

NMR

Basic Principles and Progress
Grundlagen und Fortschritte

Volume 1

Editors: P. Diehl E. Fluck R. Kosfeld

With 53 Figures



Springer-Verlag New York · Heidelberg · Berlin 1969

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Title No. 3361

Preface

Nuclear magnetic resonance spectroscopy, which has evolved only within the last 20 years, has become one of the very important tools in chemistry and physics. The literature on its theory and application has grown immensely and a comprehensive and adequate treatment of all branches by one author, or even by several, becomes increasingly difficult.

This series is planned to present articles written by experts working in various fields of nuclear magnetic resonance spectroscopy, and will contain review articles as well as progress reports and original work, its main aim, however, is to fill a gap, existing in literature, by publishing articles written by specialists, which take the reader from the introductory stage to the latest development in the field.

The editors are grateful to the authors for the time and effort spent in writing the articles, and for their invaluable cooperation.

The Editors

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NMR Studies of Molecules Oriented in the Nematic Phase of Liquid Crystals

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1. Introduction

In nuclear magnetic resonance (NMR) experiments with liquids and gases, the local magnetic fields at the sites of the nuclei, responsible for the various transition frequencies, change with the orientation of the molecules relative to the applied external magnetic field. As a consequence of rapid molecular motion only the average values of the shift and coupling parameters can be observed. For nuclei with spin $1/2$, each of the chemical shifts and the indirect spin-spin coupling constants, which are actually second rank tensors with as many as nine independent components, affect the normal high resolution NMR spectra (in isotropic media) as single parameters proportional to the trace of the tensors. This simplifies the normal NMR spectra but at the same time imposes a considerable loss of information. Furthermore, in isotropic media, the direct magnetic dipole-dipole interaction transmitted through space becomes zero when averaged. This interaction, proportional to the inverse cube of the inter-nuclear distance, is a symmetric and traceless tensor having a maximum of five independent components. The geometrical information which it carries is also lost as a consequence of the averaging process.

Similarly, the interaction of the nuclear electric quadrupole moment with the local electric field gradient for nuclei with spin $> 1/2$ averages zero in the normal high resolution spectra. The direct spin-spin coupling as well as the quadrupole interaction affect the spectra through relaxation processes only.

In solid state NMR both interactions have been directly observed since the earliest experiments, providing data on the crystal structure. However, intermolecular contributions limit the precision in this area. Several years ago, this situation induced NMR spectroscopists to search for possibilities of molecular orientation in which the direct intermolecular dipole-dipole coupling still averages zero while the intramolecular coupling is finite. This was thought to allow the study of direct dipolar and quadrupolar interactions as well as anisotropies of the indirect couplings and chemical shifts. Several types of experiments, e.g. application of an electric field [1], adsorption of molecules in polymers with subsequent stretching, or embedding in zeolite crystal channels [2] were devised. These methods met with only limited success until the use of nematic phases of liquid crystals as orienting solvents was introduced by SAUPE and ENGLERT [3, 4] in 1963.

Since then the spectroscopy of oriented molecules has developed rapidly, the primary objective being the study of direct spin-spin couplings which provide information on relative internuclear distances, bond angles and absolute signs of indirect coupling constants. In the meantime, several reviews on the subject [5-10] have appeared but the rapid development warrants the consolidation of the existing data on this fascinating and by no means difficult field of NMR spectroscopy.

2. Liquid Crystals

It was observed as early as 1888 that certain organic substances have two distinct melting points [11]. For example, cholesteryl benzoate turns into a cloudy liquid at 145°C and becomes clear at 179°C. The cloudy intermediate phase was found to have a crystal-like structure and the name 'liquid crystal' was suggested for it. Liquid crystals usually consist of rod-like molecules containing benzene rings. The intermolecular forces tend to orient the molecules in the liquid crystal phase with their longest axes parallel.

2.1. Classification of Liquid Crystal Phases

There are three basic types of liquid crystalline phases: smectic, nematic and cholesteric. They differ in the degree and type of local ordering. Molecules in the smectic phase are 'parallel' and aligned in layers (Fig. 1). Due to the thermal

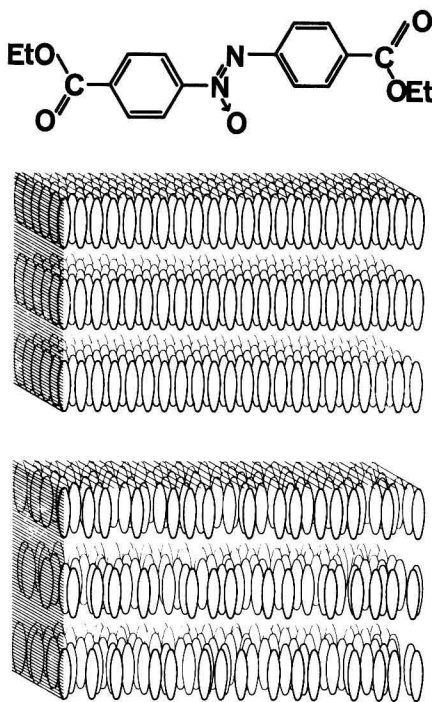


Fig. 1. The structure of a smectic phase, e. g. 4-4'-di-ethyl azoxybenzoate [9]. (Reprinted from Österreichische Chemiker-Zeitung, 4, 115 (1967), copyright (1967). Reprinted by permission of the copyright owner)

energy of the molecules, however, there is a certain scatter in the orientation of the longest molecular axes. The nematic phase is ordered to a lesser extent than

the smectic (Fig. 2) since there is no separation into layers. The cholesteric phase (Fig. 3) resembles the nematic phase. The direction of the longest mole-

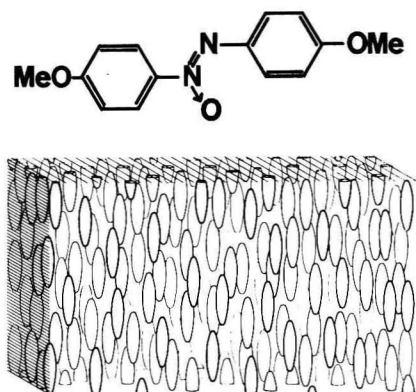


Fig. 2. Arrangement of molecules in a nematic phase, e. g. 4-4'-di-methoxy azoxy benzene [4]. (Reprinted from Österreichische Chemiker-Zeitung, **4**, 115 (1967), copyright (1967). Reprinted by permission of the copyright owner)

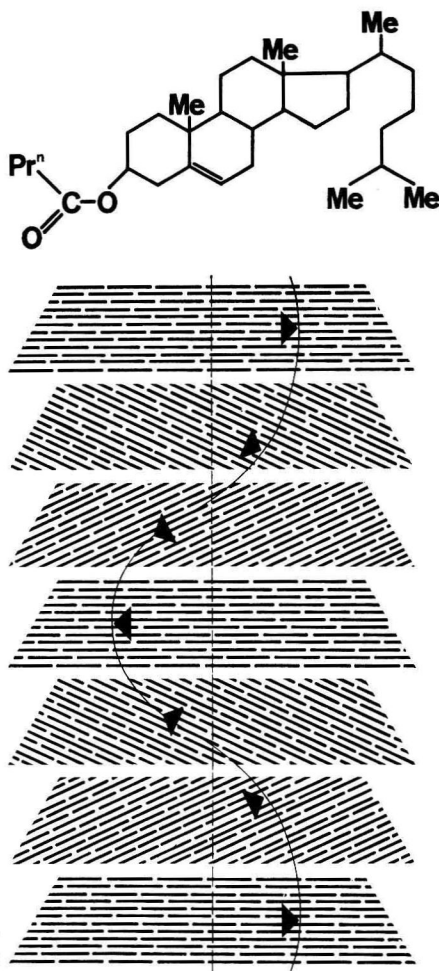


Fig. 3. The molecular arrangement in a cholesteric mesophase, e. g. cholesteryl propionate [9]. (Reprinted from Österreichische Chemiker-Zeitung, **4**, 115 (1967), copyright (1967). Reprinted by permission of the copyright owner)

cular axis in each layer is slightly displaced with respect to the neighbouring layers. The overall displacement follows a helical path (Fig. 3). A mixture of two cholesteric compounds of opposite rotatory powers may produce a nematic phase [12–15].

Of the three liquid crystalline phases, the nematic assumes the greatest importance in NMR spectroscopy. All further discussion is devoted to this type.

2.2. Theories of the Liquid Crystalline State

Two main theories have been proposed for a description of the liquid crystalline state; these are the swarm [16] and the distortion or continuum [17] theories.

According to the swarm theory, large numbers of liquid crystal molecules (approximately 10^5) aggregate in swarms. Within these clusters the molecules are arranged 'parallel' primarily due to dispersion forces, but there is no appreciable interaction between various swarms. Their life time is short, i.e. they form and decay continuously, producing a strong scatter of light leading to a cloudy appearance. Magnetic fields of several hundred GAUSS cause an alignment of the aggregates such that the longest axes of the molecules or the directions of smallest diamagnetic susceptibility are parallel to the field. The motion of a molecule dissolved in this phase is anisotropic.

The swarm theory, however, does not explain several liquid crystal properties such as the relatively continuous structure of the phase when observed between crossed NICOL prisms under a microscope, or the elastic properties evidenced by a return of the liquid crystal to its original shape after distortion. The elastic property can only be understood on the basis of a continuous change of orientation as a function of position which, contrary to swarm theory, indicates a long range interaction. These phenomena are taken into account in the continuum or distortion theory.

According to this theory also, a magnetic field orients the liquid crystal and the molecules dissolved therein.

Equivalence of the two theories when applied to NMR experiments has been demonstrated [18].

2.3. Nematic Phases

A large number of organic substances exhibit liquid crystalline properties [19]. Those which have been used in NMR are compiled in Appendix A together with the temperature range of their nematic state in the pure form. The Roman numerals in Appendix A are used to identify the liquid crystals throughout this article.

Addition of any solute to a liquid crystal usually lowers the temperature limits of the nematic range. The liquid crystal (II) for instance may be used at about 50°C and (I) at room temperature. A similar depression of the nematic range may occur in mixtures of liquid crystals [20, 21].

Another type of nematic phase is obtained by mixing cholesteric compounds of opposite optical rotatory powers. A 1:9:1 mixture by weight of cholesteryl chloride (*l*-rotatory) and cholesteryl myristate (*d*-rotatory) used as a solvent gives a characteristic spectrum of dissolved benzene (partially oriented) at 40°C [15]. The nematic range may be shifted between 23°C and 130°C by a suitable choice of cholesteryl esters.

A transition from the cholesteric to the nematic phase by application of a magnetic field has been observed [15]. The cholesteric mixture of 2.4 mole percent of optically active amyloxyazoxy benzene in the liquid crystal (III) provides a solvent displaying a typical nematic phase spectrum for dissolved benzene at about 104°C [15]. Similarly poly- γ -benzyl-L-glutamate, which forms a cholesteric phase in solutions above 12% of the polymer, has been used for observing the usual spectra of oriented molecules [22–24] such as methylene chloride, dimethylformamide and *p*-xylene in a nematic phase.

A further type of nematic phase, the lyotropic mesophase, formed by a mixture of C_8 or C_{10} alkyl sulphates plus the corresponding alcohols, sodium sulphate and water (or heavy water) in approximate ratio 8:1:1:10 respectively, has also been suggested [25] and used [26, 27] between 10°C and 75°C.

A liquid crystal molecule generally contains a large number of protons. Due to complex direct dipole-dipole interaction between the many protons, the NMR spectrum of the pure nematic phase usually gives an unresolved spectrum with little observable fine structure. The molecules which are dissolved in the nematic phase, however, give relatively sharp lines and the direct dipole-dipole interaction is manifested by line splitting in the spectra [3].

3. Experimental

NMR spectra of molecules dissolved in the nematic phase of liquid crystals can be studied with the aid of a standard high resolution spectrometer equipped with a variable temperature assembly. Ordinarily a solution of about 20 mole percent concentration of the solute in the liquid crystal is prepared. The mixture is heated above the clearing point in order to obtain a homogeneous solution. The spectrum is then recorded at the appropriate lower temperature.

Line-widths generally range from 4 to 60 Hz. They are often narrower near the centre of the spectrum than in the wings. This may be attributed to the superimposed effects of temperature-, concentration- and field-gradients. Line-width as well as degree of orientation are temperature and concentration dependent. Reduced temperature and concentration usually produce sharper lines because of smaller gradients [28]. Low concentrations, on the other hand, reduce the signal to noise ratio. The temperature gradients may in practice be lowered by using pure or mixed liquid crystals [20, 21] which form nematic solutions at room temperature.

Since the long molecular axes of the liquid crystalline nematic phase are oriented parallel to the applied magnetic field, rapid rotation of the sample about an axis perpendicular to the field destroys the orientation. Most of the experiments are therefore performed without spinning the sample. This introduces an additional contribution to the line-widths due to field inhomogeneities. In certain cases, it has been observed that slow spinning of the sample is possible without destruction of orientation; the degree of orientation, however, is reduced with increasing speed of rotation [28]. For lyotropic phases as well as for oriented liquid crystals in magnetic fields produced by superconducting magnets or for orientations produced by electric fields applied perpendicular to the magnetic field, the alignment of the mesophase is such that it is possible to spin the sample without destruction of the orientation [26, 29]. Line-widths of the order of 1 – 5 Hz have thus been obtained.

4. Basic Theory (for $I = 1/2$)

High resolution NMR spectra of molecules dissolved in a nematic phase are generally several kHz wide. If the chemical shifts are negligible, the spectra are symmetrical about the centre.

The spectra are theoretically well understood [1] and the orientation is interpreted in terms of an ordering matrix $\{S\}$ [30]. An alternative notation for the orientation has also been used and the anisotropic motion of the solute molecules expressed as an expansion of a probability function in terms of real spherical harmonics [31]. Both notations are discussed in the following section.

4.1. The Hamiltonian of Oriented Spin Systems

It has already been pointed out that the spectra of oriented molecules depend upon the direct dipole-dipole coupling (D_{ij}), the indirect coupling (J_{ij}) and the chemical shift $(1 - \sigma_i - \sigma_{ia}) \cdot \nu_0$. The Hamiltonian (\mathcal{H}) (eq. 1) of the oriented system differs from that of the isotropic one by additional terms due to direct couplings and the anisotropy of the chemical shift:

$$\mathcal{H} = - \left[\sum_i (1 - \sigma_i - \sigma_{ia}) \nu_0 \tilde{I}_{zi} + \sum_{i < j} (J_{ij} + 2 D_{ij}) \tilde{I}_{zi} \tilde{I}_{zj} + (1/2) \sum_{i < j} (J_{ij} - D_{ij}) (\tilde{I}_i^+ \tilde{I}_j^- + \tilde{I}_i^- \tilde{I}_j^+) \right]. \quad (1)$$

In eq. (1), J_{ij} and σ_i represent one third of the traces of the corresponding tensors and are identical to the indirect spin-spin coupling and chemical shift observed in normal high resolution NMR spectra in isotropic media. σ_{ia} , the anisotropy of the chemical shift, and D_{ij} , the direct spin-spin coupling, are more complex quantities. They are discussed in the text below.

Eq. (1) shows that the Hamiltonian of an isotropic case transforms easily into that of an oriented system. In the diagonal and off-diagonal contributions to all elements of the matrix, J_{ij} has been replaced by $(J_{ij} + 2 D_{ij})$ and $(J_{ij} - D_{ij})$, respectively, and $(1 - \sigma_i - \sigma_{ia})$ substituted for $(1 - \sigma_i)$.

4.2. The Direct Coupling (D_{ij}) and the Orientation Matrix $\{S\}$

The direct coupling D_{ij} may contain a contribution $D_{ij}^{\text{ind.}}$ from the anisotropy of the indirect spin-spin coupling such that:

$$D_{ij} = D_{ij}^{\text{ind.}} + D_{ij}^{\text{dir.}}. \quad (2)$$

$D_{ij}^{\text{ind.}}$ has the same directional dependence as the direct coupling ($D_{ij}^{\text{dir.}}$). It is therefore called 'pseudo dipolar coupling'. For a pair of protons this type of coupling is small or negligible because of the spherical symmetry of the predominant contact term. For fluorine, on the other hand, the electron-nuclear dipole interactions and the electron orbital current-nuclear dipole contributions to the coupling become significant. These anisotropic interactions give rise to a measurable pseudo dipolar F—F coupling ($D_{\text{FF}}^{\text{ind.}}$) [32–33]. When the interacting nuclei are protons, D_{ij} is set equal to $D_{ij}^{\text{dir.}}$ if the assumed and observed geometries coincide. Discrepancies caused by intermolecular motion have been observed [34] and are denoted by D_{ij}^{pseudo} .

$D_{ij}^{\text{dir.}}$ is defined by eq. (3):

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

where θ_{ij} is the 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 (\AA) and D_{ij} in kHz, then the constant $(h\gamma_i\gamma_j/4\pi^2)$ is equal to 120.067 kHz \AA^3 for a pair of protons. For a proton and a fluorine, it is 112.955 kHz \AA^3 ; and for a pair of fluorines, its value is 106.265 kHz \AA^3 .

If 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, (as is assumed in this article unless otherwise stated), eq. (3) can be written as:

$$D_{ij}^{\text{dir.}} = -\frac{h\gamma_i\gamma_j}{4\pi^2 r_{ij}^3} \cdot S_{ij} \quad (4)$$

where S_{ij} is the degree of orientation of the axis passing through i and j , and r_{ij} is constant, meaning that the influence of vibrational motions is neglected.

The S -values of different molecular axes are inter-dependent. The average orientation of a rigid molecule is described by a symmetrical and traceless matrix $\{S\}$ with five independent elements [30]. Using ξ, η and ζ as the axes of a Cartesian coordinate system fixed within the molecule and θ_ξ, θ_η and θ_ζ as the angles between these molecular axes and the magnetic field direction, the definition of the matrix elements is given by (5):

$$S_{pq} = (1/2) \langle 3 \cos \theta_p \cos \theta_q - \delta_{pq} \rangle \quad (5)$$

$p, q = \xi, \eta, \zeta$

where δ_{pq} is the Kronecker delta ($\delta_{pq} = 1$ for $p = q$, $\delta_{pq} = 0$ for $p \neq q$).

The matrix elements S_{pq} are related to the S -values of an axis, forming the angles $\alpha_\xi^a, \alpha_\eta^a$ and α_ζ^a with the molecule-fixed coordinate system according to eq. (6):

$$S_a = \sum_{p,q} \cos \alpha_p^a \cos \alpha_q^a \cdot S_{pq} \quad (6)$$

This shows that the degree of orientation of any axis can be derived if $\{S\}$ is known and that the matrix elements S_{pq} may be obtained given sufficient S_a values.

Eq. (5) defines the range of S as $-0.5 \leq S \leq +1$. At $S_a = 1$ the a -axis is parallel to the applied magnetic field direction, and at $S_a = -0.5$ perpendicular to it. Moreover, the absolute sign of the orientation parameter is positive when the value is larger than 0.5.

By a suitable choice of molecular axes, the number of independent S -values necessary for the description of orientation can be reduced from five to one depending upon the symmetry of the molecule. If the axis is 3-fold or more, its selection as the z -axis causes S_{zz} to be the only independent orientation parameter. If there are two perpendicular planes of symmetry both parallel to the z -axis,

a choice of x and y axes in these planes leaves only S_{zz} and $S_{xx} - S_{yy}$. If there is only one plane of symmetry, S_{xx} , S_{yy} and S_{xy} are all independent. It should be noted that in this case, contrary to normal NMR, the plane which contains all interacting nuclei constitutes a plane of symmetry. Table 1 gives the number of independent S -values as a function of molecular symmetry.

Table 1. *Number of parameters necessary for the description of orientation*
($S_{xx} + S_{yy} + S_{zz} = 0$)

Symmetry of the molecule	Number of independent elements of the S -matrix	Independent elements of the S -matrix
3-fold or greater axis	1	S_{zz}
2 perpendicular planes	2	S_{zz} , $S_{xx} - S_{yy}$
1 plane	3	S_{xx} , S_{yy} , S_{xy}
none	5	S_{xx} , S_{yy} , S_{xy} , S_{xz} , S_{yz}

The S -matrix obtained experimentally may be diagonalized so that the final number of orientation parameters does not exceed 2. This corresponds to a suitable molecular coordinate system which in general must be assigned empirically.

A more pictorial representation of orientation is obtained by describing the anisotropic motion of the molecules with a probability function $P(\theta, \varphi)$ expanded in real spherical harmonics. $P(\theta, \varphi)$ is assumed to be the probability per unit solid angle that the applied magnetic field direction is θ and φ in spherical polar coordinates relative to the molecule-fixed Cartesian coordinate system [31]. The expansion is given in formula (7):

$$P(\theta, \varphi) = (1/4\pi) \left\{ 1 + \left(\frac{5}{2}\right) [(3 \cos^2 \theta - 1) \cdot S_{zz} + \sin^2 \theta \cdot \cos 2\varphi \cdot (S_{xx} - S_{yy}) + 4 \sin \theta \cdot \cos \theta \cdot \cos \varphi \cdot S_{xz} + 4 \sin \theta \cdot \cos \theta \cdot \sin \varphi \cdot S_{yz} + 2 \sin^2 \theta \cdot \sin 2\varphi \cdot S_{xy}] \right\} \quad (7)$$

This approach is similar to a truncated expansion of an orientation probability function based on a Boltzman treatment (section 4.6) in which $\exp \{-(q/kT) \cos^2 \theta\}$ is set equal to $\{1 - (q/kT) \cos^2 \theta\}$. Consequently, $P(\theta, \varphi)$ does not rigorously describe the orientation probability except in the case of small orientations. For large orientation parameters, $P(\theta, \varphi)$ may even assume negative values. On the other hand such a truncation cannot be avoided since the NMR-experiments do not provide more information.

4.3. An Alternative Description of Orientation

In an alternative description of the orientation [31], the probability function $P(\theta, \varphi)$ (eq. (7)) is expressed as follows:

$$P(\theta, \varphi) = (1/4\pi) + c_{3z^2-r^2} \cdot D_{3z^2-r^2} + c_{x^2-y^2} \cdot D_{x^2-y^2} + c_{xz} \cdot D_{xz} + c_{yz} \cdot D_{yz} + c_{xy} \cdot D_{xy} \quad (8)$$

Here,

$$\begin{aligned}
 D_{3z^2-r^2} &= (\sqrt{5/8} \pi)(3 \cos^2 \theta - 1) \\
 D_{x^2-y^2} &= (\sqrt{15/8} \pi)(\sin^2 \theta \cdot \cos 2\phi) \\
 D_{xz} &= (\sqrt{15/4} \pi)(\sin \theta \cdot \cos \theta \cdot \cos \phi) \\
 D_{yz} &= (\sqrt{15/4} \pi)(\sin \theta \cdot \cos \theta \cdot \sin \phi) \\
 D_{xy} &= (\sqrt{15/8} \pi)(\sin^2 \theta \cdot \sin 2\phi)
 \end{aligned} \tag{9}$$

The coefficients $c_{3z^2-r^2}$, $c_{x^2-y^2}$, c_{xz} , c_{yz} and c_{xy} are called motional constants. To these, D_{ij}^{dir} is related by eq. (10):

$$\begin{aligned}
 D_{ij}^{\text{dir}} = & -\frac{h\gamma_i\gamma_j}{4\pi^2\sqrt{5}} \cdot \left\{ +c_{3z^2-r^2} \left[\left\langle \frac{(\Delta z_{ij})^2}{r_{ij}^5} \right\rangle_{\text{Av}} - (1/2) \left\langle \frac{(\Delta x_{ij})^2}{r_{ij}^5} \right\rangle_{\text{Av}} - (1/2) \left\langle \frac{(\Delta y_{ij})^2}{r_{ij}^5} \right\rangle_{\text{Av}} \right] \right. \\
 & + c_{x^2-y^2} \sqrt{3} \left[(1/2) \left\langle \frac{(\Delta x_{ij})^2}{r_{ij}^5} \right\rangle_{\text{Av}} - (1/2) \left\langle \frac{(\Delta y_{ij})^2}{r_{ij}^5} \right\rangle_{\text{Av}} \right] + c_{xz} \sqrt{3} \left[\left\langle \frac{(\Delta x_{ij})(\Delta z_{ij})}{r_{ij}^5} \right\rangle_{\text{Av}} \right] \\
 & \left. + c_{yz} \sqrt{3} \left[\left\langle \frac{(\Delta y_{ij})(\Delta z_{ij})}{r_{ij}^5} \right\rangle_{\text{Av}} \right] + c_{xy} \sqrt{3} \left[\left\langle \frac{(\Delta x_{ij})(\Delta y_{ij})}{r_{ij}^5} \right\rangle_{\text{Av}} \right] \right\}. \tag{10}
 \end{aligned}$$

where $\Delta z_{ij} = z_i - z_j$, $\Delta x_{ij} = x_i - x_j$ and $\Delta y_{ij} = y_i - y_j$ such that x_p , y_p and z_p are the coordinates of the p 'th nucleus in the molecule-fixed system and the average is taken over the internal motion. It should be noted that eq. (10) differs from that of reference [31] by a factor of 0.5. This introduces equivalence between the definitions of D_{ij}^{dir} given in references [30] and [31]. Throughout this article values of D_{ij}^{dir} obtained according to [31] have been divided by 2. The relations between the S -values and the motional constants are as follows:

$$\begin{aligned}
 c_{3z^2-r^2} &= \sqrt{5} \cdot S_{zz} \cdot (1/2)(3 \cos^2 \alpha - 1), \\
 c_{x^2-y^2} &= \sqrt{(\frac{5}{3})} \cdot (S_{xx} - S_{yy}) \cdot (1/2)(3 \cos^2 \alpha - 1), \\
 c_{xz} &= 2 \sqrt{(\frac{5}{3})} \cdot S_{xz} \cdot (1/2)(3 \cos^2 \alpha - 1), \\
 c_{yz} &= 2 \sqrt{(\frac{5}{3})} \cdot S_{yz} \cdot (1/2)(3 \cos^2 \alpha - 1), \\
 c_{xy} &= 2 \sqrt{(\frac{5}{3})} \cdot S_{xy} \cdot (1/2)(3 \cos^2 \alpha - 1),
 \end{aligned} \tag{11}$$

where α is the angle between the liquid crystal optic axis and the direction of the magnetic field.

4.4. The Anisotropy of Chemical Shift

Analogous to formulae (7) and (8), the anisotropy of chemical shift may be expressed in terms of the shielding tensor components [31]:

$$\begin{aligned}
 (\sigma_i + \sigma_{ia}) = & \left(\frac{1}{3}\right)(\sigma_{xxi} + \sigma_{yyi} + \sigma_{zzi}) + c_{3z^2-r^2} \cdot (2/3 \sqrt{5}) [\sigma_{zzi} + (1/2)(\sigma_{xxi} + \sigma_{yyi})] \\
 & + c_{x^2-y^2} \left(\frac{1}{\sqrt{15}}\right) (\sigma_{xxi} - \sigma_{yyi}) + c_{xz} \left(\frac{1}{\sqrt{15}}\right) (\sigma_{xzi} + \sigma_{zxi}) \\
 & + c_{yz} \left(\frac{1}{\sqrt{15}}\right) (\sigma_{yzi} + \sigma_{zyi}) + c_{xy} \cdot \left(\frac{1}{\sqrt{15}}\right) (\sigma_{xyi} + \sigma_{yxi}).
 \end{aligned} \tag{12}$$

Substitution of relations (11) in eq. (12) results in eq. (13) for $\alpha = 0$:

$$(\sigma_i + \sigma_{ia}) = \left(\frac{1}{3}\right)(\sigma_{xxi} + \sigma_{yyi} + \sigma_{zzi}) + \left(\frac{2}{3}\right)[(S_{zz} \sigma_{zzi} + S_{yy} \sigma_{yyi} + S_{xx} \sigma_{xxi}) + S_{xz} \cdot (\sigma_{xzi} + \sigma_{zxi}) + S_{yz} \cdot (\sigma_{yzi} + \sigma_{zyi}) + S_{xy} (\sigma_{xyi} + \sigma_{yxi})] \quad (13)$$

Molecular symmetry reduces the number of non-zero elements of the chemical shift tensor (Table 2). For example if the axis is 3-fold or higher, eq. (13) reduces to (14):

$$\begin{aligned} (\sigma_i + \sigma_{ia}) &= \left(\frac{1}{3}\right)(\sigma_{xxi} + \sigma_{yyi} + \sigma_{zzi}) + \left(\frac{2}{3}\right)S_{zz} \cdot [\sigma_{zzi} - (1/2)(\sigma_{xxi} + \sigma_{yyi})] \cdot \\ \text{or,} \quad \sigma_{ia} &= \left(\frac{2}{3}\right)S_{zz} \Delta\sigma_i \\ \text{where} \quad \Delta\sigma_i &= [\sigma_{zzi} - (1/2)(\sigma_{xxi} + \sigma_{yyi})] \cdot \end{aligned} \quad (14)$$

Table 2. *Molecular symmetry and the non-zero elements of the chemical shift tensor*

Symmetry of the molecule	Number of non-zero elements of chemical shift tensor	Non-zero elements of chemical shift tensor
3-fold or greater axis	2	$\sigma_{zz}, \sigma_{xx} + \sigma_{yy}$
2 perpendicular planes	3	$\sigma_{zz}, \sigma_{xx} + \sigma_{yy}, \sigma_{xx} - \sigma_{yy}$
1 plane	5	$\sigma_{zz}, \sigma_{xx}, \sigma_{yz}, \sigma_{xz}, \sigma_{zx}$
none	9	$\sigma_{zz}, \sigma_{xx}, \sigma_{yy}, \sigma_{xy}, \sigma_{yx}, \sigma_{xz}, \sigma_{zx}, \sigma_{yz}, \sigma_{zy}$

4.5. The Anisotropic Indirect Spin-Spin Coupling Constant (D_{ij}^{ind})

By substitution of J for each σ in eqs. (12), (13) and (14), the corresponding relations for the anisotropic indirect coupling constants are obtained. $J_i = \frac{1}{3}(J_{xx} + J_{yy} + J_{zz})$ is the isotropic value of the coupling constant, i. e. the indirect coupling. J_{ia} corresponds to $2 D_{ij}^{\text{ind}}$.

4.6. The Factors Governing Orientation of Solute Molecules in the Nematic Solvent

In principle, dispersion forces, permanent electric dipole moments, steric effects and specific interactions may affect the orientation of the solute molecules in the nematic phase. Of these only the influences of dispersion forces and permanent electric dipole moments have been studied in detail [35–36]. Investigations on a variety of chloro [35] and fluoro [36] benzenes in several solvents at various temperatures and concentrations, have shown that only the former is of major importance. The discussion of the problem has been simplified by assuming apolar orientation, validity of the dipole-dipole approximation and absence of specific solute-solvent interaction [142]. The orientation dependent part (F) of the molecular free energy is then given by eq. (15):

$$F = -a_1 \cos^2 \theta_1 - a_2 \cos^2 \theta_2 \quad (15)$$