

NMR measurement of biaxial molecular order in the smectic C phase

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Deuterium magnetic-resonance studies of spectral patterns from spinning samples are made to measure the relative contribution of various orientational order mechanisms to the biaxiality of the hydrocarbon chain in the smectic C phase. The detailed theory of motional averaging as applied to the spinning techniques is reported for the first time. Orientational order parameters measurable by this technique representing various aspects of molecular orientational order are discussed. The technique is applied to a particular compound *n*-heptyloxazoxybenzene, where it is possible to distinguish between those order parameters which result from rotational biasing about the long molecular axis and those order parameters which do not. The temperature dependence of these order parameters in this fixed-tilt-angle system is then determined.

INTRODUCTION

A particular liquid-crystal phase that is not well understood on the molecular level is that of the smectic C, S_C . This phase is characterized as being optically biaxial with the elongated molecules being tilted in the smectic layers. It has not been clear which of these two physical features, biaxiality or tilt, is the principal feature of the phase. The tilt could result from a biaxial orientational motion of the molecules or visa versa. No less than ten different theoretical models¹⁻¹⁰ have been proposed for this state of matter. Each of these models differ in the relative importance of the various kinds of possible intermolecular interactions and in the relative significance of the characteristic tilt and biaxiality.

The observed biaxiality in the S_C phase is believed to have two possible mechanisms: (a) anisotropic fluctuations in the orientation of the long axis; (b) biased rotation about the long axis. Both mechanisms could in principle be induced by the tilt structure itself; mechanism (a) because fluctuations of the long axis about the C_2 axis of the phase dilate the layer spacing whereas fluctuations about an orthogonal axis do not; mechanism (b) because rotational diffusion about the long axis of a molecule with noncylindrical symmetry could be biased towards one particular orientation in the tilted environment.

For models which place biaxiality as the primary feature of the phase it is essential that mechanism (b) be present in that intermolecular interactions transverse to the molecular long axis induce the tilt in those models.^{1,2,8} Biased rotation or "partial rotational freeze out" is necessary to prevent complete averaging of the transverse interactions. The observation of biased rotation about the long axis would not guarantee models

based on this mechanism; on the other hand, the absence of the biased motion could rule them out.

Biaxiality in the S_C is readily observed optically through conoscopy¹¹⁻¹³ or the refractometer.^{14, 16} Recent quantitative measurements by these techniques^{14, 15} have not separated the relative contribution of the two mechanisms. In another approach to the problem detailed studies have been made of the kinds of compounds from which the phase is formed.^{1, 5, 16} These compounds tend to be those which contain oxygen or nitrogen atoms at suitable sites in the molecule. Such studies^{5, 16} have favored the importance of dipoles at these sites which are transverse to the molecular long axis implying mechanism (b). In contrast, papers on x rays,^{17, 18} neutron scattering,¹⁹ and dielectric relaxation²⁰ have not been favorable to mechanism (b).

An experimental technique directly sensitive to both biaxiality and the various aspects of molecular orientational order is magnetic resonance on nuclear spins which exhibit the quadrupole interaction. Observations of the motionally averaged spin²¹⁻²⁴ interaction directly yield orientational order parameters associated with both mechanism (a) and (b) above. Seliger *et al.*²¹ have directly observed biaxiality through measurement of the asymmetry parameter of ¹⁴N spin in compounds which exhibit the S_C with a variable tilt angle. Their measured temperature dependence of that quantity was suggestive of mechanism (a) although this might be expected in that the asymmetry parameter is much more sensitive to mechanism (a) than mechanism (b), where rotational diffusion about the long axis is biased toward only one orientation "partial freeze out."²⁶ A further disadvantage of ¹⁴N NMR is that there are seldom more than one nonequivalent ¹⁴N site in the molecule. More than one nonequivalent site is necessary to separate various mechanisms for bi-

axiality. This problem is relieved by deuterium NMR studies. To observe biaxiality with deuterium, however, nonconventional NMR techniques need to be employed.²⁵ We recently reported one such NMR experimental technique on deuterium spins in the S_C phase²³ which was sensitive to parameters of both mechanism (a) and (b). In order to detect the biaxiality, the samples had to be spun about an axis normal to the applied magnetic field. A particular compound was used for this study whereby the contributions of mechanism (a) and mechanism (b) could be separated.

This paper explores that experimental method further. The detailed theory of motional averaging as applied to that technique is presented for the first time and the resulting orientational order parameters measurable by the method fully discussed. The application of the technique to the compound *n*-heptyloxazoxybenzene (HOAB- d_{30}) is carried further by examining the temperature dependence of the order parameters in this compound which has a fixed tilt angle of known value.¹⁸ These measurements allow for more detailed study and lend confidence to this experimental method as a means of further study of biaxiality and to separate various mechanisms. The results of temperature dependence studies are supportive of models in which mechanism (b) is a primary feature of the smectic C phase.

THEORY

The quadrupole Hamiltonian is given by²⁷

$$\mathcal{H}_Q = B_m^{(2)} Q_{-m}^{(2)}, \quad (1)$$

where $Q_{-m}^{(2)}$ is the quadrupole tensor and $B_m^{(2)}$ is the electric field gradient tensor at the nuclear site. Since we observe the quadrupole interaction as a perturbation on the Zeeman interaction we express $Q_{-m}^{(2)}$ in a frame (laboratory frame L) in which the z_L axis is parallel to the direction of the magnetic field, \underline{H} , where

$$\begin{aligned} Q_0^{(2),L} &= \frac{eQ}{I(2I-1)} \frac{1}{2} [3I_{z_L}^2 - I(I+1)], \\ Q_{\pm 1}^{(2),L} &= \frac{eQ}{I(2I-1)} \frac{\sqrt{6}}{4} (I_{z_L} I_{\pm} + I_{\pm} I_{z_L}), \\ Q_{\pm 2}^{(2),L} &= \frac{eQ}{I(2I-1)} \frac{\sqrt{6}}{4} I_{\pm}^2. \end{aligned} \quad (2)$$

The components of $B_{-m}^{(2)}$ in the principal axis frame of the electric field gradient (PAF-EFG) are

$$\begin{aligned} B_0^{(2),P} &= \frac{1}{2} V_{zz} = \frac{1}{2} eq, \\ B_{\pm 1}^{(2),P} &= 0, \\ B_{\pm 2}^{(2),P} &= (1/2\sqrt{6})(V_{xx} - V_{yy}) = (1/2\sqrt{6})/q\eta. \end{aligned} \quad (3)$$

For deuterium in selectively deuterated organic compounds which are in the solid state, the principal z axis is typically along the $C-D$ bond direction on the molecule.

Due to the motion of the PAF-EFG relative to the lab frame in the liquid-crystal phase the Hamiltonian in Eq. (1) is time dependent. The NMR measurement gives the *time average* of the matrix element of the quadrupole Hamiltonian, meaning that the time scale of the NMR measurement is very large compared to any characteristic time of the molecular motion. From Eqs. (2) and (3) we see that Q and B are determined from two different frames. The first step therefore is to express both of them in a common frame. If we choose this frame to be the laboratory frame we must express the components of the electric field gradient in terms of its components in the PAF-EFG. Writing Eq. (1) in the laboratory frame we have that

$$B_{m_1}^{(2),L} = D_{m',m_1}^* (\Phi, \Theta, \Psi) B_{m'}^{(2),P}, \quad (4)$$

where D_{m',m_1} are elements of the rotation matrix²⁸ and Φ, Θ, Ψ are the Euler angles of the PAF-EFG axes in the laboratory frame.

Due to the molecular motion in a liquid crystal these angles are time dependent. In order to describe this time dependence or, more precisely, the time averages of the rotation matrix elements in terms of particular types of molecular motion, it is convenient to introduce two more frames. Instead of transforming directly from the PAF-EFG to the lab or L frame as in Eq. (4), we first transform from the PAF-EFG to a new frame, M , fixed with the molecule. Naturally, since the molecule is not absolutely rigid but various parts of it move relative to one another, the notion of a frame "fixed with the molecule" is a relative one. It means that we divide the molecule into segments which move relative to a frame fixed to one of these segments. The M frame then is one in which we measure the time averaged conformation of the molecule. The orientation of the PAF-EFG in the M frame is given by the angles α, β, γ which are in general time dependent since the chemical bond that gives rise to the electric field gradient does not always belong to the segment fixed to the M frame. The field gradient components in the M frame are related to the principal ones by

$$B_m^{(2)P} = D_{m',m}(\alpha, \beta, \gamma) B_{m'}^{(2)M}. \quad (5)$$

It is to be noted that so far the frame M is *completely arbitrary* apart from the restriction that it is fixed with some part of the molecule.

We now introduce another frame, N , which is likewise *completely arbitrary* except for one restriction: it is fixed in time with the phase

(sample) and therefore with the laboratory (provided the sample is not moving in the lab). Let the orientation of the M frame in the N frame be given by the angles θ , ϕ , ψ . These angles are time dependent due to motion of the molecule as a whole, M frame, relative to the phase. The field-gradient components in the N frame are related to $B_{m'}^{(2)M}$ by the equation

$$B_{m'}^{(2)M} = D_{m', m'}(\phi, \theta, \psi) B_{m'}^{(2)N}. \quad (6)$$

In connecting the N frame to the L frame we note that in the actual experiment the L frame is basically determined by the direction of \vec{H} (z_L axis only). In this case, it is preferable to describe the orientation of the L frame in the N frame rather than the other way around. If ϕ_0 , θ_0 , ψ_0 are taken to be the angles that describe the orientation of the L frame in the N frame, the components B_m^L and B_m^N are connected by

$$B_{m_1}^{(2)L} = D_{m, m_1}(\phi_0, \theta_0, \psi_0) B_{m_1}^{(2)N}. \quad (7)$$

Combining Eqs. (5), (6), and (7) we get

$$B_{m_1}^{(2)L} = D_{m, m_1}(\phi_0, \theta_0, \psi_0) D_{m, m'}^* (\phi, \theta, \psi) \times D_{m', m'}^* (\alpha, \beta, \gamma) B_{m'}^{(2)P}. \quad (8)$$

To first order in perturbation only, the $Q_0^{(2)L}$ component gives a contribution. The significant part of the time average Hamiltonian will be of the form

$$\langle \mathcal{H}_Q \rangle = \frac{eQV_{zz}}{2I(2I-1)} \frac{1}{2} [3I^2 - I(I+1)] D_{m, 0}(\phi_0, \theta_0) \times \langle D_{m, m'}^* (\phi, \theta, \psi) [D_{m', 0}^* (\alpha, \beta, \gamma) + (\eta/\sqrt{6})(D_{m', 2}^* (\alpha, \beta, \gamma) + D_{m', -2}^* (\alpha, \beta, \gamma))] \rangle, \quad (9)$$

where the angular brackets represent a time average. The above expression can often be simplified in that $\eta \approx 0$ at most sites in the molecule. An exception to this can be the aromatic rings where even though η is small it can be a significant quantity in determining the values of some uniaxial order parameters.²⁵ Taking $\eta = 0$ the quantity of interest is

$$G(\phi_0, \theta_0) = R_m D_{m, 0}(\phi_0, \theta_0), \quad (10a)$$

where

$$R_m \equiv \langle D_{m, m'}^* (\phi, \theta, \psi) D_{m', 0}^* (\alpha, \beta, \gamma) \rangle. \quad (10b)$$

We note again that the direction of the L frame and the PAF-EFG are determined whereas the N and M frames are arbitrary. They will be chosen so that the physics of the system is made more clear and the expressions get simplified if additional symmetries exist.

We take the N frame to be the frame of the principal axes of the phase with z_N parallel to the

preferred direction of the long molecular axis. We will limit our consideration to *apolar phases*. By this we mean that there is at least one axis (which we take to x_N) about which π rotations leave Eq. (9) invariant. Consequently for apolar phases Eq. (10) must be invariant under the substitutions $\theta_0 \rightarrow \pi - \theta_0$ and $\phi_0 \rightarrow \pi + \phi_0$. Furthermore, the phase may possess a symmetry of rotation about the z_N axis by $2\pi/l$ ($l=1, 2, \dots$). In this case l gives the number of axes in the x_N, y_N plane that give twofold symmetry rotations. To see the implications of these symmetries on the time averaged quantities, namely, to answer the question: what type of molecular motion on the average would make the phase apolar or symmetric with respect to a $2\pi/l$ rotation we return to Eq. (10).

For the operation $\theta_0 \rightarrow \pi - \theta_0$ and $\phi_0 \rightarrow \pi + \phi_0$ to leave $G(\phi_0, \theta_0)$ invariant we must have

$$R_{-m} = R_m \quad (11)$$

as the condition for apolarity of the phase. Naturally, this equation refers to the particular way that the angles ϕ , θ , ψ (and not α , β , γ) average in time. Equation (11) would apply for the case of a tilted phase such as the S_C phase where x_N is parallel to the C_2 axis for that phase.

Suppose that there were a phase which also has a rotation symmetry about the z_N axis by π . In this case z_N would also be a twofold rotation axis ($l=2$ for $2\pi/l$ rotation about z_N). This means that in addition to Eq. (11) we must have

$$R_m = (-1)^m R_m \quad (12)$$

indicating, in this case, that only the R_m terms with $m=0, \pm 2$ survive. Such a phase would be a biaxial smectic A or biaxial nematic which, to these authors' knowledge, have never been observed in nature.

In the case of rotation about the z_N axis by $2\pi/l$ with $l > 2$ (threefold or higher) we have

$$R_m \neq 0 \quad \text{only for } m=0. \quad (13)$$

In this case the phase is uniaxial in the NMR sense. Such phases would be the normal nematic and smectic- A phases.

Having determined the N frame as the principal axes frame of the phase²⁹ with x_N the axis of polar inversion, we proceed to fully determine the frame M as follows. Defining

$$F_{mm'} = \langle D_{m, m'}^* (\phi, \theta, \psi) \rangle, \quad (14)$$

Eq. (11) gives

$$F_{mm'} = F_{-mm'}. \quad (15)$$

Even though the molecule is rarely ever apolar, we know that physically apolarity of the phase can still be achieved. One way is through end-for-end

flips of the molecule through rotational and translational diffusion. This is, in fact, what happens in many liquid-crystal phases and on a time scale fast compared to the NMR measurement time.³⁰ In this case it is possible to find a frame fixed to the molecule, such that the directions ϕ , θ , ψ and $\phi + \pi$, $\pi - \theta$, $-\psi$ are statistically equivalent. In other words, the molecular long axis, z_M , spends, on the average, as much time oriented in one direction as in the other. The axis of polar inversion for the molecule we take to be x_M . This frame we take to be our M frame. This choice allows us to write

$$\begin{aligned} F_{m,m'} &= \langle D_{m,m'}^*(\phi, \theta, \psi) \rangle = \langle D_{m,m'}^*(\phi + \pi, \pi - \theta, -\psi) \rangle \\ &= \langle D_{m,-m'}^*(\phi, \theta, \psi) \rangle = F_{m,-m'}; \end{aligned} \quad (16)$$

thus for this particular choice of the frame M , we have

$$F_{m,m'} = F_{-m,m'} = F_{-m,-m'} = F_{m,-m'}. \quad (17)$$

For apolar phases where the molecular long axis exchanges end-for-end faster than the time scale of the measurement we have, in general, nine different nonzero $F_{m,m'}$'s.

If the phase is apolar with equal numbers of molecules pointing, on the average, in the z_N and $-z_N$ direction but the end-for-end exchanges are slow on the NMR time scale then Eq. (11) would apply but not Eq. (16).

Returning to Eq. (10b) it has been shown experimentally²⁴ that the motions of M relative to N and of the PAF-EFG relative to M can be treated as statistically independent, in which case

$$R_m \cong \langle D_{m,m'}^*(\phi, \theta, \psi) \rangle \langle D_{m'',0}^*(\alpha, \beta, \gamma) \rangle = F_{m,m''} C_{m'',0}, \quad (18a)$$

where

$$C_{m'',0} \equiv \langle D_{m'',0}^*(\alpha, \beta, \gamma) \rangle. \quad (18b)$$

Returning to Eq. (10a), we have for the S_C phase

$$\begin{aligned} G(\phi_0, \theta_0) &= \frac{1}{16} [D_{m,0}(\phi_0, \theta_0) + D_{-m,0}(\phi_0, \theta_0)] \\ &\quad \times (F_{m,m''} + F_{-m,m''} + F_{m,-m''} + F_{-m,-m''}) \\ &\quad \times (C_{m'',0} + C_{-m'',0}). \end{aligned} \quad (19)$$

To first order in perturbation on the Zeeman interaction, the quadrupole Hamiltonian of Eq. (9) for i th spin of spin $I = 1$ will produce a doublet with a splitting of

$$\begin{aligned} \delta\nu_i &= \nu_Q^i [A_i P_2(\cos\theta_0) + B_i \sin^2\theta_0 \cos 2\phi_0 \\ &\quad + C_i \sin(2\theta_0) \sin\phi_0], \end{aligned} \quad (20a)$$

where $\nu_Q^i = e^2 q Q / h$ is the coupling constant at the deuterium site in a molecule. Its value is determined in the solid state where most of the orienta-

tional motion has been frozen out.³¹ The coefficients may be expressed as

$$\begin{aligned} A_i &= \frac{3}{2} (r_i S_{0,0} + \frac{3}{4} s_i S_{0,2} + \frac{3}{4} t_i S_{0,1}), \\ B_i &= \frac{9}{8} (r_i S_{2,0} + 2s_i S_{2,2} - \frac{3}{2} t_i S_{2,1}), \\ C_i &= \frac{9}{8} (r_i S_{1,0} - \frac{3}{2} s_i S_{1,2} + 2t_i S_{1,1}), \end{aligned} \quad (20b)$$

where

$$\begin{aligned} r &= C_{0,0} = \langle \frac{3}{2} \cos^2\beta - \frac{1}{2} \rangle, \\ s &= \frac{1}{2} \sqrt{\frac{8}{3}} (C_{2,0} + C_{-2,0}) = \langle \sin^2\beta \cos 2\alpha \rangle, \\ t &= -i \frac{1}{2} \sqrt{\frac{8}{3}} (C_{1,0} + C_{-1,0}) = \langle \sin 2\beta \sin \alpha \rangle \end{aligned}$$

are the conformation averages and the nine molecular order parameters are

$$\begin{aligned} S_{0,0} &= F_{0,0} = \langle \frac{3}{2} \cos^2\theta - \frac{1}{2} \rangle, \\ S_{0,2} &= \sqrt{\frac{8}{3}} F_{0,2} = \langle \sin^2\theta \cos 2\psi \rangle, \\ S_{0,1} &= i \sqrt{\frac{8}{3}} F_{0,1} = \langle \sin 2\theta \sin \psi \rangle, \\ S_{2,0} &= \sqrt{\frac{8}{3}} F_{2,0} = \langle \sin^2\theta \cos 2\phi \rangle, \\ S_{2,2} &= F_{2,2} = \frac{1}{2} \langle \frac{1}{2} (1 + \cos^2\theta) \cos 2\phi \cos 2\psi \\ &\quad - \cos\theta \sin 2\phi \sin 2\psi \rangle, \\ S_{2,1} &= -\frac{4}{3} i F_{2,1} = \frac{2}{3} \langle \sin\theta \cos\psi \sin 2\phi \\ &\quad + \frac{1}{2} \sin 2\theta \sin\psi \cos 2\phi \rangle, \\ S_{1,0} &= -i \sqrt{\frac{8}{3}} F_{1,0} = \langle \sin 2\theta \sin \phi \rangle, \\ S_{1,2} &= \frac{4}{3} i F_{1,2} = \frac{2}{3} \langle \sin\theta \cos\phi \sin 2\psi \\ &\quad + \frac{1}{2} \sin 2\theta \sin\phi \cos 2\psi \rangle, \\ S_{1,1} &= F_{1,1} = \frac{1}{2} \langle \cos\theta \cos\phi \cos\psi - \cos 2\theta \sin\phi \sin\psi \rangle. \end{aligned} \quad (20c)$$

Each of these parameters describe different features of the molecular-orientation order. They all have values between 0 and ± 1 depending upon the contribution of that particular aspect of the order.

For phases of higher symmetry many of these order parameters vanish. For the case of Eq. (12) the nine order parameters above reduce to at most six nonzero $S_{i,j}$'s and in the case of Eq. (13) for uniaxial phases there are at most three.

Apart from the symmetries of the phase, there can be additional symmetries associated with the molecular motion, for example,

(a) In addition to x_M being a twofold axis for end-for-end exchanges, z_M also becomes a twofold axis for rotational diffusion about the long axis ($n = 2$ for $2\pi/n$ rotations about z_M). In this case ϕ , θ , ψ and ϕ , θ , $\psi \pm \pi$ are statistically equivalent. This has been found to be the case in the nematic and smectic studies to date.²⁵

(b) z_M becomes threefold or higher (to include free rotation about the long axis) when $n > 2$. This condition coupled with uniaxiality gives the highest symmetry possible for a liquid-crystal phase as observed with NMR. Such a case would be expected

TABLE I. Surviving order parameters for various phases and molecular rotational motion about the long axes.

| Phase ^a | Molecular rotational motion about z_m ^b | Surviving order parameters |
|-------------------------|--|--|
| Uniaxial, $l > 2$ | free rotation, $n > 2$ | S_{00} |
| Uniaxial, $l > 2$ | π rotation, $n = 2$ | S_{00}, S_{02} |
| Uniaxial, $l > 2$ | partial freeze out, $n = 1$ | S_{00}, S_{02}, S_{01} |
| Biaxial S_A , $l = 2$ | free rotation, $n > 2$ | S_{00} S_{20} |
| Biaxial S_A , $l = 2$ | π rotation, $n = 2$ | S_{00}, S_{02} S_{20}, S_{22} |
| Biaxial S_A , $l = 2$ | partial freeze out, $n = 1$ | S_{00}, S_{02}, S_{01} S_{20}, S_{22}, S_{21} |
| Biaxial S_C , $l = 1$ | free rotation, $n > 2$ | S_{00} S_{20} S_{10} |
| Biaxial S_C , $l = 1$ | π rotation, $n = 2$ | S_{00}, S_{02} S_{20}, S_{22} S_{10}, S_{12} |
| Biaxial S_C , $l = 1$ | partial freeze out, $n = 1$ | S_{00}, S_{02}, S_{01} S_{20}, S_{22}, S_{21} S_{10}, S_{12}, S_{11} |

^a Rotational symmetry for $2\pi/l$ rotation about the director z_N .

^b Rotational motion for $2\pi/n$ rotations about the molecular long axis z_M .

to occur in compounds with molecules which have axial symmetry; an example being the disk-shaped molecules discussed in Chandrasekhar.³² The surviving parameters under various symmetries of the phase as well as molecular orientational motion are outlined in Table I.

EXPERIMENTAL PROCEDURE AND DATA

The basic NMR experiment has been described elsewhere.²³ Briefly the sample is spun about an axis perpendicular to the direction of the magnetic field and the resulting deuterium spectral pattern observed. If the spinning rate is fast enough, there will be a uniform distribution of z_N on a plane normal to the spinning axis. A uniform distribution of θ_0 is then obtained and a particular angle ϕ_0 is selected implying a unique alignment of the x_N axis parallel to the spinning axis. If the spinning rate is too fast, however, some deviations from a uniform distribution of θ_0 can occur as well as there being some nonplanar contributions. While these problems were avoided in the data presented here, the calculation for the spectral pattern generated from a nonplanar distribution will be presented elsewhere.³³

We can write Eq. (20a) as

$$\delta\nu = 2[E + F \cos(2\theta_0 + g_0)] = 2f(\theta_0), \quad (21a)$$

where

$$E = \frac{1}{8}A' + \frac{1}{4}B',$$

$$F = \frac{1}{2}[C'^2 + (A' - 2E)^2]^{1/2},$$

and

$$g_0 = \tan^{-1}(C'/2E - A') \quad (21b)$$

and where $A' = \nu_Q A$, $B' = \nu_Q B \cos 2\phi_0$, and $C' = \nu_Q C \sin \phi_0$. For an aligned sample, $\theta_0 = 0$, we can obtain a value for A' [see Eq. (20a)] as well as the

spectral shape function $\mathcal{L}(\nu - f(0))$ which is symmetric about the Larmor frequency.²³ A uniform distribution of θ_0 gives a spectral pattern whose shape is given by the function

$$G(\nu) = \int_0^\pi \mathcal{L}(\nu - f(\theta_0)) d\theta_0. \quad (22)$$

If the spectral lines were sharp and narrow $\mathcal{L}(\nu - f(0))$ could be approximated by a δ function $\delta(\nu - f(0))$. However, the spectral lines have a width W due to dipole-dipole interactions and in our case also due to magnetic field inhomogeneity. The individual spectral lines from the methyl groups at $\theta_0 = 0$ for HOAB- d_{30} fit well to a Gaussian line shape.

If the width of the spectral lines did not vary slightly with angle θ_0 , then the shape function $G(\nu)$ would only depend on the fitting parameters E and F . The dipole-dipole contribution, however, causes a variation in W which can be well approximated by the expression

$$W = k + N [|P_2(\cos\theta)| - 1],$$

where k is the width at $\theta_0 = 0$ (maximum width) and N is the adjustable parameter. In the fittings to the spectral patterns, this parameter only affects the width of the 90° singularities and does not shift their position as the fitting parameters E and F .²³ A fit to the experimental spectral pattern for the spinning sample gives values for E , F , and N .²³ Because of the symmetry of the spectrum about the Larmor frequency, $G(\nu)$ is invariant when $E \rightarrow -E$, thus there is an ambiguity in determining B and C from Eqs. (21) where $B' = 4E - \frac{1}{2}A'$ and

$$C' = \pm [4F^2 - (A' - 2E)^2]^{1/2}.$$

There are, therefore, four possible values of B' and two of C' , depending upon the signs of A' and E .

In the compound HOAB- d_{30} the methyl groups on each end of the molecule are inequivalent and the stationary spectra for $\theta_0 = 0$ show four spectral lines or two splittings.³⁴ The spectral patterns in spinning samples therefore show two superimposed spectral patterns. The fits to these spectral patterns were shown in an earlier publication.²³ The temperature dependence of the measured values of A'_1 and A'_2 from the methyl groups of HOAB- d_{30} are obtained from a stationary aligned sample and are shown in Fig. 1. The signs of A'_1 and A'_2 were both arbitrary and are plotted in Fig. 1 as both positive in the nematic phase. The value of A_1 changes sign, however, in the smectic phase; this is probably due to a larger dependence on $S_{0,2}$ than $S_{0,0}$ ($s_1/r_1 \ll 1$). The value of $S_{0,2}$ is expected to decrease with increasing temperature²⁵

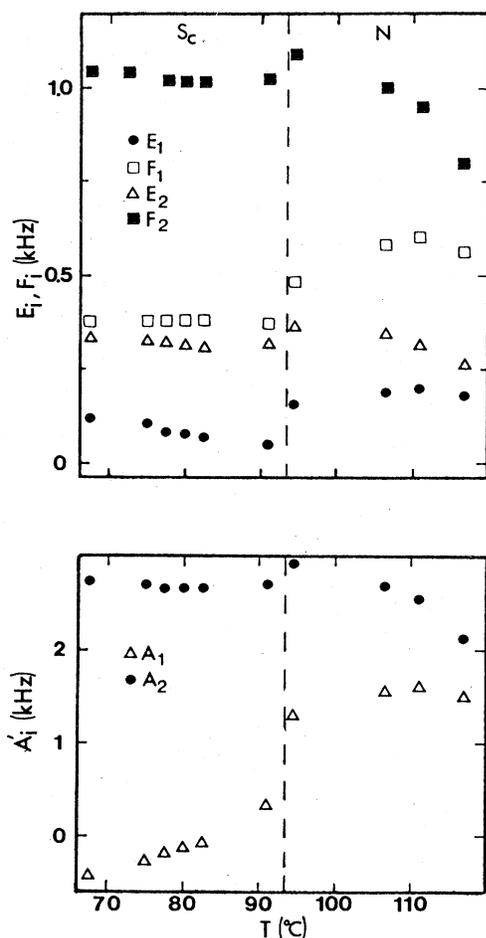


FIG. 1. Measured values of A' from the splittings of aligned samples and E and F from fits to the spectral patterns of spinning samples. The values are arbitrarily plotted as positive. The signs of these quantities are described in the text. The subscripts 1 and 2 refer to the methyl group on each end of the HOAB- d_{30} molecule.

and can go negative unlike $S_{0,0}$, which is known to remain positive in the S_c phase. The change in sign of the methyl splitting is not uncommon in the smectic phases.²⁴

The values of $E_{1,2}$ and $F_{1,2}$ and their temperature dependences obtained from the best fits to the spinning spectral patterns are shown in Fig. 1. The sign of E_1 like A_1 is arbitrarily plotted as positive. The actual relative signs of $A_1, A_2, E_1,$ and E_2 turn out to be important and can only be decided upon by choosing that sign which gives the most physically realistic values of $S_{0,0}$ and $S_{2,0}$, which is to be discussed in the next section. It is seen from Eq. (21b) that the sign of F makes no difference in the determined value of C . The sign of C cannot be determined in this experiment.

RESULTS AND DISCUSSION

Values for the order parameters $S_{i,j}$ can be obtained from the determined values of $A', B',$ and C' by use of Eq. (20b), provided that the values of $r, s,$ and t are known. It is in this regard that the terminal methyl positions, $i=1, 2,$ of HOAB- d_{30} are particularly helpful.²³ The angle β_1 and β_2 are near the magic angle³⁴ (54.7°) where small differences in β cause large changes in r but not in s and t such that $s_1 \approx s_2$ and $t_1 \approx t_2$ even though r_1 and r_2 are very different. The large difference between the character of A'_1 and A'_2 results from r_1 and r_2 not only having small values but also there being a large enough difference between them that r_1/r_2 is significantly different from 1. This particular point will be discussed again later in the section.

By taking $s_1 \approx s_2 \approx s$ and $t_1 = t_2 = t$, we get from Eqs. (20b) $\frac{2}{3}(A_1 - A_2) = (r_1 - r_2)S_{0,0} + \frac{8}{9}(B_1 - B_2) = (r_1 - r_2)S_{2,0}$, and $\frac{8}{9}(C_1 - C_2) = (r_1 - r_2)S_{1,0}$. The values and temperature dependences of the parameters $S_{0,0}, S_{2,0},$ and $S_{1,0}$ can then all be determined from the values of $A', B',$ and C' independent and separate from the other order parameters. These particular parameters depend in no way upon how the molecule is rotating about its long axis, but describe the motion of the long molecular axis. $S_{2,0}$ and $S_{1,0}$ give the contribution of asymmetric motion of the long axis about N_x toward biaxiality [mechanism (a)].

The determined temperature dependence of $S_{0,0}$ is seen to depend on the relative sign of A'_1 and A'_2 . Choosing them to have the same sign as plotted in Fig. 1 gives the temperature dependence of $S_{0,0}$ shown in Fig. 3. A choice of an opposite sign between A'_1 and A'_2 gives an $S_{0,0}$ which decreases at the N - S_c transition, further decreasing as the temperature is lowered. The latter result is believed unphysical in that the deuterium splittings on the

high ordered segments which have a strong dependence on $S_{0,0}$ always increase²⁴ as they also do in other smectic phases.²⁵ Whether A'_1 and A'_2 are both negative or positive to that in Fig. 1 turns out to be of no significance for the work presented in this paper.

Assigning a value of 0.8 for $S_{0,0}$ at the temperature of 80°C gives a value of -0.040 for $(r_1 - r_2)$ if the signs of A'_1 and A'_2 are taken as shown in Fig. 1. The value of ν_Q was taken to be 57.34 kHz for the methyl groups⁸ where $A' = \nu_Q A$. As discussed earlier there are several possible values for B'_1 and B'_2 , depending upon the relative signs of A'_1 , A'_2 , E_1 , and E_2 making a total of four possibilities for $S_{2,0}$ with the signs of A_1 and A_2 as established above. The choice of signs of E_1 and E_2 as plotted in Fig. 1 gave the only physically realistic results. The other three choices ($-E_1 + E_2$, $-E_1 - E_2$, $+E_1 - E_2$) either gave values of $S_{2,0}$ greater than 1 or gave negative values of $S_{2,0}$. A negative value of $S_{2,0}$ implies that the long molecular axis fluctuates greatest in a direction that modulates the smectic layer spacing, as opposed to a direction in which the planes slide over one another. Asym-

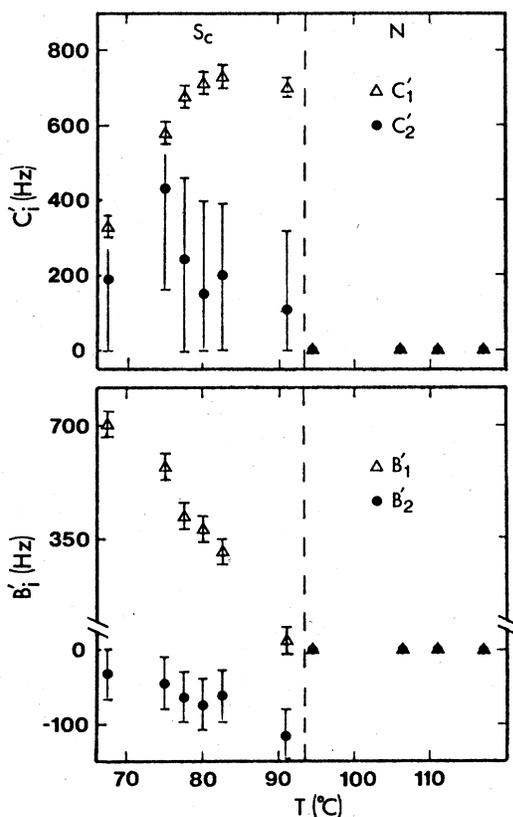


FIG. 2. Values of B' and C' determined from the data of Fig. 1 and Eq. (21b). The subscripts 1 and 2 refer to each methyl group of HOAB- d_{30} .

metric motion which gives a negative $S_{2,0}$ is believed unphysical.^{14,35}

The values of $B_{1,2}$ and $C_{1,2}$ are shown in Fig. 2 and $S_{0,0}$, $S_{2,0}$, and $S_{1,0}$ are shown in Fig. 3 for the signs of A'_1 , A'_2 , E_1 , and E_2 as chosen above. The order parameters in Fig. 3 represent the contribution of mechanism (a) discussed in the Introduction.

The temperature dependences and values of the remaining order parameters are not so well determined but estimates can be made by calculating

$$\Sigma_0 = sS_{0,2} + tS_{0,1} = \frac{4}{9} \left((A_1 + A_2) - \frac{(A_1 - A_2)(r_1 + r_2)}{(r_1 - r_2)} \right), \quad (23a)$$

$$\Sigma_2 = 2sS_{2,2} - \frac{3}{2}tS_{2,1} = \frac{4}{9} \left((B_1 + B_2) - \frac{(B_1 - B_2)(r_1 + r_2)}{(r_1 - r_2)} \right), \quad (23b)$$

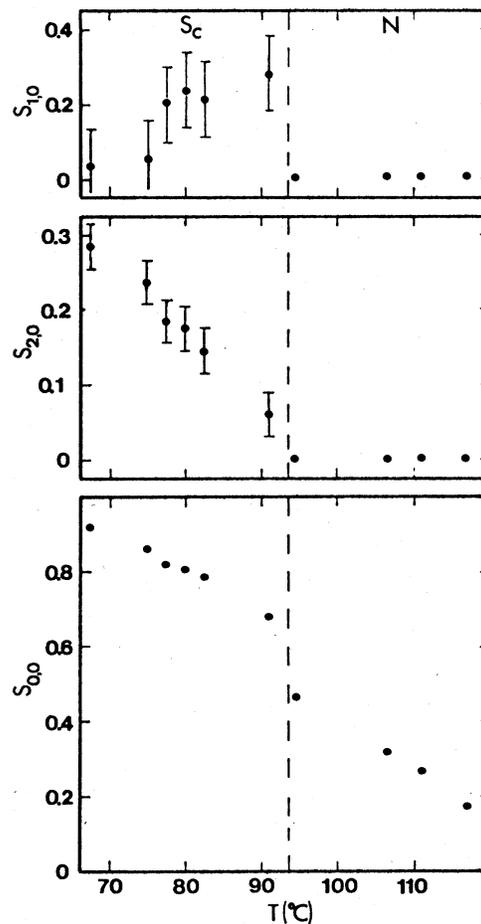


FIG. 3. Order parameters expressing the orientational order of the long molecular axis in HOAB- d_{30} . Parameters $S_{1,0}$ and $S_{2,0}$ are biaxial parameters expressing asymmetry in the orientational order of the long axis [mechanism (a)].

$$\Sigma_1 = -2sS_{1,2} + \frac{3}{2}tS_{1,1} = \frac{4}{9} \left((C_1 + C_2) - \frac{(C_1 - C_2)(r_1 + r_2)}{(r_1 - r_2)} \right). \quad (23c)$$

For perfect order of the long axis [$\theta(t) = 0$] the quantity Σ_0 will vanish, whereas Σ_1 and Σ_2 will not [see Eqs. (20b) and (20c)]. By requiring that Σ_0 decrease with decreasing temperature (increasing $S_{0,0}$) to become less than 0.1 and approach zero at the low-temperature end of the S_C phase we find $(r_1 + r_2) \approx 0.029$ which, in turn, gives the temperature dependences of Σ_i shown in Fig. 4. The form of Σ_0 which decreases with decreasing temperature is that expected for $S_{0,2}$ calculated from theory.^{36,37} The temperature dependence of $S_{0,1}$ has not been calculated.⁸

The parameters Σ_1 and Σ_2 represent a biasing of rotational diffusion about the long molecular axis described as mechanism (b). The Σ parameters are combinations of two order parameters, one in which the long molecular axis, is on the

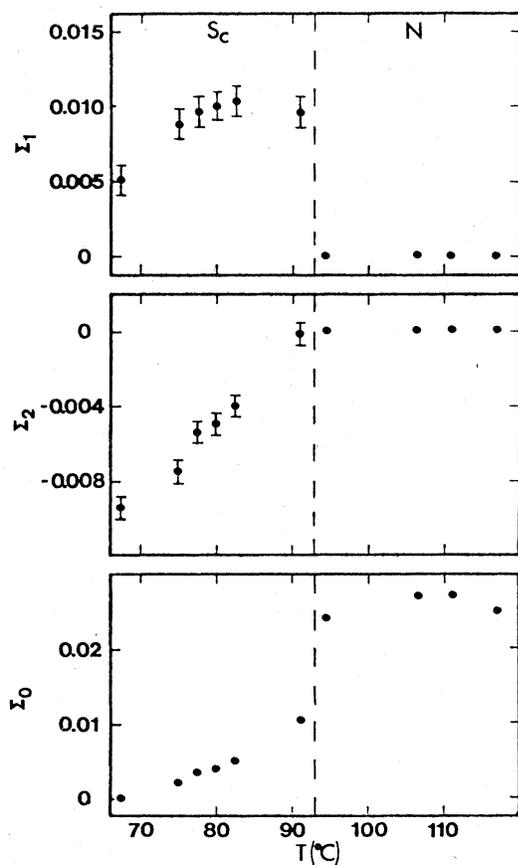


FIG. 4. Order parameters expressing biased rotational diffusion about the long molecular axis in HOAB- d_{30} . Parameters Σ_1 and Σ_2 are biaxial parameters for mechanism (b) and Σ_0 is uniaxial.

average, a twofold rotation axis and the other a onefold rotation axis "partial freeze out" (see Table I). In this compound it is not possible to unambiguously separate the onefold from the twofold contribution. However, since the long axis is reasonably well ordered, order parameters containing $\cos\theta$ in Eqs. (20c) would be expected to dominate those containing $\sin\theta$ or $\sin 2\theta$, in which case $\Sigma_1 \approx \frac{3}{2}tS_{11}$ and $\Sigma_2 \approx 2sS_{22}$. It should be pointed out, however, that the long axis is not perfectly ordered since parameters $S_{2,0}$ and $S_{1,0}$ are finite.

The values of s and t for the methyl groups cannot be determined exactly but are certainly averaged to much less than 1. From Fig. 4 $\Sigma_1 \approx 0.01 \approx \frac{3}{2}tS_{11}$, (see Ref. 38). It is not unreasonable that the value of t be as small as 0.1, which gives $S_{11} \approx 0.1$ for the hydrocarbon chain. This is a rather significant value for the freeze-out parameter.^{1,2}

An important question now arises: why was biaxiality not observed in the Luz, Hewitt, and Meiboom experiment.²² The reason is the same reason biaxial effects are much weaker on the spectra of methyl group 2 than methyl group 1 in this experiment (See Fig. 2 of Ref. 23). It is seen from Eq. (21b) that the observed biaxial effects E and F depend strongly on the value of A' which is the splitting from an aligned sample (uniaxial contribution). The effect of the biaxial order parameters B' and C' contributes most when A' is zero, but can become insignificant when A' becomes comparatively large, particularly in the smectic- C phase where B' and C' are less than 1 kHz. This is to be compared with $A'_1 \sim 0.5$ kHz and $A'_2 \sim 3$ kHz where from Eq. (21b) it is seen that the effects of B' and C' on the observed parameters E and F would be stronger for spectral lines 1 than on 2. In fact, the contribution of spectral lines 2 to the spinning spectral patterns appears nearly uniaxial,²³ as in the case of the Luz, Hewitt, and Meiboom experiment.

For deuterated segments higher up the end chain or on the body of the molecule the values of A' can be as large as 200 kHz but are typically around 25 kHz as in the Luz, Hewitt, and Meiboom experiment. The values of B and C will not increase proportionally if the freeze-out parameters contribute as s and t do not increase up the end chain as fast as r .³⁹

Since the interpretation given above depends on $s_1 \approx s_2$ and $t_1 \approx t_2$ this feature of these time-averaged conformational parameters is perhaps worthy of more discussion. The argument given earlier was that since the HOAB molecule is not chiral $\alpha_1 = \alpha_2$ in these conformational averages. Furthermore, small differences between β_1 and β_2 cause large differences between r_1 and r_2 near the magic angle but not between s_1 and s_2 or t_1 and t_2 .

The equivalence of s_1 and s_2 as well as t_1 and t_2 is also confirmed experimentally through ratios of splittings from aligned samples at various temperatures in the smectic-C phase and across the nematic-smectic-C phase transition. In another paper²⁴ it was shown that the three order parameters $S_{0,0}$, $S_{0,2}$, and $S_{0,1}$ in Eq. (20b) were required to explain the temperature dependence of the splittings from an aligned sample of another compound 4-*n*-octyl-*d*₁₇-oxybenzoic acid -*d*(OOBA-*d*₁₈) which also exhibits the nematic and smectic-C phases.²⁴ The presence of three as opposed to two order parameters is tested if ratio plots of $\delta\nu_i/\delta\nu_h$ vs $\delta\nu_j/\delta\nu_h$ are not continuous straight lines across the nematic transition.²⁴ In the case of spectral lines 1 and 2 of HOAB, however, there are only two effective parameters governing their temperature dependence since $s_1 \approx s_2$ and $t_1 \approx t_2$. A ratio plot using these spectra should yield a straight line across the transition, as it is shown to do in Fig. 5. The third splitting used in this plot comes from another segment in the hydrocarbon chain.³⁴ This fact of there being only two effective order parameters for lines 1 and 2 was also shown in an earlier paper³⁴ in another manner; there it was shown that the temperature dependence of one methyl splitting could be predicted from that of two other splittings, one of which is the other methyl group.

Finally, we would like to comment on the temperature dependence of $S_{2,0}$ and Σ_1 as determined in this experiment. The value of $S_{2,0}$ in Fig. 3 is seen to increase steadily below the *N*-*S*_c phase transition, whereas Σ_1 jumps abruptly at the phase transition and remains roughly constant, as does

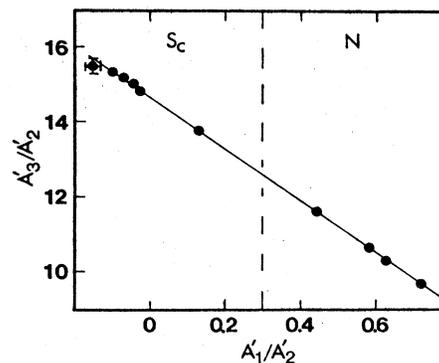


FIG. 5. Ratio plot of A_3'/A_2' vs A_1'/A_2' to illustrate $s_1 \approx s_2$ and $t_1 \approx t_2$ for the methyl groups of HOAB-*d*₃₀.

the tilt angle in this compound. This result would indicate that $S_{2,0}$ is a secondary feature of the *S*_c phase and that Σ_1 is primary. This observation is supportive of transverse interactions, contrary to model-based interpretations of other experimental data recently presented in the literature.⁴⁰ In this regard, we would like to reemphasize that our measured value of Σ_1 (≈ 0.01) could result from a significant value of the freeze-out parameter $S_{1,1}$ and at the same time not be readily observable in measurements of η from ¹⁴N spectra²⁶ or in angular dependences of DMR spectra with typical values of *A* as discussed above.

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¹W. L. McMillan, Phys. Rev. A **8**, 1921 (1975).

²A. Wulf, Phys. Rev. A **11**, 365 (1975).

³R. G. Priest, J. Phys. (Paris) **36** (1975); J. Chem. Phys. **65**, 408 (1976).

⁴D. Cabib and L. Benguigui, J. Phys. (Paris) **38**, 419 (1977).

⁵W. H. de Jeu, J. Phys. (Paris) **38**, 1265 (1977).

⁶V. L. Indenbom, S. A. Pikin, and E. B. Loginov, Sov. Phys. Crystallogr. **21**, 632 (1977).

⁷B. W. van der Meer and G. Vertogen, J. Phys. Colloq. **40**, C3-222 (1978).

⁸D. Allender and M. Kuzma, in Seventh International Liquid Crystal Conference, Bordeaux, France, 1978 (unpublished).

⁹Y. Galerne, in Ref. 8.

¹⁰A. Wulf, Mol. Cryst. Liq. Cryst. **47**, 225 (1978).

¹¹T. Taylor, J. Ferguson, and S. Arora, Phys. Rev.

Lett. **24**, 359 (1970).

¹²Y. Galerne, S. T. Lagerwall, and I. W. Smith, Opt. Commun. **19**, 147 (1976).

¹³D. Johnson and A. Saupe, Phys. Rev. A **15**, 2079 (1977).

¹⁴Y. Galerne, J. Phys. (Paris) **39**, 1311 (1978).

¹⁵T. Lockhart, D. W. Allender, E. Gelerinter, and D. L. Johnson, Phys. Rev. A **20**, 1655 (1979).

¹⁶J. W. Goodby, G. W. Gray, and D. B. McDonnell, Mol. Cryst. Liq. Cryst. Lett. **34**, 183 (1977).

¹⁷J. Doucet, A. M. Levelut, and M. Lambert, Phys. Rev. Lett. **32**, 301 (1974).

¹⁸A. J. Leadbetter and M. A. Mazid, Mol. Cryst. Liq. Cryst. **51**, 85 (1979).

¹⁹(a) F. Volino, A. J. Dianoux, and H. Hervet, J. Phys. Colloq. **37**, C3-55 (1976); (b) F. Volino and A. J. Dianoux, Phys. Rev. Lett. **39**, 763 (1977).

²⁰L. S. Chow and E. F. Carr, Phys. Rev. A **7**, 1639 (1973).

²¹(a) J. Seliger, R. Osredkar, V. Zagar and R. Blinc, Phys. Rev. Lett. **38**, 411 (1977); (b) J. Seliger, V. Zagar, and R. Blinc, Phys. Rev. A **17**, 1149 (1978).

²²Z. Luz, R. C. Hewitt, and S. Meiboom, J. Chem. Phys.

- 61, 1758 (1974).
- ²³P. J. Collings, D. J. Photinos, P. J. Bos, P. Ukleja, and J. W. Doane, *Phys. Rev. Lett.* **42**, 996 (1979).
These authors would like to note a printing error on p. 999, where it should read $sS_8 + tS_9 \approx 0.01$.
- ²⁴P. J. Bos and J. W. Doane, *Phys. Rev. Lett.* **40**, 1030 (1978).
- ²⁵J. 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, 1979).
- ²⁶(a) D. W. Allender and J. W. Doane, *Phys. Rev. A* **17**, 1177 (1978); (b) A. Wulf and J. W. Doane, *Mol. Cryst. Liq. Cryst. Lett.* **41**, 115 (1978).
- ²⁷A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1962), Chap VII.
- ²⁸M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957), p. 50.
- ²⁹The N frame thus defined does not guarantee that when the sample is aligned in the magnetic field we necessarily get $\theta_0 = 0$, although found to be nearly so ($\theta_0 \approx 0$) experimentally (Ref. 22) when cooled from the nematic into the S_C .
- ³⁰G. Meier and A. Saupe, *Mol. Cryst. Liq. Cryst.* **1**, 4 (1966).
- ³¹F. S. Millet and B. P. Dailey, *J. Chem. Phys.* **56**, 3249 (1972).
- ³²S. Chandrasekhar, B. K. Sadashiva, and K. A. Suresh, *Pramāna* **9**, 471 (1977).
- ³³P. J. Bos, D. J. Photinos, and J. W. Doane (unpublished).
- ³⁴P. J. Bos, J. Pirs, P. Ukleja, M. E. Neubert, and J. W. Doane, *Mol. Cryst. Liq. Cryst.* **40**, 59 (1977).
- ³⁵P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1975).
- ³⁶J. P. Straley, *Phys. Rev. A* **10**, 1881 (1974).
- ³⁷G. Luckhurst, C. Zannoni, P. L. Nardio, and V. Segre, *Mol. Phys.* **30**, 1345 (1975).
- ³⁸A printer's error in Ref. 23 gave the incorrect value of $\Sigma_1 \approx 0.1$ instead of its correct value $\Sigma_1 \approx 0.01$.
- ³⁹Measurements of r , s , and t along the end chain have been made in a thermotropic and lyotropic system and a manuscript is in preparation.
- ⁴⁰A. J. Dianoux and F. Volino, *J. Phys. (Paris)* **40**, 181 (1979).