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NMR methods of studying orientational order in the liquid crystalline and isotropic phases of mesogenic samples

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The understanding of how to describe the orientational order of the molecules in liquid crystalline phases, and in the isotropic phase formed by mesogens, has undergone considerable development in the past 25 years; this progress is reviewed. In parallel with the theoretical developments it has also been shown that NMR spectroscopy plays a unique role in the measurement of the orientational order of the molecules, and it is explained how biaxial ordering can be characterized for rigid molecules, and how the conformationally-dependent order parameters necessary for flexible molecules can be obtained.

1. Introduction

Over the last 30 years or so, there have been very significant changes in how the orientational order of the molecules in samples which can form a liquid crystalline phase is described, measured and explained. Geoffrey Luckhurst has played a leading role in these developments, and this article highlights those areas where his influence has been felt the most. It is not meant to be an exhaustive coverage of all the work that he and others have done, but more a tribute from one who has learned a great deal from being a close observer of the progress made by him and our colleagues at Southampton.

2. Orientational order in a liquid crystalline phase

There are strong anisotropic forces between the molecules which form liquid crystalline phases. In the liquid crystalline phase these forces lead to long range orientational order of the molecules, which in turn makes some of the physical properties of the sample anisotropic, such as the optical refractive index, n, the magnetic susceptibility, χ, and the electric permittivity, ε. To quantify the orientational order the concept of a set of director axes, x_{d}^{i}, y_{d}^{i}, z_{d}^{i} is introduced, with the origin at some point i in the sample. For simplicity only uniaxial phases will be discussed, and in this case the local symmetry about z_{d}^{i} is $D_{\infty h}$; this direction is referred to as the local director, $\mathbf{d}_i$. The two directions x_{d}^{i} and y_{d}^{i} are indistinguishable.

3. Orientational order from measurement of bulk, anisotropic properties

The simplest way to detect the presence of orientational order in a liquid sample is to view it through a polarizing microscope. The beautifully coloured and complex patterns observed reveal unambiguously that the sample is birefringent, and hence anisotropic in nature. However, this experiment does not give a way of quantifying the extent of the orientational order. This could be achieved if it was possible to measure components of the refractive index parallel, $n_{\|}^{i}$ and perpendicular, $n_{\perp}^{i}$, to the local directors: for a sample at thermal equilibrium these values should be independent of the position, i. However, it is much better first to produce a sample in which all the local directors are at the same orientation with respect to an external direction, in the case of birefringence, by containing the sample between closely spaced glass plates which, when treated appropriately, lead to the directors being all uniformly parallel to the normals to the plates, or uniformly in the plane of the surfaces of the plates. A uniform alignment of the local directors may also be obtained by application of polarized magnetic or electric fields. These uniformly, macroscopically ordered samples can now be used to measure components $A_{\|d}$ or $A_{\perp d}$ relative to the single, macroscopic director, d, where A is either n^2, χ, or ε. These values can be used to define a macroscopic order parameter, S_{mac}, as

$$S_{\mathrm{mac}}=\frac{A_{\|d}-A_{\perp d}}{\Delta A}. \tag{1}$$

ΔA is the maximum value of $\mathrm{A}_{\|d}-\mathrm{A}_{\perp d}$, which may be measurable on single crystal samples, or if unknown is a scaling parameter for S_{mac}.

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It is not always easy to measure both $A_{\parallel d}$ and $A_{\perp d}$ and an alternative is to measure one of these plus A_0, the average over all orientations, which may be equated to A_{iso} the value measured for the sample in the isotropic phase. Thus,

$$A_0 = \left(A_{\parallel d} + 2A_{\perp d}\right) \tag{2}$$

and so

$$S_{\text{mac}} = \frac{3\left(A_{\parallel d} - A_0\right)}{2\Delta A} \tag{3}$$

and

$$S_{\text{mac}} = \frac{3(A_0 - A_{\perp d})}{\Delta A}. \tag{4}$$

4. Molecular orientational order parameters

S_{mac} is certainly a very useful indication of the extent of orientational order in the liquid crystalline phase, but it is not a precise measure of the orientational order of the molecules in the phase. To appreciate why this is so, consider the orientation of a single molecule relative to the local director. In fact, since all the molecules of the same kind will have identical average orientational order, the macroscopic director **d** can be used instead of the local director $\mathbf{d}_i$. For simplicity the molecule is first considered to be rigid and cylindrically symmetric about an axis z so that the orientation of the kth molecule is specified completely by an angle β_k as shown in figure 1.

The quantities n^2, χ and ε are each second rank tensors so that

$$A_{\parallel d} - A_{\perp d} = \left[A_{zz} - \frac{1}{2}\left(A_{xx} + A_{yy}\right)\right]\left(\frac{3}{2}\cos^2\beta_k - \frac{1}{2}\right). \tag{5}$$

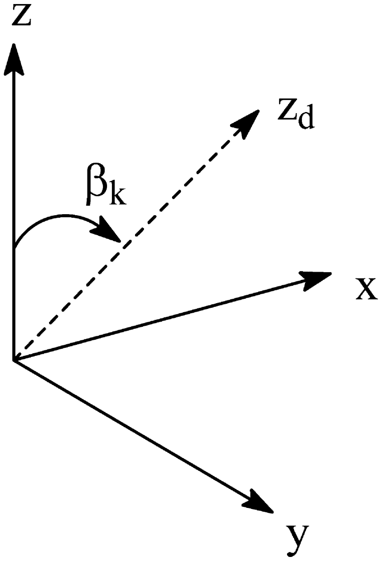


Figure 1. The orientation of the director in molecule-fixed axes xyz.

Averaging over the orientations of all the molecules then gives

$$A_{\parallel d} - A_{\perp d} = \left[A_{zz} - \frac{1}{2}\left(A_{xx} + A_{yy}\right)\right]\bar{P}_2 \tag{6}$$

where

$$\bar{P}_2 = \langle\frac{3}{2}\cos^2\beta_k - \frac{1}{2}\rangle. \tag{7}$$

The $<>$ denotes an average over either the ensemble, or time. $\bar{P}_2$ is an order parameter for rigid, cylindrically symmetric molecules, and is equal to S_{mac} if $\left[A_{zz} - \frac{1}{2}\left(A_{xx} + A_{yy}\right)\right]$ can be measured and equated to ΔA in equation (1). For rigid, cylindrically symmetric molecules, therefore, there is an equivalence between the macroscopic and molecular interpretations of an order parameter. But most molecules, even if rigid, are not cylindrically symmetric, and in these cases there are five independent, second rank order parameters, which form the Saupe matrix:

$$\begin{bmatrix} S_{xx} & S_{xy} & S_{xz} \\ S_{yx} & S_{yy} & S_{yz} \\ S_{zx} & S_{zx} & S_{zz} \end{bmatrix}$$

where

$$S_{\alpha\beta} = \langle\frac{3}{2}\cos\theta_\alpha\cos\theta_\beta - \delta_{\alpha\beta}\rangle. \tag{8}$$

The angle θ_α is that made by the director to axis α, and $\delta_{\alpha\beta}=1$ if $\alpha=\beta$, and 0 otherwise.

The nine elements are reduced to an independent set of five by the relationships:

$$S_{xx} + S_{yy} + S_{zz} = 0;\ S_{xy} = S_{yx};\ S_{xz} = S_{zx};\ S_{yz} = S_{zy}.$$

There is always one set of axes, the principal axes *abc*, for which only the diagonal elements are non-zero. Note that five independent parameters are still required to describe the second rank orientation: S_{aa}, $S_{bb} - S_{cc}$ and three Euler angles describing the relative orientations of the two axis frames. The location of some or all of the principal axes may be predicted if the rigid molecule has planes or rotation axes of symmetry.

5. Order parameters of rigid molecules from NMR spectroscopy

It is not possible to obtain the five order parameters from measurements of the anisotropies in n, χ or ε, but it is possible to do so using NMR spectroscopy. Thus, dipolar couplings, D_{ij}, between nuclei i and j in a rigid molecule are given by:

$$D_{ij} = -\left(K_{ij}/r_{ij}^3\right) \left[\begin{array}{l} S_{zz}\left(3\cos^2\theta_{ijz}-1\right)+\left(S_{xx}-S_{yy}\right)\left(\cos^2\theta_{ijx}-\cos^2\theta_{ijy}\right) \\ +4S_{xy}\cos\theta_{ijx}\cos\theta_{ijy}+4S_{xz}\cos\theta_{ijx}\cos\theta_{ijz}+4S_{yz}\cos\theta_{ijy}\cos\theta_{ijz} \end{array}\right] \quad (9)$$

with

$$K_{ij} = \frac{\mu_0 \hbar \gamma_i \gamma_i}{16\pi^2}. \quad (10)$$

The angle $\theta_{ij\alpha}$ is that between an axis α fixed in the molecule and the vector $\mathbf{r}_{ij}$ connecting the two nuclei; γ_i is the magnetogyric ratio of nucleus i, and μ_0 is the magnetic constant.

Dipolar couplings affect the spectra of all magnetic nuclei, but are not always easy to obtain when the spectra are too complex for analysis. In these cases it is more convenient to use deuterium NMR, whose spectra are dominated by the nuclear electric quadrupole interaction. The spectra yield values of the deuterium quadrupolar splittings, $\Delta\nu_i$, which are related to the order parameters by

$$\begin{aligned} \Delta\nu_i = \frac{3}{2}\, q_{\mathrm{CD}i}\Bigg[& S_{zz}\left(\frac{3}{2}\cos^2\theta_{\mathrm{CD}zi}-\frac{1}{2}\right)+ \\ & +\frac{1}{2}\left(S_{xx}-S_{yy}\right)\left(\cos^2\theta_{\mathrm{CD}xi}-\cos^2\theta_{\mathrm{CD}yi}\right) \\ & +\frac{4}{3}S_{xy}\cos\theta_{\mathrm{CD}xi}\cos\theta_{\mathrm{CD}yi} \\ & +\frac{4}{3}\,S_{xz}\cos\theta_{\mathrm{CD}xi}\cos\theta_{\mathrm{CD}zi} \\ & +\frac{4}{3}\,S_{yz}\cos\theta_{\mathrm{CD}yi}\cos\theta_{\mathrm{CD}zi}\Bigg] \end{aligned} \quad (11)$$

The deuterium quadrupole coupling constant $q_{\mathrm{CD}i}$ has to be known, and so too do the angles $\theta_{\mathrm{CD}xi}$ etc., but in practice this is not a barrier to using equation (11) to obtain the order parameters. Note that for simplicity the contribution to $\Delta\nu_i$ from terms involving the asymmetry in the quadrupole tensor have been omitted.

The ability to measure all the order parameters for a rigid molecule stimulated experimental work on solutes dissolved in liquid crystalline solvents whose aim was to test theoretical models of the origins of the anisotropic solute–solvent forces. In this regard, Luckhurst and his coworkers in a number of papers [1–7] have pointed out the advantages in studying solutes with symmetry C_{2v}. The location of the principal axes for such molecules is determined by their symmetry, whilst they are biaxial and hence there are two principal order parameters, S_{aa} and S_{bb}–S_{cc}, which can be determined from experiment for the complete temperature range of the liquid crystalline solution. Mean field theories then relate these order parameters to a mean, anisotropic potential, $U_{\mathrm{LC}}(\beta,\gamma)$, by

$$S_{aa} = Z^{-1}\int\left(\frac{3}{2}\cos^2\beta-\frac{1}{2}\right) \exp[-U_{\mathrm{LC}}(\beta,\gamma)/k_{\mathrm{B}}T]\sin\beta\,\mathrm{d}\beta\,\mathrm{d}\gamma \quad (12)$$

and

$$S_{bb}-S_{cc} = Z^{-1}\int\left(\frac{3}{2}\right)^{\frac{1}{2}}\sin^2\beta\cos 2\gamma \exp[-U_{\mathrm{LC}}(\beta,\gamma)/k_{\mathrm{B}}T]\sin\beta\,\mathrm{d}\beta\,\mathrm{d}\gamma \quad (13)$$

with

$$Z = \int \exp[-U_{\mathrm{LC}}(\beta,\gamma)/k_{\mathrm{B}}T]\sin\beta\,\mathrm{d}\beta\,\mathrm{d}\gamma. \quad (14)$$

There have been two approaches to identifying the form of $U_{\mathrm{LC}}(\beta,\gamma)$. The first is to propose a specific form for a pair potential, and then to average over the orientation and separation of the solute and solvent molecules. This clearly has the advantage of testing ideas about the origins of the anisotropic intermolecular forces, and many studies of this kind have been reported [8]. A second approach is to expand $U_{\mathrm{LC}}(\beta,\gamma)$ in terms of an orthogonal set of angular functions, such as Wigner functions, $D^L_{m,n}(\alpha,\beta,\gamma)$, or for uniaxial phases for which $m=0$, the modified spherical harmonics, $C_{L,n}(\beta,\gamma)$:

$$U_{\mathrm{LC}}(\beta,\gamma) = -\sum_{L,n}^{L\ \mathrm{even}} \varepsilon_{L,n}C_{L,n}(\beta,\gamma). \quad (15)$$

This will be a complete description of $U_{\mathrm{LC}}(\beta,\gamma)$ if the summation is over $L=2$ to ∞, but clearly it would be impossible to test a potential of infinite extent. The order tensor $\mathbf{S}$ is of second rank, and so it is appropriate to restrict the summation in equation (15) to just the terms with $L=2$, and $n=\pm 2$. This approximation improves in accuracy as the order approaches zero. The truncated form is:

$$U_{\mathrm{LC}}(\beta,\gamma) = -\varepsilon_{2,0}\,C_{2,0}(\beta)-2\varepsilon_{2,2}\,C_{2,2}(\beta,\gamma). \quad (16)$$

The measurement of the two order parameters at a particular temperature can therefore be used to obtain the two solute–solvent interaction coefficients $\varepsilon_{2,n}$.

At this point it is not immediately clear that any progress has been made in understanding the nature of the anisotropic forces contributing to $U_{\mathrm{LC}}(\beta,\gamma)$. To progress further it is necessary to consider how the $\varepsilon_{2,n}$ will depend on the orientational ordering of the solvent molecules. The solvent molecules will usually be quite complex in structure, having no symmetry and also being flexible; but neglecting these complications at the moment, and assuming them to be rigid, then two order parameters, $\bar{C}_{2,0}$ and $\bar{C}^{*}_{2,2}$ are required (averages of the modified spherical harmonics are used here rather than the Cartesian tensor **S** in order to distinguish clearly between the order of the solute and solvent molecules). The solute–solvent interaction parameters must vanish when $\bar{C}_{2,0}$ and $\bar{C}^{*}_{2,2}$ are zero, and they will be a maximum for a fully ordered liquid crystalline solvent. The simplest form, therefore, for the dependence of the $\varepsilon_{2,n}$ on the solvent order parameters $\bar{C}_{2,n}$ is:

$$\varepsilon_{2,0} = \bar{u}_{200}\,\bar{C}_{2,0} + \bar{u}_{202}\,\bar{C}^{*}_{2,2} \tag{17}$$

$$\varepsilon_{2,2} = \bar{u}_{220}\,\bar{C}_{2,0} + \bar{u}_{222}\,\bar{C}^{*}_{2,2}. \tag{18}$$

A coefficient $\bar{u}_{2mn}$ is an average over the separation of solute and solvent molecules, and for example, $\bar{u}_{200}$ refers to the tendency of the major principal axes of solute and solvent to align themselves. Measurements of $\bar{C}^{*}_{2,2}$ for the solvent, liquid crystalline molecules, albeit approximate, suggest that this biaxial order parameter is ~5% of $\bar{C}_{2,0}$. Neglecting the terms involving $\bar{C}^{*}_{2,2}$ leads to the simple result that

$$\lambda = \varepsilon_{2,2}/\varepsilon_{2,2} = \bar{u}_{220}/\bar{u}_{200}. \tag{19}$$

Thus, the strong temperature variation of the two parameters $\varepsilon_{2,n}$ arising from their dependence on $\bar{C}_{2,0}$ is removed from the ratio λ, which is therefore expected to change only weakly with temperature for a particular solute–solvent mixture. The observed temperature dependencies of values of λ determined from pairs of values of S_{aa} and S_{bb}–S_{cc} can be much stronger than this simple analysis predicts, suggesting that some of the assumptions made need re-examination in these cases [2–7].

A more striking prediction of this simple mean field theory concerns the effect produced on λ of a change in the liquid crystalline solvent. Thus, if it is assumed that a single second rank interaction determines the values of the $\bar{u}_{2mn}$, and if this obeys the relationship:

$$\bar{u}_{2mn} = B X^{\text{solute}}_{2,m}\, X^{\text{solvent}}_{2,n} \tag{20}$$

where $X^{\text{solute}}_{2,m}$ depends on some property, such as polarizability, electric quadrupolar moment, and similarly $X^{\text{solvent}}_{2,n}$ depends only on the nature of the liquid crystalline solvent, then

$$\lambda = X^{\text{solute}}_{2,2} \Big/ X^{\text{solute}}_{2,0} \tag{21}$$

and so the biaxiality parameter for a particular solute should be independent of the nature of the liquid crystalline solvent. For most solutes this prediction is incorrect, and there are large changes of experimental values of λ as the solvent is changed.

6. Orientational order of non-rigid molecules

These early studies of rigid solutes in liquid crystalline solvents stimulated many later studies, and much re-thinking of the nature of the forces governing the orientational order of dissolved solutes. But there is more interest in the orientational order of the molecules in liquid crystals themselves, and this raises another very important aspect of the structure of these molecules and its effect on both the orientational order and stability of the mesophases. The molecules which form mesophases are almost invariably flexible; that is, there is motion about single bonds so that the molecular shape is constantly changing with time. The anisotropic intermolecular forces depend on shape, and so the orientational order matrices depend on the conformation of the molecule, which is defined by a set of bond rotation angles, $\{\phi_i\}$. To extend the mean field theory to include the effects of internal motion, Luckhurst and Emsley [9] introduced a mean potential, $U_{\text{LC}}(\beta, \gamma, \{\phi_i\})$, which is a sum of an anisotropic, conformationally-dependent potential of mean torque, $U_{\text{ext}}(\beta, \gamma, \{\phi_i\})$, and $U_{\text{iso}}(\{\phi_i\})$ which depends only on the conformational state, and hence on the bond rotational potentials. Thus,

$$U_{\text{LC}}(\beta, \gamma, \{\phi_i\}) = U_{\text{ext}}(\beta, \gamma, \{\phi_i\}) + U_{\text{int}}(\{\phi_i\}). \tag{22}$$

The potential of mean torque is used to define conformationally-dependent order parameters, $S_{\alpha\alpha}(\{\phi_i\})$, thus equations (12)–(14) become:

$$S_{aa}(\{\phi_i\}) = Z^{-1}\int \left(\frac{3}{2}\cos^2\beta - \frac{1}{2}\right) \exp[-U_{\text{ext}}(\beta, \gamma, \{\phi_i\})/k_{\text{B}}T]\sin\beta\,\mathrm{d}\beta\,\mathrm{d}\gamma \tag{23}$$

and

$$S_{bb}(\{\phi_i\}) - S_{cc}(\{\phi_i\}) = Z^{-1}\int \left(\frac{3}{2}\right)^{\frac{1}{2}}\sin^2\beta\cos 2\gamma \exp[-U_{\text{ext}}(\beta, \gamma, \{\phi_i\})/k_{\text{B}}T]\sin\beta\,\mathrm{d}\beta\,\mathrm{d}\gamma \tag{24}$$

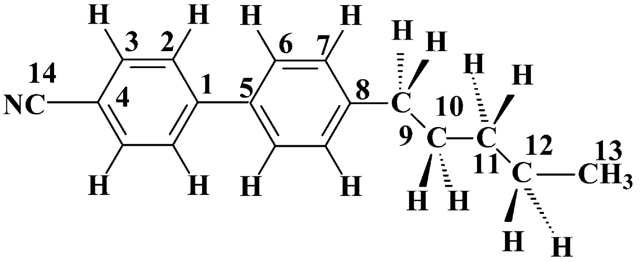
with

$$Z = \int \exp[-U_{\text{ext}}(\beta, \gamma, \{\phi_i\})/k_{\text{B}}T]\sin\beta\,\mathrm{d}\beta\,\mathrm{d}\gamma. \tag{25}$$

The same general approach to representing the potential of mean torque as an expansion in modified spherical harmonics was followed, giving

$$\begin{aligned} U_{\text{ext}}(\beta, \gamma, \{\phi_i\}) = {} & -\varepsilon_{2,0}(\{\phi_i\})C_{2,0}(\beta) \\ & -2\varepsilon_{2,2}(\{\phi_i\})C_{2,2}(\beta, \gamma). \end{aligned} \tag{26}$$

At first sight it appears that it is impossible to use equation (26) to calculate the conformationally-dependent order parameters because there are just too many interaction coefficients, $\varepsilon_{2,m}(\{\phi_i\})$ For example, consider a rather simple mesogen such as 5CB:



There are six bonds about which rotation occurs, and if a simplified, discrete conformational model is used in which the molecules are considered to move between positions of local minimum energy, there are 216 discrete conformational forms. This is based on the C–C–C–C chain segments being either in a *trans* or one of the two energetically equivalent *gauche* forms, the plane $C_8C_9C_{10}$ being orthogonal (90° or 270°) to the attached ring, and the two rings being in one of four equivalent minimum energy positions generated by rotation about the C_1–C_5 bond. Symmetry considerations reduce the number of conformations which are different in energy to 14, and so there are 28 values of the $\varepsilon_{2,m}(n)$ in equation (26), where the continuous variables $\{\phi_i\}$ are replaced by the finite set n. Luckhurst *et al.* [10] reduced this by assuming that $\varepsilon_{2,m}(\{\phi_i\})$ can be expressed as a sum of contributions from each rigid fragment in the molecules which are moved relative to one another by the rotations about the bonds. Thus:

$$\varepsilon_{2,m}(n) = \sum_{j,p} \varepsilon_{2,p}(j) D^2_{p,m}(\alpha_j, \beta_j, \gamma_j) \tag{27}$$

where $D^2_{p,m}(\alpha_j, \beta_j, \gamma_j)$ are the Wigner functions describing the orientation of fragment j relative to a reference frame fixed in one of the fragments. This model for reducing the number of variables is often referred to as the additive potential (AP) method. In 5CB these fragments are the C–C and C–H bonds in the alkyl chain, which are assigned common values of axially symmetric fragment interaction tensor, $\varepsilon_{2,0}$(C–C), and $\varepsilon_{2,0}$(C–H), and two components for the biaxial cyanobiphenyl group, $\varepsilon_{2,0}(R)$ and $\varepsilon_{2,2}(R)$. In this way the number of interaction parameters which must be found by comparison with experimental data is reduced from 28 to four, and much greater reductions are obtained for mesogens with either longer chains or more than one chain. The additional variable to be fitted by a comparison between observed NMR parameters and those calculated is the difference in energy ΔE_{tg} between a *gauche* and *trans* arrangement in the segments of the alkyl chain.

One very interesting prediction of this mean field model is that the conformational distribution should change on going from the isotropic to the liquid crystalline phase. Thus, two conformational probability densities can be defined:

$$P_{\mathrm{LC}}(\{\phi_i\}) = Q_{\mathrm{LC}}^{-1} \int \exp[-U_{\mathrm{LC}}(\beta, \gamma, \{\phi_i\})/k_{\mathrm{B}}T] \sin\beta \, \mathrm{d}\beta \, \mathrm{d}\gamma \tag{28}$$

with

$$Q_{\mathrm{LC}} = \int \exp[-U_{\mathrm{LC}}(\beta, \gamma, \{\phi_i\})/k_{\mathrm{B}}T] \sin\beta \, \mathrm{d}\beta \, \mathrm{d}\gamma \, \mathrm{d}\{\phi_i\} \tag{29}$$

and

$$P_{\mathrm{iso}}(\{\phi_i\}) = Q_{\mathrm{iso}}^{-1} \exp[-U_{\mathrm{iso}}(\{\phi_i\})/k_{\mathrm{B}}T] \tag{30}$$

with

$$Q_{\mathrm{iso}} = \int \exp[-U_{\mathrm{iso}}(\{\phi_i\})/k_{\mathrm{B}}T] \mathrm{d}\{\phi_i\}. \tag{31}$$

These two probability densities are not equal, with the difference between them increasing as the orientational order increases.

The NMR data which have been used to test this model include values of quadrupolar splittings $\Delta\nu_i$, obtained from deuteriated samples of mesogens (and which are measured very easily from 1D single pulse ^{2}H NMR spectra, but require the synthesis of deuterium labelled samples), dipolar couplings D_{ij}^{CH}, which require more sophisticated 2D or 3D experiments, and values of D_{ij}^{HH}, whose measurement involves partially deuteriating a mesogen followed by decoupling of the deuterium nuclei.

Figure 2 shows the deuterium spectrum of the partially deuterated sample 5CB-d$_{15}$ [11], and figure 3 gives the conformer probabilities $P_{\mathrm{LC}}(n)$ and $P_{\mathrm{iso}}(n)$ derived by fitting calculated to observed values of the

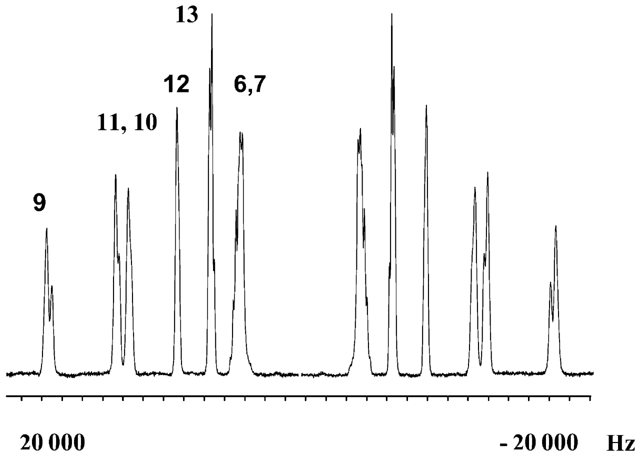


Figure 2. 30.7 MHz ^{2}H spectrum of 5CB-d$_{15}$ [11].

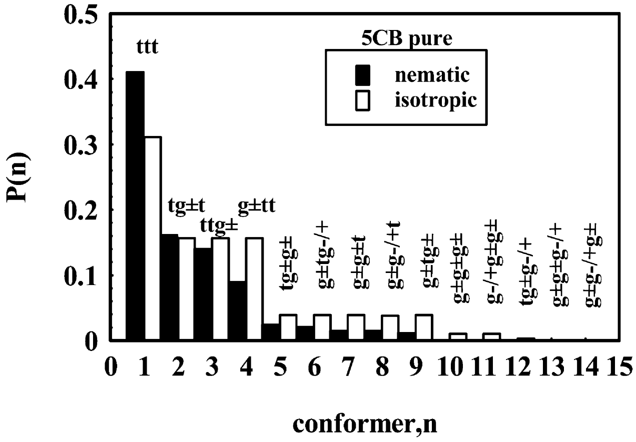


Figure 3. The probabilities *P*(*n*) of conformers in 5CB generated by rotation between *trans*(*t*) and *gauche* (*g*+ and *g*−) forms in the alkyl chain. Filled bars are values of $P_{\mathrm{LC}}(n)$ for T_{NI}–*T* of 22°C, and open bars are values of $P_{\mathrm{iso}}(n)$ predicted for the same temperature [12].

quadrupolar splittings [11, 12]. Note that some of the conformers have $P_{\mathrm{LC}}(n)$–$P_{\mathrm{iso}}(n)$ large and positive, for example the all-*trans* form *ttt*, whilst for others the difference is negative, for example $g\pm tt$.

A great many mesogens, and non-mesogenic flexible solutes, have now been studied by this combination of NMR experiments and the interpretation of the data by the model described above, or by modifications of the theoretical model, but which retain the essential feature that the orientational order of the molecules varies with their conformational state.

Luckhurst [13] has also extended the theory to include the dependence of the $\varepsilon_{2,m}(\{\phi_i\})$ on the orientational order of the liquid crystal molecules, in the same spirit as discussed for the simpler case of rigid solutes. However, this work falls outside the scope of this article.

7. Orientational order in the isotropic phase before the transition to a liquid crystalline phase

The molecules in isotropic phases are not completely without orientational order, if they are of anisometric shape. A general description of the orientational correlations between molecules is via Kirkwood g_{L} factors, and when considering the average in the phase of second rank properties only g_2 is relevant, which for rigid, cylindrically symmetric molecules is defined as:

$$g_2 = 1 + \sum_{i<j} \left\langle \left(\frac{3}{2}\cos^2\beta_{ij} - \frac{1}{2} \right) \right\rangle \tag{32}$$

where β_{ij} is the angle between the assumed symmetry axes of two molecules, and the <> denotes an average over all the molecules. When there are no orientational correlations, that is at $T \gg T_{\mathrm{NI}}$, then $g_2 = 1$, and for an ensemble of perfectly ordered molecules $g_2 = N$, the number of molecules. The Landau–de Gennes phenomenological theory for the weakly first order nematic–isotropic transition predicts that g_2 should diverge according to [14]:

$$g_2 = k_{\mathrm{B}}T/[a(T - T^*)] \tag{33}$$

where T^* is the temperature at which a second order transition to the nematic phase would occur if a first order transition at T_{NI} had not taken place. Thus, T^* is below T_{NI}. Early experiments to reveal the presence of orientational order, and to test the temperature dependence predicted by equation (33), involved the measurement of electric or magnetic field-induced birefringence. For example, application of a uniform magnetic field $\mathbf{B}_0$, polarized in one direction, leads to an induced birefringence Δn_{ind}, for a sample composed of rigid, cylindrically symmetric molecules which is predicted to depend on $\Delta\chi_{\mathrm{B}}$, the anisotropy of the magnetic susceptibility relative to the field direction, $\mathbf{B}_0^2$ and $(T$–$T^*)^{-1}$, thus [15]

$$\Delta n_{\mathrm{ind}} \propto \Delta\chi_{\mathrm{B}} \mathbf{B}_0^2/(T - T^*). \tag{34}$$

Experiments on a number of mesogens have supported the dependence of Δn_{ind} on $(T$–$T^*)^{-1}$, and on $\mathbf{B}_0^2$ over a wide temperature range in the isotropic phase, but with some significant deviations for the temperature dependence near T_{NI} for some mesogens [15].

The detection of orientational order in the pretransitional region using the measurement of a macroscopic property suffers from the same disadvantages as when these properties are used to obtain S_{mac} in the mesophase from equations (1)–(4), and which again stem from the difficulties in allowing for either lower than cylindrical symmetry, or the flexibility of the molecules. Again, NMR provides an alternative experimental method for studying pretransitional ordering, which yields enough information so that the effects of lower symmetry and molecular flexibility can be investigated.

In NMR experiments the sample is in the applied magnetic field of the spectrometer, and there is a continuous effort expended to manufacture superconducting magnets with the highest field possible. By 1978 these efforts had produced spectrometers with $\mathbf{B}_0 = 9.3$ T and Lohman and Maclean showed that with such a field strength it is possible to observe field-induced quadrupolar splittings, $\Delta\nu_i^{\mathrm{ind}}$, in the deuterium spectra of aromatic compounds dissolved in isotropic solvents, such as carbon disulphide and diethyl ether [16]. The observation of a quadrupolar splitting is direct evidence that the molecules have a net alignment, since this interaction is wholly anisotropic. The splittings observed were small, <1 Hz, and arise from the alignment effect of the magnetic field on single molecules, that is $g_2=1$. The magnetic torque U_{mag}, acting on a single, rigid molecule in a magnetic field is

$$U_{\mathrm{mag}}(\beta,\gamma)=-\frac{1}{2}\mathbf{B}_0^2\left[\chi_{2,0}C_{2,0}(\beta)+2\chi_{2,2}C_{2,2}(\beta,\gamma)\right] \quad (35)$$

and when $U_{\mathrm{mag}}(\beta,\gamma)\ll k_{\mathrm{B}}T$, which is true for these experiments, this produces orientational order parameters, $\overline{C}^{\mathrm{B}}_{2,m}$, induced by the magnetic field:

$$\overline{C}^{\mathrm{B}}_{2,m}=\mathbf{B}_0^2\chi_{2,m}/(10k_{\mathrm{B}}T). \quad (36)$$

For biaxial molecules there are two order parameters corresponding to $m=0$ and 2. For the molecules studied these are of the order of 10^{-5}.

It was quickly realised by Luckhurst *et al.* [17] that deuterium NMR should provide a means of detecting the orientational order of the molecules in the isotropic phase of mesogenic samples at these high field strengths. This was indeed found to be the case, as they first demonstrated by observing field-induced quadrupolar splittings in a sample of 5CB-d_{15} deuteriated in both ring and chain, as shown in figure 4. It can be seen that the peaks at highest field are split into doublets as T_{NI} is approached, which is unambiguous evidence for field-induced orientational order. Deuterium NMR also has the advantage that induced order in solutes dissolved in a mesogenic solvent can be studied [18]. In this case, to avoid spectral overlap, it is an advantage to use a deuteriated solute in a non-deuteriated solvent.

The main advantage in studying solutes is that they can be chosen to be rigid, and of different point group symmetries. The availability of such experimental data stimulated Luckhurst *et al.* [19, 20] to develop a mean field theory for the field-induced order. The starting point is to define a potential of mean torque for a rigid molecule in the presence of the magnetic torque given by equation (35), but also subject to anisotropic forces

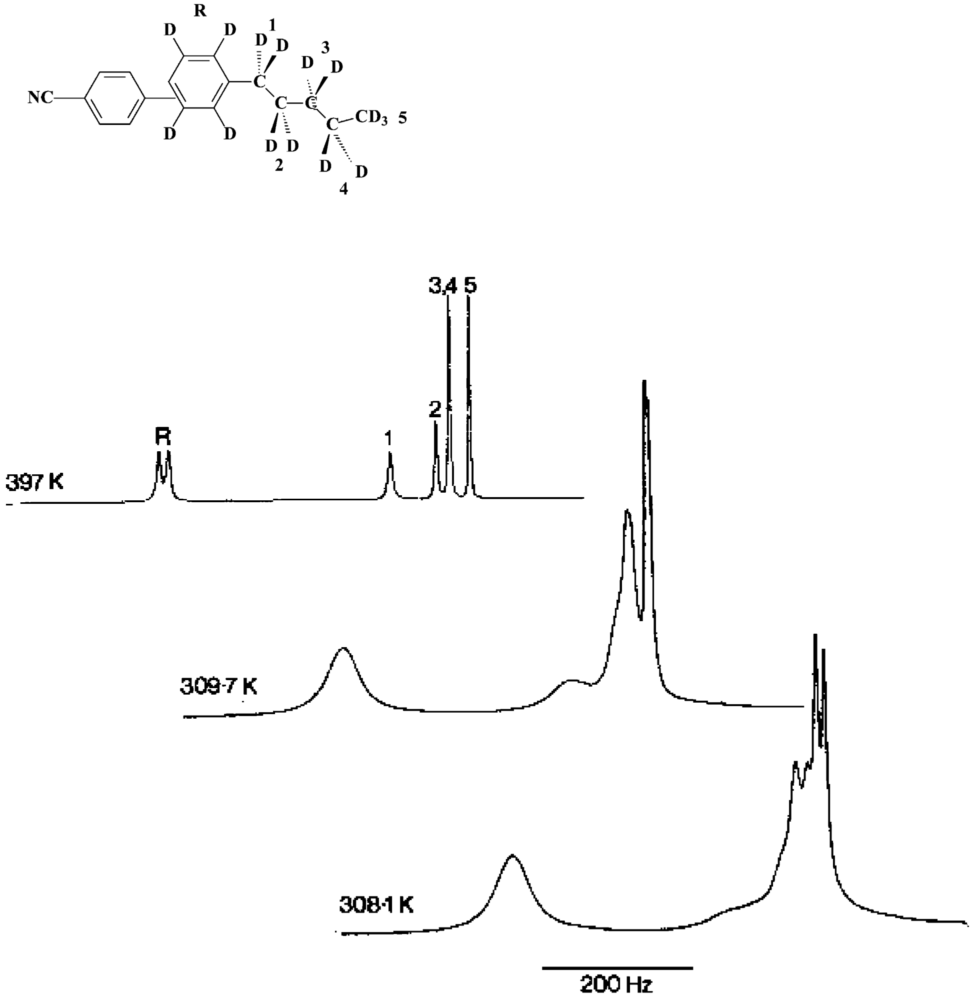


Figure 4. 61.4 MHz ^{2}H spectra of 5CB-d_{15} at the temperatures shown alongside each trace [17].

between the molecules, leading to a potential of mean torque, $U_{\mathrm{mol}}(\beta, \gamma)$, of the same form as that in equation (15), which is for the liquid crystalline phase: in both phases the symmetry is the same, $D_{\infty h}$. Both $U_{\mathrm{mol}}(\beta, \gamma)$ and U_{mag} are $\ll k_{\mathrm{B}}T$ and so the following form for the total torque, $U^{n}_{\mathrm{sum}}(\beta_n, \gamma_n, n)$, on the molecules is essentially exact:

$$U_{\mathrm{sum}}(\beta, \gamma) = -\left\{\varepsilon_{2,0} + \frac{1}{2}B_0^2\chi_{2,0}\right\}C_{2,0}(\beta) - \left\{2\varepsilon_{2,2} + B_0^2\chi_{2,2}\right\}C_{2,2}(\beta, \gamma). \tag{37}$$

In order to derive expressions for the temperature dependencies of the two order parameters, $\bar{C}^{\mathrm{B}}_{2,m}$, Luckhurst [19] together with Heaton [20] assumed a linear dependence of the interaction parameters $\varepsilon_{2,m}$ on the order parameters; cf. equations (17) and (18):

$$\varepsilon_{2,0} = \bar{u}_{200}\,\bar{C}^{\mathrm{B}}_{2,0} + \bar{u}_{202}\,\bar{C}^{\mathrm{B}}_{2,2} \tag{38}$$

$$\varepsilon_{2,2} = \bar{u}_{220}\,\bar{C}^{\mathrm{B}}_{2,0} + \bar{u}_{222}\,\bar{C}^{\mathrm{B}}_{2,2}. \tag{39}$$

Note that the $\varepsilon_{2,m}$ do not depend on the applied field strength. In the absence of a field, equations (38) and (39) still hold but with the order parameters expressed with respect to the field direction replaced by ones, $\bar{C}_{2,m}$, defined relative to a local director.

The number of proportionality constants, $\bar{u}_{2mn}$, was reduced by assuming the relationship:

$$\bar{u}_{202} = \bar{u}_{220} = (\bar{u}_{200}\bar{u}_{222})^{\frac{1}{2}}. \tag{40}$$

This leads to expressions for the dependence on temperature of the order parameters as

$$\bar{C}^{\mathrm{B}}_{2,0} = \frac{\left[\lambda\bar{u}_{200}(\chi_{2,2} - \lambda\chi_{2,0}) + 5k_{\mathrm{B}}T\chi_{2,0}\right]\mathrm{B}_0^2}{50k_{\mathrm{B}}^2T(T - T^*)} \tag{41}$$

$$\bar{C}^{\mathrm{B}}_{2,2} = \frac{\left[\bar{u}_{200}(\lambda\chi_{2,0} - \chi_{2,2}) + 5k_{\mathrm{B}}\chi_{2,2}T\right]\mathrm{B}_0^2}{50k_{\mathrm{B}}^2T(T - T^*)}. \tag{42}$$

The temperature T^* is given by:

$$T^* = \bar{u}_{200}(1 + \lambda^2)/5k_{\mathrm{B}}. \tag{43}$$

This mean field theory for rigid, biaxial molecules predicts a common divergence temperature, T^*, for both order parameters.

It is difficult to test the predictions of this theory for rigid molecules since mesogenic molecules are usually flexible. The system most closely approximating to the rigid molecule case is a rigid solute dissolved in a mesogenic solvent and this has been observed experimentally by deuterium NMR for a deuteriated solute, *para*-xylene, dissolved in a mesogenic solvent, Merck Phase 5 [18]. If the solute had been chosen to have symmetry C_{3v}, or higher, and so would have only a single, independent order parameter, $\bar{C}^{\mathrm{B}}_{2,0}$, then $\lambda=0$, and T^* is predicted to be

$$T^* = \bar{u}_{200}/5k_{\mathrm{B}}. \tag{44}$$

A comparison of equations (43) and (44) shows that the effect of biaxiality is to increase T^*, a prediction which remains to be tested experimentally.

8. The effect of molecular flexibility on pretransitional order

In order to model the behaviour of mesogenic molecules in the pretransition region it is necessary to extend the mean field theory to include the effects of the molecular non-rigidity. The approach taken by Luckhurst *et al.* [19, 20] followed the same lines as that used for the orientational order of flexible molecules in the liquid crystalline phase. If the conformational distribution is treated as a set of discrete rigid forms, then the order parameters, $\bar{C}^{n}_{2,m}$, for a molecule in conformation n, are given by

$$\bar{C}^{n}_{2,0} = \frac{\left[\lambda_n\bar{u}^{n}_{200}\left(\chi^{n}_{2,2} - \lambda_n\chi^{n}_{2,0}\right) + 5k_{\mathrm{B}}T\chi^{n}_{2,0}\right]\mathrm{B}_0^2}{50k_{\mathrm{B}}^2T(T - T^{n*})} \tag{45}$$

$$\bar{C}^{n}_{2,2} = \frac{\left[\bar{u}^{n}_{200}\left(\lambda_n\chi^{n}_{2,0} - \chi^{n}_{2,2}\right) + 5k_{\mathrm{B}}\chi^{n}_{2,2}T\right]\mathrm{B}_0^2}{50k_{\mathrm{B}}^2T(T - T^{n*})} \tag{46}$$

with

$$T^{n*} = \bar{u}^{n}_{200}(1 + \lambda_n^2)/5k_{\mathrm{B}}. \tag{47}$$

NMR experiments measure $A^{\mathrm{B}}_{2,0}$, the component along the field direction of either the deuterium quadrupolar splitting, or dipolar couplings. For a flexible molecule this is an average over all the conformations:

$$A^{\mathrm{B}}_{2,0} = \sum_n P_{\mathrm{LC}}(n)A^{\mathrm{B}}_{2,0}(n) \tag{48}$$

and since there is uniaxial symmetry about $\mathbf{B}_0$, then $A^{\mathrm{B}}_{2,0}(n)$ is related to $A^{\mathrm{mol}}_{2,m}(n)$, the components in a molecular, principal axis frame, by

$$A^{\mathrm{B}}_{2,0}(n) = \sum_{m=0,\pm 2} A^{\mathrm{mol}}_{2,m}(n)\,\bar{C}^{n}_{2,m}. \tag{49}$$

It can be concluded that all the quadrupolar and dipolar couplings in a flexible molecule should have a common dependence on $\mathbf{B}_0^2$, and a common divergence temperature T^* given by

$$T^* = \sum_n P_{\mathrm{LC}}(n, T = T^*) T^{n*}. \qquad (50)$$

There have been no attempts yet to test the dependence of T^* for flexible mesogens on $\bar{u}^n_{200}$, λ_n and $P_{\mathrm{LC}}(n, T = T^*)$, but Luckhurst and Heaton [20] have used a particular model for these quantities in order to predict how T^* should vary between members of the 4-alkyloxy-4′-cyanobiphenyl and α,ω-bis(4,4′-cyanobiphenyloxy)alkane mesogens.

9. Characterization of the conformer probabilities for mesogens in the isotropic phase

It was realised by Luckhurst *et al.* [17] that the set of field-induced quadrupolar splittings $\Delta\nu^{\mathrm{ind}}_i$, which should be available by deconvolution of the spectrum of deuteriated mesogens, such as that shown in figure 4 for 5CB-d$_{15}$, could be used to obtain the conformational distribution $P(n)$, and the conformationally-dependent order parameters $\bar{C}^n_{2,m}$ (or the Cartesian forms, $S_{aa}(n)$ and $S_{bb}(n) - S_{cc}(n)$, cf. equations (23) and (24)) for the molecules in the isotropic phase. To do this it is necessary to define a total, conformationally-dependent mean potential,

$$U^n_{\mathrm{total}}(\beta_n, \gamma_n, n) = U^n_{\mathrm{sum}}(\beta_n, \gamma_n, n) + U_{\mathrm{int}}(n) \qquad (51)$$

with

$$\begin{aligned} U^n_{\mathrm{sum}}(\beta_n, \gamma_n, n) &= U^n_{\mathrm{mol}}(\beta_n, \gamma_n, n) + U^n_{\mathrm{mag}}(\beta_n, \gamma_n, n) \\ &= -\left\{\varepsilon^n_{2,0} + \frac{1}{2}\mathbf{B}^2_0\chi^n_{2,0}\right\} C_{2,0}(\beta_n) \\ &\quad -\left\{2\varepsilon^n_{2,2} + \mathbf{B}^2_0\chi^n_{2,2}\right\} C_{2,2}(\beta_n, \gamma_n) \\ &= -X^n_{2,0} C_{2,0}(\beta_n) - 2X^n_{2,2}(\beta_n, \gamma_n) \end{aligned} \qquad (52)$$

When $T \gg T_{\mathrm{NI}}$ the coefficients $\varepsilon^n_{2,m}$ are small compared with the magnetic terms; that is, $g_2 = 1$, and the sample behaves as a collection of isolated molecules. The total potential of mean torque in this high temperature limit becomes $U_{\mathrm{mag}}(\beta_n, \gamma_n, n)$ for each conformer, just the magnetic contribution

$$\begin{aligned} (\beta_n, \gamma_n, n) = -\frac{1}{2}B^2_0\Big[&\chi^n_{2,0} C_{2,0}(\beta_n) \\ &+ 2\chi^n_{2,2} C_{2,2}(\beta_n, \gamma_n)\Big]. \end{aligned} \qquad (53)$$

This can be simplified, in the same way as used in the AP method for molecules in the liquid crystalline phase, by expressing the $\chi^n_{2,m}$ as sums of contributions $\chi_{2,p}(j)$, from rigid fragments; cf. equation (27):

$$\chi^n_{2,m} = \sum_{j,p} \chi_{2,p}(j) D^2_{p,m}(\alpha_j, \beta_j, \gamma_j). \qquad (54)$$

Fragment contributions to the total tensor χ can be found for 5CB in the paper by Bunning *et al.* [21]. For 5CB the field-induced quadrupolar splittings in the single-molecule limit are too small to be resolved, but this may not be the case for other mesogens.

When the temperature approaches T_{NI} the effect of the molecular aggregation increases, and the magnetic contributions to $U_{\mathrm{sum}}(\beta_n, \gamma_n, n)$ can be neglected and the potential of mean torque for conformer n takes on the same form as that given in equation (26) for $U_{\mathrm{ext}}(\beta_n, \gamma_n, n)$. The problem is to relate the field-induced quadrupolar, or dipolar, splittings to the conformational distributions $P(n)$, which is equivalent to $P_{\mathrm{LC}}(n)$ in that it depends on the total mean energy, and $P_{\mathrm{iso}}(n)$. The latter probability depends only on $U_{\mathrm{int}}(n)$ in both liquid crystalline and isotropic phases. In the isotropic phase, where the orientational order is very small, it is to be expected that $P_{\mathrm{iso}}(n)$ will equal $P(n)$. It is possible, therefore, to test one of the most important predictions of the theory developed by Luckhurst *et al.* [10] that in the liquid crystalline phase there may be an appreciable contribution from the anisotropic intermolecular potential to the stability of a conformer, and so $P_{\mathrm{LC}}(n)$ can differ substantially (see figure 3) from $P_{\mathrm{iso}}(n)$, which is the distribution that would exist in the absence of this anisotropic contribution, and which is predicted from the value of E_{tg} derived by fitting calculated to observed quadrupolar couplings. However, this test has not been undertaken using the field-induced quadrupolar splittings, because the severe overlapping of lines from different sites in the molecules makes deconvolution of the deuterium spectra, like that for 5CB-d$_{15}$ shown in figure 4, rather difficult. There is a further problem in that the assignment of the splittings to the molecular site is not determined from a deuterium spectrum. These two problems can be overcome by recording field-induced dipolar couplings between ^{13}C and ^{1}H nuclei. A spectrum from the 1% naturally-abundant ^{13}C for a sample having low orientational order consists of peaks from each carbon split into $n_{\mathrm{H}}+1$ lines from total spin–spin coupling, T_{CH}, with the n_{H} directly attached protons. Coupling to more distant protons may give some additional fine structure, but in the pretransitional region this is usually not resolved. The total couplings, ${}^1T_{\mathrm{CH}}$ are therefore very easily obtained, and are the sum of the scalar coupling, ${}^1J_{\mathrm{CH}}$, and the induced dipolar coupling, ${}^1D^{\mathrm{ind}}_{\mathrm{CH}}$, thus

$${}^1T_{\mathrm{CH}} = {}^1J_{\mathrm{CH}} + 2\,{}^1D^{\mathrm{ind}}_{\mathrm{CH}}. \qquad (55)$$

Figure 5 shows the ^{13}C spectra given by 5CB at $T - T_{\mathrm{NI}} = 0.2$ and 13.6°C [22]. Note that this spectrum was recorded at a field strength of 18.79 T, and it is the availability of such a high field that now makes ^{13}C an

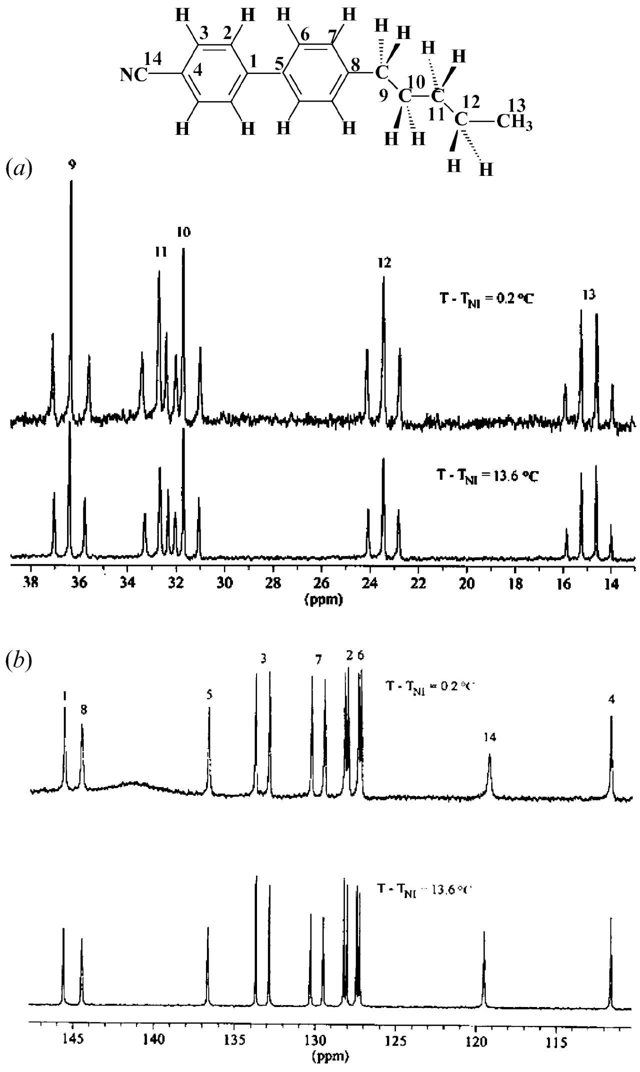


Figure 5. The 200 MHz ^{13}C spectra (B_0=18.79 T) of 5CB at T–T_{NI} of 0.2 and 13.6°C: (*a*) aliphatic, and (*b*) aromatic regions.

attractive nucleus to study: at 9.4 T, the field used for the ^{2}H spectrum in figure 4, the induced dipolar couplings are detectable, but they are small and were obtained with low precision.

There are four major advantages in using ^{13}C rather than ^{2}H to study molecules in the pretransitional region. Firstly, spectra can be obtained without isotope enrichment, so that in principal all mesogens can be studied without recourse to this often difficult procedure. Secondly, spectral overlap is much less of a problem, and indeed not a problem for 5CB, since the linewidths are small compared with the chemical shift dispersion. Thirdly, it is straightforward to assign the lines using 2D spectroscopy; and fourthly, the signs of the induced dipolar couplings are given simply by noting whether ${}^{1}T_{\mathrm{CH}}$ is larger or smaller than ${}^{1}J_{\mathrm{CH}}$, which is always positive and for 5CB larger than ${}^{1}D^{\mathrm{ind}}_{\mathrm{CH}}$.

Merlet *et al.* [22] have used the ^{13}C spectra of 5CB in the isotropic phase to show that the induced dipolar couplings for each site in the molecule all follow the predicted dependence on both $\mathbf{B}_0^2$, and $(T\text{–}T^*)^{-1}$, with a common value of T_{NI}–T^* of 0.63 ±0.01°C at $\mathbf{B}_0$=11.75 T, and 0.6±0.1°C for $\mathbf{B}_0$=18.79 T. It was also demonstrated that the set of values of ${}^{1}D^{\mathrm{ind}}_{\mathrm{CHi}}$ for positions in the alkyl chain and the attached phenyl ring, at temperatures near T_{NI}, can be used to obtain the conformational distributions, $P(n, T)$, and that these are essentially identical with the distributions $P_{\mathrm{iso}}(n, T)$ predicted by analysis with the AP method of Luckhurst *et al.* [10] of the quadrupolar splittings for 5CB-d_{15} in the nematic phase. This is a very satisfying confirmation of the prediction of the theory of the orientational order of flexible mesogens developed by Luckhurst *et al.* [9, 10] that $P_{\mathrm{LC}}(n, T) \neq P_{\mathrm{iso}}(n, T)$ for temperatures in the nematic phase.

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