SOME INVESTIGATIONS OF INTRAMOLECULAR SCREENING EFFECTS ON ^{1}H AND ^{19}F N.M.R. CHEMICAL SHIFTS

A thesis
presented to the University of Aston in
Birmingham for the degree of Doctor of
Philosophy.

by

David Callaghan B.Sc., A.R.I.C.

The Chemistry Department,
The University of Aston in Birmingham

January, 1969.

SUMMARY

The investigations reported herein concern the evaluation of ^{1}H and ^{19}F chemical shifts by semi-empirical methods. Cyclic molecules have been primarily used in these investigations. The spectral parameters required have, for some of the compounds used, been reported previously and those for the other compounds, a series of novel highly fluorinated bicyclo(2,2,1)heptanes and heptenes, are reported herein.

It has generally been assumed that ^{1}H shifts in saturated hydrocarbons depend on secondary fields produced at a resonant nucleus by magnetically anisotropic neighbouring bonds. It has been shown that a quantity, conveniently called the 'apparent' anisotropy in bond magnetic susceptibility, can be derived from n.m.r. measurements, and better used to interpret the ^{1}H shifts in a range of saturated compounds. The magnitudes of the 'apparent' anisotropies and origins of the equivalent dipoles for the C-C, C-H, C-F and C-Cl bonds have been determined. The magnitudes are found to be $+4.3 \times 10^{-6}$, between 0 and -1.2×10^{-6}, -6.0×10^{-6} and -7.8×10^{-6} $cm.^{3}mole^{-1}$ respectively and the equivalent dipole in the last three cases shown to act at the carbon atom of the bond.

^{19}F shifts in saturated compounds have been attributed to intramolecular electric fields produced by neighbouring bonds at the resonant nucleus and evaluated using an equation of the form:

$$\Delta\sigma = -A\Delta E_{z} - B(\Delta E^{2} + \Delta\langle E^{2}\rangle)$$

Significantly better correlations with experimental results are

demonstrated if the equation used is of the form:

$$\Delta\sigma = -X\Delta E_z - Y\Delta E^2 - Z\Delta\langle E^2\rangle$$

Values representing X, Y and Z and the location of the point dipole associated with the C-F bonds, have been deduced. It is found that the latter originates at c.a. 0.629Å along the bond from the carbon atom and $X = -90 \times 10^{-12}$, $Y = -1270 \times 10^{-18}$, $Z = +146.5 \times 10^{-18}$ e.s.u. Better agreement with experimental results is observed when possible contributions to $\langle E^2\rangle$ from C-C bonds are neglected.

ACKNOWLEDGEMENTS

I should like to express my thanks to my supervisor, Dr. J. Homer, for his assistance during the course of this work, and in particular for the many helpful suggestions on the interpretation of the results. I am also grateful to my colleagues, M. C. Cooke, P. J. Huck and C. J. Jackson for their helpful discussions.

My thanks are due to Dr. R. Stephens of the University of Birmingham for the gift of all of the fluorinated bicyclic compounds used for the studies reported herein. I am also grateful to Professor W. G. S. Parker for the provision of facilities for this research and to the Science Research Council for the award of a Research Studentship.

Note on Units used in this Thesis

The units used in reporting work in the scientific literature are being standardised to conform to the recently proposed S.I. (Systeme International d'Unites) convention. However, the units used throughout this thesis are those which, at the time of writing, are acceptable to The Chemical Society (London).

CONTENTS

Page

CHAPTER 1

Some Theoretical Considerations of Nuclear Magnetic Resonance Spectroscopy

CHAPTER 2

Experimental Methods for the Observation of High Resolution Nuclear Magnetic Resonance

CHAPTER 3

Some Considerations of the Chemical Shift

CHAPTER 4

The N.M.R. Spectra of Some Highly Fluorinated Bicyclo(2,2,1)heptane and Heptene Compounds

CHAPTER 5

The Anisotropy in the Magnetic Susceptibility of C-C and C-H Bonds

CHAPTER 6

The Apparent Anisotropy in the Magnetic Susceptibility of C-F and C-Cl Bonds

CHAPTER 7

Some Investigations of the Correlation Between ^{19}F Nuclear Screening and Intramolecular Electric Fields.

CHAPTER 8

Some Further Application of Electric Field Calculations.

CHAPTER 9

Some Attempts to Observe ^{13}C Resonance as a Preliminary to a Possible Interpretation of ^{13}C Shifts on Terms of Intramolecular Electric Fields

ILLUSTRATIONS

CHAPTER 1

Some Theoretical Considerations of Nuclear Magnetic Resonance Spectroscopy

1:1 Introduction

In 1924 Pauli[1] put forward the hypothesis that some atomic nuclei, in addition to acting as point electrostatic charges, possess magnetic moments. This idea was forwarded to explain the hyperfine structure observed in optical atomic spectra. When situated in an applied magnetic field the nuclear magnetic moments experience a torque and adopt specific orientations with respect to the field. These correspond to different energetic states and the application of a second rotating (oscillating) magnetic field can induce transitions between them. The quantisation of the nuclear energy levels is governed by the angular momentum of a nucleus which must be an integral or half integral multiple of $h/2\pi$ ($\hbar$) and can take $(2I + 1)$ discrete values, so that a nucleus will have $(2I + 1)$ distinct energy states in which the component of angular momentum along any direction will have values I, $(I - 1)$, ... $-I$. I is a characteristic property of each nuclear type and is referred to as the nuclear spin quantum number. The value of the nuclear spin I is seen to exhibit certain regular features which may be expressed in terms of the atomic number Z and the atomic weight A of the nucleus. If A is odd, the nuclear spin is half integral, if A and Z are both even, the spin is zero and if A is even while Z is odd, the spin is integral.

The molecular beam experiment of Stern and Gerlach[2] (1921) showed that the measurable values of an atomic magnetic moment are discrete, corresponding to the space quantisation of an atom when placed in an inhomogeneous magnetic field. Later, the magnetic moment of the hydrogen nucleus (proton) was measured by directing a beam of hydrogen molecules through a steady magnetic field[3]. This was possible because, when situated in such a magnetic field H, the nuclear energy levels are separated by an energy difference $2\mu H$ where μ is the maximum measurable value for the nuclear magnetic moment. In the general case of a nucleus with spin I, successive levels are separated by $\mu H/I$. The molecular beam method was further developed by subjecting the beam to an additional oscillating magnetic field[4] which was swept through a range of frequencies. When the frequency of the second field corresponded with $\mu H/Ih$, there was a sudden drop in the density of molecules reaching the detector, corresponding to an absorption of energy from this second oscillating field.

The first nuclear magnetic resonance (n.m.r.) signals from bulk matter were observed independently by two groups of workers in 1945; by Purcell, Torrey and Pound[5] and by Bloch, Hansen and Packard[6] using respectively samples of paraffin wax and water. Since these initial experiments were performed, the advances in instrumental design and in the theory of nuclear magnetic resonance have been such that the technique is now accepted as being invaluable for the study of certain nuclear properties and as an analytical tool for use in the determination of molecular structure[7, 8, 9, 10].

1:2 Nuclei in a Magnetic Field

The magnetic properties of a nucleus are best discussed in terms of their angular momenta and spin. Quantum mechanics requires that the maximum measurable component of the angular momentum of a nucleus must be an integral or half integral multiple of $\hbar$. The spin quantum number I governs the components of the angular momentum in a particular direction, limiting the number of spin states to $(2I + 1)$, so that the component along any direction has the values

$$I,\ (I - 1),\ \ldots.\ (-I + 1),\ -I\ (x\ \hbar)$$

It is also convenient to express magnetic properties in terms of the magnetogyric ratio γ, defined in the expression

$$\mu = \gamma I \hbar \qquad 1:1$$

From this, the magnetic moment and angular momentum can be seen to behave as parallel vectors (shown diagramatically in figure 1:1A) and therefore the observable components of the magnetic moment may be defined by a set of observable values $m\mu/I$, where $m = I, I - 1, \ldots. -I + 1, -I$ is the magnetic quantum number. The nuclear states predicted by quantum mechanics are degenerate in the absence of an external field but become separated in the presence of a field to give the predicted $(2I + 1)$ states. The energy E_z of a nucleus when introduced into a uniform magnetic field H_o in the Z direction (relative to that in zero field) is given by

$$E_z = - \mu_z H_o \qquad 1:2$$

The allowed nuclear energy levels will thus be $-m\mu H_o/I$ or

$$-\mu H_o,\ \frac{-I - 1}{I}\mu H_o\ ,\ \ldots..\ \frac{I - 1}{I}\mu H_o,\ \ \mu H_o$$

Consequently, these levels, known as nuclear Zeeman levels, are split by $\mu H_o/I$. The selection rule governing nuclear transitions is $\Delta m = \pm 1$, consequently, transitions between successive levels are the basis of n.m.r. experiments and for these to occur, the Bohr frequency condition must be observed, giving

$$h\nu = \mu H_o/I \qquad 1:3$$

or expressing equation 1.3 in terms of the magnetogyric ratio

$$\nu = \frac{\gamma H_o}{2\pi} \qquad 1:4$$

For practical observations of nuclear magnetic resonance signals the field H_o is generally of the order of 10,000 - 23,000 gauss, which necessitates a frequency ν of 40 - 100 Mc.sec.$^{-1}$ (i.e. in the radiofrequency region) for the observation of ^1H and ^{19}F resonance.

1:3 Criteria for Resonance

Nuclear magnetic resonance has been treated both classically and from a quantum mechanical view point. Both approaches are useful for an understanding of the resonance phenomenon and will be considered briefly in turn.

a) Classical Treatment of Nuclear Magnetic Resonance

Considering the motion of a magnetic dipole (nucleus) in a magnetic field, the magnetic moment μ and angular momentum p of a nucleus are related by

$$\mu = \gamma p \qquad 1:5$$

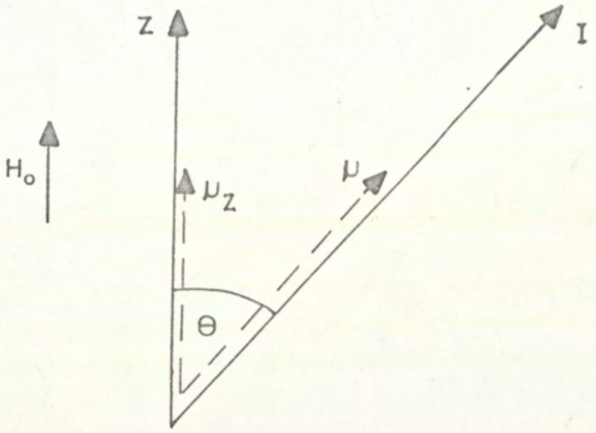
The equation of motion can be written vectorially as

$$d\mu/dt = \gamma(\mu \times H) \qquad 1:6$$

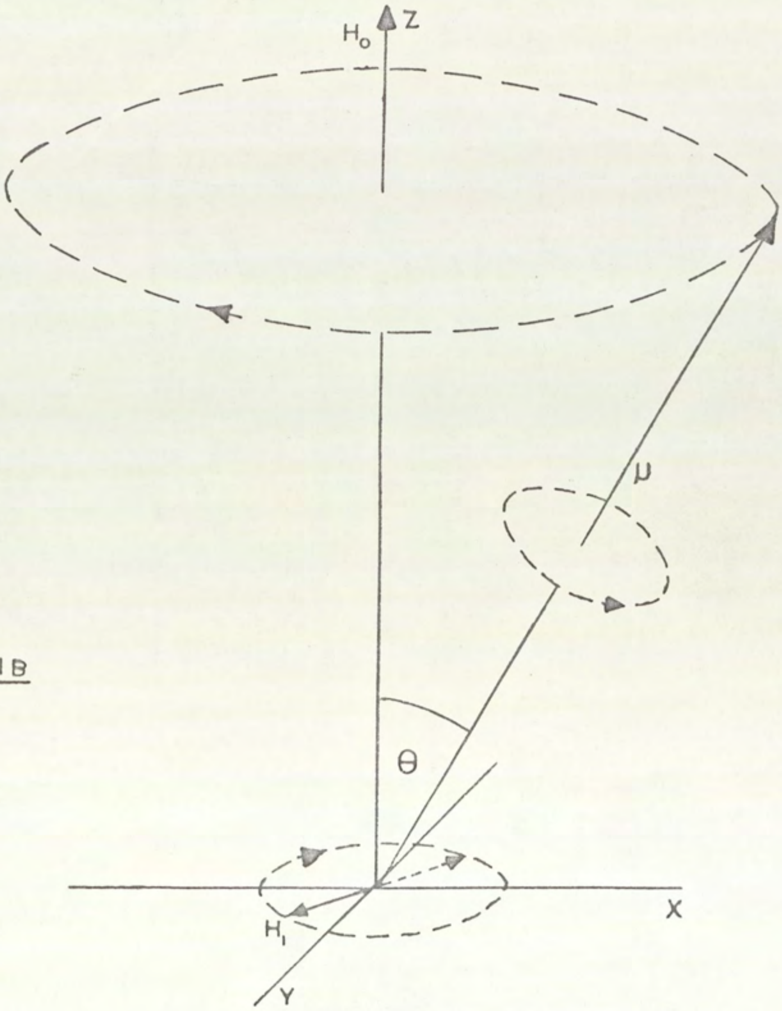
where H is the applied magnetic field. If μ is rotated with an angular frequency whose magnitude and direction are given by w, the rate of change of μ is given by

$$d\mu/dt = w \times \mu \qquad 1:7$$

Comparing equations 1:6 and 1:7, it is seen that the effect of the



1.1A



1.1B

FIGURE 1.1A The relationship between the magnetic moment and the spin angular momentum I.

FIGURE 1.1B Vectorial representation of the classical Larmor precession.

magnetic field H is equivalent to rotation with an angular frequency

$$w = -\gamma H \qquad 1{:}8$$

Thus, if H is a constant field H_o , the magnetic dipole will precess about the direction of H_o with angular frequency w , which is referred to as the Larmor frequency. Equation 1:8 may be rewritten in terms of the precession frequency ν_o as

$$\nu_o = -\gamma H_o/2\pi \qquad 1{:}9$$

If a new co-ordinate system is set up rotating with the Larmor angular frequency w and if there is no other magnetic field acting, the magnetic moment vector μ would remain stationary in the new frame. If another smaller constant magnitude field H_1 is introduced perpendicular to the original field H_o but rotating about the H_o direction, H_1 will also be rotating within the rotating co-ordinate system if the angular frequency of H_1 is not the same as w (figure 1:1B). The effect of H_1 will be to exert a torque $\mu \times H_1$ on the nucleus tending to tip the nuclear moment toward the plane perpendicular to H_o. If H_1 is moving within the rotating frame, the direction of the torque will vary rapidly and the only resultant effect will be a slight wobbling perturbation of the steady precessional motion. If, however, the field H_1 is rotating at the Larmor frequency, then in the rotating system it will behave as a constant field and the torque, always being in the same direction, will cause large oscillations in the angle between μ and H_o. If the rate of rotation of H_1 is varied through the Larmor frequency, the oscillations will increase and be greatest at the Larmor frequency itself and will show as a resonance phenomenon. It is generally not convenient to apply a pure rotating field H_1

and instead, a linearly oscillating field is applied which may be regarded as the superimposition of two fields rotating in opposite directions. Only the component having the correct sense will synchronise with the precessing magnetic moment, the other component having no effect. A purely classical model as presented here cannot predict more than a continuous absorption of energy.

b) A Quantum Mechanical Treatment of Nuclear Magnetic Resonance

If a nucleus of magnetic moment μ is placed in a magnetic field H, the Hamiltonian for the system is given by

$$\mathcal{H} = -\mu H \qquad 1:10$$

Hence, from equation 1:1

$$\mathcal{H} = -\gamma\hbar HI \qquad 1:11$$

There are m expected values of I and hence m expected values of $\mathcal{H}$, i.e. the energy levels of the system are given by

$$E = -\gamma\hbar mH \qquad 1:12$$

In order to induce transitions between the energy states, some form of perturbation must be introduced and this takes the form of an oscillating magnetic field, the necessary direction of this field being decided from the properties of spin operators and eigenfunctions appropriate to a nucleus of spin I.

A set of spin angular momentum operators I_x, I_y, I_z, I^2 can be defined for a nucleus of spin I. If, for simplicity, the nuclear spin I is restricted to $I = \pm\frac{1}{2}$, there are only two possible energy levels given by $\pm\frac{1}{2}\gamma\hbar H$. If the spin eigenfunctions are denoted by the symbols α and β, then

$$\begin{aligned} I_z\alpha &= +\tfrac{1}{2}\hbar\alpha \\ I_z\beta &= -\tfrac{1}{2}\hbar\beta \end{aligned} \qquad 1:13$$

The functions α and β are orthonormal, then

$$\alpha^2 = \beta^2 = 1$$
$$\alpha\beta = \beta\alpha = 0 \qquad 1{:}14$$

The operators I_x and I_y have the properties

$$I_x\alpha = \tfrac{1}{2}\hbar\beta; \quad I_x\beta = \tfrac{1}{2}\hbar\alpha$$
$$I_y\alpha = \tfrac{1}{2}i\hbar\beta; \quad I_y\beta = -\tfrac{1}{2}i\hbar\alpha \qquad 1{:}15$$

For the general case of a nucleus of spin I, the transition probability between two energy levels m and m' is given by

$$W^1 = (\psi_m | I_x | \psi_{m'}) \qquad 1{:}16$$

which is zero unless $m = m' \pm 1$. This gives the selection rule for nuclear transitions as $\Delta m = \pm 1$.

Considering the simpler case of a nucleus of spin $I = \pm\frac{1}{2}$, the probability of a transition between the two levels when an oscillating field is applied along the z axis is given by W^1 where

$$W^1 = (\alpha | I_z | \beta) = 0 \qquad 1{:}17$$

i.e. this arrangement of steady and oscillating fields cannot induce a transition. However, if an oscillating field is applied along the x axis, then

$$W^1 = (\alpha | I_x | \beta) = \tfrac{1}{2}\hbar \qquad 1{:}18$$

and a similar probability of transition is obtained if the oscillating field is applied along the y axis. The energy change when such a transition takes place is given by

$$E = \gamma\hbar H \qquad 1{:}19$$

and the frequency of the oscillating field is given by

$$\nu = \Delta E/h = \gamma H/2\pi \qquad 1{:}20$$

which is the equation governing the resonance condition for a nucleus of spin $I = \frac{1}{2}$.

1:4 The Distribution of Spin States

The treatment of nuclear magnetic resonance developed so far has considered only transitions between various nuclear energy levels; it is the purpose of this section to investigate the populations of the various accessible energy levels and the probabilities of transitions between them. The probabilities of the absorption or stimulated emission of energy are equal, the effect of spontaneous emission of energy being negligible[11], i.e. there is an equal probability that Δm will be ± 1. To enable the observation of nuclear resonance signals, there must be a nett change in the system, which is governed by the distribution of nuclei between the various energy levels. If only two energy levels are considered, and N_1 and N_2 are the numbers of nuclei in the low and high energy levels, then the nett change in the system is given by

$$P(N_1 - N_2) \qquad 1{:}21$$

where P is the probability of a transition occurring. In the absence of a secondary field H_1, there is a Boltzman distribution of nuclei between the various allowed energetically different nuclear levels. The probability that any nucleus will occupy a particular level of magnetic quantum number m is given by

$$\frac{1}{2I+1}\left[\exp\frac{m\mu H_o}{IkT}\right] \qquad 1{:}22$$

which approximately reduces to

$$\frac{1}{2I+1}\left[1+\frac{m\mu H_o}{IkT}\right] \qquad 1{:}23$$

It is seen that there is a distribution of nuclei favouring the lower energy state and for a nucleus of spin $I = \frac{1}{2}$, the probabilities of the nucleus being in either the upper or lower energy state respectively are given by

$$\frac{\frac{1}{2}(1 - \mu H/kT)}{\frac{1}{2}(1 + \mu H/kT)} \qquad 1:24$$

Examination of equation 1:24 shows the desirability that the nuclei should experience as high an applied field as possible for the observation of nuclear magnetic resonance signals, since the higher the field, the greater the sensitivity due to the increase in the excess population of nuclei in the lower energy state.

Equation 1:24 shows that there is normally an excess of nuclei in the lower energy state, giving rise to the possibility of nett absorption of energy for the observation of nuclear resonance signals. Nuclear magnetic resonance spectroscopy differs from optical spectroscopy[12, 13] in that in the latter case a very rapid return is normally made from an excited state to the ground state after absorption of energy, the energy being liberated in the form of heat. However, nuclear magnetic resonance signals can weaken and eventually disappear with increasing intensity of the radiofrequency field H_1 as n_{excess}, the number of excess nuclei in the lower energy state tends to zero. This phenomenon is known as saturation.

1:5 Saturation

The continued absorption of energy from the radiofrequency field will tend to reduce the excess population in the lower energy state, relative to that in the upper state, and hence reduce the nett number of nuclei that would be capable of absorbing energy from the radiofrequency field H_1. The magnitude of this effect will increase with the amplitude of the oscillating field and is referred to as saturation, which shows primarily as a reduction in signal intensity. In addition to reducing the overall magnitude of the absorption, saturation will distort the signal causing a broadening of the resonance line and, if the spectrum consists of several lines, it is possible that they may be affected non-uniformly by saturation.

An experimental feature which may result from saturation, is the appearance of multiple-quantum transitions[14]. These are transitions which are forbidden by the first order selection rules, but occur at higher order, with the absorption of two or more quanta. An example of this is shown by the spectrum of ethyl alcohol[15]; under saturation conditions a signal is observed half way between the methyl and methylene resonances due to the absorption of two quanta, causing a simultaneous change in the spin states of the methyl and methylene protons.

1:6 Relaxation Processes

In the absence of any mechanism to counteract the effects of saturation discussed in section 1:5, severe limitations would be placed on the use of the nuclear magnetic resonance. However, there are processes operating which tend to restore the original distribution of energy levels, following the absorption of energy from the radiofrequency field. The removal of excess energy from an excited spin state allowing the nucleus to return to a lower energy state, is generally referred to as a relaxation process of which there are two principal types.

a) Spin-Lattice Relaxation

Equation 1:24 gives the relative populations of the two spin states available to a nucleus of spin $\frac{1}{2}$. It is seen that there is an excess population in the lower energy state; however, the observation of nuclear magnetic resonance depends on the nett absorption of energy by this small excess population, which will obviously decrease the number of nuclei in the lower energy state.

The ratio of populations may still be described by a Boltzman factor but now there is a corresponding rise in temperature to the spin temperature T_s which is given by

$$\frac{N_1}{N_2} = \exp(2\mu H_o/kT_s) \qquad 1:25$$

which approximates to

$$\frac{N_1}{N_2} \simeq 1 + \frac{2\mu H_o}{kT_s} \qquad 1:26$$

Where N_2 and N_1 are respectively the number of nuclei in the higher and lower energy states. Nuclear spins invariably react with their surroundings, but, since the interaction is small, it is permissable to distinguish between spin temperature and Lattice temperature. However, thermal equilibrium is established eventually between the two systems due to the small interaction. Since the heat capacity of the spin system is negligible compared to that of the lattice, except at very low temperatures, the resultant temperature will be very close to that of the lattice. The absorption of radiofrequency energy tends to reduce the excess population in the lower state, but the flow of heat from the nuclei to the lattice will tend to oppose this change in population. For nuclei with spin greater than $\frac{1}{2}$ the concept of spin temperature is less precisely defined, for there will be more than two states and a unique value of T_s can be obtained only if the ratios of their populations are appropriately related. In view of the fact that there is a rise in temperature, the spin temperature T_s will be above the temperature of the lattice and hence there must be a flow of energy from the spin system to the lattice by the spin-lattice relaxation mechanism. If P is the probability of a transition occuring, then simple thermodynamics requires that

$$P_{\text{high}\longrightarrow\text{low}} > P_{\text{low}\longrightarrow\text{high}}$$

The concept of spin temperature, whilst it offers an explanation of the direction of energy flow between the nuclear spin system and the lattice, does not explain the mechanism of the process. A qualitative explanation may be given by considering that in molecules undergoing random translational and rotational motion, any nuclear magnetic moment which may be present,will experience a rapidly fluctuating magnetic field produced by neighbouring magnetic moments. If the motion contains a frequency which is synchronous with the precessional frequency of a neighbouring nucleus, then this nucleus will experience a radiofrequency field capable of inducing a transition. As discussed above in the consideration of spin temperature, this field will preferentially induce a stimulated emission of energy from the spin system rather than an absorption, thus transferring energy from the spin system to the surrounding lattice. It is the spin-lattice relaxation mechanism which is responsible for the initial distribution of spin states when a nuclear system is placed in a magnetic field.

Another feature of spin-lattice relaxation may now be considered. For an assembly of nuclear spins ($I = \frac{1}{2}$) which is initially not in a magnetic field, the populations of the two nuclear spin states are equal. When the system experiences a steady magnetic field, it requires a certain time for the populations to reach their new equilibrium value. If N_2 and N_1 are the number of nuclei per unit volume in the upper and lower states respectively, then it is possible to evaluate the excess number of nuclei per unit volume given by N,as a function of time.

$$N = N_1 - N_2 \qquad 1:27$$

Let W_1 and W_2 be the probabilities per unit time for a given nucleus to make an upward or downward transition by interaction with other molecular degrees of freedom. At equilibrium in the presence of a magnetic field, the total number of upward transitions per unit time must equal the corresponding number of downward transitions, i.e.

$$N_1W_1 = N_2W_2 \qquad 1:28$$

giving from equation 1:26

$$\frac{W_2}{W_1} = 1 + \frac{2\mu H_o}{kT} \qquad 1:29$$

Since an upward transition decreases and a downward transition increases, the excess number of nuclei N by 2 then

$$\frac{dN}{dt} = 2N_2W_2 - 2N_1W_1 \qquad 1:30$$

substituting W for $\frac{(W_2 + W_1)}{2}$ gives

$$\frac{dN}{dt} = -2W(N - N_{eq}) \qquad 1:31$$

where $N_{eq} = \frac{\mu H_o}{kT}(N_1 - N_2)$, and is the number of excess nuclei in the lower state at equilibrium. Defining a time T_1 by

$$T_1 = \tfrac{1}{2}W \qquad 1:32$$

gives

$$N - N_{eq} = (N_o - N_{eq})\exp^{-t/T_1} \qquad 1:33$$

where N_o is the initial value of N. It can be seen from equation 1:33 that the rate at which the excess population reaches its equilibrium value is governed exponentially by T_1 which is generally called the spin-lattice relaxation time.

b) <u>Spin-Spin Relaxation</u>

The precessional motion of nuclear moments will produce local fields (H_{loc}) at neighbouring nuclei, these fields having oscillating (H_{osc}) and static components (H_{stat}). A nucleus producing a magnetic field oscillating at its Larmor frequency, may induce a transition in a neighbouring nucleus in a manner similar to that induced by the applied oscillating field used to observe nuclear resonance.

The energy for this process comes from the first nucleus and a simultaneous reorientation of both nuclei results, there being an interchange of energy between the pair, whilst the total energy of the nuclear system is preserved. Only identical nuclei are capable of undergoing spin exchange and whilst the spin-spin relaxation process provides a mechanism for spin exchange, it does not help to restore the distribution of spin states following the absorption of energy, since the total spin energy remains constant throughout the process. Any phase coherence of the precessing nuclei is lost in a time T_2 which is generally referred to as the spin-spin relaxation time.

1:7 N.M.R. in Macro Samples and Line Shapes

The arguments so far have been based on the magnetic properties of isolated nuclei and these arguments can be developed to account for the observation of nuclear resonance in bulk samples. However, Bloch has treated this problem from macroscopic considerations[16, 17, 18].

An assembly of nuclei in an applied field have their various spin states occupied to different extents, which gives the sample a paramagnetic susceptibility. If M is the magnetic moment per unit volume of a substance placed in a magnetic field H_o, then this is related to the static susceptibility χ_o by

$$M = H_o \chi_o \qquad 1:34$$

Bloch[16, 18] has deduced a set of equations to describe the interaction of the nuclear magnetisation M with the radiofrequency field. These equations will not be discussed in detail, but their physical interpretation will be considered qualitatively. The bulk magnetisation is analogous to the nuclear magnetic moment μ, except that there is one important difference between these two quantities. In the absence of an applied radiofrequency field, M has only a z component, whilst μ has x, y and z components. The individual nuclei precess about the z axis and have random phases, hence the x and y components average to zero in forming M. Thus, at a condition far removed from resonance, the magnetisation vector M_o is coincident with the z axis. When the assembly of nuclei is exposed to a rotating field H_1 then as this field approaches the value required for resonance, nuclei will start to precess in phase giving non zero values to M_x and M_y. The magnetisation vector M will move away from the z direction and precess about that direction with the Larmor frequency. Depending upon which component, M_x or M_y is observed, either the absorption or dispersion curve is obtained (see section 2:4).

The effect of relaxation processes must be taken into account. M_z does not remain constant, but after resonance, approaches its equilibrium value M_o at a rate governed by the spin-lattice relaxation time T_1 which in the macroscopic system is termed the longitudinal relaxation time. The individual nuclei will become out of phase because of relaxation effects and the components M_x and M_y will decay to zero in a manner similar to that representing spin-lattice relaxation, but involving a different time T_2 which is referred to as the transverse relaxation time.

It has been shown that a nuclear magnetic absorption line can be approximately represented by a Lorentzian curve[16, 19], although this does not hold for all cases. A quantum mechanical approach to n.m.r. predicts an infinitely sharp absorption line; however, for identical nuclei, absorption occurs over a small but finite frequency range due to several line broadening effects. For most purposes, the absorption rather than the dispersion signal is displayed (see section 2:4) and the width of a line is defined as its width at half height, expressed in terms of the applied field or frequency. The various factors affecting line shape will now be discussed.

a) Magnetic Dipole Interaction

The magnetic environment of a nucleus may be modified by fields due to magnetic moments of neighbouring nuclei in fixed positions. In an amorphous solid a nucleus at distance r from the nucleus under consideration can produce a field at this nucleus of magnitude anywhere between $\pm 2\mu/r^3$. Thus, instead of all nuclei experiencing the same uniform magnetic field H_o, different nuclei in a sample will experience various fields spread over the range $\pm 2\mu/r^3$ due to the effect of their neighbours. This secondary field contributes to the (H_{stat}) field considered in the discussion of the spin-spin relaxation process (section 1:6b). Magnetic resonance will then occur over a range of frequencies and the line will be broadened[20]. These considerations only apply if the nuclei maintain the same orientations relative to each other and to the external field, as in a solid sample. In liquids and gases where the molecules are allowed rapid random motion, the magnetic field at any one nucleus due to its neighbours effectively averages to zero; the molecular motions necessary to produce this averaging being of shorter time than that required for the observation of a nuclear resonance signal. Consequently, the effect of magnetic dipole broadening is negligible in high resolution studies where the samples are liquids or gases.

b) Spin-Lattice Relaxation

The lifetime of a nucleus in a given spin state is limited by the spin-lattice relaxation mechanism and thus there is an uncertainty in the lifetime of that spin-state, which is of the order of $2T_1$

where T_1 is the spin-lattice relaxation time. The uncertainty principle requires that

$$\Delta E . \Delta T \doteq \hbar \qquad 1:35$$

i.e.

$$\Delta E \doteq \frac{\hbar}{2T_1} \qquad 1:36$$

Frequency and energy are related by the equation

$$\Delta E = h\Delta\nu \qquad 1:37$$

Then

$$\Delta\nu \doteq \frac{\hbar}{2T_1 h} \qquad 1:38$$

i.e.

$$\Delta\nu \doteq \frac{1}{4\pi T_1} \qquad 1:39$$

Equation 1:39 gives the uncertainty or spread in frequency of a given absorption line due to the limitation placed on a nucleus remaining in a particular spin state by the spin-lattice relaxation mechanism.

c) Spin-Spin Relaxation

In a manner similar to that discussed in section 1:7b the spin-spin relaxation process introduces an uncertainty into the lifetime of any nuclear spin-state and so causes an uncertainty in the frequency at which resonance will occur. This leads to the observation of resonance over a small range of frequencies giving a broadened absorption line.

d) Electric Quadrupole Effects

Nuclei of spin greater than $\frac{1}{2}$ may possess non spherically symmetrical nuclear charge distributions, resulting in their having a quadrupole moment Q. Positive and negative signs associated with Q imply that the charge distribution about the spin axis is respectively of the form of a prolate or oblate spheroid. The energy of an isolated nucleus is independent of its orientation in a uniform electric field since nuclei have no electric dipole moments. However, in the presence of an electric field gradient, the quadrupoles undergo precession which displaces the nuclear magnetic levels. For an isolated nucleus having spin $>\frac{1}{2}$ placed in a strong magnetic field, the energy levels are given[21] by

$$E = \frac{-m\mu H_o}{I} + \frac{eQ(3m^2 - I(I+1))}{4I(2I-1)} \frac{\partial^2 V}{\partial z^2} \qquad 1:4$$

The magnetic quantum number m has the values -I to +I and V is the electrostatic potential at the nucleus due to external charges. The electric field gradient $\frac{\partial V}{\partial z}$ may arise from both intramolecular and intermolecular effects, however, in liquids and gases, Brownian motion tends to reduce intermolecular electric field gradients to zero. Nevertheless, equation 1:40 places an uncertainty on level energies and consequentially causes line broadening.

e) <u>Other Causes of Line Broadening</u>

Inhomogeneity of the magnetic field H_o over the sample volume will cause line broadening due to resonance occuring not at a specific field strength, but over a range of field ΔH as different portions of the sample experience the resonance condition at slightly differing times. Rapid spinning of the sample partially overcomes this problem (see section 2:2)

Certain transient effects are responsible for distortion of the signal line shape. The steady state solution of the Bloch equation[18] assumes that equilibrium has been attained between the radiofrequency field and the nuclear magnetisation. In practise, the time taken to reach equilibrium is appreciable and thus a restriction is placed upon the rate at which resonance is traversed. The static nuclear magnetisation at thermal equilibrium is M which is reduced by $(1 + \gamma^2 H_1{}^2 T_1 T_2)^{-1}$ known as the saturation factor in the steady state where T_1 and T_2 are referred to as the longitudinal and transverse relaxation times respectively. If the resonance line is entered too rapidly, the signal will be strong at first and then become weaker as the magnetisation is reduced, leading to a distortion of the line shape.

Another transient effect when narrow resonance bands are studied using a homogeneous magnetic field, may be observed as relaxation wiggles or ringing[11]. These are damped oscillations which follow the resonance line when it is swept through rapidly, and originate from the inability of the nuclear magnetisation to follow the changing applied H_1 field. After traversing the resonance condition, a magnetic moment persists in the plane at right angles to the main field for as long as a group of nuclei continue to precess in phase. Precession about H_o induces a signal at the precession frequency, the signal amplitude decaying at a rate governed by the phase memory time T_2. After passing through the true resonance condition, the precession frequency and radiofrequency differ slightly, so that the two signals interfere with one another giving rise to a low frequency beat signal which decays exponentially with time[22].

Saturation will affect the line shape of the resonance signal (see section 1:5). Too high an R.F. power will cause a reduction in signal height accompanied by line broadening, until eventually the signal will become unobservable due to there no longer being an excess population of nuclei in the lower energy state.

1:8 The Chemical Shift

One early application of nuclear magnetic resonance was the comparison of the nuclear moments of different isotopic species by comparing their resonance frequencies in a constant applied field.

It was found that when using liquid samples for which the sharp resonance lines could be measured accurately, the resonance frequency of any isotopic nucleus depended upon its chemical environment. This phenomenon was first observed for metals and metal salts by Knight[23] and later by Proctor and Yu[24] for ^{14}N compounds and by Dickinson[25] for ^{19}F compounds. It has been discovered that this phenomenon is a general one for all nuclei and has been called 'The Chemical Shift'. The Chemical shift is observed whenever two or more nuclei of the same isotopic species have a different environment, a separate resonance usually being observed for each distinct group with an intensity proportional to the number of nuclei in that group.

The chemical shift is directly proportional to the applied field strength and arises from small intermolecular and intramolecular contributions to the actual field experienced by a particular nucleus. If H_o is the applied field, the actual field H experienced by the nucleus is given by

$$H = H_o(1 - \sigma) \qquad 1{:}41$$

where σ is the shielding constant for the nucleus. If two isotopically similar nuclei in environments i and j have shielding coefficients σ_i and σ_j respectively then for the same value of H_o, the chemical shift δ_{ij} is given by

$$\delta_{ij} = \sigma_i - \sigma_j \qquad 1{:}42$$

The measurement of absolute chemical shifts is not possible since this would require the comparison of resonance frequencies of the nuclear species in a particular molecular environment with that of the same nucleus devoid of all its electrons. Chemical shifts are therefore generally measured relative to a reference compound; in the case of proton spectra, tetramethylsilane is generally chosen as the reference compound, although such compounds as water, benzene, chloroform and cyclohexane have been used for reference purposes. On this basis, the chemical shift is defined as a dimensionless number δ,

$$\delta = \frac{(H_c - H_r)}{H_r} \times 10^6 \qquad 1:43$$

where H_c is the resonance field for the nucleus under observation and H_r is the resonance field for the reference compound. The factor of 10^6 is included to express δ in p.p.m. Alternatively, since H is proportional to ν for resonance, then equation 1:43 may be conveniently redefined as

$$\delta = \frac{(\nu_c - \nu_r) \times 10^6}{\text{oscillator frequency}} \qquad 1:44$$

where ν_c and ν_r are the frequencies corresponding to H_c and H_r in equation 1:43.

For proton spectra when using tetramethylsilane as an internal standard, a scale known as the τ scale[26] is often used, such that tetramethylsilane at infinite dilution in carbon tetrachloride is arbitrarily given the value $\tau = 10$. The τ value of any other resonance line is then given by

$$\tau = 10 + \delta \qquad 1:45$$

Using this scale, most proton resonances in organic compounds occur in the range 0 - 10 τ. The τ value of any resonance should only be quoted as such if the compound giving rise to the resonance can be considered to be at infinite dilution in carbon tetrachloride using internal tetramethylsilane, also at infinite dilution, as reference. It has been pointed out recently[27, 28] that the τ scale has been much abused in the literature and many of the quoted τ values should be treated with great caution.

1:9 Spin-Spin Coupling

Instrumental advances made after the initial observation of nuclear magnetic resonance showed that many absorption signals from specific nuclei were not single lines but contained resolvable fine structure[29]. A systematic study[30] showed that fine structure may arise in any molecule containing two or more nuclei which resonate at different field strengths, i.e. they may be chemically shifted or may be of different nuclear species. Defining an absorption band as the signal arising from one set of identical nuclei, the number of peaks, as constituent lines of such a band arising from coupling, may be predicted.

For a set of n_A equivalent nuclei of type A and n_X equivalent nuclei of type X a first-order coupling treatment will give $(2n_X I_X + 1)$ peaks for the A band and $(2n_A I_A + 1)$ peaks for the X band. The relative intensities of the peaks comprising the multiplet structure are given by the co-efficients of the terms in the general binomial expansion, i.e.

$$1,\ n,\ \frac{n(n-1)}{2},\ \frac{n(n-1)(n-2)}{3!}\ \ldots\ \frac{n(n-1)\ \ldots\ (n-r+1)}{r!}$$

where n is the number of magnetically equivalent nuclei producing the splitting. Nuclei are said to be magnetically equivalent when they have the same chemical shifts and couple equally to all other resonant nuclei in a molecule.

Consider a nucleus of spin $I = \frac{1}{2}$, the possible spin states are those with m, the magnetic quantum number equal to $\pm\frac{1}{2}$. Labelling the state $m = +\frac{1}{2}$ as α and $m = -\frac{1}{2}$ as β, a group containing say three nuclei (e.g. CH_3) has the following possible configurations of proton spin

	ααα	ααβ	αββ	βββ
		αβα	βαβ	
		βαα	ββα	
Total Spin	$+3/2$	$+\frac{1}{2}$	$-\frac{1}{2}$	$-3/2$

An adjacent nucleus will see four energy states of the group considered above and hence four values of the local field corresponding to the four values of the total spin. The two states with total spin $\pm\frac{1}{2}$ are three times as numerous as those with total spin $\pm 3/2$ and hence a quartet is observed with relative line intensities 1:3:3:1. Spin-spin coupling is a mutual effect, such that any nucleus which causes splitting of another resonance band must itself show splitting of the same magnitude and number of lines depending on the number of nuclei in the group to which it is coupled. Coupling which results in regular line spacings and intensities is said to be first order and in this case the line separations are equivalent to J, the coupling constant. The coupling mechanism may be simply described by a term $hJ_{ij}\mu_i\mu_j$ in the interaction Hamiltonian, where J_{ij} is independent of temperature and applied field (unlike the chemical shift) and has the dimensions of frequency.

When two groups of nuclei are separated by a chemical shift which is of the same order of magnitude as the coupling constant between them, the spectrum does not obey the rules of multiplicity and relative intensity given above for the case of first order spectra and a more complex pattern is obtained which requires a more detailed analysis. Such spectra are said to be second order and the convention adopted for the classification of such spectra is to use the symbols A,B,C, ... X,Y,Z, to characterise the individual nuclei within a nuclear spin system. The letters A,B,C, generally represent magnetically non equivalent nuclei of the same species, having small relative chemical shifts of the same order of magnitude as the coupling constant between them. X,Y, and Z are used to represent a similar set of nuclei; not necessarily of the same species as the first set, but having a large chemical shift from the first set. The symbols A and A^1 are used to denote nuclei which are chemically but not magnetically equivalent.

1:10 Second Order Spectra - The AB Spin System

The simplerfeatures of n.m.r. spectra have been discussed in the preceeding sections, however, in many spectra the effects of chemical shift and spin coupling give rise to a complex pattern of lines resulting from the merging of individual multiplets and having few features of regularity. The procedure for the analysis of second order spectra will now be considered.

A complete set of basic symmetry functions is required and these are evaluated as linear combinations of basic product functions. The latter for a system of nuclei take the form of products of the single eigenfunctions α and β , e.g. for two nuclei these are $\alpha\alpha, \alpha\beta, \beta\alpha, \beta\beta$; The use of basic symmetry functions, which are normalised irreducible functions, is normally necessary in order to simplify the following steps. The energy of a nucleus in a strong magnetic field H, the direction of which is the negative z direction, is given by $\gamma\hbar HI_z$ ergs or $\gamma HI_z/2\pi$ c.sec.$^{-1}$ For a set of nuclei with magnetogyric ratios γ_i acted upon by a field H_i the Hamiltonian will be

$$\mathcal{H}^{\circ} = \tfrac{1}{2\pi} \sum_i \gamma_i H_i I_z(i) \qquad 1:46$$

H_i will differ from the external field H_o because of local screening i.e.

$$H_i = H_o(1 - \sigma_i) \qquad 1:47$$

In practise the resonance condition is achieved by varying H_o, however for simplicity in the approach, H_o will be considered constant, this having little consequence to the argument. The indirect spin coupling may be represented by a Hamiltonian involving the scalar products of the spin vectors of all pairs of magnetic nuclei

$$\mathcal{H}^{(1)} = \sum_{i<j} J_{ij} \; I_{(i)} \; I_{(j)} \qquad 1{:}48$$

If the rate of rotation of the molecules is rapid enough for dipole-dipole interaction to be neglected, then the complete Hamiltonian is given by

$$\mathcal{H} = \mathcal{H}^{(o)} + \mathcal{H}^{(1)} \qquad 1{:}49$$

The matrix elements of the Hamiltonian $\mathcal{H}^{(o)}$ representing interaction of the nuclear system with the external field are given by

$$(\psi_m | \mathcal{H}^{(o)} | \psi_m) = \tfrac{1}{2}\pi \sum_i \gamma_i H_i \left[I_z (i) \right]_m \qquad 1{:}50$$

where $I_z(i)_m$ is $\frac{1}{2}$ if nucleus i has spin α in ψ_m, and $-\frac{1}{2}$ if it has β spin. Matrix elements of $\mathcal{H}^{(o)}$ between different product functions vanish, i.e. are no off-diagonal matrix elements of $\mathcal{H}^{(o)}$.

The diagonal matrix elements of the spin coupling Hamiltonian $\mathcal{H}^{(1)}$ are given by

$$(\psi_m | \mathcal{H}^{(1)} | \psi_m) = \tfrac{1}{4} \sum_{i<j} J_{ij} T_{ij} \qquad 1{:}51$$

where T_{ij} = 1 or -1 depending on whether the spins i and j are parallel or antiparallel. There will also be off-diagonal elements of $\mathcal{H}^{(1)}$ given by

$$(\psi_m | \mathcal{H}^{(1)} | \psi_n) = \tfrac{1}{2} U J_{ij} \quad (m \neq n) \qquad 1{:}52$$

where U = 1 if ψ_m differs from ψ_n by an interchange of spins i and j and is zero otherwise.

The energies of the stationary state wave functions are given by the solutions of the secular equation

$$| \mathcal{H}_{mn} - E\delta_{mn} | = 0 \qquad 1{:}53$$

where δ_{mn} = 1 if m = n and is zero otherwise. The secular equation is of order 2^P where P is the number of nuclei in the spin system but it can be factorised into a number of equations of lower order by considering that no mixing occurs between functions with different values of F_z given by

$$F_z = \sum_i I_z(i) \qquad 1:54$$

Further reduction can be made in the case of a symmetrical molecule since no mixing occurs between functions of different symmetry. If several species of nuclei X,Y, ... are present, then to a high approximation, no mixing occurs between functions which differ in any of the total spin components $F_z(X)$, $F_z(Y)$, ...

The energies can then be calculated by diagonalisation of the submatrices of the total Hamiltonian. From the stationary state eigenvalues, the corresponding eigenfunctions can be obtained. The number of possible transitions giving rise to the observed resonance lines is limited by the selection rule $\Delta F_z = \pm 1$ which applies at small values of the r.f. field and for symmetrical molecules, transitions can occur only between functions of the same symmetry. For a set of nuclei X, Y, ... of different species, or when X and Y are of the same species but have a large chemical shift compared with the coupling between them, only functions which differ by ± 1 in only one of $F_z(X)$, $F_z(Y)$, ... are allowed. The relative intensities of the remaining transitions which are not forbidden by the selection rules can be found from the squares of the matrix elements of the total X component of the nuclear moment deduced using the eigenfunctions.

The simplest system in which is observed the effects of chemical shift and spin coupling intermingled, consists of two (magnetically), non-equivalent nuclei of the same species, isolated from any other nuclei. If the chemical shift is zero, there are a pair of equivalent nuclei and only a single line is observed. At the other extreme, when the chemical shift is large enough, simple first order rules apply and the spectrum consists of a pair of doublets, the doublet splitting being equal to the spin coupling constant. Such a system is designated AX. The situation between these two extremes when the spin system is designated AB, will be of interest in subsequent chapters and the procedure discussed above will now be applied to the case of two nuclei A and B both of spin $\frac{1}{2}$.

The local field at the nuclei can be written

$$H_A = H_o(1 - \sigma_A) \qquad 1:55$$

$$H_B = H_o(1 - \sigma_B) \qquad 1:56$$

the relative chemical shift being given by $\sigma_B - \sigma_A$ and the spin coupling constant by J. In a magnetic field, the degeneracy of the spins is lifted such that $I = \pm\frac{1}{2}$ to which can be assigned the wave functions α and β respectively. The wave function for the whole system is obtained from combinations of α and β , and since there are no effective elements of symmetry, the basic functions can conveniently be taken to be the simple product functions $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, and $\beta\beta$, which are numbered 1 to 4 in table 1:1. If ν_o is the frequency of a transition for a single unscreened nucleus then

$$\nu_o = \frac{\gamma H_o}{2\pi} \qquad 1:57$$

and from equations 1:47, 1:50, 1:57 and 1:51 the corresponding diagonal matrix elements of the Hamiltonian are easily evaluated and are given in table 1:1.

n	ψ_n	F_z	$\mathcal{H}_{nn}^{(o)} + \mathcal{H}_{nn}^{(i)}$
1	$\alpha\alpha$	1	$\nu_o(1 - \frac{1}{2}\sigma_A - \frac{1}{2}\sigma_B) + \frac{1}{4}J$
2	$\alpha\beta$	0	$\nu_o(-\frac{1}{2}\sigma_A + \frac{1}{2}\sigma_B) - \frac{1}{4}J$
3	$\beta\alpha$	0	$\nu_o(\frac{1}{2}\sigma_A - \frac{1}{2}\sigma_B) - \frac{1}{4}J$
4	$\beta\beta$	-1	$\nu_o(-1 + \frac{1}{2}\sigma_A + \frac{1}{2}\sigma_B) + \frac{1}{4}J$

Table 1:1 Basic functions and diagonal matrix elements for two nuclei AB.

It is seen that there is an interchange of spins only between the product functions $\alpha\beta$ and $\beta\alpha$, giving the only non vanishing off-diagonal element as

$$\mathcal{H}_{23} = \tfrac{1}{2}J \qquad 1:58$$

The functions $\alpha\alpha$ and $\beta\beta$ will themselves be stationary state wave functions; however, mixing can occur between $\alpha\beta$ and $\beta\alpha$ since these have the same total spin F_z. To evaluate the resulting energies, it is convenient to define a positive quantity C and an angle Θ (between 0 and π) by

$$C\cos 2\Theta = \tfrac{1}{2}\nu_o(\sigma_B - \sigma_A) \qquad 1:59$$

$$C\sin 2\Theta = \tfrac{1}{2}J \qquad 1:60$$

If $\delta = \sigma_B - \sigma_A$ then

$$C = +\tfrac{1}{2}\left[(\nu_o\delta)^2 + J^2\right]^{\frac{1}{2}} \qquad 1:61$$

The energies E_n and the wave functions Φ_n may be written explicitly in terms of C and Θ as in table 1:2.

n	Φ_n	E_n
1	$\alpha\alpha$	$\nu_o(1 - \frac{1}{2}\sigma_A - \frac{1}{2}\sigma_B) + \frac{1}{4}J$
2	$\cos\Theta(\alpha\beta) + \sin\Theta(\beta\alpha)$	$-\frac{1}{4}J + C$
3	$-\sin\Theta(\alpha\beta) + \cos\Theta(\beta\alpha)$	$-\frac{1}{4}J - C$
4	$\beta\beta$	$\nu_o(-1 + \frac{1}{2}\sigma_A + \frac{1}{2}\sigma_B) + \frac{1}{4}J$

Table 1:2 Wave functions and Energy levels for two nuclei AB.

Since F_z can change by only ± 1, there are only four allowed transitions. The relative intensities are given by the squares of the appropriate matrix elements of the X component of the spin $I_x(A) + I_x(B)$, i.e. for the transition 2→1

$$\left[\cos\Theta(\alpha\beta) + \sin\Theta(\beta\alpha)\middle|I_x(A) + I_x(B)\middle|\alpha\alpha\right]^2 = \tfrac{1}{4}(\cos\Theta + \sin\Theta)^2$$

$$= \tfrac{1}{4}(1 + \sin 2\Theta) \qquad 1:62$$

The transition energies relative to the mean, $\nu_o\left[\frac{(1 - \sigma_A) + (1 - \sigma_B)}{2}\right]$,

and relative intensities are given in table 1:3.

Transition	Energy	Relative Intensity
a $3 \longrightarrow 1$	$\frac{1}{2}J + C$	$1 - \sin 2\theta$
b $4 \longrightarrow 2$	$-\frac{1}{2}J + C$	$1 + \sin 2\theta$
c $2 \longrightarrow 1$	$\frac{1}{2}J - C$	$1 + \sin 2\theta$
d $4 \longrightarrow 3$	$-\frac{1}{2}J - C$	$1 - \sin 2\theta$

Table 1:3 Transition Energies and relative intensities for two nuclei AB

The general appearance of an AB spectrum depends only on the absolute magnitude of $|J/\nu_o\delta|$, being independent of the signs of J and $\sigma_B - \sigma_A$. It can be seen that the AB spectrum consists of four lines from which J_{AB} is given by the separations of both of the outer pairs e.g. a - b or c - d . δ_A And δ_B may be obtained from the expression

$$2C = \left[(\delta_B - \delta_A)^2 + J_{AB}\right]^{\frac{1}{2}} \qquad 1:63$$

the separation of the two central lines being $2C - |J|$ The relative intensities of the outer and inner lines are given respectively by

$$1 - J_{AB}\left[(\delta_B - \delta_A)^2 + J^2_{AB}\right]^{\frac{1}{2}} \qquad 1:64$$

and

$$1 + J_{AB}\left[(\delta_B - \delta_A)^2 + J^2_{AB}\right]^{\frac{1}{2}} \qquad 1:65$$

More conveniently

$$\delta^2 = (a - d)(b - c)$$

$$\frac{\text{Relative intensity of b}}{\text{Relative intensity of a}} = \frac{a - d}{b - c}$$

CHAPTER 2

Experimental Methods for the Observation of High Resolution Nuclear Magnetic Resonance

2:1 Introduction

The fundamental requirement for the observation of a nuclear magnetic resonance signal from any nucleus is that the equation

$$\nu_0 = \frac{\gamma H_0}{2\pi} \qquad 2{:}1$$

discussed in section 2 of chapter 1 is obeyed. In order that any particular nucleus should be brought into resonance, either ν_0 or H_0 may be varied while the other is kept constant. All high resolution n.m.r. spectrometers employ some means of achieving this and, in addition, of necessity a system for the detection of nuclear resonance and a method of presenting this.

The stationary magnetic field H_0 required to observe nuclear magnetic resonance may be derived from either a permanent or an electromagnet both of which are available, operating at field strengths in the range 10-25 Killogauss. The rotating field is conveniently derived by passing a signal from an R.F. oscillator through a coil around the sample, which is situated in the stationary field. Equation 2:1 requires that either the field or frequency must be swept over a small range to observe a spectrum and it has generally been found more convenient to fix the radio frequency and sweep the magnetic field. Spectrometers, particularly those employing an electromagnet system, are now available with a field/frequency lock system, in which the field is locked onto a particular resonance signal. Any small change in the magnetic field causing a change in the resonance condition is detected and a correction applied to the steady field such that the initial resonance condition is restored. Using such a system, it is necessary to sweep the frequency to observe a spectrum. The first independent observations of the n.m.r. phenomenon in bulk samples, by the two groups Bloch, Hansen and Packard[5] and Purcell, Torrey and Pound[6] resulted in two principal techniques for its detection. These two detection techniques, known as the single coil method and crossed coil method, are both employed in commercial high resolution spectrometers.

The requirements for the individual components of a high resolution nuclear magnetic resonance spectrometer will now be discussed, followed by a consideration of a commercial spectrometer system.

2:2 The Magnet

The sensitivity S of a nuclear magnetic resonance signal is given by the equation

$$S = \frac{CNH^2\gamma^3 I(I+1)}{T} \qquad 2{:}2$$

where N is the number of nuclei under consideration, H is the applied field strength and T the absolute temperature. It is apparent from equation 2:2 that the sensitivity obtainable for any nucleus is proportional to the square of the field strength and the strongest field possible should be used. This is limited to 25 Killogauss for conventional magnet systems. Both permanent and electromagnets are available giving field strengths of 10 - 25 Killogauss. The advantage of an electromagnet is that the field strength may be set anywhere within its operating range, thus permitting the observation of many nuclei at one frequency with no additional equipment. The permanent magnet requires a separate radio frequency oscillator tuned to the appropriate frequency for each nuclear type studied. Also, an electromagnet enables the observation of a spectrum at different field strengths which sometimes facilitates its analysis. The permanent magnet is clearly not as flexible in operation as the electromagnet but it scores in its ease of operation and reliability and in that resolution, once obtained, can be maintained for long periods with only minor adjustments.

Super conducting magnets are now becoming available[31] in which fields of the required homogeneity may be produced at strengths up to c.a. 50 Killogauss. Such solenoids are very expensive in comparison to conventional magnets and require elaborate control systems to maintain the temperature of the conducting wire in the region of +10°K, this usually being achieved with liquid helium. At the time of writing, n.m.r. spectrometers employing superconducting magnets are something of a novelty, and will not be discussed further.

To obtain the required order of field strength from a conventional magnet together with the desired degree of homogeneity in a pole gap of ½" - ¾", necessary to accept the radiofrequency probe and sample, an elaborate magnet system is required. The pole pieces should be of the order of 6" - 12" diameter, so that the central portion of the field will have a 'flat' contour and not suffer from 'edge effects', i.e. bending of the lines of magnetic force near to the edge of the pole pieces. The pole faces should be parallel, free from machining marks, almost optically flat[32], and the pole cap material should be metallurgically uniform. The uniformity of field attainable with both permanent and electromagnets is comparable, both being capable of an intrinsic homogeneity of 1 part in 10^6, which may be improved with Golay Shim Coils to 1 part in 10^8. These coils are situated in pairs on the pole faces of the magnet and are arranged so that a stabilized d.c. current when passed through them, may be adjusted to produce field gradients in specific directions. These gradients are used to counteract the inhomogeneities found in the intrinsic magnetic field. Electromagnets generally require careful 'cycling' in order to obtain the degree of homogeneity required for n.m.r. experiments.

An apparent improvement in the homogeneity of the magnetic field experienced by the nuclei may be achieved by mechanical motion of the sample. One of the simplest means of providing such motion is to spin the sample about the y axis, using a small air turbine. If the main magnetic field varies over the sample by ΔH and a molecule within the sample experiences the whole of this variation ΔH in a time t, then the more rapid the motion (spinning) the more a magnetic nucleus in the molecule behaves as if it were exposed all the time to the average field $(H + \Delta H/2)$. This effect becomes appreciable when $t \leq \frac{2}{(\gamma.\Delta H)}$ where γ is the magnetogyric ratio of the nucleus. Thus, the spinning speed of the sample should be arranged such that its period of revolution is less than t.

The magnetic field is generally stabilized in some way. Permanent magnets are generally totally enclosed in a thermostated enclosure to reduce field drift to a minimum, however, such field drift can still be troublesome when the spectrometer is used continuously for long periods of time in conjuction with a time averaging computer (see section 2:10). Permanent magnets normally require, therefore, only variations in the external magnetic field to be compensated for, but electromagnets also require that slight variations in magnet current should be corrected for. It is for this reason that field/frequency lock systems are becoming favoured on spectrometers using electromagnets. When the field/frequency lock system is not used, some form of field compensator is generally employed in which coils placed on or near to the magnet pole pieces sense any variation in the magnetic field and apply a correction through further coils wound on the pole pieces.

Spectrometers employing a field sweep rather than frequency sweep mode of operation, require some means of continuously varying the field H_o over a small range. This may be achieved by passing a direct current through coils wound on the pole pieces. Alternatively, a pair of Helmholtz coils may be employed in which the separation of the coils is equal to their radius. A small direct current passed through these coils, which are situated with their axis coincident with the H_o axis and flanking the sample tube, produces the required field sweep. The variation in voltage required to supply these coils may be controlled electronically so that a linear sweep rate is obtained.

2:3 The Radiofrequency Oscillator

The practical limitations placed on the field strength obtainable from conventional magnets, requires the use of a maximum radiofrequency of c.a. 100 $Mc.sec.^{-1}$ for the observation of ^1H and ^{19}F resonance.

The stability required for the radiofrequency oscillator is of the same order as that required of the main magnetic field, i.e. 1 part in 10^8 to 10^9 per minute. Such radiofrequency signals having the required degree of stability, are generally derived by the selection and multiplication of suitable harmonics from a quartz crystal oscillator which has been carefully thermostated. The radiofrequency power delivered to the probe should have a constant level and this is generally achieved by incorporating an automatic gain control amplifier as the final stage of the radiofrequency unit, prior to its output being fed to the probe via an attenuator system.

Some spectrometers, particularly those employing an electromagnet, produce different frequencies for the observation of nuclear magnetic resonance signals by different selection and multiplication of the fundamental or harmonic frequencies derived from one quartz crystal whilst other spectrometers employ different quartz crystals, one for each frequency required. The latter system is generally used in conjunction with a permanent magnet since its field can generally only be varied by a few gauss.

2:4 The Probe and Detection System

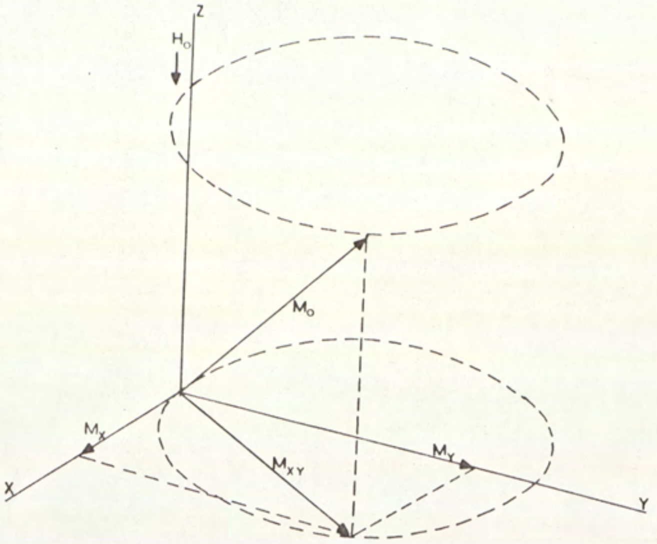
One of the major differences between the spectrometer systems available is in the method used for the detection of a resonance signal. There are two methods which differ in that one employs a crossed coil[33] and the other a single coil probe[20]. The crossed coil method was first used by Bloch, Hansen and Packard[5] and has been used since in many commercial instruments. It consists essentially of two coils, the transmitter and receiver coils, mounted almost at right angles to each other and around the sample. Electrostatic coupling between them is reduced by placing a Faraday Shield between the two coils. Some leakage between transmitter and receiver coils is essential, the amount of leakage being controlled by 'paddles', which are small pieces of metal placed in the radiofrequency field in such a manner that they can modify the lines of force due to the field, and hence vary the inductive and capacitative coupling between the two coils.

Using a system of rotating co-ordinates, as in figure 2:1A, the x y plane is rotated about the z axis and when the main field H_o has a value far removed from that required to satisfy the resonance condition, the application of a low amplitude fixed radio frequency field leaves the magnetisation vector M_o co-incident with the z axis. As the value of H_o approaches that required for resonance, the magnetisation vector will move away from the z axis and start to precess, giving projection components in the xy plane shown. The component M_y will have its maximum value when the resonance condition is reached and a further increase in H_o will cause M_y to decrease eventually to zero. The magnetisation represented by M_{xy} induces a voltage in the receiver coil which is in the same plane; this voltage is the required nuclear resonance signal and may be amplified and displayed.

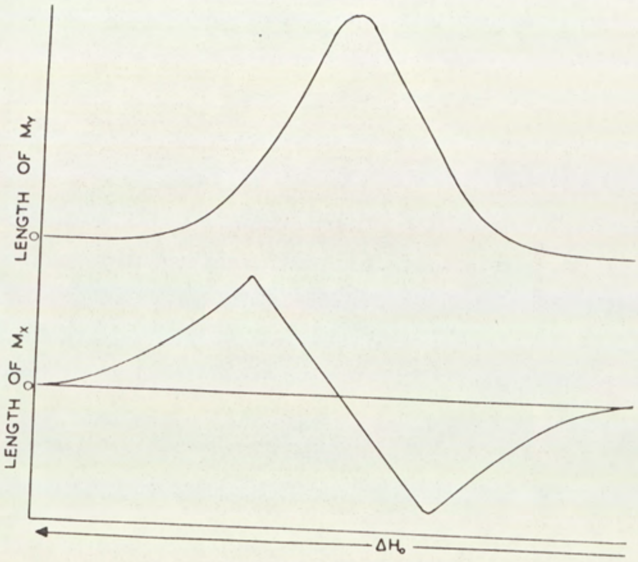
It can be seen from figure 2:1B that if the normal absorption signal (v mode) is required, then only the component M_y is of interest. The component M_x gives the dispersion (u mode) signal which results in a spectrum of more complex appearance than the absorption mode. The u mode component of the magnetisation vector is suppressed by adding a large amount of leakage from the transmitter coil in phase with the v mode. This provides a reference for the absorption signal and suppresses the unwanted u mode[11], shown diagramatically in figure 2:1C. The amount of leakage required depends on the signal strength and may be adjusted to give a suitable leakage to signal ratio.

The first successful nuclear magnetic resonance experiment, performed by Purcell, Torrey and Pound[6], used a single coil method of detection in conjunction with a bridge circuit, and much of the early work on nuclear magnetic resonance employed similar detection systems. The twin T bridge has been found most satisfactory in high resolution spectrometers in that it gives good stability of bridge balance which is required if a mixture of u and v mode signals is to be avoided. Bridge systems typically used consist of two similar circuits in parallel connected to the radio frequency oscillator, one circuit containing the sample coil and the other containing a dummy coil. The two circuits are balanced away from resonance and when resonance occurs, the out of balance e.m.f. across the bridge is amplified and displayed. The use of a single coil method of detection will be discussed later.

2.1A



2.1B



2.1C

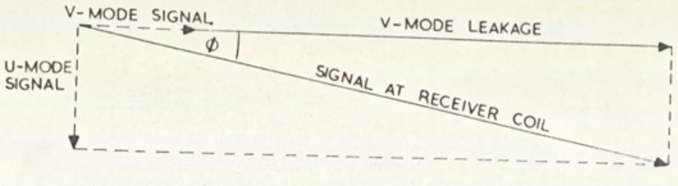


FIGURE 2.1A The magnetisation vector M_o and its components in a system of rotating co-ordinates.

FIGURE 2.1B The magnitude of the M_x and M_y vectors as a function of the field strength H_o.

FIGURE 2.1C Suppression of the u-mode (M_x) component of the magnetisation vector by adding in-phase leakage to the v-mode (M_y) component.

2:5 Presentation of a Spectrum

Most high resolution spectrometers produce a permanent record of the spectrum with a chart recorder arranged such that the field sweep (or frequency sweep) corresponds with the x axis of the recorder. Many spectrometers also employ a cathode ray oscilloscope display for the spectrum, which facilitates the rapid optimisation of the spectrometer controls prior to producing a permanent chart record of a spectrum. The field sweep is connected to the x plates of the oscilloscope. In either presentation mode, the y axis is connected to the detector output and consequently monitors the intensity of the nuclear resonance signal.

2:6 Experimental Techniques Employed

There were two spectrometers available for the investigations carried out, a Perkin Elmer R10 and an A.E.I. R.S.2; both instruments are capable of observing proton resonance at 60 Mc.sec.$^{-1}$. For ^{19}F resonance the operational frequency of the Perkin Elmer instrument is 56.462 Mc.sec.$^{-1}$ whereas that of the R.S.2 spectrometer is 60.0 Mc.sec.$^{-1}$. In fact, two frequencies were available for observations with the R.S.2 one at 15 Mc.sec.$^{-1}$ and the other at 60 Mc.sec.$^{-1}$. The major difference between the two instruments is that the R.10 utilizes a permanent magnet of 14092 gauss, whereas the R.S.2 has an electromagnet whose field may be varied over the range 2-18 Killogauss. The majority of the spectral measurements reported herein have been made using the Perkin Elmer R10 spectrometer and this instrument will now be described.

2:7 The Perkin Elmer R10 High Resolution N.M.R. Spectrometer

The Perkin Elmer R10 spectrometer employs a permanent magnet of 14,092 gauss having pole pieces of 5" dia. and a pole gap of c.a. 1". The whole magnet assembly is housed in an aluminium box which is lined with expanded polystyrene and thermostated to maintain a temperature of 33.4°C ± 0.001°C. This high degree of temperature stabilization largely overcomes the problems of field drift, provided the ambient temperature does not vary greatly. There is an ever present problem with a permanent magnet that the field will drift continuously due to the natural ageing of the magnet, and there is no provision on the R10 spectrometer to overcome this which may become troublesome when using very slow sweep rates. The field contour over a small area in the centre of the magnet is improved by passing small d.c. voltages to a set of nine printed circuit Golay coils arranged on the pole faces. The spectrometer employs the twin T bridge method of signal detection and the bridge circuitry is housed in a mu metal box attached directly to the probe unit, which is held between the magnet pole pieces by a rigid aluminium bar. The sample coil is wound on a hollow glass former in which the sample tube is spun by means of a small air turbine. The field sweep is provided by a saw tooth wave form applied to the sweep coils on the pole pieces; this voltage is also arranged to produce the time base for an oscilloscope. Alternatively, the field sweep may be derived from the recorder and synchronized with the rotation of the recorder drum. A field compensator is employed to reduce the effect of small changes in the external magnetic field.

The arrangement of the electronic components of the R10 spectrometer are shown in figure 2:2. The radiofrequency signal is obtained from an accurately thermostated quartz cyrstal, different crystals and tuned circuits being employed to produce the frequencies required to observe different nuclear resonances. For the production of 60 and 56.458 Mc.sec.$^{-1}$ required to observe ^{1}H and ^{19}F resonance respectively, the second harmonic of the crystal frequency is chosen and this is further multiplied four times to give the required frequencies, e.g. to obtain 60 Mc.sec.$^{-1}$ a quartz crystal is chosen with a fundamental

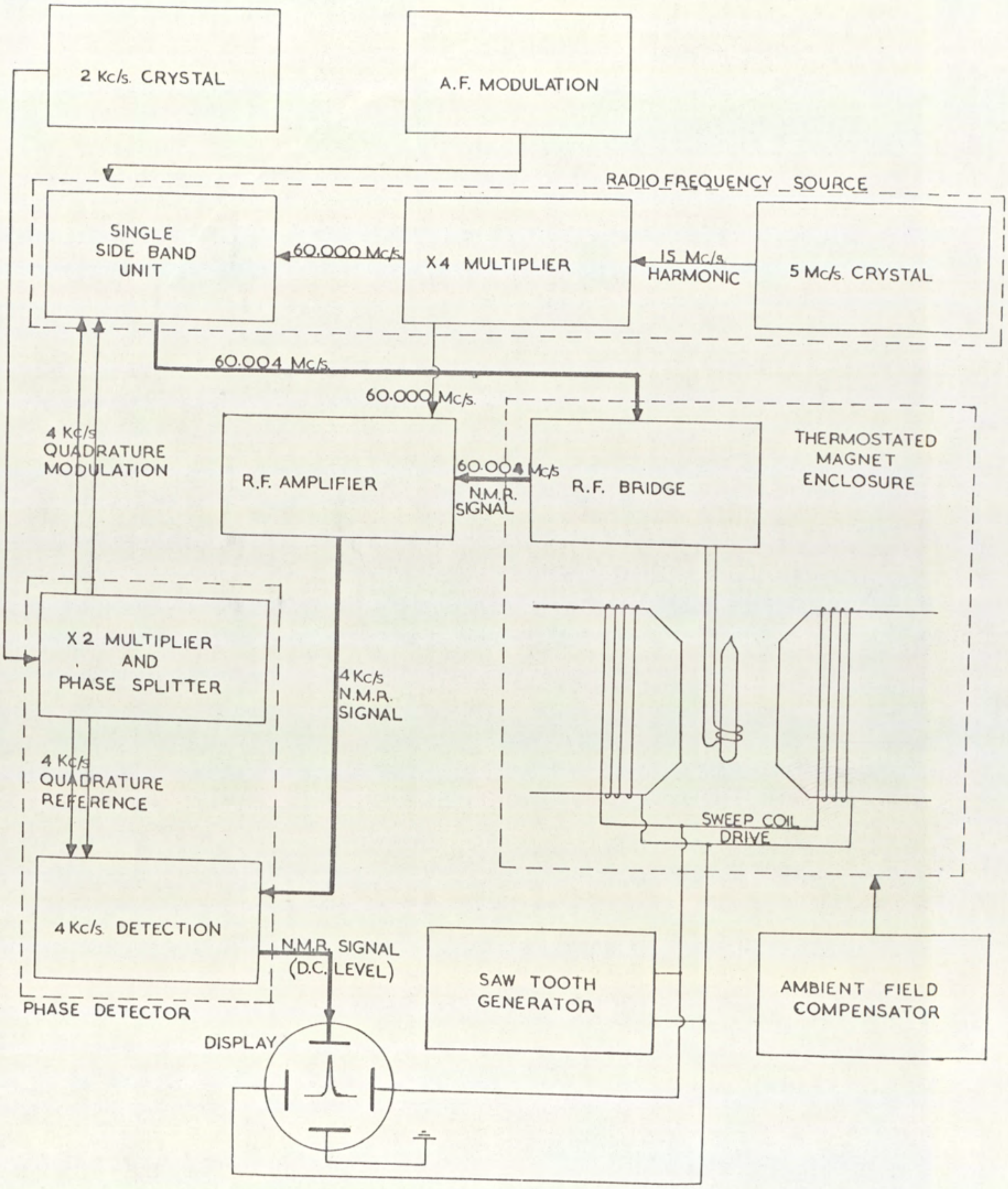


FIGURE 2.2 Schematic diagram of the Perkin-Elmer R 10 N.M.R. spectrometer.

frequency of 5 $Mc.sec.^{-1}$, the 15 $Mc.sec.^{-1}$ harmonic of which is chosen and multiplied up to 60 $Mc.sec.^{-1}$. The R10 spectrometer utilizes a single side band (S.S.B.) mode of operation rather than using the actual radiofrequency produced by multiplication of the crystal frequency. This system together with ultimate phase sensitive detection, produces a very stable baseline which is essential when using slow sweep rates. A single side band of frequency 4 $Kc.sec.^{-1}$ greater than the fundamental frequency is generated in a single side band unit which produces an amplitude modulation on the carrier at the side band frequency, but the output also contains components of the carrier and lower side band frequencies, which are rejected in two stages. The single side band unit consists of two halves, each of which is a suppressed carrier modulator. Each half is supplied with the 60 $Mc.sec.^{-1}$ radiofrequency signal and with a 4 $Kc.sec.^{-1}$ signal, the two 4 $Kc.sec.^{-1}$ signals being 90° out of phase with each other. The carrier in both circuits is first rejected, as in each half of the circuit the 60 $Mc.sec.^{-1}$ signal is fed onto the slider of a potentiometer thus dividing the carrier further into two signals which pass separately through diodes arranged to conduct in opposite directions and then onto the ends of the bifilar primary winding of a transformer. The diodes are arranged so that they are alternately conducting and cut-off by each half cycle of the 4 $Kc.sec.^{-1}$ signal which is applied to the centre tap of the transformer. The alternate anti-phase bursts of 60 $Mc.sec.^{-1}$ energy applied to the transformer can be averaged to zero by adjustment of the potentiometer, although both the upper and lower sideband frequencies remain.

The lower sideband is suppressed in the following manner. The two 4 $Kc.sec.^{-1}$ modulation supplies to the suppressed carrier modulators are arranged to be 90° out of phase with each other and further relative phase shifts are obtained by detuning the primaries of the transformers in the two halves of the circuit, so that an additional + and -45° of phase shift is obtained relative to the 60Mc.sec.$^{-1}$ input. When the outputs of the two channels are combined it is possible to eliminate the unwanted side band and cause the components of the required side band to add together and give the resulting signal at a single frequency. The single side band signal is then fed via an automatic gain control amplifier, to give a very stable output level, and an attenuation system to the input of the twin T bridge network. The bridge circuit can be adjusted for both amplitude and phase control of its output. Any out of balance of the bridge caused by a nuclear absorption is fed at the side band frequency selected into a radio frequency amplifier, where it is amplified and then combined with a signal at the carrier frequency giving a resultant signal at 4Kc.sec.$^{-1}$ which contains information about the required n.m.r. signal. This signal is then fed to an audio phase detector which is also supplied with a 4Kc.sec.$^{-1}$ reference signal (derived from that supplying the single side band unit) whose phase may be continuously varied by a phase rocking network. These two signals are combined to give zero output until a resonance signal is encountered, when a d.c. signal appears across the detector output. The signal is then fed to either an oscilloscope or pen recorder. The phase detector system gives a very stable baseline as there is no d.c. output from the detector until a nuclear signal is encountered.

The recorder on the R10 utilizes precalibrated strip charts arranged such that each chart aligns itself in the same relative position on the recorder drum. The drum is arranged such that its rotation is linked to the magnetic field sweep and the depth of field scan required for any spectrum may be pre-determined and the corresponding spectrum may be reproduced on successive charts.

2:8 Calibration of Spectra

The R10 spectrometer utilizes pre-calibrated chart paper as discussed above, but for accurate measurements of line frequencies it was considered necessary to use an audio side band modulation technique. Either the magnetic field or the radiofrequency is modulated at a known audio frequency. In the case of the R10, the latter alternative is generally chosen and an inverted replica of the portion of the spectrum under observation is produced, displaced on either side of the original by the modulation frequency. If a single line is chosen for modulation, then by suitable variation of the modulating frequency, a series of inverted sharp lines are produced in the spectrum, the frequencies of which are accurately known. The relative frequencies of unknown resonance lines are deduced by interpolation. Unless a high quality audio oscillator is employed to generate the modulation signal, it is advisable to check the frequency produced with a frequency counter giving a reading to 0.01 cycle sec.^{-1}.

The resonance which is used for modulation mormally arises from a reference material in the sample and may either be homogeneously mixed with the sample under investigation or may be in a separate container, which generally has the form of a capillary tube in the sample. In the two approaches, the reference is said to be respectively internal or external. The chemical shift of a resonance cannot be expected to be the same when measured relative to an internal standard as it is when measured relative to an external standard. The reasons for this are discussed in section 3:6.

2:9 Sample Temperature

The Perkin Elmer R10 spectrometer employs a carefully thermostated magnet system operating at 33.4°C and the basic instrument requires that the sample should also be at that temperature. There is, however, a variable temperature accessary enabling the sample temperature to be maintained anywhere in the range -100 to +200°C. Temperatures up to 40°C outside this range can be achieved by careful manipulation of the controls. An elaborate probe assembly is necessary with this system in order that changes in sample temperature are not transmitted to the magnet, which would cause the field to drift.

2:10 Computer of Average Transients

When dealing with weak solutions, or when observing signals from nuclei having a poor sensitivity or low natural abundance, it is often a problem to distinguish the nuclear resonance signals from the background noise. This situation can be improved by use of a computer of average transients[24] (C.A.T.) whereby the analogue output from the spectrometer is divided into many discrete parts (up to 3,096) each of which is converted to digital form and stored in successive memory locations in a computer. Further sweeps of the same portion of the spectrum are likewise divided and the individual outputs added to the contents of the stores containing the corresponding portions of the signal derived from previous sweeps. The n.m.r. signals should be reinforced because all additions of a positive signal are in phase, whereas the noise, being random, tends to average out. The signal to noise improvement expected from this technique is given by $n^{\frac{1}{2}}$ where n is the number of sweeps performed. The contents of the computer channels are reconverted to analogue form and reproduced on the normal instrument recorder.

The instrument available was a Digiac Computer with interface equipment for the R10 spectrometer and a limited interface for the R.S.2 instrument. The continual field drift of the R10 can be partially overcome by trigering the beginning of each sweep from a peak within the spectrum, it being possible to produce a predetermined field shift after trigering and before accumulating the required portion of the spectrum. The use of the C.A.T. with the R.S.2 spectrometer is very limited in that no baseline stabilization system is incorporated in this instrument and the baseline will generally drift to a position unsuitable for the computer after only a few minutes.

CHAPTER 3

Some Considerations of the Chemical Shift

3:1 Introduction

The actual field experienced by a nucleus when placed in a strong external magnetic field differs from the applied field by a small amount due to secondary fields induced both within the molecule containing the nucleus and in its neighbours. This may be written (see section 1:8) as

$$H = H_o(1 - \sigma) \qquad 3:1$$

where H is the field at the nucleus, H_o is the static applied field and σ is the screening constant. One of the early uses of nuclear magnetic resonance was for the measurement of nuclear magnetic moments and in conducting experiments for this purpose, it was soon discovered that the resonance condition deviated from that given by equation 3:1 because of the field dependent screening contribution $H_o\sigma$. Early attempts to correct for this shielding were based on the theory developed by Lamb[35] who considered the magnetic shielding of a nucleus due to the induced electronic currents in a free atom with no orbital or spin angular momentum. When dealing with molecules this method becomes unsuitable and the first theoretical expression for the screening of a nucleus in an isolated molecule was derived by Ramsey[36, 37]. It is not the purpose of the present work to investigate the derivation of theoretical expressions for nuclear screening; the expression derived by Ramsey for σ_λ the shielding coefficient for an orientation λ, obtained by a second order perturbation treatment will be stated without further proof.

$$\sigma_{\lambda} = (e^2/2mc^2)(0\lambda|\sum_k(x_k^2 + y_k^2)/r_k^3|0\lambda) - 2\sum_n{}'\sum_{\lambda'}{}'[1/(E_n - E_o)]$$

$$[(0\lambda|\sum_k m_{zk}^o|n\lambda')(n\lambda'|\sum_k m_{zk}^o/r_k^3|0\lambda)$$

$$+ (0\lambda|\sum_k m_{zk}^o/r_k^3|n\lambda)(n\lambda'|\sum_k m_{zk}^o|0\lambda)] \qquad 3{:}2$$

The first term of Ramsey's expression is similar to the Lamb formula for atoms and becomes identical with it when averaged over all directions. The second term, which vanishes if the system is axially symmetric about the Z axis, corresponds closely to the paramagnetic term in the Van Vleck equation[38] for magnetic susceptibility. To evaluate the second paramagnetic term precisely, it is necessary to know the energies and wave functions of all of the excited electronic states, including those in the continuum. A simpler but less exact form of the expression for the shielding of a nucleus may be obtained if $(E_n - E_o)$ is replaced by an average value[39, 40] ΔE when

$$\sigma = (e^2/3mc^2)(0|\sum_k 1/r_k|0) - (4/3\Delta E)(0|\sum_{jk} m_j^o . m_k^o/r_k^3|0) \qquad 3{:}3$$

Even in this form, however, the Ramsey formula is not suitable for the calculation of the screening constants in any but the smallest molecules. For large molecules, both terms become large and tend to cancel each other.

In order to deal with large molecules, or to make comparative studies of the shielding of nuclei, in a series of related compounds, it is convenient to make approximations to the terms of equation (3:2) and to break up the screening into several individual contributions, the sum of which will represent the total screening of the nucleus and each of which may be taken to have classical significance. This was first proposed by Saika and Slichter[41] who divided the screening of a nucleus into three separate atomic contributions as follows

1. The diamagnetic correction for the atom in question, corresponding to the Lamb equation[35].

2. The paramagnetic term for the atom in question. This term represents the contribution from magnetic fields set up by the orbital motion of the valence electrons. In the absence of an external static field, the orbital fields have a zero average value, but at any instant produce fields of several thousand gauss at the nucleus. A slight polarisation of such enormous fluctuating fields by the static magnetic field produces an appreciable magnetic shielding.

3. Contributions from other atoms. Electrons on other atoms are either tightly bound in closed shells or else are in the valence shells. The former are hard to polarise and produce only small fields and the valence electrons will generally be expected to show an effect but small compared to the paramagnetic effect above because of the r^{-3} falling off of the interaction.

It is proposed that the shielding of any nucleus K may be divided more completely and usefully into five contributions representing both intramolecular and intermolecular screening terms rather than the three proposed by Saika and Slichter and given as

$$\sigma_k = \sigma_{dia} + \sigma_{para} + \sigma_{mag} + \sigma_{del} + \sigma_{sol} \qquad 3{:}4$$

A difference in the magnitude of any one of these terms for two nuclei contributes to the Chemical shift between them. Each of the terms in equation 3:4 which are applied field dependent will be discussed in turn.

3:2 The Diamagnetic Term σ_{dia}

σ_{dia} Corresponds to term 1 proposed by Saika and Slichter[41] and is proportional to the applied magnetic field and is produced at the nucleus by the moment induced through the rotation of the electrons about the nucleus, with the Larmor precessional frequency $^{eH}/_{2mc}$. When placed in an applied magnetic field, an atom having a spherically symmetric electron distribution experiences induced currents which are wholly diamagnetic, i.e. there is no obstacle to the free circulation of induced currents. If the electron distribution is subject to some form of constraint, for example in a molecule with several attracting centres, then a paramagnetic contribution to the shielding arises.

3:3 The paramagnetic Term σ_{para}

This term is regarded as arising from the effect of mixing of ground and electronically excited states[42,43] this being induced by the applied field H_o. A simple physical representation is that σ_{para} arises from the hinderance to the Larmor precession caused by different local fields produced by the lack of axial symmetry about the field H_o; in a linear molecule, σ_{para} is zero when H_o is along the molecular axis, but in general it is non-zero for an atom in a molecule. A uniform electric field E_z distorts an atom in an S state, this distortion affecting the σ_{dia} and σ_{para} terms of equation 3:4.

The change in σ, in the case considered, due to E_z is proportional to E_z^2, the symmetry of an atom in an S state requiring that the shielding is unaffected by reversal of E_z. The contribution expected to σ for a hydrogen atom in the ground state has been calculated by Marshall and Pople[44]. When the resonant nucleus is not at a centre of molecular inversion, the screening for a fixed orientation of the molecule may be affected by reversal of E_z so that σ may be proportional to E_z rather than to E_z^2. For the case where E_z is a fixed external field, then for a gas or liquid, the shielding proportional to E_z averages to zero. However, if E_z arises from a polar group within the molecule itself or from neighbouring molecules polarised by the solute, the mean value of E_z at a particular nucleus may not be zero, giving rise to a screening constant proportional to E_z in addition to that proportional to E_z^2. Thus, the shielding of a nucleus due to an intramolecular electric field will be proportional to the first power of the field along the bond containing the nucleus and to the second power of the field perpendicular to it.

Buckingham[45], studying the effects of intramolecular electric fields on proton screenings deduced the equation

$$\sigma = 2 \times 10^{-5} - 2 \times 10^{-12} E_z - 10^{-18} E^2 \qquad 3{:}5$$

The electric field contribution to the chemical shifts of nuclei of a particular type due to the screening changes σ_{el} may be written in the form

$$\Delta \sigma_{el} = - A \Delta E_z - B \Delta E^2 \qquad 3{:}6$$

The constants A and B are a measure of the ease of polarisability of the electron distribution, along and perpendicular respectively to the bond containing the resonant nucleus. For the case of hydrogen, reasonable estimates for these quantities are the constants in equation 3:5 proposed by Buckingham[45]. The procedure for deducing E_z and E^2 is discussed in Chapter 7.

3:4 The Term σ_{mag}

The term σ_{mag} in equation 3:4 corresponds in part to term 3 proposed by Saika and Slichter[41]. This screening contribution is thought to arise principally from the neighbour-anisotropy effect[46]. The effect arises from substituents with different principal components of the magnetic susceptibilities χ_i. When placed in strong magnetic field H_i in the i direction, different magnetic moments $\chi_i H_i$ are induced along the principal axes of the substituent. The secondary fields produced at a nucleus by these induced dipoles are the origin of the neighbour-anisotropy effect. The magnitude of σ_{mag} depends solely on the nature of the atom or group in which the secondary field originates. The simplest way to estimate the magnitude of such an effect is to replace the currents on the other atoms by point magnetic dipolesat the atoms centre[46]. This corresponds to dividing up the magnetic susceptibility of a molecule into atomic contributions, χ atomic, and to finding the secondary fields produced at any nucleus by the other atoms in the molecule. The secondary fields due to the currents on neighbouring atoms are dependent on the distance r between the point dipole and the nucleus in question, and the angle between r and the inducing dipole direction. This approach may be extended when considering screening in molecules by the replacement of atomic susceptibilities with bond magnetic susceptibilities. Considering the effect of a magnetic dipole in an atom (bond) i on a nucleus j for which the distance r_{ij} is large compared with the radius of i, then

$$\sigma_j = (3N_o r^3_{ij})^{-1}(2\Delta\chi_{1(i)} - \Delta\chi_{2(i)} - \Delta\chi_{1(i)}3\cos^2\Theta_z) \qquad 3:7$$

where $\Delta\chi_1 = \chi_{zz} - \chi_{yy}$ and $\Delta\chi_2 = \chi_{zz} - \chi_{xx}$ and χ_{xx}, χ_{yy} and χ_{zz} are the three principal axes of the magnetic susceptibility tensor χ of the atom or bond i. N_o is Avagadros number and Θ_z is the angle between the radius vector r_{ij} and the axis of χ_{zz}. Equation 3:7 provides a good approximation to σ_j providing that the electrons localised on atom j do not overlap with those on atom i. It has been suggested[46] that equation 3:7 is valid only for distances of $r_{ij} > 3$Å, however, this equation has been used for shorter distances. If a group of atoms or a bond (i) is considered which is axially symmetric then $\chi_{xx} = \chi_{yy} \neq \chi_{zz}$ and equation 3:7 reduces to

$$\sigma_j = \frac{\Delta\chi_i}{3N_o r_{ij}^3}(1 - 3\cos^2\Theta_z) \qquad 3:8$$

in which $\Delta\chi_i = \chi_i^{\parallel} - \chi_i^{\perp}$, where $\chi_i^{\parallel}$ and $\chi_i^{\perp}$ are respectively the susceptibility components along and perpendicular to the axis of the bond i. The term σ_{mag} in equation 3:4 may be deduced from

$$\sigma_{mag} = \sum_i \sigma_j \qquad 3:9$$

3:5 The Term σ_{del}

The term σ_{del} in equation 3:4 arises from additional induced interatomic currents which flow around closed conjugated loops. The simplest system in which to consider this effect is the benzene molecule, having six mobile π electrons which behave much like charged particles free to move in a circular wire. If a magnetic field H_o is applied perpendicular to the wire, the electrons circulate with an angular frequency $eH_o/2\pi mc$, giving a current of

$$j = \frac{3e^2H_o}{2\pi mc} \qquad 3:10$$

The direction of this current will be such that it induces a secondary field in opposition to the applied field at the centre of the ring, the lines of force from this secondary field following circular paths at right angles to the plane of the ring. The secondary field at the positions of the aromatic protons will therefore reinforce the applied field H_o and so deshields the protons.

An estimate of this effect can be made[47] if the current j is replaced by a magnetic dipole $\frac{j\pi a^2}{c}$ at the centre of the ring and perpendicular to the plane of the ring, the radius of which is a. If the distance of a proton from the centre of the ring is R, then the secondary field at this point is given by

$$\frac{j\pi a^2}{cr^3} = \frac{3e^2H_oa^2}{2mc^2R^3} \qquad 3:11$$

Dividing by $-H_o$, the contribution for the screening constant in this direction is obtained. If the applied field was in the plane of the molecule then no current would be induced and hence there would be no contribution to the screening from this situation. The approximation to the mean screening constant from a consideration of randomly orientated molecules is obtained by dividing by 3, giving

$$\Delta\sigma = \frac{-e^2 a^2}{2mc^2 R} \qquad 3:12$$

The existance of ring currents in aromatic compounds is well established. However, little is known about the possibility of such currents existing in saturated or partly saturated rings and in calculations of nuclear screenings in saturated compounds any possible contributions from σ_{del} have in the past been neglected and a similar assumption will be made for the present work.

3:6 The Term σ_{sol}

The term σ_{sol} in equation 3:4 accounts for the interaction of solvent molecules with the molecule containing the nucleus whose screening is being evaluated. The screening due to σ_{sol} can itself be considered to arise from several intermolecular effects[48] and these may be expressed as

$$\sigma_{sol} = \sigma_b + \sigma_a + \sigma_w + \sigma_E \qquad 3:13$$

σ_b Is the contribution to σ_{sol} proportional to the bulk magnetic susceptibility of the medium. σ_a arises from the anisotropy in the molecular susceptibility of the solvent molecules, σ_w is due to van der Waals forces between the solute and solvent and σ_E is due to polar solutes causing electric charge distribution in neighbouring solvent molecules which leads to an electric field **E** acting on the solute and to a perturbation of its electronic structure. The term σ_a corresponds to the intramolecular term σ_{mag} of equation 3:4 and σ_w and σ_E may be considered to be analagous to the intramolecular effects given by the single term σ_{para} in equation 3:4. Differences in any of the terms in equation 3:13 for two nuclei can affect the σ_{sol} screening contribution. These differences may be appreciable for two nuclei in different intermolecular environments, and are thus particularly important when using an external reference for the measurement of chemical shifts. For this experimental situation σ_b and σ_a are usually the most significant contributions to $\Delta\sigma_{sol}$. These effects may be largely (but not completely) eliminated by the use of an internal reference. In the investigations reported in this work, internal references have been used and it is realised that solvent effects may have small contributions to the screening of nuclei under consideration, but these effects have been neglected in all of the calculations and no further discussion of solvent effects will be undertaken.

3:7 Some Further Assumptions Necessary for Quantitative Estimates of Chemical Shifts

For practical evaluations of screening constants, it is convenient to evaluate the screening of a nucleus k relative to that for a nucleus l of the same isotopic species, rather than evaluate the absolute screening of a nucleus, i.e. the chemical shift δ_{kl} between the resonances for the nuclei k and l is given by

$$\delta_{kl} = \sigma_k - \sigma_l \qquad 3:14$$

The contribution to the total shielding σ of a nucleus in equation 3:4 arising from the σ_{dia} term is normally assumed to be largely constant for a particular nuclear species; changes in this term constitute the major change in shielding for nuclei of different isotopic species. The small perturbations to σ_{dia} may be accounted for, together with differences in the σ_{para} term for two nuclei k and l approximately in terms of equation 3:6 which may be rewritten as

$$\Delta\sigma_{el(kl)} = -A\Delta E_{z(kl)} - B\Delta E^2_{(kl)} \qquad 3{:}15$$

The general expression for the relative screenings of the two nuclei k and l of the same nuclear species may in a molecule containing no delocalised electrons be written as

$$\Delta\sigma_{kl} = \Delta\sigma_{el(kl)} + \Delta\sigma_{mag(kl)} + \Delta\sigma_{sol(kl)} \qquad 3{:}16$$

In addition to the electric field arising from permanent dipole moments within the molecule, there is also a contribution from fluctuating electric fields whose time-averaged square $\langle E^2\rangle$ is not zero and which therefore contributes to the screening of a nucleus. This field is thought to arise from van der Waals interactions between atoms and has been determined[50] from an approximate quantum mechanical calculation to be

$$\langle E^2\rangle = \frac{3PI}{r^6} \qquad 3{:}17$$

where P and I are the polarisability and ionisation potential of the atom (bond) causing the effect, and r is the distance from the origin of the effect to the nucleus whose screening is being considered. The screening contribution given by $\langle E^2\rangle$ may be included in equation 3:15 as a separate van der Waals term or more generally it has been included in the term $\Delta\sigma_{el(kl)}$ of equation 3:15 in the form

$$\Delta\sigma_{el(kl)} = -A\Delta E_{z(kl)} - B(\Delta E^2_{(kl)} + \Delta\langle E^2\rangle_{(kl)}) \qquad 3{:}18$$

The work reported in subsequent chapters was directed towards an investigation of the use of equation 3:16 for the determination of proton and fluorine nuclear screenings in saturated compounds.

CHAPTER 4

The N.M.R. Spectra of Some Highly Fluorinated Bicyclo(2,2,1)heptane and Heptene Compounds

4:1 Introduction

The studies outlined in this work are concerned mainly with correlations between nuclear screenings as measured by the nuclear magnetic resonance technique and semi-empirical methods for the calculation of such screenings. In any of the simple methods proposed so far for the evaluation of chemical shifts, it is necessary to be able to evaluate intramolecular distances and angles, so cyclic molecules have been used extensively for these correlations as the geometry of such systems is quite easily understood. In particular, there were available a series of highly fluorinated bicyclo(2,2,1)heptanes and heptenes of which the former have been used primarily for this purpose. The numbering of the carbon skeleton in these compounds is shown in figure 4:1. These compounds, together with perfluorocyclohexane and trans-perfluorodecalin, have been used to investigate a previously proposed semi empirical method for the evaluation of ^{19}F shifts in saturated fluorinated molecules.

It is generally assumed that ^{19}F shifts in such molecules may be explained by the σ_{para} term of equation 3:4, which is investigated further in chapter 7. The contribution from σ_{mag} to fluorine shifts is thought to be negligible compared with σ_{para}, although little work has been done on evaluating the C-F bond magnetic anisotropy. This is required for the prediction of ^{19}F shifts and

4.1A

4.1B

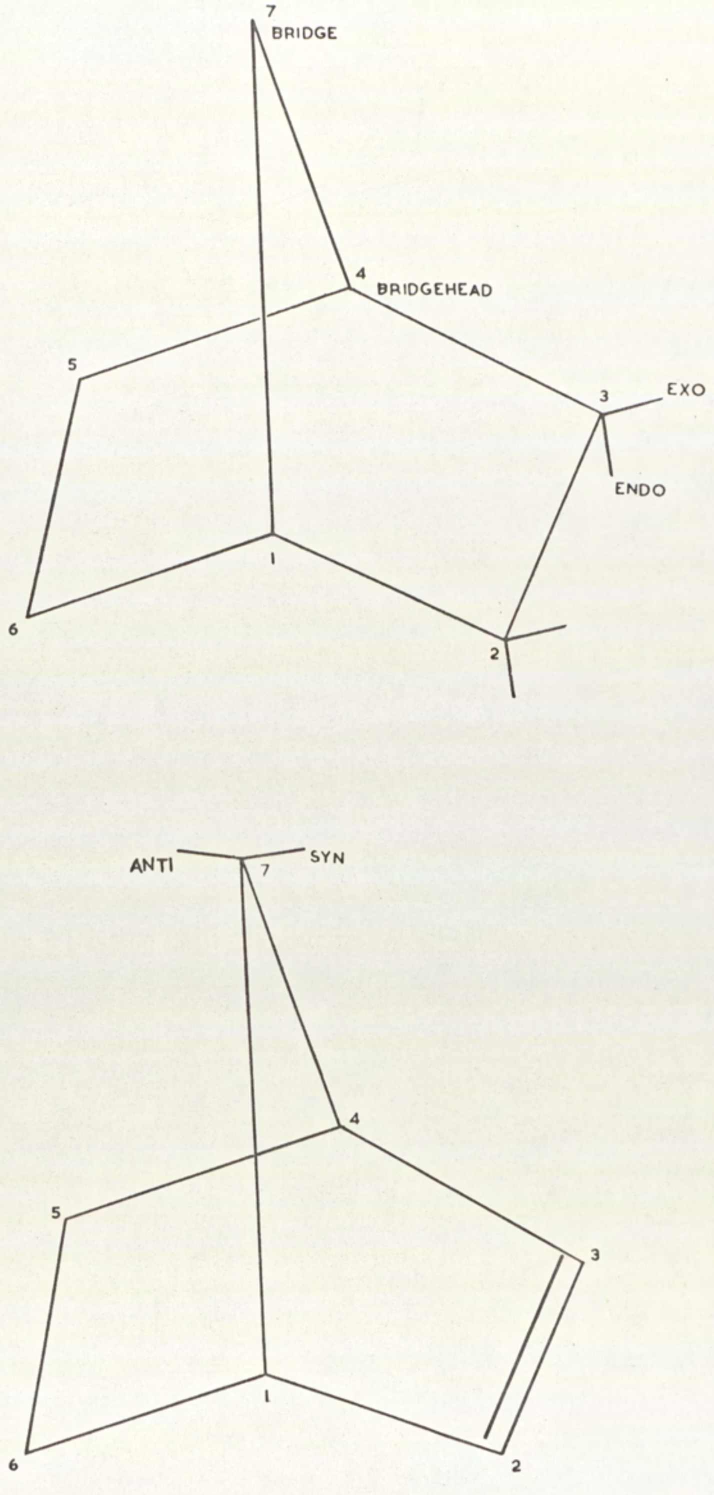


FIGURE 4.1 Nomenclature used for:

A. The bicyclo(2,2,1)heptane skeleton.

B. The bicyclo(2,2,1)heptene skeleton.

so has been investigated, and a value which apparently represents the anisotropy in the magnetic susceptibility of the C-F bond has been deduced. For detailed calculations on the molecules used it is also necessary to have values for the anisotropy in the magnetic susceptibility of C-C and C-H bonds, all of which must be derived on a self consistent basis. These have been investigated and are discussed in chapters 5 and 6, where some interesting conclusions have also been drawn on the interpretation of ^1H shifts in terms of neighbouring bond magnetic anisotropies. Before studying the semi-empirical methods for the evaluation of ^1H and ^{19}F screenings, the spectra of the highly fluorinated bicyclo(2,2,1)heptanes and heptenes used for these investigations will be discussed and the various resonances tentatively assigned on empirical grounds.

4:2 Experimental

The ^{19}F magnetic resonance spectra of a series of fluorinated bicyclo(2,2,1)heptanes and heptenes were observed at 56.462 Mc.sec.$^{-1}$ and 33.4°C on a Perkin Elmer R10 spectrometer. These fluorinated bicyclic compounds are generally solid at this temperature and therefore hexafluorobenzene has been used exclusively as the solvent in these studies. The spectrometer was fitted with a field compensator to reduce the effects of external disturbances on the magnetic field. Calibration of the spectra was by the normal audio sideband technique described in section 2:8. In general, each individual band in the spectra was measured at as slow a sweep rate as was consistent with avoiding saturation of the nuclear signals, by placing four calibration markers about it; wherever possible placing two on each side of the band being measured. The calibration markers were sidebands of the hexafluorobenzene solvent, obtained by modulating the R.F. power with an audio signal from a Muirhead-Wigan D-890A oscillator. The calibration procedure was performed six times for each band, and in each case the position of the band(s) in question was estimated by a least mean squares treatment for frequency versus absorption position on an arbitrary scale of the four calibration markers, and then interpolating for the frequency of the required peak measured on the same scale using the reference $y = mx + c$ type equation. The results from the six runs were then averaged to give an estimated error of ± 0.2 c.sec.$^{-1}$ in the frequency of the required peak(s). This averaging process was performed with the aid of either an Electronic Associates P.D.S. 1020 computer or an Elliot 803 computer and was used to overcome the small instabilities in the magnetic field which were not accounted for by the field compensator. The major source of the remaining error was then due to the accuracy with which the centre of a peak could be physically located. Most of the ^{19}F spectra studied showed a series of bands containing many overlapping and often unresolvable lines. The observation of these spectra at a higher frequency, e.g. 94 Mc.sec.$^{-1}$ might have made the measurement of the line positions more accurate. The frequency of the audio signals used for producing the calibration side bands were checked to ± 0.01 c.sec.$^{-1}$ using a Venner 3336 frequency counter. The spectra were integrated using the electronic integration circuit built into the R10 spectrometer, which is claimed to be accurate to ±1%.

4:3 The ^{19}F Magnetic Resonance Spectra of Some Highly Fluorinated Bicyclo(2,2,1)heptanes.

The compounds available for study were perfluorobicyclo(2,2,1) heptane and the following bridgehead substituted derivatives of this compound: namely the 1H-, 1;4diH-, 1Br-, 1;4diBr-, 1Br;4H- and

1I- derivatives. The ^{19}F spectra of 1D- and 1Me-undecafluorobicyclo(2,2,1)heptane have also been examined but not in such detail as those mentioned above. The ^{19}F spectrum of perfluoro-endo-2,3-cyclopentano-2,2,1-bicycloheptane has also been observed but no attempt has been made to assign the bands in the CF_2 region of the spectrum to their respective nuclei, the only point of interest in this spectrum being the doublet, obtained from the 2,3 exo fluorines, which can readily be assigned. The spectral measurements for all of the compounds studied in detail are recorded in table 4:1in which are also given the final assignments resulting from the subsequent discussion.

The ^{19}F spectrum of perfluorobicyclo(2,2,1)heptane, (figure 4:2), contains a group of absorptions to lower applied field than the hexafluorobenzene sol vent which are attributed to the fluoromethylene groups and an essentially single resonance band to high field of the hexafluorobenzene arising from the bridgehead fluoromethine nuclei. This latter assignment is unambiguously established by reference to the 1H- and 1;4diH-substituted compounds in which the corresponding resonance appears at half the relative intensity in the first case,and with no corresponding resonance in the latter case.

The portion of the spectrum of perfluorobicyclo(2,2,1)heptane to low field of the solvent appears to consist of a typical AB type pattern together with another single band containing many unresolvable lines. The latter band is assigned to the bridge CF_2 group, and the apparent AB spin pattern as arising from the 2,3,5,6 exo and endo nuclei; the AB coupling being between the exo and endo fluorines. The absorption due to the bridge CF_2 group would not be expected to show the AB type pattern shown by the exo and endo CF_2 groups,as the symmetry of the molecule would preclude the

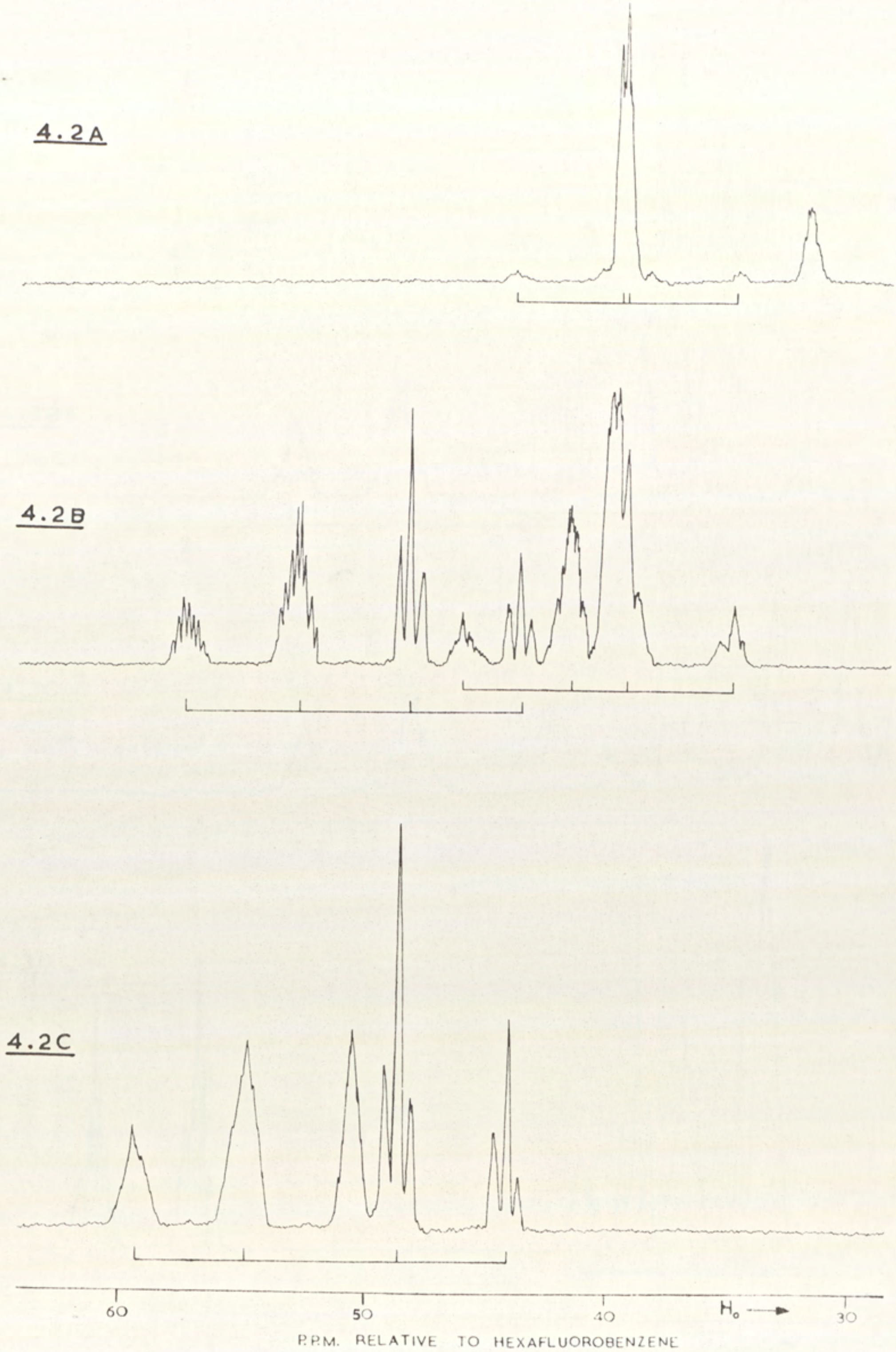


FIGURE 4.2 The ^{19}F spectra at 56.462 $Mc.sec.^{-1}$ of:

A. Perfluorobicyclo(2,2,1)heptane.

B. 1H-undecafluorobicyclo(2,2,1)heptane.

C. 1;4diH-decafluorobicyclo(2,2,1)heptane.

The spectrum to low field of the hexafluorobenzene solvent only is shown.

Table 4:1 The Chemical Shifts and approximate geminal coupling constants for perfluorobicyclo(2,2,1)heptane and some bridgehead substituted derivatives.

Nucleus	ν from hexafluorobenzene* (c.sec^{-1})	Shift p.p.m.*	J gem. (c.sec.$^{-1}$)
perfluoro-			
1,4	+3565.1	+63.15	
7	1808.9	32.04	
2,3,5,6 exo	2033.9 2244.0	39.10	256
2,3,5,6 endo	2258.2 2518.1	40.64	
1H-			
4	+3118.9	+55.25	
7	2281.8	40.41	
2,6 exo	2496.0 2756.2	47.18	259
2,6 endo	3288.6 3030.4	55.26	
3,5 exo	1991.4 2245.5	37.49	253
3,5 endo	2374.9 2626.0	43.46	

*All frequencies and chemical shifts are negative unless specifically stated otherwise.

Table 4:1 continued.

Nucleus	ν(c.sec^{-1}) from hexafluorobenzene*	Shift p.p.m.*	J gem (c.sec.$^{-1}$)
1;4diH-			
7	2854.5	50.56	
2,3,5,6 exo	2490.0 2748.5	46.90	258
2,3,5,6 endo	3102.8 3359.7	58.50	
1Br-			
4	+3155	+58.88	
7	2124	37.62	
2,6 exo	2273 2515	42.70	240
2,6 endo	3132 3370	52.57	
3,5 exo	3048 3296	42.11	248
3,5 endo	2434 3682	50.52	
1;4diBr-			
7	2449.9	43.39	
2,3,5,6 exo	2299.9 2544.2	43.16	244
2,3,5,6 endo	3321.4 3565.7	60.73	

*All frequencies and chemical shifts are negative unless specifically stated otherwise.

Table 4:1 continued.

Nucleus	ν(c.sec^{-1}) from hexafluorobenzene*	Shift p.p.m.*	J gem (c.sec.$^{-1}$)
**1Br;4H-			
7	2786.0	46.43	
2,6 exo	2392.5 2637.1	42.17	248
2,6 endo	3400.0 3650.9	58.50	
3,5 exo	2694.7 2947.8	28.45	252
3,5 endo	3400.0 3650.9	35.02	
1I-			
4	+3001.7	+53.16	
7	2315.1	41.00	
2,6 exo	2385.6 2631.9	44.64	248
2,6 endo	3677.6 3926.9	67.13	
3,5 exo	2064.0 2308.2	39.40	247
3,5 endo	2494.7 2744.4	45.71	

*All frequencies and chemical shifts are negative unless specifically stated otherwise.

**Measured at 60.0 Mc.sec.$^{-1}$ on an A.E.I. R.S.2 spectrometer.

geminal bridge fluorine coupling from appearing in the spectrum. These assignments are confirmed by relative intensity measurements. A more detailed examination of the apparent AB portion of the spectrum at a slow sweep rate, shows that it is not a true AB or even four superimposed AB's, but the AA'A''A'''BB'B''B''' portion of the complex spectrum that would be expected from the AA'A''A'''BB'B''B'''KK'XX' spin system required to fully interpret the spectrum of this compound. Spectral patterns resembling those from AB spin systems appear for all of the compounds studied, and in all cases they are not true AB's but portions of a spin system which must embrace all of the nuclei having non zero spins in the molecules. For simplicity and because the complete ten or twelve spin systems are not readily amenable to analysis, they will be referred to as AB type spectra throughout this discussion, and analysed as such, with some justification gained from the analysis of these portions of the spectra, as A_2B_2 spin systems, which is considered in section 4:4.

The portion of the ^{19}F spectrum of the 1H- compound to low field of the solvent absorption, appears considerably more complex than the corresponding portion of the perfluoro spectrum (see figure 4:2). This is due to the symmetry of the molecule about a plane perpendicular to and through the midpoint of the 2,3 and 5,6 carbon bonds being destroyed by the substituent. This portion of the spectrum contains two AB type spectra arising from the 2,6 exo/endo and 3,5 exo/endo fluorine pairs and a single band due to the bridge CF_2 group. The 1;4diH-compound has the same symmetry as the perfluoro- and it is not surprising that it gives rise to a similar spectrum, consisting of a single band due to the bridge CF_2's and an AB type pattern due to the exo and endo fluorines, although with increased chemical shift compared to that in the perfluoro spectrum. An AB analysis of the relevant portions of the spectrum of the 1H-compound gives values for the chemical shifts (see table 4:1) of the nuclei giving rise to these spin patterns. An assignment to which positions in the molecule give rise to these bands may be made using the established principle of substituent additivity to chemical shifts. The shifts for the exo and endo nuclei, relative to hexafluorobenzene, in the spectra of the perfluoro- and 1;4diH- compounds are -40.64, -39.10 and -56.73, -46.90 p.p.m. respectively, and the two pairs of exo/endo shifts in the 1H- compound are at -55.26, -47.18 and -43.46, -37.49 p.p.m. Accepting that any substituent will affect the shielding of the nuclei closest to it to a greater extent than it will influence the shielding of nuclei several bonds removed, then it is seen that the least shielded AB system may be assigned to the nuclei on the same side of the molecule as the bridgehead hydrogen and the most shielded must be on the side of the molecule having the bridgehead fluorine. The two bands in the AB portion of the spectrum due to the 1;4diH-compound arising from the more highly shielded of the exo or endo nuclei, show a well defined splitting of triplet appearance. This is also apparent on the high field bands of one of the AB type systems in the 1H-spectrum. This is the AB type, which was assigned above to the CF_2's at positions 2 and 3, i.e. adjacent to the hydrogen substituent, which supports the above assignment. The triplet splitting is not produced from first order coupling as the individual lines do not show the correct intensities or separations, and this triplet pattern must be attributed to part of the complex second order spin system expected from these molecules. The self consistency of this assignment and the substituent additivity effect are well shown in table 4:2. At this stage, no absolute assignment of shifts to exo and endo nuclei has been made.

Compound	Nucleus					
	7	1,4	Exo	or	Endo	
perfluoro	-32.04	+63.15	-39.10		-40.64	
	- 8.37	- 7.90	-8.08	+1.61	+14.62	-2.82
1H-	-40.41	+55.25	-47.18	-37.49	-55.26	-43.46
	-10.15		+0.28	-9.41	- 1.47	-13.27
1;4diH-	-50.56		-46.90		-56.73	

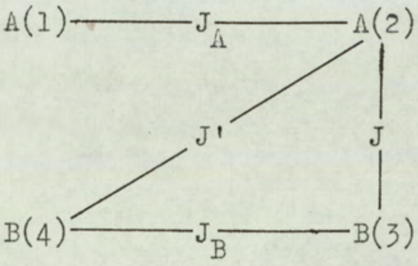
Table 4:2. The effect of bridgehead hydrogen substituents on the shielding of fluorine nuclei at other positions in fluorinated bicyclo(2,2,1)heptanes

The ^{19}F spectra obtained from the fluorobicyclo(2,2,1)heptanes with bridgehead halogen substituents other than fluorine (figure 4:3) show no features which are unexpected when compared with the spectra of the three compounds discussed above. It would appear therefore that the relative exo-endo shift is the same for the molecules having halogen bridgehead substituents as for the molecules having hydrogen at the bridgehead. This is suggested by the appearance of well defined pseudo triplet splitting on the high field bands of the AB systems assigned to the exo and endo fluorines in the compounds; this being observed when the atom at the adjacent bridgehead is anything other than fluorine.

4:4 Some Further Considerations of the Evaluation of Parameters From the Spectra which Appear as AB Type.

All of the spectra which arise from the exo and endo nuclei have been assumed to be AB and analysed according to the method given in section (1:10) to obtain an estimate for the relative chemical shifts and geminal fluorine coupling constants. These values are recorded in table 4:1. A better approximation than AB to obtain these estimates, might have been to analyse the fluorine nuclei in the two CF_2 groups on adjacent carbon atoms as A_2B_2 spin systems. The parameters obtained from the AB analysis together with estimates of the remaining couplings deduced from fluorocyclohexanes, have been used to predict the A_2B_2 spectra and this compared with that observed.

The explicit energies and intensities for the A transitions in an A_2B_2 spin system are given in ref. 7, and are reproduced in table 4:3. The transitions correspond to the numbering system used in ref. 7, the missing transitions not having explicit solutions for their energies and intensities. The spin coupling constants for the system are defined below:



The quantities K, L, M, N in table 4:3 are defined in terms of the coupling constants as:

$$K = J_A + J_B \qquad L = J - J'$$

$$M = J_A - J_B \qquad N = J + J'$$

The molecule perfluorobicyclo(2,2,1)heptane has been chosen as the model for this evaluation. The value of $(\nu_o \delta)$ has been taken as that derived from the AB analysis, i.e. 85 c.sec.$^{-1}$, and an approximate value of 250 c.sec.$^{-1}$ taken for J. The remaining coupling constants required should be similar to those found in fluorocyclohexanes[50], i.e. the J_A and J_B couplings correspond to $J_{1,2}$ gauche

Transition	Frequency Relative to $\frac{1}{2}(\nu_A + \nu_B)$	Intensity
1	$\frac{1}{2}N + \frac{1}{2}\left[(\nu_o\delta)^2 + N^2\right]^{\frac{1}{2}}$	$1 - \sin 2\phi$
3	$-\frac{1}{2}N + \frac{1}{2}\left[(\nu_o\delta)^2 + N^2\right]^{\frac{1}{2}}$	$1 + \sin 2\phi$
9	$\frac{1}{2}\left[(\nu_o\delta + M)^2 + L^2\right]^{\frac{1}{2}} + \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}$	$\sin^2(\theta_a - \psi_+)$
10	$\frac{1}{2}\left[(\nu_o\delta - M)^2 + L^2\right]^{\frac{1}{2}} + \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}$	$\cos^2(\theta_a + \psi_-)$
11	$\frac{1}{2}\left[(\nu_o\delta + M)^2 + L^2\right]^{\frac{1}{2}} - \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}$	$\cos^2(\theta_a - \psi_+)$
12	$\frac{1}{2}\left[(\nu_o\delta - M)^2 + L^2\right]^{\frac{1}{2}} - \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}$	$\sin^2(\theta_a + \psi_-)$

Table 4:3. The explicit energies and intensities for the A transitions of an A_2B_2 spin system. (The numbering corresponds to that in reference 7).

in fluorocyclohexanes, J' to $J_{1,2\ \mathrm{trans}}$, which have been found to be c.a. 14 c.sec.$^{-1}$ and 0-3 c.sec.$^{-1}$ respectively. Substituting these values into the energy functions of table 4:3 gives transitions at the following frequencies, relative to $(\nu_o\delta)$:

1	260	c.sec.$^{-1}$
3	8	
9	254	
10	254	
11	6	
12	6	

It is seen that the lines in this trial A_2B_2 spectrum will occur in two groups, between 6 - 8 c.sec.$^{-1}$ and 254 - 260 c.sec.$^{-1}$ relative to $(\nu_o\delta)$ giving a separation of 248 - 252 c.sec.$^{-1}$. This latter range of values would represent the geminal fluorine coupling constant if the system were analysed as a simple AB spectrum, and it is seen that the value obtained from such a simple AB analysis will be only of the order of 1% in error of that predicted by an A_2B_2 analysis.

This suggests that the simple AB analysis may produce estimates for the chemical shift and geminal coupling constant which, even if the remaining couplings in the molecules are considered, are not more than a few percent in error of the true values.

4:5 An Empirical Assignment of the Exo-Endo Shift in Fluorobicyclo(2,2,1)heptanes

The AB type spectra arising from the exo and endo fluorine nuclei in the fluorobicyclo(2,2,1)heptanes studied have been discussed but no assignment has yet been made as to which of the exo or endo nuclei are the more highly shielded.

A purely speculative assignment may be made following a comparison of ^{19}F and ^{1}H shifts in analogous compounds. The proton spectrum of cyclohexane at low temperature shows that in the rigid chair conformation, the axial protons are more shielded than the equatorial[57], whereas the ^{19}F spectrum of perfluorocyclohexane shows that the equatorial are more shielded than the axial fluorines[52]. The proton magnetic resonance spectrum of bicyclo(2,2,1)heptane has been reported[53] and the endo protons were observed to be more shielded than the exo. A naive analogy suggests that in perfluorobicyclo(2,2,1)heptane the exo would be more shielded than the endo fluorines.

The axial/equatorial shift in cyclohexane has been explained in terms of bond apparent magnetic anisotropy (see chapter 5). The bicyclo(2,2,1)heptane skeleton may be considered to consist of a cyclohexane ring in the boat conformation with a single carbon bridge across the 1,4 positions (figure 4:1). In both the chair and boat (if it were observable) conformations of cyclohexane, the C_1-C_2 and C_2 - C_3 bond magnetic anisotropies will contribute equally to the axial/equatorial shift for the proton at position 2 and this shift is induced almost entirely by the anisotropy in the magnetic susceptibility of C_3-C_4 and C_1-C_6 bonds. In both conformations, the C_1-C_6 bond is common, but in the chair form the C_3-C_4 bond gives an equal effect to the C_1-C_6 bond and doubles it. However, in the boat form of the cyclohexane ring, the C_3-C_4 bond bisects the angle between the two C-H bonds at C_3 and since the C-H bonds at position 3 are parallel to those at position 2 when reflected into a plane through the midpoints of the C_2-C_3 and C_5-C_6 bonds. The C_3-C_4 bond will then have an equal effect on both the axial and equatorial protons attached to C_2 in the boat conformation. This would lead to a predicted axial/equatorial shift for the boat conformation of cyclohexane of 0.46/2 p.p.m. = 0.23 p.p.m. with the same sign as for the chair conformation. The addition of a carbon bridge between C_1 and C_4 would approximately produce the bicyclo(2,2,1)heptane skeleton, with the axial protons equivalent to the endo and the equatorial equivalent to the exo. The modification to the axial/equatorial shift at carbon 2, due to the C_1-C_{bridge} and C_4-C_{bridge} bonds, which now represents the exo-endo shift in bicyclo(2,2,1)-heptane is given by

$$((0.1008 + 0.1163) - (-0.1206 + 0.1034)) \times 10^{23} \times 7.28 \times 10^{-30}$$

(The values are obtained from table 5:5) giving a resultant exo-endo shift of $(0.23 + 0.17) \times 10^{-6} = 0.39 \times 10^{-6}$. This indicates that if bicyclo(2,2,1)heptane were considered as a cyclohexane (boat) with a single carbon bridge between C_1 and C_4 then the endo protons should be 0.39 p.p.m. more shielded than the exo (c.f. observed value of 0.31 p.p.m.). If the axial/equatorial shift reversal in going from hydrogenated to fluorinated cyclic compounds is general, then in perfluorobicyclo(2,2,1)heptane, the exo fluorines would be expected to be more shielded than the endo.

The strongest empirical evidence in favour of the exo fluorines being more shielded than the endo arises from a consideration of the environments of all of the nuclei in perfluorobicyclo(2,2,1)heptane. From a model of this and related compounds, it can be seen that the exo fluorines more closely resemble those bonded to the single carbon bridge than do the endo fluorines. As a consequence of this, it would be expected that the screening of the exo fluorine muclei would more closely resemble that of the bridge fluorines than do the endo nuclei. Examination of table 4:1, in which the chemical shifts for a series of fluorinated bicyclo(2,2,1)heptanes are given, shows that the chemical shift of one of the resonances assigned to the exo and endo fluorine nuclei does more closely resemble that which can be unambiguously assigned to the bridge fluorines than does the other. The assignment obtained by this method is in agreement with that proposed above, i.e. the exo fluorines are more shielded than the endo. The empirical evidence does appear to favour this assignment to the exo-endo fluorine shift; however, it should be treated with caution at this stage. The correlations between fluorine screenings and molecular structure reported in chapters 7 and 8 give some quantitative evidence for this assignment and, indeed, the calculations do support the empirical assignment.

4:6 The ^{19}F Magnetic Resonance Spectra of Some Highly Fluorinated Bicyclo(2,2,1)heptenes.

The ^{19}F spectra of a series of bridgehead substituted fluorobicyclo(2,2,1)heptenes have been observed under similar experimental conditions to those for the fluorobicyclo(2,2,1)heptanes reported in section (4:3). The compounds studied were the 1H-, 1;4diH-, 1Br-, 1I-, 1H;4I-, 1;4diI-, 1H;4Me- and 1Me;3Me-, derivatives of perfluorobicyclo(2,2,1)heptene. The parent compound, bicyclo(2,2,1)-

heptene itself was not available due to difficulties in its synthesis. The spectra of six of these compounds are shown in figures 4:4 and 4:5 and the measurements recorded in table 4:4.

The general assignment of the spectrum of each of these compounds can be readily made by reference to the various prominent features evident throughout the series of spectra obtained from the compounds studied. The resonance from the bridgehead fluorine in those compounds having fluorine at this position can be readily identified as that occuring to highest field, in a similar position to the bridgehead fluorines in the corresponding fluorobicyclo(2,2,1)-heptanes. Each of the spectra contains an AB type spectrum with a relatively large chemical shift of 20-28 p.p.m. This would appear contradictory to the general requirements for observation of second order spectra; however, it is a prominent feature in the spectra of all of these molecules and is assigned to the bridge nuclei anti and syn to the double bond. The consistency of the shift is expected and substantiates the assignment because the two bridge fluorines must be almost symmetrically disposed to the atom at the bridgehead and hence substitution of the bridgehead atoms should have little effect on the relative shifts of the anti and syn fluorines.

There are either one or two single bands which appear consistently in all of the spectra which may be readily assigned to the olefinic fluorines. The appearance of one or two lines (half height width 10-15 $c.sec.^{-1}$) depends on whether the two bridgehead substituents are the same or different. The remaining bands in the spectra are assigned to the fluoromethylene groups at carbons 5 and 6. The appearance of these bands depends on the nature of the adjacent bridgehead substituent. When both bridgehead

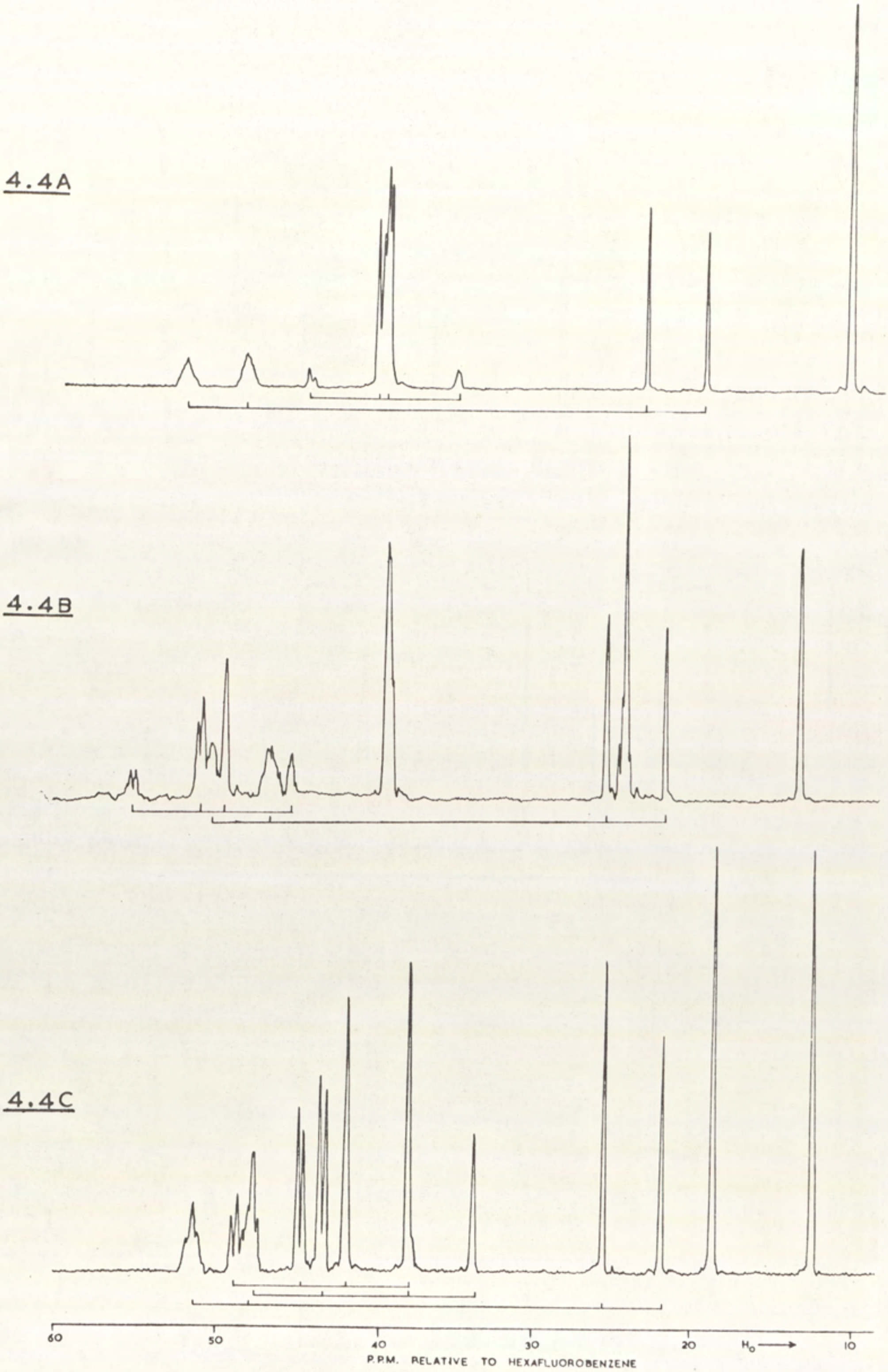


FIGURE 4.4 The ^{19}F spectra at 56.462 Mc.sec.$^{-1}$ of

A. 1;4diH-octafluorobicyclo(2,2,1)heptene.

B. 1H-nonafluorobicyclo(2,2,1)heptene.

C. 1H;4I-octafluorobicyclo(2,2,1)heptene

The spectrum to low field of the hexafluorobenzene solvent only is shown.

Table 4:4 The chemical shifts and approximate geminal coupling constants for some derivatives of perfluorobicyclo(2,2,1)heptene

Nucleus	ν(c. sec^{-1}) from hexafluorobenzene*	Shift p.p.m.*	J gem (c.sec.$^{-1}$)
1H-			
2	1365.6	24.19	
3	761.4	13.49	
4	+3042.3	+53.89	
5 exo, endo	2563.0	45.39	
6 exo	3043.9 2813.9	51.01	229
6 endo	2725.6 2497.8	47.12	
7 anti	2773.7 2567.3	47.16	205
7 syn	1428.1 1224.3	23.63	
1;4diH-			
2,3	1195.9	21.18	
5,6 exo	3028.4 2795.9	50.25	234
5,6 endo	2771.4 2537.1	48.33	
7 anti	3452.4 3245.6	59.19	207
7 syn	1898.3 1690.2	31.90	

*All frequencies and chemical shifts are negative unless specifically stated otherwise.

Table 4:4 continued.

Nucleus	ν (c.sec^{-1}) from hexafluorobenzene*	Shift p.p.m.*	J gem (c.sec.$^{-1}$)
1I-			
2	1795.4	31.80	
3	822.2	14.56	
4	+2907.5	+51.49	
5 exo, endo	2304.3	40.81	
6 exo	3350.7 3130.9	57.10	220
6 endo	2622.2 2402.1	44.79	
7 anti	2774.5 2579.7	47.27	195
7 syn	1581.6 1386.8	26.43	
1;4diI-			
2,3	1693.7	30.00	
5,6 exo	3417.2 3200.7	58.29	218
5,6 endo	2739.1 2520.0	46.89	
7 anti	3349.1 3155.7	57.47	193
7 syn	2103.0 1910.6	35.68	

*All frequencies and chemical shifts are negative unless specifically stated otherwise.

Table 4:4 continued.

Nucleus	ν (c.sec^{-1}) from hexafluorobenzene*	Shift p.p.m.	J gem (c.sec.$^{-1}$)
1H;4I-			
2	1271.0	22.51	
3	1609.9	28.51	
5 exo	3234.1 3011.7	54.68	218
5 endo	2860.2 2646.0	49.39	
6 exo	3164.7 2936.9	53.57	226
6 endo	2648.9 2424.3	45.39	
7 anti	3380.7 3186.9	58.04	196
7 syn	1983.7 1784.6	33.49	
1Br-			
2	1387.7	24.58	
3	806.0	14.27	
4	+3042.3	+53.88	
5 exo, endo	2275.4	40.3	
6 exo	2978.5 2756.8	50.33	218
6 endo	2486.3 2272.4	42.60	
7 anti	2522.3 2335.8	42.88	188
7 syn	1386.6 1196.7	23.02	

*All frequencies and chemical shifts are negative unless specifically stated otherwise.

Table 4:4 continued.

Nucleus	ν(c.sec^{-1}) from hexafluorobenzene*	Shift p.p.m.*	J gem (c.sec^{-1})
1H;4Me-			
2	1095.2	19.40	
3	853.1	15.11	
5 exo, endo	2409.3	42.67	
6 exo	3045.0 2814.6	50.98	231
6 endo	2734.8 2502.4	47.29	
7 anti	2984.7 2781.8	50.94	205
7 syn	1527.6 1319.9	25.34	
1Me;3Me-			
2	1914.0	33.90	
4	+3082.8	+54.60	
5 exo, endo	2300.8	40.75	
6 exo	2404.8 2180.0	39.76	225
6 endo	2091.1 1865.2	35.88	
7 anti	2350.9 2140.3	39.62	209
7 syn	1056.7 848.8	17.03	

*All frequencies and chemical shifts are negative unless specifically stated otherwise.

substituents are identical, only one AB type system is observed and when the bridgehead substituents are unlike, two such bands are observed one from the CF_2 group at position 5 and one from the group at position 6. In the cases where the bridgehead atom is fluorine, only a single band is observed from the CF_2 group adjacent to the fluorine, although this may be a limiting AB spectrum itself, with chemical shifts so close as to be unresolvable under the experimental conditions employed. As in the case of the fluorobicyclo(2,2,1)-heptanes, the AB type spectra have been analysed as simple AB's in an attempt to gain reasonable values for the chemical shifts and geminal coupling constants, the analysis of the complete spin systems for the molecules being too complex to attempt at present.

The assignments in the various AB spectra arising from the fluorine nuclei bonded to carbons 5 and 6 can be made by considering the additivity of substituent effects throughout the range of compounds studied. It is a reasonable assumption that a substituent at the bridgehead position will affect the shielding of the exo and endo fluorine nuclei adjacent to it more than those on the remote side of the ring. This is consistent with ideas forwarded later (chapter 7) on the mechanism for ^{19}F shieldings. An example of the use of substituent screening additivity may be demonstrated by reference to the assignment of AB type systems arising from the exo and endo nuclei bonded to carbons 5 and 6 in the 1H;4I- compound. Consider first the spectra of the two compounds having the same substituent at both bridgehead positions, as in this case there is only one AB type spectrum from the fluorines at positions 5 and 6, which can be unambiguously assigned. The AB type spectrum from the 5 and 6 position fluorines in the 1;4diH- compound has chemical shifts relative to hexafluorobenzene of -50.25 and -48.33 p.p.m. the mean of which is -49.29 p.p.m. and the corresponding resonances from the 1;4diI- compound are at -58.29 and -46.89 p.p.m. with a mean of -52.59. Considering the 1H;4I- compound, the spectrum of which contains two AB type bands, one arising from the exo and endo fluorines at carbon 5 and one from the corresponding fluorines at carbon 6. The pairs of chemical shifts relative to hexafluorobenzene are -54.68, -49.39 p.p.m., and -53.57, -45.39 p.p.m. with means of -52.04 and -49.48 respectively. The first of these two pairs clearly resemble more closely the shift found in the spectrum of the 1;4diI- compound and the second pair more closely resemble the shifts in the 1;4diH- compound. In the spectrum of the 1H;4I- compound, the AB type absorption having chemical shifts at c.a. -54.68 and -49.39 p.p.m. is assigned to the fluorines adjacent to the iodine atom, i.e. at carbon 5 and the AB type spectrum having chemical shifts of -53.57 and -45.39 p.p.m. is assigned to the fluorines at carbon 6. This assignment is substantiated from a consideration of the geminal exo-endo coupling constants found for the three molecules in question. A simple AB analysis gives $J_{gem(exo-endo)}$ for the 1;4diH- and 1;4diI- compounds as 234 and 218 $c.sec.^{-1}$ respectively. The couplings in the two different AB spectra from the 1H;4I- compound are 218 and 226 $c.sec.^{-1}$. Clearly, the coupling of 218 $c.sec.^{-1}$ corresponds to that found for the 1;4diI- compound, and supports the previous assignment that the fluorines at position 5 give rise to the AB type having chemical shifts at -54.68 and -49.39 p.p.m. Consideration of the relative chemical shifts for all of the resonances due to the fluoromethylene groups at carbons 5 and 6 will allow only one set of assignments which are entirely consistent throughout the series of compounds studied and these assignments are given in table 4:4.

4:7 Assignment of the resonance bands due to the anti-syn and exo-endo nuclei in the fluorobicyclo(2,2,1)heptenes studied

As in the analysis of the spectra of the fluorobicyclo(2,2,1)-heptanes, the initial assignment of the absorptions in the ^{19}F spectra of the fluorobicyclo(2,2,1)heptenes is relatively simple; however, as in the former case, the assignment of which of the exo and endo nuclei is the more shielded is not immediately obvious. The spectra of the unsaturated compounds is further complicated by the bridge fluorines anti and syn to the double bond being unequally shielded. An assignment as to which of the anti or syn nuclei is the more shielded cannot be made on the simple basis of the anisotropy in the magnetic susceptibility of the C=C bond[54], as this could at most only account for a very small portion of the 20-28 p.p.m. shift observed between the anti and syn fluorine nuclei. An empirical assignment to the anti-syn and exo-endo shieldings may be made by consideration of the relative chemical shifts observed for the high and low field absorption bands in each of the observed AB type spectra in these compounds. As in the case of the fluorobicyclo(2,2,1)heptanes, consideration of the symmetry of the molecule shows that in the fluorobicyclo(2,2,1)-heptenes, the exo atoms are more alike the bridge fluorine anti to the double bond, whereas the endo fluorines and the bridge fluorine syn to the double bond, show little similarity. One of the chemical shifts in the AB system due to the exo and endo fluorines should be very similar to one of the shifts in the AB type spectrum obtained from the anti-syn nuclei,whereas the other two chemical shifts need not be similar. Examination shows that only one of the bridge fluorine shifts is similar to one or both of those attributable to the exo and endo nuclei.

This indicates that the anti bridgehead nucleus is almost certainly less shielded than the nucleus syn to the double bond. The distinction between the exo and endo nuclei is, however, not so obvious. In some cases, i.e. the 1;4diH-, 1;4diI-, and 1H;4I-, this argument favours the endo as being more highly shielded than the exo nuclei whereas in other cases, i.e. the 1I-, 1H- and 1Br-, compounds it would appear that the exo are more shielded than the endo. Consideration of the general coupling patterns observed in the spectra indicates that it is most unlikely that there is a change in the relative screenings of the exo and endo nuclei for any of these compounds. The low field bands in the AB type spectra assigned to the exo and endo fluorines all show a well defined doublet splitting of c.a. 20 $c.sec.^{-1}$, whereas the high field bands of the AB spectrum in each case show very little splitting. It is interesting that in some of the spectra, the bands attributed to the bridgehead fluorine anti to the double bond exhibit a pseudo triplet splitting of similar magnitude to the doublet splitting observed for either the exo or endo fluorine resonances. It appears likely that this is a mutual coupling which intimates a strong coupling between the bridge anti fluorine and either the exo or endo fluorines. A coupling involving the endo fluorines seems unlikely due to the large number of bonds involved and 'long range' coupling appears unlikely due to the relevant intervening bonds not being in a W configuration[55,56,57]. This, of course, assumes that any long range coupling observed in ^{19}F spectra will show the same stereospecificity as is observed in ^{1}H spectra. However, coupling between the bridgehead anti fluorine and the exo fluorine is probable, such a coupling being enhanced by a 'through space' mechanism[58]. It has been estimated[59] that through space coupling for fluorine may occur for internuclear distances of up to 2.72Å. A calculation for fluorobicyclo(2,2,1)-heptenes, based on the co-ordinate system proposed by Wilcox[60] for the bicyclo(2,2,1)heptane skeleton, indicates that the 7 anti and the exo nuclei are separated by c.a. 2.73Å and these two nuclei are separated by more than three bonds[61], indicating that a 'through space' mechanism for coupling might be feasible.

The ^{19}F spectrum of perfluoro endo-2,3-cyclopentano-bicyclo-221-heptane has been observed, and the absorption due to the fluoromethine nuclei at the junction of the cycloheptane and cyclopentane rings may be readily assigned. It appears as a prominent doublet (coupling c.a. 30 $c.sec.^{-1}$) which may be compared with the doublet splitting of c.a. 20 $c.sec.^{-1}$ observed for either the exo or endo nuclei in the fluorobicyclo(2,2,1)heptenes. This suggests that as the less shielded of the bands due to the exo and endo fluorines in the fluorobicyclo(2,2,1)heptenes show this doublet splitting, the exo fluorine nuclei are less shielded than the endo, which is consistent with the argument above, based on the coupling with the bridge fluorines.

Electric field calculations (chapter 8) suggest that in 1;4-dihydro-octafluorobicyclo(2,2,1)heptene, the endo fluorine nuclei are more shielded than the exo, which is in accord with the empirical assignment for this compound, including the assignment based on the relative chemical shifts of the bridgehead anti and the exo fluorines. Since the coupling patterns observed in the spectra from the series of fluorobicyclo(2,2,1)heptenes examined, indicates that the relative exo-endo shift has the same sign throughout, it is suggested that in this series of compounds, the endo fluorines are more shielded than the exo, which is opposite to the assignment proposed for the series of fluorobicyclo(2,2,1)-heptanes (section 4:5)

4:8 Geminal CF_2 Coupling Constants

The resonances due to the exo and endo fluorine nuclei in the fluorobicyclo(2,2,1)heptanes, and in most of the fluorobicyclo(2,2,1) heptenes appear as AB type spectra as do the bridge fluorines in the latter compounds. The observed AB type spectra have been analysed as simple ABs to give reasonable estimates for the CF_2 geminal coupling constants and it is constructive to compare the values obtained with those observed for other cyclic fluorinated molecules.

Correlations have been proposed between geminal proton coupling constants and the H-C-H bond angle[62], and in the case of cyclic fluorine molecules, it appears that a correlation exists between the internal ring C_1-C_2-C_3 bond angle and the geminal CF_2 coupling constant for the fluorines bonded to C_2. The internal ring angles for fluorinated cyclohexanes, cyclopentanes, cyclobutanes and cyclopropanes are given in table 4:5 together with average values for the geminal CF_2 coupling constants observed for such molecules. There is necessarily some inaccuracy in the values quoted as the precise geometries are not known for these compounds and average coupling constants are listed for related molecules containing only small substituents other than fluorine, e.g. hydrogen which is unlikely to cause appreciable distortion of the molecules. The values in table 4:5 are plotted as the open circles of figure 4:6 from which it is seen that there is a definite trend towards larger geminal coupling constants with increase in the internal ring angle of the carbon skeleton. The

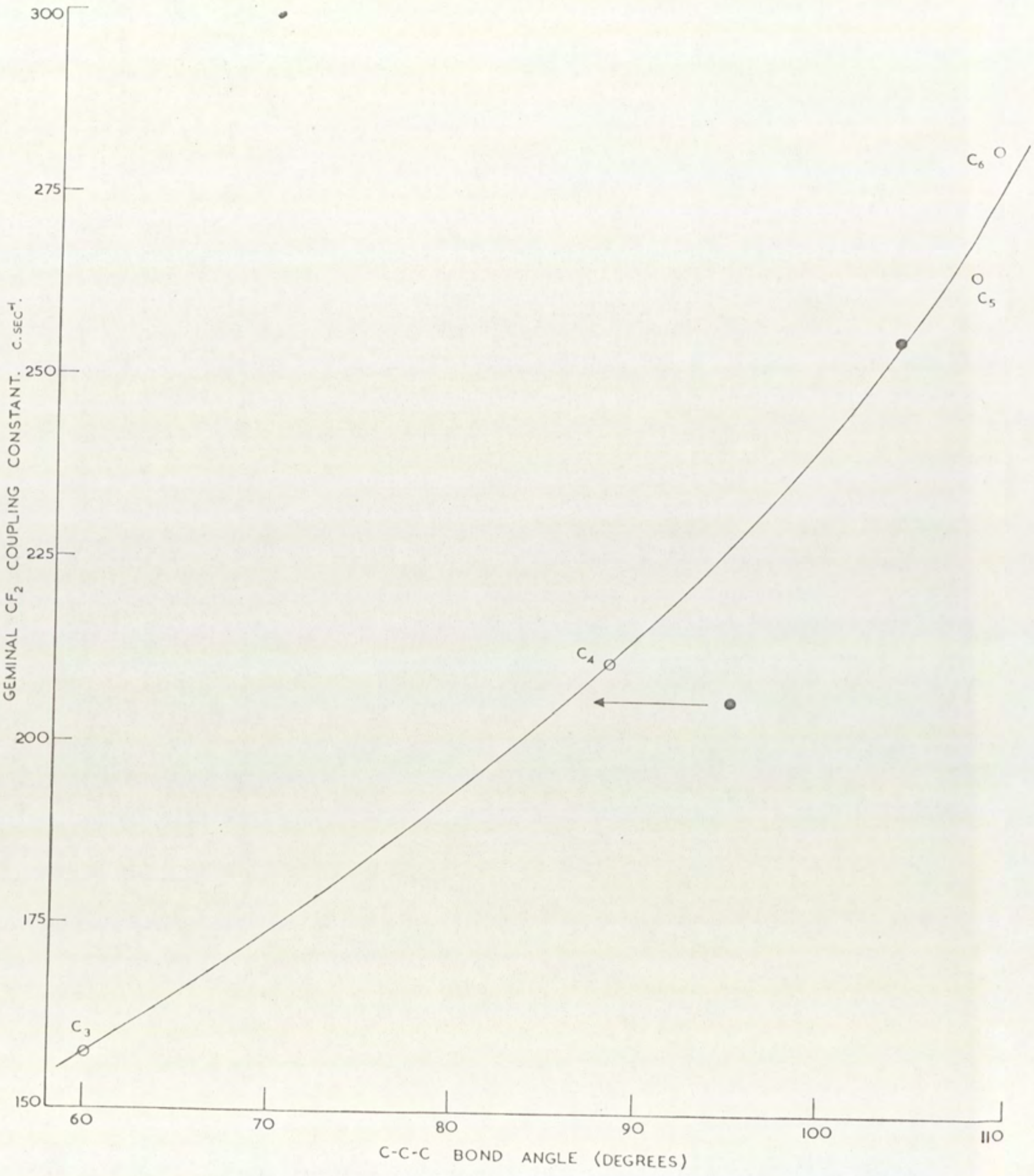


FIGURE 4.6 The correlation between C-C-C internal ring angle and CF_2 geminal coupling constant in saturated cyclic fluorocarbons.

Compound	Approximate ring angle (degrees)	Average J_{gem} coupling (c.sec.$^{-1}$)
fluorocyclohexanes	109.5	285 [63]
fluorocyclopentanes	108	265 [64]
fluorocyclobutanes	88.5*	211 [65]
fluorocyclopropanes	60	158 [65]

Table 4:5 . The approximate internal C-C-C ring angles and geminal coupling constants for some fluorinated cyclic molecules.

*Evaluated from data given in reference 66.

internal ring angle at carbons 2, 3, 5 and 6 in bicyclo(2,2,1)-heptane has been calculated by Wilcox[60] as c.a.104°. It is seen that the full circle in figure 4:6 that represents the plot of this value against 256 c.sec.$^{-1}$ for the corresponding coupling constant observed in perfluorobicyclo(2,2,1)heptane, falls almost on the line rationalizing the other data, and to some extent justifies the use of the co-ordinate system for further calculations involving fluorobicyclo(2,2,1)heptanes.

The average value of 206 c.sec.$^{-1}$ for bridge geminal CF_2 coupling constants observed in the fluorobicyclo(2,2,1)heptenes having only small bridgehead substituents, when plotted against the angle 95° proposed for the internal bridge angle in bicyclo-(2,2,1)heptane, does not lie on the line in figure 4:6. It is evident that for this full circle to fall on the line, the internal angle at the bridge in the bicyclo(2,2,1)heptenes must be smaller than in the corresponding bicyclo(2,2,1)heptanes. This should be reflected in a smaller angle at carbons 5 and 6 in the unsaturated molecules, and the appropriate coupling constants which are consistent with this suggestion indicate that the angle at carbons 5 and 6 in the fluorobicyclo(2,2,1)heptene ring is c.a. 95^{o}.

Substitution at the bridgehead in the unsaturated compounds by the relatively large bromine and iodine atoms results in significant variations in the magnitude of the geminal coupling constants compared with those found in the molecules having only fluorine or hydrogen at the bridgehead, suggesting that the larger substituents cause distortion of the carbon skeleton.

4:9 Proton Magnetic Resonance Spectra of the Fluorobicyclo(2,2,1)-heptanes and Heptenes with Hydrogen at the Bridgehead Carbons

The proton spectra of those compounds having hydrogen at the bridgehead position are all rather broad unresolved lines (half-height width 9-18 c.sec.$^{-1}$) and since with the exception of the proton spectrum of 1H-undecafluorobicyclo(2,2,1)heptane, no use is made in this work of the proton chemical shifts, they have been measured only approximately using the pre-calibrated chart recorder of the Perkin Elmer R10 Spectrometer. The chemical shift of the proton in 1H-undecafluorobicyclo(2,2,1)heptane was measured relative to internal T.M.S. using the normal audio sideband technique. The chemical shifts are given in table 4: 6.

Derivative of perfluorobicyclo(2,2,1)heptane	τ value
1H-	6.45
1;4diH-	6.38
1Br;4H-	6.17
Derivative of perfluorobicyclo(2,2,1)heptene	
1H-	6.20
1;4diH-	6.48
1H;4I-	6;65
1H;4Me	6.37 (H) 8.47 (Me)

Table 4:6 The approximate τ values for those fluorinated bicyclo(2,2,1)heptanes and heptenes containing hydrogen substituents.

CHAPTER 5

The Anisotropy in the Magnetic Susceptibility of C-C and C-H Bonds

5:1 Introduction

An empirical assignment of the spectra of some fluorobicyclo-(2,2,1)heptanes has been discussed in Chapter 4; however, some quantitative justification is required for the general assignments and in particular the relative exo-endo shift. To this end, semi-empirical methods for calculating both ^{19}F and ^{1}H shifts form the basis of the work discussed in subsequent chapters.

Whilst fluorine shifts are generally explained by the σ_{para} term[41,67,68] of equation 3:4 it was considered necessary to first consider what contribution to the fluorine shifts may be experienced from other screening mechanisms. The term σ_{dia} of equation 3:4 may be considered constant for ^{19}F nuclei, as this term is at most only of the order of 1% of the σ_{para} term for fluorine[41] and σ_{del} may be neglected for the compounds studied here as they are all saturated. This latter assumption may not be completely justified, but in the absence of direct evidence to the contrary, and from the apparent success achieved by other authors in making this assumption[66,69,70], it will be adopted here. Solvent effects will be neglected throughout these considerations and this leaves only the σ_{mag} term of equation 3:4 in addition to σ_{para} to be investigated.

The use of cyclic molecules in the investigation of σ_{mag} has produced some interesting conclusions on the values obtained for the anisotropy in the magnetic susceptibility of C-X bonds. Studies of C-C and C-H bonds in saturated hydrocarbons will be considered first in this chapter and in chapter 6 the methods employed will be extended to a study of C-F and C-Cl bonds.

5:2 Summary of Relevant Published Work on C-C and C-H Bond Magnetic Anisotropies

Interest has recently been shown in the estimation of values for the anisotropy in the magnetic susceptibility of C-C and C-H bonds from n.m.r. chemical shifts[66,69,80]. It has been assumed[69] that the total intramolecular screening constant for a particular proton in a saturated hydrocarbon can be simplified from equation 3:4 to

$$\sigma = \sigma_L + \sigma_d \qquad 5:1$$

where σ_L represents the local screening due to the electron cloud surrounding the nucleus and σ_d the screening arising from distant polarisable magnetically anisotropic bonds. For considerations of proton screenings in saturated molecules, where electric field gradients should not appreciably distort the essentially symmetrical S electron distribution about the nucleus, the term σ_L may be considered constant and differences in screenings explained in terms of σ_d. McConnell[17] has formulated an expression for σ_d in terms of the anisotropy in the magnetic susceptibility of all i neighbouring bonds, when these are axially symmetric and this is given as

$$\sigma_d = \sum_i \frac{\Delta\chi_i(1 - 3\cos^2\theta_i)}{3R_i^{\,3}} \qquad 5:2$$

This expression is based on the assumption that the electron group is sufficiently distant that the moment induced therein by the applied field may be represented with sufficient accuracy by a point dipole, and the secondary field produced at the shielded nucleus may be calculated on that basis. Equation 5:2 is generally considered valid when R, the distance between the induced magnetic dipole of bond i, and the nucleus in question, is greater than c.a.3Å. In equation 3:2 θ_i is the angle between the direction of R_i and the axis of bond i, and $\Delta\chi_i$ is the magnetic anisotropy of the bond i containing the induced magnetic dipole. For the case of a bond having axial symmetry, $\Delta\chi_i$ is given by

$$\Delta\chi_i = \chi_i^{\parallel} - \chi_i^{\perp} \qquad 5:3$$

where $\chi_i^{\parallel}$ and $\chi_i^{\perp}$ are respectively the longitudinal and transverse susceptibilities of the bond.

If the assumption[69] that $\Delta\sigma_L$ (equation 5:1) is zero for protons having similar chemical environments is justified, then it is possible in principle to evaluate bond anisotropies by equating differences in observed proton shifts to the corresponding differences between the terms representing the right hand side of equation 5:2. Using methods similar to this, Moritz and Sheppard[69] obtained the value 4.6×10^{-6} $cm^3 mole^{-1}$ for $\Delta\chi^{CC}$ and suggested that $\Delta\chi^{CH}$ is negligible. Similarly, Bothner-By and Naar-Colin deduced the values $\Delta\chi^{CC} = 3.3 \times 10^{-6}$ $cm^3 mole^{-1}$ and $\Delta\chi^{CH}$ to be zero from the shift difference between the methylene protons in cyclohexane and cyclopentane. Musher[73], investigating the resonances from tertiary hydrogens in carbocyclic molecules, found a value for $\Delta\chi^{CC}$ of 5.0×10^{-6} $cm^3 mole^{-1}$. However, in obtaining this value, the possible magnetic anisotropy shielding contributions of the substituents in these molecules were not considered. Musher also indicates that using the C-C bond magnetic anisotropy to rationalize the chemical shifts in ten bicycloheptanols[74] would require a value of $\Delta\chi^{CC} = 15 \times 10^{-6}$ $cm^3 mole^{-1}$ which is an absurdly high value, since any value of $\Delta\chi^{CC} > 4.5 \times 10^{-6}$ cm^{3}mole^{-1} would require the C-C bond to be paramagnetic in the longitudinal direction[81], since its mean susceptibility is 3.0×10^{-6} cm^{3}mole^{-1}.

Neglecting the contributions from C-H bonds, which were considered negligible in propane, Narasimhan and Rogers[80] deduced $\Delta\chi^{CC} = 4.1 \times 10^{-6}$ cm^{3}mole^{-1} and Hall[82] applying the bond magnetic anisotropy model to carbohydrates evaluated $\Delta\chi^{CC}$ as 3.9×10^{-6} cm^3-mole^{-1}. All the values quoted so far for $\Delta\chi^{CC}$ have been derived from calculations which have neglected any effects from C-H bond magnetic anisotropy and fall within a fairly narrow range of $3.3 - 5.0 \times 10^{-6}$ cm^{3}mole^{-1}.

From a consideration of Lonsdale's data[83] on molecular diamagnetic susceptibilities, together with the data of Moritz and Sheppard[69], Pople[84] has suggested that values of $\Delta\chi^{CC} = 11.0 \times 10^{-6}$ and $\Delta\chi^{CH} = 6.8 \times 10^{-6}$ cm^{3}mole^{-1} would be required to satisfy both sets of results. This value for $\Delta\chi^{CC}$ agrees quite well with the value $\Delta\chi^{CC} = 10.0 \times 10^{-6}$ cm^{3}mole^{-1} obtained by Reddy and Goldstein[72] from ^{13}C-H coupling constants. It is evident that there is little consistency between the values derived by various workers for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ using different molecular types and different approaches for their investigations. Furthermore, two theoretical estimates for $\Delta\chi^{CC}$ are both considerably smaller than the values obtained from n.m.r. measurements. The general theory of diamagnetic susceptibilities was first developed by Van Vleck[38] and later extended by Ramsey[36, 37] for a general formula for the shielding of a nucleus. These two formulae have been little used in detailed calculations on susceptibilities, primarily because of the difficulty of including contributions of all excited states, particularly those in the continuum. An alternative method, avoiding these difficulties, is a variational technique of the type first proposed by Tillieu and Guy[85, 86]. Using this method, they obtained an estimate for $\Delta\chi^{CC}$ of 1.21×10^{-6} cm^{3}mole^{-1}. Less rigorously, Zurcher[75] has calculated $\Delta\chi^{CC} = 1.04 \times 10^{-6}$ cm^{3}mole^{-1}.

In most of the evaluations of $\Delta\chi^{CC}$ (and where appropriate $\Delta\chi^{CH}$) referred to above, equation 5:2 has been employed, although some of the distances R_i involved were less than 3Å. Recently, in order to account more precisely for the effects of bonds closer than 3Å from the nucleus whose shielding is considered and thereby refine estimates for $\Delta\chi$ obtained from n.m.r. measurements, the expression formulated by McConnell[46] which is the basis of equation 5:2 has been modified to

$$\sigma = \frac{\Delta\chi}{3R^3}(1 - 3\cos^2\Theta) + \frac{S^2}{R^5}\left[\frac{-(\chi^{\parallel} - \chi^{\perp})}{2} + 5(\chi^{\parallel}\cos^2\Theta + \chi^{\perp}\sin^2\Theta) - \frac{35}{6}(\chi^{\parallel}\cos^4\Theta + \chi^{\perp}\sin^4\Theta)\right] \qquad 5{:}4$$

In this expression, the induced dipole is considered to have a finite length of 2S. Using equation 5:4 ApSimon et.al[77, 78] have derived values for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ that are apparently consistent with data obtained from both n.m.r. and magnetic birefringence measurements. The latter technique based on the theory of the Cotton Mouton effect[87] shows that the birefringence induced by a magnetic field perpendicular to a beam of light depends on χ and α, the electric polarisability tensor. A limited amount of data for α exists, but the application of this technique has been hindered by the unavailability of reliable values for this parameter. However, using the birefringence technique, Buckingham et.al[88] have recently proposed that the molecular magnetic anisotropy of ethane is -4.9×10^{-6} cm^{3}mole^{-1} and have subsequently revised this value[89] to -2.3×10^{-6} cm^{3}mole^{-1}; these authors have also commented that their technique for evaluating electric polarisabilities is less accurate than they had originally thought[89]. ApSimon et.al[77,78] assuming that bond susceptibility components are additive, have related the molecular anisotrupy of ethane to individual contributions from the C-C and C-H bonds by the equation

$$\Delta\chi^{CC} - 2\,\Delta\chi^{CH} = -4.9 \times 10^{-6} \qquad 5{:}5$$

which is a specific form of the general expression derived by Davies[79]. Zurcher[76] has proposed equation 5:6 to account for the axial-equatorial shift observed in cyclohexane (at low temperature) assuming that the observed shift may be explained wholly in terms of bond magnetic anisotropies.

$$0.114\,\Delta\chi^{CC} - 0.094\,\Delta\chi^{CH} = 0.46 \times 10^{-6} \qquad 5{:}6$$

Based on equation 5:4, ApSimon set up an expression analogous to 5:6 and using an iterative procedure analysed this, together with equation 5:5, to obtain the best values of 8.4×10^{-6} and 6.63×10^{-6} cm^3.mole^{-1} for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ respectively. It is interesting that the values obtained do not differ appreciably from the corresponding values (10.41×10^{-6} and 7.60×10^{-6} cm^3.mole^{-1}) obtained by straightforward simultaneous solution of equations 5:5 and 5:6 and in view of the spread in values mentioned previously, there appears little to be gained at this stage by using equation 5:4 to determine bond magnetic anisotropies. Nevertheless, the magnetic anisotropies obtained in this way are similar to the rationalised values suggested by Pople[84] and the value for $\Delta\chi^{CC}$ is in reasonable agreement with that based on ^{13}C-H coupling constants. They should, therefore, be capable of use in predicting differences in proton shifts in a range of saturated hydrocarbons and predicting appropriate contributions to ^{19}F shifts.

5:3 Preliminary Investigations of the Interpretation of Proton Chemical Shifts in Terms of Bond Magnetic Anisotropies.

The ^{19}F spectra of a series of fluoro compounds based on the bicyclo(2,2,1)heptane skeleton, have been observed (chapter 4) and it would appear that analogous hydrogenated compounds, in particular bicyclo(2,2,1)heptane itself, could be used in an investigation of the correlation of proton shifts with bond magnetic anisotropies. The proton spectrum of bicyclo(2,2,1)heptane has been observed[53] at 60 Mc.sec.$^{-1}$ and an assignment of the various absorptions made. Equation 5:4 has now been used in an attempt to calculate the relative shieldings of the four distinct types of proton in bicyclo(2,2,1)heptane, using the values proposed by ApSimon et. al.[77] for $\Delta\chi^{CC}$, $\Delta\chi^{CH}$, $\chi_{\parallel}^{CC}$, $\chi_{\perp}^{CC}$, $\chi_{\parallel}^{CH}$, $\chi_{\perp}^{CH}$, and S. The evaluation of the R and θ terms required for equation 5:4 is straightforward using the co-ordinates of all the atoms in bicyclo(2,2,1)heptane given in reference 60. The method of evaluation is similar to the first portion of the method given for the calculation of intramolecular electric field parameters which is discussed in section 7:2. The induced point dipoles due to $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ are assumed to act from the mid-point of the C-C bonds and 0.77Å from the carbon atom in the C-H bonds respectively, this latter value representing the electrical centre of gravity of the C-H bond. The total contributions to the shielding of the different protons in bicyclo(2,2,1)heptane arising from the anisotropy in all of the C-C and C-H bonds, except the effectively common C-H bond, containing the proton in question, are given in Table 5:1 The observed and calculated proton shifts of bicyclo(2,2,1)heptane expressed relative to the bridge protons are given in table 5:2. The difference between the observed and calculated shifts indicate

Screening contribution / due to	at H(1)	H(7)	H(exo)	H(endo)
C-C bonds	-3.499	-2.217	-2.543	-2.220
C-H bonds	+0.340	-0.698	-0.533	-0.715
C-C+C-H bonds	-3.159	-2.915	-3.076	-2.935

Table 5:1 The calculated magnetic anisotropy screening contribution (p.p.m.) to each proton in bicyclo(2,2,1)heptane due to all bonds except the effectively common C-H bond.

	$\delta_{calc.}$	δ_{obs}	$\delta_{obs} - \delta_{calc}$
H(7) - H(1)	+0.244	+0.99	$+0.74_6$
H(7) - H(exo)	+0.161	+0.28	$+0.11_9$
H(7) - H(endo)	+0.020	-0.03	-0.05_0

Table 5:2 Calculated (using equation 5:4 and observed shift (p.p.m.) for bicyclo(2,2,1)heptane.

that the values deduced by ApSimon et.al.[77] cannot in all cases be used to predict relative shifts (e.g. the sign of the shift of H(7) - H(endo) is opposite to that observed) or the magnitudes of those that are predicted with the correct sign.

Although the use of equation 5:4 together with the results of ApSimon et.al. fails to predict the correct sequence of shifts in bicyclo(2,2,1)heptane, it is evident that this molecule may be used as the basis of a method for evaluating $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ from n.m.r. measurements alone. In view of the apparent ambiguity in the results obtained using equation 5:4, there appears little justification in using this in preference to equation 5:2 for exploratory investigations of bond magnetic anisotropies.

The proton resonance spectrum of bicyclo(2,2,1)heptane shows four chemically shifted resonances from the 1, 7, exo and endo hydrogen atoms. The sum of the anisotropic effects of all of the C-C and C-H bonds in the molecule (except the effectively common C-H bond containing the resonant nucleus) on each of the four magnetically different protons, gives four screening contributions each containing $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ and these are given below. The numerical values in these terms are summarised in Table 5:3 and correspond to the coefficients of $\Delta\chi$ in equation 5:2 and were evaluated by the procedure referred to above, which is described in more detail in section 7:2.

H(1) $-2.283 \times 10^{23}\,\Delta\chi^{CC} + 0.427 \times 10^{23}\,\Delta\chi^{CH}$

H(7) $-0.888 \times 10^{23}\,\Delta\chi^{CC} - 0.499 \times 10^{23}\,\Delta\chi^{CH}$

H(exo) $-1.161 \times 10^{23}\,\Delta\chi^{CC} - 0.329 \times 10^{23}\,\Delta\chi^{CH}$

H(endo) $-0.887 \times 10^{23}\,\Delta\chi^{CC} - 0.484 \times 10^{23}\,\Delta\chi^{CH}$

The difference of any two of these expressions, together with the corresponding differences in chemical shifts from table 5:3 gives in all six possible equations representing differences in shielding constants. These equations may be arranged in three different pairs such that each pair is dependent on all four original expressions, as indicated in table 5:4.

$\Delta\chi^{CC}$ And $\Delta\chi^{CH}$ are obtained by simultaneous solution of each of the three pairs of equations. The three values obtained for both $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ would be expected to be similar and ideally the same. The values derived by this procedure together with the combinations of screening terms quoted above, are given in table 5:4.

It is evident that there is appreciable variation in each of the two sets of results in table 5:4 and two of the values in each

Effect	$\sum\left[\frac{1 - 3\cos^2\theta}{3R^3}\right] \times 10^{-23}$		observed
At nucleus	due to C-C bonds	due to C-H bonds	τ value
H_1	-2.283	+0.427	7.80
H_{exo}	-1.161	-0.329	8.51
H_{endo}	-0.887	-0.484	8.82
H_7	-0.880	-0.499	8.79

Table 5:3 Coefficients of $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ evaluated using equation 5:2 , and observed chemical shifts in bicyclo(2,2,1) heptane.

Equations derived for	$\Delta\chi^{CC}$	$\Delta\chi^{CH}$
H(1) - H(7) / H(exo) - H(endo)	+21.49	+25.92
H(1) - H(exo) / H(7) - H(endo)	+11.02	+10.69
H(1) - H(endo) / H(7) - H(exo)	+48.06	+66.91

Table 5:4 Values for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ $(\mathrm{x}10^{6}\ \mathrm{cm}^{3}.\mathrm{mole}^{-1})$ obtained from the proton shifts of bicyclo(2,2,1)heptane using equation 5:2 and considering the C-H induced magnetic dipole to act 0.77Å from the carbon atom in the bond.

set are appreciable larger than the appropriate values previously proposed for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ and it is highly improbable that these values have any real significance, particularly in view of the fact that such values for $\Delta\chi^{CC}$ would require this bond to be paramagnetic in the longitudinal direction. The inconsistent results in table 5:4 indicate that there is some basic error in the assumptions adopted in the present approach to evaluating proton screenings in terms of bond magnetic anisotropies.

C-C	H_1		H_{exo}		H_{endo}		H_7	
bond	R	Cos Θ	R	Cos Θ	R	Cos Θ	R	Cos Θ
1-2	1.586	0.786	2.743	0.778	1.539	0.749	1.539	0.748
2-3	2.784	0.774	3.288	0.000	1.538	0.748	1.538	0.748
3-4	3.279	0.062	2.743	0.778	2.602	0.657	2.602	0.656
4-5	3.279	0.062	2.310	0.309	3.459	0.481	3.070	0.006
5-6	2.784	0.774	2.537	0.000	3.572	0.322	2.771	0.415
6-1	1.585	0.786	2.310	0.309	2.750	0.808	2.241	0.257
1-7	1.586	0.785	1.555	0.761	2.402	0.440	2.697	0.755
7-4	2.727	0.716	1.555	0.761	2.898	0.225	3.147	0.104

Table 5:5

Distances and angles required for equation 5:2 to evaluate the coefficient of $\Delta\chi$ for the effect of C-C bonds in bicyclo(2,2,1)heptane.

	H_1		H_{exo}		H_{endo}		H_7	
Position of origin	R	cos Θ	R	cos Θ	R	cos Θ	R	cos Θ
1			2.363	0.888	2.537	0.579	2.476	0.487
2 exo	2.382	0.328			1.552	0.750	2.620	0.100
2 endo	2.555	0.523	1.552	0.750			3.408	0.982
3 exo	3.829	0.599	2.214	0.214	2.684	0.733	2.620	0.100
3 endo	3.939	0.723	2.684	0.733	2.214	0.214	3.408	0.982
4	4.021	0.915	3.762	0.812	3.874	0.932	2.476	0.487
5 exo	3.829	0.599	4.571	0.894	3.917	0.971	3.692	0.485
5 endo	3.939	0.723	4.108	0.360	3.135	0.072	3.963	0.792
6 exo	2.382	0.328	4.013	0.817	3.247	0.924	3.692	0.485
6 endo	2.555	0.523	3.476	0.193	2.243	-0.259	3.963	0.792
7L	2.488	0.450	3.549	0.944	3.948	0.842		
7R	2.488	0.450	2.675	-0.066	3.581	0.427	1.552	0.750

Table 5:6

Distances and angles required for equation 5:2 to evaluate the coefficient of $\Delta\chi$ for the effect of C-H bonds in bicyclo-(2,2,1)heptane, assuming dipole to originate 0.77Å along the C-H bond from the carbon atom.

5:4 The Values of $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ and the locations of equivalent dipoles required to interpret proton shifts in saturated hydrocarbons.

In previous and in the present evaluations which account for $\Delta\chi^{CH}$, it has been assumed that the point dipole resulting from the anisotropy in the magnetic susceptibility of the C-H bond is situated at a point 0.77Å from the carbon atom along the C-H bond. If this induced point dipole is considered to act at some other position in the bond, then it is possible that the three simultaneous solutions for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ obtained by the method outlined above could be the same. To investigate this possibility, the procedure detailed at the end of section 5:3 was repeated, but the induced point dipole in the C-H bond has been considered to act at various positions along the C-H bond, with the C-C bond point dipole always being assumed to act from the mid-point of the C-C bond. The calculations involved are numerous and were performed on a P.D.S. 1020 computer. For each point of action chosen for the C-H induced dipole, three solutions each were obtained for both $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ and the values are collected in table 5:7. Figure 5:1 illustrates the variation in the values obtained for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ as a function of the point of action of the C-H bond induced dipole. It is clear that there are two possible points at which the solutions become co-incident. These are at a position on the carbon atom and at a point 0.73Å along the C-H bond from the carbon atom. The corresponding values derived for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ respectively are $+4.3 \times 10^{-6}$ and -1.2×10^{-6} $cm^3 . mole^{-1}$ on the carbon atom and $+35.6 \times 10^{-6}$ and 47.0×10^{-6} $cm^3 . mole^{-1}$ at 0.73Å from the carbon atom. The two values in the second of these two pairs of results are surprisingly large, although the corresponding distance along the C-H bond from which the point dipole can be considered to act, compares very favourably with that expected (0.77Å).

There are two convenient methods of assessing the significance of these two sets of results. First, each set may be used to calculate the axial-equatorial shift for cyclohexane using an appropriate expression similar to equation 5:6. Secondly, the values

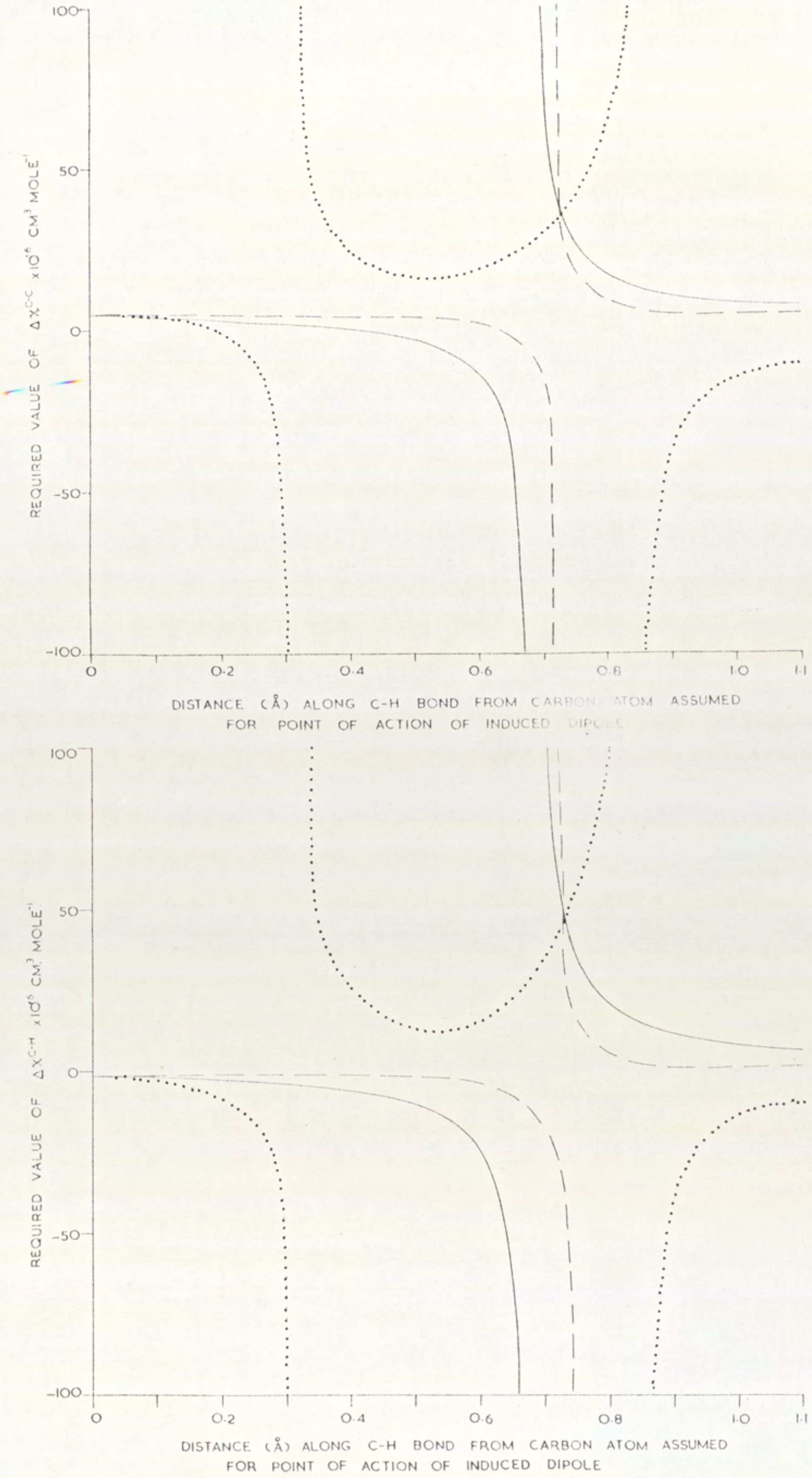


FIGURE 5.1 The dependence of $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ on the location assumed for the point of action of the C-H bond magnetic dipole. The curves are identified: ——— H(1)-H(7)/H(exo)-H(endo) – – – H(1)-H(exo)/H(7)-H(endo) ····· H(1)-H(endo)/H(7)-H(exo)

Table 5:7 Required values for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ with C-H bond induced dipole considered to act from various positions in the bond. (Values of $\Delta\chi \times 10^{6}$ cm.^{3}mole^{-1})

Distance (Å) along C-H bond	Solutions for $\Delta\chi$ from different combinations of shifts					
	(1-7) /(Exo-Endo)		(1-Exo) /(7-Endo)		(1-Endo) /(7-Exo)	
	$\Delta\chi^{CC}$	$\Delta\chi^{CH}$	$\Delta\chi^{CC}$	$\Delta\chi^{CH}$	$\Delta\chi^{CC}$	$\Delta\chi^{CH}$
0.025	+4.46	-1.70	+4.20	-1.13	+4.40	-2.14
0.05	+4.38	-1.70	+4.04	-0.90	+4.19	-2.73
0.10	+4.13	-1.74	+3.87	-0.79	+3.54	-3.56
0.20	+3.34	-2.64	+3.53	-1.05	-0.92	-7.35
0.30	+2.16	-3.89	+3.20	-1.20	-61.33	-101.34
0.35	+1.37	-4.72	+3.01	-1.33	+44.57	+56.57
0.40	+0.39	-5.84	+2.83	-1.48	+21.45	+22.70
0.45	-0.96	-7.46	+2.60	-1.71	+17.61	+17.05
0.50	-2.99	-10.09	+2.31	-2.05	+16.13	+15.02
0.55	-6.41	-14.63	+1.75	-2.78	+18.24	+17.84
0.60	-13.04	-23.91	+1.29	-3.39	+15.89	+15.08
0.66	-66.44	-99.08	-1.60	-7.43	+21.41	+23.27
0.70	+84.48	+115.41	-8.29	-16.96	+23.03	+26.74
0.73	+35.88	+45.83	+35.28	+47.34	+36.18	+44.92
0.77	+21.49	+25.91	+11.01	+10.69	+48.06	+66.91
0.85	+13.12	+14.38	+6.31	+4.03	-78.70	-142.35
0.93	+9.99	+10.13	+5.14	+2.37	-8.41	-25.09
1.00	+8.51	+8.19	+4.69	+1.73	-1.79	-13.91
1.10	+7.24	+6.57	+4.40	+1.33	+1.03	-9.53

can be used to predict the molecular magnetic anisotropy of ethane.

The situation in which the C-H bond dipole is considered to act 0.73Å from the carbon atom will be appraised first. For this case, the axial-equatorial proton shift in cyclohexane is given in terms of the anisotropy in the magnetic susceptibility of the C-C and C-H bonds by

$$0.1025\,\Delta\chi^{CC} - 0.0911\,\Delta\chi^{CH} = \delta_{a-e} \qquad 5{:}7$$

This expression was derived using the co-ordinate system proposed recently for cyclohexane[90] and which accounts for the bond angles being not strictly tetrahedral. Substituting the values $\Delta\chi^{CC} = 35.6 \times 10^{-6}$ $cm^3.mole^{-1}$ and $\Delta\chi^{CH} = 47.0 \times 10^{-6}$ $cm^3.mole^{-1}$ into equation 5:7, gives $\delta_{a-e} = -2.51$ p.p.m. which is inconsistent with the required value of +0.46 p.p.m. Substitution for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ in the left hand side of equation 5:5 provides a value of -58.4×10^{-6} $cm^3.mole^{-1}$ for the molecular magnetic anisotropy of ethane which differs considerably from the value of -4.9×10^{-6} $cm^3.mole^{-1}$ obtained by Buckingham et.al[88] (this value has subsequently been refined[89] to -2.3×10^{-6} $cm^3.mole^{-1}$).

The alternative values of $+4.3 \times 10^{-6}$ and -1.2×10^{-6} cm^3 $mole^{-1}$ for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ respectively will now be considered. The theoretical arguments against having $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ of opposite sign will be neglected for the purpose of the present argument and some justification for this will be given later. Re-evaluation of the expression relating the axial-equatorial shift to the C-C and C-H bond magnetic anisotropies in cyclohexane with the C-H bond dipole acting from the carbon atom, gives

$$0.1025\,\Delta\chi^{CC} - 0.1890\,\Delta\chi^{CH} = \delta_{a-e} \qquad 5{:}8$$

Substitution of the values $\Delta\chi^{CC} = 4.3 \times 10^{-6} cm^3.mole^{-1}$ and $\Delta\chi^{CH}$

$= -1.2 \times 10^{-6}$ cm.^{3}mole^{-1} into equation 5:8 gives $\delta_{a-e} = +0.78$ p.p.m. which, whilst not in absolute agreement with the experimental value of +0.46 p.p.m., is of the correct order of magnitude. The values for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ when substituted into equation 5:5 give a value for the molecular magnetic anisotropy of ethane of $+6.7 \times 10^{-6}$ cm.^{3}mole^{-1}, which is incompatible with the observations of Buckingham e.al.[88, 89].

It is evident that of the various values that have been suggested for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ there are none that enable extensive prediction of proton shifts and at the same time are compatible with the results of magnetic birefringence measurements. There are three immediately obvious reasons for this incompatibility of data from the two techniques, which are:-

(i) The σ_d contribution to proton shifts in equation 5:1 should not be interpreted in terms of the anisotropy in the magnetic susceptibility of neighbouring bonds or

(ii) there is some other contribution to σ_d in addition to that due to bond magnetic anisotropy which is fortuitously accommodated by equation 5:2 so that only apparent values are obtained for $\Delta\chi$, these values having no real physical significance or

(iii) there is some fallacy in the method for comparing the results of magnetic birefringence and n.m.r. measurements. Suggestion (i) seems unlikely in view of the theoretical arguments which advocate the interpretation of proton shifts in terms of bond magnetic anisotropy and in view of the consistent results obtained by such workers as Moritz and Sheppard[69]. It is possible that suggestion (ii) might rationalize the situation, although it is difficult to conceive a plausible additional contribution to proton screenings that possesses magnetic susceptibility characteristics. It is possible that electric field contributions to proton screenings may be fortuitously and approximately included due to the similar angular and R^{-3} dependence of such effects (see section 7:1). Such effects are likely to be small in proton screenings in saturated hydrocarbons due to the difficulty in polarising the inherently symmetrical electron density about the hydrogen nuclei in these compounds. Suggestion (iii) could offer a possible explanation of the incompatibility of n.m.r. and magnetic birefringence results. The fundamental requirement for comparison of the results obtained by the two methods is that bond magnetic susceptibility components may be added vectorially. A suggestion has been made previously by Narisimhan and Rogers[80] that the normal method of summation may be erroneous. If (ii) and/or (iii) above make the present method for comparison of n.m.r. and magnetic birefringence results fallacious, then it is reasonable to obtain apparent values for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ from n.m.r. data alone, which may be used to calculate proton shifts in a wide range of molecular situations.

Of the two sets of values obtained for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ from the proton shifts observed for bicyclo(2,2,1)heptane, the pair of values $\Delta\chi^{CC} = 35.6 \times 10^{-6}$ cm^3.mole^{-1} and $\Delta\chi^{CH} = 47.0 \times 10^{-6}$ cm^3.-mole^{-1} are almost certainly incorrect because they predict an axial equatorial shift in cyclohexane having both the wrong sign and magnitude. The other pair of values do, on the other hand, predict a shift of the correct sign and almost the right magnitude. The negative sign for $\Delta\chi^{CH}$ at first sight causes some concern in that the sign is opposite to that predicted by Tillieu[85]. However, it has been suggested above that the value of $\Delta\chi^{CH} = -1.2 \times 10^{-6}$ cm^3.mole^{-1} need not entirely represent the anisotropy in the magnetic susceptibility of the C-H bond, but may contain shielding contributions from other effects. For this reason, the term 'apparent' will be used to prefix the anisotropies obtained from n.m.r. measurements. It is interesting that Zurcher[75] deduced $\Delta\chi^{CH} = -0.74 \times 10^{-6}$ cm.^{3}mole^{-1} from a least squares treatment of ten sets of data concerned with polarisability and susceptibility properties of both C-C and C-H bonds. Zurcher's negative value for $\Delta\chi^{CH}$ depends on the assumption that the equivalent dipole acts from a point 0.77Å from the carbon atom and does not therefore bear direct comparison with the value for $\Delta\chi^{CH}$ deduced herein. Nevertheless, this author provides extensive evidence that $\Delta\chi^{CH}$ derived from n.m.r. measurements is negative or that, due to inaccuracies in the data used, it is zero. Furthermore, it is shown that these conclusions are unaffected by varying the effective position for the centre of gravity of the electron distribution in the C-H bond. It must also be concluded from the present investigation that either $\Delta\chi^{CH}$ has a small negative value or is zero, in which case the three lines in figure 5:1 representing $\Delta\chi^{CH}$ should intersect at $\Delta\chi^{CH} = 0$ at a position on the carbon atom and the value -1.2×10^{-6} cm.^{3}mole^{-1} actually obtained represents the inaccuracy of the chosen model. To investigate which of the two values, zero and -1.2×10^{-6} cm.^{3}mole^{-1} can be taken to best represent $\Delta\chi^{CH}$, equation 5:8 can be used to calculate the axial-equatorial proton shift in cyclohexane. The shifts predicted are +0.44 and +0.78 p.p.m. respectively and when compared with the observed value of +0.46 p.p.m. it appears that $\Delta\chi^{CH}$ can most reasonably be taken as zero.

5:5 Comparison of Derived Values of $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ with those obtained by other Workers.

The value $\Delta\chi^{CC} = +4.3 \times 10^{-6}$ cm^3.mole^{-1} which results from the present investigation is consistent with the values found by other workers who assumed $\Delta\chi^{CH}$ to be zero. In particular, it is interesting to compare this result with those of Moritz and Sheppard[69], who correlated the C-C bond anisotropy contributions with τ values for a number of hydrocarbons. However, rather than making a direct comparison, these results have been re-interpreted since when considering only C-C bond magnetic anisotropy contributions to proton screening, the coefficients of $\Delta\chi^{CC}$ should be plotted against the appropriate observed shifts for each molecule relative to that of some compound which itself has no contribution from C-C anisotropy shielding and not against τ values. A suitable reference compound is methane.

The coefficients of $\Delta\chi^{CC}$ for the axial and equatorial protons in cyclohexane have been re-evaluated as -8.282×10^{22} and -14.462×10^{22} cm^3.mole^{-1} respectively and these have been replotted together with the remaining values of Moritz and Sheppard against the appropriate shifts expressed relative to methane (τ 9.774)[48]. The relationship is illustrated by the open circles of figure 5:2 where the line represents a least mean squares treatment on all these points, except the origin through which the line would be expected to pass. The fact that the line does not meet the origin is presumably due to the difference between the σ_L terms of equation 5:1 for the protons of methane and for those of molecules containing C-C bonds. If it is assumed that the difference in σ_L for the protons of methane and the hydrocarbons containing C-C bonds is approximately constant, then the

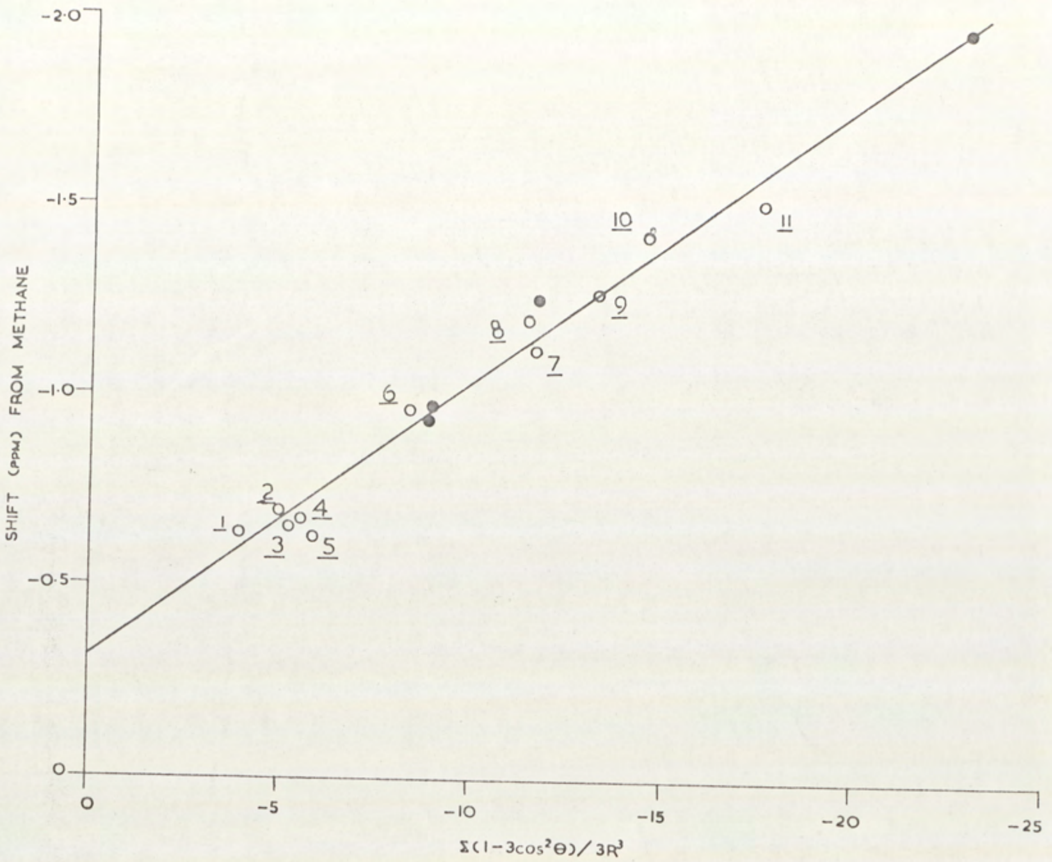


FIGURE 5.2 The coefficients of $\Delta\chi^{CC}$ derived using equation 5:2 versus proton shifts (p.p.m.) relative to methane for various hydrocarbons. The full circles correspond to the parameters for bicyclo-(2,2,1)heptane evaluated herein, and the open circles correspond to those given in reference 69.

Key

1. $(CH_3)_6C_2$ [91]
2. $(CH_3)_4C$ [91]
3. $(C\underline{H}_3)_3CH$ [92]
4. $(C\underline{H}_3)_2CH_2$ [93]
5. CH_3CH_3 [94]
6. C_6H_{12}(axial) [51]
7. $(CH_3)_2C\underline{H}_2$ [93]
8. C_6H_{12}(average) [95]
9. C_5H_{10} [96]
10. C_6H_{12}(equatorial) [51]
11. $(CH_3)_3CH$ [92]

slope of the line in figure 5:2 should reasonably represent $\Delta\chi^{CC}$ which is thus found to be 7.263×10^{-30} $cm^3.molecule^{-1}$ or 4.3×10^{-6} $cm^3.mole^{-1}$. The close agreement between this value and that (4.3×10^{-6} $cm^3.mole^{-1}$) obtained earlier from bicyclo-(2,2,1)heptane alone is emphasized by the small deviation of the full circles, which represent the four points for bicyclo(2,2,1)-heptane, from the least mean squares line in figure 5:2. The shift deviations from this line for the four points are 0.00, -0.02, -0.11 and 0.00 p.p.m. for the 1, 7, exo and endo hydrogens respectively. Expressed relative to the position 7 proton resonance the shifts corresponding to those in table 5:2 are:

	$\delta_{calc.}$	$\delta_{obs.}$	$\delta_{obs} - \delta_{calc}$
H(7) - H(1)	+1.013	+0.99	-0.02_3
H(7) - H(exo)	+0.198	+0.28	-0.08_2
H(7) - H(endo)	-0.001	-0.03	-0.02_9

It is seen that the deviations between observed and calculated shifts are considerably less than those in table 5:2 which depend on calculated shifts obtained from equation 5:4 using the C-C and C-H bond susceptibilities given by ApSimon et.al.[77]. A least mean squares treatment of all the points in figure 5:2, including those for bicyclo(2,2,1)heptane, enables the apparent value for $\Delta\chi^{CC}$ to be refined to $+4.39 \times 10^{-6}$ $cm^3.mole^{-1}$.

5:6 Conclusions

It is concluded that for the purpose of calculating proton n.m.r. shifts $\Delta\chi^{CC} = 4.39 \times 10^{-6}$ $cm^3.mole^{-1}$ and that the C-H bond can be considered to be magnetically isotropic. In the absence of a rigorous explanation for the incompatibility of these values, with the results of magnetic birefringence measurements, it may be wise at present to refer to the values for $\Delta\chi$ obtained from n.m.r. studies as apparent bond magnetic anisotropies, as it seems likely that the values derived in this manner do not represent the true values of $\Delta\chi$ for the bonds considered. Nevertheless, it is evident that relative shifts for protons with similar local screening in saturated hydrocarbons can be calculated quite adequately using equation 5:2 in terms of the secondary fields at the protons in question which arise from the apparent anisotropy in the magnetic susceptibility of all of the C-C bonds in the molecules.

This model accounts very well for the observed shifts in bicyclo(2,2,1)heptane. Hence, the contribution from C-C bond apparent magnetic anisotropy to the total screening of the fluorine nuclei in fluorobicyclo(2,2,1)heptane molecules should not account for shielding contributions much larger than in the hydrogen substituted molecule. These are insignificant when compared with the large differences in screening observed for the fluorinated molecules.

CHAPTER 6

The Apparent Anisotropy in the Magnetic Susceptibility of C-F and C-Cl Bonds

6:1 Introduction

In Chapter 5, proton screenings in a range of saturated hydrocarbons were explained in terms of an intramolecular screening effect, the origin of which has been attributed to the so-called 'apparent' magnetic anisotropy in the neighbouring bonds. The screening effect of this quantity is dependent upon the same intramolecular parameters as the previously accepted magnetic anisotropy induced in bonds by magnetic fields. The concept will now be further developed to investigate whether similar apparent anisotropies in magnetic susceptibilities may be deduced for C-F and C-Cl bonds, that may be used to interpret the observed proton shifts in saturated molecules containing only fluorine or chlorine substituents.

6:2 Chemical Shift Values Used in the Investigation

Whilst the chemical shifts for ten of the compounds used in this investigation have been previously reported two of these have been re-examined and refined values used in the calculations; the proton spectrum of 1H-undecafluorobicyclo(2,2,1)heptane has been reported earlier in this investigation (section 4:9) All of the τ values used in this investigation are collected in Table 6:1.

The shift of the axial protons in β-1,2,3,4,5,6,hexachlorocyclohexane has been previously measured relative to dioxan and a value[99] of 5.79τ obtained. For this investigation, the shift has

Compound	τ Value
Methane	9.774[48]
Fluoroform	3.76 [97]
Chloroform	2.75
Cyclohexane (Time average)	8.564[95]
Cyclohexane (H axial)	8.80 [51]
1H-undecafluorocyclohexane	4.96 [64]
Cyclohexyl chloride	6.04 [98]
β-1,2,3,4,5,6,hexachlorocyclohexane	5.81
-1,2,3,4,5,6,hexachlorocyclohexane (H equatorial)	5.12
Bicyclo(2,2,1)heptane ($H_{1,4}$)	7.80 [53]
1H-undecafluorobicyclo(2,2,1)heptane	6.52

Table 6:1 The ^{1}H Chemical shifts used in the investigation

been remeasured in dioxan relative to internal tetramethyl silane, using the normal audio sideband method of calibration. The shift observed was 5.8τ. The 40 Mc.sec.$^{-1}$ proton spectrum of δ-1,2,3,4,5,6,hexachlorocyclohexane has been previously reported to consist of broad singlets at -1.2 p.p.m. (equatorial) and -0.69 p.p.m. (axial) relative to dioxan. This spectrum has been re-examined at 60 Mc.sec.$^{-1}$ using dioxan as solvent and is observed to be considerably more complex than previously reported, showing second-order pseudo-triplet splittings on each resonance band. It is noteworthy that this spectrum is less second-order in chloroform, but no direct use could be made of this observation because insufficient of the β isomer could be dissolved in chloroform to obtain a spectrum for comparison. However, some use was made of the spectrum of the δ isomer in chloroform in that it facilitated an assessment of the equatorial proton shift in dioxan as τ 5.12 ± 0.02, which is slightly different from the previously reported value of τ 5.23.

6:3 The 'Apparent' Anisotropy in the Magnetic Susceptibility of the C-F Bond

The general procedure adopted to estimate the 'apparent' $\Delta\chi^{CF}$ and the effective point of action of the C-F bond dipole is governed by the assumption that electronegativity and electric field effects can be accounted for in the apparent magnetic anisotropy of the bond. Whether this is true for bonds such as C-F and C-Cl is difficult to ascertain, primarily because of the lack of information concerning the magnitude of screening contributions arising from electronegativity effects. However, it has been often assumed that the most significant electric field contribution to nuclear screening results from mean square electric fields due to fluctuating dipoles in a molecule[49,66,70,100,101], and is given by

$$\sigma_E = -B\sum_i \left[\frac{3P_i I_i}{r_{ij}^6}\right] \qquad 6:1$$

where P_i and I_i are respectively the polarisability and first ionisation potential of the contributing bond, r_{ij} corresponds to R_{ij} in equation 5:2 and B is a constant to which an approximate value of $+1.0 \times 10^{-18}$ e.s.u. can be assigned when proton screenings are considered[45]. Using equation 6:1 with the appropriate data recorded in table 7:5 it can be seen that σ_E for a proton due to similarly disposed C-H and C-F bonds will be of the same order of magnitude, whereas that due to a comparable C-Cl bond ($P = 2.60 \times 10^{-24}$ cm.^{3} and $I = 20.8 \times 10^{-12}$ erg) should be very slightly larger because of the higher bond polarisability. In view of this similarity, particularly in the C-H and C-F cases, and the success achieved in calculating proton shifts in terms of the apparent C-C bond magnetic anisotropy, it appears justifiable at this stage to adopt a similar approach to C-F and C-Cl bonds as was used for C-C and C-H bonds.

The procedure for investigating $\Delta\chi^{CF}$ is to compare proton shifts in several pairs of molecules which are selected such that in each pair the molecules have the same basic carbon skeleton but differ in the number of substituent fluorine atoms. One molecule of each pair is fully hydrogenated and the other fully fluorinated with the exception of one hydrogen whose shift is measured. It was concluded earlier that $\Delta\chi^{CH}$ may best be taken to be zero and since the carbon skeleton is the same in each case, the differences in shift between the fluorinated and hydrogenated molecules may be attributed entirely to $\Delta\chi^{CF}$ apparent. Various points along the C-F bond have been chosen to represent the point of action of the induced dipole. These, as distances from the carbon atom are then plotted against the values for $\Delta\chi^{CF}$ that are required by the appropriate co-efficients in equation 5:2 to account for the chosen proton shift differences. If there is a point of mutual intersection of the curves, this provides values for the 'apparent' $\Delta\chi^{CF}$ and for the effective position of the induced point dipole in the C-F bond.

Such a study is restricted by the number of pairs of molecules that are readily available for comparison. Suitable available pairs of molecules are methane and fluoroform, bicyclo(2,2,1)-heptane and 1H-undecafluorobicyclo(2,2,1)heptane and cyclohexane and 1H-undecafluorocyclohexane. The last compound is thought to interconvert between the two possible conformers which are taken to exist in the ratio 3:2 favouring the hydrogen in the axial position[63], and has been accounted for in the calculations. The coefficients of $\Delta\chi^{CF}$ in equation 5:2 were evaluated for each of the molecules containing fluorine substituents. For the cyclohexanes and bicyclo(2,2,1)heptanes, the co-ordinate systems suggested in references 90 and 60 respectively, and the molecular parameters for fluoroform given in reference 102, were used for this purpose. The observed difference in screening of a proton in similar positions in each of the pairs of molecules discussed above, together with the appropriate coefficients in equation 5:2, enabled a value to be deduced for $\Delta\chi^{CF}$ that would be required to satisfy the relationship given in equation 5:2 between nuclear screening and the secondary fields induced by magnetically anisotropic bonds. The calculations were performed for a number of locations for the equivalent dipole along the C-F bond using the shift values given in table 6:1. The resulting values required for $\Delta\chi^{CF}$ for each molecular pair are collected in table 6:2 and these are plotted against distance along the C-F bond from the carbon atom, taken for the origin of the induced point dipole in figure 6:1. It is evident that there is only one point in figure 6:1 at which the values obtained for $\Delta\chi^{CF}$ from the three sets of calculations become consistent. This corresponds to the value $-6.0_3 \times 10^{-6}$ $cm^3.mole^{-1}$ for $\Delta\chi^{CF}$ with the equivalent dipole originating on the carbon atom. This result is particularly interesting, not so much for the value derived for the apparent bond magnetic anisotropy, but for its position of origin on the carbon atom, which is identical to the position required in the C-H bond for its equivalent dipole to originate if it has a significant value.

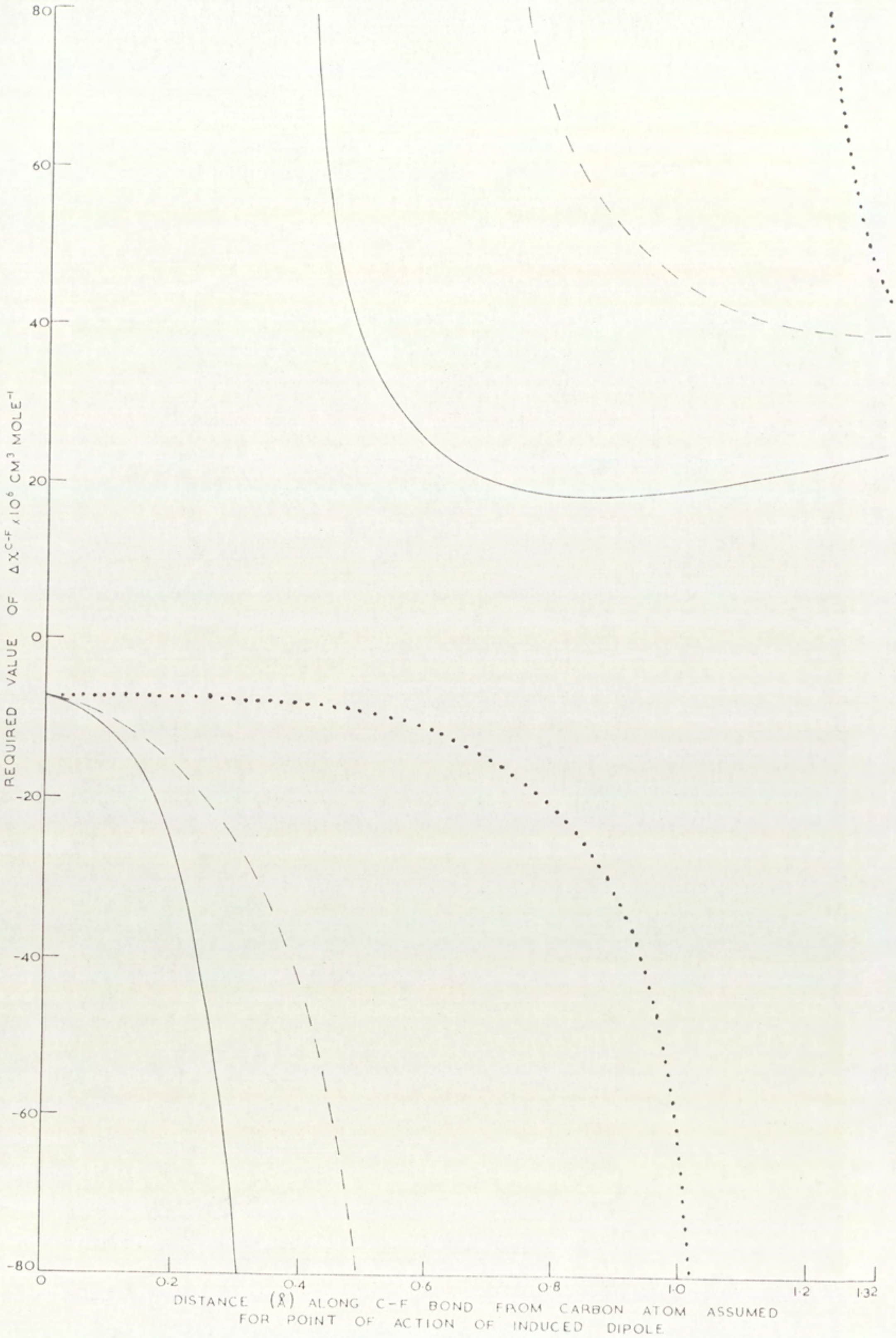


FIGURE 6.1 The dependence of $\Delta\chi^{CF}$ (evaluated using equation 5:2) on the location assumed for the point of action of the C-F bond magnetic dipole. The curves are identified:

——— methane/fluoroform – – – – cyclohexane/1Hundecafluorocyclohexane ······ bicyclo(2,2,1)heptane/1Hundecafluorobicyclo-(2,2,1)heptane.

	Required Value of $\Delta\chi^{CF} \times 10^6$ cm^{3}mole^{-1}		
Distance along bond from C atom (Å)	Methane/ Fluoroform	Cyclohexane/ 1H-undecafluoro cyclohexane	Bicyclo(2,2,1)heptane/ 1H-undecafluoro bicyclo(2,2,1)heptane
0.1	-11.39	-11.5	-5.4
0.2	-21.1	-15.9	-6.0
0.3	-71.1	-39.8	-6.8
0.4	+89.6		
0.5	+34.6	-103.4	-9.3
0.6	+24.8		
0.7	+21.3	+100.0	-14.6
0.8	+19.9		
0.9	+19.6	+52.6	-30.7
1.0	+20.0	+44.6	-60.1
1.1	+70.8	+41.5	-435.6
1.2	+22.0	+39.1	+95.6
1.32	+24.0	+37.3	+42.3

Table 6:2

Representative values of $\Delta\chi^{CF}$ required to explain proton screenings wholly in terms of bond magnetic anisotropy.

6:4 The apparent anisotropy in the Magnetic Susceptibility of the C-Cl Bond.

A value for the apparent anisotropy in the magnetic susceptibility of the C-Cl bond could not be determined by precisely the same technique as was used for $\Delta\chi^{CF}$ because the chlorine analogues of the molecules used previously were not readily available, with the exception of the chloroform - methane pair. Together with this pair of compounds, three other pairs were examined. The first was cyclohexane and cyclohexyl chloride, where the shifts and coefficients of the α proton in cyclohexyl chloride were compared with those of cyclohexane. For this purpose, both molecules were considered to exist as a 1:1 mixture of the possible chair conformers, although it is most probable that the cyclohexyl chloride should be represented as a weighted average favouring the axial orientation of the α hydrogen atom[103]. This assumption is reasonable for the present purpose because any slight deviation from actuality in the chosen situation should not necessitate any significant correction to the relatively large shift (-2.32 p.p.m.) measured by Bothner-By and Naar-Colin[98] for the α proton in cyclohexyl chloride relative to cyclohexane. The second additional pair of molecules was β-1,2,3,4,5,6-hexachlorocyclohexane and cyclohexane, for which the shifts and co-efficients of the axial protons were compared using the revised shift value for the β-isomer given in section 6:2. The third additional pair of molecules considered was δ-1,2,3,4,5,6,-hexachlorocyclohexane and β-1,2,3,4,5,6,-hexachlorocyclohexane, for which the co-efficients and shifts were compared for the equatorial hydrogen in the δ-isomer and the axial hydrogens in the β isomer. Again, the revised shift values for the β and δ isomers given in section 6:2 were used. The axial hydrogens in the β isomer were chosen for comparison with the equatorial hydrogen of the δ isomer rather than comparing the internal axial-equatorial shift in the δ-isomer, because the axial resonance can be measured to a greater accuracy for the β isomer than for the δ isomer where axial resonance overlap probably occurs. Because in this case axial and equatorial hydrogens were compared, it was necessary to account for the different screening contributions to these, arising from the magnetic anisotropy of the C-C bonds in the two molecules. Using the value of $\Delta\chi^{CC} = +4.39 \times 10^{-6}$ cm^3.mole^{-1} derived in section 5:4, δ axial-equatorial has been calculated as +0.45 p.p.m. which is in good agreement with that observed[57] (0.46 p.p.m.). Appropriate account has been taken of this contribution when evaluating $\Delta\chi^{CCl}$ from this pair of molecules and, as in previous calculations, $\Delta\chi^{CH}$ has been taken to be zero. The proton shifts used in these calculations are those given in table 6:1. As for the case of the C-F bond, the position of origin assumed for the induced point dipole, was varied along the C-Cl bond and the value required of $\Delta\chi^{CCl}$ to satisfy equation 5:2 was evaluated for each position chosen for each of the four pairs of molecules. The required values of $\Delta\chi^{CCl}$ are collected in table 6:3 and these are plotted in figure 6:2 against the distance from the carbon atom along the C-Cl bond chosen for the position of origin of the induced point dipole. It is seen that there is only one position at which the four lines in figure 6:2 become co-incident, again requiring that the point dipole should originate at the carbon atom. The value for the apparent anisotropy in the magnetic susceptibility of the C-Cl bond deduced from figure 6:2 is $-7.8 \pm 1.0 \times 10^{-6}$ cm^3.mole^{-1} which appears to be quite compatible with the values derived previously for $\Delta\chi^{CC}$, $\Delta\chi^{CH}$ and $\Delta\chi^{CF}$ apparent.

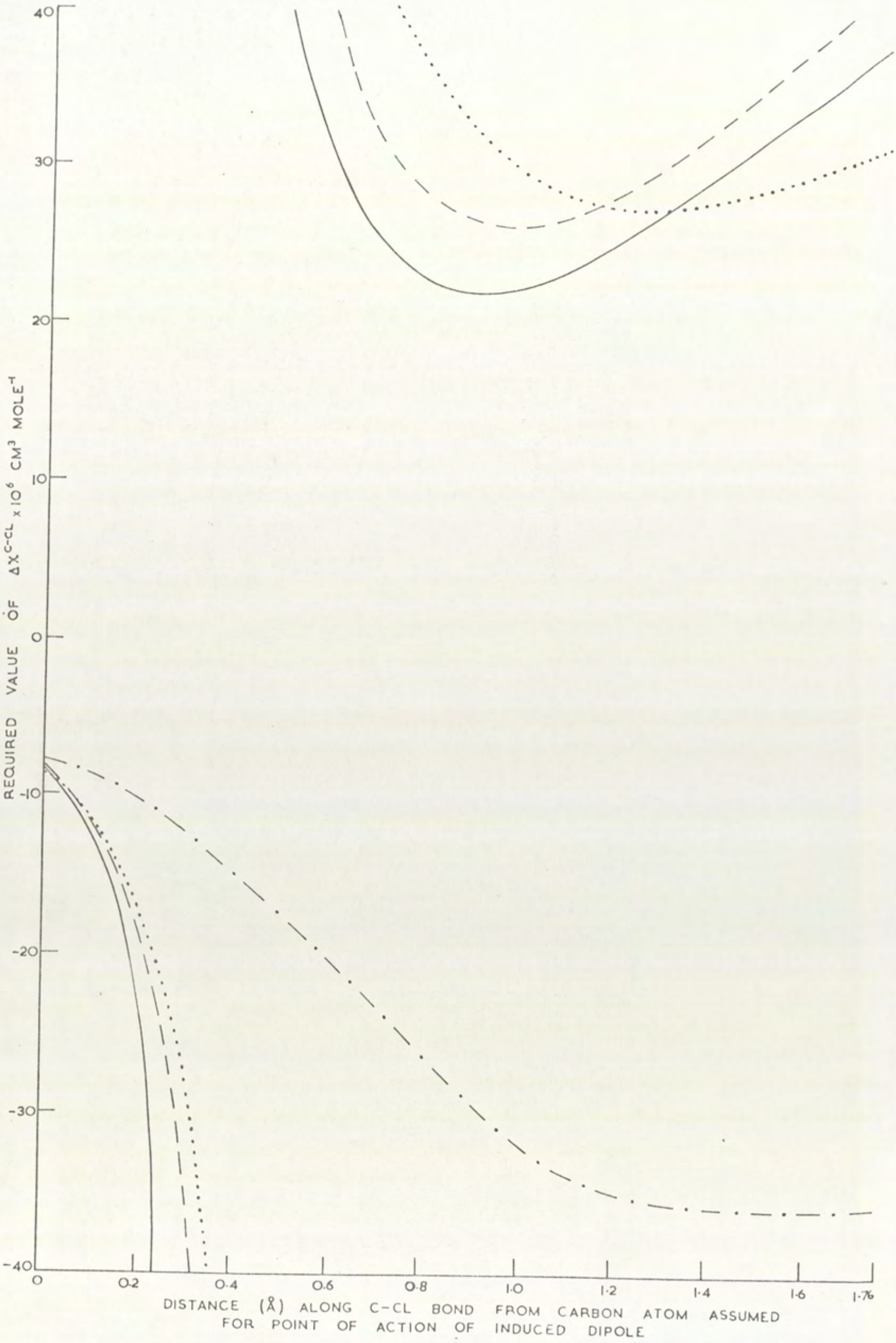


FIGURE 6.2 Dependence of $\Delta\chi^{CCl}$ (evaluated using equation 5:2) on the location assumed for the point of action of the C-Cl bond magnetic dipole. The curves are identified:

——— methane/chloroform, – – – cyclohexane/cyclohexylchloride,

····· cyclohexane/β 1,2,3,4,5,6-hexachlorocyclohexane,

–·–·–· β/δ 1,2,3,4,5,6-hexachlorocyclohexane

	Required Value of $\Delta\chi^{CCl} \times 10^6$ cm^3.mole^{-1}			
Distance along bond from C atom (Å)	CH_4/ $CHCl_3$	C_6H_{12}/ $C_6H_{11}Cl$	C_6H_{12}/ $C_6H_6Cl_6$(β isomer)	$C_6H_6Cl_6$ (β/δ isomer)
0.1	-11.0	-11.6	-11.6	
0.2	-19.2	-18.7	-17.1	-9.7
0.4	+202.9	-338.4	-74.1	-13.6
0.6	+29.3	+40.0	+70.8	-19.5
0.8	+22.5	+27.5	+35.2	-26.3
1.0	+22.4	+26.2	+28.8	-32.2
1.2	+24.5	+28.0	+27.4	-35.5
1.4	+28.9	+31.7	+27.4	-36.4
1.6	+33.1	+36.7	+27.4	-36.3
1.76		+41.7	+30.0	

Table 6:3 Representative values of $\Delta\chi^{CCl}$ required to explain proton screenings wholly in terms of bond magnetic anisotropy.

6:5 Conclusions

It is most surprising that the apparent values deduced for the C-H, C-F and C-Cl bond magnetic anisotropies should all require the induced point dipole to act from the carbon atom in the bond. Either this is a genuine feature or there is an over-riding effect in all the molecular situations chosen that results in this as a false requirement. The most obvious effect is that when a substituent X is attached to the same carbon as the hydrogen being investigated, the C-X bond anisotropic screening contribution either produces the dominant effect at this hydrogen or cannot be calculated sufficiently precisely[46,77,78] by use of equation 5:2 because of R_{ij} being less than 3Å. Certainly, from the calculations reported herein, it appears that the effect of such a substituent is large and of the order of three times greater than the sum of the effects of the remaining substituents of a similar type in the molecule. However, it would appear that such an effect is not the cause of the point dipole appearing to originate from the carbon atom, as this effect is not present in all cases and occurs to varying degrees in others. For example, in the C-F bond investigations the effect is not present for the bicyclo-(2,2,1)heptanes whereas it is singly present in the cyclohexane pair and triply present in the methane-fluoroform pair. Similarly, in the chlorine case, there is no contribution from this effect in the hexachlorocyclohexane β and δ isomer pair but there are single and triple contributions in the remaining molecular pairs. Because of the varying extents to which this geminal effect contributes in the different molecular systems and the fact that there is only one point of intersection in figures 6:1 and 6:2, it appears that the suggestion that this effect cannot be calculated adequately by use of equation 5:2 is unimportant although the R_{ij} values are considerably less than 3Å.

All of the calculations so far have neglected any specific contributions to proton screening due to electonegativity and electric field effects. It is therefore, necessary to emphasize that the various $\Delta\chi$ values derived can only be considered to be apparent values that satisfy the observed shifts if these can be wholly accounted for by the bond anisotropy approach. It is therefore difficult to assess the magnetic anisotropies from n.m.r. studies. Even a rigorous quantitative investigation of combined electric field and magnetic anisotropy effects would be unprofitable at this stage owing to the uncertainty in assessing the position of origin of the electric dipoles of the C-X bonds. From equation 6:1, an estimate of the effect of including electric field terms in the calculations shows that the various lines in figures 6:1 and 6:2 would still intersect at a point representing action at or very near to the carbon atom. In each case, the inclusion of these terms would make $\Delta\chi^{CX}$ more positive resulting in values for the C-F and C-Cl bonds about half the current values and in addition, the spread in the intersection of the curves for $\Delta\chi^{CCl}$ in figure 6:2 would also be reduced if account were taken of this electric field effect. In the light of more recent work on intramolecular electric fields (see chapters 7 and 8), it would appear doubtful if equation 6:1 does represent the major contribution to nuclear screening from the electric field effect. However, it is difficult at present to extend to proton screenings the method which has been found most successful for interpreting ^{19}F screenings due to the difficulty in obtaining suitable estimates for the constants in equation 7:10 when protons are considered. It is possible that if the contributions to proton screening from electronegativity and electric field effects were subtracted from the observed screening before attempting to derive values for $\Delta\chi$, then the resulting values could become compatible with those derived from magnetic birefringence measurements and further, it is possible that the point of origin for the induced dipole might be at some other position in the bond rather than on the carbon atom.

Nevertheless, apparent values for $\Delta\chi^{CC}$, $\Delta\chi^{CH}$, $\Delta\chi^{CF}$ and $\Delta\chi^{CCl}$ have been derived and the equivalent dipoles for the last three of these have been shown to act from the carbon atom of the bond containing the substituent. The values derived are almost certainly not true bond magnetic anisotropies, but some quantity, the physical significance of which is not immediately obvious, which must contain contributions from, for example electronegativity and electric field effects, both of which are fortuitously included in the quantity called the apparent bond magnetic anisotropy. Because the parameters were deduced from proton shifts in a diverse range of molecules, they should enable relative proton screenings to be calculated for other saturated compounds containing hydrogen, fluorine or chlorine, provided that the geometries of the molecules are known sufficiently precisely to enable the evaluation of the R_{ij} and Θ_{ij} terms in equation 5:2.

The value obtained for $\Delta\chi^{CF}$ apparent, indicates that the contribution to ^{19}F chemical shifts from secondary fields due to the anisotropy in the magnetic susceptibility of neighbouring C-F bonds, is only very small when compared with the observed range of values for ^{19}F shifts. In chapters 7 and 8, the chemical shifts in some saturated fluorinated molecules have been accounted for by the effect of intramolecular electric fields and it would seem unwise to use the value derived herein for $\Delta\chi^{CF}$ apparent in an evaluation of the combined effect on ^{19}F shifts of electric fields and bond magnetic anisotropy. This is because it has been suggested above that the apparent values for the anisotropy in the magnetic susceptibility of bonds derived herein, must themselves fortuitously contain a contribution from intramolecular electric fields.

CHAPTER 7

Some Investigations of the Correlation Between ^{19}F Nuclear Screening and Intramolecular Electric Fields

7:1 Introduction

It has been reported recently that ^{19}F screenings in fluoroaromatic compounds can be explained in terms of π electron densities and the resultant electric fields at the fluorine nuclei, so that intramolecular fluorine screening constants may be written in the form[104,105]

$$\sigma = \sigma(\text{electric}) + \sigma(\text{electronic}) \qquad 7{:}1$$

Some authors[66,70] have used this approach to calculate shifts in saturated fluorinated molecules by assuming that σ(electronic) is zero and that the shifts can be attributed entirely to the electric field effects embodied in the σ(electric) term of equation 7:1. For differences in screening of a particular nuclear type, in this case fluorine, in two different molecular situations, the electric term corresponding to that in equation 7:1 has been given in terms of differences in electric fields by

$$\Delta\sigma(\text{electric}) = -A\Delta E_z - B(\Delta E^2 + \Delta\langle E^2\rangle) \qquad 7{:}2$$

where A and B are constants and E is the electric field at the resonant nucleus arising from point dipoles associated with all of the polar bonds in the molecule, except that containing the nucleus in question. E_z is the component of E acting along the direction of the bond containing the resonant nucleus and may together with E^2 be deduced by appropriate summation from the individual components of E, which classically are given[106,107] by

$$E_{i(x)} = \mu_i(3\cos^2\theta_i - 1)/\ r_i^3 \qquad 7{:}3$$

$$E_{i(y)} = (3\mu_i\cos\theta_i\sin\theta_i)/\ r_i^3 \qquad 7{:}4$$

where $E_{i(x)}$ is taken in the direction of the polar bond, r_i is the length of the radius vector between the point dipole i and the resonant nucleus, θ_i is the angle between the radius vector and the x direction, and ϵ, the dielectric constant of the intervening medium, is taken to be unity. The angles and distances are shown in figure 7:1A. The non zero time average contribution to E^2 given by $\langle E^2 \rangle$ arises from the presence of time dependent dipole moments in neighbouring electron groups. These time dependent moments give rise to van der Waals forces between non-bonded atoms and their effect is known as the van der Waals shift. The value of $\langle E^2 \rangle$, the non-zero time average field, can be obtained approximately from an expression that was derived for intermolecular solution effects[49] and given by

$$\langle E^2 \rangle = \frac{3PI}{r^6} \qquad 7{:}5$$

in which P is the polarisability of the electron group, I is the first ionisation potential and r is the distance separating the fluorine atom from the electron group and corresponds to the R given in figure 7:1A. Bothner-By[108] has derived an equation which reduces to half the expression given in equation 7:5, however, this latter equation will be used in the present work as other authors have achieved some success when using it.

It has been shown previously[104] that the ortho effects observed for fluorobenzenes can be accounted for satisfactorily using equation 7:2. This equation has also been used to calculate[70] the axial/equatorial shift in perfluorocyclohexane, giving a value of 10.87 p.p.m. compared with the observed[52] value of

18.2 p.p.m. Equation 7:5 has been used alone to predict changes in the shielding of fluorine nuclei when fluorine atoms at other positions in the molecule are replaced by other atoms.[66,70,101,104] Equation 7:5 has been assumed to be equally valid for both polar and non-polar bonds, although in only one of the previously reported works[70] has equation 7:5 been specifically applied to non-polar bonds, in the perfluorocyclohexane investigation. In all of the other work, equation 7:5 has been applied only to polar bonds, as most of these investigations have been concerned with the effect on a fluorine nucleus of changing substituents at other positions in the molecule. Any effect from the essentially non-polar C-C bonds was then constant and no account was taken of it.

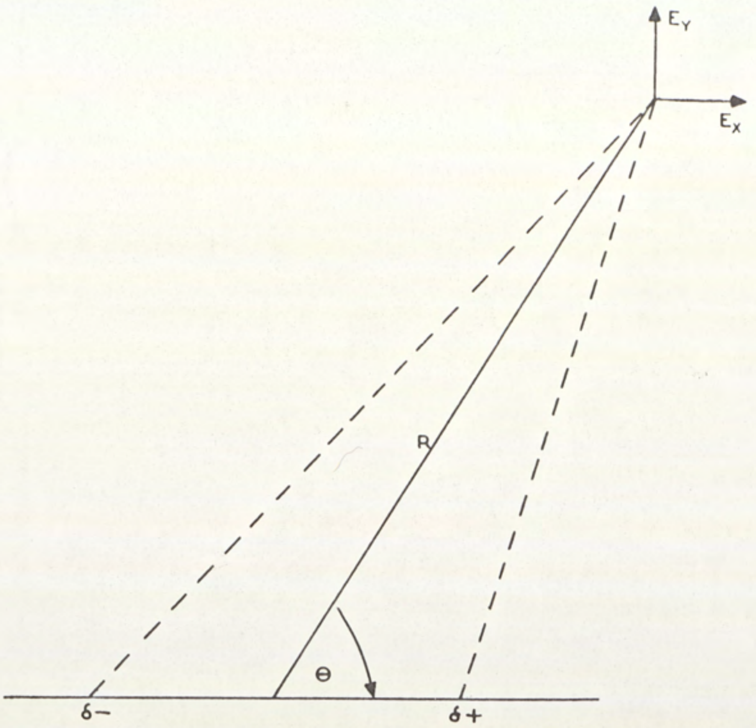
A simpler empirical correlation has been reported[109] for substituent (X) effects on fluorine shifts in unsaturated compounds with a quantity Q given by

$$Q = P/Ir^3 \qquad 7{:}6$$

where P and r are respectively the polarisability and length of the C-X bond and I is the first ionisation potential of the substituent X. However, in a subsequent publication[110], it was indicated that the electric field model would be expected to be more successful and widely applicable than that involving Q for calculating ^{19}F shifts in saturated compounds and that the 'Q' effect appeared to be a through bond effect which was transmitted via the double bond of the unsaturated systems studied.

The use of any equation such as 7:2 based on a point dipole approximation, suffers from the problem that some of the distances r_i are smaller than is consistent with the point dipole basis of the calculations. This is not easily overcome. Nevertheless, in view of the general success achieved in estimating chemical shifts

7.1A



7.1B

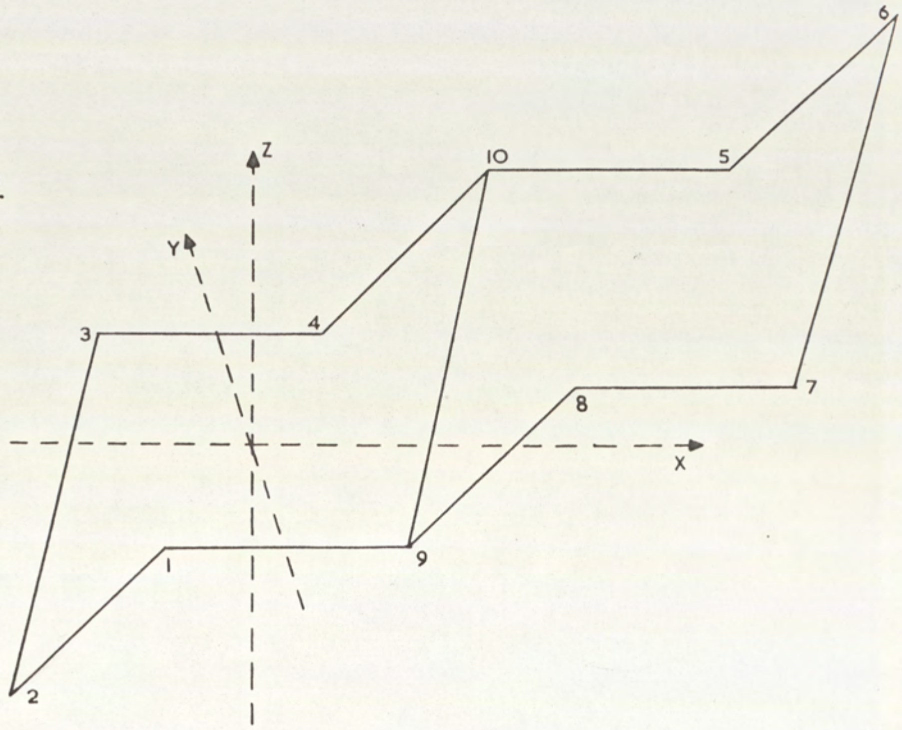


FIGURE 7.1A The electric field components E_x and E_y produced at a distance R from a dipole.

FIGURE 7.1B The numbering and co-ordinate system used for the trans-decalin structure.

using equations similar to 7:2, in particular when calculating anomalous ortho shifts in substituted benzenes[104,105] where the relevant distances are small, it would appear that its basis and use for consistent empirical calculations of chemical shifts may be justified. Even so, it is difficult to decide on the appropriate values of A and B to substitute into equation 7:2 and to decide on the position in any particular bond which should be taken for the point of origin of the electric field associated with that bond. In previous calculations[66,70,101,104,105] involving the C-F bond, the electric field has been assumed to originate from the centre of the bond, although this is almost certainly incorrect. However, it should in principle be possible to derive values for A and B and to determine the best position along a C-F bond at which the electric dipole can be considered to act.

For this purpose, fluorinated cyclic molecules are of particular interest because in general their conformations are fairly well known, making it relatively simple to evaluate the intramolecular geometrical parameters that are necessary in any of the methods proposed so far for the evaluation of ^{19}F shifts. Three molecules which are particularly suitable for these investigations are perfluorobicyclo(2,2,1)heptane, trans-perfluorodecalin and perfluorocyclohexane. Before discussing the correlation between intramolecular electric fields and fluorine screenings, the evaluation of the intramolecular parameters required in equations 7:3 and 7;4 will be discussed.

7:2 The Calculation of Intramolecular Geometrical Parameters

For the three molecules chosen for these investigations, the co-ordinates are available or readily evaluated for all of the atoms. The co-ordinates for molecules based on the bicyclo(2,2,1) heptane skeleton[60] and the cyclohexane skeleton[90] have been published previously and the co-ordinates of the atoms in the perfluorodecalin may be evaluated from those of cyclohexane, assuming an idealised configuration of the trans fused cyclohexane rings. The co-ordinates used in these investigations for the decalin ring system are given in tables 7:1 and 7:2 and the co-ordinate axes are shown in figure 7:1B.

Carbon atom	Co-ordinates x	of carbon y	atoms z
1	-0.764	-1.263	0
2	-1.325	0	-0.651
3	-0.764	+1.263	0
4	+0.764	+1.263	0
5	+2.853	0	+0.651
6	+3.414	-1.263	+1.302
7	+2.853	-2.526	+0.651
8	+1.325	-2.526	+0.651
9	+0.764	-1.263	0
10	+1.325	0	+0.651

Table 7:1 The co-ordinates of the carbon atoms in trans-perfluorodecalin.

The distance between any two points in a molecule (corresponding to r in equations 7:3 and 7:4) is simply the scalar magnitude of the vector joining the points. The distance between two points defined by the co-ordinates $x_1y_1z_1$ and $x_2y_2z_2$ is given by

$$\text{separation} = \left[(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2\right]^{\frac{1}{2}} \qquad 7{:}7$$

The co-ordinates x, y, z of any atom or any position in the bond containing that atom are derived from the co-ordinates of the carbon atom of that bond, plus the unit vector co-ordinates of the substituent atom multiplied by the length of the bond or the distance along the bond for which the co-ordinates are required. The angle Θ in equations 7:3 and 7:4 may be easily determined since the distance r from the point dipole to the nucleus

Substituent	Co-ordinates of substituents		
	x	y	z
1ax	-0.333	-0.067	+0.940
1eq	-0.333	-0.804	-0.492
2ax	+0.223	0	-0.975
2eq	-0.997	0	+0.077
3ax	-0.333	+0.067	+0.940
3eq	-0.333	+0.804	-0.492
4ax	+0.333	+0.067	-0.940
4eq	+0.333	+0.804	+0.940
5ax	+0.333	+0.067	-0.940
5eq	+0.333	+0.804	+0.492
6ax	-0.223	0	+0.975
6eq	+0.997	0	-0.077
7ax	+0.333	-0.067	-0.940
7eq	+0.333	-0.804	+0.492
8ax	-0.333	-0.067	+0.940
8eq	-0.333	-0.804	-0.492
9ax	+0.333	-0.067	-0.940
10ax	-0.223	0	+0.975

Table 7:2 The unit vector co-ordinates (i.e. assuming a bond length of 1Å) of the substituent atoms in *trans*-perfluorodecalin.

in question may be determined by the procedure outlined above, as can the distance between the carbon atom of the bond containing the dipole and the nucleus, and the distance along the C-X bond of the point dipole is pre-determined. Thus three sides of a triangle, one of the internal angles of which is θ, are known and hence θ is easily evaluated. The two contributions E_x and E_y of equations 7:3 and 7:4 must be resolved into the direction of the bond containing the resonant nucleus and the resolving angles may be determined in a manner similar to that outlined for θ above. The angle required to determine the component of E_x in the bond direction is simply evaluated by considering a hypothetical situation where the carbon atoms of the C-F bond containing the resonant nucleus and the carbon of the C-F bond whose influence is being investigated are considered to be coincident. The lengths of the two bonds are known and the distance between the two fluorine nuclei in this hypothetical situation is easily evaluated, giving the lengths of the three sides of a triangle. The angle between E_x and the bond direction is identical to one of the angles of this triangle and may be evaluated. The angle required to determine the component of E_y in the bond direction may be evaluated, although the procedure is somewhat more complicated than that outlined above. The co-ordinates of an imaginary point are evaluated, such that it is in the plane containing the nucleus whose screening is considered, and the carbon and fluorine atoms of the bond in which the electric field is considered to originate, and is also on a line through the carbon atom of this bond and perpendicular to the bond. The distance of this point from the carbon atom is conveniently taken to be the same as the C-F bond length. If the bond containing the resonant nucleus is then considered to originate from the same carbon as the bond causing the electric field (by transposing co-ordinates), then the angle between the imaginary point, the carbon atom and the resonant nucleus in this new hypothetical position, is identical to the required resolving angle for E_y and can be evaluated by using the same procedure discussed above for the angle appropriate to E_x.

Due to the large number of calculations involved, all of the required parameters have been evaluated using an Elliot 803 computer and an 'Algol' program called 'Intramolicon'. This program requires the co-ordinates of all the atoms in the molecule as input data together with the bond lengths and the distance along the bond at which the point dipole is assumed to originate. A modified form of this computer program also evaluates the electric field contributions and arranges these together with observed shifts and solves for the constants A and B. The use of this latter facility is discussed in section 7:4. All of the computer programs used were checked by hand calculations and the geometrical parameters were further checked as being of the right magnitude by measurement on a model of one of the compounds.

The R and Θ terms in equation 5:2 that has been used in chapters 5 and 6 were evaluated by similar procedures to those outlined above.

7:3 Comments on the ^{19}F Resonance Spectra of the Compounds used in the Investigation.

The ^{19}F spectrum of perfluorobicyclo(2,2,1)heptane has been discussed in sections 4:3 and 4:5 and empirical assignments made to the various resonances. The ^{19}F spectrum of perfluorocyclohexane has been previously reported by Tiers[52].

The ^{19}F spectrum of trans-perfluorodecalin has also been reported previously[111]; however, only a single shift value of 47.00 p.p.m. from external trifluoroacetic acid was quoted for the 1,4,5,8 axial and equatorial fluorines which arise from a near limiting AB type spectrum. The axial and equatorial shifts have been estimated from band intensity measurements. The intensities and line separations are given for the general AB spin system in section 1:10. If I_{inner} and I_{outer} are respectively the intensities of the inner and outer lines of the AB spectrum, and since $C \sin 2\Theta = \frac{1}{2}J$ (from section 1:10) then

$$\frac{I_{inner}}{I_{outer}} = \frac{1 + J/2C}{1 - J/2C} \qquad 7:8$$

and

$$C = \frac{1}{2}\left[(\nu_0\delta)^2 + J^2\right]^{\frac{1}{2}} \qquad 7:9$$

From equations 7:8 and 7:9 and the spectrum of trans-perfluorodecalin, it has been estimated that $(\nu_0\delta) = 242$ c.sec.$^{-1}$ which at 30 Mc.sec.$^{-1}$ operating frequency gives an axial-equatorial shift of 8 p.p.m. The chemical shifts used for trans-perfluorodecalin in this investigation are axial 43.0 p.p.m.

equatorial 51.0 p.p.m. from external

trifluoroacetic acid.

7:4 Attempts to correlate ^{19}F nuclear Screenings with Electric Fields and an Investigation of the Position of Origin of the Point Dipole.

Equation 7:2 or modified forms of this equation, have been used to predict fluorine shifts in a range of molecules; however, there have been no theoretical estimates for A and B when considering fluorine as the resonant nucleus. The constants A and B depend upon the ease of distortion of the electronic charge distribution along the bond direction and perpendicular to it. Petrakis and Bernstein[112, 113] have determined these constants experimentally by observing the pressure dependence of chemical shifts of gaseous samples of fluorine containing compounds. They find that A is negative and has the value of $(-9.9 \pm 3.3) \times 10^{-12}$ e.s.u. for the molecule CHF_3. Whereas B is positive and varies from $(15.1 \pm 3.0) \times 10^{-18}$ e.s.u. in CHF_3 to $(43.5 \pm 5.1) \times 10^{-18}$ e.s.u. in SiF_4. They suggest that the B values for X-F bonds depend upon the double bond character. It should be possible to determine the constants A and B and the effective position of origin of the point dipole in the C-F bond purely from n.m.r. measurements.

Considering the perfluorobicyclo(2,2,1)heptane molecule, there are four magnetically dissimilar types of fluorine, for which the chemical shifts have been evaluated in section 4:3. Any position along the C-F bond may be taken for the origin of the C-F dipole and the mid point of the C-C bond chosen for evaluating its contributions from equation 7:2. The relevant C-C bond contributions to $\langle E^2 \rangle$ are listed in table 7:3 and the total contributions to each of the terms in equation 7:2 from all of the C-F bonds in the molecule, except that containing the resonant nucleus in question, are listed in table 7:4. The electric fields associated with each of the C-F bonds in the molecule are assumed to originate from varying positions in all the bonds to obtain the data in table 7:4.

It is possible to set up three pairs of simultaneous equations from which each pair may be solved to give the values of A and B that would be required to satisfy equation 7:2 for the observed shifts, with the electric fields originating from the

C-C Bond	Contribution to $\langle E^2 \rangle$ field x 10^{-12} e.s.u. at:			
	F1	Fexo	Fendo	F7
1-2	1.0654	1.2647	1.2653	0.1619
2-3	0.0499	1.2659	1.2654	0.1031
3-4	0.0193	0.0766	0.0766	0.1619
4-5	0.0193	0.0148	0.0323	0.0544
5-6	0.0499	0.0120	0.0641	0.0191
6-1	1.0654	0.0540	0.1993	0.0544
1-7	1.0668	0.1263	0.0605	1.1928
4-7	0.0555	0.0433	0.0254	1.1928
Total	3.3915	2.8576	2.9888	2.9404

Table 7:3 Contributions from C-C bonds to the $\langle E^2 \rangle$ field at the resonant fluorine nuclei in perfluorobicyclo-(2,2,1)heptane.

position in the C-F bonds chosen. If the position of origin of the dipole has been chosen correctly, then the three solutions for A and B would be expected to be the same, or at least very close, bearing in mind the inherent inaccuracies in the chosen co-ordinate systems. The four shifts observed for perfluorobicyclo(2,2,1)-heptane, together with the appropriate electric field contributions have been substituted into equation 7:2 and arranged in the following manner for solution of A and B

$$(F_1 - F_{exo}) \text{ with } (F_1 - F_{endo})$$

$$(F_1 - F_{exo}) \text{ with } (F_1 - F_7)$$

$$(F_1 - F_{endo}) \text{ with } (F_1 - F_7)$$

Table 7:4 The electric field contributions at the various resonant fluorine nuclei in perfluorobicyclo(2,2,1)heptane due to the remaining C-F bonds in the molecule with the position of origin of the point dipole located at varying distances along the C-F bonds.

(Å) along C-F bond assumed for dipole	Resonant Nucleus.	$\Sigma E_z x10^{-6}$	$\Sigma E^2 x10^{-12}$	$\Sigma<E^2>x10^{-12}$
0.1	1,4	0.1980	0.0701	1.7810
	2,3,5,6 exo	0.6694	0.5424	10.5542
	2,3,5,6 endo	0.7895	0.5682	10.7769
	7	0.5751	0.5466	10.4936
0.2	1,4	0.2397	0.0689	1.7052
	2,3,5,6 exo	0.6306	0.4938	8.8571
	2,3,5,6 endo	0.7370	0.5180	9.0634
	7	0.5635	0.4957	8.7726
0.3	1,4	0.2788	0.0675	1.6200
	2,3,5,6 exo	0.5793	0.4404	7.3507
	2,3,5,6 endo	0.6696	0.4634	7.5509
	7	0.5329	0.4408	7.2470
0.4	1,4	0.3141	0.0659	1.5278
	2,3,5,6 exo	0.5230	0.3861	6.0612
	2,3,5,6 endo	0.5950	0.4081	6.2648
	7	0.4915	0.3853	5.9433

Table 7:4 continued

(Å) along C-F bond assumed for dipole	Resonant Nucleus	$\Sigma E_z \mathrm{x}10^{-6}$	$\Sigma E^2 \mathrm{x}10^{-12}$	$\Sigma \langle E^2 \rangle \mathrm{x}10^{-12}$
0.5	1,4	0.3449	0.0641	1.4306
	2,3,5,6 exo	0.4672	0.3339	4.9850
	2,3,5,6 endo	0.5189	0.3551	5.2015
	7	0.4457	0.3323	4.8574
0.6	1,4	0.3709	0.0621	1.3306
	2,3,5,6 exo	0.4154	0.2860	4.1053
	2,3,5,6 endo	0.4453	0.3065	4.3406
	7	0.3999	0.2837	3.9698
0.7	1,4	0.3920	0.0599	1.2297
	2,3,5,6 exo	0.3697	0.2434	3.3923
	2,3,5,6 endo	0.3765	0.2634	3.6536
	7	0.3567	0.2406	3.2529
0.8	1,4	0.4080	0.0575	1.1298
	2,3,5,6 exo	0.3307	0.2065	2.8182
	2,3,5,6 endo	0.3139	0.2260	3.1105
	7	0.3178	0.2033	2.6779
0.9	1,4	0.4193	0.0549	1.0323
	2,3,5,6 exo	0.2983	0.1751	2.3566
	2,3,5,6 endo	0.2577	0.1941	2.6831
	7	0.2839	0.1716	2.2179

Table 7:4 continued

(Å) along C-F bond assumed for dipole	Resonant Nucleus	$\Sigma E_z x10^{-6}$	$\Sigma E^2 x10^{-12}$	$\Sigma \langle E^2 \rangle x10^{-12}$
1.0	1,4	0.4260	0.0521	0.9384
	2,3,5,6 exo	0.2721	0.1487	1.9844
	2,3,5,6 endo	0.2080	0.1673	2.3466
	7	0.2550	0.1450	1.8495
1.1	1,4	0.4285	0.0492	0.8493
	2,3,5,6 exo	0.2512	0.1267	1.6829
	2,3,5,6 endo	0.1645	0.1449	2.0802
	7	0.2309	0.1228	1.5534
1.2	1,4	0.4273	0.0462	0.7655
	2,3,5,6 exo	0.2348	0.1084	1.4369
	2,3,5,6 endo	0.1268	0.1262	1.8670
	7	0.2110	0.1044	1.3139
1.3	1,4	0.4228	0.0433	0.6875
	2,3,5,6 exo	0.2220	0.0932	1.2344
	2,3,5,6 endo	0.0948	0.1107	1.6932
	7	0.1949	0.0891	1.1189

Key to Curves in Figures 7.2-7.11

Figures 7.2, 7.3, 7.5, 7.6, 7.8 and 7.9

________ $(F_1-F_{exo})/(F_1-F_{endo})$
- - - - - $(F_1-F_{exo})/(F_1-F_7)$
.... $(F_1-F_{endo})/(F_1-F_7)$

Figures 7.4 and 7.7

________ $(F_9-F_{2ax})/(F_9-F_{2eq})$
- - - - - $(F_9-F_{2ax})/(F_9-F_{1ax})$
.... $(F_9-F_{2ax})/(F_9-F_{1eq})$
. - . - . $(F_9-F_{2eq})/(F_9-F_{1ax})$
+ + + + + $(F_9-F_{2eq})/(F_9-F_{1eq})$
+ - + - + $(F_9-F_{1ax})/(F_9-F_{1eq})$

Figures 7.10 and 7.11

________ $(F_9-F_{1ax})/(F_9-F_{1eq})/(F_9-F_{2ax})$
- - - - - $(F_9-F_{1ax})/(F_9-F_{1eq})/(F_9-F_{2eq})$
.... $(F_9-F_{1ax})/(F_9-F_{2ax})/(F_9-F_{2eq})$
. - . - . $(F_9-F_{1eq})/(F_9-F_{2ax})/(F_9-F_{2eq})$

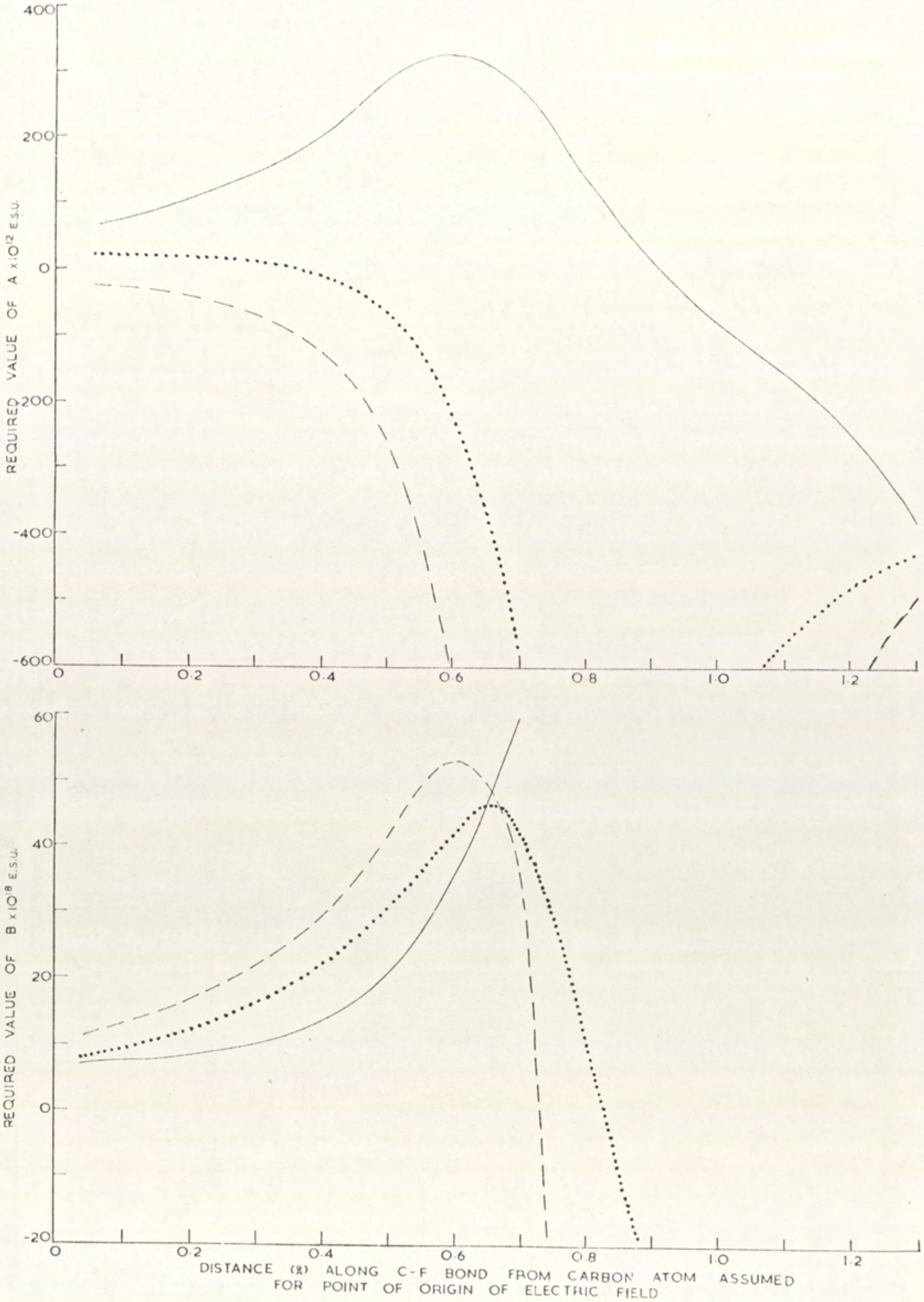


FIGURE 7.2 The dependence of the constants A and B in equation 7:2 on the location assumed for the point of origin of the electric field associated with the C-F bonds in perfluoro-bicyclo(2,2,1)heptane, including contributions to $\langle E^2 \rangle$ from C-C bonds and assuming $\delta_{\text{exo-endo}} = +\ 1.54$ p.p.m. For identification curves see preceding page.

The bridgehead position has been chosen as reference since it is one of the resonances which can be unambiguously assigned and also since it has the form $\geqslant CF$ as opposed to $> CF_2$ for all of the other positions. It is almost certain that the dipole moment and possibly the polarisability and ionisation potential of a C-F bond in the former situation will be different from those of a C-F bond in the latter situation. Since all the measurements are made relative to the bridgehead fluorines, such inaccuracies will disappear in the solution of the resulting equations and errors made in assigning values to the C-F bond constants should be accounted for in the resulting values for A and B.

Assuming firstly that the empirical assignment of the exo-endo shift given in section 4:5 is correct, i.e. the exo nuclei are more shielded than the endo, the values of A and B required to satisfy the three pairs of simultaneous equations defined above were evaluated using the computer program discussed in section 7:2. The molecular data used in the calculations are given in Table 7:5. The calculations were repeated at 0.1Å intervals along the C-F bonds for the position taken for the origin of their associated electric fields. Because the computational data and results are so numerous, these have not been fully tabulated herein, but the relevant resultant electric fields at the various nuclei are listed in table 7:4 and the resulting solutions for A and B have been plotted as a function of distance along the C-F bond assumed for the point of origin of its electric field and are shown in figure 7:2. The contribution to equation 7:5 from the C-C bonds is taken to originate from the bond centre in each case. It is seen from figure 7:2 that there is no point of mutual intersection for the three lines representing the values required

X	r_{c-x}(Å)[102]	μ_{c-x}(Debye)	P_{c-x}($\times 10^{24}$ cm^3)	I_{c-x}($\times 10^{12}$ erg)
C	1.55	-	0.620[114]	19.2[115]
F	1.32	1.40[116]	0.683[117]	28.5[118]
Br		1.56[116]	3.754[119]	18.8[118]
I		1.20[119]	5.72[119]	16.7[118]
H	1.09	±0.5[119]	0.650[114]	23.2[120]

Table 7:5 Bond parameters used in the calculations.

for A. There is, however, a point of near intersection for B requiring that the C-F dipole should originate c.a. 0.65Å along the bond (its mid point) and giving a value of B = c.a. 45×10^{-18} e.s.u. which is in accord with the values assumed for B by other authors[66] in interpreting fluorine shifts in terms only of equation 7:5. Because of the possible ambiguity concerning the exo-endo shift assignment, the alternative has also been tried. The resulting plots for A and B shown in figure 7:3 are seen to be very similar to those obtained using the empirical exo-endo shift assignment. There is no point of mutual intersection observed for A, but B gives a point of near intersection at c.a. 0.65Å along the bond with a value of B = c.a. 45×10^{-18} e.s.u.

A similar type of solution has been attempted using trans-perfluorodecalin as the model. The total contribution from C-C bonds to $\langle E^2 \rangle$ at the various resonant fluorine nuclei in this molecule, derived using equation 7:5, are listed in table 7:6. The resultant electric field contributions at the various fluorine

Resonant Fluorine Nucleus	$\Sigma\langle E^2\rangle \times 10^{-12}$ e.s.u. due to C-C Bonds
F9,10	5.1109
F1,4,5,8 ax	3.1963
F1,4,5,8 eq	2.9610
F2,3,6,7 ax	3.0242
F2,3,6,7 eq	2.7871

Table 7:6 Total $\langle E^2\rangle$ electric field contributions at the various resonant fluorine nuclei from C-C bonds in trans-perfluorodecalin derived using equation 7:5.

nuclei due to the remaining C-F bonds in the molecule are listed in table 7:7, assuming the effect to originate at various positions along the C-F bonds.

Since there are five types of fluorine nuclei in trans-perfluorodecalin, there are six possible ways of substituting the data into equation 7:2 and arranging in pairs for simultaneous solution, i.e.

$(F_9 - F_{2ax})$ with $(F_9 - F_{2eq})$

$(F_9 - F_{2ax})$ with $(F_9 - F_{1ax})$

$(F_9 - F_{2ax})$ with $(F_9 - F_{1eq})$

$(F_9 - F_{2eq})$ with $(F_9 - F_{1ax})$

$(F_9 - F_{2eq})$ with $(F_9 - F_{1eq})$

$(F_9 - F_{1ax})$ with $(F_9 - F_{1eq})$

The solutions for A and B are shown in figure 7:4 and it is seen that there is no point of mutual intersection of the lines for A or B.

Table 7:7 The electric field contributions at the various resonant fluorine nuclei in trans-perfluorodecalin due to the remaining C-F bonds in the molecule, with the position of origin of the point dipole located at varying distances along the C-F bonds.

(Å) along C-F bond assumed for dipole	Resonant Nucleus.	$\Sigma E_z x10^{-6}$	$\Sigma E^2 x10^{-12}$	$\Sigma \langle E^2 \rangle x10^{-12}$
0.1	9,10	-0.5037	0.1969	2.7635
	2,3,6,7 ax	0.3006	0.5508	11.1793
	2,3,6,7 eq	0.6609	0.5004	11.0620
	1,4,5,8 ax	0.4024	0.5540	11.1153
	1,4,5,8 eq	0.6351	0.5105	10.9706
0.2	9,10	-0.4974	0.1745	2.5363
	2,3,6,7 ax	0.3059	0.5086	9.5535
	2,3,6,7 eq	0.7029	0.4685	9.5168
	1,4,5,8 ax	0.3911	0.5115	9.4885
	1,4,5,8 eq	0.6624	0.4695	9.4372
0.3	9,10	-0.4873	0.1558	2.3470
	2,3,6,7 ax	0.2917	0.4610	8.0506
	2,3,6,7 eq	0.7212	0.4294	8.0654
	1,4,5,8 ax	0.3583	0.4636	7.9898
	1,4,5,8 eq	0.6650	0.4304	8.0019
0.4	9,10	-0.4750	0.1401	2.1862
	2,3,6,7 ax	0.2645	0.4107	6.7190
	2,3,6,7 eq	0.7226	0.3862	6.7632
	1,4,5,8 ax	0.3117	0.4130	6.6681
	1,4,5,8 eq	0.6507	0.3871	6.7190

Table 7:7 continued

(Å) along C-F bond assumed for dipole	Resonant Nucleus.	$\Sigma E_z \mathrm{x}10^{-6}$	$\Sigma E^2 \mathrm{x}10^{-12}$	$\Sigma \langle E^2 \rangle \mathrm{x}10^{-12}$
	9,10	-0.4611	0.1269	2.0471
	2,3,6,7 ax	0.2301	0.3606	5.5777
0.5	2,3,6,7 eq	0.7126	0.3418	5.6332
	1,4,5,8 ax	0.2578	0.3625	5.5406
	1,4,5,8 eq	0.6255	0.3427	5.6108
	9,10	-0.4464	0.1156	1.9241
	2,3,6,7 ax	0.1932	0.3129	4.6222
0.6	2,3,6,7 eq	0.6957	0.2988	4.6758
	1,4,5,8 ax	0.2017	0.3146	4.6022
	1,4,5,8 eq	0.5943	0.2998	4.6766
	9,10	-0.4309	0.1060	1.8133
	2,3,6,7 ax	0.1570	0.2693	3.8355
0.7	2,3,6,7 eq	0.6750	0.2589	3.8777
	1,4,5,8 ax	0.1473	0.2708	3.8348
	1,4,5,8 eq	0.5606	0.2600	3.0923
	9,10	-0.4149	0.0976	1.7115
	2,3,6,7 ax	0.1236	0.2305	3.1946
0.8	2,3,6,7 eq	0.6525	0.2230	3.2191
	1,4,5,8 ax	0.0970	0.2319	3.2143
	1,4,5,8 eq	0.5265	0.2242	3.2672
	9,10	-0.3983	0.0925	1.6166
	2,3,6,7 ax	0.0941	0.1968	2.6755
0.9	2,3,6,7 eq	0.6294	0.1915	2.6786
	1,4,5,8 ax	0.0522	0.1982	2.7159
	1,4,5,8 eq	0.4934	0.1929	2.7492

Table 7:7 continued

(Å) along C-F bond assumed for dipole	Resonant Nucleus.	$\Sigma E_z x10^{-6}$	$\Sigma E^2 x10^{-12}$	$\Sigma \langle E^2 \rangle x10^{-12}$
1.0	9,10	-0.3808	0.0838	1.5267
	2,3,6,7 ax	0.0690	0.1680	2.2557
	2,3,6,7 eq	0.6062	0.1642	2.2360
	1,4,5,8 ax	0.0138	0.1694	2.3160
	1,4,5,8 eq	0.4622	0.1659	2.3273
1.1	9,10	-0.3624	0.0780	1.4405
	2,3,6,7 ax	0.0483	0.1436	1.9155
	2,3,6,7 eq	0.5832	0.1409	1.8732
	1,4,5,8 ax	-0.0181	0.1451	1.9943
	1,4,5,8 eq	0.4330	0.1428	1.9830
1.2	9,10	-0.3429	0.0727	1.3572
	2,3,6,7 ax	0.0320	0.1230	1.6387
	2,3,6,7 eq	0.5605	0.1211	1.5753
	1,4,5,8 ax	-0.0436	0.1247	1.7340
	1,4,5,8 eq	0.4061	0.1233	1.7009
1.3	9,10	-0.3221	0.0680	1.2761
	2,3,6,7 ax	0.0195	0.1059	1.4119
	2,3,6,7 eq	0.5381	0.1042	1.3297
	1,4,5,8 ax	-0.0628	0.1078	1.5212
	1,4,5,8 eq	0.3815	0.1068	1.4682

The failure of the A and B curves for either molecule to intersect at points requiring the electric fields to originate at one **fixed** position in the C-F bond may be due to one or more of the following reasons:

(i) The principle assumption made by other authors[66,70,101] that σ(electronic) for saturated molecules is zero for the direct use of equation 2, may be incorrect. It is certainly untrue for fluoroaromatic compounds, but in the absence of substantiated evidence to the contrary for saturated compounds, and because of the apparent success achieved when adopting it for these compounds, it would appear that this assumption is not unrealistic.

(ii) Errors may have been introduced in the calculations by neglecting the effects of modifications to the electric moments of each of the C-F bonds by permanent dipoles induced in them by the fields arising from the other polar bonds in the molecules. For perfluorobicyclo(2,2,1)heptane, the maximum difference due to this in the total non-fluctuating fields at two resonant nuclei, should not be more than c.a. 10% of that calculated on the simple dipole basis and hence the contribution by this to the total shift will be considerably less. It would appear therefore, that this suggestion cannot entirely explain the inadequacy of equation 7:2 to predict on a consistent basis the observed shifts.

(iii) Other workers[66,70,101,104,105] have used equation 7:5 successfully to evaluate $\langle E^2 \rangle$ contributions of carbon-halogen bonds to ^{19}F shifts. However, of the previously reported calculations only in one, performed by Emsley[70], have $\langle E^2 \rangle$ contributions from C-C bonds been specifically included, as has been done here. It is possible that the disappointing results of the calculations so far may have arisen because equation 7:5 is not equally applicable to C-F and C-C bond effects as has been assumed. The equation was originally derived by an approximate quantum mechanical approach[49] to explain the effect on n.m.r. chemical shifts of intermolecular dispersion forces due to the oscillating dipoles present in both polar and non-polar molecules. The equation was in fact used to interpret the interaction of both like and unlike molecules. It can also be deduced classically[107] but in so doing it can only be considered to be strictly applicable to the interaction of like molecules, and should be modified to account for the interaction of unlike molecules. Because the dispersion interaction of a C-F bond with a neighbouring fluorine atom may be likened to the interaction of like molecules, an equation similar to 7:5 may be applicable to this situation. However, from a classical standpoint, the interaction of a C-C bond with a fluorine atom is analogous to that of unlike molecules and the equation equivalent to 7:5 would no longer be applicable to this. In view of this, the importance of the C-C bond $<E^2>$ contributions to the ^{19}F shifts has been investigated by adopting the extreme approach of neglecting them in additional calculations of the type discussed above for perfluorobicyclo(2,2,1)heptane and trans-perfluorodecalin.

The resulting plots of the required values for A and B against distance along the bond assumed for the position of origin of the point dipole for perfluorobicyclo(2,2,1)heptane are shown in figures 7:5 and 7:6 and the plots for trans-perfluorodecalin are shown in figure 7:7. The resulting plots for both possibilities for the exo-endo shift in perfluorobicylo(2,2,1)heptane are very similar to the case where C-C contributions to $<E^2>$ were

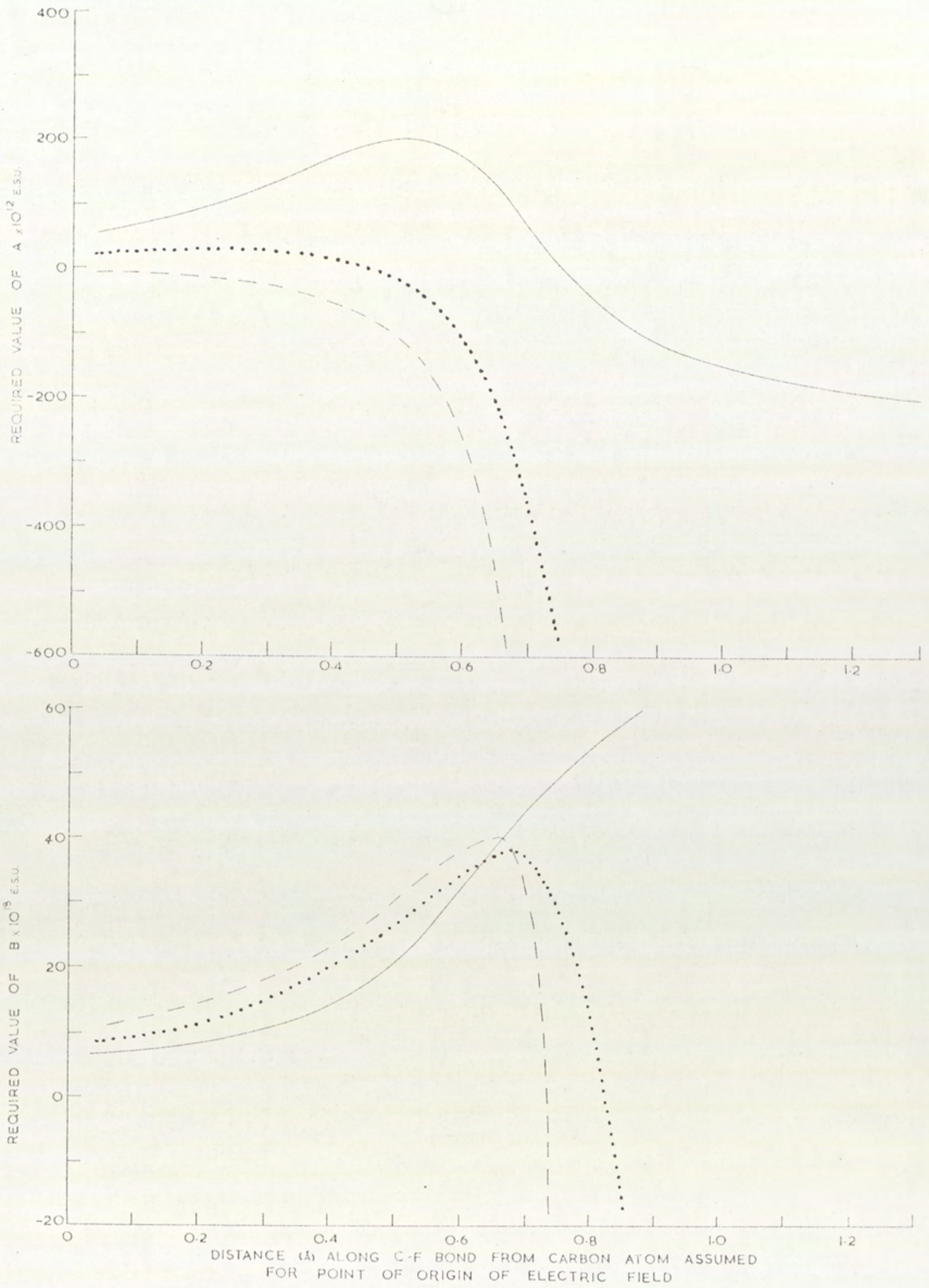


FIGURE 7.5 The dependence of the constants A and B in equation 7:2 on the location assumed for the point of origin of the electric fields associated with the C-F bonds in perfluorobicyclo(2,2,1)heptane, excluding any contributions to $\langle E^2 \rangle$ from C-C bonds and assuming $\delta_{\text{exo-endo}} = + 1.54$ p.p.m.

For identification of curves see page preceding figure 7:2.

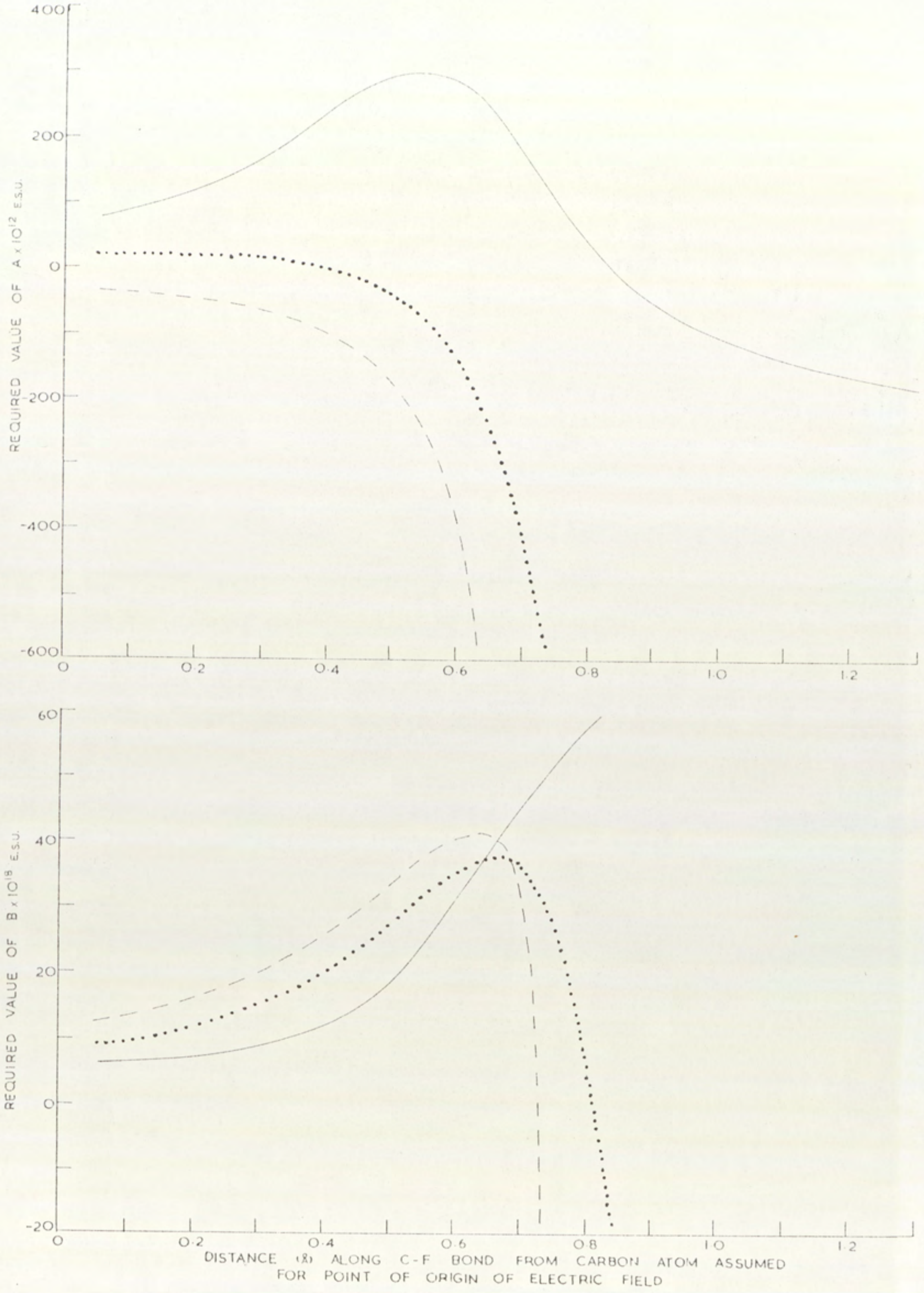


FIGURE 7.6 The dependence of the constants A and B in equation 7:2 on the location assumed for the point of origin of the electric fields associated with the C-F bonds in perfluorobicyclo(2,2,1)heptane, excluding any contributions to $\langle E^2 \rangle$ from C-C bonds and assuming $\sigma_{exo-endo}$ = - 1.54 p.p.m.

For identification of curves see page preceding figure 7:2.

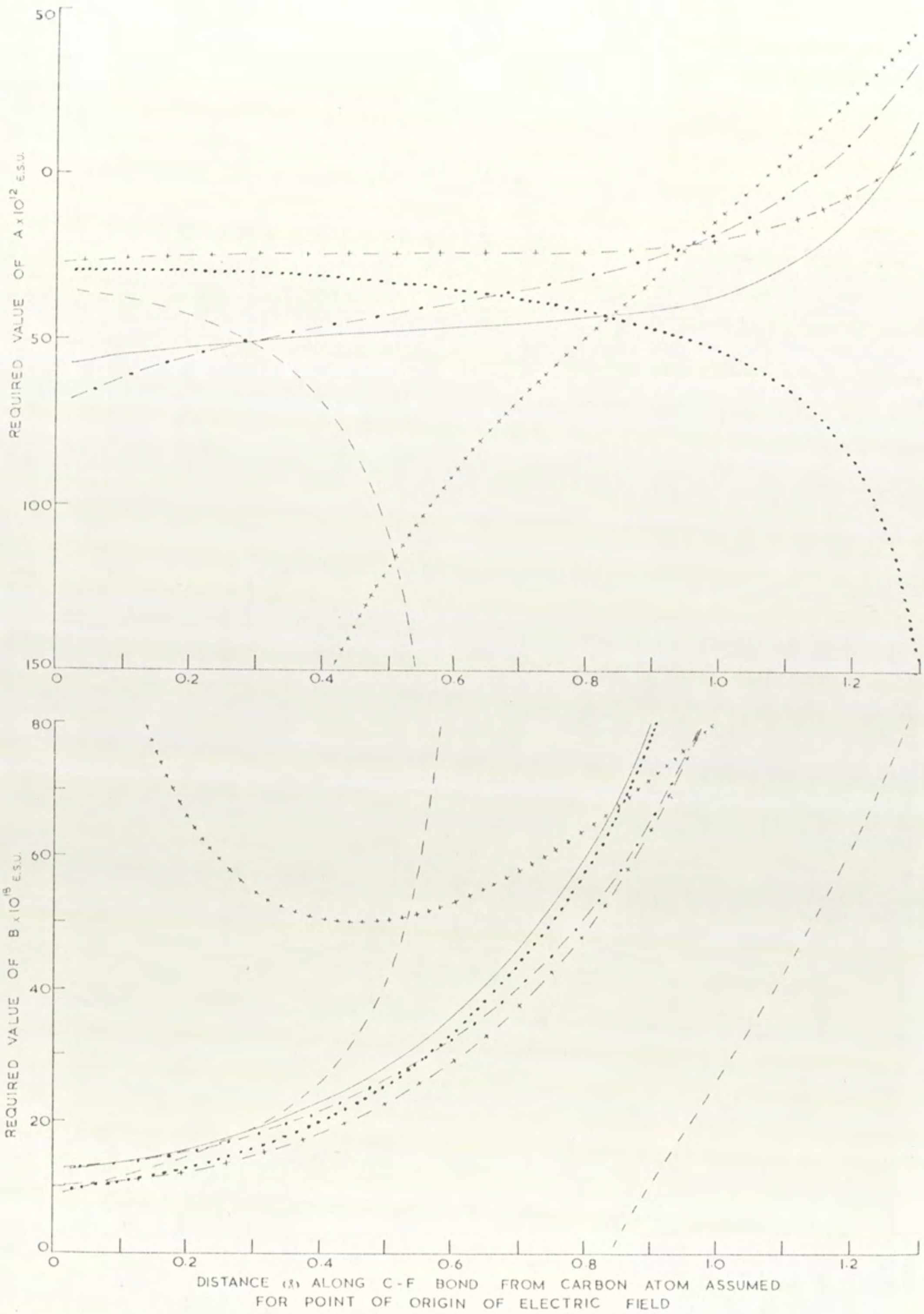


FIGURE 7.7 The dependence of the constants A and B in equation 7:2 on the location assumed for the point of origin of the electric fields associated with the C-F bonds in trans-perfluorodecalin, excluding any contributions to $\langle E^2 \rangle$ from C-C bonds.
For identification of curves see page preceding figure 7:2.

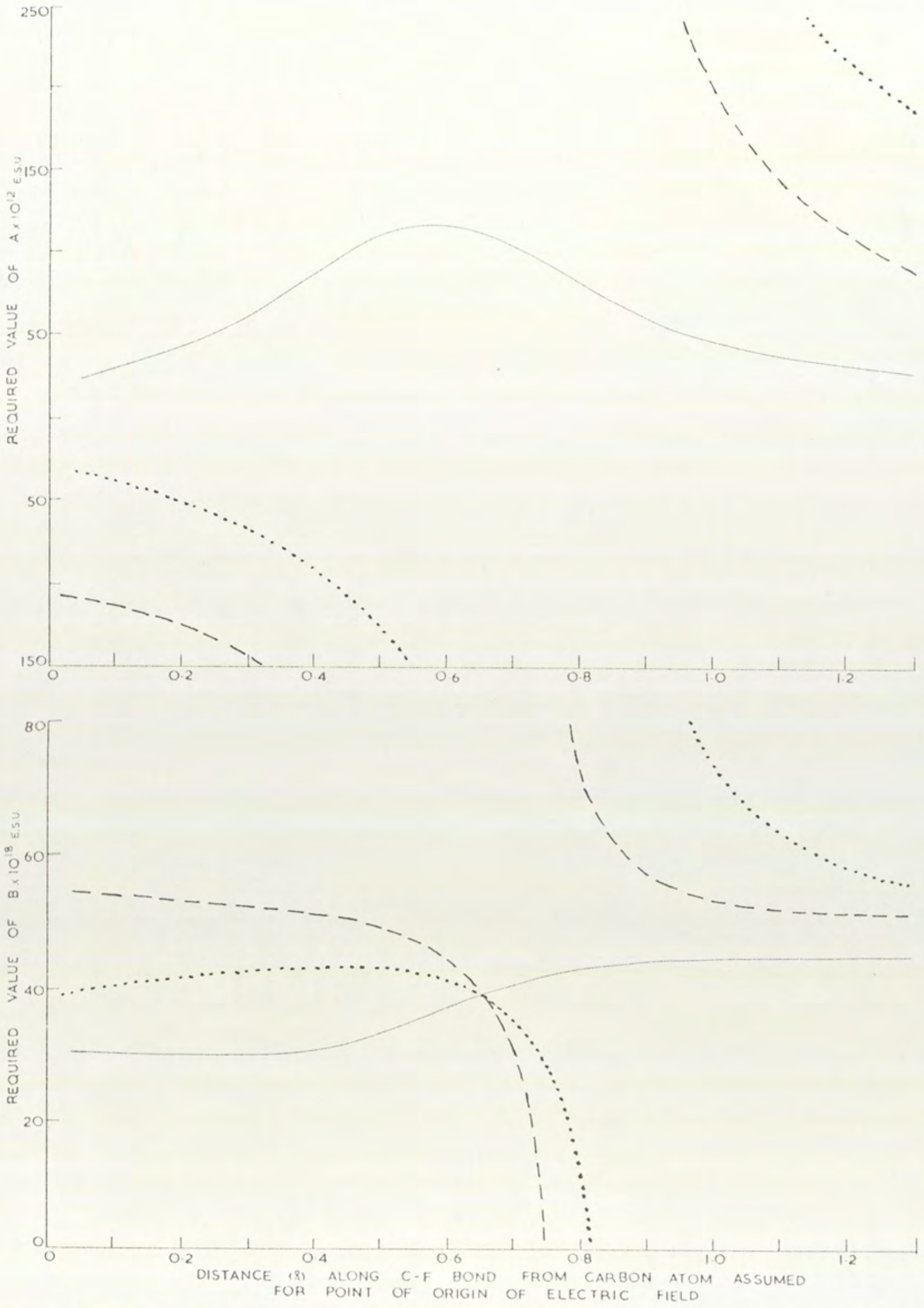


FIGURE 7.8 The dependence of the constants A and B for perfluorobicyclo(2,2,1)heptane on the location assumed for the point of origin of the electric field term associated with E in equation 7:2, while the term associated with $\langle E^2 \rangle$ is kept constant at 0.6Å from the carbon atom. Any contributions to $\langle E^2 \rangle$ from C-C bonds are excluded and $\delta_{\text{exo-endo}}$ is assumed + 1.54 p.p.m.

For identification of curves see page preceding figure 7:2.

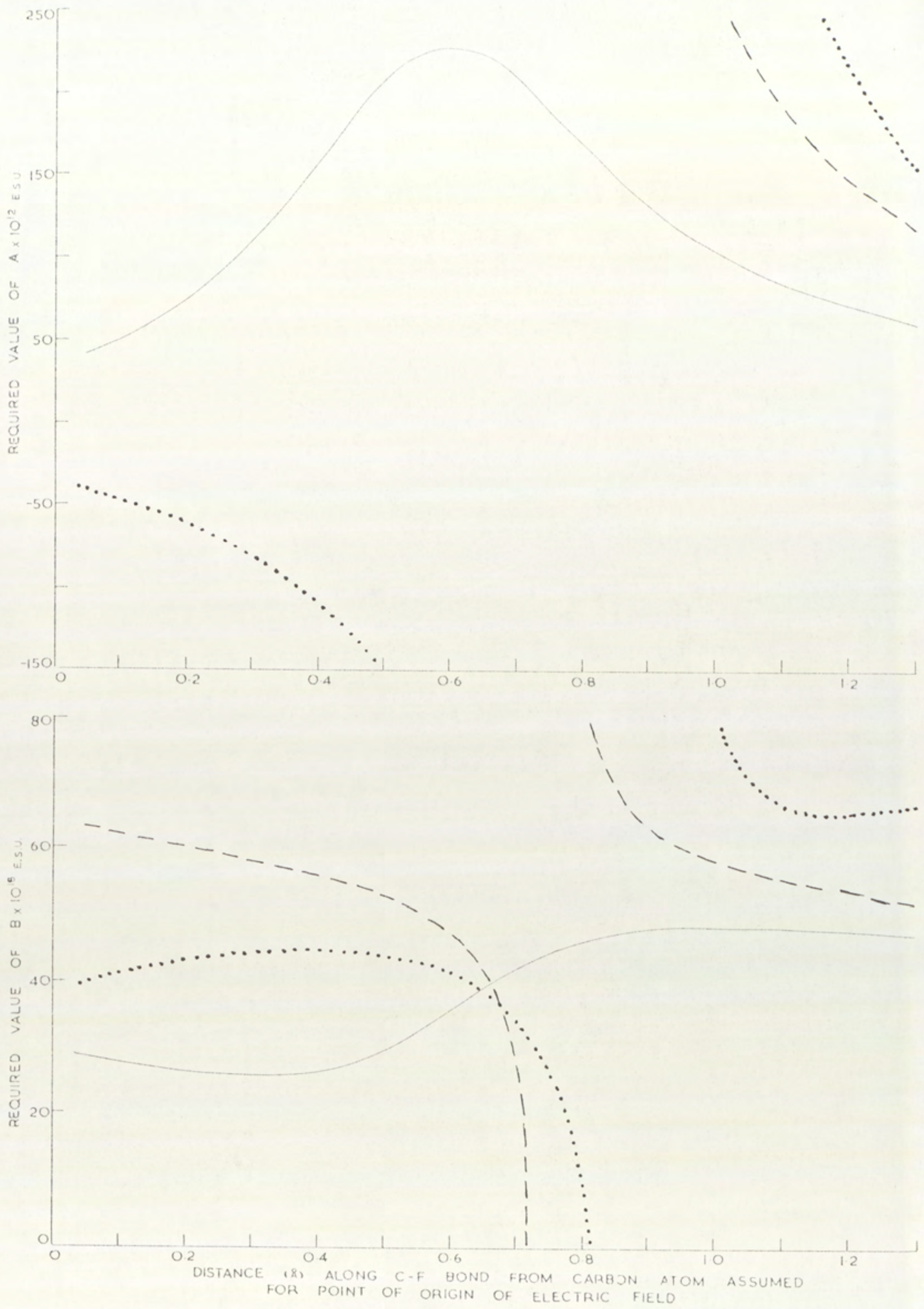


FIGURE 7.9 The dependence of the constants A and B for perfluorobicyclo(2,2,1)heptane on the location assumed for the point of origin of the electric field term associated with E in equation 7:2, while the term associated with $\langle E^2 \rangle$ is kept constant at 0.6Å from the carbon atom. Any contributions to $\langle E^2 \rangle$ from C-C bonds are excluded and $\delta_{\text{exo-endo}}$ is assumed - 1.54 p.p.m.
For identification of curves see page preceding figure 7:2.

included; there being no cross over for A but a point of near cross for B at c.a. 0.66Å along the C-F bond, giving a value of B = c.a. 38×10^{-18} e.s.u. irrespective of the sign chosen for the exo-endo shift. In the case of trans-perfluorodecalin, the plot for B is very similar to that in figure 7:4 showing no definite cross over, the plot for the values of A is slightly different to that in figure 7:4 but still shows no point of mutual intersection.

(iv) The two types of electric fields, the one associated with the A term and the other $<E^2>$ in the B term of equation 7:2 may have different origins in the C-F bond. Because in the B term, the contributions from $<E^2>$ generally far outweigh those from E^2, the intersection of the B curves of perfluorobicyclo(2,2,1)-heptane was taken to indicate the origin of the former field at 0.6Å along the C-F bond. This was fixed at this position and the origin of the field E varied along the bond. Contributions to $<E^2>$ from C-C bonds were not included in this solution and again it was found that, as expected, the solutions for B became nearly co-incident at a point 0.66Å along the C-F bond, but again there was nothing approaching a point of mutual intersection for the A solutions. These results are shown in figures 7:8 and 7:9 for both possibilities of the exo-endo shift.

In view of the results of the considerations (i) to (iv) above, it would appear that the calculations of ^{19}F shifts using equation 7:2 cannot be entirely satisfactory.

There can be little doubt that the time dependent dipole moments in C-F bonds give rise to electric fields at neighbouring fluorine nuclei and the best approximation available for these at present is given by equation 7:5. There seems, however, little justification for the step taken by previous authors on this subject, of including the electric field contribution due to $<E^2>$ together with that due to the square of the steady field as in equation 7:2. It is suggested that a more realistic approach would be to combine the electric field contributions as in equation 7:10.

$$\Delta\sigma = -X\Delta E_z - Y\Delta(E^2) - Z\Delta<E^2> \qquad 7{:}10$$

The constants have been labled X, Y and Z to avoid confusion with the A and B used previously. If the previous assumption that the 'square' field terms should be combined is justified, then in a solution for X, Y and Z equivalent values should be found for Y and Z.

The constants X, Y and Z in equation 7:10 have been solved for in a manner similar to that outlined above and the values required of these to satisfy the observed shifts have been studied as a function of the distance along the C-F bond taken for the point of origin of its associated electric fields. The molecule <u>trans</u>-perfluorodecalin has been chosen for this purpose since three combinations of electric field parameters are now required for solution of the three unknowns X, Y and Z. Using this molecule there are four ways of arranging the data in three sets for solution, i.e.

$(F_9 - F_{1ax})$ with $(F_9 - F_{1eq})$ with $(F_9 - F_{2ax})$

$(F_9 - F_{1ax})$ with $(F_9 - F_{1eq})$ with $(F_9 - F_{2eq})$

$(F_9 - F_{1ax})$ with $(F_9 - F_{2ax})$ with $(F_9 - F_{2eq})$

$(F_9 - F_{1eq})$ with $(F_9 - F_{2ax})$ with $(F_9 - F_{2eq})$

The values required for X, Y and Z in each of these combinations are plotted in figure 7:10 as the point of origin of the electric fields is varied along the C-F bond. The steady field and the square field due to fluctuating dipoles are assumed to originate at the same point and in this solution any possible contributions to $<E^2>$ from C-C bonds have been included. It is seen from figure 7:10 that there is a point of mutual intersection of the curves at a position c.a. 0.13Å from the carbon atom along the C-F bond giving values of $X = -108 \times 10^{-12}$ e.s.u., $Y = -978 \times 10^{-18}$ e.s.u. and $Z = +84.8 \times 10^{-18}$ e.s.u. This procedure has been repeated with the exclusion of any possible fields from C-C bonds to $<E^2>$ and the resulting values required for X, Y and Z plotted against distance along the C-F bond taken for the origin of its electric fields, are shown in figure 7:11. Again, it is seen that there is a point of mutual intersection at 0.629Å from the carbon atom along the C-F bond giving values of $X = -90 \times 10^{-12}$ e.s.u., $Y = -1270 \times 10^{-18}$ e.s.u. and $Z = +146.5 \times 10^{-18}$e.s.u. For both of the solutions discussed above, the required values for X, Y and Z were determined at 0.01Å intervals in the region of the crossover points to improve the accuracy to which the point of mutual intersection could be located and to determine the most reliable values for X, Y and Z in each case.

To evaluate which, if either, of these two solutions is realistic, the values derived for X Y and Z above have been used to predict the internal shifts in perfluorobicyclo(2,2,1)heptane and perfluorocyclohexane using the appropriate electric field parameters and with the C-F electric field originating at the appropriate position along the C-F bond in each case, i.e. with or without C-F C-F contributions to $<E^2>$. Inherent in this approach is the assumption that the values for X, Y and Z do not vary significantly for different molecules when virtually identical resonant

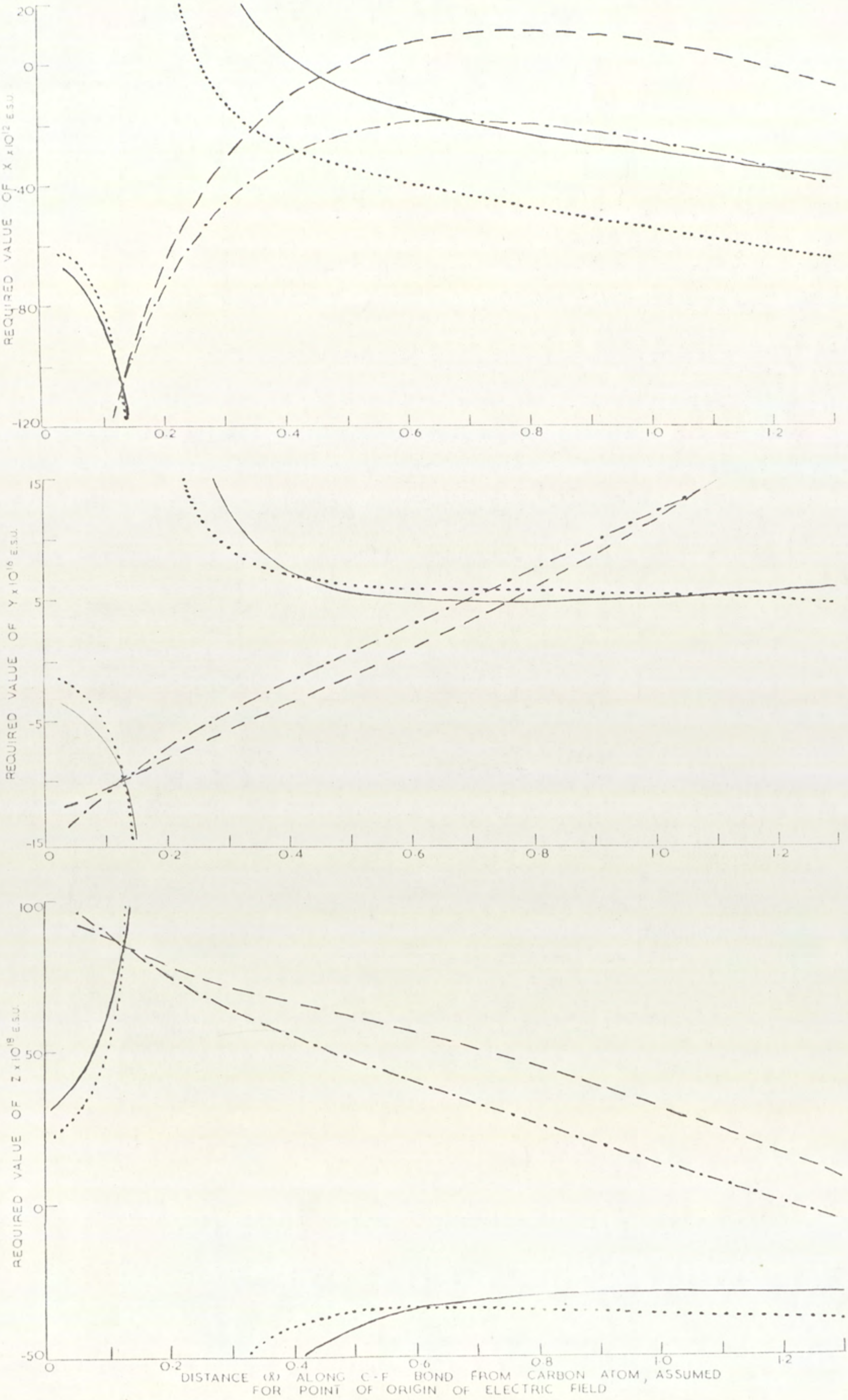


FIGURE 7.10 The dependence of the constants X, Y and Z in equation 7:10 on the location assumed for the point of origin of the electric fields associated with the C-F bonds in trans-perfluorodecalin. Any contributions to $\langle E^2 \rangle$ from C-C bonds are included.

For identification of curves see page preceding figure 7:2.

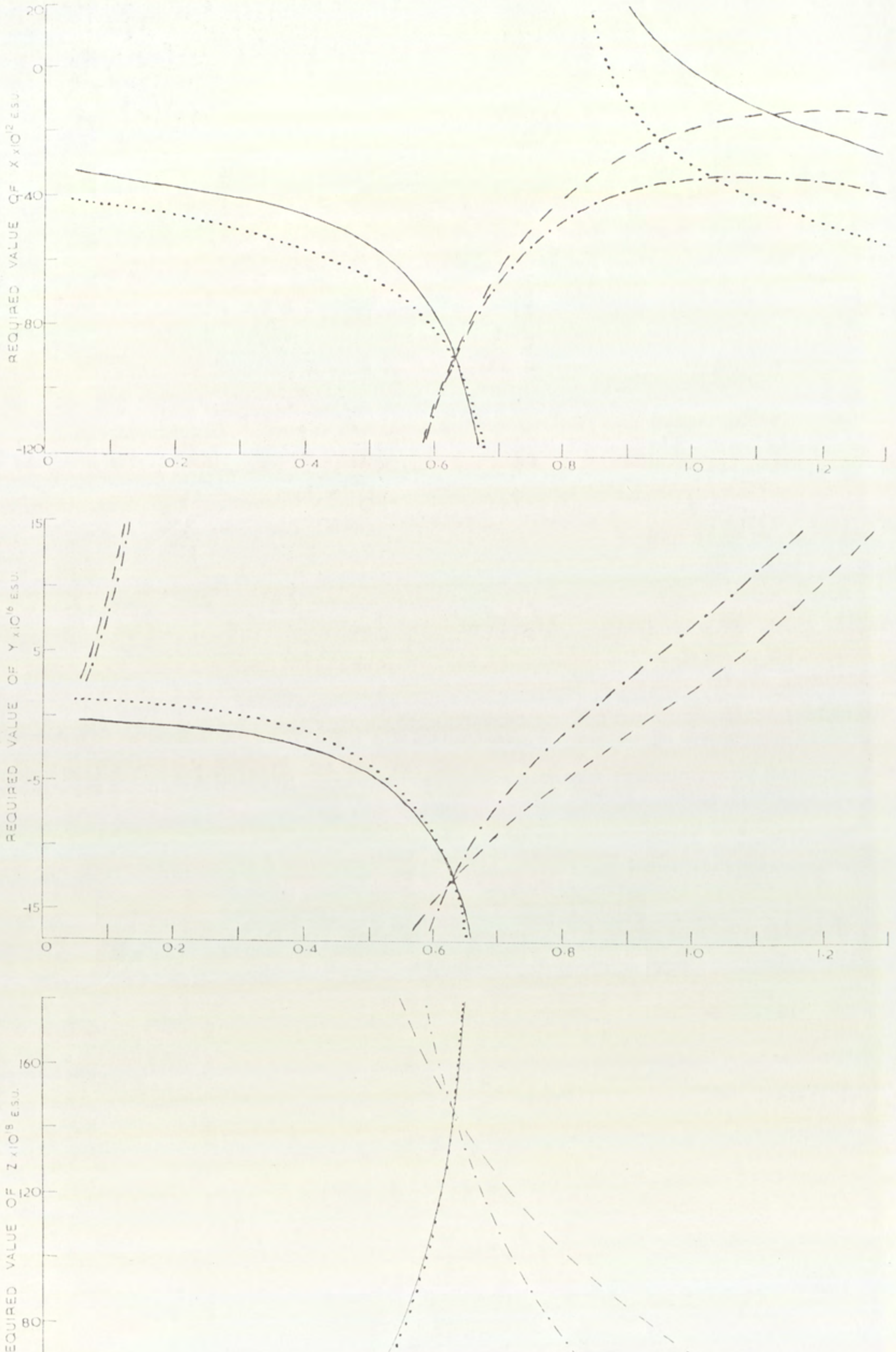


FIGURE 7.11 The dependence of the constants X, Y and Z in equation 7:10 on the location assumed for the point of origin of the electric fields associated with the C-F bond in trans-perfluorodecalin. Any contributions to $\langle E^2 \rangle$ from C-C bonds are excluded.
For identification of curves see page preceding figure 7:2.

fluorine nuclei are considered. The results for perfluorobicyclo(2,2,1)heptane with the bridgehead fluorines as the reference nuclei are given in table 7:8 together with the observed shifts. It is seen that the agreement is not very good for the case where the effect of C-C bonds are included in $<E^2>$ but for the case where they are omitted, agreement is very good and allows an assignment of the exo-endo shift in this compound. The axial-

Fluorine Nucleus	$\delta_{calc.}$ (p.p.m.)		$\delta_{obs.}$ (p.p.m.)
	Including C-C Contributions	Excluding C-C Contributions	
Perfluorobicyclo (2,2,1)heptane			
2,3,5,6 exo	158.4	107.4	102.3
2,3,5,6 endo	150.6	114.9	103.8
7	165.4	91.6	95.2
<u>trans</u>-perfluorodecalin			
1,4,5,8 ax		65.9	66.8
1,4,5,8 eq		58.0	58.8
2,3,6,7 ax		70.5	71.3
2,3,6,7 eq		48.7	49.4

<u>Table 7:8</u> Calculated and observed ^{19}F shifts for perfluorobicyclo(2,2,1)heptane and <u>trans</u>-perfluorodecalin, expressed relative to the $F_{1,4}$ and $F_{9,10}$ resonances respectively.

equatorial shift for perfluorocyclohexane is given for the two cases where the electric field is assumed to originate at 0.13Å and 0.629Å from the carbon atom by equations 7:11 and 7:12 respectively.

$$+0.3193 \times 10^{6} \times X - 0.0535 \times 10^{12} \times Y - 0.3311 \times 10^{12} \times Z \qquad 7{:}11$$

$$+0.4448 \times 10^{6} \times X - 0.0154 \times 10^{12} \times Y + 0.0371 \times 10^{12} \times Z \qquad 7{:}12$$

Substituting the appropriate values for X, Y and Z into these equations gives the calculated axial-equatorial shift in each case as:

(i) Including C-C bond contributions -10.25 p.p.m.

(ii) Excluding C-C bond contributions -15.06 p.p.m.

compared with the observed value[52] of -18.2 p.p.m. Again, the agreement in the case where possible contributions from C-C bonds to $\langle E^2 \rangle$ are neglected is very good, considering the inaccuracies inherent in the method. The observed and calculated shifts for trans-perfluorodecalin are also given in table 7:8.

7:5 Conclusions

The fact that intersection of the curves in figures 7:10 and 7:11 is found, together with the success achieved in calculating the shifts for the other molecules using the data derived from figure 7:11 is significant. This is because it indicates either that the basic assumption that σ(electronic) is zero is valid, or that deviations from this may be accommodated in the procedure adopted for calculating ^{19}F shifts even though this could be purely empirical.

With the exception of a previous attempt to calculate the axial-equatorial shift in perfluorocyclohexane, most of the previous calculations on fluorine shifts using an electric field approach have considered only the effect on a fluorine nucleus of substituting other halogens for neighbouring fluorine atoms. Equation 7:10 has been used to successfully predict all of the internal fluorine shifts in three different fully fluorinated molecules and it should be possible to extend the use of this equation to other fluorinated molecules. It would appear that the same values of X, Y and Z and the same point of origin of the C-F electric dipole (obtained from figure 7:11) can be used in compounds in which the hybridisation states of the various atoms are similar, provided C-C bond contributions to $\langle E^2 \rangle$ are omitted. From the calculations, it would appear that the point taken for the origin of the C-F electric dipole is very critical, only small deviations from the value of 0.629Å from the carbon atom causes large discrepancies between the predicted and observed shifts. This is obvious from an inspection of figure 7:11 where it is seen that the curves have a very steep gradient at and near to the point of mutual intersection. This could present a serious limitation to this method of predicting fluorine shifts, due to the idea mentioned previously that the C-F bond dipole and electrical centre in a $\geqslant$CF group may be different to that in a $>CF_2$ group due to inductive loading by the extra fluroine atom.

It is difficult to relate the values of A and B obtained by other workers from the pressure dependence of chemical shifts in gaseous fluorine compounds to the values obtained finally for X, Y and Z. This stems primarily from the fact that the other authors have assumed the validity of equation 7:2 so that for the polar solutes they considered, for which all three field terms are effective, A and B bear no relation to X, Y and Z. However, when non-polar solutes were examined, for which only the

$<E^2>$ term is effective, comparison of the value obtained for B with that for Z would be justifiable. The value obtained for Z is a factor of ten greater than that deduced previously for B although it is of the same sign.

It is interesting that in a recent attempt to calculate the effect of electric interactions on proton magnetic shielding by a perturbation method[121] an expression was derived consisting of three terms expressed as:

$$\Delta\sigma = \Delta\sigma(1) + \Delta\sigma(2) + \Delta\sigma(W) \qquad 7:13$$

where $\Delta\sigma(1)$ is the part proportional to the steady electric field strength at the proton, $\Delta\sigma(2)$ is dependent on the square of the steady field and its Z component and $\Delta\sigma(W)$ is a van der Waals contribution. Because of the similarity between equations 7:10 and 7:13, the validity of the former empirically derived equation is further confirmed, and its present use, for the determination of the point of action of bond electric dipole moments and values for X, Y and Z, justified. Consequently, it would appear that extensive use of equation 7:10 for calculation of fluorine shifts may be reasonable and therefore its application facilitates the assignment of the perfluorobicylco(2,2,1)heptane spectrum, in particular it confirms the empirical assignment of the exo-endo shift discussed in section 4:5 for this compound.

CHAPTER 8

Some Further Application of Electric Field Calculations

8:1 Introduction

In Chapter 7, it was seen that equation 7:10 could be used to successfully predict all of the internal shifts for three fully fluorinated molecules and also enabled a confirmation of the exo-endo shift in perfluorobicyclo(2,2,1)heptane. This approach will now be extended to other similar molecules and the effect of introducing substituents such as hydrogen and halogens other than fluorine will be investigated.

8:2 Prediction of ^{19}F Shifts in 1H-undecafluoro- and 1;4diH-decafluorobicyclo(2,2,1)heptane

Equation 7:10 together with the values derived in section 7:4 for X, Y and Z have been used to calculate the relative fluorine shifts in 1H-undecafluoro- and 1;4diH-decafluorobicyclo(2,2,1)-heptane. In this connection, the co-ordinate system[60] referred to earlier for bicyclo(2,2,1)heptane was adopted. The origin of the point dipole in the C-F bond has been taken at 0.629Å along the bond from the carbon atom, and the point dipole for the C-H bond has been assumed to originate from the bond centre, this position being chosen due to the lack of any evidence to suggest a better position. Any possible contributions to $<E^2>$ from C-C bonds were omitted from the calculations, for the reasons given in section 7:4. The various bond parameters used in the calculations are listed in table 7:5 and the electric field contributions at the various resonant nuclei are listed in table 8:1.

Resonant Nucleus.	$\Sigma E_z \times 10^{-6}$ (μ_{CH}=+0.5D)	$\Sigma E_z \times 10^{-6}$ (μ_{CH}=-0.5D)	$\Sigma E^2 \times 10^{-12}$	$\Sigma\langle E^2\rangle \times 10^{-12}$
1H-undecafluoro-				
4	0.3872	0.3902	0.0597	1.2689
7	0.3274	0.2809	0.2483	3.4931
2,6exo	0.3652	0.3534	0.2500	3.6154
2,6endo	0.3497	0.2876	0.2707	3.8894
3,5exo	0.3683	0.3442	0.2582	3.6573
3,5endo	0.4120	0.4223	0.2784	3.9081
1;4diH-decafluoro-				
7	0.2812	0.1882	0.2395	3.4652
2,3,5,6 exo	0.3463	0.3104	0.2485	3.6135
2,3,5,6endo	0.3584	0.3065	0.2691	3.8880
perfluoro-				
1,4	0.3776		0.0615	1.3014
7	0.3870		0.2707	3.7456
2,3,5,6 exo	0.4015		0.2730	3.8826
2,3,5,6endo	0.4248		0.2934	4.1248

Table 8:1 Evaluated contributions to the total electric fields at the resonant fluorine nuclei in perfluoro-, 1H-undecafluoro- and 1;4diH-decafluoro-bicyclo(2,2,1)heptane, assuming the C-F bond dipole to be 0.629Å along the bond from the carbon atom.

Nucleus	Calculated shift (p.p.m.)		Observed shift (p.p.m.)
	μ_{CH}^{+ve}	μ_{CH}^{-ve}	
Perfluoro-			
1	-	-	-
7	91.63	91.63	95.19
2,3,5,6 exo	107.37	107.37	102.25
2,3,5,6endo	114.86	114.86	103.79
1;4diH-decafluoro-			
7	103.95	112.23	113.71
2,3,5,6 exo	108.34	111.57	110.05
2,3,5,6endo	121.40	128.77	121.65
1H-undecafluoro-			
4	1.02	0.76	7.90
7	92.65	96.75	103.56
2,6 exo	105.03	106.09	110.33
2,6endo	120.36	126.95	118.41
3,5 exo	100.46	102.63	100.64
3,5endo	107.69	106.77	106.61

Table 8:2 Calculated and observed shifts for perfluoro-, 1;4diH-decafluoro- and 1H-undecafluoro-bicyclo(2,2,1)heptane, evaluated with $\mu_{CH} = \pm 0.5D$. All shifts are quoted relative to that of the bridgehead fluorines in perfluorobicyclo(2,2,1)-heptane.

There is some difficulty in calculations involving hydrogen substituents due to the lack of consistent data for the C-H bond dipole moment[119], both in its magnitude and sign in different molecular situations. It appears[119] that a small value of c.a. 0.5 D for a hydrogen atom attached to a tertiary carbon atom would not be unreasonable, and the calculations have been performed using both the values ± 0.5 D.

The calculated shifts relative to the bridgehead fluorines in perfluorobicyclo(2,2,1)heptane are compared with the observed shifts in table 8:2. It can be seen that very good agreement is obtained whichever sign is chosen for μ^{CH} in this type of molecule and there is little to choose between the two sets of results to advocate the use of either sign. Whilst nothing can be deduced about the sign of μ^{CH} from this investigation, it would appear that its magnitude is small when the carbon atom of the bond is a tertiary one. Together with the previously reported results for trans-perfluorodecalin and perfluorocyclohexane given in section 7:4, the three fluorobicyclo(2,2,1)heptanes give five molecules for which all of the internal fluorine screenings can be satisfactorily explained by a consistent approach, using equation 7:10.

8:3 ^{19}Fluorine Nuclear Screening and the Electronegativity of Substituents.

The ^{19}F resonance spectra of a series of highly fluorinated bicyclo(2,2,1)heptanes with other halogens at the bridgehead positions were discussed in section 4:3. It can be seen from the data given in table 4:1 that there are very definite trends in the shifts of a fluorine nucleus at any specific position in the fluorobicyclo(2,2,1)heptanes with the electronegativity of the bridgehead substituent. For example, increasing the electronegativity of the bridgehead fluorine substituents generally leads to increased shielding of the bridge fluorines. This variation is inconsistent with the results of a study of binary fluorides[122; 123], from which it was concluded that increasing the electronegativity of the substituent decreased the screening of a fluorine nucleus. A similar apparent reversal of expected shielding trends with the electronegativity of the substituents is exhibited also by both the exo and endo fluorine nuclei in these compounds and by the remaining bridgehead fluorine in the monosubstituted compounds. Where the substituent is hydrogen, the shifts do not fall into the pattern produced by halogen substituents.

Substituent electronegativity effects have been found in some cases previously to be opposite to that expected[124,125,126] whereas corresponding anomalies in the variation of proton shifts appear to be less common. This may be attributable to the fact that essentially different mechanisms are thought to predominate in producing proton and fluorine shifts (see Chapter 3). To rationalize this it is necessary to investigate the composition of the total screening σ of any nucleus. Neglecting any solvent effects, the screening may be split up into four components (as in section 3:1) and represented by an expression such as

$$\sigma = \sigma_{dia} + \sigma_{para} + \sigma_{mag} + \sigma_{del} \qquad 8:1$$

The screening of a nucleus at a particular position in a series of molecules which differ only in the substituent at one other position, is modified in three ways by changing the substituent providing that σ_{del} is zero, which is a reasonable assumption for most saturated molecules. Firstly, changing the electronegativity of the substituent will modify the electron density at the nucleus and hence σ_{dia}. Secondly, the electric fields produced by the different bonds to the substituents can differ and result in modifications to both σ_{dia} and σ_{para}. Thirdly, changes in magnetic susceptibility characteristics of the bonds to the substituents can modify σ_{mag}. When the resonant nucleus is a proton, the changes in σ_{dia}, σ_{para} and σ_{mag} on changing the substituent may be of similar significance and whilst it has often been assumed that changes in σ_{mag} have the dominant effect in proton shift variations, it has been indicated in Chapters 5 and 6 that changes in all three terms may be explained by variations in the apparent bond magnetic anisotropies. It is evident that although possible, only under certain limiting conditions can absolute correlations of substituent electronegativity with proton shifts be expected. When fluorine is the resonant nucleus, changes in σ_{para} dominate the observed shifts, and it might therefore be considered surprising that successful correlations between substituent electronegativities and shifts have been achieved. Whilst it is not always expected to find correlations of this type, that are consistent with the long range inductive effects of the substituents, it it quite probable that more complex relationships can occur fortuitously. That this is possible is evident when it is considered that trends in substituent electronegativities are often accompanied by trends in the values of parameters characteristic of the bonds to the substituents. In particular, parameters such as electric dipole moment, polarisability and ionisation potential, on which intramolecular electric fields depend, vary in this way. It is not altogether unexpected therefore, that in many cases an apparent correlation exists between the substituent electronegativities and the shielding of an adjacent nucleus, even though the shielding may be considered to have its origin in intramolecular electric fields. If this is so, a particular trend in substituent electronegativity could result, as often observed, in a progressive increase <u>or</u> decrease in the shielding of an adjacent nucleus, depending on the relative magnitude of the various terms contributing to the electric field at that nucleus. It has been shown in sections 7:4 and 8:2 that ^{19}F screenings in some saturated cyclic molecules may be accounted for by equation 7:10. This equation has now been used in an attempt to explain the trends in shielding of the various nuclei with variation of the bridgehead substituent in the perfluoro-, 1H-undecafluoro-, 1Br-undecafluoro- and 1I-undecafluoro-bicyclo(2,2,1)heptane, using the values of X, Y and Z proposed in section 7:4. In each case, the electric field associated with the substituent is assumed to originate at a point 0.66Å along the bond from the carbon atom, and although a better position has been evaluated for the C-F bond, this has not been used in these calculations due to the uncertainty in the point of origin in the other bonds. It is primarily for the last reason that only the series of mono-substituted compounds were considered so that accumulative inaccuracies could be avoided. The values for the various bond parameters required for equation 7:10 are given in table 7:5. For each nucleus in each molecule, the shielding relative to the corresponding nucleus in the perfluoro compound has been evaluated and it is found that in general, the numerical agreement between observed and

Nucleus	Shift (p.p.m.) relative to corresponding nucleus in perfluorobicyclo(2,2,1)heptane						
	1H			1Br		1I	
	$\mu_{CH}+0.5$	$\mu_{CH}-0.5$	obs.	calc	obs.	calc	obs.
F4	+0.8	+0.6	+7.9	+6.2	+7.3	+10.3	+10.0
F7	+9.4	+13.9	+8.5	+85.0	+5.6	+136.6	+9.0
F2,6 exo	+6.1	+7.9	+8.1	+112.5	+3.6	+177.7	+5.5
F2,6endo	+11.6	+17.1	+8.6	+64.0	+16.6	+119.8	+26.5
F3,5 exo	+3.2	+5.2	+4.4	+7.3	+3.0	+13.1	+0.3
F3,5endo	+0.8	-0.1	+2.8	+6.4	+9.9	+10.6	+5.1

Table 8:3 Calculated and observed shifts in mono-substituted fluorobicyclo(2,2,1)heptanes.

Nucleus	Influence of substituent on shielding	
	Calculated	Observed
F4	F>H>Br>I	F>Br>I>H
F7	F>H>Br>I	F>Br>H>I
F2,6 exo	F>H>Br>I	F>Br>I>H
F2,6endo	F>H>Br>I	F>H>Br>I
F3,5 exo	F>H>Br>I	F>I>Br>H
F3,5endo	F>H>Br>I	F>H>I>Br

Table 8:4 Calculated and observed order of effects of bridgehead substituents on the shielding of neighbouring fluorine atoms.

calculated screenings is very poor, as shown in table 8:3. However, this is not surprising considering the inaccuracies in the approach that stem primarily from the uncertainty in the point of origin of the electric fields. It is interesting, however, to compare the orders of shielding observed for a nucleus in any position in the four compounds considered with those calculated. The orders of relative shieldings are given in table 8:4 from which it can be seen that a hydrogen substituent generally causes the calculated screening of fluorines at other positions in the molecule to fall out of step with the observed sequence. Changing the sign, which is uncertain, of the C-H dipole has little effect on this. The predicted orders of relative screenings when the substituent is a halogen agrees with the observed order, except for the $F_{exo\ 3,5}$ and $F_{endo\ 3,5}$ nuclei, where the differences between the calculated and observed screenings that are out of sequence are sufficiently small to be easily accounted for by the position of origin of the electric fields not being known. It would appear that the correlation of ^{19}F shifts with substituent electronegativity may be usefully superceeded by the more practical correlation with electric fields associated with the bonds to the substituents. This is indicated further by the results of the following section.

8:4 Some Electric Field Calculations for Fluorobicyclo(2,2,1) Heptenes.

The relative shielding of the exo-endo and anti-syn fluorine nuclei were discussed empirically in section 4:7 for a series of fluorobicyclo(2,2,1)heptenes. It is now possible to make a semi-quantitative estimate of these relative shieldings, using the electric field approach to fluorine nuclear screening. In order to calculate the resultant electric fields at the resonant nuclei, an approximate co-ordinate system was estimated for the bicyclo-(2,2,1)heptene skeleton based on that proposed by Wilcox[60] for bicyclo(2,2,1)heptane. The fluoro-olefinic nuclei were assumed to lie on a line bisecting the corresponding exo and endo nuclei in the saturated compound, and an allowance was made for the C=C bond being shorter than the corresponding C-C bond. However, in trial calculations, it was found that the electric fields arising from the fluoro-olefinic bonds evaluated by this method were sufficiently close to those obtained by simply taking the average of the fields produced by the corresponding bonds to the exo and endo atoms in the saturated compounds, to justify the latter, simpler approximation being used. It was further assumed that the differences between the co-ordinates defining the remaining geometries of the saturated and unsaturated molecules are sufficiently small to be neglected in view of the necessarily approximate nature of the calculations.

The appropriate electric fields for the relevant nuclei were calculated using the values for the molecular parameters given in table 7:5 the values for X, Y and Z in equation 7:10 are those deduced in section 7:4 and the origin of the electric fields associated with the C-F bond located at 0.629Å from the carbon atom in the bond. The C-C bond contributions to the $\langle E^2 \rangle$ term of equation 7:2 were neglected for the reasons given in section 7:4. Using the above criteria, it has been calculated that in perfluoro-bicyclo(2,2,1)heptene, the bridge fluorine anti to the double bond should be 2.72 p.p.m. less shielded, and that syn to the double bond should be 27.04 p.p.m. more shielded than the corresponding fluorines in perfluorobicyclo(2,2,1)heptane. Whilst the compound perfluorobicyclo(2,2,1)heptene itself, was not available for any experimental measurements to be performed, any pair of saturated and unsaturated compounds having the same substituents at the bridgehead should suffice for comparison. This is because a bridgehead substituent should affect almost equally the screening of the anti and syn nuclei, due to the almost symmetrical disposition of these two nuclei with respect to the one carbon bridge. The same bridgehead substituent in the corresponding bicyclo(2,2,1) heptane molecule should also affect the screening of the bridge fluorine nuclei to an extent very similar to that for the bridgehead nuclei in the unsaturated molecule. It can be seen from tables 4:1 and 4:4 that there are four pairs of molecules which satisfy this criterion, namely those having 1H-, 1H;4H-, 1Br-, and 1I- substituents. For each of these pairs, one of the bridge fluorines in the unsaturated molecules is deshielded by 5.3-8.3 p.p.m. and the other shielded by 14.6 - 19.9 p.p.m. relative to the bridge fluorine in the corresponding saturated compound. These shifts are in agreement both in sign and in approximate magnitude with those calculated, and this therefore suggests that the fluorine syn to the double bond gives rise to the high field lines and that anti to the double bond to the low field lines in the appropriate AB band in each of the spectra. The results of this calculation are in agreement with the empirical assignments given in section 4:7.

The exo-endo shift derived empirically for the fluorobicyclo-(2,2,1)heptenes in section 4:7 is a little uncertain and an attempt to predict this shift on a semi-quantitative basis for one of the compounds, will now be given. The screening difference between the exo and endo fluorine nuclei at positions 5 and

6 in 1;4diH-octafluorobicyclo(2,2,1)heptene have been evaluated using equation 7:10 and the parameters used in the evaluation of the anti-syn shift above. The dipole giving rise to the electric field associated with the C-H bond has been assumed to originate from the mid-point of the bond. It has been calculated that in the unsaturated compound, the endo are 10.36 p.p.m. more shielded than the exo fluorines (observed shift 1.92 p.p.m.). Whilst the numerical agreement between the calculated and observed shifts is not very good, it does suggest that the exo-endo shift in 1;4 diH-octafluorobicyclo(2,2,1)heptene, is reversed relative to that in 1;4diH-decafluorobicyclo(2,2,1)heptane, which is in agreement with the empirical assignment for this compound.

8:5 A Correlation Between Intramolecular Electric Fields and Nuclear Screening in Some Highly Fluorinated Cyclohexanes

There have been reported a number of rules concerning the axial-equatorial shift in fluorocyclohexanes[63] when neighbouring fluorines are replaced by hydrogen atoms. The rules state that

a) In a group flanked by CF_2 groups, $\delta_{ax} - \delta_{eq} = 17.7$ p.p.m. (c.f. 18.2 p.p.m. observed for perfluorocyclohexane[52])

b) Replacement of an α axial fluorine atom by hydrogen shields F_{ax} by 2.3 p.p.m. and deshields F_{eq} by 15.0 p.p.m.

c) Replacement of an α equatorial fluorine atom by hydrogen deshields F_{ax} by 4.3 p.p.m. and deshields F_{eq} by 10.5 p.p.m.

d) Substitution of an α equatorial $-CF_3$ group for a fluorine atom deshields by 5.7 p.p.m. and deshields F_{eq} by 10.9 p.p.m.

e) Substitution of a β axial hydrogen atom for a fluorine atom shields F_{eq} by c.a. 4 p.p.m.

It may be possible to explain these rules in terms of the electric fields given by equation 7:10. Rule (a) has already been assessed and a value of $\delta_{eq - ax}$ = 15.1 p.p.m. obtained. No attempt has been made at this stage to appraise rule (d) due to the difficulty in handling the geometrical parameters required by a CF_3 group. In evaluating the effect of hydrogen substituents, the values $\pm$ 0.5 D for the C-H dipole were used in the first instance, together with the values of P and I given in table 7:5, and the electric field was assumed to originate from the mid-point of the C-H bond. The shieldings predicted by this method

Position of Hydrogen	Effect on axial fluorine			Effect on equatorial fluorine		
	$\mu^{CH}{}_{+}$	$\mu^{CH}{}_{-}$	obs.	$\mu^{CH}{}_{+}$	$\mu^{CH}{}_{-}$	obs.
2ax	+14.3	+ 9.0	-2.3	+22.15	+24.4	+15.0
2eq	+22.0	+24.3	+4.3	+23.0	+26.9	+10.5
3ax	-16.3	-20.9	-4.0	-	-	-

Table 8:5 Calculated and observed effects on fluorine screening due to the substitution of one hydrogen atom into perfluorocyclohexane. (Screenings in p.p.m.)

are collected in table 8:5. Replacement of an α axial fluorine by hydrogen predicts that F_{eq} should be deshielded by 14.3 p.p.m. and F_{ax} deshielded by 22.1 p.p.m. if μ^{CH} is +0.5 D and F_{eq} is deshielded by 9.0 p.p.m. and F_{ax} deshielded by 24.4 p.p.m. if the alternative value μ^{CH} = -0.5 D is used. At first sight, these values seem rather disappointing when compared to the observed shifts. However, the calculations do predict that the axial-equatorial shift is decreased by 7.8 p.p.m., or 15.4 p.p.m. (depending on whether μ^{CH} is taken as + or - 0.5 D respectively), compared with the observed decrease of 17.3 p.p.m. The calculated effects for substitution of an α equatorial fluorine by hydrogen predicts a deshielding of either 22.0 p.p.m. or 24.3 p.p.m. for the axial and a deshielding of either 23.0 p.p.m. or 26.9 p.p.m. for the equatorial fluorines depending on whether μ^{CH} is positive or negative. Direct comparison with the observed shieldings is again not good (axial and equatorial fluorines deshielded by 4.3 and 10.5 p.p.m. respectively) but the magnitude of the relative screenings is again in reasonable agreement with the observed value. Substituting a β axial hydrogen atom for a fluorine atom gives a predicted shielding of F_{eq} by 16.3 p.p.m. or 20.9 p.p.m. compared with the observed shielding of c.a. 4 p.p.m. and whilst the magnitude of the calculated and observed shifts are once more not very good, the signs are in agreement.

The poor agreement noted above could be due to the approximations made for the magnitude of the C-H bond dipole and the position of origin of the point dipole within the bond. It would appear possible to investigate whether a better value for the C-H bond dipole and its point of origin might be evaluated from these compounds and such an investigation has been attempted. For a particular value of μ^{CH} and location of the equivalent dipole, the effect on the α axial and equatorial fluorines has been calculated when a fluorine is replaced by hydrogen in either the axial or equatorial position. This has been repeated (μ^{CH} constant) for a number of points of origin in the bond assumed for the C-H bond dipole and the calculated shift for each of the four cases considered (given in b and c above) plotted against the position in the bond assumed for the point dipole. The best position for the dipole to act may then be obtained from each graph by interpolation as that position which gives the correct value for the observed shift for the particular point chosen for the origin of the C-H dipole.

The C-H bond dipole was then varied between + and -1.0 D and the procedure above repeated for each value chosen. The values for μ were then plotted against the best distance obtained for the origin of the C-H dipole from the method outlined above and these plots are shown in figure 8:1. It would be expected that the four lines should intersect, or nearly intersect at a point representing the best value of, and the origin of its dipole. However, it can be seen that there is no such point of mutual intersection in figure 8:1. An examination of this figure suggests that it is probable that μ^{CH} should be in the range -0.5 to -0.9 D and the point of origin of the dipole between 0.65Å and the hydrogen atom in the C-H bond, although no appreciable significance should be attached to this result at present.

It appears that the calculations involving one hydrogen substituent in the fluorocyclohexanes are not as successful as those involving one or two hydrogen substituents in the fluorobicyclo(2,2,1)heptanes. This may, in part, be due to the different inductive effects of the differing numbers of fluorine atoms on the properties of the bond to the hydrogen atom directly attached to the same carbon as the fluorine in the cyclohexane cases. It seems quite possible that the highly electronegative fluorine atom attached to the same carbon could seriously effect the electron distribution in the C-H bond and hence its polarisability and ionisation potential and would also affect the position of origin of any electric fields that may be associated with a C-H bond, compared to the case where the hydrogen is attached to a tertiary carbon atom.

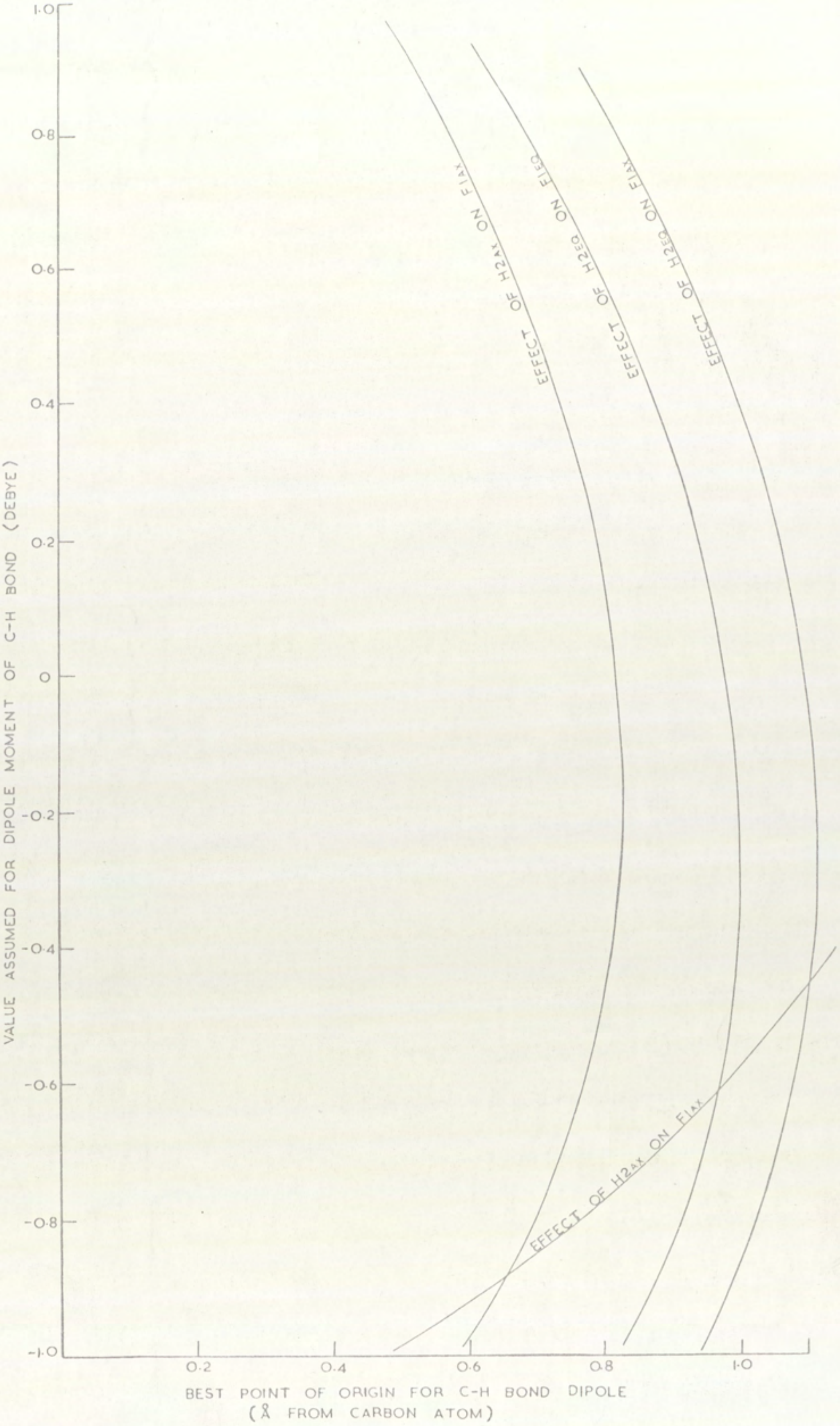


FIGURE 8.1 Plot of best point of origin for C-H bond dipole versus value assumed for dipole moment of C-H bond in mono hydrogen substituted fluorocyclohexanes.

8:6 Conclusions

The empirical electric field approach developed in section 7:4 has been applied to a number of highly fluorinated molecules with varying degrees of success. The calculations involving fully fluorinated molecules are quite successful and the introduction of one or two hydrogen atoms attached to a tertiary carbon can be treated by this approach. However, when halogens other than fluorine are introduced, or when hydrogen is present and attached to the same carbon as a fluorine atom, the results are not so encouraging. This could be due to the lack of knowledge of critical values for the bond parameters for these C-X bonds and the position of origin of the point dipole within the bond. Any small errors in the bond parameters chosen for the C-F bonds will have been accommodated in the values of X, Y and Z deduced for equation 7:10. This, of course, means that the constants X, Y and Z have no real physical significance and the point of origin for the C-F bond dipole is only an approximation which together with the values derived for X, Y and Z gives the best overall fit. It will therefore be difficult to include other halogens into this scheme, as this would require that values representing the ionisation potential, polarisability and dipole moment of these bonds would be required that are compatible with the values of X, Y and Z derived from a study of C-F bonds. It would be surprising if such values would correspond with those derived by other physical methods. The apparent success achieved when C-H bonds are substituted into the fluorobicyclo(2,2,1)heptane molecule could in part be due to the apparently small value of μ^{CH} that is required.

The conclusions that have been drawn from the results reported in Chapters 5-8 may be summarized. Proton shifts in a range of saturated molecules may be satisfactorily accounted for by the apparent anisotropy in the magnetic susceptibility of neighbouring bonds, but when considering ^{19}F screenings, this mechanism could account for only an insignificantly small portion of the observed shifts. It has, however, been shown that ^{19}F shifts in a range of highly fluorinated molecules may be explained in terms of the resultant electric fields at the various resonant nuclei.

It is interesting to speculate that ^{13}C shieldings in saturated molecules may also be capable of explanation in terms of intramolecular electric fields, and it is proposed that the method used herein to explain ^{19}F screenings should now be extended to include ^{13}C screenings. The modification of the n.m.r. equipment available to enable the observation of ^{13}C resonance is discussed in the following chapter, as a preliminary to undertaking such an investigation.

CHAPTER 9

Some Attempts to Observe ^{13}C Resonance as a Preliminary to a Possible Interpretation of ^{13}C Shifts in Terms of Intramolecular Electric Fields

9:1 Introduction

The majority of n.m.r. studies are carried out on organic compounds, by observing the resonances from hydrogen or fluorine substituents. As carbon is naturally present in the form of 98.9% ^{12}C and only 1.1% ^{13}C, the latter nuclear species has little effect on the appearance of ^{1}H or ^{19}F spectra due to its low abundance. The ^{12}C isotope, of course, has no effect on the appearance of the spectrum as for this $I = 0$. However, ^{13}C has a nuclear spin of $\frac{1}{2}$, and since by definition all organic compounds contain carbon, this nucleus offers the possibility of providing much valuable information regarding molecular skeletal structure. Such studies have been hindered until recently by the difficulty in observing ^{13}C resonances due to the low natural abundance, low sensitivity (1.59×10^{-2} compared with the proton at the same field strength) and ease of saturation. This latter problem, coupled with the need to use high R.F. power to be able to observe the signals from such a low abundance isotope, presents great experimental difficulties. The problems are being overcome by the introduction of magnets capable of operating at higher field strengths and by the use of time averaging computers to enhance the signal to noise ratio. It is also possible to enrich the sample with ^{13}C, however, this is very expensive and in some cases undesirable. The use of a low abundance isotope can be useful, as with ^{13}C there is only a 1.1% chance that the carbon atom adjacent to a ^{13}C atom will also be of the ^{13}C isotope, so that the effect of ^{13}C-^{13}C spin couplings in the resulting spectrum will be negligible, and such spectra are generally first order[127], and therefore easy to analyse.

There have been few attempts to correlate ^{13}C shieldings with molecular structure, possibly due to the lack of experimental data for such correlations, but it has been observed that ^{13}C chemical shifts are spread over a range[127,128] of 300-500 p.p.m. Carbon nuclei in many of their compounds are quite isolated and are therefore only slighly influenced by interactions with other molecules. Spiesecke and Schneider[129] have measured the ^{1}H and ^{13}C chemical shifts for a series of alkyl-X and aryl-X compounds, and have attempted to rationalise the observed shifts in terms of intramolecular parameters. They correlated the observed shifts with substituent (X) electronegativity, and suggested that deviations from the correlation may be explained by bond magnetic anisotropy contributions. However, these authors recognise that this is not the complete answer, but were unable to suggest a better mechanism. In aromatic compounds, correlations have been proposed between ^{13}C chemical shifts and π electron densities[130,131] and chemical reactivity parameters[132] such as Hammett σ constants - such correlations showing only a limited success.

It has been shown that the paramagnetic contribution to nuclear screening (see equation 3:4) must be the major factor influencing ^{13}C shieldings[133-136]. A molecular orbital approach to the calculation of ^{13}C chemical shifts by Karplus and Pople[137] lead to the conclusion that the local paramagnetic term would be expected to dominate, and it was shown that the shielding is a function of the free valance of the atom under consideration and of the polarity of the sigma bonds to it. Recently, Feeney, Sutcliffe and Walker[66] have shown the existence of a correlation between differences in ^{13}C shieldings and the intramolecular electric field given by

$$\delta = -B\Delta\langle E^2\rangle \qquad 9{:}1$$

This latter consideration, together with the ideas proposed in section 8:3 regarding the interpretation of ^{19}F shifts in terms of intramolecular electric fields, rather than substituent electronegativities, suggests that the screening of ^{19}F and ^{13}C nuclei might be largely due to the same mechanism. It would be an interesting extension of the work reported in Chapters 7 and 8 to enquire into the possibility of interpreting ^{13}C shifts in terms of an equation similar to equation 7:10. Since the constants X, Y and Z are a function of the bond containing the resonant nucleus (i.e. of the electron distribution about that nucleus), these constants would need to be evaluated for the case of ^{13}C using an approach similar to that adopted for the investigation of ^{19}F screenings. This would necessitate the observation of ^{13}C chemical shifts in suitable molecules of known geometry and it would appear that rigid cyclic molecules or cyclic molecules which interconvert between two conformers would be particularly suitable for this investigation. Very little work has been published on the ^{13}C shifts in such compounds and it would appear necessary to be able to measure ^{13}C chemical shifts before such an investigation can be undertaken. Subsequent sections outline attempts to expedite this.

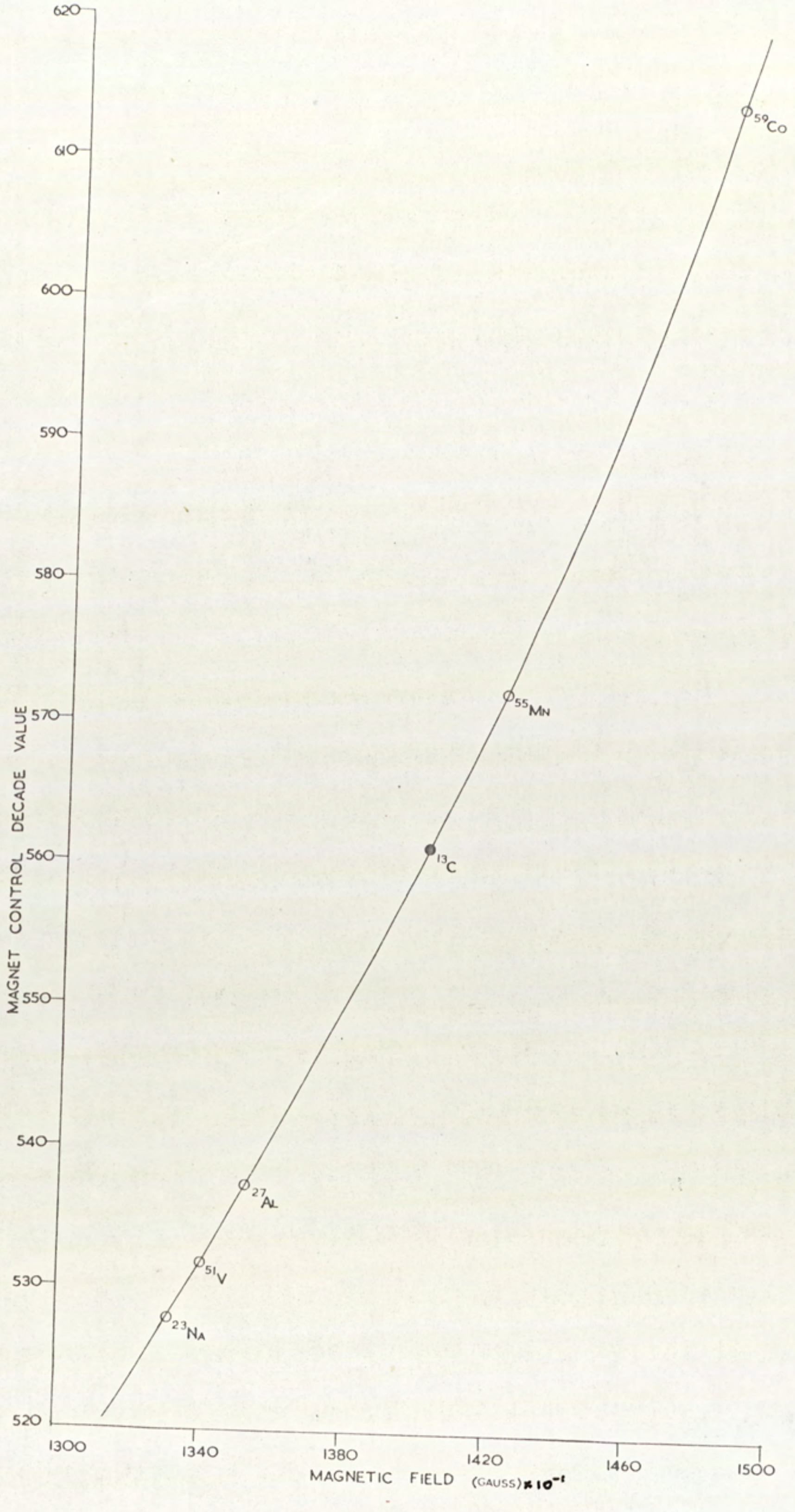


FIGURE 9.1. Plot of magnetic field (gauss) required to satisfy known resonance condition for various nuclei at 15 Mc.sec.$^{-1}$ versus magnet control decade value for A.E.I. RS2 spectrometer.

9:2 Attempts to Observe ^{13}C Resonance Signals with the A.E.I. R.S.2 Spectrometer

The R.S.2 spectrometer having an electromagnet, should be capable of detecting resonance signals from ^{13}C nuclei, although the manufacturers of this instrument have no record of this nucleus ever being observed with their equipment. There was available a radiofrequency source operating at 15Mc.sec.$^{-1}$ and suitable for ^{13}C investigations. This necessitated an applied field of c.a. 14000 gauss, very close to that required to observe proton signals at 60Mc.sec.$^{-1}$. The necessary probe and bridge assembly for operation at 15Mc.sec.$^{-1}$ were also available, the former requiring sample tubes of 9mm. diameter. It was anticipated that considerable difficulty would be experienced in locating the very weak signal from natural abundance ^{13}C, and therefore it was necessary to locate the field quite precisely before attempting to search for a ^{13}C resonance. This problem was overcome by calibrating the magnetic field in the region of 14000 gauss using resonances which could be easily located. In practise, the decade settings on the magnet control unit were plotted against the field required to observe the following resonances: ^{27}Al, ^{23}Na, ^{55}Mn, ^{59}Co and ^{51}V. Concentrated or saturated solutions of the compounds listed in table 9:1 were used for this calibration. The field versus decade settings are plotted in figure 9:1 from which it should be possible to accurately locate the ^{13}C resonance position by interpolation. The internal chemical shifts in the compounds[138-140] which may amount to several hundred p.p.m. should not seriously affect the accuracy of this method, as at best it would only be possible to locate the ^{13}C resonance position to ± 500 p.p.m. Some degree of 'operator technique' is required when using this method of field calibration, as the actual field produced for a given decade setting depends somewhat on the manner in which a particular setting is approached, and it was necessary to adopt a standard technique. It was found convenient to first locate the ^{59}Co resonance and then drop the field onto the resonance condition required for each of the other nuclei in turn, this method giving good reproducibility. The field homogeneity was adjusted using either ^{27}Al or ^{55}Mn signals, as these gave relatively sharp signals from the solutions studied.

After developing this field calibration technique, it was attempted to locate the natural abundance ^{13}C signal from benzene, this being a particularly suitable sample as it contains 92% of carbon, and each molecule has a c.a. 6.6% chance of containing one ^{13}C nucleus. Repeated searches for a ^{13}C signal were unsuccessful despite particular care being taken on repeated runs to avoid saturation due to the high R.F. power levels employed.

One major problem encountered when searching for this signal was that of baseline instability when using high R.F. power levels and high amplifier gain. This baseline stability problem also made it impractical to utilize the C.A.T. for signal to noise enhancement during these searches. It was considered that inclusion of an A.F. phase detection system should overcome this baseline instability. There was available an A.F. phase detector unit identical to that employed in the Perkin Elmer R10 spectrometer and it was attempted to include this unit in the R.S.2. A 4Kc sec.$^{-1}$ modulation signal from a Muirhead-Wigan D890A oscillator was introduced into the 15Mc.sec.$^{-1}$ supplied to the probe, via the normal R.F. modulation channel. A similar signal was introduced into the A.F. phase detector unit at a suitable position, i.e.

^{27}Al	Aluminium Chloride
^{23}Na	Sodium Ortho Vanadate
^{55}Mn	Sodium Permanganate
^{59}Co	Potassium Cobalti Cyanide
^{51}V	Sodium ortho Vanadate

Table 9:1

The compounds used for calibration of the magnetic field of the R.S.2 spectrometer.

after the x 2 multiplication stages (see figure 2:1) this unit being incorporated into the spectrometer between the diode detection and the signal presentation. This arrangement was shown to work for ^{55}Mn resonance, however, whilst the baseline was now quite stable, the resulting signal to noise was considerably worse than when using the straightforward R.F. diode detection. This reduction in signal to noise was quite unacceptable when attempting to locate the very weak ^{13}C resonance, even though the stability was improved to the extent of being able to control the spectrometer with a C.A.T. With the lack of success achieved in using the R.S.2 spectrometer to locate the ^{13}C resonance, attention was now directed towards using the Perkin Elmer R10 spectrometer to this end.

9:3 Attempts to locate ^{13}C resonance Signals with a Perkin Elmer R10 Spectrometer

Perkin Elmer Ltd. market the necessary radiofrequency equipment to observe ^{13}C signals, however, this was not available in this laboratory for these studies. There was available radiofrequency equipment, i.e. source, amplifier, and bridge, designed to observe ^{11}B signals at 19.2519 Mc.sec.$^{-1}$. It was decided that this equipment could be modified to operate at c.a. 15.1Mc.sec.$^{-1}$ necessary for ^{13}C observations.

The method of operation was somewhat more complicated than that normally employed with this spectrometer, and the arrangement of the radiofrequency equipment used is shown in figure 9:2 The crystal in the ^{11}B source was disconnected and the required fundamental frequency of c.a. 15Mc.sec.$^{-1}$ was obtained by mixing the 15Mc.sec.$^{-1}$ intermediate frequency from the proton source (normally used for spin decoupling) with a signal of c.a. 100Kc. sec.$^{-1}$ obtained from a Venner TSA625/2 oscillator. The mixer circuit used is shown in figure 3:3A. The required signal at c.a. 15Mc.sec.$^{-1}$ was selected and amplified with a simple tuned circuit (figure 3:3B) similar to that used in the final R.F. amplification stage of the Perkin-Elmer R.F. sources. The resulting signal was then fed into the single side band unit of the ^{11}B source, in which the fixed capacitors were changed from 100 pf. and 110 pf. to 184.7 pf. and 208.2 pf. on the advice of Perkin-Elmer Ltd. The various tuned circuits in the final automatic gain control amplifier were retuned to c.a. 15Mc.sec.$^{-1}$ by changing some of the fixed capacitors and adjusting the tuning slugs of the three coils. The various voltage levels were adjusted as closely as possible to those suggested by the manufacturers.

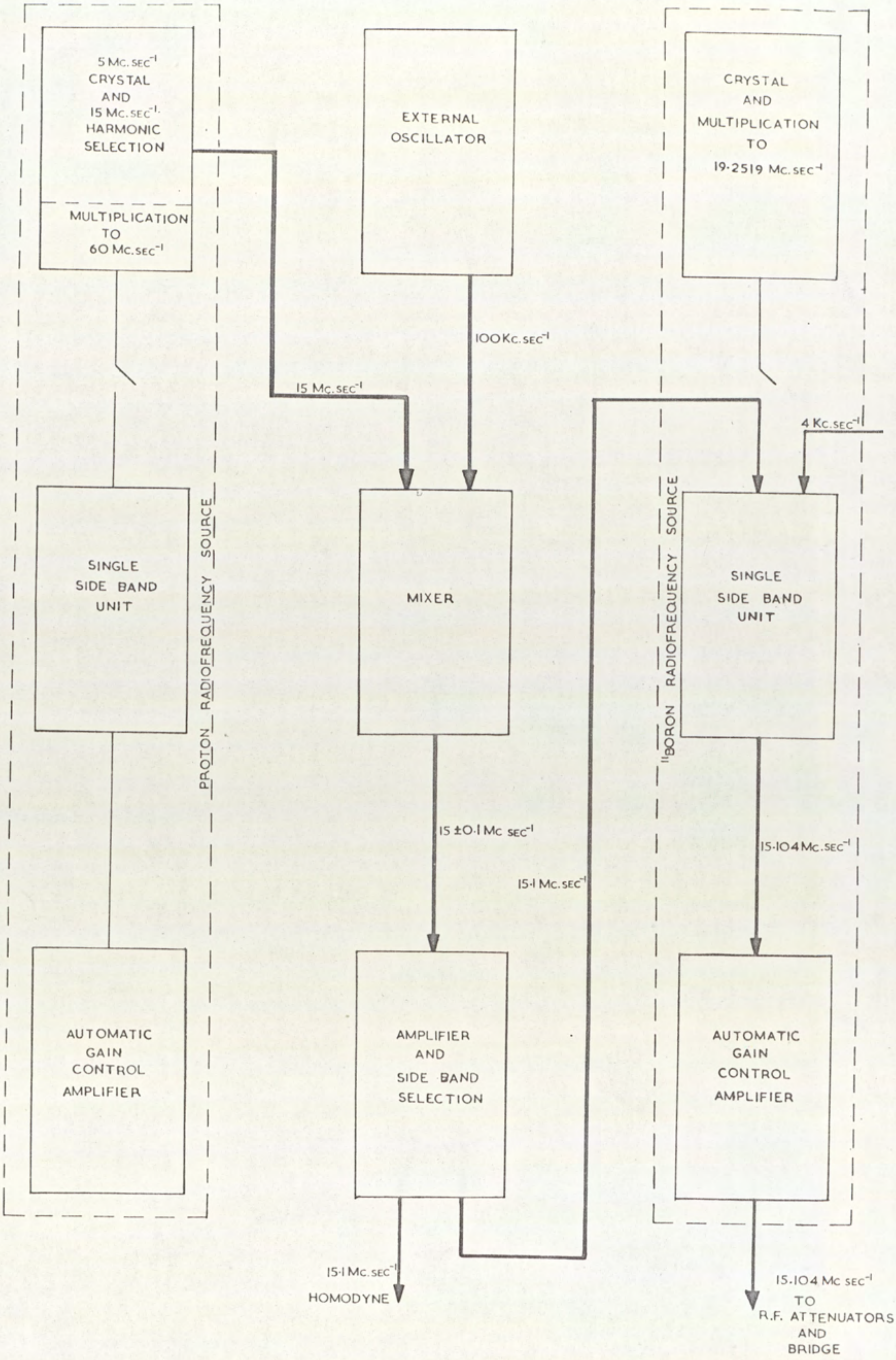
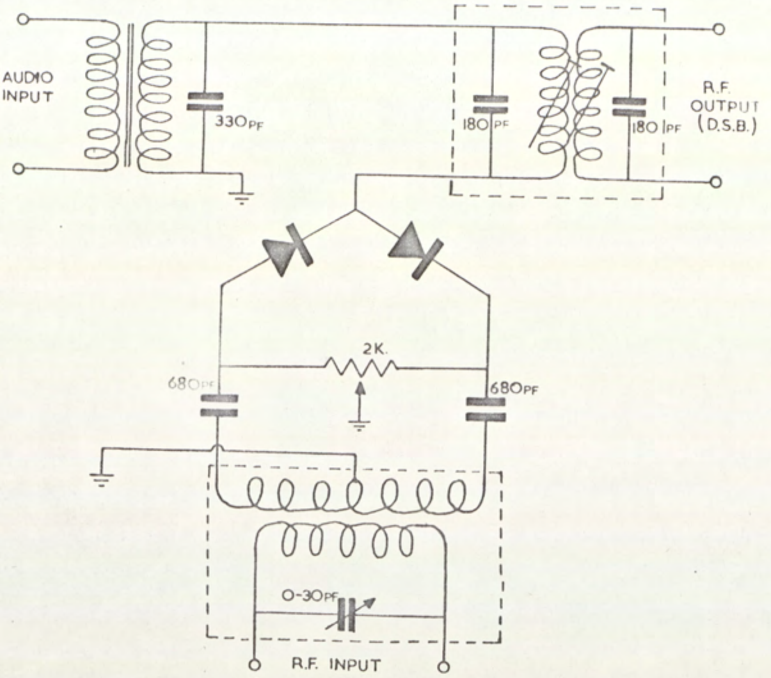


FIGURE 9.2. Schematic diagram of method used to obtain 15.1 Mc.sec.$^{-1}$ from Perkin-Elmer R 10 radiofrequency equipment.



9.3A.

9.3B.

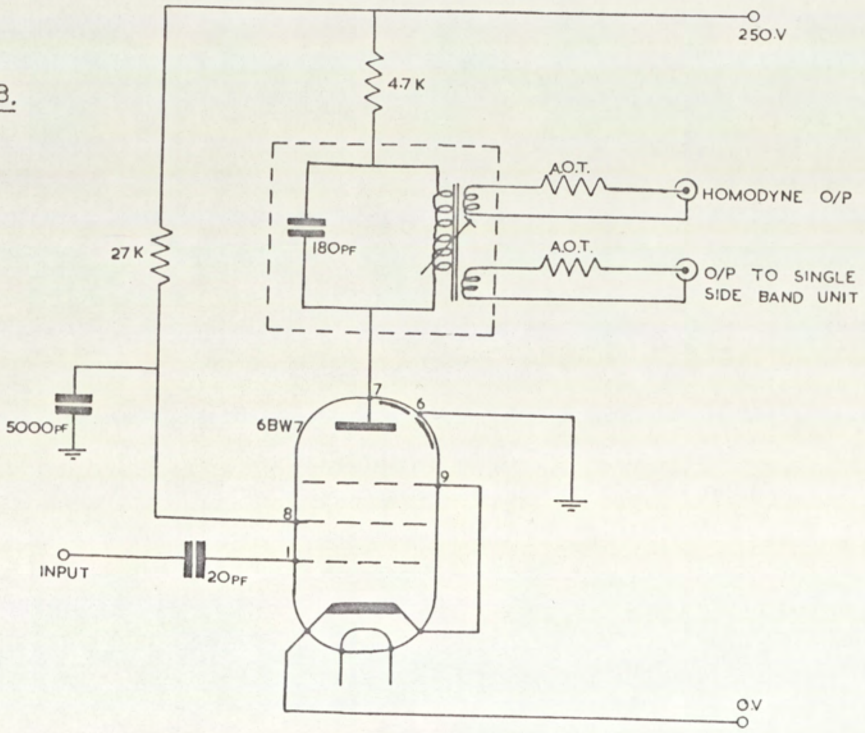


FIGURE 9.3A. Circuit diagram of simple mixer used to obtain 15 $\pm$ 0.1 Mc.sec.$^{-1}$.

FIGURE 9.3B. Circuit diagram for simple tuned amplifier used to select 15.1 Mc.sec.$^{-1}$ sideband.

The R.F. amplifier was retuned to 15.1Mc.sec.$^{-1}$ by replacing the fixed capacitors of the various tuned L.C. circuits with ones of the appropriate value, which may be evaluated approximately for a constant coil by the relationship

$$\nu_1/\nu_2 = (C_2/C_1)^{\frac{1}{2}} \qquad 9:2$$

where ν_1 and ν_2 are the initial and final frequencies and C_1 and C_2 are the corresponding initial and final capacitor values. Final tuning was achieved by moving the slug in each of the coils to its optimum position.

The manufacturers advised that the same probe should be suitable for ^{13}C as is used for ^{11}B studies, this being capable of accepting unspun sample tubes of 9mm. diameter. The R.F. bridge was retuned to 15Mc.sec.$^{-1}$ using a Wayne Kerr capacitance bridge, the output impedence being adjusted to 50 ohms to eliminate formation of standing waves in the connecting cables. The tuning of the bridge is something of a trial and error process, the values of the various capacitors labelled A.O.T. (adjust on test) on the circuit diagram, being varied until the desired result was obtained. All of the retuned equipment was assembled and after the initial screening of the cables and coils was improved and some final adjustments made to the equipment as a whole, the instrument seemed to be functioning normally.

9:4 Attempts to Locate a Resonance Signal at c.a. 15Mc.sec.$^{-1}$

It was decided unwise to attempt to locate a ^{13}C signal immediately with this modified equipment, due to the difficulty of locating such a signal even when using equipment which is known to be functioning correctly. Therefore, attempts were made to prove the system by first locating a ^{55}Mn signal from a sample of $NaMnO_4$ dissolved in water. This necessitated mixing a signal of 129Kc.sec^{-1} from the external oscillator with the 15Mc.sec^{-1} frequency from the proton source, the lower side band then being selected, i.e. 15.000-0.129Mc.sec^{-1}. This required only minor adjustments to the various tuned circuits from the settings necessary for ^{13}C resonance. After some initial difficulty, a signal from ^{55}Mn was located, which was then used for adjustment of the Golay shim coils and for further adjustment of the various tuned circuits to obtain maximum signal strength. A signal was eventually obtained that was somewhat better than that obtained on the R.S.2 instrument, having a signal to noise ratio of c.a. 50:1 with a stable baseline. This performance cannot however, be compared with the 15Mc.sec^{-1} equipment produced by Perkin Elmer, as these manufacturers have no knowledge of a ^{55}Mn resonance ever being observed with such equipment, and hence no comparison signal to noise figures are available. Nevertheless, after retuning the equipment to the ^{13}C frequency, the benzene ^{13}C resonance could not be located. In fact, despite the initial success, it was then discovered that the instrument was not working in the prescribed manner. Changing the 4Kc.sec^{-1} sideband in the modified ^{11}B source from +4 Kc.sec^{-1} to -4 Kc.sec^{-1} gave no change in the position of the ^{55}Mn resonance signal, which should have moved by 8 Kc.sec^{-1} It would appear that a tuned amplifier having higher selectivity for the desired side-band than that shown in figure 3:3B should be used prior to feeding the signal at c.a. 15.1Mc.sec^{-1} into the single side-band unit of the modified ^{11}B unit.

With minor modifications to the equipment, it should be possible to locate ^{13}C resonance signals. This would enable the suggestion made at the end of Chapter 8, that ^{13}C screenings may be correlated with intramolecular electric fields, to be investigated.

REFERENCES

1. W. Pauli, Naturwiss, (1924), 12, 741.

2. O. Stern, Z.Phys., (1921), 7, 249.

3. I. I. Rabi, S. Millman, P. Kusch and J. R. Zacharias, Phys. Rev., (1939), 55, 526.

4. N. F. Ramsey, 'Molecular Beams', Oxford University Press, (1956).

5. F. Bloch, W. W. Hansen and M. Packard, Phys. Rev., (1946), 69, 127.

6. E. M. Purcell, H. C. Torrey and R. V. Pound, Phys. Rev., (1946), 69, 37.

7. J. A. Pople, W. G. Schneider and H. J. Bernstein, 'High Resolution Nuclear Magnetic Resonance Spectroscopy', McGraw Hill Book Co., N. Y., (1959).

8. J. W. Emsley, J. Feeney and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy, Vol. I', Pergamon Press, Oxford (1965).

9. J. W. Emsley, J. Feeney and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy Vol. II', Pergamon Press, Oxford (1966).

10. L. M. Jackman, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry', Pergamon Press, Oxford (1959).

11. N. Bloembergen, E. M. Purcell and R. V. Pound, Phys. Rev., (1948), 73, 679

12. A. Einstein, Phys. Z., (1917), 18, 121.

13. E. M. Purcell, Phys. Rev., (1946), 69, 681.

14. W. A. Anderson, Phys. Rev., (1956), 104, 850.

15. J. I. Kaplan and S. Meiboom, Phys. Rev., (1957) 106, 499.

16. F. Bloch, Phys. Rev., (1946), 70, 460.

17. F. Bloch, Phys. Rev., (1956), 102, 104.

18. R. K. Wagsness and F. Bloch, Phys. Rev., (1953), 89, 728.

19. G. V. D. Tiers, J. Phys. Chem., (1961), 65, 1916.

20. E. R. Andrew, 'Nuclear Magnetic Resonance', Cambridge University Press, N. Y., (1955).

21. R. V. Pound, Phys. Rev., (1950), 79, 685.

22. N. Bloembergen, 'Nuclear Magnetic Relexations', W. A. Benjamin, N. Y. (1960).

23. W. D. Knight, Phys. Rev., (1949) 76, 1259.

24. W. G. Proctor and F. C. Yu, Phys. Rev., (1950) 77, 717.

25. W. C. Dickinson, Phys. Rev., (1950), 77, 736.

26. G. V. D. Tiers, J. Phys. Chem., (1959), 63, 1379.

27. J. Homer, Tetrahedron, (1967), 23, 4065.

28. P. Laszlo, A. Speert, R. Ottinger and J. Reisse, J. Chem. Phys., (1968), 48, 1732.

29. W. G. Proctor and F. C. Yu, Phys., Rev., (1951), 81, 20.

30. H. S. Gutowsky and D. W. McCall, Phys. Rev., (1951), 82, 748.

31. Chem. Eng. News, (1964), 23, 55.

32. A. L. Bloom and M. E. Packard, Science, (1955), 122, 738.

33. J. T. Arnold, Phys. Rev., (1956), 102, 136.

34. L. C. Allen and L. F. Johnson, J. Amer. Chem. Soc., (1963), 85, 2668.

35. W. E. Lamb, Phys. Rev., (1941), 60, 817.

36. N. F. Ramsey, Phys. Rev., (1950), 78, 699.

37. N. F. Ramsey, Phys. Rev., (1952), 86, 243.

38. J. H. Van Vleck, 'Electronic and Magnetic Susceptibilities', Oxford University Press, N. Y. (1932).

39. J. H. Van Vleck and A. Frank, Proc. Nat. Acad. Sci., (1929), 15, 539.

40. N. F. Mott and I. N. Sneddon, 'Wave Mechanics and its Applications', Clarendon Press Oxford, (1948).

41. A. Saika and C. P. Slichter, J. Chem. Phys., (1954), 22, 26.

42. T. P. Das and R. Bersohn, Phys. Rev., (1956), 104, 476.

43. C. P. Slichter, 'Principles of Magnetic Resonance', Harper and Row, N. Y..

44. W. T. Marshall and J. A. Pople, Mol. Phys., (1958), 1, 223.

45. A. D. Buckingham, Canad. J. Chem., (1960), 38, 300.

46. H. M. McConnell, J. Chem. Phys., (1957), 27, 226.

47. J. A. Pople, J. Chem. Phys., (1956), 24, 1111.

48. A. D. Buckingham, T. Schaefer and W. G. Schneider, J. Chem. Phys., (1960), 32, 1227.

49. A. D. Buckingham, H. J. Bernstein and W. T. Raynes, J. Chem. Phys., (1963), 36, 3481.

50. A. Peake and L. F. Thomas, Trans. Faraday Soc., (1966), 62, 2980.

51. E. R. Jenson, D. S. Noyce, C. H. Sederholm and A. J. Berlin, J. Amer. Chem. Soc., (1960), 82, 1256.

52. G. V. D. Tiers, Proc. Chem. Soc., (1960), 389.

53. K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji and H. Tanida, Tetrahedron Letters, (1966), 9.

54. K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji and H. Tanida, Canad. J. Chem., (1964), 42, 928.

55. F. A. L. Anet, Canad. J. Chem., (1961), 39, 789.

56. J. Meinwald and Y. C. Meinwald, J. Amer. Chem. Soc., (1963) 85, 2514.

57. K. L. Williamson and J. C. Fenstermaker, J. Amer. Chem. Soc., (1968), 90, 342.

58. L. Petrakis and C. H. Sederholm, J. Chem. Phys., (1961), 35, 1243.

59. C. H. Sederholm and Soon Ng. J. Chem. Phys. (1964), 40, 2090

60. C. F. Wilcox Jr., J. Amer. Chem. Soc., (1960), 82, 414.

61. N. Boden, J. Feeney and L. H. Sutcliffe, J. Chem. Soc., (1965), 3482.

62. H. S. Gutowsky, M. Karplus and D. M. Grant, J. Chem. Phys., (1959), 31, 1278.

63. J. Homer and L. F. Thomas, Trans. Faraday Soc., (1963), 59, 491.

64. J. Homer, Ph.D. Thesis, University of Birmingham (1962)

65. D. W. Phillips, J. Chem. Phys., (1956), 25, 949.

66. J. Feeney, L. H. Sutcliffe and S. M. Walker, Mol. Phys., (1966), 11, 117.

67. M. Karplus and T. P. Das, J. Chem. Phys., (1966), 34, 1683

68. F. Prosser and L. Goodman, J. Chem. Phys., (1963), 38, 374.

69. A. G. Moritz and N. Sheppard, Mol. Phys., (1962), 5, 361.

70. J. W. Emsley, Mol. Phys., (1965), 9, 381.

71 A. A. Bothner-By and C. Naar-Colin, Ann. New York Acad. Sci., (1958), 70, 833.

72. G. S. Reddy and J. H. Goldstein, J. Chem. Phys., (1963), 38, 2786.

73. J. I. Musher, J. Chem. Phys., (1961), 35, 1159.

74. J. I. Musher, Mol. Phys., (1963), 6, 93.

75 R. F. Zurcher, J. Chem. Phys., (1962), 37, 2421.

76. R. F. Zurcher, Helv. Chim. Acta., (1961), 44, 1755.

77. J. W. Ap Simon, W. G. Craig, P. V. Demarco, D. W. Mathieson, L. Saunders and W. B. Whalley, Chem. Comm., (1966), 359.

78. J. W. Ap Simon, W. G. Craig, P. V. Demarco, D. W. Mathieson, L. Saunders and W. B. Whalley, Tetrahedron, (1967), 23, 2339.

79. D. W. Davies, Mol. Phys., (1963), 6, 489.

80. P. T. Narasimhan and M. T. Rogers, J. Chem. Phys., (1959), 31, 1302.

81. A. A. Bothner-By and J. A. Pople, Ann. Rev. Phys. Chem., (1965), 16, 45.

82. D. L. Hall, Tetrahedron Letters, (1964), 1457.

83. K. Lonsdale, Proc. Roy. Soc., (1939), A 171, 541.

84. J. A. Pople, Discuss Faraday Soc., (1962), 34, 68.

85. J. Tillieu and J. Guy, Compt. Rend., (1934), 239, 1203; (1955), 241, 382; (1956), 242, 1279, 1436. J. Chem. Phys., (1956), 24, 1117.

86. J. Tillieu, Ann. Phys. (Paris), (1957), 2, 471, 631.

87. A. D. Buckingham and J. A. Pople, Proc. Phys. Soc., (1956), 69 B, 1133.

88. A. D. Buckingham, W. H. Prichard and D. W. Whiffen, Chem.Comm. (1965), 51.

89. A. D. Buckingham, W. H. Prichard and D. W. Whiffen, Trans. Faraday Soc., (1967), 63, 1057.

90. E. L. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison, 'Conformational Analysis', Interscience, N.Y., (1965).

91. M. P. Brown and D. E. Webster, J. Phys. Chem., (1960), 64, 698.

92. J. S. Waugh and F. W. Dobbs, J. Chem. Phys., (1959), 31, 1235.

93. N. Sheppard and J. J. Turner, Mol. Phys., (1960), 3, 168.

94. R. M. Lynden-Bell - quoted as private communication in reference 69.

95. G. V. D. Tiers, J. Phys. Chem., (1958), 62, 1151.

96. K. B. Wiberg and B. J. Nist, J. Amer. Chem. Soc., (1961), 83, 1226.

97. C. J. Creswell and A. L. Allred, J. Amer. Chem. Soc., (1963) 85, 1723.

98. A. A. Bothner-By and C. Naar-Colin, J. Amer. Chem. Soc., (1958), 80, 1728.

99. R. U. Lemieux, R. K. Kullnig, H. J. Bernstein and W. G. Schneider, J. Amer. Chem. Soc., (1958), 80, 6098.

100. J. Feeney, L. H. Sutcliffe and S. M. Walker, Mol. Phys., (1966), 11, 129.

101. J. Feeney, L. H. Sutcliffe and S. M. Walker, Mol. Phys., (1966), 11, 137.

102. 'Interatomic Distances', Chem. Soc. Special Publication, No. 11, (1958)

103. L. W. Reeves and K. O. Strømme, Canad. J. Chem., (1960), 38, 1241.

104. N. Boden, J. W. Emsley, J. Feeney and L. H. Sutcliffe, Mol. Phys., (1964), 8, 133.

105. N. Boden, J. W. Emsley, J. Feeney and L. H. Sutcliffe, Mol. Phys., (1964), 8, 467.

106. J. W. Smith, 'Electric Dipole Moments', Butterworth's Scientific Publications', (1965).

107. E. A. Moelwyn Hughes, 'Physical Chemistry', Pergamon Press, London 1957.

108. A. A. Bothner-By, J. Mol. Spec., (1960), 5, 52.

109. F. Hruska, H. M. Hutton and T. Schaefer, Canad. J. Chem., (1965), 43, 2392.

110. T. Schaefer, F. Hruska and H. M. Hutton, Canad. J. Chem., (1967), 45, 3143.

111. J. Homer and L. F. Thomas, Proc. Chem. Soc., (1961), 139.

112. L. Petrakis and H. J. Bernstein, J. Chem. Phys., (1962), 37, 2731.

113. L. Petrakis and H. J. Bernstein, J. Chem. Phys., (1963), 38, 1562.

114. C. G. Le Fevre and R. J. W. Le Fevre, Rev. Pure. Appl. Chem. Australia, (1955), 5, 261.

115. V. I. Vedneyev, L. V. Gurvich, V. M. Kondrat'yev, V. A. Medvelev, and Y. L. Frankerich, 'Bond Energies, Ionisation Potentials and Electron Affinities', Edward Arnold (Publishers), London, (1966).

116. L. E. Sutton, 'Determination of Organic Structures by Physical Methods', Eds. E. A. Brande and F. C. Nachod, Academic Press, N. Y. (1955).

117. R. J. W. Le Fevre, J. Proc. Roy. Soc., New South Wales, (1961), 95, 1.

118. H. H. Landholt and R. Bernstein, 'Zahlenverte und Functionen', Julius Springen-Verlag, Berlin, 1 Band, 1 Teil.

119. C. P. Smyth, 'Dielectric Constant and Molecular Structure", Mc.Graw-Hill Book Co., N.Y. (1955).

120. 'Handbook of Chemistry and Physics', The Chemical Rubber Publishing Co., 45th edition, (1964).

121. T. Yonemoto, Canad. J. Chem. (1966), 44, 223.

122. H. S. Gutowsky and C. J. Hoffman, J. Chem. Phys. (1951), 19, 1259.

123. E. L. Muettertieg and W. D. Phillips, J. Amer. Chem. Soc., (1959), 81, 1084.

124. B. B. Howard, B. Linder and M. T. Emerson, J. Chem. Phys., (1962), 36, 485.

125. L. H. Meyer and H. S. Gutowsky, J. Phys. Chem., (1953), 57, 481.

126. T. S. Smith and E. A. Smith, J. Phys. Chem., (1959), 63, 1701.

127. J. B. Stothers, Quart. Rev., Chem. Soc., (1965), 19, 144.

128. C. H. Holm, J. Chem. Phys., (1957), 26, 707.

129. H. Spiesecke and W. G. Schneider, J. Chem. Phys., (1961), 35, 722.

130. P. C. Lauterbur, Tetrahedron Letters, (1961), 274.

131. H. Spiesecke and W. G. Schneider, Tetrahedron Letters, (1961), 468.

132. P. C. Lauterbur, J. Amer. Chem. Soc., (1961), 83, 1846.

133. J. A. Pople, Discuss. Faraday Soc., (1960), 34, 7.

134. J. A. Pople, Mol. Phys., (1964), 7, 301.

135. B. V. Cheney and D. M. Grant, J. Amer. Chem. Soc., (1967), 89, 5319.

136. W. M. Litchman and D. M. Grant, J. Amer. Chem. Soc., (1968), 90, 1400.

137. M. Karplus and J. A. Pople, J. Chem. Phys., (1963), 38, 2803.

138. D. E. O'Reilley, J. Chem. Phys., (1960), 82, 1007.

139. W. G. Proctor and F. C. Yu, Phys. Rev., (1951), 81, 20.

140. J. E. Wertz and O. Jardetzky, J. Chem. Phys., (1956), 25, 357.

ERRATA

Page 59

Table 4:1

The chemical shift of the 2,3,5,6 endo fluorine nuclei in 1:4dihydro-decafluorobicyclo(2,2,1)heptane quoted as 58.50 p.p.m. should read 56.73 p.p.m.

The spectral parameters for 1Br-undecafluorobicyclo(2,2,1)heptane should read:

Nucleus	ν (c.sec.$^{-1}$) from hexafluorobenzene	Shift p.p.m.	J gem c.sec.$^{-1}$
4	+3155	+55.88	
7	2124	37.62	
2,6 exo	2273 2515	42.70	240
2,6 endo	3132 3370	57.27	
3,5 exo	2048 2296	39.26	248
3,5 endo	2434 2682	44.50	

The amended chemical shift values quoted require the following corrections to be made:

Page 147 Table 8:2

The chemical shift of the 2,3,5,6 endo fluorines in 1:4diH-decafluorobicyclo(2,2,1)heptane, quoted as 121.65 p.p.m., replace by 119.88 p.p.m.

Page 152 Table 8:3

The observed chemical shift differences for 1Br-undecafluorobicyclo(2,2,1)heptane

F3,5 exo for +3.0 read +0.2

F3,5endo for +9.9 read +3.8

Page 152 Table 8:4

The observed influence of substituent on shielding

F4, for F>Br>I>H read F>Br>H>I

F3,5 exo for F>I>Br>H read H>F>Br>I

3,5 endo for F>H>I>Br read F>H>Br>I

Thus, the method discussed in section 8:3 for the correlation of observed shielding trends, with differences in resultant electric fields produced at the various resonant nuclei by substituents, rather than a correlation with substituent electronegativity, predicts the correct order of observed shielding in each case studied where the substituents are halogens. However, when the substituent is hydrogen, the observed order of shielding is still out of sequence with that calculated.

Intramolecular Screening Effects on n.m.r. Chemical Shifts. Part I. The Anisotropy in the Magnetic Susceptibility of the C–C and C–H bonds

By **J. Homer** and **D. Callaghan**, Department of Chemistry, The University of Aston in Birmingham, Birmingham 4

Reprinted from

JOURNAL
OF
THE CHEMICAL SOCIETY

SECTION A
Inorganic, Physical, and Theoretical Chemistry

1968

Intramolecular Screening Effects on n.m.r. Chemical Shifts. Part I. The Anisotropy in the Magnetic Susceptibility of the C–C and C–H bonds

By **J. Homer** and **D. Callaghan**, Department of Chemistry, The University of Aston in Birmingham, Birmingham 4

The intramolecular screening contributions to proton resonance shifts arising from the anistropy in the magnetic susceptibility of the C–C and C–H bonds are investigated. The values $+4{\cdot}39 \times 10^{-6}$ cm.^{3} mole^{-1} and approximately zero, apparently representing $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$, are obtained from proton resonance measurements and compared with magnetic birefringence data. It is concluded that the values obtained from n.m.r. chemical shifts are incompatible with those obtained from Cotton–Mouton constants, but can be used to predict proton shifts for a range of saturated hydrocarbons.

RECENTLY, interest has been shown in the estimation of values for the anisotropy in the magnetic susceptibility of C–C and C–H bonds from n.m.r. shielding constants.[1-10] It is assumed that the total screening constant for a particular nucleus is given [2] by

$$\sigma = \sigma_l + \sigma_d \qquad (1)$$

where σ_l represents the screening due to the electron cloud surrounding the nucleus in question and σ_d the screening arising from distant polarisable magnetically anisotropic bonds. The approximate expression

$$\sigma_d = \sum_i \frac{\Delta\chi^i(1 - 3\cos^2\theta_i)}{3R_i^3} \qquad (2)$$

based on that formulated by McConnell,[11] is obtained by summing the contributions of all i bonds in a molecule to the screening of the resonating nucleus. The expression is valid providing each value of R_i, the distance between the induced magnetic dipole of bond i and the nucleus in question, is greater than about 3 Å. In equation (2), θ_i is the angle between the direction of R_i and the axis of bond i, and $\Delta\chi^i$ is the magnetic anisotropy of the bond i containing the induced magnetic dipole. Providing the bond has axial symmetry, $\Delta\chi^i$ is given by

$$\Delta\chi^i = \chi^i_{\parallel} - \chi^i_{\perp} \qquad (3)$$

---

[1] A. A. Bothner-By and C. Naar-Colin, *Ann. New York Acad. Sci.*, 1958, **70**, 833.

[2] A. G. Moritz and N. Sheppard, *Mol. Phys.*, 1962, **5**, 361.

[3] G. S. Reddy and J. H. Goldstein, *J. Chem. Phys.*, 1963, **38**, 2736.

[4] J. A. Pople, *Discuss. Faraday Soc.*, 1962, **34**, 68.

[5] J. I. Musher, *J. Chem. Phys.*, 1961, **35**, 1159.

[6] R. F. Zürcher, *J. Chem Phys.*, 1962, **37**, 2421.

[7] R. F. Zurcher, *Helv. Chim. Acta*, 1961, **44**, 1755.

[8] J. W. ApSimon, W. G. Craig, P. V. Demarco, D. W. Mathieson, L. Saunders, and W. B. Whalley, *Chem. Comm.*, 1966, 359.

[9] D. W. Davies, *Mol. Phys.*, 1963, **6**, 489.

[10] J. I. Musher, *Mol. Phys.*, 1963, **6**, 93.

[11] H. M. McConnell, *J. Chem. Phys.*, 1957, **27**, 226.

where $\chi^i_{\parallel}$ and $\chi^i_{\perp}$ are respectively the longitudinal and transverse susceptibilities of the bond.

In order to obtain information regarding σ_d, and thence $\Delta\chi$, from shift comparisons the values of σ_l for the nuclei concerned must be similar. This is most probable in the case of protons because for these, intramolecular screening contributions such as those due to electric field effects, can be considered to be small.

Normally, it is assumed that σ_l is the same for all protons having similar chemical environments and that σ_d provides the dominant contribution to proton shifts. If these assumptions are justified it is possible, in principle, to evaluate bond anisotropies by equating differences in observed proton shifts to the corresponding differences between the terms representing the right-hand side of equation (2). In this way Moritz and Sheppard [2] obtained the value $4{\cdot}6 \times 10^{-6}$ cm.^{3} mole^{-1} for $\Delta\chi^{CC}$ and suggested that $\Delta\chi^{CH}$ is neligible. Similarly, Bothner-By and Naar-Colin [1] deduced $\Delta\chi^{CC} = 3{\cdot}3 \times 10^{-6}$ cm.^{3} mole^{-1} and $\Delta\chi^{CH}$ to be zero from the shift difference between the methylene protons in cyclohexane and cyclopentane. By investigating the resonances arising from tertiary hydrogens in carbocyclic molecules, Musher [5] found $\Delta\chi^{CC} = 5{\cdot}0 \times 10^{-6}$ cm.^{3} mole^{-1} in these systems. However, in obtaining this value the possible magnetic anisotropy shielding contributions of substituents in these molecules were not considered. Neglecting contributions from the anisotropy of C–H bonds Narasimhan and Rogers [12] deduced $\Delta\chi^{CC} = 4{\cdot}1 \times 10^{-6}$ cm.^{3} mole^{-1} in propane. Pople,[4] by considering Lonsdale's data [13] on molecular diamagnetic susceptibilities together with Moritz and Sheppard's data [2] has suggested that $\Delta\chi^{CC} = 11{\cdot}0 \times 10^{-6}$ and $\Delta\chi^{CH} = 6{\cdot}8 \times 10^{-6}$ cm.^{3} mole^{-1} would be required to satisfy both sets of data. The last value for $\Delta\chi^{CC}$ agrees quite well with that ($\Delta\chi^{CC} = 10 \times 10^{-6}$ cm.^{3} mole^{-1}) obtained by Reddy and Goldstein [3] from ^{13}C–H coupling constants. Nevertheless, it is evident that agreement between the various values obtained for both $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ is poor. Furthermore, two theoretical estimates of $\Delta\chi^{CC}$ are both considerably smaller than the values obtained from n.m.r. measurements. Tillieu,[14] using a variation method, calculated a value of $1{\cdot}21 \times 10^{-6}$ cm.^{3} mole^{-1} and, less rigorously, Zurcher [6] calculated $1{\cdot}04 \times 10^{-6}$ cm.^{3} mole^{-1} for $\Delta\chi^{CC}$.

Recently,[8] in order to account for the effects of bonds closer than 3 Å to the nucleus in question, and thereby refine estimates of $\Delta\chi$ obtained from n.m.r. measurements, the expression, formulated by McConnell, which is the basis of equation (2) has been modified to

$$\sigma = \frac{\Delta\chi}{3R^3}(1 - 3\cos^2\theta) + \frac{S^2}{R^5}\left[\frac{-(\chi_{\parallel} + 2\chi_{\perp})}{2} + 5(\chi_{\parallel}\cos^2\theta + \chi_{\perp}\sin^2\theta) - \frac{35}{6}(\chi_{\parallel}\cos^4\theta + \chi_{\perp}\sin^4\theta)\right] \quad (4)$$

In this, S is referred to as half the length of the induced dipole. Using this expression ApSimon *et al.*[8] have derived values for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ that are apparently consistent with data obtained from both n.m.r. and magnetic birefringence measurements. Zurcher [7] proposed equation (5) to account for the axial–equatorial proton shift in cyclohexane. From magnetic birefringence measurements Buckingham *et al.*[15] were able to

$$0{\cdot}114\Delta\chi^{CC} - 0{\cdot}094\Delta\chi^{CH} = 0{\cdot}46 \times 10^{-6} \quad (5)$$

$$\Delta\chi^{CC} - 2\Delta\chi^{CH} = -4{\cdot}9 \times 10^{-6} \quad (6)$$

show that the molecular magnetic anisotropy of ethane is $-4{\cdot}9 \times 10^{-6}$ cm.^{3} mole^{-1}. Assuming that bond susceptibility components are additive, they related the molecular anisotropy to the C–C and C–H bond anisotropies by equation (6) which is a specific form of the general expression derived by Davies.[9] Based on equation (4) ApSimon *et al.* set up an expression analogous to (5) and using an iterative procedure analysed this together with equation (6) to obtain the best values of $8{\cdot}4 \times 10^{-6}$ and $6{\cdot}63 \times 10^{-6}$ cm.^{3} mole^{-1} for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$, respectively. It is worthy of mention that these values do not differ appreciably from the corresponding values ($10{\cdot}41 \times 10^{-6}$ and $7{\cdot}60 \times 10^{-6}$ cm.^{3} mole^{-1}) obtained by straightforward simultaneous solution of equations (5) and (6). Consequently, in view of the spread in the values mentioned previously, there appears to be little gained, at this stage, by using equation (4) to determine bond anisotropies. Nevertheless, the magnetic anisotropies obtained in this way are similar to the rationalised values suggested by Pople [4] and the value for $\Delta\chi^{CC}$ is in reasonable agreement with that based on ^{13}C–H coupling constants.[3] They should, therefore, be capable of use in predicting differences in proton shifts in a range of saturated hydrocarbons.

We have studied the n.m.r. spectra of compounds based on the bicyclo[2,2,1]heptane skeleton, and consider that the different proton shifts observed for the parent compound, bicyclo[2,2,1]heptane (norbornane), itself could be explained in terms of the shielding due to the magnetically anisotropic C–C and possibly C–H bonds within the molecule. To test this we considered, in the first instance, the anisotropic shielding due to both C–C and C–H bonds and calculated the appropriate σ_d values using equation (4) to include the effects of dipoles closer than 3 Å to the resonating nuclei. The values for $\Delta\chi^{CC}$, $\Delta\chi^{CH}$, $\chi^{CC}_{\parallel}$, $\chi^{CC}_{\perp}$, $\chi^{CH}_{\parallel}$, $\chi^{CH}_{\perp}$, and S are those proposed by ApSimon *et al.*[8] The evaluation of the R and θ terms required for equation (4) is straightforward using the co-ordinates of all the atoms in norbornane given in reference 16. The induced point dipoles due to $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ are assumed to act from the mid-point of the C–C bonds and 0·77 Å from the carbon atom in the C–H bonds, respectively. The total contributions to the shielding of the different protons in norbornane arising from the anisotropy of all the C–C

---

[12] P. T. Narasimhan and M. T. Rogers, *J. Chem. Phys.*, 1959, **31**, 1302.

[13] K. Lonsdale, *Proc. Roy. Soc.*, 1939, *A*, **171**, 541.

[14] J. Tillieu, *Ann. Phys.*, 1957, **2**, 471, 631.

[15] A. D. Buckingham, W. H. Prichard and D. W. Whiffen, *Chem. Comm.*, 1965, 51.

[16] C. F. Wilcox, jun., *J. Amer. Chem. Soc.*, 1960, **82**, 414.

and C–H bonds, except the effectively common C–H bond containing the protons in question, are given in Table 1.

TABLE 1

The calculated magnetic anisotropy screening contribution (p.p.m.) to each proton in bicyclo[2,2,1]heptane due to all bonds except the effectively common C–H bond

Screening contribution/ at: due to	H(1)	H(7)	H(*exo*)	H(*endo*)
C–C bonds	−3·499	−2·217	−2·543	−2·220
C–H bonds	+0·340	−0·698	−0·533	−0·715
C–C + C–H bonds	−3·159	−2·915	−3·076	−2·935

TABLE 2

Calculated [using equation (4)] and observed proton shifts (p.p.m.) for bicyclo[2,2,1]heptane

	$\delta_{\text{calc.}}$	$\delta_{\text{obs.}}$	$\delta_{\text{obs.}} - \delta_{\text{calc.}}$
H(7)–H(1)	+0·244	+0·99	$+0{\cdot}74_6$
H(7)–H(*exo*)	+0·161	+0·28	$+0{\cdot}11_9$
H(7)–H(*endo*)	+0·020	−0·03	$-0{\cdot}05_0$

The observed and calculated proton shifts of norbornane, expressed relative to the resonance of the protons at position 7, are given in Table 2. The difference between the observed and calculated shifts indicate that the values deduced by ApSimon *et al.* cannot, in all cases, be used to predict relative shifts (*e.g.*, the sign of the shift of H(7)–H(*endo*) is opposite to that observed) or the magnitudes of those that are predicted with the correct sign.

Although the use of equation (4) together with the results of ApSimon *et al.* fails to predict the correct sequence of shifts for norbornane, it is evident that studies of this molecule afford a possible method for evaluating $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ from n.m.r. measurements alone. The proton resonance spectrum of norbornane shows four chemically shifted resonances, from the 1,7, *exo*, and -*endo* hydrogen atoms. Considering the sum of the anisotropic effects of all the C–C and C–H bonds in the molecule (except the effectively common C–H bond) on each of the four magnetically different protons in turn enables four expressions, each containing $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$, to be obtained. The contributions, derived using equation (2), are given below, together with the appropriate observed proton shifts.[17]

H(1)	$-2{\cdot}283 \times 10^{23}\Delta\chi^{CC} + 0{\cdot}427 \times 10^{23}\Delta\chi^{CH}$	τ 7·80
H(7)	$-0{\cdot}888 \times 10^{23}\Delta\chi^{CC} - 0{\cdot}499 \times 10^{23}\Delta\chi^{CH}$	τ 8·79
H(*exo*)	$-1{\cdot}161 \times 10^{23}\Delta\chi^{CC} - 0{\cdot}329 \times 10^{23}\Delta\chi^{CH}$	τ 8·51
H(*endo*)	$-0{\cdot}887 \times 10^{23}\Delta\chi^{CC} - 0{\cdot}484 \times 10^{23}\Delta\chi^{CH}$	τ 8·82

The difference of any two of these expressions provides in all six possible equations representing differences in shielding constants. From these, it is possible to set up three different pairs of equations, such that each pair is dependent on four different original expressions. $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ Can be obtained by the simultaneous solution of each of the three pairs of equations. The three values for both $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ obtained from the three solutions would be expected to be similar and ideally the same. The values derived by this procedur are given in Table 3. It can be seen that there i appreciable variation in each of the two sets of results, and two values in each set are also considerably large than the appropriate values previously proposed fo $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$. These facts indicate some basic erro in the assumptions adopted in the present approach t the problem.

TABLE 3

Values for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ ($\times$ 10^6 cm.^{3} mole^{-1}) obtaine from the proton shifts of norbornane using equation (2 and by considering the C–H induced magnetic dipol to act 0·77 Å from the carbon atom in the bond

Equations derived for	$\Delta\chi^{CC}$	$\Delta\chi^{CH}$
H(1)–H(7)/H(*exo*)–H(*endo*)	+21·49	+25·92
H(1)–H(*exo*)/H(7)–H(*endo*)	+11·02	+10·69
H(1)–H(*endo*)/H(7)–H(*exo*)	+48·06	+66·91

In previous and present evaluations which account for $\Delta\chi^{CH}$ it has been assumed that the point dipole resulting from the anisotropy in the magnetic susceptibility of the C–H bond acts from a point 0·77 Å from the carbon atom along the C–H bond.[6,7,14] If this induced dipole is considered to act from some other point in the bond it is possible that the three different simultaneous solutions for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$, obtained by the method outlined above, could be the same. To investigate this possibility the induced point dipole of the C–H bond was considered to act at various points along the C–H bond and the C–C point dipole was assumed to act from the mid-point of the C–C bond in each case. For each point of action chosen for the C–H induced dipole three solutions each were obtained for both $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$. Figures 1 and 2 illustrate the variation in the values obtained for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ as a function of the point of action of the C–H bond induced dipole. It is clear that there are two possible points at which the three solutions become coincident. These are at a position on the carbon atom and also at a point 0·73 Å along the C–H bond from the carbon atom. The corresponding best values derived for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$, respectively, are $+4{\cdot}3 \times 10^{-6}$ and $-1{\cdot}2 \times 10^{-6}$ cm.^{3} mole^{-1} on the carbon atom and $+35{\cdot}6 \times 10^{-6}$ and $+47{\cdot}0 \times 10^{-6}$ cm.^{3} mole^{-1} at 0·73 Å from the carbon atom. The two values in the second of these two pairs of results are surprisingly large although the corresponding distance along the C–H bond from which the point dipole can be considered to act compares very favourably with that expected (0·77 Å). There are two convenient methods of assessing the significance of these two sets of results. First, each set can be used to calculate the axial–equatorial shift for cyclohexane using an appropriate expression similar to equation (5). Secondly, the values can be used to predict the molecular magnetic anisotropy of ethane.

The situation in which the C–H bond dipole is considered to act 0·73 Å from the carbon atoms is appraised

---

[17] K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Letters*, 1966, 9.

first. In this case the axial–equatorial proton shift in cyclohexane is given by

$$0{\cdot}1025\Delta\chi^{CC} - 0{\cdot}0911\Delta\chi^{CH} = \delta_{a-e} \qquad (7)$$

This expression was derived using the co-ordinate system for cyclohexane which has been proposed recently[18] and accounts for bond angles being not strictly tetrahedral. Substituting the values $\Delta\chi^{CC} = 35{\cdot}6 \times 10^{-6}$ cm.^{3} mole^{-1} and $\Delta\chi^{CH} = 47{\cdot}0 \times 10^{-6}$ cm.^{3} mole^{-1} into equation (7) gives $\delta_{a-e} = -2{\cdot}51$ p.p.m. which is inconsistent with the required value of $+0{\cdot}46$ p.p.m. Substitution into the left-hand side of equation (6) provides a value of $-58{\cdot}4 \times 10^{-6}$ cm.^{3} mole^{-1}, for the molecular magnetic anisotropy of ethane, that differs considerably from the value of $-4{\cdot}9 \times 10^{-6}$ cm.^{3} mole^{-1} obtained by Buckingham *et al.*[15] It would appear from these comparisons that the values of $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ deduced with the C–H bond dipole acting at a point 0·73 Å from the carbon atom cannot be considered to represent real bond anisotropies.

The alternative values of $+4{\cdot}3 \times 10^{-6}$ and $-1{\cdot}2 \times 10^{-6}$ cm.^{3} mole^{-1} for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ respectively, are considered next. For the purpose of the following discussion the theoretical reasons against having $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ with opposite sign will be neglected. Re-evaluation of the relationship between $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ and the axial–equatorial shift in cyclohexane, with the C–H bond dipole acting from the carbon atom, gives

$$0{\cdot}1025\Delta\chi^{CC} - 0{\cdot}1890\Delta\chi^{CH} = \delta_{a-e} \qquad (8)$$

Substituting the values $\Delta\chi^{CC} = +4{\cdot}3 \times 10^{-6}$ cm.^{3} mole^{-1} and $\Delta\chi^{CH} = -1{\cdot}2 \times 10^{-6}$ cm.^{3} mole^{-1} in equation (8) gives $\delta_{a-e} = +0{\cdot}78$ p.p.m. which, whilst not in absolute agreement with the experimental value, is of the correct order of magnitude. When substituted into the left-hand side of equation (6) these values enable $+6{\cdot}7 \times 10^{-6}$ cm.^{3} mole^{-1} to be obtained for the molecular magnetic anisotropy of ethane. This is incompatible with the value obtained by Buckingham *et al.*

It now becomes evident that of the various values that have been suggested for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ there are none that enable extensive prediction of proton shifts and at the same time are compatible with the results of magnetic birefringence measurements. Consequently, it is necessary to suggest that, (i) the σ_d contribution to proton shifts is not due to the anisotropy in the magnetic susceptibility of bonds, or (ii) there is some other contribution to σ_d in addition to that due to bond magnetic anisotropy which is fortuitously accommodated by equation (2), so that only apparent values are obtained for $\Delta\chi$ having no real physical significance or (iii) there is some fallacy in the method for comparing the results of n.m.r. and magnetic birefringence measurements. Dealing with these possibilities in turn; (i) seems unlikely in view of the consistent results obtained by Moritz and Sheppard.[2] If suggestion (ii) does afford a rationalisation of the situation it is difficult to conceive a plausible additional contribution that possesses magnetic susceptibility characteristics. Suggestion (iii) could offer a possible starting point for an explanation of the incompatibility of n.m.r. and magnetic birefringence results. The fundamental requirement for the comparison of the results obtained by the two methods is that bond magnetic susceptibility components are truly additive. The evidence to date suggests either that this may not be the case or that the normal method of summation is erroneous. A similar suggestion has been made previously by Narisimhan and Rogers.[12] If (ii) and (iii) make the present method of comparing n.m.r. and magnetic birefringence results fallacious then it is reasonable and expedient to ascertain apparent values for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ that will allow of the calculation of proton shifts in a wide range of molecular situations.

Of the two sets of values obtained for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ from the proton shifts observed for norbornane $\Delta\chi^{CC} = 35{\cdot}6 \times 10^{-6}$ and $\Delta\chi^{CH} = 47{\cdot}0 \times 10^{-6}$ cm.^{3} mole^{-1} are almost certainly incorrect because they predict an axial–equatorial shift in cyclohexane which has both the wrong sign and magnitude. The other values ($\Delta\chi^{CC} = +4{\cdot}3 \times 10^{-6}$ cm.^{3} mole^{-1} and $\Delta\chi^{CH} = -1{\cdot}2 \times 10^{-6}$ cm.^{3} mole^{-1}), do, on the other hand, predict a shift of the correct sign and almost the right magnitude. The negative value obtained for $\Delta\chi^{CH}$, at first sight, causes some concern in that the sign is opposite to that predicted by Tillieu.[14] However, there is some consolation in the fact that Zurcher[6] deduced $\Delta\chi^{CH} = -0{\cdot}74 \times 10^{-6}$ cm.^{3} mole^{-1} from a least-squares treatment of ten sets of data concerned with polarisability and susceptibility properties of both the C–C and C–H bonds. It could be argued that Zurcher's negative value for $\Delta\chi^{CH}$ depends on the assumption that the equivalent dipole acts from a point 0·77 Å from the carbon atom in the C–H bond and, therefore, direct comparison with our value need not be completely justified. Nevertheless, he provides extensive evidence that either $\Delta\chi^{CH}$ is negative or that, in view of possible inaccuracies in his data, it is zero: furthermore, he shows that these conclusions are unaffected by varying the effective position for the centre of gravity of the electron distribution in the C–H bond. We must conclude also that either $\Delta\chi^{CH}$ has a small negative value or is zero in which case the three lines in Figures 1 and 2 should intersect at a point representing $\Delta\chi^{CH} = 0$ acting at the carbon atom, and the value $-1{\cdot}2 \times 10^{-6}$ cm.^{3} mole^{-1} actually obtained represents the inaccuracy of the chosen model. If it is accepted that $\Delta\chi^{CH}$ may have a very small value then because the C–H magnetic susceptibility is composed of a contribution from the σ electrons in the bond and another from one quarter of the susceptibility of the carbon 1*s* electrons, it is evident from our results that the σ electron cloud must be very nearly magnetically isotropic. To test which of the values, zero and $-1{\cdot}2 \times 10^{-6}$ cm.^{3} mole^{-1}, can be taken to best represent $\Delta\chi^{CH}$ equation (8) can be used to calculate the axial–equatorial proton shift for cyclohexane; the

---

[18] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, 'Conformational Analysis,' Interscience, New York, 1965.

shifts predicted are, respectively, +0·44 and +0·78 p.p.m. It appears, therefore, that $\Delta\chi^{CH}$ can reasonably be taken to be zero.

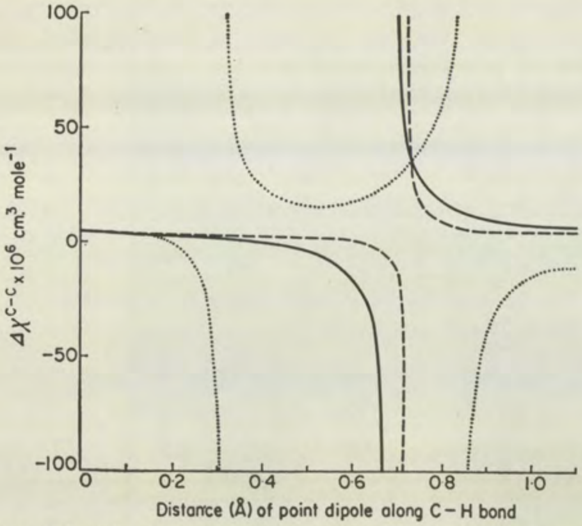


Figure 1 The dependence of $\Delta\chi^{CC}$ [evaluated using the proton shifts of norbornane with equation (2)] on the location assumed for the point of action of the C–H bond magnetic dipole. The curves ——, – – –, and ··· correspond to equations derived for H(1)–H((7)/H(*exo*)–H(*endo*), H(1)–H(*exo*)/H(7)–H(*endo*), and H(1)–H(*endo*)/H(7)–H(*exo*), respectively

The value $\Delta\chi^{CC} = +4{\cdot}3 \times 10^{-6}$ cm.^{3} mole^{-1} which results from the present investigation should be, and is, consistent with the values found by previous workers who assumed $\Delta\chi^{CH}$ to be zero. In particular, it is constructive to compare our results with those of Moritz and Sheppard [2] who correlated the C–C bond anisotropy contributions with τ values for a number of hydrocarbons. However, rather than making a direct comparison we consider that their results should first be re-interpreted. The necessity for this arises due to the fact that because only C–C bond magnetic anisotropy contributions to proton screening are calculated, the coefficients of $\Delta\chi^{CC}$ in σ_d should be plotted against the appropriate observed shifts for each molecule relative to that of some compound which itself has no contribution from C–C anisotropy shielding and not against τ values. A suitable reference appears to be afforded by methane.

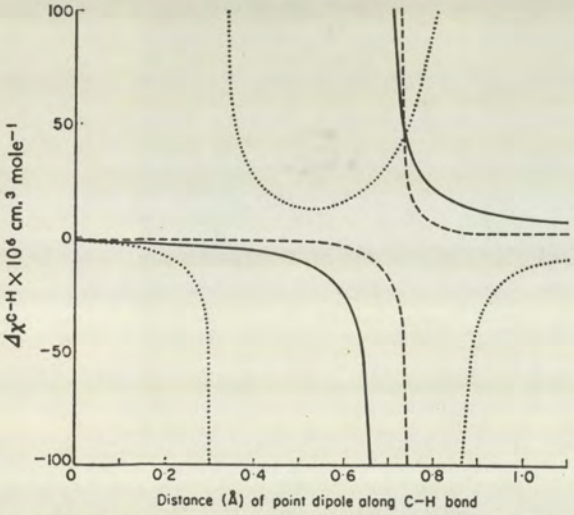


Figure 2 The dependence of $\Delta\chi^{CH}$ [evaluated using the proton shifts of norbornane with equation (2)] on the location assumed for the point of action of the C–H bond magnetic dipole. The curves are identified similarly to those in Figure 1

We have re-evaluated the coefficients of $\Delta\chi^{CC}$ for the axial and equatorial protons in cyclohexane as $-8{\cdot}282 \times 10^{22}$ and $-14{\cdot}462 \times 10^{22}$ cm.^{3} molecule^{-1}, respectively, and replotted these, together with the remaining values of Moritz and Sheppard, against the appropriate shifts expressed relative to methane (τ 9·774).[19] It should be noted that all the coefficients quoted by these authors should be negative. The relationship is illustrated by the open circles of Figure 3. In this the line represents a least-mean-squares treatment on all the points, except the origin, through which the line would be expected to pass. The fact that the line does not meet the origin is due presumably to the difference between the σ_l terms of equation (1) for the protons of methane and for those of molecules containing C–C linkages. Assuming the difference in σ_l for the protons of methane and the hydrocarbons containing C–C bonds is approximately constant the slope of the line in Figure 3 should reasonably represent $\Delta\chi^{CC}$ which is thus found to be $7{\cdot}263 \times 10^{-30}$ cm.$^{-3}$ molecule or $4{\cdot}38 \times 10^{-6}$ cm.^{3} mole^{-1}. The close agreement between this value and that ($4{\cdot}3 \times 10^{-6}$ cm.^{3} mole^{-1}) obtained earlier from norbornane alone is emphasised by the small deviation of the full circles which represent the four points for norbornane, from the least-mean-squares line in Figure 3. The shift deviations from this line for the four points are 0·00,

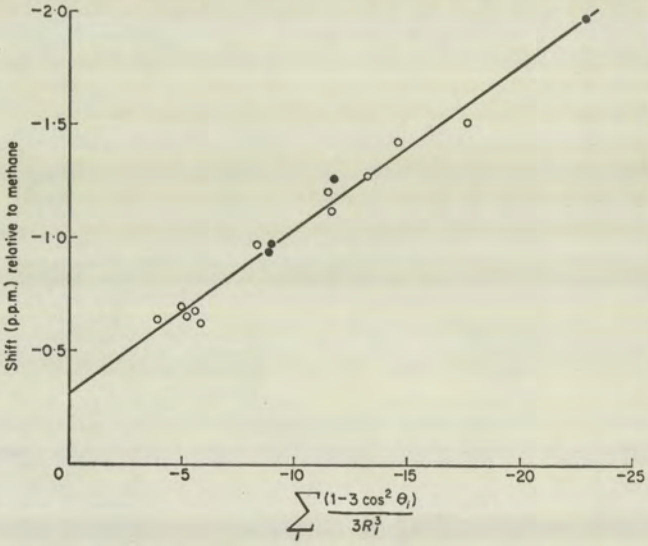


Figure 3 The plot of coefficients of $\Delta\chi^{CC}$, derived using equation (2), versus proton shifts (p.p.m.) relative to methane for various hydrocarbons. The open circles correspond to those given in reference 2 and the full circles to the parameters for norbornane evaluated herein

---

[19] A. D. Buckingham, T. Schaefer and W. G. Schneider, *J. Chem. Phys.*, 1960, **32**, 1227.

—0·02, —0·11, and 0·00 p.p.m. for the 1,7-*exo*- and 1-*endo*-hydrogens, respectively. Expressed relative to the position 7 proton resonance the shifts corresponding to those in Table 2 are

	$\delta_{\text{calc.}}$	$\delta_{\text{obs.}}$	$\delta_{\text{obs.}} - \delta_{\text{calc.}}$
H(7)–H(1)	$+1·013$	$+0·99$	$-0·02_3$
H(7)–H(*exo*)	$+0·198$	$+0·28$	$-0·08_2$
H(7)–H(*endo*)	$-0·001$	$-0·03$	$-0·02_9$

It can be seen that these deviations between observed and calculated shifts are considerably less than those in Table 2 which depend on calculated shifts obtained from equation (4) using the C–C and C–H bond susceptibilities given by ApSimon *et al.* A least-mean-squares treatment of all the points in Figure 3, including those for norbornane, enables the value for $\Delta\chi^{\text{CC}}$ to be refined to $+4·39 \times 10^{-6}$ cm.^{3} mole^{-1}.

We conclude that for the purpose of calculating ^{1}H n.m.r. shifts $\Delta\chi^{\text{CC}} = +4·39 \times 10^{-6}$ cm.^{3} mole^{-1} and that the C–H bond can be considered to be magnetically isotropic. In the absence of a rigorous explanation for the apparent incompatibility of these values with the results of magnetic birefringence measurements, it may be wise at present to refer to the values obtained from ^{1}H n.m.r. studies as apparent bond magnetic anisotropies. Nevertheless it is evident that relative shifts for protons with similar local screening in saturated hydrocarbons can be calculated quite adequately, using equation (2), in terms of the secondary fields at the protons in question which arise from the apparent anisotropy in the magnetic susceptibility of all of the C–C bonds in the molecules.

Note added in proof.—During the course of the publication of this Paper ApSimon *et al.* reported (J. W. ApSimon, P. V. Demarco, D. W. Mathieson, and W. B. Whalley, *Tetrahedron*, 1967, **23**, 2357) revised values for $\Delta\chi^{\text{CC}}$ and $\Delta\chi^{\text{CH}}$ based on refined magnetic birefringence data (A. D. Buckingham, W. H. Prichard, and D. H. Whiffen, *Trans. Faraday Soc.*, 1967, **63**, 1057). Consequently, we have repeated our calculations for bicyclo[2,2,1]heptane using these revised bond anisotropy values with equation (4), and found no better agreement between the observed and calculated shifts than that demonstrated in Table 2. Moreover, because Buckingham *et al.* have suggested that the anisotropy in the molecular magnetic susceptibility derived from magnetic birefringence data is less certain than had been hoped, it becomes evident that attempts either to derive bond anisotropies from these results or compare them with n.m.r. anisotropy data must in any event be treated with caution.

The authors thank Professor W. G. Parker for the provision of facilities and one of them (D. C.) the S.R.C. for a Research Studentship.

[7/645 *Received, May 3rd,* 1967]

Intramolecular Screening Effects on Nuclear Magnetic Resonance Chemical Shifts. Part II.[1] The Anisotropy in the Magnetic Susceptibility of C–F and C–Cl Bonds

By J. Homer * and D. Callaghan, Department of Chemistry, University of Aston in Birmingham, Birmingham 4

Reprinted from

JOURNAL
OF
THE CHEMICAL SOCIETY

SECTION A
Inorganic, Physical, and Theoretical Chemistry

1968

Intramolecular Screening Effects on Nuclear Magnetic Resonance Chemical Shifts. Part II.[1] The Anisotropy in the Magnetic Susceptibility of C–F and C–Cl Bonds

By **J. Homer** * and **D. Callaghan**, Department of Chemistry, University of Aston in Birmingham, Birmingham 4

Values, apparently representing the anisotropies in the magnetic susceptibilities of the C–F and C–Cl bonds, are determined from ^{1}H n.m.r. shifts. It is suggested that apparent $\Delta\chi$ values for some bonds may fortuitously accommodate electronegativity and electric-field effects characteristic of the bonds. Because of this it is concluded that the values for $\Delta\chi^{\mathrm{CF}}$ and $\Delta\chi^{\mathrm{CCl}}$ deduced herein and for $\Delta\chi^{\mathrm{CH}}$ and $\Delta\chi^{\mathrm{CC}}$ reported previously, need not represent actual bond anisotropies. Even so, it is shown that the values deduced to represent $\Delta\chi^{\mathrm{CF}}$ and $\Delta\chi^{\mathrm{CCl}}$ can be used to account for differences in proton shifts in diverse molecular situations by using a bond-induced point magnetic dipole approach. The points of action of the effective dipoles induced in the bonds are determined.

RECENTLY we have derived values for the apparent anisotropy in the magnetic susceptibility of the C–C and C–H bonds from ^{1}H n.m.r. measurements[1] and shown that they enable relative proton shifts to be calculated by use of the expression (1), in which R_{ij} is the separation

$$\sigma_d = \sum_i \frac{\Delta\chi^i(1 - 3\cos^2\theta_{ij})}{3R_{ij}^3} \qquad (1)$$

of the equivalent dipole in bond *i*, having anisotropy $\Delta\chi^i$, and the resonating proton (*j*) and θ_{ij} is the angle between this radius vector and the axis of bond *i*. Whilst equation (1) was derived[2] for situations where $R_{ij} >$ *ca.* 3 Å, our previous work[1] indicates that, other limitations in the use of the equation aside, when $R_{ij} < 3$ Å this equation approximates well to the more rigorous expression[3] which includes a correction term for those cases where $R_{ij} < 3$ Å. In addition to the inherent conceptual limitations of any anisotropy expression, such as equation (1), there can be other major restrictions to the use of this for determining true values for $\Delta\chi$ directly from ^{1}H n.m.r. measurements. Unless contributions to proton shifts, arising from the effects of, for example, substituent electronegativities, intramolecular electric fields, and ring currents can, where appropriate, be accounted for, the bond magnetic anisotropies which are evaluated must necessarily be far from real. In the absence of suitable procedures for estimating the magnitudes of the contributions from these effects to proton screenings, it is evident that little is to be gained at present by using expressions more precise than equation (1). Further, because it would be difficult to find molecular systems where all screening effects, other than that due to bond magnetic anisotropy, are absent, any $\Delta\chi$ value obtained by use of equation (1) is unlikely to represent a real magnetic anisotropy, and should therefore, be

---

[1] Part I, J. Homer and D. Callaghan, *J. Chem. Soc.* (*A*), 1968, 439.

[2] H. M. McConnell, *J. Chem. Phys.*, 1957, **27**, 226.

[3] J. W. ApSimon, W. G. Craig, P. V. Demarco, D. W. Mathieson, L. Saunders, and W. B. Whalley, *Chem. Comm.*, 1966, 359; *Tetrahedron*, 1967, **23**, 2339.

termed apparent and treated in this context. However, it was shown [1] that apparent anisotropies of this type can be determined readily and used to calculate proton shifts in a range of molecules. The values obtained [1] for $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ are respectively $+4{\cdot}39 \times 10^{-6}$ cm.^{3} mole^{-1} and either zero or a small negative value, not exceeding $-1{\cdot}2 \times 10^{-6}$ cm.^{3} mole^{-1}. The position of the C–H bond induced point dipole was investigated and it was concluded that if $\Delta\chi^{CH}$ is finite it should be considered to act from the carbon atom. It appears in the case of some bonds that the contributions to the screening of a remote proton, arising from real magnetic anisotropy and other effects characteristic of the bond, may be accommodated fortuitously in the so-called apparent anisotropy attributed to that bond. The present investigation was to determine whether the shielding afforded by bonds other than C–C and C–H can be treated similarly.

Our approach for determining $\Delta\chi^{CC}$ and $\Delta\chi^{CH}$ should be capable of extension for the evaluation of $\Delta\chi^{CX}$ where X is any substituent atom or group. The apparent anisotropies thus derived could then be used to facilitate the calculation of chemical shifts in a wider range of compounds than so far considered. The halogens offer a convenient starting point in these investigations and the C–F and C–Cl bonds have been considered first.

The general procedure adopted to estimate the apparent $\Delta\chi^{CX}$ and the effective point of action of the equivalent C–X bond dipole is governed by the assumption that electronegativity and electric field effects can be accounted for in the apparent magnetic anisotropy of the bond. Whether this is true for bonds such as C–F and C–Cl is difficult to ascertain, primarily because of the lack of information concerning the magnitude of screening contributions arising purely from electronegativity effects. However, the most significant electric field contribution to nuclear screening often results from mean square electric fields due to fluctuating dipoles in a molecule [4-6] and is given by (2),

$$\sigma_E = -B\sum_i \frac{3P_iI_i}{r_{ij}^6} \qquad (2)$$

where P_i and I_i are respectively the polarisability and first ionisation potential of the contributing bond, r_{ij} corresponds to R_{ij} in equation (1), and B is a constant to which an approximate value of $+1{\cdot}0 \times 10^{-18}$ e.s.u. can be assigned when proton screenings are considered.[7] Using equation (2) we can show readily that σ_E for a proton due to similarly disposed C–H and C–F bonds will be of the same order of magnitude, whereas that due to a comparable C–Cl bond should be very slightly larger because of the higher bond polarisability. In view of this and the success achieved in calculating proton shifts in our previous work, it appears justifiable at this stage to adopt a similar approach to C–F and C–Cl bonds as was used for C–C and C–H bonds. Relative proton shifts should then be capable of evaluation by use of equation (1). The procedure for investigating $\Delta\chi^{CX}$ is to compare proton shifts in each of several pairs of molecules which are selected such that in each pair the molecules have the same basic skeleton but differ either in the number of substituents X or in their geometric arrangement. Various points along the C–X bond are chosen to represent the point of action of the induced dipole. These, as distances from the carbon atom, are then plotted against the values for $\Delta\chi^{CX}$ that are required by the appropriate coefficients in equation (1) to account for the chosen proton shift differences. From the intersection of the various lines both $\Delta\chi^{CX}$ and its effective point of action can be determined.

Suitable pairs of molecules for studying the C–F magnetic anisotropy are methane and fluoroform, bicyclo[2,2,1]heptane and 1*H*-undecafluorobicyclo[2,2,1]-heptane, and cyclohexane and 1*H*-undecafluorocyclohexane. The last compound is considered to interconvert between the two possible conformers which are taken to exist in the ratio 3 : 2, favouring the hydrogen in the axial position.[8] The coefficients of $\Delta\chi^{CF}$ in equation (1) were evaluated for each molecule. For the cyclohexanes and bicyclo[2,2,1]heptanes the co-ordinate systems suggested in refs. 9 and 10, respectively, and the molecular parameters for fluoroform given in ref. 11 were used for this purpose. From the differences in appropriate coefficients, values were determined for $\Delta\chi^{CF}$ which account for the observed difference in proton shifts in the fluorinated and protonated molecules. The calculations were performed for a number of locations for the equivalent dipole along the C–F bond. The values used in these calculations are in the Table and the results, obtained by considering the three pairs of molecules, are shown in Figure 1. It is evident that there is only one point on the diagram at which the values obtained for $\Delta\chi^{CF}$ from the three sets of calculations become consistent. This corresponds to the value $-6{\cdot}0_3 \times 10^{-6}$ cm.^{3} mole^{-1} for $\Delta\chi^{CF}$, with the equivalent dipole originating on the carbon atom.

$\Delta\chi^{CCl}$ could not be evaluated by precisely the same technique as was used for $\Delta\chi^{CF}$ because the chlorine analogues of the molecules used previously were not readily available, with the exception of the chloroform–methane pair. Together with this pair of compounds three other pairs were examined. The first was cyclohexane and cyclohexyl chloride. In this case the shifts and coefficients of the α-proton in cyclohexyl chloride were compared with those of cyclohexane. For this

---

[4] A. D. Buckingham, H. J. Bernstein, and W. T. Raynes, *J. Chem. Phys.*, 1962, **36**, 3481.

[5] J. W. Emsley, *Mol. Phys.*, 1965, **9**, 381.

[6] J. Feeney, L. H. Sutcliffe, and S. M. Walker, *Mol. Phys.*, 1966, **11**, 117, 129, and 137.

[7] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' vol. 1, Pergamon Press, Oxford, 1965.

[8] J. Homer and L. F. Thomas, *Trans. Faraday Soc.*, 1963, **59**, 2431.

[9] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, 'Conformational Analysis,' Interscience Publishers, New York, 1965.

[10] C. F. Wilcox, jun., *J. Amer. Chem. Soc.*, 1960, **82**, 414.

[11] 'Interatomic Distances,' *Chem. Soc. Special Publ.* No. 11, 1958.

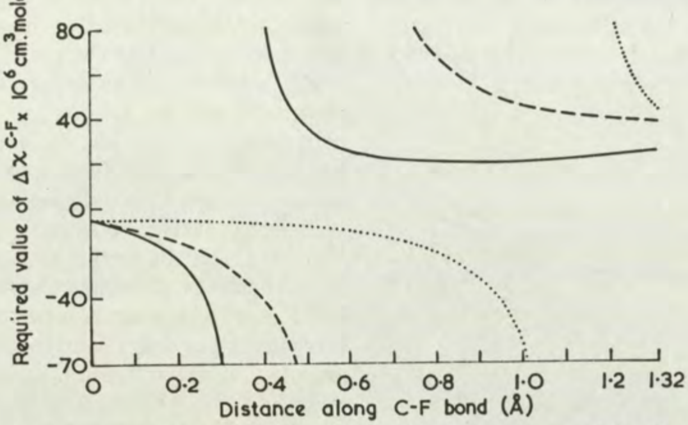


FIGURE 1 The dependence of $\Delta\chi^{CF}$ [evaluated by use of eqn. (1)] on the location assumed for the point of action of the C–F bond magnetic dipole: —— methane–fluoroform, – – – – cyclohexane–1*H*-undecafluorocyclohexane, · · · · bicyclo[2,2,1]heptane–1*H*-undecafluorobicyclo[2,2,1]heptane

purpose both molecules were considered to exist as a 1 : 1 mixture of the possible chair conformers even though, in fact, it is most probable that the cyclohexyl chloride should be represented as a weighted average favouring the axial orientation of the α-hydrogen atom.[12] This assumption is reasonable for the present purpose because any slight deviation in actuality from the chosen situation should not necessitate any significant correction to the relatively large shift (−2·52 p.p.m.) measured by Bothner-By and Naar-Colin [13] for the α-proton in cyclohexyl chloride relative to cyclohexane. The second additional pair of molecules was β-1,2,3,4,5,6-hexachlorocyclohexane and cyclohexane. For these molecules the shifts and coefficients of the axial protons were compared. The shift of the axial proton in the β-hexachlorocyclohexane, previously measured relative to dioxan,[14] is equivalent to τ 5·79. We have remeasured this shift in dioxan relative to internal tetramethylsilane, and obtained the value of τ 5·81. The third additional pair of molecules considered was δ-1,2,3,4,5,6-hexachlorocyclohexane and β-1,2,3,4,5,6-hexachlorocyclohexane. For these, the coefficients and shifts were compared for the equatorial hydrogen in the δ-isomer and the axial hydrogens in the β-isomer. The 40 Mc./sec. proton spectrum of the δ-isomer has been reported to consist of broad singlets at −1·2 p.p.m. (equatorial) and −0·69 p.p.m. relative to dioxan.[14] However, we have re-examined this spectrum in dioxan at 60 Mc./sec. and found that it is considerably more complex than previously reported and shows second-order pseudo-triplet slittings on each resonance band. It is noteworthy that this spectrum is less second-order in chloroform, but no direct use could be made of this fact because insufficient of the β-isomer could be dissolved in chloroform to obtain a spectrum for comparison. However, some use was made of the spectrum of the δ-isomer in chloroform in that it facilitated an assessment of the shift in dioxan as τ 5·12 ± 0·02 which is slightly different from the previously reported value. This equatorial shift was compared with that of the axial hydrogens in the β-isomer rather than taking the internal axial–equatorial shift in the δ-isomer, because the axial resonance can be measured to a much greater accuracy for the β-isomer than for the δ-isomer where axial-resonance overlap probably occurs. Because axial and equatorial hydrogens were compared, it was necessary to account for the different screening contributions to these arising from the magnetic anisotropy of the C–C bonds in the two molecules. Using our previously reported value of $+4{\cdot}39 \times 10^{-6}$ cm.^{3} mole^{-1} for $\Delta\chi^{CC}$, we found σ_{a-e} to be +0·45 p.p.m., in fair agreement with that

Chemical shifts * used in the evaluation of $\Delta\chi^{CF}$ and $\Delta\chi^{CCl}$

	Shift (τ)
Methane	9·774 [a]
Fluoroform	3·76 [b]
Chloroform	2·75
Cyclohexane (time average)	8·564 [c]
Cyclohexane (H_{axial})	8·80 [d]
1*H*-Undecafluorocyclohexane	4·96 [e]
Cyclohexyl chloride	6·04 [f]
β-1,2,3,4,5,6-Hexachlorocyclohexane	5·81
δ-1,2,3,4,5,6-Hexachlorocyclohexane ($H_{equatorial}$)	5·12
Bicyclo[2,2,1]heptane (H_1 resonance)	7·80 [g]
1*H*-Undecafluorobicyclo[2,2,1]heptane	6·52

[a] A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, 1960, **32**, 1227. [b] C. J. Creswell and A. L. Allred, *J. Amer. Chem. Soc.*, 1963, **85**, 1723. [c] G. V. D. Tiers, *J. Phys. Chem.*, 1958, **62**, 1151. [d] F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *J. Amer. Chem. Soc.*, 1960, **82**, 1256. [e] J. Homer, Ph.D. Thesis, Birmingham, 1962. [f] See ref. 13. [g] K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Letters*, 1966, 9.

* Whilst all of the shifts were not measured under the same ideal solution conditions any inaccuracies in the quoted τ values should only cause minor errors in the relatively large shifts required for eqn. (1) and so should not affect significantly the points of intersection of the curves in Figures 1 and 2.

---

[12] L. W. Reeves and K. O. Strømme, *Canad. J. Chem.*, 1960, **38**, 1241.

[13] A. A. Bothner-By and C. Naar-Colin, *J. Amer. Chem. Soc.*, 1958, **80**, 1728.

[14] R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Amer. Chem. Soc.*, 1958, **80**, 6098.

observed (+0·46 p.p.m.). Appropriate account was taken of this value when evaluating $\Delta\chi^{\mathrm{CCl}}$ from this pair of molecules. As in other calculations $\Delta\chi^{\mathrm{CH}}$ was taken as zero. The proton shifts required for the evaluation of $\Delta\chi^{\mathrm{CCl}}$ are included in the Table. Figure 2 illustrates, for the four stysems studied, the variation in the calculated values of $\Delta\chi^{\mathrm{CCl}}$ with the distance along the C–Cl bond chosen for the point of action of the induced dipole. It can be seen from this that, similarly to the C–F and C–H cases, the C·Cl graphs are concurrent at a point requiring the equivalent dipole to act at the carbon atom. Although not so precise as in the other cases, the corresponding value for $\Delta\chi^{\mathrm{CCl}}$ is found to be $-7{\cdot}8 \pm 1{\cdot}0 \times 10^{-6}$ cm.^{3} mole^{-1}.

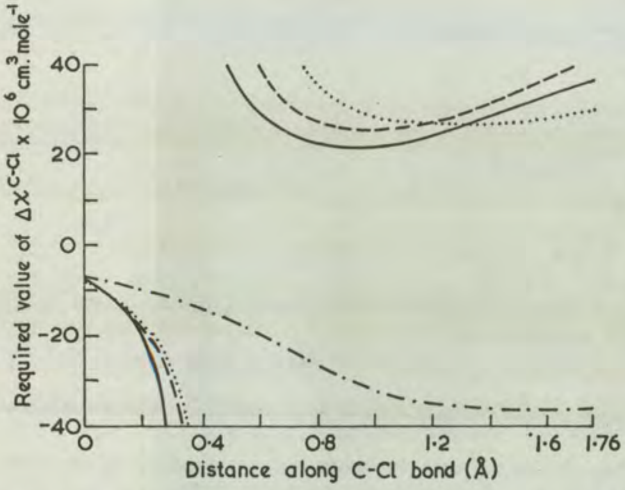


FIGURE 2 The dependence of $\Delta\chi^{\mathrm{CCl}}$ [evaluated by use of eqn. (1)] on the location assumed for the point of action of the C–Cl bond magnetic dipole: —— methane–chloroform, – – – – cyclohexane–cyclohexyl chloride, · · · · cyclohexane–β-1,2,3,4,5,6-hexachlorocyclohexane, — · — · — β–δ-1,2,3,4,5,6-hexachlorocyclohexane

It is most surprising that the apparent values deduced for the C–H, C–F, and C–Cl bonds should all require the point dipole to act from the carbon atom in the bond. Either this is a genuine feature, or there is an overriding effect in all the molecular situations chosen that results in this as a false requirement. The most obvious effects are that when a substituent X is attached to the same carbon as the hydrogen being investigated, the C–X bond anisotropic screening contribution either produces the dominant effect at this hydrogen, or cannot be calculated sufficiently precisely [2,3] by use of equation (1) because of R_{ij} being less than 3 Å. Certainly, from our calculations it appears that the effect of such a substituent is large and of the order of three times greater than the sum of the effects of the remaining substituents of a similar type in the molecule. However, we consider that the effect cannot materially affect the conclusions that have been drawn because it is not present in all cases, and occurs to varying degrees in others. For example, in the C–F bond investigations the effect is not present for the bicyclo[2,2,1]heptanes, whereas it is singly present in the cyclohexane pair and triply present in the methane–fluoroform pair. Similarly, in the chlorine case there is no contribution from this effect in the hexachlorocyclohexane β- and δ-isomer pair but there are single and triple contributions in the remaining molecular pairs. Because of the varying extents to which this geminal effect contributes in the different molecular systems, and the fact that there is only one point of intersection in each of Figures 1 and 2, it appears that the suggestion that this effect cannot be calculated adequately by use of equation (1) is unimportant as indicated earlier, although the R_{ij} values are considerably less than 3 Å.

All our calculations so far have neglected any specific contributions to proton screening due to electronegativity and electric field effects. Consequently, it has been necessary to emphasise that the various $\Delta\chi$ values derived can only be considered to be apparent values that satisfy observed shifts if these can be wholly accounted for in terms of bond magnetic anisotropy. It is, therefore, difficult to assess the magnitudes of real bond magnetic anisotropies. Even a rigorous quantitative investigation of combined electric field and magnetic anisotropy effects would be unprofitable at this stage owing to the uncertainty in assessing the position of action of the electric dipoles of the C–X bonds. Nevertheless, from equation (2), an estimate of the effect of including electric field terms in our calculations shows that the various lines in Figures 1 and 2 would still intersect at a point representing action at or very near to the carbon atom. In each case the inclusion of these terms would make $\Delta\chi^{\mathrm{CX}}$ more positive, resulting in values for the C–F and C–Cl bonds about half the current values. In addition the spread in the intersection of the curves for C–Cl in Figure 2 would also be reduced if account were taken of the electric field effect. Further, whereas in Part I the apparent incompatibility of the values for $\Delta\chi^{\mathrm{CC}}$ and $\Delta\chi^{\mathrm{CH}}$ derived from n.m.r. and magnetic birefringence measurements accounted for by two possible explanations of which one implied limitations in the procedure for comparing the results obtained from the two techniques, it now appears that the other explanation may be more probable. This is that no account has been taken of, for example, electric field contributions from C–H and possibly C–C bonds to proton shifts. In fact, inclusion of these terms in the evaluation of $\Delta\chi^{\mathrm{CH}}$ could cause the resulting value to become positive and then quite possibly compatible with magnetic birefringence data.[15] This does not, however, affect our earlier conclusions that proton shifts in hydrocarbons can be predicted simply in terms of the apparent magnetic anisotropy of the C–C bonds in these molecules.

Apparent values for $\Delta\chi^{\mathrm{CC}}$, $\Delta\chi^{\mathrm{CH}}$, $\Delta\chi^{\mathrm{CF}}$, and $\Delta\chi^{\mathrm{CCl}}$ have now been derived and the equivalent dipoles for the last three of these have been shown to act from the carbon atom of the bond containing the substituent. Because the parameters were deduced from proton

---

[15] A. D. Buckingham, W. H. Prichard, and D. W. Whiffen, *Chem. Comm.*, 1965, 51.

shifts in a diverse range of molecules, they should enable relative proton screenings to be calculated for other saturated compounds containing hydrogen, fluorine, or chlorine, provided, of course, that the geometries of these molecules are known sufficiently precisely to enable the evaluation of the R_{ij} and θ_{ij} terms in equation (1).

EXPERIMENTAL

The proton spectra of 1*H*-undecafluorobicyclo[2,2,1]-heptane and the β- and δ-hexachlorocyclohexanes were observed at 60·004 Mc./sec. and 33° on a Perkin-Elmer R10 spectrometer. The spectra were calibrated by the usual side-band technique with audiofrequency signals derived from a Muirhead-Wigan D-890-A oscillator; the frequencies of these were assessed to ±0·05 c./sec. with a Venner 3336 counter.

We thank Dr. R. Stevens, University of Birmingham, for the gift of a sample of 1H-undecafluorobicyclo[2,2,1]-heptane and Professor W. G. S. Parker for facilites. One of us (D. C.) thanks the S.R.C. for a Research Studentship.

[7/643 *Received, May 23rd,* 1967]