Study of Medium Effects by
Nuclear Magnetic Resonance

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of Manitoba

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the Requirements for the
Degree of Master of Science

BY
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ABSTRACT

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The chemical shift of the single peak proton magnetic resonance spectrum of cis and trans dibromoethylene and cis and trans dichloroethylene was determined in a variety of media, including a series of dioxane-water solutions, of varying dielectric constants and in various aliphatic and aromatic solvents with a wide range of dielectric constants. The difference in the chemical shifts of the polar cis haloethylene and nonpolar trans haloethylene, measured in an identical medium, is a measure of the effect of the reaction field at the protons in the cis form if other solvent interactions with the two forms are identical.

Buckingham's treatment of electric field effects is studied. The modification of the above by Diehl and Freeman is considered.

TO MY FAMILY

I would like to thank Dr. T. Schaefer for his generous assistance and excellent advice given during the course of this research.

I would also like to express my gratitude to the National Research Council of Canada for their financial assistance.

I would also like to thank Dr. E. Bock for some helpful suggestions.

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THEORETICAL INTRODUCTION

THEORETICAL INTRODUCTION

CHAPTER I

A) Nuclear Magnet

It is believed that all nuclei possessing an even number of protons and neutrons have spin zero. For lighter elements this is confirmed from band spectra. Nuclei whose mass number is odd have a half integral spin quantum number, while those of even mass number but odd charge number have an integral spin.[1]

The rotation of a nucleus involves charge circulation and hence one might expect that a magnetic moment be associated with nuclei having a spin. Classic determinations of this minute magnetic dipole have been carried out.[2,3] It can be shown that the magnetic moment vector is proportional to the nuclear angular momentum. Therefore, the two vectors are collinear. From classical ideas on the circulation of charge one expects a proportionality constant equal to

$$\frac{e}{2m_pc} \qquad (1)$$

where e is the electronic charge, m_p the mass of the proton, and c the velocity of light. However, it is found that an additional characteristic constant must be inserted for equality, the nuclear g factor. This g factor is the counterpart of the Landé factor for electrons. The value of g, which is determinable only from experiment, cannot be explained in any simple way.[4] Hence we write

$$\underline{\mu} = g \frac{e}{2m_p c} \underline{I}\hbar \qquad (2)$$

where $\underline{\mu}$ is the magnetic moment vector and $\underline{I}$ the spin vector in the direction of the angular momentum. The nuclear magneton, μ_0 , may be written

$$\mu_0 = \frac{e\hbar}{2m_p c} \qquad (3)$$

Equation (2) may be written

$$\underline{\mu} = g\,\mu_0 \underline{I} \qquad (4)$$

It is frequently convenient to specify magnetic properties in terms of the magnetogyric ratio γ defined by

$$\underline{\mu} = \gamma\,\underline{I}\,\hbar \qquad (5)$$

The spin I is the value of the maximum component of the magnetic moment, in units of $g\,\mu_0$, along any direction. The magnetic moment vector may align itself in certain directions and the directions are such that the components of the vector along the reference direction are

I, (I-1) ------ (-I+1), -I in units of $g\,\mu_0$.

B) Interaction With a Magnetic Field

In the absence of a magnetic field the orientations of the magnetic moments are random. However, the moment will interact with a magnetic field. The interaction energy is given by

$$E = -\underline{\mu}.\underline{H}_0 \qquad (6)$$

where H_0 is the vector magnetic field. This may be rewritten

$$E = -\mu \cos\theta\, H_0 \qquad (7)$$

where θ is the angle between the magnetic moment and magnetic field vectors. $\mu \cos\theta$ is the value of the component of $\underline{\mu}$ along H_0. Hence

$$E = -mg\,\mu_0\,H_0 \qquad (8)$$

where m = I, (I-1) ----- (-I+1), -I. Hence there are 2I+1 energy levels available to nuclear spins, the populations of which are determined by the Boltzman Distribution Law. This splitting of energy levels in a magnetic field is referred to as nuclear Zeeman splitting, (Fig. 1, p. 3). The energy difference between adjacent levels (only transitions between adjacent levels are allowed transitions) is given by

$$\Delta E = g \mu_0 H_0 \qquad (9)$$

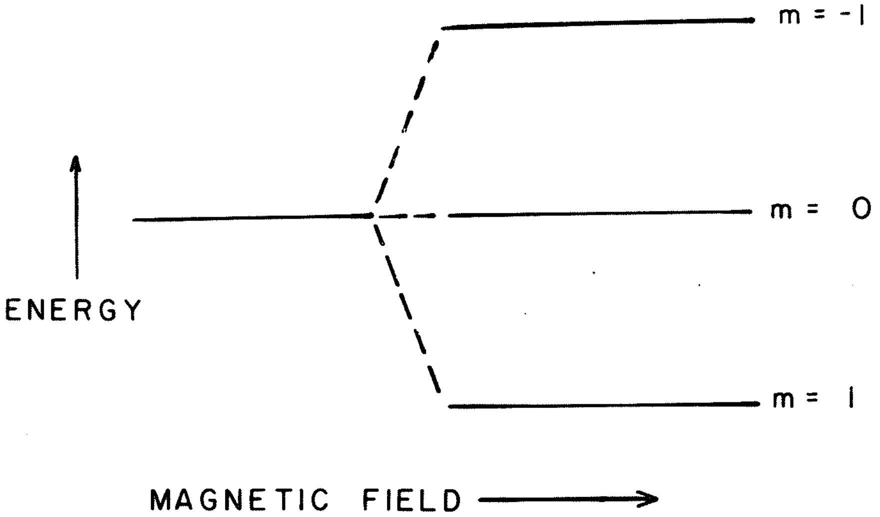


Figure 1: Nuclear Zeeman levels for I=1

The NMR phenomenon arises from induced transitions between these Zeeman levels. The frequency of the quanta or photons inducing these transitions is given by

$$\nu = \frac{\Delta E}{h} \qquad (10)$$

Substituting (2), (3) and (4) into (10), we arrive at

$$\nu = \frac{\gamma H_o}{2\pi} \qquad (11)$$

For a bare proton in a field of 10,000 gauss, the frequency is 42.6 megacycles, in the radio frequency portion of the electromagnetic spectrum.

C) Classical Description of NMR

On a purely classical basis it can be shown that the effect of a static field H_o is to cause the angular momentum vector, and hence the magnetic moment vector, to precess about the direction of the field. J. Larmor was able to show that the angular frequency of this precession, called Larmor precession, was proportional to the strength of the magnetic field, with γ the gyromagnetic ratio as the proportionality constant.[5] It is in this precessional motion that the energy of interaction between $\underline{\mu}$ and H_o is stored. The relationship between angular frequency and the magnetic field may be written

$$w_o = \gamma H_o \qquad (12)$$

Thus the frequency of quanta absorbed or emitted upon transition from one energy level to another is equal to the Larmor precessional frequency of the nucleus.

Suppose now a second magnetic field H_1 is imposed, perpendicular to H_o and rotating about it with a constant angular frequency.

This second field tends to tip the magnet moment vector $\underline{\mu}$ but if the angular frequencies of H_1 and $\underline{\mu}$ are not the same, they interact only slightly. The result is that the precessional motion of $\underline{\mu}$ is changed to a nutational motion, the amplitude of which depends on the difference between their angular frequencies. If the frequencies are the same (with a zero phase angle) large oscillations in the angle between $\underline{\mu}$ and H_o result in transitions from a lower level to an upper level, with absorption of a characteristic quantum of energy. This describes the resonance condition of a single nucleus.

The tendency for nuclei to orient themselves with their magnetic moment vectors along the direction of a magnetic field can be associated with a static paramagnetic susceptibility[6] given by

$$x = \frac{I+1}{3\,I} \; \frac{N\mu^2}{k\,T} \qquad (13)$$

where x is the paramagnetic susceptibility, N is the number of nuclei in one cm^3, T, absolute temperature and k is the Boltzman constant. Upon suitable substitution we arrive at

$$x = \frac{N\,I\,(I+1)}{3\,k\,T} \; \hbar^2 \gamma^2 \qquad (14)$$

One cm^3 of water at $25^{o}C.$ in a magnetic field of 10,000 gauss has induced in it, due to the orientation of the proton spins, a magnetic moment of 3.4×10^{-10} erg/gauss.

The nuclear susceptibility is many orders of magnitude smaller than either the electronic paramagnetic or diamagnetic susceptibility and thus can hardly be determined by classical methods.[7]

Since the protons in a given sample are precessing with random phases, the resultant magnetic moment is parallel to the field H_o. The presence of H_1 tends to bring the precessing nuclear moments $\underline{\mu}$ into phase, with the result that the field H_1 may, under suitable conditions, interact with the macroscopic moment $\underline{M}$ which now has components in the plane in which H_1 rotates.

If the frequency of the precession of the macroscopic moment is altered towards that of H_1, the average component of the magnetization in the plane perpendicular to H_o gradually increases and at resonance a rapid increase is expected since H_1 may now exert a steady torque on $\underline{M}$. If we choose two arbitrary perpendicular fixed directions, x and y, in the plane, it can be shown that the components of the magnetization are given by

$$\begin{aligned} Mx &= M \sin \theta \cos w T \\ My &= M \sin \theta \sin w T \qquad (15) \\ Mz &= M \cos \theta \end{aligned}$$

where θ is the angle between H_o, the z direction, and $\underline{M}$, given by

$$\sin \theta = H_1 / \sqrt{(H_o - \frac{w}{\gamma})^2 + H_1^2} \qquad (16)$$

w is the angular frequency of $\underline{M}$ and $M = |\underline{M}| = xH_o$

Corresponding to the magnetization M_y there is a magnetic induction

$$Hy = 4\pi My \qquad (17)$$

A coil of area A consisting of n turns, oriented with its axis along the y axis would see a magnetic flux

$$\Phi = 4\pi n A M_y \tag{18}$$

This alternating flux induces at resonance a voltage in the coil given by

$$V \text{ (volts)} = \frac{-1}{10^8}\dot{\Phi} = \frac{-1}{10^8} 4\pi n A M \cos \omega t \tag{19}$$

This voltage is of the order of 1 millivolt if the resonant frequency is 42.6 megacycles using a coil with n = 10 and A = 1 cm^2. Apparatus which can produce this phenomenon and measure its effect has been available for some time. For a description of such apparatus see references (8), (9) and (10).

NMR PARAMETERS

CHAPTER II

NMR PARAMETERS

The first NMR parameter was initially observed by a group of physicists observing the N-15 resonance of aqueous ammonium nitrate. Much to their surprise a pair of peaks was observed as the field was scanned. A physical chemist came to their rescue by postulating that the two peaks of equal intensity were due to the presence of two kinds of nitrogen nuclei situated, respectively, in the ammonium and nitrate ions. This shift in the resonant field is known as the chemical shift.

In 1951 the second parameter to be used in labelling NMR spectra was observed.[11] When an NMR spectrogram of pure ethanol was obtained at 40 megacycles and 9,400 gauss, three broad peaks were noticed with a separation of about 20 milligauss. One may assume correctly that three chemically different types of protons are present. Using the intensities measured by the areas under each peak (in the ratio 1: 2: 3) one would ascribe the low field signal to the hydroxyl proton, the one at slightly higher field to the methylene and that at highest field to the methyl group protons whose number are in the ratio 1: 2: 3 respectively. However, in a high resolution spectrum of impure ethanol at 40 megacycles we find that the signals associated with the methylene and methyl protons are now split into a symmetrical quartet and triplet respectively, while that of the -OH proton remains unchanged. (A trace of water catalyzes the exchange of the hydroxyl protons, and does not allow splitting of the hydroxyl proton to be noticeable). This splitting of signals is due to the presence of a second NMR parameter, the coupling constant. Although the object of this thesis is not concerned with this parameter, the coupling constant warrants at least a short discussion.

THE COUPLING CONSTANT

CHAPTER III

THE COUPLING CONSTANT

Andrew[12] attempted to explain the fine structure of the NMR spectrum of Sb-121 and Sb-123 which consisted of a symmetrical set of seven equally spaced lines. He postulated restricted rotation of the SbF_5 molecules was causing this splitting. However, no temperature effects on the splitting was discovered in all compounds studied with this view in mind. In addition, the fine structure persisted when gaseous samples were studied. Gutowsky *et al*[13] proposed the first satisfactory hypothesis--the splittings resulted from an interaction between nuclear magnetic moments. They proposed the following evidence in support of their claim:

1. The splitting of a signal by a neighbouring nucleus was proportional to the magnetic moment of the second nucleus.
2. Chemically equivalent nuclei did not appear to interact.
3. Relative intensities and the number of components of a line A are determined by the statistical weights, and number, of possible spin states of the neighbouring nucleus B.
4. Splittings were independent of temperature and applied field strength.

Ramsey and Purcell[14] pointed out that the magnetic interaction of the nuclei with the electron spin magnetic moments resulted in an effective coupling of the nuclei. This coupling gives rise to a scalar interaction of the proper magnitude. This interaction was explained using a simple diatomic molecule HD. Because neighbouring spins may interact, the spin state of the proton may be telegraphed magnetically to the deuteron via the electrons. The spin of the deuteron (I=1) may be oriented in three directions with respect to an applied field, corresponding to three projections of its magnetic moment along the field. When this component is parallel to the field, the resultant magnetic field at the proton is somewhat larger than that impressed. Hence the proton will resonate at a lower impressed field. When the spin of the deuteron has no component along H_o, the proton will resonate at an impressed field equal to that if no coupling were present. When the component is antiparallel, the spin magnetic moment detracts from the field at the proton, causing a proton in this configuration to resonate at higher field. The number of deuterons, under a field of 14,000 gauss, are distributed almost equally between the three orientations ($m = 1, 0, -1$). The differences in energy of interactions of the deuteron with the magnetic field is so small that the Boltzman distribution is almost identical; an excess of 6 protons per 10 million is found in the lower energy level in a sample of water at room temperature. Hence, as a result of the 3 spin orientations of the deuteron, the proton signal will be split into a symmetrical triplet. Similarly the deuteron can "see" the proton in $2I + 1 = 2$ orientations; hence we expect its signal to consist of a pair of lines of equal intensity. It has been shown that the interaction energy between spins of nuclei is given by the scalar quantity

$$J\,\underline{I}_1 \cdot \underline{I}_2 \qquad (20)$$

where J is the coupling constant in cycles per second. In fact in the above case the value of J may be determined by simply evaluating the separation of two adjacent peaks in either the proton or deuteron set. J has been shown to be 43.5 cps between H and D in HD.[15]

In a similar fashion the fine structure of the ethanol spectrum may be explained.[16] The three methyl protons may be arranged in eight possible ways, with resultant spin components along H_o corresponding to 3/2, 1/2, - 1/2 or - 3/2 (fig. 2, p. 14). The methylene proton may see one of the possible arrangements, all of which are equally probable. Hence we expect the methylene proton

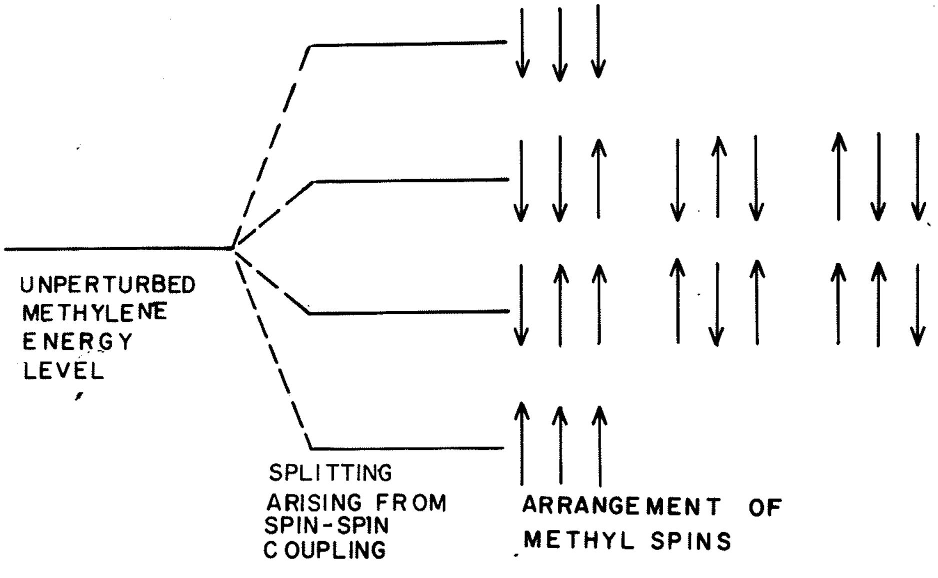

UNPERTURBED METHYLENE ENERGY LEVEL
SPLITTING ARISING FROM SPIN-SPIN COUPLING
ARRANGEMENT OF METHYL SPINS

Figure 2: The splitting of the signal from the methylene group protons in ethanol by spin-spin interaction with the protons of the methyl group.

signal to be composed of 4 lines whose relative intensities are in the ratio of 1: 3: 3: 1. The intensities, in fact, are nearly in this proportion. Similarly the methylene protons may arrange themselves in four ways, two of which are equivalent. The spin arrangements 1, 0, -1 respectively increase the field seen by the methyl group, have no effect, or decrease the field (fig. 3, p. 15). Hence, for a collection of ethanol molecules there will be three equally spaced transition energies for the methyl protons. Since the probabilities of existence of each of the four spin arrangements are equal, the intensities of the three transitions will be 1: 2: 1. This splitting will not be

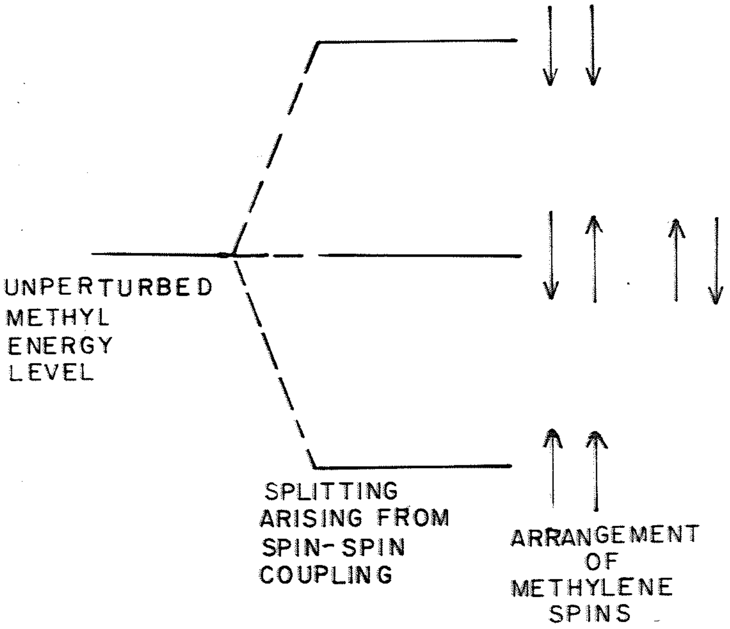

UNPERTURBED METHYL ENERGY LEVEL
SPLITTING ARISING FROM SPIN-SPIN COUPLING
ARRANGEMENT OF METHYLENE SPINS

Figure 3: The splitting of the signal from the methyl group protons in ethanol by spin-spin interaction with the protons of the methylene group.

observable if the nuclei responsible for it do not spend a certain time in a given arrangement. The minimum time required is the reciprocal of the separation in cycles per second of the multiplet components. If this time is shorter, an average effect is recorded and it appears as if no coupling were present.

Coupling occurs across one, two or three bonds in singly bonded systems. Widely separated nuclei are not expected to couple since there is little chance of electron exchange between the two groups. Coupling across four to six bonds has been observed in conjugated systems; however, the coupling constants usually decrease as the number of intermediate bonds is increased.

This has been a description of first order coupling of nuclear moments. Actually, very often more lines than are predicted by this simple treatment are observed. Such spectra can be accounted for by the exact solution of the Schroedinger equation for the system.[17]

THE CHEMICAL SHIFT

CHAPTER IV

THE CHEMICAL SHIFT

The magnetic field experienced by a nucleus in a physical system is not the external magnetic field. The largest single factor modifying the magnetic environment of a nucleus in a completely rigid system is the presence of other magnetic nuclei which may alter the field by as much as $-\frac{2\mu}{r^3}$ where μ is the magnetic moment of the neighbouring nucleus and r the separation.[1] These fields become effective only in solids; in liquids and gases where a random motion of the molecules exists, this magnetic effect averages to zero.

Physical and organic chemists are interested mainly in effects on chemical shifts which may be listed under

1) Intramolecular effects
2) Intermolecular effects

The first concerns itself with the electronic structure of the molecule and the manner in which variations in this structure affect the chemical shifts of a particular nucleus; the latter studies the effect of variations in the magnetic and electric properties of the medium in which the molecule is found.

A) Intramolecular Effects

1) The Screening Constant and Chemical Shift Parameter

If it were possible to measure the resonant fields at a fixed frequency of both an isolated nucleus and of the nucleus in an isolated molecule, one would find that the latter was considerably larger. In a static field a diamagnetic moment is induced in the molecule as a result of a circular movement of the electrons about an axis along the field. (The impressed field may in general induce both diamagnetic and paramagnetic moments; the latter, however, are less important). Because of this induced moment isolated nuclei "resonate" at lower fields.

The screening constant parameter has been defined by

$$H = H_o\ (1 - \sigma) \qquad (21)$$

where σ is the screening constant, H_o the field seen by the molecule and H the field seen by the nucleus. σ is then a measure of the magnetic shielding produced by the electrons. σ is a nondimensional constant independent of the applied field but dependent on the environment of a specific nucleus. Values of σ vary from 10^{-5} for protons to 10^{-2} for bismuth nuclei. For theoretical purposes σ is separated into a number of contributions which may be of either sign, that is, shielding and deshielding contributions.

We may readily show, using the above relationship, that the separation of the signals from two nuclei will be directly proportional to the field seen by the molecule and to the difference between the screening constants of the two nuclei. Because chemical shifts are proportional to the applied field strength, it has been found useful to express line positions in terms of the chemical shift parameter δ which is independent of the field.

$$\delta = \frac{(H_s - H_r)}{H_r} \qquad (22)$$

where H_r is the resonant field of a suitable reference and H_s is the resonant field of the nucleus. δ is then related to the shielding constants of the reference and sample. Spectra are generally calibrated in cycles per second, using a side band technique; δ is then related to the peak separations in cps by

$$\delta = \frac{\Delta 10^6}{f} \qquad (23)$$

(in units of parts per million) where Δ is the separation in cps and f the resonant frequency.

2) Theory of Electronic Shielding

The theory necessary for an understanding of chemical shifts was developed as part of the theory of diamagnetic susceptibilities. The extension to NMR was initiated in the early 1950's. Ramsey[18] developed an expression for the magnetic field at a nucleus resulting from the application of an external magnetic field to a polyatomic molecule having no resultant electronic angular momentum in the absence of the field. Electronic motion set up by the field was assumed to make a dual contribution to the shielding:

1) diamagnetic and

2) paramagnetic contribution

These contributions were increased to three and clarified by Pople[19] in 1957:

a) local diamagnetic circulation in each atom.

b) paramagnetic currents set up corresponding to a mixing of ground and excited electronic states by a magnetic field. These cannot occur in an atom in the S state or a linear molecule in a Σ state if the field is along the axis.

c) Interatomic circulation of electrons along closed circuits around a molecular path. These are of prime importance in aromatic molecules.

3) Effect of a Magnetic Field on an Electron

In the presence of a uniform magnetic field the electron will move in a circular path whose axis is along the applied field. The angular velocity of the electron is given by

$$w = \frac{e\ H}{2\ mc} \tag{24}$$

where the symbols have their usual meaning.

Associated with this circulation will be a current given by

$$i = \frac{e^2 H}{4 \pi mc} \tag{25}$$

This electric current produces a magnetic field which is proportional to the applied field and directed against it, i.e. a diamagnetic moment is introduced.

If the electron is not free to move in a completely circular path, a paramagnetic contribution will also result. The relative sizes of the diamagnetic and paramagnetic contributions will depend on the amount of asymmetry in the path that the electron follows.

After a rigorous quantum mechanical treatment, Pople[20] was able to arrive at a value of the diamagnetic currents resulting from the spherically symmetrical nature of the electron density of an atom. This circulation was shown to result in a positive shielding on a proton (high field shift from a bare proton) and the only way to reduce this shielding is by a removal of charge density from the nucleus. Hence one might expect that proton resonant fields in the series

$-CH_2 I$, $-CH_2Br$,$-CH_2Cl$ and $-CH_2F$

should decrease from left to right. Assuming the diamagnetic contribution to be predominant, the removal of charge with increasing electronegativity should cause low field shifts. Dailey and Shoolery[21] obtained the expected trend of internal chemical shifts with increasing electronegativity in the series $CH_3 - CH_2X$

4) Circulations About Neighbouring Sites

Although for most nuclei the magnitude of the shift is determined by local diamagnetic currents the electron density about a proton is so small that circulations in other parts of the molecule make significant contributions to the overall proton shift. However, only paramagnetic terms on neighbouring sites contribute to the shielding of a nucleus. If an electron not directly associated with the proton can move in a circular path no matter what its orientation in a magnetic field, the induced moment will be independent of the orientation of the molecule. If the relative orientations of the nucleus and the electron vary in a random fashion, the average field at the nucleus due to this induced moment is zero. If the electron can move in a circular path only in certain orientations with respect to the field--anisotropy in the diamagnetism--the average effect over all orientations has a finite value and hence contributes to the shielding of the nucleus.

Paramagnetic terms must be considered when one attempts to interpret the shifts of aldehydic and acetylenic protons. To explain the low field shift of -CHO on the basis of reduced diamagnetic circulation one must conclude that the electron density about a proton has been reduced by $\frac{1}{2}$ by the presence of the oxygen atom.[22] Similarly, considering only diamagnetic currents, one might expect some relationship between shift and acidity of the proton in ethane, ethylene and acetylene. However, none is found; the acetylenic protons resonate at a field lower than that of ethane but higher than ethylenic protons. (This is true in general for saturated, ethylenic and acetylenic protons). On the basis of acidity, one should expect the acetylenic proton signal at the lowest field. These anomolous shifts are explained by paramagnetic circulations associated with the neighbouring carbon - carbon triple bond or carbon-oxygen double bond.

Pople[20] treats the acetylene molecule to some extent. Since the molecule is linear there is no paramagnetic polarization due to the component of the field along the molecular axis. The electrons are able to circulate freely within the axially symmetrical π orbitals. A field perpendicular to the molecular axis induces a paramagnetic moment at the carbon atom; however, the lines of flux of this paramagnetic moment are, at the protons, opposite to the direction of the applied field. The net effect is a shielding of the protons. McConnell[23] derived a relation between the contribution to the nuclear magnetic screening of a proton and the anisotropy in the diamagnetism of an axially symmetric group of electrons. The difference in susceptibilities in the axial and transverse directions is a measure of this anisotropy. Using his relation, it is easily shown that the presence of anisotropy may result in shielding or deshielding of a neighbouring nucleus. The acetylenic proton is found in the region of positive contribution to the shielding.

In an analogous fashion, the unusually low field resonance of aldehydic protons is explained. In this instance the proton is located in the deshielding, or negative, region about the anisotropic C=O bond.

5) Interatomic Circulations

Certain diamagnetic crystals have a normal susceptibility in a certain plane but an unusually large susceptibility in a direction perpendicular to this plane, i.e. they have a pronounced diamagnetic anisotropy. Aromatic crystals show this effect. Values of the anisotropy of benzene and other aromatic molecules were calculated,[24] on the assumption that the π electrons are free to move from carbon atom to adjoining carbon atom. Under the influence of a magnetic field perpendicular to the plane, the mobile π electrons circulate with an angular frequency, given by (24), giving rise to a current.[25]

$$i = \frac{3e^2H}{2\pi mc} . \qquad (26)$$

The direction of flow is such that the magnetic field set up inside the ring is parallel to H_0 and opposed to it. The lines of flux outside the ring are along the field and thus give rise to a negative contri-

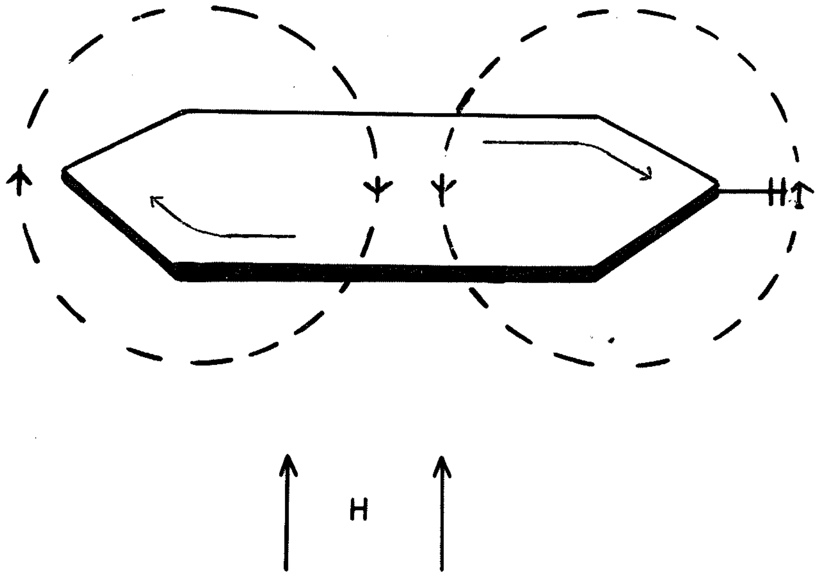


Figure 4: Aromatic ring current and associated magnetic lines of flux.

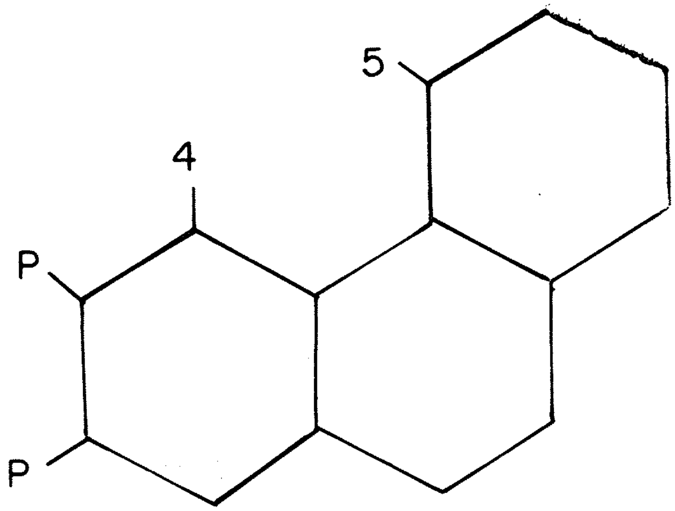


Figure 5: A condensed ring system.

bution to the screening constant of aromatic protons (fig. 4, p. 25). This ring current effect results in a low field shift[26] of 7.37 ppm for benzene protons (7% in $CDCl_3$) from tetramethylsilane, whereas the protons in cyclohexane (where no ring current is possible) are found only 1.43 ppm to low field from TMS.[27]

An estimate was made of the ring current effect by Pople,[28] assuming the moment induced in the ring may be replaced by a point dipole. The theoretical difference in proton shifts of benzene and ethylene was given by

$$\delta\,(\text{benzene}) - \delta\,(\text{ethylene}) = 10^5\,\frac{e^2a^2}{2mc^2(a^2+b^2)} \qquad (27)$$

where a is the radius of the benzene ring and b the C-H bond length in benzene. Using reasonable values for a and b, $\delta\,(B) - \delta\,(E)$ was found to be 1.7 ppm as compared to the experimental value of 1.5 ppm with the benzene protons to low field.

Further investigations[29] on polymethylene benzenes along with predictions based on Pople's model contributed strong support for the ring current effects. Similarly, it has been found that internal protons, 4 and 5, in condensed ring systems (figure 5, p. 25) are found up to 0.5 ppm to low field from the peripheral protons (P).[30] The internal protons are closer to more rings than the peripheral protons and hence suffer an enhanced deshielding due to the ring currents.

B) Intermolecular or Medium Effects

Thus far we have discussed chemical shifts as functions of the properties of the molecule in which the nucleus is found.

However, large shifts arise from the magnetic shielding, or deshielding, of a nucleus due to the medium in which the molecule is found. Reference points for these shifts should be the gaseous phase where medium effects are in most cases negligible. However, experimental difficulties limit the determination of gas phase shifts. Hence shifts for magnetically different nuclei are compared at infinite dilution in an inert solvent.[31]

Medium effects may be classified under two headings:

1) Magnetic effects
   a) bulk susceptibility of the medium
   b) anisotropy in the diamagnetic susceptibility of the medium
2) Electrical effects (van der Waals forces)
   a) orientation effects
   b) induction effects
   c) dispersion effects

1) Magnetic Effects

a) Bulk Susceptibility

In the presence of an external magnetic field, the solvent molecules are diamagnetically polarized. (Certain substances like liquid oxygen and iron are paramagnetic, that is, more permeable to lines of flux than a vacuum; the majority however are diamagnetic, that is, less permeable). A resultant moment is produced in the bulk of the solution given by

$$\underline{M} = X_V \underline{H_0} \qquad (28)$$

where $\underline{M}$ is the induced magnetization vector and X_V the volume susceptibility tensor of the bulk. If X_V is positive, the substance is paramagnetic; if negative, diamagnetic. X_V is anisotropic if its components are different in different directions.[32] This polarization of the bulk produces a magnetic field which contributes to the screening of a nucleus. If the sample is contained in a spherical tube, this contribution is zero; if the sample is contained in a cylindrical tube the contribution from the bulk susceptibility σ_b is given by[33]

$$(\sigma_b) = \frac{2}{3} X_V \qquad (29)$$

The use of external references necessitates a bulk susceptibility correction to chemical shift measurements. If the solution and reference are contained in cylindrical tubes, the correction is given by

$$\frac{2}{3} \pi X_V \qquad (30)$$

No correction is required when an internal reference is used since the susceptibilities of sample and reference are the same,[34] equal to the susceptibility of the solution.

Pascal[35] first realized that susceptibilities were constitutive properties. He arrived at a set of atomic contributions to the molar diamagnetic susceptibility by correlating existing experimental data. These contributions, called Pascal's constants, may be used to determine susceptibilities for substances with unknown X_m (molar susceptibilities). Reference 7 lists the various methods of determining susceptibilities of liquids, solutions, and crystals.

An NMR technique[36] has recently been employed to determine magnetic susceptibilities. A microtechnique[37,38] for measuring the paramagnetic susceptibilities of compounds in solution has been described.

b) Anisotropy in the Susceptibility

Anisotropy in the susceptibility of the solvent molecules may result in large shifts to either high or low field. For example, a high field shift of 56.8 cycles at 60 megacycles has been observed[39] for the proton resonance of CH_3CN in benzene solution with respect to the resonant field in the inert solvent neopentane. Buckingham et al[33] found that the proton resonance of methane (corrected for differences in bulk susceptibility) was shifted to low field by 34 cps in CS_2 and to high field by 16.1 cps in nitrobenzene. These shifts may readily be attributed to anisotropy in shape and diamagnetic susceptibility.

i) Rod-Shaped Solvent Molecules

The effects of anisotropy, as an intramolecular effect, has been discussed; anisotropy in the solvent molecules is treated, as an intermolecular effect, in an analogous fashion. However, we must approach the problem by postulating a preferred orientation of solute and solvent molecules, which may be brought about by complex formation, dipolar interaction or other causes.[40] Acetylenic protons were shown to be in a region where the contribution from the anisotropy in the $C \equiv C$ bond to the proton shielding constants was positive. In the preferred orientation of an elongated molecule like CS_2 or C_2H_2, and a solute molecule (assumed to be spherical), we find the solute above rather than along the axis of the rod. A magnetic field perpendicular to the axis induces a paramagnetic moment due to the restricted motion of the electrons. Averaging over all possible orientations of this rod in the field, we find that a nucleus will experience a deshielding and hence a low field shift from its resonant field in a completely isotropic medium.

Buckingham, Schaefer and Schneider[33] related the contribution to the screening of a nucleus to $X_{\parallel} - X_{\perp}$, the difference in susceptibilities along and perpendicular to the axis of the rod. This difference is a measure of the anisotropy. They predicted a low field shift of 0.5 ppm for the proton peak of CH_4 in CS_2, relative to CH_4 in n-hexane; the observed shift was 0.42 ppm.

Schneider, Bernstein and Pople[41] were able to show that whereas methane and ethane suffered no association shifts, ethylene at -60°C and acetylene at -82°C suffered shifts to low field of 0.43 and 1.30 ppm respectively. (Association shifts were defined as the difference between chemical shifts of the liquid at a temperature just above the melting point and that of the gas). Weak hydrogen bonding between the proton and the triple bond would tend to keep the associated molecules above the axis of the rod-like acetylene molecule. The low field shift of acetylene in the liquid state could then be ascribed to a contribution from the weak hydrogen bond and the strong anisotropy effect of the triple bond. The low field shift for ethylene is smaller because of the smaller anisotropy of a double bond; in addition we might expect the hydrogen bonding which always causes low field shifts to be of lesser importance in ethylene because of the only faintly acidic nature of ethylenic protons as compared to acetylenic protons which are readily replaced by metals to form acetylides.

ii) Disc-shaped Solvent Molecules

The disc-like molecule is the other extreme in anisotropy in molecular shape. The classical example is the benzene molecule. The benzene ring has large induced magnetic moments when the field is perpendicular to the plane. A solute molecule may approach nearer to this dipole when the molecule is found above rather than in the plane. Since the moment induced is diamagnetic an increase in the shielding of a nucleus in this region is expected. A shift to high field in aromatic solvents is found.

Chloroform forms a weak hydrogen bond with the benzene electrons.[42] The fact that a high field shift of the proton is observed in benzene may be explained only by the presence of the anisotropy in the diamagnetism. If none existed, the average contribution to the screening constant, over all orientations of the complex, would be zero.

A second type of interaction exists between the rod-like acetonitrile molecule and benzene.[39] Acetonitrile has a large dipole moment, the negative end of which is concentrated on the nitrogen atom. Since benzene has a large polarizability in the plane of the ring a dipole is induced as illustrated in figure 6. The interaction will tend to locate the CH_3 group over the ring and hence a high field shift is produced.

In general, the shift produced due to anisotropic effects were found to be very irregular and depended quite strongly on the solvent and solute employed.

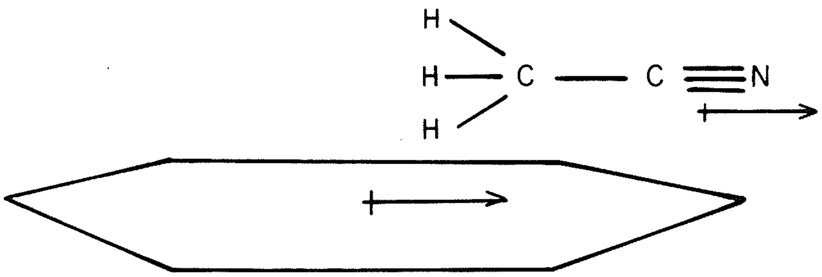


Figure 6: Interaction of CH_3CN with the benzene electrons.

2) Electrical Interactions - van der Waals Forces

The most obvious evidence for intermolecular forces is the existence of the liquid state. There is no interpretation of these forces which suggests they are anything but electrical. The interactions involving polar molecules are easily visualized; however, even molecules having no permanent electric moment may be liquified and hence some interaction must be present.

Intermolecular van der Waals forces are generally attributed to three types of interactions[43]

a) Interaction between permanent dipoles (orientation effect)

b) Interaction between permanent and induced dipoles (induction effect)

c) Interaction arising from mutual polarization of neighbouring atoms or molecules (dispersion effect)

a) Dipole-Dipole Interaction - Hydrogen Bonding

The energy of interaction of two dipoles will depend on the magnitude of the dipole moment[44]. The Boltzman Distribution Law demands that these randomly moving dipoles, when under the influence of each other, be found more often in the position of lowest energy than in that of greatest energy. The position of lowest energy is that in which the dipoles are opposed. Thus on the average there is a net attractive force between two molecules with a dipole moment.

The energy of interaction between two polar molecules is given by

$$U = -\frac{2}{3}\frac{\mu^4}{r^6}\frac{1}{kT} \qquad (31)$$

where μ is the dipole moment of the molecules, r is the separation between centres of the dipoles, k is the Boltzman constant, and T is the absolute temperature.

As the temperature is increased the energy of interaction is decreased. That is, as the temperature is increased, the thermal motion of the molecules is increased. This tends to hinder the orientation of dipoles. As a result their attraction decreases rapidly with temperature rise.

These dipole-dipole interactions are not adequate to explain the phenomenon of hydrogen bonding which occurs most strongly when H is bonded to F, O, N, or Cl. In these instances a better approximation is obtained if we postulate a small positive charge on the proton, which will be strongly attracted to the electron-rich atom. These types of bonds are possible only with hydrogen because of its small size and high density of positive charge when bonded to a strongly electronegative atom.[45]

Thus far the hydrogen bond has been studied mainly by infrared and Raman spectroscopy and dielectric constant techniques.[46] Almost immediately after the chemical shift was observed chemists realized NMR would prove to be an additional tool for H-bond studies. In 1951 hydrogen bonding effects were recorded by a PMR experiment;[11] it was found that the hydroxyl proton signal of ethyl alcohol was distinctly dependent on the temperature. Liddel and Ramsey[47] suggested that hydrogen bonding, known to exist in ethyl alcohol, might explain this dependence. An equilibrium was known to exist between the associated and unassociated molecules but if the correlation time for the life times is small resonance at one frequency should be observed corresponding to the average shielding of the states. The suggested experiment to verify this was the effect of dilution of ethyl alcohol in a solvent like carbon tetrachloride on the chemical shift. Like temperature increase, dilution tends to shift the equilibrium towards the unassociated form. The predictions were shown to be valid. In fact it was found[48] that the degree of association, according to the resonance experiment, of alcohol at its boiling point corresponded to that in a 10% solution in carbon tetrachloride (both dilution and temperature increase send the signal to high field). Cohen and Reid[49] found that at extreme dilution the hydroxyl proton appears at a higher field than do the methyl protons, whereas in pure alcohol it appears to low field. Hence hydrogen bonding accounts for a shift of 2 ppm (a small fraction of this is attributed to dispersion interactions).

In addition to being able to observe hydrogen bonding, Korinek and Schneider[50] showed that relative strengths of hydrogen bonding could be correlated with chemical shifts. The effect of dilution of $CHCl_3$ in a variety of virtually nonassociated solvents on its proton chemical shift was determined. The shift to low field increased in the series propylfluoride, propionitrile, diethyl ether and triethylamine, the same order as expected hydrogen bonding. No absolute values of these bond strengths are known for the above donors. However, Pople, Bernstein and Schneider[51] compare these shifts with other relevant properties of these solvents (ionization potential, lone-pair dipole, and IR data). Reasonable agreement exists between the low field shifts and expected hydrogen bonding power of the members in the above series.

Similarly, Schneider, Bernstein and Pople[41] have correlated degrees of interaction with association shifts of simple hydrides. HF and H_2O suffered the largest association shifts; CH_4 and C_2H_6, the least. Conner and Reid[52] extended the study of concentration dependence of -OH proton shifts to a variety of alcohols. Association shifts and IR data in the series tertiary butyl, n-propyl, methyl and benzyl alcohols were related similarly to the electron attracting power of the R groups. In general association shifts were found to be proportional to IR stretching frequency shifts.

The hydrogen bond shift arises because the magnetic field experienced by the proton is altered by the presence of the donor group. Two general effects must be considered:[41]

1. The donor group behaves like an anisotropic neighbour. This effect leads to a high field shift and is important for hydrogen bonding with aromatic π electrons.
2. Hydrogen bonding is usually interpreted as being primarily electrostatic in nature. The low field shift may be explained if the primary function of the donor atom is to produce a strong electric field in the vicinity of the bond. As the proton is drawn closer to the donor atom its electron density is reduced; in addition to this, the spherical symmetry of the electron cloud about the proton is reduced. Both effects result in low field shifts.

b) The Reaction Field of a Polar Molecule

1) Form of the Reaction Field

The electric field associated with a polar molecule tends to polarize the surrounding medium. This polarization which is proportional to the magnitude of the dipole and depends on the dielectric nature of the medium, gives rise to an electric field at the dipole; because of molecular motion, this reaction field, as it is called, is parallel to the dipole moment.

The effect of this reaction field is to cause a secondary polarization of the dipolar molecule; this secondary polarization depends on the strength of the reaction field (and hence on the dipole moment of the molecule and on the dielectric constant of the medium) and on the polarizability α of the molecule.

The total dipole moment is then given by

$$m = \mu + \alpha R \qquad (32)$$

where μ is the permanent dipole of the isolated molecule and R the reaction field.

Many attempts have been made to evaluate the reaction field of a dipole and the energy of interaction, using approximate models for calculations. The most useful model[53], the Onsager model, represents the molecule by a sphere of a certain radius with a point dipole moment μ at the centre and represents the medium as a continuum of uniform dielectric constant. Basically the method consists of calculating the work done in transferring an isolated polar spherical molecule to a spherical cavity in the continuum.

The reaction field, as calculated by Onsager's model, is given by

$$R = \frac{2(\epsilon - 1)}{2\epsilon + 1} \frac{m}{r^3} \qquad (33)$$

where ϵ is the dielectric constant of the medium, m the total dipole moment of the molecule and r the radius of the sphere. The polarizability of the sphere is given by[54]

$$\alpha \doteq \frac{n^2 - 1}{n^2 + 2} r^3 \qquad (34)$$

where n is the refractive index of the solute for sodium - D light. Hence

$$R = \frac{2(\epsilon - 1)}{2\epsilon + 1} \frac{\mu + \alpha R}{\frac{n^2 + 2}{n^2 - 1}\alpha} \qquad (35)$$

Solving for R and simplifying, we arrive at

$$R = \frac{2(\epsilon - 1)(n^2 - 1)}{3(2\epsilon + n^2)} \frac{\mu}{\alpha} \qquad (36)$$

For most solutes (solid or liquid) n = 1.5. The expression for R then reduces to

$$R = \frac{2.5(\epsilon - 1)}{3(2\epsilon + 2.25)} \frac{\mu}{\alpha} \qquad (37)$$

ii) Nuclear Magnetic Shielding and the Reaction Field

The influence of electric fields on shielding parameters has been studied in some detail by workers in the solvent effects field. Marshall and Pople[55] have shown that the application of an electric field reduces both diamagnetic and paramagnetic contributions to the screening constant of atomic hydrogen, the reduction in both cases being proportional to the square of the magnitude of E. The symmetry of the atom requires the shielding to be unaffected by a reversal of the field.

Buckingham[56] focused attention on the shielding of a proton in an X-H bond. The effect of a field acting along the bond will either increase or decrease the electron density about the proton depending on its direction and thus may either increase or decrease the nuclear magnetic shielding. The lack of symmetry in this direction requires this directional effect. A field perpendicular to the X-H bond serves only to destroy the axial symmetry of the electron density. This destruction of symmetry, spherical or axial, results in all instances in a reduction in shielding. The symmetry, however, in this direction requires that reversal of this perpendicular field should not result in a change in sign of the shielding contribution. Therefore the shielding due to this field is expected to be proportional to the square of the field.

Buckingham was able to derive an expression for the contribution of an electric field to the shielding of a proton in an X-H bond

$$\sigma_E = -2 \times 10^{-12} E \cos \theta - 10^{-18} E^2 \qquad (38)$$

where E is the magnitude of the field and θ the angle between the field and the X-H bond. Inserting the expression (36) for the reaction field of a polarizable dipole into this equation we arrive at

$$\sigma_E = -1.6\times10^{-12}\,\frac{\epsilon - 1}{2\epsilon + 2.25}\,\frac{\mu\cos\theta}{\alpha} - 0.7\times10^{-18}\,\frac{(\epsilon - 1)^2}{(2\epsilon + 2.25)^2}\,\frac{\mu^2}{\alpha^2} \qquad (39)$$

where θ is now the angle between μ and the X-H bond.

One might expect that this expression approximates the contribution to the screening constant of, say, carbon - 13 more accurately than it does of protons. The latter are normally at the surface of molecules exposed to direct contact with surrounding medium and not at the centre of a sphere as required by Onsager's model.

Buckingham's equation predicts that for small fields the shielding contribution is proportional to E. In addition, for small E, one predicts a linear relationship between the chemical shift of a proton and the dielectric function

$$\frac{\epsilon - 1}{2\epsilon + n^2} \qquad (40)$$

of the medium. Furthermore, for a given change in the function a "shift in the chemical shift" of the proton proportional to the value of $(n^2 - 1)\frac{\mu}{\alpha}$ for the solute molecule is expected.

iii) Molecular Shape and the Reaction Field

Very few molecules may be considered spherical or even nearly so. G. Scholte[57] attempted to evaluate the reaction field of a nonpolarizable dipole located at the centre of a nonspherical cavity.

Diehl and Freeman[58] considered a nonspherical (ellipsoidal) cavity and extended the calculations to a polarizable dipole. The value of the reaction field is given by the expression

$$E = \frac{\mu}{abc} \quad 3\xi_a \left[1 + (n^2 - 1)\,\xi_a\right] \frac{\epsilon - 1}{\epsilon + \dfrac{n^2 \xi_a}{1 - \xi_a}} \qquad (41)$$

where μ is the permanent dipole moment of the molecule in the ellipsoidal cavity, a, b, c are the principle axes of the ellipsoid, n is the refractive index of the solute, ϵ is the dielectric constant of the medium and ξ_a is the solute shape factor given by

$$\xi_a = \tfrac{1}{2}\, abc \int \frac{d\lambda}{(a^2 + \lambda)^{3/2}\,(b^2 + \lambda)^{\frac{1}{2}}\,(c^2 + \lambda)^{\frac{1}{2}}} \qquad (42)$$

where λ is a dummy variable of integration. Values of ξ_a have been evaluated by Ross and Sack[59] for molecules of various shapes.

iv) Previous Work on Polar Effects

Several polar solutes have been studied in a wide variety of solvents. Possibly one of the more interesting cases is that of monosubstituted benzenes.[60] When the substituent is a nitro group the protons in positions 3 and 4 on the ring suffer a low field shift from their resonant field in benzene, while those in the 2 position, a high field shift. If the direction of the dipole, and hence direction of the electric field due to the substituent, is reversed (with NH_2 on the ring) high field shifts are expected. The directional effect is clearly observable.

Buckingham et al[33] observed good agreement with theoretical calculations between the displacement of the proton chemical shift of CH_3CN, assumed to be due largely to polar effects, and changes in the dielectric constant of the medium. Diehl and Freeman[58] and Abraham[61] obtained similar results using the shape corrected expression for the reaction field.

c) The Dispersion Effect

The dispersion interactions are the most general of the intermolecular interactions since they are exerted by all types of atoms and molecules, whether polar or not. In actual magnitude they are exceeded by polar interactions; in the absence of polar groups they are the sole contributors to association shifts.

London[62] was the first to give a satisfactory explanation of the origin of the attractive forces. These forces were traced to the coupling of electrical oscillators within neighbouring molecules. A small oscillating electric moment that varies such that its time average is zero induces in its neighbour an opposite but parallel moment and a small attraction called a dispersive force results. (London called these forces dispersive forces since they were thought to be responsible for dispersion of light).

The attractive force will depend on the magnitude of the induced dipole moment and hence on the polarizability of the neighbouring atom or molecules. Thus we might expect that attraction increases with the size of an atom. These forces are expected to lead to an expansion of the electron cloud about a nucleus and to decreased nuclear magnetic shielding. Thus far only negative association shifts have been observed for substances exerting mainly dispersive interactions.

London showed that these forces resulted in an energy expressible as a sum of terms varying inversely as the sixth power of the separation of the interacting moments. Equating London's expression with the classical energy of a polarizable body in an electric field, Bothner-By[40] found the electric field acting on a proton due to these dispersion forces. Marshall and Pople[55] evaluated the contribution to the proton magnetic shielding from an electric field at the molecule. Using this relationship between the field and the shielding contribution Bothner-By obtained a proton shift of 0.1 ppm, of the same order of magnitude observed for proton shifts in nonpolar media.

M. Martin[63] has studied a large number of halogenated ethanes and methanes. It was observed that the PMR shift of $CHCl_3$ from a C_6H_{12} reference suffered a low field displacement when pure chloroform was diluted with $CHBr_3$ and a high field shift when diluted with C_6H_{12}. In the pure state dispersive forces exist between the proton and the chlorine atoms; upon dilution in $CHBr_3$ the interaction between the hydrogen and the more polarizable bromine atom becomes predominant. The dispersive forces are thus increased and a low field shift results. Upon dilution in C_6H_{12} the interaction between hydrogen and chlorine atoms is reduced and replaced by the very weak proton-proton interaction; the high field shift is then expected.

Similarly, dilution effects on the proton shift of CH_2Cl_2 were studied. Dilution in $CHCl_3$ produced no displacement of the signal whereas dilution in $CHBr_3$ resulted in a low field shift from pure CH_2Cl_2. The environment of the methylene protons is changed only slightly in $CHCl_3$; the $CHBr_3$, however, presents a more polarizable medium as dilution increases.

These effects are clearly dispersive and not due to changes in dipole-dipole or dipole-induced dipole interaction. If the latter two predominated we would expect a high field shift of the methylene group upon dilution in brominated hydrocarbons whose dipole moments are smaller than that of the chlorinated hydrocarbon. We might expect the chloroform proton signal to move to high field upon dilution in $CHBr_3$ for similar reasons.

Buckingham et al[33] studied nonpolar interactions using methane gas as a solute in a variety of solvents, polar and nonpolar, aliphatic and aromatic. A measure of molecular interaction in a pure solvent is the heat of vaporization at the boiling point; when the solvent is isotropic and nonpolar, ΔH_V is a measure of the dispersive interactions. A close proportionality between solvent-solvent and solvent-solute molecular interaction was assumed. With this assumption in mind they plotted proton chemical shifts of CH_4, in the various solvents, from the resonance signal of gaseous CH_4 (corrected for susceptibility differences) against the heat of vaporization of the solvent. A linear plot was obtained for solvents expected to exert mainly dispersive forces. Aromatic solvents displayed positive deviations; linear molecules with large anisotropies in shape and diamagnetic susceptibilities displayed excess low field shifts.

PURPOSE OF THIS INVESTIGATION

CHAPTER V

PURPOSE OF THIS INVESTIGATION

The purpose of this investigation was to study the effect of the medium on the nuclear magnetic shielding of a proton. In particular, the effect of the reaction field at a polar molecule on the shielding is considered.

The difficulty involved in this study was the isolation of the contribution to the overall chemical shift attributable to the reaction field. Two similar pairs of compounds were employed for the study--cis and trans-dichloroethylene and cis and trans-dibromoethylene (to be called cis, trans Cl cis Br and trans Br). The trans forms have no dipole moment and hence will not experience a reaction field; the cis forms, however, have a dipole moment and will experience this effect. We might expect that in similar solutions at the same concentration the cis and trans forms experience very similar dispersion interactions with the solvent molecule. Thus by taking differences in chemical shift (δ cis - δ trans in cycles per second) we obtain the proton chemical shift due to the reaction field at the cis forms, provided that an additional difference in interaction does not exist between the two forms. As a first approximation, this is expected to be true.

Both Buckingham's treatment, and Diehl and Freeman's solute-shape refinement will be tested.

EXPERIMENTAL

CHAPTER VI

EXPERIMENTAL

A) Apparatus

All measurements of the proton chemical shift were made at approximately 23°C using a Varian High Resolution Spectrometer with a fixed frequency of 60 megacycles. Chemical shifts from suitable internal references using the convenient side band technique were made with the Hewlett-Packard audio oscillator and electronic counter. Samples were contained in identical glass sample tubes of 4 mm inner diameter and 5 mm outer diameter. Results are the average of 10 runs; the standard deviation was about 0.1 cycles per second and never larger than 0.2 cycles per second.

B) Solutions

Since only solute-solvent interactions were of interest, solute-solute interactions had to be minimized. The solute concentration was in all cases 5 ± 0.5 mole percent, approximating infinite dilution where no solute-solute interactions exist.

A wide variety of solvents was chosen so that all the medium effects could be observed. A series of dioxane-water solutions of known dielectric constant were prepared ranging from pure dioxane to 15 weight percent water. This series seemed particularly appropriate for the study of the reaction field effect.

An internal reference was used for all measurements in order that no susceptibility corrections had to be applied. Chloroform was used though considered a poor internal reference because its proton chemical shift is affected strongly by small changes in the solvent properties. However, only the difference in chemical shifts of cis and trans forms, $\Delta\delta$ was of any significance. By taking differences, one removes all solvent effects on the chloroform. Cyclohexane, which like chloroform shows only a single peak, is considered a more desirable reference. Absolute shifts measured from cyclohexane in a series of solvents have more significance since this molecule is affected to a lesser degree by solvent changes. Tetramethylsilane was used when the cyclohexane signal was obscured by the solvent peaks. The concentration of the reference was 2% in all solutions.

RESULTS

CHAPTER VII

RESULTS

TABLE I

CHEMICAL SHIFTS (CPS) OF CIS AND TRANS DICHLOROETHYLENE (INTERNAL REFERENCE, CHLOROFORM)

	Solvent	Chemical Shift of cisCl	Chemical Shift of transCl	Separation of cis and trans
1.	n-Pentane	51.9	52.7	-0.8
2.	Cyclohexane	51.1	52.5	-1.4
3.	n-Hexane	51.7	52.4	-0.7
4.	n-Octane	51.6	52.7	-1.1
5.	Acetone	74.2	79.1	-4.9
6.	Acetonitrile	58.8	-	-
7.	Ethyl Acetate	69.4	73.9	-4.5
8.	Ethyl Glycol	70.9	76.4	-5.5
9.	Formic Acid	57.7	62.9	-5.2
10.	p-Dioxane	65.2	66.7	-1.5
11.	Isopropanol	80.3	87.3	-7.0
12.	n-Butanol	75.5	82.5	-7.0
13.	Diethylamine	116.5	118.1	-1.6
14.	Chloroform	50.1	54.1	-4.0
15.	Carbon Tetrachloride	50.6	53.9	-3.3
16.	Dibromomethane	50.3	55.3	-5.0
17.	Dibromochloromethane	49.2	-	-
18.	Bromochloromethane	51.0	56.9	-5.9
19.	Diiodomethane	53.3	58.4	-5.1
20.	Benzene	38.4	31.8	6.8

Table I (cont'd.)

	Solvent	Chemical Shift of cisCl	Chemical Shift of transCl	Separation of cis and trans
21.	Toluene	33.9	29.5	4.4
22.	1,1,2,2,-Tetrachloroethane	50.3	54.4	-4.1
23.	1,1,2,2,-Tetrabromoethane	48.8	54.2	-5.4
24.	Ethyl Ether	74.7	77.1	-2.4
25.	Carbon Disulfide	50.4	54.5	-4.1

TABLE II

CHEMICAL SHIFTS (CPS) OF CIS AND TRANS DICHLOROETHYLENE (INTERNAL REFERENCE CYCLOHEXANE AND TETRAMETHYLSILANE (*)

	Solvent	Chemical Shift of cisCl	Chemical Shift of transCl	Separation of cis and trans
1.	Carbon Disulfide	-296.8	-292.5	-4.35
2.	Cyclohexane	-288.2	-287.1	-1.3
3.	Ethylene Bromide	-304.9	-301.4	-3.5
4.	1-Bromo, 2-Chloroethane	-304.5	-300.4	-3.7
5.	1,1,2,2,-Tetrachloroethane	-301.3	-297.3	-3.9
6.	1,1,2,2,-Tetrabromoethane	-307.3	-302.1	-5.3
7.	Dibromomethane	-305.8	-300.8	-5.0
8.	Bromochloromethane	-303.8		
9.	Chloroform	-299.7	-295.7	-4.1
10.	Tetrachloroethylene	-294.7	-293.5	-1.6
11.	Carbon Tetrachloride	-298.9	-294.5	-3.3
12.	Benzene	-249.8	-257.8	8.0
13.	Ethnyl Benzene	-277.4	-278.6	1.2
14.	Bromobenzene	-276.2	-275.5	-0.7
15.	Toluene	-251.0	-255.6	4.6
16.	Aniline	-266.1	-270.2	4.2
17.	O-Toluidine	-263.2	-266.8	3.5
18.	Benzonitrile	-308.4	-297.2	-11.3
19.	Mesitylene			0.0
20.	O-Dibromobenzene	-290.8	-286.6	-4.2
21.	Phenyl Isocyanate	-280.8	-276.5	-4.4

Table II (cont'd.)

Solvent	Chemical Shift of cisCl	Chemical Shift of transCl	Separation of cis and trans
22. Pyridine	-319.7	-315.0	-4.7
23. O-Xylene	-251.7	-254.2	2.4
24. Hexachloro 1,3-Butadiene			-2.2
25. Ethyl Ether			-2.4*
26. n-Pentane			-0.8*
27. Ethyl Acetate			-4.4*
28. n-Hexane			-0.9*
29. n-Octane			-1.1*
30. Acetonitrile			-3.7*
31. Dioxane	-309.7	-308.2	-1.4
32. Dioxane-water #1	-310.7	-308.9	-1.9
33. Dioxane-water #2	-310.9	-308.9	-2.0
34. Dioxane-water #3	-311.4	-309.0	-2.4
35. Dioxane-water #4			
36. Dioxane-water #5	-312.5	-309.5	-3.1
37. Dioxane-water #6	-312.9	-309.4	-3.3
38. Dioxane-water #7	-313.3	-309.7	-3.6

TABLE III

CHEMICAL SHIFT OF CIS AND TRANS DIBROMOETHYLENE (INTERNAL REFERENCE CYCLOHEXANE AND TETRAMETHYLSILANE (*)

	Solvent	Chemical Shift of cisBr	Chemical Shift of transBr	Separation of cis and trans
1.	Carbon Disulfide	-333.4	-310.4	-23.0
2.	Cyclohexane	-324.9	-304.4	-20.5
3.	Dibromomethane	-341.3	-317.3	-24.0
4.	Methyl Iodide	-342.5	-318.5	-24.0
5.	Hexachloro 1,3,-butadiene	-331.6	-310.3	-21.3
6.	Tetrachloroethylene	-331.6	-310.8	-20.7
7.	Chloroform	-335.2	-312.5	-22.7
8.	Ethyl Acetate			-22.4*
9.	n-Pentane			-20.1*
10.	n-Hexane			-20.4*
11.	n-Octane			-20.6*
12.	Benzene	-286.4	-273.6	-12.7
13.	Toluene	-286.9	-271.0	-15.9
14.	Bromobenzene	-312.4	-291.9	-20.6
15.	Ethynl Benzene	-313.4	-294.9	-18.4
16.	Phenyl Cyanide	-342.2	-312.4	-30.8
17.	Mesitylene	-287.4	-265.4	-22.1
18.	Phenyl Isocyanate	-314.6	-289.7	-25.9
19.	Chlorobenzene	-309.9	-289.5	-20.4
20.	O-Xylene	-285.4	-267.4	-17.9
21.	Dioxane	-344.1	-325.3	-19.1
22.	Dioxane-water #1	-345.6	-325.9	-19.9

Table III (cont'd.)

Solvent	Chemical Shift of cisBr	Chemical Shift of transBr	Separation of cis and trans
23. Dioxane-water #2	-345.9	-326.0	-20.1
24. Dioxane-water #3	-346.3	-326.2	-20.1
25. Dioxane-water #4	-346.9	-326.6	-20.3
26. Dioxane-water #5	-347.4	-326.8	-20.6
27. Dioxane-water #6	-347.7	-326.7	-21.0
28. Dioxane-water #7	-347.9	-326.8	-21.1

TABLE IV

PHYSICAL CONSTANTS

	cisCl	transCl	cisBr	transBr
Molecular weight[64]	96.95	96.95	185.87	185.87
Refractive index[64]	1.4519	1.4490	1.528	
Density[64]	1.291	1.265	2.271	
Dielectric constant[65]	9.2	2.14	7.1	2.9
Dipole moment[66]	1.89 D	0	1.35 D	0
Shape factor[67]	0.34		0.32	
C-H bond length[68]	1.08 Å		1.08 Å	
C-X bond length[68]	1.67 ± .02 Å		1.91 ± .01 Å	
C=C bond length[68]	1.38 Å		1.34 Å	
XCC bond angle[68]	123.5 ± 1°		121 ± 3°	
HCC bond angle[68]	120°		120°	

TABLE V

DIELECTRIC FUNCTIONS

$A = \dfrac{\epsilon - 1}{2\epsilon + 2.10}$ (in Buckingham's expression for dichloroethylene)

$B = \dfrac{\epsilon - 1}{2\epsilon + 2.37}$ (in Buckingham's expression for dibromoethylene)

$C = \dfrac{\epsilon - 1}{\epsilon + 1.09}$ (in Diehl and Freeman's expression for dichloroethylene)

$D = \dfrac{\epsilon - 1}{\epsilon + 1.12}$ (in Diehl and Freeman's expression for dibromoethylene)

$E = \dfrac{\epsilon - 1}{3\epsilon + 2}$ (in Buckingham's quadrupolar reaction field expression)

	Solvent	ϵ	A	B	C	D	E
1.	Cyclohexane	2.019	.166	.159			
2.	Acetone	20.91	.453	.451			
3.	Chloroform	4.76	.323	.316			
4.	Carbon disulfide	2.63	.221	.214			
5.	1,2-Dibromoethane	4.79	.324	.317			
6.	1,2-Bromochloroethane	7.08	.374	.368			
7.	1,1,2,2,-Tetrachloroethane	8.2	.389	.384			
8.	1,1,2,2-Tetrabromoethane	7	.373	.367			
9.	Dibromomethane	7.41	.379	.373			
10.	Tetrachloroethylene	2.30	.194	.187			
11.	Carbon Tetrachloride	2.23	.188	.180			
12.	n-Hexane	1.89	.151	.148			
13.	n-Pentane	1.84	.145	.139			

Table V (cont'd.)

Solvent	ϵ	A	B	C	D	E
14. n-Octane	1.95	.158	.152			
15. Ethyl Acetate	6.05	.356	.349			
16. Acetonitrile	37.05	.473	.471			
17. Dioxane	2.21	.186	.178	.367	.364	.140
18. Dioxane-water #1	2.82	.235	.227	.466	.462	.174
19. Dioxane-water #2	3.18	.258	.250	.511	.507	.189
20. Dioxane-water #3	3.76	.287	.279	.569	.566	.208
21. Dioxane-water #4	5.00	.331	.323	.657	.654	.235
22. Dioxane-water #5	5.83	.351	.344	.698	.696	.248
23. Dioxane-water #6	7.24	.376	.370	.749	.747	.263
24. Dioxane-water #7	9.56	.403	.398	.804	.802	.279
25. Formic Acid	57.	.482	.481			
26. Ethyl Ether	4.28	.308	.300			
27. Hexachloro 1,3-butadiene	2.55	.215	.207			
28. O-Xylene	2.56	.216	.208			
29. Ethnyl benzene	2.98	.246	.238			
30. Bromobenzene	5.43	.342	.335			
31. Toluene	2.38	.201	.194			
32. Benzene	2.28	.192	.194			
33. Aniline	6.84	.370	.364			
34. O-Toluidine	6.3	.361	.354			
35. Benzonitrile	25.4	.461	.458			
36. m-Chloroaniline	13	.427	.422			
37. O-Dibromobenzene	7.35	.378	.372			
38. Pyridine	12.3	.423	.418			
39. Phenyl Isocyanate	8.8	.395	.391			
40. Mesitylene	2.27	.191	.184			

Table V (cont'd.)

Solvent	ϵ	A	B	C	D	E
41. Chlorobenzene	5.6	.346	.339			
42. Ethylene glycol	37.42	.473	.472			
43. Methyl iodide	6.91	.371	.365			
44. n-Butyl alcohol	17.38	.444	.441			
45. Isopropanol	18.59	.448	.445			
46. Diethyl amine	3.6	.280	.271			

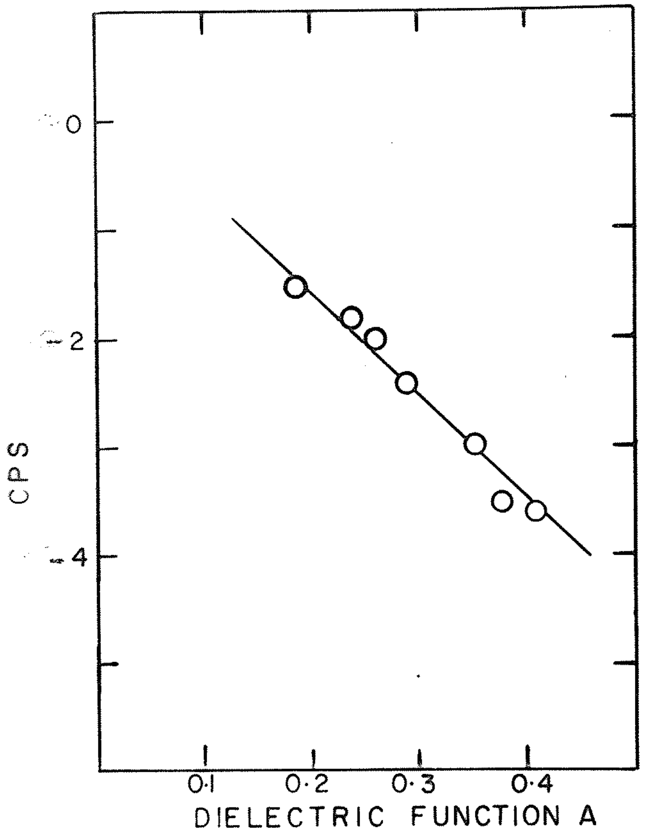
The dielectric constants of the dioxane-water solutions are found in reference (69); the remaining values were obtained from reference (65). The values are those for approximately 23°C.

Figure 7:

Difference in the chemical shift between cis and trans dichloroethylene versus the dielectric function A of several dioxane-water solutions.

Figure 8:

Chemical shift of cis dichloroethylene from cyclohexane versus the dielectric function A of several dioxane-water solutions.


0
-2
-4
CPS
0·1
0·2
0·3
0·4
DIELECTRIC FUNCTION A

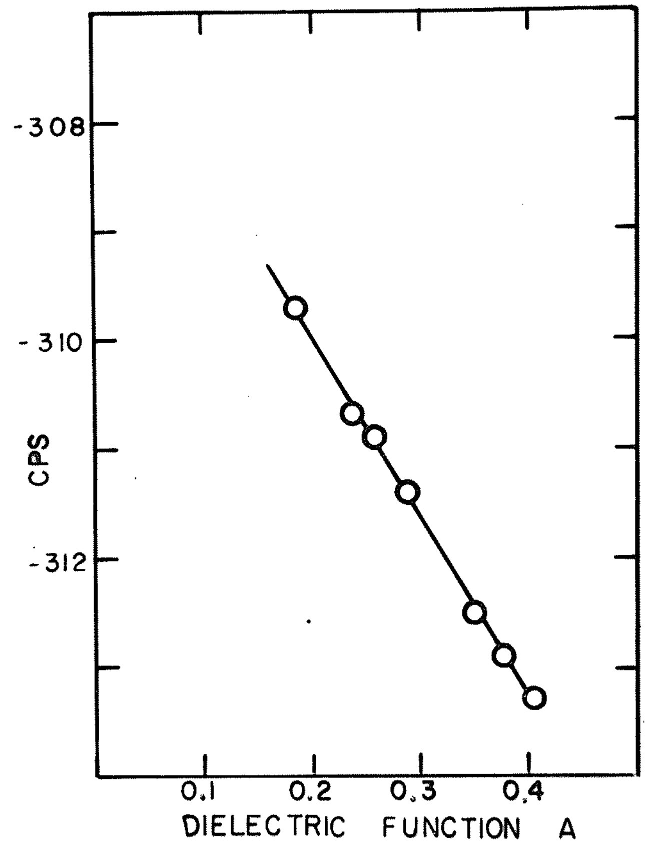
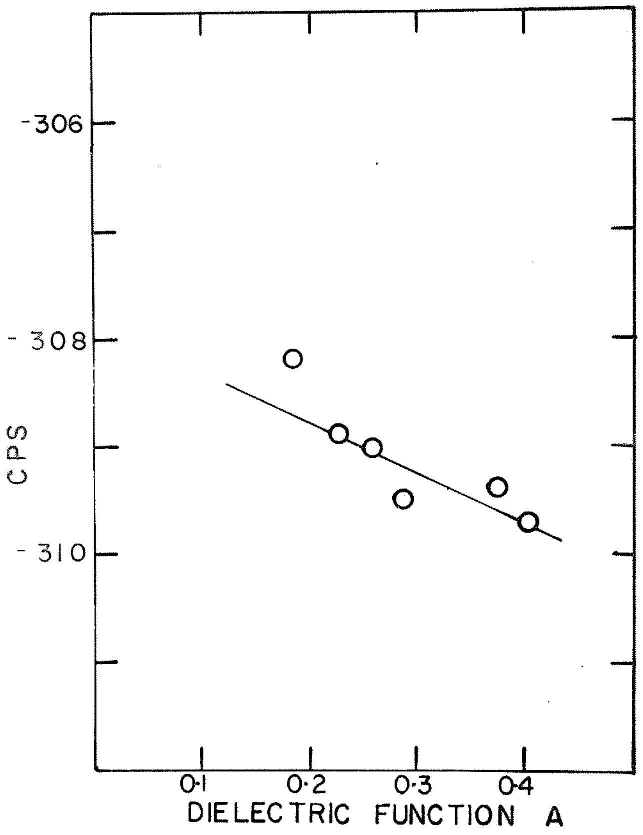

-308
-310
CPS
-312
0.1
0.2
0.3
0.4
DIELECTRIC FUNCTION A

Figure 9

Chemical shift of trans dichloroethylene from cyclohexane versus the dielectric function A of several dioxane-water solutions.

Figure 10

Difference in chemical shift between cis and trans dibromoethylene versus the dielectric function B of several dioxane-water solutions.


-306
-308
-310
CPS
0·1
0·2
0·3
0·4
DIELECTRIC FUNCTION A

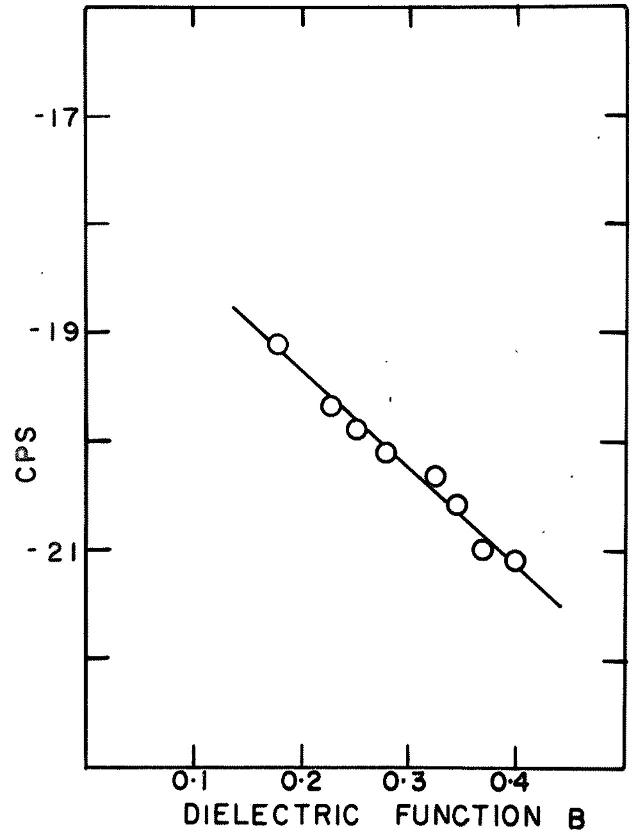
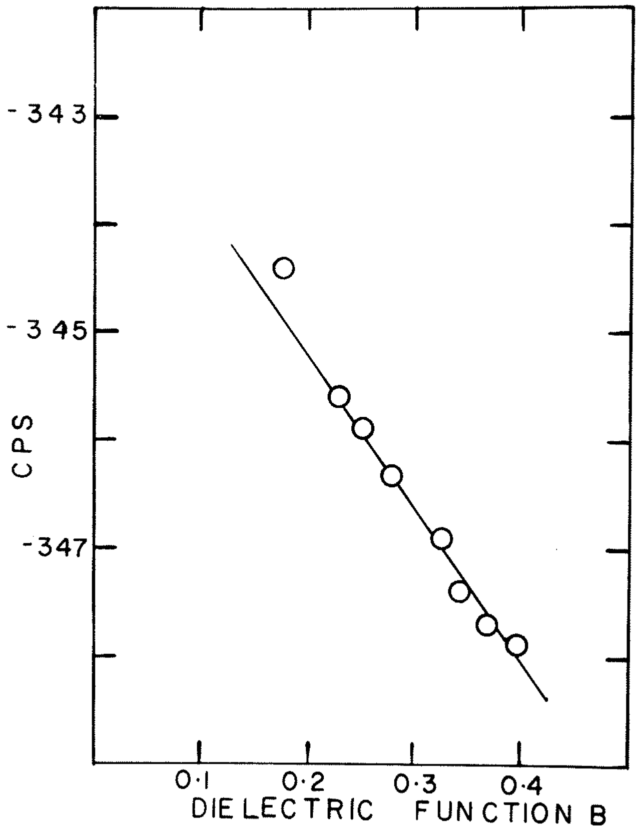

-17
-19
-21
CPS
0·1
0·2
0·3
0·4
DIELECTRIC FUNCTION B

Figure 11

Chemical shift of cis dibromoethylene from cyclohexane versus the dielectric function B of several dioxane-water solutions.

Figure 12

Chemical shift of trans dibromoethylene from cyclohexane versus the dielectric function B of several dioxane-water solutions.


-343
-345
-347
CPS
0·1
0·2
0·3
0·4
DIELECTRIC FUNCTION B

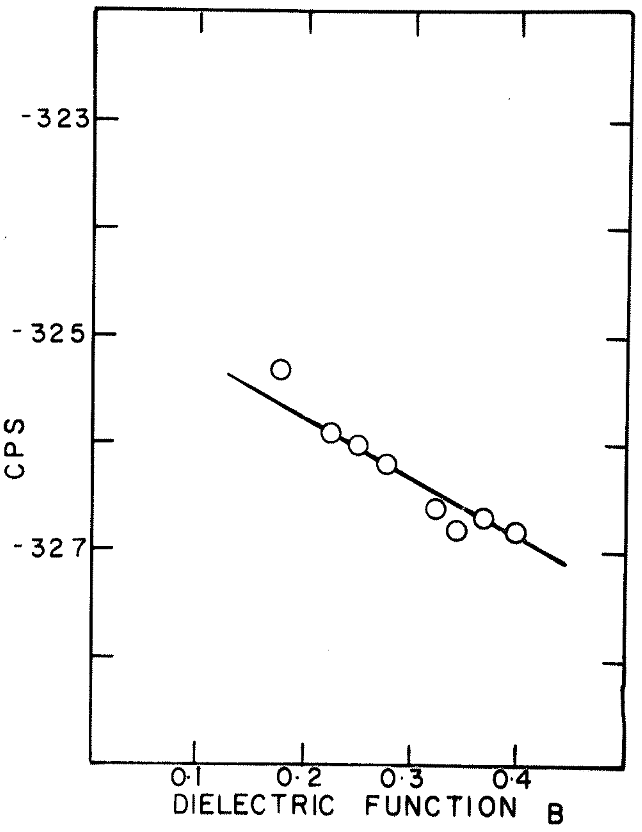
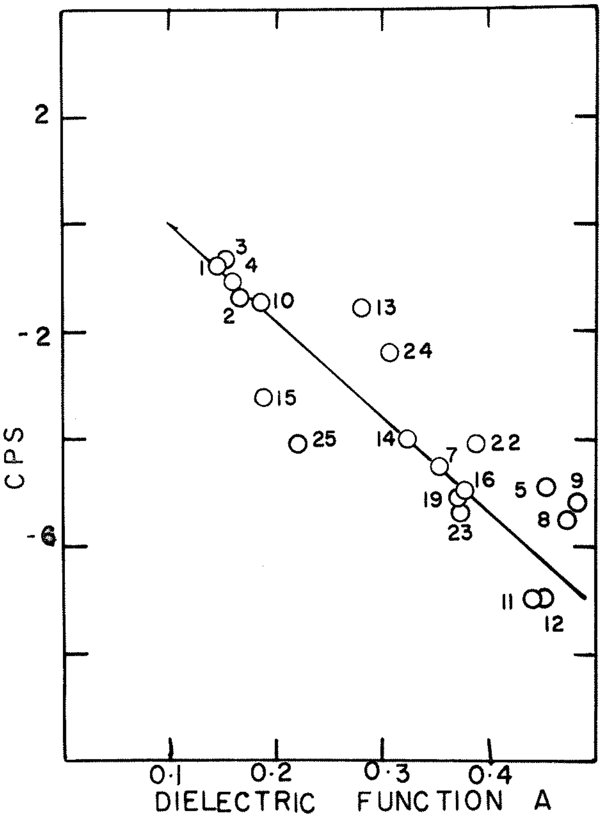

-323
-325
-327
CPS
0·1
0·2
0·3
0·4
DIELECTRIC FUNCTION B

Figure 13

Difference in chemical shift from chloroform between cis and trans dichloroethylene versus the dielectric function A of various aliphatic solvents.

Figure 14

Difference in chemical shift from cyclohexane between cis and trans dichloroethylene versus the dielectric function A of various aliphatic solvents.


2
-2
-6
CPS
0·1
0·2
0·3
0·4
DIELECTRIC FUNCTION A
1
3
4
2
10
13
24
15
25
14
7
22
16
5
9
19
23
8
11
12

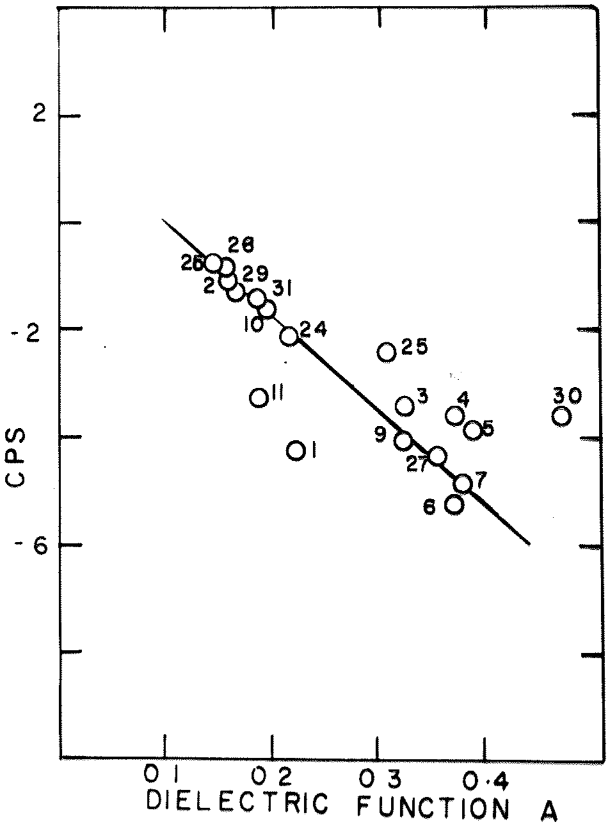
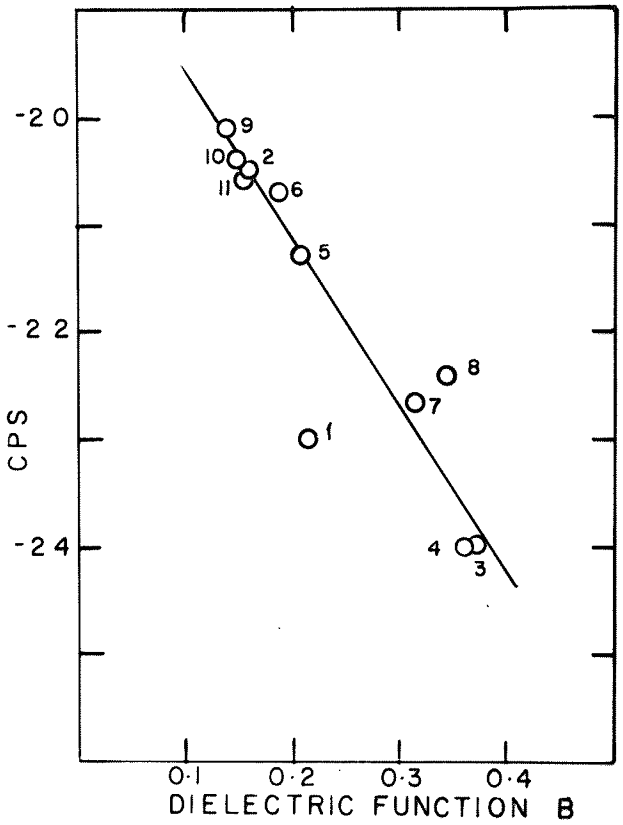

2
-2
-6
CPS
0 1
0 2
0 3
0·4
DIELECTRIC FUNCTION A
28
26
29
2
31
10
24
25
11
3
4
5
30
9
1
27
7
6

Figure 15

Difference in chemical shift from cyclohexane between cis and trans dibromoethylene versus the dielectric function B of various aliphatic solvents.

Figure 16

Difference in chemical shift between cis and trans dichloroethylene versus the dielectric function C of several dioxane-water solutions.


-20
-22
-24
CPS
9
10
2
11
6
5
8
7
1
4
3
0·1
0·2
0·3
0·4
DIELECTRIC FUNCTION B

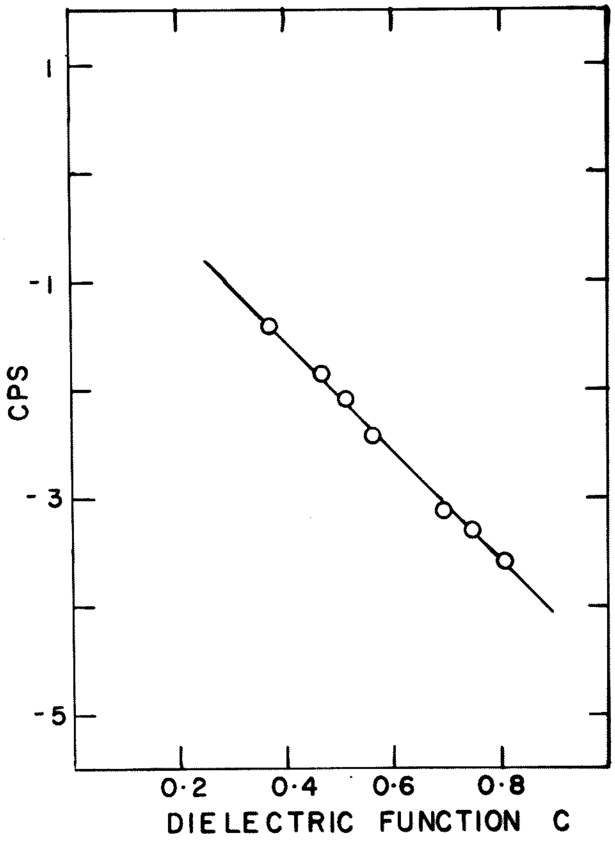
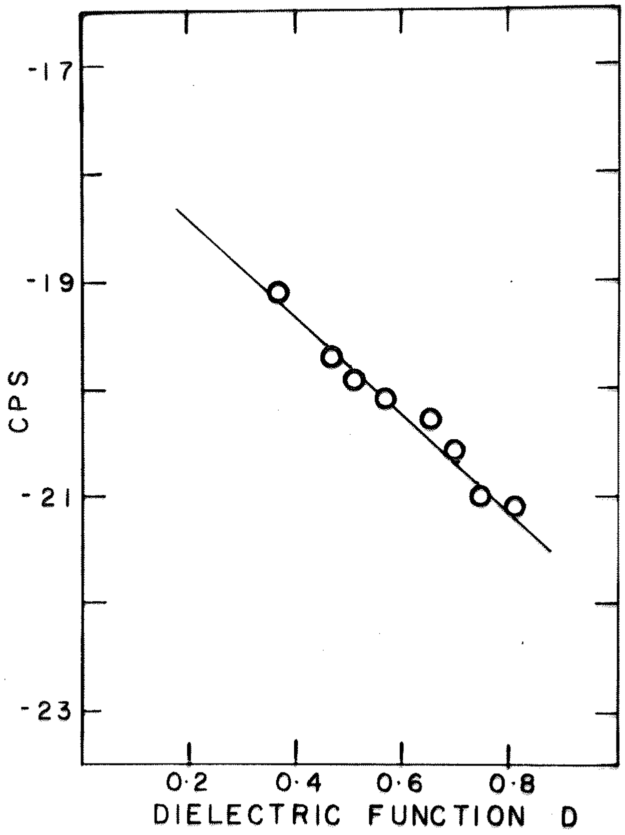

1
-1
-3
-5
CPS
0·2
0·4
0·6
0·8
DIELECTRIC FUNCTION C

Figure 17

Difference in chemical shift between cis and trans dibromoethylene versus the dielectric function D of several dioxane-water solutions.

Figure 18

Difference in chemical shift between cis and trans dichloroethylene versus the dielectric function A of various aromatic solvents.


-17
-19
-21
-23
CPS
0·2
0·4
0·6
0·8
DIELECTRIC FUNCTION D

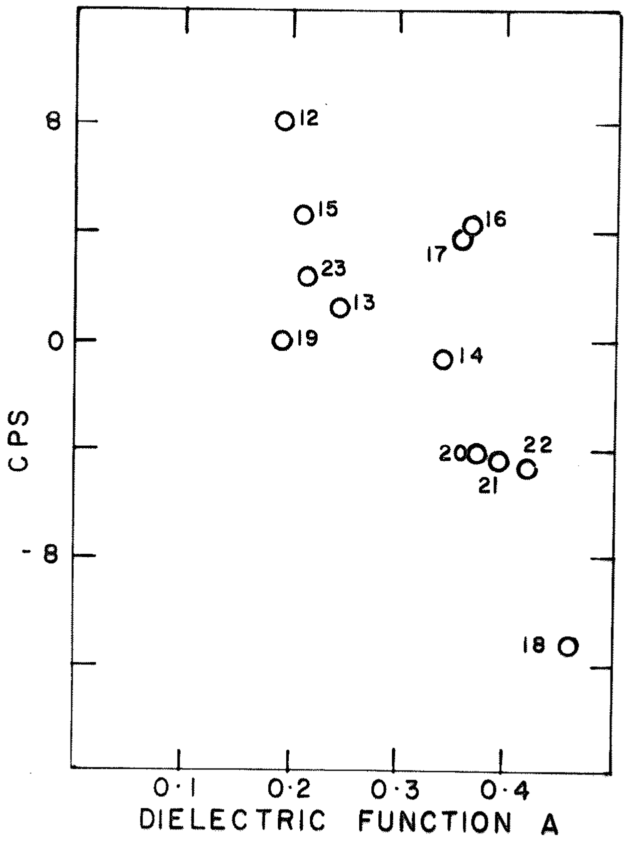
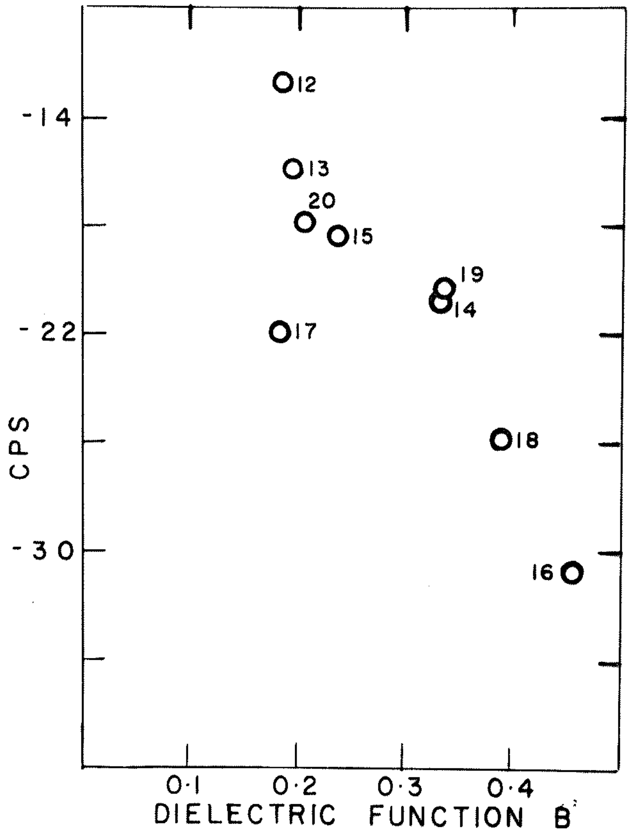

8
0
-8
CPS
12
15
23
13
19
16
17
14
20
21
22
18
0·1
0·2
0·3
0·4
DIELECTRIC FUNCTION A

Figure 19

Difference in chemical shift between cis and trans dibromoethylene versus the dielectric function B of various aromatic solvents.

Figure 20

Chemical shift from cyclohexane of trans dichloroethylene versus dielectric function E of several dioxane-water solutions.


-14
-22
-30
CPS
12
13
20
15
19
14
17
18
16
0·1
0·2
0·3
0·4
DIELECTRIC FUNCTION B

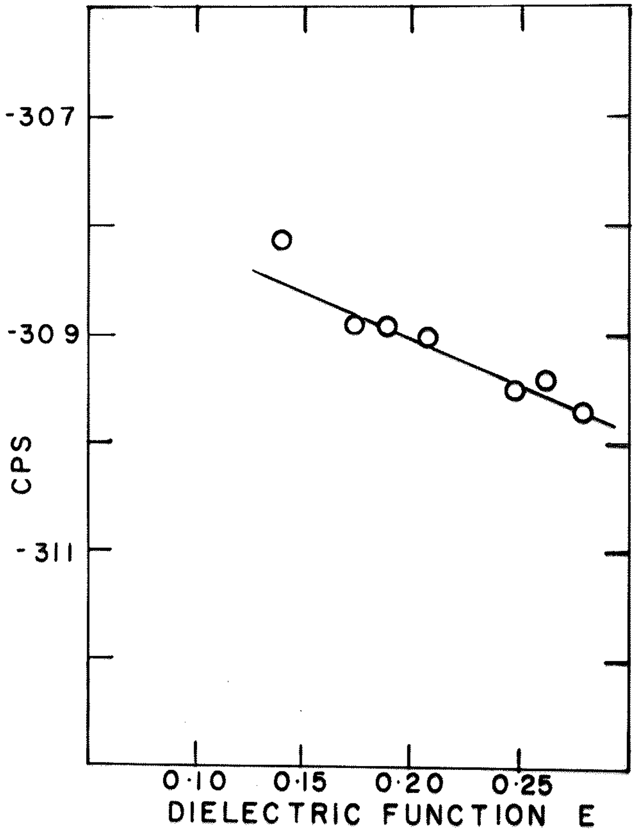
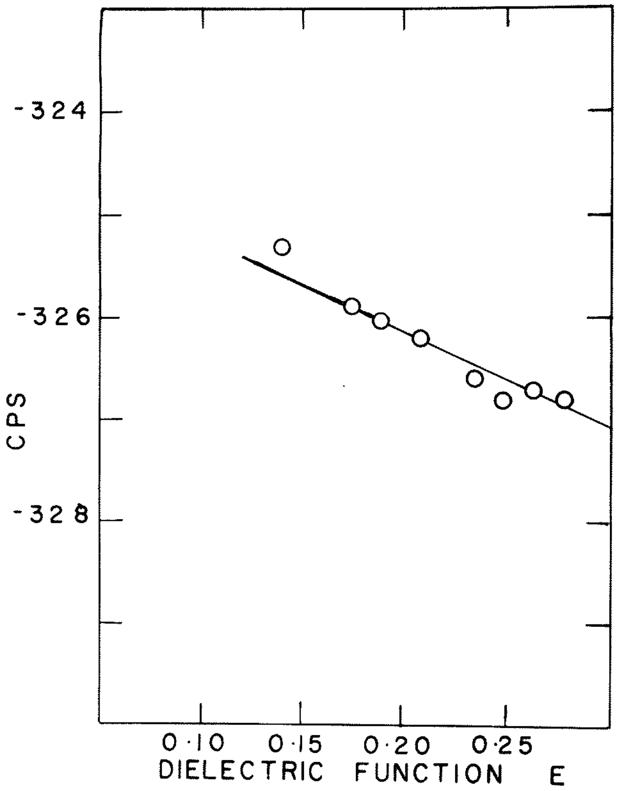

-307
-309
-311
CPS
0·10
0·15
0·20
0·25
DIELECTRIC FUNCTION E

Figure 21

Chemical shift from cyclohexane of trans dibromoethylene versus the dielectric function E of several dioxane-water solutions.

Figure 22

Difference in chemical shift between cis and trans dichloroethylene versus the molar volume of the aromatic solvent.


-324
-326
-328
CPS
0·10
0·15
0·20
0·25
DIELECTRIC FUNCTION E

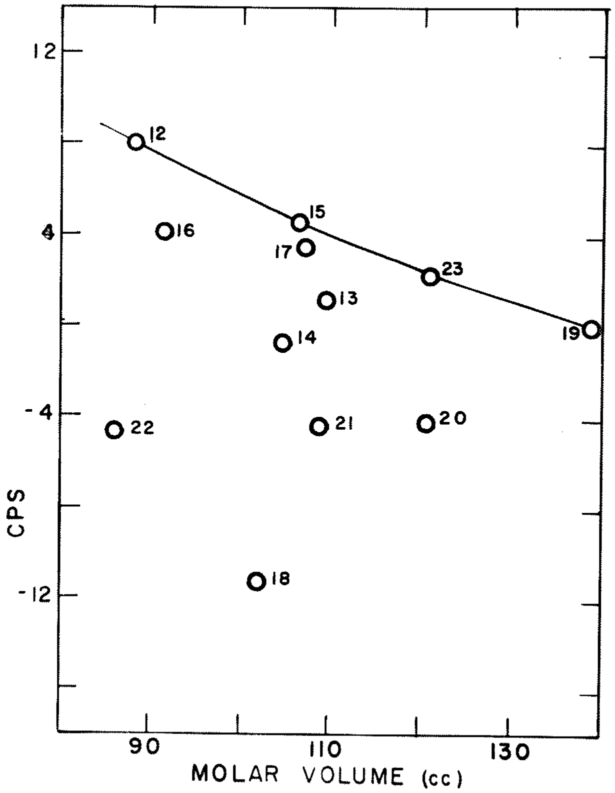
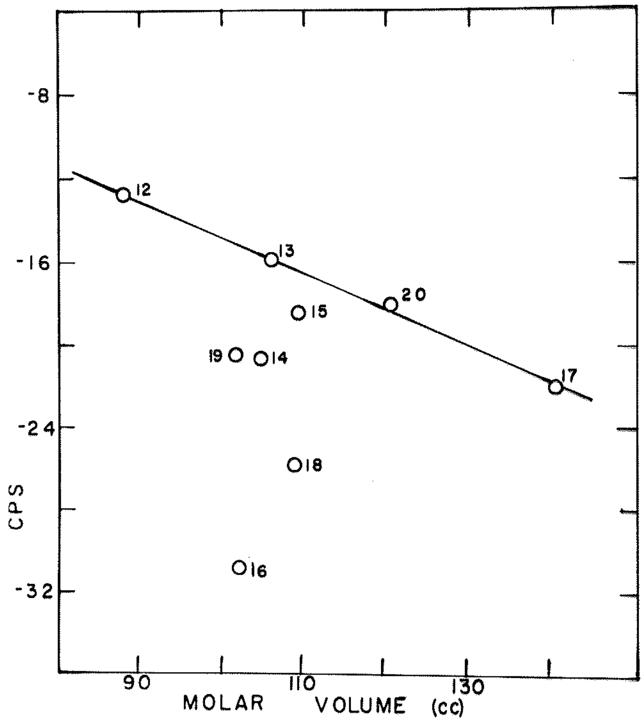

12
4
-4
-12
CPS
90
110
130
MOLAR VOLUME (cc)
12
15
16
17
13
23
14
19
22
21
20
18

Figure 23

Difference in chemical shift between cis and trans dibromoethylene versus the molar volume of the aromatic solvent.

Figure 24

Difference in chemical shift, corrected for solvent-volume effects, between cis and trans dichloroethylene versus the dielectric function A of various aromatic solvents.


-8
-16
-24
-32
CPS
90
110
130
MOLAR VOLUME (cc)
12
13
20
15
19
14
17
18
16

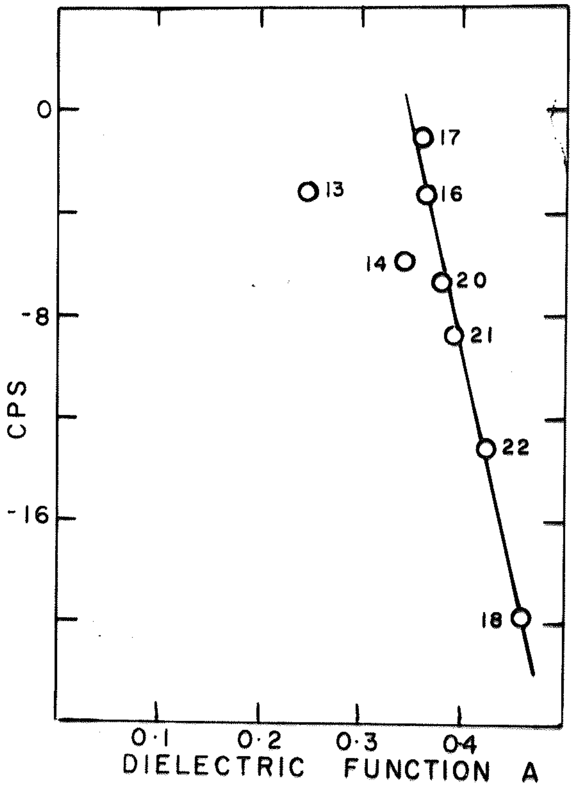
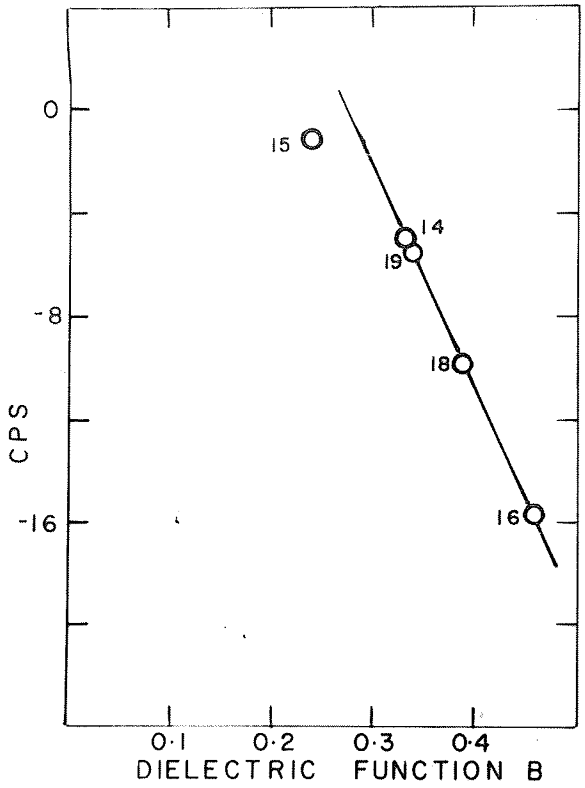

0
-8
-16
CPS
0·1
0·2
0·3
0·4
DIELECTRIC FUNCTION A
17
13
16
14
20
21
22
18

Figure 25

Difference in chemical shifts, corrected for solvent-volume effects between cis and trans dibromoethylene versus dielectric function B of various aromatic solvents.

Figure 26

Chemical shift from cyclohexane of cis dichloroethylene in various aromatic solvents versus the Hammett para σ constant of the ring substituent.


0
-8
-16
CPS
15
14
19
18
16
0·1
0·2
0·3
0·4
DIELECTRIC FUNCTION B

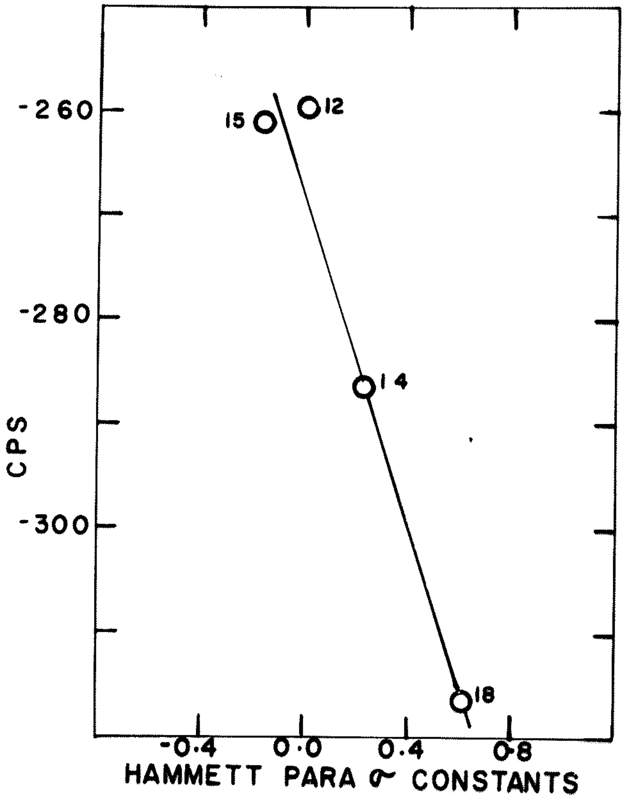
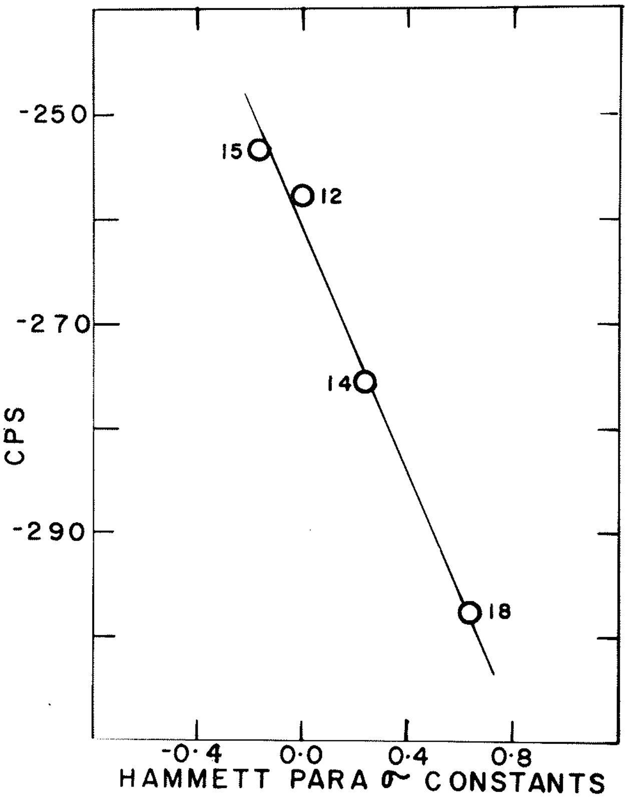

-260
-280
-300
CPS
15
12
14
18
-0·4
0·0
0·4
0·8
HAMMETT PARA σ CONSTANTS

Figure 27

Chemical shift from cyclohexane of trans dichloroethylene in various aromatic solvents versus the Hammett para σ-constant of the ring substituent.

Figure 28

Chemical shift from cyclohexane of cis dibromoethylene in various aromatic solvents versus the Hammett para σ-constant of the ring substituent.


-250
-270
-290
CPS
15
12
14
18
-0·4
0·0
0·4
0·8
HAMMETT PARA σ CONSTANTS

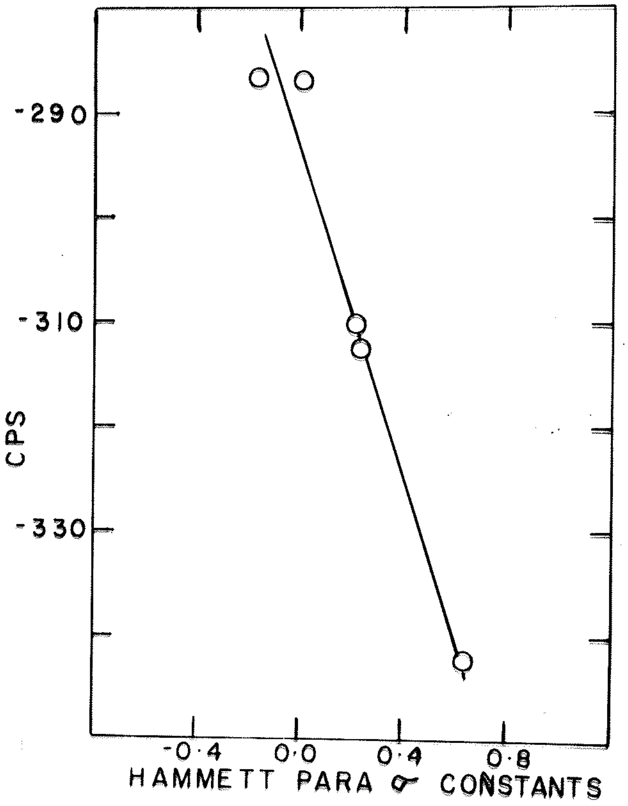
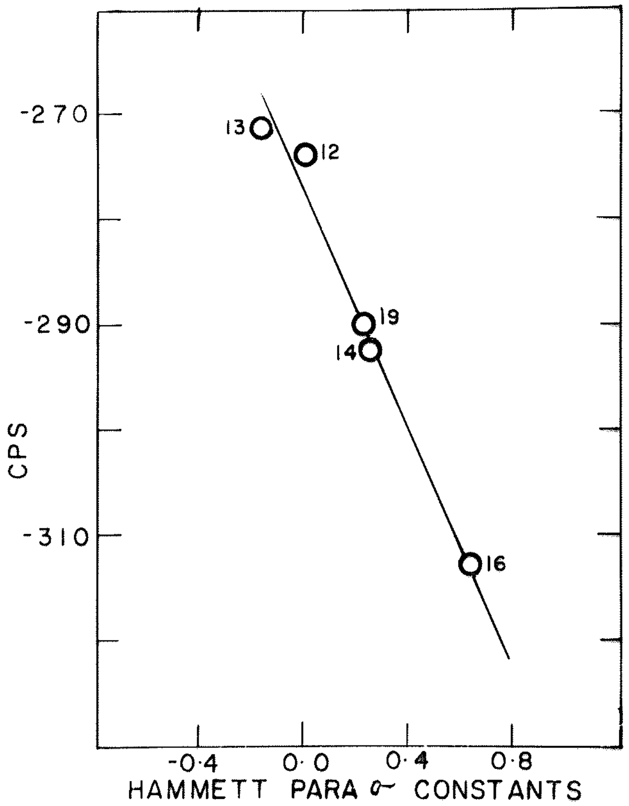

-290
-310
-330
CPS
-0·4
0·0
0·4
0·8
HAMMETT PARA σ CONSTANTS

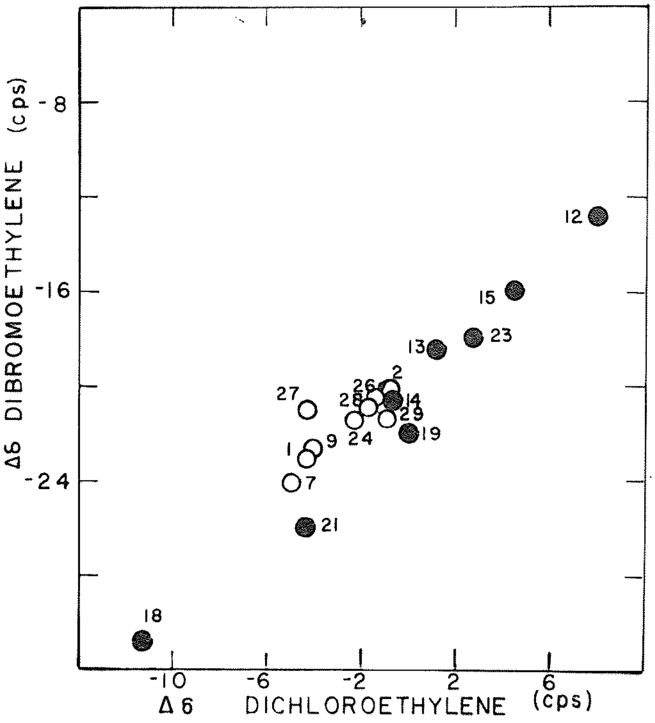
Figure 29

Chemical shift from cyclohexane of trans dibromoethylene in various aromatic solvents versus the para σ constants of the ring substituent.

Figure 30

Difference in chemical shift between cis and trans dibromoethylene versus the difference in chemical shift between cis and trans dichloroethylene.


-270
-290
-310
CPS
-0·4
0·0
0·4
0·8
HAMMETT PARA σ CONSTANTS
13
12
19
14
16


Δδ DIBROMOETHYLENE (cps)
-8
-16
-24
-10
-6
-2
2
6
Δδ DICHLOROETHYLENE (cps)
12
15
23
13
2
26
28
14
29
27
24
9
19
1
7
21
18

DISCUSSION

CHAPTER VIII

DISCUSSION

A) Intramolecular Effects

Before proceeding to a discussion of medium effects whose determination we are primarily concerned with, a short discussion of intramolecular effects is in order.

From tables II and III we observe that in all the solvents studied the chemical shift from the internal reference cyclohexane or tetramethylsilane of cisCl is smaller than that of cisBr; that is, the protons in cisCl are more strongly shielded than those in cisBr and hence resonate at higher field. In a similar fashion the protons in transCl resonate to high field from transBr. If the predominant effect were the induction by the substituent X (Cl or Br), we should expect the reverse to be true.

It seems, therefore, that it is not the electron withdrawing power of X but the anisotropy in the diamagnetic susceptibility of the C-X bond that largely determines the resonant field of the protons. The magnetic environment of the ethylenic protons is similar to that of an aldehydic proton which experiences a strong deshielding due to the large anisotropy in the carbonyl double bond.

Using McConnell's treatment[23] we also expect a deshielding of the ethylenic protons due to the anisotropy of the C-X bond. However, since the C-Br bond is less ionic its anisotropy is larger. In addition to this the low field shift due to dispersion interactions is expected to be larger in the brominated rather than the chlorinated form. The combination of dispersive and anisotropic effects overcomes the larger inductive power of the chlorine atom.

B) Reaction Field Effects

Assuming that the reaction field at the ethylenic protons is not large,[71] that is, E^2 terms may be neglected in Buckingham's equation, we expect that the "shift in the chemical shift" of cisCl and cisBr and therefore $\Delta\delta$ should vary linearly with an appropriate function of the dielectric constant of the solvent. Given (p. 38)

$$R = \frac{2(\epsilon - 1)\,(n^2 - 1)}{3(2\epsilon + n^2)}\,\frac{\mu}{\alpha} \qquad (36)$$

$n = 1.45$ for cisCl

$$R = \frac{2(\epsilon - 1)\,(2.10 - 1)}{3(2\epsilon + 2.10)}\,\frac{\mu}{\alpha} = \frac{.73(\epsilon - 1)}{2\epsilon + 2.1}\,\frac{\mu}{\alpha} \qquad (43)$$

and $n = 1.54$ for cisBr

$$R = .91\,\frac{\epsilon - 1}{2\epsilon + 2.37}\,\frac{\mu}{\alpha} \qquad (44)$$

The polarizability α was calculated using an empirical equation[72] relating the polarizability of a pure liquid to its dielectric constant and its dipole moment. This equation is a slight modification of Debye's equation[73] which must, however, be used solely for gases and vapors. This empirical equation has been found to give fairly accurate results with a variety of liquids.

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3}\,N\left\{\alpha + \frac{\mu^2}{3kt + CN\mu^2}\right\} \qquad (45)$$

where ϵ is the dielectric constant of the liquid, N is the number of molecules in one cm^3, α is the polarizability, μ is the dipole moment of the molecule, k is the Boltzman constant per molecule, T is the absolute temperature and C is a constant. Except for the term $CN\mu^2$, this equation is identical to Debye's equation.

In most instances C may be replaced by $\frac{4\pi}{3}$. Isolating the polarizability we arrive at

$$\alpha = \frac{3}{4\pi N} \frac{\epsilon - 1}{\epsilon + 2} - \frac{\mu^2}{3kT + \frac{4\pi N}{3} \mu^2} \qquad (46)$$

To evaluate the polarizabilities, appropriate values from table IV are substituted.

Therefore

$$\alpha \text{ (cisCl)} = 0.71 \times 10^{-23} \text{ cm}^3 \qquad (47)$$

$$\alpha \text{ (cisBr)} = 1.17 \times 10^{-23} \text{ cm}^3 \qquad (48)$$

It is realized that these values may not be the best possible, mainly because the values of μ for cisCl and cisBr were not obtained in identical environments. (The former value is a gaseous dipole moment whereas the latter is that in a benzene environment;[66] μ values are found to vary considerably with the surroundings of the polar molecule).

Now

$$\frac{\mu}{\alpha} \text{ (cisCl)} = \frac{1.89 \times 10^{-18}}{0.71 \times 10^{-23}} = 2.7 \times 10^{5} \frac{\text{esu}}{\text{cm}^2} \qquad (49)$$

$$\frac{\mu}{\alpha} \text{ (cisBr)} = \frac{1.35 \times 10^{-18}}{1.17 \times 10^{-23}} = 1.2 \times 10 \frac{\text{esu}}{\text{cm}^2} \qquad (50)$$

Substituting these values into the reaction field, we arrive at

$$R = 1.97 \times 10^{5} \frac{\epsilon - 1}{2\epsilon + 2.1} \qquad (51)$$

$$= -0.341 \times 10^{-6} \frac{\epsilon - 1}{2\epsilon + 2.1} \quad \text{for} \quad (\text{Cl}) \qquad (52)$$

and

$$R = 1.08 \times 10^{5} \frac{\epsilon - 1}{2\epsilon + 2.3} \qquad (53)$$

$$= -0.187 \times 10^{-6} \frac{\epsilon - 1}{2\epsilon + 2.37} \quad \text{for} \ (\text{Br}) \qquad (54)$$

The theoretical slopes of $\Delta\delta$ versus the dielectric functions are therefore

-0.341 ppm (-20 cps) for the chloro and

-0.187 ppm (-11 cps) for the bromo.

1) Dioxane-Water Solutions

Measured slopes were found to be -9.5 cps for $\Delta\delta$ Cl and -8.9 cps for $\Delta\delta$ Br as compared with theoretical slopes of -20 cps and -11 cps respectively (figure 7, figure 10). Although there is reasonable agreement for the bromo, the experimental chloro slope is only 50% of that given by Buckingham's reaction field expression. However, many approximations have been made in arriving at these expressions. The coefficient of the first order electric field term, -2×10^{-12}, is reliable to only one significant figure.[74] The uncertainty, therefore, in the theoretical slope may well be 50%. We must also remember that the dipole moment of a molecule depends quite strongly on the nature of the medium.[75] Both dioxane and water are strong hydrogen bond forming solvents which should reduce the effective dipole moment of the solute, and hence the reaction field at the ethylenic protons. These two factors may well account for the discrepancies.

Because of the approximations involved (considering the medium to be a continuum, the dipole to be a point dipole, the proton to be at the centre of a spherical cavity, etc.), more significance should be placed on the relative slopes and less on the absolute. We might state that the mere fact that experimental and theoretical slopes are of the same order is evidence for the validity of Buckingham's equation. In addition the linearity of plots seems to indicate that the assumption about the size of the E effect was reasonable.

According to the expression for R (36), the slopes should be proportional to $(n^2-1)\frac{\mu}{\alpha}$. The theoretical ratio, cisCl to cisBr, is 1.8 as compared to the experimental ratio of 1.1.

We expect Buckingham's equation to be a poor approximation for protons which are generally at the surface of a molecule. Upon closer examination, one concludes that, assuming Buckingham's equation is accurate and does hold for protons, the net dipole moment of the two polar molecules is an inappropriate value to substitute into the reaction field expression. The ethylenic protons are in the immediate vicinity of a bond dipole due to the C-Cl or C-Br bond, which does not act in the same direction as the resultant μ, and a larger distance from a second, equal but differently oriented, dipole.

Some weighted average of both magnitude and orientation, with respect to the C-H bond, of the two bond dipoles seems more appropriate for evaluation of R. However, this value is beyond determination and an additional approximation does not seem in order.

Evidence for the above is the fact that δ of both transCl and transBr showed pronounced variation with the dielectric constant of the solution (figure 9, p. 58; figure 12, p. 59). These ethylenic protons experience a low field shift with increasing ϵ because they experience a reaction field; from the point of view of the ethylenic protons the net dipole moment of transCl and transBr is not zero, and the actual moment seen by these protons does not act perpendicular to the double bond as it does in the polar pair of molecules.

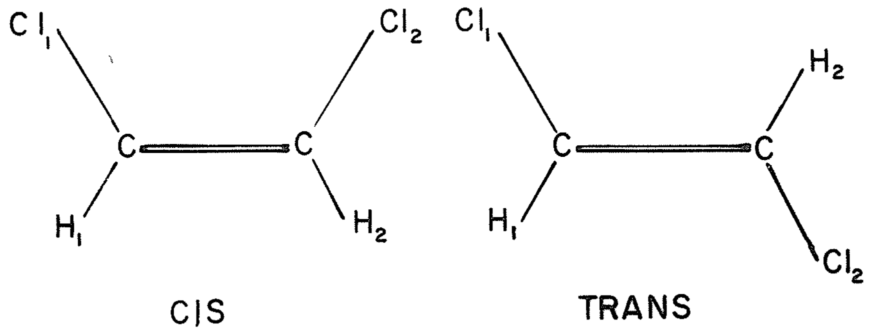


Figure 31: Cis and trans dichloroethylene.

Consider cisCl and transCl (figure 31, p. 74). As far as H_1 is concerned, the only difference between the two forms is the arrangement of the H_2- C_2 - Cl_2 group. We can rightly assume that the reaction field at $H_{(1)}$ due to the bond dipole in $C_{(1)}$—$Cl_{(1)}$ is approximately the same in both cis and trans form. Therefore, the difference should be determined not by the total dipole moment of the cis form, but by the orientation, relative to a C-H bond, of a C-Cl bond dipole at the opposite end of the molecule.

The field produced by a dipole decreases as the third power of separation, and the effect on the shielding of a proton increases as the cosine of the angle between the dipole and the X-H bond. Therefore, we might expect respective slopes of chemical shift of cisCl and of transCl versus the dielectric function to be proportional to $\cos \phi/r^3$ where ϕ is the angle between $C_{(1)}$- $H_{(1)}$ and $C_{(2)}$- $Cl_{(2)}$ and r the distance between the midpoints of the two bonds, determined from scale models. This ratio, cisCl to transCl, was found to be 3.1 as compared to the experimental value of 3.6; for cisBr and transBr the theoretical ratio was again 3.1 as compared to 2.6 experimentally.

When calculations are made of the electric field at a certain distance from a dipole, the assumption is made that this distance is large compared to the separation of the two poles, that is, the dipole is considered to be a point dipole. This assumption is not valid for our solutes when the two distances are almost identical. We must conclude that local effects describe qualitatively the situation more reasonably than a net dipole effect, though the latter, by virtue of several approximations, may be formulated, as has been done by Buckingham.

2) Quadrupolar Moments

Buckingham[56] considers electric field effects in non-polar molecules in terms of a quadrupole moment. TransCl and transBr have no net dipole moment but have a quadrupole moment by virtue of the two equal but opposed bond dipoles. Whereas the potential of a charge near a dipole varies as the reciprocal of the third power of the separation, the potential of the charge near a quadrupole varies as the reciprocal of the fifth power of separation. Thus we might expect quadrupolar effects to be much weaker than dipolar effects.

The reaction field gradient R^1 for a model similar to Onsager's is given by[76]

$$R^1 = \frac{6(\epsilon - 1)}{3\epsilon + 2} \frac{\theta}{r^5} \tag{55}$$

where θ is the molecular quadrupole moment; for a molecule with two opposed dipolar groups of moment μ separated by a distance d,

$$\theta = 2\mu d \tag{56}$$

The bond dipoles may be calculated from the dipole moment of the polar cis form. By simple trigonometry

$$\mu\ (\text{C-Cl}) = \frac{1.89 \times 10^{-18}}{2 \cos 33.5^\circ} = 1.13 \times 10^{-18} \text{ esu-cm} \tag{57}$$

$$\mu\ (\text{C-Br}) = \frac{1.35 \times 10^{-18}}{2 \cos 31^\circ} = 0.79 \times 10^{-18} \text{ esu-cm} \tag{58}$$

The value d (the separation between midpoints of C-X bonds in the trans form) was obtained from scale models of transCl and transBr.

$$dCl = 2.36 \text{ Å} \qquad \theta\, Cl = 5.33 \times 10^{-26} \text{ esu-cm}^2 \tag{59}$$

$$dBr = 2.43 \text{ Å} \qquad \theta\, Br = 3.84 \times 10^{-26} \text{ esu-cm}^2 \tag{60}$$

The magnitude of r^5 may readily be determined from the molecular volume of the molecule assuming that the solute molecule is approximately spherical and completely fills the cavity.

The molecular volume is given by

$$\frac{M}{dN} = \frac{4}{3}\pi r^3 \tag{61}$$

$$r^5 = \left(\frac{3M}{4\pi dN}\right)^{5/3} \text{cm}^5 \tag{62}$$

where M is the molecular weight of the trans form and d is its density (approximately that at room temperature). Substituting values and solving we find that

$$r^5 = 2.96 \times 10^{-38} \text{ cm}^5 \quad \text{for transCl} \tag{63}$$

and $$r^5 = 3.3 \times 10^{-38} \text{ cm}^5 \quad \text{for transBr} \tag{64}$$

The reaction field of the quadrupolar moment is then given by

$$R = 0.847 \times 10^5 \; \frac{\epsilon - 1}{3\epsilon + 2} \quad \text{for transCl} \tag{65}$$

and $$R = 0.554 \times 10^5 \; \frac{\epsilon - 1}{3\epsilon + 2} \quad \text{for transBr} \tag{66}$$

and the contributions to the shielding constants of the ethylenic protons by

$$\sigma_E = -0.17 \times 10^{-6} \; \frac{\epsilon - 1}{3\epsilon + 2} \quad \text{for transCl} \tag{67}$$

and $$\sigma_E = -0.11 \times 10^{-6} \; \frac{\epsilon - 1}{3\epsilon + 2} \quad \text{for transBr} \tag{68}$$

Thus we expect slopes of -0.17 ppm (-10.2 cps) for transCl and -0.11 ppm (-6.6 cps) for transBr. The observed slopes were -8.5

cps and -9.1 cps respectively (figure 20, p. 63; figure 21, p. 64). Thus results of the proper order of magnitude are predicted.

3) Solute Shape and the Reaction Field

The theory for the reaction field of a polar solute predicts that solute shape should be important. Using the models proposed by Scholte,[57] Dekker,[77] and Diehl and Freeman[58] extended the reaction field equation, as given by the Onsager model, to a polarizable, but nonspherical, cavity. Their derived expression is identical to that based on a spherical polarizable cavity except for the insertion of the shape factor ξ_a which depends on the specific solute used.

Using the same values of chemical shift of our two pairs of halogenated ethylenes, we have tested the validity of the Diehl and Freeman expression, or at least its applicability to our solutes.

The reaction field for a nonspherical (ellipsoidal) polarizable cavity is given by

$$E = \frac{\mu}{abc} \; 3\xi_a \left[1 + (n^2 - 1)\xi_a\right] \frac{\epsilon - 1}{\epsilon + \frac{n^2 \xi_a}{1 - \xi_a}} \qquad (41)$$

The values of a, b and c the axes of the cavity ellipsoid were evaluated from a scale model of the cisCl and cisBr molecules using known bond lengths and bond angles.

Using appropriate values for both cisCl and cisBr, the equation reduces to the following for cisCl

$$E = 0.197 \times 10^6 \; \frac{\epsilon - 1}{\epsilon + 1.09} \qquad (69)$$

and for cisBr

$$E = 0.112 \times 10^6 \frac{\epsilon - 1}{\epsilon + 1.12} \qquad (70)$$

Insertion of these quantities into Buckingham's reaction field expression (38) predicts slopes of the plots of $\Delta\delta$ versus the appropriate dielectric function of -0.341 ppm (-20 cps) and -0.194 ppm (-12 cps) for cisCl and cisBr respectively. The experimental values (figure 16, p. 61; figure 17, p. 62) are -5.0 and -4.6 cps respectively for cisCl and cisBr. Diehl and Freeman's expression predicts that the shape correction is slight, at least for our solutes. However, our results show that the shape correction reduces the slopes by a factor of 2 or 3.

4) Aliphatic Solvents

The effects of aliphatic media on the chemical shift differences are shown on pages 60 and 61. In general the proton chemical shift was displaced to low field from its value in cyclohexane which exerts only small dispersion forces on the solute. Except for the bulk susceptibility correction, the shift in this medium should approximate closely that in the gas phase. Thus the low field shift in CS_2 of 8.6 cps and 8.4 cps for cisCl and cisBr, and of 5.4 and 6.0 cps for transCl and transBr may be attributed largely to the diamagnetic anisotropy effect of the CS_2 molecule. In view of the fact that Abraham[78] attributes a low field shift due to this effect of about 14 cps for CH_4 in CS_2, we may conclude that the ethylenic protons are almost as accessible to the solvent interaction as are the protons in the methane.

When $\Delta\delta$ for both dichloro and dibromoethylene was plotted against proper dielectric functions for a series of aliphatic solvents, a trend (pp. 60, 61) identical to that observed in dioxane-water solutions was observed. $\Delta\delta$, the measure of the reaction field at the cis protons, increased with increasing dielectric constant of the solvent. Since the cis and trans forms differ with respect to arrangement of the atoms, we might expect $\Delta\delta$ to be a measure of the reaction field at the cis form with a contribution due to difference in dispersion interaction, if any, due to this difference in arrangement. Whereas the trend of $\Delta\delta$ versus the dielectric function was linear, over a short range, for simple hydrocarbons in which the dispersion interaction is small, a spread of 2 or 3 cycles in the points was noticed. These deviations should be a measure of the difference in interaction between solvent and cis form and solvent and trans form. As these deviations do not exceed 3 cycles, we must conclude that the difference in the arrangement of the atoms in cis and trans form is of little consequence as far as solvent interactions is concerned.

Best straight lines were drawn through the points and their slopes were determined: -17.5 cps for dichloroethylene as compared to the theoretical value of -20 cps. The observed slope for dibromoethylene was -16 cps as compared to the theoretical value of -11 cps.

Though the uncertainty in these experimental slopes may be as large as 5 or 6 cycles, nevertheless they are of the order predicted. The ratios of these slopes, chloro to bromo, is 1.1 (identical to that obtained for dioxane-water measurements) as compared to the theoretical ratio of 1.8. We must therefore conclude that the predictions on the relationship between shielding constants of the protons and the dielectric nature of the medium, as given by Buckingham's equation (38) are reasonably valid.

5) Aromatic Solvents

When $\Delta\delta$ for both pairs of solutes were plotted against the appropriate dielectric function of the aromatic solvents, a wide scatter of points was observed with only a trend to decreasing values of $\Delta\delta$ with increasing dielectric function (pp. 62, 63). The conclusion is that solvent effects in aromatic liquids depend more strongly on the shape of the solute than do aliphatic solvent effects. The largest effect in these ring compounds, the anisotropy in the diamagnetism of the π electrons, depends quite strongly on the preferred orientation of the solute with respect to the ring and any slight hindrance to this orientation, as might occur in the rearrangement of halogen atoms in proceeding from one form of dihaloethylene to the other, produces a large change in the shielding of the ethylenic protons. $\Delta\delta$ must therefore be a measure of difference in shielding constants between cis and trans forms due to the presence of an electric reaction field at the cis form and due to the difference in ring current shielding.

The magnetic shielding of a nucleus near the π electrons of an aromatic molecule varies inversely as the third power of the separation of the nucleus from the centre of the ring. The effect of adding a ring substituent is to hinder the approach of a solute molecule and hence to reduce the shielding produced by the ring current. Some relationship is then expected between the molar volume of the solvent and chemical shift of cis and trans, chloro and bromo ethylenes.

Molar volumes of the aromatic solvents were obtained from molecular weights and densities of the pure solvent at or near room temperature.

When $\Delta\delta$ for both chloro and bromoethylene was plotted against molar volume a smooth relationship was obtained for the series benzene, toluene, O-xylene and mesitylene (pp. 64, 65). This suggests that the molecular volume of the solvent may be correlated with the distance of closest approach of solute and solvent molecules. Evidently this smooth trend is present in this series of simple aromatic solvents because they have low dielectric constants. For this reason reaction field effects are expected to be small as compared to the volume effects.

Points corresponding to more polar solvents lay beneath the line drawn through the above simply substituted benzenes. Assuming that reaction field effects in benzene and its methyl homologues are small, one can conclude that deviations from this line should be a measure of the magnetic shielding of the protons in cisBr and cisCl due to the presence of a net dipole moment. Using this line as the zero point for electric effects, $\Delta\delta'$, the volume corrected differences were plotted against proper dielectric functions (pp. 65,66).

The slopes of these new plots were found to be -172 cps for cisCl and -88 cps for cisBr. It seems the shielding contribution to cis protons is ten times more sensitive to changes in the dielectric function in aromatic than in aliphatic solvents. The coefficient of the linear E term in Buckingham's equation must depend to some extent on the nature of the medium; whereas its value of -2×10^{-12} holds reasonably well for aliphatic solvents, -2×10^{-11} would fit our data for aromatic solvents.

It is interesting to note that some relationship exists between the chemical shifts of the four solutes and the electron withdrawing power of the substituent on the aromatic ring. Since the high field shift in aromatic solvents is attributed to the moment induced in the π electrons, the high field shift is expected to decrease if the π electron density is decreased. When the chemical shifts of the four solutes were plotted against the Hammett para σ constant of the substituent, which is a measure of its withdrawing power, a trend to low field with increasing σ was observed (pp. 66, 67, 68).

SUMMARY AND CONCLUSIONS

CHAPTER IX

SUMMARY AND CONCLUSIONS

We set out to test the validity of Buckingham's equation which relates the contribution to the magnetic shielding of a proton in an X-H bond from an electric field at the bond. More specifically, this electric field is the reaction field of a polar molecule.

Buckingham's equation predicts a linear variation of the contribution to the shielding with

$$\frac{\epsilon - 1}{2\epsilon + n^2} \tag{40}$$

where ϵ is the dielectric constant of the medium and n the refractive index of the solute. The chemical shifts of cis and trans dichloroethylene and cis and trans dibromoethylene were obtained in a wide variety of media. By subtracting the shift of the trans form from that of the cis form, in the same medium, we can reasonably assume that we have isolated the effect of the reaction field at the cis protons. This assumption held in dioxane-water and aliphatic media, where the deviations from linearity were of the order of 1 or 2 cps. We concluded therefore that in aromatic solvents, where deviations were much larger, that the arrangement of atoms of a solute is of greater consequence than it is in nonaromatic solvents. The difference in shifts of the two forms of both pairs of solute varied as predicted with changing dielectric constant and the variation was of the order expected. The differences $\Delta\delta'$ in aromatic solvents, corrected for volume effects also varied linearly with the dielectric functions but with slopes a factor ten larger than predicted.

The variation of shift of transCl and transBr with the dielectric constant of the medium was explained on the basis of local effects. Though the net dipole of the trans forms is zero, the effective moment seen by the trans protons is not. On this basis, the ratio between the slopes of cisCl and transCl were evaluated and found to agree reasonably with the experimental ratio.

The presence of a quadrupolar moment in transCl and transBr also accounts for the variation with the dielectric constant of the shifts of these nonpolar molecules. Reasonable agreement between theory and experiment was obtained.

It was also found that shape corrections as proposed by Diehl and Freeman did not result in better agreement between theory and experiment.

We may conclude that Buckingham's equation approximates quite reasonably the actual shielding contributions observed; it is difficult, however, to say whether the shape corrections are actually an improvement of the above equation.

In figure 30, page 68, are plotted the values $\Delta\delta$(Br) versus $\Delta\delta$(Cl). The majority of the points have only small deviations from a straight line with unit slope. This means that the difference in $\Delta\delta$(Br) for two media is approximately equal to the change in $\Delta\delta$ (Cl) observed for the same two media. One may conclude that solvent interactions are not strongly affected by the size of the halogen atom.

SUGGESTED RESEARCH

CHAPTER X

SUGGESTED RESEARCH

Measurements of chemical shifts of cis and trans difluoro and diiodo ethylene will complete this series. The effect of size of the substituent on solute-solvent interaction may be to some extent clarified.

Also, the determination of actual dipole moments of the solutes in any one medium should be carried out along with the measurement of the actual dielectric constant of the solutions.

Measurements of proton chemical shifts of the four trihaloethylenes should be carried out. These would enable us to determine the polar effects of a single bond dipole. The difference between these shifts and the corresponding cis and trans shifts in identical solutions should be a measure of the reaction field at the latter protons due to a single carbon-halogen bond in two different orientations. The assumption that the dipole in question is a point dipole is then less severe.

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