The University of Manitoba

A STUDY OF AROMATIC SOLVENT INDUCED SHIFTS IN THE PROTON MAGNETIC RESONANCE SPECTRA OF SOME POLYHALOSUBSTITUTED BENZENES

by

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A Thesis

Submitted to

the Faculty of Graduate Studies and Research

University of Manitoba

In Partial Fulfillment

of the Requirements for the Degree

MASTER OF SCIENCE

Winnipeg, Manitoba

June, 1968

- TO MY PARENTS -

- ACKNOWLEDGEMENTS -

I would like to thank Dr. T. Schaefer who patiently guided me throughout this research project. I would also like to thank him for his generous giving of both time and advice in order to aid me in other areas of my education.

My appreciation is also due to Dr. H. Hutton, Dr. E. Bock and to my colleagues Dr. Chris MacDonald and Dr. George Kotowycz for many valuable discussions.

I am grateful to Mr. A.J. teRaa for his assistance and advice during the course of some lab preparations and to Mr. J.W.S. Lee for his assistance in some computer work.

I am indebted to the National Research Council of Canada for their financial support.

- ABSTRACT -

The benzene solvent induced shift in the proton magnetic resonance spectra of some thirty polyhalosubstituted benzenes were examined. It was found that the magnitude of the solvent shift is subject to steric effects, charge effects and shape effects.

Steric effects are evident but are not of major importance.

Simple electrostatic charge effects are important in determining both the magnitude and the sign of the solvent shift. Several $\frac{\mu}{r}$ functions (where μ is the dipole moment of and r is the C-X bond length in the phenyl halides) were defined and used to represent a measure of the amount of charge removed from the ring region by a substituent X. The benzene solvent shifts correlate well with these $\frac{\mu}{r}$ functions for all compounds in which there are no ortho hydrogens.

Polyhalobenzenes in which there are ortho hydrogens experience, at these ortho hydrogens, a solvent shift over and above that predicted by the $\frac{\mu}{r}$ functions. This was concluded to be due to a shape or packing effect. The magnitude of this additional solvent shift is approximately constant for a given proton in a given substitution pattern.

From the $\frac{\mu}{r}$ values of the halogen substituents solvent shift parameters Δ_o, Δ_m, and Δ_p were derived. These parameters represent the effect a halogen substituent has on the solvent shift at a proton ortho, meta or para to it. Combining these Δ values with a packing parameter permits the approximate calculation of the solvent shift. Highest ac-

curacy is observed for protons between two halogens.

A number of substituted benzenes with substituents other than halogen were also tested with a fair amount of success.

- TABLE OF CONTENTS -

- LIST OF TABLES -

- LIST OF FIGURES -

CHAPTER I

- Introduction -

A- THE RESONANCE PHENOMENON

The basic theory of nuclear magnetic resonance (N.M.R.) is covered in many books (1-6). Only a brief review will be presented in this chapter.

All electrons and some nuclei possess a property conveniently called "spin". Electron spin was postulated to account for the way in which electrons group themselves about a nucleus to form atoms. Electron spin also accounted for fine structure in atomic spectra. In the same manner, it was necessary to invoke a nuclear spin to account for the hyperfine structure observed in the spectra of some atoms.

Both protons and neutrons are spin $\frac{1}{2}$ particles. If a particular nucleus is composed of p protons and n neutrons its total spin will be a vector combination of p + n spins each of magnitude $\frac{1}{2}$. Each nuclear isotope, being composed of a different number of protons and neutrons, will have its own total spin value. The spin of a particular nucleus cannot be predicted in general, but observed spins can be rationalized, and some empirical rules have been formulated:

(i) Nuclei with both p and n even (hence charge and mass even) have zero spin, e.g., ^{4}He, ^{12}C, ^{16}O.

(ii) Nuclei with both p and n odd (hence charge odd but mass = p + n, even), have integral spin, e.g., ^{2}H, ^{14}N(spin = 1), ^{10}B(spin = 3).

(iii) Nuclei with odd mass have half-integral spins, e.g., ^{1}H, ^{15}N(spin = $\frac{1}{2}$), ^{17}O(spin = $\frac{5}{2}$).

The spin of a nucleus is usually given the symbol I, called the spin quantum number. Quantum mechanics shows that the angular momentum of a nucleus is given by the expression

$$\text{angular momentum } \underline{I} = \sqrt{I(I+1)}\ \hbar \qquad = \sqrt{I(I+1)} \quad \text{a.m. units} \qquad (1\text{-}1)$$

where $\hbar$ is Planck's constant divided by 2π. For each nucleus I takes one of the values $0, \frac{1}{2}, 1, \frac{3}{2}$ ---.

It is not possible to describe the "state" of a nucleus by giving the direction of its angular momentum, but only by giving the component of the angular momentum along some arbitrary direction, commonly taken as the Z axis. Quantum mechanically, the component of angular momentum along the Z axis is quantized according to the equation

$$I_Z = m\hbar \qquad (1\text{-}2)$$

where $m = I, (I-1), \text{---}\ 0, \text{---}\ -(I-1), -I$.

Coupled to the spin angular momentum $\underline{I}$ of the nucleus is the spin magnetic moment $\underline{\mu}$, given by

$$\underline{\mu} = \gamma\ \underline{I} \qquad (1\text{-}3)$$

where γ is the magnetogyric ratio. Classically, the value of γ is calculated as

$$\gamma = \frac{e}{2M_n c} \qquad \text{(classically)} \qquad (1\text{-}4)$$

where e is the protonic charge, c is the speed of light and M_n is the mass of the nucleus. However, in order to explain experimental results γ is given the value

$$\gamma = g\ \frac{e}{2M_n c} \qquad \text{(experimental)} \qquad (1\text{-}5)$$

where g is the nuclear analogue of the Lande g factor for electrons and

hence is called the nuclear g factor. If the nucleus in question is the hydrogen nucleus (proton)

$$\frac{e\hbar}{2M_p c} = 5.049 \times 10^{-24} \quad \text{ergs/gauss}$$

and

$$g = 5.85.$$

$\frac{e\hbar}{2M_p c}$ is often given the symbol μ_o, and is called the nuclear magneton. Thus, for the proton

$$\gamma = \frac{g \mu_o}{\hbar} \tag{1-6}$$

If the nucleus is placed in a magnetic field $\underline{H}_o$, there is an energy of interaction between the spin magnetic moment vector $\underline{\mu}$ of the nucleus and the magnetic field $\underline{H}_o$, given classically as

$$E = -\underline{\mu} \cdot \underline{H}_o = -\gamma \, \underline{I} \cdot \underline{H}_o \tag{1-7}$$

If the direction of $\underline{H}_o$ is taken to define the Z-axis of the nucleus, equation (1-7) may be rewritten

$$E = -\gamma \, I_Z H_o \tag{1-8}$$

Thus the Hamiltonian for a nucleus in the presence of a magnetic field may be written

$$\mathcal{H} = T - \gamma I_Z H_o \tag{1-9}$$

where T represents the kinetic energy operator of the nucleus. Partitioning out the kinetic energy gives

$$\mathcal{H} = -\gamma \, I_Z H_o \tag{1-10}$$

The eigenfunctions of this Hamiltonian may be written symbolically as

$$\psi_{spin} = \left| I, I_Z \right\rangle \tag{1-11}$$

If the nucleus is a spin $\frac{1}{2}$ nucleus (e.g. the hydrogen nucleus or proton),

the eigenfunctions are

$$\psi_{(1)\ \text{spin}} = \left| \tfrac{1}{2},\tfrac{1}{2} \right\rangle$$

and

$$\psi_{(2)\ \text{spin}} = \left| \tfrac{1}{2},-\tfrac{1}{2} \right\rangle$$

The energy of interaction of such a spin $\frac{1}{2}$ nucleus with a magnetic field $\underline{H}_o$ is thus given by

$$E_{(1)} = \left\langle \tfrac{1}{2},\tfrac{1}{2} \right| -\gamma H_o I_Z \left| \tfrac{1}{2},\tfrac{1}{2} \right\rangle = -\tfrac{1}{2}\gamma H_o \hbar \left\langle \tfrac{1}{2},\tfrac{1}{2} \right| \left. \tfrac{1}{2},\tfrac{1}{2} \right\rangle = -\tfrac{1}{2}\gamma H_o \hbar$$

and

$$E_{(2)} = \left\langle \tfrac{1}{2},-\tfrac{1}{2} \right| -\gamma H_o I_Z \left| \tfrac{1}{2},-\tfrac{1}{2} \right\rangle = \tfrac{1}{2}\gamma H_o \hbar \left\langle \tfrac{1}{2},-\tfrac{1}{2} \right| \left. \tfrac{1}{2},-\tfrac{1}{2} \right\rangle = \tfrac{1}{2}\gamma H_o \hbar$$

Thus, in the presence of a magnetic field $\underline{H}_o$, the energy of a proton splits into two levels (see Fig. 1) with energy separation

$$\triangle E = \gamma H_o \hbar = g \mu_o H_o \qquad (1\text{-}12)$$

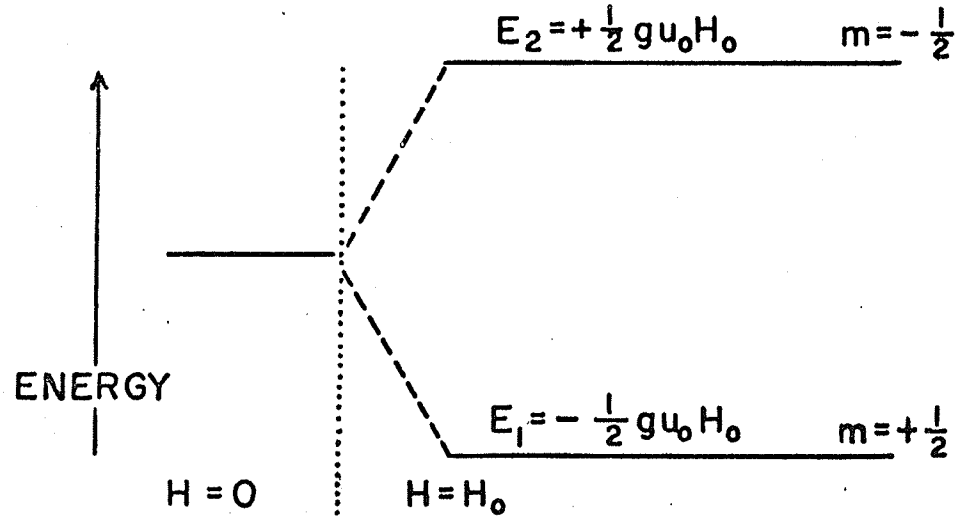

Figure 1: Energy levels for $I=\frac{1}{2}$.

It follows from equations (1-2) and (1-11) that the number of energy

levels produced will be equal to the number of allowable values of I_Z.

In the N.M.R. experiment a proton containing substance is placed in a magnetic field; this gives rise to the two available energy levels, as described above. The nuclei distribute themselves between the two energy levels according to a Boltzmann distribution and hence there is a slight excess of nuclei in the lower energy level. The sample is then subjected to electromagnetic radiation whose frequency is made to vary in a uniform manner. When the frequency ν_1 of the radiation is such that

$$\triangle E = h\nu = \gamma H_o \hbar$$

or

$$\nu = \frac{\gamma H_o}{2\pi} \tag{1-13}$$

transitions take place between the two energy levels (for nuclei with $I > \frac{1}{2}$ these transitions are subject to the selection rule $\triangle m = \pm 1$). The greater population of spins in the lower energy level leads to a net absorption of energy. This is the resonance phenomena commonly observed in the N.M.R. experiment.

From a classical point of view, the nuclear magnetic moment vector $\underline{\mu}$ precesses about the direction of the magnetic field $\underline{H}_o$ as a result of the torque that $\underline{H}_o$ exerts on $\underline{\mu}$ in an attempt to align $\underline{\mu}$ parallel to $\underline{H}_o$. In the experimental procedure a second, rotating magnetic field $\underline{H}^1$, is applied perpendicular to $\underline{H}_o$. The field $\underline{H}^1$ also exerts a torque on $\underline{\mu}$, changing the precession to a nutation. If the field $\underline{H}^1$ is colinear with $\underline{\mu}$ and rotating with the same angular frequency

$$\omega = 2\pi\nu = \gamma H_o$$

or

$$\nu = \frac{\gamma H_o}{2\pi}$$

the torque on $\underline{\mu}$ due to $\underline{H}^1$ is continually applied in one direction and eventually "flips" the magnetic moment vector into a new orientation with respect to $\underline{H}_o$. This process leads to an absorption of energy, and the resonance phenomena is observed.

B- THE CHEMICAL SHIFT

The discussion of section (1-A) referred to a "bare"nucleus. Such a situation is not realized in practise, for each nucleus has associated with it a certain number of electrons. These electrons also precess about the applied field $\underline{H}_o$ and this precession gives rise to an induced field $\underline{H}_i$ which partially shields the nucleus from "feeling" the full value of $\underline{H}_o$. The induced field $\underline{H}_i$ is proportional to the applied field $\underline{H}_o$ and is thus written as

$$\underline{H}_i = -\sigma \underline{H}_o \qquad (1\text{-}14)$$

where σ is the screening constant and is a positive quantity. The field, H_{local}, "felt" by the nucleus is, therefore, written

$$H_{local} = H_o + H_i = H_o(1 - \sigma) \qquad (1\text{-}15)$$

The magnitude of σ depends on the electronic environment of the nucleus and, therefore, so does the magnitude of H_{local}. Hence, it follows from equation (1-13) that the frequency at which the resonance phenomenon is observed varies for nuclei with different electronic environments. This difference in resonance frequency is referred to as the chemical shift.

Resonance frequencies are usually reported with respect to a reference. In N.M.R. the most commonly used reference is tetramethylsilane (T.M.S.). In order to avoid having to state the field at which the resonance experiment was carried out, the chemical shift with respect to the reference is generally reported in terms of the dimensionless parameter (in units of parts per million - p.p.m.)

$$\delta_{sr} = \frac{H_s - H_r}{H_r} \qquad (1\text{-}16)$$

where H_s and H_r are the resonance fields of the sample and reference, respectively.

Another commonly used convention is the τ scale, where

$$\tau = 10 - \delta \qquad (1\text{-}17)$$

Chemical shifts were first observed in 1949 by Knight (7), who found differences in the ^{31}P resonance position of several salts. Lindstrom (8) and Thomas (9) were the first to observe proton chemical shifts.

CHAPTER II

- The Shielding Constant -

A- INTRODUCTION

The chemical shift of the resonance position of any particular type of proton in solution is affected by the surrounding molecules. Thus, it has been proposed (10) that the screening constant for a sample in solution be written

$$\sigma = \sigma_G + \sigma_B + \sigma_A + \sigma_E + \sigma_W + \sigma_C \qquad (2\text{-}1)$$

or

$$\sigma = \sigma_G + \sigma_{solvent}$$

where σ_G is the screening constant for the isolated gaseous molecule, σ_B is the contribution due to the bulk diamagnetic susceptibility of the solvent, σ_A is the contribution due to the anisotropy in the susceptibility of the solvent, σ_E is the contribution due to the reaction field of the medium, σ_W is the contribution due to dispersion (van der Waals) interactions and σ_C is the contribution due to complex formation or, specific molecular interactions.

In this chapter the first five of the six terms making up equation (2-1) will be discussed. Since this thesis is concerned primarily with the nature of the final term in equation (2-1) - σ_C, it will be discussed in a separate chapter.

B- THE HAMILTONIAN

Before proceeding with a discussion of equation (2-1) it will be of use to consider the nature of the Hamiltonian for a charged particle in the presence of electric and magnetic fields.

A particle of mass m and charge q moving with a velocity $\underline{v}$ in the presence of an electric field $\underline{E}$ and a magnetic field $\underline{H}$ is subject to a force

$$\underline{F} = q \left(\underline{E} + \frac{1}{c} \left[\underline{V} \times \underline{H}\right]\right) \tag{2-2}$$

From equation (2-2), making use of Maxwell's, Lagrange's and Hamilton's equations, it may be shown (11) that the Hamiltonian operator corresponding to the energy of the particle is

$$\mathcal{H} = \frac{1}{2m} \left(-\hbar^2 \nabla^2 + 2 i \hbar \frac{q}{c} \underline{A} \cdot \underline{\nabla} + i \hbar \frac{q}{c} \underline{\nabla} \cdot \underline{A} + \frac{q^2}{c^2} |\underline{A}|^2\right) + q\phi \tag{2-3}$$

where $\underline{\nabla}$ is the gradient operator, $\underline{A}$ is a vector potential such that

$$H = \underline{\nabla} \times \underline{A} \tag{2-4}$$

and ϕ is a scalor potential such that

$$\underline{E} = -\frac{1}{c} \frac{\partial A}{\partial t} - \underline{\nabla} \phi \tag{2-5}$$

Equations (2-4) and (2-5) are a direct result of Maxwell's equations.

If the vector potential is chosen so as to satisfy the conditions of the Coulomb guage (12), that is

$$\underline{\nabla} \cdot \underline{A} = 0$$

then equation (2-3) becomes

$$\mathcal{H} = \frac{1}{2m} \left(\hbar^2 \nabla^2 + 2 i \hbar \frac{q}{c} \underline{A} \cdot \underline{\nabla} + \frac{q^2}{c^2} |\underline{A}|^2\right) + q\phi \tag{2-6}$$

Upon generalizing to a systems of n particles of charge q, equation (2-6) becomes

$$\mathcal{H} = -\sum_j \frac{\hbar^2}{2m_j} \nabla_j^2 + \sum_j \frac{i\hbar}{m_j} \frac{q}{c} \underline{A}_j \cdot \underline{\nabla}_j + \sum_j \frac{1}{2m_j} \frac{q^2}{c^2} |\underline{A}_j|^2 + \sum_j q\phi_j \quad (2\text{-}7)$$

In the absence of a permanent electric field $\underline{E}$ (13), ϕ is zero for all particles. Thus for a system of charged particles with an internal potential energy V, in the presence of a magnetic field $\underline{H}$, the Hamiltonian operator may be written

$$\mathcal{H} = \mathcal{H}_o + \mathcal{H}^1$$

where

$$\mathcal{H}_o = \sum_j \frac{i\hbar}{2m_j} \nabla_j^2 + V \quad (2\text{-}8)$$

and

$$\mathcal{H}^1 = \sum_j \frac{i\hbar}{m_j} \frac{q}{c} \underline{A}_j \cdot \underline{\nabla}_j + \sum_j \frac{1}{2m_j} \frac{q^2}{c^2} |A_j|^2 \quad (2\text{-}9)$$

If the magnetic field is weak or of moderate strength, second order terms in the perturbation Hamiltonian $\mathcal{H}^1$ will be small and hence under these conditions

$$\mathcal{H}^1 = \sum_j \frac{i\hbar}{m_j} \frac{q}{c} \underline{A}_j \cdot \underline{\nabla}_j \quad (2\text{-}10)$$

From an elementary consideration of Ampere's Law it may be shown that an electron executing orbital motion in an orbit of radius a may be thought of as a point dipole $\underline{M}$ of strength

$$|\underline{M}| = \frac{-ea}{2c} |\underline{v}| \quad (2\text{-}11)$$

where $\underline{v}$ is the velocity of the electron. Due to its motion the electron will also have associated with it an angular momentum $\underline{\mathcal{L}}$ whose magnitude is

$$|\underline{\mathcal{L}}| = ma |\underline{v}| \quad (2\text{-}12)$$

where m is the mass of the electron. The magnetic dipole moment may now be written

$$\underline{M} = \frac{-e}{2mc} \underline{\mathcal{L}} \tag{2-13}$$

The potential energy of interaction between this magnetic moment and an external magnetic field $\underline{H}$ is given by

$$E = -\underline{M} \cdot \underline{H} = \frac{e}{2mc} \underline{\mathcal{L}} \cdot \underline{H} \tag{2-14}$$

The angular momentum may be written

$$\underline{\mathcal{L}} = \underline{r} \times \underline{p} \tag{2-15}$$

where $\underline{r}$ is the radius vector to the electron from some origin and $\underline{p}$ is the electron's momentum. Generalizing to n electrons, equation (2-14) thus becomes

$$E = \frac{e}{2mc} \sum_j (\underline{r}_j \times \underline{p}_j) \cdot \underline{H} \tag{2-16}$$

or

$$E = -\frac{e}{mc} \sum_j \left[\tfrac{1}{2} (\underline{r}_j \times \underline{H})\right] \cdot \underline{p}_j \tag{2-17}$$

Upon comparing the energy expressed by equation (2-17) with the perturbation Hamiltonian given by equation (2-10), it follows that for an electron in a magnetic field $\underline{H}$

$$\underline{A} = -\tfrac{1}{2} (\underline{r} \times \underline{H}) \tag{2-18}$$

Consideration must also be given to the magnetic field $\underline{H}^1$ which is associated with the electrons motion. Further consideration of Ampere's Law shows that if the electron in its orbit is treated as a point dipole $\underline{M}$, then the field $\underline{H}^1$ is

$$\underline{H}^1 = \frac{2\underline{M}}{R^3} \tag{2-19}$$

where R is the distance from the point dipole. Substituting equation (2-19) into equation (2-18) gives

$$\underline{A} = \frac{\underline{M} \times \underline{R}}{R^3} \tag{2-20}$$

Thus, for an electron executing orbital motion in the presence of a magnetic field $\underline{H}$

$$\underline{A} = \tfrac{1}{2} (\underline{H} \times \underline{r}) + \frac{\underline{M} \times \underline{R}}{R^3} \tag{2-21}$$

or

$$\underline{A} = \underline{A}^{1} + \underline{A}^{11} \tag{2-22}$$

If the electron is also under the influence of a permanent electric field $\underline{E}$ the value of the scalor potential ϕ is non-zero. If conditions are chosen to satisfy the Coulomb guage (14), ϕ satisfies the equation

$$\nabla^2 \phi = -4\pi\rho \tag{2-23}$$

where ρ is an electron density function. Also, from Maxwell's equations

$$\underline{\nabla} \cdot \underline{E} = 4\pi\rho \tag{2-24}$$

Equations (2-23) and (2-24) give

$$\underline{E} = -\underline{\nabla} \phi \tag{2-25}$$

which has the solution

$$\phi = - \underline{E} \cdot \underline{r} \tag{2-26}$$

On substituting equations (2-18) and (2-26) into equation (2-7), one finds that for an atom under the influence of a uniform electric field $\underline{E}$ and a uniform magnetic field $\underline{H}$, the complete Hamiltonian (neglecting spin) may be written as

$$\mathcal{H} = \mathcal{H}_{oo} + \mathcal{H}_{lo} + \mathcal{H}_{ol} + \mathcal{H}_{o2} \tag{2-27}$$

using a double suffix notation, the first suffix representing the order in E and the second the order in H. The separate parts are

$$\mathcal{H}_{oo} = -\sum_j \frac{\hbar^2}{2m_j} \nabla_j^2 - \sum_j \frac{Ze^2}{|\underline{r}_n - \underline{r}_j|}$$

$$\mathcal{H}_{lo} = \sum_j e\,\underline{E} \cdot \underline{r}$$

$$\mathcal{H}_{ol} = \sum_j \frac{e}{2m_j c}\,\underline{H} \cdot \underline{L}_j \qquad (2\text{-}28)$$

$$\mathcal{H}_{o2} = \sum_j \frac{e^2}{8m_j c^2} \left\{ H^2 r^2 - (\underline{H} \cdot \underline{r})^2 \right\}$$

where $\underline{L}_j$ is the orbital angular momentum operator for the j^{th} electron.

$$\underline{L}_j = -\,i\,h\,\underline{r}_j \times \underline{\nabla}_j \qquad (2\text{-}29)$$

C- THE SHIELDING CONSTANT OF THE ISOLATED MOLECULE $-\sigma_G$ *

1. Approach of Lamb

Lamb (16) first attempted to calculate the screening constant for a free atom in an S state. In an external magnetic field the entire spherical electron cloud precesses about the field direction as if it were a rotating rigid sphere of electricity (see Figure 2).

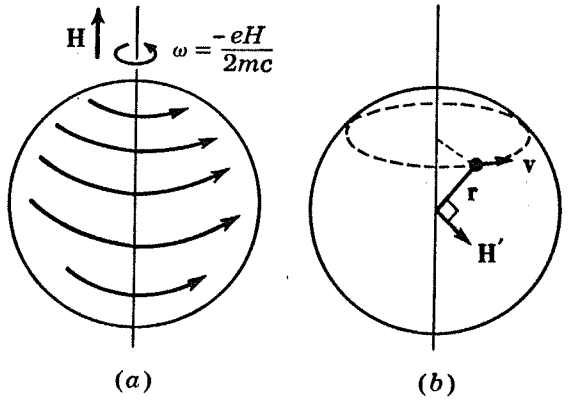

Figure 2: Chemical Shielding in the Helium Atom.

(a) Precession of the electron cloud.
(b) The screening magnetic field.

The angular velocity of precession is

$$\omega = -\frac{eH}{2mc} \qquad (2\text{-}30)$$

The motion of the electron produces a secondary magnetic field, calculated from Ampere's Law

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* Refer to reference 15 from which the substance of Section C is taken.

$$\underline{H}^1 = i\int \frac{d\underline{l} \times \underline{r}}{r^3} = \frac{e}{c}\int \frac{\underline{r} \times \underline{v}}{r^3} \qquad (2\text{-}31)$$

On the average the electrons are distributed over the atom with a probability density $\rho(r)$ and, therefore, the average secondary field is

$$\underline{H}^1 = \frac{e}{c}\int \frac{\underline{r} \times \underline{v}}{r^3}\ \rho(r)\, d\tau \qquad (2\text{-}32)$$

Since

$$\underline{v} = \underline{\omega} \times \underline{r} = -\frac{e}{2mc}\ \underline{H} \times \underline{r} \qquad (2\text{-}33)$$

equation (2-32) may be written as

$$\underline{H}^1 = -\frac{e^2}{2mc^2}\int \frac{\underline{r} \times (\underline{H} \times \underline{r})}{r^3}\ \rho(r)d\tau \qquad (2\text{-}34)$$

For a field $\underline{H}$ in the Z direction equation (2-34) becomes

$$\underline{H}^1 = -\frac{e^2 H}{2mc^2}\int \frac{(x^2 + y^2)}{r^3}\ \rho(r)\, d\tau \qquad (2\text{-}35)$$

for a spherically symmetric system. The screening constant σ is defined as

$$\sigma = -\frac{H^1}{H} \qquad (2\text{-}36)$$

and hence

$$\sigma = \frac{e^2}{2mc^2}\int \frac{(x^2 + y^2)}{r^3}\ \rho(r)d\tau \qquad (2\text{-}37)$$

Equation (2-37) may be rewritten as

$$\sigma = \frac{4\pi e^2}{3mc^2}\int_0^\infty r\, \rho(r)dr \qquad (2\text{-}38)$$

Equation (2-38) is Lamb's formula for the shielding constant in a closed shell atom.

If the atom in question is the hydrogen atom, equation (2-38) becomes

$$\sigma = \frac{e^2}{3mc^2 a_o} \qquad (2\text{-}39)$$

where ao is the Bohr radius (.529 A^{o}).

2. Approach of Ramsey

Ramsey (17) carried out a second order perturbation calculation which considered the magnetic interactions between the electrons and nuclei of an isolated molecule placed in a uniform static magnetic field. If the nucleus is part of the molecule, the electrons, in general, are nolonger free to rotate about the direction of $\underline{H}$. This gives rise to two new effects: first, the secondary field $\underline{H}^{1}$ is not necessarily parallel to $\underline{H}$ and the shielding constant must be replaced by an anisotropic tensor $\underline{\sigma}$; secondly, the theoretical expression for the screening involves an additional term which often is of opposite sign to the Lamb term.

In quantum mechanics an electron in a state ψ has a probability distribution $\rho(r) = \psi\psi^{*}$ and in the absence of a magnetic field there is an electric current density (18)

$$\underline{j} = \frac{e\hbar i}{2mc} \left(\psi^{*} \underline{\nabla} \psi - \psi \underline{\nabla} \psi^{*}\right) \qquad (2\text{-}40)$$

which corresponds to the classical expression

$$\underline{j} = -\left(\frac{e}{c}\right) \rho \, \underline{v} \qquad (2\text{-}41)$$

For simplicity it may be supposed that there is only one electron in the molecule. Call the ground state spatial wave function ψ_{o}. In any closed-shell nondegenerate state ψ_{o} is a real function and so the current density $\underline{j}_{o}(\underline{r})$ vanishes in every part of the molecule. A steady

magnetic field $\underline{H}$, on the other hand, sets up currents in two distinct ways.

In the first place the electron wave function changes and has to satisfy a modified Schrodinger equation (see Section B of this chapter)

$$\left(\frac{-\hbar^2}{2m}\nabla^2 + V\right)\psi + \left(\frac{e}{mc}\underline{A}\cdot\underline{P} + \frac{e^2}{2mc^2}\left|\underline{A}\right|^2\right)\psi = E\psi \qquad (2\text{-}42)$$

where

$$\underline{A} = \tfrac{1}{2}\left(\underline{H} \times \underline{r}\right)$$

If the field is small we neglect $\left|\underline{A}\right|^2$. Also, from equation (2-28)

$$\frac{e}{mc}\underline{A}\cdot\underline{P} = \frac{e\hbar}{2mc}\underline{H}\cdot\underline{L} \qquad (2\text{-}43)$$

which was shown to be the energy of interaction between the orbital angular momentum and the external magnetic field $\underline{H}$. Time independent perturbation theory shows that in the presence of a time invariant perturbation described by $\mathcal{H}^1$, the wave function may be written (to first order)

$$\psi = \psi_o + \sum_n \frac{\langle n|\mathcal{H}^1|o\rangle}{E_o - E_n}\psi_n \qquad (2\text{-}44)$$

where ψ_o is the unperturbed wave function which describes the ground state whose energy is E_o, and ψ_n is an excited state wave function which describes the n^{th} excited state whose energy is E_n. Hence, the electronic wave function becomes

$$\psi = \psi_o - \frac{e\hbar}{2mc}H\sum_n \frac{\langle n|L_z|o\rangle}{E_n - E_o}\psi_n \qquad (2\text{-}45)$$

for a field in the Z direction. This change gives rise to a change in the current distribution $\underline{j}$ (sometimes called the paramagnetic current).

The second effect is more subtle. The current density $\underline{j}$ is proportional to $\underline{v}$, the velocity of the electron. Classically $\underline{v} = \frac{\underline{P}}{m}$ where there is no field, but in the presence of a magnetic field

$$\underline{v} = \frac{1}{m} \left(\underline{P} + \frac{e}{c} \underline{A}\right) \tag{2-46}$$

In the same way the formula for the quantum mechanical current density changes in the presence of the field (19), becoming

$$\underline{j} = \frac{e\hbar i}{2mc} (\psi^* \underline{\nabla} \psi - \psi \underline{\nabla} \psi^*) - \frac{e^2}{mc^2} \underline{A} \psi^* \psi \tag{2-47}$$

Thus, even when the wave function does not change at all, there still exists an induced current

$$\underline{j} = \frac{e^2}{2mc^2} \psi_o^* \psi_o (\underline{H} \times \underline{r}) \tag{2-48}$$

which corresponds to a free precession of the entire electron cloud about the field direction (this is usually called the diamagnetic current).

The magnetic field $\underline{H}^1$ produced by the induced currents is

$$\underline{H}^1 = -\left(\frac{e}{c}\right) \frac{\underline{r} \times \underline{v}}{r^3} = \frac{-e}{mc} \frac{\underline{r} \times \left[\underline{P} + \frac{e}{c} \underline{A}\right]}{r^3} \tag{2-49}$$

Substituting

$$\underline{\mathcal{L}} \hbar = \underline{r} \times \underline{P}$$

and

$$\underline{A} = \tfrac{1}{2} (\underline{H} \times \underline{r})$$

gives

$$\underline{H}^1 = -\left(\frac{e\hbar}{2mc}\right) \frac{2\underline{\mathcal{L}}}{r^3} - \left(\frac{e^2}{2mc^2}\right) \frac{\underline{r} \times (\underline{H} \times \underline{r})}{r^3} \tag{2-50}$$

The classical expression (2-50) has to be replaced by a quantum mechanical average over the perturbed electron state ψ, and for simplicity only the

Z component of $\underline{H}^1$ is worked out, giving

$$H_Z^1 = -\sigma_{ZZ}H = -\left(\frac{e\hbar}{2mc}\right)\left\langle\psi\left|\frac{2\mathcal{L}_Z}{r^3}\right|\psi\right\rangle - \left(\frac{e^2}{2mc^2}\right)H\left\langle\psi\left|\frac{x^2+y^2}{r^3}\right|\psi\right\rangle \qquad (2\text{-}51)$$

Substituting for ψ from equation (2-45) gives

$$\sigma_{ZZ} = \left(\frac{e^2}{2mc^2}\right)\left\langle 0\left|\frac{x^2+y^2}{r^3}\right|0\right\rangle - \left(\frac{e\hbar}{2mc}\right)^2 \sum_n \left\{ \frac{\left\langle 0\left|\mathcal{L}_Z\right|n\right\rangle\left\langle n\left|\frac{2\mathcal{L}_Z}{r^3}\right|0\right\rangle}{E_n - E_o} + \frac{\left\langle 0\left|\frac{2\mathcal{L}_Z}{r^3}\right|n\right\rangle\left\langle n\left|\mathcal{L}_Z\right|0\right\rangle}{E_n - E_o}\right\} \qquad (2\text{-}52)$$

This is Ramsey's shielding formula and applies to any closed shell molecule. The quantities $\mathcal{L}_Z$ and $\frac{(x^2+y^2)}{r^3}$ must be summed over all electrons. One may derive similar expressions for σ_{xx} and σ_{yy} and then work out one average isotropic σ. The two parts of σ in equation (2-52) are usually called the diamagnetic and paramagnetic terms. Thus

$$\sigma = \sigma_d + \sigma_p \qquad (2\text{-}53)$$

σ_d is fairly easy to estimate theoretically as it depends only on the electron distribution in the electronic ground state. The paramagnetic term also depends on the excited states. It is equal to zero for electrons in s orbitals and, therefore, of zero angular momentum, but it may become very large when there is an asymmetric distribution of p and d electrons close to the nucleus and these electrons have low lying excited states. Fluorine chemical shifts, for example, are largely dominated by the paramagnetic term.

D- THE EFFECT OF BULK SUSCEPTIBILITY - σ_B

When the reference compound is kept external from the solute-solvent system being studied (for example, by placing reference and solution in separate concentric tubes) a correction to the chemical shift is required in order to account for the differences in the bulk diamagnetic susceptibility of the reference and the solution.

However, when the reference is also placed in the solution studied (internal reference), then the susceptibility of the sample and reference are the same, equal to the susceptibility of the solution. Under these conditions no correction is required. Since most N.M.R. experiments are run using an internal reference, this topic shall not be discussed further.

E- THE EFFECTS OF MAGNETICALLY ANISOTROPIC SOLVENTS - σ_A

It is well known that aromatic solvents tend to produce high field shifts in the resonance position of a solute, relative to the solute resonance position in non-aromatic, "inert" solvents such as cyclohexane. Similarily, carbon disulfide produces low field shifts. These phenomena may be interpreted in terms of the shapes of these solvent molecules, along with their large diamagnetic anisotropy.

The physical properties of a single molecule in general depend upon the direction along which they are measured relative to the molecular axis; this phenomena is called anisotropy. The reason for the anisotropy lies in the pattern of the atoms. Along any direction through a molecule, the atoms occur at different intervals and different angles than they do along another direction; also, the atoms in general do not lie symmetrically about the direction. Any physical property dependent on the pattern of the atoms will vary with this direction. Thus, in defining a magnetic field $\underline{H}^1$ induced by an applied field $\underline{H}$, assumption of a linear relationship between cause and effect does not require the magnitude of $\underline{H}^1$ to be independent of direction, nor the vector $\underline{H}^1$ to be parallel to the vector $\underline{H}$. Thus, in describing $\underline{H}^1$, one writes

$$H^1_\alpha = X_{\alpha\beta} H_\beta \qquad (2\text{-}54)$$

where $X_{\alpha\beta}$ is known as the susceptibility tensor. Onsager (20) has shown that this tensor is symmetric and, therefore, has principal axes. By referring the tensor to these principal axes all the off-diagonal elements become zero, and, hence

$$\begin{aligned} H^1_x &= X_{xx} H_x \\ H^1_y &= X_{yy} H_y \\ H^1_z &= X_{zz} H_z \end{aligned} \qquad (2\text{-}55)$$

The anisotropy of such a system is observed in the fact that, in general $X_{xx} \neq X_{yy}$, $X_{xx} \neq X_{zz}$ and $X_{yy} \neq X_{zz}$.

There are several approaches to calculating the effect of the induced field $\underline{H}^1$ in the shielding of a molecule for magnetically anisotropic systems. These will now be discussed.

1. The Approach of Stephen

If a molecule is placed in a uniform magnetic field $\underline{H}$, which is in the negative Z direction, by Lenzs' Law, a field $\underline{H}^1$ will be induced in the positive Z direction, the magnitude of the field being given by

$$H_z^1 = X_{zz}H \tag{2-56}$$

(see Figure 3).

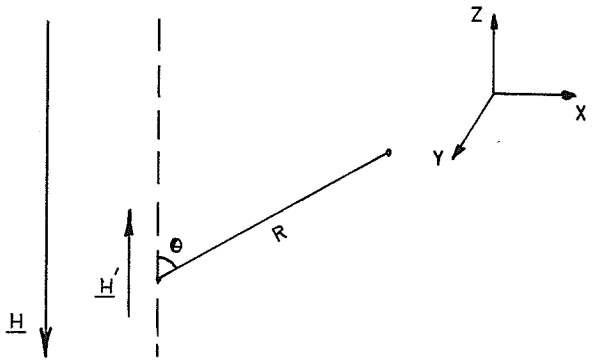

Figure 3: The induced field in an anisotropic system.

From equations (2-19) and (2-20), the vector potential corresponding to the induced field is

$$\underline{A} = \frac{\underline{M} \times \underline{R}}{R^3} \tag{2-20}$$

Thus

$$\underline{A} = \frac{1}{R^3} \left\{ (-y\, XH)\, \underline{i} + (x XH)\, \underline{j} + 0\underline{k} \right\} \tag{2-57}$$

where $\underline{i}$, $\underline{j}$, and $\underline{k}$ are unit vectors in the x, y and z directions, respectively. Thus

$$H_z^1 = (\text{curl } \underline{A})_z = \frac{2\, X\, H}{R^3} - \frac{3\, X\, H}{R^5} (R^2 - Z^2) \tag{2-58}$$

or

$$H_z^1 = \frac{XH}{R^3} (3 \cos^2 \theta_z - 1) \tag{2-59}$$

Therefore,

$$-\Delta \sigma_z H = \frac{XH}{R^3} (3 \cos^2 \theta_z - 1) \tag{2-60}$$

and hence

$$\Delta \sigma_z = \frac{X}{R^3} (1 - 3 \cos^2 \theta_z) \tag{2-61}$$

If now $\underline{H}$ is in a direction i, and we have $X^{(i)}$ atomic and θ_i, the mean contribution to the screening tensor is

$$\Delta \sigma = \frac{1}{3R^3} \sum_{i=1,2,3} X^i_{\text{atomic}} (1 - 3 \cos^2 \theta_i) \tag{2-62}$$

If X is referred to its principal axes, equation (2-62) becomes

$$\Delta \sigma = \frac{1}{3R^3} \left[(1 - 3 \cos^2 \theta_x) X_{xx} + (1 - 3 \cos^2 \theta_y) X_{yy} + (1 - 3 \cos^2 \theta_z) X_{zz} \right] \tag{2-63}$$

If R is taken in the yz plane, $\cos \theta_x = 0$ and

$$\Delta \sigma = \frac{1}{3R^3} \left[2(X_{xx} - X_{yy}) - (X_{zz} - X_{xx}) - 3 \cos^2 \theta_z (X_{xx} - X_{yy}) \right] \tag{2-64}$$

Call $X_{xx} - X_{yy} = \Delta X_1$, and $X_{zz} - X_{xx} = \Delta X_2$. Hence,

$$\Delta\sigma = \frac{1}{3R^3}\left[2\Delta X_1 - \Delta X_2 - 3\cos^2\theta_z \Delta X_1\right] \qquad (2\text{-}65)$$

If the molecule has axial symmetry, $X_{xx} = X_{yy}$, and then

$$\Delta\sigma = \frac{\Delta X}{3R^3}(1 - 3\cos^2\theta_z) \qquad (2\text{-}66)$$

where

$$\Delta X = X_{zz} - X_{xx} = X_{zz} - X_{yy} = X_{ll} - X_{\perp} \qquad (2\text{-}67)$$

and θ_z equals the angle between R and the anisotropy (Z) axis.

Equation (2-66) describes how the chemical shift of a solute molecule will be affected by the presence of a solvent molecule, when the solute molecule has coordinates R and θ_z with respect to the solvent molecule. For a magnetically isotropic solvent molecule $\Delta X = 0$ and there will be no change in the screening constant of the solute molecule. If the solvent molecule is magnetically anisotropic, $\Delta X \neq 0$ and a change in screening will result. Equation (2-66) is equivalent to a result first presented by Stephen (21).

ΔX must be measured experimentally. If a crystal of the substance in question is obtainable, the ordinary Gouy method is used. If crystals are unobtainable, the experimental technique is somewhat more difficult as it involves the measurement of the magnetic birefringence (Cotton-Mouton effect), from which ΔX may be calculated (22).

Buckingham, et. al., (23), applied equation (2-66) to the example of CH_4 in benzene and carbon disulfide (see Figure 4)

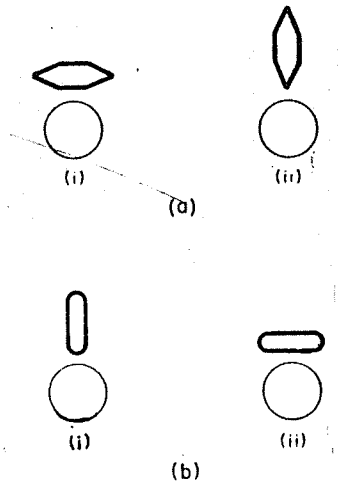

Figure 4: Relevant arrangements for (a) discs and (b) rods in relation to a spherical solute molecule.

For benzene as solvent, collisions of the type (i-a) are predominant, while for CS_2 as solvent, collisions of the type (ii-b) are predominant, simply due to the shape of the molecule. Taking, for benzene, $X_{11} - X_{\perp} = -9 \times 10^{-29}$ ergs gauss^{-2}, $R \sim 4.5 A^{o}$, and assuming that for this value of R two benzene molecules are in the relevant range of R, Buckingham, et. al., calculated $\triangle\sigma = 1.3$ p.p.m. The experimental value is 0.33 p.p.m. Taking, for CS_2, $X_{11} - X_{\perp} = -5 \times 10^{-29}$ ergs gauss^{-2}, $R \sim 4A^{o}$ and again assuming that two solvent molecules are in the relevant range of R, they calculated $\triangle\sigma = -0.5$ p.p.m. The experimental value is -0.42 p.p.m.

2. The Classical Ring Current Model

Benzene and other aromatic hydrocarbons are characterized by a π electron system which is not localized. The abnormally large diamagnetic anisotropy of such aromatic molecules has come to be explained as arising from the Larmor precession of electrons in orbits containing many nuclei (the π electrons) (24). Pople (25) applied this idea to

a benzene molecule placed in a magnetic field $\underline{H}$. The six π electrons undergo Larmor precession with the Larmor frequency

$$\omega = -\frac{eH}{2mc} \tag{2-68}$$

for each electron. The moving electrons are equivalent to a current, whose value per electron is

$$i = -\frac{e\omega}{2\pi} = \frac{e^2H}{4\pi mc} \tag{2-69}$$

or, for 6 electrons

$$i = \frac{3e^2H}{2\pi mc} \tag{2-70}$$

Pople assumes that the precessing π electrons are equivalent to a point dipole at the centre of the benzene ring. The dipole moment $\underline{M}$ of the current loop is given by

$$M = i \times (\text{area of the loop perpendicular to } H).$$

Thus

$$M = \frac{3e^2H}{2\pi mc}\,\pi\,(a\cos\theta)^2 \tag{2-71}$$

where a is the radius of the π electron orbit (taken as the C-C bond distance) and θ is the angle between the direction of H and the hexagonal axis of the benzene ring. Averaging over all values of θ gives

$$M = \frac{e^2a^2H}{2mc} \tag{2-72}$$

The dipole lies parallel and opposed to the applied field (see Figure 5).

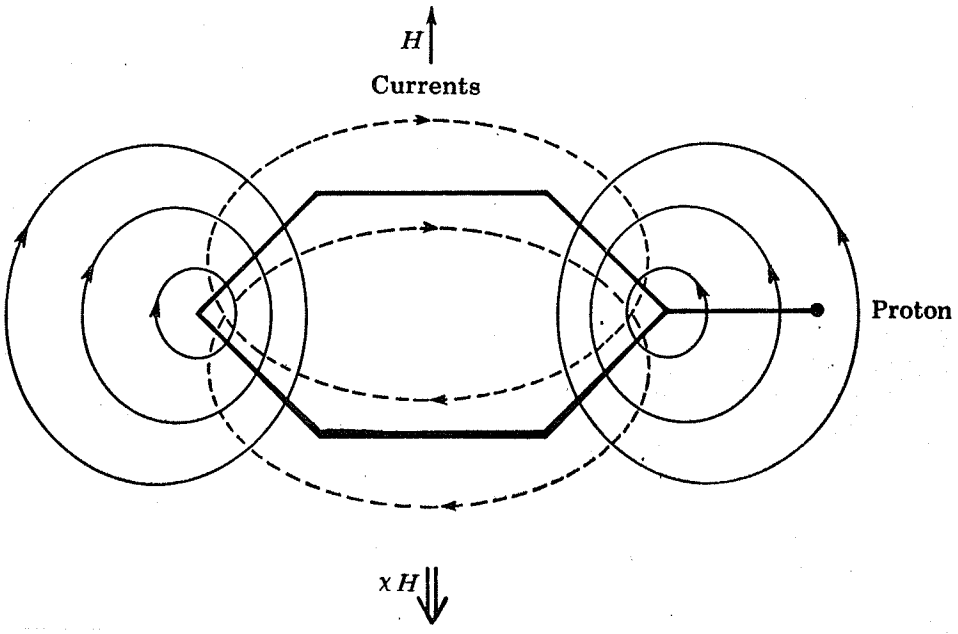

Figure 5: Free Electron Ring Currents in Benzene.

The field produced is thus opposed to the applied field at the centre of the ring but reinforces it at the position of the hydrogen atom. The effect of the interatomic current is to produce a low-field chemical shift for protons found near the periphery of the benzene ring, and a high field chemical shift for protons found near the centre of the benzene ring.

The magnitude of the induced field at the position of the benzene protons is

$$H^1 = \frac{e^2 a^2 H}{2mc\ (a+b)^3} \qquad (2\text{-}73)$$

where b is the C-H bond distance. Hence, for these protons, the change in the shielding with respect to an ordinary aliphatic ethylenic proton is

$$\Delta\sigma = \frac{e^2a^2}{2mc\,(a+b)^3} \qquad (2\text{-}74)$$

Pople calculated the difference in the shift between benzene and ethylene protons to be -1.75 p.p.m. as compared to the experimental value of -1.4 p.p.m.

Waugh and Fessenden (26,27) recalculated the ring current effect using the free electron model. On this basis, they found that $\Delta\sigma$ = -2.2 p.p.m. The negative sign denotes that the ring current shift is to low field with respect to the ethylene resonance. To check this value experimentally they found the difference in shift between the benzene protons and the ethylenic protons of cyclohexadiene -1,3 in carbon tetrachloride to be 1.48 p.p.m. with the benzene protons appearing at low field. Schaefer and Schneider (28) redetermined this difference in shift using cyclohexane as solvent, and found it to be 1.5 p.p.m., in agreement with the value of Waugh and Fessenden. The difference in shift is the ring current shift for a single aromatic ring.

In general, the predicted values for the ring current shifts are too high, since the calculation overestimates the ring current effect.

3. The Quantum Mechanical Ring Current Model

Pople (29), using the method of London (30), attempted to calculate the ring current produced in polycyclic aromatic hydrocarbons.

In the independent electron model it is assumed that the molecular orbitals ψ_i are eigenfunctions of a one-electron Hamiltonian, which

takes the form (see Section B of this chapter)

$$\mathcal{H} = \frac{1}{2m} \left(\underline{P} + \frac{e}{c} \underline{A}\right)^2 + V \qquad (2\text{-}75)$$

where, for a uniform magnetic field $\underline{H}$

$$\underline{A} = -\tfrac{1}{2} (\underline{r} \times \underline{H}) \qquad (2\text{-}76)$$

In the absence of a magnetic field the general approach is usually to express the molecular orbitals as linear combinations of the 2 $P\pi$ carbon atomic orbitals ϕ_s. This is the L.C.A.O. approximation. When there is a magnetic field present, however, this is not satisfactory for it is found that the best linear combination will depend on the guage transformation of the vector potential $\underline{A}$. Pople overcomes this difficulty by adopting London's technique of expressing the molecular orbitals ψ as linear combinations of modified atomic orbitals

$$X_s = \phi_s \exp\left\{ - \frac{2\pi i e}{hc} \underline{A}_s \cdot \underline{r} \right\} \qquad (2\text{-}77)$$

where $\underline{A}_s$ is the vector potential at the centre of atom S. Whenever ψ is replaced by $e^{i\lambda}\psi$, that is

$$\psi \longrightarrow e^{i\lambda}\psi \qquad (2\text{-}78)$$

then the Hamiltonian is transformed, such that

$$\mathcal{H} \longrightarrow (e^{-i\lambda} \mathcal{H} e^{i\lambda} - i\hbar e^{-i\lambda} \frac{\partial e^{i\lambda}}{\partial t}) \qquad (2\text{-}79)$$

Thus replacing ϕ_s by X_s as expressed by equation (2-77) has the effect (31) of transforming the Hamiltonian expressed by equation (2-75) so that

$$\left(\underline{P} + \frac{e}{c} \underline{A}\right)^2 X_s = \exp\left\{ \frac{-2\pi i e}{hc} \underline{A}_s \cdot \underline{r} \right\} \left[\underline{P} + \frac{e}{c} (\underline{A} - \underline{A}_s) \right]^2 \phi_s \qquad (2\text{-}80)$$

and hence the exponential factor in equation (2-77) eliminates guage difficulties because $(\underline{A} - \underline{A}_s)$ is a local vector potential independent of the choice of origin.

Thus

$$\psi_j = \sum_s C_{js} X_s \tag{2-81}$$

where the coefficients C_{js} are determined by the usual variation procedure. The variation treatment for the coefficients C_{js} leads to the secular equation

$$\left| \mathcal{H}_{st} - E\, S_{st} \right| = 0 \tag{2-82}$$

where

$$\mathcal{H}_{st} = \int X_s^* \mathcal{H} X_t d\tau \tag{2-83}$$

and

$$S_{st} = \int X_s^* X_t d\tau \tag{2-84}$$

In the simplest version of the theory, which is the approach used by Pople, the overlap integral S_{st} is neglected if $s \neq t$. That is, it is assumed that the overlap between these modified P orbitals is small if the orbitals are located on non-adjacent carbon atoms.

From equations (2-77) and (2-80), $\mathcal{H}_{st}$ takes the form

$$\begin{aligned}
\mathcal{H}_{st} &= \int \exp\left\{\frac{2\pi ie}{hc}\, \underline{A}_s \cdot \underline{r}\right\} \phi_s^* \left\{\frac{1}{2m}\left(\underline{P} + \frac{e}{c}\underline{A}\right)^2 + V\right\} \exp\left\{\frac{-2\pi ie}{hc}\, \underline{A}_t \cdot \underline{r}\right\} \phi_t d\tau \\
&= \int \exp\left\{\frac{2\pi ie}{hc}\, \underline{A}_s \cdot \underline{r}\right\} \phi_s^* \exp\left\{\frac{-2\pi ie}{hc}\, \underline{A}_t \cdot \underline{r}\right\} \left\{\frac{1}{2m}\left[\underline{P} + \frac{e}{c}(\underline{A} - \underline{A}_t)\right]^2 + V\right\} \phi\, t d\tau \\
&= \int \exp\left\{\frac{2\pi ie}{hc}(\underline{A}_s - \underline{A}_t) \cdot \underline{r}\right\} \phi_s^* \left\{\frac{1}{2m}\left[\underline{P} + \frac{e}{c}(\underline{A} - \underline{A}_t)\right]^2 + V\right\} \phi_t d\tau
\end{aligned} \tag{2-85}$$

If s=t, the exponential factor is unity and the rest of the expression measures the basic energy of the atomic orbital, as modified by

the local diamagnetic circulation represented by the $(\underline{A} - \underline{A}_t)$ term. Since Pople is interested only in the interatomic currents he omits these terms and chooses the zero of energy so that all diagonal terms $\mathcal{H}_{ss}$ are zero.

In London's analysis $\underline{r}$ is replaced by its values at the mid-point of the bond where

$$r = \tfrac{1}{2} (\underline{R}_s + \underline{R}_t) \tag{2-86}$$

$\underline{R}_s$ and $\underline{R}_t$ being the position vectors of the nuclei of atoms s and t. If the term $(\underline{A} - \underline{A}_t)$ is also omitted (since magnetic energies are small in comparison to electronic energies), equation (2-85) becomes

$$\mathcal{H}_{st} = \beta_{st} \exp\left\{\frac{\pi ie}{hc} (\underline{A}_s - \underline{A}_t) (\underline{R}_s - \underline{R}_t)\right\} \tag{2-87}$$

where

$$\beta_{st} = \int \phi_s^* \left[\frac{1}{2m} p^2 + V\right] \phi_t d\tau \tag{2-88}$$

is the corresponding matrix element in the non-magnetic theory, usually known as the resonance integral. To a first approximation, Pople takes β_{st} to have a common value β for all C-C bonds. Energies may be measured in units of β and the secular equation written

$$\left|\mathcal{H}_{st} - x \beta \delta_{st}\right| = 0 \tag{2-89}$$

where x is the dimensionless eigenvalue and δ_{st} is the Kronecker delta.

Expansion of the secular determinant gives a polynomial in x, the coefficients all being expressible in terms of closed cyclic products of the type

$$\mathcal{H}_{ij} \mathcal{H}_{jk} \mathcal{H}_{kl} \cdots \mathcal{H}_{pq} \mathcal{H}_{qi} \Big/ \beta^n \tag{2-90}$$

where n equals the number of factors. The simplest such product is $\mathcal{H}_{ij}\,\mathcal{H}_{ji} \,/\, \beta^2$ which is real and independent of the magnetic field. If there are no closed cycles of bonds (as in linear polyenes, for example) all solutions of equation (2-89) will be independent of the magnetic field, corresponding physically to the absence of ring currents. If closed cycles do exist, there will be complex expressions (2-90) dependent on the magnetic field.

From equation (2-87), the numerator of equation (2-90) may be written

$$\mathcal{H}_{ij}\,\mathcal{H}_{jk}\,\mathcal{H}_{kl}\cdots\mathcal{H}_{pq}\,\mathcal{H}_{qi} = \beta^n \exp(2\pi i f) \qquad (2\text{-}91)$$

where

$$f = \frac{e}{2hc}\sum\nolimits^{1} (\underline{A}_s - \underline{A}_t) \cdot (\underline{R}_s + \underline{R}_t) \qquad (2\text{-}92)$$

the sum $\sum^{1}$ being over ordered pairs around the ring. Since

$$(\underline{A}_s - \underline{A}_t) = \left[(\underline{R}_s - \underline{R}_t) \cdot \underline{\nabla} \right] \underline{A} \qquad (2\text{-}93)$$

equation (2-92) may be rewritten

$$f = \frac{e}{2hc}\sum\nolimits^{1} \left\{ \left[(\underline{R}_s - \underline{R}_t) \cdot \underline{\nabla} \right] \underline{A} \right\} \cdot (\underline{R}_s + \underline{R}_t) \qquad (2\text{-}94)$$

which, upon switching to tensor notation becomes

$$f = \frac{e}{2hc}\sum\nolimits^{1} (R_{s\alpha} - R_{t\alpha}) \nabla_\alpha A_\beta (R_{s\beta} + R_{t\beta}) \qquad (2\text{-}95)$$

$\underline{R}_s$ and $\underline{R}_t$ represent vectors to adjacent nuclei from a common origin and hence

$$R_{s\alpha} - R_{t\alpha} = \triangle R_\alpha \qquad (2\text{-}96)$$

If $\triangle R_\alpha \longrightarrow dR_\alpha$ the summation in equation (2-95) may be replaced by a

closed line integral, so that

$$f = \frac{e}{hc} \oint R_\beta \left(\nabla_\alpha A_\beta \right) dR_\alpha \tag{2-97}$$

Since

$$\underline{\nabla} \left(\underline{A} \cdot \underline{R} \right) = \underline{A} \tag{2-98}$$

f becomes

$$f = \frac{e}{hc} \oint A_\alpha \, dR_\alpha \tag{2-99}$$

Stokes theorem states that

$$\oint \underline{V} \cdot \underline{dr} = \iint_s \left(\underline{\nabla} \times \underline{V} \right) \cdot dS \tag{2-100}$$

where $\underline{V}$ is any vector and equation (2-100) is for clockwise rotation.

Therefore

$$f = \frac{e}{hc} \oint A_\alpha dR_\alpha = - \frac{e}{hc} \iint_s \left(\underline{\nabla} \times \underline{A} \right) \cdot \underline{dS} = - \frac{e}{hc} \iint_s \underline{H} \cdot \underline{dS} \tag{2-101}$$

where $\underline{H}$ is the magnetic field and equation (2-101) is for counter clockwise rotation. The quantity f is, therefore, proportional to the flux of the magnetic field through the ring. For a uniform magnetic field H, the numerical value will be

$$f = \frac{eHS}{hc} \tag{2-102}$$

where S is the closed area of the ring.

From the Hermitian nature of the secular determinant, it is clear that only the real part of the cyclic products (2-91) will appear. Thus if the f values corresponding to the irreducible circuits are f_1, f_2 --- f_n, the secular equation when expanded will involve quantities such as $\cos 2\pi f_1$, $\cos 2\pi (f_1 + f_2)$ etc. If the applied magnetic field is treated as a small perturbation the secular equation can be written

$$P(x) = 4\pi^2 \sum_{ij} Q_{ij}(x)\, f_i f_j \qquad (2\text{-}103)$$

where $P(x)$ is the unperturbed determinant and Q_{ij} is a set of polynomials such that $Q_{ij} = Q_{ji}$. The solutions to order f^2 can be written

$$X^{(p)} = X_o^{(p)} + 4\pi^2 \sum_{ij} x_{ij}^{(p)}\, f_i f_j \qquad (2\text{-}104)$$

where p represents the p^{th} solution, $X_o^{(p)}$ the unperturbed eigenvalue and

$$X_{ij}^{(p)} \equiv \frac{- Q_{ij}(X_o^{(p)})}{P^1(X_o^{(p)})} \qquad (2\text{-}105)$$

where $P^1(X)$ is the first derrivative of $P(X)$.

Pople now considers adding to the primary field $\underline{H}$, a secondary testing field $\underline{H}^1$. Since the total field is now $\underline{H} + \underline{H}^1$, the quantities f_i have to be replaced by the sums $f_i + f_i^1$. Equation (2-104) then takes the form

$$X^{(p)} = X_o^{(p)} + 4\pi^2 \sum_{ij} x_{ij}^{(p)} \left[f_i f_j + 2 f_i^1 f_j + f_i^1 f_j^1 \right] \qquad (2\text{-}106)$$

The terms of the type $f_i^1 f_j$ give the energy (in units of β) due to the interaction of the testing field with the magnetic polarization due to the primary field. Since f_i^1 is proportional to the flux of the testing field through circuit i, we may say that the system, in the presence of the primary field only, behaves as if the i^{th} circuit were replaced with a magnetic shell of strength equal to $-\beta e / hc$ times the coefficient of f^1 in equation (2-106). This may then be interpreted as the current in-circuit i divided by c.

That is, the energy of interaction between the testing field $\underline{H}^1$

and the magnetic dipole $\underline{M}$ induced by the primary field $\underline{H}$ is

$$E = - \underline{M} \cdot \underline{H}^1 = 8\pi^2 \sum_{ij} X_{ij} f_j \frac{eS}{hc} H^1 \beta \qquad (2\text{-}107)$$

since, from equation (2-102)

$$f^1 = \frac{eH^1}{hc} S \qquad (2\text{-}108)$$

Thus

$$M = -8\pi^2 \sum_{i\ j} X_{ij} f_j \frac{eS}{hc} \beta \qquad (2\text{-}109)$$

Also

$$M = \frac{i}{c} S \qquad (2\text{-}110)$$

where i is the current flowing in the ring of area S. Hence

$$i = - \frac{8\pi^2 e\beta}{h} \sum_{i\ j} X_{ij} f_j \qquad (2\text{-}111)$$

From equation (2-101), for counter clockwise rotation

$$f_j = - \frac{eH}{hc} \iint_s \cdot \underline{dS} \qquad (2\text{-}112)$$

Thus

$$i(p) = - \frac{8\pi^2 \beta e^2}{hc} \underline{H} \iint \cdot \underline{dS} \sum_{i\ j} X_{ij}(p) \qquad (2\text{-}113)$$

Equation (2-113) applies to each orbital separately. For the total effective current in one circuit, it has to be summed over electrons

$$\sum_p \lambda_p \sum_j X_{ij}(p)$$

where $\sum_p$ is over occupied orbitals ψ_p, and λ_p is the number of electrons in ψ_p (1 or 2).

From equation (2-113) it has been calculated that

$$i_{benzene} = \frac{8\pi^2 \beta e^2}{9h^2 c} H \cdot S_6 \qquad (2\text{-}114)$$

This ring current is then substituted into the classical expression for the induced field and the effect on the shielding constant calculated, as described in Section E-2.

Jonathan et al (32) determined the current intensity in each ring of some polycyclic hydrocarbons employing the molecular orbital method described above. They also studied the ring current effect experimentally and found the agreement between predicted and observed values only fair, the predicted chemical shifts being always larger than the experimental. Some of this discrepancy was later explained by Pople, in a series of papers, to be due to the fact that a significant contribution to $\triangle \sigma$ arises from a significant contribution to the anisotropy due to localized $P\pi$ electrons. Thus too large a chemical shift is attributed to ring currents and hence predicted values for the ring current shift are larger than experimental values.

F- THE EFFECTS OF THE REACTION FIELD - σ_E

The development of an expression for σ_E is the result of the work of Buckingham, who, in turn, extended the work of Marshall and Pople.

Marshall and Pople (33,34) attempted to calculate the screening in a hydrogen atom under the influence of an electric field $\underline{E}$, neglecting any effect of the spin of the electron. This represents perhaps the simplest situation for which the "paramagnetic" effect has to be taken into account.

Marshall and Pople used the Hamiltonian for an atom in a uniform electric field $\underline{E}$ and a uniform magnetic field $\underline{H}$, given by equations (2-27) and (2-28)

$$\mathcal{H} = \mathcal{H}_{oo} + \mathcal{H}_{1o} + \mathcal{H}_{o1} + \mathcal{H}_{o2} \tag{2-27}$$

where

$$\mathcal{H}_{oo} = -\frac{\hbar^2}{2m}\nabla^2 - \left(\frac{e^2}{r}\right)$$

$$\mathcal{H}_{1o} = e\,\underline{E}\cdot\underline{r}$$

$$\mathcal{H}_{o1} = \left(\frac{e}{2mc}\right)\,\underline{H}\cdot\underline{L} \tag{2-28}$$

$$\mathcal{H}_{o2} = \left(\frac{e^2}{8mc^2}\right)\left[H^2r^2 - (\underline{H}\cdot\underline{r})^2\right]$$

where equation (2-28) is written specifically for the hydrogen atom, in this case.

They then expanded the wave function in a similar manner

$$\psi = \psi_{oo} + \psi_{1o} + \psi_{o1} + \psi_{o2} + \cdots \tag{2-115}$$

in which case the complete Schrödinger equation breaks up into separate equations in each order in E and H.

Since the hydrogen atom in an electric field is an axially symmetric system, Marshall and Pople considered only the two cases of $\underline{H}$ parallel or perpendicular to $\underline{E}$. These give rise to different shielding constants which are denoted $\sigma_{\parallel}$ and $\sigma_{\perp}$. If the x, y and z axes are taken as the principal axes of the shielding tensor, the shielding tensor is diagonal when referred to these axes. If $\underline{H}$ lies along a direction whose direction cosines are l_x, l_y and l_z with respect to the principal axes, then

$$\underline{H} = (l_x H, l_y H, l_z H) \tag{2-116}$$

Thus, the induced field $\underline{H}^1$ is given by

$$\underline{H}^1 = (\sigma_{xx} l_x H, \sigma_{yy} l_y H, \sigma_{zz} l_z H) \tag{2-117}$$

The component of the induced field in the direction of $\underline{H}$ is

$$H_{\parallel}^1 = \sigma_{xx} l_x^2 H + \sigma_{yy} l_y^2 H + \sigma_{zz} l_z^2 H \tag{2-118}$$

Thus

$$\sigma = \frac{H_{\parallel}^1}{H} = \sigma_{xx} l_x^2 + \sigma_{yy} l_y^2 + \sigma_{zz} l_z^2 \tag{2-119}$$

If $\underline{E}$ lies along the Z axis, the spherical symmetry of the hydrogen atom will be distorted so that

$$\sigma_{xx} = \sigma_{yy} \neq \sigma_{zz} \tag{2-120}$$

In this case

$$\sigma = \sigma_{xx} (l_x^2 + l_y^2) + \sigma_{zz} l_z^2 = \sigma_{xx} (1 - l_z^2) + \sigma_{zz} l_z^2 \tag{2-121}$$

or

$$\sigma = \sigma_{\perp} \sin^2 \theta + \sigma_{\parallel} \cos^2 \theta \tag{2-122}$$

where σ is the shielding constant along any direction i which is at an angle θ from the direction of $\underline{E}$ (symmetry axis) and $\sigma_\perp = \sigma_{xx} = \sigma_{yy}$ and $\sigma_{ll} = \sigma_{zz}$.

Marshall and Pople then express the Hamiltonian in terms of polar coordinates with the direction of $\underline{H}$ as the polar axis. The separate parts of $\mathcal{H}$ then become

$$\begin{aligned}
\mathcal{H}_{oo} &= -\frac{\hbar^2}{2m}\nabla^2 - \left(\frac{e^2}{r}\right) \\
\mathcal{H}_{o1} &= \frac{e}{2mc}\,\underline{H}\cdot\underline{L} = \frac{\hbar eH}{2imc}\frac{\partial}{\partial\phi} \\
\mathcal{H}_{o2} &= \frac{e^2}{8mc^2}\left[H^2r^2 - (\underline{H}\cdot\underline{r})^2\right] = \frac{e^2H^2r^2}{8mc^2}\sin^2\theta \\
\mathcal{H}_{1o} &= e\,\underline{E}\cdot\underline{r} = eEr\begin{cases}\cos\theta - \parallel \text{ fields}\\ \sin\theta\cos\phi - \perp \text{ fields}\end{cases} \\
&= eEr\,P(\theta,\phi)
\end{aligned} \tag{2-123}$$

The components of ψ, which are eigenfunctions of the components of the Hamiltonian that are considered are (unnormalized)

$$\begin{aligned}
\psi_{oo} &= \exp(-r) \\
\psi_{o1} &= 0 \\
\psi_{1o} &= -\tfrac{1}{2}e^{-1}a^2E\,(r^{1^2} + 2r^1)\exp(-r^1)\,P(\theta,\phi) \\
\psi_{2o} &= \frac{1}{48}e^{-2}a^4E^2\left\{(2r^{1^3} + 21r^{1^2}) + (6r^{1^4} + 30r^{1^3} + 45r^{1^2})P^2(\theta,\phi)\right\}\exp(-r^1) \\
\psi_{11} &= \begin{cases}0 \text{ (parallel fields)}\\ \dfrac{ia^4EH}{24\hbar c}(2r^{1^3} + 11r^{1^2} + 22r^1)\exp(-r^1)\sin\theta\sin\phi \text{ (perpendicular fields)}\end{cases}
\end{aligned} \tag{2-124}$$

where $r^1 = \frac{r}{a}$ and a is the Bohr radius (= .529A°).

The current density vector $\underline{j}$ is written (see Section C, equation (2-47))

$$\underline{j} = -\frac{e^2}{2mcN}(\underline{H} \times \underline{r})\psi^*\psi - \frac{e\hbar}{2miN}\left\{\psi^* \underline{\nabla}\psi - \psi \underline{\nabla}\psi^*\right\} \quad (2\text{-}47)$$

where $$N = \int \psi^* \psi \, d\tau.$$

This in turn gives rise to a magnetic field

$$\underline{H}^1 = \int \frac{\underline{r} \times \underline{j}}{cr^3} \, d\tau \quad (2\text{-}125)$$

Marshall and Pople then write the secondary field

$$\underline{H}^1 = \underline{H}_1^1 + \underline{H}_2^1 \quad (2\text{-}126)$$

corresponding to the two parts of $\underline{j}$. The first part leads to the diamagnetic term in the general theory of Ramsey (see Section C, part 2). This is given by (see equation (2-37))

$$\sigma^d = \frac{e^2}{2mc^2} \int \frac{\rho \sin^2\theta}{r} \, d\tau \quad (2\text{-}37)$$

where ρ is the electron density in the absence of a magnetic field. In the present situation

$$\rho = \frac{\psi^2}{\int \psi^2 d\tau} = \frac{\psi_{oo}^2 + 2\psi_{oo}\psi_{1o} + 2\psi_{oo}\psi_{2o} + \psi_{1o}^2 + \cdots}{\int (\psi_{oo}^2 + 2\psi_{oo}\psi_{1o} + \cdots) \, d\tau} \quad (2\text{-}127)$$

Using equations (2-124), (2-127) and (2-37) and carrying the expansion of σ^d in E as far as E^2, Marshall and Pople obtain

$$\sigma_{11}^d = \frac{e^2}{3mc^2a}\left[1 - \frac{439}{40}\frac{a^4E^2}{e^2}\right]$$
$$\sigma_{\perp}^d = \frac{e^2}{3mc^2a}\left[1 - \frac{641}{80}\frac{a^4E^2}{e^2}\right] \quad (2\text{-}128)$$

The paramagentic contribution, σ^p, is then evaluated from the second term in the expression for ~~j~~, equation (2-47). Since the component of $\underline{r} \times \nabla$ in the direction of $\underline{H}$ is $\frac{\partial}{\partial \phi}$, the corresponding part of the secondary magnetic field is

$$H_2^1 = - \frac{e\hbar}{2mcNi} \int \left(\psi^* \frac{\partial \psi}{\partial \phi} - \psi \frac{\partial \psi^*}{\partial \phi} \right) \frac{1}{r^3} \, d\tau \qquad (2\text{-}129)$$

which on substitution becomes

$$H_2^1 = \frac{2e\hbar}{mcNi} \int \psi_{11} \frac{\partial \psi_{1o}}{\partial \phi} \frac{1}{r^3} \, d\tau \qquad (2\text{-}130)$$

Substituting for ψ_{11} and ψ_{1o} and evaluating σ^p up to terms in E^2, Marshall and Pople obtain

$$\begin{aligned} \sigma_{11}^p &= 0 \\ \sigma_{\perp}^p &= \frac{-233}{144} \frac{a^3 E^2}{mc^2} \end{aligned} \qquad (2\text{-}131)$$

Combining equations (2-128) and (2-131), they obtain

$$\begin{aligned} \sigma_{11} &= \frac{e^2}{3mc^2 a} \left[1 - \frac{439}{40} \frac{a^4 E^2}{e^2} \right] \\ \sigma_{\perp} &= \frac{e^2}{3mc^2 a} \left[1 - \frac{193}{15} \frac{a^4 E^2}{e^2} \right] \end{aligned} \qquad (2\text{-}132)$$

On comparing equation (2-132) with the Lamb formula, equation (2-39), one sees that the magnetic screening of the nucleus by the electrons is reduced in all directions by the application of a uniform electric field, the reduction being greatest when the magnetic field is perpendicular to the electric field. This lowering of the screening constant is only partly due to the paramagnetic term, for the diamagnetic Lamb term is also reduced. This corresponds to the partial removal of

electrons from the vicinity of the nucleus by the electric field and the consequent reduction of the mean value of $\frac{1}{r}$.

Buckingham (35) extended the theory to the situation where the resonant nucleus is not at the molecular centre of inversion. He argues that under these circumstances the screening for a fixed orientation of the molecule may be affected by a reversal of E_z, so that in weak electric fields σ may be proportional to E_z rather than E_z^2. If E_z is a fixed external field, the shielding proportional to E_z averages to zero in a gas or a liquid, but if E_z arises from a polar group from within the molecule itself, or from neighbouring solvent molecules polarized by the solute, then the mean value of E_z at a particular nucleus may be non-zero. A shielding constant proportional to E_z as well as E_z^2 is, therefore, possible.

In the presence of a primary uniform magnetic field $\underline{H}$, there will be at a particular nucleus an induced secondary field $\underline{H}^1$, and the screening constant tensor $\sigma_{\alpha\beta}$ for this nucleus is defined by

$$H^1_\alpha = \sigma_{\alpha\beta} H_\beta \qquad (2\text{-}133)$$

A uniform electric field $\underline{E}$ will perturb the electron distribution, and therefore, $\sigma_{\alpha\beta}$ will be a function of $\underline{E}$. Buckingham supposes that $\sigma_{\alpha\beta}$ is affected in such a way that it can be expanded in a power series in E

$$\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^{(0)} + \sigma_{\alpha\beta\gamma}^{(1)} E_\gamma + \tfrac{1}{2} \sigma_{\alpha\beta\gamma\delta}^{(2)} E_\gamma E_\delta \; t\ldots \qquad (2\text{-}134)$$

If the molecule is symmetric in x (that is, if $\sigma_{\alpha\beta}$ is unaffected by an inversion in the YZ plane), then $\sigma^{(1)}_{\alpha\beta X} = 0$, that is σ will not depend

on the direction of E with respect to the YZ plane (see reference 36). Thus $\sigma^{(1)} = 0$ for an atom in a molecule which is symmetric about the Z axis (an X-H bond is usually approximately symmetric about the bond direction).

The observed screening constant σ for a molecule in a gas or liquid corresponds to an average of $\sigma_{\alpha\beta}$ over all orientations and hence

$$\langle \sigma \rangle_{AV} = \frac{1}{3}\sigma_{\alpha\alpha} = \frac{1}{3}\left\{ \sigma_{\alpha\alpha}^{(0)} + \sigma_{\alpha\alpha\gamma}^{(1)} E_\gamma + \frac{1}{2}\sigma_{\alpha\alpha\gamma\delta} E_\gamma E_\delta + \cdots \right\} \quad (2\text{-}135)$$

Buckingham then considers an atom in an S state (spherically symmetric, and, therefore $\sigma^{(1)} = 0$) in order to apply equation (2-135) to the equation of Marshall and Pople, equation (2-132). For an atom in an S state in a uniform electric field in the Z direction, there will be two independent $\sigma^{(2)}$ tensor components. Equation (2-134) gives

$$\sigma_{zz} = \sigma^{(0)} + \frac{1}{2}\sigma_{zzzz} E_z^2 + \cdots$$

and (2-136)

$$\sigma_{xx} = \sigma_{yy} = \sigma^{(0)} + \frac{1}{2}\sigma_{xxzz} E_z^2 \cdots$$

whence from equation (2-132)

$$\sigma^{(0)} = \frac{e^2}{3mc^2 a}$$

$$\sigma_{zzzz}^{(2)} = \sigma_{11}^{(2)} = -\frac{439}{60}\frac{a^3}{mc^2} \quad (2\text{-}137)$$

and

$$\sigma_{xxzz}^{(2)} = \sigma_{\perp}^{(2)} = -\frac{386}{45}\frac{a^3}{mc^2}$$

The $\sigma^{(2)}$ tensor may be generalized to

$$\sigma^{(2)}_{\alpha\beta\gamma\delta} = \sigma_{\perp}{}^{(2)}\delta_{\alpha\beta}\delta_{\gamma\delta} + \frac{1}{2}(\sigma^{(2)}_{ll} - \sigma_{\perp}{}^{(2)})(\delta_{\alpha\gamma}\,\delta_{\beta\delta} + \delta_{\alpha\delta}\,\delta_{\beta\gamma}) \quad (2\text{-}138)$$

where $\delta_{\alpha\beta}$ is the substitution tensor (= 1 if $\alpha = \beta$, = 0 if $\alpha \neq \beta$).

In an axially symmetric X - H bond there is no screening proportional to the first power of the field at right angles to the bond (symmetry demands that screening be independent of the direction of E with respect to the XZ or YZ plane). Thus, $\sigma^{(1)}_{\alpha\beta x} = \sigma^{(1)}_{\alpha\beta y} = 0$. But, these will be components of $\sigma^{(1)}$ for fields parallel to the Z axis and on rotational averaging one obtains from equation (2-135) the two independent $\sigma^{(1)}$ tensors

$$\sigma^{(1)}_{zzz} = \sigma^{(1)}_{ll}$$

and (2-139)

$$\sigma^{(1)}_{xxz} = \sigma_{yyz}{}^{(1)} = \sigma^{(1)}_{\perp}.$$

Thus

$$\sigma = \sigma^{(0)} + \sigma^{(1)}E_z + \frac{1}{2}\sigma^{(2)}E^2 + \ldots \quad (2\text{-}140)$$

where

$$\sigma^{(0)} = \frac{1}{3}(\sigma_{ll}{}^{(0)} + 2\sigma_{\perp}{}^{(0)}) \quad (2\text{-}141)$$

and

$$\sigma^{(1)} = \frac{1}{3}(\sigma_{ll}{}^{(1)} + 2\sigma_{\perp}{}^{(1)}) \quad (2\text{-}142)$$

due to rotational averaging.

Buckingham then considers a model in which a hydrogen atom is at a distance R from a point change λ. In the presence of a uniform electric field $\underline{E}$, the total electric field $\underline{F}$ acting on the atom is

$$\underline{F} = \left\{E_x,\ E_y,\ E_z + \left(\frac{\lambda}{R}\right)^2\right\} \quad (2\text{-}143)$$

From equation (2-134) the screening constant is

$$\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^{(0)} + \sigma_{\alpha\beta\gamma}^{(1)} F_\gamma + \frac{1}{2} \sigma_{\alpha\beta\gamma\delta} F_\gamma F_\delta + \cdots \qquad (2\text{-}144)$$

$\sigma^{(1)} = 0$ for this model (that is, for a hydrogen atom). Substituting equation (2-138) into equation (2-144) thus, gives

$$\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^{(0)} + \frac{1}{2}\left\{\sigma_\perp^{(2)} \delta_{\alpha\beta}\delta_{\gamma\delta} F_\gamma F_\delta + \frac{1}{2}(\sigma_{11}^{(2)} - \sigma_\perp^{(2)})(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma})F_\gamma F_\delta\right\}$$

$$= \sigma_{\alpha\beta}^{(0)} + \frac{1}{2}\left\{\sigma_\perp^{(2)} \delta_{\alpha\beta} F^2 + \frac{1}{2}(\sigma_{11}^{(2)} - \sigma_\perp^{(2)})(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma})F_\gamma F_\delta\right\} \qquad (2\text{-}145)$$

Substituting for $\sigma_\perp^{(2)}$ and $\sigma_{11}^{(2)}$ from equation (2-137) gives

$$\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^{(0)} + \frac{1}{2} \frac{a^3}{mc^2}\left\{-\frac{386}{45}\delta_{\alpha\beta}F^2 + \frac{1}{2}\left(\frac{454}{360}\right)(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma})F_\gamma F_\delta\right\} \qquad (2\text{-}146)$$

Since the average value of σ consists only of components where $\alpha = \beta$, equation (2-146) becomes

$$\sigma_{\alpha\beta} = \frac{e^2}{3mc^2 a} - \frac{1510}{360}\frac{a^2 F^2}{mc^2} \qquad (2\text{-}147)$$

on substitution for $\sigma_{\alpha\beta}^{(0)}$ and choosing $\alpha = \beta$ and $\gamma = \delta$.

Because of the form of $\underline{F}$, equation (2-147) leads to screening proportional to E_z and E^2, and it can be shown that

$$\sigma_{11}^{(1)} = \frac{\lambda}{R^2}\sigma_{11}^{(2)}$$

and $\qquad (2\text{-}148)$

$$\sigma_\perp^{(1)} = \frac{\lambda}{R^2}\sigma_\perp^{(2)}$$

Thus, equation (2-140) becomes

$$\sigma = \sigma^{(0)} + \sigma^{(1)} E_z + \frac{1}{2}\sigma^{(2)} E^2 + \cdots \qquad (2\text{-}140)$$

where

$$\sigma^{(0)} = \frac{1}{3}\left(\sigma_{11}^{(0)} + 2\sigma_{\perp}^{(0)}\right) = \frac{e^2}{3mc^2 a}$$

$$\sigma^{(1)} = \frac{1}{3}\left(\sigma_{11}^{(1)} + 2\sigma_{\perp}^{(1)}\right) = \frac{1}{3}\,\frac{\lambda}{R^2}\left(\sigma_{11}^{(2)} + 2\sigma_{\perp}^{(2)}\right) = \frac{-881}{108}\,\frac{\lambda}{R^2}\,\frac{a^3}{mc^2} \qquad (2\text{-}149)$$

and

$$\sigma^{(2)} = \frac{1}{3}\left(\sigma_{11}^{(2)} + 2\sigma_{\perp}^{(2)}\right) = \frac{-881}{108}\,\frac{\lambda}{R^2}\,\frac{a^3}{mc^2}$$

Buckingham chooses the parameters $\lambda = 10^{-10}$ e.s.u. and $R = 10^{-8}$ cm., whence equation (2-140) becomes

$$\sigma = 2 \times 10^{-5} - 2 \times 10^{-12} E_z - 10^{-18} E^2 \ldots \qquad (2\text{-}150)$$

This may be rewritten

$$\sigma = 2 \times 10^{-5} - 2 \times 10^{-12} E \cos\theta - 10^{-18} E^2 \ldots \qquad (2\text{-}151)$$

where θ is the angle between the field and the X-H bond axis.

When a polar molecule is dissolved it polarizes the surrounding medium, and this polarization leads to an electric field - the "reaction field" - at the solute. If the molecule is sufficiently symmetrical the mean reaction field is parallel and proportional to the dipole moment. The total dipole moment is given by

$$\underline{M} = \underline{\mu} + \alpha \underline{R} \qquad (2\text{-}152)$$

where $\underline{\mu}$ is the permanent dipole moment of the isolated solute molecule, α is the polarizability of the solute molecule and $\underline{R}$ is the reaction field.

Many attempts have been made to evaluate the reaction field of a dipole. The most useful model (37), the Onsager model, represents the molecule as a sphere of a certain radius a, with a point dipole moment $\underline{\mu}$ at the centre and represents the medium as a continuum of

uniform dielectric constant ϵ . Basically, the method consists of calculating the work done in transferring an isolated, polar, spherical molecule to a spherical cavity in the continum.

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

$$\underline{R} = \frac{2(\epsilon - 1)}{2\epsilon + 1} \quad \frac{\underline{m}}{a^3} \tag{2-153}$$

The polarizability of a sphere, as given by the Clausius - Mossotti equation, is

$$\alpha = \frac{n^2 - 1}{n^2 + 2} \; a^3 \tag{2-154}$$

where n is the refractive index of the solute for the Na - D line. Hence

$$\underline{R} = \frac{2(\epsilon - 1)}{2\epsilon + 1} \quad \frac{\underline{\mu} + \alpha \underline{R}}{\frac{n^2 + 2}{n^2 - 1}\,\alpha} \tag{2-155}$$

Solving for $\underline{R}$ and simplifying gives

$$\underline{R} = \frac{2(\epsilon - 1)(n^2 - 1)}{3(2\epsilon + n^2)} \quad \frac{\underline{\mu}}{\alpha} \tag{2-156}$$

For most solutes $n \sim 1.5$ and hence the expression reduces to

$$\underline{R} = \frac{\epsilon - 1}{2\epsilon + 2.5} \quad \frac{\underline{\mu}}{\alpha} \tag{2-157}$$

Substituting this expression into equation (2-151) gives

$$\sigma_E = -2 \times 10^{-12} \left[\frac{(\epsilon - 1)}{(2\epsilon + 2.5)}\right] (\mu \cos\theta/\alpha) - 10^{-18} \left[\frac{(\epsilon - 1)}{(2\epsilon + 2.5)}\right]^2 \left(\frac{\mu^2}{\alpha^2}\right) \tag{2-158}$$

where θ is the angle between the direction of $\underline{\mu}$ and the direction of the X-H bond. When cos θ is positive, increasing the dielectric constant

of the solvent will tend to shift the proton signals from polar molecules to lower fields.

Buckingham (35) tested equation (2-158) by applying it to a 50:50 cyclohexane - nitrobenzene mixture. The calculated shifts for the ortho, meta and para protons of nitrobenzene were in very good qualitative agreement with the experimental results. The model was then applied to di- and trisubstituted benzenes in CCl_4 with similar good agreement.

G- THE EFFECTS OF DISPERSION INTERACTIONS - σ_W

For non-polar solvents of the type generally used in N.M.R., the van der Waals attraction forces are generally attributed to two types of long range interactions:

(1) interactions between permanent (solute) and induced-dipoles (induction effect); and

(2) interactions arising form the mutual polarization of electron clouds of neighbouring atoms or molecules (dispersion effect).

The dispersion effect is, by far, the most important constituent of the van der Waals interaction. It generally outweighs the induction effect, and is in the absence of permanent dipoles the sole contribution to the total attractive force.

The induction effect has already been treated in this thesis in Section F of this chapter. Expressions for the effect of the dispersion interaction on the chemical shift arose chiefly due to the work of Linder, Howard and Emerson (38,39).

Linder et. al. attempt to extend the Onsager model to non-polar molecules by treating the non-polar molecules as oscillating dipoles. If placed at the centre of an Onsager cavity this oscillating dipole sets up an oscillating electric field which induces oscillating dipoles in the surrounding medium. The induced oscillating dipoles in turn set up oscillating electric fields which interact with the oscillating dipole at the centre of the Onsager cavity. Linder approaches the

problem by considering this interaction.

If $\underline{M}_{ok}$ represents the transition probability from the o^{th} to the k^{th} state

$$\underline{M}_{ok} = \int \phi_o \, e \, \underline{r} \, \phi_k \, d\tau \qquad (2\text{-}159)$$

where ϕ_o and ϕ_k are the wave functions describing the o^{th} and the k^{th} state, respectively, then the polarizability of the molecules in the medium surrounding the Onsager cavity (see for example reference 40) is

$$\alpha^* = \frac{2}{3} \sum_k \frac{|\underline{M}_{ok}| \, (E_k - E_o)}{(E_k - E_o)^2 - (h\nu)^2} \qquad (2\text{-}160)$$

The asterisk serves to indicate that the polarizability is not static.

The "centre" molecule is assumed to have a moment $\underline{M}$ with a frequency of oscillation ν_i — denoted $\underline{M}(\nu_i)$. This moment gives rise to an electric field at a distance $\underline{r}_k$ from the centre, which may be written (41)

$$\underline{E}_k = (3 \, \underline{M}(\nu_i) \cdot \underline{r}_k / r_k^5) \, \underline{r}_k - (\underline{M}(\nu_i) / r_k^3) \qquad (2\text{-}161)$$

This field will fluctuate with the same frequency as $\underline{M}(\nu_i)$ and induce a moment in each molecule of which the dielectric (surrounding medium around the Onsager cavity) is composed.

For the k^{th} molecule the moment is

$$\underline{M}_k = \alpha_k^* \, \underline{E}_k \qquad (2\text{-}162)$$

If all the molecules of the dielectric medium have the same frequency, say ν_j, then the induced moment of the k^{th} molecule is

$$\underline{M}_k = \alpha_j \, \underline{E}_k \left[\frac{\nu_j^2}{(\nu_j^2 - \nu_i^2)} \right] \qquad (2\text{-}163)$$

where

$$\alpha_j = \frac{2}{3} \left|\underline{M}_{ok}\right|^2 / (E_k - E_o) \qquad (2\text{-}164)$$

Each moment $\underline{M}_k$ gives rise to a field $\underline{E}_k^1$ at the centre of the Onsager cavity, which can be represented by

$$\underline{E}_k^1 = \left\{ \left(\frac{3\alpha_j \underline{E}_k \cdot \underline{r}_k}{r_k^5}\right) \underline{r}_k - \left(\frac{\alpha_j \underline{E}_k}{r_k^3}\right) \right\} \times \left[\frac{\nu_j^2}{(\nu_j^2 - \nu_i^2)}\right] \qquad (2\text{-}165)$$

The resultant field $\sum_k \underline{E}_k^1$ is the analogue of the reaction field of a static dipole and is denoted by the symbol $\underline{R}^*$. If $\nu_i \longrightarrow 0$ the frequency drops out and the resultant field $\sum_k \underline{E}_k^1$ ($\nu_i = 0$) is simply the reaction field of a static dipole moment $\underline{M}$ ($\nu_i = 0$):

$$\underline{R} = \sum_k \underline{E}_k^1 \ (\nu_i = 0) = g_j \ \underline{M} \ (\nu_i = 0) \qquad (2\text{-}166)$$

where from equation (2-153)

$$g = \left[\frac{2(\epsilon - 1)}{(2\epsilon + 1)}\right] \left(\frac{1}{a^3}\right) \qquad (2\text{-}167)$$

Comparison of equations (2-165) and (2-166) gives

$$\underline{R}^* = g_j \underline{M} (\nu_i) \left[\frac{\nu_j^2}{(\nu_j^2 - \nu_i^2)}\right] \qquad (2\text{-}168)$$

The work obtained in bringing a sphere inside the dielectric is obtained by coupling $\underline{M}(\nu_j)$ with $\underline{R}^*$ and is

$$W = -\frac{1}{2} M^2 (\nu_i) \ g_j \left[\frac{\nu_j^2}{(\nu_j^2 - \nu_i^2)}\right] \qquad (2\text{-}169)$$

or, if $M^2(\nu_i)$ is replaced by the average square of the dipole moment (which is a function of ν_i)

$$W = -\frac{1}{2} \left\langle M^2(\nu_i) \right\rangle_{AV} g_j \left[\frac{\nu_j^2}{(\nu_j^2 - \nu_i^2)} \right] \qquad (2\text{-}170)$$

However, equation (2-170) is really an oversimplification of the true situation because in the solution the molecules perturb each other sufficiently so as to give rise to a range of frequencies, even though the molecules may all have the same frequency in empty space. Thus the uniquely defined frequencies ν_i and ν_j should be replaced by a distribution of frequencies (even though the average frequency may be close to the natural frequency of a single oscillator). Thus equation (2-170) is rewritten

$$W = -\frac{1}{2} \iint \rho(\nu_i)\, \rho(\nu_j) \left\langle M^2(\nu_i) \right\rangle_{AV} g_j \left[\frac{\nu_j^2}{(\nu_j^2 - \nu_i^2)} \right] d\nu_i d\nu_j \qquad (2\text{-}171)$$

where $\rho(\nu_i)$ and $\rho(\nu_j)$ are the distribution functions of the frequencies of the "centre" sphere and the dielectric medium. This formula is not applicable when $\nu_i = \nu_j$, but the probability that this will occur is small.

The nature of equation (2-171) is such that it exhibits complete reciprocal character for there is a term $\left\langle M^2(\nu_i) \right\rangle_{AV} g_j \left[\frac{\nu_j^2}{(\nu_j^2 - \nu_i^2)} \right]$ for every term $\left\langle M^2(\nu_j) \right\rangle_{AV} g_i \left[\frac{\nu_i^2}{(\nu_i^2 - \nu_j^2)} \right]$ and vice versa.

For the ground state of a quantum mechanical oscillator

$$\left\langle M^2(\nu_i) \right\rangle_{AV} = \frac{3}{2} h \nu_i \alpha_i \qquad (2\text{-}172)$$

where h is Planck's constant. Substituting equation (2-172) into equation (2-171) gives

$$W = -\frac{3}{4} h \iint \rho(\nu_i)\, \rho(\nu_j) \nu_i\, \alpha_i\, g_j \left[\frac{\nu_j^2}{(\nu_j^2 - \nu_i^2)}\right] d\nu_i d\nu_j \quad (2\text{-}173)$$

which due to the reciprocal nature described above, may be written as

$$W = -\frac{3}{8} h \iint \rho(\nu_i)\, \rho(\nu_j)\, \alpha_i\, g_j \left[\frac{\nu_i\, \nu_j}{(\nu_i + \nu_j)}\right] d\nu_i\, d\nu_j \quad (2\text{-}174)$$

In the limit of infinite dilution when a solute molecule is surrounded only by solvent molecules, equation (2-174) becomes (39)

$$W = -\frac{3}{8} h \alpha g \left[\frac{\nu_1\, \nu_2}{(\nu_1 + \nu_2)}\right] \quad (2\text{-}175)$$

or

$$W = -\frac{1}{4} \left\langle M_2^2 \right\rangle g \left[\frac{\nu_1}{(\nu_1 + \nu_2)}\right] \quad (2\text{-}176)$$

where 1 and 2 refer to solvent and solute respectively and ν is a mean absorption frequency. The radius of the solute molecule, a_2, should be used in the expression for g (equation (2-167)).

Linder considers the previously described treatment of Marshall and Pople, which is for a static electric field $\underline{E}$. The potential energy of a non-polar molecule in a static field $\underline{E}$ is

$$W = -\int_0^E \alpha_2 E\, d E = -\frac{1}{2} \alpha_2 E^2 \quad (2\text{-}177)$$

Combining equations (2-176) and (2-177) gives for the equivalent static electric field acting on the molecule which would give the same free energy

$$E^2 = \frac{1}{2} \frac{\langle M_2^2 \rangle_{AV}\, g}{\alpha_2} \left[\frac{\nu_1}{(\nu_1 + \nu_2)} \right] \qquad (2\text{-}178)$$

and since

$$\langle M^2 \rangle_{AV} = \frac{3}{2} h \nu \alpha \qquad (2\text{-}172)$$

Linder gets

$$E^2 = \frac{3}{4} h g \left[\frac{\nu_1 \nu_2}{(\nu_1 + \nu_2)} \right] \qquad (2\text{-}179)$$

Marshall and Pople (see equation (2-132) showed that

$$\sigma_E = \phi E^2 \qquad (2\text{-}180)$$

where for a bound hydrogen atom Buckingham (see equation (2-151)) showed that

$$\phi = -1 \times 10^{-12} \text{ cm}^2 \text{ e.s.u.}^{-1} \text{p.p.m.} \qquad (2\text{-}181)$$

Combining equations (2-179) and (2-180) gives

$$\sigma_W = \frac{3}{4} \phi h g \left[\frac{\nu_1 \nu_2}{(\nu_1 + \nu_2)} \right] \qquad (2\text{-}182)$$

ν_1 and ν_2 may be calculated if the bulk diamagnetic susceptibilities, X, of the solvent and solute are known. It may be shown (42) that

$$\langle M^2 \rangle_{AV} = \left(\frac{6mec^2}{N} \right) X \qquad (2\text{-}183)$$

where N is Avagadro's number and the other terms are as previously defined and hence by the use of equations (2-183) and (2-172), ν may be calculated.

Linder et al (38) tested equation (2-182) by plotting corrected experimental gas to solvent shifts against the square of the effective dispersion field for methane and cyclopentane in various solvents. A rough linear correlation was observed, the deviations being greatest for highest values of E^2.

CHAPTER III

- Specific Molecular Interactions -

A- INTRODUCTION*

1. The Aromatic Solvent Induced Shift

Due to the large anisotropy in the susceptibility of benzene (see Chapter II), protons situated near the symmetry axis of the benzene ring resonate at higher fields than ordinary ethylenic protons. Thus the resonance positions of the various types of protons of any particular compound, when that compound is dissolved in benzene, will usually appear to high field of the resonance positions of the same protons when the compound is dissolved in an "inert", non-anisotropic solvent such as cyclohexane or neopentane. This upfield shift caused by the benzene solvent is known as the "aromatic solvent induced shift", abbreviated ASIS. The ASIS is often referred to as $\Delta\delta$ or just Δ.

2. The 1:1 Complex

When an internal reference is used one would expect no net ASIS because the resonance position of the reference should experience the same ASIS as the solute protons. However, for certain types of compounds even when an internal reference is used, a net ASIS is observed. Schneider and Schaefer (44,45) were the first to present an explanation for this phenomenon. With respect to the ASIS of acetonitrile, Schneider wrote:

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* See reference 43 from which most of Chapter III finds its substance.

"The most probable explanation of this is one which involves an induced dipole interaction with the benzene. Acetonitrile has a large dipole moment, the negative end of which is concentrated mainly in the N atom. This will be repelled by the π - electron distribution of the benzene and will tend to be off the ring. Since benzene has a large polarizability in the plane of the ring, a dipole is induced (as is shown in Figure 6 of this thesis) and the resulting attraction will tend to locate the CH_3 group of the acetonitrile over the aromatic ring.

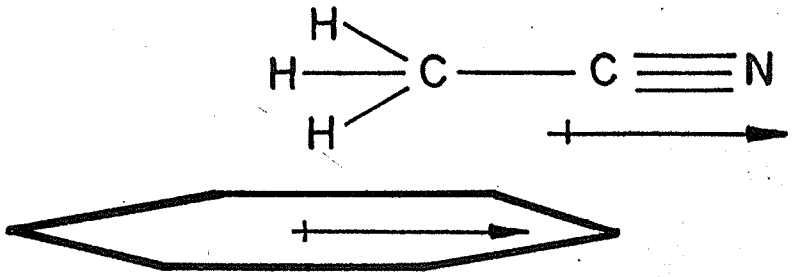


Figure 6: Interaction of Acetonitrile with the Benzene π Electrons.

In this orientation the ring current effect will then cause a pronounced high-field shift of the acetonitrile proton resonance. Now if there were no specific interaction between benzene and acetonitrile involving preferred mutual orientations of these molecules, i.e. if we had complete randomization of this system, both the acetonitrile and the reference

neopentane molecules would experience the same environment due to the solvent benzene. To a first approximation both should be affected in the same way by the magnetic anisotropy of the benzene solvent. The observed high-field shift of the acetonitrile leads us to conclude there is a preferred mutual interaction between benzene and acetonitrile."

The net ASIS is then explained in terms of equation (3-1) (see equation (2-1))

$$\delta\left(\begin{matrix}\text{benzene}\\ \text{solution}\end{matrix}\right) - \delta\left(\begin{matrix}\text{neopentane}\\ \text{solution}\end{matrix}\right) = \Delta\delta = \delta_A + \delta_W + \delta_E + \delta_C \qquad (3\text{-}1)$$

Here δ_A is the shift due to the magnetic anisotropy effects of the benzene solvent, δ_W is the shift arising from the different van der Waals interaction of the solute with neopentane and with benzene, δ_E is the shift due to the difference in the reaction field effects associated with the two solvents and δ_C is the shift due to specific molecular interaction or complex formation in the benzene solution. Schneider assumes terms δ_W and δ_E are small and, therefore, neglects them. If $\delta_C = 0$ then $\delta_A = 0$ for reasons explained above. If $\delta_C \neq 0$, then $\delta_A \neq 0$ and the quantity measured is then $\Delta\delta = \delta_A + \delta_C$. δ_C is generally negative, and since for acetonitrile in benzene $\Delta\delta$ is a large positive quantity, $\delta_A \gg \delta_C$. In other words small proton chemical shifts of solute molecules resulting from specific complex formation with benzene molecules are effectively "amplified" because of the large magnetic anisotropy of the solvent molecules.

In three studies Klinck and Stothers (46-48) have produced strong evidence that the benzene solvent molecule acts as an electron donor to an electron deficient region in the solute molecule. In their

study of parasubstituted benzaldehydes, for example, they find that the parent grouping experiences an increased shielding as the electronic character of the substituent is changed progressively from a strongly electron-releasing type to a strongly electron-withdrawing species. In addition, those substituents bearing protons show the expected trend in that the shielding decreases as the electron releasing power diminishes. They attribute this to the fact that strong electron-withdrawing substituents aid association at the carbon bearing the formyl proton since this carbon would be expected to be slightly positive. At the other limit, strong electron-donating substituents would be slightly positive and thus would attract the solvent molecule preferentially.

Ronayne and Williams (49) upon studying the ASIS for certain steroids concluded that "the plane of the aromatic ring is steeply inclined with respect to the plane of the steroid molecule. In this way the region of high π - electron density in the benzene can interact with the electron - deficient site with a minimum of steric interference." In the same paper, from a consideration of the chemical shifts of the various protons of 1 - iodobutane, they concluded that although the α - CH_2 would provide the main site for the solvation in terms of the above hypothesis, one would also expect some solvation at more distant sites which would also be electron deficient. They thus postulate an association at each electron-deficient site in a polyfunctional compound, that is, local dipole - induced dipole interactions. They support their argument by referring to the large ASIS experienced by parabenzoquinone.

Although the total net dipole for this compound is zero, there will be local dipoles at each carbonyl group and the benzene solvent molecule is pictured as forming a 1:1 complex at each of these positions. They also support their argument by reference to certain concentration and temperature studies, which will be discussed later in this chapter. With respect to aromatic compounds they conclude that the concept of stoichiometry becomes now less meaningful because a partial positive charge may be extensively delocalized.

3. Steric Effects

To test the existence of a 1:1 complex between a polar solute and an aromatic solvent it has been proposed by several authors that hindrance of this association by steric congestions of either member of the pair would be expected to lead to decreased solvent shifts.

Diehl (50) established that there is a reduction in the magnitude of the ASIS of about .7 upon the ring protons meta or para to the substituent in mesitylenes and durenes, compared with the monosubstituted benzenes.

Williams, Ronayne and Wilson (51) while considering non-polar solutes postulated that if the proton being studied is sterically hindered in comparison to the non-hindered T.M.S. protons, then the T.M.S. resonance should experience a higher ASIS than the solute proton resonance. This should lead to a net downfield solvent shift. This was indeed found to be so; benzene experienced a positive Δ on passing from

C_6H_{12} to C_6D_6 as solvent whereas p - xylene, mesitylene, 1,4-di-t-butylbenzene and 1,3,5,-tri-t-butylbenzene all experienced a negative Δ, the magnitude of which increased as the steric hindrance of the solute increased.

The general approach to the investigation of steric effects has been to use polymethylsubstituted benzenes as solvents. Hatton and Richards (52) noted that the ASIS of the methyl resonances of dimethyl formamide generally decreased with increasing molar volume of the solvent (benzene, toluene, p-xylene, t-butylbenzene and mesitylene).

Brown and Stark (53) noted a decrease in the ASIS for the organometallic compounds they studied, in the order

benzene $>$ toluene $>$ mesitylene

Laszlo (43) claims that the steric interpretation is, in fact, erroneous. For example, Connolly and McCrindle (54) found that although the geminal methyls of the ketone derived from caryophyllene alcohol and the geminal methyls of camphor strongly hinder the approach of benzene molecules to the rear of the carbonyl in the formation of a preferred collision complex, they, in both cases, show appreciable upfield shifts. Also the benzene shifts of simple methylcyclohexanones are almost identical to those for much more hindered steroidal ketones. There are even examples where the ASIS is slightly increased with the donor aptitude of the solvent towards polar solutes as are the formyl resonances of the parasubstituted benzaldehydes studied by Klinck and Stothers (47). The author of this thesis feels that Laszlo's criticism is subject to discussion.

4. Concentration Studies

Bowie, Ronayne and Williams (55) postulated that if a 1:1 complex existed, a plot of Δ vs the mole fraction of benzene in an inert solvent should yield a straight line. This hypothesis was tested by plotting Δ for the methoxyl resonance of p-nitroanisole vs the mole fraction of benzene in CCl_4. A reasonably straight line was obtained, at least much more linear than that obtained in the plot of Δ vs the square of the mole fraction.

Ronayne and Williams (49) in support of their hypothesis of a 1:1 complex at each polar functional group state that the dilution curve will be independent of the number of sites of association provided that there exists no phase relationship between the various 1:1 associations. This is because the net dilution curve is a superimposition of the dilution curves for each independent site.

Klinck and Stothers (47) in their previously mentioned study of parasubstituted benzaldehydes plotted the chemical shifts for the N-methyl and formyl protons of p-NMe_2 - and p-NO_2-benzaldehydes, respectively, in chloroform - benzene mixtures. The curves were approximately linear and parallel. Klinck and Stothers concluded that "clearly the causes for these parallel shifts can be assumed to be similar".

Foster and Fyfe (56) developed a technique for the determination of the association constants of the organic charge-transfer complexes by N.M.R. The same idea can be applied to the benzene complexes now

under discussion. Given the equilibrium

$$\text{acceptor} + \text{donor} \rightleftharpoons \text{complex} \tag{3-2}$$

the association constant is

$$K = \frac{(A\,D)}{(A)\,(D)} \tag{3-3}$$

where (A), (D) and (A D) are respectively the concentrations of the acceptor, the donor and the complex. Now

$$(A) = \alpha\, A_o \tag{3-4}$$

$$(D) = D_o - \beta\, A_o \tag{3-5}$$

$$(AD) = \beta\, A_o \tag{3-6}$$

where α is the fraction of solute (acceptor) existing as monomer, β is the fraction of solute existing as complex, A_o is the initial solute monomer concentration and D_o is the initial solvent monomer concentration. Thus

$$K = \frac{\beta\, A_o}{\alpha\, A_o(D_o - \beta\, A_o)} = \frac{\beta}{\alpha\,(D_o - \beta\, A_o)} \tag{3-7}$$

If $D_o \gg A_o$, equation (3-7) becomes

$$K = \frac{\beta}{\alpha\, D_o} \tag{3-8}$$

Thus

$$\beta = K\,\alpha\, D_o \tag{3-9}$$

Now

$$\delta_{OBS} = \alpha\, \delta_A + \beta\, \delta_{AD} \tag{3-10}$$

where δ_{OBS} is the observed chemical shift, δ_A is the chemical shift of

pure solute monomer and δ_{AD} is the chemical shift of pure complex.

Thus

$$\Delta = \delta_{OBS} - \delta_A = (\alpha - 1)\,\delta_A + \beta\delta_{AD} \qquad (3\text{-}11)$$

or

$$\Delta = \beta\,(\delta_{AD} - \delta_A) \qquad (3\text{-}12)$$

If

$$\Delta_o = \delta_{AD} - \delta_A \qquad (3\text{-}13)$$

then

$$\Delta = \alpha\, K\, D_o\, \Delta_o \qquad (3\text{-}14)$$

Now

$$\alpha = \frac{(A)}{(A) + (AD)} = \frac{1}{1 + \frac{(AD)}{(A)}} \qquad (3\text{-}15)$$

and

$$\frac{(AD)}{(A)} = K\,(D) \qquad (3\text{-}16)$$

so that

$$\alpha = \frac{1}{1 + K\,(D)} \qquad (3\text{-}17)$$

If $D_o \gg A_o$, $(D) \doteqdot D_o$ and

$$\alpha = \frac{1}{1 + K\,D_o} \qquad (3\text{-}18)$$

Thus from equations (3-14) and (3-18) it follows that

$$\Delta = \frac{K\,D_o\,\Delta_o}{1 + K\,D_o} \qquad (3\text{-}19)$$

Thus

$$\frac{1}{\Delta} = \frac{1}{\Delta_o} + \frac{1}{K\Delta_o D_o} \qquad (3\text{-}20)$$

Hence if a complex of 1:1 stoichiometry exists, a plot of $\frac{1}{\Delta}$ against $\frac{1}{\Delta_o}$ should give a straight line from which K can be calculated. Fort

(57) pointed out, however, that the reverse of the statement is not necessarily true; a linear relationship is not a proof of complex formation.

This technique was used by Laszlo and Williams (58) in a study of 5 α - androstan -6- one in toluene solution. A straight line was obtained which gave an apparent equilibrium constant K = 0.20 M^{-1} at 33°C, in fair agreement with the results of an alternative temperature method (see next section of this thesis).

Tyrrell (59), in his investigation of complex formation between propargyl chloride and benzene, used an equivalent approach to derive an equilibrium constant of K = 1.01 ± 0.02 M^{-1} from the methylene proton and K = 0.96 ± 0.06 M^{-1} from an independent consideration of the ethynyl proton.

5. Temperature Studies

The basic model presented for the 1:1 complex is

$$\text{solute} + \text{solvent} \rightleftharpoons \text{complex} \qquad (3\text{-}21)$$

The prediction can therefore be made, to test the quality of this model, that by lowering the temperature the equilibrium (3-21) would be shifted to the right and the ASIS resulting from complex formation would be enhanced. In addition, the temperature variation for the equilibrium constant K for the equilibrium (3-21) would permit an evaluation of the enthalpy of formation of the complex.

Before testing this idea it was necessary to show that variations

with temperature were not an intramolecular effect. Laszlo (43) demonstrates this to be so by presenting the variation with temperature of the chemical shifts of the 8-Me, 9-Me and 10-Me groups of camphor in toluene solution and in carbon disulfide solution. The variation of the 8-Me and 9-Me resonance position in toluene solution is positive while in carbon disulfide solution it is negative. The resonance position of the 10-Me is approximately constant in both. Thus solvent effects are implied.

The actual increase in $\triangle$ with increase in temperature has been observed in many instances. For example, Klinck and Stothers (47) in their study of parasubstituted benzaldehydes noted an increase in $\triangle$ with decrease in temperature for the formyl proton when the parasubstituent was electron releasing (the example considered was p-N, N-dimethylbenzaldehyde). However, the $\triangle$ value for the aminomethyl groups for the latter compound changed with temperature in approximately the same way as the formyl shifts of the other compounds.

For the calculation of thermodynamic parameters on the basis of an assumed 1:1 complex, Abraham (60) has suggested the following method. If, in dilute solution, a fraction p of the solute is in the complex form, then

$$K = \frac{p}{1 - p} = \exp\left(\frac{\triangle S}{R}\right) \exp\left(-\frac{\triangle H}{RT}\right) \qquad (3\text{-}22)$$

where $\triangle S$ is the entropy of formation, $\triangle H$ is the enthalpy of formation and R is the universal gas constant. The fraction of solute molecules complexed, p, is given at any temperature (t) by

$$p = \frac{\delta_t - \delta_o}{\delta_c - \delta_o} \qquad (3\text{-}23)$$

where δ_t is the observed chemical shift at temperature t, δ_o is the

chemical shift of the uncomplexed solute and δ_c is the chemical shift of the pure complex.

If the position of the resonance in an "inert" solvent is taken to be δ_o, and this arbitrarily taken as zero, then equation (3-23) becomes

$$p = \frac{\delta_t}{\delta_c} \qquad (3\text{-}24)$$

Estimates of δ_c can be made by measuring δ_t as a function of temperature and extrapolating to $0^{\circ}K$. At this point all of the solute molecules are assumed to be complexed so that $\delta_{t=o} = \delta_c$. Hence, K may be calculated and then $\triangle H$ may be calculated from the slope of a plot of log K against $\frac{1}{T}$.

Fort (57), for example, applied this technique in his study of the system t-butylbromide - chlorobenzene. A very good straight line for δ_t as a function of T was obtained.

Laszlo and Williams (58) also applied this technique to their previously mentioned study of 5 α-androstan -11- one. From the δ_t vs T study of the 12 α -H and 1 β -H, for example, precisely parallel plots of log K vs $\frac{1}{T}$ were obtained, giving the same value for $\triangle H = -0.65 \pm 0.15$ kcal. per mole.

Such extrapolations of δ_t to $0^{\circ}K$ may be of doubtful validity, however, for recent work in this laboratory shows that some of these δ_t vs. T plots are definitely curved, especially at lower temperatures.

Ronayne and Williams (49), in support of the local dipole - induced dipole hypothesis, consider the case where several sites of solvation are important. They argue that a given proton may be shielded by benzene

molecules which are complexed at different sites and the variation of this shielding from one of these solvent molecules with temperature may differ with the variation from the other solvent molecules. A similar argument holds for other protons in the solute so that the net result is that different protons within a polyfunctional molecule should give different values for the variation of K with temperature and hence different values for $\triangle H$. This is precisely the situation found by Klinck and Stothers (48) for their parasubstituted benzaldehydes; for example, $-\triangle H$ (kcal per mole) for collision-complex formation of p-nitrobenzaldehyde is 0.74 ± 0.06, 0.69 ± 0.04 and 0.59 ± 0.03, from data for the formyl and ortho- and meta- protons, respectively.

An interesting point that arose from the determination of these equilibrium constants was the fact that when one goes from benzene to polymethylsubstituted benzenes as the aromatic solvent, the equilibrium constant in general increased, in direct contrast to the fact that the ASIS in general decreased. This fact is attributed to the increased donor force of the methyl-substituted aromatic compound.

B- CORRELATIONS

1. Correlations With The Solute Dipole Moment

If the concept of a dipole-induced dipole complex is correct, the ASIS should increase as the dipole moment of the solute increases. This is indeed found to be so in many cases.

Schneider (45) tested the hypothesis by plotting the ASIS for polar solutes of the type CH_3X against $\frac{\mu}{V}$, where μ is the solute dipole moment and V is the molar volume of the solute. The dipole moment was divided by the molar volume to allow for varying distances between the centres of gravity of the solute and of the benzene molecule. A fairly linear correlation was observed with the notable exception of chloroform, due to hydrogen bonding with the aromatic π electrons.

Bowie, Ronayne and Williams (55) obtained a fairly linear plot between the solvent shift for the methoxyl resonance of p - X· C_6H_4 · O Me (X = NO_2, COMe, CHO, Br, SMe, H, Me, OM_e, NH_2, NMe_2) and the dipole moment of the compound.

Brown and Stark (53) achieved similar success with the ASIS of the organometallic compounds they studied and have actually presented this technique as a method of determining dipole moments.

Diehl (50) has successfully correlated the ASIS at the meta position of substituted benzenes with the substituent dipole moment.

2. Additivity

An interesting property of the ASIS is the remarkable additivity which is exhibited in many cases. Williams (49) and other workers have observed this additivity in the ASIS of steroids. A typical example is illustrated in Figure 7.

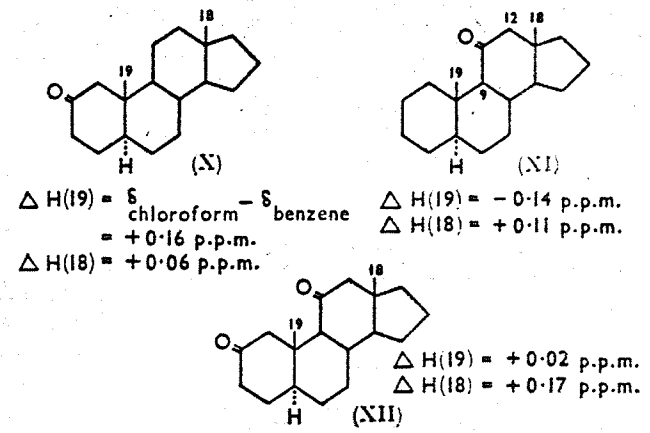


Figure 7: The additivity of the ASIS of Steroids.

Murrell and Gil (61) also observed this phenomenon in the ASIS of the cyclazines they studied, as is shown in Figure 8.

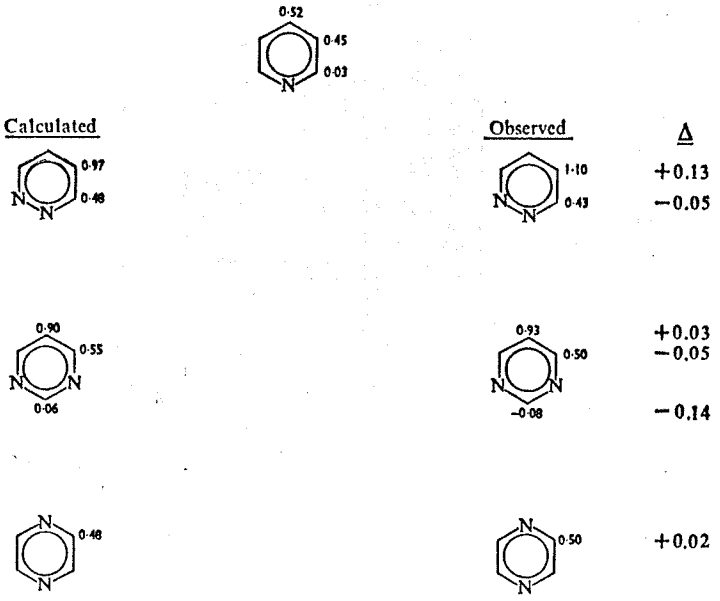


Figure 8: Observed and calculated values for the ASIS of the Cyclazines.

Laszlo and Soong, Jr. (62) extended the work of Murrell and Gil to substituted pyridines and cyclazines with a similar sort of success.

Diehl (50,63) has also reported upon the additivity of solvent effects for substituted benzenes. The total ASIS at a certain position of a substituted benzene is simply the sum of the individual ASIS relative to each substituent.

C- CONCLUSIONS

The model of the 1:1 complex has been presented in this chapter along with several pieces of evidence presented by various workers in its support. However, there are at present several arguments against the 1:1 complex.

The idea of a dipole-induced dipole type of association has been disputed by Laszlo and Soong, Jr. (62) who carried out the previously mentioned study of the ASIS of various cyclazines. The fact that these compounds showed a definite ASIS appeared to Laszlo to be "incompatible with the hypothesis of a dipole-induced dipole complex" for "local dipoles cannot be defined for the molecules of the present study".

Laszlo (43) presents the following argument against the 1:1 complex: "It is known that, in the liquid phase, the time a molecule spends in a given orientation, between two collisions, is of the order of 10^{-10} - 10^{-11} sec., and this is the true minimum duration for any complex. The NMR measurement is much slower and, for separate "free" and "complexed" resonances to be present in a spectrum, the lifetime of the complex has to be longer than the reciprocal of their frequency difference. In the examples we have discussed here, the ASIS were of the order of 0 - 60 c/s, the reciprocal of this shift fixes a limit of 10^{-2} sec. for the observation of individual bands. These have not been observed. The life time of such an association, between one molecule of the solute and one molecule of the solvent, is therefore very small, certainly much smaller than 10^{-2} sec., and there is no such thing as the permanence of these 1:1 complexes in solution."

Fort and Lindrstrom (64) present the alternative model of "a slight structuring of the solvent about each solute molecule, a sort of 'cage construction'. An indeterminate number of solvent molecules would be involved, each rapidly changing places with molecules from the bulk of the solvent." The author of this thesis prefers this model over the 1:1 complex model.

Laszlo (43) concludes his discussion with:

> "This model, if it is too simple to account for all the observations (it is probably that admixing of a quantum mechanical term to the simple electrostatic, will provide a correct description), or to reflect the complexity of the ordering process taking place in the liquid around the polar solute, has led to predictions, which have generally been shown to be true. Now it is clearly obsolete."

CHAPTER IV

- The Nature of the Problem -

A- THE NATURE OF THE PROBLEM

Additivity has been observed in the ASIS of certain classes of compounds (49,61,62) including substituted benzenes (50,63). In certain cases (45,50,53,55) the ASIS can be correlated with the dipole moment of the compound. However, no method, aside from the emperical method of Diehl (50,63), has yet been proposed to allow the calculation of the ASIS of substituted benzenes from properties of their substituents.

Thus the purpose of this investigation is to attempt to correlate the ASIS of some polyhalosubstituted benzenes with some property of the halogen substituents and from this correlation to provide a means of predicting the ASIS of other halobenzenes. An attempt to extend any correlation found to substituents other than halogen will also be made.

CHAPTER V

- Experimental -

A- MATERIALS

The chemicals used were obtained from the following companies:- (1) Aldrich Chemical Co., Inc.; (2) Ansul Chemical Company; (3) Columbia Organic Chemicals, Co., Inc.; (4) Eastman Organic Chemicals; (5) K & K Laboratories Inc.; (6) Koch-Light Laboratories, Ltd.; (7) Matheson, Coleman and Bell; (8) Merck, Sharp and Dohme, Ltd.; and (9) Pierce Chemical Company. They were used without further purification, since any lines due to impurities were easily recognized.

1-bromo-3-chloro-5-iodobenzene was prepared according to the eight step procedure of Ault and Kraig (65). The procedure was reduced to two steps by starting with an intermediate compound, 2-chloro-4-bromoaniline, obtained from the Chemicals Procurement Laboratories.

B- MEASUREMENT OF THE SPECTRA

The samples were prepared as 3 mole percent solutions in benzene - d_6. In a few cases, samples were also prepared as 3 mole percent solutions in carbon tetrachloride, and cyclohexane. A small number of solutes were not soluble enough in benzene - d_6 to allow the preparation of a 3 mole percent solution. In these cases a saturated solution was used. The samples were contained in glass tubes of 4 mm inner diameter and 5 mm outer diameter. Most samples, especially those which gave rise to multiline spectra, were degassed on a vacuum line.

The spectra were measured and calibrated by period averaging techniques on a Varian DA - 60I spectrometer operated in the frequency-sweep mode. Tetramethylsilane (TMS) was used as an internal reference. The temperature of the sample, as determined by an ethyleneglycol calibration graph, was 28.5°C.

CHAPTER VI

- Results -

A- RESULTS

The results of the measurements are presented in this chapter. In Table I the proton chemical shift(s) (ppm to low field of TMS) of 30 polyhalosubstituted benzenes in C_6H_{12} and in C_6D_6 are given, along with $\Delta_{C_6H_{12}} = \delta_{C_6H_{12}} - \delta_{C_6D_6}$. In Table II the proton chemical shift(s) (ppm to low field of TMS) of several other compounds in the same two solvents are given, along with $\Delta_{C_6H_{12}}$. A discussion of these results will be presented in the next chapter.

Table I

Proton Chemical Shifts of Polyhalosubstituted Benzenes

(PPM To Low Field of TMS)*

COMPOUND	PROTON	IN C_6H_{12}	IN C_6D_6	$\Delta_{C_6H_{12}} = \delta_{C_6H_{12}} - \delta_{C_6D_6}$	REFERENCE**
(1) benzene	--	7.211	7.149	.062	66
(2) 1,4-difluorobenzene	--	6.869	6.517	.352	--
(3) 1,4-dichlorobenzene	--	7.150	6.743	.416	67
(4) 1,4-dibromobenzene	--	7.240	6.743	.497	67
(5) 1,4-diiodobenzene	--	7.300	6.893	.407	67
(6) 1,3,5-trichlorobenzene	--	7.163	6.778	.385	66
(7) 1,3,5-tribromobenzene	--	7.521	7.159	.362	66
(8) 1,2,3,4-tetrafluorobenzene	--	6.761	6.016	.745	66
(9) 1,2,3,4-tetrachlorobenzene	--	7.162	6.472	.690	66
(10) 1,2,4,5-tetrafluorobenzene	--	6.887	6.192	.695	66
(11) 1,2,4,5-tetrachlorobenzene	--	7.432	6.848	.584	66
(12) 1,2,4,5-tetrabromobenzene	--	7.768	7.239	.529	66
(13) 1,4-difluoro-2,5-dibromobenzene	--	7.206	6.558	.648	66
(14) 1,2,3,5-tetrafluorobenzene	--	6.593	6.055	.538	66
(15) 2,4,6-tribromoiodobenzene	--	7.605	7.155	.450	66
(16) pentafluorobenzene	--	6.719	5.854	.865	66
(17) pentachlorobenzene	--	7.407	6.727	.680	66
(18) 1,2,3-trichlorobenzene	H_4,H_6	7.225	6.748	.477	66
	H_5	6.945	6.258	.687	66

Table I (continued)

COMPOUND	PROTON	IN C_6H_{12}	IN C_6D_6	$\Delta_{C_6H_{12}} = \delta_{C_6H_{12}} - \delta_{C_6D_6}$	REFERENCE**
(19) 3,5-dichlorobromobenzene	H_2, H_6	7.325	6.949	.376	66
	H_4	7.203	6.810	.393	66
(20) 1-bromo-3-chloro-5-iodobenzene	H_2	7.367	6.987	.380	66
	H_4	7.367	6.987	.380	66
	H_6	7.484	7.128	.356	66
(21) 1,2,4-trichlorobenzene	H_3	7.355	6.974	.381	66
	H_5	7.042	6.465	.577	66
	H_6	7.223	6.667	.556	66
(22) 1,2,4-tribromobenzene	H_3	7.682	7.346	.336	66
	H_5	7.149	6.545	.604	66
	H_6	7.331	6.808	.523	66
(23) 1-bromo-2,5-dichlorobenzene	H_3	7.227	6.711	.516	66
	H_4	7.086	6.469	.617	66
	H_6	7.533	7.180	.353	66
(24) 1-bromo-3,4-dichlorobenzene	H_2	7.513	7.137	.376	66
	H_5	7.164	6.572	.592	66
	H_6	7.187	6.640	.547	66
(25) 1-iodo-2,4-dichlorobenzene	H_3	7.771	7.461	.310	--
	H_5	7.050	6.508	.542	--
	H_6	7.283	6.736	.547	--

Table I (continued)

COMPOUND	PROTON	IN C_6H_{12}	IN C_6D_6	$\Delta_{C_6H_{12}} = \delta_{C_6H_{12}} - \delta_{C_6D_6}$	REFERENCE**
(26) 1-iodo-2,5-dichlorobenzene	H_3	7.213	6.646	.567	--
	H_4	7.119	6.572	.547	--
	H_6	7.772	7.456	.316	--
(27) 1-iodo-3,4-dichlorobenzene	H_2	7.698	7.348	.350	66
	H_5	7.010	6.396	.614	66
	H_6	7.380	6.889	.491	66
(28) 1-iodo-2,3-dichlorobenzene	H_4	7.297	6.826	.471	--
	H_5	6.707	6.046	.661	--
	H_6	7.658	7.205	.453	--
(29) 1-fluoro-3,4-dichlorobenzene	H_2	7.084	6.675	.409	66
	H_5	7.268	6.708	.560	66
	H_6	6.782	6.215	.567	66
(30) 1-fluoro-2,4-dibromobenzene	H_3	7.612	7.259	.353	66
	H_5	7.262	6.705	.557	66
	H_6	6.827	6.202	.625	66

* The proton chemical shifts quoted have a maximum standard deviation of $\pm$ 0.005 ppm. The actual standard deviation, however, is generally of the order of $\pm$ 0.0005 ppm.

** The reference quoted refers to the source from which the C_6H_{12} values were taken. When no reference is given, the value was determined by the author.

Table II

Proton Chemical Shifts of Various Polysubstituted Benzenes

(PPM To Low Field of TMS)*

	COMPOUND	PROTON	IN C_6H_{12}	IN C_6D_6	$\Delta_{C_6H_{12}}$	REFERENCE**
(1)	toluene	ring	7.110	7.065	.045	68
(2)	p-xylene	ring	6.980	6.958	.022	68
(3)	mesitylene	ring	6.672	6.709	-.037	--
(4)	p-dimethoxybenzene	ring	6.681	6.738	-.057	--
(5)	p-dinitrobenzene***	--	8.375	7.363	1.012	--
(6)	2,4,6-trichlorophenol	ring	7.153	6.772	.381	--
(7)	2,4,6-triiodophenol	ring	7.865	7.569	.296	--
(8)	2,6-dinitro-4-chlorophenol	ring	8.121	7.250	.871	--
(9)	1,2,5,6-tetrachloronitrobenzene	--	7.572	6.539	1.033	--
(10)	3,5 dichlorotoluene	H_2, H_6	6.947	6.651	.296	--
		H_4	7.082	7.003	.079	--

* The proton chemical shifts quoted have a maximum standard deviation of $\pm$ 0.005 ppm, except where the spectra was analysed approximately (see AppendixII). The actual standard deviation, however, is generally of the order of $\pm$ 0.0005 ppm.

** The reference quoted refers to the source from which the C_6H_{12} values were taken. When no reference is given, the value was determined by the author.

*** The value for C_6H_{12} was estimated by subtracting 0.075 ppm from the shift in CCl_4.

The values quoted in Tables I and II were obtained by analysing the spectra according to the standard methods outlined in Appendix II. The coupling constants which were also obtained from these analyses are listed in Appendix I.

Many of the spectra consisted merely of a single line or a single shift position. The non-trivial spectra were of several types, including: (1) an AB_2 such as 1,2,3-trichlorobenzene; (2) an ABX such as 1,2,4-trichlorobenzene: (3) an ABC such as 2,3-dichloroiodobenzene; (4) an ABC that approximated very close to an AB_2, such as 1-chloro-3-bromo-5-iodobenzene; (5) an ABXR such as 2,4-dibromofluorobenzene; (6) an ABCR such as 3,4-dichlorofluorobenzene; (7) spectra which would be expected to be complex but which are rather simple, such as 1,2,4,5-tetrafluorobenzene, and (8) an AB_2X_3 such as 3,5-dichlorotoluene. Some of these spectra are reproduced on the following pages.

Figure 9: The complete proton spectrum of a 3 mole % solution of 1,2,3-trichlorobenzene in C_6D_6... a typical AB_2 spectrum.

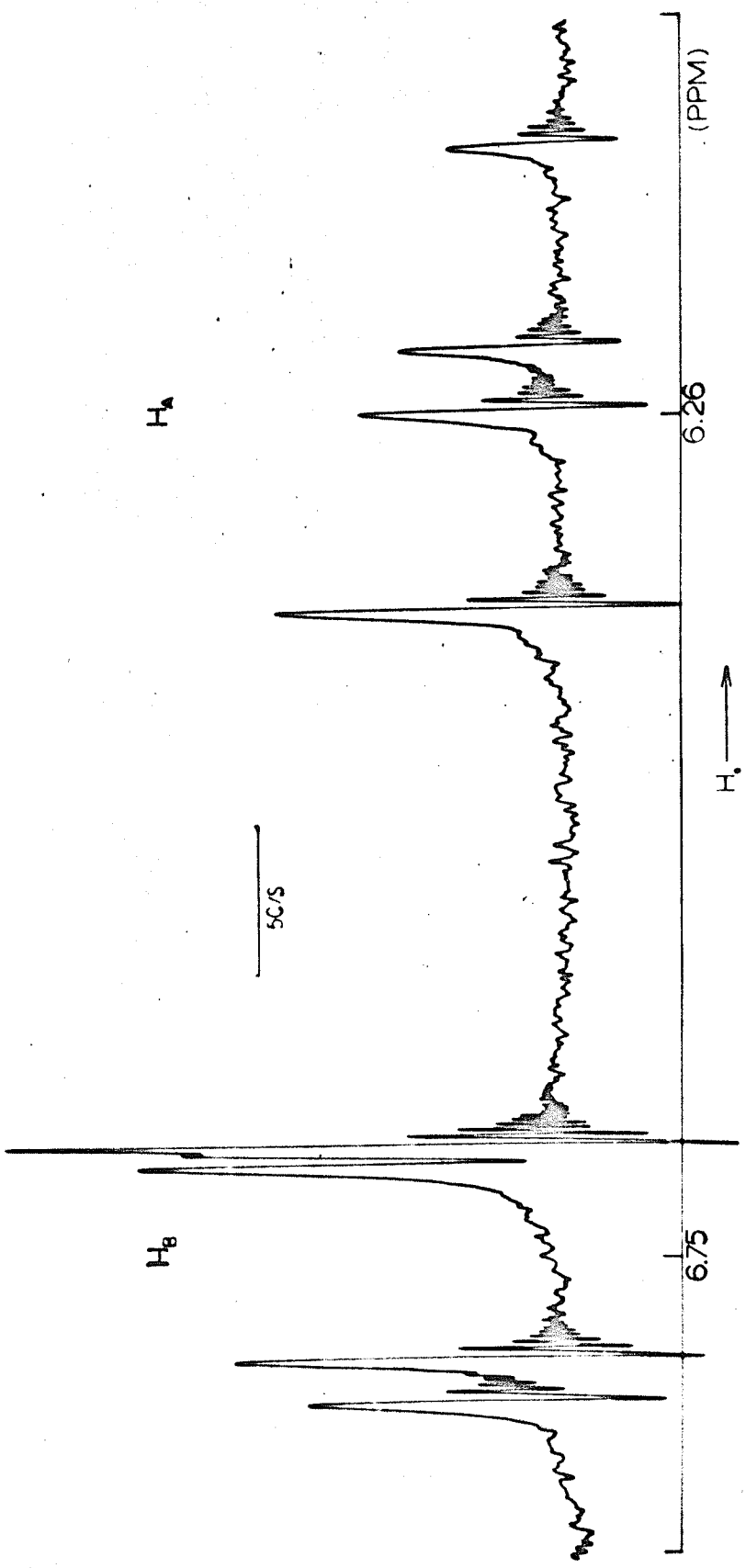

H_A
H_B
6.26
6.75
(PPM)
H
5c/s

Figure 10: The complete proton spectrum of a 3 mole % solution of 1,2,4-trichlorobenzene in C_6D_6... a typical ABX spectrum.

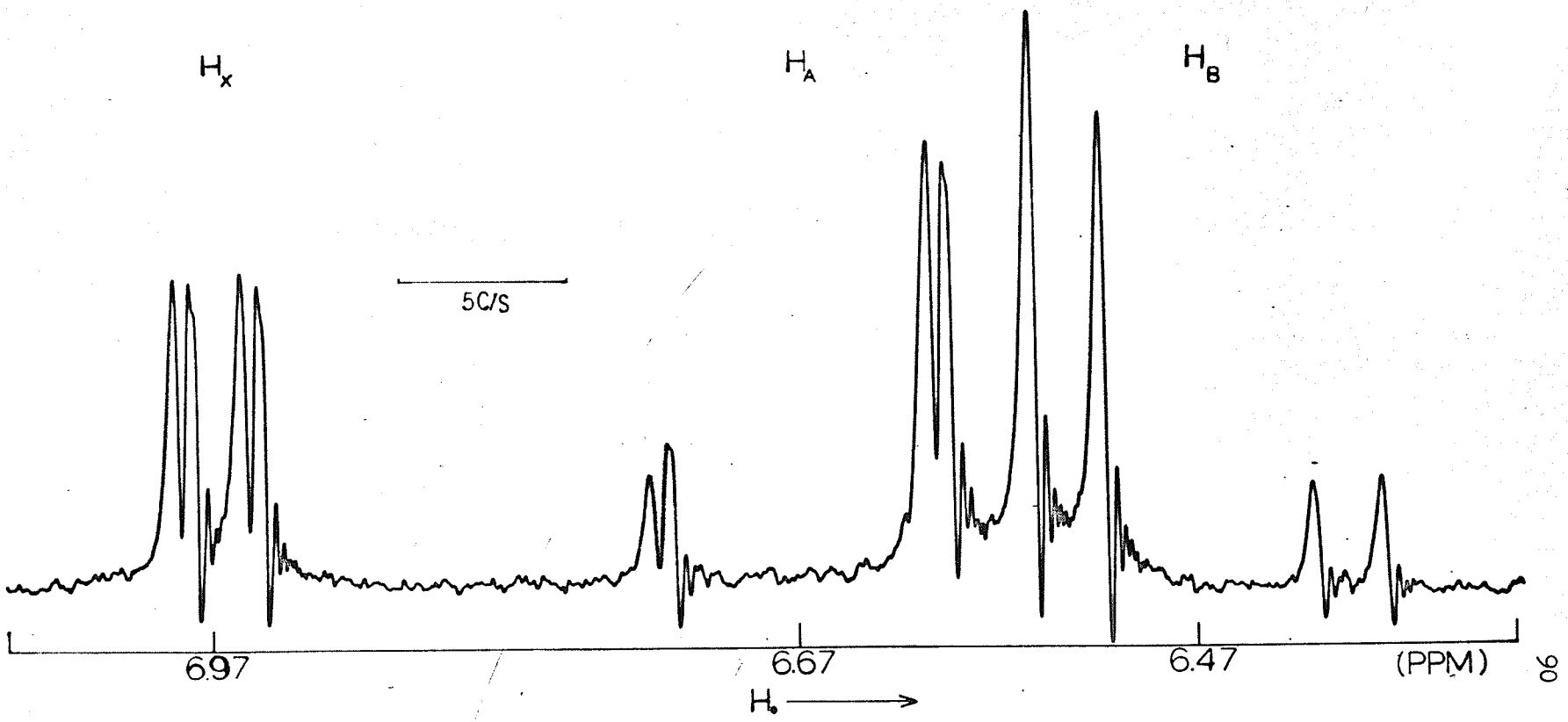
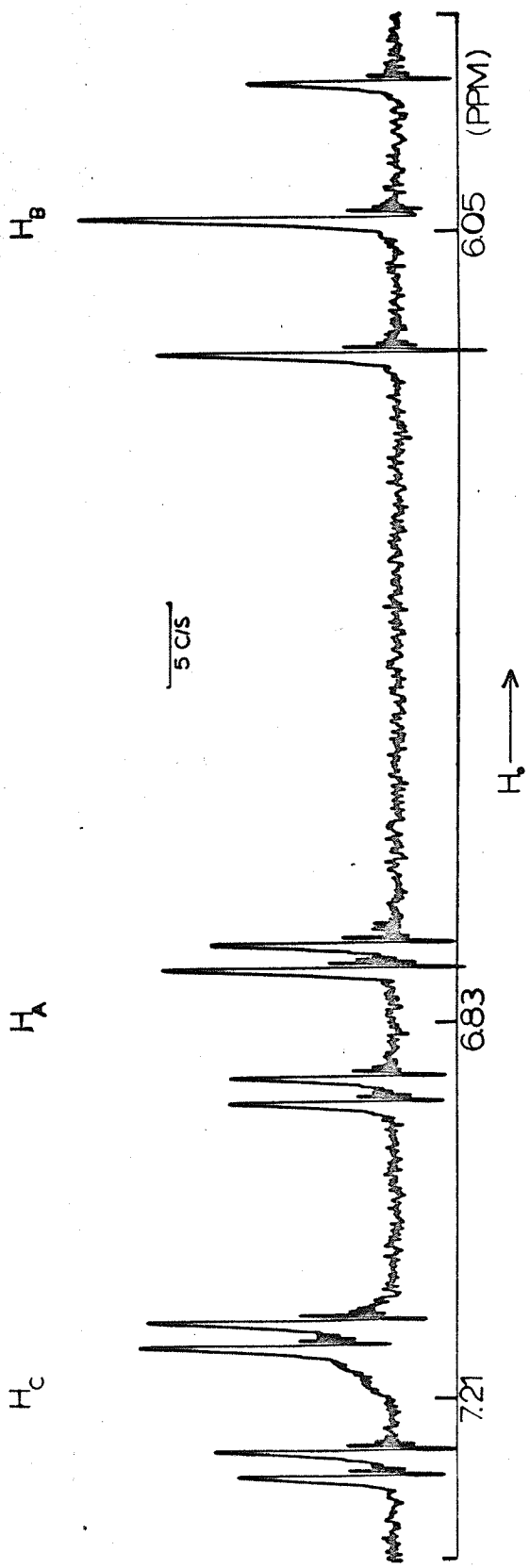

H_X
H_A
H_B
5C/S
6.97
6.67
6.47
(PPM)
H_o ⟶

Figure 11: The complete proton spectrum of a 3 mole % solution of 2,3-dichloroiodobenzene in C_6D_6... a typical ABC spectrum.


H_B
H_A
H_C
6.05
6.83
7.21
(PPM)
5 c/s
H.

CHAPTER VII

- Discussion -

A- INTRODUCTION

Before trying to correlate the benzene solvent shifts given in Tables I and II with some property or properties of the solute molecules, it is first necessary to decide what factors give rise to the benzene solvent shift. According to equation (3-1) such a solvent shift may arise from: (1) the shift due to the differences in the reaction field effects in changing the solvent medium from cyclohexane to benzene; (2) the shift corresponding to the different van der Waals interaction of the solute with the different solvents; (3) the shift due to the magnetic anisotropy effects of the benzene solvent and (4) specific molecular interactions.

It may easily be shown that the shift due to the differences in the reaction field effects is small. The dielectric constants (69) of benzene and cyclohexane are 2.284 (20°C) and 2.023 (20°C), respectively. Substituting these values along with reasonable values for μ, θ and α into equation (2-158) for the reaction field shift shows that the contribution to the solvent shift arising from reaction field effects is of the order of -0.01 ppm.

Several pieces of evidence also suggest that the shift corresponding to the different van der Waals interactions of the solute with the two solvents is small. Homer (70) calculated the contribution to the shielding constant of TMS arising from dispersion interactions. The value for benzene as solvent differed from the value for cyclohexane as solvent by only -0.005 ppm. Laszlo, Speert, Ottinger and Reisse (71) found that

on changing from CS_2 to C_6H_6 as solvents, the chemical shifts of cyclohexane, di-t-butylmethane and neopentane only changed by around 0.01 ppm. Since these are non-polar solutes the differences in shifts in passing from one solvent to another may be attributed to the differences in dispersion interactions (with both the solute and the reference). Because the change in dielectric constant on passing from CS_2 to C_6H_6 is similar to the change in dielectric constant on passing from C_6H_6 to C_6H_{12}, one would expect similar results. Hutton, Bock and Schaefer (72) concluded that the solvent dependence of the Si-F coupling constant in SiF_4 arose from dispersion interactions. They found that the magnitude of the coupling correlated linearly with the heat of vapourization of the solvent in the same way that Linder (39) found that dispersion free energies correlated with heat of vapourization. The value of the Si-F coupling was the same, in C_6H_{12} and in C_6H_6, suggesting that the dispersion interaction of the solute with these two solvents was the same.

It is thus evident that the benzene solvent shift must arise from the magnetic anisotropy effect of the benzene solvent which amplifies the chemical shift arising from specific molecular interactions of benzene with the solute, as was discussed in Chapter III. Such interactions of the solute with cyclohexane as solvent are presumably absent since cyclohexane is "inert".

In Chapter III it was pointed out that steric effects were evidently important in determining the magnitude of the ASIS. Also the ASIS

appeared in many cases to correlate with the solute dipole moment. It was thus thought that this would be a good place to start the investigation of the ASIS of the compounds given in Table I.

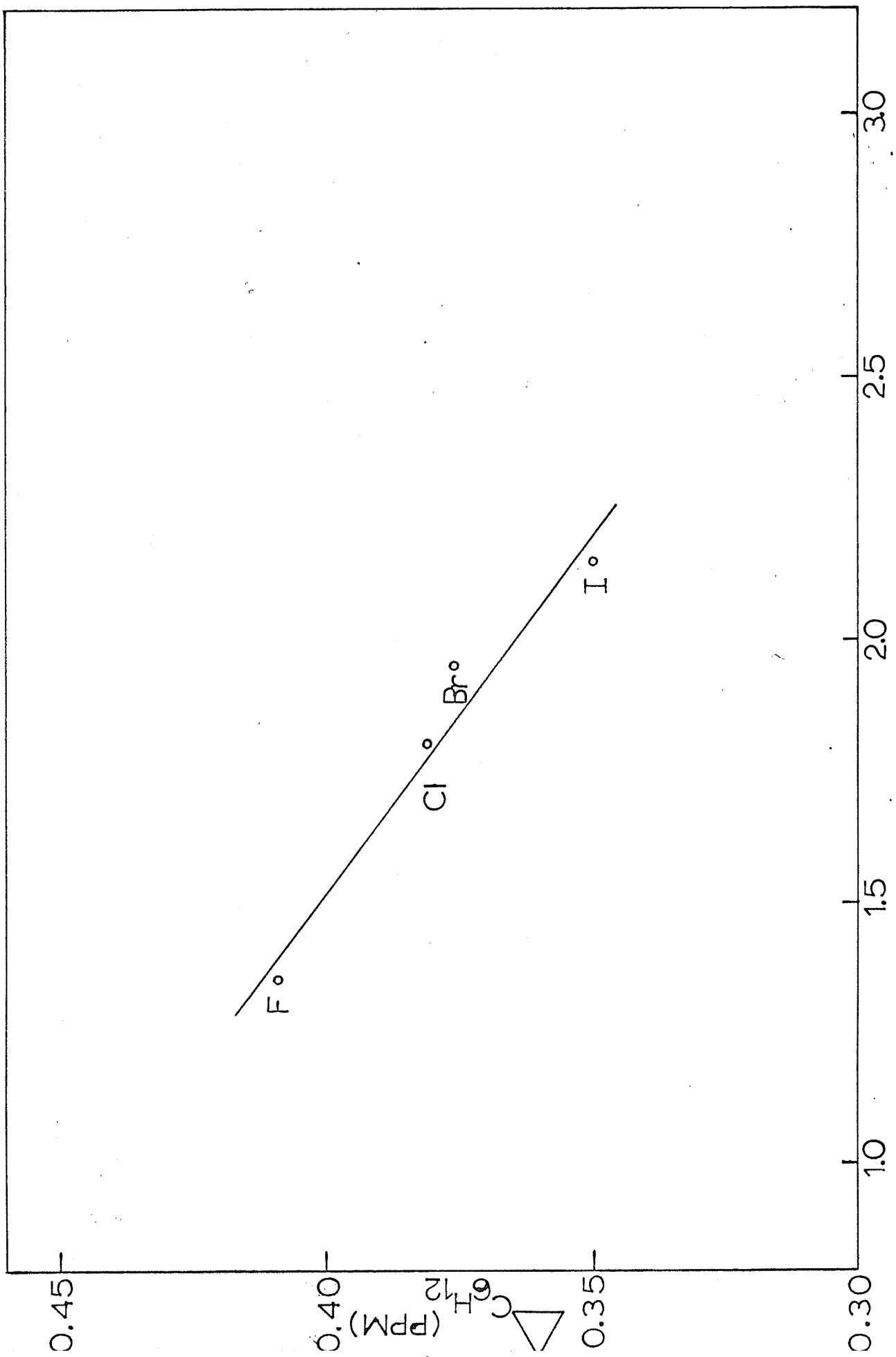
1. Steric Effects

The presence of steric effects is demonstrated in Figure 12 where the $\Delta_{C_6H_{12}}$ values of the 2-protons in 1-X-3,4-dichlorobenzenes plot approximately linearly against the van der Waals radius of X. The steric effect seems to be present only for the proton with two ortho substituents, although a somewhat similar plot is exhibited by the 6-protons. The values for the 5-protons show no such correlation (the charge effect discussed next may counteract the steric effect of the more distant neighbours).

2. Charge Effects

Steric effects are not sufficient to explain the solvent shifts listed in Tables I and II. Another approach to interpreting the magnitudes of these solvent shift is, of course, that of "complex formation". The benzene π-electrons form a region of high electron density and this part of the benzene solvent molecule will therefore tend to avoid the electron-rich regions of the solute molecule (such as the halogen substituents), and will tend to orientate towards the regions of low electron density. The exact nature of this specific interaction (as discussed in

Figure 12: A plot of $\Delta_{C_6H_{12}}$ in ppm for the 2-protons in the 1-X-3,5-dichlorobenzenes, versus the van der Waals radius, R_x of the substituent X.


0.45
0.40
0.35
0.30
(PPM) C_6H_{12}
1.0
1.5
2.0
2.5
3.0
R_X (A°)
F°
Cl°
Br°
I°

Chapter III) is not being proposed. This charge effect is in some way superimposed upon the steric effect in determining the magnitude of the solvent shift.

There is no certain way of determining exactly how much the charge distribution in the immediate vicinity of the C-H bond is altered by a substituent. Hückel molecular orbital calculations are probably too crude for polyhalobenzenes. The semiquantitative approach used in this thesis is to allow $\frac{\mu}{r}$ to represent a measure of the amount of charge removed from the ring region by a substituent X. Here μ is the dipole moment of the C-X bond and r is the C-X bond length. The $\frac{\mu}{r}$ values of 1.14, 0.93, 0.84 and 0.68 e.s.u. units are used for F, Cl, Br and I, respectively. They are obtained from the dipole moments (73), and the bond lengths (74) in the phenyl halides. The ortho substituent is naturally most effective at removing charge from the region near the C-H bond.

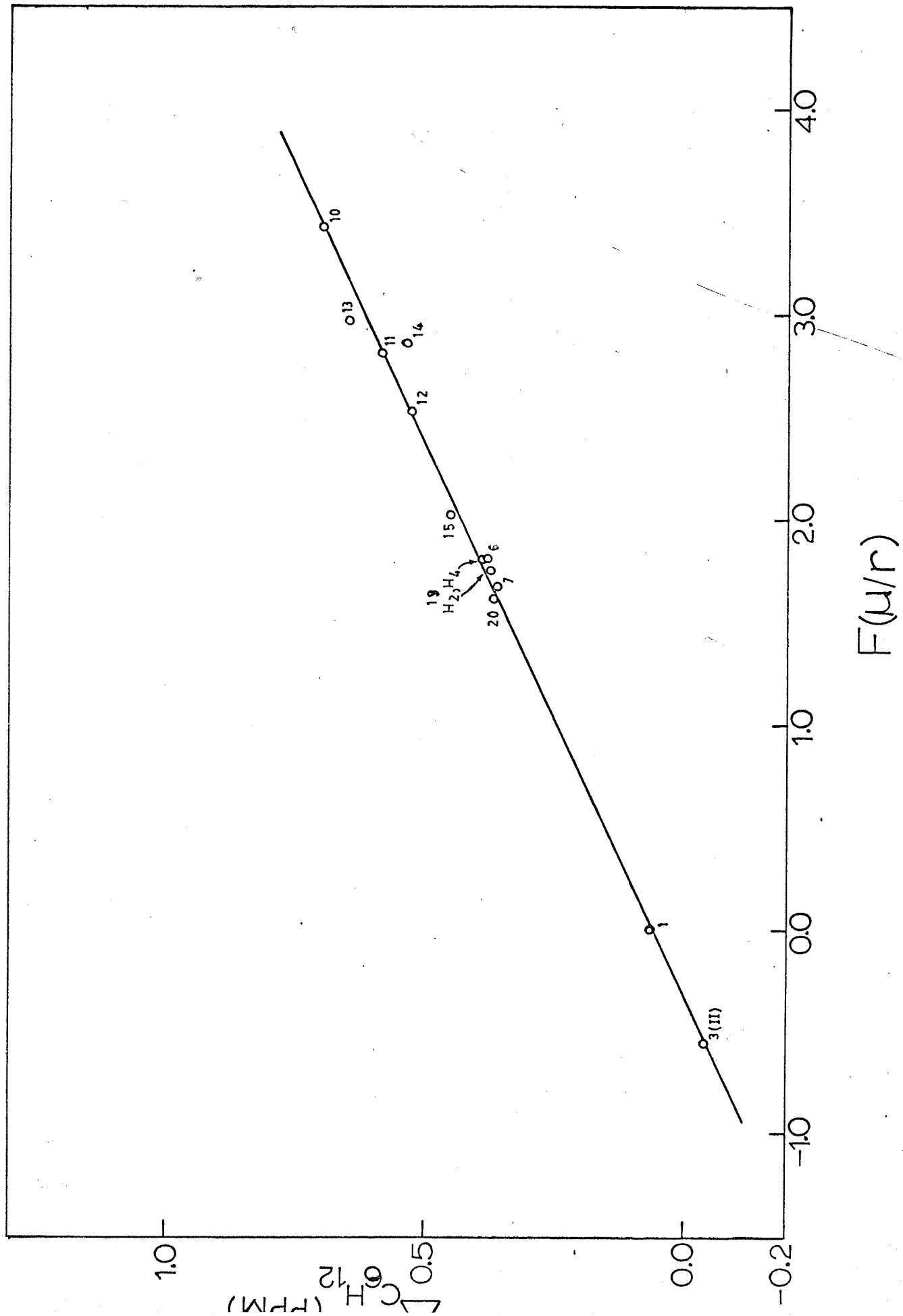
In this thesis the expression

$$F\left(\frac{\mu}{r}\right) = \sum_{o} \frac{\mu}{r} + 0.5 \sum_{m} \frac{\mu}{r} \qquad (7\text{-}1)$$

is presented as an approximation to the change in the charge distribution induced by the substituent. The sums are over ortho (o) and meta (m) substituents.

The charge effect is illustrated in Figure 13 where the solvent shifts, $\Delta_{C_6H_{12}}$, for those polyhalobenzenes in which no protons occur ortho to each other, are plotted versus $F(\frac{\mu}{r})$. From the approximate linearity of this plot it is evident that a charge effect is indeed important

Figure 13: A plot of $\Delta_{C_6H_{12}}$ in ppm versus $F(\frac{\mu}{r})$ (defined in text) for the protons of the polyhalobenzenes in which there are no orthohydrogens. The numbering of the points corresponds to the numbering used in Table I, with the exception of point 3 (II) which corresponds to the numbering used in Table II.


1.0
0.5
0.0
-0.2
$C_{6H_{12}}$ (PPM)
-1.0
0.0
1.0
2.0
3.0
4.0
F(μ/r)
3(II)
1
10
13
11
14
12
15
19
H_2, H_4
6
8
7
20

in determining the magnitude of the solvent shift.

For this plot the value of the dipole moment for the C-H bond in C_6H_6 was taken as zero. However, there is a net solvent shift of 0.063 ppm for benzene. This may be attributed to two things. First, the hybridization of the carbon atom in C_6H_6 is sp^2 while that in TMS is sp^3. Hence there is a lower electron density near the benzene proton than near the TMS proton. Thus the π-electron density of the benzene "solvent" molecules would (on a time averaged scale) tend to approach closer to the benzene "solute" protons than to the TMS protons. This would give rise to a small, positive, upfield shift. Secondly, there may be a slight packing effect. The benzene molecules in solution may tend to lie slightly stacked on top of one another in such a manner that the π-electron densities avoid each other. No such stacking would exist between benzene and TMS. This would therefore lead to a small, positive, upfield shift.

The value for mesitylene is also plotted in Figure 13, merely to illustrate that the plot extends to negative values. Such negative values will be discussed later in this chapter.

By taking the best slope of the line in Figure 13, and then multiplying the terms in equation (7-1) by this slope, the Δ parameters given in Table III were calculated

Table III

ASIS Parameters For Polyhalobenzenes (ppm)

HALOGEN	Δ_o	Δ_m	Δ_p
F	0.212	0.106	0
Cl	0.173	0.087	0
Br	0.156	0.078	0
I	0.126	0.063	0

If to these parameters is added a stacking parameter Φ (which is the $\Delta_{C_6H_{12}}$ value for benzene as solute), the solvent shifts plotted in Figure 13 may then be calculated from equation (7-2).

$$\Delta_{C_6H_{12}} = \sum_o \Delta_o + \sum_m \Delta_m + \Phi \qquad (7\text{-}2)$$

The calculated and observed values are given in Table IV. The mean standard deviation between calculated and observed values is ± 0.014 ppm.

Table IV

Calculated and Observed ASIS Values (ppm)

For Polyhalobenzenes With No Ortho Hydrogens*

Compound	Proton	$\Delta_{C_6H_{12}}$ (calc.)	$\Delta_{C_6H_{12}}$ (obs.)	Deviation
(1) benzene	-	0.063	0.063	0.000
(2) 1,3,5-trichlorobenzene	-	0.408	0.385	+0.023
(3) 1,3,5-tribromobenzene	-	0.375	0.362	+0.013
(4) 1,2,4,5-tetrafluorobenzene	-	0.698	0.695	+0.003
(5) 1,2,4,5-tetrachlorobenzene	-	0.581	0.584	-0.003
(6) 1,2,4,5-tetrabromobenzene	-	0.531	0.529	+0.002
(7) 1,4-difluoro-2,5-dibromobenzene	-	0.614	0.648	-0.034
(8) 1,2,3,5-tetrafluorobenzene	-	0.592	0.538	+0.054
(9) 2,4,6-tribromoiodobenzene	-	0.438	0.450	-0.012
(10) 3,5-dichlorobromobenzene	H_2,H_6,	0.391	0.376	+0.015
	H_4	0.408	0.393	+0.015
(11) 1-bromo-3-chloro-5-iodo-benzene	H_2,H_4**	0.377	0.380	-0.003
	H_6	0.345	0.356	-0.011

* The values were initially calculated from the parameters in Table III expressed in $\frac{c}{s}$. They were then converted to ppm.

** Separate values were calculated for H_2 and H_4 and then these were averaged.

3. Shape Effects

Whenever two or more protons occur ortho to one another there seems to be another factor determining the magnitude of the solvent shift

not accounted for by the steric or charge effects. In the case of the 1,2,4-trihalobenzenes the $\Delta_{C_6H_{12}}$ values of the 5 and 6-protons seem to be greatly increased over what is predicted by the parameters given in Table III. The $\Delta_{C_6H_{12}}$ values for the 3-proton seems to be slightly decreased. This fact suggests that bulky distant substituents force the benzene solvent molecules towards the unsubstituted regions of the benzene ring of the solute molecule. Also, this may be the result of a packing effect in which the benzene solvent molecules, in a time averaged fashion, tend to pack in the unsubstituted, "empty" region of the benzene ring of the solute molecule. Such a packing or shape effect has been observed by Fenby and Scott (75) in their study of the excess heats of mixing of thirty-four fluorobenzenes. Excess heats of mixing are heats of mixing over and above that predicted by the formation of an ideal solution and, therefore, represent specific interactions in a somewhat similar fashion that the ASIS does. In their study they found that matching "lock and key" systems (o-$C_6H_4F_2$ + 1,2,3,4-$C_6H_2F_4$, m-$C_6H_4F_2$ + 1,2,3,5-$C_6H_2F_4$, p-$C_6H_4F_2$ + 1,2,4,5-$C_6H_2F_4$ and C_6H_5F + C_6HF_5) have algebraically lower heats of mixing (that is, more exothermic) than non-matching systems. This suggests a packing effect in solution which gives rise to stronger interactions.

The deviation of the observed solvent shifts for the 1,2,4-trihalobenzenes from that calculated from equation (7-2) appear to be approximately constant for a given proton. Averaging the observed deviations gives the values listed below (the parameter Φ from equation (7-2) is included in these values).

Proton	Shape Parameter (ppm)
H_3	-0.059
H_5	+0.310
H_6	+0.233

It is interesting to note that H_5, the proton farthest removed from the two ortho halogens, has the highest value.

Combining these shape parameters with the values given in Table III provides a means of approximately calculating the solvent shifts for the protons of the 1,2,4-trihalobenzenes, as is shown in Table V.

Table V

Calculated and Observed ASIS Values (ppm)

For The 1,2,4-Trihalobenzenes*

Compound**	Proton	$\Delta_{C_6H_{12}}$ (calc.)	$\Delta_{C_6H_{12}}$ (obs.)	Deviation
(1) 1,2,4-trichlorobenzene	H_3	0.372	0.381	-0.009
	H_5	0.569	0.577	-0.008
	H_6	0.578	0.556	+0.022
(2) 1,2,4-tribromobenzene	H_3	0.331	0.336	-0.005
	H_5	0.544	0.604	-0.060
	H_6	0.545	0.523	+0.022
(3) 1,4-dichloro-2-bromobenzene	H_3	0.356	0.353	+0.003
	H_5	0.569	0.617	-0.048
	H_6	0.570	0.516	+0.054
(4) 1,2-dichloro-4-bromobenzene	H_3	0.356	0.376	-0.020
	H_5	0.552	0.547	+0.005

Table V (cont.)

Compound**	Proton	$\Delta_{C_6H_{12}}$ (calc.)	$\Delta_{C_6H_{12}}$ (obs.)	Deviation
	H_6	0.570	0.592	-0.022
(5) 1-iodo-2,4dichlorobenzene	H_3	0.349	0.310	+0.039
	H_5	0.546	0.542	+0.004
	H_6	0.532	0.547	-0.015
(6) 1,4-dichloro-2-iodobenzene	H_3	0.326	0.316	+0.010
	H_5	0.569	0.547	+0.022
	H_6	0.555	0.567	-0.012
(7) 1,2-dichloro-4-iodobenzene	H_3	0.326	0.350	-0.024
	H_5	0.523	0.491	+0.032
	H_6	0.555	0.614	-0.059
(8) 1,2-dichloro-4-fluorobenzene	H_3	0.411	0.409	+0.002
	H_5	0.608	0.567	+0.041
	H_6	0.598	0.560	+0.038
(9) 1-fluoro-2,4-dibromobenzene	H_3	0.359	0.353	+0.006
	H_5	0.572	0.557	+0.015
	H_6	0.600	0.625	-0.025

* The values were first calculated from both the Δ parameters (Table III) and the shape parameters expressed in $\frac{c}{s}$. They were then converted to ppm.

** The nomenclature, inconsistent with that used in Table I, was chosen so the protons could be labelled H_3, H_5, H_6.

The mean standard deviation is $\pm$0.023 ppm. The mean standard deviation for the 3-protons is $\pm$0.013 ppm, considerably smaller. This is presumably because these protons, being situated between two halogens, most closely resemble the type of proton used to derive the parameters given in Table III.

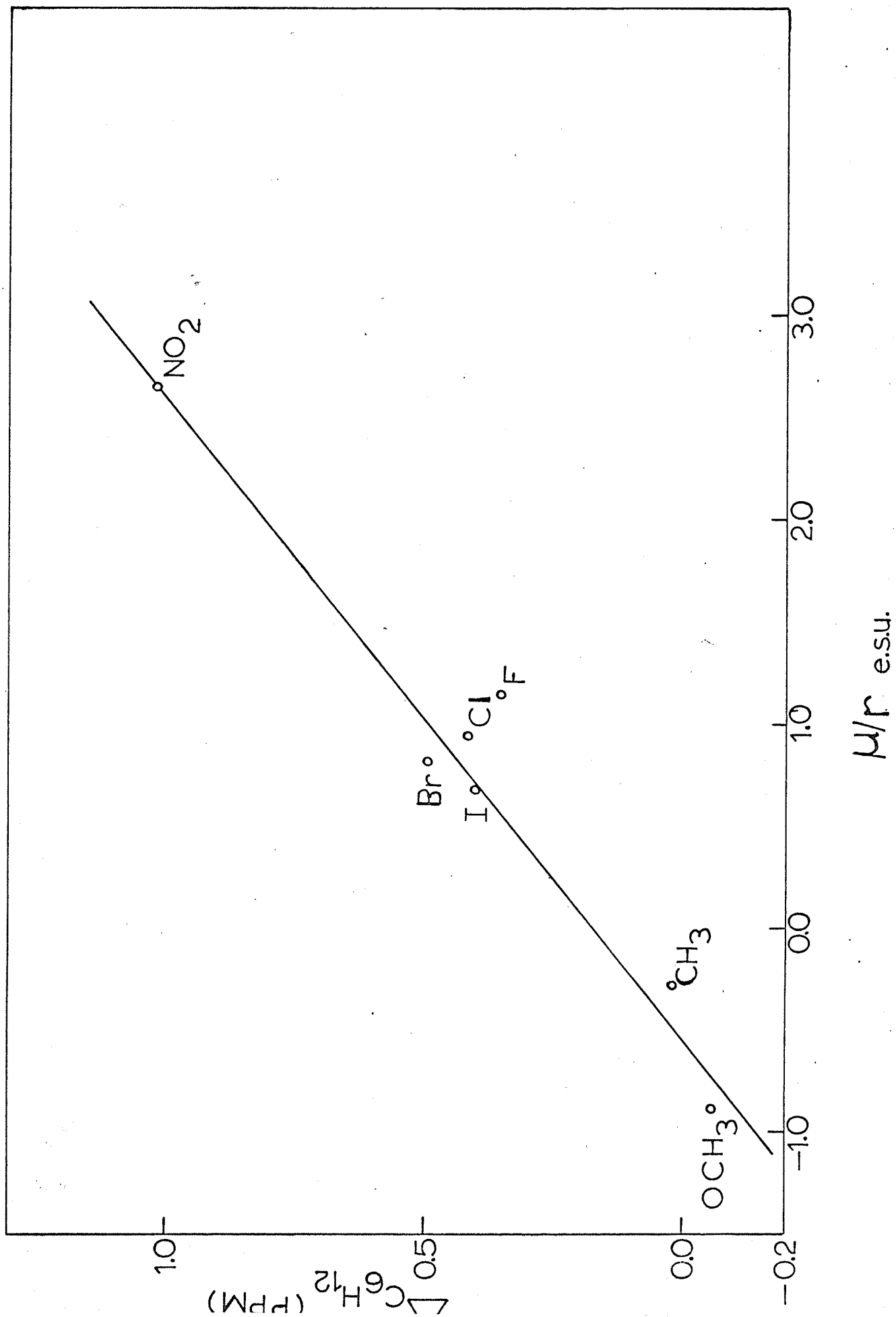
A similar, constant, shape parameter seems to be evident for the 1,2,3-trihalobenzenes. At least, the deviation of the observed solvent shift for 1,2,3-trichlorobenzene from that calculated from the parameters in Table III is consistent with the same deviation for 1-iodo-2,3-dichloro-benzene.

B- TESTING SUBSTITUENTS OTHER THAN HALOGEN

Some preliminary experiments have been performed to test whether the previous ideas apply to substituents other than halogen. The $\frac{\mu}{r}$ values (obtained from references 73 and 74 (when the C-X bond distance in C_6H_5X was not given, it was estimated from the C-X bond distance in similar compounts)), are -1.15 for -OH, -1.12 for $-N(CH_3)_2$, -1.11 for $-NH_2$, -0.89 for $-OCH_3$, -0.28 for $-CH_3$ and 2.64 for $-NO_2$. Negative values correspond to substituents which are electron donors. For $-N(CH_3)_2$ and $-NO_2$, only the C-N bond distance was used for the r value. For $-OCH_3$ only the C-O bond distance was used. There are several justifications for this: (1) The dipole moments of $C_6H_5N(CH_3)_2$ and $C_6H_5NH_2$ are approximately the same. The C-N bond distance is approximately the same. Choosing only the C-N bond distance for r thus gives approximately the same $\frac{\mu}{r}$ value for the two groups. If choosing only the C-N bond distance is justified, both groups, therefore, should have the same effect in determining the magnitude of the ASIS. From Figures 15 and 16 it appears that this is the case. (2) The more distant groups (e.g. the N-methyls for $-N(CH_3)_2$) are probably too distant to cause steric hindrance. (3) This approach seems to work.

The preliminary experiments indicate that the approach applied to halogen substituents as given in Section A of this chapter, also apply to other substituents. In Figure 14 the solvent shifts for some sym-p-disubstituted benzenes are plotted versus the $\frac{\mu}{r}$ value for the substituent. The near linearity of the plot suggests a similar charge effect for all substituents. Also, the p-disubstituted halobenzenes

Figure 14: A plot of $\triangle_{C_6H_{12}}$ in ppm for some sym-p-disubstituted benzenes versus the $\frac{\mu}{r}$ value of the substituent.


1.0
0.5
0.0
−0.2
$\Delta_{C_6H_{12}}$ (PPM)
−1.0
0.0
1.0
2.0
3.0
μ/r e.s.u.
NO2
Br
I
Cl
F
CH3
OCH3

do not fit the plot given in Figure 13. Presumably this is due to a shape effect, and, from Figure 14 it appears that this shape effect is independent of the substituent.

In Figure 15 the solvent shifts for the ortho protons of some monosubstituted benzenes are plotted versus the $\frac{\mu}{r}$ value of the substituent. Again a linear relationship is observed. In Figure 16 the average of the solvent shifts for the ortho, meta and para protons of the same monosubstituted benzenes is plotted versus the $\frac{\mu}{r}$ value of the substituent. Again a linear plot is obtained. Also the slope of the line in Figure 16 is greater than the slope of the line in Figure 15, suggesting a constant additional shift due to a shape effect.

When the benzene solute molecule is substituted so that there are no ortho hydrogens, substituents other than halogen appear to have the same effect as halogen, at least for those molecules tested, providing equation (7-1) is modified to

$$F\left(\frac{\mu}{r}\right) = \left[\sum_{o} \frac{\mu}{r}\right]_{\substack{\text{MESO.}\\ \text{IND.}}} + \frac{1}{2}\left[\sum_{m} \frac{\mu}{r}\right]_{\text{IND.}} + \frac{1}{3}\left[\left(\frac{\mu}{r}\right)_{p}\right]_{\text{MESO.}} \qquad (7\text{-}3)$$

The modification necessary is to consider substituents which are mainly inductive contributors when they are ortho and meta to the proton in question, and to consider substituents which are mainly mesomeric contributors when they are ortho or para to the proton in question. Inductive contributors are considered only in the ortho and meta position because the magnitude of inductive charge transfer drops off rapidly with the number of bonds. Also this seems to be justified by the halogen

Figure 15: A plot of $\triangle_{C_6H_{12}}$ in ppm for the ortho protons of some monosubstituted benzenes versus the $\frac{\mu}{r}$ value of the substituents. The values for $-N(CH_3)_2$, $-NH_2$ and $-NO_2$ are taken from reference 45.

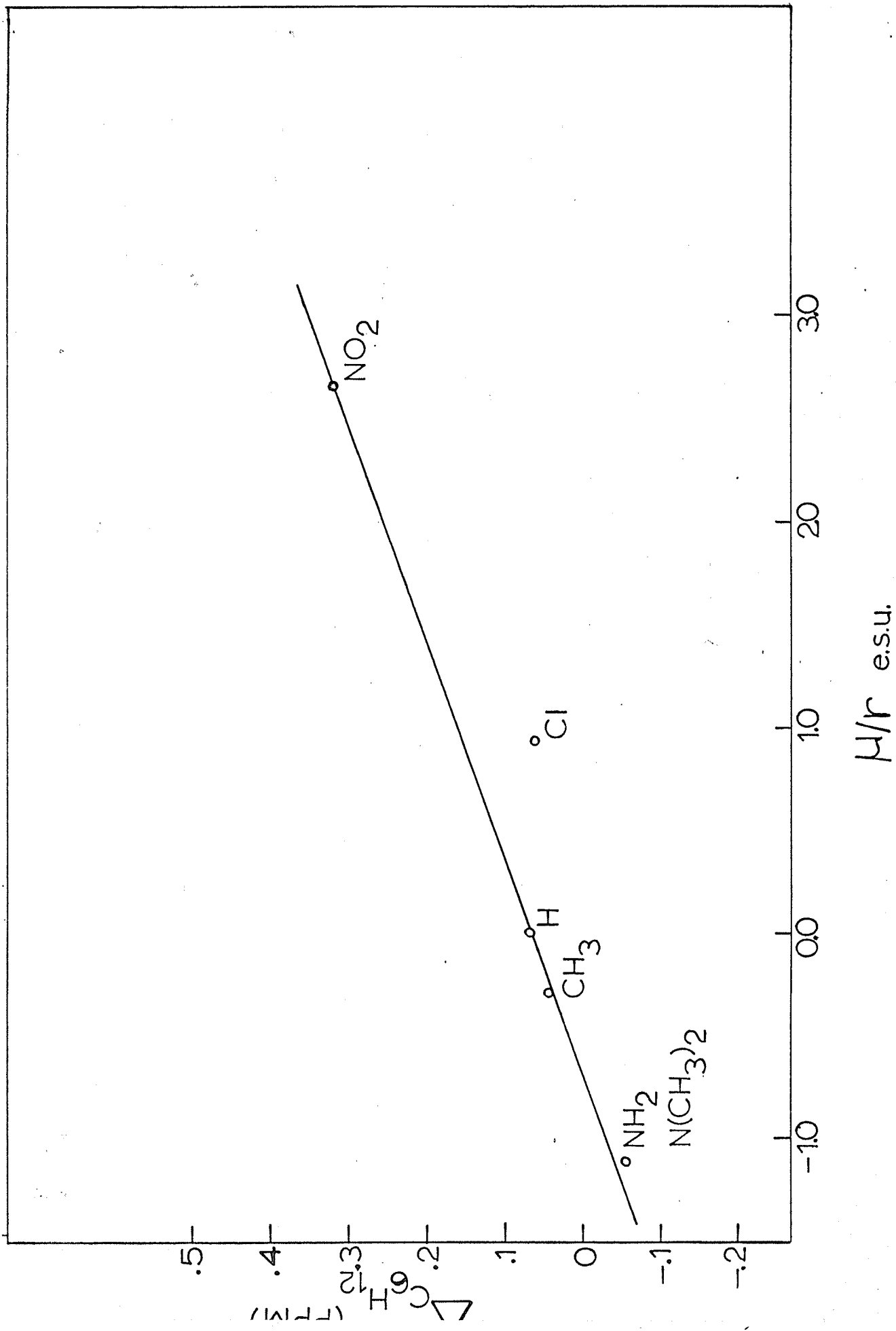
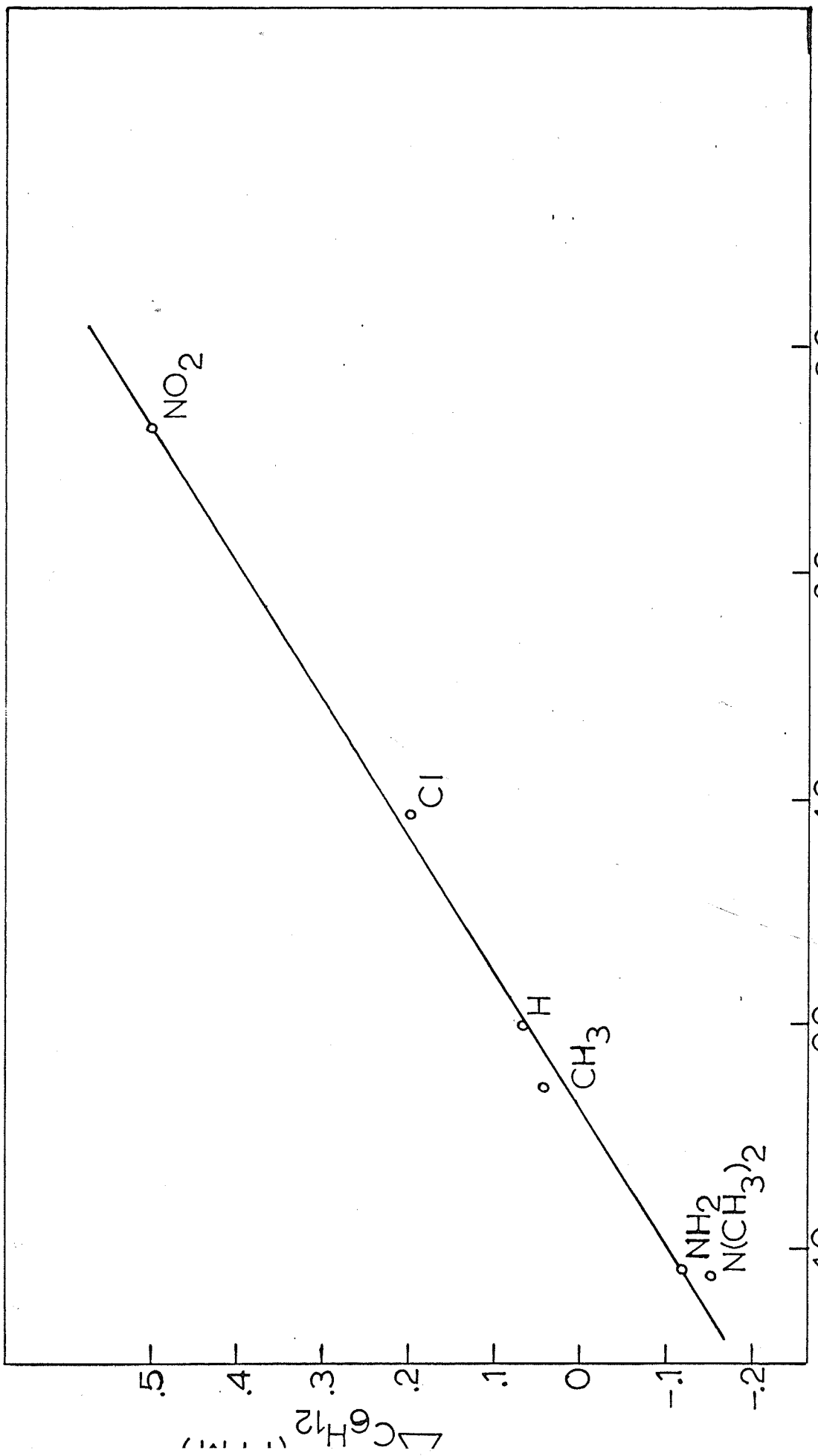

.5
.4
.3
.2
.1
0
-.1
-.2
-1.0
0.0
1.0
2.0
3.0
μ/r e.s.u.
ΔC_6H_{12} (FPM)
NO_2
Cl
H
CH_3
NH_2
$N(CH_3)_2$

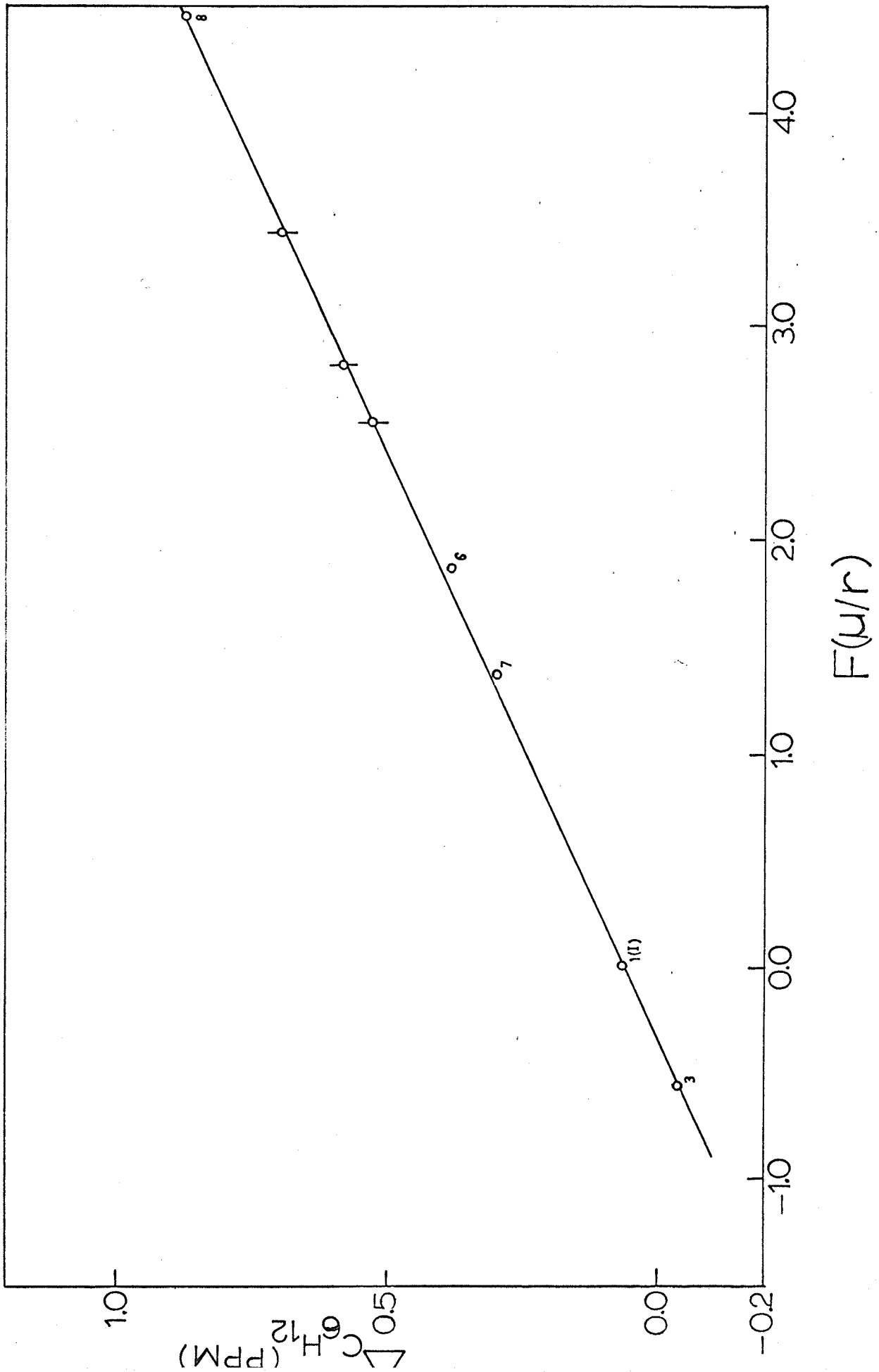
Figure 16: A plot of the average $\triangle_{C_6H_{12}}$ value, in ppm, of the ortho, meta and para protons of some monosubstituted benzenes versus the $\frac{\mu}{r}$ value of the substituent.


NO_2
Cl
H
CH_3
NH_2
$N(CH_3)_2$
5.
4.
3.
2.
1.
0
-.1
-.2
-1.0
0.0
1.0
2.0
3.0
μ/r e.s.u.

results. Considering mesomeric contributors only when the substituent is in the ortho and para position is perhaps justified by the fact that resonance structures for these molecules shows that mesomeric contributors affect charge distribution only in the ortho and para position. Thus - $N(CH_3)_2$, $-NH_2$, $-OH$, $-OCH_3$ and $-NO_2$ are considered only when ortho and para to the proton in question. CH_3 is considered an inductive contributor, although a dipole involving this substituent may arise from hyperconjugation. The solvent shifts for molecules containing some of these substituents is plotted versus $F(\frac{\mu}{r})$, as expressed by equation (7-3), in Figure 17. The points plot on the same line as that for the halogens in Figure 13. This is illustrated by replotting a few of the halogen values (represented by circles, ϕ).

From Figures 14,15,16 and 17 it is important to note that electron donors seem to have the same type of effect as electron withdrawers. This fact will be discussed in the next section.

Figure 17: A plot of $\Delta_{C_6H_{12}}$ in ppm versus $F(\frac{\mu}{r})$ (defined in text) for the protons of some polysubstituted benzenes. The numbering of the points corresponds to the numbering used in Table II, with the exception of point 1 (I) which corresponds to the numbering used in Table I.


1.0
0.5
0.0
-0.2
$C_{6H_{12}}$ (PPM)
-1.0
0.0
1.0
2.0
3.0
4.0
F(μ/r)
8
6
9
7
1(1)
3

C- SUMMARY AND CONCLUSIONS

From the polyhalobenzenes studied it appears that the magnitude of the benzene solvent induced shift is subject to steric effects, charge effects and shape effects. Charge effects also appear to determine the sign of the solvent shift.

The shape effect appears to be approximately constant for a given substitution pattern and probably is a result of packing.

It appears that the charge effect is merely electrostatic in nature. This is suggested for two reasons. First of all, as described previously, $\frac{\mu}{r}$ represents charge transfer. Secondly, and most important, is the fact that electron withdrawing substituents seem to have precisely the same (equal in magnitude but opposite in sign) effect as electron donors. If a local dipole-induced dipole type of interaction were the true mechanism giving rise to the solvent shift, it does not seem probable that benzene solvent molecules solvated at a positive substituent (as would be the case for electron donors) should produce a downfield shift equal in magnitude to the upfield shift caused by benzene solvent molecules solvated at the positive carbon atom bonded to an electron withdrawing substituent with an equivalent $\frac{\mu}{r}$ value. However, for the data presented, such shifts are observed. It would seem that some mechanism other than complex formation is necessary to explain the results. The mechanism presented by Fort and Lindstrom (64) (see Chapter III) perhaps would more reasonably explain the results presented in this thesis.

All the factors determining the benzene solvent induced shift have, however, not been uncovered. The pentasubstituted compounds examined

do not correlate with the other compounds. They do, however, correlate among themselves provided the parasubstituent is included whether it is an inductive or mesomeric contributor. At least this is the case for the three compounds examined. Perhaps when there is only one electron deficient region in the benzene solute molecule all substituents become important.

Also the observed and calculated values for the ASIS of the protons in 3,5-dichlorotoluene differ greatly. The protons ortho to the positive methyl group experience a much larger upfield shift than calculated while the proton ortho to the two chlorines experiences a much smaller upfield shift than calculated. This may be due to the fact that the methyl group acts as a positive centre causing more benzene solvent molecules to orientate towards this end of the solute molecule. In mesitylene there was no such preference because the substitution was symmetrical.

D- SUGGESTIONS FOR FUTURE RESEARCH

The model developed for polyhalobenzenes in this thesis has only briefly been applied to polysubstituted benzenes containing substituents other than halogen. Equation (7-3) was applied only to a few compounds. It should obviously be tested on many more compounds. A much more detailed study of compounds like 3,5-dichlorotoluene is also needed to test the effect of positive centres.

Further extensions of this work may also lead to a useful method for approximately determining the dipole moments of substituted benzenes. At present it appears that this is so for monosubstituted benzenes, at least.

Sufficient refinement of the ideas presented in this thesis may also lead to a new method for investigating interactions between substituents, such as hydrogen bonding.

- APPENDIX I -

- Compilation of Coupling Constants -

TABLE VI

Coupling Constants In Polyhalosubstituted Benzenes (H_Z)*

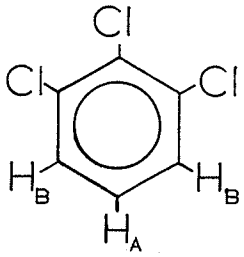
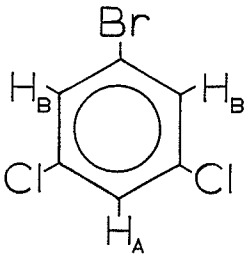
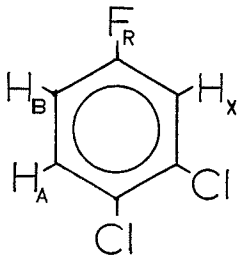
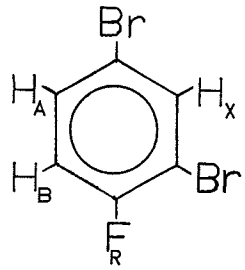
COMPOUND	J	IN CCl_4 +	IN C_6H_{12} +	IN C_6D_6
	J_{AB}	8.16	8.14	8.11
	J_{AB}	1.81	1.84	1.82
	J_{AB}	8.81	8.83	8.88
	J_{AX}	0.30	0.31	0.35
	J_{BX}	2.91	2.94	3.06
	J_{AR}	5.44	5.33	5.38
	J_{BR}	7.47	7.46	7.77
	J_{RX}	8.08	7.99	8.22
	J_{AB}	8.71	8.70	8.75
	J_{AX}	2.45	2.40	2.46
	J_{BX}	0.30	0.30	0.24
	J_{AR}	4.26	4.23	4.35
	J_{BR}	7.94	7.93	8.25
	J_{RX}	6.06	6.05	6.11

Table VI (Continued)

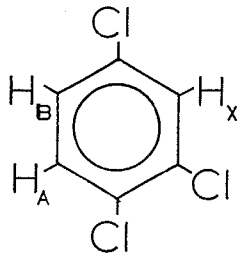
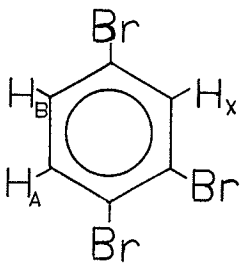
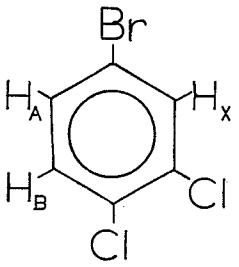
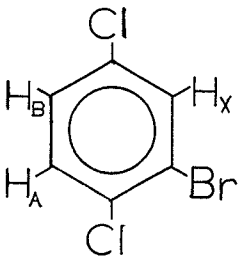
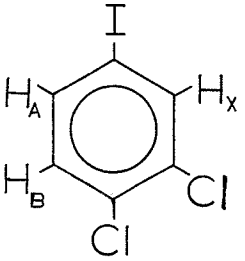
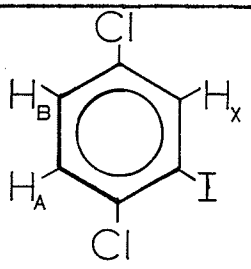
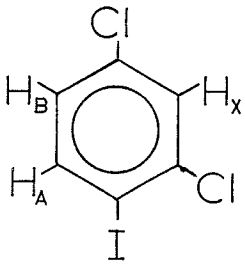
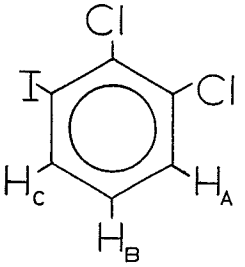
COMPOUND	J	IN CCl_4	IN C_6H_{12}	IN C_6D_6
	J_{AB} J_{AX} J_{BX}	8.60 0.23 2.42	8.58 0.32 2.39	8.59 0.24 2.46
	J_{AB} J_{AX} J_{BX}	8.47 0.22 2.26	8.52 0.20 2.26	8.49 0.21 2.26
	J_{AB} J_{AX} J_{BX}	8.55 2.22 0.34	--- --- ---	8.54 2.31 0.25
	J_{AB} J_{AX} J_{BX}	8.59 0.26 2.41	8.56 0.25 2.40	8.61 0.30 2.41
	J_{AB} J_{AX} J_{BX}	8.43 2.05 0.23	8.39 2.02 0.24	8.43 2.05 0.26

Table VI (Continued)

COMPOUND	J	IN CCl_4	IN C_6H_{12}	IN C_6D_6
	J_{AB} J_{AX} J_{BX}	8.53 0.27 2.43	8.54 0.28 2.43	8.55 0.26 2.43
	J_{AB} J_{AX} J_{BX}	8.55 0.25 2.41	8.54 0.33 2.38	8.53 0.22 2.48
	J_{AB} J_{AC} J_{BC}	8.01 1.43 7.95	8.01 1.46 7.96	8.05 1.44 7.95

* Standard deviations are in all cases less than $\pm$ 0.03 H_Z.

+ The coupling constants quoted for carbon tetrachloride and cyclohexane as solvents are taken from references 66 and 76, with the exception of those for the last three compounds. All values for the last three compounds were determined by the author.

- APPENDIX II -

- The Analysis of the NMR Spectra -

- APPENDIX II - *

In single line spectra, the proton chemical shift corresponds to the frequency of the line position.

The AB_2 and ABX spectra were analysed according to procedures given in standard texts (2,4,5).

The chemical shifts for most of the spectra complicated by fluorine splittings were obtained from symmetry considerations. The spectra of 2,4-dibromo fluorobenzene and 3,4-dichlorofluorobenzene were analysed as ABXR spectra according to the procedure given in reference 77. The spectrum of the lattercompound is actually an ABCR spectrum which approximates very closely to an ABXR spectrum.

The spectrum of 1-bromo-3-chloro-5-iodobenzene (an ABC which approximates closely to an AB_2) was analysed as an AB_2 spectrum.

The spectrum of 2,3-dichloroiodobenzene was analysed as an ABC spectrum by means of an IBM 360/65 computer using the LAOCOON III program of S. Castellano and A.A. Bothner-By. When C_6H_{12} and C_6D_6 were used as solvents, two of the B lines were unresolvable. Treating these lines as degenerate in the computer input data produced parameters (shifts and coupling constants) with an average probable error of 0.025 c/s for C_6H_{12} as solvent and 0.027 c/s for C_6D_6 as solvent. In the computer input statements the unresolvable lines were then reported as being two resolvable lines separated by 0.24 c/s (by adding and substracting 0.12 c/s from the unresolvable line position). The analysis was repeated and this gave rise to a new set of parameters (shifts and coupling constants)

with an average probable error of 0.014 c/s for C_6H_{12} as solvent and 0.015 c/s for C_6D_6 as solvent. The average of the two sets of parameters was reported.

The spectrum of 3,5-dichlorotoluene was analysed as an AB_2 spectrum by treating the methyl splitting as being first order.

The spectra of toluene and mesitylene appeared as several broad peaks over a region of about 5 c/s. The chemical shift, in both cases, was taken to be the centre of these groups of peaks.

The spectrum of chlorobenzene appeared as several broad peaks of varying intensity over a region of about 5 c/s for all solvents used (see Appendix III) except C_6D_6. The spectra were analysed by taking the centre of the group of signals as the chemical shift if the spectrum was close to a typical multiplet. If the signals had a structure far from a simple multiplet, the chemical shift was assumed to be given by the location of the area-weighted centre of the appropriate signals. The chemical shifts of the ortho and meta protons of chlorobenzene in C_6D_6 were gotten approximately by using chlorobenzene-4d_1 (an AA^1BB^1X system), treating the deuterium coupling as being first order; and then analysing the spectrum approximately as an AB spectrum.

* This appendix applys only to the C_6D_6 values reported in the thesis, with the exception of the discussion of the analysis of the spectrum of 2,3-dichloroiodobenzene, which applys to the CCl_4, C_6H_{12} and C_6D_6 values.

- APPENDIX III -

- The Benzene Solute Experiment -

- APPENDIX III -

In order to obtain further insight into the nature of the benzene solvent shift, the following investigation was carried out. The solvent - solute systems previously studied were reversed, that is, 3 mole percent solutions of C_6H_6 were made up using some of the halobenzenes listed earlier as the solvent. The position of the benzene resonance was then studied. The results of this experiment are given in Table VII.

TABLE VII

Benzene Chemical Shifts in Halobenzene Solutions

SOLVENT	BENZENE CHEMICAL SHIFT*
Carbon Tetrachloride	7.253
Cyclohexane	7.211
Benzene-d_6	7.149
Hexafluorobenzene	7.183
Pentafluorobenzene	7.219
1,2,3,5-tetrafluorobenzene	7.233
1,2,4,5-tetrafluorobenzene	7.257
1,2,3,4-tetrafluorobenzene	7.262
1,2,4-trichlorobenzene	7.234
2,4-dichlorobromobenzene	7.238
2,4-dichloroiodobenzene	7.253
2,5-dichloroiodobenzene	7.255

* PPM to low field of internal TMS.

The average benzene chemical shift for the halobenzene solvent samples is 7.237 ppm. With the exception of the hexafluorobenzene sample, all halobenzene samples have a benzene chemical shift value to low field of the benzene chemical shift for the cyclohexane solvent system. The

results in Table VII indicate that for solvents in chemical shift work the halobenzenes behave more like a polar than a nonpolar, anisotropic solvent. Certainly they are not similar to benzene.

It was thought that there were two possible explanations for the above results. When benzene is solvent, the benzene molecules encounter essentially only one solute molecule at any given time. Because of this it experiences only one net dipolar force which in turn can induce a preferentially directed dipole in the benzene π-electron system. This leads to specific interaction as discussed previously. On the other hand, when benzene is the solute, it encounters several polar molecules at any instant of time and these polar solvent molecules presumably have their dipole moments orientated randomly about the solute molecule. Hence it does not seem probable that any preferentially directed dipole will be induced in the benzene π-system. Thus there would be no specific interaction and no net solvent shift. To test this hypothesis several solutions of chlorobenzene (a molecule with a permanent dipole moment) were examined. With chlorobenzene there should be direct dipole-dipole interaction and hence a net solvent shift should be observed. The results of this experiment are given in Table VIII.

TABLE VIII

Chlorobenzene Chemical Shifts in Halobenzenes Solutions

SOLVENT	CHLOROBENZENE CHEMICAL SHIFT*
Carbon Tetrachloride	7.232
Cyclohexane	7.161
Benzene - d6	7.100 (ortho) 6.829 (meta)
Hexafluorobenzene	7.183
Pentafluorobenzene	7.214
1,2,4-trichlorobenzene	7.190

* PPM to low field of TMS.

From the results given in Table VIII it appears that even with a polar solute the halobenzenes behave as polar isotropic solvents.

The second possible explanation for the anomalous behaviour of the halobenzene solvents is that the halogen substituents are having an effect on the ring current such that these compounds have a much different magnetic anisotropy than benzene. Figeys (78) recently calculated that substituents tend to decrease the ring current in monosubstituted benzenes. Corfield and Buckingham are at present measuring the magnetic anisotropy of hexafluorobenzene with their Cotton-Mouton apparatus. Until their results are known it is not of much further use to speculate on the reason for the anomolous behaviour of the halobenzene solvents.

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