Optical and X-ray Studies on the Twisted Smectic C and Twisted Nematic Phases: Evidence for a Skew-Cybotactic Type of Cholesteric Structure

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Optical and X-ray Studies on the Twisted Smectic C and Twisted Nematic Phases

Evidence for a Skew-Cybotactic Type of Cholesteric Structure

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The optical rotation ρ and the pitch P of mixtures of *p-n*-heptyloxyazoxybenzene and cholesteryl benzoate have been measured as function of temperature in the twisted smectic C and the twisted nematic phases for two compositions (10 % and 15 % of cholesteryl benzoate by weight). Both ρ and P change discontinuously at the twisted smectic C–twisted nematic point, the values being higher in the lower-temperature phase. The birefringence δn of pure HOAB has also been determined in the nematic and smectic C phases.

The observed ρ in the twisted nematic phase cannot be accounted for in terms of the measured values of δn and P. The calculated value is too high indicating that, in contrast to the classical cholesteric structure, the molecules in this phase are not normal but inclined with respect to the helical axis. This has been confirmed directly by X-ray studies; the diffraction pattern has an inner ring characteristic of a skew-cybotactic structure with a tilt angle of 39° with respect to the layer normal. However the calculated rotatory power for such a structure turns out to be only about 0.5 of the observed value. The discrepancy decreases slightly with increasing sample thickness suggesting that it may be due to a boundary layer in which the molecules tend to align themselves parallel to the glass surface.

INTRODUCTION

Saupe[1] pointed out that the smectic C phase bears some similarities with the nematic in regard to its elastic properties and that there should therefore exist a twisted form of this structure resembling the twisted nematic or cholesteric phase. Subsequent studies[2–4] have established the occurrence of the twisted smectic C modification in mixtures as well as in pure compounds. Figure 1 gives a schematic representation of the structure. Optical rotatory
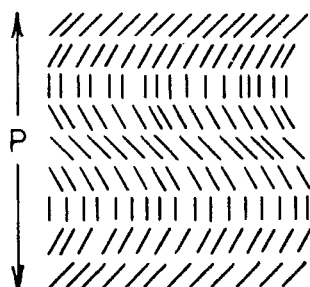
FIGURE 1   A schematic diagram of the twisted smectic *C* phase.

power measurements on the twisted smectic C (TSC) and twisted nematic (TN) phases of a mixture of bis-(4'-*n*-decyloxybenzal) 2 chloro-1-4-phenyl-enediamine and cholesteryl cinnamate have been reported by Brunet.[5] We present here detailed optical and X-ray studies on the TSC and TN phases of a mixture of 4,4'-di-*n*-heptyloxyazoxybenzene (HOAB) and cholesteryl benzoate (CB) for 2 compositions (0.9 HOAB + 0.1 CB and 0.85 HOAB + 0.15 CB by weight). The results show that the TN phase of the mixture has a skew-cybotactic structure in which the molecules are tilted with respect the helical axis, and not normal to it as in the classical cholesteric.

The differential scanning calorimetric (Perkin Elmer DSC-2) traces showing the smectic C–nematic and nematic–isotropic transitions in pure HOAB and the TSC–TN and TN–isotropic transitions in the HOAB-CB mixtures are shown in Figure 2. As can be seen the transitions are all of first order.

Optical measurements

Optical rotatory power   The optical rotatory power as a function of temperature was measured for both mixtures using a standard polarimetric arrangement (Model No. 103071, Winkel Zeiss, Gottingen) and a sodium lamp (λ = 589.3 nm). Thin films of the sample were prepared between two optically flat ($\lambda/5$) glass plates with mylar spacers (~ 6.4 μm). The actual sample thickness was measured by the channelled spectrum technique to an accuracy $\pm 2\%$. The sample temperature was maintained by an electrically controlled heater and measured to $\pm 0.1°C$ by means of a previously calibrated constantan-chromel thermocouple. In the TN phase, well aligned plane texture films could easily be obtained in the usual manner by mechanical displacement of the upper glass plate. In the TSC phase this method did not work satisfactorily; an aligned film could be obtained only by slow cooling of a plane texture TN film, but the alignment was not as perfect as in the TN phase. The uncertainty in the optical rotation measurement was therefore somewhat larger for the TSC phase ($\pm 3\%$ as compared with
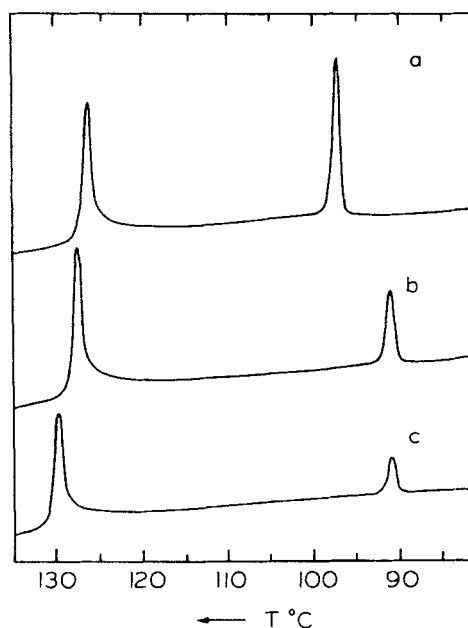
FIGURE 2   Differential scanning calorimeter traces showing (a) the smectic C–nematic and nematic–isotropic transitions for HOAB, (b) & (c) the twisted smectic C–twisted nematic and twisted nematic–isotropic transitions for the 0.9 HOAB + 0.1 CB and 0.85 HOAB + 0.15 CB mixtures respectively.

$\pm 0.5\%$ for the TN phase). The experimental data are given in Figures 3 and 4. The sign of optical rotation is negative in all cases.

Pitch   The pitch (P) measurement was carried out by the "oblique reflection" method developed by Fergason.[6] The sample was sandwiched between two glass plates, the lower one being coated with aluminium to make it highly reflecting. The method allows one to determine pitch values higher than λ provided the helical axes of the reflecting domains are aligned approximately parallel to the substrate. However, it is more suitable for materials whose birefringence is small whereas in the present case the birefringence is large. It was found that the reflection is not sharp, but still measurements were possible both in the TSC and TN phases. The observed pitch as a function of temperature are presented in Figures 5 and 6. The pitch in the TN phase was also measured by recording the transmission through a plane texture film using a Leitz double beam IR spectrophotometer (Model 081). When $\lambda = nP$ there is a diminution in the transmitted intensity. This technique yields a more precise estimate of the pitch. These experimental values are also given in Figures 5 and 6.
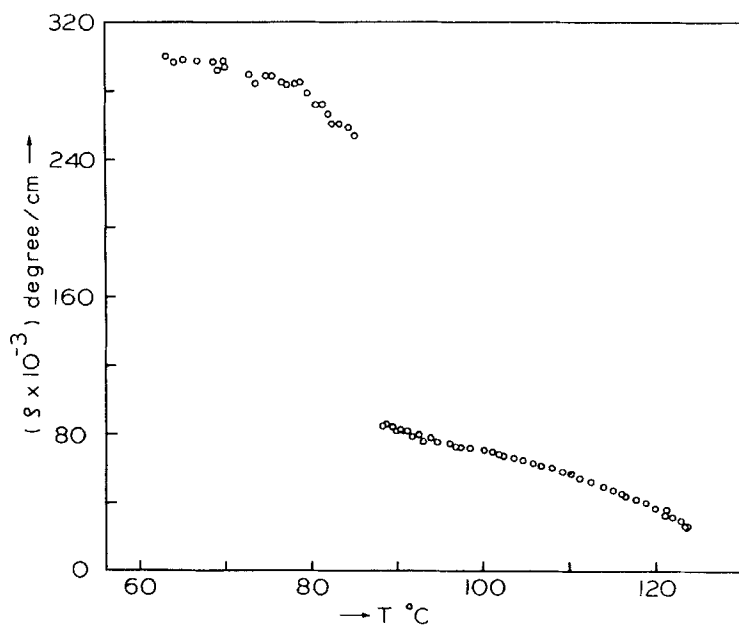
FIGURE 3   Optical rotatory power as a function of temperature for a mixture of 0.9 HOAB + 0.1 CB.
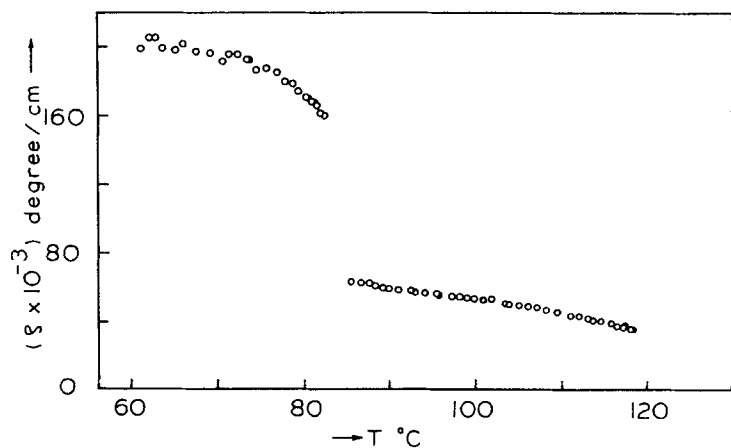
FIGURE 4   Optical rotatory power as a function of temperature for a mixture of 0.85 HOAB + 0.15 CB.
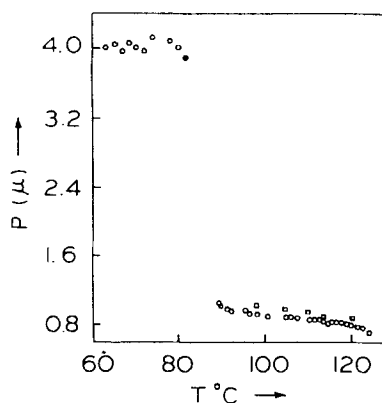
FIGURE 5 Pitch as a function of temperature for a mixture of 0.9 HOAB + 0.1 CB. Circles represent the data obtained by the oblique reflection method and squares by the infrared transmission method.

Birefringence The birefringence of pure HOAB was determined in the nematic and smectic C phases by measuring the phase retardation of a sample of known thickness using a Babinet compensator. The sample was taken between two optically flat glass plates which were cleaned thoroughly and given a very thin aluminium coating to eliminate wall effects. The sample was aligned by a magnetic field of strength 7.5 kG and all measurements were made in the presence of the field after the specimen had remained in it for 2 hours. A spacer of thickness ~38 μm was used, but the actual sample thickness was measured by the channelled spectrum technique. Figure 7 shows the experimental values.
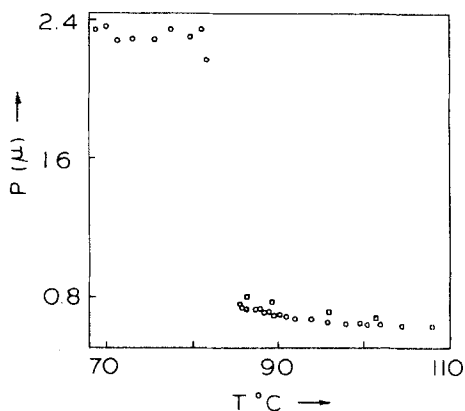
FIGURE 6 Pitch as a function of temperature for a mixture of 0.85 HOAB + 0.15 CB (see legend of Figure 5).
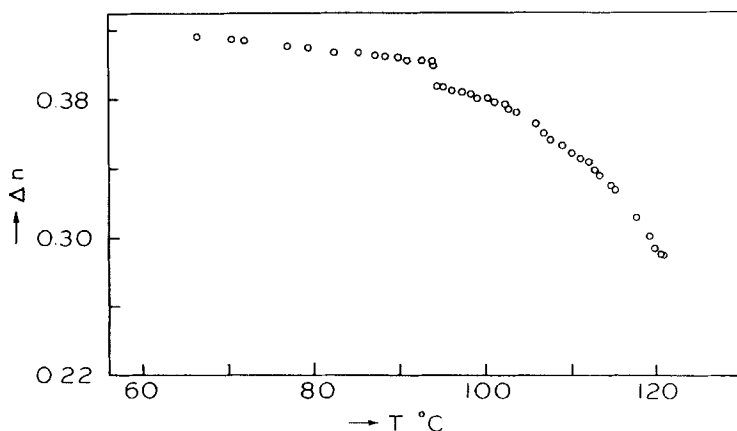
FIGURE 7   Birefringence versus temperature for pure HOAB oriented in a magnetic field.

Using the observed values of P, taking the birefringence of cholesteryl benzoate to be 0.05 and assuming a simple additivity law for the birefringence of the mixture, the rotatory power ρ of the TN phase was calculated using the rigorous equation[7]

$$\rho = \frac{\pi}{P}\left(2 + \frac{m'_1 - m'_2}{\lambda'}\right), \tag{1}$$

where

$$\lambda' = \frac{\lambda}{P[\frac{1}{2}(n_1^2 + n_2^2)]^{1/2}},$$

$$m'_1 = [1 + \lambda'^2 - (4\lambda'^2 + \alpha^2)^{1/2}]^{1/2},$$

$$m'_2 = [1 + \lambda'^2 + (4\lambda'^2 + \alpha^2)^{1/2}]^{1/2},$$

$$\alpha = \frac{n_e^2 - n_0^2}{n_e^2 + n_0^2},$$

n_e and n_0 are principal refractive indices of the layer and λ is the wavelength of light in vacuum. It was found that (1) gave a rotatory power which was nearly twice the experimental value. This indicated that the molecules are probably not normal to the helical axis (as in the usual cholesteric) but tilted (as in the TSC) resulting in a reduction of the effective birefringence for this direction of propagation. X-ray studies were undertaken to verify this conclusion.
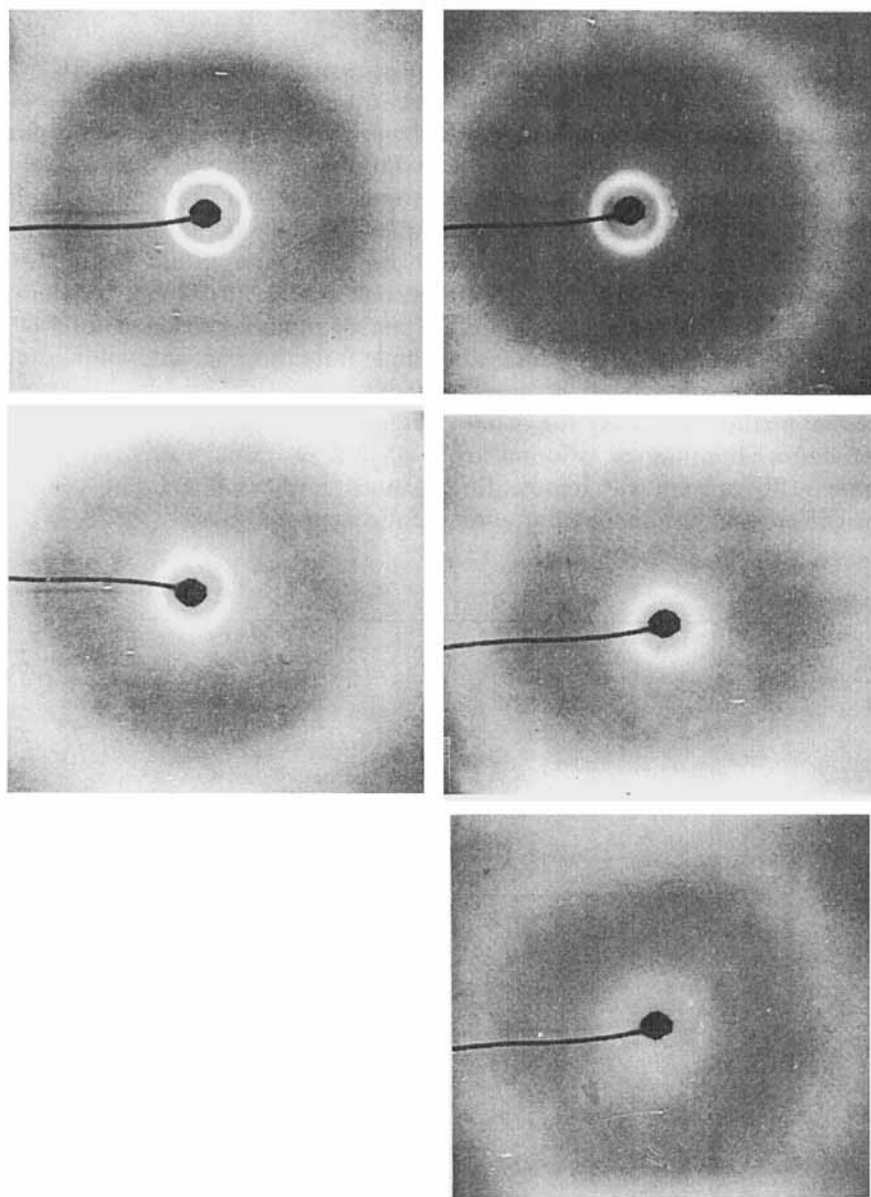
FIGURE 8   X-ray diffraction patterns for unaligned samples. Pure HOAB in the smectic C phase (top left) and in the nematic phase (bottom left). The 0.9 HOAB + 0.1 CB mixture in the twisted smectic C phase (top right), twisted nematic phase (middle right) and isotropic phase (bottom right). The spots in the photographs on the right are due to the sample holder.

X-ray studies

X-ray diffraction photographs of randomly oriented samples of pure HOAB and of the mixtures were taken at different temperatures using Ni-filtered CuK_α radiation. The specimen was in the form of a free film about 2 mm diameter on a loop of wire and its temperature was controlled by a suitably designed heater. The diffraction photographs are shown in Figure 8. In all cases, there occurs a relatively intense inner ring and a faint outer ring. For the smectic C phase of pure HOAB and the TSC phase of the mixture, the inner ring is quite sharp as would be expected of a smectic layered structure. Taking the molecular length to be 33 Å,[8] the tilt angle is calculated to be 44° and 41.5° respectively and practically temperature independent within each phase. On the other hand for the nematic phase of HOAB and the TN phase of the mixture, the inner ring is more diffuse, characteristic of a cybotactic structure. The tilt angle is found to be 41° and 39° respectively, and again practically constant with temperature. A much more weak and diffuse inner ring is present even in the photograph of the isotropic phase.
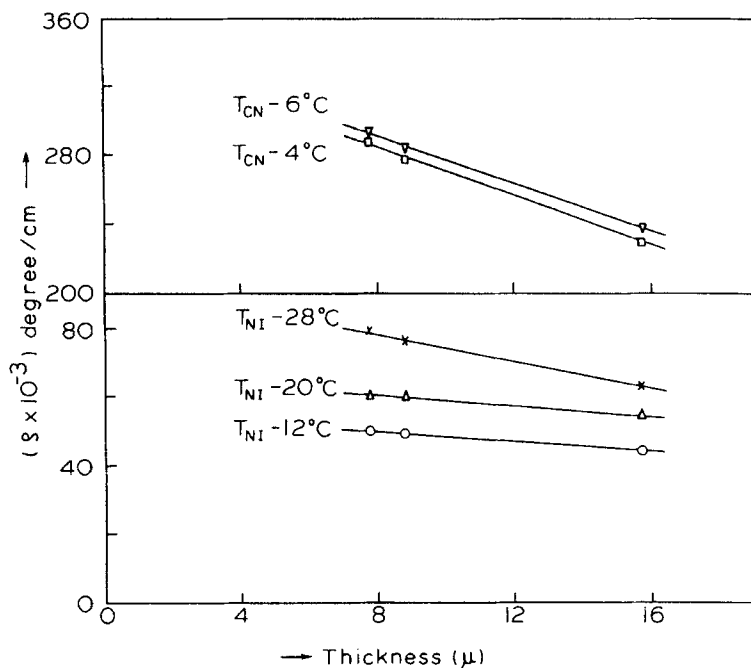

FIGURE 9   Optical rotatory power as a function of thickness for the 0.9 HOAB + 0.1 CB mixture.

Discussion

On the basis of this evidence, the theoretical rotatory power of the TN phase was recalculated taking the molecules to be tilted at 39° to the helical axis. The effective birefringence for propagation along the helical axis was evaluated from the well known equation:

$$\frac{1}{n^2} = \frac{\cos^2 \theta}{n_0^2} + \frac{\sin^2 \theta}{n_e^2} \tag{2}$$

where θ is the tilt angle with respect to the helical axis. It was assumed that $n_0 = 1.55$ which is the approximate value of the ordinary index for p-azoxy-anisole and other similar compounds. Surprisingly, the theoretical value now turned out to be only about 0.5 of the observed value. A similar discrepancy was found for the TSC phase also. Measurements on samples of different thicknesses showed that the rotatory power (i.e., the rotation per unit thickness) decreases with increasing thickness suggesting that there may be a boundary layer effect (Figure 9). It seems possible that near the boundary the molecules tend to align parallel to the glass surfaces, thus enhancing the effective optical rotation. This may partly account for the discrepancy between the experimental and calculated values.

Despite this difficulty, the optical evidence together with the X-ray results appear to show fairly conclusively that the twisted–nematic phase of the mixture has a structure quite different from the usual cholesteric in that the molecules are not normal but tilted with respect to the helical axis.

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