(1958); G. S. Schnoknecht, Z. Naturforsch. 12a, 983 (1960).

[7] R. Narayan and S. Ramaseshan, to be published.

[8] This surprising fact has not been recognized so far. The belief is that only ionic crystals with exceptionally large radius ratios can occur in the ZnS structure with its open fourfold coordination (correspondingly low Madelung constant α). However, the lower coordination number also shifts the equilibrium to smaller interionic distances, rendering the structure competitive with the NaCl structure.

[9] See, for example, F. Seitz, *The Modern Theory of Solids* (McGraw Hill, New York and London, 1940), p. 331.

[10] The radius ratio r_+/r_- varies in different phases of a crystal and also with temperature and pressure in the same phase.

[11] This assumption is good enough for the present purpose since the term $T\beta/K$ corresponds to a small effective negative pressure of only a few kilobars.

[12] The values of C and D were taken from F. Hajj, J. Chem. Phys. 44, 4618 (1966), and J. E. Mayer, J. Chem. Phys. 1, 270 (1933), respectively. A simplifying approximation was made of replacing each ionic polygonal face by a circle of equivalent area so that the integral (5) is simplied. Also, the radius r_+ of Na$^+$ in NaCl was held fixed at the electron-density map value of 1.18 Å.

[13] The high-temperature expressions given by W. F. Weston and A. V. Granato, Phys. Rev. B 12, 5355 (1975), were used.

[14] K. J. Rao, G. V. S. Rao, and C. N. R. Rao, Trans. Faraday Soc. 63, 1013 (1967).

[15] The calculations are at 0°K while the experiments were at 300°K. However, there is experimental evidence [R. B. Jacobs, Phys. Rev. 54, 468 (1938)] that the transition pressures are quite insensitive to temperature.

[16] Jacobs, Ref. 15.

[17] S. N. Vaidya and G. C. Kennedy, J. Phys. Chem. Solids 32, 951 (1971); P. W. Bridgman, Proc. Am. Acad. Arts Sci. 76, 9 (1945).

[18] W. A. Bassett, T. Takahashi, H. K. Mao, and J. S. Weaver, J. Appl. Phys. 39, 319 (1968).

[19] A. L. Ruoff and L. C. Chhabildas, J. Appl. Phys. 47, 4867 (1976).

[20] No pressure transitions have been reported.

[21] P.-O. Löwdin, Philos. Mag. Suppl. 5, 1 (1956).

[22] E. Lombardi, L. Jansen, and R. Ritter, Phys. Rev. 185, 1150 (1960).

[23] A. H. Cohen and R. G. Gordon, Phys. Rev. B 12, 3228 (1975).

NMR in Spinning Samples of Biaxial Liquid Crystals

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(Received 29 December 1978)

Magnetic resonance measurements on a spinning sample of deuterated n-heptyloxyazoxybenzene (HOAB-d_{30}) 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, S_C, phase. The lack of experimental data on molecular order is evidenced by the numerous and varied models[1] 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.[2] 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[3,4] who used an ingenius technique to measure the asymmetry parameter of the ^{14}N nucleus in TBBA (terephthal-*bis*-butylaniline). 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.[5-7]

This paper introduces a simple NMR experiment which is more sensitive to biased 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 order parameters.

The theory of motionally averaged quadrupole spectra in biaxial liquid crystals has been described elsewhere.[5,8] Basically, the theory involves successive coordinate transformations of the spatial part of the quadrupole Hamiltonian. In our development we define four coordinate systems. The angles (φ_0, θ_0) describe the orientation of the magnetic field in the reference frame fixed with respect to the liquid-crystal directors.[5,8] The Euler angles (φ, θ, ψ) describe the orientation of a coordinate system fixed to the molecule with respect to the director frame. These angles are time dependent, with suitable averages representing order parameters. The Euler angles (α, β, γ) give the orientation of a particular deuterium-carbon bond relative to the molecular frame. Intramolecular motion also causes these angles to be time dependent. In terms of these angles, the motionally averaged deuterium quadrupole splitting for the ith spectral pair in a biaxial liquid crystal which is apolar, on the average, may be expressed in the following form:

$$\Delta\nu_i = \nu_Q{}^i [A_i P_2(\cos\theta_0) + B_i \sin^2\theta_0 \cos(2\varphi_0) + C_i \sin(2\theta_0)\sin\varphi_0], \qquad (1)$$

where $\nu_Q{}^i$ is the coupling constant for the ith 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

$$A_i = \tfrac{3}{2}(r_i S_1 + \tfrac{3}{4} s_i S_2 + \tfrac{3}{4} t_i S_3), \qquad (2a)$$

$$B_i = \tfrac{9}{8}(r_i S_4 + s_i S_5 - t_i S_6), \qquad (2b)$$

$$C_i = \tfrac{9}{8}(r_i S_7 - s_i S_8 + t_i S_9), \qquad (2c)$$

where $r = \langle \tfrac{3}{2}\cos^2\beta - \tfrac{1}{2}\rangle$, $s = \langle \sin^2\beta \cos 2\alpha\rangle$, and $t = \langle \sin 2\beta \sin\alpha \rangle$ are the conformation averages and the nine order parameters are

$$S_1 = \langle \tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}\rangle, \quad S_2 = \langle \sin^2\theta \cos 2\psi\rangle,$$

$$S_3 = \langle \sin 2\theta \sin\psi\rangle, \quad S_4 = \langle \sin^2\theta \cos 2\varphi\rangle,$$

$$S_5 = \langle \tfrac{1}{2}(1+\cos^2\theta)\cos 2\varphi \cos 2\psi - \cos\theta \sin 2\varphi \sin 2\psi\rangle,$$

$$S_6 = \langle \sin\theta \sin 2\varphi \cos\psi + \tfrac{1}{2}\sin 2\theta \cos 2\varphi \sin\psi\rangle,$$

$$S_7 = \langle \sin 2\theta \sin\varphi\rangle,$$

$$S_8 = \langle \sin\theta \cos\varphi \sin 2\psi + \tfrac{1}{2}\sin 2\theta \sin\varphi \cos 2\psi\rangle,$$

$$S_9 = \langle (1 - 2\cos^2\theta)\sin\varphi \sin\psi + \cos\theta \cos\varphi \cos\psi\rangle .$$

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 $(\theta_0 = 0)$ the splittings only depend on these order parameters.[8] The order parameters S_4 through S_9 are biaxial order parameters of which S_7, S_8, and S_9 are only present in tilted phases. Parameters which express a biased rotation about the long molecular axis are S_2, S_5, and S_8 (twofold rotation) and S_3, S_6, and S_9 (partial freezeout). Parameters S_1, S_4, and S_7 are the only parameters which survive under free rotation about the molecular axis.

In order to observe the biaxial order parameters the angle θ_0 in Eq. (1) must be nonzero. This can be achieved experimentally by spinning the sample about an axis perpendicular to the magnetic field. If the rate of spinning is rapid enough the angle θ_0 becomes uniformly distributed.[9] Instead of a splitting, a spectral pattern results. In the uniaxial case, the shape of the spectral pattern can be calculated without the use of fitting parameters.[10] In the biaxial case the shape of the pattern can also be calculated when the biaxial coefficients *B* and *C* are fitting parameters.

Using a pulsed NMR spectrometer operating at 9.4 MHz, we have recorded the quadrupolar spectrum of selectively deuterated *n*-heptyloxyazoxybenzene (HOAB-d_{30}).

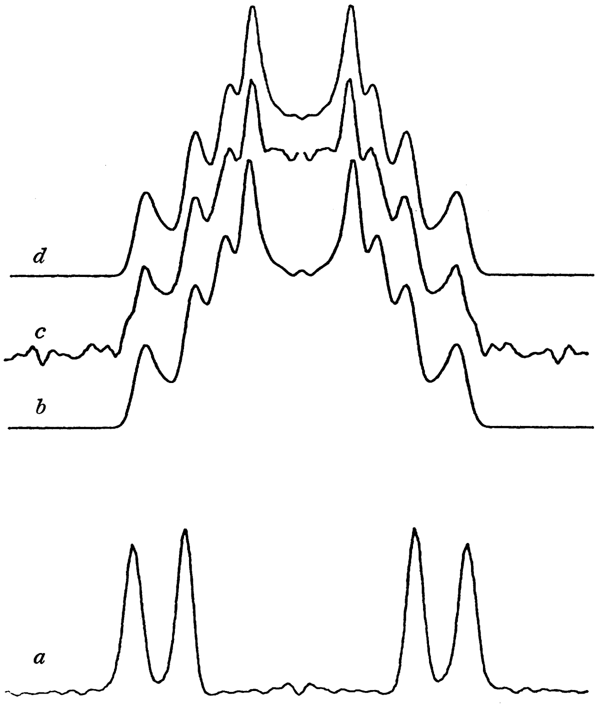

FIG. Deuteron nuclear-magnetic-resonance spectrum of the methyl groups in HOAB-d_{30} in the nematic phase at 115°C. Trace *a*, the stationary spectrum, $\theta_0 = 0$, where $\delta\nu_1$ is the splitting of the inner two lines and $\delta\nu_2$ the outer. Trace *b*, the calculated spectral pattern only using the stationary spectrum and assuming uniaxiality. 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.

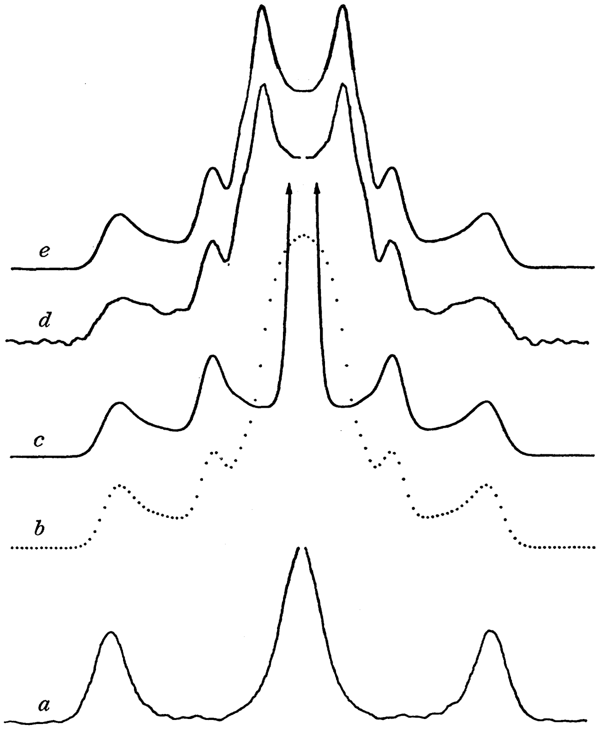

FIG. 2. Deuteron nuclear-magnetic-resonance spectrum of HOAB-d_{30} in the S_c phase at 82°C. Trace *a*, stationary spectrum where $\delta_1 = 0$ and $\delta\nu_2$ is the large splitting; *b*, calculated spectral pattern in which φ was assumed to be distributed; *c*, calculated spectral pattern assuming uniaxiality; *d*, recorded spinning spectral pattern; and *e*, calculated spectral pattern with the best fitted values given in Table I. All recordings range over 4.0 kHz.

Figure 1, 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 ~30 Hz, or lower rates down to ~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 uniaxial 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 uniaxial 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 θ_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

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

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-

TABLE I. Best-fit values (in kilohertz) for the spectral patterns.

Parameter[a]	Nematic phase (115°C) Line 1	Nematic phase (115°C) Line 2	Smectic-C phase (82°C) Line 1	Smectic-C phase (82°C) Line 2
A'	1.56 ± 0.02	2.26 ± 0.02	0.02 ± 0.02	2.65 ± 0.02
B'	0.00 ± 0.02	0.00 ± 0.02	-0.24 ± 0.03	0 ± 0.03
C'	0.0 ± 0.1	0.0 ± 0.1	0.75 ± 0.03	0.4 ± 0.2
k	0.068	0.079	0.10	0.12
N	0.016	0.005	0.045	0.05

[a] $A' = \nu_Q A$, $B' = \nu_Q B \cos 2\varphi_0$, $C' = \nu_Q C \sin\varphi_0$, and $\nu_Q = 57.34$ kHz (Ref. 11). The values of A and k used were obtained from stationary spectra.

perature, a fact observed earlier.[11] 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 $(\frac{1}{2}A' + \frac{1}{4}B') \pm \frac{1}{2}[(\frac{3}{4}A' - \frac{1}{2}B')^2 + C'^2]^{1/2}$, where A', 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 φ_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 ($\varphi_0 = 90$) 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 β_1 and β_2 are near the magi magic angle[11] (54.7°) where small differences β cause large changes in r but not in s and t such that $s_1 \simeq s_2$ and $t_1 \simeq t_2$ even though r_1 and r_2 are very different.[12] Using this fact alone and taking $S_1 \simeq 0.8$ give $S_4 \simeq 0.10$ and $S_7 \simeq 0.15$. Furthermore, assuming $sS_2 + tS_3 \lesssim 0.1$, which is reasonable both theoretically[13] and experimentally,[11] gives $sS_5 - tS_6 \sim -sS_8 + tS_9 \sim 0.1$. Taking $0.1 < |s| < 1$ and $0.1 < |t| < 1$, one finds that the parameters expressing biased rotation appear at best comparable in magnitude to S_4 and S_7 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_4 is not inconsistent with the measurements of Refs. 4 and 7 as S_4 appears in the asymmetry parameter[5] and could account for the unique temperature dependence of that quantity.

This research was supported in part by the National Science Foundation under Grant No. DMR-76-21365.

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[1] W. L. McMillan, Phys. Rev. A 8, 1921 (1975); A. Wulf, Phys. Rev. A 11, 365 (1975); R. G. Priest, J. Phys. (Paris) 36, 437 (1975), and J. Chem. Phys. 65, 408 (1976); D. Cabib and L. Benguigui, J. Phys. (Paris) 38, 419 (1977); W. H. de Jeu, J. Phys. (Paris) 38, 1265 (1977).

[2] T. Taylor, J. Fergason, and S. Arora, Phys. Rev. Lett. 24, 359 (1970).

[3] J. Seliger, R. Osredkar, V. Zagar, and R. Blinc, Phys. Rev. Lett. 38, 411 (1977).

[4] J. Seliger, V. Zagar, and R. Blinc, Phys. Rev. A 17, 1149 (1978).

[5] D. W. Allender and J. W. Doane, Phys. Rev. A 17, 1177 (1978).

[6] A. Wulf and J. W. Doane, Mol. Cryst. Liq. Cryst. 41, 115 (1978).

[7] F. Volino and A. J. Dianoux, Phys. Rev. Lett. 39, 763 (1977).

[8] J. W. Doane, in Magnetic Resonance Studies of Phase Transitions, edited by F. J. Owens, C. P. Poole, Jr., and H. A. Farach (Academic, New York, to be published).

[9] P. J. Bos and J. W. Doane, Phys. Rev. Lett. 40, 1030 (1978).

[10] J. Pirs, P. Ukleja, and J. W. Doane, Solid State Commun. 19, 877 (1976).

[11] P. J. Bos, J. Pirs, P. Ukleja, M. E. Neubert, and J. W. Doane, Mol. Cryst. Liq. Cryst. 40, 59 (1977).

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

[13] G. R. Luckhurst, C. Zannoni, P. L. Nordio, and V. Segre, Mol. Phys. 30, 1345 (1975).