PHYSICAL REVIEW A VOLUME 17, NUMBER 6 JUNE 1978

Orientational phase transition of tilted molecules moving in a planar layer—tentative model for the smectic-*C* phase

A. Wulf*

Department of Applied Mathematics, Research School of Physical Sciences, The Australian National University,
Canberra ACT 2600, Australia

(Received 1 December 1977)

A recent x-ray study, by De Jeu and De Poorter, of the smectic phases of heptyloxybenzylidene-pentylaniline shows that the individual molecules are tilted with respect to the layer normal in both the smectic-*A* and the smectic-*C* phases. We demonstrate here that a system of long molecules, moving within a planar layer, and making a fixed angle $\epsilon > 0$ with the layer normal, has a second-order transition from a phase with disordered tilt directions to a phase with the tilt directions aligned along some axis.
It is suggested that this model phase transition underlies the smectic-*A*–smectic-*C* transition, at least in those cases where the smectic-*A* layer thickness is significantly smaller than the molecular length. In this model the effective tilt angle α, as measured in optical and magnetic resonance experiments, grows continuously with increasing order of the tilt directions, and saturates at the value $\alpha = \epsilon$. On the other hand, the biaxiality (Δ) in the molecular orientational order passes through a maximum and remains small at all temperatures; e.g., we find $|\Delta| < 6 \times 10^{-2}$ for $\epsilon = 30°$. The phase transition is driven by the gains in translational entropy and total attractive energy which accompany an increase in order of the tilt directions. (At the transition temperature these effects balance the loss in orientational entropy.)

I. INTRODUCTION

The striking behavior of the smectic-*C* phase, observed in optical and magnetic resonance experiments as the smectic-*A*–smectic-*C* transition is passed, is conventionally explained by a gradual tilting of the molecules away from the normal to the smectic planes, all the molecules (within a given domain) remaining parallel as they tilt.[1,2] A recent x-ray study by De Jeu and De Poorter[3] shows that this interpretation cannot always be valid. These workers found that the layer thickness in the smectic-*A* and smectic-*C* phases of heptyloxybenzylidene-pentylaniline (abbreviated 70.5) are equal and less than the molecular length (the layer thickness in the smectic-*C* phase of 70.5 was found not to vary significantly with temperature). The angle between the molecules and the layer normal was deduced to be about 17° in both phases.

We propose a new interpretation of the smectic-*C* phase which is consistent with these results. It is suggested that the change from smectic *A* to smectic *C* is the result of a second-order phase transition in which long-range order in the molecular tilt directions develops. In the smectic-*A* phase the tilt directions are disordered; in the smectic-*C* phase the tilt directions tend to align along a preferred axis.

A simple model for this phase transition is given in Sec. II. This model considers rodlike molecules packed in a planar layer and making a fixed angle ϵ with the layer normal. The phase transition is driven by the gains in translational entropy and *total* attractive interaction energy (assumed isotropic) which accompany the growth of orientational order in the tilt directions—below the transition temperature these effects overcome the loss in orientational entropy. The same type of mechanism has recently been proposed to explain the isotropic-nematic phase transition.[4-6]

In Sec. III it is shown that this model exhibits the usual optical behavior associated with the smectic-*C* phase. This behavior is characterized by an effective tilt angle which grows continuously from zero at the smectic-*A*–smectic-*C* phase transition.

The simple model of Sec. II is appropriate for cases, like that of 70.5, where the layer thickness in the smectic-*C* phase may be taken as fixed (it is not known at present whether this case is a common one). In another case that has been extensively studied, that of terephtal-bis-butylaniline (TBBA), the angle ϵ in the smectic-*A* phase is small[7] and the layer thickness in the smectic-*C* phase varies approximately like $\cos\alpha$, where α is the optically measured tilt angle.[8] Thus, TBBA seems to conform to the usual interpretation of the smectic-*C* phase. However, it is conceivable that even in cases like that of TBBA the basic picture of an orientational ordering of the molecular tilt directions remains valid, the change of ϵ with temperature amounting to only an additional complication.

De Jeu and De Poorter[3] offered a different interpretation for the smectic-*A*–smectic-*C* transition of 70.5. They suggested that while each layer in the smectic-*A* and smectic-*C* phases has a well established tilt direction, the tilt directions of the layers are randomly distributed in the smectic-*A* phase. The smectic-*A*–smectic-*C* transition represents, they suggest, the onset of coupling of the tilt directions of the various layers. We believe that this interpretation is unlikely to be correct. The reason is that the entropy per molecule associated with the tilt direction of a layer is of order k/N (k is the Boltzmann constant, N is the number of molecules in a layer) while the coupling energy, per molecule, between adjacent layers is presumably independent of N (for large N). Under these conditions, it is difficult to see how a sharp phase transition, involving layer tilt directions, can occur.

Several mechanisms for the smectic-*A*–smectic-*C* phase transition have been proposed in the last few years,[9-11] but none of them is consistent with all the experimental data now available. The electric dipole model of McMillan[9] and the steric model[10] of the author both predict a large anisotropy in the orientations of the transverse molecular axes when the tilt angle in the smectic-*C* phase becomes large. This contradicts a series of experiments which have now established that the anisotropy is quite small (of the order of 10^{-2} instead of 10^{-1}).[2,12-15] Further, studies of molecular structure and the occurrence of the smectic-*C* phase do not confirm either of these models. The study of Goodby and Gray[16] makes the McMillan model doubtful; the study of De Jeu[17] makes the author's steric model doubtful. The model of Cabib and Benguigui[11] is consistent with isotropic rotation of the molecules about their long axes, but is not supported by either of the above structural studies.

II. MODEL PLANAR LAYER AND ORIENTATIONAL PHASE TRANSITION

The N molecules composing the planar layer will be assumed for simplicity to be ellipsoids of revolution of length and diameter l and d, respectively. The mass centers of the molecules move only on a plane of area A, and the long axis of each molecule is inclined at the angle ϵ to the plane normal. In addition to the hard-core repulsion between the molecular ellipsoids, we assume an attractive interaction $-K/r_{12}^6$ between pairs of molecules (r_{12} is the distance between the molecular mass centers).

Let the plane normal be the Z axis of a rectangular coordinate system X, Y, Z, and let the X axis be the direction of alignment of the tilts in the ordered phase. The unit vector $\vec{e}_i$ along the long axis of molecule i can be written

$$\vec{e}_i = \hat{Z}\nu_i \cos\epsilon + (\hat{X}\cos\psi_i + \hat{Y}\sin\psi_i)\sin\epsilon \, , \tag{1}$$

where $\nu_i = \pm 1$ and ψ_i is the azimuthal angle of $\vec{e}_i$ measured from the X axis. Similarly, we write the radius vector $\vec{r}_{12}$ between the mass centers of molecules 1 and 2 as

$$\vec{r}_{12} = \hat{X} r_{12}\cos\phi + \hat{Y} r_{12}\sin\phi \, . \tag{2}$$

The orientational distribution function $f(\psi, \nu)$ can be expanded in a trigonometric series

$$f(\psi,\nu) = (1/4\pi)[1 + 2a\nu\cos\psi + 2b\cos 2\psi + \cdots] \, , \tag{3}$$

where no sines appear because the XZ plane is a plane of symmetry. However, this expansion is only useful near the second-order phase transition where it is sufficient to keep one or two nontrivial terms in Eq. (3). Since we want to study the behavior of the model also for high degrees of order (when a, b, etc., are of order 1) we adopt instead the trial form

$$f(\psi,\nu) = [1/4\pi I_0(p)]e^{p\nu\cos\psi} \, , \tag{4}$$

where p is a variational parameter and I_0 is the zeroth-order modified Bessel function of the first kind:

$$I_0(p) = \frac{1}{\pi}\int_0^\pi e^{p\cos u}\,du \, . \tag{5}$$

It may be verified that near the transition, where $|p| \ll 1$, Eq. (4) and Eq. (3)—suitably truncated—give much the same results.

Let the system be at constant volume (i.e., constant area A), so that the appropriate thermodynamic potential is the Helmholtz free energy $F = U - TS$. As usual, we set the entropy S equal to the entropy of the hard rods without attraction.[18,19] Then the attraction between molecules enters F only through the internal energy U. This procedure is acceptable for liquids far from the critical point.[20]

For the hard-rod entropy we employ the Onsager approximation,[21]

$$\frac{S}{Nk} \approx 1 + \ln\sigma - \sum_{\nu_1}\int d\psi_1\, f_1 \ln 4\pi f_1 + \frac{\sigma}{2}\sum_{\nu_i}\int d\psi_1\, d\psi_2\, f_1 f_2 B_{12} \, , \tag{6}$$

where $\sigma = N/A$, $f_i \equiv f(\psi_i, \nu_i)$, and $-B_{12}$ is the pair excluded area of molecules with orientations ψ_1, ν_1 and ψ_2, ν_2. Since the intermolecular radius vector $\vec{r}_{12}$ lies in the XY plane, we have

$$-B_{12} = \frac{d^2}{2}\int_0^{2\pi}\left(\frac{\rho_{12}}{d}\right)^2 d\phi \, , \tag{7}$$

where we use the contact radius ρ_{12} given by the Gaussian overlap model of Berne and Pechukas[22]:

$$\rho_{12} = d\left[1 - \frac{1}{2}\chi\left(\frac{(\hat{r}\cdot\vec{e}_1 + \hat{r}\cdot\vec{e}_2)^2}{1+\chi\vec{e}_1\cdot\vec{e}_2} + \frac{(\hat{r}\cdot\vec{e}_1 - \hat{r}\cdot\vec{e}_2)^2}{1-\chi\vec{e}_1\cdot\vec{e}_2}\right)\right]^{-1/2}, \qquad (8)$$

$$\hat{r} = \vec{r}_{12}/r_{12}, \quad \chi = (l^2 - d^2)/(l^2 + d^2).$$

Similarly, we evaluate the internal energy by using just the low-density form of the hard-rod correlation function g_{12},

$$g_{12} = \begin{cases} 1, & r_{12} \geqslant \rho_{12} \\ 0, & r_{12} < \rho_{12}. \end{cases} \qquad (9)$$

Thus,

$$\frac{U}{N} \approx \frac{\sigma}{2} \sum_{\nu_i} \int d\psi_1\, d\psi_2\, f_1 f_2 \int d\vec{r}_{12} \frac{-K}{r_{12}^6} g_{12}$$

$$= -\frac{\sigma d^2 K}{8d^6} \sum_{\nu_i} \int d\psi_1\, d\psi_2\, f_1 f_2 \int d\phi \left(\frac{d}{\rho_{12}}\right)^4. \qquad (10)$$

The above expressions for the entropy and energy neglect the molecular correlations that must exist at liquid densities. As a consequence, the dependence of the translational entropy and U on the orientational order is exaggerated and, as will be seen below, this results in a gross overestimate of the transition temperature for large values of l/d and ϵ.

The evaluation of the integrals over ϕ in Eqs. (7) and (10) is difficult for general orientations $\vec{e}_1$ and $\vec{e}_2$. However, we can expand

$$J_m \equiv \left(\frac{1}{2\pi}\right) \int_0^{2\pi} d\phi \left(\frac{\rho_{12}}{d}\right)^m$$

$$= A_m + B_m \nu_1 \nu_2 \cos\psi_{12} + C_m \cos 2\psi_{12} + \cdots, \qquad (11)$$

where $\psi_{12} = \psi_1 - \psi_2$ and the coefficients $A_m, B_m, C_m, \ldots$ are functions of ϵ and χ. We truncate the series after the third term and determine the coefficients A, B, C by fitting to J_m at the three points (a) $\nu_1 = \nu_2$, $\psi_{12} = 0$; (b) $\nu_1 = \nu_2$, $\psi_{12} = \pi$; and (c) $\nu_1 = \nu_2$, $\psi_{12} = \frac{1}{2}\pi$. In these configurations it is easy to calculate J exactly by elementary trigonometric integrals [$\int (q^2 - r^2\cos^2 x)^{-1}\,dx$ for (a) and (b), and $\int (q + r\sin x)^{-1}\,dx$ for (c), in the case $m = 2$. For $m = -4$ the integrals are simpler still.] Values for A_m, B_m, C_m are given in Table I. It appears from the table that the series (11) converges quite rapidly, especially for the smaller values of ϵ and l/d.

TABLE I. Values of coefficients in expansion of J_m [Eq. (11)].

l/d	ϵ	A_2	B_2	C_2	A_{-4}	B_{-4}	C_{-4}
$\frac{3}{2}$	20°	1.05	−0.019	−0.001	0.905	0.029	0.004
$\frac{3}{2}$	30°	1.12	−0.034	−0.003	0.814	0.043	0.012
3	10°	1.06	−0.050	−0.001	0.891	0.077	0.007
3	20°	1.24	−0.168	−0.013	0.711	0.148	0.041
3	30°	1.49	−0.299	−0.060	0.569	0.148	0.079
5	10°	1.17	−0.149	−0.004	0.778	0.163	0.031
5	20°	1.55	−0.445	−0.040	0.587	0.213	0.093

With the help of Eqs. (7) and (11), the translational entropy S_t [the last term on the right-hand side of Eq. (6)] is easily seen to be given by

$$S_t/Nk \approx -2\tilde{\sigma}(A_2 + B_2 a^2 + C_2 b^2), \qquad (12)$$

where $\tilde{\sigma} = \pi(\frac{1}{2}d)^2\sigma$ and

$$a = \langle \nu\cos\psi\rangle, \quad b = \langle\cos 2\psi\rangle, \qquad (13)$$

with the brackets denoting the average with respect to $f(\psi, \nu)$: $\langle W\rangle = \sum_\nu \int d\psi\, f W$. Similarly, with the notation $\tilde{K} = K/d^6$, we have

$$U/N \approx -\tilde{\sigma}\tilde{K}(A_{-4} + B_{-4}a^2 + C_{-4}b^2). \qquad (14)$$

Combining Eqs. (6), (12), and (14) we get

$$F/NkT \approx \text{const} + \langle \ln 4\pi f\rangle - (\gamma_1 a^2 + \gamma_2 b^2), \qquad (15)$$

where

$$\gamma_1/\tilde{\sigma} = (\tilde{K}B_{-4}/kT) - 2B_2,$$
$$\gamma_2/\tilde{\sigma} = (\tilde{K}C_{-4}/kT) - 2C_2. \qquad (16)$$

Note $\gamma_2 < \gamma_1$ since $C_{-4} < B_{-4}$ and $|C_2| < |B_2|$ (Table I).

Using expression (4) for f, we find

$$\langle \ln 4\pi f\rangle = pI_1(p)/I_0(p) - \ln I_0(p) \qquad (17)$$

and

$$a = I_1(p)/I_0(p), \quad b = I_2(p)/I_0(p). \qquad (18)$$

In deriving Eqs. (17) and (18), the following relations for the first kind modified Bessel functions I_n are used[23]: $2I_n' = I_{n-1} + I_{n+1}$, $4I_n'' = I_{n-2} + 2I_n + I_{n+2}$ and $I_{-n} = I_n$, where the primes indicate differentiation. For small p, Eqs. (17) and (18) can be expanded in a power series in p, using the series expansion

$$I_n(p) = \sum_0^\infty \left(\frac{p}{2}\right)^{n+2s} \Big/ s!\,(n+s)!;$$

then Eq. (15) becomes, to order p^4,

$$F/NkT = \text{const} + (\tfrac{1}{2}p)^2(1-\gamma_1) + (\tfrac{1}{2}p)^4(\gamma_1 - \tfrac{3}{4} - \tfrac{1}{16}\gamma_2). \qquad (19)$$

Equation (19) indicates a continuous phase transition at $\gamma_1 = 1$, with

$$p \approx \frac{2^{3/2}(\gamma_1 - 1)^{1/2}}{(1 - \frac{1}{4}\gamma_2)^{1/2}}$$

$$\approx \left(\frac{8(1 + 2\tilde{\sigma}B_2)}{1 - \frac{1}{4}\gamma_2}\right)^{1/2} \left(1 - \frac{T}{T_c}\right)^{1/2}, \qquad (20)$$

TABLE II. Equilibrium properties of the model as functions of T/T_c.

		$\epsilon=20°$, $l/d=3$			$\epsilon=20°$, $l/d=5$			$\epsilon=30°$, $l/d=3$		
T/T_c	1	0.99	0.90	0.80	0.99	0.90	0.80	0.99	0.90	0.80
p	0	0.26	0.90	1.4	0.23	0.74	1.1	0.25	0.86	1.3
a	0	0.13	0.41	0.57	0.11	0.35	0.49	0.12	0.40	0.54
$10b$	0	0.08	0.90	1.86	0.06	0.62	1.32	0.08	0.82	1.66
α	0	2.9	8.9	12	2.5	7.6	10	4.7	15	19
η_e	[a]	0.83	0.86	0.88	0.83	0.85	0.87	0.63	0.69	0.74
$-10^2\Delta$	0	0.08	0.77	1.4	0.06	0.56	1.1	0.18	1.7	2.9

[a] At $T/T_c=1$, $\eta_e=\frac{1}{2}(3\cos^2\epsilon-1)$.

for $0 \leqslant p \ll 1$. The transition temperature is given by $\gamma_1=1$, i.e.,

$$T_c=\frac{\tilde{K}}{k}\,\frac{\tilde{\sigma}B_{-4}}{1+2\tilde{\sigma}B_2}\,. \tag{21}$$

For large p, Eq. (15) is evaluated numerically using Eqs. (17) and (18). Table II gives the value of p which minimizes F for several values of T/T_c, ϵ, l/d, and $\tilde{\sigma}=\frac{1}{2}$; corresponding values of a and b are also given. [Note $\gamma_1=(1+2\tilde{\sigma}B_2)\times T_c/T-2\tilde{\sigma}B_2$ and a similar expression for γ_2 (with C's instead of B's) are evaluated using Table I.]

From Eq. (14), it is seen that $\tilde{\sigma}\tilde{K}A_{-4}$ represents the mean attractive energy per molecule for $a=b=0$. As an estimate, an approximate value appropriate for p-azoxyanisole[19] may be taken:

$$\tilde{\sigma}\tilde{K}A_{-4}\sim 20kT_0 \quad (T_0\approx 400\ °\mathrm{K})\,.$$

This enables us to rewrite Eq. (21) as

$$T_c=\frac{\tilde{\sigma}\tilde{K}A_{-4}}{k}\,\frac{B_{-4}/A_{-4}}{1+2\tilde{\sigma}B_2}\sim 20T_0\left(\frac{B_{-4}/A_{-4}}{1+B_2}\right), \tag{22}$$

where we have again taken $\tilde{\sigma}=\frac{1}{2}$. It has been seen previously for nematic liquid crystals that the use of the correlation function (9) for long rods (e.g., $l/d=3$) grossly overestimates the change of U/N with orientational order, but that for $l/d\sim\frac{3}{2}$ the correct order of magnitude for this change is obtained.[6] Therefore, since B_{-4}/A_{-4} measures the rate of change of U/N with a^2, it is not too surprising that Eq. (22), together with Table I, gives values of T_c too large by about a factor of 5 for $l/d=3$. For $l/d=\frac{3}{2}$, on the other hand, we get

$$T_c\sim\begin{cases}\frac{6}{10}T_0, & \epsilon=20°\\ T_0, & \epsilon=30°\end{cases}$$

which is about right. This suggests that the ordering transition of the molecular tilt directions may indeed occur at typical smectic-A temperatures.

III. OPTICAL PROPERTIES OF THE MODEL

In this section we show that the orientational properties of the model are characterized by an effective tilt angle α which vanishes in the high-temperature (disordered) phase and grows continuously from zero in the low-temperature (ordered) phase. In addition, it is seen that the orientational distribution of the long molecular axes in the ordered phase is biaxial, but the associated biaxial order parameter remains small at all temperatures. We employ the language of the optical experiments, but everything said applies also to the magnetic resonance experiments provided $P_\parallel$ and $P_\perp$ (defined below) are suitably reinterpreted.[24]

As mentioned in Sec. I, rotation of the molecules about their long axes appears to be nearly isotropic.[2,12–15] Therefore, the molecular polarizability may be taken to be cylindrically symmetric, with components $P_\parallel$ and $P_\perp$ parallel and perpendicular to the molecular axis. Then the average polarizability tensor is[25]

$$\langle\overleftrightarrow{\mathrm{P}}\rangle=P_0\overleftrightarrow{1}+(P_\parallel-P_\perp)\overleftrightarrow{\mathrm{Q}}\,, \tag{23}$$

where $P_0=(P_\parallel+2P_\perp)/3$ and

$$\overleftrightarrow{\mathrm{Q}}=\langle\vec{e}\,\vec{e}-\overleftrightarrow{1}/3\rangle\,. \tag{24}$$

The angle α between the layer normal and the major principal axis of $\overleftrightarrow{\mathrm{Q}}$ is the optically measured tilt angle.

With the help of Eqs. (1) and (13) we obtain

$$\langle\vec{e}\,\vec{e}\rangle=\cos^2\epsilon\hat{Z}\hat{Z}+\tfrac{1}{2}(1+b)\sin^2\epsilon\hat{X}\hat{X}+\tfrac{1}{2}(1-b)\sin^2\epsilon\hat{Y}\hat{Y}+\tfrac{1}{2}a\sin 2\epsilon(\hat{Z}\hat{X}+\hat{X}\hat{Z})\,. \tag{25}$$

We diagonalize expression (25) by transforming to the tilted frame $\hat{Z}'$, $\hat{X}'$, $\hat{Y}$, where

$$\begin{aligned}\hat{Z}&=\hat{Z}'\cos\alpha-\hat{X}'\sin\alpha,\\ \hat{X}&=\hat{Z}'\sin\alpha+\hat{X}'\cos\alpha.\end{aligned} \tag{26}$$

Substituting Eqs. (26) into Eq. (25), we find that the condition which diagonalizes $\langle\vec{e}\,\vec{e}\rangle$ is

$$[\cos^2\epsilon - \tfrac{1}{2}(1+b)\sin^2\epsilon]\tan 2\alpha = a\sin 2\epsilon \tag{27}$$

or

$$\alpha = \tfrac{1}{2}\,\mathrm{Tan}^{-1}\frac{a\sin 2\epsilon}{\cos^2\epsilon - \frac{1}{2}(1+b)\sin^2\epsilon}\,. \tag{28}$$

Then we have

$$\overleftrightarrow{Q} = \eta_e(\hat{Z}'\hat{Z}' - \overleftrightarrow{1}/3) + \Delta(\hat{X}'\hat{X}' - \hat{Y}\hat{Y})\,, \tag{29}$$

where

$$\eta_e = \tfrac{3}{2}[\cos^2\epsilon\cos^2\alpha - \tfrac{1}{3} + \tfrac{1}{2}(1+b)\sin^2\epsilon\sin^2\alpha + \tfrac{1}{2}a\sin 2\epsilon\sin 2\alpha]\,, \tag{30}$$

and the biaxiality Δ is

$$\Delta = (\tfrac{1}{2})\cos^2\epsilon\sin^2\alpha + (\tfrac{1}{2}b)\sin^2\epsilon - \tfrac{1}{4}[a\sin 2\epsilon\sin 2\alpha + (1+b)\sin^2\epsilon\sin^2\alpha]\,. \tag{31}$$

It is seen that $\Delta = 0$ for vanishing order of the tilt directions ($\alpha = a = b = 0$), and again for perfect alignment of the tilts ($\alpha = \epsilon$, $a = b = 1$). Values of α, η_e, and Δ as functions of T/T_c for several values of ϵ and l/d are given in Table II. For very large values of p (not shown in Table II) we observe $|\Delta|$ passing through a maximum and then decreasing very slowly. The maximum values of $|\Delta|$ are about 3×10^{-2} for $\epsilon = 20°$, and 6×10^{-2} for $\epsilon = 30°$. Biaxialities of order 10^{-2} in smectic-C phases have been measured in nuclear-magnetic-resonance[14] and nuclear-quadrupole-resonance[15] experiments.

IV. COMMENTS

The model for the smectic-A–smectic-C transition given here is, of course, very idealized. Interactions between smectic layers and fluctuations of the angle ϵ are not considered, and the smectic layer ordering is assumed perfect. In addition, the energy and entropy of the model system were evaluated neglecting all correlations between molecules except for the nonoverlapping of the rodlike hard cores. Nevertheless, the conclusion that an ordering transition of the molecular tilt directions can take place in smectic layers whose thickness is less than the molecular length, is probably valid. As shown in Sec. III, if this phase transition occurs, it is observed experimentally as a smectic-A–smectic-C transition.

It remains to be seen whether the case of 70.5—smectic-A and smectic-C layer thicknesses about the same and independent of temperature—occurs frequently. Clearly, it would be very useful to have measurements of both tilt angle and layer thickness as a function of temperature in a variety of systems with smectic-A–smectic-C transitions.

It is interesting that the present model gives new meaning to Saupe's remark that the smectic-C phase is analogous to a two-dimensional nematic liquid crystal.[26]

Note: Very recently De Vries[27] has found that the layer thickness in the smectic-A and -C phases of n-pentyl-(n-decyloxybenzylidenamino)-cinnamate shows the same behavior as in 70.5.

ACKNOWLEDGMENTS

I thank Professor J. W. Doane and Dr. W. H. De Jeu for sending me preprints of their recent publications.

---

[*] Permanent address: Centro de Fisica, Instituto Venezolano de Investigaciones Cientificas (IVIC), Apartado 1827, Caracas 101, Venezuela.

[1] T. R. Taylor, J. L. Fergason, and S. L. Arora, Phys. Rev. Lett. 25, 722 (1970); G. R. Luckhurst and F. Sundholm, Mol. Phys. 21, 349 (1971); E. Gelerinter and G. Fryburg, Appl. Phys. Lett. 18, 84 (1971); R. A. Wise, D. H. Smith, and J. W. Doane, Phys. Rev. A 7, 1366 (1973); Z. Luz and S. Meiboom, J. Chem. Phys. 59, 275 (1973).

[2] Z. Luz, R. C. Hewitt, and S. Meiboom, J. Chem. Phys. 61, 1758 (1974).

[3] W. H. De Jeu and J. A. De Poorter, Phys. Lett. 61A, 114 (1977).

[4] A. Wulf, J. Chem. Phys. 64, 104 (1976).

[5] W. M. Gelbart and B. A. Baron, J. Chem. Phys. 66, 207 (1977).

[6] A. Wulf, J. Chem. Phys. 67, 2254 (1977).

[7] A. De Vries, Mol. Cryst. Liq. Cryst. 16, 311 (1972).

[8] D. Guillon and A. Skoulios, J. Phys. 38, 79 (1977).

[9] W. L. McMillan, Phys. Rev. A 8, 1921 (1973).

[10] A. Wulf, Phys. Rev. A 11, 365 (1975).

[11] D. Cabib and L. Benguigui, J. Phys. 38, 419 (1977).

[12] H. Hervet, F. Volino, A. J. Dianoux, and R. E. Lechner, J. Phys. Lett. 35, L-151 (1974).

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

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

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

[16] J. W. Goodby and G. W. Gray, J. Phys. C 3, 17 (1976).

[17] W. H. De Jeu, J. Phys. (to be published).

[18] R. Alben, Mol. Cryst. Liq. Cryst. 13, 193 (1971).

[19] M. A. Cotter, J. Chem. Phys. 66, 1098 (1977).

[20] H. C. Longuet-Higgins and B. Widom, Mol. Phys. 8, 549 (1964).

[21] L. Onsager, Ann. N. Y. Acad. Sci. 51, 627 (1949).

[22] B. J. Berne and P. Pechukas, J. Chem. Phys. 56, 4213 (1972).

[23] See, for example, H. B. Dwight, *Tables of Integrals and Other Mathematical Data*, 4th ed. (MacMillan, New York, 1965).

[24] T. C. Lubensky, Phys. Rev. A 2, 2497 (1970).

[25] Equation (23) disregards local-field effects [P. G. de Gennes, *Physics of Liquid Crystals* (Clarendon, Oxford, 1974), Sect. 2.1.2.3]; however, these should

be unimportant for our purposes because we are mainly interested in the principal axes of $\overleftrightarrow{Q}$ and not the actual magnitude of the optical polarizability anisotropy. In the magnetic case the local field corrections are negligible.

[26] A. Saupe, Mol. Cryst. Liq. Cryst. 7, 59 (1969).

[27] A. De Vries, Mol. Cryst. Liq. Cryst. Lett. 41, 27 (1977).