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NMR in Spinning Samples of Biaxial Liquid Crystals

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Magnetic resonance measurements on a spinning sample of deuterated 8-heptyloxyazoxybenzene (HOAB-<\textit{d}_{12}>.) are presented. The resulting spectral patterns for the deuterated terminal methyl groups display the biaxial character of the smectic-C phase. Values for those biaxial order parameters which survive under free molecular rotation are directly determined from the shape of the spectral patterns. Parameters expressing biased rotation are also present and contribute significantly to the biaxiality.

In spite of the intense interest in the nature of molecular orientational order in liquid crystals, uncertainty still remains concerning its role in the biaxial character of the smectic-C, \textit{S}_\textit{C}, phase. The lack of experimental data on molecular order is evidenced by the numerous and varied models that have been proposed for this phase. Some of these models are principally based on the biaxial property, while others are not. Experimentally, the biaxial condition is most readily observed optically by the characteristic "baseball" figure seen conoscopically under a polarizing microscope. While this has been a common method of identification, little quantitative information has come from these studies. NMR techniques, on the other hand, have more potential for quantitative measurements; however, they suffer from the fact that the biaxiality is not readily observed in the usual NMR measurement of spectral splittings where the samples...
are aligned by the magnetic field. Unusual NMR experiments are called for in the study of biaxiality. One experiment in this regard is that of Seliger and co-workers\textsuperscript{5,6} who used an ingenious technique to measure the asymmetry parameter of the $^{14}$N nucleus in TBBBA (terephthal-bis-butyloxyaniline). These measurements have been exceedingly helpful; however, there has remained uncertainty as to the contribution of biased rotation to the observed biaxiality in the smectic-C phase.\textsuperscript{5,7}

This paper introduces a simple NMR experiment which is more sensitive to biaxial rotation than the measurement of the asymmetry parameter. Furthermore, the effects of biaxiality on deuterium spins at different selected sites in the molecule can be examined to extract specific order parameters and reduce the uncertainties due to modeling. The experiment takes advantage of quadrupole spectral patterns obtained when a liquid-crystal sample is spun in a magnetic field. The shape of the pattern depends on the biaxial orientational order and thus can be used to obtain

$$\Delta \nu_i = \nu_0^f \left[ A_i \sin^2 \theta_0 \cos(2\varphi_0) + B_i \sin \varphi_0 \cos \theta_0 \sin(2\theta_0) \sin \varphi_0 \right],$$

where $\nu_0^f$ is the coupling constant for the $i$th deuterium site in a molecule in the solid state where much of the orientational motion has been frozen out. The coefficients may be expressed as

$$A_i = \frac{1}{2} (v' \cos \theta - t \sin \theta),$$
$$B_i = \frac{1}{2} (v' \cos \theta + t \sin \theta),$$
$$C_i = \frac{1}{2} (v' \sin \theta + t \cos \theta),$$

where $r = \left( \frac{1}{2} \sin^2 \theta + \frac{1}{2} \right)$, $s = \langle \sin^2 \theta \cos 2\alpha \rangle$, and $t = \langle \sin 2\theta \sin \alpha \rangle$ are the conformation averages and the nine order parameters are

$$S_1 = \left( \frac{1}{2} \cos^2 \theta - \frac{1}{2} \right), \quad S_2 = \langle \sin \theta \cos \theta \rangle, \quad S_3 = \langle \sin^2 \theta \rangle, \quad S_4 = \langle \sin \theta \cos 2\theta \rangle, \quad S_5 = \langle \sin \theta \cos \varphi \sin \theta \rangle, \quad S_6 = \langle \sin \theta \cos \varphi \sin \theta \rangle, \quad S_7 = \langle \sin \varphi \rangle, \quad S_8 = \langle \sin \theta \cos \varphi \sin \theta \rangle, \quad S_9 = \langle 1 - 2 \cos^2 \theta \rangle.$$

The brackets denote a time average. The order parameters $S_1$, $S_2$, and $S_3$ are uniaxial order parameters. In stationary samples where the director is aligned parallel to the magnetic field ($\varphi_0 = 0$)
Deuteron nuclear-magnetic-resonance spectrum of the methyl groups in HOAB-\(d_3\) in the nematic phase at 115°C. Trace \(a\), the stationary spectrum, \(\theta_0 = 0\), where \(\delta v_1\) is the splitting of the inner two lines and \(\delta v_2\) the outer. Trace \(b\), the calculated spectral pattern only using the stationary spectrum and assuming unaxiality. Trace \(c\), the recorded spectral pattern. Trace \(d\), the calculated spectral pattern with the best fitted values given in Table I and with time averaging due to the spinning sample taken into account. All recordings range over 4.0 kHz.

Trace \(a\), shows the stationary recorded NMR spectrum at 115°C, in the nematic phase. Trace \(c\) is the recorded spectral pattern at the same temperature, but with the sample spinning at 13.7 Hz. Spinning the sample at significantly higher rates, up to \(\sim 30\) Hz, or lower rates down to \(\sim 8.0\) Hz, did not significantly alter the shape of the spectral pattern. The spinning sample did, however, produce small observable effects as a result of partial time averaging. As long as the rate of spinning was slow compared to NMR frequency of the interaction, these effects were small and could be accounted for precisely. Figure 1, trace \(b\), shows the calculated spectral pattern for the unaxial case \((B = C = 0)\). It is seen that the two inner peaks do not coincide exactly with those of the recorded pattern (trace \(c\)). Trace \(d\) shows the unaxial spectral pattern recalculated with the effects of averaging due to the spinning taken into account. If the width of spectral lines did not vary slightly with the angle \(\theta_0\), then no fitting parameters would be necessary at all to generate traces \(b\) and \(d\). Because of the dipole-dipole interaction, however, the linewidth does vary but not appreciably because the inhomogeneity in the magnetic field is the principal contributor. The linewidth of the \(i\)th line was taken to follow the expression

\[
W_i = k_i + N_i \left[ |P_2(\cos\theta_0)| - 1 \right],
\]

where \(k_i\) is the width at \(\theta_0 = 0\) (maximum width) and \(N_i\) is the adjustable parameter. This parameter only has the effect of varying the width of the two inner peaks on the pattern (90° singularities); it does not shift their location.

Figure 2, trace \(a\), shows the recorded stationary NMR spectrum at 82°C, in the \(S_C\) phase. Notice that one methyl line is not split at this tem-
temperature, a fact observed earlier. Trace d is the recorded spectral pattern with the sample spinning at 13.7 Hz. Note the splitting of the center line, indicating a strong biaxial effect. A uniaxial spectral pattern would have a huge central component, c. Figure 2, trace e, shows the calculated spectral pattern with the best-fit values shown in Table I. Each spectral line of the $\theta_0=0$ spectrum produces two singularities in the spinning pattern, with frequencies $(\frac{1}{2}A'+\frac{1}{2}B')$, $B$ and $C'$ are defined in Table I. The dependence of this expression on the parameter $C'$ explains the insensitivity of the pattern to relatively large variations of $C'$ when $A'$ is large.

A surprising feature is that $\varphi_0$ does not appear to be distributed; see Fig. 2, trace b. This suggests that the $C_2$ axis aligns parallel to the spinning axis ($\varphi_0=90^\circ$) of the sample when it is spinning in the presence of a magnetic field.

By comparing measured values of $A_2-A_1$, $B_2-B_1$, and $C_2-C_1$, ratios between several of the order parameters can be obtained because of a unique feature of the methyl groups on each end of HOAB. The angles $\beta_1$ and $\beta_2$ are near the magic angle $11^\circ$ ($54.7^\circ$) where small differences $\beta$ cause large changes in $r$ but not in $s$ and $t$ such that $s_1=s_2$ and $t_1=t_2$ even though $r_1$ and $r_2$ are very different. Using this fact alone and taking $S_1=0.8$ give $S_1=0.10$ and $S_2=0.15$. Furthermore, assuming $sS_2+tS_3 \leq 0.1$, which is reasonable both theoretically and experimentally, gives $sS_2-tS_3 \leq 0.1$. Taking $0.1 < |s| < 1$ and $0.1 < |r| < 1$, one finds that the parameters expressing biased rotation appear at best comparable in magnitude to $S_2$ and $S_3$, which are present for a freely rotating molecule.

Contributions to biaxiality of the end chain appear, therefore, to be due to both biased rotation and other orientational motion as well. The large value of $S_3$ is not inconsistent with the measurements of Refs. 4 and 7 as $S_3$ appears in the asymmetry parameter and could account for the unique temperature dependence of that quantity.

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<table>
<thead>
<tr>
<th>Parameter</th>
<th>Nematic phase (115°C)</th>
<th>Smectic-C phase (82°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A'$</td>
<td>1.56 ± 0.02</td>
<td>0.02 ± 0.02</td>
</tr>
<tr>
<td>$B'$</td>
<td>0.00 ± 0.02</td>
<td>-0.24 ± 0.03</td>
</tr>
<tr>
<td>$C'$</td>
<td>0.00 ± 0.01</td>
<td>0.75 ± 0.03</td>
</tr>
<tr>
<td>$k$</td>
<td>0.068</td>
<td>0.10</td>
</tr>
<tr>
<td>$N$</td>
<td>0.016</td>
<td>0.045</td>
</tr>
</tbody>
</table>

$A'=v_0A$, $B'=v_0B\cos\varphi_0$, $C'=v_0C\sin\varphi_0$, and $v_0=57.34$ kHz (Ref. 11). The values of $A$ and $k$ used were obtained from stationary spectra.

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In fact $r_1$ and $r_2$ are of opposite signs, thus explaining why $|C_1| > |C_2|$ even though $|A_1| < |A_2|$.