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Undulation instabilities in smectic C phases*

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Microscopic studies on thermally induced undulation instabilities of the smectic C phase of pentyloxybenzylideneheptylaniline ($\bar{5}$BA7) and pentylphenyloctylthiobenzoate (5PTB$\bar{8}$) are reported. The A-C transitions of these compounds appear to be second order. The tilt angle in smectic C is strongly temperature dependent. The biaxial order is small. Layer undulations can be produced with suitable samples by a stepwise reduction of the temperature. A few hundredths of a degree are sufficient. The preferred undulation mode has a wave vector parallel to the C_2 axis. A theoretical analysis and comparison with data from the smectic A phase shows that the dilation modulus of smectic C is about two orders of magnitude smaller than that of smectic A. The temperature dependence of the modulus near the transition to smectic A is discussed theoretically on the basis of a Landau expansion.

I. INTRODUCTION

Smectic films of a planar layered structure can sustain a stress normal to the layers over an extended period of time. Plastic deformations will eventually occur but they require a formation of additional layers which apparently cannot nucleate readily. Their propagation starts from boundaries or existing defects and is associated by climbing of dislocation lines. Since the formation of new layers is relatively slow, elastic properties can be conveniently studied under the constraint of a constant layer number. In the following we assume in general that this constraint applies.

There exists an instability threshold stress for the planar structure that is proportional to the square root of the film thickness. For stresses above the threshold, undulations form. Mechanically induced undulations in smetic A have been studied by Ribotta and Durand[1,3,4] and by Clark and Meyer.[2,10] In this paper we report on undulation instabilities in the smectic C phase of 4-n-pentyloxybenzylidene-4′-n-heptylaniline ($\bar{5}$BA7) and of 4-n-pentylphenyl-4′-n-octylthiobenzoate (5PTB$\bar{8}$).

The instabilities are observed on thin films with a Schlieren texture. They are induced by cooling presumably by the following mechanism. The contraction of the layers of the smectic C films can be expected to be exceptionally large because of the increase of tilt upon cooling. As the spacers which hold the glass plates apart contract less strongly, a mechanical stress results that induces the instability.

The experimental observations are presented in Sec. II. They include studies of the temperature variation of tilt and optical biaxiality. The relation between biaxiality and molecular order are analyzed in Sec. III. Section IV contains a theoretical treatment of undulation instabilities in smectic C. It is based on the free-energy expression given by de Gennes[5] which is slightly extended to include a tilt-angle variation. The final Sec. V contains a discussion of the temperature dependence of the dilation modulus near the A-C transition based on a mean-field Landau expansion. The experimental data and the theoretical analysis shows that there is sharp decrease of the dilation modulus at the transition to the smectic C phase. It is understood as an effect resulting from the coupling between dilation and tilt.

II. EXPERIMENTAL RESULTS

A. Compounds and sample preparations

Both compounds $\bar{5}$BA7 and 5PTB$\bar{8}$ form a nematic phase and several smectic phases including smectic A and smectic C. The transition temperatures are summarized in Table I. The classification of the smectic phases as far as given in Table I is based on the textures. The compounds were prepared for us by Dr. Mary Neubert. They had been carefully purified by recrystallization.

The observations were made on thin films sandwiched between glass plates using a Leitz polariz-

TABLE I. Transition temperatures in °C.

	Compound	
Transition	$\bar{5}$BA7	5PTB$\bar{8}$
Isotropic		
	78.0	85.7
Nematic		
	64.0	62.6
Smectic A		
	55.4	55.6
Smectic C		
	52.7	
Smectic B		
	37.3	
Smectic X		
	29.5	58.6
Crystal		

ing microscope equipped with a Mettler heat stage. The surfaces of the glass slides were coated with a silane as described by Kahn.[6] This surface treatment leads to homotropic nematic and smectic *A* textures and upon cooling to Schlieren textures of the smectic *C* phase. Wire spacers were used to control the thickness of the films which varied from 50 to 150 μm.

B. Microscopic observations

We are interested here only in the smectic *C* phase and in the *A* to *C* transition. Conoscopic observations were used to study the temperature dependence of the tilt in the smectic *C* phase. A well-centered positive uniaxial conoscopic figure is observed in the smectic *A* phase. Upon cooling, when the transition to smectic *C* is reached the figure moves out of center first without any other noticeable change. This motion is due to the tilt of the molecular alignment axis and allows a direct determination of the tilt angle. Within the accuracy of our observation the tilt angle changes continuously starting from zero at the transition point. We made particularly careful studies with compound $\bar{5}$BA7 and we estimate that any discontinuous change that might occur at the transition is smaller than 1° in angle. This is the lowest tilt angle that we could observe. However, the temperature dependence close to the transition is very strong. The tilt angle at 0.4 °C below the transition is about 12°.

The biaxial splitting of the conoscopic figure becomes observable a few tenths of a degree below the transition. It increases noticeably with increasing tilt. The two optical axes lie perpendicular to the C_2 axis which is the twofold rotation axis.

Under orthoscopic observations the phase transition is recognizable by a change from the homotropic texture to a Schlieren texture that usually contains singularities of strength ±1. The structure of the +1 points is characterized by a $\vec{C}$-director field which tends to form circles around the singularity. This can be easily verified using a λ plate (the $\vec{C}$ director coincides with the axis of the larger refractive index). It shows that the splay constant of the *C* field for our materials is larger than the bend elastic constant ($b_3 > b_1$).

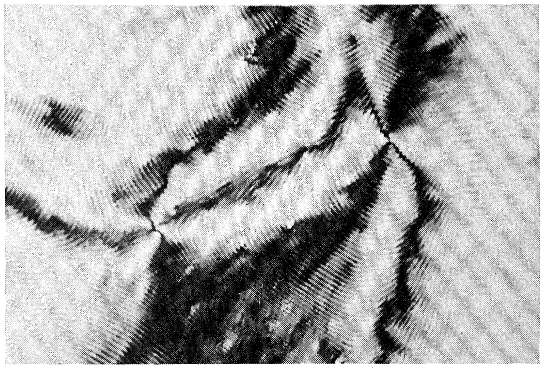

FIG. 1. Smectic *C* Schlieren texture with undulation lines. $\bar{5}$BA6, 52.7 °C, 133×, crossed polarizers.

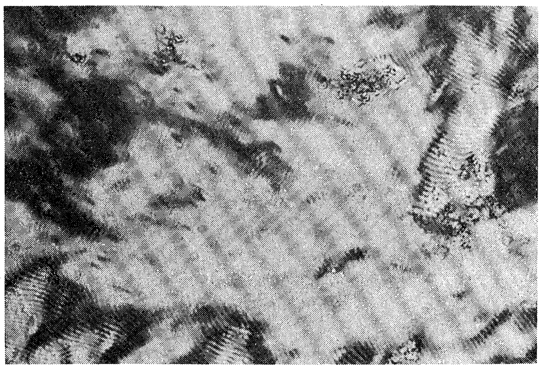

FIG. 2. Smectic *C* Schlieren texture with undulation lines. $\bar{5}$BA6, 52.8 °C, 133×, parallel polarizers, polarization horizontal.

Upon further cooling the texture becomes "dressed" by parallel lines following the *C* field. Figure 1 shows an example. As mentioned in the Introduction we interpret the lines as layer undulations caused by stresses due to thermal contraction.

The line patterns correspond to metastable textures. When kept sufficiently long at the same temperature a boundary will move across behind which the striped pattern is less pronounced or has disappeared. The boundary apparently is a dislocation line at the edge of a number of new layers that grow in starting from some disturbance.

Figure 2 shows a micrograph taken with parallel polarizers. The stripes parallel to the direction of vibration remain easily visible while the perpendicular stripes are hardly recognizable. In the areas with parallel stripes only the ordinary (or quasiordinary) ray is excited. It has a constant refractive index and remains to a good approximation unmodulated. Upon further cooling of the sample a second set of stripes develops running perpendicular to the first set. Figure 3 shows an example of the resulting cross-hatched texture. The spacing of the second set is larger. In Fig. 3 it is about 1.6 times as large. Occasionally the secondary set appears first as can be seen in Fig. 1 at the right edge. In this case the ratio between the spacings is about 2:1.

The spacing depends on the thickness of the film.

FIG. 3. Smectic *C* Schlieren texture with cross-hatched patterns due to double undulation. $\overline{5}$BA6, 53.3 °C, 133×, crossed polarizers.

It seems to be proportional to the square root of the thickness as one expects for undulations. A quantitative verification of the dependence is difficult because the observed spacing may deviate by 20% or more from its equilibrium value. Variations in spacing between different areas of the same sample were found to be of this magnitude. Repeated measurements were made with 5PTB$\overline{8}$ on a 150 μm thick film at a temperature 0.14 K^0 below the transition ($T_{AC} - T = 0.14$ K^0) the (mean) spacing is $\frac{1}{2}\lambda = 3.75$ μm. Assuming the square-root dependence this gives

$$\tfrac{1}{2}\lambda = 3.1 \times 10^{-3}\sqrt{d}$$

when λ and the thickness d are measured in cm. We will show later that the actual undulation period is λ. The temperature dependence of λ was studied qualitatively. It does not seem to increase strongly near the transition.

III. BIAXIALITY AND MOLECULAR ORDER

Relations between molecular order and birefringence have been successfully used with uniaxial liquid crystals, in particular nematics. We will use in the following a similar approach to discuss some qualitative aspects of the biaxial order in smectic *C* phases.

We denote by α_i ($i = 1, 2, 3$) the principle polarizabilities of the molecule with $\alpha_1 > \alpha_2 > \alpha_3$. The highest polarizability α_1 is in general parallel to the long axis of the molecule and α_3, when we consider molecules with a planar aromatic center part, perpendicular to the plane. Typical values for the anisotropy of molecules such as considered here are

$$\alpha_a = \alpha_1 - \tfrac{1}{2}(\alpha_2 + \alpha_3) = 3 \times 10^{-23}\,\text{cm}^3 , \tag{1}$$

$$\alpha_b = \alpha_2 - \alpha_3 = 1 \times 10^{-23}\,\text{cm}^3 . \tag{2}$$

We assume for an estimate of α_b that it is about twice the anisotropy of a benzene molecule. We denote by $\overline{\alpha}_i$ the principle average polarizabilities in a suitable lab system and by θ_{ij} the angle between the x_i axis of the lab system and the molecular ξ_j axis. A straightforward calculation gives $\overline{\alpha}_i = \sum_j \langle \cos^2\theta_{ij}\rangle \alpha_j$ and

$$\overline{\alpha}_a = \eta_{11}\alpha_a + \tfrac{1}{2}(\eta_{12} - \eta_{13})\alpha_b , \tag{3}$$

$$\overline{\alpha}_b = \gamma_1\alpha_a + \tfrac{1}{2}(\gamma_2 - \gamma_3)\alpha_b , \tag{4}$$

with the following abbreviations

$$\eta_{ij} = \tfrac{1}{2}\langle 3\cos^2\theta_{ij} - 1\rangle , \tag{5}$$

$$\gamma_i = \langle \cos^2\theta_{2i} - \cos^2\theta_{3i}\rangle . \tag{6}$$

In nematics and uniaxial smectic liquid crystals with x_1 as the symmetry axis we have $\gamma_i = 0$. The leading term on the right side of (3) is $\eta_{11}\alpha_a$. We assume that for ideal nematic order all molecules are parallel with their long axes (ξ_1). The second term on the right side of (3) is usually neglected. The difference $\eta_{12} - \eta_{13}$ will indeed be in general small when η_{11} is close to 1 since $\eta_{12} - \eta_{13} \rightarrow 0$ for $\eta_{11} \rightarrow 1$. (We estimate $|\eta_{12} - \eta_{13}| < 0.01$ for smectic phases where $\eta_{11} \approx 0.80$.)

The parameters γ_i correspond to the differences between the average square projections of a unit vector parallel to the molecule ξ_i axis on x_2 and x_3. γ_2 or γ_3 may serve as an order parameter for biaxial order. The third parameter γ_1 will in general be small in smectic phases because of the high value of γ_{11}. Neglecting γ_1 Eq. (4) becomes

$$\overline{\alpha}_b = \gamma_2\alpha_b , \tag{4'}$$

where we have used the fact that $\gamma_3 = -\gamma_2$. Using the Lorenz-Lorentz formula we obtain now the relations for η_{11} and the biaxial order γ_2 in terms of the refractive indices:

$$\eta_{11} = \frac{3}{4\pi N\alpha_a}\left(\frac{n_1^2 - 1}{n_1^2 + 2} - \frac{1}{2}\frac{n_2^2 - 1}{n_2^2 + 2} - \frac{1}{2}\frac{n_3^3 - 1}{n_3^2 + 2}\right) , \tag{7}$$

$$\gamma_2 = \frac{3}{4\pi N\alpha_b}\left(\frac{n_2^2 - 1}{n_2^2 + 2} - \frac{n_3^2 - 1}{n_3^2 + 2}\right) . \tag{8}$$

We are interested here only in γ_2. Let the x_2 axis be parallel to the C_2 axis of the smectic *C* phase. The difference $n_2 - n_3$ can be estimated from the conoscopic figures. It is positive for both compounds. For $\overline{5}$BA7 at $T - T_{AC} = 0.4$ °C we find $n_2 - n_3 \approx 1 \times 10^{-3}$. It follows that γ_2 is positive and of the order of 1%.

The positive sign indicates that the molecules tend to orient with their planes parallel to C_2. The small value shows that the biaxial order is not a proper feature of the smectic *C* phase but induced by the tilt. The same conclusions can be made for the smectic *C* phase of 5PTB$\overline{8}$. An analysis of the optical observations on 4,4′-heptyloxyazoxybenzene[7] and on terephthal-bis-(4-n-butylaniline)[8] suggests that their smectic C phases also have the same basic features.

Finally, it should be noticed that the low values for $|\gamma_2|$ makes the use of (4′) instead of (4) questionable since this requires $|\gamma_1| \ll |\gamma_2|$, but (4′) remains good for an estimate of the magnitude.

IV. THEORY OF UNDULATION INSTABILITY

A. Undulation modes and critical dilation

The mechanism of an undulation instability in smectic C is similar to that in smectic A phases studied theoretically by Clark and Meyer[2] and by de Gennes.[5] In smectic C's the situation is somewhat more complicated because of the coupling between layer curvature and tilt orientation. Following de Gennes[5] we write for the free energy per unit volume.

$$\begin{aligned} F = {} & \tfrac{1}{2}(b_1\phi_x^2 + b_2\phi_y^2 + b_3\phi_z^2 + 2b_{13}\phi_x\phi_z) \\ & + \tfrac{1}{2}(\tilde{B}\gamma^2 + C_1u_{xx}^2 + C_2u_{yy}^2 + 2C_{12}u_{xx}u_{yy}) \\ & + d_1u_{yx}\phi_x + d_2u_{yy}\phi_y \ . \end{aligned} \tag{9}$$

The y axis of the selected coordinate system coincides with the C_2 axis of the undisturbed liquid crystal. ϕ denotes the angle between the local C_2 axis and the y axis or equivalently between $\vec{C}$ director and x axis, γ the dilation (fractional change of layer distance), and u the displacement of the layers in direction of the z axis. The subscripts indicate partial derivatives, e.g., $\phi_x = \partial\phi/\partial x$, $u_{xx} = \partial^2u/\partial x^2$, etc. It is assumed that the displacements from equilibrium are small.

The first part on the right side of Eq. (9) is the curvature elasticity of the director field,[9] the second part dilation energy plus curvature elasticity of the layers, and the last two terms contain the coupling between layer curvature and director field.

The dilation in second order is given by

$$\gamma = u_z - \tfrac{1}{2}(u_x^2 + u_y^2) \ . \tag{10}$$

Equation (9) is a reduced expression for the free energy in which the lateral stretching of layers and the variation of the tilt angle do not explicitly appear. The energy is already minimized with respect to these two variables. This elimination of variables affects the value of the dilation modulus B which for that reason has been marked by a tilde. All other coefficients remain unchanged.

In later discussions the tilt variation will be considered explicitly. The free-energy expression, including the tilt variable, is obtained by replacing $\frac{1}{2}\tilde{B}\gamma^2$ with

$$\tfrac{1}{2}\bar{B}\gamma^2 + \tfrac{1}{2}\bar{A}\omega^2 + A_{11}\gamma\omega \ . \tag{11}$$

The tilt variation is given by $\omega = \theta - \theta_0$, where θ denotes the local tilt angle and θ_0 its equilibrium value. Minimizing the free energy with respect to ω gives

$$\omega = -(A_{11}/\bar{A})\gamma \ , \tag{12}$$

$$\tilde{B} = \bar{B} - A_{11}^2/\bar{A} \ . \tag{13}$$

For $T \to T_{AC}$: $A_{11} \to 0$ and $\bar{A} \to 0$. Our measurements were made within a few degrees of the transition. The limit of the ratio $A_{11}^2/\bar{A}$ is therefore of interest. It will be discussed in the last section.

We return to Eq. (9). We assume the existence of a uniform dilation γ_0 and consider instabilities due to undulations of the form

$$u = u_0 \sin pz \sin\vec{q}\cdot\vec{r} + \gamma_0 z \ . \tag{14}$$

The layer curvature couples with the $\vec{C}$-director field. We must therefore also consider the variation of the director field. It will be of the form

$$\phi = \phi_0 \sin pz \sin(\vec{q}\cdot\vec{r} + \beta) \ . \tag{15}$$

The boundary conditions corresponding to our experiments are taken into account by selecting the z axis perpendicular to the film and setting

$$p = \pi/d, \quad q_z = 0 \ ,$$

where d is the thickness of the film.

Using Eqs. (14) and (15) we find for the average energy per unit volume

$$\begin{aligned} \langle F\rangle = {} & \tfrac{1}{2}\tilde{B}\gamma_0^2 + \tfrac{1}{8}u_0^2\{\tilde{B}[p^2 - \gamma_0(q_x^2 + q_y^2)] \\ & + C_1q_x^4 + C_2q_y^4 + 2C_{12}q_x^2q_y^2\} \\ & + \tfrac{1}{4}u_0\phi_0q_y(d_1q_x^2 + d_2q_y^2)\sin\beta \\ & + \tfrac{1}{8}\phi_0^2(b_1q_x^2 + b_2q_y^2 + b_3p^2). \end{aligned} \tag{16}$$

Minimizing with respect to β and ϕ_0 gives

$$\phi_0 = \frac{|q_y(d_1q_x^2 + d_2q_y^2)|}{b_1q_x^2 + b_2q_y^2 + b_3p^2}u_0 \tag{17}$$

and $\beta = \pm\frac{1}{2}\pi$ for $q_y \neq 0$ with $\operatorname{sgn}\beta = -\operatorname{sgn}q_y(d_1q_x^2 + d_2q_y^2)$. For $q_y = 0$ the coupling between layer curvature and tilt orientation disappears.

In order to study the effect of the orientation of $\vec{q}$ we set

$$q_x = q\cos\alpha, \quad q_y = q\sin\alpha. \tag{18}$$

This gives using the relation (17)

$$\langle F\rangle = \tfrac{1}{2}\tilde{B}[\gamma_0^2 + \tfrac{1}{4}u_0^2(p^2 - \gamma_0q^2)] + \tfrac{1}{8}u_0^2q^4Q(\alpha) \tag{19}$$

with

$$\begin{aligned} Q(\alpha) = {} & C_1\cos^4\alpha + C_2\sin^4\alpha + 2C_{12}\sin^2\alpha\cos^2\alpha \\ & - \sin^2\alpha\,\frac{(d_1\cos^2\alpha + d_2\sin^2\alpha)^2}{b_1\cos^2\alpha + b_2\sin^2\alpha + b_3(p/q)^2}\,. \end{aligned} \tag{20}$$

$Q(\alpha)$ has extremes for $\alpha=0$ and $\alpha=\frac{1}{2}\pi$. Expansion into a power series gives in second order

$$Q(\alpha)\approx C_1+\alpha^2\left[2(C_{12}-C_1)-\frac{d_1^2}{b_1+b_3(p/q)^2}\right], \tag{21}$$

$$Q\tfrac{1}{2}\pi+\alpha')\approx C_2-\frac{d_2^2}{b_2+b_3(p/q)^2}+\alpha'^2\left[2(C_{12}-C_2)+\frac{d_1^2+2d_1d_2}{b_2+b_3(p/q)^2}-\frac{d_2^2(b_1-b_2)}{(b_2+b_3(p/q)^2)^2}\right]. \tag{22}$$

The considered extremes correspond to energy minima when the expressions in brackets on the right side of (21) and (22) are positive. We cannot determine the sign theoretically. The experimental results indicate, however, that both are positive at least near the *C-A* transition.

The critical dilation and the critical q value are found by setting the partial derivatives $\partial\langle F\rangle/\partial u_0^2$ and $\partial\langle F\rangle/\partial q^2$ equal to zero. It gives

$$\gamma_c=(2\pi/d)\Lambda, \tag{23}$$

$$\lambda_c=2\pi/q_c=2(\pi d\Lambda)^{1/2}. \tag{24}$$

Here Λ corresponds to the "penetration" length introduced for smectic *A* by de Gennes.[5] For the two extremes considered above we have

$$\Lambda=(C_1/\bar{B})^{1/2},\quad \alpha=0; \tag{25}$$

$$\Lambda=(1/\sqrt{\bar{B}})(C_2-d_2^2/b_2)^{1/2},\quad \alpha=\tfrac{1}{2}\pi. \tag{26}$$

We assumed in the case $\alpha=\frac{1}{2}\pi$ that $\pi\Lambda/d\ll 1$.

B. Optical effect of undulations

It is convenient here and also justified to neglect the weakly biaxial character of the smectic *C* phase. We assume that geometrical optic can be applied and that the light is decomposed into ordinary and extraordinary rays.

Under deformations which produce only a rotation of the index ellipsoid the ordinary ray suffers no phase modulation since its refractive index remains constant. The direction of its polarization will, however, in general be affected because it is linked to the orientation of the index ellipsoid. The refractive index of the extraordinary ray depends on the angle θ between the wave normal and the optical axis.

$$n_e=(\epsilon_1\epsilon_2)^{1/2}/(\epsilon_a\cos^2\theta+\epsilon_2)^{1/2}. \tag{27}$$

Here ϵ_1 and ϵ_2 denote the two principle dielectric constants and $\epsilon_a=\epsilon_1-\epsilon_2$.

We consider now normal incidence and a small modulation of θ of the form

$$\theta=\theta_0+\omega. \tag{28}$$

In the first approximation for small ω we may assume that the wave normal remains parallel to the z axis. The modulation of n in the first approximation is then

$$\Delta n=-\frac{\epsilon_a(\epsilon_1\epsilon_2)^{1/2}\sin 2\theta_0}{(\epsilon_a\cos^2\theta_0+\epsilon_2)^{3/2}}\,\omega. \tag{29}$$

The phase modulation has therefore the same periodicity as the modulation of the angle between the z axis and the optical axis.

The effect of a layer undulation depends on the orientation of the undulation vector. In the first approximation $\omega=-u_x$. The undulation with $\alpha=0$ gives an optical pattern which is produced by a first-order effect and which has the same periodicity as the undulation. In contrast to this the undulation with $\alpha=\frac{1}{2}\pi$ has no first-order effect. The optical pattern is due to a second-order effect. For small θ_0 we obtain in second order

$$\omega=\tfrac{1}{2}u_y^2\cot\theta_0. \tag{30}$$

Therefore, the modulation of n has a periodicity which is only half as long as that of the undulation.

It remains to discuss the effect of the coupling between tilt angle and dilation. According to Eq. (12) and (10) we have to consider an additional variation of θ given by

$$\omega=-(A_{11}/\bar{A}_2)[u_z-\tfrac{1}{2}(u_x^2+u_y^2)]. \tag{31}$$

This gives a first-order effect on the modulation of n. The integrated optical effect will, however, disappear in first order. The optical path for perpendicular incidence is proportional to the integral $\int\omega' dz$ over film thickness and this integral is zero. The previous conclusions remain therefore valid.

V. DISCUSSION AND CONCLUSION

The undulation instability that tends to occur first has a wave vector parallel to the C_2 axis, that means [see Eq. (18)] $\alpha=\frac{1}{2}\pi$. It follows $\gamma_c(\pi/2)<\gamma_c(0)$ or with Eq. (23) $\Lambda(\pi/2)<\Lambda(0)$. The difference between the threshold dilations is however small since the sequence of the appearance is occasionally reversed.

The theoretical relations (24)–(26) show that $\lambda\sim\sqrt{d}$ for $\alpha=0$ and that this relation also holds for $\alpha=\frac{1}{2}\pi$ provided $\Lambda/d\ll 1$. In the range of thicknesses covered in our experiments Λ/d is indeed small. Using Eq. (24) we obtain from the observed periodicity for 5PTB8 at 55.5 °C (see Sec. II)

$$\Lambda=300\times 10^{-8}\text{ cm}.$$

The value for 5PTB$\bar{8}$ has a similar magnitude. No strong temperature dependence of Λ was observed and there is no indication for a divergence for $T \to T_{AC}$.

In smectic A phases Λ is about one order of magnitude smaller. This in particular is also true for a homologous compound[4] where $\Lambda = 25$ Å in smectic A. There is, therefore, a discontinuous change of Λ at the transition. This change must be due to a discontinuous change of the dilation constant $\tilde{B}$ since the splay constant can be expected to vary continuously in case of a second-order transition.

In order to discuss this problem in detail we expand the free energy as a function of γ and θ about $\theta = 0$.

For a second-order transition the relevant terms of the expansion are

$$F(\gamma, \theta^2) = F_0 + \tfrac{1}{2}a_{20}\theta^2 + \frac{1}{4!}a_{40}\theta^4 + \tfrac{1}{2}a_{02}\gamma^2 + \tfrac{1}{2}a_{21}\theta^2\gamma. \tag{32}$$

Here $\gamma = 0$ corresponds to the equilibrium dilation for $\theta = 0$. We first take γ as independent parameter and eliminate θ^2. By minimization of the free energy we find $\theta^2 = -6(a_{20} + a_{21}\gamma)/a_{40}$ and

$$F(\gamma) = F_0 + \tfrac{1}{2}\bar{a}_{02}\gamma^2 \tag{33}$$

with the dilation modulus

$$\bar{a}_{02} = a_{02}(1 - 3a_{21}^2/a_{02}a_{40}). \tag{34}$$

It is related to the modulus in Eq. (9) by an equation of the form $\tilde{B} = \bar{a}_{02} + O(\theta_0^2)$ and similarly we have $\tilde{B}_2 = a_{02} + O(\theta^2)$. By comparison with Eq. (13) we find accordingly for $T \to T_{AC}$

$$A_{11}^2/\bar{A}\bar{B} \to 3a_{21}^2/a_{02}a_{40}. \tag{35}$$

The coefficients a_{21}, a_{02}, and a_{40} do not in general change sign at the transition so that the limit remains finite.

We take now θ^2 as independent parameter and eliminate γ. It gives

$$F(\theta) = F_0(\theta_0) + \frac{1}{4!}\bar{a}_{40}(\theta^2 - \theta_0^2)^2 \tag{36}$$

with

$$\bar{a}_{40} = a_{40}(1 - 3a_{21}^2/a_{02}a_{40}). \tag{37}$$

In general it will be true that $\bar{a}_{40} \ll a_{40}$ because a change of θ^2 at fixed γ results in a change of density while for an adaptable dilation the density may remain constant. The energy change in the first case which is proportional to a_{40} will therefore be much larger than in the second case where it is proportional to $\bar{a}_{40}$. Using Eq. (37) to replace the expression in parenthesis on the right of Eq. (34) we obtain

$$\tilde{B} = \bar{a}_{02} = (a_{02}/a_{40})\bar{a}_{40} = \tfrac{1}{3}(a_{02}^2/a_{21}^2)\bar{a}_{40}. \tag{38}$$

The last relation is obtained using Eq. (37) and $\bar{a}_{40} \ll a_{40}$. The ratio a_{02}/a_{21} can be estimated assuming that the equilibrium layer distance is equal to the length of the projection of the molecules on the layer normal. For a small tilt and for molecules of the shape of a rotation ellipsoid one obtains neglecting thermal fluctuations, $a_{21}/a_{02} = 1 - b^2/a^2$, where b and a are the axes of the ellipsoid. For the molecules of interest $b/a \approx \frac{1}{5}$ and $a_{21}/a_{02} \approx 1$.

Equation (33) and (34) apply for $\gamma < -a_{20}/a_{21}$. For $\gamma > -a_{20}/a_{21}$ the tilt is zero and the coupling disappears. The dilation modulus in this range is $\bar{B} \approx a_{20}$. When $T < T_{AC}$ the ratio $a_{20}/a_{21} < 0$ and Eq. (33) applies for $\gamma \approx 0$, but when $T > T_{AC}$ $a_{20}/a_{21} > 0$ and γ must surpass a minimum negative value before the coupling is effective. This explains the change of the modulus at the transition.

The abrupt change for $\tilde{B}$ to $\bar{B}$ at the transition is true only for the mean-field approach. The actual change will be somewhat smoothed out because of fluctuations. Even in the mean-field approach some pretransitional effects on the undulation wavelength can be expected. Equations (23)–(24) apply only when $\gamma_c < -a_{20}/a_{21}$. Using our experimental data we estimate that deviation should result in the range

$$0 < T_{AC} - T < 10^{-2}.$$

We can also give a numerical estimate of $\tilde{B}$. When we assume that the effective splay constant is as usually found in the order of 10^{-6} dyn we find $\tilde{B} \approx 10^5$ erg/cm^3. This is about two orders of magnitude smaller than the modulus $\bar{B}$ that is observed in smectic A phases.[4,10] It will be of interest to study a dependence that may exist between molecular structure and $\tilde{B}$. Some of our observations still need a quantitative verification. In particular, an experimental investigation of the temperature dependence of the undulation wavelength will be of interest.

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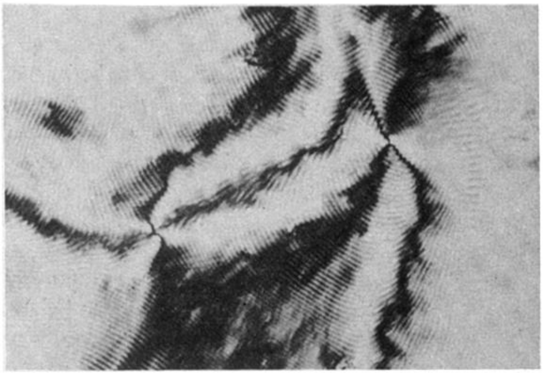

FIG. 1. Smectic *C* Schlieren texture with undulation lines. $\overline{5}$BA6, 52.7 °C, 133×, crossed polarizers.

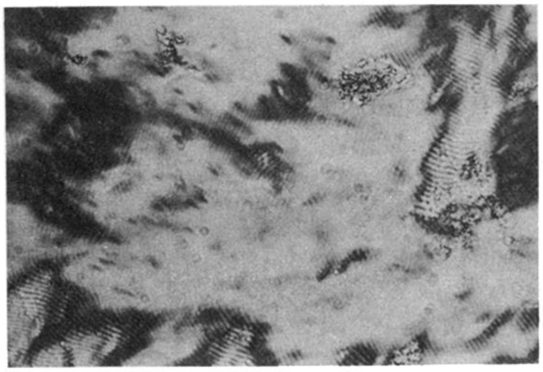

FIG. 2. Smectic *C* Schlieren texture with undulation lines. $\overline{5}$BA6, 52.8 °C, 133×, parallel polarizers, polarization horizontal.

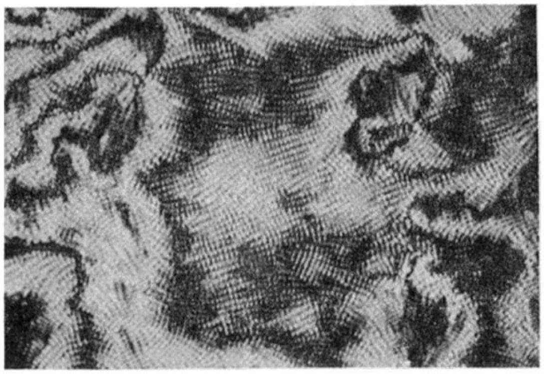

FIG. 3. Smectic *C* Schlieren texture with cross-hatched patterns due to double undulation. $\overline{5}$BA6, 53.3 °C, 133×, crossed polarizers.