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Direct Nuclear-Magnetic-Resonance Measurements of Biaxiality in the Cholesteric Liquid Crystalline Phase

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(Received 7 April 1981)

We report what we believe is the first experimental measurement of biaxiality in a cholesteric phase. This observation is made in a selectively deuterated nematic that was twisted by the addition of a chiral compound. A theoretically predicted biaxial order parameter (measured in terms of an asymmetry in the time-averaged deuterium quadrupole interaction) was found to be $\sim 10^{-3}$ for a pitch $\sim 3\ \mu$m and to increase both with decreasing pitch and as the isotropic phase is approached.

PACS numbers: 64.70.Ew, 61.30.Gd

The possibility of observing biaxial molecular order in a twisted nematic has been a topic of discussion for several years.[1] The nematic liquid crystal is normally uniaxial, but when it is twisted the cylindrical symmetry is broken by the helical twist defined by the pitch axis and biaxial ordering, though perhaps very weak, has been expected in such systems. Several theoretical investigations have regarded biaxiality as an important feature of cholesterics[2-4] and of the blue phases[5,6] which often intercede between the cholesteric and the isotropic phase. In an experiment on light scattering[7] the data could be interpreted as a result of competing fluctuations of both uniaxial and biaxial order parameters, but no values of the biaxial order parameters were reported. On the other hand, other optical experiments[1] have not revealed any observable biaxiality. Nevertheless, theory has been encouraging for further experimental study with some authors suggesting the use of NMR to observe this feature.[3,5]

In this paper we report a direct deuterium NMR measurement of biaxial order in a nematic that has been twisted by an optically active compound added to the sample. The nematic material is a binary mixture of 75 wt.% 4-methoxybenzylidene-4′-n-butylaniline (MBBA) and 25 wt.% 4-n-butyloxybenzylidene-4′-n-heptyl-d_4-analine (4.O7-d_4) selectively deuterated on one aromatic ring. To this material was added various concentrations of chiral 4-cyano-4′-(2-methyl)butylbiphenyl (CB-15) to yield the twisted structure.

In the untwisted material, the nematic aligns in the magnetic field yielding the typical deuterium spectrum illustrated in Fig. 1(a). Of interest in

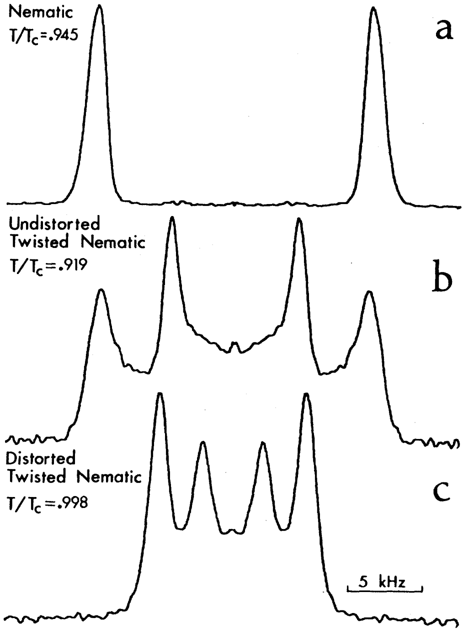

FIG. 1. Experimental NMR spectral patterns of (a) untwisted nematic (0 mol% CB-15), T_c = 324.1°K; (b) undistorted twisted nematic (6.1 mol% CB-15), T_c = 322.23 °K; (c) same as (b) at a temperature just below the isotropic transition and showing the distortion effects due to the applied magnetic field.

such a spectrum is the splitting between the spectral lines which, in general, is given by the expression[8]

$$\delta\nu = \tfrac{3}{2}\nu_Q[(\tfrac{3}{2}\cos^2\theta_0 - \tfrac{1}{2}) + \tfrac{1}{2}\eta \sin^2\theta_0 \cos 2\varphi_0]. \quad (1)$$

The basic parameters to be determined from the splitting are the time-averaged coupling constant $\nu_Q = eQ\langle V_{zz}\rangle/h$ and the motionally induced asymmetry parameter $\eta = \langle V_{xx} - V_{yy}\rangle/\langle V_{zz}\rangle$, where $\langle V_{ii}\rangle$ are the time-averaged electric-field–gradient components along the respective principal axes x, y, and z. The parameter η is directly related to biaxial order and in the uniaxial nematic $\eta \equiv 0$. The angles θ_0 and φ_0 are the polar and aximuthal angles of the direction of the magnetic field in the principal-axes frame. The untwisted nematic aligns in the magnetic field such that the principal z axis is parallel to $\vec{H}$ ($\theta_0 = 0$).

When a sufficient quantity of CB-15 is added to the sample the nematic becomes twisted to yield the spectral pattern illustrated in Fig. 1(b). This spectral shape is that expected where the pitch axis of the helical twist is perpendicular to the direction of the magnetic field and results from a distribution of θ_0 in Eq. (1) as V_{zz} is twisted about that axis.[9] The spectral pattern is characterized by two sets of edge singularities with splittings $|\delta\nu_1|$ and $|\delta\nu_2|$ which correspond to the locations along the pitch axis where in Eq. (1), $\theta_0 = 0°$ and 90°, respectively. It is easily recognized from the experimental patterns such as Fig. 1(b) that $|\delta\nu_2| < \frac{1}{2}|\delta\nu_1|$. This important feature can be understood as a result of two independent effects: (i) a nonvanishing asymmetry parameter, η, in Eq. (1), and (ii) self-diffusion along the pitch axis. In the latter case, V_{zz} becomes further time averaged as diffusion along the pitch axis changes its orientation relative to $\vec{H}$. During the time scale of the NMR measurement, $\tau \simeq \nu_Q^{-1} \sim 10^{-4}$ sec, the molecule can diffuse an rms distance along the pitch axis $\sim (D\tau)^{1/2} \sim 0.1$ μm, where D is the diffusion constant. It can be shown that the singularities are calculated to become[10]

$$\delta\nu_{1,2} = \tfrac{3}{2}\nu_Q[\tfrac{1}{4}(1 + \eta\cos 2\varphi_0) \pm \tfrac{1}{4}(3 - \eta\cos 2\varphi_0)K], \quad (2)$$

where the factor K is due to diffusion and is given by $K = [1 - \exp(-X)]/X$, where $X = (-16\pi^2 D\tau/p^2)$ and where p is the pitch of the twist.[10] It is seen from Eq. (2) that the effect of diffusion can be eliminated by considering the quantity

$$\Delta = 2(|\delta\nu_1| - |\delta\nu_2|) = \tfrac{3}{2}|\nu_Q|(1 + \eta\cos 2\varphi_0). \quad (3)$$

There are two other effects that can affect the shape of the spectral pattern. One is the effect of a twist distortion[11] which occurs when the sample is under the action of a magnetic field of strength very near the critical field, H_c, that unwinds the cholesteric.[12] This effect is easily recognized in that it gives a preponderance of orientations of V_{zz} at $\theta_0 = 0°$ over those at $\theta_0 = 90°$ and as a result the intensity of the outer set of singularities becomes enhanced over that of the inner set as evidenced in Fig. 1(c). In the absence of diffusion the positions of the singularities are not affected, only the intensities. In the presence of diffusion in the distorted case Eq. (3) is no longer strictly valid and, as a result, its use was avoided when distortion was evident from the peak intensities. Another effect which can alter the spectral pattern is when the pitch axis is not perpendicular to $\vec{H}$.[9] Again, this effect is easily recognized in that the outer singularities are shifted inward while the inner singularities remain unshifted, such that $|\delta\nu_2| > \frac{1}{2}|\delta\nu_1|$ contrary to that observed in our experiments.

Experimental values for the temperature dependences of $|\delta\nu_1|$ are shown in Fig. 2(a) for

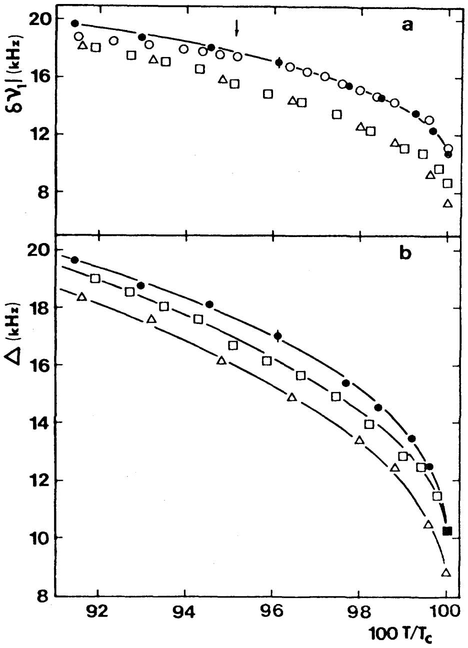

FIG. 2. Plot of the (a) outermost splittings, $|\delta v_1|$, and of the (b) parameter $\Delta = 2(|\delta v_1| - |\delta v_2|)$ vs T/T_c. Solid circles, untwisted nematic (0 mol% CB-15), $T_c = 324.10\,^\circ\mathrm{K}$. Open circles, twisted nematic (3.5 mol% CB-15) $T_c = 315\,^\circ\mathrm{K}$. The arrow shows where this sample becomes untwisted by the magnetic field at $T = 299\,^\circ\mathrm{K}$. Squares, twisted nematic (6.1 mol% CB-15) ($p = 3.3\ \mu\mathrm{m}$), $T_c = 322.23\,^\circ\mathrm{K}$. Triangles, twisted nematic (8.0 mol% CB-15) ($p = 2.5\ \mu\mathrm{m}$), $T_c = 317.76\,^\circ\mathrm{K}$. The solid lines are drawn to aid the eye.

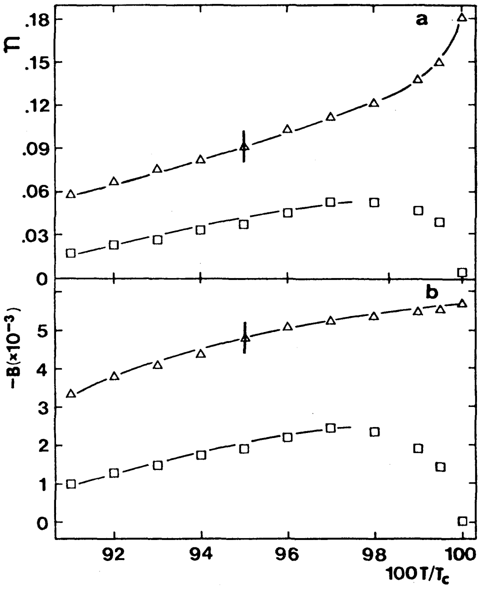

FIG. 3. Plot of (a) the asymmetry parameter η, and (b) the biaxial order parameter, B as a function of T/T_c. Same convention of symbols as in Fig. 2. The solid lines are drawn only in the temperature range where there is no evidence of distortion effects (see text).

several different concentrations of CB-15. Using the Cano wedge method[13] we measured a pitch length of 3.3 μm for the 6.1 mol% concentration. The sample containing the 3.5 mol% concentration of CB-15 exhibited an induced cholesteric-nematic phase transition at a temperature of $T = 299\,^\circ\mathrm{K}$, where $H_c(T) = H = 47$ kG. The values of $|\delta\nu_1|$ vs T/T_c are the same in the untwisted nematic for both the zero and 3.5 mol% samples indicating that changing the concentration of CB-15 from 0 to 3.5 mol% had no effect on ν_Q in the nematic phase on a T/T_c plot. It was likewise assumed that this was also true for the other samples since the concentration of CB-15 was no larger than 8% and impurities generally have little effect on the degree of order, S, on a T/T_c plot. At the N-Ch transition where the 3.5 mol% sample becomes untwisted, the value of $|\delta\nu_1|$ drops below that of the 0 mol% sample primarily because of averaging by diffusion. In the 6.1 ($p = 3.3\ \mu$m) and 8.0 ($p = 2.5\ \mu$m) mol% samples the nematic is twisted throughout the nematic temperature range and $|\delta\nu_1|$ is reduced by both η and D.

In Fig. 2(b) the effect of diffusion is eliminated by the plot of Δ vs T/T_c. Using values of ν_Q obtained from $\delta\nu_1{}^0 = \frac{3}{2}\nu_Q$ of the 0 mol% (CB-15) sample, Eq. (3) is then used to obtain the values of η shown in Fig. 3(a). The values of $\eta\cos2\varphi_0$ are found to be negative from Eq. (3). Since, by definition, η is positive we chose the value of $\cos2\varphi_0 = -1$ which would fix the pitch axis along the x axis. This is the axis of the smallest component of the time-averaged electric-field gradient.

In Fig. 3 we have drawn solid lines only in the temperature range where there is no evidence of distortion due to the unwinding of the twist. No distortion was observed at all in the 8.0 mol% sample ($p \simeq 2.5\ \mu$m), where η becomes enhanced near T_c. In the 6.1 mol% sample distortion is observed between $T = T_c$ and $T/T_c = 0.98$ where η reaches a maximum. Equation (3) is not strictly valid in this region and the values of η may become more incorrect as T_c is approached.

The asymmetry parameter can be directly related to the biaxial order parameter B by the expression[14] $B = \frac{9}{8}\langle\sin^2\sigma\cos2\xi\rangle$, or[15] $B = 3\eta\nu_Q/4\nu_Q{}^s$, where $\nu_Q{}^s$ is the coupling constant of the C-D bond measured in a solid where all orientational motion is frozen out. The time-dependent angles

σ and ξ are the polar and azimuthal angles of the C-D bond in the principal x, y, z axes frame. The values obtained for B are shown in Fig. 3(b). Likewise, the order parameter $S = \langle \frac{3}{2} \cos^2\sigma - \frac{1}{2} \rangle$ of the C-D bond can be obtained by the relation $S = \nu_Q / \nu_Q{}^s$. Since the C-D bond is at a large angle ($\sigma \simeq 60°$) relative to the molecular long axis, the value of S and hence the ratio $\nu_Q/\nu_Q{}^s$ is negative. Taking values of $\nu_Q{}^s$ from the literature we can then write $\nu_Q/\nu_Q{}^s = -\frac{2}{3} |\delta\nu_1{}^0| / 193$. This gives negative values of B as shown in Fig. 3(b) but, as shown later, when transformed from the C-D bond to the molecular long axis the order parameters become positive as expected.

Since B is a direct measure of biaxiality, it is useful to comment on Fig. 3(b). Firstly, in the region far from T_c it appears that $|B| \simeq \text{const} p^{-2}$, a result predicted in the literature.[6] Secondly, in the 8.0 mol% sample which was not untwisted by the field, $|B|$ continually increases as T_c is approached, also an expected result.[6]

More meaningful order parameters than S and B of the C-D bond are those associated with the molecular long axis, z_m. We can assume this to be near the para-axis of the aromatic ring so that the C-D bond is oriented 60° away from that axis. Taking the molecular short axis, x_m, to be normal to the plane of the ring and transforming to the x_m, y_m, z_m frame yields $S \simeq -0.12 S_{0,0}$ and $B \simeq 9(-0.12 S_{2,0} - 1.5 S_{2,2})/8$, where $S_{0,0} = \langle 3 \cos^2\theta - 1 \rangle / 2$ is the degree of order of the long axis; $S_{2,0} = \langle \sin^2\theta \cos 2\varphi \rangle$ gives the biaxiality associated with anisotropic fluctuations of the long axis and $S_{2,2} \simeq \frac{1}{2} \langle \cos 2(\varphi + \psi) \rangle$ gives the contribution of birotational freezeout to biaxiality.[15] The Euler angles φ, θ, ψ give the instantaneous orientation of the molecular frame x_m, y_m, z_m in the laboratory x, y, z frame. From Fig. 2(a), at temperatures far from T_c, $\nu_Q = 12$ kHz which gives a reasonable value for $S_{0,0} \simeq 0.52$. Unfortunately, there is not enough information in this experiment to separate the contributions from $S_{2,0}$ and $S_{2,2}$. This would require another measurement of B on a differently oriented C-D bond. However, it is seen that since B is negative the values of $S_{2,0}$ and $S_{2,2}$ are positive as one might expect for these parameters. If $S_{2,2}$ were negligible, the value of $S_{2,0}$ could be ~0.03 possibly increasing an order of magnitude to a sizable value of ~0.3 for tighter pitches. On the other hand, $S_{2,2}$ is a likely contributor particularly in regions far from T_c since small values of $S_{2,2} \simeq 0.003$ can account for the measured values of B.

More experiments are in progress on different deuterated segments to separate the values of $S_{2,0}$ and $S_{2,2}$ as well as to obtain values for shorter pitch lengths.

We are indebted to Dr. Mary E. Neubert for the deuterated compound. This work was supported in part by the National Science Foundation under Grants No. DMR-78-09046 and No. DMR-79-04393. One of us (G.C.) is a recipient of a NATO Fellowship.

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