

A Computational Investigation of Local Interactions Within Ionic Liquids and Ionic Liquid Analogues

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Declaration of Originality

All research work reported herein was, unless clearly stated, undertaken by Claire Ashworth between October 2011 and June 2015 within the Department of Chemistry, Imperial College London.

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Abstract

The potential applications of ionic liquids and related analogues are diverse. However, for large-scale industrial applications low cost ionic liquids are required. Moreover, for the full potential of ionic liquids to be realised, a fundamental link between molecular level interactions, structuring and the bulk phase properties must be established.

Deep eutectic solvents (DESs) and protic ionic liquids have been identified as candidates for the potential application of chalcopyrite leaching. The choline chloride – urea DES and 1-butylimidazolium hydrogensulphate protic ionic liquid were selected as systems of primary interest. Local structuring within the selected systems has been investigated, with an emphasis on the hydrogen bonding interactions.

The choline chloride – urea mixture is a prototypical example of a DES. Using DFT, the pairwise interactions between the constituent components, and within clusters composed of n .urea.choline-chloride ($n = 1-3$), have been evaluated. Many different types of hydrogen bond have been identified, exhibiting flexibility in both strength and number. The formation of the commonly proposed $[2\text{urea}\cdot\text{Cl}]^-$ complexed anion has been scrutinised and found to be energetically competitive with other interactions. Moreover, contrary to existing proposals, the negative charge is found to remain localised on chloride.

The cation-anion and anion-anion interactions within $[\text{C}_4\text{Him}][\text{HSO}_4]$ and related systems have been compared and contrasted; ion pairs were evaluated using DFT and the bulk systems modelled using classical MD. Local structuring within $[\text{C}_4\text{Him}][\text{HSO}_4]$ exhibits features of both the aprotic analogue and alkylammonium protic ionic liquids. $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ interactions have been considered and found to be a notable feature of the $[\text{HSO}_4]^-$ ionic liquids studied. It is anticipated that the formation of $[\text{HSO}_4]^-$ aggregates influences the properties of the bulk systems.

A QM/MM method for the study of ionic liquids is introduced. Preliminary analysis suggests that this is a viable approach for the investigation of local structuring within ionic liquids.

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Table of contents

Abstract.....	3
Acknowledgments.....	4
Chapter 1 Introduction	17
1. Ionic Liquids and Ionic Liquid Analogues	17
1.1 Background.....	17
1.2 Classification of ionic liquids	19
1.3 Interactions and structuring within ionic liquids.....	27
2. Hydrogen Bonding	53
2.1 What is a hydrogen bond?	53
2.2 Hydrogen bonding concepts	56
2.3 The ionic liquid hydrogen bond criteria	65
3. The Chalcopyrite Problem: Project Background	66
3.1 Background.....	66
3.2 Application of ionic liquids in extractive metallurgy	67
3.3 The cost issue: choosing an ionic liquid	69
Chapter 2 Computational Methods	77
1. Introduction	77
2. Quantum Chemistry and Density Functional Theory	79
2.1 The Schrödinger equation	79
2.2 Approximating the solutions to the Schrödinger equation	80
2.3 Electron correlation: Improving upon Hartree-Fock theory	88
2.4 Density functional theory	89
2.5 Comment on method used here	99
3. Population Analysis.....	100
3.1 Mulliken population analysis	100
3.2 Natural Bond Orbitals	102
3.3 Charges derived from molecular electrostatic potentials	103
3.4 Quantum Theory of Atoms in Molecules.....	104
4. Molecular Dynamics	109
4.1 The force field	109
4.2 Periodic boundary conditions.....	111
4.3 Long-ranged forces.....	112
4.4 The Verlet algorithms.....	113
4.5 Ensembles and averaged properties	115
4.6 Radial distribution functions	116
5. QM/MM	117
5.1 The energy expression and QM/MM coupling schemes.....	118

5.2 Computational considerations	122
Chapter 3 Interactions Within the Choline Chloride – Urea Deep Eutectic Solvent...	127
1. Background	127
1.1 Eutectics	128
1.2 Phase behaviour and speciation of deep eutectic solvents	130
2. Method	131
3. Individual Species and Pairwise Interactions	132
3.1 The choline cation.....	132
3.2 Choline chloride ion pairs	134
3.3 Urea monomers and dimers	144
3.4 Urea – chloride complexes	147
3.5 Choline – urea pairs.....	157
3.6 Comparison of hydrogen bonding and pairwise interactions	160
4. Choline Chloride – n Urea Clusters	167
4.1 Method.....	167
4.2 B3LYP clusters	168
4.3 B3LYP-D2 clusters	171
5. Conclusion.....	179
Chapter 4 Comparing and Contrasting Aprotic and Protic Imidazolium Ionic Liquids	185
1. Introduction	185
2. Ion Pairs and Ion Pair Dimers	188
2.1 Method.....	188
2.2 Ion pairs: Comparison of protic and aprotic analogues	189
2.3 Anion-anion hydrogen bonding	212
3. Molecular Dynamics Simulations	220
3.1 Method.....	220
3.2 Comparison of hydrogensulphate force fields	223
3.3 Cation – anion interactions	226
3.4 Anion-anion interactions	232
3.5 Using QM/MM to investigate ionic liquid structuring: A preliminary study	243
4. Conclusion.....	256
Conclusion	263
Appendix	267

List of Figures

Figure 1.1. Examples of common ionic liquid ions. “C_n” represents an alkyl chain with n corresponding to the chain length e.g. C₄ equates to a butyl chain.

Figure 1.2. Suggested classification system for ionic liquids. An example of each “type” of ionic liquid is given underneath (a-e).

Figure 1.3. The relative fraction of anionic species present in the [C₂C₁im]Cl-AlCl₃ mixture with variation in the mole fraction of AlCl₃ at 200°C. Calculated using a thermodynamic model. Reproduced from Ref. 18 with permission from The Royal Society of Chemistry.

Figure 1.4. Possible speciation within the choline chloride - urea DES at the 1:2 eutectic composition.

Figure 1.5. Potential energy surfaces for different H-bond types.

Figure 1.6. Complexed anions (a) [Cl(HCl)]⁻, (b) [HSO₄(H₂SO₄)]⁻ and (c) [urea·Cl]⁻, together with proposed reaction coordinates for proton transfer: X-H + :Y⁻ → X:⁻ + H-Y

Figure 1.7. (a) [C₄C₁im]⁺, a typical ionic liquid cation with the most acidic C-H unit depicted in red. (b) [C₄C₁C₁]⁺, a methylated analogue of [C₄C₁im]⁺.

Figure 1.8. A representation of the possible H-bond interactions within an alkylammonium ionic liquid (a) and a trialkylammonium ionic liquid (b). Influence of the ionic liquid environment on the PES for the proton transfer reaction, where R=H or an alkyl group (c).

Figure 1.9. (a) A simplified representation of the quadrupole moment within benzene. π-π structural arrangements: (b) T-shape, (c) displaced parallel and (d) stacked. Possible imidazolium π⁺-π⁺ structures (e) and (f). Stable cation-π arrangement with the cation above the centre of the ring (g). Possible anion – arene binding motifs: (h) H-bonding with C-H groups of the ring, (i) anion above the ring centroid or (j) anion above the periphery of the ring.

Figure 1.10. Examples of anion-arene structural motifs, shown here for the 1,3,5-triazine and chloride combination: (a) centred anion-π, (b) displaced and (c) in-plane H-bonded motif. Structures optimised here at the MP2(full)/aug-cc-pVDZ level.

Figure 1.11. Analysis of the centred anion-π and displaced 1,3,5-triazine-chloride structural motifs (at the MP2(full)/aug-cc-pVDZ level). Electron density isosurfaces for (a) centred anion-π and (b) displaced motifs. Electron density reported in eÅ⁻³. Selected MOs for (c) centred anion-π and (d) displaced motifs. MOs generated at the 0.02 eÅ⁻³ isosurface.

Figure 1.12. A [C₄C₁im]⁺ cation with the possible anion positions indicated by filled black circles. Five in-plane positions indicated in (a), a simplified representation of the two out-of-plane positions shown in (b) and H-bonding interactions associated with the top out-of-plane position shown in (c). Primary H-bond interactions with ring C-H units depicted in red. Secondary H-bonds with alkyl C-H groups depicted in blue.

Figure 1.13. Analysis of the front and top ion pair configurations of [C₁C₁im]Cl. Selected MOs generated at the 0.02 eÅ⁻³ isosurface, (a) and (b). Partial charge distributions according to the NBO scheme (at the B3LYP-D3/6-311+G(d,p) level), (c) and (d). Red is negative and green is positive. Scale = +/- 0.85 e. (e) and (f) Electron density isosurfaces computed at the MP2(full)/aug-cc-pVTZ level. Electron density reported in eÅ⁻³.

Figure 1.14. Spatial distribution functions from an MD simulation showing the favourable locations of Cl⁻ around the [C₂C₁im]⁺ cation (128 ion pairs at 450 K), provided by Dr Richard Matthews (Hunt research group). (a) SDF at 30% above bulk density and (b) SDF at 20% above bulk density.

Figure 1.15. Low energy [C₁C₁im]Cl dimer obtained at the B3LYP-D3BJ/6-311+G(d,p) level. Structure provided by Dr Richard Matthews.

Figure 1.16. (a) Front and top [C₁C₁im]Cl configurations. (b) Combined front/top ion pair configurations of [C₁C₁im][PF₆] and [C₁C₁im][C₁SO₄]. Structures obtained here at the B3LYP-D3BJ/6-311+G(d,p) level.

Figure 1.17. (a) Conventional chelated and bifurcated H-bond motifs. (b) H-bond motif variations accessible within ionic liquid systems. Primary H-bonds indicated with red, secondary H-bonds with blue.

Figure 1.18. (a) Traditional representation of a quaternary ammonium cation. (b) Simplified representation of a quaternary ammonium cation as a tetrahedron with four “faces”. Anion positions are indicated using filled-in black circles. (c) $[\text{NC}_1\text{C}_1\text{C}_1\text{C}_1]\text{Cl}$ ion pair, with the chloride anion sitting at one of the four possible faces. (d) and (e) $[\text{NC}_1\text{C}_1\text{C}_1\text{H}]\text{Cl}$ ion pairs with chloride sitting at a face or forming a directional $\text{N-H}\cdots\text{Cl}$ H-bond respectively. Structures computed here at the B3LYP-D3BJ/6-311+G(d,p) level.

Figure 1.19. Comparison of the simulated radial distribution functions for the cation-anion and cation-cation distributions within $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ (using the centre of mass of the ions). Classical MD simulation of 256 ion pairs performed here at 400.15 K (further details in Chapter 4).

Figure 1.20. Pictorial representation of the variation in H-bond components. Figure from “Hydrogen bonding in ionic liquids”.⁶¹ Reproduced by permission of The Royal Society of Chemistry.

Figure 1.21. Electron density difference contour plot for $[\text{NC}_1\text{C}_1\text{C}_1\text{H}]\text{Cl}$. Structure optimised at the B3LYP-D3/aug-cc-pVTZ level, provided by Dr Richard Matthews (Hunt research group). Pink and blue contour lines indicate an increase and decrease in $\rho(r)$ respectively (with respect to the isolated ions in the geometry of the ion pair). Contour lines drawn at densities between 0.0005 and 20 au (0.0005 – 0.01 in 0.0005 intervals, 0.02-0.1 in 0.02 intervals, 0.2, 0.04, 0.08, 2, 4, 8 and 20 au).

Figure 1.22. Resonance forms of (a) neutral and doubly ionic H-bonds and (b) ionic H-bonds.

Figure 1.23. Relief map of the electron density in the molecular plane of the 4-nitropyridine $\cdots\text{HCl}$ complex (structure optimised here at the B3LYP-D3BJ/6-311+G(d,p) level). (a) Relief map of entire complex and (b) close-up view of the electron density topology in the H-bond region.

Figure 1.24. QTAIM molecular graph for the 4-nitropyridine and HCl H-bonded dimer (B3LYP-D3BJ/6-311+G(d,p)). Small pink spheres correspond to BCPs. Values of ρ_{BCP} ($\text{e}\text{\AA}^{-3}$) and $\nabla^2\rho_{\text{BCP}}$ (in brackets, $\text{e}\text{\AA}^{-5}$) provided.

Figure 1.25. Simplified qualitative MO diagrams for H-bond formation: (a) interaction between a Y lone pair (LP) fragment orbital (FO) and a X-H σ^* FO and (b) interaction between a Y LP FO and a X-H σ FO. Based on a diagram from “Hydrogen bonding in ionic liquids”. Reproduced by permission of The Royal Society of Chemistry.

Figure 1.26. Comparison of the bonding and antibonding H-bond MOs for the (a) “NH” and (b) “face” configurations of the trimethylammonium chloride ion pair. Structures optimised here at the B3LYP-D3BJ/6-311+G(d,p) level. MOs generated at the $0.02 \text{ e}\text{\AA}^{-3}$ isosurface.

Figure 2.1. Comparison of a 1s Slater type orbital (STO, $\zeta = 1$) and the Gaussian type orbital of best fit (GTO, $\alpha = 0.270950$).²⁰

Figure 2.2. Molecular graph for the HCN molecule. Structure optimised here at the B3LYP-D3BJ/6-311+G(d,p) level. BCPs represented by pink spheres and thick grey line indicates the bond path. Thin purple lines are the atomic basin paths and the thick purple lines are the interatomic surface paths.

Figure 2.3. Simplified pictorial representation of a QM/MM system.

Figure 2.4. Model system with two regions.

Figure 2.5. Graphical representation of the subtractive QM/MM coupling scheme.

Figure 2.6. Mechanical embedding within an additive coupling scheme.

Figure 2.7. Electrostatic embedding within an additive coupling scheme.

Figure 3.1. Simplified phase diagram for a binary mixture of solid A and solid B.

Figure 3.2. Experimentally determined phase diagram for the choline chloride – urea mixture. Plot of freezing temperature (T_f) against mole fraction of urea. Reproduced from Ref. 4 with permission of The Royal Society of Chemistry.

Figure 3.3. Gas phase choline cation conformations: (a) gauche, (b) trans and (c) trans-rotated.

Figure 3.4. C-H $\cdots$ O interaction distances indicated within (a) gauche choline and (b) gauche *N,N*-dimethylethanolamine.

Figure 3.5. Choline chloride ion pairs ($\Delta E_{\text{rel}} / \text{kJ mol}^{-1}$).

Figure 3.6. Simplified representation of the gauche choline cation.

Figure 3.7. Example of a high energy choline chloride ion pair.

Figure 3.8. QTAIM molecular graphs of (a) A_ChG and (b) B_ChG. BCPs are shown as pink dots.

Figure 3.9. QTAIM molecular graphs for (a) chloroform – chloride, $\text{Cl}_3\text{CH}\cdots\text{Cl}^-$ and (b) the choline chloride ion pair E_ChG.

Figure 3.10. HOMO-2 of (a) E_ChG, (b) A_ChG and (c) A_ChT, generated at the 0.02 au isosurface.

Figure 3.11. Relative energies of ion pairs, ΔE_{rel} (kJ mol^{-1}) plotted against charge transfer, CT, (NBO and CHELPG). Red circles = A_ChG, blue circles = B_ChG and green circles = A_ChT.

Figure 3.12. Electrostatic potential mapped onto the 0.0004 au density isosurfaces of choline chloride ion pairs (a) A_ChG, (b) B_ChG and (c) C_ChT. Charge range = ± 0.09 e (positive = blue, negative = red).

Figure 3.13. The electrostatic potential for ion pair C_ChT mapped onto isodensity surfaces of different values. Charge range = ± 0.09 e (positive = blue, negative = red).

Figure 3.14. Intermolecular H-bonds within ion pairs A_ChT and E_ChG.

Figure 3.15. Conformers of urea: (a) C_2 with anti pyramidal NH_2 groups, (b) planar C_{2v} and (c) C_s with syn NH_2 groups. The labelling of the H atoms within a single NH_2 group as syn and anti, with respect to C=O , is shown in (a).

Figure 3.16. Structures of gas phase urea dimers: (a) ribbon and (b) distorted chain.

Figure 3.17. Molecular graphs shown in (a) and (b). BCPs indicated by small pink spheres. RCPs omitted. MOs indicating $\text{N-H}\cdots\text{O=C}$ H-bond formation shown in (c) and (d). MOs generated at the 0.02 au isosurface.

Figure 3.18. Simplified representation of (a) urea and (b) chloride. Coordination sphere with respect to chloride shown in (c).

Figure 3.19. Simplified representation of the urea - chloride complexes. Structures labelled X.Y.Z with respect to the number of urea molecules in the 1st, 2nd and 3rd coordination spheres. Relative energies in kJ mol^{-1} .

Figure 3.20. Geometries of selected urea-chloride complexes.

Figure 3.21. Examples of urea-chloride complexes featuring linear and distorted urea-urea chain motifs.

Figure 3.22. HOMO-1 of (a) 1.0.0_A, (b) 2.0.0_A and (c) 3.0.0_A. MOs generated at the 0.02 au isosurface.

Figure 3.23. A H-bonded ring found within the 2.1.0_A structure. $\text{N-H}\cdots\text{Cl}$ H-bonds indicated in green, $\text{N-H}\cdots\text{O=C}$ H-bonds in red and $\text{N-H}\cdots\text{N}$ H-bonds in blue.

Figure 3.24. Example bonding MOs for (a) the $[\text{AlCl}_4]^-$ complexed anion and (b) the 1.0.0_A [urea-Cl]⁻ pair.

Figure 3.25. Choline-urea pairs (relative energy/ kJ mol^{-1}).

Figure 3.26. Plot of mean $E^{(2)}$ against mean ρ_{BCP} values for each H-bond type.

Figure 3.27. Plot of $E^{(2)}$ against ρ_{BCP} values for each individual H-bond.

Figure 3.28. Plot of $\Sigma E^{(2)}$ against $\Sigma \rho_{\text{BCP}}$ for the intermolecular H-bonds found in each complex.

Figure 3.29. Plot of the total association energy, E_a , against $\Sigma \rho_{\text{BCP}}$ for each complex. The choline-chloride ion pairs have not been included in the linear fit.

Figure 3.30. Correlation between ρ_{BCP} and $\nabla^2 \rho_{\text{BCP}}$ for all H-bonds identified in the complexes.

Figure 3.31. Relative energies of the B3LYP 1:2 choline chloride - urea clusters.

Figure 3.32. Pairwise interactions within an example 1:2 cluster.

Figure 3.33. Selected 1:1 B3LYP-D2 clusters. Relative energies in kJ mol^{-1} .

Figure 3.34. Selected 1:2 B3LYP-D2 clusters. Relative energies in kJ mol^{-1} .

Figure 3.35. Selected 1:3 B3LYP-D2 clusters. Relative energies in kJ mol^{-1} .

Figure 3.36. QTAIM molecular graph of cluster 1:3_B. BCPs shown as pink dots, RCPs and CCPs omitted for clarity.

Figure 3.37. Ranges in the values of ρ_{BCP} for the different H-bond types identified within the isolated pairs and clusters.

Figure 3.38. Plot of relative energy against total sum of ρ_{BCP} for the intermolecular H-bonds within the selected clusters of each composition.

Figure 4.1. The 1-butylimidazolium cation (a) and hydrogensulphate anion (b).

Figure 4.2. Torsion angles within the $[\text{C}_4\text{Him}]^+$ cation.

Figure 4.3. (a) Comparison of the NBO partial charge distributions of the $[\text{C}_4\text{Him}]^+$ and $[\text{C}_4\text{C}_1\text{im}]^+$ cations. For the methyl and methylene groups the sum of atomic charges is represented. A grey circle represents an atom or group that is essentially charge neutral. (b) Electrostatic potential mapped onto the $0.001 \text{ e}\text{\AA}^{-3}$ isodensity surfaces.

Figure 4.4. Lowest energy examples (at B3LYP/6-311+G(d,p)) of the six stable chloride configurations with respect to the $[\text{C}_4\text{Him}]^+$ cation. Relative energies in kJ mol^{-1} .

Figure 4.5. Comparison of the stable chloride positions about the $[\text{C}_4\text{C}_1\text{im}]^+$ and $[\text{C}_4\text{Him}]^+$ cations.

Figure 4.6. NBO partial charge distributions for (a) H_2SO_4 and (b) $[\text{HSO}_4]^-$.

Figure 4.7. Selected $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ ion pairs optimised at the B3LYP/6-311+G(d,p) level. Relative energies in kJ mol^{-1} .

Figure 4.8. Selected $[\text{C}_4\text{Him}][\text{HSO}_4]$ ion pairs optimised at the B3LYP/6-311+G(d,p) level. Relative energies in kJ mol^{-1} .

Figure 4.9. Relative energies of the B3LYP ion pairs. Cation-anion configurations corresponding to the energy “band” shown alongside.

Figure 4.10. Relative energies of the B3LYP-D2 ion pairs (open circles) plotted against the relative energies of the B3LYP ion pairs (filled circles).

Figure 4.11. H-C²...S angle distributions for $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ ion pairs with a front or top configuration.

Figure 4.12. QTAIM molecular graphs for selected B3LYP-D2 $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ ion pairs. BCPs shown as pink dots, RCPs and CCPs omitted for clarity. Values of ρ_{BCP} (au) for selected interactions indicated. ϕ and the relative energy of the structure in kJ mol^{-1} detailed beneath each system.

Figure 4.13. Selected FOs of $[\text{C}_4\text{C}_1\text{im}]^+$ and $[\text{HSO}_4]^-$. $[\text{C}_4\text{C}_1\text{im}]^+$ LUMO (a), HOMO (b) and deep π FO (c). $[\text{HSO}_4]^-$ HOMO (d) and π type FO (e).

Figure 4.14. $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ MOs indicating alkyl C-H...O H-bond formation.

Figure 4.15. $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ MOs suggestive of H-bond formation with C²-H.

Figure 4.16. Additional anion FO interactions with a C²-H σ FO.

Figure 4.17. Examples of high energy anion- π^+ interactions.

Figure 4.18. Examples of deeper energy anion- π^+ interactions.

Figure 4.19. Selected crystal structures featuring $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ H-bonding: (a) pyridinium hydrogensulphate⁴⁵ and (b) 1-butyl-2,3-dimethyl hydrogensulphate.⁴⁶

Figure 4.20. The $[\text{HSO}_4]^-$ cyclic dimer (a), QTAIM molecular graph (b) and example MO generated at the $0.02 \text{ e}\text{\AA}^{-3}$ isosurface (c).

Figure 4.21. Low energy ion pair dimer motifs, (a) diagonal and (b) middle.

Figure 4.22. Example $[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4]$ ion pair dimers. Relative energies in kJ mol^{-1} . Anion-anion contacts indicated *via* pink dotted lines.

Figure 4.23. Example $[\text{C}_1\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ ion pair dimers. Relative energies in kJ mol^{-1} . Anion-anion contacts indicated *via* pink dotted lines.

Figure 4.24. $E^{(2)}$ and ρ_{BCP} values for H-bonds in selected ion pair dimers.

Figure 4.25. Atom labelling used here for (a) $[\text{C}_4\text{C}_1\text{im}]^+$, (b) $[\text{C}_4\text{Him}]^+$, (c) $[\text{C}_1\text{SO}_4]^-$ and (d) $[\text{HSO}_4]^-$.

Figure 4.26. Radial distribution functions comparing the influence of the $[\text{HSO}_4]^-$ force field on $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ (a) cation-anion and (b) anion-anion interactions. (c) Influence of modifications to FFA on anion-anion interactions.

Figure 4.27. Selected cation-anion site-site radial distribution functions for systems at both 300.15 and 400.15 K.

Figure 4.28. Cation-anion site-site radial distribution functions. Terminal anion oxygen atoms ($\text{O}^2\text{-O}^4$) about cation the (a) C^2 , (c) C^4 and (d) C^5 positions. Bridging oxygen atoms (O^1) about the cation C^2 position (b). Terminal and bridging oxygen atoms about N^3 for $[\text{C}_4\text{Him}][\text{HSO}_4]$ (e). All systems at 400.15 K.

Figure 4.29. Spatial distribution functions of selected anion oxygen atoms about the $[\text{C}_4\text{C}_1\text{im}]^+$ or $[\text{C}_4\text{Him}]^+$ cations: O^2 terminal oxygen atom (red) and O^1 bridging oxygen atom (blue). All systems at 400.15 K.

Figure 4.30. Observed cation-anion motifs featuring anion interaction with the N-H group of $[\text{C}_4\text{Him}]^+$.

Figure 4.31. Possible $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ interactions. Black dotted line represents $\text{C}^2\text{-H}\cdots\text{O}$ H-bond formation. Red dotted line indicates a non-interacting terminal oxygen within the 4 Å cut-off.

Figure 4.32. Distribution of angles $\phi(\text{O}^2\cdots\text{C}^2\text{-H})$ and $\phi(\text{O}^2\cdots\text{N}^3\text{-H})$ for atoms within the values of r_{cut} . All systems at 400.15 K.

Figure 4.33. Selected anion-anion site-site radial distribution functions. All systems at 400.15 K.

Figure 4.34. Possible anion interactions. Cations are represented by circles with a positive charge at the centre.

Figure 4.35. Distribution of the angle $\phi(\text{O}^2\cdots\text{O}^1\text{-H})$ within $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ and $[\text{C}_4\text{Him}][\text{HSO}_4]$, for atoms within the values of r_{cut} . Both systems at 400.15 K.

Figure 4.36. Anion-anion interactions observed within the 400.15 K simulation of $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$: (a) – (c) example structures showing the three $[\text{HSO}_4]^-$ dimer motifs and (d) an example of an $[\text{HSO}_4]^-$ trimer.

Figure 4.37. Series of snapshots showing the dynamic nature of H-bond motifs between three anions.

Figure 4.38. Examples of anion tetramers observed within the 300.15 K simulation of $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$.

Figure 4.39. Simplified representation of the H-bond donor and acceptor groups of selected ions: (a) ethylammonium, (b) nitrate, (c) 1-butylimidazolium and (d) hydrogensulphate. (e) Simplified representation of an example $[\text{C}_4\text{Him}][\text{HSO}_4]$ ion pair.

Figure 4.40. Examples of cation-anion configurations observed within the $[\text{C}_4\text{Him}][\text{HSO}_4]$ 400.15 K trajectory: (a) one anion with two cations and (b) one anion with three cations. Pink arrows indicate available groups for extension of the H-bond network.

Figure 4.41. Examples of cation-anion configurations observed within the $[\text{C}_4\text{Him}][\text{HSO}_4]$ 400.15 K trajectory: (a) cyclic anion dimer with one cation, (b) chain anion dimer with two cations and (c) chain anion dimer with three cations. Pink arrows indicate available groups for extension of the H-bond network.

Figure 4.42. Examples of cation-anion configurations observed within the $[\text{C}_4\text{Him}][\text{HSO}_4]$ 400.15 K trajectory: (a) an anion trimer with one cation, (b) an anion trimer with two cations, (c) an anion trimer with three cations, (d) an anion trimer with four cations and (e) an anion chain composed of four anions.

Figure 4.43. Example QM/MM cluster of 50 $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ ion pairs: 4 ion pairs in the QM region (balls and sticks), 16 ion pairs in the MM active region (pink sticks) and 30 ion pairs in the MM frozen region (black lines).

Figure 4.44. Central QM region of selected QM/MM clusters of $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$: the MD geometry (blue) and QM/MM optimised geometry (red) for (a) Cluster A and (b) Cluster B. (c) Comparison of the MD geometry (blue), the QM/MM B3LYP geometry (red) and QM/MM B3LYP-D2 geometry (green) for

Cluster B. (d) Comparison of the QM/MM B3LYP geometry (cyan) and gas phase B3LYP-D3BJ/6-311+G(d,p) geometry (orange) for Cluster B.

Figure 4.45. QTAIM molecular graphs of the QM region for an example QM/MM cluster of $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$: (a) with a cut-off value for ρ_{BCP} of 0.001 au and (b) with a higher cut-off value for ρ_{BCP} of 0.008 au.

Figure 4.46. Fragments taken from the larger QM regions of selected QM/MM clusters: (a) – (c) examples of structural motifs within the $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ system and (d) the $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ system.

Figure 4.47. Examples of fragments showing different cation-anion $[\text{C}_4\text{C}_1\text{im}]^+ \cdots [\text{HSO}_4]^-$ H-bond motifs.

Figure 4.48. Plot of ρ_{BCP} against H-bond distance (r) for all H-bonds identified within the selected clusters.

Figure 4.49. Comparison of the exponential relationship between ρ_{BCP} and r for the C-H $\cdots$ O H-bonds identified in the clusters, with analogous correlations for N-H $\cdots$ O and O-H $\cdots$ O H-bonds taken from the literature.⁹⁵

Figure 4.50. (a) Plot of ρ_{BCP} against ϕ , the H-bond angle and (b) plot of ϕ against H-bond length, r .

List of Tables

Table 1.1. Criteria use to classify H-bonds, taken from “Hydrogen bonding in ionic liquids”.⁶¹

Table 2.1. Summary of the different types of CP.

Table 2.2. Approximate classification of different types of interaction based on the electron density, $\rho(r)$, Laplacian of the electron density, $\nabla^2\rho(r)$, and total energy density, $H(r)$.

Table 3.1. Relative energies (ΔE_{rel} / kJ mol^{-1}) of the choline chloride ion pairs. Amount of charge transfer, CT, from chloride to choline computed using NBO and CHELPG population analysis methods.

Table 3.2. Estimated Coulomb interaction within each choline chloride ion pair. Δr is the separation between the ions (i.e. the distance between the N centre of choline and Cl), E_a is the total association energy of the ion pair and E_C is the estimated Coulomb potential. ΔE corresponds to the difference between the total association energy and the estimated Coulomb potential.

Table 3.3. Relative energies (ΔE_{rel} / kJ mol^{-1}) of the urea-chloride complexes. Total charge transfer (CT) from chloride computed using NBO and CHELPG.

Table 3.4. Association energies (E_a / kJ mol^{-1}), and difference between successive association energies (ΔE_a / kJ mol^{-1}), for complexes with urea in the 1st coordination shell of chloride.

Table 3.5. Relative energies (ΔE_{rel} / kJ mol^{-1}) of the choline-urea pairs. Total charge transfer (CT) from urea computed using the NBO and CHELPG schemes.

Table 3.6. Maximum association energies, E_a , for the pairwise interactions. nU corresponds to the number of urea molecules in the 1st coordination sphere of chloride.

Table 3.7. Summary of selected H-bond properties for the different types of H-bond: Values of ρ_{BCP} in au, H-bond lengths (r) in Å, and $E^{(2)}$ for the donor (D) $\rightarrow$ acceptor (A) interaction in kJ mol^{-1} .

Table 3.8. The H-bond types ordered according to the descending value of mean ρ_{BCP} . For the intramolecular C-H $\cdots$ O H-bonds, values of $E^{(2)}$ were not obtained in four cases.

Table 3.9. The approximated choline chloride separation within the B3LYP ion pairs and clusters. Charge transfer (CT) from chloride computed using the NBO scheme.

Table 3.10. Mean values and ranges of ρ_{BCP} for the H-bonds identified in the B3LYP-D2 subset of clusters shown in Figures 3.33-35. “No.” is the number of H-bonds of a given type identified.

Table 3.11. Relative energies of selected clusters (ΔE_{rel}), total number (No.) of H-bonds identified and sum of ρ_{BCP} for each cluster, the number of H-bonds with ρ_{BCP} above a value of 0.020 au and the percentage contribution of these “stronger” H-bonds to the total value of $\Sigma \rho_{\text{BCP}}$.

Table 4.1. Computed association energies (kJ mol^{-1}) of the lowest energy ion pairs of $[\text{C}_4\text{C}_{1\text{im}}][\text{HSO}_4]$, $[\text{C}_4\text{Him}][\text{HSO}_4]$, $[\text{C}_4\text{Him}]\text{Cl}$ and for reference, $[\text{C}_4\text{C}_{1\text{im}}]\text{Cl}$ at the B3LYP/6-311++G(d,p) level.

Table 4.2. Reported melting points (T_m) and viscosities (η) of selected ionic liquids.

Table 4.3. Computed association energies (kJ mol^{-1}) of the lowest energy ion pairs of $[\text{C}_4\text{C}_{1\text{im}}][\text{HSO}_4]$, $[\text{C}_4\text{Him}][\text{HSO}_4]$, $[\text{C}_4\text{Him}]\text{Cl}$ and for reference, $[\text{C}_4\text{C}_{1\text{im}}]\text{Cl}$ at the B3LYP-D2/6-311++G(d,p) level.

Table 4.4. Selected properties of the $[\text{HSO}_4]^-$ cyclic dimer in the gas phase and in an implicit solvation environment (CPCM) with different solvent parameters: association energies (E_a), H-bond lengths (r), NBO partial charges on the H-atoms (q), values of ρ_{BCP} and $E^{(2)}$ for the O-H $\cdots$ O H-bonds.

Table 4.5. Sum of ρ_{BCP} for different types of H-bond (anion-anion and cation-anion) within selected ion pair dimers. All values of ρ_{BCP} in au.

Table 4.6. Final values of the cell vectors, calculated densities (ρ_{calc}), experimental densities (ρ_{exp}) and the percentage difference between the calculated and experimental densities.

Table 4.7. Positions of the first peak maxima (r_{max}) and peak minima (r_{cut}) for the C²-H $\cdots$ O²-O⁴ and N³-H $\cdots$ O²-O⁴ RDFs and the calculated coordination numbers (N_c).

Table 4.8. Positions of the first peak maxima (r_{max}) and peak minima (r_{cut}) for the $\text{S}^1\cdots\text{S}^1$ and $\text{O}^1\cdots\text{H}\cdots\text{O}^2\cdots\text{O}^4$ RDFs and the calculated coordination numbers (N_C).

Table 4.9. The number (No.) of H-bonds of each type identified within the clusters and mean values and ranges for the H-bond angles (ϕ), H-bond distances (r), and ρ_{BCP} .

List of Abbreviations

$[\text{C}_2\text{C}_1\text{im}]^+$		1-ethyl-3-methylimidazolium
$[\text{C}_4\text{C}_1\text{im}]^+$		1-butyl-3-methylimidazolium
$[\text{C}_4\text{Him}]^+$		1-butylimidazolium
$[\text{NC}_1\text{C}_1\text{C}_1\text{C}_1]^+$		tetramethylammonium
$[\text{NC}_1\text{C}_1\text{C}_1\text{H}]^+$		trimethylammonium
$[\text{C}_1\text{SO}_4]^-$		methysulphate
$[\text{HSO}_4]^-$		hydrogensulphate
$[\text{OAc}]^-$		acetate
$[\text{NTf}_2]^-$		bis(trifluoromethylsulphonyl)imide
$[\text{OTf}]^-$		trifluoromethanesulphonate
6-311+G(d,p)		Pople augmented, polarisable, triple-zeta split valence basis set
ADF		Angular Distribution Function
AO		Atomic Orbital
B3LYP		Becke's three parameter exchange functional with the correlation functional of Lee, Yang and Parr
BCP		Bond Critical Point
BJ		Becke-Johnson damping function
BSSE		Basis Set Superposition Error
CHELPG		CHarges from Electrostatic Potentials using a Grid-based method
CP		Counterpoise correction <i>or</i> Critical Point
CPCM		Conductor-like Polarizable Continuum Model
CT		Charge Transfer
D2		Grimme's second generation dispersion correction
D3		Grimme's third generation dispersion correction
DES		Deep Eutectic Solvent
DFT		Density Functional Theory
ESP		Electrostatic Potential
FFA		Force Field A for $[\text{HSO}_4]^-$
FFB		Force Field B for $[\text{HSO}_4]^-$
FO		Fragment Orbital
GGA		Generalised Gradient Approximation
GTO		Gaussian Type Orbital
H-bond		Hydrogen bond
HOMO		Highest Occupied Molecular Orbital
L(S)DA		Local (Spin) Density Approximation
LP		Lone Pair

LUMO		Lowest Unoccupied Molecular Orbital
MD		Molecular Dynamics
MO		Molecular Orbital
MP2		Second order Møller-Plesset perturbation theory
NBO		Natural Bond Orbital
NPA		Natural Population Analysis
NPT		Isothermal-isobaric ensemble
NVE		Microcanonical ensemble
NVT		Canonical ensemble
OPLS-AA		Optimised Potentials for Liquid Simulations -all atom
PES		Potential Energy Surface
QM/MM		Quantum Mechanics/Molecular Mechanics
QTAIM		Quantum Theory of Atoms in Molecules
RDF		Radial Distribution Function
SDF		Spatial Distribution Function
STO		Slater Type Orbital
ZPE		Zero-Point Energy

Chapter 1

Introduction

1. Ionic Liquids and Ionic Liquid Analogues

1.1 Background

Ionic liquids are room temperature liquids, or low melting point solids, composed solely of ions.^{1, 2} Traditional ionic salts, such as sodium chloride, exhibit very high melting points ($\approx 801\text{ }^{\circ}\text{C}$ for NaCl). However, through careful selection and engineering of the constituent ions, it is possible to not only control the melting point, but also influence a wide range of physico-chemical properties.

The constituent ions of traditional, high melting point, ionic salts are small with a high charge density and high packing efficiency. In contrast, typical constituent ions of ionic liquids are bulkier, with a much lower charge density and a reduced propensity to form efficiently packed crystal lattices. Moreover, the move away from inorganic monoatomic ions to those more organic in nature, introduces the possibility of additional intermolecular interactions, most notably hydrogen bonding. Examples of common ionic liquid ions are shown in **Figure 1.1**. A vast number of possible ion combinations, resulting in an ionic liquid, are conceivable.

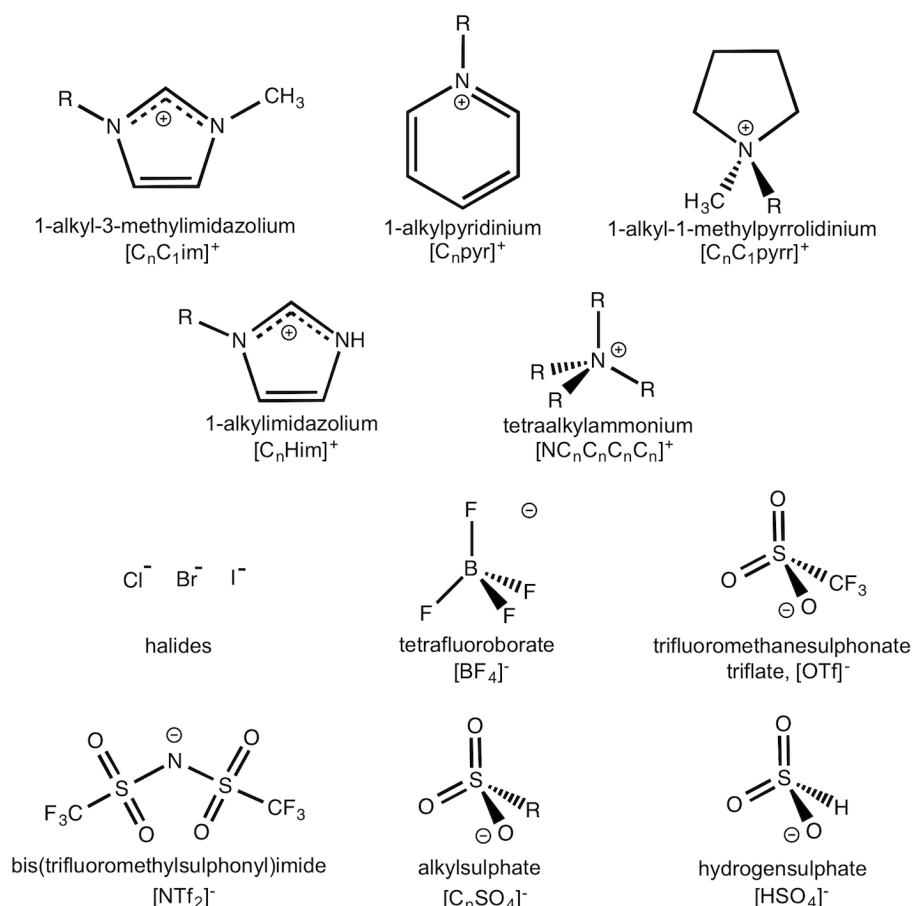


Figure 1.1. Examples of common ionic liquid ions. “ C_n ” represents an alkyl chain with n corresponding to the chain length e.g. C_4 equates to a butyl chain.

The interest in ionic liquids continues to grow, driven by the potential for the unusual combination of physico-chemical properties exhibited by ionic liquids to be exploited in a wide range of areas. Favourable properties include a wide liquidus range, electrical conductivity, moderate to high thermal and electrochemical stability, low volatility and the ability to solubilise a diverse range of materials.³⁻⁵ The term “designer solvents” is often affiliated with ionic liquids,⁶ referring to the increased synthetic flexibility associated with a two component system, and thus the increased possibility of tailor-making a solvent for a specific purpose. Potential applications are many and span a manifold of research fields, from the engineering through to the biological ends of the spectrum. Examples of potential applications include: engineering fluids,⁷ electrolytes for energy storage devices,⁸ CO₂ capture,⁸ biomass pretreatment,^{9, 10} electrodeposition,¹¹ as well as solvents for separations,^{12, 13} synthesis and catalysis.^{1, 2}

Nevertheless, despite the demonstrated potential for ionic liquids in new and established areas, the cost of many of the ionic liquids currently employed at the lab scale is prohibitive to large scale industrial processes. This has driven the search for cheaper ionic liquids.¹⁴

The term “designer solvent” invokes the idea of *a priori* design. Given the huge number of possible ion combinations, the ability to predict the properties of an ionic liquid prior to synthesis becomes almost a necessity. However, our predictive capabilities depend on there being a well developed understanding of the fundamental link between the molecular level structuring and interactions, and the bulk phase properties. At present, our fundamental understanding is limited. Thus, for the full potential of ionic liquids to be realised, our fundamental knowledge at the molecular level must be advanced. In terms of furthering our understanding of the molecular level interactions within ionic liquids, computational chemistry has become an invaluable tool.

1.2 Classification of ionic liquids

Over the last two decades, the expansion in the field of ionic liquids has seen the introduction of a number of different “types” of ionic liquid. Some systems do not strictly adhere to the definition of an ionic liquid as consisting solely of ions, but do exhibit the typical physical properties associated with ionic liquids. These systems can be referred to as “ionic liquid analogues”, and thus, are considered here as part of the ionic liquids family.

There are a number of ways in which the different ionic liquids can be categorised. The nature of the anionic component will be used here, in the first instance, to separate ionic liquids into two broad classes, *simple* ionic liquids and *complex* ionic liquids. The anions within simple ionic liquids are discrete, whereas complex ionic liquids feature complexed anions. The majority of cations are common to both classes. The classification system used here is graphically represented in **Figure 1.2**.

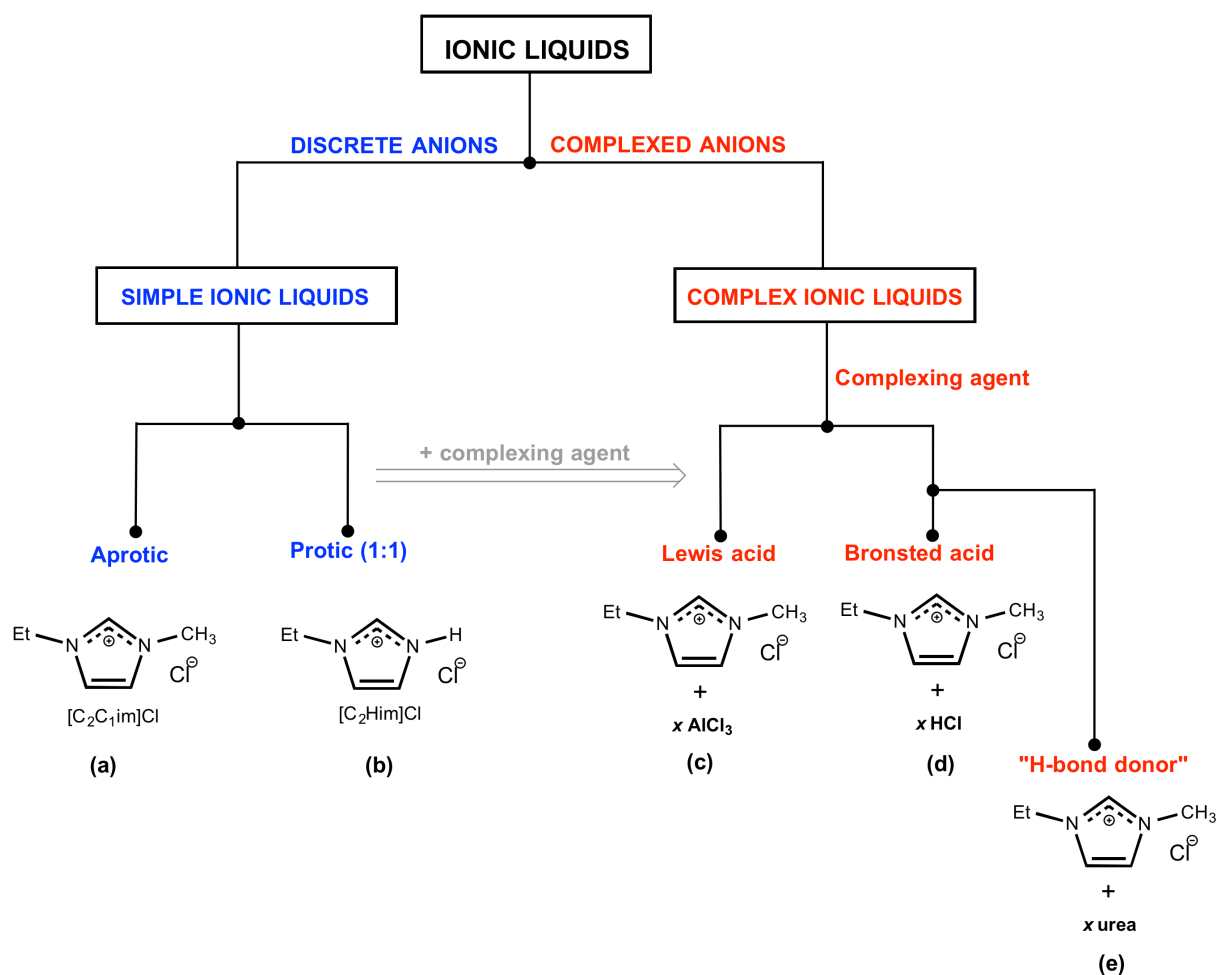


Figure 1.2. Suggested classification system for ionic liquids. An example of each “type” of ionic liquid is given underneath (a-e).

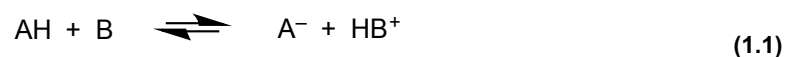
The anion influences numerous properties of the resultant ionic liquid, including solvation capability, hydrophobicity, viscosity and the melting point.⁵ As the anion gets larger, the separation between the oppositely charged ions increases and the Coulombic interactions decrease, along with a concomitant decrease in lattice packing efficiency. Subsequently, a decrease in the melting point is observed.

Larger, singly charged, anions will also have a lower total charge *density*. Increased charge delocalisation is also frequently cited as a factor contributing to a lowering of the melting point.⁵ Therefore, the aim, when synthesising a low melting point ionic liquid, is usually to introduce a bulky anion with a low charge density. This can be achieved through the selection of an appropriate *discrete* anion, or through the formation of a *complexed* anion.

The simplest ionic liquids with respect to speciation are those composed only of discrete ions, where a discrete ion is taken to be a distinct entity not in effective equilibrium with another ionic species. Thus, for an ionic liquid with discrete anions, it is presumed that only one anionic species will be present. As such, ionic liquids with discrete anions are considered here as *simple* ionic liquids. 1-ethyl-3-methyl-imidazolium chloride, [C₂C₁im]Cl, **Figure 1.2 a**, is a prototypical example, although the melting point of [C₂C₁im]Cl is still relatively high ($\approx 87\text{ }^{\circ}\text{C}$).¹⁵ There are, however, a huge number of possible discrete ions that can be introduced to meet the bulky/low charge density criteria (to varying extents), leading to a class of ionic liquid with a very diverse chemistry. Some common examples of discrete anions are shown in the bottom half of **Figure 1.1**.

[C₂C₁im]Cl is also an example of an ionic liquid belonging to the *aprotic* subcategory. The cations within aprotic ionic liquids have quaternary (or pseudo quaternary, if aromatic) centres, usually formed through the alkylation of the parent base e.g. alkylation of methylimidazole with a haloalkane to form [C_nC₁im]X. Simple aprotic ionic liquids are also the most well studied class of ionic liquid to date.

Protic ionic liquids constitute the second subcategory within the simple ionic liquid class. In contrast to aprotic ionic liquids, protic ionic liquids are formed through the reaction of a Brønsted acid with a Brønsted base in a 1:1 ratio, **Equation 1.1**. The protic analogue of [C₂C₁im]Cl is [C₂Him]Cl, shown in **Figure 1.2 b**. A distinguishing feature of protic ionic liquids is the introduction of a more acidic (N-H) proton donor site on the cation.



As protic ionic liquids are derived from a simple acid-base reaction, the ions resulting from proton transfer are therefore in equilibrium with the neutral parent acid and base, with the position of equilibrium depending on the acid and base combination. Use of a strong acid/base will increase the extent of proton transfer, although quantifying this is more difficult. A qualitative estimate of the degree of proton transfer can be obtained by determining the difference in the (aqueous) $\text{p}K_{\text{a}}$ values, $\Delta\text{p}K_{\text{a}}$, between the acid and base. Although there are questions relating to the transferability of aqueous measures of acidity to non-aqueous systems, the work of Angell *et al.* suggests that when $\Delta\text{p}K_{\text{a}} > 10$, proton transfer is nearing completion.¹⁶ Protic ionic liquids formed with strong acids, such as H₂SO₄, would be expected to be largely ionic, whereas those formed from weaker acids, such as carboxylic acids, may have a lower ionicity and a larger percentage of neutral species present. Some protic “ionic liquids” are therefore complicated mixtures of neutral and ionic species and are more correctly ionic liquid analogues. As a guide, MacFarlane and Seddon suggest that less than 1% neutral species should be present for a protic ionic liquid to be considered “pure”.¹⁷

According to the classification scheme represented in **Figure 1.2**, the second major branch of ionic liquids consists of those featuring complexed anions. A complexed anion can be formed when a

small, charge localised, anion, X^- , is “complexed” by a neutral species, N, **Equation 1.2**. The ionic liquids with anions formed in this manner are referred to here as *complex* ionic liquids. As indicated in **Figure 1.2**, a simple ionic liquid with a small anion, such as chloride, can be turned into a complex ionic liquid through the addition of a complexing agent.

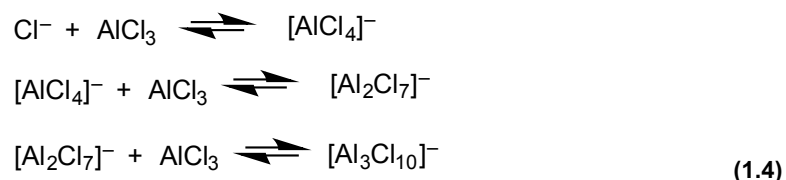


Subdivision of the complex ionic liquid class can be achieved on the basis of the nature of the neutral complexing agent, N, typically a Lewis or Brønsted acid. A key characteristic of a complex ionic liquid is the existence of a complicated set of equilibria governing the anionic speciation, dependent on the identity and mole fraction of the complexing agent. Consequently, unlike simple ionic liquids, more than one anionic species could be present. Understanding the anionic speciation is therefore key to understanding the bulk physical properties of these ionic liquids, from phase behaviour, to acid/base properties.

Traditionally the complexing agent has been a Lewis acidic metal halide, MX_y . The term halometallate is frequently used to describe ionic liquids formed from the eutectic mixture of an organic salt and a metal halide according to the generalised reaction, **Equation 1.3**.¹⁸



The identity of the anionic species present will depend on the Lewis acidity and mole fraction, χ_m , of the metal halide. Representative equilibria for a chloroaluminate system ($MX_y = AlCl_3$) are shown below, **Equation set 1.4**. As $AlCl_3$ is added to the organic chloride salt, $[AlCl_4]^-$ is the only complexed anion to form when $\chi_m(AlCl_3) < 0.5$. Above $\chi_m(AlCl_3) = 0.5$, a complicated mix of larger complexed anions are predicted to exist, as shown in **Figure 1.3** for the archetypal $[C_2C_1im]Cl-AlCl_3$ system.¹⁸ Only when the mole fraction of $AlCl_3$ is exactly 0.5 is there predicted to be only one anionic species present. As the $\chi_m(AlCl_3)$ increases to > 0.5 , there is insufficient Cl^- present to convert all $AlCl_3$ into $[AlCl_4]^-$. Conceptually, one can think of chloride as having to be “shared” between more $AlCl_3$ units (e.g. $AlCl_3 + Cl^- + AlCl_3$), leading to the formation of higher order complexed anions e.g. $[Al_2Cl_7]^-$. The ability to tune the bulk phase properties simply through changing the mole fraction of metal halide is an attractive feature. The melting point, for example, and the well known “W-shaped” phase diagram for the $[C_2C_1im]Cl-AlCl_3$ system is directly attributable to the anionic speciation.^{19, 20} Furthermore, the ionic liquid can be readily changed from being Lewis basic (excess Cl^-) to Lewis acidic (excess $AlCl_3$).¹⁹



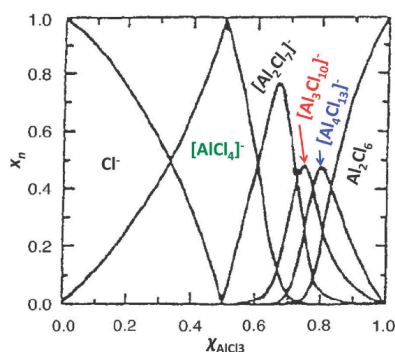


Figure 1.3. The relative fraction of anionic species present in the [C₂C₁im]Cl-AlCl₃ mixture with variation in the mole fraction of AlCl₃ at 200°C. Calculated using a thermodynamic model. Reproduced from Ref. 18 with permission from The Royal Society of Chemistry.

Although the original chloroaluminate ionic liquids remain the most documented, halometallate ionic liquids have been formed using metal halides from across the periodic table. Examples include MCl₃ (M = Ga, In, Fe, Au) and MCl₂ (M = Sn, Fe, Co, Ni, Zn, Cr, Cu).¹⁸ The use of less Lewis acidic metal halides, such as ZnCl₂, results in ionic liquids more tolerant to the air and moisture.²¹ Hydrated metal halides, e.g. CrCl₃·6H₂O,²² have also been employed, another example of a system not strictly meeting the ionic liquid definition.

Whilst the use of Lewis acidic metal halides as complexing agents is more commonplace, a number of examples employing a Brønsted acid to form complexed anions have been published. In contrast to the halometallates, where the interactions leading to complexed anion formation are presumably covalent in nature, the complexed anions formed with Brønsted acids are hydrogen bonded (H-bonded) clusters, generally of the form [A(HA)_x]⁻ (where A⁻ is typically the conjugate base of acid HA). However, akin to the halometallates, complex equilibria, dependent on the identity and ratio of the components are also expected to govern anionic speciation.

For a protic ionic liquid, formed from an acid-base mixture, complexed anions have been shown to form when excess acid is added e.g. [(HSO₄)(H₂SO₄)_x]⁻,²³ [(CF₃COO)(CF₃COOH)_x]⁻,¹⁶ [(CF₃SO₃)(CF₃SO₃H)]⁻,²⁴ and [Br(HBr)_x]⁻.²⁵ However, a Brønsted acid could also conceivably be added to an aprotic ionic liquid. For example, HCl has previously been added to [C₂C₁im]Cl resulting in the formation of complexed anions according to [Cl(HCl)_x]⁻.²⁶ Whether or not such systems are ionic liquids, or ionic liquid analogues, has been questioned.²⁷ The answer to this clearly depends on the extent to which the (neutral) Brønsted acid is complexed.

Interest in protic ionic liquids is rapidly growing, being easy to synthesise and potentially employing low cost starting materials. As with halometallates, the possibility of readily tuning the properties of the ionic liquid simply through altering the ratio of components is a desirable attribute.

Mixtures of base with acetic acid in a 1:1 ratio leads to the formation of a “poor” ionic liquid i.e. of low ionicity.²⁷ One way of conceptualising ionicity is as the effective fraction of ions available to participate in conduction.²⁸ Thus, the equimolar base : acetic acid mixtures are not as ionic as they should be. However, it has been demonstrated for mixtures of *N*-methylpyrrolidine with acetic acid, that the ionicity increases with the addition of excess acid, with a maximum ionicity at a 1:3 ratio.²⁷ This behaviour has been attributed to the formation of complexed anions of the form [(CH₃COO)(CH₃COOH)_x]⁻.²⁷ Relative to the acetate anion, the complexed anions are thought to be

weaker bases, thus driving the equilibrium in **Equation 1.1** to the ionic side. Moreover, using Guttmann acceptor numbers as a measure, it was shown that the Brønsted acidity of mixtures of various bases with H₂SO₄ could be tailored, influenced by both the identity of the base and the mole fraction of H₂SO₄ and thus the anionic species, [(HSO₄)(H₂SO₄)_x][−], present.²³ These examples illustrate the potential tunability of such systems.

For a protic ionic liquid, the properties can also be readily tuned through the addition of excess base.^{29, 30} However, the speciation of such systems is even less well established than the excess acid analogues. The addition of excess base to a protic ionic liquid formed from a polyprotic acid may just lead to deprotonation of the protic anion (e.g. deprotonation of [HSO₄][−] to [SO₄]^{2−}). In theory, there is also the possibility of complexed cation formation. Certainly there are indications of cations H-bonding to excess base molecules. For example, the conductivity of [HHim][NTf₂] was found to increase upon addition excess imidazole.²⁹ This has been attributed to enhanced intermolecular proton transfer through a Grotthuss like mechanism between the cation and neutral imidazole.²⁹ Addition of neutral organic species (e.g. urea, ethylene glycol) to ZnCl₂ has been shown to lead to eutectic “ionic liquid” formation, with systems composed of both complexed cations (e.g. [ZnCl•urea]⁺) and anions (e.g. [ZnCl₃][−]).³¹ However, complexed cation formation is an area that has not been well explored within the ionic liquids field.

The existence of a secondary branch of the Brønsted acid – complex ionic liquid category is intimated within **Figure 1.2**. The systems in question are eutectic mixtures of organic salts with neutral organic species capable of acting as a H-bond donor, typically an amide,³² carboxylic acid³³ or polyol.^{34, 35} Whilst the organic salt could be a simple ionic liquid, such as [C₂C₁im]Cl,³⁶ quaternary ammonium halides (with higher melting points) are usually employed. The neutral “H-bond donor” species is thought to act as a complexing agent and binds to the anion of the salt, reducing the cation – anion interaction, resulting in a decrease in the melting point of the system.³⁷ A pictorial representation of this speciation is shown for the archetypal choline chloride – urea system in **Figure 1.4**. The resultant liquid, or low melting point solid, has similar physical properties to a more conventional simple ionic liquid, but an unknown concentration of neutral species.³⁷ These ionic liquid analogues have been termed deep eutectic solvents (DESs).³³ Within the literature, the term DES is used to apply to a wider range of systems,^{31, 37} but will be taken here to explicitly refer to eutectic mixtures of an organic salt with a neutral H-bond donor species.

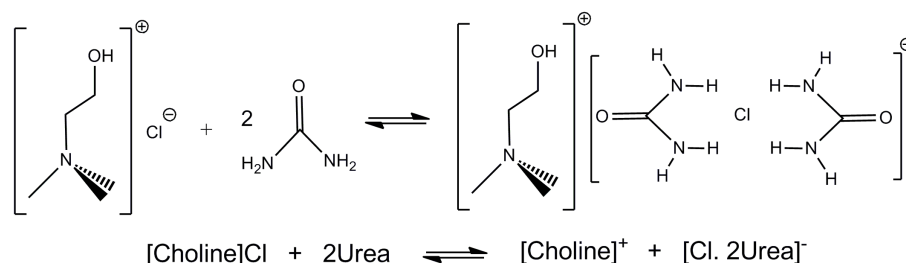


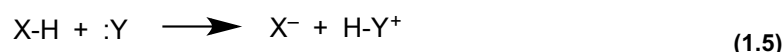
Figure 1.4. Possible speciation within the choline chloride - urea DES at the 1:2 eutectic composition.

Many of the commonly employed quaternary ammonium salts and neutral H-bond donor species are bulk commodity chemicals, choline chloride and urea being prototypical examples.³² Therefore DESs,

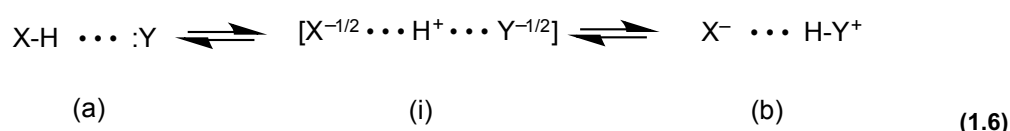
easy to synthesise from cheap, and usually relatively benign starting materials, could be suitable candidates for large-scale industrial applications. Thus, interest in DESs has grown significantly in the last few years, with a continuously diversifying range of applications being explored.^{37, 38}

In terms of classification, is there a difference between these DESs and the aforementioned systems with $[A(HA)_x]^-$ anionic clusters? In both cases a neutral species capable of acting as a H-bond donor, whether that be HCl or urea, is added to an organic salt and through H-bond formation a new anionic species is thought to form. Thus, one could argue that there is no real difference. However, upon consideration of the nature of the complexed anions formed, a possible distinguishing feature can be identified; arising as a consequence of the ΔpK_a difference between the donor and acceptor.

One way of conceptualising the H-bond is as a stage in the proton transfer reaction between the H-bond donor (XH) and the acceptor (Y), e.g. **Equation 1.5**. The position of the H-bond on the proton transfer reaction coordinate will determine whether it is a weak or strong H-bond. A weaker H-bond will correspond to an early stage in the proton transfer, whilst a stronger H-bond will represent a more advanced stage.³⁹



This can be illustrated through examination of the potential energy surface (PES) for the proton transfer reaction. However, first it must be recognised that the proton transfer reaction is an equilibrium between two tautomers, (a) a neutral form ($X-H \cdots Y$) and (b) a (doubly) ionic form ($X:^- \cdots H-Y^+$), passing through an intermediate (i) in which the proton is shared equally between the donor and acceptor (e.g. $[X^{-1/2} \cdots H^+ \cdots Y^{-1/2}]$), **Equation 1.6**. The PESs for different possible H-bond scenarios are shown in **Figure 1.5**.



The shape of the PES for a weak or very weak H-bond is asymmetric with a very high barrier to proton transfer, thus is effectively single-welled. This is shown for form (a), a neutral H-bond, in **Figure 1.5 A**. At the other end, post proton transfer, a weak H-bond between two ionic species may occur, form (b) **Figure 1.5 F**. The PES shown in **Figure 1.5 F** is essentially the mirror image of that shown in **Figure 1.5 A**, in both cases one of the two tautomeric forms is substantially lower in energy than the other, with no mixing between the two forms. Note that a correspondence between the barrier to proton transfer and the H-bond strength has also been identified.^{40, 41}

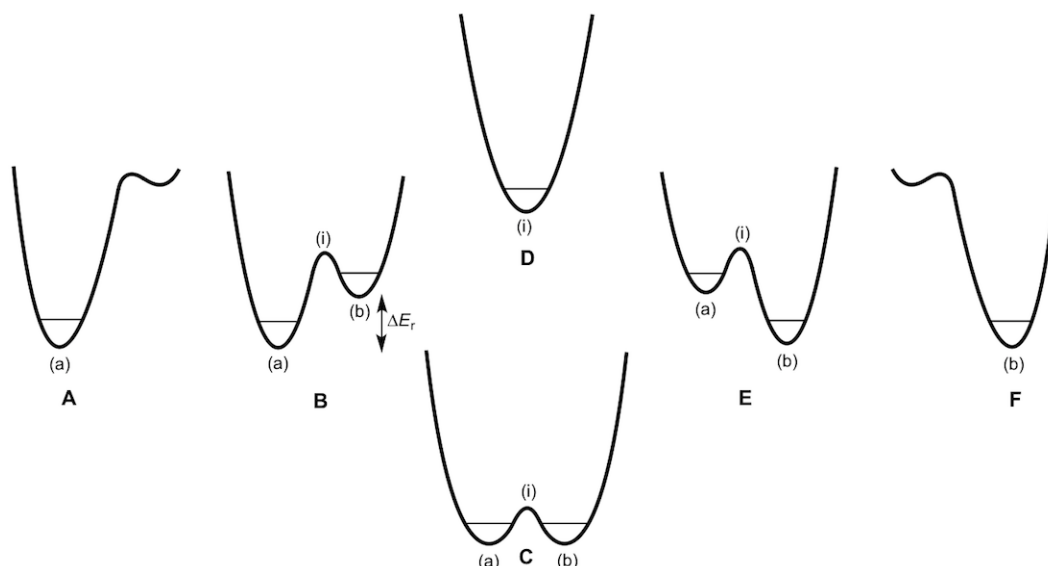


Figure 1.5. Potential energy surfaces for different H-bond types.

However, as the energy difference, ΔE_r , between the two forms decreases, e.g. **Figure 1.5 B and E**, increased mixing between the two tautomers will occur.⁴² This results in a decreased X...Y separation, and consequently a shorter H-bond of moderate strength. Nevertheless, the double-welled PES is still asymmetric, with one of the two forms energetically favoured, i.e. either **Figure 1.5 B or E**.

For the scenario where the two tautomers are isoenergetic, i.e. $\Delta E_r \approx 0$, the mixing between the two forms will be at a maximum.⁴² This could lead to one of two possible PESs, the first being double-welled but symmetric, typically with a low barrier to proton transfer, **Figure 1.5 C**, resulting in strong H-bonds. The second scenario, exhibited by the very strongest H-bonds, is a single-welled PES, in which the “intermediate” (i) with the proton shared equally between the donor and acceptor, is now the minimum, **Figure 1.5 D**.

Therefore, it can be established that the thermodynamic driving force dictating the strength of the resultant H-bond is the energy difference, ΔE_r , between the two tautomeric forms.⁴² However, which physico-chemical variable determines this energy difference?

It has been found that there exists a good correlation between the strength of a H-bond and the difference in pK_a (or gas phase proton affinity, PA) between the H-bond donor and the conjugate acid of the H-bond acceptor, ΔpK_a (where $\Delta pK_a = pK_a(XH) - pK_a(YH^+)$).⁴³ In effect, it has been established that ΔpK_a (or ΔPA) represents ΔE_r , or, in other words, these are just different ways of quantifying the same difference.⁴³ Therefore, to move from a weak to a strong H-bond, ΔpK_a needs to be minimised, with the strongest H-bonds forming when ΔpK_a is negligible. This principle has been termed pK_a “matching”.⁴²

The most common situation in which the pK_a values of the donor and acceptor are matched, that is chemically and energetically equivalent tautomeric forms achieved, is for H-bonds formed between an acid and its conjugate base, where ΔpK_a is zero by definition. This could, therefore, be the case for the $[A(HA)]^-$ complexed anions, formed from the association of an acid and corresponding conjugate base, under consideration.

The gas phase structures of two example $[A(HA)]^-$ anions are shown in **Figure 1.6** together with a proposed reaction coordinate for the proton transfer reaction. The $[Cl(HCl)]^-$ complexed anion, **Figure 1.6 a**, is totally symmetric, with H^+ positioned equidistant between the Cl^- atoms. The associated reaction coordinate is thus single wellled, typical of the very strongest H-bonds. In contrast, the complex formed between H_2SO_4 and $[HSO_4]^-$ in the gas phase, $[HSO_4(H_2SO_4)]^-$ **Figure 1.6 b**, does not exhibit H-bonds with H^+ positioned midway between the donor and acceptor atoms. The reaction coordinate is thus double wellled, albeit symmetric and with a low barrier (calculated here to be $\approx 7 \text{ kJ mol}^{-1}$), also typical of stronger H-bonds.

For our urea-chloride example, however, **Figure 1.6 c**, there is a sizeable difference in the pK_a values (pK_a (amide) $\approx +15-17$ and pK_a (HCl) $= -7$).⁴² Thus, an individual $N-H\cdots Cl$ H-bond within the urea-chloride complex is likely to be early stage on the proton transfer coordinate, with a highly asymmetric PES and a high barrier to proton transfer anticipated. A weaker H-bond is therefore expected.

A difference between the complexed anions in a DES and the $[A(HA)_x]^-$ anionic clusters, could therefore be the extent to which the neutral Brønsted acid is associated in the mixture. However, it is not known how transferrable theories based on aqueous pK_a values, or gas phase proton affinities, are to the ionic liquid environment. Moreover, the established PESs for H-bonds have been developed based on single, linear H-bonds. How is the PES influenced when more complex H-bond motifs are considered? Finally, H-bonding is not the only contribution to intermolecular association, other factors (e.g. electrostatics, dispersion, polarisation) must also be considered in addition to H-bonding. Clearly, there are many questions that remain to be answered in relation to the speciation of these systems.

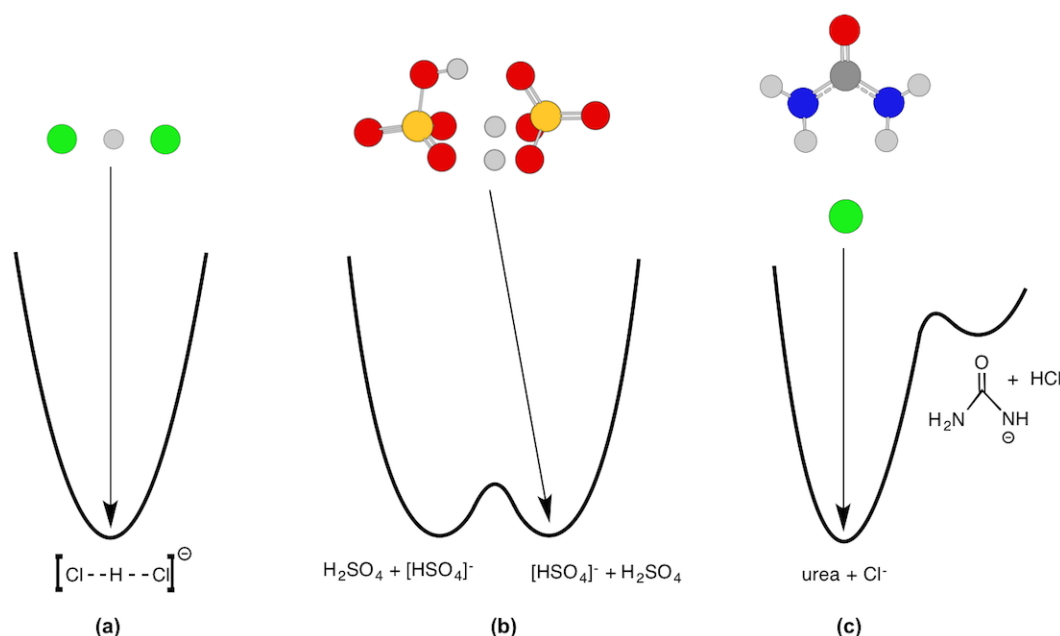


Figure 1.6. Complexed anions (a) $[Cl(HCl)]^-$, (b) $[HSO_4(H_2SO_4)]^-$ and (c) $[urea-Cl]^-$, together with proposed reaction coordinates for proton transfer: $X-H + :Y^- \rightarrow X:^- + H-Y$

1.3 Interactions and structuring within ionic liquids

Elucidating the structure of liquids is vital for understanding both the macroscopic properties and solvation behaviour in the liquid. A range of experimental and theoretical techniques have been employed to investigate structuring in ionic liquids. Key interactions within ionic liquids will first be introduced, followed by a discussion of local cation-anion interactions within the first solvation shell and finally a brief consideration of longer range ordering.

1.3.1 Intermolecular interactions

The structuring, and hence properties, of ionic liquids are governed by a complex interplay of intermolecular forces: electrostatics, dispersion, H-bonding and, for some systems, π type interactions. The subtle balance between these interactions is dependent on the constituent ions. Changes in macroscopic properties of ionic liquids upon ion modification are not always intuitive and unravelling the relative contributions of the different intermolecular forces to rationalise observed phenomenon can be complicated, at times leading to debate within the field.

Electrostatics

The electrostatic interaction is determined to be the major contributor to the total association energy of an ionic liquid.⁴⁴ Symmetry Adapted Perturbation Theory (SAPT)⁴⁵ has been used to decompose the association energy of ion pairs for a small number of systems. For the different configurations of [C₂C₁im]Cl, the electrostatic contribution to the total attractive association energy varied between 75 to 78%.⁴⁶

Although a reduction in the Coulombic association energy has been proposed to explain the lower melting point of ionic liquids relative to higher melting point molten salts, computed association energies of gas phase ion pairs (i.e. one cation and one anion) reveal that for typical ionic liquid ion combinations, the total association energy is still very large, on the order of -300 to 400 kJ mol⁻¹ (for reference, the association energy of a NaCl ion pair is reported as $\approx$ -550 kJ mol⁻¹).⁴⁴ However, within the gas phase there is no attenuation of the Coulomb interaction between the oppositely charged ions, leading to very strong associations. Therefore, gas phase association energies of isolated ion pairs represent an “upper limit”.

Within an ionic solid, each ion will “feel” a Coulomb attraction to all oppositely charged ions and repulsion with all like charged ions. The total Coulombic interaction is the sum of the individual interactions, resulting in a net attraction.⁴⁷ The total lattice energy therefore depends on the charge of the ions (z), the ion separation (d) and the packing arrangement (*via* the Madelung constant, A). The minimum total potential energy (E_P), including consideration of repulsions arising from orbital overlap, can be expressed using the Born-Mayer equation, **Equation 1.7**, where e is the elementary charge, ϵ_0 the permittivity of free space, N_A Avogadro's constant and d^* a constant.⁴⁷

$$E_P = -\frac{N_A |z_A z_B| e^2}{4\pi\epsilon_0 d} \left(1 - \frac{d^*}{d} \right) A \quad (1.7)$$

Within an ionic liquid, each ion will also experience the net effect of the attractive and repulsive interactions with the neighbouring ions. The interactions between any two ions are therefore highly

screened. This charge screening effect has important implications for the behaviour and properties of ionic solutes in ionic liquids.

The point charge model of electrostatic interactions is, however, slightly simplistic. For a more accurate description of the total electrostatic energy, E_{es} , a consideration of higher order multipoles may be required, **Equation 1.8**.⁴⁸ Although, for an ionic liquid the leading term is clearly the first, ion-ion term. Significantly, the interaction of monopoles is both long ranged ($1/r$) and isotropic. This has previously been used to suggest that the electrostatic interactions within an ionic liquid are essentially orientation independent.⁴⁹

$$\begin{aligned}
 E_{\text{es}} = & E_{\text{ion-ion}} + E_{\text{ion-dipole}} + E_{\text{ion-quadrupole}} \dots \\
 & + E_{\text{dipole-dipole}} + E_{\text{dipole-quadrupole}} \dots \\
 & + E_{\text{quadrupole-quadrupole}} \dots
 \end{aligned}
 \tag{1.8}$$

However, ionic liquid ions are typically molecular ions with a complicated charge distribution. For example, the prototypical imidazolium cation has been found to have local regions of both positive and negative charge (at least according to the NBO method).⁵⁰ This anisotropic charge distribution could introduce a degree of orientation and configuration dependence. Moreover, charge transfer from the anion to the cation can lead to a reduction in the total charge on the individual ions, resulting in a reduction in the Coulombic interaction and also influencing the charge distribution within the ions. Therefore, a simple point charge treatment of ionic liquid ions may not recover the subtleties of the electrostatic interactions within these systems.

Induction and Dispersion

While the electrostatic term may determine the overall magnitude of the association energy, induction and dispersion terms are found to be non negligible. The extent to which both inductive and dispersive effects contribute will be dependent on the size and polarisability of the constituent ions, with polarisability determining how readily the electron distribution of a molecule can be distorted in an electric field. There is a correlation between the polarisability of a system and the size of the HOMO-LUMO gap, with a smaller HOMO-LUMO separation corresponding to a larger polarisability.⁴⁷ Typically, larger systems with many electrons will exhibit small HOMO-LUMO separations. This is of relevance to many of the “bulky” constituent species of an ionic liquid.

Induction refers to the distortion of the charge distribution of an entity in the electric field of its surrounding neighbours and is always attractive.⁴⁸ The net electric field felt by the entity is dependent on whether the individual electric fields of the neighbouring species reinforce or oppose each other. Induction is therefore a many-body effect and inherently non-additive. The importance of cooperativity in ionic liquids has been demonstrated, affecting, for example, local structuring, such as H-bonding, interaction energies, dipole moment distributions and partial charges.⁵¹⁻⁵³ Using SAPT, the contribution from induction to the total attractive association energy of $[\text{C}_2\text{C}_1\text{im}]\text{Cl}$ ion pairs is found to be between 10-11%.⁴⁶

Dispersion is quantum in origin, arising from the correlated movement of electrons.⁴⁸ In a classical model this can be represented as an instantaneous dipole on one molecule inducing a dipole

on another molecule, the attraction between the induced dipoles lowering the energy of the system.⁴⁷ With a distance dependence of $\approx r^{-6}$, dispersion effects occur over a much shorter range than ion-ion interactions. Computationally, obtaining an adequate description of electron correlation at a feasible cost can be problematic. However, the importance of accounting for dispersion in QM calculations of ionic liquid systems is now well documented and shall be discussed in more detail in **Chapter 2**.^{54, 55}

A breakdown of the total association energy of both NaCl and [C₁C₁im]Cl using SAPT demonstrated that whilst electrostatics, exchange and induction contribute to both systems, for [C₁C₁im]Cl only is there a contribution from dispersion.⁴⁴ While this could indicate that the presence of dispersion within ionic liquids marks a clear distinction from more traditional ionic salts, it is recognised that even for alkali halides, dispersion does become more important for the larger, more polarisable ions. For example, dispersion may help to explain why caesium halides do not adopt the NaCl crystal structure favoured by most other alkali halides.⁵⁶ Therefore, the importance of dispersion within ionic liquids is consistent with the size and polarisability of the constituent species.

The contribution from dispersion to the total association energy of a single ionic liquid ion pair is estimated to be 5-10%,^{51, 54} but has been shown to increase for clusters built from multiple ion pairs,⁵¹ where a wider range of intermolecular interactions are recovered. Dispersion can be shown to influence structuring, such as the aggregation of alkyl chains into non-polar domains and both cation – cation (i.e. $\pi^+ - \pi^+$) and cation – anion interactions.^{57, 58}

The combined influence of induction and dispersion on the potential energy surface (PES) could be central to rationalising physical properties of ionic liquids. As part of the SAPT analysis of NaCl and [C₁C₁im]Cl, the interaction energy, and individual contributions to the interaction energy, were examined as a function of distance from the equilibrium geometry.⁴⁴ It was found that the minimum in each of the contributing terms for NaCl coincided with the equilibrium position. In contrast, for [C₁C₁im]Cl the equilibrium distance was found to be shifted to smaller distances with respect to the minimum in the electrostatic component (i.e. the equilibrium position is within the repulsive regime of the hypothetical, purely electrostatic potential). Thus, unlike for NaCl, the dominating electrostatic interactions within [C₁C₁im]Cl do not exclusively determine the equilibrium structuring. It is suggested that the overall “compensation” of the interactions within the ionic liquid leads to a flatter potential, thus increasing the flexibility, and “liquid-like” nature, of the system. A shallower potential in the repulsive region is possibly linked to lower melting points.

Further links between the dispersion component and macroscopic properties of ionic liquids have been identified. Correlations between computed association energies of gas phase ion pairs and experimentally determined melting points are known to be poor. However, an improved correlation with the melting point can be established when the *ratio* of the association energy to the dispersion component of the ion pair is instead considered.⁵⁹ Furthermore, the dispersion component of the ion pair association energy has been found to correlate with selected transport properties (viscosity and conductivity).⁵⁹ In contrast to the long range Coulombic interactions, the shorter range dispersion interactions could be significantly perturbed by ion motion. Therefore, some correlation with the transport properties should perhaps be anticipated. A more accurate description of the transport

properties of [C₂C₁im][SCN] using *ab initio* MD with an improved treatment of dispersion has also been reported.⁵⁷

Electrostatic forces and dispersion are also intrinsic to other types of non-covalent interaction of significance within ionic liquids, including H-bonding and, where relevant, interactions with aromatic π systems.

Hydrogen Bonding

H-bonding has a long history of being a divisive subject. However, the view of H-bonding as an entirely electrostatic interaction has been dispelled, with it now recognised that there are electrostatic, dispersion and covalent contributions to a H-bond.⁶⁰ The nature of H-bonds is discussed in more detail in **Chapter 1, Section 2**. The existence of H-bonds within ionic liquids is now well documented, evidence of H-bond formation having been obtained from a range of sources, including: X-ray diffraction, mid and far infrared spectroscopy, NMR spectroscopy, MD (*ab initio* and classical) and QM calculations.⁶¹⁻⁶⁸ The influence of H-bonds on the properties of ionic liquids, however, is still debated within the community. Nevertheless, it is generally understood that H-bonding does play some role in the structuring, networking and, therefore, properties of ionic liquids.

Within an ionic liquid, the H-bond donor is typically the cation and the H-bond acceptor, the anion.⁶⁹ For an aprotic ionic liquid, the most common donor functionality is therefore C-H, often thought of as a relatively poor H-bond donor within the established H-bond field. There are a wide range of possible anions, however, the H-bond acceptor atom tends to be a halogen, N, O, or possibly, S. For a protic ionic liquid, a more acidic N-H donor unit is introduced. Moreover, both the cation and anion could potentially be functionalised, allowing for the introduction of further common H-bond functionalities, such as O-H and COOH.

Many ionic liquid cations have multiple H-bond donor sites, albeit of primary and secondary importance. With the exception of the simplest halide anions, ionic liquid anions are multivalent, with multiple potential H-bond acceptor sites. A recurring observation, both within the literature and this work, is the propensity for the formation of more complex H-bond motifs within ionic liquids; bifurcated and chelated H-bond motifs are common occurrences.⁶¹ In contrast, the formation of single, linear H-bonds, at least within unfunctionalised aprotic ionic liquids, is rare. The potential to form multiple H-bonds also introduces the possibility of H-bond networking.

For some time it has been recognised that H-bonding in ionic liquids is “different” compared to H-bonding in conventional molecular solvents. However, a deeper understanding of those differences is only now beginning to be developed. Given that the H-bond donor and acceptor species are usually not the same, there is the potential for a more chemically diverse range of H-bond functionalities within ionic liquids. Furthermore, it has been established that H-bonding within an ionic liquid is often less directional than in a molecular solvent. For example, the conventional angle based criteria for assessing H-bonds within MD simulations has been shown to be insufficient for capturing all H-bonding within ionic liquids.^{61, 70, 71} Thus, a wider angle distribution is now employed. The main exceptions to this are protic ionic liquids, where the introduction of a stronger N-H donor group can lead to greater directionality in the H-bond interactions.^{72, 73}

More fundamentally, the H-bonds within a molecular solvent are formed between two neutral molecules, within an ionic liquid, H-bonding occurs between two charged species. Thus, H-bonding within an ionic liquid is of the *doubly ionic* type.⁶¹ Understanding how the charge of the donor and acceptor influences the properties of the H-bond formed is a challenge. Whilst both neutral and ionic H-bonds (i.e. the H-bonds formed between two neutral and, one charged and one neutral species, respectively) have been extensively investigated in the literature, the doubly ionic H-bond has largely been overlooked. A recent review of H-bonding within ionic liquids establishes that the doubly ionic H-bond shares many basic similarities with neutral H-bonds, but also exhibits a number of unique features.⁶¹ A more in depth discussion of the nature of neutral, ionic and doubly ionic H-bonds is undertaken in **Chapter 1, Section 2**.

Determining the contribution of H-bonding to the total association energy, and establishing the individual strengths of the H-bonds, is problematic. For neutral H-bonded systems, the total association energy of a H-bonded complex is often used as a measure of the energy of the H-bond.⁷⁴ For a doubly ionic H-bond, the total association energy will obviously be much larger and dominated by the Coulombic contribution. Moreover, theoretical methods, such as SAPT, used to partition the total association energy into contributing terms, do not explicitly account for H-bonding.

Estimates of the H-bond contribution to the total association energy have been obtained for a small number of systems through comparison of the computed gas phase association energies of related ion pairs (or larger clusters) with, and without, appreciable H-bonding interactions e.g. comparison of $[\text{NC}_1\text{C}_1\text{C}_1\text{H}][\text{NO}_3]$ with $[\text{NC}_1\text{C}_1\text{C}_1\text{C}_1][\text{NO}_3]$. For the protic $[\text{NC}_1\text{C}_1\text{C}_1\text{H}][\text{NO}_3]$ system at the B3LYP/6-31+G(d) level, the H-bond contribution is estimated to be approximately 10% of the total association energy.⁷⁵ This is consistent with the earlier estimates of 10 and 16% for aprotic and protic tetramethylimidazolioium $[\text{NTf}_2]$ systems, at the lower HF/3-21G level.⁷⁶ Thermodynamic cycles have been employed to evaluate the ionic and H-bonding contributions within ion pairs of guanadinium chloride, $[\text{C}_1\text{C}_1\text{im}]\text{Cl}$ and $[\text{NC}_1\text{C}_1\text{C}_1\text{H}]\text{Cl}$ at the MP2/aug-cc-pVDZ level.⁶¹ The H-bonding contributions were estimated to be 23, 25 and 13% respectively.

For many practical applications, however, only a qualitative estimate of the capability of an ionic liquid to donate or accept H-bonds is required. For this purpose, the Kamlet-Taft α and β parameters, corresponding to H-bond acidity and basicity respectively, are commonly employed. The Kamlet-Taft linear energy solvation relationship is an empirical polarity scale, of which α and β are constituent parameters.⁷⁷⁻⁷⁹ The Kamlet-Taft parameters are usually determined by measuring the solvatochromic shift in the absorption spectra of a set of probe dye molecules, although, more recently, a number of computational descriptors for the prediction of α and β have been proposed.⁸⁰ Using the Kamlet-Taft approach, the relative H-bonding ability of ionic liquids can be established.^{69, 81} Whilst there must clearly be a connection between α and β values and the strength of H-bonds *within* an ionic liquid, establishing a direct correlation between computed properties of H-bonds within ion pairs and, for example, β , is not straightforward.⁸²

Unequivocally establishing the influence of H-bonding on the properties of ionic liquids is also a complex issue. There is significant evidence to indicate that H-bonding influences local structuring, at the very least in a secondary manner, if one takes the Coulombic interaction to be the primary

structural driver. Therefore, it is reasonable to assume that H-bonding must, to some degree, influence physical properties, such as viscosity, as well as chemical properties, such as the ability of an ionic liquid to interact with a solute. In terms of rationalising physical properties of ionic liquids on the basis of H-bonding there is some debate in the field, although, there does now appear to be a general agreement that H-bonding does have a secondary influence.

As one example, the influence of H-bonding on the properties of $[\text{C}_4\text{C}_1\text{im}]\text{Br}$ has been investigated using MD, with the results suggesting that H-bonding influences the dynamic properties in a “secondary or indirect manner”.⁷¹ Within classical MD simulations H-bonding is a purely electrostatic interaction, therefore altering the atomic partial charges allows the H-bonding ability to be modulated; either increased or decreased. Overall, it was found that H-bonding had a significant effect on local structuring, but a weaker effect on the dynamic properties (diffusion and viscosity). For example, compared to the structuring, a more significant change in the H-bonding ability was required to observe an effect on the diffusion coefficient.

The link between H-bonding and viscosity, in particular, has been a controversial issue. A reduction in H-bonding might be expected to lead to a reduction in viscosity. In numerous cases such a rationale would appear to hold. For example, there is a strong link between the composition and viscosity of chloroaluminate ionic liquids. Basic compositions, rich in Cl^- , are more viscous than acidic compositions with larger, and weaker H-bond accepting, anions.¹⁹ A reduction in viscosity upon fluorination of anion alkyl groups would also appear to be linked to a reduction in cation-anion H-bonding.⁸³ In a few cases, *anion-anion* H-bonding may also influence the viscosity. For example, $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ is less viscous than $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$.⁸⁴

However, when a methyl group replaces the most acidic C-H unit of an aprotic dialkylimidazolium cation, e.g. **Figure 1.7**, the opposite is observed, the viscosity is found to increase.⁸⁵ A number of explanations have been proposed to rationalise this phenomenon, all supporting the argument for a secondary influence of H-bonding on properties.

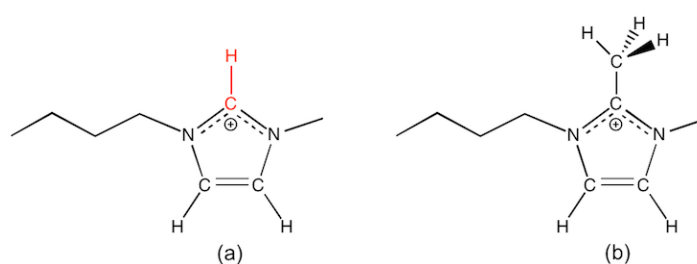


Figure 1.7. (a) $[\text{C}_4\text{C}_1\text{im}]^+$, a typical ionic liquid cation with the most acidic C-H unit depicted in red. (b) $[\text{C}_4\text{C}_1\text{C}_1]^+$, a methylated analogue of $[\text{C}_4\text{C}_1\text{im}]^+$.

One argument is that the introduction of the methyl group leads to a reduction in the number of possible cation-anion configurations and therefore results in reduced disorder and the loss of entropy.⁸⁶ Moreover, as the methyl group is sterically more demanding, it is proposed that this leads to restricted rotation of the longer butyl chain, again resulting in entropy reduction.

However, a Boltzmann distribution of the stable configurations of $[\text{C}_3\text{C}_1\text{im}]\text{I}$ and the methylated analogue, $[\text{C}_3\text{C}_1\text{C}_1\text{im}]\text{I}$, suggests that there is not a significant difference in the conformational space of these systems.⁸⁷ Although, it should be noted that the relative energies of the two lowest energy

configurations of $[C_3C_1im]I$ shows some method dependence, which could influence the Boltzmann distribution. Comparison of the PESs for the interconversion between the stable cation-anion configurations reveals that the protonated form has a number of low energy local minima separated by low energy barriers.⁸⁷ In contrast, the methylated form has much larger energy barriers (greater than the thermal energy) between a reduced number of stable configurations. Similar results have been obtained for the $[C_1C_1im]Cl$ and $[C_1C_1C_1im]Cl$ pair.⁸⁸

In Goldstein's "potential energy barrier picture", it is suggested that the viscosity of a liquid is related to the PES; the number of local minima and the height of the barriers between the minima.⁸⁹ When the barrier heights are below the available thermal energy, the structure can move from one local minimum to another, resulting in a fluid system. The results for the $[C_3C_1im]I/[C_3C_1C_1im]I$ and $[C_1C_1im]Cl/[C_1C_1C_1im]Cl$ pairs could suggest that the higher energy barriers between stable configurations for the methylated systems are the origin of the reduced ion mobility and hence higher viscosity.

An alternative hypothesis is that the formation of H-bonds leads to a disruption of the charge symmetry within the ionic liquids, creating "defects" in the Coulomb network.⁹⁰ It is therefore suggested that increased H-bonding within ionic liquids leads to fluidisation, thus an increase in viscosity upon methylation would be expected. For a series of polymethylated imidazolium ionic liquids, this "defect hypothesis" was used to rationalise trends in the measured melting points, viscosities and enthalpies of vapourisation.⁷⁶

Most of the ideas relating to the links between H-bonding and physical properties, however, have been developed for aprotic ionic liquids. For protic ionic liquids, H-bonding may have an even more significant function.

Many of the physical properties of protic ionic liquids are influenced by the ionicity of the system. Although there is no standard method of determining ionicity, an approach based on the Walden rule ($\Lambda\eta=\kappa$, where Λ is the molar conductivity, η is the viscosity and κ a temperature dependent constant) is commonly employed to provide a qualitative measure.⁹¹ A Walden plot (the plot of the log of molar conductivity against the log of viscosity) can be used to establish the deviation between conductivity and ion mobility. Data for a 0.01M KCl solution, in which the ions are fully dissociated, is often used as a reference. Ionic liquids that show significant negative deviation from ideal Walden behaviour have been termed "poor" ionic liquids,⁹¹ with many protic ionic liquids falling into this category.¹⁶ There is more than one possible explanation for the origin of this behaviour, including, incomplete proton transfer, aggregation with neutral species or strong ion correlation.⁹² In all cases, H-bonding could play a central role.

For protic ionic liquids, partial proton transfer is perhaps the most obvious factor that could result in reduced ionicity. However, quantifying the extent of proton transfer is not straightforward. Based on a relation between boiling point and the difference in the aqueous pK_a values of the acid and base, ΔpK_a , it is suggested that for complete proton transfer within a protic ionic liquid the ΔpK_a needs to be greater than 10.¹⁶ Within an aqueous solution however, it is estimated that for $\Delta pK_a \approx 4$, proton transfer is nearing completion.⁹³ This infers that the solvation environment of the ionic liquid could have a significant effect on the energy of proton transfer.

For mixtures of different acids and bases with similar values of ΔpK_a , it would be expected that the degree of proton transfer is approximately equivalent. However, for mixtures of a range of amines of similar pK_a with acetic acid, this was not found to be the case, with a clear disparity in the behaviour of primary and tertiary amines observed.⁹⁴ Despite similar ΔpK_a values, the resultant systems with primary amines showed behaviour indicative of a significant degree of proton transfer, whilst the tertiary amine systems showed behaviour indicative of a low degree of proton transfer. To explain this observation, differences in the solvation environment of the ions, as a result of differences in H-bonding, was proposed.

An alkylammonium cation has three potential N-H H-bond donor sites, compared to only one for a trialkylammonium cation. Therefore, for the alkylammonium system there is the potential for a larger number of cation-anion H-bond interactions. A graphical representation of the possible differences in the H-bond interactions between an alkylammonium and trialkylammonium system is shown in **Figure 1.8**. The increase in the number of possible H-bond interactions for the alkylammonium system potentially leads to increased stabilisation of the ions, resulting in increased proton transfer. In other words, increased H-bonding in the ionic liquid environment may lead to stabilisation of the ionic tautomer in the proton transfer equilibrium, as indicated in the PES shown in **Figure 1.8 c**.

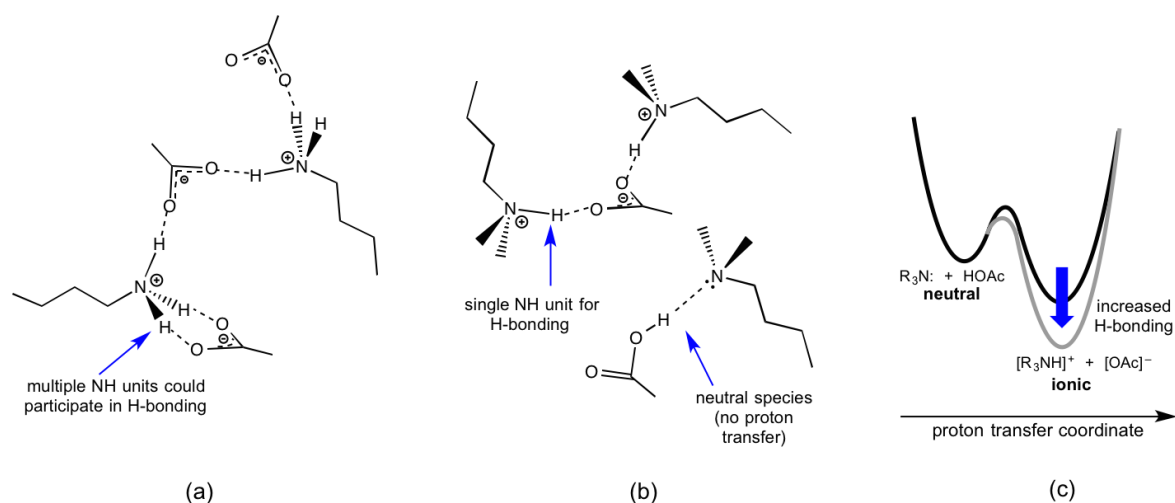


Figure 1.8. A representation of the possible H-bond interactions within an alkylammonium ionic liquid (a) and a trialkylammonium ionic liquid (b). Influence of the ionic liquid environment on the PES for the proton transfer reaction, where R=H or an alkyl group (c).

The conclusion that H-bonding can help to stabilise the ionic species is supported by the finding that, for some systems, the addition of excess acid can lead to an increase in the ionicity through the formation of complexed anions. Such an effect is observed, for example, upon the addition of excess acetic acid to an equimolar mixture of *N*-methylpyrrolidine and acetic acid.²⁷ The complexed anion is stabilised through H-bond interactions, resulting in a weaker base and therefore shifting the equilibrium to favour the ionic, over neutral, species.

However, if aggregation between neutral and ionic species were to occur at the equimolar ratio, then there would be a reduced number of ionic species, compared to the theoretical maximum, which could lead to a lower ionicity. The formation of aggregates at equimolar ratios has previously been

observed for mixtures of amines with carboxylic acids. At the equimolar ratio, the tertiary amine systems examined showed a preference for the formation of aggregates of acid to base ratio 3:1, in the presence of free base.^{95, 96} In contrast, the primary amines showed the preference for the formation of 1:1 acid to base aggregates.^{95, 96} This behaviour could be consistent with the “H-bond stabilisation” argument provided to explain the increased ionicity of alkylammonium systems.

Even for a system with a higher degree of proton transfer, the ionicity could be reduced if the motions of the ions are strongly correlated. A strong association between ions, possibly through ion pair formation or the clustering of ions into larger aggregates, has also been used to rationalise the low ionicity of some aprotic ionic liquids.^{28, 97} From reported examples the association energies of ion pairs of protic systems are often larger than ion pairs for analogous aprotic systems. For example the computed association energy of $[\text{NC}_2\text{C}_2\text{C}_1\text{H}][\text{BF}_4]$ is $\approx 54 \text{ kJ mol}^{-1}$ greater than for $[\text{NC}_2\text{C}_1\text{C}_1\text{C}_1][\text{BF}_4]$.⁷³ The introduction of a stronger H-bond donor (N-H) could contribute to an increase in the association energy. Therefore, the possibility of increased H-bonding within a protic ionic liquid could also result in increased ion association, a factor proposed to reduce ionicity.

More recently, the effect of charge transfer on the ionicity of aprotic ionic liquids was investigated.⁹⁸ Charge transfer leads to fluidisation of the liquid (reduced Coulomb interactions) but also a reduction in conductivity (reduced charge being carried by the ions). Overall, it was suggested that charge transfer effects, in tandem with ion pairing, are needed to explain the lower than expected conductivity of many aprotic ionic liquids.⁹⁸ As partial charge transfer can occur through orbital interaction, as found for H-bond interactions, it would seem logical to suggest that there might be a correlation between the magnitude of charge transfer and the degree of H-bonding within the ionic liquid. However, for the systems investigated, a clear correlation was not established.⁹⁸ Although, as far as can be determined, the extension of this charge transfer concept to protic ionic liquids has not yet been reported.

H-bonding therefore has the potential to increase the ionicity of a protic ionic liquid, increasing proton transfer through stabilisation of the ionic species, but, could also have a negative effect on ionicity, through increased ion association.

H-bonding does not only influence the physical properties of ionic liquids, but also the interactions with solute species. In the capacity of solvent, the ability of an ionic liquid to H-bond with a solute can strongly influence both the solubility and reactivity. The miscibility of some common classes of molecular solvent, such as alcohols, shows a dependence on the H-bonding ability of the ionic liquid.² The hydrophilicity of ionic liquids has also been linked to the H-bond accepting ability of the anion.² Moreover, solvent-solute H-bonding is of significance for many potential practical applications of ionic liquids, such as in the dissolution of recalcitrant materials^{9, 99-101} or extraction/separation processes.^{12, 13} For example, the solubility of cellulose has been linked to the H-bond accepting ability of the ionic liquid anion⁹, whereas the extraction of sulphur compounds from fuels using protic ionic liquids was shown to be more dependent on the H-bond donating ability of the cation.¹⁰² It has been recently demonstrated that through tuning the ionic liquid – solute H-bond interactions with the addition of a co-solvent, the solubility of the solute could be tailored and crystallisation initiated.¹⁰³

H-bonding has also been shown to influence the selectivity and rate of certain reactions within ionic liquids. The influence of the H-bond donating ability of the cation on the *endo/exo* selectivity of the Diels Alder reaction is one of the most commonly cited examples.^{104, 105} However, a number of other reaction types have also been found to show a dependence on the H-bonding ability of the ionic liquid.²

The on-going uncertainty in the role of H-bonding on the physical properties of ionic liquids and the significance of H-bonding for many practical applications provides strong justification for the continued exploration of H-bonding within ionic liquids.

π -interactions

Some of the most common ionic liquid cation families, including imidazolium and pyridinium, are heteroaromatic species, therefore introducing the possibility of π -type interactions within ionic liquids. Aromatic interactions are a feature of many biological systems and can roughly be divided into three main types: π - π ,¹⁰⁶ cation- π ¹⁰⁷ and anion- π .¹⁰⁸ Within ionic liquids, two main types of π interaction have been recognised: a π^+ - π^+ interaction between two cations or an anion- π^+ interaction, with π^+ used here to refer to the π system of a cationic species.¹⁰⁹

π^+ - π^+ interactions have been seen in a small number of crystal structures (e.g. [C₂C₁im][NO₃],¹¹⁰ [C₂C₁im]₂[SO₄]-H₂O¹¹⁰ and [C₁C₁im][OTf]¹¹¹), observed within MD¹¹² and *ab initio* MD simulations (e.g. [C₂C₁im][X], [X]⁻ = Cl⁻, [SCN]⁻)¹¹³ and inferred from NOE experiments (e.g. [C₄C₁im][BF₄]).¹¹⁴ Moreover, the possibility of anion- π^+ interactions could help to rationalise one of the most favourable anion-imidazolium cation configurations, in which the anion locates above the π system of the ring.¹⁰⁹ Solvent-solute π - π interactions could also influence the solubility of aromatic solutes such as benzene,¹¹⁵ or even more complex systems such as lignin.⁹ Interactions with, and between, π^+ systems, however, show some differences compared to more traditional neutral π systems.

Electrostatics and dispersion are found to be the driving forces leading to the formation and structuring of traditional π - π interactions.¹¹⁶⁻¹¹⁸ Benzene is the prototypical neutral π system. With no dipole moment, the electrostatic contribution to the interaction between two benzene molecules comes from the interaction of the quadrupole moments of the rings.¹¹⁹ The quadrupole moment of benzene arises as a result of the uneven electron distribution; increased electron density above and below the plane of the ring, and reduced electron density around the peripheral edge of the ring, **Figure 1.9 a**. Given the electron distribution, the attractive structural arrangements of benzene dimers are the so-called “T-shape” and “displaced parallel” motifs, **Figure 1.9 b** and **c**.¹¹⁶ A third motif, in which the rings adopt a face-to-face “stacked” structure is repulsive in terms of electrostatics, but is stabilised through dispersion interactions. However, when the quadrupole moment of one of the rings is reversed, e.g. for perfluorobenzene, C₆F₆, the face-to-face stacked structure is electrostatically favoured, **Figure 1.9 d**.¹¹⁹ Nevertheless, even for benzene, where the stacked structure is an energetic saddle point, the energy differences between the three configurations is relatively small,¹¹⁷ the result of the interplay between the electrostatic and dispersion effects. Deficiencies in the purely electrostatic model are

particularly evident when considering the influence of substituents (e.g. electron withdrawing vs. electron donating) on the structuring, with dispersion identified as playing a key role.¹¹⁸

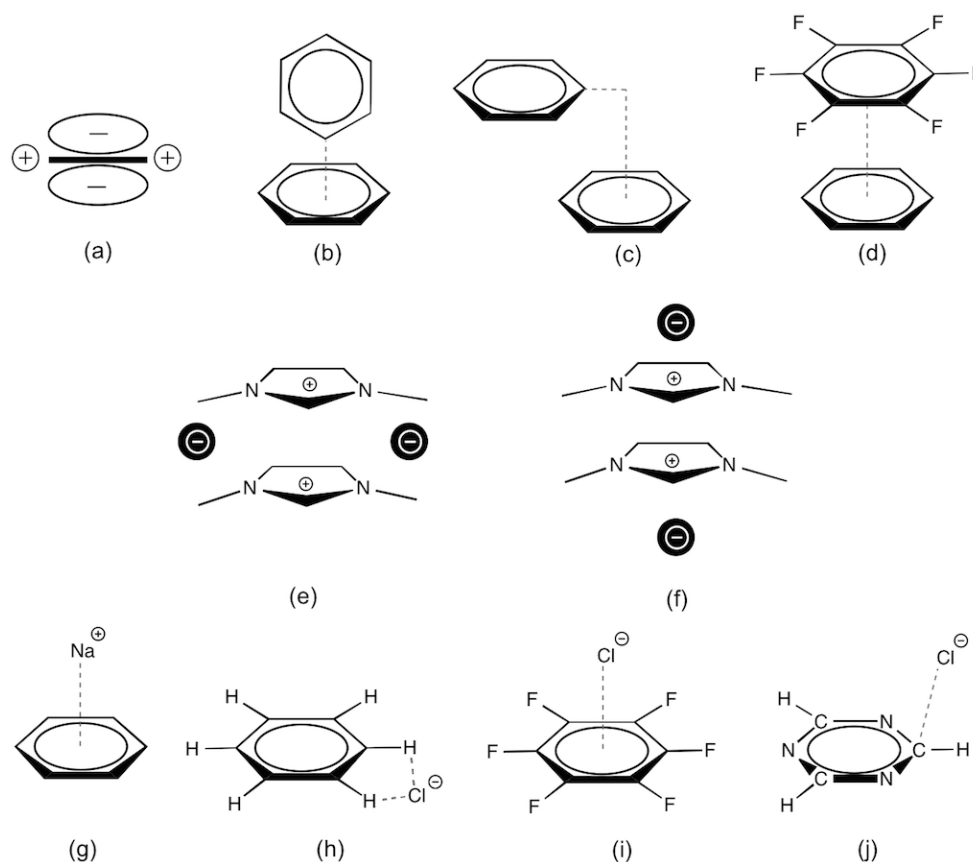


Figure 1.9. (a) A simplified representation of the quadrupole moment within benzene. π - π structural arrangements: (b) T-shape, (c) displaced parallel and (d) stacked. Possible imidazolium $\pi^+-\pi^+$ structures (e) and (f). Stable cation- π arrangement with the cation above the centre of the ring (g). Possible anion – arene binding motifs: (h) H-bonding with C-H groups of the ring, (i) anion above the ring centroid or (j) anion above the periphery of the ring.

The most notable difference with cationic $\pi^+-\pi^+$ interactions is the introduction of permanent monopoles, resulting in a large repulsive Coulombic force between the charged rings. Possible $\pi^+-\pi^+$ motifs include variations of stacked, displaced and T-shaped.¹⁰⁹ However, inclusion of counter ions is necessary to reduce the Coulombic repulsion.^{109, 120} An example of both a low energy and a high energy $\pi^+-\pi^+$ configuration for an imidazolium dimer is provided in **Figure 1.9 e** and **f** respectively. In both examples, the motif is stabilised through charge screening *via* inclusion of the counterions. Cation – anion H-bonding may also play a role in the stabilisation of $\pi^+-\pi^+$ interactions within ionic liquids.

Two other key types of π interaction within the field of supramolecular chemistry are the cation- π and anion- π interactions. For a typical neutral aromatic system, positively charged species can interact favourably with the π cloud, sitting above the plane of the ring, **Figure 1.9 g**.¹⁰⁷ In contrast, anionic species preferably locate in the plane of the ring, forming H-bonds, **Figure 1.9 h**. Generally, only when the π system is electron deficient (e.g. C_6F_6) are anions found to locate above the π system, **Figure 1.9 i**. For both cation- π and anion- π interactions, induction is found to make a sizable

contribution to the stabilisation.^{121, 122} Dispersion however, is of more significance for anion- π interactions, increasing for larger anions.¹²¹

Whilst much attention has been focussed on the anion- π motif with the anion above the ring centroid, an additional structural motif, with the anion located above the periphery of the ring has also been observed.¹²³ In these “displaced” structures, the anion is often found to locate above a C-H unit of the ring, e.g. **Figure 1.9 j**. Whilst analysis of the Cambridge Structural Database for anion- π interactions shows dependence on the search criteria, there are indications that the displaced structure is much more common than the centred anion- π structure.¹²³ Moreover, a review of computed centred anion- π structures *circa* 2008 revealed that 50% of the reported structures were not true minimum.¹²³ In some of these cases it has been acknowledged that, without symmetry constraints, the anion undertakes “nucleophilic attack” at one of the ring carbon centres, suggesting formation of a displaced motif.¹²¹

Therefore, for arene-anion combinations there is the possibility of three structural motifs, a centred anion- π interaction, a displaced interaction or an in-plane H-bonded interaction. The relative stability of these motifs, or even whether the structures are minima, is highly dependent on the arene-anion combination. For some systems, such as 1,3,5-triazine with the chloride anion, all three motifs can be located as stable minima e.g. **Figure 1.10**, with the displaced motif energetically favoured.¹²⁴ However, for 1,3,5-triazine with bromide, the centred anion- π motif is reported to be the lowest in energy.¹²⁴

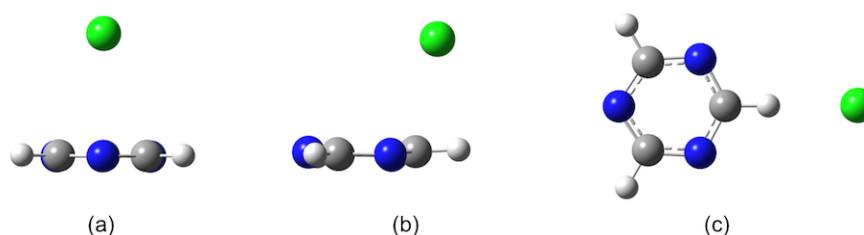


Figure 1.10. Examples of anion-arene structural motifs, shown here for the 1,3,5-triazine and chloride combination: (a) centred anion- π , (b) displaced and (c) in-plane H-bonded motif. Structures optimised here at the MP2(full)/aug-cc-pVDZ level.

In terms of the nature of the displaced structure, there is some debate over whether or not this is an example of an anion- π interaction. With the most nucleophilic anions, e.g. fluoride, nucleophilic attack at a carbon centre leading to the formation of an anionic σ complex occurs, akin to the formation of a Meisenheimer intermediate in the S_NAr reaction.¹²³ Such structures are identifiable by the short C-X bonds, typical of a covalent interaction, and the change from sp^2 to sp^3 hybridisation at the carbon centre. The displaced structures, formed with less nucleophilic anions, exhibit longer C-X distances and no change in the hybridisation of the carbon centre, suggesting that a new covalent bond has not formed.¹²³ However, there is evidence to indicate that the displaced motif has a larger covalent contribution than the centred anion- π motif.

Visualisation of electron density isosurfaces allows for the maximum electron density, $\rho_{\max}$, between two interacting species to be determined. The magnitude of $\rho_{\max}$ has been linked to the covalency of an interaction, with a larger value indicating a higher degree of covalency. For the

centred anion- π motif, $\rho_{\max}$ is found to be $< 0.012 \text{ e}\text{\AA}^{-3}$ in the cases examined (at the MP2/aug-cc-pVDZ level).¹²³ For reference, covalent bonds typically have $\rho_{\max} > 0.1 \text{ e}\text{\AA}^{-3}$.¹²³ The $0.012 \text{ e}\text{\AA}^{-3}$ isodensity surface for the centre anion- π 1,3,5-triazine chloride structure is shown in **Figure 1.11 a**. It is evident that there is a discontinuity in the isosurface in the region between Cl^- and the ring plane. In contrast, the $0.012 \text{ e}\text{\AA}^{-3}$ isodensity surface for the displaced analogue is continuous, **Figure 1.11 b**, and does not show a discontinuity until $\approx 0.018 \text{ e}\text{\AA}^{-3}$, suggesting an enhanced covalent contribution to the interaction.

Molecular orbitals (MOs) are also useful for assessing the covalency of an interaction. Limited interaction between the orbitals of two fragments is indicative of an interaction with minimal covalent contribution. Minimal fragment orbital interaction has been used to support the argument for the centred anion- π interaction as an essentially non-covalent interaction.¹²³ For example, a bonding and antibonding MO combination for the 1,3,5-triazine – chloride pair is shown in **Figure 1.11 c**. The antibonding HOMO-2 is clearly dominated by a contribution from a 3p AO of chloride, whilst the bonding, HOMO-8, is dominated by the triazine π system. However, in other cases, slightly more significant fragment orbital interactions have been observed, which could indicate an increased covalent contribution, particularly for larger anions.^{121, 123, 125} Typically the two fragment orbitals are occupied, resulting in the formation of an occupied bonding and antibonding pair, which has been interpreted by some as resulting in an overall non-bonding interaction and not as evidence for a covalent contribution to the anion- π interaction.^{108, 125} However, this interpretation may require further validation. Interactions between occupied fragment orbitals are not unknown, potentially also occurring in some H-bonded systems.⁶¹

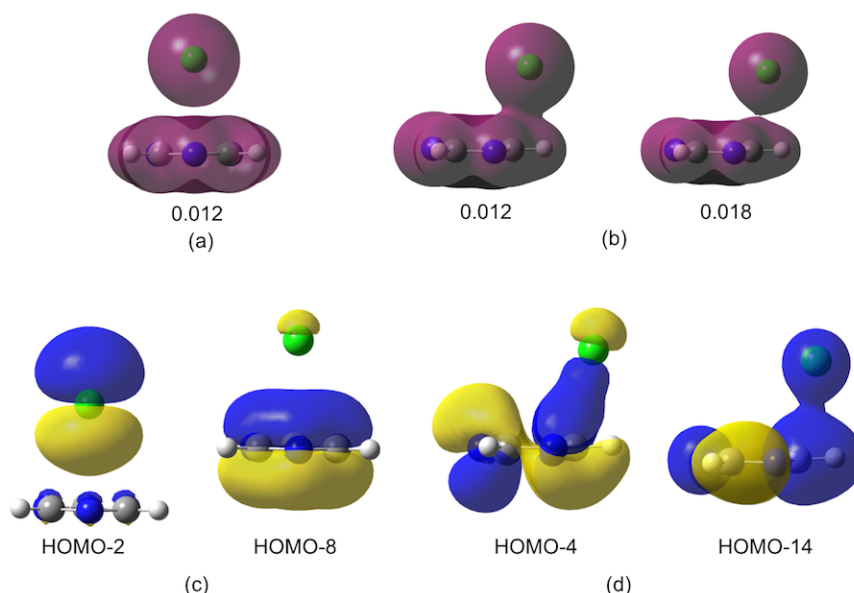


Figure 1.11. Analysis of the centred anion- π and displaced 1,3,5-triazine-chloride structural motifs (at the MP2(full)/aug-cc-pVDZ level). Electron density isosurfaces for (a) centred anion- π and (b) displaced motifs. Electron density reported in $\text{e}\text{\AA}^{-3}$. Selected MOs for (c) centred anion- π and (d) displaced motifs. MOs generated at the $0.02 \text{ e}\text{\AA}^{-3}$ isosurface.

For the reported examples of the displaced motif, there is greater orbital interaction between the two fragments.¹²³ Exemplars of bonding MOs for the triazine-chloride example are shown in **Figure 1.11 d**. The HOMO-4 shows a directional interaction between a 3p AO of Cl⁻ and the π -manifold, whilst the HOMO-14 reveals a much deeper energy interaction between the 3s AO of Cl⁻ and the σ -manifold of the ring. Therefore, the MOs are indicative of an increased covalent contribution to the displaced motif.

Evidence of charge transfer for anion-arene complexes in solution has been obtained through UV-Vis spectroscopy.^{108, 123} The appearance of charge transfer bands in the visible region is indicative of donor- π -acceptor interactions. The enhancement of electron donor π -acceptor charge transfer for the displaced structural motif has also been validated using TD-DFT.¹²³ An increase in charge transfer is consistent with increased orbital interaction and a more significant covalent contribution.

Owing to the increased covalency, it has been suggested that the displaced motif is not an example of an anion- π interaction, which is argued should be non-covalent¹²³ on the basis of the early definition of the anion- π interaction as belonging to the “non-covalent” family of interactions.¹²⁶ As the MOs, e.g. the HOMO-4 **Figure 1.11 d**, are of σ symmetry, it has been suggested that the displaced structure be termed a weak σ interaction.¹²³ Similar discussions can be found within the cation- π field, where a consideration of MOs and thus degree of covalency, led to the introduction of the term cation- π *bonding* to distinguish from the (non-covalent) cation- π *interaction*.¹²⁷

However, this is perhaps just an issue of semantics and how the anion- π interaction is defined. H-bonds are also considered as “non-covalent” interactions, although it is established that H-bonds can have a variable covalent contribution.⁶⁰ Thus, it seems unreasonable to claim that the displaced motif is not an example of an anion- π interaction because it is “too covalent”. There is clear evidence (e.g. MOs) to establish that within the displaced motif there is an interaction between the anion and the π -system. Herein, an interaction will be considered as anion- π when there is evidence of interaction between the anion and the π system, therefore not limited to the anion situating above the centre of an aromatic ring.

For ionic liquids with heteroaromatic cations, there is the potential for the anion to interact with the electron deficient π system, an anion- π^+ interaction. Examples of anion- π^+ interactions have previously been observed outside of the ionic liquids field e.g. anion interactions with the tropylium cation.¹²⁸ Compared to anion- π interactions, the anion- π^+ interaction will have an enhanced attractive electrostatic contribution. However, as found for the anion- π interactions, the stability of the complexed anion- π^+ motif is dependent on the anion. For the tropylium cation with halide anions, it can be inferred that the stable minima correspond to the displaced motif (or in the case of F⁻, the formation of a σ -complex).¹²⁸ With larger anions, [NO₃]⁻ and [BF₄]⁻, stable centred anion- π structures were located.¹²⁸ However, the multidentate anions were found to bridge between both centred and displaced motifs.

Within imidazolium ionic liquids, there is evidence to suggest the existence of the displaced anion- π^+ motif,^{46, 109, 120} although larger anions may show an increased preference for the centred

anion- π^+ motif.⁸² The nature of anion- π^+ interactions within ionic liquids is discussed in more detail shortly. However, for the displaced anion- π^+ motif, dispersion has been shown to influence the position of the anion above the C-H bond.⁶² As an increasing amount of dispersion is recovered by *ab initio* methods, the anion shifts further toward the carbon atom. This is suggestive of an interaction between the anion and the π cloud of the ring, which would indicate that this structural motif, as found in imidazolium ionic liquids, meets our criteria for an anion- π^+ interaction. Furthermore, the increased preference for larger anions to position above the ring is consistent with an increase in the dispersion interaction.

A further factor to consider is the role of H-bonding. As shall be revealed in the following discussion on local structuring, H-bonds could help to stabilise proposed anion- π^+ configurations.¹⁰⁹ However, when there is the potential for anion- π^+ and in plane H-bonding interactions to co-exist, there may be synergistic effects between the two, e.g. the formation of an anion- π^+ interaction could weaken H-bond interactions.⁸² Such effects have previously been observed for anion- π systems.¹²⁹

Summary

There exists a complex interplay between different interactions within an ionic liquid, including electrostatics, dispersion, induction, H-bonding and π -type interactions. The electrostatic interaction between monopoles is the primary intermolecular force within a traditional salt. Dispersion, H-bonding and the interaction between higher order multipoles (e.g. dipole-dipole) are common intermolecular forces within a molecular solvent. In terms of intermolecular interactions, an ionic liquid therefore exhibits features of both salts and molecular solvents.

The association of the oppositely charged ions within an ionic liquid is large and dominated by the electrostatic contribution. However, the contribution from dispersion and induction is found to be non-negligible. Together, dispersion and induction could play a key role in influencing the PES, and hence properties, of an ionic liquid. Electrostatics and dispersion are also intrinsic components of other important types of interaction, including H-bonding and π interactions.

Ionic liquids potentially exhibit a wide range of H-bond functionalities and motifs. H-bonding in an ionic liquid is of the doubly ionic type, occurring between two charged species. To date, the doubly ionic H-bond has not been explored in depth. Furthermore, traditional H-bond criteria derived for neutral systems may not always be suitable for assessing H-bonds within an ionic liquid.

For ionic liquids with aromatic cations, $\pi^+-\pi^+$ and anion- π^+ interactions could feature. The repulsive interaction between two π^+ systems is stabilised by the counter ions. The anion- π^+ interaction is electrostatically favoured, however, as with anion- π interactions, more than one stable binding motif may be exhibited.

While the key intermolecular interactions within an ionic liquid have been identified, unravelling the interdependence of the interactions and quantifying the relative contributions to the total association energy remains a challenge.

1.3.2 Local structuring

The ion pair, the combination of one cation and one anion, is the most basic building block of an ionic liquid. Many studies have been undertaken using gas phase ion pairs as a starting point for understanding local cation-anion interactions within ionic liquids.^{46, 49, 50, 59, 66, 87, 130, 131}

The dialkylimidazolium cation is the prototypical example of an ionic liquid cation, with the imidazolium family of cations being the most well studied to date. $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$, **Figure 1.12**, shall be used here to illustrate stable anion configurations with respect to the imidazolium cation.

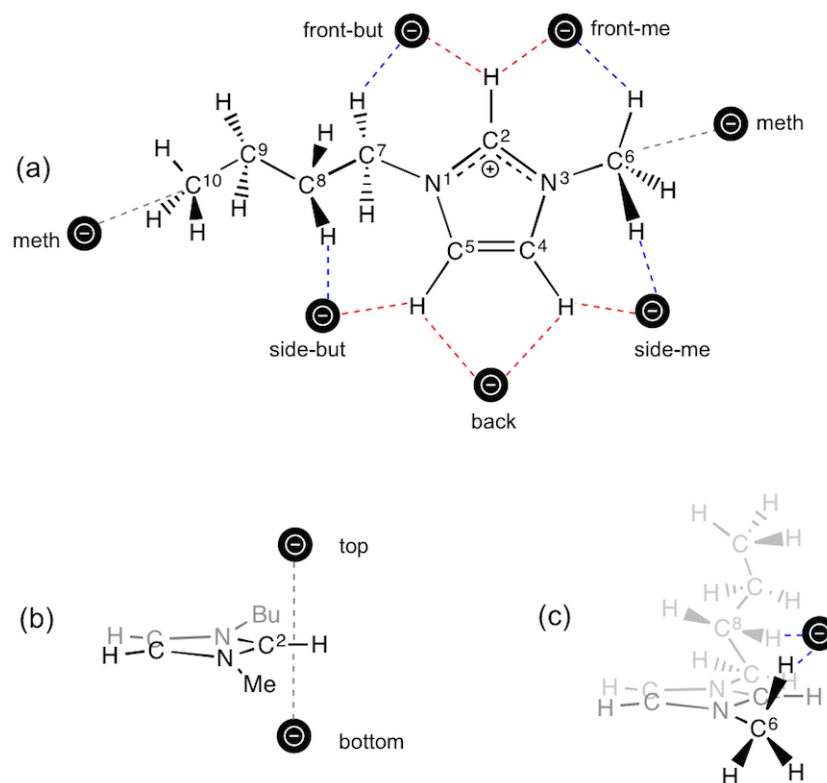


Figure 1.12. A $[\text{C}_4\text{C}_1\text{im}]^+$ cation with the possible anion positions indicated by filled black circles. Five in-plane positions indicated in (a), a simplified representation of the two out-of-plane positions shown in (b) and H-bonding interactions associated with the top out-of-plane position shown in (c). Primary H-bond interactions with ring C-H units depicted in red. Secondary H-bonds with alkyl C-H groups depicted in blue.

An (aprotic) imidazolium cation has a number of potential C-H H-bond donor groups, which can be divided into two main types, of the imidazolium ring, or of the alkyl side chains. The C-H groups of the imidazolium ring are stronger H-bond donors compared to the alkyl C-H units.⁵⁰ Therefore, H-bond interactions with the ring will be termed here as primary H-bonds, with H-bonds with the methyl or methylene groups considered as secondary. Of the ring positions, it is well established that the $\text{C}^2\text{-H}$ unit is the most acidic, and therefore the preferred H-bonding site.¹³⁰

For a dialkylimidazolium cation with two different side chains e.g. $[\text{C}_4\text{C}_1\text{im}]^+$, there are five non-equivalent positions in the plane of the ring that an anion, such as chloride, could “occupy”, **Figure 1.12 a**.^{50, 130} In each case a primary H-bond is formed with the ring. There is a marked deviation from linearity for these primary H-bonds through the formation of additional stabilising secondary H-bond interactions with the alkyl chain. Depending on the conformation of the alkyl chain, a range of

secondary H-bonds can form. However, the alkyl chain can also play a role in restricting anion access to sites about the cation.⁶¹

Two further anion positions are possible, in which the anion “sits” out of plane of the ring, **Figure 1.12 b**. In these top and bottom configurations, the anion locates above or below either the C²-H bond or ring respectively. Whilst small anions, such as chloride, locate above the C²-H bond, larger anions show an increased tendency to locate above the ring plane.¹³² Secondary H-bonds, as shown in **Figure 1.12 c**, also partake in the stabilisation of these out-of-plane-configurations.^{50, 61, 120}

Although the computed relative energies of the ion pair configurations show some method dependence, the top and front configurations are the lowest in energy and are essentially energetically degenerate, with the side positions at $\approx 30 \text{ kJ mol}^{-1}$ and the back position at $\approx 60 \text{ kJ mol}^{-1}$ above the lowest energy configuration.¹³⁰

A further motif, in which the anion interacts with one of the terminal methyl groups, has also been identified, **Figure 1.12 a**. For gas phase ion pairs this motif is very high in energy, $\approx 100 \text{ kJ mol}^{-1}$ above the lowest energy structure. However, a study of gas phase ion pair dimers (i.e. two cations and two anions) suggests that this motif can be stabilised through the formation of additional interactions.¹⁰⁹ Interaction with a terminal methyl group has also been observed within MD simulations.⁶² Within this terminal-meth structure the anion is positioned directly along a C-C or C-N bond vector, consistent with the recently proposed “carbon bond” interactions.

Although usually very close in energy, the nature of the front and top interactions is established to be different. It is recognised that the front structure is a H-bonding motif, whereas the top structure could be an example of an anion- π^+ interaction.¹⁰⁹

For the front structure, the observation of a red shift in the C²-H stretching frequency is typical of a H-bond interaction.⁵⁰ Moreover, analysis of the MOs of the front structure reveals a fragment orbital interaction between the anion and primary C²-H group. For example, the HOMO-2 of [C₁C₁im]Cl shown in **Figure 1.13 a**, reveals an interaction between a 3p AO of Cl⁻ and a σ^* type C²-H fragment orbital. This MO is dominated by the Cl⁻ AO, consistent with this being a primarily ionic H-bond. Analysis of the partial charge distribution shows that the C²-H unit as a whole is highly positively charged, **Figure 1.13 c**, which could lead to enhancement of the electrostatic contribution to the C²-H...Cl⁻ H-bond.¹³⁰ The computed anion to cation charge transfer is dependent on the charge partitioning method, but is typically slightly greater when the anion is in a front position, than the charge transfer obtained for the side configurations (also H-bonding interactions).¹³⁰

Evidence to support the case for the top structure being an example of an anion- π^+ interaction includes the finding that there is a small (blue) shift in the calculated C²-H stretching frequency, consistent with a donor- π acceptor type interaction.⁵⁰ Depending on the charge partitioning scheme, the total charge transfer is approximately equivalent to, or very slightly reduced, compared to the front structure. Analysis of the MOs further supports the case for an anion- π^+ interaction. The HOMO-3 of [C₁C₁im]Cl, shown in **Figure 1.13 b**, demonstrates the interaction of a 3p AO with the π system of the imidazolium ring. This interaction is analogous to that shown in **Figure 1.11 d** for the displaced anion- π interaction between chloride and 1,3,5-triazine. The influence of dispersion has already been noted.

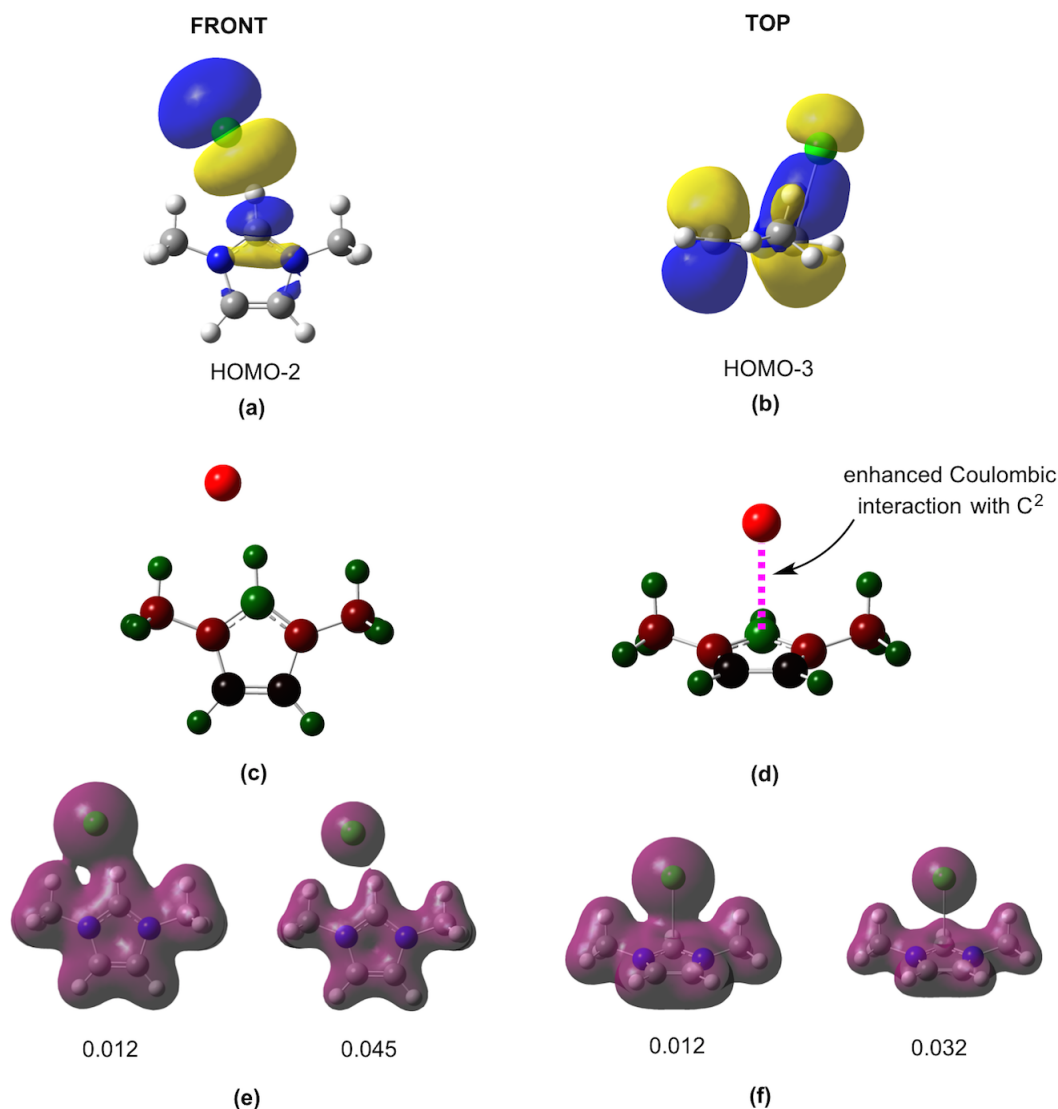


Figure 1.13. Analysis of the front and top ion pair configurations of $[\text{C}_1\text{C}_1\text{im}]\text{Cl}$. Selected MOs generated at the $0.02 \text{ e}\text{\AA}^{-3}$ isosurface, (a) and (b). Partial charge distributions according to the NBO scheme (at the B3LYP-D3/6-311+G(d,p) level), (c) and (d). Red is negative and green is positive. Scale = $\pm 0.85 \text{ e}$. (e) and (f) Electron density isosurfaces computed at the MP2(full)/aug-cc-pVTZ level. Electron density reported in $\text{e}\text{\AA}^{-3}$.

However, the positioning of chloride above the C^2 atom, the most positively charged heteroatom of the imidazolium ring, **Figure 1.13 d**, also points to an increased Coulombic interaction. SAPT analysis of the $[\text{C}_2\text{C}_1\text{im}]\text{Cl}$ top and front configurations suggests that there is a marginally greater electrostatic contribution within the top configuration, in addition to a slightly greater dispersion component. The top configuration does therefore show features characteristic of a (displaced) anion- π^+ interaction, as well as the potential for an enhanced Coulombic interaction.

Visualisation of the electron density isosurfaces shows that, as for the displaced anion- π interactions, the anion- π^+ interaction has a ρ_{max} greater than the suggested “non covalent” cut-off of $0.012 \text{ e}\text{\AA}^{-3}$, **Figure 1.13 f**. Comparison of the values of ρ_{max} for the top $[\text{C}_1\text{C}_1\text{im}]\text{Cl}$ structure ($\approx 0.032 \text{ e}\text{\AA}^{-3}$) with the 1,3,5-triazine-chloride exemplar ($\approx 0.018 \text{ e}\text{\AA}^{-3}$) demonstrates there to be quite a significant increase in the value of ρ_{max} . However, this probably reflects the closer $\text{C}\cdots\text{Cl}^-$ contact within the anion- π^+ system ($2.64 \text{ \AA}$ cf. $2.88 \text{ \AA}$ within the 1,3,5-triazine-chloride example at the

MP2/aug-cc-pVDZ level). Interestingly, a similar analysis for the front structure, **Figure 1.13 e**, shows a further increase in $\rho_{\max}$.

The spatial distribution of chloride anions about the $[\text{C}_2\text{C}_1\text{im}]^+$ cation, as obtained from MD simulations, shows both similarities and differences compared to the gas phase ion pairs, **Figure 1.14 a and b**. The stable anion positions determined in the gas phase are clearly evidenced in the reported spatial distribution functions (SDFs). A higher probability for anion location about the $\text{C}^2\text{-H}$ position is also evident. However, the MD simulations show that anions in the front and side positions can also sit out of plane of the ring. Moreover, the SDFs suggest that the established back position is not occupied in the liquid. An apparent “meth” interaction is, however, identified, **Figure 1.14 b**.

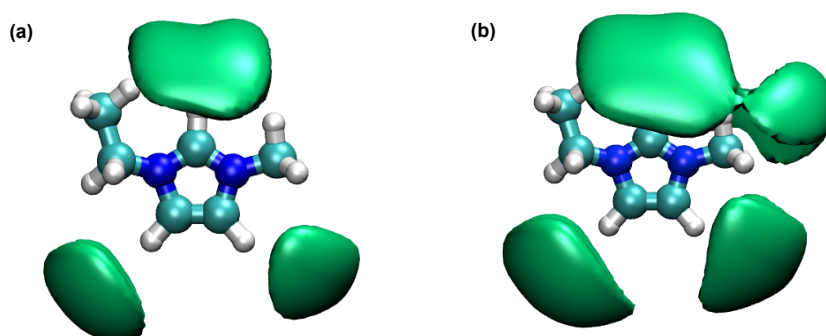


Figure 1.14. Spatial distribution functions from an MD simulation showing the favourable locations of Cl^- around the $[\text{C}_2\text{C}_1\text{im}]^+$ cation (128 ion pairs at 450 K), provided by Dr Richard Matthews (Hunt research group). (a) SDF at 30% above bulk density and (b) SDF at 20% above bulk density.

Simple ion pairs do not, therefore, recover all possible cation – anion interactions of the bulk phase and have been found to lead to an overestimation of the cation-anion interaction. Moreover, with a single ion pair, possible cation-cation, or anion-anion, interactions cannot be examined. However, as computational resources have increased, there has been a move toward higher level investigations of larger aggregates built from multiple ion pairs. For example, a comprehensive study of ion pair dimers of the simple $[\text{C}_1\text{C}_1\text{im}]\text{Cl}$ system has recently been undertaken.¹⁰⁹

Within ion pair dimers, low energy structures with the anions sitting out-of-plane have been identified.¹⁰⁹ For example, one of the key structural motifs established for $[\text{C}_1\text{C}_1\text{im}]\text{Cl}$ dimers features two stacked cations with the anions lying in the mid-plane, stabilising the repulsive Coulombic interaction between the rings e.g. **Figure 1.15**. These results would suggest, perhaps not unsurprisingly, that ion pair dimers are able to recover more structural features of the bulk phase.

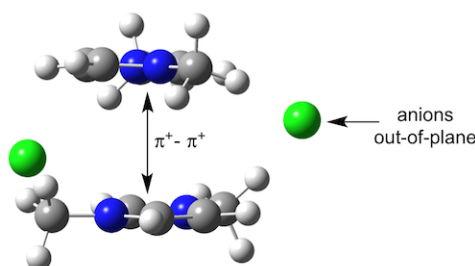


Figure 1.15. Low energy $[\text{C}_1\text{C}_1\text{im}]\text{Cl}$ dimer obtained at the B3LYP-D3BJ/6-311+G(d,p) level. Structure provided by Dr Richard Matthews.

So far in this report, only the situation with the simple chloride anion has been considered. However, the majority of ionic liquid anions are larger, polyatomic species with multiple H-bond acceptor sites, thus introducing an additional level of complexity. Many of these larger anions are able to “bridge” between more than one of the stable anion positions defined in **Figure 1.12** for Cl^- . The larger anions show an increased preference for the top position,¹³³ but can span between both the front and top positions. This can be observed for anions with quite different characters e.g. “spherical” $[\text{PF}_6]^-$, with a low β value, as well as tetrahedral $[\text{C}_1\text{SO}_4]^-$, with a mid β value, **Figure 1.16 b**.

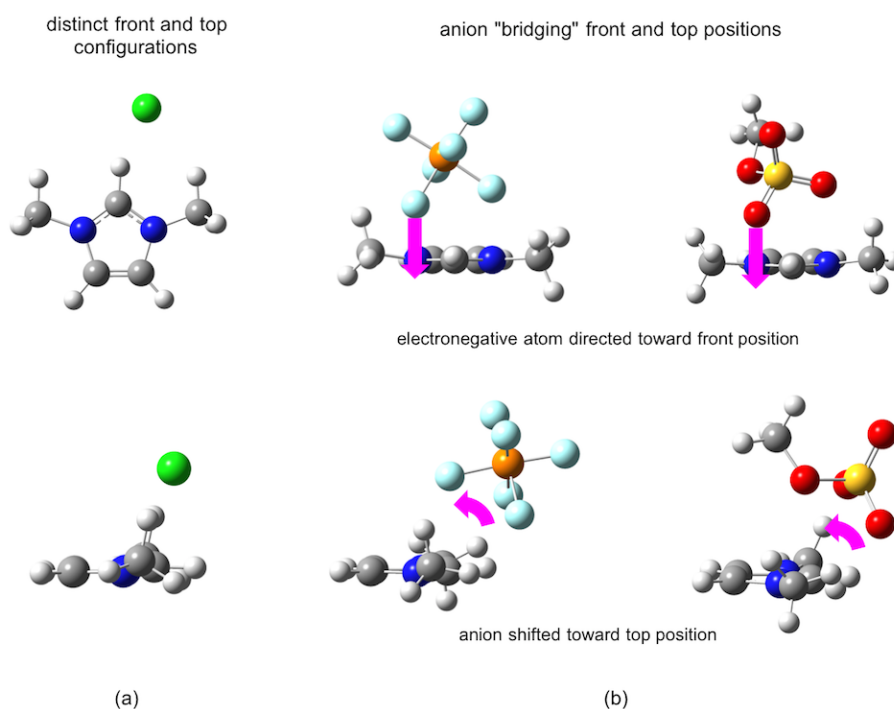


Figure 1.16. (a) Front and top $[\text{C}_1\text{C}_1\text{im}]\text{Cl}$ configurations. (b) Combined front/top ion pair configurations of $[\text{C}_1\text{C}_1\text{im}][\text{PF}_6]$ and $[\text{C}_1\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$. Structures obtained here at the B3LYP-D3BJ/6-311+G(d,p) level.

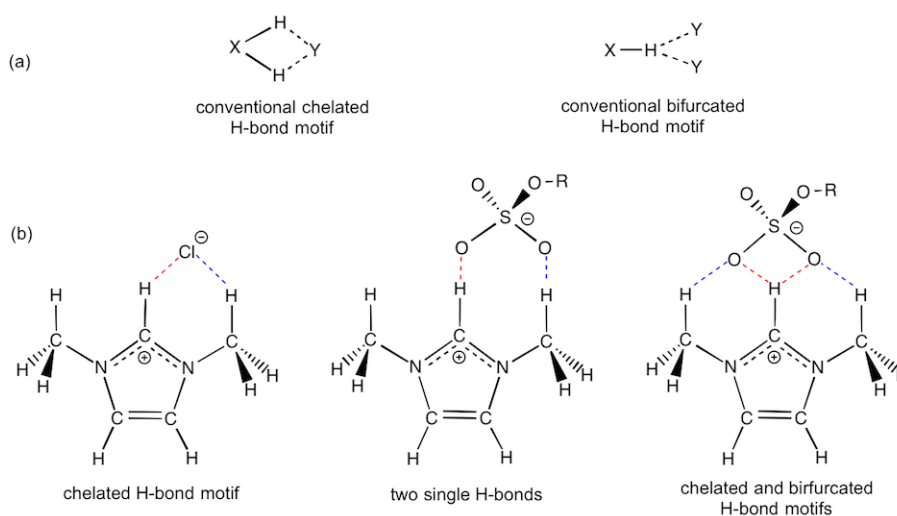


Figure 1.17. (a) Conventional chelated and bifurcated H-bond motifs. (b) H-bond motif variations accessible within ionic liquid systems. Primary H-bonds indicated with red, secondary H-bonds with blue.

The introduction of multiple H-bond acceptor sites on the anion also leads to a wider range of accessible H-bond motifs. $[C_nC_1im]Cl$ systems frequently exhibit a chelated H-bond motif, **Figure 1.17**. With multidentate anions, there is also the possibility of forming multiple single H-bonds as well as mixed bifurcated and chelated motifs, **Figure 1.17**. A variety of different motifs were recently observed within ion pair dimers of $[C_1C_1im]X$ ($X = Cl^-$, $[BF_4]^-$, $[OTf]^-$, $[C_1SO_4]^-$ and $[NO_3]^-$).⁸²

The identity of the cation will, of course, also have a significant effect on the local structuring. Whilst other cation types have been investigated, to date, the number and depth of these investigations is more limited compared to the imidazolium systems. However, of interest to this work is a consideration of how the introduction of an N-H donor unit within a protic ionic liquid influences the local structuring. To date, investigations into structuring within protic ionic liquids have largely been limited to protic ammonium systems. Although both are relatively high melting point solids, tetramethylammonium and trimethylammonium chloride are used here, for simplicity, to illustrate key structural features.

A quaternary ammonium cation can be considered as a tetrahedron with four “faces”, as shown in **Figure 1.18 a** and **b**. Depending on the identity of the four alkyl groups, there may be a chain appended to one, or more, of the four vertices of the tetrahedron. Analysis of the crystal structures of quaternary ammonium salts indicates that anions have a strong tendency to sit at one of the four faces of the cation, **Figure 1.18 b**.¹³⁴ A stable ion pair configuration, with the anion sitting at one of the four faces, is shown for $[NC_1C_1C_1C_1]Cl$ in **Figure 1.18 c**. Similar observations have been made for asymmetric quaternary ammonium cations with a number of different anions in the gas phase.⁷³ For both solid state and gas phase structures it is suggested that occupying one of the four facial positions allows for closer approach of the anion to the cation, thus maximising the Coulombic association.^{73, 134} However, a contribution from dispersion in stabilising these ion pair configurations has also been observed, with some dependence on the length of the alkyl chains.¹³⁵ As far as can be determined, the potential role of H-bonding, despite the evident C-H...X close contacts, has not been fully explored.

For a trialkylammonium cation, there are typically two stable configurations; one in which the anion sits at the remaining face and one in which the anion forms a H-bond with the N-H unit.⁷³ Examples of such configurations are shown for $[N_1C_1C_1C_1H]Cl$ in **Figure 1.18 d** and **e** respectively. The nature of the N-H...X interaction has been studied using, for example, far-infrared spectroscopy combined with DFT calculations.^{135, 136} It has been shown that the N-H...X H-bond is both directional and moderate to strong in strength, dependent on the cation – anion combination.¹³⁷ For example, the isolated N-H stretching frequency for a given cation shows an increased red shift as the H-bond accepting ability of the anion, and therefore the H-bond strength, increases.¹³⁷ The introduction of a more traditional, linear H-bond is a marked difference from the non-linear C-H...X H-bonds more typically observed in aprotic imidazolium ionic liquids.

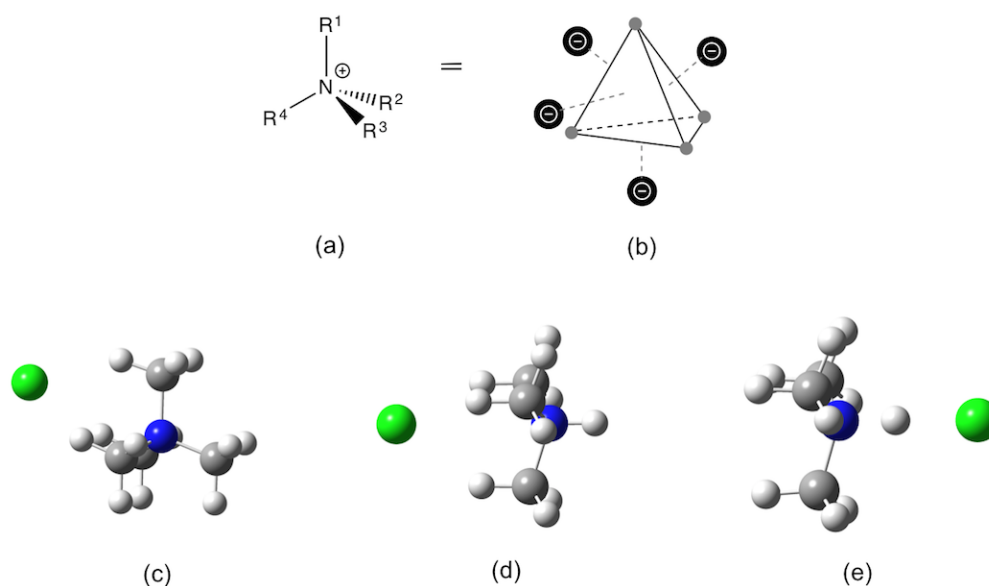


Figure 1.18. (a) Traditional representation of a quaternary ammonium cation. (b) Simplified representation of a quaternary ammonium cation as a tetrahedron with four “faces”. Anion positions are indicated using filled-in black circles. (c) $[\text{NC}_1\text{C}_1\text{C}_1\text{C}_1]\text{Cl}$ ion pair, with the chloride anion sitting at one of the four possible faces. (d) and (e) $[\text{NC}_1\text{C}_1\text{C}_1\text{H}]\text{Cl}$ ion pairs with chloride sitting at a face or forming a directional $\text{N-H}\cdots\text{Cl}$ H-bond respectively. Structures computed here at the B3LYP-D3BJ/6-311+G(d,p) level.

For reported asymmetric quaternary ammonium cation – anion ion pairs, energy differences between configurations were found to be relatively small, $< 17 \text{ kJ mol}^{-1}$. Reports for trialkylammonium – anion ion pairs suggest that the “NH” configuration is between 34 to 75 kJ mol^{-1} more stable than the alternative “face” configuration. Therefore, although based on a limited number of examples, it would appear that the energy difference between the “NH” and “face” configurations of protic ionic liquid systems may show large system dependent variations. At the lower end, an energy difference of $\approx 34 \text{ kJ mol}^{-1}$ is of the order observed between front/top and side positions of aprotic imidazolium ion pairs. At the higher end, an energy difference of $\approx 75 \text{ kJ mol}^{-1}$ is above that which would typically be found between the front/top and back imidazolium configurations.

To rationalise the system dependent variation, it is necessary to consider the variation in the intermolecular interactions on going from the “face” to “NH” configuration. The formation of a stronger $\text{N-H}\cdots\text{X}$ H-bond would be anticipated to stabilise the “NH” configuration. However, the magnitude of the dispersion interactions could play an important role in the relative stabilisation of the “face” configuration. For example, the energy difference between the NH and face configurations of $[\text{NC}_6\text{C}_6\text{C}_6\text{H}][\text{OTf}]$ was found to be $\approx 34 \text{ kJ mol}^{-1}$, but increased to $\approx 61 \text{ kJ mol}^{-1}$ for $[\text{NC}_2\text{C}_2\text{C}_2\text{H}][\text{OTf}]$. Note that for both $[\text{NC}_6\text{C}_6\text{C}_6\text{H}][\text{OTf}]$ and $[\text{NC}_2\text{C}_2\text{C}_2\text{H}][\text{OTf}]$ in the “face” configuration, the anion does interact with the tripodal arrangement of methylene C-H groups closest to the nitrogen centre. Making the assumption that the $\text{N-H}\cdots\text{X}$ H-bond is of approximately the same strength in both cases, the difference in these two relative energies was attributed to a reduction in the dispersion interaction for the shorter chain system. Subtle differences in the electrostatic contribution may also need to be accounted for.

In terms of local structuring, trialkylammonium cations correspond to the simplest possible protic systems. Many of the most commonly employed protic cations, including the prototypical

ethylammonium cation, feature multiple N-H sites, leading to more varied H-bonding motifs. Moreover, many of the alkylammonium cations have differing alkyl groups and/or functionalised groups. Analysis of neutron diffraction data reveals that the number of H-bond contacts formed, and the linearity, is dependent on the identity of the anion.²⁰⁸ Such variations could lead to differences in the three dimensional H-bond networking. One suggestion is that the number of cation H-bond donor sites must nearly equal the number of anion H-bond acceptor sites for efficient H-bond networking, that is, a “matching” of the donor and acceptor sites.²⁰⁹ However, a miss-match in the number of donor and acceptor sites could introduce more flexibility into a H-bond network.⁶¹

As far as we are aware, an in depth analysis of the local structuring with a protic imidazolium cation has not been conducted in the context of ionic liquids. Within the H-bonding community, however, it is known that protic imidazolium cations can form moderate-strong, linear H-bonds.¹³⁸ The local structuring for a protic imidazolium cation may therefore be somewhere between a trialkylammonium and aprotic imidazolium cation; a directional N-H...X H-bond is introduced, but a larger number of alternative configurations, including interaction with the π^+ system, are conceivable. The influence of the introduction of the N-H moiety on the well established anion positions for an aprotic imidazolium remains to be investigated.

Summary

Gas phase ion pairs provide key information relating to the most favourable cation-anion configurations. To date, our understanding of local structuring is most developed for aprotic imidazolium systems, for which the stable cation-anion configurations are well established. The importance of H-bonding, anion- π^+ interactions and dispersion in influencing imidazolium – anion interactions has been elucidated. However, ion pairs cannot recover all structural features of the bulk phase, such as possible $\pi^+ \cdots \pi^+$ and out-of-plane interactions. Recent studies suggest that ion pair dimers can recover more structural features of the bulk phase.

There is a growing interest in potentially cheaper protic ionic liquids. The introduction of an N-H group results in the formation of stronger, and more linear, H-bonds compared to aprotic ionic liquids. The N-H...X interaction leads to an increase in association energy for protic trialkylammonium systems compared to the tetraalkylammonium analogues, but also typically results in a reduction in the number of stable configurations. Local structuring within protic alkylammonium systems with multiple N-H groups is more complex, with the multiple H-bond donor sites facilitating H-bond networking. As far as can be determined, an extensive study of local structuring within imidazolium protic ionic liquids has not yet been reported.

1.3.3 Charge and intermediate range ordering

Neutron diffraction studies of a series of $[C_1C_1im][X]$ salts ($X = Cl^-$, $[PF_6]^-$ and $[NTf_2]^-$) have revealed the presence of significant charge ordering in the liquid phase.^{132, 139, 140} Such charge ordering is reminiscent of more traditional molten salts, such as molten alkali halides.¹⁴¹ MD simulations have supported experimental observations of charge ordering in ionic liquids.

Charge ordering can be readily inferred through comparison of cation-anion and like ion (i.e. cation-cation or anion-anion) probability distribution functions.¹⁴¹ Such a comparison is made in **Figure 1.19** with the simulated radial distribution functions for the cation-anion and cation-cation distributions within $[C_4C_1im][C_1SO_4]$ (at 400.15 K). The out of phase oscillations between the cation-anion and cation-cation distributions are evident and strongly indicative of charge ordering.

Oscillations in the probability distribution can be relatively long ranged, extending up to, and sometimes over, 20 Å, suggesting the presence of multiple solvation shells.¹⁴² The ordering in ionic liquids therefore extends over a greater range than would be expected for a molecular solvent.¹⁴²

The extent of charge ordering is, however, found to be dependent on the ion combination. For the $[C_1C_1im][X]$ series, ordering for $[C_1C_1im][NTf_2]$ was found to be less pronounced than within its congeners, attributed to the larger, more charge delocalised, anion.^{133, 140} The introduction of functionalised side chains may also lead to a reduction in long –ranged ordering. For example, for a sequence of $[NC_nC_2C_1C_1][NTf_2]$ ionic liquids, ether functionalisation of an alkyl side chain on the cation led to a disturbance of the charge ordering.¹⁴³ Nevertheless, the authors emphasised that the charge ordering still remained the dominant structural motif in the functionalised systems.

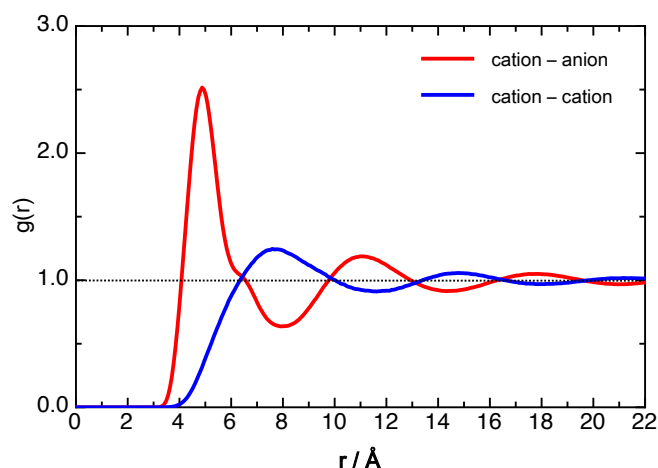


Figure 1.19. Comparison of the simulated radial distribution functions for the cation-anion and cation-cation distributions within $[C_4C_1im][C_1SO_4]$ (using the centre of mass of the ions). Classical MD simulation of 256 ion pairs performed here at 400.15 K (further details in Chapter 4).

While charge ordering in ionic liquids indicates a degree of similarity with higher temperature molten salts, the observation of mesoscopic domains within ionic liquids reveals a notable difference. Dispersion plays a key role in the formation of non-polar domains through the aggregation of alkyl groups, with polar domains composed of the charged groups associated through Coulombic interactions. The existence of nanoscale heterogeneities could play an important role in determining the solvation behaviour, for example, the ability to interact with both polar and non-polar solutes.

For ionic liquids with long alkyl chains, with $C_n \geq 12$, liquid crystalline behaviour has been directly observed using small angle X-ray scattering,¹⁴⁴ differential scanning microscopy and polarising optical microscopy.^{145, 146} For ionic liquids with shorter chains, molecular dynamics simulations, of differing levels of “detail”, have played a central role in the exposure of nanostructural organisation.

Whether employing coarse graining methods, a united atom force field or more sophisticated all atom force field, the general observations are largely in agreement; for $[C_nC_1im][X]$ systems with $n \geq 4$, heterogeneous domain formation can be observed.²¹⁴⁻²¹⁶ Moreover, the non-polar domain size and connectivity has been found to be proportional to alkyl chain length.²¹⁶ The presence of nanoscale heterogeneities in $[C_nC_1im][X]$ ionic liquids with intermediate chain lengths ($4 \leq n \leq 10$) has been corroborated using X-ray diffraction.²¹⁷

Whilst initial studies focussed on imidazolium based ionic liquids, indications of nanostructuring has now been observed for a range of systems, including quaternary ammonium,²¹⁸ phosphonium,²²⁰ piperidinium,²¹⁹ as well as protic ionic liquids.²¹⁰ Results for protic ionic liquids are particularly interesting as it is proposed that nanostructuring can occur within short chain systems, such as the prototypical protic ionic liquids ethylammonium and propylammonium nitrate.²¹⁰ Using X-ray diffraction, the formation of polar and non-polar domains with the short chain $[C_2C_1im]^+$ cation has also been detected when the counter anion is an alkylsulphate ($[C_nSO_4]^-$, $n = 2-8$).²¹¹ MD simulations support the conclusion that the non-polar domains in the alkylsulphate systems are formed through association of the cation and anion alkyl groups, with the size of the non-polar domain increasing with extension of the anion alkyl chain.^{212, 213} However, further investigation is required to ascertain the nature of the structure of the non-polar domain.

The existence of nanoscale heterogeneities has been exposed within a wide range of ionic liquids. Although only very briefly considered here, the topic of self-assembly within ionic liquids is of increasing interest within the field and may be important for many practical applications. As the structuring will influence the properties of the ionic liquids, understanding how to control the self - assembly of ionic liquids is necessary for practical advancement. Much progress has been made in this area, however, further development of structure-property relationships is required.

1.3.4 Concluding summary

Ionic liquids are a novel class of fluids with a wide range of potential applications. There are many different types of ionic liquid and numerous ways of classifying them. For example, using the nature of the anion, ionic liquids can be classed as either simple ionic liquids, with discrete anions, or complex ionic liquids, with complexed anions.

Simple aprotic ionic liquids are commonly employed at the lab scale and constitute the most well studied class of ionic liquid. However, protic ionic liquids and deep eutectic solvents are of increasing interest as potentially cheaper alternatives for larger scale applications.

Much progress has been made in understanding ionic liquids at the molecular level, using a combination of theory and experiment. The subtle balance between electrostatics, induction, dispersion, H-bonding and possibly π -type interactions determines the structuring and properties of ionic liquids. For example, the interplay between the different interactions can be used to rationalise the stable ion pair configurations and the formation of nanoscale domains. However, the dominating electrostatic interaction and the fundamental coupling between the different interactions (e.g. H-bonds are intrinsically associated with the electrostatic component) can make it difficult to “separate out” individual contributions to the total energy. Moreover, observed macroscopic properties can be difficult to rationalise, resulting in different interpretations of how factors such as H-bonding influence the properties of ionic liquids.

The *a priori* prediction of ionic liquid properties therefore remains a challenge. Further investigation of the links between molecular structure and bulk phase properties, and for a wider range of ionic liquids, is required for this to be achieved.

2. Hydrogen Bonding

2.1 What is a hydrogen bond?

H-bonds are ubiquitous within chemistry and the importance of H-bonding in many areas cannot be overstated. However, H-bonding has arguably been one of the most controversial and difficult types of interaction to define. In part, this is because of the huge diversity in the interactions now recognised as H-bonds and the corresponding variation in features. For example, H-bonds span an energy range of $\approx 1 - 170 \text{ kJ mol}^{-1}$,³⁹ from the energy of a (London) dispersion interaction to the energy of a (weak) covalent bond.

The concept of H-bonding, in some form, has been under discussion since the early 20th century.^{42, 147, 148} During this time, numerous working definitions of the H-bond have been proposed based on a range of criteria e.g. energetic, spectroscopic and geometric. Whilst many of these definitions are useful within the context for which they were originally intended, a universal definition of the H-bond has proven elusive.



The traditional “picture” of H-bonding is of an electrostatic (closed shell) interaction between a H-bond donor, X-H, and a H-bond acceptor Y, where X and Y are highly electronegative elements (e.g. N, O, F), **Equation 1.9**. The O-H $\cdots$ O H-bond interaction within water would be a prototypical example. However, this view is now rather out-dated. While all H-bonds will have an electrostatic component, the size of the electrostatic contribution varies. It is now recognised that the H-bond interaction is an amalgam of different components: electrostatics, polarisation, van der Waals (dispersion and repulsion) and covalency.^{39, 149} The variable contribution in each of these components has a significant effect on the H-bond characteristics, and can, for example, explain the wide energy range spanned by the H-bond.³⁹ The weakest H-bonds will have a reduced electrostatic component, replaced by an increased van der Waals contribution. In contrast, the strongest H-bonds can have a sizeable covalent contribution.

Moreover, the limitations placed upon the identities of the H-bond donor and acceptor have relaxed significantly since the early formalisation of the classical electrostatic H-bond. It is now accepted that neither X nor Y need be a highly electronegative element, extending the list of H-bond donors to include, for example, C-H and P-H groups.¹⁵⁰ The only limitation upon X is that it must be more electronegative than H, such that the X-H unit is slightly polar, with the hydrogen bearing the δ^+ charge.³⁹ Furthermore, the H-bond acceptor Y does not need to be a conventional Lewis base with a lone pair, but only has to be a region of high electron density, which could be a multiple bond,^{151, 152} or even an electron rich metal centre.¹⁵³

IUPAC revisited the subject of defining the H-bond in 2011.^{147, 154} To try to encompass the wide range of possible interactions, a very generalised definition was proposed, with the emphasis instead placed on providing evidence of H-bond formation:

*"The hydrogen bond is an attractive interaction between a hydrogen atom from one molecule or a molecular fragment X-H in which X is more electronegative than H, and an atom or a group of atoms in the same or different molecule, in which there is evidence of bond formation."*¹⁵⁴

With the focus on providing evidence of H-bond formation, the IUPAC technical report provides a list of suggested H-bond criteria and characteristics.¹⁴⁷ Importantly, it is not required that all criteria are met for an interaction to be accepted as a H-bond. However, the larger the number of criteria satisfied, the stronger the case for H-bond formation. The suggested criteria and characteristics involve a mix of both experimental and theoretical properties. Some of the characteristics are well established, such as the red shift in the infrared X-H stretching frequency (with a caveat for blue shifted H-bonds), the deshielding of the X-H proton as determined using ¹H NMR spectroscopy and the link between linearity and H-bond strength. Characteristics commonly assessed using theoretical methods include the link between charge transfer and strength of the H-bond, as well as specific features of the topology of the electron density. Both charge transfer and characteristics of the topology of the electron density are used extensively in this work as H-bond descriptors and shall be discussed in more detail shortly.

The classification of H-bonds into types based on strength (e.g. weak, moderate or strong) is often undertaken by imposing cut-offs in spectroscopic, geometric or energetic criteria, such as in the popularised classification scheme of Jeffrey.¹⁴⁹ However, H-bonds sit on a continuous energy scale. The suggested groupings are therefore arbitrary, with there being no natural borderlines between the proposed types of H-bond. At the extreme ends, the variation in the components of a H-bond can lead to transition to other types of intermolecular interactions, at one end a van der Waals interaction, and at the other extreme a covalent bond.⁶⁰ Desiraju has represented the interplay between the different contributions of the H-bond schematically.⁶⁰ An adapted version of the original schematic is shown in **Figure 1.20**.⁶¹ Therefore, classification schemes are useful, but should be regarded as guidelines rather than strict rules.

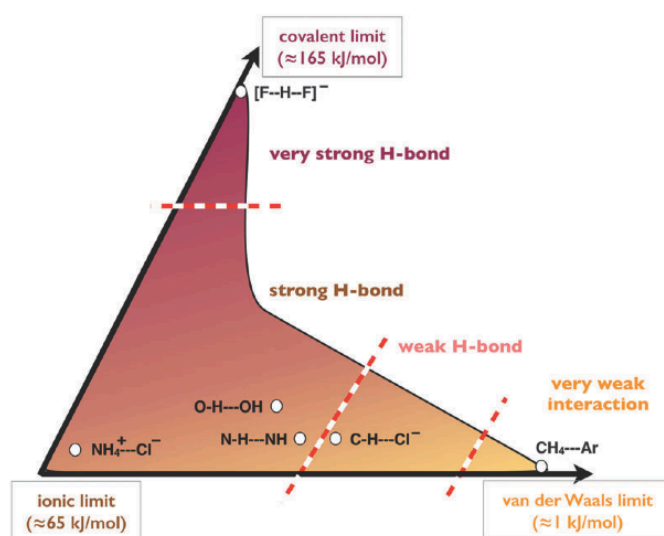


Figure 1.20. Pictorial representation of the variation in H-bond components. Figure from "Hydrogen bonding in ionic liquids".⁶¹ Reproduced by permission of The Royal Society of Chemistry.

A further problem with many existing classification schemes for application to ionic liquids is that they have been developed based on, and for, conventional neutral H-bonds. As has been noted, H-bonding within ionic liquids may differ in some aspects and as such, established schemes may not be valid for ionic liquid systems.

2.1.1 Doubly ionic hydrogen bonds

Considering the charge of the H-bond donor and H-bond acceptor species, there are three main types of H-bond: neutral, ionic and doubly ionic. Neutral H-bonds are formed through the interaction of two neutral species. When one component, either the H-bond donor or acceptor, is charged (i.e. an ion) an ionic H-bond is formed. When both the donor and the acceptor species are charged, a doubly ionic H-bond is formed.

Neutral and ionic H-bonds are ubiquitous and well studied.^{39, 147, 155} To date, doubly ionic H-bonds have not been as extensively examined, often having either been overlooked or considered as an example of an ionic H-bond interaction. However, within the field of ionic liquids, the H-bonds will predominantly be of the doubly ionic type. Therefore, it is necessary to better understand the nature of the doubly ionic H-bond and how it compares to the ionic and neutral analogues.

Outside the field of ionic liquids, there are a limited number of reported examples of doubly ionic H-bond interactions. Some of these examples, however, have been recognised for a relatively long period of time. For example, the so-called “salt bridge” is one of the strongest H-bond interactions identified within biological systems.¹⁴⁹ Typically a salt bridge corresponds to an N-H...O=C interaction, between a positively charged ammonium group and a negatively charged carboxylate group within a protein.

Returning to the view of H-bonds as stages on the proton transfer coordinate, **Equation 1.5**, a doubly ionic H-bond may arise between the ions formed upon complete proton transfer. In a small number of cases, where the donor and acceptor are “pK_a matched”, strong H-bonds of the form $O^{\cdot-} \cdots H^+ \cdots O^{-1/2}$ have been identified.¹⁵⁶ These have previously been referred to as “double charge assisted H-bonds”.⁴² The H-bond formed between pyridine-*N*-oxide and trichloroacetic acid is an example of such an interaction. With the restriction that the donor and acceptor be pK_a matched, this particular type of doubly ionic H-bond is relatively esoteric.

A recent review of H-bonding in ionic liquids reveals that doubly ionic H-bonds are more commonplace than has previously been appreciated.⁶¹ From the work undertaken to date, it was established that doubly ionic H-bonds share many similarities with the neutral and ionic counterparts. However, unique features of the doubly ionic interaction were also identified. Therefore, whilst progress has been made in understanding these interactions, it has been recognised that there is much scope for further investigation into doubly ionic H-bonding within ionic liquids.⁶¹

2.2 Hydrogen bonding concepts

2.2.1 Components of the hydrogen bond

Establishing the energy of a H-bond and the relative contributions of the constituent components is challenging. There exist a number of different decomposition schemes. Morokuma's decomposition scheme is one of the most well known.¹⁵⁷ More recently, Symmetry Adapted Perturbation Theory (SAPT) has increasingly been employed to decompose the total association energy of H-bonded complexes.^{45, 158, 159} However, the partitioning of the total energy into the different components is highly dependent on the scheme employed. For ionic liquids, there is the added complication of "decoupling" the H-bond contributions from the more general ion-ion interactions.

Constituent components of the H-bond include: an electrostatic term, a polarisation and induction term, a van der Waals term and a charge transfer term.³⁹ Each component shows a different dependence on the separation, r , and therefore the relevant significance of each term varies as a function of the separation.

The electrostatic term corresponds to the interaction between the undistorted charge distributions of the H-bond donor and H-bond acceptor. The total electrostatic component can be described using a multipole expansion.⁴⁸ The interaction between point charges (i.e. the ion-ion term) decays slowly as $\approx -r^{-1}$ and is therefore very significant at longer distances. The ion-dipole and dipole-dipole terms decay as $\approx -r^{-2}$ and $-r^{-3}$ respectively. Higher order multipoles are therefore of increased importance at shorter distances.

Upon H-bond formation, there is a distortion of the charge distribution of both the H-bond acceptor and donor. The energy associated with the change in the charge distribution is typically recovered within the polarisation and induction terms, with polarisation decaying as $\approx -r^{-4}$.³⁹

The van der Waals component of the H-bond is a combination of the dispersion and exchange-repulsion terms. Dispersion, associated with the correlated movement of electrons (a quantum effect), is always attractive.^{48, 160} Dispersion can be approximated using a series expansion in terms of r . However, often only the leading $-r^{-6}$ term is employed. Overall, the exchange-repulsion term is repulsive; there is an energy penalty associated with the interaction of two closed shell electron clouds i.e. Pauli repulsion.¹⁶¹ The repulsive term is frequently modelled as $+r^{-12}$. The commonly employed Lennard-Jones potential combines the attractive $-r^{-6}$ and repulsive $+r^{-12}$ terms to provide an approximate description of the van der Waals interaction.

For charge transfer to occur there needs to be an orbital interaction between the donor and acceptor. The relationship between charge transfer and the separation can be modelled using an exponential relationship i.e. as $\approx e^{-r}$.^{39, 48} Thus, charge transfer is of most relevance at equilibrium geometries.

2.2.2 The ionic component

In the majority of H-bonds there is expected to be a large electrostatic component. It can be anticipated that this would be larger for ionic and doubly ionic H-bonds where an acceptor, donor, or potentially both, are charged species. However, it has been shown that oversimplified electrostatic models can fail to predict the correct geometries of simple H-bonded dimers.⁴⁸ For example, if only dipole-dipole interactions are considered, the geometry of the HF dimer is incorrectly predicted to be linear.⁴⁸ This finding therefore suggests the importance of “other” terms in rationalising the orientational dependence of H-bonds. However, there is some debate over the relative importance of these “other” contributions. There are two main arguments proposed; one based on charge transfer¹⁶² and the other on the inclusion of higher order multipoles.⁴⁸

There is evidence to suggest that the failure of simple electrostatic models is the result of the covalent (charge transfer) contribution being ignored.¹⁶² This will be discussed in more detail shortly. Alternatively, it can be shown that when higher order multipoles are included there are cases where the correct geometry of H-bonded dimers can be predicted using a purely electrostatic model.⁴⁸ For example, HF is found to have a significant quadrupole moment in addition to the dipole moment. A simple electrostatic model including both dipole-quadrupole and quadrupole-quadrupole terms correctly predicts the non-linear geometry of the HF dimer.^{48, 163} However, there are also a number of issues associated with a multipole analysis of H-bonding that may need to be considered.⁶¹

Nevertheless, regardless of the relative importance of higher order multipoles, it is clear that the ionic component of the H-bond will be highly dependent on the charge distribution within the donor and acceptor species. For example, there is an established correlation between the strength of a H-bond and the partial charges on the donor (H) and acceptor (Y) atoms both before and after H-bond formation.¹⁶⁴ For a doubly ionic H-bond, it can be anticipated that the positive charge of the cation would increase the positive charge on the H atom, while the negative charge of the anion would lead to increased negative charge on the acceptor Y atom. However, it has been found that the influence of the cation charge on the donor X atom is more difficult to predict.⁶¹

The relative H-bond donor strengths and partial charges of the C²-H and C^{4/5}-H groups of aprotic imidazolium cations illustrate the complexity of the issue. The H atoms associated with C², C⁴ and C⁵ bear similar positive charges.¹³⁰ Therefore, with the same H-bond acceptor, the H-bond strength would be predicted to be similar. The C²-H group is, however, found both experimentally and theoretically to be the stronger H-bond donor group.^{69, 130, 165} Both C⁴ and C⁵ bear a negative charge, such that overall the C⁴-H and C⁵-H groups are effectively neutral. In contrast, the C² atom is positively charged. Overall, it can be shown that the combined positive charge distributed over the C²-H group contributes to an increase in strength of the H-bond acidity of this group.¹³⁰

The charge distribution of the H-bond donor and acceptor groups do not remain static upon H-bond formation. The combined effects of polarisation and induction (and charge transfer) result in a redistribution of charge upon forming a H-bond. For neutral, ionic and doubly ionic H-bonds it can be shown that H-bond formation results in a build up of electron density in the internuclear region between the donor and acceptor i.e. between H and Y.^{61, 155} This occurs concomitantly with a decrease in electron density on H and an increase in electron density on both X and Y. The

magnitude of the gains and losses of electron density are associated with both the relative strength of the H-bond donor and acceptor groups, in addition to the total charge of the interacting species. For example, changes upon ionic H-bond formation are found to be greater than changes upon neutral H-bond formation.¹⁵⁵ A simple “push-pull” interpretation has recently been proposed as a way of understanding these effects.⁶¹

Comparison of electron density difference maps for ion pairs reveals that upon H-bond formation, electron density is typically polarised away from the anion further “into” the cation.⁶¹ For example, the electron density contour plot for an $[\text{NC}_1\text{C}_1\text{C}_1\text{H}]\text{Cl}$ ion pair is shown in **Figure 1.21**; the polarisation of electron density to the “back” of the cation can be seen. Therefore, electron density redistribution is not necessarily localised in the region of the H-bond. Such non-local charge redistributions have previously been associated with blue-shifted H-bonds.^{166, 167} Furthermore, electron density difference maps demonstrate the anisotropic electron redistribution about some atoms, highlighting the approximate nature of partial charge descriptions of charge redistribution.

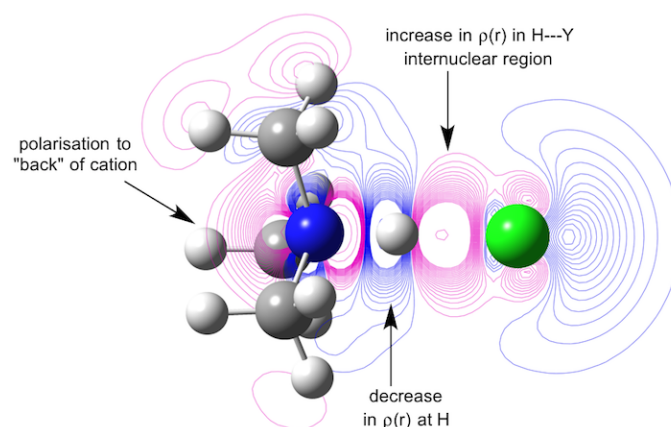


Figure 1.21. Electron density difference contour plot for $[\text{NC}_1\text{C}_1\text{C}_1\text{H}]\text{Cl}$. Structure optimised at the B3LYP-D3/aug-cc-pVTZ level, provided by Dr Richard Matthews (Hunt research group). Pink and blue contour lines indicate an increase and decrease in $\rho(r)$ respectively (with respect to the isolated ions in the geometry of the ion pair). Contour lines drawn at densities between 0.0005 and 20 au (0.0005 – 0.01 in 0.0005 intervals, 0.02-0.1 in 0.02 intervals, 0.2, 0.04, 0.08, 2, 4, 8 and 20 au).

2.2.3 The covalent component

The resonance description of hydrogen bonding

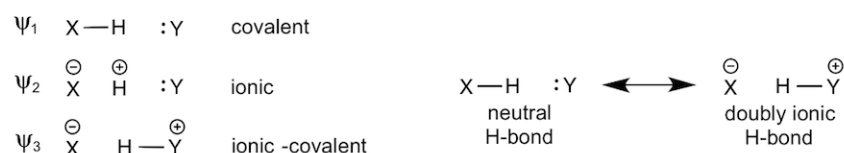
With a 1s valence orbital hydrogen can only form a single pure (2-centre–2-electron) covalent bond. Hence, many early theories of H-bonding were based predominantly on ionic arguments.¹⁶⁸ However, it was recognised that H-bonding could also be described using the concept of, what is now known as, a 3-centre–4-electron interaction.^{169, 170} For example, the valence bond description of H-bonding was one of the first formalisms to incorporate a covalent component.^{171, 172}

A H-bond can be considered to be a mixture of different resonance forms. Each resonance form contributes to the H-bond, with the individual contributions weighted by a coefficient ω , **Equation 1.10**. The relative contribution of each of the resonance forms therefore determines the nature of the H-bond. Neutral and ionic H-bonds are on the same PES and can be treated using the same main three representations, **Figure 1.22 a**. For ionic H-bonds, different representations need to be invoked, **Figure 1.22 b**.⁶¹

$$\Psi_{HB} = \omega_1\varphi_1 + \omega_2\varphi_2 + \omega_3\varphi_3 \quad (1.10)$$

Mixing between two resonance forms will be greater when the energy difference between the two forms is reduced. The strongest H-bonds are formed when the ionic and covalent forms are energetically equivalent.⁴² This infers that the strongest H-bonds will be symmetric and will have a significant covalent component.

(a) Neutral and doubly ionic H-bonds



(b) Ionic H-bonds



Figure 1.22. Resonance forms of (a) neutral and doubly ionic H-bonds and (b) ionic H-bonds.

The strongest H-bonds known are examples of ionic H-bonds and are determined to be symmetric with the proton located mid-way between the donor and acceptor atoms (i.e. between X and Y).⁴² $[H\cdots F\cdots H]^-$ is the prototypical example of a very strong and symmetric H-bonded dimer. In contrast, doubly ionic H-bond interactions are not symmetric. Therefore, it is not expected that a doubly ionic H-bond will be as strong as a symmetric ionic H-bond.⁶¹

Electron density description of hydrogen bonding

Experimentally, X-ray and neutron diffraction have been widely used to examine the electron density, $\rho(r)$, of H-bonded systems.¹⁷³ Theoretically, the Quantum Theory of Atoms in Molecules (QTAIM)¹⁷⁴ is now commonly employed to analyse and interpret the topology of $\rho(r)$ within a system. This analysis can be used to interrogate both experimental and computed electron densities. Moreover, features of the QTAIM analysis are some of the foremost descriptors for assessing the covalency of a H-bond interaction.⁷⁴ A more detailed description of the QTAIM theory is provided in **Chapter 2**.

Within a molecule, the maximum values of $\rho(r)$ correspond to the positions of the nuclei, with decay in $\rho(r)$ away from the atomic centres. However, this decay is less rapid in the internuclear region. A relief map of the electron density in the molecular plane of a H-bonded complex between 4-nitropyridine and HCl is shown in **Figure 1.23 a**. The huge peaks corresponding to the nuclei dominate, but significantly, the topology of $\rho(r)$ in the internuclear regions is not featureless, e.g. **Figure 1.23 b**.

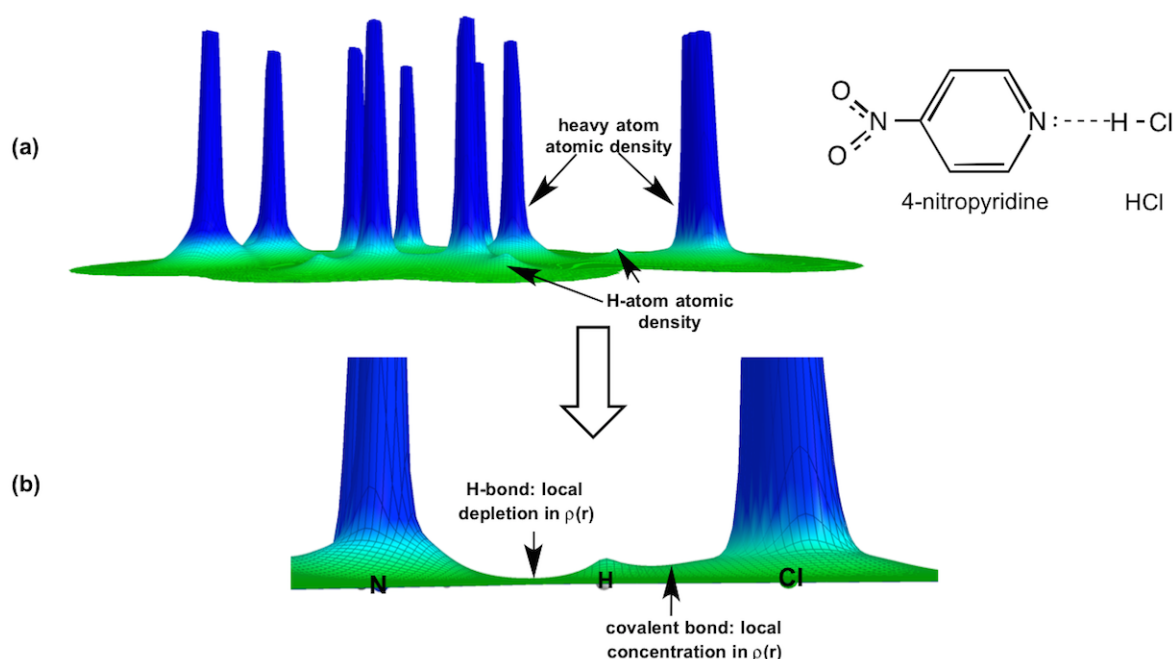


Figure 1.23. Relief map of the electron density in the molecular plane of the 4-nitropyridine...HCl complex (structure optimised here at the B3LYP-D3BJ/6-311+G(d,p) level). (a) Relief map of entire complex and (b) close-up view of the electron density topology in the H-bond region.

Through assessment of the gradient of $\rho(r)$, critical points (i.e. where the gradient is zero) can be identified.¹⁷⁵ A bond critical point (BCP) is a saddle point in $\rho(r)$, a minimum along the bond path connecting two atomic centres and a maximum in the two perpendicular directions. The identification of a bond path and the associated BCP is suggestive of the presence of a bond or "interaction". The magnitude of $\rho(r)$ at the BCP, ρ_{BCP} , has been associated with the strength and covalency of the intermolecular interaction.^{74, 175} The value of ρ_{BCP} for a shared interaction (i.e. a covalent bond) is typically much larger than for a closed shell interaction (e.g. a H-bond).⁷⁴ For example, within the 4-

nitropyridine and HCl complex, **Figure 1.24**, the value of ρ_{BCP} for the Cl-H $\cdots$ N H-bond is 0.054 eÅ⁻³. The corresponding value of ρ_{BCP} for the covalent H-Cl bond is much larger, 0.211 eÅ⁻³.

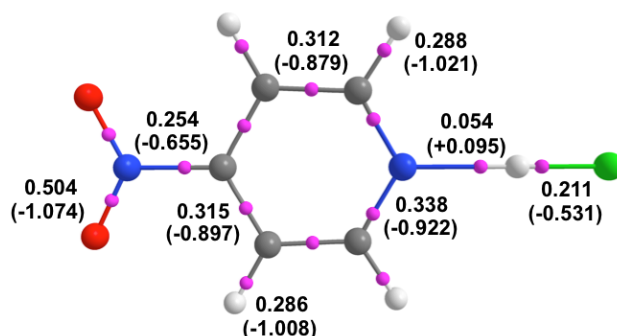


Figure 1.24. QTAIM molecular graph for the 4-nitropyridine and HCl H-bonded dimer (B3LYP-D3BJ/6-311+G(d,p)). Small pink spheres correspond to BCPs. Values of ρ_{BCP} (eÅ⁻³) and $\nabla^2\rho_{\text{BCP}}$ (in brackets, eÅ⁻⁵) provided.

The Laplacian of $\rho(r)$ at the BCP, $\nabla^2\rho_{\text{BCP}}$, is also useful in characterising the nature of an interaction. $\nabla^2\rho_{\text{BCP}}$ provides information relating to the curvature of $\rho(r)$ in the vicinity of the BCP. For covalent bonds, $\nabla^2\rho_{\text{BCP}}$ is usually negative, indicating local concentration and therefore sharing of $\rho(r)$ in the internuclear region.¹⁷⁵ In contrast, for closed shell interactions, $\nabla^2\rho_{\text{BCP}}$ is typically small and positive, indicating local depletion in $\rho(r)$.¹⁷⁵ Small values of ρ_{BCP} for a H-bond are therefore consistent with the interaction being dominated by electrostatic and/or dispersive contributions.

The total electron energy density at the BCP, H_{BCP} , is often used in conjunction with $\nabla^2\rho_{\text{BCP}}$ to classify interactions, including H-bonds.^{175, 176} A value of $H_{\text{BCP}} < 0$ is usually associated with a covalent interaction, whilst $H_{\text{BCP}} > 0$ typically corresponds to a closed shell interaction. For H-bonds, there are three main scenarios. Weak H-bonds are usually classified by $\nabla^2\rho_{\text{BCP}} > 0$ and $H_{\text{BCP}} > 0$. At the other end of the scale, the strongest H-bonds, with significant covalent contributions, are associated with $\nabla^2\rho_{\text{BCP}} < 0$ and $H_{\text{BCP}} < 0$. An intermediate case, with $\nabla^2\rho_{\text{BCP}} > 0$ and $H_{\text{BCP}} < 0$ is indicative of a H-bond with at least partial covalent character.

For neutral and ionic H-bonds, correlations between characteristics of the topology of $\rho(r)$ (e.g. ρ_{BCP} , $\nabla^2\rho_{\text{BCP}}$ and H_{BCP}) and other established H-bond descriptors, such as the H-bond length, have been found.^{74 177} Within this work we investigate, and compare, the relationships between ρ_{BCP} and other H-bond descriptors for neutral, ionic and doubly ionic H-bond interactions.

The orbital description and charge transfer component of hydrogen bonding

H-bonding can be described using molecular orbital (MO) theory at various levels of sophistication. The simplest qualitative MO description of H-bond formation assumes the interaction between a lone pair (LP) fragment orbital (FO) on Y, Y_{LP} , and a σ^* orbital of X-H, σ^*_{XH} , e.g. **Figure 1.25 a**. The resultant bonding MO is occupied and hence, electron density is shared between the H-bond donor and acceptor.

The relative stabilities of the FOs will influence the degree of FO interaction. It has been recognised that in some cases the Y_{LP} FO is very stable and/or the σ^*_{XH} orbital is relatively unstable.⁶¹

In such cases, there is the potential for interaction between the Y_{LP} and σ_{XH} FOs, **Figure 1.25 b**. As both FOs are occupied this interaction is destabilising. However, overall the energy of the system must be lowered. For this to be achieved, it has been proposed that the stabilisation of the bonding MO must be significant and that the antibonding MO (also occupied) undergoes significant mixing with higher energy unoccupied orbitals.⁶¹ From our own examination of H-bonding in ion pairs, it appears that the interaction of two occupied FOs is not uncommon.

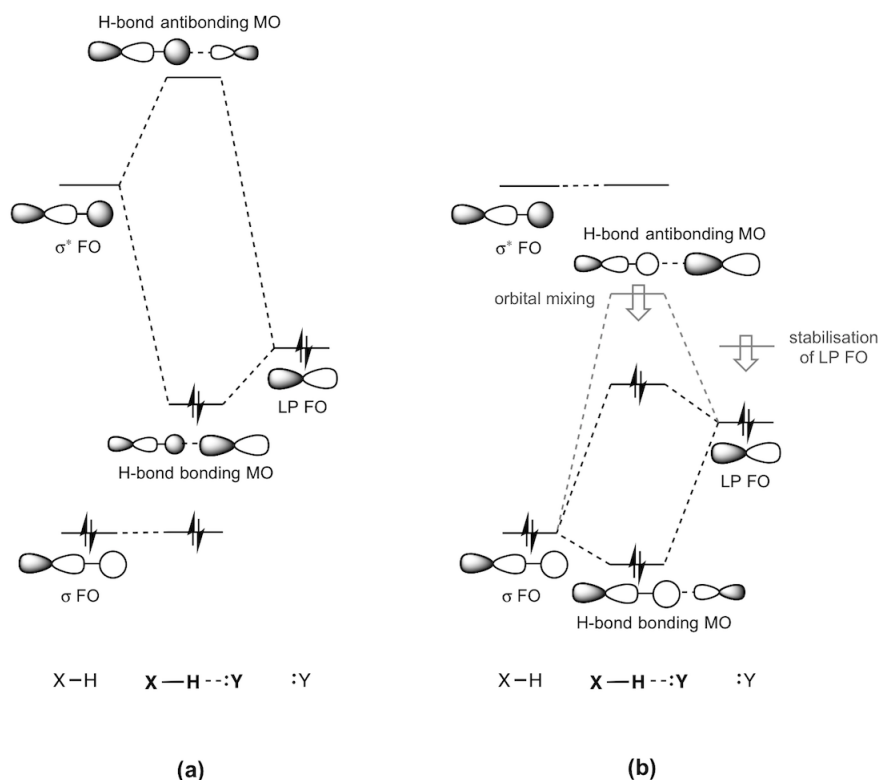


Figure 1.25. Simplified qualitative MO diagrams for H-bond formation: (a) interaction between a Y lone pair (LP) fragment orbital (FO) and a X-H σ^* FO and (b) interaction between a Y LP FO and a X-H σ FO. Based on a diagram from “Hydrogen bonding in ionic liquids”. Reproduced by permission of The Royal Society of Chemistry.

Compared to the simplified FOs employed in **Figure 1.25**, the computed (delocalised) FOs of the H-bond donor and acceptor are significantly more complex. Moreover, the formation of more complicated H-bond motifs can further increase the intricacies of the associated MOs. It can therefore be difficult to reconcile the complex computed MOs with the simplified qualitative MO description. Nevertheless, the identification of FO interactions between the H-bond donor and acceptor species indicates some degree of delocalisation between the two fragments. Thus, the extent to which the computed FOs interact can give a qualitative “feel” for the covalent contribution to the H-bond interaction.

As an example of a “real” system, MOs associated with H-bond formation within the “NH” and “face” configurations of the trimethylammonium chloride ion pair are shown in **Figure 1.26**. Firstly, it can be seen that the cation FOs are delocalised over the entire cation i.e. the cation FO is not localised entirely on the X-H donor unit. Within the NH configuration, **Figure 1.26 a**, a single, linear N-H $\cdots$ Cl H-bond is formed. The σ and σ^* bonding and antibonding combinations of the Cl^- and cation

FOs can readily be identified. Moreover, the contributions from the Cl^- and cation FOs to the H-bond MOs are relatively equal.

Within the face configuration, a more complex H-bonding motif is present; Cl^- appears to interact concurrently with three C-H donor groups, **Figure 1.26 b**. In contrast to the case for the NH configuration, within the face configuration, the Cl^- and cation FO contributions to the H-bond MOs are not equal e.g. the antibonding combination is clearly dominated by the Cl^- FO.

Comparing these two systems, there is more significant FO interaction for the $\text{N-H}\cdots\text{Cl}$ H-bond compared to the individual $\text{C-H}\cdots\text{Cl}$ interactions. This would suggest that the $\text{N-H}\cdots\text{Cl}$ H-bond has a larger covalent contribution, consistent with N-H (typically) being the stronger H-bond donor.

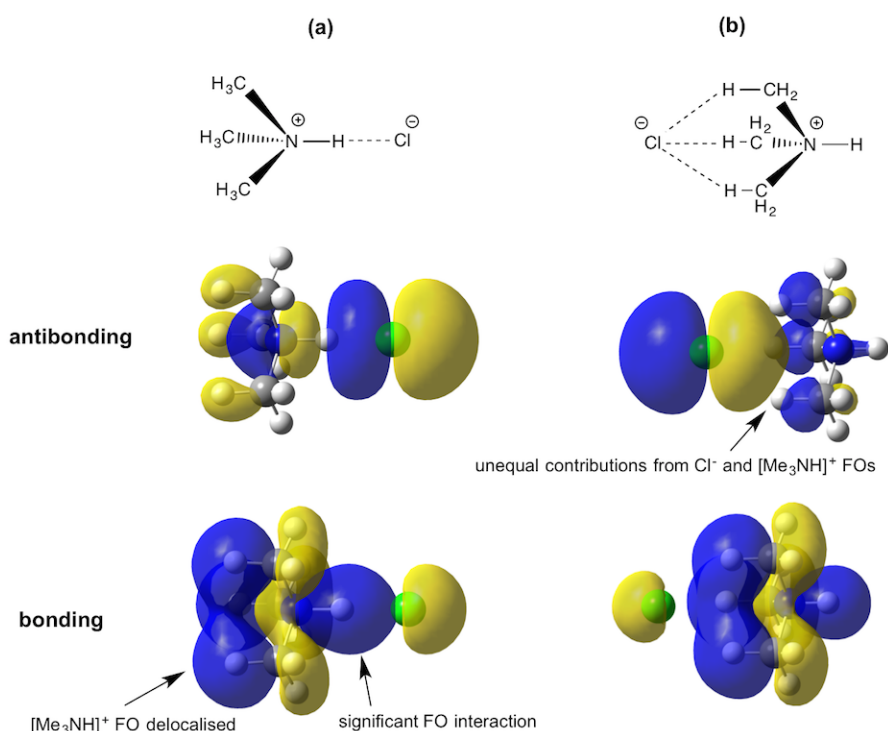


Figure 1.26. Comparison of the bonding and antibonding H-bond MOs for the (a) “NH” and (b) “face” configurations of the trimethylammonium chloride ion pair. Structures optimised here at the B3LYP-D3BJ/6-311+G(d,p) level. MOs generated at the $0.02 \text{ e}\text{\AA}^{-3}$ isosurface.

Natural Bond Orbitals (NBOs) are localised orbitals, typically on one or two centres.¹⁶² Within the NBO scheme, a H-bond interaction can be associated with a donor-acceptor interaction between the lone pair NBO on Y (n_{LP}) and a σ^* NBO of X-H i.e. $n_{\text{LP}} \rightarrow \sigma^*_{\text{XH}}$.¹⁶² The schematic representation of the interaction of the NBOs is very similar to that presented in **Figure 1.25 a** (with the canonical orbitals replaced with the appropriate NBOs). The recognition of a $n_{\text{LP}} \rightarrow \sigma^*_{\text{XH}}$ donor-acceptor interaction invokes the idea of resonance –type charge transfer.¹⁶⁹

The strength of the donor-acceptor interaction can be quantified using the charge transfer component of the NBO analysis i.e. $E^{(2)}$ stabilisation energies.¹⁶² The $E^{(2)}$ stabilisation energy for a donor-acceptor interaction is computed using **Equation 1.11**, where q_i is the donor orbital occupancy, ε_i and ε_j are the orbital energies and $F(i,j)$ is the off diagonal NBO Fock matrix element. The theory relating to NBOs is discussed in more detail in **Chapter 2**. Correlations between other H-bond

descriptors and the magnitude of $E^{(2)}$ associated with H-bond formation have been established for neutral and ionic H-bonds.^{162, 178}

$$E^{(2)} = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i} \quad (1.11)$$

For a given interaction, the magnitude of $E^{(2)}$ can be related, in part, to the strength of the orbital interaction.¹⁷⁹ Within a doubly ionic H-bond, the cationic charge of the X-H donor stabilises the σ_{XH}^* orbital, whilst the anionic charge destabilises the acceptor n_{LP} orbital. Both of these effects contribute to a decrease in the energy separation ($\Delta\varepsilon = \varepsilon_j - \varepsilon_i$) between the donor and acceptor orbitals. Moreover, for an ion pair, there is expected to be an enhanced Coulombic attraction, decreasing the separation between the fragments, and increasing $F(i,j)$. Therefore, for a doubly ionic H-bond, compared to a neutral analogue, an enhancement of $E^{(2)}$ is expected.⁶¹

Properties relating to $n_{\text{LP}} \rightarrow \sigma_{\text{XH}}^*$ (e.g. $E^{(2)}$) are now routinely employed as H-bond descriptors. However, there are those that vehemently argue against placing significant emphasis on the charge transfer component, instead advocating the multipole analysis of H-bonding.¹⁶¹ In part this is due to the success of pure electrostatic models in describing some H-bonded dimers.⁴⁸ However, it is also claimed that charge transfer is a poorly defined quantity, in most cases merely an “ill-defined part of the induction (polarization) energy” that “vanishes in the limit of a complete basis set”.¹⁶¹ Moreover, in cases where the charge transfer component can be separated, it is found to be notably less sensitive to the geometry compared to the electrostatic component.⁴⁸

To the contrary, Weinhold *et al* provide evidence to directly contradict the view of charge transfer as an insignificant contribution of the H-bond. For example, within the NBO scheme, it can be shown that when the $n_{\text{LP}} \rightarrow \sigma_{\text{XH}}^*$ charge transfer component of the H-bond is deleted the H-bond is effectively “lost”.¹⁷⁹ Furthermore, very strong correlations between properties associated with charge transfer and experimental H-bond descriptors (e.g. H-bond energy, bond length and IR stretching frequency) have been demonstrated.¹⁷⁹

The debate between the competing arguments is ongoing, both cases potentially associated with strengths and weaknesses. Nevertheless, due to the strength of the evidence linking charge transfer with H-bond strength, we employ $E^{(2)}$ extensively herein to characterise H-bond interactions.

2.3 The ionic liquid hydrogen bond criteria

From a recent review of H-bonding in ionic liquids, a set of theoretical criteria, modified for application to ionic liquids, has been proposed.⁶¹ One small change to the original criteria was made upon consideration of results in this work. The “ionic –liquid H-bond criteria” provided in **Table 1.1** shall be employed herein to classify H-bonds.

Table 1.1. Criteria use to classify H-bonds, taken from “Hydrogen bonding in ionic liquids”.⁶¹

	Strong	Moderate	Weak
Energy H-bond/ kJ mol ⁻¹	63 - 167	17-63	< 17
Density ρ_{BCP} / au (eÅ ⁻³)	>0.05 very strong > 0.085	0.02-0.05	0.002-0.02
Laplacian $\nabla^2 \rho_{BCP}$ / au (eÅ ⁻⁵)	most often –ve but can be +ve	+ve or -ve	+ve and small <0.07
Energy density H_{BCP}	$H_{BCP} < 0$	$H_{BCP} < 0$	$H_{BCP} > 0$
$E^{(2)}$ / kJ mol ⁻¹	> 150	30-150	< 30

3. The Chalcopyrite Problem: Project Background

Ionic liquids could offer new approaches to the extraction of metals from metal ore. The *Rio Tinto – Imperial College London* collaboration was established to investigate, and improve upon, the extraction of copper from chalcopyrite. This work constitutes a contribution to “blue skies” research into the application of ionic liquids in the leaching of chalcopyrite.

3.1 Background

Copper is a versatile material with a wide range of desirable properties and applications.¹⁸⁰ The expansion of developing markets, such as China and India, has led to an increase in the demand for copper.¹⁸¹ Given that both the quality and accessibility of known copper ore deposits is decreasing, being able to supply the future demand for this base metal is a topical issue within the metallurgical industry.^{181, 182} Therefore, to ensure production remains economically viable, cheaper extraction processes, more suitable for lower grade ores, are required.

Chalcopyrite, $CuFeS_2$, is the world’s most abundant copper mineral.¹⁸³ To date, mined chalcopyrite has almost exclusively been subjected to pyrometallurgical processing. This is an energy intensive process, requiring the mined ore to be ground and concentrated *via* floatation methods before being smelted and subsequently electrorefined to produce high purity copper cathodes.¹⁸⁴ Pyrometallurgical treatment is therefore only viable for higher grade ores.

An alternative to pyrometallurgy is hydrometallurgy, which involves the extraction of metal ions from ore into the solution phase (usually aqueous).¹⁸⁴ Heaps of crushed ore are irrigated with a leaching solvent and the metal species are extracted, leaving behind the unwanted gangue material. Subsequently, the leaching liquor is collected from the bottom of the heap and a process of extraction and refining is undertaken to obtain the pure metal. For copper extraction the leaching solvent is usually a dilute acidic aqueous solution; sulphuric acid is most commonly employed, there being an available supply from the pyrometallurgical processing of sulphide ores.¹⁸⁵

The hydrometallurgical processing of ore is reported to require both lower initial capital investment and lower long term running costs.¹⁸⁶ Therefore, hydrometallurgy is seen as a viable alternative to pyrometallurgy for the processing of lower grade copper ores and copper waste materials. However, only $\approx 20\%$ of copper is currently obtained *via* hydrometallurgical processing.¹⁸⁶ Moreover, at present, most copper obtained in this way is extracted from either copper oxides or secondary copper sulphides, such as chalcocite, Cu_2S , and waste materials.¹⁸⁶ A major obstruction to the increase in copper production *via* hydrometallurgy is the reticence of chalcopyrite to the aqueous leaching process. The development of a commercially viable chalcopyrite leaching process has been described as the “holy grail” of copper metallurgy.¹⁸⁶

Despite a wealth of research, no consensus has been reached to explain the slow kinetics of chalcopyrite leaching.^{187, 188} However, it is generally accepted that mildly acidic and oxidising conditions are required for the leaching process.¹⁸⁹ Nevertheless, for chalcopyrite leaching to become competitive with the current pyrometallurgical treatment, an increase in the percentage extraction of copper from chalcopyrite is necessitated. Potentially, the relatively novel application of ionic liquids to chalcopyrite leaching could provide the “game changing” increase required.

3.2 Application of ionic liquids in extractive metallurgy

In the field of metal processing, ionic liquids have been employed in a number of areas. The wide electrochemical window, conductivity, good thermal and electrochemical stability and large liquidus range make ionic liquids particularly attractive for electrochemical applications.¹⁹⁰ There are a number of reports of ionic liquids being employed for the electrodeposition or electrefining of metals.^{11, 191} The wide electrochemical window of ionic liquids can allow for the electroprocessing of metals not accessible using aqueous electrolytes due to the limited electrochemical window of water.¹⁹¹

Ionic liquids can also be utilised in the areas of extraction and separation. For example, ionic liquids have been shown to be efficient at extracting heavy metal ions from wastewater streams (e.g. spent nuclear fuel),^{192, 193} and in recovering, and separating, target metals from composite effluents.^{194, 195} To date, there are fewer reports relating to the application of ionic liquids in the digestion or leaching of recalcitrant minerals. However, there are toxicological issues associated with some current aqueous leaching processes for precious metals, such as the use of cyanide as a leaching agent.¹⁹⁶ Therefore, there is an incentive to identify “greener” alternatives. A few key studies suggest that ionic liquids do have the potential to also be employed in these areas.

Both precious metals and base metals have successfully been leached from the respective ores using ionic liquid based leaching solvents. $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ has been identified as a potential candidate for the extraction of copper, gold and silver.^{195, 197-199} Significantly, this ionic liquid is Brønsted acidic.

For the extraction of copper from chalcopyrite using $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ with the addition of Fe(III) as an oxidant at 70°C, a percentage extraction of 86.6 % can be achieved.¹⁹⁸ In contrast, the percentage extraction of copper with 1M H_2SO_4 under the same conditions was only 23.3 %. The use of the related Brønsted acidic ionic liquid $[\text{C}_4\text{C}_1\text{im}][\text{H}_2\text{PO}_4]$ in the leaching of chalcopyrite has also been reported and patented.²⁰⁰

With the addition of thiourea (leaching agent) and Fe(III) (oxidant) to $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, the percentage extraction of gold from a gold and silver containing sulphide ore is reported to be competitive with that achieved with acidic aqueous leachates under analogous conditions.²⁰¹ Moreover, the percentage extraction of silver with the ionic liquid leaching solvent showed a significant increase compared to the aqueous solvent.²⁰¹ Importantly, the recyclability of $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ was also found to be good; no loss in the percentage extraction or degradation of the ionic liquid over repeated leaching cycles was observed.²⁰¹ However, despite the initial “proof of concept” no satisfactory explanations for the observed influence of ionic liquids on the leaching process have yet been proposed.

Metal oxides are typically very difficult to dissolve, usually only soluble in strongly acidic or basic aqueous media. However, a number of metal oxides have been shown to be partially soluble in a range of different ionic liquids and DESs.^{194, 202}

The dissolution of lanthanide and actinide oxides is a particular area of interest due to the prevalence of these materials in the nuclear fuel industry. Such materials have been shown to be soluble in both chloroaluminate ionic liquids and simple ionic liquids.^{203, 204} For example, UO_3 and UO_2 have been dissolved in $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$ with the addition of nitric acid.²⁰⁴

Task specific simple ionic liquids for the dissolution of transition metal oxides have also been reported.²⁰⁵ Moreover, it has been established that transition metal oxides can show relatively high solubility in DESs.^{202, 206} One of the attractive features of DESs is the flexibility in the combination of the salt and complexing agent. Potential complexing agents, such as urea and thiourea, are well known ligands for metals. The choice of the organic complexing agent has been shown to affect the relative solubility of the metal oxides, imparting a degree of selectivity in the dissolution process.³³ Thus, there could be the potential to create a DES with a high selectivity for a particular metal species. The potential technological application of DESs in separating metal oxides within a complex mixture has been demonstrated.²⁰⁷

3.3 The cost issue: choosing an ionic liquid

A major limitation to the practical application of ionic liquids in large scale processes is the prohibitively high cost of many ionic liquids. The “heaps” of ore involved in leaching are vast, requiring very large volumes of leaching solvent; typical flat-topped heaps are reportedly ≈ 7 m high with surface areas of $0.1 - 1 \text{ km}^2$.¹⁸⁶ Safety and environmental concerns relating to the solvent must also be considered. Moreover, there are practical, and cost, issues associated with the transportation of large volumes of reagents to relatively remote areas.

Any potential ionic liquid employed in a leaching solvent capacity must be cost effective i.e. as cheap as possible, as well as efficient at leaching and recyclable. To minimise the cost of the ionic liquid, the synthesis will need to be straightforward and the starting materials readily available bulk commodity chemicals. Ideally, both the reagents and final ionic liquid will be relatively non-toxic.

Two “types” of ionic liquid have been identified as cheaper alternatives to more traditional ionic liquids; protic ionic liquids and DESs. Both protic ionic liquids and DESs can be synthesised in a simple, “one-pot” process. Furthermore, many of the potential starting materials are bulk commodity chemicals, including a number of simple amines, mineral acids, ammonium salts and typical organic complexing agents (e.g. carboxylic acids and amides).

It has been demonstrated that copper can be leached from chalcopyrite with the Brønsted acidic ionic liquid, $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$.^{199, 201} A cheaper alternative would be the protic analogue, $[\text{C}_4\text{Him}][\text{HSO}_4]$. H_2SO_4 , used in the synthesis of $[\text{C}_4\text{Him}][\text{HSO}_4]$, is a by-product of the mining industry and therefore readily accessible. Furthermore, if leaching with a protic imidazolium ionic liquid can be demonstrated to be viable, there is the scope to replace the imidazolium cation with cheaper ammonium analogues.

DESs have been shown to solubilise a range of inorganic materials.^{32, 194} Choline chloride is the most commonly employed quaternary ammonium salt and is a mass produced chemical used as an additive in animal feed. Urea, a common example of a complexing agent, is also produced on an industrial scale for use in many applications, including fertilisers. Both choline chloride and urea are non-toxic reagents. Furthermore, with DESs, there could be the potential for a combination of a quaternary ammonium salt and complexing agent to be “tailored” for the selective extraction of copper.

Therefore, both mineral acid derived protic ionic liquids and DESs were initially proposed for investigation by the “ionic liquids” contingent of the *Rio Tinto – Imperial College London* collaboration. Experimentally, the focus has been on the application of mineral acid derived protic ionic liquids, such as $[\text{C}_4\text{Him}][\text{HSO}_4]$ and protic ionic liquid – water mixtures.

Computationally, one of our aims has been to achieve an improved fundamental understanding of the molecular level interactions within an exemplar DES, the choline chloride – urea mixture, and the protic ionic liquid, $[\text{C}_4\text{Him}][\text{HSO}_4]$. Understanding of the pure systems provides a good foundation for the investigation of more complex systems, such as ionic liquid – water mixtures, and eventually, metal speciation in the ionic liquid environment.

We present here the results from a quantum chemical study of the molecular level interactions within the choline chloride – urea DES and a combined quantum chemical and molecular dynamics investigation of $[\text{C}_4\text{Him}][\text{HSO}_4]$ and related systems.

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Chapter 2

Computational Methods

1. Introduction

A range of computational methodologies can be employed to investigate ionic liquids; each method is associated with inherent benefits and drawbacks. However, when different methods are employed to study the same system, a more complete “picture” can be obtained. Classical molecular dynamics (MD) and quantum chemical calculations, as used here, are two of the methodologies most routinely encountered in the computational study of ionic liquids.

Through classical MD the structure and thermodynamic and transport properties of the bulk ionic liquid can be evaluated.¹ However, the wave function is not explicitly included, therefore information relating to the electronic structure cannot be acquired. Moreover, the fixed charge, two-body potentials commonly employed are unable to capture many body effects, such as electronic polarisation. With the use of a polarisable force field more realistic dynamic properties can be obtained,^{1,2} but with an associated increase in the computational cost. Charge scaling of the atomic partial charges has also been shown to improve the computed dynamic properties.³⁻⁵

Ab initio quantum chemical methods allow for the in-depth interrogation of the electronic structure and properties associated with the electronic wave function or density. However, due to cost-scale considerations, calculations are usually restricted to a small number of ion pairs. One of the criticisms of such an approach is that a cluster of limited size may not adequately recover structural features of the bulk.⁶

Although larger clusters (up to at least 8 ion pairs) have been reported and novel approaches to the *ab initio* calculation of larger clusters are being developed,⁷ the feasibility of undertaking a systematic and comprehensive search for stable configurations decreases significantly with system size. One approach is to build larger clusters from the lowest energy ion pair motif. However, for ion pair dimers it has been shown that the lowest energy ion pair configurations are not necessarily adopted in the lowest energy ion pair dimers.⁶ This “building block” approach could therefore lead to key, low energy, structures being overlooked. Moreover, how large does a gas phase cluster need to be to be representative of the bulk?

An alternative methodology showing great potential for determining the structural and dynamic properties of ionic liquids is *ab initio* MD.⁸⁻¹¹ This method effectively couples key features of classical MD and *ab initio* methods and both some information regarding the dynamics of the system and information relating to the electronic properties can be acquired. A major drawback to routine application, however, is the high cost of *ab initio* MD simulations, placing a limit on the size of the system that can be modelled and restricting simulations to short timescales.

In this work we have used quantum chemical methods to study small ion pairs and ion pair dimers, as well as classical MD to model the bulk phase of selected ionic liquids. H-bonding in the ion

pairs and dimers has been examined using descriptors derived from the electronic wave function (e.g. ρ_{BCP} and $E^{(2)}$), whilst H-bonding in the MD simulations has been examined on a structural basis.

One of the criticisms of the study of ion pairs and dimers is that the structures are not sufficiently large enough to recover the structural features of the bulk. Furthermore, properties such as charge distribution are influenced by polarisation as a result of the bulk environment, potentially affecting the H-bond properties. Whilst the structure of the bulk ionic liquid is recovered using MD, information relating to the electronic structure (including relevant H-bond descriptors) cannot be obtained. Ideally it would be possible, using quantum chemical methods, to examine a cluster of ion pairs of feasible size in the “solvation environment” of the bulk ionic liquid.

Solvation is a complex process with a number of different contributions, including: the electrostatic interaction between the solvent and solute, cavity formation, dispersion interactions, structural reorganisation of the bulk solvent and specific interactions, including H-bonding.¹² The solvent influence can typically be broken down into long-ranged macroscopic effects, namely the mutual polarisation of the solvent and solute, and short-ranged effects, including H-bonding and the preferential reorientation of the solvent molecules. The specific effects are usually limited to the first few solvation shells, however, in order to recover the macroscopic influence of the bulk solvent, many solvent molecules are required.¹³ A cost effective approach for recovering some of the polarisation effects of the bulk solvent is to employ a quantum mechanical continuum solvation model, in which the solvent environment is treated implicitly as a dielectric continuum.¹⁴ Such implicit solvation models have previously been applied to the study of ionic liquids e.g. modelling of the reaction pathways for the thermal decomposition of $[\text{C}_2\text{C}_1\text{im}][\text{OAc}]$.¹⁵

However, a deficiency of continuum solvation models in the application to ionic liquids is the fact that many of the models were developed exclusively for neutral molecular solvents. Additionally, whilst solvent parameters for molecular solvents are generally well documented, there is the lack of parameters available for ionic liquids. Particularly problematic is the dearth of dielectric constant (ϵ) values.¹⁶ Moreover, the dielectric constant of ionic liquids has been found to have a strong dependence on the method used, resulting in a variation in the reported values of ϵ for the same ionic liquid. Some progress has been made with the introduction of the SMD model,¹⁷ which has been parameterised using both ionic and neutral species. Nevertheless, one of the major limitations of implicit solvation models is that they cannot recover direct solute-solvent interactions, such as H-bonding.

A possible approach, in which both the long-range electrostatic effects of the bulk environment and the short-range H-bonding could be approximated, would be to implement a hybrid QM/MM method. QM/MM has previously been employed to model reactions in an ionic liquid environment, with the reactants modelled at the semi-empirical PM3 level^{16, 18} However, a major drawback in the application of semi-empirical methods is that they are limited in application to systems and properties similar to those employed in the parameterisation procedure. Moreover, methods such as PM3 are unable to systematically recover electron exchange and correlation effects.

As far as can be established, the structuring and H-bonding within an ionic liquid has not been the subject of detailed investigation using a hybrid QM/MM method. We investigate here the possible

application of a QM/MM method in this context and aim to extend the evaluation of the QM region beyond the lowest level quantum mechanical treatments to more sophisticated methods, specifically DFT.

2. Quantum Chemistry and Density Functional Theory

2.1 The Schrödinger equation

One of the foremost aims of modern quantum chemistry is to obtain highly accurate information relating to the properties of molecular systems. Much of this “information” is effectively “stored” within the molecular wave function. Therefore, to access the information describing the properties of a system, the wave function describing the system must typically be computed. This can be achieved by obtaining the solution to the Schrödinger equation. The non-relativistic, time independent Schrödinger equation (**equation 2.1**) is:

$$\hat{H}\Psi(\mathbf{q}) = E\Psi(\mathbf{q}) \quad (2.1)$$

The wave function, Ψ , is dependent on the spin and spatial coordinate $\mathbf{q}$. $\hat{H}$ is the Hamiltonian operator, describing all nuclear and electronic interactions and E , the eigenvalue of the Schrödinger equation, has the units of energy.

The true molecular wave function is dependent on both the electronic and nuclear coordinates. However, given that the nuclei are much heavier than the electrons, the nuclei move much more slowly. Hence, the electrons can be approximated as moving in a field of fixed nuclei, known as the *clamped-nuclei approximation*. Through the *Born-Oppenheimer approximation* it can be demonstrated that the electronic and nuclear motions can be uncoupled. When $(m_e/m_n)^{1/4} \ll 1$ (where m_e and m_n are the electron and nuclear masses respectively), the molecular wave function can be approximated as (**equation 2.2**)¹⁹:

$$\Psi(\mathbf{q}_i, \mathbf{q}_\alpha) = \Psi_{el}(\mathbf{q}_i; \mathbf{q}_\alpha) \Psi_n(\mathbf{q}_\alpha) \quad (2.2)$$

Within **equation 2.2**, the total molecular wave function has been written as a product of the electronic wave function, Ψ_{el} , and the nuclear wave function, Ψ_n . The nuclear wave function depends on the nuclear coordinates ($\mathbf{q}_\alpha$) only, whereas the electronic wave function depends explicitly on the electronic coordinates ($\mathbf{q}_i$) but also parametrically on the nuclear coordinates (i.e. for a different nuclear configuration, the electronic energy will vary).²⁰

The full molecular Hamiltonian (**equation 2.3**) features terms for the kinetic energy of both the electrons and nuclei (first two terms respectively) and terms for the potential energy of the nuclear-nuclear, nuclear-electron and electron-electron interactions (last three terms respectively).

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee} \quad (2.3)$$

However, within the fixed nuclei framework, the kinetic energy of the nuclei can be neglected and the potential energy of the nuclear-nuclear interactions treated as a constant for a given nuclear

configuration. The remaining terms correspond to the electronic Hamiltonian, $\hat{H}_{el}$, as given in **equation 2.4**, or expressed more fully (in atomic units), **equation 2.5**:

$$\hat{H}_{el} = \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} \quad (2.4)$$

$$\hat{H}_{el} = -\sum_{i=1}^{N_e} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N_e} \sum_{\alpha=1}^{N_\alpha} \frac{Z_\alpha}{r_{i\alpha}} + \sum_{i=1}^{N_e} \sum_{j>1}^{N_e} \frac{1}{r_{ij}} \quad (2.5)$$

Within **equation 2.5**, N_e and N_α correspond to the number of electrons and nuclei respectively and Z_α to the nuclear charge. The electron – nuclear separation (i.e. $|r_i - R_\alpha|$) is expressed as $r_{i\alpha}$ and the electron-electron separation (i.e. $|r_i - r_j|$) as r_{ij} . When the electronic Hamiltonian is employed, the solution to the Schrödinger equation is the electronic wave function. All further discussion here is restricted to the treatment of the electronic wave function.

For many-electron systems the Schrödinger equation cannot be solved exactly, requiring approximations to be invoked. There are various “levels” of approximation, and often the choice of method is dependent on the size of the system and the accuracy required.

2.2 Approximating the solutions to the Schrödinger equation

To describe an electron it is necessary to consider both the spatial coordinates and “spin” of the electron. The orthonormal spin functions $\alpha(\omega)$ and $\beta(\omega)$, corresponding to the electron either being “spin up” and “spin down”, are therefore introduced. The three spatial coordinates, $\mathbf{r}$, and the spin coordinate, ω , are collectively represented by $\mathbf{q}$, **equation 2.6**. The electronic wave function of an N electron system is therefore a function of $\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N$ (**equation 2.7**).

$$\mathbf{q} = \{\mathbf{r}, \omega\} \quad (2.6)$$

$$\Psi_{el}(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N) \quad (2.7)$$

In addition to satisfying the Schrödinger equation, any molecular wave function must also satisfy the antisymmetry principle, as expressed in **equation 2.8**.²⁰ In other words, the wave function must change sign when the coordinates of any two electrons are interchanged.

$$\Psi(\mathbf{q}_1, \dots, \mathbf{q}_i, \dots, \mathbf{q}_j, \dots, \mathbf{q}_N) = -\Psi(\mathbf{q}_1, \dots, \mathbf{q}_j, \dots, \mathbf{q}_i, \dots, \mathbf{q}_N) \quad (2.8)$$

An approximate molecular wave function can be written as a Slater determinant of singly occupied one electron spin orbitals, where the one electron spin orbitals, $\chi(\mathbf{q})$, describe both the spatial distribution of the electron ($\psi(\mathbf{r})$) and the spin of the electron (either $\alpha(\omega)$ and $\beta(\omega)$), **equation 2.9**.

$$\chi(\mathbf{q}) = \begin{cases} \psi(\mathbf{r})\alpha(\omega) \\ \psi(\mathbf{r})\beta(\omega) \end{cases} \quad (2.9)$$

For a system with N electrons in N spin orbitals this is generalised as (**equation 2.10**):

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(q_1) & \chi_j(q_1) \cdots & \chi_k(q_1) \\ \chi_i(q_2) & \chi_j(q_2) \cdots & \chi_k(q_2) \\ \vdots & \vdots & \vdots \\ \chi_i(q_N) & \chi_j(q_N) \cdots & \chi_k(q_N) \end{vmatrix} \quad (2.10)$$

When expressed in this form, the wave function satisfies the antisymmetry principle. The rows of the Slater determinant are labelled according to the electrons (q_N) and the columns according to the spin orbitals (χ_i). Upon swapping the coordinates of any two electrons, two rows within the determinant are interchanged, thus resulting in the required change in sign of the determinant.

The anti-symmetrisation of the wave function introduces an effect known as exchange correlation, meaning that the movement of two electrons with parallel spins are correlated. However, the movement of two electrons with opposite spins are uncorrelated within this framework. This can be demonstrated by considering the electron probability densities.²⁰

$P(r_1, r_2)dr_1dr_2$ corresponds to the probability of finding electron one in a region of space defined by dr_1 at position r_1 simultaneously as finding a second electron in a region of space defined by dr_2 at position r_2 , **equation 2.11**.

$$P(r_1, r_2)dr_1dr_2 = \int |\Psi|^2 dr_1dr_2d\omega_1d\omega_2 \quad (2.11)$$

It can be shown that for two electrons with opposite spins, $P(r_1, r_2)$ is (**equation 2.12**)²⁰:

$$P(r_1, r_2) = \frac{1}{2} \left[|\psi_i(r_1)|^2 |\psi_j(r_2)|^2 + |\psi_i(r_2)|^2 |\psi_j(r_1)|^2 \right] \quad (2.12)$$

The first term of **equation 2.12** corresponds to the probability of finding electron 1 in spatial orbital ψ_i at the same time as electron 2 occupying ψ_j . The second term is the opposite, the probability of electron 2 occupying ψ_i simultaneously as electron 1 occupying ψ_j . The electrons are indistinguishable; therefore the two arrangements are equally likely. Hence, $P(r_1, r_2)$ is simply the average of the two terms. As each of the terms is simply the product of the probability of finding electron 1 in one region of space and electron 2 in another, the motions of two electrons with opposite spins are not correlated. Moreover, for the case where $\psi_i = \psi_j$ (**equation 2.13**):

$$P(r_1, r_2) = |\psi_i(r_1)|^2 |\psi_j(r_2)|^2 \quad (2.13)$$

Therefore, there is a non-zero probability of finding two electrons with opposite spins in the same region of space. However, for electrons with parallel spins, $P(\mathbf{r}_1, \mathbf{r}_2)$ can be shown to be (**equation 2.14**):

$$P(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} \left\{ \left| \psi_i(\mathbf{r}_1) \right|^2 \left| \psi_j(\mathbf{r}_2) \right|^2 + \left| \psi_i(\mathbf{r}_2) \right|^2 \left| \psi_j(\mathbf{r}_1) \right|^2 - \left[\psi_i^*(\mathbf{r}_1) \psi_j(\mathbf{r}_1) \psi_j^*(\mathbf{r}_2) \psi_i(\mathbf{r}_2) + \psi_i(\mathbf{r}_1) \psi_j^*(\mathbf{r}_1) \psi_j(\mathbf{r}_2) \psi_i^*(\mathbf{r}_2) \right] \right\} \quad (2.14)$$

The additional cross term ensures that two electrons with the same spin are correlated. For example, for the case where $\psi_i = \psi_j$, $P(\mathbf{r}_1, \mathbf{r}_2) = 0$. Hence, there is no probability of finding two electrons with parallel spins at the same position, consistent with the Pauli exclusion principle.

2.2.1 The Hartree-Fock approach

The energy of a system described by a given wave function is obtained by taking the expectation value of the Hamiltonian operator, **equation 2.15**:

$$E[\Psi] = \int \Psi^* \hat{H} \Psi d\mathbf{q} = \langle \Psi | \hat{H} | \Psi \rangle \quad (2.15)$$

According to the variational theorem, unless the wave function is the ground state wave function, then the energy of the system will be higher than the ground state energy (**equation 2.16**):

$$E[\Psi] \geq E_0[\Psi_0] \quad (2.16)$$

Therefore, one approach to finding the ground state wave function is to search for the wave function that minimises the total energy. Within the Hartree-Fock approximation, the initial “guess” wave function is assumed to be of the form given in **equation 2.10** i.e. an antisymmetric Slater determinant of one electron spin orbitals. Substitution of the guess wave function into the **equation 2.15** yields the Hartree-Fock energy (**equations 2.17**).

$$E_{HF} = \sum_i^{N_e} \langle \chi_i | \hat{h} | \chi_i \rangle + \frac{1}{2} \sum_i^{N_e} \sum_j^{N_e} \langle \chi_i \chi_j | \chi_i \chi_j \rangle - \langle \chi_i \chi_j | \chi_j \chi_i \rangle \quad (2.17)$$

$$\langle \chi_i | \hat{h} | \chi_i \rangle = \int \chi_i^*(\mathbf{q}_1) \left\{ -\frac{1}{2} \nabla^2 - \sum_{\alpha}^{N_a} \frac{Z_{\alpha}}{r_{1\alpha}} \right\} \chi_i(\mathbf{q}_1) d\mathbf{q}_1 \quad (2.18)$$

$$\langle \chi_i \chi_j | \chi_i \chi_j \rangle = \iint \chi_i^*(\mathbf{q}_1) \chi_i(\mathbf{q}_1) \frac{1}{r_{12}} \chi_j^*(\mathbf{q}_2) \chi_j(\mathbf{q}_2) d\mathbf{q}_1 d\mathbf{q}_2 \quad (2.19)$$

$$\langle \chi_i \chi_j | \chi_j \chi_i \rangle = \iint \chi_i^*(\mathbf{q}_1) \chi_j(\mathbf{q}_1) \frac{1}{r_{12}} \chi_j^*(\mathbf{q}_2) \chi_i(\mathbf{q}_2) d\mathbf{q}_1 d\mathbf{q}_2 \quad (2.20)$$

The first term (**equation 2.18**) corresponds to the kinetic energy and the electron-nuclear attraction. The second term (**equation 2.19**) is the classical Coulomb energy due to the electron-electron repulsions. The final term (**equation 2.20**) is the exchange energy, arising from the antisymmetrisation of the Slater determinant. The exchange interaction is attractive and modifies the Coulomb repulsion; two electrons with parallel spins have a tendency to “avoid” each other, thus reducing the Coulomb repulsion and lowering the energy. The sum of the Coulomb and exchange energies corresponds to the *mean* potential energy of an electron in the presence of $N_e - 1$ other electrons.

Considering the expression for the Coulomb interaction, the term $i=j$ is allowed. This implies that an electron can interact with itself, which is physically non-realistic. However, within the Hartree-Fock framework, when $i=j$, the Coulomb and exchange contributions cancel exactly. The Hartree-Fock approach is therefore free of *self-interaction* errors.

Through minimisation of the energy with respect to the set of spin orbitals, and under the condition that the spin orbitals are orthonormal, the optimal set of spin orbitals can be identified. The optimal Hartree-Fock orbitals must satisfy the Hartree-Fock equation, **equation 2.21**, where $\hat{f}$ is the Fock operator and is defined in **equation 2.22**.

$$\hat{f}|\chi_i\rangle = \varepsilon_i \chi_i \quad (2.21)$$

$$\hat{f} = \hat{h}_1 + \sum_j (\hat{J}_j - \hat{K}_j) \quad (2.22)$$

The first term within the Fock operator, $\hat{h}_1$, is the operator for the kinetic energy and electron-nuclear potential energy, **equation 2.23**. $\hat{J}_j$, and $\hat{K}_j$ are the Coulomb and exchange operators respectively, easier to define by the respective effects on a spin orbital, $\chi_i(\mathbf{q}_1)$, **equations 2.24** and **2.25**.

$$\hat{h}_1 = \left[-\frac{1}{2} \nabla_i^2 - \sum_{\alpha=1}^{N_\alpha} \frac{Z_\alpha}{r_{i\alpha}} \right] \quad (2.23)$$

$$\hat{J}_j(\mathbf{q}_1) \chi_i(\mathbf{q}_1) = \left[\int \chi_j^*(\mathbf{q}_2) \frac{1}{r_{12}} \chi_j(\mathbf{q}_2) \right] \chi_i(\mathbf{q}_1) d\mathbf{q}_2 \quad (2.24)$$

$$\hat{K}_j(\mathbf{q}_1) \chi_i(\mathbf{q}_1) = \left[\int \chi_j^*(\mathbf{q}_2) \frac{1}{r_{12}} \chi_i(\mathbf{q}_2) \right] \chi_j(\mathbf{q}_1) d\mathbf{q}_2 \quad (2.25)$$

The Coulomb operator, $\hat{J}_j$, is an example of a local operator and determines the average potential at position $\mathbf{q}_1$ due to an electron in χ_j . In contrast, the exchange operator, $\hat{K}_j$ is a non-local operator; the result of the application of $\hat{K}_j(\mathbf{q}_1)$ on $\chi_i(\mathbf{q}_1)$ depends on the value of χ_i at all points in space.

The solutions of the Hartree-Fock equations yield the exact spin orbitals. However, obtaining exact solutions to the Hartree-Fock equations is only viable for atoms.²⁰ Typically, it is necessary to expand the spatial part of the spin orbitals as a linear combination of known spatial basis functions.

The form of these basis functions is discussed in more detail shortly (**section 2.2.2**). The Hartree-Fock equation, **equation 2.21**, can be considered a *pseudo*-eigenvalue equation as the Fock operator has a functional dependence on the spin orbitals.²⁰ Therefore, the process of solving the Hartree-Fock equations is iterative.

2.2.2 Basis sets

The spatial component of the Hartree-Fock spin orbitals is typically expressed as a linear combination of K basis functions, ϕ , **equation 2.26**.²⁰

$$\psi_i = \sum_{\mu=1}^K c_{\mu i} \phi_{\mu} \quad (2.26)$$

For H_2 , for example, the ground state molecular orbitals could be expressed as a linear combination of 1s atomic orbitals. For the exact orbitals of a system to be obtained an infinite number of basis functions would be required. However, due to the computational cost, a finite basis of K functions, resulting in K spatial wave functions, is instead employed. As the basis set nears completeness, the expansion provides a more accurate description of the true orbitals. The error introduced as a result of using an incomplete basis set is known as the *basis set truncation error*.²¹ However, employing a large basis set, particularly one with diffuse functions, can generate issues of linear dependency.¹³ Invoking the variational theorem, the coefficients of the basis functions, $c_{\mu i}$, that give the lowest energy wave function need to be found. Therefore, for a given basis set, the coefficients that minimise the energy, **equation 2.27**, are the optimal coefficients.

$$\frac{\partial E}{\partial c_{\mu i}} = 0 \quad (2.27)$$

When choosing a set of basis functions, two main factors need to be considered; the accuracy with which the basis functions represent the true molecular orbitals and the efficiency with which the calculations can be undertaken.²⁰

In principle many different types of functions could be employed. In practice for molecular systems (i.e. ignoring the solid state), the functions employed approximate the form of the known hydrogen atomic orbitals and are associated with, and centred on, a single atom, in an “atomic orbital like” manner. Two main types of basis function are commonly encountered: *Slater* type functions and *Gaussian* type functions.

The mathematical form of a normalised Slater type function and a normalised Gaussian type function for a 1s atomic orbital are given in **equations 2.28** and **2.29**.²⁰ The exponents of the functions (ζ for the Slater and α for the Gaussian functions) determine the diffuseness of the function; a small exponent leads to a diffuse function, whilst a large exponent results in a tight function. An example Slater function (with $\zeta = 1$) is plotted in **Figure 2.1** together with a Gaussian function, fitted to best approximate the Slater function.

$$\phi_{1s}^{SF}(\zeta, \mathbf{r} - \mathbf{R}_A) = \left(\frac{\zeta^3}{\pi} \right)^{\frac{1}{2}} e^{-\zeta|\mathbf{r} - \mathbf{R}_A|} \quad (2.28)$$

$$\phi_{1s}^{GF}(\alpha, \mathbf{r} - \mathbf{R}_A) = \left(\frac{2\alpha}{\pi} \right)^{\frac{3}{4}} e^{-\alpha|\mathbf{r} - \mathbf{R}_A|^2} \quad (2.29)$$

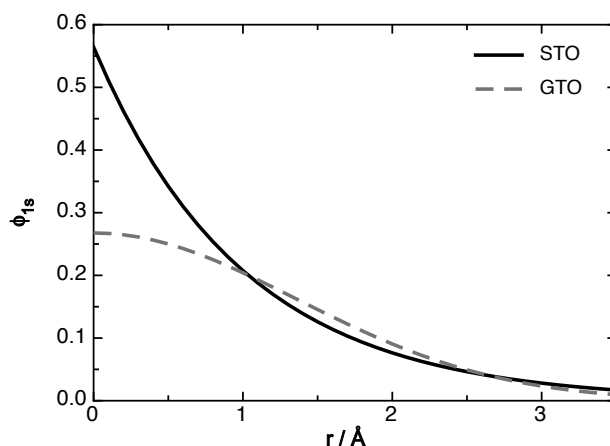


Figure 2.1. Comparison of a 1s Slater type orbital (STO, $\zeta=1$) and the Gaussian type orbital of best fit (GTO, $\alpha=0.270950$).²⁰

From **equations 2.28** and **2.29** and **Figure 2.1**, it can be seen that there are key differences in the Slater and Gaussian type functions. Slater functions have an exponential in $e^{-\zeta r}$, while Gaussian functions have an exponential in $e^{-\alpha r^2}$. This leads to slightly different behaviour, most evident at $r = 0$ and at large values of r .²⁰ At the nucleus (i.e. at $r = 0$), a Slater function has a cusp, in agreement with the form of the hydrogen 1s atomic orbital (AO). In contrast, a Gaussian function has a finite value at the nucleus. Moreover, at long ranges, the Gaussian function decays more rapidly than a Slater function. Overall, therefore, a single Slater type function provides a better representation of the behaviour of “real” AOs compared to a single Gaussian type function.

With respect to the efficiency of the calculation, the speed is often limited by the number and complexity of the two electron integrals that need to be evaluated. At worst, these two electron integrals involve a basis function on four *different* atomic centres, the so-called two-centre-four-electron integral problem. With Slater type functions, these integrals are costly to compute.²⁰ However, as the product of two Gaussian functions is simply another Gaussian, this four-centre problem can be effectively reduced to a two-centre problem. Therefore, Gaussian functions are computationally “cheaper” to employ.²⁰

An effective solution to this basis function dilemma is to use multiple Gaussian type functions to model a single Slater type function, the principle behind the STO-nG series of basis sets (STO = Slater Type Orbital and G = Gaussian).²²

A minimal STO basis employs just one STO to describe each AO of an atom e.g. H would require just 1x1s STO, whereas, C would require 1x1s STO, 1x2s STO and 3x2p STOs. Within an STO-nG basis, a linear combination of n-primitive Gaussian functions is used to model each single

STO. An STO-3G basis, for example, uses three Gaussian functions to model each STO i.e. **equation 2.30**. The exponents (α) and contraction coefficients (c) of each Gaussian are fitted to best approximate the STOs. These pre-determined parameters remain fixed during a calculation. Only the coefficient that corresponds to the effective contribution from each STO (i.e. d_i , **equation 2.31**) is varied during the course of the calculation.

$$STO = c_1 g(\alpha_1) + c_2 g(\alpha_2) + c_3 g(\alpha_3) \quad (2.30)$$

$$d_i[STO] = d_i[c_1 g(\alpha_1) + c_2 g(\alpha_2) + c_3 g(\alpha_3)] \quad (2.31)$$

A careful choice for the exponent (ζ) for the STO must also be made. The optimal value of ζ for an atom in a molecule differs from that of a free atom,²² and typically improved results for molecular calculations are obtained when larger values of ζ are employed for the valence electrons.²³ However, once the Gaussian expansion has been fitted to an STO with $\zeta=1$, a straightforward scaling procedure can be employed to determine the values of the Gaussian exponents for an STO with a different exponent.²⁰ For the STO-nG basis sets, the core orbitals of heavy atoms use the Slater exponents derived for free atoms.²² However, the exponents for the valence orbitals are obtained by averaging over the optimal exponents determined for the atom in a number of different molecules.²² For example, for hydrogen $\zeta=1$ is the optimum value in the free atom, but $\zeta=1.24$ in an average molecular environment, consistent with the hydrogen 1s orbital being “denser” on average within a molecule.²⁰

Minimal basis sets constitute the bottom rung of the basis set hierarchy and are very limited in terms of flexibility. An improvement on the minimal basis set can be made by using two STOs to describe each AO, a *double-zeta* (DZ) basis set. Relative to the minimal basis set, the exponents of one of the two functions for a given atomic orbital is slightly larger and one slightly smaller.²⁰ Through optimisation of the coefficients of the two functions, either a tight or diffuse orbital can be obtained in response to the surrounding environment.

n-Zeta basis sets also form a hierarchy, with an increasing number of “n” basis functions being used to describe each orbital; triple-zeta, quadruple-zeta etc. However, this is associated with an increase in computational cost. Introduction of valence-zeta and split-valence basis sets aids in moderating the computational cost.

It is recognised that the valence orbitals of an atom are more important for the description of chemical bonding than the core orbitals, although the latter make a significant contribution to the total energy.¹² A split-valence basis set distinguishes between the core and valence orbitals and uses a different contraction pattern for each. Within a split-valence basis set, each core orbital is described using a single contracted function.¹² In contrast, the valence orbitals are described using multiple functions in which only the internal component of the valence orbital is contracted, and thus have more flexibility. Although each core orbital is described using only a single contracted function, the number of primitive functions may be equal to, or larger than, the number of primitive functions used in the description of the valence orbitals.

There are a number of different “families” of basis sets. Pople basis sets are some of the most commonly employed and are built upon the minimal STO-nG basis sets. The simplest Pople basis

set, 3-21G, uses three contracted primitive Gaussian functions to describe the core orbitals, and three primitive Gaussian functions contracted in a 2:1 pattern to describe each of the valence orbitals. The number of contracted primitive Gaussian functions used for the core and valence orbitals can be increased. For example, the 6-311G basis set uses six contracted primitive Gaussian functions for each core orbital and five primitive Gaussian functions contracted in a 3:1:1 pattern for each valence orbital.

Further improvements to the flexibility of a basis set can be made through the introduction of *polarisation* and *diffuse* basis functions.¹² Upon bond formation, atomic orbitals become distorted by the surrounding atoms. Polarisation functions are functions of higher angular momentum that allow for a more anisotropic distribution of electron density about an atomic centre e.g. the addition of a “p” type function to an H atom allows for the distortion of the s orbital, or a “d” type function to a C atom can describe the polarisation of a p orbital. Polarisation functions are often considered necessary for a good description of H-bonding and polar bonding.^{12, 23}

Diffuse functions are basis functions with small exponents and allow for the movement of electron density further away from the atomic centre.²³ This is particularly important for electron rich species e.g. those with lone pairs or anions. Thus, diffuse functions are often required for the study of ionic liquids.

Using Pople notation, addition of “+”, as in 6-311+G, indicates the inclusion of diffuse functions on the heavy atoms. Addition of (d,p), e.g. 6-311+G(d,p), indicates the inclusion of one set of polarisation functions for the heavy atoms as well as polarisation functions on the hydrogen atoms.

An important consideration when deciding on a basis set for a system is to ensure that it is well balanced.¹³ This means that the description of each orbital is of equal quality. If the basis set is not well balanced, and is too small, then a problem known as basis set superposition error (BSSE) may occur. For the case of two interacting monomers, BSSE arises when one monomer uses basis functions from the second monomer to describe its own electron distribution, compensating for basis set incompleteness.¹³ This results in artificial stabilisation of the dimer relative to the two isolated monomers. For weakly bound complexes, the BSSE may be significant relative to the total interaction energy.²⁴ However, in the limit of the complete basis set, the BSSE would vanish.¹³

An (approximate) procedure for assessing the magnitude of the BSSE error is to employ the counterpoise correction (CP) proposed by Boys and Bernardi.²⁵ The CP approach approximates the BSSE as the difference in the energy of the two monomers computed with the respective basis sets of the monomers, and the energy of the monomers computed with the basis functions of the entire complex.¹³ The CP correction energy is defined in **equation 2.32** for two interacting monomers A and B, where the subscript indicates the basis set (either of the monomer or the complex) and the asterisk indicates that the monomers are in the geometries found in the complex.

$$\Delta E_{CP} = E(A)_{ab}^* + E(B)_{ab}^* - E(A)_a^* - E(B)_b^* \quad (2.32)$$

There is some debate regarding the CP correction, some arguing that it overestimates the BSSE, others that it is a rigorous and correct procedure.²⁶ Moreover, for intramolecular systems, it is more difficult to define the BSSE¹³ and for intermolecular complexes featuring many monomer units,

assessing the BSSE in this manner becomes increasingly questionable. Nevertheless, the CP correction is still widely employed.

2.3 Electron correlation: Improving upon Hartree-Fock theory

Within Hartree-Fock theory, the electron-electron interactions are treated in an average way; the non-interacting electrons are influenced by the electrostatic field of the nuclei and the mean field of the $N_e - 1$ electrons. Hartree-Fock does not, therefore, recover the *instantaneous* interactions between electrons, neither the instantaneous Coulomb nor quantum mechanical effects. As such, Hartree-Fock theory can be said to ignore electron correlation.²³

The electron correlation energy is defined as the energy difference between the Hartree-Fock energy and the true (exact) energy of the system, ε_0 , **equation 2.33**.²⁰ The correlation energy is negative and therefore lowers the total energy of the system.

$$E_{corr} = \varepsilon_0 - E_{HF} \quad (2.33)$$

Electron correlation can crudely be partitioned into two different types, although strictly the correlation effects are difficult to separate.¹³ The first is commonly referred to as either dynamic or short-range correlation. This refers to the instantaneous correlated movement of electrons and includes the tendency of one electron to “avoid” another electron, thus lowering the Coulomb repulsion.

The second type of correlation is static or long-range correlation. This is usually more significant for systems with a number of low-lying, near degenerate states. In such cases, a description of the system using only the single Hartree-Fock ground state determinant is not sufficient. Static correlation can be important for the correct description of bond dissociation¹³ and, for example, systems featuring transition metals,²⁷ with only a very small energy separation between the nd and $(n+1)s$ orbitals.

The deficiencies of Hartree-Fock limit its application. However, Hartree-Fock does provide the foundation upon which better approximations for the molecular wave function can be built, so-called *post-Hartree-Fock* methods. Much emphasis is placed on recovering the “missing” electron correlation. There is more than one approach to accounting for electron correlation (to varying degrees), although the incorporation of excited state determinants into the description of the ground state wave function is a common feature.¹³ Typical approaches include Møller-Plesset perturbation theory, configuration-interaction (CI) and coupled-cluster (CC) methods.

The highest-level methods are capable of predicting chemical properties within experimental accuracy. However, the cost of many of the post-Hartree-Fock methods scales quickly with the number of electrons. Moreover, these methods often require the use of very large and flexible basis sets, further increasing the computational cost. As such, the cost of post-Hartree-Fock methods is prohibitively high for many applications.

2.4 Density functional theory

One alternative approach to Hartree-Fock and post-Hartree-Fock methods is to employ Density Functional Theory (DFT). The use of DFT as an alternative to true *ab initio* methods is now widespread within computational chemistry, where it is routinely used to investigate a diverse range of systems, from materials in the solid state to gas phase molecular systems, including complex biological species.

2.4.1 Background

The foundations of DFT are the Hohenburg-Kohn theorems.²⁸ The first theorem establishes that the Hamiltonian operator can be uniquely determined by the electron density $\rho(r)$. It can subsequently be demonstrated that the energy of a system is a functional of the electron density, **equation 2.34**:

$$E[\rho(r)] \quad (2.34)$$

Significantly, the total electron density is dependent on only 3 spatial coordinates (i.e. the x, y and z coordinates). Therefore, within the DFT framework, the problem of a many-electron system with $3N$ spatial coordinates (*ab initio* methods) is reduced to a problem with only 3 spatial coordinates. However, this advantage is lost in modern DFT methodology due to the reintroduction of an orbital (χ_i) based basis set. In practice, a DFT calculation has a similar computational cost to a Hartree-Fock calculation, but is able to produce more accurate results.¹³

The second theorem is simply a variant of the variational theorem (i.e. **equation 2.16**). It establishes that for any trial density, $\rho(r)_t$ (also satisfying **equation 2.35**, where N is the total number of electrons), **equation 2.36** is applicable.²⁸ Therefore, the electron density that minimises the energy corresponds to the electron density of the ground state.

$$N = \int \rho(r)_t dr \quad (2.35)$$

$$E[\rho_t] \geq E_0 \quad (2.36)$$

Through the Hohenburg-Kohn theorems it can be surmised that there should exist a universal functional, $E[\rho(r)]$, which if it could be determined, would allow the exact ground state electron density and energy to be computed.

With reference to the Schrödinger equation, $E[\rho(r)]$ can be partitioned into constituent terms, **equation 2.37**. As before, the kinetic energy of the nuclei can be neglected and the nuclear-nuclear repulsions treated as a constant for a given configuration of the nuclei.

$$E[\rho(r)] = T_e[\rho(r)] + V_{ne}[\rho(r)] + J_{ee}[\rho(r)] + K_{ee}[\rho(r)] \quad (2.37)$$

Both the energy of the electron-nuclear interaction, V_{ne} , and the classical Coulomb contribution to the electron-electron interaction, J_{ee} , can be readily expressed in terms of the electron density, **equations 2.38** and **2.39** respectively.

$$V_{ne}[\rho(r)] = -\sum_{i=1}^{N_e} \sum_{\alpha=1}^{N_\alpha} \int \frac{Z_\alpha \rho(r_1)}{r_{1\alpha}} dr_1 \quad (2.38)$$

$$J_{ee}[\rho(r)] = \sum_{i=1}^{N_e} \sum_{j=1}^{N_e} \frac{1}{2} \iint \frac{\rho(r_1)\rho(r_2)}{r_{12}} dr_1 dr_2 \quad (2.39)$$

However, the exact forms of the kinetic energy and exchange energy functionals are not known, and an approach to approximating these functionals is required. The approach proposed by Kohn and Sham was to assume a system of non-interacting electrons (i.e. $V_{ee} = 0$) which reproduce the same ground state electron density as the real system.²⁸ A Slater determinant of singly occupied one electron orbitals is employed as a basis to describe the system of non-interacting (ni) electrons. Within this framework, the exact (non-interacting) kinetic energy can be calculated, **equation 2.40**, where the orbitals reproduce the true ground state electron density, **equation 2.41**.

$$T_{ni}[\rho(r)] = -\frac{1}{2} \sum_{i=1}^{N_e} \langle \chi_i | \nabla^2 | \chi_i \rangle \quad (2.40)$$

$$\rho(r) = \sum_{i=1}^{N_e} |\chi_i|^2 \quad (2.41)$$

Using the non-interacting kinetic energy, the expression for the total energy functional can be rewritten, **equation 2.42**, where an additional term $E_{xc}[\rho(r)]$ has been introduced. $E_{xc}[\rho(r)]$ is referred to as the *exchange-correlation functional* and is effectively the error resulting from assuming a system of non-interacting electrons and a classical treatment of electron-electron interactions, **equation 2.43**.

It should be noted that the Coulomb repulsion, J_{ee} , also includes the interaction of the electron density with itself. For this to cancel (as in the Hartree-Fock scheme), $J_{ee}[\rho(r)]$ would have to exactly equal minus $E_{xc}[\rho(r)]$. However, due to the approximate nature of the exchange-correlation functional, this is typically not the case. Thus, the self-interaction error is an issue for DFT.²⁸

$$E[\rho(r)] = T_{ni}[\rho(r)] + V_{ne}[\rho(r)] + J_{ee}[\rho(r)] + E_{xc}[\rho(r)] \quad (2.42)$$

$$E_{xc}[\rho(r)] = \left[(T[\rho(r)] - T_{ni}[\rho(r)]) + (V_{ee}[\rho(r)] - J_{ee}[\rho(r)]) \right] \quad (2.43)$$

The orbitals that minimise the energy, under the constraint that the orbitals are orthonormal, are found through application of the variational theorem and must satisfy **equation 2.44**. V_{xc} is the potential derived from the exchange-correlation energy functional, **equation 2.45**. It should be noted that unlike in Hartree-Fock and post-Hartree-Fock methods, the physical relevance of the (Kohn-Sham) orbitals is not clear and the interpretation of these orbitals is debated.²⁸

$$\left[-\frac{1}{2} \nabla^2 - \sum_{\alpha=1}^{N_\alpha} \frac{Z_\alpha}{r_{1\alpha}} + \int \frac{\rho(r_2)}{r_{12}} dr_2 + V_{xc}(r_1) \right] \chi_i(r_1) = \varepsilon_i \chi_i(r_1) \quad (2.44)$$

$$V_{xc}(\mathbf{r}) = \frac{\partial E_{xc}[\rho(\mathbf{r})]}{\partial \rho(\mathbf{r})} \quad (2.45)$$

If $E_{xc}[\rho(\mathbf{r})]$ were known, the ground state density, and therefore energy, could be determined exactly. However, the form of $E_{xc}[\rho(\mathbf{r})]$ is not known and must instead be modelled. In practice, the accuracy and applicability of DFT to a system is inherently dependent on the choice of the exchange-correlation functional employed.

Typically, $E_{xc}[\rho(\mathbf{r})]$ is written in terms of separate exchange and correlation components, **equation 2.46**. However, this is something of a misnomer, as these two contributions do not correspond directly to exchange and correlation as the terms would apply within Hartree-Fock and post-Hartree-Fock theories.

$$E_{xc}[\rho(\mathbf{r})] = E_x[\rho(\mathbf{r})] + E_c[\rho(\mathbf{r})] \quad (2.46)$$

2.4.2 Exchange-correlation functionals

Much work has been undertaken in the field of exchange-correlation functional development and this continues to be an active area of research. However, one of the drawbacks of DFT is that there is no systematic way of improving the approximations to the exchange-correlation functional.²⁸ Nevertheless, progress in improving the performance of exchange-correlation functionals has been made. There now exists a number of different “families” of density functional, forming an approximate hierarchy.²⁹ To date, however, there is still no one functional that can be said to outperform all others for application across the entire periodic table and for all properties.

In this context, the thorough testing and benchmarking of functionals becomes very important. However, even here there are issues. For example, what reference data is most appropriate for a functional to be benchmarked against? Older functionals were usually benchmarked using test sets that were predominated by atomic properties, e.g. atomisation energies. Modern functionals are typically benchmarked against test sets that include arguably more “chemically relevant” properties, e.g. barrier heights, spectroscopic properties and interaction energies of non-covalently bound species, and include systems with a wider range of elements, e.g. transition metals. Significantly, there are indications that there is not a significant correlation between the performance in predicting atomisation energies and in chemically more relevant energies.³⁰

Based on recent assessments of functional performance, two generalised statements can be made. Firstly, newer functionals *on average* perform better than older functionals.²⁹ Secondly, *on average* there is improved functional performance as “Jacob’s ladder” of functionals is ascended.³⁰ However, given the very large number of available functionals, and the variation in functional performance for different applications, choosing the “best” functional for a given problem can be difficult. Often a number of factors may need to be considered and a compromise made. The different “families” of exchange-correlation functional are briefly introduced in the following.

The local (spin) density approximation

The *local density approximation* (LDA) is the simplest approach to the approximation of the exchange-correlation functional. Central to the LDA approach is the assumption that the exchange-correlation energy at a given point is a local function of the electron density. Moreover, it is assumed that the exchange-correlation energy at this point corresponds to that of a homogeneous electron gas of the same electron density.²⁸

With LDA, the approximate exchange-correlation energy can be expressed as:

$$E_{xc}^{LDA}[\rho(\mathbf{r})] \approx \int \rho(\mathbf{r}) \varepsilon_{xc}[\rho(\mathbf{r})] d\mathbf{r} \quad (2.47)$$

Where $\varepsilon_{xc}[\rho(\mathbf{r})]$ within **equation 2.47** is the exchange-correlation energy per particle of a homogeneous electron gas of density $\rho(\mathbf{r})$. $\varepsilon_{xc}[\rho(\mathbf{r})]$ can be partitioned into two terms, one corresponding to the exchange contribution (ε_x) and one to the correlation contribution (ε_c). The form of $\varepsilon_x[\rho(\mathbf{r})]$, the exchange energy of an electron in a homogeneous electron gas of a given density, was initially derived by Bloch and Dirac, **equation 2.48**.²⁸ When inserted into **equation 2.47**, the exchange energy can be written exactly as in **equation 2.49**. The constant C_x is defined in **equation 2.50**.

$$\varepsilon_x[\rho(\mathbf{r})] = -C_x \rho(\mathbf{r})^{1/3} \quad (2.48)$$

$$E_x^{LDA}[\rho(\mathbf{r})] = -C_x \int \rho(\mathbf{r})^{4/3} d\mathbf{r} \quad (2.49)$$

$$C_x = \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \quad (2.50)$$

There is no analogous explicit expression for the correlation energy. However, results from high-level Monte Carlo simulations of the homogeneous electron gas at a number of different densities have allowed analytical expressions of ε_c to be developed. Commonly employed expressions include those established by Vosko, Wilk and Nusair (VWN)³¹ and by Perdew and Wang.³²

A more general form of the LDA approach is the local spin density approximation (LSDA) in which the total electron density is expressed in terms of the individual α and β spin densities, **equation 2.51**.²⁸ The LSDA approach is particularly useful for open shell systems where the α and β spin densities are not equal.

$$E_x^{LSDA}[\rho(\mathbf{r})] = -2^{1/3} C_x \int \left[\rho_\alpha(\mathbf{r})^{4/3} + \rho_\beta(\mathbf{r})^{4/3} \right] d\mathbf{r} \quad (2.51)$$

A homogeneous electron gas is an acceptable physical approximation for a simple metal, but is not a good approximation of the electron density in a real system, which will exhibit significant variations. It is therefore surprising that the LDA approach can perform reasonably well in some cases. Results obtained with LDA methods are often of a similar accuracy to those obtained with Hartree-Fock methods.¹³ In part, the reasonable success of the LDA approach is due to the fortuitous cancellation

of errors; the overestimation in E_c is balanced by the underestimation in E_x .³³ Nevertheless, LDA usually performs poorly in the estimation of energies, for example, having a tendency to overestimate binding energies.^{28, 33} Generally, LDA functionals are not good enough for the treatment of most problems of interest in molecular chemistry.

The generalised gradient approximation

For an improvement on the LDA approach to be made, it is necessary to account for the spatial inhomogeneity in the electron distribution of real systems. This can be achieved by making the exchange-correlation energy dependent on both $\rho(\mathbf{r})$ at point $\mathbf{r}$ and the gradient of $\rho(\mathbf{r})$, $\nabla\rho(\mathbf{r})$, **equation 2.52**. This is the approach taken by all *Generalised Gradient Approximation* (GGA) methods.²⁸

$$E_{xc}^{GGA}[\rho(\mathbf{r})] \approx \int \rho(\mathbf{r}) \varepsilon_{xc}[\rho(\mathbf{r}), \nabla\rho(\mathbf{r})] d\mathbf{r} \quad (2.52)$$

There are two main approaches to the development of GGA functionals. The first approach employs a test set of data and a numerical fitting procedure to determine specific parameters. The resultant functionals are therefore partially empirical in nature. Given the data used to parameterise the functionals, it is not surprising that this class of GGA functional typically performs well in the prediction of atomisation energies and reaction barriers for molecules. However, these fitted functionals often perform poorly in describing the properties of solid-state systems.³³

A notable example of an exchange functional derived using this approach is the Becke88 (B) functional,³⁴ in which a correction to the LSDA exchange energy is introduced, **equation 2.53**. The B88 exchange functional contains one empirically determined parameter, β (0.0042 a.u), obtained through a least squares fit to atomic data. x is defined in **equation 2.54**.

$$E_x^{B88}[\rho(\mathbf{r})] = E_x^{LSDA}[\rho(\mathbf{r})] - \beta \sum_{\sigma=\alpha,\beta} \int \rho_{\sigma}(\mathbf{r})^{4/3} \frac{x_{\sigma}^2}{(1 + 6\beta x_{\sigma} \sinh^{-1} x_{\sigma})} d\mathbf{r} \quad (2.53)$$

$$x = \frac{|\nabla\rho_{\sigma}(\mathbf{r})|}{\rho_{\sigma}(\mathbf{r})^{4/3}} \quad (2.54)$$

The second class of GGA functional consists of functionals with no semiempirical parameters, instead having been developed with a stricter adherence to first principles.³³ These functionals perform better in the prediction of solid-state properties but generally do not perform as well as the fitted GGA functionals in the prediction of, for example, reaction barriers for molecules.³³ One of the most commonly encountered exchange functionals of this second class is the PBE functional of Perdew, Burke and Ernzerhof.³⁵

The GGA correlation functionals have complex analytical expressions. Examples include P86,³⁶ with a single empirical parameter, parameter free PW91,³⁷ and the well-known LYP functional of Lee, Yang and Parr.³⁸ LYP differs from the other examples, as it has not been based upon the homogeneous electron gas. Instead, LYP was developed from the correlation energy of a helium

atom, as determined using high level correlated wave function theory and contains one empirical parameter.

Generally, GGA functionals do improve upon the performance of LDA functionals.¹³ For example, GGA methods typically give better predictions of energies.³³ As an estimate the GGA approach improves calculated binding energies by roughly an order of magnitude relative to the LDA.³⁹ However, there can be significant variation in the performance of GGA functionals. Moreover, for solid-state systems GGA functionals do not necessarily out-perform LDA functionals.³³

Meta-GGA functionals are an extension of GGA functionals and have been developed to include a dependence on higher order gradients of the electron density, **equation 2.55**. This is either *via* a dependence on the Laplacian of $\rho(r)$, $\nabla^2\rho(r)$, or more typically on the related kinetic energy density, τ , **equation 2.56**.¹²

$$E_{xc}^{mGGA}[\rho(r)] \approx \int \rho(r) \varepsilon_{xc}[\rho(r), \nabla\rho(r), \nabla^2\rho(r), \tau] dr \quad (2.55)$$

$$\tau = \frac{1}{2} \sum_i^{occ} |\nabla \chi_i|^2 \quad (2.56)$$

Meta-GGA functionals may offer an improvement over GGA functionals,¹² however, relative to GGA functionals, meta-GGA functionals typically require the use of a finer integration grid.²⁹

Hybrid functionals

In terms of energy, the exchange contribution is usually significantly larger than the correlation contribution.²⁸ Therefore, a good approximation for the exchange functional is particularly important to the accuracy of any DFT method.

Within Hartree-Fock theory, the exchange energy for a Slater determinant of non-interacting electrons is exact and by definition a non-local quantity. In contrast, approximate LDA and GGA exchange-correlation functionals are local entities, dependent only on the electron density and gradient of the electron density at one point in space. In order to better approximate the true density functional, which will have non-local character,²⁹ a percentage of the exact Hartree-Fock exchange can be included in the approximate exchange-correlation functional. Such functionals are known as *hybrid* functionals.

It is possible for the approximate exchange functional to be replaced with 100% of Hartree-Fock exchange. However, within DFT errors in the exchange and correlation functionals approximately cancel.²⁸ Replacing the approximate exchange with the exact exchange removes this cancellation. Subsequently, the percentage of exact exchange to be incorporated must be carefully determined.

The exchange functional is commonly expressed as a combination of contributions from LSDA, exact exchange and a gradient correction term.¹³ The correlation functional can also be expressed as a combination of LSDA and a suitable gradient correction. One approach to obtaining the optimal functional is to introduce semiempirical coefficients to determine the respective weighting of the different components.²⁸

One of the most well known functionals of this type is B3LYP, a combination of Becke's three-parameter exchange functional with the LYP correlation functional.^{38, 40, 41} To date, B3LYP has been the most widely employed functional within the field of computational chemistry. The form of the B3LYP functional is given in **equation 2.57**. The coefficient a determines the amount of exact exchange (E_x^{HF}), and b and c determine the size of the contributions of the gradient corrections to the local density approximation. Becke's original parameters are $a = 0.20$, $b = 0.72$ and $c = 0.81$, obtained through fitting to the heats of formation of small molecules.

$$E_{xc}^{B3LYP}[\rho(\mathbf{r})] = (1-a)E_x^{LSD} + aE_x^{HF} + bE_x^{B88} + cE_c^{LYP} + (1-c)E_c^{VWN} \quad (2.57)$$

Another class of hybrid functionals are *parameter free* hybrid functionals. Theoretically, there is justification for the suggestion that the percentage of exact exchange should be between 20-25%.^{42, 43} Perdew, Burke and Ernzerhof recommend the implementation of 25% exact exchange and the form of the hybrid functional can be expressed as in **equation 2.58**.⁴² When the GGA functional is PBE, the resultant hybrid functional is known as PBE1PBE (or PBE0).

$$E_{xc}^{hybrid}[\rho(\mathbf{r})] = E_{xc}^{GGA} + 0.25(E_x^{HF} - E_x^{GGA}) \quad (2.58)$$

In the computation of molecular properties, hybrid functionals do generally result in improvements over GGA analogues.^{12, 33} However, for functionals parameterised against a specific dataset, there are questions relating to the transferability of the functional to systems different to those included within the dataset.

A more recent extension of the hybrid family, are the *hybrid-meta* GGA functionals. Instead of development upon a parent GGA functional, hybrid-meta-GGA functionals are built upon meta-GGA functionals. Some of the most promising hybrid-meta GGA functionals belong to the Minnesota suite of density functionals e.g. M06 and M06-2X.⁴⁴ There are questions relating to the robustness of the Minnesota functionals.³⁰ However, benchmark studies often find hybrid-meta GGA members of the Minnesota class of functional to be amongst the top performing examples. M05-2X, for example, was found to perform reasonably well in the prediction of ionic liquid ion pair binding energies, relative to MP2 reference values.⁴⁵

The hybrid functionals discussed so far are all examples of *global* hybrid functionals. These functionals do exhibit some non-local character *via* the incorporation of a percentage of Hartree-Fock exchange. However, global hybrid functionals still fail to describe the correct long-range behaviour of the exchange-correlation potential.⁴⁶ *Long-range corrected* (LC) hybrid density functionals possibly offer a solution to this problem.

Within long-range corrected hybrid density functionals, the Coulomb operator is partitioned into a short-ranged (SR) and long-ranged (LR) operator.⁴⁶ The LR component can be treated using wave function theory and the SR component using DFT. The form of an exchange-correlation functional for a simple LC scheme is given in **equation 2.59**.⁴⁶

$$E_{xc}^{LC} = E_x^{LR-HF} + E_x^{SR-DFT} + E_c^{DFT} \quad (2.59)$$

Within this scheme the exchange energy is partitioned into two components; LR exchange corresponding to exact HF exchange and SR exchange approximated using DFT. The correlation energy is also treated using a density functional approximation. This type of scheme is computationally efficient and a number of LC functionals have been developed.⁴⁶ Some of the most well known are those centred on Becke's B97 GGA functional.⁴⁷ A dispersion corrected variant, known as ω B97XD,⁴⁸ is emerging as a very promising functional for a wide range of applications.^{30, 49, 50}

2.4.3 Dispersion corrections

Dispersion interactions are quantum in origin, arising from the effects of electron correlation.⁵¹ Classically this can be thought of as an instantaneous dipole, resulting from fluctuations in the electron density, inducing a dipole in another atom. Thus, dispersion is an attractive interaction and is an important contribution to many systems, including ionic liquids.

When higher order multipoles are also considered, the dispersion interaction can be approximated as a series expansion, **equation 2.60**, with the leading r^{-6} term corresponding to the dipole-dipole interaction.⁵¹

$$E_{disp} = \frac{-C_6}{r^6} + \frac{-C_8}{r^8} + \frac{-C_{10}}{r^{10}} + \dots \quad (2.60)$$

Dispersion interactions are most significant over medium ($\approx 2\text{-}5$ Å) and long (>5 Å) separations. A deficiency of DFT is the failure to adequately describe interactions in this mid to long range. This is largely due to the inability of the components of most functionals to act over the required range. The incorporation of exact Hartree-Fock exchange introduces some long-range character; however, the correlation remains local. As such, even for hybrid functionals, the r^{-6} distance dependence of dispersion interactions is not correctly described.

Approaches to improving the description of dispersion interactions within the DFT framework are actively being researched. In recent years, a number of new functionals have been developed offering an improved description of dispersion. However, one of the most widely implemented approaches is to use a simple "dispersion correction", the DFT-D approach.^{52, 53}

Within the DFT-D approach, an empirical dispersion correction (E_{Disp}) is added to the Kohn-Sham energy (E_{KS-DFT}), **equation 2.61**.⁵² As the dispersion correction is an "add-on" term, it only directly alters the energy of the system i.e. does not directly influence the electronic structure. However, through changes in the forces, the dispersion correction will indirectly influence the geometry and electron density of the system. The dispersion corrections developed have been parameterised for use with a number of different functionals and are now implemented in popular computational chemistry codes.

$$E_{DFT-D} = E_{KS-DFT} + E_{Disp} \quad (2.61)$$

The form of Grimme's second generation "D2" dispersion correction is given in **equation 2.62**.⁵³ The dispersion correction accounts for all pairwise (AB) interactions, summed over all atoms (N_{at}). r_{AB} is

the atom-atom separation and C_6^{AB} the atom pair specific dispersion coefficient, taken to be the geometric mean of the individual atom specific values, **equation 2.63**. A damping function, f_{damp} **equation 2.64**, is introduced to avoid electron correlation double counting effects at intermediate distances and near singularities at small separations.

$$E_{Disp}^{D2} = -\frac{1}{2} \sum_{A \neq B}^{N_{at}} s_6 \frac{C_6^{AB}}{r_{AB}^6} f_{damp}(r_{AB}) \quad (2.62)$$

$$C_6^{AB} = \sqrt{C_6^A C_6^B} \quad (2.63)$$

$$f_{damp}^{D2}(r_{AB}) = \frac{1}{1 + e^{-\alpha(r_{AB}/s_{r,n} R_{AB}^0 - 1)}} \quad (2.64)$$

The “D3” dispersion correction, **equation 2.65**, is a refinement of the D2 correction and includes an r^{-8} term, with a corresponding adjustment of the C_6^{AB} coefficient and damping function, **equation 2.66**.⁵⁴

$$E_{Disp}^{D3} = -\frac{1}{2} \sum_{n=6,8} s_n \sum_{A \neq B}^{N_{at}} \frac{C_n^{AB}}{r_{AB}^n} f_{damp}(r_{AB}, s_{r,n}) \quad (2.65)$$

$$f_{damp}^{D3}(r_{AB}) = \frac{1}{1 + 6 \left(r_{AB} / (s_{r,n} R_{AB}^0) \right)^{-\alpha}} \quad (2.66)$$

Within both **equations 2.62** and **2.65**, s_6 and s_8 are global scaling factors used to adjust the repulsive behaviour of the density functional and are dependent on the functional being employed. Within the damping functions, α is a “steepness parameter”, determining the steepness of the damping function. R_{AB}^0 is the sum of the van der Waal radii for atoms A and B , which for consistency have been determined theoretically for all elements up to $Z=94$. $s_{r,n}$ is an order dependent radii scaling factor for atom pair AB .

The D2 and D3 damping functions are known as “zero-order” damping functions. In both cases the damping function approaches zero as $r_{AB} \rightarrow 0$. Therefore, within DFT-D2 and DFT-D3, E_{disp} also approaches zero as $r_{AB} \rightarrow 0$. However, it has been suggested that E_{disp} should approach a constant, finite value as $r_{AB} \rightarrow 0$.^{55, 56}

Becke and Johnson proposed a new damping function to address this problem.⁵⁶ When the Becke-Johnson (BJ) damping function is employed there is a constant contribution of E_{disp} to the total correlation energy for spatially close pairs of atoms. The form of E_{disp} with the BJ damping function is given in **equation 2.67**, with the associated damping function provided in **equation 2.68**. a_1 and a_2 are additional parameters introduced by Becke and Johnson and must be determined for each density functional. The cut-off radius for atom pair AB , R_{AB}^0 is defined in **equation 2.69**. The R_{AB}^0 values used in the DFT-D3 approach can be employed, however the R_{AB}^0 values obtained with the relation given in **equation 2.69** were found to give slightly better results within the DFT-D3BJ approach.⁵⁵

The benchmark testing of the DFT-D3BJ variant reveals that compared to DFT-D3, the use of the BJ damping function does result in slight improvements.⁵⁵ For example, improved results for non-bonded distances and the description of intramolecular dispersion were found. Both variants perform well in determining the structures of non-covalently bonded systems. However, on average DFT-D3BJ shows a slight improvement in the predicted non-covalent association energies and in the prediction of thermodynamic data. It should be noted, however, that any differences between the results with the DFT-D3 and DFT-D3BJ approaches were notably smaller than the differences between either of the DFT-D approaches and the uncorrected DFT results.

$$E_{disp}^{D3BJ} = -\frac{1}{2} \sum_{A \neq B} \sum_{n=6,8} s_n \frac{C_n^{AB}}{R_n^{AB} + [f_{damp}]^n} \quad (2.67)$$

$$f_{damp}^{D3BJ}(R_{AB}^0) = a_1 R_{AB}^0 + a_2 \quad (2.68)$$

$$R_{AB}^0 = \sqrt{\frac{C_8^{AB}}{C_6^{AB}}} \quad (2.69)$$

A recent evaluation of quantum mechanical methods for the treatment of non-covalent interactions found that DFT-D corrected methods performed very well against the CCSD(T)/CBS reference data.⁵⁰ For example, inclusion of a D3 dispersion correction significantly reduced the underbinding found with non-corrected functionals. Across all test systems, a notable improvement on going from B3LYP to B3LYP-D3 was observed. A small improvement on going from B3LYP-D3 to B3LYP-D3BJ was also identified.

With regard to ionic liquids, the inclusion of the D3 correction was found to improve the computed binding energies of ion pairs relative to the CCSD(T)/CBS reference values.¹¹⁰ However, an earlier investigation with the D2 correction found that there is some inconsistency in the improvement depending on the identity of the ions.⁴⁵ For computed ion pair dissociation potential energy curves, DFT-D3BJ was found to correct for the deviations observed with the standard DFT functionals.⁵⁷

2.5 Comment on method used here

DFT has been used extensively in this work to investigate intermolecular interactions within the selected ionic liquid systems. The Gaussian 09 (G09) suite of programmes has been used exclusively for all quantum chemical calculations. Becke's three parameter exchange functional in conjunction with the correlation functional of Lee, Young and Parr, B3LYP, has been employed throughout as the "parent functional". However, throughout the course of this project, increasing evidence demonstrating the importance of dispersion interactions within ionic liquids has been made apparent.

Early, preliminary calculations were undertaken with the conventional B3LYP functional with a medium sized Pople basis set, 6-311+G(d,p). Subsequent calculations were undertaken with the inclusion of Grimme's D2 dispersion correction, the only correction available within the B.01 version of G09. Only within the more recent D.01 revision of G09 have the D3 and D3BJ corrections been implemented. Work from within the group has demonstrated that structures obtained at the B3LYP-D3BJ level with a moderate sized Pople basis set are in good agreement with MP2 geometries.⁶ As such, the most recent quantum chemical calculations have been undertaken here at the B3LYP-D3BJ level.

Ideally, all systems optimised here at the B3LYP-D2 level would have been subjected to further optimisation at the B3LYP-D3BJ level. However, due to the large number of structures and given time constraints, this was not feasible. Moreover, it is anticipated that the differences between the B3LYP-D2 and B3LYP-D3BJ structures would be smaller than those between the uncorrected B3LYP and B3LYP-D structures.

The exact method employed (i.e. combination of dispersion correction and basis set) for a given set of structures is clearly indicated throughout the results chapters. For all quantum chemical calculations undertaken here optimisation convergence criteria of 10^{-9} on the density matrix and 10^{-7} on the energy matrix were employed together with a pruned numerical integration grid of 99 radial shells and 590 angular points per shell. All structures have been optimised without enforcing symmetry constraints. A frequency analysis of each structure was undertaken to confirm it as a minimum on the PES and determine the zero-point energy correction (ZPE). Where undertaken, the basis set superposition errors (BSSE) between pairs of species have been calculated using the counterpoise correction method of Boys and Bernardi.²⁵

3. Population Analysis

Methods of population analysis apportion the electron density of a molecule between the nuclei, such that each nucleus has an associated number of electrons (this can be non-integer). This allows properties, such as the net atomic charge on an atom to be calculated. However, atomic charges are not quantum mechanical observables and the concept of an atomic partial charge is not well defined. As such, numerous different methods of population analysis have been proposed.

Mulliken was the first to propose a method for undertaking such a population analysis.⁵⁸ However, the Mulliken analysis suffers from a number of shortcomings and is no longer recommended for use.⁵⁹ A relatively large number of alternative charge partitioning schemes have subsequently been developed. These typically fall into one of two main categories; those derived from consideration of the one-electron density matrix (e.g. Mulliken,⁵⁸ NBO⁶⁰) or electrostatic potential (ESP) based methods (e.g. CHELPG,⁶¹ MK^{62, 63}). Atomic charges can also be obtained *via* the Quantum Theory of Atoms in Molecules (QTAIM) approach, which relies entirely on an assessment of the properties of the electron density.⁶⁴

Between the different charge partitioning schemes there can be significant variation in the magnitude of partial charges determined for a given system. However, trends are often more important than absolute values.⁶⁵ There is on-going discussion over which method is “best” for a given application. For example, a number of charge partitioning schemes have recently been evaluated for application to ionic liquids.⁶⁶

As the assignment of partial charges to an atom is artificial, it could be suggested that computed partial charges should not be over relied upon or over interpreted. Moreover, a simple point charge model does not give a good representation of the anisotropic nature of the charge distribution. Nevertheless partial charges, as a first approximation of the charge distribution within a system, are conceptually easy for most chemists to understand and have proven useful. For example, partial charges can be used to help rationalise preferred sites of interaction e.g. the relative strength of H-bonds within imidazolium ionic liquids. For ionic liquids, partial charges also allow the anion to cation charge transfer to be approximated and correlations with experimental descriptors of charge transfer have previously been established.⁶⁷ Moreover, computed partial charges are typically used in the construction of molecular dynamics force fields.

Additional to atomic partial charges, schemes such as the Natural Bond Orbital method and QTAIM provide further descriptors useful in the characterisation of bonding interactions. A brief overview of Mulliken population analysis, Natural Bond Orbitals, ESP charge partitioning and QTAIM is provided in the following.

3.1 Mulliken population analysis

Using the Born interpretation of the wave function, the electron density at a position r can be expressed as in **equation 2.70**, where there are N electrons in $N/2$ spatial orbitals. Integrating over all space yields the total number of electrons, N , **equation 2.71**.

$$\rho(\mathbf{r}) = 2 \sum_{i=1}^{N/2} |\psi_i(\mathbf{r})|^2 \quad (2.70)$$

$$N = \int \rho(\mathbf{r}) d\mathbf{r} = 2 \int \sum_{i=1}^{N/2} |\psi_i(\mathbf{r})|^2 d\mathbf{r} \quad (2.71)$$

Equation 2.70 can be re-written expanding the spatial orbitals as a linear combination of basis functions, ϕ , **equation 2.72**.

$$\begin{aligned} \rho(\mathbf{r}) &= 2 \sum_{i=1}^{N/2} \left(\sum_{\mu=1}^K c_{\mu i} \phi_{\mu}(\mathbf{r}) \right) \left(\sum_{v=1}^K c_{v i} \phi_v(\mathbf{r}) \right) \\ &= 2 \sum_{i=1}^{N/2} \sum_{\mu=1}^K c_{\mu i} c_{\mu i} \phi_{\mu}(\mathbf{r}) \phi_{\mu}(\mathbf{r}) + 2 \sum_{i=1}^{N/2} \sum_{\mu=1}^K \sum_{v=\mu+1}^K 2 c_{\mu i} c_{v i} \phi_{\mu}(\mathbf{r}) \phi_v(\mathbf{r}) \end{aligned} \quad (2.72)$$

The expanded form of **equation 2.72** can be simplified by re-writing it in terms of the overlap integral $S_{\mu\nu}$ (**equation 2.73**) and in terms of the elements of the charge density matrix, $P_{\mu\nu}$ (**equation 2.74**). Noting that the overlap integral is normalised (i.e. $S_{\mu\mu} = 1$), the total number of electrons is then given by **equation 2.75**.

$$S_{\mu\nu} = \int \phi_{\mu}(\mathbf{r}) \phi_{\nu}(\mathbf{r}) d\mathbf{r} \quad (2.73)$$

$$P_{\mu\nu} = 2 \sum_{i=1}^{N/2} c_{\mu i} c_{v i} \quad (2.74)$$

$$N = \int \sum_{\mu=1}^K P_{\mu\mu} + 2 \sum_{\mu=1}^K \sum_{v=\mu+1}^K P_{\mu\nu} S_{\mu\nu} \quad (2.75)$$

The Mulliken approach to partitioning the electron density assumes that the basis functions are centred on the atoms. The electron density, $P_{\mu\mu}$, is simply “given” to the atom on which the basis function ϕ_{μ} is centred. For electron density associated with the overlap between ϕ_{μ} and ϕ_{ν} , Mulliken proposed that for each element of the density matrix, the atom on which ϕ_{μ} is located obtains half of the electron density, the other half going to the atom on which ϕ_{ν} is located.

The net atomic charge on atom A is then readily calculated by subtracting N_A (i.e. the total number of electrons partitioned to atom A) from the nuclear charge, Z_A , **equation 2.76**.

$$q_A = Z_A - N_A = Z_A - \sum_{\mu=1}^K P_{\mu\mu} - \sum_{\mu=1}^K \sum_{v=1; v \neq \mu}^K P_{\mu\nu} S_{\mu\nu} \quad (2.76)$$

One of the problems of the Mulliken population analysis is immediately obvious; the shared electron density is partitioned without any consideration of the relative electronegativities of the atoms to which the basis functions belong. Secondly, Mulliken population analysis is found to be highly basis set dependent.^{12, 13, 68} Use of an unbalanced basis set, or a diffuse basis,¹³ combined with the electronegativity issue, can lead to spurious results.

Nevertheless, one of the benefits of the Mulliken approach is that it is easy to calculate once the density matrix has been computed. It is perhaps because of this simplicity that Mulliken atomic charges are still routinely encountered.

3.2 Natural Bond Orbitals

The Natural Bond Orbital (NBO) analysis method is a powerful tool used in the study of bonding concepts. NBOs are localised one or two centre orbitals that relate closely to the Lewis-like electron pair description of chemical bonding.^{69, 70} The computed NBOs form an orthonormal set of localised maximum occupancy (i.e. close to two electrons) orbitals. For an N electron system, the $N/2$ leading NBOs typically contain > 99.9% of the electron density and correspond to the optimal Lewis-like representation of the system.⁷⁰ Non Lewis-like character is accounted for through resonance delocalisation effects.

Central to the NBO analysis is the one-electron reduced density matrix, which is used to determine the nature of the atomic orbitals *in the molecular environment*. These atomic orbitals are termed *Natural Atomic Orbitals* (NAOs) and are used in the formation of the NBOs.

The one-electron reduced density matrix of an N electron system, $\gamma(r_1, r_1')$, is given in **equation 2.77**. This can subsequently be expanded in terms of an orthonormal set of orbitals, **equation 2.78**, where γ_{ij} is an element of the density matrix.

$$\gamma(r_1, r_1') = N \int \Psi(r_1, r_2, \dots, r_N) \Psi^*(r_1', r_2, \dots, r_N) dr_2 \dots dr_N \quad (2.77)$$

$$\gamma(r_1, r_1') = \sum_{ij} \gamma_{ij} \phi_i(r_1) \phi_j^*(r_1') \quad (2.78)$$

Assuming that the basis functions can be ordered such that those centred on atom A are before those centred on atom B, etc., the full density matrix, **D**, can be written in terms of blocks of basis functions associated with a given atomic centre, **equation 2.79**.¹³

$$\mathbf{D} = \begin{pmatrix} \mathbf{D}^{AA} & \mathbf{D}^{AB} & \mathbf{D}^{AC} & \dots \\ \mathbf{D}^{BA} & \mathbf{D}^{BB} & \mathbf{D}^{BC} & \dots \\ \mathbf{D}^{CA} & \mathbf{D}^{CB} & \mathbf{D}^{CC} & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \quad (2.79)$$

Each of the diagonal blocks (e.g. $\mathbf{D}^{AA}$) can subsequently be diagonalised; the corresponding eigenvectors are the NAOs for that atom, with the occupancies given by the eigenvalues. For example, the NAOs of atom A are those that diagonalise block $\mathbf{D}^{AA}$. However, these NAOs are not orthogonal and the total sum of the occupancies does not equate to the total number of electrons. The orbitals must therefore be orthogonalised.¹³

The diagonal elements of the density matrix in the basis of the final orthogonalised NAOs are the orbital populations. The populations of the NAOs satisfy the Pauli constraints i.e. $0 \leq p_k^{(A)} \leq 2$.⁶⁰ The total sum of these orbital populations does equate to the total number of electrons in the system, and can therefore be used to determine the *natural atomic charge* of each atom. The natural atomic

charge of atom A, for example, is simply the sum of the populations of the NAOs of atom A ($p_k^{(A)}$) subtracted from the nuclear charge Z_A , **equation 2.80**.

$$q_A = Z_A - \sum_k p_k^{(A)} \quad (2.80)$$

With regard to the partial atomic charges, the *Natural Population Analysis* (NPA)⁶⁰ method has largely superseded Mulliken population analysis. The NPA scheme is less basis set dependent and generally a more robust method. However, the NBO partial charges (as we shall term them here) have previously been criticised for being too large relative to partial charges obtained *via* other approaches.^{12, 66, 71}

3.3 Charges derived from molecular electrostatic potentials

One of the criticisms of population analysis methods based on the partitioning of the wave function in terms of basis functions is that the partial atomic charges have not been determined to reproduce physical properties, such as multipole moments. An alternative approach to assigning charges to atoms within a molecule is to do so according to some physical criteria.

The electrostatic potential around a molecule is an important property in determining intermolecular interactions. Therefore, charges that have been derived to accurately reproduce the molecular electrostatic potential may provide an improved description of how one molecule “appears” to another molecule in terms of the charge distribution.

The electrostatic potential at a position r , $\phi(r)$, corresponds to the work done in bringing a test unit positive charge from a position of infinity to locate at r . In terms of a molecule, the total electrostatic potential will have contributions from both the nuclei and the electrons; the positive unit charge will experience attraction to the electron density and repulsion from the nuclei. The electrostatic potential is a property that can be directly obtained from the wave function and is simply expressed as in **equation 2.81**.

$$\phi(r) = \sum_{\alpha=1}^{N_a} \frac{Z_{\alpha}}{|r - R_{\alpha}|} - \int \frac{\rho(r')}{|r - r'|} dr' \quad (2.81)$$

The aim of ESP charge partitioning methods is to determine the partial atomic charges that most accurately reproduce the calculated electrostatic potential at a defined set of points about the molecule. At each of the defined points $\phi(r)$ is evaluated. A fitting procedure is then employed to derive the best set of partial atomic charges for reproducing the electrostatic potential at each point, under the condition that the total sum of the partial charges must equate to the total charge of the molecule.²³ Depending on the scheme, typically either an iterative non-linear or Lagrange multiplier least-squares fitting procedure is employed.

There are a number of different ESP charge partitioning schemes, differing primarily in where the points at which the electrostatic potential is to be evaluated are located. It has been found that both how, and where, these points are selected can have a significant influence on the resultant atomic partial charges.⁷²

Points are ideally taken from a region where it is most important to describe the intermolecular interactions correctly, corresponding to a region just beyond the van der Waals radii of the constituent atoms.²³ Typically points within the van der Waals radii and beyond a defined exclusion limit are not included. The CHELPG scheme, for example, uses a cubic grid of points, with a spacing of 0.3 to 0.8 Å between each grid point.⁶¹ Any grid point that lies within the van der Waals radius of an atom is removed, together with all points that lie further than 2.8 Å away from an atom, effectively creating a 2.8 Å headspace about the molecule. Alternatives include the use of shells centred on each atom with the points symmetrically distributed (e.g. CHELP)⁷³, or points distributed over a set of nested Connolly surfaces (e.g. MK).⁶³

ESP charge partitioning methods are a popular choice for deriving the atomic charges used within molecular force fields. However, there are a number of potential issues. For example, ESP schemes are typically reliant on predefined values for the van der Waals radii. However, van der Waals radii are approximate and the defined values differ according to the ESP scheme employed, contributing to a variation in the computed charges.⁷² To varying degrees, ESP charges also show some dependence on the molecular conformation.^{13, 23, 72} Furthermore, ESP methods can perform poorly in determining the charges on atoms “buried” in the interior of a large system.¹³ A modified ESP method, known as RESP (restrained electrostatic potential fit), potentially improves the description of buried charges and reportedly shows less variation with molecular conformation.²³

3.4 Quantum Theory of Atoms in Molecules

The Quantum Theory of Atoms in Molecules (QTAIM) aims to link properties of the electron density to concepts of chemical bonding.⁶⁴ QTAIM is now used widely in the study of “bonding” interactions, including in the analysis of H-bonding.⁷⁴

The molecular wave function, Ψ , contains all information relating to a quantum system. However, Ψ cannot be directly observed and is a complex function of $4N_e$ variables (where N_e is the total number of electrons). The electron density, $\rho(r)$, is directly related to the wave function through **equation 2.82**, where $\int \tau'$ denotes integration over the spin coordinates of all electrons and the spatial coordinates of all electrons except one.

$$\rho(r) = N_e \int \Psi^*(q) \Psi(q) d\tau' \quad (2.82)$$

Compared to Ψ , $\rho(r)$ is much simpler, depending on only 3 variables (i.e. the x, y and z coordinates). Furthermore, $\rho(r)$ can be observed experimentally e.g. through X-ray diffraction. QTAIM analysis can be undertaken using either experimentally or theoretically derived electron densities.⁷⁵ The electron distribution of a molecular system is dependent on the number and identity of the nuclei, in addition to the interactions between the nuclei. Examination of the *topology* of $\rho(r)$ allows these interactions to be characterised.

The gradient vector of the electron density, $\nabla\rho(r)$ (**equation 2.83**) always points in the direction of steepest ascent in $\rho(r)$ and a gradient path therefore corresponds to the path of steepest ascent in $\rho(r)$. Gradient paths only intersect when $\nabla\rho(r) = 0$. The special points in the electron density where

the gradient vanishes are referred to as *critical points* (CPs). A gradient path has both an origin and a terminus and can be shown to always connect two critical points.⁷⁵

$$\nabla\rho(\mathbf{r})=i\frac{\partial\rho}{\partial x}+j\frac{\partial\rho}{\partial y}+k\frac{\partial\rho}{\partial z} \quad (2.83)$$

Most gradient paths will originate at infinity and terminate at a nucleus, a maxima in $\rho(\mathbf{r})$. Each nucleus attracts gradient paths towards itself and the gradient paths are therefore found to partition the molecule into regions of space dominated by a single nucleus. Within QTAIM, a nucleus and the associated region of space defined by the gradient paths (the atomic basin) are used to define an atom within the molecule.⁷⁵ The boundary between two atoms is defined by a collection of gradient paths that originate at infinity but terminate at a CP *between* the two nuclei. This boundary is known as the interatomic surface.⁷⁵

Within **Figure 2.2**, the atomic basins corresponding to the three atoms within the HCN molecule can be seen. The thin purple lines correspond to the atomic basin paths (i.e. the gradient paths) and the thick purple lines are the interatomic surface paths, demarking the boundaries between the atoms.

Once the atomic basin has been defined, the total number of electrons, N , associated with the atom, and subsequently the net atomic charge, can readily be computed. The total electron population is simply the integral of the electron density over the basin of the atom.⁶⁴ QTAIM derived partial charges have previously been criticised, for example for being too large.^{68, 76, 77} However, Bader himself published a retort strongly refuting such criticisms.⁷⁸

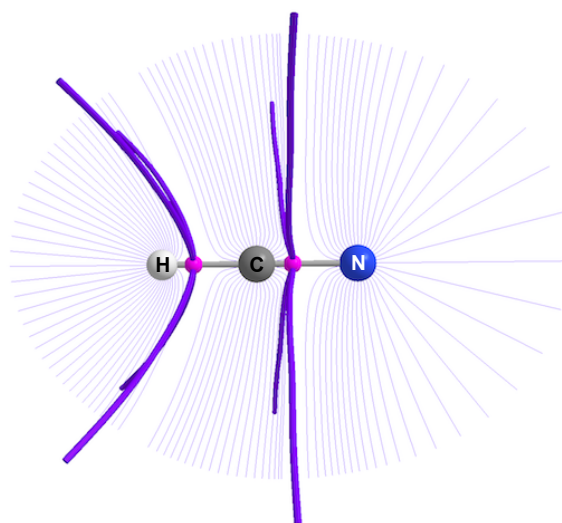


Figure 2.2. Molecular graph for the HCN molecule. Structure optimised here at the B3LYP-D3BJ/6-311+G(d,p) level. BCPs represented by pink spheres and thick grey line indicates the bond path. Thin purple lines are the atomic basin paths and the thick purple lines are the interatomic surface paths.

The CP found at a nucleus is a maximum in $\rho(\mathbf{r})$ in 3D. However, CPs can be maxima, minima or saddle points in $\rho(\mathbf{r})$. For example, the CP found at the centre of an interatomic surface is a maximum in $\rho(\mathbf{r})$ in the 2D of the surface, but a minimum in the orthogonal direction and is thus a saddle point in

$\rho(r)$. This type of CP is known as a *bond critical point* (BCP) and is associated with a bond. The BCPs for HCN are indicated by small pink spheres within **Figure 2.2**.

For each BCP there is a set of two gradient paths, both paths originate at the BCP and terminate at one of the two nuclei “connected” by the BCP (i.e. the “bonded” nuclei). Under the condition that the forces acting on the nuclei are zero, the two gradient paths are referred to collectively as a *bond path*. Therefore, within the QTAIM framework, the identification of a BCP and associated bond path between two atoms is suggestive of a bonding interaction.^{75, 79} The thick grey lines shown in **Figure 2.2** correspond to the bond paths within HCN.

Further types of CP include ring critical points (RCPs) and cage critical points (CCPs).⁷⁵ In order to distinguish between the different types of CP, it is necessary to consider the Hessian of second derivatives of $\rho(r)$ with respect to all possible combinations of coordinates calculated at a CP, i.e. **equation 2.84**.

$$\nabla\nabla\rho = \begin{pmatrix} \frac{\partial^2\rho}{\partial x^2} & \frac{\partial^2\rho}{\partial x\partial y} & \frac{\partial^2\rho}{\partial x\partial z} \\ \frac{\partial^2\rho}{\partial y\partial x} & \frac{\partial^2\rho}{\partial y^2} & \frac{\partial^2\rho}{\partial y\partial z} \\ \frac{\partial^2\rho}{\partial z\partial x} & \frac{\partial^2\rho}{\partial z\partial y} & \frac{\partial^2\rho}{\partial z^2} \end{pmatrix} \quad (2.84)$$

The Hessian can be diagonalised, with the three diagonal matrix elements corresponding to the eigenvalues, **equation 2.85**.⁷⁵ The three eigenvalues are labelled as λ_1 , λ_2 and λ_3 and can be interpreted as the curvature of $\rho(r)$ in the x, y and z directions respectively. Therefore, when λ is positive, it indicates that the CP is a minimum in that direction, whereas a negative λ indicates that the CP is a maximum in that one direction.

$$\nabla\nabla\rho' = \begin{pmatrix} \frac{\partial^2\rho}{\partial x'^2} & 0 & 0 \\ 0 & \frac{\partial^2\rho}{\partial y'^2} & 0 \\ 0 & 0 & \frac{\partial^2\rho}{\partial z'^2} \end{pmatrix} = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix} \quad (2.85)$$

Together, the three eigenvalues correspond to the spectrum of a CP and can be used to classify the type of CP.⁷⁵ The rank of the CP, r , is the number of non-zero eigenvalues. Using -1 for a negative λ and +1 for a positive λ , the sum of these values corresponds to the signature, s , of the CP. This information is summarised in **Table 2.1** for the different types of CP.

The properties of BCPs are central to this work. A BCP is classified as a (3, -1) CP, **Table 2.1**. Identification of a (3, -1) CP is included in IUPAC's most recent list of properties for the characterisation of H-bonds.⁸⁰

The magnitude of $\rho(r)$ at a BCP also provides information relating to the nature of the interaction. A large value of $\rho(r)$ is synonymous with an interaction involving the sharing of $\rho(r)$. Therefore, the magnitude of $\rho(r)$ at a BCP is a descriptor of the covalency of the interaction. Usually, $\rho(r)$ is also a good measure of the strength of the interaction.

Table 2.1. Summary of the different types of CP.

Critical Point	λ_1	λ_2	λ_3	(<i>r</i> , <i>s</i>)
Nuclear attractor	-	-	-	(3, -3)
Bond critical point	-	-	+	(3, -1)
Ring critical point	-	+	+	(3, +1)
Cage critical point	+	+	+	(3, +3)

The Laplacian of $\rho(r)$, $\nabla^2\rho(r)$, provides further information relating to the local curvature of $\rho(r)$. The Laplacian can be defined as the sum of the three eigenvalues of the Hessian of the electron density, **equation 2.86**.⁷⁵

$$\nabla^2\rho(\mathbf{r}) = \frac{\partial^2\rho}{\partial x^2} + \frac{\partial^2\rho}{\partial y^2} + \frac{\partial^2\rho}{\partial z^2} = \lambda_1 + \lambda_2 + \lambda_3 \quad (2.86)$$

At a BCP, both λ_1 and λ_2 are negative, while λ_3 is positive. The eigenvalues λ_1 and λ_2 therefore represent the curvature in the plane of the interatomic surface with λ_3 corresponding to the curvature along the bond path. The sign of the Laplacian therefore indicates which of these curvatures dominates.

A negative $\nabla^2\rho(r)$ indicates that the λ_1 and λ_2 curvatures dominate and that $\rho(r)$ is locally concentrated in the internuclear region. This is indicative of a shared interaction, such as a covalent bond. In contrast, for a positive value of $\nabla^2\rho(r)$, λ_3 must dominate. This indicates that $\rho(r)$ is locally depleted, with $\rho(r)$ concentrated away from the internuclear region towards the two nuclei. This is characteristic of a closed shell interaction and is typical for many H-bonds. Cases where $\nabla^2\rho(r) \approx 0$ could indicate an interaction with partial covalent character.

The total energy density, $H(r)$, is an additional descriptor that can provide information about the nature of the interaction at a BCP.⁷⁵ $H(r)$ corresponds to the sum of the kinetic energy density, $G(r)$, and the potential energy density, $V(r)$, **equation 2.87**. The kinetic and potential energy densities are related to $\nabla^2\rho(r)$ through the local virial theorem, **equation 2.88**.

$$H(\mathbf{r}) = G(\mathbf{r}) + V(\mathbf{r}) \quad (2.87)$$

$$V(\mathbf{r}) + 2G(\mathbf{r}) = \frac{1}{4}\nabla^2\rho(\mathbf{r}) \quad (2.88)$$

$G(r)$ is a positive quantity and $V(r)$ a negative quantity. Therefore, the sign of $H(r)$ reveals whether the kinetic energy or potential energy density term is dominant. Through **equation 2.88**, an excess of

kinetic energy is associated with a positive value of $\nabla^2\rho(r)$ and therefore a closed shell interaction. In contrast, a dominant potential energy term relates to a negative value of $\nabla^2\rho(r)$ and therefore a shared interaction. A dominant potential energy term indicates that the localisation of $\rho(r)$ in the internuclear region is overall stabilising for the system.⁷⁴

At a BCP, when $H(r) > 0$, it is indicative of a closed shell interaction e.g. a weak, predominantly electrostatic H-bond. When $|V(r)| > G(r)$ and subsequently $H(r) < 0$, it is suggestive of an interaction with *any* degree of covalent character. In many cases, the sign of $\nabla^2\rho(r)$ and $H(r)$ are in agreement, and infer the same conclusions regarding the nature of the interaction.

However, this is not always the case. Examples of interactions with $H(r) < 0$, but $|V(r)| < 2G(r)$ and therefore $\nabla^2\rho(r)$ is positive, have been reported. Cases where this has been observed include both conventional covalent interactions as well as strong H-bonds.^{81, 82} The situation has previously been described as indicating partial covalent character.^{83, 84} Furthermore, it is clear that in some cases it is necessary to consider multiple properties of the electron density topology to assess the nature of an interaction.⁸¹ The properties of $\rho(r)$ discussed here are some of the QTAIM descriptors most commonly employed to analyse bond interactions and are roughly summarised in **Table 2.2**.

Table 2.2. Approximate classification of different types of interaction based on the electron density, $\rho(r)$, Laplacian of the electron density, $\nabla^2\rho(r)$, and total energy density, $H(r)$.

	Covalent	Partial covalent	Ionic
$\rho(r)$	high	intermediate	low
$\nabla^2\rho(r)$	-ve	-ve or +ve	+ve
$H(r)$	-ve	-ve	+ve

Some of the first criteria for evaluating H-bonding using QTAIM were proposed by Koch and Popelier in 1995.⁸⁵ These original criteria were largely based on the evaluation of C-H...O interactions. Since the initial criteria were proposed, the number and variety of H-bond interactions investigated using QTAIM has increased. Therefore, some of the original criteria have been modified. For example, the known ranges in the values of $\rho(r)$ and $\nabla^2\rho(r)$ for H-bonds have widened. Moreover, it is now accepted that depending on the strength of the H-bond, the Laplacian may be positive or negative.

The QTAIM criteria employed here for classifying H-bonds is provided in **Chapter 1, Table 1.1**.

4. Molecular Dynamics

Molecular dynamics (MD) simulations have been employed widely in the study of ionic liquids, both in understanding the structure-property relationships and in a predictive capacity.^{1, 86} In terms of MD simulations, ionic liquids present a number of challenges. As ionic liquids are highly charged systems, the issue of long-range electrostatic interactions is important. Furthermore, ionic liquids can exhibit slow dynamics. As a result, long simulations may be required to allow for adequate sampling to determine the dynamic properties.¹ These factors must be taken into consideration when determining the system size (i.e. the number of ion pairs) and the simulation time period. Both the structure and dynamic properties of ionic liquids have been found to show size dependence.⁸⁷

The choice of force field is also important and force fields for ionic liquids are still being developed. Polarisable force fields improve the description of dynamic properties, but are associated with higher computational demands.¹ For non-polarisable force fields, the choice of atomic partial charges can be important.^{1, 88}

Brief descriptions of features pertinent to the MD simulations undertaken here are provided in the following.

4.1 The force field

Invoking the Born-Oppenheimer approximation it is possible to separate the nuclear and electronic motions of a system. Under this approximation, force fields can be developed that describe the potential energy of the system as a function of the nuclear coordinates. Force fields are determined empirically, and the electronic influence on the nuclear motions is incorporated implicitly.

Most force fields consist of a number of relatively simple terms that describe the bonded (i.e. intramolecular) and non-bonded (i.e. intermolecular) interactions within a system. The total potential energy, $V(\mathbf{r}^N)$, is a function of the positions $\mathbf{r}$ of N particles, **equation 2.89**.

$$\begin{aligned} V(\mathbf{r}^N) &= V_{\text{bonded}} + V_{\text{non-bonded}} \\ V_{\text{bonded}} &= \sum v_{\text{bonds}} + \sum v_{\text{angles}} + \sum v_{\text{torsions}} \\ V_{\text{non-bonded}} &= \sum v_{\text{vdW}} + \sum v_{\text{Coulomb}} \end{aligned} \tag{2.89}$$

The total potential associated with bonded interactions typically includes individual terms to describe how the energy varies as the bonds, angles and torsion angles are deformed away from defined reference values. The non-bonded terms typically comprise a term to describe the van der Waals (vdW) interactions in addition to a term to describe the longer-ranged electrostatic interactions. Some force fields may include additional terms. Moreover, there are a number of ways in which the individual terms within **equation 2.89** can be defined.

The force fields employed in this work have largely been based on the established frame work of the OPLS and Amber force fields. We define here the form of the force field employed in this work, as implemented in DL_POLY Classic.⁸⁹

Bonded terms

Simple harmonic potentials have been used to describe both the bond stretching and angle bending terms, **equations 2.90** and **2.91** respectively.

$$v(r_{ij}) = \frac{k}{2} (r_{ij} - r_0)^2 \quad (2.90)$$

$$v(\theta_{jik}) = \frac{k}{2} (\theta_{jik} - \theta_0)^2 \quad (2.91)$$

Within **equations 2.90** and **2.91**, r_{ij} is the distance between atoms i and j and θ_{jik} is the angle between bond vectors r_{ij} and r_{ik} . r_0 and θ_0 correspond to the reference bond length and reference angle respectively. The force constant, k , determines the energy required to stretch/compress a bond or deform an angle away from the reference value. Typically less energy is required to distort an angle; therefore the associated force constants are typically smaller than for the bond stretching term.²³

The form of the torsion potential is defined in **equation 2.92**, where ϕ_{ijkn} is the torsion angle defined by the atomic positions of atoms i, j, k and n .

$$v(\phi_{ijkn}) = \frac{1}{2} \{ V_1 (1 + \cos(\phi)) + V_2 (1 - \cos(2\phi)) + V_3 (1 + \cos(3\phi)) \} \quad (2.92)$$

V_n is sometimes, misleadingly, referred to as the barrier height. However, the barrier to rotation is not independent of the other terms within the force field. V_n does, however, provide a measure of the relative barriers to rotation about different torsion angles.²³

Non-bonded terms

The dispersive and exchange-repulsive interactions between particles constitute the vdW interaction. Although these effects are quantum in origin, they can be modelled using empirically derived potential functions. The most well known is the Lennard-Jones potential, **equation 2.93**, and has been employed here.

$$v_{vdW}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (2.93)$$

The Lennard-Jones potential contains two components, an attractive component varying as r^{-6} and a repulsive component varying as r^{-12} . Within **equation 2.93** there are two adjustable parameters, σ , the collision diameter, and ϵ , the potential well depth. It is typically assumed that the values of σ and ϵ for the interactions between two different atom types (i.e. ϵ_{ij} and σ_{ij}) can be obtained from the values of ϵ and σ for the pure atoms. There are a number of different “mixing rules” that can be used. Here we adopt the convention employed within the OPLS force field and use the geometric mean to determine σ_{ij} and ϵ_{ij} , **equations 2.94** and **2.95**.

$$\sigma_{ij} = \sqrt{\sigma_{ii}\sigma_{jj}} \quad (2.94)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \quad (2.95)$$

To determine the long-ranged electrostatic interactions, a point charge model is commonly employed. Within this model atomic partial charges are employed to represent the charge distribution within a molecule. The electrostatic interactions between, for example, molecules *A* and *B* is then taken to be the sum of the interactions between all pairs of atoms according to Coulomb's law, **equation 2.96**. N_A and N_B refer to the number of partial charges in molecules *A* and *B*, and q_i and q_j are the partial atomic charges of atoms *i* and *j*.

$$v_{Coulomb}(r_{ij}) = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \quad (2.96)$$

However, whilst the direct Coulomb summation can be employed in MD simulations, it is generally not recommended for use with a periodic system (introduced shortly). A number of more sophisticated techniques have been developed for dealing with long-ranged interactions. The technique employed here is the Ewald summation method.

The non-bonded interactions between atoms separated by three bonds (i.e. 1,4 interactions) must be given special consideration. The error due to the use of an r^{-12} term to describe the repulsive interactions is largest for the 1,4 interactions.²³ Moreover, the non-bonded interactions between 1,4 atoms are often reduced by a through bond redistribution of charge.²³ It is therefore common practice to employ a scaling factor to reduce the vdW and electrostatic terms for the 1,4 interactions. The vdW and electrostatic terms have been scaled by 0.5 for the 1,4 interactions herein.

4.2 Periodic boundary conditions

With MD, simulations are usually performed using a relatively small number of particles with the aim of obtaining macroscopic properties. For the simulation of a bulk liquid, this is only achievable if periodic boundary conditions are introduced.

For a system of N particles within a container, a large proportion of the particles will experience an interaction with the container walls. Therefore, a large number of particles will not be experiencing the forces representative of the bulk liquid.

To overcome this problem, the cubic cell can be replicated in all directions to produce an infinite lattice. As a molecule moves in the central box, its periodic image moves accordingly in all of the neighbouring boxes. Therefore, if a particle were to leave the central box during the simulation, a corresponding image particle would enter the cell from the opposite face.

Periodic boundary conditions are widely employed and if the system is not near a phase transition and the interactions are relatively short ranged, then the periodic boundary conditions typically do not have an undesirable effect on the properties of the system. However, the use of periodic boundary conditions does inhibit fluctuations in the system. For example, fluctuations with

wavelengths longer than the length of the cell cannot occur. Moreover, for systems with long-ranged interactions, e.g. electrostatic, there is the possibility that a particle in the central box will interact with one of its own images. Subsequently, a degree of anisotropy in the form of long-ranged ordering may be induced in the system. This effect is more significant the smaller the system size.

4.3 Long-ranged forces

For a given system, long-ranged interactions are interactions that decay no faster than r^{-d} , where d is the dimensionality of the system. These interactions may lead to a problem where the range of the interaction is greater than half the length of the box. Charge-charge interactions, decaying as $\approx r^{-1}$, are particularly problematic.

One solution to this problem would be to significantly increase the size of the system, with the increase in the charge screening decreasing the effective range of the electrostatic potential. However, given the associated computational cost this is rarely a feasible option.

The Ewald summation method was initially developed for treating the electrostatic interactions within ionic crystals. This technique can provide an effective solution to the problem of calculating electrostatic interactions in periodic systems in MD simulations.

With the Ewald method and in a periodic system, a particle will interact with all other particles in the central simulation cell, and with all the image particles in the array of periodic cells. The Coulomb (charge-charge) contribution to the potential energy can then be calculated as the sum of all pairwise interactions within the central simulation cell and all interactions between the central cell and the image boxes. When the simulation cell is located at a cubic lattice point $\mathbf{n}$ (where $\mathbf{n} = (n_x L, n_y L, n_z L)$ and n_x, n_y and n_z are integers), the potential energy can be expressed as in **equation 2.97**. The prime on the first summation indicates that the term for $i=j$ at $\mathbf{n}=0$ has been omitted.

$$v = \frac{1}{2} \sum_{\mathbf{n} \neq 0} \sum_{i=1}^N \sum_{j=1}^N \frac{q_i q_j}{4\pi\epsilon_0 |\mathbf{r}_{ij} + \mathbf{n}|} \quad (2.97)$$

Equation 2.97 converges very slowly; when taken alone both the positive and negative terms form a divergent series. The Coulomb sum is also problematic in that it decays very rapidly for small values of r , but decays very slowly for large values of r .²³

Full details of how the Ewald technique deals with this summation are not provided here. However, the approach taken does involve replacing the conditionally convergent summation in real space with two finite sums, one in real space and one in reciprocal space. Importantly, both of these terms converge more quickly than the summation in **equation 2.97**. Within the MD simulation, a cut-off can also be introduced to limit the summation in real space. This approach also requires the introduction of a corrective term in the interaction potential. The final form of the potential expression is more complex than the direct Coulomb sum given in **equation 2.97**. However, the Ewald method has proven to be one of the most effective ways of incorporating long-ranged interactions in MD simulations.

Nevertheless, the Ewald method can be computationally demanding.²³ However, A number of modifications of the original Ewald method have been developed to increase the computational efficiency.

4.4 The Verlet algorithms

In molecular dynamics, the trajectory of a system is determined by solving Newton's equation of motion. Newton's second law is a differential equation, as expressed in **equation 2.98**, and describes the motion of a particle (i) with mass m_i , travelling along coordinate x_i , under a force F_{xi} .

$$\frac{d^2 x_i}{dt^2} = \frac{F_{xi}}{m_i} \quad (2.98)$$

Within a molecular system, the force acting on any one particle will be dependent on the relative positions of all other particles and is described by a continuous potential. As the motion of the particles is coupled, the resulting many-body problem cannot be described analytically. Therefore, numerical methods of integration are required to solve the classical equations of motion.

A finite difference method is a standard numerical method for solving ordinary differential equations. There are a number of different algorithms for solving the equations of motion that employ a finite difference approach. However, the Verlet algorithm⁹⁰ and variants of the Verlet algorithm are some of the most commonly employed.

The Verlet algorithm utilises the positions $r(t)$, accelerations $a(t)$, and the positions from the previous step $r(t-\delta t)$, where δt is the timestep selected by the user.⁹¹ The equation used to move forward the positions of the particles is (**equation 2.99**):

$$r(t + \delta t) = 2r(t) - r(t - \delta t) + \delta t^2 a(t) \quad (2.99)$$

From **equation 2.99** it can be seen that the velocities are not required to determine the trajectory of the system. However, the velocity is required for estimating the kinetic energy. One way of obtaining the velocity is to divide the difference in r at time $t+\delta t$ and time $t-\delta t$ by $2\delta t$, **equation 2.100**.

$$v(t) = \frac{r(t + \delta t) - r(t - \delta t)}{2\delta t} \quad (2.100)$$

The benefits of the Verlet algorithm are that it requires only a moderate amount of storage and is relatively straightforward to implement and program.⁹¹ Furthermore, the algorithm is time reversible and, even with relatively large timesteps, has been shown to do well in conserving energy.⁹¹ However, the form of **equation 2.99**, in which a small term ($\delta t^2 a(t)$) is added to the difference of two larger terms, may introduce some numerical imprecision.⁹¹ Furthermore, treatment of the velocity is not ideal, and according to **equation 2.100** can only be determined once $r(t+\delta t)$ is known.

The original Verlet algorithm has been modified in an attempt to overcome the above issues. The *leap-frog* Verlet algorithm employs the following relationships (**equations 2.101 and 2.102**) and requires the current positions, accelerations and *mid-step* velocities⁹¹:

$$\mathbf{r}(t + \delta t) = \mathbf{r}(t) + \delta t \mathbf{v}(t + \frac{1}{2} \delta t) \quad (2.101)$$

$$\mathbf{v}(t + \frac{1}{2} \delta t) = \mathbf{v}(t - \frac{1}{2} \delta t) + \delta t \mathbf{a}(t) \quad (2.102)$$

Equation 2.102 is initially implemented, resulting in the velocities “leap-frogging” over the coordinates to give the velocities at the next half-step. The positions at $t + \delta t$ can subsequently be calculated using the velocities at $t + \frac{1}{2} \delta t$ and values of $\mathbf{r}(t)$. The acceleration can then be re-evaluated for use in **equation 2.102**, and so on in a series of “leap-frog” advancements.

In order to calculate the kinetic energy at time t , the velocity at time t can be obtained by taking the average of the velocities at a mid-step either side of t , **equation 2.103**.

$$\mathbf{v}(t) = \frac{1}{2} (\mathbf{v}(t + \frac{1}{2} \delta t) + \mathbf{v}(t - \frac{1}{2} \delta t)) \quad (2.103)$$

Relative to the original Verlet algorithm, the leap-frog variant does explicitly include the velocities. Moreover, the loss of numerical precision is reduced as the leap-frog algorithm does not require the difference of two large numbers to be taken to give a small number. However, the positions and velocities are not synchronised.

Another modified Verlet algorithm, the *velocity* Verlet algorithm,⁹² does store the positions, velocities and accelerations at the same time t , with no loss in precision, **equations 2.104** and **2.105**.

$$\mathbf{r}(t + \delta t) = \mathbf{r}(t) + \delta t \mathbf{v}(t) + \frac{1}{2} \delta t^2 \mathbf{a}(t) \quad (2.104)$$

$$\mathbf{v}(t + \delta t) = \mathbf{v}(t) + \frac{1}{2} \delta t [\mathbf{a}(t) + \mathbf{a}(t + \delta t)] \quad (2.105)$$

Numerous other integration schemes have been developed. However, DL_POLY Classic employs either the leap-frog or velocity Verlet algorithms. The leap-frog variant has been employed in this work.

Bond constraints

The choice of timestep is of central importance to the quality of the simulation; too long and accuracy is lost, too short and the computational demands are too high. Ideally, we would be able to increase the size of the timestep without any loss of accuracy.

One of the factors that determines the choice of timestep is the frequency of the vibrations, the timestep should not be longer than the time taken for the highest frequency vibration.²³ Typically the high frequency vibrations correspond to bond vibrations e.g. X-H stretching modes. However, often these are not of as much interest as lower frequency motions, such as the conformational changes occurring from rotations about the torsion angles.

The introduction of constraint dynamics allows selected degrees of freedom to be held fixed (at a user defined value) throughout the simulation. However, degrees of freedom to be constrained should be relatively independent of other degrees of freedom.

The general approach taken is to introduce a set of (undetermined) multipliers that will determine the magnitude of the constraint forces.⁹¹ The constraint forces lie along the bonds to be

constrained and ensure that the bond lengths remain fixed. The process typically involves two steps. Firstly, the motions of the atoms in the system are calculated in the absence of the constraint forces. Secondly, the magnitudes of the constraint forces are determined and the positions of the atoms corrected.

When the leap-frog Verlet algorithm is employed to integrate the equations of motion, the SHAKE procedure is used to apply constraints.⁹³ The SHAKE method employs an iterative process to ensure that all constraints are satisfied to within a specified tolerance.

4.5 Ensembles and averaged properties

The thermodynamic state of a macroscopic system is defined by a set of fixed macroscopic variables e.g. the number of particles, N , the pressure, P , the temperature, T and the volume, V . The specific set of fixed parameters determines the ensemble.

The positions and momenta of the atoms define the mechanical state of the system. These can be considered as coordinates in a multidimensional space, the phase space. For a system with N atoms, the phase space will have $6N$ dimensions.

The instantaneous value of a property A at a given point in the phase space is $A(\Gamma)$, where Γ denotes a point in the phase space. Over time, the value of $A(\Gamma)$ will fluctuate. The observed value, A_{obs} , is the average of A over the time period of the measurement. As the time period approaches infinity, the true average of A is approached, **equation 2.106**.⁹¹

$$A_{obs} = \langle A \rangle_{time} = \left\langle A(\Gamma(t)) \right\rangle_{time} = \lim_{t_{obs} \rightarrow \infty} \frac{1}{t_{obs}} \int_0^{t_{obs}} A(\Gamma(t)) dt \quad (2.106)$$

In MD, where the trajectory is of a finite length of τ timesteps of δt , the time average of A can be calculated as (**equation 2.107**):

$$\langle A \rangle_{time} = \frac{1}{\tau} \sum_{\tau=1}^{\tau} A(\Gamma(\tau)) \quad (2.107)$$

However, in statistical mechanics, averages correspond to ensemble averages, where an ensemble can be considered to be a collection of points Γ in the phase space.⁹¹ The phase space includes every possible configuration of the system. The average of property A is obtained by integrating over the entire phase space (**equation 2.108**), where $\rho_{ens}(\Gamma)$ is the probability density of the ensemble and determines the probability of finding a configuration with Γ .²³

$$\langle A \rangle_{ens} = \int A(\Gamma) \rho_{ens}(\Gamma) d\Gamma \quad (2.108)$$

Through MD we obtain the time-averaged values of properties. However, experimentally the ensemble average is also commonly measured. The *ergodic hypothesis* states that the time average is equal to the ensemble average, and thus, the computed time-averaged properties obtained *via* MD simulations are experimentally relevant.

Traditionally, MD simulations have been performed in the microcanonical (NVE) ensemble, that is, a fixed number of particles in a fixed volume giving a constant energy.⁹⁴ However, there are a number of reasons why a different ensemble might be preferable. For example, under experimental conditions the pressure and temperature are commonly a constant. There are a number of methods through which MD simulations with constant temperature and/or pressure can be enabled.^{91, 94-97} Two of the most commonly encountered ensembles are the canonical (NVT) and isothermal-isobaric (NPT) ensembles. Both are widely employed in the prediction of ionic liquid properties.

4.6 Radial distribution functions

Radial pair distribution functions (RDFs) are often calculated as a means of gaining insight into the structuring within a system, and are particularly useful in the study of liquid systems. RDFs can be determined experimentally, e.g. through neutron diffraction, or obtained through analysis of a MD trajectory.

The RDF, $g(r)$, gives the probability of finding a particle (e.g. an observed atom or molecule) a distance r from another (reference) particle, relative to the uniform density. The uniform density is the density that would be obtained if there were an entirely uniform distribution of the particle being observed in the cell volume i.e. effectively an ideal gas distribution, and should correspond to $g(r) = 1$.

Values of $g(r) > 1$, therefore, indicate that the probability of finding the observed particle at a distance r from the reference particle is greater than the average probability. At long distances, $g(r)$ will tend towards one; the value of r at which this occurs gives an indication of the extent of the long-range ordering within the system.

To calculate an RDF from an MD simulation, it is necessary to sort the neighbouring particles around a reference particle into bins of width ω . The number of neighbours within each bin can then be averaged over the duration of the simulation.

The TRajjectory Analyzer and VISualiser package (TRAVIS) has been employed here to compute the required RDFs.⁹⁸ The RDF is defined in **equation 2.109**. $\mathbf{r}_i$ and $\mathbf{r}_j$ define the position vectors of the i^{th} and j^{th} particles. $\delta=1$ in the interval defined by $[-\omega, \omega)$ and is zero elsewhere.

$$g_{ab}(r) = \frac{V}{N_a N_b} \sum_{i=1}^{N_a} \sum_{j=i+1}^{N_b} \left\langle \delta(r - |\mathbf{r}_i(t) - \mathbf{r}_j(t)|) \right\rangle_t \quad (2.109)$$

5. QM/MM

Many chemical systems and problems of interest are too large in size to be examined purely using electronic structure theory methods. Examples could include the modelling of biomolecular systems, such as enzymes, and the exploration of chemical reactions in solution. Molecular mechanics force fields are widely employed to simulate large and complex systems. However, (most) force fields are unable to describe the changes in the electronic structure necessary to investigate chemical reactivity.

One step towards addressing this problem is to recognise that for many systems there is a smaller “key” region of interest that needs to be modelled at high accuracy, whereas it is sufficient to treat the surroundings at a lower level of theory. A classic example of such a system is an enzyme. In terms of chemical reactivity, the active site of the enzyme is the key region of interest, while the surrounding protein plays an important role in constraining the geometry of the active site and providing an electrostatic background.^{99, 100} For such systems, hybrid computational methods can be employed.

Hybrid approaches combine two (or in some cases more) computational techniques in a single calculation. Most commonly, hybrid methods couple quantum mechanical (QM) with molecular mechanical (MM) modelling, termed QM/MM. However, the combination of high and low level QM methods (i.e. QM/QM) is also possible. Within a QM/MM simulation, the central region about which information about the electronic properties is required is modelled at the QM level, **Figure 2.3**. The surrounding environment is modelled at the cheaper MM level. The aim of such hybrid methods is to achieve increased accuracy and a more physically reasonable model at a significantly reduced computational cost.

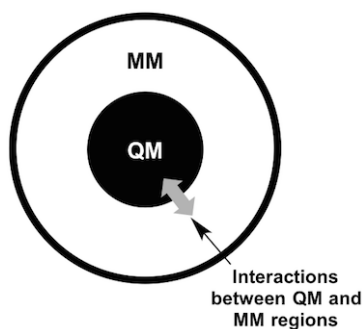


Figure 2.3. Simplified pictorial representation of a QM/MM system.

Within the QM/MM framework there are three sets of interactions that need to be considered: interactions within the central QM region, interactions within the surrounding MM region and interactions *between* the QM and MM regions. It is the latter that is most difficult to evaluate.⁹⁹ There are a number of different variations of QM/MM methods, differing primarily in the treatment of the QM and MM regions and in the approach taken to modelling the coupling between them.

5.1 The energy expression and QM/MM coupling schemes

One way of classifying the different QM/MM methods is *via* the scheme used for the QM/MM coupling. There are two main approaches, *subtractive* or *additive* coupling. It should be noted that the energy expressions for the subtractive and additive schemes given here represent the two extremes, and that intermediate models are also employed.¹⁰¹

We consider here a model system comprised of two regions, region A, the region of primary interest to be modelled at a higher level of theory (i.e. at the QM level), and the surrounding region, B, to be modelled at a lower level of theory (i.e. at the MM level), **Figure 2.4**.

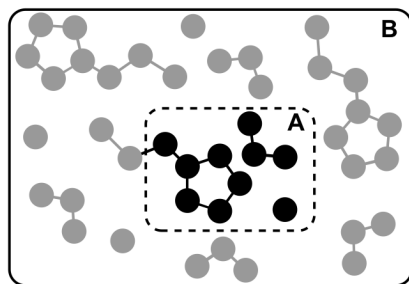


Figure 2.4. Model system with two regions.

5.1.1 Subtractive

With the subtractive approach, the QM/MM energy ($E_{\text{QM/MM}}$) of the entire system (i.e. A and B) is determined in a three-step process, **equation 1.110**. Firstly, the entire system is evaluated at the MM level and $E_{\text{MM}}(\text{A+B})$ is determined. Secondly, the energy of region A in isolation (i.e. gas phase) is determined at the QM level, $E_{\text{QM}}(\text{A})$. Finally, the energy of region A, again in isolation, is evaluated at the MM level, $E_{\text{MM}}(\text{A})$. $E_{\text{MM}}(\text{A})$ is subsequently subtracted from the sum of $E_{\text{MM}}(\text{A+B})$ and $E_{\text{QM}}(\text{A})$, to avoid double counting the energy of the QM region. A graphical representation of this procedure is shown in **Figure 2.5**.

$$E_{\text{QM/MM}} = E_{\text{MM}}(\text{A+B}) + E_{\text{QM}}(\text{A}) - E_{\text{MM}}(\text{A}) \quad (2.110)$$

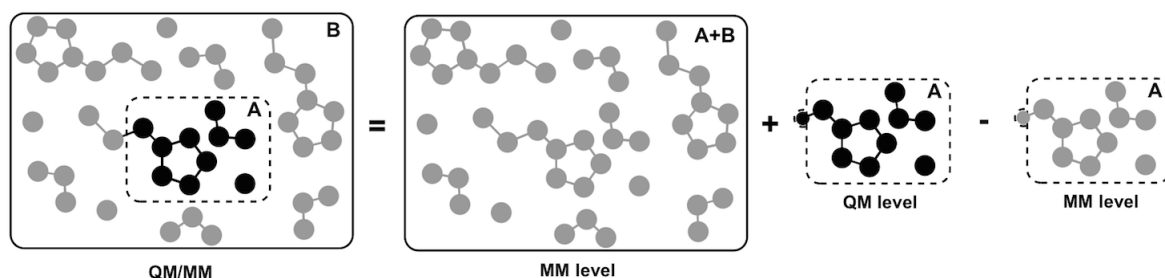


Figure 2.5. Graphical representation of the subtractive QM/MM coupling scheme.

The subtractive scheme is typically relatively straightforward to apply.⁹⁹ However, as the coupling between the QM and MM subsystems is treated purely at the MM level, the QM calculation is effectively an isolated gas phase calculation. In other words, the electron density within the QM region is not polarised by the atoms in the MM region. As a result, electronic properties influenced by the

surroundings cannot be evaluated. Furthermore, a force field of sufficient flexibility to describe the QM region and any chemical changes in the system is required.

One of the most well known hybrid methods employing a subtractive scheme is the ONIOM (Our own N-layered Integrated molecular Orbital and Molecular mechanics) method.¹⁰² However, unlike the simplest subtractive schemes, ONIOM has been modified to allow for polarisation of the QM region *via* electrostatic embedding (to be explained shortly).¹⁰³

5.1.2 Additive

With the additive approach, the QM subsystem is “embedded” within the MM region. The *generalised* equation for the total energy contains terms for the energy of region A at the QM level, region B at the MM level and a term for the interaction *between* the two subsystems, **equation 2.111**. Therefore, unlike the subtractive schemes, the coupling between the two subsystems is explicitly considered.

$$E_{QM/MM} = E_{MM}(B) + E_{QM}(A) + E_{QM-MM}(A+B) \quad (2.111)$$

However, there is more than one way in which the QM/MM energy of the system can be determined within the additive coupling scheme. The different approaches differ in the treatment of the interactions between the two regions. The three main approaches, in order of increasing sophistication, are mechanical embedding, electrostatic embedding and polarisation embedding.

Embedding schemes

Mechanical embedding is the simplest approach. With mechanical embedding, the energy of region A in isolation (i.e. gas phase) is evaluated at the QM level. The energy of region B is determined at the MM level, with the addition that the interactions *between* region A and region B are also evaluated at the MM level, **Figure 2.6**. Both bonded and non-bonded interactions between the two regions must be considered. Any covalent bonds between atoms in region A and region B are simply described using the bond harmonic potential of the force field, with the angle and torsion terms evaluated in an analogous manner. The van der Waals interactions between the two regions are modelled using the Lennard-Jones potential and the corresponding electrostatic interactions with the Coulomb potential.

The Lennard-Jones parameters for the QM atoms are typically kept the same throughout the course of the simulation. For the charges on the QM atoms used in calculating the Coulomb potential, there are two options.⁹⁹ The first is to employ a fixed set of charges; the second is to update the atomic charges during the simulation. The latter is typically achieved using an ESP approach i.e. fitting the atomic charges to reproduce the electrostatic potential at the surface of the QM region.

With mechanical embedding the energy expression given in **equation 2.111** can be rewritten as presented in **equation 2.112**, where $E_{MM}(B+“A-B”)$ is the energy of region B at the MM level with the addition of the MM evaluation of all interactions (i.e. all bonded and non-bonded terms) *between* regions A and B.

$$E_{QM/MM} = E_{MM}(B+“A-B”) + E_{QM}(A) \quad (2.112)$$

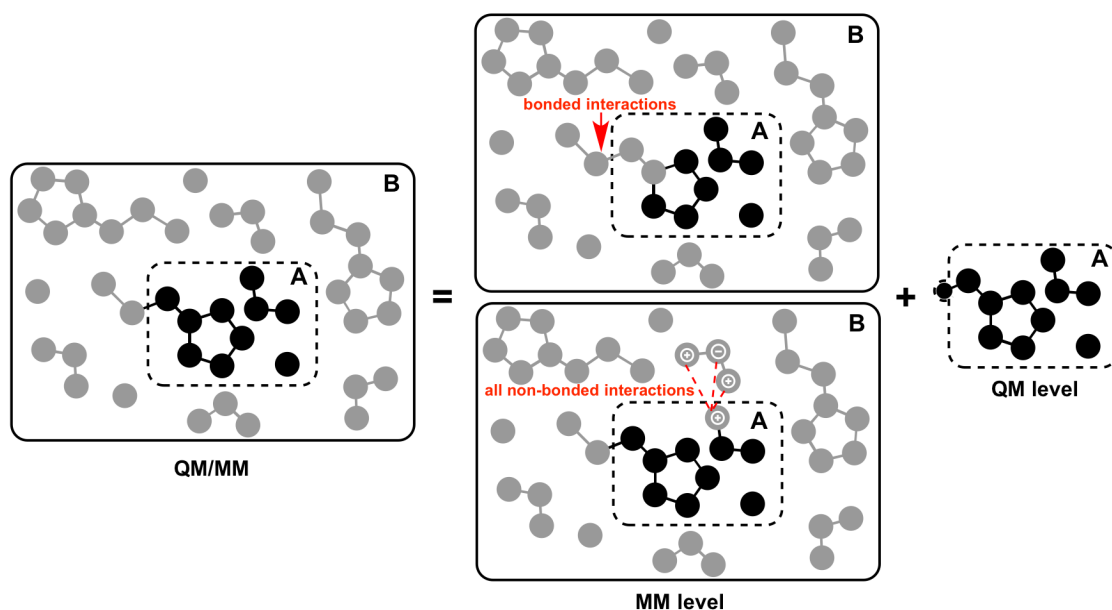


Figure 2.6. Mechanical embedding within an additive coupling scheme.

An improvement upon the mechanical embedding approach is to include the polarisation of region A in the calculation, and is known as *electrostatic embedding*. The difference between mechanical and electrostatic embedding is that in the latter the electrostatic interaction between the two regions is treated at the QM level. This is achieved by allowing the wave function for region A to optimise with respect to a point charge representation of the atoms of region B. The charged atoms of region B are included in the electronic Hamiltonian as one electron operators. The expression for the full electronic Hamiltonian within this QM/MM framework is given in **equation 2.113**.

$$\hat{H}_{el(QM/MM)} = -\sum_{i=1}^{N_e} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N_e} \sum_{\alpha=1}^{N_a} \frac{Z_{\alpha}}{r_{i\alpha}} + \sum_{i=1}^{N_e} \sum_{j>1}^{N_e} \frac{1}{r_{ij}} - \sum_{i=1}^{N_e} \sum_{K=1}^{N_{MM}} \frac{q_K}{r_{iK}} \quad (2.113)$$

Compared to the pure QM electronic Hamiltonian, as given in **equation 2.5**, the QM/MM Hamiltonian contains one additional term to account for the Coulombic interaction between the electrons in the QM region A and the charged atoms in the MM region B (where N_{MM} is the number of MM atoms in region B and q_K is the charge on the MM atoms). Within electrostatic embedding schemes, the vdW, and where relevant the bonded terms, between regions A and B are still treated using the MM force field, **Figure 2.7**.

The energy expression given in **equation 2.111** can therefore be rewritten as presented in **equation 2.114**, where $E_{MM}(B+“A-B”)$ is the energy of region B at the MM level, with the addition of the MM evaluation of the vdW and bonded interactions *between* regions A and B, and $E_{QM}(A+“A-B”)$ is the energy of region A at the QM level in the environment of the point charges of region B.

$$E_{QM/MM} = E_{MM}(B+“A-B”) + E_{QM}(A+“A-B”) \quad (2.114)$$

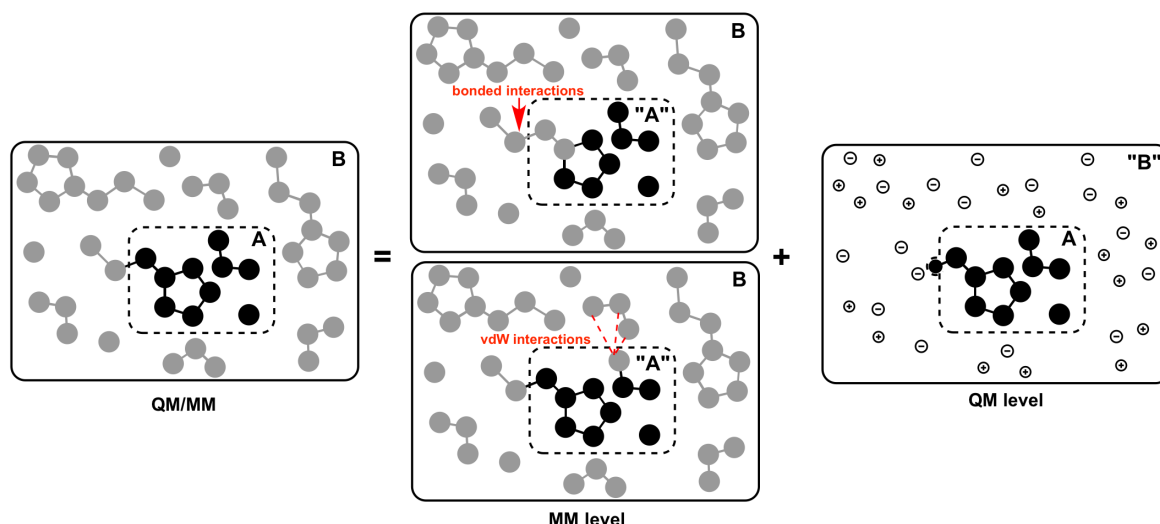


Figure 2.7. Electrostatic embedding within an additive coupling scheme.

Electrostatic embedding schemes can successfully account for the polarisation of the QM region, but do not account for any potential charge polarisation of the MM region. For a solute in solution, for example, there is expected to be mutual polarisation of both the solute *and* the solvent molecules.¹² Polarisation embedding schemes have been developed to allow for mutual polarisation of both the QM and MM regions and thus provide a more realistic description of the interactions between the subsystems. For this approach to be implemented, a polarisable force field is a necessity. For many systems, polarisable force fields are not yet available. Moreover, the self-consistent treatment of the polarisation is associated with an increase in computational cost.¹⁰⁰

Of the three embedding schemes, electrostatic embedding is most routinely employed, and has also been used herein. However, there are a number of issues that must be considered.⁹⁹ Firstly, due to the added terms in the electronic Hamiltonian, the quantum chemistry code may need to be modified. Additionally, there are questions relating to the validity of the polarisation induced in the QM region by the fixed MM point charges. For example, the MM force field has been parameterised to reproduce properties of the MM system. Therefore, the MM point charges do not necessarily provide an accurate description of the true physical charge distribution. In some cases, the original charges of the MM force field may need to be replaced.

A further problem is that of “charge leakage”, or over-polarisation near the QM/MM boundary.⁹⁹ This arises due to the use of simple point charges to model the charge distribution in the MM region; simple point charges do not provide a good description of the smeared distribution of the electron density.¹⁰⁰ Charge leakage occurs when electron density in the QM region spills out onto the positive point charges in the MM region. Typically this problem is only highly significant when very large and flexible basis sets (or plane waves) are in use.⁹⁹ A number of approaches for addressing this problem have been proposed, including the use of eliminated and scaled-charge schemes, a shifted-charge scheme or the introduction of Gaussian charge distributions for selected atoms of the MM region.⁹⁹⁻¹⁰¹

For some systems, the treatment of covalent bonds crossing the QM/MM boundary is also an issue and is relevant to both mechanical and electrostatic embedding schemes. Simply “cutting” thought a covalent bond creates “dangling ends” and results in an unpaired electron in the QM

region.⁹⁹ The simplest approach is to “cap” the dangling bond with a link atom, most typically hydrogen.⁹⁹ The localised orbital approach is a commonly employed alternative.⁹⁹ For systems where covalent bonds do not cross the QM/MM boundary, for example in the study of the solvation of an ion in water, this is obviously not an issue. Moreover, in such cases, the evaluation of the QM-MM interaction energy reduces to only the non-bonded terms. However, there does remain the potential issue of whole molecules moving in and out of the QM region. For example, this can be problematic if solvent molecules are included in the QM region.

5.2 Computational considerations

With respect to the implementation of QM/MM codes, three main types of programming architecture are in use¹⁰⁰: established QM codes modified to allow for the inclusion of an MM environment (e.g. ONIOM¹⁰² in Gaussian¹⁰⁴), MM packages extended to include the required MM functionality (e.g. CHARMM¹⁰⁵) or a central control program that acts as an interface between the MM and QM codes (e.g. ChemShell^{101, 106}).

It is noted that each approach has associated advantages and disadvantages.¹⁰⁰ However, it is suggested that the latter option is the most flexible and requires the least modification of the existing QM and MM codes. Nevertheless, such an approach may suffer from reduced efficiency due to the large amount of data that needs to be transferred between the QM and MM packages.¹⁰⁰

For the QM/MM calculations undertaken in this work, ChemShell has been employed as the interface between the Gaussian and DL_POLY modules. An electrostatic embedding coupling scheme has been employed for all QM/MM calculations. The force fields used in the classical MD simulations have also been used for the evaluation of the interactions within the MM regions and the Lennard-Jones parameters used for the assessment of the vdW interactions between the QM and MM regions. The QM regions have been evaluated using DFT.

With Gaussian employed as the QM module, a slight modification of the energy expression given in **equation 2.114** is required. In addition to computing the electrostatic interaction between the point charges in region B with the electron density of the atoms in region A, Gaussian also evaluates the Coulomb interactions between the MM point charges of region B. Therefore, to avoid double counting the energy for the electrostatic interaction within the MM region, the energy for the Coulomb interaction between the atoms in the MM region must be subtracted once from the total energy of the system. DL_POLY computes the energy of the MM region in addition to the energy of the vdW interactions between the MM and QM regions. During the MM evaluation the charges on the atoms in the QM region are set to zero.

DL_FIND is the optimisation library within ChemShell used for QM/MM geometry optimisations.^{101, 107} The default optimisation procedure has been employed here. Gaussian is first called by ChemShell to run a single point calculation and compute the forces on the atoms in the QM region. DL_POLY is subsequently called to compute the forces on the atoms in the MM region. It is ChemShell that combines these forces and determines the step to be taken in the geometry. New input files with the updated coordinates are generated and fed back to Gaussian and DL_POLY. The cycle continues until the convergence criteria have been satisfied.

An alternative approach would be to employ a microiterative optimisation procedure, an approach aimed at reducing the computational cost of a QM/MM geometry optimisation.¹⁰⁹ The computational cost associated with a QM/MM optimisation is usually dictated by the evaluation of the QM region, despite the fact that the MM region is typically much larger. With a microiterative optimisation, the number of required evaluations of the QM region, and hence cost, is reduced. For each step in the inner QM region, multiple steps (microiterations) in the outer MM region are taken, allowing the MM region to fully relax. Further investigation is required to assess the extent to which the microiterative optimisation procedure would reduce the computational cost of the QM/MM calculations undertaken here.

We have considered the basic theory relating to quantum chemical, classical MD and hybrid QM/MM methodologies. Within this work, DFT has been employed to investigate the choline chloride-urea system and a combination of DFT, classical MD and a QM/MM approach has been employed to investigate the selected imidazolium ionic liquids.

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Chapter 3

Interactions Within the Choline Chloride – Urea Deep Eutectic Solvent

1. Background

Deep eutectic solvents (DESs) are of interest as both cheaper alternatives to conventional ionic liquids, as well as solvents for new applications.^{1,2} The possible application of DESs in the area of metal processing has been introduced. There are a number of different types of system termed as “DESs”,^{1,3} however, only the eutectic mixtures of quaternary ammonium salts with organic complexing agents, capable of acting as H-bond donors, shall be considered here.

There are numerous favourable features of DESs, including the simple preparation, air and moisture stability and flexibility in terms of the large number of possible combinations of quaternary ammonium salts and organic H-bond donors. As such, there has been a notable increase in the number of publications relating to DESs since these systems were introduced in the early 2000s.^{1,4} However, much focus has been on the potential applications of DESs,^{1,2} and/or reporting properties of novel combinations of organic salts and H-bond donors.^{2, 5-10} Fewer examples of in-depth studies of intermolecular interactions within DESs have been reported. Recently, however, there has been an increase in the use of computational methods to investigate DESs, although the number of reported studies is still limited.¹¹⁻¹⁴

Many questions regarding the speciation and intermolecular interactions within DES systems remain, including questions relating to the role of H-bonding and nature of the complexed anion. More generally, H-bonding has been recognised as playing a central role in influencing the secondary structuring and properties of conventional ionic liquids, where H-bonding is almost exclusively of the doubly ionic type.¹⁵ However, as a DES features neutral, cationic and anionic species, there is the potential for neutral, ionic and doubly ionic H-bond formation. Examination of H-bonding within a DES provides the opportunity to compare and contrast these different types of H-bond interaction within a single system.

As far as can be established, we present here the first in-depth examination, employing quantum chemical methods, of intermolecular interactions within an example DES. The archetypal DES, the choline chloride – urea system,⁴ was selected for study. The relative rigidity of urea, in comparison to other commonly employed complexing agents (e.g. glycols), makes this system a good choice for an initial computational assay.

Each of the individual components of the choline chloride – urea DES has been examined, with a particular focus on H-bonding. For a conventional ionic liquid, the most basic building block is the ion pair. For a DES there is an additional component, the neutral H-bond donor species. The pairwise interactions between each of the constituent species therefore correspond to the most basic level of interaction within a DES. An examination of the pairwise interactions also lays the foundation for understanding more complex “clusters” built from choline chloride : *n* urea.

We present first an analysis of the isolated choline cation and the pairwise interactions between the constituent species of the DES i.e. choline- chloride, urea-urea, urea-chloride and choline-urea. A comparison of the interactions across the pairs of species is then made. Finally, an analysis of small clusters of composition choline chloride : n urea ($n = 1-3$) is presented.

However, before results are discussed, a brief introduction to the phase behaviour of eutectic systems, and current understanding of speciation and phase behaviour of DESs is provided.

1.1 Eutectics

Eutectic mixtures have a long history of being used in the molten salt – ionic liquids field to create lower melting point systems. For example, a eutectic mixture of alumina (Al_2O_3) and cryolite (Na_3AlF_6) is still used in the Hall-Héroult process (*circa* 1880s) for the electrolytic reduction of alumina to aluminium.¹⁶ More recent developments include electrolytes for thermal batteries,¹⁷ halometallate ionic liquids,^{18, 19} as well as DESs.⁴

A simplified phase diagram for a binary eutectic mixture of solid A and solid B, at constant pressure, is shown in **Figure 3.1**. The liquidus lines ae and be define the phase boundary between the region of homogeneous liquid and biphasic regions of liquid and solid. At all compositions, the mixture of component A and component B melts at a lower temperature than either of the pure components. Line ae can effectively be viewed as the depression in the melting point of A as the percentage of component B increases, and *vice versa* for line be . Below the solidus phase boundary, demarked by line ced , no liquid can exist.

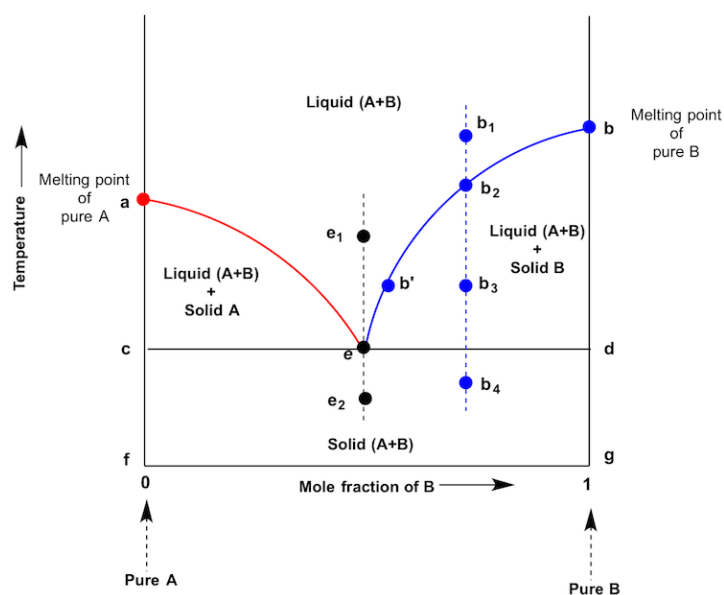


Figure 3.1. Simplified phase diagram for a binary mixture of solid A and solid B.

Point **e** corresponds to the eutectic point, the composition of A and B with the lowest melting point and the only point on the phase diagram at which three phases can coexist (solid A, solid B and liquid). The composition and temperature associated with the eutectic point are referred to as the eutectic composition and eutectic temperature respectively. Considering the isopleth (line passing through points of the same composition) passing through **e**, point e_1 corresponds to a homogeneous liquid of

the eutectic composition. Upon cooling of this liquid mixture to just below the eutectic temperature, the system will solidify at a single temperature without any change in composition. Typically, the solid at e_2 will be a fine mix of A and B in the eutectic ratio.²⁰

Only for liquids of the eutectic composition does cooling occur without a change in composition of the liquid phase. For example, consider the isopleth passing through points b_1 to b_4 . Cooling of the homogeneous liquid b_1 initially occurs without any change in composition until point b_2 on the liquidus line is reached. At, and below point b_2 , solid B will begin to precipitate out of the liquid phase, such that the liquid is proportionally richer in component A, with the composition of the liquid determined by the liquidus line. Continued cooling occurs with a concomitant precipitation of solid B. At point b_3 the liquid phase will be of the composition defined at point b' and relative proportions of liquid and solid can be determined using the lever rule. When point b_4 is reached, the liquid is of the eutectic composition and therefore freezes. The solid system at this point is a mixture of pure solid B and the solid eutectic structure, a fine mix of A and B. There are therefore also two solid sub-regions; one to the right of the eutectic composition, a mixture of solid B and the eutectic solid, and one to the left of the eutectic composition, a mixture of solid A and the eutectic solid.²⁰

The solid-liquid phase diagram of a simple binary mixture can be predicted theoretically. It is assumed that the two components (A and B) are completely miscible in the liquid phase but completely immiscible in the solid phase, that the enthalpy of fusion is constant over the temperature range and that the system is an ideal mixture.²¹ The Schroeder – van Laar equation, **equation 3.1**, relates the temperature at which crystallisation occurs (T) to the mole fraction of component B in the liquid (x_B). ΔH_{fus} is the enthalpy of fusion of pure B, T_f the melting point of pure B and R is the gas constant. There is a decrease in the solubility of component B as the temperature is lowered from the melting point of B. A crystallisation curve can be plotted for both components of the mixture and the point at which the two independent curves meet corresponds to the predicted eutectic point.

$$\ln x_B = \frac{\Delta H_{fus}}{R} \left(\frac{1}{T_f} - \frac{1}{T} \right) \quad (3.1)$$

The form of the Schroeder – van Laar equation presented in **equation 3.1** is strictly only applicable to ideal mixtures, and even then is an approximation only.²¹ Nevertheless, for mixtures of two very similar components (e.g. *ortho*-chloronitrobenzene and *para*-chloronitrobenzene) a good agreement between the theoretical and experimental phase diagrams can be established.²¹ For mixtures where there is expected to be a significant deviation from ideality, a concomitant deviation between the predicted and actual phase diagrams will be observed. Formation of addition compounds can also lead to more complex phase diagrams. For the DESs under consideration, notable deviations from ideality could be anticipated.

1.2 Phase behaviour and speciation of deep eutectic solvents

For DESs, complexed anion formation *via* H-bond interaction between the anion (of the quaternary ammonium salt) and neutral organic species is proposed.^{1, 4} Formation of a complexed anion is thought to reduce the cation – anion association, contributing to a sizeable decrease in the solid-liquid phase transition temperature of the system. However, it is not fully understood how the interaction between the H-bond donor and the anion reduces the cation-anion association. The most common proposal is that complexation of the charge localised anion (e.g. Cl^-) by the complexing agent results in charge delocalisation, and thus reduces the Coulombic interaction with the cation.¹

The exemplar choline chloride – urea DES is a good example of a system with a relatively large depression in freezing point, the reported freezing point is 12°C at the eutectic composition of 1:2 choline chloride (mpt. $\approx 302^\circ\text{C}$) to urea (mpt. = 133°C).⁴ The partial phase diagram for the choline chloride – urea system is shown in **Figure 3.2**, the liquid-solid phase behaviour of this DES appears to closely resemble that of a simple binary eutectic (e.g. **Figure 3.1**).

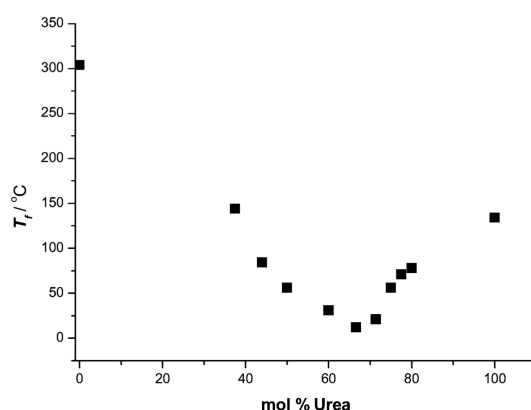


Figure 3.2. Experimentally determined phase diagram for the choline chloride – urea mixture. Plot of freezing temperature (T_f) against mole fraction of urea. Reproduced from **Ref. 4** with permission of The Royal Society of Chemistry.

Larger deviations from the phase diagram of an ideal binary mixture of components can be expected for systems with significant interactions between the components. For example, for a range of choline chloride based eutectics, there appears to be a link between the magnitude of the freezing point depression and the strength of the interaction between the chloride anion and complexing agent i.e. covalent interactions lead to a larger freezing point depression compared to H-bond interactions. For example, the choline chloride – zinc chloride eutectic, with covalent interactions leading to complexed anion formation, has a reported freezing point depression of 272°C relative to the (approximated) ideal mixture.^{8, 22} This is significantly larger than the corresponding freezing point depression of 178°C reported for the choline chloride – urea system,⁴ with H-bond interactions. Moreover, tetramethylurea, unable to act as a significant H-bond donor, does not form a homogeneous liquid with choline chloride.⁴ Further factors that potentially contribute to a lowering of the freezing point include the H-bond accepting ability of the anion,⁴ in addition to the asymmetry and functionality of the cation.²²

The eutectic composition, i.e. the ratio of salt to complexing agent, may also show a dependence on the number of H-bond donor groups on the complexing agent. For a series of choline

chloride : carboxylic acid mixtures, the mole fraction of carboxylic acid at the eutectic point decreases with an increase in the number of COOH functional groups; e.g. monofunctional phenylpropionic acid (67%), difunctional oxalic acid (50%) and trifunctional citric acid (33%).⁸ These observations emphasise the importance of H-bonding in the formation of DESs, the H-bonding ability of the components appears to influence both the eutectic temperature and eutectic composition of a DES. However, at present, there is not a clear model to rationalise the influence of the H-bond donor complexing agent on either properties of the system.

To rationalise the properties of these DES systems, a deeper understanding of the molecular speciation is required. Evidence for the interaction between the anion and the complexing agent has been obtained from both experimental and theoretical sources. For example, for the choline chloride – urea mixture, the infrared stretching frequencies associated with the NH₂ groups of urea show a small red shift upon formation of the DES, consistent with H-bond interactions.^{4, 12} For the related choline trimethylfluoride ((CH₃)₃F)) – urea eutectic, heteronuclear Overhauser effect spectroscopy (HOSEY), suggested the direct interaction between the NH₂ groups of urea and the F atom of the anion.⁴ Mass spectrometry also indicates the presence of both urea·Cl[−] and 2urea·Cl[−] complexes for the eutectic composition of choline chloride - urea,⁴ albeit this is not direct evidence for the existence of these species in the liquid phase. However, more recently, MD simulations have revealed there to be a high probability of interaction between urea and the chloride anion in the liquid phase.¹²

Given that the complexing agents are typically able to act as both H-bond donors and acceptors, there is the potential for self-interaction. Carboxylic acids, for example, are known to dimerise. It has previously been suggested that the very high viscosity of the choline chloride – malonic acid eutectic could be related to self-association of the malonic acid units.²³ MD simulations of a number of choline chloride based DESs suggest that there is a variation in the degree of self-association with the identity of the complexing agent.¹³ Moreover, cation-anion, and cation-complexing agent interactions could feature within the liquid. All possibilities have been considered here.

2. Method

The initial geometries of all species have been obtained employing Becke's three parameter exchange functional²⁴ with the correlation functional of Lee, Yang and Parr (B3LYP)²⁵ in conjunction with the 6-311+G(d,p) basis set. Grimme's D2 dispersion correction²⁶ was appended to the B3LYP functional, henceforth denoted as B3LYP-D2, to improve the description of long range dispersion interactions. The B3LYP/6-311+G(d,p) geometries of all individual species, pairwise interacting species and selected clusters were subsequently optimised at the B3LYP-D2 level together with the 6-311++G(d,p) basis set.

All the electronic energies reported for choline, choline–chloride ion pairs, urea, urea-urea dimers, urea-chloride complexes and choline–urea pairs are at the B3LYP-D2/6-311++G(d,p) level and are BSSE and ZPE corrected. The reported energies of selected clusters, at both the B3LYP/6-311+G(d,p) and B3LYP-D2/6-311++G(d,p) levels, are ZPE corrected only. The relative energies of all systems, with and without corrections, can be found in the **Appendix**.

3. Individual Species and Pairwise Interactions

3.1 The choline cation

A conformational analysis of the choline cation has been undertaken here. β -substituted ethyltrimethylammonium cations, such as choline and acetylcholine, are of biological importance.²⁷ As such, the conformational preferences of this class of cation have been previously investigated experimentally. With regard to the N-C-C-X torsion angle ($X = \beta$ substituent), β -substituted ethyltrimethylammonium cations adopt either a trans or gauche conformation. For choline ($X=OH$), the gauche conformer has been shown to predominate in both the gaseous and solid phases, and additionally in solution.²⁸⁻³¹

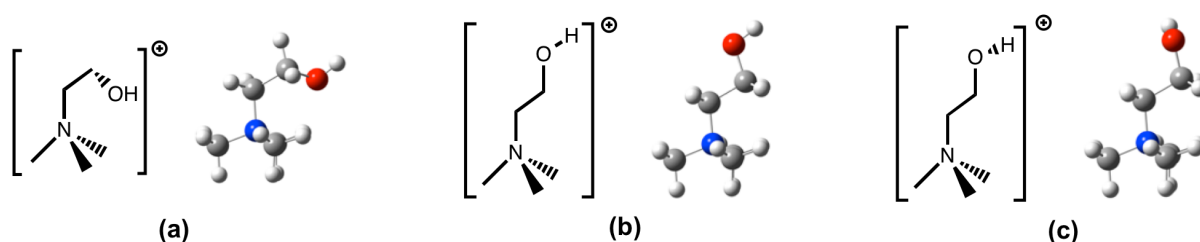


Figure 3.3. Gas phase choline cation conformations: (a) gauche, (b) trans and (c) trans-rotated.

Stable gas phase conformations of the choline cation are shown in **Figure 3.3**. The gauche conformer (**Figure 3.3 a**) is found to be $\approx 18 \text{ kJ mol}^{-1}$ lower in energy than the trans conformer (**Figure 3.3 b**). The C-C-O-H torsion angle can be rotated and constrained to 90° to isolate a second stable trans conformer (**Figure 3.3 c**), which lies approximately a further 5 kJ mol^{-1} higher in energy, **Appendix Table A.1**. Although constrained, vibrational analysis returned no negative frequencies. For all systems featuring the choline cation, the reported association energies are referenced with respect to the minimum energy gauche conformer.

Within a polar solvation environment, the energy difference between the gauche and trans conformers of choline decreases. For example, when optimised in a CPCM (H_2O) environment, the relative energy difference, ΔE_{rel} between gauche and trans choline decreases to only $\approx 6 \text{ kJ mol}^{-1}$, **Appendix Table A.1**. Trans choline has a larger computed dipole moment (3.66 D) relative to gauche choline (1.90 D) and is therefore stabilised to a greater extent in a polar environment. This finding is consistent with other reports and could explain the increased conformational flexibility of choline in *ab initio* MD simulations of choline carboxylate ionic liquids.³² With both gauche and trans choline potentially accessible in the DES environment, it is important to screen intermolecular interactions with both conformers.

Considering steric arguments alone, the trans conformer of choline would be anticipated to be energetically more favourable than the gauche conformation. For the related neutral analogue of choline, *N,N*-dimethylethanolamine, the energy difference between the gauche and lowest energy trans conformer is reduced, with the gauche conformer lying $\approx 2 \text{ kJ mol}^{-1}$ higher in energy. As the trans conformer is not energetically favoured in choline, electronic factors must influence the conformational preference.

Previous ^1H NMR studies observed that the gauche conformer of β -substituted ethyltrimethylammonium cations predominated when the substituent X was polar and able to occupy a position close to the cationic head group.³⁰ In contrast, when the substituent was non-polar/of lower electronegativity, the trans conformation was favoured. These results would suggest a favourable, non-specific, electrostatic interaction between the electronegative substituents and the positive charge distributed over the ammonium head group i.e. an “electrostatic gauche effect”.

In the case of choline, the computed partial charge distribution provides evidence to support such a hypothesis. With both the NBO and CHELPG charge partitioning schemes, the electronegative oxygen atom of the hydroxyl group is found to bear a negative partial charge (≈ -0.65 to -0.75 e), with the positive charge being largely distributed over the hydrogen atoms of the alkyl groups (**Appendix, Table A.2**). Therefore, the negative oxygen atom “sees” the positive charge smeared out over the periphery of the ammonium head group, resulting in a favourable electrostatic interaction.

Within the gauche conformer, there is also the possibility of an intramolecular H-bond contributing to the total stabilisation. One of the C-H $\cdots$ O distances in choline is found to be notably shorter than the others (**Figure 3.4 a**). Moreover, this C-H $\cdots$ O interaction is the only one for which a BCP is identified, $\rho_{\text{BCP}}=0.016$ au (**Appendix, Table A.3**). Together with the magnitude and signs of $\nabla^2\rho_{\text{BCP}}$ and H_{BCP} , this finding is indicative of the formation of a weak, predominantly electrostatic H-bond. An $E^{(2)}$ value of only 5.23 kJ mol^{-1} for the associated $n_{\text{O}}\rightarrow\sigma_{\text{CH}}^*$ interaction further supports this argument (to put this in context, the $E^{(2)}$ values associated with the geminal $n_{\text{O}}\rightarrow\sigma_{\text{CH}}^*$ interactions are found to be over four times greater).

A comparative analysis of the C-H $\cdots$ O interactions within neutral *N,N*-dimethylethanamine reveals that this system exhibits a weaker H-bond, (**Figure 3.4 b** and **Appendix, Table A.3**). This indicates that the positive charge of choline strengthens the intramolecular H-bond, and thus contributes to the preference for the gauche conformation. Similar behaviour has been reported for other functionalised cationic/neutral systems.^{33, 34}

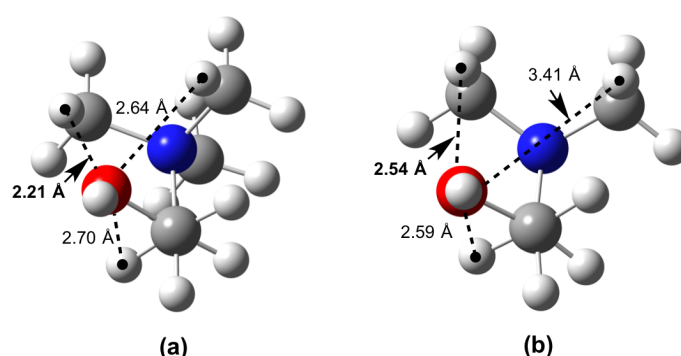


Figure 3.4. C-H $\cdots$ O interaction distances indicated within (a) gauche choline and (b) gauche *N,N*-dimethylethanamine.

A $\sigma_{\text{C-H}}\rightarrow\sigma_{\text{C-X}}^*$ hyperconjugative interaction is one of the two main arguments proposed as the origin of the so-called “gauche effect” in some systems,³⁵ most commonly disubstituted alkanes. Whilst there is some debate on this matter,³⁶ only within the gauche conformation of choline is a $\sigma_{\text{C-H}}\rightarrow\sigma_{\text{C-N}}^*$

donor-acceptor interaction observed (26.5 kJ mol^{-1}). Therefore, hyperconjugation could also play a role in stabilising the gauche conformation.

In summary, the gauche conformer of choline is found to be energetically favoured with respect to the trans conformer in the gas phase. Through analysis of the electronic structure, a non-specific electrostatic interaction between the δ^- oxygen atom and the positive charge across the ammonium head group, a specific C-H $\cdots$ O intramolecular H-bond, facilitated by the positive charge of the cation, and a hyperconjugative interaction have been identified as factors contributing to the stabilisation of the gauche conformer.

3.2 Choline chloride ion pairs

Structure – energy relationships

A search for stable positions of the chloride anion about the isolated gauche and trans choline conformers was undertaken. The stable choline chloride ion pairs are shown in **Figure 3.5**, with the relative energies detailed in **Table 3.1**. Relative energies of the ion pairs with and without ZPE and BSSE corrections can be found in the **Appendix, Table A.4**. The ion pairs are labelled alphabetically in order of ascending relative energy, in conjunction with a label to denote the conformation of the choline cation in the ion pair. ChG and ChT are used to label gauche and trans choline respectively. Thus, A_ChG is the lowest energy ion pair featuring gauche choline, whilst A_ChT is the lowest energy ion pair featuring trans choline. The association energies of the ion pairs are calculated as: $E_a = E(\text{ion pair}) - E(\text{gauche choline}) - E(\text{chloride})$, where $E(\text{gauche choline})$ is the energy of the isolated gauche choline conformer.

Typical for an organic salt in the gas phase, the association energies of the choline chloride ion pairs are large, ranging from -371 to -409 kJ mol^{-1} .³⁷ The high values are the result of the strong, attractive Coulombic association between the oppositely charged ions which is unscreened in the gas phase. To rationalise the energy differences between the ion pairs, more than one factor must be considered; differences in the global Coulomb interaction energy, a result of the different partial charge distributions and varying distances between the ions, in combination with changes in local electronic and structural interactions, such as H-bonding.

Table 3.1. Relative energies ($\Delta E_{\text{rel}} / \text{kJ mol}^{-1}$) of the choline chloride ion pairs. Amount of charge transfer, CT, from chloride to choline computed using NBO and CHELPG population analysis methods.

Ion Pair	$\Delta E_{\text{rel}} / \text{kJ mol}^{-1}$	CT(NBO) / e	CT (CHELPG) / e
A_ChG	0.00	0.150	0.249
B_ChG	0.81	0.130	0.250
C_ChG	12.21	0.099	0.213
A_ChT	21.46	0.102	0.231
D_ChG	28.74	0.107	0.203
E_ChG	29.79	0.111	0.217
B_ChT	33.11	0.115	0.221
C_ChT	37.50	0.108	0.193

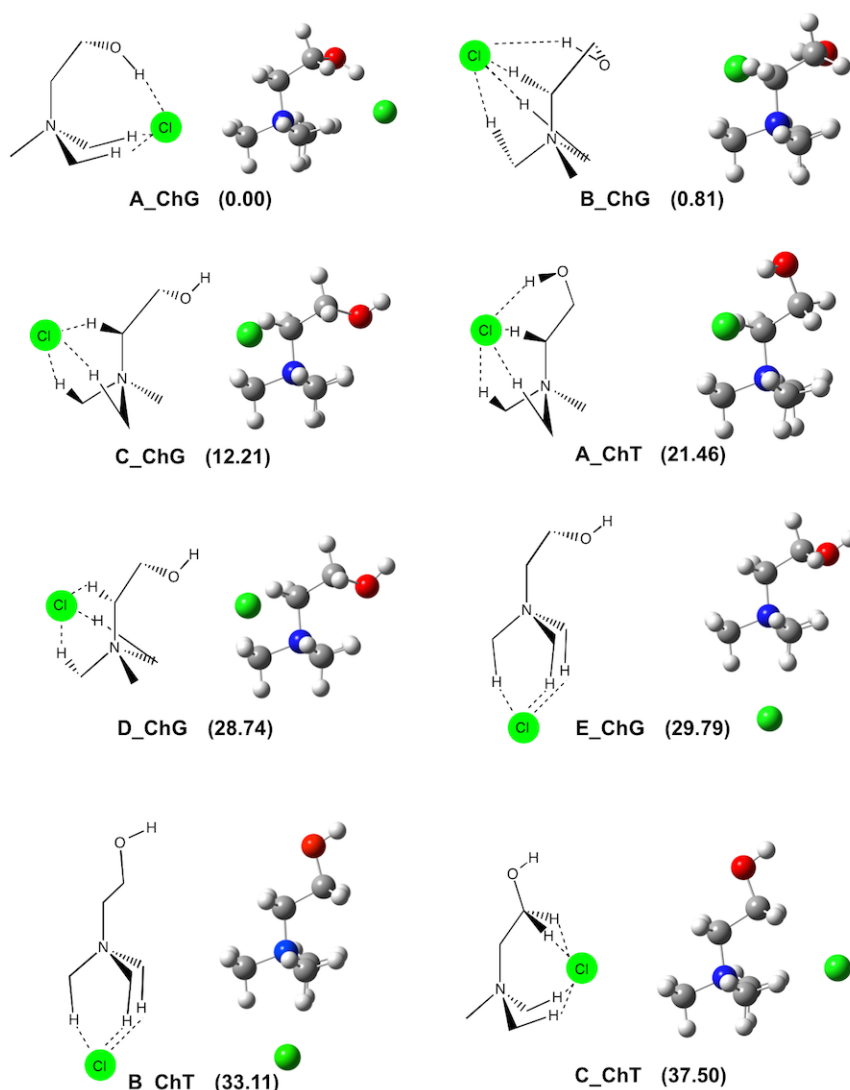


Figure 3.5. Choline chloride ion pairs ($\Delta E_{\text{rel}} / \text{kJ mol}^{-1}$).

The global Coulomb association energies can be crudely estimated assuming that the ions are point charges, with the positive charge of the choline cation located at the nitrogen centre. The average separation, r , between the nitrogen centre of choline and the chloride anion is 3.65 Å, but ranges from 3.84 Å (A_ChG) to 3.55 Å (C_ChG), **Table 3.2**. Using charges, q , of ± 1 e and the average separation, an electrostatic potential energy of $\approx 380 \text{ kJ mol}^{-1}$ is recovered. The variation in the separation, r , of 0.29 Å across the ion pairs results in a corresponding variation in the estimated Coulomb association energy of $\approx 29.6 \text{ kJ mol}^{-1}$, **Table 3.2**. However, the average NBO charge on each ion following charge transfer is approximately ± 0.9 e, **Table 3.1**. Using values of ± 0.9 e and the average separation, the corresponding Coulomb potential is $\approx 310 \text{ kJ mol}^{-1}$ with a reduced variation of $\approx 23.9 \text{ kJ mol}^{-1}$ across the ion pairs, **Table 3.2**.

Although this is a crude approximation, the results suggest that variation in the global Coulomb association energy is of the same order of magnitude as the relative energy differences between the ion pairs.

Table 3.2. Estimated Coulomb interaction within each choline chloride ion pair. Δr is the separation between the ions (i.e. the distance between the N centre of choline and Cl), E_a is the total association energy of the ion pair and E_c is the estimated Coulomb potential. ΔE corresponds to the difference between the total association energy and the estimated Coulomb potential.

Ion Pair	Δr (N...Cl)/ Å	E_a /kJ mol ⁻¹	$ q = 1\text{ e}$		$ q = 0.9\text{ e}$	
			E_c / kJ mol ⁻¹	ΔE ($E_c - E_a$) /kJ mol ⁻¹	E_c / kJ mol ⁻¹	ΔE ($E_c - E_a$) /kJ mol ⁻¹
A_ChG	3.84	-409	-362	+47	-293	+116
B_ChG	3.60	-408	-386	+22	-313	+95
C_ChG	3.55	-397	-391	+6	-317	+80
A_ChT	3.63	-387	-383	+4	-310	+77
D_ChG	3.59	-380	-387	-7	-314	+66
E_ChG	3.60	-379	-386	-7	-313	+66
B_ChT	3.58	-376	-388	-12	-314	+62
C_ChT	3.77	-371	-369	+2	-299	+72

A simplified representation of the choline cation, as a tetrahedron with four faces formed by the methyl/methylene groups of the quaternary ammonium head, is shown in **Figure 3.6**. Owing to the CH₂OH chain extending from the apical vertex, one face is partially blocked, albeit to a greater extent in the gauche conformation (blocked face shaded in **Figure 3.6**).

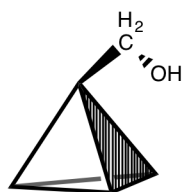


Figure 3.6. Simplified representation of the gauche choline cation.

For a gauche or trans choline conformer, there are a number of stable positions in which the anion can locate. The chloride anion can either “sit” at one of the three unhindered faces of the tetrahedron (ion pairs (B-E_ChG, A-B_ChT) or at the hindered face (A_ChG and C_ChT), **Figure 3.5**. As trans choline is symmetric, the optical isomer of ion pair A_ChT can also be isolated. The stable positions of chloride about choline, found here in the gas phase, are consistent with the anion positions about quaternary ammonium cations in the solid state.³⁸

Additional to the structures shown in **Figure 3.5**, a high energy structure ($\Delta E_{\text{rel}} \approx 100\text{ kJ mol}^{-1}$) in which chloride does not sit at a face of the tetrahedron, but along a N-C bond vector of a methyl group, can also be obtained, **Figure 3.7**. It is likely that analogous structures with chloride positioned at the alternate methyl groups would exist. However, due to the high energy, a structural search for these configurations has not been undertaken. Nevertheless, structures of this type are also observed in the solid state of quaternary ammonium salts.³⁸

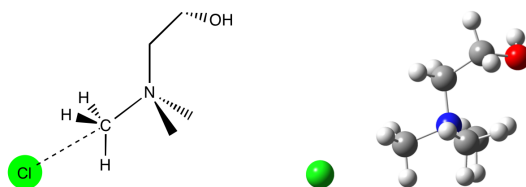


Figure 3.7. Example of a high energy choline chloride ion pair.

A_ChG is the lowest energy ion pair, with the conformation of the choline cation showing reasonable agreement with that found for choline in the choline chloride crystal structure.²⁹ Within A_ChG, the hydroxyl group is orientated to form a favourable interaction with the chloride anion. For both gauche and trans choline, the lowest energy ion pairs (A_ChG, B_ChG and A_ChT) all feature an O-H...Cl H-bond.

For the ion pairs featuring an O-H...Cl interaction, the hydroxyl group has been rotated away from the gas phase minimum energy conformation. A partial energy profile for the rotation about the C-C-O-H torsion angle within gauche choline is shown in the **Appendix, Figure A.2**. The C-C-O-H torsion angles adopted by A_ChG and B_ChG are associated with an increase in torsional strain, estimated at $\approx + 20 \text{ kJ mol}^{-1}$. As A_ChG and B_ChG are the lowest energy ion pairs, the energy associated with this deformation must be more than recouped by the formation of the O-H...Cl H-bond.

The remaining ion pairs only exhibit specific C-H...Cl interactions. The lowest energy ion pair of this type, C_ChG, is only $\approx 12 \text{ kJ mol}^{-1}$ higher in energy than A_ChG. The interaction of chloride with a “tripodal” (i.e. akin to the legs of a tripod) arrangement of hydrogen atoms is observed to be a recurrent motif in these higher energy ion pairs. An examination of the literature reveals the tripodal motif to be relatively prevalent, particularly for systems with quaternary ammonium cations.^{32, 39-42} Nevertheless, the significance, and interplay of interactions underpinning this structural motif have typically been overlooked.

Covalent contribution to H-bonding

A detailed examination of the H-bonding within the choline chloride ion pairs has been conducted. The H-bonds with the choline chloride ion pairs are of the doubly ionic type. However, an examination of H-bonding with the choline cation allows for a comparison of H-bonds of more traditional functionality (i.e. O-H...O) with C-H...X H-bond interactions, commonly observed within aprotic ionic liquids.

As examples, the QTAIM molecular graphs for ion pairs A_ChG and B_ChG are shown in **Figure 3.8**. Information relating to the individual H-bonds within each ion pair is provided in the **Appendix, Table A.5**.

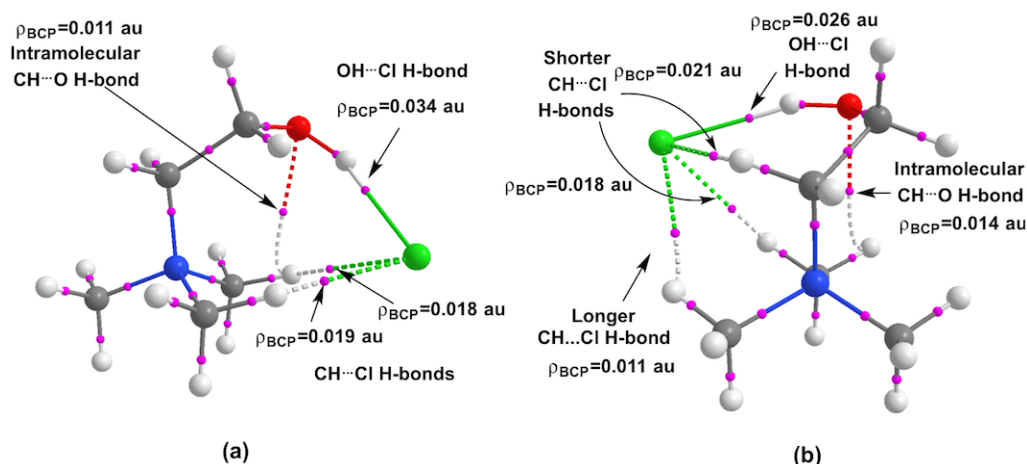


Figure 3.8. QTAIM molecular graphs of (a) A_ChG and (b) B_ChG. BCPs are shown as pink dots.

The weak intramolecular C-H...O H-bond found within isolated gauche choline is preserved upon ion pair formation, with an average value of ρ_{BCP} (0.014 au) only marginally reduced from the value in the isolated cation (0.016 au), e.g. the examples in **Figure 3.8**.

A BCP has been identified for each of the C-H...Cl interactions within the ion pairs. The mean value of ρ_{BCP} for a C-H...Cl interaction is found to be 0.018 au, although ranges from 0.008 – 0.022 au. In all cases, associated values of $\nabla^2 \rho_{\text{BCP}}$ and H_{BCP} are both positive. According to our criteria, the majority of the C-H...Cl interactions are therefore within the weak H-bond category. Nevertheless, whilst each of the C-H...Cl H-bonds is weak, multiple C-H...Cl H-bonds exist within each ion pair.

As a result of the cation structure, tripodal arrangements of δ^+ hydrogen atoms are presented on the three unhindered tetrahedron faces of the cation. By sitting at (or near) the centre of the face, chloride is able to maximise the number of H-bonds formed; three C-H...Cl H-bond interactions are observed within ion pairs B-E_ChG and A-B_ChT. However, at one of the three unhindered faces, the hydroxyl group can rotate to form an additional O-H...Cl H-bond. However, this “pulls” the chloride anion slightly off-centre, leading to a reduction in one of the C-H...Cl H-bond interactions, e.g. B_ChG, **Figure 3.8 b**.

The chloroform (Cl_3CH) – chloride complex has been computed to substantiate the assertion that H-bonding to chloride is “maximised” within the tripodal motif, **Figure 3.9 a**. Chloride forms a single, linear H-bond of moderate strength ($\rho_{\text{BCP}} = 0.033$ au) with chloroform. The molecular graph for ion pair E_ChG, an example of a structure exhibiting the tripodal motif, is shown in **Figure 3.9 b**. Within E_ChG, each of the individual C-H...Cl H-bonds (mean $\rho_{\text{BCP}} = 0.020$ au) is weaker than the single H-bond in the chloroform-chloride example. However, the total sum of ρ_{BCP} for the three C-H...Cl contacts is 0.059 au. Therefore, if $\sum \rho_{\text{BCP}}$ is used as a measure of the total H-bonding, this finding indicates that the formation of three slightly bent H-bonds in the doubly ionic system is competitive with the formation of a single linear H-bond in the ionic system. Similar observations regarding the preference for the tripodal motif have been made elsewhere. For example, for the interaction of *N*-methylacetamide with $[\text{NC}_1\text{C}_1\text{C}_1\text{C}_1]^+$, the formation of three slightly bent C-H...O H-

bonds in the tripodal arrangement is energetically favoured over the formation of a single, linear C-H...O H-bond.⁴⁰

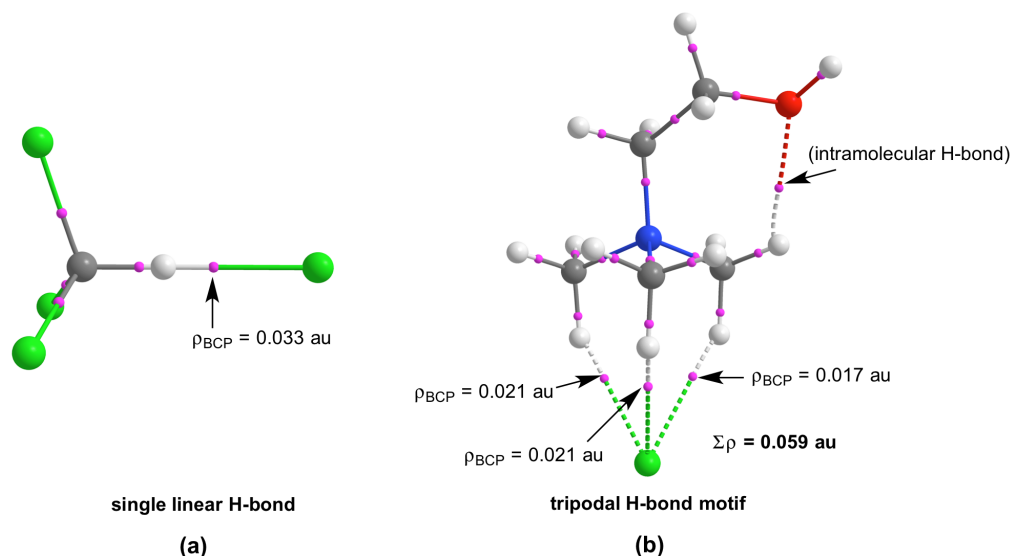


Figure 3.9. QTAIM molecular graphs for (a) chloroform – chloride, $\text{Cl}_3\text{CH}\cdots\text{Cl}^-$ and (b) the choline chloride ion pair E_ChG.

However, does chloride sit at the centre of one of the tripodal faces in order to maximise H-bonding, or is H-bonding maximised as a result of chloride sitting at the centre of the face? If each of the tripodal hydrogen atoms is considered as a positive point charge, from the perspective of an approaching anion (a negative point charge), the charge distribution would be analogous to placing a positive charge at the centre of the triangle formed by the three hydrogen atoms. This could explain why the anion approaches along the vector passing through the centre of a tetrahedron face. Furthermore, by locating at the centre of the face, it is possible that steric interactions are minimised, allowing the anion to approach closer to the cation. Therefore, the combination of electrostatics, H-bonding and sterics influences the chloride positioning.

A qualitative analysis of the MOs can be undertaken to evaluate the degree of orbital interaction between the cation and anion fragments. For the ion pairs exhibiting only C-H...Cl interactions, the HOMO, HOMO-1 and HOMO-2 of the ion pairs are dominated by orbital contributions from the three 3p AOs of chloride, with minor contributions from each of the C-H fragments of the cation. For example, the HOMO-2 of E_ChG, shown in **Figure 3.10 a**, reveals limited interaction between the tripodal face of C-H based fragment orbitals (FOs) and the chloride p AO. Localisation of the orbital contribution on one fragment is indicative of this being a highly ionic interaction, in agreement with the QTAIM analysis of the C-H...Cl H-bonds.

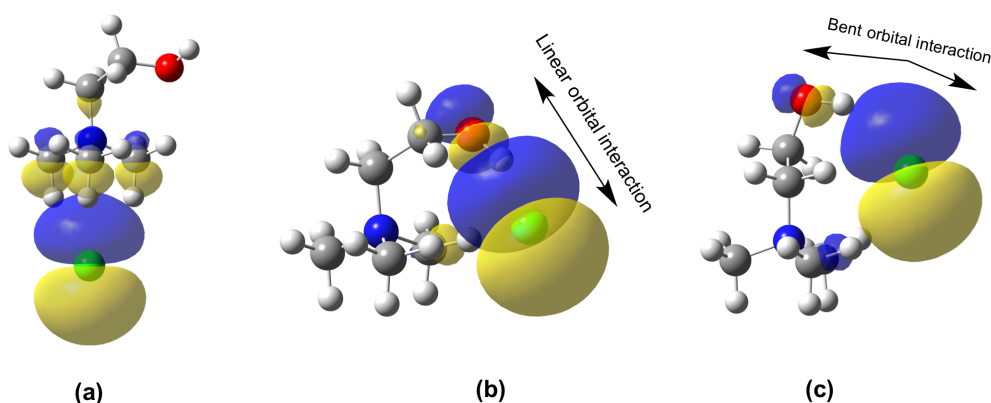


Figure 3.10. HOMO-2 of (a) E_ChG, (b) A_ChG and (c) A_ChT, generated at the 0.02 au isosurface.

For the high-energy ion pair structure shown in **Figure 3.7**, chloride sits at the face of a methyl group (i.e. along the N-C_{methyl} bond vector), rather than at a face of the tetrahedron. Whilst similar interactions have been observed in other systems,^{40, 43} the nature of this interaction is debateable. However, all evidence obtained here suggests that this is not an alternative tripodal H-bond motif, with the H-bond criteria detailed in **Table 1.1** not being satisfied. For example, neither C-H...Cl BCPs, nor $n_{\text{Cl}} \rightarrow \sigma^*_{\text{CH}}$ interactions in the NBO analysis, were identified. Rather, a BCP is located between chloride and the methyl carbon centre, indicating that this interaction is an example of the recently proposed “carbon bond”.⁴⁴

For ion pairs featuring O-H...Cl H-bonds, the strength of the interaction varies as A_ChG ($\rho_{\text{BCP}} = 0.034$ au) > B_ChG ($\rho_{\text{BCP}} = 0.026$ au) > A_ChT ($\rho_{\text{BCP}} = 0.013$ au). The decrease in the magnitude of ρ_{BCP} occurs concurrently with an increase in the O-H...Cl H-bond length and decrease in the value of $E^{(2)}$ for $n_{\text{Cl}} \rightarrow \sigma^*_{\text{OH}}$, **Appendix, Table A.5**. For each case $\nabla^2 \rho_{\text{BCP}}$ is positive, however, the sign of H_{BCP} changes from positive (A_ChT), to approximately zero (B_ChG) to negative (A_ChG). In all, this would indicate that the O-H...Cl H-bond is of moderate strength within ion pairs A_ChG and B_ChG, but weak within A_ChT.

In terms of orbital interactions, for ion pairs with an O-H...Cl H-bond one of the 3p AOs of chloride interacts with an O-H based FO e.g. the HOMO-2 of A_ChG and A_ChT, **Figure 3.10 b and c**. Whilst the HOMO-2 of A_ChG is still dominated by the chloride FO, the O-H FO makes a slightly larger contribution than the individual C-H contributions within the HOMO-2 of E_ChG. Furthermore, the orbital interaction is linear, in contrast to the “bent” orbital interaction seen in the HOMO-2 of A_ChT. A decrease in linearity leads to a reduction in orbital overlap, and thus a lower value of ρ_{BCP} . The gauche conformation of choline allows for the formation of more linear, and therefore stronger, O-H...Cl H-bonds.

A recurrent theme when investigating H-bonding is the concept of number versus strength of H-bond interactions; there is a balance between forming a smaller number of stronger H-bonds and a larger number of weaker H-bonds. A comparison of the H-bonding in the choline chloride ion pairs therefore requires that both the number *and* strength of the observed H-bond interactions be assessed. Ion pairs A_ChG (0.00 kJ mol⁻¹) and C_ChT (+ 37.5 kJ mol⁻¹) can be used to illustrate the balance between number and strength of individual H-bond interactions.

For example, within C_ChT, four C-H...Cl H-bonds are formed. Within A_ChG, **Figure 3.8 a**, only two C-H...Cl H-bonds form, however, additional stabilisation occurs through formation of an O-H...Cl H-bond. Across the choline chloride ion pairs, a single C-H...Cl H-bond is on average weaker than an O-H...Cl H-bond. However, the sum of ρ_{BCP} for three C-H...Cl H-bonds (e.g. 0.059 au for E_ChG, **Figure 3.9 b**) is more than competitive with the maximum ρ_{BCP} for a single OH...Cl H-bond (0.034 au), but not greater than the sum of ρ_{BCP} for the formation of an O-H...Cl H-bond in conjunction with multiple CH...Cl H-bonds, e.g. $\Sigma \rho_{\text{BCP}} = 0.071$ au within A_ChG.

The number of H-bonds is not, therefore, necessarily maximised in the lowest energy structure. However, due to the formation of a stronger O-H...Cl H-bond, the total sum of ρ_{BCP} is maximised in the two lowest energy choline chloride ion pairs.

Charge transfer contribution to H-bonding

Charge transfer from the anion to the cation is known to occur within ion pairs. The amount of NBO charge transfer has also been linked to the strength of H-bond formation.^{45, 46} Within the choline chloride ion pairs, charge transfer ranges from 0.099 – 0.150 e according to the NBO method, and 0.193 – 0.250 e with the CHELPG scheme, **Table 3.1**. ESP charge partitioning methods (e.g. CHELPG and MK) have previously been reported to predict more significant charge transfer when compared to the NBO method.⁴⁷ The range in charge transfer across the ion pairs, however, shows only a small difference (0.051 e and 0.057 e for NBO and CHELPG respectively).

Within the two lowest energy ion pairs, A_ChG and B_ChG, charge transfer is the greatest. Nevertheless, a strong correlation between charge transfer and the relative energy across all ion pairs is not obtained, **Figure 3.11**. Although the general trend is similar with both schemes, qualitative differences are observed in some cases. For example, the data points for the ion pairs with O-H...Cl H-bonds, A_ChG, B_ChG and A_ChT are circled in **Figure 3.11**. With the NBO scheme, the magnitude of total charge transfer for these ion pairs decreases in line with the strength of the O-H...Cl H-bond (based on ρ_{BCP} and $E^{(2)}$ values). With the CHELPG scheme, the magnitude of charge transfer is approximately the same across the three examples.

One possible explanation for the observed disparity is that the NBO scheme is more sensitive to the changes in orbital interactions. The electrostatic potential description, however, may provide a better “picture” of how the charge distribution of a system would appear to another, approaching molecule. For example, the ESP surfaces for A_ChG, B_ChG and C_ChT are shown in **Figure 3.12**. Overall, the charge distributions for A_ChG and B_ChG are very similar. For comparison, the charge distribution of C_ChT exhibits subtle differences. For example, within C_ChT, the region of negative charge is relatively localised on the chloride centre. In contrast, within A/B_ChG, both featuring O-H...Cl interactions, the negative charge is distributed over both the oxygen and chloride centres.

The “picture” of the charge distribution of a system will also be dependent on how close an approaching molecule is. This can be demonstrated by considering the electrostatic potential computed at different isodensities, e.g. for C_ChT, **Figure 3.13**. At lower isodensities, i.e. “further out”, the system appears more neutral, whilst at higher isodensities, i.e. “further in”, greater charge separation can be observed. In the extreme, at the atomic centres, the ESP partial charges are

obtained. The NBO and ESP charge partitioning methods potentially provide us with complementary information.

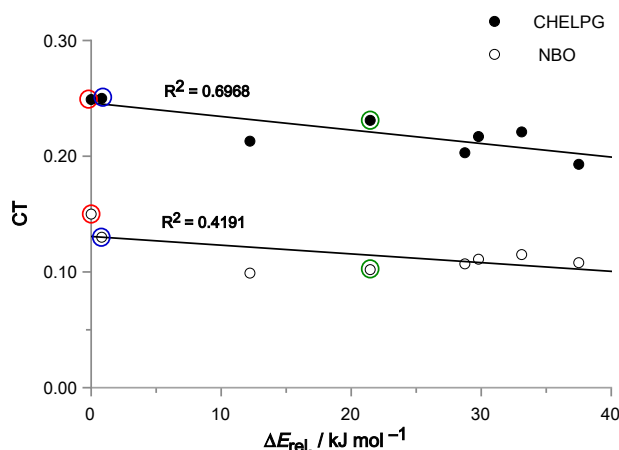


Figure 3.11. Relative energies of ion pairs, ΔE_{rel} (kJ mol^{-1}) plotted against charge transfer, CT, (NBO and CHELPG). Red circles = A_ChG, blue circles = B_ChG and green circles = A_ChT.

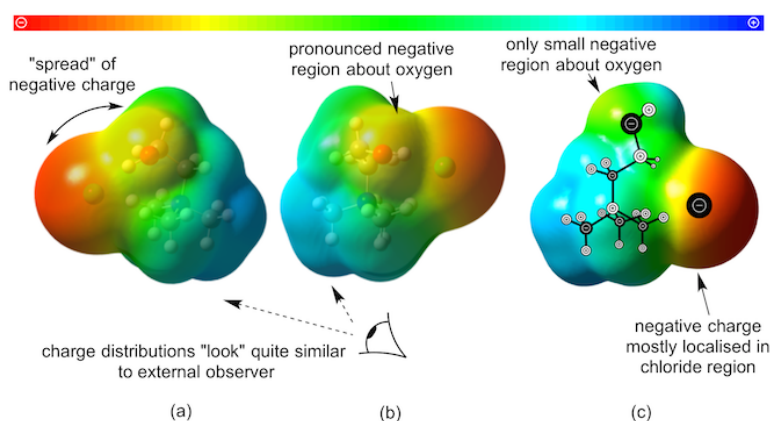


Figure 3.12. Electrostatic potential mapped onto the 0.0004 au density isosurfaces of choline chloride ion pairs (a) A_ChG, (b) B_ChG and (c) C_ChT. Charge range = ± 0.09 e (positive = blue, negative = red).

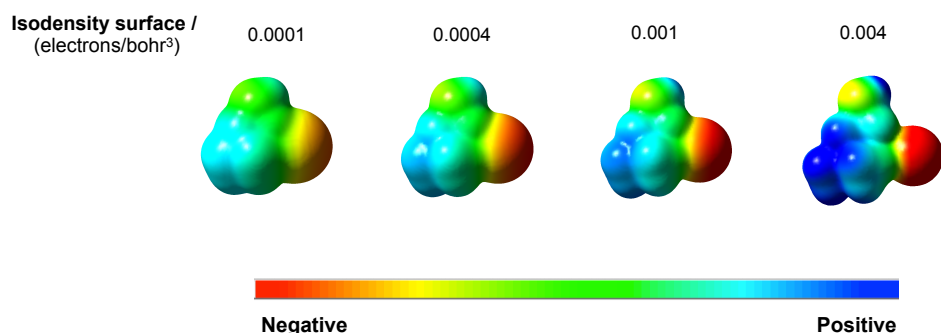


Figure 3.13. The electrostatic potential for ion pair C_ChT mapped onto isodensity surfaces of different values. Charge range = ± 0.09 e (positive = blue, negative = red).

An initial assumption was that ion pairs featuring an O-H $\cdots$ Cl interaction (A_ChG, B_ChG and A_ChT) would exhibit greater charge transfer than those with only C-H $\cdots$ Cl interactions. However, the presence of an O-H $\cdots$ Cl H-bond does not necessarily lead to larger charge transfer. According to the

NBO scheme, charge transfer for a number of ion pairs with only C-H...Cl H-bonds approaches that of A_ChT, or exceeds that of A_ChT according to the CHELPG scheme. However, it has been established that the O-H...Cl H-bond within A_ChT is particularly weak, with ρ_{BCP} (0.013 au) less than the mean ρ_{BCP} for the C-H...Cl H-bonds in this system (0.018 au). Furthermore, the O-H FO contribution to the HOMO-2 of A_ChT, **Figure 3.10**, is approximately equivalent to each of the individual C-H FO contributions within the HOMO-2 of E_ChG. The methyl groups are close to, or “carry”, the positive charge of the choline cation. However, the O-H group is essentially decoupled from the charged head group and in effect is a neutral donor. The charge of the system can, therefore, result in the formation of C-H...Cl H-bonds stronger than those with a functional group usually considered to be the stronger H-bond donor.

The total charge transfer can be shown to be the result of the combined contributions from the individual H-bonds. Importantly, to account for the total charge transfer the C-H...Cl interactions must be accounted for. For example, a representation of the intermolecular H-bonding for ion pairs A_ChT and E_ChG is shown in **Figure 3.14**. The total sum of ρ_{BCP} for the intermolecular H-bonds (1 x O-H...Cl and 3 x CH...Cl) within A_ChT is 0.062 au. For E_ChG, the sum of ρ_{BCP} is 0.059 au (3 x C-H...Cl), thus is very similar to the value obtained for A_ChT. However, the value of $E^{(2)}$ for all $n_{\text{Cl}} \rightarrow \sigma^*_{\text{CH}}$ interactions within E_ChG totals 105.31 kJ mol⁻¹, approximately 20 kJ mol⁻¹ greater than the total sum of 83.3 kJ mol⁻¹ for the combined $n_{\text{Cl}} \rightarrow \sigma^*_{\text{OH}}$ and $n_{\text{Cl}} \rightarrow \sigma^*_{\text{CH}}$ interactions in A_ChT. Therefore, the slightly greater NBO charge transfer within ion pair E_ChG (0.111 e compared to 0.102 e) is a result of the combined effect of the individual interactions.

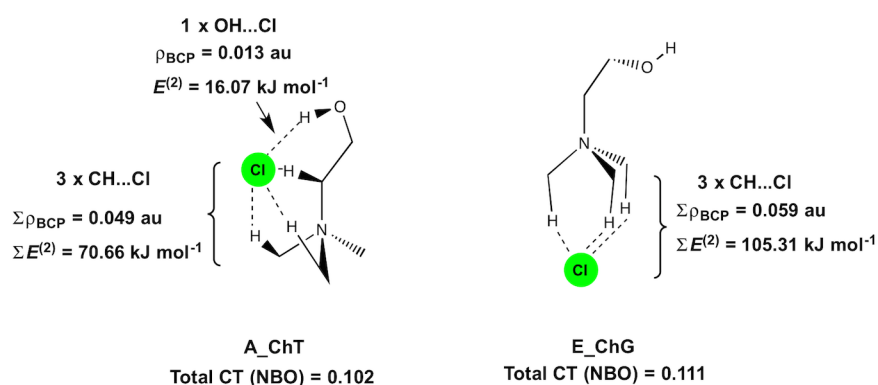


Figure 3.14. Intermolecular H-bonds within ion pairs A_ChT and E_ChG.

In summary, the choline chloride ion pairs can assume a relatively wide range of configurations. The choline cation can adopt either a trans or, the slightly more stable, gauche conformation and the chloride anion can sit at one of the four faces of the tetrahedron head group. Within these ion pairs, the tripodal C-H...Cl H-bond motif was found to be a recurrent feature. However, the lowest energy ion pairs, with either gauche or trans choline, feature a stabilising O-H...Cl interaction. On average, the O-H...Cl interactions are found to be stronger than the individual C-H...Cl H-bonds. However, the O-H...Cl interactions are found to be sensitive to the conformation of the choline cation, and linearity of the interaction. The sum of ρ_{BCP} or $E^{(2)}$ for three C-H...Cl H-bonds in the tripodal motif can be greater

than for a single O-H...Cl interaction. The charge of the cation therefore facilitates the formation of C-H...Cl H-bond motifs that are competitive with more traditional “strong” H-bond donors. The balance between forming a larger number of weaker, or smaller a number of stronger H-bonds was emphasised. As would be expected, the overall association of the choline chloride ion pairs is dominated by the electrostatic contribution. However, each ion pair finds a balance between maximising the Coulombic interaction and maximising local, specific interactions, including H-bonding.

3.3 Urea monomers and dimers

The geometries of amides have been the subject of numerous experimental and theoretical studies, the amide linkage being the basic building block of a polypeptide chain, and amides having important roles in crystal engineering and as anion receptors.⁴⁸⁻⁵²

In the gas phase the geometries of amides show some variability, usually with respect to pyramidalisation about the nitrogen centre(s). Urea, for example, has been found to adopt a non-planar equilibrium structure in the gas phase; whilst the heavy atoms (O-C-N) are co-planar, the NH₂ groups are pyramidal.⁴⁹⁻⁵¹ This results in two stable conformers, C₂ (**Figure 3.15 a**), with anti NH₂ groups, and C_s (**Figure 3.15 c**), with syn NH₂ groups. In contrast, the planar C_{2v} conformer (**Figure 3.15 b**) has been shown to be a second order saddle point on the PES.⁵¹ The energy differences between the conformers are reported to be small and dependent on both the level of theory and the inclusion of ZPE and thermal corrections. Both C₂ and C_s urea have been isolated here as, effectively degenerate, stable minima (C₂ < 0.5 kJ mol⁻¹ lower in energy). Two imaginary frequencies were returned for the C_{2v} conformer, consistent with previous reports. Relative energies of the conformers with, and without, ZPE corrections can be found in the **Appendix, Table A.6**.

Recently, it has been reported that intermolecular H-bonding can influence the planarity of simple amides, with the deformation away from the equilibrium geometry more than recompensed through the formation of stabilising H-bonds.⁵³ Change in the geometry of urea monomers has also been observed here, upon interaction with other species. For consistency, all association energies involving urea have therefore been computed using the energy of the C₂ conformer.

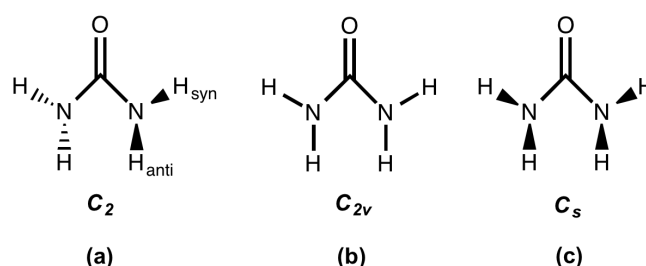


Figure 3.15. Conformers of urea: (a) C₂ with anti pyramidal NH₂ groups, (b) planar C_{2v} and (c) C_s with syn NH₂ groups. The labelling of the H atoms within a single NH₂ group as syn and anti, with respect to C=O, is shown in (a).

Studies to investigate gas phase oligomeric structures of urea have previously been undertaken.^{51, 54} Here, the interaction of urea with a second urea molecule (i.e. a urea dimer) is of most interest. For the urea dimer in the gas phase, there are two primary motifs, the ribbon (**Figure 3.16 a**) and the distorted chain (**Figure 3.16 b**). Within both structures examined here, the urea monomer adopts the

C_2 conformation. Alternate combinations of urea monomer conformers have been reported at different levels of theory.⁵¹

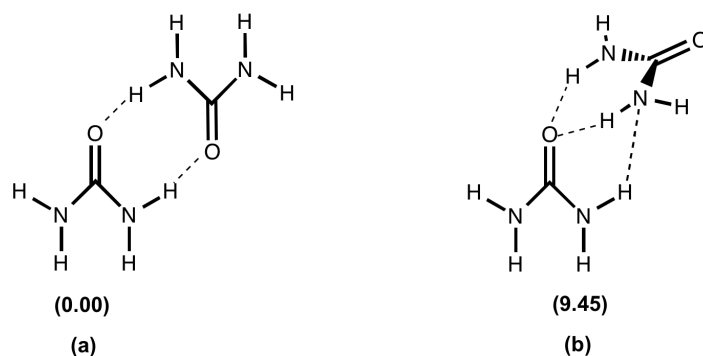


Figure 3.16. Structures of gas phase urea dimers: (a) ribbon and (b) distorted chain.

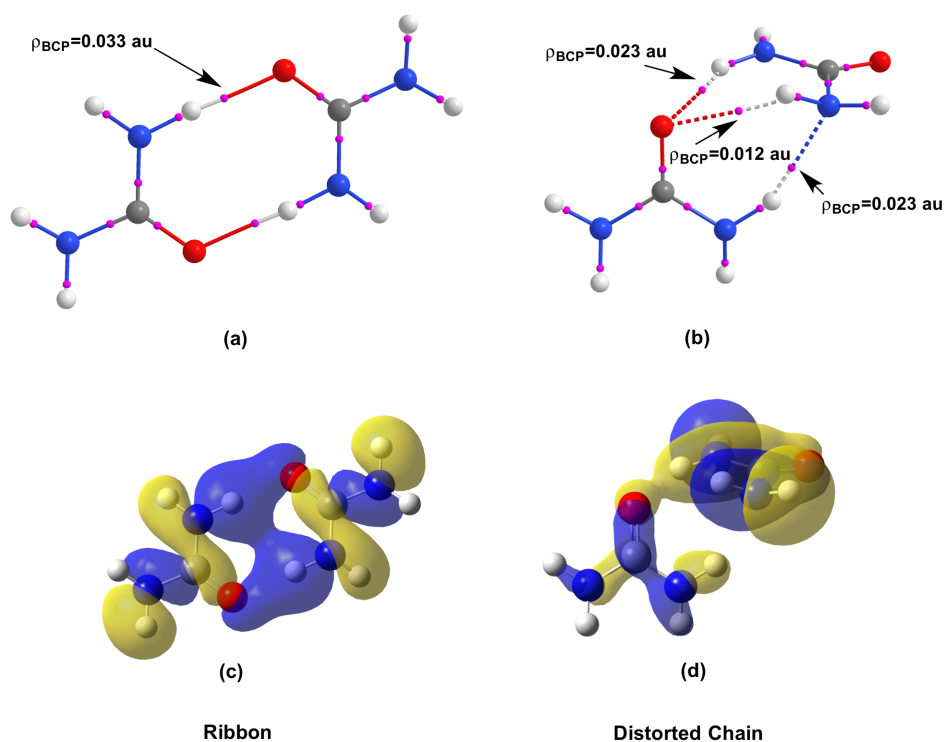


Figure 3.17. Molecular graphs shown in (a) and (b). BCPs indicated by small pink spheres. RCPs omitted. MOs indicating N-H...O=C H-bond formation shown in (c) and (d). MOs generated at the 0.02 au isosurface.

Of the two structures, the ribbon dimer is found to be $\approx 9.5 \text{ kJ mol}^{-1}$ lower in energy, with an association energy of $\approx -59 \text{ kJ mol}^{-1}$, **Appendix, Table A.7**. The ribbon dimer has approximate C_2 symmetry, and thus the urea monomers are equivalent. Two moderate single (and identical) N-H...O=C H-bonds are formed, each with $\rho_{\text{BCP}} = 0.033 \text{ au}$, **Figure 3.17 a** and **Appendix, Table A.8**. The sum for the combined interaction is therefore 0.066 au. Based on ρ_{BCP} , these neutral N-H...O=C H-bonds are the same strength as the strongest O-H...Cl H-bond identified within a choline chloride ion pair ($\rho_{\text{BCP}} = 0.034 \text{ au}$, A_ChG). Analysis of the MOs reveals there to be a reasonable amount of delocalisation over the whole system i.e. each urea fragment contributes equally to the MOs (not unsurprising given the symmetry of the dimer). As an example, a σ type MO indicating H-bond

formation is shown in **Figure 3.17 c**. The concept of delocalisation between the urea fragments is supported by the magnitude of the stabilisation energies associated with the $n_{\text{O}} \rightarrow \sigma_{\text{NH}}^*$ interactions, 68.7 kJ mol⁻¹ from one urea to the other, **Appendix, Table A.8**. However, as the system is symmetrical, the total stabilisation energy associated with electron delocalisation equates to 137.4 kJ mol⁻¹.

Within the solid state, urea monomers form linear, H-bonded chains.^{55, 56} For a gas phase dimer, a distortion of the linear chain motif occurs through the formation of an additional N-H...N H-bond, leading to a reduction in symmetry and resulting in the distorted chain motif. The distorted chain configuration is found here to be ≈ 9.5 kJ mol⁻¹ higher in energy than the ribbon configuration, **Appendix, Table A.7**.

A non-symmetrical chelating H-bond motif is identified within the distorted chain structure (**Figure 3.17 b**), the oxygen of one urea interacting with the two anti-NH units of the other. However, each of these N-H...O=C H-bonds is weaker than those found in the ribbon dimer, with the total sum of ρ_{BCP} , 0.035 au, almost the same as ρ_{BCP} for a single N-H...O=C interaction within the ribbon configuration. The additional stabilising N-H...N H-bond has a ρ_{BCP} of 0.023 au, and thus, is of approximately the same strength as the stronger of the two N-H...O=C H-bonds within the distorted chain. The sum of ρ_{BCP} for the combined interaction is 0.058 au.

Unlike the ribbon dimer, analysis of the MOs for the distorted chain reveals disparate contributions from each of the urea fragments to the dimer MOs e.g. **Figure 3.17 d**. Furthermore, the stabilisation energy associated with electron delocalisation between the fragments, $n_{\text{O}}/\pi_{\text{C=O}} \rightarrow \sigma_{\text{NH}}^*$ and $n_{\text{N}} \rightarrow \sigma_{\text{NH}}^*$, totals only 63.2 kJ mol⁻¹ (**Appendix, Table A.8**), ≈ 46 % of the value in the ribbon dimer. Therefore, there is reduced delocalisation within the distorted chain dimer.

To summarise, for gas phase urea dimers, the ribbon motif is energetically favoured over the alternate distorted chain motif. To form a dimer, urea must act as both a H-bond donor and H-bond acceptor. In terms of H-bonding, the total ρ_{BCP} for the two moderate H-bonds within the ribbon dimer (0.066 au) is greater than the combined ρ_{BCP} for the three weaker H-bonds within the distorted chain dimer (0.058 au). Furthermore, through analysis of the MOs and $E^{(2)}$ values, it can be established that there is a greater degree of electron delocalisation within the ribbon dimer.

3.4 Urea – chloride complexes

The interaction of urea with chloride is thought to be key to the formation of the choline chloride – urea DES.⁴ Amides, such as urea and thiourea, have long been known to form inclusion compounds with quaternary ammonium salts.^{57, 58} Crystal structures of such guest-host lattices vary, but indicate the formation of amide-anion H-bond interactions.^{59, 60} The ability of amides to complex a range of anions, from monoatomic halides to Y shaped carboxylates, is capitalised upon to build receptors for the purpose of anion recognition.^{61, 62} H-bonding is evidently central to the amide – anion interaction, with the strength of the complex formation in solution, for a given amide, related to the strength of the anion basicity.⁶³ In an aprotic solvent, the interaction of a functionalised urea derivative with two equivalents of F⁻ resulted in deprotonation of the urea analogue.⁶³ Thus, there is the potential for the amide – anion interaction to be very strong.

A number of questions remain to be answered regarding anion speciation within DESs. For example, for the system considered here, what is the nature of the urea-chloride interaction within the environment of a DES and what complexes form when the ratio of urea to chloride increases? To try to answer such questions, complexes of composition *n*.urea. : chloride (*n*=1-3) have been considered here. The first urea molecule to be “added” interacts directly with the chloride centre. Complex formation with a second or third urea molecule could occur either *via* formation of additional urea – chloride interactions, or through the formation of urea-urea interactions. It has been necessary to consider both possibilities here.

A simplified representation, emphasising the shell filling model of solvation, is used here to represent the urea-chloride complexes, **Figures 3.18** and **19**. The actual optimised structures are shown in the **Appendix, Figure A.3**. Structures have been labelled as X.Y.Z, with X, Y and Z corresponding to the number of urea molecules in the first, second and third coordination spheres of chloride respectively. Where relevant, square brackets have been used to indicate the formation of an *n*-urea-chloride complex in which all *n* urea locate in the first solvation sphere of chloride. Relative energies are detailed in **Table 3.3**. Further information can be found in the **Appendix, Table A.9**. Association energies have been computed according to: $E_a = E(\text{complex}) - n.E(\text{urea}) - E(\text{chloride})$.

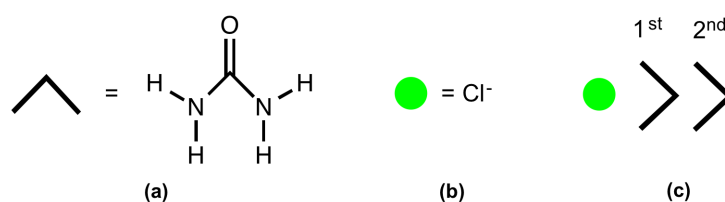


Figure 3.18. Simplified representation of (a) urea and (b) chloride. Coordination sphere with respect to chloride shown in (c).

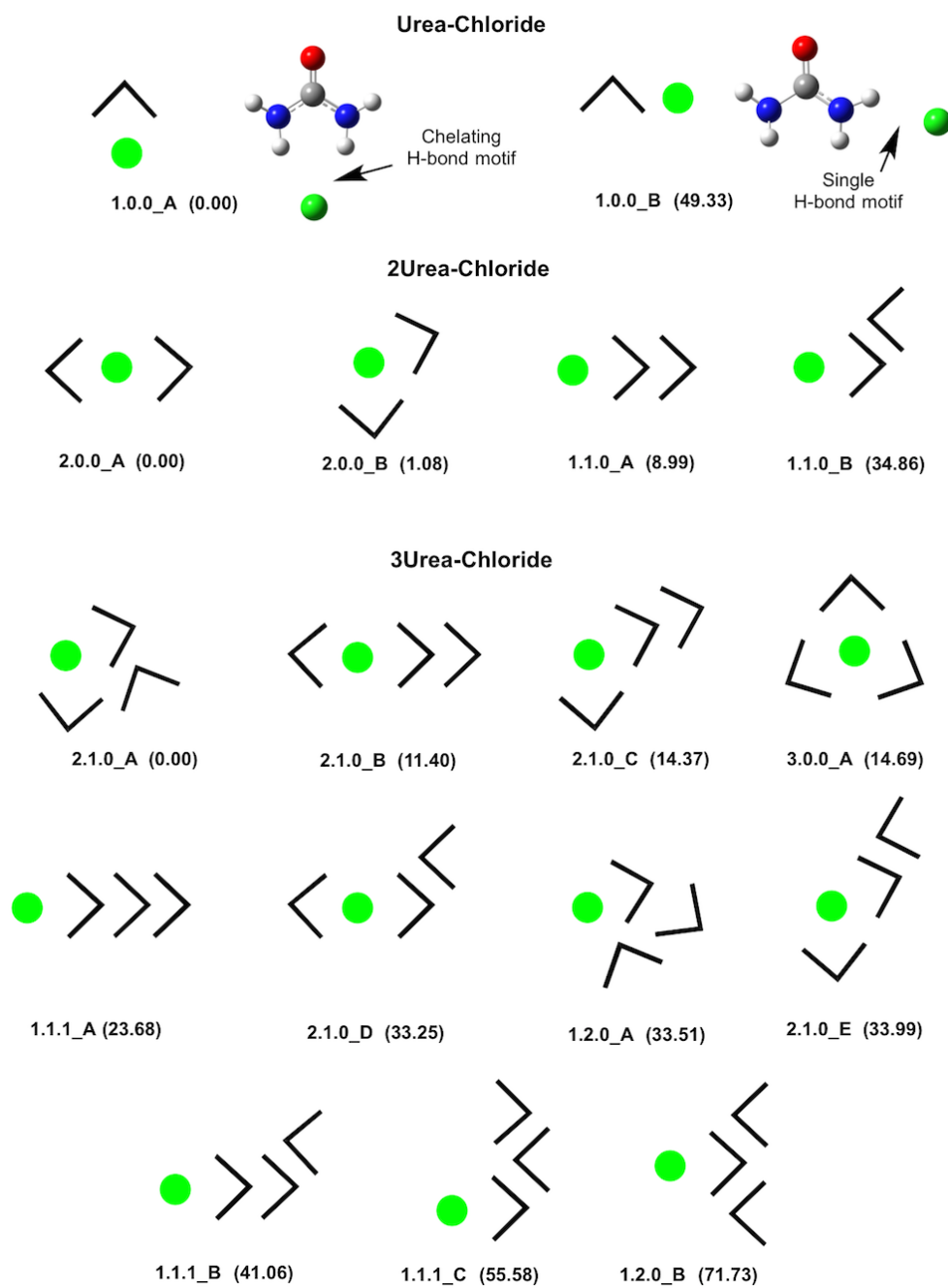


Figure 3.19. Simplified representation of the urea - chloride complexes. Structures labelled X.Y.Z with respect to the number of urea molecules in the 1st, 2nd and 3rd coordination spheres. Relative energies in kJ mol⁻¹.

Table 3.3. Relative energies ($\Delta E_{\text{rel}} / \text{kJ mol}^{-1}$) of the urea-chloride complexes. Total charge transfer (CT) from chloride computed using NBO and CHELPG.

Complex	$\Delta E_{\text{rel}} / \text{kJ mol}^{-1}$	(NBO) / e	(CHELPG) / e
1.0.0_A	0.00	0.076	0.109
1.0.0_B	49.33	0.040	0.060
2.0.0_A	0.00	0.097	0.136
2.0.0_B	1.08	0.107	0.185
1.1.0_A	8.99	0.098	0.130
1.1.0_B	34.86	0.080	0.108
2.1.0_A	0.00	0.105	0.171
2.1.0_B	11.40	0.106	0.125
2.1.0_C	14.37	0.117	0.194
3.0.0_A	14.69	0.104	0.178
1.1.1_A	23.68	0.103	0.137
2.1.0_D	33.25	0.101	0.128
1.2.0_A	33.51	0.104	0.136
2.1.0_E	33.99	0.111	0.183
1.1.1_B	41.06	0.097	0.126
1.1.1_C	55.58	0.079	0.106
1.2.0_B	71.73	0.083	0.094

Structure-energy relationship

Complex formation with one urea molecule occurs preferentially *via* the formation of a chelating H-bond motif, the two anti N-H units forming two single H-bonds with the chloride centre, structure 1.0.0_A. The association energy for complex 1.0.0_A is quite large (-106 kJ mol^{-1}), although only $\approx 26\%$ of the maximum choline-chloride association. The alternative H-bond motif, with urea acting as a single H-bond donor (structure 1.0.0_B), is 50 kJ mol^{-1} higher in energy than the chelating H-bond motif. At the B3LYP-D2 level, the single H-bond motif could only be obtained with the N-H...Cl distance fixed, although vibrational analysis returned no negative frequencies.

The C_2 conformer of urea is calculated here to have a relatively large dipole moment of 3.9 D. Therefore, there is the potential for a sizeable ion-dipole contribution to the association energy. Using the ion-dipole equation, the magnitude of this contribution can be estimated. Assuming a charge of -1 e on Cl, the computed dipole moment of urea, and using the Cl...C_{urea} distance (3.78 Å) as an estimate of the separation, r , the approximated ion-dipole contribution is -79 kJ mol^{-1} within 1.0.0_A. This value is large and supports the earlier hypothesis.

For the addition of a second urea molecule, there is a “choice” in where to locate, interaction with either chloride or with urea. Two complexes with two urea molecules interacting with chloride, that is both urea molecules in the 1st coordination sphere, have been obtained (2.0.0_A and B), **Figure 3.19**. When instead a urea-urea interaction takes place i.e. one urea in the 1st and one in the 2nd coordination sphere, two motifs are possible, the chain (1.1.0_A) and the ribbon (1.1.0_B). For the situation with three urea molecules, the third urea can situate in either the 1st solvation shell (3.0.0_A), 2nd solvation shell (e.g. 2.1.0_A) or, if added to one of the 1.1.0 structures, the 3rd solvation shell (e.g. 1.1.1_A).

For the n .urea-chloride complexes with two and three urea molecules, there is therefore found to be a fine balance between the preferences for chloride-urea or urea-urea interactions, reflected in

the range of configurations. The three lowest energy configurations with $n=2$ or 3 are separated by only ≈ 9 and 15 kJ mol^{-1} respectively.

With two urea molecules, the 2nd urea also preferentially resides in the 1st coordination shell, forming additional urea-chloride interactions, e.g. 2.0.0_A, over the possibility of forming urea-urea interactions. Nevertheless, structure 1.1.0_A, with one urea in both the 1st and 2nd coordination shells, is only 9 kJ mol^{-1} higher in energy than 2.0.0_A.

A complex with three urea molecules in the 1st coordination shell has been located, 3.0.0_A, but is $\approx 15 \text{ kJ mol}^{-1}$ higher in energy than the lowest energy 3.urea-chloride complex, 2.1.0_A. Within 2.1.0_A, the formation of urea-urea interactions leads to the creation of a “H-bonded ring”. Thus, with three urea molecules, the formation of a urea-urea interaction has (just) become more favourable for the system than formation of further urea-chloride interactions.

Typical for complex formation, successive addition of urea to chloride occurs with a concomitant decrease in ΔE_a , the difference in the energy of association between the $[n^{\text{th}} \text{ urea} \cdot \text{Cl}]^-$ and $[(n+1)^{\text{th}} \text{ urea} \cdot \text{Cl}]^-$ complexes, **Table 3.4**. ΔE_a between $[2\text{urea} \cdot \text{Cl}]^-$ (2.0.0_A) and $[3\text{urea} \cdot \text{Cl}]^-$ (3.0.0_A) is $\approx -69 \text{ kJ mol}^{-1}$. This is of a similar magnitude to the maximum association of the isolated urea dimer, ($\approx -59 \text{ kJ mol}^{-1}$). Thus, whilst the interaction of chloride with a single urea molecule is strongly favourable, the interaction with multiple urea molecules could potentially be competitive with other interactions.

Table 3.4. Association energies ($E_a / \text{kJ mol}^{-1}$), and difference between successive association energies ($\Delta E_a / \text{kJ mol}^{-1}$), for complexes with urea in the 1st coordination shell of chloride.

Urea-Chloride Complex	$E_a / \text{kJ mol}^{-1}$	$\Delta E_a / \text{kJ mol}^{-1}$
$[\text{urea} \cdot \text{Cl}]^-$ (1.0.0_A)	-106.43	-106.43
$[2\text{urea} \cdot \text{Cl}]^-$ (2.0.0_A)	-190.88	-84.46
$[3\text{urea} \cdot \text{Cl}]^-$ (3.0.0_A)	-259.75	-68.87

Our findings indicate that for eutectic mixtures at ratios of urea greater than 1:1, there could be a certain degree of flexibility in the urea-chloride association. For example, at the 1:2 ratio, the second urea molecule could be entering and leaving the first coordination sphere of chloride without there being a significant energy penalty, although this would be highly dependent on the barrier to reorganisation of the 1st coordination shell. This idea is consistent with reported MD findings, where urea was found to be more mobile than chloride in the 1:2 eutectic mixture.¹²

Complex 2.0.0_A, and the distorted variant 2.0.0_B, relate to the hypothesised complexed anions occurring at the eutectic composition. Low energy structures for the 1:3 system also feature the $[2\text{urea} \cdot \text{Cl}]^-$ “complexed anion motif”, but with the addition of urea-urea interactions. Conformers with all three urea molecules in either the ribbon or chain motifs are not favoured ($> 24 \text{ kJ mol}^{-1}$). Therefore, whilst the association of chloride with multiple urea molecules may be dynamic, the $[\text{urea} \cdot \text{Cl}]^-$ and, at higher concentrations of urea, $[2\text{urea} \cdot \text{Cl}]^-$ “complexed anion motifs” could feature prominently in these eutectic mixtures.

Geometries

The simplified representations do not illustrate the full complexity of the geometries of the urea-chloride complexes. For example, within 2.0.0_A, where the two urea molecules are in the 1st coordination sphere, the four N-H...Cl H-bonds form a tetrahedral arrangement about the chloride centre, **Figure 3.20 a**. Structure 2.0.0_B is a variant of 2.0.0_A, in which the urea molecules have “slipped”, leaving one side of chloride exposed, **Figure 3.20 b**. Within structure 3.0.0_A, the six N-H...Cl H-bonds form a distorted octahedral arrangement about the chloride centre, **Figure 3.20 c**. Structure 2.0.0_B is therefore effectively an intermediate between 2.0.0_A and 3.0.0_B. Furthermore, the geometry of urea also shows some variability in the complexes, mostly adopting either an approximate C_s or C_2 conformation, with the C_s conformer favoured when interacting directly with chloride.

Cooperative effects are thought to play a key role in influencing the geometry of urea oligomers, leading to the stabilisation of the chain motif over the ribbon motif for larger aggregates.^{54, 64} For example, at the Hartree-Fock level it has been found that for aggregates consisting of four or more urea molecules, the energy for the successive addition of urea favours the growth of the chain motif.⁵⁴ In the solid state of pure urea the chain motif is exclusively observed.⁵⁶ In contrast, within guest-host inclusion compounds, urea ribbons have also been identified.⁵⁹

For the *n*.urea-chloride (*n*=2,3) complexes studied here, the urea-urea chain motif is found to be energetically favoured with respect to the ribbon motif. This is despite the finding that the ribbon motif of the isolated urea dimer is more stable than the (distorted) chain dimer. As an example, complex 1.1.0_A (chain) is $\approx 26 \text{ kJ mol}^{-1}$ more stable than 1.1.0_B (ribbon). This finding suggests that the introduction of chloride could lead to an enhancement of the cooperativity in short urea chains.

Moreover, the urea-urea chain interaction within structure 1.1.0_A is linear rather than distorted, **Figure 3.21 a**. Again, this could indicate increased cooperative effects within the Cl-urea-urea subunit. However, this effect is found to be short-ranged. For example, within structure 1.1.1_A the chain interaction between urea in the 1st and 2nd coordination spheres is linear, but is distorted for the urea-urea interaction between the 2nd and 3rd shells, **Figure 3.21 b**. The influence of chloride on the urea-urea chain interaction can also be moderated by the complexation of a second urea molecule directly to chloride, as in complex 2.1.0_B, **Figure 3.21 c**, where the urea-urea chain interaction is distorted. Within 2.1.0_B, chloride is effectively “pulled” in opposite directions; the long-range influence of chloride in one direction is therefore reduced. This is consistent with the cancellation of the effects of induced polarisation.

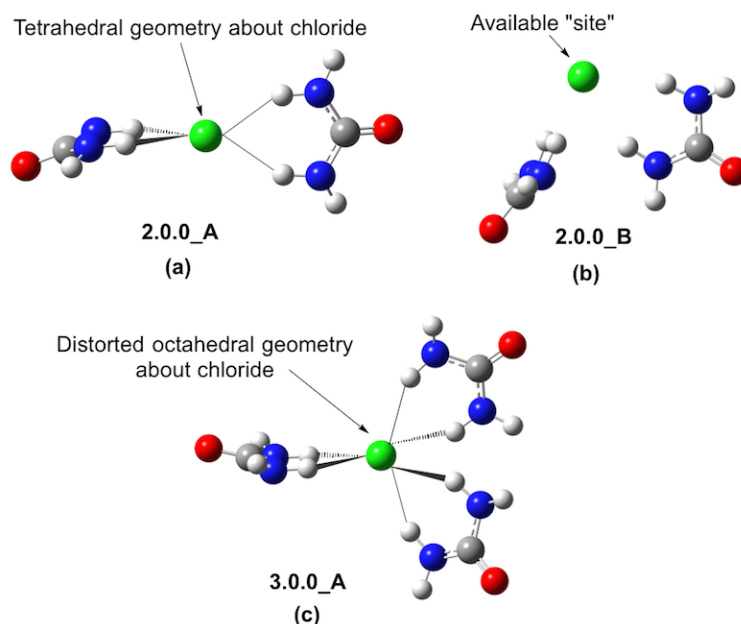


Figure 3.20. Geometries of selected urea-chloride complexes.

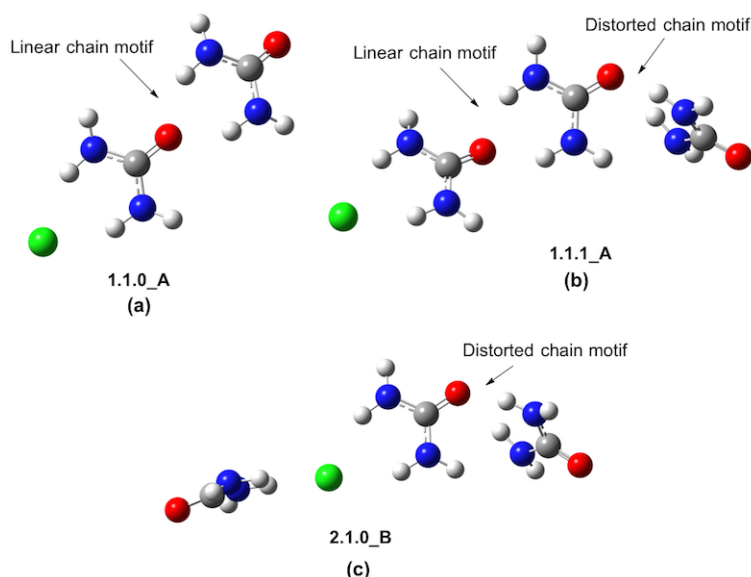


Figure 3.21. Examples of urea-chloride complexes featuring linear and distorted urea-urea chain motifs.

H-bonding

Selected properties of all H-bonds found in the urea-chloride complexes can be found in the **Appendix, Table A.10**. For the N-H $\cdots$ Cl interactions there is a range in the values of both ρ_{BCP} (0.012 – 0.028 au) and $E^{(2)}$ (15 – 73 kJ mol $^{-1}$). This indicates a relatively high degree of flexibility for the N-H $\cdots$ Cl interaction, varying from weak to moderate in strength depending on the local coordination environment.

However, the average value of ρ_{BCP} for the N-H $\cdots$ Cl interaction, across all the urea-chloride complexes, is 0.019 au. This is very close to the average value of ρ_{BCP} for the C-H $\cdots$ Cl interactions in the choline chloride ion pairs (0.018 au), despite the N-H group typically being thought of as the superior H-bond donor. This comparison reveals that doubly ionic H-bonds with a weaker donor group

can be competitive, in terms of strength, with ionic H-bonds with a stronger donor group. Additionally, if ρ_{BCP} and $E^{(2)}$ are used as a measure of the covalency of a H-bond interaction, the doubly ionic C-H $\cdots$ Cl interactions are, on average, as covalent as the ionic N-H $\cdots$ Cl interactions. However, on the scale of H-bond interactions, both the C-H $\cdots$ Cl and N-H $\cdots$ Cl interactions are still relatively ionic.

Analysis of the MOs provides further evidence of the relatively ionic nature of the N-H $\cdots$ Cl interactions; with there being limited orbital overlap between the urea and chloride fragments. Furthermore, the FO interactions that are observed occur between the filled 3p AOs of chloride and combinations of the HOMO, HOMO-1 and HOMO-2 of the urea fragments, e.g. **Figure 3.22**, indicative of a closed shell interaction. From visual inspection of the HOMO-1 orbitals of 1.0.0_A, 2.0.0_A and 3.0.0_A, **Figure 3.22**, it appears that the relative contribution of the urea FOs increases with the number of urea coordinated to chloride. This could indicate increased delocalisation.

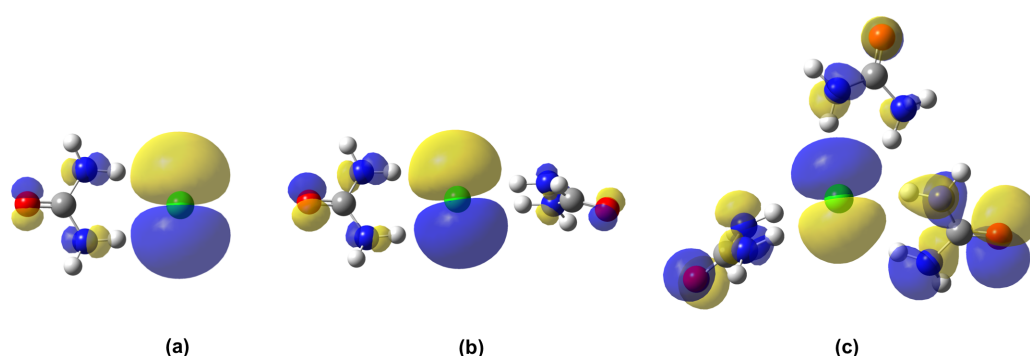


Figure 3.22. HOMO-1 of (a) 1.0.0_A, (b) 2.0.0_A and (c) 3.0.0_A. MOs generated at the 0.02 au isosurface.

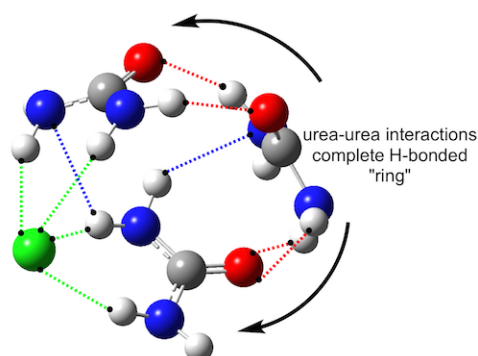


Figure 3.23. A H-bonded ring found within the 2.1.0_A structure. N-H $\cdots$ Cl H-bonds indicated in green, N-H $\cdots$ O=C H-bonds in red and N-H $\cdots$ N H-bonds in blue.

Maximisation of H-bonding between two interacting species may lead to increased stabilisation for many systems. However, for complex molecules, and particularly ions with anisotropic charge distributions, the total electrostatic interaction (including polarisation and inductive effects) will also be dependent on the configuration. Therefore, there will be a balance between maximising H-bonding and maximising other contributions to the total association energy. In this context, the lowest energy 3urea $\cdot$ Cl $^-$ complex, 2.1.0_A, is of interest.

Within 2.1.0_A, chloride and the three urea molecules form a “H-bonded ring”, **Figure 3.23**. For complexes of the 3:1 composition, the number of H-bonds is maximised within 2.1.0_A (in total 10 H-bonds). However, maximising the number of H-bonds does not necessarily equate to maximisation of the total H-bond interaction. For this to be established the strength of the individual H-bonds must be examined. Here we use the sum of ρ_{BCP} as a measure of the total H-bonding within a system. Within 2.1.0_A, the sum of ρ_{BCP} is 0.167 au and is only the third largest value for a 3urea·Cl⁻ complex. Both 1.2.0_A (0.171 au, 9 H-bonds) and 1.1.1_C (0.175 au, 6 H-bonds) have slightly larger values of $\Sigma\rho_{\text{BCP}}$, despite having fewer H-bonds. This demonstrates that H-bonding is not necessarily maximised in the lowest energy structure.

Therefore, why is 2.1.0_A the lowest energy example of a 3urea·Cl⁻ complex? Within bulk water, chloride has previously been found to polarise, with the water molecules of hydration “grouping” on one side of chloride i.e. an anisotropic cluster is formed.⁶⁵ Possible explanations for this phenomenon include dipole moment formation, the relative polarisability of chloride, entropy, as well as water-water H-bonding.⁶⁵ Potentially, a combination of similar effects could contribute to the “grouping” of urea within 2.1.0_A.

Charge transfer

Charge delocalisation across large bulky ions is frequently cited as a contributing factor to the low melting points of ionic liquids.⁶⁶ For DESs it has been suggested that charge delocalisation occurs upon complexation of the halide ion by the H-bond donor species.¹ This would suggest that charge is transferred from the localised chloride ion to the complexing urea moieties.

However, we find the magnitude of charge transfer within the urea-chloride complexes to be relatively small, albeit not negligible **Table 3.3**. With one urea in the 1st coordination shell, 1.0.0_A, charge transfer from chloride is 0.076 e according to NBO (0.109 e CHELPG), increasing to 0.107 e for 2.0.0_B (0.185 e CHELPG). The maximum charge transfer (0.117 e NBO, 0.194 e CHELPG) is found with three urea present (2.1.0_C) although only two urea molecules are in the 1st coordination sphere. Therefore, for complexes under 15 kJ mol⁻¹, there is an increase in charge transfer with the increase in the number of urea molecules.

In terms of charge transfer, the association of urea with chloride follows typical “solvation” behaviour. The solvation of charged species (e.g. [NH₄]⁺ and [OH]⁻) with water molecules is also found to occur with charge transfer, increasing with the number of added solvent molecules, but with less charge transfer for each successive addition.⁶⁷ In all cases, it was found that a significant amount of charge remained localised on the ionic centre within the solvated cluster.

Comparing to the choline chloride ion pairs, according to both NBO and CHELPG, the maximum charge transfer within the urea-chloride complexes is ≈ 78% of the maximum charge transfer within a choline chloride ion pair. Using the NBO partial charges, the average charge on chloride within the two [2urea·Cl]⁻ “complexed anion” structures, 2.0.0_A and B, is ≈ 0.90 e. In comparison, the average charge on chloride within the choline chloride ion pairs is ≈ 0.88 e. Thus, there is not a significant difference in the charge on chloride within isolated choline chloride relative to the isolated “complexed anion”. This would suggest that in terms of charges alone, the strength of the

Coulomb interaction between choline and chloride in an ion pair, and choline and the $[2\text{urea}\cdot\text{Cl}]^-$ complexed anion, are not notably different. This could suggest that the hypothesised decrease in Coulombic interaction between the choline cation and the anionic species within the DES is not due to a significant reduction in charge on the chloride centre.

To try and put the limited charge transfer from chloride to urea in context, we have computed the charge transfer upon formation of the prototypical eutectic ionic liquid complexed anion, $[\text{AlCl}_4]^-$. Using NBO charges, upon formation of $[\text{AlCl}_4]^-$, chloride donates ≈ 0.162 e to the Lewis acidic aluminium centre, and ≈ 0.092 e to each of the three other Cl atoms. Each of the four symmetrically equivalent Cl atoms bears a charge of ≈ 0.561 e. Thus, total charge transfer from chloride totals 0.433 e. The maximum charge transfer within the urea - chloride complexes is only $\approx 27\%$ of this value.

However, charge transfer is expected to be greater upon covalent bond, as opposed to H-bond, formation, associated with a greater degree of FO interaction. Examples of bonding MOs for $[\text{AlCl}_4]^-$ and $[\text{urea}\cdot\text{Cl}]^-$ (1.0.0_A) are shown in **Figure 3.24**. Within the $[\text{AlCl}_4]^-$ example, **Figure 3.24 a**, the relative contributions from the fragments are equal, indicative of delocalisation. In contrast, **Figure 3.24 b** reveals the disparate contributions from the Cl anion and urea fragments within the H-bonded complex. Localisation of orbital contributions is typical for relatively ionic H-bond interactions, and helps to rationalise the limited charge transfer observed.

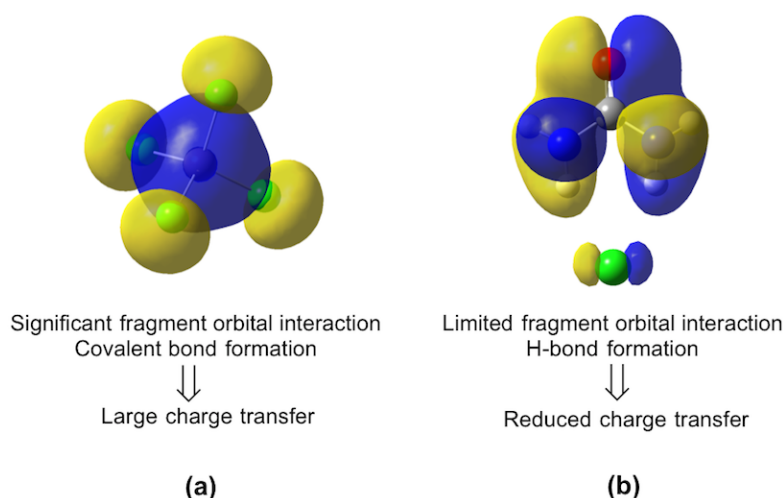


Figure 3.24. Example bonding MOs for (a) the $[\text{AlCl}_4]^-$ complexed anion and (b) the 1.0.0_A $[\text{urea}\cdot\text{Cl}]^-$ pair.

A key question relating to the *n*.urea-chloride “complexed anions” is whether to consider them as systems in which urea coordinates to chloride in a solvating capacity or coordinates to form a fully delocalised complex. Our findings suggest the former to be more appropriate; the urea-chloride complexes are not highly delocalised.

In summary, the association of urea and chloride is found to be strong, however, this is attributable to both H-bonding *and* a large ion-dipole interaction. Moreover, the direct association of chloride with multiple urea molecules is competitive with the formation of urea-urea interactions, resulting in a number of low energy configurations. This flexibility in the urea-chloride association could have important implications for the anion speciation within the DES mixtures. The N-H $\cdots$ Cl H-bonds are also found to be flexible, showing a variation in strength. Based on values of ρ_{BCP} the

mean N-H...Cl interaction is almost equivalent to the average C-H...Cl interaction. However, although maximising H-bond interactions is important in the stabilisation of the larger urea-chloride complexes, other factors must also contribute. Finally, we observe limited charge transfer within the n.urea-Cl⁻ systems, suggesting that charge delocalisation is not the primary origin of the proposed decrease in the choline – chloride Coulombic interaction and subsequently the low melting point of this DES.

3.5 Choline – urea pairs

For the choline chloride – urea system, focus has typically been on the interaction between urea and chloride. However, we find here that the choline – urea interaction is also significant and additionally provides an example of a system featuring cationic H-bonds. The choline-urea complexes, **Figure 3.25**, were obtained in a similar manner to the choline chloride ion pairs, through strategic placement of urea about the choline cation. Relative energies of the choline-urea complexes are listed in **Table 3.5** (further details in the **Appendix, Table A.11**).

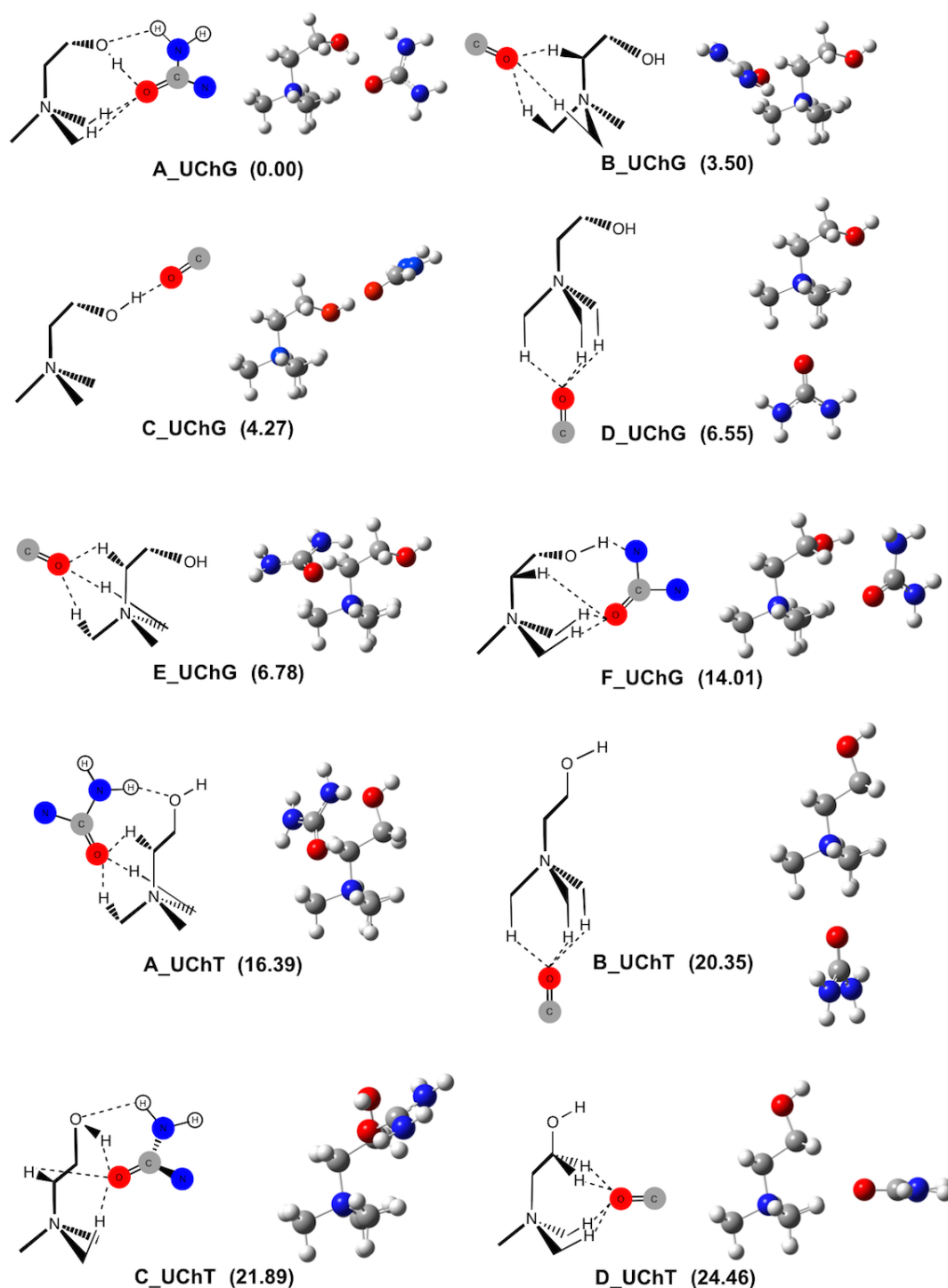


Figure 3.25. Choline-urea pairs (relative energy/ kJ mol^{-1}).

Table 3.5. Relative energies ($\Delta E_{\text{rel}} / \text{kJ mol}^{-1}$) of the choline-urea pairs. Total charge transfer (CT) *from* urea computed using the NBO and CHELPG schemes.

Choline-Urea Pair	$\Delta E_{\text{rel}} / \text{kJ mol}^{-1}$	(NBO) / e	(CHELPG) / e
A_UChG	0.00	0.066	0.074
B_UChG	3.50	0.019	0.081
C_UChG	4.27	0.060	0.067
D_UChG	6.55	0.020	0.089
E_UChG	6.78	0.020	0.049
F_UChG	14.01	0.030	0.071
A_UChT	16.39	0.019	0.080
B_UChT	20.35	0.021	0.083
C_UChT	21.89	0.033	0.075
D_UChT	24.46	0.020	0.047

Five of the ten stable choline-urea configurations are within 10 kJ mol^{-1} of the lowest energy structure (A_UChG), suggesting flexibility in the choline-urea interaction. The relative energies of the choline-urea pairs span $\approx 25 \text{ kJ mol}^{-1}$, only slightly reduced compared to the spread in the relative energies of the choline chloride ion pairs ($\approx 38 \text{ kJ mol}^{-1}$).

The maximum association energy of a choline – urea pair is calculated to be -82 kJ mol^{-1} , $\approx 20\%$ of the maximum association of a choline chloride ion pair. However, this is $\approx 24 \text{ kJ mol}^{-1}$ less than the association energy of $[\text{urea}\cdot\text{Cl}]^-$, but almost equivalent to the association of $[\text{urea}\cdot\text{Cl}]^-$ with a second urea molecule (-85 kJ mol^{-1}). Furthermore, the choline-urea association is greater than the maximum urea-urea interaction (-59 kJ mol^{-1}). Therefore, the choline-urea interaction can be energetically competitive with both urea-urea interactions and, significantly, the association of a second urea molecule to the $[\text{urea}\cdot\text{Cl}]^-$ complex. As $[\text{2urea}\cdot\text{Cl}]^-$ is usually assumed to form at the eutectic point, a competitive interaction between choline and urea could have important implications.

Within the choline – urea complexes, urea predominantly acts as a H-bond acceptor through the δ^- oxygen of the carbonyl group. Analogous to the preferred positioning of chloride in the choline-chloride ion pairs, the δ^- oxygen is found to locate at the approximate centre of the tetrahedron faces formed by the methyl/methylene C-H groups of the choline cation. Thus, the tripodal H-bond motif is also apparent in the choline-urea systems i.e. B_UChG, D_UChG, E_UChG, A_UChT, B_UChT. However, as found for choline chloride, the lowest energy choline-urea pair, A_UChG, has the δ^- oxygen sitting at the hindered face of gauche choline, with the formation of an additional stabilising O-H $\cdots$ O=C H-bond. Furthermore, a configuration exhibiting only a O-H $\cdots$ O=C interaction has been obtained (C_UChG), in contrast to choline chloride where an analogous structure could not be located.

Urea has more than one possible mode of interaction with choline. Additional to acting as a H-bond acceptor through the carbonyl oxygen, urea can act as a H-bond donor, leading to the formation of an N-H $\cdots$ O-H H-bond (A_UChT) or act as a H-bond acceptor *via* one of the nitrogen centres, resulting in a O-H $\cdots$ N-H H-bond (F_UChG). Although O-H $\cdots$ N interactions have been observed in MD simulations of this system, it was reported to be one of the least probable interactions involving the hydroxyl group of choline.¹²

With a mean ρ_{BCP} value of 0.044 au , the O-H $\cdots$ O=C H-bonds are one of the strongest types of interaction identified across all pairs within this system. Based on ρ_{BCP} , the O-H $\cdots$ O=C interactions within A_UChG and C_UChG are within the moderate H-bond strength range. Moreover, the sum of

the $E^{(2)}$ stabilisation energies associated with the $n_{\text{O}} \rightarrow \sigma^*_{\text{OH}}$ interactions are ≈ 114 and 125 kJ mol^{-1} for A_UChG and C_UChG respectively, **Appendix, Table A.12**, and feature amongst the largest values for a single H-bond identified here.

The C-H $\cdots$ O=C H-bonds, however, represent the opposite end of the scale, being amongst the weakest type of H-bond located here. The mean value of ρ_{BCP} is 0.013 au for the C-H $\cdots$ O=C interactions and is below that for the intramolecular C-H $\cdots$ O H-bonds within gauche choline and the C-H $\cdots$ O interactions within choline chloride. The N-H $\cdots$ O-H H-bonds have ρ_{BCP} values of a similar magnitude.

Charge transfer is also found to occur within the choline-urea ion pairs, **Table 3.5**. However, as urea predominantly acts as a H-bond acceptor for a cationic H-bond donor species, the charge transfer occurs *from* urea *to* choline, resulting in a small positive charge on the urea molecules. Using the NBO values, total charge transfer is found to vary from 0.019 e (B_UChG), to a maximum of 0.066 e in the lowest energy choline-urea pair (A_UChG). Therefore, the maximum amount of charge transfer with urea acting as a H-bond acceptor in a [choline-urea] $^+$ pair is similar to the maximum amount of charge transfer with urea acting as a H-bond donor in a [urea-Cl] $^-$ pair. This suggests that urea is equally able to act as both a donor and acceptor of small amounts of charge.

The flexibility in the choline-urea association and the finding that the choline-urea interaction is energetically competitive with both urea-urea interactions and the interaction of chloride with a second urea molecule are key results. Based on the pairwise association energies, it could be suggested that the choline-urea interaction should be a prominent feature of the eutectic mixture. The prominent mode of interaction within the choline-urea pairs involves the δ^- oxygen, forming either moderately strong O-H $\cdots$ O=C H-bonds or weak C-H $\cdots$ O=C H-bonds. As with the choline-chloride ion pairs, the choline-urea ion pairs can feature the tripodal motif. The dual functionality of urea, as either a H-bond donor or H-bond acceptor, results in urea either accepting or donating small amounts of charge.

3.6 Comparison of hydrogen bonding and pairwise interactions

A comparison of the H-bonding and interactions within the examined systems is undertaken here. The maximum association energies (E_a) of the pairwise interactions are detailed in **Table 3.6**. Selected information related to the H-bond interactions is provided in **Table 3.7**.

The maximum E_a for the pairwise interactions is found to decrease as: choline-chloride >> urea-chloride > urea-choline > urea-urea. The decrease in E_a reflects the change in the leading term for the electrostatic interaction: ion-ion >> ion-dipole > dipole-dipole. The large E_a for the choline chloride ion pairs is expected; a result of the strong attractive interaction between the oppositely charged ions. However, the energies of association for pairs featuring urea are also quite large. This is the result of the relatively large dipole moment of urea, in conjunction with the H-bond interactions.

Table 3.6. Maximum association energies, E_a , for the pairwise interactions. nU corresponds to the number of urea molecules in the 1st coordination sphere of chloride.

Interaction		Maximum E_a / kJ mol^{-1}
Choline-Chloride	ion (+)⋯ion (-)	-409
Urea-Chloride	dipole (δ^+)⋯ion (-)	-106(1U), -85(2U), -69(3U)
Urea-Choline	dipole (δ^-)⋯ion (+)	-82
Urea-Urea	dipole (δ^+)⋯dipole (δ^-)	-59

The number of low energy configurations (e.g. within 15 kJ mol^{-1} of the lowest energy structure) provides an indication of the flexibility in the interactions between the constituent species of this DES. For choline chloride, there are 3 ion pairs with $\Delta E_{\text{rel}} < 15 \text{ kJ mol}^{-1}$. For urea- Cl^- there is only a single low energy configuration, however, for 2urea- Cl^- and 3urea- Cl^- there are 3 and 4 configurations respectively. The choline-urea pairs, however, exhibit the largest number of low energy configurations, with 6 pairs within 15 kJ mol^{-1} of the lowest energy structure. Flexibility in the pairwise interactions could indicate a reasonable degree of disorder within the liquid system.

Typical for coordination complexes, there is a decrease in the association energy for the successive addition of urea to the 1st solvation shell of chloride. Using square brackets here to indicate the 1st coordination sphere, ΔE_a for the addition of a second urea molecule to $[\text{urea-Cl}]^-$ is $\approx 85 \text{ kJ mol}^{-1}$. This is almost equivalent to the E_a for the interaction between choline and urea ($\approx 82 \text{ kJ mol}^{-1}$). Furthermore, with an E_a of $\approx 59 \text{ kJ mol}^{-1}$, the maximum association for the urea-urea dimer approaches ΔE_a for the addition of a third urea to $[2\text{urea-Cl}]^-$ ($\approx 69 \text{ kJ mol}^{-1}$). The association of chloride with multiple urea molecules in the 1st coordination sphere is therefore energetically competitive with other pairwise interactions. Whilst $[\text{urea-Cl}]^-$ is strongly favoured, the formation of $[2\text{urea-Cl}]^-$ is not significantly favoured over the formation of $[\text{urea-choline}]^+$. This could have implications for the speciation within the 1:2 eutectic mixture.

An analysis of the H-bond interactions has been central to our assay of the pairwise interactions. A key finding is the large number of different H-bond types. Moreover, using the ρ_{BCP} and $E^{(2)}$ criteria, the H-bond interactions are found to span a relatively wide range in terms of strength, from very weak to moderate-strong. The mean value and ranges for selected H-bond descriptors (H-

bond length, ρ_{BCP} and $E^{(2)}$) are detailed in **Table 3.7**. The different H-bond types are listed in **Table 3.8** in order of decreasing value of mean ρ_{BCP} . For a given H-bond type, mean values of ρ_{BCP} (or $E^{(2)}$) refers to the average across *all* H-bonds of that type, thus includes values for H-bonds in different systems e.g. N-H...O=C H-bonds are found in both urea-urea dimers and in the urea-chloride complexes.

Table 3.7. Summary of selected H-bond properties for the different types of H-bond: Values of ρ_{BCP} in au, H-bond lengths (r) in Å, and $E^{(2)}$ for the donor (D) $\rightarrow$ acceptor (A) interaction in kJ mol⁻¹.

Choline Chloride Ion-Pairs							
H-bond	Mean ρ_{BCP}	Range ρ_{BCP}	Mean r	Range r	D $\rightarrow$ A	Mean $E^{(2)}$	Range $E^{(2)}$
CH...Cl	0.018	0.008 – 0.022	2.46	2.31 – 2.90	$n_{\text{Cl}} \rightarrow \sigma_{\text{C-H}}^*$	29.28	1.55 – 47.95
OH...Cl	0.024	0.013 – 0.034	2.28	2.09 – 2.55	$n_{\text{Cl}} \rightarrow \sigma_{\text{O-H}}^*$	55.08	16.07 – 89.37
CH...OH (intra.)	0.014	0.011 – 0.015	2.36	2.25 – 2.52	$n_{\text{O}} \rightarrow \sigma_{\text{C-H}}^*$	3.47	2.09 – 4.56
Choline - Urea Pairs							
H-bond	Mean ρ_{BCP}	Range ρ_{BCP}	Mean r	Range r	D $\rightarrow$ A	Mean $E^{(2)}$	Range $E^{(2)}$
CH...O=C	0.013	0.008 – 0.024	2.04	2.20 – 2.64	$n_{\text{O}} \rightarrow \sigma_{\text{C-H}}^*$ $\pi_{\text{C=O}} \rightarrow \sigma_{\text{C-H}}^*$	7.91	0.46 – 25.65
OH...O=C	0.044	0.032 – 0.050	1.74	1.65 – 1.88	$n_{\text{O}} \rightarrow \sigma_{\text{O-H}}^*$ $\pi_{\text{C=O}} \rightarrow \sigma_{\text{O-H}}^*$	94.75	45.06 – 124.81
NH...OH	0.012	0.009–0.016	2.34	2.14 – 2.48	$n_{\text{O}} \rightarrow \sigma_{\text{N-H}}^*$	9.69	3.72 – 19.71
OH...NH	0.019	-	2.17	-	$n_{\text{N}} \rightarrow \sigma_{\text{O-H}}^*$	20.08	-
CH...OH (intra)	0.015	0.012 – 0.018	2.30	2.18 – 2.47	$n_{\text{O}} \rightarrow \sigma_{\text{C-H}}^*$	5.59	4.31 – 8.83
Urea-Urea Dimers							
H-bond	Mean ρ_{BCP}	Range ρ_{BCP}	Mean r	Range r	D $\rightarrow$ A	Mean $E^{(2)}$	Range $E^{(2)}$
NH...O=C	0.025	0.012 – 0.033	2.01	1.83 – 2.40	$n_{\text{O}} \rightarrow \sigma_{\text{N-H}}^*$ $\pi_{\text{C=O}} \rightarrow \sigma_{\text{N-H}}^*$	42.18	4.52 – 68.91
NH...NH	0.023	-	2.09	-	$n_{\text{N}} \rightarrow \sigma_{\text{N-H}}^*$	31.97	-
Urea-Chloride Complexes							
H-bond	Mean ρ_{BCP}	Range ρ_{BCP}	Mean r	Range r	D $\rightarrow$ A	Mean $E^{(2)}$	Range $E^{(2)}$
NH...Cl	0.019	0.012 – 0.028	2.36	2.18 – 2.59	$n_{\text{Cl}} \rightarrow \sigma_{\text{N-H}}^*$	36.79	14.77 – 72.97
NH...O=C	0.027	0.011 – 0.046	1.96	1.68 – 2.48	$n_{\text{O}} \rightarrow \sigma_{\text{N-H}}^*$ $\pi_{\text{C=O}} \rightarrow \sigma_{\text{N-H}}^*$	44.69	2.38 – 118.16
NH...NH	0.010	0.006 – 0.017	2.59	2.21 – 2.92	$n_{\text{N}} \rightarrow \sigma_{\text{N-H}}^*$	5.27	0.50 – 19.46

Table 3.8. The H-bond types ordered according to the descending value of mean ρ_{BCP} . For the intramolecular C-H...O H-bonds, values of $E^{(2)}$ were not obtained in four cases.

H-bond donor	H-bond acceptor	Mean ρ_{BCP} / au	Mean $E^{(2)}$ / kJ mol ⁻¹	Max. ρ_{BCP} / au	No. of occurrences
OH cation	O=C neutral	0.044	94.75	0.050	3
NH neutral	O=C neutral	0.026	44.44	0.046	41
OH cation	Cl anion	0.024	55.08	0.034	3
NH neutral	Cl anion	0.019	36.79	0.028	51
OH cation	NH neutral	0.019	20.08	0.019	1
CH cation	Cl anion	0.018	29.28	0.022	24
CH cation	OH cation	0.015	4.68	0.018	11
CH cation	O=C neutral	0.013	7.91	0.024	26
NH neutral	OH cation	0.012	9.69	0.016	3
NH neutral	NH neutral	0.011	8.23	0.023	9

The ordering of the H-bonds within **Table 3.8** is not definitive. For example, using a different descriptor (e.g. $E^{(2)}$), or using the maximum value of ρ_{BCP} for a given H-bond, the ordering subtly changes. However, regardless of the descriptor employed, the O-H...O=C interaction is found to be the strongest type of H-bond within this system and is of upper moderate strength. The N-H...Cl and O-H...Cl interactions follow and are of lower moderate strength. The remaining interactions all fall within the weak H-bond category, however, there is a split within this, the N-H...Cl and C-H...Cl interactions typically being stronger (i.e. upper weak) than the C-H...O=C and N-H...N interactions (lower weak).

The mean values do not, however, present the whole picture, with a number of the H-bond types showing a relatively sizeable range of values resulting from the different H-bond motifs. The variation for the N-H...O=C H-bonds is particularly large. For example, the values of ρ_{BCP} for the N-H...O=C interactions varies from 0.011 to 0.046 au i.e. from less than the mean value of ρ_{BCP} for the weak intramolecular C-H...O interactions within gauche choline, to one of the strongest H-bonds within this system. The associated values for $E^{(2)}$ and r show similarly large variations (i.e. 116 kJ mol⁻¹ and 0.80 Å respectively). Thus, there is flexibility in the H-bond interactions.

In addition to the different functionalities of the H-bond donor and acceptor groups, the H-bonds within the DES system are also a mix of doubly ionic, ionic and neutral H-bond types. However, in some cases, the distinction between doubly ionic, ionic and neutral interactions is blurred. For example, whilst in the following analysis we treat the O-H...Cl H-bonds identified within the choline chloride ion pairs as examples of doubly ionic interactions, as the hydroxyl group is effectively decoupled from the charged head group, it could be argued that this is an example of a neutral interaction. Furthermore, the N-H...O=C interactions, whether within the neutral urea dimers, or overall negatively charged urea-chloride complexes, have been treated as examples of neutral H-bonds. This is justified based on the limited amount of charge transfer found within the urea-chloride complexes. However, a more in-depth analysis of the influence of chloride on the individual N-H...O=C urea-urea interactions has not yet been conducted.

For both neutral and ionic H-bonds, a relationship between $E^{(2)}$ and ρ_{BCP} has previously been reported.^{68, 69} A plot of the mean values of $E^{(2)}$ against the mean values of ρ_{BCP} for the different H-bond types examined here is shown in **Figure 3.26**. A reasonable correlation, across the neutral, ionic and doubly ionic interactions, is observed. The plot of the values of $E^{(2)}$ against ρ_{BCP} for the 168 individual H-bonds, for which both properties could be determined, is shown in **Figure 3.27**. The evident “band” reveals that for a given value of ρ_{BCP} there is some variation in $E^{(2)}$, or vice versa.

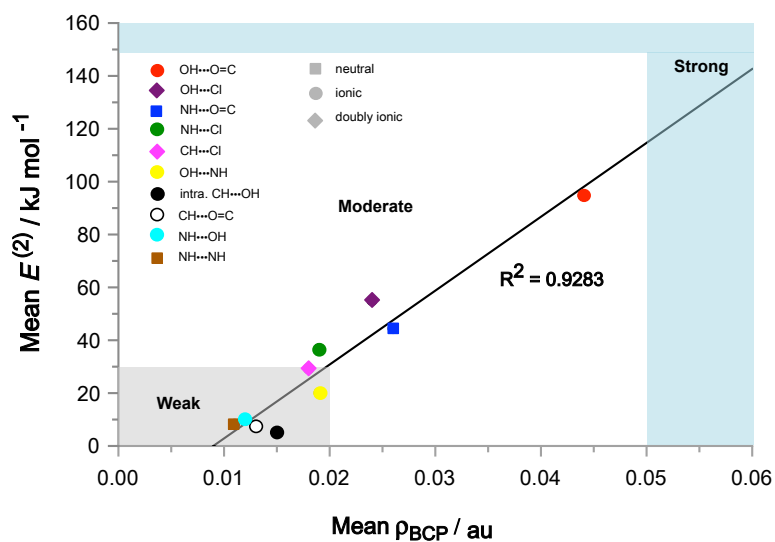


Figure 3.26. Plot of mean $E^{(2)}$ against mean ρ_{BCP} values for each H-bond type.

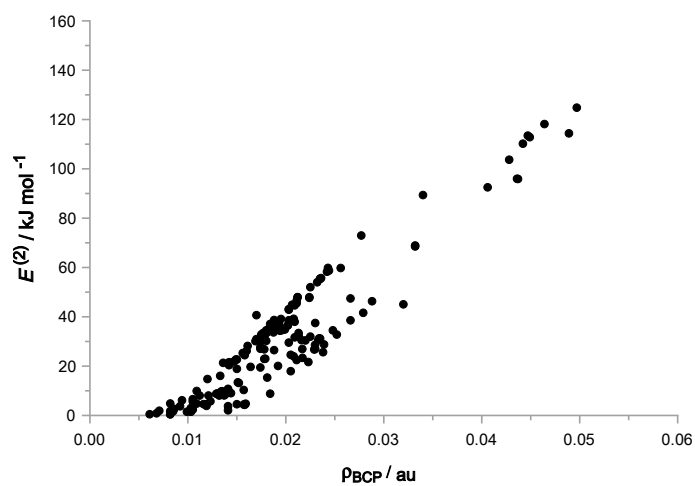


Figure 3.27. Plot of $E^{(2)}$ against ρ_{BCP} values for each individual H-bond.

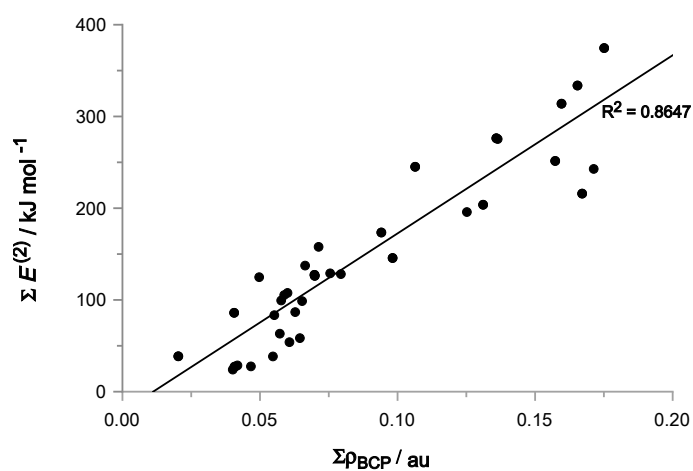


Figure 3.28. Plot of $\Sigma E^{(2)}$ against $\Sigma \rho_{\text{BCP}}$ for the intermolecular H-bonds found in each complex.

Given the reasonable correlation between individual $E^{(2)}$ and ρ_{BCP} values, there should be a correlation between the total sum of $E^{(2)}$ and the total sum of ρ_{BCP} for the multiple H-bond interactions found within each H-bonded complex. Consistent with previous reports,⁷⁰ a correlation between $\Sigma E^{(2)}$ and $\Sigma \rho_{\text{BCP}}$ is found here, **Figure 3.28**. Therefore, all trends established here suggest that, at least in terms of the $E^{(2)}$ and ρ_{BCP} descriptors, doubly ionic H-bonds are consistent with neutral and ionic H-bond interactions.

The total association energy of a H-bonded complex has often been used as a measure of the strength of the intermolecular H-bond(s). Equations relating E_a to ρ_{BCP} (or $\Sigma \rho_{\text{BCP}}$) have previously been derived for neutral and ionic systems, and typically for systems with H-bonds of closely related functionality.⁷⁰ The relationship between E_a and $\Sigma \rho_{\text{BCP}}$ has been established for the complexes examined here, **Figure 3.29**. The clustering of the data points corresponding to the choline chloride ion pairs, away from the data points for the other systems, is evident. However, even when the choline chloride data points are excluded from the fit, the correlation is poor.

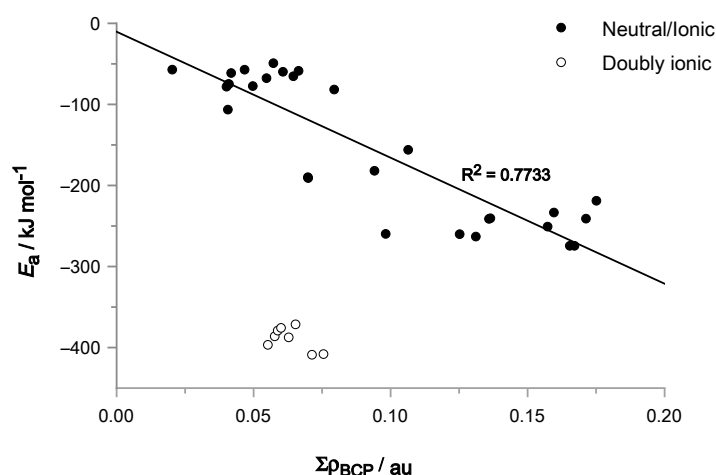


Figure 3.29. Plot of the total association energy, E_a , against $\Sigma \rho_{\text{BCP}}$ for each complex. The choline-chloride ion pairs have not been included in the linear fit.

However, in addition to the different functionalities of the H-bonds, there is a variation in the H-bond motifs coupled with interdependence in the H-bond interactions; a strengthening of one H-bond, could lead to a weakening of another H-bond interaction in the same system. Furthermore, the total association energy is an agglomeration of different components, including electrostatics, polarisation, dispersion and H-bonding. H-bonding, quantified here using $\Sigma \rho_{\text{BCP}}$, is just one component of E_a . For the choline chloride ion pairs the deviation between the H-bond contribution and E_a is the largest, as would be anticipated for a system dominated by the Coulombic interaction. However, there is clearly also variation across the neutral and ionic systems. Correlating $\Sigma \rho_{\text{BCP}}$ with E_a ignores inherent variations in the other contributions to the total association energy.

Although the correlation between E_a and $\Sigma \rho_{\text{BCP}}$ is relatively poor, the extent to which the choline chloride ion pairs deviate from the linear regression can be used to approximate the ion-ion electrostatic contribution to the ion pair association. The mean value for $\Sigma \rho_{\text{BCP}}$ for the choline chloride ion pairs is 0.0633 au. Using **equation 3.2**, the predicted value of E_a would be $\approx -109 \text{ kJ mol}^{-1}$. This

values differs by almost -280 kJmol^{-1} from the mean of the actual computed values of E_a (-389 kJ mol^{-1}). Therefore, this suggests that approximately 72 % of the interaction energy of a choline chloride ion pair results from the ion-ion electrostatic term.

$$E_a = -1554.3(\Sigma \rho_{BCP}) - 10.37 \quad (3.2)$$

The large number of H-bonds isolated here, and examined using QTAIM, has allowed us to assess the criteria recently proposed for classification of H-bonds in ionic liquids. An upper limit of 0.02 au in ρ_{BCP} for weak H-bonds is consistent with other H-bond classification schemes. However, upon examination of the values of $\nabla^2 \rho_{BCP}$ herein, the associated cut-off of 0.01 au in $\nabla^2 \rho_{BCP}$ was found to be too low. A correlation between ρ_{BCP} and $\nabla^2 \rho_{BCP}$ is found here, **Figure 3.30**. Assuming a cut-off in ρ_{BCP} of 0.02 au for weak H-bonds, a corresponding upper limit in $\nabla^2 \rho_{BCP}$ of 0.07 au is obtained. However, for a given value of ρ_{BCP} , there is clearly some variation in $\nabla^2 \rho_{BCP}$, or *vice versa*. Moreover, there appears to be two divergent correlations within **Figure 3.30**. The divergent group of data points all correspond to H-bond interactions involving the chloride anion (i.e. doubly ionic C-H $\cdots$ Cl and O-H $\cdots$ Cl, and anionic N-H $\cdots$ Cl). This could indicate that $\nabla^2 \rho_{BCP}$ is more sensitive to functionality and charge of the system relative to ρ_{BCP} .

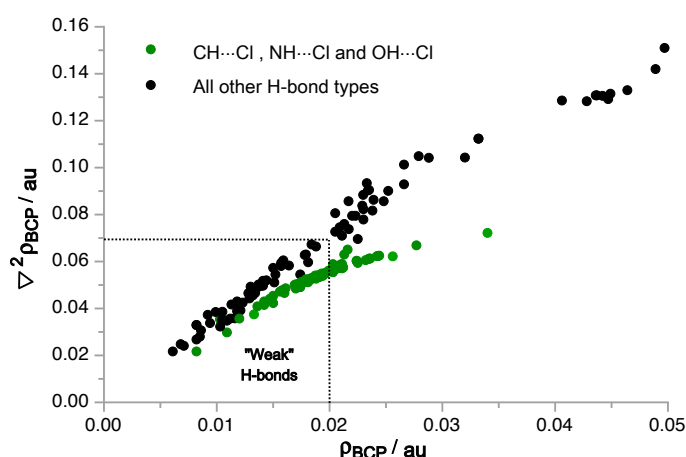


Figure 3.30. Correlation between ρ_{BCP} and $\nabla^2 \rho_{BCP}$ for all H-bonds identified in the complexes.

We have gained much insight into the types and nature of potential H-bond interactions within the choline chloride – urea system. However, how do the H-bond interactions influence the properties of this DES? As found more generally for ionic liquids, this is not a straightforward question to answer.

Within the choline chloride – urea DES there is the potential for many different, and possibly competitive, types of H-bond. Moreover, there is a balance between forming a smaller number of stronger H-bonds against forming a larger number of weaker H-bonds. This flexibility in the H-bond interactions could result in a large number of accessible configurations, increasing the overall disorder of the system. However, a large number of H-bond interactions, and the formation of a H-bond network, could also lead to an increase in the overall structuring, and therefore, rigidity of the system. The relative balance between “disorder” and “rigidity” could vary with composition, and may help to explain the phase behaviour of this DES.

Nevertheless, compared to the pure components, the mixtures will be more disordered. Solid urea is a highly ordered H-bonded network, while choline chloride is an ionic solid. Upon addition to choline chloride, urea could have more than one role. For example, the addition of urea to choline chloride could disrupt the regular crystal packing of choline chloride, as well as increase the separation between the choline cation and chloride anion. We find only minimal charge transfer, however, the role of urea in dispersing the charge (of the anionic component) has often been assumed. Further investigation is required to establish both the predominant role of urea and the overall influence of H-bonding.

4. Choline Chloride – n Urea Clusters

The examination of the isolated pairwise interactions provides insight into the relative strength and potentially competitive nature of the interactions in this DES. However, how are the strengths of the pairwise interactions and bonding motifs affected when all three species, choline, chloride and urea, are present, as in the liquid?

For the choline chloride – urea DES, the smallest unit representative of a given composition is a cluster composed of choline, chloride and urea in a fixed ratio, e.g. a cluster consisting of choline, chloride and two molecules of urea corresponds to the eutectic composition for this system. Thus, relative to a conventional ionic liquid, for which the ion pair is representative of the composition, there is an additional degree of complexity for a DES and a larger number of possible configurations.

We have sampled a large number of clusters of the 1:2 choline chloride to urea composition. The melting points of the integer compositions either side of the eutectic point i.e. the 1:1 and 1:3 compositions, are higher.⁴ To explore this phenomenon, we have computed a reduced number of clusters of the 1:1 and 1:3 compositions.

4.1 Method

Initial geometries were obtained using the B3LYP functional together with the 6-311+G(d,p) basis set. In total, 67 clusters of 1:2 composition, 27 of 1:1 composition and 33 of 1:3 composition have been obtained at the B3LYP level. A subset of B3LYP clusters (12-14 of each composition) were subjected to a second optimisation and frequency analysis using B3LYP appended with Grimme's D2 dispersion correction²⁶ and the 6-311++G(d,p) basis set.

The majority of clusters showed only subtle changes in geometry before and after inclusion of the D2 correction. Only in a small number of cases were significant changes in the geometry observed. However, the inclusion of the D2 correction does affect the relative energy ordering of the clusters, in comparison to the order established at the B3LYP level.

The clusters of choline chloride : *n* urea were constructed in different ways. Starting from an optimised choline chloride ion pair, additional urea molecules were introduced successively. Alternatively, the choline cation was introduced to an optimised *n*.urea-chloride complex (*n* = 1-3). Clusters with both gauche and trans choline have been considered.

The relative energy of a cluster has been defined relative to the energy of the lowest energy cluster of that composition i.e. $\Delta E_{\text{rel}} = E(\text{lowest } E \text{ } 1:n \text{ cluster}) - E(1:n \text{ cluster})$, where *n* is the number of urea molecules. All clusters (B3LYP and B3LYP-D2) can be found in the **Appendix, Figures A.4 – 9**, together with relative energies, with and without ZPE correction, **Appendix, Tables A.13-18**. All B3LYP-D2 clusters selected for further analysis will be clearly identified in the text.

4.2 B3LYP clusters

4.2.1 General comments

The relative energy spanned by the clusters of a given composition can be large. For example, the 1:2 clusters span a relative energy range of $\approx 60 \text{ kJ mol}^{-1}$, **Figure 3.31**. Stable clusters featuring both gauche and trans choline have been isolated and are identified within **Figure 3.31**. There is significant overlap in the relative energies of the “gauche” and “trans” clusters. However, the very lowest energy clusters feature gauche choline, whilst the very highest energy clusters (obtained to date) feature trans choline. This finding is consistent with the relative energies of the isolated choline conformers and the choline chloride ion pairs.

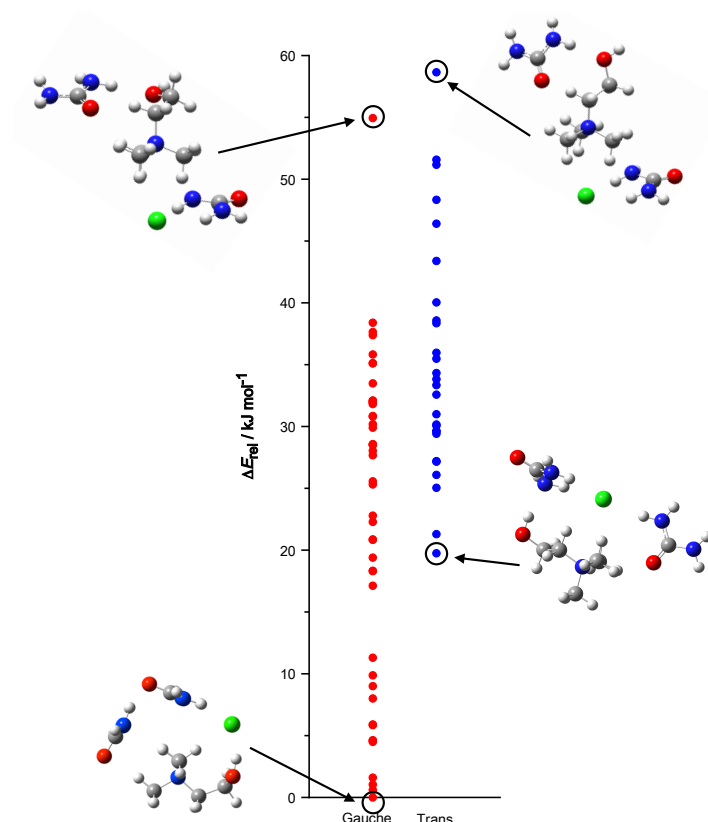


Figure 3.31. Relative energies of the B3LYP 1:2 choline chloride - urea clusters.

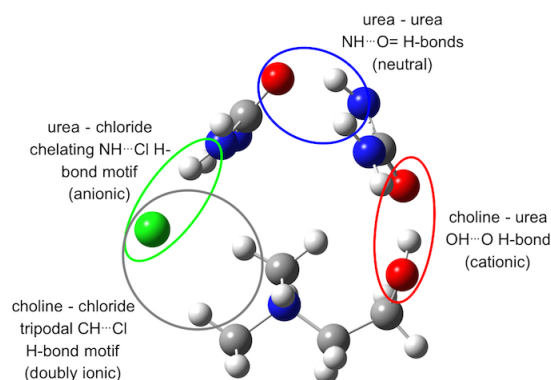


Figure 3.32. Pairwise interactions within an example 1:2 cluster.

Many of the key bonding motifs identified within the choline-chloride, urea-urea, urea-chloride and choline – urea pairs are also evident in the clusters. As an example, the 1:2 cluster shown in **Figure 3.32** can be decomposed into the individual pairwise interactions: the tripodal choline - chloride C-H...Cl motif, a chelating urea-chloride interaction, a urea-urea chain interaction and a choline – urea O-H...O=C interaction.

All clusters (of each composition) with a relative energy below 10 kJ mol⁻¹ feature an O-H...X interaction (X = Cl⁻ or O=C) and (with one exception) a urea – chloride interaction. These clusters can be found both with, and without, urea-urea interactions. As the number of urea molecules increases, urea - urea interactions become more prevalent. All clusters of the 1:3 composition, across the entire energy range, feature interactions between the urea molecules.

A general observation is that lower energy clusters have the tendency to exhibit fewer “loose ends”, relative to the higher energy counterparts. The lowest energy 1:2 cluster, for example, is a H-bonded ring, **Figure 3.31**, with the ends of each component “tied up” in H-bond formation. Thus, the H-bonding capacity is effectively saturated within this structure. In contrast, the highest energy 1:2 “gauche” cluster, **Figure 3.31**, features components with “free ends” i.e. the N-H groups of one urea, the carbonyl group of the second urea and O-H group of choline are not participating in H-bond formation. However, although the clusters with a larger number of unsaturated fragments are high energy in the gas phase, it can be anticipated that these structures would be stabilised in the bulk through the formation of interactions with additional molecules within the liquid.

4.2.2 Choline chloride separation and charge transfer

A reduction in the choline – chloride association is hypothesised upon addition of urea to form the eutectic mixture. Considering Coulomb’s law, two factors could contribute to this reduction; a decrease in the magnitude of charge on the ions, and/or an increase in the separation between the ions. A rough approximation of the Coulombic interaction between choline and chloride in the clusters can be obtained by using the N(choline)...Cl separation as an approximation of the ion separation, *r*, and assuming no charge transfer (therefore, *q* = +/- 1 *e*). The mean N(choline)...Cl distances within the B3LYP choline chloride ion pairs and clusters of each composition, together with the charge transfer from chloride, are listed in **Table 3.9**.

Table 3.9. The approximated choline chloride separation within the B3LYP ion pairs and clusters. Charge transfer (CT) from chloride computed using the NBO scheme.

System	Mean N...Cl separation/ Å	Range N...Cl separation/ Å	Mean CT (NBO) / e
Choline Cl ion pairs	3.67	3.57 – 3.85	0.114
1:1 Clusters	3.88	3.69 – 4.27	0.120
1:2 Clusters	4.10	3.69 – 6.72	0.129
1:3 Clusters	4.27	3.66 – 7.16	0.111

Within the choline chloride ion pairs, the mean N...Cl separation is 3.67 Å. Upon addition of a single urea molecule to form a 1:1 cluster, the average N...Cl separation increases to 3.88 Å. The increase in separation of 0.21 Å upon addition of urea results in a corresponding decrease in the Coulomb

association of $\approx 20 \text{ kJ mol}^{-1}$. Addition of a second urea molecule leads to approximately the same successive increase in the separation and corresponding reduction in the Coulomb interaction. The addition of a third urea molecule, however, has a slightly reduced effect, with a successive increase of $0.17 \text{ \AA}$ in the separation and associated reduction in the Coulomb interaction of $\approx 14 \text{ kJ mol}^{-1}$.

The average charge transfer from chloride in the ion pairs is 0.114 e , **Table 3.9**. The magnitude of charge transfer increases slightly upon addition of one ($+0.06 \text{ e}$) and two ($+0.15 \text{ e}$) urea molecules i.e. within the 1:1 and 1:2 clusters. For the 1:3 clusters, however, there is a very slight decrease in the magnitude of charge transfer (-0.03 e).

Although relatively simple, this analysis indicates that addition of one equivalent of urea to choline chloride does result in an increase in the choline – chloride separation, if not a significant increase in the charge transfer away from chloride. The addition of multiple equivalents of urea may further increase the average separation. However, the maximum successive increase potentially peaks for the 1:2 (eutectic) composition.

4.3 B3LYP-D2 clusters

Selected examples of 1:1, 1:2 and 1:3 clusters optimised at the B3LYP-D2 level are shown in **Figures 3.33, 3.34 and 3.35** respectively. All B3LYP-D2 structures can be seen in the **Appendix, Figures A.5, A.7 and A.9**.

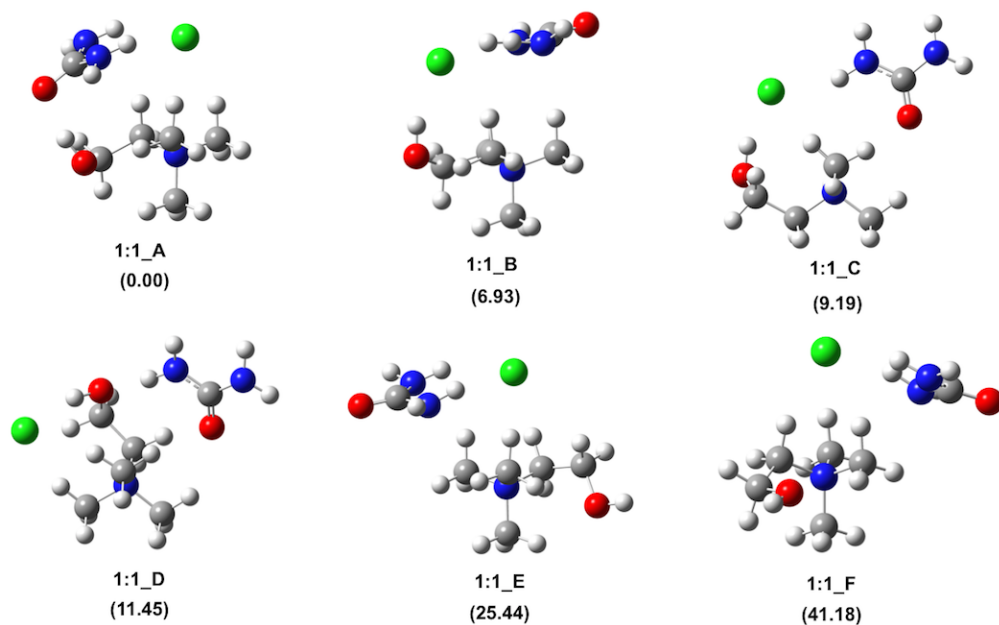


Figure 3.33. Selected 1:1 B3LYP-D2 clusters. Relative energies in kJ mol^{-1} .

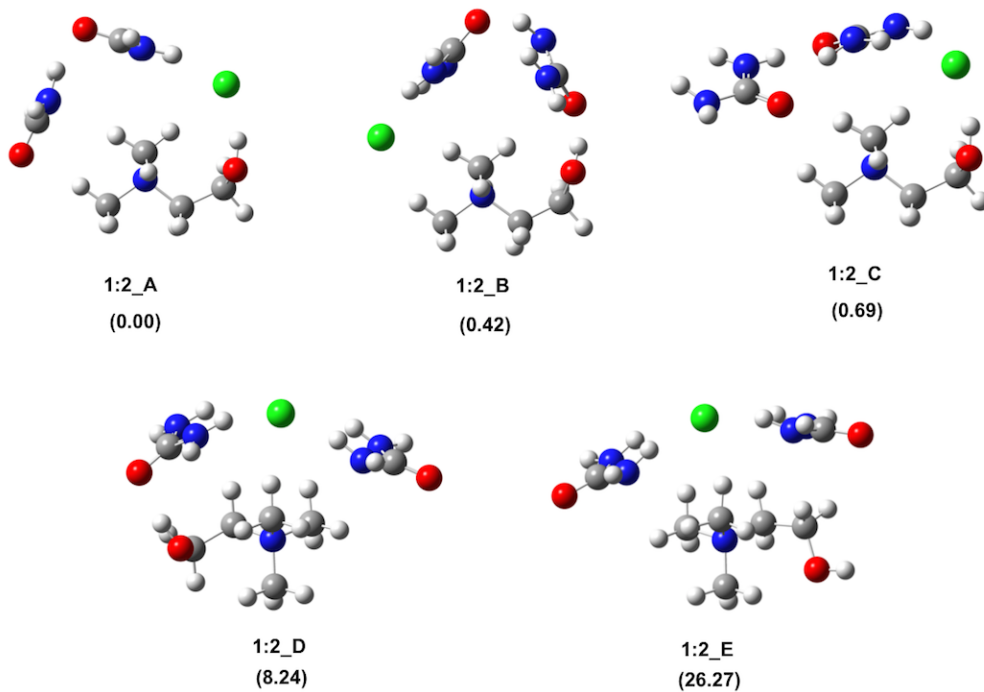


Figure 3.34. Selected 1:2 B3LYP-D2 clusters. Relative energies in kJ mol^{-1} .

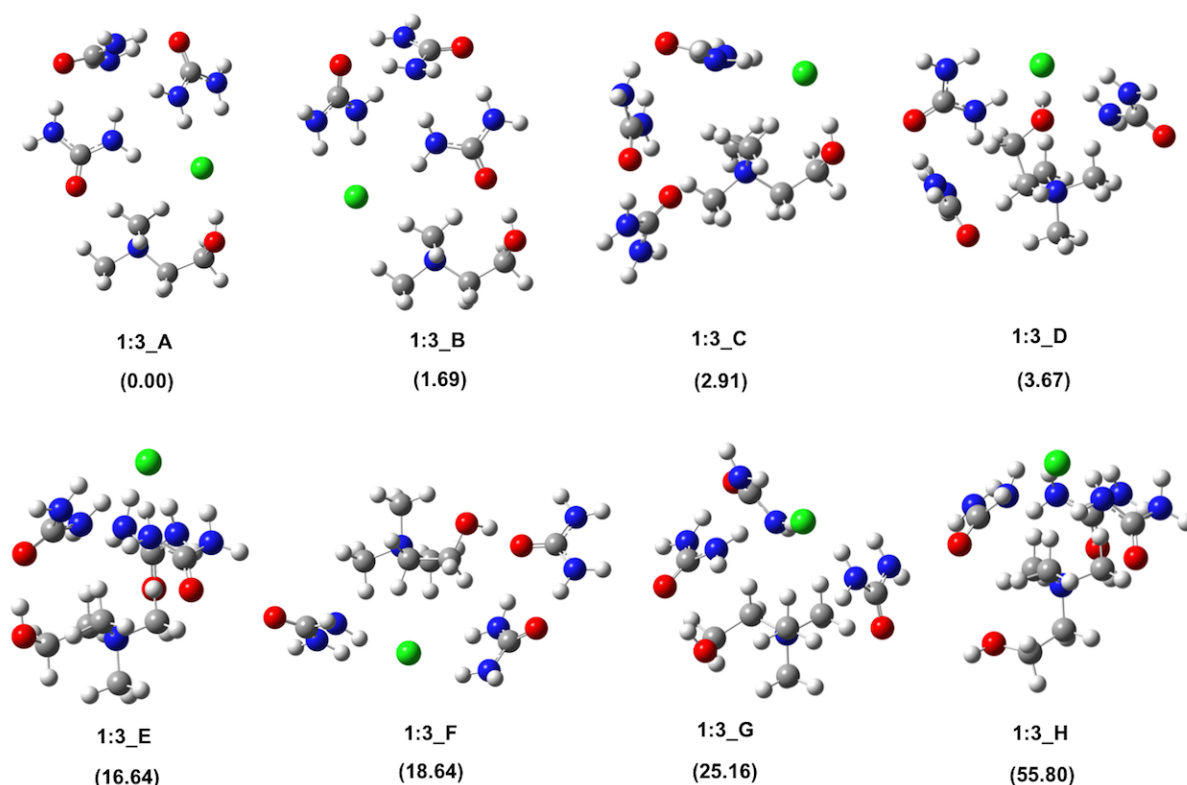


Figure 3.35. Selected 1:3 B3LYP-D2 clusters. Relative energies in kJ mol^{-1} .

Structural motifs of selected clusters

1:1_A to 1:1_C are examples of clusters exhibiting low energy “H-bonded rings”. Within each “ring”, the H-bond donor-acceptor, and dipole-dipole/ion-dipole, interactions are matched. Both clusters 1:1_A and 1:1_B feature the $[\text{urea}\cdots\text{Cl}]^-$ complexed anion, but differ in the order of interaction: 1:1_A features a primary H-bonded chain consisting of $\text{O-H}(\text{choline})\cdots\text{O}=\text{C}(\text{urea})\cdots\text{N-H}(\text{urea})\cdots\text{Cl}$, whereas, 1:1_B features a primary chain consisting of $\text{O-H}(\text{choline})\cdots\text{Cl}\cdots\text{H-N}(\text{urea})$.

On average, the $\text{O-H}\cdots\text{O}=\text{C}$ H-bond was found to be the strongest type of H-bond within the pairs. However, isolated choline chloride, in both the solid state and lowest energy gas phase ion pairs, features a stabilising $\text{O-H}\cdots\text{Cl}$ interaction. Upon addition of one equivalent of urea to choline chloride, insertion of urea between the choline and chloride ions, as in 1:1_A, is potentially the most energetically favourable motif. However, formation of a urea-chloride interaction could also occur without breaking the existing $\text{O-H}\cdots\text{Cl}$ interaction, e.g. 1:1_B. Dependent on the barrier to insertion of urea between choline and chloride, this latter motif is potentially more probable upon addition of urea to choline chloride or *vice versa*, due to the pre-existence of the ion pair.

Within 1:1_C, urea forms a single H-bond with chloride. This single H-bond motif was found to be high energy (49 kJ mol^{-1}), with respect to the chelating H-bond motif (1:0.0_A, **Figure 3.19**) within the isolated pairs. However, cluster 1:1_C is only $\approx 9 \text{ kJ mol}^{-1}$ above the lowest energy 1:1 cluster at the B3LYP-D2 level (and is the lowest energy structure at the B3LYP level, **Appendix, Table A.13** and **Figure A.4**), suggesting that the additional interactions within the clusters have stabilised this motif. This finding also emphasises the importance of screening both low and high energy isolated pairs.

Cluster 1:1_D is an example of a low energy cluster ($\Delta E_{\text{rel}} \approx 11.5 \text{ kJ mol}^{-1}$) that does not feature a urea-chloride interaction. Within 1:1_D urea interacts with the O-H group of choline forming a N-H...OH H-bond. The O-H group also acts as a H-bond donor, concurrently forming a H-bond with the Cl anion. The individual O-H...Cl ($\rho_{\text{BCP}} = 0.041 \text{ au}$, $E^{(2)} = 128.1 \text{ kJ mol}^{-1}$) and N-H...OH ($\rho_{\text{BCP}} = 0.033 \text{ au}$, $E^{(2)} = 66.4 \text{ kJ mol}^{-1}$) H-bonds within this cluster are stronger than the strongest analogous interactions identified within the isolated pairs. Thus indicating that there is the potential for cooperativity to enhance the H-bonding within the clusters.

The [urea-Cl]⁻ complexed anion is also found to be a feature of mid – high energy clusters, e.g. 1:1_E and 1:1_F. However, in contrast to 1:1_A and 1:1_B, the involvement of the O-H group of choline has been “switched off”. Thus, in both 1:1_E and 1:1_F, the hydroxyl and carbonyl groups are unsaturated. Despite appearing very similar, there is an energy difference of $\approx 16 \text{ kJ mol}^{-1}$ between 1:1_E and 1:1_F. However, the location of the [urea-Cl]⁻ complexed unit with respect to choline differs between the two structures. As with the choline chloride ion pairs, the location of the anion influences the relative energy of the system.

The lowest energy 1:2 clusters, similar to the 1:1 clusters, are also H-bonded rings. In comparison to the 1:1 clusters, the low energy H-bond rings within the 1:2 clusters feature an additional urea – urea, rather than urea-chloride, interaction. Clusters 1:2_A-C are essentially energetically degenerate despite exhibiting different motifs. A urea-urea chain can insert between the Cl anion and choline O-H group, e.g. 1:2_B, or form with the O-H...Cl interaction preserved, e.g. 1:2_A. Structure 1:2_C is very similar to 1:2_A, with the exception that the urea-urea interaction is of the ribbon, rather than chain, type. The degeneracy of these clusters illustrates the flexibility in terms of specific interactions within this system. The dual ability of urea to act as an effective H-bond donor and acceptor plays an important role in increasing the flexibility of the system.

The [2urea-Cl]⁻ complexed anion is a feature of both 1:2_D and 1:2_E. Conceptually, 1:1_E is most similar to the “picture” of molecular speciation within this DES at the eutectic composition as proposed in **Chapter 1, Figure 1.4**. Within 1:2_E, chloride is complexed by the two urea molecules, with no additional urea-urea interactions or involvement of the choline O-H group, but this structure is $\approx 26 \text{ kJ mol}^{-1}$ above the lowest energy structure. The formation of an O-H...O=C H-bond can, however, help to stabilise the [2urea-Cl]⁻ motif, with 1:2_D only $\approx 8 \text{ kJ mol}^{-1}$ above the minimum for this composition.

With three urea molecules, the low energy H-bonded rings observed at the 1:1 and 1:2 compositions can expand to accommodate additional urea – urea interactions; both distorted chain (e.g. 1:3_A and B) and distorted ribbon (e.g. 1:3_C). The extent of H-bond aggregation within these small units, e.g. **Figure 3.36**, hints at the possibility for extensive H-bond networking within this mixture.

For the isolated *n*.urea-chloride complexes, it was found that upon addition of a third urea molecule to [2urea-Cl]⁻, the formation of urea-urea, rather than urea-chloride, interactions had just become energetically favoured. Within the 1:3 clusters, low – mid energy structures with both two (e.g. 1:3_D and F) and three (e.g. 1:3_E and G) urea molecules in the 1st coordination shell of chloride have been identified.

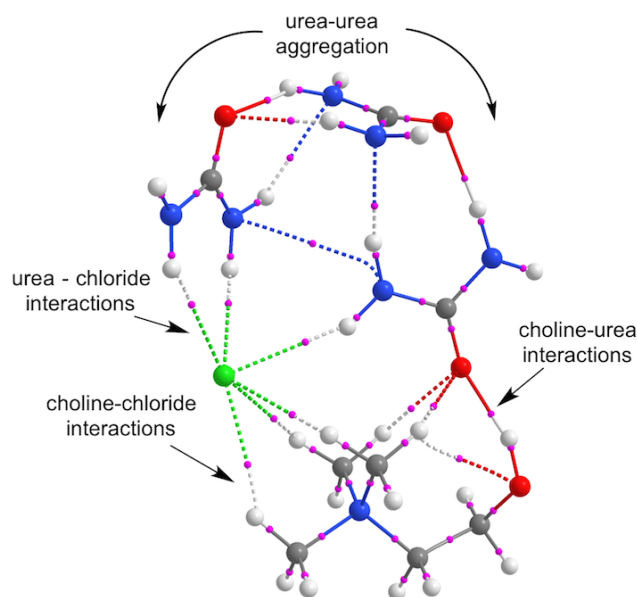


Figure 3.36. QTAIM molecular graph of cluster 1:3_B. BCPs shown as pink dots, RCPs and CCPs omitted for clarity.

Cluster 1:3_D with the $[2\text{urea}\cdot\text{Cl}]^-$ complexed anion is energetically competitive with the H-bonded rings. The clusters with three urea molecules in the 1st coordination shell of chloride (e.g. 1:3_E, G and H), exhibit a pseudo $[3\text{urea}\cdot\text{Cl}]^-$ complexed anion motif, with five, rather than six, N-H $\cdots$ Cl H-bonds. The high energy structure 1:3_H ($\Delta E_{\text{rel}} \approx 56 \text{ kJ mol}^{-1}$) has many unsaturated ends. However, the formation of a O-H $\cdots$ O=C H-bond can contribute to stabilisation of structures featuring the pseudo $[3\text{urea}\cdot\text{Cl}]^-$ motif, as in 1:3_G ($\Delta E_{\text{rel}} \approx 25 \text{ kJ mol}^{-1}$) and 1:3_E ($\Delta E_{\text{rel}} \approx 17 \text{ kJ mol}^{-1}$).

Considering all the 1:3 clusters obtained to date, no structures have been identified with the chloride anion fully “buried” (i.e. fully solvated) within the centre of the cluster. Instead chloride is found to preferentially locate on the periphery of the cluster. This behaviour was also observed in the lowest energy isolated $3\text{urea}\cdot\text{Cl}^-$ complex (i.e. 2.1.0_A) and reference made to the anisotropic solvation of chloride in water.

QTAIM analysis of H-bond interactions

QTAIM analysis of the H-bond interactions has been undertaken for the selection of B3LYP-D2 clusters shown in **Figure 3.33 –35**. For the subset of clusters analysed, the range and mean values of ρ_{BCP} for each H-bond type are detailed in **Table 3.10**. For a larger set of clusters, there is likely to be an extension of the given ranges of ρ_{BCP} . Moreover, given the small and selective nature of the data set, the mean values of ρ_{BCP} are guidelines only.

All H-bond types previously observed within the isolated pairs (including the *n*.urea-chloride complexes ($n=2,3$)) are also identified within the clusters. Additionally, choline-urea C-H $\cdots$ NH H-bonds, not observed in the pairs, are found within the clusters.

Table 3.10. Mean values and ranges of ρ_{BCP} for the H-bonds identified in the B3LYP-D2 subset of clusters shown in Figures 3.33-35. "No." is the number of H-bonds of a given type identified.

Donor	Acceptor	Mean $\rho_{\text{BCP}}/\text{au}$	Range $\rho_{\text{BCP}}/\text{au}$	No.
OH	O=C	0.038	0.034 – 0.050	7
NH	OH	0.033	-	1
OH	Cl	0.030	0.030 - 0.041	8
NH	O=C	0.026	0.016 - 0.044	21
NH	Cl	0.017	0.008 – 0.028	55
NH	NH	0.014	0.010 – 0.026	9
CH	OH (intra)	0.014	0.011 – 0.017	19
CH	Cl	0.012	0.005 – 0.017	45
CH	O=C	0.012	0.005 – 0.020	34
CH	NH	0.008	0.004 – 0.014	57

The values of ρ_{BCP} for many of the individual H-bonds identified within the subset of clusters are within the ranges previously established for the different H-bond types within the pairs. A comparison of the ranges of ρ_{BCP} in the pairs and clusters is made in **Figure 3.37**. The overlap in the ranges of ρ_{BCP} for the different H-bond types indicates that many of the interactions are competitive in terms of strength (as represented by the magnitude of ρ_{BCP}). For some of the H-bond types (i.e. N-H...Cl, C-H...O=C and C-H...Cl), the minimum value of ρ_{BCP} is lowered in the clusters. However, for the O-H...Cl, N-H...NH and N-H...OH H-bonds stronger examples are identified within the clusters. Thus, there is the possibility of both enhancement and weakening of the H-bond interactions within the larger systems.

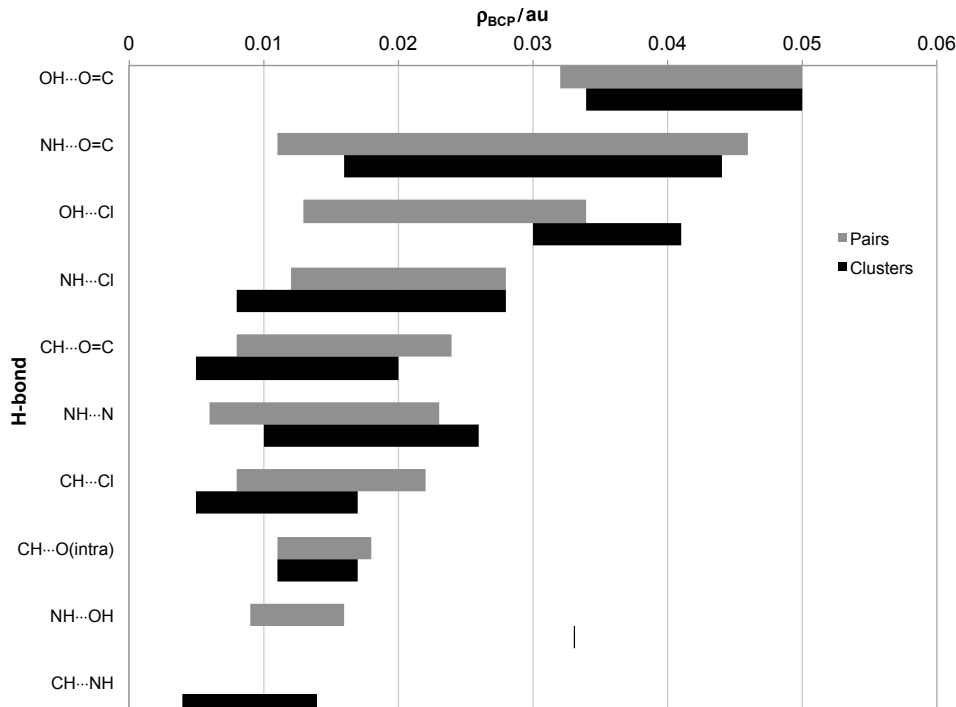


Figure 3.37. Ranges in the values of ρ_{BCP} for the different H-bond types identified within the isolated pairs and clusters.

Based on the mean values of ρ_{BCP} , the O-H...O=C interaction is the strongest H-bond type within the clusters, consistent with the findings for the pairs. The "new" C-H...NH H-bonds are very weak, but

prolific in number. However, using ρ_{BCP} , the ordering of the remaining H-bond types varies slightly compared to the ordering established for the pairs. For example, within the clusters there is a greater disparity between the doubly ionic C-H...Cl (mean $\rho_{\text{BCP}} = 0.012$ au) and ionic N-H...Cl (mean $\rho_{\text{BCP}} = 0.017$ au) interactions. This could indicate that when combined, there is a degree of “competition” between choline and urea for the chloride anion.

The total number and sum of ρ_{BCP} for the intermolecular H-bonds within each cluster are detailed in **Table 3.11**, together with the relative energy for each cluster. As would be expected, the average number of H-bonds increases with the number of urea molecules within the clusters. However, for clusters of the same composition, there is no apparent trend between the relative energy of the cluster and the total number of H-bonds. As found for the *n*.urea-chloride complexes, the total number of H-bonds is not necessarily maximised in the lowest energy structure. For example, cluster 1:3_H ($\Delta E_{\text{rel}} \approx 56$ kJ mol⁻¹) has 20 H-bonds, while the lowest energy cluster of the same composition, 1:3_A, features only 14 H-bonds.

Table 3.11. Relative energies of selected clusters (ΔE_{rel}), total number (No.) of H-bonds identified and sum of ρ_{BCP} for each cluster, the number of H-bonds with ρ_{BCP} above a value of 0.020 au and the percentage contribution of these “stronger” H-bonds to the total value of $\Sigma \rho_{\text{BCP}}$.

Cluster	$\Delta E_{\text{rel}} / \text{kJ mol}^{-1}$	Total No. of H-bonds	$\Sigma \rho_{\text{BCP}} / \text{au}$	No. H-bonds with $\rho_{\text{BCP}} \geq 0.020 \text{ au}$	% contribution to $\Sigma \rho_{\text{BCP}}$
1:1_A	0.00	8	0.132	2	44.6
1:1_B	6.93	9	0.127	2	39.5
1:1_C	9.19	7	0.122	2	40.8
1:1_D	11.45	7	0.146	2	50.4
1:1_E	25.44	8	0.103	0	0
1:1_F	41.18	8	0.105	0	0
1:2_A	0.00	12	0.187	4	50.3
1:2_B	0.42	11	0.201	3	49.9
1:2_C	0.69	11	0.195	2	36.8
1:2_D	8.24	13	0.173	1	21.6
1:2_E	26.27	14	0.155	0	0.0
1:3_A	0.00	14	0.249	6	56.1
1:3_B	1.69	14	0.265	5	49.7
1:3_C	2.91	15	0.249	5	55.0
1:3_D	3.67	18	0.238	3	32.5
1:3_E	16.64	15	0.223	4	47.9
1:3_F	18.64	14	0.234	2	33.2
1:3_G	25.16	17	0.220	2	28.2
1:3_H	55.80	20	0.208	2	19.1

Using $\Sigma \rho_{\text{BCP}}$ as a measure of H-bonding, a correlation between “total H-bonding” and ΔE_{rel} can be observed for clusters of each composition, **Figure 3.38**. Nevertheless, the trends are quite poor, although it should be noted that only a small number of clusters have to date been examined in this manner. For each composition, $\Sigma \rho_{\text{BCP}}$ is not a maximum for the lowest energy structure. For example, $\Sigma \rho_{\text{BCP}}$ is 0.014 au larger for 1:1_D ($\Delta E_{\text{rel}} = 11.5$ kJ mol⁻¹) compared to the lowest energy cluster of the 1:1 composition. Thus, as with the pairs, H-bonding is not necessarily maximised in the lowest energy structures, indicating the importance of other structure directing interactions.

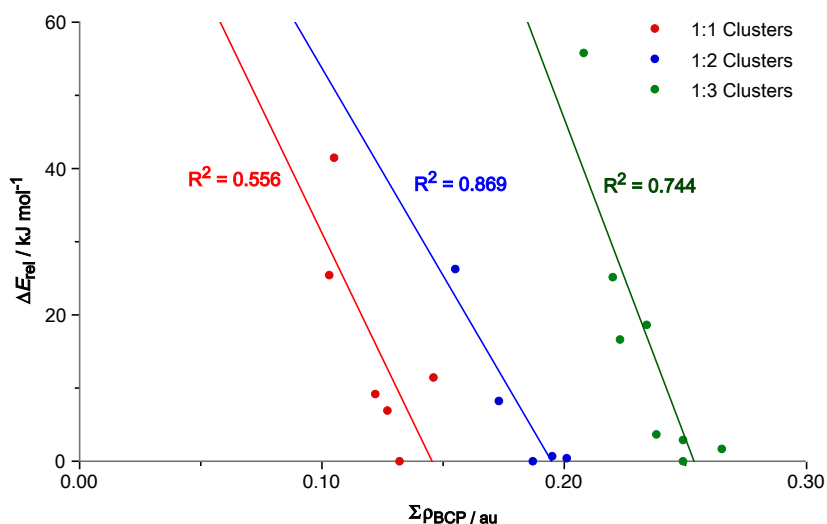


Figure 3.38. Plot of relative energy against total sum of ρ_{BCP} for the intermolecular H-bonds within the selected clusters of each composition.

The H-bonds identified within the clusters span from very weak to moderate-strong. However, is there any variation in the relative contributions of “stronger” H-bonds across clusters of different compositions and clusters of different relative energies? The formation of stronger individual H-bonds and/or highly structured motifs, e.g. the tripodal and chelated H-bond motifs, potentially favours the formation of a more “rigid” and ordered H-bond network. However, the formation of a large number of weak and very weak H-bonds, in less structured configurations, potentially contributes to an increase in disorder in the system. A balance between “rigidity” and “disorder” could influence the physical properties of the system. The number of H-bonds with values of $\rho_{\text{BCP}} \geq 0.02$ au (i.e. above the weak H-bond cut-off) are listed in **Table 3.11**, together with the percentage contribution of these “stronger” H-bonds to the total value of $\Sigma\rho_{\text{BCP}}$.

The maximum number of “stronger” H-bonds increases with the number of urea molecules. A maximum of 2 H-bonds with $\rho_{\text{BCP}} \geq 0.02$ au are found in the 1:1 clusters, 4 in the 1:2 clusters and 6 in the 1:3 clusters. Contrary to any assumption that increasing the size of a cluster results in a decrease in the H-bond strengths, increasing the number of urea molecules increases not only the total number of H-bonds, but also the number of stronger H-bond interactions. Thus, the increase in the number urea-urea interactions upon increasing the concentration of urea, could contribute to an increase in rigidity of the system.

With exception of the lowest energy 1:3 clusters, the number of “stronger” H-bond interactions above the weak H-bond cut-off is small with respect to the total number of H-bonds. For 1:1_A, for example, only 2 of the 8 H-bonds have values of $\rho_{\text{BCP}} \geq 0.02$ au. However, in terms of the percentage contribution to the total sum of ρ_{BCP} , the small number of stronger H-bond interactions is significant e.g. $\approx 45\%$ within 1:1_A. Thus, there are generally a small number of stronger interactions within a “soup” of weak, or very weak, H-bond interactions. Moreover, the very highest energy clusters examined, do not feature any H-bonds with values of $\rho_{\text{BCP}} \geq 0.02$ au. Tentatively, it could be suggested that stronger H-bond interactions make a more significant contribution to the total H-bonding within the lower energy clusters.

Charge transfer

Employing the NBO scheme, the charge transfer away from chloride within the selection of B3LYP-D2 clusters presented here varies from 0.105 to 0.160 e, **Appendix, Table A.19**. Thus, the maximum charge transfer within these clusters is very slightly increased with respect to the maximum charge transfer found for the isolated choline chloride ion pairs (0.150 e). The minimum charge transfer is approximately of the same order of magnitude as found within the isolated [2urea-Cl]⁻ complex 2.0.0_B (0.107 e). However, within the clusters, the charge transferred from chloride could be accepted by either choline or urea. Therefore, consistent with the conclusions drawn for the pairwise interactions, the negative charge of chloride is not highly delocalised within the clusters.

The charge on the individual urea molecules varies from -0.040 to +0.035 e (**Appendix, Table A.20**), thus is slightly reduced from the maximum amount of charge transfer to and from urea in the isolated *n*.urea-chloride complexes and choline-urea pairs respectively. Whether urea is slightly positive, negative or effectively neutral is dependent on the local coordination environment. For example, within cluster 1:1_B, urea forms a primary interaction with chloride, acting as a H-bond donor, and thus is slightly negative (-0.032 e). Within 1:1_A, urea acts as both a H-bond acceptor and H-bond donor, forming primary interactions with both choline and urea. Thus, with respect to 1:1_B, the negative charge on urea is reduced in 1:1_A (-0.008 e). Within 1:2_A there is a slight negative charge on both of the urea molecules in the H-bond chain (-0.017 and -0.014 e), thus there is a small amount of charge delocalisation over a longer range. Cluster 1:2_B features both a slightly negative and slightly positive urea molecule (-0.032 and +0.035 e), with one urea in the H-bond chain forming a primary interaction with chloride (H-bond donor mode), whilst the other forms a primary interaction with the O-H group of choline (H-bond acceptor mode).

5. Conclusion

We have undertaken an in-depth examination of the pairwise interactions between the constituent species of the choline chloride – urea DES, including small *n*.urea-chloride complexes, and a preliminary analysis of larger clusters of *n*.urea.choline-chloride. H-bonding has been proposed to be central to the formation of DESs. Therefore, a major focus of this work has been on understanding the H-bonding within the system. Moreover, DESs provide a good example of a system featuring neutral, ionic and, the poorly explored, doubly ionic H-bonds.

The relative ordering of the maximum association energies, E_a , of the pairs of components can be rationalised by considering the dominant electrostatic contribution (choline-chloride $\gg$ urea-chloride $>$ choline-urea $>$ urea-urea). Due to the anisotropic charge distribution of the interacting species, variations in the electrostatic interactions for different configurations are anticipated. Within the pairs and higher *n*.urea-chloride complexes, a total of 172 H-bonds were identified, increasing to 235 within the small subset of clusters (19 clusters in total). This provides an indication that a very large number of H-bonds could form within this DES. However, neither the total number of H-bonds, nor the total H-bonding contribution (quantified here using $\Sigma\rho_{\text{BCP}}$) is necessarily maximised in the lowest energy pairs and clusters. Therefore, a balance between maximising H-bonding and maximising local electrostatic interactions controls the relative stability of the different configurations.

Consistent with previous reports, we find that E_a cannot be used to quantify doubly ionic H-bond interactions, which are clouded by the dominant Coulombic contribution. Local descriptors of H-bonding, such as ρ_{BCP} and $E^{(2)}$, can be employed for all H-bonds, regardless of the global charge of the system. A correlation between $\Sigma\rho_{\text{BCP}}$ and E_a for the neutral and ionic systems was obtained, however, was found to be relatively poor, potentially reflecting the complex interplay of interactions contributing to the total association energy.

The choline cation has two stable configurations, gauche and trans. The gauche conformer is stabilised through the formation of an intramolecular C-H $\cdots$ OH H-bond, facilitated by the positive charge of the cation. The energy difference between the gauche and trans conformations is potentially reduced in a polar environment. Therefore, it is important to assess interactions with both gauche and trans choline; pairs and clusters with both conformations of choline have been located and examined.

Both chloride and urea form a relatively large number of low energy configurations with choline. Intermolecular interactions with the choline cation can occur *via* interaction with the C-H groups of the ammonium head group and/or with the hydroxyl group of the functionalised chain. For both the choline-chloride and choline-urea pairs, the very lowest energy configurations feature interactions with the hydroxyl group, O-H $\cdots$ Cl and O-H $\cdots$ O=C respectively. For the O-H $\cdots$ Cl interaction, the gauche conformation allows for better orbital overlap and consequently more linear, and stronger, H-bonds. Within the clusters of each composition, an O-H $\cdots$ Cl or O-H $\cdots$ O=C interaction is a key element of the lowest energy structures. The hydroxyl group of choline could therefore play an important role in structuring within DESs.

H-bond formation with the C-H groups of ammonium cations is often overlooked. However, C-H...X interactions are a prominent feature of the system examined here. The positive charge of the choline cation facilitates the formation of C-H...X interactions that would likely be too weak to be identified with a neutral donor. For the choline chloride system in particular, the doubly ionic nature of the system strengthens the C-H...Cl interaction. The tripodal motif was found to be a recurring feature of pairwise interactions with choline, and is also preserved within the clusters. For choline chloride, the concurrent formation of three C-H...Cl H-bonds in the tripodal arrangement can lead to a stronger H-bond interaction than a single O-H...Cl H-bond. This emphasises the importance of considering the *total* H-bonding.

Moreover, within the pairs, the doubly ionic C-H...Cl H-bonds are found to be competitive in terms of strength with the ionic N-H...Cl H-bonds, despite N-H groups typically being considered as the stronger H-bond donor. However, within the clusters, where both choline and urea can form H-bonds simultaneously with the chloride anion, a greater disparity in the C-H...Cl and N-H...Cl interactions is revealed. The N-H...Cl interactions are generally found to be stronger than the C-H...Cl interactions within the clusters.

A key finding of this work is the large number of different H-bond types identified, a “soup” of possible intermolecular interactions: O-H...O=C, N-H...O=C, O-H...Cl, N-H...Cl, O-H...NH, C-H...Cl, C-H...O=C, N-H...OH and N-H...NH. In addition, relatively large numbers of C-H...NH interactions were observed in the clusters. Therefore, at least 12 different types of intermolecular H-bond could form within the (pure) choline-chloride-urea DES. Within the bulk liquid, a potential choline-choline, O-H...OH interaction may also occur.

Typically, H-bonding within a molecular solvent, and even a conventional aprotic ionic liquid, is relatively homogeneous i.e. limited in the number of different H-bond types (e.g. C-H...Cl within [C₄C₁im]Cl, and O-H...O within water). The large number of different H-bond types identified within this DES could have two important consequences. Firstly, the large number of different H-bond types could increase the disorder within the system, favouring the formation of a liquid. Secondly, the different H-bond donor and acceptor groups could play an important role in influencing the solvation behaviour of the system. The choline chloride – urea DES has been found to solubilise a wide range of materials, including salts and polar organics.^{1, 4} The ability of this DES to “adapt” to the solute in terms of H-bonding could be central to this.

Additional to variation in the functionality of the H-bond interactions, there is found to be a relatively large variation in the strength within each type of H-bond interaction. Relative to the pairs, examples of weaker and stronger H-bond interactions were identified within the clusters. Furthermore, there is a considerable overlap in the relative strengths of many of the different types of H-bond interaction. Thus, there appears to be a high degree of flexibility in terms of the H-bond interactions. Moreover, within the pairs we find that there is no strong energetic preference for either a smaller number of stronger H-bonds or a larger number of weaker H-bonds. Examination of the H-bonding in the clusters suggests that within this DES there are a small number of moderate to strong interactions within a “soup” of weaker interactions.

Determining the overall impact of H-bonding on the system is difficult. A large number of H-bonds, and the formation of a H-bond network, could lead to an increase in structuring of the liquid. However, the diversity and variation in the H-bond interactions could increase the total entropy of the system. Thus, H-bonding could lead to both “rigidity” and “disorder” within the system. Potentially there is a balance between these two competing effects. Changing the composition of the eutectic mixture could alter this balance.

The formation of the $[2\text{urea}\cdot\text{Cl}]^-$ complexed anion at the eutectic composition of 1:2 choline chloride to urea has been suggested. Delocalisation of the negative charge on chloride over the complexing urea molecules is proposed to lead to a reduction in the choline – chloride association, contributing to the decrease in the freezing point of the system.

The formation of a $[\text{urea}\cdot\text{Cl}]^-$ complex is strongly favourable ($E_a \approx 106 \text{ kJ mol}^{-1}$). However, interaction with a second urea molecule, leading to the formation of a $[2\text{urea}\cdot\text{Cl}]^-$ complex is not necessarily favoured. The formation of a $[\text{urea}\cdot\text{choline}]^+$ complex ($E_a \approx 82 \text{ kJ mol}^{-1}$) is energetically competitive with the formation of $[2\text{urea}\cdot\text{Cl}]^-$ ($E_a \approx 85 \text{ kJ mol}^{-1}$). Moreover, the choline – urea O-H $\cdots$ O=C H-bond, not the N-H $\cdots$ Cl H-bond, is found to be the strongest in this system. These results emphasise the importance of recognising the dual ability of urea to act as an effective H-bond donor and H-bond acceptor.

The $[\text{urea}\cdot\text{Cl}]^-$ complex is a dominant structural motif within the clusters of each composition. For the higher 1:2 and 1:3 clusters, the $[2\text{urea}\cdot\text{Cl}]^-$ is also observed. However, $[2\text{urea}\cdot\text{Cl}]^-$ is not necessarily a feature of the lowest energy structures. In the gas phase, formation of H-bonded rings, that maximise the local electrostatic and H-bond interactions are favoured. The number of low energy structures for each composition again highlights the flexibility, and competitive nature, of interactions within this DES.

Charge delocalisation within the isolated *n*.urea-chloride complexes, assessed using partial charges, is not large. This is consistent with the limited delocalisation observed within the MO interactions and the formation of largely electrostatic H-bond interactions. Moreover, urea is both able to accept or donate a small amount of charge. Examples of slightly negative and slightly positive urea molecules were identified within the clusters, varying according to the bonding motif. We therefore find no evidence to support the case for a highly charge delocalised $[2\text{urea}\cdot\text{Cl}]^-$ complexed anion. This could suggest that urea either acts to increase the average choline – chloride separation or potentially “shields” the relatively localised charge on the chloride anion. Preliminary analysis of the choline-chloride separation in the clusters suggests that urea may act as a “spacer”.

Our analysis of the interactions within the choline-chloride-urea DES suggests that H-bonding is central to this system. There is the potential for many H-bond interactions to form, varying in functionality, charge, motif and strength. It is expected that this flexibility in the H-bond interactions will influence both the physical and chemical properties of the eutectic.

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Chapter 4

Comparing and Contrasting Aprotic and Protic Imidazolium Ionic Liquids

1. Introduction

The protic ionic liquid $[\text{C}_4\text{Him}][\text{HSO}_4]$ was identified as a potential candidate for application in chalcopyrite leaching. Therefore, an increased understanding of the local structuring within this system is a key aim here. Furthermore, $[\text{C}_4\text{Him}][\text{HSO}_4]$ is also of interest from the perspective of H-bonding, as both the cation *and* the anion have the potential to act as good H-bond donors, **Figure 4.1**. As the $[\text{HSO}_4]^-$ anion is both a H-bond acceptor and H-bond donor, there is the additional possibility of anion-anion H-bond interactions.

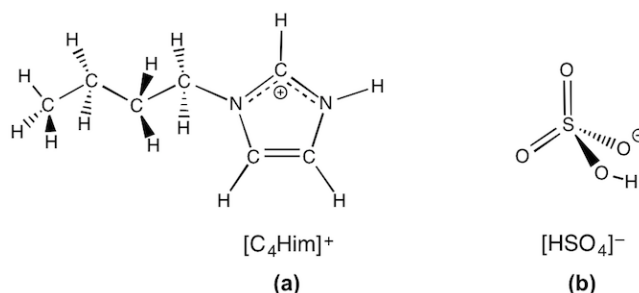


Figure 4.1. The 1-butylimidazolium cation (a) and hydrogensulphate anion (b).

To fully understand how the presence of an acidic proton on both the cation and the anion influences the local structuring, a number of related ionic liquid systems were chosen for comparison. Moreover, a combination of QM calculations, MD simulations and a preliminary investigation employing a QM/MM method have been employed to gain insight into the selected systems.

The terms aprotic and protic ionic liquid are used throughout this chapter. The use of the term protic ionic liquid applies strictly to ionic liquids formed through an acid-base neutralisation reaction. By default, all protic ionic liquids will feature an acidic N-H group on the cation. The term “protic” therefore does not account for the nature of the anion, which may, or may not, feature an acidic proton e.g. $[\text{HSO}_4]^-$ and $[\text{C}_1\text{SO}_4]^-$ respectively. As such, an “aprotic” ionic liquid could also feature an anion with an acidic proton, e.g. $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$.

The hydrogensulphate anion, $[\text{HSO}_4]^-$, can be considered as the smallest member of the alkylsulphate, $[\text{C}_n\text{SO}_4]^-$, family. Aprotic imidazolium alkylsulphate ionic liquids are of increasing interest for practical application. The synthesis of aprotic alkylsulphate ionic liquids *via* alkylation of an imidazolium base with a dialkylsulphate is both atom economic and halide free.¹ Halide impurities are inherent to ionic liquids synthesised *via* the metathesis of halide salts and can be difficult to remove.² As halide impurities can influence both the physical properties of the ionic liquid³ and impinge chemical reactivity within the system,² use of halide free ionic liquids is important for many practical

applications. Moreover, variation of the anion alkyl chain length, and functionality, also allows for the tuning of the ionic liquid properties e.g. $[\text{C}_n\text{SO}_4]^-$ anions with longer alkyl chains are more stable to hydrolysis.⁴ Generally, favourable properties of alkylsulphate ionic liquids include low melting points,⁴⁻⁶ acceptable viscosities,⁷ and depending on the cation, relatively low toxicities.⁸

Aprotic imidazolium hydrogensulphate ionic liquids can be obtained *via* high temperature hydrolysis of the parent $[\text{C}_n\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ system,^{9, 10} although alternative synthesis methods have been reported.^{11, 12} The protic equivalent, $[\text{C}_n\text{Him}][\text{HSO}_4]$ is readily obtained *via* a simple acid-base reaction, although achieving an exact 1:1 ratio can be difficult. Additional to the potential application as leaching agents for the extraction of metals from ore,¹³ $[\text{HSO}_4]^-$ ionic liquids are also of interest in the field of biomass deconstruction¹⁴, as well as providing (mildly) acidic medium for catalytic reactions.¹⁵ Furthermore, proton conducting ionic liquids (e.g. $[\text{HSO}_4]^-$ ionic liquids) have previously been considered in the active search for non-aqueous electrolytes for fuel cells.¹⁶ Other potential candidates include protic heterocycles (e.g. imidazole)¹⁷ as well as solid inorganic acids (e.g. $\text{Cs}[\text{HSO}_4]$).¹⁸

In terms of elucidating the structure and interrogating the intermolecular interactions, the aprotic alkylsulphates have received the most attention. Classical MD, *ab initio* MD and X-ray diffraction have all been used to probe the structuring within $[\text{C}_2\text{C}_1\text{im}][\text{C}_n\text{SO}_4]$ ($n \geq 2$) systems.¹⁹⁻²² To the best of our knowledge, only a single MD study of an aprotic imidazolium hydrogensulphate ionic liquid, $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, has been reported.²³

For a series of $[\text{C}_2\text{C}_1\text{im}][\text{C}_n\text{SO}_4]$ ($n=1, 4, 6$ and 8) ionic liquids, the viscosity was found to be dependent on the length of the anion alkyl chain, increasing as the chain length was extended.⁷ $[\text{C}_2\text{C}_1\text{im}][\text{HSO}_4]$ however, was found to be over twice as viscous as $[\text{C}_2\text{C}_1\text{im}][\text{C}_8\text{SO}_4]$ and approximately an order of magnitude more viscous than $[\text{C}_2\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$.⁷ Initially, it was suggested that the cation-anion interactions were enhanced in the $[\text{HSO}_4]^-$ system, compared to the $[\text{C}_n\text{SO}_4]^-$ analogues.⁷ However, a Raman spectroscopy study of $[\text{C}_2\text{C}_1\text{im}][\text{HSO}_4]$ and $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ revealed the presence of Raman bands characteristic of H-bonded $[\text{HSO}_4]^-$ chains, thus indicating that anion-anion interactions were the origin of the increased viscosity.²⁴ The line broadening in the ^{17}O NMR spectrum of $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ is also consistent with anion-anion H-bond interactions.²³ Furthermore, $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ interactions were observed in the MD simulation of $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$.²³ However, these interactions were found to result in the formation of “anion pairs” surrounded by a cation cage, rather than the formation of longer H-bonded chains.

The computed vibrational spectrum of $[\text{C}_6\text{C}_1\text{im}][\text{HSO}_4]$ (as isolated ions) was used to help interpret the experimental IR and Raman spectra.²⁵ In this case, bands suggestive of the presence of H_2SO_4 in the liquid were observed. Although the possibility of this being due to the residual H_2SO_4 from the synthesis was acknowledged, the presence of H_2SO_4 was tentatively attributed to cation - anion proton transfer (i.e. carbene formation at the C^2 position). However, later IR and Raman studies found no indication of H_2SO_4 and as far as we can determine, there are no other reports of cation - anion proton transfer for a $[\text{C}_n\text{C}_1\text{im}][\text{HSO}_4]$ ionic liquid.

Despite $[\text{HSO}_4]^-$ ionic liquids (both aprotic and protic) receiving much interest for practical application, the structuring and interactions within these systems has not been fully interrogated.

Although evidence of anion-anion H-bonding has been reported for aprotic $[C_nC_1im][HSO_4]$ systems, the nature and strength of these interactions has not been established. Furthermore, the influence on the anion-anion interactions through replacing the aprotic imidazolium cation with a protic imidazolium has not been investigated.

2. Ion Pairs and Ion Pair Dimers

An examination of ion pairs of protic and aprotic analogues was undertaken to help elucidate how the established local structuring of an aprotic $[\text{C}_4\text{C}_1\text{im}][\text{X}]$ ionic liquid changes when the cation methyl group is replaced by a proton. The chloride anion, being monatomic and small, has often been used to perform an initial assay of a system, with the $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$ system being a prototypical exemplar of an aprotic ionic liquid. Therefore, an initial assay of stable anion configurations with respect to the $[\text{C}_4\text{Him}]^+$ cation was undertaken using the chloride anion as a “probe”. A subsequent study of aprotic $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ and protic $[\text{C}_4\text{Him}][\text{HSO}_4]$ was then carried out. Ion pairs have been obtained with and without a dispersion correction to the density functional, allowing for the influence of increased dispersion on ion pair interactions to be assessed.

However, although ion pairs are useful for probing the nature of cation-anion interactions, it is not possible to examine potential anion-anion interactions. Therefore, a comparative analysis of $[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4]$ ion pair dimers (i.e. $[\text{C}_1\text{C}_1\text{im}]_2[\text{HSO}_4]_2$), where anion-anion H-bonding might be expected, with the $[\text{C}_1\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ analogue, where anion-anion H-bonding would be anticipated to be minimal, was initiated.

2.1 Method

During the course of this work, the available dispersion corrections implemented for use within G09 were updated. For more recent work we have employed the improved D3BJ correction. For our earlier work the D2 correction was used.

A conformational analysis of the isolated $[\text{C}_4\text{Him}]^+$ cation was initially conducted at the B3LYP/6-311+G(d,p) level. B3LYP conformers were subsequently optimised using MP2(full) in conjunction with the 6-311+G(d,p) basis set. Ion pair geometries were initially obtained at the B3LYP/6-311+G(d,p) level. All ion pairs were then subjected to a second optimisation with the B3LYP functional appended with Grimme's D2 dispersion correction²⁶ (B3LYP-D2) in combination with the 6-311++G(d,p) basis set. All reported ion pair energies are ZPE corrected.

For consistency with recently published results from the group,²⁷ $[\text{C}_1\text{C}_1\text{im}][\text{X}]$ ion pair dimer structures (i.e. $[\text{C}_1\text{C}_1\text{im}]_2[\text{X}]_2$) have been obtained using the B3LYP functional appended with Grimme's D3 dispersion correction with the Becke and Johnson (BJ) damping function²⁸ (B3LYP-D3BJ), in combination with the 6-311+G(d,p) basis set. Analysis of $[\text{HSO}_4]^-$ dimers was conducted at the same level. All reported energies for the ion pair dimers are ZPE and BSSE corrected.

2.2 Ion pairs: Comparison of protic and aprotic analogues

Analysis of the B3LYP ion pairs is presented first, with a comparison of the $[\text{C}_4\text{Him}]\text{Cl}$ and $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$ systems initially undertaken, followed by examination of the more complex $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ and $[\text{C}_4\text{Him}][\text{HSO}_4]$ systems. The influence of dispersion on the ion pair structures is subsequently considered.

2.2.1 Local structuring: The influence of introducing an N-H group

The $[\text{C}_4\text{Him}]^+$ cation

An in depth analysis of the $[\text{C}_4\text{C}_1\text{im}]^+$ cation has previously been reported.^{29, 30} To determine the influence of replacing the methyl group with a proton on the geometry and electronic structure, a comparative analysis of the $[\text{C}_4\text{Him}]^+$ cation has been undertaken here.

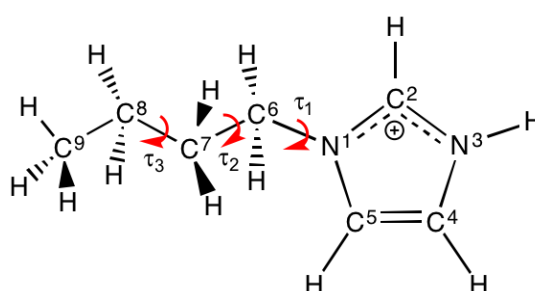


Figure 4.2. Torsion angles within the $[\text{C}_4\text{Him}]^+$ cation.

In line with previous reports for $[\text{C}_4\text{C}_1\text{im}]^+$,²⁹ the rotational profiles for the three torsion angles τ_1 , τ_2 and τ_3 , as defined in **Figure 4.2**, were examined. τ_1 ($\text{C}^2\text{-N}^1\text{-C}^6\text{-C}^7$) determines the orientation of the butyl chain with respect to the plane of the ring, with τ_2 ($\text{N}^1\text{-C}^6\text{-C}^7\text{-C}^8$) and τ_3 ($\text{C}^6\text{-C}^7\text{-C}^8\text{-C}^9$) corresponding to internal rotations of the butyl chain. Consistent with findings for $[\text{C}_4\text{C}_1\text{im}]^+$, the barriers to rotation are low ($< 23 \text{ kJ mol}^{-1}$), **Appendix, Figure A.10**, thus suggesting that butyl chain rotation is relatively facile.

A search for stable conformations of $[\text{C}_4\text{Him}]^+$ was undertaken, using the respective combinations of local minima of $\tau_1\text{-}\tau_3$ to establish input structures. Following optimisation, a total of 11 stable conformations of $[\text{C}_4\text{Him}]^+$ were isolated within an energy range of $\approx 12 \text{ kJ mol}^{-1}$, **Appendix, Figure A.11** and **Table A.21**. The relative energy ordering of $[\text{C}_4\text{C}_1\text{im}]^+$ conformers is known to be dependent on the amount of correlation recovered by the method and the basis set employed.²⁹ Optimisation of the $[\text{C}_4\text{Him}]^+$ B3LYP structures at the MP2 level resulted in subtle changes in the relative energies, **Appendix, Table A.22**. However, two of the B3LYP conformations (both with $\tau_1 \approx 0$) are not stable minima at the MP2 level.

A comparison of the NBO partial charges (at the B3LYP level) reveals that the partial charge distribution is very similar within the $[\text{C}_4\text{Him}]^+$ and $[\text{C}_4\text{C}_1\text{im}]^+$ cations, **Figure 4.3 a** and **Appendix, Table A.24**. The exception to this is the increased polarisation of the N-H unit of $[\text{C}_4\text{Him}]^+$ compared to the N-CH₃ unit of $[\text{C}_4\text{C}_1\text{im}]^+$.

Electrostatic potential (ESP) surfaces are useful for providing a “picture” of how the charge distribution of a system appears to an approaching molecule. Example ESP surfaces for $[\text{C}_4\text{Him}]^+$ and

$[\text{C}_4\text{C}_1\text{im}]^+$ are shown in **Figure 4.3 b**. The majority of the positive charge is clearly distributed over the heteroaromatic ring in both cases. For $[\text{C}_4\text{C}_1\text{im}]^+$ the local regions of highest positive charge are the $\text{C}^2\text{-H}$ unit and the $(\text{C}^4)\text{-H}$ and $(\text{C}^5)\text{-H}$ ring protons. For $[\text{C}_4\text{Him}]^+$, there is a region of increased positive charge corresponding to the N-H proton, in agreement with the NBO partial charges. However, whilst the NBO charge partitioning method, by definition, produces a localised picture of the charge distribution, the ESP surface for $[\text{C}_4\text{Him}]^+$ suggests that there is a “smearing” of the high positive charge in the region of the N-H proton toward the $\text{C}^2\text{-H}$ and $\text{C}^4\text{-H}$ regions.

Not unexpectedly, replacing the methyl group of $[\text{C}_4\text{C}_1\text{im}]^+$ with a proton does not significantly affect the butyl chain rotation nor the charge distribution, except in the locality of the N-H unit. The increased polarisation of the N-H group is consistent with this being a good H-bond donor group.

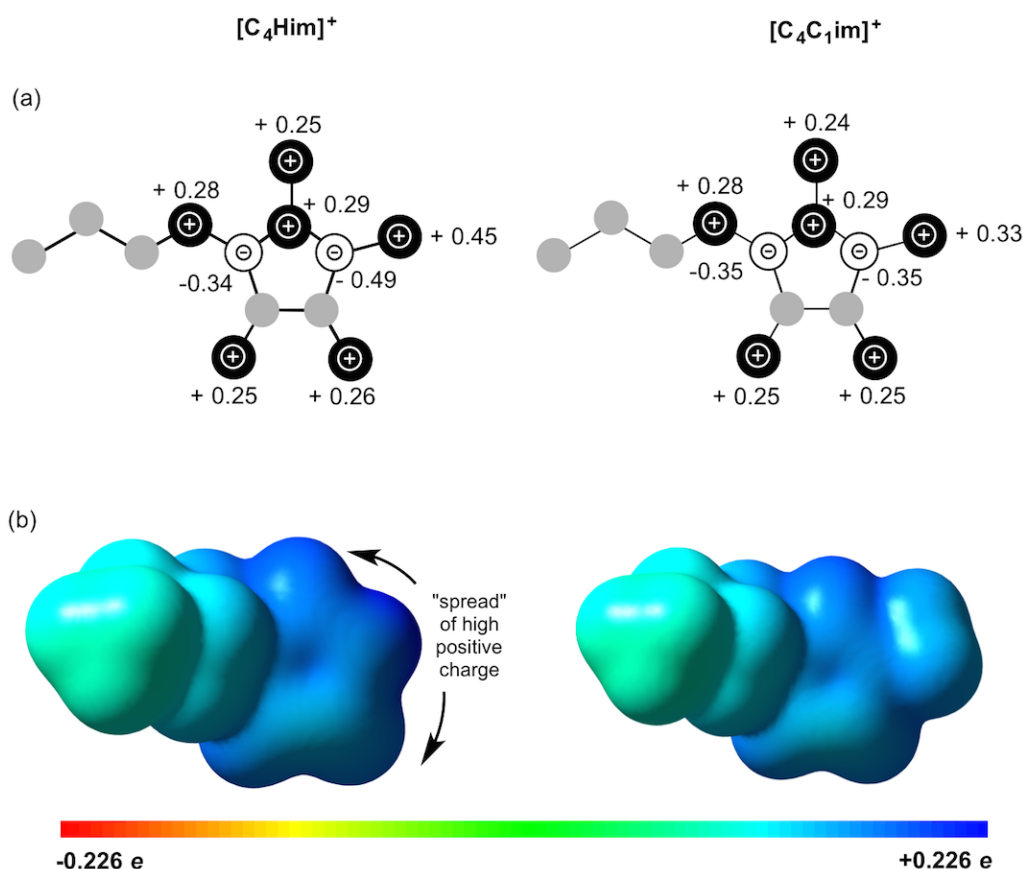


Figure 4.3. (a) Comparison of the NBO partial charge distributions of the $[\text{C}_4\text{Him}]^+$ and $[\text{C}_4\text{C}_1\text{im}]^+$ cations. For the methyl and methylene groups the sum of atomic charges is represented. A grey circle represents an atom or group that is essentially charge neutral. (b) Electrostatic potential mapped onto the 0.001 $\text{e}\text{\AA}^{-3}$ isodensity surfaces.

Comparison of $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$ and $[\text{C}_4\text{Him}]\text{Cl}$

A search for stable $[\text{C}_4\text{Him}]\text{Cl}$ ion pairs has been undertaken for each of the isolated conformers of the $[\text{C}_4\text{Him}]^+$ cation. Starting ion pair structures for each conformer were obtained by placing the chloride anion in the stable anion positions established for $[\text{C}_n\text{C}_1\text{im}]^+$ e.g. **Figure 4.5**.³⁰ In addition, a starting configuration in which chloride was positioned to form a linear interaction with the N-H group was also examined. Therefore, a minimum of eight starting configurations for each $[\text{C}_4\text{Him}]^+$ conformer were submitted for optimisation at the B3LYP/6-311+G(d,p) level. In total, 51 stable $[\text{C}_4\text{Him}]\text{Cl}$ ion pairs

have been isolated, spanning an energy range of $\approx 129 \text{ kJ mol}^{-1}$, **Appendix, Figure A.13**. Relative energies with, and without, ZPE corrections are listed in the **Appendix, Table A.25**.

Six stable chloride positions with respect to the $[\text{C}_4\text{Him}]^+$ cation have been determined. The lowest energy structure of each configuration type, together with the relative energy, is provided in **Figure 4.4**. For each stable chloride position, the alkyl chain conformation is found to influence the relative energy. The 51 stable $[\text{C}_4\text{Him}]\text{Cl}$ ion pairs therefore show variation in both the chloride position and alkyl chain rotation.

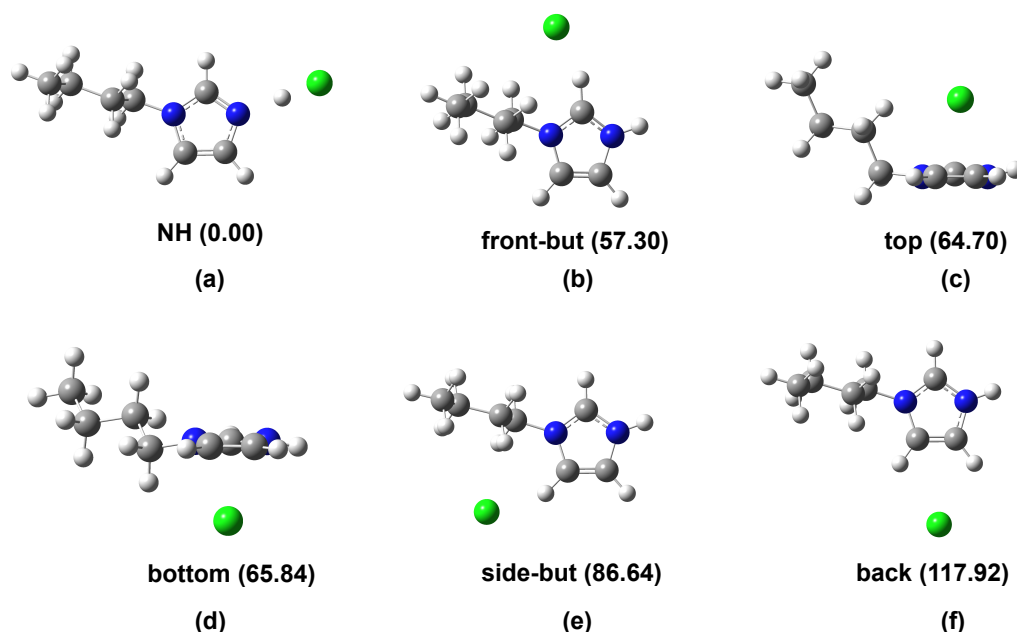


Figure 4.4. Lowest energy examples (at B3LYP/6-311+G(d,p)) of the six stable chloride configurations with respect to the $[\text{C}_4\text{Him}]^+$ cation. Relative energies in kJ mol^{-1} .

Within the lowest energy configuration, chloride forms a linear H-bond with the N-H group, **Figure 4.4 a**. This will be termed here as the “NH” configuration. Within **Figure 4.4 a**, it can be seen that the interaction of the N-H group with the basic Cl^- anion in the gas phase leads to partial proton transfer. However, it can be anticipated that the inclusion of a polar solvation environment would stabilise the ionic species, resulting in a decrease in proton transfer. For example, optimisation of the lowest energy ion pair with the “NH” configuration in a polarisable continuum (SMD, parameters for $[\text{C}_4\text{C}_1\text{im}][\text{PF}_6]$), results in a decrease in the N-H separation of $\approx 0.56 \text{ \AA}$.

The five higher energy configurations correspond to the established front-but, top, bottom, side-but and back configurations, **Figure 4.4 b to f** respectively. The front-but and top configurations, the lowest energy configurations with an aprotic imidazolium cation, are found to be ≈ 57 and 65 kJ mol^{-1} higher in energy than the lowest energy NH configuration. The side-but and back configurations are at a higher energy still, ≈ 87 and 118 kJ mol^{-1} respectively. Reports for trialkylammonium ion pairs suggest that the NH configuration is stabilised by ≈ 34 to 75 kJ mol^{-1} with respect to the alternative configuration.^{31, 32} The stabilisation of the NH configuration of $[\text{C}_4\text{Him}]\text{Cl}$, with respect to the alternative configurations of lowest energy (front-but/top), is therefore within this range.

The introduction of the NH configuration therefore leads to a significant increase in the energy difference between the two lowest energy configurations of $[\text{C}_4\text{Him}]\text{Cl}$ ($\approx 57 \text{ kJ mol}^{-1}$) compared to $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$ (typically $< 10 \text{ kJ mol}^{-1}$). However, replacing the methyl group with a proton does not have a significant influence on the relative energy ordering of the other configurations. Within $[\text{C}_4\text{Him}]\text{Cl}$, the front-but and top (or bottom) configurations are close in energy ($< 9 \text{ kJ mol}^{-1}$ for the examples shown in **Figure 4.4**), with the side-but and back configurations ≈ 29 and 61 kJ mol^{-1} higher in energy than the front-but configuration. The relative energy differences between these configurations are therefore very similar to the analogous configurations found for $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$ ion pairs.³⁰

A further notable difference between $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$ and $[\text{C}_4\text{Him}]\text{Cl}$ ion pair configurations is that stable front-me and side-me configurations could not be isolated for the latter. For all attempts to isolate either a front-me or side-me structure the chloride anion is “pulled” toward the NH configuration. A comparison of the stable $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$ and $[\text{C}_4\text{Him}]\text{Cl}$ configurations is made in **Figure 4.5**, with the “loss” of the front-me and side-me configurations, in favour of the NH configuration, emphasised. The absence of the front-me and side-me configurations suggests that the formation of a linear $\text{N-H}\cdots\text{Cl}^-$ interaction is strongly favoured over the formation of two non-linear interactions. This is in contrast to aprotic imidazolium systems, where the formation of multiple non-linear $\text{C-H}\cdots\text{Cl}^-$ interactions is favoured.³³ However, this behaviour does correspond to findings for protic trialkylammonium systems, where the NH configuration, with a linear $\text{N-H}\cdots\text{X}$ interaction, is energetically preferred.³²

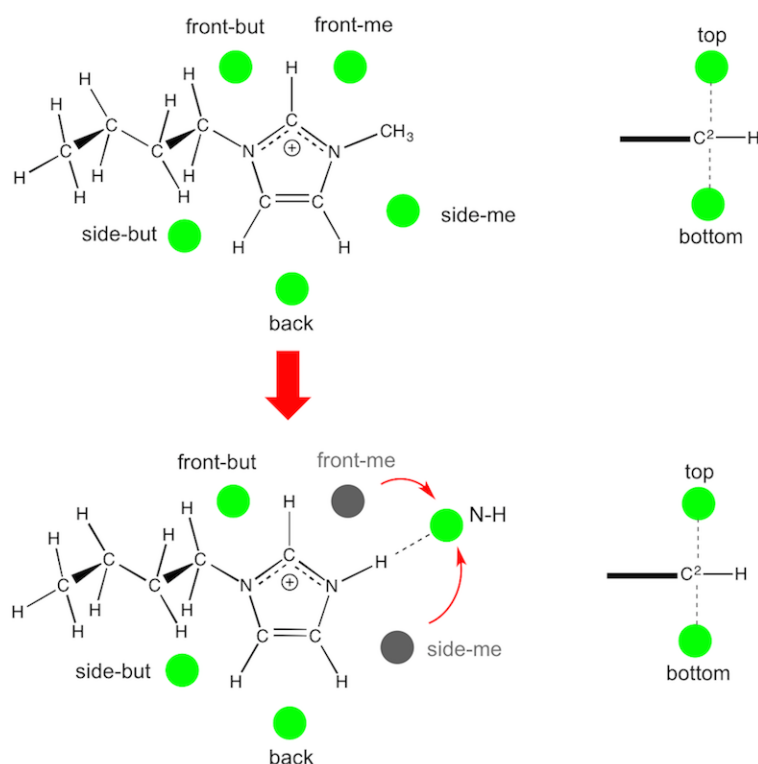


Figure 4.5. Comparison of the stable chloride positions about the $[\text{C}_4\text{C}_1\text{im}]^+$ and $[\text{C}_4\text{Him}]^+$ cations.

The ion pair configurations of $[\text{C}_4\text{Him}]\text{Cl}$ therefore exhibit an admixture of features of aprotic imidazolium and protic trialkylammonium systems. As with protic trialkylammonium ion pairs, the NH configuration is strongly favoured. For $[\text{C}_4\text{Him}]\text{Cl}$, this results in destabilisation (or loss) of the side-me and front-me configurations. However, unlike the trialkylammonium case, where there is typically only one alternative configuration (i.e. “face”, **Chapter 1, Figure 1.18**), for $[\text{C}_4\text{Him}]^+$ the established aprotic imidazolium front-but, top/bottom, side-but and back configurations can be isolated. Potentially therefore, the properties of $[\text{C}_4\text{Him}]\text{Cl}$ might also lie between those of aprotic $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$ and a protic $[\text{NC}_n\text{C}_n\text{C}_n\text{H}]\text{Cl}$ system.

Comparison of $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ and $[\text{C}_4\text{Him}][\text{HSO}_4]$

A comparison of aprotic and protic imidazolium chloride ion pairs is useful for gaining initial insight into the differences in local structuring. However, the simple monoatomic chloride anion is not prototypical of the larger multidentate anions typically found within ionic liquids. As an understanding of ionic liquids with the $[\text{HSO}_4]^-$ anion is of interest here, a comparison of aprotic $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ and protic $[\text{C}_4\text{Him}][\text{HSO}_4]$ has been undertaken.

The hydrogensulphate anion has four potential H-bond acceptor sites and one acidic proton (i.e. H-bond donor site). Hence, $[\text{HSO}_4]^-$ has the potential to form multiple specific interactions. The NBO partial charge distribution of $[\text{HSO}_4]^-$ is compared to the parent acid, H_2SO_4 , in **Figure 4.6**. As would be anticipated, upon loss of a proton the resulting negative charge is distributed across the electronegative oxygen centres. The three “terminal” oxygen atoms bear only marginally more negative charge than the “bridging” oxygen atom. This would suggest that, based on charges alone, there may not be a significant difference in the preference for interaction with a terminal or the bridging oxygen atom.

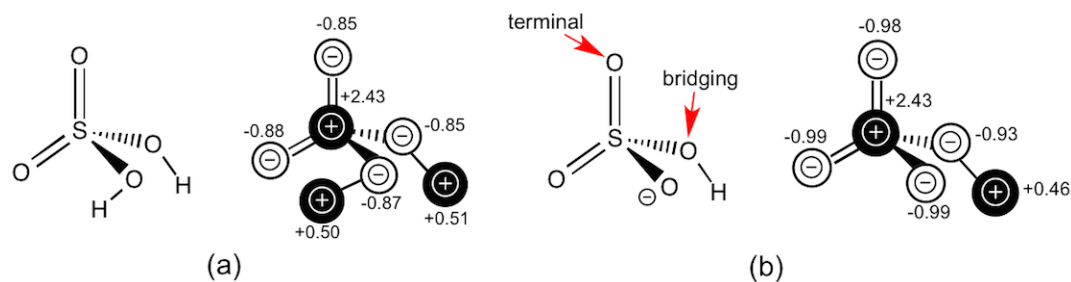


Figure 4.6. NBO partial charge distributions for (a) H_2SO_4 and (b) $[\text{HSO}_4]^-$.

Using the $[\text{C}_4\text{C}_1\text{im}]\text{Cl}/[\text{C}_4\text{Him}]\text{Cl}$ systems as a guide, a systematic search for $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ and $[\text{C}_4\text{Him}][\text{HSO}_4]$ ion pairs was undertaken, with each stable conformation of the $[\text{C}_4\text{Him}]^+$ and $[\text{C}_4\text{C}_1\text{im}]^+$ cations considered. Moreover, for a given cation – anion configuration, the orientation of the $[\text{HSO}_4]^-$ anion could also vary e.g. interaction *via* a terminal or bridging oxygen. A total of 70 $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ ion pairs and 68 $[\text{C}_4\text{Him}][\text{HSO}_4]$ ion pairs have been isolated spanning energy ranges of ≈ 55 and 92 kJ mol^{-1} respectively, **Appendix, Figures A.15 and 17**. Relative energies with, and without, ZPE corrections are provided in the **Appendix, Tables A.27 and 29**. The $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ system shall be considered first and then comparison made with the $[\text{C}_4\text{Him}][\text{HSO}_4]$ system.

Selected examples of $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ ion pairs, chosen to illustrate key structural features, are presented in **Figure 4.7**. With $[\text{HSO}_4]^-$, one of the oxygen atoms of the anion is often found to locate in an established “Cl⁻” position. Therefore, the same labelling convention (i.e. front, top, side and back) is used to identify the stable $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ ion pair configurations. Upon examination of the $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ ion pairs, similarities to the $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$ system can be identified. Namely, the relative energy ordering of the stable configurations follows the same trend; front/top configurations are found to be the lowest in energy, e.g. **Figure 4.7 a-c**, followed by the side configurations ($\approx +30 \text{ kJ mol}^{-1}$), e.g. **Figure 4.7 f and g**, and lastly the back configurations ($\approx +40 \text{ kJ mol}^{-1}$) e.g. **Figure 4.7 j**.

However, the established chloride positions about the $[\text{C}_4\text{C}_1\text{im}]^+$ cation are less well defined for $[\text{HSO}_4]^-$. That is, the multidentate $[\text{HSO}_4]^-$ anion is able to span, and therefore occupy, more than one of the chloride positions simultaneously. For example, an oxygen atom can be located in both the front-but and front-me positions, e.g. **Figure 4.7 b**, the side-but and back positions, e.g. **Figure 4.7 h**, as well as “bridge” between a front and top configuration, e.g. **Figure 4.7 d**. The partial negative charge on the oxygen atoms of (isolated) $[\text{HSO}_4]^-$ is considerable, (-0.99 to -0.93 e) and only slightly reduced from the charge of -1 e on (isolated) chloride. In effect, the oxygen atoms of $[\text{HSO}_4]^-$ can act as “pseudo Cl⁻” ions.

Of the 70 $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ ion pairs, 44 are within the front/top category. Due to the facile rotation of the butyl chain, in conjunction with the different orientations of the $[\text{HSO}_4]^-$ anion, many stable configurations have been isolated within a relatively small energy range ($< 21 \text{ kJ mol}^{-1}$). Within this group of structures, a variety of structural motifs can be seen. Examples of structures in which the anion sits in the plane of the ring have been identified, e.g. **Figure 4.7 b**. However, the formation of secondary interactions with the butyl chain can lead to the anion being “pulled” slightly out of the plane, e.g. **Figure 4.7 a**. As well as examples where the anion bridges between a front and top configuration, structures in which the entire anion sits above (or below) the plane of the ring have also been observed. Within the structure shown in **Figure 4.7 c**, the anion appears to locate over the C² atom of the imidazolium ring. However, within the structure shown in **Figure 4.7 e**, one of the terminal oxygen atoms is positioned over the centre of the ring. In both examples, secondary interactions with the butyl chain would appear to be important in stabilising these structures. The nature of the differing front/top configurations is investigated further for the B3LYP-D2 ion pairs.

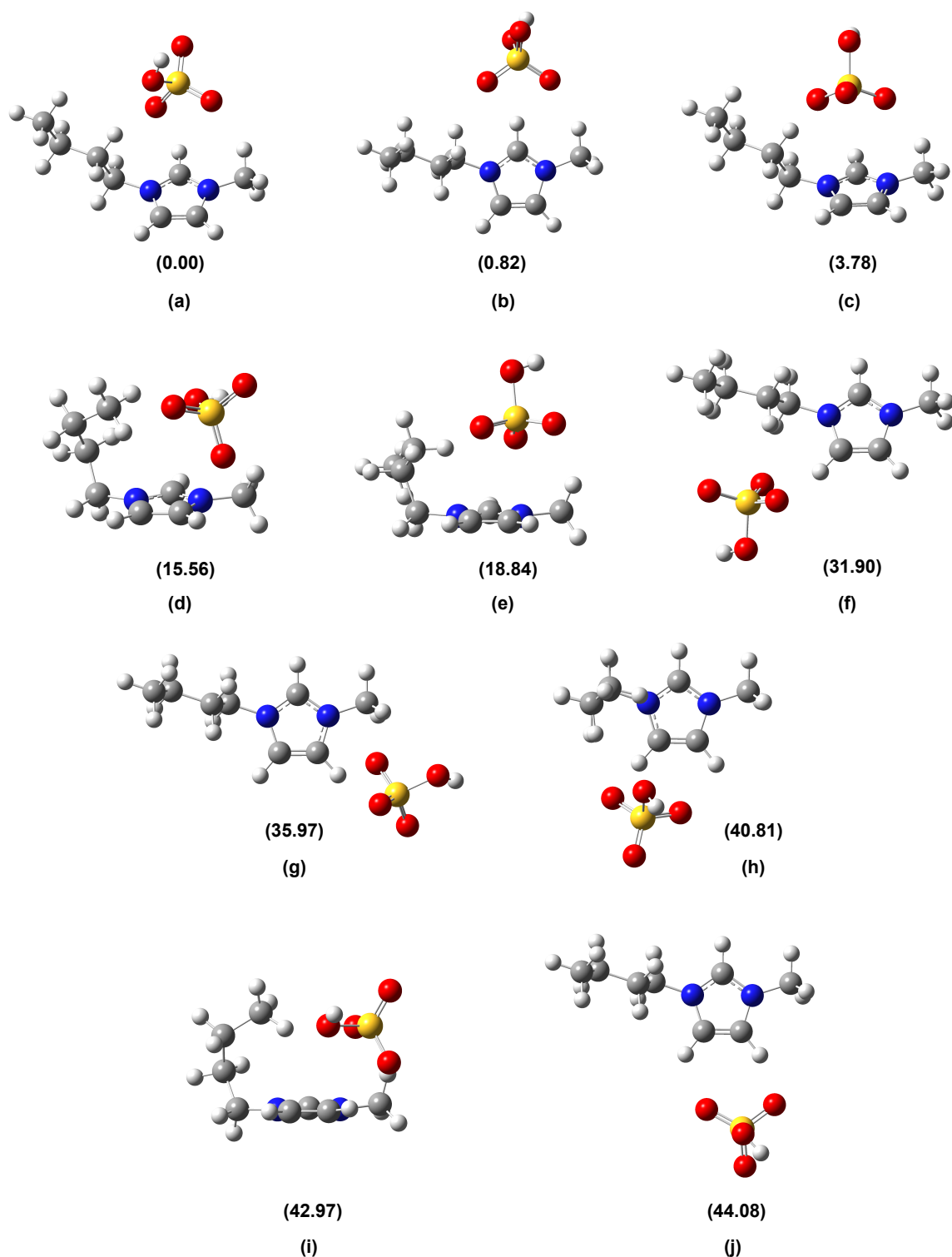


Figure 4.7. Selected $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ ion pairs optimised at the B3LYP/6-311+G(d,p) level. Relative energies in kJ mol^{-1} .

Secondary interactions with the alkyl groups are also of significance for stabilising the higher energy configurations. For example, within the side-but structure shown in **Figure 4.7 f**, $[\text{HSO}_4]^-$ is orientated to interact with the $\text{C}^5\text{-H}$ group, as well as form secondary interactions with more than one of the methylene groups of the butyl chain. Moreover, interaction with the butyl chain may also be important for the stabilisation of out-of-plane side configurations, e.g. **Figure 4.7 i**.

A mutual interdependence between the alkyl chain conformation and anion position can be established. However, it is difficult to separate the influence of the anion on the alkyl chain conformation from the influence of the alkyl chain on the anion position. The former might be anticipated to dominate; maximisation of the interaction with the ring foremost, followed by maximisation of secondary interactions with the alkyl chain. However, examples of ion pairs in which the anion does not locate in the “optimal Cl⁻” position with respect to the ring plane, instead appearing to be “pulled” out-of-plane through interaction with the alkyl chain can also be observed e.g. **Figure 4.7 i**. For the gas phase ion pairs, the importance of the anion-alkyl chain interactions could, however, be overestimated. In the liquid there is also the possibility of the formation of competing alkyl-alkyl chain interactions, in addition to the anion maximising interactions with multiple cations.

A range of different H-bond motifs can be observed within the [C₄C₁im][HSO₄] ion pairs. The in-plane front structure shown in **Figure 4.7 b**, exhibits a mixed chelated/bifurcated motif. A structure in which the anion is shifted from this central position, forming two more linear H-bonds, one with the C²-H group and one with either the methyl or butyl group, has not been found. This would suggest that the formation of four non-linear, and presumably weaker, interactions is overall favoured in this instance. As with the front in-plane example, within the side-me structure shown in **Figure 4.7 g**, an oxygen atom is located in the approximate position that Cl⁻ would occupy, resulting in formation of a chelated H-bond motif. However, for the side-but structure in **Figure 4.7 f**, rather than form a chelated H-bond motif, the anion orientates to form multiple single (and approximately linear) H-bond interactions using more than one of the oxygen atoms. Similarly, for the back structure, **Figure 4.7 j**, rather than position such that one oxygen atom forms a chelated motif (as would be the case for Cl⁻), [HSO₄]⁻ is located so that two single C-H...O interactions occur *via* two different oxygen atoms. Overall, [C₄C₁im][HSO₄] ion pairs therefore feature a large number of non-linear H-bond interactions, as found for the chloride analogue, but also an increased number of single, more linear, interactions due to the ability of [HSO₄]⁻ to act as a H-bond acceptor using multiple oxygen atoms.

Selected examples of [C₄Him][HSO₄] ion pairs are shown in **Figure 4.8**. All the lowest energy structures feature a linear N-H...O interaction. However, as [HSO₄]⁻ is a multidentate anion, a second interaction, with either a C²-H (**Figure 4.8 a**) or C⁴-H (**Figure 4.8 b**) group is formed. These shall be termed the “NH-front” and “NH-side” configurations respectively. While there is some interleaving in the relative energy of these two motifs, for a given cation conformation and anion orientation, the NH-front motif is lower in energy than the NH-side motif, suggesting that interaction with the C²-H unit is energetically more favourable than interaction with C⁴-H. For example, for the “all-trans” conformation of the butyl chain, the NH-front configuration, **Figure 4.8 a**, is $\approx 9.4 \text{ kJ mol}^{-1}$ more stable than the NH-side configuration, **Figure 4.8 b**.

However, although the majority of the NH-front and NH-side structures are relatively low in energy ($< 20 \text{ kJ mol}^{-1}$), examples of higher energy structures ($25\text{--}40 \text{ kJ mol}^{-1}$) featuring these motifs have also been identified. The origin of the increase in energy can be attributed to the orientation of the anion, that is, whether the H-bond acceptor is a terminal or bridging oxygen atom. This can be demonstrated by considering the series of structures (with the same butyl chain conformation) shown in **Figure 4.8 a-e**. In the lowest energy examples of both the NH-front and NH-side motifs, **a** and **b**

respectively, the $[\text{HSO}_4]^-$ anion interacts *via* two terminal oxygen atoms. When the interaction with either $\text{C}^2\text{-H}$ or $\text{C}^4\text{-H}$ is *via* a bridging oxygen, there is a slight increase in energy; $\approx 12 \text{ kJ mol}^{-1}$ in the case of the $\text{C}^2\text{-H}$ interaction (**c**) and $\approx 6 \text{ kJ mol}^{-1}$ in the case of the $\text{C}^4\text{-H}$ interaction (**d**). However, when the interaction with the N-H group is *via* a bridging oxygen (**e**), the increase in energy is more significant, $\approx 25 \text{ kJ mol}^{-1}$. From this it can be inferred that, not surprisingly, the $\text{N-H}\cdots\text{O}$ interaction is the primary interaction within these motifs, with the $\text{C-H}\cdots\text{O}$ interactions being secondary. Moreover, the earlier suggestion, based on the partial charge distribution of the $[\text{HSO}_4]^-$ anion, that there might not be a notable difference in H-bond interactions with the terminal and bridging oxygen atoms is evidently incorrect.

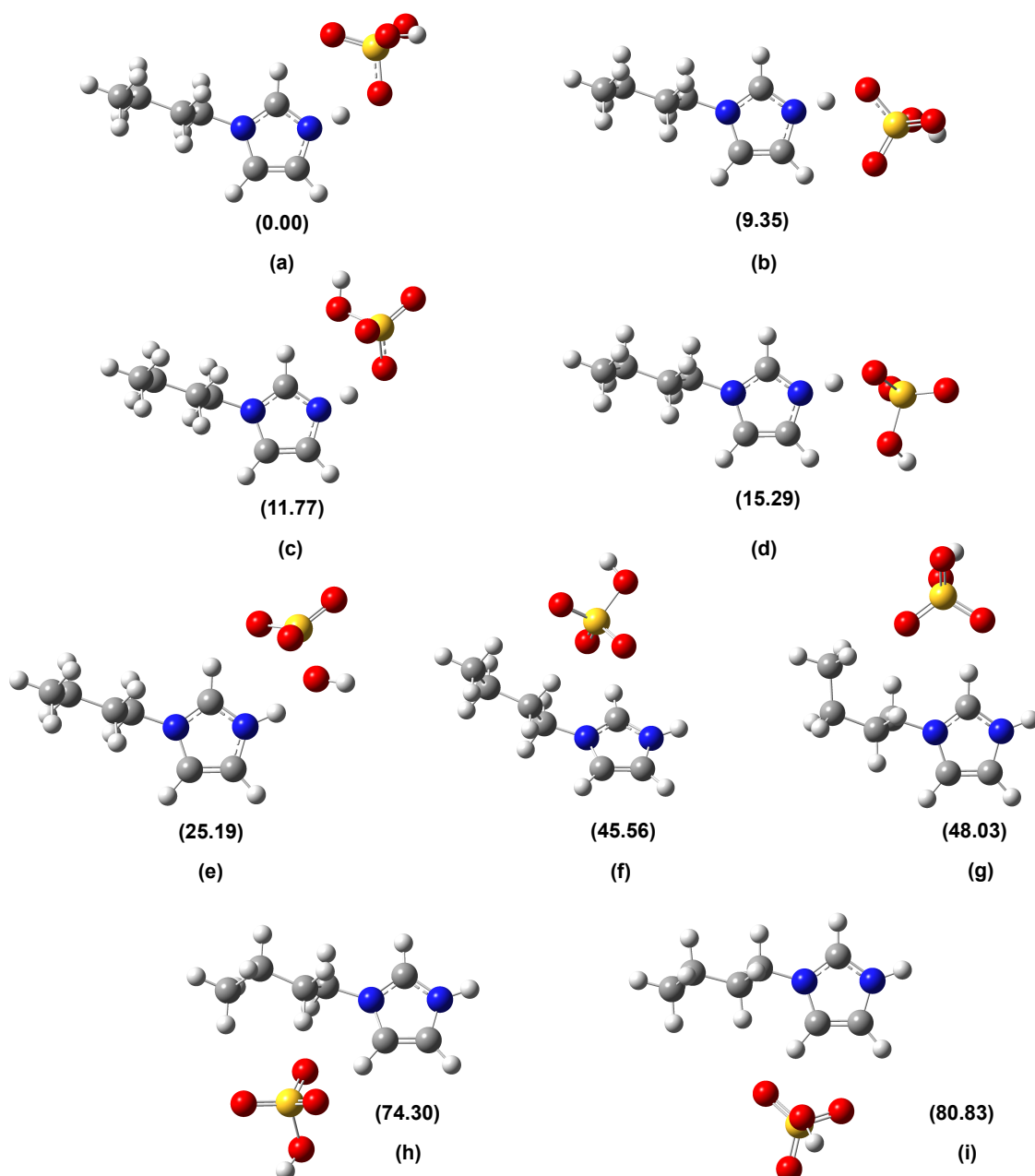


Figure 4.8. Selected $[\text{C}_4\text{Him}][\text{HSO}_4]$ ion pairs optimised at the B3LYP/6-311+G(d,p) level. Relative energies in kJ mol^{-1} .

As with $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, examples of front/top, side-but and side-but/back configurations can also be isolated for $[\text{C}_4\text{Him}][\text{HSO}_4]$. The most stable front/top structure is $\approx 46 \text{ kJ mol}^{-1}$ higher in energy than the lowest energy structure (**Figure 4.8 f**), increasing to $\approx 74 \text{ kJ mol}^{-1}$ for the side-but configuration (**Figure 4.8 h**) and $\approx 81 \text{ kJ mol}^{-1}$ for the side-but/back configuration (**Figure 4.8 i**). Therefore, as found for $[\text{C}_4\text{Him}]\text{Cl}$, the front/side/back motifs are shifted to higher relative energies compared to the aprotic analogues through introduction of the “NH” motifs.

However, unlike for $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, no true top structure has been obtained for $[\text{C}_4\text{Him}][\text{HSO}_4]$, suggesting that the secondary interactions with the methyl group may be key to stabilising this motif. Nevertheless, structures in which $[\text{HSO}_4]^-$ bridges between a front-but and top configuration were obtained, e.g. **Figure 4.8 f**. Replacing the methyl group with a proton also influences the in-plane front interactions. The mixed bifurcated/chelated motif observed within $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ is replaced by a motif in which the $[\text{HSO}_4]^-$ anion forms two single and more linear interactions, one with the $\text{C}^2\text{-H}$ group and a second with a methylene group of the butyl chain, e.g. **Figure 4.8 g**.

The structure shown in **Figure 4.8 i** is an example of a bridged side-but/back motif, with one oxygen forming an approximately linear interaction with the $\text{C}^5\text{-H}$ group and a second oxygen sitting between $\text{C}^5\text{-H}$ and $\text{C}^4\text{-H}$ in the approximate position that chloride would occupy, also observed within $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$. However, unlike for $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, an analogous interaction shifted toward $\text{C}^4\text{-H}$, i.e. a structure in which the anion interacts almost equally with both $\text{C}^4\text{-H}$ and $\text{C}^5\text{-H}$, could not be obtained for $[\text{C}_4\text{Him}][\text{HSO}_4]$.

The $[\text{C}_4\text{Him}][\text{HSO}_4]$ ion pairs therefore reflect both features of the aprotic analogue and protic $[\text{C}_4\text{Him}]\text{Cl}$. As with $[\text{C}_4\text{Him}]\text{Cl}$, interaction with the N-H group is strongly favoured. However, as with $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, the stable anion configurations are less well defined, with the multidentate $[\text{HSO}_4]^-$ anion able to “span” between two positions. Compared to $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, the orientation of the $[\text{HSO}_4]^-$ anion has a more significant influence on the relative energy of the $[\text{C}_4\text{Him}][\text{HSO}_4]$ ion pairs.

Energy “band” diagram and discussion

The relative energies of all the B3LYP $[\text{C}_4\text{Him}]\text{Cl}$, $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ and $[\text{C}_4\text{Him}][\text{HSO}_4]$ ion pairs are plotted in **Figure 4.9**. The most obvious feature of this plot is the existence of energy “bands”, with each band corresponding to particular cation-anion configurations. The configurations associated with an energy band are illustrated within **Figure 4.9**.

For $[\text{C}_4\text{Him}]\text{Cl}$, four well defined bands are evident. All structures with the NH configuration are contained within the lowest energy band, with the three higher energy bands corresponding to the front/top, side-but and back configurations respectively. The large energy difference between structures with the NH configuration and the front/top structures is apparent.

For $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ there are two bands, with the lower energy band consisting of all front and top structures and the higher energy band corresponding to side and back configurations. The analogous bands are shifted to higher energies for $[\text{C}_4\text{Him}][\text{HSO}_4]$, with the lowest energy band for $[\text{C}_4\text{Him}][\text{HSO}_4]$ consisting of the NH-front and NH-side structures. However, compared to $[\text{C}_4\text{Him}]\text{Cl}$, the energy difference between the NH structures and the front structures is significantly reduced.

The anion position with respect to the cation is evidently the most significant factor in determining the relative energy of an ion pair. However, the relative energy within a band is influenced by the conformation of the butyl chain, and for the $[\text{HSO}_4]^-$ systems, the anion orientation. For the NH configurations of $[\text{C}_4\text{Him}]\text{Cl}$, the butyl chain conformation leads to a variation in the relative energy of $\approx 11.5 \text{ kJ mol}^{-1}$. The influence of the anion orientation can be small. For $[\text{C}_4\text{Him}][\text{HSO}_4]$, it was found that within the lowest energy NH structures, the $[\text{HSO}_4]^-$ anion interacts *via* two terminal oxygen atoms. In these cases, the orientation, or positioning, of the (non-interacting) hydroxyl group has little influence on the relative energy. However, when one of the specific interactions with a ring proton occurs *via* a bridging oxygen, an increase in energy of between $6\text{--}25 \text{ kJ mol}^{-1}$ was observed. Thus, the influence of the anion orientation on the relative energy of an ion pair can be greater than that of the butyl chain. When the anion orientation and chain conformation are considered together, the wide energy range ($\approx 40 \text{ kJ mol}^{-1}$) spanned by the NH configurations of $[\text{C}_4\text{Him}][\text{HSO}_4]$ can be explained.

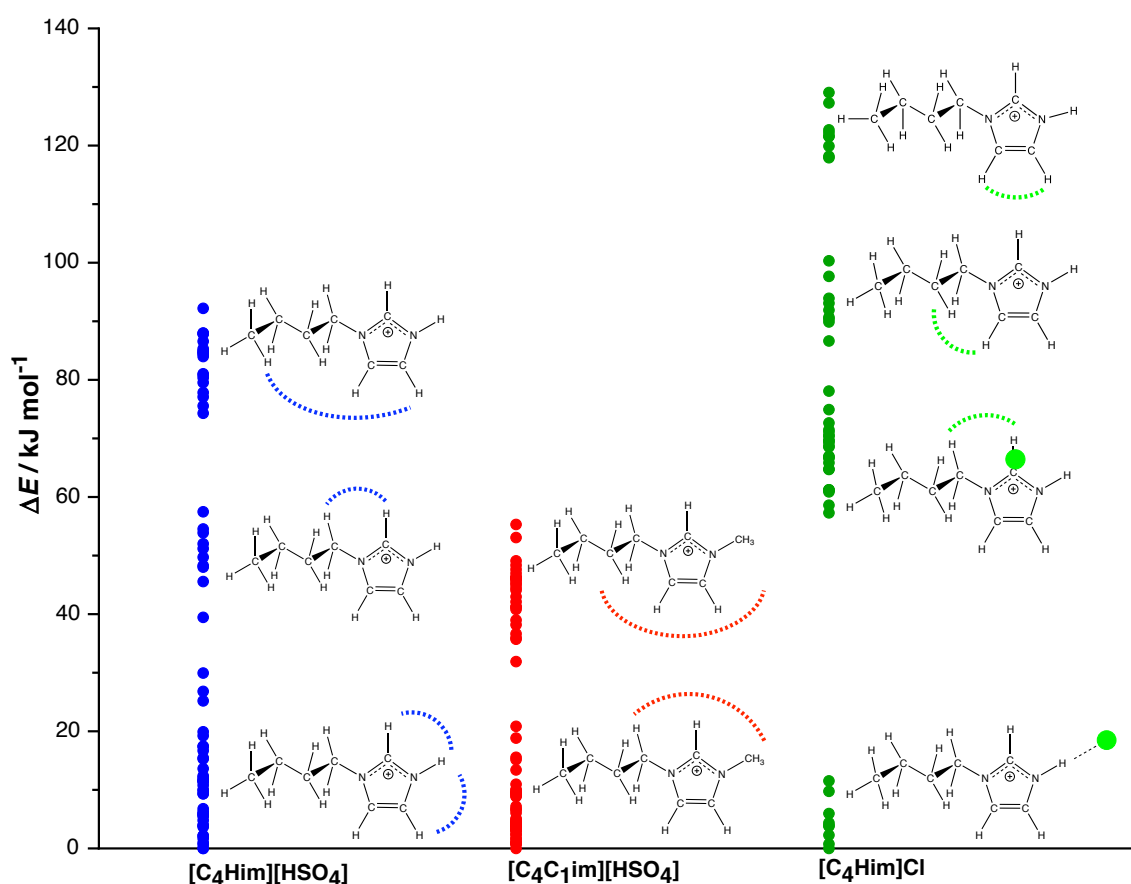


Figure 4.9. Relative energies of the B3LYP ion pairs. Cation-anion configurations corresponding to the energy “band” shown alongside.

Whilst **Figure 4.9** is useful for comparing the relative energy ordering of the ion pairs, the association energies of these systems have not yet been considered. The computed association energies, E_a , for lowest energy ion pairs of $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, $[\text{C}_4\text{Him}][\text{HSO}_4]$, $[\text{C}_4\text{Him}]\text{Cl}$ and, for comparison, $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$

are provided in **Table 4.1**, where $E_a = E(\text{ion pair}) - E(\text{cation}) - E(\text{anion})$. Association energies have been computed with respect to the lowest energy cation conformation.

With both the Cl^- and $[\text{HSO}_4]^-$ anions, the association with the protic cation is greater than with the aprotic analogue (by $\approx 65 \text{ kJ mol}^{-1}$ in the case of Cl^- and $\approx 47 \text{ kJ mol}^{-1}$ in the case of $[\text{HSO}_4]^-$). Additionally, the change in E_a upon changing the anion is greater for the protic cation compared to the aprotic. In both cases, association with Cl^- is moderately stronger (by $\approx 24 \text{ kJ mol}^{-1}$ for $[\text{C}_4\text{C}_1\text{im}]^+$ and $\approx 43 \text{ kJ mol}^{-1}$ for $[\text{C}_4\text{Him}]^+$). The ordering of these association energies could be anticipated using simple arguments based on H-bonding; stronger H-bonding with the protic cation and with the Cl^- anion.

Based on these values it might be suggested that the melting points/viscosities of the protic systems would be higher than the aprotic analogues. However, correlations between the computed association energies of ion pairs and such properties are known to be poor.³⁴ Moreover, the additional complication of possible anion-anion interactions within the $[\text{HSO}_4]^-$ systems cannot be accounted for using simple ion pairs.

Table 4.1. Computed association energies (kJ mol^{-1}) of the lowest energy ion pairs of $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, $[\text{C}_4\text{Him}][\text{HSO}_4]$, $[\text{C}_4\text{Him}]\text{Cl}$ and for reference, $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$ at the B3LYP/6-311+G(d,p) level.

Anion	Cation	
	$[\text{C}_4\text{C}_1\text{im}]^+$	$[\text{C}_4\text{Him}]^+$
Cl^-	-377.6	-443.0
$[\text{HSO}_4]^-$	-353.5	-400.4

Some of the difficulties in rationalising observed macroscopic properties of ionic liquids in terms of H-bonding were introduced in **Chapter 1**. In some cases an increase in viscosity, for example, could be explained by an increase in cation-anion H-bonding. In other cases, namely the increase in viscosity when the C^2 position of an imidazolium ring is methylated, are more difficult to interpret. The different arguments used to explain this phenomenon were considered.

A further problem in trying to establish structure-property relationships for protic ionic liquids is the current lack of reliable experimental data for many systems. Moreover, macroscopic properties of ionic liquids, both aprotic and protic, can be significantly influenced by the presence of water (amongst other contaminants).³ For protic ionic liquids, the difficulties in ensuring that an exact 1:1 acid to base ratio is achieved can introduce an additional source of error. Nevertheless, the melting points and/or viscosity of selected protic and aprotic analogues are presented in **Table 4.2**, with values sourced from both within the Welton research group and the literature.

According to the values in **Table 4.2**, the melting point of $[\text{C}_4\text{Him}]\text{Cl}$ is $\approx 25^\circ\text{C}$ lower than the melting point of $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$. This is relatively consistent with the reported melting points of $[\text{C}_2\text{Him}]\text{Cl}$ and $[\text{C}_2\text{C}_1\text{im}]\text{Cl}$, with the melting point of $[\text{C}_2\text{C}_1\text{im}]\text{Cl}$ $\approx 27^\circ\text{C}$ lower. Therefore, contrary to what might be expected based on the computed association energies, the protic $[\text{C}_n\text{Him}]\text{Cl}$ systems have lower melting points than the aprotic analogues. This observation could be consistent with the argument suggesting that the introduction of strong and directional H-bonds results in disruption of the Coulomb network.

However, reports for the equivalent systems with the trifluoromethanesulphonate anion, [C₄C₁im][OTf] and [C₄Him][OTf], suggest that both the melting point and viscosity are higher for the protic system. The viscosity of [C₄Him][HSO₄] is also higher than for [C₄C₁im][HSO₄]. Assuming there is no difference in the potential anion-anion interactions, the higher viscosity of [C₄Him][HSO₄], could be attributable to the increase in the cation-anion H-bonding interactions. The same could be said for the analogous [OTf][−] systems.

That there is a difference in the melting point behaviour of the chloride and trifluoromethanesulphonate systems is not wholly unexpected. Establishing common trends for related ionic liquid systems is known to be problematic. However, the origin of this behaviour cannot yet be fully explained. Therefore, whilst examination of the ion pairs of [C₄Him]Cl, [C₄C₁im][HSO₄] and [C₄Him][HSO₄] indicates that replacing the methyl group with a proton does result in key changes to the local structuring, as well as an increase in the association energy of the ion pairs, the influence on properties such as melting point and viscosity is harder to discern.

Table 4.2. Reported melting points (T_m) and viscosities (η) of selected ionic liquids.

Ionic liquid	$T_m/^\circ\text{C}$	η/cP (T in $^\circ\text{C}$)
1-butyl-3-methyl-imidazolium chloride [C ₄ C ₁ im]Cl	65 ³⁵	-
1-butylimidazolium chloride [C ₄ Him]Cl	40 ³⁵	-
1-ethyl-3-methyl-imidazolium chloride [C ₂ C ₁ im]Cl	87 ³⁶	-
1-ethylimidazolium chloride [C ₂ Him]Cl	58 ³⁷	-
1-ethyl-3-methyl-imidazolium trifluoromethanesulphonate [C ₄ C ₁ im][OTf]	-11 ³⁸	43 (25) ³⁹ 36 (30) ³⁹
1-ethylimidazolium trifluoromethanesulphonate [C ₄ Him][OTf]	8 ³⁷	58 (27) ³⁷
1-butyl-3-methyl-imidazolium hydrogensulphate [C ₄ C ₁ im][HSO ₄]	-	286 (25) ⁴⁰
1-butylimidazolium hydrogensulphate [C ₄ Him][HSO ₄]	-	5690 (25) ⁴⁰

2.2.2 Local structuring: The influence of dispersion

The importance of dispersion within ionic liquids has been established. Whilst the B3LYP ion pairs are useful for providing initial insight into the differences in local structuring between related aprotic and protic imidazolium systems, dispersion interactions are not well recovered. To establish the influence of dispersion on the structuring of these systems, all B3LYP ion pairs were re-optimised, starting from the B3LYP structures, at the B3LYP-D2 level. In total, 44 [C₄Him]Cl, 61 [C₄C₁im][HSO₄] and 62 [C₄Him][HSO₄] ion pairs were obtained at the B3LYP-D2 level, **Appendix, Figures A.14, 16 and 18** respectively. Relative energies with, and without, ZPE corrections are provided in the **Appendix, Tables 26, 28 and 30**.

In many cases, particularly for the protic systems, no significant change in geometry is observed upon optimisation with the dispersion correction. For [C₄Him]Cl and [C₄Him][HSO₄], the same cation-anion configurations, as identified at the B3LYP level, can also be observed at the

B3LYP-D2 level. For $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, there is an increased preference for out-of-plane front, or top, structures, resulting in a reduction in the number of in-plane front structures. For all systems it was more difficult to isolate stable back structures.

The relative energies of the B3LYP-D2 ion pairs are plotted alongside the relative energies of the B3LYP ion pairs in **Figure 4.10**. From **Figure 4.10** it can be seen that the energy bands for the B3LYP-D2 ion pairs are “compressed” relative the B3LYP counterparts i.e. a given band is shifted to a lower energy with a reduction in the relative energy spanned by structures of a given configuration. For example, the 9 $[\text{C}_4\text{Him}]\text{Cl}$ ion pairs with the NH configuration span a relative energy range of 11.5 kJ mol^{-1} at the B3LYP level, decreasing to 5.5 kJ mol^{-1} at the B3LYP-D2 level. For $[\text{C}_4\text{Him}][\text{HSO}_4]$, the already small energy difference (at B3LYP) between structures with the front/top configuration and the higher energy examples of NH-front/side structures is further reduced, such that the NH structures and front/top structures effectively form a continuum. The clear exceptions to the general trend for a lowering of energy are the $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ side and back structures, which are shifted to higher energies compared to the B3LYP analogues.

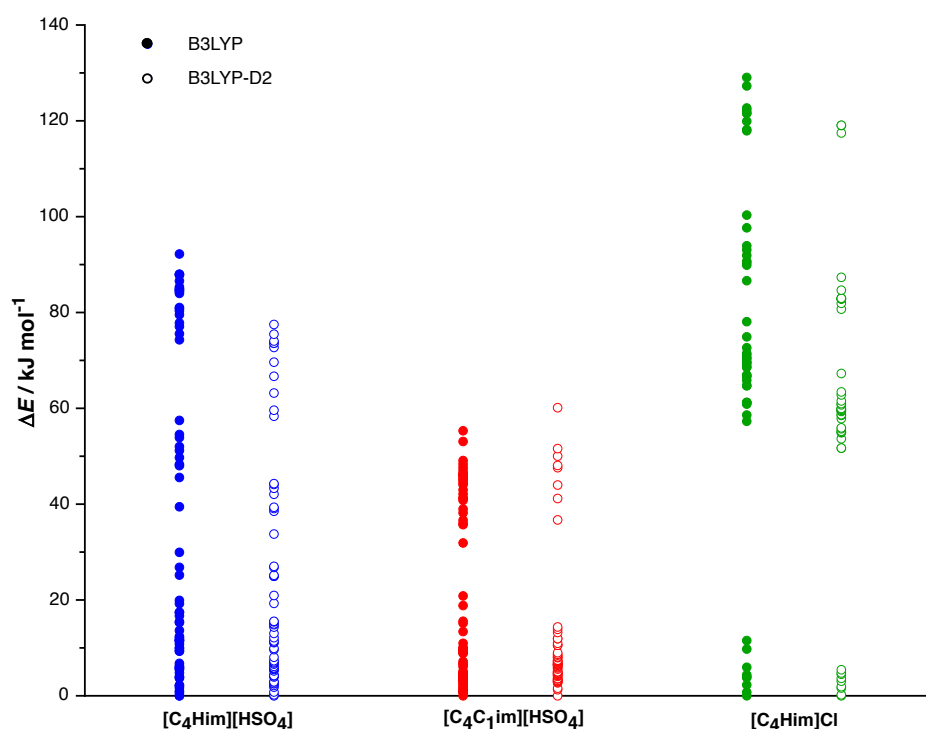


Figure 4.10. Relative energies of the B3LYP-D2 ion pairs (open circles) plotted against the relative energies of the B3LYP ion pairs (filled circles).

In all cases, the association energies, E_a , of the lowest energy ion pairs increase upon inclusion of the dispersion correction, **Table 4.3**. However, the increase is smaller for the Cl^- systems compared to the $[\text{HSO}_4]^-$ systems, and smaller for systems with the $[\text{C}_4\text{Him}]^+$ cation relative to $[\text{C}_4\text{C}_1\text{im}]^+$. This likely reflects the link between the size of the dispersion contribution and the size of the ions. The largest increase in E_a ($\approx +31 \text{ kJ mol}^{-1}$) is therefore found for $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, which is also the system that exhibits the largest changes in geometry at the B3LYP-D2 level.

Overall, the net effect is to decrease the difference in the values of E_a between the Cl^- and $[\text{HSO}_4]^-$ systems (reduced to $< 5 \text{ kJ mol}^{-1}$ between $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$ and $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, and to $\approx 33 \text{ kJ mol}^{-1}$ between $[\text{C}_4\text{Him}]\text{Cl}$ and $[\text{C}_4\text{Him}][\text{HSO}_4]$). Likewise, a decrease in the difference in E_a between the protic and aprotic analogues is observed ($\approx 62 \text{ kJ mol}^{-1}$ between $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$ and $[\text{C}_4\text{Him}]\text{Cl}$, and $\approx 33 \text{ kJ mol}^{-1}$ between $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ and $[\text{C}_4\text{Him}][\text{HSO}_4]$).

Table 4.3. Computed association energies (kJ mol^{-1}) of the lowest energy ion pairs of $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, $[\text{C}_4\text{Him}][\text{HSO}_4]$, $[\text{C}_4\text{Him}]\text{Cl}$ and for reference, $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$ at the B3LYP-D2/6-311++G(d,p) level.

Anion	Cation	
	$[\text{C}_4\text{C}_1\text{im}]^+$	$[\text{C}_4\text{Him}]^+$
Cl^-	-389.0	-450.5
$[\text{HSO}_4]^-$	-384.6	-417.6

The influence of dispersion on the geometry of ion pairs was most significant for the $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ system. Upon inclusion of the dispersion correction there was found to be an increased preference for the $[\text{HSO}_4]^-$ anion to move from an in-plane front position towards an out-of-plane top position. However, as the $[\text{HSO}_4]^-$ anion is able to bridge between these two configurations, there is a spectrum of different structures. The angle, ϕ , between the vector passing along the $\text{C}^2\text{-H}$ bond and the vector between C^2 and the S of $[\text{HSO}_4]^-$ (inset **Figure 4.11**) can be used as a measure of the extent to which the anion sits out of plane (0°). The influence of dispersion can be demonstrated by comparing the angle distribution for all B3LYP and B3LYP-D2 ion pairs falling into the front/top category, **Figure 4.11**. At the B3LYP level, the majority of ion pairs within this category have a value of ϕ below 40° . In contrast, the majority of the B3LYP-D2 ion pairs in this category have ϕ values of 50 to 70° . The observed increase in ϕ could be consistent with there being increased interaction with the π system of the ring.

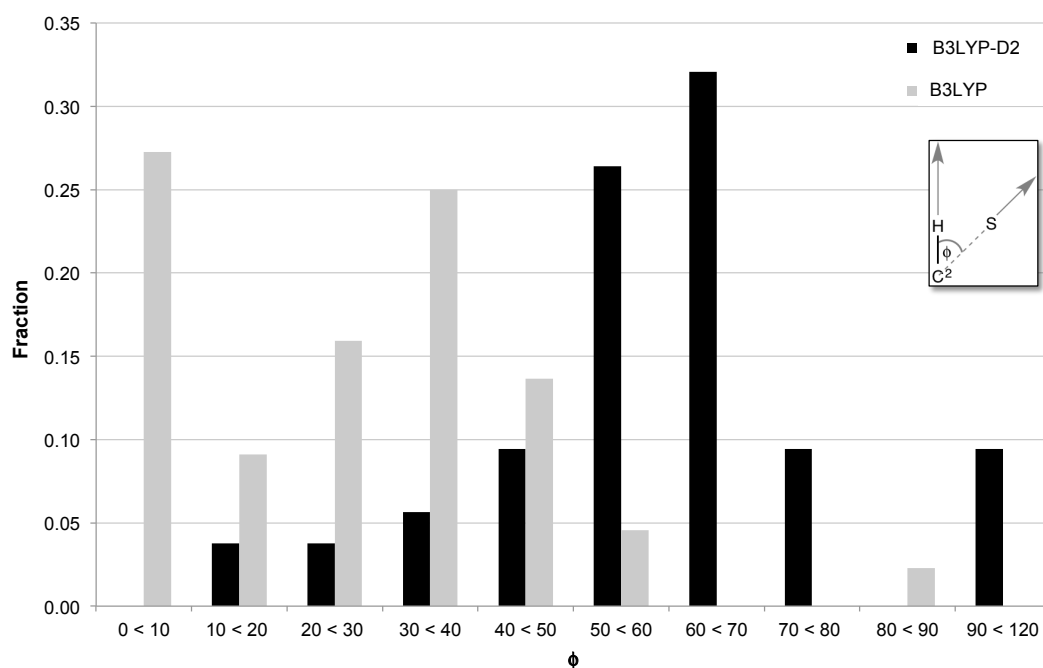


Figure 4.11. H-C²...S angle distributions for $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ ion pairs with a front or top configuration.

The inclusion of the dispersion correction therefore has a moderate influence on both the association and relative energies of the ion pairs; association energies show a small increase and there is, in the majority of cases, a small decrease in the relative energy differences between different cation-anion configurations. In terms of geometries, many of the cation-anion configurations obtained at the B3LYP level could also be isolated at the B3LYP-D2 level. However, for all systems it becomes more difficult to isolate structures with a back configuration after addition of the dispersion correction. Overall, the most notable effect in terms of geometry is found for the low energy [C₄C₁im][HSO₄] ion pairs, where an increased preference for out-of-plane configurations is apparent.

Analysis of selected [C₄C₁im][HSO₄] ion pairs: interactions within front and top configurations

To further understand the nature of the interactions influencing the structuring, a small number of B3LYP-D2 [C₄C₁im][HSO₄] ion pairs with differing values of ϕ were selected for a more in depth analysis using QTAIM and through examination of the MOs. Due to the variation in ϕ , it can be difficult to determine whether a structure is an example of a front, top or possibly a mixed front/top configuration through visual inspection alone. The possibility of anion- π^+ interactions was introduced in **Chapter 1**, where we suggested that evidence of an interaction between an anion and the π system of the ring could be used to identify an anion- π^+ interaction.

QTAIM molecular graphs of the selected ion pairs, labelled (a) – (f) in ascending order of ϕ , are shown in **Figure 4.12**. Full details of the QTAIM analysis can be found in the **Appendix, Table A.31**. Using our outlined criteria (**Chapter 1, Table 1.1**), values of ρ_{BCP} for weak, moderate and strong H-bonds are 0.002-0.02 au, 0.02-0.05 au and >0.05 au respectively.

Ion pairs (a) and (b) both appear to be examples of structures with a “front” type configuration. (a) is a relatively rare example (at the B3LYP-D2 level) of a structure with the [HSO₄][−] anion sitting in the plane of the ring ($\phi \approx 13^\circ$). One oxygen atom is positioned in the approximate front-me position, forming a chelated H-bond motif. Values of ρ_{BCP} reveal that the secondary C-H...O interaction with the methyl group (0.009 au) is significantly weaker than the primary interaction with C²-H (0.033 au). While the second oxygen atom in the plane of the ring initially appears to be in an approximate front-but position, it is shifted such that no interaction with C²-H occurs. Instead, two H-bonds with the butyl group are formed, although again relatively unequal in strength, the interaction with the methylene C-H group ($\rho_{\text{BCP}} = 0.018$ au) being stronger than the interaction with the terminal methyl group ($\rho_{\text{BCP}} = 0.008$ au).

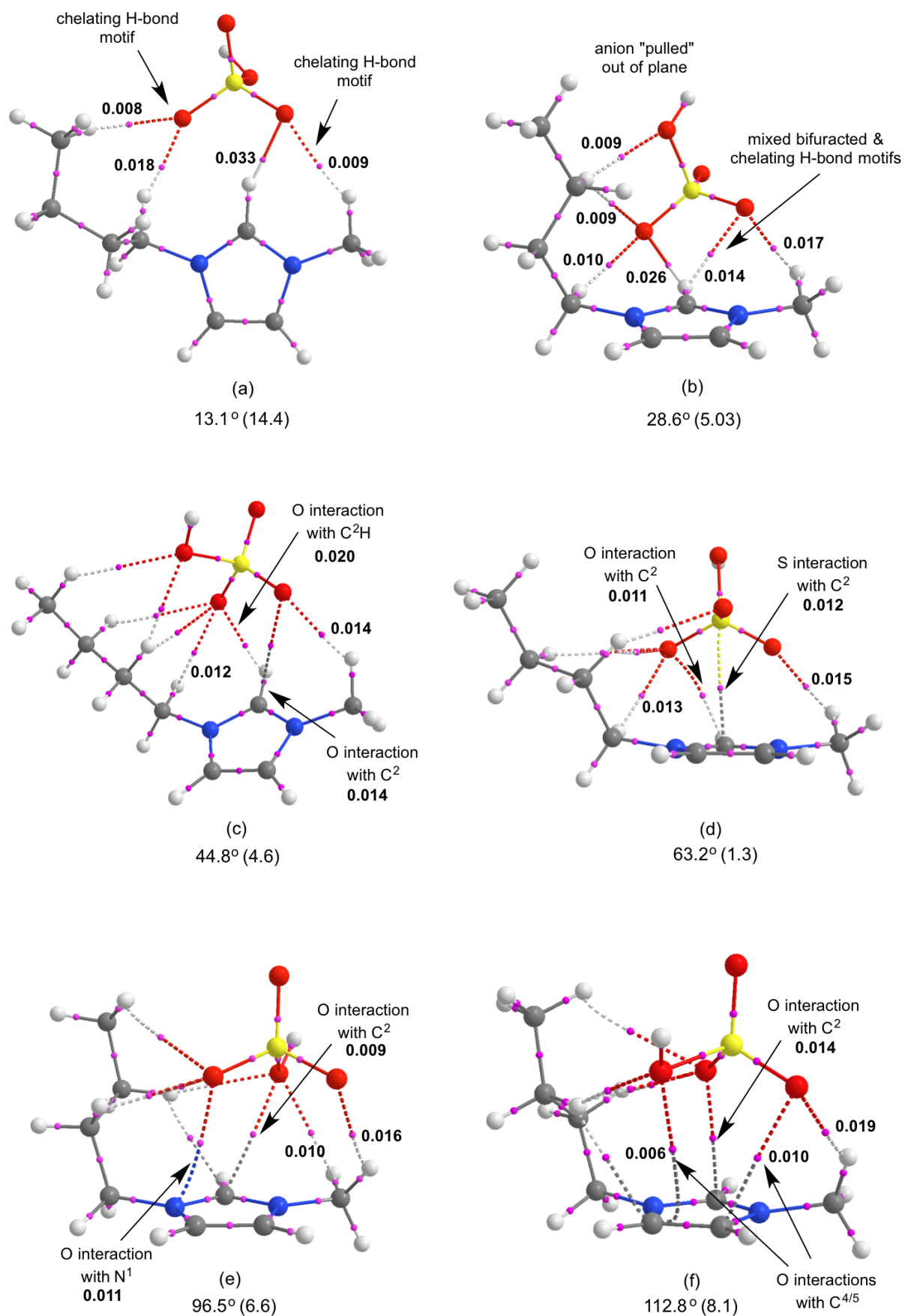


Figure 4.12. QTAIM molecular graphs for selected B3LYP-D2 [C₄C₁im][HSO₄] ion pairs. BCPs shown as pink dots, RCPs and CCPs omitted for clarity. Values of ρ_{BCP} (au) for selected interactions indicated. ϕ and the relative energy of the structure in kJ mol⁻¹ detailed beneath each system.

Within ion pair (b), two oxygen atoms also occupy approximate front-me/but positions, albeit with $\phi \approx 29^\circ$, slightly further out of the plane relative to structure (a). (b) features the mixed bifurcated and chelated H-bond motif. Two oxygen atoms form a H-bond with the C²-H unit (bifurcated motif), although not of equal strength. Asymmetry in anionic bifurcated C-H...O⁻ H-bond motifs has previously been reported elsewhere.⁴¹ In this example, one of the oxygen atoms forms a moderately strong H-bond with C²-H ($\rho_{\text{BCP}} = 0.026$ au) and weaker secondary interactions with the butyl chain, whilst the second oxygen forms a weak H-bond with C²-H ($\rho_{\text{BCP}} = 0.014$ au) and a slightly stronger H-bond with one of the methyl C-H moieties ($\rho_{\text{BCP}} = 0.017$ au). Moreover, a third oxygen of [HSO₄]⁻ forms a very weak H-bond interaction ($\rho_{\text{BCP}} = 0.009$ au) with the butyl chain. The formation of secondary H-bond interactions with the butyl chain, in the observed conformation, could perhaps explain why the anion is seemingly “pulled” from the plane of the ring. Nevertheless, the QTAIM analysis of ion pairs (a) and (b) is consistent with these structures being termed front configurations.

As shown for structures (a) and (b), the multidentate anion can span more than one of the established anion positions. However, rather than spanning between the two front positions, the [HSO₄]⁻ anion within ion pair (c) ($\phi \approx 45^\circ$) appears to “bridge” between the front-but and top configurations. The oxygen directed towards the front-but position forms a borderline weak/moderate H-bond with C²-H ($\rho_{\text{BCP}} = 0.020$ au) in addition to a number of secondary H-bond interactions with the butyl chain. A second oxygen atom locates above the C²-H bond, with a BCP detected between O and the C² atom of the ring. The value of ρ_{BCP} (0.014 au) for the O...C² interaction is of the same magnitude as the value of ρ_{BCP} for the secondary H-bond formed with the methyl C-H group. As with ion pair (b), a third oxygen atom also forms secondary H-bonds with the butyl chain.

Ion pairs (d) – (f) are all examples of structures in which the anion locates above the plane of the ring and thus would be classified as “top”. However, are the interactions the same within these examples?

Within (d) ($\phi \approx 65^\circ$), [HSO₄]⁻ is positioned over the C²-H bond, with two oxygen atoms sitting directly above the approximate front-me/but positions. Interestingly, despite one of the oxygen atoms of [HSO₄]⁻ being situated almost perpendicular to C², QTAIM detects an interaction between the sulphur atom of [HSO₄]⁻ and C² ($\rho_{\text{BCP}} = 0.012$ au). H-bond interactions with the methyl group ($\rho_{\text{BCP}} = 0.015$ au) and butyl group ($\rho_{\text{BCP}} = 0.005 - 0.013$ au) are also observed. Moreover, even in this out-of-plane configuration, a weak H-bond with C²-H is found ($\rho_{\text{BCP}} = 0.011$ au).

Ions pairs (e) and (f) ($\phi \approx 97^\circ$ and 113° respectively) differ, in that the anion does not locate directly over the C²-H bond. Within (e) one of the oxygen atoms of [HSO₄]⁻ is situated approximately over the ring centroid, with a BCP between O and N¹ located ($\rho_{\text{BCP}} = 0.011$ au). However, an O...C² interaction ($\rho_{\text{BCP}} = 0.009$ au) is also identified. Within (f) an O...C² interaction with a slightly larger value of ρ_{BCP} (0.014 au) is found in conjunction with O...C⁴ and O...C⁵ interactions ($\rho_{\text{BCP}} = 0.006$ and 0.010 au respectively). As with the other selected ion pairs, H-bond interactions with the butyl and methyl groups can be identified. The strongest of these, in both cases, is with a methyl C-H (0.014 au for (e) and 0.019 au for (f)).

The QTAIM analysis of the selected ion pairs therefore reveals a subtle change in the interplay of H-bond and possible anion- π^+ interactions as the anion moves from a front in-plane position to locate above the ring (i.e. as ϕ increases).

An increased preference for the top position for larger anions has previously been observed.⁴² One possible explanation for this phenomenon is an increase in the dispersion interaction between a larger anion and the π -system. With QTAIM an interaction between the anion and a heteroatom of the ring (i.e. a BCP) could be suggestive of a possible anion- π^+ interaction. However, unlike for Cl^- , which forms very directional interactions with C^2 when in the top position, the findings here suggest that for the larger multidentate $[\text{HSO}_4]^-$ anion, the “top” configuration is more varied. For example, the QTAIM analysis suggests possible interaction with both the front N-C-N and back C=C moieties of the ring. The small values of ρ_{BCP} for these interactions (approximately the same as for a weak H-bond), is consistent with these interactions being largely electrostatic and/or dispersive.

The front structures (a) and (b) exhibit the expected combination of primary ($\text{C}^2\text{-H}\cdots\text{O}$) and secondary (methyl/butyl $\text{C-H}\cdots\text{O}$) H-bond interactions. Interestingly, complete loss of the $\text{C}^2\text{-H}\cdots\text{O}$ interaction does not occur until quite large values of ϕ . However, the strength of the $\text{C}^2\text{-H}\cdots\text{O}$ interaction does decrease concomitantly with the decrease in the linearity of the interaction. For example the values of ρ_{BCP} decrease as 0.033 au (a) > 0.026 au (b) > 0.020 au (c) and 0.011 au (d).

H-bond interactions with the alkyl groups are significant for all six of the ion pairs examined; front, “bridging” and top configurations. The maximum value of ρ_{BCP} for an alkyl $\text{C-H}\cdots\text{O}$ contact stays relatively consistent across the selected ion pairs i.e. 0.018 au (a), 0.017 au (b), 0.014 au (c), 0.015 au (d), 0.016 au (e) and 0.019 au (f). This possibly reflects the ability of the alkyl groups to rotate in order to form stronger H-bond interactions. These “secondary” H-bond interactions are evidently important for stabilisation of out-of-plane, as well as in-plane, configurations.

As has been established, MOs can also be used to support the case for H-bond and anion- π^+ interactions. Selected fragment orbitals (FOs) of the $[\text{C}_4\text{C}_{1\text{im}}]^+$ cation and $[\text{HSO}_4]^-$ anion are shown in **Figure 4.13** with selected MOs of ion pairs (a) to (f) shown in **Figures 4.14-18** (for reference, the ion pair HOMO corresponds to MO 63). Ion pair MOs are labelled according to the ion pair (i.e. a-f) and the MO number. For example, a-MO40 corresponds to MO 40 of ion pair (a).

For each ion pair, the LUMO corresponds to the LUMO FO of $[\text{C}_4\text{C}_{1\text{im}}]^+$ (**Figure 4.13 a**) and the HOMO to the HOMO FO of $[\text{HSO}_4]^-$ (an antibonding combination of 2p-AOs, **Figure 4.13 d**). This is not uncommon for ionic liquid systems. However, a relatively large number of $[\text{C}_4\text{C}_{1\text{im}}][\text{HSO}_4]$ ion pair MOs show cation – anion FO mixing. In contrast, for $[\text{C}_4\text{C}_{1\text{im}}]\text{Cl}$ there are relatively few examples of MOs featuring contributions from both cation and anion FOs. This would suggest that the cation and anion FOs within $[\text{C}_4\text{C}_{1\text{im}}][\text{HSO}_4]$ are relatively well “matched” in energy and indicates a larger degree of delocalisation.

π -type FOs of $[\text{C}_4\text{C}_{1\text{im}}]^+$ include the HOMO FO (**Figure 4.13 b**) as well as deeper energy orbitals e.g. the all in-phase π -orbital, **Figure 4.13 c**. Anion- π^+ interactions with Cl^- involve the directional interaction between a Cl^- 3p-AO with the HOMO of the anion (e.g. **Chapter 1, Figure 1.13**). The tetrahedral geometry of $[\text{HSO}_4]^-$ results in a tripodal arrangement of oxygen atoms, each of which can contribute a 2p-AO to form a π -type FO, **Figure 4.13 e**. Moreover, the π -type FO of $[\text{HSO}_4]^-$

lies deeper in energy than the p-AO of Cl^- . Potentially, there could be interaction between the “ π -face” of the $[\text{C}_4\text{C}_1\text{im}]^+$ cation and the $[\text{HSO}_4]^-$ anion.

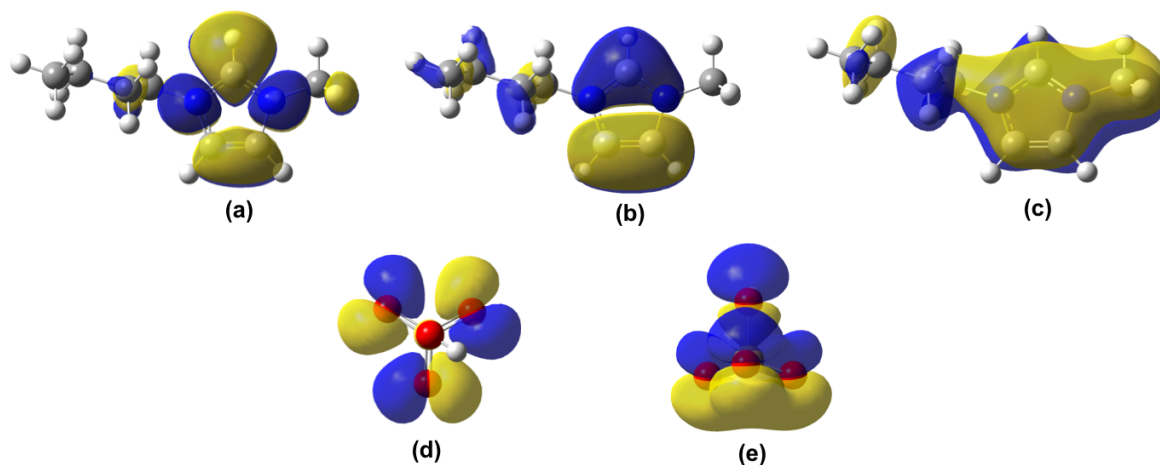


Figure 4.13. Selected FOs of $[\text{C}_4\text{C}_1\text{im}]^+$ and $[\text{HSO}_4]^-$. $[\text{C}_4\text{C}_1\text{im}]^+$ LUMO (a), HOMO (b) and deep π FO (c). $[\text{HSO}_4]^-$ HOMO (d) and π type FO (e).

For each of the ion pairs examined, MOs indicating the formation of alkyl $\text{C-H}\cdots\text{O}$ H-bonds can be identified. Such examples include relatively high energy orbitals, e.g. b-MO54 **Figure 4.14 i**, as well as deeper energy orbitals, e.g. a-MO44, **Figure 4.14 ii**. Interactions with $\text{C}^2\text{-H}$ σ type FOs are also apparent for ion pairs (a) – (c), e.g. a-MO40, b-MO39 and c-MO39 **Figure 4.15 i-iii**. A simplified representation of the interaction with the $\text{C}^2\text{-H}$ σ FO is shown in **Figure 4.15 iv**. MO 57 of ion pair (a), **Figure 4.15 v**, corresponds to a higher energy interaction between an anion FO and a σ^* $\text{C}^2\text{-H}$ FO, with a simplified representation shown in **Figure 4.15 vi**. This interaction is reminiscent of the $\text{C}^2\text{-H}\cdots\text{Cl}^-$ orbital interaction within $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$.³⁰

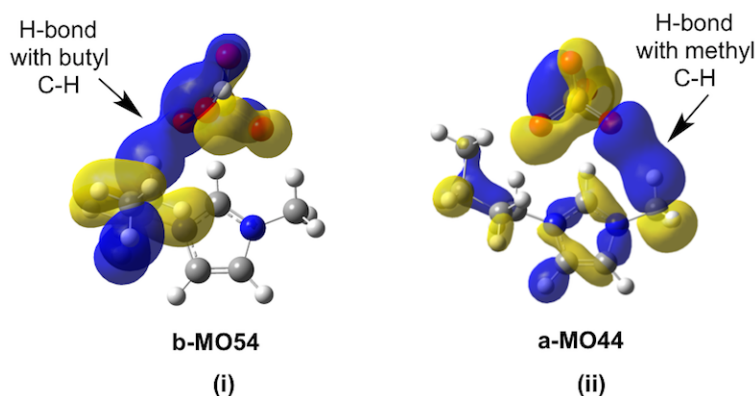


Figure 4.14. $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ MOs indicating alkyl $\text{C-H}\cdots\text{O}$ H-bond formation.

Additional anion FO interactions with a $\text{C}^2\text{-H}$ σ based FO have also been identified for ion pairs (a) to (d) e.g. a-MO41, c-MO41 and d-MO38, **Figure 4.16**. These MOs are more difficult to interpret, seemingly revealing an interaction between an S=O fragment with the $\text{C}^2\text{-H}$ group. The orbital interaction between S and the $\text{C}^2\text{-H}$ unit in d-MO38, **Figure 4.16 iii**, would appear to be consistent with the detection of a $\text{C}^2\cdots\text{S}$ BCP for ion pair (d).

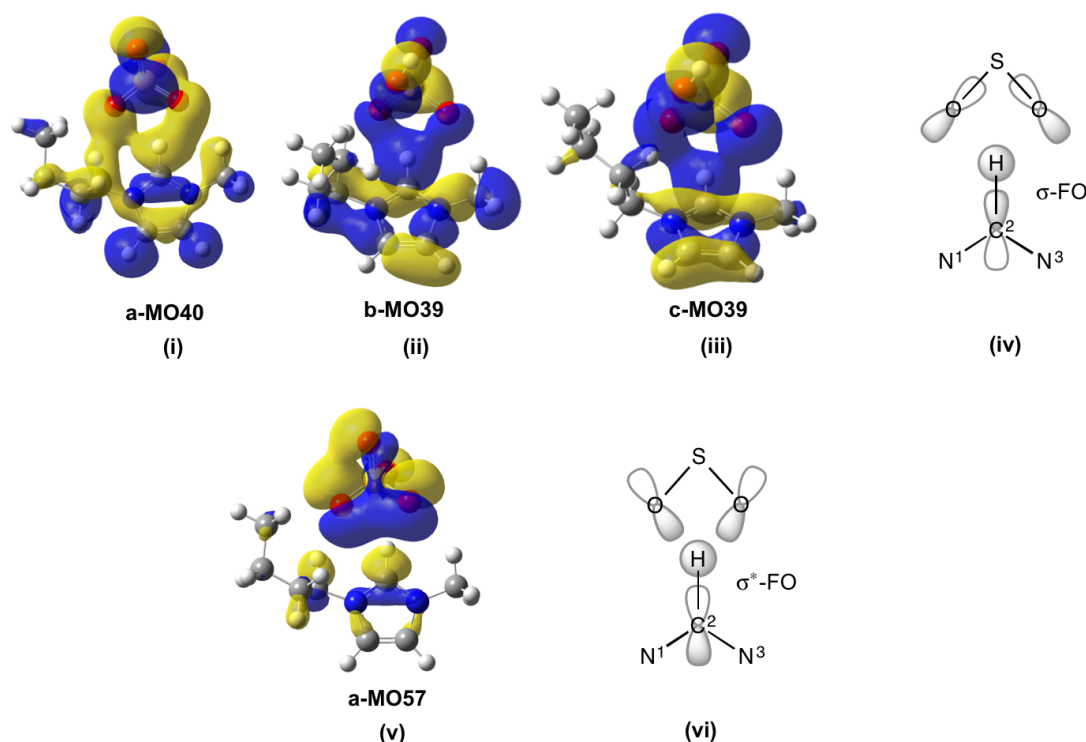


Figure 4.15. $[\text{C}_4\text{C1im}][\text{HSO}_4]$ MOs suggestive of H-bond formation with $\text{C}^2\text{-H}$.

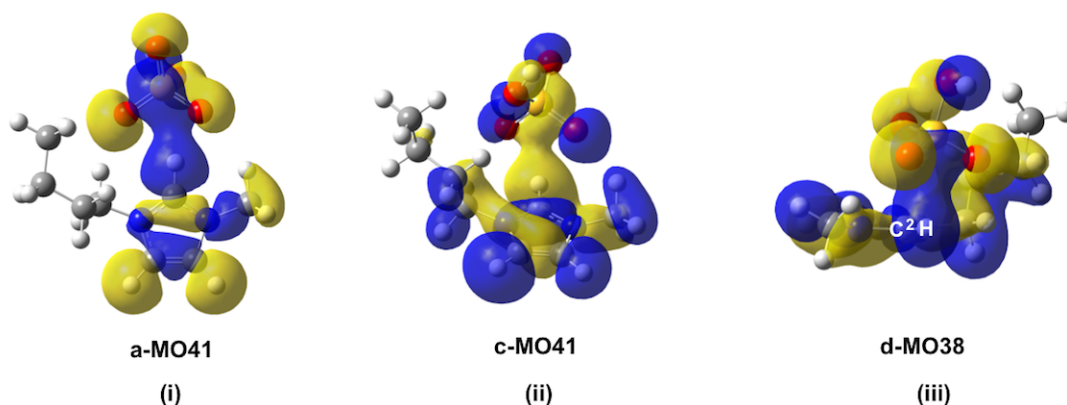


Figure 4.16. Additional anion FO interactions with a $\text{C}^2\text{-H}$ σ FO.

The MOs were also examined for evidence of anion- π^+ interactions. For all ion pairs FO interaction between the anion and the cation HOMO FO (**Figure 4.13 b**) was found, **Figure 4.17**. Most surprisingly, an interaction between the cation HOMO FO and the anion “ π ” orbital (**Figure 4.13 e**) was observed for ion pair (a), a-MO58 **Figure 4.17 i**. This in-plane interaction is of π symmetry and could perhaps be termed a $\pi^+-\pi^-$ interaction. For ion pairs (b) to (d), the anion gradually shifts out-of-plane, nevertheless, one of the anion FOs remains able to form an interaction with the front N-C-N π system of the ring, **Figure 4.17 ii-iv**. For ion pairs (e) and (f) there is also an anion FO interaction with the cation HOMO FO, but, the interaction is with the back C=C moiety, **Figure 4.17 v** and **vi**. FO interactions with the back C=C moiety of the ring have also been observed in $[\text{C}_1\text{C1im}][\text{C}_1\text{SO}_4]$ ion pair dimers.²⁷ Ion pairs (e) and (f) are the only ion pairs examined here to also feature lower energy π -type interactions, **Figure 4.18**. Orbital e-MO57, **Figure 4.18 i**, shows a weak interaction between the low-

lying all in-phase cation π FO (**Figure 4.13 c**) and the anion π -face. This is also observed in f-MO57, **Figure 4.18 ii**, but the anion contribution is further reduced.

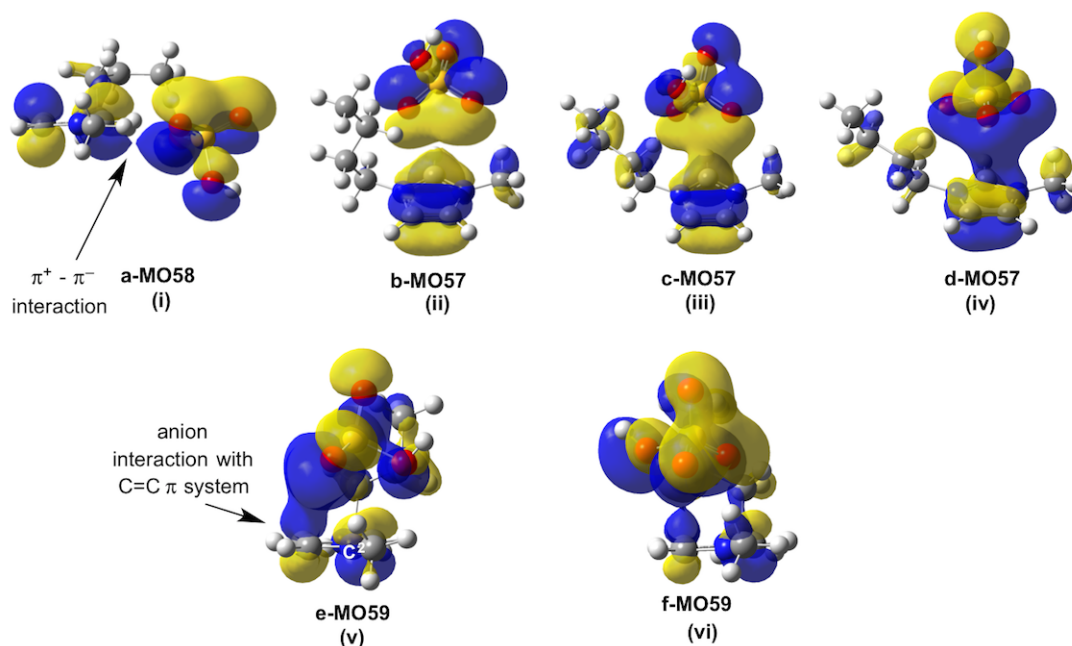


Figure 4.17. Examples of high energy anion- π^+ interactions.

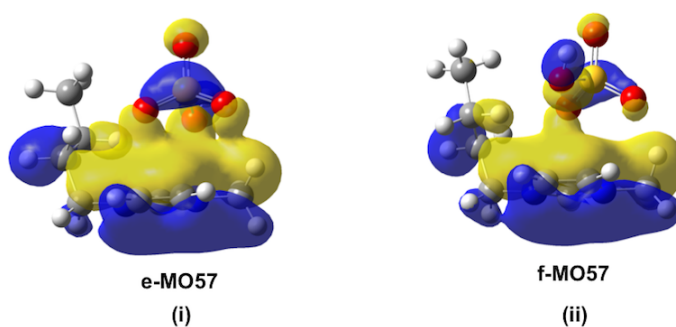


Figure 4.18. Examples of deeper energy anion- π^+ interactions.

The MO analysis therefore supports the case for a subtle interplay between H-bonding and anion interactions with the cation π system in the examined $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ ion pairs. In agreement with the QTAIM analysis, the MOs suggest that H-bond formation with the alkyl groups is significant for all the examined cation-anion configurations. Moreover, the MOs reflect the changing nature of the anion- π^+ interaction as the anion moves from an in-plane position to locate above the imidazolium ring.

2.2.3 Concluding summary

A large number of ion pairs of $[\text{C}_4\text{Him}]\text{Cl}$, $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ and $[\text{C}_4\text{Him}][\text{HSO}_4]$ have been obtained at both the B3LYP and B3LYP-D2 levels. Similarities and differences in the cation-anion configurations between the protic and aprotic systems have been determined, and the influence of dispersion on the ion pair geometries and energies established.

A number of stable cation-anion configurations have been identified for the protic imidazolium ion pairs. These include the established front/top, side-but and back configurations. However, interaction with the N-H group of the protic imidazolium cation is strongly favoured. This leads to an increase in the energy difference between the lowest energy configurations of the protic systems compared to the aprotic systems. The formation of a strong and directional interaction with the N-H unit also leads to an increase in the cation-anion association energies of the protic ion pairs.

Key differences between the Cl^- and $[\text{HSO}_4]^-$ ion pairs were also observed. Namely, the ability of the multidentate anion to “bridge” between more than one position and to use more than one oxygen atom to form multiple single H-bonds rather than the chelated H-bonds favoured with Cl^- .

Examination of the B3LYP ion pairs also established that the butyl chain conformation, and for the $[\text{HSO}_4]^-$ systems anion orientation, each have a small to moderate influence on the ion pair energies. However, the combined effect, particularly for $[\text{C}_4\text{Him}][\text{HSO}_4]$, can be more significant, up to $\approx 40 \text{ kJ mol}^{-1}$. Moreover, the secondary interactions with the butyl chain were found to be important for all systems in stabilising cation-anion configurations. Therefore, where relevant, examination of the alkyl chain conformation on the cation-anion interactions is recommended.

The differences in the local structuring and association energies can be expected to lead to differences in the physical properties between the aprotic and protic systems. However, based on the limited available data, no clear trend could be established. Further investigation and more experimental data for related aprotic and protic systems are required.

Dispersion was found to result in an increase in the association energy of all systems, with the most significant increase ($\approx 31 \text{ kJ mol}^{-1}$) found for $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, consistent with the size of the ions. Moreover, the most significant effect on the geometries was also found for $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, where a clear increase in the preference for the top position was identified. The interactions with selected examples of front and top structures of $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ were analysed using QTAIM and through examination of the MOs. The subtle balance between primary H-bonds, secondary H-bonds and anion- π^+ interactions is found to vary as the anion moves from the front in-plane position to locate above the ring plane.

2.3 Anion-anion hydrogen bonding

The $[\text{HSO}_4]^-$ protic anion could potentially lead to anion-anion H-bonding within $[\text{HSO}_4]^-$ ionic liquids. Anion-anion H-bonding is known to occur in the solid state with protic anions, such as $[\text{HSO}_4]^-$ or $[\text{H}_2\text{PO}_4]^-$, and a search of the Cambridge Structure Database reveals numerous examples. For $[\text{HSO}_4]^-$ there appears to be two primary modes of interaction, formation of an infinite chain, e.g. **Figure 4.19 a**, or formation of a discrete cyclic dimer, **Figure 4.19 b**. However, for some systems, an increase in temperature leads to phase transitions and structural changes. For example, for $\text{Cs}[\text{HSO}_4]$ there is a conversion from infinite chains of $[\text{HSO}_4]^-$ at room temperature, to cyclic dimers at higher temperatures.⁴³ Increased pressure and the absorption of water also leads to a disruption of the infinite H-bonded $[\text{HSO}_4]^-$ chains.⁴⁴

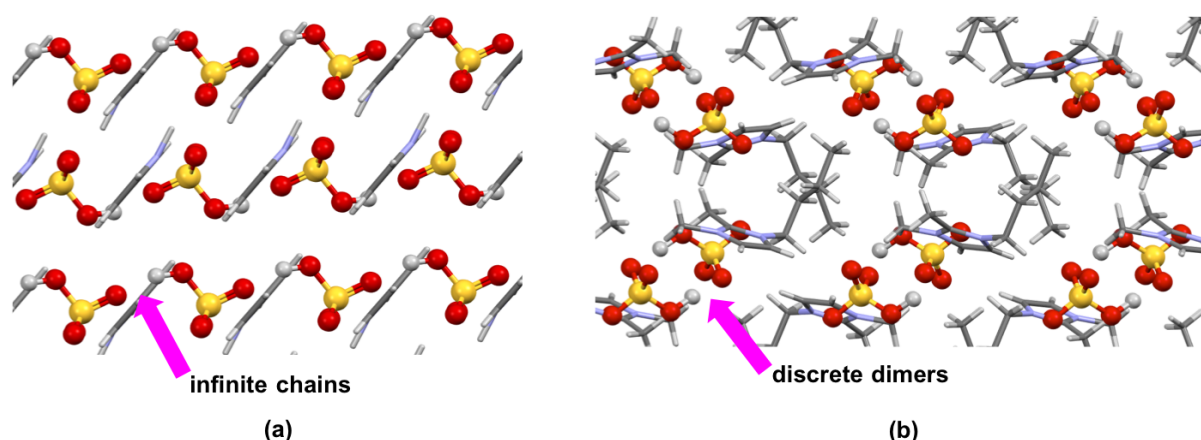


Figure 4.19. Selected crystal structures featuring $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ H-bonding: (a) pyridinium hydrogensulphate⁴⁵ and (b) 1-butyl-2,3-dimethyl hydrogensulphate.⁴⁶

The presence of $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ H-bonds in an ionic liquid was initially identified using Raman spectroscopy.²⁴ Comparison of the Raman spectra of $[\text{C}_2\text{C}_1\text{im}][\text{HSO}_4]$ and $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ to the Raman spectra of simple crystalline $[\text{HSO}_4]^-$ salts (e.g. $\text{K}[\text{HSO}_4]$ and $\text{Cs}[\text{HSO}_4]$), suggested the presence of H-bonded $[\text{HSO}_4]^-$ chains, rather than dimers, in the ionic liquids. However, $[\text{HSO}_4]^-$ dimers (although not necessarily the cyclic dimers seen in **Figure 4.19 b**) were reported for a recent MD simulation of $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ (298.15 K).²³

The observation of anion-anion H-bond interactions in ionic liquids is perhaps not surprising considering the charge screening of the ionic environment, with the screening effect leading to a reduction in the Coulomb repulsion between like charged ions. The effectiveness of ionic liquids in screening the electrostatic repulsions between probe solute ions of like-charge has previously been demonstrated.⁴⁷ For example, the electrostatic repulsion between two negative probe anions was computed to decrease to $\approx 66\%$ of the unscreened value in the $[\text{C}_1\text{C}_1\text{im}]\text{Cl}$ environment.⁴⁷

Despite the large electrostatic repulsion, stable H-bonded anion-anion dimers have also been computed in the gas phase.⁴⁸⁻⁵² Although found to have positive association energies, reported gas phase H-bonded anionic dimers are found to be kinetically stable, with a barrier to dissociation.^{49, 50} Examples include, $[\text{F} \cdots \text{HCO}_3]^{2-}$,⁵⁰ $[\text{H}_2\text{PO}_4 \cdots \text{H}_2\text{PO}_4]^{2-}$,⁴⁸ $[\text{H}_2\text{AlO}_3 \cdots \text{H}_2\text{AlO}_3]^{2-}$, and $[\text{HSO}_4 \cdots \text{HSO}_4]^{2-}$.⁴⁹

The origin of the stability of these gas phase complexes is, however, debated. One suggestion is that the short-range charge transfer arising from donor-acceptor interactions overcomes the unfavourable long-range electrostatic forces.⁵⁰ Thus, it has been proposed that the electrostatic contributions typically associated with H-bond formation (i.e. dipole-dipole) are “inessential” for these “anti-electrostatic” H-bonds.⁵⁰

However, the use of the classical Coulomb potential (e^2/r) to estimate the electrostatic interaction in a region where orbital overlap occurs has been criticised.⁵¹ Instead, it is stated that a quasi-classical treatment of the electrostatic interactions in the H-bond region is more appropriate. Using this approach, a *decrease* in the electrostatic repulsion is reported upon H-bond formation.⁵¹ This is consistent with arguments suggesting that the electron-nuclear attraction between the H-bond acceptor and donor at the H-bond distance is able to overcompensate for the electron-electron repulsion.^{48, 51} In this context, the charge transfer interaction is suggested to confer additional stabilisation, but not be the sole determining factor in stabilising these *doubly anionic* H-bonds.⁴⁸

Nevertheless, analysis of doubly anionic H-bonds in both the solid state and gas phase suggests that the properties of these H-bonds (e.g. geometric and spectroscopic features, topology of $\rho(r)$) are consistent with more traditional H-bond analogues.^{49, 50, 53, 54}

2.3.1 Hydrogensulphate dimers

The discrete cyclic $[\text{HSO}_4]^-$ dimer, **Figure 4.20 a**, has been isolated here with a computed association energy, E_a , of $\approx +150 \text{ kJ mol}^{-1}$ (where $E_a = E(\text{dimer}) - 2E(\text{monomer})$). The cyclic dimer is symmetric, with two symmetrically equivalent $\text{O-H}\cdots\text{O}$ H-bonds, e.g. **Figure 4.20 b**. The values of ρ_{BCP} (0.040 au) and $E^{(2)}$ ($\approx 92 \text{ kJ mol}^{-1}$) for each of the $\text{O-H}\cdots\text{O}$ interactions suggests that these are moderately strong. As the interactions are symmetric, the total stabilisation energies associated with electron delocalisation between the $[\text{HSO}_4]^-$ fragments is $\approx 184 \text{ kJ mol}^{-1}$. The effective interactions between the fragment orbitals, e.g. **Figure 4.20**, are consistent with there being a significant amount of electron delocalisation in this system. An alternative configuration, with only one $\text{O-H}\cdots\text{O}$ contact (i.e. as would be found in a H-bonded chain) could not be isolated for a gas phase dimer.

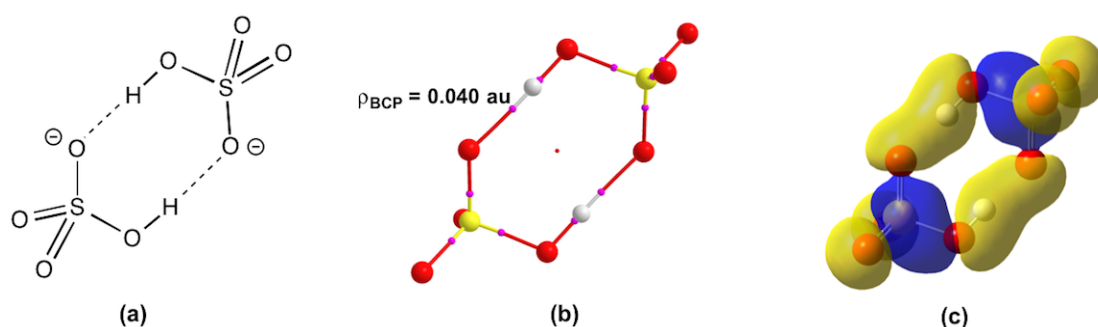


Figure 4.20. The $[\text{HSO}_4]^-$ cyclic dimer (a), QTAIM molecular graph (b) and example MO generated at the 0.02 eA^{-3} isosurface (c).

Using the ideas of charge screening, it would be anticipated that the anionic dimers would be stabilised in a polar solvation environment. Use of an implicit solvation model (a polarisable continuum model (PCM)) has previously been reported to lead to favourable (i.e. negative) association

energies for anionic dimers.⁴⁹ However, although the negative association energies reveal an overall stabilising effect of the solvation environment, it was also suggested that the charge screening effect would reduce the proposed attractive electrostatic contribution to the H-bond, resulting in a slight destabilisation of the H-bond interaction relative to the gas phase.⁴⁹

The cyclic $[\text{HSO}_4]^-$ dimer has been re-optimised here employing the conductor-like polarisable continuum model (CPCM) with parameters for solvents of differing polarity, dichloromethane (DCM) ($\epsilon = 8.93$), methanol ($\epsilon = 32.61$) and water ($\epsilon = 78.36$). The computed association energies and selected properties of the H-bonds are detailed in **Table 4.4**. Further information is provided in the **Appendix**, **Tables A.32** and **A.33**. As the two H-bonds within a dimer are symmetric, properties of only one of the O-H...O H-bonds for each case is listed.

Table 4.4. Selected properties of the $[\text{HSO}_4]^-$ cyclic dimer in the gas phase and in an implicit solvation environment (CPCM) with different solvent parameters: association energies (E_a), H-bond lengths (r), NBO partial charges on the H-atoms (q), values of ρ_{BCP} and $E^{(2)}$ for the O-H...O H-bonds.

$[\text{HSO}_4]^-$ cyclic dimer	$E_a / \text{kJ mol}^{-1}$	$r_{\text{OH}\cdots\text{O}} / \text{\AA}$	$q_{\text{H (NBO)}} / e$	$\rho_{\text{BCP}} / \text{au}$	$\Sigma E^{(2)}_{\text{no}} \rightarrow \sigma^*(\text{O-H}) / \text{kJ mol}^{-1}$
Gas phase	+149.5	1.718	0.522	0.040	91.8
DCM ($\epsilon = 8.93$)	-42.2	1.644	0.519	0.050	127.4
Methanol ($\epsilon = 32.61$)	-59.4	1.640	0.518	0.051	129.7
Water ($\epsilon = 78.36$)	-63.2	1.639	0.518	0.051	130.2

As anticipated, the association energies of the $[\text{HSO}_4]^-$ dimer are negative in the implicit solvation environment, with a slight increase in the magnitude of the association energy as the dielectric of the solvent increases, with $E_a \approx -42 \text{ kJ mol}^{-1}$ in DCM increasing to $\approx -63 \text{ kJ mol}^{-1}$ in water. This is consistent with an increase in the electrostatic screening.

However, contrary to the literature suggestions, the O-H...O H-bonds are found to increase in strength within the solvation environment, compared to the gas phase. On going from the gas phase to the DCM CPCM environment, there is a slight decrease in the H-bond lengths ($\approx 0.074 \text{ \AA}$), very slight decrease in positive charge on the hydrogen atoms, increase in the value of ρ_{BCP} ($\approx 0.010 \text{ au}$) and an increase in the $n_{\text{O}} \rightarrow \sigma^*_{\text{OH}}$ stabilisation energy ($\approx 35.6 \text{ kJ mol}^{-1}$). There is evidence of a very slight relative increase in H-bond strength on going from DCM to water, however, this is significantly reduced compared to the change from gas phase to DCM.

Based on these findings it would be predicted that $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ interactions are energetically favoured in the ionic liquid environment. Moreover, the O-H...O H-bonds could be enhanced in strength compared to the gas phase values. However, within the ionic liquid there is also the potential to form additional, and potentially competitive, cation-anion C-H...O H-bonds.

2.3.2 Ion pair dimers: comparison of $[\text{C}_1\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ and $[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4]$

Ion pair dimers, e.g. $[\text{C}_n\text{C}_n\text{im}]_2[\text{X}]_2$, are the smallest systems for which it is possible to examine both cation-anion and anion-anion interactions. Ion pair dimers of $[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4]$ could therefore provide insight into the $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ interaction in the presence of the ionic liquid cation. $[\text{C}_1\text{C}_1\text{im}]^+$ is used to reduce the computational expense and avoid the additional complication of multiple alkyl chain conformations.

An in depth assay of $[\text{C}_1\text{C}_1\text{im}]\text{Cl}$ ion pair dimers has previously been reported.⁵⁵ Two low energy motifs were identified, the diagonal motif and the middle motif, **Figure 4.21 a** and **b** respectively. Within the diagonal motif the ions are in a chequer board arrangement, with ions of like charge in opposite corners. Within this configuration each anion is in the front position with respect to one cation and in the top configuration with respect to a second cation, therefore simultaneously occupying the most favourable ion pair configurations. Within the middle motif, the cations adopt a $\pi^+ - \pi^+$ stacked configuration with the anions located in the mid-plane. Therefore, in the middle motif, the anions are out-of-plane with respect to the imidazolium rings.

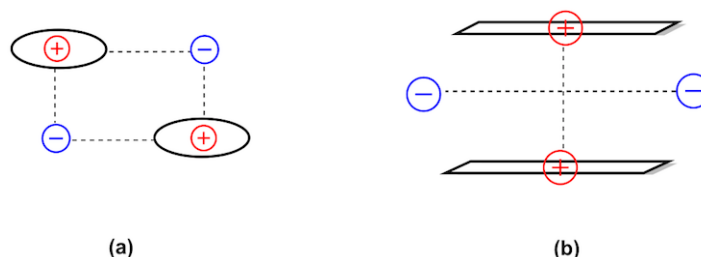


Figure 4.21. Low energy ion pair dimer motifs, (a) diagonal and (b) middle.

Subsequently, we examined the anion influence on the structuring of the low energy dimer motifs.²⁷ The six lowest energy $[\text{C}_1\text{C}_1\text{im}]\text{Cl}$ ion pair dimers were re-optimised with the Cl^- anion replaced by a range of anions with different sizes and charge distributions: $[\text{BF}_4]^-$, $[\text{OTf}]^-$, $[\text{C}_1\text{SO}_4]^-$ and $[\text{NO}_3]^-$. The larger anions show a slight increase in preference for the diagonal motif, consistent with previous reports suggesting an increased preference for the top configuration with larger anions.^{56, 57}

Replacing $[\text{C}_1\text{SO}_4]^-$ with $[\text{HSO}_4]^-$ has no significant effect on the previously reported ion pair dimer structures. However, our assay of the $[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4]$ and $[\text{C}_1\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ systems has been extended here to include a search for stable configurations exhibiting anion-anion interactions. Fourteen $[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4]$ ion pair dimers, six featuring $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ interactions, are shown in the **Appendix, Figure A.20**, with relative energies with, and without, ZPE and BSSE corrections listed in the **Appendix, Table A.34**. For $[\text{C}_1\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$, two new ion pair dimers featuring $[\text{C}_1\text{SO}_4]^- \cdots [\text{C}_1\text{SO}_4]^-$ interactions have been obtained here. These are compared to the previously reported lowest energy $[\text{C}_1\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ ion pair dimer, **Figure 23** and **Appendix, Table A.35**.

The lowest energy $[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4]$ ion pair dimer features a cyclic $[\text{HSO}_4]^-$ dimeric unit, **Figure 4.22 a**, and is termed here the “anion-cyclic” motif. Within the anion-cyclic structure, the $[\text{HSO}_4]^-$ cyclic dimer is “sandwiched” between the two $[\text{C}_1\text{C}_1\text{im}]^+$ cations. Four ion pair dimers of the anion-cyclic motif have been isolated, **Appendix Figure A.20**, differing primarily in the rotation of the cations and therefore subtle differences in the cation-anion interactions. The very small energy difference

between these four structures ($\approx 4 \text{ kJ mol}^{-1}$) suggests that there can be a reasonable degree of flexibility in the relative cation orientations without a significant energy penalty.

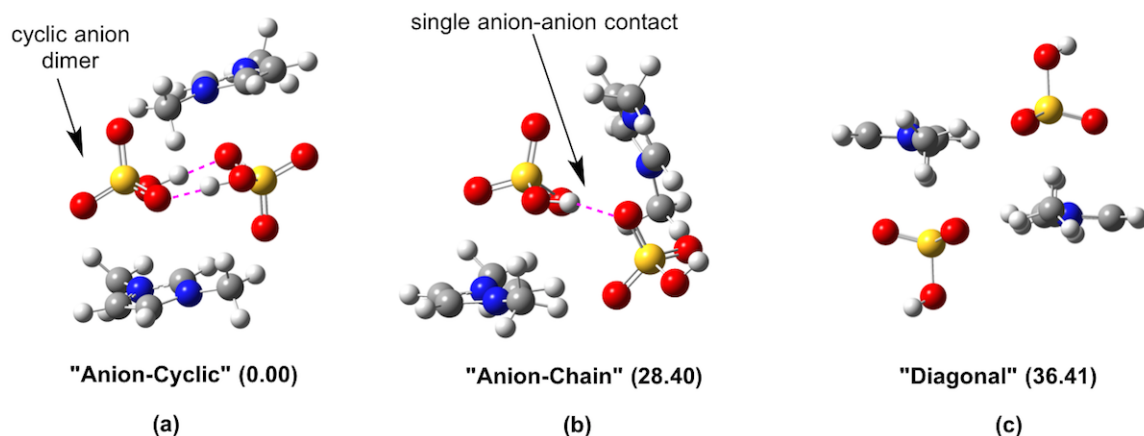


Figure 4.22. Example $[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4]$ ion pair dimers. Relative energies in kJ mol^{-1} . Anion-anion contacts indicated *via* pink dotted lines.

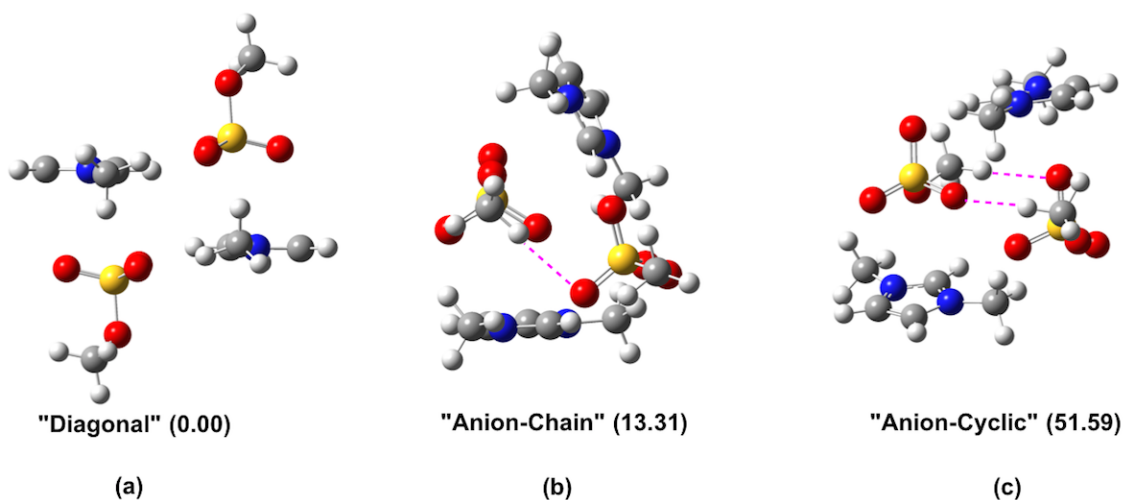


Figure 4.23. Example $[\text{C}_1\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ ion pair dimers. Relative energies in kJ mol^{-1} . Anion-anion contacts indicated *via* pink dotted lines.

The lowest energy $[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4]$ ion pair dimer *not* featuring any anion-anion interaction is the diagonal structure shown in **Figure 4.22 c**, and is $\approx 36 \text{ kJ mol}^{-1}$ higher in energy than the low energy anion-cyclic structure. This suggests that the formation of inter anion $\text{O-H}\cdots\text{O}$ H-bonds could be very favourable for $[\text{C}_n\text{C}_n\text{im}][\text{HSO}_4]$ systems.

An additional motif in which there is a single $\text{O-H}\cdots\text{O}$ interaction between the $[\text{HSO}_4]^-$ anions has also been isolated, **Figure 4.22 b**. This motif is termed the “anion-chain” motif and lies $\approx 28 \text{ kJ mol}^{-1}$ above the lowest energy ion pair, and is therefore only slightly ($\approx 8 \text{ kJ mol}^{-1}$) stabilised with respect to the diagonal structure.

Within the cyclic $[\text{HSO}_4]^-$ dimer, both of the O-H groups are involved in H-bond formation. As only one $\text{O-H}\cdots\text{O}$ interaction is found in the chain dimer motif, there is an unsaturated H-bond donor group. Therefore, in the gas phase, formation of the cyclic dimer and maximisation of the anion-anion H-bonding is energetically favourable. However, in the liquid there is the potential to form additional

[HSO₄]⁻...[HSO₄]⁻ interactions, leading to an extension of the anion chain. Within chain-like structures, there is the possibility of co-operative effects. Therefore, based on the gas phase ion pair dimers alone, it is not possible to state whether dimers or chains would be energetically preferred in the bulk phase.

For [C₁C₁im][C₁SO₄], ion pair dimers with the anion-cyclic and anion-chain motifs could also be isolated. The presence of [C₁SO₄]⁻... [C₁SO₄]⁻ H-bonds within ionic liquid systems has previously been proposed.²⁴ However, the energy ordering of the [C₁C₁im][C₁SO₄] dimer motifs is reversed compared to the [C₁C₁im][HSO₄] case. With [C₁C₁im][C₁SO₄], the lowest energy dimer is a diagonal structure, **Figure 4.23 a**, analogous to the [C₁C₁im][HSO₄] diagonal structure in **Figure 4.22 c**. The anion-chain configuration (**Figure 4.23 b**) is $\approx 13 \text{ kJ mol}^{-1}$, and the anion-cyclic configuration (**Figure 4.23 c**) $\approx 52 \text{ kJ mol}^{-1}$, higher in energy than the lowest energy structure.

Analysis of the H-bond interactions helps to explain the relative energy ordering of the [C₁C₁im][HSO₄] and [C₁C₁im][C₁SO₄] ion pairs. Within the [C₁C₁im][HSO₄] ion pair dimers, the value of ρ_{BCP} for the O-H...O H-bonds varies between 0.037 and 0.057 au, suggesting that these interactions are moderate to strong in strength. Compared to the gas phase cyclic dimer ($\rho_{\text{BCP}} = 0.040 \text{ au}$), the O-H...O interactions within the ion pair dimers are both enhanced and weakened. Based on ρ_{BCP} (0.007-0.013 au), the anion-anion C-H...O H-bonds within the [C₁C₁im][C₁SO₄] anion-cyclic and anion-chain dimers are weak interactions. Nevertheless, the formation of additional H-bonds, strong or weak, might have been predicted to lead to a stabilisation for both the [C₁C₁im][HSO₄] and [C₁C₁im][C₁SO₄] systems.

However, the formation of anion-anion interactions does appear to come at a cost, a reduction in the cation-anion H-bond interactions. The sum of ρ_{BCP} for the anion-anion and for the cation-anion H-bonds within the selected dimers are given in **Table 4.5**, (full details in the **Appendix, Table A.36**). The total sum of ρ_{BCP} for the cation-anion interactions is the sum of the contributions from both the alkyl C-H...O and ring C-H...O interactions. Interestingly, for both [C₁C₁im][HSO₄] and [C₁C₁im][C₁SO₄] dimers, $\Sigma \rho_{\text{BCP}}$ for the alkyl C-H...O H-bonds is greater than for the ring C-H...O H-bonds, again indicating the importance of the secondary H-bonds in stabilising cation-anion configurations.

Table 4.5. Sum of ρ_{BCP} for different types of H-bond (anion-anion and cation-anion) within selected ion pair dimers. All values of ρ_{BCP} in au.

Ion pair dimer	$\Sigma \rho_{\text{BCP}}$ anion CH/OH...O	$\Sigma \rho_{\text{BCP}}$ alkyl CH...O	$\Sigma \rho_{\text{BCP}}$ ring CH...O	Total $\Sigma \rho_{\text{BCP}}$ cation-anion
[C ₁ C ₁ im][HSO ₄] Anion-cyclic	0.110	0.072	0.041	0.113
[C ₁ C ₁ im][HSO ₄] Anion-chain	0.037	0.075	0.046	0.121
[C ₁ C ₁ im][HSO ₄] Diagonal	-	0.080	0.069	0.149
[C ₁ C ₁ im][C ₁ SO ₄] Anion-cyclic	0.025	0.061	0.050	0.111
[C ₁ C ₁ im][C ₁ SO ₄] Anion-chain	0.015	0.076	0.055	0.131
[C ₁ C ₁ im][C ₁ SO ₄] Diagonal	-	0.081	0.069	0.150

For the $[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4]$ system, the total $\Sigma \rho_{\text{BCP}}$ for the cation-anion H-bonds decreases as, diagonal (0.149 au) > anion-chain (0.121 au) > anion-cyclic (0.113 au). This would suggest that as the anion-anion interactions increase, diagonal (none) < anion-chain (0.037 au) < anion-cyclic (0.110 au), there is a concomitant decrease in the cation-anion H-bonding.

The same trend in the cation – anion H-bonding is observed for the analogous $[\text{C}_1\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ dimers. However, for the $[\text{HSO}_4]^-$ system, the strong O-H $\cdots$ O interactions are able to compensate for the loss in the cation-anion H-bonding. This is not the case for the $[\text{C}_1\text{SO}_4]^-$ system, where the C-H $\cdots$ O interactions are not sufficient to recoup the loss of the stabilising cation-anion interactions. These findings emphasise the competitive nature of H-bonding in ionic liquids.

To demonstrate the variation in the H-bond strengths within these systems, the values of ρ_{BCP} are plotted against the corresponding values of $E^{(2)}$ for all H-bonds identified within selected ion pair dimers, **Figure 4.24**. This analysis was undertaken for the nine lowest energy $[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4]$ dimers together with both the anion-cyclic and anion-chain $[\text{C}_1\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ dimers. The H-bonds were classified as either cation-anion alkyl C-H $\cdots$ O (black data points), cation-anion ring C-H $\cdots$ O (blue data points), or anion-anion C/O-H $\cdots$ O (red data points). In total, 74 alkyl C-H $\cdots$ O, 31 ring C-H $\cdots$ O and 16 anion-anion C/O-H $\cdots$ O H-bonds were identified. The weak, moderate and strong H-bond regions, as defined here, are indicated in **Figure 4.24**.

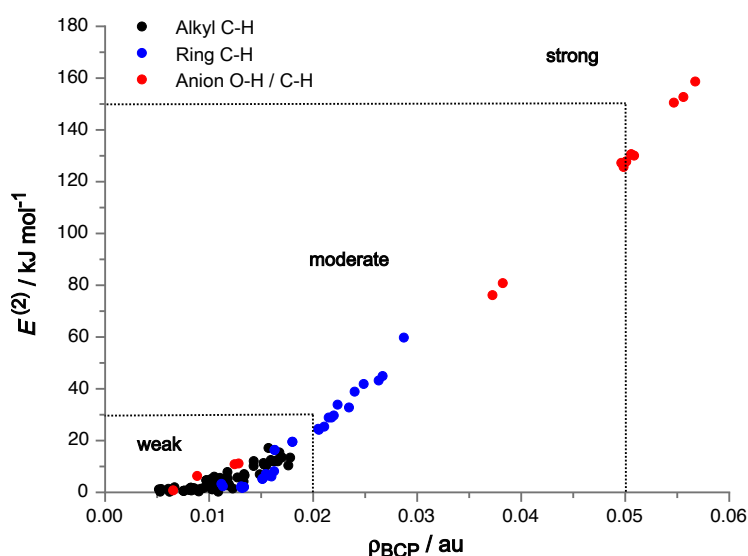


Figure 4.24. $E^{(2)}$ and ρ_{BCP} values for H-bonds in selected ion pair dimers.

Importantly, it can be seen that the doubly anionic H-bonds, both weak and strong, follow the same correlation between ρ_{BCP} and $E^{(2)}$ as the cation-anion H-bonds. Moreover, the introduction of the O-H $\cdots$ O interactions leads to a significant increase in the variation of H-bond strength for the $[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4]$ system. Although there is some overlap in the alkyl C-H $\cdots$ O and ring C-H $\cdots$ O H-bond strengths, all the alkyl C-H $\cdots$ O interactions fall within the weak band, whereas the ring C-H $\cdots$ O interactions (typically with C²-H as the donor) extend up to the middle of the moderate band, justifying the choice to describe these interactions as secondary and primary respectively. If we take a value of $\rho_{\text{BCP}} = 0.030$ au and $E^{(2)} = 60$ kJ mol⁻¹ to demark the upper limit of a “normal” H-bond interaction within

an archetypal ionic liquid, it can be seen that even the weakest $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ interaction is above this limit. Thus, the $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ H-bonds are atypical for an aprotic ionic liquid.

In summary, a review of the literature reveals anion-anion H-bonding to be relatively common in the solid state and even viable in the gas phase. Although the association energy is positive, the gas phase cyclic dimer of $[\text{HSO}_4]^-$ is stabilised through the formation of two linear and moderately strong O-H $\cdots$ O H-bonds. The charge screening effect of a solvation environment leads to an overall stabilisation of the ion pair dimer and an increase in the strength of the H-bonds. The O-H $\cdots$ O H-bonds are found to remain of moderate to strong in strength within the $[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4]$ dimers, despite competitive cation-anion interactions. The anion-anion interactions therefore lead to a stabilisation of the $[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4]$ dimers, suggesting that formation of $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ interactions is likely favourable in the bulk ionic liquid.

3. Molecular Dynamics Simulations

To further investigate the interplay between cation-anion and anion-anion interactions, three related systems were selected for study using classical MD: $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$, $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ and $[\text{C}_4\text{Him}][\text{HSO}_4]$. The key difference between these systems is the potential capacity for H-bonding.

$[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ is the “parent” system, a conventional aprotic ionic liquid, with neither a strongly acidic proton on the cation nor anion. Aprotic imidazolium alkylsulphate ionic liquids have previously been studied using MD^{19, 20} and thus $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ is used here as a reference system. Anion interaction with the cation, particularly the ring C-H groups, is expected. Anion-anion interactions are a possibility, however, analysis of the ion pair dimers suggests that the anion-anion C-H $\cdots$ O H-bonds are of approximately the same strength as the weaker examples of cation alkyl C-H $\cdots$ O H-bonds. Therefore, it is not expected that anion-anion interactions would be dominant within this system.

$[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ is the “intermediate” system and features an anion with an acidic proton. Theoretical and experimental evidence suggests that $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ interactions are present and could be significant in influencing the properties of this ionic liquid. For example, the formation of anion-anion O-H $\cdots$ O H-bonds was found here to result in stabilisation of the $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ ion pair dimers. $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ interactions were also identified within a previous MD simulation of this ionic liquid.²³ Experimentally, $[\text{C}_n\text{C}_1\text{im}][\text{HSO}_4]$ ionic liquids have been found to be more viscous than the $[\text{C}_n\text{SO}_4]^-$ analogues.²⁴ The experimentally determined Raman $\nu(\text{S}=\text{O})$ bands are also indicative of O-H $\cdots$ O H-bond formation.²⁴ However, it is not clear whether $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ interactions within the liquid result in the formation of chains or cyclic dimers.

The final ionic liquid in the sequence is the protic ionic liquid, $[\text{C}_4\text{Him}][\text{HSO}_4]$, with both an acidic N-H group on the cation and an acidic proton on the anion. Based on the QM ion pairs, replacing the aprotic imidazolium cation with a protic imidazolium leads to an increase in the cation-anion interaction. However, how does a potential increase in the cation-anion association influence the anion-anion interactions (or *vice versa*)?

3.1 Method

All simulations of $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$, $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ and $[\text{C}_4\text{Him}][\text{HSO}_4]$ were performed using the DL_POLY Classic simulation code.^{58, 59} All three of the selected systems is a liquid at room temperature (only the melting point of $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ (≈ 296 K) is reported⁵). However, due to the viscosity, of $[\text{C}_4\text{Him}][\text{HSO}_4]$ in particular, heating may be required for practical application. Therefore, for each of the ionic liquids, simulations at 300.15 K and 400.15 K have been undertaken i.e. just above room temperature and at a possible “working” temperature (and at least 100 K above the melting point).

All potentials used here are based on the OPLS-AA framework. The potential models of Canongia Lopes, Padua *et al* have been used to describe $[\text{C}_4\text{C}_1\text{im}]^+$, $[\text{C}_4\text{Him}]^+$ and $[\text{C}_1\text{SO}_4]^-$.⁶⁰⁻⁶² Two different force fields for the $[\text{HSO}_4]^-$ anion were identified in the literature and have been examined: one developed for the study of $[\text{HSO}_4]^- \cdots \text{H}_2\text{O}$ interactions in the field of atmospheric chemistry,⁶³ and a

second, adapted from the Lopes-Padua $[C_nSO_4]^-$ potential.²³ These shall be identified here as force field A (FFA) and force field B (FFB) respectively. Parameters for each force field are detailed in the **Appendix, Tables A.37 and 38**. The geometric mean was used to combine the Lennard Jones potential parameters for pairs of atoms, **Equations 2.94 and 2.95**.

For $[C_4C_1im][HSO_4]$ both FFA and FFB were tested, with potential FFA selected for further investigation of $[C_4C_1im][HSO_4]$ structuring. Subsequently, FFA was employed for $[C_4Him][HSO_4]$. The origin of the two $[HSO_4]^-$ potentials shall be discussed in more detail in the following section. A cut-off radius of 16 Å was used for the Lennard Jones interactions. Long-range electrostatic forces were treated using the Ewald summation method. The leapfrog Verlet algorithm was used to integrate the equations of motion with a 1 fs timestep and a modified SHAKE algorithm was used to constrain the X-H bonds (X = C, N or O).

Each simulation consisted of 256 pairs of cations and anions in a cubic simulation cell with periodic boundary conditions. Initial configurations were generated by randomly packing the ions into cubic boxes with low densities using Packmol.⁶⁴ Systems were initially relaxed at constant volume and energy (NVE) at 5.15 K, and subsequently at 200 and 300 K. A short simulation (up to 1 ns) at constant pressure and temperature (NPT) was then undertaken at 300 K and the energy and cell behaviour assessed. A process of simulated annealing was subsequently undertaken. Starting from 300 K, and at constant volume and temperature (NVT), each system was systematically heated for 100 ps at 50 K intervals up to 500-550 K. Systems were then gradually cooled to the required simulation temperature in 25 K intervals. Each system was then equilibrated at constant pressure and temperature (NPT), at either 300.15 or 400.15 K, for 1-2 ns until a constant volume was obtained. A Nosé-Hoover thermostat and barostat was used to constrain the temperature and pressure with relaxation times of 0.1 and 0.5 ps respectively. Final cell parameters and densities are provided in **Table 4.6**. A further 15 ns equilibration at constant volume and temperature (NVT), employing the Nosé-Hoover thermostat (0.1 ps relaxation time) was undertaken before moving to the production phase.

The production simulations were run within the NVT ensemble in sequential 5 ns blocks. For $[C_4C_1im][C_1SO_4]$ and $[C_4C_1im][HSO_4]$ a 10 ns production phase was used for analysis of the structure. For $[C_4Him][HSO_4]$ the energy drift was found to be slightly higher, although not exceeding 0.04 % of the total energy. For $[C_4Him][HSO_4]$ the simulation was therefore extended to a total of 55 ns at 300.15 K and 70 ns at 400.15 K in an attempt to reduce the energy drift. Whilst the drift in total energy did not reduce during these time periods, analysis of the structure at different time intervals revealed no significant change, suggesting that the structure had been equilibrated. It is anticipated that due to the highly viscous nature of $[C_4C_1im][HSO_4]$, much longer simulation times could be required for the energy to stabilise. In the interests of time, a 10 ns block over which the energy was constant was selected for further analysis of the structure.

Structural analysis, that is computation of the radial, angular and spatial distribution functions, (RDFs, ADFs and SDFs respectively) was undertaken using the Trajectory Analyzer and Visualizer package (TRAVIS).⁶⁵ The labelling used here for the heavy atoms for each of the ions is shown in

Figure 4.25. The hydrogen atoms are referred to in conjunction with the associated heavy atom e.g. C²-H or N³-H.

Table 4.6. Final values of the cell vectors, calculated densities (ρ_{calc}), experimental densities (ρ_{exp}) and the percentage difference between the calculated and experimental densities.

Ionic liquid	T /K	Cell vector / Å	$\rho_{\text{calc}} / \text{g dm}^{-3}$	$\rho_{\text{exp}} / \text{g dm}^{-3}$ (T in K)	% difference
[C ₄ C ₁ im][C ₁ SO ₄]	300.15	44.64	1196	1204 (300.2) ⁶⁶	-0.65
[C ₄ C ₁ im][C ₁ SO ₄]	400.15	45.45	1133	-	-
[C ₄ C ₁ im][HSO ₄] (FFA)	300.15	42.72	1288	1276 (303) ⁶⁷	+0.90
[C ₄ C ₁ im][HSO ₄] (FFA)	400.15	44.34	1233	-	-
[C ₄ C ₁ im][HSO ₄] (FFB)	300.15	43.01	1263	1276 (303) ⁶⁷	-1.06
[C ₄ C ₁ im][HSO ₄] (FFB)	400.15	43.92	1186	-	-
[C ₄ Him][HSO ₄]	300.15	41.26	1345	1295 ^a (RT) ⁶⁸	+3.87
[C ₄ Him][HSO ₄]	400.15	41.93	1282	-	-

^a estimated from polynomial fit of data for plot of density against molar % excess H₂SO₄.⁶⁸

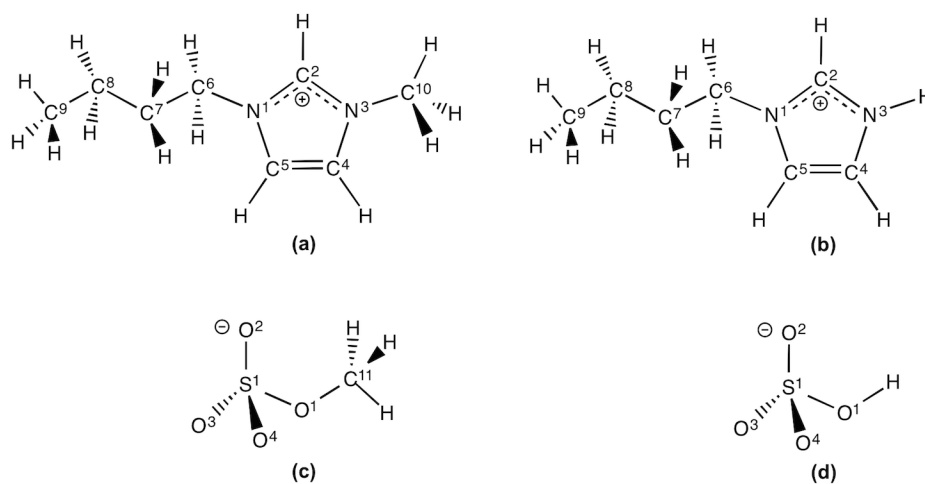


Figure 4.25. Atom labelling used here for (a) [C₄C₁im]⁺, (b) [C₄Him]⁺, (c) [C₁SO₄]⁻ and (d) [HSO₄]⁻.

3.2 Comparison of hydrogensulphate force fields

Two different force fields for the $[\text{HSO}_4]^-$ anion have been examined here. One force field (FFA) was generated by Loukonen *et al* to investigate the nucleation process of sulphuric acid in water.⁶³ Parameters for FFA were derived using the OPLS-AA procedure.⁶⁹ Loukonen *et al* obtained Lennard-Jones parameters from related functional groups in the literature. Partial charges, equilibrium bond lengths, angles and associated harmonic stretching and bending force constants were computed using *ab initio* methods.

The second potential (FFB) was generated by Schwenzer *et al* specifically for the investigation of structuring within $[\text{C}_4\text{C}_{1\text{im}}][\text{HSO}_4]$.²³ FFB is a modification of the Canongia Lopes – Padua potential for alkylsulphates.⁶² The partial charge on the O-H hydrogen of $[\text{HSO}_4]^-$ was obtained by Schwenzer *et al* through summation of the atomic charges on the methyl group of $[\text{C}_1\text{SO}_4]^-$. All other partial charges correspond to those of $[\text{C}_1\text{SO}_4]^-$. Parameters for the equilibrium O-H bond length, S-O-H angle and the associated force constants are reported, however, it is not stated in the original article how these values were obtained.

Notable differences between FFA and FFB include the magnitude of the angle bending force constants, the Lennard-Jones parameters for the oxygen atoms and the partial charges on the O¹-H group. For FFA the partial charges on O¹ and H are -0.64 e and +0.38 e respectively. For FFB, the corresponding values are -0.45 e and +0.22 e. The O-H group is therefore significantly (0.35 e) more polarised within FFA.

To determine the influence of the $[\text{HSO}_4]^-$ potential on cation-anion and anion-anion interactions, two initial simulations of $[\text{C}_4\text{C}_{1\text{im}}][\text{HSO}_4]$ were undertaken, one using FFA and one using FFB. For both simulations the same potential for $[\text{C}_4\text{C}_{1\text{im}}]^+$ was employed. The simulations were run at 400.15 K with a 5 ns NVT production phase. The computed liquid densities, **Table 4.6**, are quite similar and in reasonable agreement with the experimental value. However, it is well established that different force fields can produce very similar densities and that density alone is not a good measure of the quality of a force field.⁷⁰

The liquid structure has been compared *via* examination of the computed RDFs. Example RDFs are shown in **Figure 4.26 a** and **b**, note the difference in the vertical scale. The C²...O²-O⁴ site – site RDFs, **Figure 4.26 a**, are representative of the cation-anion interactions. The intensities and positions of the peak maxima are in close agreement with the two force fields, suggesting that the $[\text{HSO}_4]^-$ potential does not have a significant influence on the cation-anion interactions.

Comparison of the anion-anion S¹...S¹ site-site RDFs (**Figure 4.26 b**) does, however, reveal a significant difference in the anion-anion interactions between the two potentials. The difference is particularly evident in the short-range. With FFA, there is a well-defined peak at ≈ 4.24 Å with a second, less intense peak at ≈ 4.46 Å. For FFB, there is a broader peak with a reduced intensity at ≈ 5.22 Å. Analysis of the RDFs therefore suggests that with FFB, there is a reduction in the number of anion-anion interactions.

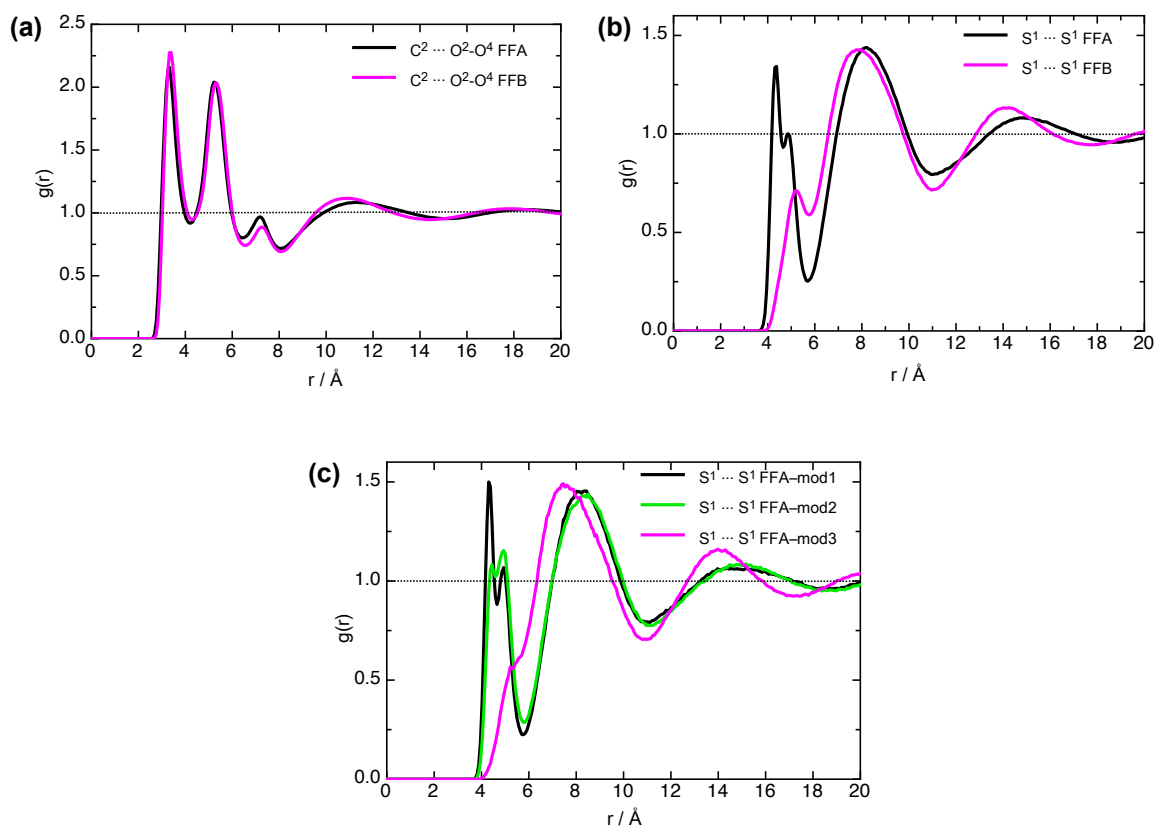


Figure 4.26. Radial distribution functions comparing the influence of the $[HSO_4]^-$ force field on $[C_4C_{7im}][HSO_4]$ (a) cation-anion and (b) anion-anion interactions. (c) Influence of modifications to FFA on anion-anion interactions.

To establish the most significant factor leading to the observed variation in the anion-anion interactions a series of short test simulations with modified forms of the FFA potential were undertaken. Three modifications to FFA have been made, each through replacement of a set of FFA parameters with those of FFB: firstly, the force constants for the angle bend terms (FFA-mod1), secondly, the Lennard-Jones parameters (FFA-mod2) and lastly, the atomic partial charges (FFA-mod3). The equilibrated FFA system was used as the starting structure in each case. The FFA force field was replaced with a modified version and the system subjected to a period of heating and then cooling, followed by a 1 ns NPT and then 1 ns NVT simulation (at 400.15 K).

The anion-anion $S^1 \cdots S^1$ site-site distribution functions were subsequently computed and are shown in **Figure 4.26 c**. In terms of peak positions, results with FFA-mod1 appear very similar to those with the parent FFA potential, although there is a slight increase in the intensity of the peak maximum at ≈ 4.24 Å. With FFA-mod2, the peak positions are also in good agreement with those obtained with the original FFA potential; however, there is an evident decrease in the intensity of the peak maximum at ≈ 4.24 Å. The most significant effect however, is found with FFA-mod3, with the overall “shape” of the distribution more closely resembling that obtained with FFB.

Overall, it can therefore be established that it is the combined effect of the variation in the Lennard-Jones parameters, and most significantly the partial charges, that leads to the discrepancies in the anion-anion interactions. Variation in the observed H-bonding, local structuring and dynamic

properties of ionic liquid MD simulations has previously been observed upon modification of the partial charge distributions of the ions.^{71, 72}

Without further comparison to experimental properties it is difficult to state which of the two force fields is more accurate for the study of $[\text{HSO}_4]^-$ containing ionic liquids. However, from our own QM work we have established that the O-H group of $[\text{HSO}_4]^-$ is more polarised than the O-CH₃ group of $[\text{C}_1\text{SO}_4]^-$ (e.g. NBO partial charges: O-H (O = -0.77e, H = +0.46e), O-CH₃ (O = -0.77e, ΣCH_3 = +0.29e)). The partial charges within FFA account for the increased polarisation of the O-H group. It is possible that the increased polarisation within FFA results in over-structuring, while FFB leads to under-structuring (i.e. too many and too few anion-anion interactions respectively). The extent of anion-anion interactions within the “real” system could lie somewhere between the two. However, it is my opinion that FFB has not been suitably parameterised, while FFA has been parameterised in a manner consistent with other commonly employed ionic liquid potentials. Based on this judgement, FFA was selected as the force field to be used for a more in depth analysis of the local structuring within $[\text{C}_4\text{C}_{1\text{im}}][\text{HSO}_4]$ and $[\text{C}_4\text{Him}][\text{HSO}_4]$.

3.3 Cation – anion interactions

3.3.1 Comment on temperature effect

Simulations for each system have been undertaken here at both 300.15 and 400.15 K. Comparison of the site-site interactions through analysis of the RDFs reveals that the short range interactions within the system at 300.15 and 400.15 K are very similar in terms of the peak positions e.g. the example $C^2-H \cdots O^2-O^4$ and $N^3-H \cdots O^2-O^4$ RDFs shown in **Figure 4.27**. A small decrease in the intensity of the first peak maxima at the higher temperature can, however, typically be observed. It can be anticipated that an increase in temperature leads to an increase in the mobility of the ions, thus resulting in a less structured liquid. Unless otherwise stated, structural analysis has been conducted here for the ionic liquid simulations obtained at 400.15 K.

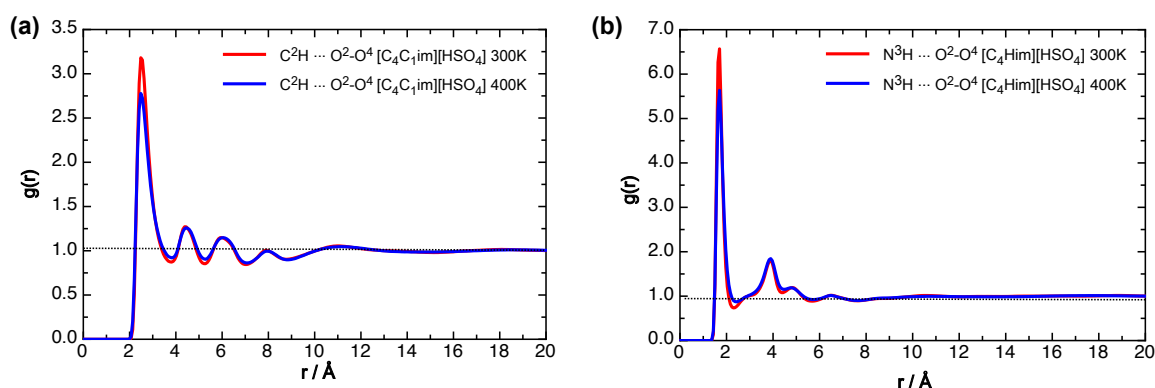


Figure 4.27. Selected cation-anion site-site radial distribution functions for systems at both 300.15 and 400.15 K.

3.3.2 Comparison of local cation – anion interactions

Selected cation-anion site-site RDFs are shown in **Figure 4.28**. The preferred interaction sites about an (aprotic) imidazolium cation are now well established. For all three systems examined here, including protic $[C_4Him][HSO_4]$, there is a relatively high probability of finding a terminal anion oxygen atom (O^2 , O^3 or O^4) in the vicinity of the C^2 , C^4 and C^5 positions of the imidazolium ring, **Figure 4.28 a, c and d** respectively. For $[C_4Him][HSO_4]$, the introduction of the N-H group also leads to a high probability of finding an anion oxygen atom in the vicinity of N^3 , **Figure 4.28 e**.

For the systems with an aprotic imidazolium cation, the relative intensities of the first peak maxima for the ring positions correspond to the relative acidities of the C-H groups; there is a greater probability of interaction at the more acidic C^2-H position compared to $C^{4/5}-H$. Moreover, for an aprotic imidazolium cation the probability of interaction at C^4 and C^5 is approximately the same i.e. these positions are effectively equivalent. For the protic imidazolium cation, the C^4 and C^5 positions are not equivalent. The introduction of the “NH” configurations results in an increase in interaction at the C^4 position relative to C^5 , such that the intensity of the first peak maxima for interaction at C^4 is similar to that at C^2 .

The bridging oxygen atom of the anion (O^1) is also able to interact with the cation. However, for $[C_4C_1im][C_1SO_4]$ the probability of interaction with O^1 is much lower compared to interaction with a terminal oxygen atom, e.g. **Figure 4.28 b**. For the systems with $[HSO_4]^-$, while there is also a reduction in the intensity of the cation interaction with the bridging oxygen, for example at the C^2

position **Figure 4.28 b**, the relative difference between the terminal and bridging oxygen atoms is not as great as with the $[\text{C}_1\text{SO}_4]^-$ anion. This could be due to the differences in the potential (e.g. the larger negative partial charge at O^1 for the $[\text{HSO}_4]^-$ anion) or reflect a reduction in steric hindrance (i.e. methyl vs. H).

For $[\text{C}_4\text{Him}][\text{HSO}_4]$ however, there is a very large decrease in the interaction between $\text{N}^3 \cdots \text{O}^2-\text{O}^4$ and $\text{N}^3 \cdots \text{O}^1$, **Figure 4.28 e**. This is consistent with analysis of the QM ion pairs, where it was found that the interaction between the N-H group and a terminal oxygen atom is energetically favoured over interaction with a bridging oxygen atom by $\approx 25 \text{ kJ mol}^{-1}$. In contrast, there was found to be less of an energy difference (up to $\approx 12 \text{ kJ mol}^{-1}$) between the C^2 -H terminal oxygen and bridging oxygen interactions, possibly reflected here in the relative intensities of the peak maxima.

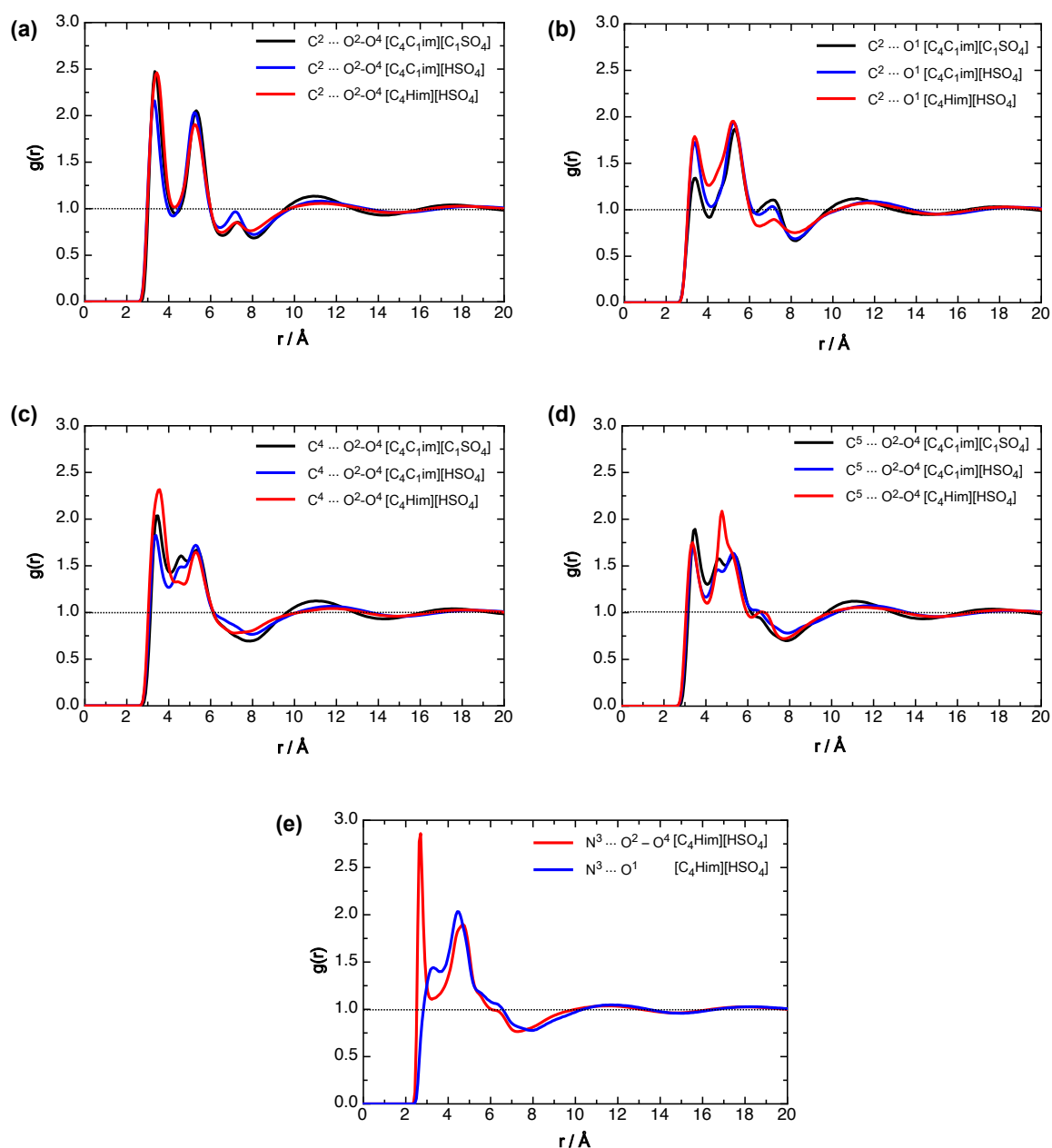


Figure 4.28. Cation-anion site-site radial distribution functions. Terminal anion oxygen atoms (O^2-O^4) about cation the (a) C^2 , (c) C^4 and (d) C^5 positions. Bridging oxygen atoms (O^1) about the cation C^2 position (b). Terminal and bridging oxygen atoms about N^3 for $[\text{C}_4\text{Him}][\text{HSO}_4]$ (e). All systems at 400.15 K.

On going from $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ to $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ it could be expected that there would be an increase in the anion-anion interactions (to be discussed shortly) resulting in a possible decrease in the corresponding cation-anion interactions. Comparing the RDFs for the $\text{C}^2\cdots\text{O}^2\text{-O}^4$ and $\text{C}^{4/5}\cdots\text{O}^2\text{-O}^4$ site-site interactions it can be seen that there is a slight decrease in the intensities of the first peak maxima in each case for $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ compared to $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$. However, the increase in interaction with the O^1 bridging oxygen of $[\text{HSO}_4]^-$ must also be considered. Overall, it is therefore difficult to determine if an increase in anion-anion interaction does lead to a decrease in the cation-anion interaction. For $[\text{C}_4\text{Him}][\text{HSO}_4]$ however, the computed RDFs are consistent with there being an overall increase in the cation-anion interaction compared to the aprotic analogues. However, between all three systems differences are only observed in the local region, the radial distributions at longer ranges are almost identical.

Comparison of the computed spatial distribution functions (SDFs) allows for a more visual, albeit qualitative, interrogation of the local cation-anion configurations. Computed SDFs for the terminal O^2 and the bridging O^1 oxygen atoms about the imidazolium cations are shown in **Figure 4.29** at both twice the average background density (a-c) and 2.5 times the average background density (d-f).

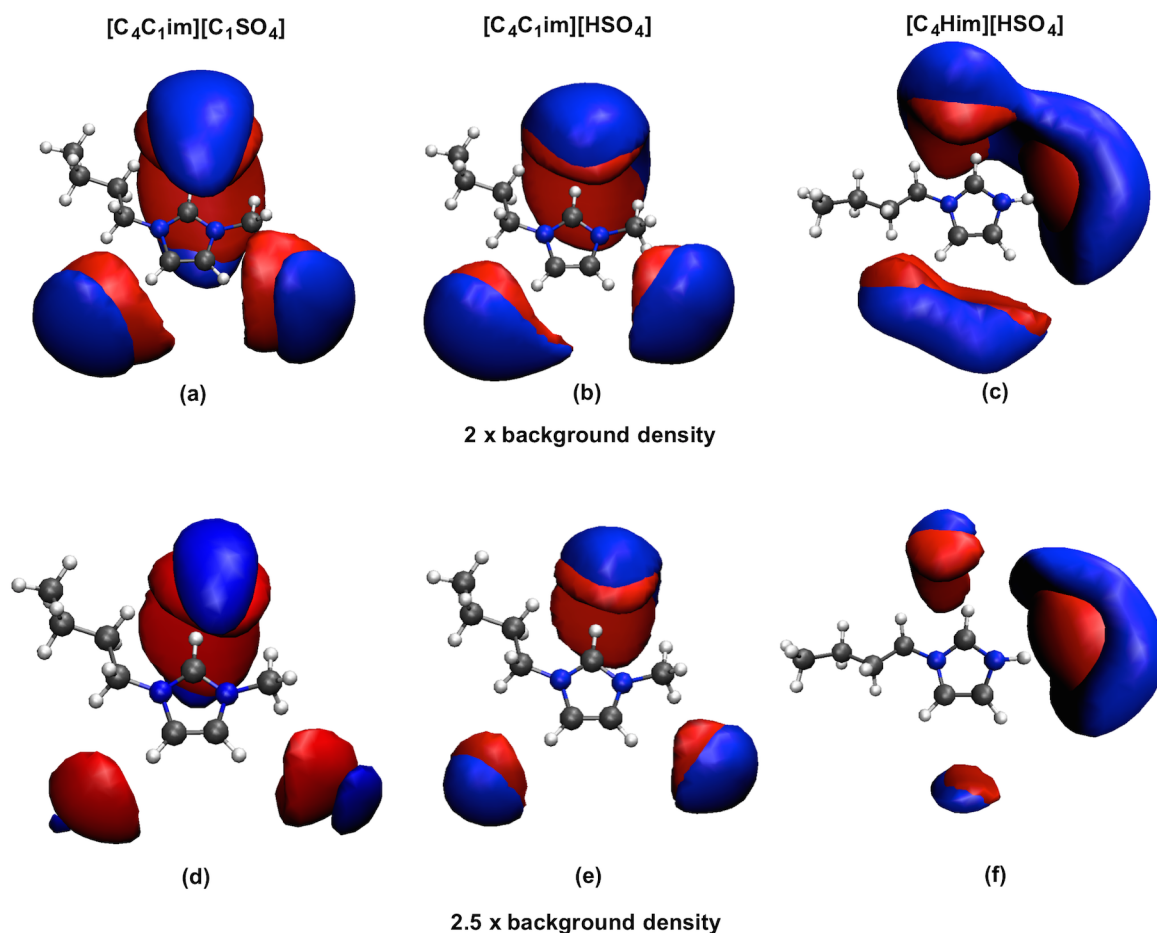


Figure 4.29. Spatial distribution functions of selected anion oxygen atoms about the $[\text{C}_4\text{C}_1\text{im}]^+$ or $[\text{C}_4\text{Him}]^+$ cations: O^2 terminal oxygen atom (red) and O^1 bridging oxygen atom (blue). All systems at 400.15 K.

From **Figure 4.29 a and b** it can be seen that the $[\text{C}_1\text{SO}_4]^-$ and $[\text{HSO}_4]^-$ anions preferably locate in the front and side positions with respect to the aprotic imidazolium cation. As previously established for other aprotic imidazolium ionic liquids, there is an absence of ions in the “back” position and a probability of anions locating out-of-plane in the front and side positions, the latter not (typically) recovered through examination of ion pairs.⁵⁵

Comparing the SDFs shown in **Figures 4.29 d and e**, the differences in the probability of interaction with terminal O^2 and bridging O^1 , as evidenced in the RDFs, can be seen. For $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ the probability of interaction with O^2 is clearly greater than interaction with O^1 . For $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, however, the relative probabilities of interaction with O^2 and O^1 are more similar.

Figures 4.29 c and f show the analogous SDFs for the $[\text{C}_4\text{Him}][\text{HSO}_4]$ system. About the protic cation, **Figure 4.29 c**, there is a “smeared” anion distribution, stretching from the front-but position, through to the apparent NH-front to the NH-side positions. There is also a probability of the anion locating in the side-but position and, interestingly, unlike the aprotic analogues, in the back position. Higher above the average bulk density, the dominance of the anion interaction with the N-H group of the cation is evident, **Figure 4.29 f**.

Through visual inspection of the $[\text{C}_4\text{Him}][\text{HSO}_4]$ trajectory, it is possible to identify examples of different cation-anion configurations involving the N-H group. For example, the NH-front motif, **Figure 4.30 a** and the NH-side motif, **Figure 4.30 b**, have been identified here. These motifs were initially identified through examination of the QM ion pairs and are consistent with the “smeared” anion distribution seen in **Figure 4.29 c**. However, there are many examples where the anion interaction occurs *only* via the N-H group, e.g. **Figure 4.30 c**. For gas phase ion pairs such a motif is not stable, the anion preferring to maximise H-bonding through formation of a second H-bond with either $\text{C}^2\text{-H}$ or $\text{C}^4\text{-H}$. In the bulk phase, a single anion can also maximise H-bond interactions through interaction with multiple different ions.

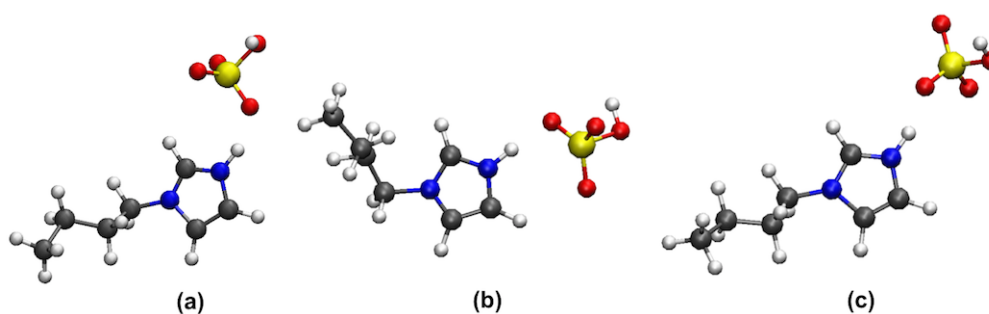


Figure 4.30. Observed cation-anion motifs featuring anion interaction with the N-H group of $[\text{C}_4\text{Him}]^+$.

3.3.3 Hydrogen bonding

Computed RDFs (now centred on H) for the $\text{C}^2\text{-H}\cdots\text{O}^2\text{-O}^4$ site-site interactions for each system, and additionally $\text{N}^3\text{-H}\cdots\text{O}^2\text{-O}^4$ for $[\text{C}_4\text{Him}][\text{HSO}_4]$, are shown in **Figure A.23** of the **Appendix**. The values for the radial distance to the first peak maxima (r_{max}) and radial distance to the first peak minima (r_{cut}), for systems at both 300.15 and 400.15 K, are listed in **Table 4.7**. The coordination numbers, N_c , were obtained through integrating up to the first peak minimum for each interaction.

Table 4.7. Positions of the first peak maxima ($r_{\max}$) and peak minima (r_{cut}) for the $\text{C}^2\text{-H}\cdots\text{O}^2\text{-O}^4$ and $\text{N}^3\text{-H}\cdots\text{O}^2\text{-O}^4$ RDFs and the calculated coordination numbers (N_c).

	300.15 K			400.15 K		
	$r_{\max} / \text{\AA}$	$r_{\text{cut}} / \text{\AA}$	N_c	$r_{\max} / \text{\AA}$	$r_{\text{cut}} / \text{\AA}$	N_c
$[\text{C}_4\text{C}_{1\text{im}}][\text{C}_1\text{SO}_4]$ $\text{C}^2\text{-H}\cdots\text{O}^2\text{-O}^4$	2.60	4.00	3.01	2.60	4.00	2.75
$[\text{C}_4\text{C}_{1\text{im}}][\text{HSO}_4]$ $\text{C}^2\text{-H}\cdots\text{O}^2\text{-O}^4$	2.49	3.82	2.86	2.49	3.82	2.66
$[\text{C}_4\text{Him}][\text{HSO}_4]$ $\text{C}^2\text{-H}\cdots\text{O}^2\text{-O}^4$	2.50	3.30	2.18	2.50	3.30	2.03
$[\text{C}_4\text{Him}][\text{HSO}_4]$ $\text{N}^3\text{-H}\cdots\text{O}^2\text{-O}^4$	1.70	2.30	1.03	1.70	2.43	1.09

The values of $r_{\max}$ for the $\text{C}^2\text{-H}\cdots\text{O}^2\text{-O}^4$ interactions ($\approx 2.49 - 2.60 \text{ \AA}$) are relatively consistent across the three systems. However, $r_{\max}$ for the $\text{N}^3\text{-H}\cdots\text{O}^2\text{-O}^4$ interaction is significantly shorter ($1.70 \text{ \AA}$), consistent with this being a stronger H-bond interaction. Increasing the temperature from 300.15 to 400.15 K does not have a significant effect on the position of the peak maxima.

In contrast, the coordination numbers show some temperature dependence. The decrease in N_c for the $\text{C}^2\text{-H}\cdots\text{O}^2\text{-O}^4$ interactions upon increasing the temperature suggests a reduction in H-bonding and subsequently a reduction in structuring. The value of N_c for the $\text{N}^3\text{-H}\cdots\text{O}^2\text{-O}^4$ interaction is the exception to this, not exhibiting notable temperature dependence. Within the temperature range studied, there is not a significant change in the number of $\text{N-H}\cdots\text{O}$ H-bonds, while the weaker $\text{C}^2\text{-H}\cdots\text{O}^2\text{-O}^4$ interactions are affected.

The calculated $\text{C}^2\text{-H}\cdots\text{O}^2\text{-O}^4$ coordination numbers are much higher than those for the analogous $\text{C}^2\text{-H}\cdots\text{Cl}$ interaction within $[\text{C}_4\text{C}_{1\text{im}}]\text{Cl}$.⁷³ Given the values of r_{cut} (up to $4 \text{ \AA}$), the large values of N_c could suggest that non-interacting terminal oxygen atoms of the anion are also being captured. Pictorial representations of possible cation – anion interaction motifs in which non-interacting terminal oxygen atoms could also be captured by r_{cut} are shown in **Figure 4.31**. Therefore, the values of N_c for the $\text{C}^2\text{-H}\cdots\text{O}^2\text{-O}^4$ interactions do not equate to the number of H-bonds.

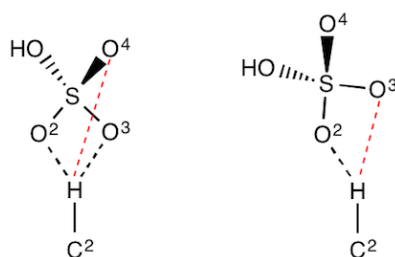


Figure 4.31. Possible $[\text{C}_4\text{C}_{1\text{im}}][\text{HSO}_4]$ interactions. Black dotted line represents $\text{C}^2\text{-H}\cdots\text{O}$ H-bond formation. Red dotted line indicates a non-interacting terminal oxygen within the $4 \text{ \AA}$ cut-off.

For $\text{N}^3\text{-H}\cdots\text{O}^2\text{-O}^4$, the value of r_{cut} is much lower, with a corresponding value of $N_c \approx 1$. Therefore, on average, each N-H group forms a single H-bond. In contrast, the larger values of N_c for the $\text{C}^2\text{-H}\cdots\text{O}^2\text{-O}^4$ interactions may also reflect an increased tendency for the formation of bifurcated H-bond motifs.

With the exception of the $\text{N}^3\text{-H}\cdots\text{O}^2\text{-O}^4$ interactions, temperature is not found to affect the values of r_{cut} . For $\text{N}^3\text{-H}\cdots\text{O}^2\text{-O}^4$ only a broadening of the first peak is observed.

The angle distribution functions (ADFs) for the $\text{C}^2\text{-H}\cdots\text{O}^2$ and $\text{N}^3\text{-H}\cdots\text{O}^2$ interactions have also been computed, i.e. the distribution of the angles $\phi(\text{O}^2\cdots\text{C}^2\text{-H})$ and $\phi(\text{O}^2\cdots\text{N}^3\text{-H})$, for interactions with a radial cut-off below the first peak minimum (r_{cut}). The computed ADFs for the systems at 400.15 K are shown in **Figure 4.32**, for each case the area under the curve has been normalised to unity.

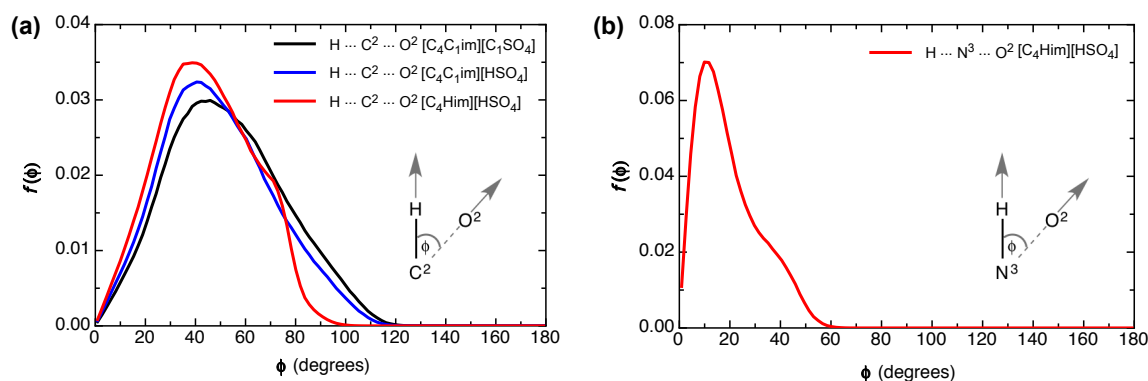


Figure 4.32. Distribution of angles $\phi(\text{O}^2\cdots\text{C}^2\text{-H})$ and $\phi(\text{O}^2\cdots\text{N}^3\text{-H})$ for atoms within the values of r_{cut} . All systems at 400.15 K.

The distribution of ϕ for each of the $\text{C}^2\text{-H}\cdots\text{O}^2$ interactions, **Figure 4.32 a**, is characterised by a broad peak with a maximum between 39 and 50°. By comparison, the $\text{N}^3\text{-H}\cdots\text{O}^2$ angle distribution is relatively narrow, with a maximum at 9.9°, **Figure 4.32 b**. The ADFs therefore support the conclusion that the N-H group of the protic imidazolium cation forms a single, linear H-bond interaction, as previously found for protic alkylammonium ionic liquids. In contrast, the $\text{C-H}\cdots\text{O}$ H-bonds show a reduction in linearity, as is typical for an ionic liquid and more generally for weaker H-bonds. For example, a widening of the conventional 30° H-bond angle cut-off has previously been suggested for both $[\text{C}_4\text{C}_1\text{im}]\text{Cl}^{73}$ and $[\text{C}_4\text{C}_1\text{im}]\text{Br}^{71}$.

3.4 Anion-anion interactions

3.4.1 Comparison between systems

The RDFs for the $S^1 \cdots S^1$ site-site interactions can be used to gauge the extent of the anion-anion interactions within the selected ionic liquid systems, **Figure 4.33 a**.

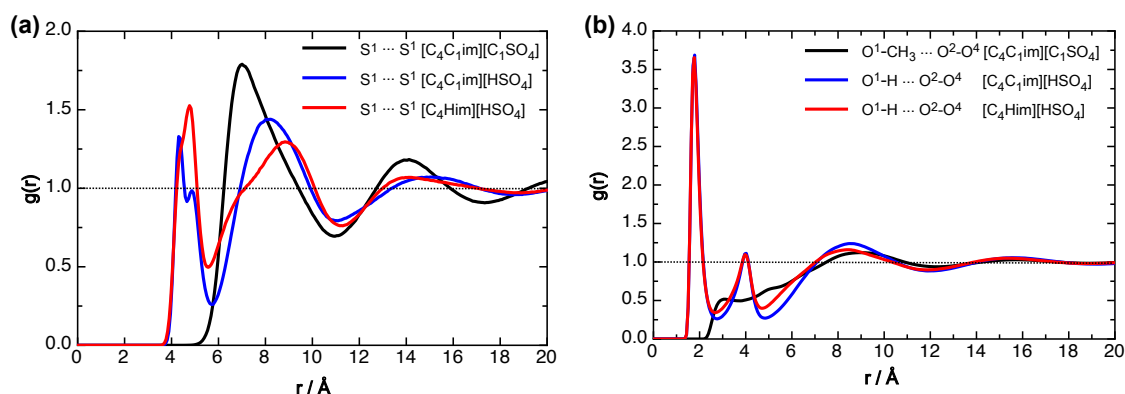


Figure 4.33. Selected anion-anion site-site radial distribution functions. All systems at 400.15 K.

For $[C_4C_1im][C_1SO_4]$ there is a broad peak with a maximum at ≈ 6.93 \AA. The $S^1 \cdots S^1$ distribution for $[C_4C_1im][C_1SO_4]$ is therefore very similar to the $S^1 \cdots S^1$ distributions previously reported for the related $[C_2C_1im][C_nSO_4]$ ($n=2,4,6$ and 8) series of aprotic imidazolium alkylsulphate ionic liquids.²⁰ For the $[C_2C_1im][C_nSO_4]$ systems, the broad peak in question was attributed to situations in which two anions are found to interact with the same cation.²⁰ Broad peaks, albeit with a reduced intensity and shifted to slightly longer radial distances, are also observed for $[C_4C_1im][HSO_4]$ and $[C_4Him][HSO_4]$, presumably also corresponding to configurations with multiple anions interacting with a single cation.

However, for both of the $[HSO_4]^-$ ionic liquids, there is an additional, narrower, peak with a maximum at a shorter radial distance ($\approx 4.24 - 4.77$ \AA). Within the gas phase $[C_1C_1im][HSO_4]$ ion pair dimers, the $S \cdots S$ separation for the lowest energy structure featuring a cyclic anion dimer is found to be ≈ 4.15 \AA. The corresponding $S \cdots S$ separation for the lowest energy dimer with an anion chain motif is ≈ 4.43 \AA. The positions of the first peak maxima for the computed $S^1 \cdots S^1$ RDFs could therefore suggest the formation of $[HSO_4]^- \cdots [HSO_4]^-$ interactions.

Similar conclusions can be drawn through a comparative analysis of the (intermolecular) $O^1-H \cdots O^2-O^4$ and $O^1-CH_3 \cdots O^2-O^4$ RDFs, **Figure 4.33 b**. For the $O^1-H \cdots O^2-O^4$ interactions within both $[C_4C_1im][HSO_4]$ and $[C_4Him][HSO_4]$, there is a very intense and sharp peak with a maximum at ≈ 1.77 \AA, indicating the formation of $O-H \cdots O$ H-bonds. By contrast, the RDF for the $O^1-CH_3 \cdots O^2-O^4$ interactions within $[C_4C_1im][C_1SO_4]$ exhibits an ill-defined, weak distribution, below the average background density. It is possible that there are some weak $[C_1SO_4]^- \cdots [C_1SO_4]^-$ interactions occurring within $[C_4C_1im][C_1SO_4]$, however, these are evidently significantly reduced in number relative to the analogous $[HSO_4]^- \cdots [HSO_4]^-$ interactions.

Numerous crystal structures of systems with $[HSO_4]^- \cdots [HSO_4]^-$ interactions have been reported. Typically the $S \cdots S$ distances are not discussed, however the H-bond $O \cdots O$ donor-acceptor distances have been used to assess the H-bonding in some cases. Within $[C_4C_1im][HSO_4]$, the H-bond $O \cdots O$

separation within the $[\text{HSO}_4]^-$ cyclic dimers is reported to be 2.61 Å.⁴⁶ H-bond O $\cdots$ O distances for $[\text{HSO}_4]^-$ chains within $\text{Cs}[\text{HSO}_4]$ are dependent on the phase, with reports up to 2.64 Å.⁷⁴ The computed $\text{O}^1\cdots\text{O}^2\cdots\text{O}^4$ RDFs for $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ and $[\text{C}_4\text{Him}][\text{HSO}_4]$ with the associated values of r_{max} are provided in the **Appendix, Figure A.24** and **Table A.39**. The computed values of r_{max} for the $\text{O}^1\cdots\text{O}^2\cdots\text{O}^4$ interactions are between 2.63 and 2.70 Å. These values are relatively consistent with the H-bond O $\cdots$ O distances reported for solid state systems in the literature, supporting our argument for $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ H-bonding within $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ and $[\text{C}_4\text{Him}][\text{HSO}_4]$.

Increased anion association with the protic $[\text{C}_4\text{Him}]^+$ cation could lead to differences in the $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ interactions compared to the aprotic analogue. The $\text{O}^1\cdots\text{H}\cdots\text{O}^2\cdots\text{O}^4$ RDFs for the two systems are effectively indistinguishable, however, the $\text{S}^1\cdots\text{S}^1$ radial distributions do show subtle differences.

For $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, there is a sharp peak at ≈ 4.24 Å followed by a subtle secondary peak at ≈ 4.46 Å. It is possible that these two peaks correspond to different $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ configurations (e.g. cyclic vs. chain). Within the $[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4]$ ion pair dimers, the S $\cdots$ S separation for structures featuring a cyclic $[\text{HSO}_4]^-$ dimer is found to be between 4.15 and 4.32 Å. In contrast the S $\cdots$ S separation within structures with the chain $[\text{HSO}_4]^-$ dimer is found to be slightly larger, between 4.43 to 4.49 Å. However, a larger number of structures need to be sampled to validate this observation. Furthermore, the observed relative S $\cdots$ S separations in the gas phase may not reflect the relative S $\cdots$ S separations in the bulk phase. Within the liquid there is the possibility of interactions between multiple $[\text{HSO}_4]^-$ anions. For the chain motif, this could lead to cooperative effects and a concomitant decrease in the S $\cdots$ S separation.

The $\text{S}^1\cdots\text{S}^1$ radial distribution for $[\text{C}_4\text{Him}][\text{HSO}_4]$ features a single peak with a maximum at ≈ 4.77 Å, possibly due to the merging of the two distinguishable peaks observed for $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$. This could suggest a slight difference in the $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ interactions within the two $[\text{HSO}_4]^-$ ionic liquids.

The average $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ coordination numbers, N_C , for both $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ and $[\text{C}_4\text{Him}][\text{HSO}_4]$ have been estimated through integrating up to the first (significant) peak minimum observed in the $\text{S}^1\cdots\text{S}^1$ RDFs. The corresponding $\text{O}^1\cdots\text{H}\cdots\text{O}^2\cdots\text{O}^4$ coordination numbers have also been calculated. Radial distances for the peak maxima, minima and the associated values of N_C are listed in **Table 4.8**, for the systems at both 300.15 and 400.15 K. The $\text{S}^1\cdots\text{S}^1$ and $\text{O}^1\cdots\text{H}/\text{CH}_3\cdots\text{O}^2\cdots\text{O}^4$ RDFs for the systems at 300.15 K are provided in the **Appendix, Figure A.25**.

The anion-anion coordination numbers for both systems decrease upon an increase in temperature. This is also reflected in the $\text{O}^1\cdots\text{H}\cdots\text{O}^2\cdots\text{O}^4$ coordination numbers, suggesting a decrease in the anion-anion H-bonding. Nevertheless, for both ionic liquids, at both temperatures, the total anion-anion coordination numbers (i.e. N_C for $\text{S}^1\cdots\text{S}^1$) are greater than one. This indicates the formation of anion aggregates larger than anion dimers (i.e. more than two $[\text{HSO}_4]^-$ anions). For the formation of $([\text{HSO}_4]^-)_n$ aggregates, with $n>2$, the anion chain motif must feature. Moreover, the values of N_C for $[\text{C}_4\text{Him}][\text{HSO}_4]$ are higher than for $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, suggesting a possible increase in the size of the anion chains.

Table 4.8. Positions of the first peak maxima ($r_{\max}$) and peak minima (r_{cut}) for the $\text{S}^1\cdots\text{S}^1$ and $\text{O}^1\text{-H}\cdots\text{O}^2\text{-O}^4$ RDFs and the calculated coordination numbers (N_c).

	300.15 K			400.15 K		
	$r_{\max} / \text{\AA}$	$r_{\text{cut}} / \text{\AA}$	N_c	$r_{\max} / \text{\AA}$	$r_{\text{cut}} / \text{\AA}$	N_c
$[\text{C}_4\text{C}_{1\text{im}}][\text{HSO}_4]$ $\text{S}^1\cdots\text{S}^1$	4.31	5.64	1.31	4.24	5.71	1.21
$[\text{C}_4\text{Him}][\text{HSO}_4]$ $\text{S}^1\cdots\text{S}^1$	4.83	5.50	1.71	4.77	5.57	1.64
$[\text{C}_4\text{C}_{1\text{im}}][\text{HSO}_4]$ $\text{O}^1\text{-H}\cdots\text{O}^2\text{-O}^4$	1.72	2.63	0.93	1.79	2.77	0.80
$[\text{C}_4\text{Him}][\text{HSO}_4]$ $\text{O}^1\text{-H}\cdots\text{O}^2\text{-O}^4$	1.77	2.57	0.93	1.77	2.70	0.87

The coordination numbers for the $\text{O}^1\text{-H}\cdots\text{O}^2\text{-O}^4$ interactions are all below one, suggesting that the O-H groups form single H-bonds only. Moreover, N_c values < 1 indicates the presence of free O-H groups, suggesting that, on average, not all anions are involved in H-bond donation to another anion. Therefore, not all $[\text{HSO}_4]^-$ anions are “tied up” in the formation of cyclic dimers. Importantly, cation-anion interactions are not precluded by the formation of anion-anion interactions. Pictorial representations of possible scenarios are shown in **Figure 4.34**: (a) “anion free” $[\text{HSO}_4]^-$ (i.e. not interacting with another anion), (b) a $[\text{HSO}_4]^-$ chain dimer leaving one O-H group free and (c) a $[\text{HSO}_4]^-$ cyclic dimer with both O-H groups involved in H-bonding. In each case, anion interactions with cations are possible.

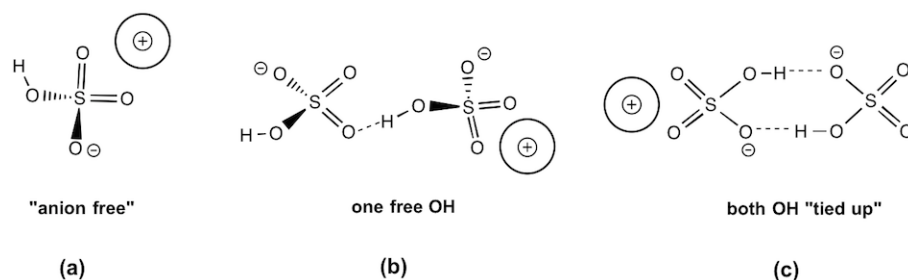


Figure 4.34. Possible anion interactions. Cations are represented by circles with a positive charge at the centre.

The computed distributions of angle ϕ ($\text{O}^2\cdots\text{O}^1\text{-H}$) for $[\text{C}_4\text{C}_{1\text{im}}][\text{HSO}_4]$ and $[\text{C}_4\text{Him}][\text{HSO}_4]$, **Figure 4.35**, exhibit peak maxima at 11.7° . Thus, as anticipated, the $\text{O-H}\cdots\text{O}$ interactions are highly directional, consistent with the formation of single, linear H-bonds.

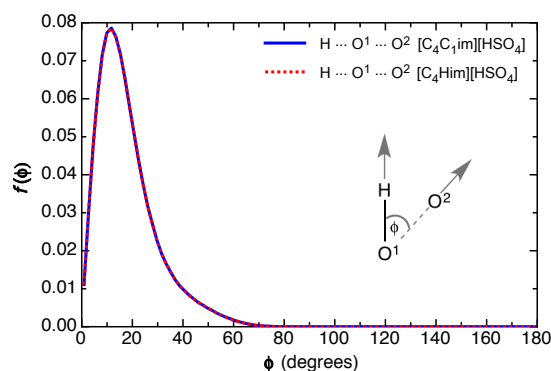


Figure 4.35. Distribution of the angle $\phi(\text{O}^2\cdots\text{O}^1\text{-H})$ within $[\text{C}_4\text{C}_{1\text{im}}][\text{HSO}_4]$ and $[\text{C}_4\text{Him}][\text{HSO}_4]$, for atoms within the values of r_{cut} . Both systems at 400.15 K.

3.4.2 Anion-anion hydrogen bond motifs within [C₄C₁im][HSO₄]

To further investigate the nature of the [HSO₄][−]⋯[HSO₄][−] interactions, a qualitative assessment, through visual inspection of the [C₄C₁im][HSO₄] trajectories (at both 300.15 and 400.15 K) has been undertaken. A quantitative analysis has not yet been performed.

For a given timestep of the [C₄C₁im][HSO₄] trajectory at 400.15 K, the presence of “anion free” [HSO₄][−] can be observed. However, the existence of anion dimers can also be detected. The [HSO₄][−] dimers exhibit one of three main motifs, **Figure 4.36**; the cyclic motif (**a**), the chain motif (**b**) or the intermediate motif (**c**), in which one of the O-H⋯O H-bonds of the cyclic motif has effectively been “switched off”. For the intermediate motif, formation of a second O-H⋯O interaction would therefore lead to formation of a cyclic dimer, whilst rotation of one of the anions would lead to formation of the chain motif.

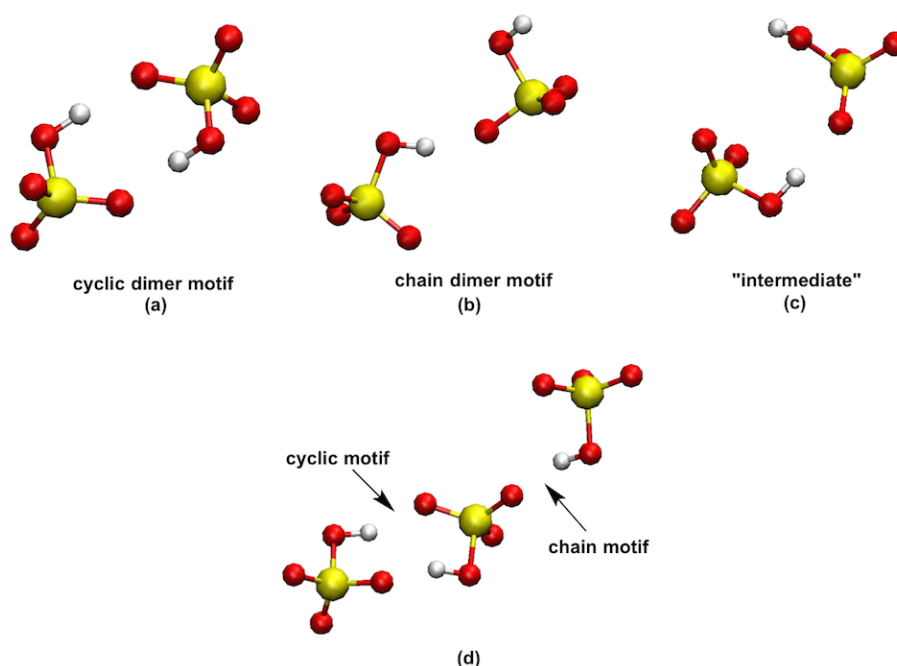


Figure 4.36. Anion-anion interactions observed within the 400.15 K simulation of [C₄C₁im][HSO₄]: (a) – (c) example structures showing the three [HSO₄][−] dimer motifs and (d) an example of an [HSO₄][−] trimer.

Larger [HSO₄][−] aggregates, particularly anion trimers, can also form. However, these are not typically examples of a simple ([HSO₄][−])₃ chain motif; rather, the observed anion trimers feature a combination of the cyclic *and* chain motifs. An example [HSO₄][−] trimer of this type is shown in **Figure 4.36 d**. Within the example structure shown in **Figure 4.36 d**, two [HSO₄][−] are associated in the cyclic motif. With both of the O-H H-bond donor groups involved in formation of the cyclic dimer, interaction with a third [HSO₄][−] can only occur *via* H-bond formation with one of the four free terminal oxygen atoms i.e. through a chain-type interaction.

The lifetime of the anion dimers and higher aggregates has not yet been determined, however, even through visual inspection, it can be established that the anion-anion interactions and associated H-bond motifs are dynamic. For example, in **Figure 4.37**, a series of snapshots shows how the interactions between three [HSO₄][−] anions change over a short period of time. From a cyclic anion

dimer (a), interaction with a third $[\text{HSO}_4]^-$ anion leads to a temporary dissociation of the dimer (b). The dimer partially reforms, i.e. the intermediate motif (c), followed by transient formation of an anion trimer (d). Thus, there is flexibility in the $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ interactions.

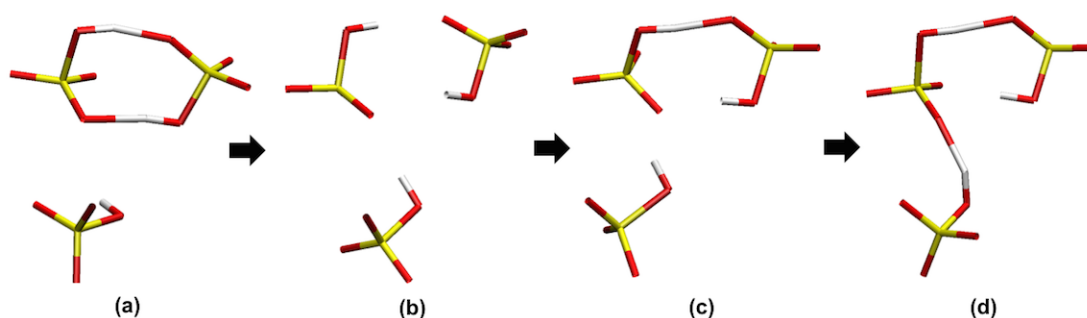


Figure 4.37. Series of snapshots showing the dynamic nature of H-bond motifs between three anions.

Anion-anion interactions within the 300.15 K simulation of $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ show similarities to those observed at the higher temperature, in that the three primary anion – anion motifs (cyclic, chain and intermediate) are also evident. However, a key difference at the lower temperature is the increase in the probability of forming larger anion aggregates, i.e. trimers and above. This is consistent with the increase in the average anion-anion coordination number at the lower temperature.

As well as anion trimers, numerous examples of anion tetramers could be identified. As established for the anion trimers, the anion tetramers also typically feature an anion cyclic dimer as a central unit. Starting from an anion trimer, composed of anions A, B and C (with A and B forming the central cyclic dimer), a fourth $[\text{HSO}_4]^-$ (anion D) could potentially interact with A, B or C, allowing for the formation of a wider range of anion aggregate motifs. For example, the fourth $[\text{HSO}_4]^-$ anion could interact with anion C, leading to the extension of the anion chain motif in one direction, as in **Figure 4.38 a**. Alternatively, introduction of a fourth $[\text{HSO}_4]^-$ unit could initiate anion chain formation in the opposite direction, e.g. **Figure 4.38 b**. A branched motif is formed when anions C and D interact with the two terminal oxygen atoms of the *same* $[\text{HSO}_4]^-$ (anion A in this case), **Figure 4.38 c**. A variation of the central anion dimer unit is seen in **Figure 4.38 d**, where a central cyclic anion trimer can instead be seen.

The results from the MD simulations of $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ undertaken here suggest the co-existence of $[\text{HSO}_4]^-$ cyclic dimers and chains. The combination of these two motifs allows for the formation of larger anion aggregates.

In concordance with the previously reported MD analysis of $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, we observe the existence of anion dimers in the bulk phase.²³ However, the formation of larger aggregates, as seen here, was not previously commented upon. This difference likely arises as a result of the different force fields employed. The increased polarisation of the O-H group within FFA (as used here) results in an increase in anion-anion H-bonding; the formation of $\text{O-H} \cdots \text{O}$ H-bonds is more favourable, leading to the formation of larger aggregates.

The existence of larger anion aggregates within $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ was suggested on the basis of Raman spectra.²⁴ However, it was proposed, through comparison to the solid state spectra of simple

$[\text{HSO}_4]^-$ salts, that the aggregation of the $[\text{HSO}_4]^-$ anions occurs *via* the chain motif. Given the complex interplay between the different anion motifs observed here, experimentally distinguishing between the motifs could be challenging. Nevertheless, our results do corroborate the suggestion that the anion-anion interactions, and therefore the size of the anion aggregates, decreases as the temperature of the system increases.

The findings presented here are therefore in partial agreement with both the previous MD results and the interpretation of the experimental Raman spectra. However, perhaps most importantly, we can provide further evidence to substantiate the claim that when protic anions are present, anion-anion H-bonding could play an important role in influencing the properties of the ionic liquid.

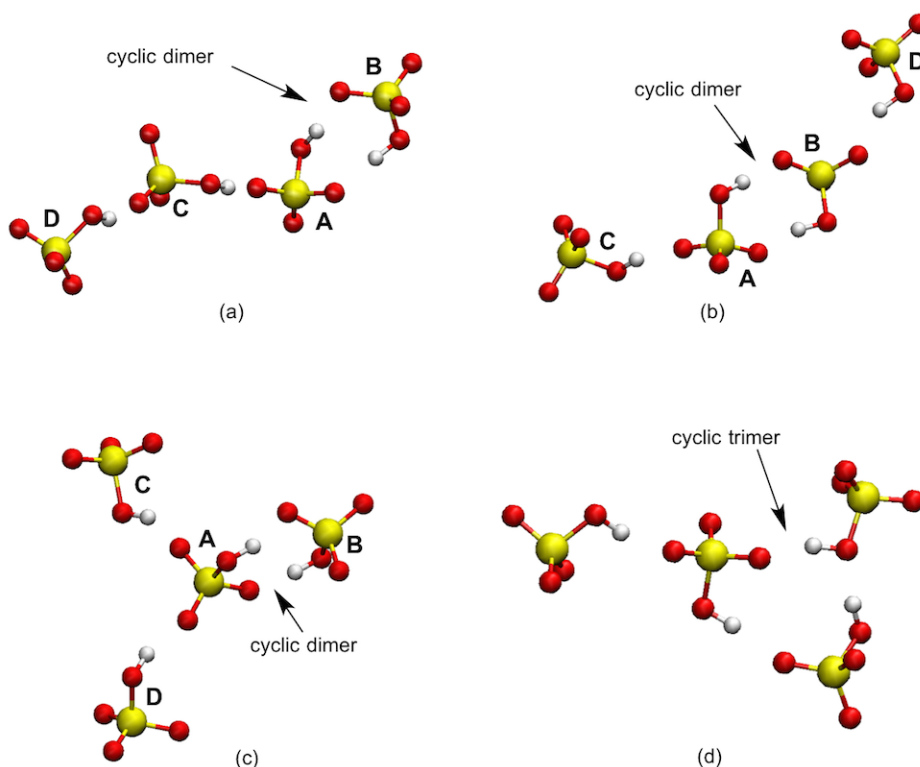


Figure 4.38. Examples of anion tetramers observed within the 300.15 K simulation of $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$.

3.4.3 Hydrogen bond networking within $[\text{C}_4\text{Him}][\text{HSO}_4]$

It has previously been suggested that H-bonding within ionic liquids could induce formation of a three dimensional H-bonded network.⁷⁵⁻⁷⁷ Water is the prototypical exemplar of a liquid system with a H-bonded network. With each water molecule having two H-bond donor groups and two H-bond acceptor sites, a tetrahedral H-bond network can be established.^{78, 79} The classical view of a tetrahedral network within liquid water is still strongly favoured,⁸⁰ although there is some debate relating to the symmetry of the network.^{79, 81, 82} Some of the anomalous (and yet characteristic) properties of water have long been associated with the formation of a H-bond network; typical examples including the high melting and boiling points, high heat capacity and the decrease in molar volume upon melting.⁷⁸ Therefore, H-bond networking within ionic liquids could influence and give rise to unique properties.

Although H-bond networking could potentially occur within aprotic ionic liquids *via* C-H...X H-bond formation, H-bond networking within protic ionic liquids, *via* N-H...X interactions, is more evident. We restrict our discussion here to “primary” H-bond networking *via* N-H...X interactions, and although present, do not consider the influence of the “secondary” C-H...X interactions.

For effective multidimensional H-bond networking within a protic ionic liquid, the ions must be able to partake in the formation of multiple H-bonds; the cations typically have multiple N-H donor groups and the anions multiple H-bond acceptor sites. This is the case for the prototypical protic ionic liquid, ethylammonium nitrate; the cation has three potential H-bond donor sites and the anion three potential H-bond acceptor sites, thus both ions can act as “linker” groups in terms of H-bond networking. Simplified representations of the ethylammonium and nitrate ions, emphasising the donor and acceptor groups, are shown in **Figure 4.39 a** and **b** respectively. Through analysis and deconvolution of the far-infrared spectra, the H-bond network within ethylammonium nitrate, and related systems, were found to be “reminiscent” of the networking in water.⁷⁷

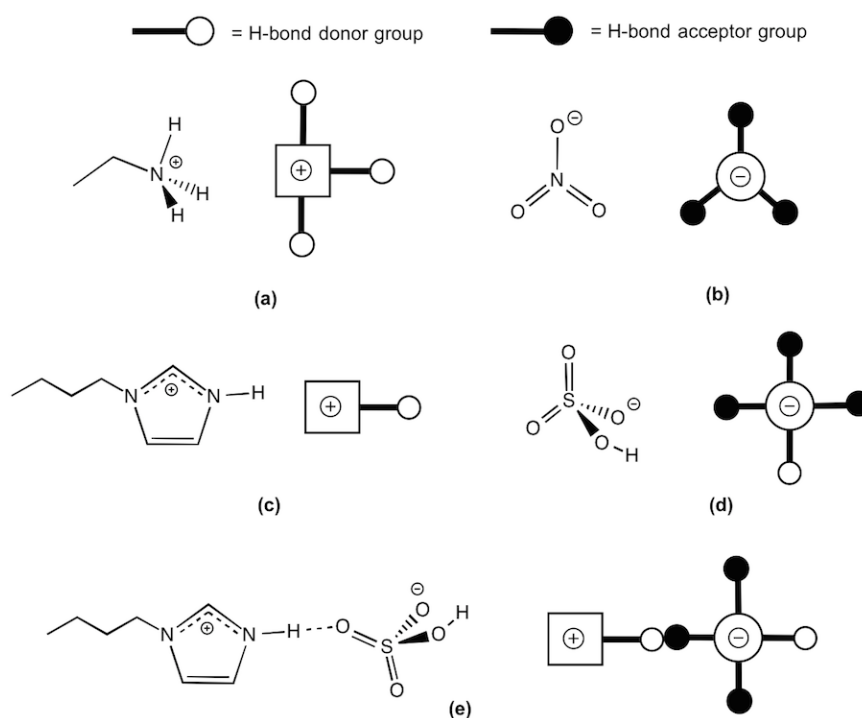


Figure 4.39. Simplified representation of the H-bond donor and acceptor groups of selected ions: (a) ethylammonium, (b) nitrate, (c) 1-butylimidazolium and (d) hydrogensulphate. (e) Simplified representation of an example [C₄Him][HSO₄] ion pair.

It has been suggested that H-bond networking is most effective when the number of H-bond donor groups on the cation and H-bond acceptor groups on the anion are nearly matched.⁷⁶ However, a “miss-match” in terms of the number of donor and acceptor groups could introduce flexibility into the H-bond network.³³ Moreover, even when the number of donor and acceptor groups is matched, not all of the donor and acceptor groups are necessarily involved in H-bond network formation.^{83, 84} It has been proposed that incomplete, or highly asymmetrical, H-bond networks could introduce increased disorder within an ionic liquid.^{33, 84}

Neutron diffraction has been used to investigate the structuring within a series of alkylammonium protic ionic liquids featuring anions with different numbers of H-bond acceptor sites.⁸⁵ Whilst all systems were found to form H-bond networks, the local H-bond motifs varied according to the identity of the anion. Ethylammonium thiocyanate, for example, featured linear H-bonds, whilst ethylammonium nitrate exhibited bifurcated H-bonds. Ethylammonium hydrogensulphate was also examined and found to form strong and linear N-H...O H-bonds. Whilst anion-anion O-H...O H-bonds were also detected, these were found to be “rarer” than the cation-anion H-bond interactions and deemed less significant. The potential contribution of the anion-anion H-bond to the networking was not discussed.

Nevertheless, regardless of the variations in the number and linearity of the H-bonds, for a traditional protic ionic liquid, such as ethylammonium nitrate, the H-bond network is built up and extended through cation-anion interactions. This is not the case for [C₄Him][HSO₄].

The N-H...O H-bonds between [C₄Him]⁺ and [HSO₄]⁻ have been found here to be both strong and directional. However, the [C₄Him]⁺ cation only has a single N-H H-bond donor group. Therefore, [C₄Him]⁺ acts as a terminal, rather than linker group in terms of network formation, **Figure 4.39 c**.

The protic anion has one H-bond donor group and three H-bond acceptor groups (not including O¹). [HSO₄]⁻ can therefore act as a linker unit (**Figure 4.39 d**). As demonstrated for [C₄C₁im][HSO₄], this allows for the formation of anion dimers and higher aggregates. Therefore, any primary H-bond network within [C₄Him][HSO₄] *must* be built up through O-H...O anion-anion interactions.

Unlike for the gas phase ion pairs, an [HSO₄]⁻ anion in the bulk phase can maximise H-bond interactions through the formation of multiple H-bonds with different ions: multiple cations, multiple anions or a mix of cation and anion interactions. Through visual inspection of the 400.15 K trajectory of [C₄Him][HSO₄], a wide variety of different cation-anion configurations can be identified; selected examples are shown in **Figures 4.40, 4.41 and 4.42**. These examples are effectively “fragments” of a larger H-bond network that will also involve C-H...O H-bond interactions.

Interaction of a cation with a single anion *via* an N-H...O H-bond is a strongly favoured motif, **Figure 4.39 e**. Given the N-H...O²-O⁴ coordination number of approximately one and the relatively linear orientation of the interactions, it is likely that on average each of the cation N-H groups is involved in H-bond formation with an anion. However, it is also possible for a single anion to interact with more than one cation.

Figure 4.40 shows two examples where a single anion is found to interact with multiple [C₄Him]⁺ cations. Interaction with two cations, **Figure 4.40 a**, leaves one H-bond acceptor and one H-bond donor group free, therefore, there is the potential for the H-bond network to grow in two directions upon interaction with an additional anion. Although most likely a rare event, interaction with three cations, **Figure 4.40 b**, is a possibility. However, such an arrangement is not conducive to H-bond network formation, with each of the three terminal H-bond acceptor groups “blocked” through interaction with a cation. Therefore, for effective H-bond networking in this system, interactions between a single anion and multiple terminal cation units must be restricted in number.

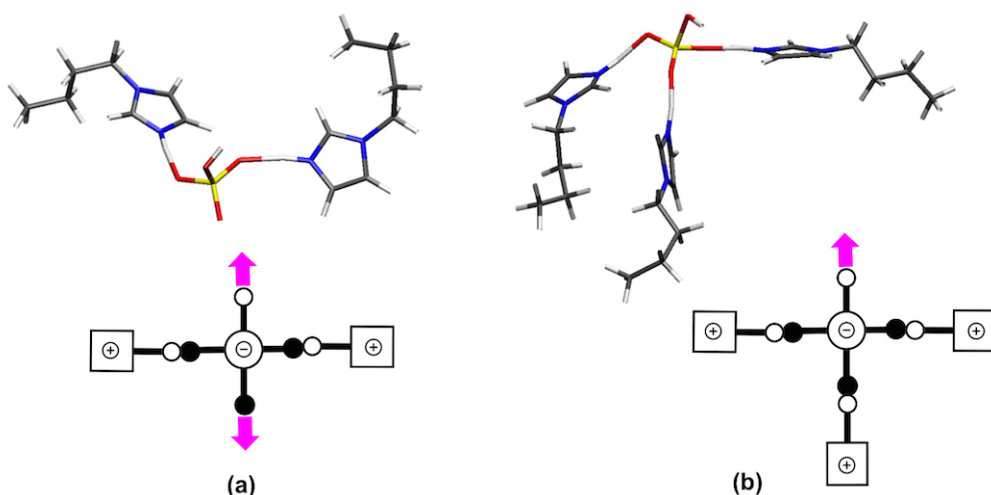


Figure 4.40 Examples of cation-anion configurations observed within the $[\text{C}_4\text{Him}][\text{HSO}_4]$ 400.15 K trajectory: (a) one anion with two cations and (b) one anion with three cations. Pink arrows indicate available groups for extension of the H-bond network.

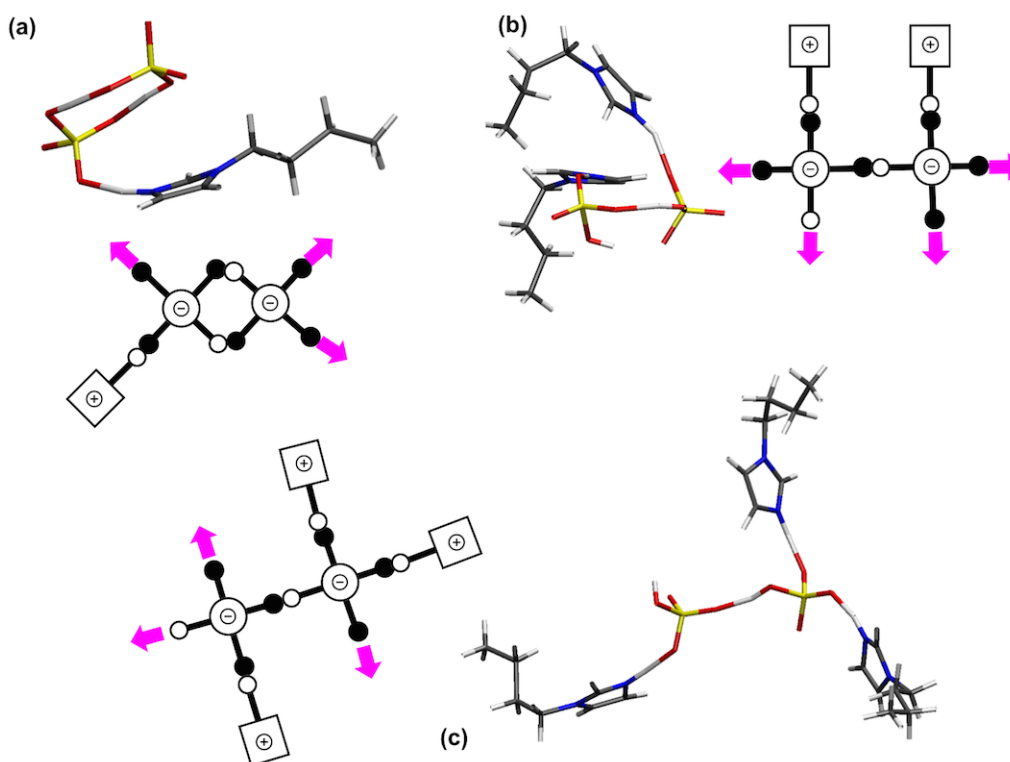


Figure 4.41 Examples of cation-anion configurations observed within the $[\text{C}_4\text{Him}][\text{HSO}_4]$ 400.15 K trajectory: (a) cyclic anion dimer with one cation, (b) chain anion dimer with two cations and (c) chain anion dimer with three cations. Pink arrows indicate available groups for extension of the H-bond network.

Within **Figure 4.41**, three configurations featuring anion dimers are shown. The structure that is shown in **Figure 4.41 a** exhibits a cyclic dimer motif, interacting with a single cation *via* one of the terminal oxygen atoms. In this configuration, the anions can only act as H-bond acceptors; the remaining available terminal oxygen atoms could interact with further cations, or, as seen for $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, interact with the O-H group of an anion *via* the chain motif. The structures shown in **Figure 4.41 b** and **c** both feature anion chain dimers, interacting with two and three cation units

respectively. In both cases, the anion dimer is still able to act as both a H-bond acceptor and H-bond donor.

Examples of structural motifs featuring anion trimers are shown in **Figure 4.42**. As with the anion trimers observed within $[\text{C}_4\text{C}_{1\text{im}}][\text{HSO}_4]$, examples of trimers featuring a cyclic dimer as a central unit can also be observed within $[\text{C}_4\text{Him}][\text{HSO}_4]$, e.g. **Figure 4.42 a**. However, strong interaction with one or more cations, e.g. **Figure 4.42 b**, potentially results in disruption of the cyclic dimer motif, favouring the formation of chains. The structure shown in **Figure 4.42 d** shows how the interaction with four cations has resulted in a more “open” anion aggregate, compared to the anion trimer shown in **Figure 4.42 a**. Moreover, although four of the H-bond acceptor groups are blocked, terminal oxygen atoms and one O-H group are still available for extension of the H-bond network.

The structure shown in **Figure 4.42 c**, a cluster of three cations and three anions, is an interesting example as it features a highly branched motif. This illustrates how the tetrahedral geometry of the $[\text{HSO}_4]^-$ anion could be very effective in building a multidimensional network.

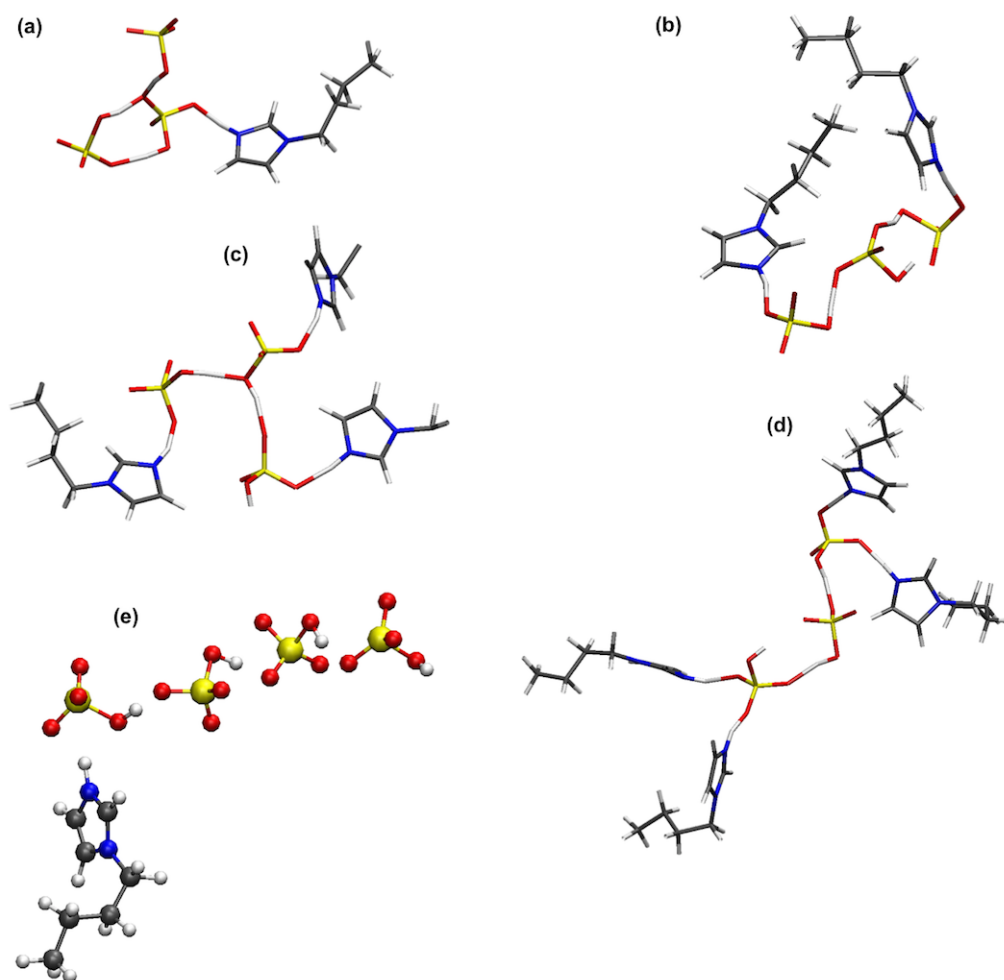


Figure 4.42. Examples of cation-anion configurations observed within the $[\text{C}_4\text{Him}][\text{HSO}_4]$ 400.15 K trajectory: (a) an anion trimer with one cation, (b) an anion trimer with two cations, (c) an anion trimer with three cations, (d) an anion trimer with four cations and (e) an anion chain composed of four anions.

Comparing the anion-anion coordination numbers of $[\text{C}_4\text{Him}][\text{HSO}_4]$ and $[\text{C}_4\text{C}_{1\text{im}}][\text{HSO}_4]$, **Table 4.8**, it was found that the average value of N_c is slightly higher for $[\text{C}_4\text{Him}][\text{HSO}_4]$. This is counterintuitive on

the basis that cation-anion interactions within $[\text{C}_4\text{Him}][\text{HSO}_4]$ block terminal oxygen positions, resulting in fewer H-bond acceptor groups for extension of the anion aggregates. However, the example structures shown in **Figure 4.42** reveal how the $[\text{C}_4\text{Him}]^+ \cdots [\text{HSO}_4]^-$ interactions result in a disruption of the cyclic dimer motif, leading to more open aggregates, more favourable for chain extension. For example, the anion chain composed of four units, **Figure 4.42 e**, is potentially facilitated by the cation interactions. Therefore, contrary to initial assumptions, increased cation-anion interaction could also result in increased anion-anion associations.

However, there is a balance between cation-anion interactions enhancing anion-anion association through facilitation of anion chain formation, and increased cation-anion interactions prohibiting anion aggregation. For example, increasing the number of N-H donor groups on the cation would lead to an increased number of cation - anion interactions. If the N-H $\cdots$ O interactions occur at the expense of the slightly weaker anion-anion O-H $\cdots$ O interactions, then the potential for anion aggregation would be reduced. This could explain why the H-bond network within ethylammonium hydrogensulphate is built upon cation-anion interactions, with the anion-anion interactions purported to be of less significance.⁸⁵

$[\text{C}_4\text{Him}][\text{HSO}_4]$ is evidently a highly structured ionic liquid featuring both strong cation-anion and anion-anion interactions. Unlike the more established alkylammonium protic ionic liquids, potential H-bond networking within $[\text{C}_4\text{Him}][\text{HSO}_4]$ occurs *via* anion-anion interactions. The viscosity of $[\text{C}_4\text{Him}][\text{HSO}_4]$ is approximately twenty times greater than that of $[\text{C}_4\text{C}_{1}\text{im}][\text{HSO}_4]$ at 25°C (5690 cP and 286 cP respectively).⁴⁰ This can be rationalised on the basis of both increased cation-anion and potentially anion-anion interactions.

3.5 Using QM/MM to investigate ionic liquid structuring: A preliminary study

Using MD, averaged properties and the structuring within a bulk system can be obtained. However, as the wavefunction is not explicitly treated, information relating to the electronic structure cannot be acquired. For example, H-bond interactions within a classical MD simulation are purely ionic and quantification of the individual H-bonds is restricted to geometric descriptors (e.g. H-bond lengths and angles).

With quantum chemical methods, we can routinely examine the electronic structure of small systems. For ionic liquids this is usually an ion pair or ion pair dimer. However, how representative of the bulk are the geometries of these smaller systems? Common computational H-bond descriptors, such as ρ_{BCP} and $E^{(2)}$, are highly sensitive to distance. Moreover, cooperative H-bond networking cannot be adequately recovered with small systems. Thus, is our interpretation of H-bonding in ionic liquids, based on ion pairs and dimers, consistent with H-bonding in the bulk liquid?

Ideally, we would like to undertake electronic structure analyses of large clusters of ions in geometries representative of the bulk system. Such calculations are not yet routinely viable using quantum chemical methods. However, using a hybrid QM/MM based approach, there is the potential to examine an ion pair cluster of moderate size at the QM level in the surrounding environment of the bulk liquid. We present here initial results from an investigation into the application of QM/MM, using the ChemShell interface, to examine H-bonding in small clusters of ion pairs surrounded by an ionic liquid environment. The preliminary and limited nature of this investigation must be emphasised. However, the results are informative and therefore we have chosen to include them here. The purpose of these calculations is to provide a more accurate solvation environment for the central QM region and not to recover thermodynamic parameters. Thus, the central QM region is the focus of our initial study.

To obtain structures representative of the bulk liquid, clusters of ions have been cut from the MD trajectories of $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ and $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ and subsequently partitioned into QM and MM regions. We use a three-layer approach here, with the MM region divided into two, an active MM region surrounding the central QM subsystem and an outer frozen MM region. A preliminary assay of the structuring and H-bonding within the optimised central QM regions has been undertaken.

3.5.1 Method

All clusters for QM/MM optimisation were prepared using the in-house MolCluster cutting tool.⁸⁶ Neutral spherical clusters of 50 ion pairs (i.e. 50 cations and 50 anions) were cut at regular time intervals (every 250 ps) from the last 5 ns of the 300.15 K trajectories of $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ and $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, generating 20 input structures for each system.

The origin of each of the clusters was defined to be a C^2 atom of a central $[\text{C}_4\text{C}_1\text{im}]^+$ cation. The specified numbers of ions in each of the three regions (QM, $\text{MM}_{\text{active}}$ and $\text{MM}_{\text{frozen}}$) were identified with respect to the distance to the origin. For example, if four cations were required in the QM region, the closest four cations to the origin (including the cation at which the origin is located) would have been selected. In total, each of the clusters is composed of 4 ion pairs in the central QM region, 16 further ion pairs in the $\text{MM}_{\text{active}}$ region and the remaining 30 ion pairs in the $\text{MM}_{\text{frozen}}$ region. The $\text{MM}_{\text{active}}$ and $\text{MM}_{\text{frozen}}$ regions form approximate first and second solvation shells about the central QM

region respectively. An example QM/MM $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ input cluster, with the three regions clearly identified, is shown in **Figure 4.43**.

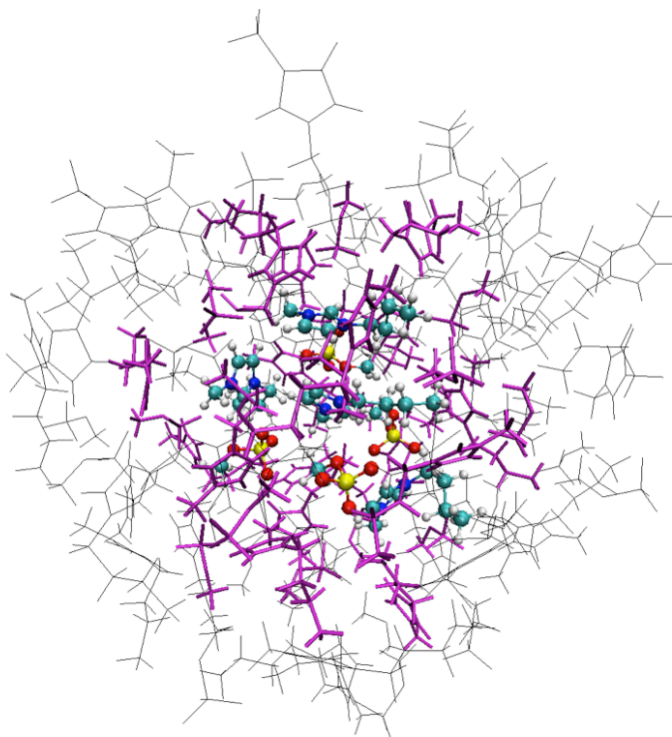


Figure 4.43. Example QM/MM cluster of 50 $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ ion pairs: 4 ion pairs in the QM region (balls and sticks), 16 ion pairs in the MM active region (pink sticks) and 30 ion pairs in the MM frozen region (black lines).

QM/MM optimisations of selected clusters were undertaken within the ChemShell^{87, 88} environment employing the DL_FIND optimiser.⁸⁹ Gaussian 09 (revision D.01)⁹⁰ was used as the QM interface and DL_POLY Classic^{58, 59} as the MM interface. The electrostatic interactions between the QM and MM region were treated using the electrostatic embedding coupling scheme. The Canongia Lopes-Padua force fields for $[\text{C}_4\text{C}_1\text{im}]^+$ and $[\text{C}_1\text{SO}_4]^-$, and the FFA force field for $[\text{HSO}_4]^-$ (i.e. the same potentials as used for the MD simulations) were employed for the MM evaluation.^{60, 62, 63} As within the MD simulations, the X-H bonds ($\text{X} = \text{C}, \text{O}$) within the MM regions were constrained. The central QM regions were initially optimised at the B3LYP/6-31G(d,p) level. Starting from the optimised B3LYP/6-31G(d,p) geometries, the QM regions were subsequently optimised at the B3LYP/6-311G(d,p) level with tighter convergence criteria of 10^{-9} on the density matrix and 10^{-7} on the energy matrix. Frequency analyses of the optimised clusters have not yet been performed. QTAIM analyses of the isolated QM region (i.e. without the surrounding MM environment) of selected clusters have been undertaken using AIMAll at the B3LYP/6-311G(d,p) level of theory.

In total, 20 $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ and 5 $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ clusters have been optimised using this QM/MM method.

Comment on choice of QM method

On increasing the basis set size from 6-31G(d,p) to 6-311G(d,p) we typically found there to be a notable increase in the time taken for the geometry optimisation of the QM region. Starting the 6-311G(d,p) optimisation from the 6-31G(d,p) optimised structure was an attempt to reduce the

computational time. Ideally we would employ a triple split-valence basis with both diffuse and polarisation functions. However, just the addition of diffuse functions to the 6-31G(d,p) basis (i.e. to give the 6-31+G(d,p) basis) was also found to result in a notable increase in the calculation time. The 6-311G(d,p) basis was therefore chosen as a compromise. This triple split-valence basis set increases the flexibility and improves the description of the electron density at a distance further away from the atomic centre, even without the addition of diffuse functions. Moreover, this is applicable to all atoms, including hydrogen.

The importance of dispersion in influencing the structuring within ionic liquids has been established. Within ChemShell, currently only the D2 dispersion correction is implemented and modification of the code is required to introduce the more recent D3(BJ) correction. For the calculations presented here, we chose not to include the D2 correction. Our choice was based on results from some very early test calculations (not included here) where we found that the addition of the D2 correction could lead to small, but slightly unpredictable, changes in the structure. For example, in one instance it was found that relative to the “MD geometry”, both optimisation with and without the D2 correction resulted in small shifts in the structure, but in opposite directions. In other cases this was not observed. The type of dispersion correction employed in conjunction with the underlying functional have also previously been found to affect the relative stabilities of ionic liquid ion pairs and ion pair dimers e.g. the energy ordering of the top and front ion pair configurations with B3LYP-D3BJ and ω B97XD is reversed.⁵⁵ A more systematic study is required to establish the influence of dispersion corrections (and choice of functional) on the structuring within the QM/MM clusters.

3.5.2 Comparison of geometries: before and after QM/MM optimisation

To assess the extent to which the geometry of the QM region changes relative to the geometry in the bulk MD simulation, it is necessary to compare the geometry before and after QM/MM optimisation. Two examples of [C₄C₁im][C₁SO₄] clusters for which the pre and post QM/MM optimised geometries of the QM regions are overlaid are shown in **Figure 4.44** (N.B. the MM regions are present, but are not shown for clarity).

Typically, changes between the pre-QM/MM geometry (that is, the geometry adopted in the bulk MD simulation) and the post-QM/MM geometry are relatively small, although in some cases, slightly larger changes in the geometries can be observed. For example, Cluster A, **Figure 4.44 a**, shows a mix of small and slightly more significant differences, while Cluster B, **Figure 4.44 b**, shows only small changes between the MD and QM/MM geometries.

Not enough testing has yet been conducted for the origin of the observed geometry differences to be established; there are a number of possible contributing factors. Is the origin of the differences due to the inability of the fixed charge MD simulation to account for electronic effects? For example, polarisation could be influencing the local structuring. Alternatively, is the MM surrounding region insufficient in size to capture the long-range effects of the bulk environment? Another possibility is that the level of theory used to evaluate the QM region is not accurate enough to obtain a good geometry. For example, dispersion effects are not adequately recovered at the B3LYP level.

Optimisation of the B3LYP/6-311G(d,p) geometry of Cluster B at the B3LYP-D2/6-311G(d,p) level does result in small geometry changes, **Figure 4.44 c**.

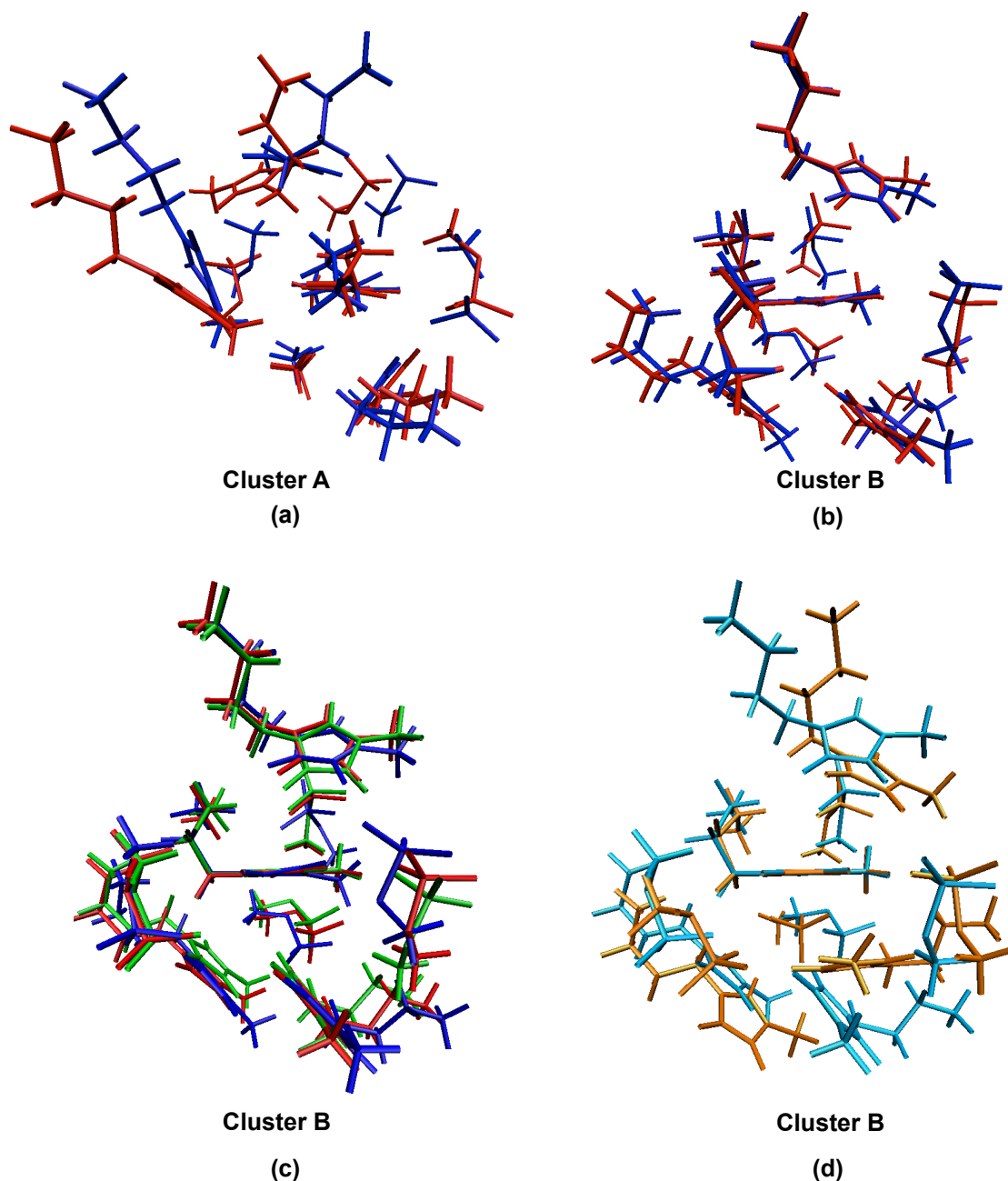


Figure 4.44. Central QM region of selected QM/MM clusters of $[C_4C_{1im}][C_1SO_4]$: the MD geometry (blue) and QM/MM optimised geometry (red) for (a) Cluster A and (b) Cluster B. (c) Comparison of the MD geometry (blue), the QM/MM B3LYP geometry (red) and QM/MM B3LYP-D2 geometry (green) for Cluster B. (d) Comparison of the QM/MM B3LYP geometry (cyan) and gas phase B3LYP-D3BJ/6-311+G(d,p) geometry (orange) for Cluster B.

The importance of the surrounding MM environment can be evaluated; removal of the MM environment and subsequent optimisation of the isolated ion pairs of the central QM region in the gas phase leads to more significant geometry changes. The central QM region of Cluster B was optimised *in vacuo* at the B3LYP-D3BJ/6-311+G(d,p) level (i.e. at the same level of theory as used here for the ion pair dimers). Comparison of the isolated gas phase and QM/MM B3LYP/6-311G(d,p) geometries is shown in **Figure 4.44 d**. Compared to the small differences observed between the MD and QM/MM

geometries for Cluster B, the optimised QM/MM and gas phase geometries exhibit larger discrepancies. Therefore, the structures of the QM region of the QM/MM clusters computed here are in closer accordance with the geometries observed in the bulk MD, compared to geometries obtained in the gas phase at a level of theory now used as standard to examine ion pairs and ion pair dimers within the Hunt research group. However, this conclusion is based on results from a limited sample size and further investigation is needed.

The QM regions of the clusters examined here using QM/MM therefore appear to be representative of the structuring in the bulk phase. The choice of the system size was a compromise between computational feasibility and the number of ions needed to begin to recover bulk properties. We have established that on going from an ion pair to an ion pair dimer more structural features of the bulk can be recovered. Doubling of the system size again, i.e. to form an ion pair tetramer, is anticipated to recover still further features of the bulk. Therefore, central QM regions consisting of four ion pairs were defined in this initial assay. Importantly, the size of the system in conjunction with the level of theory employed for the QM region was found to be viable given time constraints.

For $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, however, a problem in limiting the QM region to only four ion pairs became apparent; the larger $[\text{HSO}_4]^-$ aggregates observed in the MD trajectories were effectively “cut” upon defining the QM and MM regions. Nevertheless, the ionic component of the H-bond through which the QM/MM boundary passes can still be recovered.

Numerous questions relating to the size of the system and level of theory therefore remain to be answered. For example, how large a QM region can be examined using this method and still remain computationally feasible? How many ion pairs are needed in the MM region to recover the effect of the bulk environment and are point charges needed around the $\text{MM}_{\text{frozen}}$ region to account for the long-range electrostatic effects? In terms of theory, the influence of basis set size (e.g. inclusion of diffuse functions) and functional need to be established. In particular, the influence of the dispersion correction to the functional in this QM/MM environment needs to be determined.

3.5.3 Structural motifs and hydrogen bonding within clusters

For five $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ and five $[\text{C}_1\text{C}_4\text{im}][\text{HSO}_4]$ QM/MM clusters, a QTAIM analysis of the isolated central QM region (i.e. without the surrounding point charges of the MM region) has been undertaken. Single point calculations on the geometries of the QM regions in the gas phase were used to obtain the electron densities for the QTAIM evaluations. Each QM cluster effectively equates to a snapshot of the liquid structure of the four ion pairs in a moment in time. An initial evaluation of selected structural motifs and the strength and nature of the H-bonds formed is presented here.

Visualisation of a QTAIM molecular graph for an example $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ cluster, **Figure 4.45 a**, reveals a high density, and complex network, of intermolecular interactions. However, many of these interactions are very weak based on values of ρ_{BCP} . Included in this are a relatively large number of bond paths and associated BCPs linking H atoms. There is an on-going debate over the interpretation of these $\text{H}\cdots\text{H}$ interactions. Some argue that such interactions are (locally) stabilising.⁹¹⁻⁹³ However, it has also been argued that $\text{H}\cdots\text{H}$ “bonding” is not “real” and that such interactions are consistent with more conventional steric Pauli repulsions.⁹⁴ Nevertheless, visualisation of the molecular graph for the same structure but with a higher cut-off for ρ_{BCP} (0.008 au) shows a significant

reduction in the number of observable intermolecular interactions, **Figure 4.45 b**. However, a multidimensional network of H-bonds is still evident. Unlike the H-bond networking found within protic ionic liquids, H-bond networking within an aprotic ionic liquid will typically be based upon C-H...X interactions e.g. C-H...O interactions, as seen in **Figure 4.45 b**.

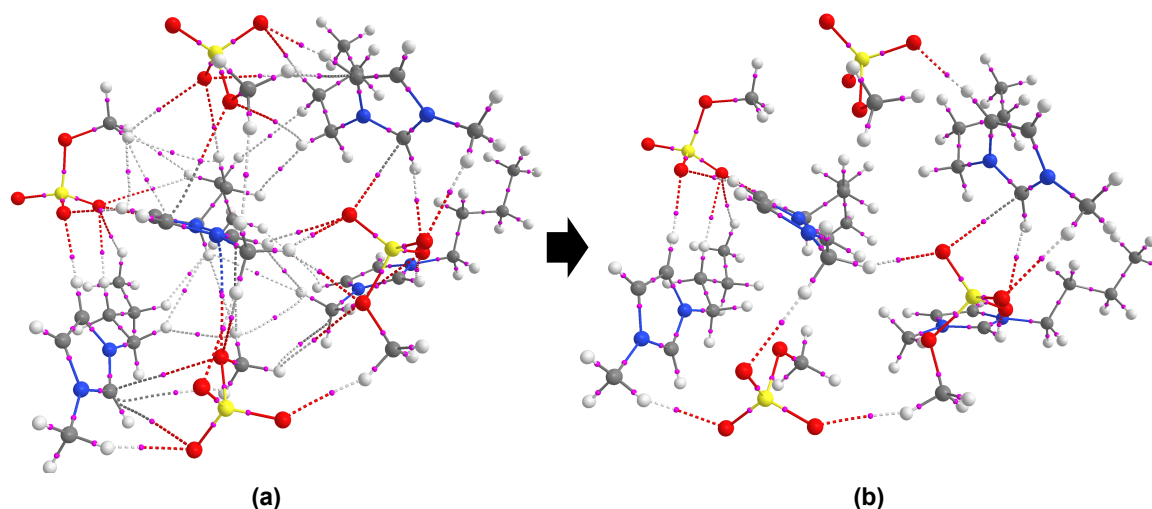


Figure 4.45. QTAIM molecular graphs of the QM region for an example QM/MM cluster of $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$: (a) with a cut-off value for ρ_{BCP} of 0.001 au and (b) with a higher cut-off value for ρ_{BCP} of 0.008 au.

Key structural features of the selected QM clusters are easier to discern when smaller fragments of the larger clusters are visualised. Example fragments of selected QM clusters, chosen to highlight particular structural features, are shown in **Figures 4.46** and **4.47**.

Within all of the clusters examined using QTAIM, the $[\text{C}_1\text{SO}_4]^-$ or $[\text{HSO}_4]^-$ anions act as linkers, bridging between multiple cations. For example, within the fragment shown in **Figure 4.46 a**, three $[\text{C}_4\text{C}_1\text{im}]^+$ cations are connected *via* interleaving $[\text{C}_1\text{SO}_4]^-$ anions.

As deduced from MD SDFs and inferred from previous reports for IP dimers, anions can adopt both in-plane or out-of-plane configurations with respect to the imidazolium cation. The fragment within **Figure 4.46 b** resembles a “middle” type ion pair dimer structure in which both in-plane and out-of-plane interactions can be identified. However, unlike Cl^- , multidentate $[\text{C}_1\text{SO}_4]^-$ can simultaneously form in-plane H-bonds and out-of-plane “bent” H-bond interactions *via* multiple oxygen atoms. Moreover, a number of structures feature configurations in which the anion is located in an out-of-plane top (e.g. **Figure 4.46 c**) or even bridging (e.g. **Figure 4.46 a**) position, as identified in the QM ion pair structures.

Anion-anion interactions, both $[\text{C}_1\text{SO}_4]^- \cdots [\text{C}_1\text{SO}_4]^-$ and $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ have been observed. Within **Figure 4.46 d**, an $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ intermediate dimer is found to bridge between three cations. Within **Figure 4.46 a**, a $[\text{C}_1\text{SO}_4]^- \cdots [\text{C}_1\text{SO}_4]^-$ C-H...O H-bond is detected. Whilst the MD simulations suggest that this is not a highly prominent feature of the liquid, the QTAIM analysis does confirm that there is the potential for (weak) $[\text{C}_1\text{SO}_4]^- \cdots [\text{C}_1\text{SO}_4]^-$ interactions to form.

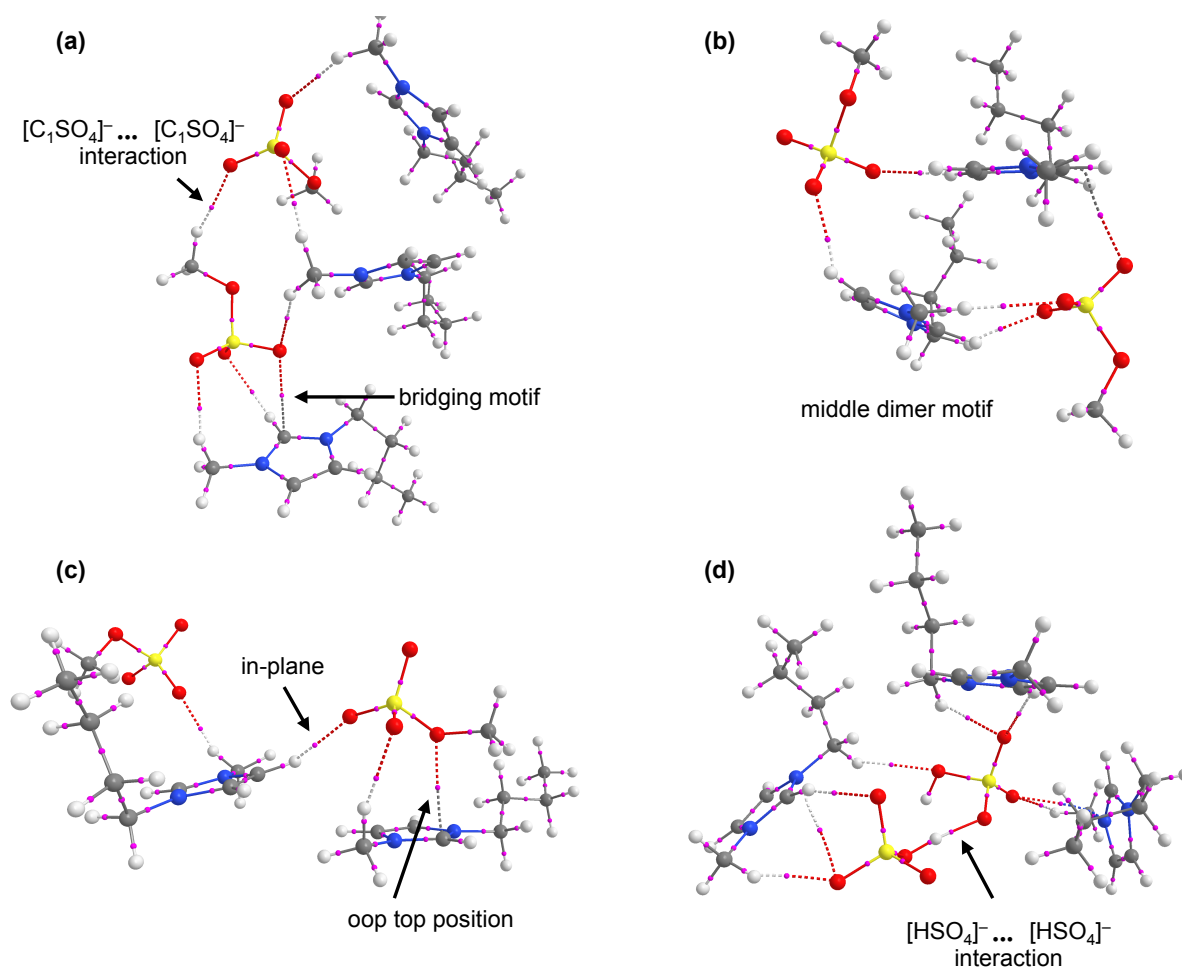


Figure 4.46. Fragments taken from the larger QM regions of selected QM/MM clusters: (a) – (c) examples of structural motifs within the $[C_4C_{1im}][C_1SO_4]$ system and (d) the $[C_4C_{1im}][HSO_4]$ system.

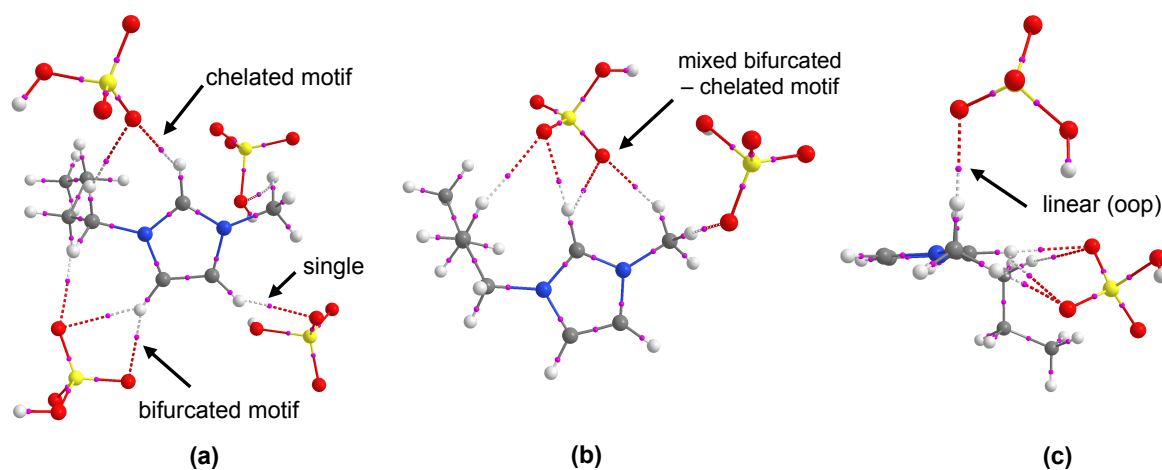


Figure 4.47. Examples of fragments showing different cation-anion $[C_4C_{1im}]^+ \dots [HSO_4]^-$ H-bond motifs.

A variety of different cation-anion H-bond motifs can be observed within the clusters, involving both the ring and alkyl C-H groups. The fragment within **Figure 4.47 a**, for example, shows a single cation H-bonding with four anions, with three different anions forming primary H-bonds with the ring C-H groups, each with a different H-bond motif; chelated, bifurcated and single. The mixed bifurcated-chelated motif identified within the QM ion pairs can also be detected within the clusters e.g. **Figure**

4.47 b. An anion within the bulk is therefore able to form H-bond interactions with multiple cations as well as multiple H-bond interactions with a single cation. Moreover, both non-linear and linear H-bonds can be observed. The fragment within **Figure 4.47 c** shows an $[\text{HSO}_4]^-$ anion sitting above the plane of the imidazolium ring but forming an approximately linear H-bond with the methyl group. It has previously been suggested that the ability of the alkyl groups to rotate, in comparison to the fixed ring C-H groups, allows for more linear H-bond interactions.^{33, 55} Comparison of the “bent” H-bonds with the ring C-H groups in the fragment shown in **Figure 4.46 b** with the linear interaction in **Figure 4.47 c** supports such an argument.

A notable feature of all the clusters examined is that they are very asymmetric (e.g. **Figure 4.45 b**), although in some cases small fragment units may exhibit a more symmetric arrangement (e.g. **Figure 4.46 b**). Further sampling of different clusters is required to determine if the $[\text{C}_1\text{SO}_4]^-/[\text{HSO}_4]^-$ anions are typically saturated, e.g. all donor/acceptor groups are involved in H-bond formation, or if, on average, one or more of the groups is “free”, creating a H-bond “defect”. However, it can be established that when a single anion forms multiple H-bonds, they are typically very unequal in strength.

To further examine the H-bonding within the ten clusters, the relationship between three commonly employed H-bond descriptors has been assessed; the H-bond distance (r), the H-bond angle (ϕ) and the value of ρ_{BCP} . In total, 165 H-bonds with values of ρ_{BCP} above the 0.002 au cut-off, as per our criteria, were identified; 162 examples of C-H $\cdots$ O interactions (including ring C-H, alkyl C-H and $[\text{C}_1\text{SO}_4]^-$ C-H donors) and 3 examples of $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ O-H $\cdots$ O interactions. Mean values and ranges for r , ϕ and ρ_{BCP} for the different H-bond types are provided in **Table 4.9**.

Table 4.9. The number (No.) of H-bonds of each type identified within the clusters and mean values and ranges for the H-bond angles (ϕ), H-bond distances (r), and ρ_{BCP} .

H-bond type	No.	Mean $\phi/^\circ$	Range $\phi/^\circ$	Mean $r/\text{\AA}$	Range $r/\text{\AA}$	Mean $\rho_{\text{BCP}}/\text{au}$	Range $\rho_{\text{BCP}}/\text{au}$
ring CH $\cdots$ O	56	30.3	4.9-55.3	2.43	1.93-3.17	0.012	0.002-0.028
alkyl CH $\cdots$ O	98	25.4	1.0-56.0	2.54	2.07-3.38	0.010	0.002-0.019
anion CH $\cdots$ O	8	22.7	10.1-52.3	2.49	2.19-2.91	0.009	0.004-0.014
OH $\cdots$ O	3	4.2	2.3-5.8	1.61	1.58-1.67	0.053	0.045-0.057

The O-H $\cdots$ O interactions are of moderate to strong strength based on ρ_{BCP} (0.045 – 0.057 au). However, all the C-H $\cdots$ O interactions are within the weak to moderate H-bond categories and exhibit a wider distribution in H-bond strength. For example, the variation in the C-H $\cdots$ O H-bond length is $\approx 1.45 \text{ \AA}$, with a corresponding variation in ρ_{BCP} of $\approx 0.026 \text{ au}$. As was observed for the ion pair dimers, the properties for the doubly anionic $[\text{C}_1\text{SO}_4]^- \cdots [\text{C}_1\text{SO}_4]^-$ C-H $\cdots$ O H-bonds fall within the values for the cation-anion doubly ionic C-H $\cdots$ O H-bonds.

The mean value of r for the ring C-H $\cdots$ O interactions is slightly shorter than for the alkyl C-H $\cdots$ O interactions ($\approx 0.11 \text{ \AA}$), consistent with a very slight increase in the mean value of ρ_{BCP} ($\approx 0.002 \text{ au}$). Moreover, the very strongest C-H $\cdots$ O interactions (up to $\rho_{\text{BCP}} = 0.028 \text{ au}$), involve the ring C-H groups. Therefore, within these clusters the H-bond interactions with the ring C-H groups are, on average, slightly stronger than H-bond interactions with the alkyl groups. However, the number of alkyl C-H $\cdots$ O

H-bonds identified within the clusters is almost twice as large as the number of ring C-H...O H-bonds. The H-bond interactions with the alkyl groups are therefore prolific and make a sizeable contribution to the total H-bonding within these ionic liquid systems.

For clusters built from ion pairs it might be expected that as the size of the clusters (i.e. the number of ion pairs) increases, there would be a decrease in the strength of the H-bond interactions, either due to an increase in separation or due to competitive H-bond formation, i.e. a larger number of weaker H-bonds. On going from ion pairs to ion pair dimers of [C₁C₁im]Cl, for example, there was found to be a sizeable decrease (over 40 %) in the strength of the C²-H...Cl interactions, although the methyl C-H...Cl interactions were not as significantly affected.⁹⁹ If the H-bonding within the QM region of the QM/MM clusters is representative of the liquid phase, then comparison of the H-bonds with those observed within the gas phase ion pair dimers would allow for an assessment of the extent to which the smaller systems overestimate the H-bond strengths.

For the ion pair dimers examined here, the ring C-H...O H-bonds were also found to be on average stronger than the alkyl C-H...O H-bonds. However, the mean values of ρ_{BCP} and the corresponding ranges differ slightly between the dimers and larger clusters. For the 31 ring C-H...O H-bonds identified within the [C₁C₁im][C₁SO₄] and [C₁C₁im][HSO₄] dimers, the mean value of ρ_{BCP} was found to be 0.018 au, $\approx$ 0.006 au greater than for the analogous interactions in the clusters. In contrast, the mean ρ_{BCP} for the 75 methyl C-H...O H-bonds within the dimers is 0.011 au, only $\approx$ 0.001 au greater than in the clusters.

The ranges in ρ_{BCP} for the ring and methyl C-H...O H-bonds in the dimers are 0.011 – 0.029 au and 0.005 – 0.018 au respectively. The upper limit for both types of interactions in the dimers is very similar to those found for the analogous interactions in the larger clusters. The C-H...O interactions in the clusters are not, therefore, all inherently weaker relative to those in the dimers. The lower limits, however, are found to be higher in the dimers, although the difference is less significant for the alkyl C-H...O H-bonds. Within the clusters C-H...O interactions can be detected at the H-bond minimum (0.002 au). However, the minimum value of ρ_{BCP} for the equivalent interactions in the dimers is $\approx$ 0.009 au larger.

The decrease in the minimum values of ρ_{BCP} within the clusters is consistent with a larger number of weaker H-bonds being formed. The mean values of the ring C-H...O interactions, in particular, are affected. Within the clusters there are an increased number of occurrences of structures in which the ring C-H groups are involved in the formation of two H-bonds simultaneously (i.e. a chelated or bifurcated type motif). Typically, such motifs are found to be quite asymmetric; one stronger H-bond forms simultaneously with a second, weaker bond.

Interestingly, the values of ρ_{BCP} for the alkyl (methyl) C-H...O interactions are relatively consistent across the dimers and larger clusters. Relative consistency in alkyl C-H...X H-bonds has also previously been reported between ion pairs and ion pair dimers.⁹⁹ Alkyl C-H...X H-bonds could therefore be proportionally more significant in the bulk phase. Combined with the large number of alkyl C-H...X interactions that could form, increased importance should therefore be placed on these “secondary” H-bond interactions.

Therefore, based on this very limited sample of clusters and dimers, a tentative hypothesis is that the ion pair dimers are able to capture the “upper limit” in the H-bond interactions, but cannot recover the larger network of weak (or very weak) H-bonds. The larger clusters also “cut” through the extended H-bond network. However, the cluster size (i.e. 4 ion pairs) appears just large enough to gain a representation of the networking.

It should be noted however that the QTAIM analysis was undertaken using slightly different methods for the dimers and clusters. The $[\text{C}_1\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ and $[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4]$ ion pair dimers were computed here at the B3LYP-D3BJ/6-311+G(d,p) level, and the QM region of the QM/MM clusters at the B3LYP/6-311G(d,p) level. Therefore, an assessment of the difference between values of ρ_{BCP} for a given structure with the different basis sets needs to be determined. Values of ρ_{BCP} have previously been found to be relatively independent of the method/basis set employed.⁹⁶ Moreover, the inclusion of the D3BJ correction influences the energy and geometry of a system, and thus only influences $\rho(r)$ indirectly. Therefore, computed values of $\rho(r)$ for the same geometry, with and without the D3BJ correction, should be identical. For the example diagonal $[\text{C}_1\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ dimer (**Figure 4.23 a**), a QTAIM analysis, of the B3LYP-D3BJ/6-311+G(d,p) geometry, at the B3LYP/6-311G(d,p) level of theory has been undertaken. For each of the BCPs, there is a negligible difference in the values of ρ_{BCP} (mean difference is 9×10^{-5} au).

An exponential relationship between ρ_{BCP} and H-bond distance is well established within the H-bond community.⁹⁵ Values of ρ_{BCP} are plotted against the corresponding H-bond distances for all 165 H-bonds in **Figure 4.48**, where a very strong correlation between ρ_{BCP} and r is evident. An exponential relationship for the H-bonds in our clusters is therefore consistent with “normal” H-bonds. Moreover, using values of ρ_{BCP} , the H-bond strength categories are indicated within **Figure 4.48**, where it can be seen that the vast majority of the H-bond interactions fall within the weak or very weak ($\rho_{\text{BCP}} < 0.01$ au) categories. Only the O-H $\cdots$ O interactions and fewer than 6% of the C-H $\cdots$ O interactions are above the 0.02 au moderate H-bond threshold.

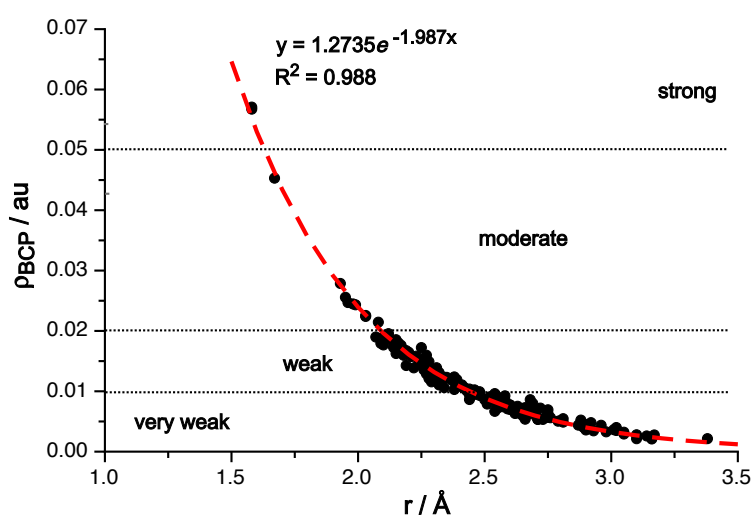


Figure 4.48. Plot of ρ_{BCP} against H-bond distance (r) for all H-bonds identified within the selected clusters.

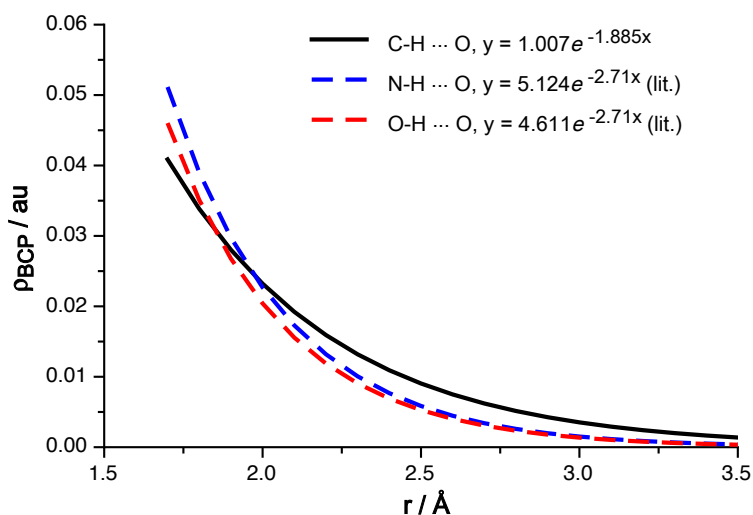


Figure 4.49. Comparison of the exponential relationship between ρ_{BCP} and r for the C-H...O H-bonds identified in the clusters, with analogous correlations for N-H...O and O-H...O H-bonds taken from the literature.⁹⁵

As equations for the exponential correlation between ρ_{BCP} and r for neutral gas phase N-H...O and O-H...O H-bonds have previously been reported, a comparison with the analogous relationship for the 162 doubly ionic C-H...O H-bonds identified here can be made.⁹⁵ The exponential decay in ρ_{BCP} with H-bond distance for N-H...O and O-H...O H-bonds are very similar, **Figure 4.49**. However, the analogous relationship for the C-H...O H-bonds shows a slightly slower decay, **Figure 4.49**, which could suggest that the C-H...O H-bonds are marginally less sensitive to the H-bond distance compared to the more traditional H-bonds.

It should be noted, however, that additional to the differences in functionality, there are a number of other differences between the H-bonds examined here and those reported in the literature, including the level of theory, charge (i.e. neutral vs. doubly ionic) and size of the system (i.e. small dimer vs. larger cluster). Nevertheless, for a given H-bond distance, values of ρ_{BCP} have previously been found to be both relatively insensitive to the method and basis set employed,⁹⁶ as well as independent of the charge of the system; neutral, ionic and doubly ionic H-bonds of a given H-bond functionality have been shown to obey the same exponential correlation.^{97, 98} These reports lend credence to the argument suggesting that the primary origin of the differences in the exponential relationships between ρ_{BCP} and r is due to the different functionality of the H-bond donor.

The linearity of a H-bond, together with the H-bond length, are two of the most established (geometric) descriptors of H-bond strength. Water is the prototypical example of a H-bonded liquid and a good correlation between the O-H...O H-bond length and the H-bond angle has been established.¹⁰⁰ Given the strong correlation between ρ_{BCP} and r for the H-bonds examined here, it could be anticipated that there would be a good correlation between ρ_{BCP} and the H-bond angle, ϕ , (where ϕ is the angle between the X-H vector and the X...O vector). Plots of ρ_{BCP} against ϕ , and r against ϕ , are shown in **Figure 4.50 a** and **b** respectively. In both cases, the correlations with ϕ are very poor. At most, a weak trend can be observed, for example the stronger O-H...O H-bonds are amongst the most linear H-bonds with the shortest H-bond distances. However, for the C-H...O H-bonds there is great variability in the linearity of the H-bond for a given value of ρ_{BCP}/r . The correlation

between the H-bond angle and H-bond distance has previously been found to be dependent on the polarity of the X-H donor group.^{101, 102} Therefore, a stronger correlation for the more polar O-H...O interactions, compared to the C-H...O interactions, is anticipated. Moreover, this finding provides further justification for the use of larger cut-off values in ϕ to assess H-bonding within bulk MD simulations.⁷³

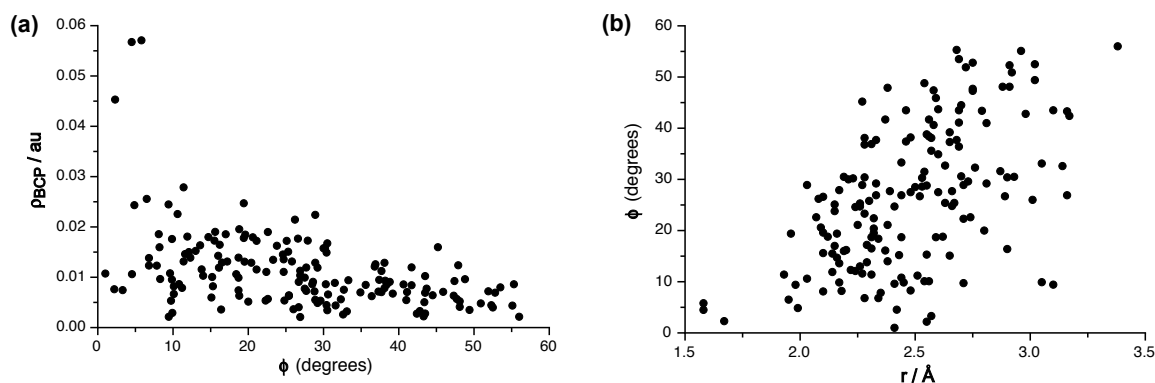


Figure 4.50. (a) Plot of ρ_{BCP} against ϕ , the H-bond angle and (b) plot of ϕ against H-bond length, r .

The different relative flexibilities and acidities of the C-H donor groups could be a factor contributing to the poor correlation. The ring C-H groups are more acidic, and therefore in theory stronger H-bond donors, however, the alkyl C-H groups have more flexibility to rotate and form more linear interactions. The mean value of ϕ for the alkyl C-H...O H-bonds is $\approx 5^\circ$ smaller than for the ring C-H...O interactions, despite the ring C-H...O H-bonds, on average, being slightly shorter and correspondingly associated with slightly larger values of ρ_{BCP} . Therefore, a stronger ring C-H donor group could form a H-bond of reduced linearity, but of equivalent strength (e.g. ρ_{BCP}) as a more linear H-bond with a weaker alkyl C-H donor. Moreover, the complex H-bond motifs and network of H-bonds may also contribute to the large variation in ϕ . The formation of bifurcated H-bonds, for example, has previously been associated with a reduction in the correlation between H-bond length and angle.¹⁰²

The wide diversity in the possible H-bond motifs coupled with a relatively wide variation in the C-H...O H-bond strengths and directionality, suggests a highly flexible H-bond network within these ionic liquids. Such flexibility could lead to increased disorder within the ionic liquid systems. However, for [C₄C₁im][HSO₄] the introduction of stronger, more directional O-H...O interactions could introduce an increased degree of rigidity into the H-bond network, consistent with the increase in viscosity.

3.5.4 Concluding Summary

Clusters of 50 ion pairs of [C₄C₁im][C₁SO₄] and [C₄C₁im][HSO₄] have been successfully optimised using a QM/MM method, with 4 ion pairs in the central QM region and the remaining 46 ion pairs partitioned between the MM_{active} and MM_{frozen} regions. The geometries of the optimised QM regions were typically found to show only small deviations from the MD geometries. Therefore, it can be suggested that the QM regions of the QM/MM clusters are representative of structuring within the bulk ionic liquid.

Many of the individual cation-anion configurations and H-bond motifs observed within the QM regions have also been observed here within the isolated gas phase ion pairs or ion pair dimers. Moreover, the relationship between ρ_{BCP} and H-bond length in the clusters is consistent with H-bonds in smaller gas phase dimers. Thus, there is justification for the continued study of small ion pair systems to gain initial insight into local interactions within ionic liquids. However, the smaller systems cannot recover the extended network of H-bonds that begins to become apparent in these larger ion pair “tetramers”. For example, the wider range in the values of ρ_{BCP} for the C-H $\cdots$ O H-bonds within the clusters reflects the greater structural variation in the larger systems.

In contrast with reports of conventional H-bonded systems (e.g. water), we find a very poor correlation between both ρ_{BCP} and the H-bond length against the H-bond angle. However, our results for the C-H $\cdots$ O H-bonds examined here are relatively consistent with reports for weak C-H $\cdots$ O interactions in other systems.¹⁰¹ The origin of the poor correlation has not yet been fully established and further investigation is required. Nevertheless, our findings substantiate the use of non-conventional angle criteria in assessing H-bonding in ionic liquids.

From the QTAIM analysis of the QM regions of selected clusters emerges a “picture” of the H-bonding within the bulk systems; a “scaffold” of weak to moderate H-bond interactions in a “soup” of very weak to weak H-bond interactions. H-bonds within the larger clusters are not necessarily weaker than those found in the smaller dimers. However, there is an increase in the number of very weak H-bond interactions arising from the multidimensional networking.

Our preliminary investigation suggests that application of QM/MM to the study of structuring and H-bonding within clusters of ion pairs is a viable approach. Further testing is required to establish the optimum system size and level of theory. However, there is the potential for this approach to be applied to more complex systems, such ionic liquid/water mixtures and the study of the solvation behaviour of solute species in an ionic liquid.

4. Conclusion

The interactions within related aprotic and protic ionic liquids have been examined using different computational methods. The complementary information obtained can be used to build a “picture” of the structuring within the selected systems. Analysis of ion pairs ($[\text{C}_4\text{Him}]\text{Cl}$, $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4^-]$ and $[\text{C}_4\text{Him}][\text{HSO}_4^-]$) using DFT provided information relating to the local cation-anion arrangements; relative energies of the different configurations, favourable H-bond motifs and the influence of dispersion, have all been considered. An extension to ion pair dimers ($[\text{C}_1\text{C}_1\text{im}][\text{C}_1\text{SO}_4^-]$ and $[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4^-]$) allowed for an initial assessment of possible $[\text{HSO}_4^-] \cdots [\text{HSO}_4^-]$ interactions. Through MD simulations of $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4^-]$, $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4^-]$ and $[\text{C}_4\text{Him}][\text{HSO}_4^-]$ further information relating to the anion distribution about the imidazolium cations, the extent of anion-anion interactions and the H-bond networking within $[\text{C}_4\text{Him}][\text{HSO}_4^-]$ was acquired. Finally, our preliminary study using a QM/MM method applied to $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4^-]$ and $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4^-]$ enabled for a comparison of H-bond interactions in the bulk with those found in smaller ion pairs and ion pair dimers.

Ion pairs of $[\text{C}_4\text{Him}]\text{Cl}$ were used as a starting point. Through comparison to the well studied $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$ system, an initial assay of the differences in the cation-anion configurations within protic and aprotic imidazolium ionic liquids was undertaken. Comparison of the $[\text{C}_4\text{Him}]\text{Cl}$ and $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$ ion pairs suggests that the structuring within a protic imidazolium ionic liquid shows similarities to both aprotic imidazolium ionic liquids and protic (tri)alkylammonium ionic liquids. Similar to protic alkylammonium cations, anion interaction with the N-H group of the protic imidazolium cation is strongly favoured and contributes to the increase in the association energy for the protic system. Introduction of the stable “NH” configuration also results in a loss of the established front-me and side-me configurations and an increase in ΔE_{rel} between the lowest energy ion pair configuration (NH) and the next most stable configurations (front-but/top). Nevertheless, compared to a protic alkylammonium ionic liquid, there is potentially a larger number of cation-anion configurations within a protic imidazolium system.

Through a comparison of $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4^-]$ and $[\text{C}_4\text{Him}][\text{HSO}_4^-]$ ion pairs, featuring a larger, multidentate anion, similar conclusions were drawn. However, multidentate $[\text{HSO}_4^-]$ can use multiple oxygen atoms to interact with the cation, effectively spanning between two established “Cl⁻ positions” e.g. $[\text{HSO}_4^-]$ can bridge between a front and top position. With $[\text{C}_4\text{Him}]^+$ this results in two favourable configurations in which the anion can interact with the NH group of the cation; NH-front and NH-side. Thus, cation-anion configurations are less-well defined with larger anions.

Moreover, for each system studied using ion pairs, a large number of different structures were obtained which could be categorised into energy “bands”. For a given cation-anion configuration (e.g. front or side) there is a distribution in the energy of the ion pairs resulting from the orientation of the butyl chain. Interactions with the butyl chain were found to be important for stabilising both low and higher energy (including out-of-plane) ion pair configurations. For the $[\text{HSO}_4^-]$ systems, the relative orientation of the anion can also affect the energy of the system. Therefore, when screening ion pairs, a consideration of the alkyl chain rotation could be significant.

The influence of dispersion has also been assessed. For $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4^-]$ in particular, the introduction of a dispersion correction can lead to a change in the dominant ion pair configurations;

increasing dispersion results in an increase in the preference for the top configuration. This is consistent with an increase in the anion interaction with the π manifold of the imidazolium ring. Using QTAIM, and through qualitative analysis of the MOs, there appears to be a subtle change in the balance between H-bonding and anion- π^+ interactions as the anion moves from the front positions in the plane of the ring to locate above the imidazolium ring.

The anion distributions about the imidazolium cations were also determined from the MD trajectories for $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$, $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ and $[\text{C}_4\text{Him}][\text{HSO}_4]$. The distribution of $[\text{C}_1\text{SO}_4]^-$ about $[\text{C}_4\text{C}_1\text{im}]^+$ are consistent with reports for other alkylsulphate ionic liquids. Replacing the methyl group on the anion with a proton is not found to have a significant influence on the cation-anion distribution. In contrast, replacing the methyl group on the $[\text{C}_4\text{C}_1\text{im}]^+$ cation with a proton does have a notable affect on the cation-anion distribution. The distribution of $[\text{HSO}_4]^-$ about $[\text{C}_4\text{Him}]^+$, as determined using MD, is in accordance with the conclusions drawn from the ion pairs. Namely, a predominance of the anion interaction with the N-H group and a “smeared out” distribution stretching from the front-but to NH-side positions is observed.

For $[\text{HSO}_4]^-$ ionic liquids there is the potential for anion-anion interactions. The formation of $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ O-H $\cdots$ O H-bonds was found to result in stabilisation of the surveyed $[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4]$ ion pair dimers. However, the formation of the anion-anion interactions occurs at the cost of a slight reduction in the cation-anion H-bond interactions. For the related $[\text{C}_1\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ system $[\text{C}_1\text{SO}_4]^- \cdots [\text{C}_1\text{SO}_4]^-$ C-H $\cdots$ O H-bonds can also form. However, for this system a reduction in the cation-anion H-bond interactions is not recouped by the formation of the anion-anion H-bonds. This is consistent with analysis of selected anion-anion site-site radial distribution functions for the MD trajectories of $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ and $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$. $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ interactions are a prominent structural feature of $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$. In contrast, $[\text{C}_1\text{SO}_4]^- \cdots [\text{C}_1\text{SO}_4]^-$ interactions are, at most, a minor feature of $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$. As there is not a notable variation in the cation-anion association between the two systems, the significant increase in viscosity on going from $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ to $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ is most likely attributable to $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ H-bond formation.

Qualitative analysis of the $[\text{HSO}_4]^- \cdots [\text{HSO}_4]^-$ interactions within $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ reveals the presence of aggregates formed of mixed chain and dimer motifs. Initially it had been presumed that on going from $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ to $[\text{C}_4\text{Him}][\text{HSO}_4]$, the increased cation-anion interactions would lead to a decrease in the anion-anion interactions. In contrast, we find that there is potentially an increase in the size of the anion aggregates within $[\text{C}_4\text{Him}][\text{HSO}_4]$. It is proposed that interactions between $[\text{C}_4\text{Him}]^+$ and $[\text{HSO}_4]^-$ leads to a disruption of anion cyclic dimers, favouring the chain motif and hence larger anion aggregates. In terms of H-bond networking, the frame of the H-bond network within $[\text{C}_4\text{Him}][\text{HSO}_4]$ is based upon anion-anion interactions. The large increase in viscosity on going from $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ to $[\text{C}_4\text{Him}][\text{HSO}_4]$ is most likely attributable to the increase in cation-anion and potentially also anion-anion interactions.

A comparison and analysis of the H-bonding has been a central focus of this investigation. Considering the series $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$, $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ and $[\text{C}_4\text{Him}][\text{HSO}_4]$, C-H $\cdots$ O H-bonds are a common feature of all three systems. These can be segregated into C-H $\cdots$ O H-bonds with the ring and C-H $\cdots$ O interactions with the alkyl chain. Both $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ and $[\text{C}_4\text{Him}][\text{HSO}_4]$ feature O-H $\cdots$ O

H-bonds while [C₄Him][HSO₄] additionally features N-H...O interactions. Both the O-H...O and N-H...O interactions are typically short and relatively linear. This is consistent with these being moderate to strong H-bond interactions. The C-H...O interactions show a much wider variation in linearity and length. This is possibly due to the weaker nature of these interactions and the formation of more varied H-bond motifs (e.g. single, bifurcated and chelated).

The preliminary results from our QM/MM approach to the investigation of interactions in ionic liquids has provided us with the opportunity to compare using a descriptor based on the $\rho(r)$, H-bonds in clusters with geometries representative of the bulk, with H-bonds found in smaller ion pairs and dimers. To date, this analysis has only been undertaken for [C_nC₁im][C₁SO₄] and [C_nC₁im][HSO₄] systems. Analysis of the strength of the H-bond interactions based on ρ_{BCP} suggests that within these ionic liquids there are a small number of moderately strong interactions in a flexible “sea” of weak and very weak H-bonds. Small ion pairs can recover the upper end of the H-bond interactions found in the large clusters, but do not capture the “sea” of weaker interactions associated with extended H-bond networking.

On average C-H...O ring interactions are slightly stronger than the analogous interactions with the alkyl chain, however, the latter are more prolific. As such, H-bond interactions with the alkyl chain make a sizeable contribution to the total H-bonding within a system. In addition, through analysis of the ion pairs it appears that interactions with the alkyl chain can play a key role in the stabilisation of cation-anion configurations. Therefore, we suggest that these “secondary” interactions are more important than previously thought in influencing the structuring within the selected ionic liquid systems.

Fully understanding how our “picture” of H-bonding in these systems relates to the bulk phase physical properties is not straight forward. In some cases, such as in the comparison of [C₄C₁im][C₁SO₄] with [C₄C₁im][HSO₄], and [C₄C₁im][HSO₄] with [C₄Him][HSO₄], we can present a justifiable case to claim that an increase in anion-anion and cation-anion H-bonding respectively results in an increase in structuring, leading in this instance to an increase in viscosity. More generally, it is possible that the flexible sea of weak H-bonds results in increased disorder and favours the liquid state. In contrast, the formation of stronger interactions, such as N-H...X, could have the opposite effect. However, if this were the case, then it would be expected that the melting point of [C₄C₁im]Cl would be lower than that of [C₄Him]Cl. From the available melting point values, this is not the case. Establishing the link between H-bonding, amongst other interactions, and the bulk phase properties of ionic liquids is thus an on-going area of investigation.

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Conclusion

DESs and mineral acid derived ionic liquids were identified as low cost ionic liquids for the potential application of chalcopyrite leaching. Ionic liquids and related analogues are complicated systems in which a subtle balance between different interactions affects the structuring and properties. Determining and quantifying the relative contributions, and establishing how the different interactions influence the properties of the bulk system remains a key objective of ionic liquids research.

The choline chloride – urea DES and the $[\text{C}_4\text{Him}][\text{HSO}_4]$ protic ionic liquid were selected as target systems of interest. Our aim has been to further the fundamental understanding of the interactions and local structuring within the exemplar systems.

H-bonding is thought to play a central role in the formation of DESs, primarily in the formation of a complexed anion. For example, at the 1:2 eutectic composition of the choline chloride – urea mixture, the formation of the H-bonded $[\text{2urea}\cdot\text{Cl}]^-$ complexed anion is proposed. H-bonding is also recognised as a key contributor to the structuring within protic ionic liquids, potentially resulting in the formation of a multidimensional H-bond network. Analysis of the H-bond interactions within the systems of study has therefore been a central theme of this work. We have identified and examined a large number of H-bonds, differing in functionality, charge and local motif. Local (quantum chemical) descriptors of H-bonding, namely $E^{(2)}$ and ρ_{BCP} , have proven to be robust and reliable tools in the quantification of the H-bond interactions across *all* different types of H-bond.

The choline chloride – urea deep eutectic solvent

Employing DFT the possible pairwise combinations of the constituent species of the choline chloride – urea DES have been explored (i.e. choline-chloride, urea-urea, urea-chloride and choline-urea interactions) and an initial assay of clusters of composition $n.\text{urea}.\text{choline-chloride}$ ($n=1-3$) has been undertaken. For the choline-chloride and choline-urea pairs a relatively large number of low energy configurations were isolated. The clusters also exhibit a large number of nearly degenerate low energy structures, indicating flexibility in the intermolecular interactions within this system.

For the pairwise interactions the global electrostatic contribution determines the approximate magnitude of the association energies. However, the anisotropic charge distributions of the constituent species leads to local variations in the electrostatic interactions. Within the molecular pairs and clusters a large number of H-bonds have been identified and quantified using local descriptors. The large number of H-bonds suggests that there is a significant H-bonding contribution within this system. However, H-bonding is not necessarily maximised in the lowest energy configurations and in order to rationalise the relative energies of structures, we propose there to be a balance between maximising both H-bonding and local electrostatic interactions. Moreover, for both the molecular pairs and clusters, a relatively large number of low energy configurations were identified, indicating that there could be a high degree of flexibility within this DES.

A relatively large number of different H-bond types can form within the choline chloride - urea DES, differing in both the functionality and charge. Both pure molecular solvents and conventional ionic liquids are typically very homogeneous with respect to the H-bond functionality. The diverse

range of H-bond types is therefore a relatively unique feature of these eutectic mixtures that could increase disorder within the system.

Moreover, the different H-bond types cover a range of strengths, from very weak to moderately strong. We have characterised the H-bonding within the clusters as exhibiting a small number of stronger interactions within a “soup” of weaker interactions. For a given H-bond type a variation in the strength was found. The competitive nature of different H-bond types also increases flexibility within the system. Furthermore, we find evidence to suggest that a larger number of weaker H-bonds can be competitive with a smaller number of stronger H-bonds.

The strongest H-bonds within this system are the choline – urea $\text{O-H}\cdots\text{O}=\text{C}$ interactions, and not the urea-chloride $\text{N-H}\cdots\text{Cl}$ interactions. Furthermore, the formation of either a $\text{O-H}\cdots\text{O}=\text{C}$ or $\text{O-H}\cdots\text{Cl}$ H-bond is a common feature of low energy pairs and clusters. Thus, the hydroxyl group of choline could play an important role in the structuring of this DES.

The positive charge of the choline cation facilitates the formation of $\text{C-H}\cdots\text{X}$ H-bonds. These interactions are often overlooked but are found to be prevalent here. The doubly ionic nature of the choline chloride interaction leads to an enhancement of the $\text{C-H}\cdots\text{Cl}$ H-bond strength. Furthermore, it is typical for multiple $\text{C-H}\cdots\text{X}$ H-bonds to form concurrently, with the tripodal motif identified as a recurrent feature. Whilst the individual $\text{C-H}\cdots\text{Cl}$ interactions are weak, in terms of the *total* H-bonding contribution, the formation of multiple $\text{C-H}\cdots\text{Cl}$ interactions can be stronger than the more conventional $\text{O-H}\cdots\text{Cl}$ interaction.

The formation of the $[\text{urea}\cdot\text{Cl}]^-$ complex was found to be energetically very favourable and was also found to be a key feature within many of the clusters. However, the addition of a second urea molecule, leading to the formation of $[\text{2urea}\cdot\text{Cl}]^-$, was found to be energetically competitive with the formation of $[\text{choline}\cdot\text{urea}]^+$. This has potential implications for the speciation within this system and emphasises the importance of considering all possible interactions.

The potential role of urea in the formation of the DES has been considered. It is commonly proposed that the complexation of urea to chloride leads to delocalisation of the negative charge. We do not find evidence to support this. Instead, analysis of the partial charges and MOs indicates that the charge remains relatively localised on the chloride centre. However, the analysis of a limited sample of clusters suggests that the addition of urea to choline chloride could result in the increase in the average choline $\cdots$ chloride separation. Moreover, there is the potential for urea to insert between choline and chloride and thus screen the electrostatic interaction.

We therefore confirm that H-bonding is inherently important to the choline chloride – urea DES. However, the role of H-bonding is not limited to the formation of complexed anions and H-bonding may have additional influence on the chemical and physical properties of this system.

Comparison of selected aprotic and protic ionic liquids

$[\text{C}_4\text{Him}][\text{HSO}_4]$ was identified as a primary ionic liquid of interest. However, in order to deconvolute the influence of the $[\text{C}_4\text{Him}]^+$ cation and $[\text{HSO}_4]^-$ anion on the local structuring, a comparison to related ionic liquids was made, specifically $[\text{C}_4\text{Him}]\text{Cl}$, $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4]$ and $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$. A range of different approaches (i.e. QM ion pairs, ion pair dimers, MD and QM/MM) has been employed, with

the different methods providing complimentary insight into the systems of study. Using DFT, ion pairs of $[\text{C}_4\text{Him}][\text{HSO}_4^-]$, $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4^-]$ and $[\text{C}_4\text{Him}]\text{Cl}$ have been compared and contrasted and a small number of larger $[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4^-]$ and $[\text{C}_1\text{C}_1\text{im}][\text{C}_1\text{SO}_4^-]$ ion pair dimers evaluated. Bulk systems of $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4^-]$, $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4^-]$ and $[\text{C}_4\text{Him}][\text{HSO}_4^-]$ have been modelled using classical MD and a qualitative analysis of the structuring undertaken. Moreover, a preliminary investigation of the interactions within $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4^-]$ and $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4^-]$ has been conducted employing a hybrid QM/MM method.

A comparison of the anion interactions with the aprotic and protic imidazolium cations has been made. The “NH” configurations of the gas phase $[\text{C}_4\text{Him}][\text{X}]$ ($\text{X} = \text{Cl}^-$ or $[\text{HSO}_4^-]$) ion pairs were identified as the lowest energy configurations for these systems. Anion interaction with the acidic N-H group is therefore energetically very favourable and contributes to the increase in the ion pair association energy with respect to the aprotic $[\text{C}_4\text{C}_1\text{im}][\text{X}]$ analogues. This is consistent with the analysis of the SDF for the MD simulation of $[\text{C}_4\text{Him}][\text{HSO}_4^-]$, which indicates that the anion preferentially locates to interact with the N-H unit.

Compared to the small chloride anion, the anion positioning and interactions with multidentate $[\text{HSO}_4^-]$ are less well defined. Consistent with reports for other large anions, there is an increased preference for $[\text{HSO}_4^-]$ to locate in the top position, particularly with the $[\text{C}_4\text{C}_1\text{im}]^+$ cation. Of the systems studied using ion pairs, $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4^-]$ was the system most affected by the addition of a dispersion correction to the density functional. The influence of dispersion in this case is consistent with the presence of an anion- π^+ interaction. QTAIM and MO analysis of a range of front/top $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4^-]$ structures suggests there to be a subtle interplay between both H-bonding and anion- π^+ interactions.

The possibility of anion-anion $[\text{HSO}_4^-] \cdots [\text{HSO}_4^-]$ interactions was assessed. A $[\text{HSO}_4^-] \cdots [\text{HSO}_4^-]$ dimer can be isolated in the gas phase and these anion-anion interactions are likely further stabilised in the charge screening environment of the bulk ionic liquid. The doubly ionic O-H $\cdots$ O H-bonds are also found to be moderate to strong and contribute to the stabilisation of $[\text{C}_1\text{C}_1\text{im}]_2[\text{HSO}_4^-]_2$ ion pair dimers.

Consistent with the QM findings, $[\text{HSO}_4^-] \cdots [\text{HSO}_4^-]$ interactions were found to be a prominent feature of the MD simulations of both $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4^-]$ and $[\text{C}_4\text{Him}][\text{HSO}_4^-]$, where mixed cyclic dimer and chain $[\text{HSO}_4^-]$ aggregates were observed. However, the extent of the anion-anion H-bonding was found to be dependent on the partial atomic charges of the $[\text{HSO}_4^-]$ potential, and thus further validation of the force field is required. Nevertheless, we propose that in both $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4^-]$ and $[\text{C}_4\text{Him}][\text{HSO}_4^-]$ there is the potential for a primary H-bonded network based on $[\text{HSO}_4^-] \cdots [\text{HSO}_4^-]$ interactions.

A preliminary study employing a hybrid QM/MM method to investigate the local structuring within ionic liquids has been undertaken. Whilst still in its infancy, our approach has the potential to allow for the QM analysis of ion pair clusters in the environment of the bulk ionic liquid. Based on our preliminary assessment of the H-bond interactions within a limited sample of $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{SO}_4^-]$ and $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4^-]$ clusters, we propose that smaller gas phase ion pair dimers are able to capture the stronger H-bond interactions, but cannot recover the extensive network of weaker secondary

interactions. These secondary interactions are identified as playing an important role in the structuring of these systems.

Final comments

The complexity of the ionic liquid “H-bond problem” is such that no entirely satisfactory explanation to rationalise the influence of H-bonding on the macroscopic properties of ionic liquids has yet been presented. The central question that remains to be answered is *how do the H-bond interactions influence the bulk properties of ionic liquids?*

For the systems studied herein, we have succeeded in obtaining new insight and have established a foundation upon which further investigations can be based. H-bonding has been demonstrated to be of significance to all the systems studied; in order to rationalise local structuring, and hence the bulk phase properties, H-bonding must be accounted for.

However, there is much further insight to be gained through the theoretical exploration of H-bonding in ionic liquids. The development of methods that allow for the high-level assessment of H-bonding in structures representative of the bulk phase (e.g. QM/MM and *ab initio* MD) is particularly promising. In conjunction with an increased availability of good quality experimental data on the physical properties of related ionic liquids, an answer to the “H-bond problem” may soon be achievable.

Appendix

Interactions within the Choline Chloride – Urea Deep Eutectic Solvent

The choline cation

Relative energies

Table A. 1. Relative energies of the choline conformers with and without the ZPE correction.

Choline Conformer	E / au	$\Delta E_{\text{rel}} / \text{kJ mol}^{-1}$	E+ZPE / au	ΔE_{rel} (with ZPE correction) / kJ mol^{-1}
Gauche	-328.819938	0.000	-328.623147	0.000
Trans	-328.812538	19.429	-328.616231	18.158
Trans-rotated	-328.810428	24.968	-328.614307	23.209
Gauche-cpcm (H ₂ O)	-328.867746	0.000	-328.670834	0.000
Trans-cpcm (H ₂ O)	-328.865192	6.705	-328.6684271	6.319

Partial charge analysis and H-bond data

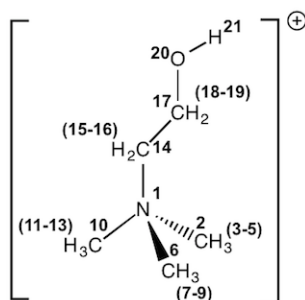


Figure A. 1. Atomic numbering scheme used for the choline cation.

Table A. 2. Partial charge analysis of gauche choline.

	q / e	
	NBO	CHELPG
N ¹	-0.347	0.211
C ²	-0.353	-0.250
H ³	0.256	0.170
H ⁴	0.218	0.139
H ⁵	0.221	0.147
C ⁶	-0.358	-0.266
H ⁷	0.236	0.164
H ⁸	0.222	0.154
H ⁹	0.228	0.144
C ¹⁰	-0.347	-0.306
H ¹¹	0.227	0.150
H ¹²	0.227	0.165
H ¹³	0.224	0.162
C ¹⁴	-0.176	-0.161
H ¹⁵	0.229	0.151
H ¹⁶	0.228	0.105
C ¹⁷	-0.053	0.240
H ¹⁸	0.205	0.065
H ¹⁹	0.177	0.021
O ²⁰	-0.757	-0.654
H ²¹	0.493	0.448

Table A. 3. H-bond lengths (r) and selected topological properties of $\rho(r)$ at the BCPs for the intramolecular H-bonds within choline (cationic) and *N,N*-dimethylethanolamine (neutral). No $n_O \rightarrow \sigma^*_{CH}$ interaction was found for the C-H $\cdots$ O contact in question within the neutral system.

	Cationic	Neutral
$r_{C-H\cdots O} / \text{\AA}$	2.21	2.54
$/ \text{kJ mol}^{-1}$	5.23	-
ρ_{BCP} / au	0.0164	0.0103
$\nabla^2 \rho_{BCP} / \text{au}$	0.0629	0.0366
H_c / au	0.00237	0.00121

Energy profile for rotation about selected torsion angles

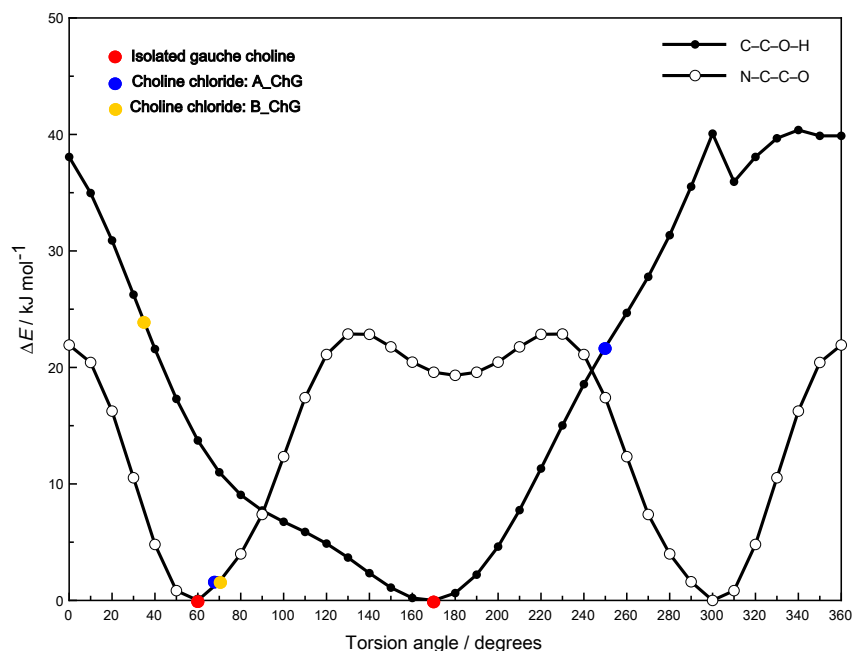


Figure A. 2. Energy profiles for rotation about the C-O-O-H and N-C-C-O torsion angles of isolated choline. Torsion angles found in gauche choline and the A_ChG and B_ChG choline chloride ion pairs indicated using coloured circles.

Choline chloride ion pairs

Relative energies

Table A. 4. Absolute and relative energies of the urea-chloride complexes: without any corrections, with ZPE corrections and with both ZPE and CP corrections.

Ion Pair	E / au	$\Delta E_{\text{rel}} / \text{kJ mol}^{-1}$	E+ZPE / au	ΔE_{rel} (with ZPE correction) / kJ mol^{-1}	BSSE / kJ mol^{-1}	ΔE_{rel} (with ZPE + CP correction) / kJ mol^{-1}
A_ChG	-789.281345	0.000	-789.083878	0.000	3.370	0.000
B_ChG	-789.281068	0.726	-789.083596	0.739	3.444	0.814
C_ChG	-789.276470	12.799	-789.0791408	12.436	3.146	12.213
A_ChT	-789.273526	20.529	-789.075726	21.403	3.424	21.457
D_ChG	-789.269489	31.128	-789.0727456	29.227	2.883	28.740
E_ChG	-789.269206	31.870	-789.072290	30.423	2.738	29.792
B_ChT	-789.267669	35.906	-789.071038	33.711	2.778	33.119
C_ChT	-789.266262	39.600	-789.069471	37.825	3.045	37.501

H-bond data

Table A. 5. H-bond lengths, $E^{(2)}$ values and selected topological properties of the $\rho(r)$ at the BCPs for the individual H-bonds within the choline chloride ion pairs

A ChG					
H-bond	r/Å	$\Sigma E^{(2)}/\text{kJ mol}^{-1}$	$\rho_{\text{BCP}}/\text{a.u.}$	$\nabla^2 \rho_{\text{BCP}}/\text{a.u.}$	$H_{\text{BCP}}/\text{a.u.}$
Intra CH...O(H)	2.519	-	0.0113	0.0417	0.00142
CH...Cl (a)	2.417	30.25	0.0180	0.0514	0.00176
CH...Cl (b)	2.381	38.24	0.0193	0.0540	0.00167
OH...Cl	2.090	89.37	0.0340	0.0722	-0.00315
B ChG					
H-bond	r/Å	$\Sigma E^{(2)}/\text{kJ mol}^{-1}$	$\rho_{\text{BCP}}/\text{a.u.}$	$\nabla^2 \rho_{\text{BCP}}/\text{a.u.}$	$H_{\text{BCP}}/\text{a.u.}$
Intra CH...O(H)	2.432	-	0.0141	0.0512	0.00157
CH...Cl (a)	2.433	26.82	0.0178	0.0513	0.00178
CH...Cl (b)	2.714	9.92	0.0109	0.0298	0.00123
CH...Cl (c)	2.353	32.47	0.0213	0.0630	0.00170
OH...Cl	2.214	59.79	0.0256	0.0622	-0.00011
C ChG					
H-bond	r/Å	$\Sigma E^{(2)}/\text{kJ mol}^{-1}$	$\rho_{\text{BCP}}/\text{a.u.}$	$\nabla^2 \rho_{\text{BCP}}/\text{a.u.}$	$H_{\text{BCP}}/\text{a.u.}$
Intra CH...O(H)	2.289	3.77	0.0141	0.0518	0.00190
CH...Cl (a)	2.375	34.85	0.0199	0.0561	0.00164
CH...Cl (b)	2.532	18.90	0.0150	0.0423	0.00163
CH...Cl (c)	2.381	29.54	0.0203	0.0589	0.00173
D ChG					
H-bond	r/Å	$\Sigma E^{(2)}/\text{kJ mol}^{-1}$	$\rho_{\text{BCP}}/\text{a.u.}$	$\nabla^2 \rho_{\text{BCP}}/\text{a.u.}$	$H_{\text{BCP}}/\text{a.u.}$
Intra CH...O(H)	2.254	4.56	0.0150	0.0573	0.00216
CH...Cl (a)	2.444	27.07	0.0174	0.0492	0.00170
CH...Cl (b)	2.388	34.35	0.0194	0.0539	0.00164
CH...Cl (c)	2.351	37.99	0.0209	0.0584	0.00155
E ChG					
H-bond	r/Å	$\Sigma E^{(2)}/\text{kJ mol}^{-1}$	$\rho_{\text{BCP}}/\text{a.u.}$	$\nabla^2 \rho_{\text{BCP}}/\text{a.u.}$	$H_{\text{BCP}}/\text{a.u.}$
Intra CH...O(H)	2.319	2.09	0.0141	0.0508	0.00176
CH...Cl (a)	2.443	27.66	0.0174	0.0491	0.00170
CH...Cl (b)	2.350	39.20	0.0208	0.0572	0.00151
CH...Cl (c)	2.356	38.45	0.0206	0.0569	0.00155
A ChT					
H-bond	r/Å	$\Sigma E^{(2)}/\text{kJ mol}^{-1}$	$\rho_{\text{BCP}}/\text{a.u.}$	$\nabla^2 \rho_{\text{BCP}}/\text{a.u.}$	$H_{\text{BCP}}/\text{a.u.}$
CH...Cl (a)	2.378	35.27	0.0196	0.0551	0.00168
CH...Cl (b)	2.898	4.85	0.0082	0.0217	0.00084
CH...Cl (c)	2.354	30.54	0.0216	0.0651	0.00176
OH...Cl	2.545	16.07	0.0133	0.0375	0.00140
B ChT					
H-bond	r/Å	$\Sigma E^{(2)}/\text{kJ mol}^{-1}$	$\rho_{\text{BCP}}/\text{a.u.}$	$\nabla^2 \rho_{\text{BCP}}/\text{a.u.}$	$H_{\text{BCP}}/\text{a.u.}$
CH...Cl (a)	2.367	36.53	0.0202	0.0559	0.00157
CH...Cl (b)	2.367	36.53	0.0202	0.0559	0.00157
CH...Cl (c)	2.382	34.60	0.0196	0.0548	0.00163
C ChT					
H-bond	r/Å	$\Sigma E^{(2)}/\text{kJ mol}^{-1}$	$\rho_{\text{BCP}}/\text{a.u.}$	$\nabla^2 \rho_{\text{BCP}}/\text{a.u.}$	$H_{\text{BCP}}/\text{a.u.}$
CH...Cl (a)	2.312	47.95	0.0224	0.0603	0.00130
CH...Cl (b)	2.312	47.70	0.0224	0.0603	0.00129
CH...Cl (c)	2.835	1.55	0.0103	0.0354	0.00160
CH...Cl (d)	2.835	1.55	0.0103	0.0354	0.00160

Urea monomers and urea-urea dimers

Relative energies

Table A. 6. Relative energies of the urea conformers with and without ZPE correction.

Urea Conformer	E / au	$\Delta E_{\text{rel}} / \text{kJ mol}^{-1}$	E+ZPE / au	ΔE_{rel} (with ZPE correction) /kJ mol ⁻¹
C₂	-225.353480	0.000	-225.289997	1.357
C_{2v}	-225.351956	4.00	-225.290514	0.000
C_s	-225.352295	3.11	-225.289862	1.712

Table A. 7. Absolute and relative energies of the urea-urea dimers: without any corrections, with ZPE corrections and with both ZPE and CP corrections.

Dimer	E /au	$\Delta E_{\text{rel}} / \text{kJ mol}^{-1}$	E+ZPE /au	ΔE_{rel} (with ZPE correction) /kJ mol ⁻¹	BSSE /kJ mol ⁻¹	ΔE_{rel} (with ZPE + CP correction) /kJ mol ⁻¹
Ribbon	-450.732052	0.000	-450.603139	0.000	2.193	0.000
Distorted Chain	-450.728823	8.476	-450.599592	9.314	2.325	9.446

H-bond data

Table A. 8. H-bond lengths (r), $E^{(2)}$ values and selected topological properties of the $\rho(r)$ at the BCPs for the individual H-bonds within the urea dimers.

Ribbon					
H-bond	r/Å	$\Sigma E^{(2)} / \text{kJ mol}^{-1}$	$\rho_{\text{BCP}} / \text{a.u.}$	$\nabla^2 \rho_{\text{BCP}} / \text{a.u.}$	$H_{\text{BCP}} / \text{a.u.}$
NH...O=C (a)	1.826	68.53	0.0332	0.1123	0.00059
NH...O=C (b)	1.825	68.91	0.0332	0.1124	0.00057
Distorted Chain					
H-bond	r/Å	$\Sigma E^{(2)} / \text{kJ mol}^{-1}$	$\rho_{\text{BCP}} / \text{a.u.}$	$\nabla^2 \rho_{\text{BCP}} / \text{a.u.}$	$H_{\text{BCP}} / \text{a.u.}$
NH...O=C (a)	1.990	26.74	0.0229	0.0838	0.00232
NH...O=C (b)	2.397	4.52	0.0118	0.0389	0.00108
NH...N	2.088	31.97	0.0225	0.0696	0.00167

Urea – chloride complexes

Relative energies

Table A. 9. Absolute and relative energies of the urea-chloride complexes: without any corrections, with ZPE corrections and with both ZPE and CP corrections.

Complex	E /au	ΔE_{rel} /kJ mol ⁻¹	E+ZPE /au	ΔE_{rel} (with ZPE correction) /kJ mol ⁻¹	BSSE /kJ mol ⁻¹	ΔE_{rel} (with ZPE + CP correction) /kJ mol ⁻¹
1.0.0_A	-685.699365	0.000	-685.634804	0.000	1.428	0.000
1.0.0_B [‡]	-685.679640	51.790	-685.615991	49.394	1.360	49.325
2.0.0_A	-911.087208	0.000	-910.958020	0.000	4.186	0.000
2.0.0_B	-911.086767	1.158	-910.957573	1.174	4.089	1.077
1.1.0_A	-911.083968	8.507	-910.954439	9.402	3.772	8.987
1.1.0_B	-911.074102	34.410	-910.944666	35.062	3.980	34.855
2.1.0_A	-1136.478947	0.000	-1136.281542	0.000	8.642	0.000
2.1.0_B	-1136.470841	21.282	-1136.276361	13.602	6.441	11.401
2.1.0_C	-1136.469377	25.128	-1136.275091	16.939	6.074	14.370
3.0.0_A	-1136.468913	26.344	-1136.275124	16.851	6.486	14.694
1.1.1_A	-1136.466189	33.496	-1136.271542	26.255	6.070	23.683
2.1.0_D	-1136.462255	43.825	-1136.267980	35.607	6.286	33.251
1.2.0_A	-1136.465543	35.193	-1136.268539	34.140	8.009	33.507
2.1.0_E	-1136.462038	44.394	-1136.267728	36.268	6.363	33.988
1.1.1_B	-1136.459629	50.719	-1136.264902	43.688	6.001	41.056
1.1.1_C	-1136.454424	64.385	-1136.259575	57.674	6.543	55.575
1.2.0_A	-1136.448052	81.116	-1136.253382	73.935	6.436	71.729

[‡] Structure 1.0.0_B can be obtained at the B3LYP level without constraints. Re-optimisation of B3LYP 1.0.0_B with inclusion of the D2 dispersion correction returned a structure with the chelating H-bond motif (i.e. 1.0.0_A). To isolate 1.0.0_B at the B3LYP-D2 level it was necessary to constrain the N-H...Cl distance; vibrational analysis of this structure returned no negative frequencies.

Optimised structures

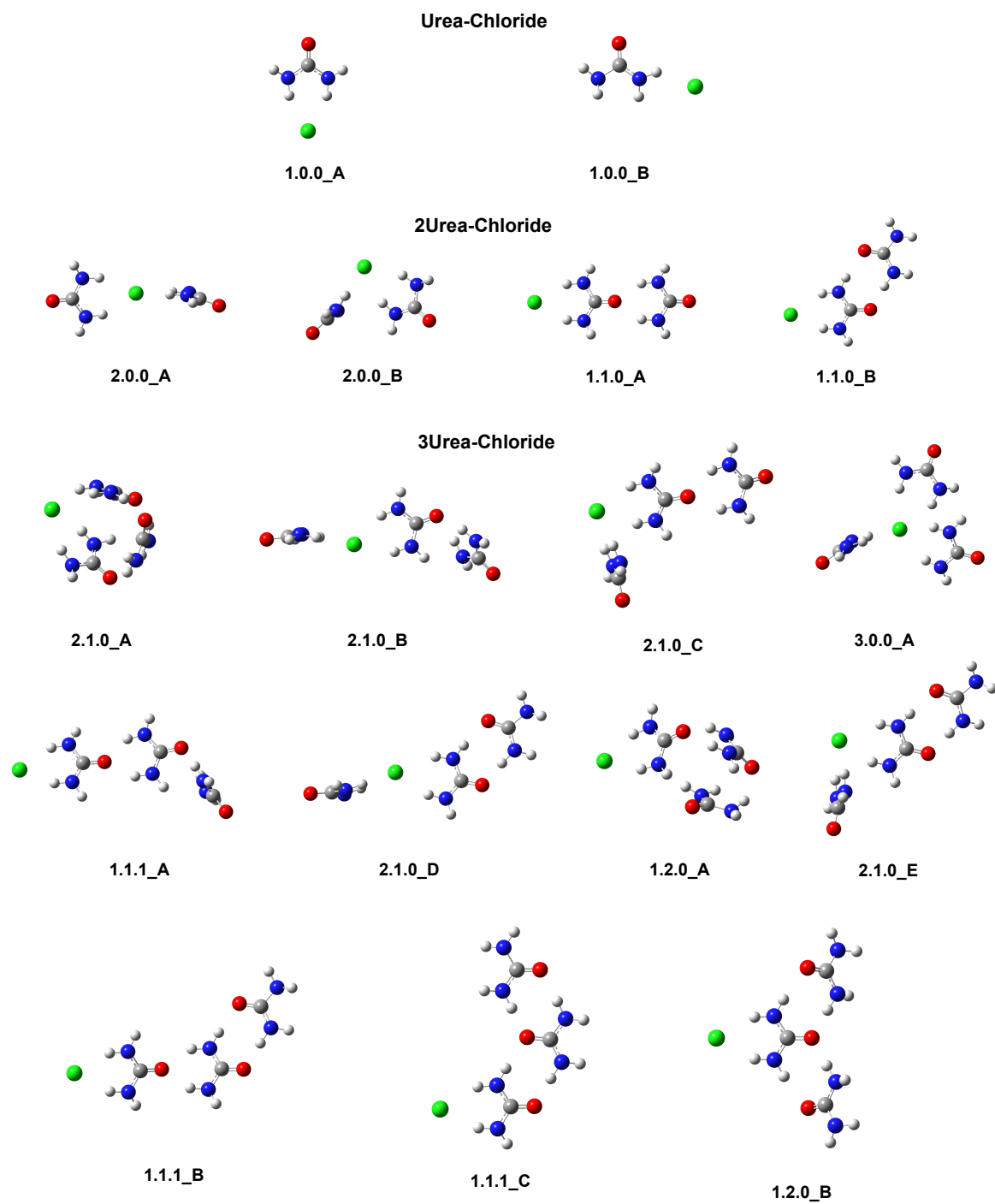


Figure A. 3. Urea-chloride complexes optimised at the B3LYP-D2/6-311++G(d,p) level.

H-bond data

Table A. 10. H-bond lengths (r), $E^{(2)}$ values and selected topological properties of the $\rho(r)$ at the BCPs for the individual H-bonds within the urea-chloride complexes.

1.0.0_A					
H-bond	$r/\text{\AA}$	$\Sigma E^{(2)}/\text{kJ mol}^{-1}$	$\rho_{\text{BCP}}/\text{a.u.}$	$\nabla^2 \rho_{\text{BCP}}/\text{a.u.}$	$H_{\text{BCP}}/\text{a.u.}$
NH...Cl (a)	2.321	43.10	0.0203	0.0555	0.00137
NH...Cl (b)	2.322	42.89	0.0203	0.0555	0.00137
1.0.0_B					
H-bond	$r/\text{\AA}$	$\Sigma E^{(2)}/\text{kJ mol}^{-1}$	$\rho_{\text{BCP}}/\text{a.u.}$	$\nabla^2 \rho_{\text{BCP}}/\text{a.u.}$	$H_{\text{BCP}}/\text{a.u.}$
NH...Cl (a)	2.320	38.58	0.0203	0.0577	0.00154
2.0.0_A					
H-bond	$r/\text{\AA}$	$\Sigma E^{(2)}/\text{kJ mol}^{-1}$	$\rho_{\text{BCP}}/\text{a.u.}$	$\nabla^2 \rho_{\text{BCP}}/\text{a.u.}$	$H_{\text{BCP}}/\text{a.u.}$
NH...Cl (a)	2.382	29.83	0.0174	0.0510	0.00170
NH...Cl (b)	2.379	32.84	0.0175	0.0512	0.00171
NH...Cl (c)	2.381	31.38	0.0174	0.0510	0.00170
NH...Cl (d)	2.380	32.22	0.0175	0.0511	0.00171
2.0.0_B					
H-bond	$r/\text{\AA}$	$\Sigma E^{(2)}/\text{kJ mol}^{-1}$	$\rho_{\text{BCP}}/\text{a.u.}$	$\nabla^2 \rho_{\text{BCP}}/\text{a.u.}$	$H_{\text{BCP}}/\text{a.u.}$
NH...Cl (a)	2.34385	37.15	0.0193	0.0549	0.00156
NH...Cl (b)	2.36547	35.31	0.0183	0.0528	0.00168
NH...Cl (c)	2.50221	20.38	0.0142	0.0415	0.00172
NH...Cl (d)	2.36629	34.52	0.0180	0.0521	0.00173
1.1.0_A					
H-bond	$r/\text{\AA}$	$\Sigma E^{(2)}/\text{kJ mol}^{-1}$	$\rho_{\text{BCP}}/\text{a.u.}$	$\nabla^2 \rho_{\text{BCP}}/\text{a.u.}$	$H_{\text{BCP}}/\text{a.u.}$
NH...Cl (a)	2.252	55.69	0.0236	0.0613	0.00072
NH...Cl (b)	2.253	55.40	0.0235	0.0612	0.00074
NH...O=C (a)	1.968	31.25	0.0234	0.0903	0.00262
NH...O=C (b)	1.968	31.17	0.0235	0.0905	0.00262
1.1.0_B					
H-bond	$r/\text{\AA}$	$\Sigma E^{(2)}/\text{kJ mol}^{-1}$	$\rho_{\text{BCP}}/\text{a.u.}$	$\nabla^2 \rho_{\text{BCP}}/\text{a.u.}$	$H_{\text{BCP}}/\text{a.u.}$
NH...Cl (a)	2.406	40.67	0.0170	0.0485	0.00174
NH...Cl (b)	2.236	59.83	0.0243	0.0624	0.00054
NH...O=C (a)	2.077	26.48	0.0188	0.0664	0.00219
NH...O=C (b)	1.697	118.16	0.0464	0.1330	-0.00047
2.1.0_A					
H-bond	$r/\text{\AA}$	$\Sigma E^{(2)}/\text{kJ mol}^{-1}$	$\rho_{\text{BCP}}/\text{a.u.}$	$\nabla^2 \rho_{\text{BCP}}/\text{a.u.}$	$H_{\text{BCP}}/\text{a.u.}$
NH...Cl (a)	2.594	14.77	0.0120	0.0357	0.00096
NH...Cl (b)	2.356	35.61	0.0191	0.0534	0.00154
NH...Cl (c)	2.361	37.11	0.0184	0.0525	0.00165
NH...Cl (d)	2.386	34.02	0.0181	0.0512	0.00160
NH...O=C (a)	1.971	34.52	0.0248	0.0857	0.00183
NH...O=C (b)	2.033	23.97	0.0208	0.0728	0.00213
NH...O=C (c)	2.155	15.36	0.0181	0.0597	0.00149
NH...O=C (d)	2.058	17.95	0.0205	0.0727	0.00203
NH...N (a)	2.646	1.72	0.0085	0.0280	0.00096
NH...N (b)	2.783	0.88	0.0068	0.0248	0.00100
2.1.0_B					
H-bond	$r/\text{\AA}$	$\Sigma E^{(2)}/\text{kJ mol}^{-1}$	$\rho_{\text{BCP}}/\text{a.u.}$	$\nabla^2 \rho_{\text{BCP}}/\text{a.u.}$	$H_{\text{BCP}}/\text{a.u.}$
NH...Cl (a)	2.393	30.13	0.0169	0.0500	0.00176
NH...Cl (b)	2.391	30.96	0.0170	0.0503	0.00176
NH...Cl (c)	2.293	45.48	0.0211	0.0590	0.00129
NH...Cl (d)	2.368	32.97	0.0179	0.0524	0.00168
NH...O=C (a)	2.060	23.35	0.0217	0.0738	0.00175
NH...O=C (b)	1.959	32.80	0.0252	0.0901	0.00200
NH...N	2.432	8.08	0.0112	0.0357	0.00143

2.1.0 C					
H-bond	r/Å	$\Sigma E^{(2)}/\text{kJ mol}^{-1}$	$\rho_{\text{BCP}}/\text{a.u.}$	$\nabla^2 \rho_{\text{BCP}}/\text{a.u.}$	$H_{\text{BCP}}/\text{a.u.}$
NH...Cl (a)	2.359	33.68	0.01874	0.054047	0.001643
NH...Cl (b)	2.372	33.60	0.01807	0.0524	0.00172
NH...Cl (c)	2.444	26.19	0.01600	0.0466	0.00172
NH...Cl (d)	2.304	44.89	0.02064	0.0577	0.00140
NH...O=C (a)	1.995	26.95	0.02168	0.0857	0.00281
NH...O=C (b)	1.977	28.58	0.02298	0.0884	0.00262
NH...N	2.672	1.92	0.00708	0.0241	0.00099
3.0.0 A					
H-bond	r/Å	$\Sigma E^{(2)}/\text{kJ mol}^{-1}$	$\rho_{\text{BCP}}/\text{a.u.}$	$\nabla^2 \rho_{\text{BCP}}/\text{a.u.}$	$H_{\text{BCP}}/\text{a.u.}$
NH...Cl (a)	2.415	28.20	0.0161	0.0486	0.00185
NH...Cl (b)	2.471	21.88	0.0147	0.0441	0.00175
NH...Cl (c)	2.468	22.68	0.0149	0.0446	0.00172
NH...Cl (d)	2.453	22.68	0.0150	0.0454	0.00182
NH...Cl (e)	2.431	25.31	0.0156	0.0472	0.00182
NH...Cl (f)	2.423	24.44	0.0158	0.0478	0.00182
NH...N	2.915	0.50	0.0061	0.0217	0.00092
1.1.1 A					
H-bond	r/Å	$\Sigma E^{(2)}/\text{kJ mol}^{-1}$	$\rho_{\text{BCP}}/\text{a.u.}$	$\nabla^2 \rho_{\text{BCP}}/\text{a.u.}$	$H_{\text{BCP}}/\text{a.u.}$
NH...Cl (a)	2.238	58.74	0.0244	0.0625	0.00052
NH...Cl (b)	2.240	58.28	0.0242	0.0623	0.00057
NH...O=C (a)	1.959	30.46	0.0233	0.0934	0.00287
NH...O=C (b)	1.897	41.63	0.0279	0.1049	0.00215
NH...O=C (c)	1.981	28.79	0.0239	0.0863	0.00211
NH...O=C (d)	2.030	26.99	0.0230	0.0779	0.00170
NH...N	2.464	6.61	0.0105	0.0347	0.00147
2.1.0 D					
H-bond	r/Å	$\Sigma E^{(2)}/\text{kJ mol}^{-1}$	$\rho_{\text{BCP}}/\text{a.u.}$	$\nabla^2 \rho_{\text{BCP}}/\text{a.u.}$	$H_{\text{BCP}}/\text{a.u.}$
NH...Cl (a)	2.377	32.93	0.0176	0.0513	0.00170
NH...Cl (b)	2.376	33.47	0.0177	0.0514	0.00170
NH...Cl (c)	2.296	44.64	0.0209	0.0585	0.00133
NH...Cl (d)	2.478	21.59	0.0142	0.0430	0.00180
NH...O=C (a)	2.018	33.43	0.0213	0.0760	0.00227
NH...O=C (b)	1.715	110.21	0.0442	0.1306	-0.00366
1.2.0_A					
H-bond	r/Å	$\Sigma E^{(2)}/\text{kJ mol}^{-1}$	$\rho_{\text{BCP}}/\text{a.u.}$	$\nabla^2 \rho_{\text{BCP}}/\text{a.u.}$	H/a.u
NH...Cl (a)	2.305	46.48	0.0211	0.0571	0.00124
NH...Cl (b)	2.179	72.97	0.0277	0.0669	-0.00046
NH...O=C (a)	2.316	8.08	0.0121	0.0392	0.00123
NH...O=C (b)	2.020	21.67	0.0223	0.0795	0.00204
NH...O=C (c)	1.896	46.32	0.0288	0.1042	0.00174
NH...O=C (d)	2.476	2.38	0.0105	0.0354	0.00114
NH...O=C (e)	2.066	22.47	0.0211	0.0710	0.00175
NH...N (a)	2.555	2.97	0.0103	0.0323	0.00110
NH...N (b)	2.211	19.46	0.0174	0.0545	0.00185
2.1.0 E					
H-bond	r/Å	$\Sigma E^{(2)}/\text{kJ mol}^{-1}$	$\rho_{\text{BCP}}/\text{a.u.}$	$\nabla^2 \rho_{\text{BCP}}/\text{a.u.}$	$H_{\text{BCP}}/\text{a.u.}$
NH...Cl (a)	2.352	35.02	0.0190	0.0542	0.00159
NH...Cl (b)	2.362	35.40	0.0185	0.0531	0.00167
NH...Cl (c)	2.342	39.12	0.0195	0.0548	0.00150
NH...Cl (d)	2.504	21.34	0.0136	0.0409	0.00184
NH...O=C (a)	2.027	31.67	0.0209	0.0746	0.00226
NH...O=C (b)	1.709	112.84	0.0449	0.1315	-0.00394
1.1.1 B					
H-bond	r/Å	$\Sigma E^{(2)}/\text{kJ mol}^{-1}$	$\rho_{\text{BCP}}/\text{a.u.}$	$\nabla^2 \rho_{\text{BCP}}/\text{a.u.}$	H/a.u
NH...Cl (a)	2.260	54.10	0.0232	0.0606	0.00083
NH...Cl (b)	2.253	55.44	0.0235	0.0612	0.00074
NH...O=C (a)	2.023	24.60	0.0205	0.0806	0.00275
NH...O=C (b)	1.913	38.58	0.0266	0.1013	0.00236
NH...O=C (c)	1.983	37.49	0.0230	0.0823	0.00223
NH...O=C (d)	1.728	103.70	0.0428	0.1283	-0.00300

Choline – Urea Pairs

Relative energies

Table A. 11. Absolute and relative energies of the choline urea pairs: without any corrections, with ZPE corrections and with both ZPE and CP corrections.

Ion Pair	E /au	ΔE_{rel} /kJ mol ⁻¹	E+ZPE /au	ΔE_{rel} (with ZPE correction) /kJ mol ⁻¹	BSSE /kJ mol ⁻¹	ΔE_{rel} (with ZPE + CP correction) /kJ mol ⁻¹
A_UChG	-554.207244	0.000	-553.945257	0.000	2.674	0.000
B_UChG	-554.204551	7.070	-553.943473	4.683	1.489	3.499
C_UChG	-554.204543	7.091	-553.943287	5.172	1.769	4.267
D_UChG	-554.203266	10.444	-553.942222	7.968	1.258	6.552
E_UChG	-554.203337	10.258	-553.942235	7.935	1.517	6.778
F_UChG	-554.202443	12.604	-553.940014	13.765	2.921	14.012
A_UChT	-554.200689	17.209	-553.939064	16.258	2.804	16.389
B_UChT	-554.197555	25.437	-553.936973	21.748	1.276	20.350
C_UChT	-554.199468	20.416	-553.936970	21.757	2.807	21.891
D_UChT	-554.196133	29.172	-553.935585	25.394	1.737	24.458

H-bond data

Table A. 12. H-bond lengths (r), $E^{(2)}$ values and selected topological properties of the $\rho(r)$ at the BCPs for the individual H-bonds within the choline-urea pairs.

A_UChG					
H-bond	r/Å	$\Sigma E^{(2)}$ / kJ mol ⁻¹	ρ_{BCP} /a.u	$\nabla^2 \rho_{\text{BCP}}$ /a.u	H_{BCP} /a.u
Intra CH...O(H)	2.474	-	0.0118	0.0430	0.00165
CH...O=(a)	2.298	6.15	0.0094	0.0338	0.00132
CH...O=(b)	2.434	3.89	0.0119	0.0426	0.00168
OH...O=	1.683	114.39	0.0489	0.1420	-0.00565
NH...O(H)	2.477	3.72	0.0092	0.0373	0.00162
B_UChG					
H-bond	r/Å	$\Sigma E^{(2)}$ / kJ mol ⁻¹	ρ_{BCP} /a.u	$\nabla^2 \rho_{\text{BCP}}$ /a.u	H_{BCP} /a.u
Intra CH...O(H)	2.229	4.77	0.0159	0.0605	0.00228
CH...O=(a)	2.279	9.71	0.0134	0.0466	0.00171
CH...O=(b)	2.319	5.73	0.0123	0.0425	0.00154
CH...O=(c)	2.245	9.04	0.0144	0.0520	0.00195
C_UChG					
H-bond	r/Å	$\Sigma E^{(2)}$ / kJ mol ⁻¹	ρ_{BCP} /a.u	$\nabla^2 \rho_{\text{BCP}}$ /a.u	H_{BCP} /a.u
Intra CH...O(H)	2.179	8.83	0.0184	0.0673	0.00226
OH...O=	1.648	124.81	0.0497	0.1510	-0.00579
D_UChG					
H-bond	r/Å	$\Sigma E^{(2)}$ / kJ mol ⁻¹	ρ_{BCP} /a.u	$\nabla^2 \rho_{\text{BCP}}$ /a.u	H_{BCP} /a.u
Intra CH...O(H)	2.240	4.44	0.0157	0.0593	0.00221
CH...O=(a)	2.297	8.79	0.0129	0.0443	0.00160
CH...O=(b)	2.241	8.12	0.0137	0.0502	0.00120
CH...O=(c)	2.239	10.38	0.0141	0.0507	0.00194
E_UChG					
H-bond	r/Å	$\Sigma E^{(2)}$ / kJ mol ⁻¹	ρ_{BCP} /a.u	$\nabla^2 \rho_{\text{BCP}}$ /a.u	H_{BCP} /a.u
Intra CH...O(H)	2.237	4.31	0.0158	0.0598	0.00223
CH...O=(a)	2.286	8.08	0.0132	0.0456	0.00165
CH...O=(b)	2.258	9.83	0.0135	0.0485	0.00188
CH...O=(c)	2.238	9.46	0.0142	0.0513	0.00194
F_UChG					
H-bond	r/Å	$\Sigma E^{(2)}$ / kJ mol ⁻¹	ρ_{BCP} /a.u	$\nabla^2 \rho_{\text{BCP}}$ /a.u	H_{BCP} /a.u
Intra CH...O(H)	2.458	-	0.0128	0.0465	0.00154
CH...O=(a)	2.384	4.81	0.0109	0.0348	0.00113

CH...O=(b)	2.240	8.91	0.0130	0.0493	0.00210
CH...O=(c)	2.440	4.60	0.0116	0.0358	0.00089
OH...N	2.165	20.08	0.0192	0.0587	0.00152
A_UChT					
H-bond	r/Å	$\Sigma E^{(2)}$/kJ mol⁻¹	ρ_{BCP}/a.u.	$\nabla^2 \rho_{BCP}$/a.u.	H_{BCP}/a.u.
CH...O=(a)	2.185	10.33	0.0157	0.0581	0.00222
CH...O=(b)	2.480	2.68	0.0086	0.0307	0.00116
CH...O=(c)	2.041	25.65	0.0238	0.0817	0.00205
NH...O(H)	2.136	19.71	0.0164	0.0583	0.00206
B_UChT					
H-bond	r/Å	$\Sigma E^{(2)}$/kJ mol⁻¹	ρ_{BCP}/a.u.	$\nabla^2 \rho_{BCP}$/a.u.	H_{BCP}/a.u.
CH...O=(a)	2.248	10.79	0.0141	0.0497	0.00186
CH...O=(b)	2.249	9.37	0.0139	0.0496	0.00187
CH...O=(c)	2.246	8.45	0.0138	0.0499	0.00191
C_UChT					
H-bond	r/Å	$\Sigma E^{(2)}$/kJ mol⁻¹	ρ_{BCP}/a.u.	$\nabla^2 \rho_{BCP}$/a.u.	H_{BCP}/a.u.
CH...O=(a)	2.559	1.76	0.0082	0.0268	0.00089
CH...O=(b)	2.464	1.51	0.0099	0.0385	0.00148
OH...O=	1.879	45.06	0.0320	0.1043	0.00001
NH...O(H)	2.403	5.65	0.0105	0.0386	0.00153
D_UChT					
H-bond	r/Å	$\Sigma E^{(2)}$/kJ mol⁻¹	ρ_{BCP}/a.u.	$\nabla^2 \rho_{BCP}$/a.u.	H_{BCP}/a.u.
CH...O=(a)	2.204	13.43	0.0151	0.0511	0.00208
CH...O=(b)	2.204	13.18	0.0152	0.0545	0.00207
CH...O=(c)	2.641	0.50	0.0082	0.0329	0.00137
CH...O=(d)	2.642	0.46	0.0082	0.0330	0.00138

Clusters: Structures and energies

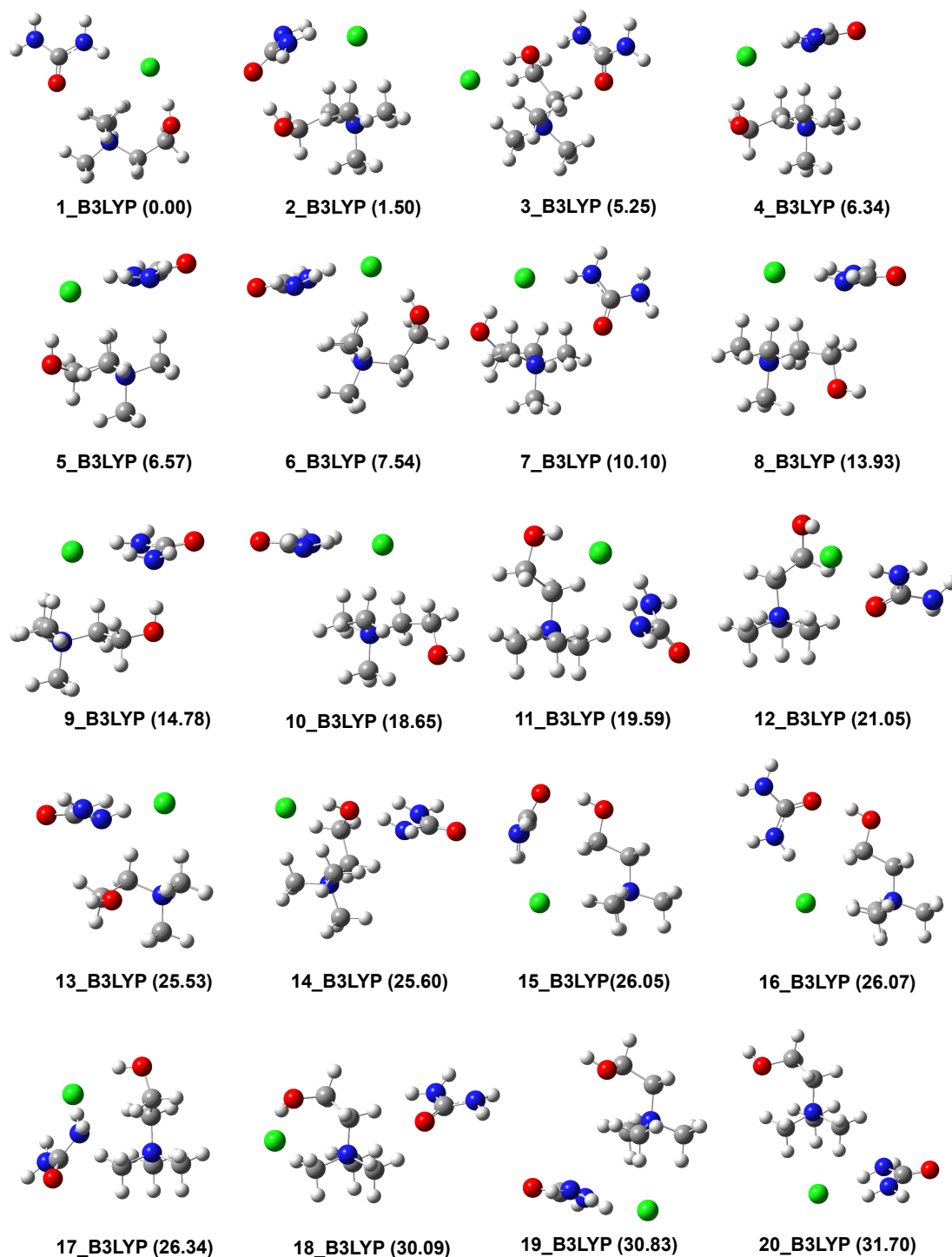
1:1 Clusters

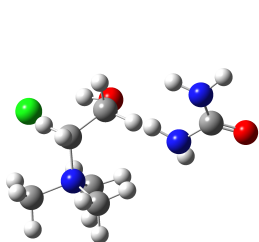
B3LYP/6-311+G(d,p)

Table A. 13. Absolute and relative energies of the B3LYP/6-311+G(d,p) 1:1 clusters with, and without, ZPE corrections.

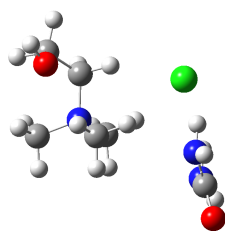
Cluster	E /au	ΔE_{rel} /kJ mol ⁻¹	$E+ZPE$ /au	ΔE_{rel} (with ZPE correction) /kJ mol ⁻¹
1_B3LYP	-1014.619000	0.896	-1014.356787	0.000
2_B3LYP	-1014.619342	0.000	-1014.356218	1.496
3_B3LYP	-1014.617281	5.409	-1014.354786	5.253
4_B3LYP	-1014.617498	4.840	-1014.354372	6.341
5_B3LYP	-1014.617201	5.621	-1014.354284	6.571
6_B3LYP	-1014.616521	7.406	-1014.353915	7.542
7_B3LYP	-1014.614854	11.783	-1014.352942	10.096
8_B3LYP	-1014.614221	13.443	-1014.351481	13.930
9_B3LYP	-1014.614529	12.633	-1014.351158	14.779
10_B3LYP	-1014.612197	18.759	-1014.349686	18.645
11_B3LYP	-1014.612206	18.733	-1014.349324	19.594
12_B3LYP	-1014.610954	22.017	-1014.348769	21.051
13_B3LYP	-1014.609564	25.672	-1014.347063	25.532
14_B3LYP	-1014.609597	25.585	-1014.347037	25.600
15_B3LYP	-1014.609461	25.940	-1014.346864	26.052
16_B3LYP	-1014.608778	27.736	-1014.346859	26.068
17_B3LYP	-1014.609630	25.493	-1014.346755	26.340
18_B3LYP	-1014.606908	32.644	-1014.345328	30.086
19_B3LYP	-1014.607337	31.517	-1014.345046	30.825
20_B3LYP	-1014.607151	32.006	-1014.344715	31.696
21_B3LYP	-1014.607052	32.267	-1014.344517	32.217
22_B3LYP	-1014.606618	33.405	-1014.344418	32.475
23_B3LYP	-1014.605251	36.995	-1014.34301	36.173
24_B3LYP	-1014.604614	38.667	-1014.342702	36.981
25_B3LYP	-1014.601752	46.183	-1014.339005	46.689
26_B3LYP	-1014.601752	46.174	-1014.339002	46.694
27_B3LYP	-1014.599752	51.431	-1014.337910	49.561

Figure A. 4. 1:1 Clusters optimised at the B3LYP/6-311+G(d,p) level. Relative energies (kJ mol^{-1}) are ZPE corrected.

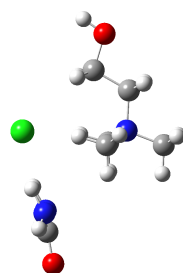




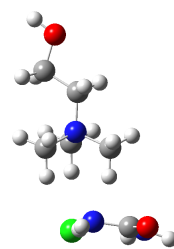
21_B3LYP (32.22)



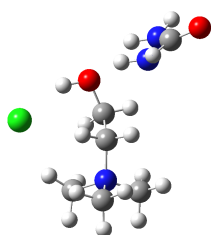
22_B3LYP (32.48)



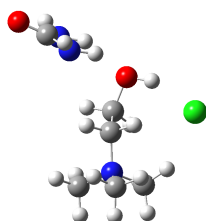
23_B3LYP (36.17)



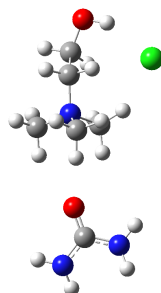
24_B3LYP (36.98)



25_B3LYP (46.69)



26_B3LYP (46.69)



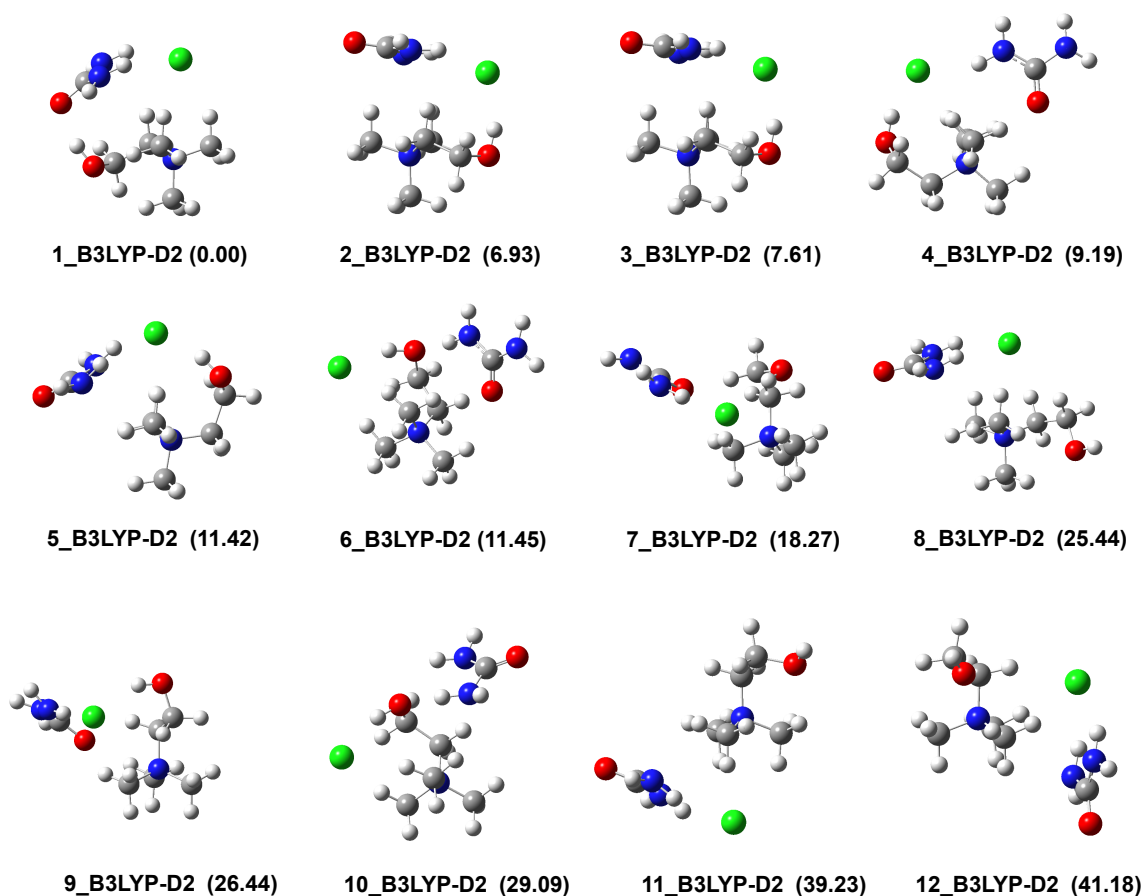
27_B3LYP (49.56)

B3LYP-D2/6-311++G(d,p)

Table A. 14. Absolute and relative energies of the B3LYP-D2/6-311++G(d,p) 1:1 clusters with, and without, ZPE corrections. The B3LYP cluster from which each B3LYP-D2 cluster is derived listed. Structures marked with * underwent significant change in geometry upon optimisation at the B3LYP-D2 level.

B3LYP-D2 Cluster	Parent B3LYP Cluster	E /au	ΔE_{rel} /kJ mol ⁻¹	$E+ZPE$ /au	ΔE_{rel} (with ZPE correction) /kJ mol ⁻¹
1_B3LYP-D2	2_B3LYP	-1014.670247	0.000	-1014.407099	0.000
2_B3LYP-D2	5_B3LYP	-1014.667716	6.645	-1014.40446	6.928
3_B3LYP-D2	4_B3LYP	-1014.667464	7.307	-1014.404201	7.609
4_B3LYP-D2	1_B3LYP	-1014.666250	10.496	-1014.403599	9.191
5_B3LYP-D2	6_B3LYP	-1014.666299	10.366	-1014.402749	11.421
6_B3LYP-D2	3_B3LYP	-1014.665788	11.709	-1014.402738	11.451
7_B3LYP-D2	17_B3LYP *	-1014.662798	19.559	-1014.400138	18.277
8_B3LYP-D2	10_B3LYP	-1014.660411	25.826	-1014.397409	25.442
9_B3LYP-D2	25_B3LYP *	-1014.659803	27.423	-1014.397031	26.436
10_B3LYP-D2	14_B3LYP	-1014.659677	27.751	-1014.396019	29.090
11_B3LYP-D2	19_B3LYP	-1014.655193	39.524	-1014.392159	39.225
12_B3LYP-D2	20_B3LYP	-1014.654449	41.479	-1014.391415	41.180

Figure A. 5. 1:1 Clusters optimised at the B3LYP-D2/6-311++G(d,p) level. Relative energies (kJ mol⁻¹) are ZPE corrected.



1:2 Clusters

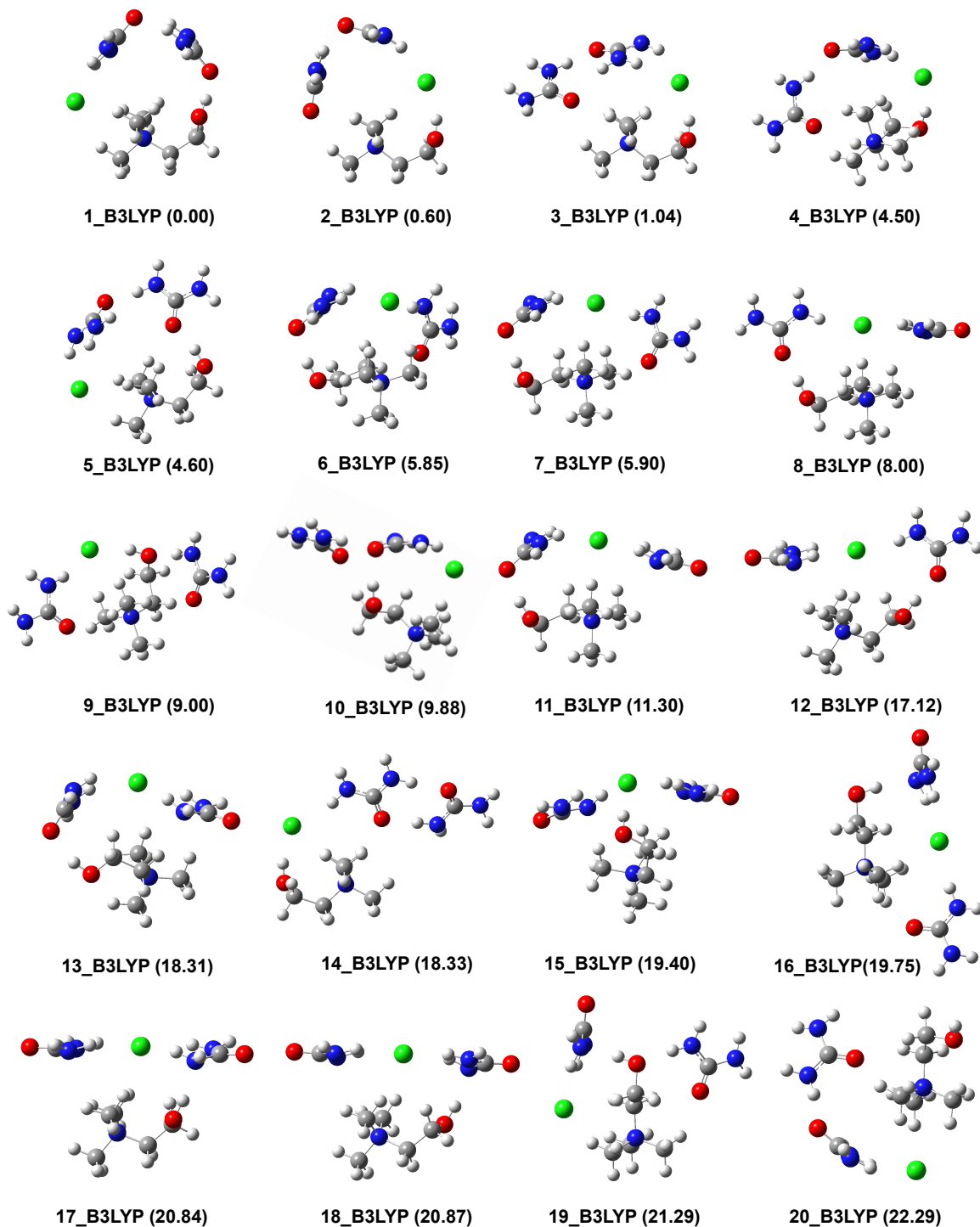
B3LYP/6-311+G(d,p)

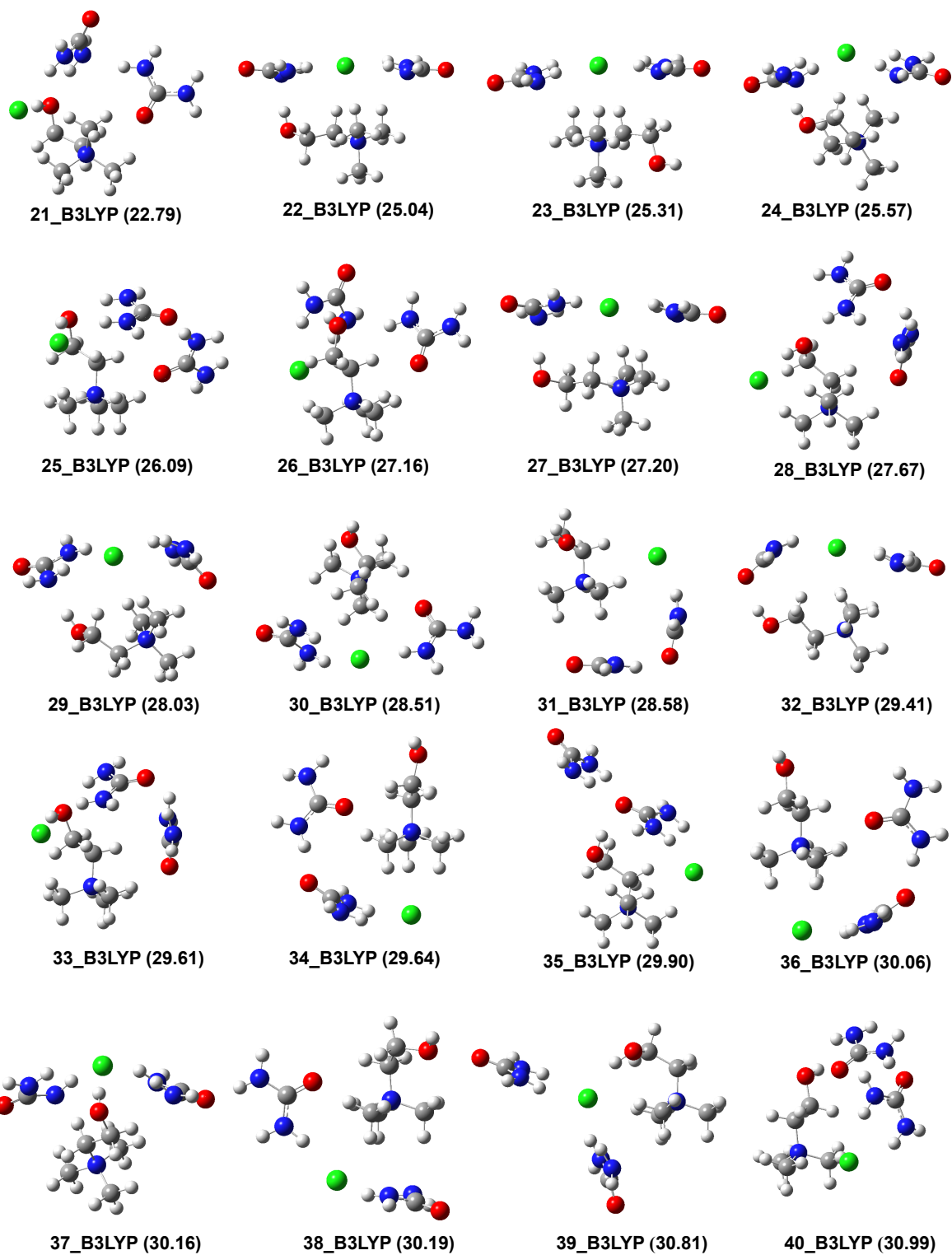
Table A. 15. Absolute and relative energies of the B3LYP /6-311+G(d,p) 1:2 clusters with, and without, ZPE corrections

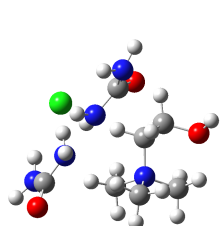
Cluster	E /au	ΔE_{rel} / kJ mol ⁻¹	$E+\text{ZPE}$ /au	ΔE_{rel} (with ZPE correction) /kJ mol ⁻¹
1_B3LYP	-1239.992811	0.000	-1239.665123	0.000
2_B3LYP	-1239.992136	1.772	-1239.664894	0.601
3_B3LYP	-1239.992589	0.582	-1239.664726	1.042
4_B3LYP	-1239.990396	6.341	-1239.663411	4.495
5_B3LYP	-1239.990645	5.687	-1239.663370	4.603
6_B3LYP	-1239.990765	5.371	-1239.662895	5.849
7_B3LYP	-1239.990684	5.585	-1239.662875	5.902
8_B3LYP	-1239.989665	8.259	-1239.662075	8.002
9_B3LYP	-1239.989173	9.551	-1239.661695	9.000
10_B3LYP	-1239.990173	6.926	-1239.661362	9.875
11_B3LYP	-1239.988965	10.098	-1239.660819	11.300
12_B3LYP	-1239.986056	17.736	-1239.658602	17.122
13_B3LYP	-1239.986941	15.412	-1239.658151	18.306
14_B3LYP	-1239.985567	19.020	-1239.658143	18.327
15_B3LYP	-1239.985352	19.584	-1239.657736	19.395
16_B3LYP	-1239.985723	18.609	-1239.657602	19.746
17_B3LYP	-1239.985545	19.077	-1239.657187	20.836
18_B3LYP	-1239.985519	19.145	-1239.657176	20.865
19_B3LYP	-1239.985431	19.375	-1239.657012	21.294
20_B3LYP	-1239.983844	23.542	-1239.656635	22.285
21_B3LYP	-1239.984374	22.150	-1239.656442	22.790
22_B3LYP	-1239.984004	23.124	-1239.655585	25.043
23_B3LYP	-1239.983165	25.325	-1239.655482	25.312
24_B3LYP	-1239.984057	22.982	-1239.655385	25.566
25_B3LYP	-1239.982803	26.275	-1239.655187	26.086
26_B3LYP	-1239.983609	24.160	-1239.654780	27.156
27_B3LYP	-1239.983102	25.490	-1239.654764	27.197
28_B3LYP	-1239.982730	26.468	-1239.654583	27.673
29_B3LYP	-1239.982634	26.719	-1239.654445	28.034
30_B3LYP	-1239.981603	29.427	-1239.654264	28.511
31_B3LYP	-1239.981505	29.683	-1239.654239	28.575
32_B3LYP	-1239.981927	28.58	-1239.653921	29.411
33_B3LYP	-1239.981581	29.48	-1239.653846	29.606
34_B3LYP	-1239.980665	31.89	-1239.653833	29.640
35_B3LYP	-1239.981460	29.802	-1239.653733	29.904
36_B3LYP	-1239.980427	32.51	-1239.653673	30.062
37_B3LYP	-1239.981671	29.247	-1239.653634	30.163
38_B3LYP	-1239.980792	31.554	-1239.653624	30.189
39_B3LYP	-1239.979845	34.041	-1239.653388	30.809
40_B3LYP	-1239.980414	32.55	-1239.653319	30.991
41_B3LYP	-1239.981279	30.277	-1239.653006	31.813
42_B3LYP	-1239.980717	31.753	-1239.652962	31.929
43_B3LYP	-1239.981455	29.815	-1239.652946	31.971
44_B3LYP	-1239.979425	35.143	-1239.652900	32.090
45_B3LYP	-1239.979864	33.99	-1239.652715	32.577
46_B3LYP	-1239.979184	35.78	-1239.652422	33.346
47_B3LYP	-1239.980712	31.765	-1239.652368	33.488
48_B3LYP	-1239.980323	32.787	-1239.652238	33.829
49_B3LYP	-1239.980147	33.249	-1239.652050	34.323
50_B3LYP	-1239.979782	34.207	-1239.651752	35.105
51_B3LYP	-1239.980322	32.790	-1239.651609	35.481
52_B3LYP	-1239.979386	35.248	-1239.651478	35.825
53_B3LYP	-1239.979316	35.431	-1239.651425	35.964
54_B3LYP	-1239.977697	39.680	-1239.650883	37.385
55_B3LYP	-1239.978286	38.136	-1239.650787	37.640
56_B3LYP	-1239.978728	36.97	-1239.650516	38.351
57_B3LYP	-1239.978714	37.012	-1239.650500	38.393
58_B3LYP	-1239.978569	37.39	-1239.650430	38.576
59_B3LYP	-1239.978701	37.045	-1239.649874	40.035
60_B3LYP	-1239.977110	41.22	-1239.648597	43.388
61_B3LYP	-1239.974407	48.318	-1239.647449	46.402

62_B3LYP	-1239.975423	45.653	-1239.646714	48.333
63_B3LYP	-1239.972766	52.63	-1239.645634	51.169
64_B3LYP	-1239.972545	53.209	-1239.645590	51.285
65_B3LYP	-1239.973685	50.22	-1239.645478	51.579
66_B3LYP	-1239.971446	56.094	-1239.644196	54.944
67_B3LYP	-1239.969983	59.935	-1239.642786	58.646

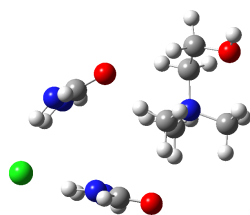
Figure A. 6. 1:2 Clusters optimised at the B3LYP /6-311+G(d,p) level. Relative energies (kJ mol^{-1}) are ZPE corrected.



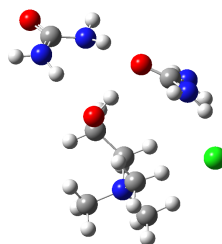




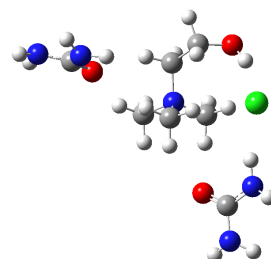
41_B3LYP (31.81)



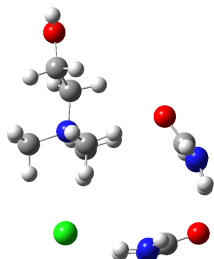
42_B3LYP (31.93)



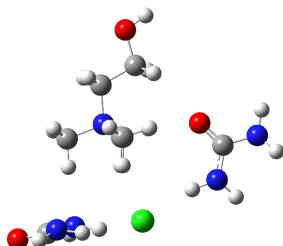
43_B3LYP (31.97)



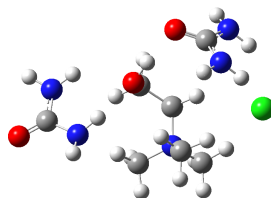
44_B3LYP (32.09)



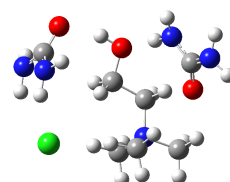
45_B3LYP (32.58)



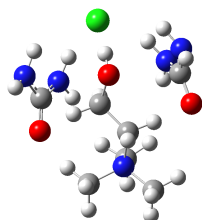
46_B3LYP (33.35)



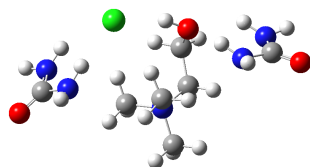
47_B3LYP (33.49)



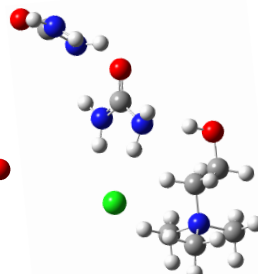
48_B3LYP (33.83)



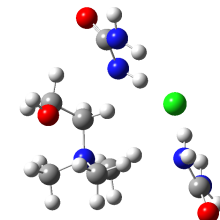
49_B3LYP (34.32)



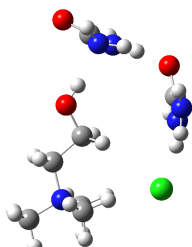
50_B3LYP (35.11)



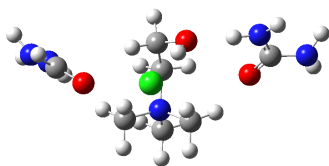
51_B3LYP (35.48)



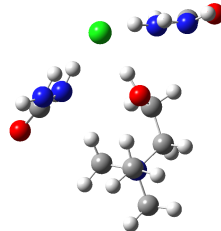
52_B3LYP (35.83)



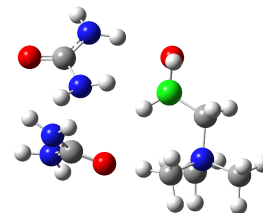
53_B3LYP (35.96)



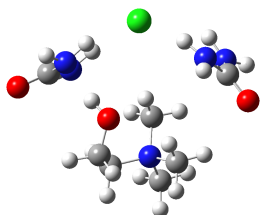
54_B3LYP (37.39)



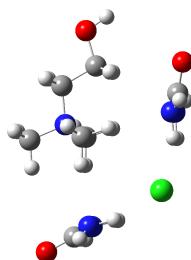
55_B3LYP (37.64)



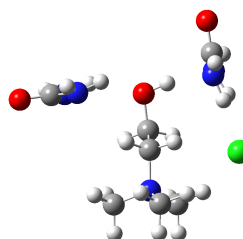
56_B3LYP (38.35)



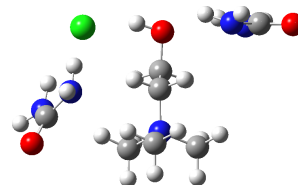
57_B3LYP (38.39)



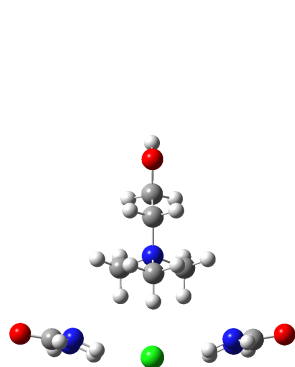
58_B3LYP (38.58)



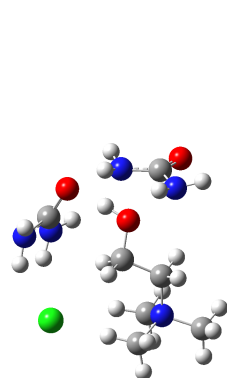
59_B3LYP (40.04)



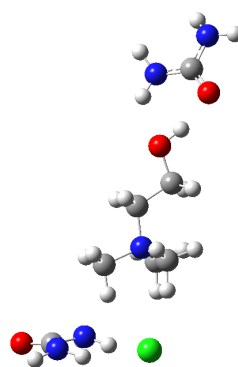
60_B3LYP (43.39)



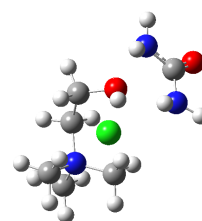
61_B3LYP (46.40)



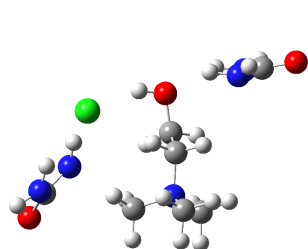
62_B3LYP (48.33)



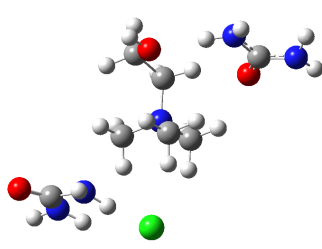
63_B3LYP (51.17)



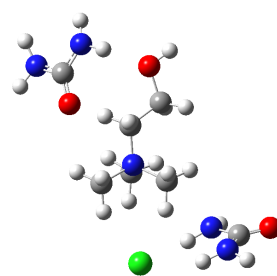
64_B3LYP (51.29)



65_B3LYP (51.58)



66_B3LYP (54.94)



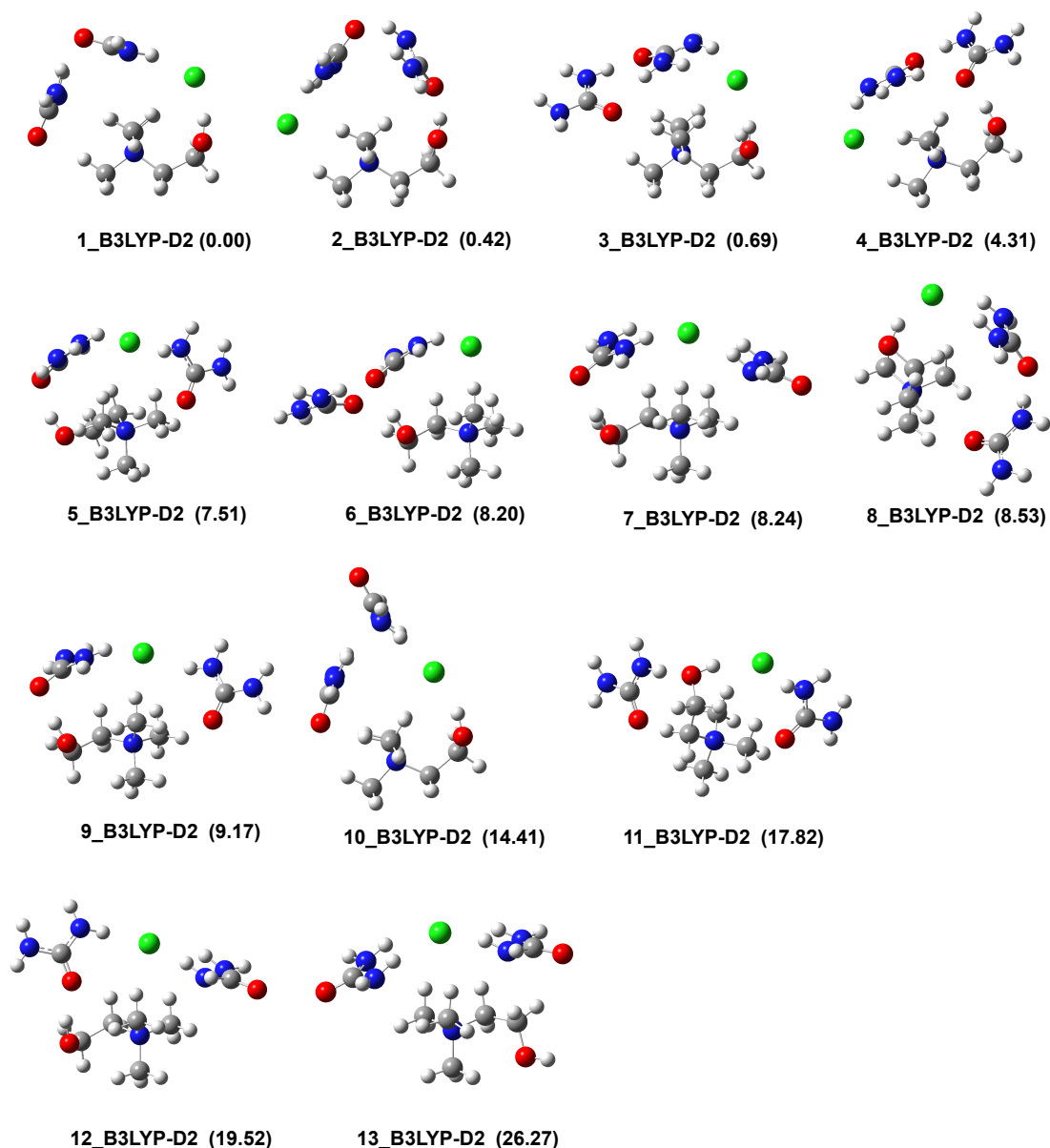
67_B3LYP (58.65)

B3LYP-D2/6-311++G(d,p)

Table A. 16. Absolute and relative energies of the B3LYP-D2/6-311++G(d,p) 1:2 clusters with, and without, ZPE corrections. The B3LYP cluster from which each B3LYP-D2 cluster is derived listed. Structures marked with * underwent significant change in geometry upon optimisation at the B3LYP-D2 level.

B3LYP-D2 Cluster	Parent B3LYP Cluster	E /au	ΔE_{rel} /kJ mol ⁻¹	$E+ZPE$ /au	ΔE_{rel} (with ZPE correction) /kJ mol ⁻¹
1_B3LYP-D2	2_B3LYP	-1240.055022	0.000	-1239.726178	0.000
2_B3LYP-D2	1_B3LYP	-1240.054964	0.152	-1239.72602	0.415
3_B3LYP-D2	3_B3LYP	-1240.054873	0.391	-1239.725917	0.685
4_B3LYP-D2	5_B3LYP	-1240.053623	3.673	-1239.724537	4.309
5_B3LYP-D2	6_B3LYP	-1240.051514	9.210	-1239.723318	7.509
6_B3LYP-D2	10_B3LYP	-1240.052208	7.388	-1239.723056	8.197
7_B3LYP-D2	11_B3LYP	-1240.051472	9.322	-1239.723039	8.243
8_B3LYP-D2	4_B3LYP	-1240.051275	9.838	-1239.722929	8.531
9_B3LYP-D2	7_B3LYP	-1240.050626	11.542	-1239.722685	9.171
10_B3LYP-D2	34_B3LYP *	-1240.049995	13.200	-1239.720692	14.405
11_B3LYP-D2	9_B3LYP	-1240.047575	19.552	-1239.719389	17.824
12_B3LYP-D2	8_B3LYP	-1240.047301	20.271	-1239.718744	19.518
13_B3LYP-D2	23_B3LYP	-1240.044794	26.854	-1239.716174	26.266

Figure A. 7. 1:2 Clusters optimised at the B3LYP-D2 /6-311++G(d,p) level. Relative energies (kJ mol⁻¹) are ZPE corrected.



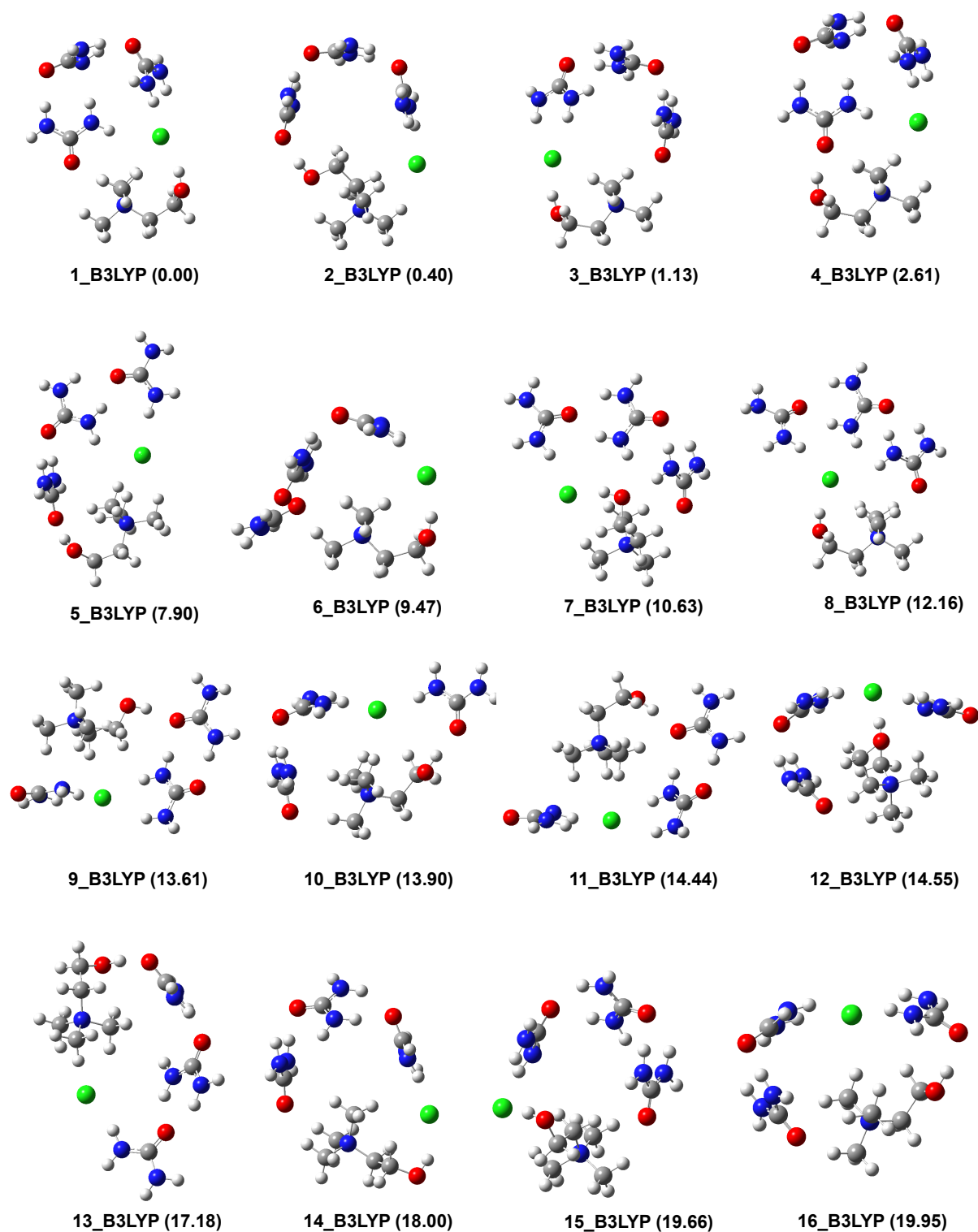
1:3 Clusters

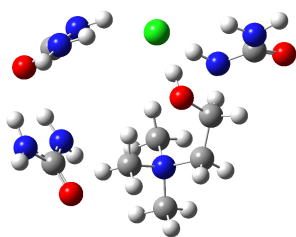
B3LYP/6-311+G(d,p)

Table A. 17. Absolute and relative energies of the B3LYP /6-311+G(d,p) 1:3 clusters with, and without, zero point energy corrections.

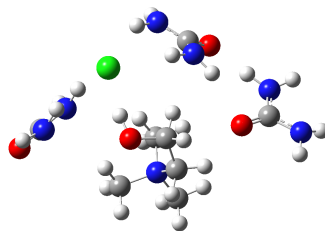
Cluster	E /au	ΔE_{rel} /kJ mol ⁻¹	E+ZPE /au	ΔE_{rel} (with ZPE correction) /kJ mol ⁻¹
1_B3LYP	-1465.366923	0.000	-1464.973249	0.000
2_B3LYP	-1465.365799	2.953	-1464.973098	0.399
3_B3LYP	-1465.365891	2.711	-1464.972819	1.130
4_B3LYP	-1465.36653	1.020	-1464.972254	2.614
5_B3LYP	-1465.362911	10.534	-1464.970239	7.903
6_B3LYP	-1465.362369	11.958	-1464.969644	9.466
7_B3LYP	-1465.362643	11.239	-1464.969201	10.630
8_B3LYP	-1465.362020	12.874	-1464.968617	12.162
9_B3LYP	-1465.361956	13.042	-1464.968065	13.612
10_B3LYP	-1465.360583	16.647	-1464.967956	13.898
11_B3LYP	-1465.360964	15.646	-1464.967751	14.435
12_B3LYP	-1465.359542	19.381	-1464.967707	14.553
13_B3LYP	-1465.359162	20.378	-1464.966707	17.178
14_B3LYP	-1465.359618	19.180	-1464.966394	17.999
15_B3LYP	-1465.359113	20.506	-1464.96576	19.663
16_B3LYP	-1465.358428	22.305	-1464.965651	19.950
17_B3LYP	-1465.357788	23.985	-1464.965556	20.199
18_B3LYP	-1465.357734	24.128	-1464.965147	21.274
19_B3LYP	-1465.358164	22.998	-1464.964432	23.151
20_B3LYP	-1465.357376	25.068	-1464.964303	23.490
21_B3LYP	-1465.354837	31.733	-1464.962151	29.139
22_B3LYP	-1465.355125	30.977	-1464.961964	29.630
23_B3LYP	-1465.35508	31.096	-1464.961767	30.148
24_B3LYP	-1465.353598	34.985	-1464.961581	30.635
25_B3LYP	-1465.354619	32.305	-1464.961474	30.916
26_B3LYP	-1465.352987	36.590	-1464.959617	35.792
27_B3LYP	-1465.350867	42.157	-1464.957544	41.235
28_B3LYP	-1465.350415	43.344	-1464.957266	41.965
29_B3LYP	-1465.349277	46.332	-1464.955759	45.922
30_B3LYP	-1465.344975	57.626	-1464.952965	53.257
31_B3LYP	-1465.345514	56.212	-1464.952212	55.235
32_B3LYP	-1465.339654	71.597	-1464.94863	64.640
33_B3LYP	-1465.338116	75.635	-1464.947141	68.548

Figure A. 8. 1:3 Clusters optimised at the B3LYP/6-311+G(d,p) level. Relative energies (kJ mol^{-1}) are ZPE corrected.

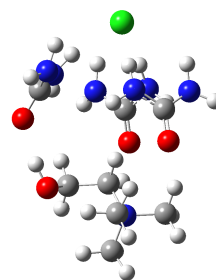




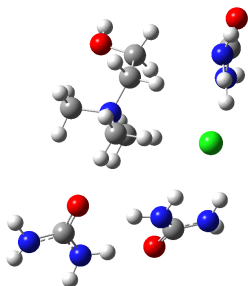
17_B3LYP (20.20)



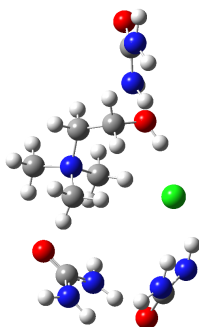
18_B3LYP (21.27)



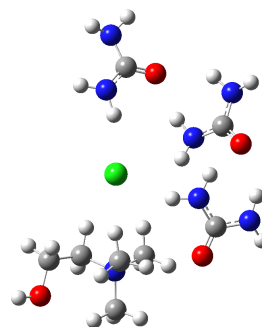
19_B3LYP (23.15)



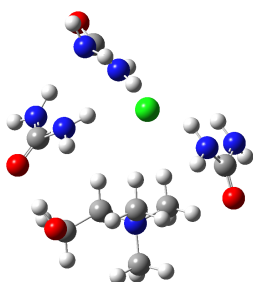
20_B3LYP (23.49)



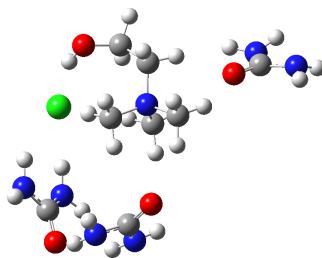
21_B3LYP (29.14)



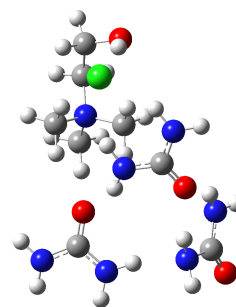
22_B3LYP (29.63)



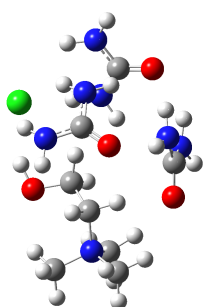
23_B3LYP (30.15)



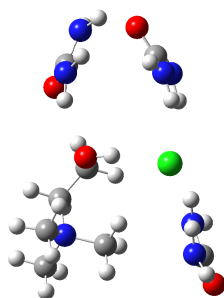
24_B3LYP (30.64)



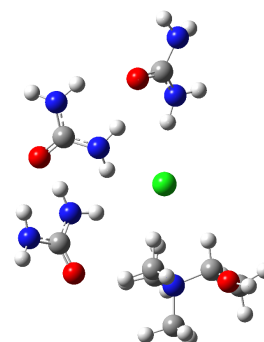
25_B3LYP (30.92)



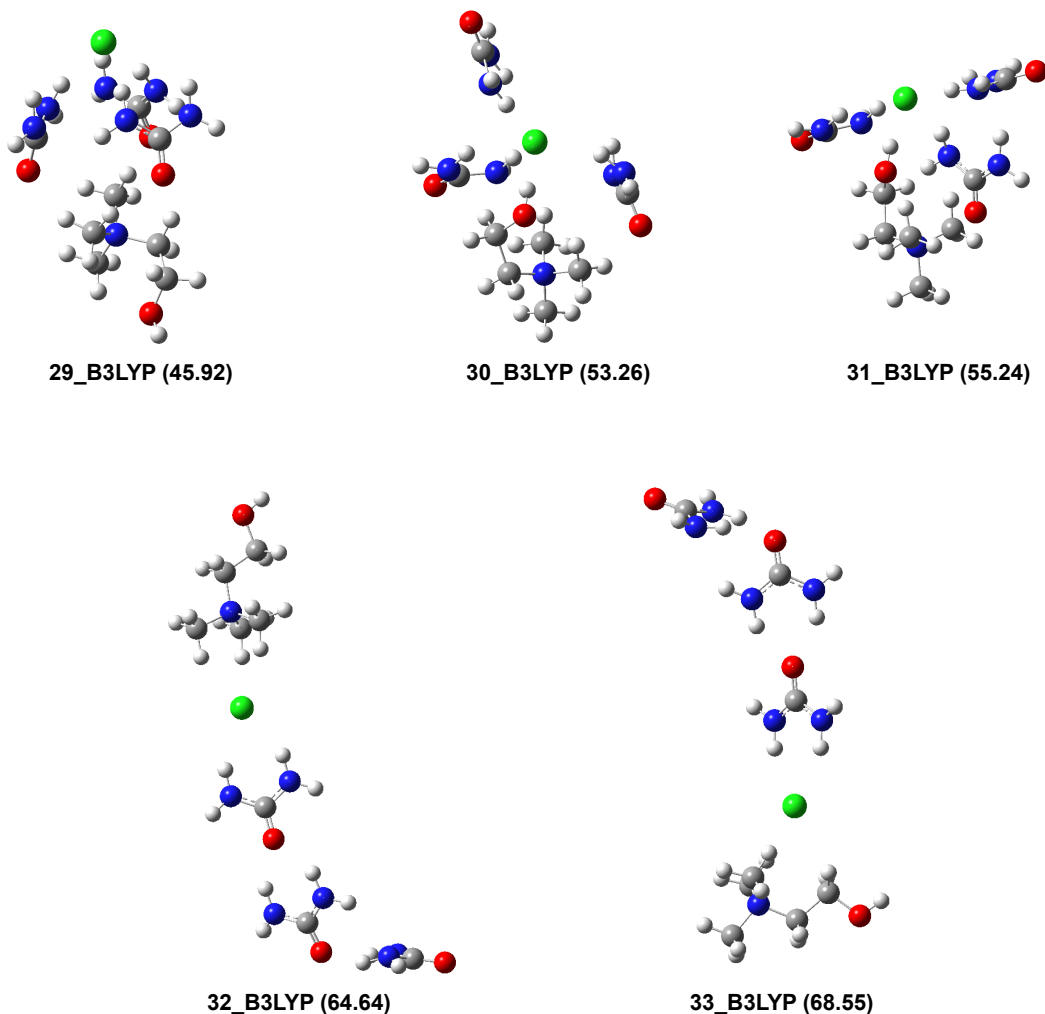
26_B3LYP (35.79)



27_B3LYP (41.24)



28_B3LYP (41.97)

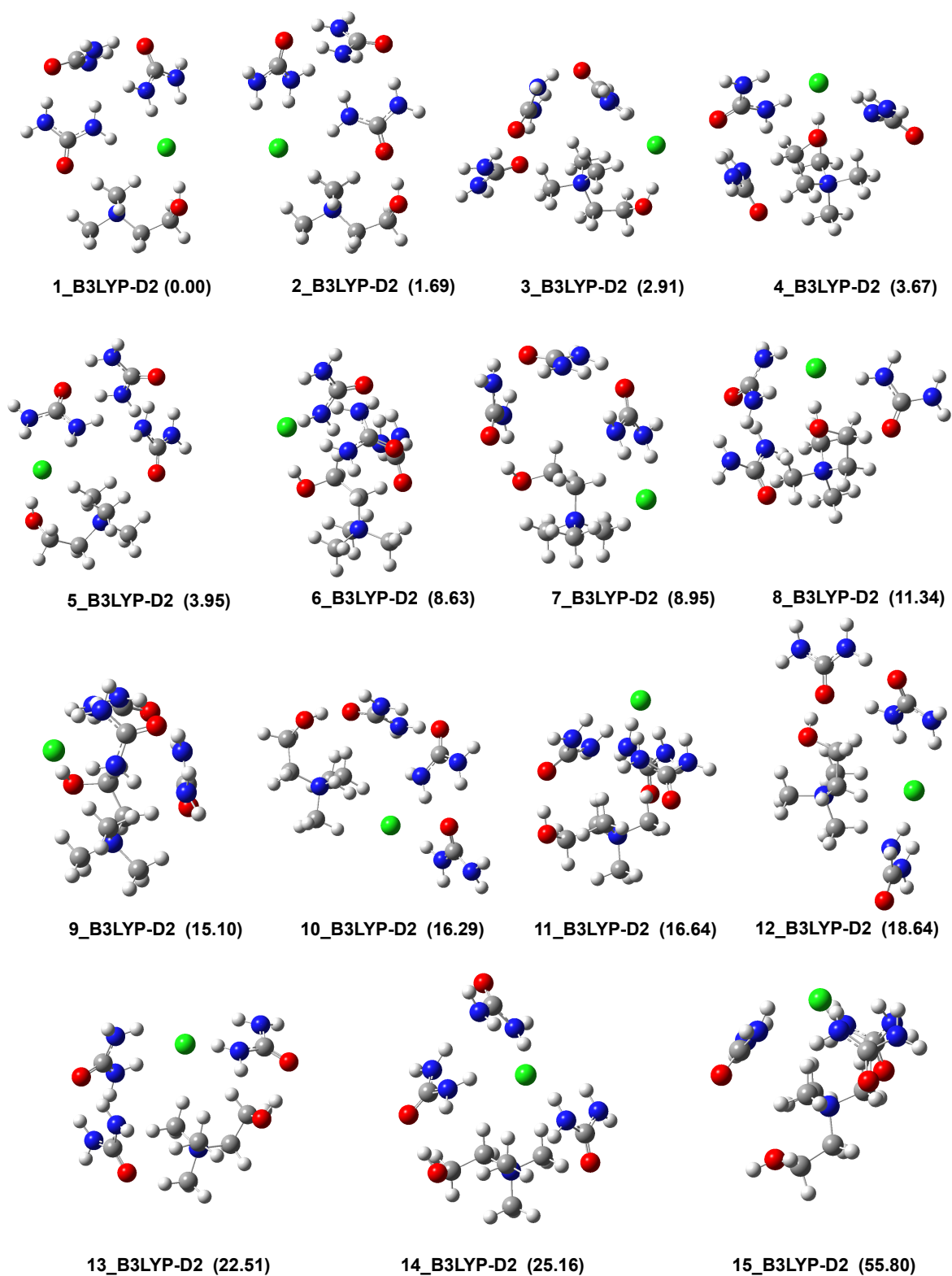


B3LYP-D2/6-311++G(d,p)

Table A. 18. Absolute and relative energies of the B3LYP-D2 /6-311++G(d,p) 1:3 clusters with, and without, zero point energy corrections. * Indicates significant change in B3LYP geometry upon optimisation at the B3LYP-D2 level. † Indicates structure first optimised at the B3LYP-D2 level and then re-optimised at the B3LYP level.

B3LYP-D2 Cluster	Parent B3LYP Cluster	E /au	ΔE_{rel} /kJ mol ⁻¹	E+ZPE /au	ΔE_{rel} (with ZPE correction) /kJ mol ⁻¹
1_B3LYP-D2	1_B3LYP	-1465.440194	0.000	-1465.044929	0.000
2_B3LYP-D2 [†]	4_B3LYP	-1465.439843	0.923	-1465.044285	1.692
3_B3LYP-D2	5_B3LYP	-1465.438651	4.052	-1465.043821	2.910
4_B3LYP-D2	6_B3LYP	-1465.43722	7.8103	-1465.043531	3.673
5_B3LYP-D2	3_B3LYP	-1465.438417	4.667	-1465.043425	3.951
6_B3LYP-D2 [†]	25_B3LYP	-1465.437472	7.147	-1465.041643	8.627
7_B3LYP-D2	2_B3LYP	-1465.436447	9.838	-1465.041521	8.948
8_B3LYP-D2	23_B3LYP *	-1465.434476	15.014	-1465.040612	11.336
9_B3LYP-D2	30_B3LYP *	-1465.435577	12.123	-1465.039179	15.098
10_B3LYP-D2	4_B3LYP	-1465.432561	20.042	-1465.038725	16.290
11_B3LYP-D2 [†]	18_B3LYP	-1465.434454	15.072	-1465.038593	16.637
12_B3LYP-D2	8_B3LYP	-1465.431911	21.749	-1465.03783	18.640
13_B3LYP-D2	15_B3LYP	-1465.431098	23.883	-1465.036357	22.508
14_B3LYP-D2 [†]	22_B3LYP	-1465.430012	26.73	-1465.035347	25.157
15_B3LYP-D2 [†]	28_B3LYP	-1465.418493	56.978	-1465.023675	55.804

Figure A. 9. 1:3 Clusters optimised at the B3LYP-D2/6-311++G(d,p) level. Relative energies (kJ mol^{-1}) are ZPE corrected.



B3LYP-D2 Clusters: Population analysis

Total charge transfer from chloride

Table A. 19. Charge on the chloride centre, and charge transfer (CT) from chloride, determined using NBO and CHELPG (at B3LYP/6-311+G(d,p) for selected clusters optimised at B3LYP-D2/6-311++G(d,p)

Cluster	q Cl (NBO) / e	CT (NBO) / e	q Cl (CHELPG) / e	CT (CHELPG) / e
1:1_A	-0.885	0.115	-0.789	0.211
1:1_B	-0.866	0.134	-0.775	0.225
1:1_C	-0.855	0.145	-0.751	0.249
1:1_D	-0.840	0.160	-0.744	0.256
1:1_E	-0.889	0.111	-0.762	0.238
1:1_F	-0.884	0.116	-0.770	0.230
1:2_A	-0.860	0.140	-0.740	0.260
1:2_B	-0.870	0.130	-0.776	0.224
1:2_C	-0.868	0.133	-0.776	0.224
1:2_D	-0.891	0.109	-0.796	0.204
1:2_E	-0.887	0.113	-0.765	0.235
1:3_A	-0.878	0.122	-0.773	0.227
1:3_B	-0.895	0.105	-0.801	0.199
1:3_C	-0.858	0.142	-0.755	0.245
1:3_D	-0.859	0.141	-0.776	0.224
1:3_E	-0.840	0.160	-0.750	0.250
1:3_F	-0.895	0.105	-0.804	0.196
1:3_G	-0.890	0.110	-0.807	0.193
1:3_H	-0.895	0.105	-0.831	0.169

Charge on urea molecules

Table A. 20. Sum of charge (NBO) on the urea molecules within selected B3LYP-D2 clusters.

Cluster	Charge on Urea (NBO) / e		
	Urea 1	Urea 2	Urea 3
1:1_A	-0.008	-	-
1:1_B	-0.032	-	-
1:1_C	-0.019	-	-
1:1_D	-0.014	-	-
1:1_E	-0.037	-	-
1:1_F	-0.040	-	-
1:2_A	-0.017	-0.014	-
1:2_B	-0.032	0.034	-
1:2_C	0.003	-0.025	-
1:2_D	0.008	-0.024	-
1:2_E	-0.023	-0.027	-
1:3_A	-0.002	-0.025	0.009
1:3_B	-0.007	-0.012	-0.034
1:3_C	-0.022	0.004	-0.015
1:3_D	-0.005	-0.014	-0.016
1:3_E	-0.025	-0.026	-0.034
1:3_F	0.014	-0.012	-0.023
1:3_G	-0.012	-0.010	0.004
1:3_H	-0.018	-0.004	-0.014

Comparing and Contrasting Aprotic and Protic Imidazolium Ionic Liquids

QM: Isolated ions

Conformational analysis of the $[\text{C}_4\text{Him}]^+$ cation

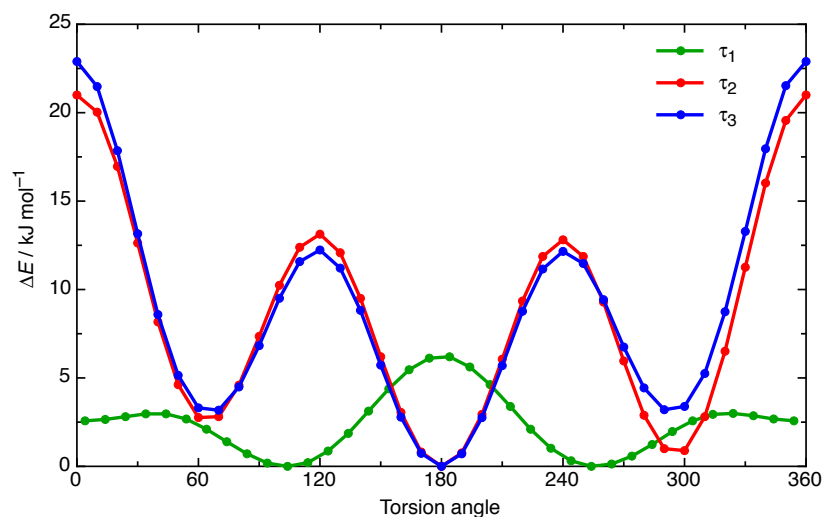


Figure A. 10. Energy profile for rotation about the torsion angles τ_1 , τ_2 and τ_3 at the B3LYP/6-311+G(d,p) level.

Table A. 21. Electronic and relative energies of the conformations of $[\text{C}_4\text{Him}]^+$ at the B3LYP/6-311+G(d,p) level with, and without, ZPE corrections.

Conformer	E /au	ΔE_{rel} / kJ mol ⁻¹	$E+\text{ZPE}$ /au	ΔE_{rel} (with ZPE correction) /kJ mol ⁻¹
a	-383.962210	0.000	-383.764636	0.000
b	-383.961941	0.707	-383.764256	0.999
c	-383.961237	2.555	-383.763562	2.820
d	-383.961239	2.549	-383.763541	2.875
e	-383.961049	3.048	-383.763363	3.342
f	-383.961035	3.086	-383.763363	3.343
g	-383.960684	4.008	-383.762919	4.510
h	-383.960025	5.738	-383.762256	6.250
i	-383.959970	5.882	-383.762192	6.418
j	-383.958403	9.996	-383.760637	10.500
k	-383.957748	11.716	-383.759961	12.275

Table A. 22. Electronic and relative energies of the conformations of $[\text{C}_4\text{Him}]^+$ at the MP2(full)/6-311+G(d,p) level with, and without, ZPE corrections.

Conformer	E /au	ΔE_{rel} / kJ mol ⁻¹	$E+\text{ZPE}$ /au	ΔE_{rel} (with ZPE correction) /kJ mol ⁻¹
a	-382.972802	0.000	-382.772851	0.000
b	-382.974499	-4.453	-382.774367	-3.978
c (1 x imag. freq)			-382.771493	3.566
d	-382.973657	-2.243	-382.773552	-1.839
e	-382.972261	1.421	-382.772173	1.781
f	-382.972303	1.310	-382.772188	1.740
g	-382.974306	-3.948	-382.773959	-2.908
h	-382.973515	-1.871	-382.773179	-0.860
i (1 x imag. freq)	-382.970790	5.285	-382.770685	5.689
j	-382.972692	0.291	-382.772381	1.236
k	-382.971991	2.130	-382.771662	3.122

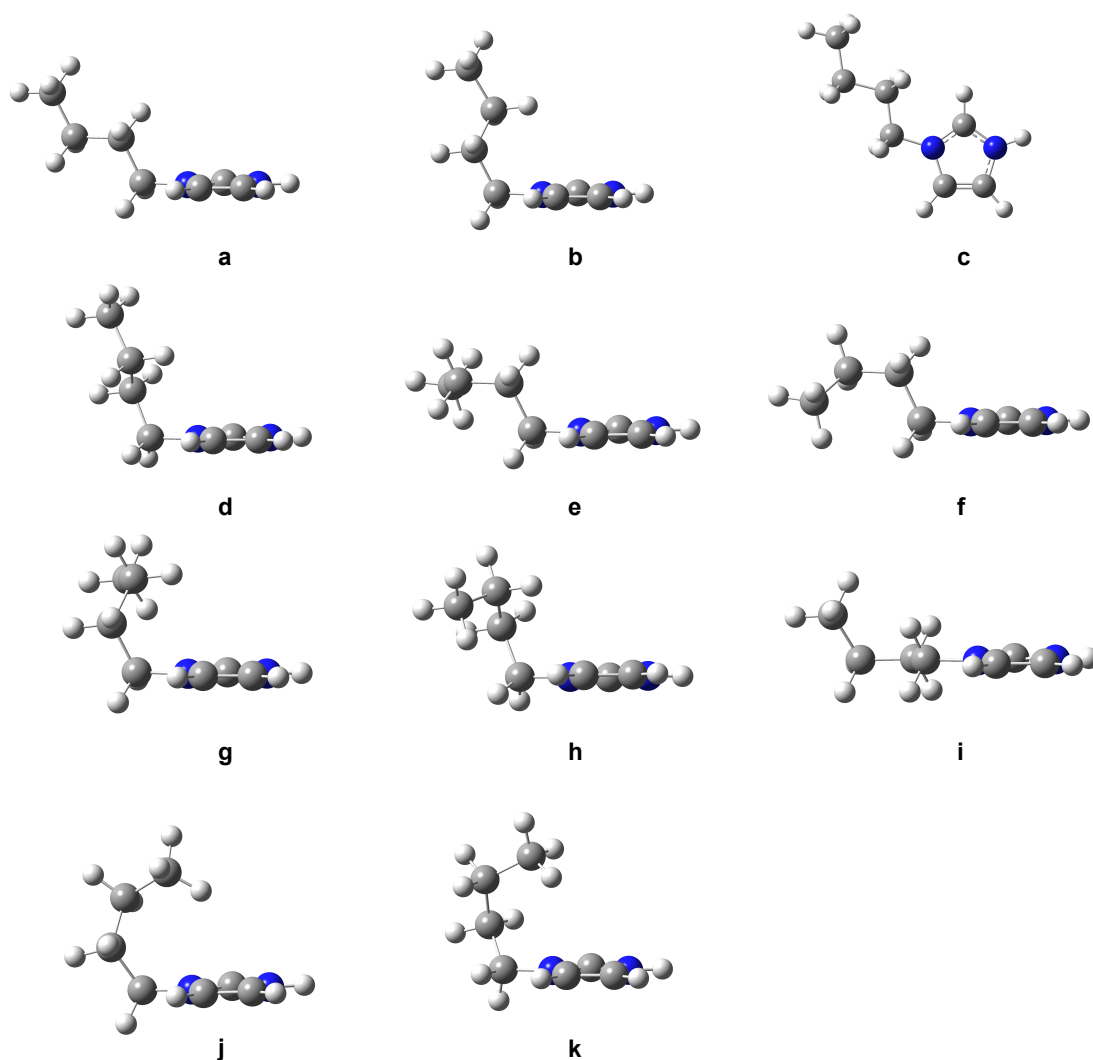


Figure A. 11. $[\text{C}_4\text{Him}]^+$ conformers optimised at the B3LYP/6-311+G(d,p) level.

Table A. 23. Torsion angles within the B3LYP and MP2 [C₄Him]⁺ conformers.

Conformer	B3LYP			MP2		
	τ_1	τ_2	τ_3	τ_1	τ_2	τ_3
a	-104.1	179.8	179.9	-110.2	178.3	179.5
b	-107.4	64.3	177.0	-109.4	58.0	175.3
c	-0.5	-180.0	-179.9	-1.6	-179.7	-179.9
d	-83.4	-64.7	-176.5	-109.4	-58.1	-175.3
e	-104.0	-178.7	-65.7	-108.4	-178.6	-62.6
f	-102.6	178.7	66.2	-109.0	175.3	62.4
g	-108.0	64.3	65.2	-68.4	-58.5	86.1
h	-84.1	-65.1	-64.9	-111.9	56.7	61.5
i	3.9	177.9	65.7	108.4	178.6	62.6
j	-116.1	69.2	-79.9	-106.8	60.2	-86.4
k	-60.1	-70.2	76.1	-67.7	-56.9	-62.1

Population analysis of the [C₄Him]⁺ cation

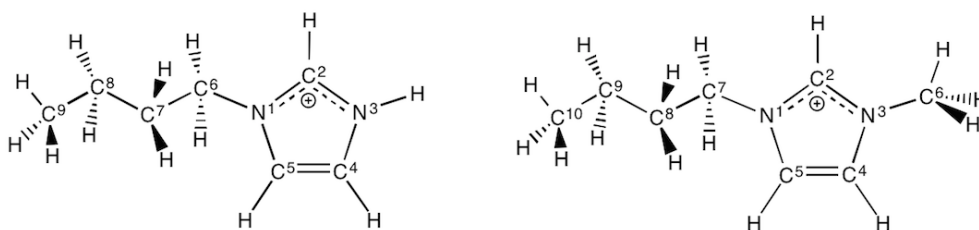


Figure A. 12. Numbering scheme for the [C₄Him]⁺ and [C₄C₁im]⁺ cations.

Table A. 24. Computed NBO partial charges at the B3LYP/6-311+G(d,p).

[C ₄ Him] ⁺		[C ₄ C ₁ im] ⁺	
Atom	q / e	Atom	q / e
N ¹	-0.341	N ¹	-0.346
C ²	0.289	C ²	0.294
C ² -H	0.246	C ² -H	0.240
N ³	-0.488	N ³	-0.350
N-H	0.451	C ⁴	-0.009
C ⁴	-0.012	C ⁴ -H	0.250
C ⁴ -H	0.256	C ⁵	-0.005
C ⁵	-0.009	C ⁵ -H	0.250
C ⁵ -H	0.253	C ⁶	
C ⁶	-0.090	C ⁶ -H	-0.164
C ⁶ -H	0.190/0.198	C ⁷	0.217/0.223
C ⁷	-0.346	C ⁷ -H	-0.395
C ⁷ -H	0.180/0.178	C ⁸	0.205/0.205
C ⁸	-0.337	C ⁸ -H	-0.388
C ⁸ -H	0.171/0.173	C ⁹	0.198/0.199
C ⁹	-0.502	C ⁹ -H	-0.574
C ⁹ -H	0.176/0.194/0.177	C ¹⁰	0.201/0.219/0.202
		C ¹⁰ -H	

QM: Ion Pairs

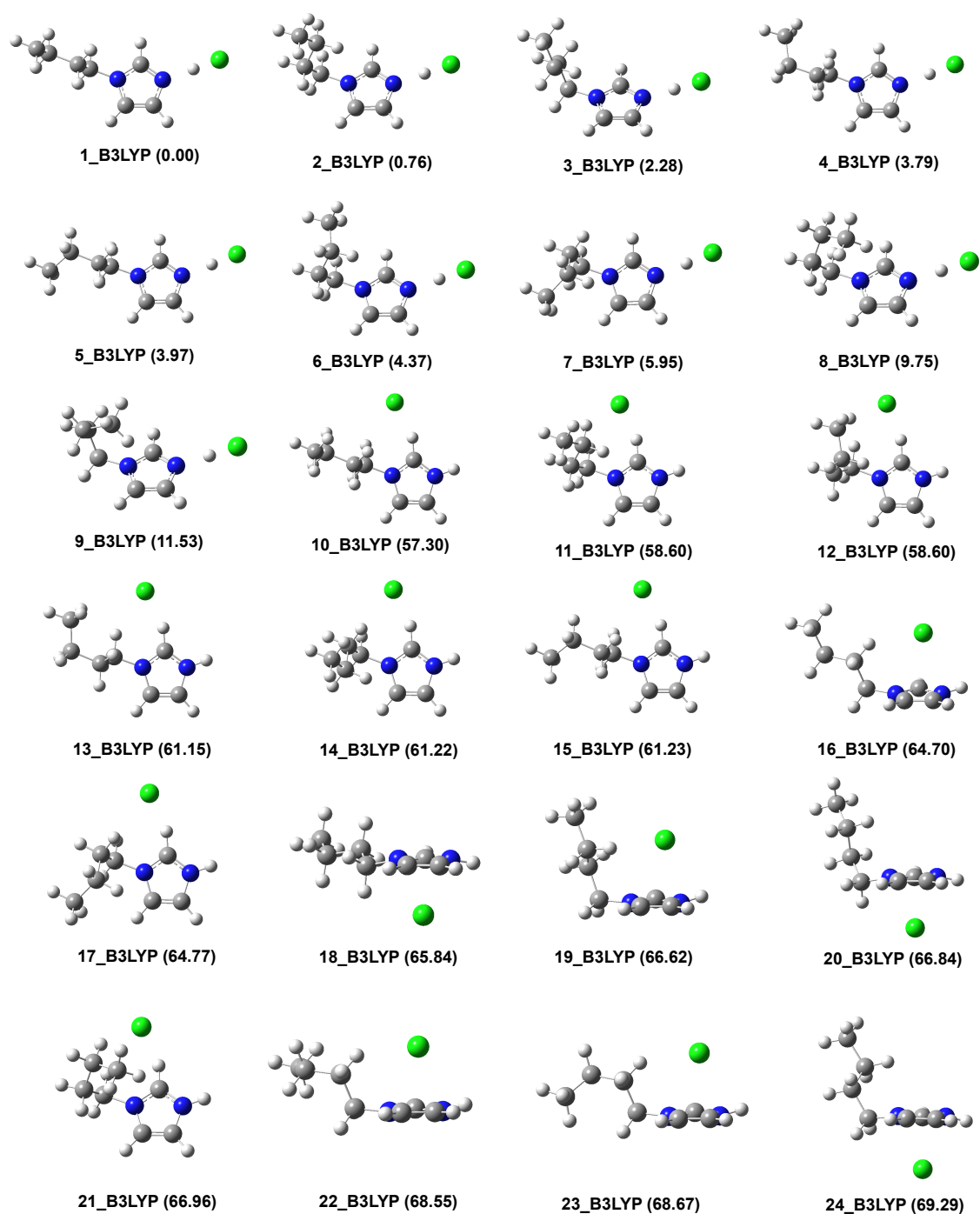
[C₄Him]Cl

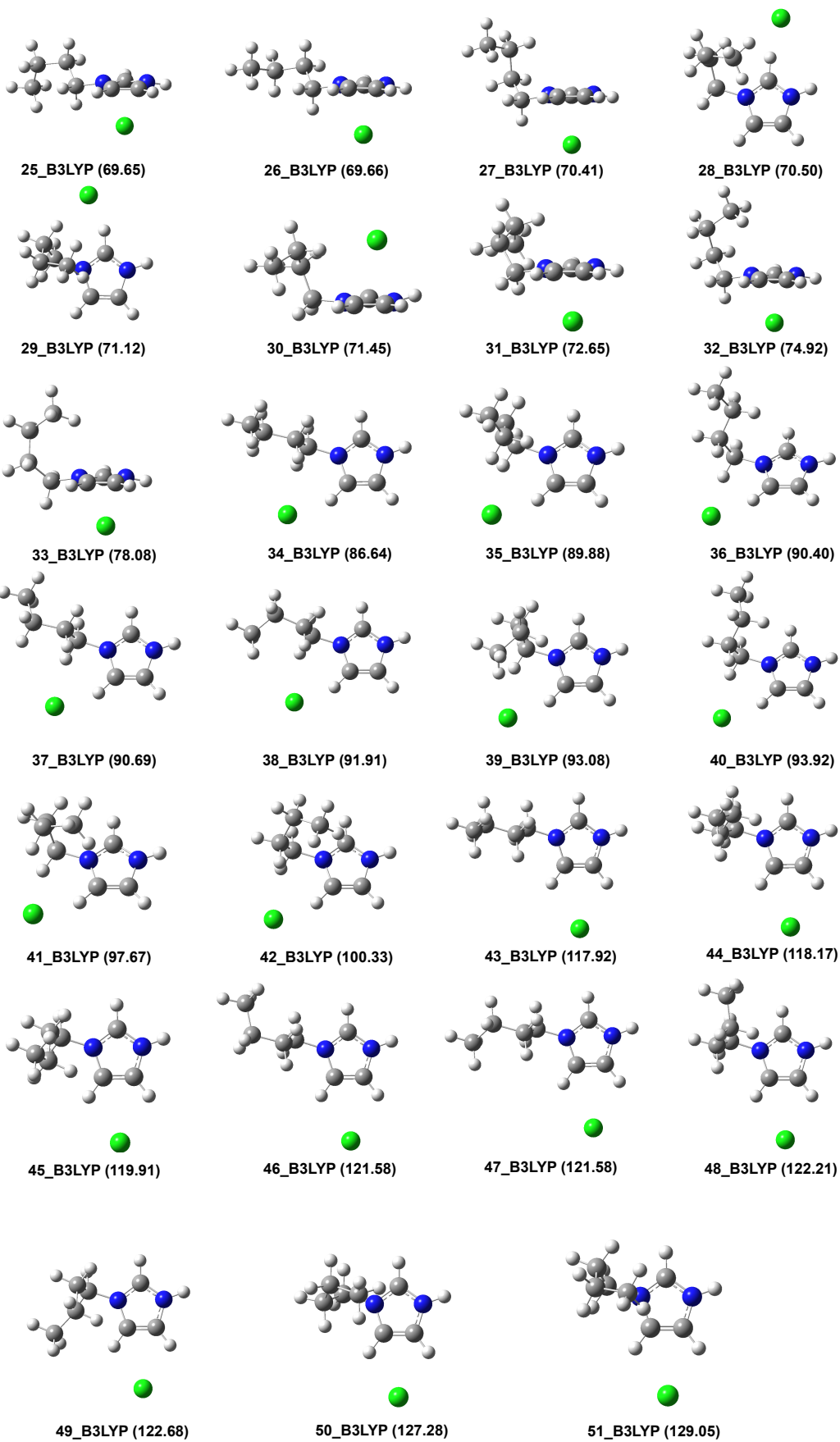
B3LYP/6-311+G(d,p)

Table A.25. Electronic and relative energies of the B3LYP/6-311+G(d,p) [C₄Him]Cl ion pairs with, and without, zero point energy corrections.

Ion Pair	<i>E</i> / au	ΔE_{rel} / kJ mol ⁻¹	<i>E</i> +ZPE / au	ΔE_{rel} (with ZPE
				correction) /kJ mol ⁻¹
1_B3LYP	-844.429855	0.000	-844.237078	0.000
2_B3LYP	-844.429745	0.288	-844.236789	0.758
3_B3LYP	-844.429126	1.914	-844.236211	2.276
4_B3LYP	-844.428536	3.463	-844.235633	3.794
5_B3LYP	-844.428475	3.622	-844.235578	3.937
6_B3LYP	-844.428496	3.566	-844.235412	4.372
7_B3LYP	-844.427844	5.279	-844.234810	5.954
8_B3LYP	-844.426409	9.047	-844.233363	9.753
9_B3LYP	-844.425719	10.859	-844.232686	11.531
10_B3LYP	-844.411957	46.990	-844.215255	57.295
11_B3LYP	-844.411635	47.836	-844.214758	58.601
12_B3LYP	-844.410935	49.673	-844.213891	60.876
13_B3LYP	-844.410640	50.449	-844.213789	61.145
14_B3LYP	-844.410500	50.817	-844.213762	61.216
15_B3LYP	-844.410577	50.614	-844.213755	61.234
16_B3LYP	-844.410127	51.795	-844.212435	64.699
17_B3LYP	-844.409239	54.128	-844.212410	64.766
18_B3LYP	-844.409648	53.052	-844.212002	65.835
19_B3LYP	-844.409416	53.661	-844.211704	66.618
20_B3LYP	-844.409275	54.032	-844.211621	66.836
21_B3LYP	-844.408549	55.937	-844.211575	66.956
22_B3LYP	-844.408713	55.509	-844.210969	68.550
23_B3LYP	-844.408676	55.605	-844.210923	68.669
24_B3LYP	-844.408296	56.601	-844.210688	69.285
25_B3LYP	-844.408231	56.774	-844.210551	69.647
26_B3LYP	-844.408289	56.621	-844.210547	69.657
27_B3LYP	-844.408076	57.181	-844.210260	70.411
28_B3LYP	-844.407164	59.574	-844.210225	70.501
29_B3LYP	-844.406794	60.547	-844.209990	71.120
30_B3LYP	-844.407685	58.207	-844.209849	71.489
31_B3LYP	-844.407321	59.163	-844.209409	72.645
32_B3LYP	-844.406306	61.828	-844.208543	74.919
33_B3LYP	-844.405022	65.199	-844.207337	78.084
34_B3LYP	-844.401153	75.357	-844.204079	86.638
35_B3LYP	-844.400039	78.282	-844.202843	89.884
36_B3LYP	-844.399730	79.093	-844.202647	90.398
37_B3LYP	-844.399696	79.183	-844.202536	90.690
38_B3LYP	-844.399169	80.566	-844.202072	91.909
39_B3LYP	-844.398956	81.124	-844.201624	93.083
40_B3LYP	-844.398461	82.424	-844.201304	93.924
41_B3LYP	-844.397160	85.840	-844.199877	97.671
42_B3LYP	-844.396031	88.804	-844.198865	100.327
43_B3LYP	-844.389168	106.822	-844.192163	117.923
44_B3LYP	-844.389225	106.673	-844.192069	118.170
45_B3LYP	-844.388528	108.505	-844.191407	119.910
46_B3LYP	-844.387870	110.230	-844.190771	121.577
47_B3LYP	-844.387856	110.269	-844.190770	121.582
48_B3LYP	-844.387789	110.443	-844.190532	122.205
49_B3LYP	-844.387616	110.897	-844.190351	122.680
50_B3LYP	-844.385863	115.500	-844.188598	127.283
51_B3LYP	-844.385051	117.633	-844.187924	129.054

Figure A. 13. [C₄Him]Cl ion pairs optimised at the B3LYP/6-311+G(d,p) level. Relative energies (kJ mol⁻¹) are ZPE corrected.

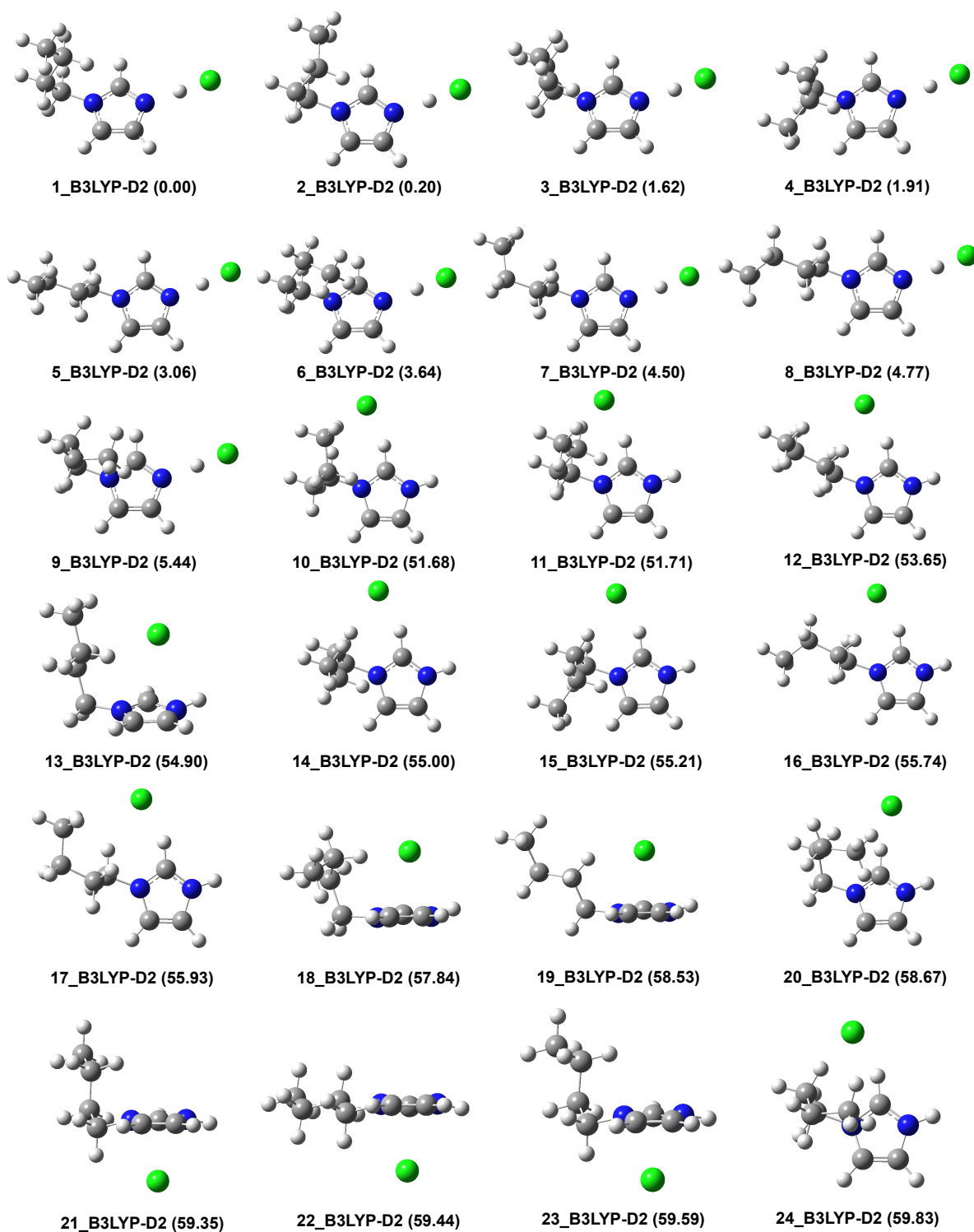


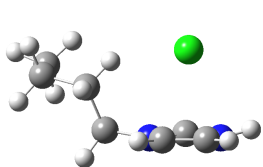


B3LYP-D2/6-311++G(d,p)**Table A. 26.** Electronic and relative energies of the B3LYP-D2/6-311++G(d,p) [C₄Him]Cl ion pairs with, and without, zero point energy corrections.

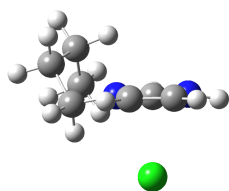
Ion Pair	E / au	ΔE_{rel} / kJ mol ⁻¹	E +ZPE /au	ΔE_{rel} (with ZPE correction) /kJ mol ⁻¹
1_B3LYP-D2	-844.454827	0.000	-844.262753	0.000
2_B3LYP-D2	-844.455050	-0.586	-844.262675	0.204
3_B3LYP-D2	-844.454173	1.715	-844.262134	1.623
4_B3LYP-D2	-844.454411	1.091	-844.262026	1.907
5_B3LYP-D2	-844.453459	3.592	-844.261589	3.056
6_B3LYP-D2	-844.453869	2.515	-844.261365	3.644
7_B3LYP-D2	-844.453088	4.564	-844.261038	4.501
8_B3LYP-D2	-844.452979	4.850	-844.260935	4.771
9_B3LYP-D2	-844.453188	4.303	-844.260682	5.437
10_B3LYP-D2	-844.439465	40.332	-844.243069	51.680
11_B3LYP-D2	-844.439266	40.855	-844.243059	51.706
12_B3LYP-D2	-844.438463	42.962	-844.242319	53.647
13_B3LYP-D2	-844.439047	41.431	-844.241842	54.902
14_B3LYP-D2	-844.437909	44.418	-844.241804	55.001
15_B3LYP-D2	-844.438185	43.692	-844.241723	55.213
16_B3LYP-D2	-844.437773	44.775	-844.241524	55.736
17_B3LYP-D2	-844.437611	45.200	-844.241451	55.928
18_B3LYP-D2	-844.438200	43.653	-844.240721	57.844
19_B3LYP-D2	-844.437400	45.754	-844.240461	58.527
20_B3LYP-D2	-844.437082	46.588	-844.240405	58.673
21_B3LYP-D2	-844.437321	45.961	-844.240147	59.352
22_B3LYP-D2	-844.437243	46.167	-844.240112	59.444
23_B3LYP-D2	-844.437434	45.664	-844.240056	59.590
24_B3LYP-D2	-844.436497	48.125	-844.239965	59.829
25_B3LYP-D2	-844.437107	46.522	-844.239927	59.928
26_B3LYP-D2	-844.437886	44.477	-844.239914	59.963
27_B3LYP-D2	-844.436711	47.562	-844.239623	60.726
28_B3LYP-D2	-844.436868	47.151	-844.239527	60.979
29_B3LYP-D2	-844.436652	47.716	-844.239311	61.545
30_B3LYP-D2	-844.435996	49.440	-844.238836	62.793
31_B3LYP-D2	-844.435902	49.686	-844.238597	63.420
32_B3LYP-D2	-844.434351	53.759	-844.237130	67.273
33_B3LYP-D2	-844.428511	69.091	-844.232016	80.699
34_B3LYP-D2	-844.428002	70.428	-844.231553	81.915
35_B3LYP-D2	-844.427599	71.485	-844.231213	82.807
36_B3LYP-D2	-844.427745	71.103	-844.231187	82.876
37_B3LYP-D2	-844.427819	70.908	-844.231186	82.878
38_B3LYP-D2	-844.427845	70.840	-844.231162	82.941
39_B3LYP-D2	-844.427775	71.025	-844.231152	82.969
40_B3LYP-D2	-844.427317	72.226	-844.230508	84.658
41_B3LYP-D2	-844.426321	74.843	-844.229488	87.338
42_B3LYP-D2	-844.414180	106.718	-844.218009	117.474
43_B3LYP-D2	-844.413777	107.775	-844.217415	119.033
44_B3LYP-D2	-844.413794	107.730	-844.217399	119.075

Figure A. 14. $[\text{C}_4\text{Him}]\text{Cl}$ ion pairs optimised at the B3LYP-D2/6-311++G(d,p) level. Relative energies (kJ mol^{-1}) are ZPE corrected.

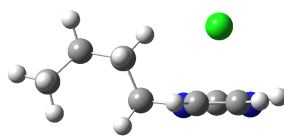




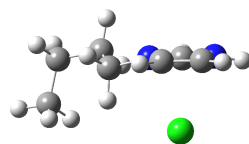
25_B3LYP-D2 (58.67)



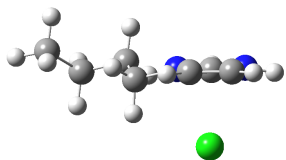
26_B3LYP-D2 (59.96)



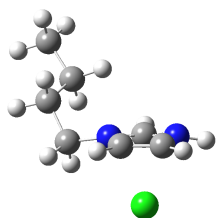
27_B3LYP-D2 (60.73)



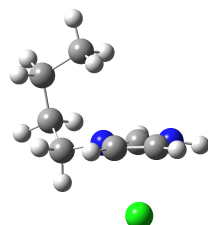
28_B3LYP-D2 (60.98)



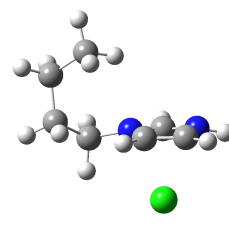
29_B3LYP-D2 (61.55)



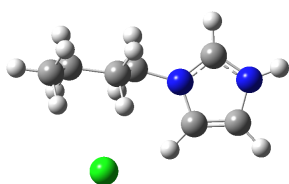
30_B3LYP-D2 (62.79)



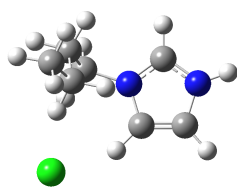
31_B3LYP-D2 (63.42)



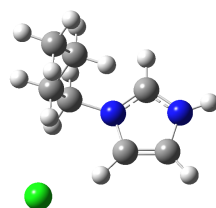
32_B3LYP-D2 (67.27)



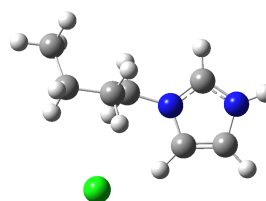
33_B3LYP-D2 (80.70)



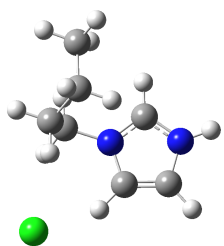
34_B3LYP-D2 (81.92)



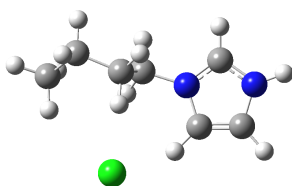
35_B3LYP-D2 (82.81)



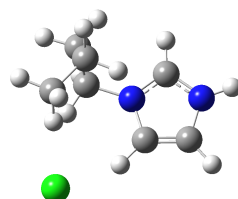
36_B3LYP-D2 (82.88)



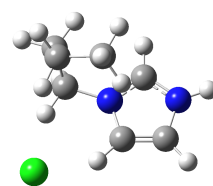
37_B3LYP-D2 (82.88)



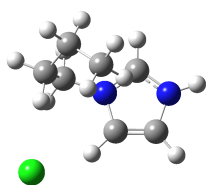
38_B3LYP-D2 (82.94)



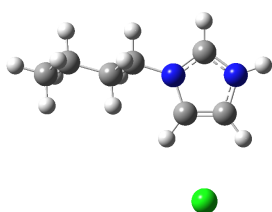
39_B3LYP-D2 (82.97)



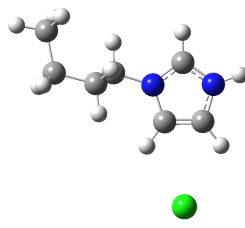
40_B3LYP-D2 (84.66)



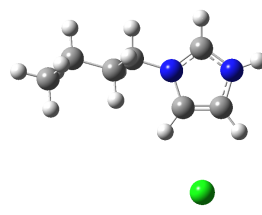
41_B3LYP-D2 (87.34)



42_B3LYP-D2 (117.45)



43_B3LYP-D2 (119.03)



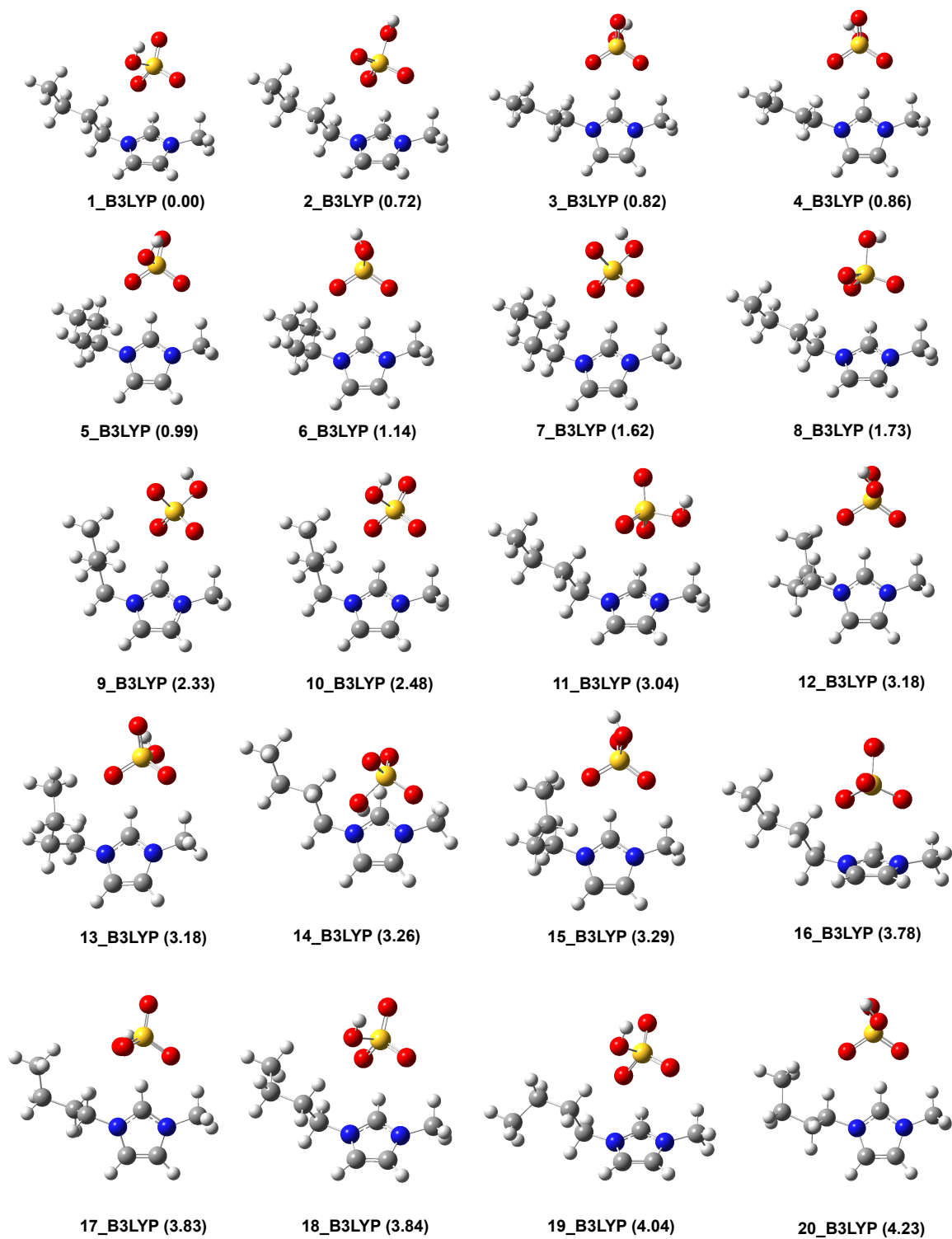
44_B3LYP-D2 (119.08)

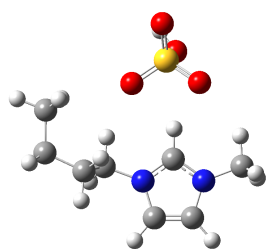
[C₄C₁im][HSO₄]**B3LYP/6-311+G(d,p)****Table A. 27.** Electronic and relative energies of the B3LYP /6-311+G(d,p) [C₄C₁im][HSO₄] ion pairs with, and without, zero point energy corrections.

Ion Pair	<i>E</i> / au	ΔE_{rel} / kJ mol ⁻¹	<i>E</i> +ZPE /au	ΔE_{rel} (with ZPE correction) /kJ mol ⁻¹
1_B3LYP	-1123.260594	0.000	-1123.007838	0.000
2_B3LYP	-1123.260325	0.707	-1123.007564	0.720
3_B3LYP	-1123.259850	1.953	-1123.007525	0.822
4_B3LYP	-1123.259836	1.992	-1123.007513	0.855
5_B3LYP	-1123.260021	1.504	-1123.007460	0.992
6_B3LYP	-1123.259781	2.136	-1123.007403	1.143
7_B3LYP	-1123.259853	1.945	-1123.007220	1.622
8_B3LYP	-1123.260029	1.484	-1123.007179	1.731
9_B3LYP	-1123.259883	1.867	-1123.006949	2.334
10_B3LYP	-1123.259764	2.181	-1123.006896	2.475
11_B3LYP	-1123.259436	3.042	-1123.006679	3.044
12_B3LYP	-1123.259341	3.291	-1123.006629	3.176
13_B3LYP	-1123.259341	3.291	-1123.006626	3.183
14_B3LYP	-1123.259456	2.988	-1123.006597	3.258
15_B3LYP	-1123.259189	3.690	-1123.006586	3.288
16_B3LYP	-1123.259227	3.591	-1123.006398	3.782
17_B3LYP	-1123.259269	3.480	-1123.006380	3.829
18_B3LYP	-1123.259269	3.480	-1123.006378	3.835
19_B3LYP	-1123.259115	3.884	-1123.006299	4.041
20_B3LYP	-1123.258737	4.877	-1123.006227	4.231
21_B3LYP	-1123.258738	4.873	-1123.006216	4.259
22_B3LYP	-1123.258902	4.444	-1123.006144	4.449
23_B3LYP	-1123.258508	5.477	-1123.006131	4.482
24_B3LYP	-1123.258492	5.519	-1123.006040	4.721
25_B3LYP	-1123.258547	5.376	-1123.005975	4.893
26_B3LYP	-1123.258405	5.749	-1123.005893	5.108
27_B3LYP	-1123.258469	5.579	-1123.005525	6.072
28_B3LYP	-1123.257924	7.010	-1123.005318	6.616
29_B3LYP	-1123.257901	7.071	-1123.005282	6.711
30_B3LYP	-1123.257860	7.180	-1123.005104	7.180
31_B3LYP	-1123.257102	9.169	-1123.004464	8.859
32_B3LYP	-1123.257456	8.239	-1123.004425	8.961
33_B3LYP	-1123.257089	9.204	-1123.004278	9.348
34_B3LYP	-1123.256630	10.407	-1123.004229	9.475
35_B3LYP	-1123.256700	10.225	-1123.004229	9.477
36_B3LYP	-1123.256896	9.711	-1123.004218	9.506
37_B3LYP	-1123.256815	9.923	-1123.004055	9.934
38_B3LYP	-1123.256901	9.697	-1123.004007	10.059
39_B3LYP	-1123.256691	10.247	-1123.003663	10.962
40_B3LYP	-1123.255583	13.157	-1123.002733	13.404
41_B3LYP	-1123.254955	14.806	-1123.002063	15.163
42_B3LYP	-1123.254825	15.146	-1123.001910	15.563
43_B3LYP	-1123.253402	18.883	-1123.000663	18.839
44_B3LYP	-1123.252376	21.578	-1122.999898	20.848
45_B3LYP	-1123.248044	32.950	-1122.995688	31.900
46_B3LYP	-1123.246609	36.718	-1122.994233	35.720
47_B3LYP	-1123.246274	37.60	-1122.994139	35.967
48_B3LYP	-1123.246141	37.947	-1122.993878	36.652
49_B3LYP	-1123.245798	38.847	-1122.993295	38.182
50_B3LYP	-1123.245431	39.811	-1122.992991	38.982
51_B3LYP	-1123.244657	41.842	-1122.992294	40.810
52_B3LYP	-1123.244527	42.185	-1122.992134	41.232
53_B3LYP	-1123.244706	41.714	-1122.992120	41.267
54_B3LYP	-1123.244052	43.433	-1122.991803	42.101
55_B3LYP	-1123.243948	43.704	-1122.991471	42.971
56_B3LYP	-1123.242979	46.248	-1122.991050	44.077
57_B3LYP	-1123.242952	46.319	-1122.990897	44.478
58_B3LYP	-1123.242721	46.925	-1122.990692	45.017

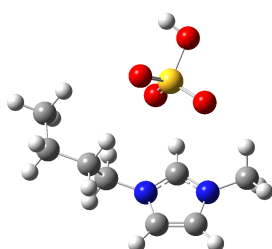
59_B3LYP	-1123.243109	45.907	-1122.990567	45.345
60_B3LYP	-1123.242532	47.423	-1122.990396	45.795
61_B3LYP	-1123.241660	49.712	-1122.990282	46.093
62_B3LYP	-1123.242287	48.064	-1122.990274	46.114
63_B3LYP	-1123.242414	47.732	-1122.990203	46.301
64_B3LYP	-1123.242414	47.732	-1122.990203	46.301
65_B3LYP	-1123.242223	48.234	-1122.989951	46.963
66_B3LYP	-1123.241675	49.673	-1122.989696	47.633
67_B3LYP	-1123.241559	49.977	-1122.989421	48.355
68_B3LYP	-1123.241806	49.330	-1122.989137	49.101
69_B3LYP	-1123.239854	54.452	-1122.987621	53.079
70_B3LYP	-1123.238840	57.115	-1122.986771	55.312

Figure A. 15. $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ ion pairs optimised at the B3LYP/6-311+G(d,p) level. Relative energies (kJ mol^{-1}) are ZPE corrected.

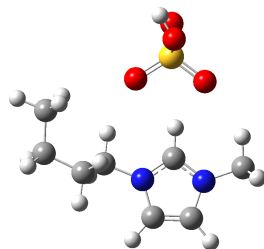




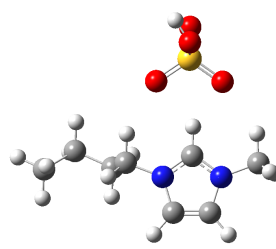
21_B3LYP (4.26)



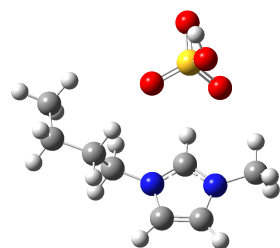
22_B3LYP (4.45)



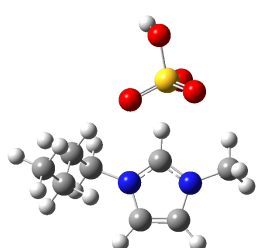
23_B3LYP (4.48)



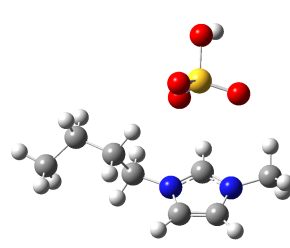
24_B3LYP (4.72)



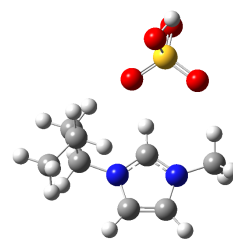
25_B3LYP (4.89)



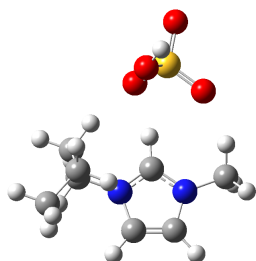
26_B3LYP (5.11)



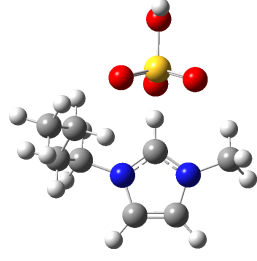
27_B3LYP (6.07)



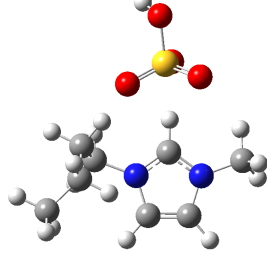
28_B3LYP (6.62)



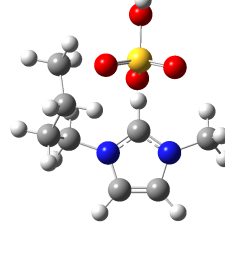
29_B3LYP (6.71)



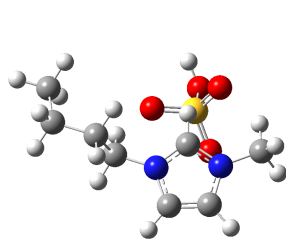
30_B3LYP (7.18)



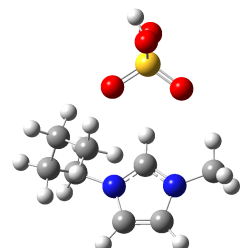
31_B3LYP (8.86)



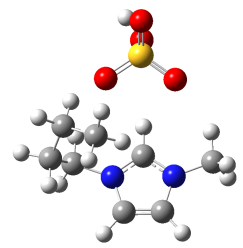
32_B3LYP (8.96)



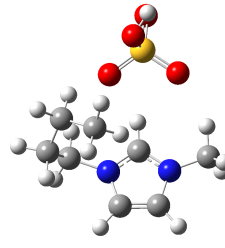
33_B3LYP (9.35)



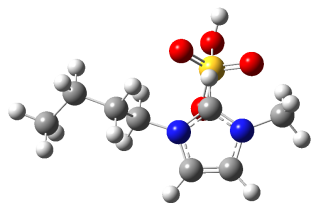
34_B3LYP (9.48)



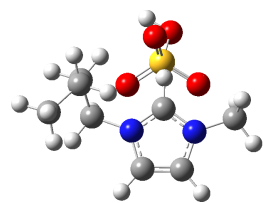
35_B3LYP (9.48)



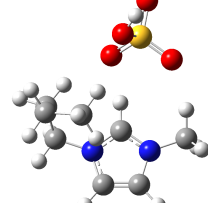
36_B3LYP (9.51)



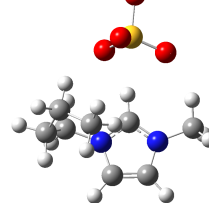
37_B3LYP (9.93)



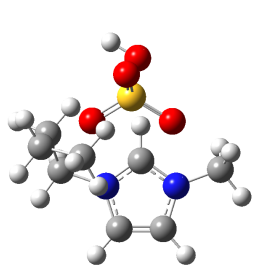
38_B3LYP (10.06)



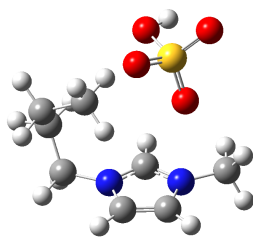
39_B3LYP (10.96)



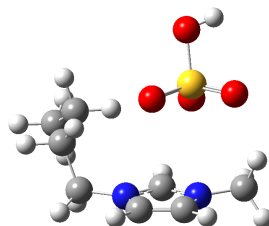
40_B3LYP (13.40)



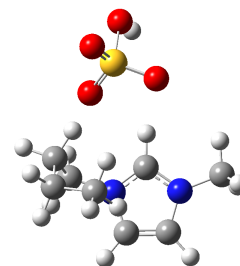
41_B3LYP (15.16)



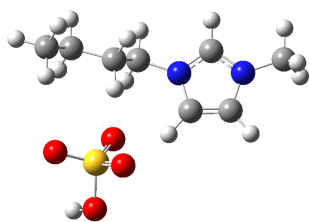
42_B3LYP (15.56)



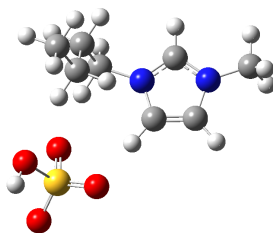
43_B3LYP (18.84)



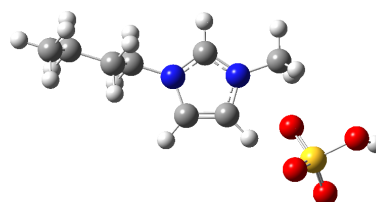
44_B3LYP (20.85)



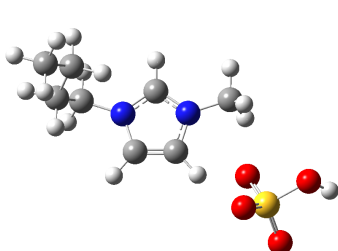
45_B3LYP (31.90)



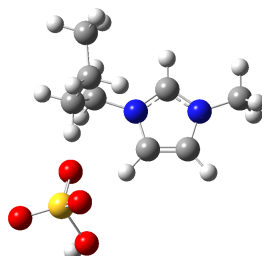
46_B3LYP (35.72)



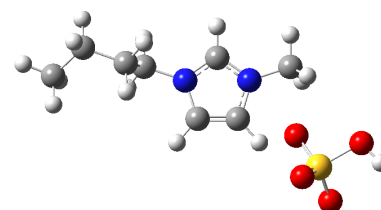
47_B3LYP (35.97)



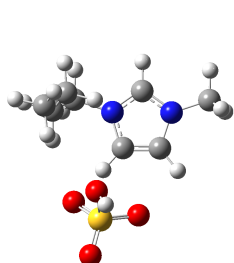
48_B3LYP (35.97)



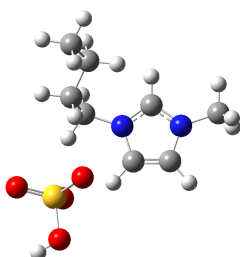
49_B3LYP (38.18)



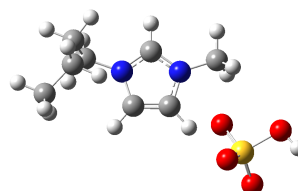
50_B3LYP (38.18)



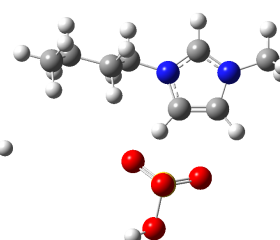
51_B3LYP (40.81)



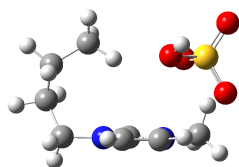
52_B3LYP (41.23)



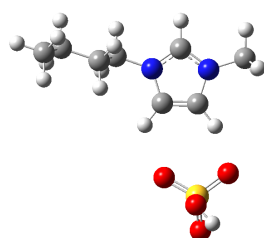
53_B3LYP (41.27)



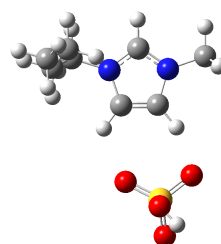
54_B3LYP (42.10)



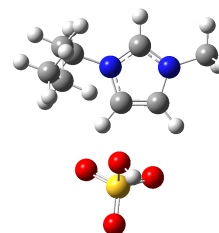
55_B3LYP (42.97)



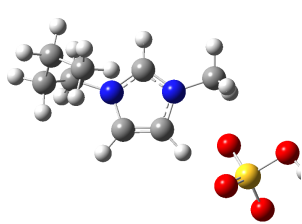
56_B3LYP (44.08)



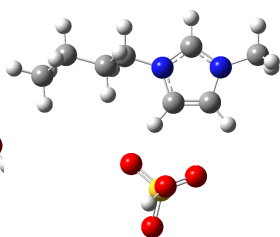
57_B3LYP (44.48)



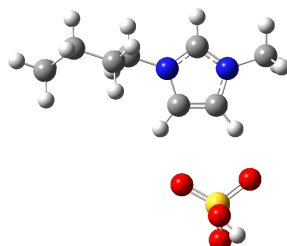
58_B3LYP (45.02)



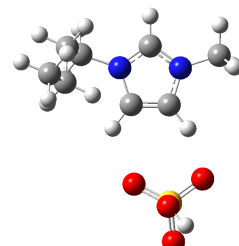
59_B3LYP (45.35)



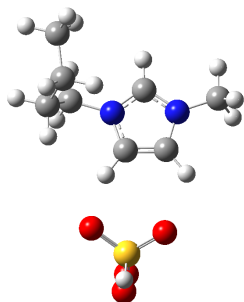
60_B3LYP (45.80)



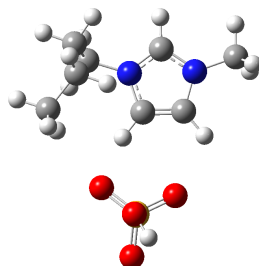
61_B3LYP (46.09)



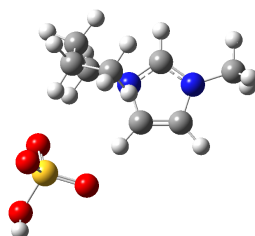
62_B3LYP (46.11)



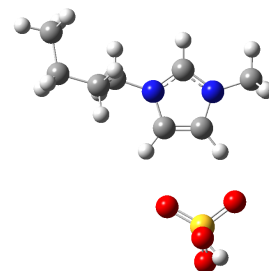
63_B3LYP (46.30)



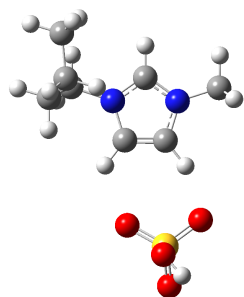
64_B3LYP (46.30)



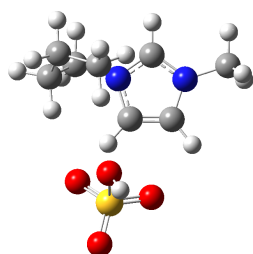
65_B3LYP (46.96)



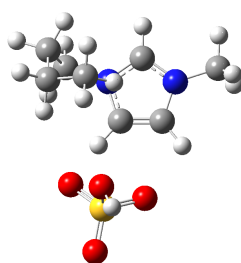
66_B3LYP (47.63)



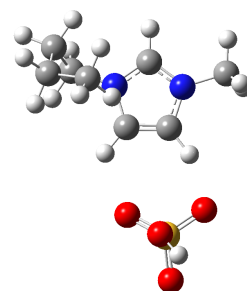
67_B3LYP (48.36)



68_B3LYP (49.10)



69_B3LYP (49.10)

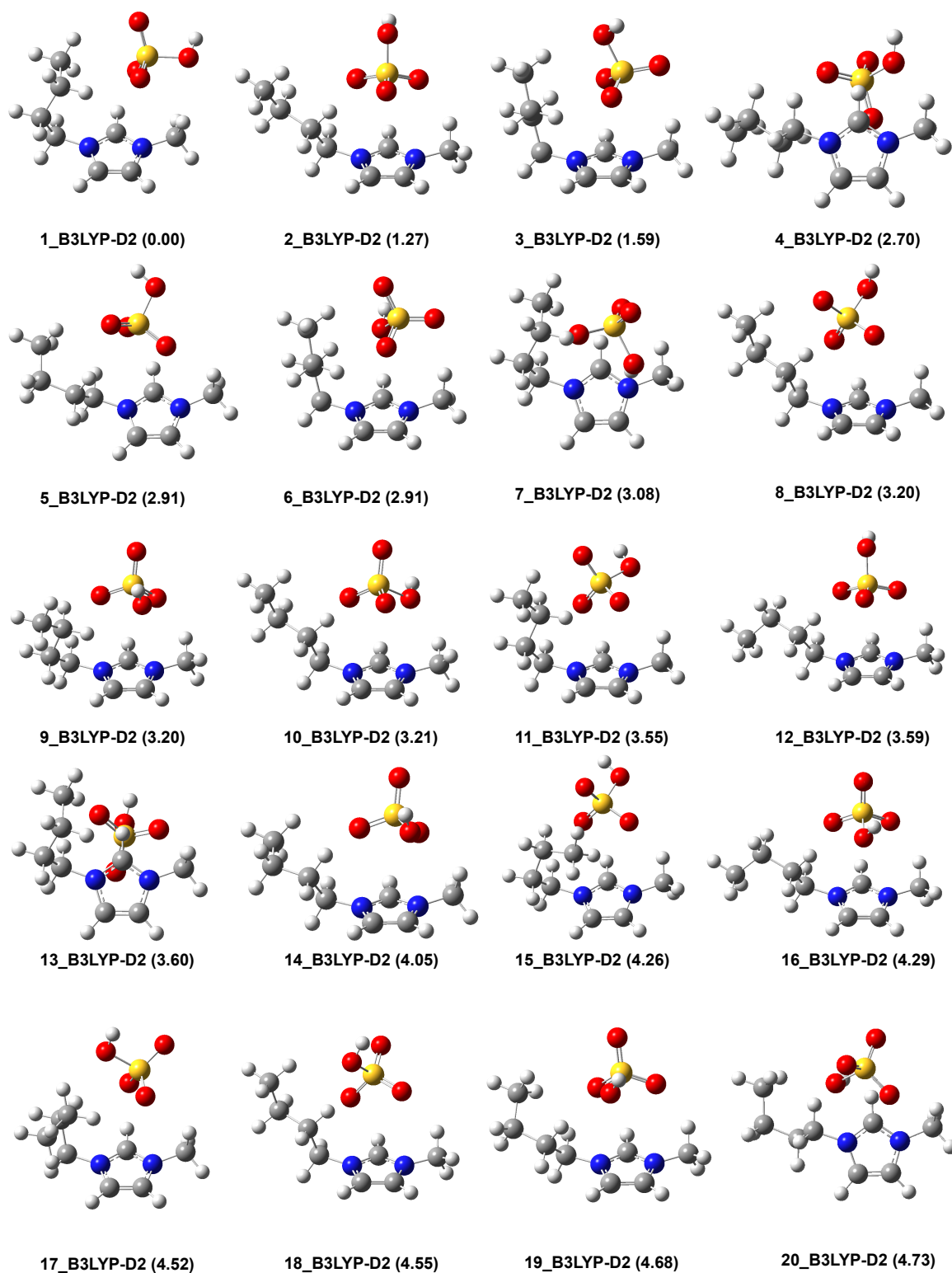


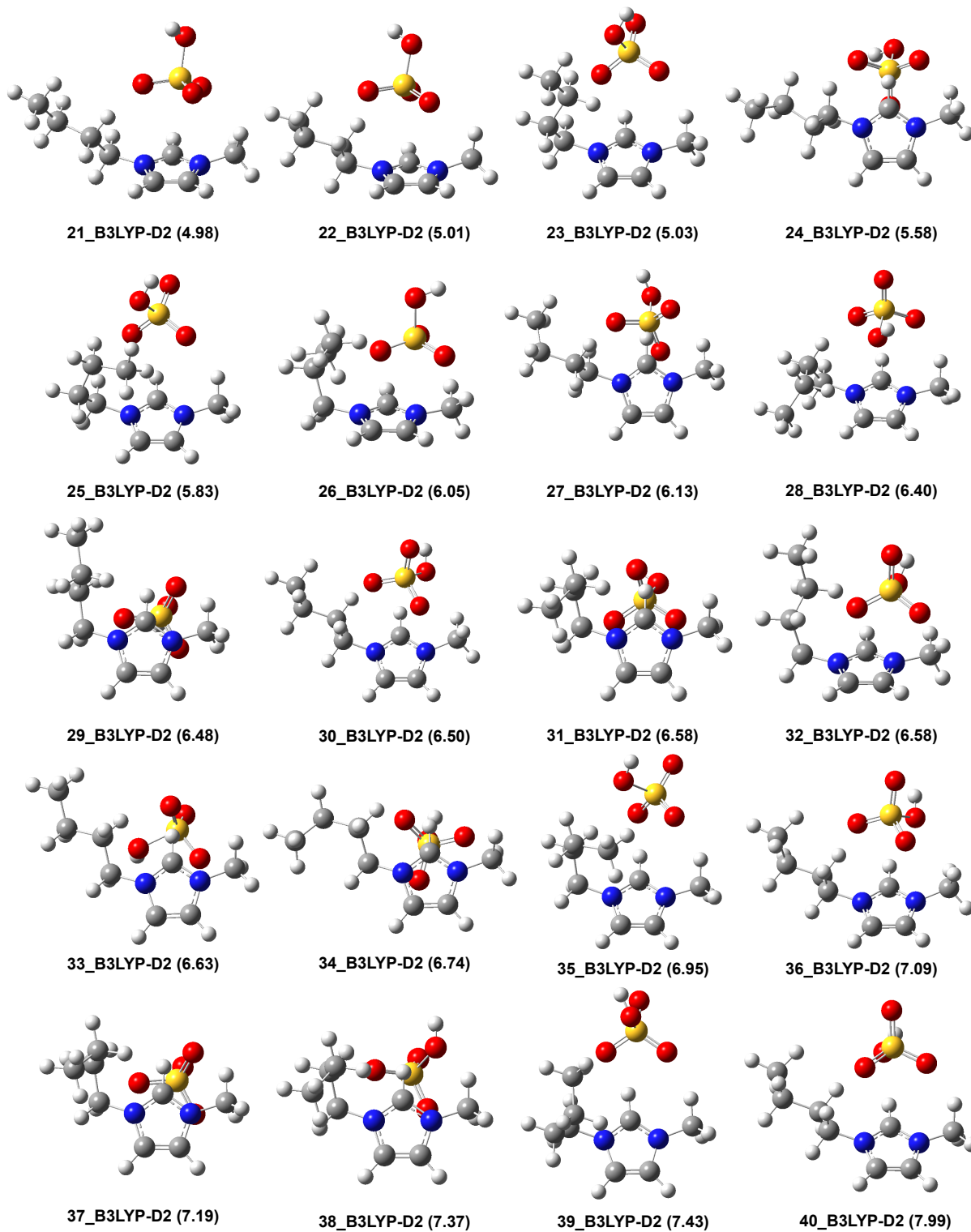
70_B3LYP (55.31)

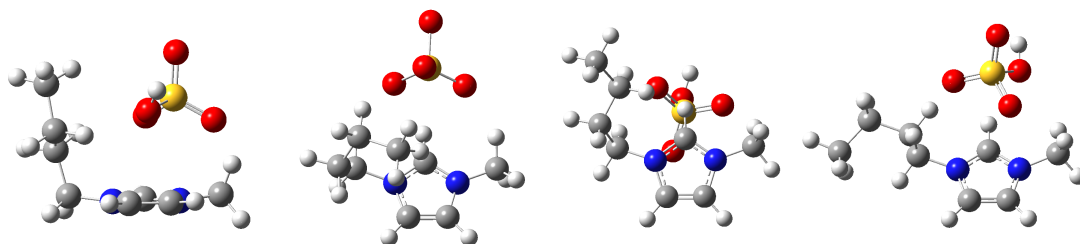
B3LYP-D2/6-311++G(d,p)**Table A. 28.** Electronic and relative energies of the B3LYP-D2 /6-311++G(d,p) [C₄C₁im][HSO₄] ion pairs with, and without, zero point energy corrections.

Ion Pair	<i>E</i> / au	ΔE_{rel} / kJ mol ⁻¹	<i>E</i> +ZPE /au	ΔE_{rel} (with ZPE correction) /kJ mol ⁻¹
1_B3LYP-D2	-1123.302001	-2.204	-1123.049211	0.000
2_B3LYP-D2	-1123.301144	0.047	-1123.048728	1.270
3_B3LYP-D2	-1123.301162	0.000	-1123.048605	1.593
4_B3LYP-D2	-1123.300790	0.976	-1123.048183	2.700
5_B3LYP-D2	-1123.300766	1.040	-1123.048104	2.908
6_B3LYP-D2	-1123.300683	1.256	-1123.048103	2.909
7_B3LYP-D2	-1123.300917	0.643	-1123.048038	3.081
8_B3LYP-D2	-1123.300498	1.742	-1123.047993	3.198
9_B3LYP-D2	-1123.300458	1.846	-1123.047992	3.200
10_B3LYP-D2	-1123.300675	1.278	-1123.047990	3.206
11_B3LYP-D2	-1123.300317	2.217	-1123.047858	3.552
12_B3LYP-D2	-1123.300391	2.022	-1123.047843	3.591
13_B3LYP-D2	-1123.300533	1.651	-1123.047840	3.601
14_B3LYP-D2	-1123.300452	1.864	-1123.047670	4.047
15_B3LYP-D2	-1123.300349	2.134	-1123.047590	4.257
16_B3LYP-D2	-1123.300077	2.848	-1123.047576	4.293
17_B3LYP-D2	-1123.299864	3.406	-1123.047488	4.523
18_B3LYP-D2	-1123.299840	3.471	-1123.047477	4.554
19_B3LYP-D2	-1123.300095	2.801	-1123.047428	4.682
20_B3LYP-D2	-1123.300081	2.838	-1123.047410	4.730
21_B3LYP-D2	-1123.299687	3.870	-1123.047316	4.975
22_B3LYP-D2	-1123.299721	3.782	-1123.047302	5.013
23_B3LYP-D2	-1123.299344	4.773	-1123.047296	5.029
24_B3LYP-D2	-1123.299519	4.311	-1123.047086	5.578
25_B3LYP-D2	-1123.299589	4.129	-1123.046989	5.834
26_B3LYP-D2	-1123.299970	3.128	-1123.046908	6.046
27_B3LYP-D2	-1123.299716	3.794	-1123.046877	6.127
28_B3LYP-D2	-1123.299705	3.823	-1123.046774	6.398
29_B3LYP-D2	-1123.299376	4.689	-1123.046744	6.478
30_B3LYP-D2	-1123.299465	4.456	-1123.046737	6.497
31_B3LYP-D2	-1123.299179	5.206	-1123.046706	6.578
32_B3LYP-D2	-1123.299257	4.999	-1123.046703	6.584
33_B3LYP-D2	-1123.299052	5.539	-1123.046688	6.625
34_B3LYP-D2	-1123.299217	5.107	-1123.046643	6.744
35_B3LYP-D2	-1123.299248	5.023	-1123.046564	6.949
36_B3LYP-D2	-1123.299522	4.304	-1123.046510	7.091
37_B3LYP-D2	-1123.299290	4.913	-1123.046473	7.188
38_B3LYP-D2	-1123.299379	6.886	-1123.046406	7.366
39_B3LYP-D2	-1123.298354	7.371	-1123.046381	7.430
40_B3LYP-D2	-1123.298886	5.975	-1123.046169	7.987
41_B3LYP-D2	-1123.298584	6.768	-1123.046161	8.008
42_B3LYP-D2	-1123.298764	6.294	-1123.046117	8.123
43_B3LYP-D2	-1123.298484	7.029	-1123.045976	8.493
44_B3LYP-D2	-1123.298822	6.141	-1123.045906	8.677
45_B3LYP-D2	-1123.298630	6.645	-1123.045784	8.997
46_B3LYP-D2	-1123.298058	8.149	-1123.045195	10.545
47_B3LYP-D2	-1123.297677	9.149	-1123.045189	10.560
48_B3LYP-D2	-1123.297523	9.553	-1123.045036	10.962
49_B3LYP-D2	-1123.297266	10.229	-1123.044671	11.921
50_B3LYP-D2	-1123.297114	10.626	-1123.044665	11.935
51_B3LYP-D2	-1123.296547	12.115	-1123.044176	13.220
52_B3LYP-D2	-1123.296966	11.015	-1123.043924	13.881
53_B3LYP-D2	-1123.295614	14.566	-1123.043740	14.366
54_B3LYP-D2	-1123.287549	35.740	-1123.035230	36.707
55_B3LYP-D2	-1123.285505	41.106	-1123.033527	41.178
56_B3LYP-D2	-1123.284470	43.823	-1123.032456	43.990
57_B3LYP-D2	-1123.282798	48.214	-1123.031078	47.609
58_B3LYP-D2	-1123.283189	47.187	-1123.030899	48.078
59_B3LYP-D2	-1123.281885	50.609	-1123.030160	50.018
60_B3LYP-D2	-1123.281772	50.906	-1123.029560	51.593
61_B3LYP-D2	-1123.278208	60.266	-1123.026309	60.131

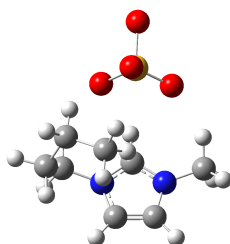
Figure A. 16. $[\text{C}_4\text{C}_{1\text{im}}][\text{HSO}_4]$ ion pairs optimised at the B3LYP-D2/6-311++G(d,p) level. Relative energies (kJ mol^{-1}) are ZPE corrected.



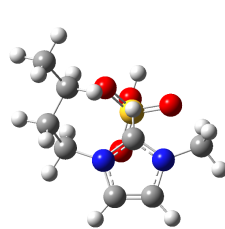




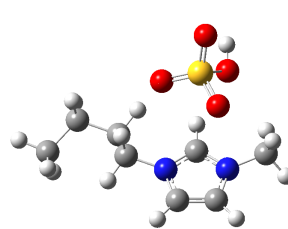
41_B3LYP-D2 (8.01)



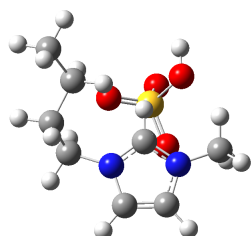
42_B3LYP-D2 (8.12)



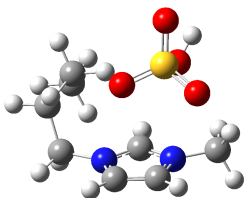
43_B3LYP-D2 (8.49)



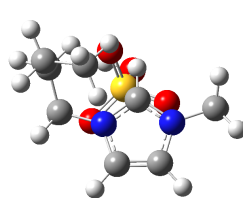
44_B3LYP-D2 (8.68)



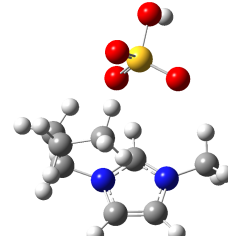
45_B3LYP-D2 (9.00)



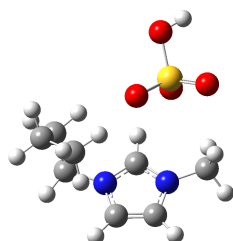
46_B3LYP-D2 (10.55)



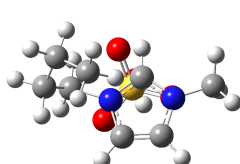
47_B3LYP-D2 (10.56)



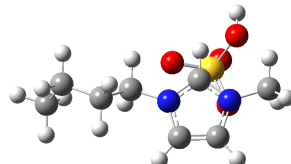
48_B3LYP-D2 (10.96)



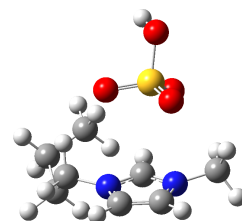
49_B3LYP-D2 (11.92)



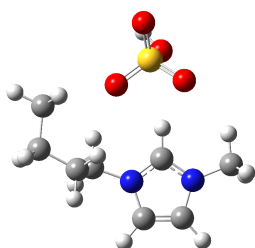
50_B3LYP-D2 (11.94)



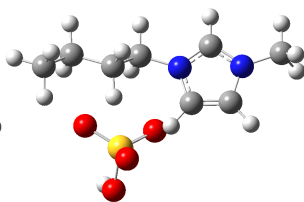
51_B3LYP-D2 (13.22)



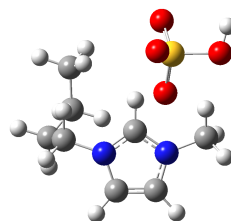
52_B3LYP-D2 (13.88)



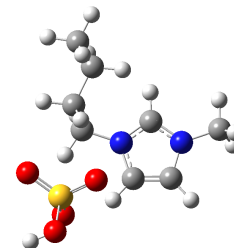
53_B3LYP-D2 (14.47)



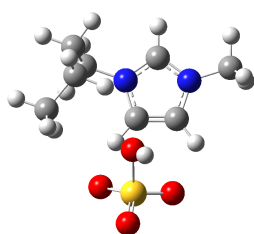
54_B3LYP-D2 (36.71)



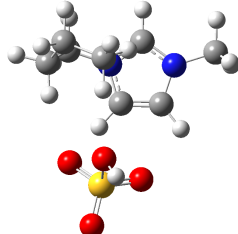
55_B3LYP-D2 (41.18)



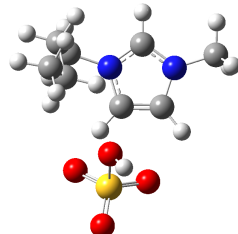
56_B3LYP-D2 (43.99)



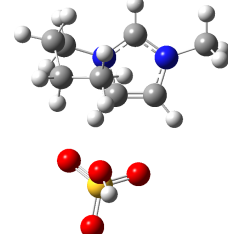
57_B3LYP-D2 (47.61)



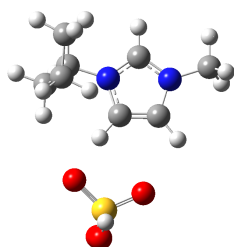
58_B3LYP-D2 (48.08)



59_B3LYP-D2 (50.02)



60_B3LYP-D2 (51.59)



61_B3LYP-D2 (60.13)

[C₄Him][HSO₄]

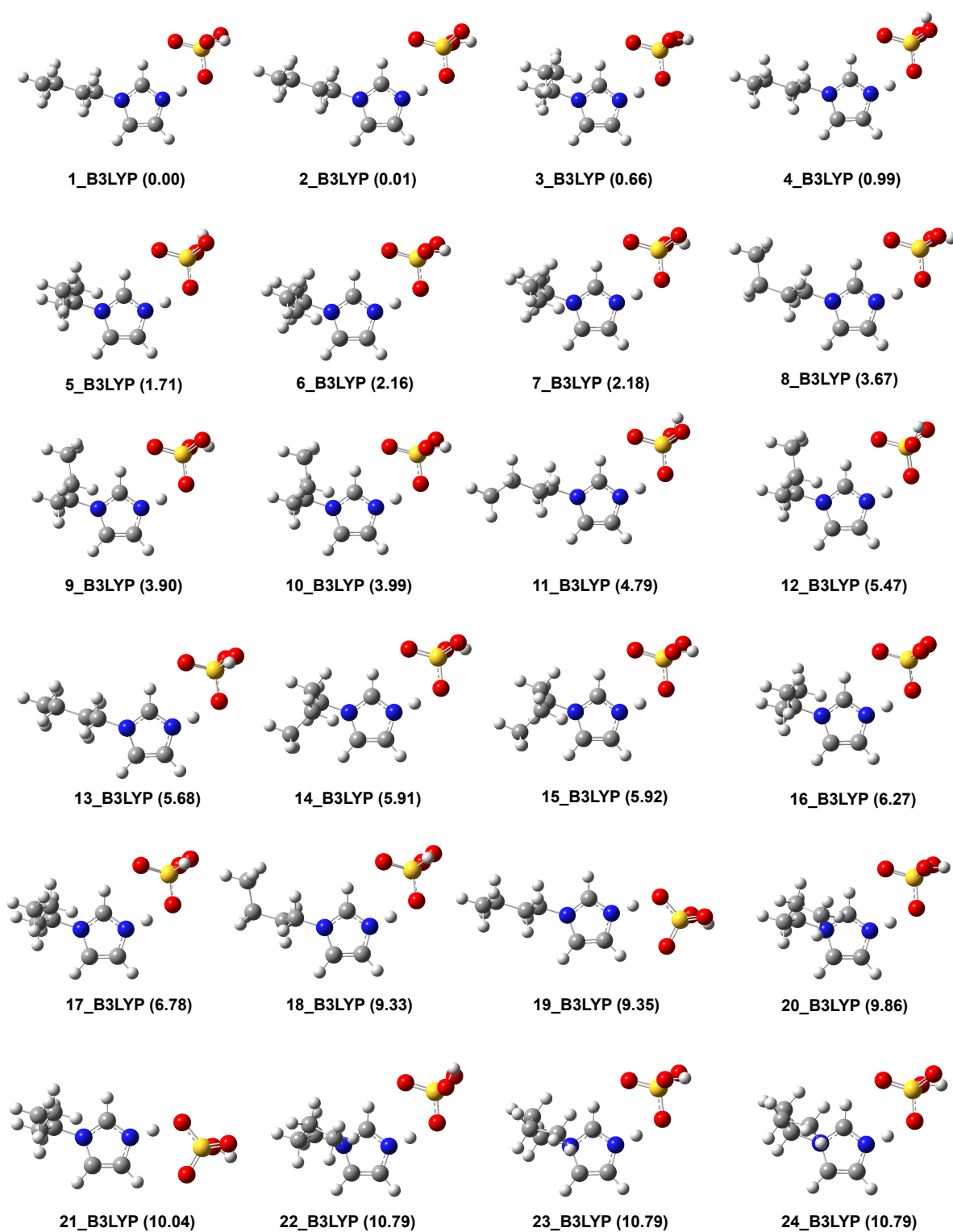
B3LYP/6-311+G(d,p)

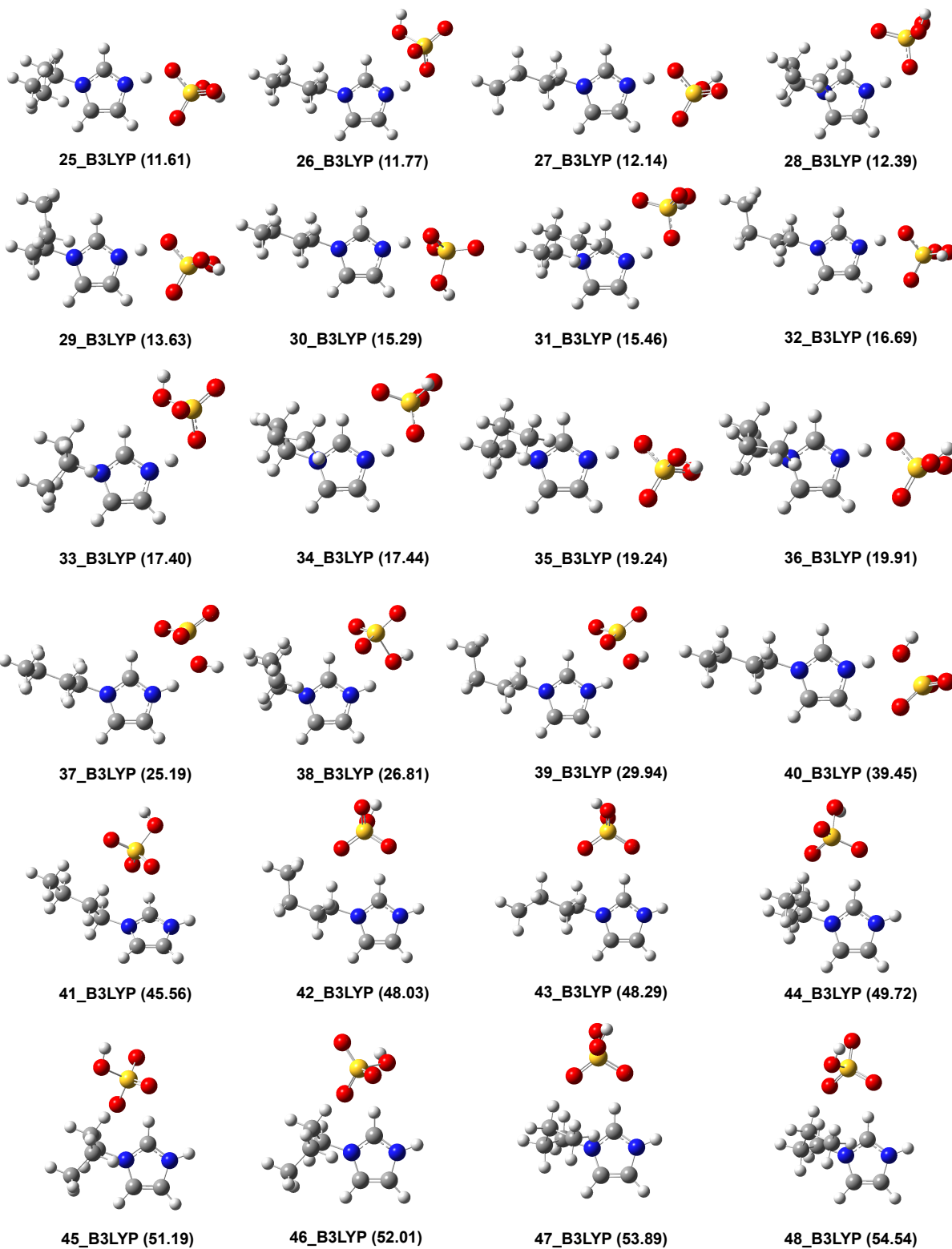
Table A. 29. Electronic and relative energies of the B3LYP /6-311+G(d,p) [C₄Him][HSO₄] ion pairs with, and without, zero point energy corrections.

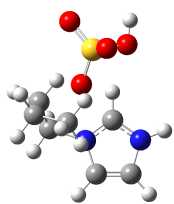
Ion Pair	<i>E</i> /au	ΔE_{rel} / kJ mol ⁻¹	<i>E</i> +ZPE /au	ΔE_{rel} (with ZPE correction)/kJ mol ⁻¹
1_B3LYP	-1083.951150	0.000	-1083.727700	0.000
2_B3LYP	-1083.951137	0.033	-1083.727697	0.007
3_B3LYP	-1083.951026	0.325	-1083.727449	0.659
4_B3LYP	-1083.950700	1.183	-1083.727322	0.994
5_B3LYP	-1083.950590	1.472	-1083.727051	1.705
6_B3LYP	-1083.950444	1.854	-1083.726877	2.161
7_B3LYP	-1083.950445	1.851	-1083.726871	2.177
8_B3LYP	-1083.949851	3.410	-1083.726302	3.670
9_B3LYP	-1083.949922	3.224	-1083.726213	3.904
10_B3LYP	-1083.949933	3.196	-1083.726179	3.994
11_B3LYP	-1083.949364	4.690	-1083.725875	4.792
12_B3LYP	-1083.949271	4.935	-1083.725616	5.473
13_B3LYP	-1083.949008	5.625	-1083.725542	5.667
14_B3LYP	-1083.949134	5.294	-1083.725449	5.911
15_B3LYP	-1083.949136	5.289	-1083.725447	5.916
16_B3LYP	-1083.948933	5.822	-1083.725311	6.273
17_B3LYP	-1083.948742	6.322	-1083.725119	6.776
18_B3LYP	-1083.947719	9.007	-1083.724148	9.325
19_B3LYP	-1083.946846	11.301	-1083.724139	9.350
20_B3LYP	-1083.947581	9.370	-1083.723943	9.864
21_B3LYP	-1083.946765	11.512	-1083.723874	10.044
22_B3LYP	-1083.947139	10.531	-1083.723589	10.794
23_B3LYP	-1083.947108	10.613	-1083.723347	11.430
24_B3LYP	-1083.947074	10.702	-1083.723341	11.445
25_B3LYP	-1083.946103	13.252	-1083.723279	11.609
26_B3LYP	-1083.946379	12.525	-1083.723215	11.774
27_B3LYP	-1083.945816	14.005	-1083.723078	12.136
28_B3LYP	-1083.946637	11.849	-1083.722981	12.390
29_B3LYP	-1083.945499	14.837	-1083.722510	13.627
30_B3LYP	-1083.943905	19.022	-1083.721876	15.291
31_B3LYP	-1083.945476	14.898	-1083.721812	15.460
32_B3LYP	-1083.943939	18.931	-1083.721341	16.694
33_B3LYP	-1083.944462	17.559	-1083.721071	17.404
34_B3LYP	-1083.944789	16.700	-1083.721059	17.435
35_B3LYP	-1083.943296	20.620	-1083.720371	19.241
36_B3LYP	-1083.942932	21.576	-1083.720115	19.914
37_B3LYP	-1083.942607	22.430	-1083.718105	25.192
38_B3LYP	-1083.942408	22.952	-1083.717488	26.812
39_B3LYP	-1083.941057	26.499	-1083.716295	29.944
40_B3LYP	-1083.936598	38.206	-1083.712673	39.453
41_B3LYP	-1083.935435	41.261	-1083.710346	45.564
42_B3LYP	-1083.934105	44.751	-1083.709406	48.030
43_B3LYP	-1083.933964	45.121	-1083.709308	48.288
44_B3LYP	-1083.933647	45.955	-1083.708763	49.720
45_B3LYP	-1083.933103	47.382	-1083.708201	51.194
46_B3LYP	-1083.932831	48.096	-1083.707889	52.013
47_B3LYP	-1083.931948	50.415	-1083.707176	53.886
48_B3LYP	-1083.931847	50.679	-1083.706926	54.541
49_B3LYP	-1083.930898	53.173	-1083.705809	57.476
50_B3LYP	-1083.924505	69.957	-1083.699402	74.297
51_B3LYP	-1083.923709	72.046	-1083.698924	75.551
52_B3LYP	-1083.923561	72.435	-1083.698340	77.085

53_B3LYP	-1083.922933	74.083	-1083.698056	77.830
54_B3LYP	-1083.922245	75.891	-1083.697407	79.535
55_B3LYP	-1083.921965	76.625	-1083.697094	80.356
56_B3LYP	-1083.921462	77.945	-1083.696912	80.833
57_B3LYP	-1083.921480	77.899	-1083.696835	81.036
58_B3LYP	-1083.920164	81.353	-1083.695712	83.983
59_B3LYP	-1083.920193	81.279	-1083.695544	84.427
60_B3LYP	-1083.920238	81.159	-1083.695500	84.541
61_B3LYP	-1083.920102	81.516	-1083.695400	84.803
62_B3LYP	-1083.920042	81.674	-1083.695345	84.948
63_B3LYP	-1083.919910	82.020	-1083.695206	85.313
64_B3LYP	-1083.919686	82.609	-1083.694726	86.574
65_B3LYP	-1083.919388	83.392	-1083.694250	87.824
66_B3LYP	-1083.919357	83.472	-1083.694208	87.933
67_B3LYP	-1083.919083	84.191	-1083.694182	88.000
68_B3LYP	-1083.917376	88.673	-1083.692579	92.210

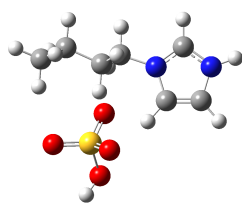
Figure A. 17. [C₄Him][HSO₄] ion pairs optimised at the B3LYP /6-311+G(d,p) level. Relative energies (kJ mol⁻¹) are ZPE corrected.



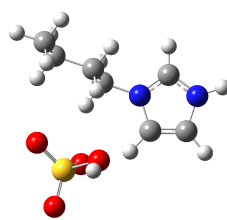




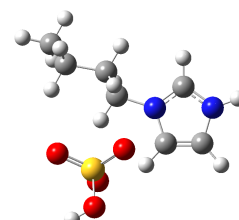
49_B3LYP (57.48)



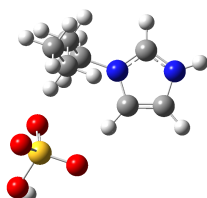
50_B3LYP (74.30)



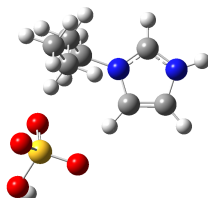
51_B3LYP (75.55)



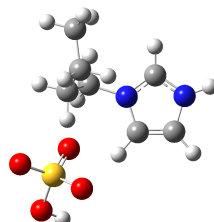
52_B3LYP (77.09)



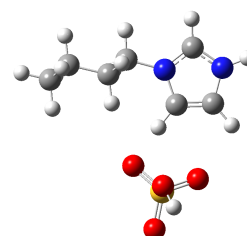
53_B3LYP (77.83)



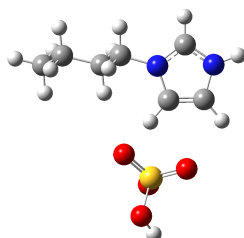
54_B3LYP (79.54)



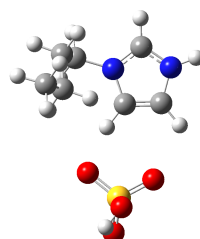
55_B3LYP (80.36)



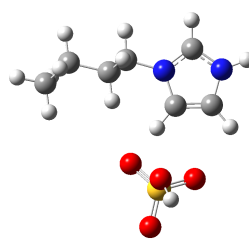
56_B3LYP (80.83)



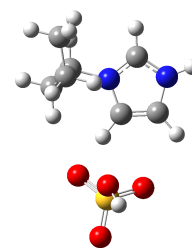
57_B3LYP (81.04)



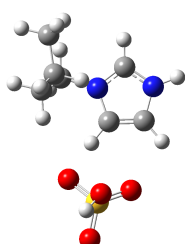
58_B3LYP (83.98)



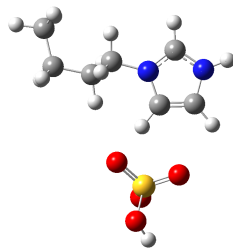
59_B3LYP (84.43)



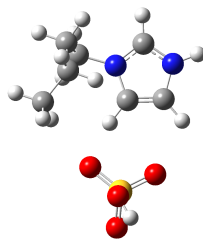
60_B3LYP (84.54)



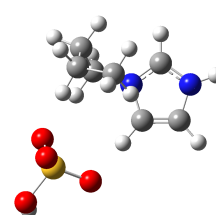
61_B3LYP (84.80)



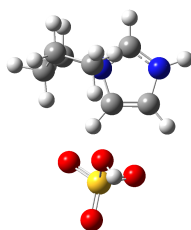
62_B3LYP (84.95)



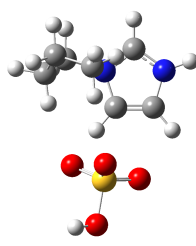
63_B3LYP (85.31)



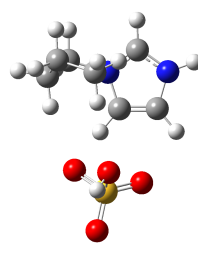
64_B3LYP (86.57)



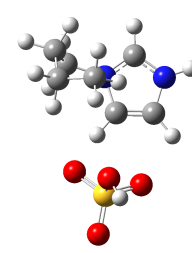
65_B3LYP (86.57)



66_B3LYP (87.93)



67_B3LYP (88.00)



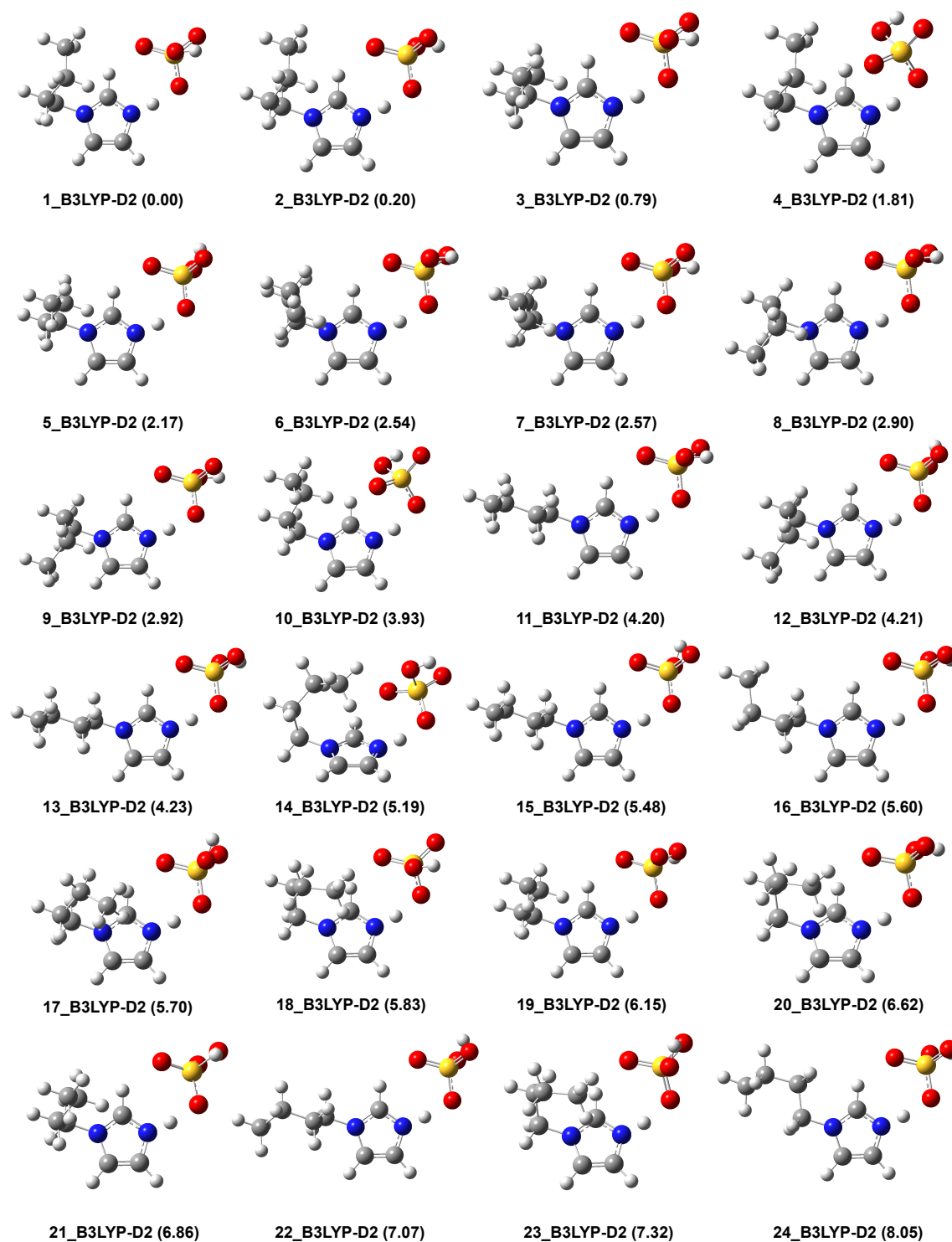
68_B3LYP (92.21)

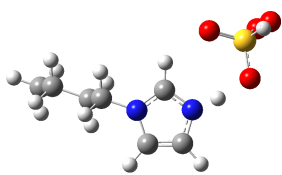
B3LYP-D2/6-311++G(d,p)

Table A. 30. Electronic and relative energies of the B3LYP-D2 /6-311++G(d,p) [C₄Him][HSO₄] ion pairs with, and without, ZPE corrections.

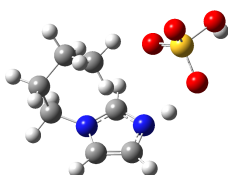
Ion Pair	<i>E</i> /au	ΔE_{rel} / kJ mol ⁻¹	<i>E</i> +ZPE /au	ΔE_{rel} (with ZPE correction) /kJ mol ⁻¹
1_B3LYP-D2	-1083.982714	-2.112	-1083.759474	0.000
2_B3LYP-D2	-1083.982596	-1.802	-1083.759397	0.202
3_B3LYP-D2	-1083.981910	0.000	-1083.759172	0.794
4_B3LYP-D2	-1083.982967	-2.777	-1083.758785	1.809
5_B3LYP-D2	-1083.981344	1.484	-1083.758649	2.166
6_B3LYP-D2	-1083.981241	1.756	-1083.758508	2.538
7_B3LYP-D2	-1083.981186	1.899	-1083.758496	2.567
8_B3LYP-D2	-1083.981357	1.451	-1083.758369	2.901
9_B3LYP-D2	-1083.981333	1.515	-1083.758363	2.918
10_B3LYP-D2	-1083.981739	0.447	-1083.757978	3.927
11_B3LYP-D2	-1083.980374	4.032	-1083.757873	4.204
12_B3LYP-D2	-1083.980852	2.775	-1083.757870	4.210
13_B3LYP-D2	-1083.980357	4.077	-1083.757863	4.231
14_B3LYP-D2	-1083.981273	1.672	-1083.757497	5.191
15_B3LYP-D2	-1083.979875	5.341	-1083.757385	5.484
16_B3LYP-D2	-1083.980043	4.900	-1083.757340	5.602
17_B3LYP-D2	-1083.980403	3.955	-1083.757302	5.703
18_B3LYP-D2	-1083.981030	2.308	-1083.757253	5.830
19_B3LYP-D2	-1083.979939	7.286	-1083.757133	6.147
20_B3LYP-D2	-1083.980761	3.015	-1083.756953	6.619
21_B3LYP-D2	-1083.979580	6.116	-1083.756863	6.855
22_B3LYP-D2	-1083.979448	6.462	-1083.756782	7.067
23_B3LYP-D2	-1083.980351	4.091	-1083.756684	7.324
24_B3LYP-D2	-1083.979436	6.494	-1083.756407	8.052
25_B3LYP-D2	-1083.978312	9.445	-1083.755803	9.638
26_B3LYP-D2	-1083.979880	5.330	-1083.755703	9.902
27_B3LYP-D2	-1083.978001	10.262	-1083.755249	11.093
28_B3LYP-D2	-1083.977302	12.097	-1083.755207	11.203
29_B3LYP-D2	-1083.977533	11.491	-1083.755116	11.442
30_B3LYP-D2	-1083.978229	9.663	-1083.754851	12.137
31_B3LYP-D2	-1083.976610	13.913	-1083.754512	13.027
32_B3LYP-D2	-1083.975898	15.783	-1083.754010	14.346
33_B3LYP-D2	-1083.975789	16.069	-1083.753821	14.842
34_B3LYP-D2	-1083.976245	14.873	-1083.753759	15.006
35_B3LYP-D2	-1083.978231	9.659	-1083.753596	15.434
36_B3LYP-D2	-1083.975888	15.811	-1083.753553	15.547
37_B3LYP-D2	-1083.973999	20.769	-1083.752125	19.295
38_B3LYP-D2	-1083.973035	23.299	-1083.751498	20.940
39_B3LYP-D2	-1083.973917	20.985	-1083.749972	24.949
40_B3LYP-D2	-1083.974608	19.170	-1083.749969	24.956
41_B3LYP-D2	-1083.974156	20.356	-1083.749892	25.157
42_B3LYP-D2	-1083.973419	22.292	-1083.749267	26.799
43_B3LYP-D2	-1083.973609	21.794	-1083.749183	27.020
44_B3LYP-D2	-1083.971674	26.873	-1083.746615	33.761
45_B3LYP-D2	-1083.969815	31.755	-1083.744802	38.522
46_B3LYP-D2	-1083.969604	32.307	-1083.744585	39.090
47_B3LYP-D2	-1083.969637	32.222	-1083.744487	39.349
48_B3LYP-D2	-1083.966825	39.605	-1083.743451	42.069
49_B3LYP-D2	-1083.967148	38.757	-1083.742976	43.316
50_B3LYP-D2	-1083.967108	38.862	-1083.742672	44.115
51_B3LYP-D2	-1083.967706	37.292	-1083.742608	44.282
52_B3LYP-D2	-1083.963145	49.267	-1083.737248	58.355
53_B3LYP-D2	-1083.961603	53.316	-1083.736772	59.605
54_B3LYP-D2	-1083.960316	56.693	-1083.735406	63.190
55_B3LYP-D2	-1083.958979	60.204	-1083.734074	66.688
56_B3LYP-D2	-1083.957570	63.904	-1083.732954	69.629
57_B3LYP-D2	-1083.956714	66.152	-1083.731783	72.704
58_B3LYP-D2	-1083.955917	68.243	-1083.731449	73.580
59_B3LYP-D2	-1083.956438	66.875	-1083.731439	73.605
60_B3LYP-D2	-1083.956250	67.369	-1083.731271	74.047
61_B3LYP-D2	-1083.955152	70.251	-1083.730728	75.472

Figure A. 18. [C₄Him][HSO₄] ion pairs optimised at the B3LYP-D2 /6-311++G(d,p) level. Relative energies (kJ mol⁻¹) are ZPE corrected.

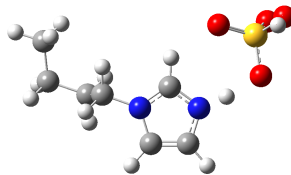




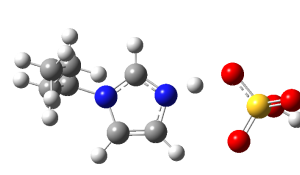
25_B3LYP-D2 (9.64)



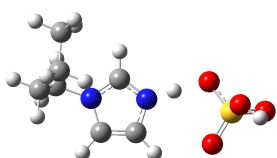
26_B3LYP-D2 (9.90)



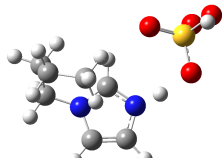
27_B3LYP-D2 (11.09)



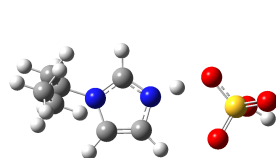
28_B3LYP-D2 (11.20)



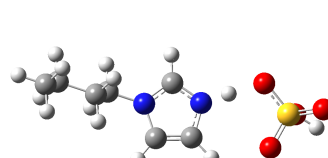
29_B3LYP-D2 (11.44)



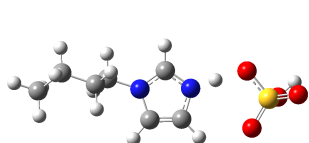
30_B3LYP-D2 (12.14)



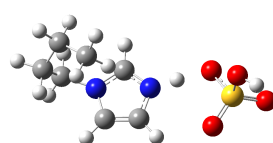
31_B3LYP-D2 (13.03)



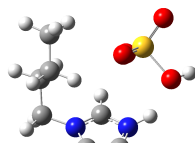
32_B3LYP-D2 (14.35)



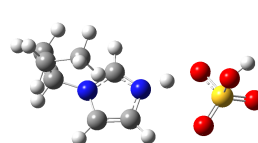
33_B3LYP-D2 (14.84)



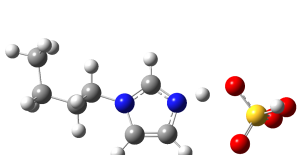
34_B3LYP-D2 (15.01)



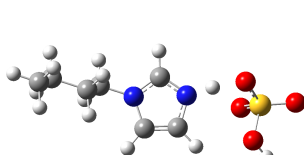
35_B3LYP-D2 (15.43)



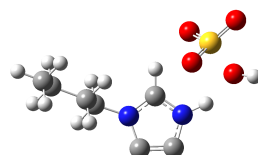
36_B3LYP-D2 (15.55)



37_B3LYP-D2 (19.30)



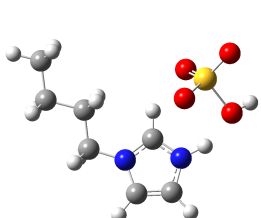
38_B3LYP-D2 (20.94)



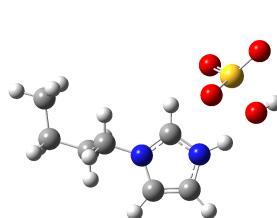
39_B3LYP-D2 (24.95)



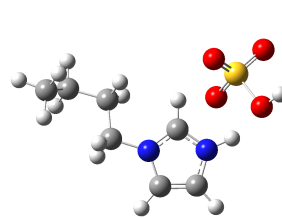
40_B3LYP-D2 (24.96)



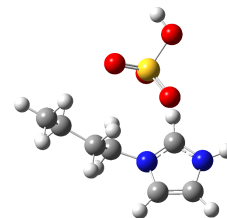
41_B3LYP-D2 (25.16)



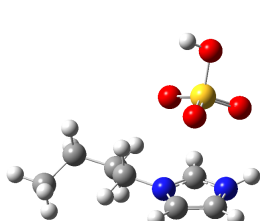
42_B3LYP-D2 (26.80)



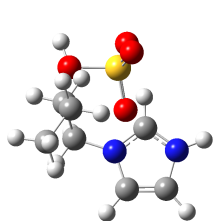
43_B3LYP-D2 (27.02)



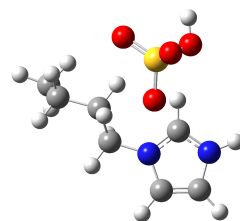
44_B3LYP-D2 (33.76)



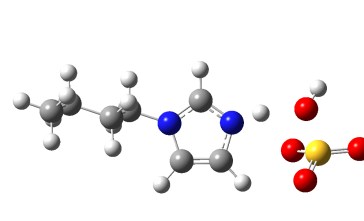
45_B3LYP-D2 (38.52)



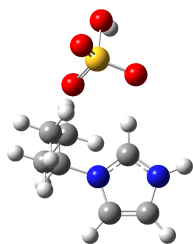
46_B3LYP-D2 (39.09)



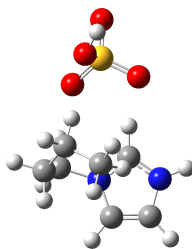
47_B3LYP-D2 (39.35)



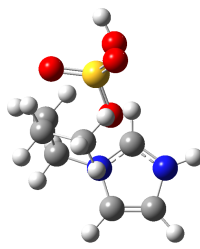
48_B3LYP-D2 (42.07)



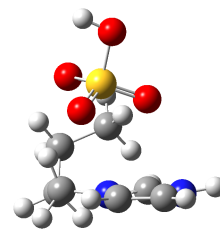
49_B3LYP-D2 (43.32)



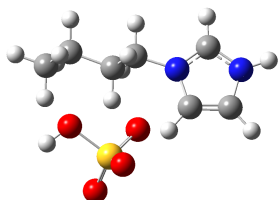
50_B3LYP-D2 (44.12)



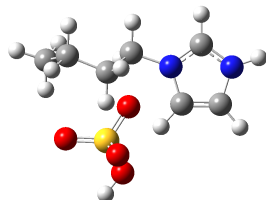
51_B3LYP-D2 (44.28)



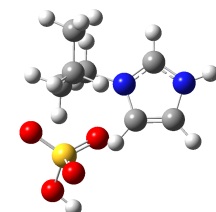
52_B3LYP-D2 (58.34)



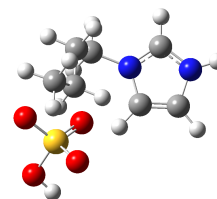
53_B3LYP-D2 (59.61)



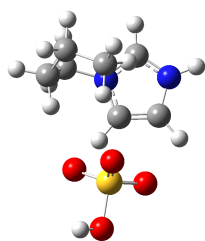
54_B3LYP-D2 (63.19)



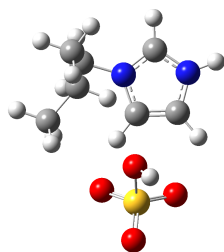
55_B3LYP-D2 (66.69)



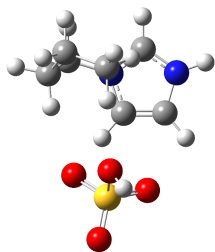
56_B3LYP-D2 (69.63)



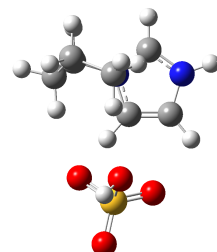
57_B3LYP-D2 (72.70)



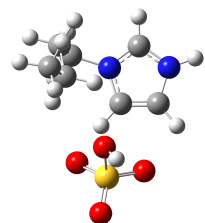
58_B3LYP-D2 (73.58)



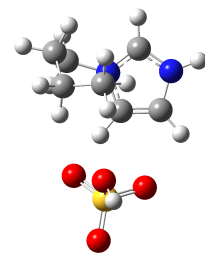
59_B3LYP-D2 (73.61)



60_B3LYP-D2 (74.05)



61_B3LYP-D2 (75.47)



62_B3LYP-D2 (77.50)

QTAIM data for selected [C₄C₁im][HSO₄] ion pairs

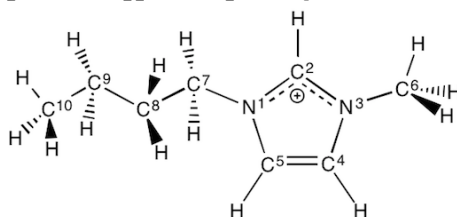


Figure A. 19. Numbering scheme for the [C₄C₁im]⁺ cation.

Table A. 31. Selected topological properties of intermolecular interactions within selected [C₄C₁im][HSO₄] ion pairs (shown in Chapter 4, Figure 4.12).

Interaction	$\rho_{\text{BCP}} / \text{a.u.}$	$\nabla^2 \rho_{\text{BCP}} / \text{a.u.}$	$H_{\text{BCP}} / \text{a.u.}$
Ion pair (a)			
C ¹⁰ H...O	0.0085	0.0274	0.0009
C ⁶ H...O	0.0087	0.0303	0.0012
C ⁷ H...O	0.0181	0.0681	0.0025
C ² H...O	0.0331	0.1140	0.0010
Ion pair (b)			
C ⁹ H...O	0.0088	0.0307	0.0011
C ⁹ H...O	0.0089	0.0274	0.0007
C ⁷ H...O	0.0102	0.0354	0.0013
C ² H...O	0.0138	0.0511	0.0017
C ⁶ H...O	0.0169	0.0646	0.0025
C ² H...O	0.0258	0.0927	0.0022
Ion pair (c)			
C ⁹ H...O	0.0054	0.0192	0.0007
C ¹⁰ H...O	0.0055	0.0184	0.0006
C ⁹ H...O	0.0072	0.0263	0.0009
C ⁹ H...O	0.0115	0.0389	0.0013
C ⁷ H...O	0.0117	0.0421	0.0015
C ⁹ H...O	0.0140	0.0513	0.0020
C ² ...O	0.0141	0.0517	0.0016
C ² H...O	0.0200	0.0718	0.0022
Ion pair (d)			
C ⁹ H...O	0.0007	0.0194	0.0007
C ⁹ H...O	0.0079	0.0288	0.0009
C ⁹ H...O	0.0111	0.0338	0.0009
C ² ...S	0.0117	0.0468	0.0020
C ² H...O	0.0119	0.0433	0.0016
C ⁷ H...O	0.0128	0.0441	0.0014
C ⁶ H...O	0.0170	0.0586	0.0019
Ion pair (e)			
C ¹⁰ H...O	0.0063	0.0223	0.0008
C ² ...O	0.0092	0.0368	0.0014
C ⁶ H...O	0.0097	0.0351	0.0012
C ⁹ H...O	0.0101	0.0305	0.0008
N ¹ ...O	0.0106	0.0414	0.0014
C ⁹ H...O	0.0109	0.0382	0.0011
C ⁹ H...O	0.0113	0.0432	0.0016
C ⁶ H...O	0.0162	0.0564	0.0018
Ion pair (f)			
C ¹⁰ H...O	0.0053	0.0188	0.0007
C ⁵ ...O	0.0062	0.0213	0.0009
C ⁵ H...O	0.0086	0.0300	0.0014
C ⁹ H...O	0.0087	0.0311	0.0010
C ⁴ ...O	0.0097	0.0328	0.0009
C ⁹ H...O	0.0106	0.0387	0.0014
C ⁹ H...O	0.0115	0.0379	0.0012
C ² ...O	0.0136	0.0503	0.0013
C ⁶ H...O	0.0187	0.0661	0.0021

QM: Anion-Anion H-bonding:

The $[\text{HSO}_4]^-$ discrete dimer

Relative energies

Table A. 32. Electronic energies, with and without the ZPE correction, for the $[\text{HSO}_4]^-$ dimer in the gas phase and in an implicit solvation environment at the B3LYP-D3BJ/6-311+G(d,p) level.

$[\text{HSO}_4]^-$ discrete dimer	E /au	$E+\text{ZPE}$ /au	BSSE/ kJ mol^{-1}
Gas phase	-1399.634958	-1399.579589	9.48
cpcm DCM	-1399.880923	-1399.826054	-
cpcm Methanol	-1399.903700	-1399.848921	-
cpcm Water	-1399.908722	-1399.853960	-

H-bonding

Table A. 33. Selected topological properties of the O-H...O H-bonds within the $[\text{HSO}_4]^-$ discrete dimers. The two H-bonds within a dimer are symmetrically equivalent.

$[\text{HSO}_4]^-$ discrete dimer	ρ_{BCP} / a.u	$\nabla^2\rho_{\text{BCP}}$ / a.u	H /a.u
Gas phase	0.0404	0.1322	-0.0021
cpcm DCM	0.0499	0.1483	-0.0062
cpcm Methanol	0.0505	0.1491	-0.0065
cpcm Water	0.0506	0.1492	-0.0066

Ion Pair Dimers

Relative energies

Table A. 34. Electronic and ZPE and BSSE corrected relative energies of the B3LYP-D3BJ /6-311+G(d,p) $[\text{C}_i\text{C}_i\text{im}][\text{HSO}_4]$ ion pair dimers.

Ion pair dimer	E /au	$E+\text{ZPE}$ /au	BSSE/ kJ mol^{-1}	ΔE_{rel} (with ZPE and BSSE correction) / kJ mol^{-1}
Dimer_1	-2010.719617	-2010.379757	34.2	0.000
Dimer_2	-2010.718554	-2010.378754	34.6	2.948
Dimer_3	-2010.718119	-2010.378507	34.4	3.408
Dimer_4	-2010.718447	-2010.378760	35.0	3.410
Dimer_5	-2010.717760	-2010.378148	34.0	3.965
Dimer_6	-2010.705767	-2010.366959	29.0	28.401
Dimer_7	-2010.703928	-2010.365192	29.2	33.230
Dimer_8	-2010.699461	-2010.362004	24.0	36.411
Dimer_9	-2010.697295	-2010.359840	22.8	40.846
Dimer_10	-2010.696774	-2010.359114	23.5	43.442
Dimer_11	-2010.697866	-2010.360285	26.6	43.446
Dimer_12	-2010.694797	-2010.357377	20.0	44.546
Dimer_13	-2010.695814	-2010.358633	26.5	47.753
Dimer_14	-2010.692645	-2010.354665	23.2	54.819

Table A. 35. Electronic and ZPE and BSSE corrected relative energies of selected B3LYP-D3BJ /6-311+G(d,p) $[\text{C}_7\text{C}_{10}\text{im}][\text{C}_7\text{SO}_4]$ ion pair dimers (shown in **Figure 4.22**).

Ion pair dimer	E /au	E +ZPE /au	BSSE/ kJ mol^{-1}	ΔE_{rel} (with ZPE and BSSE correction) / kJ mol^{-1}
"Diagonal"	-2089.330390	-2088.936340	25.301	0.00
"Anion-Chain"	-2089.327433	-2088.932768	29.231	13.31
"Anion-Cyclic"	-2089.312803	-2088.917793	28.196	51.59

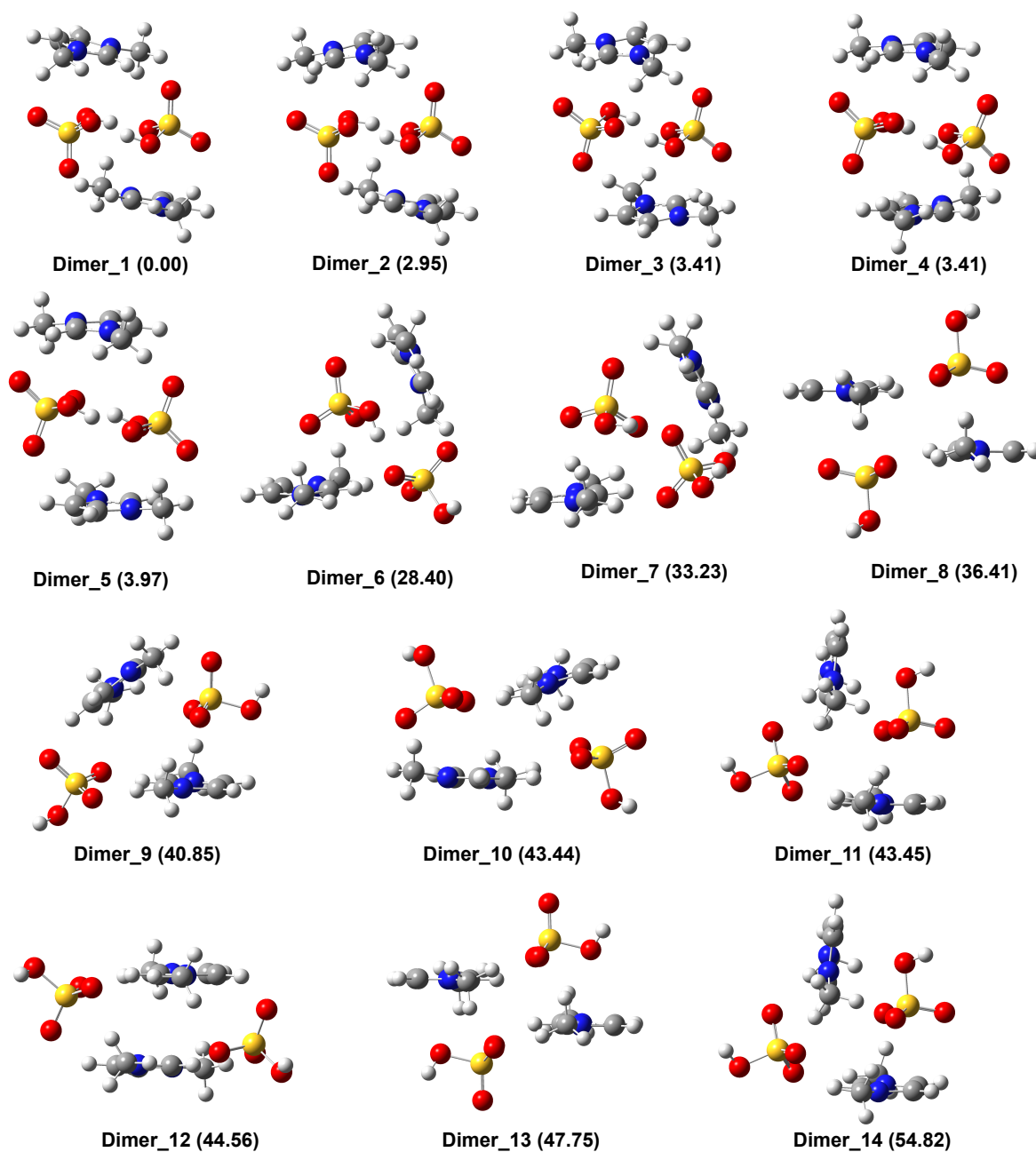


Figure A. 20. $[\text{C}_7\text{C}_{10}\text{im}][\text{HSO}_4]$ ion pair dimers at B3LYP-D3BJ/6-311+G(d,p). Relative energies in kJ mol^{-1} .

H-bonding

Table A. 36. $E^{(2)}$ values and associated topological properties of H-bond BCPs within selected B3LYP-D3BJ/6-311+G(d,p) $[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4]$ and $[\text{C}_1\text{C}_1\text{im}][\text{CSO}_4]$ ion pair dimers.

Interaction	$E^{(2)} / \text{kJ mol}^{-1}$	$\rho_{\text{BCP}} / \text{a.u.}$	$\nabla^2 \rho_{\text{BCP}} / \text{a.u.}$	$H_{\text{BCP}} / \text{a.u.}$
$[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4]$ Dimer 1				
methyl CH...O	0.25	0.0062	0.0222	0.0009
methyl CH...O	0.29	0.0109	0.0416	0.0015
methyl CH...O	5.40	0.0116	0.0377	0.0011
methyl CH...O	5.36	0.0117	0.0384	0.0012
methyl CH...O	10.71	0.0153	0.0506	0.0015
methyl CH...O	12.51	0.0159	0.0535	0.0016
$\text{C}^2\text{H}\cdots\text{O}$	24.56	0.0205	0.0745	0.0024
$\text{C}^2\text{H}\cdots\text{O}$	24.18	0.0205	0.0755	0.0025
OH...O	150.54	0.0547	0.1568	-0.0084
OH...O	152.72	0.0556	0.1580	-0.0090
$[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4]$ Dimer 2				
methyl CH...O	0.96	0.0081	0.0312	0.0012
methyl CH...O	0.38	0.0090	0.0324	0.0012
methyl CH...O	1.21	0.0103	0.0378	0.0014
$\text{C}^2\text{H}\cdots\text{O}$	2.38	0.0113	0.0388	0.0012
methyl CH...O	5.40	0.0118	0.0392	0.0012
$\text{C}^{4/6}\text{H}\cdots\text{O}$	2.34	0.0131	0.0498	0.0020
methyl CH...O	11.34	0.0152	0.0508	0.0016
methyl CH...O	13.51	0.0170	0.0590	0.0019
$\text{C}^2\text{H}\cdots\text{O}$	25.40	0.0211	0.0776	0.0025
OH...O	125.69	0.0498	0.1502	-0.0061
OH...O	158.70	0.0567	0.1582	-0.0098
$[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4]$ Dimer 3				
methyl CH...O	0.59	0.0075	0.0308	0.0012
methyl CH...O	0.59	0.0075	0.0308	0.0012
methyl CH...O	2.34	0.0099	0.0347	0.0012
methyl CH...O	2.34	0.0099	0.0347	0.0012
methyl CH...O	1.72	0.0105	0.0361	0.0012
methyl CH...O	1.72	0.0105	0.0361	0.0012
$\text{C}^{4/6}\text{H}\cdots\text{O}$	2.09	0.0133	0.0515	0.0021
$\text{C}^{4/6}\text{H}\cdots\text{O}$	2.09	0.0133	0.0515	0.0021
$\text{C}^2\text{H}\cdots\text{O}$	5.23	0.0151	0.0525	0.0017
$\text{C}^2\text{H}\cdots\text{O}$	5.23	0.0151	0.0525	0.0017
methyl CH...O	12.13	0.0164	0.0563	0.0018
methyl CH...O	12.13	0.0164	0.0563	0.0018
OH...O	130.58	0.0506	0.1514	-0.0065
OH...O	130.58	0.0506	0.1514	-0.0065
$[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4]$ Dimer 4				
methyl CH...O	0.71	0.0076	0.0293	0.0011
methyl CH...O	1.55	0.0086	0.0292	0.0010
methyl CH...O	1.72	0.0095	0.0341	0.0012
methyl CH...O	3.51	0.0115	0.0383	0.0012
methyl CH...O	5.77	0.0127	0.0423	0.0014
$\text{C}^{4/6}\text{H}\cdots\text{O}$	2.01	0.0131	0.0489	0.0019
$\text{C}^{4/6}\text{H}\cdots\text{O}$	1.72	0.0132	0.0501	0.0019
$\text{C}^2\text{H}\cdots\text{O}$	7.11	0.0154	0.0535	0.0017
$\text{C}^2\text{H}\cdots\text{O}$	8.20	0.0162	0.0564	0.0018
methyl CH...O	12.22	0.0164	0.0568	0.0019
methyl CH...O	12.01	0.0166	0.0581	0.0019
OH...O	127.28	0.0496	0.1511	-0.0060
OH...O	130.08	0.0508	0.1516	-0.0066
$[\text{C}_1\text{C}_1\text{im}][\text{HSO}_4]$ Dimer 5				

methyl CH...O	1.80	0.0082	0.0272	0.0009
methyl CH...O	1.80	0.0082	0.0272	0.0009
methyl CH...O	2.72	0.0112	0.0378	0.0012
methyl CH...O	2.72	0.0112	0.0378	0.0012
C ^{4/5} H...O	1.72	0.0137	0.0536	0.0021
C ^{4/5} H...O	1.72	0.0137	0.0536	0.0021
C ² H...O	6.57	0.0157	0.0541	0.0017
C ² H...O	6.57	0.0157	0.0541	0.0017
methyl CH...O	12.13	0.0161	0.0543	0.0017
methyl CH...O	12.13	0.0161	0.0543	0.0017
OH...O	127.82	0.0501	0.1511	-0.0062
OH...O	127.82	0.0501	0.1511	-0.0062
[C₁C₁im][HSO₄] Dimer 6				
methyl CH...O	0.29	0.0053	0.0196	0.0009
methyl CH...O	1.17	0.0081	0.0307	0.0012
methyl CH...O	5.19	0.0115	0.0368	0.0011
methyl CH...O	2.68	0.0118	0.0429	0.0016
methyl CH...O	3.10	0.0119	0.0441	0.0016
methyl CH...O	4.23	0.0133	0.0469	0.0018
methyl CH...O	6.57	0.0134	0.0456	0.0015
C ² H...O	28.91	0.0218	0.0830	0.0028
C ² H...O	38.91	0.0240	0.0867	0.0023
OH...O	76.19	0.0372	0.1282	-0.0008
[C₁C₁im][HSO₄] Dimer 7				
methyl CH...O	1.97	0.0067	0.0227	0.0008
methyl CH...O	0.75	0.0083	0.0301	0.0011
methyl CH...O	6.07	0.0105	0.0342	0.0011
C ² H...O	3.31	0.0112	0.0414	0.0014
methyl CH...O	7.07	0.0134	0.0431	0.0013
methyl CH...O	10.21	0.0143	0.0473	0.0015
methyl CH...O	6.99	0.0149	0.0527	0.0018
C ² H...O	28.91	0.0215	0.0850	0.0030
C ² H...O	29.71	0.0220	0.0798	0.0024
OH...O	80.83	0.0382	0.1317	-0.0010
[C₁C₁im][HSO₄] Dimer 8				
methyl CH...O	4.69	0.0097	0.0333	0.0012
methyl CH...O	4.69	0.0097	0.0333	0.0012
methyl CH...O	2.76	0.0101	0.0346	0.0011
methyl CH...O	2.76	0.0101	0.0346	0.0011
methyl CH...O	5.06	0.0102	0.0355	0.0013
methyl CH...O	5.06	0.0102	0.0355	0.0013
methyl CH...O	3.35	0.0102	0.0336	0.0011
methyl CH...O	3.35	0.0102	0.0336	0.0011
C ² H...O	16.40	0.0163	0.0573	0.0018
C ² H...O	16.40	0.0163	0.0573	0.0018
C ² H...O	19.54	0.0180	0.0639	0.0019
C ² H...O	19.54	0.0180	0.0639	0.0019
[C₁C₁im][HSO₄] Dimer 9				
methyl CH...O	1.30	0.0054	0.0191	0.0007
methyl CH...O	1.38	0.0061	0.0214	0.0008
methyl CH...O	1.34	0.0081	0.0276	0.0009
methyl CH...O	1.63	0.0085	0.0323	0.0012
methyl CH...O	3.10	0.0104	0.0376	0.0014
methyl CH...O	3.72	0.0109	0.0351	0.0010
methyl CH...O	12.09	0.0143	0.0510	0.0019
C ² H...O	6.15	0.0160	0.0553	0.0018
methyl CH...O	13.43	0.0178	0.0605	0.0019
C ^{4/5} H...O	33.89	0.0223	0.0800	0.0024
C ² H...O	41.88	0.0249	0.0892	0.0022

[C ₁ C ₁ im][C ₁ SO ₄] "Anion-Chain" Dimer				
methyl CH...O	1.17	0.0052	0.0185	0.0007
anion CH...O	0.79	0.0065	0.0218	0.0007
anion CH...O	6.36	0.0088	0.0263	0.0007
methyl CH...O	1.21	0.0103	0.0384	0.0014
methyl CH...O	1.51	0.0123	0.0445	0.0015
methyl CH...O	10.42	0.0155	0.0522	0.0016
methyl CH...O	17.15	0.0157	0.0538	0.0018
methyl CH...O	15.44	0.0167	0.0615	0.0023
C ² H...O	43.22	0.0263	0.0957	0.0023
C ² H...O	59.79	0.0287	0.1066	0.0023
[C ₁ C ₁ im][C ₁ SO ₄] "Anion-Cyclic" Dimer				
methyl CH...O	0.84	0.0088	0.0313	0.0011
methyl CH...O	1.38	0.0092	0.0312	0.0009
methyl CH...O	3.72	0.0100	0.0339	0.0011
methyl CH...O	4.77	0.0102	0.0317	0.0009
methyl CH...O	5.61	0.0110	0.0362	0.0011
methyl CH...O	7.87	0.0118	0.0375	0.0011
anion CH...O	10.88	0.0124	0.0385	0.0010
anion CH...O	11.17	0.0128	0.0456	0.0017
methyl CH...O	10.42	0.0176	0.0707	0.0028
C ² H...O	32.80	0.0234	0.0994	0.0036
C ² H...O	44.94	0.0267	0.0958	0.0022

Molecular Dynamics

Force fields

Cations

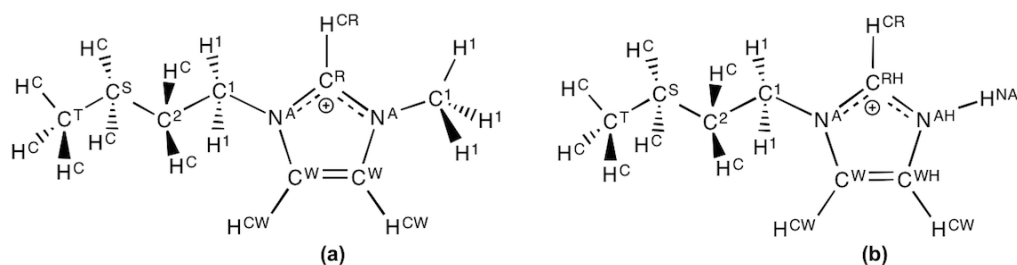


Figure A. 21. Atom labelling used for the (a) $[C_4C_1im]^+$ and (b) $[C_4Him]^+$ cations within the DL_POLY MD simulations.

Table A. 37. Force field parameters for the $[C_4C_1im]^+$ and $[C_4Him]^+$ cations.

Atoms	q / e	$\epsilon / \text{kJ mol}^{-1}$	$\sigma / \text{\AA}$	Bonds	$r_{eq} / \text{\AA}$	$k_r / \text{kJ mol}^{-1} \text{\AA}^{-2}$
1-butyl-3-methylimidazolium						
CR	-0.11	0.29288	3.55	CR - HCR	1.080	constrained
NA	0.15	0.71128	3.25	CW - HCW	1.080	constrained
CW	-0.13	0.29288	3.55	CR - NA	1.315	3992
HCR	0.21	0.12552	2.42	CW - NA	1.378	3574
HCW	0.21	0.12552	2.42	CW - CW	1.341	4352
C1	-0.17	0.27614	3.50	NA - C1	1.466	2820
H1	0.13	0.12552	2.50	C - H	1.090	constrained
C2	0.01	0.27614	3.50	C - C	1.529	2242
HC	0.06	0.12552	2.50			
CS	-0.12	0.27614	3.50			
CT	-0.18	0.27614	3.50			
1-butylimidazolium						
NAH	-0.21	0.71128	3.25	NAH - HNA	1.010	constrained
HNA	0.37	0.00000	0.00			
CWH	-0.03	0.29288	3.55			
CRH	0.00	0.29288	3.55			
Angles	$\theta_{eq} / ^\circ$	$k_\theta / \text{kJ mol}^{-1} \text{rad}^{-2}$	Dihedrals	$V_1 / \text{kJ mol}^{-1}$	$V_2 / \text{kJ mol}^{-1}$	$V_3 / \text{kJ mol}^{-1}$
1-butyl-3-methylimidazolium						
CW-NA-CR	108.0	585.8	CW-NA-CR-NA	0.0000	19.4600	0.0000
CW-NA-CT	125.6	585.8	CW-NA-CR-HCR	0.0000	19.4600	0.0000
CR-NA-CT	126.4	585.8	C1-NA-CR-NA	0.0000	19.4600	0.0000
NA-CR-HCR	125.1	292.9	C1-NA-CR-HCR	0.0000	19.4600	0.0000
NA-CR-NA	109.8	585.8	CR-NA-CW-CW	0.0000	12.5500	0.0000
NA-CW-CW	107.1	585.8	CR-NA-CW-HCW	0.0000	12.5500	0.0000
NA-CW-HCW	122.0	292.9	C1-NA-CW-CW	0.0000	12.5500	0.0000
CW-CW-HCW	130.9	292.9	C1-NA-CW-HCW	0.0000	12.5500	0.0000
NA-C1-H1	110.7	313.8	NA-CW-CW-NA	0.0000	44.9800	0.0000
NA-C1-C2	112.7	488.3	NA-CW-CW-HCW	0.0000	44.9800	0.0000
C-C-C	112.7	488.3	HCW-CW-CW-HCW	0.0000	44.9800	0.0000
C-C-H	110.7	313.8	CW-NA-C1-H1	0.0000	0.0000	0.5190
H-C-H	107.8	276.1	CR-NA-C1-H1	0.0000	0.0000	0.0000
			CW-NA-C1-C2	-7.1535	6.1064	0.7939
			CR-NA-C1-C2	-5.2691	0.0000	0.0000
			NA-C1-C2-CS	-7.4797	3.1642	-1.2026
			NA-C1-C2-HC	0.0000	0.0000	0.3670
			H-C-C-H	0.0000	0.0000	1.3305
			C-C-C-H	0.0000	0.0000	1.5313
			C-C-C-C	7.2800	-0.6569	1.1673
			CR-CW-NA-C1	0.0000	8.3700	0.0000

			NA-NA-CR-HCR	0.0000	9.2000	0.0000
			NA-CW-CW-HCW	0.0000	9.2000	0.0000
1-butylimidazolium						
CRH-NAH-HNA	125.4	292.9	HNA-NAH-CR-NA	0.0000	19.4600	0.0000
CWH-NAH-HNA	126.6	292.2	HNA-NAH-CR-HCR	0.0000	19.4600	0.0000
			HNA-NAH-CWH-CW	0.0000	12.5500	0.0000
			HNA-NAH-CWH-HCW	0.0000	12.5500	0.0000
			CR-CWH-NAH-HNA	0.0000	8.3700	0.0000

Anions

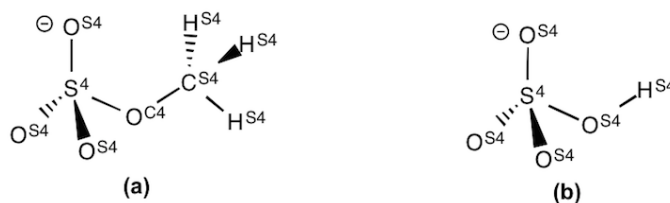


Figure A. 22. Atom labelling used for the (a) $[C_1SO_4]^-$ and (b) $[HSO_4]^-$ anions within the DL_POLY MD simulations.

Table A. 38. Force field parameters for the $[C_1SO_4]^-$ and $[HSO_4]^-$ anions.

Atoms	q/e	$\epsilon / \text{kJ mol}^{-1}$	$\sigma / \text{\AA}$	Bonds	$r_{\text{eq}} / \text{\AA}$	$k_r / \text{kJ mol}^{-1} \text{\AA}^{-2}$
Methylsulphate						
S4	1.18	1.04600	3.55	CS4-OC4	1.402	745.8
OS4	-0.65	0.83700	3.15	OS4-S4	1.455	5331.0
OC4	-0.45	0.58600	2.90	OC4-S4	1.633	1789.6
CS4	0.22	0.27600	3.50	CS4-HS4	1.090	constrained
HS4		0.12600	2.50			
Hydrogensulphate FFA						
S4	1.27	1.04600	3.55	OS4-S4	1.438	5239.9
OS4	-0.67	0.71176	3.00	OH4-S4	1.634	2328.3
OH4	-0.64	0.71176	3.00	OH4-HS4	0.949	constrained
HS4	0.38	0.00000	0.00			
Hydrogensulphate FFB						
S4	1.18	1.04600	3.50	OS4-S4	1.455	5331.00
OS4	-0.65	0.83700	3.15	OH4-S4	1.633	1789.6
OH4	-0.45	0.58600	2.90	OH4-HS4	1.00	constrained
HS4	0.22	0.00000	0.00			
Angles	$\theta_{\text{eq}} / ^\circ$	$k_\theta / \text{kJ mol}^{-1} \text{rad}^{-2}$	Dihedrals	$V_1 / \text{kJ mol}^{-1}$	$V_2 / \text{kJ mol}^{-1}$	$V_3 / \text{kJ mol}^{-1}$
Methylsulphate						
OS4-S4-OC4	114.0	969.00	OS4-S4-OC4-CS4	0.0000	0.0000	2.4815
OC4-S4-CS4	103.5	1239.62	S4-OC4-CS4-HS4	0.0000	0.0000	1.6858
CS4-OC4-S4	116.6	300.45				
HS4-CS4-S4	109.70	488.68				
HS4-CS4-OC4	107.8	276.14				
Hydrogensulphate FFA						
OS4-S4-OS4	114.76	456.97	OS4-S4-OS4-HS4	0.0000	0.0000	0.0000
OH4-S4-OS4	103.45	814.48				
S4-OH4-OS4	106.39	398.12				
Hydrogensulphate FFB						
OS4-S4-OS4	114.0	969.00	OS4-S4-OS4-HS4	0.0000	0.0000	0.0000
OH4-S4-OS4	103.5	1239.62				
S4-OH4-OS4	109.5	1046.00				

Selected radial distribution functions

Cation – anion

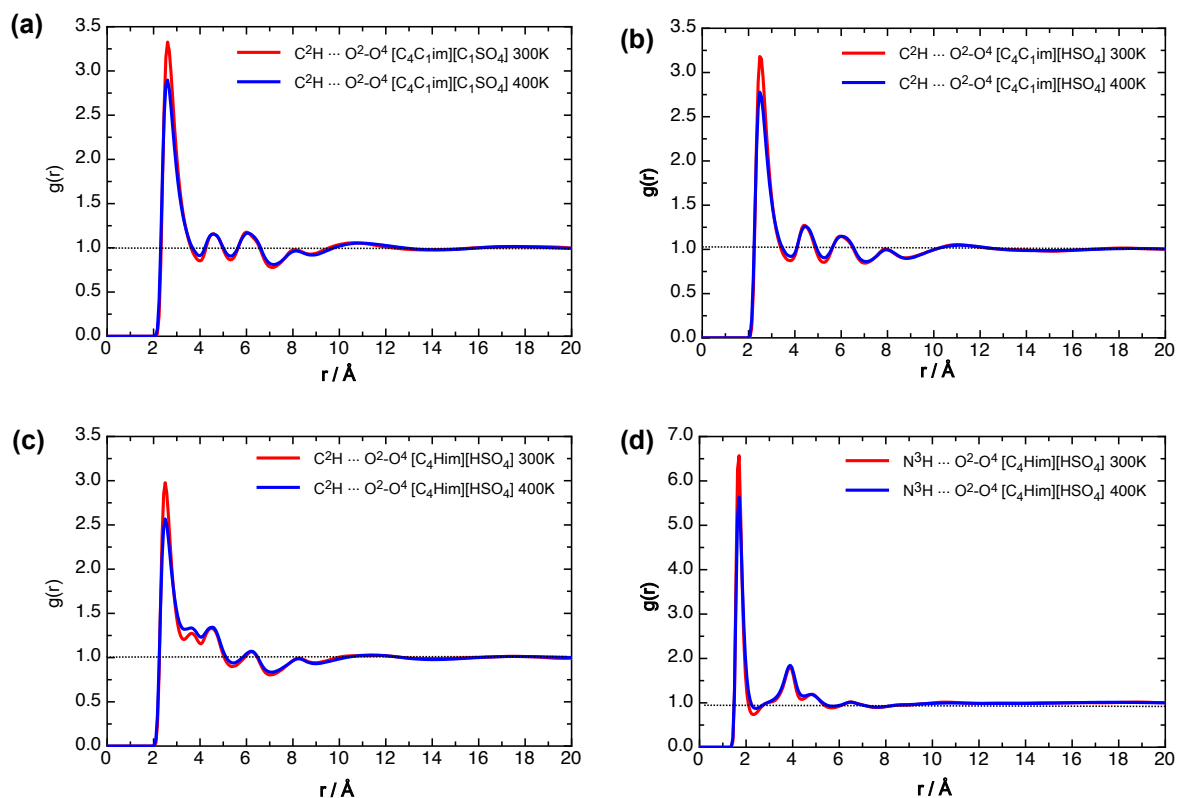


Figure A. 23. Selected cation – anion site-site radial distribution functions for systems at 300.15 and 400.15 K.

Anion – anion

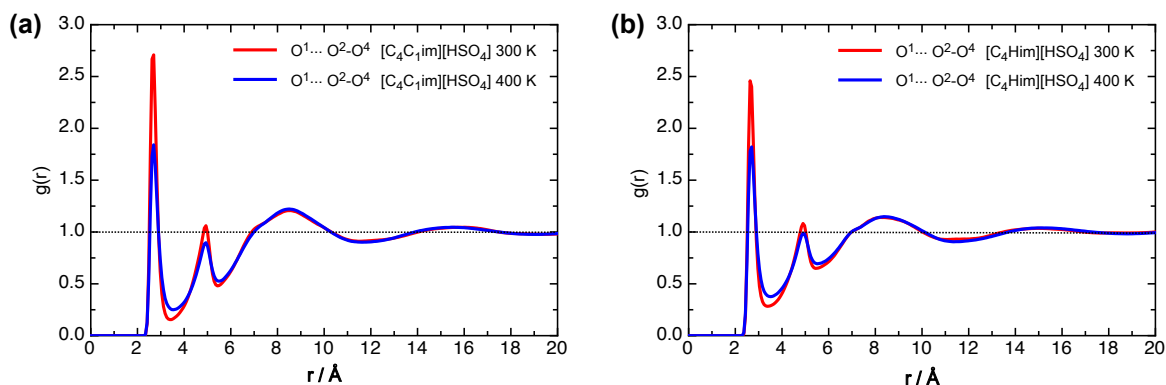


Figure A. 24. Anion – anion H-bond O (donor) ...O (acceptor) site-site radial distribution functions for (a) $[C_4C_1im][HSO_4]$ and (b) $[C_4Him][HSO_4]$ at 300.15 and 400.15 K.

Table A. 39. Positions of 1st peak maxima (r_{max}) for the $O^1...O^2-O^4$ RDFs.

	$r_{max} / \text{\AA}$	
	300.15 K	400.15 K
$[C_4C_1im][HSO_4] O^1...O^2-O^4$	2.70	2.70
$[C_4Him][HSO_4] O^1...O^2-O^4$	2.63	2.70

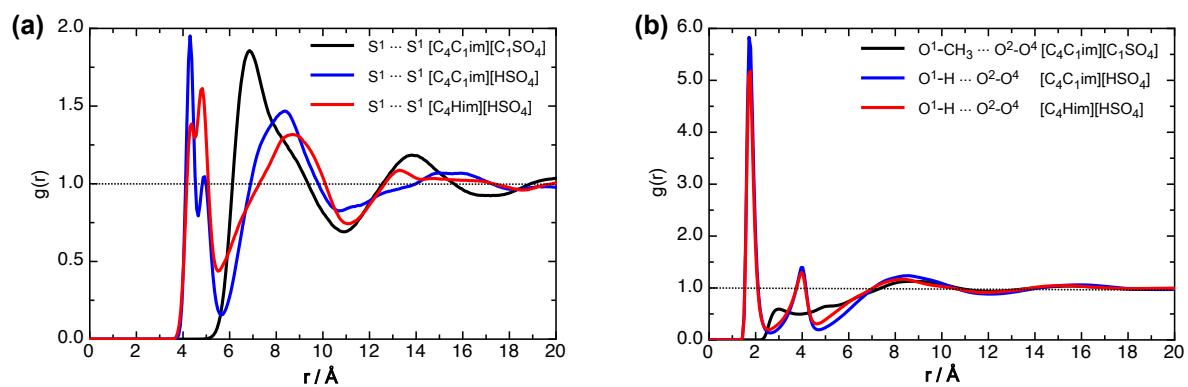


Figure A. 25. Selected anion – anion site-site radial distribution functions for systems at 300.15 K.

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