STUDIES IN NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

A Thesis submitted by

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ABSTRACT

In part 1, the quantum mechanical and semi-empirical methods employed in the calculation of the magnetic shielding of protons are first reviewed.

The magnetic shielding of nuclei due to distant chemical groups may be calculated from the knowledge of the magnetic anisotropy of the bonds in these groups. The reverse procedure, namely, the calculation of the magnetic anisotropy of bonds from NMR relative chemical shifts seems to offer some hope, and has been employed here to estimate the magnetic anisotropy of -C≡C-, -C≡N, and -N≡C triple bonds. The paramagnetic contribution to the shielding of the acetylene proton was estimated from the calculated value of $\Delta\chi^{C\equiv C}$, and from the known geometry of the molecule. The value thus obtained is compared with that calculated by quantum mechanical methods.

We have also shown that electrostatic effects in the case of -C≡N and -N≡C triple bonds are very important in determining the chemical shift of a particular proton.

In part 11, a kinetic analysis of the protolysis reactions of ethyl, diethyl, triethyl, isopropyl, isobutyl, and neopentyl-ammonium ions in aqueous solutions has been carried out using the nuclear magnetic resonance technique. Reaction rates were measured

as a function of the alkylammonium ion concentration and of the hydrogen ion concentration. Detailed informations on the reaction mechanism was obtained by correlating the rate constants obtained from the α-hydrogen, the NH_3^+ , and the H_2O resonances of the NMR spectra.

We have noted in this study, that steric hindrance, electrostatic interactions, and inductive effects play a dominant role in the exchange reactions between the ion and the corresponding base.

NOTE

In this thesis, numbers in paranthesis prefixed by the letter N refer to page number in the experimental note books. Numbers without a prefix refer to the list of references.

All the ultra-violet absorption spectra were determined in ethanol and all melting points are "uncorrected". TMS, refer to tetramethylsilane, and NMR to nuclear magnetic resonance.

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PART 1.

1. INTRODUCTION.

Up to the present time rather little progress has been made in the development of quantitative treatment for the chemical shifts observed in high resolution proton magnetic resonance spectra.

In principle , the shielding of a proton in a molecule can be calculated by quantum mechanical methods. The alternative approach is the development of semiempirical methods which would presumably be suggested by quantum mechanical studies of magnetic shielding of protons in molecules.

In this introductory section , the various quantum mechanical treatments are first reviewed. It is shown that these treatments suggest ways in which the complex problem of proton magnetic shielding can be broken down into simple terms which then form the bases of semiempirical methods. Subsequent sections report attempts to test and apply these semiempirical methods.

QUANTUM MECHANICAL METHODS.

A general theory of nuclear magnetic shielding has been given by Ramsey.[1] He accounts for the effect and calculates its magnitude in the case of molecular hydrogen in terms of the ground and excited-state wave functions of the molecule, using second-order perturbation theory. Unfortunately, it is quite difficult to extend the theory to more complicated molecules, and while a number of approximate calculations have been made, not all of them have been completely successfull.

The variational method has also been employed by several authors,[2,3] and many of them have limited themselves to the case of the proton magnetic shielding in the hydrogen molecule. Applications of the second-order perturbation theory to this problem is possible only if the excited-state wave functions in addition to the ground-state wave functions are available for the molecule in question.

At present, it is very difficult to obtain accurate ground-state wave functions of molecules. Hence, very few direct theoretical calculations of the shielding have been made.

In extending the theory to more complex molecules than

molecular hydrogen , it appears profitable to separate the contributing factors into a number of terms.

Several workers have considered this problem. Saika and Slichter[4] developed a quantitative theory of the atomic contributions to the chemical shifts observed in high resolution fluorine magnetic resonance experiments. They devided the total shielding into three parts:

1. The diamagnetic correction for the atom in question.
2. The paramagnetic correction for the atom in question.
3. The contribution from other atoms.

Pople[5] and McConnell[6] have studied acetylene and benzene respectively , and have indicated how the unusual chemical shifts of their protons can be attributed to calculated magnetic anisotropies.

In order to explain the anomalous chemical shifts of the protons in acetylene and benzene , Pople[5,7] separated the circulations of the electrons in a molecule into three types of circulations:

a. Local diamagnetic circulations.

These circulations involve the <u>1s</u> electrons of the protons and are induced by the applied magnetic field. They produce a secondary magnetic field which opposes the direction

of the applied magnetic field at the proton. The effective field at the nucleus is thus less than the applied field and is given by the relation:

$$H_{eff.} = H_o(1 - \xi)$$

Where, ξ is a constant called the magnetic screening of the nucleus. Diamagnetic currents are a source of positive shielding of the proton.

b. Paramagnetic circulations.

This term corrects for the anisotropy in the magnetic susceptibility of a molecule. Paramagnetic circulations produce a magnetic field which may have a component which is either parallel or anti-parallel to the direction of the applied magnetic field, and is a source of either positive or negative shielding of the protons. This can not occur for an atom in the ground-state, or for a linear molecule in an excited-state if the applied magnetic field is along the axis, but elsewhere such currents may be important.

c. Interatomic diamagnetic currents.

There may be interatomic currents flowing in closed circuits around a molecular path as in the case of the pi-electron system in benzene. This type of current is particularly important in aromatic compounds, and is responsible for the anomalous chemical

shifts of their protons.

For most nuclei the magnitude of the chemical shift of a nucleus is determined particularly by the local circulations around its own atom. Protons are exceptional, however, in that, the total electron density on a hydrogen atom is relatively small, so that circulations in other parts of the molecule will be of comparable importance.

The anomalous positions of the acetylenic and the aromatic protons can be explained by means of these three types of circulations. In the case of acetylene , when the applied magnetic field is coincident with the axis of the molecule , the pi-electron system will circulate within the pi-molecular orbitals around the direction of the applied field, in such a way as to produce a magnetic field opposing the direction of the applied field. Thus , the acetylenic proton, which is along the axis of the molecule , or in the diamagnetic part of the field, will experience a field which is significantly less than the applied field and hence be additionally shielded. On the other hand , when the applied field is perpendicular to the axis of the molecule , the pi-electron system can not circulate within the pi-molecular orbitals and therefore do not contribute to the shielding of the protons . The total contribution

of the pi-electrons to the shielding of a proton is the average over all orientations and will , therefore , be positive. For this reason the acetylenic protons are more shielded than the olefinic protons even though the local diamagnetic contribution is greater for the later.

To explain the relative chemical shifts of the protons of ethylene and benzene , Pople[7] assumed that the magnetic anisotropy of the benzene will allow for this difference. The principle magnetic difference between an open chain system of double bonds and the aromatic system lies in the fact , that , in the aromatic ring an electronic current can flow around a closed conjugated path of relatively large radius. The pi-electrons will circulate around the benzene ring when the magnetic field is applied perpendicular to the plane of the molecule. This will produce a secondary magnetic field which will oppose the direction of the applied field at the centre of the ring and will reinforce the magnetic field near the aromatic protons. This means that the effective magnetic field experienced by the proton will be more than the applied field , and resonance will occur at a lower applied field than otherwise . Pople[7] has calculated the difference in shielding between ethylene and benzene by replacing the ring current by a point dipole located at the

centre of the benzene ring.

Waugh and Fessenden[8] refined the calculation by eliminating the point dipole approximation and by noting that the pi-electron current is not confined to the plane of the benzene ring , but has its maximum density in two regions on either side separated by 0.9 A°. Strong support of this theory is provided by the measurments of polymethylenebenzenes in which the central methylene groups , which lies above the plane of the ring , are more highly shielded than the normal saturated cyclic polymethylenes.

There are many references to quantum mechanical methods used in the calculation of the shielding effects, and explanations for the deviations from the expected shielding as observed in acetylene and simple hydrides.[5] Pople has developed an approximate molecular orbital theory which enables the electronic currents induced by the applied field to be devided up under cirtian conditions into local diamagnetic and paramagnetic circulations about the individual atoms. The method has been applied to the acetylene molecule.

A general quantum mechanical theory of the effect was given by Ramsey.[1] However , his complete formula is not suitable for applications to complex molecules , as it consist of two terms which largely cancel.

The positions of the proton signals in a large number of organic compounds were measured by Meyer , Gutowsky , and Saika.[9] The simplest concept in terms of which these results might be interpreted is the local diamagnetic effect, proportional to the electronic charge on the hydrogen . This could lead to a direct correlation with the ionic character of the C-H bond. There are difficulties in interpreting all the data in this way. The total chemical shift values are too large to be explained by the magnitude of the electron density in the hydrogen orbital. Pople[5] has considered the effect theoretically and has calculated the chemical shifts of the acetylenic protons. In view of the various approximations made , the values obtained could be regarded as an order of magnitude for the effect , but is clearly enough to account for the anomalous positions of acetylene protons. In his quantum mechanical calculations,Pople , has accounted for the chemical shifts of the CH_4 , NH_3 , and HF molecules, and has shown that , there is an increasing paramagnetic effect on the proton resonance frequency , which is in the opposite direction to the electronegativity effect which tends to withdraw electrons from the hydrogen orbital. The calculated shifts are of the correct order of magnitude,

so it seems reasonable to propose that the relatively small variations in the total shift along the series CH_4 , NH_3 , and HF is largely due to the cancelations of these two effects.

The general variational method was applied by Stephen[3] to the problem of calculating the magnetic shielding in molecules. Approximate variational functions together with simple molecular-orbital and valence-bond wave functions were used. Calculations have been made for molecular hydrogen , methane , ethylene , and acetylene. The results for the hydrogen molecule are in good agreement with other reported values. The large numerical values obtained probably arise because of the approximations in using the diamagnetic susceptibility for small distances which rather overestimate the contribution of these electrons to the shielding. It is interesting to note that the shielding of acetylene protons is predicted correctly as lying between the values for CH_4 , and $CH_2{=}CH_2$. In each case Stephen has used a wave function which is symmetric . In the case of the hydrogen molecule , where there are only two electrons , the result using an anti-symmetric wave function was shown to be exactly the same . In more complicated molecules this is not the case. In using this approximation , Stephen has regarded

electrons as completely localised in bonds, and all electron currents induced by the applied magnetic field are considered to be due to electron circulations in the bonds and not extending to other atoms. In view of the results of Stephen and Tillieu[10] this picture does appear to be a good approximation in the molecules CH_4 , $CH_2{=}CH_2$, and $CH{\equiv}CH$.

McGarvey[2] has employed a variational method using the unperturbed ground-state wave function of the molecule to calculate the shielding of the proton in hydrogen and hydrogen halide molecules. Surprisingly good results where obtained in view of the approximations employed in the calculations. The theory developed shows that the shielding depends on the ionic character of the bond , the bond distance , and the number of electrons on the atom to which the hydrogen is bonded.

Marshall and Pople[11] have studied the effect of an electric field on the magnetic shielding of an atom. They showed that the shielding is reduced by the electric field for all directions of the applied magnetic field , and the reduction is greatest if the two fields are perpendicular. This is the simplest problem in which the paramagnetic effect has to be taken into account . This lowering of the screening constant is

only partly due to the paramagnetic term , for the diamagnetic Lamb-type term is also reduced . This corresponds to the partial removal of the electrons from the vicinity of the nucleus by the electric field . The large reduction in the screening constant of protons which are involved in hydrogen bonding is due , in part , to similar effects.[12]

Recently , a theory of proton magnetic shielding has been given by Fixman[13] in which he has used an unsymmetrised product of molecular orbitals to represent the ground-state of a molecule . This method has been applied to the proton magnetic shielding in H_2 , in the C-H bond in CH_4 , $CH_2 = CH_2$, and $CH \equiv CH$, in group VI hydrides (H_2O , H_2S , H_2Se) , and in hydrogen halides (HF , HCl , HBr , and HI). The accuracy of the calculations given by Fixman is well below the precision frequently attained in the experimental determinations of chemical shifts . For other molecules , the conclusions drawn about the position of charge centroids or hybridization from the experimental shielding are in reasonable agreement with other estimates. It seems reasonable to conclude that the formalism extracted from Stephen's variational calculations and the simple wave functions used by Fixman , provide a reliable

and usefull basis for semiquantitative discussion of proton magnetic shielding. The most important result one can obtain from calculations of this sort is the demonstration of those features in the bonding which have the greatest influence on the magnitude of the shielding . In the hydrogen halides , the bond distsnce and the ionic character,have pronounced effect on the value of the diamagnetic and the second-order paramagnetic terms. The effect of the bond distance on the two terms is similar , so that the net shielding appears to be independent of the bond distance in the hydrogen halides and gives the appearance that the ionic character is the only important parameter in the system . McGarvey showed that in the case of multiatomic systems , the shielding will depend to a small extend on the ionic character of other bonds involving the atom to which the hydrogen is bonded . McGarvey's calculations for the compounds involving group Vl elements demonstrated this effect . Although this effect is not too large,changes in the ionic character of adjacent bonds are probably the main cause of many small chemical shifts that are observed.

SEMIEMPIRICAL METHODS.

In this section all the empirical approaches to the problem of chemical shifts are reviewed ,and it is shown how some of the terms come from the last section , and some are suggested by the electronic theory of organic chemistry.

Several workers have attempted to express the chemical shifts observed in high resolution proton magnetic resonance spectra as a summation of terms which contribute to the chemical shift .

Heel and Zeil[14] have suggested an equation of the form :

$$\xi = a + b + c + d \qquad (1)$$

Where , a , is the diamagnetic shielding due to the electrons around the nucleus itself . This corresponds to Pople's local diamagnetic term , or the Lamb term of Ramsey if the origin is the nucleus . b , is the bulk diamagnetic correction for the substance under invistigation and is eliminated by proper choice of the experimental conditions. c , is the shift due to the anisotropy of the atom or group of atoms . This last term is analogous to the paramagnetic term , and

and to Pople's interatomic diamagnetic term , and this depends on the geometry of the molecule and the anisotropy in the magnetic susceptibility of the bond or group (Long-range shielding) . d , is the shift due to the van der Waals forces.

Later , Cavanaugh and Daily[15] suggested that an equation of the following form:

$$\xi n = \xi ed + \xi ep + \xi an \qquad (2)$$

might be found to describe the behaviour of chemical shifts in related series of molecules . This is similar to Eq.(1) but neglects the term involving interatomic van der Waals forces. Here , ξed , is a term proportional to the electron density and therefore to the effective nuclear charge of the atom to which the proton is bonded ; ξep , is the paramagnetic term involving electrons surroundind the nucleus ; ξep , includes terms arising from second-order paramagnetic term in the Ramsey equation ; ξan , is the long-range shielding term dependent on the anisotropy of neighboring groups . It corresponds to Pople's neighboring paramagnetic and interatomic diamagnetic terms . The local paramagnetic contribution ξep ,

to hydrogen is generally thought to be small and it will be considered latter in relation to Pople and Marshall's theory relating to the effect of an electric field on proton shielding. The neighboring contribution to ξ_{ep} is very important and is dealt with in some detail below. In Eq.(2) , it is assumed that ring current effects for alkyl shains are negligible.

A number of attempts have been made to fit an equation of the last form to data obtained for a series of molecules. In cirtain cases correlations have been made between the chemical shift and electron densities , thus emphasising the role of the first term in the equation , and showing the effect of electronegativity of the substituent on the chemical shifts of the protons in the molecules. The more tightly the electrons are held by another atom chemically bonded to the nucleus , the less effective they are in shielding the nucleus , so that the shielding should be effected by the degree of ionic character of the bond and by inductive and resonance donation or withdrawals of electrons by neighboring groups . The effect of the electron withdrawing groups , which tend to cause chemical shifts

to lower fields , was demonstrated for F^{19} resonance by Gutowsky , McCall , McGarvey , and Meyer[16] ; and by Meyer and Gutowsky[17] who obtained definite correlations between resonance line positions and Hammett's ξ-constant in a large number of substituted fluorobenzenes. A similar study was made for the proton resonance in an early study of ethyl derivatives by Shoolery[18] and in an extensive collection of simple organic compounds by Meyer, Saika and Gutowsky.[9]

Daily and Shoolery[19] have shown the direct dependence of the proton chemical shift as measured in benzene solution of the methyl derivatives and the internal chemical shift of the ethyl derivatives on the electronegativity of the substituent.

The methyl derivatives shift as measured at infinite dilution in carbon tetrachloride has also been shown by Allerd and Rochow[20] to correlate with the electronegativity of the substituent . However , cases in which there is this agreement appears to be small in number.

In a study of the chemical shifts in a series of methyl , ethyl , propyl , and isopropyl derivatives, Cavanaugh

and Daily[15] have attempted to determine the distance and the angular dependence of any contribution to the chemical shift arising from magnetically anisotropic substituent group . They found that the electron withdrawal effects play a major role in determining the chemical shifts for methyl derivatives. The linear relation of the methyl shifts with electronegativity for the methyl halides seems to cancel any large influence due to magnetic anisotropy . The ethyl shifts were found to be determined by electron withdrawal effects and a factor which acted equally at the α- and β-positions . They found that this factor arises from the carbon-carbon single bonds.

The contributions to ξed first discussed are assumed to be inductive in origin . However , the possibility of electric polarization of an X-H bond by direct electrostatic interactions through space with neighboring poles and dipoles requires consideration. A treatment of this problem has been given by Buckingham.[21] In some bonds the centre of negative charge on the electrons and of positive charge on the nuclei do not coincide and such bonds are known as polar bonds , and are accompanied with a constant dipole moment . Buckingham has shown that molecules containing polar bonds produce an electric

field at a particular nucleus and this leads to chemical shifts proportional to the first power of the field strength . It has been shown that a field along the X-H bond draws the electrons in the enriched region between the nuclei away from the proton, thus causing its resonance to occur at lower fieldstrengths ; while a field in the H-X direction leads to resonance at higher fields . The electric field produced by the polarization of neighbouring solvent molecules may also be important and may lead to solvent shift related to the dielectric constant of the solvent . The direction of this field could be easily estimated when the molecule is rigid and the model is usefull in assigning bands in spectra . Buckingham has shown that these effects give a reasonably accurate account of the observed spectra of substituted benzenes and of some solvent effects on the proton resonances of cis-and trans-1,2-dichloroethane . If the nucleus under consideration is not at a molecular centre of inversion , the shielding for a fixed orientation may be effected by a reversal of the electric field , so that for weak fields the screening constant ,ζ, is proportional to E_z rather than E_z^2 , where , E_z^2 is the component of the electric field along the direction of the bond . If E_z is a

fixed external field , the screening constant proportional to E_z averages to zero in a gas or liquid. But if E_z arises from a polar group within the molecule itself , or from neighbouring solvent molecules polarised by the solute , then the mean value of E_z at a particular nucleus will be non-zero . A screening constant proportional to E_z in addition to one proportional to E_z^2 is possible .

The proton magnetic shielding represent a difficult problem. Because of the low nuclear charge of the proton , the associated fields will be small , since only a few electrons can be localised close to a given proton in a molecule. For this reason long-range effects (i.e. the term ξan), due to magnetically anisotropic groups relatively far removed from the protons , can make significant shielding contribution . Certainly , the absence of a smooth correlation between proton acidity and proton shielding suggests this possibility .[7,9] A shielding will be considered to be long-range if it originates from electrons which are not involved in the bonding of the proton to the molecule .

McConnell[6] has derived a quantum mechanical expression for calculating the chemical shifts due to long-range bonds

or groups. The equation expresses the chemical shift as a function of the geometry of the molecule and the diamagnetic anisotropy of the electronic distribution situated further away from the proton under consideration. The equation derived by McConnell for an axially symmetric bond appears in the form:

$$\xi_N^G = \Delta\chi^G(1 - 3\cos\theta z^2)/3LoR^3 \qquad (3)$$

Where, R, is the radius vector for the proton, or the line joining the proton to the centre of gravity of the group G; θz, is the angle between R and the symmetry axis of the bond(usually the bond axis itself). The scalar $\Delta\chi^G = \chi_L^G - \chi_T^G$, where, the scalars χ_L^G and χ_T^G are the average of the susceptibility components parallel and perpendicular to the symmetry axis.

This theory has been extended by Narasimhan and Rogers[22] to the three dimentional case, where, all the three principal magnetic susceptibilities are different. These workers have also derived expressions for the case of a rotating methyl group, in which the shielding is averaged over all possible orientations. They have applied this theory to the calculation of the magnetic anisotropy of the C=O bond from the internal chemical shift between the protons which are <u>cis</u>- and <u>trans</u>- with respect to the C=O bond in acetamide and similarly the internal chemical shift between the two N-methyl groups in dimethylacetamide.

The theory of McConnell for long-range proton shielding appears capable of fairly general applicability ,although it is not very well suited to quantitative calculations of aromatic proton shieldings , since it has been developed only to the extent that the shielding fields are approximated by dipolar fields .

Quantitative applications of the shielding equation due to the magnetic anisotropy of a long-range bond in a molecule suffer from two very important difficulties . The first difficulty is that the shielding of a proton is a function of the anisotropy in the magnetic susceptibility of the group G , and only very few data for the magnetic anisotropies of bonds are known . The second difficulty is that R appears in the equation as R^{-3} , so that with decreasing R , the shielding becomes larger and more important , and the dipolar approximation becomes less and less accurate.

The present work represents an attempt to investigate the role of the neighbor-anisotropy effect , and calculate the electrostatic effects due to electric fields at a particular nucleus arising from polar groups in other parts of the molecule.

From the relative chemical shifts and the known molecular geometries , we determine the anisotropy in the magnetic susceptibilities of the C≡C , C≡N , and N≡C triple bonds based on the McConnell dipolar expression . In doing so , we have shown experimentally that long-range shielding does exist and that it is correctly explained to lower order of accuracy by the McConnell expression . We have also showed that the electrostatic effects in the case of C≡N , and N≡C triple bonds are very important in determining the chemical shift of a particular proton.

11. REVIEW OF PROTON MAGNETIC RESONANCE STUDIES OF ACETYLENES, CYANIDES, AND ISOCYANIDES.

Most of the work which has been reported in the literature on compounds containing the three groups, $C\equiv C$, $C\equiv N$, and $N\equiv C$, concerns studies of the effects of solvents on the resonance frequencies of protons in molecules possessing these groups . Since for all, but small molecules , measurments of chemical shifts must be made on solutions , this work will now be considered in detail .

Early work relating to NMR solvent effects has been discussed by Pople , Schneider , and Bernstein .[23] Bothner-By and Glick ,[24] and Zimmermann and Foster[25] examined the effects of aromatic solutes and solvents , and have shown that an environment of aromatic molecules tends to lead to an increased solute screening constant .

Buckingham , Schaefer , and Bernstein,[26] have studied the problem of solvent effects in greater detail and have divided the screening constant due to solvents into four different contributions as follows :

$$\xi solvent = \xi b + \xi a + \xi w + \xi E \qquad (4)$$

Where, ξb is the contribution to ξ proportional to the bulk susceptibility of the medium; ξa arises from anisotropy in the molecular susceptibility of the solvent molecules; ξw is due to the van der Waals forces between the solute and solvent; and ξE is the polar effect caused by the charge distributions in the neighbouring solvent molecules , contributing an electric field E acting on the solute and thereby perturbing its electronic structure , and hence the nuclear screening constant. They have found that ξb and ξw are negative (that is , they lead to resonance at lower applied field strength), ξa is positive for disc-shaped solvents (like benzene), and negative for rod-shaped ones (like carbon disulphide) ; while ξE can be either positive or negative depending on the position of the nucleus relative to the polar groups in the solute molecules .[21]

The chemical shifts of the acetylenic hydrogen in monosubstituted acetylenes have been recorded in a variety of solvents by Hatton and Richards .[27] They have shown that some

solvents cause the acetylenic proton resonance to shift to lower applied field , while others produce a high-field shift. The chemical shift of the acetylenic proton resonance in propargyl chloride , phenylacetylene , and benzoylacetylene were measured over a range of concentrations in different solvents . The shifts were extrapolated to infinite dilution of the acetylenes . It was shown that the acetylenic resonance of propargyl chloride and phenylacetylene exibited small negative shifts in the pure liquids. The shifts may be produced by the anisotropic effects of the medium in the pure acetylene.

Hatton and Richards have divided the solvents into two classes , those which cause the acetylenic resonance to shift to lower applied fields , and others which produce high-field shifts . Solvents of the first class contain strongly electronegative groups which can act as proton acceptors. They have discussed the low field shifts produced by these solvents in terms of the formation of weak hydrogen bonds. When the hydrogen bond is formed , the acetylenic proton experiences a strong electric field from the electronegative

group ; diamagnetic circulations around the hydrogen atom are inhibited , and the resonance shifts to lower applied fields.These workers have pointed out that these shifts cannot be regarded as a simple measure of the strength of the associates , because of the many contributing factors of which , the magnetic anisotropy of the solvent is a very important effect.

Whipple , Goldstein , Mandel , Reddy , and McClure[28] have studied the effects of various solvents on the spectra of propargyl halides . They have observed that the relative intramolecular shielding for compounds in the liquid state is complicated by the high sensitivity of the NMR shifts toward environmental medium shifts.[29]

Whipple , Goldstein , and Steward[30] have determined the NMR spectra of the protons in allene and methylacetylene both in the vapor phase and at high dilution in innert solvents. Differences in shifts between vapor and solvent are used to measure the medium effects in the solution state , and indicate a non-vanishing but approximately constant medium shifts for

several proton types .

From the foregoing review , we have seen that the NMR spectra are very sensitive to solvent effects . The chemical shift should ideally be determined in the vapor phase . Accurate chemical shifts in solvents such as carbon tetrachloride and chloroform and extrapolated to infinite dilution, are considered as fairly approximate to measurments in an ideal solvent , whose influence on the chemical shift of the solute is negligible.

In the remaining part of this section , work on the shielding of protons and the attempts to calculate the magnetic anisotropy of the C≡C bond will be discussed .

During the course , when the present work was in progress , a paper was published by Heel and Zeil,[14] in which they have prepared a series of simple acetylenic derivatives and have examined their NMR spectra , at infinite dilution in carbon tetrachloride . Their results represents an extensive approach to the problem of calculating the diamagnetic anisotropy of the C≡C bond . They have set up equations relating the

chemical shift of a particular proton to different parameters involved in the shielding of a nucleus as was shown on page 13.

Recently , Reddy , Mandell , and Goldstein [31] have prepared propargyl cyanide and have examined its NMR spectrum. They have calculated the diamagnetic shielding of all the protons in the molecule due to both the C≡C , and C≡N ,triple bonds . The value of the diamagnetic anisotropy of the C≡C bond has been calculated by Whipple[32] and the same value was adopted for the C≡N triple bond .

Complete analysis of the NMR spectra of acrylonitrile and α-D-acrylonitrile were carried out by Reddy , Goldstein , and Mandell .[33] The shifts and the coupling constants were determined at infinite dilution in tetramethylsilane (TMS) which also served as an internal reference . They have shown that the diamagnetic anisotropy of the C≡N bond give rise to additional shielding on all the protons in the molecule , and corrections to this will bring the protons to lower applied field.

Several workers have analysed the spectrum of acrylonitrile.[33-36] The results of Banwell and Sheppard[34] are different from that of Reddy , Goldstein , and Mandell[33] and Brugel,[35] in that , the two protons at the β-position have been interchanged . There are also some variations in the values of the chemical shifts of the three protons.

The NMR spectrum of acrylonitrile was considered above in great detail because of its importance in the calculation of the diamagnetic anisotropy of the C≡N bond . The most reliable analysis of acrylonitrile is that of Castellano and Waugh .[36] They find two sets of coupling constants , both of which would be accepted as reasonable if reached by the usual iterative method . They suggest that a final decision be made by running the spectrum in a magnetic field strength considerably different from the one they use . Our results on the analysis of the spectrum of acrylonitrile will be presented later .

111. EXPERIMENTAL.

p-Tolylacetylene.[37] (N 31-33).

p-Methylacetophenone (15g.) was added slowly (1hr.) to solid phosphorus pentachloride (20g.) at 0° . The reaction mixture was allowed to stand for 1hr. at 0°, and then 12hrs. at room temperature . Removal of the phosphorus oxychloride under reduced pressure and distillation of the residue afforded α-chloro-p-methylstyrene (12g. ; 68 %), b.p. 92-4°/13mm.; n_D^{25} 1.5139.

The above chloroethylene (9g.) was refluxed for 24 hrs. with potassium hydroxide (50g.), in dry ethanol(100ml.). The reaction mixture was poured into ice-water (250ml.). The oil was separated and the aqueous layer extracted with ether. The oil and the ethereal extracts were combined together and dried ($MgSO_4$) . Removal of the solvent and distillation of the residue gave p-tolylacetylene (4.46g. ; 65 %) , as a colourless oil, b.p. 68°/23mm. , n_D^{25} 1.5441 . $\lambda_{max.}$ (in ethanol), 250mμ , 240mμ , (ϵ , 13,100 ; 13,400).
(Found:C,92.53;H,7.48. Calc.for C_9H_8: C,93.05;H,6.94 %).

o-Tolylacetylene[40] (N 20).

A solution of methyl lithium[39] (from 2.4g. of lithium and 23g. methyl iodide , estimated titrimetrically to 0.67 N) in ether (175ml.) , was added to o-toluic acid (4g.) in ether (150ml.) , under an atmosphere of nitrogen . A vigorous reaction took place . After the addition was complete , the solution was then refluxed for ½hr. After cooling to room temperature , water was slowly added .The aqueous alkaline layer containing the lithium salt of the unreacted acid was removed , and the ethereal layer washed three times with water . Removal of the solvent from the dried extract ($MgSO_4$) , and distillation of the product furnished o-methylacetophenone[38] (3.7g. ; 94.5 %) , b.p. 104-5°/20mm. , n_D^{25} 1.5434.

o-Methylacetophenone (3.7g.) was added during ½hr. under vigorous stirring to phosphorus pentachloride (4.8g.). when addition was complete , the mixture was refluxed for 2hrs. at 60° , after which time phosphorus oxychloride was removed at 60° under vacuum.

The above chloride (5.5g.) was added to a stirred mixture of dried , powdered , potassium hydroxide (4.9g.) , and absolute ethanol (2.5ml.) at 125°. When addition was complete , the reaction mixture was kept at this temperature with continuous stirring for 2½hr. The reaction mixture was cooled to room temperature , water (80ml.) was added , boiled once , and cooled again . The product was extracted with ether , dried (KOH) , and distilled . o-Tolylacetylene (1.6g. ;46.5%) had , b.p. 54-6°/14mm. , n_D^{25} 1.5436 , $\lambda_{max.}$ 243,238mμ .
(Found:C,92.91;H,6.97 . C_9H_8 requires C,93.05;H,6.94 %)

Mesitylenic acid.[41] (N 60).

This acid was prepared by the method described by Zaugg and Rapala[41]. Mesitylene (160g.) , water (500ml.) , and concentrated nitric acid (320ml.), were heated under reflux at 145-155° for 26hrs. (This was found to be the optimum time needed for completion of the reaction). The hot mixture was poured onto ice (400g.) and the solid product was filtered ,

mixed with water and steam distilled . The distillate was ether extracted , dried ($MgSO_4$) , and the solvent removed . The solid residue was recrystallised from ethanol to give mesitylenic acid (14g.) , m.p. 168-170.

3,5-Dimethylacetophenone.[42] (N 63).

This ketone was prepared by the method described by Tagner[39] for the preparation of methyl ketones from the free acid. A solution of methyl lithium (from 4.8g. of lithium and methyl iodide 46g. in ether , 350ml.) , was added to a solution of mesitylenic acid (7.5g.) , in ether (300ml.) , under an atmosphere of nitrogen . The product was hydrolysed with water , extracted with ether , and dried ($MgSO_4$) . Removal of the solvent and distillation of the residue gave 3,5-dimethylacetophenone (7g. ; 93.3 %) , b.p. 100-2°/23mm. , n_D^{25} 1.5205 .(lit.[42] n_D^{25} 1.5276.).

3,5-Dimethylphenylacetylene (N 64).

This acetylene was prepared for the first time by the same method as that used for the preparation of o-tolylacetylene.[40] 3,5-Dimethylacetophenone (6.5g.) was added to phosphorus pentachloride (13 g.) . The chloro-compound was added to potassium hydroxide (25g.) at 125° . The reaction mixture was hydrolysed , ether extracted , dried (KOH) , and distilled .The product (3 g. ; 51.7 %) , had b.p. 64-5°/23mm., n_D^{25} 1.5137 , $\lambda_{max.}$ 249mμ .
(Found : C,92.12;H,7.52 ; $C_{10}H_{10}$ requires , C,92.25,H,7.75 %).

3,5-Dimethylbenzonitrile (N 69).

Mesitylenic acid (5g.) was mixed with phosphorus pentachloride (10g.) and heated at 60° for 2hrs. Phosphorus oxychloride was distilled off , and the resulting acid chloride was added to ice-cold ammonia . The amide separated immediately. It was filtered, washed with dilute ammonia , and recrystallised from water when it had m.p. 150-151°.

3,5-Dimethylbenzamide (1.7g.) was suspended in dry pyridine (25ml.) for 24hrs. Carbonyl chloride was bubbled into the rapidly stirred suspension .[44] The temperature was maintained at 65-70° by control of the gas and by external cooling . (Using small quantities of the amide , it is necessary to warm the flask with a hot water bath). When the reaction was complete (ca. 1hr.) , water was added slowly , the mixture was acidified with concentrated hydrochloric acid (Congo red) , and continuously extracted with ether for 72hrs. Removal of the solvent from the dried ($MgSO_4$) extract and subsequent distillation of the residue furnished 3,5-dimethylbenzonitrile (1.3g.;86.7%) , b.p. 108-9°/15mm.; m.p.51°.

(Found: C,82.5;H,6.84;N,10.7, C_9H_9N requires ,C,82.24;H,6.89;N,10.87%)

3,5-Dimethylaniline (sym-xylidine) (N 71).

This amine was prepared as described by Herbert and Adams .[45] To a solution of sodium hydroxide (19g.), water(80ml.) cooled to 5° , was added bromine (18g.). 3,5-Dimethylbenzamide (7g.) was made into a paste with a solution of sodium hydroxide(10%),

and was added to the hypobromite solution . The reaction mixture was steam distilled , the distillate was ether extracted , dried ($MgSO_4$) , and distilled . The product , 3,5-dimethylaniline (3.9g.; 70 %) , had b.p. 221°/760mm., n_D^{25} 1.5580. (lit.[42] n_D^{25} 1.5581).

o-Tolylisocyanide[46] (N 152).

o-Toluidine (53.5g.) , chloroform (13ml.) , and methyl alcohol (20ml.) , were heated nearly to boiling . Powdered sodium hydroxide (3g.) was added and the mixture started boiling gently. When the reaction was nearly over , a mixture of chloroform (40ml.), methyl alcohol (60ml.) , and powdered sodium hydroxide (60g.), was added . The reaction mixture was filtered , the salt washed with ether , the solvent removed , and the residue steam distilled. The distillate was ether extracted , washed with sulphuric acid (1:10), sodium carbonate , and water respectively . Removal of the solvent from the dried extract (KOH), and sublimation of the residue at high vacuum at ordinary temperature gave o-tolylisocyanide (40g.;70 %) , b.p.30-2°/0.5mm., n_D^{25} 1.5260.

p-Tolylisocyanide (N 160).

This isocyanide was prepared by the same general procedure described above. p-Tolylisocyanide was obtained as a colourless oil b.p. 40-1°/0.5mm., n_D^{25} 1.5246.

3,5-Dimethylbenzoisocyanide (N 162).

The method adopted for the preparation of o-and p-tolyl-isocyanide was used in this case as well . 3,5-Dimethylbenzoisocyanide was obtained as a colourless oil , b.p.40-1°/0.5mm., n_D^{25} 1.5243.

Endo-cis-bicyclo-(2:2:1)-hept-5ene-2,3-dicarbonitrile(N 191-4).[47]

Maleamide (8g.) was suspended in dry pyridine (125ml.), and carbonyl chloride was bubbled into the rapidly stirred suspension for 2 hr. at 65-70° . The mixture was poured onto ice , acidified with concentrated hydrochloric acid (Congo red), continuously extracted with ether , and dried ($MgSO_4$). Removal of the solvent and distillation of the residue furnished maleonitrile

(6.1g. ; 85%) , b.p.69-70°/14mm., m.p. 31°.

Freshly distilled cyclopentadiene (6.6g.) was added slowly to a cooled solution (0°) of maleonitrile (7.8g.) in absolute ethanol (50ml.). The reaction mixture was kept at room temperature for 12 hrs. Removal of the solvent and recrystallization of the residue from absolute ethanol gave endo-cis-bicyclo-(2:2:1)-hept-5ene-2,3-dicarbonitrile (14g. ; 98.5 %) , m.p. 158-9°.
(Found: C,74.78;H,5.63;N,20.26. Calc.for $C_9H_8N_2$,C,75;H,5.55; N,19.45 %).
Trans-bicyclo-(2:2:1)-hept-5-ene-2,3-dicarbonitrile[47](N 103-104).

Fumaronitrile was prepared by the same method described for maleonitrile. Freshly distilled cyclopentadiene (6.6g.) was added slowly to a cooled (0°) solution of fumaronitrile (7.8g.) in absolute ethanol (50ml.) . The reaction mixture was kept at room temperature for 12 hrs. Removal of the solvent and recrystallization of the residue from absolute ethanol afforded trans-bicyclo-(2:2:1)-hept-5-ene-2,3-dicarbonitrile (14g. ; 97 %),m.p.96-7°
(lit.[47]m.p. 95°).
(Found:C,74.56;H,6.09;N,19.42.Calc.for $C_9H_8N_2$,C,75;H,5.55;N,19.45).

Endo-bicyclo-(2:2:1)-hept-5-ene-2-carbonitrile[48](N 108).

This cyanide was prepared as described by Herman and Bruson[48]. Acrylonitrile (26.5g.) was added dropwise to freshly distilled cyclopentadiene (33g.) . After standing for 10 minutes, the reaction mixture began to boil , and lasted for about ½ hr. Distillation gave endo-bicyclo-(2:2:1)-hept-5-ene-2-carbonitrile (58g. ; 97.7 %) , b.p.85-6°/20mm., n_D^{25} 1.4865.(lit.,[48] n_D^{25}1.4863). (Found:C,80.46;H,7.94;N,11.61.Calc.for C_8H_9N,C,80.19;H,8.11;N,11.69).

4-Methylpent-3-ene-1-yne[49](N 166).

A mixture of propargyl bromide (48g.) , dry acetone (30ml.) , and anhydrous ether (50ml.), was added to zinc wool (28g.) . The solution was heated gently , a clear brown solution was finally obtained . Hydrolysis of the product ,ether extraction , drying ($MgSO_4$) , removal of the solvent and distillation of the residue gave 4-methylpent-1-yne-4-ol (22g. ; 71 %) , b.p.120-2°/755mm. , n_D^{25} 1.4350 .

Phosphorus oxychloride (20g.) in pyridine (40ml.) was added during ½ hr. to a stirred mixture of the above alcohol (16g.) in pyridine (40ml.) at 0°. The mixture was stirred for ½ hr., ether extraction ,drying , removal of the solvent , and subsequent distillation of the residue gave 4-methylpent-3-ene-1-yne (4.5g. ; 31.7 %) , b.p.73-4°/765mm., n_D^{25} 1.4384. The acetylene was purified through its mercury salt, m.p.162°.

Ethylisocyanide (N 224).

This isocyanide was prepared as described by Hammick, New , Sidgwick , and Sutton .[46] Ethylisocyanide was obtained as colourless liquid , b.p. 79-80°/760mm. , n^{25} 1.3655.

Bicyclo-(2:2:1)-hept-2,5-diene-2,3-dicarbonitrile (N 253-255).

Acetylenedicarboxylic acid was prepared according to the procedure given by Abbott , Arnold , and Thompson .[50] The acid (100g.) was heated with absolute methyl alcohol (200ml.) ,

sodium dried benzene (300ml.) , and concentrated sulphuric acid (16ml.) , for 12hrs. The reaction mixture was poured into excess water (2-3 volumes) , and the benzene layer separated , washed with a saturated solution of sodium carbonate , water , and dried ($MgSO_4$) . Removal of the solvent and distillation of the residue furnished , dimethylacetylenedicarboxylate (87g.; 85.5%), b.p. 98°/20mm.

Dimethyl acetylenedicarboxylate (25g.), was added slowly to freshly distilled cyclopentadiene (16.4ml.) , at 0° C. The reaction mixture was kept at room temperature for 12hrs. The resulting impure adduct was added to a concentrated ammonia solution (200ml.), and the mixture stirred for 8hrs. The precipitated diamide was filtered , washed with cold water . Recrystallization of the product from absolute ethanol furnished bicyclo-(2:2:1)--hept-2,5-diene-2,3-dicarboxylic amide (25g. ; 83 %), m.p. 218--219° . (lit.,[47] m.p. 211-212).

The above diamide (7.9g.) was suspended in dry pyridine (125ml.) , and carbonyl chloride was bubbled into the rapidly stirred suspension for 1hr. at 65-70°. When the reaction was complete

concentrated hydrochloric acid was added (Congo red), and the cherry red solution was continuously extracted with ether for 72 hrs. Removal of the solvent from the dried extract($MgSO_4$), and recrystallization of the residue gave bicyclo-(2:2:1)-hept-2,5-diene-2,3-dicarbonitrile (3.5g.; 55.5 %), m.p. 41-2°.

Endo-bicyclo-(2:2:1)-hept-2,3-dicarbonitrile (N 260).

Freshly distilled cyclopentadiene(6.6g.), was added slowly to a cooled solution of maleamide (11.2g.), in absolute ethanol (100ml.). The mixture was kept at room temperature for 12hrs. Removal of the solvent and recrystallization of the residue from absolute ethanol furnished endo-bicyclo-(2:2:1)-hept-5-ene-2,3-dicarboxylic amide (15g. ; 84.5 %), m.p.210-11°,

To a solution of the above diamide (6g.), in ethanol (80ml.), placed in a hydrogenation apparatus was added Adam's catalyst (40mg.). The mixture was stirred at room temperature untill the uptake of hydrogen had ceased. The catalyst was removed by filteration through a layer of charcoal, and the alcohol was distilled off. Recrystallization of the residue from absolute ethanol

afforded , endo-bicyclo-(2:2:1)-hept-2,3-dicarboxylic amide (5.8g.; 95 %), m.p. 199-200°.

Phosphorus oxychloride (6.5g.) , was added during ½hr. to a suspension of the above diamide (5.8g.) , in pyridine (27ml.) at 50-55° . On heating to 70° , a spontaneous temperature rise occur , after which the mixture was maintained at 70-80° for 3hrs. The reaction mixture was cooled , poured onto ice-cold hydrochloric acid , and filtered . The filterate was continuously extracted with ether for 72hrs. , and dried ($MgSO_4$). Removal of the solvent and crystallization of the residue from absolute ethanol gave endo-bicyclo-(2:2:1)-hept-2,3-dicarbonitrile (3.2g. ; 72 %), m.p. 144-145° .

(Found:C,73.72;H,6.83;N,19.36.$C_9H_{10}N_2$requires,C,74;H,6.85;N,19.25 %).

3-Exo-methyl-bicyclo-2:2:1)-hept-5-ene-2-carbonitrile (211-212).

Crotonamide (13g.) was suspended in dry pyridine (130ml.), and carbonyl chloride was bubbled through the rapidly stirred suspension The mixture was poured onto ice , and acidified with concentrated hydrochloric acid (Congo red), and continuously extracted with

with ether . Removal of the solvent from the dried extract ($MgSO_4$), and distillation of the residue afforded crotononitrile (9.6g.;89%), b.p.118-119°/760mm.

Freshly distilled cyclopentadiene (6.6g.) , was added to crotononitrile (8.3g.) at 0°C. The reaction mixture was kept at room temperature for 12hrs. Distillation of the residue gave 3-~~endo~~ exo-methyl-bicyclo-(2:2:1)-hept-5-ene-2-carbonitrile (9.2g.;62%), b.p.68-9°/20mm., n_D^{25} 1.4020.

(Found:C,73.2;H,7.36;N,19.24.$C_9H_{11}N$ requires, C,73.5;H,7.5;N,19.0 %).

THE NMR SPECTROMETER.

The measurements were made on a Varian Associates high-resolution spectrometer, operating at a fixed frequency of 56.45 Mc/s. The measurements of the NMR spectra of the bicyclo-compounds were made at 60Mc/s. The frequency separations between lines were measured using the usual audio-modulation side-band technique. The chemical shifts were measured with respect to tetramethylsilane (TMS), used as an internal standard and are quoted as τ-values.[61] All τ-values which were employed in the calculations are the average of four determinations and are accurate to ± 0.6 c/s.

Table 1. The chemical shift of all identifiable protons in compounds 1-1X. (Measured in τ-values at 56.45 Mc/s, relative to TMS as an internal standard).

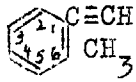
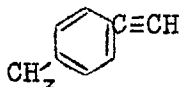
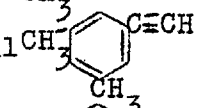
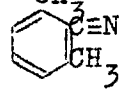
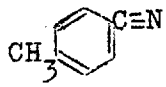
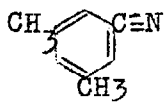
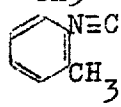
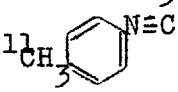
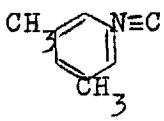
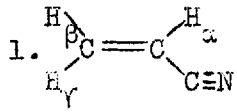
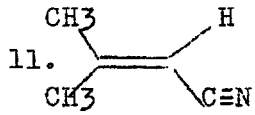
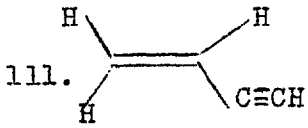
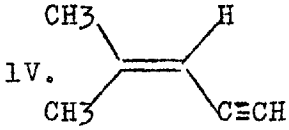
	Compound	CH_3	H-2	H-3	H-4	H-5	≡CH
1.		7.578					6.90
11		7.690	2.804	2.896			7.13
111		7.725	3.25		3.071		6.655
1V		7.485					
V		7.590	2.531	2.769			
V1		7.627	2.817	2.817	2.817	2.817	
V11		7.622	2.817	"	"	"	
V111		7.655	2.900	2.900			
1X		7.752	3.007	2.989			

Table 11. The chemical shift of all identifiable protons in compounds I-VII. (Measured in τ-values at 56.45 Mc/s, relative to TMS as an internal standard).

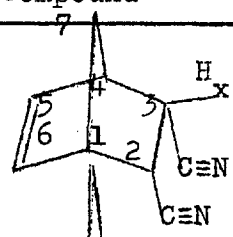
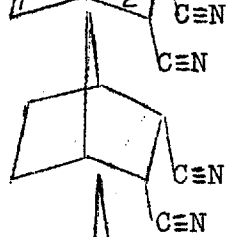
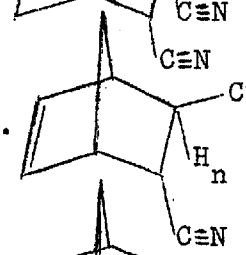
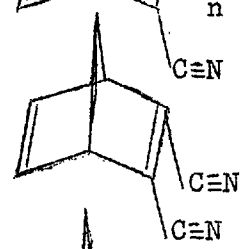
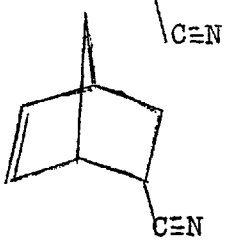
Compound	α-H	β-H(or CH_3)	γ-H(or CH_3)	$(\xi_T^\beta - \xi_T^\gamma) \times 10^{-6}$
I. 	4.525	4.215	4.03	0.1775
II. 	4.892	7.630	8.063	0.433
III. 				0.180[x]
IV. 	4.830	8.18or8.11	8.11or8.18	0.07
V. $\overset{\gamma}{C}H_3\overset{\beta}{C}H_2C\equiv CH$		8.1	9.04	0.94[†]
VI. $CH_3CH_2C\equiv N$		7.00	8.040	1.04[*]
VII. $CH_3CH_2N\equiv C$		7.19	8.775	1.585

x Reference 58.

† " 14.

* " 15.

Table III. The chemical shifts of all identifiable protons in compounds I-V. (Measured in τ-values at 60 Mc/s, relative to TMS as an internal standard.

Compound	Olefinic	Bridgehead	H_x(exo)	H_n(endo)	C_7-H_2
I. 	3.50	6.67	6.575		8.67,8.37
II. 	(C-5,6) 8.21	7.33	6.82		8.44
III. 	3.517	6.60	7.485	6.83	8.31,8.27
IV. 	3.02	5.93			7.627
V. 		7.03,6.86			

3. CALCULATIONS.

Introduction.

In the following section, the methods used in calculating the diamagnetic anisotropies of bonds, and the magnetic shielding of protons are discussed.In order to do this systematically, this section is devided into three parts:

(1). Diamagnetic anisotropy.

(2). Electrostatic effects.

(3). Electronegativity effects.

1. DIAMAGNETIC ANISOTROPY.

As we have seen in the introduction, the magnetic shielding ξ, of a proton in a molecule can be calculated theoretically using the second-order perturbation theory of Ramsey,[1] or the variational method.[2,3] Application of the second-order perturbation theory to this problem is possible only if the exited-state wave functions, in addition to the ground-state wave functions are available for the molecule in question. Hence, very few direct theoretical calculations of ξ have been made.

In order to overcome the foregoing difficulty, Narasimhan and Rogers,[22] have adopted the following procedure. For a given proton in a molecule, the net observed shielding ξ, can be written as the sum of two quantities, namely, ξ_l and ξ_d, where ξ_l , denotes the shielding due to the immediately surrounding electron colud (primary shielding), and it corresponds to Pople's local diamagnetic term. The second term ξ_d, arises from distant electron distributions within the molecule itself(secondary shielding) , and corresponds to Pople's neighbor-anisotropy effect. ξ_l can be evaluated by using the wave functions of the bond attached to the proton of interest.[3] ξ_d, can be evaluated from a knowledge of the diamagnetic anisotropy $\Delta\chi$ of the various charge distributions in the molecule.[3,6,7] Thus, we may write,

$$\xi = \xi_l + \xi_d$$

Where, ξ, is the net shielding of the nucleus in the molecule.

The reason for this separation of the total shielding into local and distant ones, is that, it is easier to estimate ξ_d from the knowledge of the diamagnetic anisotropies of the distant groups. It is then necessary to carry out the perturbation or variational calculations for the region nearest to the nucleus only. In this

manner, the problem of calculating magnetic shielding is simplified. However, in the present work, we shall not be concerned with details for calculating ξ_1, since our principal interest is in the magnetic anisotropies $\Delta\chi$'s of the -C≡CH, -C≡N, and -N≡C bonds. We shall consider in detail the quantity ξ_d, this being directly related to $\Delta\chi$.

The expression for ξ_d in terms of the diamagnetic anisotropies of distant groups can be derived from the general equation for the shielding tensor, on the bases of both perturbation and variational methods, as has been demonstrated by McConnell,[6] and Stephen.[3] In a classical sense, the externally applied uniform magnetic field may be thought of as inducing magnetic dipoles in these distant groups, and the secondary field at the nucleus due to these dipoles as contributing to ξ_d. For purposes of calculation we may approximate these induced dipoles by point dipoles, when the distances between them and the nucleus is large. In high resolution NMR spectroscopy, with which we are presently concerned, the samples are in the form of liquids or gases and, due to thermal motion, the molecules containing the nuclei under consideration are randomly oriented with respect to the applied field. The secondary field from the induced dipoles is thus averaged. In order to observe a finite

shielding, $\xi_d \neq 0$, the distant groups must be magnetically anisotropic .

A difference in the net shielding, or an internal chemical shift $\Delta\xi$ between two protons A and B in a molecule may originate from difference in ξ_l and/or ξ_d, ($\Delta\xi_l$ and $\Delta\xi_d$ respectively). Thus we have,

$$\Delta\xi = (\xi^A - \xi^B) = (\xi_l^A - \xi_l^B) + (\xi_d^A - \xi_d^B)$$
$$= \Delta\xi_l + \Delta\xi_d$$

Since the magnitude of the shielding contribution from distant groups depend on their diamagnetic anisotropy, and on molecular geometry, we have calculated the magnetic anisotropy of the C≡C, C≡N, and N≡C groups, using the internal chemical shift between protons. However, before proceeding further, we shall consider the rather classical problem of the secondary field due to an induced dipole, and thus derive a general expression for ξ_d, in terms of the diamagnetic anisotropy of a bond, when this bond is distant from the nucleus under consideration.

Let us now consider the shielding of the nucleus N due to an anisotropic bond A-B, formed between the two atoms A and B.

We choose a point 'O' somewhere along the bond, as the location of the induced dipole due to the external uniform magnetic field H_o , which is taken to be applied along A-B (Z-axis), with 'O' as the origin of the cartesian coordinates. The radius vector between 'O' and N is denoted by R. We can write the secondary field[51] at N due to the ideal dipole at 'O' as ,

$$\vec{H}_N = -T\vec{\mu} \tag{1}$$

Where the tensor T is ,

$$T = 1/R^3(1 - 3\vec{R}..\vec{R}/R^2) \tag{2}$$

In Eq.(2), 1 is the unit dyad and $\vec{R}..\vec{R}$ is the dyad from the radius vector. Now, the components of the magnetic moment are:

$$\left.\begin{aligned} \mu x &= \chi_{xx} H_x \\ \mu y &= \chi_{yy} H_y \\ \mu z &= \chi_{zz} H_z \end{aligned}\right\} \tag{3}$$

Where χ_{xx}, χ_{yy}, and χ_{zz}, are the principal magnetic susceptibilities of the bond A-B. The magnetic field $\vec{H}_N$ at the nucleus N is related to the externally applied uniform magnetic

field $\vec{H}_o$ by the shielding tensor ξN as follows:

$$\vec{H}_N = \vec{H}_o - \xi N \vec{H}_o \qquad (4)$$

and hence we may write ξ_d as,

$$\xi_d = \vec{T}\mu/3\ H_o \qquad (5)$$

Where, the factor 1/3 has been introduced in order to average the shielding due to molecular motion in liquids and gases. In the case of an axially symmetric bond, that is one with $\chi_{zz} \neq \chi_{yy} = \chi_{xx}$,

$$\xi_d = \Delta\chi(1 - 3\cos^2\theta_z)/3L_oR^3 \qquad (6)$$

Where, θ_z is the angle between the z-axis and the radius vector R. $\Delta\chi$ is the molar diamagnetic anisotropy , namely, $\chi_{zz} - \chi_{yy} = \chi_{zz} - \chi_{xx}$, and L_o is the Avogadro number. Equation (6) has been used by McConnell in discussing proton shifts in benzene and methyl halides.

In some cases the value of θ and/or R may change with internal molecular motions and here one must use appropriately averaged values, as will be discussed bellow.

When a given nucleus is involved in internal molecular motions, the average shielding of that nucleus due to a point dipole must be used in Eq.(6). The component ,

$$T_z = (1 - 3\cos^2\theta_z)/R^3$$

was evaluated numerically in the following manner.

Let us consider the case of a nucleus N which is free to move in a circular path around the axis A-B , this axis being taken to be in the Z-Y plane, with the point dipole placed at 'O' as shown in Fig.(1).

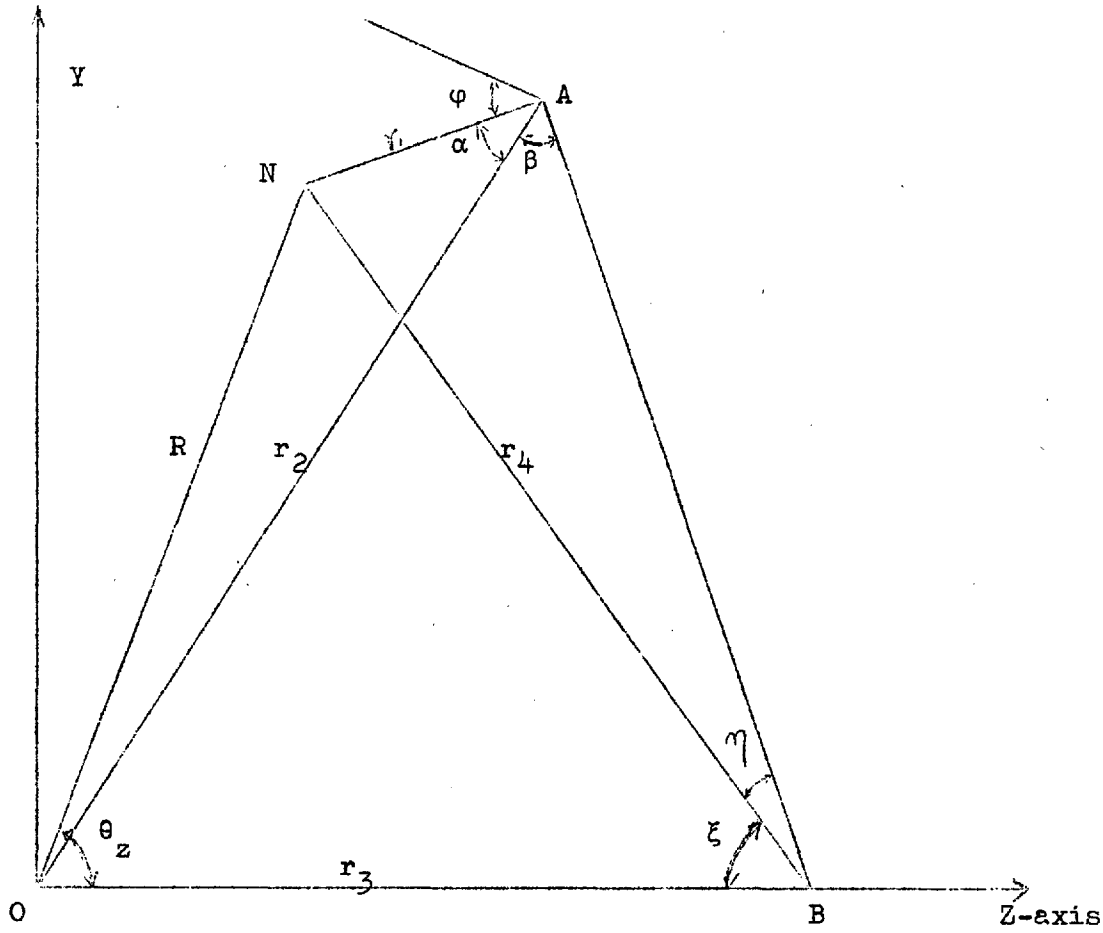


Fig.1. Evaluation of T_z value. The dipole is located at 'O', and nucleus N is free to rotate around the axis A-B.

The quantities of interest to us now are:

the radius vector R and θ_z. Since AN (= r_1), and AB are chosen to be at right angles to each other, we can express α in terms of β and φ (φ is the angle of rotation of r_1 in its plane). Thus it can be shown that,

$$\cos\alpha = \sin\beta\cos\varphi \tag{9}$$

and hence, we can express R as,

$$R = (r_1^2 + r_2^2 - 2r_1r_2\sin\beta\cos\varphi)^{1/2} \tag{10}$$

Now we also have,

$$\cos\theta_z = (R^2 + r_3^2 - r_4^2)/2Rr_3 \tag{11}$$

and hence, we can write,

$$T_z = (1 - 3\cos\theta z)/R^3$$
$$= \left\{R^{-3}\left[1 - 3\,(R^2 + r_3^2 + r_4^2)^2/(2Rr_3)^2\right]\right\}_{av.} \tag{12}$$

Since φ varies from 0 to 2π, we can find the average value by integrating the left-hand side of Eq.(12), after substituting Eq.(10) for R and deviding finally by 2π, thus after rearranging we obtain,

$$Tz = 1/2\pi\left\{J_B - 3/4r_3^2\left[(r_3^2 - r_4^2)^2 J_C + 2(r_3^2 - r_4^2)\,J_B + J_A\right]\right\}_{av.} \tag{13}$$

Where,

$$J_A = \int_0^{2\pi}(a + b\cos\varphi)^{-1/2}d\varphi$$
$$J_B = \int_0^{2\pi}(a + b\cos\varphi)^{-3/2}\,d\varphi \qquad \text{With, } a = r_1^2 + r_2^2 \text{ , and}$$
$$J_C = \int_0^{2\pi}(a + b\cos\varphi)^{-5/2}\,d\varphi \qquad b = -2\,r_1r_2\sin\beta.$$

The above case is sufficient to deal with the averages required for the case of ethylacetylene.

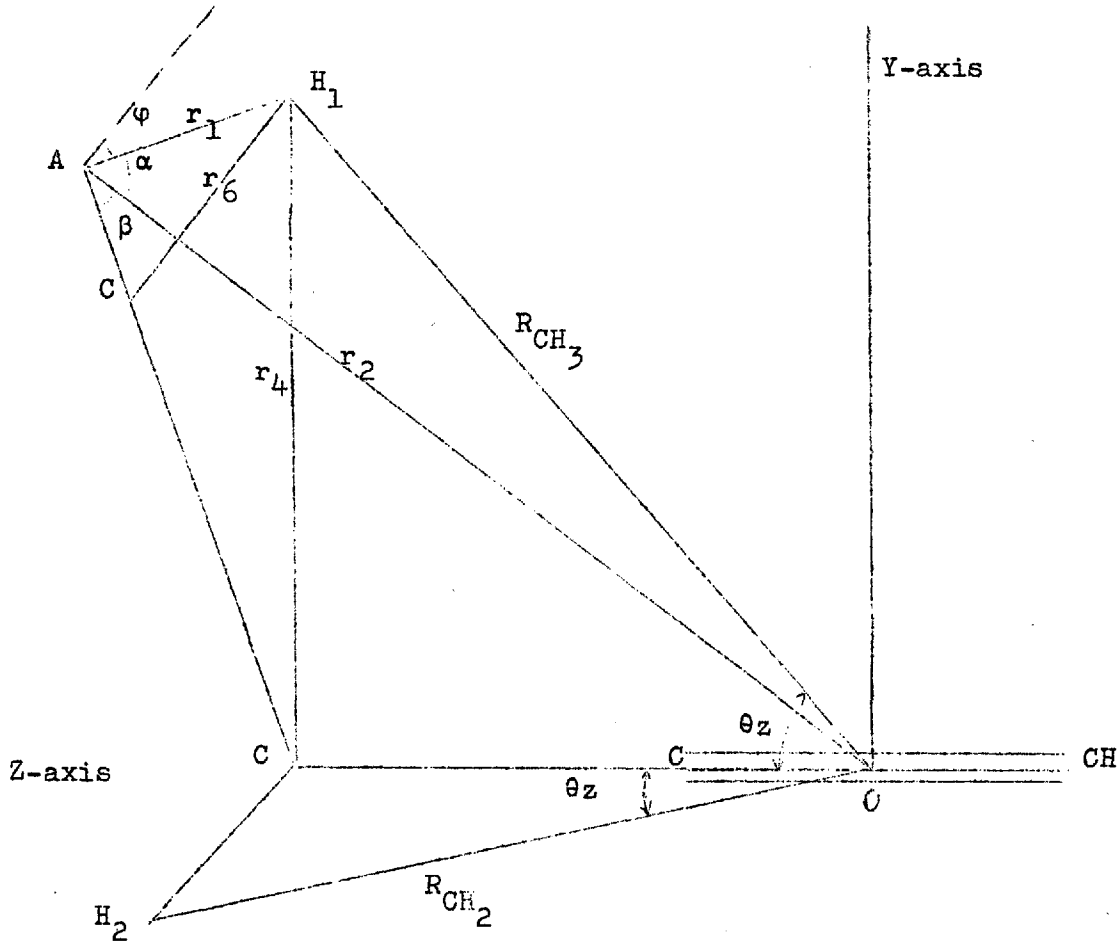


Fig.2. Structure used for calculating diamagnetic anisotropy effects in ethylacetylene. R_{CH3}=2.79A°, r_1=1.05A°, r_3=2.09A°, r_2=3.24A°, r_4=2.20A°, r_6=1.07A°, R_{CH2}=2.67A°, $\theta z(CH_2)$=22.9°.

Refereing to Fig.(2), the secondary field at proton 1 and 2 due to the -C≡CH bond at 'O' is required. The Z-axis is chosen along the bond and the X-axis is perpendicular to the plane of the molecule (i.e. Z and Y are in the plane of the paper).

An examination of Fig.2, shows that Tz can be obtained in the same manner as was shown in the general case. For the proton 2, the radius vector R and the angle θ are constants, therefore, we can use Eq.(6) to calculate the secondary field due to the -C≡CH bond.

The evaluation of the integrals in equation (13) is necessary for the calculation of Tz for the methyl group. These integrals are of the elleptical type and cannot be evaluated in a closed form. These were calculated numerically using the Gauss quadrature method.

2. ELECTROSTATIC EFFECTS.

In dealing with bonds which are more highly polar than the carbon-carbon triple bond, account must be taken of direct electrostatic contributions to ξe. This problem arises in the case of the carbon-nitrogen and nitrogen-carbon triple bonds, and the way in which it is treated is now discussed.

(a). Dipole field.[21]

In the presence of a primary uniform magnetic field $\underline{H}$, there will be at a particular nucleus an induced secondary magnetic field $\underline{H}'$, and the screening tensor $\xi\alpha\beta$ for this nucleus is defined by:

$$H'\alpha = -\xi\alpha\beta\ H\beta \qquad (1)$$

Where the Greek subscripts denote tensor components (α and β can be x, y, or z, and repeated subscripts indicate a summation over x, y, and z-components). Thus $\xi\alpha\beta H\beta = \xi\alpha x\ Hx + \xi\alpha y\ Hy + \xi\alpha z\ Hz$.

It is supposed that if the molecule is in a uniform electric field E, the screening is effected in such a way that ξ can be expanded as a power series in E,

$$\xi\alpha\beta = \xi^{o}\alpha\beta + \xi^{1}\alpha\beta\gamma E\gamma + \tfrac{1}{2}\ \xi^{2}\alpha\beta\gamma\delta E\gamma E\delta + \ldots\ldots\ldots \qquad (2)$$

In an axially symmetric X→H bond, there can be no screening proportional to the first power of the field at right angles

to the bond, so that expression (2) is reduced to,

$$\xi = \xi^{o} + \xi^{1}E_{z} + \tfrac{1}{2}\xi^{2}E^{2} + \ldots\ldots\ldots\ldots \quad (3)$$

To estimate the importance of the proton shielding proportional to E , and to E^2 in an X⟶H bond, use can be made of the results of Marshall and Pople,[11] for the E^2 effect on an H-atom. Their theory leads to an expression for the screening of a proton to,

$$\xi = 2 \times 10^{-5} - 2 \times 10^{-12} E_{z} - 10^{-18}E^{2}\ldots\ldots\ldots \quad (4)$$

In most X⟶H bonds, it is reasonable to assume that there is an increased electronic charge between the nuclei, so that an electric field in the X⟶H direction will tend to draw this excess charge further away from the proton, thereby decreasing its screening constants. Equation (4), indicates that the change in ξ arrising from the action of an electric field on an X⟶H bond is approximately,

$$-2 \times 10^{-2}E_{z} - 10^{-18}E^{2}$$

(b). Reaction field of solvent.

When a polar molecule is dissolved, it polarises the surrounding medium and this polarization leads to an electric field ' the reaction field ' at the solute.

If the molecule is sufficiently symmetrical, the mean reaction field is parallel and proportional to its dipole moment. For the Onsager model,[52] in which the solute molecule is represented by a sphere of radius r containing a point dipole of moment μ, at its centre, and the solvent by a continuum of dielectric constant ϵ, the reaction field R is,

$$R = 2(\epsilon - 1).\ m/(2\epsilon + 1)r^3 = 2(\epsilon - 1)(n^2-1).\mu/2(2\epsilon + n^2)\alpha \qquad (5)$$

Where, $m = \mu + \alpha R$, is the total dipole moment, $\alpha = (n^2-1)r^3/(n^2+2)$, being the polarizability of the sphere, and n is the refractive index of the pure solvent (as a liquid or solid). If the polarizabilit α is not available, we can use the following expression:

$$\text{Molecular refraction}(R) = 4\pi N\alpha/3 = (n^2-1).M/(n^2+2).d \qquad (6)$$

(i.e.),

$$\alpha = 3M(n^2-1)/4\pi N\alpha(n^2+2) = (n^2-1).r^3/(n^2+2),$$

or,

$$r^3 = 3M/4\pi Nd \qquad (7)$$

$$R = (\epsilon-1)(8\pi Nd/\mu)(n^2+2)/2\epsilon + n^2(9M) \qquad (8)$$

(c). Partial point charge approximation.

An improved approximation for the electrostatic effect can be made by replacing the point dipole by partial positive and negative point charges on the two atoms of the bond. These partial charges are derived from the dipole moment and length of the bond.

The electric field at any point is defined as the force exerted on unit charge placed at that point. To determine the field exerted at the point H by the two charges(+e)and(-e), placed at the carbon and nitrogen atoms respectively; we shall proceed as follows:

According to coulomb's law, the force exerted by the positive charge (+e) on the unit charge placed at the proton H, is

$$E_1 = e/R_1^2 ,$$

The component of this force along the C⟶H bond is given by,

$$E_1^{C\rightarrow H} = e/R_1^2 \cdot \cos\lambda \qquad (1)$$

The field due to the negative charge (-e), at the proton H, is given by,

$$E_2 = -e/R_2^2 ,$$

The component of this force along the C⟶H bond is,

$$E_2^{C\longrightarrow H} = -e/R_2^2 \cdot \cos\omega \qquad (2)$$

The electrical field at the point H is completely defined by the total force exerted at the proton H, by the two charges (+e) and (-e), and is given by,

$$E_T = e/R_1^2 \cdot \cos\lambda - e/R_2^2 \cdot \cos\omega \qquad (3)$$

From the geometry of the figures bellow, we can show that ,

$$\cos\lambda = (R_1^2 + r_4^2 - r_3^2)/(2R_1r_4) \qquad (4)$$

and,

$$\cos\omega = (R_2^2 + r_4^2 - r_3'^2)/(2R_2r_4) \qquad (5)$$

Therefore,

$$\langle E_T\rangle = e/R_1^2\left[(R_1^2+r_4^2-r_3^2)/(2R_1r_4)\right] - e/R_2^2\left[(R_2^2+r_4^2-r_3^2)/(2R_2r_4)\right] \qquad (6)$$

Since $\mu = el$, and $e = \mu/l$,

Therefore,

$$E_T = \mu/2lr_4\left\{(R_1^{-1}+R_1^{-3}(r_4^2-r_3^2) - R_2^{-1}-R_2^{-3}(r_4^2-r_3'^2)\right\}_{AV.} \qquad (7)$$

Since φ varies from 0 to 2π , we can find the average value by integrating the left-hand side of this equation and substituting the values of R_1 and R_2 given by,

$$R_1 = (r_1^2 + r_2^2 - 2r_1r_2\sin\beta\cos\varphi)^{1/2}$$

$$R_2 = (r_1^2 + r_2'^2 - 2r_1r_2'\sin\beta'\cos\varphi)^{1/2}$$

$$\langle E_T\rangle = 1/2\pi\int_0^{2\pi}\langle E\rangle\, d\varphi \ ,$$

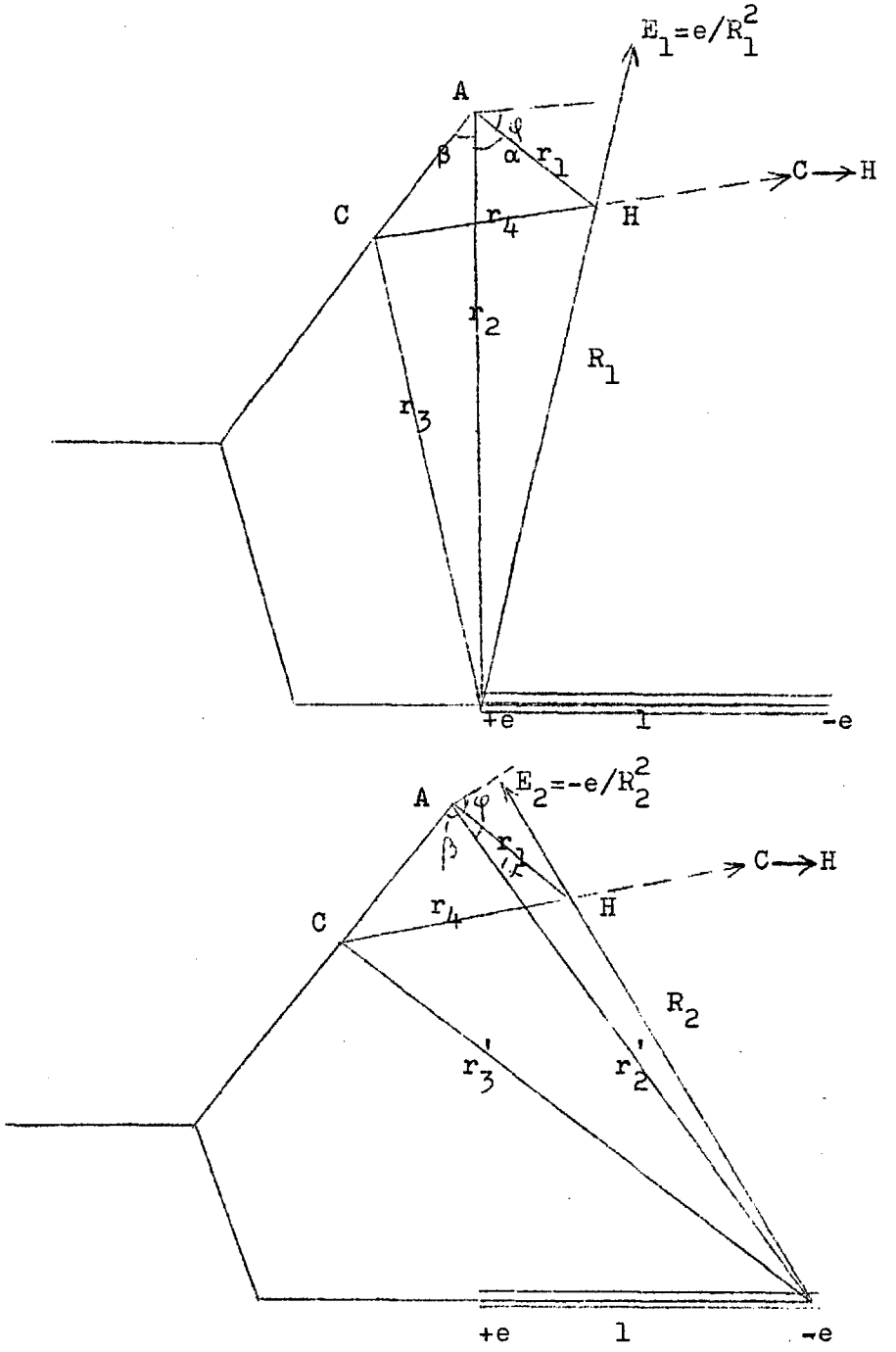


Fig.3. Calculation of electrical shielding for rotating methyl groups, based on the point charge approximation.

Thus after rearranging, we obtain,

$$\langle E_T \rangle = \mu/4l\ r_4 \left\{ J_{A1} + J_{B1}(r_4^2 - r_3^2) - J_{A2} - J_{B2}(r_4^2 - r_3'^2) \right\}_{AV.} \qquad (8)$$

Where,

$$J_{A1} = \int_0^{2\pi} (a_1 + b_1\cos\varphi)^{-1/2}\, d\varphi$$

$$J_{A2} = \int_0^{2\pi} (a_2 + b_2\cos\varphi)^{-1/2}\, d\varphi$$

and,

$$J_{B1} = \int_0^{2\pi} (a_1 + b_1\cos\varphi)^{-3/2}\, d\varphi$$

$$J_{B2} = \int_0^{2\pi} (a_2 + b_2\cos\varphi)^{-3/2}\, d\varphi$$

With,

$$a_1 = r_1^2 + r_2^2 \quad , \quad b = -2\, r_1 r_2 \sin\beta$$

$$a_2 = r_1^2 + r_2'^2 \quad , \quad b' = -2\, r_1 r_2' \sin\beta'$$

3. Electronegativity effects.

Following the original invistigations of Meyer, Saika, and Gutowsky,[9] it was found empirically by Daily and Shoolery,[19] that for a series of ethyl derivatives , a linear relation exists between the internal chemical shift of the ethyl group protons and the electronegativity of the substituent . Cavanaugh and Daily,[15] have re-examined this relation, in which , they replaced the solvent

(benzene), by carbon tetrachloride, since benzene has been shown to exhibit anomalous dilution effects. These results were reviewed, and measurements were made on dilute solutions of these compounds in carbon tetrachloride, and extrapolated to infinite concentration of the solutes. The internal chemical shifts of the ethyl derivatives as measured in carbon tetrachloride differ slightly from those measured in benzene. However, the correlations of the internal chemical shifts with the electronegativity of the substituents is still apparant. A revised Daily and Shoolery equation was set up using the new data.

Electronegativity = 0.0114δ internal + 1.78

Where, δ is in cycles/second at 60 Mc/s.

Since the electronegativity of the substituent determines the electron distribution around the protons, this equation may be taken as an empirical expression for estimating $\Delta\xi_1$ between the methyl and methylene protons in ethylacetylene.

Narasimhan and Rogers,[53] have determined the diamagnetic anisotropy of the C—C and C—H single bonds in propane. They considered propane as CH_3CH_2X. Using a modified Daily-Shoolery equation, they estimated the empirical value of $\Delta\xi_1$, with X being the methyl

group in this instant , and assuming the electronegativity of the methyl group to be 2.32.[54] They estimated $\Delta\xi_1$ in this manner and was found to be + 0.317 x 10^{-6}, which compares favourably with the theoretical value , +0.338 x 10^{-6} calculated from electron density distribution in propane. The electron density distribution in propane was invistigated by Sandorfy,[55] who has given the so-called "atom charges" in this molecule following the definitions of McWeeny,[56]

4. APPLICATIONS.

(a). The anisotropy of -C≡C- bond.

(i). Ethylacetylene.

We have followed the general approach outlined above in the calculations of the inductive contribution to $\Delta\xi_1$ in ethylacetylene, and have neglected the term arising from the electrostatic effect. Using the value of 3.29 for the electronegativity of the -C≡CH bond,[57] and the modified Daily-Shoolery equation, we have estimated $\Delta\xi_1$ in ethylacetylene, and thus obtained a value of +2.207 x 10^{-6} for

the difference in the chemical shift between the methyl and methylene protons due to the electronegativity of the -C≡CH bond.

Since the total chemical shift (0.94×10^{-6} observed) between the methyl and methylene protons is equal to the difference due to the magnetic anisotropy of the -C≡CH group and the electronegativity difference, we have,

$$\Delta \xi_T = \Delta \xi_d + \Delta \xi_l$$

Therefore,

$$\Delta \xi_d = 0.94 \times 10^{-6} - 2.207 \times 10^{-6} = -1.267 \times 10^{-6}$$

$$\Delta \xi_d = \Delta \chi^{C\equiv C} / 3L_o \; (T_z^{CH3} - T_z^{CH2})$$

Where,

$$Tz = (1 - 3\cos^2 \theta_z)/R^3$$

$$-1.267 \times 10^{-6} = 0.0359 \, \Delta \chi^{C\equiv C}$$

$$\therefore \Delta \chi^{C\equiv C} = -35.3 \times 10^{-6} \text{cm.}^3 \text{mole.}^{-1}$$

(ii). <u>3,5-Dimethylphenylacetylene</u>.

We have also calculated the diamagnetic anisotropy of the C≡CH group in 3,5-dimethylphenylacetylene , from the internal chemical shift between the <u>o</u>-and <u>p</u>-protons, using McConnell expression.

$$(\xi_o^H - \xi_p^H) = \xi_d^{o-p} = \Delta\chi^{C\equiv C}/3L_o(\ T_z^o - T_z^p\ )$$

$$+0.179 \times 10^{-6} = -0.00561\ \Delta\chi^{C\equiv C}$$

$$\therefore \Delta\chi^{C\equiv C} = -31.9 \times 10^{-6}\ \text{cm.}^3\text{mole.}^{-1}$$

(iii). Vinylacetylene.

Very recently Hirst and Grant,[58] have determined the NMR spectra, and have calculated the chemical shift and spin-spin coupling constants in vinylacetylene. The chemical shift difference between the two protons at the β-carbon atom was used in the calculation of the diamagnetic anisotropy of the C≡C bond in vinylacetylene. The structure used in the calculation is shown in Fig.4.[59]

$$\xi_d^C - \xi_d^B = \Delta\chi^{C\equiv C}/3L_o\left\{(1 - 3\cos^2\theta_z^C)/R_C^3 - (1 - 3\cos^2\theta_z^B)/R_B^3\right\}$$

$$-0.18 \times 10^{-6} = 0.005076\ x\Delta\chi^{C\equiv C}$$

$$\therefore \Delta\chi^{C\equiv C} = -35.4 \times 10^{-6}\ \text{cm.}^3\text{mole.}^{-1}$$

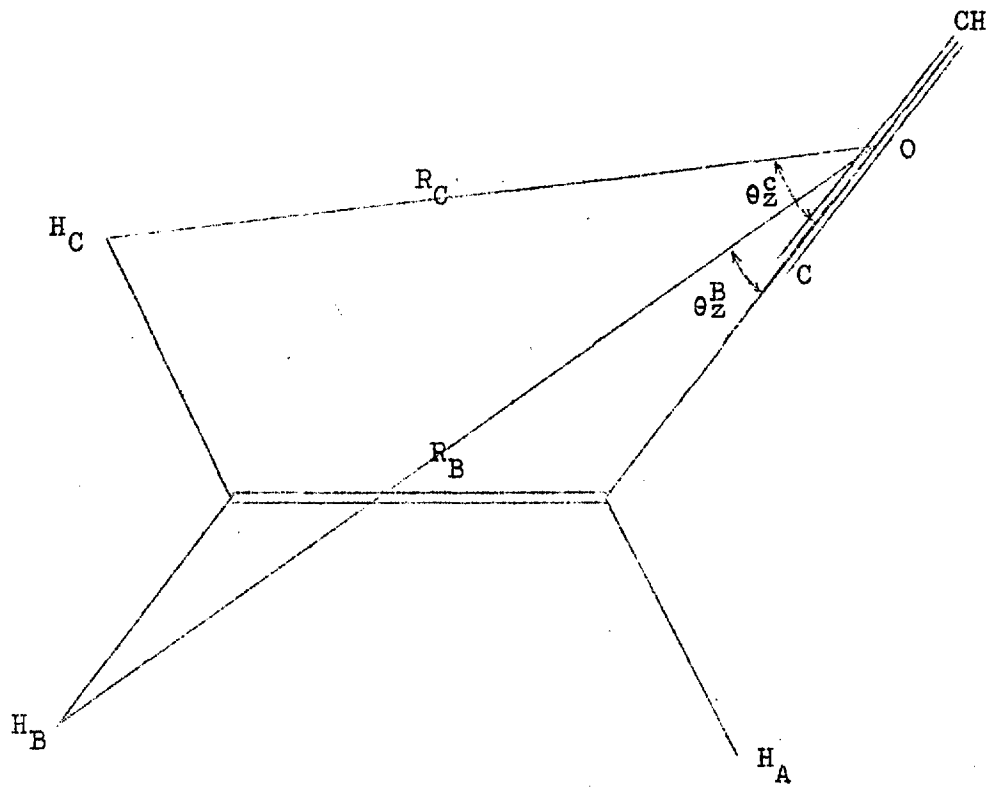


Fig.4. Structure used for calculating diamagnetic anisotropy effects in vinylacetylene. R_C =2.9 A°, R_B = 3.84 A°, θ_Z^C = 44.6°, and θ_Z^B = 17.5°.

b. The anisotropy of -C≡N bond.

(i). Propionitrile.

The difference in the shielding between the methyl and methylene protons due to the dipole field of the -C≡N group was estimated as follows:

The mid point of the -C≡N bond is taken as the position of the dipole, as an approximation , and the positive direction of the axis of the dipole is drawn from the negative to the positive charge.[60] R, is the radius vector to the rotating nucleus; θz, is the angle made by the radius vector and the positive dipole direction, other distances are shown in Fig. 5. A line is drawn perpendicular to the radius vector at the proton H, to meet the dipole axis (in this case at the point p). The electrical field experienced by the nucleus H, due to the -C≡N dipole, may now be resolved into a radial E_r and a transverse component E_θ. The radial and the transverse resolutes of the electric field are respectively,

$$Er = 2\mu\cos\theta z/R^3 \qquad \text{and,} \qquad E\theta = \mu\sin\theta z/R^3$$

each taken positive in the direction of increasing R and θ. The electric field at the nucleus H, is completely defined by $E_r + E_\theta$.

The component of E_r in the direction of the C⟶H bond is given by:

$$E_r^{C\to H} = 2\mu\cos\theta z.\ \cos\gamma/R^3, \quad \text{and similarly,}$$

$$E_\theta^{C\to H} = \mu\sin\theta z\ .\cos w/R^3.$$

The total field at the point H in the direction of the C⟶H bond is then given by:

$$E_T^{C\to H} = 2\mu\cos\theta z.\ \cos\gamma/R^3 + \mu\sin\theta z.\ \cos w/R^3$$

$$\cos\gamma = (R^2 + r_6^2 - r_7^2)/2Rr_6$$

$$\therefore\quad E_r^{C\to H} = 2\mu\cos\theta z\left\{(R^2 + r_6^2 - r_7^2)/2R^4 r_6\right\}$$

$$= \mu\cos\theta z/2r_6R^4\left\{2R^2 + 2(r_6^2 - r_7^2)\right\}$$

$$\cos w = r_6^2 + (Rp)^2 - (CP)^2\ /2r_6(HP)$$

Since,

$$HP = R\tan\theta \quad , \quad \text{and} \quad OP = R\sec\theta,$$

Also,

$$\cos\xi = r_7^2 + (OP)^2 - (CP)^2\ /\ 2r_7(OP)$$

$$\therefore\quad (CP)^2 = r_7^2 + R^2\sec^2\theta z - 2r_7R\sec\theta z.\cos\xi$$

Therefore,

$$\cos w = r_6^2+R^2\tan^2\theta-r_7^2-R^2\sec^2\theta z+2r_7R\sec\theta.\cos\xi/2r_6R\tan\theta z$$

$$\cos w = \left[(r_6^2 - r_7^2) - R^2 + 2r_7 R \sec\theta z . \cos\xi\right] / 2r_6 R \tan\theta z$$

$$\therefore E_\theta^{C\rightarrow H} = \cos\theta z / 2r_6 R^4 \left[(r_6^2 - r_7^2) - R^2 + 2r_7 R \sec\theta z . \cos\xi\right]$$

Since,

$$\cos\theta z = (R^2 + r_3^2 - r_4^2)/2Rr_3$$

We get,

$$E_T = \mu/4r_3 r_6 \left[R^{-1} + R^{-3}(r_3^2 - r_4^2) + 3(r_6^2 - r_7^2)R^{-3} + 3(r_6^2 - r_7^2)(r_3^2 - r_4^2)R^{-5} + 4r_3 r_7 R^{-3}\cos\xi\right.$$

Now,

$$R = (r_1^2 + r_2^2 - 2r_1 r_2 \sin\beta . \cos\varphi)^{1/2}$$

Hence the average value of E_T over a full revolution of φ is:

$$\langle E_T\rangle_{av.} = 1/2\pi \int_0^{2\pi} \langle E_T\rangle d\varphi$$

$$\therefore \langle E\rangle_{av.} = \mu/8\pi r_3 r_6 \left[JA + JB(r_3^2 - r_4^2) + 3(r_6^2 - r_7^2)JB + 3(r_6^2 - r_7^2)(r_3^2 - r_4^2)JC + 4r_3 r_7 \cos\xi . JB\right]_{av.}$$

$$= \mu/8\pi r_3 r_6 \left\{ JA + JB\left[(r_3^2 - r_4^2) + 3(r_6^2 - r_7^2) + 4r_3 r_7 \cos\xi\right] + JC\left[3(r_6^2 - r_7^2)(r_3^2 - r_4^2)\right]\right\}_{av.}$$

Where, JA, JB, and JC represents the elleptical integrals as defined on page 57.

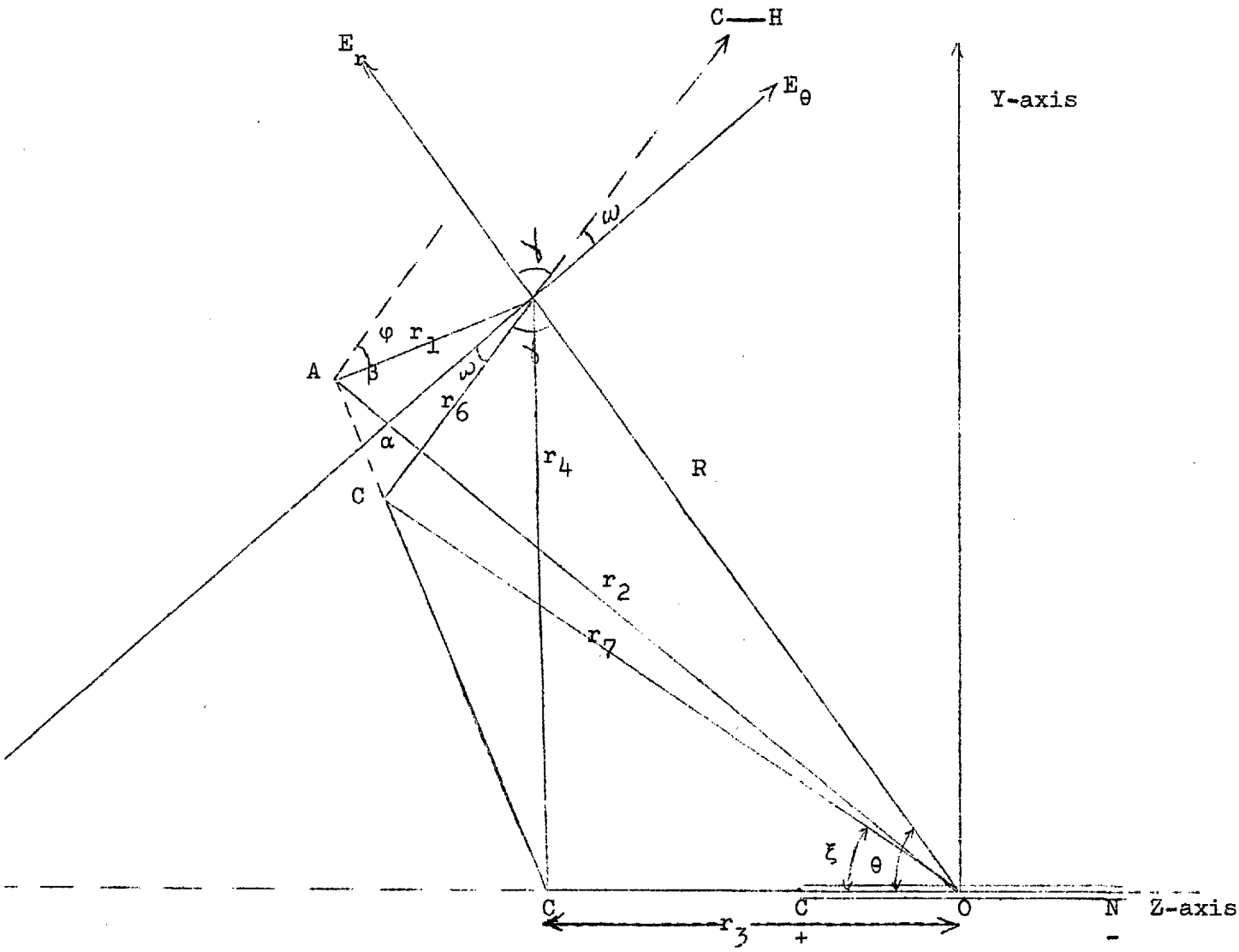


Fig. 5. Estimation of electrical shielding due to the dipole field of the -C≡N group on the methyl group in propionitrile. R=2.79A°, r_1=1.05, r_2=3.24, r_3=2.09, r_4=2.20, r_6=1.09, r_7=2.98, ξ=29.4°. JA=1.89579 x 10^8, JB= 1.80776 x 10^{23}, JC= 1.8354 x 10^{38}. Tz= -1.84762 x 10^{22}.

For α-hydrogens, R= 2.67A°, r_1=1.09, r_6=1.09, r_7=2.09, θz=22.9°, Tz= -0.8121 x 10^{23}.

The same general method was used to derive an expression for the electrical field at the methylene protons due to the -C≡N group. The following expression is obtained,

$$E_T^{\alpha H} = \mu/2r_6R^4\left[R^2\cos\theta z + 3(r_6^2 - r_7^2)\cos\theta z + 2r_7R\right]$$

Substituting the appropriate values in the two expressions we get:

$$\langle E_T\rangle^{CH_3} = +0.118 \times 10^6$$

$$\Delta\xi(CH_3) = -0.25 \times 10^{-6}$$

and,

$$\langle E_T\rangle^{CH2} = +0.3098 \times 10^6$$

$$\Delta\xi(CH_2) = -0.715 \times 10^{-6}$$

In propionitrile, the methyl resonance is shifted by -0.25 p.p.m.; and the $-CH_2-$ resonance by -0.715 p.p.m. to lower applied field strength by the electrical field of the -C≡N dipole. In the calculation of the diamagnetic anisotropy of the -C≡N bond in propionitrile, we have allowed for the effect of the electrical field at the methyl and methylene protons. We have included the term $\Delta\xi e$ in the shielding expression,(i.e) ,

$$\Delta\xi_T = \Delta\xi d + \Delta\xi 1 + \Delta\xi e$$

Where, $\Delta\xi e$, represents the chemical shift difference between the

methyl and methylene protons due to the electric field of the -C≡N bond. Using a value of 3.11 for the electronegativity of the -C≡N bond,[57] we have estimated empirically $\Delta\xi_1$ due to the difference in electronegativity at the two carbon atoms, and found that this difference is equal to 1.94 p.p.m. The observed chemical shift between the $-CH_3$ and $-CH_2-$ protons in propionitrile, as measured in carbon tetrachloride is +1.03 p.p.m.

$$\therefore \Delta\xi_d = +1.03 \times 10^{-6} - 1.94 \times 10^{-6} - 0.465 \times 10^{-6}$$
$$= -1.376 \times 10^{-6}$$

$$\Delta\xi_d = \Delta\chi^{C\equiv N}/3L_o \left(T_z^{CH3} - T_z^{CH2} \right)$$

Where,

$$T_z = (1 - 3\cos^2\theta_z)/R^3$$

$$\therefore \Delta\xi_d = +0.0347\,\Delta\chi^{C\equiv N}$$

$$-1.376 \times 10^{-6} = +0.0347\,\Delta\chi^{C\equiv N}$$

$$\therefore \Delta\chi^{C\equiv N} = -39.6 \times 10^{-6} \text{ cm.}^3\text{mole.}^{-1}$$

(ii). Acrylonitrile-dipole approximation.

The electrical field at the nucleus C, due to the -C≡N dipole was calculated in the following manner:

The electrical field at the proton H_C is completely defined by the radial E_r and the transverse component E_θ. The radial and transverse resolutes of the electric field are respectively,

$$E_r = 2\mu\cos\theta z/R^3 , \qquad E\theta = \mu\sin\theta z/R^3$$

each taken positive in the direction of increasing R and θ.

Now,

$$E_T^{C\rightarrow H} = E_r + E_\theta = 2\mu\cos\theta z.\cos\gamma/R^3 + \mu\sin\theta z.\cos w/R^3$$

$$\cos\gamma = (R^2 + r_4^2 - r_3^2)/2Rr_4$$

$$E_r = \cos\theta z/2R^4 r_6\left[2R^2 + 2(r_4^2 - r_3^2)\right]$$

and,

$$\cos w = \left[r_4^2 + R^2\tan^2\theta z - (R\sec\theta z - r_3)^2\right]/2r_4 R\tan\theta z$$

$$= \left[(r_4^2 - r_3^2) - R^2 + 2r_3 R\sec\theta z\right]/2r_4 R\tan\theta z$$

$$\therefore E_\theta = \mu\cos\theta z/2r_4 R^4\left[(r_4^2 - r_3^2) - R^2 + 2r_3 R\sec\theta z\right]$$

$$\therefore E_T = \mu/2r_4 R^4\left[R^2\cos\theta z + 3(r_4^2 - r_3^2)\cos\theta z + 2r_3 R\right]$$

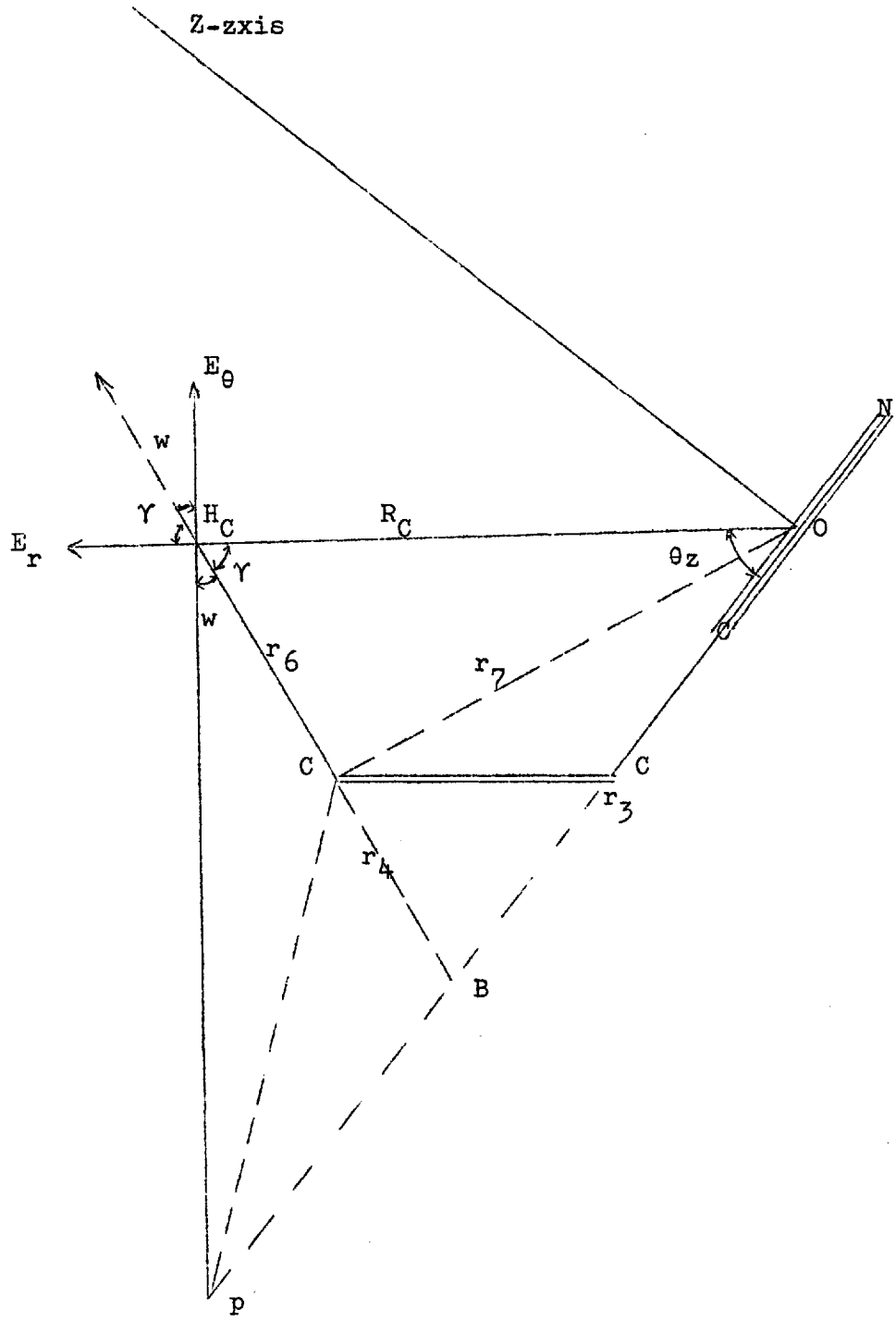


Fig.6. Structure used for calculating the electrical field at the proton C in acrylonitrile due to the -C≡N dipole. R_c=2.9A°, r_3=3.34, r_4(=H_CB)=2.4, r_6=1.10, r_7=2.96, θ_z=43.24°.

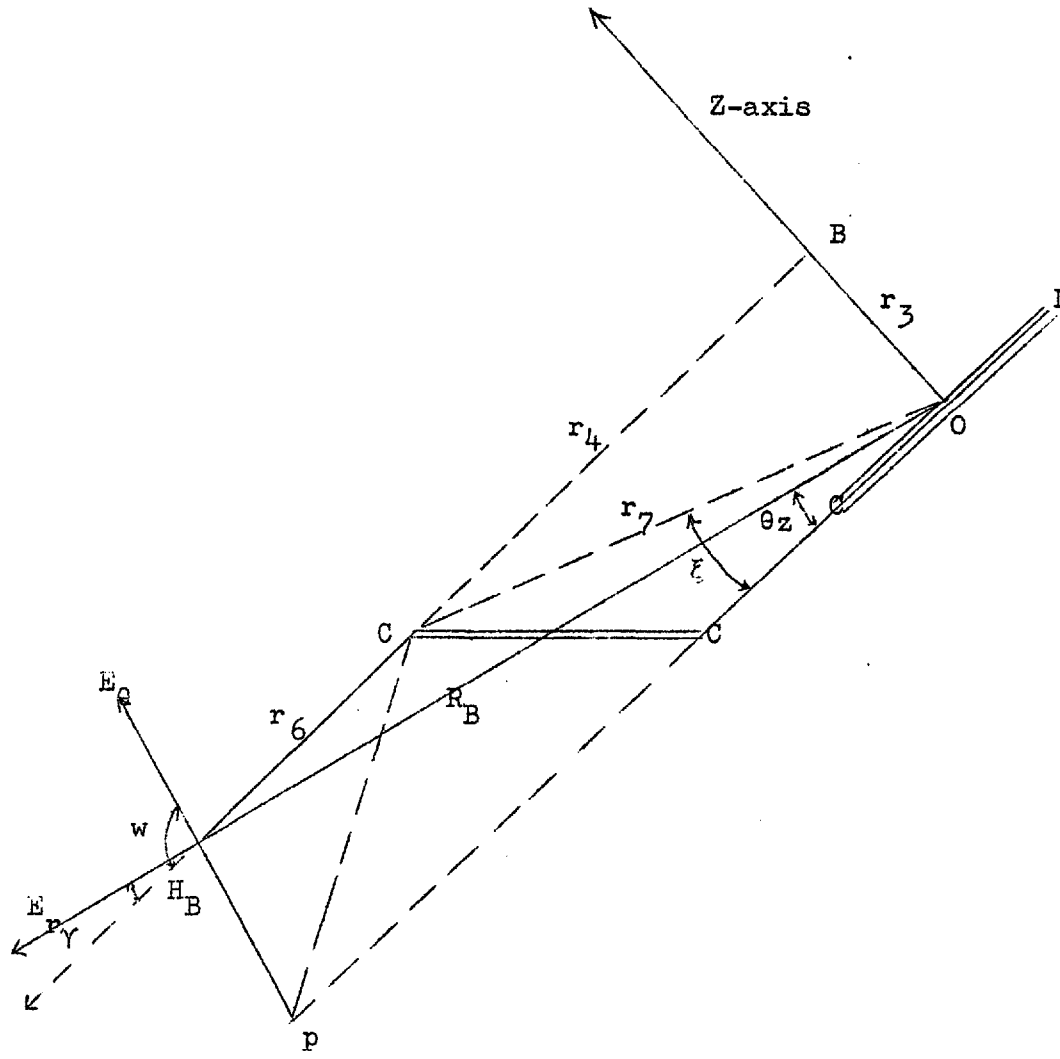


Fig.7. Structure used for calculating the electrical field at the proton H_B in acrylonitrile due to the -C≡N dipole, based on the point dipole approximation. R_B=3.987A°, r_4=3.68, r_6=1.10, r_7=2.96, θz=16°, ξ=23°.

Since,

$$\cos\vartheta z = (R^2 + r_3^2 - r_4^2)/2r_3R$$

$$\therefore E_T^{HC} = \mu/4r_3r_4R^5\left[R^4 - 2R^2(r_3^2 - r_4^2) - 3(r_3^2 - r_4^2) + 4r_3^2R^2\right]$$

This formula leads to:

$$E^C = +0.155 \times 10^6$$

$$(\Delta\xi)_e^C = -0.334 \times 10^{-6}$$

The same general method was applied in the case of the proton H_B, and an expression was derived for the electrical field at this proton,

$$E_T^B = \mu/2r_6R^4\left[R^2\cos\vartheta z + 3(r_6^2 - r_7^2)\cos\vartheta z + 2r_7R\cos\xi\right]$$

Since,

$$\cos\theta z = r_4/R$$

We obtain the final expression for the shielding:

$$E_T^B = \mu/2r_6R^5\left[R^2(r_4 + 2r_7\cos\xi) + 3r_4(r_6^2 - r_7^2)\right]$$

Substituting the appropriate values in this expression we obtain:

$$E_T^B = +0.108 \times 10^6$$

$$(\Delta\xi)_e^B = -0.227 \times 10^{-6}$$

The chemical shift difference between the two protons at the β-position is related to the geometrical factor and the anisotropy in the magnetic susceptibility of the -C≡N bond by the following expression:

$$(\xi_c - \xi_B)_d = \Delta\chi^{C\equiv N}/3L_o \left[(1 - 3\cos^2\theta^C_z)/R_C^3 - (1 - 3\cos\theta^B_z)/R_B^3 \right]$$

Substituting the values of the various parameters in the above expression , we obtain,

$$(\xi_C - \xi_B)_d = 0.0037\,\Delta\chi^{C\equiv N}$$

$$(\xi_C - \xi_B)_d = \Delta\xi^d_{CB} = \Delta\xi^T_{CB} - \Delta\xi^e_{CB}$$

Where,

$\Delta\xi^T_{CB}$, is the difference in shielding between protons C and B, as observed experimentally; $\Delta\xi^e_{CB}$, is the difference between these two protons due to the electrical field of the -C≡N bond.

Substituting the values of $\Delta\xi^T_{CB}$ and $\Delta\xi^e_{CB}$, we get:

$$\Delta\xi^d_{CB} = -0.177 \times 10^{-6} - (-0.1 \times 10^{-6}) = -0.077 \times 10^{-6}$$

$$\therefore \quad -0.077 \times 10^{-6} = 0.0037 \times \Delta\chi^{C\equiv N}$$

$$\therefore \Delta\chi^{C\equiv N} = -20.8 \times 10^{-6} \text{ cm.}^3\text{mole.}^{-1}$$

(iii). Acrylonitrile-partial point charge approximation.

Application of the partial point charge approximation to the problem of calculating the electrical shielding of the C and B protons in acrylonitrile, proves to be a better approximation to the field of the -C≡N bond, particularly at the β-proton. The following expressions are obtained for the electrical field at the protons C and B, due to the two charges (+e) and (-e) placed at the carbon and nitrogen atoms respectively; the expressions are:

$$E_T^C = \mu/2 l r_4 \left[(R_1^2 + r_4^2 - r_3^2)/R_1^2 - (R_2^2 + r_4^2 + r_3')/R_2^3 \right]$$

The same expression is applied also in the case of the proton H_B. Substituting the values of the various parameters in the above expression, we obtain:

$$E_T^C = +0.151 \times 10^6$$

$$\Delta\xi_e^C = -0.325 \times 10^{-6}$$

and ,

$$E_T^B = +0.125 \times 10^6$$

$$\Delta\xi_d^B = -0.265 \times 10^{-6}$$

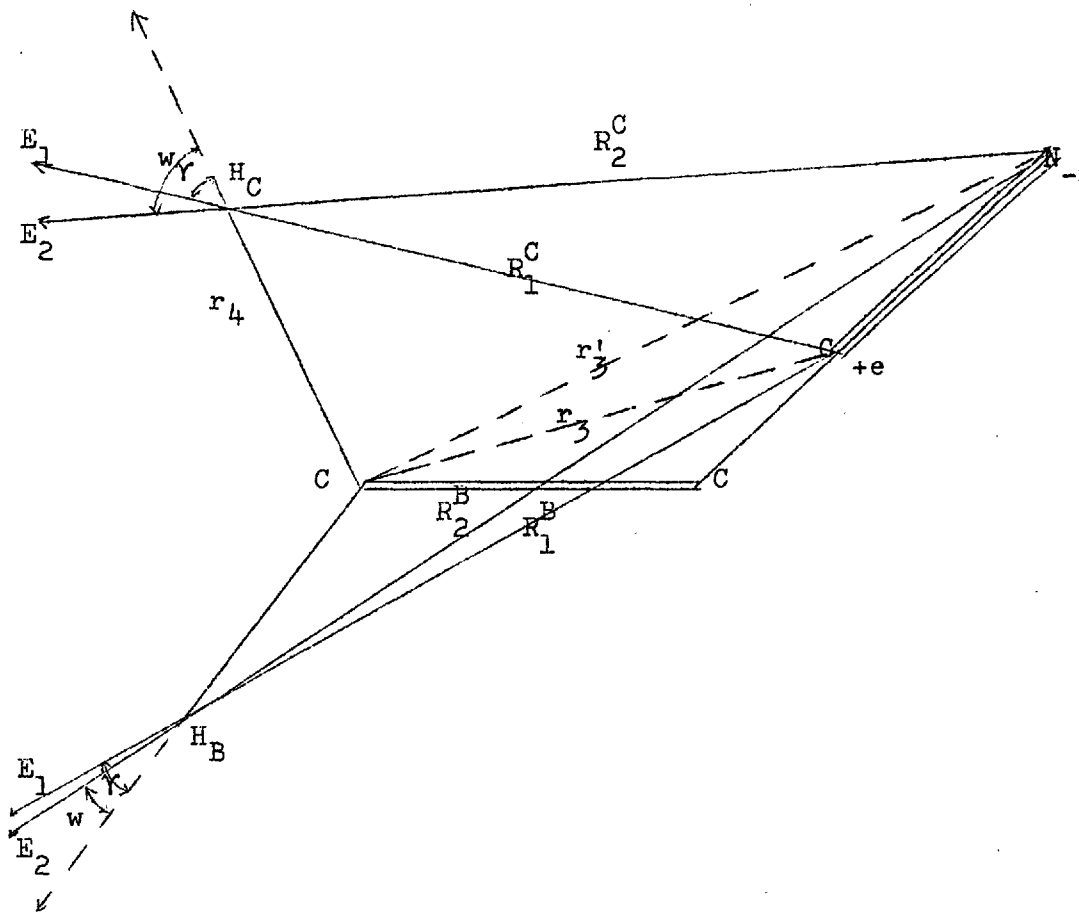


Fig.8. Structure used for calculating the electrical field at the two protons C and B in acrylonitrile, due to the dipole -C≡N, based on the partial point charge approximation. R_1^C=2.64A°, R_2^C=3.45, r_3=2.42, r_3'=3.47, r_4=1.09, w_C=81.25°, γ_C=65.25°; R_1^B=3.4A°, R_2^B=4.49, w_B=14.5°, γ_B=20°. C≡N =1.159A°, μ =3.84 x 10^{-18}D.

$$\xi_e^C - \xi_e^B = -0.325 - (-0.265) = -0.06 \times 10^{-6}$$

$$\therefore \Delta\xi_e^{CB} = -0.06 \times 10^{-6}$$

Since,

$$\Delta\xi_T^{CB} = \Delta\xi_d^{CB} + \Delta\xi_e^{CB}$$

$$\Delta\xi_d^{CB} = -0.177 \times 10^{-6} - (-0.06) = -0.117 \times 10^{-6}$$

$$\Delta\xi_d^{CB} = 0.0037\,\Delta\chi^{C\equiv N}$$

$$\therefore \Delta\chi^{C\equiv N} = -31.6 \times 10^{-6}$$

(iv). Bicyclo-(2:2:1)-hept-5-ene dinitrile. (3 sets of protons).

The magnetic anisotropy of the -C≡N bond is calculated in several bicyclo-(2:2:1)-hept-5-ene dinitriles from the internal chemical shift of protons having exactly the same electronic environment , but differ with respect to their orientation to the -C≡N bonds. In all these compounds, the shielding was corrected for the electrostatic effects of the -C≡N bonds.

The electrical shielding for the bridge-protons , enumerated 2 and 3 in the diagram , was calculated using the general expression

based on the point dipole approximation. Since the distances R_2 and R_3 are large and hence, the error encountered is negligible.

$$E_T = \mu / R^3 \ (2\cos\theta z.\cos\gamma + \sin\theta z.\cos w)$$

Substituting the appropriate values in the foregoing expression, the following values are obtained for these two protons.

$$E^{H2} = +0.0324 \times 10^{6}$$
$$\Delta\xi_e^{H2} = -0.065 \times 10^{-6}$$

and,

$$E^{H3} = +0.0399 \times 10^{6}$$
$$\Delta\xi_e^{H3} = -0.0798 \times 10^{-6}$$

The total electrical shielding due to the two nitrile groups is :

$$\Delta\xi_e^{H2} = -0.129 \times 10^{-6}$$
$$\Delta\xi_e^{H3} = -0.159 \times 10^{-6}$$

$$\therefore \Delta\xi_e^{H2} - \Delta\xi_e^{H3} = \Delta\xi_e^{H2-3} = -0.129 \times 10^{-6} - (-0.159 \times 10^{-6})$$
$$= +0.03 \times 10^{-6}$$

Since,

$$\Delta\xi_T = \Delta\xi_d + \Delta\xi_e$$

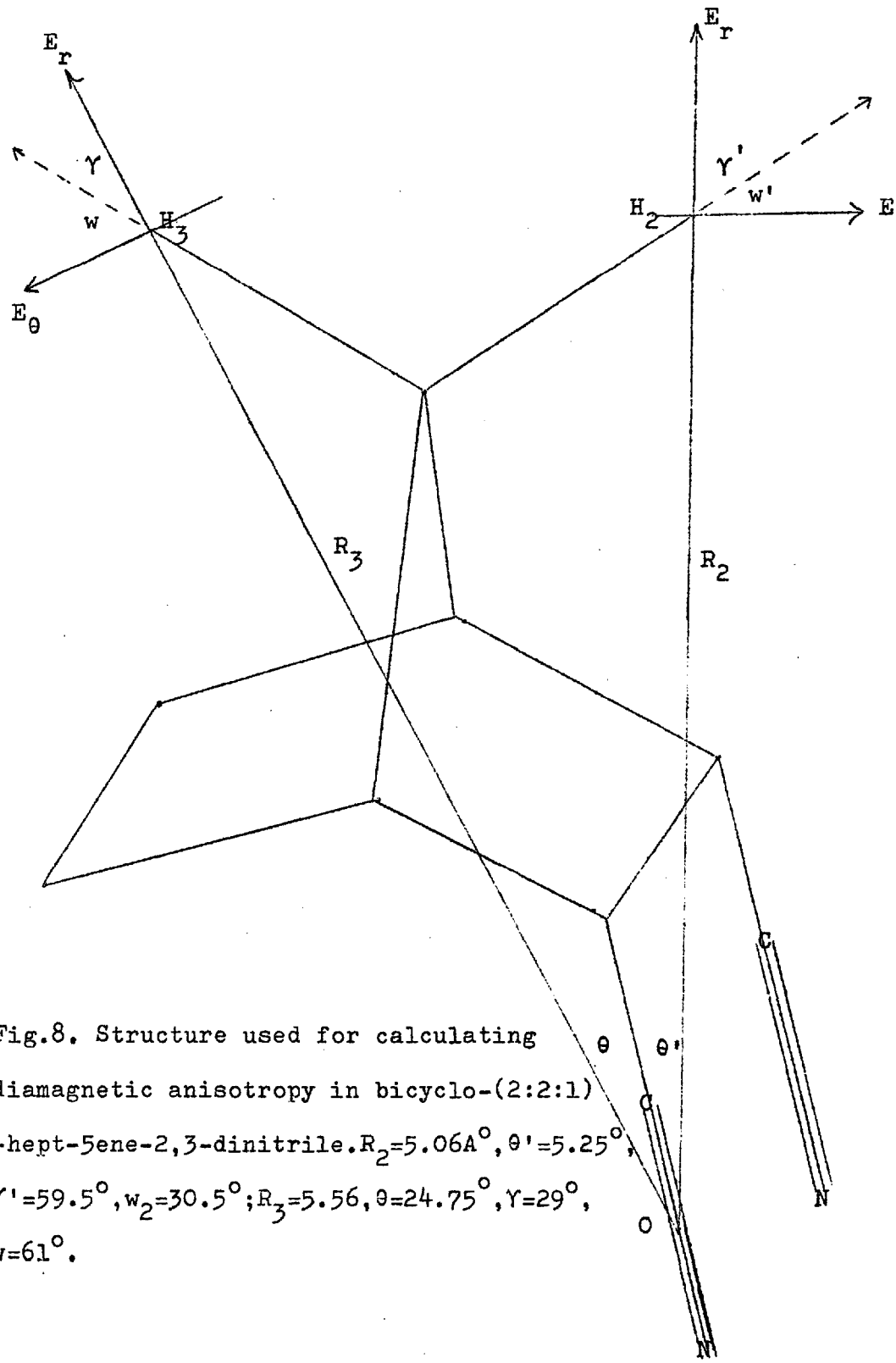


Fig.8. Structure used for calculating diamagnetic anisotropy in bicyclo-(2:2:1) -hept-5ene-2,3-dinitrile. R_2=5.06A°, θ'=5.25°, γ'=59.5°, w_2=30.5°; R_3=5.56, θ=24.75°, γ=29°, w=61°.

Where, T, d, and e, refer to total chemical shift difference, the chemical shift difference due to distant anisotropic groups, and the difference in electrical shielding due to the -C≡N bond respectively.

$$\therefore \Delta\xi_d = 0.315 \times 10^{-6} - 0.03 \times 10^{-6} = +0.285 \times 10^{-6}$$

$$\Delta\xi_d = 2\Delta\chi^{C\equiv N}/3L_o \left[(1 - 3\cos^2\theta z)/R_2^3 - (1 - 3\cos^2\theta z)/R_3^3 \right]$$

$$+0.285 \times 10^{-6} = -0.00736\, \Delta\chi^{C\equiv N}$$

$$\therefore \Delta\chi^{C\equiv N} = -38.77 \times 10^{-6} \text{ cm.}^3\text{mole.}^{-1}$$

The electrical shielding of the H_2 proton due to the exo-nitrile group was calculated using the partial point charge approximation, since R_2 is appreciably smaller than R_3.

$$E_T^{H2} = e/R_1^2 \cdot \cos\alpha - e/R_2^2 \cdot \cos\beta$$

Since, $\mu = el$, $\therefore e = \mu/l$,

$$\therefore E_T^{H2} = \mu/l \left[(\cos\alpha)/R_1^2 - (\cos\beta)/R_2^2 \right]$$

Substituting the values of the various parameters in this equation

we obtain,

$$E^{H2} = -0.104 \times 10^{6}$$

$$\Delta\xi_e^{H2} = +0.198 \times 10^{-6} \quad \text{(due to the exo-nitrile group),}$$

Since the electrical shielding of the H_2 proton due to the endo-nitrile group is -0.065×10^{-6},

$$\therefore \Delta\xi_T^{H2} = 0.198 \times 10^{-6} + (-0.065 \times 10^{-6})$$

$$= +0.133 \times 10^{-6}$$

and similarly,

$$\Delta\xi_T^{H3} = -0.105 \times 10^{-6} + (-0.0798 \times 10^{-6}) = -0.185 \times 10^{-6}$$

$$\Delta\xi_e^{H2} - \Delta\xi_e^{H3} = 0.133 \times 10^{-6} + 0.185 \times 10^{-6}$$

$$= +0.318 \times 10^{-6}$$

$$\Delta\xi_d = \Delta\xi_T - \Delta\xi_e$$

Since $\Delta\xi_T = 0$,

$$\therefore \Delta\xi_d = -0.318 \times 10^{-6}$$

$$-0.318 \times 10^{-6} = +0.00845\,\Delta\chi^{C\equiv N}$$

$$\therefore \Delta\chi^{C\equiv N} = -37.65 \times 10^{-6}$$

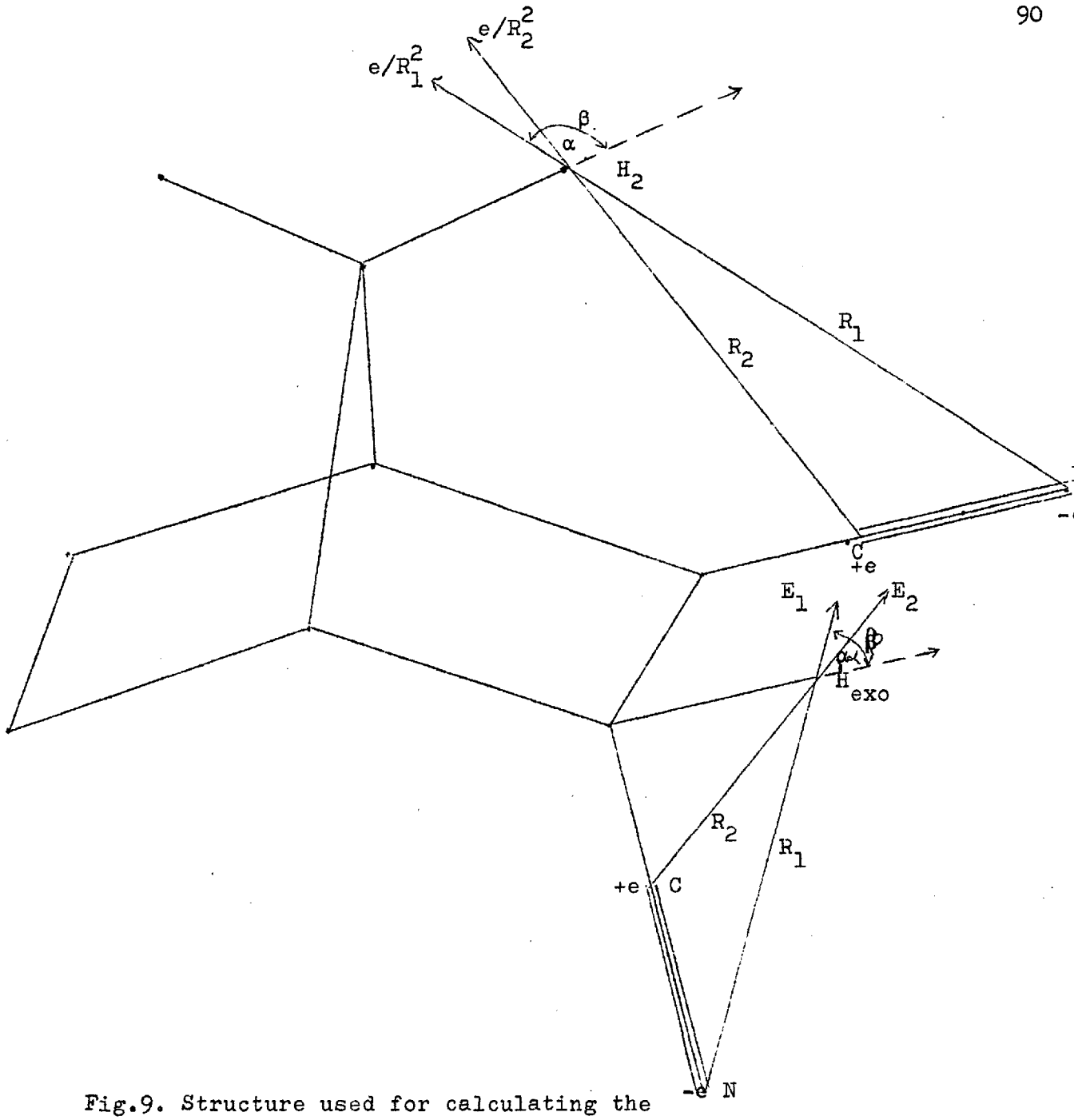


Fig.9. Structure used for calculating the electrical shielding of the protons in bicyclo-(2:2:1)-hept-5-ene-2,3-trans dinitrile. For H_2; R_1=3.27A°, R_2=2.84, α=113.5°, β=93°. For H(exo); R_1=2.26A°, R_2=3.36, α=36.5°, β=45°.

Estimation of the electrical shielding for the endo-proton at position 3, in trans-bicyclo-(2:2:1)-hept-5-ene-dinitrile.

1. Shielding due to the endo C≡N group at position 2.

$R_1 = 2.4A^\circ$, $R_2 = 3.09A^\circ$, $\alpha = 79^\circ$, $\beta = 98.5^\circ$.

$$E = /1\ (\cos\alpha/R_1^2 - \cos\beta/R_2^2)$$

$$E = +0.161 \times 10^6$$

$$\Delta\xi_e = -0.348 \times 10^{-6}$$

2. Shielding due to the exo -C≡N group at position 3.

$R_1 = 2.25A^\circ$, $R_2^2 = 3.32A^\circ$, $\alpha = 32^\circ$, $\beta = 39.5^\circ$.

$$E = +0.323 \times 10^6$$

$$\Delta\xi_e = -0.75 \times 10^{-6}$$

The total electrical shielding of the endo proton at position 3, due to both -C≡N groups is:

$$\xi_T^{en\text{-}H} = -0.348 \times 10^{-6} + (-0.75 \times 10^{-6})$$

$$= -1.098 \times 10^{-6}$$

Estimation of electrical shielding for the exo-proton at position 2, in trans-bicyclo-(2:2:1)-hept-5-ene-2,3-dinitrile.

1. Shielding due to the endo -C≡N group at position 2.

$R_1 = 2.26A^\circ$, $R_2 = 3.36A^\circ$, $\beta = 45^\circ$, $\alpha = 36.5^\circ$.

$$E = +0.314 \times 10^6$$

$$\Delta\xi_e = -0.726 \times 10^{-6}$$

2. Electrical shielding due to the exo -C≡N group at position 3.

$R_1 = 3.04A^{\circ}$, $R_2 = 3.90A^{\circ}$, $\alpha = 59.5^{\circ}$, $\beta = 72^{\circ}$.

$$E = \mu/1\ (\cos\alpha/R_1^2 - \cos\beta/R_2^2)$$

$$E = +0.115 \times 10^{6}$$

$$\Delta\xi_e = -0.242 \times 10^{-6}$$

The total electrical shielding of the exo-proton at position 2, due to both -C≡N groups at positions 2 and 3 is:

$$\xi_{T_e}^{ex\text{-}H} = -0.726 \times 10^{-6} + (-0.24 \times 10^{-6})$$

$$= -0.969 \times 10^{-6}$$

$$\xi_{T_e}^{en\text{-}H} - \xi_{T_e}^{ex\text{-}H} = -1.098 \times 10^{-6} + 0.969 \times 10^{-6}$$

$$= -0.129 \times 10^{-6}$$

$$\xi_d^{en\text{-}H} - \xi_d^{ex\text{-}H} = \Delta\chi^{C\equiv N}/3L_o\left[(1 - 3\cos\theta_{en}^2)/R_{en}^3 - (1 - 3\cos^2\theta_{ex})/R_{ex}^3\right]$$

$$= -0.05\,\Delta\chi^{C\equiv N} + 0.051\,\Delta\chi^{C\equiv N}$$

$$= +0.001\,\Delta\chi^{C\equiv N}$$

Since $\xi_T^{en\text{-}H} - \xi_T^{ex\text{-}H} = -0.17 \times 10^{-6}$

$$\therefore\ \xi_d^{en\text{-}H} - \xi_d^{ex\text{-}H} = -0.17 \times 10^{-6} + 0.129 \times 10^{-6}$$

$$= -0.04 \times 10^{-6}$$

$$\therefore\ \Delta\chi^{C\equiv N} = -40.4 \times 10^{-6}$$

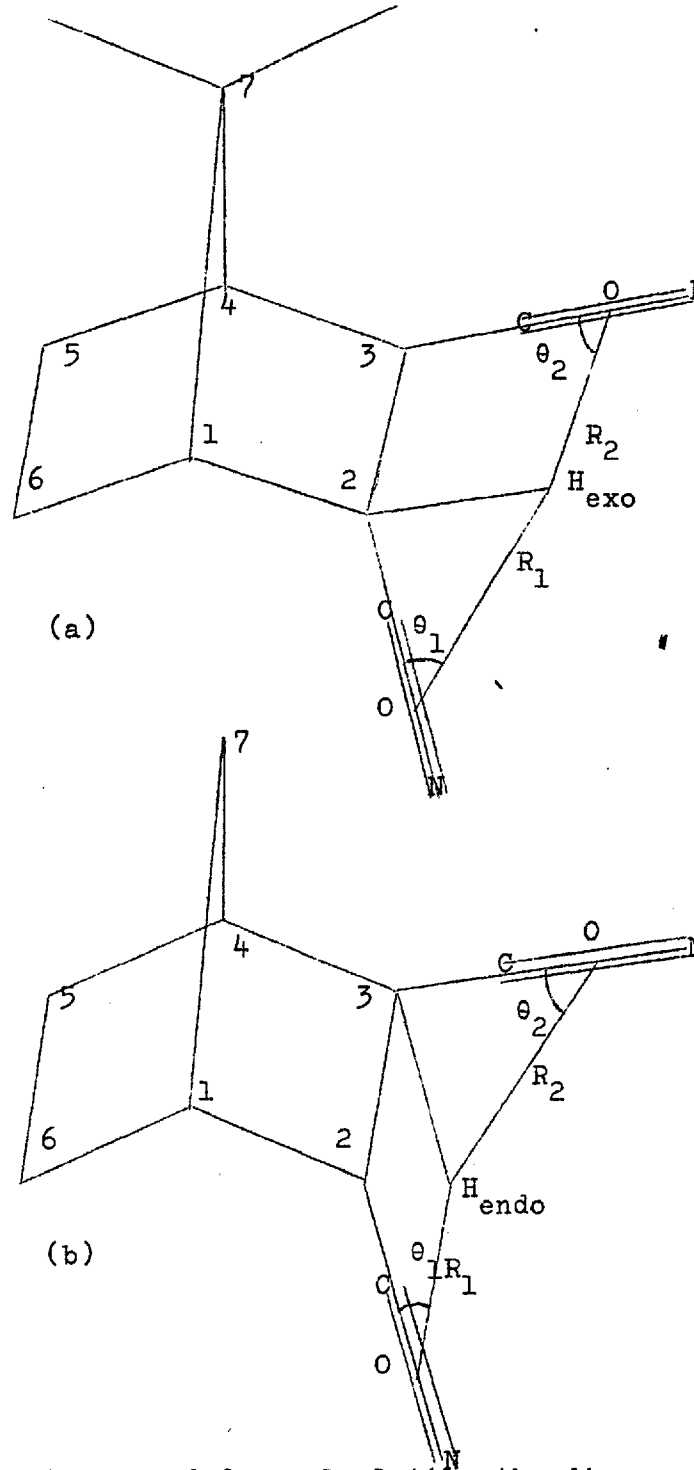


Fig.10. (a). Structure used for calculating the diamagnetic anisotropy of the -C≡N bond in <u>trans</u>-bicyclo-(2:2:1)-hept-5-ene-2,3-dinitrile. R_1 = 2.8A°, R_2=3.45A°, θ_1=20.3°, θ_2=41.3°. (b). R_1=2.72A°, R_2=2.78A°, θ_1=51.5°, θ_2=19°.

(v). Toluonitriles.

The electrical shielding of the o-and m-protons in p-toluonitrile was calculated by the same general method described previously, based on the partial point charge approximation.

For o-proton,

$R_1 = 2.57A^\circ$, $R_2 = 3.36A^\circ$, $\alpha = 61.5^\circ$, $\beta = 79^\circ$.

$$E = \mu/1\ (\cos\alpha/R_1^2 - \cos\beta/R_2^2)$$

$$E^o = +0.183 \times 10^6,$$

$$\Delta\xi_e^o = -0.399 \times 10^{-6}$$

For m-proton,

$R_1 = 4.38A^\circ$, $R_2 = 5.45A^\circ$, $\alpha = 30.5^\circ$, $\beta = 36.5^\circ$.

$$E^m = +0.059 \times 10^{+6}$$

$$\Delta\xi_e^m = -0.118 \times 10^{-6}$$

$$\Delta\xi_e^o - \Delta\xi_e^m = -0.399 \times 10^{-6} - (-0.118 \times 10^{-6})$$

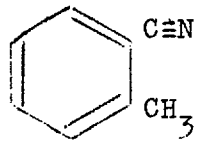
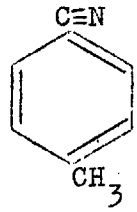
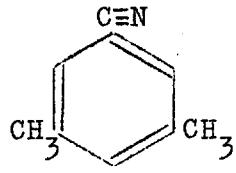
$$= -0.282 \times 10^{-6}$$

Since, $\xi_T^o - \xi_T^m = -0.209 \times 10^{-6}$

$$\therefore\ \xi_d^o - \xi_d^m = -0.209 \times 10^{-6} - (-0.282 \times 10^{-6})$$

$$= +0.0709 \times 10^{-6}$$

Table IV. The magnetic anisotropy of the -C≡N bond derived from NMR chemical shift data on o-, p-,and m-Tolunitrile.

Compound	distance "O" from carbon	$\Delta\chi^{C\equiv N} 10^6$	$\xi_d \times 10^6$	$\xi_e \times 10^6$
	0.579A°	-28.73	-0.0802	+0.0333
	0.620	-27.25	-0.0837	"
	0.660	-29.89	-0.0780	"
	0.700	-32.91	-0.0706	"
	0.770	-31.71	-0.0768	"
	0.780	-32.69	-0.0758	"
	"	"	+0.0955	-0.0371
	"	"	+0.0884	"
	"	"	+0.0966	"
	"	"	+0.1048	"
	"	"	+0.0985	"
	"	"	+0.0996	"
	"	"	+0.1084	-0.0153
	"	"	+0.1070	"
	"	"	+0.1126	"
	"	"	+0.1200	"
	"	"	+0.1138	"
	"	"	+0.1178	"

and,

$$\xi_d^{C-m} = \Delta\chi^{C\equiv N}/3L_o\left[(1 - 3\cos^2\vartheta_z/R_o^3 - (1 - 3\cos^2\vartheta_z/R_m^3\right]$$

$R_o = 3.04A^o$, $\vartheta_o = 46.7^o$,

$R_m = 5.10A^o$, $\theta_m = 25.5^o$.

$$\therefore \quad \xi_d^o - \xi_d^m = -0.00207\ \Delta\chi^{C\equiv N}$$

$$\therefore \quad \Delta\chi^{C\equiv N} = -34.18 \times 10^{-6}\ cm.^3 mole.^{-1}$$

(vi). ββ-Dimethylacrylonitrile.

Expressions for the electrical shielding of the two methyl groups in ββ-dimethylacrylonitrile were derived , using the point dipole approximation. The method is exactly similar to that described previously. Figs. 11 and 12 shows the structural parameters used in the calculations. The expressions for the two methyl groups are:

$$E^A = \mu/8\pi r_3 r_6\left\{JA + \left[(r_3^2 - r_4^2) + 3(r_6^2 - r_7^2) + 4r_3 r_7\cos\gamma\right] JB + \left[3(r_6^2 - r_7^2)(r_3^2 - r_4^2)\right] JC\right.$$

and,

$$E^B = \mu/4\pi r_6 \left[(3r_4\cos\xi - 2r_7\cos\Upsilon)JB + r_4(r_6^2 - r_7^2)\cos\xi \; JC \right]$$

Where, JA, JB, and JC are the elliptical integrals defined previously, and the other parameters are shown in Figs. 11 and 12. Substituting the appropriate values in the above expressions, we obtain,

$$E^A = +0.0927 \times 10^6$$

$$\xi_e^A = -0.194 \times 10^{-6}$$

and,

$$E^B = +0.066 \times 10^{+6}$$

$$\xi_e^B = -0.136 \times 10^{-6}$$

$$\therefore \quad \xi_e^A - \xi_e^B = (-0.193 - (-0.136)) \times 10^{-6}$$

$$= -0.057 \times 10^{-6}$$

Since, $\xi_T^A - \xi_T^B = -0.433 \times 10^{-6}$

$$\therefore \quad \xi_d^A - \xi_d^B = -0.433 \times 10^{-6} - (-0.057 \times 10^{-6})$$

$$= -0.376 \times 10^{-6}$$

$$\xi_d^A - \xi_d^B = \Delta\chi^{C\equiv N}/3L_o \; (T_z^A - T_z^B)$$

Where, $T_z = (1 - 3\cos^2\theta z)/R^3$

$$-0.376 \times 10^{-6} = 0.01189 \; \Delta\chi^{C\equiv N}$$

$$\therefore \quad \Delta\chi^{C\equiv N} = -31.6 \times 10^{-6} \text{ cm.}^3\text{mole.}^{-1}$$

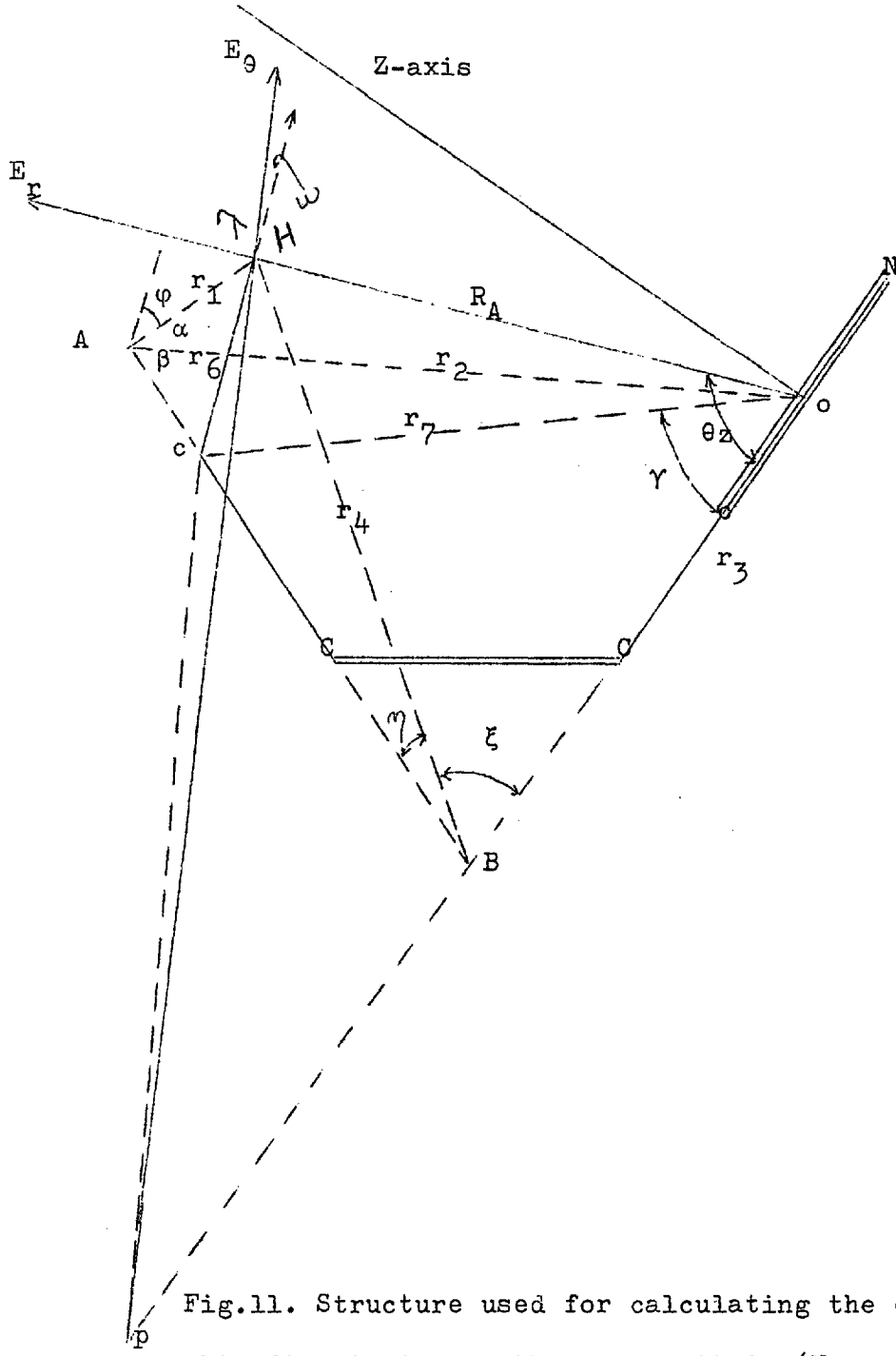


Fig.11. Structure used for calculating the electrical shielding in ββ-dimethylacrylonitrile(Nucleus A).

R_A=2.58A°, r_1=0.96, r_2=3.32, r_3=3.25, r_4=3.36, β=59°, γ=50°, r_6=1.10, r_7=3.08, =3.84 x 10^{-18} e.s.u. JA=1.7349x10^{8}, JB=1.90272 x10^{23}, JC=2.1247x10^{38}, T_z^A=+1.37118 x 10^{22}.

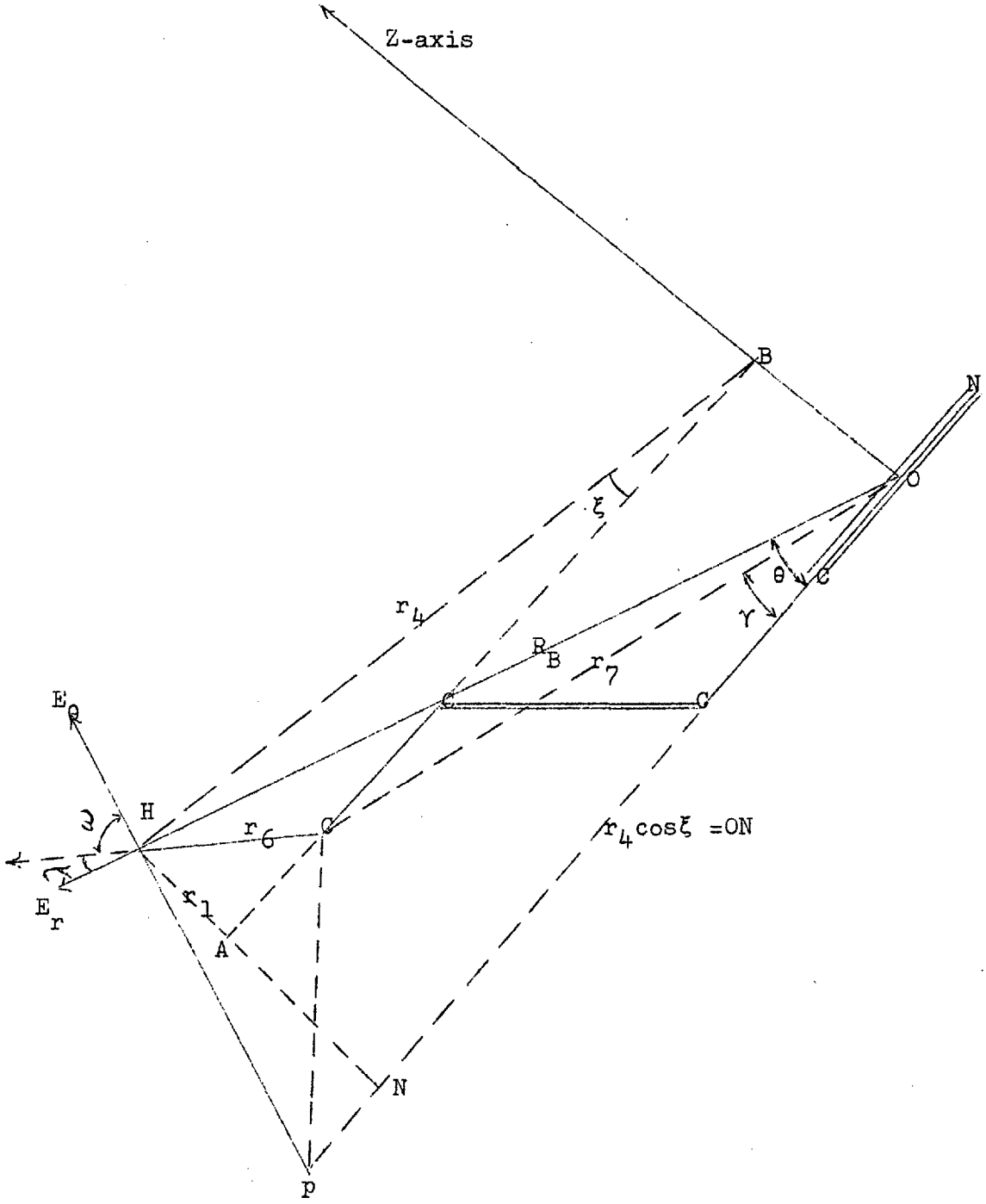


Fig. 12. Structure used for calculating the electrical shielding in ββ-dimethylacrylonitrile(Nucleus B). r_1=0.96Å°, r_2=4.74, r_3=1.22, r_4=4.74, r_6=1.10, r_7=4.24, β=15°, ξ=11.5°, γ=14.5°. JA=1.3036 x 10^8, JB=5.61709 x 10^{22}, JC=2.432676 x 10^{37}, T_Z^B = -0.776289 x 10^{22}.

C. THE ANISOTROPY OF THE -N≡C BOND.

The same general method, which were used to calculate $\Delta\xi_1$ in ethylacetylene, was applied in this case as well, using the value of 3.49 for the electronegativity of the -N≡C group.[57]

$$\Delta\xi_T = \Delta\xi_d + \Delta\xi_1 + \Delta\xi_e$$

Where, the subscripts d, 1, and e, represents the shift due to the magnetic anisotropy, the local shielding due to the electron cloud around the nucleus itself, and the electrical shielding respectively. Since,

$$E = 0.0114(\xi_{CH3} - \xi_{CH2}) + 1.78$$

$(\xi_{CH3} - \xi_{CH2})$ is in cycles/second, at 60 Mc./s.

$$3.49 = 0.0114(\xi_{CH3} - \xi_{CH2}) + 1.78$$

$$(\xi_{CH3} - \xi_{CH2}) = 150 \text{ c/s} = +2.5 \times 10^{-6} \text{ p.p.m.}$$

$$\therefore \Delta\xi_1 = +2.5 \times 10^{-6}$$

The electrical shielding of the methyl and methylene protons due to the -N≡C dipole was estimated and found to be:

$$E^{CH3} = +0.112 \times 10^{6}$$

$$\Delta\xi_e^{CH3} = -0.237 \times 10^{-6}$$

and,

$$E^{CH2} = +0.294 \times 10^{6}$$

$$\xi_e^{CH2} = -0.674 \times 10^{-6}$$

$$\therefore \quad \xi_e^{CH3} - \xi_e^{CH2} = +0.437 \times 10^{-6}$$

$$\Delta\xi_{\ } = 1.585 \times 10^{-6} - 0.437 \times 10^{-6} - 2.50 \times 10^{-6}$$

$$= -1.352 \times 10^{-6}$$

$$\Delta\xi_d = \Delta\chi^{N\equiv C}/3L_o(T_z^{CH3} - T_z^{CH2})$$

$$-1.352 \times 10^{-6} = 0.0347\ \Delta\chi^{N\equiv C}$$

$$\therefore \Delta\chi^{N\equiv C} = -38.92 \times 10^{-6}\ \text{cm.}^3\text{mole.}^{-1}$$

Estimation of the electrical shielding for the o-, m-, and p-, protons in Toluisonitriles.

The electrical field at the o-, m-, and p- protons in toluisonitriles was estimated by the method of partial point charge approximation, using the value of 3.64×10^{-18} e.s.u. for the dipole moment of the -N≡C bond.[46] The structural parameters used in the calculation, and the electrical shielding of these protons are shown bellow:

1. Electrical shielding for the o-proton.

$R_1 = 2.66A^\circ$, $R_2=3.5A^\circ$, $\alpha=65.5^\circ$, $\beta=81.5^\circ$, $R_0 =3.06A^\circ$, $\theta z =44.5^\circ$.

$E = \mu/1(\cos\alpha/R_1^2 - \cos\beta/R_2^2)$

$E^o = +0.144 \times 10^6$

$\xi_e^o = -0.308 \times 10^{-6}$

$\xi_d^o = -0.01016 \Delta\chi^{N\equiv C}$

2. Electrical shielding for the m-proton.

$R_1=4.59A^\circ$, $R_2=5.66A^\circ$, $R_m=5.13A^\circ$, $\alpha=31^\circ$, $\beta=36.6^\circ$, $\theta z=24.5^\circ$.

$E^m = +0.0486 \times 10^6$

$\xi_e^m = -0.099 \times 10^{-6}$

$\xi_d^m = -0.00608 \times \Delta\chi^{N\equiv C}$

3. Electrical shielding for the p-proton.

$R_1=5.26A^\circ$, $R_2=6.44A^\circ$, $R_p=5.86A^\circ$, $\alpha=0$, $\beta=0$, $\theta z=0$.

$E^p = +0.0371 \times 10^6$

$\xi_e^p = -0.0742 \times 10^{-6}$

$\xi_d^p = -0.0055 \Delta\chi^{N\equiv C}$

$\xi_e^o - \xi_e^p = -0.308 \times 10^{-6} + 0.0742 \times 10^{-6}$

$= -0.234 \times 10^{-6}$

$$\xi_e^o - \xi_e^m = -0.308 \times 10^{-6} + 0.0996 \times 10^{-6}$$

$$= -0.209 \times 10^{-6}$$

$$(\xi_d^o - \xi_d^p) = (\xi_1^o - \xi_1^p) - (\xi_e^o - \xi_e^p)$$

$$= -0.044 \times 10^{-6} + 0.234 \times 10^{-6}$$

$$= +0.19 \times 10^{-6}$$

$$+0.19 \times 10^{-6} = -0.00466 \, \Delta\chi^{N\equiv C}$$

$$\therefore \Delta\chi^{N\equiv C} = -40.75 \times 10^{-6} \text{ cm.}^3\text{mole.}^{-1}$$

also we have,

$$\xi_d^o - \xi_d^m = +0.208 \times 10^{-6} - 0.0436 \times 10^{-6}$$

$$= +0.165 \times 10^{-6}$$

$$+0.165 \times 10^{-6} = -0.00408 \, \Delta\chi^{N\equiv C}$$

$$\therefore \Delta\chi^{N\equiv C} = -40.45 \times 10^{-6} \text{ cm.}^3\text{mole.}^{-1}$$

Table V. The magnetic anisotropy of the -N≡C bond derived from NMR chemical shift data on o-, m-, and p-Toluisonitriles.

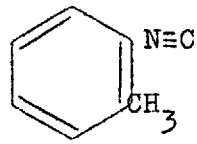
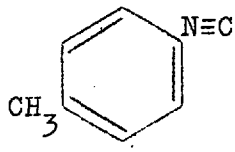
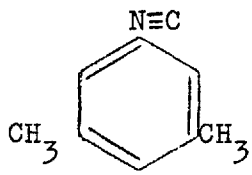
Compound	distance of"O" from carbon	$\Delta\chi^{N\equiv C}\ 10^{+6}$	$\xi_e \times 10^6$	$\xi_d \times 10^6$
	0.46	-35.72	+0.032	-0.006
	0.50	-35.71	"	-0.002
	0.54	-35.53	"	+0.007
	0.579	-33.43	"	+0.006
	0.62	-34.91	"	+0.013
	0.46	"	-0.035	+0.093
	0.50	"	"	+0.098
	0.54	"	"	+0.107
	0.579	"	"	+0.109
	0.60	"	"	+0.113
	0.46	"	-0.015	+0.170
	0.50	"	"	+0.174
	0.54	"	"	+0.184
	0.579	"	"	+0.182
	0.62	"	"	+0.190

Table VI. Observed chemical shift difference between the protons A and B, and the values of $\Delta T_z^{A-B}/3Lo$ for these protons, together with the values of the magnetic anisotropy of the -C≡C- bond.($cm.^3 mole.^{-1}$).

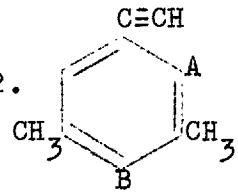
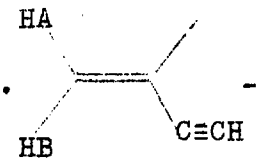
Compound	$10^6 \Delta\xi_d$	$10^6 \Delta\xi_l$	$10^6 \Delta\xi_T$	$T_z^{A-B}/3Lo$	$\Delta\chi^{C\equiv C} \times 10^6$
1. $CH_3^B CH_2^A C\equiv CH$	-1.268	+2.208	+0.94	+0.0359	- 35.26
2. 	+0.179	Assumed "0"	+0.179	-0.0056	-31.90
3. 	-0.18	0	-0.18	+0.0051	-35.40

Table V11. Observed chemical shift difference between the protons A and B, and the values of $\Delta T_z^{A-B}/3L_o$ for these protons, together with the values of the magnetic anisotropy of the -C≡N bond.($cm^3 mole.^{-1}$)

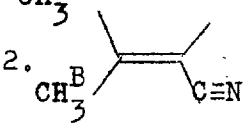
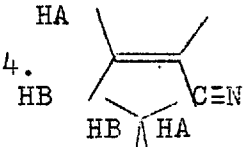
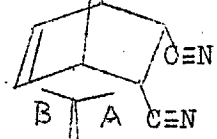
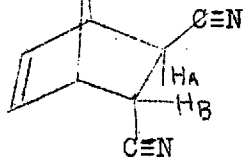
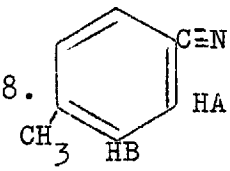
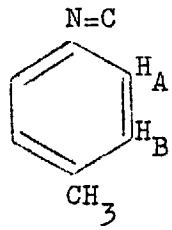
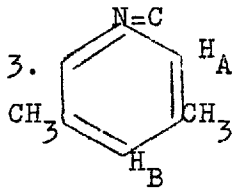
Compound	$10^6\Delta\xi_T^{A-B}$	$10^6\Delta\xi_e^{A-B}$	$10^6\Delta\xi_d^{A-B}$	$10^6\Delta\xi_l^{A-B}$	$\Delta T_z^{A-B}/3Lo$	$\Delta\chi^{-C\equiv N}/10^6$
1. $CH_3^B CH_2^A C\equiv N$	+1.033	+0.465	-1.376	1.944	+0.0347	-39.62
2. 	-0.177	-0.10	-0.077		+0.0037	-20.8
3. " "	-0.177	-0.061	-0.117		+0.0037	-31.6
4. 	-0.433	-0.057	+0.376		+0.0119	-31.6
5. 	+0.315	+0.03	+0.285		-0.00736	-38.77
6. 	0	+0.318	-0.318		+0.0085	-37.65
7. HA & Hb above	-0.17	-0.129	-04		+0.001	-40.4
8. 	-0.209	-0.282	+0.071		-0.00207	-34.18

Table Vlll. Observed chemical shift difference between the ptotons A and B, and the values of $\Delta T_z^{A-B}/3Lo$ for these protons, together with the values of the magnetic anisotropy of the -N≡C bond.($cm.^3 mole.^{-1}$)

Compound	$10^6\Delta\xi_T^{A-B}$	$10^6\Delta\xi_e^{A-B}$	$10^{+6}\Delta\xi_d^{A-B}$	$10^6\Delta\xi_l^{A-B}$	$\Delta T_z^{A-B}/3Lo$	$10^6\Delta\chi^{-N\equiv C}$
1. $CH_3\overset{B}{C}H_2\overset{A}{N}\equiv C$	+1.585	+0.437	-1.352	+2.50	+0.0347	-38.92
2. 	+0.045	-0.209	+0.165		-0.0041	-40.45
3. 	+0.044	-0.234	+0.19		-0.0047	-40.75

5. DISCUSSION.

We wish now to demonstrate experimentally the presence of these long-range contributions to the shielding of a proton in a molecule. At the same time, we demonstrate the existence and determine the magnitude of a definite anisotropy in the magnetic susceptibility of the average -C≡C-, -C≡N, and -N≡C triple bonds, from which such long-range contributions originate. The molecules are assumed to be in the liquid state, and summation , in the shielding expression, is over all long-range triple bonds, which are assumed to be axially symmetric with magnetic anisotropies $\Delta\chi^{X\equiv Y}$, Therefore,

$$\Delta\xi_d^{A-B} = \Delta\chi^{X\equiv Y} \sum'(T_z^A - T_z^B)/3Lo$$

Thus from the calculated value of $\sum'(T_z^A - T_z^B)/3Lo$, and the experimentally observed values of $\Delta\xi^{A-B}$, we determine $\Delta\chi^{X\equiv Y}$, Where, X≡Y represents a triple bond.

In tables 6, 7, and 8, are listed the values of $\sum'(T_z^A - T_z^B)/3Lo$ for specific nuclei, also are listed in the tables the appropriate experimental NMR relative chemical shifts for these nuclei, in a series of molecules containing the three different triple bonds.

The values from tables 6, 7, and 8, are plotted in Figs.13, 14, and 15, with $\Delta \xi_d^{A-B}$ as abscissa and $\sum(T_z^A - T_z^B)/3Lo$ as the ordinate. A marked linear dependence of these points is found, enabling us to conclude that such long-range bonds do contribute to the shielding and there is an anisotropy in the magnetic susceptibility of an average C≡C, -C≡N, and -N≡C triple bonds. Drawing the line of best fit through these points, we obtain from its slope the values of:

$$\Delta\chi^{C\equiv C} = \chi_L^{C\equiv C} - \chi_T^{C\equiv C} = -35.27 \pm 0.23 \times 10^{-6} \text{ cm.}^3\text{mole.}^{-1}$$
$$= -5.859 \pm 0.039 \times 10^{-29} \text{ cm.}^3\text{molecule}^{-1}.$$

$$\Delta\chi^{-C\equiv N} = \chi_L^{-C\equiv N} - \chi_T^{-C\equiv N} = -39.75 \pm 0.33 \times 10^{-6} \text{ cm.}^3\text{mole.}^{-1}$$
$$= -6.60 \pm 0.055 \times 10^{-29} \text{ cm.}^3\text{molecule}^{-1}$$

$$\Delta\chi^{-N\equiv C} = \chi_L^{N\equiv C} - \chi_T^{N\equiv C} = -39.05 \pm 0.19 \times 10^{-6} \text{ cm.}^3\text{mole.}^{-1}$$
$$= -6.48 \pm 0.032 \times 10^{-29} \text{ cm.}^3\text{molecule}^{-1}$$

The fact that these points do not lie exactly on a straight line, indicates that the assumptions we have made are not frequently valid. We feel, however, that our conclusions are justified and give every indication that other contributing effects are of higher order.

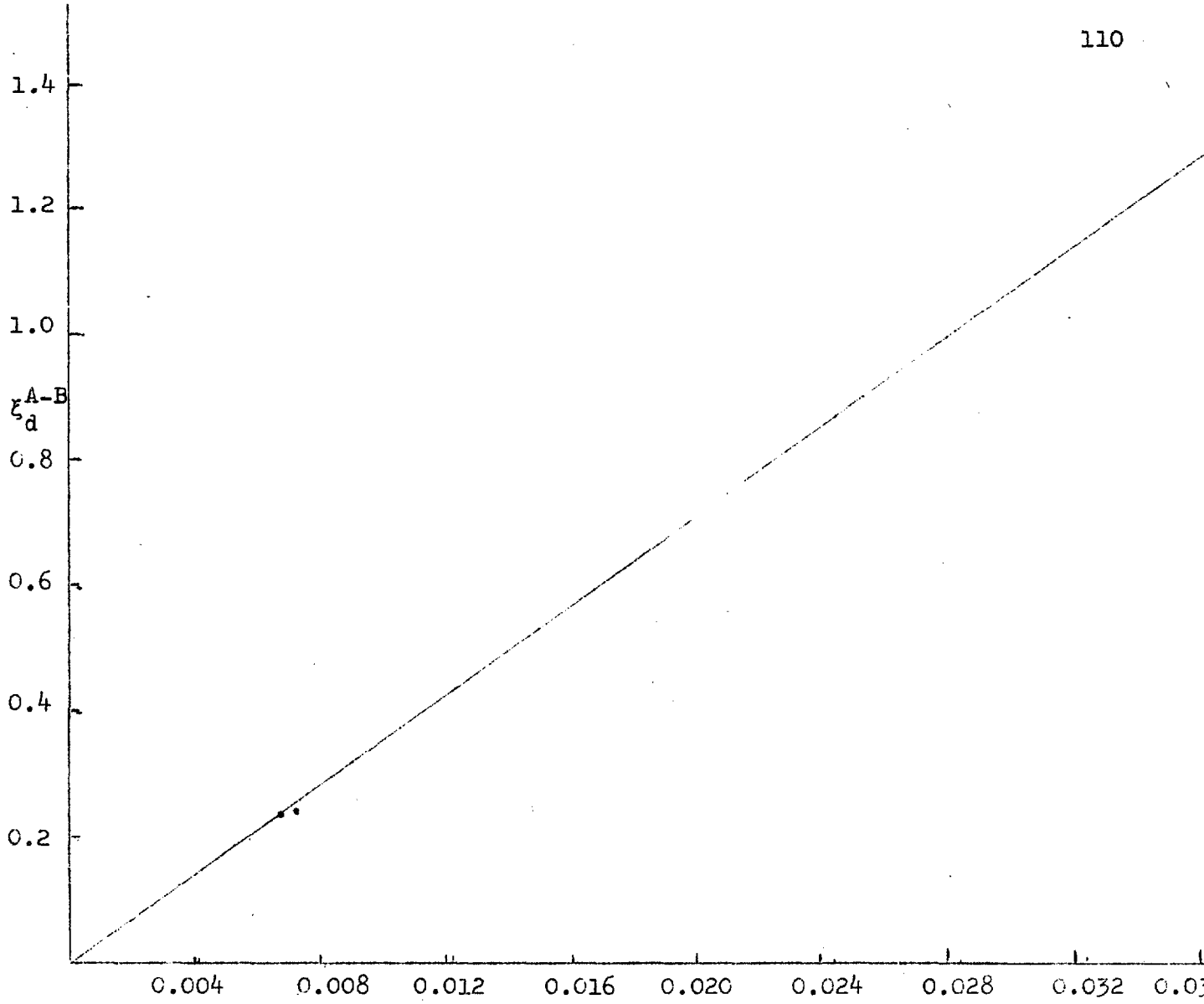


Fig. 13. Plot of $\sum(T_z^A - T_z^B)$ vs. $\Delta\xi_d^{A-B} \times 10^{-6}$ for acetylenes. $\sum(T_z^A - T_z^B)$

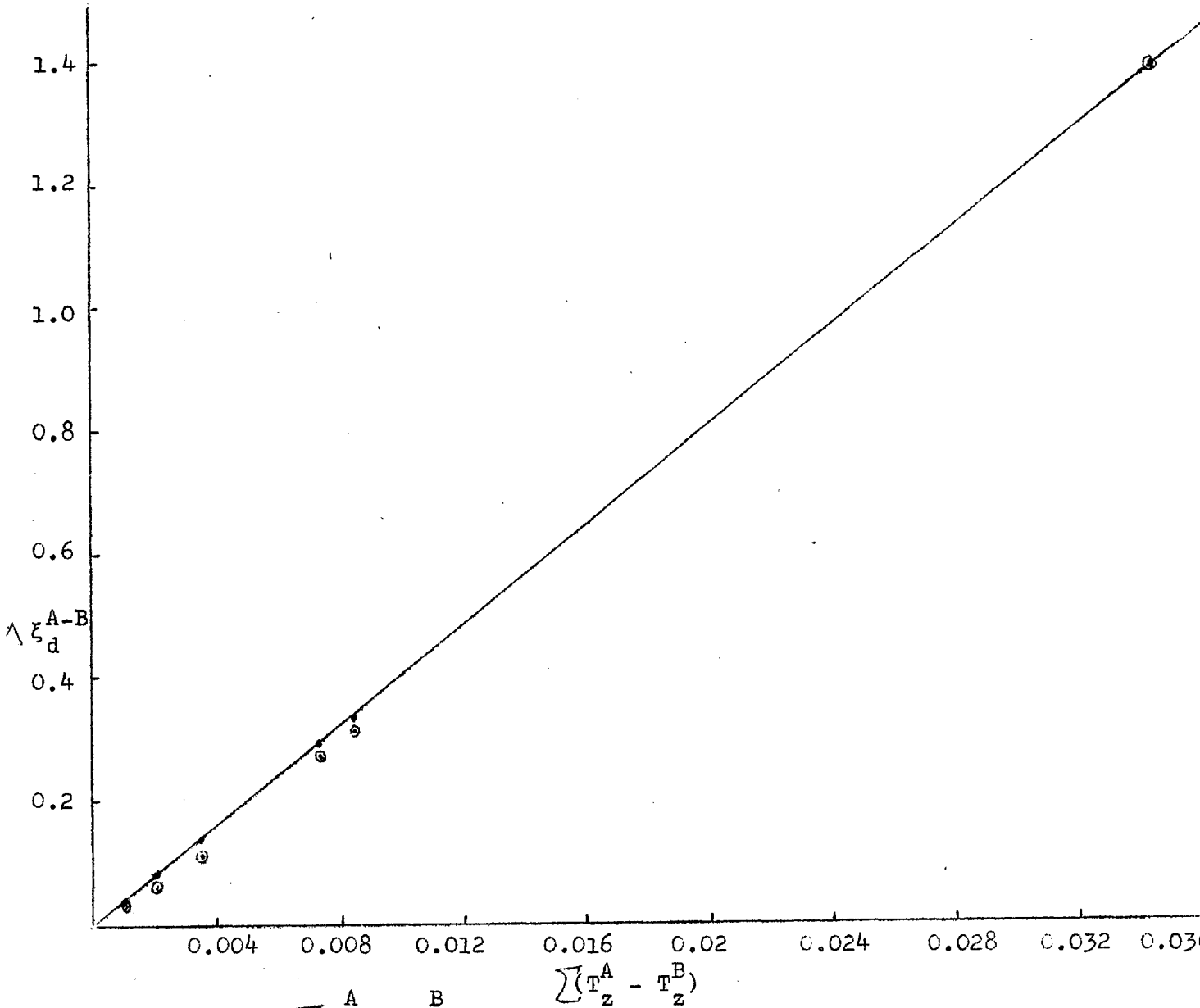


Fig.14 Plot of $\sum(Tz^A - Tz^B)$ vs. $\Delta\xi_d$ for nitriles.

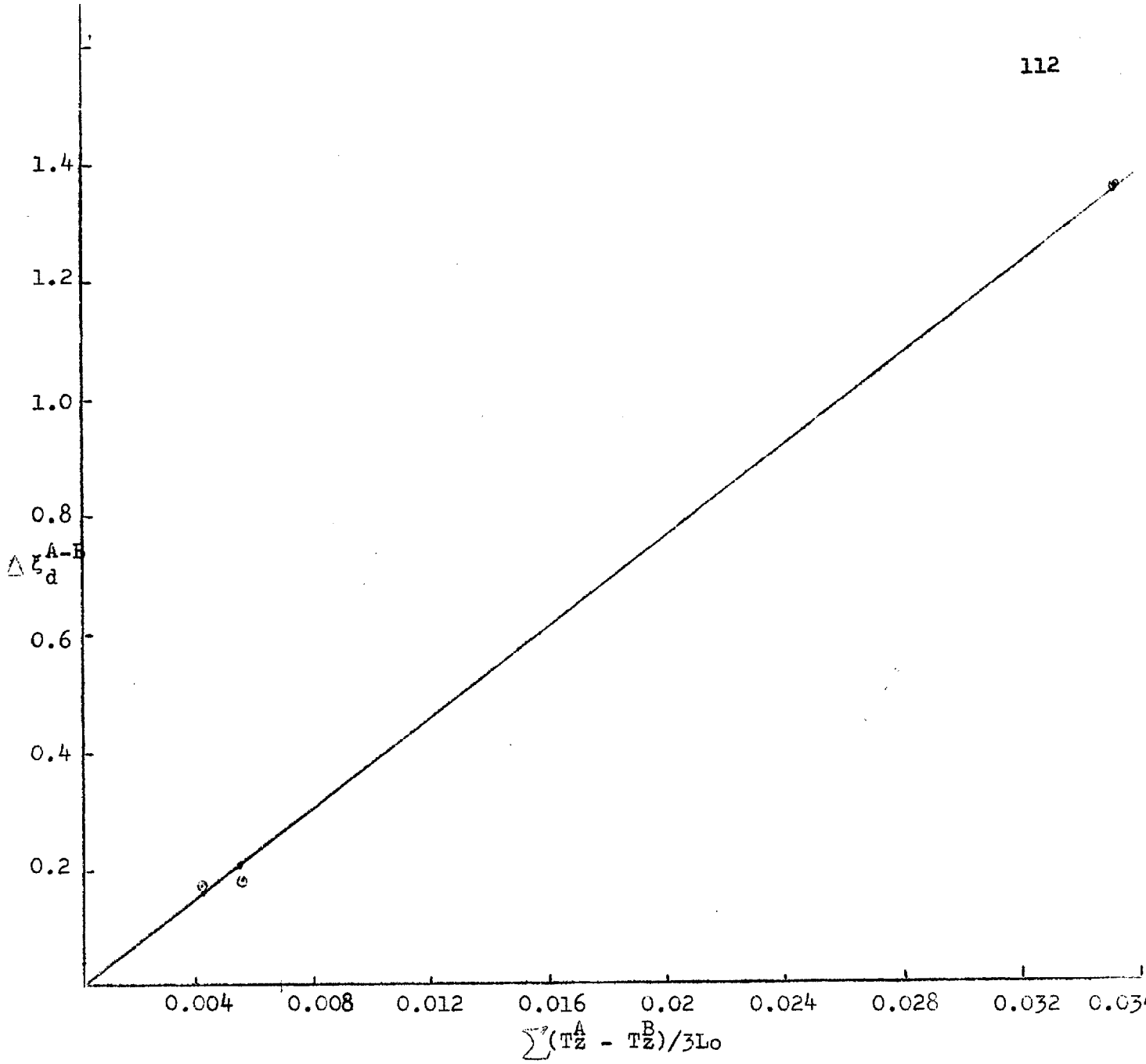


Fig.15. Plot of $\sum'(T_Z^A - T_Z^B)/3Lo$ vs. $\Delta \xi_d^{A-B}$ in isonitriles.

An examination of tables IV and V, shows the dependence of $\Delta\chi$ values for the -C≡N and -N≡C triple bonds on various parameters such as the location of the -C≡N and -N≡C dipoles. It was mentioned earlier, that, for mathematical simplicity we have idealized the induced dipoles by point dipoles, and such an idealization is valid when we consider the field due to these dipoles at very large distances. For actual calculations, it is customary to locate this dipole somewhere along the bond by making certain assumptions; one such assumption is to locate the dipole at the electrical centre of gravity of the electron distribution constituting the bond. Unfortunately, the task of locating the dipole in this manner is not as trivial as it appears at first sight. From theoretical studies on dipole moments of bonds,[62] it is well known that the location of the centre of gravity of a charge distribution in a bond is dependent, among other things, on two important factors, namely, the hybridization and the ionic character of the bond. At present, these two quantities are not as accurately known as one would desire, and hence, the location of the dipole in this manner is subject to some error.

In the case of the purely covalent bond, one can, without serious error place the dipole along the bond at a distance

corresponding to the covalent radii of the two atoms forming the bond. In fact, this assumption is true for the case of the C-H bond. But in the case of the more polar bonds, the electrical centre of gravity is likely to shift toward the more electronegative atom, while the exact location of this point is not easily determined. In the present case of the -C≡N, the nitrogen atom being much more electronegative than carbon, the centre of gravity is likely to be very near the nitrogen atom. While, in the case of the -N≡C bond, the centre of gravity is shifted toward the carbon atom as being the negative pole of the $\overset{+}{N}\equiv\overset{-}{C}$ dipole.[63] Hence, calculations have been made with the -C≡N and -N≡C dipoles at different locations near the nitrogen atom in the first case, and near the carbon atom in the second case. Owing to this uncertainty in the location of the induced dipole, the anisotropy values differ widly, although, it must be mentioned that the values themselves are of reasonable order of magnitude. It is indeed rather unfortunate, that, no direct experimental measurements of the principal magnetic susceptibilities of these bonds is possible at present. Also if the electronic

centre of gravity of the -C≡N and -N≡C bonds in these molecules could be located more precisely by other methods, it might then be possible to limit the choice of $\Delta\chi$ values more satisfactorally.

From considerations of the graph of $\Delta\xi_d^{A-B}$ vs. $\sum(T_z^A - T_z^B)/3Lo$, most of the points lie rather close to this line, and evidence appears good that we are justified in drawing the relavent conclusions:

(a). There is a definite contribution for long-range -C≡C-, -C≡N, and -N≡C triple bonds in the form of an effective field, at the nucleus N, of a pair of point dipoles located parallel and perpendicular to each triple bond axis. The perpendicular chosen in the plane of the radius vector R and the bond axis.

(b). There is a definite anisotropy in the magnetic susceptibility of each of the three triple bonds, such that the longitudinal susceptibility is smaller than the transverse susceptibility or that χ L is diamagnetic relative to χ T. It is this anisotropy which makes the dipoles of (a) of different strengths, thus providing a net or observable effect in molecules rapidly reorienting relative to the applied magnetic field. The negative sign of $\Delta\chi$, indicates that the diamagnetic susceptibility perpendicular to the axis of

symmetry $|\chi_T^D|$, must be considerably smaller in magnitude than $|\chi_L^D|$. This is so because in an axially symmetric system $\chi_L^P = 0$, and only $\chi_T^P (>) \neq 0$. Therefore,

$\Delta\chi^{X\equiv Y} = \chi_L - \chi_T = \chi_L^D - \chi_T^D - \chi_T^P < 0$, $|\chi_L^D|$ must be large and negative.

In carrying out the calculations, we have taken into account two important points:

(a). In most of the model compounts chosen, we have used the internal chemical shift between two protons which are located on the same carbon atom, or on two different carbon atoms with the same electron distribution around(for example, the o-and p-positions in monosubstituted benzenes). Hence, $\Delta\xi_1$ for such protons will be zero. Therefore, the difference in the chemical shift ($\Delta\xi_T$), will be due to the difference in the magnetic anisotropy effect alone.

(b). The two protons under consideration are symmetrically placed with respect to all other single or double bonds or any other group in the molecule, but the triple bonds. The two β-protons in vinylacetylene and acrylonitrile are typical examples for such calculations. Hence, the value of $\Delta\chi^{C\equiv C}$ and $\Delta\chi^{C\equiv N}$ obtained from these

calculations are considered of high validity.

The measurement of $\Delta\chi$ for a triple bond by this method accomplishes what would be very difficult to do by any other method. The ideal experiment for measuring the susceptibility of a triple bond in both the transverse and longitudinal directions would be to freeze acetylene, as an example, in a crystal in which all the acetylenic bonds were parallel, and such that all molecules were sufficiently far apart to eliminate nuclear dipole fields and then performing the magnetic susceptibility measurements. By using the experimental values of $\Delta\chi$, and the quantum mechanical expression for $\Delta\chi$, the validity of different possible wave functions for the triple bonds can be determined.

At this point a few comments must be made on the previous attempts to obtain the magnetic anisotropy of the -C≡C- bond. There is only one paper, which could be considered as an extensive attempt to give experimental magnetic anisotropies. In this paper, Heel and Zeil,[14] have calculated $\Delta\chi^{C\equiv C}$ for a -C≡C- bond, and they give a value of -5.24×10^{-29} cm.^{3}molecule^{-1} = -32.69×10^{-6} cm.^{3}mole.$^{-1}$. They base this value on the internal chemical shift difference

between the methyl and methylene protons in ethylacetylene. They have used the value of 3.1 for the electronegativity of the -C≡C- bond, and have calculated the internal chemical shift due to the difference in electronegativity at the two carbon atoms by the use of Daily and Shoolery equation.[19]

Again, one has to comment on the value of group electronegativity (3.1), which these authors have used in their calculations. Wilmshurst,[57] have calculated group electronegativities by utilizing and extending Gordy's expression,[66] relating the electronegativity of an atom with the number of electrons in the valence shell and the covalent bond radius. Both the state of hybridization and the effect of the electronegativity property of other atoms on the bonding atom in the radical have been accounted for. The group electronegativities calculated by this expression are in good agreement with those obtained from the sensitive C-H bending vibrational frequencies, but disagree with group electronegativities obtained from other spectroscopic data. Wilmshurst have discussed the cause of these deviations in detail.

In the case of electronegativities of groups derived from studies of the change of a double bond vibrational stretching frequency

with the electronegativity of substituents, anomalies may be expected to occur.[67-70] Inter or intramolecular bonding is very common with these molecules, especially if one of the substituents attached to the double bond is an OH, NH, C≡CH, -N≡C, or -C≡N groups,[74-76] and in such cases the double bond frequency is more sensitive to the intermolecular bonding than to the electronegativity of the substituents On the other hand, group electronegativities obtained from the relation of the C-H bending frequencies against the electronegativity of the substituent in substituted methanes are not effected by inter or intramolecular bonding effects, and depend on the electronegativity of the substituent and not on their ionization potential(or electron affinity) alone.[70-72] A study of the relation between the difference in methyl and methylene proton magnetic resonance shift ($\delta CH_3 - \delta CH_2$), and the electronegativity of the substituent in the monosubstituted ethanes, as suggested by Daily and Shoolery,[19] should lead to good electronegativity values. However, when the substituent group is capable of intermolecular bonding, its group electronegativity will depend on the degree of association, and in these cases the molecules must be invistigated in the gas phase or at infinite dilution in an

inert solvent to obtain correct group electronegativities. It is not surprising, therefore, that the data of Daily and Shoolery, which applies to 50% solutions in benzene, gives group electronegativities for the radicals -OH, $-NH_2$, $-C\equiv N$, and $-\varphi$, in poor agreement with the values reported by Wilmshurst.

In fact, the electronegativity value for the $-C\equiv C-$ bond as calculated by Wilmshurst is 3.29 and the value which have been used by Heel and Zeil is 3.1 , and it does not appear in the table given by Wilmshurst for the electronegativities of a large number of radicals. In their calculations, Heel and Zeil have used the original Daily-Shoolery equation for 50% solutions in benzene. Consequently, since benzene has been shown to have anomalous dilution effects, their results have been reviewed by Cavanaugh and Daily,[15] on dilute solutions of a series of ethyl, proryl, and <u>iso</u>-propyl derivatives in carbon tetrachloride and extrapolated to infinite concentration. A revised Daily-Shoolery equation have been set up by Cavanaugh and Daily using their own data and it appears in the following form:

$$\text{Electronegativity} = 0.0114\ d_{\text{internal}} + 1.78$$

Where, d is in c/s at 60 Mc/s.

These authors have used this equation to calculate the electronegativity values for a number of radicals. Their results differ slightly from those obtained by Daily an Shoolery.

It is interesting to compare our results with those obtained theoretically by Guy and Tillieu,[72,73] who have calculated by a variational method, the two principal magnetic susceptibilities of the C-C bond for different states of hybridization of the carbon atom. They obtained a value of -1.16×10^{-6} cm.^{3}mole.$^{-1}$ for the magnetic anisotropy of the -C≡C- bond. This value agrees in sign with our experimental results but is decidedly different in magnitude.

It is interesting to note certain remarks made by Bothner-By and Naar Colin,[64] regarding proton shielding in alkanes bases on their work on haloalkanes. These authors noted that the internal chemical shift in alkanes could be explained on the assumption of a large magnetic anisotropy for the C-C single bond, or on the basis of electronegativity differences. Since the electronegativity of carbon as calculated from NMR shielding data on alkanes by the use of Daily-Shoolery equation, is much lower than the generally accepted values, Bothner-By and Naar Colin concluded, that, in these molecules

the observed shift cannot be accounted for by electronegativity considerations alone. The present semi-quantitative treatment indicates that in the case of ethylacetylene, ethylcyanide, and ethylisocyanide, the major contribution to the internal chemical shift comes from $\Delta\xi_1$, and that the observed shift cannot be satisfactorally explained on the basis of bond magnetic anisotropy alone.

It seems probable from the present work, that, both bond magnetic anisotropies and electronegativity differences contribute to the chemical shift between the methyl and methylene protons in these three molecules, and that both effects are of the same order of magnitude. The local shielding differences perhaps being somewhat the more important.

The value of $\xi_d^{\equiv CH}$ contribution to the shielding of the proton in acetylene could be estimated from the calculated value of $\Delta\chi^{-C\equiv C-}$ and the known geometry of the molecule.[59] The shielding expression is,

$$\xi_d = \Delta\chi^{C\equiv C}/3Lo\left[(1 - 3\cos\theta z)/R^3\right]$$

If we treat this as a point dipole and substituting, R=1.644A°, θ=0, in the above relation, the corresponding paramagnetic contribution

to ξ is $+7.8 \times 10^{-6}$. This means that the paramagnetic effect will displace the proton signal in acetylene by +7.8 p.p.m. towards high fields. It is interesting to compare this value with that obtained by Pople,[5] in a quantum mechanical study of the proton chemical shift in acetylene, Pople found that the paramagnetic contribution to the shielding of the acetylenic proton is 10×10^{-6}. Pople, has emphasised that this value is only an order of magnitude for the effect and is clearly large enough to account for the anomalous position of the acetylenic proton. Using this value of $\xi_d^{\equiv CH}$ and the experimentally observed chemical shift of the acetylenic proton, we can calculate the local shielding ξ_l as follows:

$$\xi_T = \xi_l + \xi_d$$

$$-2.2 = \xi_l + 7.8 \times 10^{-6}$$

$$\therefore \quad \xi_l^{\equiv CH} = -10 \times 10^{-6} \text{ (p.p.m. relative to TMS as reference),}$$

This means that the acetylenic proton will be shifted by 10 p.p.m. to lower fields if the local shielding was the only contributing factor to the total shielding constant. Again, we may notice that both bond magnetic anisotropy and electronegativity of the $-C\equiv CH$ group contribute to the chemical shift of the acetylene proton. The local shielding effect being somewhat the more important.

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PART II.

1. INTRODUCTION.

Nuclear magnetic resonance spectroscopy (NMR) ,provides a powerful and direct tool for the measurement of fast exchange rates . The method has the advantage that it gives data on the chemical kinetics while the measured system is in chemical equilibrium , and that it indicates directly the atoms that are exchanging. The first mention of the influence of chemical exchange on the NMR spectrum was made in papers by Hahn and Maxwell[1], and by Gutowsky, McCall , and Slichter .[2] Slichter, Gutowsky , and Saika,[3] have published a theory of the effect, and quantitative results have been reported for a number of specific compounds.[4-7] Gutowsky and Holm,[8] have extended the theory and reported a quantitative study of dynamic processes by NMR methods. Later, Grunwald , Loewenstein, and Meiboom,[9] developed a method to give quantitative results for the protolysis kinetics of methyl, dimethyl, and trimethylammonium chloride in aqueous solutions under conditions where the half-lives are betw en 0.2 and 0.002 sec. Relatively little is known about the protolysis kinetics of amines. Brodskii and Sulima,[10] have measured the exchange rates of ND_4^+ in strong acidic aqueous solutions and have reported half-lives of the order of several minutes.Their

results have been verified by Kaplan and Wilzback.[11] These authors and Swain and co-workers,[12] have studied the exchange between ammonium salts and alcohols in several nonaqueous solvents.Swain and co-workers , found that the rates were measurable in dimethyl formamide and toluene , and that they were inversly proportional to the concentration of added strong acid. Eigen and Schoen,[13] useing the electrical impulse method, estimated the rate constant for the reaction,

$$NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$$

to be 3.0×10^{10} sec.$^{-1}$ M.$^{-1}$ at 20°. Ogg,[4] useing the NMR technique, found that in aqueous solutions of ammonium nitrate ,the proton exchange with water is too slow to measure at low pH's and speeds up with increasing pH.

Grunwald , Loewenstein , and Meiboom,[9,14] have studied acid-base equilibria in aqueous solutions of methyl-,dimethyl-, and trimethylammonium chloride. These equilibria can be represented schematically by:

$$R_3NH^+ \rightleftharpoons R_3N + H^+$$

Where R represents either a methyl group or a hydrogen. Under conditions in which both components are present , the spectra consist of two sharp signals , one for the methyl protons , and the other for the protons exchanging between water , hydronium ions, hydroxide ions , and the ionizable positions on nitrogen.Grunwald, Loewenstein , and Meiboom ,[9] have investigated the chemical shift of the methyl signal as a function of acid to base ratio as measured by titration. They found that the shift measured relative to tetramethyammonium ion as a reference, was a linear function of the concentration ratio of acid to base plus acid for all three systems.

In addition to the equilibrium studies described above , nuclear magnetic resonance has been used by Grunwald , Loewenstein , and Meiboom,[9] to investigate the kinetics of protolysis of methylammonium ion. The results can be described as follows: at low pH , the methyl signal shows a sharp 1:3:3:1 quartet structure due to coupling with the NH_3^+ protons , so that the rate of protolysis is slow. As the pH value is increased , the methyl quartet collapses into a single line , while the NH_3^+ triplet (due to coupling with N^{14}) diminishes in intensity and ultimately disappears.

The water signal broadens and then narrows again, while shifting slightly to lower field.

These changes provide quantitative information about the protolysis rate and mechanism. Exchange in the CH_3 group can be ruled out since the reactivity of the C-H bonds toward bases is generally too low to be of consequence here.[15] The broadening of the water line at intermeadiate pH's and the disappearance of the NH_3^+ triplet at higher pH values indicate that at least part of the protolysis reactions involve water. At high pH , the water line also includes the NH_3^+ protons, which exchange rapidly with the water protons and cause the shift of the water line which was mentioned above.

The protolysis reactions which may occur in the system under consideration , are of the type shown in equations, 1, 2 , and 3.

$$CH_3NH_3^+ + B \xrightarrow{k_1} CH_3NH_2 + BH \qquad (1)$$

$$CH_3NH_2 + BH' \xrightarrow[\text{slow}]{k_2} (CH_3NH_2H')^+ + B \qquad (2)$$

$$CH_3NH_2 + B \xrightarrow[\text{fast}]{k_3} (CH_3NH_2H)^+ + B' \qquad (3)$$

Where B indicates a basic molecule such as H_2O , CH_3NH_2 , OH^- , and the prime on B' indicates that one of its hydrogens has been replaced.

In any mechanism , CH_3NH_2 is a short lived intermeadiate, since its concentration under the conditions of the kinetic experiments is very low. The rate determining step for proton exchange is reaction (1) , whose rate constant was measured. Exchange may occur by the cycle of reactions (1) and (2) , and in addition reaction (3) , which includes all mechanisms for proton exchange in methylamine that do not proceed via methylammonium ion. In order to simplify the problem , Grunwald , Loewenstein , and Meiboom,[9] have considered the following possible mechanisms:

$$CH_3NH_3^+ + H_2O \xrightarrow{k_4} CH_3NH_2 + H_3O^+ \qquad (4)$$

$$CH_3NH_3^+ + OH^- \xrightarrow{k_5} CH_3NH_2 + HOH \qquad (5)$$

$$CH_3NH_3^+ + NH_2CH_3 \xrightarrow{k_6} CH_3NH_2 + {}^+NH_3CH_3 \qquad (6)$$

$$CH_3NH_3^+ + HOH + NH_2CH_3 \xrightarrow{k_7} CH_3NH_2 + HOH + NH_3^+CH_3 \qquad (7)$$

The total rate constant of reaction (1) is given by :

$$\frac{\text{Rate}}{(CH_3NH_3^+)} = k_4 + k_5 K_W/(H^+) + (K_6+k_7) K_A (CH_3NH_3^+)/(H^+) \qquad (8)$$

Where , $K_W = (H^+)(OH^-)$, and $K_A = (H^+)(CH_3NH_2)/(CH_3NH_3^+)$

and the quantities in brackets denote the molar concentrations of the respective substances. From measurments of the CH_3-quadruplet at different values of (H^+) and ($CH_3NH_3^+$) , values of k_4 , k_5 , and ($k_6 + k_7$) are obtained.

From measurments of the broadening of the water line , separation of the latter into k_6 and k_7 is accomplished. From the measurments of the broadening of the NH_3^+ triplet , the correctness of the rate constants and the unimportance of reaction (3) are confirmed.

The value of k_4 is negligible in the time range covered by the NMR method (0.2 - 0.002). This is consistant with the fact that the CH_3-quadruplet is not collapsed at low pH's and low concentrations of $CH_3NH_3^+$, where equation (4) would be the only mechanism. Grunwald , Loewenstein , and Meiboom ,[9] were also able to estimate the relative importance of process (6) and (7) , by

examining the broadening of the water line , since this could be caused by (7), but not (6). The extra broadening of the water line can be used to measure the mean time a proton spends on a water molecule before returning to nitrogen. Combined with the over-all rate measurment , this enables one to make an estimate of the fraction of protolysis that proceeds by transfer of a proton to a water molecule and so to distinguish between the two mechanisms.

An exactly parallel investigation of di-, and trimethyl-ammonium ions was carried out by Loewenstein and Meiboom.[16] They have shown the importance of exchange via the solvent increases with methyl substitution. Also, the rate constant , k_4 ,(direct exchange with water molecules) , becomes detectable in trimethylammonium ion. This may be connected with greater basicity.[17] These workers have also observed that trimethylammonium ion has a much lower k_6 than methylammonium ion. From the decrease in the pK_A value alone, the opposite would be expected. They have concluded that other effects such as steric hindrance ,[18] or electrostatic interactions,[19] play a dominant role in the direct interaction between the ion and the free base.

More recently , Grunwald , Karabatsos , Kromhout , and Purlee,[20]

have measured the rate constants for the reactions:

$$CH_3NH_3^+ + NH_2CH_3 \xrightarrow{k_6} CH_3NH_2 + HNH_2^+CH_3$$

$$CH_3NH_3^+ + H_2O + NH_2CH_3 \xrightarrow{k_7} CH_3NH_2 + H_2O + NH_3^+CH_3$$

by precise nuclear magnetic resonance technique , in aqueous acid at 25°. They found that the ratio k_6/k_7 remains virtually constant between 1.7 and 8.1 M. concentrations of methylammonium ion. They concluded that the magnitude of k_7 as well as the constancy of k_6/k_7 indicate that the most probable rate-determining step for the reaction with rate constant ,k_7, is proton transfer from a water molecule in the solvation shell of $CH_3NH_3^+$ to a molecule of CH_3NH_2 to produce the triple ion ,

$$CH_3NH_3^+ .OH^-.HNH_2^+CH_3$$

In the following sections , we report the results on the protolysis reactions of the following ammonium ions:

1. Ethylammonium ion.
2. Diethylammonium ion.

3. Triethylammonium ion.

4. Isopropylammonium ion.

5. Isobutylammonium ion .and,

6. Neopentylammonium ion.

It was felt, that, a comparison of the kinetics of these ammonium ions would contribute to the understanding of characteristics of these ions , such as, basic strength , ionic solvation , and steric effects. We have noted in this study , that , steric hindrance, electrostatic interactions , and inductive effects , play a dominant role in the exchange reactions between the ion and the corresponding base.

11. EXPERIMENTAL.

1. REAGENTS AND SOLUTIONS.

Neopentylamine hydrochloride.

This amine was prepared from pinacol hydrate, converting it to pinacolone with 6N sulphuric acid. Pinacolone was treated with sodium hypobromite , trimethylacetic acid was obtained in 90 % yield, b.p. 68°/10mm. , m.p.35-6°.

Trimethylacetic acid was treated with an equal weight of phosphorus pentachloride to give the acid chloride. The chloride was poured into ice-cold ammonia , the amide separated immediately, and was recrystallized from water to give needles, m.p.155-6°.

The amide was reduced to the amine with lithium aluminium hydride , by continuously extracting the amide into the well stirred suspension of lithium aluminium hydride in ether. The complex was distroyed by the addition of an excess of water, and the amine was obtained by distillation from the alkaline solution. The amine hydrochloride was formed by passing hydrogen chloride gas in an ethereal solution of the amine. The amine hydrochloride was obtained

in 69 % yield, m.p.275-6°.

All the other amine hydrochlorides were prepared from aqueous solutions of the corresponding amines. The solutions were acidified with concentrated hydrochloric acid and then evaporated on a steam bath under reduced pressure. The resulting material was recrystallized several times, the last crystallization being from absolute ethanol, and dried in vacuo. Hydrochloric acid was constant boiling material prepared according to the method of Foulk and Hollingsworth.[21] Its titre was checked by Volhard titration with standard silver nitrate solution. All solutions were prepared using triply distilled water.

Since the hydrochlorides are quite hygroscopic , their concentrations in the solutions were determined by Volhard titration with silver nitrate. The hydrochloric acid concentration in the solutions could not be obtained with sufficient accuracy by dilution of standard acid with the amine hydrochloride solutions. The concentration of the latter was so much greater than that of the hydrochloric acid , that very small amounts of amine impurity could cause appreciable error. The procedure finally adopted was to add a known amount of acid about 1×10^{-3} M. , to the amine hydrochlodide

and to titrate the acidity potentiometrically with 0.007N sodium hydroxide. In this way , the concentration of the amine impurity , which ranged from (2 to 8) x 10^{-5}M. , was determined with a standard error of 1 x 10^{-5}M. Having determined the amine impurity, other reaction mixtures could be prepared by standard dilution techniques. In several cases a check of the hydrochloric acid concentration was made by titrating potentiometrically the acidic solutions with standard sodium hydroxide to an end point , where , hydrochloric acid is neutralised but the amine hydrochloride is not. This procedure would also detect the presence of acidic or basic impurities in the water or the amine hydrochloride used in preparing the solutions.

2. DETERMINATION OF ACID DISSOCIATION CONSTANT.

We use K_A to denote the acid dissociation constant in terms of molar concentrations , and K_A^o to denote the thermodynamic constant in terms of activities. Since the rate measurments were made in acidic solutions in which the concentration of the free amine was extremely small, the K_A measurments were made under conditions

as nearly comparable as possible. A Beckman model G pH meter and glass and calomel electrods were used. pK_A values were measured by the differential potentiometric method,[22] at a number of the amine hydrochloride concentrations. The concentration of the amine hydrochloride was kept constant in each pK_A measurement.

In this method , a known amount of the strong acid (in this case , HCl) , is added to a solution of the weak acid HA ; and the e.m.f. is measured. Sufficient sodium hydroxide then is added to neutralize all of the strong acid and some of the HA; and the e.m.f. is again measured. In the first case , C_H depends chiefly on the amount of the strong acid added, since it represses the ionization of the weak acid HA; whereas in the second solution C_H depends on the $HA = H^+ + B$ equilibrium , and hence on K_A. If we define a quantity ϵ by the equation,

$$\epsilon = (\text{Eq.HA} + \text{Eq.HCl} - \text{Eq.NaOH})/(\text{Eq.HA}) \qquad (1)$$

Where, Eq.= equivalents added to the cell. The fundamental expression for K_A is ,

$$\frac{C_H(C_H-(\epsilon - 1)\, C)}{(\epsilon C - C_H)} = K_A \frac{Y_{HA}}{Y_A\, Y_H} = k_A \qquad (2)$$

Where $C = C_{HA} + C_{B}$, and the Y's are molar activity coefficients.[23]

Experimentally we measure the ratio C'_H/C''_H of the hydrogen ion concentration in the two solutions. Upon solving Eq.(2). for C_H , we find ,

$$C'_H/C''_H = Z'/Z'' \qquad (3)$$

Where ,

$$Z = (\epsilon - 1)C - K_A + (\epsilon(\epsilon - 1)^2 C^2 + 2K_A C(1+\epsilon) + K_A^2)^{-\frac{1}{2}} \qquad (4)$$

Z' and Z'' are the values of Z at the two experimental points. Since Z'/Z'' is a function of K'_A and K''_A , and hence of K_A , the later may be evaluated. The calculations are based on equations (3) and (4) ; C'_H/C''_H is obtained from the experimental values of E' , E'', C'_{CL} , C''_{Cl} , μ' , and μ''. Next a plausible first estimate is made for K_A , k'_A and k''_A , Z' and Z'' are computed from equations (2) and (4). To obtain the correct value of K_A , Z'/Z'' is plotted VS. the assumed K_A. K_A is correct when eq.(3) is satisfied.

3. DETERMINATION OF THE RELAXATION TIME T_2.

There are two contributions to the effective value of the transverse relaxation time T_2: the natural line width , and the inhomogeneity of the magnetic field over the sample. At high acid concentrations, where the exchange is very slow , the lines of the quadruplet were not appreciably broader than the water line. Moreover , the effective T_2 of the water line in the absence of exchange or at high acid concentrations ranged from 1.4-1.9 sec., which is very little shorter than the value of ca. 2 sec.corresponding to the natural line width of water. The transverse relaxation time T_2 was measured from the decay envelope following rapid passage through the water line . The actual decay envelopes were nearly but not exactly exponential , and effective averages had to be estimated for T_2. The wiggles decay as e^{-t/T_2} , their amplitude can be plotted VS. time on a semi-logarithmic paper; the slope of the straight line thus obtained gives $1/T_2$. The figure below shows a picture of wiggles from the original tracing of the recorder.

4. KINETIC MEASUREMENT.

Rates of exchange were measured by the nuclear magnetic resonance technique. A Varian Associates high resolution NMR spectrometer was used at 56.45 Mc./sec.

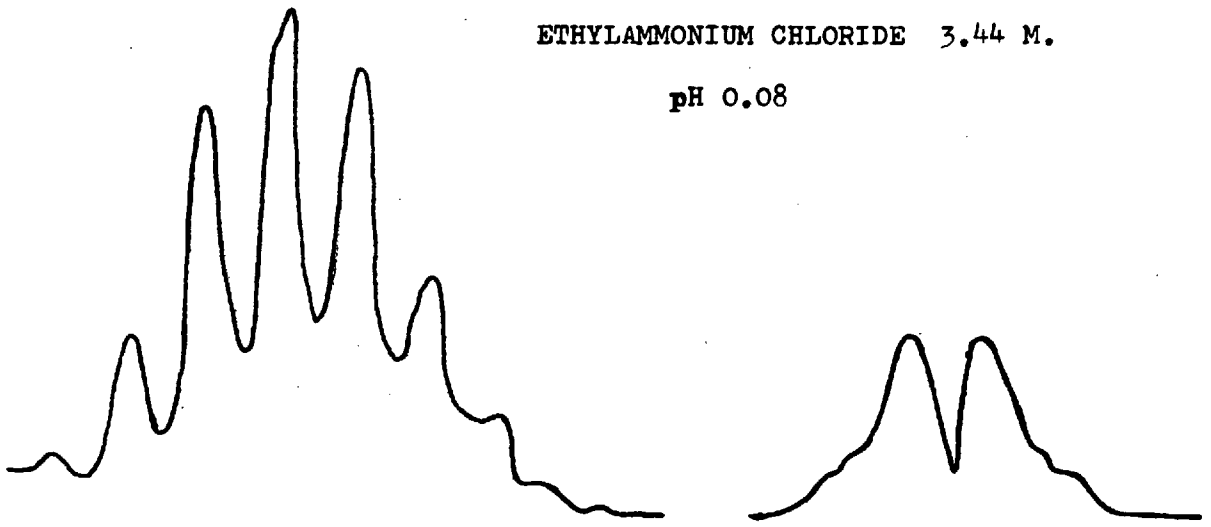
In all the amines studied , there are other groups in the molecule which could interact with the protons on the carbon atom next to the NH_3^+ group. Thus complicating the observed spectra. The procedure adopted in this case was to decouple the protons next to the NH_3^+ from other groups in the molecule. Thus , we could obtain simple doublets , triplets , or quadruplets, from which the rate constants were measured.

Spectra typical of those used in the final rate determinations are shown in Figs. (1) and (2) : also shown in the figure are typical spectra of the undecoupled nuclei.

The NMR measurments were made in an air-conditioned room. During any one series of measurments , the variation in temperature was less than $1^{\circ}C$. Most of the measurements were made at $20 \pm 0.5^{\circ}C$.

ETHYLAMMONIUM CHLORIDE 3.44 M.

pH 0.08



UNDECOUPLED

DECOUPLED

+95 c/s.

pH 3.23

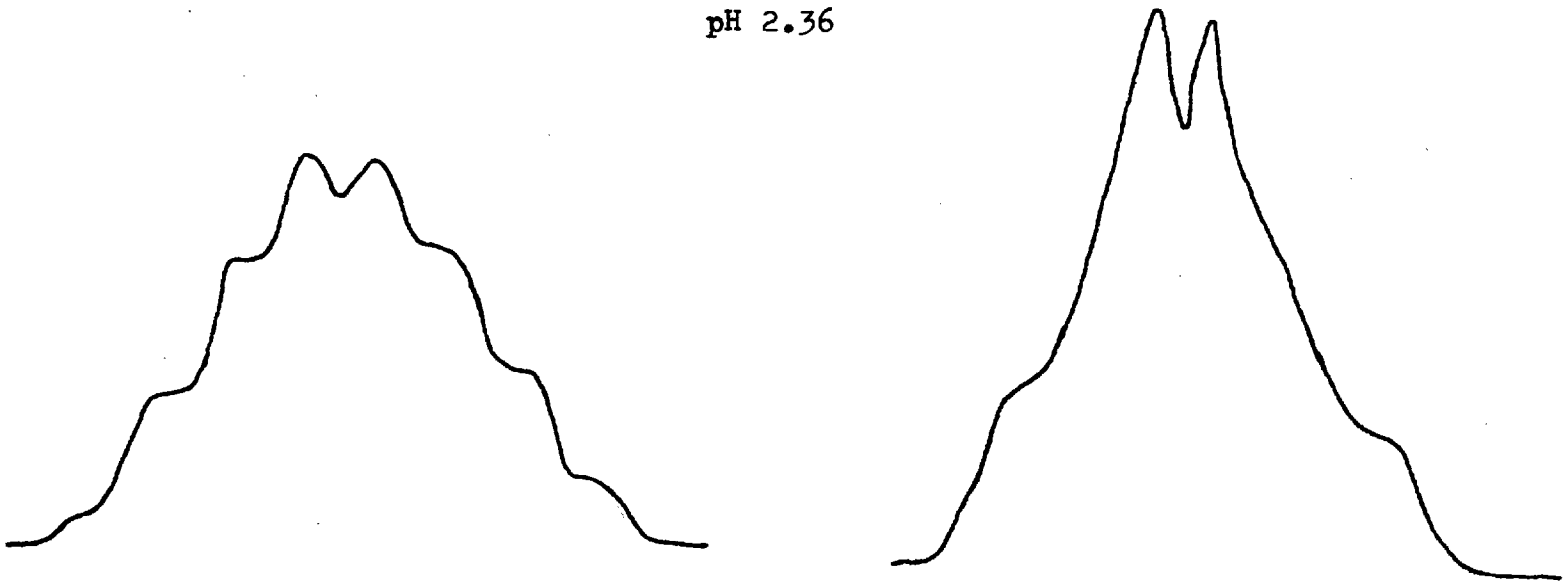
UNDECOUPLED

DECOUPLED

Fig. 1

ISOPROPYL AMMONIUM CHLORIDE 5.614 M.

pH 2.36



UNDECOUPLED

DECOUPLED

FIG. 2

III. CALCULATIONS.

A. METHODS.

1. MEASURMENT OF RATE CONSTANTS.

The theory of exchange broadening of Gutowsky , McCall , and Slichter,[2] and of Gutowsky and Saika,[3] which is based on the Bloch equations, was used by Grunwald , Loewenstein , and Meiboom,[9] to calculate the shape of the CH_3-group resonance in methylammonium ion as a function of the exchange rate of the NH_3^+ protons. An outline of this calculation as adopted to the case of methyl, dimethyl, and trimethylammonium ions has been given by Grunwald , Loewenstein , and Meiboom,[9] and by Loewenstein and Meiboom.[16] The derivation is valid only in the case that the spin-spin interaction is small compared with the chemical shift.

In these calculations it is necessary to make a specific assumption concerning the relative rates of reactions (2) and (3), because these determine the number of protons that are replaced each time reaction (1) occurs. It will be assumed in this discussion that $k_3 \ll k_2$. Some theoretical line shapes of the CH_3-group resonance obtained on this basis are shown in Fig.(3),(4),(5),(6),(7) and (8).

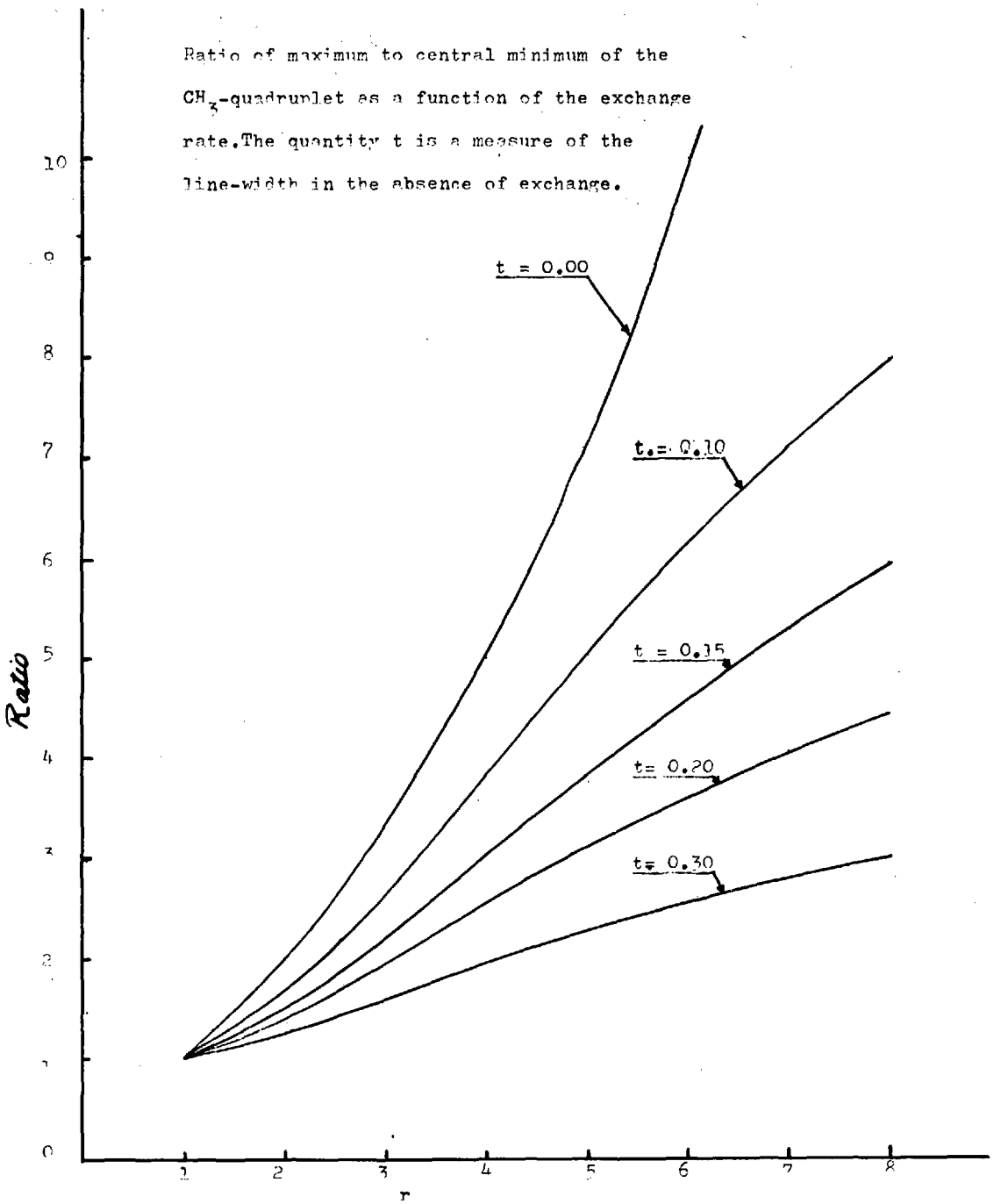

Ratio of maximum to central minimum of the CH_3-quadruplet as a function of the exchange rate. The quantity t is a measure of the line-width in the absence of exchange.
t = 0.00
t = 0.10
t = 0.15
t = 0.20
t = 0.30
Ratio
r
0
1
2
3
4
5
6
7
8
9
10

Fig. 3

Half-width of the CH_3-resonance as a function of the exchange rate. The ordinate is the quantity U = /dw, where, , is the width of the line at half amplitude.

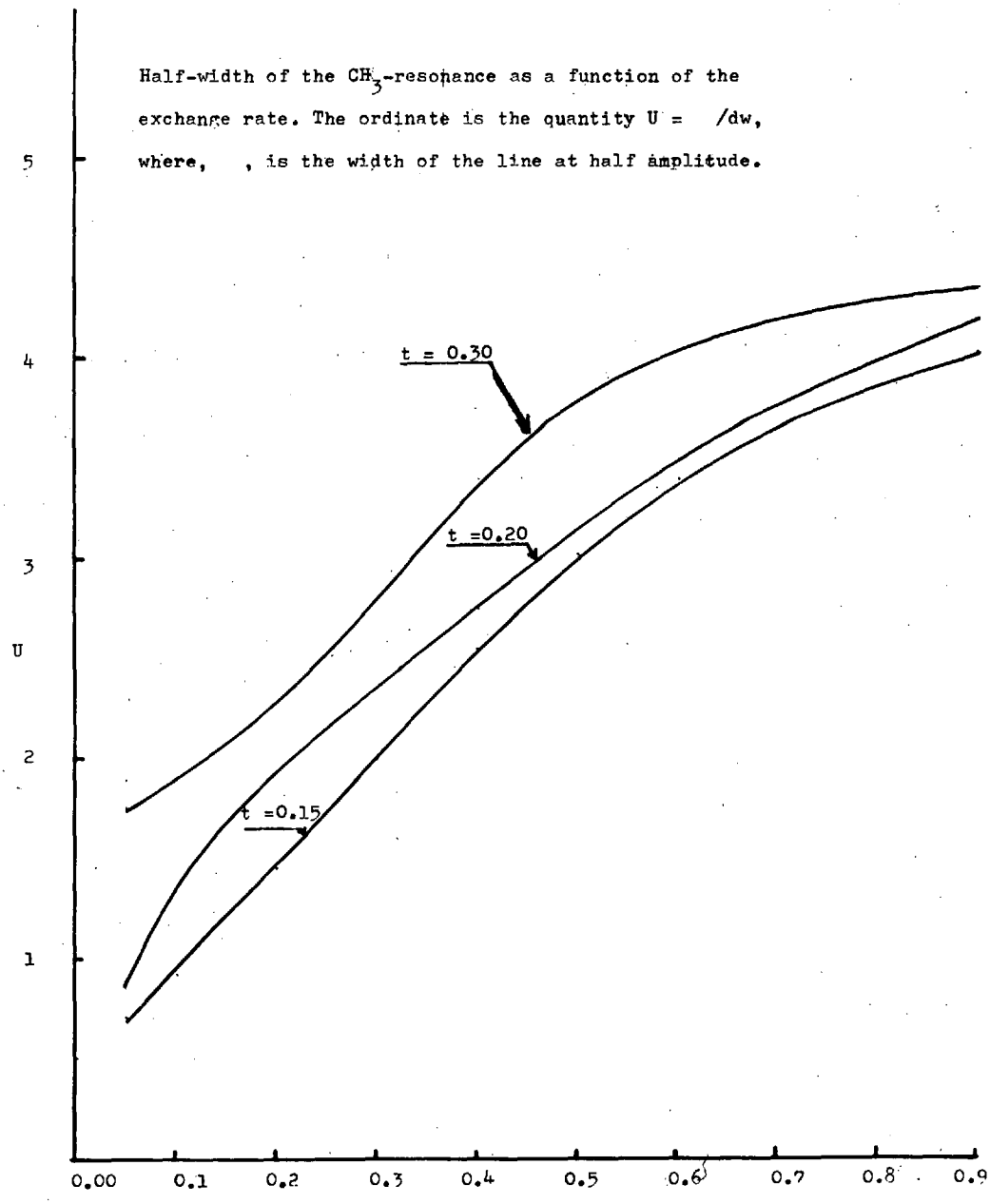


Fig. 4

THEORETICAL CURVES USED IN OBTAINING EXCHANGE RATE FROM OBSERVED LINE SHAPE. THE CURVES ARE FOR A BROADENED SPIN-SPIN TRIPLET. THE RATIO OF MAXIMUM TO CENTRAL MINIMUM IS PLOTTED AGAINST THE EXCHANGE PARAMETER $r=2\tau dw$, WHERE τ IS THE MEAN LIFE-TIME BETWEEN EXCHANGES, AND $2dw$ THE ANGULAR FREQUENCY OF THE SPIN-SPIN SPLITTING.

$t = 1/T_2 dw$

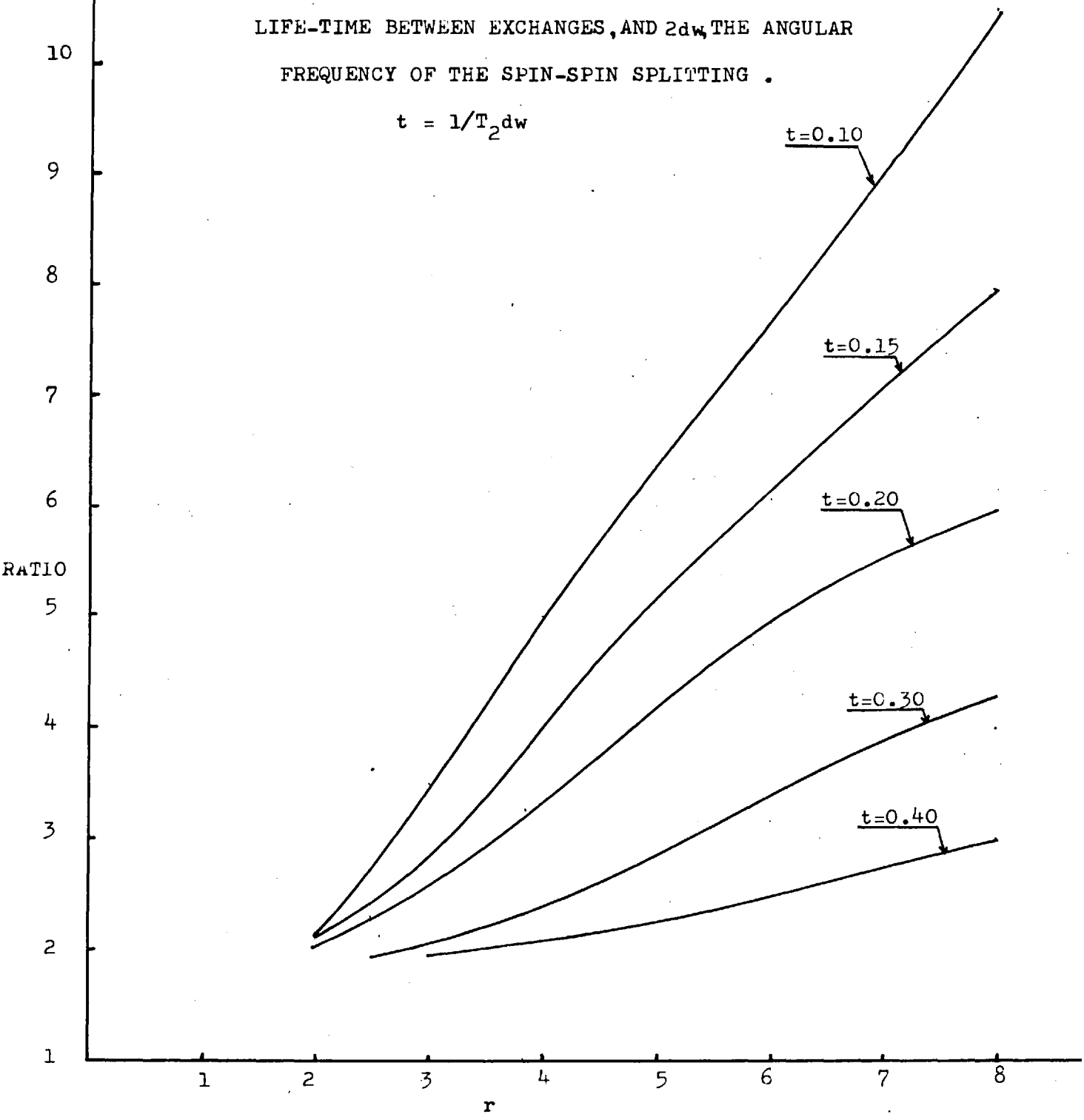


Fig.5

THEORETICAL CURVES USED IN OBTAINING THE EXCHANGE RATE FROM OBSERVED LINE SHAPE.THE CURVES ARE FOR THE CASE OF A SPIN-SPIN TRIPLET,WHICH IS COLLAPSED INTO A SINGLE BROADENED LINE.THE ORDINATE IS THE QUANTITY $U = \Delta/dw$,WHERE Δ IS THE HALF-WIDTH OF THE LINE,AND dw IS HALF THE SPIN-SPIN SPLITTING.

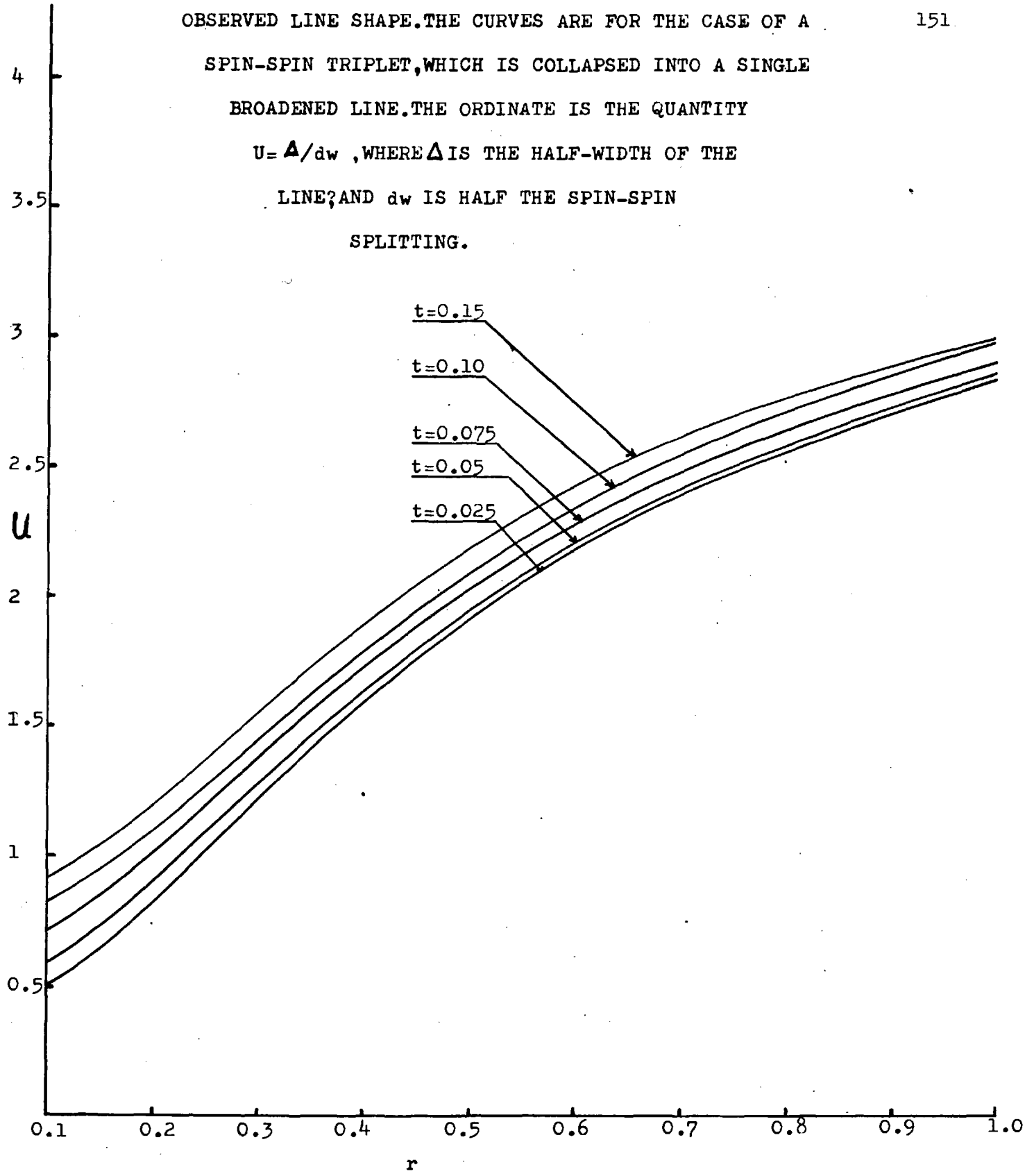


FIG.6

THEORETICAL CURVES USED IN OBTAINING THE EXCHANGE RATE FROM OBSERVED LINE-SHAPE. THE FIGURE IS FOR THE CASE OF SPIN-SPIN DOUBLET. $U = \Delta/dw$, Δ IS THE HALF-WIDTH OF THE LINE, dw =HALF THE PEAK-TO-PEAK SEPARATION OF THE CH3-QUADRUPLET IN UNITS OF ANGULAR FREQUENCY.

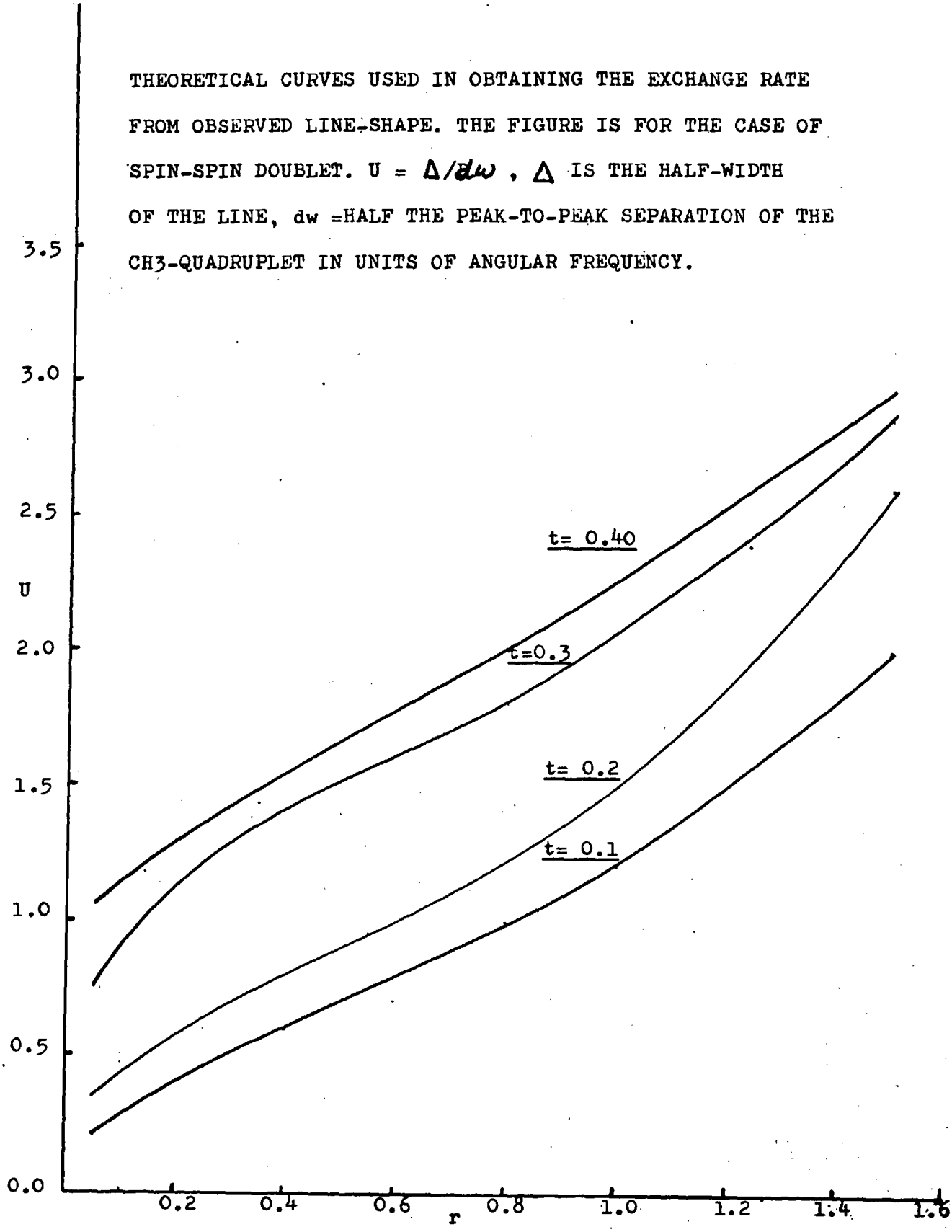


Fig.8.

Theoretical curves used in obtaining the exchange rate from observed line-shape. The figure is for spin-spin doublet. The ratio of max. to min. is plottet against r.

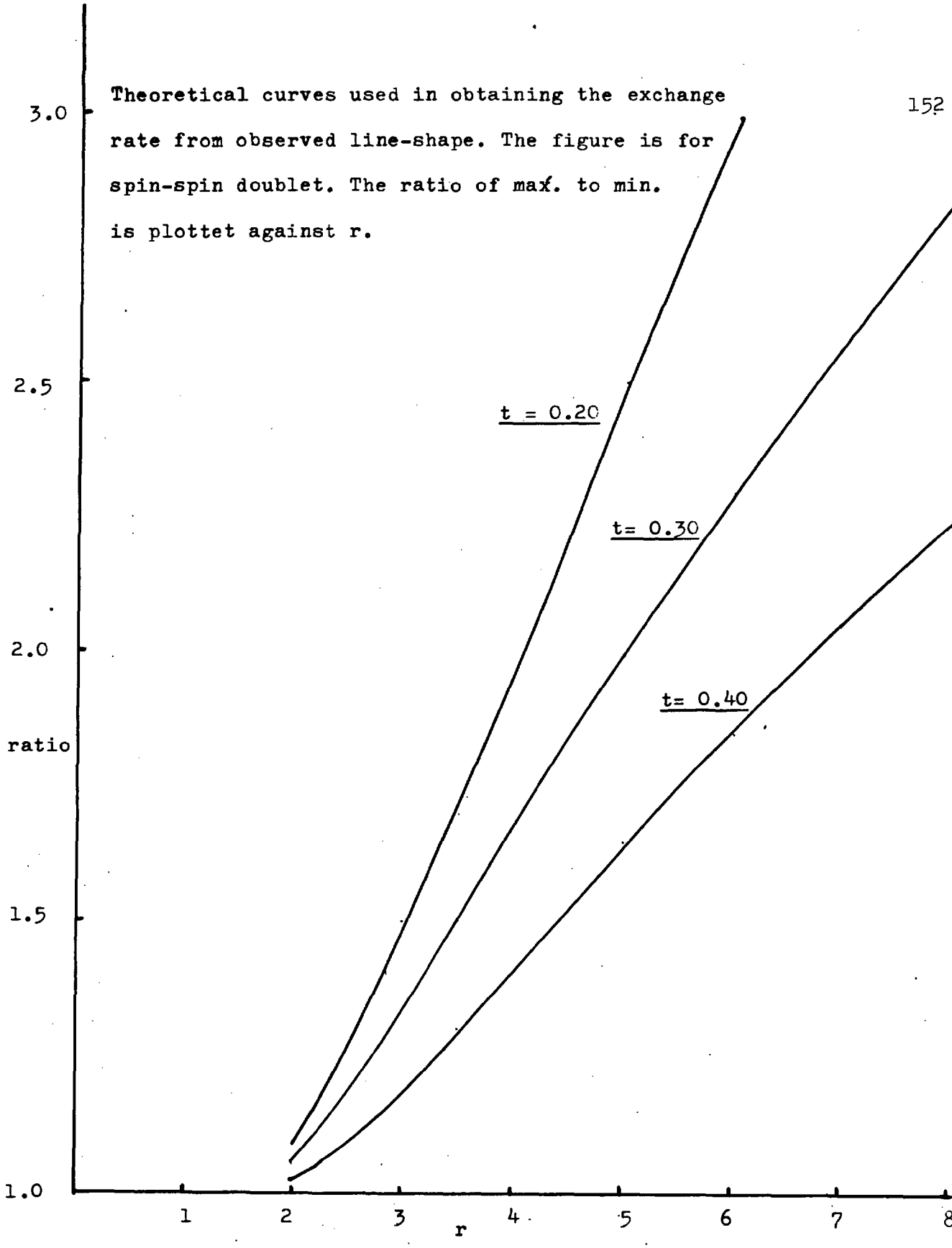


Fig.7.

The line shapes depend on the values of the parameters,

$$t = 1/T_2 dw \text{ , and } r = 2\tau dw \text{ ,}$$

where T_2 is the transverse relaxation time in the absence of exchange. τ, is the mean time interval between proton exchange of the NH_3^+ group , and dw is one-half of the peak-to-peak separation and is equall to one-half of the spin-spin coupling constant J_{MN} between the methyl group protons and the NH_3^+ protons (in units of angular frequency), in the absence of any exchange effects. Since the change of the spin configuration of the NH_3 protons is a first-order process in methylammonium ion concentration , one can calculate from τ , the pseudo-first-order rate constant, k , for reaction(1), by means of Eq.(1).

$$(\text{Rate})/(CH_3NH_3^+) = k = 1/\tau = 2dw/r \qquad (1)$$

r, is evaluated by comparing the observed line shapes with the calculated line shapes. At the lower exchange rates , where the line shapes are as in the upper curves of Fig.(2), the ratio of the maximum to the central minimum could be measured satisfactorily and was taken as the characteristic quantity. This ratio was obtained

from the theoretical curves and was plotted as a function of r , for a number of t values as shown in Figs. (3),(5), and (7). At the faster exchange , where the central minimum has disappeared , the half-width of the lines could be measured conveniently and was used as the characteristic quantity. Plots of u = Δ/dw VS. r, for various values of t are shown in Figs. (4), (6), and (8).

The tables of lineshapes of exchange broadened NMR multiplets give calculated lineshapes of NMR multiplets as a function of exchange rate of the interacting nuclei.[24] The equations on which the tables are based have been derived on the following assumptions:

a. Chemical shifts large compared to spin-spin interaction.

b. Nuclei with spin one half.

c. Absence of saturation.

There are several difficulties connected with the use of Figs.(3),(4),(5),(6),(7), and (8). First, the theoretical curves are obtained for the limiting case of slow passage and small H_1 , whilst the experimental curves are necessarily obtained at finite sweep and H_1 values that may be too large for strict conformity to the theory. In order to estimate the magnitude of the error so

introduced , we measured the lineshapes for several solutions at various sweep speed and H_1 values. The values of the ratio of maximum to central minimum were essentially constant.

2. KINETIC ANALYSIS USING THE WATER LINE.

It is clear from the broadening of the water line and from the merging of the H_2O and NH_3^+ resonances into a single line at the higher pH's , that at least part of the protolysis reactions involve direct proton transfer from nitrogen to oxygen. Since reaction (3) will be shown to be negligible , the broadening is attributed to reaction (5) , and possibly to additional reactions such as (7) , involving mathylammonium ion , methylamine , and one or several water molecules. The total rate of these reactions will now be reported. It is not practicable to set up general equations for the broadening of the H_2O and NH_3^+ lines, since this would have required prior knowledge of the relative rates. However , for the special case where the exchange is so slow, that, these lines do not appreciably overlap , Grunwald , Loewenstein , and Meiboom ,[9] gives the following

equation as an approximate one:

$$1/T_2' = 1/T_2 + 1/\tau \text{ (water)} \qquad (2)$$

T_2', is the effective relaxation time , as measured from the actual half-width , or decay of the wiggles of the water line; T_2 , the relaxation time in the absence of exchange , as measured with an unbroadened water sample; and τ (water) , the mean lifetime of the protons bonded in water before returning to nitrogen. τ' , the mean lifetime of the NH_3^+ group before a proton is transfered to water is then given by Eq.(3) ,

$$\tau' = \tau(\text{water}) \ (RNH_3^+)/2(H_2O) \qquad (3)$$

The fraction of protolysis p, involving direct proton transfer from NH_3^+ to H_2C , is then given by the following equation:

$$p = 1/k\tau' \qquad (4)$$

Where, k, is obtained from the data for the R-group resonance at the same pH and (RNH_3^+).

3. RATE MEASURMENT USING THE NH_3^+ TRIPLET.

The kinetic information obtained from the broadening of the NH_3^+ triplet is of lower accuracy than that obtained from the other lines. There are two reasons for this: the large natural line width due to quadrupole relaxation of the N^{14} nucleus makes the experimental determination of the exchange broadening less accurate; and the superposed quadruplet and triplet structures of the lines makes an exact theoretical interpretation in terms of the exchange rate very difficult. In the following discussion the quadruplet structure was ignored, and an equation was derived by Grunwald , Loewenstein , and Meiboom,[9] relating the increase in half-width with increasing pH , to the decrease in the mean time τ'', during which a proton is bonded to a nitrogen atom of a given spin,

$$\pi (df_2 - df_1) = 1/\tau''_2 - 1/\tau''_1 \qquad (5)$$

In Eq.(5) , df, is the full width of a given line at half of its maximum height(half-width), in cycles/second. This equation was derived also for the special case where the various lines do not appreciably overlap . Since all the rates were inversely proportional to the hydrogen ion concentration, the same must be true for $1/\tau''$,

and a rate constant k_{16} is calculated from equation (6),

$$1/\tau''_2 - 1/\tau''_1 = k_{16}(1/(H^+)_2 - 1/(H^+)_1) \qquad (6)$$

Measurements were made only for concentrated solutions of the various alkylammonium ions used. The intensity of the lines being too small at low concentrations.

B. RESULTS.

In the following sections, the rate constants for the various possible mechanisms of amine protolysis will be reported. In principle, all rate constants are functions of the ammonium ion concentrations. Therefore, a number of measurements were made in which the alkylammonium ion concentration was constant and the hydrogen ion concentration varied from 10^{-3} to 10^{-5}M. The results are shown in the tables below.

k, is the pseudo first-order rate constant, $\tau_{(water)}$, the mean lifetime of the proton bonded in water before returning to nitrogen, τ', the mean lifetime of the NH_3^+ group before a proton is transfered to water, p, is the fraction of protolysis involving direct proton transfer from NH_3^+ to H_2O, and $m_2/111.$, is one half the molar ratio, i.e. $(RNH_3^+)/2(H_2O)$.

Table 1. Kinetic data for ethylammonium ion in water at 20 ± 0.5°.

T_2 = 0.4 sec.

$CH_3CH_2NH_3^+$ M.	$10^3(H^+)$M.	k(sec.$^{-1}$)	τ(water)	τ'(sec.)	m_2/111.
4.827	512.87	18.10	1.0111	0.068	0.0678
	257.03	27.05	0.2337	0.0158	
	9.55	34.84	0.392	0.0266	
	3.98	43.55	0.193	0.0131	
	3.09	45.9	0.444	0.0300	
	0.064	76.25	0.123	0.0838	
3.44	831.73	5.80	2.029	0.085	0.0415
	21.877	28.99	1.059	0.044	
	4.677	33.50	0.768	0.0322	
	0.589	58.80	1.181	0.0490	
	0.039	67.90	0.54	0.0220	
7.24	112.20	25.60	2.721	0.385	0.1415
	33.112	16.7 0	0.207	0.0292	
	4.365	27.20	0.578	0.0820	
	1.905	36.20	0.186	0.0263	
	0.281	77.75	0.187	0.0264	
	0.0038	217	0.0577	0.00817	

Table 11. Kinetic data for diethylammonium ion in water at 20±0.5°.

$(CH_3CH_2)_2NH_2^+M.$	$10^3(H^+)M.$	$k(sec.^{-1})$	τ(water)	τ'(sec.)	$m_2/111.$
4.04	123.03	16.558	0.808	0.00518	0.0642
	58.880	23.457	0.5514	0.00352	
	11.90	100.00	0.4520	0.00198	
	9.616	140.74	0.932	0.00590	
	6.250	175.00	0.821	0.00525	
	2.750	129.92	0.590	0.00378	
	1.318	48.600	0.642	0.00411	
	0.324	201.06	0.286	0.00132	
3.50	208.92	21.990	0.237	0.01180	
	22.387	20.106	0.225	0.01130	
	9.330	20.900	0.338	0.01690	
	3.715	22.824	0.235	0.01190	
	3.162	18.766	0.2106	0.01050	
	2.454	767.70	0.2880	0.01440	
	0.588	469.15	0.2120	0.01060	
	0.489	527.80	0.1980	0.00995	
2.02	166.00	19.870	1.7680	0.04130	0.0234
	8.510	153.54	1.0830	0.02520	
	5.370	175.93	0.8100	0.01890	
	1.778	222.23	1.6250	0.03790	
	0.141	272.40	0.7750	0.01840	
	0.0300	767.70	0.0950	0.00220	

Table 111. Kinetic data for triethylammonium ion in water at 20±0.5°. T_2 = 0.3 sec.

$(CH_3CH_2)_3NH^+M.$	$10^3(H^+)M.$	$k(sec.^{-1})$	τ(water)	τ'(sec.)	$m_2/111.$
1.95	190.54	16.69	0.314	0.0076	0.0241
	10.00	22.80	0.236	0.0057	
	3.31	24.70	0.194	0.0046	
	0.758	33.40	0.262	0.0063	
	0.389	34.70	0.245	0.0059	
	0.134	28.60	0.264	0.0064	
	0.0019	62.00	0.061	0.0015	
1.775	13.35	19.20			0.0193
	2.50	28.01			
	0.635	59.80			
	0.834	58.00			
1.60	223.80	17.75			0.0186
	8.71	18.06			
	5.13	17.33	1.245	0.0232	
	6.76	21.10	1.656	0.0310	
	2.82	32.80	1.769	0.0320	
	0.104	28.20	0.208	0.0038	
	0.10	28.20	0.214	0.00398	
	0.085	43.30	0.0612	0.00113	
	0.0911	48.20	0.143	0.00260	

Table IV. Kinetic data for isopropylammonium ion in water at 20±0.5°.

$(CH_3)_2CHNH_3^+$M.	$10^3(H^+)$M.	k(sec.$^{-1}$)	τ(water)	τ'(sec.)	m_2/111.
5.614	724.42	13.90	7.155	1.073	0.106
	22.387	16.65	8.56	0.908	
	4.365	20.60	1.298	0.138	
	0.331	21.80	0.213	0.0226	
	0.0014	31.80	0.039	0.0280	
	0.29×10^{-4}	500	0.268	0.0280	
3.66	263.03	7.90	1.473	0.073	0.0495
	9.119	8.90	4.580	0.222	
	7.412	9.79	2.680	0.133	
	1.148	21.90	0.762	0.037	
	0.501	35.12	0.09	0.0045	
	0.36×10^{-5}	501	1.213	0.0505	
2.80	269.15	5.31	4.334	0.147	0.0341
	19.50	6.25	3.44	0.111	
	5.011	8.56	2.089	0.071	
	1.38	27.99	1.255	0.042	
	0.741	46.70	1.101	0.037	

Table V. Kinetic data for isobutylammonium ion in water at 20±0.5°.

$(CH_3)_2CHCH_2NH_3^+$ M.	$10^3(H^+)$ M.	k (sec.$^{-1}$)	m_2/111.
4.468	38.90	21.655	0.074
	19.49	22.858	
	2.95	45.717	
	1.778	62.34	
	0.512	80.677	
	0.229	114.29	
3.892	165.97	15.825	0.0585
	100	27.43	
	28.84	23.51	
	2.379	25.70	
	12.02	24.20	
	10.0	23.50	
	7.244	24.20	
	2.45	30.47	
	1.318	59.20	
	0.758	84.83	
	0.407	117.50	
	0.071	146.90	

Table VI. Kinetic data for neopentylammonium ion in water at 20±0.5°

$(CH_3)_3CCH_2NH_3^+$ M.	$10^3(H^+)$ M.	k ($sec.^{-1}$)	$m_2/111$.
3.848	6.61	35.806	0.0525
	6.31	32.719	
	4.79	44.133	
	4.37	47.440	
	1.66	69.000	
	1.122	75.909	
3.684	79.43	6.325	0.048
	15.49	12.243	
	12.88	14.057	
	9.77	16.50	
	8.70	22.72	
	5.62	29.19	
	3.89	42.17	
	2.88	46.20	
	2.09	69.00	
	1.95	72.99	
2.94	104.70	3.795	0.0354
	47.86	4.744	
	6.025	23.143	
	3.801	30.122	
	2.344	42.172	
	1.995	58.39	
	1.479	60.63	

Table V11. Summary of rate processes in dilute aqueous acid.

Reaction	Rate constant
$R_3NH^+ + H_2O$	k_4 ($sec.^{-1}$)
$R_3N + H_3O^+$	k_{-4} ($sec.^{-1}M.^{-1}$)
$R_3NH^+ + OH^-$	k_5 ($sec.^{-1}M.^{-1}$)
$R_3N + H_2O$	k_{-5} ($sec.^{-1}$)
$R_3NH^+ + NR_3$	k_6 ($sec.^{-1}M.^{-1}$)
$R_3NH^+ + H_2O + NR_3$	k_7 ($sec.^{-1}M.^{-1}$)

MEASUREMENT OF ($k_6 + k_7$)

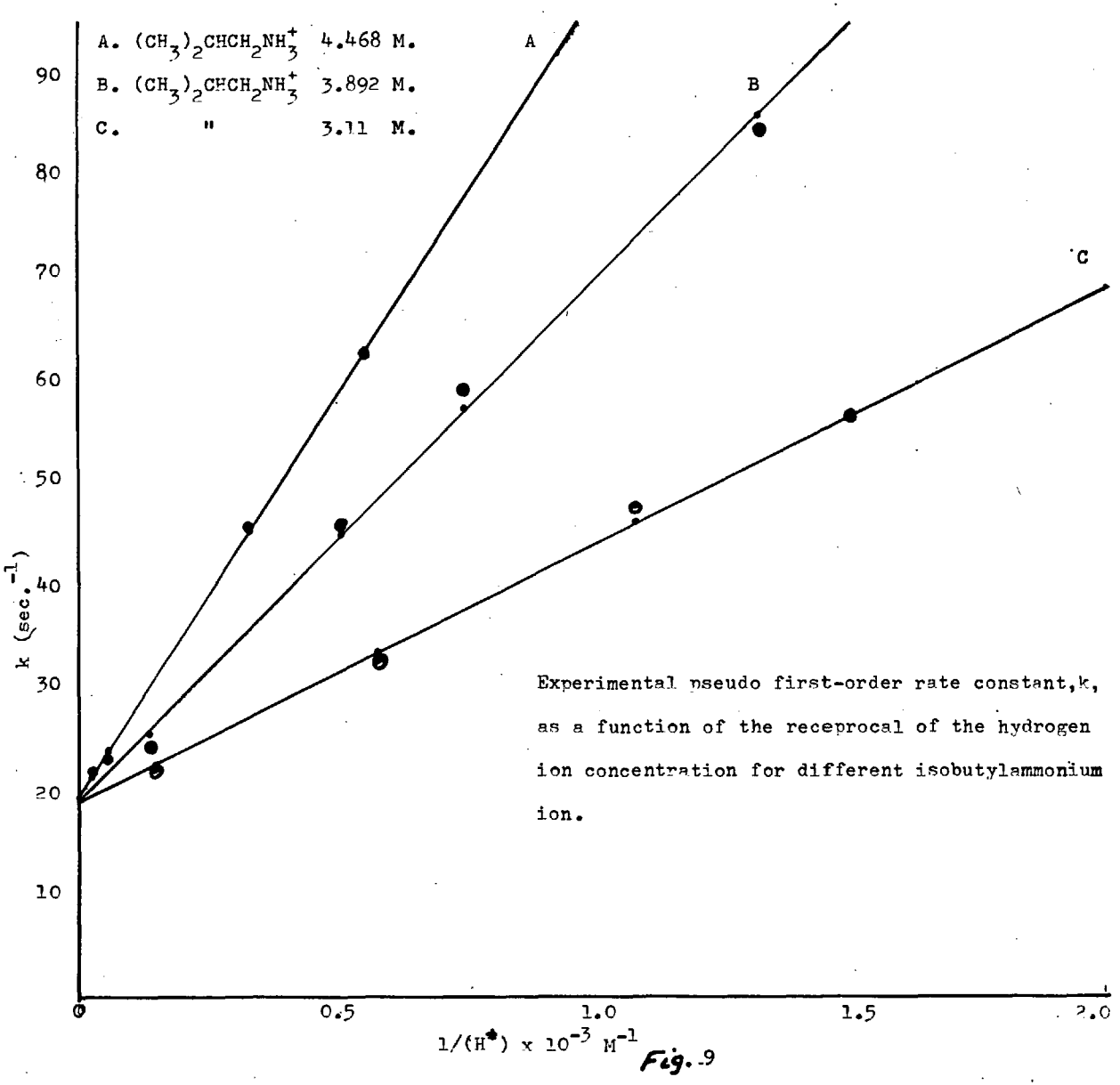
The rate constant ($k_6 + k_7$) for all these ammonium ions was determined as follows:

The pseudo first-order rate constant k, defined by the equation,

$$k = k_4 + k_5K_W/(H^+) + (k_6 + k_7)K_A(RNH_3^+)/(H^+) \qquad (1)$$

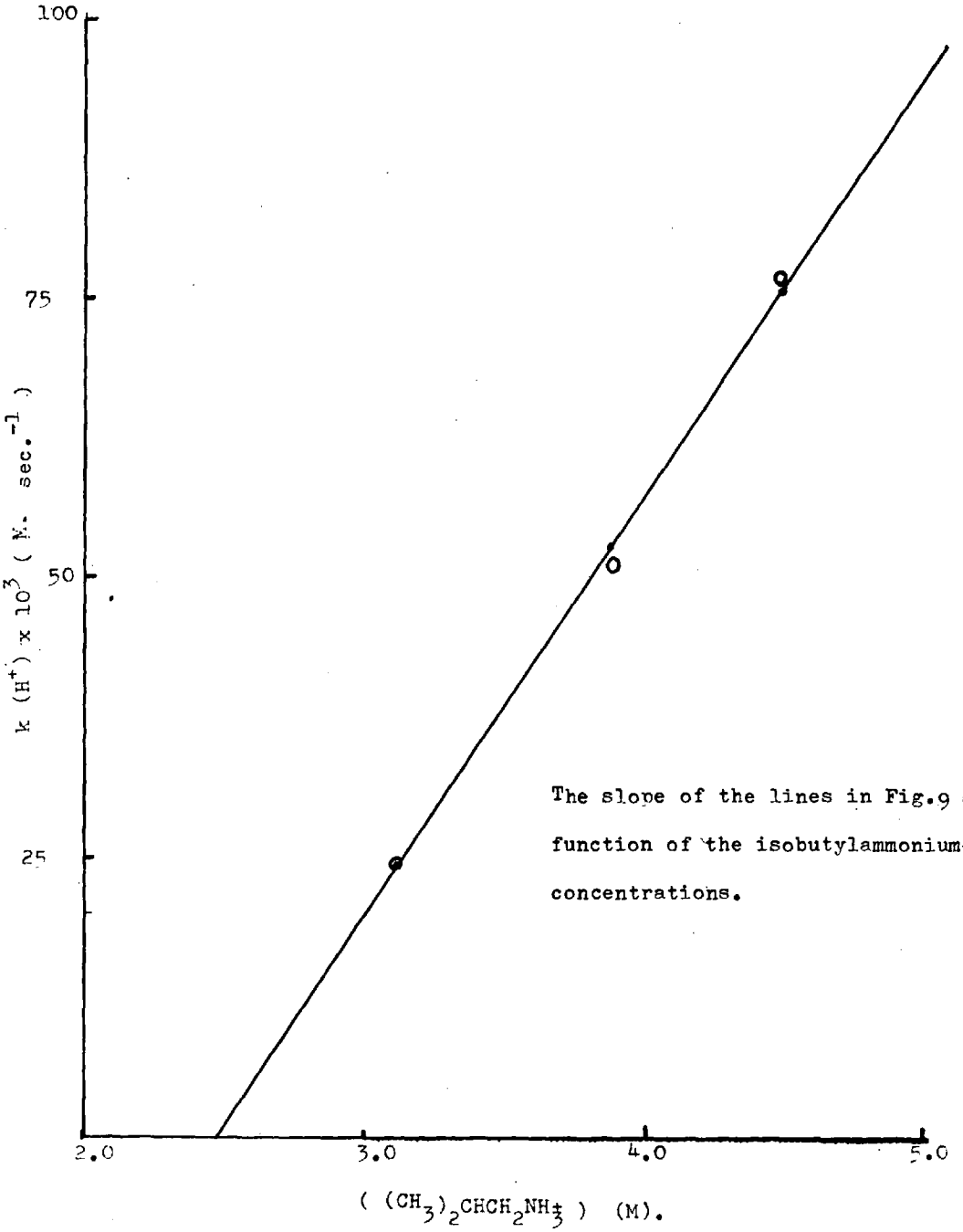
is plotted against the reciprocal of the hydrogen ion concentration. Within the experimental accuracy , all the figures shows linear dependence of k on $1/(H^+)$, in accordance with the above equation.

For all these ammonium ions , the graphs shows definite intercepts with the Y-axis. In accordance with Eq.(1) , this intercept is interpreted as due to a direct reaction with water. The rate constant k_4 , for this reaction was estimated in this manner and is reported in tablelX for the various ammonium salts studied. The slopes of the lines in Figs. (9), (11),(13),(15), and (17) , has been plotted against the concentration of the amine hydrochlorides. The slopes of Figs. (10),(12),(14),(16), and (18) , give the value of $(k_6 + k_7)\ K_A$, The values of $(k_6 + k_7)K_A$, together with the values of acid dissociation constants are given in table V111, for the different ammonium ions under consideration.



Experimental pseudo first-order rate constant, k, as a function of the receprocal of the hydrogen ion concentration for different isobutylammonium ion.

Fig. 9



The slope of the lines in Fig.9 as a function of the isobutylammonium ion concentrations.

Fig. 10

Experimental pseudo first-order rate constant ,k, as a function of the reciprocal of the hydrogen ion concentration for different isopropylammonium ion.

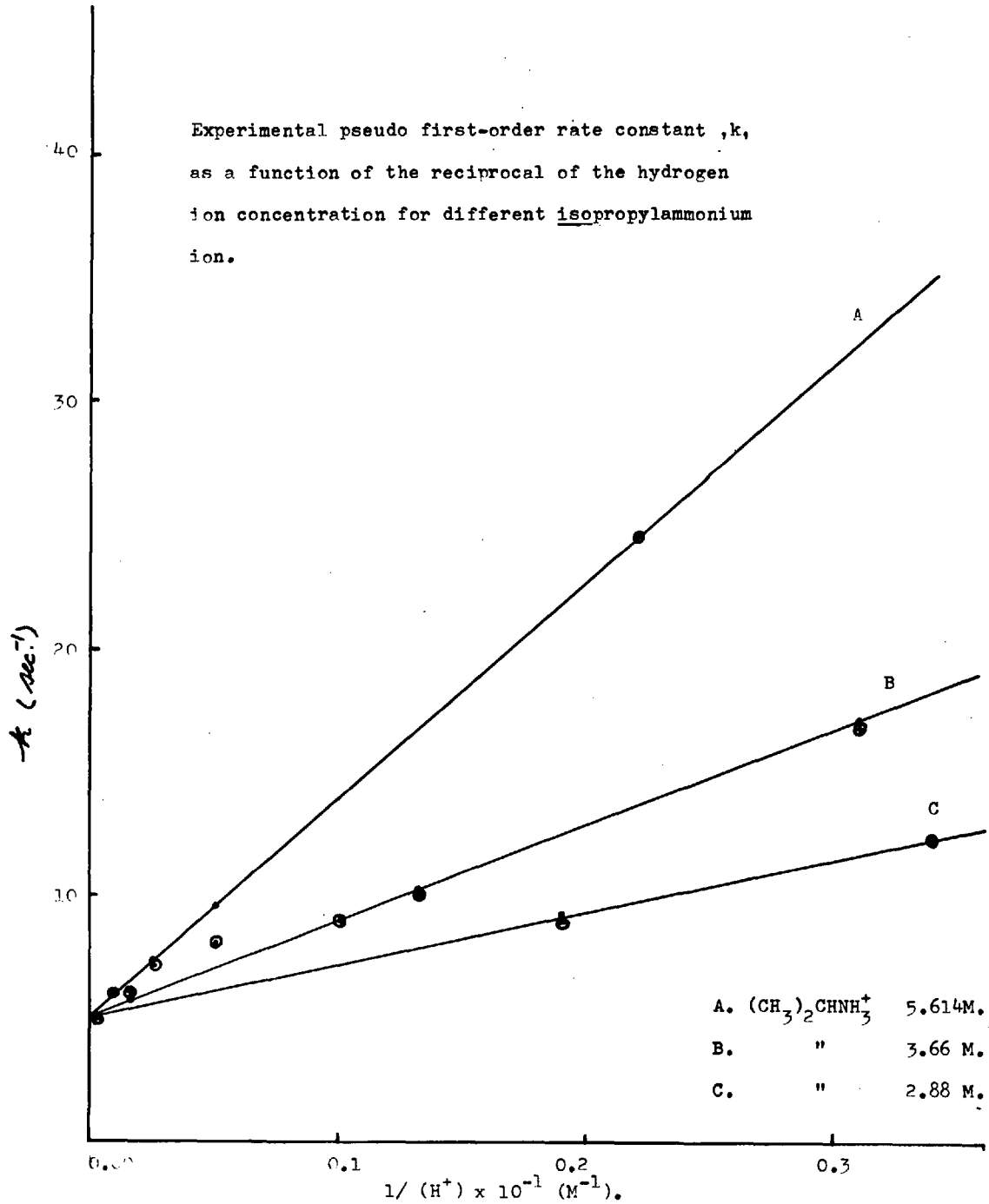


Fig. 11

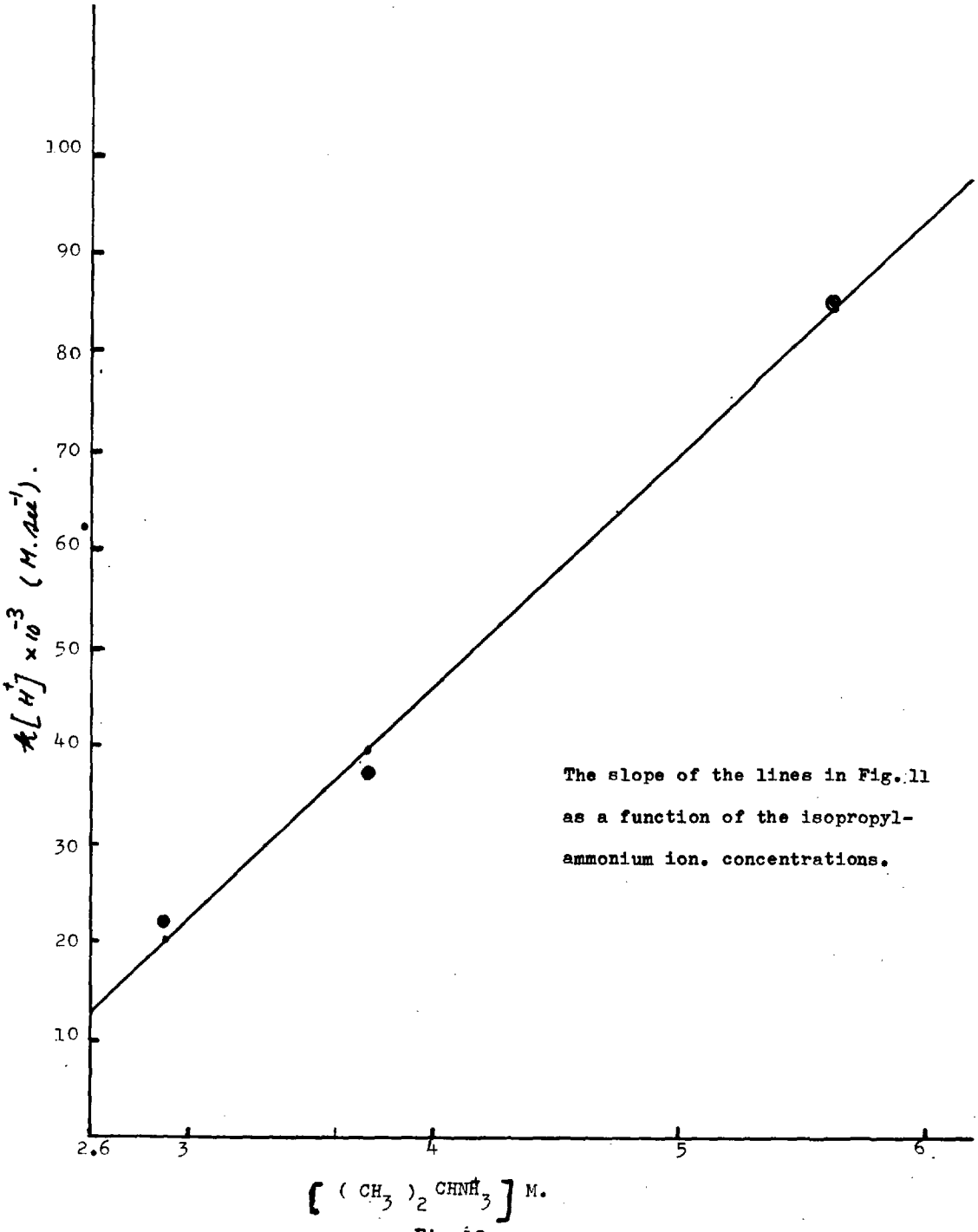
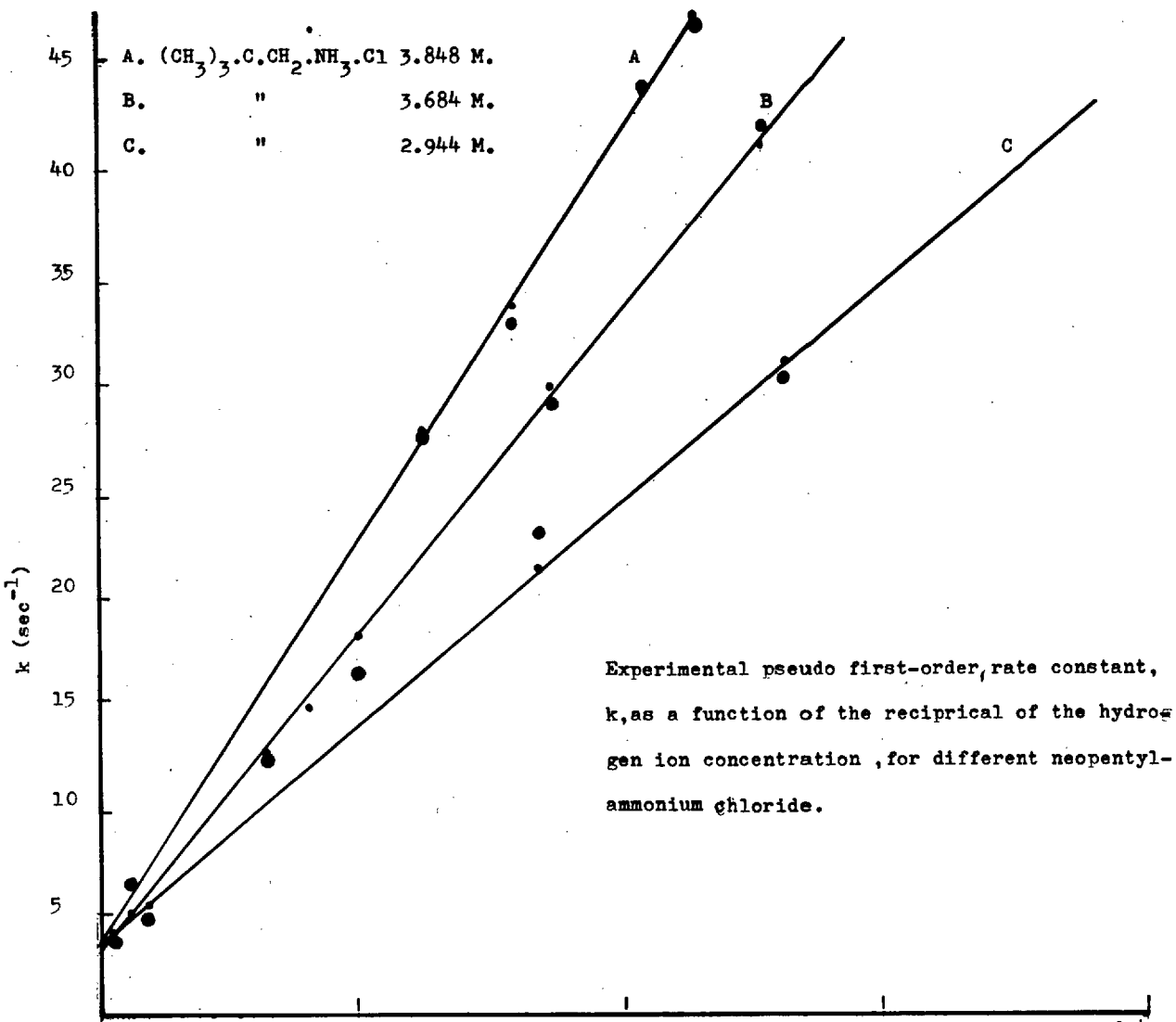


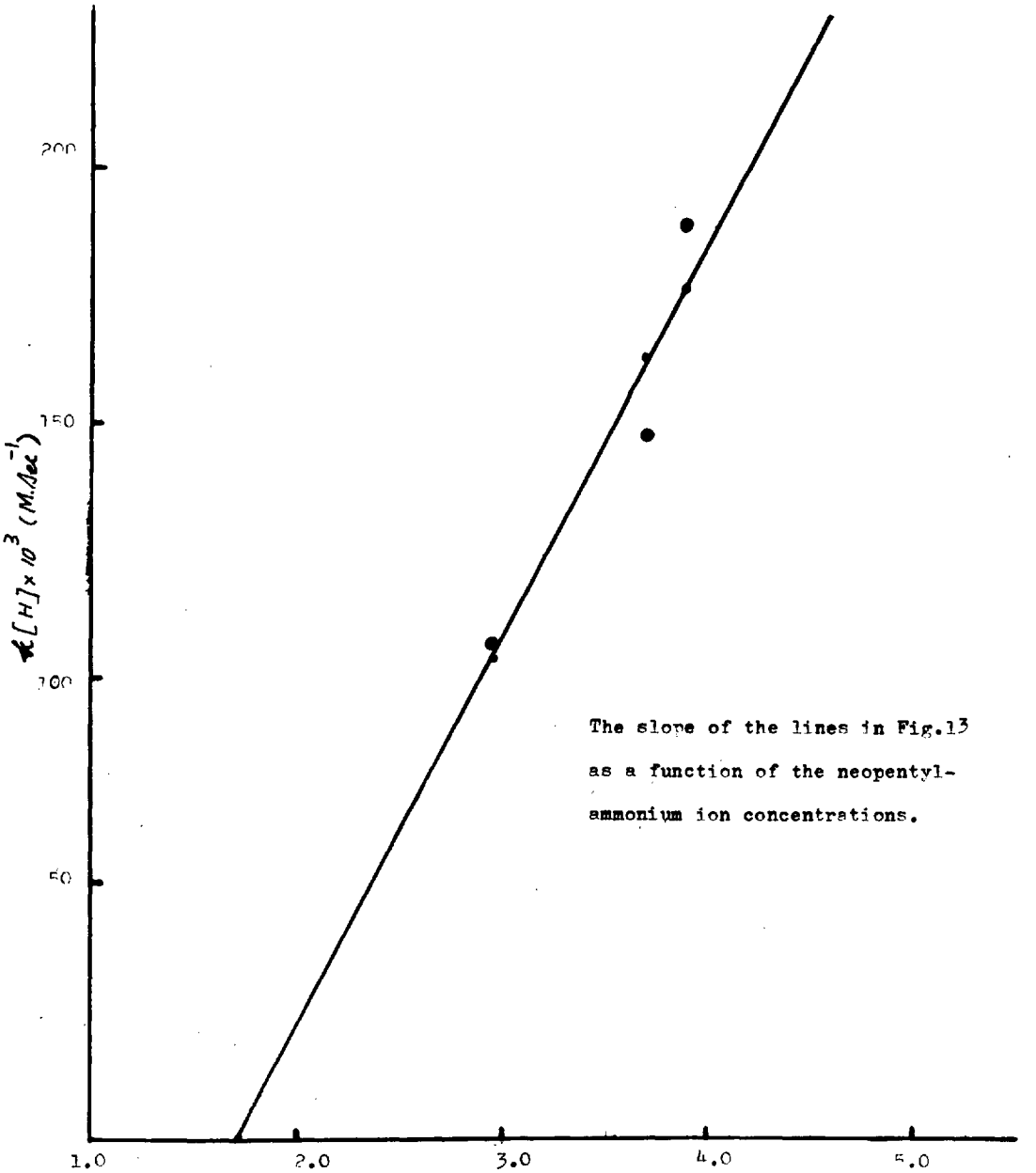
Fig.12

The slope of the lines in Fig.11 as a function of the isopropyl-ammonium ion. concentrations.



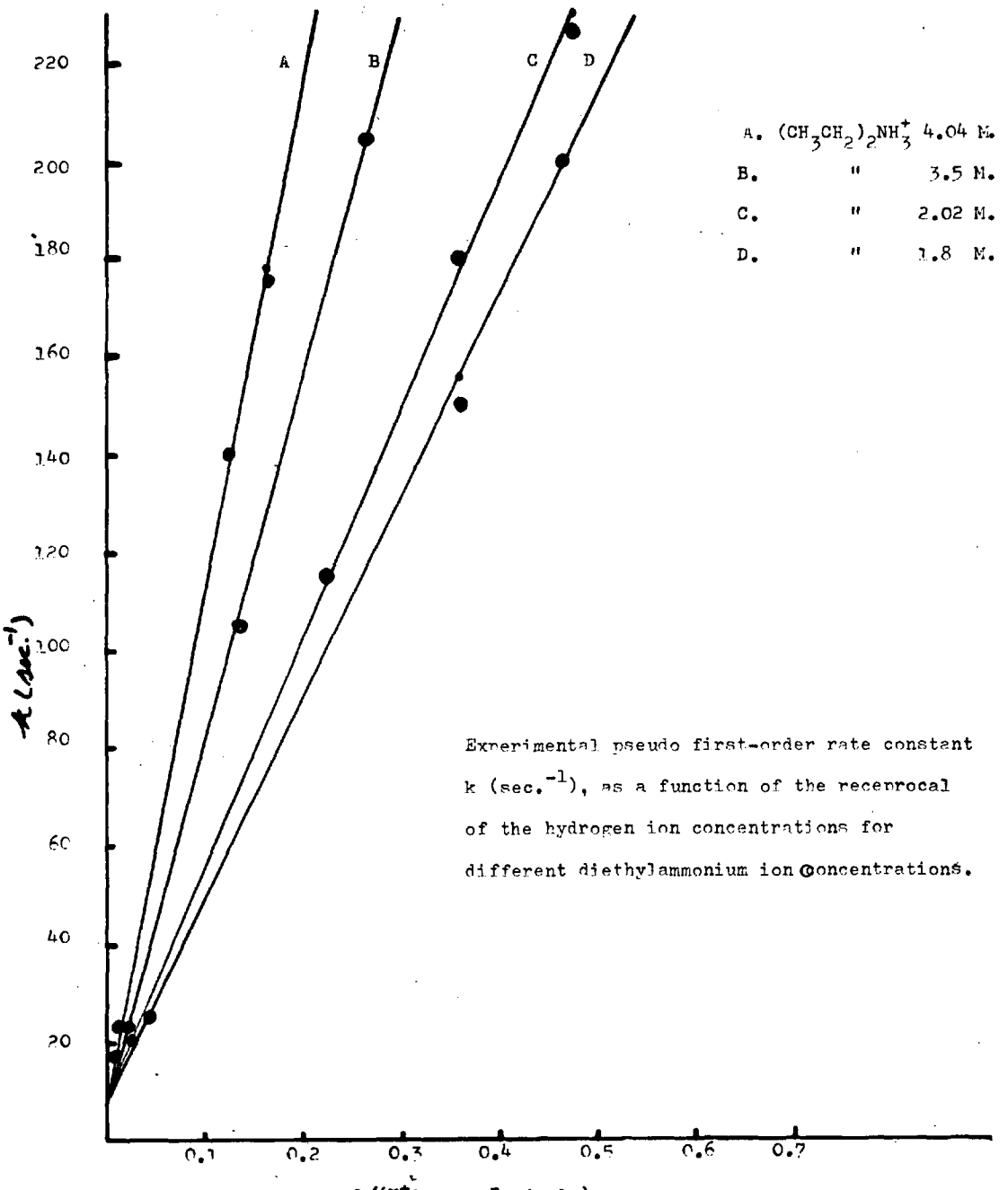
Experimental pseudo first-order rate constant, k, as a function of the reciprical of the hydrogen ion concentration, for different neopentylammonium chloride.

Fig.13



The slope of the lines in Fig.13 as a function of the neopentylammonium ion concentrations.

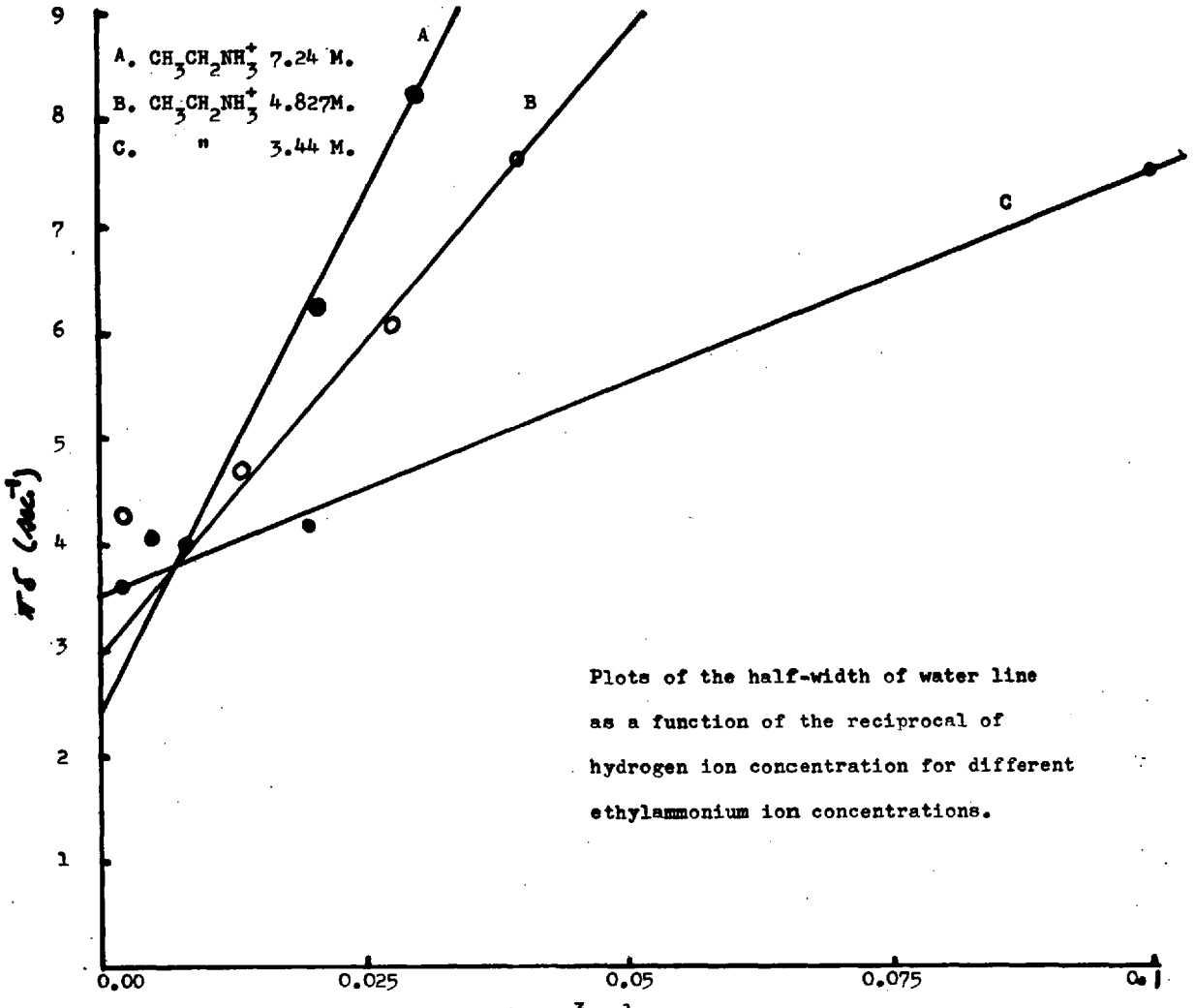
Fig.14



A. $(CH_3CH_2)_2NH_3^+$ 4.04 M.
B. " 3.5 M.
C. " 2.02 M.
D. " 1.8 M.

Experimental pseudo first-order rate constant k (sec.$^{-1}$), as a function of the reciprocal of the hydrogen ion concentrations for different diethylammonium ion concentrations.

Fig. 15



Plots of the half-width of water line as a function of the reciprocal of hydrogen ion concentration for different ethylammonium ion concentrations.

Fig. 15

THE SLOPE OF THE LINES IN FIG.15 AS A FUNCTION OF THE DIETHYLAMMONIUM ION CONCENTRATIONS.

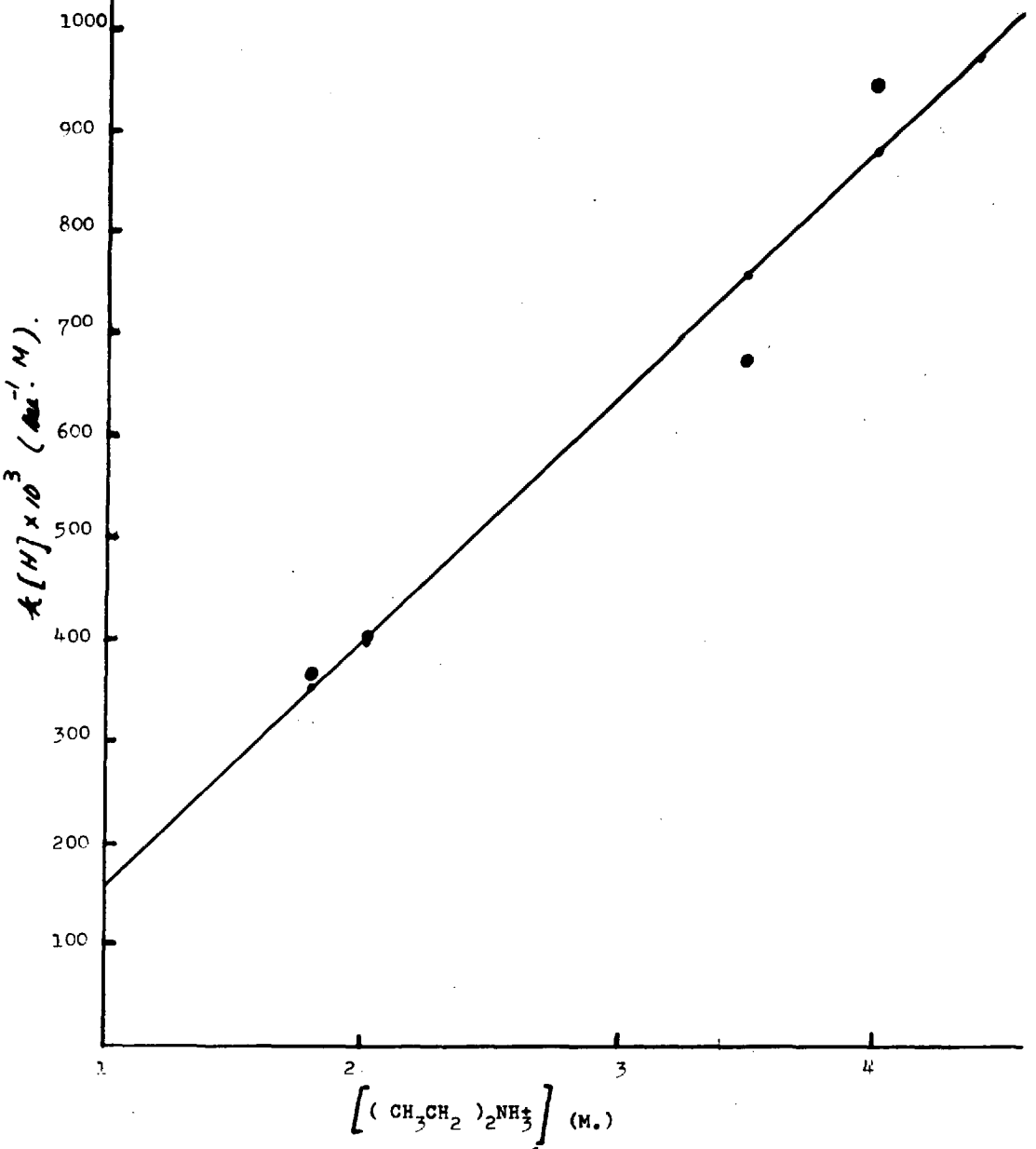
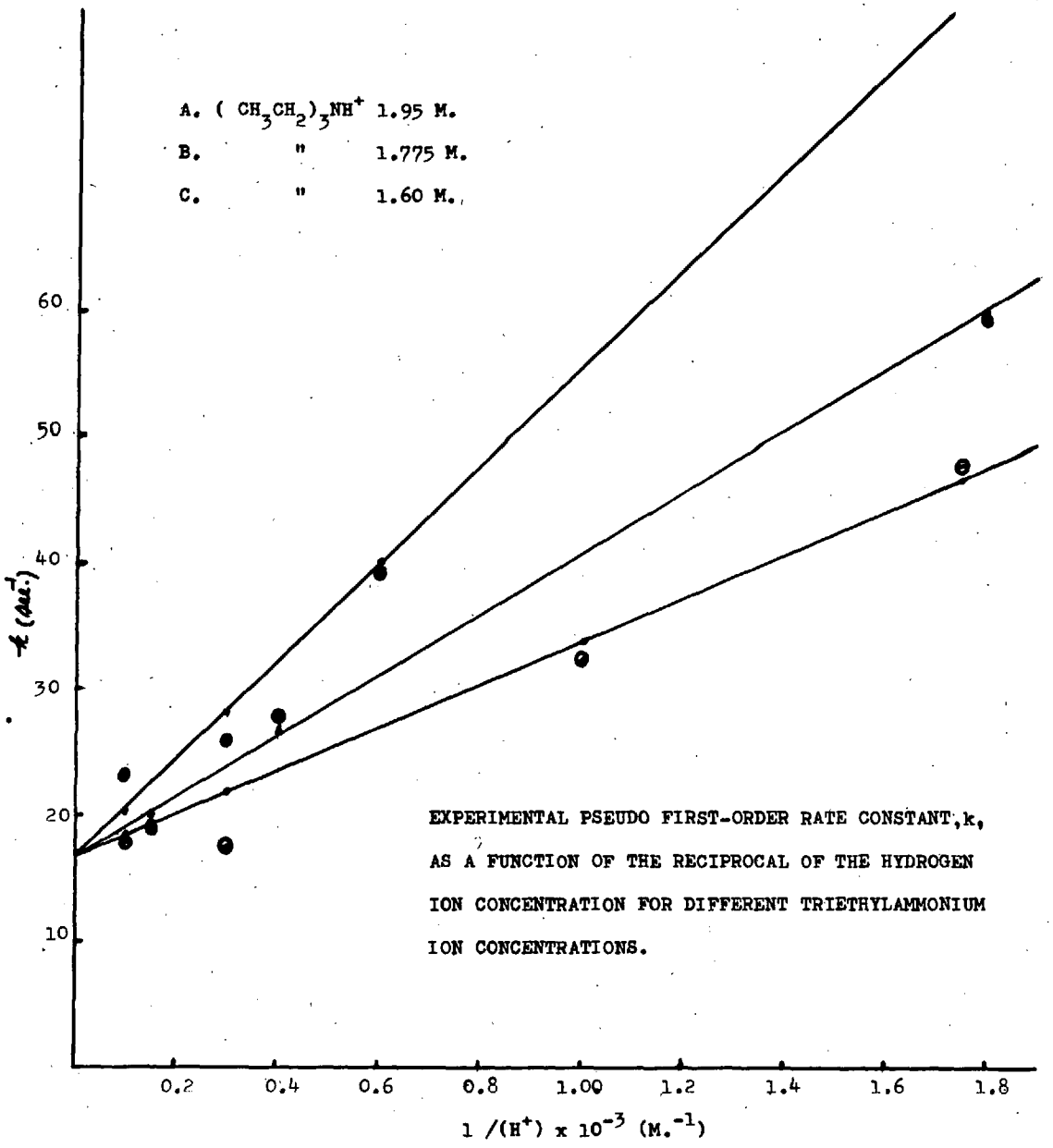


Fig. 16



EXPERIMENTAL PSEUDO FIRST-ORDER RATE CONSTANT, k, AS A FUNCTION OF THE RECIPROCAL OF THE HYDROGEN ION CONCENTRATION FOR DIFFERENT TRIETHYLAMMONIUM ION CONCENTRATIONS.

Fig.17

THE SLOPE OF THE LINES IN FIG.17 AS A FUNCTION OF THE TRIETHYLAMMONIUM ION CONCENTRATIONS.

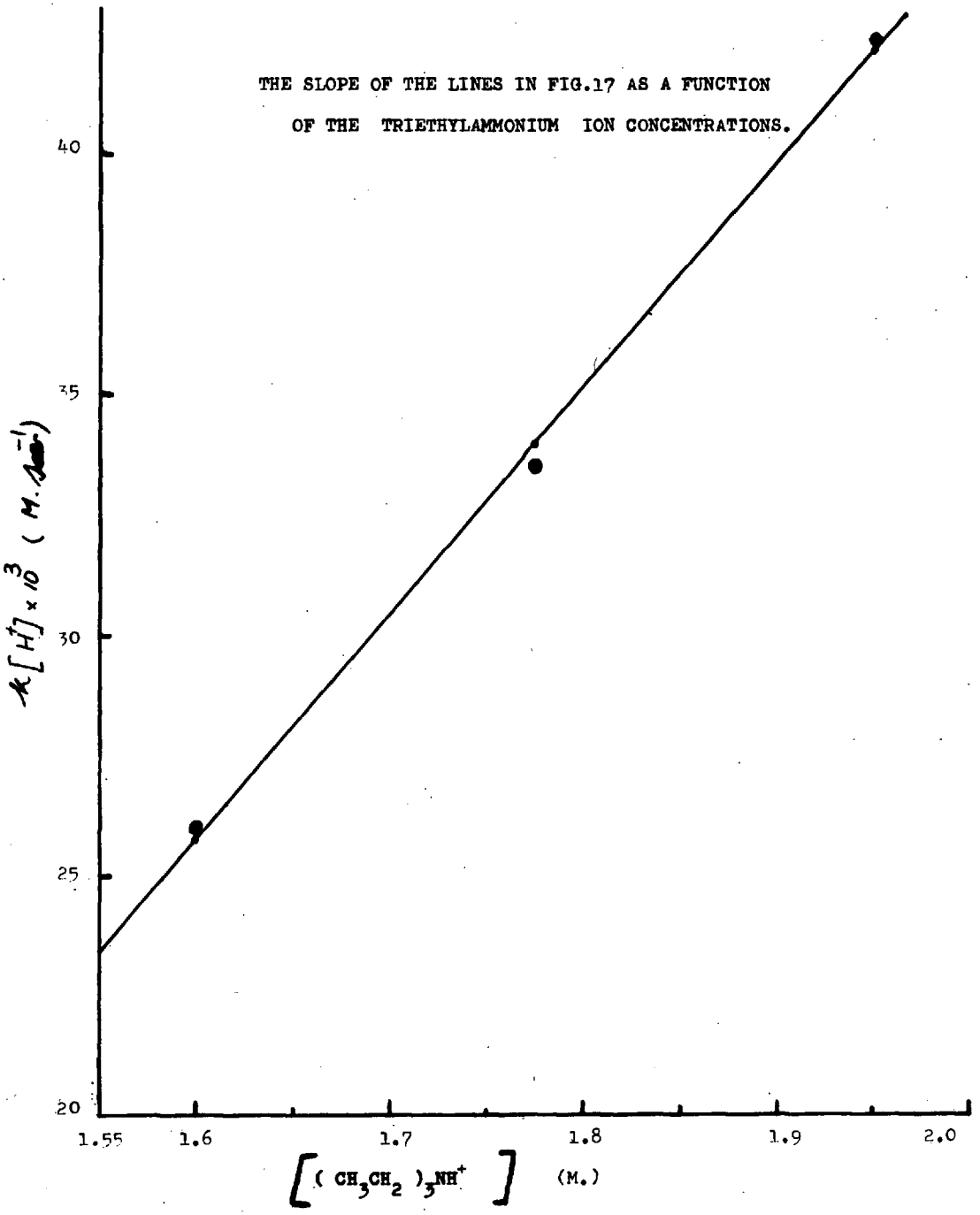


Fig.18

MEASUREMENT OF k_7/k_6

In order to separate $(k_6 + k_7)$ into the individual rate constants, we have measured the exchange broadening of the water line. Grunwald, and his co-workers,[20] define a quantity p by :

$$p = k_5K_W + k_7K_A(RNH_3^+)/k_5K_W + (k_6+k_7)K_A(RNH_3^+) \qquad (2)$$

from which the ratio k_7/k_6 can be deduced since the small term k_5K_W is already known from conductivity measurements. The quantity p, may be measured by two different methods:

(i). From the initial broadening of the water line at relatively high hydrogen ion concentrations.

(ii). From the final narrowing of the water line at relatively low hydrogen ion concentrations.

The first of these methods will be considered here. If δ is the full width of the water line at half of its maximum height (half-width), then it can be shown that $\pi\delta$ approaches the unbroadened line width $1/T_2$, its value is given in good approximation by the following formula, which was also derived by Grunwald and his co-workers,[20]

$$\pi\delta = 1/T_2 + (m_2k_4/111.) + p\, m_2[k_5K_W + (k_6+k_7)K_A(RNH_3^+)]/111.(H^+) \qquad (3)$$

In this equation, m_2 is the molality of the alkylammonium ion, and $m_2/111.$, is one half the molar ratio $(RNH_3^+)/(H_2O)$. Thus , according to the foregoing equation, the plot of π against $1/(H^+)$ should be linear in the region of initial broadening. The slope of this line in conjunction with the data listed in table V111. , permits evaluation of p. Typical experimental plots are shown in Figs.(19), (21), and (23). The results are shown in table 1X.

EXPERIMENTAL PLOT OF HALF-WIDTH OF THE WATER LINE, , vs. 1/ (H^+) FOR SOLUTIONS OF NEOPENTYL-AMMONIUM ION CONTAINING

A. 3.849 M. $(CH_3)_3C-CH_2NH_3^+$.

B. 3.684 M. "

C. 2.944 M. "

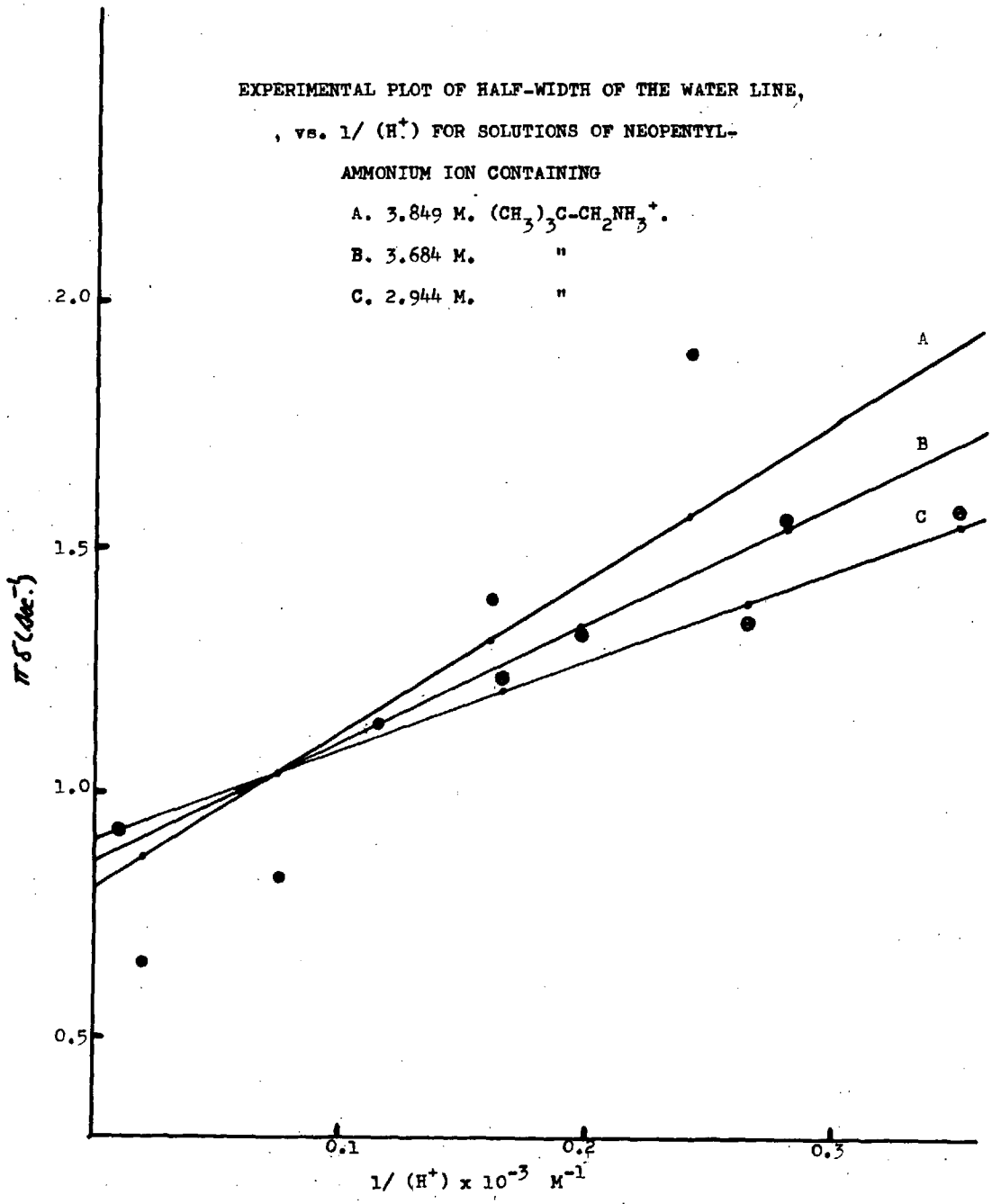


Fig.19

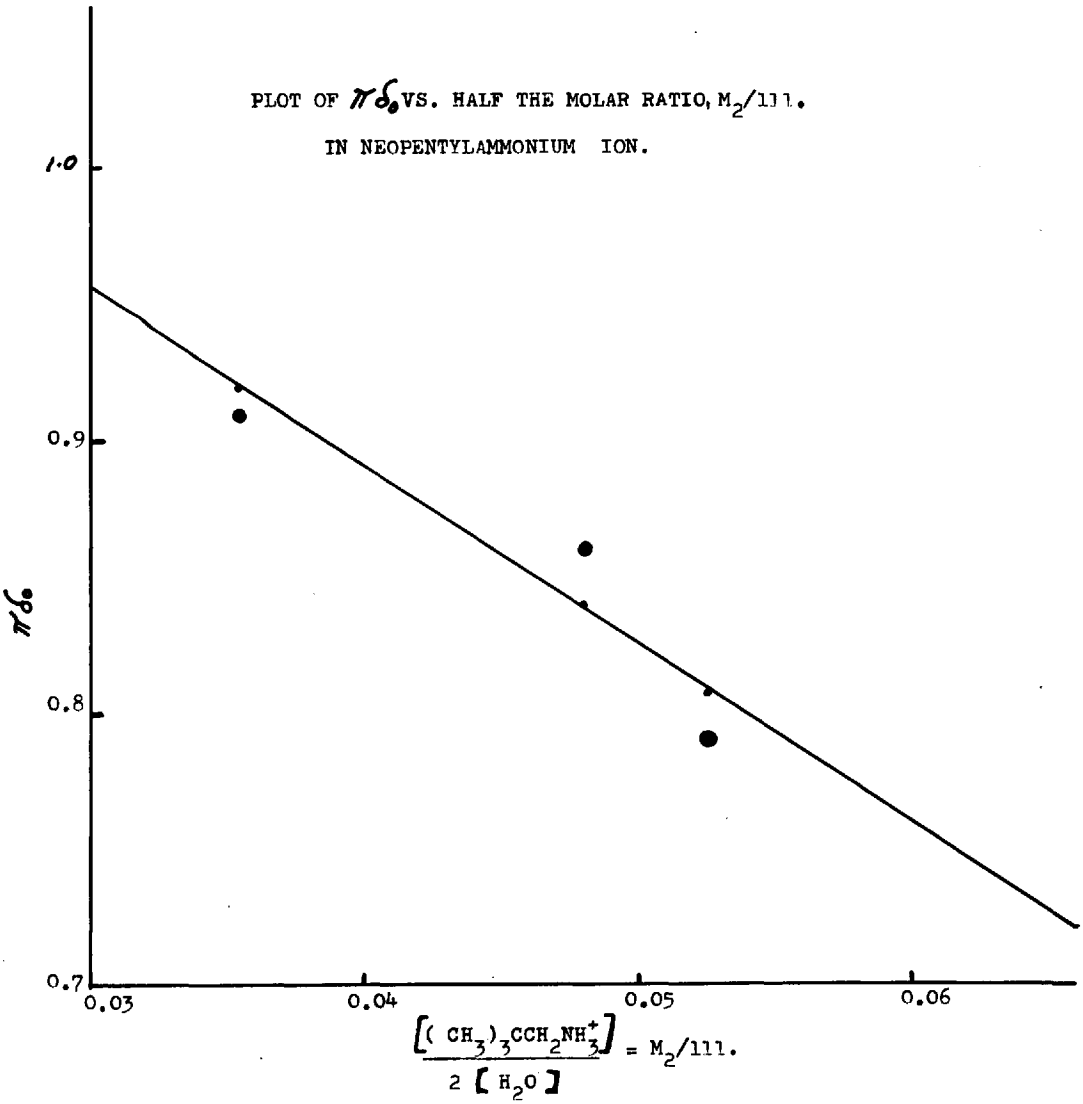

PLOT OF $\pi\delta_o$ VS. HALF THE MOLAR RATIO, $M_2/111$.
IN NEOPENTYLAMMONIUM ION.
1.0
0.9
0.8
0.7
$\pi\delta_o$
0.03
0.04
0.05
0.06
$\frac{[(CH_3)_3CCH_2NH_3^+]}{2[H_2O]} = M_2/111.$

Fig.20

PLOT OF $\pi\delta$ VS. $1/(H^+)$ FOR SOLUTIONS OF ISOPROPYL-AMMONIUM ION AT DIFFERENT CONCENTRATIONS.

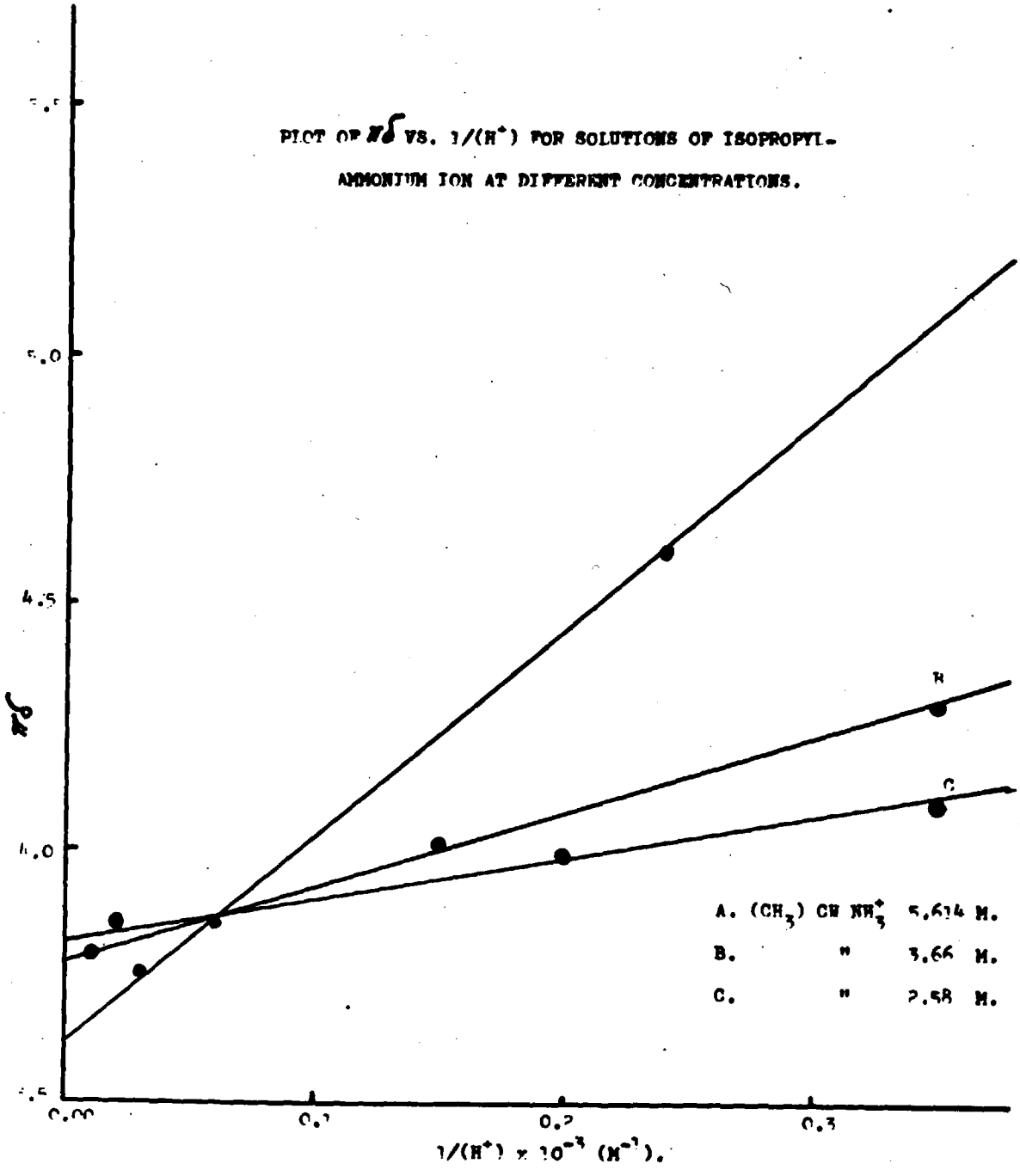


Fig.21

PLOT OF γd_o VS. HALF THE MOLAR RATIO, $M_2/111$.
IN ISOPROPYLAMMONIUM ION.

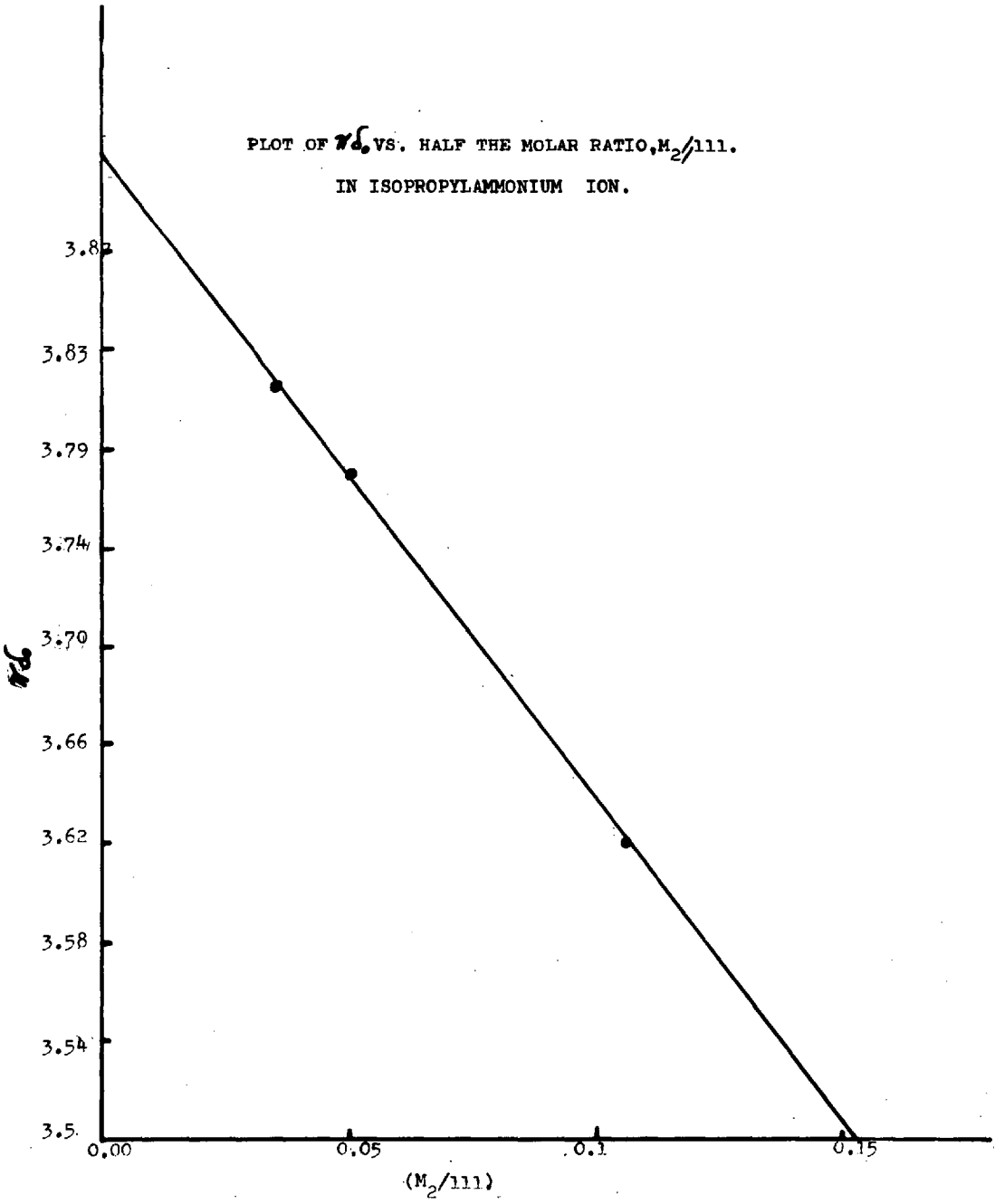


Fig.22

EXPERIMENTAL PLOT OF HALF-WIDTH OF WATER LINE VS. $1/(H^+)$ FOR SOLUTIONS OF ISOBUTYLAMMONIUM ION.

A. $(CH_3)2CHCH_2NH_3^+$ 4.468 M.

B. " 3.684 M.

C. " 3.11 M.

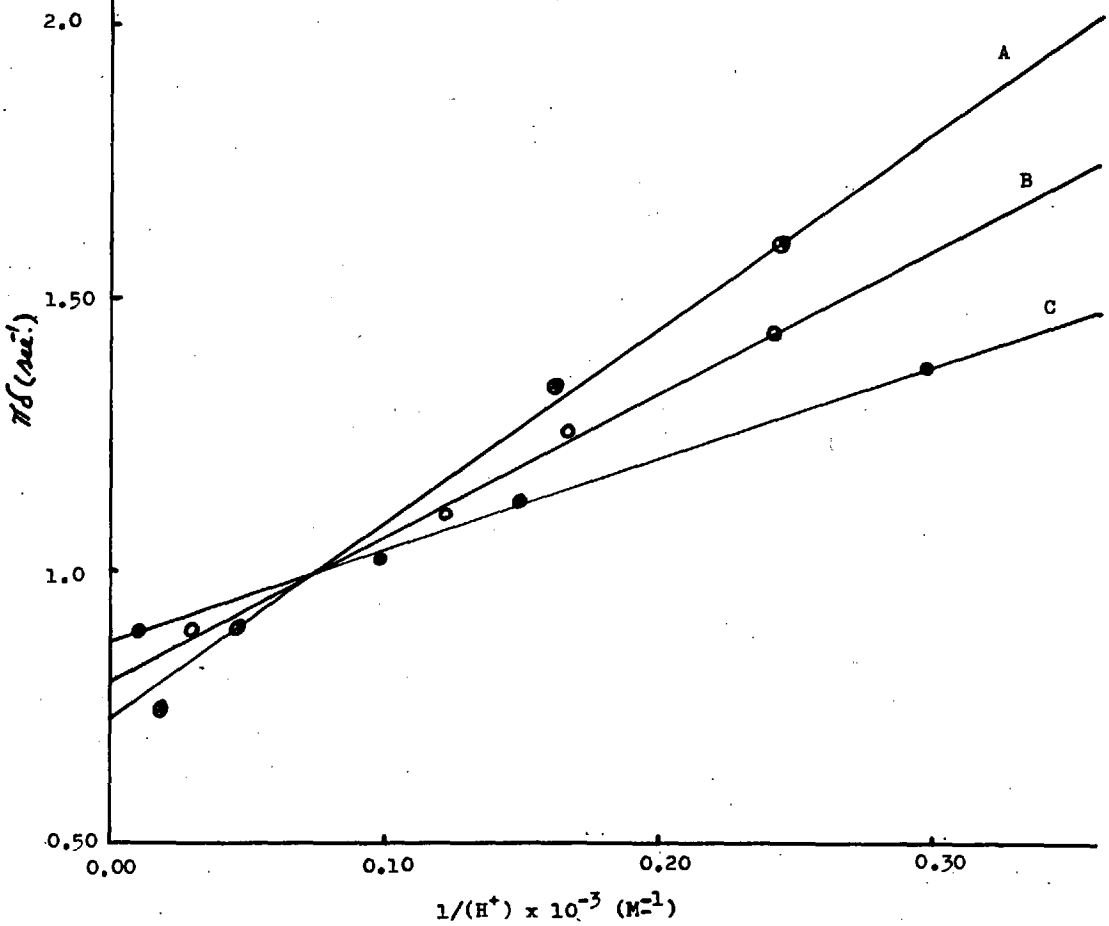


Fig.23

EXPERIMENTAL PLOT OF HALF-WIDTH OF WATER LINE VS.

$1/(H^+)$ FOR SOLUTIONS OF ISOBUTYLAMMONIUM ION.

A. $(CH_3)2CHCH_2NH_3^+$ 4.468 M.

B. " 3.684 M.

C. " 3.11 M.

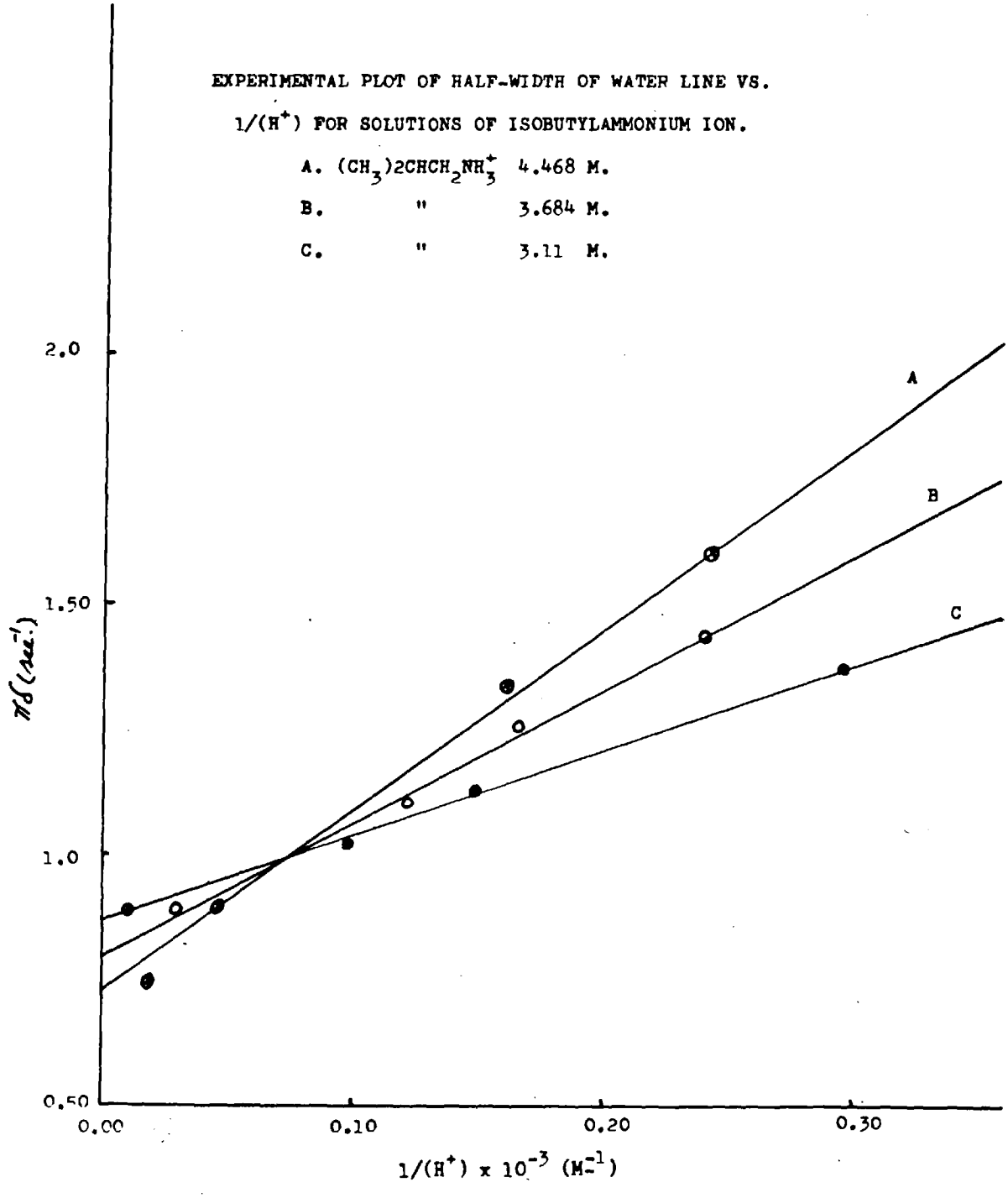


Fig.23

PLOT OF $\pi\delta_o$ VS. HALF THE MOLAR RATIO, $M_2/111$.
IN ISOBUTYLAMMONIUM ION.

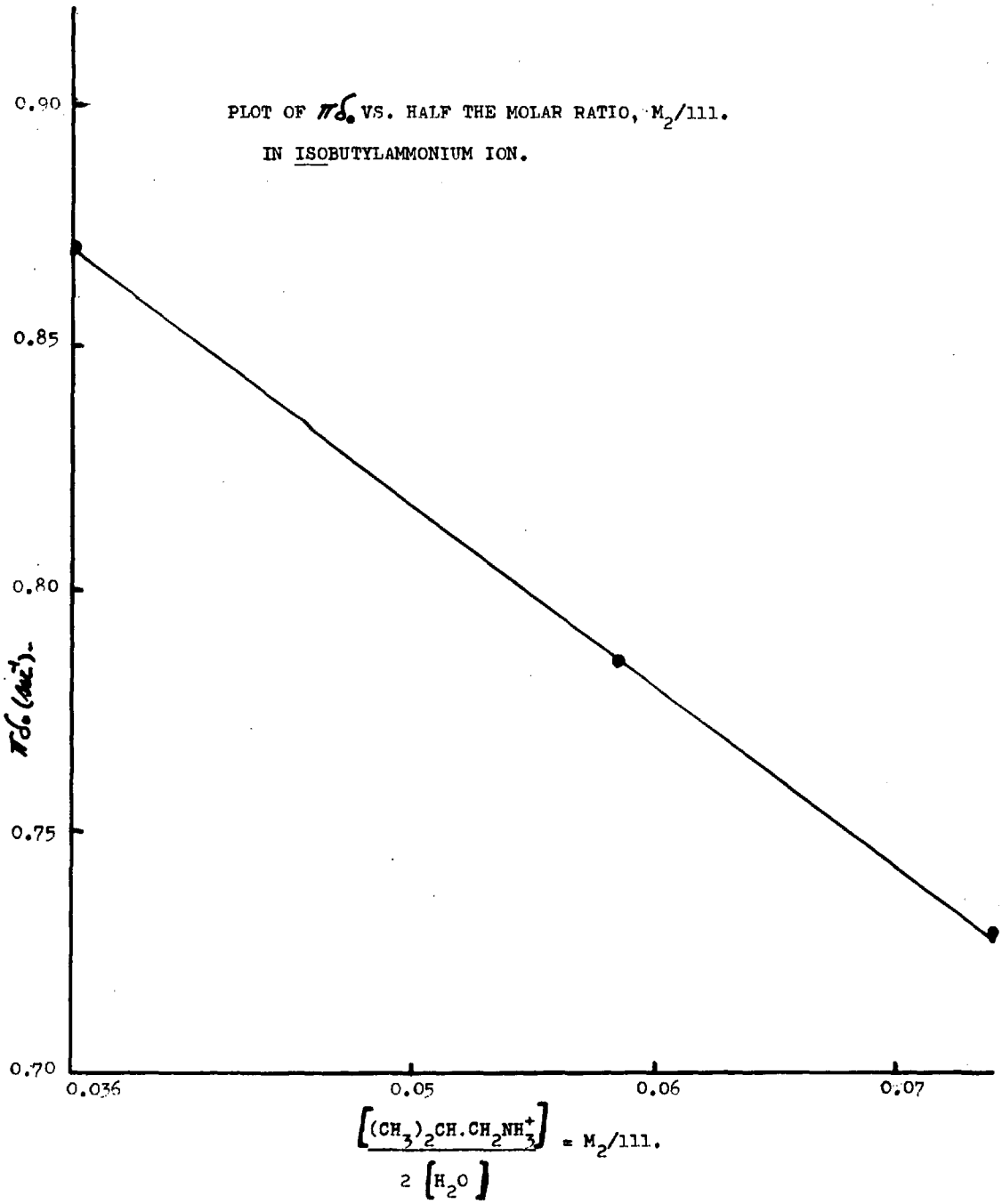


Fig.24

PLOT OF $\pi\delta_o$ VS. HALF THE MOLAR RATIO , $M_2/111.$,
IN ETHYLAMMONIUM ION.

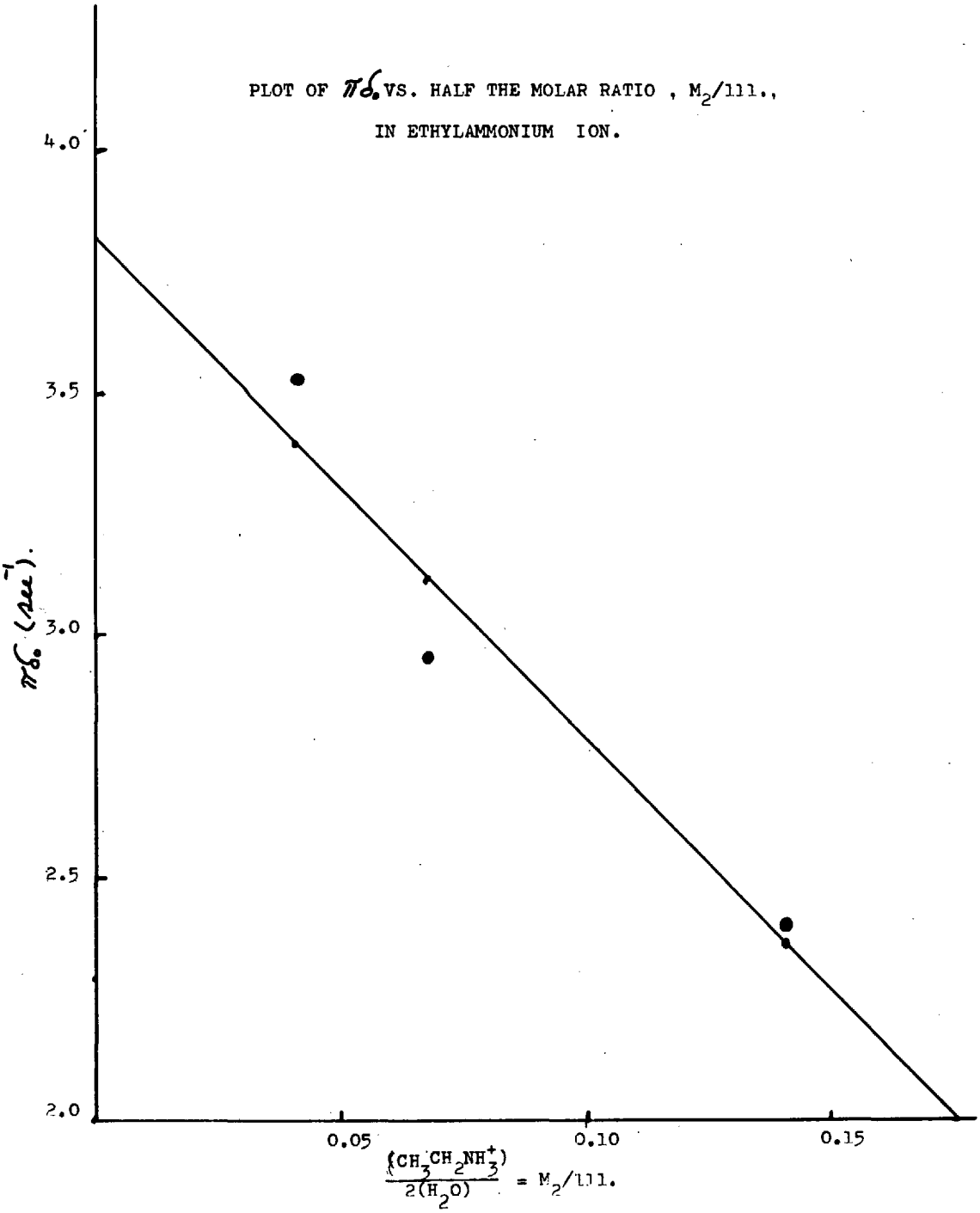


Fig.25

Table VIII. Rate and equilibrium constants for proton transfer reactions of alkylammonium ions in water at 20 0.5°.

Compound	(RNH_3^+)	$(k_6+k_7)K_A10^3$	$10^8(k_6+k_7)$	$10^8\ k_6$	$10^8\ k_7$
$CH_3CH_2NH_3^+$	7.24	45.98 ± 1.3	38.89±1.05	26.02±0.34	12.87±0.7
	4.827	"	38.22±1.03	25.65±0.33	12.57±0.7
	3.440	"	37.17±1.01	24.31±0.33	12.86±0.68
$(CH_3CH_2)_2NH_2^+$	4.040	23.75±0.17	41.57±0.28	29.06±0.09	12.54±0.20
	3.500	"	41.07±0.27	27.93±0.09	13.14±0.18
	2.020	"	39.50±0.26	26.47±0.09	13.04±0.17
	1.800	"	39.12±0.26	26.48±0.08	12.63±0.18
$(CH_3CH_2)_3NH^+$	1.950	46.87±1.05	40.89±0.91	28.71±0.27	12.19±0.64
	1.755	"	40.72±0.90	27.69±0.28	13.03±0.62
	1.600	"	40.51±0.90	27.99±0.90	12.52±0.62
$(CH_3)_2CHNH_3^+$	5.614	23.18±0.5	17.70±0.38	12.09±0.26	5.61 ± 0.12
	3.660	"	17.26±0.37	11.22±0.24	6.04 ± 0.13
	2.880	"	16.92±0.36	11.82±0.26	5.10 ± 0.10
$(CH_3)_2CHCH_2NH_3^+$	4.468	38.57±0.93	17.87±0.43	11.90±0.37	5.97 ± 0.06
	3.684	"	17.71±0.42	10.54±0.38	7.17 ± 0.04
	3.110	"	17.44±0.42	6.38 ± 0.38	11.06±0.04
$(CH_3)_2CCH_2NH_3^+$	3.848	79.48±12.7	43.86±7.0	35.0 ± 3.55	8.86 ± 1.4
	3.684	"	43.67±6.9	35.98±5.7	7.68 ± 1.22
	2.944	"	43.07±6.89	33.38±5.3	9.68 ± 1.50

MEASUREMENT OF k_4.

The above expression (Eq.3), derived by Grunwald, and his co-workers,[20] relating the half-width of the water line to k_4, k_6, and k_7 enables one to calculate k_4 as follows:

According to this equation, the intercepts $\pi\delta_o$ of the plots of the half-width of the water line against $1/(H^+)$, are equall to $1/T_2 + m_2k_4/111.0$. Experimental values are shown in table 1X. The values of $\pi\delta_o$ decreases sharply with increase in alkylammonium ion concentration. The decrease is not due to decrease in $1/T_2$, we conclude that k_4 is decreasing with increase in concentration.

At very high acid concentration, where the term $1/(H^+)$ is equall to zero, the above expression reduces to:

$$\pi\delta_o = 1/T_2 + m_2k_4/111.0 \qquad (4)$$

Where, $\pi\delta_o$ is the intercept of the plot of $\pi\delta$ (half-width of the water line), VS. $1/(H^+)$, and $m_2/111.0$ is one half the molar ratio i.e. $(RNH_3^+)/2(H_2O)$. In this equation the plot of $\pi\delta_o$ against $m_2/111.0$ should be linear , the slope of which should give the value of k_4. The intercept of this line is equall to the half-width of the water line in the absence of exchange. In fact, this value is in good

agreement with the value of $1/T_2$ found in this study.

EVALUATION OF k_5.

Regarding the prediction of k_5, there are experimental values for analogous reactions of hydroxide ion with ammonium ion and with hydronium ion. If in these reactions, protolysis occur at every encounter, the rate constants should be closely similar to those for the formation of short-range ion pairs, that is , for the approach of these ions to distances within 3.5 A^{o} in aqueous solutions. The later rate constant can be estimated from a theory developed by Onsager.[25] For uniunivalent electrolytes, the value is given by :

$$k = 1.130 \times 10^{10} \Lambda_o / D \qquad (5)$$

Where, D is the dielectric constant for the medium, and Λ_o , the sum of the equivalent conductance of cation and anion.

Table 1X. Determination of k_4 and k_{-4} for aqueous solutions of alkylammonium ions at 20 ± 0.5°.

Compound	(RNH_3^+) M.	$10^{11} K_A$	k_4	$10^{-11} k_{-4}$	p
$CH_3CH_2NH_3^+$	7.24	1.182	5.757	8.822	0.331
	4.827	1.203	5.858	8.669	0.329
	3.440	1.237	6.024	8.431	0.346
$(CH_3CH_2)_2NH_3^+$	4.040	0.570	5.335	16.421	0.301
	3.500	0.577	5.400	16.221	0.320
	2.020	0.600	5.616	15.600	0.330
	1.800	0.606	5.672	15.445	0.323
$(CH_3CH_2)_3$	1.950	1.146	5.913	8.595	0.298
	1.775	1.151	5.939	8.557	0.320
	1.600	1.157	5.970	8.513	0.309
$(CH_3)_2CHNH_3^+$	5.614	1.309	1.165	1.586	0.317
	3.440	1.343	1.195	1.546	0.350
	2.588	1.369	1.218	1.516	0.302
$(CH_3)_2CHCH_2NH_3^+$	4.468	2.158	2.115	1.728	0.334
	3.684	2.178	2.134	1.713	0.405
	3.110	2.211	2.167	1.687	0.634
$(CH_3)_3CCH_2NH_3^+$	3.848	1.812	3.914	3.773	0.202
	3.684	1.820	3.931	3.756	0.176
	2.944	1.845	3.985	3.705	0.225

Table X. Rate constants for proton transfer reactions in water at 25°. All rate constants are in sec.$^{-1}$M.$^{-1}$, except k_4 and k_{-5} which is sec.$^{-1}$

Reactions	Temp.	A_o	$10^{-10}k_5$(sec.$^{-1}$M.$^{-1}$)	$10^{-5}k_{-5}$sec.$^{-1}$
$CH_3CH_2NH_3^+ + OH^-$	25°	252.55	3.657	170.5
$(CH_3CH_2)_2NH_2^+ + OH^-$	"	249.35	3.614	361.4
$(CH_3CH_2)_3NH^+ + OH^-$	"	252.20	3.660	191.5

Table XI. Determination of k_4^o and k_{-4}^o for aqueous solutions of alkylammonium ions at 20 0.5°.

Compound	$10^{11}K_A^o$	$10^{-11}k_{-4}^o$(sec.$^{-1}$M.$^{-1}$)	k_4^o (sec.$^{-1}$)
$CH_3CH_2NH_3^+$	2.14	4.87± 0.62	10.43 ± 1.33
$(CH_3CH_2)_2NH_2^+$	1.00	9.36± 0.86	9.36 ± 0.86
$(CH_3CH_2)_3N\overset{+}{H}$	1.91	5.16± 0.22	9.85 ± 0.40
$(CH_3)_2CHNH_3^+$	2.34	0.89± 0.05	2.08 ± 0.12
$(CH_3)_2CHCH_2NH_3^+$	3.80	0.98±0.12	3.73 ± 0.46
$(CH_3)_3CCH_2NH_3^+$	3.16	2.16± 0.12	6.84 ± 0.34

Table XI. Rate and equilibrium constants for proton transfer reactions of alkylammonium ions in water at 20 = 0.5°.in sec.$^{-1}$M.$^{-1}$.

Compound	$10^{-8}(k_6^o + k_7^o)$	$10^{-8}\ k_6^o$	$10^{-8}\ k_7^o$	pK_A
$CH_3CH_2NH_3^+$	21.49 ± 0.58	14.28 ± 0.19	7.21 ± 0.39	10.67
$(CH_3CH_2)_2NH_2^+$	23.75 ± 1.66	16.19 ± 0.55	7.56 ± 1.11	11.00
$(CH_3CH_2)_3N\overset{+}{H}$	24.54 ± 0.55	16.96 ± 0.16	7.58 ± 0.39	10.72
$(CH_3)_2CHNH_3^+$	9.903 ± 0.12	6.71 ± 0.04	3.20 ± 0.09	10.63
$(CH_3)_2CHCH_2NH_3^+$	10.15 ± 0.24	5.51 ± 0.10	4.65 ± 0.14	10.42
$(CH_3)_3CCH_2NH_3^+$	25.14 ± 4.01	20.08 ± 3.21	5.06 ± 0.80	10.50

CONFORMATION FROM THE NH_3^+ TRIPLET.

This method is closely analogous to that employed in the case of ammonium ion,[26] but is less precise because of the broad and complex nature of these lines even in the absence of exchange. However, the plots of half-width vs. $1/(H^+)$, for these lines were linear in the range of initial broadening, and the slopes were calculated by the least-square method. If the kinetic scheme is correct we see,

$$3\pi(\text{slope}) = k_5K_W + (k_7 + 2/3k_6)K_A(\ RNH_3^+\ ) \qquad (6)$$

The right side of equation (6) , can be calculated from data presented previously. The results are shown in table X11. The agreement is satisfactory.

Table X11. Rate measurement based on the broadening of the NH_3-triplet.

Compound	(RNH_3^+)M.	3π slope(obs.)	3π slope(calc.)
$CH_3CH_2NH_3^+$	4.827	0.174 ± 0.003	0.172 ± 0.0025
	3.44	0.123 ± 0.002	0.124 ± 0.0031

C. DISCUSSION.

The exchange reactions considered in this study are the ones given by Grunwald, Loewenstein, and Meiboom.[9] The two major mechanisms for protolysis of aqueous alkylammonium ions are reactions (6) and (7). The simplest mechanisms for reaction (7) are as follows:

(a). Proton transfer from RNH_3^+ to H_2O, followed rapidly by proton transfer to RNH_2.

(b). Concerted transfer of both protons; and,

(c). Proton transfer from H_2O to RNH_2, followed rapidly by release of a proton from RNH_3^+.

Mechanism (a) can be ruled out because the rate is not expected to be much faster than that of reaction (4), and hence much slower than the observed rate, (k_7). In mechanism (b), the rate determining step is either the reorientation of the water molecule between the alkylammonium ion and alkylamine, so as to permit the concerted proton transfer or it is the proton transfer itself. In the former, the rate should depend on the extent of the required reorientation. In mechanism (c), the electrostatic field of the ion is expected to increase the acid strength of adjacent water molecules by, at least, a few orders of magnitude.[27] The increase in acid strength of the water

facilitates the proton transfer to the alkylamine, and the observed magnitude of k_7 is reasonable relative to the values of k_{-5} listed in tableX. Since the field produced by the ion at the nearest water molecules is the same for NH_4^+ and $CH_3CH_2NH_3^+$, the rate should parallel the base strength of the proton-accepting amine as is observed. Thus mechanism (c) is most consistent with the experimental facts.

It is interesting to compare the trend of the rate constants with the pK_A values , because the latter give some measure of the proton donating capacity of the ion. Table Xl shows that k_4 increases as the pK_A decreases (i.e.), as the ion becomes a stronger acid, and is more capable of donating its exchangable protons to water.

In the series ethyl, diethyl, and triethylammonium ions, ethylammonium ion has the smallest pK_A value, and it has a lower k_6 than di-, and triethylammonium ions. Triethylammonium ion has a higher k_6 than diethylammonium ion, as was expected from the small value of pK_A for the former. The value of k_7 has no correlation with pK_A. In the above series of the three ammonium ions , ethylammonium ion has a much lower k_7 than would be expected from its low pK_A.

Organic acids and bases have played a significant role in the development of modern physical theories.[28,29] The influence which structure and substituents exert on the relative strengths of acids and bases are an important part of the foundations upon which such theories as those of the inductive effect and the resonance effect are constructed.

One such phenomenon is the anomalous behaviour of the methylamines. The introduction of a methyl group into the ammonia molecule, produces an increase in base strength , which is ascribed to the positive inductive effect (+ I) of the methyl group. The introduction of a second methyl group causes a further increase which is ascribed to the same effect. Introduction of a third methyl group, however , markedly reduces the strength of the tertiary amine formed.

If we go along the series ammonia, methylamine, ethylamine, and propylamine, the base strength rises with the first three, but falls in the latter. According to the current theories,[30] introduction of a given substituent influences the properties of the parent molecule in two ways:

(1). By changing the charge distribution.

(2). By changing the steric relationships within the molecule.

The first of these effects is due primarily to the electrostatic properties of the substituent. The second, to its space requirments. The former effect has been called the ' polar factor ' associated with a given substituent, the second is termed the 'steric factor'. The influence of the polar factor on the strength of acids and bases has long been realized. The importance of the steric factor, with respect to these properties, has only recently been recognised.

The increase in base strength of methylamine over ammonia and the further increase of dimethylamine over methylamine are ascribed to the polar factor. The inductive effect of two successive methyl groups (+ I), increases the electron density on the nitrogen atom and thus augments the ability of that atom to donate an electron pair to an exceptor such as the proton. There is, however, no apparent explanations in terms of the polar factor for the marked decrease in the donor properties of the nitrogen atom associated with the introduction of a third methyl group. It is reasonable, therefore, to seek the reason for this phenomenon in the steric factor.

There are theoretical reasons for believing that the three bonds of a trivalent nitrogen atom should be directed in space at angles of 90° to each other. In all cases which have been investigated, however, the angles are considerably greater, probably because, they must increase to accomodate the attached groups.[32] An electron diffraction investigation of trimethylamine led Brockway and Jenkens,[33] to the conclusion that the C-N-C angle in the molecule is 108 ± 4°. In the explanation proposed by Brown, Bartholomay, and Taylor,[30] it is assumed that the bond angle in trimethylamine is somewhat greater than the tetrahedral angle, probably close to the upper limit set by Brockway and Jenkins. In other words, the three rather bulky methyl groups spread the bonds from their prefered configuration (90°) to a value greater than the tetrahedral angle.

In the trivalent nitrogen derivatives , such spreading of the bond angles is relatively easy, since the fourth position in the valence shell is not occupied. However, the addition of a fourth group to the vacant position, such as a proton, forces the nitrogen atom toward the tetrahedral configuration and results in a reduction of the expanded angles. The methyl groups are therefore crowded toward each other setting up a strain which reduces the stability

of the ammonium ion.

The following qualitative effects of substituents are considered to influence the pK_A values of the alkylammonium ions.

(1). The mesomeric and inductive effects of the substituent. Any effect which shifts negative charge toward the nitrogen atom will enhance its proton attracting power and hence the strength of the base by increasing the electron density in the lone-pair orbital.

(2). The bulk effect of the substituent , causing hindrance to the approach of the proton.

(3). The combination effect of more than one substituent.

(4). A direct spacial effect due to interactions between the electron clouds of the amino group and the substituent.

(5). Steric hindrance to solvation of the alkylammonium ion.

In the case of trimethyl or triethylammonium ions, since the methyl groups have a positive inductive effect (+ I) , they will be slightly positively charged and it is suggested that electrostatic interactions may occur between the partially unscreened nuclei of the methyl hydrogens and the lone-pair orbital causing its distortion , and reduction of the electron density around the nitrogen atom, thus decreasing its basicity.

It is interesting to compare the basicity of ethyl and isopropylamines, in which we have introduced another methyl group at the α-carbon atom. If the inductive effect alone was the only important factor in determining the basicity of alkylamines, isopropylamine would be the stronger base. In fact it is a weaker base than ethylamine, and this suggests that electrostatic interactions are very important in determining the basicity of alkylamines.

Isopropylammonium ion has a much lower k_6 than ethylammonium ion. From the decrease in the pK_A alone, the opposite would be expected. It is clear that other factors such as electrostatic interactions and steric hindrance play an important role in the direct interaction between the ion and the free base.

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