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Direct NMR observation of rotational freeze-out in the smectic C phase

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We report here a simple and direct observation that the molecular long axis is not, on the average, a rotation axis for the entire molecule in the smectic C phase (rotational freeze-out). This observation is made in the compound 4-*n*-heptyl-*d*₁₅-oxybenzoic acid-*d*₁ where experiment clearly shows that the principal axes of the time-averaged deuterium quadrupole interactions at specific sites of the hydrocarbon chain are not all parallel, demonstrating that they do not share a common axis of rotation.

There are two contributions to biaxial orientational order that are often discussed in the literature; rotational freeze-out and asymmetric fluctuations of the molecular long axis about its director.¹ The relative contribution of each of these mechanisms is of considerable value in examining proposed models for the smectic C phase.²⁻⁸ The experimental task of measuring the relative contributions has been of interest to several investigators.⁹⁻¹⁶

In deuterium magnetic resonance studies there is a direct way to observe the contribution of each mechanism separately. Rotational freeze-out will manifest itself in the relative orientation of the principal axes associated with the deuterium quadrupole interaction at different deuterated sites in the molecule. Two contrasting examples are the solid and the nematic liquid crystal. In the solid, where there is no rotation, the principal axis at each site is along each corresponding C-D bond. Since the bonds are not all parallel in the molecule, the crystalline solid will exhibit principal axes along several different directions. In the nematic, on the other hand, where the molecule is rotating about its long axis, all of the quadrupole interactions will time average along the axis of rotation, yielding principal-axis systems which are parallel to that axis. The smectic C, as we shall show, is somewhere in between these two contrasting examples where rotation is only very weakly frozen out.

The other mechanism for biaxiality, asymmetric fluctuations of the molecule, will show itself in terms of an asymmetry parameter η , for the deuterium quadrupole interaction.¹⁷ This asymmetry parameter

is induced by such asymmetric motion which is of long range and is a measurable quantity in quadrupole magnetic resonance.^{17,18} Values for this parameter are also reported in this paper.

The compound we studied in this paper is 4-*n*-heptyl-*d*₁₅-oxybenzoic acid-*d*₁ (70BA-*d*₁₆). It possesses a nematic-smectic C transition at 95 °C. This deuterated compound has the desirable feature that the quadrupole interaction at the terminal methyl site is strongly time averaged and as a result very sensitive not only to partial freeze-out, but also asymmetric motion.

The NMR experiment is performed in the presence of a magnetic field \vec{H} . The orientations of the principal axes are observed relative to the direction of \vec{H} . The magnetic field also has the effect of aligning the sample. In the nematic phase, the molecular long axis aligns, on the average, parallel to \vec{H} . This is readily observed by NMR in that the principal axes from all deuterated sites are always found to be in the direction of \vec{H} .¹⁹ This means that the axis, $z_{\vec{N}}$, which aligns in the field, is also an axis about which the molecule is rotating (usually a twofold-type rotation).¹⁹ Upon cooling the sample from the nematic into the smectic C phase in the presence of \vec{H} , we find the interesting feature that most of the principal axes appear to remain very nearly parallel to \vec{H} , but one of them, namely, the terminal methyl group, is grossly different, pointing 51° away from the alignment of the others and $z_{\vec{N}}$. We shall show that this does not mean that some parts of the molecule are rotating while others are not, but that the rotation of the molecule as a whole is only weakly frozen out and

that the terminal methyl site is the site most sensitive to this feature since it is the site which suffers most time averaging.

The quadrupole interaction for deuterium is observed by a pair of spectral lines with a splitting commonly described by the equation²⁰

$$\delta\nu_Q = \frac{3}{2} \nu_Q \left[\left(\frac{3}{2} \cos^2 \theta_0 - \frac{1}{2} \right) + \frac{\eta}{2} \sin^2 \theta_0 \cos 2\phi_0 \right], \quad (1)$$

where θ_0 and ϕ_0 are the polar and azimuthal angles giving the direction of the applied magnetic field in the frame of the principal-axis system of the electric field gradient. When observed in the solid where the molecule is rigid, the quadrupole coupling constant is given by $\nu_Q^s = eQV_{zz}/h$, where V_{zz} is the electric field gradient along the C–D bond. In addition the asymmetry parameter $\eta_s = (V_{xx} - V_{yy})/V_{zz} \approx 0$ for the C–D bonds on the hydrocarbon chain.²¹ The coordinates x, y, z refer to the principal axes associated with the C–D bond of the rigid molecule. In the liquid crystal, on the other hand, V_{zz} becomes time averaged to yield an average coupling constant $\nu_Q^l = eQV_{zz}^l/h$ and a motionally induced asymmetry parameter²² $\eta^{lc} = (V_{x'x'}^{lc} - V_{y'y'}^{lc})/V_{z'z'}^{lc}$, where the primed coordinates refer to the principal-axis system observed in the liquid crystal, different from that of the C–D bond. The time-averaged quantities ν_Q^l and η^{lc} are related to the instantaneous ν_Q^s by the expressions $\nu_Q^l = S \delta\nu_Q^s$ and $\eta^{lc} = 4B \nu_Q^s / 3 \nu_Q^l$, where S and B are orientational order parameters.^{1,22} The parameter S is the usual degree of order,²¹ which in this case is the order of the C–D bond along the z' axis with values $0 \leq S \leq 1$. The order parameter B represents the degree of asymmetry in fluctuation of the C–D bond about the z' axis²² with values limited to $0 \leq B \leq \frac{3}{4}$. In uniaxial phases $B = 0$.

A feature of Eq. (1) is that the splitting is maximum when $\theta_0 = 0$ where $\delta\nu_{\max} = \frac{3}{2} \nu_Q^l$. It is easy to demonstrate experimentally in the nematic phase that a sample, when held stationary in a field, aligns such that $\theta_0 = 0$ ($\delta\nu = \delta\nu_{\max}$) for each deuterated site. To do this one needs a measure of ν_Q^l . One way to achieve this is by spinning a sample at a rate fast enough that $z_{\overline{N}}$ cannot follow \overline{H} , in which case $z_{\overline{N}}$ becomes randomly distributed in a plane containing \overline{H} .²³ Under this distribution, the deuterium spectrum also becomes distributed, and there is developed a characteristic spectral pattern containing two sets of singularities or peaks corresponding to $\theta_0 = 0^\circ$ and 90° , yielding a large splitting, $\delta\nu' = \frac{3}{2} \nu_Q^l$ and a small splitting $\delta\nu'' = \frac{3}{4} \nu_Q^l (\eta \cos \phi_0 - 1)$, respectively.¹ In the nematic phase, $\delta\nu' = \delta\nu_{\max}$, indicating that $\theta_0 = 0$ in the stationary sample and that the principal axis aligns parallel to \overline{H} . Another feature characteristic of nematics is that it is found that $\delta\nu' = 2\delta\nu''$, indicating $\eta^{lc} \cos \phi_0 = 0$, which is expected for uniaxial phases

where $\eta^{lc} = 0$.

We now turn to the smectic C phase. Figure 1(a) shows an unresolved splitting from the deuterated methyl group 70BA- d_{16} . This site is strongly time averaged. The spectral line is two partially overlapped lines with a splitting $\delta\nu = 100 \pm 50$ Hz, which is less than the linewidth of the individual lines measured to be 250 Hz in the nematic phase, where they are totally resolved.²⁴ When the sample is spun about an axis perpendicular to \overline{H} at a rate of ~ 1 revolution/sec, a spectrum characteristic of a spinning sample is observed, as shown in Fig. 1(b). It is first of all readily obvious that the spectrum from the spinning sample, is broader than that from the stationary sample indicating that the principal axis in the stationary sample is not aligned parallel to \overline{H} . Furthermore, it is seen from Fig. 1(b) that $\delta\nu' = 2\delta\nu''$, indicating $\eta^{lc} \cos 2\phi_0 = 0$.

If the principal axis in the stationary sample is aligned at an angle $g_0/2$ with respect to \overline{H} , then from Eq. (1) $\delta\nu = 3\nu_Q^l [3 \cos^2(g_0/2) - 1]/4 = 100$ Hz. From Fig. 1(b) $\delta\nu' = \frac{3}{2} \nu_Q^l = 1200$ Hz, giving a value of $g_0/2 = 51^\circ \pm 3^\circ$ for the terminal methyl group.

We now turn to the other sites, which show a totally different behavior. Spectra from a stationary sample of the other sites of the hydrocarbon chain are shown in Fig. 2(a). The spectrum from the spinning sample [Fig. 2(b)], when compared with that of the stationary sample, is "nematiclike" in that $\delta\nu_{\max}$ in the stationary sample equals $\delta\nu'$ of the spinning sam-

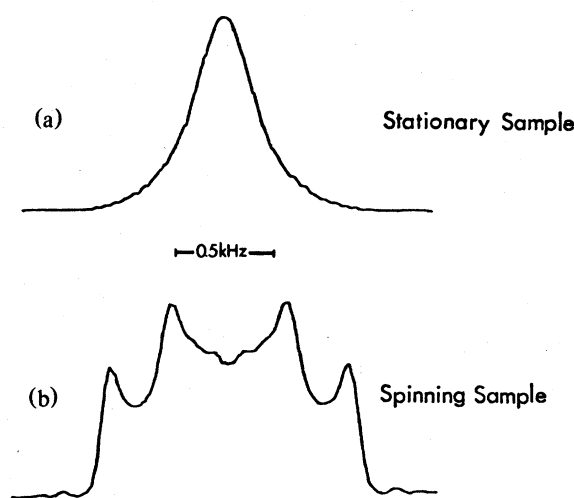


FIG. 1. Deuterium spectra for the methyl group of 70BA- d_{16} recorded in the smectic C phase at 92°C , where the sample was cooled in the magnetic field from the nematic phase into the smectic C phase and recorded while (a) the sample was stationary and (b) the sample was spinning at a rate of 1 Hz about a direction perpendicular to the direction of the magnetic field.

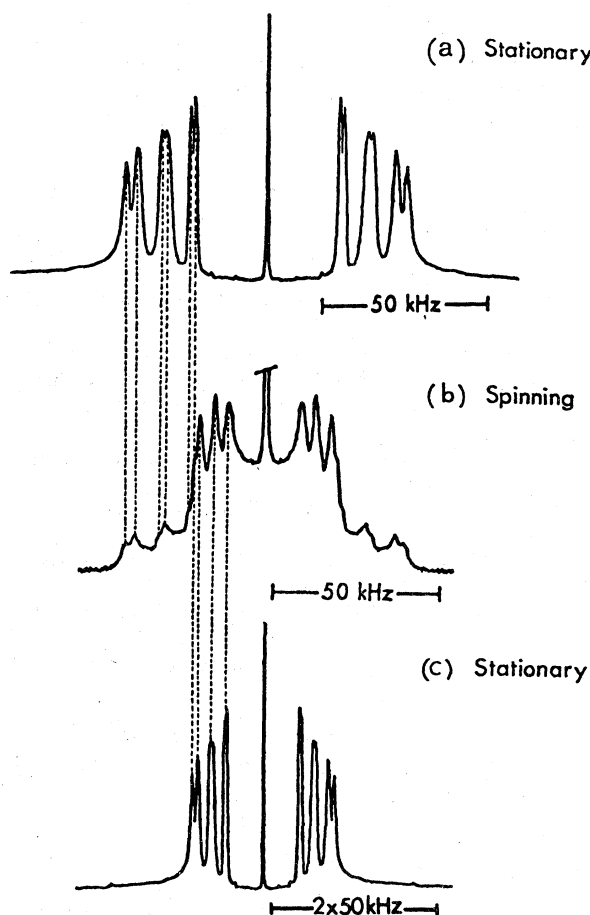


FIG. 2. Deuterium spectra for 70BA- d_{16} recorded in the smectic C phase at 92°C after the sample was cooled from the nematic into the smectic C phase for (a) sample stationary in the field, (b) spinning about an axis 90° to the field direction at a rate of 10 Hz, and (c) same as (a) except recorded on a scale of twice that of (a) in order to identify the peaks in Fig. 1(b) corresponding to the 90° orientation, i.e., for the case where $\delta\nu'' = \delta\nu'/2$. The vertical dashed lines are drawn to identify the peaks where visible in the spectra of the spinning sample. The details of the central line are shown in Fig. 1. The outer peaks in Fig. 1(b) corresponding to $\delta\nu'$ are suppressed somewhat in amplitude in that a perfect planar distribution was not achieved at the 10-Hz rotation rate, but such a deviation from planarity does not affect the location of the peaks or $\delta\nu'$ (Ref. 29). The sites corresponding to the spectral lines of Fig. 1(a) are reported in Ref. 24.

ple and $\delta\nu' = 2\delta\nu''$. At these sites, unlike the methyl site, $g_0/2 = 0 \pm 5^\circ$. This particular feature, that the more ordered sites on the molecule align with their principal axes essentially along \vec{H} , was reported earlier by Luz *et al.*,²⁵ but we shall show that this result might be expected.

The contrasting large value of $g_0/2$ for the methyl

site reflects the high sensitivity of that site for partial freeze-out because it is the site of the molecule most strongly time averaged. This is easily demonstrated by the use of an additional order parameter, C , to represent the degree of freeze-out. Instead of describing the splitting in the smectic C phase by a shift $g_0/2$ in the principal axis, it can be described by an off-diagonal element of the field-gradient tensor in the same frame which was the principal axis frame in the nematic.¹ In this case¹ $V_{yz}^{lc}/V_{zz}^{lc} = 2\nu_D^c C/3\nu_Q^c$, where C has values limited to $0 \leq C \leq \frac{2}{3}$. The value of $g_0/2$ is related to C by the expression¹

$$\sin g_0 = 9C\nu_D^c/8\nu_Q^c \quad (2)$$

Applying Eq. (2) to the methyl group, $\nu_D^c = 51$ kHz (Ref. 26), and from Fig. 1(b) one obtains $\nu_Q^c = 800$ kHz, yielding a value of $C = 0.01$. If we assume that C does not change appreciably from segment to segment (probably much less than does S for example¹), the value of $g_0/2$ can be estimated for the segment next to the methyl group on the hydrocarbon chain where $\nu_D^c = 168$ kHz (Ref. 27) and where $\nu_Q^c = 43$ kHz from Fig. 2(b). Equation (2) gives $g_0 \approx 3^\circ$ for that group which is below experimental uncertainty to observe in this experiment. It is therefore seen why weak freeze-out is only observable on the methyl group.²⁸

Equation (2), for g_0 , like the expression for η^{lc} , both contain the ratio (ν_D^c/ν_Q^c) and both are measures of biaxial order. Biaxial order in the smectic C is so weak that it can only be observed by NMR on those sites of the molecule which have large values of (ν_D^c/ν_Q^c) and small values of ν_Q^c . This is why some previous NMR experiments such as that by Luz *et al.*²⁵ report no observable effects of freeze-out on other sites of the molecules in the smectic C phase and perhaps why the experimental problem of observing freeze-out has been so difficult in general.

The result that $\eta^{lc} \approx 0$ is a result unique to the compound 70BA. In some difficult ¹⁴N experiments by Seliger *et al.*,¹⁷ were found small but finite values for η^{lc} in the smectic C phase of terephthal-*bis*-butylaniline (TBBA). Their measurements show η^{lc} to go through a maximum at $\eta_{\max} \sim 0.1$ then rapidly decrease toward zero as the tilt angle increases. Since the compound 70BA has a large tilt angle $\sim 45^\circ$, this could explain why our observed value of η^{lc} is below detection.

A more detailed description of the NMR spinning sample technique is planned to be given in a subsequent paper.²⁹

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