NMR as a tool in the investigation of fundamental problems in ordered liquids

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Received 3 June 2005; received in revised form 31 August 2005
Available online 2 November 2005

Abstract

An overview is presented of modern NMR techniques and a variety of experimental and theoretical tools employed in the study of solutes dissolved in liquid crystals. The NMR techniques involve multiple quantum and spectral subtraction methods. In addition, various experimental and theoretical tools are discussed, including: the theoretical background of observed order parameters; the use of ‘magic mixtures’ to separate orientational contributions; the reorientation–vibration interaction; the use of model calculations based on size and shape of the various solutes; and the use of computer simulations. Applications to the benchmark probe molecules hydrogen, methane, ethane, and butane and their isotopomers are treated.

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Keywords: NMR; Hydrogen; Methane; Ethane; Butane; Liquid crystal; Order parameter

1. Introduction

Among the abundance of scientific meetings in the area of magnetic resonance that one can visit, the Zakopane NMR Summer School is one that many of us would very much hesitate to miss. Of course meeting international colleagues at any conference is usually a pleasure but, as many of us have learned to appreciate over the many years that Jerzy Blicharski and Barbara Blicharska have organized this annual event, the Zakopane meeting has something special to offer. Starting off as a scientific meeting where for the first time East met West, it soon developed into an occasion where on a regular basis colleagues got together in Poland in an atmosphere of international friendship that the initiators know so well how to create. It is only fitting that on the occasion of the last Zakopane meeting that Jerzy and Barbara will organize, a journal volume will be published in recognition of their invaluable contributions to the world of magnetic resonance. As long time participants and contributors it is our pleasure to give an overview of the research that we have presented, usually jointly, at a succession of Zakopane meetings. Since the organizers have always insisted on calling their conference a Summer School, it seems only fitting on this occasion to stress the general aspects of our work over the years. Moreover, part of the work that will be described in this contribution would not have been possible without a number of essential scientific contacts that were established for the first time in Zakopane.

Our research is concerned with partially ordered liquids such as liquid crystals. In an anisotropic environment the molecular rotational motion is somewhat perturbed, leading to a degree of molecular orientational order. Since observables in nuclear magnetic resonance (NMR) are essentially represented by second-rank tensors, the degree of molecular orientational order in a liquid crystal leads to NMR spectra in which dipolar and quadrupolar couplings, as well as anisotropies in chemical shielding and indirect couplings, no longer average to zero as is the case in an isotropic liquid. Clearly, NMR is a uniquely suitable tool for the study of ordered liquids because the NMR spectra of solutes in anisotropic media contain detailed...
information about solute properties. However, there is much more. Since the details of the interaction between solute and liquid crystal solvent are not known a priori, for many years the ensuing degree of orientational order was essentially unpredictable. From our work it has become apparent that small, well-characterized solutes are eminently suited to act as probes of the anisotropic environment caused by the solvent liquid crystal. In this way the solute orientational order serves to monitor and study the intermolecular potential. In the same spirit, a key result has been the discovery that the relative contributions of the mechanisms that lead to overall solute orientational order can be varied by forming mixtures of liquid crystals. In particular, the use of the so-called ‘magic mixtures’ allows separation of various orientational mechanisms and has contributed immensely to our understanding and to the predictability of the degree of solute partial orientation [1,2].

In this paper, we highlight results obtained for a series of key probe molecules that range from hydrogen, via methane and ethane, to butane. The elementary physical properties, such as geometrical and electronic structures and vibrational data, of the members of this series are relatively well known. Moreover, each member of the series is chosen for a specific reason. Hydrogen [3–5] with its deuterated [6,7] and tritiated [8] isotopomers is the simplest molecule in nature and is expected to hardly perturb the anisotropic environment when dissolved in a liquid crystal. Results obtained for this solute probe molecule have been crucial to our understanding of the various orientational mechanisms that play a role. The experiments on tritiated hydrogens originated at one of the Zakopane meetings where discussions with Prof. AnnaLaura Segre led to subsequent collaboration and extensive 3H NMR experiments at CNR in Monterotondo, Italy. Our studies on methane and its isotopomers deserve special mention. Since methane possesses tetrahedral symmetry, this solute is not expected to show partial orientation when dissolved in a liquid crystal, nevertheless it does. The mechanism underlying the observed dipolar and quadrupolar couplings in the methane series is that of reorientation–vibration interaction and derives quantum mechanically from the correlation between both types of motion [9–11]. Although at first thought to be an elusive effect, it gradually transpired that neglect of such correlation contributions in solutes other than the methanes was unwarranted. In this context we mention detailed studies on acetylene [12], benzene [13], and methyl fluoride [14] and their isotopomers. For an analysis of the hydrogen and methane results, molecular vibrations, of the members of this series are measured that require sophisticated subtraction techniques to obtain the observables for each molecule [17]; and (ii) the many-line spectra measured for a solute with 10 protons such as butane is very difficult to solve without sophisticated NMR approaches such as multiple quantum (MQ) techniques, in particular frequency-selective MQ excitation [18] and selective MQ detection [16]. In this context scientific contacts established at one of the Zakopane meetings with Prof. Jean Jeener from Brussels are acknowledged with great pleasure. The ensuing collaboration has resulted in a novel three-dimensional (3D) MQ-NMR method that proved highly applicable to problems of solutes in nematic phases [19].

In the following, we shall review how modern NMR techniques can be applied successfully to the study of orientationally ordered solutes in liquid crystals. Moreover, the various tools developed to obtain an understanding of the prevalent orientation mechanisms, such as the theoretical background of observed order parameters, reorientation–vibration interactions, the use of ‘magic mixtures’ to separate orientational contributions, model calculations based on size and shape of the various solutes, as well as computer simulations will be discussed in some detail.

2. NMR techniques

2.1. The spectra

The NMR spectra of orientationally ordered molecules can provide a vast array of information on anisotropic properties. The Hamiltonian (in Hz) that describes the spectrum is

\[ \mathcal{H} = \sum_{\mu} \nu_{\mu} I_{Z,\mu} + \sum_{\mu < v} J_{\mu v} I_{\mu} \cdot I_{v} + \sum_{\mu < v} D_{\mu v} \]

\[ \times (3I_{Z,\mu} I_{Z,v} - I_{\mu} \cdot I_{v}) + \frac{1}{3} B_{\mu} (3I_{Z,\mu}^{2} - I_{\mu}^{2} - I_{v}^{2}). \]  

(1)

where \( \nu_{\mu} \) is the resonance frequency of nucleus \( \mu \), \( J_{\mu v} \) and \( D_{\mu v} \) are the indirect spin–spin and the direct dipolar coupling between nuclei \( \mu \) and \( v \), and \( B_{\mu} \) is the quadrupolar coupling for nucleus \( \mu \) if its spin is greater than \( \frac{1}{2} \). The \( \nu_{\mu} \) term can have both isotropic and anisotropic parts, while...
the $D_{\mu\nu}$ and $B_{\mu}$ terms are completely anisotropic and hence do not influence the familiar spectra of isotropic liquids. We omit the effect of anisotropy in $J_{\mu\nu}$ which is to modify slightly the observed value of $D_{\mu\nu}$. This anisotropy is negligible for proton–proton couplings.

The anisotropic terms in Eq. (1) are all second-rank tensorial in nature and can be expanded in terms of the second-rank Saupe order matrix $S_{kl}$ as for example:

$$D_{\mu\nu} = -\frac{h^2}{4\pi^2} (r_{\mu\nu}^{-3}) \sum_{k,l} S_{kl} \cos \theta_k \cos \theta_l,$$

where $\theta_l$ is the angle between the $k$ molecule-fixed axis and the vector joining nuclei $\mu$ and $\nu$ which have internuclear separation $r_{\mu\nu}$, and the angle brackets denote an average. For spin $I = 1$

$$B_{\mu} = \frac{3eV_{zz}^{int} Q_{\mu}}{4\hbar} \sum_{k,l} S_{kl} \cos \theta_k \cos \theta_l,$$

where $-V_{zz}^{int}$ is the principal component of a molecule-fixed axially symmetric electric field gradient tensor, $eQ_{\mu}$ is the nuclear quadrupole coupling constant of nucleus $\mu$, and $\cos \theta_l$ is the angle between the symmetry axis of $V_{zz}$ and $k$. Eqs. (2) and (3) assume that the averaging over rotational and vibrational motions can be carried out independently, see Section 3.2.

The Hamiltonian of Eq. (1) is an excellent predictor of observed NMR spectra, such as those given in Fig. 1. These spectra demonstrate the complexity associated with an increase in the number of coupled spins $\frac{1}{2}$ associated with a solute molecule in a nematic liquid-crystal solvent. The top row demonstrates the spectra of fully equivalent 2-, 3- and 4-spin systems which are interpreted intuitively in terms of one spin of dihydrogen splitting the other into a doublet, two spins of 1,3,5-tri-chlorobenzene (TCB) splitting the other one into a 1:2:1 triplet, and the coupling between the four equivalent spins of methane leading to a 1:3:3:1 quartet. The other, more complicated spectra are from molecules in which the spins are not fully equivalent.

For example, the six non-fully equivalent protons in benzene ($D_{ortho} \neq D_{meta} \neq D_{para}$) give rise to a 74-line spectrum. The figure demonstrates that spectra get very complicated when eight or more spins are coupled, and in the case of the liquid crystal itself there are so many overlapping lines that fine structure is no longer observed.

Analysis of the more complicated spectra in Fig. 1 is often difficult and time-consuming. A major problem is that initial values of the spectral parameters that depend on knowledge of the molecular structure and especially of the order parameters are required. In favourable cases models for the anisotropic intermolecular interactions (vide infra Section 4.1) can be used to give excellent predictions of the order parameters and a calculated spectrum that is close to the experimental one is obtained (see Fig. 2). The calculated lines are then readily assigned to the experimental ones, leading to an excellent fit to the experimental spectrum and very accurate values of the coupling parameters. Other approaches to spectral analysis are the use of MQ-NMR and spectral subtraction techniques.

### 2.2. Multiple-quantum NMR

The normal high-resolution single-pulse proton NMR spectrum of molecules such as butane (CH₃CH₂CH₂CH₃ in Fig. 1), which contains ten coupled protons, consists of over 1000 lines all of which satisfy the selection rule $\Delta M_Z = \pm 1$, where $M_Z = \sum m_{Z,i}$, $m_{Z,i}$ being the $Z$ component of spin $i$. The large number of lines results from the $2^{10} = 1024$ energy levels and the directly observed NMR spectrum consists of many transitions between these energy levels. However, it is possible to use MQ-NMR (see Fig. 3 for pulse sequence) to observe indirectly transitions involving $\Delta M_Z > 1$. If the phase $\phi$ of the first pulse is $0^\circ$ (i.e. it is an $X$ pulse), it generates $Y$ magnetization ($T_Y = \sum T_{Y,j}$) that evolves during the time $\tau$ according to the Hamiltonian of Eq. (1). This evolution produces terms such as $T_{X,1} T_{Z,2}$ (resulting from $T_{Y,1}$ evolving under $D_{12}$) with more complicated terms then being produced via
coupling to other spins. These terms are all coherences involving only $\Delta M_Z = \pm 1$, or 1Q coherences, and the Fourier transform of the observable $T_x$ and $T_y$ components gives the usual one-pulse high-resolution NMR spectrum.

The second pulse at time $\tau$ rotates the 1Q coherences into coherences between all energy levels; these MQ coherences evolve during the time $t_1$ after which the third pulse rotates some of the magnetization back into 1Q coherences which refocus (as a stimulated echo) after a time $\tau$. A 2D Fourier transform of the echo with respect to incremented values of $t_1$ gives the MQ spectrum, as demonstrated in Fig. 4 for the 7-spin $\frac{1}{2}$ system para-chlorotoluene. The spectrum was obtained using pulse sequence A of Table 1. The $N$ (i.e. 7Q) transition should be a single line because there is only one energy level for each of the $M_Z = +\frac{1}{2}$ and $M_Z = -\frac{1}{2}$ quantum states. As there are three chemically distinct protons in para-chlorotoluene, the 6Q spectrum should consist of three doublets. However, these 7Q and 6Q transitions are not observed in Fig. 4 because of the wide spectral width required for this method of obtaining all orders of the MQ spectrum in one experiment.

An alternative approach is to acquire lines selectively for only one MQ order by using pulse sequence B of Table 1 which involves phase cycling the first two pulses so that addition (with the indicated receiver phase cycling) of the echo signal cancels all but the selected MQ order. When this was presented at a previous AMPERE NMR School, Jean Jeener rose and asked “why throw away all that information—why not collect all MQ orders using a 3D NMR experiment (pulse sequence C of Table 1) in which the Fourier transform with respect to the phase of the first two pulses gives one slice for each of the $-NQ$ to $+NQ$ spectra?” This question led to a Zakopane collaboration and the successful result is presented in Fig. 5. The spectra are equivalent in every way to those obtained with the selective experiment of pulse sequence B, but are collected in the time required to collect only one of the selective orders [19].

As can be seen, higher-order MQ-NMR spectra have considerably fewer lines than do their 1Q counterparts, and spectral fitting is considerably easier. However, the parameters obtained are less accurate than those from analysis of the one-pulse high-resolution spectrum because of the considerable line widths of the MQ spectra (often of order 50 Hz). However, the spectral parameters obtained from analysis of the MQ spectra do provide an excellent starting spectrum for analysis of the high-resolution spectrum: in most cases almost all lines in the high-resolution spectrum can be assigned directly from those predicted from the MQ ones. One excellent example is the spectrum of ortho-xylene [17] presented in Figs. 6A–C; the expansion demonstrates both the spectral complexity and the excellent prediction obtained from analysis of the $N = 2$ (i.e. 8Q) spectrum. The excellent fit to the high-resolution...
spectrum yields very accurate spectral parameters (vide infra Section 5 on more complicated systems for a discussion of a seminal example, butane).

It is worth mentioning one additional MQ-NMR experiment. The one-pulse high-resolution spectrum of the 6-spin 1,3-dichloro-2-ethenylbenzene (fourth row of Fig. 1) proved particularly difficult to analyse. The outer lines of this spectrum are pure aromatic proton resonances. If the first two pulses of MQ sequence A of Table 1 are made frequency selective for the outer lines (e.g. by using a Dante pulse sequence), then MQ coherences involving only these protons will be generated. Because there are three aromatic protons, 3Q is the highest-order coherence generated. This 3Q order is affected by the eight possible spin states of the three ethenyl protons, and eight transitions are observed (see Fig. 7). These transitions gave valuable information about the small, long-range dipolar couplings between the ethenyl and aromatic protons and hence enabled analysis of the normal MQ spectrum [18] and eventually the one-pulse high-resolution spectrum [20].

![Fig. 4. Multiple-quantum spectrum of para-chlorotoluene in ZLI-1132. This spectrum was collected in 14 h, 5 m using sequence A (Fig. 3, Table 1) with \( t \) set to 20 ms, four scans/\( t_1 \) increment, 8192 \( t_1 \) increments, \( F_2 \) spectral width of 83 333 Hz, and \( F_1 \) spectral width of 1 MHz. The absolute value of the projection of the complex \( F_2 \) spectra onto the \( F_1 \)-axis gives the \( F_1 \) spectrum, which is the entire MQ-NMR spectrum. The spectrometer frequency was offset by 60 000 Hz from the centre of the spectrum in order to separate the various orders. Under these conditions, the higher-order coherences are poorly detected, presumably due to the combination of the large offset with the long duration (10 \( \mu \)s) of the 90° pulses. (Reproduced with permission from [19]. Copyright 2002 Academic Press.)

Table 1

<table>
<thead>
<tr>
<th>Sequence</th>
<th>Phase list</th>
</tr>
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<tbody>
<tr>
<td>A&lt;sup&gt;b&lt;/sup&gt;</td>
<td>( \phi = 0 )</td>
</tr>
<tr>
<td></td>
<td>( \theta = 0 )</td>
</tr>
<tr>
<td>B&lt;sup&gt;c&lt;/sup&gt;</td>
<td>( \phi = 0, 90/N, 2 \times 90/N, 3 \times 90/N \ldots (4N - 1) \times 90/N )</td>
</tr>
<tr>
<td></td>
<td>( \theta = 0, 90, 180, 270 )</td>
</tr>
<tr>
<td>C&lt;sup&gt;d&lt;/sup&gt;</td>
<td>( \phi = 0, 360/n, 2 \times 360/n, 3 \times 360/n \ldots (n - 1) \times 360/n )</td>
</tr>
<tr>
<td></td>
<td>( \theta = 0 )</td>
</tr>
</tbody>
</table>

<sup>a</sup>As defined in Fig. 3, \( \phi \) refers to the phase of pulses 1 and 2, and \( \theta \) refers to the receiver phase. (Reproduced with permission from [19]. Copyright 2002 Academic Press.)

<sup>b</sup>Sequence A gives all MQ orders in a single, wide spectrum (see e.g. Fig. 4). For this experiment the phases \( \phi \) and \( \theta \) can be any arbitrary constant angle. Zero degrees was chosen for convenience.

<sup>c</sup>Sequence B is used for the selective detection of the \( NQ \) (and \( 2NQ, 3NQ \ldots \)) spectrum. \( N \) is the quantum order being selectively detected.

<sup>d</sup>Sequence C is used for the 3D experiment, where \( n \) is an arbitrary integer that should be at least \( 2N_{\text{max}} + 1 \). A separate signal is acquired and stored for each value of \( n \), giving a 3D interferogram that is a function of \( t_1, \phi, \) and \( t_2 \).
2.3. Spectral subtraction

Series of solutes are often used to investigate the anisotropic intermolecular interactions that are responsible for orientational order in liquid crystals. Liquid-crystal orientational order varies greatly with both temperature and solute concentration. Hence, it is essential to utilize the spectra of solutes that are obtained under precisely identical experimental conditions. An excellent way to do this is to co-dissolve several solutes in the same NMR tube. Obviously the resulting spectrum is even more complicated than that obtained from a single solute. An example is the NMR spectrum from the partially ordered mixture of ortho-xylene, ortho-chlorotoluene, ortho-di-chlorobenzene and 1,3,5-tri-chlorobenzene dissolved in the liquid-crystal solvent Merck ZLI 1132 (spectrum A of Fig. 6). MQ-NMR was used to provide initial starting parameters for the analysis of the 10-spin spectrum of ortho-xylene. Because the other solutes have seven or fewer protons, the 8Q, 9Q and 10Q spectra contain lines from ortho-xylene only. The parameters obtained from analysis of the 8Q spectrum led to an excellent prediction (spectrum B of Fig. 6) of the 1Q transitions which can immediately be assigned and the one-pulse high-resolution spectrum simulated accurately (spectrum C of Fig. 6). The resulting calculated spectrum is subtracted from the experimental one, leaving only lines from the remaining three solutes (and an impurity, spectrum D of Fig. 6). Successive fitting and subtraction gives accurate spectral parameters.
for all the solutes [17]. The dipolar couplings were used to
determine the molecular geometry and order parameters.
The order parameters were used in a study similar to the
one discussed in Section 4 to investigate anisotropic
intermolecular forces.

3. Simple probe molecules in nematic liquid crystals

In this paper we shall focus on the simplest possible
liquid crystals, viz. nematic phases which in an external
electric or magnetic field form a highly anisotropic liquid
with uniaxial, cylindrical symmetry along an axis that is commonly called the director, and with the opposing directions along this axis indistinguishable. To describe the intermolecular potential present in such an anisotropic phase, simplifying assumptions cannot be avoided. The basic model commonly used to describe orientational ordering in nematics is the ‘mean field’ potential of Maier and Saupe [21,22], in which each molecule is viewed as moving in a ‘field’ generated via its interactions with all the surrounding molecules. It is assumed that this ‘field’ is independent of the degrees of freedom of every molecule except the one being considered. In this theory the physical nature of the intermolecular forces does not need to be specified. Its key feature is the $P_2(\cos \theta)$ dependence of the ‘mean field’ on the degree of molecular orientation. The appreciable success of this approach underlines the dominance of second-rank tensorial interactions.

In order to obtain experimental knowledge about the intermolecular potential, NMR studies of simple, small, well-characterized probe molecules and their isotopomers dissolved in nematic phases have proved to be crucial. Through such studies the essential physical interaction mechanisms that contribute to orientational order could be unraveled, and models could be developed that under appropriate experimental conditions are capable of predicting solute degrees of order with reasonable accuracy. In the following we shall discuss these exciting developments.

A solute dissolved in a nematic liquid crystal experiences an intermolecular potential $U$ that can be described as a ‘mean field’ with cylindrical symmetry around the direction of the space-fixed magnetic field direction $Z$. The interaction potential can be written as [11]

$$ U = -\frac{1}{3} G \sum_{k,l} \beta_{kl}(Q_m) S_{kl}(\Omega) $$

(4)

with the orientation operator

$$ S_{kl}(\Omega) = \frac{i}{2} \cos \theta_{kZ} \cos \theta_{lZ} - \frac{1}{2} \delta_{kl}, $$

(5)

where $k$ and $l$ are molecule-fixed axes $x, y, z$ for the solute and $\cos \theta_{kZ}$ is the direction cosine between the molecule-fixed $k$-axis and the space-fixed $Z$-axis. The quantity $G = F_1 - F_\perp$ is the anisotropy of the liquid-crystal ‘mean field’ interacting with the solute. The $\beta$-tensor signifies some electronic property of the solute that can couple with the liquid-crystal solvent ‘field’. At this point there is no need to specify $\beta$ any further. The potential $U$ is a function of both the vibrational normal modes $Q_m$ of the solute and of the Euler angles $\Omega$ that describe its orientation. In principle this potential couples reorientational and vibrational motions, a notion that will turn out to have important consequences (vide infra). The potential is treated as a perturbation on the freely rotating and vibrating solute molecule. The unperturbed wave functions are taken to be simple products of harmonic oscillator and rigid rotor wave functions, and standard perturbation theory is used to obtain the perturbed wave functions where the orienting potential of Eq. (4) is taken as the perturbation. NMR observables such as dipolar and quadrupolar couplings are obtained by calculating expectation values of the corresponding operators using the perturbed wave functions for the rotational and vibrational motions of the solute and by computing thermal averages [5,11].

At this point we want to make an important observation. Assuming that the above description of the orienting...
potential has some validity, the use of molecular hydrogen as a probe molecule leads to a particularly simple situation. Essentially the only influence that the ‘mean field’ exerts on the solute is through a uniaxial, apolar perturbation. In this picture the solute can be treated at an ab initio level and the extent to which this perturbation affects reorientational and vibrational motion can be calculated in detail. It appears that the degree of perturbation of the rigid rotor and harmonic oscillator wave functions of molecular hydrogen is surprisingly small. Clearly, there is ample justification to consider the solute as an isolated species in a liquid-phase environment that only slightly perturbs its gas-phase behaviour and properties [5].

3.1. \( \ce{H2} \) and its isotopomers

It is hardly surprising that molecular hydrogen (see Fig. 1 top left for NMR spectrum) was used as a probe molecule at an early stage [3]. Later this molecule and its deuterated and tritiated isotopomers (see Fig. 8 for the spectra of \( \ce{T2}, \ce{HT} \) and \( \ce{DT} \)) were investigated in various liquid crystals in a much more systematic fashion [4,6–8]. The observed dipolar and quadrupolar couplings contain detailed information about how the solute responds to the intermolecular potential. We shall show how these studies have contributed significantly to an understanding of the mechanisms that underlie solute orientation, and to the design of novel liquid-crystal mixtures that allow a detailed information about how the solute responds to the rotational levels of the solute to be taken into account.

Homonuclear isotopomers that contain nuclei with \( I = \frac{1}{2} \) (\( \ce{H2}, \ce{T2} \)) occur either in the ortho (total nuclear spin \( I = 1 \)) or in the para (total nuclear spin \( I = 0 \)) form, with only ortho-\( \ce{H2} \) and \( \ce{T2} \) observable with NMR. For these isotopomers only the odd-numbered \( J \) states exist. A similar distinction can be made for ortho-\( \ce{D2} \) (total nuclear spin \( I = 0 \) or 2, with even \( J \)) or para-\( \ce{D2} \) (total nuclear spin \( I = 1 \), with odd \( J \)). These Pauli restrictions do not apply to diatomics built from two different isotopic nuclei, and both even and odd \( J \) levels exist. As a consequence, the values of \( S_{zz} \) must be calculated using the appropriate \( J \) levels for the various isotopomers. It is noteworthy that the isotopomer dependence of the degree of orientation would not be obtained for classical averaging over the rotational degree of freedom. In that sense these observations are a clear illustration of a quantum-mechanical effect in the liquid phase that persists at room temperature. Results on the asymmetrical isotopomers HD, HT, and DT could not be fully reproduced by the quantum-mechanical averaging over the rotational degree of freedom and a small liquid-crystal independent contribution to the solute orientational order was invoked. A simple model provides evidence that the somewhat deviant behaviour of the asymmetrical isotopomers could be due to the fact that the centre of mass around which these species rotate does not quite coincide with the geometrical centre [8,23].

In NMR studies of partially oriented species only the magnitudes of dipolar couplings (but not their signs) are observed and the signs of the Saupe orientation parameters do not in general follow directly from experiment. However, when \( \ce{D2} \) is employed as a probe molecule, the sign of its orientation parameter \( S_{zz} \) can be gleaned immediately from its NMR spectrum. The \( \ce{2H} \) NMR spectrum of \( \ce{D2} \) (see Fig. 9) contains transitions arising from ortho- and para-\( \ce{D2} \), because of its relative simplicity, the spin system can be solved analytically [4]. The indirect \( J \) coupling between both nuclei is seen to lead to two transitions with unequal intensities that in the spectrum are separated by \( |3J| \). The order in which these lines occur is directly related to the relative signs of \( J \) and \( S_{zz} \). The value of \( J \) arises predominantly from the Fermi contact interaction and is known to be positive [24]. Hence, the sign of \( S_{zz} \) is determined by the spectrum. In some nematic phases the degree of orientation of \( \ce{D2} \) is found to be positive, in others negative. As we shall see, this simple experimental fact has unexpected implications.

It is apparent that both the dipolar coupling \( D \) and the quadrupolar coupling \( B \) can be obtained from the experimental \( \ce{2H} \) NMR spectrum in Fig. 9. If the averaging over reorientational and vibrational motions can be carried out independently, the dipolar coupling \( D_{\mu \nu} \), between nuclei \( \mu \) and \( \nu \) is given by [11]

\[
D_{\mu \nu} = -\frac{\hbar}{4\pi^2} (1/r_{\mu \nu}^3) S_{zz},
\]

where the angular brackets signify averaging over vibrational motion. The quadrupolar coupling \( B_{\mu} \), for nucleus \( \mu \)
with $B^\text{int}_D$ the second derivative of the intramolecular potential with respect to the position co-ordinate $z$, which corresponds to the negative of the $zz$-component of the intramolecular electric field gradient ($efg$) tensor, and $eQ_D$ the deuteron nuclear quadrupole moment. Clearly, the quantity $B/D$ is independent of the degree of orientation and can be obtained from D$_2$ molecular properties alone. The value of $B/D$ obtained from an NMR experiment can now be compared to an accurate $B/D$ value measured in a molecular beam magnetic resonance experiment on D$_2$ in the gas phase [25]. There is a significant disagreement between these $B/D$ values.

One possible way out of the above $B/D$ dilemma could be the notion that the observed quadrupolar splitting does not only arise from an intramolecular term $B_D = B^\text{int}_D$ as given by Eq. (7), but also contains an external contribution $B^\text{ext}_D$ caused by the liquid-crystal environment. The quadrupolar coupling observed from the NMR spectrum is then given by [11]

$$B_D^{\text{obs}} = B_D^{\text{int}} + B_D^{\text{ext}}$$  

(8) with

$$B_D^{\text{ext}} = \frac{3}{4} \frac{eV^{zz}_D Q_D}{\hbar},$$  

(9)

where $Z$ is the direction of the nematic director. By adjusting $B^\text{int}_D$ the disagreement between $B/D$ obtained from NMR and $B/D$ obtained from molecular beam magnetic resonance can now be removed. From this procedure a value for the $efg$ present in the liquid-crystal solvent and felt by the quadrupolar nuclei of the solute can be estimated. Of course, without additional support for such a supposition, this course of action has little justification. However, as will be discussed in the following, similar discrepancies in the quadrupolar couplings of the deuterated methanes [10,11] and ethanes [15] can be explained on exactly the same basis.

If the concept of an external $efg$ in the liquid crystal experienced by the solute is realistic, one would expect that the interaction between this $efg$ and the overall solute quadrupole moment would represent an orientation mechanism that might be able to explain part or all of the observed degree of orientation of the D$_2$ molecule dissolved in a nematic phase. The interaction potential is [11]

$$U = \frac{1}{2} V^{zz}_D Q_{zz} S_{zz},$$  

(10)

where $V^{zz}_D$ can be estimated from Eq. (9), $Q_{zz}$ is the known D$_2$ molecular quadrupole moment, and $S_{zz}$ can be obtained from the observed dipolar coupling. When the solute-solvent interaction is assumed to have the form of Eq. (10), ab initio calculations with $V^{zz}_D$ as the only adjustable parameter indicate that ~90% of the observed orientation can be explained for values of $V^{zz}_D$ close to what was estimated in the above procedure [5]. However, this observation by itself again does not prove that an external $efg$ exists.

As was already mentioned above, the sign of the degree of orientation $S_{zz}$ of D$_2$ dissolved in a nematic phase can be determined unambiguously and is found to differ in different liquid crystals. If the concept of an external $efg$ is correct, this would suggest that by mixing two liquid crystals in which D$_2$ orients with different signs in appropriate amounts, a novel liquid-crystal solvent with essentially zero external $efg$ could be formed. Moreover, because the ab initio calculations suggest that the interaction between external $efg$ and D$_2$ molecular quadrupole moments causes most of its orientation [5], D$_2$ would be expected to show virtually zero $S_{zz}$ in such a ‘magic mixture’. The fact that both these expectations are borne out can be viewed as a breakthrough and lends strong credence to the concept of an external $efg$ that can be controlled at will by creating suitable liquid-crystal mixtures [7].

As an example, in the liquid crystals N-(4-ethoxybenzylidene)-4’-$n$-butylaniline (EBBA) and Merck ZLI-1132 (1132, a eutectic mixture of alkylcyclohexylecyanobenzene and alkoxycyclhexyl-cyanobiphenyls) the degrees of orientation of D$_2$ have opposite signs. In Fig. 10 the $^2$H NMR spectra of D$_2$ dissolved in various mixtures of EBBA and 1132 at 310 K are shown. At all compositions the mixtures form nematic liquid crystals. For the 61.3 wt% 1132/38.7 wt% EBBA mixture the degree of orientation of D$_2$ is essentially zero. These experimental facts indicate that: (i) liquid-crystal mixtures with zero external $efg$ can be formed; and (ii) D$_2$ dissolved in such a ‘magic mixture’ shows close to zero degree of orientation (in fact $S_{zz}$ is

![DEUTERIUM NMR OF D$_2$](image)

Fig. 10. 61.4 MHz deuteron NMR spectra of D$_2$ dissolved in nematic mixtures of EBBA and ZLI 1132 at 310 K. (Reproduced with permission from [7]. Copyright 1984 Elsevier Science.)
slightly negative) [7]. Other zero $efg$ mixtures that support these allegations have also been discovered [26].

The mechanisms that generally play a role in determining the degree of average orientation of solutes dissolved in nematic liquid crystals are normally divided into long- and short-range interactions. Long-range interactions are usually described as terms that arise from the multipole expansion. This series expansion of the potential between two charge distributions converges rapidly when the distance between both distributions is large. For small distances the multipole expansion fails to converge and short-range interactions that predominantly depend on size and shape of the solute become dominant. From a large body of data it has now become apparent that the leading term in the long-range interactions is the interplay between the external solvent $efg$ and the solute molecular quadrupole moment. For a solute such as $D_2$ dissolved in a typical liquid crystal (e.g. EBBA, 1132) this long-range interaction dominates completely and the short-range contribution appears to be quite small [5]. In zero $efg$ ‘magic mixtures’ the long-range contribution to solute orientation disappears. For somewhat larger solutes (such as benzene, see Fig. 1 third from top) dissolved in a ‘magic mixture’ removal of the long-range interactions does not lead to zero orientation, but to a non-zero degree of orientational order intermediate between those in 1132 and EBBA. The remaining orientational mechanism is ascribed to a size- and shape-dependent short-range interaction. This short-range interaction can be modeled adequately (see Section 4.1) with a small number of adjustable parameters. Generally, the Saupe orientation parameters of solutes dissolved in ‘magic mixtures’ can now be predicted at ~ the 10% level [1,2].

3.2. $CH_4$ and its isotopomers

Methane, $CH_4$, is the simplest hydrocarbon and is a molecule with an equilibrium tetrahedral configuration. Because of its symmetry, one would not expect this solute to show dipolar or quadrupolar splittings when dissolved in a nematic liquid crystal. Nevertheless, significant splittings of typically 10 Hz (see Fig. 1 top right for NMR spectrum of $CH_4$) have been observed and analysed [27]. The mechanism underlying these observations in the methanes is interesting, particularly because it has broader implications in the realm of accurate structure determination [12,14,15].

Methane with tetrahedral symmetry possesses four vibrational normal modes, viz. a symmetric breathing mode of $A_1$ symmetry, a bending mode of $E$ symmetry, and two modes of $F_2$ symmetry, one predominantly bending, one stretching. The observed splittings arise from the interplay between vibrational and reorientational motion, often called ‘correlation’. The importance of methane and its isotopomers lies in the fact that this ‘correlation’ effect is the sole reason behind the observed splittings. In less symmetrical molecules the role of ‘correlation’ is often obscured by the presence of other vibrational effects. There are two equivalent ways of understanding this interesting process, either from a kinetic point of view [28,29], or via perturbation theory [9,11]. In either approach the non-totally symmetric vibrations of $E$ and $F_2$ symmetry play a central role.

In the kinetic approach the vibrational motion takes place on a much faster time scale than reorientation. If methane undergoes an $E$ or $F_2$ vibration, there is an instantaneous lowering of the symmetry of the molecule away from tetrahedral. The degree of orientation of the methane molecule in this instantaneous non-tetrahedral geometry will then evolve via a characteristic reorientation time constant towards an equilibrium orientation that corresponds to that particular non-tetrahedral shape. Long before this degree of orientation has been reached, another non-symmetrical vibrational deformation takes place. This kinetic process can be viewed as a Markov chain, and if the ratio between the relevant vibrational and reorientational time scales is $>0$ (hence both degrees of freedom are somewhat coupled) a non-zero average degree of orientation results [29].

In an equivalent quantum-statistical picture, we shall focus on the dipolar couplings. The general expression for a dipolar coupling $D_{\mu\nu}$ between two nuclei $\mu$ and $\nu$ is

$$D_{\mu\nu} = \left( \sum_{k,l} d_{kl,\mu\nu} S_{kl}(\Omega) \right)_{\text{vibrations, rotations}}$$

(11)

with

$$d_{kl,\mu\nu} = -\frac{\hbar Y_{l\mu}\cos \theta_{\mu E}\cos \theta_{\mu F_2}}{4\pi^2} \frac{1}{r_{\mu\nu}^3}.$$  

(12)
There are two sorts of terms: those where averaging over vibrations and reorientations can be carried out independently, leading to contributions of the type

\[ D_{\nu \tau} = \sum_{k, l} \langle d_{E_{k \tau}^{\nu \mu}} \rangle_{\text{vibrations}} \langle S_{k \ell} (\Omega) \rangle_{\text{rotations}} \tag{13} \]

and a contribution \( D_{\nu \tau}^{\text{non-rigid}} \) where this separation cannot be made. Employing the expression of Eq. (4) as a perturbation, we obtain [10, 11]:

\[ D_{\nu \tau}^{\text{non-rigid}} = \frac{1}{3} G \sum_{i, j, k, l} \sum_{m} \left( \frac{\partial \beta_{ij}}{\partial Q_m} \right) \left( \frac{\partial d_{E_{k \tau}^{\nu \mu}}}{\partial Q_m} \right) \left( \frac{1}{\alpha_m^2} \right) \times \langle S_{ij} (\Omega) S_{k \ell} (\Omega) \rangle_{\text{rotations}}. \tag{14} \]

In this expression \( Q_m \) stands for the \( m \)th vibrational normal mode, \( \omega_m \) is its frequency, and \( i, j, k, l \) signify molecule-fixed axes. The derivatives are calculated at the equilibrium geometry. \( D_{\nu \tau}^{\text{non-rigid}} \) can be calculated assuming knowledge of the molecular \( \beta \) tensor, and on the basis of a force field obtained from a normal mode analysis. Alternatively, the quantities \( \langle \frac{\partial \beta_{ij}}{\partial Q_k} \rangle_k \) can be used as fitting parameters [11].

Extensive experimental [27] and theoretical [9–11] studies on methane and its isotopomers have been performed and the crucial role of the reorientation–vibration interaction mechanism has been elucidated. In order to discuss the various isotopomers on the same basis, the equilibrium geometry (corresponding to the bottom of the potential energy well) is used as a starting point. This particular geometry is identical for all isotopomers. However, a real molecule undergoes internal vibrations, and its average geometry therefore deviates from the equilibrium one. To achieve the best possible separation between reorientational and vibrational motions, the so-called Eckart conditions must be met. Subtle issues arising from the close connection between these Eckart conditions and isotope dependencies are beyond the scope of this paper [9–11]. However, it is clear that, in addition to work on CH₄, much can be learned from work on deuterated and tritiated methanes. A very recent example of the latter isotopomers dissolved in the liquid crystal 5CB (4-n-pentyl-4’-cyanobiphenyl) can be seen in Fig. 11 [30].

For the deuterated methanes, in addition to dipolar splittings discussed above, quadrupolar splittings have also been observed [10, 11, 27]. Again, these splittings are due to the reorientation–vibration interaction mechanism. However, just as was the case for the deuterated hydrogens, discrepancies between observed and predicted quadrupole couplings arose. These discrepancies could be removed by again invoking the notion of an external \( \epsilon_{fg} \) in the liquid-crystal solvents used. Moreover, if it was assumed that identical \( \epsilon_{fg} \)’s were experienced by hydrogens and methanes alike, excellent agreement was obtained in all cases. This is taken as additional proof that external \( \epsilon_{fg} \)’s in typical liquid crystals have a significant effect on quadrupolar splittings in solute atoms and molecules containing quadrupolar nuclei.

### 3.3. Acetylene, methyl fluoride and their isotopomers

In the previous section, it has been shown how the correlation between reorientational and vibrational motion leads to unexpected dipolar and quadrupolar splittings when methane and its isotopomers are dissolved in a liquid crystal. The dipolar couplings observed are described by \( D_{\nu \tau}^{\text{non-rigid}} \), quantities defined in Eq. (14). However, methane is a rather special case, and it is worthwhile to investigate to what extent accurate structural parameters of molecules with lower symmetry dissolved in nematic phases can be obtained from the observed dipolar couplings. Despite the multitude of studies that have been carried out, the extent to which the liquid-crystal environment affects solute structure is still a matter of debate. Since zero-point vibrations typically have amplitudes of 0.1 Å, bond lengths accurate to better than 0.01 Å can only be obtained if averaging over the vibrational motion is dealt with appropriately. Not only do we have to contend with the correlation effect of Eq. (14), but also we must include various terms from Eq. (13) where separate averages over vibrational and rotational motion contribute to the observed dipolar couplings. Omitting details of the derivation, the observed dipolar couplings can be expressed as follows [12, 14]:

\[ D_{\nu \tau} = D_{\nu \tau}^e + D_{\nu \tau}^\text{a} + D_{\nu \tau}^b + D_{\nu \tau}^{\text{non-rigid}}. \tag{15} \]

Higher-order terms can be included when necessary [14]. The term \( D_{\nu \tau}^e \) is the contribution that occurs if the solute is in its rigid equilibrium configuration. \( D_{\nu \tau}^b \) signifies the so-called anharmonic contribution that is proportional to \( \langle Q_m^2 \rangle \) and depends on the cubic and higher-order anharmonic force field. For most but the simplest molecules detailed information on higher-order force fields is not known. In the case of a purely harmonic vibrational potential \( \langle Q_m^2 \rangle = 0 \). The term \( D_{\nu \tau}^\text{a} \) stands for the harmonic contribution to the dipolar couplings and is proportional to \( \langle Q_m^2 \rangle \). This term depends on the harmonic force field which is usually rather well known, especially in the case of small molecules. In Eq. (15) \( D_{\nu \tau}^e \) is usually the dominant contribution, but the other terms are by no means negligible if one wants to extract accurate bond distances and bond lengths. Nevertheless, the \( D_{\nu \tau}^{\text{non-rigid}} \) term, which is admittedly complicated to obtain, has been omitted in the majority of structural studies of solutes in nematic phases.

The benchmark molecule acetylene is a case in point. Acetylene-1,1³C and acetylene-1,2,1³C₂ have been studied in a number of nematic liquid crystals, and the observed dipolar couplings were analysed in terms of the vibrationally averaged structure, but with the neglect of the correlation term [31]. The ratios of the C–H and C–C bond lengths as determined from the dipolar couplings were found to be strongly solvent and temperature dependent, and this result was explained in terms of a two-site model. In this model acetylene was envisaged as occupying different environments with different structures.
and degrees of orientation. For acetylene in EBBA a negative order parameter $S_2$ was found. This observation was also discussed in terms of the two-site model [31].

A subsequent $^1$H, $^2$H, and $^{13}$C NMR study of acetylene and various isotopomers in the nematic liquid crystals EBBA, 1132, and a ‘magic mixture’ of these component liquid crystals in which the solute D$_2$ possesses essentially zero orientation has shown very interesting results [12]. To ensure identical experimental conditions, all isotopomers studied were co-dissolved in each liquid crystal. Firstly, the degree of orientation of the acetylenes in the ‘magic mixture’ was found to be intermediate between those obtained in EBBA and 1132, but not equal to zero. Secondly, in addition to the first three terms of Eq. (15) the $D_{mn}^\text{non-rigid}$ correlation term was included in the analysis of the dipolar couplings. It was concluded that the ordering of acetylene could be described adequately as resulting from two mechanisms: (i) the interaction between the solvent $efg$ and the solute molecular quadrupole moment that is operational in EBBA and 1132, but not equal to zero. (ii) a second mechanism which depends on the solute molecular quadrupole moment that is operational in both component liquid crystals as well as the ‘magic mixture’, and which can be modeled (see Section 4.1). Moreover, from our D$_2$ experiments in EBBA and 1132 it had become apparent that the $efg$’s in these nematic phases are of similar magnitude but of opposite sign. Assuming that acetylene and D$_2$ experience identical $efg$’s, the negative ordering of acetylene in EBBA can be understood in a natural way, without taking recourse to a two-site model. Finally, inclusion of the correlation effect leads to structural parameters for acetylene dissolved in these liquid crystals that are very similar to the known gas-phase values. These results support the notion that the perturbations exerted by the solvent ‘mean field’ on the solute are relatively small.

In a $^1$H, $^2$F, and $^3$H NMR study of eight isotopomers of fluoromethane (CH$_3$F) an extensive set of dipolar couplings was obtained. The nematic liquid crystals employed were again EBBA, 1132, and their ‘magic mixture’. To ensure identical experimental conditions, all isotopomers studied were co-dissolved in each liquid crystal. As in the case of acetylene, methyl fluoride is a very well-characterized molecule, and all the contributions to the dipolar couplings given in Eq. (15) could be included. The structural parameters for methyl fluoride dissolved in these nematic phases, obtained in this way from the observed dipolar couplings, are again very similar to those accurately known in the gas phase. A slight remaining discrepancy could be ascribed tentatively to an anisotropy in the $J_{CF}$ indirect coupling [14].

### 3.4. Ethane and its isotopomers

In order to obtain accurate structural parameters for solutes dissolved in nematic liquid crystals, the molecular vibrations must be dealt with appropriately. Until now we have discussed effects due to small-amplitude vibrational motions. However, large-amplitude internal motions can also occur, and ethane is a benchmark example of a system showing internal rotation of a methyl group. It is of interest to study the effects of this type of internal motion.

Ethane, CH$_3$CH$_3$, and five of its isotopomers, viz. $^{13}$CH$_3$CH$_3$, CH$_3$CD$_3$, CH$_3$CH$_2$D, $^{13}$CH$_3$CH$_2$D, and CH$_3$$^{13}$CH$_2$D, were studied as solutes mostly in the nematic liquid crystal 1132 and in one experiment in EBBA [15]. When a series of molecules is considered a comparison of observed NMR coupling parameters (such as dipolar and quadrupolar couplings) can only be made if the various species are studied under exactly the same experimental conditions. This is particularly true for isotopomers of the same molecule, since isotope dependences are generally small compared to changes arising from slight variations in the experimental conditions. It would therefore be preferable to study all species in the same NMR sample tube. In the case of the ethanes this is not feasible because the NMR spectra consist of a large number of transitions: too much spectral overlap of signals from different species poses an assignment problem. Hence, it was necessary to dissolve the isotopomers in more than one sample tube. Under such conditions great care must be exercised in scaling the results obtained in the different tubes. In our study we have obtained a consistent set of carefully scaled experimental NMR dipolar and quadrupolar couplings for ethane and its isotopomers.

For ethane in its stable staggered conformation no equilibrium structure $r_e$ is available, only the so-called $r_z$ structure is known [32,33]. Also, no experimental data for the cubic and quartic anharmonic force constants have been obtained. However, the experimental harmonic force field, based on the $r_z$ structure, is available [34]. The contributions to the dipolar couplings in Eq. (15) that can be calculated are therefore the ones from the ‘rigid’ $r_z$ structure $D^\text{reg}_{mn}$ and the harmonic vibrational corrections $D^\text{h}_{mn}$. The anharmonic contributions $D^\text{a}_{mn}$ were neglected. The torsional mode, that belongs to the A$_{1u}$ irreducible representation of the D$_{3d}$ symmetry group, cannot couple with any of the small-amplitude vibrations and is therefore treated separately.

The torsional potential energy $V(\tau)$ possesses threefold periodicity as a function of the torsional angle $\tau$, and can be expanded in a Fourier series truncated after the second term as

$$V(\tau) = \frac{V_1}{2} (1 - \cos 3\tau) + \frac{V_6}{2} (1 - \cos 6\tau).$$

(16)

Experimental values for the quantities that determine the height and the shape of the barrier are known, and are $V_1 = 2.882$ kcal/mol and $V_6 = 0.020$ kcal/mol [35]. Since the torsional motion does not couple to any other vibrational mode, a separation of variables can be performed leading to a 1D Schrödinger equation for the torsional motion where $V(\tau)$ represents the potential energy. Truncating $V(\tau)$ after the $V_3$ term, this differential
equation reduces to the so-called Mathieu equation whose eigenvalues and eigenfunctions have been tabulated. In principle the $V_\kappa$ term can then be taken into account with perturbation theory. At a given temperature the dipolar couplings can then be calculated as an expectation value of the dipole operator, while obtaining the thermal average over all the torsional levels populated according to the appropriate Boltzmann factors. Hence, the full quantum-mechanical treatment of the torsional problem can be performed, albeit with a considerable amount of effort. Alternatively, the effect of the torsional motion on the mechanical treatment of the torsional problem can be performed, albeit with a considerable amount of effort.

As we have seen, inclusion of the correlation term $D_{\mu
u}^\text{non-rigid}$ is usually vitally important. Rather than attempting to calculate this contribution from Eq. (14) an alternative strategy was developed. There are ample indications that the harmonic and anharmonic force fields for a methyl group do not depend strongly on the molecule that the methyl group is part of [36]. Since the correlation effect has been determined in detail for methyl fluoride [14], this notion provides justification for the transferability of the quantities $D_{\mu
u}^\text{non-rigid}$ from methyl fluoride to ethane. Some of these contributions can be transferred immediately, for others some degree of improvisation is required. For details the reader is referred to Ref. [15].

Excellent agreement between the full set of experimental and calculated dipolar couplings was obtained on the basis of the ethane gas-phase structure and gas-phase barrier height with the classical treatment of the large-amplitude internal rotation, and with the inclusion of the correlation effects transferred from the methyl fluoride case. These results are completely in line with those obtained for acetylene, methyl fluoride and their isotopomers.

One final point concerns the quadrupolar couplings observed in the deuterated ethanes. It was found that again external $e\!f\!g$’s in the solvents 1132 and EBBA had to be taken into account, with magnitudes very similar to those required in the case of the deuterated hydrogens and methanes. Again, a consistent picture emerges [15] from our study on ethane and its deuterated isotopomers.

4. Short-range size and shape interactions

4.1. Models

As discussed above, solute order parameters determined from NMR dipolar (and quadrupolar) couplings provide an excellent means of testing theories and models of orientational order in liquid crystals. The simplest approach is to describe the solute as interacting with the ‘mean field’ of the solvent (see Section 3). It is convenient to divide the interactions into short- and long-range ones so that the solute intermolecular potential is

$$U(\Omega) = U_{\text{ext}}^{\text{iso}} + U(\Omega)_{\text{short-range}} + U(\Omega)_{\text{long-range}},$$

where $\Omega$ represents the Euler angles between the molecule-fixed and space-fixed axis systems. The isotropic term $U_{\text{ext}}^{\text{iso}}$ becomes important when considering molecules that exist in several different conformers, each of which has a distinct set of order parameters (see Section 5 for a discussion of butane).

The order parameter for a molecular axis (in a ‘rigid’ molecule) that makes angle $\theta$ with the director is calculated classically as

$$S = \frac{1}{Z} \int \frac{3}{2} \cos^2 \theta - \frac{1}{2} \cos^2 \frac{\Omega}{2} e^{-U(\Omega)/k_B} d\Omega,$$

where the partition function is

$$Z = \int e^{-U(\Omega)/k_B} d\Omega.$$

The test of a model is to what extent the intermolecular potential used in Eq. (18) gives calculated order parameters that are consistent with those determined from NMR experimental anisotropic parameters. An excellent test is to compare results from series of solutes in the same liquid crystal and to see to what extent the same liquid-crystal ‘mean field’ can rationalize the entire set of experimental results. A particularly interesting example is provided by experiments using ‘magic mixture’ liquid crystals (see Section 3) for which long-range interactions appear to be negligible and solute orientational order appears to be dominated by short-range interactions that depend on the solute size and shape.

We have proposed several approaches to modeling the short-range interactions [37]. The C model assumes that the liquid crystal imposes an anisotropic Hooke’s law elastic restoring force on the solute such that solute orientations that give the smallest projection onto the plane perpendicular to the director are favoured. The interaction is written

$$U_C(\Omega) = \frac{1}{k} C^2(\Omega),$$

where $C$ is the minimum circumference of the projection and $k$ a constant.

The I model has the form of an anisotropic surface interaction and is written

$$U_I(\Omega) = -\frac{1}{2} k_s \int_{Z_{\text{min}}}^{Z_{\text{max}}} C_{Z}(\Omega) dZ,$$

where for a given molecular orientation $C_{Z}(\Omega)$ is the minimum circumference at position $Z$ which is the molecular distance along the director direction and $k_s$ is a constant.

NMR measurements on a collection of 46 solutes dissolved in the ‘magic mixture’ 55 wt% 1132/45 wt% EBBA were fitted to both models. In general the C model overestimates and the I model underestimates the orientational
order of more asymmetric particles. Combining the two potentials into a two-parameter CI model
\[ U_{CI}(\Omega) = \frac{1}{2} k C^2(\Omega) - \frac{1}{2} k_s \int_{Z_{\text{min}}}^{Z_{\text{max}}} C_Z(\Omega) dZ \] (22)
leads to calculated order parameters that are in excellent agreement with those obtained from the NMR experiments (vide infra).

The situation with the ‘magic mixture’ is that order parameters can now be predicted to about the 10% level. This is demonstrated in Fig. 2 where the \( k \) and \( k_s \) constants obtained from the fit to the 46 solutes were used to give an excellent prediction of the spectrum of \textit{meta}-chlorotoluene in the ‘magic mixture’.

4.2. Monte Carlo computer simulations

Monte Carlo (MC) and Molecular Dynamics simulations provide an excellent means of testing models for intermolecular interactions. An important example is the MC simulation of hard ellipsoidal particles which give a nematic phase at sufficiently low packing density [38]. The only interactions included in these simulations are hard-body ones—i.e. the interparticle potential energy is zero if particles do not overlap, and is infinite if they do. In other words, the simulations of the hard particles are based solely on excluded volume or entropic considerations and do not include additional attractive or repulsive energy terms.

The NMR results discussed above suggest that only hard-body anisotropic intermolecular interactions are important for the description of solute orientational order in ‘magic mixture’ liquid crystals. Hence, it is interesting to ask whether MC simulations of a hard ellipsoid solute/solvent liquid-crystal system are consistent with these NMR results. Fig. 12 shows the results of such MC simulations (solid squares) of a single solute hard ellipsoid in a solvent of 95 or 239 liquid-crystal hard ellipsoids. The liquid-crystal particle is a 5\( \times \)1\( \times \)1 ellipsoid and the solutes are of differing dimensions as indicated in the figure.

In order to compare the MC simulation results with the models used in the previous section, they were fitted to the potentials of Eqs. (20)–(22). The order parameters calculated from the fits are shown in Fig. 12. The results of the fitting are similar to those observed with fitting to the NMR experiments: the C model overestimates and the I model underestimates the orientational order of more symmetric particles. For the CI model calculations the ratio \( k_s/k \) was either varied (\( k_s/k = 38.1 \), solid line), or fixed to the value obtained from the fit of Eq. (22) to the NMR results for the 46 solutes in ‘magic mixture’ (\( k_s/k = 23.5 \), dashed line). Both fits are excellent, indicating that the CI model that best fits solute order parameters also provides the best fit to MC simulation results [39].

Fig. 13 further emphasizes the agreement between MC simulations of ellipsoidal particles and NMR experiments on real molecules. The difference between simulated (or experimental) and calculated (from the models) order parameters is plotted versus the simulated (or experimental) value. This graph emphasizes the strong correlation between the simulations and the NMR experiments.

The most noteworthy result of the simulations is that the combined CI model, using precisely the same ratio \( k_s/k \) as obtained from analysis of the NMR experiments, gives an excellent fit to both the simulated and the NMR experimental solute order parameters. This is strong evidence that orientational order of solutes in the ‘magic mixture’ is governed by short-range interactions and that long-range anisotropic electrostatic interactions are not important in this mixture [39].

5. More complicated systems

An excellent demonstration of how NMR spectral parameters can be used for the elucidation of physical information about solutes in anisotropic media is provided by butane [16]. Direct analysis of the complicated butane spectrum (second from bottom in Fig. 1) would be very difficult. Selectively detected 7Q and 8Q MQ-NMR spectra were obtained using pulse sequence B of Table 1. The starting point for analysis of these MQ spectra involved the
CI model with parameters from Ref. [37] along with a trial trans-gauche energy difference of 3.0 kJ/mol. Parameters from fitting the 7Q and 8Q MQ spectra provided an excellent starting spectrum for analysis of the one-pulse high-resolution spectrum which yielded seven very accurate dipolar couplings as well as two chemical shifts.

Butane is an excellent molecule for studying flexible hydrocarbon systems because only one bond is involved in the conformer changes. Using Flory’s rotational isomeric state (RIS) model [40] of hydrocarbon chains, the internal motion about the central C–C bond in butane is described by the conformers trans (φ = 0), gauche+ and gauche−. The relative trans:gauche population depends on both intra- and extra-molecular energy contributions. Statistical mechanical calculations of hydrocarbon chains predict an increase in gauche populations (over the gas-phase value) resulting from short-range packing considerations in the liquid [41,42]. In addition, conformer populations could be affected by the orientational ordering present in liquid-crystal solutions where elongated conformers might be expected to be favoured [43,44]. Because the methyl-methylene dipolar couplings in butane are a sensitive function of geometry, NMR is an excellent tool for the investigation of such a conformational problem (see e.g. [2, Part III]).

As is often the case with flexible molecules, butane interconverts among conformers sufficiently rapidly that a single motionally averaged NMR spectrum is observed. The NMR couplings are then averages over all conformers which in the case of dipolar couplings gives (taking each conformer to be rigid)

$$D_{ij} = \sum_n p_n^s \sum_{kl} d_{xkl}^n s_{kl}^t,$$

where each conformer $n$ has $d_{xkl}^n$ which depend on its structure. It is not possible to separate the probability $p_n^s$ of conformer $n$ from its order matrix $s_{kl}^t$ and only the product is obtainable from analysis of the motionally averaged NMR spectrum [45,46]. In order to proceed, it is necessary either to find values for the probabilities or to use a model for the order parameters. Here we are interested in how the trans and gauche probabilities: (i) change from the gas to the liquid phase; and (ii) are affected by the orientational ordering in anisotropic liquids. Hence, we need to use some model (in conjunction with Eq. (18)) to calculate how the order parameters vary with conformational change. In this regard it is important to note that the butane NMR spectrum was run using the 55 wt% 1132/45 wt% EBBA ‘magic mixture’ for which (as discussed above) there is overwhelming evidence that short-range interactions dominate the orientational potential. Hence, it makes sense to use potentials that have been designed to model short-range anisotropic interactions, such as the C, I and CI models of Section 4.1.

In order to deal with the molecular flexibility, the mean-field potential of Eq. (17) is expanded to include an intramolecular contribution $U_{int,n}^{iso}$ for each conformer

$$U_n = U_{int;n}^{iso} + U_n(\Omega).$$

The trans-gauche energy difference is defined

$$E_{tg} = (U_{int;gauche}^{iso} + U_{ext;gauche}^{iso}) - (U_{int;trans}^{iso} + U_{ext;trans}^{iso}).$$

In principle, the presence of the $U_{ext}$ terms in Eq. (25) explains the result that experimental values of $E_{tg}$ obtained from pure liquid butane and from butane in solution are in the range 2.1–2.5 kJ/mol, while values obtained from gas-phase experiments of hydrocarbons are higher, being in the range 3.3–3.7 kJ/mol (see [16] and references therein).

The conformer probabilities are calculated

$$p_n^s = \frac{G^0 e^{-\frac{(U_{int;gauche}^{iso} + U_{ext;gauche}^{iso})}{kT}} d\Omega}{\sum_n G^0 e^{-\frac{(U_{int;trans}^{iso} + U_{ext;trans}^{iso})}{kT}} d\Omega},$$

where the term $U_n(\Omega)_{long-range}$ is taken to be zero in the magic mixture, and $G^0 = \sqrt{I_{xx}^0 I_{yy}^0 I_{zz}^0}$ is a rotational kinetic energy factor that depends on the conformer principal moment of inertia tensor values $I_{kk}^0$ [16].

We note that the C, I and CI potentials of Eqs. (20)–(22) are not completely anisotropic. In order to obtain the value of $E_{tg}$ as defined by Eq. (25) when using these models, the isotropic contribution to $U_{iso}^{excl}$ from the C, I or CI
potential must be added to the value \( E_{fg}^\text{fit} \) that is obtained from the fit to the experimental dipolar couplings [16].

Fitting to the dipolar couplings was carried out using the equations above in conjunction with eight different models for the anisotropic intermolecular potential. The models used were the C, I and CI models discussed in Section 4.1, three additional models related to the C, I and CI ones, a model based on conformer moments of inertia [47], and a chord model that was specifically designed to deal with hydrocarbon chains [48]. Each model employed only one adjustable parameter. Calculations were performed with the three-state RIS model and with an extended-RIS model [49] in which the shape of the torsional probability distribution about each of the \( \text{trans} \) and \( \text{gauche} \) energy minima was approximated by including states with \( \phi \) and \( \phi \pm 20^\circ \) with relative populations of the extended-RIS triplet being 1:2:1. As there is uncertainty surrounding the correct value of \( \phi_{\text{gauche}} \), calculations were also performed for values \( \phi_{\text{gauche}} = 112^\circ, 116^\circ \) and \( 120^\circ \) [16].

The inertial model gave a poor fit to the experimental dipolar couplings. For the other models the results obtained depend on the model used for the intermolecular potential. The \( \text{trans-gauche} \) energy difference varied from 2.1 to 3.0 kJ/mol for the most acceptable models, with the chord model having the lower value—in all cases these values are significantly lower than the gas-phase values 3.3–3.7 kJ/mol. These results are indicative of enhanced \( \text{gauche} \) state probability in the liquid state. Both variation of the \( \text{gauche} \) state dihedral angle \( \phi_{\text{gauche}} \) and inclusion of torsional fluctuations about the \( \text{trans} \) and \( \text{gauche} \) energy minima had little effect on the results. All calculations indicated that the anisotropic potential causes a very slight increase in the \( \text{trans} \) state probability in ordered phases. However, this increase is far less than differences associated with using different models for the potential. It is clear that conformational studies using NMR of orientationally ordered, flexible molecules require that the ‘correct’ model for the potential must be used in order to account for order matrix changes with conformation.

6. Conclusions

We have shown that the study of probe molecules, ranging from hydrogens, via methanes and ethanes to butanes, dissolved in nematic liquid crystals, in combination with sophisticated multiple-quantum NMR and spectral subtraction techniques leads to two types of important results.

First, essential information about the solvent intermolecular potential is obtained. The solvent ‘mean field’ approach is found to be an excellent framework for discussing the interaction with probe molecules. There are two main mechanisms that contribute to solute orientational order, viz. the long-range interaction between the solvent \( efg \) and the solute molecular quadrupole moment, and a short-range mechanism that depends on the size and shape of the solute. In zero \( efg \) ‘magic mixtures’ the long-range contribution can be neglected and only the size and shape contribution remains. Since the short-range mechanism can be modeled effectively by relatively simple phenomenological models, solute order parameters in ‘magic mixtures’ can now be predicted to approximately the 10% level. Moreover, the experimental NMR results show excellent agreement with those of computer simulations. A large body of data supports the notion of a solvent \( efg \), especially because its presence in a nematic liquid crystal can explain discrepancies in quadrupolar couplings observed for quadrupolar nuclei in many probe molecules in a consistent manner.

Secondly, the dipolar and quadrupolar couplings observed in the NMR spectra of probe molecules contain detailed information about structural parameters such as bond lengths and bond angles. When the solvent ‘mean field’ is taken as a uniaxial, apolar perturbation on the rigid rotor and harmonic oscillator wave functions of the probe molecules, the perturbations are found to be surprisingly small. In order to obtain accurate structural parameters, averaging over rotational and vibrational motions has to be performed with great care. If the reorientation–vibration interaction, also called ‘correlation’, is included, it is found consistently that the geometrical parameters obtained for solutes dissolved in liquid-crystal phases are in excellent agreement with the corresponding gas-phase values. This observation again supports the idea that the perturbation of the solute by the solvent ‘field’ is relatively small. Finally, when ‘correlation’ effects are taken into account, curious ‘discrepancies’ disappear. In order to explain the NMR observations there is no longer the need to resort to elusive chemical interactions such as two-site models.

Acknowledgments

The authors acknowledge all the students, post-docs and co-workers that over many years have contributed to this project. Their names appear as co-authors on many papers. We express our special thanks to Prof. Jaap G. Snijders (deceased in 2004) who contributed immensely to the theory developed for the project. Thanks are also due to Profs. Annalaura Segre and Jean Jeener for the fruitful collaborations that originated at Zakopane meetings, and to Jerzy Blicharski and Barbara Blicharska for organizing these meetings in the first place.

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