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Molecular Orientational Order and NMR in the Uniaxial and Biaxial Phases†

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(*Received December 6, 1976*)

Although of fundamental interest, orientational order is a property of the liquid crystalline phases which has not been well determined. Only that order which is described by the parameter $S_{zz} = \langle \frac{3}{2}\cos^2\theta - \frac{1}{2} \rangle$ has been given intensive study. There are other useful order parameters. This paper discusses some of those parameters and their measurement. Like S_{zz}, the parameters described come from the transformation properties of the spherical harmonics of order two. In the uniaxial phases a parameter which describes the asymmetry in the order of the molecular long axis is discussed and a measurement of its temperature dependence presented. The technique used in the measurement is deuteron magnetic resonance and the compound is selectively deuterated *n*-heptyloxyazoxybenzene (HOAB). In addition the conformation of the molecule and its temperature dependence throughout the liquid crystalline phase is discussed. The order parameter concept is extended to the biaxial phases where the influence of some of these parameters on deuteron resonance spectra is presented. Finally, the measurement of a parameter which describes partial rotational freeze out in the smectic C phase of HOAB is shown.

INTRODUCTION

The liquid crystalline phases are characterized by the preferred orientational and translational order of their elongated molecules. X-ray studies have been successful in determining the translational order and giving reliable models for many of the phases.[1] The orientational order, on the other hand, has not

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been as well determined. A classic example in recent years has been the smectic C phase where there has been considerable speculation in the literature as to what the molecular orientational order in that phase might be and what role that order might play.[2–5] Even in the uniaxial phases, the understanding of the orientational order has not been all that satisfying to some.[6–9]

It has been usual practice to express orientational order in terms of parameters. These parameters are usually time averages of functions which depend on the orientation of a molecule and its specified coordinate axes in some fixed director frame. These functions often come from the transformation properties of the spherical harmonic functions. The most commonly used spherical harmonics are those of order two of which the degree of order $S_{zz} = \langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \rangle$ is a well known example.[2] There are others. Even in the uniaxial phases there is another parameter $(S_{xx} - S_{yy})$ which expresses the asymmetry in the order of the molecular long axis.[7] Sometimes this order parameter is written as $\langle \frac{3}{2} \sin^2 \theta \cos 2\psi \rangle$ where the angles (ϕ, θ, ψ) are the Euler angles giving the orientation of a molecular frame in the frame of the director.[8,9] While this parameter gives an important feature of the orientational order it is a difficult parameter to determine and literature on its measurement is meager. Perhaps even a more serious problem is that, in the case of NMR, the influence of this parameter on the spectra is often neglected giving erroneous values and temperature dependences for S_{zz}.

In the biaxial phases the order parameter description of orientational order becomes much more complex.[10,11] For example, spherical harmonics of order two as described above now transform to give twenty-five possible order parameters. This number can often be reduced, however, by symmetry considerations. Of current interest are those parameters which express "partial rotational freeze out" for rotation about the molecular long axes.[3–5,12] Parameters which express this motion have eluded direct measurement in spite of an intense interest in their values in recent years.[13]

In this paper we will show how the orientational order parameters follow directly from NMR studies. We confine the NMR discussion to the Zeeman perturbed quadrupole interaction as is seen in deuteron spectra of selectively deuterated liquid crystalline compounds. We will discuss both the uniaxial and biaxial phases. Experimental examples will then be shown using *n*-heptyloxyazoxybenzene (HOAB-d_{30}) in which the alkyl end chains on both ends of the molecule have been fully deuterated.

In this study we show measurements of the order parameters S_{zz} and $(S_{xx} - S_{yy})$ and their temperature dependences in both the nematic and smectic C phases. These measurements are made on one rigid segment of the molecule. We further show that neither conformation of the molecule nor

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the internal relative vibrational or rotational motion of its segments appear to change through the temperature range of the nematic and smectic C phases nor at the phase transition.

Finally, we show a direct NMR observation of biaxial order and obtain a value for a biaxial order parameter which expresses rotational freeze out.

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MOTIONAL AVERAGING OF THE QUADRUPOLE INTERACTION

The concept behind the NMR measurement of orientational order is basically quite simple. Internal to the molecule is an electric field gradient at each deuteron nuclear site. As the orientation of the molecule is undergoing thermal motion a time average of that field gradient is observed through the quadrupole interaction. How the field gradient time averages depends directly on the orientational order parameters. The field gradient, like the orientational order, is described by a set of principal axes, a magnitude for the gradient and an asymmetry. If, for example, in the biaxial phases there is a two-fold rotation about the molecular long axis then there will be an asymmetry in the electric field gradient which can be measured.

To be more quantitative it is convenient to start with the familiar Hamiltonian for the quadrupole interaction:

$$\mathscr{H}_Q = \frac{e^2qQ}{4I(2I-1)}[3I_Z^2 - I(I+1) + \tfrac{1}{2}\eta(I_+^2 + I_-^2)] \tag{1}$$

where the (X, Y, Z) axes are the principal axes of the tensor V_{ij} that describes the electric field gradient and the symbols in Eq. (1) are the usual symbols for the quantities as given, for example, in the book by Abragam.[14] The asymmetry parameter, η, is the intrinsic value or the value of the asymmetry parameter $(V_{XX} - V_{YY})/V_{ZZ}$. This is the value that would be measured in a molecule that was rigidly ordered.

In the liquid crystal phases, however, the orientation of the molecule is thermally agitated and $\mathscr{H}_Q$ becomes time averaged. In order to account for the averaging we therefore wish to transform the Hamiltonian to include the molecular and the director (crystal) frames. In addition, we would like to have the operators given with respect to the frame of the applied magnetic field (x, y, z) since we often observe $\mathscr{H}_Q$ as a perturbation on the Zeeman interaction. In this case the truncated Hamiltonian is written:

$$\begin{aligned}\mathscr{H}_Q = \frac{e^2qQ}{4I(2I-1)} \sum_{m,m'=-2}^{2} \Bigg\{ &\left(\frac{4\pi}{5}\right) Y_{2m}^*(\beta, \alpha) + \frac{\eta}{2}\left(\frac{8\pi}{15}\right)^{1/2} \\ &\times [D^{(2)}_{m,2}(\alpha, \beta, \gamma) + D^{(2)}_{m,-2}(\alpha, \beta, \gamma)]\Bigg\} \\ &\times \langle D^{(2)}_{m',m}(\phi, \theta, \psi)\rangle Y_{2m'}(\theta_0, \phi_0)[3I_z^2 - I(I+1)]\end{aligned} \tag{2}$$

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where, I_z is now defined in the frame of the magnetic field. In the final result of the transformation, the off diagonal terms of $\mathscr{H}_Q$ have been left off since it will be treated as a perturbation on the Zeeman interaction. The Euler angles (ϕ, θ, ψ) describe the orientation of the molecular frame in the fixed director frame (see Figure 1) and hence the rotation matrix $\langle D^{(2)}_{m'm}(\phi, \theta, \psi)\rangle$ is time averaged because of the partial orientation of the molecule. The symbols Y_{2m} are the standard spherical harmonics of order two where the spherical coordinate angles θ_0, ϕ_0 give the direction of the magnetic field in the director frame. The Euler angles (α, β, γ) give the orientation of the field gradient principal axes in the molecular frame.

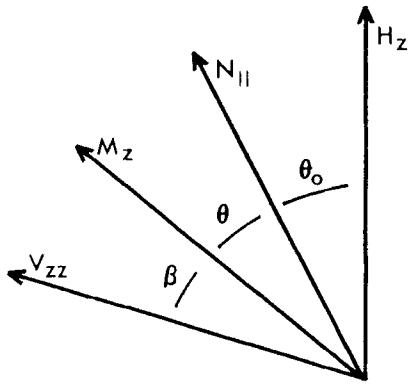

FIGURE 1 Illustration of the z-axes of the various reference frames where $\mathbf{H}_z$, $\mathbf{N}_\parallel$ and $\mathbf{M}_z$ are the frames of the magnetic field, director and molecule respectively. V_{zz} is the principal z-axis of the electric field gradient.

UNIAXIAL PHASES

In the typical NMR experiment $\theta_0 = 0$, that is, the director N_z is parallel to the magnetic field. In this case, Eq. (2) becomes:

$$\mathscr{H}_Q = \frac{e^2qQ}{4I(2I-1)} \sum_{M=-2}^{2} \left\{ \left(\frac{4\pi}{5}\right) Y^*_{2m}(\beta, \alpha) + \frac{\eta}{2}\left(\frac{8\pi}{15}\right)^{1/2} \times [D^{(2)}_{m,2}(\alpha, \beta, \gamma) + D^{(2)}_{m-2}(\alpha, \beta, \gamma)] \right\} \times (-1)^m \langle Y^*_{2m}(\theta, \psi)\rangle [3I_z^2 - I(I+1)]. \quad (3)$$

In order to simplify Eq. (3) a common practice is to assume a cylindrically shaped molecule or a cylindrical distribution for the orientation of the long molecular axis about the director. In this case Eq. (3) gives a splitting

to the first order in perturbation on the Zeeman interaction as:

$$\delta\nu = \tfrac{3}{2}\nu_Q\left[(\tfrac{3}{2}\cos^2\beta - \tfrac{1}{2}) + \frac{\eta}{2}\sin^2\beta\cos 2\gamma\right]\langle\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}\rangle \qquad (4)$$

where $\nu_Q = e^2qQ/h$. It is noted that when $\eta = 0$, Eq. (4) gives the familiar simple result often seen in the literature.[16]

If, on the other hand, we don't have cylindrical symmetry then the result is more complex.[17] If the symmetry is such that one can guess the principal axes of the order (molecular shapes which possess twofold rotation axes or planes of reflection) then there is one additional order parameter $\langle\frac{3}{2}\sin^2\theta\cos 2\psi\rangle$ and the splitting obtained from Eq. (3) becomes:

$$\begin{aligned}\delta\nu = \tfrac{3}{2}\nu_Q\Big\{&(\tfrac{3}{2}\cos^2\beta - \tfrac{1}{2})\langle\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}\rangle + \tfrac{1}{2}\sin^2\beta\cos 2\alpha\langle\tfrac{3}{2}\sin^2\theta\cos 2\psi\rangle \\ &+ \frac{\eta}{2}\sin^2\beta\cos 2\gamma\,\langle\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}\rangle + \frac{\eta}{6}[(1 + \cos^2\beta)\cos 2\alpha\cos 2\gamma \\ &- 2\cos\beta\sin 2\alpha\sin 2\gamma]\langle\tfrac{3}{2}\sin^2\theta\cos 2\psi\rangle\Big\} \qquad (5)\end{aligned}$$

The order parameter $\langle\frac{3}{2}\sin^2\theta\cos 2\psi\rangle$ expresses the asymmetry in the molecular order and is sometimes expressed as $(S_{xx} - S_{yy})$[7] where these parameters have their usual definition in terms of direction cosines. Knowing the structural constants and molecular configuration it is then possible to determine the values of the two order parameters in Eq. (5). While these order parameters have been measured for simple solute molecules dissolved in liquid crystals,[17] the literature is nearly void of measurements on the liquid crystal molecules themselves.

BIAXIAL PHASES

In the biaxial phases the splitting takes on a more complicated form. In the first place, there are no less than 25 possible order parameters to consider. This number comes from the dimensionality of the 5×5 rotation matrix $\langle D^{(2)}_{m'm}(\phi, \theta, \psi)\rangle$ in Eq. (2). This number can be reduced by considering liquid crystalline phases which are apolar. That is, the molecule can exchange end-for-end. The molecule, however, may only be able to exchange end-for-end about one axis.[3,4] In possible models that have been considered[3,4] the molecule contains, on the average, a mirror plane which contains the plane of the aromatic rings and the C—C bonds of the end chains in their preferred trans configuration.[18] If we take the molecular x-axis, M_x, as normal to

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that plane, then an end-for-end exchange about that x-axis would give the invariant operations; $\phi \to \pi + \phi$, $\theta \to \pi - \theta$ and $\psi \to -\psi$. While these operations reduce the number of order parameters to a more manageable number we can simplify it even further for the case where the long axis of the molecule is well ordered. If the value of $S_{zz} \gtrsim 0.7$, as is usually the case in the smectic phases, then the long axis of the molecule does not fluctuate, on the average, to very large angles away from the director. Terms in the rotation matrix $\langle D^{(2)}_{m'm}(\phi, \theta, \psi)\rangle$ which contain $\sin\theta$ will in general be small. If we neglect these terms then the order parameters in the biaxial phase simplify. If we take $\eta = 0$ then Eq. (2) gives the splitting in the biaxial phase as

$$\begin{aligned}\delta\nu = {} & \tfrac{3}{2}\nu_Q\{[(\tfrac{3}{2}\cos^2\beta - \tfrac{1}{2})S_{zz} + \tfrac{1}{2}\sin^2\beta\cos 2\alpha(S_{xx} - S_{yy})](\tfrac{3}{2}\cos^2\theta_0 - \tfrac{1}{2}) \\ & - \tfrac{3}{4}\sin 2\beta\cos(\alpha - \phi_0)\langle\cos\xi\rangle\sin 2\theta_0 \\ & + \tfrac{3}{4}\sin^2\beta\cos 2(\alpha - \phi_0)\langle\cos 2\xi\rangle\sin^2\theta_0\}. \end{aligned} \tag{6}$$

The angles β and α are, as before, the polar and azimuthal angles giving the orientation of the principal z axis of the field gradient in the molecular frame. The angles θ_0 and ϕ_0 give the orientation of $\mathscr{H}$ in the director frame. The angle ξ is the angle between the molecular x axis, M_x, and the director x-axis, N_x. The order parameter $\langle\cos\xi\rangle$ describes the extent of partial rotational freeze out for rotation about the long molecular axis, M_z. The order parameter $\langle\cos 2\xi\rangle$ describes a preferred two fold rotation about M_z.

The first term in Eq. (6) is just the term we had earlier in the uniaxial case. The remaining terms are the two biaxial terms. In the last term, the factor of $\sin^2\theta_0$ is an effective asymmetry in the electric field gradient which is induced by the time averaging of biaxial order. The second term in Eq. (6) which contains $\langle\cos\xi\rangle$ reflects the fact that the principal axis of the time averaged field gradient is not parallel to the director N_z. This is what would be expected for partial rotational freeze out. It is important to recognize that each of these terms have a different angular dependence. This dependence will be used later as a means to distinguish them experimentally.

UNIAXIAL ORIENTATIONAL ORDER IN HOAB-d_{30}

An interesting compound is selectively deuterated *n*-heptyloxyazoxybenzene (HOAB-d_{30}).[19] This compound exhibits the nematic and smectic C phases. We deuterated the end chains of this compound to examine the orientational order and conformation of the molecule in each of these phases and at the phase transition. The spectra at one particular temperature as well as a diagram of the molecule is illustrated in Figure 2. This spectrum has been observed by others[20] and is at first sight a little surprising in that it shows a double set of spectra. This is interpreted as coming from each inequivalent

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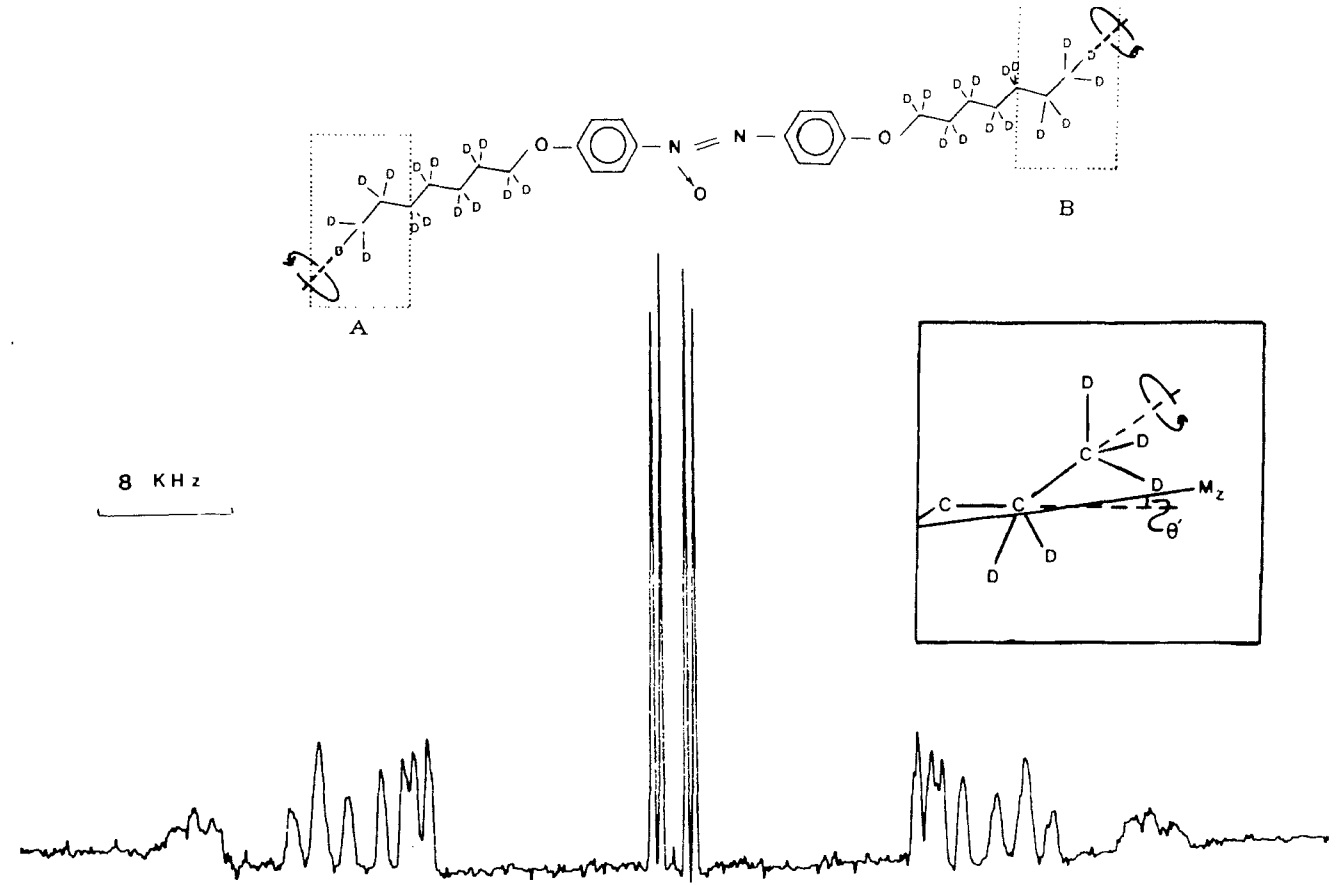

FIGURE 2 Deuteron spectrum and molecular diagram of the compound HOAB-d_{30}. The four central lines are identified with the methyl groups on each end of the molecule. The inset illustrates the terminal segment of the end chain and the molecular z-axis.

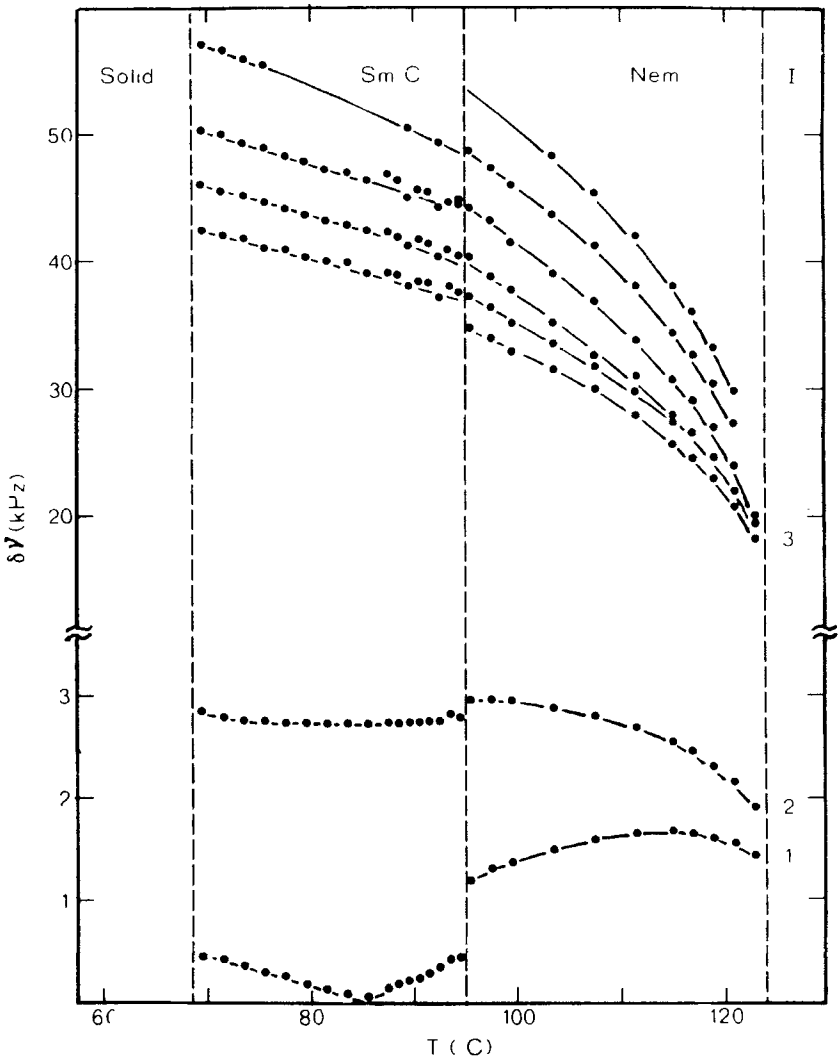

FIGURE 3 Temperature dependence of the splittings of the deuteron spectra in HOAB-d_{30}. The lines $\delta\nu_1$ and $\delta\nu_2$ are identified as the methyl group from each end of the asymmetric molecule. Lines $\delta\nu_3$, $\delta\nu_4$ etc. are identified with each chain segment progressing from the end segment toward the aromatic rings.

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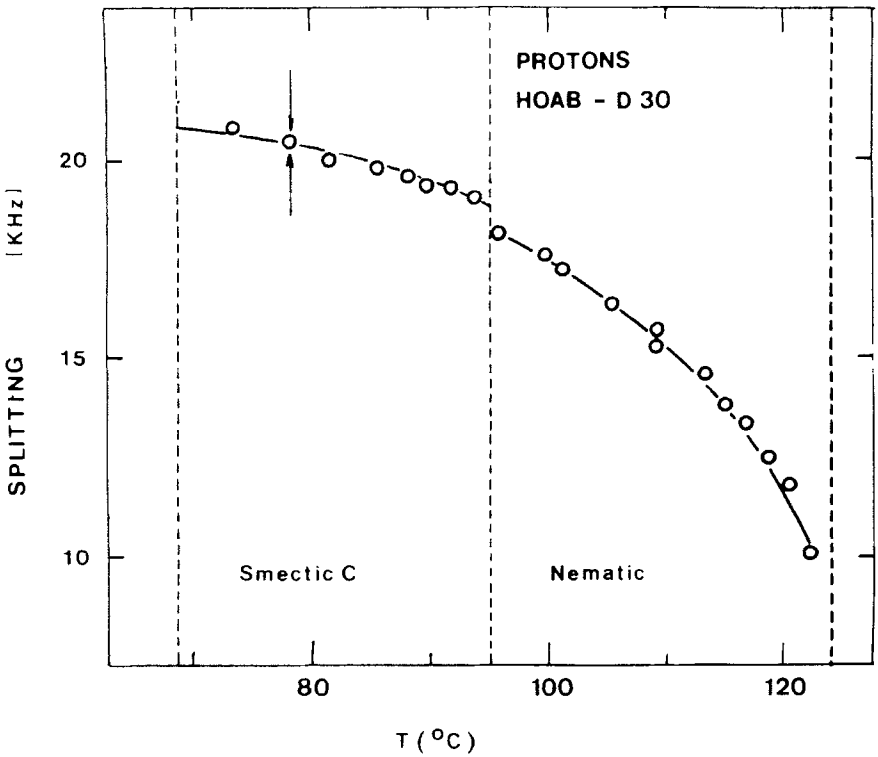

FIGURE 4 Temperature dependence of the proton splitting from the aromatic rings in HOAB-d_{30}.

end chain of the molecule. The temperature dependence of some of the quadrupolar splittings are shown in Figure 3 and that of the proton lines from the aromatic ring are shown in Figure 4. It is noted that the temperature dependence of the three smallest splittings are all unalike. These peculiar dependences could in principle be explained by either one of, or a combination of, two possible effects:

1) more than one order parameter, each of which have different temperature dependences,

2) a molecule in which the preferred conformation is changing with temperature.

The latter interpretation has been used by others to explain similar dependences in other deuterated systems.[21]

It is, however, possible to distinguish between the above two effects. This can be done by attempting to construct the temperature dependence of one

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splitting that is coming from a deuterated site on one portion of the molecule from the temperature dependences of two other splittings which come from deuterated sites in some other portion of the molecule. If these dependences are only determined by the order parameters then the construction is possible. If, on the other hand, the molecule is changing its conformation this would not be possible. This follows from Eq. (5) which can be written as:

$$\delta\nu_i = A_i S_{zz} + B_i(S_{xx} - S_{yy}) \tag{7}$$

for the ith splitting where A_i and B_i are constants which depend on the time averaged conformation of the molecule. Since the temperature dependence of the order parameters are a property of the molecule as a whole and if the conformation or the relative internal motions in the molecule do not change over the temperature range of the phases, then one can construct the homogeneous equation:

$$\delta\nu_3 = C_1\delta\nu_1 + C_2\delta\nu_2 \tag{8}$$

in which the temperature dependence of a third line can be determined from two others. The constants C_1 and C_2 only depend on the conformation of the molecule and are related to the parameters of Eq. (5) and (7) by

$$C_1 = \frac{A_3/A_2 - B_3/B_2}{A_1/A_2 - B_1/B_2}$$

and

$$C_2 = \frac{A_3/A_1 - B_3/B_1}{A_2/A_1 - B_2/B_1}.$$

The values of the C_i are obtained from the data. The prediction of the temperature dependence of one of the quadrupole splittings (bottom curve of Figure 3) has been made in Figure 5. It is seen that the temperature dependence of this splitting is made with remarkable accuracy not only from two other quadrupolar splittings coming from sites on the other end of the molecule but also from the proton splitting of the aromatic rings. In this case it is seen that the preferred conformation of the molecule appears to be rather constant even across the nematic–smectic C phase transition and the temperature dependence of the splittings are governed primarily by the molecular orientational order parameters.

The values of the order parameters themselves are more difficult to obtain for this involves a detailed knowledge of the molecular structure and conformation. Some segments of the molecule, particularly the end chain segments have freedom to rotate or librate about a bond axis. The amount

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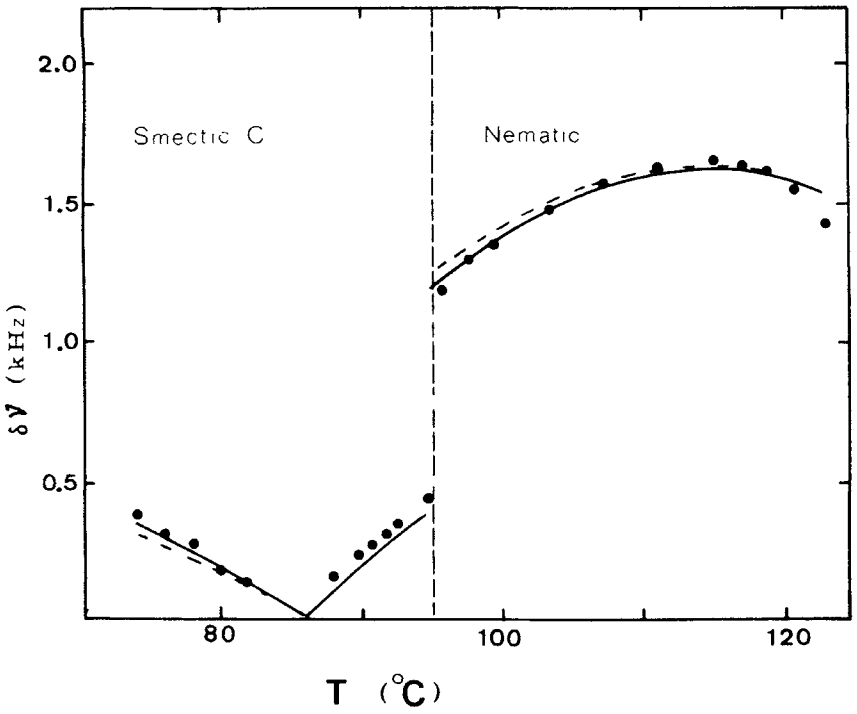

FIGURE 5 Temperature dependence of the deuteron spectral line $\delta\nu_1$ in HOAB-d_{30}. Solid line is the dependence calculated from $\delta\nu_2$ and the proton splittings from the aromatic ring. Dashed line is that calculated from $\delta\nu_2$ and $\delta\nu_3$.

of freedom for rotational motion a particular segment has is often not known. To circumvent this problem it is common practice to write an order parameter or set of parameters for each segment. While the magnitude of the order parameters will be different for each segment they all will have the same temperature dependence. That is, the ratio of the order parameters from one segment to another would be a constant if the molecular conformation and the internal motions within the molecule are not temperature dependent over the temperature range of the nematic phase. This is apparently very close to the actual case in HOAB as illustrated by Figure 5. The internal motion of the molecule could be accounted for in Eq. (2) by introducing another transformation to a segment frame. Through such a transformation, one could in principle determine the amount of internal molecular motion.

If one has made the correct choice for the molecular axes then there are only two order parameters (for the case where $\theta_0 = 0$) to consider. In order to determine the values of these two order parameters it would require two quadrupole interactions with differently oriented principal gradient axes

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within a molecular segment. In the case of deuteron this means that there should be a minimum of two C—D bonds per each rigid segment each of which make a different angle β with respect to the molecular z-axis. Unfortunately, this condition does not exist for most of the end chain segments and one cannot determine the order of each segment with the deuteron quadrupole interaction alone. It is, however, possible to do this with the quadrupole interactions of the deuterons associated with the last C—C bond terminating the alkyl end chain. That this is possible results from the fact that the terminating methyl group is rotating about that bond yielding, on the average, an effective interaction in the direction of that C—C bond as illustrated by the inset on Figure 2. This interaction along with the deuterons on the second carbon from the end can then be used to determine S_{zz} and $(S_{xx} - S_{yy})$ for that group.

The determination of numerical values for these order parameters from the data requires that we provide a molecular model. We chose a model which has, on the average, a mirror plane containing all the C—C bonds of the alkyl end chains in a preferred *trans* configuration. The x-axis is taken as normal to that plane with M_y and M_z in the plane. There is some uncertainty in choosing M_z. It is normally taken to be along a line connecting the centers of the aromatic rings[22] as indicated by the angle θ' in the inset of Figure 2. Within the framework of this model, the reason the two methyl groups show different splittings is that the value of θ' is different on each end of the molecule.

In the use of Eq. (5) to determine the order parameters we first of all set $\eta = 0$. This is probably a reasonable approximation since the segment under consideration is near tetrahedral and the values of η for the deuterons under consideration are estimated[23,24] to be ~ 0.01. In the use of Eq. (5) the magnitude of the coupling constant for the methyl splittings is time averaged by rotating about the terminal C—C bond axis. A value of $(\frac{3}{2}\cos^2 70.53 - \frac{1}{2})$ 172 kHz is therefore used for ν_Q for the splittings of $\delta\nu_1$ and $\delta\nu_2$. This factor comes from an additional transformation to the C—C bond axis not included in Eq. (2). A value of 172 kHz is used for $\delta\nu_3$. The angles for β and α are then derived from θ' and assuming a tetrahedral shape for the segment in question. The values of β_1 and β_2 then depend on the value used for θ' on each end of the molecule.

In order to obtain values for S_{zz} and $S_{xx} - S_{yy}$ we must choose a value for one of these angles. From the splitting $\delta\nu_1$ in Figure 3 we argue that A_1 of Eq. (7) must be small and negative. This follows in that based on our model B_1 is positive ($\alpha_1 = 90°$ and ν_Q is negative) and that $\delta\nu_1$ is observed to change sign for decreasing temperatures of the sample. As the temperature decreases S_{zz} increases whereas $(S_{xx} - S_{yy})$ is expected to decrease.[8,9] This forces A_1 to be small and negative which requires $\beta_1 \lesssim 54.7°$.

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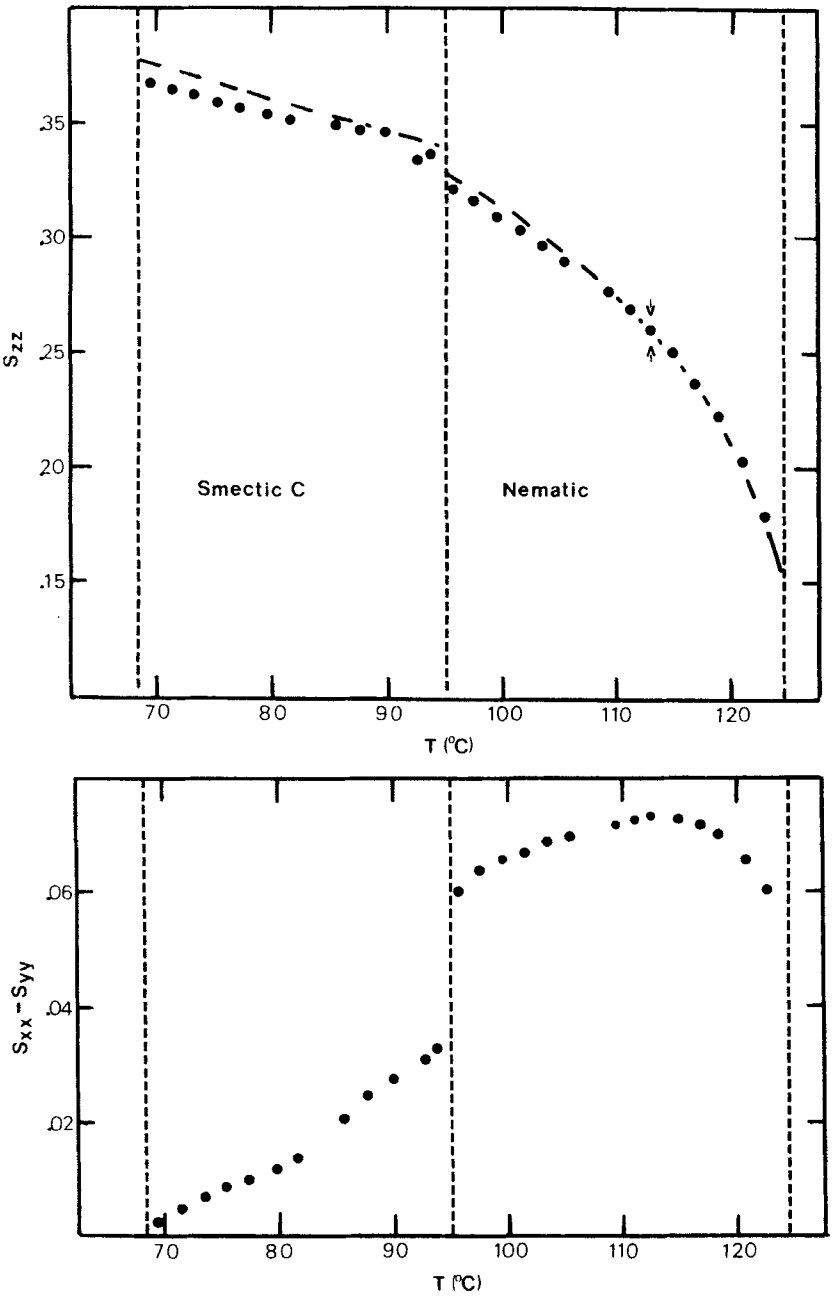

FIGURE 6 Temperature dependence of the order parameters S_{zz} and $S_{xx} - S_{yy}$ as determined from the deuteron splittings from terminal end chain segments of HOAB-d_{30}. The dashed line is the temperature dependence of S_{zz} determined from the proton splitting and fitted at the arrow.

Using a value of $\beta_1 = 54.0°$ the order parameters are determined as shown in Figure 6. The temperature dependence of S_{zz} is found to be consistent with that determined from the dipolar splitting of the protons on the aromatic ring. The proton line splitting is directly proportional to S_{zz}[25] and nearly independent of $S_{xx} - S_{yy}$ since the dipole–dipole vector is nearly parallel to the molecular z-axis.[22]

BIAXIAL ORIENTATIONAL ORDER IN HOAB

In the uniaxial case it was seen that it is only necessary to measure the magnitude of the time averaged quadrupole interaction to determine the orientational order. This is because there is no asymmetry in the time averaged field gradient and its principal z-axis is parallel to the director, N_-. This is not the case in the biaxial phases. In these phases the asymmetry parameter must be measured and the location of the principal axes determined for each C—D bond. This is not a trivial experiment to do even in the case of solids where the samples are easier to work with. The complications which arise are as follows:

1) A monodomain liquid crystal sample or a polydomain sample of known domain distribution or distribution of directors is required.

2) When the quadrupole interaction is observed as a perturbation on the Zeeman interaction, as is described in this paper, large magnetic fields are required which can influence the orientation of the directors in the sample. In order to determine the location of the principal axes as well as measure the time averaged asymmetry in the field gradient, it is necessary to vary the magnetic field relative to the director in a known way. Often the directors want to follow the direction of the magnetic field[26] and a mechanism to compete with this field in the director alignment is required.

3) Adding to the complications described above is that the asymmetry in the field gradient which is induced by motional averaging is small. This is also true of the averaging effect on the orientation of its principal axes.

We found that in the case of HOAB, we could solve the first two problems above with the use of applied a.c. electric fields. By cooling HOAB from the nematic to the smectic C phase in the presence of both a magnetic and a.c. electric field, we found it to be possible to make a monodomain smectic C sample. Since this compound has a negative dielectric anisotropy the direction of the applied electric field must be perpendicular to that of the magnetic field.

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The monodomain feature of the sample can be observed with NMR. If the sample is polydomain as has been observed by cooling only in the presence of a magnetic field alone, then the spectral lines become distributed[26,27] when the sample is reoriented in the magnetic field. In a monodomain sample, on the other hand, the spectral lines don't distribute but either shift or don't move at all depending upon which axis the sample is reoriented.

The top spectrum of Figure 7 shows the spectral lines of the methyl groups of HOAB in the smectic C phase at $\theta_0 = 0$. The temperature of the sample has been adjusted to the temperature where one of the lines is not split at all (see Figure 3 where $\delta\nu_1 = 0$). These lines were recorded in a monodomain sample created in a 8 kv/cm, 1 kHz electric field (defining a y-axis) and in an 8 kG magnetic field (defining a z-axis).

After the monodomain was formed, the electric field was turned off. When the sample was reoriented about the x-axis in the magnetic field, the spectral lines did not appear to change and remained as shown in the upper spectrum of Figure 7. No variation in the splittings were observed for angles as large as 40°. This we interpreted as due to the fact that the director could follow the field when rotated about this axis.[23,24] If, on the other hand, the sample was reoriented about the y-axis, then the central line split as shown in the lower spectrum of Figure 7.

The splitting of the central line can only come from biaxial order. This can be seen from Eq. (6). The first term (uniaxial term) in Eq. (6) is zero for the central line because the angle β is near the magic angle and because of the unique combination of order parameters S_{zz} and $S_{xx} - S_{yy}$, and their coefficients.

Upon the adjustment of the angle θ_0, the second and third biaxial terms, if present, will split the line. The relative contribution of each term can be determined through the angular dependence of the splitting as is shown in Figure 8 where the $\sin 2\theta_0$ term is shown to be dominant at small angles. Also shown in Figure 8 is the absence of any splitting for rotation about the x-axis when the electric field is turned on during the NMR measurement to prevent the director from following the magnetic field. In this case the outer spectral lines shift inward but the central line does not split since $\alpha - \phi_0$ in Eq. (6) is 90°.

From the slope of the line in Figure 8 and from the second term in Eq. (6) an estimate of the order parameter can be obtained. Since we are using the methyl lines, we must use a value of $(\frac{3}{2}\cos^2 70.53 - \frac{1}{2})$ 172 kHz for ν_Q to account for rotation about the C—C bond. Using the values $\beta = 54°$ and $\alpha - \phi_0 = 0$, we obtain a value of $\langle\cos\xi\rangle \simeq 0.008$. This value is, of course, very small but it must be realized that because of internal molecular rotations the value of $\langle\cos\xi\rangle$ would be expected to be smaller for the terminal

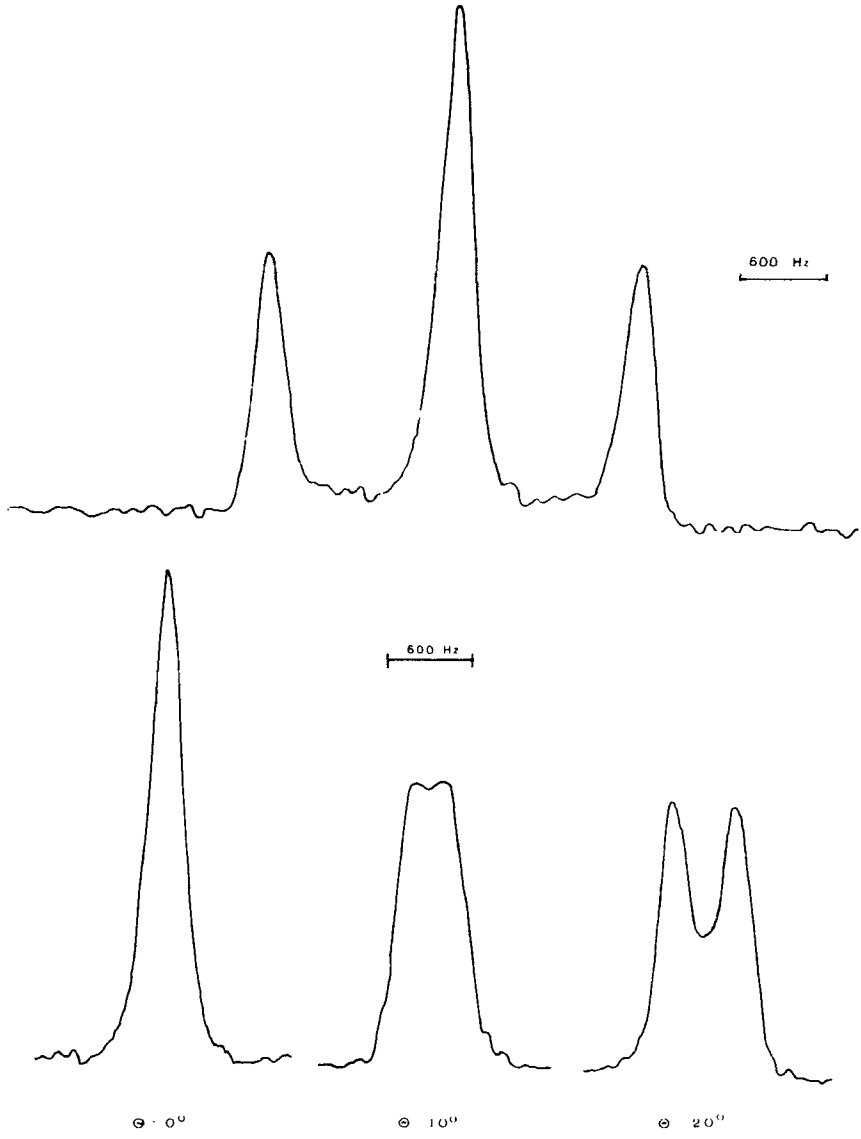

FIGURE 7 Recorded deuteron spectra of the methyl lines of HOAB-d_{30} in the smectic C phase at the temperature where $\delta\nu_1 = 0$ the lower spectra shows only $\delta\nu_1$ for various angles of the director N_z in the magnetic field.

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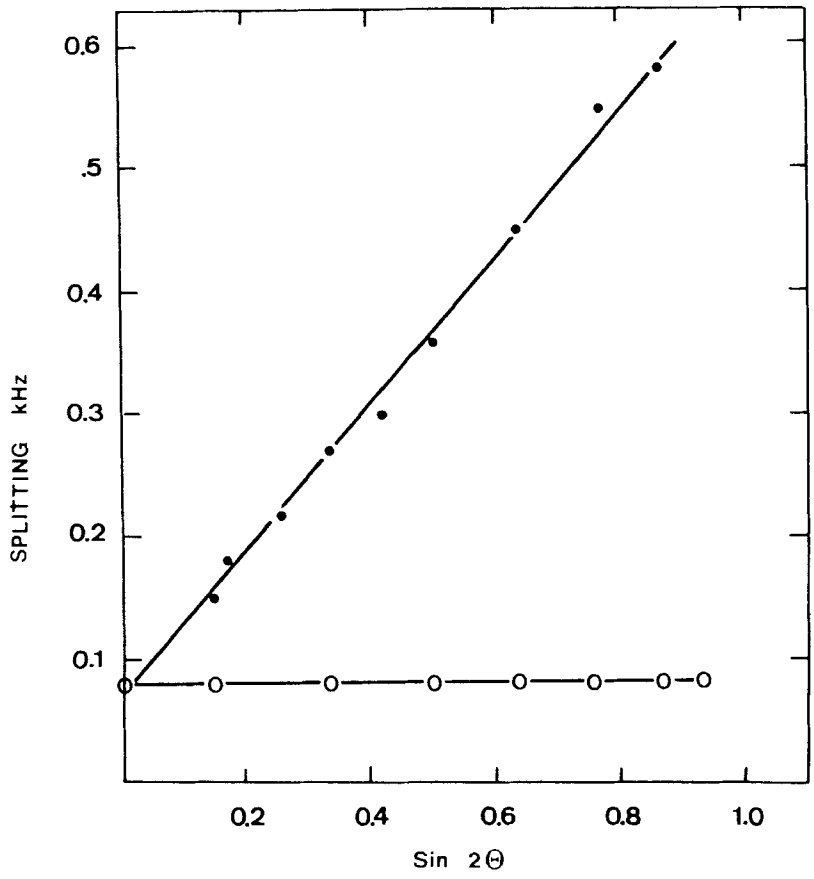

FIGURE 8 Angular dependence of $\delta\nu_1$ for reorientation of the sample about the y-axis (defined in the text) solid dots and for reorientation about the x-axis open circles.

end chain group than on the aromatic ring. In addition, Eq. (6) is an approximation for a highly ordered molecule. A possible interpretation of this rather small value for $\langle \cos \xi \rangle$ will be discussed in the next section.

SUMMARY

By observing the deuterated terminal groups on the alkyl end chain of the compound HOAB, we have determined temperature dependences for the uniaxial order parameters S_{zz} and $S_{xx} - S_{yy}$. The data strongly indicates that these temperature dependences are representative of the entire molecule and not just characteristic of the end group. The magnitudes vary, however,

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from segment to segment because of internal molecular motion but these data suggest that the motion is not strongly dependent on temperature over the range of the liquid crystal phases in HOAB.

Contrary to other suggestions in the literature[21] we believe that the inclusion of two order parameters successfully explains the quadrupolar data without including changes in molecular conformation.

Our value of the biaxial order parameter must be looked upon as an estimate. We believe that its rather small value, however, cannot be overlooked. This suggests that it is induced by the symmetry of the smectic C phase rather than the phase being determined by it. This seems to be consistent with the pure quadrupole study by Blinc, *et al.*[28] in TBBA.

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19. 4-4′-di-*n*-heptyloxyazoxybenzene was synthesized in our laboratories and was prepared by a three-step synthesis involving (1) alkylation of 4-hydroacetanilide with commerically available (Merck) perdeuterated heptylbromide, (2) basic hydrolysis of the acetanilide to the amine and (3) oxidation of this amine to the azoxy compound. The product was purified by recrystallization from abs. EtOH. Transition temperatures (microscope) were 72.0–73.7° ($C \rightarrow S_c$), 93.5–93.6° ($S_c \rightarrow N$) and 122° ($N \rightarrow I$). Mass spectral and NMR analysis indicated that this material was both chemically and isotopically pure.
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$$\nu_M = 2\left(\frac{\gamma}{2\pi}\right)^2 \frac{h}{r^3}$$

in which γ is the gyromagnetic ratio and r the internuclear spearation distance. The angles β and α are the spherical coordinates of r in the molecular frame.
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