Molecular Order Versus Conformation Changes in Liquid-Crystal Phases

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Molecular Order versus Conformation Changes in the Liquid-Crystal Phases

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Deuteron magnetic resonance splittings and their temperature dependence from deuterated liquid-crystal compounds are analyzed in terms of molecular conformation and orientational order. Three order parameters are found to be necessary to explain the smectic-C (S_C) spectra whereas only two are required for the nematic (N), S_A, and S_B phases. The data are consistent with the concept that the preferred conformation of the molecule remains unchanged at the N-S_C, N-S_A, and S_A-S_B phase transitions as well as throughout the temperature range of these phases.

During the past several years there has appeared in the literature a substantial amount of deuteron magnetic resonance data from several of the thermotropic liquid-crystal phases.1-5 These data were obtained from a variety of different compounds in which one or both of the end-
chains were completely deuterated along with other selected groups in the molecule. In cases where the temperature dependence of the spectra are recorded, these data show the interesting feature that the splitting of each set of spectral lines is often not at all proportional to one another, particularly at discontinuous changes at the phase transitions. In fact, this dependence is markedly different for some lines giving the general appearance that there may be occurring a change in the preferred or most probable conformation of the molecule. This is the conclusion that would be drawn if the spectral splittings were assumed to be proportional to a single order parameter $S = \langle \frac{1}{2} \cos^2 \theta - \frac{1}{2} \rangle$ which is an approximation often made by NMR workers. In this Letter we show that these relative temperature dependences can be fully explained in terms of more than one orientational order parameter defined from the preferred orientation of a single molecular-axis system.

The quadrupole interaction of the deuteron spin is normally observed as a perturbation on the Zeeman interaction in which a spin of $I = 1$ will show a spectrum of two lines with a splitting given by

$$\delta \nu_1 = \frac{3}{2} \frac{e^2 q Q}{h} \left( \frac{1}{2} \cos^2 \beta_i - \frac{1}{2} \right),$$

where $\beta_i$ is the angle between the instantaneous principal $z$ axis of the electric field gradient, $q = V_{zz}$, and the direction of the magnetic field. In this expression we have taken the electric-field-gradient tensor to be axially symmetric about the principal $z$ axis which can in turn usually be taken to be the direction of the particular carbon-deuteron bond in question (6 bond) in the molecule.\textsuperscript{7} Writing the expression for the most general nonaxial case would not change the argument which follows but would only complicate the appearance of the equations.\textsuperscript{7}

Since we wish to compare the temperature dependence of each deuterated site we will transform the spherical-harmonic function of Eq. (1) to a common rectangular-axis system $M_x$, $M_y$, $M_z$, which we shall refer to as the molecular-axis system. We identify $M_x$ as the long molecular axis defined such that in an apolar liquid-crystal phase $M_x$ and $-M_x$ are equivalent. We may not know precisely the physical position of $M_x$ on the molecule itself, but this is not a relevant feature of this paper. Transforming the spherical-harmonic function of Eq. (1), that equation now becomes

$$\delta \nu_1 = \frac{3}{2} \frac{e^2 q Q}{h} \sum_{m=-2}^{2} \langle D_{m1}^{(2)} \rangle \langle \alpha_i \rangle \langle \beta_i \rangle \langle \theta, \psi \rangle,$$

where the $D_{m1}^{(2)}$ are the elements of the Wigner rotation matrix\textsuperscript{8} of order two. The angles $\theta$ and $\psi$ are the spherical coordinates which give the instantaneous orientation of the molecular axes relative to the director. Since the NMR experiments are performed in a strong magnetic field, the director (preferred direction of $M_x$) is normally parallel to the direction of the magnetic field uniformly throughout the liquid-crystal sample. The angles $\beta_i$ and $\alpha_i$ are the spherical coordinates of the $i$th C-D bond direction in the molecular frame. The liquid-crystal molecules are flexible so that $\beta_i$ and $\alpha_i$ are likewise time dependent. In this picture then we have fluctuations in the conformation of the molecule relative to a common molecular frame which modulates $\beta_i$ and $\alpha_i$ and, in addition, thermal fluctuation in the orientation of the molecular frame relative to the director which modulates $\theta$ and $\psi$. One purpose of this paper is to show experimentally that these two motions can be treated as independent, that is,

$$\langle D_{m1}^{(2)} \rangle \langle \beta_i \rangle \langle \alpha_i \rangle \langle \theta, \psi \rangle \rangle = \langle D_{m1}^{(2)} \rangle \langle \beta_i \rangle \langle \alpha_i \rangle \langle \theta, \psi \rangle.$$

The five terms of Eq. (2) can be immediately reduced to three by the apolar condition that $M_x$ and $-M_x$ are equivalent. In choosing this reorientation to occur about $M_x$, Eq. (2) must be invariant under the operation $\theta \rightarrow -\theta$ and $\psi \rightarrow -\psi$, in which case

$$\delta \nu_1 = \frac{3}{2} \frac{e^2 q Q}{h} \left[ \langle \frac{1}{2} \cos^2 \beta_i - \frac{1}{2} \rangle \langle \sin^2 \beta_i \cos 2\alpha_i \rangle \langle \sin 2\theta \cos 2\psi \rangle + \frac{1}{2} \langle \sin^2 \beta_i \sin \alpha_i \rangle \langle \sin 2\theta \sin \psi \rangle \right].$$

In some uniaxial phases, however, no distinction may be possible as to whether the reorientation $M_x$ can occur about $M_x$ or $M_y$, in which case a second invariance under the operation $\theta \rightarrow -\theta$, $\psi \rightarrow -\psi$ would leave only the first two terms of Eq. (3) for such phases. We shall see later that this is the
case for the nematic, smectic-\(A\), and smectic-\(B\) phases but not the case for the biaxial smectic-\(C\). If only the two order parameters \(\left< \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right>\) and \(\left< \sin \theta \cos \phi \right>\) are required, Eq. (3) has the form \(\delta \nu_i = a_i A + b_i B\). Since the order parameters are common to the entire molecule, we can express one splitting in terms of two others by the homogeneous equation

\[
\delta \nu_i = C_i \delta \nu_j + C_j \delta \nu_k,
\]

where the \(C\)'s are conformation constants which depend on the \(a\)'s and \(b\)'s. We now come to a central feature of this paper. It is to be noted that if the values of \(C\) were independent of temperature the ratios \(\delta \nu_i/\delta \nu_j\) vs \(\delta \nu_j/\delta \nu_k\) should yield a straight line.

A dramatic illustration that this is indeed the case is given in Fig. 1. The upper inset in Fig. 1 is a sketch of the temperature dependence of the spectral splittings in the compound \(\beta\)-butyl-oxybenzylidene-\(p\)-d_{15}-octyl-2,6-d_{19} aniline (BOBOA-\(d_{19}\)) obtained by Deloche and Charvolin.\(^3\) The ratio plots show a remarkably straight line throughout the full temperature range of the nematic, smectic-\(A\), and smectic-\(B\) phases of that compound without deviation at the transitions. Ratio plots of other splittings all show similar straight lines.

In Fig. 2 we show the deuterium spectral splittings and their temperature dependence from the compound 4-\(\alpha\)-octyl-\(d_{19}\)-oxybenzoic acid-\(d\) (OBOA-\(d_{19}\)) which we have obtained in our laboratory. This compound exhibits the nematic and smectic-\(C\) phases. Figure 3 shows ratio plots.

**FIG. 1.** Plots of various ratios of the deuterium spectral splittings obtained at various temperatures from the compound BOBOA-\(d_{19}\). The lower inset shows an expanded plot in the smectic-\(A\) and -\(B\) phases. The upper inset shows a sketch of the data of Deloche and Charvolin (Ref. 3) from which the splittings were obtained. The nonproportionality is clearly evident in the lower splittings.

**FIG. 2.** Deuterium spectral splittings in OBOA-\(d_{19}\) and their temperature dependence. One-half of the spectrum recorded at 125°C is shown. This spectrum is symmetric about zero.
obtained from these spectra. The nematic phase again shows the same feature as the previous compound; however, there appears a dramatic break in the plot at the nematic–smectic-C phase transition. We do not believe this to be a change in the molecular conformation but instead the onset of the third order parameter in Eq. (3). The presence of three order parameters would require that three splittings instead of two is necessary to determine any others, i.e., \( \delta V_1 = C_j \delta V_j + C_\delta \delta V_\delta + C_\beta \delta V_\beta \). In Fig. 4 we have made use of this equation assuming temperature-independent conformation coefficients to fit the temperature dependence of \( \delta V_1 \) from Fig. 2. The solid curve shows the temperature dependence determined from that of three other splittings. We found that any three splittings chosen would work equally as well even at the nematic–smectic-C phase transition whereas two splittings were insufficient. It can likewise be shown that Cartesian plots of \( (\delta V_1/\delta V_1, \delta V_2/\delta V_1, \delta V_3/\delta V_1) \) all lie in a plane as required by the above equation,\(^9\)

We conclude affirmatively, therefore, concerning the presence of the third order parameter \( (\sin 2\theta \sin \phi) \) for the smectic-C phase. In the sense that only one laboratory or space-fixed axis (director) is required in its definition, it is a uniaxial order parameter even though it only shows itself in the biaxial smectic-C phase. We have also observed this order parameter in the smectic-C phase of compounds with a smectic-A–smectic-C phase transition and determined its temperature dependence.\(^9\)

Finally, we discuss the temperature independence of the conformation coefficient, \( C \). The fact that one can predict the temperature dependence of a spectral splitting coming from some region of the molecule from the spectra obtained from an entirely different region of the same molecule is suggestive that the preferred or most probable conformation of the molecule is not changing even at the phase transition. The constant coefficients \( C \) of Eq. (4) are related to the molecular conformational averages \( a_i \) and \( b_i \) by \( C_j = (a_i b_j - a_j b_i) / (a_j b_j - a_i b_j) \). The fact that the spectral lines are resolved along the alkyl endchain results from different values of \( a_i \) and \( b_i \) for each segment, that is, more averaging occurs toward the terminal end of the endchain. Even though the preferred conformation of the molecule may not change, the averages \( a_i \) and \( b_i \) are expected to be temperature dependent.\(^10,11\)

The coefficient \( C \), however, is not seen to vary measurably with temperature, which might provide a useful test of endchain models.\(^12\) Since some portions of the molecule are more rigid than others, it is still nonetheless surprising that the value of \( C \) remains constant throughout

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**FIG. 3.** Plots of the ratios of \( \delta V_2/\delta V_1 \) and \( \delta V_3/\delta V_1 \) vs \( \delta V_2/\delta V_1 \) from the compound OOBA–d_{18}.

**FIG. 4.** Temperature dependence of \( \delta V_1 \) from the compound OOBA–d_{18}. Solid dots are experimental; solid line is the calculated temperature dependence obtained from the temperature dependence of any three splittings other than \( \delta V_2 \). Long and short dashed lines show the failure of two splittings alone (\( \delta V_1, \delta V_2 \) and \( \delta V_3, \delta V_4 \)) to fit at the nematic–smectic-C phase transition.

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the thermotropic phases studied.

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12S. Marcelja, private communication.