Deuterium NMR spectra of the cholesteric and blue phases: A study of biaxiality

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(Received 18 July 1983)

Deuterium NMR spectra from a set of cholesteric materials differing in pitch length have been interpreted in terms of a biaxial ordering of the molecules. It is found that, in these materials, the biaxiality in the cholesteric phase is a universal function of the reduced temperature (independent of pitch length) only when there is a blue phase present in the material. In contrast, when the cholesteric phase transforms directly into the isotropic phase without the presence of a blue phase the biaxiality on a reduced-temperature plot is strongly pitch-length dependent. By the study of different deuterated sites of the same molecule, the mechanism for biaxiality is examined. Deuterium NMR spectra are also used to measure the pitch dependence of the self-diffusion constant. Finally, the NMR technique of measuring biaxiality in the cholesteric phase is discussed and a critique made. The materials used in the study were selectively deuterated 4-methoxybenzylidene-4'-butylaniline (MBBA) twisted by the addition of chiral 4-methoxybenzylidene-4'-[(+)-2-methylbutyl]aniline (MBMBA) in various weight percentages to obtain samples of different pitch lengths.

I. INTRODUCTION

A subtle but nonetheless important feature of cholesteric liquid crystals is the biaxial ordering of the molecules. It is subtle in that it is a weak effect except near the isotropic or blue-phase transition[1] and it is difficult to observe by standard optical techniques.[2] It is deemed to be important in that it is a significant feature of some theories of the blue phases which can appear between the cholesteric and isotropic phases.[3,4] A measure of the biaxiality in the cholesteric phase can therefore be an important test of these theoretical concepts.

Recently, we showed that pronounced features of deuterium NMR spectral patterns observed in cholesteric liquid crystals can be suitably explained by biaxial ordering.[1,5,6] Using this technique we demonstrated how the biaxiality could be measured in terms of an asymmetry parameter η for the time-averaged deuterium quadrupole interaction. Interpreting the deuterium NMR spectral patterns in terms of η we showed that (1) the biaxiality increases with increasing temperature and decreasing pitch length,[1] (2) the mechanism for biaxiality appears to be a result of anisotropic fluctuations of the molecular long axis,[6] and (3) the long molecular axis is least ordered relative to a direction parallel to the direction of the pitch axis.[1] Features (1) and (2) above appeared to be consistent with the Landau theory of Hornreich and Shtrikman[4] and a recent molecular field theory of Lin-Liu and Lee[7] although the measured values of biaxiality were slightly larger than would be expected from the Landau theory. Feature (3) turned out to be entirely consistent with the simple concepts involved in the molecular field theory.[7]

In this paper we show detail measurements of η in the cholesteric phase in a set of binary mixtures of materials consisting of selectively deuterated 4-methoxybenzylidene-4'-butylaniline (MBBA) and chiral 4-methoxybenzylidine-4'-[(+)-2-methylbutyl]aniline (MBMBA).

With these materials we were able to perform a controlled set of experiments with different pitch lengths p ranging over $\infty > p > 0.32 \ \mu$m, well into the range where the blue phases occur. Perhaps the most interesting result of these studies is that we find two different behaviors of the biaxiality depending upon whether there is a cholesteric-isotropic or cholesteric—blue-phase transition. In cholesteric materials which exhibit long pitch lengths and a cholesteric-isotropic phase transition at the temperature T_c we observe that, on a reduced temperature plot, T/T_c the biaxiality is dependent upon the pitch length. In contrast, for short pitch length materials which exhibit a cholesteric—blue-phase transition at the temperature $T_{c'}$ the biaxiality is a universal function of temperature on a reduced temperature plot $T/T_{c'}$. Such a feature has not yet been reported earlier from previous experimental or theoretical studies. In this paper we also examine further the mechanism for biaxiality at two different pitch lengths and we discuss and examine in more detail the deuterium NMR measurement. The role of self-diffusion and the effects of the orientation of the pitch axis in the NMR magnetic field on the deuterium spectrum are discussed.

II. ^{2}H-NMR THEORY

Spectral frequencies

When observed in the presence of a large magnetic field, a spin-1 deuterium nucleus will show a simple spectrum of only two lines.[8] If we start with the axis of quantization x,y,z chosen with $Z||H$ and x,y at an arbitrary orientation, then the spectral frequencies $\nu^{\pm}$ of each of the lines relative to the Zeeman frequency[9] ν_0 can be expressed by the following equation[10]:

$$\nu^{\pm} = \pm \frac{1}{2} \left(\frac{3}{2} \right)^{1/2} \frac{eQ}{h} R^z_{2,0} \ , \tag{1}$$

where Q is the deuterium quadrupole moment and $R_{2,0}^z = (\frac{3}{2})^{1/2} V_{zz}$ in which V_{zz} is the z component of the electric-field-gradient tensor. In our development we will assume that all of the internal motions of the system are either sufficiently rapid or sufficiently slow compared to $|v^{\pm}|^{-1} \lesssim 10^{-5}$ sec that we can always express these frequencies in terms of the components of the field gradient tensors V_{ij}.

In the cholesteric phase, the z component of the time-averaged electric-field-gradient tensor is distributed in a unique way relative to the direction of H whereby it is necessary to express $v^{\pm}$ relative to two frames of reference: a sample frame a,b,c in which we describe the orientation of $\vec{H}$ in terms of the polar angles (θ_0, ϕ_0) and a second frame x,y,z which is the principal axes frame of the time-averaged electric-field-gradient tensor. Relative to the x,y,z frame, the a,b,c frame is expressed in terms of the Euler angles $(\phi_1, \theta_1, \psi_1)$. A transformation of $R_{2,0}^z$ to these frames can be expressed as

$$R_{2,0}^z = \sum_{m,m_1 = -2}^{2} D_{m,0}(\theta_0, \phi_0) D_{m,m_1}^*(\phi_1, \theta_1, \psi_1) R_{2,m_1}^p ,$$

(2)

where $R_{2,0}^p = (\frac{3}{2})^{1/2} V_{zz} = (\frac{3}{2})^{1/2} eq$, $R_{2\pm 2}^p = \frac{1}{2}(V_{xx} - V_{yy}) = \frac{1}{2} eq\eta$, and $R_{2\pm 1}^p = 0$ since we have chosen x,y,z to be a principal axis frame. The $D_{m,m'}$ are the Wigner rotation matrices of order two.[10]

In the cholesteric model we must define a pitch axis which we choose to be the b axis of our sample frame. The helicity of the cholesteric requires that the z axis be distributed uniformly about b whereby $\phi_1 = 0$. We sacrifice no generality if we confine H to be in the b,c plane whereby $\phi_0 = 90°$. The pitch axis is a symmetry axis for the cholesteric phase and as such we expect this symmetry to reflect itself in the time-averaged electric-field-gradient tensor and thereby be also a principal axis of this tensor. We do not know prior to experiment whether this is the x or y axis defined such that $|V_{xx}| < |V_{yy}| < |V_{zz}|$. Under these constraints the spectral frequencies become

$$\omega^{\pm} = \frac{v^{\pm}}{3/16 v_Q} = f + g \cos(2\theta_1) .$$

(3)

In the absence of diffusion effects

$$f = (3\cos^2\theta_0 - 2)[1 + \eta \cos(2\psi)] ,$$

$$g = \cos^2\theta_0 [3 - \eta \cos(2\psi)] ,$$

and $v_Q = eqQ/h$. The above equation is only exact for the case where ψ_1 takes on either one of two values, 0 or 90° depending upon whether the y or x axis is parallel to the pitch axis, respectively. An arbitrary value of ψ_1 adds another term to Eq. (3). The angle $\pi/2 - \theta_0$ describes the orientation of the pitch axis of the helix, b axis, relative to the direction of the magnetic field H.

Effects of self-diffusion

As b is defined as the pitch axis, the angle θ_1 is uniformly distributed in the (a,c) plane. Molecular diffusion

along the direction of the pitch axis will therefore have the effect of making the angle θ_1, and hence the spectral frequencies, time dependent. As described in a previous publication,[5] this effect on the spectral frequencies can be conveniently accounted for by multiplying the $\cos(2\theta_1)$ term of Eq. (3) by the factor $e^{-\rho}$, where $\rho = 16\pi^2 Dt/p^2$ with D being the self-diffusion constant in the direction of the pitch axis, p the pitch length, and t the time. If t_m is the time scale of the NMR measurement (for example, the length of the free induction decay) then one can calculate the average frequency as[5]

$$\bar{\omega}(\theta, t_m) = f + gK \cos(2\theta_1) ,$$

(4)

where $K = (1 - e^{-\rho_m})/\rho_m$ and where $\rho_m = 16\pi^2 Dt_m/p^2$. It is important to note that no matter what model we choose for the effect of self-diffusion only the $\cos(2\theta_1)$ term of Eq. (3) is modulated and the f term is unaffected. We shall show next that it is normally possible to measure only the f term of Eq. (4).

Spectral patterns and positions of the singularity peaks

A uniform distribution of θ_1 in the a,c plane characteristic of the cholesteric phase has the effect of producing a spectral pattern with a distribution of frequencies $F(\omega) = F_0 d\theta_1/d\omega$, where F_0 is constant.[5,11] When applied to Eq. (4),

$$F(\omega) = F_0 [2gK \sin(2\theta_1)]^{-1}$$

which is discontinuous at the angles $\theta = 0°$ and 90°. This has the effect of producing a spectral pattern with two sets of edge singularities symmetrically displaced about the center of the pattern. One set of singularities are at the frequencies $\pm(f + Kg)$ corresponding to the angle $\theta = 0°$ with a splitting $\bar{\omega}_1 = 2(f + Kg)$. The other set of edge singularities are at the frequencies $\pm(Kg - f)$ corresponding to $\theta = 90°$ with a splitting of $\bar{\omega}_2 = 2(Kg - f)$.

Normally the values of D and η are such that when $\theta_0 = 0°$ (pitch axis perpendicular to H) then $Kg > f$ and $\bar{\omega}_1$ corresponds to the splitting of the outer set of singularities and $\bar{\omega}_2$ to the inner set.[5] As we have noted in previous papers[1,5] one can eliminate the effect of diffusion by measuring the difference $\bar{\omega}_1 - \bar{\omega}_2 = 4f$. Following our previous work we define

$$\Delta = 2(\bar{v}_1 - \bar{v}_2) = \frac{3}{8} v_Q (\bar{\omega}_1 - \bar{\omega}_2) .$$

For the case where the pitch axis is perpendicular to $\vec{H}(\theta_0 = 0)$ we have

$$\Delta = \frac{3}{2} v_Q [1 + \eta \cos(2\psi_1)] .$$

(5)

This equation is the central result upon which we base the interpretation of our data on the cholesteric phase. As mentioned above the quantity Δ is independent of diffusion effects. If we can assume that $\theta_0 = 0$ at all temperatures in the cholesteric phase (this assumption to be examined later) then Eq. (5) will give us a dependable measure of $v_Q [1 + \eta \cos(2\psi_1)]$.

A more detailed study of the spectral patterns requires that we calculate the free induction decay $G(t)$ whereby[5]
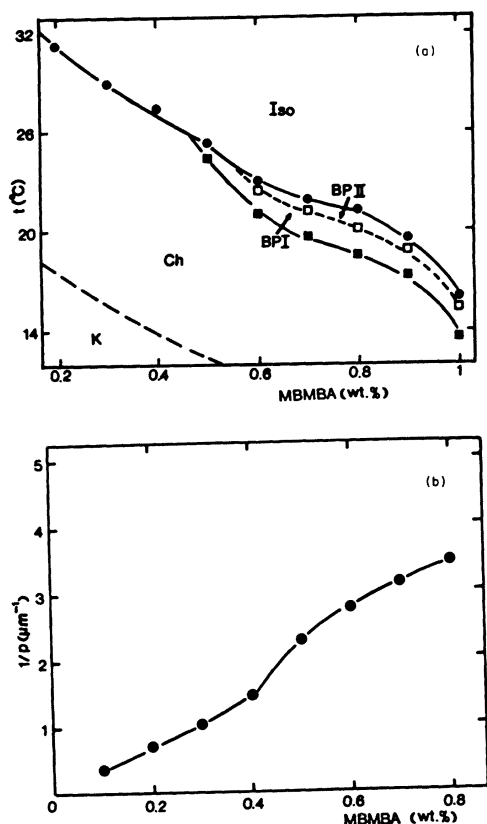
FIG. 1. (a) Phase diagram of mixtures of MBMBA in MBBA obtained from textures under a polarizing microscope observed by a slow cooling process from the isotropic phase. (b) Chirality p^{-1} for mixtures of MBMBA in MBBA obtained by the Cano optical method.
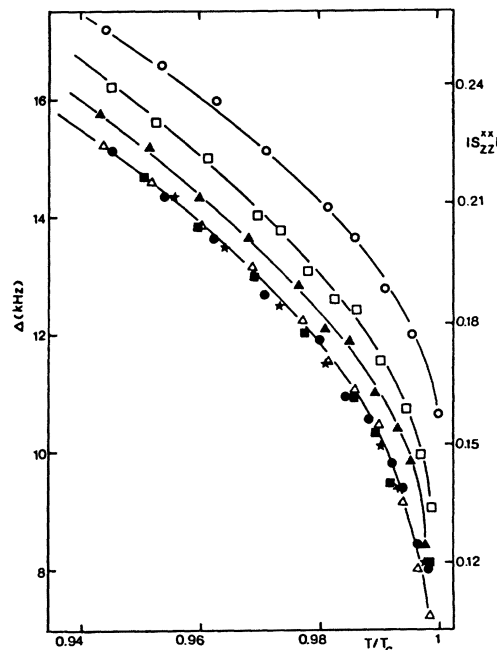

FIG. 2. A plot of the experimentally measured parameter $\Delta = 2(\bar{v}_1 - \bar{v}_2)$ vs reduced temperature T/T_c, where T_c is the temperature of the cholesteric-isotropic or cholesteric-phase transition, whichever occurs. The parameter Δ can also be interpreted in terms of the order S_{ZZ}^{xx} of the molecular axis Z relative to the pitch x axis. The symbols are as follows: $\bigcirc$, nematic, $p = \infty$; $\square$, $p = 1.4 \, \mu$m; $\blacktriangle$, $p = 0.95 \, \mu$m; $\triangle$, $p = 0.68 \, \mu$m; $\bullet$, $p = 0.43 \, \mu$m; $\blacksquare$, $p = 0.36 \, \mu$m; $*$, $p = 0.32 \, \mu$m.

$$G(t) = G_0 \int_0^{\pi/2} [\cos\Omega(\theta_1,\tau)\theta_1] R(\theta_1,\tau) d\theta_1 , \qquad (6)$$

where $R(\theta_0,\tau) = \exp[-t^2\sigma^2(\theta)/2]$ is a line broadening function with

$$\sigma(\theta_0) = W' + W''[P_2(\cos\theta_0) - 1] ,$$

where W' and W'' are fitting parameters. A calculation of $G(t)$ and its Fourier transform has demonstrated that experimental spectral patterns from materials which align with their pitch axis perpendicular to the direction of the magnetic field, $\pi/2 - \theta_0 = \pi/2$, can be nicely fit and that Eq. (5) and, though remarkably simple, can be applied to study motional averaging.[5] In the use of Eq. (5) we must only guard against the possibility that pitch axis always remains perpendicular to $\vec{H}$. The modification of Eq. (5) in which this does not happen is discussed later.

III. MATERIALS

The materials used in this study were the compounds 4-methoxybenzylidene-4'-butylaniline (MBBA) where one compound was selectively deuterated in the α position of the butyl chain (MBBA-α-d_2) and another deuterated on one aromatic ring (MBBA-2',3',5',6'-d_4). To each of these materials was added the chiral compound 4-meth-

oxybenzylidene-4'-[(+)-2-methylbutyl]aniline (MBMBA) (Ref. 12) in various quantities to obtain samples of different pitch length. These compounds are chemically very similar such that homogeneous mixtures for all possible concentrations and a wide range of pitch lengths could be obtained. Furthermore, with these materials we could obtain the blue phases at temperatures near room temperature, thereby avoiding high-temperature gradients in the probe.

Microscope studies were performed on the Ortholux-Leitz polarizing microscope. The samples were sandwiched between glass plates, generally with untreated surfaces. The phase diagram obtained for the MBBA-MBMBA system after cooling from the isotropic phase (in order to match the experimental conditions in the DMR experiment) is shown in Fig. 1(a). The phases were easily identified by their characteristic textures,[13] and their transition temperatures were recorded through several cycles of heating and cooling. Transition temperatures were reproducible even after long periods of time. A strong supercooling effect was observed in the cholesteric phase and no crystallization was seen until below $-10\,^\circ$C.

The blue phase was identified by the distinctive platelet texture[14] occurring in a narrow range between the cholesteric and the isotropic phases. This texture was clearly visible under the transmission mode. In this phase diagram presented in Fig. 1(a), the blue phase appears for

a pitch length ≤ 4500 Å, confirming that there is an upper limit to the pitch of a cholesteric compound exhibiting the blue phase.[15] In certain mixtures the first texture that appears upon cooling from the isotropic phase is a faint green "fog" which persists over a temperature range of less than 0.1 °C before being replaced by platelets. This green fog is very similar to the blue or gray fog observed by Marcus.[16] Upon further cooling bright blue and green platelets were observed to nucleate and grow until they impinged on each other. This was identified as blue phase II (BP II). Further cooling yielded small red patches appearing in the blue-green background. This phase was identified as blue phase I (BP I) because in most mixtures the phase transition BP II→BP I does not occur by the nucleation mechanism just described but starts at a certain temperature at one side of the field view and sweeps over the sample in a frontal movement. Changing the temperature very slowly so that the front moves slowly, the shape of the original grains (in the high-temperature phase, BP II) will be retained in the new phase (BP I). Otherwise the grain structure of the new phase has no relation to the old one. Cooling slowly from the isotropic, the temperature range of the blue phase is enlarged because of a supercooling effect.

When heating the cholesteric phase toward the isotropic, the blue phase occurs in a smaller temperature range and the identification of the two blue phases is more difficult and unclear. The focal conic cholesteric texture decomposes in batonnets which eventually disappear, condensing into platelets.

Figure 1(b) shows the pitch length for the different mixtures of MBMBA in MBBA measured by the Cano lines method.[17,18] The variation of the inverse pitch versus concentration is approximately linear over the entire range of compositions. The variation of the pitch length with temperature for a specific composition was observed to be negligible, changing by less than 5% over the entire cholesteric phase.

IV. DATA AND MOLECULAR ORDERING IN THE CHOLESTERIC PHASE

In the magnetic field of 47 kG the MBBA materials with MBMBA concentrations $\underset{\sim}{<}4$ wt. % ($p \underset{\sim}{\geq} 6.5$ μm) are untwisted by the field. In this case, both MBBA-α-d_2 and MBBA-$2',3',5',6',$-d_4 gave a two-line spectrum characteristic of an aligned nematic. All four deuterated sites of MBBA-$2',3',5',6'$-d_4 are nearly equivalent and produce a two-line spectrum like that reported earlier for the material 40.8-d_4 4-n-butyloxybenzylidene-4'-n-octyl-d_4-aniline similarly deuterated.[1] The splitting between the lines gives a value for the quantity $\frac{3}{2}\nu_Q$. This splitting for MBBA-$2',3',5',6'$-d_4 as a function of reduced temperature is shown in Fig. 2 (upper curve with open circles). Such a plot is identical for all concentrations of MBMBA less than the critical concentration ($\sim$4 wt. %) where the materials are untwisted by the magnetic field.

In a small concentration range ($\sim$4—6 wt. %) just above critical concentration of MBMBA the material is twisted but the cholesteric helix is distorted by the magnetic field at some temperatures. This distortion is clearly

visible on the ^{2}H-NMR spectral pattern as reported earlier.[19] In this paper we use MBMBA concentrations above 20 wt. % which is well above that where distortions are evident on the spectral patterns.

The spectral patterns of MBBA-α-d_2 and MBBA-$2',3',5',6'$-d_4 in the cholesteric phase for MBMBA concentrations above 20 wt. % are typical of those of a uniformly twisted material in which the pitch axis is aligned in a direction perpendicular to the direction of the magnetic field [$\theta_0=0°$ in Eqs. (3)—(5)]. The value Δ which is twice the value of the difference in the splitting between the outer and inner edge singularities is plotted in Fig. 2 as a function of reduced temperature for several concentrations of MBMBA. In the reduced temperature plot in Fig. 2 we have taken the transition temperature T_c to be that of the cholesteric-isotropic phase transition or the cholesteric—blue-phase transition whichever occurs. It is noted in Fig. 2, that at MBMBA concentrations in which T_c is the cholesteric—blue-phase transition, the reduced temperature plot of Δ becomes independent of concentration. This result is central to this study and will be discussed in detail later in the paper.

In our analysis of Δ we will start by assuming that the pitch axis is aligned exactly perpendicular to the direction of the magnetic field whereby $\cos^2\theta_0=1$ in the functions f and g of Eq. (3) and we apply Eq. (5). We shall also start by attributing the decrease in the value of Δ with decreasing pitch length to an increase in the value of η. If we use the value of $\frac{3}{2}\nu_Q$ obtained from the untwisted nematic, then using the measured values of Δ at the same reduced temperature yields values of $\eta \cos2\psi$ which are negative in sign. Since the pitch axis is an axis of symmetry for the cholesteric phase we might expect that it is also a principal axis of the electric-field-gradient tensor. Since η is positive under the convention of $|V_{xx}| < |V_{yy}|$ we are forced to choose $\psi=90°$ whereby the pitch axis is also the x axes of the tensor. As mentioned in the Introduction, this experimental observation is in agreement with that predicted by simple theoretical considerations.[7]

We now note that the measured quantity Δ can be expressed as

$$\Delta = \tfrac{3}{2}\nu_Q(1-\eta) = \frac{3eQ}{h}|V_{xx}|. \tag{7}$$

The component V_{xx} is the only component not affected by self-diffusion of the molecules. At $\theta_0=90°$ (pitch axis parallel to $\vec{H}$) one can only measure the component $|V_{xx}|$ as the spectrum consists of only two lines.[5] The quantity Δ is also a measure of the order of the long molecular axis relative to the x or pitch axis direction. This is so because V_{xx} results from a time average due to molecular motion of the z' component $V^s_{z'z'}$ associated with the C—D bond on the aromatic ring in a "frozen" molecule measured by measuring $\nu^s_Q=eQV_{z'z'}/h$ in the solid state. Under a suitable transformation then $V_{xx}=V^s_{z'z'}\langle(\tfrac{3}{2}\cos^2\sigma_x-\tfrac{1}{2})\rangle$, where σ_x is the angle between pitch axis (x axis) and the C—D bond direction (z axis) which is modulated by the orientational motion of the molecules. In the case of MBBA-$2',3',5',6'$-d_4 there is an additional averaging which results from a nearly
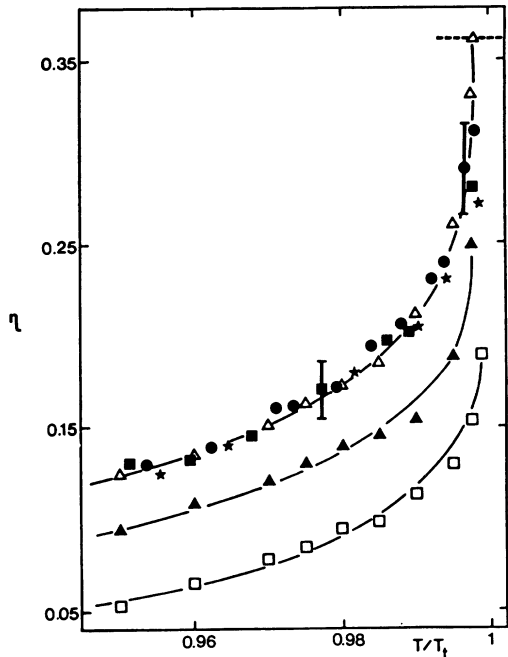
FIG. 3. Biaxiality vs reduced temperature, where the biaxiality is expressed in terms of the monotonically induced asymmetry parameter η of the deuterium spin quadrupole interaction and where T_c is the cholesteric-isotropic or cholesteric—blue-phase transition temperature, whichever occurs. The symbols are identical to those of Fig. 2.

FIG. 4. Reduced temperature plot of the asymmetry parameter for binary mixtures of MBMBA in MBBA: ■ = MBMBA + MBBA-α-d_2, $p = 1.8$ μm; □ = MBMBA + MBBA-2',3',5',6'-d_4, $p = 1.8$ μm; ● = MBMBA + MBBA-α-d_2, $p = 1.4$ μm; ○ = MBMBA + MBBA-2',3',5', 6'-d_4, $p = 1.4$ μm.

unhindered rotational diffusion of the aromatic ring around the para-axis as well as a nearly free rotational diffusion of the molecule about its long axis.[20,21] It is a good approximation to assume that the molecule, on the average, is cylindrically symmetric and to take the long molecular axis, Z (most ordered axis of the molecule), to be nearly parallel to the para-axis. Under these simplifying approximations[10]

$$\Delta \simeq 3 v_Q^s (\tfrac{3}{2} \cos^2\beta - \tfrac{1}{2}) S_{ZZ}^{xx} , \tag{8}$$

where $S_{ZZ}^{xx} = \langle (\tfrac{3}{2} \cos^2\theta_x - \tfrac{1}{2}) \rangle$ is the orientational order of the log molecular Z axis relative to the pitch x axis; v_Q^s is the quadrupole coupling constant of the C—D bond (~ 180 kHZ) as measured in a solid where there is negligible motional averaging. The angle β is the angle between the C—D bond direction and the para-axis which in the case of MBBA-2',3',5',6'-d_4 is $\sim 60°$.

Similarly, in the case of the untwisted nematic, the splitting between the spectral lines is $\tfrac{3}{2} v_Q = e Q V_{zz}/h$. Since the nematic phase is uniaxial, $V_{xx} = V_{yy} = -V_{zz}/2$ and

$$\tfrac{3}{2} v_Q = \frac{3eQ}{h} |V_{xx}| = 3 v_Q^s (\tfrac{3}{2} \cos^2\beta - \tfrac{1}{2}) S_{ZZ}^{xx} .$$

Taking β to be $60°$ for MBBA-2',3',5',6'-d_4, we calculate the values of S_{ZZ}^{xx} for the twisted and untwisted cases which are shown in Fig. 2. From this we conclude that the order of the molecules relative to the pitch axis is affected by the pitch length until one has a blue-phase tran-
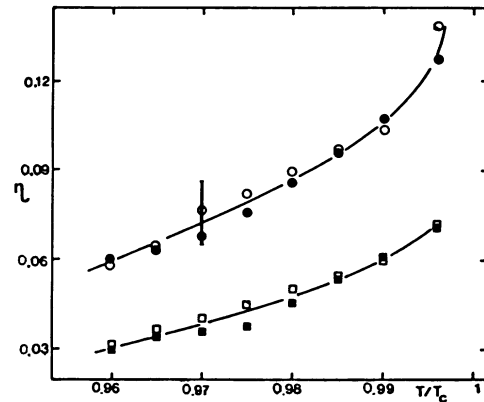
sition at which point it becomes a universal function of reduced temperature.

We now apply another point of view to these data. We assume that $|V_{zz}|$ (or v_Q) and consequently the order of the long molecular Z axis relative to the director (z axis), S_{ZZ}^{zz}, is unaffected by the pitch length. This appears to be a likely assumption as optical measurements report no dependence of S_{ZZ}^{zz} on the pitch length.[4,22] It is recalled here that we cannot measure V_{zz} directly as it is affected by self-diffusion of the molecule. Using the value of $\tfrac{3}{2} v_Q$ obtained from the untwisted nematic on a reduced temperature plot we can then determine the value of η from Eq. (5), the results of which are plotted in Fig. 3. Using η as our measure of biaxiality we see that the biaxiality in the cholesteric also appears to predict the onset of the blue phase in that its value on a reduced temperature plot becomes universal.

V. MECHANISMS FOR BIAXIAL ORDERING

In Fig. 4 we show the values of η measured for both MBBA-α-d_2 and MBBA-2',3',5',6'-d_4 at two different pitch lengths on a reduced temperature plot. The interesting feature of this plot is that it shows that the two different deuterated sites yield the same value for η at a given pitch length and reduced temperature. We can use this information to distiguish between two possible mechanisms for biaxial ordering: (1) anisotropic fluctuations of the molecular long axis and (2) ordering of the short molecular axis relative to the pitch axis[23] (sometimes referred to as a "birotational freeze out").

We have reported earlier that a motionally induced asymmetry parameter can be expressed in terms of two order parameters[6,24]

$$\eta^i = \frac{3}{2} \frac{v_Q^s}{v_Q^i} (s_{0,0}^i S_{2,0} + s_{0,2}^i S_{2,2}) , \tag{9}$$

where η^i and v_Q^i are values measured for the i deuterated

TABLE I. Value of the activation energies for different pitch lengths for the system MBBA + MBMBA as well as the values of Dt_m/p and at the reduced temperature of $T/T_c = 0.99$. A value of 10^{-3} sec was used for t_m.

wt. % of MBMBA in MBBA	$P(\mu m)$	ΔE(kcal/mole)	Dt_m/p^2 at $T/T_c = 0.99$	D (cm^2 sec^{-1}) at $T/T_c = 0.99$
20	1.4	6.1 ±0.3	0.0048	9.4×10^{-8}
30	0.95	6.45	0.0061	5.5×10^{-8}
40	0.68	7.1	0.0079	3.6×10^{-8}
50	0.43	7.5	0.0098	1.8×10^{-8}
60	0.36	8.1	0.0108	1.4×10^{-8}
70	0.32	8.35	0.0106	1.1×10^{-8}

site, $v_Q^s \approx 180$ kHz. The parameters

$$S_{2,0} = \langle \sin^2\theta \cos(2\phi) \rangle$$

and

$$S_{2,2} = \langle [\tfrac{1}{2}(1+\cos^2\theta)\cos(2\phi)\cos(2\psi)$$
$$-\cos\theta \sin(2\phi)\sin(2\psi)] \rangle ,$$

where the Eular angles (θ,ϕ,ψ) express the orientation of the molecular X,Y,Z frame in the principal axis x,y,z frame of the time-averaged electric field gradient. In the molecular frame Z represents the most ordered axis (long axis) and x the least ordered short axis. The parameter $S_{2,0}$ represents anisotropic fluctuations of the molecular long axis. The parameter $S_{2,2}$ represents the ordering of the short molecular axis. This identification is most easily understood in the case where the long axis is well ordered where $S_{2,2} \approx \langle \cos[2(\phi+\psi)] \rangle$. If the short axis were not ordered $S_{2,2}=0$. The conformation parameters

$$s_{0,0}^i = (\tfrac{3}{2}\cos^2\beta_i - \tfrac{1}{2})$$

and $s_{0,2}^i = \sin^2\beta_i \cos(2\alpha_i)$, where the polar angles α_i and β_i give the orientation of the C—D bond in the molecular X,Y,Z frame.[6,24]

We now point out a useful result that if $S_{2,2} \simeq 0$ then the value of η is independent of the deuterated site.[24] This follows from Eq. (9) in that $v_Q^i \simeq s_{0,0}^i S_{0,0}$, where

$$S_{0,0} = \langle \tfrac{3}{2}\cos^2\theta - \tfrac{1}{2} \rangle = S_{ZZ}^z$$

and is the order of the molecular long axis relative to the director (z principal axis).[24] If $S_{2,2} \simeq 0$ then

$$\eta = \tfrac{3}{2}(S_{2,0}/S_{0,0}) \tag{10}$$

and, hence, is independent of the position of the ith site.

This is what is observed in Fig. 4 for two different pitch lengths and hence suggests that anisotropic fluctuations of the molecular long axis relative to the x,y,z frame. For a more detailed discussion of this feature the reader is referred to Ref. 7.

VI. SELF-DIFFUSION MEASUREMENTS

If instead of measuring the difference, we measure the sum of the splittings of the outer and inner singularities we obtain

$$2(\bar{v}_1 + \bar{v}_2) = \tfrac{3}{8}v_Q(\bar{\omega}_1 + \bar{\omega}_2) = \tfrac{3}{2}v_Q Kg .$$

Such a measurement allows us to determine a value for K and hence a value for the self-diffusion constant D along the direction of the pitch axis. Using this expression we obtained the values of K by assuming, as earlier, that the pitch axis is very nearly perpendicular to the direction of the magnetic field. Also as in the previous sections, we obtained the value of $\tfrac{3}{2}v_Q$ from the splittings of the untwisted nematic at a common reduced temperature and used the values of η as presented in Fig. 3.

At temperatures which are not in the vicinity of the iso-tropic or blue-phase transition plots of the measured values of the $\ln(Dt_m/p^2)$ vs T^{-1} (K^{-1}) were found to be linear and an activation energy could be obtained.[25] In Table I we show our measured values of the activation energies as well as the values of the diffusion constant at a reduced temperature of $T/T_c = 0.99$ and taking t_m to be the length of the free induction decay and equal to 10^{-3} sec. The measured values of the diffusion constant are in general agreement with those measured by other workers in cholesteric systems by other techniques. The decreasing value of D with decreasing pitch length is also in agreement with viscosity measurements[26] in cholesteric systems and the recent measurement of Hakemi et al.[27]

VII. BLUE-PHASE SPECTRAL PATTERN

In Fig. 5(a) and 5(b) we show two spectral patterns recorded from a sample of MBBA-2',3',5',6'-d_4 twisted by the addition of 60-wt.% MBMBA at the same temperature of 21.3 °C but at different times. The blue-phase [Fig. 5(a)] spectrum was obtained after cooling 2.0 °C below the isotropic phase. At this temperature the blue phase is supercooled and will eventually transform into the cholesteric phase [see Fig. 5(b)]. This sample was particularly well suited to obtain the blue-phase spectrum as this phase occurred at room temperature where the temperature gradients across the sample were minimal.

We found that it was possible to obtain a reasonable good fit to this blue-phase spectra pattern by assuming the same model as we used for the cholesteric phase but with a random orientation of the pitch axis in the magnetic field. Under this model the angle θ_0 in the functions f and g of Eqs. (3) and (4) is spherically distributed in addi-
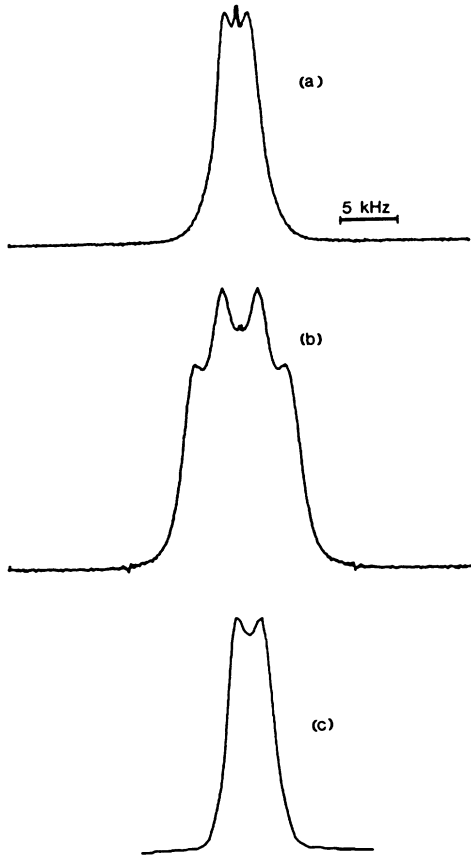
FIG. 5. (a) Spectral pattern from the binary mixture of MBMBA, 60 wt. % + MBBA-2',3',5',6'-d_4 recorded in the supercooled blue phase at 21.3 °C. (b) Spectral pattern recorded at the same temperature but after sufficient time had elapsed for the sample to transform from the supercooled blue phase into the cholesteric phase. (c) Calculated blue-phase spectrum based on a model of randomly oriented pitch axes.

tion to there being a planar distribution of the angle θ_1 like in the cholesteric phase in order to account for the helical structure. The calculation of the blue-phase spectrum is considerably simplified if we set $\eta = 0$. This simplification is justified in that the shape of the spectral pattern is most strongly affected by the value of D and ν_Q. Also, since the blue-phase spectrum is nearly void of any distinguishable features, the addition of a third fitting parameter η appeared to be of little significance.

With these conditions the free induction decay is calculated following Eq. (6) but with an additional average over the angles θ_0:

$$G(t) = \int_0^{2\pi} \int_0^\pi [\cos\Omega(\theta_1,\theta_0 t_m)t]R(\theta_1,t_m)$$

$$\times \sin\theta_0 d\theta_0 d\theta_1 \ . \tag{11}$$

A Fourier transform of the equation above yields the spectral pattern shown in Fig. 5(c) with the fitting parameters D and ν_Q having the values 5×10^{-8} cm^2/sec and 8.0 kHz, respectively. The fitted value $\nu_Q = 8.0$ kHz corresponds to that of the untwisted nematic (see Fig. 2) at the reduced temperature of 0.995, very near the cholesteric

isotropic phase transition. The value of $D = 5 \times 10^{-8}$ cm^2/sec is near that ($D = 2 \times 10^{-8}$ cm^2/sec) measured for the cholesteric phase at the same value of the pitch at a reduced temperature of 0.995. It appears, therefore, that the motional averaging in the blue phase is very similar to that of the cholesteric phase with the only added feature that the pitch axis is randomly distributed in the magnetic field. We note here that it is highly unlikely that we have a single-crystal blue phase, and the random value of θ probably indicates a polycrystalline sample.

VIII. DISCUSSION

An interesting aspect of this work is the behavior of the measured parameter Δ on a reduced temperature plot. As noted earlier Δ can be interpreted as the order of the molecular long axis relative to the pitch axis. Figure 2 clearly shows that Δ becomes independent of the pitch length on a reduced temperature plot and hence a universal function of reduced temperature when T_c is the cholesteric—blue-phase transition but is dependent on the pitch length when T_c is the cholesteric-isotropic phase transition. As seen from Eq. (5) the parameter Δ measures the product $\nu_Q(1-\eta)$ where we assume in Fig. 3 that (1) ν_Q and hence $|V_{zz}|$ is not affected by the pitch length, and (2) that we are justified in obtaining the values of ν_Q from the untwisted samples. Here we can turn to optical studies of the cholesterol derivatives which do not report any changes in the degree of order S_{ZZ}^{zz} in materials where the pitch length is varied.[21,22] Since ν_Q depends directly on S_{ZZ}^{zz} this would imply that our assumption is valid. Based upon the above arguments we have therefore plotted Fig. 3 which attributes our observed variation in Δ strictly to the asymmetry parameter η and hence the biaxiality. It is supporting evidence in this regard that we obtain measured values of η independent of the deuterated site and hence independent of the value ν_Q. As described in the text, this result is that expected where the biaxiality is due to anisotropic fluctuation in the molecular long axis. Also the mechanism of anisotropic fluctuations have been justified on theoretical grounds by Lee and Lin-Liu.[7]

It has been pointed out to us by Shtrikman[28] that the Landau theory predicts that the biaxiality when normalized to its value at the cholesteric-isotropic transition (η/η_{C-I}) should be a universal function of $(T - T_c)$. Our data appear to follow this prediction although we have not been able to obtain an accurate value of η at T_c as η strongly diverges near T_c and the singularities of the spectral patterns from which we obtain values of η become poorly resolved. Figure 3 clearly indicates, however, two interesting features: (i) the blue phase appears when $\eta = \eta_{C-BP} = 0.34$, and (ii) η is a universal function of reduced temperature T/T_c when T_c is taken as the cholesteric—blue-phase transition temperature. A plot of η/η_{C-BP} is therefore also universal. In the material studied here the biaxiality in the cholesteric can be used to predict the onset of the blue phase. This is a new concept in cholesteric behavior and a feature which should be examined in other materials.

We now discuss an assumption made in the interpretation of our spectral patterns that the pitch axis remain

perpendicular to the direction of $\vec{H}$ [i.e., $\theta_0 = 0$ in Eq. (3)]. If we allow for a variation in θ_0 then Eq. (5) becomes

$$\Delta = \tfrac{3}{2}\nu_Q(3\cos^2\theta_0 - 2)[1 + \eta\cos(2\psi)] . \qquad (12)$$

We see from this equation that a measurement of Δ does not distinguish between a variation in θ_0 and a variation in $\nu_Q[1 + \eta\cos(2\psi)]$. We now discuss the possibility that variations in Δ could be caused by changes in the angle θ_0. First of all, one might expect that there be some distribution in θ_0 about $\theta_0 = 0$. In the case of cholesterol materials which are not so strongly aligned by the magnetic field, a distribution about $\theta_0 = 90°$ reported by Luz et al.[29] was clearly visible on the spectra. On the other hand, a distribution about $\theta_0 = 0$ would not alter the position of the singularities and affect our measurement of Δ. It is clearly illustrated in the data on the cholesterol material reported by Luz et al.[29] that a large distribution about $\theta_0 = 90°$ preserves the edge singularities. A second possibility, that could affect our measurement, though it does not appear likely, is that there would be a change in the diamagnetic tensor such that θ_0 would shift uniformly. In order to account for the data in Fig. 2, a variation of θ_0 from $0°-20°$ would be required. To the knowledge of these authors no such feature has been reported in the literature. It therefore does not appear likely that the ob-

served variations in Δ were caused by the function $(3\cos^2\theta_0 - 1)$ in Eq. (5) but instead by the biaxiality η as we have assumed.

The measured values of the diffusion constant D in Table I are consistent with those reported by Hakemi[27] using other experimental methods. There appears to be reasonable agreement both in the magnitude and in the pitch dependence. The decrease in D with decreasing pitch length is also consistent with the viscosities of cholesteric crystals.[26]

Finally, we discuss the spectral pattern observed in the blue phase shown in Fig. 5. Since we are able to fit this pattern with a random distribution of θ_0 indicates that we have a polycrystalline blue-phase sample as might be expected.

ACKNOWLEDGMENTS

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[1]Z. Yaniv, N. A. P. Vaz, G. Chidichimo, and J. W. Doane, Phys. Rev. Lett. 47, 46 (1981).

[2]D. W. Berreman and T. J. Scheffer, Phys. Rev. A 5, 1397 (1972).

[3]H. Grebel, R. M. Hornreich, and S. Shtrikman, Phys. Rev. A (in press).

[4]R. M. Hornreich and S. Shtrikman, in Liquid Crystals of One- and Two-Dimensional Order, edited by W. Helfrich and G. Heppke (Springer, Berlin, 1980), p. 196.

[5]G. Chidichimo, Z. Yaniv, N. A. P. Vaz, and J. W. Doane, Phys. Rev. A 25, 1077 (1982).

[6]Z. Yaniv, M. E. Neubert, and J. W. Doane, in Liquid Crystals and Ordered Fluids, edited by A. C. Griffin and J. F. Johnson (Plenum, New York, in press), Vol. 4.

[7]M. A. Lee and Y. R. Lin-Liu, Bull. Am. Phys. Soc. 28, 372 (1983).

[8]M. H. Cohen and F. Reif, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 5, pp. 321–448.

[9]We consider ν_0 as expressed here to be the Zeeman frequency where the appropriate shield interaction has been included.

[10]J. W. Doane, in Magnetic Resonance of Phase Transitions, edited by F. J. Owens, C. P. Poole, and H. A. Farach (Academic, New York, 1979), pp. 171–246.

[11]An analogous distribution is that of nematics in spinning samples. See J Pirs, P. Ukleja, and J. W. Doane, Solid State Commun. 19, 877 (1976).

[12]D. Dolphin, Z. Muljiani, J. Cheng, and R. B. Meyer, J. Chem. Phys. 58, 413 (1973).

[13]D. Demus and Z. Richter, Textures of Liquid Crystals (Chemie, Berlin, 1978).

[14]D. L. Johnson, J. H. Flack, and P. P. Crooker, Phys. Rev. Lett. 45, 641 (1980).

[15]H. Stegemeyer and K. Bergmann, Springer Ser. Chem. Phys, 11, 161 (1980).

[16]M. Marcus, J. Phys. (Paris) 42, 61 (1981).

[17]R. Cano, Bull. Soc. Franc Mineral Crist. 91, 20 (1968).

[18]G. Heppke and F. Oestreicher, Z. Naturforsch. 32a, 899 (1977).

[19]N. A. P. Vaz, G. Chidichimo, Z. Yaniv, and J. W. Doane, Phys. Rev. A 26, 637 (1982).

[20]J. C. Rowell, W. C. Phillips, L. R. Melby, and M. J. Panar, J. Chem. Phys. 43, 3442 (1965).

[21]N. Chao, K. C. Chu, and Y. R. Shen, Mol. Cryst. Liq. Cryst. 67, 261 (1981).

[22]P. Adamski, L. A. Dylik-Gromiec, and M. Wojcaehowski, Mol. Cryst. Liq. Cryst. 75, 33 (1981).

[23]P. G. de Gennes, The Phyiscs of Liquid Crystals (Oxford University Press, London, 1974).

[24]See page 162 and Appendix A of D. J. Photinos and J. W. Doane, Mol. Cryst. Liq. Cryst. 76, 159 (1981).

[25]Z. Yaniv, G. Chidichimo, N. Vaz, and J. W. Doane, Phys. Lett. 86A, 297 (1981).

[26]W. Helfrich, Phys. Rev. Lett. 23, 372 (1969).

[27]H. Hakemi, J. Chem. Phys. (in press); H. Hakemi and M. M. Labes, ibid. 63, 3708 (1975); H. Hakemi, J. Appl. Phys. (in press).

[28]S. Shtrikman (private communication).

[29]Z. Luz, R. Poupko, and E. T. Samulski, J. Chem. Phys. 74, 5825 (1980).