

Supplementary material for: “Predicting solvatochromic shifts and colours of a solvated organic dye: The example of Nile Red”

T. J. Zuehlsdorff,^{*,†} P. D. Haynes,^{‡,¶} M. C. Payne,[§] and N. D. M. Hine^{||}

[†]*School of Natural Sciences, University of California Merced, 5200 N. Lake Road, Merced, CA 95343, USA*

[‡]*Department of Physics, Imperial College London, Exhibition Road, London SW7 2AZ, UK*

[¶]*Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, UK*

[§]*Cavendish Laboratory, University of Cambridge, J. J. Thomson Avenue, Cambridge CB3 0HE, UK*

^{||}*Department of Physics, University of Warwick, Coventry, CV4 7AL, UK*

E-mail: tzuehlsdorff@ucmerced.edu

March 9, 2017

1 Fitting experimental data to a classical model for the solvatochromic shift of Nile Red

Following McRae,¹ a semiclassical model can be derived from perturbation theory that relates the solvatochromic shift of a dye in solution to macroscopic properties of the solvent expressed through the relative static permittivity ϵ_0 and the relative optical permittivity ϵ_{opt} , as well

as parameters A and B that are solvent-independent:

$$\Delta E_{\text{solv}} = A \frac{\epsilon_{\text{opt}} - 1}{2\epsilon_{\text{opt}} + 1} + B \left(\frac{\epsilon_0 - 1}{\epsilon_0 + 2} - \frac{\epsilon_{\text{opt}} - 1}{\epsilon_{\text{opt}} + 2} \right) \quad (1)$$

Rearranging the above equation we obtain

$$\Delta E_{\text{solv}} \left(\frac{\epsilon_{\text{opt}} - 1}{2\epsilon_{\text{opt}} + 1} \right)^{-1} = B \left(\frac{\epsilon_0 - 1}{\epsilon_0 + 2} - \frac{\epsilon_{\text{opt}} - 1}{\epsilon_{\text{opt}} + 2} \right) \left(\frac{\epsilon_{\text{opt}} - 1}{2\epsilon_{\text{opt}} + 1} \right)^{-1} + A \quad (2)$$

which is in a suitable format to determine constants A and B through a linear fit to experimental results. The experimental data used for the fit is taken from Deye *et al.*² and we have used the reported maximum absorption wavelength of Nile red in CO₂ as the gas phase benchmark with respect to which solvent-dependent solvatochromic shifts ΔE_{solv} are measured. A selection of 20 solvents is taken from the published data,² ranging from non-polar solvents like n-hexane and cyclohexane to strongly polar solvents like water and formamide. Fitting to the experimental data yields constants $A = -0.51$ eV (± 0.16 eV) and $B = -0.32$ eV (± 0.06 eV). After the constants A and B have been determined through fitting to experiment, Eqn. 1 can be used to calculate solvatochromic shifts predicted by the model under the assumption that no solvent-solute interactions occur and that the net effect of the solvent on the excitation energies of the solute can be expressed through macroscopic quantities ϵ_0 and $\epsilon_{\text{opt}} = n^2$ alone. Strong discrepancies between the results predicted by Eqn. 1 and the experimental results can then be ascribed to and used as an indicator for the presence of strong solute-solvent interactions for Nile red and that particular solvent.

2 Reparameterisation of classical force field parameters for Nile Red

Nile red consists of a 2-diethylamino group connected to a conjugated system via a C-N bond. Previous computational studies have demonstrated that the excited state potential

energy surface of the bright S_1 state responsible for the strong absorption peak in the visible region has two distinct minima with respect to rotations of the 2-diethylamino group. The excited state of the flat conformation has a relatively local character, while the conformation corresponding to a twist around the C-N bond by 90° has a charge transfer character in semi-local functionals.³ Since the energy of the S_1 state is influenced by the twist angle around the C-N bond, a classical force field that accurately reproduces the relative movements of the group with respect to the rest of the dye is of central importance. This was pointed out by Singh *et al.*,⁴ who performed a 2-dimensional reparameterisation of two dihedral force field parameters, using both density-functional theory (DFT) with the B3LYP⁵ functional and second order Møller-Plesset perturbation theory (MP2).⁶

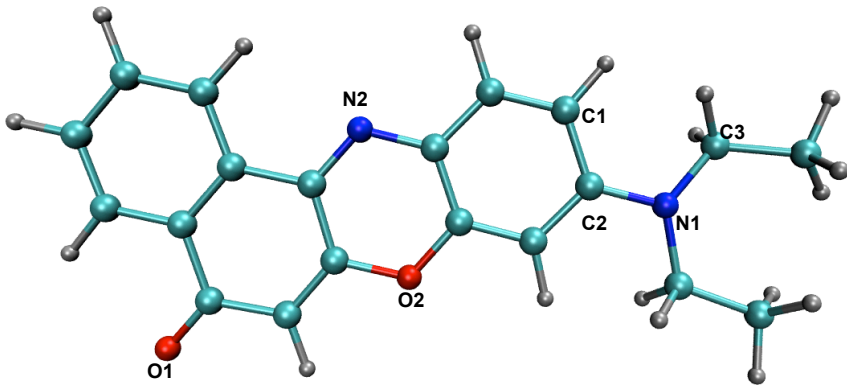


Figure 1: Ball and stick representation of nile red. The reparameterised dihedral angle in the classical force field is defined via C1-C2-N1-C3, while the oxygen and nitrogen atoms involved in hydrogen bonding with ethanol (see Section 6) are labelled as N2, O1 and O2 respectively. The figure was produced using VMD.⁸

For the purpose of this work, we choose a slightly different approach to the one selected in the work by Singh *et al.*⁴ Since the DFT and TDDFT calculations reported in this work are carried out using the PBE exchange-correlation functional,⁷ we choose the same functional to produce a potential energy surface to fit our force field to. The reason for this is to generate a force field that reproduces the ground state PBE potential energy surface with as much accuracy as possible, thus ensuring greater consistency between the structures obtained from classical MD and the TDDFT calculations. We also do not perform a 2-dimensional

potential energy scan but rather focus on the dihedral angle that controls the positioning of the diethylamino groups with respect to the conjugated ring structure. This angle is labelled as C1-C2-N1-C3 in Fig. 1.

In order to perform the DFT potential energy scan, we use NWChem⁹ in conjunction with a 6-311++G** Gaussian basis set. The dihedral angle is varied from 180° to 60° in steps of 10° and a full geometry optimisation is carried out at each step. Therefore, the second diethyl amino group is optimised to be in its minimum energy configuration for the given dihedral angle C1-C2-N1-C3 controlling the first diethylamino group. This is done in order to ensure that the AMBER force field is parameterised along a realistic low energy twist path rather than fixing both groups to the same dihedral angle and is the reason why the DFT potential energy surface is not expected to be symmetric around 90° of twist angle. The relaxed DFT structures for each dihedral angle are then used as input for the classical AMBER force field,¹⁰ and the AMBER potential energy surface is computed with the force constant for the dihedral angle set to zero. The force constant is then fitted to the difference in potential energy surfaces, where it is assumed that the potential energies for the dihedral angle equal to 180° (corresponding to the fully flat conformation) for both NWChem and the AMBER classical force field coincide. However, we stress that while the parameterisation is done by scanning over the C1-C2-N1-C3 dihedral angle, the dihedral angles of the two diethylamino groups have the same force constant associated with them, both in the standard AMBER force field and in the reparameterised one.

The results for the DFT potential energy surface and the AMBER force field both before and after the force constant was refitted can be found in Fig. 2. As can be seen the original AMBER force field underestimates the potential energy barrier height by almost 4 kcal/mol. The fitted force field parameter yields a much better agreement for larger deviation from the minimum of the potential energy surface (130° to 80°) but slightly underestimates the potential energy barrier to small deviations from the flat conformation (170-140°). This shortcoming can likely be ascribed other parameters in the AMBER force field not connected

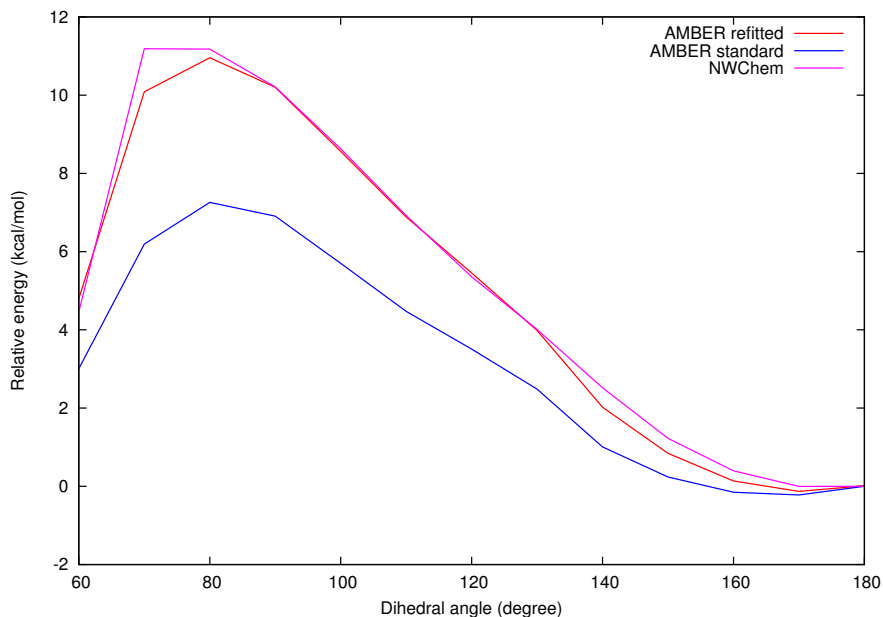


Figure 2: Relative potential energy surfaces of Nile Red under rotation of the dihedral angle C1-C2-N1-C3. Shown in the figure are the potential energy surface obtained through a DFT scan at the PBE level (purple), the potential energy surface given by standard AMBER force field parameterisation (blue) and the potential energy surface obtained after refitting the force constant of the dihedral angle.

to the dihedral angle in question, as the AMBER scan with the dihedral force constant set to zero reveals a small decrease in energy for small twist angles rather than a completely flat profile. Overall however, we thus expect the reparameterised force field to yield a much improved sampling of twisted conformations of Nile Red, apart from a potential minor over-sampling of small deviations from the fully flat conformation.

3 Average dihedral angle distribution of Nile Red in different solvents

Given the important role the dihedral angle that was parameterised in the previous section plays in the dominant excitation in the visible region of the spectrum, it is interesting to analyse how the angle distribution gets influenced by the solvent environment. For this purpose, we record the average dihedral angle, defined as the average between the angle

given by C1-C2-N1-C3 in Fig. 1 and the corresponding equivalent angle for the second diethylamino group for each snapshot studied. Furthermore, for the purpose of this section we define the average dihedral angle in such a way that an angle of 0° corresponds to a flat conformation, while an angle of 90° signifies the fully twisted conformation where the C-N bonds are pointing out of the plane defined by the aromatic ring system.

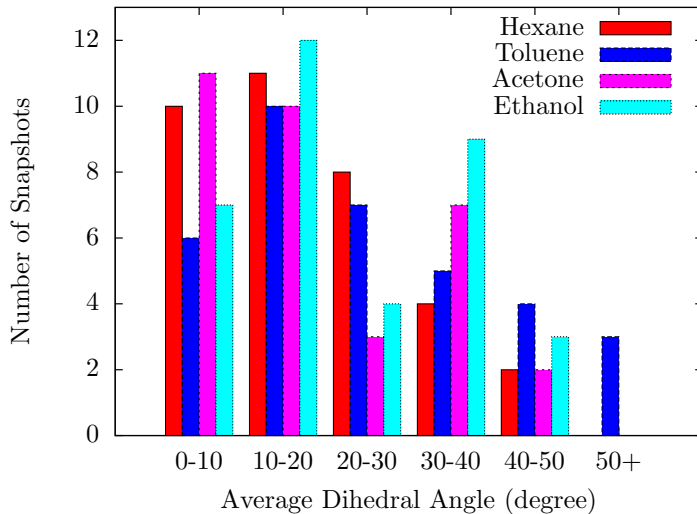


Figure 3: Distribution of the average dihedral angle of Nile Red defined through C1-C2-N1-C3 in Fig. 1 and the corresponding equivalent angle for the second diethylamino group for all 35 snapshots taken in all four solvents. Here, we define an angle of 0° as corresponding to a flat conformation. The dihedral angle is found to be solvent-dependent, with increasing solvent polarity stabilising more twisted conformations of the 2-diethylamino group, especially in the $30-40^\circ$ region.

The results for the dihedral angle distribution of all snapshots in all solvents can be found in form of a histogram in Fig. 3. As can be seen, in hexane the preferred conformation is flat (angles $0-10^\circ$) to slightly twisted (angles $10-20^\circ$), while larger twist angles have a considerably lower probability. For toluene, the dominant conformation is the lightly twisted one, but similar trends compared to Nile Red in hexane can be found, with the main difference that very twisted ($>40^\circ$) conformations do appear in toluene, albeit with a relatively low probability. For the more polar solvents acetone and ethanol, a twisted conformation ($30-40^\circ$) is found to be stabilised, up to the point that it becomes a more probable conformation than the fully flat conformation in ethanol. Thus in general it is found that increasingly polar solvents stabilise

a twisted conformation of the diethylamino group with respect to the aromatic ring system in Nile Red. Furthermore, toluene is the only solvent that supports very twisted conformations with any significant likelihood, a finding that is most likely related to the strong interactions between Nile Red and toluene favouring π -stackings either in flat or T-shape conformations around the aromatic rings (see Section 6).

4 ONETEP calculation parameters

In the ONETEP code,^{11,12} the ground state density matrix is expanded in terms of atom-centered, localised orbitals (referred to as non-orthogonal generalised Wannier functions or NGWFs) that are themselves expressed on a grid of psinc (periodic sinc) functions¹³ equivalent to a plane wave basis. The flexible representation of the atom-centered support functions means that they can be optimised *in situ* during a calculation, resulting in the property that only a minimal number (1 for hydrogens, 4 for carbons, oxygens, nitrogens etc.) is necessary to yield an exact representation of the DFT single-particle density matrix. In TDDFT calculations,¹⁴ a second set of localised orbitals is optimised in order to yield an ideal representation of a certain range of the low energy conduction space manifold in the system.¹⁵ For all calculations presented in this work, all well-bound conduction states of the system in question (defined as all Kohn-Sham states with negative eigenvalues) are explicitly optimised, while unbound conduction states are included in the TDDFT calculation in form of a projector onto the entire unoccupied space manifold expressed in the joint representation of valence and conduction NGWFs.¹⁶

The accuracy of a ONETEP TDDFT calculation is then controlled by two parameters only. The size of the underlying psinc basis that, due to its analogy to plane wave basis sets, can be formally expressed in terms of a kinetic energy cutoff and the localisation radius of the atom-centered conduction and valence NGWFs. The kinetic energy cutoff required is dependent only on the ion species in the calculation and the nature of the pseudopotentials

used. In line with previous results,¹⁷ all calculations are performed at an 800 eV kinetic energy cutoff to correctly account for the relatively hard norm-conserving pseudopotential of the oxygen species. The localisation region of all NGWFs is set to 10.0 a_0 . While this radius is insufficient to correctly treat very delocalised transitions like Rydberg states, results for the relatively localised low energy excited states of organic dyes have been shown to be fully converged.¹⁷ Excited state energies obtained in the ONETEP code have generally been demonstrated to be comparable to those obtained with large diffuse Gaussian basis sets like aug-cc-pVTZ.^{14,16,18}

5 The S_1 excited state potential energy surface

As has been noted in previous work,³ the character of the S_1 excited state of interest in nile red is heavily influenced by a rotation around the C-N bond that controls the alignment of the 2-diethylamino group with respect to the aromatic ring system. It was noted that for a torsion angle of 0°, corresponding to a flat conformation, the S_1 state has a local character, while for larger rotations it gains some intermolecular charge transfer (ICT) character.³ Since the semi-local PBE functional used in this work is expected to represent the S_1 state with local character well but might struggle with the ICT character state, it is worth investigating how the S_1 excited state potential energy surface under rotation around the dihedral angle C1-C2-N1-C3 (see Fig. 1) for semi-local functionals behaves in comparison to range-separated hybrid functionals.

To do so, we perform two sets of calculations with NWChem⁹ where we scan through the dihedral angle in steps of 10°, with a full ground state geometry optimisation carried out at each step, and calculate the S_1 excited state. For one set of calculations, the PBE exchange-correlation functional is used throughout, while for the other set we make use of the CAM-B3LYP range-separated hybrid functional.¹⁹ The resulting potential energy surfaces are plotted in Fig. 4, where the PBE results have been shifted upwards in energy such

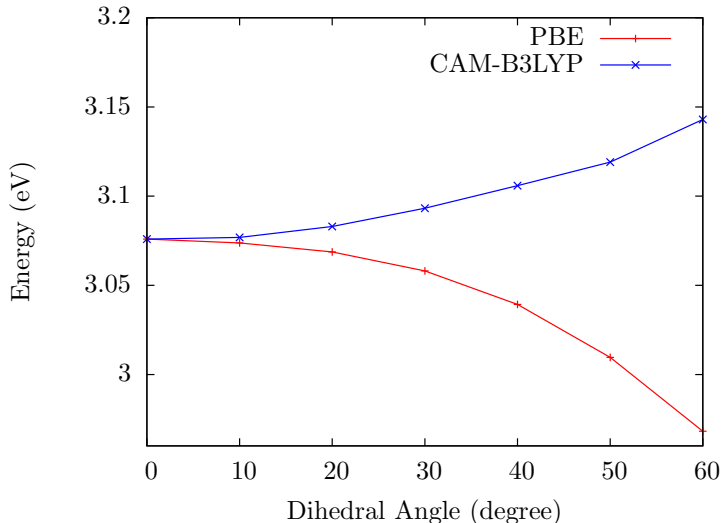


Figure 4: Figure showing the S_1 excited state potential energy surface computed with both CAM-B3LYP and the PBE, under a torsion around the dihedral angle C1-C2-N1-C3 (see Fig. 1). The PBE potential energy surface has been rigidly shifted up in energy such that the energies of the two surfaces coincide at an angle of 0° .

that they coincide with the CAM-B3LYP results for a 0° dihedral angle. As can be seen, for the PBE functional the excitation energy of the S_1 state decreases for increasing twist angle, while the CAM-B3LYP results produce an increase in excitation energy. This can be straightforwardly explained by the fact that the PBE functional will strongly underestimate excitation energies for states with large charge-transfer character. The CAM-B3LYP results however correctly predict an increase of excitation energy with increasing twist angle, in line with more sophisticated quantum chemistry methods.³

In order to visualise the difference in behaviour of the two excited state potential energy surfaces, we subtract the rigidly shifted PBE excited state potential energy surface from the CAM-B3LYP surface. The results of the energy difference can be found in Fig. 5. It is found that the angle-dependent difference between the CAM-B3LYP excited-state potential energy surface and the corresponding PBE surface follows a simple quadratic function of the form $f(\phi) = \alpha\phi^2$ for dihedral angle ϕ to a high degree of accuracy in the range of dihedral angles of interest for the purpose of this work. Here, we find the parameter α is given by $0.138 \text{ eV}(\text{rad})^{-2}$ when ϕ is measured in radians.

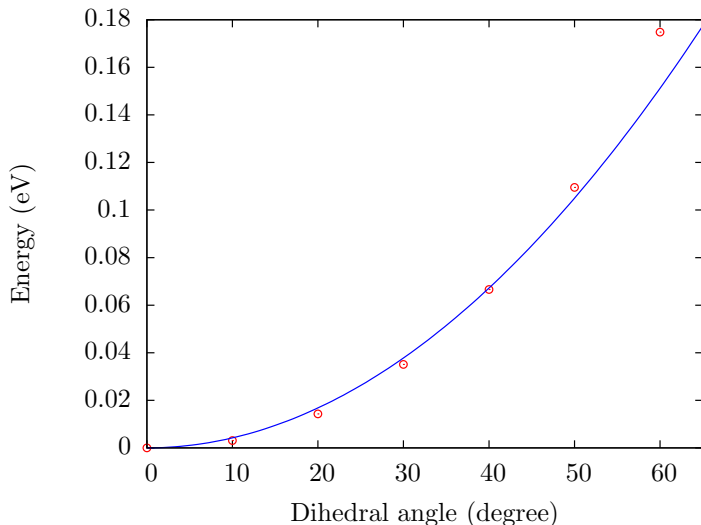


Figure 5: Figure showing the energy difference between the CAM-B3LYP S_1 excited state potential energy surface and the PBE excited state potential energy surface, under a torsion around the dihedral angle C1-C2-N1-C3 (see Fig. 1), where the PBE potential energy surface has been rigidly shifted up in energy such that the energies of the two surfaces coincide at an angle of 0° . The red circles correspond to calculated potential energy surface values, while the blue line represents a quadratic fit of the form $f(\phi) = \alpha\phi^2$ for dihedral angle ϕ .

6 Analysing π -stackings and hydrogen bonding in solvent environments

In order to quantify how ordered the first solvation shell of Nile red in ethanol and Nile red in toluene is, we analyse the number of hydrogen bonds formed between the solute and the solvent in the case of ethanol and the number of π -stackings observed in the case of toluene. This analysis is carried out for all 35 snapshots of the 140 ps trajectories studied.

There is some level of ambiguity in how to define what classifies as hydrogen bonding and π -stacking. For the purpose of this work we define a hydrogen bond through the distance R_H between the oxygen of the OH group in ethanol and the two oxygens or the nitrogen in Nile red that is not part of the 2-diethylamino group (labelled as N2 in Fig. 1). If $R_H < 3.5 \text{ \AA}$ and the angle $\left| \angle \left(\overrightarrow{H_{\text{eth}}O_{\text{eth}}}, \overrightarrow{H_{\text{eth}}X_{\text{Nile}}} \right) - 180^\circ \right| < 25^\circ$, where X_{Nile} refers to either the two oxygens or the nitrogen in Nile red (labelled as O1, O2 and N2 in Fig. 1), the ethanol molecule in question is considered to be interacting with the Nile red via a hydrogen bond

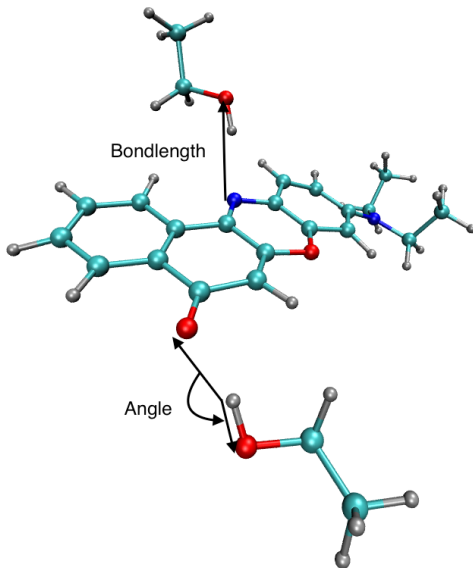


Figure 6: Figure showing the definition of the H-bond length R_H , as well as the angle $\angle \left(\overrightarrow{H_{\text{eth}}O_{\text{eth}}}, \overrightarrow{H_{\text{eth}}X_{\text{Nile}}} \right)$ used for classifying H-bonds for the purpose of this work.

(see Fig. 6 for an example H-bond configuration of nile red in ethanol, with the relevant bond length and angle labelled).

For the toluene, we consider the distance R_π between the centre of the aromatic ring in the toluene molecule and the centres of the two aromatic rings in the nile red molecule. We furthermore define A_π as the angle between the plane defined by the aromatic ring in the nile red that produces the smallest R_π and the aromatic ring in toluene. If $R_\pi < 5.5 \text{ \AA}$ and $|A_\pi| < 15^\circ$, the toluene molecule in question is said to be in a flat π -stacking conformation. If $R_\pi < 5.5 \text{ \AA}$ and $|A_\pi - 90^\circ| < 15^\circ$, the toluene molecule is considered to be in a T-stacking conformation (See Fig. 8 for an example π -stacking conformation of nile red in toluene, with the relevant vectors for defining R_π and A_π labelled).

The resulting analysis of the solvent environments of nile red in toluene and nile red in ethanol can be found in Fig. 7 to Fig. 10. The results suggest that in both cases, the first solvation shell is highly ordered and strong solute-solvent interactions can be observed. Only around 25 % of analysed frames of nile red in ethanol show no evidence of solute-

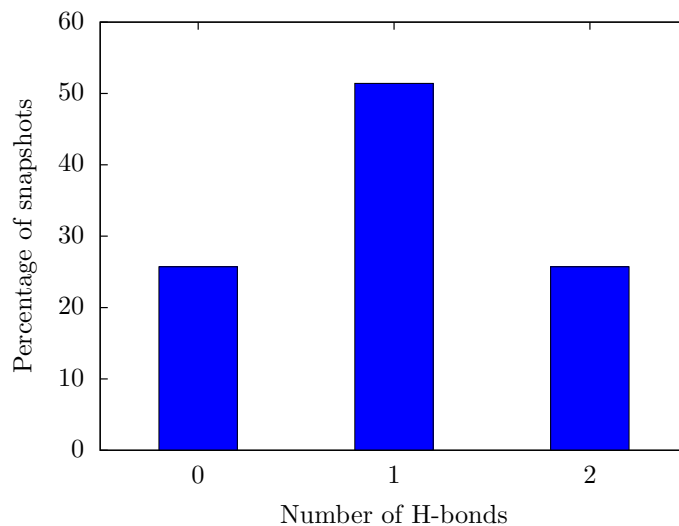


Figure 7: Figure detailing the percentage of snapshots of Nile Red in ethanol showing zero, one or two hydrogen bonds between an ethanol molecules and Nile Red.

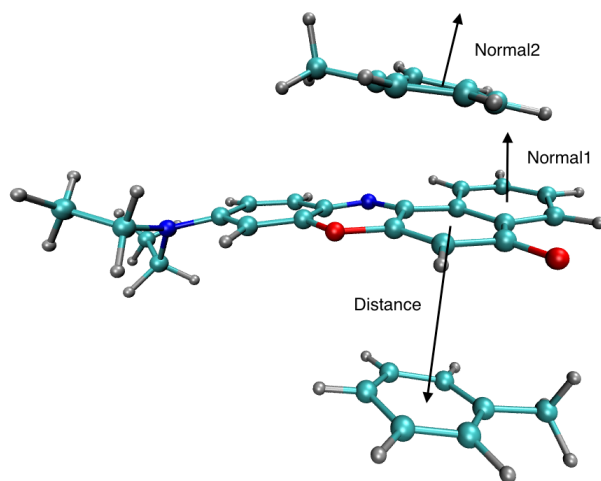


Figure 8: Figure showing an example structure of Nile Red with two toluene molecules, detailing the definition of the distance R_π and showing the normal vectors to the aromatic rings in the toluene and Nile Red structure. A_π is given by the angle between the two normal vectors for a given toluene molecule and aromatic ring in Nile Red.

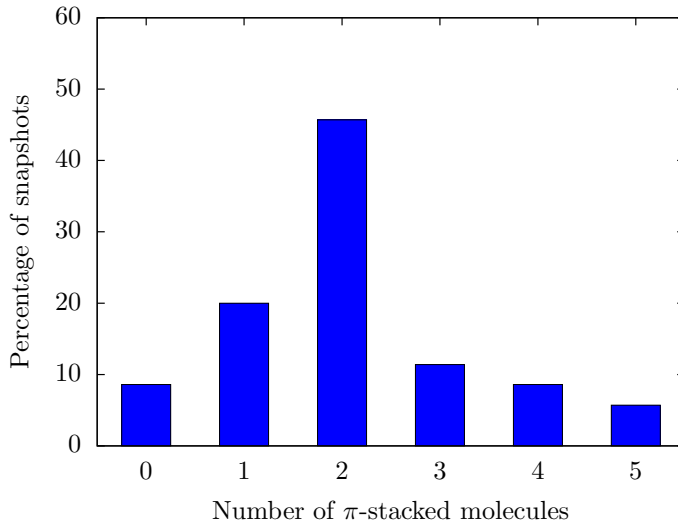


Figure 9: Figure detailing the percentage of snapshots of nile red in toluene showing zero, one, two, three, four or five toluene molecules in π -stacking conformation around the nile red.

solvent hydrogen bonding, while around 25 % show two hydrogen bonds being formed. In the case of toluene, less than 10 % of all frames show no evidence of π -stacking, with most frames containing two or more molecules in the π -stacking conformation. The flat stacking conformation is preferred by about 3:1 compared to the T-shape conformation.

The high degree of ordering of solvent molecules belonging to the first solvation shell of nile red in toluene and ethanol suggests that a simple description of the solvent environment in terms of macroscopic quantities ϵ_0 and n alone is insufficient for this system. The origin of the ordered solvent environment around nile red can be seen in its aromatic rings and the capability of its oxygen and nitrogen atoms to accept hydrogen bonds. It is therefore a property of the atomic structure of both the solute and the solvent and can therefore not be accounted for without some atomistic level of description of some part of the solvent environment.

We note that the force field of nile red was parameterised in vacuum and that we cannot rule out that there is a solvent-dependent change in the potential energy surface of the rotation of the 2-diethylamino group in the dye that could be driven by hydrogen bonding interactions between ethanol and the nitrogen labelled N1 in Fig. 1. Thus there is a possibil-

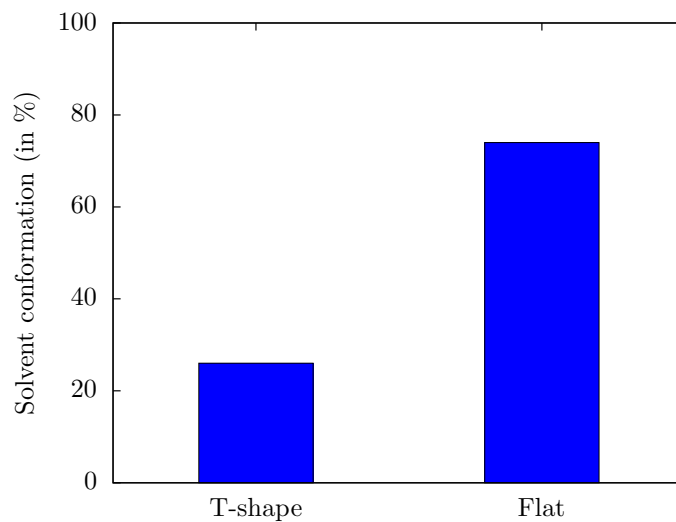


Figure 10: Figure comparing the percentage of occurrence of toluene molecules around nile red in the T-shape and the flat π -stacking conformation.

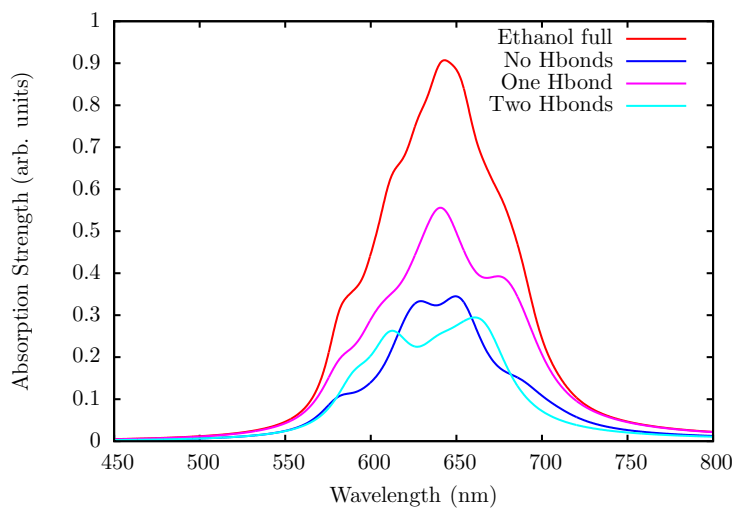


Figure 11: Full absorption spectrum of nile red in ethanol plotted together with spectral contributions due to snapshots containing zero, one or two h-bonds between ethanol molecules and nile red.

ity that a sample of snapshots derived from QM/MM molecular dynamics simulations would show a slightly different distribution of the number of solvent-solute hydrogen bonds compared to the method used in our work. In Fig. 11 we break down the absorption spectrum of nile red in ethanol according its contributions from snapshots containing no, one or two hydrogen bonds between ethanol and nile red respectively. It is evident that while snapshots containing hydrogen bonds do contribute significantly to the broadening of the absorption peak, small changes in the distribution of the number of hydrogen bonds in a given sample of snapshots are unlikely to have a strong effect on the location of the absorption maximum of the dye in solution.

7 Calculated values for $\lambda_{\max}$ for all TDDFT approaches in comparison with experiment

In this work, theoretical spectra are computed in three different approaches: In the implicit solvent model, with the full solvent environment represented by macroscopic solvent properties, the explicit solvent model where large regions of the solvent environment are treated at first principles, and the warped explicit solvent results, where the deficiencies of the semi-local exchange correlation functional in describing the S_1 potential energy surface are corrected for. The calculated spectra allow us to compute $\lambda_{\max}$, the wavelength at which the absorption maximum occurs, for all solvents and models and compare it to the experimental values.² The results can be found in the table 1.

Table 1: Calculated absorption maxima in nm, as compared to experimental data.²

	Implicit	Explicit	Warped	Exp. ²
ethanol	613	640	508	548
acetone	601	620	495	530
toluene	587	591	481	522
<i>n</i> -hexane	582	583	470	484
vacuum	556	556	450	480

8 Experimental data used for colour prediction

The experimental colors reported in this work are directly obtained by using experimental spectra as input to the tristimulus colometry theory procedure. For this purpose, the experimental spectra of nile red in cyclohexane, benzene, acetone and ethanol in the visible region are extracted from the results published by Davis *et. al*²⁰ and are reproduced in Fig. 12.

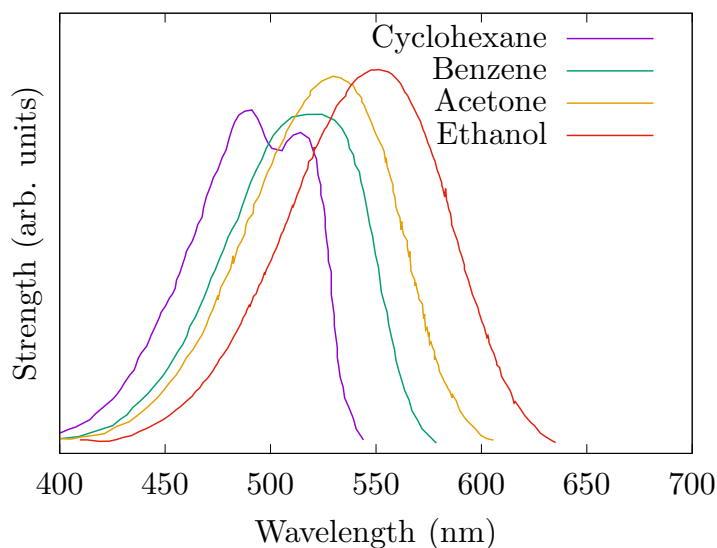


Figure 12: Experimental spectra for Nile Red in four different solvents in the visible region (reproduced with permission from M. M. Davis, and H. B. Helzer, *Anal. Chem.* **38** (3), 451-461 (1966), Copyright 2017 American Chemical Society.)

References

- (1) E. G. McRae, *J. Phys. Chem.* **61** (5), 562-572 (1957).
- (2) J. F. Deye, and T. A. Berger, *Anal. Chem.* **62**, 615-622 (1990).
- (3) A. Y. Freidzon, A. A. Safonov, A. A. Bagaturyants, and M. V. Alfimov, *Int. J. Quantum Chem.* **112**, 3059-3067 (2012).
- (4) G. Singh, A. C. Chamberlin, H. R. Zhekova, S. Y. Noskov, and D. P. Tieleman, *J. Chem. Theory Comput.* **12**, 364-371 (2016).

- (5) A. D. Becke, J. Chem. Phys. **98**, 5648-5652 (1993).
- (6) M. Head-Gordon, J. A. Pople, and M. J. Frisch, Phys. Lett. **153** (6), 503-506 (1988)
- (7) J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
- (8) W. Humphrey, A. Dalke, and D. Schulten, J. Molec. Graphics **14**, 33-38 (1996).
- (9) M. Valiev, E. J. Bylaska, N. Govind, K. Kowalski, T. P. Straatsma *et al.*, Comput. Phys. Commun. **181**, 1477 (2010).
- (10) D. A. Case, T. J. Berryman, R. M. Betz, D. S. Cerutti *et. al.*, AMBER 2015, University of California, San Francisco (2015).
- (11) C.-K. Skylaris, P. D. Haynes, A. A. Mostofi, and M. C. Payne, J. Chem. Phys. **122**, 084119 (2005).
- (12) P. D. Haynes, C.-K. Skylaris, A. A. Mostofi, and M. C. Payne, Psi-k Newsletter **72**, 78-91 (2005).
- (13) A. A. Mostofi, C.-K. Skylaris, P. D. Haynes, and M. C. Payne, Comput. Phys. Commun. **147**, 788-802 (2002).
- (14) T. J. Zuehlsdorff, N. D. M. Hine, J. S. Spencer, N. M. Harrison, D. J. Riley, and P. D. Haynes, J. Chem. Phys. **139**, 064104 (2013).
- (15) L. E. Ratcliff, N. D. M. Hine, and P. D. Haynes, Phys. Rev. B. **84**, 165131 (2011).
- (16) T. J. Zuehlsdorff, *Computing the Optical Properties of Large Systems*; Publisher: Springer International Publishing, Switzerland, 2015; 97-165.
- (17) T. J. Zuehlsdorff, P. D. Haynes, F. Hanke, M. C. Payne, and N. D. M. Hine, J. Chem. Theory Comput. **12** (4), 1853-1861 (2016).

- (18) T. J. Zuehlsdorff, N. D. M. Hine, M. C. Payne, and P. D. Haynes, J. Chem. Phys. **143**, 204107 (2015).
- (19) T. Yanai, D. P. Tew, and N. C. Handy, Chem. Phys. Lett. **393**, 51-57 (2004).
- (20) M. M. Davis, and H. B. Helzer, Anal. Chem. **38** (3), 451-461 (1966).