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Biaxial Ordering of Deuterochloroform in a Smectic G Phase

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The biaxial symmetry of the low temperature smectic phase of *N*-(4-*n*-hexyloxybenzylidene)-4-*n*-hexylaniline is demonstrated through observation of the deuterium NMR resonance of $CDCl_3$ probe molecules dissolved in this phase. The biaxial ordering is revealed in the observed powder spectrum as well as in a complete rotation study of a uniformly aligned sample.

SECTION 2:

Introduction:

Nuclear Magnetic Resonance provides an excellent method for the investigation of the morphology and dynamics of liquid crystalline phases.[1] The observation of ^2H labeled liquid crystal molecules[2,3] and small solute molecules[4,5] demonstrate that deuterium resonances are especially useful. This is due to the rather large quadrupolar interaction which dominates the observed fine structure and relaxation mechanisms.

Of recent interest is the direct observation of biaxial character in the lower symmetry smectic phases, primarily the smectic C phase. Attempts at revealing the biaxial behavior are difficult, however, due to the unique inhomogeneous broadening that occurs in the smectic C phases, as a result of the tilted structure of this phase.[3,6] The liquid crystal directors may also reorient to maintain a fixed relationship with respect to the magnetic field as a sample is rotated and special methods must be employed to prevent this.[2] Biaxiality can also be observed through Nuclear Quadrupole Resonance[7] but a more detailed picture is possible with NMR.[8] In this paper, we report the observation of biaxially ordered deuterochloroform in the low temperature smectic phase of *N*-(4-*n*-hexyloxybenzylidene)-4-*n*-hexylaniline (60·6)[9] as revealed through a rotation study similar to those used in solid state single crystals, and appears to be the first observation of a solute molecule biaxially ordered in a liquid crystal phase.

Experimental:

The (60·6) homologue was synthesized from commercially obtained 4-*n*-hexyloxybenzaldehyde (Eastman, N.Y.) and para-*n*-hexylaniline Frinton Labs, N.J.) both of which were distilled under reduced pressure before use. Equimolar amounts were refluxed for two hours in absolute ethanol and the product was then recrystallized twice from absolute ethanol. The liquid crystal has a wax-like consistency at room temperature and the observed clearing point was 79 ± 1°C. The reported temperature for the nematic–isotropic transition as determined by differential scanning calorimetry and thermal microscopy is 80.7°C.[9]

Approximately 1 gram of (60·6) was placed in a small 10 mm diameter ampule with a ground glass joint and placed on a glass vacuum line. The liquid crystal was degassed and a small quantity (~2 wt.%) of ^{2}H labeled chloroform was distilled into the ampule. The sample was then sealed and tested for high temperature work.

All NMR spectra were obtained on a home built pulsed spectrometer operating at the ^{2}H resonance of 23 MHz produced by a 3.5 Tesla superconducting wide bore magnet (Nalorac Inc., California). A special transverse solenoid probe was constructed and used so that the sample axis is perpendicular to the applied field. By rotating the sample tube an arbitrary angle between the director and field direction is possible. The sample tube was fitted with a pointer and one end of the probe dewar was marked in 5° intervals from 0° to 90°. The orientation of the sample could be set to within ±1°. The free induction decays were accumulated on a Nicolet 1080 data system with disk storage. The 90° pulse length was 8 μs, providing sufficiently uniform excitation.

Results and discussion:

After preparation, the sample was heated to the isotropic phase and allowed to cool to 24°C in the absence of a magnetic field. This procedure produces a random distribution of liquid crystal directors. Because the liquid crystal phase is highly viscous at 24°C, the random distribution of directors should be preserved in the presence of a magnetic field. That this is indeed the case is revealed by the spectrum of the oriented $CDCl_3$. The $CDCl_3$ spectrum yields a powder lineshape, characteristic of an asymmetrical electric field gradient (EFG),[10] as shown in Figure 1. As the $CDCl_3$ molecule is highly symmetric, the molecular EFG is axially symmetric and the asymmetry observed is due to the biaxial averaging of the liquid crystal. The spectrum was taken at a temperature of 24°C and 15,000 accumulations were required. At this temperature the phase has been classified as smectic G. The powder lineshape is characterized by the quadrupole coupling constant, ν_Q and asymmetry parameter, η, as illustrated in Figure 2. In this figure, the inhomogeneous lineshape for each of the two $\Delta m \pm 1$ transitions are shown and the observed spectrum is given by their sum. The small outer step discontinuities are separated by ν_Q. The separation of the inner shoulder steps and intense singularities are given by $\frac{1}{2}\nu_Q(1 + \eta)$ and $\frac{1}{2}\nu_Q(1 - \eta)$ respectively. For an axially symmetric pattern $\eta = 0$.

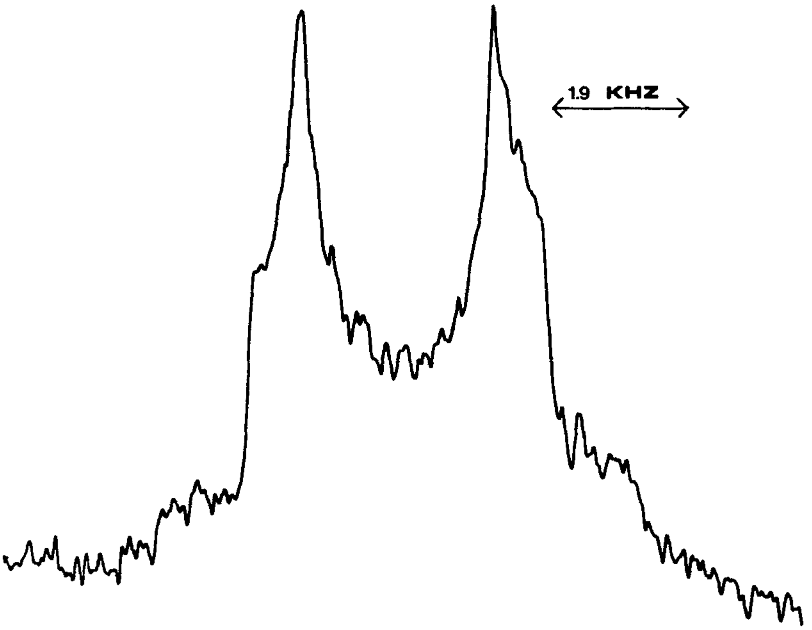

FIGURE 1 Deuterium spectrum of $CDCl_3$ in (60.6) at 24°C. with a random distribution of directors.

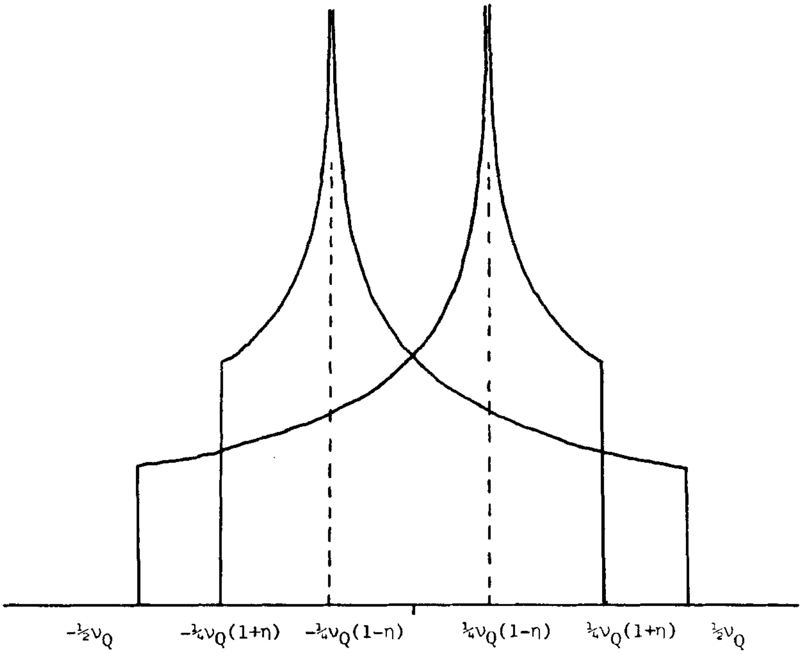

FIGURE 2 Theoretical Powder Spectrum for a Spin ONE Nucleus with an Asymmetric EFG Tensor.

For the case as a cylindrically shaped molecule, the theory of biaxial rotational averaging[8] gives for these averaged EFG parameters

$$\nu_Q = \frac{3}{2}\left(\frac{e^2qQ}{h}\right)S_1 \tag{1}$$

and

$$\eta = S_2/S_1 \tag{2}$$

where $(e^2qQ)/h$ is the quadrupole coupling constant of $CDCl_3$. In terms of the angles (ϕ, θ) that give the polar direction of the $CDCl_3$ symmetry axis with respect to the liquid crystal principal axes, the order parameters S_1 and S_2 are

$$S_1 = \langle \tfrac{1}{2}(3\cos^2\theta - 1)\rangle \tag{3}$$

$$S_2 = \tfrac{3}{2}\langle \sin^2\theta \cos 2\phi\rangle \tag{4}$$

The angular brackets indicate the time averaging imparted to the solute by the liquid crystal solvent and the order parameters are those re-

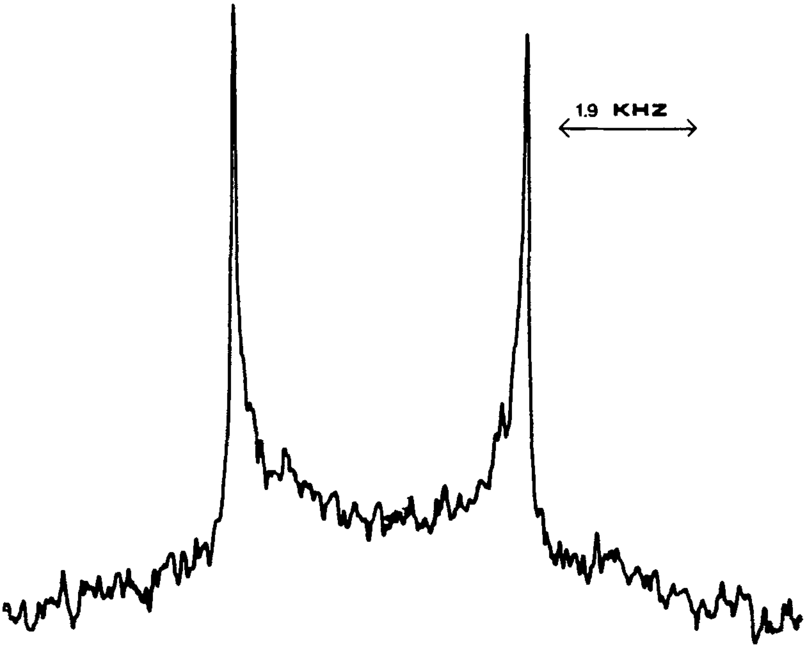

FIGURE 3 Deuterium Spectrum of $CDCl_3$ (60.6) at 45°C.

quired assuming free rotation about the symmetry axis.[8] From the measured spectral splittings we obtain $\nu_Q = 6.81 \pm 0.2$ KHz and $\eta = 0.20 \pm 0.10$. The large value of 0.2 for the asymmetry parameter cannot be due to some asymmetry of the molecular EFG as even in less symmetrical molecules as CD_2Cl_2, observations of pure quadrupole resonances set a limit of $\eta \lesssim 0.05$.[11] Using these values with reported measurement of 167.5 KHz for $(e^2qQ)/h$ gives $S_1 = 0.027$ and $S_2 = 0.0054$. S_1 is very small in this case which helps magnify the effect of the nonzero biaxial ordering as measured by η. When the sample was heated to 45°C, the spectrum results in an axially symmetric powder lineshape as shown in Figure 3. The axially symmetric lineshape, as characterized by the sharpening of the intense singularities, with a separation of $\frac{1}{2}\nu_Q$ as given by Eq. 1, gives $S_1 = 0.033$. The increase of S_1 with temperature has also been observed with CH_2Cl_2 oriented in the S_B phases of Terephthal-bis-(butylaniline) and di-ethylazoxy cinnamate.[4] The small step discontinuities separated by ν_Q were not observed in the symmetric case. This is probably due to the directors becoming more fluid. At 45°C the phase of 60 • 6 has been classified as a S_B phase. No attempt was made to determine the temperature at which the transition to the axially symmetric spectrum occurred.

After heating the sample to the clearing point and cooling slowly back down to 24°C in the presence of the magnetic field, a sharp doublet spectrum is observed indicating a uniform alignment of the liquid crystal. The initial orientation of the sample tube is designated as 0°. Upon rotation of the sample tube by 90°, four peaks are observed with linewidths significantly larger than those observed for the initial orientation. This result indicates a strong departure from uniaxial behavior. In the uniaxial case, sharp lines are expected for 0° and 90° since a distribution of directors has no first order effect on the doublet splitting at these angles.[4] Spectra were therefore obtained for a complete set of orientations between 0° and 90° in 5° increments. The spectra resulting from this rotation study are shown in Figures 4 and 5. The extremely sharp doublet at 0° quickly broadens as the sample is rotated and at 40° shoulders to the doublet become apparent. At 50° two sets of doublets can be distinguished, a strong inner doublet and an outer doublet with approximately half the intensity. At 65° these doublets have crossed each other with the more intense doublet on the outside. It can be noted that these spectra do not resemble those observed in the smectic C phase[4,6] where the reorientation about the tilt direction produces a characteristic broadening. This behavior seems to be only weakly present as suggested by the slightly sharper outside edges of the doublet for small angles of rotation away from the initial orientation.[4] This suggests, along with the observation of an asymmetric powder spectrum for the unaligned case, that the rotation study is exhibiting biaxial behavior. The doublet splitting in this case can be analyzed by fitting to the functional form[12]

$$\Delta\nu(\theta_0)/\Delta\nu(0) = P_2(\cos\theta_0) + A\sin^2\theta_0 + B\sin 2\theta_0 \tag{5}$$

with

$$\Delta\nu(0) = \frac{3}{2}(e^2qQ/h)S_1$$

$$A = \frac{1}{2}\frac{S_2}{S_1}\cos 2\psi_0 \tag{6}$$

$$B = \frac{3}{4}\frac{S_3}{S_1}\sin\psi_0$$

The new order parameter, S_3, is given by $\langle\sin^2\theta\sin\phi\rangle$ and is characteristic of tilted phases.[12] Equation 5 is the expression appropriate for

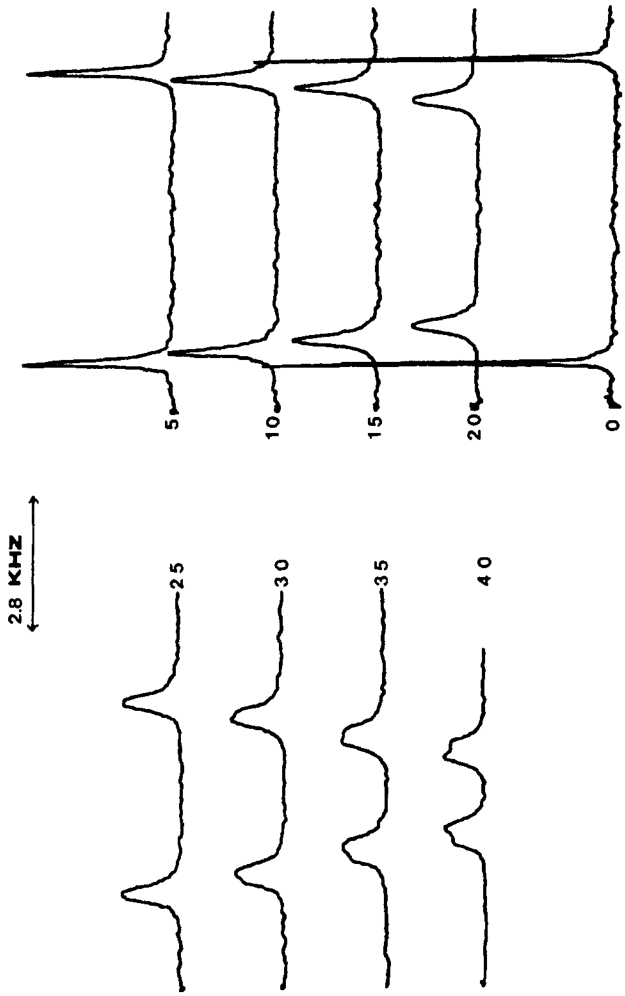

FIGURE 4 Observed $CDCl_3$ Spectra as a Function of Angle for 0°–40° (T = 24.0°C.)

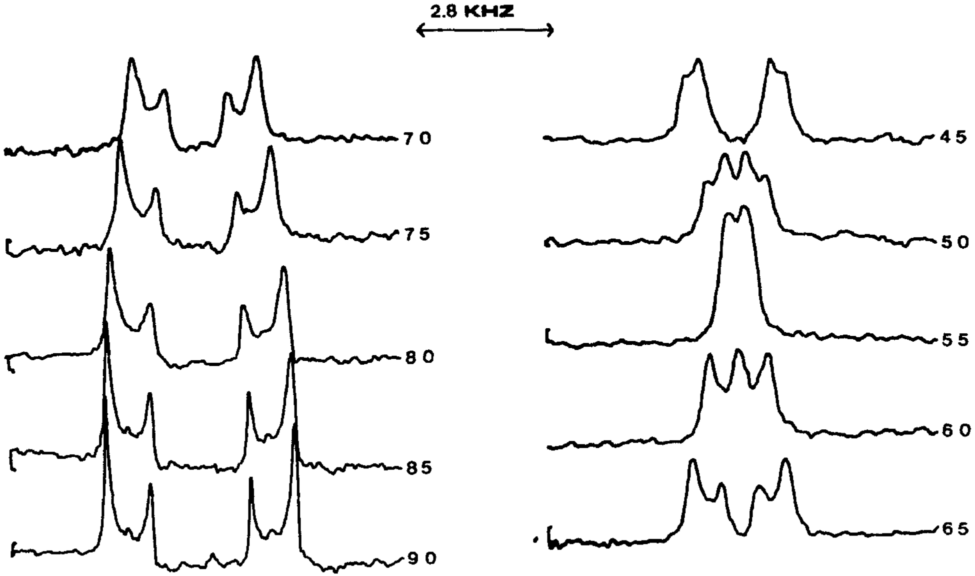

FIGURE 5 Observed $CDCl_3$ Spectra as a Function of Angle for 45°–90° (T = 24.0°C.)

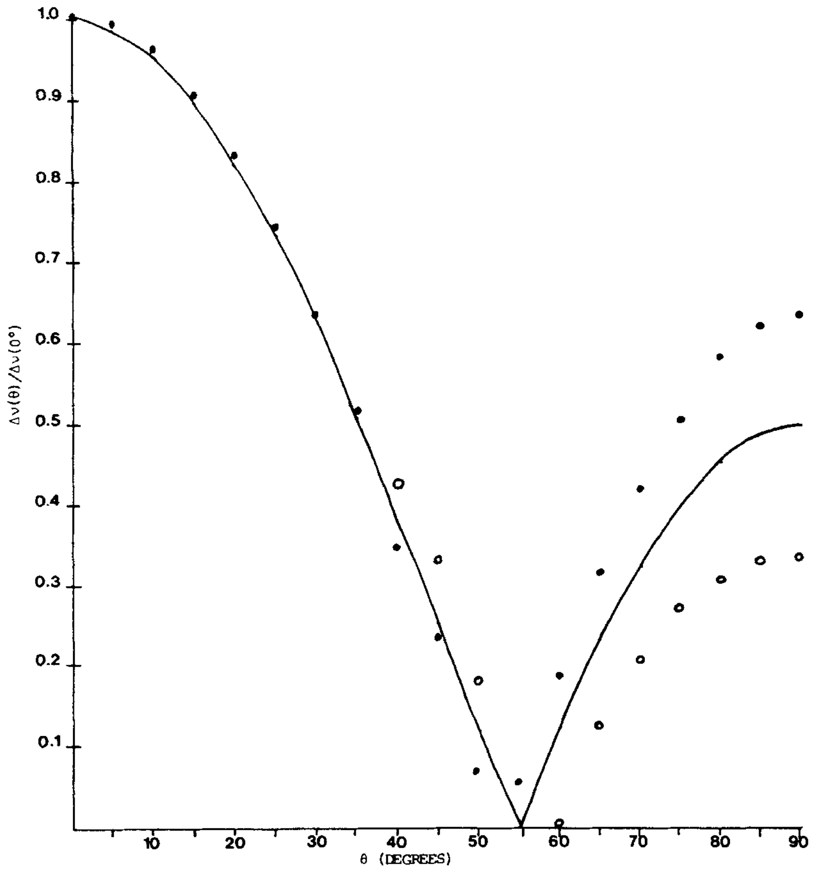

FIGURE 6 Plot of the Normalized Experimental Doublet Separation. The Solid Curve Indicator, the Theoretical Separation for Uniaxial Behavior.

molecules possessing a C_3 or greater symmetry axis. The angles (θ_0, ψ_0) give the orientation of the magnetic field in the principal axis frame of the liquid crystal, if $B = 0$. In a uniaxial phase, A and B are zero. The separation into two sets of doublets is interpreted as resulting from a distribution in the angle ψ_0 with maxima at two different values of the angle. The absolute value of the normalized splittings for each set of doublets is plotted along with the theoretical angular dependence for uniaxial phases in Figure 6. The deviation from uniaxial dependence is clearly indicated, especially for angles approaching 90° due to the extra $\sin^2 \theta_0$ dependence. The open circle data points in Figure 4 refer to the small doublet peaks (Set A) while the solid points give the doublet

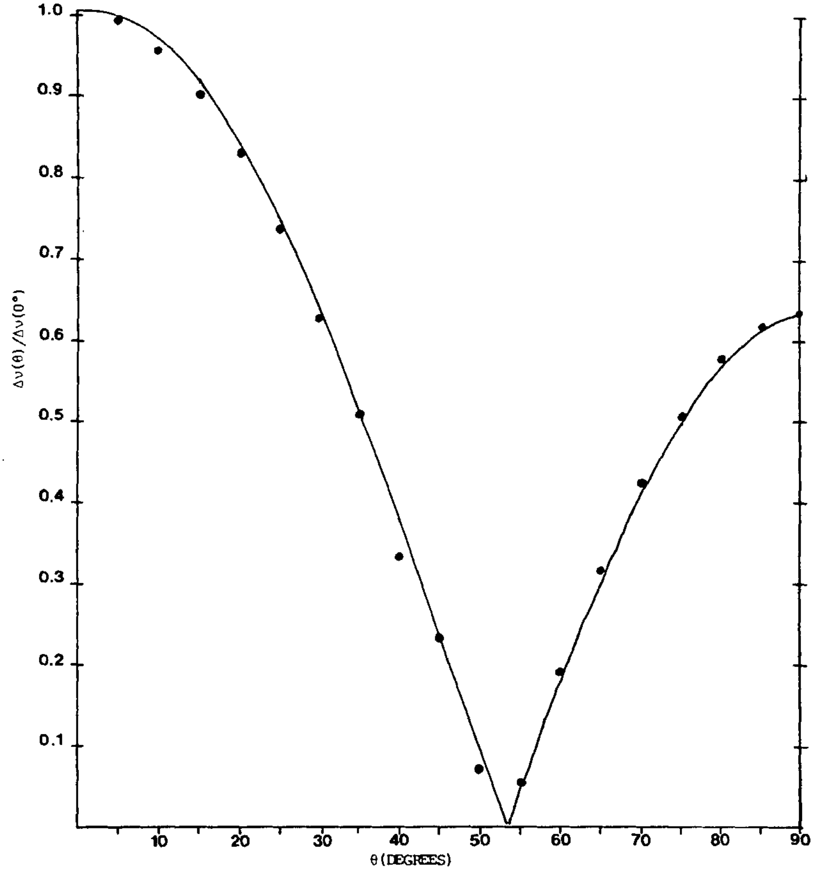

FIGURE 7 Normalized *B* set Doublet Separation with the Solid Curve Calculated from Equation 5.

splittings for the larger peaks (Set *B*). For angles smaller than 30° these two sets are unresolved and the solid data points refer to some average doublet splitting. The doublet separation as a function of angle for the larger peaks is plotted in Figure 7 along with a curve calculated from Eq. 5 where A and B parameters were determined from the experimental splittings observed for 90° and 45° which yield $2A = -.27 \pm 0.02 = \eta \cos 2\psi_0$ and $B = 0.054$. It was observed that a curve with $B = 0$ produced a fit with a systematic difference between the observed splittings that increased for angles approaching 45°. However, B may actually be zero since the spectral peaks are badly overlapped at 45°.

In order to locate the direction pertaining to the angle ψ_0, another rotation study was attempted. In this case, the sample was cooled from the isotropic phase (to 24°C) in the magnetic field while the sample tube axis was parallel to the field direction. This was accomplished by using a commercial probe designed for 20 mm tubes. The sample was then placed back into the transverse solenoid probe and the spectrum obtained was very similar to that shown for the 90° orientation in Figure 4. Upon rotation of the sample axis, however, no shifts in the doublet splittings were observed. This behavior has also been observed in rotation studies on *n*-heptyloxyazoxybenzene[2] where an electric field was required to prevent the liquid crystal from realigning with the magnetic field. This behavior precludes a determination of the order parameters except S_1, for which a 0° splitting of 6.69 KHz gives $S_1 = 0.0266$. The value for S_1 is in good agreement with the value of 0.027 determined from the powder spectrum. A similar analysis of the rotation behavior of the *A* set doublets also shows that the normalized splitting as a function of θ_0 follows the expression given by Eq. 5. The *A* set analysis gives $\eta \cos 2\psi_0 = 0.33 \pm 0.02$ which is larger and of opposite sign than the same parameter given by the *B* set doublets. In connection with the absence of changes in the doublet splittings in the second type of rotation experiment, an alternative explanation to magnetic field realignment exists, namely that there is a uniform or nearly uniform distribution in the angle ψ_0. A theoretical analysis of this case predicts spectra not unlike those shown in Figures 4 and 5.[13] This model also provides a natural explanation for the equality of $\eta \cos \psi_0$ for both sets of doublets and that they are opposite in sign. Because of the unequal intensities in the observed doublets the ψ_0 distribution is not completely uniform, but the deviation from uniformity appears to be small.

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References

1. J. W. Doane in "Magnetic Resonance of Phase Transitions," F. J. Owend, C. P. Poole, Jr., H. A. Farach, eds. (Academic Press, New York, 1979) Chap. IV, "NMR of Liquid Crystals," pp. 171–245.
2. P. J. Box, J. Pirs, P. Ukleja, J. W. Doane and M. E. Neubert, *Mol. Cryst. Liq. Cryst.*, **40**, 59 (1979).

3. Z. Luz, R. C. Hewitt and S. Meiboom, *J. Chem. Phys.*, **61**, 1758 (1974).
4. Z. Luz and S. Meiboom, *J. Chem. Phys.*, **59**, 275 (1973).
5. R. R. Vold and R. L. Vold, *J. Chem. Phys.*, **66**, 4018 (1977).
6. R. Wise, D. H. Smith and J. W. Doane, *Phys. Rev. A*, **7**, 1366 (1973).
7. J. Seliger, R. Osredkar, V. Zaga and R. Blinc, *Phys. Rev. Lett.*, **38**, 411 (1977).
8. D. W. Allender and J. W. Doane, *Phys. Rev. A.*, **17**, 1177 (1978).
9. G. W. Smith and Z. G. Garlund, *J. Chem. Phys.*, **59**, 3214 (1973).
10. R. G. Barnes in "Advances in Nuclear Quadrupole Resonance," J. A. S. Smith, Ed. (Heydan, New York, 1972) Vol. 1, Part VII, "Deuteron Quadrupole Coupling Constants," pp. 342.
11. J. L. Ragle and K. L. Skerk, *J. Chem. Phys.*, **50**, 3553 (1969).
12. P. J. Collings, D. J. Photinos, P. J. Bos, P. Ukleja and J. W. Doane, *Phys. Rev. Lett.*, **42**, 996 (1979).
13. Z. Yaniv, J. W. Doane, T. Barbara and B. P. Dailey, *Mol. Cryst. Liq. Cryst.* (to appear).