possible if the field energy is transferred only to a fraction of plasma particles, for instance to particles matching some resonance condition similar to the static-corkscrew conditions; complications are introduced by field self-consistency and time dependence at the focus.

[10] J. P. Baconnet, G. Cesari, A. Coudeville, and J. P. Watteau, in *Proceedings of the Ninth International Conference on Phenomena in Ionized Gases, Bucharest, 1969*, edited by G. Musa *et al.* (Institute of Physics, Bucharest, Romania, 1969), p. 643; H. L. L. van Paassen, Phys. Fluids 12, 2193 (1969).

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TEMPERATURE-DEPENDENT TILT ANGLE IN THE SMECTIC *C* PHASE OF A LIQUID CRYSTAL*

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Measurement of the tilt angle of the smectic *C* phase of terephthal-bis-(4-*n*-butylaniline) has been made using conoscopic observation and circularly polarized light. The new phenomenon of a smectic *C* phase with a temperature-dependent tilt angle is reported. Terephthal-bis-(4-*n*-butylanaline) has nematic, smectic *A*, smectic *C*, and smectic *B* liquid-crystalline phases. The tilt angle of smectic *C* changes from 0° at the smectic-*A*–smectic-*C* transition to approximately 26° at the smectic-*C*–smectic-*B* transition temperature.

The most commonly occurring smectic phases have been classified according to optical texture as smectic *A*, *C*, and *B* by Sackmann and Demus.[1] Smectic phases are considered to be layered and smectic *A* has a molecular arrangement such that the long molecular axis is perpendicular to the layers; smectic *C* has the molecular axis tilted with respect to the layer normal. Smectic *B* can have the molecular axis perpendicular or tilted and, in addition, has an order within the layers.

The optical properties of terephthal-bis-(4-*n*-butylaniline) (TBBA) are of special interest because it has nematic, smectic *A*, smectic *C*, and smectic *B* phases. TBBA was prepared by refluxing 4-*n*-butylaniline (2 mole) and terephthalaldehyde (1 mole) in absolute ethanol for 5-6 h. The product after isolation was recrystallized several times from alchohol until the transition temperatures remained constant. Analysis calculated for $C_{28}H_{32}N_2$ was N, 7.07; found, N, 7.15. The phase-transition temperatures are isotropic-nematic, 236.5°; nematic–smectic *A*, 199.6°; smectic *A*–smectic *C*, 172.5°; smectic *C*–smectic *B*, 144.1°; and smectic *B*–solid, 113.0°C. The absolute error in the temperatures is estimated to be less than ±1.0°C with a repeatablility of ±0.2°C. A differential thermal analysis (du Pont DTA 900) is shown for heating and cooling in Fig. 1. From the thermogram it is apparent that the smectic *A*–smectic *C* (S_A-S_C) transition energy is very low compared with any of the other mesophase transition energies. The assignments of the phases were made by optical texture[1] using a polarizing microscope with a heated stage. Smectic *A* can exhibit the focal-conic texture in thick sections but generally orients normally spontaneously in sections less than 0.1 mm thickness. Smectic *C* exhibits the smectic schlieren texture[1] with thickness less than 0.1 mm and smectic *B* gives a mosaic texture.

In examining TBBA we found that the smectic *C* schlieren texture showed a striking change in the order of the birefringence as a function of temperature when observed with white light. In smectic *C* phases which we have reported,[2] we had not observed a temperature dependence of

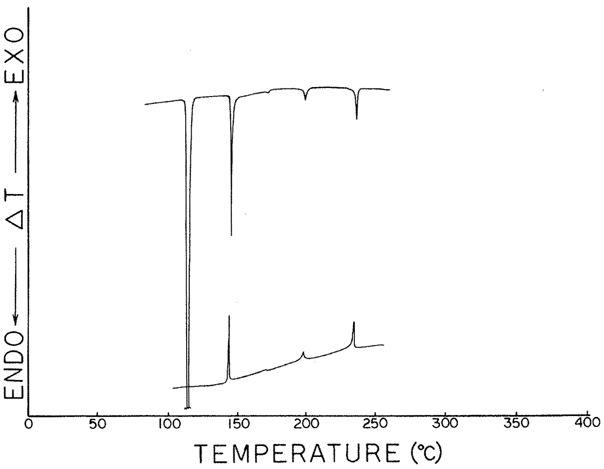

FIG. 1. Differential thermal analyzer thermogram of TBBA for heating and cooling.

the texture. The temperature dependence of the texture was such that the interference colors of the sample increased from near zero at the S_A-S_C transition to second- or third-order colors at lower temperatures. In other words, the color of the sample between crossed polarizers was a strong function of temperature. The effect was accentuated by the fact that the color changes appeared to be discontinuous. That is, a wave would pass across the optical field with the interference colors changing behind the wave. It occurred to us that this change in birefringence could indicate that the tilt angle of smectic *C* was changing with temperature, a phenomenon that has not been reported.

The apparent wave motion which was observed could possibly be attributed to a change in the number of layers in a fixed sample thickness. As the sample is cooled the number of layers increases since the layer thickness L is given by $L = d\cos\theta$, where d is the molecular length and θ the tilt angle. TBBA has a length of approximately 20 Å and there would be an increase of approximately 3000 layers if we assume that the tilt angle changes from 0° to 25° over the 30° temperature range with a fixed thickness of 0.05 mm.

In order to investigate whether the smectic *C* tilt angle was a function of temperature, conoscopic observations on well-oriented samples of TBBA have been made. Since with undefined surface conditions the director (unit vector in the direction of the long axis) can vary continuously over the sample area, the director must be uniformly oriented to make conoscopic observations. Uniform orientation of the director was obtained by rubbing glass slides as described by Taylor, Fergason, and Arora.[2] With uniformly oriented samples a high quality interference figure was obtained, which definitely established that the tilt angle is a function of temperature. Figure 2 shows a series of interference figures from a temperature of 172.5 to 169.0°C. In the temperature range 172.4 to 169.0°C the center of the cross changes from an angle of 0° to 12°. At the S_A-S_C transition there appears to be no discontinuous change in optical properties; at the transition, the cross begins to move off center without any other apparent change.

The change of 12° in the position of the center of the cross corresponds to a change in tilt angle of 12° if the very reasonable assumption is made that the acute bisectrix can be identified as lying along the long molecular axis. The absolute magnitude of the tilt angle is dependent on the value of the maximum index of refraction γ, for which a value of 1.7 was assumed. Also shown in Fig. 2 is an interference figure off the extinction position showing the biaxial character of smectic *C*. Within the field of view of our objective the angle $2V$ between the optic axes was not a function of temperature. The angle $2V$ was calculated to be approximately 6° using a value of 1.5 for the intermediate index of refraction. There was no measurable dispersion of $2V$ with wavelength and both smectic *A* and smectic *C* were found to be optically positive.

All conoscopic observations were made using a Leitz Panphotpol microscope with a Mettler FP-2 heated stage. The objective had a magnification of 32× and a numerical aperture of 0.4 corresponding to an angular field of view of 45° in air. Because of working distance, we were limited to a numerical aperture of 0.4.

The interference figures conclusively prove that the tilt angle does change with temperature in the smectic *C* phase of TBBA but is of limited use in measuring the complete temperature dependence of the tilt angle, since the interference figure is out of the field of view in 4°C and smectic *C* has a complete range of 30°C. In order to measure the tilt angle at lower temperatures, circularly polarized light has been used. The experiment was done using two circular polarizers of opposite sense, which gives extinction when no sample is between the polarizers. We obtain circularly polarized light by inserting one quarter-wave plate after the polarizer and one before the analyzer of the microscope. When the quar-

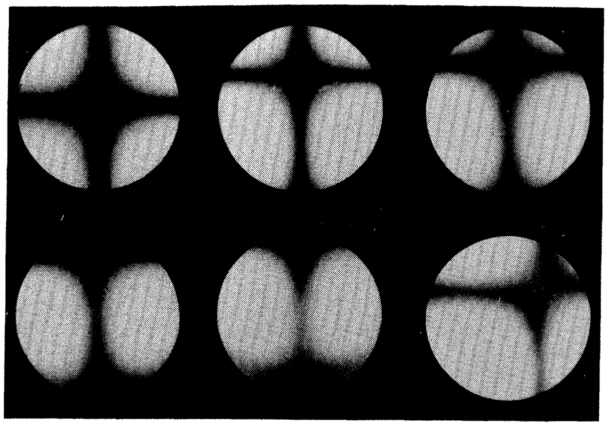

FIG. 2. Interference figures showing temperature dependence of tilt angle of smectic *C*. From left to right, top to bottom: smectic *A* phase 172.5°C; smectic *C* phase at temperatures of 172.0, 171.5, 170.5, 169.0, and 171.5°C.

ter-wave plates are correctly oriented with respect to the privileged direction of the polarizer and analyzer, circular polarizers of opposite sense are obtained.

When a birefringent material is observed between circular polarizers of opposite sense the transmitted intensity is given by

$$I = I_0 \sin^2(\tfrac{1}{2}\delta), \qquad (1)$$

where

$$\delta = 2\pi z(\gamma - \alpha)\sin(\theta - v)\sin(\theta + V)/\lambda$$
$$= 2\pi z(\gamma - \alpha)(\sin^2\theta - \sin^2 V)/\lambda.$$

The maximum index of refraction is γ; the minimum, α; z is the thickness of the sample; θ, the tilt angle; and λ, the wavelength. The derivation of a similar formula for circular polarizers of like sense is given by Preston.[3] The use of circular polarizers allows a deviation of the director over the optical field of view since the intensity depends only on the tilt angle and not on the direction of the director. This is not so for linearly polarized light. From Eq. (1) it can be seen that the intensity will go through a series of maxima and minima at different temperatures.

To investigate the intensity as a function of temperature a Bausch and Lomb high-intensity monochromator, EMI photomultiplier with S-20 surface, and the Mettler heated stage were used. The photomultiplier output was fed to the Y axis of an X-Y recorder and the time base of the X-Y recorder was synchronized with the 2°C per minute temperature rate of the Mettler stage. A typical curve of intensity versus temperature is shown in Fig. 3. Figure 3 is for a decreasing temperature but the curves were repeatable if the temperature was reversed before the solid phase was reached. Data were taken at 4500, 5250, and 6250 Å for a large number of sample thicknesses. As can be seen from Fig. 3, the curves do not agree completely with the theoretical Eq. (1) as the intensities of subsidiary maxima and minima are not those predicted by Eq. (1). We attribute this to a number of factors. First, to obtain sufficient intensity, wide monochromator slits must be used and thus there was a relatively large wavelength band which would tend to smear out the minima. Also, the quarter-wave plates are exactly quarter wave only for 5400 Å. Lastly, it appears that as the temperature is lowered, the parallelism of the layers to the glass surfaces decreases.

For the above reasons, values of the tilt angle were calculated only at maxima and minima. By varying the thickness and wavelength, it is easy to obtain sufficient data to compute the tilt angle at a number of temperatures. In order to compute the tilt angle it is necessary to know $\gamma - \alpha$. Since this is extremely difficult to determine directly with accuracy, the temperature at which the first maximum occurred, along with the tilt angle determined from the interference figure at that temperature, was used to calculate $z(\gamma - \alpha)$ for each wavelength and thickness. Then Eq. (1) was used to obtain the tilt angle at lower temperatures from the subsidary maxima and minima.

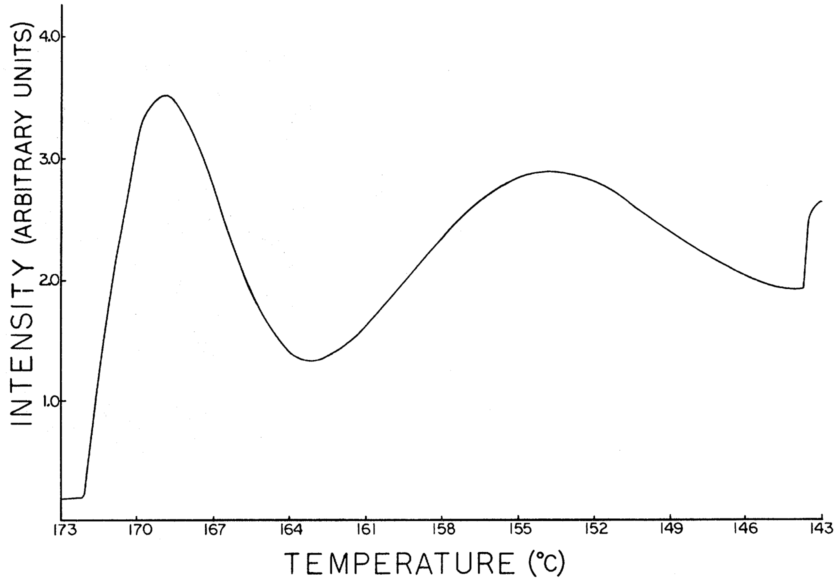

FIG. 3. Transmitted intensity of 5250-Å circularly polarized light as a function of temperature in the smectic C phase.

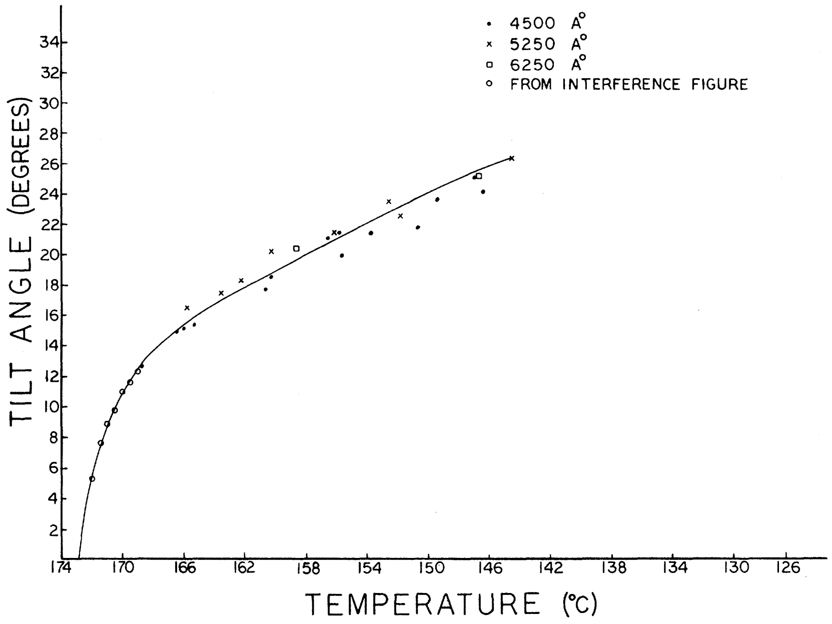

FIG. 4. Variation of tilt angle in smectic *C* phase as a function of temperature.

It was assumed for the calculations that the optic axial angle remained constant and equal to that obtained from the interference figure. It was apparent from these calculations that there was some dispersion in $\gamma-\alpha$ with wavelength.

Figure 4 shows the variation of tilt angle over the complete temperature range. As can be seen, there is scatter in the data but the points represent data from four different sample thickness. The scatter between points from individual sample thickness is much less than the scatter from different samples, thus the repeatability is not particularly good. The tilt changes from nearly 0° at the S_A-S_C transition to approximately 26° at the smectic *C*–smectic *B* (S_C-S_B) transition. The tilt increases very rapidly in the first five degrees after the S_A-S_C transition and then increases much more slowly to the S_C-S_B transition temperature. The curve raises the question of whether the S_A-S_C transition in the case of TBBA is of first order. Within the limit of our measuring technique there does not appear to be a discontinuous change in tilt at the S_A-S_C transition although it is possible that it is too small for our methods to detect. If the tilt does change continuously from 0° to 26°, it would seem that the S_A-S_C transition could just as well be identified as a second-order transition.

In our studies of smectic phases, we should point out that we have found very few smectic *C* phases with variable tilt. In fact, TBBA was the only one at the start of this study but since that time we have found two other compounds. (Studies are in progress for these compounds.) The interesting point is that all variable-tilt smectic *C* phases we have found are preceded by a smectic *A* phase. It is possible that this is necessary for the variable-tilt smectic *C* to occur. Also, we would point out that TBBA tends to oxidize with exposure to air, so that care must be exercised that a decomposed sample is not used in measurements.

There are several features of TBBA which allow conclusions to be drawn about the nature of smectic *C* and smectic *B* phases. In the smectic *C* schlierien texture, lines of optical discontinuities can be observed. In the ideal case of a uniformly aligned sample there are two equally probable directions of the director, each director lying in the same plane but having an angle between them equal to twice the tilt angle. Either direction of the director would give the same interference colors and optical texture. In uniformly aligned samples, using conoscopic observation, we have observed the sample on either side of these discontinuities. It was found that the direction of tilt of the interference figure changed from one side of the field of view to the other as we traversed the discontinuity. This indicates that these discontinuities are inversion walls in which the director reverses itself by twice the tilt angle. Observations were also made on smectic *B* with circularly polarized white light. When the uniformly oriented smectic *C* makes the transition to the mosaic texture of smectic *B* we find that the mosaic blocks are of a uniform interference color although the outline of the blocks can still be seen. This indicates that the blocks all have the same tilt angle but that the director changes discontinuously from block to block giving an optical discontinuity which forms the outline of each block. In plane-polarized light they would then give the usual pattern of mosaic blocks of different interference colors which show extinction at different stage positions. The tilt angle of smectic *B* probably remains the same as at the end of the smectic *C* range, namely, 26°. We could not determine the tilt angle of smectic *B* by our previous method[2] because we could not obtain the center of the interference figure in the field of view. Thus the tilt angle must certainly be less than 35°.

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*Research supported in part by the National Aeronautics and Space Administration under Contract No. NGR-36-007-025.

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[2] T. R. Taylor, J. L. Fergason, and S. L. Arora, Phys. Rev. Lett. $\underline{24}$, 359 (1970).

[3] T. Preston, *The Theory of Light* (Macmillian, London, 1928), 5th ed.

LOW-TEMPERATURE BEHAVIOR FOR THE QUANTUM VIRIAL COEFFICIENTS*

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The low-temperature behavior of all the quantum cluster integrals b_l is calculated by using a perturbation scheme in which a hyperspherical representation for the many-body problem is used. Definitions of the usual equations for the *T*, *R*, and *S* scattering matrices as well as the many-body eigenphase shift are given. The technique for calculating the energy eigenvalues is outlined and a relationship between the level shift and the eigenphase shift is given. It is found that for an everywhere-finite short-ranged potential without bound states, b_l behaves as a polynomial in $\lambda = h/(2\pi mkT)^{1/2}$ in the low-temperature limit.

We would like to report a new method of calculating the low-temperature behavior of the quantum virial coefficients[1] which involves a perturbation scheme based on representation in terms of hyperspherical coordinates.[2]

We consider first the canonical transformation

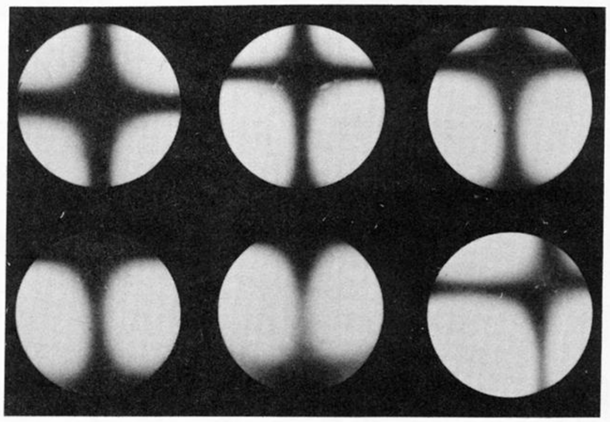
$$\vec{Q} = \mathcal{O}\vec{q}, \quad \vec{P} = \mathcal{O}m\dot{\vec{q}},$$

where $\vec{q}$ and $m\dot{\vec{q}}$ are the standard vectors in a $3N$-dimensional phase space which specify the position and momentum, respectively, of the system composed of N particles of mass m, and where $\mathcal{O}$ can be chosen as

$$\mathcal{O} = \begin{bmatrix} N^{-1/2} & N^{-1/2} & N^{-1/2} & N^{-1/2} & \cdots & N^{-1/2} \\ -(2^{-1/2}) & -(2^{-1/2}) & 0 & 0 & \cdots & 0 \\ -(6^{-1/2}) & -(6^{-1/2}) & (\frac{2}{3})^{1/2} & 0 & \cdots & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ -[N(N-1)]^{-1/2} & -[N(N-1)]^{-1/2} & -[N(N-1)]^{-1/2} & -[N(N-1)]^{-1/2} & \cdots & [(N-1)/N]^{1/2} \end{bmatrix}$$

(The component $\vec{q}_l$ of the vector $\vec{q}$ specifies the position vector of the particle l.)

We factor out the coordinates of the center of mass and write $\vec{r}$ and $\vec{p}$ for the new reduced canonical vectors. We then introduce hyperspherical coordinates where a vector is specified by its modulus and



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