

3. ANALYSIS OF NMR SPECTRA OF ORIENTED MOLECULES :

3.1 The NMR Spin-Hamiltonian for oriented molecules:

The most important observable in NMR spectroscopy is the energy of the spin system due to the applied magnetic field and the corresponding operator is called the NMR Spin Hamiltonian $\mathcal{H}$, the quantum mechanical operator. In isotropic liquid solvent the contributions due to nuclear Zeeman interaction causing chemical shift and indirect spin-spin interaction giving effect of electron-coupled spin-spin coupling are only observable, the anisotropic contributions being nearly absent. The isotropic liquid solvent NMR spin Hamiltonian can be written as the sum of two terms a time-independent Schrödinger equation involving the Hamiltonian

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_I \quad (3.1)$$

Where $\mathcal{H}_Z$ and $\mathcal{H}_I$ are respectively, the contributions from the nuclear Zeeman interaction and the indirect Spin-Spin interaction.

The Spin Hamiltonian of oriented molecules differ from that in isotropic media and has to be modified to include the anisotropic contributions due to direct dipole-dipole interactions. The modified Hamiltonian

for oriented molecules will be

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_1 + \mathcal{H}_d. \quad (3.2)$$

Where $\mathcal{H}_d$ is the direct dipole-dipole interaction contributing Hamiltonian operator. For nuclei with spins greater than $\frac{1}{2}$ nuclear quadrupole interactions do contribute the resultant Hamiltonian but the present work considers only the compounds of nuclear spin $\frac{1}{2}$; hence and quadrupole interaction is not considered in equation (3.2). These terms are discussed separately in the following sections.

3.2 The Direct Dipole-Dipole Interaction ($\mathcal{H}_d$):

The direct coupling (D_{ij}) observed in a spectrum is sum of the anisotropic contribution of the indirect spin-spin coupling (D_{ij}^{ind}) and the direct dipolar coupling (D_{ij}^{dir}) i.e.

$$D_{ij} = D_{ij}^{(ind)} + D_{ij}^{(dir)} \quad (3.3)$$

both have the same directional dependence and hence therefore, $D_{ij}^{(ind)}$ is sometimes called 'pseudo dipolar coupling'. For pair of protonsⁱⁿ this type of coupling is small or negligible because of the spherical symmetry of the predominant Fermi contact term. On the other hand, for Fluorine compounds, the electron-nuclear dipole interactions and the electron orbital current-nuclear dipole contributions

to the coupling became significant. These anisotropic interactions give rise to a measurable pseudo dipolar F-F coupling (35). Present work concerns with protons for which D_{ij} is set equal to $D_{ij}^{(dir)}$ as the assumed and observed geometries coincide. Hence direct dipole-dipole coupling is given by (3.4)

$$D_{ij}^{(dir)} = D_{ij} = - \frac{h}{4\pi^2} \frac{\gamma_i \gamma_j}{r_{ij}^3} \left\langle \frac{(3\cos^2\theta_{ij} - 1)}{r_{ij}^3} \right\rangle \quad (3.4)$$

Where θ_{ij} = angle between the magnetic field direction and the axis connecting the two nuclei i and j separated by a distance r_{ij} . γ is the magnetogyric ratio and the average is taken over the inter-and intra-molecular motion. If r_{ij} is measured in Angstroms ($\text{\AA}$) and D_{ij} in HZ, then the constant $K = \frac{(h \gamma_i \gamma_j)}{4\pi^2} = 120067.0 \text{ HZ. \AA}^3$ for a pair of protons. When all possible values of θ_{ij} are equally probable (Which is the case in isotropic solutions) due to random rapid molecular motions, the average value of $(3\cos^2\theta_{ij} - 1)$ is zero and hence dipolar couplings are not observed.

If the nuclei i and j belong to the same rigid part of the molecule and the optic axis of the liquid crystal is parallel to the magnetic field, then $\left\langle \frac{1}{r_{ij}^3} \right\rangle$ can be replaced by $\frac{1}{r_{ij}^3}$ and $\left\langle \frac{1}{2} (3\cos^2\theta_{ij} - 1) \right\rangle = S_{ij}$ the degree of orientation of the axis passing through i and j for



constant $\sqrt{ij}$. S_{ij} is also sometimes referred as the orientation parameter. Hence eq. (3.4) can be written as

$$D_{ij} = \frac{-K}{\sqrt{ij}^3} S_{ij} \quad (3.5)$$

It may be emphasized that the influence of all the types of molecular vibrations (36-38) and the complications arising out of the assumptions of the independence of the average order parameter and $\left\langle \frac{1}{\sqrt{ij}^3} \right\rangle$ are neglected in eq. (3.5) and throughout this work.

The S_{ij} values of different molecular axes are interdependent. The average orientation of a rigid molecule is described by a symmetrical and traceless matrix $\{S\}$ with five independent elements (39). If X , Y and Z are the axes of a Cartesian co-ordinate system fixed within the molecule and Q_x , Q_y and Q_z as the angles between the molecular axes and the optic axis of the nematic liquid crystal (or the magnetic field direction which is assumed parallel to the optic axis which is in general true for thermotropic nematic liquid crystal solvents. However, for most of the lyotropic liquid crystals, the optic axis may be perpendicular to the magnetic field direction). In general, the order parameter should include a factor which relates the above S_{ij} values to that with respect to the optic axis (i.e. S_{ij}^0) such that $S_{ij} = \frac{1}{2} (3 \cos^2 \alpha - 1) S_{ij}^0$

where α is the angle that the optic axis makes with the magnetic field direction. However, as suggested in literature (13), the convention of expressing the order parameter with respect to the magnetic field direction is followed through out this work.

$$S_{pq} = \left(\frac{1}{2} \right) \left\langle (3 \cos \alpha_p \cos \alpha_q - \delta_{pq}) \right\rangle \quad (3.6)$$

where $p, q = x, y, z$ and δ_{pq} is the Kronecker delta, having the property $\delta_{pq} = 1$ for $p = q$ and $\delta_{pq} = 0$ for $p \neq q$.

The matrix elements S_{pq} are related to the S values of an axis, forming the angles $\alpha_x, \alpha_y, \alpha_z$ with the molecule-fixed co-ordinate system according to equation (3.7)

$$S = \sum_{p,q} \cos \alpha_p \cos \alpha_q (S_{pq}) \quad (3.7)$$

Where $p, q = x, y, z$ and $\alpha_x, \alpha_y, \alpha_z$ are the angles which the axis connecting nuclei i, j make with the axes of the Cartesian co-ordinate system.

A suitable choice of the co-ordinate system may reduce the independent number of order parameters necessary to describe the molecular orientation. If the molecule has a three-fold or higher fold axis of symmetry, the number reduces to 'one' provided that the symmetry axis is chosen as one of the axes of the co-ordinate system. For molecule

with two perpendicular planes of symmetry, with a choice of the coordinate system where each these planes contain two of the axes, the number of independent order parameters reduce to 'two'. For a molecule having one plane of symmetry containing two of the axes of the co-ordinate system, the number of order parameters reduce to 'three'.

Equation (3.5) suggests that the dipolar coupling constants always contain the ratio of S_{ij} to r_{ij}^3 , consequently, experimental D-values can provide the information on r_{ij} only when S_{ij} are known. Since, no method is yet available to determine S_{ij} precisely without the knowledge of an internuclear distance, it follows that the NMR method would provide only the relative distances and the bond angles. From the above considerations, it is clear that the number of independent dipolar couplings should exceed the number of independent parameters needed to describe the molecular orientation, in order to obtain any information on the molecular geometry.

3.3 Nuclear Zeeman Interaction ($\mathcal{H}_Z$)(Chemical shift) :

The chemical shift as derived from the spectra of oriented molecules differ from that determined from those of isotropic cases (ie. $\delta_i = (\delta_s - \delta_i) = \frac{(\nu_s - \nu_i)}{\nu_i} \times 10^6$ ppm. eq. 2.4) in that it contains information about the anisotropic contribution (δ_{ia}). (δ_{ia}) is related to

the chemical shift elements of the order matrix given in terms of tensor components as eq. (3.8)

$$\delta_{ia} = \frac{1}{3} \sum_{p,q} S_{pq} (\delta_{pqi} + \delta_{qpi}) \quad (3.8)$$

Where $p, q = x, y, z$, the axes of the Cartesian co-ordinate system. The presence of symmetry in the molecule reduces the number of independent elements of the chemical shift tensor as discussed in literature (39). The total contribution of nuclear Zeeman interaction along with anisotropy factor will be

$$\mathcal{H}_Z = - \frac{1}{\hbar} H_0 \sum_i \delta_i (1 - \delta_{ia}) I_{zi} \quad (3.9)$$

The total chemical shift ($\delta_i + \delta_{ia}$) in the nematic phase can be written in terms of elements of the S matrix as follows:

$$\begin{aligned} \delta_i + \delta_{ia} = & \left(\frac{1}{3} \right) (\delta_{xx} + \delta_{yy} + \delta_{zz}) + \left(\frac{2}{3} \right) \left[(S_{xx} \delta_{xx} + S_{yy} \delta_{yy} + S_{zz} \delta_{zz}) \right. \\ & + S_{xy} (\delta_{xy} + \delta_{yx}) + S_{yz} (\delta_{yz} + \delta_{zy}) \\ & \left. + S_{xz} (\delta_{xz} + \delta_{zx}) \right] \end{aligned} \quad (3.10)$$

In a molecule with three-fold or higher-fold axis of symmetry, with Z axis chosen along the axis of symmetry, the number of independent elements in equation (3.10) reduces to just two and equation (3.10) becomes

$$\delta_i + \delta_{ia} = \left(\frac{1}{3}\right)(\delta_{xx} + \delta_{yy} + \delta_{zz}) + \left(\frac{2}{3}\right)S_{zz} \left[\delta_{zz} - \left(\frac{1}{2}\right)(\delta_{xx} + \delta_{yy}) \right] \\ \text{with } \delta_{ia} = \frac{2}{3} S_{zz} \Delta\sigma \quad (3.11)$$

Where $\Delta\sigma = \left[\delta_{zz} - \left(\frac{1}{2}\right)(\delta_{xx} + \delta_{yy}) \right]$ called the anisotropy of chemical shift. Therefore, for the determination of in a molecule with three fold or higher-fold axis of $\Delta\sigma$ symmetry, S_{zz} and the chemical shift in the nematic phase with respect to its value in the isotropic medium should be determined.

3.4 Indirect Spin-Spin Interaction (1):

The indirect spin-spin coupling constants J_{ij} derived from the spectra of oriented molecules are the same as those obtained from isotropic systems. The anisotropic contribution (D_{ij}^{ind}) which is contained in the symmetrically determined direct dipole-dipole couplings (D_{ij}^{dir}) is related to the elements of the S-matrix given by equation (3.12) as

$$D_{ij}^{\text{ind}} = \frac{1}{6} \sum_{p,q} S_{pq} \langle J_{pq} + J_{qp} \rangle_{ij} \quad (3.12)$$

Where $p, q = x, y, z$.

For pair of protons (D_{ij}^{ind}) is usually neglected since the major contribution to indirect Spin-Spin coupling comes from the spherically symmetric Fermi contact term. This (D_{ij}^{ind}) the anisotropic, interaction term is considerably large for fluorine compounds and can not be neglected. The present work deals only with protons hence neglecting the anisotropic interaction or Pseudo-dipolar coupling constant, the actual indirect spin-spin interaction can be written as

$$\begin{aligned}
 \mathcal{H}_i &= \sum_{i,j} J_{ij} \left[I_{zi} \cdot I_{zj} + \frac{1}{2} (I_{1i}^+ I_{1j}^- + I_{1i}^- I_{1j}^+) \right] \\
 &+ \sum_{i,j} J_{ij}^a \left[2I_{zi} I_{zj} - \frac{1}{2} (I_{1i}^+ I_{1j}^- + I_{1i}^- I_{1j}^+) \right] \\
 &= J_{ij} + J_{ij}^a \\
 &= J_{ij} + D_{ij}^{\text{ind}} \text{ -- neglect.} \\
 &= J_{ij}.
 \end{aligned} \tag{3.13}$$

3.5 Analysis of the Spectra :

The nuclear spin Hamiltonian describing the NMR spectra of spin $\frac{1}{2}$ nuclei in diamagnetic molecules oriented in nematic liquid crystal solvents can be written on the basis of equation (3.2) with the consideration of equations (3.9), (3.13) and (3.4) as

$$\begin{aligned}
 \mathcal{H} = & - \sum_i (1 - \delta_i - \delta_{ia}) \gamma_i \hbar I_{zi} + \sum_{i < j} (J_{ij} + 2D_{ij}) \tilde{I}_{zi} \tilde{I}_{zj} \\
 & + \frac{1}{2} \sum_{i < j} (J_{ij} - D_{ij}) (\tilde{I}_{i+} \tilde{I}_{j-} + \tilde{I}_{i-} \tilde{I}_{j+})
 \end{aligned} \tag{3.14}$$

with the symbols having their usual meaning.

Once the spectrum has been properly recorded, the line positions determined, the line intensities observed, the spectrum is interpreted in terms of chemical shifts, indirect couplings and direct dipole-dipole couplings. The spectrum of oriented molecules are dominantly influenced by direct dipolar couplings, specifically for protons. Therefore, for obtaining an estimate of the direct dipole-dipole couplings, the chemical shifts and the indirect spin-spin couplings are usually taken from the literature on the spectra in isotropic media for the same or similar compounds.

The direct dipole-dipole couplings are written in terms of the molecular geometry and order parameters. A rough estimate of the molecular geometry on the same or similar compounds is then introduced into these relations. In the next step, one of the S-values is fixed and several trial spectra are calculated by varying other S-values using computer programme.

Many computer programmes are now available for the spectral analysis. The one most commonly used is "LAOCOONOR" (40) which is the modification of the "LAOCOON PART II" (41) and "LAOCN III" for isotropic systems. The recent and commonly used computer programme "LEQUOR" (42) considers magnetic equivalence factorisation dipolar couplings along with chemical shifts and indirect spin-spin couplings. It requires short running time. For the present work "LAOCOONOR" computer programme is used.

The programme in the first part computes the spectrum from the guessed values of the chemical shift, indirect spin-spin couplings and direct dipole-dipole couplings. The part I of 'LAOCOONOR' programme is carried on till a visual resemblance between calculated and the observed spectra is obtained. Some of the lines in this spectrum can then be identified with the corresponding lines in the observed spectrum and they can be used to compute the parameters using part II of the "LAOCOONOR" programme. In the spectrum thus computed, many more lines can usually be identified with those in the observed ones. This new assignment is then used to obtain 'betterfit' parameters. The procedure is repeated by assigning more and more lines, till a satisfactory agreement between the observed and the calculated spectrum is obtained which

makes use of the pre-stored output of part I. The root mean square error (RMS error) between the experimental and the calculated¹ line positions usually corresponds to the statistical error of the line position measurements since in most cases the number of observed lines is must² larger than the number of parameters to be derived. The indirect spin-spin couplings are usually assumed to be the same as in the isotropic media and the iterations are carried out only on the chemical shifts and direct dipole-dipole couplings. The "maximum error" between the experimental and calculated line positions in the spectra of the molecules should be less than 3Hzs.

The NMR spectra of oriented molecules do not provide the absolute signs of D's and J's. If the sign of J is assumed from the work in isotropic media, those of D's can be obtained from the 'best fit' iterations. For the estimation of the errors in the parameters the following procedures are followed (40, 43). In one of the methods, the line positions are changed randomly by amount³ of statistical error in the line position measurements. These line positions are then used for calculating the parameters iteratively. Many such calculations are carried out. The largest difference between the parameters so obtained are taken as error in the respective parameters

(40). In the other method (43) only one such calculation is carried out and that is to change the experimental line positions by the amount of the statistical error of the line position measurements such that it produces a larger deviation between the experimental and the calculated line positions. The parameters are then obtained iteratively using these line positions and the difference between these and the correct parameters gives the error. The errors obtained by these two methods are then compared with the most probable error of the parameters obtained from the "LAOCOONOR" programme.

3.6 Interpretation of Dipolar couplings and- molecular Geometry of Solute :

If the number of independent dipolar couplings is equal to the sum of number of independent orientation parameters and the distance ratios necessary to describe the geometry, the explicit relations between the D-values, internuclear distance ratios and order parameters can be used to derive the molecular geometry depending on the symmetry of molecule (39). However, if the number of independent D-values exceeds the sum of the number of independent parameters necessary to specify the orientation and molecular geometry, a "least square"

method is used. For this purpose, the computer programme "SHAPE" (44) was used. In this programme, the dipolar couplings may be given different weights and a weighted least square fit can be obtained iteratively. In the present work equal weights to all the dipolar coupling constants were given.

3.7 Influence of molecular vibrations :

In general, the molecules are not perfectly rigid and when solute is dissolved in nematic liquid crystal solvent the molecules have random motion along with molecular vibrations. In NMR we get the averaged result of molecular random motion and vibrations within the solution. Geometrical data thus derived with NMR is not directly comparable unless corrections for the influence of molecular vibrations are applied.

The problem of applying vibrational corrections to geometries derived from NMR experiments was first discussed as early as 1967(45) and has since attracted considerable attention. A very simple model for such a purpose is one in which only the vibrations of hydrogen are taken into account and those of the heavy atoms are neglected (46). The direct dipolar coupling is expanded in a Taylor series about the equilibrium geometry and

the terms higher than quadratic can be neglected such that

$$D_{\text{NMR}} = D_e + \sum_q \left(\frac{\partial D}{\partial q} \right)_e \langle \Delta q \rangle + \frac{1}{2} \sum_q \left(\frac{\partial^2 D}{\partial q^2} \right)_e \langle \Delta q^2 \rangle \quad (3.15)$$

Where D_{NMR} is the direct dipolar coupling measured by NMR; e is equilibrium configuration

$\langle \Delta q \rangle$ is average vibrational amplitude along the direction of the cartesian coordinate system.

$\langle \Delta q^2 \rangle$ is corresponding mean square average.

It is found that the corrections are small for H-H couplings. However, it has now been shown that for comparison of geometries obtained from different techniques, an average structure ~~is~~ derived by applying purely the harmonic corrections is sufficient (47-49). computer programmes are now available that allow the calculations of the average structure provided mean square amplitudes are known (50).

In the present work, only H-H distances are studied; such influences have therefore been neglected.

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