STUDIES IN NUCLEAR MAGNETIC RESONANCE

- I. ANISOTROPY OF THE FLUORINE SHIELDING CONSTANTS IN SUBSTITUTED FLUOROBENZENES
- II. MOLECULAR MOTIONS IN BORANE AND BORONTRIHALIDE COMPLEXES

by

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ABSTRACT

PART I

Proton and fluorine magnetic resonance spectra of eleven substituted fluorobenzenes oriented in a mixed nematic liquid crystal solvent have been measured. The spectra were analysed with either a first order perturbation treatment or a computer simulation technique.

Expressions for the anisotropy of fluorine chemical shift were obtained. For meta- and para-substituted derivatives the changes in anisotropies relative to fluorobenzene have been correlated with Taft's inductive and resonance parameters. It has also been concluded that the fluorine nucleus in these molecules is most shielded when the applied field is perpendicular to the molecular plane and least when the applied field is parallel to the plane and perpendicular to the C-F bond.

Information about the anisotropy of proton chemical shift, absolute sign of indirect spin coupling constant, mean orientation of the solute molecule, and molecular geometry, was also obtained.

PART II

Wide-line proton and fluorine nuclear magnetic resonance studies were made on the compounds of the type $(CH_3)_3 \ N \ BX_3$, where X = H, F, Cl and Br. Comparisons of theoretical and experimental second moments reveal the nature of the rotational motions responsible for the observed line width transitions. The barriers to the rotational motions were estimated from the line width data and the results were compared with those in the similar compounds. The influence of the molecular shape and the dipolar interaction energy on the reorientation freedom in these solid complexes was considered.

A similar study on ammonia borontrifluoride has shown that molecular rotation occurs in this complex.

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PART I

ANISOTROPY OF THE FLUORINE SHIELDING CONSTANTS IN SUBSTITUTED FLUOROBENZENES

CHAPTER I

INTRODUCTION

I-1 Nuclear Magnetic Resonance Phenomena

Certain nuclei possess non-zero spin angular momentum $\dot{I}h$ and an associated magnetic moment $\dot{\mu}$. The two vectors are parallel, so that we can write

where χ is a scalar called the "magnetogyric ratio". When placed in a magnetic field, H_o, the spin energy levels are split and transitions between these sublevels can be induced by an oscillating magnetic field of the appropriate frequency. For a nucleus of spin 1/2 the resonance condition is

$$f_{k} y = 2\mu H_{loc}$$

or $W = 2\pi y = \gamma H_{loc}$ (1-2)

The local field H_{loc} is the sum of the external magnetic field H_{o} and the small contributions due to the various interactions between the nucleus and its surroundings. It is these contributions that make NMR spectroscopy interesting, as they give information on the environment of the nucleus.

The nuclear magnetic resonance spectra of diamagnetic molecules depend on four types of interaction: (1) the interaction between external magnetic fields and nuclear magnetic moments (2) the indirect spin-spin couplings, (3) the direct dipole-dipole couplings between nuclei and (4) the interaction of nuclear quadrupole moments with the electric field gradients at the nuclei. All these interactions involving the product

of two vector functions are influenced by the translational and rotational motions of the molecules, and thus they are strongly dependent on the aggregate state of the system. In isotropic liquids and gases, the intermolecular dipole-dipole coupling vanishes because of translational motion, and the intramolecular dipole-dipole coupling and quadrupole interaction vanish because of rotaional motion. It is possible, therefore, to obtain the high resolution NMR spectra in gaseous and liquid states and to study the smaller effects of the chemical shifts and indirect spin-spin couplings. These parameters have directional properties, that is , their magnitude depends on the orientation of the molecule with respect to the external magnetic field. In fact they are second-rank tensors and may have as many as nine independent components. In the ordinary high resolution NMR experiments only mean shielding constants and coupling constants, $\sigma_i = \frac{1}{3} (\sigma_{aai})$ + σ_{cci} + σ_{cci}) and $J_{ij} = \frac{1}{3}(J_{aaij} + J_{bbij} + J_{ccij})$, can be determined and information about the components $\sigma_{\alpha\beta i}$ and $J_{\alpha\beta ij}$ along various molecular axes is lost due to the isotropic molecular motion. It is, nevertheless, desirable to measure experimentally these anisotropic properties since these components of the tensor contain potentially useful information concerning the electronic structure of the molecule. These measurements will also be of fundamental importance to the further development of the theory of magnetic resonance. The first part of this thesis describes the determination of the anisotropy of the fluorine shielding constants in a series of substituted fluorobenzenes.

In solids, the restrictions on molecular motion do not average to zero the numerous intermolecular dipole interactions and this results in a broad line of several gauss width with little or no structure.

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However, the dipole-dipole couplings of intramolecular origin can be reduced by either internal rotation or rotation of the molecule as a whole; the study of wide-line NMR gives valuable information about molecular motion in solid state and this will be the subject of the second part of this thesis.

<u>I-2 Experimental Methods for Determination of Anisotropy of Fluorine</u> <u>Shielding Constants</u>

A determination of the anisotropy in the fluorine shielding tensor was first attempted by examining its effect upon the spin-lattice relaxation time T_1 of liquids. As the molecules tumble, the nuclei experience a fluctuating field as the shift runs randomly through its range of values. By measuring the field dependence of the fluorine relaxation time in 1,3,5-trifluorobenzene, Gutowsky and Woessner¹) obtained a value of 750 ppm for the anisotropy AC. However, since the two values of applied field used in these experiments differed by only 33% and the contribution of the spin-rotation mechanism to the spin-relaxation time had been neglected, the accuracy of this estimation has been questioned².

Information concerning the anisotropy of the shielding tensor can be obtained from the asymmetric field-dependent broadening of the resonance spectrum of a polycrystalline solid. Eloembergen and Rowland³) first gave a detailed treatment of the theoretical line shapes which result from anisotropic chemical shifts alone. Later the same authors⁴) calculated the second moment of a polycrystalline line including chemical shift anisotropy, dipolar and scalar coupling perturbations. They found

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that the second moment is separable into two contributions, one due to a field-dependent, anisotropic chemical shift interaction alone, and the other due to field-independent effects. These results have been applied by Andrew and Tunstall²⁾ to obtain both sign and magnitude of the fluorine chemical-shift anisotropies for three organic fluorides, 1,2,4-trifluorobenzene, $\text{CFCl}_2\text{CFCl}_2$ and $\text{CF}_2\text{BrCF}_2\text{Br}$. Recently MacLean and Mackor⁵⁾ have pointed out that the asymmetry of the line shape may be strongly dependent on the origin of the dipolar local field and emphasized the need of simultaneously accounting for the dipolar perturbation as well as the chemical shift interaction in the analysis of the line shape. This method has been further examined by Gutowsky and co-workers^{6,7)}.

Another method of measuring the anisotropy of the shielding constant depends upon the orientation of guest molecules trapped in a single crystal of a clathrate compound at low temperatures (about $1^{\circ}K$)^{8,9}. The shift of the resonance line was measured as a function of angle as the crystal was rotated with respect to the applied magnetic field. Anisotropies of the fluorine shielding were obtained for CH_3F , NF_3 and CHF_3 .

The disadvantage of methods employing crystalline solids lies in the need to measure small changes in a broad resonance. To avoid this difficulty attempts have been made to obtain the high resolution NMR spectra of oriented molecules^{10,11}. For such a purpose a macroscopically anisotropic medium is required which permits extensive translational motion while favouring certain molecular orientations. The possession of sufficient translational freedom by the molecule eliminates the intermolecular dipolar broadening. If the rotational motion is

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sufficiently fast and the sample is homogeneously oriented, the magnetic fields from the nuclei within the molecule will be averaged to definite non-vanishing values which lead to observable splittings. The observation of these intramolecular dipolar couplings then permits the degree of orientation to be measured as well as the absolute signs of indirect spin coupling constants. Since the dipole-dipole interaction is proportional to the inverse cube of the separation of the interacting nuclei, information about relative bond lengths and bond angles can also be obtained from the experimentally measured direct dipole coupling constants¹².

An apparently simple method to obtain such high resolution NMR spectra of oriented molecules is to apply a large static electric field, in addition to the magnetic field, to a fluid sample consisting of polar molecules. This technique has been applied to molten p-nitrotoluene by Buckingham and McLauchlan¹³⁾, but unfortunately this only produced a rather weak orientation effect at easily attainable electric field strengths and is only applicable to fluids of high resistivity. A much more powerful and useful orienting medium, as demonstrated by Saupe and Englert in 1963^{14,15,16,17)}, is a liquid crystal solvent. Certain types of liquid crystal become homogeneously oriented in a field of a few hundred gauss and a solute molecule dissolved in such a solvent can become partially oriented as a result of the angular dependence of the intermolecular forces¹⁸⁾. Usually liquid crystal molecules contain large numbers of protons and the NMR spectrum consists of many lines and it appears as a rather broad envelope, so that only the sharp lines arising from the solute resonance can be seen¹⁹⁾.

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In this investigation a mixture of p-p!-di+d+m!koxyazoxy-benzenes was used as a liquid crystal solvent to obtain high resolution spectra of oriented fluorobenzenes.

1-3 Theoretical Calculation of Fluorine Chemical Shift in Fluorobenzenes

The general theory of the nuclear shielding was developed by Ramsey²⁰⁾. For systems that do not have spherical symmetry he showed that, in addition to the first-order diamagnetic shielding (the Lamb term²¹⁾), one has to include a second-order term, which is often called the paramagnetic or high frequency term.

By using an order of magnitude argument Saika and Slichter²²) have shown that chemical shift of fluorine is usually dominated by the second-order contribution. They expressed this contribution in terms of localized bond properties and obtained a useful correlation between ionic character and fluorine resonance shift.

Based on Saika and Slichter's work, Karplus and Das²³⁾ have presented a molecular orbital method for calculating fluorine chemical shifts. By the introduction of suitable approximations, they expressed the shielding tensor in terms of localized bond properties; ionic character, s orbital hybridazation and double bond character of the X-F bond. This approach has been fairly successfully applied in a semiempirical fashion to the calculation of isotropic fluorine chemical shifts in substituted fluorobenzenes^{23,24}). For systems containing essentially covalent X-F bonds, the theory predicts that the magnetic shielding of fluorine nuclei will be greatest when the applied field is along the bond direction.

Prosser and Goodman²⁵⁾ have extended the Karplus and Das treatment specifically to chemical shifts in conjugated fluorine compounds. They include terms arising from changes in the carbonfluorine pi-bond order and changes in the pi-charge density on the neighbouring carbon atom. The substituent effects on the sigma framework of the molecule are not considered in this treatment and all changes in shielding in the aromatic fluorides are ascribed to changes in the pi-electron distribution. The importance of pi-charge densities demonstrated by this work and the difficulties involved in calculating the sigma-charge densities have led to the various attempts 26-30) to correlate the calculated pi-densities with isotropic fluorine chemical shifts. Such approaches have been fairly successful providing no ortho substituents are present. These methods, however, are aimed at correlating the isotropic chemical shifts, furthermore, changes in the sigma framework are ignored or included empirically. To compare anisotropies of fluorine chemical shifts it seemed more appropriate to employ the original Karplus and Das theory. The detailed mathematical formulation of this theory will be presented in Chapter VI.

I-4 A Summary of the Results on Anisotropies of Fluorine Shielding Constants

A summary of measured anisotropies of fluorine chemical shifts is given in Table I.

Several points about these results are worth mentioning. In at least three cases, CH_3F , $CHFCl_2$ and XeF_4 , the sign of the anisotropy differs from that predicted by the Karplus and Das theory. The values

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TABLE I

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Measured Anisotropies (ppm) of Fluorine Chemical Shifts

Compounds	Results	Experimental Method
CFC12CFC12	$\Delta \sigma = 240^{*}$	Wide line ²⁾
$CF_2Br - CF_2Br$	$\Delta \sigma = 260$	Wide line ²⁾
CHFC12	$\Delta \sigma = -210$	Wide line ⁵⁾
CH3 F	$\Delta \sigma = -66$	Clathrate ⁸⁾
	$\Delta \sigma = -159$	Liquid-crystal solution ³¹⁾
CH2F2	$\Delta \sigma = 159$	Liquid-crystal solution ³¹⁾
CHF3	$\Delta \sigma = 105$	Clathrate g)
	$\Delta \sigma = 249$	Liquid-crystal solution ³¹⁾
NF ₃	$\Delta \sigma = 390$	Clathrate ⁹⁾
^{CF} 3 ^{C≡CH}	$\Delta \sigma = 149$	Liquid-crystal solution ³²⁾
CF ₃ C≡CICF ₃	$\Delta \sigma = 147$	Liquid-crystal solution 33)
XeF ₄	$\Delta \sigma = -570$	Wide line ³⁴⁾
XeF ₂	$ \Delta \sigma = 105$ (negative sign preferred)	Wide line ³⁵⁾
BaFPO 3	$\Delta \sigma = 182$	Wide line ⁷⁾
1,2,4-C6 ^H 3 ^F 3	$\Delta \sigma = 250$	Wide line ²⁾
C_6F_6 and C_6H_5F	$\sigma_{aa} = \sigma_{bb} = 30^{**}$	Liquid crystal solution 36,37)
	$\sigma_{aa} - \sigma_{cc} = 289$	
^с 6 ^н 5 ^ғ	∆ € = 160	Molecular beam ³⁸⁾
	$\sigma - \sigma = -9$	
	s the shielding constant for	a magnetic field
parallel (perpen	dicular) to the X-F bond.	
**		

For the assignment of molecular axes a, b and c see text.

for the same compound determined by different methods are not consistent, for example, -66 ppm and -159 ppm have been obtained for methylfluoride. It is rather difficult to understand why ΔG will be so different for two similar compounds such as CHFCl₂ and (CCl₂F)₂; the fact becomes more surprising if one notices that both values were obtained with the same method.

The anisotropies of ¹⁹F shielding tensor in fluorobenzenes have been studied by different experimental methods. With the assumption of axial symmetry of shielding tensor, a value of +250 ppm for $\Delta \sigma$ was obtained from the field dependence of fluorine second moment in 1,2,4trifluorobenzene by Andrew and Tunstall²⁾.

From a molecular beam magnetic resonance study of mono-fluorobenzene, Chan and Dubin³⁸⁾ have determined the spin-rotational interaction constants $C_{\alpha\alpha}^{I}$ etc. The spin-rotational constants $C_{\alpha\alpha}^{I}$ are composed of two contributions. The first is from the rotation of adjacent charged nuclei about the nucleus under consideration, the second from the circulating electron currents. The expression of the second contribution, except for multiplicative constants and vibrational corrections, is identical with that for the paramagnetic shielding term $\sigma_{\alpha\alpha}^{(2)}$. Since the contribution $\sigma_{\alpha\alpha}^{(2)nuclear}$ from the rotating nuclei can be easily calculated, one can relate $\sigma_{\alpha\alpha}^{(2)}$ directly to experimentally determined $\sigma_{\alpha\alpha}^{(2)CI}$. The results for $\sigma_{\alpha\alpha}^{(2)CI}$, $\sigma_{\alpha\alpha}^{(2)nuclear}$ and $\sigma_{\alpha\alpha}^{(2)}$ for fluorobenzene are listed in Table II (a axis - perpendicular to the plane of ring, b axis - along C-F bond and c axis - in the molecular plane and perpendicular to the C-F bond).

Based on both experimental data and theoretical considerations, Chan and Dubin further suggested that the anisotropy of the shielding

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TABLE IT

Fluorine Shielding Anisotropy (ppm) in Fluorobenzene from Molecular Beam Measurement³⁸⁾

g	$\sigma_{gg}^{(2) \text{ nuclear}}$	6 gg (2) CI	6 _gg ⁽²⁾
a	-222	-193	-415
b	- 33	- 31	- 64
с	-189	-184	-373

tensor can be directly obtained from $\sigma_{\alpha\alpha}^{(2)CI}$. With either $\sigma_{\alpha\alpha}^{(2)}$ or $\sigma_{\alpha\alpha}^{(2)CI}$ their results indicates $\sigma_{bb} \gg \sigma_{cc} > \sigma_{aa}$, while the Karplus and Das theory predicts $\sigma_{bb} \gg \sigma_{aa} > \sigma_{cc}^{23}$.

The anisotropic spectra of hexafluorobenzene³⁷⁾ and fluorobenzene³⁶⁾ oriented in a nematic p-p'-di-n-hexyloxyazoxybenzene have been studied by Snyder and Anderson. For hexafluorobenzene a value of 159 ppm was obtained for $\sigma_{aa} - \frac{1}{2} (\sigma_{bb} + \sigma_{cc})$. Combining this value with the result for fluorobenzene and assuming that C-F bonds in these two compounds are similar, Snyder obtained $\sigma_{aa} - \sigma_{bb} = 30$ ppm and $\sigma_{aa} - \sigma_{cc} = 289$ ppm i.e. $\sigma_{aa} > \sigma_{bb} > \sigma_{cc}$.

The three experimental results disagree not only in magnitude but also in sign. Neither do they agree with the prediction of the semiempirical theory. More important, assumptions were made in all three measurements in obtaining anisotropic values from experimental data. These assumptions need to be verified.

CHAPTER II

LIQUID CRYSTALS

When some organic substances are "melted", a turbid liquid is produced instead of a clear isotropic liquid. On further heating a well defined phase transition to the isotropic liquid is observed. These turbid liquids, called liquid crystals, or mesophases, are welldefined phases having properties intermediate between those of isotropic liquid and crystalline material 17,39,40). There are three different types of liquid crystal, namely nematic, smectic and cholesteric. Molecules that give liquid crystals are more or less elongated. Fig. 1 shows the schematic structure of these three mesophases. A homogeneously oriented layer of a liquid crystal behaves optically as an uniaxial crystal. The nematic mesophase differs structurally from normal isotropic liquid only in the spontaneous orientation of the molecules with their long axes parallel (Fig. 1). In the absence of any external restraint, the preferred direction of the long axis is not uniform over a large volume. In order to obtain high resolution NMR spectra, a homogeneously oriented sample is required. A nematic phase can readily be homogeneously oriented by magnetic field of a few hundred gauss; the preferential direction of the long axis - the optical axis - becomes parallel to the field direction. This requirement is automatically fulfilled when the sample has been introduced into a NMR spectrometer. The viscosity of a nematic mesophase is comparable with that of a normal liquid, such as benzene, which implies that the molecular motion is sufficiently rapid to average out the intermolecular dipolar coupling.



Fig. 1. The local molecular arrangements in mesophases:

- (a) nematic, e.g. p-azoxyanisole,
- (b) smectic, e.g. ethyl p-azoxybenzoate,
- (c) cholesteric, e.g. cholesteryl propionate.

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A given substance may give one or more smectic phases as well as the nematic phase. The smectic phases, in agreement with the higher order, always occur at lower temperatures. By comparison with the nematic phases, the arrangement of molecules in smectic phases shows the existence of an additional degree of order i.e. the arrangement of the centers of gravity of molecules in planes perpendicular to the preferred direction of the long axis of the molecule. The additional order makes the structure of the smectic mesophase more similar to a solid, and as might be expected the mesophase is rather viscous. The smectic mesophase can not be oriented by magnetic fields with attainable strength. There is also no commonly applicable method which can be used to establish a homogeneously oriented layer in the smectic phase.

A cholesteric phase occurs only in optically active substances. It may be regarded as a special case of a nematic phase, since its molecular arrangement corresponds to a twisted nematic layer (Fig. 1). In a homogeneously oriented layer, the preferred direction of the long axis is no longer constant over the entire volume, there are instead parallel planes in which the preferred direction is constant. As one proceeds along a line perpendicular to these planes, the preferred direction rotates uniformly. The pitch of this rotation (rotation through 2%) varies widely, and is generally between 0.2 and 20µ. The resulting helical structure is responsible for the observed high optical activity of the cholesteric mesophase. As a twisted nematic layer, the cholesteric phase can also be oriented by a field of several thousand

- 14 -

gauss. Depending on the nature of the compound, the long axis of the molecules may tend to align either parallel or perpendicular to the magnetic field. The examples for these two cases are optically active amyloxyazoxybenzene and cholesteric derivatives respectively⁴¹⁾.

For the reasons given above, nematic liquid crystals provide the most useful solvents for obtaining the high resolution NMR spectra of oriented molecules. Due to the difficulties involved in obtaining a homogeneously oriented layer, and its high viscosity, the smectic mesophase may not be a useful solvent for alignment experiments. The possibility of using cholesteric phases has not yet been fully exploited although recently a high resolution NMR spectrum of a solute molecule has been observed in a cholesteric phase⁴¹.

Another group of liquid crystals occurs in solution, these are more accurately described as lyotropic liquid crystals. The bestknown representatives of this group are aqueous soap solutions. The molecular order is a function of composition and can resemble either that of smectic or nematic phase. Although the viscosity of the mesophase is often extremely high, it has been found that methyl alcohol is highly oriented and gives a high-resolution NMR spectra in such a solvent system⁴²⁾. Lyotropic liquid crystal solvent could be particularly valuable for orienting lyophilic solutes.

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CHAPTER III

BASIC THEORY OF NUCLEAR MAGNETIC RESONANCE SPECTRA OF ORIENTED MOLECULES

<u>III-1 The Mean Orientation of the Solute Molecule - the Order Matrix</u> and Motional Constants

To describe the mean orientation of a solute molecule in a nematic solvent, Saupe¹⁵⁾ introduced the order matrix, which will now be discussed.

Let X'_1 , X'_2 , X'_3 be specific space-fixed cartesian co-ordinates, the X'_3 axis is parallel to the optical axis (the preferred direction of long molecular axis) of the homogeneously oriented liquid crystal layer. Consider a rigid molecule in the layer. α_1 , α_2 and α_3 are the axes of a molecular fixed co-ordinate system, and at the same time α_1 , α_2 , α_3 denote the components of a molecular-fixed vector and in space-fixed system these components are expressed by X'_1 , X'_2 , X'_3 . β_1 , β_2 , β_3 are the components of a second molecular fixed vector, and Y'_1 , Y'_2 , Y'_3 are its components in space-fixed system. Since we are mainly concerned with the type of interactions between two vectors, the expressions for the average value of $< X'_1 Y'_1 >$ in terms of the components in the molecular fixed system i.e. $\alpha_1\beta_1$ need to be computed.

Due to the rotational symmetry about the optical axis $\langle X'_{1}Y'_{j} \rangle$ are all equal to zero for $i \neq j$ and also $\langle X'_{1}Y'_{1} \rangle = \langle X'_{2}Y'_{2} \rangle$. From the invariance of the trace we obtain

$$< x'_{1} y'_{1} > = < x'_{2} y'_{2} > = (\sum_{i} \alpha_{i} \beta_{i} - < x'_{3} y'_{3} >)/2$$
 (3-1)

fixed axis α_i as $\underline{\phi}_i$, then

$$\langle x_{3}' x_{3}' \rangle = \sum_{ij} \alpha_{i} \beta_{j} \langle \cos \phi_{i} \cos \phi_{j} \rangle$$
 (3-2)

and equation (3-1) becomes

$$\langle \mathbf{x}_{1}'\mathbf{Y}_{1}' \rangle = \langle \mathbf{x}_{2}'\mathbf{Y}_{2}' \rangle = \frac{1}{2} \sum_{\mathbf{i}} \alpha_{\mathbf{i}} \beta_{\mathbf{i}} - \frac{1}{2} \sum_{\mathbf{i}} \alpha_{\mathbf{i}} \beta_{\mathbf{j}} \cdot \langle \cos \phi_{\mathbf{i}} \cos \phi_{\mathbf{j}} \rangle$$

$$\langle \cos \phi_{\mathbf{i}} \cos \phi_{\mathbf{j}} \rangle \qquad (3-3)$$

Equations (3-2) and (3-3) can be rewritten as

$$\langle x'_{3} Y'_{3} \rangle = \frac{1}{3} \sum_{i=1}^{3} \alpha_{i} \beta_{i} + \frac{2}{3} \sum_{i=1}^{3} S_{i} \beta_{i} \beta_{i}$$
(3-4)

$$< x'_{1} x'_{1} > = < x'_{2} x'_{2} > = \frac{1}{3} \sum_{i=1}^{\infty} \alpha_{i} \beta_{i} - \frac{1}{3} \sum_{i=1}^{\infty} \beta_{i} \alpha_{i} \beta_{j}$$
 (3-5)

where S_{ij} is defined as follows

$$S_{ij} = \frac{1}{2} < 3 \cos \phi_i \cos \phi_j - \delta_{ij} > \qquad (3-6)$$

and δ_{ij} is the Kronecker symbol.

If a new space-fixed co-ordinate system X_{i} is chosen and

$$X_{l} = \sum_{i}g_{li}X'_{i}, \text{ thus}$$

$$< X_{k}Y_{l} > = \sum_{ij}g_{ki}g_{lj} < X'_{i}Y'_{j} >$$

$$= \frac{1}{3}\delta_{kl}\sum_{i}\alpha_{i}\beta_{i} + (g_{3k}g_{3l} - \frac{1}{3}\delta_{kl})\sum_{ij}s_{ij}\alpha_{i}\beta_{j}$$

$$= \frac{1}{3}\delta_{kl}\sum_{i}\alpha_{i}\beta_{i} + (\cos \eta_{k}\cos \eta_{l})$$

$$- \frac{1}{3}\delta_{kl}\sum_{ij}s_{ij}\alpha_{i}\beta_{j} \qquad (3-7)$$

Here η_i is the angle between X_i axis and the optical axis X_j .

The expression for the average value in a space-fixed co-ordinate system can be applied to every molecular-fixed tensor of second rank, since every tensor can be expressed as linear superposition of basic tensors, for which equation (3-7) is derived.

As far as it is of importance to magnetic resonance experiments, the mean orientation of the solute in nematic solvents can be described by the matrix (S_{ij}), which is called the order matrix. This matrix is symmetrical by definition and $S_{11} + S_{22} + S_{33} = 0$. Thus there remain only five independent elements. The limiting ranges of the matrix elements are:

> $-\frac{1}{2} \leq S_{ii} \leq 1$ $-\frac{3}{4} \le S_{i,j} \le \frac{3}{4}$ for i≠j only

Snyder³⁶⁾ has adopted a different approach to treat the average orientation of the molecule. In Snyder's method, the probability $P(\Theta, \phi)$ that the magnetic field is at the spherical polar angles θ and ϕ relative to the molecular-fixed cartesian axes **x**, **y**, $\ddot{\mathbf{z}}$, may be written as a series of spherical harmonics (Fig. 2):

$$P(\Theta, \phi) = (4\pi)^{-1} + C_{x}P_{x} + C_{y}P_{y} + C_{z}P_{z} + C_{3z}^{2} - r^{2} D_{3z}^{2} - r^{2}$$
$$+ C_{x^{2}-y^{2}} D_{x^{2}-y^{2}} + C_{xz}D_{xz} + C_{yz}D_{yz} + C_{xy}D_{xy} + \dots (3-8)$$
$$P_{x} = (4\pi)^{-1} (3)^{-1/2} SIN \Theta COS \phi \qquad (3-9)$$

where

$$P_y = (4\pi)^{-1} (3)^{-1/2} \sin \theta \sin \phi$$
 (3-10)

(3-9)

$$P_{z} = (4\pi)^{-1} (3)^{-1/2} \cos \theta \qquad (3-11)$$

$$D_{3z}^2 r^2 = (4\pi)^{-1} (2)^{-1} (5)^{1/2} (3 \cos^2 \theta - 1)$$
 (3-12)

$$D_x^2 - y^2 = (4\pi)^{-1} (2)^{-1} (15)^{1/2} (SIN^2 \Theta \cos 2\phi)$$
 (3-13)

$$D_{xy} = (4_{T7})^{-1} (15)^{1/2} (\sin^2 \theta \sin \phi \cos \phi)$$
 (3-14)

$$D_{xz} = (4\pi)^{-1} (15)^{1/2} (SIN \oplus COS \oplus COS \phi)$$
 (3-15)



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Fig. 2 The orientation of the magnetic field H o in a molecular - fixed coordinate system.

$$D_{yz} = (4\pi)^{-1} (15)^{1/2} (SIN \oplus COS \oplus SIN \phi)$$
 (3-16)

The C-coefficients in the above expansion describe the orientation. Since $P(\Theta, \phi)$ is a probability density function, $\int_{0}^{2\pi} \int_{0}^{\pi} P(\Theta, \phi) \text{ SIN } \Theta \ d\Theta \ d\phi = 1, \text{ and the mean value of any}$ function $f(\Theta, \phi)$ of the orientation is $\overline{f} = \int_{0}^{2\pi} \int_{0}^{\pi} f(\Theta, \phi) P(\Theta, \phi) \text{ SIN } \Theta \ d\Theta \ d\phi \qquad (3-17)$

It will be shown later that all the interactions observed in a nuclear magnetic resonance experiment are only dependent on the five C-coefficients: $C_{3z}2_{-r}2$, $C_{x}2_{-y}2$, C_{xy} , C_{xz} and C_{yz} . For this reason, we will neglect all the other C-coefficients in the equation (3-8), and refer to these five C-coefficients as motional constants in subsequent discussions.

As expected, the five motional constants are closely related to the elements of the order matrix:

$$C_{3z^2-r^2} = (5)^{1/2} (2)^{-1} S_{33} (3 \cos^2(H) - 1)$$
 (3-18)

$${}^{C}x^{2}-y^{2} = (5)^{1/2} (3)^{-1/2} (S_{11}-S_{22}) (3 \cos^{2} \mathbb{H} - 1)/2 (3-19)$$

$${}^{C}xy = (5)^{1/2} (3)^{-1/2} S (3 \cos^{2} \mathbb{H} - 1) (3-19)$$

$$\nabla = (5)^{1/2} (3)^{-1/2} s_{12} (3 \cos^2 (\mathbb{H} - 1))$$
 (3-20)

$$C_{xz} = (5)^{1/2} (3)^{-1/2} S_{13} (3 \cos^2(H) - 1)$$
 (3-21)

$$C_{yz} = (5)^{1/2} (3)^{-1/2} S_{23} (3 \cos^2(H) - 1)$$
 (3-22)

Here (H) is the angle between the liquid crystal optical axis and the applied field direction. These relations can be easily verified with equation (3-7) by computing the average value $< X_3Y_3 > of$ two unit vectors along molecular-fixed cartesian axes, the X_3 axis is taken to be parallel to the field direction.

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If a molecule is symmetrical, a suitable choice of molecularaxes can reduce the number of motional constants. For a molecule with a 3-fold or higher axis of symmetry a choice of this as the z-axis causes only $C_{3z^2-y^2}$ to be non-zero. If a molecule has two perpendicular planes of symmetry, and if one axis is parallel to them both, with second and third axes in the planes, the $C_{3z^2-r^2}$ and $C_{x^2-y^2}^2$ are the only non-vanishing motional constants. If the molecule has a single plane of symmetry, the choice of a co-ordinate system with one axis perpendicular to this plane leaves only three coefficients to be non-zero.

III-2 The Spin Hamiltonian

The complete Hamiltonian determining the energy levels and spin wave functions of a set of nuclei in a molecule in a fixed orientation in space can be written as (using Hz as the energy unit)

$$\mathcal{H} = -\frac{H_{o}}{2\pi r} \sum_{i}^{r} \gamma_{i} (I_{Zi} = \sum_{\alpha = X, \tilde{Y}, Z} \sigma_{Z\alpha i} I_{\alpha i}) + \sum_{i > j}^{r} \vec{I}_{i} (\vec{A}_{ij}) \vec{I}_{j}$$
(3-23)

where, as usual, the direction of external magnetic field H_0 is taken as to be the Z axis. The term $\sigma_{\alpha\beta i}$ is the shielding tensor of nucleus i; the total magnetic field at nucleus i in the β direction due to an external magnetic field H_{α} is H_{α} ($\delta_{\alpha\beta} - \sigma_{\alpha\beta i}$), where $\delta_{\alpha\beta}$ is the unit second rank tensor. The constant tensor \widehat{A}_{ij} represents the indirect spin coupling \widehat{J}_{ij} and the intramolecular dipole-dipole coupling $\widehat{D}_{ij}^{\text{dir}}$ between nuclei i and j for $i \neq j$, and the quadrupole interaction for i = j.

The elements of direct dipole-dipole coupling $\overset{\leftrightarrow}{\underset{j}{\text{D}}}$ between two

magnetic moments of $\pi_{\gamma_i} \vec{I}_i$ and $\pi_{\gamma_j} \vec{I}_j$ of nuclei i and j with separation \vec{R}_{ij} are

$$D_{\alpha\beta ij}^{dir} = \frac{n}{2\pi} \frac{\gamma_{i} \gamma_{j}}{R_{ij}^{5}} [(R_{ij})^{2} \delta_{\alpha\beta} - 3(R_{ij\alpha})(R_{ij\beta})] \quad (3-24)$$

Thus the tensor $D_{ij}^{\leftarrow dir}$ is traceless (i.e. $\sum_{\alpha} D_{\alpha\alpha ij} = D_{XXij}$ + $D_{YXij} + D_{ZZij} = 0$) and symmetrical (i.e. $D_{XYij} = D_{YXij}$ etc.)

In all practical cases, H_0 is of the order of 10^4 gauss, and the Zeeman term is much bigger than any of the remaining interactions, so mixing of the states with different values of $I_Z = \sum_i I_{Zi}$ can be neglected. Thus, in the high field approximation, one can write

$$\begin{aligned} \mathcal{H} &= -\frac{H_{0}}{2\pi} \sum_{i} \gamma_{i} (1 - \sigma_{ZZi}) I_{Zi} \\ &+ \sum_{i > j} \frac{1}{3} (A_{XXij} + A_{YYij} + A_{ZZij}) \vec{I}_{i} \vec{I}_{j} \\ &+ \sum_{i > j} \frac{1}{3} (2 A_{ZZij} - A_{XXij} - A_{YYij}) \\ &\quad (\frac{2}{2} I_{Zi} I_{Zj} - \frac{1}{2} \vec{I}_{i} \vec{I}_{j}) \end{aligned}$$
(3-25)

For a molecule in constant rotational motion, the average values of σ_{ZZi} and $A_{\alpha\beta ij}$ have to be used in equation (3-25). The average values can relate either to the order matrix (S_{ij}) through equation (3-7) or to the motional constants through equation (3-17). In this thesis Snyder's treatment³⁶ is adopted to analyze the observed spectra.

For any molecular-fixed second order tensor A it can be shown

$$\frac{(A_{ZZij} + A_{YYij} + A_{ZZij})}{(2A_{ZZij} - A_{YYij} - A_{XXij})} = (A_{xxi} + A_{yyij} + A_{zzij}) \quad (3-26)$$

$$\frac{(2A_{ZZij} - A_{YYij} - A_{XXij})}{(2A_{ZZij} - A_{YYij} - A_{XXij})} = 2(3)^{-1}(5)^{-1/2}c_{3z}^{2}-r^{2} \quad [A_{zzij} - \frac{1}{2}(A_{xxij} + A_{yyij})] \\
+ (3)^{-1/2}(5)^{-1/2}c_{x}^{2}-y^{2} \quad [A_{xxij} - A_{yyij}] \\
+ (3)^{-1/2}(5)^{-1/2}c_{xy} \quad [A_{xyij} + A_{yxij}] \\
+ (3)^{-1/2}(5)^{-1/2}c_{xz} \quad [A_{xzij} + A_{zxij}] \\
+ (3)^{-1/2}(5)^{-1/2}c_{yz} \quad [A_{yzij} + A_{zyij}] \quad (3-27)$$

In equations (3-26) and (3-27), X, Y, Z, and x, y, z, are referred to the axes of space-fixed and molecularfixed co-ordinate system respectively.

With equations (3-25), (3-26) and (3-27), the spin Hamiltonian for a set of nuclei of spin 1/2 can then be written as

$$\begin{aligned} \mathcal{H} &= - \frac{H_0}{2\pi} \sum_{i} \gamma_i (1 - \overline{\sigma}_{ZZi}) I_{Zi} \\ &+ \sum_{i > j} J_{ij} \vec{I}_i \vec{I}_j \\ &+ \sum_{i > j} D_{ij} (\frac{3}{2} I_{Zi} I_{Zj} - \frac{1}{2} \vec{I}_i \vec{I}_j) \end{aligned} (3-28)$$

The dipole coupling constant D_{ij} can be taken as the sum of two terms; D_{ij}^{dir} , the contribution from the intramolecular dipole-dipole interaction, and D_{ij}^{pseudo} , the contribution due to the anisotropy of the indirect spin-spin coupling constant. The indirect spin coupling constant J_{ij} , the direct dipole coupling constant D_{ij}^{dir} and the pseudo-dipole coupling constant D_{ij}^{pseudo} can be computed from equation (3-26) and (3-27):

$$J_{ij} = (J_{xxij} + J_{yyij} + J_{zzij})/3$$
(3-29)

$$D_{ij}^{dir} = -2(5)^{-1/2}(2\pi)^{-1} \gamma_{i} \gamma_{j} + \left\{ C_{3z^{2}-r^{2}} \left[< z_{ij}^{2}/R_{ij}^{5} > - (1/2) < x_{ij}^{2}/R_{ij}^{5} > - (1/2) < y_{ij}^{2}/R_{ij}^{5} > \right] + C_{x^{2}-y^{2}} (3)^{+1/2}(2)^{-1} \left[x_{ij}^{2}/R_{ij}^{5} > - < y_{ij}^{2}/R_{ij}^{5} > \right] + C_{xy} (3)^{1/2} \left[< x_{ij} y_{ij}/R_{ij}^{5} > \right] + C_{xz} (3)^{1/2} \left[< x_{ij} z_{ij}/R_{ij}^{5} > \right] + C_{yz} (3)^{1/2} \left[< y_{ij} z_{ij}/R_{ij}^{5} > \right] + C_{yz} (3)^{1/2} \left[< y_{ij} z_{ij}/R_{ij}^{5} > \right]$$
(3-30)

$$D_{ij}^{pseudo} = C_{3z^{2}-r^{2}} (2/3) (5)^{-1/2} \left[J_{zzij} - \frac{1}{2} (J_{xxij} + J_{yyij}) \right] + C_{x^{2}-y^{2}} (15)^{-1/2} (J_{xyij} + J_{yyij}) + C_{xy} (15)^{-1/2} (J_{xyij} + J_{yxij}) + C_{xy} (15)^{-1/2} (J_{xzij} + J_{zyij}) + C_{xz} (15)^{-1/2} (J_{yzij} + J_{zyij})$$
(3-31)

 $x_{ij} y_{ij}$ and z_{ij} are the components of the distance vector \overrightarrow{R}_{ij} in the molecular-fixed co-ordinate system. The angular brackets indicate averages over the internal motion.

The average $\overline{\sigma}_{ZZi}$ can be expressed in terms of the components of the shielding tensor in the molecular-fixed co-ordinate system:
$$\overline{\sigma}_{ZZi} = (\sigma_{xxi} + \sigma_{yyi} + \sigma_{zzi})/3
+ c_{3z}^2 r^2 (2/3)(5)^{-1/2} [\sigma_{zzi} - (\sigma_{xxi} + \sigma_{yyi})/2]
+ c_{x}^2 r^2 (15)^{-1/2} (\sigma_{xxi} - \sigma_{yyi})
+ c_{xy} (15)^{-1/2} (\sigma_{xyi} + \sigma_{yxi})
+ c_{xz} (15)^{-1/2} (\sigma_{xzi} + \sigma_{zxi})
+ c_{yz} (15)^{-1/2} (\sigma_{yzi} + \sigma_{zyi})$$
(3-32)

The first term is the average value of the shielding tensor and is the quantity usually measured in the isotropic solution. By combining the results from nematic solution with those from isotropic solution an additional relation among various components of the shielding tensor can be obtained.

CHAPTER IV

EXPERIMENTAL

IV-1 General Consideration

If a nematic mesophase is mixed with other substances the resulting phase will remain nematic over a definite concentration range. The maximum obtainable concentration depends on the nature of the solute and of the nematic solvent. With p-p'-di-n-alkoxyazoxybenzenes as solvents, up to 40 mole % of a substituted benzene can be dissolved. Usually low solubility is observed for solutes with melting points higher than the nematic range of the solvent.

Many liquid crystals have been used as solvents, but most of them exist in nematic phases at elevated temperatures. The solution must therefore be heated in the NMR probe and great care taken to eliminate thermal gradients within the sample and to ensure a constant temperature. This necessity arises because the direct dipole coupling depends on the degree of orientation which is in turn temperature-dependent. Thus molecules in different regions would have slightly different NMR transition frequencies and a line width variation across the entire spectrum is observed⁴³⁾. For protons, the minimum line width usually occurs within 10-20 Hz of the spectrum center. For fluorine spectra, due to the large anisotropy of the chemical shift, this region of minimum line width may be several hundred cycles from the center. Since the linebroadening degrades both the resolution and the intensity of the signal, nematic solvents with lower melting points are obviously preferred.

In most commercial NMR spectrometers the sample is spun about

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an axis perpendicular to the magnetic field in order to reduce field inhomogeneity. A liquid crystal sample is homogeneously oriented with the optical axis parallel to the magnetic field and therefore such a rotation is expected to destroy the alignment. Hence, in most of the experiments using liquid crystals as solvents, the sample is not spun, and the minimum line-width attainable, about 2-5 Hz, is limited by the field inhomogeneity. Recently it has been found that a sample rotation of 5 c.p.s. or less does not destroy the orientation and improves the resolution^{44,33)}. But this improvement is probably due to the reduction of temperature gradients across the whole sample.

The presence of an additional interaction, the direct dipole couplings, causes the spectra of oriented molecules to be much more complex and also to have a much greater spread than normal high resolution spectra. This fact coupled with the above-mentioned experimental requirements greatly reduces the signal to noise ratio of the spectrum. In order to increase the magnitude of the signal, an r.f. field as high as possible (limited by the saturation) needs to be used.

IV-2 Modification of the Spectrometer

The use of high r.f. powers usually results in a serious base-line drift. To overcome this difficulty and at the same time to calibrate a spectrum of several thousand cycles in width, the field modulation technique was used 45,46.

Separate side band resonances are obtained, when the magnetic field is modulated with an audio signal having a frequency large compared to the line width. The side bands are separated from the usual resonance frequency by nY_m , where Y_m is the modulation frequency and n is any positive or negative integer. If the magnetic field H_o is swept slowly signals are found at the field value given by $H_o = 2\pi V_o/V$ and also at $H_o = 2\pi (V_o + nV_m)/V$, where V_o is the transmitter frequency. This result is shown in Fig. 3. Under conditions of low r.f. field strength, these side band resonances are useful in calibrating the spacing between high resolution NMR lines.

If a Fourier analysis is made of the signal components from any one of these separate resonance signals it is found that each resonance signal contains a number of frequency components which differ from the transmitter frequency V_0 by multiples of the modulation frequency V_m . Above one of the resonances in Fig 3, the frequency components contained in that resonance is sketched. In the detector of the receiver all of the components are mixed with reference signal from the transmitter converting signals at transmitter frequency V_0 to d.c. and signals at frequency $V_0 \pm nV_m$ to nV_m . Thus the signals contain audio components as well as d.c. component . Any change in balance of the probe will change the d.c. level but leave the a.c. components unaffected. By selecting only the a.c. component of the signal, the effect of base-line drift can be minimized.

To perform the selection of the a.c. component at the frequency \mathcal{V}_{m} , a unit consisting of an audio amplifier, a narrow-band amplifier and a lock-in detector was constructed. The circuitry is given in Fig. 4.

The block diagram of the modified DP-60 spectrometer (the transmitter frequency is 56.4 MHz) is given in Fig. 5. In actual operation, the center band and the second side bands were recorded; the first side band was minimized by careful adjustment of the modulation amplitude and

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Fig. 4 Circuit for field modulation and signal detection

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Fig. 5 Block diagram of NMR spectrometer

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phase. Under such conditions the two second side bands are 180° out of phase with the center band and they appear as negative peaks on two sides of the main spectrum, and are used for calibration. Generally the distance between the center band and up-field and down-field side bands are not exactly the same; the difference corresponds to about 10 Hz over a range of 2500 to 3000 Hz. The average of the two was then taken to calculate the frequencies of the peaks in the center band. With the modified spectrometer, it has been found that a modulation frequency higher than ~2000 Hz produces some false signals on the output recorder. In most of the spectra measured, modulation frequencies of 1200-1500 Hz were used.

All the spectra were recorded using a Varian V-4340 variable temperature NMR probe accessory and a Dewar probe insert V-4331-THR. As stated above, the appearance of the spectra is extremely sensitive to iemperature gradients across the sample. Therefore, the sample was equilibrated in a thermostat at the desired temperature before transferring to the probe, and the sample position and the flow rate of heating gas were carefully adjusted to give a minimum line width across the spectrum. The temperature within Dewar probe insert was measured with a calibrated thermocouple.

IV-3 Preparation of Samples

p-Nitrophenol and l-bromoalkanes were used as starting materials to synthesize p-p-di-n-alkoxyazoxybenzenes. The solid potassium salt of p-nitrophenol was prepared by pouring excess conc. potassium hydroxide into a solution of p-nitrophenol in aqueous KOH. The precipitate was filtered and dried under vacuum.

The procedure of Weygaud and Gabler⁴⁷⁾ was used to prepare p-alkoxynitrobenzene. The potassium salt of p-nitrophenol (40 gm), 1-bromoalkane (45 cc) and cyclopentanone (130 cc) were refluxed with stirring for about 12 hours. Ether was added to the cooled reaction mixture, which was then washed successively with 10% aqueous KOH and water. The ether layer was treated with anhydrous $CaCl_2$ and allowed to stand overnight. After filtration the solution was distilled under reduced pressure. The yield of purified p-alkoxynitrobenzene was about 50%.

p-p'-di-n-alkoxyazoxybenzenes were prepared through the electrolytic reduction of p-alkoxynitrobenzene. Both cathode and anode were made of pure lead and the cathode was treated in 20% H_2SO_4 solution before electrolysis. The catholyte was first prepared by dissolving 7% p-alkoxynitrobenzene into a saturated solution of sodium acetate in 96% ethanol. The catholyte was then poured into a porous cup situated in a beaker which was filled with a 10% solution of sodium carbonate. The current density used was 0.02 A/cm^2 . The electrolysis was stopped when 95% nitrobenzenes was expected to be reduced.

The crude products were recrystallized from a mixture of benzene and ethanol. The melting points and clear points of purified samples are given in Table III.

A preliminary study by differential scanning calorimetry showed that a mixture containing 3.5% butoxy-, 34.8% pentyloxy- and 61.7% hexyloxy-derivatives had a lowest melting point of 69°C. A mixture

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TABLE III

Transition Temperatures (°C) of p-p-Di-n-butoxy-, p-p-Di-n-pentyloxy-, and p-p-Di-n-hexyloxy-azoxybenzene

	<u>Solid-Ne</u>	matic	Nematic-Is	-Isotropic		
	This Work	<u>Lit.48</u>)	This Work	Lit.48)		
Butoxy-	108	106	133	134		
Pentyloxy-	.81	81	122	122		
Hexyloxy-	82	82	128	129		

of such composition was used as the solvent.

Samples of fluorobenzenes were obtained from commercial sources (Table IV) and used without further purification. Deuterated p-fluorophenol (C_6H_4FOD) and p-fluoroaniline ($C_6H_4FND_2$) were prepared by repeated treatment with heavy water. Solutions containing fluorobenzenes were sealed under vacuum in standard 5 mm 0.D. NMR tubes. Solution concentrations and the temperatures of measurement are listed in Table IV.

For proton chemical shift measurements a small amount of tetramethylsilane was added to the samples and used as an internal standard. Trifluoroacetic acid was used as an external reference for fluorine resonances. A solution of carbon tetrafluoride (4%) in the same liquid crystal solvent showed a 13 Hz low field shift on going from the isotropic phase (104°C) to the nematic phase (65°C) and a corresponding correction was made to all observed fluorine anisotropic shifts 49,50.

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TABLE IV

Solution Concentrations (Mole %) and

Temperatures (°C) of Measurement

Compounds	Supplier	Concentration	Temperature
1,3,5-Trifluorobenzene	Pierce Chem. Co.	30	62
0-Difluorobenzene	Aldrich	36	64
m-Difluorobenzene	Eastman	37	64
p-Difluorobenzene	Aldrich	33	67
p-Chlorofluorobenzene	J.T. Baker	33	67
p-Bromofluorobenzene	Eastman	31	65
p-Nitrofluorobenzene	Eastman	33	65
p-Fluorobenzonitrile	Aldrich	33	64
p-Fluorophenol (-OD)	Eastman	33	67
p-Fluoroaniline (-ND ₂)	Eastman	34	65
3,5-Difluoroiodobenzene	Aldrich	27	67

CHAPTER V

RESULTS AND ANALYSIS OF THE SPECTRA

To analyse the spectra of molecules oriented in a nematic solvent, one starts from the spin Hamiltonian

$$\mathcal{H} = -\frac{H_{o}}{2\pi} \sum_{i} \gamma_{i} (1 - \overline{\sigma}_{ZZi}) I_{Zi} + \sum_{i>j} J_{ij} \overrightarrow{I}_{i} \overrightarrow{I}_{j} + \sum_{i>j} (D_{ij}^{dir} + D_{ij}^{pseudo}) (\frac{3}{2} I_{Zi} I_{Zj} - \frac{1}{2} \overrightarrow{I}_{i} \overrightarrow{I}_{j})$$
(5-1)

The quantum-mechanical methods⁵¹⁾ commonly used for normal high resolution spectra are equally applicable. The main difference is the presence of the direct dipole couplings D_{ij}^{dir} , which play a dominant role in determining the major features of the spectra. All the fluorobenzenes to be studied contain at least five magnetically nonequivalent nuclei and generally it is not possible to obtain analytical expressions for line frequencies and intensities and a computer technique has to be used to extract spectral parameters from the rather complex spectra. However, for the p-substituted fluorobenzenes rather precise analytical expressions can be obtained for all the observed transitions with a first order perturbation treatment. Subsequent refinement can be conveniently carried out with higher order perturbation theory or with a computer program.

V-1 Computer Simulation Technique

In principle, the computer simulation technique is a trial and error method. For systems with a large number of different spectral parameters such as substituted fluorobenzenes, the success of the method depends on the possibility of developing a systematic approach based on a knowledge of the relative magnitude of the various parameters entering the spin Hamiltonian.

The spectra of molecules oriented in a nematic liquid crystal are usually dominated by the direct dipole coupling constants D_{ij}^{dir} . Equation (3-30) shows that D_{ij}^{dir} are determined by the molecular geometry and the degree of orientation. If the approximate molecular geometry is known, the direct dipole coupling constants will be determined by the values of non-zero motional constants. The molecules studied here have symmetry C_{2v} or higher and, therefore, at most two motional constants are required to describe the average orientation of the molecules.

The existing large volume of information about chemical shifts and indirect spin-spin coupling constants obtained from the analysis of isotropic spectra is of great value in estimating these parameters for the computer simulations of the anisotropic spectra. In fact, rather accurate (absolute) values for J_{ij} can be obtained in this way. The anisotropy of the indirect spin coupling constant is expected to be small for all the compounds studied here.

The program given by Wiberg⁵²⁾ for normal high resolution NMR spectra was rewritten to include the dipole coupling constants D_{ij}^{dir} and D_{ij}^{pseudo} . The modified program accepts the values of J_{ij} , D_{ij}^{pseudo} and $\overline{\mathcal{T}}_{ZZi}$, atomic positions in a molecular-fixed co-ordinate system, and the motional constants as the input. The direct dipole coupling constants are calculated from the assumed molecular geometry and motional constants. For each system it constructs basic product

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functions and the Hamiltonian matrix for each value of $I_Z = \sum_i I_{Zi}$. Nuclear stationary state wave functions and energies are computed as the eigen-vectors and eigen-values of that matrix. Energies and relative intensities of transitions are then computed for each system. Depending on the choice of the user, the output of the program may consist of 1. a list of transition frequencies and relative intensities, 2. a plot of the calculated spectrum, and 3. both list and plot. A complete listing of the program is given in the Appendix.I.

1,3,5-Trifluorobenzene

The observed proton and fluorine spectra are reproduced in Fig. 6, since the spectra are symmetric about the centre only one-half is shown in each case. The centre of the proton spectrum in the nematic phase was 6.24 ppm to low field from internal TMS. The centre of the fluorine spectrum was 35.19 ppm to high field from carbon-tetrafluoride. In the isotropic phase at 102°C the shifts were - 6.53 ppm and 45.16 ppm respectively.

Since the proton resonance position shifts to <u>lower</u> field in the isotropic relative to the nematic phase, the solute molecules are aligned with their molecular planes parallel to the applied field¹⁶) and therefore the sign of the only motional constant required, $C_{3z}^2_{-r}^2$, is negative. For the first trial calculation only the direct dipole coupling constants were included, with values based on a structure with D_{3h} symmetry and bond distances C-C = 1.39Å, C-H = 1.08Å, and C-F = 1.31Å. The theoretical spectra obtained with an arbitrarily chosen value of $-0.25 \text{ for } C_{3z}^2_{-r}^2$ were in approximate agreement with experiment



Fig. 6 Proton and fluorine magnetic resonance spectra of 1,3,5-trifluorobenzene. The spectra are symmetric about the center and only one-half is shown.

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except for a scale factor. Examination of the theoretical line positions and the values of D_{ij}^{dir} showed the lines J(H), Q(H), T(H) and L(F), S(F) and U(F) correspond to transitions of the a_3 subspectra of the isotropic case analyzed by Jones <u>et al.</u>⁵³⁾, with the addition of the direct dipole couplings. Similarly lines M(H) and O(F) are the transitions between the A_2 symmetry levels, plus dipolar coupling.

$$\begin{aligned} \mathcal{V}(J(H)) &= (J_{HF} + D_{HF}) + \frac{1}{2} (J_{HF}' + D_{HF}') - \frac{3}{2} D_{HH} \\ \mathcal{V}(T(H)) &= (J_{HF} + D_{HF}) + \frac{1}{2} (J_{HF}' + D_{HF}') + \frac{3}{2} D_{HH} \\ \mathcal{V}(L(F)) &= (J_{HF} + D_{HF}) + \frac{1}{2} (J_{HF}' + D_{HF}') - \frac{3}{2} D_{FF} \\ \mathcal{V}(U(F)) &= (J_{HF} + D_{HF}) + \frac{1}{2} (J_{HF}' + D_{HF}') + \frac{3}{2} D_{FF} \\ \mathcal{V}(Q(H), S(F)) &= (J_{HF} + D_{HF}) + \frac{1}{2} (J_{HF}' + D_{HF}') + \frac{3}{2} D_{FF} \\ \mathcal{V}(M(H), O(F)) &= (J_{HF} + D_{HF}) - \frac{1}{2} (J_{HF}' + D_{HF}') \end{aligned}$$

For the second stage of spectrum calculation, the indirect spin-spin coupling constants J_{ij} with the absolute values taken from Ref.⁵³⁾ were included in the calculation. The absolute signs of J_{ij} were varied and, at the same time, the most reasonable fit to the positions of the above eight lines was obtained with the variation of the magnitude of the motional constant. Closest agreement was found with $J_{\rm HH}$, $J_{\rm FF}$ and $J_{\rm HF}$ (ortho) all positive, and $J'_{\rm HF}$ (para) negative (see Table V). Changes in the magnitudes of the indirect coupling constants from the values given by Jones <u>et al.</u>⁵³⁾ did not improve the agreement.

The final refinement of the theoretical spectrum included the pseudo-dipole coupling constants D_{ij}^{pseudo} to give the best overall

TABLE V

Signs of Spin-Spin Coupling Constants in

1,3,5-Trifluorobenzene

J _{HF} (ortho)	J _{HF} '(:pa <i>r</i> a)	J _{HH}	J _{FF}	RMS deviation over all observed lines
+	÷	+	+	3.1
-	+	+	÷	3.9
+	-	+	÷	1.9
+	+	-	+	4.0
+	+	+		7.0
-	-	+	+	4.1
-	+	-	+	5.4
-	+	+	-	6.8
÷	-	-	+	3.3
+	-	+		8.0
+	+	-	-	6.9
-	-	-	+	4.2
-	-	+	-	7.0
-	+	-	-	7.8
+	-	-	-	8.1
-	-	-	-	7.5

fit to both spectra. The experimental (mean of five spectra) and calculated line positions are compared in Table VI. The root mean square deviation of all observed lines from their calculated frequencies was 1.2 Hz. Final parameters are listed in Table VII.

3.5-Difluoroiodobenzene

The proton and fluorine magnetic resonance spectra of 3,5difluoroiodobenzene are given in Fig. 7. The spectra are not symmetrical with respect to their centres due to the difference between proton chemical shifts. Theoretical spectra were computed with initial values of the direct dipole coupling constants calculated for a regular molecular structure with bond distances of $C-C = 1.39 \mathring{A}_{,}$ $C-H = 1.08\text{\AA}$ and $C-F = 1.31\text{\AA}$, all bond angles were assumed to be 120°C. Since the molecule has a C_{2v} symmetry, a suitable choice of molecular axes leads to two non-zero motional constants, $C_{3z}^2 - r^2$ and $C_{x}^2 - y^2$. Except for a scale factor, the major structure of the spectra will depend on the ratio of these two motional constants. Several trial calculations were carried out by varying C_{x-y}^2 with an arbitrarily chosen value of -0.25 for $C_{3z}^2 - r^2$ and neglecting the indirect spin coupling constants and the proton chemical shift. After approximate values of $C_{3z}^2 - r^2$ and $C_x^2 - v^2$ were obtained the proton chemical shift and the indirect spin coupling constants, with values estimated from the data given by Loemker et al⁵⁴⁾, were inserted into calculations. At this stage, an examination of the theoretical line positions and the values of $D_{i,j}$ and $J_{i,j}$ showed that certain lines bore simple fixed relationship to the coupling constants, VIZ (for numbering see Table VIII).

TABLE VI

Experimental and Calculated Line Positions of 1,3,5-Trifluorobenzene in Hz from Centre of Resonance, at 56.4 MHz

Proton Spectrum				Fluoring Speet-			
Line	Exp. Freqn.	Calc. Freqn.	Calc. Intensity	Exp. Freqn.	Calc. Freen		
А	5.49+0.2	5 02				care. Intensity	
		9.03	2.9	6.35+0.5	5,05	0.0	
В	30,90+0 5	7.78 21.00	0.4	-	10.0	<i>L.L</i>	
С	105.9 ± 0.5	JL.07	1.6	31.55+1.0	31.09	1.4	
•		100.8	4.0	90.53+1.5	88.3	1.0	
מ	150 L _1 E	110.0	0.7			<u>~.4</u>	
2	1)2.4 <u>1</u> 1.)	153.4	2.5	96.45+1.5	95 6	1.0	
ਤ	102 7 .17 6	154.3	0.7		//•0	1.9	
	17) •(<u>T</u> 1•)	195.3	2.4	108.5 + 1.5	106 g	0 (
न	250 2 11 0	077 0			110.2	2.6	
Ģ	260.7 ± 1.0	251.2	3.6	154.5 +1.5	153 /	1.6	
н		2/1.8	1.5	166.4 + 2.0	161. 8	4.5	
T	570.7 ± 2.0	3/1.4	3.1	193.7 +1.5	192 5	1.5	
1	665 0 + 2.0	623.8	1.6	209.1 +2.5	207 5	2.2	
ĸ	$759 0 \pm 0$	666.8	3.0	313.5 +2.0	312.6	1.2	
T.	700 7 17 5	759.6	0.6	683.1 +3.5	682 6	2.7	
м	870 7 JO 0	783.2	1.2	774.4 +3.0	772 0	1.9	
••	077.7 ± 2.0	878.0	1.0	783.3 +3.0	783.2	3.0	
N	005 F 10 0	880.0	1.0			2.4	
0	007.5 ± 2.0	888.4	1.0	867.9 +3.0	866 5	0 (
P	741.0 ±3.0	923.7	0.8	879.2 +2.0	878 0	0.6	
Ď	3001.6 ± 3.0	985.2	0.8	923.7 +3.0	923 8	1.0	
vc R		1000.3	6.0	935.7 +3.0	035 0	0.8	
S	1041.7 ± 3.0	1042.2	1.5	986.2 +3.0	755.2 085.2	1.5	
ר קי	1222 1 12 0	1144.6	2.3	1001.3 + 3.0		1.5	
т П	0. <u>ر+</u> ۲.ررز	1333.7	3.0	1085.2 + 3.0		6.0	
0				1226.9 ± 3.0	1002.7 1006 7	2.0	
					1220. /	3.0	

Spectrum Centre: - 6.24+0.02 ppm (int. TMS)

+ 35.19+0.05 ppm (CF₄)

3.0

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TABLE VII

Spectral Parameters: for 1,3,5-Trifluorobenzene

	D _{ij}	J ij	D ^{pseudo} ij
F-F	-152.0	5.8	1.0
H - H	-224.3	2.3	2.0
H-F ortho	-948.1	9.0	
H-F para	-119.6	-1.7	-1.0

 ${}^{C}_{3z}{}^{2}-r^{2} = -0.3269$ $\triangle \sigma_{F} = \pm 102 \pm 2 \text{ ppm}$ $\triangle \sigma_{H} = -2.98 \pm 0.3 \text{ ppm}$

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Fig. 7a The proton magnetic resonance spectra of 3,5-difluoroiodobenzene. Computer simulated spectrum is shown below the experimental spectrum.



Fig. 7b The fluorine magnetic resonance spectra of 3,5-difluoroiodobenzene. Computer simulated spectrum is shown below the experimental spectrum.

TABLE VIIT

Spectral Parameters for 3,5-Difluoroiodobenzene



i	j	D _{ij}	D ^{pseudo} ij	J _{ij}
2	3	-1040.3	-	8.5
2	4	- 221.8	6.0	2.5
2	5	- 91.6	-	-1.0
2	6	- 146.9	-	1.5
3	4	- 699.6	-	9.0
3	5	- 99.5	_	7.2

 $C_{3z}^2 - r^2 = -0.2869$ $C_{x}^2 - y^2 = -0.0420$

 $\mathcal{Y}_{\rm H_2} = 0 \qquad \qquad \mathcal{Y}_{\rm H_L} = 5.0 \,\, \rm Hz$

¹⁹_F Chemical shift (nematic 67°C) = 37.74 ± 0.04 ppm int. CF₄ (isotropic 95°C) = 45.95 ± 0.02 ppm

$$\mathcal{V}(\mathbf{L}'(\mathbf{H}), \mathbf{M} (\mathbf{H})) = \mathbf{D}_{34} + \mathbf{J}_{34}$$

$$\mathcal{V}(\mathbf{K}(\mathbf{F}), \mathbf{K}'(\mathbf{F})) = \frac{1}{2} (\mathbf{J}_{23} + \mathbf{J}_{34} + \mathbf{J}_{36}) + \frac{1}{2} (\mathbf{D}_{23} + \mathbf{D}_{34} + \mathbf{D}_{36})$$

$$- \frac{3}{4} \mathbf{D}_{35}$$

$$\mathcal{V}(\mathbf{O}(\mathbf{F}), \mathbf{O}'(\mathbf{F})) = \frac{1}{2} (\mathbf{J}_{23} + \mathbf{J}_{34} + \mathbf{J}_{36}) + \frac{1}{2} (\mathbf{D}_{23} + \mathbf{D}_{34} + \mathbf{D}_{36})$$

$$+ \frac{3}{4} \mathbf{D}_{35}$$

Further calculations were carried out by keeping a reasonable fit to the frequencies of these lines while changes of spectral parameters were made. Theoretical spectra were computed for both possible signs of J_{ij} relative to D_{ij} . With all J_{ij} except J_{25} being positive, a much better fit to both proton and fluorine spectra can be achieved by varying the motional constants and chemical shift. The last stage of calculation included the pseudo-dipole coupling constants and the variation of motional constants and chemical shift to give the best overall fit to the experimental spectra. The final spectral parameters are given in Table VIII and the computer simulated spectra given in Fig. 7. The experimental and calculated line positions are compared in Table IX. The root mean square deviation of all observed lines from their computed frequencies was 2.5 Hz.

Ortho- and Meta-difluorobenzene

The proton and fluorine spectra of these two compounds are given in Fig. 8 and Fig. 9. The procedures used for 3,5-difluoroiodobenzene were employed for analysis. A better fit was obtained with most of J_{ij} being positive in both compounds. The final parameters are listed in Table X and the computer simulated spectra

TABLE IX

Experimental and Calculated Line Positions of 3,5-Difluoroiodobenzene in Hz at 56.4 MHz

Proton Spectrum

Line	Exp. Freqn.	Calc. Freqn.	Calc. Intensity	Line	Exp. Freen.	Calc From	
Α	0	0	9.8		1 • • • • 1 • • •	varu rrequ.	Calc. Intensity
В	213.1 <u>+</u> 1.7	209.7 212.7	1.7	Bı	213.0 <u>+</u> 1.0	210.0	1.7
C	265.9 <u>+</u> 2.1	263.4	1.5	0.		213.0	1.9
D	307.3+1.7	304.9	±•)		277.9+2.3	273.3	1.5
Ε	324.5+1.8	303 5	2.8	D.	318.3 <u>+</u> 0.5	313.2	5.8
F	18 1+1 0		1.4	E٩	336.8 <u>+</u> 0.8	333.4	1.4
- C	440.411.0	419.1	1.6	F*	429 .3<u>+</u>2. 0	429.0	
u u	400.041.7	466.9	1.5	G†	476.7+1.1	176 7	
п -	480.7+2.4	476.3	2.4	H+	<u> </u>	1.96 0	1.5
Ŧ	537.2 <u>+</u> 2.4	533.4	2.1	I.	546 5+2 5	400.2	2.3
J	560.4 <u>+</u> 2.5	554.8 559.4	2.2 6.5	1:	570.4 <u>+</u> 1.3	543.2	2.1 2.1
К	631.6 <u>+</u> 3.0	629.0	2.9	V·		569.3	6.5
L	681.2+3.2	679.7	~• /		639.0 <u>+</u> 1.3	638.8	2.9
М	693.3+3.0	690 5	2.5	Γŧ	689.2 <u>+</u> 1.4	689.6	2.5
N	740.4+2.6	727.2	2.0			690.4	2.0
0	765 8+2 6	()(.)	1.5	M•	746.6 <u>+</u> 2.5	746.4	1. <i>1</i> ,
ں م		762.4	1.3	N*	767.1+1.3	766.1	+
•	744•4 <u>+</u> 2•7	940.3	4.5	01	942.5 <u>+</u> 1.7	942.2	4.6

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Fluorine Spectrum

Line	Exp. Freqn.	Calc. Freqn.	Calc. Intensity	Line	Exp. Freqn.	Calc. Freqn.	Calc. Intensity
А	49.7 <u>+</u> 1.0	47.7	2.0	A •	49.1 <u>+</u> 1.0	47.6	2.0
В	87.8 <u>+</u> 1.0	86.9	1.6	B.	89.3+1.0	88.8	1.6
C	110.9 <u>+</u> 0.7	106.6 111.0	3.3 2.2	C۹	110.9 <u>+</u> 0.7	109.5 110.2	2.2 3.3
D	215.4 <u>+</u> 1.2	214.9	1.9	D*	214.1 <u>+</u> 1.7	215.1	1.9
Е	253.7 <u>+</u> 2.2	251.3	3.0	E↑	250.4 <u>+</u> 1.5	249.8	3.0
F	308.0 <u>+</u> 2.5	309.8	0.6	F1	313.4<u>+</u>2. 2	317.8	0.5
G	457.8 <u>+</u> 2.5	454.3	0.8	G٩	446.0 <u>+</u> 3.0	446.6 0	0.9
Н	654.5 <u>+</u> 3.0	651.7	0.5	H 4	646.8+3.0	643.7	0 . 5 ប្រ
I	669.9 <u>+</u> 2.5	670.6	0.8	I.	677.4+3.0	678.6	0.8
J	7 37.1<u>+</u>2. 8	738.0	2.0	J۴	737.5+3.0	738.2	2.0
К	832 . 5 <u>+</u> 3.0	832.7	4.0	K۴	830.9+2.5	832.7	4.0
L	851.5 <u>+</u> 2.0	852.9	1.2	Γŧ	846.0 <u>+</u> 1.7	851.3	1.3
М	873.3 <u>+</u> 2.5	873.6	1.5	M۴	871.4+2.5	875.4	1.5
N	903.7 <u>+</u> 2.2	905.5	1.9	N۴	901.0 <u>+</u> 2.5	905.4	1.9
0	981.8 <u>+</u> 3.0	981.9	4.0	01	978.8+2.0	981.9	4.0

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Fig. 8a The proton magnetic resonance spectra of ortho-difluorobenzene. Computer simulated spectrum is shown below the experimental spectrum.



Fig. 8b The fluorine magnetic resonance spectra of ortho-difluorobenzene. Computer simulated spectrum is shown below the experimental spectrum.



Fig. 9a The proton magnetic resonance spectra of meta-difluorobenzene. Computer simulated spectrum is shown below the experimental spectrum. י קל י



Fig. 9b The fluorine magnetic resonance spectra of meta-difluorobenzene. Computer simulated spectrum is shown below the experimental spectrum.

- 56 -<u>TABLE Xa</u>





i	្វ	D_{ij}	J _{ij}	J _{ij} (ref. 72)
1	2	-970.1	11.0	10.44
l	3	- 98.0	9.0	7.87
l	4	- 41.6	0	0.29
1.	5	-115.0	1.5	1.62
l	6	-1108.4	8.3	8.30
2	3	-225.5	-20.0	-20.43
2	5	-115.6	- 1.5	-] 30
2	6	-219.4	3.5	4. 33
5	6	-332.8	7.6	7.62

 $C_{3z}^{2}-r^{2} = -0.2418$ $C_{x}^{2}-y^{2} = 0.0857$ $I_{F}^{9} \sigma \text{ nematic } (64^{\circ}C) = 67.87 \pm 0.05 \text{ ppm int. } CF_{4}$ $\sigma \text{ isotropic } (90^{\circ}C) = 78.81 \pm 0.04 \text{ ppm}$ $L_{H}^{1} \mathcal{V}_{1,4} = 0 \text{ Hz}$ $V_{5,6}^{2} = -4.0 \text{ Hz at } 56.4 \text{ MHz}$

TABLE Xb







i	j	D ij	J ij	J _{ij} (ref. 71)			
1	2	-917.0	9.2	9.23			
1	3	-100.2	2.5	2.45			
l	4	- 31.4	0.3	0.33			
2	3	-209.8	8.2	8.16			
2	4	- 86.0	6.5	6.46			
2	5	-108.7	-0.9	-0.86			
2	6	-173.2	6.6	6.57			
3	4	-1028.0	8.4	8.4			
3	5	-216.1	0.9	0.86			
$^{C}_{3z}^{2}-r^{2} = -0.2216$ $C_{x}^{2}-y^{2} = 0.0872$							
$19_{\rm F} \sigma$ nematic (64°C) = 43.10 ± 0.06 ppm int. CF.							
σ isotropic (85°C) = 48.00 ± 0.02 ppm							

 $V_{\rm H} = 25.0 \text{ Hz}$ $V_{3,5} = 15.0 \text{ Hz}$ $V_4 = 0 \text{ Hz at } 56.4 \text{ MHz}$

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in Fig. 8 and Fig. 9 respectively.

V-2 Perturbation Method

The possibility of using the first order perturbation_method to treat the spectra of p-substituted fluorobenzenes and para-difluorobenzene arises from the fact that the dipole coupling constant between ortho-protons is usually an order of magnitude greater than any of the other coupling constants in the system. Therefore, one can write the spin Hamiltonian as (for numbering see Table XI)

$$\mathcal{H} = \mathcal{H}^{\circ} + \mathcal{H}'$$
(5-2)
where $\mathcal{H}^{\circ} = -\frac{H_{\circ}}{2\pi} \sum_{i} \mathcal{H}_{i} \mathbf{I}_{Zi} + \mathbf{D}_{HH}^{\circ} [\frac{2}{2} (\mathbf{I}_{Z2} \mathbf{I}_{Z3} + \mathbf{I}_{Z5} \mathbf{I}_{Z6} - \frac{1}{2} (\mathbf{I}_{2} \mathbf{I}_{3} + \mathbf{I}_{5} \mathbf{I}_{6})]$ (5-3)

and the term \mathcal{H} contains remaining coupling constants and chemical shifts.

p-Substituted Fluorobenzenes

The eigen-functions of the zero-th order spin Hamiltonian, equation (5-3), can be constructed by using the D_{2h} symmetry of \mathcal{H}° , and are listed in Table XI (only given for states with $I_Z(H) = 2$, 1, 0). Since there are no degeneracies in the zeroth order symmetry wave functions the effect of \mathcal{H}' can be treated as a perturbation. The calculated first order energies are also listed in Table XI.

In the first order approximation, the proton spectra should consist of twenty-four lines symmetrically placed relative to the center at $\frac{1}{2}$ ($V_{H2} + V_{H3}$). Energies and intensities for only twelve hydrogen transitions are given in Table XII. Among them, two pairs of lines, C and D, TABLE XI

Zeroth-Order Wave Functions and First-Order Energies for p-Substituted Fluorobenzenes

 F_{1} H_{0} H_{2} H_{1} H_{2} H_{3} R_{4} Y_{1} X

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TABLE XI page 2

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Symmetry	Wave functions [*]	У _{Н2}	\mathcal{V}_{H3}	$\mathcal{V}_{\mathbf{F}}$	d _{HH}	D ^m HĻ	D ^m [♥] HH	$D_{\rm HH}^{ m p}$
^S 2, <u>+</u> 1/2	$\mathbf{p}_{\boldsymbol{\beta}_{\mathbf{F}}}^{\boldsymbol{\alpha}_{\mathbf{F}}}$	1	1	<u>+</u> 1/2	1/2	1/4	1/4	1/2
¹⁵ 1, <u>+</u> 1/2	$(2)^{-1}(a+b+c+d)^{\alpha}_{\beta_{F}}$	1/2	1/2	<u>+</u> 1/2	-1/4	-1/8	-1/8	-1/4
²⁵ 1, <u>+</u> 1/2	(2) ⁻¹ (a-b-c+d) $^{\alpha}_{\beta_{F}}$	1/2	1/2	<u>+</u> 1/2	1/4	-1/8	-1/8	1/4
^{1A} 1, <u>+</u> 1/2	$(2)^{-1}(a+b-c-d)^{\alpha}_{\beta_{F}}$	1/2	1/2	<u>+</u> 1/2	-1/4	1/8	1/8	1/4
^{2A} 1, <u>+</u> 1/2	(2) ⁻¹ (a-b+c-d) $^{\alpha}_{\beta_{F}}$	1/2	1/2	<u>+</u> 1/2	1/4	1/8	1/8	-1/4
^{1S} 0, <u>+</u> 1/2	$(2)^{-1}(f+j+g+h)^{\alpha}_{\beta_{F}}$	0	0	<u>+</u> 1/2	-1	0	0	0
^{2S} 0, <u>+</u> 1/2	$(2)^{-1}(f+j-g-h)^{\alpha}_{\beta_{F}}$	0	0	<u>+</u> 1/2	0	0	0	0
³⁵ 0 <u>,+</u> 1/2	(2) ^{-1/2} (e+k) $^{\alpha}_{\beta_{\rm F}}$	0	0	<u>+</u> 1/2	1/2	-1/4	-1/4	-1/2
^{4S} 0, <u>+</u> 1/2	$(2)^{-1/2}(g-h)^{\alpha}_{\beta_{\rm F}}$	0	0	<u>+</u> 1/2	-1/2	1/4	1/4	-1/2
1A _{0,+1/2}	$(2)^{-1/2}(f-j)^{\alpha}_{\beta_{F}}$	0	0	<u>+</u> 1/2	1/2	-1/4	-1/4	-1/2
^{2A} 0, <u>+</u> 1/2	$(2)^{-1/2} (e-k)^{\alpha}_{\beta}_{F}$	0	0	<u>+</u> 1/2	-1/2	-1/4	-1/4	1/2
TABLE XI page 3

Symmetry ⁺	$D_{ m HF}^{ m o}$	D ^m HF	J ^o HH	J ^m HH	J ^m ' HH	J ^p HH	J ^o _{HF}	J ^m HF
^S 2, <u>+</u> 1/2	<u>+</u> 1/2	<u>+</u> 1/2	1/2	1/4	1/4	1/2	+1/2	+1/2
^{1S} 1, <u>+</u> 1/2	<u>+</u> 1/4	<u>+</u> 1/4	1/2	1/4	1/4	1/2	 +1/4	+1/4
^{2S} 1, <u>+</u> 1/2	<u>+</u> 1/4	<u>+</u> 1/4	-1/2	1/4	1/4	1/2	<u>+1/4</u>	+1/4
^{1A} 1, <u>+</u> 1/2	<u>+</u> 1/4	<u>+</u> 1/4	1/2	-1/4	-1/4	-1/2	+1/4	+1/4
^{2A} 1, <u>+</u> 1/2	<u>+</u> 1/4	<u>+</u> 1/4	-1/2	-1/4	-1/4	1/2	<u>+</u> 1/4	+1/4
^{1S} 0, <u>+</u> 1/2	0	0	1/2	0	0	0	0	0
^{2S} 0, <u>+</u> 1/2	0	0	-3/2	0	0	0	0	0
^{3S} 0, <u>+</u> 1/2	0	0	1/2	-1/4	-1/4	-1/2	0	0
4\$0, <u>+</u> 1/2	0	0	-1/2	1/4	1/4	-1/2	0	0
¹ , <u>+</u> 1/2	0	0	1/2	-1/4	-1/4	-1/2	0	0
^{2A} 0, <u>+</u> 1/2	0	0	-1/2	-1/4	-1/4	1/2	0	0

+ The symbols S and A are used to denote symmetric and antisymmetric functions. The values of $I_Z(H)$ and $I_Z(F)$ are appended as suffix.

* $\mathbf{p} = \alpha(2)\alpha(3)\alpha(5)\alpha(6)$

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TABLE XII

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Transition Energies and Relative Intensities of the Spectrum of p-Substituted Fluorobenzenes Hydrogen Transitions

Line	Tra	insition		Energy*	Relative Intensit	v
a	24	04				•
ë 	²⁴ 1, <u>+</u> 1/2	^{2A} 0, <u>+</u> 1/2	±	$\Delta/4-3D_{HH}^{o}/4-3(D_{HH}^{m}+D_{HH}^{m})/8 + 3D_{HH}^{p}/4$	2	
<u>h</u> _	^S 2, <u>+</u> 1/2	^{lS} 1, <u>+</u> 1/2	<u>+</u>	$\Delta/4-3D_{HH}^{o}/4-3(D_{HH}^{m}+D_{HH}^{m'})/8 - 3D_{HH}^{p}/4$	4	
c i	^{1S} 1, <u>+</u> 1/2	^{1S} 0, <u>+</u> 1/2	±	$\Delta/4-(J_{HH}^{m} + J_{HH}^{m^{*}})/4 - J_{HH}^{p}/2 - 3D_{HH}^{o}/4 + (D_{HH}^{m} + D_{HH}^{m^{*}})/8 + D_{HH}^{p}/4$	4 ¹⁰	•
ā -	^{3S} o, <u>+</u> 1/2	^{1S} _1, <u>+</u> 1/2	<u>+</u>	$\triangle/4 + (J_{HH}^{m} + J_{HH}^{m^{*}})/2 + J_{HH}^{p} - 3D_{HH}^{o}/4 + (D_{HH}^{m} + D_{HH}^{m^{*}})/8 + D_{HH}^{p}/4$	2	
e k - -	14. ., <u>+</u> 1/2	^{1A} -1, <u>+</u> 1/2	<u>+</u>	$\triangle /4$ - $3D_{HH}^{o}/4$ + $3(D_{HH}^{m} + D_{HH}^{m^{e}})/8$ + $3D_{HH}^{p}/4$	2	
1	^{2S} 1, <u>+</u> 1/2	^{4S} 0, <u>+</u> 1/2	+	$\Delta/4-3D_{HH}^{o}/4 + 3(D_{HH}^{m} + D_{HH}^{m*})/8 - 3D_{HH}^{p}/4$	2	
	* Measured	from $(y_{H2} + y_{H3})$)/2;	$\triangle = (J_{HF}^{o} + J_{HF}^{m} + D_{HF}^{o} + D_{HF}^{m})$		

TABLE XII page 2

3

Fluorine Transitions Line Transition Energy ** Relative Intensity ^{1S}0,1/2 ^{1S}0,-1/2 ^{2S}0,1/2 ^{2S}0,-1/2 ^{3S}0,1/2 ^{3S}0,-1/2 a 0 ^{4S}0,1/2 ^{4S}0,-1/2 6 ^{1A}0,1/2 ^{1A}0,-1/2 ^{2A}0,1/2 ^{2A}0,-1/2 ^{1S}1,1/2 ^{1S}1,-1/2 ^{2S}1,1/2 ^{2S}1,-1/2 Ъ △ /2 ^{1A}1,1/2 ^{1A}1,-1/2 4 ^{2A}1,1/2 ^{2A}1,-1/2 ^s2,1/2 ^s2,-1/2 С Δ 1 $\Delta = (J_{HF}^{o} + J_{HF}^{m} + D_{HF}^{o} + D_{HF}^{m})$ **

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I and J, separated by $\frac{3}{4} (J_{HH}^{m} + J_{HH}^{m'}) + \frac{3}{2} J_{HH}^{p}$, a quantity of about 4 to 5 Hz, can not be resolved in the spectra. The proton half spectrum thus consists of five doublets separated by $\frac{1}{2} (J_{HF}^{o} + J_{HF}^{m} + D_{HF}^{o} + D_{HF}^{m})$. The general appearance of the spectra depends upon the relative signs and magnitudes of the two quantities $\frac{1}{2} (D_{HH}^{m} + D_{HH}^{m'})$ and D_{HH}^{p} , and on their signs relative to D_{HH}^{o} .

The fluorine magnetic resonance spectra, as shown in Table XII, should consist of a quintet (1:4:6:4:1) separated by $\frac{1}{2}$ ($J_{HF}^{o} + J_{HF}^{m}$ + $D_{HF}^{o} + D_{HF}^{m}$). The proton and fluorine spectra of p-chlorofluorobenzene are shown in Fig. 10. Analysis of the spectra gives values for $\frac{1}{2}$ (D_{HH}^{m} + $D_{HH}^{m'}$, D_{HH}^{p} , D_{HH}^{o} , and $\frac{1}{2}(J_{HF}^{o} + J_{HF}^{m} + D_{HF}^{o} + D_{HF}^{m})$. Based on the results for benzene¹⁶⁾ and 1,3,5-trifluorobenzene, it seems reasonable to assume that D_{HH}^{O} is negative. Then the observed proton magnetic resonance spectra of p-chloro-, p-bromo-, p-nitro-fluorobenzene and p-fluorobenzonitrile correspond to the case with opposite signs for $\frac{1}{2} (D_{HH}^{m} + D_{HH}^{m'})$ and D_{HH}^{p} , and with the positive term having the larger magnitude. The actual signs of these two terms and the signs and magnitudes of $D_{\mathrm{HF}}^{\mathrm{O}}$ and D_{HF}^{m} were made on the basis of reasonable geometry, R(C-C) = 1.39 Å, $R(C-H) = 1.08\text{\AA}$, $R(C-F) = 1.31\text{\AA}$. Literature values were used for respective J_{HF}° and J_{HF}^{m} values 54,55,56). The motional constants were then obtained from equation (3-30) by fitting $\frac{1}{2} (D_{HH}^{m} + D_{HH}^{m'})$ and $\frac{1}{2}$ ($D_{HF}^{o} + D_{HF}^{m}$) to the observed spectra.

In order to eliminate one of the chemical shift terms, and to reduce the dipolar coupling between the ring protons and those of the substituent, the spectra of p-fluorophenol and p-fluoroaniline deuterated in the subsituent position, were recorded. The proton



Fig. 10 The proton and fluorine magnetic resonance spectra of p-chlorofluorobenzene. Only the high-field half of the proton spectrum is shown. spectrum of p-fluoroaniline-d₂ showed only two very broad peaks with a separation of about 3600 Hz. The fluorine spectrum showed a quintet with each peak further split into quintet of separation 22 Hz and intensity ratio 1:2:3:2:1 (Fig. 11). All these phenomena can be explained by the presence of deuterium-proton and deuteriumfluorine coupling. Since it was impossible to derive a value for $\frac{1}{2}$ ($D_{HH}^{m} + D_{HH}^{m'}$), the motional constants were determined from the experimental values of ($D_{HF}^{o} + D_{HF}^{m}$) and $\frac{2}{2} D_{HH}^{o}$, which was assumed to be equal to the separation of the two broad peaks in the proton spectrum. The spectrum of p-fluorophenol-d did not show any evidence of deuterium-proton or deuterium-fluorine coupling but the proton spectrum showed only three doublets due to the coincidence of lines caused by the near equality of $\frac{1}{2} |(D_{HH}^{m} + D_{HH}^{m'})|$ and $|D_{HH}^{p}|$.

It can be shown with the second order perturbation theory that the difference in chemical shift between the two pairs of protons in the para-substituted fluorobenzenes should shift the center of the inner ten lines of the proton spectrum relative to the center of the outer ten lines. Within the experimental errors only the spectrum of p-nitrofluorobenzene required such a correction. A chemical shift difference between H_2 and H_3 of 90 Hz was required to account for the spectral asymmetry of 4 Hz.

The various spectral parameters thus obtained were further refined with the computer program described before. The results show that the first order perturbation treatment gave almost exact frequencies for most of the observedle transitions. The corrections were generally less than 3 Hz and the largest correction was 7 Hz for the two lines



Fig. 11 The fluorine magnetic resonance spectrum of p-fluoroaniline-d₂.

(C and I) in the spectrum of p-nitrofluorobenzene. Final parameters are given in Table XIII.

Para-difluorobenzene

A table, such as Table XI, can be constructed for para-difluorobenzene merely by addition of D_{FF} and J_{FF} . The presence of a second fluorine atom, on the one hand, changes the symmetry of the molecule from C_{2v} to D_{2h} and therefore simplifies the treatment by making some of the zeroth order spin wave functions become the eigenfunctions of the full spin Hamiltonian of the system. On the other hand, it brings in two additional sets of states corresponding to $I_F = 1$, $m_F = 0$, and $I_F = 0$, $m_{F} = 0$, and the possible mixing between these two sets of states has to be considered⁵⁷⁾. However, this mixing is forbidden in the zeroth order of approximation. In the first order approximation, the proton half spectrum should consist of five triplets with a splitting equal to (1/2) $(D_{HF}^{O} + D_{HF}^{m} + J_{HF}^{O} + J_{HF}^{m})$. In the actual spectrum, Fig. 12, only four triplets were observed due to coincidence of lines C and D, H and I, M and N. The fluorine spectrum, Fig. 12, consisted essentially of ten lines based on a quintet, with a splitting (1/2) $(D_{HF}^{O} + D_{HF}^{m} + J_{HF}^{O} + J_{HF}^{m})$, each line of which was further split into a doublet with separation $(3/2)D_{FF}$. A further small splitting due to second order effects was also observed. Analysis of the spectra only gave values of D_{HH}^{O} , D_{HH}^{m} , D_{HH}^{p} , D_{FF} and (1/2) $(D_{HF}^{m} + D_{HF}^{o} + J_{HF}^{m} + J_{HF}^{o})$ and the magnitudes and signs of the remaining indirect spin coupling constants could not be obtained. A complete list of transition frequencies and relative intensities, based on the firstorder treatment, is given in Table XIV.

TABLE XITI



Substituent	D ^O HH	$\frac{1}{2}(D_{HH}^{m}+D_{HH}^{m'})$	D ^p HH	$D_{\rm HF}^{\rm O}$	D ^m HF	J ^O HF	J ^{nı} HF	$C_{3z}^2 - r^2$	^C 2 2 x -y	c* nematic	o isotropic
p-chloro	-2754.5	133.9	-26.4	-346.3	-317.9	8.1	4.7	-0.2974	-0.2843	$\frac{ppm}{51.13 \pm .04}$	ppm 53.64 + .05
p-bromo	-3044.4	161.8	-21.3	-337.5	-346.3	8.2	4.8	-0.3158	-0.3185	50.41 <u>+</u> .07 (65°C)	53.09 <u>+</u> .05
p-cyano	-3341.5	184.4	-19.2	-338.2	-374.2	8.6	5.8	-0.3357	-0.3499	37.40 <u>+</u> .05 (64°C)	(1, 0) $(1, 21 \pm .04)$
p −nitro	-3246.3	128.2	-46.8	-492.6	-380.4	8.2	4.8	-0.3721	-0.3230	34.44 <u>+</u> .05 (65°)	40.97 ± .02
p-hydroxy-d	-1787.9	45.4	-45.4	- 391.5	-236.3	8.1	5.0	-0.2489	-0.1819	$61.62 \pm .04$	$63.12 \pm .02$
p-amino-d ₂	-2428 <u>+</u> 50	-	-	-304.7	-271.6	8.1	5.0	-0.2560	-0.2411	65.58 <u>+</u> .02 (65°C)	65.77 <u>+</u> .04
	* Bolo	tive to OT	10								(71.0)

Relative to CF₄. Mean of five determinations.

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Fig. 12 The proton and fluorine magnetic resonance spectra of para-difluorobenzene. Only the high-field half of the proton spectrum is shown. Computer simulated spectra are shown below the experimental spectra. - 70

	Hydrogen trans	itions		
Line	Trans	ition **	Energy*	Relative Intensity
A 	(A ₂) _{0,-1,1}	(A ₂) _{1,-1,1}	$-\frac{1}{2} \bigtriangleup + \frac{3}{4} (D_{HH}^{o} + D_{HH}^{m} - D_{HH}^{p})$	1
B 	(A ₁) _{1,-1,1}	(A ₁) _{2,-1,1}	$-\frac{1}{2} \bigtriangleup + \frac{3}{4} (D_{HH}^{o} + D_{HH}^{m} + D_{HH}^{p})$	2
С	(A'1)0,-1,1	(A ₁) _{1,-1,1}	$-\frac{1}{2} \triangle + \frac{1}{2}(J_{HH}^{m} + J_{HH}^{p}) + \frac{3}{4}D_{HH}^{o} - \frac{1}{4}(D_{HH}^{m} + D_{HH}^{p})$	2
	(A ₁)-1,-1,1	(A ₁ ''') _{0,-1,1}	$-\frac{1}{2} \bigtriangleup - \frac{1}{2} (J_{HH}^{m} + J_{HH}^{p}) + \frac{2}{\lambda} D_{HH}^{o} - \frac{1}{\lambda} (D_{HH}^{m} + D_{HH}^{p})$	l
D.	(B ₁)-1,-1,1	(B ₁) _{0,-1,1}	$-\frac{1}{2} \bigtriangleup + \frac{2}{4} (D_{HH}^{5} - D_{HH}^{p} - D_{HH}^{m})$	l
E 	(B ₂) _{0,-1,1}	(B ₂) _{1,-1,1}	$-\frac{1}{2} \bigtriangleup + \frac{2}{4} (D_{HH}^{o} + D_{HH}^{p} - D_{HH}^{m})$	l
	^{(A} 2 ⁾ 0,0,1	(A ₂)1,0,1		
F			$\frac{3}{L}(D_{HH}^{o} - D_{HH}^{p} + D_{HH}^{m})$	2
	(B ₁) _{0,0,0}	(B ₁) _{1,0,0}		~
	(A ₁) _{1,0,1}	(A ₁) _{2,0,1}		
G			$\frac{3}{L}(D_{HH}^{O} + D_{HH}^{P} + D_{m}^{m})$	L.
	(B ₂) _{1,0,0}	^{(B} 2 ⁾ 2,0,0		4

TABLE XIV

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Transition Energies and Relative Intensities of the Spectrum of Para-Difluorobenzene

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Line Transtion (A[†])_{0,0,1} (A₁)_{1,0,1} (B^{*}2)_{0,0,0} (B₂)_{1,0,0} H (A₁)_1,0,0 (A1''')0,0,0 (B₂)_1,0,0 (B2''')0,0,0 (B₁)_1,0,1 (B₁)_{0,0,1} Ι (A₂)_1,0,0 ^{(A}2⁾0,0,0 (B₂)_{0,0,1} (B₂)_{1,0,1} J (A₁)_{0,0,0} (A₁)_{1,0,0} (A₂)_{0,1,1} K (A₂)_{1,1,1} (A₁)_{1,1,1} (A₁)_{2,1,1} L (A'₁)_{0,1,1} (A₁)_{1,1,1} М (A₁)_1,1,1 (A1''')0,1,1 (B₁)_1,1,1 (B₁)_{0,1,1} N (B₂)_{0,1,1} 0 (B₂)_{1,1,1}

$$\begin{array}{c} \operatorname{Energy}^{*} & \operatorname{Relative}_{\text{Intensity}} \\ \frac{1}{2} \left(J_{\text{HH}}^{\mathbf{p}} + J_{\text{HH}}^{\mathbf{m}} \right) + \frac{3}{4} D_{\text{HH}}^{\mathbf{o}} - \frac{1}{4} \left(D_{\text{HH}}^{\mathbf{p}} + D_{\text{HH}}^{\mathbf{m}} \right) & 4 \\ - \left(J_{\text{HH}}^{\mathbf{m}} + J_{\text{HH}}^{\mathbf{p}} \right) + \frac{3}{4} D_{\text{HH}}^{\mathbf{o}} - \frac{1}{4} \left(D_{\text{HH}}^{\mathbf{p}} + D_{\text{HH}}^{\mathbf{m}} \right) & 2 \\ \frac{3}{4} \left(D_{\text{HH}}^{\mathbf{o}} - D_{\text{HH}}^{\mathbf{p}} - D_{\text{HH}}^{\mathbf{m}} \right) & 2 \\ \frac{3}{4} \left(D_{\text{HH}}^{\mathbf{o}} - D_{\text{HH}}^{\mathbf{p}} - D_{\text{HH}}^{\mathbf{m}} \right) & 2 \\ \frac{3}{4} \left(D_{\text{HH}}^{\mathbf{o}} + D_{\text{HH}}^{\mathbf{p}} - D_{\text{HH}}^{\mathbf{m}} \right) & 2 \\ \frac{1}{2} \Delta + \frac{3}{4} \left(D_{\text{HH}}^{\mathbf{o}} - D_{\text{HH}}^{\mathbf{p}} + D_{\text{HH}}^{\mathbf{m}} \right) & 1 \\ \frac{1}{2} \Delta + \frac{3}{4} \left(D_{\text{HH}}^{\mathbf{o}} + D_{\text{HH}}^{\mathbf{p}} + D_{\text{HH}}^{\mathbf{m}} \right) & 2 \\ \frac{1}{2} \Delta + \frac{3}{4} \left(D_{\text{HH}}^{\mathbf{o}} + D_{\text{HH}}^{\mathbf{p}} + D_{\text{HH}}^{\mathbf{m}} \right) & 1 \\ \frac{1}{2} \Delta - \left(J_{\text{HH}}^{\mathbf{m}} + J_{\text{HH}}^{\mathbf{p}} \right) + \frac{3}{4} D_{\text{HH}}^{\mathbf{o}} - \frac{1}{4} \left(D_{\text{HH}}^{\mathbf{p}} + D_{\text{HH}}^{\mathbf{m}} \right) \\ \frac{1}{2} \Delta + \frac{3}{4} \left(D_{\text{HH}}^{\mathbf{o}} + D_{\text{HH}}^{\mathbf{p}} \right) + \frac{3}{4} D_{\text{HH}}^{\mathbf{o}} - \frac{1}{4} \left(D_{\text{HH}}^{\mathbf{p}} + D_{\text{HH}}^{\mathbf{m}} \right) \\ 1 \\ \frac{1}{2} \Delta + \frac{3}{4} \left(D_{\text{HH}}^{\mathbf{o}} + D_{\text{HH}}^{\mathbf{p}} \right) + \frac{3}{4} D_{\text{HH}}^{\mathbf{o}} - \frac{1}{4} \left(D_{\text{HH}}^{\mathbf{p}} + D_{\text{HH}}^{\mathbf{m}} \right) \\ 1 \\ \frac{1}{2} \Delta + \frac{3}{4} \left(D_{\text{HH}}^{\mathbf{o}} + D_{\text{HH}}^{\mathbf{p}} - D_{\text{HH}}^{\mathbf{m}} \right) \\ 1 \\ \frac{1}{2} \Delta + \frac{3}{4} \left(D_{\text{HH}}^{\mathbf{o}} + D_{\text{HH}}^{\mathbf{p}} - D_{\text{HH}}^{\mathbf{m}} \right) \\ 1 \\ \frac{1}{2} \Delta + \frac{3}{4} \left(D_{\text{HH}}^{\mathbf{o}} + D_{\text{HH}}^{\mathbf{p}} - D_{\text{HH}}^{\mathbf{m}} \right) \\ 1 \\ \frac{1}{2} \Delta + \frac{3}{4} \left(D_{\text{HH}}^{\mathbf{o}} + D_{\text{HH}}^{\mathbf{p}} - D_{\text{HH}}^{\mathbf{m}} \right) \\ 1 \\ \frac{1}{2} \Delta + \frac{3}{4} \left(D_{\text{HH}}^{\mathbf{o}} + D_{\text{HH}}^{\mathbf{p}} - D_{\text{HH}}^{\mathbf{m}} \right) \\ 1 \\ \frac{1}{2} \Delta + \frac{3}{4} \left(D_{\text{HH}}^{\mathbf{o}} + D_{\text{HH}}^{\mathbf{p}} - D_{\text{HH}}^{\mathbf{m}} \right) \\ 1 \\ \frac{1}{2} \Delta + \frac{3}{4} \left(D_{\text{HH}}^{\mathbf{o}} + D_{\text{HH}}^{\mathbf{p}} - D_{\text{HH}}^{\mathbf{m}} \right) \\ 1 \\ \frac{1}{2} \Delta + \frac{3}{4} \left(D_{\text{HH}}^{\mathbf{o}} + D_{\text{HH}}^{\mathbf{p}} - D_{\text{HH}}^{\mathbf{m}} \right) \\ 1 \\ \frac{1}{2} \Delta + \frac{3}{4} \left(D_{\text{HH}}^{\mathbf{o}} + D_{\text{HH}}^{\mathbf{p}} \right) \\ 1 \\ \frac{1}{2} \Delta + \frac{3}{4} \left(D_{\text{HH}}^{\mathbf{o}} + D_{\text{HH}$$

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TABLE XIV page 3

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Fluorine transitions

Line

(A [†])	~ t >	Energy*	Relative Intensity
(*1'0,0,1 /.")	(^A 1 ⁾ 0,1,1		
(A1)0,0,1	(A ^{¨)} D,1,1		
(A1)) _{0,0,1}	(A1)) _{0,1,1}	3	
(A ₂) _{0,0,1}	(A ₂) _{0,1,1}	$\overline{\mathcal{A}}^{\mathrm{D}}_{\mathrm{FF}}$	6
(B ₁) _{0,0,1}	(B ₁) _{0,1,1}		
(B ₂) _{0,0,1}	(B ₂) _{0,1,1}		
(A ₁) _{1,-1,1}	(A ₁) _{1,0,1}		
(A ₂) _{1,-1,1}	(A ₂) _{1,0,1}] ^ 3	
(B ₁) _{1,-1,1}	(B ₁) _{1,0,1}	$\overline{2} \stackrel{\frown}{-} \overline{4}^{D}_{FF}$	4
(B ₂) _{1,-1,1}	(B ₂) _{1,0,1}		
(A ₁) _{1,0,1}	(A ₁) _{1,1,1}		
(A ₂) _{1,0,1}	(A ₂) _{1,1,1}		
(B ₁) _{1,0,1}	(B ₁) _{1,1,1}	$\frac{1}{2}$ $\triangle - \frac{3}{4}D_{FF}$	4
(B ₂) _{1,0,1}	(B ₂) _{1,1,1}		
	$(A_1)_{0,0,1}$ $(A_1)_{0,0,1}$ $(A_1)_{0,0,1}$ $(A_2)_{0,0,1}$ $(B_1)_{0,0,1}$ $(B_2)_{0,0,1}$ $(A_1)_{1,-1,1}$ $(A_2)_{1,-1,1}$ $(A_2)_{1,-1,1}$ $(B_1)_{1,-1,1}$ $(B_2)_{1,-1,1}$ $(A_2)_{1,0,1}$ $(B_1)_{1,0,1}$ $(B_1)_{1,0,1}$ $(B_2)_{1,0,1}$ $(B_2)_{1,0,1}$	$(A_{1}^{'})_{0,0,1} \qquad (A_{1}^{'})_{0,1,1} \\ (A_{1}^{'})_{0,0,1} \qquad (A_{1}^{''})_{0,1,1} \\ (A_{1}^{'''})_{0,0,1} \qquad (A_{1}^{'''})_{0,1,1} \\ (A_{2})_{0,0,1} \qquad (A_{2})_{0,1,1} \\ (B_{1})_{0,0,1} \qquad (B_{1})_{0,1,1} \\ (B_{2})_{0,0,1} \qquad (B_{2})_{0,1,1} \\ (A_{2})_{1,-1,1} \qquad (A_{1})_{1,0,1} \\ (A_{2})_{1,-1,1} \qquad (A_{1})_{1,0,1} \\ (A_{2})_{1,-1,1} \qquad (A_{2})_{1,0,1} \\ (B_{2})_{1,0,1} \qquad (B_{2})_{1,0,1} \\ (B_{2})_{1,0,1} \qquad (B_{1})_{1,1,1} \\ (A_{2})_{1,0,1} \qquad (A_{2})_{1,1,1} \\ (A_{2})_{1,0,1} \qquad (A_{2})_{1,1,1} \\ (B_{2})_{1,0,1} \qquad (B_{1})_{1,1,1} \\ (B_{2})_{1,0,1} \qquad (B_{2})_{1,1,1} \\ (B_{2})_{1,1,1} \qquad (B_{2})_{1,1,1} \\ (B_{2})_{1,1,1} \qquad (B_{2})_{1,1,1} \\ (B_{2})_{1,1,1} \qquad (B_{2})_{1,1,1} \\ (B_{2})_{1,0,1} \qquad (B_{2})_{1,1,1} \\ (B_{2})_{1,1,1} \qquad (B_{2})_{1,1,1$	Energy* $ \begin{array}{cccccccccccccccccccccccccccccccccccc$

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TABLE XIV page 4



$$^{*} \bigtriangleup = (D_{HF}^{O} + D_{HF}^{m} + J_{HF}^{O} + J_{HF}^{m})$$

хх

The states are designated by the symmetry properties of their corresponding eigenfunctions which form bases for the irreducible representations of point group C_{2v} . Subscripts in the symmetry notation indicate m m F and I respectively.

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While this work was in progress, Bulthuis <u>et al</u>.⁵⁸⁾ published proton and fluorine NMR spectra of para-difluorobenezene dissolved in nematic p-p¹di-n-hexyloxyazoxybenzene. Their analysis of the spectra was based on a perturbation treatment of p-dichlorobenzene, but exactly the same results were obtained.

Final parameters for **p**-difluorobenzene are given in Table XV.



 $D_{HF}^{0} = -344.5$ $D_{HF}^{m} = -233.2$ $D_{HH}^{0} = -1907.9$ $D_{HH}^{m} = 59.9$ $D_{HH}^{p} = -35.8$ $D_{FF} = -170.8$

 $J_{\rm HF}^{0} = 8.1$ (7.6 Ref. (57)) $J_{\rm HF}^{\rm m} = 4.6$ (4.6 Ref. (57))

$$C_{3z}^2 - r^2 = -0.2413$$
 $C_x^2 - y^2 = -0.1899$

¹⁹_F nematic (67°C) = 55.32 ± 0.05 ppm (CF₄) isotropic (90°C) = 57.62 ± 0.02 ppm

¹_H nematic (67°C) = -6.31 ± 0.03 ppm int. TMS isotropic (93°C) = -6.46 ± 0.03 ppm

CHAPTER VI

DISCUSSION

VI-1 Theory of Fluorine Chemical Shift

For a nucleus of magnetic moment $\vec{\mu}$ in a uniform magnetic field \vec{H}_{O} , the shielding tensor \vec{O} is defined by the relation

$$\Delta \mathbb{E} \left(\mu, \mathcal{H}_{O} \right) = -\overrightarrow{\mathcal{H}}_{O} \left(\overrightarrow{\mathbf{I}} - \overrightarrow{\sigma} \right) \overrightarrow{\mu}$$
(6-1)

where $\Delta E(\mu, H_0)$ is the energy contributed to the molecule by the coupling of $\vec{\mu}$ and \vec{H}_0 , and \vec{T} is the unit dyadic. Ramsey²⁰⁾ has shown that the chemical shift can be written as the sum of two terms

$$\overrightarrow{\Theta} = \overrightarrow{\Theta} \overrightarrow{1} + \overrightarrow{\Theta} \overrightarrow{2}$$

$$(6-2)$$

$$\mathbf{g}^{(1)} = (\mathbf{e}^2/2\mathbf{m}\mathbf{c}^2) \langle \Psi_{\mathbf{o}} | \frac{\sum_{\mathbf{k}} (\mathbf{r}_{\mathbf{k}}^2 \mathbf{\vec{1}} - \mathbf{\vec{r}}_{\mathbf{k}} \mathbf{\vec{r}}_{\mathbf{k}})/\mathbf{r}_{\mathbf{k}}^3 | \Psi_{\mathbf{o}} \rangle$$
(6-3)

$$\begin{aligned} \widehat{\sigma}^{(2)} &= \left(e^{2}/2m^{2}c^{2} \right) \sum_{m} \left(E_{o} - E_{m} \right)^{-1} \\ &\left[\langle \Psi_{o} \middle| \sum_{k} \vec{1}_{k} \middle| \Psi_{m} \rangle \langle \Psi_{m} \middle| \sum_{k} \left(\vec{1}_{k} / r_{k}^{3} \right) \middle| \Psi_{o} \rangle \right. \\ &\left. + \langle \Psi_{o} \middle| \sum_{k} \left(\vec{1}_{k} / r_{k}^{3} \right) \middle| \Psi_{m} \rangle \langle \Psi_{m} \middle| \sum_{k} \vec{1}_{k} \middle| \Psi_{o} \rangle \right] \end{aligned}$$

$$(6-4)$$

where \vec{l}_k is the orbital angular momentum of electron k, and \vec{r}_k is the vector from the magnetic nucleus to electron k. \underline{Y}_0 and \underline{Y}_m are the wave functions of ground and excited states with energies of \underline{F}_0 and \underline{F}_m respectively. Implicit in equations (6-3) and (6-4) is the choice of the magnetic nucleus as the origin for the vector potential. $\vec{\sigma}^{(1)}$ and $\vec{\sigma}^{(2)}$ are often referred to as diamagnetic and paramagnetic terms, but although $\vec{\sigma}^{(1)}$ is always diamagnetic $\vec{\sigma}^{(2)}$ need not be paramagnetic. Both terms are important in determining proton chemical shifts. In attempts to calculate fluorine chemical shifts, it is usually assumed that paramagnetic contribution is dominant; consequently we restrict most of the following discussion to $\sigma^{(2)}$.

 $\overline{\sigma^{(2)}}$ is generally very difficult to evaluate exactly because of the appearance of matrix elements between ground and all excited states which do not yield zero contribution due to symmetry. The so-called "average excitation energy approximation" consists of rewriting a component of the paramagnetic term as

 $\sigma_{\alpha\alpha}^{(2)} = -(e^2/m^2c^2)(\Delta E_{\alpha})^{-1} \langle \Psi_{\alpha} | \sum_{kk'} 1_{\alpha k} 1_{\alpha k'} / r_k^{-3} | \Psi_{0} \rangle \qquad (6-5)$ where ΔE_{α} is an average excitation energy which is formally defined as the quantity required to make equation (6-5) exact. In another approximation often used, one assumes the presence of an expectation value $\langle r^{-3} \rangle$ such that

$$\begin{aligned}
\sigma^{(2)} &= -\left(e^{2}/m^{2}c^{2}\right) < r^{-3} > \sum_{m} (E_{m} - E_{o})^{-1} \\
&\leq \underline{\Psi}_{o} | \sum_{k} \vec{1}_{k} | \underline{\Psi}_{m} > < \underline{\Psi}_{m} | \sum_{k} \vec{1}_{k} | \underline{\Psi}_{o} > \\
\text{Through constion (6.6)} \quad \widehat{\Phi}^{(2)} \text{ is used to be}
\end{aligned}$$
(6-6)

Through equation (6-6), σ^{\times} is related to paramagnetic term in the diamagnetic susceptibility, in fact magnetic shielding and diamagnetic susceptibility are different phenomena caused by the same intramolecular currents. In most semi-empirical theories^{23,24,30)} of ¹⁹F chemical shifts both approximations are used.

Further simplification of equations (6-5) and (6-6) can be made with the application of the LCAO approximation for the molecular wave function $\underline{\Psi}_{0}^{23,24,25,30}$. By considering only the atomic orbitals centered on the fluorine atom, Karplus and Das²³⁾ expressed the chemical shift in terms of the localized bond parameters:

$$\sigma_{aa} = \sigma_{o} (1 - s - I + Is + \rho_{c}(s + I))$$
(6-7)

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$$\sigma_{bb} = \sigma_{o}(\rho_{a} + \rho_{c} - \rho_{a}\rho_{c})$$
 (6-8)

$$\sigma_{cc} = \sigma_{o}(1 - s - I + Is + \rho_{a}(s + I)) \qquad (6-9)$$

where s denotes the extent of s-hybridization of the fluorine sigmabonding orbital in the X-F bond and I is its ionic character. ρ_a and ρ_c denotes the double bond character of the X-F bond in the directions orthogonal to the bond axis (b-axis). The constant σ_o is $(e^2h^2/m^2c^2\Delta E) < r^{-3} >_{2p}$; $\langle r^{-3} >_{2p}$ is the expectation value of r^{-3} for fluorine 2p-orbital and ΔE is the average excitation energy which is assumed to be isotropic. The dependence of $\langle r^{-3} >_{2p}$ on the electron density of the fluorine atom is neglected in their formulation^{61,24}).

The rotational average of the shift tensor is

$$\sigma = (1/3) (\sigma_{aa} + \sigma_{bb} + \sigma_{cc}) = (2/3)\sigma_{o} (1 - s - I - (1/2)(\rho_{a} + \rho_{c}))$$
$$- (1/2)(2Is + (\rho_{a} + \rho_{c}) (I + s) - \rho_{a}\rho_{c})$$
(6-10)

Taking mono-fluorobenzene as a reference compound, Karplus and Das applied their theory particularly to the fluorine chemical shift in polyfluorobenzenes. With σ_0 chosen empirically equation (6-10) does provide an explanation of the experimental results for non-orthopolyfluorobenzenes. For ortho-polyfluorobenzenes, an "ortho-correction" of ~17 ppm has to be introduced for every ortho-neighbour in order to achieve the agreement between the experimental and calculated chemical shifts.

The principal components of the 19 F shift tensor in any system can be calculated according to equation (6-7) (6-8) and (6-9); the numerical results, of course, depend on the choice of the values for s, I and ρ and also on the actual anisotropy of the average excitation energy. However, for compounds containing essentially covalent X-F bonds i.e. bonds in which ρ , I and s are expected to be small, these equations predict $\sigma_{\rm bb} > \sigma_{\rm aa} \cong \sigma_{\rm cc}$.

<u>VI-2 Anisotropies of Fluorine Chemical Shifts in Fluorobenzenes and the</u> <u>Solvent Effect</u>

For molecules for which only two motional constants are required the chemical shift in the nematic phase is given by

$$\sigma_{ZZi} = (1/3) (\sigma_{xxi} + \sigma_{yyi} + \sigma_{zzi}) + C (2/3)(5)^{-1/2} (\sigma_{zzi} - (1/2)(\sigma_{xxi} + \sigma_{yyi})) + C (2/3)(5)^{-1/2} (\sigma_{zzi} - \sigma_{zyi})$$
(6-11)

The first term in equation (6-11) is given by the chemical shift in the isotropic phase, thus the anisotropies of the chemical shift can be written as

$$A(\sigma_{aa} - (1/2)(\sigma_{bb} + \sigma_{cc})) + B(\sigma_{bb} - \sigma_{cc}) = C \qquad (6-12)$$

where the molecular fixed axes x, y, and z have been transformed to axes; a (perpendicular to the molecular plane), b (along the C-F bond), and c (in the molecular plane and perpendicular to the C-F bond). In this transformation it is assumed that a, b and c are the principal axes of the shielding tensor. In Table XVI the values of the coefficients A, B and C in equation (6-12) are listed for compounds studied here and also for fluorobenzene³⁶⁾ and hexafluorobenzene³⁷⁾. The errors given are standard deviations of five measurements.

In the interpretation of the results in Table XVI, the solvent

TABLE XVI

Coefficients A, B and C for Equation (6-12)

	A	В	c*
p-fluoro	1.0	-0.684	31.7 <u>+</u> 1.0 ppm
p-chloro	1.0	-0.827	28.2 <u>+</u> 1.0
p-bromo	1.0	-0.873	28.5 <u>+</u> 1.3
p-cyano	1.0	-0.903	38.0 <u>+</u> 1.0
p-nitro	1.0	-0.752	58.8 <u>+</u> 1.2
p-hydroxy	1.0	-0.633	20.1 <u>+</u> 1.0
p-amino	1.0	-0.816	2.4 <u>+</u> 1.0
m-fluoro	1.0	-0.170	74.4 <u>+</u> 2.0
3,5-difluoroiodo	1.0	0.063	95.5 <u>+</u> 1.5
1-3,5-trifluoro	1.0	0	102.0 <u>+</u> 1:5
fluorobenzene	1.0	-0.424	50.0
ortho difluorobenzene	1.0	-0.1534	123.9 <u>+</u> 2.0
hexa fluorobenzene	1.0	-	154.0

* Standard deviation of 5 measurements

contribution to the chemical shift has to be considered. The chemical shift anisotropy is determined from the shift of the mean NMR frequency on going from the isotropic to the nematic phase. The assumption underlying the experiment is that the measured mean frequencies are influenced to the same extent by the liquid crystal solvent, i.e., that the displacement of the center of the spectrum is due only to incomplete averaging of anisotropic shielding interactions. Thus the important problem is not one of whether solvent interacts with the solute, but rather one of whether the solvent-solute interaction is significantly different in random and ordered phases of the same solvent. However, since no quantitative theory on the solvent contribution to the chemical shift is available at the present time, the estimation of the magnitude of this solvent effect on the present results can only be made on the basis of known experimental data.

(1) Bernheim and Krugh⁴⁹⁾ reported that there is a down-field shift of 0.24 ppm in CF_4 resonance (with respect to an external reference) when going from nematic to isotropic phase. They attributed this mainly to the solvent anisotropic effect as suggested by Buckingham and Burnell⁵⁰⁾.

(2) Bernheim and Lavery⁵⁹⁾ studied ¹⁹F shielding anisotropy in CH₃F in two different nematic solvents with respect to an external reference. Their results shows a solvent effect of the order of 0.2 ppm.
(3) Buckingham <u>et al.</u>⁶⁰⁾ measured the chemical shift of CF₄ relative to internal SF₆ in two different nematic solvents. They found a nematic → isotropic shift of ~0.1 ppm and temperature-dependent shift of ~0.008 ppm/degree in both phases.

(4) Buckingham et al.³²⁾ studied fluorine shielding anisotropy in

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trifluoropropyne in several different nematic solvents and used $ext{CF}_4$ as an internal standard. Their result implies a solvent effect of ± 0.1 ppm which corresponds to an error of ± 6 ppm in their final values for $\triangle \sigma_{\rm F}^{-}$. (5) In both isotropic and nematic phases, the rodlike solvent molecules are oriented nearly parallel to each other, but in the normal liquid a specific orientation persists only for a short distance and a short time, while in the ordered liquid it persists over a long range. In terms of this model the immediate environment of a solute molecule looks very much the same in the normal and the nematic liquid phases. Therefore, the variation of the chemical shift caused by the change of the solvent effects during the phase transition is expected to be smaller compared with those observed in different solvents. Taft et al. 62) investigated the solvent effect on the 19 F isotropic chemical shift of substituted fluorobenzenes in twenty widely varied solvents and C_{65}^{H} was used as an internal reference; they found a variation of 0.5 ppm for +R substituents, for -R substituents the range increases to about 2 ppm. Emsley and Phillips 63) reported that the solvent dependence of ¹⁹F chemical shift between two similar compounds (chemical type, size, shape) is about three to four times smaller than that of dissimilar compounds (0.6 ppm v.s. 2 ppm).

Since the importance of solvent effect in a determination of $\triangle 0_F^{F}$ by liquid crystal method depends on the degree of orientation an error of ± 0.1 ppm (as in the case of trifluoropropyne) will only cause an uncertainty of 1.4 ppm in our results. However, the fluorine atoms in trifluoropropyne and carbontetrafluoride may have similar environment which differs from that of fluorine atom in fluorobenzenes. If we take the same proportionality constant as found by Emsley and Phillips⁶³⁾, this leads to an uncertainty

of 5.6 ppm in the absolute values of C in equation (6-12). This estimation is also consistent with the other data discussed above. To a certain degree, this solvent effect will be expected to cause a more or less constant change in the anisotropic values in a series of similar compounds such as fluorobenzenes. Therefore, the relative uncertainty in the values of C caused by the difference in the solvent effects on different fluorobenzenes is estimated to be \sim 3 ppm.

VI-3 Anisotropies of Fluorine Shielding Constants in Non-ortho-substituted Fluorobenzenes and a Correlation with Taft Parameters

The results listed in Table XVI provide a test of Snyder's assumption. By assuming that the results on fluorobenzene and hexafluorobenzene are consistent he obtained $\sigma_{aa} - \sigma_{bb} = 30$ ppm and $\sigma_{bb} - \sigma_{cc} = 259$ ppm. If this is true, then the expressions for any two molecules can be used to determine the anisotropy. With the most favourable cases; i.e. by combining the expressions for 1,3,5-trifluorobenzene and those without ortho-substituents, the values of $\sigma_{bb} - \sigma_{cc}$ vary from -102 ppm to +162 ppm. The assumption that the carbon-fluorine bonds are sufficiently similar is not justified and therefore approximate anisotropic relations between components of the shielding tensor in fluorobenzenes can not be obtained by simply combining the results of any two compounds.

As pointed out earlier, for compounds such as fluorobenzenes the semiquantitative theory of Karplus and Das predicts $\sigma_{bb} > \sigma_{aa} \cong \sigma_{cc}$. Experimentally, large positive values were obtained for the anisotropies $\sigma_{aa} - (1/2)(\sigma_{bb} \neq \sigma_{cc})$ in 1,3,5-trifluorobenzene and hexafluorobenzene (See Table XVI); thus either of the two qualitative relations, $\sigma_{aa} \cong \sigma_{bb} > \sigma_{cc}$ and $\sigma_{aa} > \sigma_{bb} \cong \sigma_{cc}$, should hold for these two compounds. Furthermore, in the original paper by Karplus and Das, values of s, I and ρ have been calculated for monofluorobenzene and nonortho-polyfluoro benzene; if these values are substituted into equations (6-7) - (6-9) and the resulting σ_{aa} , σ_{bb} and σ_{cc} substituted in equation (6-12) for the corresponding compounds, acceptable values of σ_{o} are not obtained (See Table XVII). The calculated anisotropy in 1,3,5trifluorobenzene is zero. Several causes can be responsible for the inadequacy of Karplus and Das' treatment. The theory may be oversimplified by the neglect of all orbitals except those on the central atom. The **parameters** chosen may not be the most suitable. The assumption has been made that the average excitation energy is constant and isotropic.

Although the direct calculation has failed, it would still be possible to seek a correlation between the shielding anisotropies in fluorobenzenes and the changes in electron distribution. According to the theory of Karplus and Das the changes in the components of the chemical shifts, relative to the reference compound fluorobenzene, are given by

 $\Delta \sigma_{aa} = \sigma_{oa} (s_r - 1) \Delta I \qquad (6-13)$

$$\Delta \sigma_{bb} = \sigma_{ob} (\Delta \rho) \qquad (6-14)$$

 $\Delta \sigma_{cc} = \sigma_{oc} \left[\left(\dot{s}_r - \rho_r - 1 \right) \Delta I + \left(\dot{s}_r + I_r \right) \Delta \rho \right] \quad (6-15)$ where \dot{s}_r is the s-hybridization of the reference compound, $\Delta I = I - I_r$ and $\Delta \rho = \rho - \rho_r$ are the changes in ionic character and double bond character. The terms σ_{oa} etc. are given by $\sigma_{oa} = -\frac{e^2 \Lambda^2}{m^2 c^2 \Delta E_a} < \frac{1}{r^3} >_{2p}$; i.e. the average excitation energy

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TABLE XVII

Calculated σ_{o} by Karplus and Das Theory

	A	В	C	σ o calcd.	(ppm)
fluorobenzene	1.0	-0.424	50.0	524	
meta-difluorobenzene	1.0	-0.170	74.4	3560	
para-difluorobenzene	1.0	-0.684	31.7	234	
1,3,5-trifluorobenzene	1.0	0	102.0	-	

is taken to be anisotropic. In writing equations (6-13) to (6-15) small changes in s are neglected and so are all the terms that are quadratic in ΔI and $\Delta \rho$. The lack of suitable values for ΔI and $\Delta \rho$ and the absence of any data on the anisotropy of the average excitation energy make it difficult to apply these equations.

Taft^{64,65)} has correlated his inductive and resonance parameters, $\sigma_{\rm I}$ and $\sigma_{\rm R}$, with the isotropic ¹⁹F chemical shifts with success for a large number of meta- and para-substituted fluorobenzenes. The isotropic chemical shifts, relative to fluorobenzene, is given by equation (6-16)^{*} with $\sigma_{\rm R}$ equal to zero for meta-substituents.

$$\overline{\mathbf{0}} = -29.7 \overline{\mathbf{0}}_{\mathrm{R}} - 6.1 \overline{\mathbf{0}}_{\mathrm{I}}$$
(6-16)

In order to obtain some insight into this empirical correlation, Taft <u>et al</u>.²⁶⁾ have examined the experimental results on ¹⁹F chemical shifts for several p-substituted fluorobenzenes in terms of Prosser and Goodman's semiempirical theory²⁵⁾ of fluorine chemical shifts. The results indicate that there is a reasonable degree of theoretical justification for relating the $\sigma_{\rm R}$ values with pi-charge density of the fluorine atom. On the other hand, in their treatment of polyfluorobenzenes, Karplus and Das determined $\Delta \rho$ with Hückel MµO. calculations and they found that the terms involving $\Delta \rho$ give negligible contribution to the chemical shift in all meta-derivatives. If this is true^{**}, then $\sigma_{\rm T}$ could be a rather

This equation is preferred to a later expression ⁶²⁾ since it led to smaller deviations. The results, however, are unchanged.

** Recent calculation with the CNDO/2 method shows that the pi-charge density on fluorine atoms in m-difluorobenzene is quite different from that in fluorobenzene²⁸.

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good measure of the values of $\triangle I$, at least for the meta-substituted fluorobenzenes. Therefore, for both meta- and para-substituted fluorobenzenes a direct proportionality is assumed between $\triangle I$ and σ_I and between $\triangle \rho$ and σ_R . With this assumption the Taft parameters can be incorporated into equations (6-13) to (6-15). A least squares fit was made to the experimental data for eleven non-ortho-substituted fluorobenzenes with the constants of proportionality and $(\sigma_{aa} - (1/2)(\sigma_{bb} + \sigma_{cc}))$ and $(\sigma_{bb} - \sigma_{cc})$ for fluorobenzene as the unknown parameters, to give

$$\Delta \sigma_{aa} = 18.2 \sigma_{T} \tag{6-17}$$

$$\Delta \sigma_{\rm bb} = -58.7 \sigma_{\rm R} \tag{6-18}$$

$$\Delta \sigma_{cc} = -36.5 \sigma_{I} - 30.4 \sigma_{R}$$
(6-19)

The sum of equations (6-17) to (6-19), of course, equals equation (6-16)

Table XVIII lists the values of the anisotropy terms, the calculated values of C from substitution in equation (6-12), and the calculated and experimental isotropic chemical shifts. The standard deviation in C is 3.0 ppm and in $\overline{\sigma}$ is 1.4 ppm. The largest deviations occur for p-nitrofluorobenzene and p-fluorobenzonitrile. This is not unexpected since these +R substituents do not obey equation (6-16) strictly.

The values obtained for the anisotropy of fluorobenzene may be compared with those of $\operatorname{Snyder}^{37}$ and Chan and $\operatorname{Dubin}^{38}$. Since $\operatorname{Snyder's}$ results are based upon the invalid assumption that the results for fluorobenzene and hexafluorobenzene are consistent, thus the

TABLE XVIII

Anisotropy Values of Fluorine Chemical Shifts of Substituted Fluorobenzenes

Compounds	$\begin{bmatrix} \sigma_{aa} - \frac{1}{2}(\sigma_{bb} + \sigma_{cc}) \end{bmatrix}$ (ppm)	[σ _{bb} - σ _{cc}] (ppm)	C calc. (ppm)	C exp. (ppm)	で calc. (ppm)	o exp. (ppm)	
Fluorobenzene	62.5	30.1	49.7	50.0	0	0	
p-Fluoro-	67.2	58.1	27.4	31.7	6.3	6.6	
p-Chloro-	71.7	52.4	28.3	28.2	2.5	2.7	
p-Bromo-	71 . 7	51.0	27.1	28.5	2.1	2.1	
p-Cyano-	84.4	44.7	43.2	38.0	-6.0	-9.8	ŧ
p-Nitro-	90.1	46.0	55.4	58.8	-8.2	-10.0	88
p-Hydroxy-	52.5	51.7	19.9	20.1	11.2	12.1	
p-Amino-	41.5	44.0	5.6	2.4	14.2	14.8	
m-Fluoro-	81.5	48.0	73.1	74.4	-3.2	-3.0	
3,5-Difluoroiodobenzer	ne 95.4	63.0	99.3	95.5	-5.5	-5.0	
1,3,5-Trifluoro -	100.5	68.0	100.5	102.0	-6.3	-5.8	

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lack of quantitative agreement is not surprising. However, qualitatively our results do verify Snyder's conclusion, i.e., the fluorine nucleus in fluorobenzene is most diamagnetically shielded when the applied field is perpendicular to the molecular plane and least when the applied field is parallel to the plane and perpendicular to the C-F bond.

Our results disagree with those of the molecular beam magnetic resonance determination, both in sign and magnitude. A substitution of Chan and Dubin's values for $\sigma_{\alpha\alpha}^{(2)CI}$ into equation (6-12) for fluorobenzene gives a value of -150 ppm for C. Any anisotropy based on Snyder's value (C = 50 ppm) can not be expected to be in agreement with those from the molecular beam magnetic resonance study. It is unrealistic to hold that the environmental effects on a solute molecule on going from the nematic to the isotropic phase are responsible for such a large discrepancy between the anisotropies of fluorobenzene determined by the two different methods. The liquid crystal experiment gives the anisotropic relations including both diamagnetic and paramagnetic terms, while the molecular beam resonance experiment is concerned only with part of the para-magnetic contribution. The discrepancy is probably due to the different assumptions used in the two treatments.

VI-4 The Average Excitation Energy Approximation

According to equation (6-17) and (6-19), a change in ionic character of the carbon-fluorine bond has opposite effects upon $\Delta \sigma_{aa}$ and $\Delta \sigma_{cc}$ as shown by their dependence on σ_{I} . Within the context of the Karplus and Das theory, both σ_{aa} and σ_{cc} should increase with increasing ΔI . Since ΔI is proportional to the negative σ_{T}

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(comparing equation (6-13) and (6-15) with (6-16)), the effect of σ_{I} on $\Delta \sigma_{aa}$ is unexpected and could be interpreted in terms of a negative average excitation energy ΔE_{a} .

The occurrence of negative average excitation energies has been recognized as a consequence of this approximation $^{66,67)}$. By combining equation (6-5) and (6-6) we obtain

$$\sigma_{\alpha\alpha}^{(2)} = \left(-e^{2}/m^{2}c^{2}\Delta E_{\alpha}\right) < r^{-3} < \Psi_{0} \left| \left(\sum_{k} l_{\alpha k}\right) \left(\sum_{k} l_{\alpha k}\right) \right| \Psi_{0} > \qquad (6-20)$$

Since the expectation value of the square of $L_{\alpha k} = \sum_{k=\alpha k} 1_{\alpha k}$ is always positive, the equation predicts a paramagnetic $\sigma_{\alpha\alpha}^{(2)}$ with a positive ΔE_{α} . However, $\sigma_{\alpha\alpha}^{(2)}$ need not be paramagnetic as shown directly by equation (6-4) and recently both experimental and theoretical analyses have shown that a diamagnetic $\sigma_{\alpha\alpha}^{(2)}$ exists in the compound ClF^{68} . In such cases, the use of equation (6-20) as an approximation to $\sigma_{\alpha\alpha}^{(2)}$ may lead to a negative ΔE_{α} .

A comparison of equation (6-4) and (6-5) leads to

$$-(\Delta E_{\alpha})^{-1} = \frac{\sum_{m} (E_{o} - E_{m})^{-1} \operatorname{Re}[\langle \Psi_{o} | \sum_{k} l_{\alpha k} | \Psi_{m} \rangle \langle \Psi_{m} | \sum_{k} l_{\alpha k} / r_{k}^{3} | \Psi_{o} \rangle]}{\sum_{m} \operatorname{Re}[\langle \Psi_{o} | \sum_{k} l_{\alpha k} | \Psi_{m} \rangle \langle \Psi_{m} | \sum_{k} l_{\alpha k} / r_{k}^{3} | \Psi_{o} \rangle]$$
(6-21)

In this sense $\triangle E_{\alpha}$ is defined as an average excitation energy weighted by the corresponding matrix elements. The constancy of every $E_m - E_o$ is not the only condition for obtaining the same $\triangle E_{\alpha}$ for two similar compounds; in addition the corresponding matrix elements have to remain constant or change with increments proportional to their original values. Alternatively one may define the average excitation energy as

$$\frac{1}{\Delta E_{\alpha}}_{a} = -\frac{d(\sum_{m} (E_{o} - E_{m})^{-1} \operatorname{Re} [\langle \Psi_{o} | \sum_{k} 1_{\alpha k} | \Psi_{m} \rangle \langle \Psi_{m} | \sum_{k} 1_{\alpha k} / r_{k}^{3} | \Psi_{o} \rangle 1)}{d(\sum_{m} \operatorname{Re} [\langle \Psi_{o} | \sum_{k} 1_{\alpha k} | \Psi_{m} \rangle \langle \Psi_{m} | \sum_{k} 1_{\alpha k} / r_{k}^{3} | \Psi_{o} \rangle 1)}$$

$$(6-22)$$

As an illustration of the difference between these two definitions, equations (6-21) and (6-22), consider the **calculation** of $\int_{\Omega\Omega}^{-}$ for two similar compounds A and B. A continuous dependence of $O_{\Omega\Omega}^{(2)}$ on

$$s_{m} (\underline{\Psi}_{o}) = \left(\sum_{\underline{m}} \operatorname{Re}[\langle \underline{\Psi}_{o} | \sum_{\underline{k}} \mathbf{1}_{\alpha k} | \underline{\Psi}_{m} \langle \underline{\Psi}_{m} | \sum_{\underline{k}} \mathbf{1}_{\alpha k} / \mathbf{r}_{k}^{3} | \underline{\Psi}_{o} \rangle \right)$$
$$= \langle \underline{\Psi}_{o} | \left(\sum_{\underline{k}} \mathbf{1}_{\alpha k} \right) (\sum_{\underline{k}} \mathbf{1}_{\alpha k} / \mathbf{r}_{k}^{3}) | \underline{\Psi}_{o} \rangle$$
(6-23)

in a small range is assumed and is shown in Fig. 13. For calculation of $\mathbb{G}_{\alpha\alpha}^{(2)}$ from $\underline{\Psi}_{0}$, the correct $(\Delta E_{\alpha})^{-1}$ can be found from the slopes of lines OA and OB for these two compounds. If we assume that the $\Delta E_{\alpha}'$ S are same for A and B, then a reasonably good calculation can be made with the choice of line OC. But, if one is interested in $\Delta \mathbb{G}_{\alpha\alpha}$ between compounds A and B, then $(\Delta E_{\alpha})_{d}^{-1}$ should be used. Generally the value of $(\Delta E_{\alpha})_{d}^{-1}$ will be different from that of $(\Delta E_{\alpha})^{-1}$. Referring back to fluorobenzenes a negative ΔE_{a} for $\Delta \mathbb{G}_{aa}$ in equation (6-17) does not mean that $\mathbb{G}_{\alpha\alpha}^{(2)}$ is diamagnetic, but it may be responsible for the high shielding components along the a-axis.

In view of the uncertain nature of the average excitation energies it could be argued that this concept should be discarded entirely in the calculation of chemical shifts. The approximation, however, does avoid the difficult task of dealing with excited states. Furthermore, in a series of sufficiently similar compounds, $(\Delta E)_d^{-1}$ may be fairly constant and thus a correlation of changes in chemical shift with the



Fig. 13 The dependence of $\mathbf{\sigma}_{\alpha\alpha}^{(2)}$ on $s_{m}^{(\overline{\Psi}_{0})}$

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ground state properties may be expected. For this purpose, it is proper to treat $\triangle E$ as an empirical parameter.

VI-5 Ortho-Substituted Fluorobenzenes

In the isotropic phase the fluorine resonance of 1,3,5- trifluorobenzene is 56 ppm to low field from hexafluorobenzene. When this result is combined with the anisotropic data (Table XVI), then

> $\Delta \sigma_{aa} (C_6 F_6 - C_6 H_3 F_3) = 90 \text{ ppm}$ $\Delta (\frac{1}{2} (\sigma_{cc} + \sigma_{bb})) (C_6 F_6 - C_6 H_3 F_3) = 39 \text{ ppm}$

The orthofluorine substituents effect the shielding in hexafluorobenzene perpendicular to the molecular plane to a greater extent than the shielding parallel to the plane.

The observation is further supported by the comparison of anisotropic data for meta- and ortho-difluorobenzene. Since the term involving $\sigma_{bb} - \sigma_{cc}$ has only a small coefficient in both cases, the rather large difference of ~50 ppm in the values of C can only be attributed to the change of $\sigma_{aa} - \frac{1}{2} (\sigma_{bb} + \sigma_{cc})$ due to the presence of the orthofluorine atom.

As pointed out above, Karplus and Das have found that an empirical "ortho-effect" contribution of ~17 ppm has to be introduced in order to obtain agreement between experimental and calculated shifts. With the intention of perserving their theory, they suggested that the "ortho-effect" is most probably due to the reduction of the amount of double bond character and such a change in ρ can be attributed to a steric effect caused by the ortho-substituents. According to equations (6-13) to (6-15) a large negative $\triangle \rho$ increases both $\triangle \sigma_{bb}$ and $\triangle \sigma_{cc}$. This in turn decreases, not increases as observed experimentally, the values for $\sigma_{aa} - \frac{1}{2} (\sigma_{bb} + \sigma_{cc})$. Therefore, in view of the present results, this steric effect does not provide a satisfactory explanation of the presence of the "ortho-effects" within the context of Karplus and Das theory. This conclusion is consistent with the results on other ortho-halogen substituted fluorobenzenes⁶⁹.

VI-6 Anisotropy of Proton Chemical Shift

The anisotropies of proton chemical shifts were only measured for 1,3,5-trifluorobenzene and p-difluorobenzene. They are

The value for $C_6H_3F_3$ is surprisingly similar to that of benzene itself, -2.88 ppm⁴³⁾. A value closer to that of 1,3,5-trichlorobenzene, -4.90 ppm¹⁶⁾, might be expected due to presence of the ortho-halogen substituents in each case. However, too much significance should not be attached to these values at the present time since the change in solvent effect with change of phase may contribute a significant part to the proton-shift anisotropy value determined by this method^{49,50,70}.

VI-7 Absolute Signs of Indirect Spin-Spin Coupling Constants

For high resolution nuclear magnetic resonance of both oriented and non-oriented molecules, a reversal of the signs of all J_{ij} , D_{ij}^{dir} D_{ij}^{pseudo} does not affect the observed spectrum and a direct analysis of these spectra only yields the relative signs of the coupling constants. However, in certain favourable cases, when the signs of $D_{i,j}^{dir}$ can either be obtained from other methods or estimated with reasonable certainty from a knowledge of molecular geometry, it is possible to determine the absolute signs of the indirect spin-spin coupling constants from the anisotropic spectrum. With the assumption that the fluorobenzenes are aligned with their molecular planes parallel to the applied field the absolute signs of indirect coupling constants in 1,3,5-trifluorobenzene, 3,5-difluoroiodobenzene, ortho-, meta-, and para-difluorobenzene have been determined. The results are listed in Tables VII, VIII, X, XV and are consistent with those reported by other workers^{53,57,58,71,72}).

Recently there has been some confusion about the absolute sign of J_{FF}^{meta} in fluorobenzenes. By assuming that hexafluorobenzene tends to orient its molecular plane parallel to magnetic field Snyder and Anderson $^{37)}$ have found $J_{FF}^{meta} = -4$ Hz, which is in contradiction with the signs of J_{FF}^{meta} in substituted trifluorobenzenes obtained from double resonance experiments⁷³⁾. The measured anisotropy of the proton chemical shift in 1,3,5-trifluorobenzene supports the assumed orientation of hexafluorobenzene in nematic p-p'-di-n-hexyloxyazoxybenzene but J^{meta} was found to be +5.6 Hz. Based on the study of several 2,6-difluorobenzenes Abraham, Macdonald and Pepper⁷⁴⁾ have correctly pointed out that J_{FF}^{meta} may vary appreciably and may be of either sign. According to an additive scheme of substituent contributions suggested by those authors, $J_{\rm FF}^{\rm meta}$ should be +5.6 Hz in 1,3,5-trifluorobenzene and -2.3 Hz in hexafluorobenzene. The results from liquid crystal solution measurements, therefore, directly verify these predictions. Among the various coupling constants in substituted benzenes, J_{HH} , J_{HF} and J_{FF} , J_{FF}^{meta} is

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unique in its sensitivity to the nature of the substituents, but the mechanism underlying this strong effect has not yet been fully examined.

VI-8 Molecular Geometry

As mentioned in Chapter III, the dipole coupling constant D_{ij} consists of two independent parts, the direct dipole coupling D_{ij}^{dir} and the pseudo-dipole coupling D_{ij}^{pseudo} . Previous studies^{12,43} indicate that the contribution from the anisotropy of the indirect spin coupling constant J_{ij} is negligible for H-H coupling, and here it is assumed that this is also true for H-F coupling. With this assumption, the optimized dipole coupling constants have been used to calculate the molecular geometries of the three difluorobenzenes and of 1,3,5-trifluorobenzene.

It should be noted that the motional constants and the nuclear co-ordinates always enter equation (3-30) as products of the first power in the motional constants and the inverse third power of the co-ordinates; and a linear change in the molecular geometry with a compensating change in motional constants will leave D_{ij}^{dir} unchanged. Thus the derived distances are all relative and it is necessary to assume fixed values for certain co-ordinates.

The direct dipole constants, calculated for ideal geometry based on a regular hexagonal carbon skeleton, with $C-C = 1.390\text{\AA}$, and $C-H = 1.080\text{\AA}$, and $C-F = 1.310\text{\AA}$, all bond angles 120°, disagreed with experimental values in some cases. For para-difluorobenzene a positive pseudo-dipole coupling constant of about 100 Hz occurred for ortho-hydrogen atoms, the geometry, therefore, is not ideal. The hydrogen atom positions were determined with respect to fixed fluorine atoms placed 2.700Å from the origin at the center of the molecule. Trial values of the x and y co-ordinates were used to

determine the motional constants from experimental values of D_{HH}^{σ} and D_{HH}^{m} , and then the motional constants and trial co-ordinates were used to calculate the D_{HH}^{p} and $(D_{HF}^{o} + D_{HF}^{m})$ which were compared with the observed values. The process was repeated until agreement was within the experimental The final co-ordinates are 2.141Å and 1.261Å for x and y respectively, error. the estimated error is about 0.005Å. The departure from ideal geometry is such that the hydrogen atoms are displaced towards neighbouring fluoring atoms. It is interesting to note that this positional change can not be accounted for by altering the C-C-H bond angle only. With the assumption that C-H = 1.080Å, an increase in either the distance $C_1 - C_2$ relative to that of C_2-C_3 , or the angle $C_6-C_1-C_2$ from 120°, or both, are required (for numbering see Table XV). The increase in the $C_1 - C_2$ bond distance and decrease in the $C_2 - C_3$ distance are changes expected from a contribution of the quinoid type structure arising from conjugation of the fluorine substituent with the ring. The increase in bond angles shows a resemblance to models constructed for monofluorobenzene from the microwave spectrum.⁷⁵⁾ To determine these actual changes would require further assumptions regarding nuclear co-ordinates and is not justified.

McLean <u>et al.</u>⁵⁸⁾ have computed the geometry of para-difluorobenzene from their experimental dipolar coupling constants but by a different procedure. They compared the ratios of the distances R_{26} to R_{23} and R_{14} to R_{13} . These ratios are 1.6988 and 2.1335, respectively. The corresponding values from our analysis are 1.6979 and 2.1412.

The nuclear co-ordinates of ortho- and meta-difluorobenzene were calculated by a similar procedure and are given in Table XIX, together with those of para-difluorobenzene. A similar effect was observed. The hydrogen

TABLE XIX

Nuclear Co-ordinates in Difluorobenzenes*

	or	tho	met	. .	para		
	x	У	x	У	x	У	
1	0.008	2.480	0	2.470	(0)	(2.700)	
2	2.338	1.350	(2.338)	(1.350)	2.141	1.261	
3	2.338	-1.350	2.166	-1.228	2.141	-1.261	
4	0.008	-2.480	0	-2.470	(0)	(-2.700)	
5	(-2.139)	(-1.235)	- 2.166	-1.228	-2.141	-1.261	
6	(-2.139)	(1.235)	(2.338)	(1.350)	-2.141	1.261	

* Assumed coordinates are in parentheses.

atoms ortho to fluorine were displaced towards the fluorine atom. If only the distortion of the carbon skeleton is assumed for ortho-difluorobenzene it is in the direction opposite to that expected as a result of fluorine conjugation. The displacements are small but consistent, and similar effects have been reported for para-dichlorobenzene and para-di-bromobenzene 18,58.

In 1,3,5-trifluorobenzene, the ratio of the distances from fluorine and hydrogen to the center of molecule was found to be 1.087. This ratio is in good agreement with the value 1.086 obtained from an electron diffraction study 76 .

Since the direct dipole coupling constants D_{ij}^{dir} are averages over all vibrations, the internuclear distances derived from NMR spectra in nematic solvents are values for $\langle R^{-3} \rangle_{molecular}$ vibration \cdot It is convenient to express R, the separation at any given time, as the sum of the equilibrium internuclear distance R_e and an extension δR . Provided the vibration is small, we may write

$$D_{ij} \propto (R_e + \delta R)^{-3}$$

$$\propto R_e^{-3} (1 - 3 < \delta R > /R_e + 6 < \delta R^2 > /R_e^2 + - - - -) \quad (6-24)$$
where $\langle \delta R^n \rangle = \int P(\delta R) (\delta R)^n dR$. $P(\delta R)$ is the normalized probability
function for stretching by an amount δR from its equilibrium distance R_e .

Thus the value from NMR will be related to R by

$$R_{\text{NMR}} = \langle R^{-3} \rangle^{-1/3}$$

= $R_{\text{e}} [1 + \langle \delta R \rangle / R_{\text{e}} - 2 \langle \delta R^{2} \rangle / R_{\text{e}}^{2} + - - -]$ (6-25)

Equation (6-25) shows that the anharmonic correction $\langle \mathbf{\delta} \mathbf{R} \rangle$ and harmonic correction $\langle \mathbf{\delta} \mathbf{R}^2 \rangle$ are of opposite sign; with a harmonic oscillator function the second term in the bracket is zero and $R_{NMR} \langle R_e$ is predicted, but with a Morse wave function it has been shown that the anharmonic correction is usually dominant, i.e. $R_{NMR} > R_e^{-77}$. The relationship between R_{NMR} and R_e , is therefore, critically dependent upon the probability function P(3R) and a correction can not be applied without this knowledge from a complete vibrational analysis.

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PART II

MOLECULAR MOTIONS IN BORANE AND BORONTRIHALIDE COMPLEXES

CHAPTER I

INTRODUCTION

The existence of liquid crystals, as discussed in the first part of this thesis, provides an example of how that melting process can occur by stages. When the thermal energy becomes sufficiently high that the molecules are no longer able to maintain themselves in their regular arrangement then the substance liquefies; if there is room, the free molecules then begin to turn in all directions, giving an isotropic liquid. However for rod-like molecules much space is needed to rotate freely. Some directions in the liquid state are therefore less favourable than others and an anisotropic liquid is formed and only at a higher transition does it become isotropic.

If the molecules are globular in shape, such as neopentane, hindrance to the rotation of the whole molecule is expected to be small. Molecules of this type usually form so-called plastic crystals¹⁾ in which the orientational freedom is acquired first in a solid-solid phase transition, but the coherence of the crystal is broken only at a higher temperature, the melting point. For this reason most plastic crystals have low entropy of melting, usually less than 5 e.u.; this quantity, in fact, is a criterion of the "plasticity" of a crystal.

The first direct experimental evidence that the molecules can rotate relatively freely in plastic phase came from dielectric constant measurements^{2,3)}. Usually upon freezing, the dielectric constant of a polar substance drops sharply; but with many plastic crystals the dielectric constants are similar in size and in temperature dependence to those of the liquid phase. The abrupt change in dielectric constant only occurs at the lower transition point. Since the high dielectric constants of liquids consisting of dipolar molecules are known to be due to the rotational orientation of the molecules in the alternating electric field used in measuring the dielectric constant, these high dielectric constants of dipolar molecular solids show the existence of molecular rotation in the plastic phase.

The line shape and line width of the nuclear magnetic resonance spectrum of a solid substance are critically dependent on the nature of any molecular motion which may occur. Thus the study of the resonance spectrum gives insight into the nature of the motion involved. Sometimes it is also possible to correlate the onset of certain molecular motions with the occurrence of a phase transition. The application of the NMR technique to systems consisting of spherical or near-spherical molecules, was first reported by Gutowsky et al. 4,5) for six tetrasubstituted They found that the rotation of the CH_3 group around its C_3 methanes. axis, more complex internal rotation, the overall molecular reorientation (isotropic rotation), and self-diffusion appear progressively with increasing temperature. In all the polar materials the line becomes very narrow at the thermal transition at which the dielectric constants rise to a high value, marking the onset of isotropic rotation. The work was recently further extended to the related series $Si(CH_3)_4$, Ge(CH₃)₄, Sn(CH₃)₄ and Pb(CH₃)₄ by G.W. Smith⁶⁾. The heavier molecules were found to become progressively less mobile. This phenomenon, on the basis of Pople-Karasz theory 7,8), has been

qualitatively explained by the gradual increase of the orientational energy barrier relative to that for self-diffusion as the central atom becomes heavier.

In the present work, wide-line nuclear magnetic resonance studies of solids of the type $(CH_3)_3 \ N \ BX_3$, where X = H, F, Cl and Br, have been made to gain information about the motions of the molecules. These compounds have high dipole moments (Table I). They are roughly spherical in shape and the deviation from such a shape increases gradually as X changes from hydrogen to bromine. It was hoped that this study would give insight into the effect of these factors on the motional freedom in the solid state.

The results of a wide-line NMR study of the solid ammoniaborontrifluoride complex will also be presented in this thesis.

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TABLE I

Dipole Moments	of	(CH ₃) ₃	N	^{BX} 3 ⁹⁾	
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Compounds	<u>Dipcle Moments (Debye</u>)
(CH ₃) ₃ N B H ₃	4.62
(CH ₃) ₃ N BF ₃	4.04
(CH ₃) ₃ N BCl ₃	5.13
(CH ₃) ₃ N BBr ₃	5.57

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CHAPTER II

THE INFLUENCE OF MOLECULAR MOTION ON NUCLEAR MAGNETIC RESONANCE LINE SHAPES

II-1 Nuclear Dipole-Dipole Interaction

With nuclei of spin 1/2 the dominant contribution to the broadening of the resonance spectrum of solids comes from the magnetic interaction between nuclear dipoles. Referring to equation (3-28) of Part I, this means that those terms involving chemical shifts and indirect spin coupling constants can be neglected and the spin Hamiltonian can be rewritten as

$$\begin{aligned}
\iint_{i=} -(2\pi)^{-1} \sum_{i} \gamma_{i}^{HI}_{Zi} \\
+ \sum_{i>j} (1/2) D_{ij} [2I_{Zi}I_{Zj} - (I_{Xi}I_{Xj} + I_{Yi}I_{Yj})] \\
D_{ij} = (2\pi)^{-1} \gamma_{i} \gamma_{j} f_{i} (1-3\cos^{2}\theta_{ij}) R_{ij}^{-3}.
\end{aligned}$$
(2-1)

and

where R is the distance between nuclei i and j and
$$\Theta_{ij}$$
 the angle

between the vector ${\bf R}_{\mbox{ij}}$ and the applied field ${\bf H}_{\mbox{\cdot}}$

If i and j are two different nuclei, e.g. ^{L}H and ^{19}F , it can be shown that the spin-exchange term, i.e. the term involving $(I_{Xi}I_{Xj} + I_{Yi}I_{Yj})$ does not contribute because of the different Larmor precessional frequencies of the two nuclei¹⁰, thus this part of the spin Hamiltonian can be simplified to

$$\mathcal{H} = -(2\pi)^{-1} \sum_{i} \gamma_{i} I_{Zi} [H + \sum_{j} \gamma_{j} n I_{Zj} (1 - 3 \cos^{2} \theta_{ij}) R_{ij}^{-3} + - - -]$$
(2-3)

The presence of nucleus j modifies the field experienced by nucleus i by a quantity

$$H_{loc, ij} = \chi_{fi} I_{Zj} (1 - 3 \cos^2 \theta_{ij}) R_{ij}^{-3}$$
 (2-4)

where I_{Zj} can take values +1/2 or -1/2 corresponding to the two possible orientations of the nuclear dipole j in the external magnetic field.

For the case of identical nuclei, the effect of the spin-exchange term has to be taken into account. A quantummechnical perturbation calculation, performed by $Pake^{10}$ for two protons showed that equation (2-4) must be multiplied by a factor 3/2 to obtain the dipolar magnetic field between two identical nuclei.

Since the summation in equation (2-1) is supposed to be taken over all the nuclei present in the crystal, a calculation of line shape from a known structure model presents, in general, a forbidden task. However, where the nuclei are localized in small groups it is possible to calculate the line shape in the following way: transition frequencies and intensities are first computed as if these groups were isolated, then the effect of the field due to the more remote nuclei is introduced by broadening the individual transitions with a suitable Gaussian function. In such a way the line shapes have been calculated for two spin-¹⁰⁾, three spin-¹¹⁾, and to a limited extent four spin-systems¹²⁾. As the number of nuclei in the group increases the calculation becomes extremely complicated and the result would be less rewarding since the line structure becomes so complex as to be unresolved in detail. Comparison between structural models and experiment is possible for more complicated systems by employing the second moment¹³⁾.

II-2 Second Moment of the Resonance Line

For a normalized resonance curve described by a shape function g(H) with maximum at H_o , the nth moment M_n with respect to H_o is defined as

$$M_{n} = \int_{-\infty}^{\infty} (H-H_{o})^{n} g(H) dH \qquad (2-5)$$

If g(H) is symmetrical about H_0 , then all odd moments vanish. Van Vleck¹³⁾ has derived expressions for the second moment in terms of internuclear distances. For a single crystal his result for the second moment M_2 , which is just the mean-square width of the spectrum about its center is

$$M_{2} = \frac{3}{4} I(I+1) g^{2} \mu_{0}^{2} N^{-1} \sum_{i \neq j} (3 \cos^{2} \theta_{ij} - 1)^{2} R_{ij}^{-6} + \frac{1}{3} \mu_{0}^{2} N^{-1} \sum_{if} I_{f} (I_{f} + 1) g_{f}^{2} (3 \cos^{2} \theta_{if} - 1)^{2} R_{if}^{-6}$$
(2-6)

where I is the spin number, μ_0 is the nuclear magneton, $g\mu_0I$ is the nuclear magnetic moment and N is the number of resonance nuclei in the system over which the sum is taken. The suffix f is referred to the other species of magnetic nuclei besides those at resonance. The first term arises from the resonant nuclei in the sample and the second comes from their interaction with the nonresonant spins I_f . It is to be noticed that the numerical coefficient in (2-6) for the contribution to the second moment from pairs of identical nuclei is 9/h times greater than that for unlike pairs. This is merely the square of the factor 3/2 caused by the mutual spin exchange process discussed earlier. Strictly speaking, N should be summed over the entire crystal. However, since the inverse sixth power of distance enters into every term in equation (2-6), important contributions to the sum are only obtained from pairs of nuclei in the same unit cell or in the adjacent cells. The environment of all unit cells is therefore effectively identical; the number N may therefore be reduced to the number of nuclei in one unit cell, and the sum taken over all the nuclei in this cell and their neighbours, both inside and outside the cell. Frequently the symmetry of the unit cell provides two or more nuclei with the same environment, in this case N may be reduced still further.

For a polycrystalline sample, equation (2-6) has to be averaged over all values of θ and this gives

$$M_{2} = \frac{3}{5} I(I+1) g^{2} \mu_{0}^{2} N^{-1} \sum_{i \neq j} R_{ij}^{-6} + \frac{4}{15} \mu_{0}^{2} N^{-1} \sum_{if} I_{f}(I_{f}+1) g_{f}^{2} R_{if}^{-6}$$
(2-7)

If the nuclear positions in the crystal lattice are known, then a straight forward calculation of the theoretical second moment can be made. More commonly, however, they are not well defined, especially for protons, and estimates must be made. It is usual to divide the second moment into intra- and inter-molecular contributions. The former is calculated on the basis of reasonable molecular bond lengths, angles and conformation. The intermolecular contribution is estimated by comparison with known similar structures.

II-3 Effect of Molecular Motion on the Line Width and Second Moment

In many solids constituent molecules or atomic groups undergo translational or rotational motion with a frequency which increases with

Such motion modifies the interactions between nuclear temperature. magnetic dipoles and as a result the local field experienced by any resonant nucleus is time-variant. If this variation is sufficiently rapid, the time average of the local field must be used in expressing the dipolar interaction. Since this average will in general be smaller than the steady local field for a rigid system, a narrowing of the line width will result.

In the presence of fast molecular motion the second moment can be calculated from Van Vleck's formula with the terms (3 $\cos^2 \theta_{ij} - 1$) R_{ij}^{-3} averaged over the particular type of molecular motion. For a single crystal containing a system of atomic groups each reorienting about one axis only, the intra-group contribution S1 to the second moment can be calculated by averaging the angular term only. The result is 14) $S_1 = (3 \cos^2 \theta' - 1)^2 [\frac{2}{4} I (I + 1) g^2 \mu_0^2 N^{-1} \sum_{i \neq j} F(\beta_{ij})^2 R_{ij}^{-6}]$ + $\frac{1}{3} \mu_0^2 N^{-1} \sum_{if} I_f (I_f + 1) g_f^2 F(\beta_{if}) R_{if}^{-6}$] (2-8) $F(\beta) = \frac{1}{h} (3 \cos^2 \beta - 1)^2$ (2 - 8a)

where

 θ' is the angle between the axis of reorientation and the applied field H, and $\beta_{i,j}$ is the angle between the axis of rotation and R.

If the material is polycrystalline, there is an isotropic distribution of axes of reorientation, and the factor (3 $\cos^2 \theta' - 1$)² occurring in equation (2-8) must be replaced by its mean value of 4/5 giving

$$S_{1} = \frac{3}{5} I (I + 1) g^{2} \mu_{0}^{2} N^{-1} \sum_{i \neq j} F (\beta_{ij}) R_{ij}^{-6} + \frac{4}{15} \mu_{0}^{2} N^{-1} \sum_{if} I_{f} (I_{f} + 1) g^{2}_{f} F(\beta_{if}) R_{if}^{-6}$$
(2-9)

Comparison of (2-9) with equation for a rigid structure shows that each term in the intragroup contribution is reduced by a factor $F(\beta)$. This factor decreases from unity at $\beta = 0^{\circ}$ to zero at 54°44' and increases to 1/4 at $\beta = 90^{\circ}$.

The effect on the intragroup second moment by simultaneous rotations about two or more axes has been investigated by Powles and Gutowsky⁴⁾. They gave the following general formula for the average value of the angular term

The distance vector \overrightarrow{R} between the two nucleic considered makes an angle Θ with respect to the main magnetic field H and Θ_1 , with respect to an axis of rotation which we designate the lst axis of rotation. Θ_i is the angle: between ith and (i - 1)th axes of rotation and $\Theta^{(n)}$ the angle between magnetic field H and the nth axis.

Calculation of inter-group and intermolecular contributions to the second moment is complicated by the fact that both angle and distance vary during the motion. Andrew and Eades¹⁵⁾ have derived expressions which can be used to estimate the intermolecular second moment during rotation. The essence of their method is to average the term $(3 \cos^2 \theta - 1) \ \text{R}^{-3}$ over the equivalent positions of minimum potential energy; it is supposed that the molecule spends on the average an equal length of time in each position.

The intramolecular second moment will be zero for isotropic rotational motion of the molecule as a whole^{16,17)}, but as long as the centers-of-mass remain fixed, an intermolecular contribution will still arise. If, in addition, diffusion through the lattice occurs, then the overall second moment tends to zero.

For ths simple case of nuclei grouped in pairs or in triangles, it is also possible to calculate the change in line width and shape caused by molecular rotations^{10,11}.

It is important to consider the frequency of molecular motion which is necessary to cause the narrowing of the resonance line. For this purpose, it would be better to use the so-called spin-spin relaxation time, T2, which is an alternative measure of line width. In a solid, the nuclei experience a range of magnetic fields about H loc and, therefore, a corresponding range of Larmor frequencies $\Delta W = \gamma H_{loc}$. If all the nuclei process initially in phase, then they will gradually lose phase because of the differences in their precessional frequencies. The spin-spin relaxation time T2, defined as the time required for this dephasing to occur, is clearly in the order of $1/\gamma H$ loc. The variation of the local fields caused by the molecular motion interrupts the dephasing process, increasing the spin-spin relaxation time and so narrowing the line. In order that the molecular motion may be effective, the local field must change before the nuclei can lose phase by spin-spin relaxation, and it follows, therefore, that the motion must occur at a frequency greater than $1/T_2$, i.e., greater than line width expressed in frequency units.

The theoretical calculation of second moments has been discussed for cases where frequency of molecular motion is either very fast or very slow compared with the line width. However, in the intermediate region between these two extremes, the interpretation of the observed second moment becomes extremely difficult. The root of this difficulty lies in the fact that, theoretically, the second moment is not affected by the molecular motion. Andrew and Newing¹⁸⁾ have shown that a rapid reorientation of similar groupings of nuclei yields a spectrum consisting of a central part and side bands separated by frequencies equal to the frequency of molecular motion. As the frequency of molecular motion increases, the side bands move outward and decrease in intensity so that the overall second moment remains constant. The central portion has a second moment calculable using the modification of the Van Vleck formula. When the molecular motion is very rapid, the intensities of the side bands are too low to be observed experimentally. However, when the frequency of the molecular motion is the same order as the line width, i.e. in the region of the line width transition, the side bands may well be strong enough to be observed. The measured value of the second moment will depend on how far in the wings it is possible to measure the absorption and the significance of the observed second moment in this region becomes very uncertain. For this reason, the line-width data are used exclusively in the literature for discussions concerning the transition region.

The variation in local field can be quantitatively described by a correlation time, T_c , or by a correlation frequency $\gamma_c = (2\pi T_c)^{-1}$.

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An equation for the dependence of the line width on the correlation frequency of the molecular motion has been given by Bloembergen, Purcell and Pound¹⁹⁾. This equation was further modified by Gutowsky and Pake¹⁴⁾. The modified form reads

$$(\delta H)^2 = (A^2 - B^2)(2/\pi) TAN^{-1} [\alpha(\gamma \delta H/2\pi V_c)] + B^2$$
 (2-11)

where δH is the line width, γ is the magnetogyric ratio, A is the rigid lattice line width; and B is the limiting value of the line width above the transition. The line widths are expressed in gauss. The correlation frequency γ_c can be calculated from the expression

$$V_{\rm c} = (\alpha_7 \delta_{\rm H}/2\Omega) [TAN(\Omega/2)((\delta_{\rm H}^2 - B^2)/(A^2 - B^2))]^{-1} (2-12)$$

It is usually assumed that the variation of correlation frequency with the temperature is governed by an activation energy E_{o} according to the equation

$$V_{\rm c} = V_{\rm o} \exp(-E_{\rm o}/{\rm RT})$$
 (2-13)

By fitting the experimental measurements with equation (2-12) and (2-13), an estimation of the activation energy (energy barrier) for the molecular motion can be obtained.

The factor α in equation (2-11) and (2-12) arises from the uncertainties in the limits of integration used in obtaining the equations and is rather ill-defined. Since α will affect γ_0 rather than E_0 , it can be incorporated as $(\alpha\gamma_0)$ or set equal to unity.

In writing equation (2-11) it is implied that a single correlation frequency, rather than a distribution, may be used to describe the motion. Furthermore, changes in line shape are ignored, as are the relative magnitudes of the inter- and intramolecular contributions to the line width. Due to these assumptions, the results thus obtained should be carefully examined and comparisons between activation energies should be limited only to a series of similar compounds.

Waugh and Fedin²⁰⁾ have suggested another treatment to determine the hindered-rotation barrier from NMR experiments. Based on an assumed relation between $\frac{1}{0}$ and E_0 they obtained two equations for the energy barrier.

$$E_{o} = 1.8RT_{c} \quad \ln \left[(n/\Delta) (kT_{o}/2I)^{1/2} \right]$$
 (2-14)

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and $E_o = 37T_c$ (cal/mole) (2-15)

where reorientation occurs about an n-fold axis. T_c is the temperature at which line narrowing commences; \triangle is the "excess" rigid lattice line width over the narrowed line width in radian per second, and I is the molecular moment of inertia for the reorientation. Equation (2-15) is, in fact, an approximate form of equation (2-14) and the results obtained differ, for the most part, by only 10%. This method is of particular value when the B-P-P equation (2-11) gives absurd results²⁰⁾.

CHAPTER III

EXPERIMENTAL

III-1 Nuclear Magnetic Resonace Spectrometer and its Calibration

Proton and fluorine nuclear magnetic resonance spectra were obtained with a Varian Dual Purpose Spectrometer. A block diagram of this spectrometer is shown in Fig. 1.

In recording the derivative trace of an absorption line, the r.f. transmitter was held at a constant frequency (56.4 M Hz), while the main magnetic field H was slowly scanned through the resonance and, at the same time, sinusoidally modulated with a andio-frequency magnetic field. Since the sweep-amplitude of this field modulation was purposely chosen to be much less than the line width, the output of the r.f. detector consisted of an audiofrequency signal with an amplitude proportional to the slope of the resonance signal at the center of the modulation. This signal was then fed through a phase-sensitve detector and the resulting d.c. signal was recorded.

To calibrate the scan-rate of the main magnetic field as a function of distance along the baseline of the recorder, the frequencymodulation technique was applied to a sample of liquid water. While the transmitter was frequency-modulated with an audio oscillator, the recorded signal consisted of a center peak and a series of side bands. By measuring the spacing between a particular set of side bands in centimetres and by measuring exactly the modulation frequency with an electronic counter, the scanning field was calibrated in gauss per cm of the chart paper.

The calibration of the sweep modulation amplitude, H_m , was performed



Fig. 1 Block diagram of wide-line NMR spectrometer

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for each setting by slowly scanning through the signal from a sample of water. Since the water-signal has a very narrow line width, the observed line width in gauss could be taken as H_m . The sweep modulation frequency was kept constant at 80 cps for all the experiments.

For variable temperature work a Dewar assembly shown in Fig. 2 was used. The temperature control was achieved by passing around the sample either heated air or tank nitrogen cooled by liquid nitrogen; the flow of the gas was monitored by means of a flow-meter. Temperatures were measured with a calibrated copper/constantan thermocouple. For measurements at temperatures below the lower limit of the flow system the sample tube was immersed directly in liquid nitrogen or oxygen inside a simply designed Dewar vessel. This vessel has a wide top-portion and a tubular bottom which fits inside the receiver coil.

III-2 The Measurement of Line Width and Second Moment

The line width, SH, is defined as the interval between the slope extrema of a resonance signal and corresponds to the horizontal distance between positive and negative peaks of a derivative trace. The distance was measured and recorded in units of gauss for each of the resonance spectra. To reduce the line width distortion the sweep modulation amplitudes, H_m , were chosen to be $0.3 \ SH^{21}$.

The experimental second moment defined by equation (2-5) was computed directly from the derivative trace of the absorption signal according to the equation²²

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$$M_{2} = \frac{1}{3} - \frac{\int_{-\infty}^{\infty} g'(H)(H-H_{0})^{3} dH}{\int_{-\infty}^{\infty} g'(H)(H-H_{0}) dH}$$
(3-1)

where g'(H) was the intensity of the derivative curve in arbitrary units. The denomination is introduced to normalize the resonance curve. A Fortran IV program was written to compute the second moment according to equation (3-1) by numerical integration. The modulation effect was also corrected for according to Andrew's formula²³⁾. A listing of this program is given in Appendix II.

III-3 Preparation and Purification of Materials

Sources or preparation of reagents and compounds, method or their purification and the means of determination of their purity are summarized in Table II.

The purified polycrystalline sample was tightly packed into a 9 mm O.D. sample tube and then sealed under vacuum.

TABLE II	

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Preparation and Purification of Reagents and Compounds

Compound	Supplier or Preparation	Technique of Purification	Physical Found	Properties	Dof
(^{Cn} 3 ³ 3 ¹	Fisher Scientific (highest purity grade)	-	-	-	TUET .
BF 3 (CH) OBF	Matheson (99.0%)	-	-	-	_
(°2"5′2°"3	J. T. Baker	Distillation in			
BC13	Matheson (99.0%)	atmosphere	-	-	-
BBr ₃	Alfa Inorganic (99.9%)	-	-	-	-
(CH ₃) ₃ NBH ₃	Matheson Coleman and Bell	Vac. Sublimation	M.P.		
(CH ₃) ₃ NBF ₃	$\frac{Me_{3}N(g) + BF_{3}(g)}{in^{3}cold}$	Vac. Sublimation	93-95°C	94	24
	and dried C6H6		147-149°C I.R.	145-146°C	25 26
(CH ₃) ₃ NBC1 ₃	$Me_{3}N(g) + BCl_{3}(g)$ in ³ cold and dried C ₆ H ₆	Recryst. from hot ethanol	M.P. 242-245°C I.R.	242-243°C	26
(CH ₃) ₃ NBBr ₃	$Me_{3}N(g) + BBr_{3}(1)$ in ³ cold and dried $C_{6}H_{6}$	Recryst. from hot ethanol	M.P. 236-240°C	238 [°] C	26
NH ₃ BF ₃	$NH_{g}(g) + (C_{2}H_{5})_{2}OBF_{3}(1)$ in ³ cold absolute ether	Recryst. from cold water	I.R. power x-ray	-	28 29 30

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CHAPTER IV

RESULTS AND DISCUSSION

IV-1 Trimethylamine Borontrifluoride

The experimental second moment and line width of proton and fluorine resonances are plotted against temperature in Fig. 3 and Fig. 4 respectively. As the temperature is increased from 77° K, the proton second moment decreases sharply from 18 gauss² to~8 gauss² at 110°K, which is followed by a slow decrease to 2.2 gauss² at about 160°K. It is evident that two different but partially overlapping transitions are involved. Over the same temperature range (77° K - 160°K) the fluorine second moment decreases from 7.4 gauss² to 3.2 gauss². Above 160°K both the proton and fluorine second moments remain constant up to the melting point.

The compound has been shown³¹⁾ to crystallize in a rhombohedral unit cell, (space group $C_{3v}^5 - R_{3m}$), one molecule per unit cell and the crystallographic positions of the nuclei, except hydrogens, have been given. There are two possible orientations: for the methyl groups within the molecule consistent with symmetry, i.e. the plane passing through six hydrogen atoms can be either away from or toward the center of gravity of the molecule. In the first orientation the distance between hydrogen atoms attached to adjacent carbon atoms is about 0.4 Å less than the normal Van der Waals separation and therefore this possibility has been ruled out³¹⁾. With the assumption that methyl groups adopt the second orientation, the crystallographic positions of hydrogen atoms were found using a C-H bond length of 1.08Å and a H-C-H bond angle



Fig. 3 Temperature dependence of the line width and second moment of the proton resonance in trimethylamine borontrifluoride. 128

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of 109°28'.

For the theoretical calculation of second moment a Fortran IV program was written. This program consists of three independent parts. The first part computes various contributions to the rigidlattice second moment from known crystallographic positions of the nuclei; the contributions over distances greater than 7\AA are estimated by an integral^{32,33}). In the presence of various types of molecular motion the second part can be used to compute the inter-group and intermolecular contributions to the second moments according to Andrew and Eades'formulae¹⁵⁾; the intra-group contribution can be easily computed according to equations (2-9) and (2-10). The third part computes the second moment for isotropic rotation^{16,17)}. A complete list of this program is given in Appendix II**L**.

With this program the various contributions to the proton and fluorine second moments of $(CH_3)_3 \ N \ BF_3$, in the presence of different molecular motions were calculated and the results are listed in Table III.

The theoretical values for the molecular motion where both the - BF_3 and - CH_3 groups rotate about their three-fold axes and $He NMe_3$ group rotates about the B-N bond, are 2.5 gauss² and 3.4 gauss² for proton and fluorine respectively. This is in good agreement with the experimental second moments above 160°K, 2.2 gauss² (¹H) and 3.2 gauss² (¹⁹F), therefore, it is concluded that this type of rotational motion occurs between the melting point and 150°K in the solid (CH_3)₃N BF_3 . The reorientation process of -NMe₃ and - BF_3 groups at room temperature probably involves a jump mechanism as no evidence for the rotational

					(0045)	, ion (cu	3 ⁷ 3 ^{N BF} 3		
	сн [*] 3	NMe.	3 [*] BF [*] ₃	Intram	olecular		Inter	nolecular	Total
				Intra-group	Inter-group	Total	< 7Å	> 7Å	
	S	S	S	22.50	3.42	25.92	5.96	0.085	32 1
٦	R	S	S	5.63	1.78	7.41	3.13		J~•1
тн	R	S	R	5.63	1.67	7.29	2,89		10.7
	R	R	S	0.90	0.41	1.31	1.27		10.4
	R	R	R	0.90	0.40	1.30	1 18		2.6
	Is	otrop	ic				4.40		2.5
	S	S	S	5,00	16 02	07 00			1.1
	R	S	S	5.00	10,95	21.93	3.92	0.076	20.9
19 _F	q	G	2	5.00	11.21	16.21	2.59		18.9
-		3	R	1.25	1.73	2.98	1.64		4.7
	R	R	S	5.00	10.27	15.26	1.53		16 0
	R	R	R	1.25	1.14	2.39	1.05		2.1
	Iso	tropi	с						3•4
*s		- St	ationary						0.7

TABLE III Calculated Second Moments (gauss²) for (CH₃)₃ N BF₃

R - - - - - Rotating

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motions of these groups has been observed by the x-ray study 31 .

The comparison between the experimental and theoretical moments further reveals the nature of the two partially overlapping transitions observed below 160°K; the high temperature transition corresponds to the reorientation of $-NMe_3$ group and the low temperature transition involves the methyl group rotation. The latter is not complete even at 77°K. In the neighbourhood of 77°K the rotational motion of $-BF_3$ starts to slow down as evidenced from the sharp upward trend in the fluorine second moment.

When this work was in progress, Dunell et al.³⁴⁾ reported the results of a wide-line study on this complex. In general, their experimental data and conclusion are in agreement with the present studies. However, from the data presented in Fig. 3 and 4, no evidence can be found for the premelting phenomenon which has been observed at 390° K by Dunell et al.³⁴⁾ with both the NMR and DSC (differential scanning calorimetry) techniques. A DSC study by this author also failed to detect a phase transition below the melting point.

IV-2 Trimethylamine Borontrichloride and Trimethylamine Borontribromide

The temperature dependence of the proton second moment and line width of the trimethylaming complexes with borontrichloride and borontribromide are shown in Fig. 5 and Fig. 6 respectively. Fig. 7 shows typical derivative traces of proton resonance spectra of $(CH_3)_3$ N BCl₃.

The behaviour of the second moment, line width and also line shape with temperature is remarkably similar for these two complexes. As the temperature is increased from 77° K the second moments first decrease rapidly and then level off at a value of ~ 7.6 gauss²; at still higher



Fig. 5 Temperature dependence of the line width and second moment of the proton resonance in trimethylamine borontrichloride. Line width dependences were obtained from the assumed values for rigid lattice line width: 21.5 gauss (curve A), 20.5 gauss (curveB), 20.0 gauss (curve C) and 19.5 gauss (curve D) (see Table VII).

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Fig. 7 Derivative traces of the proton resonance in $(CH_3)_3 N BCl_3$.

temperature, around 210°K for $(CH_3)_3$ N BCl₃ and 230°K for $(CH_3)_3$ N BBr₃, there appears a second transition which gradually reduces the proton second moment to 1.25 gauss². The second moment then remains at this value for both compounds up to ~ 200°C. At just below 200°C the white solid samples became slightly darkened under prolonged heating in the NMR probe and measurements at higher temperature were, therefore, not attempted.

Since the detailed crystal structures of these two compounds have not been reported, the theoretical second moments were estimated based on the values for borontrifluoride complex. The results are compared with experimental values in Table IV.

The experimental second moments at high temperatures, 1.25 gauss², lies between the estimated values for the isotropic rotation, 0.7 gauss², and the simultaneous rotation of $-CH_3$ group about its C_3 axis and B-N bond, 1.8 gauss². However, in view of the conclusions drawn for the borontrifluoride complex, it is reasonable to suggest that the latter motion is actually responsible for the observed low second moments. The discrepancy between the experimental and estimated values is ascribed partly to the difference between the actual and assumed molecular geometry, and partly to the approximate method used in the estimation of inter-group contribution (see discussion below).

The second moment plateau between 100° K and 200° K corresponds to the methyl group reorientation around its C_3 axis. The fact that the experimental second moments, 7.6 gauss², is less than the theoretical value could be attributed to two different factors. (1) In the calculation of the contribution to the second moment from the interaction between two

TABLE IV

Calculated and Observed Second Moments (gauss²)

for (CH₃)₃ N BCl₃ and (CH₃)₃ N BBr₃

сн3	NMe [*] 3	Calculated Second Moment	Observed Second Moment for (CH ₃) ₃ N BCl ₃	Observed Second Moment for (CH ₃) ₃ N BBr ₃
S	S	30.2	26.2 (77°K)	25.5 (77°K)
R	S	9.52	7.7 (140°–200°K)	7.5 (130°-220°K)
R	R	1.8	1.25 (>280°K)	1.25 (>300°K)
Isot	ropic	0.7		

*S - - - - - - Stationary R - - - - - Rotating

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rotating methyl groups, the Andrew and Eades formulae were used and the average was taken over the assumed $3^2 = 9$ equilibrium positions with minimum potential energy. However, these positions were assumed mainly on the basis of crystal symmetry. In the case of methyl group reorientation, it is obvious that the preferred orientation of a particular methyl group at a particular instant will depend on the orientation of the neighbouring groups at that time. Therefore the rotations of the different methyl groups are correlated. It is possible that the correlation is such as to prevent the protons on neighbouring groups occupying some of the immediately adjacent sites³²⁾; this in turn reduces the observed second moments. A comparison with the experimental and theoretical results for similar compounds: $(CH_3)_2 C (NO_2)_2^4$, $(CH_3)_2$ C ClNO₂⁴⁾, (CH₃)₄ Si⁶⁾ etc., indicates the calculated values for -CH3 rotation in (CH3)3 N BF3, (CH3)3 N BCl3 and (CH3)3 N BBr3 are probably too high by ~ 1 gauss². (2) The existence of additional molecular motions could lead to the reduction of the experimental second moment. Most likely this motion would be a torsional oscillation of the NMe3 group about the B-N bond. Based on Fig. 10 in Ref. 36 an angle of oscillation of 15° to 20° should cause a sufficient reduction in intra- and inter-molecular second moment to produce agreement with experiment.

The transition below 100°K involves the on-set of methyl group reorientation. The proton resonance spectrum at 77°K shows a structure similar to that of a stationary three-spin system. However, the transition may not be complete at 77°K as the difference between the observed second moments (.26 gauss²) and estimated rigid lattice values (30 gauss²) is larger than the expected limits of error.

IV-3 Trimethylamine Borane

The proton second moment and line width of this complex are plotted against temperature in Fig. 8. Their behaviour below room temperature is similar to those of the other three complexes. However, at 325° K, the second moment and line width decrease steadily with increasing temperature until 358°K. There is no apparent change at 350° K where a thermal transition has been observed by Douslin <u>et al.</u>³⁷⁾. At 358° K there is an abrupt <u>increase</u> in line width and second moment. The latter changes from 1.8 gauss² to 2.7 gauss². This is a rather unusual behaviour and similar phenomena have only been reported for cyclopentane³⁸⁾ octamethylcyclotetrasiloxane and hexamethylcyclotrisiloxane³⁹⁾.

In Fig. 9 are shown derivative curves of proton resonance absorption at several selected temperatures.

It has been shown from thermal measurements that three different solid phases exist for: this complex³⁷⁾. Unit cell dimensions and the space group of the room temperature phase have been determined by an x-ray diffraction study⁴⁰⁾. Partial molecular structure data have also been obtained by Bauer⁴¹⁾ from a gas-phase electron diffraction experiment. The theoretical second moment was calculated, using the program described before, based on a molecular structure with the following bond distances and bond angles: $C-N = 1.53^{(L1)}_{A}$, $N-B = 1.62^{(L1)}_{A}$, $B-H = 1.194^{(L2)}_{A}$, $C-H = 1.09^{*}_{A} < HBH = 113 \circ 42$), $<BNC = 105 \circ 31$, $<HCH = 109 \circ 28^{\circ}$. The values for B-H bond distance and <BHB were taken from the reported structure of a similar complex BH₃ CO^(L2). The results are listed in Table V. For comparison, the experimental second





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Fig. 9 Derivative traces of the proton resonance in $(CH_3)_3 N BH_3$.

TABLE V

Calculated and Observed Second Moments (gauss²)

for $(CH_3)_3 N BH_3$

сн [*] 3	^{BH} 3	NMe [*] 3	Calculated Second Moment	Observed Second Moment
S	S	S	37.0	35.2 (77°K)
R	S	S	19.3	
R	R	S	11.8	8.5 (120°K)
R	S	R	12.2	8.5 (120°K)
R	R	R	4.0	3.0 (220°-320°К)
Isot	tropic		1.4	

* S - - - - - - Stationary R - - - - - Rotating

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moments below the room temperature are also included in the same table.

It is evident that the lattice is almost rigid at 77° K. From 200°K to room temperature the observed value, 3.1 gauss², is compatible with the case that the -CH₃ and the -BH₃ groups rotate about their C₃ axes and -NMe₃ rotates about B-N bond. The second moment value, ~8.5 gauss², at 110°K may be interpreted as corresponding to one of two possible molecular rotations: 1. rotation of both the -CH₃ and -BH₃ groups about their C₃ axes, 2. simultaneous rotation of the -CH₃ group around its C₃ axis and the B-N bond but with the -BH₃ group stationary. Based on the results for the other three complexes the first interpretation is preferred. In view of the discrepancy between the experimental second moment (8.5 gauss²) and the calculated value (12 gauss²), the torsional oscillation of the -NMe₃ group about the B-N bond, suggested for (CH₃)₃N BCl₃ and (CH₃)₃N BBr₃, probably occurs in this compound as well.

The decrease in the second moment with increase in temperature above 320° K can be explained by the gradual onset of isotropic rotational motion. An alternative interpretation of this line narrowing in terms of the "wobbling" of the B-N axis about its equilibrium position, would require an angle of 30° or more⁴³ to account for the observed reduction in the second moment. Such a motion, although it occurs about a preferred axis, represents a mode of attack upon the barrier to isotropic rotation.

Another possible molecular motion would be diffusion through the crystal lattice. This process reduces intermolecular dipole-dipole coupling, but leaves the intramolecular coupling unchanged; the situation is similar to that observed in the liquid crystal phase. However, as pointed out in the introduction, the liquid crystal phase can only occur for rod-like molecules; the presence of a diffusion process without orientation disorder is considered as less likely for the spherical $(CH_3)_3$ N BH₃.

At the present time, no satisfactory explanation can be proposed for the abrupt increase of the second moment and the line width observed at $358^{\circ}K$ ($\pm 2^{\circ}K$). However, since this occurs at the temperature at which the thermal transition I has been observed³⁷⁾, it is possible that the change of crystal structure during this transition may play an important role in causing this unusual behaviour.

IV-4 Comparison of NMR and Thermal Data on (CH3)3 N BH3

A complete thermal study of solid trimethylamine-borane was made by Douslin <u>et al</u>.³⁷⁾ They measured the heat capacity from $ll \cdot K$ to the melting point, determined the various thermodynamic functions and showed that two solid-solid phase transitions occurred in this compound. For the convenience of later discussion the heat capacities, as a function of temperature, are reproduced in Fig. 8. The transition temperatures, enthalpies and entropies are listed in Table VI.

It is well known that NMR is sensitive to a much lower frequency $(10^4 - 10^5 \text{ cps})$ as compared with the thermodynamic properties $(10^{11} - 10^{12} \text{ cps})$. However, thermodynamics is also sensitive to the appearance of orientational disorder, whatever its rate. As a consequence, the onset of a reorientation process among several "thermo-dynamically" indistinguishable orientations does not contribute appreciably to the thermodynamic functions; while a similar process

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TABLE VI

Transition Temperatures, Enthalpies and Entropies in Solid Trimethylamine Borane 36)

Transition	Transition Temperature	\triangle H(cal/mole)	∆ S(e.ı	ı.)
II	350.1	605.9 <u>+</u> 1.1	1.73	\$
I	360.4	1419.5 <u>+</u> 1.5	3.94	÷
Melting	368.7	1182.4 <u>+</u> 0.8	3.21	
			Total 8.88	i

among several distinguishable orientations, such as the isotropic rotation of $(CH_3)_3$ N BH₃, increases the disordering and, therefore, the entropy of the system. Based on these arguments, Darmon and Brot⁶⁰⁾ concluded that a thermal transition is, in principle, necessary to liberate the reorientation process if the molecule has lower symmetry than that of its allowed orientations. According to their theory, Darmon and Brot⁶⁰⁾ successfully classified the known thermal and NMR data of many compounds, including those of t-butylchloride and t-butylbromide. This theory has a "all or nothing" nature as it is assumed that the crystal can only exist in either a perfectly ordered or in a completely disordered state.

The x-ray diffraction experiments on $(CH_3)_3$ N BH₃ showed that in the room temperature phase nitrogen and boron atoms lie on the three threefold axis of the rhombohedral unit cell⁴⁰⁾. Between ll°K and 320°K the heat-capacity measurements did not reveal any thermal transition³⁷⁾. These experimental results indicate that the room temperature phase is essentially an ordered state. To interpret the observed line narrowing above 320°K by an isotropic rotation means that a reorientation among distinguishable positions occurs without a preceding thermal transition. To reconcile the basic nature of the thermodynamic functions with the NMR results it is necessary to discard the "all or nothing" model and, instead, to suppose a progressive, co-operative establishment of the disorder. It is interesting to note that at the neighbourhood of 210°K an upward trend in the heat-capacity curve (Fig. 8) can be noticed; since the contribution of the rather slow isotropic rotation $(10^4 - 10^5 \text{ cps})$ to the thermodynamic functions is negligible, the abnormal increase of the heat capacity is at least compatible with a progressive establishment of the disorder. The

entropy increase for transition II is 1.73 e.u. This value, even corrected for the high heat capacities below the transition temperature is still much smaller than the minimum requirement, 2.78 e.u. (= R ln4), needed for achieving a completely disordered state. A certain degree of ordering persists even in phase II.

The low entropy of melting, 3.21 e.u. - a value typical of a plastic crystal, indicates that orientational disorder exists in the crystal phase I of $(CH_3)_3$ N BH3. On account of the high experimental second moment in this phase, the isotropic reorientation process, if it occurs, should not be fast enough to effect the NMR spectrum. Usually, in the plastic phase, both isotropic rotational motion and self-diffusion are found by NMR techniques 44). The only exception known to the author is the plastic phase of perfluorocyclohexane⁴⁵⁾, in which neither isotropic rotation nor self-diffusion can be detected immediately above the transition. The present study of solid $(CH_3)_3$ N BH₃ provides a second example of this kind. In his dielectric studies of "rotator" phase, Baker and Smyth⁴⁶⁾ also observed a long relaxation time of $10^{-4} - 10^{-5}$ sec for the rotational process in $(CH_3)_3$ CI as compared with 10^{-12} sec in $(CH_3)_3$ CCl and he attributed this to the greater asymmetry of the t-butyl iodide molecule. At the present time, the author is unable to suggest a satisfactory explanation as to why trimethylamine borane and perfluorocyclohexane behave differently from other systems. Certainly a careful crystal structure study of phase I and phase II of this complex will be helpful in answering this question and possibly would provide an explanation for the observed sudden increase in both the second moment and line width at thermal transition I.

IV-5 Barriers to the Rotation in Trimethylamine-Borontrihalide Complexes

The line width data in Fig. 3, Fig. 5, Fig. 6 and Fig. 8 were used to calculate the rotational barrier, E_0 , and V_0 with the modified B-P-P equation (2-12) and the Waugh and Fedin equation (2-15). The results are listed in Table VII and VIII respectively.

The limiting line width for stationary $-CH_3$ groups required in the B-P-P treatment was first estimated from the experimental values of $(CH_3)_3N^{35}$, $(CH_3)_3CC1$ and $(CH_3)_3CBr^4$ and computations were subsequently carried out with the variation of this value within a reasonable limit. A similar procedure was used to treat the rotations about the B-N bond in $(CH_3)_3NBH_3$ and $(CH_3)_3N$ BF₃. In the transition region, the theoretical line widths from B-P-P treatment were plotted against temperature in Fig. 3, Fig. 5, Fig. 6 and Fig. 8.

For the $-CH_3$ rotation the numerical values of the energy barriers obtained with two treatments differ by 30% - 40%. At the present time, it is not possible to judge which set is more dependable, although equation (2-15) results in a better agreement with energy barriers for the similar motion in neopentane and t-butyl chloride (see Table IX). However, both sets of values show that the barrier is essentially the same for all four complexes. Since all of them contain the same group -NMe₃, and the barrier to $-CH_3$ rotation will generally be dependent on the immediate environment of the methyl group $\frac{47,48,49}{}$; this result is expected.

In Table IX energy barriers for methyl group reorientation in this series are compared with those in several related compounds. With the known values of bond length and bond angle for $(CH_3)_3 N BF_3$ the distance between the methyl groups was calculated to be the same as in

TABLE VII

Energy Barriers (E₀) and Frequency Factors ($\alpha / _{0}$) From B-P-P Treatment

Compounds	Line width below transition (gauss)	Line width above transition (gauss)	E _o (Kcal/Mole)	a)/o (Sec ⁻¹)
$-CH_3$ rotation				
-BH3**	20.0-22.0	5.4-5.8	1.7-2.3	2.0x10 ⁹ -5.1x10 ¹⁰
** ^{B#} 3	~20.0	~5.6	~1.7	~1.0x10 ¹⁰
-BC13	19.5-21.0	5.5	1.6-1.9	$4.7 \times 10^8 - 2.0 \times 10^9$
- ^{BBr} 3	19.25-20.75	5.25	1.7-2.0	8.6x10 ⁸ -3.7x10 ⁹
-MMe ₃ rotation				
- ^{BH} 3	5.4-5.8	4.3	1.9-2.2	$1.9 \times 10^7 - 3.2 \times 10^7$
^{-BF} 3	5.4-5.7	3.75	1.6-1.8	$3.2 \times 10^7 - 6.7 \times 10^7$
-BC1 ₃	5.5	2.7	10.8	6.3x10 ¹⁴
-BBr ₃	5.25	2.5	7.7	7.9x10 ¹⁰

* Estimated Values

хх

Including rotations of both the $-CH_3$ group and $-BH_3$ group about their axes.

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TABLE VIII

Energy Barriers (E₀) and Frequency Factors ($\not\!\!\!/_0$) from the Waugh and Fedin Treatment

			Δ	E	
	Compounds	т _с	(Sec ⁻¹)	o (Kcal/Mole))∕₀(Sec ⁻¹)
-CH3	Rotation				
-	-BH3*	77 ° K	6.3x10 ⁴	2.8	5.8x10 ¹²
	-BF3	~67 ° K	~5.3x10 ⁴	~2.5	$\sim 7.4 \times 10^{12}$
	-BC13	7 5° K	6.2x10 ⁴	2.8	8.9x10 ¹²
	-BBr ₃	7 5° K	6.3x10 ⁴	2.8	9.1x10 ¹²
-Me3	Rotation				
	- ^{BH} 3	130° K	4.3x10 ³	4.8	5.7x10 ¹¹
	-BF3	110° K	6.4x10 ³	4.1	7.9x10 ¹¹
	-BC13	215°K	1.2x104	8.0	1.6x10 ¹²
	-BBr ₃	235°K	1.2x104	8.7	1.5x10 ¹²

* Including rotations of both the -CH₃ group and -BH₃ group about their axes.

TABLE IX

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Barriers to the Methyl Group Reorientation

E		
(Kcal/Mole)	Methods	Lit.
2.0 (B-P-P) 2.8 (W-F)	Line width	This work
1.7 (B-P-P) 2.5 (W-F)	Line width	This work
1.8 (B-P-P) 2.8 (W-F)	Line width	This work
1.9 (B-P-P) 2.8 (W-F)	Line width	This work
2.8-3.0	T _l measurement	(5)(6)
1.3	Calorimetric measurement	(47)
0.65	T ₁ measurement	(6)
0 .4 6	T ₁ measurement	(6)
0.18	T ₁ measurement	(6)
2.8-3.7	- T _l measurement	(5)
4.1	- T ₁ measurement	(5)
	E (Kcal/Mole) 2.0 (B-P-P) 2.8 (W-F) 1.7 (B-P-P) 2.5 (W-F) 1.9 (B-P-P) 2.8 (W-F) 2.8 (W-F) 2.8-3.0 1.3 0.65 0.46 0.18 2.8-3.7 4.1	E_o (Kcal/Mole)Methods2.0 (B-P-P) 2.8 (W-F)Line width1.7 (B-P-P) 2.5 (W-F)Line width1.8 (B-P-P) 2.8 (W-F)Line width1.9 (B-P-P) 2.8 (W-F)Line width2.8-3.0 T_1 measurement1.3Calorimetric measurement0.65 T_1 measurement0.46 T_1 measurement0.18 T_1 measurement2.8-3.7 T_1 measurement4.1 T_1 measurement

neopentane, i.e. 1.50Å. It is rather interesting to note that the same agreement is observed between energy barriers calculated by the Waugh and Fedin equation (2-15) and observed in $(CH_3)_4C$. This result supports the opinion 47,48,49,6 about the importance of methyl group separation in determining the energy barriers to methyl reorientation.

For rotations of the -NMe₃ group around the B-N bond, the energy barriers from the two different treatments show a large discrepancy. Judging from the magnitude of both E_0 and V_0 , the values in Table VIII seem to be more realistic. From values in either of the two tables, it can be concluded that rotational motion of the -NMe₃ group is less hindered in $(CH_3)N$ BH₃ and $(CH_3)_3N$ BF₃ than in $(CH_3)_3N$ BCl₃ and $(CH_3)_3N$ BBr₃. This trend is consistent with the spatial molecular models as shown in Fig. 10.

The two low temperature transitions in $-BH_3$ and $-BF_3$ complexes appear in immediate succession; the similar situation has been observed in t-butylchloride and t-butylbromide⁴⁾. These facts suggest that in these compounds the rotational motion of the $-CH_3$ group facilitates the reorientation process of the $-NMe_3$ group and thus the two different motions are closely coupled to each other.

In order to investigate the effect of electrostatic energy on the isotropic rotational freedom in these complexes, a calculation based on a model of point dipoles was made on $(CH_3)_3N$ BH₃. The interaction energy of a central molecule with all its neighbours was computed for a series of varying cut-off distances. The energies (in Kcal/mole) are plotted against the cut-off distance in Fig. 11, which clearly shows the convergence properties of this calculation. Surprisingly; the total energy



(CH₃)₃N BH₃

(CH₃)₃N BF₃



(CH3)3N BC13

 $(CH_3)_3N BBr_3$

Fig. 10 Molecular models for the complexes $(CH_3)_3N \xrightarrow{BX_3}$



(CH₃)₃N BH₃



(CH₃)₃N BF₃





(CH₃)₃N BCl₃

 $(CH_3)_{3}N$ BBr₃

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Fig. 10 Molecular models for the complexes $(CH_3)_3N BX_3$



ad

20

40

60

CUT - OFF DISTANCE (Å)

Fig. 11 The dependence of dipolar interaction energy on the cut - off distance.

80

100

0

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is positive,~0.16 Kcal/mole, and if the result were correct the structure as determined by x-ray crystallography would be unstable. Since the distance between the nearest neighbours is obviously comparable to the molecular dimensions, the validity of the point-dipole approximation is suspected to be the cause of this absurd result. An analysis of the calculation immediately reveals that the interaction with the 14 nearest neighbours (with distances less than 9\AA) is, in fact, critically dependent on the assumed dimension of the molecular dipole. If the dimension of the dipole is taken to be 2\AA , the interaction energy with 14 nearest neighbours will be -0.16 Kcal/mole and the total dipolar interaction energy becomes negative.

Although no definite conclusion can be obtained from the calculation, a comparison of the experimental results of this series with that of the similar carbon containing compounds suggests that the tendency to align the relatively high dipole moments of the complexes is an important factor affecting the hindrance of the isotropic rotational motion. Those molecular motions which have little or no effects upon the alignment of the molecular dipoles, such as rotations of -CH₃ groups and -NMe₃ groups, are observed in comparable temperature ranges for the boron-nitrogen complexes and their carbon anologues⁴: such as neopentane ($\mu=0$), t-butylchloride ($\mu=2.14^{50}$) and t-butyl-bromide ($\mu=2.17^{51}$); while the isotropic rotation can be detected in only one of the four complexes studied and at a much higher temperature than those of the hydrocearbons^{44,52}. However, in relation to the effect of dipole moments, it should be pointed out that the electrostatic energy of a system, as shown by the calculation described earlier, depends upon

the details of the charge distribution in the molecule.

The distances between the central nitrogen atom and the Van der Waals surfaces of the substituents are given in Table X. Following the suggestion by $Smyth^{52}$ the ratio of the two distances, $N-BX_3/N-CH_3$, is taken as a measure of the asymmetry of the molecular shape. The fact that the isotropic rotation or similar motion occurs only in $(CH_3)_3$ N BH₃ but not in other three complexes demonstrates the importance of the molecular shape in determining the orientation freedom of the molecule in the solid state. From dielectric studies on several halogenated hydrocarbons, Smyth⁵² concluded that the isotropic rotation ceases where the ratio of two C-X values is greater than 1.20; this is in rough agreement with the trend observed in this series.

<u>IV-6 Molecular Motion in NH3-BF3</u>

The variations in line width and second moment of the 1 H and 19 F resonances with temperature are shown in Fig. 12 and Fig. 13. Both the fluorine second moment and line width show a quite sharp transition centred at 200°K. Over the same temperature range there is a similar but much smaller change in the proton values.

With the computer program described before, the theoretical proton and fluorine second moments were computed for various cases based on the crystal structure reported by Hoard, Geller and Cashin⁵⁴. The results are compared with experimental values in Table XI.

The experimental second moments at 77°K, 11.0 gauss² and 20.4 gauss² for ¹H and ¹⁹F respectively; are in good agreement with the



	N-CH3	N-BH3	^{N-BF} 3	N-BC13	N-BBr ₃
R(Å)	3.53	3.98	4.24	5.21	5.52
N-BX3 N-CH ³		1.12	1.20	1.47	1.56

* Calculated according to the bond lengths data and Van der Waals radii given in Ref. (53). SECOND MOMENT (GAUSS²) AND LINE WIDTH (GAUSS)



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TABLE XI

Calculated and Observed Second Moments

(gauss²) of NH₃BF₃

^{NH} 3	^{BF} 3	Calculated Second Moments		Obse Second	erved 1 Moments
		J ^H	19 _F	1 ^H	19 _F
S	S	38.2	22.3		
S	R	11.9	20.6	11.0 (77°К)	20 .4 (77°К)
R	R	10.7	5.3	8.9 (~300°K)	4.6 (~300°K)

* S - - - - - - Stationary R - - - - - Rotating theoretical values for a rotating $\rm NH_3$ group and stationary $\rm BF_3$ group. Above the transition, the second moments reduce to values in agreement with a molecular motion involving the reorientation of both groups around their C₃ axis. Therefore, the transition centered at 200°K is associated with the onset of BF₃ group reorientation.

It is interesting to note that the observed proton second moments, both below and above the transition, are smaller than the calculated values. The crystallographic positions of the protons were not obtained by Hoard, Geller and Cashin⁵⁴⁾. These authors included contributions based on an N-H distance of 1.02Å and an HNH angle of 107° which seemed "in general to improve slightly the agreement with observed amplitudes". The basis of these assumed values were from an earlier structure for $CH_3NH_2BF_3^{55)}$, where the N-H distance was assumed to be 0.01Å longer than in NH₃. There appear to be very few measured (N-H) distances for a four co-ordinate nitrogen atom⁵⁶⁾. From a line shape analysis of the proton resonance in $CD_3^{TH_3}Cl$ at 77°K a value of 1.035Å has been obtained by Tsau⁵⁷⁾. Using this value for the N-H distance in NH₃BF₃, analysis of the experimental second moment leads to an HNH angle of 104°.

The fluorine line width data in the transition region has been used to obtain the energy barrier to rotation with the modified B-P-P equation (2-12). This yields values of $E_0 = 7.0$ Kcal/mole and $\alpha \not{\!/}_0 = 2.3 \times 10^{13}$ sec⁻¹ for the reorientation of the BF₃ group.

Several years ago, the proton and fluorine nuclear magnetic resonance spectra of this: complexe: were studied at several selected

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temperatures by Leane and Richards⁵⁸⁾. However, the second moments reported for ¹⁹F at 95°K, 25 gauss², and for ¹H at 293°K, 11 gauss², disagree with our values. At the present time, it is difficult to explain the discrepancy. When this work was in progress, Dunell <u>et al</u>.³⁴⁾, Ragle and Yeh⁵⁹⁾, separately reported that similar disagreements with the values reported by Leane and Richards were found in their recent wide-line NMR studies of NH_3BF_3 complex.

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CONTRIBUTIONS TO ORIGINAL KNOWLEDGE

PART I

The anisotropies of 19 F chemical shifts have been measured for a series of substituted fluorobenzenes dissolved in a nematic liquid crystal solvent. The values obtained do not agree with those calculated from the Karplus and Das theory. For meta- and parasubstituted derivatives the changes in the fluorine shift anisotropies, relative to fluorobenzene, have been correlated with Taft's inductive and resonance parameters. It has been concluded that the fluorine nucleus in these molecules is most shielded when the applied field is perpendicular to the molecular plane and least when the applied field is parallel to the plane and perpendicular to the C-F bond. This result disagrees, both in sign and magnitude, with that of the molecular beam magnetic resonance determination.

It has been shown that the presence of ortho-fluorine substituents effects the fluorine shielding perpendicular to the molecular plane to a greater extent than the shielding parallel to the plane. This result is in contrast with the suggestion that the "ortho-effect" is due to the reduction of the double bond character of the carbonfluorine bond caused by the steric hindrance between the neighbouring fluorine atoms.

For para-substituted fluorobenzenes quite precise analytical expressions have been obtained for all the observed transition energies and intensities with a first order perturbation treatment.

The absolute signs of the indirect coupling constants in

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1,3,5-trifluorobenzene, 3,5-difluorobenzene, ortho-difluorobenzene, meta-difluorobenzene and para-difluorobenzene have been determined. The results confirm predictions regarding the sign and magnitude of J_{FF}^{meta} .

The relative molecular geometry obtained for 1,3,5-trifluorobenzene agrees with the electron diffraction data. It has been found that in all the difluorobenzenes, the hydrogen atoms ortho to fluorine are displaced toward the fluorine atom.

PART II

Wide-line proton and fluorine nuclear magnetic resonance studies were made on $(CH_3)_3$ N EH₃, $(CH_3)_3$ N EF₃, $(CH_3)_3$ N ECl₃ and $(CH_3)_3$ N EBr₃ Below the room temperature the behaviour of proton resonances with temperature is more or less similar for all four complexes. The narrowing of the absorption lines in the neighbourhood of 77°K is attributed to the increasing rate of motion of the -CH₃ groups about their C₃ axis. At higher temperatures, a composite motion occurs which involves both the rotation of the -CH₃ groups about their C₃ axis and the rotation about the molecular three-fold symmetry axis, the B-N bond. Barriers for methyl group reorientation are essentially constant in the series but for the rotation about the B-N bond much greater energies are required in $(CH_3)_3$ N BCl₃ and $(CH_3)_3$ N BBr₃ than in $(CH_3)_3$ N BH₃ and $(CH_3)_3$ N BF₃.

In the complex $(CH_3)_3$ N BF₃ the BF₃ group reorients about its C₃ axis over the entire temperature range.

Above room temperature there are indications of isotropic rotation in solid $(CH_3)_3$ N BH₃, however, no similar motion could be

detected in $(CH_3)_3$ N BF₃ below the melting point, and in $(CH_3)_3$ N BCl₃ and $(CH_3)_3$ N BBr₃ below 470°K. This phenomenon is attributed to the decrease of the "symmetry" of the molecular shape, as the hydrogen atoms are replaced by much larger halogen atoms.

A similar study on the ammonia-borontrifluoride complex showed that the $-NH_3$ group reorientation occurs at temperatures as low as $77^{\circ}K$. Rotation of the $-BF_3$ group commences at $200^{\circ}K$. APPENDIX I

THIS PROGRAM WAS WRITTEN FOR SIMULATING THE NMR SPECTRUM OF ORIENTED MOLECULES. IT ACCEPTS THE VALUES OF INDIRECT SPIN COUPLING CONSTANTS, PSEUDO-DIPOLE COUPLING CONSTANTS AND CHEMICAL SHIFTS, ATOMIC POSITIONS IN A MOLECULAR FIXED COORDINATE SYSTEM, AND THE MOTIONAL CONSTANTS AS INPUT. CEPENDING ON THE CHOICE OF THE USER, THE OUTPUT OF THE PROGRAM MAY CONSIST OF (A) A LIST OF TRANSITION FREQUENCIES AND RELATIVE INTENSITIES, (B) A PLOT OF THE CALCULATED SPECTRUM AND (C) BOTH LIST AND PLOT. TITLE-TITLE OF THE WHOLE SYSTEM. NSYTEM-NO. OF SYSTEM TO BE ADDED TOGETHER. MODE-OUTPUT INCICATOR (=1 PRINT ONLY, =2 PLOT ONLY, =3 PRINT AND PLOT). STITLE-TITLE OF THE SUBSYSTEM. SPWGHT-SPECTRUM WEIGHT OF THE SUBSYSTEM. IZ-NUMBERING OF THE SUBSYSTEM (=1,2,3,---). NUCLEI-TOTAL NO. OF NUCLEI. NUCLEA-TOTAL NO. OF NUCLEI OF TYPE A (FOR EXAMPLE HYDROGEN). NUCLEM-TOTAL NO. OF NUCLEI OF TYPE B (FOR EXAMPLE FLUORINE). IFANY-NO. OF EXTRA NUCLEI (0 OR 1)(FCR EXAMPLE C(13)). NGEFM-NO. OF DIFFERENT GEOMETRICAL FORM. MODP-OUTPUT INCICATOR CONCERNING A AND M (=1 GIVING LIST OR PLOT FOR A AND M TOGETHEP . = 2 GIVING LIST OR PLOT FOR A AND M SEPARATELY). I-NUMBERING SEQUENCE OF NUCLEI. NATO(I)-ATOMIC NC. OF NUCLEUS I. CS(I)-CHEMICAL SHIFT(CPS) OF NUCLEUS I. XMAG(I)-NUCLEAR MAGNETIC MOMENT OF NUCLEUS I. CUP(ID, IP)-INDIRECT COUPLING CONSTANT BETWEEN NUCLEI ID AND IP. PCUP(IO, IP)-PSEUDO-DIPOLE COUPLING CONSTANT BETWEEN NUCLEI IC AND IP. XA(L), YA(L) AND ZA(L)-COORDINATES OF THE NUCLEUS L. C1,C2,C3,C4 AND C5-MOTIONAL CONSTANTS. WIDTH-WIDTH OF THE LINES TO BE PLOTTED. HEIGHT-MAXIMUM HEIGHT OF THE PLOTTING. NPLGT-NO. OF PLOTS TO BE MADE. IPBEN-INDEX FOR STARTING POINT OF THE FLCT (≐L STARTING POINT CHOSEN BY THE USER, =1 STARTING POINT DETERMINED BY THE PROGRAM). IPEND-INDEX FOR END POINT OF THE PLOT (=) END POINT CHOSEN BY THE USER, =1 END POINT DETERMINED BY THE PROGRAM). START-FREQUENCY OF STARTING POINT OF THE PLOT. ENC-FREQUENCY OF END POINT OF THE PLCT. DIMENSION TITLE(18), STITLE(15), LIN(2) COMMON CS(10), CUP(10,10), DCUP(10,10), PDCUP(10,10), BB(25,25), C(25, 125), S(25,25), NEG(256), FREQ(1000), AMP(1000), IFANY, KORDER(25), 2 LINE, LINEA, LINEB, MCCE, MODP, NUCLEI, NUCLEA, NUCLEM, NUCM1, NUCM2, 3 NGEFM, SPWGHT, STATE, CHEMST, CHEM 1 REAC(5,1002)TITLE WRITE(6,1001) WRITE(6,10)3)TITLE READ(5,1704)NSYTEM, MCDE LINEA=0 LINEB=0 LINE=0 DO 2 IBC=1,NSYTEM

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READ(5,1005)STITLE,SPWGHT,IZ WRITE(6,1006) IZ, STITLE, SPWGHT READ(5,1007)NUCLEI, NUCLEA, NUCLEM, IFANY, NGEFM, MODP ITEST=C NUCM2=NUCLEI+IFANY NUCM1=NUCM2-1 SPWGHT=100.*SPWGHT/2.**NUCM2 WRITE(6,1008)NUCLEI, NUCLEA, NUCLEM, IFANY IF (MCDP-?) 5, 3, 5 3 READ(5,1011)CHEMST, CHEM 5 CALL BINPUT 6 STATE=1. IFANY1=IFANY+1 DO 12 IAB=1, IFANY1 CALCULATION OF THE EIGENVALUES AND EIGENVECTORS. С CALL DIAMAT(ITEST) IF(ITEST- 99)7,999,7 CALCULATION OF TRANSITION FREQUENCIES AND INTENSITIES. С 7 CALL CALFRE(ITEST) IF(ITEST- 99)9,999,9 9 IF(ITEST- 100)12,1000,12 12 STATE=-1. 2 CONTINUE LIN(1)=LINE LIN(2)=LINEB+500 MIN=1CALL PLOTON DO 10 IAC=1, MODP MAX=LIN(IAC) С PRINT LINE FREQUENCIES AND INTENSITIES. CALL PRINT (MIN, MAX, IAC) GO TO (10,8,8),MCDE 8 CALL APLC(MIN, MAX) 10 MIN=MIN+500 С PLOTTING THE SIMULATING SPECTRUM. CALL PLOT(0.0,0.0,999) GO TO 1 1000 WRITE(6,1009) GO TO 11 999 WRITE(6,1010) 1001 FORMAT (1H1,40X,27HANALYSIS OF NMR SPECTRUM OF) 1002 FORMAT(18A4) 1003 FORMAT(1H ,40X,18A4) 1004 FORMAT(215) 1005 FORMAT(15A4,F10.4,I2) 1006 FORMAT(1H0,50%,6HSYSTEM,12/10%,15A4,16HSPECTRUM WEIGHT=,2PE9.2) 1007 FORMAT(615) 1008 FORMAT(10X,20HTOTAL NO. OF NUCLEI=,12,20X,15HSCLVE AS AB---(,12, 11H),6HMN---(,12,1H),2HX(,12,1H)/52X,24HNC X TRANSITION INCLUDED) 1009 FORMAT(1H0,10X,1SHINPUT DATA IS WRENG) 1010 FORMAT(1H0,10X,40HTHE SYSTEM IS TOC LARGE FOR THIS PROGRAM) 1011 FORMAT(2F10.5) 11 STOP END

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SUBRCUTINE BINPUT
      DIMENSION NATO(10), XMAG(10), XA(10), YA(10), ZA(10)
      COMMON CS(10), CUP(10,10), DCUP(10,10), PDCUP(10,10), BB(25,25), C(25,
     125), S(25,25), NEG(256), FREQ(1000), AMP(1000), IFANY, KORDER(25),
     2 LINE, LINEA, LINEB, MODE, MCDP, NUCLEI, NUCLEA, NUCLEM, NUCM1, NUCM2,
     3 NGEFM, SPWGHT, STATE, CHEMST, CHEM
      WRITE(6,2011)
      READ(5,2009)(I,NATU(I),CS(I),XMAG(I),J=1,NUCM2)
      WRITE(6, 2015)(J, NATO(J), CS(J), XMAG(J), J=1, NUCM2)
      DO 1 I=1.NUCM1
      IPP1=I+1
      DO 1 J=IPP1,NUCM2
      READ(5,2017)IO, IP, CUP(IO, IP), PDCUP(IG, IP)
    1 \text{ DCUP}(I,J)=0.
      DO 2 I=1,NGEFM
      REAC(5,2013)GWEGHT
      REAC(5,2014)(L,XA(L),YA(L),ZA(L),K=1,NUCM2)
      REAC(5,2012)C1,C2,C3,C4,C5
      WRITE(6,2022)I,GWEGHT
      WRITE(6,2025)
      WRITE(6,2023)(L,XA(L),YA(L),ZA(L),L=1,NUCM2)
      WRITE(6,2024)C1,C2,C3,C4,C5
      CDE=2./2.236068*15399.74*GWEGHT
      DO 3 J=1,NUCM1
     COEF=XMAG(J)*CCE
     IPP1=J+1
     DO 3 K=IPP1, NUCM2
     DX = XA(J) - XA(K)
     DY=YA(J)-YA(K)
     DZ=ZA(J)-ZA(K)
     R=(SQRT(DX**2+CY**2+CZ**2))**5
     SUMA=C1*(DZ**2-0.5*(DY**2+DX**2))/R+(C2*0.5*(DX**2-DY**2)+C3*DX*DZ
    1+C4*DY*DZ+C5*DX*DY)*1.73205/R
   3 DCUP(J,K)=-COEF*SUMA*XMAG(K)+DCUP(J,K)
   2 CONTINUE
     WRITE(6,2026)
     DO 6 I=1,NUCM1
     JPP1=I+1
     DO 6 J=JPP1, NUCM2
   6 WRITE(6,2927)I, J, CUP(I, J), PDCUP(I, J), DCUP(I, J)
2009 FORMAT(215,2F10.4)
2010 FORMAT(215,2F10.4)
2011 FORMAT(1H0,50X,10HINPUT DATA//14X,6HNUCLEI,20X,7HAT. ND.,20X,14HCH
    1EMICAL SHIFT, 20X, 15H MAGNETIC MCMENT)
2012 FORMAT(5F10.5)
2013 FORMAT(F10.4)
2014 FCRMAT(110,3F10.4)
2015 FORMAT(1H ,15X,12,25X,12,25X,F1C.2,25X,F1U.5)
2022 FORMAT(1H0,15X,16HGECMETRICAL FORM,13,30X,16HSPECTRUM WEIGHT=,
    12PE9-21
2023 FORMAT(1F ,22X,12,12X,F10.4,12X,F10.4,12X,F10.4)
2024 FORMAT (1H0,30X,39HCONSTANT TO DESCRIBE ANISOTROPIC MOTION/
    116X,2HC1,15X,2HC 2,15X,2HC3,15X,2HC4,15X,2HC5/
    213X,F8.4,9X,F8.4,9X,F8.4,9X,F8.4,9X,F8.4)
2025 FORMAT(1H ,20X,6HNUCLEI,15X,1HX,21X,1HY,21X,1HZ)
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2026 FORMAT(1HD,30X,41HCOUPLING CONSTANTS BETWEEN NUCLEI I AND J/16X,
     11HI, 10X, 1HJ, 20X, 8HINDIRECT, 22X, 6HPSEUDC, 21X, 7HDIPOLAR)
 2027 FCRMAT(15X,12,9X,12,16X,F10.3,18X,F10.3,18X,F10.3)
      RETURN
       ENC
      SUBROUTINE DIAMAT(ITEST)
      DIMENSION NS(256), SW(256), SA(256), KB(50), DME(50)
      COMMON CS(10), CUP(10,10), DCUP(10,10), PDCUP(10,10), BB(25,25), C(25,
     125), S(25,25), NEG(256), FREQ(1000), AMP(1000), IFANY, KORDER(25),
     2 LINE, LINEA, LINEB, MCCE, MODP, NUCLEI, NUCLEA, NUCLEM, NUCM1, NUCM2,
     3 NGEFM, SPWGHT, STATE, CHEMST, CHEM
С
      CALCULATION OF DIAGONAL ELEMENTS
      REWIND 1
      SA(1)=0.
      SA(2)=0.
      NEG(1) = 1
      NEG(2)=0
      IF(IFANY)1,17,1
    1 DO 16 I=1, NUCLEI
  16 CS(I)=CS(I)+STATE*0.50*(CUP(I,NUCM2)+FDCUP(I,NUCM2)+DCUP(I,NUCM2))
  17 SW(1) = -CS(1)
      SW(2)=CS(1)
      DO 33 N=2, NUCLEI
      N3=2**(N-1)
      DO 33 J=1,N3
      I = N3 - J + 1
      IT2=2*I
      IT2M1=IT2-1
      SW(IT2) = SW(I) + CS(N)
     SW(IT2M1) = SW(I) - CS(N)
     NEG(IT2)=NEG(I)
     NEG(IT2M1) = NEG(I)+1
     COUP=0.
     NM1=N-1
     DO 31 M=1,NM1
     SOM=2*MOD(((I-1)/2**(N-M-1)),2)-1
  31 COUP=COUP+SOM*(CUP(M,N)+DCUP(M,N)+PDCUP(M,N))
     SA(IT2)=SA(I)+COUP
  33 SA(IT2M1)=SA(I)-COUP
     N4=2**NUCLEI
     C(1,1)=0.5*SW(N4)+0.25*SA(N4)
     ZA=1.0
     KORDER(1)=1
     WRITE(1) C(1,1)
     WRITE(1) ZA
     CALCULATION OF OFF DIAGONAL MATRIX ELEMENTS
     NNEG=1
     N1 = N4 - 1
     N2=NUCLEI-1
     N7 = N1 - 1
   IF(NUCLEM)19,34,19
 34 DO 59 K=1,N2
     FLAG=0.
    KOUNT=0
```

С

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11=1
    J1=2
    DO 57 I = 2.N7
    IF(NEG(I)-NNEG) 57,38,57
 38 IP1=I+1
    DO 54 J=IP1,N1
    IF(NEG(I)-NEG(J)) 54,39,54
 39 INVER=0
    DO 50 N=1,NUCLEI
    MXCTH1=2*MOD((((I-1)/2**(NUCLEI-N)),2)-1
    MXCTH2=2*MOD((((J-1)/2**(NUCLEI-N)),2)-1
    K1=1-MXOTH1*MXCTH2
    IF(K1) 50,50,41
41 INVER=INVER+K1
    IF(INVER-2) 50,44,43
43 IF(INVER-4) 50,46,50
44 MΔ=N
    GO TO 50
46 MB=N
50 CONTINUE
   IF(INVER-4) 52,51,52
51 C(I1,J1)=0.5*CUP(MA,MB)-0.25*(DCUP(MA,MB)+PDCUP(MA,MB))
   GO TO 53
52 C(I1,J1)=0.
53 C(J1,I1)=C(I1,J1)
   KOUNT=KOUNT+1
   J1=J1+1
   J2=J
54 CONTINUE
   C(I1_{9}I_{1})=0.5*SW(I)+0.25*SA(I)
   IF(FLAG) 56,55,56
55 NCRDER=KOUNT+1
   FLAG=1.C
56 I1=I1+1
   J1=I1+1
57 CONTINUE
   C(I1,I1)=0.5*SW(J2)+0.25*SA(J2)
   IF(NCRDER-25)58,58,70
58 KCRDER(K+1)=NORDER
   CALL EVALUE(C, 25, 25, S, 25, 25, NORDER, 0.0001, 1)
   WRITE(1) (C(J,J), J=1, NCRDER)
   WRITE(1) ((S(I,J),I=1,NCRDER),J=1,NORDER)
59 NNEG=NNEG+1
   GO TO 72
19 DO 27 LA=1,N4
20 NS(LA)=0
   DO 21 LA=1,N4
   DO 21 LB=1,NUCLEA
   MXC=2*MOD(((LA-1)/2**(NUCLEI-LB)),2)-1
21 NS(LA) = NS(LA) + MXC
  L10=2*NUCLEA+1
  L11=NUCLEA+1
  DO 159 K=1,N2
  KOUNTB=0
  KCUNTC =1
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DO 130 LB=1, L10, 2L12=LB-L11 I1=1 J1=2 KOUNT=0 KOUNTA=0 DO 157 I=2,N1 IF(NEG(I)-NNEG) 157,138,157 138 KOUNT=KOUNT+1 KB(KCUNT)=0 NSAB=NS(I) IF(NSAB- L12)157,140,157 140 KOUNTA=KOUNTA+1 KCUNTB=KOUNTB+1 KB(KCUNT)=KB(KCUNT)+1 IP1=I+1DO 154 J=IP1,N4 IF(NEG(I)-NEG(J)) 154,139,154 139 NSAB=NS(J) IF(NSAE- L12)154,239,154 239 INVER=0 DO 150 N=1,NUCLEI MXCTH1=2*MOD((((I-1)/2**(NUCLEI-N)),2)-1 MXCTH2=2*MOD(((J-1)/2**(NUCLEI-N)),2)-1 K1=1-MXOTH1*MXCTH2 IF(K1) 150,150,141 141 INVER=INVER+K1 IF(INVER-2) 150,144,143 143 IF(INVER-4) 150,146,150 144 MA=N GO TO 150 146 MB=N 150 CONTINUE IF(INVER-4) 152,151,152 151 C(I1,J1)=0.5*CUP(MA,MB)-0.25*(DCUP(MA,MB)+PDCUP(MA,MB)) GC TO 153 152 C(11,J1)=0. 153 C(J1,I1)=C(I1,J1)Jl = Jl + 1**154 CONTINUE** C(I1,I1)=0.5*SW(I)+0.25*SA(I)I 1 = I 1 + 1J1 = I1 + 1**157 CONTINUE** IF (KOUNTA) 158, 130, 158 158 IF(KOUNTA- 1)160,24,160 160 IF (KOUNTA-25)161,161,70 161 CALL EVALUE(C, 25, 25, S, 25, 25, KCUNTA, 0, 0001, 1) GO TO 25 24 S(1,1)=1. 25 L13=0 DO 26 L2=KCUNTC, KOUNTB KC = 0L13=L13+1DME(L2)=C(L13,L13)

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DO 22 L3=1,KOUNT
      KKB = KB(L3)
      IF(KKB)27,23,27
  27 KC=KC+1
      BB(L3, L2) = S(KC, L13)
      GO TO 22
  23 BB(L3,L2)=0.
  22 CONTINUE
  26 CUNTINUE
 130 KOUNTC=KOUNTC+KOUNTA
     KORDER(K+1)=KOUNT
     WRITE(1) (CME(J), J=1, K(UNT)
     WRITE(1) ((BB(I,J),I=1,KOUNT),J=1,KOUNT)
 159 NNEG=NNEG+1
  72 C(1,1)=0.5*SW(1)+0.25*SA(1)
     N5=NUCLEI+1
     KCRDER(N5)=1
     WRITE(1) C(1,1)
     WRITE(1) ZA
     END FILE 1
     GO TO 71
  70 ITEST=99
  71 RETURN
     END
     SUBROUTINE CALFRE(ITEST)
     DIMENSION FREQ 8(500,2), FMULT(25,25), MULT(25,25), EIGENA(25),
    1EIGENB(25), AMPB(500,2)
    COMMON CS(10), CUP(10,10), DCUP(10,10), PECUP(10,10), BB(25,25), C(25,
   125), S(25,25), NEG(256), FREQ(1000), AMP(1000), IFANY, KORDER(25),
   2 LINE, LINEA, LINEB, MCCE, MODP, NUCLEI, NUCLEA, NUCLEM, NUCM1, NUCM2,
    3 NGEFM, SPWGHT, STATE, CHEMST, CHEM
    EQUIVALENCE (FREQ(1), FREQB(1,1)), (FMULT(1,1), BB(1,1)), (AMP(1), AMPB
   1(1,1)
    REWIND 1
    NEGA=0
    NEGB=1
    DO 310 K=1,NUCLEI
    KORDRA=KCRDER(K)
    KCRDRB=KORCER(K+1)
    N1=2**NUCLEI
    I]=1
    J1=1
    DO 371 I=1,N1
    IF (NEG(I)-NEGA) 301, 302, 301
302 DO 303 J=1,N1
    IF(NEG(J)-NEGB) 303,304,303
304 K2=0
    DO 306 N=1,NUCLEI
    MXOTH1=2*MOD(((I-1)/2**(NUCLEI-N)),2)-1
    MXCTH2=2*MOD(((J-1)/2**(NUCLEI-N)),2)-1
    IF (MXOTH1*MXOTH2) 308,352,306
308 K2=K2+1
306 CONTINUE
    IF(K2-1) 312,311,312
```

```
311 FMULT(11,J1)=1.
      GO TO 313
  312 FMULT(11,J1)=0.
  313 J1=J1+1
  303 CONTINUE
      J1=1
      I1 = I1 + 1
  301 CONTINUE
      READ(1) (EIGENA(K1), K1=1, KCRDRA)
      READ(1) ((C(I2,J2),J2=1,KORDRA),I2=1,KCRCRA)
      REAC(1) (EIGENB(K1), K1=1, KCRDRB)
      READ(1) ((S(I2,J2),J2=1,KORDRB),I2=1,KCRDRB)
      IF(MODP- 2)300,400,300
 300 DO 305 I=J,KORDRA
      DO 305 J=1,KORDRB
      SUM=r.
     DO 324 I3=1,KORDRA
     DO 324 J3=1,KORDRB
 324 SUM=C(I,I3)*S(J,J3)*FMULT(I3,J3)+SUM
     LINEA=LINEA+1
     SUMQR=SUM*SUM
     IF(SUMQR- C.0001)305,325,325
 325 LINE=LINE+1
     AMP(LINE)=SUMQR*SPWGHT
     FREQ(LINE) = EIGENA(I) - EIGENB(J)
 305 CONTINUE
     IF(LINE- 4996)309,309,351
 400 DO 405 I=1,KORDRA
     DO 405 J=1,KORDRB
     SUM=0.
     DO 424 I3=1,KORDRA
     DO 424 J3=1,KORDRB
424 SUM=C(I,I3)*S(J,J3)*FMULT(I3,J3)+SUM
    LINEA=LINEA+1
     SUMQR=SUM*SUM
    IF(SUMQR- 0.0001)405,425,425
425 SFREQ=EIGENA(I)-EIGFNB(J)
    IF(SFREQ- CHEMST)426,426,402
426 LINE=LINE+1
    FREQB(LINE,1)=SFREQ
    AMPB(LINE, 1)=SUMGR*SPWGHT
    GO TO 405
402 LINEB=LINEB+1
    FREQB(LINEB, 2) = SFREQ-CHEM
    AMPB(LINEB, 2) = SUMQR * SPWGHT
405 CONTINUE
440 IF(LINE- 2500)441,441,351
441 IF(LINEB- 2500)309,3(9,351
309 NEGA=NEGA+1
    NEGB=NEGB+1
    PACK SPACE 1
310 BACKSPACE 1
    GO TC 353
351 ITEST=99
    GO TC 353
```



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352 ITEST=100
  353 RETURN
       END
       SUBROUTINE PRINT (MIN, MAX, IAC)
      COMMON CS(10), CUP(10,10), DCUP(10,10), PDCUP(10,10), BB(25,25), C(25,
     125), S(25,25), NEG(256), FREQ(1000), AMP(1000), IFANY, KORDER(25),
     2 LINE, LINEA, LINEB, MCDE, MCDP, NUCLEI, NUCLEA, NUCLEM, NUCM1, NUCM2,
     3 NGEFM, SPWGHT, STATE, CHEMST, CHEM
      MAXR = MAX - MIN + 1
       JLINE=MAX+1
      KLINE=MAX+4
      DO 81 I=JLINE,KLINE
      FREQ(I)=0.
   81 AMP(I)=0.
      DO 70 L=MIN, MAX
      POS=FREQ(L)
      VAL = AMP(L)
      K=L
      DO 71 M=L,MAX
      IF(PCS-FREQ(M)) 71,71,72
   72 POS=FREQ(M)
      VAL=AMP(M)
      K = M
   71 CONTINUE
      FREQ(K)=FREQ(L)
      FREQ(L)=POS
      AMP(K) = AMP(L)
   70 AMP(L)=VAL
      GO TO (80,90,80), MODE
  80 IF(IAC- 1)82,73,82
  82 IF (NUCLEM) 76,83,76
  83 WRITE(6,3005)MAXR
      GO TO 74
  76 WRITE(6,3006)MAXR
     GO TO 74
  73 WRITE(6,3000)LINEA,MAXR
  74 GO TO (101,101,101,104,104,104,104,104),NUCLEI
 101 WRITE(6,3001)
     WRITE(6,3002)(I, FREQ(I), AMP(I), I=MIN, MAX)
     GO TO 90
 104 IJ=MAXR/4+1
     IM=MIN-1
     II=IJ+IM
     IK=IJ*2
     IL=IJ*3
     WRITE(6,3003)
     DO 180 I=MIN.II
     JK=I+IJ
     KK = I + IK
     LK=I+IL
 180 WRITE(6,3004) I, FREQ(I), AMP(I), JK, FREQ(JK), AMP(JK), KK, FREQ(KK),
    1 AMP(KK), LK, FREQ(LK), AMP(LK)
3000 FCRMAT(1H1,2X,18HTCTAL NC. OF LINES,110/3X
    153HTOTAL NO. OF A-TRANSITION WITH INTENSITIES GT. 0.0001,110)
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3001 FORMAT (1H0,10X,4HLINE,10X,4HFREQ,10X,5FINTEN)
3002 FORMAT(1H ,12X,12,6X,F1C.2,6X,F9.4)
3003 FORMAT(1H0,4HLINE,4X,4HFREC,6X,5HINTEN,7X,4HLINE,4X,4HFREC,6X,
    15HINTEN,7X,4HLINE,4X,4HFREQ,6X,5HINTEN,7X,4HLINE,4X,4HFREQ,6X,
     25HINTEN)
3004 FORMAT(1H , 14, F10.2, F10.4, 3(110, F10.2, F10.4))
3905 FURMAT(1H0,2X,
    153HTOTAL NO. OF B-TRANSITION WITH INTENSITIES GT. 0.0001,110)
3006 FORMAT(1H0,2X,
    153HTOTAL NO. OF M-TRANSITION WITH INTENSITIES GT. 0.0001,110)
  90 RETURN
     ENC
     SUBROUTINE APLO(MIN, MAX)
     DIMENSION X(1600), Y(1600)
     COMMON CS(10), CUP(10,10), DCUP(10,10), PCCUP(10,10), BB(25,25), C(25,
    125), S(25,25), NEG(256), FREQ(1000), AMP(1000), IFANY, KORDER(25),
    2 LINEE, LINEA, LINEB, MCDE, MODP, NUCLEI, NUCLEA, NUCLEM, NUCM1, NUCM2,
    3 NGEFM, SPWGHT, STATE, CHEMST, CHEM
 101 READ 4001, WIDTH, HEIGHT, NAPLOT, IPBEN, IPEND
     B=FREQ(MIN)
     CAB = FREQ(MAX)
     IF(MODE.NE.2) GO TO 614
     PRINT 4004, B, CAB
614 DO 626 JK=1, NAPLCT
     IF(IPBEN.EQ.1) GO TO 601
     READ 4002, START
     GO TO 602
601 IST=(INT(B))/10+10-3C
     START=FLOAT(IST)
602 IF(IPEND.EC.1) GC TO 603
    READ 4003, END
    GO TO 604
603 ENC=CAB
604 D=END-START
    IF(D.GT.155.) GO TO 625
    DIF=0.1
    GO TO 641
625 IF(D.GT.310.) GO TO 605
    DIF=C.2
    GO TO 641
605 IF(D.GT.620.) GO TO 606
    DIF=0.4
    GC TC 641
606 IF(D.GT.1550.) GO TO 607
    DIF=1.0
    GO TO 641
607 IF(D.GT.3100.) GC TO 608
    DIF=2.0
    GO TC 641
608 IF(D.GT.6200.) GD TD 609
    DIF=4.C
641 ZDM=100.*DIF
    F=1./DIF
    GFU=1./(3.1415926*WIDTH)
```

- 180 -

SQW=1./WIDTH KRANGE=INT(WIDTH/DIF*1C.+1.) KCOMP=KRANGE*2-1 DO 644 I = 1,1550644 Y(I)=0. DO 645 I=MIN,MAXV=DIF*FLOAT(INT(F*FREQ(I))) W=FREQ(I)-V L=(V-START)*F L=L-KRANGE IF(L.LT.) GO TO 645 IF(L.GT.1550) GO TO 645 •. DO 645 K=1,KCCMP LL=L+K Y(LL)=Y(LL)+AMP(I)*GFU/(1.+(((FLOAT(K-KRANGE))*DIF-W)*SQW)**2) 645 CONTINUE IF(JK.NE.1) GO TO 653 SIZE=Y(1)KBIG=1 DO 651 I=1,1550 IF(Y(I)-SIZE) 651,651,652 652 SIZE=Y(I)KBIG=I651 CONTINUE PROP=HEIGHT/Y(KBIG) 653 DO 661 I=1,1550 X(I)=FLOAT(I)*0.01 661 Y(I)=Y(I)*PROP CALL PLOT(1.0,0.0,-3) CALL AXIS(0.0,0.0,9HFREQUENCY,9,16.0,0.0,START,ZDM) CALL AXIS(0.0,0.0,9HINTENSITY,9,10.0,90.0,0.0,1.0) CALL LINE(X,Y,1550,-1) CALL PLOT(18.0,0.0,-3) 626 CONTINUE 609 PRINT 4005,D 4001 FORMAT(2F10.2,315) 4002 FORMAT(F10.2) 4003 FORMAT(F10.2) 4004 FCRMAT(1H1,17HMINIMUM FREQUENCY,F10.2,20X,17HMAXIMUM FREQUENCY, 1F10-2) 4005 FORMAT(1H0, J9HTHE FREQUENCY RANGE, F10.2, 13H IS TOO LARGE) 610 RETURN ENC

APPENDIX II

CALCULATION OF EXP. SECOND MOMENT BY NUMERICAL INTERGRATION OF EQUTION (3-1). ANME-TITLE OF THE SYSTEM. T-TEMTERATURE. N-NC. OF TRACES TO BE AVERAGEC. ITRA-NUMBERING OF THE TRACE. K-TETAL NO. OF DATA IN A PARTICULAR TRACE (=5,10,15,20,25---). HM-MCDULATION AMPLITUDE. SCA-(GAUSS/CM) OF THE X-AXIS. SCX-LENTH OF THE UNIT (CM) TAKEN TO MEASURE THE X-AXIS. Y-FEIGHT OF THE ABSCRPTICN CURVE. DIMENSION Y(2,40), ANNE(9), SA(30,2) 8 REAC(5,108) ANME 4 REAC(5,101) T.N IF (T - 0.) 31,8,31 31 WRITE(6,109)ANME WRITE(6,102)T 3 READ(5,103)ITRA,K,HM,SCA,SCX,((Y(I,J),J=1,K),I=1,2) WRITE(6,104) ITRA, HM, SCA, SCX DC 1 I=1.K 1 WRITE(6,105) I,Y(1,I),I,Y(2,I) B = SCA + SCXDO 7 I=1,2SB=0 SC=0 C=0 DO 2 J=1,K C = C + BIF(Y(I,J) - 0.001) 2,33,3333 SB=SB+C**3*Y(I,J) SC=SC+C*Y(I,J) 2 CONTINUE 7 SA(ITRA, I)=SB/(3.*SC)-HM**2/4. WRITE(6,106) ITRA, (SA(ITRA, I), I=1,2) IF(ITRA - N) 3,32,3232 SUM=0. D=2*N DO 5 I=1,N DO 5 J=1,2 5 SUM=SUM+SA(I,J) S = SUM/D

```
ST=0
D0 6 I=1,N
```

C C

С

С

С

С

C

С

С

C C

```
DO 6 J=1,2
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6 ST=ST+(S-SA(I,J))**2
STC=SQRT(ST/(D-1.))
WRITE(6,107) N,S,STD
GO TO 4
```

```
101 FORMAT (F10.5, 110)
```

```
102 FORMAT (1HD, 15HTEMPERATURE(K)=,F6.1)
```

```
103 FORMAT (2110,3F10.3/(5F10.4))
```

```
104 FORMAT(1HL,5HTRACE,I3,5X,14HMCD. FIELD(G)=,F6.3,5X,16HSCALE(GAUSS/
1CM)=,F6.3,5X,8HX-SCALE=,F6.3/10X,4HX(1),10X,4HY(1),1^X,4HX(2),10X,
24HY(2))
```

```
105 FORMAT(11X,12,11X,F6.2,9X,12,10X,F6.2)
106 FORMAT(1H0,5HTRACE,12,10X,18HSECGND MOMENT S1=,F7.2,10X,3HS2=,F7.
12/)
107 FORMAT(1HL,10HAVERAGE CF,12,22H TRACE, SECOND MOMENT=,F7.2,5X,2CH
1STANCARD DEVIATION=,F7.3//)
108 FORMAT (15A4)
109 FORMAT (1H1,22FEXP. SECOND MOMENT CF , 15A4)
100 STOP
ENC
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APPENDIX III

THIS PROGRAM CONSISTS OF THREE INDEPENDENT PARTS. С PART 1 CALCULATES THE RIGID LATTICE SECOND MOMENT, PART 2 COMPUTES THE С С INTER-GROUP CONTRIBUTION TO THE SECOND MOMENT IN THE PRESENCE OF MOLECULAR ROTATION, PART 3 CALCULATES THE SECOND MOMENT FOR С С **ISOTROPIC ROTATION.** PART 1--- CALCULATION OF RIGID LATTICE SECOND MOMENT ACCORDING TO С С VAN VLECK. С ANME-TITLE OF THE SYSTEM. С NTA-ATCMIC NO. OF THE NUCLEUS INTERESTED. ATME-THE NUCLEUS FOR WHICH THE SECOND MCMENT IS CALCULATED. С N-TOTAL NO. OF THE CENTRAL ATOMS INCLUDED IN THE CALCULATION. С С M-TOTAL NO. OF ATOMS IN A MOLECULE. NC-NO. OF UNIT CELL INCLUDED IN THE CALCULATION. С С ONM-NO. OF EQUIVALENT MOLECULES IN AN UNIT CELL. С XA, XB, XC AND ANGLE-LATTICE CONSTANTS. IND-INPUT INDEX FOR ATOMIC POSITIONS (=0 INPUT COCRDINATES IN С TERMS OF LATTICE COORDINATES, =1 INPUT COORDINATES IN TERMS OF С С ANGSTROM). С KA-ATCMIC NO. С AX, AY, AZ AND BX, BY, BZ-COORDINATES OF ATCMS. С AW-FACTORS FOR CALCULATING SECOND MOMENT. BXIM, BYIM AND BZIM-MULTIPLYING FACTORS IN TRANSFORMATION OF C C CRYSTALLCGRAPHIC POSITIONS BXI, BYI AND BZI-ACDING FACTORS IN TRANSFORMATION OF CRYSTALLO-С С **GRAPHIC POSITIONS.** С ID, IP AND IQ-UNIT CELL INDEX. DIMENSION ANME(8), ATME(8) COMMON AX(30), AY(30), AZ(30), BX(30), BY(30), BZ(30), AW(30,2), KA(30), 1R(30,30),B,S,M,N,XA,XB,XC,F(30),O,P,G 15 READ 101, ANME, NTA, ATME, N, M, NC, NNEA, ONM, XA, XB, XC, ANGLE, IND, (KA(I), 1AX(I), AY(I), AZ(I), (AW(I,J), J=1,2), I=1, M)PRINT 102, ANME, ATME, XA, XB, XC, ANGLE, (KA(I), AX(I), AY(I), AZ(I), (AW(I, $1J_{J}, J=1, 2$, I=1, MNEEM=ONM **PRINT 103** CONVERT THE UNIT OF COORDINATES AND DEFINE B С IF(IND.EQ.1) GO TO 1 DO 2 I=1,M $A \times (I) = A \times (I) * X A$ AY(I) = AY(I) * XB2 AZ(I) = AZ(I) * XC1 DO 6 I = 1.M $B \times (I) = \Delta \times (I)$ BY(I) = AY(I)6 BZ(I) = AZ(I)С ASSIGN CALCULATION FACTORS DO 20 I=1,M IF(KA(I).EG.NTA) GO TO 13 F(I) = AW(I,2)GC TO 20 13 F(I)=AW(I,1)/2.

```
20 CONTINUE
        B=COS(3.1416*(1.-ANGLE/189.))
        S=0
        CALCULATION OF INTRA-GROUPE SECOND MOMENT
       DO 3 I=1.N
        DO 3 J=1,N
       IF(I.EC.J) GO TO 4
       IF(I.GT.J) GO TO 5
       R(I,J)=SQRT((BX(J)-AX(I))**2+(BZ(J)-AZ(I))**2-2.*B*(BX(J)-AX(I))*
      1(BZ(J)-AZ(I))+(BY(J)-AY(I))**2)
       S=S+2.*F(J)/R(I,J)**6
       GO TO 3
     4 R(I,J)=0
       GO TO 3
     5 R(I,J)=R(J,I)
     3 CONTINUE
       D = N
       SAA=S/D
С
      CALCULATION OF INTRAMOLECULAR CONTRIBUTION
      READ 104, (BXI(I), BXIM(I), BYI(I), BYIM(I), BZIM(I), I=1, NEMIUC)
      KOB=N+1
      CALL CMOMEN(NNEA,KOB)
      SAB=S/D
      IF(NC .EQ.0) GO TO 14
С
      CALCULATION OF INTERMOLECULAR CONTRIBUTION
      S=0
      KB=1
      0=0.
      P=0.
      0=0-
  10 PRINT 106, KB, IO, IP, IC
      DO 40 I=1,NEEM
     IF(KB.GT.1) GO TO 41
     IF(I.EQ.1) GO TO 40
  41 CALL TRAN(BXIM(I), BYIM(I), BZIM(I), BXI(I), BYI(I), BZI(I))
     CALL CMOMEN(NNEA,1)
  40 CONTINUE
     IF(KB.GE.NC) GO TO 30
     IF(KB/2*2-KB.EQ.0) GO TO 8
     READ 105, IC, IP, IQ
     GO TC 9
   8 IO=-10
     IP = -IP
     IQ = -IQ
   9 O=IO
     P = IP
    Q = IQ
    DO 7 I=1,M
    BX(I) = AX(I) + O * XA
    BY(I) = AY(I) + P * XB
  7 BZ(I) = AZ(I) + Q * XC
    KB=KB+1
    GO TO 10
    CAL. OF THE CONTRIBUTION FROM THE ATOMS WITH A DISTANCES GT. 7
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J.

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<u>- 185 -</u>
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30 SOB=0.
      DO 12 I=1.N
   12 SOB=SOB+F(I)
      SIB=ONM*4.0*3.1416*SCB/(3.0*7.**3*XA*XB*XC*SIN(3.1416*(1.-ANGLE/
     1180.)))
С
      PRINT THE RESULT
      SA=SAA+SAB
      SIA=S/D
      S=SIA+SIB
      ST=SA+S
      PRINT 107, ST, SA, SAA, SAB, S, SIA, SIB
      GO TO 15
  14 SA=SAA→SAB
      PRINT 108, SA, SAA, SAB
      GO TO 15
 101 FORMAT(8A6/15,8A6/4110,F10.5/4F10.5,11C/(110,5F10.5))
 102 FORMAT(1H1, 30HRIGID LATTICE SECOND MOMENT OF, 1X, 8A6/22X, 7HELEMENT,
    12X,8A6/18H LATTICE CONSTANT,5X,2HA=,F7.3,5X,2HB=,F7.3,5X,2HC=,F7.
    23,5X,6HANGLE=,F7.2/2X,7HAT. NO.,10X,14HAT. COORDINATE,14X,25HFACTO
    3RS FOR SECOND MOMENT/(15,5x,3F10.4,10x,2F10.3))
 103 FORMAT(1H1,21HINTERATOMIC DISTANCES//2X,3HND.,10X,1HX,10X,1HY,10X,
    11HZ,15X,5HR1,R6,7X,5HR2,R7,7X,5HR3,R8,7X,5HR4,R9,7X,6HR5,R10)
 104 FORMAT(6F10.5)
 105 FORMAT(312)
 106 FORMAT(1H0,4HCELL,13,1H(,12,1H,,12,1H,,12,1H))
 107 FORMAT(1H1,13HSECOND MOMENT,F10.3//28H INTRAMOLECULAR CONTRIBUTION
    1,F10.3/21X,6HPART 1,F10.3/21X,6HPART 2,F10.3/28H INTERMOLECULAR CO
    2NTRIBUTION, F10.3/21X, 6HPART 1, F10.3/21X, 6HPART 2, F10.3)
 108 FORMAT( 1H0,28HINTRAMOLECULAR SECOND MOMENT, F10.3/22X,6HPART 1,F10
    1.3/22X,6HPART 2,F10.3)
 100 STOP
     END
     SUBROUTINE CMOMEN(L,K)
     COMMON AX(30), AY(30), AZ(30), BX(30), BY(30), BZ(30), AW(30,2), KA(30),
    1R(30,30),B,S,M,N,XA,XB,XC,F(30),O,P,Q
     DO 1 I=1,L
     DO 1 J=K,M
     R(I,J)=SQRT((BX(J)-AX(I))**2+(BZ(J)-AZ(I))**2-2.*B*(BX(J)-AX(I))*
    1(BZ(J)-AZ(I))+(BY(J)-AY(I))**2)
     IF(K.GT.1) GO TO 2
     IF(R(I,J).GT.7.) GO TO 1
   2 S=S+F(J)/R(I,J)**6
   1 CONTINUE
     DO 10 J=1,M
     IF(K.GT.1) GO TO 8
     IDAN=0
     DO 9 I=1,L
     IF(R(I,J).GT.7.) GD TO 9
     IDAN=IDAN+1
   9 CONTINUE
     IF(IDAN.EQ.C) GO TO 10
   8 PRINT 104, J, BX(J), BY(J), BZ(J), (R(I, J), I=1, N)
 10 CONTINUE
104 FORMAT(1H ,2X,12,5X,3F10.4,5X,5F12.4/45X,5F12.4)
```

	R ETURN END
	<pre>SUBROUTINE TRAN(TI,UI,VI,T,U,V) COMMCN AX(30),AY(30),AZ(30),BX(30),BY(30),BZ(30),AW(30,2),KA(30), IR(30,30),B,S,M,N,XA,XB,XC,F(30),0,P,C DO 1I=1,M BX(I)=TI*AX(I)+(T+0)*XA BY(I)=UI*AY(I)+(U+P)*XB 1 BZ(I)=VI*AZ(I)+(V+Q)*XC RETURN END</pre>
с с с с с с	PART 2 CALCULATION OF INTERGROUP SECOND MOMENT BY ANDREW- EADES FORMULAEMOLECULAR REORIENTATION. ANME-TITLE OF THE SYSTEM. SORTE-TYPE OF THE MOLECULAR MOTION. NTA-ATOMIC NO. OF THE NUCLEUS INTERESTED.
C C	ATME-THE NUCLEUS FOR WHICH THE SECOND MOMENT IS CALCULATED.
Č	MA-NO. OF GROUPS IN A MOLECULE (EQUIVALENT POSITIONS IN A ROTATUON
C	TREATED AS A GROUP). NA-NO. OF CENTRAL GROUPS INCLUDED IN THE CALCULATION
C	NEMIUC-NO. OF EQUIVALENT MOLECULES IN AN UNIT CELL.
C C	IND-INPUT INDEX FOR ATOMIC POSITIONS (=0 INPUT COORDINATES IN
č	ANGSTROM).
С	XA, XB, XC AND ANGLE-LATTICE CONSTANTS.
C C	MB(I)-ND. OF ATOMS IN GROUP I.
č	AX+AY+AZ AND BX+BY-B7-COORDINATES OF ATOMS
С	AWA AND AWB-FACTORS FOR CALCULATING SECOND MOMENT.
C	SINTRA-INTRAMOLECULAR-INTERGROUP CONTRIBUTION TO THE SECOND
C r	
č	BXIM.BYIM AND BZIM-MULTIPLYING FACTORS IN TRANSFORMATION OF
C	CRYSTALLOGRAPHIC POSITIONS
C	BXI, BYI AND BZI-ADDING FACTORS IN TRANSFORMATION OF CRYSTALLO-
C	GRAPHIC POSITIONS.
C	DIMENSION ANME(12) ATME(2) SPOTE(12) CINTOACCOL CONTERNO
	1, BYI(10), BZI(10), BXIN(10), BYIN(10), BZIN(10)
	COMMON MB(40), KA(40, 10), AX(40, 10), AY(40, 10), AZ(40, 10), BX(40, 10),
	1BY(40,10),BZ(40,10),AWA(40,10),AWB(40,10),F(40,10),KB,KC,XA,XB,
С	ZACHDAHCBHBCHUHPHUHNCIHMA INPUT DE DATA
-	99 READ 101, ANME, SROTE, NTA, ATME, LA, MA, NA, NEM THE, TND, VA, VB, VC, ANGLE
	PRINT 201, ANME, SROTE, ATME, XA, XB, XC, ANGLE
	PRINT 202
	$\frac{1}{1} = \frac{1}{10} MA$
	KB=MB(I)
	READ 103, (KA(I,J), AX(I,J), AY(I,J), AZ(I,J), AWA(I,J), AWB(I,J), I=1, KB

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С

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1)
     1 PRINT 203, (I, (KA(I, J), AX(I, J), AY(I, J), AZ(I, J), AWA(I, J), AWB(I, J),
      1J=1.KB))
       CONVERSION OF UNIT OF COORDINATES, DEFINE ANGLE FACTORS AND ASSIGN
       CALCULATION FACTORS
       IF(IND.EQ.1) GO TO 2
       DO 3 I=1, MA
       KB=MB(I)
       DO 3 J=1,KB
       A \times (I, J) = A \times (I, J) + X A
       AY(I,J) = AY(I,J) = XB
    3 AZ(I,J)=AZ(I,J)*XC
    2 BA=COS(3.1416*(1.-ANGLE/180.))
       BB=COS(3.1416*ANGLE/180.)
       BC=SIN(3.1416*ANGLE/180.)
       DO 4 I=1,MA
       KB=MB(I)
      DO 4 J=1, KB
       BX(I,J)=AX(I,J)
      BY(I,J) = AY(I,J)
      BZ(I,J)=AZ(I,J)
      IF(KA(I,J).EQ.NTA) GO TO 6
      F(I,J) = 1.25 \times AWB(I,J)
      GO TO 4
    6 F(I,J)=0.625*AWA(I,J)
    4 CONTINUE
С
      CALCULATION OF INTRAMOLECULAR-INTERGROUP CONTRIBUTION
      TSRA=0
      TSER=0
      DD 29 I=1, MA
      SINTRA(I)=0
   29 SINTER(I)=0.
      PRINT 211
      FNA=NA
      NAI=NA+1
      DO 8 J=NAI,MA
      KC=MB(J)
      DO 9 I=1.NA
      NCI = I
      KB=MB(I)
    9 CALL CMOMEN(SINTRA(J),0,J,I)
    8 SINTRA(J)=SINTRA(J)/FNA
      READ 104, (BXI(I), BXIM(I), BYI(I), BYIM(I), BZIM(I), BZIM(I), I=1, NEMIUC)
      0=0.
      P=C.
      Q=0.
      KD=1
      GO TO 11
   10 KD=KD+1
      PRINT 204, KD, IO, IP, IC
      0 = I O
      P = IP
      Q = IQ
   11 DO 13 I=1,NEMIUC
      IF(KC.GT.1) GO TO 14
```

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IF(I.EQ.1) GO TO 13
 14 CALL TRANS(BXIM(I), BYIM(I), BZIM(I), BXI(I), BYI(I), BZI(I))
    DO 12 K=1,MA
    KC = MB(K)
    DO 12 J=1,NA
    NCI = J
    KB=MB(J)
    CALL CMOMEN(SINTER(K),1,K,J)
 12 CONTINUE
 13 CONTINUE
    READ 105, IO, IP, IQ
    IF(IC.NE.0)GO TO 10
    IF(IP.NE.0) GO TO 10
    IF(IQ.NE.0) GO TO 10
    PRINT 206
    DO 15 I=1,MA
    SINTER(I)=SINTER(I)/FNA
    TSRA=TSRA+SINTRA(I)
    TSER=TSER+SINTER(1)
 15 PRINT 205, I, SINTRA(I), SINTER(I)
    PRINT 212, TSRA, TSER
    GO TO 99
101 FORMAT (12A6/12A6/15,8A6/5110/4F10.5)
102 FORMAT(I2)
103 FORMAT(110,5F1C.5)
104 FORMAT(6F10.5)
105 FORMAT(312)
201 FORMAT(1H1,16HSECOND MOMENT OF,1X,12A6/16X,12A6/8X,7HELEMENT,2X,
   18A6/18H LATTICE CONSTANT, 5X, 2HA=, F7.3, 5X, 2HB=, F7.3, 5X, 2HC=, F7.3,
   25X, 6HANGLE=, F7.2
202 FORMAT(1H0,2X,9HGROUP NO.,10X,7HAT. NO.,10X,14HAT. COORDINATE,16X,
   125HFACTORS FOR SECOND MOMENT)
203 FORMAT(1H ,5X,I2,15X,I2,5X,3F10.4,10X,2F10.3/(23X,I2,5X,3F10.4,
   110 \times 2F10.3
204 FORMAT(1H0,4HCELL, I3,1H(,I2,1H,,I2,1H,,I2,1H))
205 FORMAT(1H ,8X,12,18X,F10.4,18X,F10.4)
206 FORMAT(1H1,13HSECOND MCMENT/4X,9HGROUP NO.,10X,25HINTRAMOLECULAR-I
   INTERGROUP, 10X, 14HINTERMOLECULAR)
211 FORMAT(1H1,9HGROUP NO.,10X,3HNO.,20X,1HX,20X,1HY,20X,1HZ)
212 FORMAT(1H0, 3X, 5HTOTAL, 30X, F10, 4, 18X, F10, 4)
98 STOP
    END
    SUBROUTINE CMCMEN(S, ICAL, K, J)
    DIMENSION R(20,20)
   COMMON MB(40), KA(40,10), AX(40,10), AY(40,10), AZ(40,10), BX(40,10),
  1BY(40,10),BZ(40,10),AWA(40,1C),AWB(40,10),F(40,10),KB,KC,XA,XB,
  2XC_{P}BA_{P}BB_{P}BC_{P}O_{P}O_{P}O_{P}NCI_{P}A
    DO 1 L=1, KB
    DO 1 M=1,KC
 1 R(L,M)=SQRT( (BX(K,M)-AX(J,L))**2+(BY(K,M)-AY(J,L))**2-2,*BA*
  1(BX(K,M)-AX(J,L))*(BY(K,M)-AY(J,L))+(BZ(K,M)-AZ(J,L))**2)
    IF(ICAL.EQ.O) GO TO 5
   RS = R(1,1)
   DO 2 L=1,KB
```

```
DO 2 M=1.KC
     IF(RS.LE.R(L,M)) GO TO 2
     RS=R(L,M)
   2 CONTINUE
     IF(RS.GT.7.) GO TO 4
     GO TO 7
   5 IF(NCI.GT.1) GO TO 6
  7 PRINT 210,K, (M, BX(K, M), BY(K, M), BZ(K, M), M=1,KC)
  6 A=0.
     B=0.
     C=n.
     D=0.
     E=0.
     FZ=0.
    G=0.
     DO 3 L=1,KB
    DO 3 M=1.KC
    RZ=BZ(K,M)-AZ(J,L)
    RX = (BX(K,M) - AX(J,L)) + (BY(K,M) - AY(J,L)) + BB
    RY = \{BY(K,M) - AY(J,L)\} * BC
    RXY=SQRT(R(L,M)**2-RZ**2)
    ACOSA=RZ/R(L.M)
    ASINA=RXY/R(L,M)
    ACOSB=RX/RXY
    ASINB=RY/RXY
    RISP=1./R(L,M)**3
    A=A+ACOSA**2*RISP
    B=B+ASINA*ACOSA*ACOSB*RISP
    C=C+ASINA*ACOSA*ASINB*RISP
    D=D+ASINA**2*ACOSB**2*RISP
    E=E+ASINA**2*ASINB*ACOSB*RISP
    FZ=F2+ASINA**2*ASINB**2*RISP
  3 G=G+RISP
    H=1./FLOAT(KB*KB*KC)
    S=S+H*F(K,1)*(1.8*(A*A+D*D+F2*F2)+G*G+2.4*(B*B+C*C+E*E)
   1+1.2*(A*D+A*FZ+D*FZ)-2.0*G*(A+D+FZ))
210 FORMAT(1H ,4X,12,14X,12,13X,F1C.4,11X,F1C.4,11X,F10.4/
   1(21X, I2, 13X, F10, 4, 11X, F10, 4, 11X, F10, 4))
  4 RETURN
    END
    SUBROUTINE TRANS(TI,UI,VI,T,U,V)
    COMMON MB(40), KA(40,10), AX(40,10), AY(40,10), AZ(40,10), BX(40,10),
   1BY(40,10), BZ(40,10), AWA(40,10), AWB(40,10), F(40,10), KB, KC, XA, XB,
   2 \times C_{9} B A_{9} B B_{9} B C_{9} O_{9} P_{9} G_{9} N C I_{9} M A
    DO 1 IL=1.MA
    KBI=MB(IL)
    DO 1 JK=1,KBI
    BX(IL, JK) = TI * AX(IL, JK) + (T+C) * XA
    BY(IL, JK) = UI * AY(IL, JK) + (U+P) * XB
 1 BZ(IL,JK)=VI*AZ(IL,JK)+(V+C)*XC
    RETURN
    END
```

PART 3--- CALCULATION OF SECOND MOMENT FOR ISOTROPIC ROTATION. С C ANME-TITLE OF THE SYSTEM. С NTA-ATOMIC NO. OF THE NUCLEUS INTERESTED. С ATME-THE NUCLEUS FOR WHICH THE SECOND MOMENT IS CALCULATED. C LA-TOTAL NO. OF ATOMS IN A MOLECULE. С NEMIUC-NO. OF EQUIVALENT MOLECULES IN AN UNIT CELL. IND-INPUT INDEX FOR ATOMIC POSITIONS (=0 INPUT COORDINATES IN C С TERMS OF LATTICE COORDINATES, =1 INPUT COORDINATES IN TERMS OF C ANGSTROM). С XA, XB, XC AND ANGLE-LATTICE CONSTANTS. С KA-ATOMIC NO. С AK-ATOMIC WEIGHT. С AX, AY, AZ AND BX, BY, BZ-COORDINATES OF ATOMS. С AWA AND AWB-FACTORS FOR CALCULATING SECOND MOMENT. C BXIM, BYIM AND BZIM-MULTIPLYING FACTORS IN TRANSFORMATION OF С CRYSTALLOGRAPHIC POSITIONS BXI, BYI AND BZI-ADDING FACTORS IN TRANSFORMATION OF CRYSTALLC-С С GRAPHIC POSITIONS. С ID, IP AND IQ-UNIT CELL INDEX. DIMENSION ANME(12), ATME(8), KA(20), AK(20), AX(20), AY(20), AZ(20), 1AWA(20),AWB(20),BXI(10),BXIM(10),BYI(10),BYIM(10),BZI(10),BZIM(10) С INPUT OF DATA 20 REAC(5,101)ANME, NTA, ATME, LA, NEMIUC, INC, XA, XB, XC, ANGLE WRITE(6,201)ANME,ATME,XA,XB,XC,ANGLE WRITE(6,202) READ(5,103)(KA(I),AK(I),AX(I),AY(I),AZ(I),AWA(I),AWB(I),I=1,LA) WRITE(6,203)(KA(I),AK(I),AX(I),AY(I),AZ(I),AWA(I),AWB(I),I=1,LA) С DEFINE ANGLE FACTORS AND ASSIGN CALCULATION FACTORS F=0. BA=COS(3.1416*(1.-ANGLE/180.)) DO 1 I=1,LA IF(KA(I).EQ.NTA) GO TO 2 F=AWB(I)+F GO TO 1 2 F=AWA(I)/2.+F **1** CONTINUE С CALCULATION OF CENTER OF MASS CM=0. CMX=Q. CMY=0. CMZ=0. DO 4 I=1, LACM=AK(I)+CM CMX = AK(I) * AX(I) + CMXCMY = AK(I) * AY(I) + CMY4 CMZ=AK(I)*AZ(I)+CMZ IF(IND.EQ.1) GO TO 3 CX=CMX/CM*XA CY=CMY/CM*XB CZ=CMZ/CM*XC .GO TO 8 3 CX=CMX/CM CY=CNY/CM CZ=CMZ/CM

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8 READ(5,104)(BXI(I),BXIM(I),BYI(I),BYIM(I),BZI(I),BZIM(I),I=1, 1NEMIUC) WRITE(6,207) KC = 1S=0. 0=?. P=0. Q=?. GO TO 11 10 KC=KC+1 WRITE(6,205)KC, IO, IP, IQ 0=10P = IPC = IQ11 DO 5 I=1, NEMIUC IF(KC.NE.1) GO TO 6 IF(I.EQ.1) GO TO 5 6 BXC=BXIM(I)*CX+(BXI(I)+0)*XA BYC=BYIM(I)*CY+(BYI(I)+P)*XBBZC=BZIM(I)*CZ+(BZI(I)+Q)*XC R=SQRT((BXC-CX)**2+(BYC-CY)**2-2.*BA*(BXC-CX)*(BYC-CY)+(BZC-CZ) 1**2)WRITE(6,204)BXC, BYC, BZC, R IF(R.GT.8.) GO TO 5 S=S+F/R**6 **5 CONTINUE** READ(5,105)IO, IP, IQ IF(I0.NE.0) GO TO 10 IF(IP.NE.C) GO TO 1C IF(IQ.NE.0) GO TO 10 WRITE(6,206)S GO TO 20 101 FORMAT (12A6/15,8A6/3110/4F10.5) 103 FORMAT(110,6F1C.5) 104 FORMAT(6F10.5) 105 FORMAT(312) 201 FORMAT(1H1,16HSECOND MCMENT OF,1X,12A6/8X,7HELEMENT,2X,8A6/18H LA 1TTICE CONSTANT, 5X, 2HA=, F7.3, 5X, 2HB=, F7.3, 5X, 2HC=, F7.3, 5X, 6HANGLE=, 2F7.2) 202 FORMAT(1H0,2X,7HAT. NO.,10X,7HAT. WT.,10X,14HAT. COORDINATE,16X, 125HFACTORS FOR SECOND MOMENT) 203 FORMAT (1H ,6X,12,7X,F10.3,8X,3F10.3,10X,2F10.3) 204 FORMAT(1H ,5X,3F10.4,5X,F10.4) 205 FORMAT (1H0,4HCELL, I3,1H(,I2,1H,,I2,1H,,I2,1H)) 206 FORMAT(1H1,23HSECOND MOMENT-ISOTROPIC,F10.4) 207 FORMAT(1H1,21HINTERATOMIC DISTANCES//10X,1HX,10X,1HY,10X,1HZ,15X, 11HR) 99 STOP END