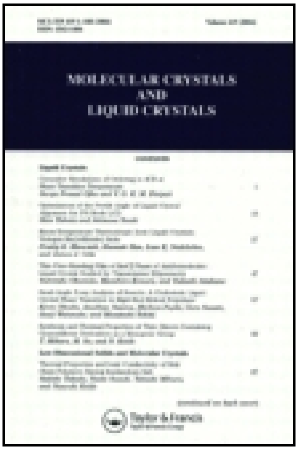

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Optical Anisotropy of Cholesteryl Oleyl Carbonate

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Density and refractive index data of cholesteryl oleyl carbonate in the smectic, cholesteric and isotropic phases are reported and the effective principal polarizabilities in the cholesteric and smectic phases are calculated and correlated. There is a systematic decrease in the effective optical anisotropy with increase in temperature owing to the decrease in orientational order.

INTRODUCTION

In the following are discussed the results of measurements on the refractive indices of cholesteryl oleyl carbonate (COC) which exhibits the smectic A and cholesteric phases, the smectic-cholesteric transition point being 15.5°C and the cholesteric-isotropic transition point being 28°C. The COC used here was obtained from M/s E. Merck, West Germany and the purity of the sample is quoted as better than 98%. Owing to the limited quantity of the substance available, no further purification of the substance was attempted. Refractive indices of cholesteryl oleyl carbonate in the cholesteric and isotropic phases had been earlier determined by Adamski and Dylik-Gromiec [1-3] using an Abbe refractometer. However, they have not reported any index data in the smectic mesophase. Here, the present authors report the density and the index data for the smectic, cholesteric and isotropic phases. It may be remarked that the index data for the liquid and cholesteric phases reported by Adamski and Dylik-Gromiec[1,2] are for white light. Our data obtained for sodium light (5893 Å) are in reasonable agreement, indicating that the samples are of comparable purity. The values of the refractive indices are correct to within ±0.0005. The experimental data are analysed in the following to correlate the effective principal polarizabilities of cholesteryl oleyl carbonate in the cholesteric and smectic mesophases.

EXPERIMENTAL DETERMINATION OF REFRACTIVE INDICES AND DENSITIES

The density measurements for the specimen were carried out at different temperatures between 4 and 45°C using a density bottle of volume about 3 cc and by making measurements of the mass of the sample and that of water (as the standard substance) at each temperature. The variation of the density as a function of temperature, is shown in Figure 1. The experimental values are correct to ±0.0005. It is surprising that the values of the densities do not show discontinuities at the phase transitions. This feature may be explained tentatively on the basis that owing to the flexible nature of the end chains the close packing of the molecules in the different phases corresponds to the same packing fraction. The agreement between the calculated values of the mean polarizability $\overline{\alpha}$ in Table II provides indirect support to the genuine nature of the variation of density.

The refractive indices were measured using an Abbe refractometer in which the temperature could be controlled by circulation of water. The measurements of the temperature were carried out using a calibrated thermocouple and the values of the temperatures were correct to within ±0.2°C.

Adamski and Dylik-Gromiec refer to the indices of the cholesteric phase as extraordinary and ordinary, n_e and n_o respectively. However, here we avoid the use of such a notation for the cholesteric phase, because the so called "ordinary" refractive index (in the case of a oriented sample) is variable depending upon the direction of the electric vector relative to the long axes of the molecules within the cholesteric layers. We prefer to use the notation (n_1 and n_2) used by Pelzl and Sackmann.[5] In order to facilitate the interpretation of the data, the optics involved in the experimental determination is discussed here in some detail.

As is well-known, the specimen is sandwiched between two right angled prisms of the Abbe refractometer (Figure 2). The following remarks refer to the cholesteric phase which is considered first. For angles of incidence greater than the critical angle, the beam does not enter the specimen, but is totally reflected backwards. On the other hand, the beam which is incident at an angle slightly less than the critical angle propagates through the specimen almost tangentially in the plane of the thin specimen before emerging into the top prism (see Figure 2). Associated with the propagation of light in the plane of the specimen i.e., normal to the optic (helical) axis, there are two refractive indices n_1 and n_2 respectively, (i) for the electric vector lying in the plane of the specimen and (ii) for the electric vector along the helical axis (normal to the thin specimen). In the cholesteric phase the long axes of the molecules are lying approximately in the plane of the thin layer and normal to helical axis so that n_2 will clearly involve $\alpha_\perp$, the polarizability transverse to the long axes of the molecules. On the other hand, for propagation of light normal to the helical axis (Z), with the electric vector transverse to the helical axis, the refractive

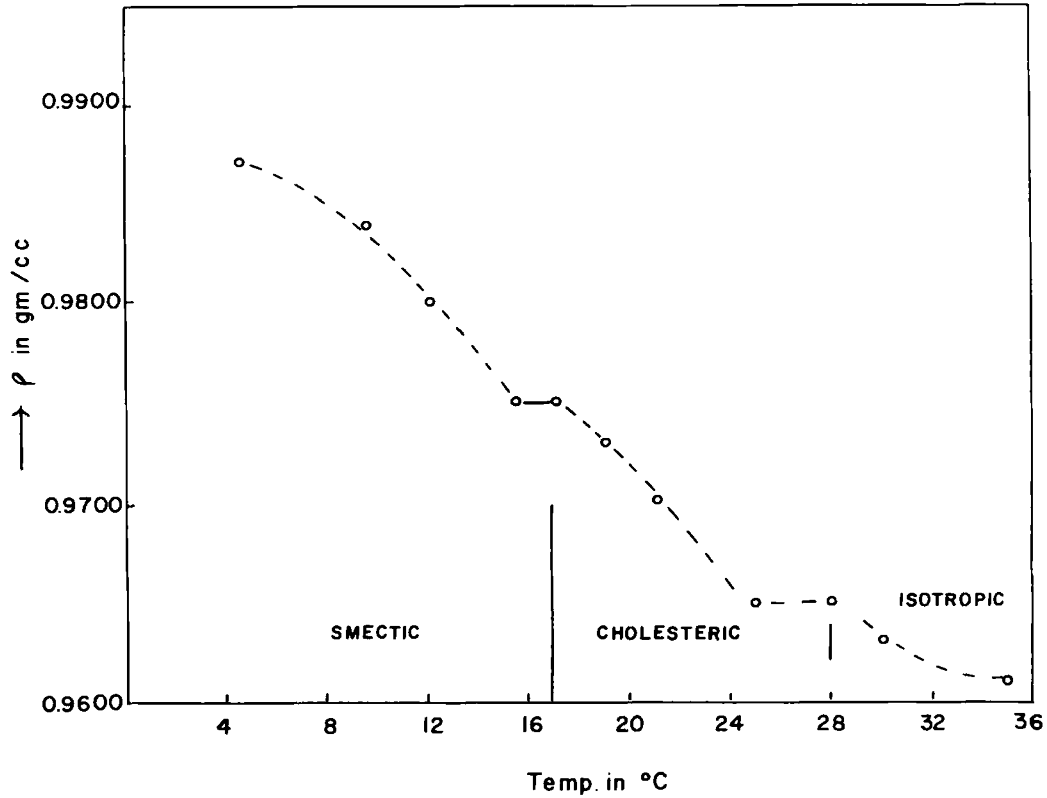

FIGURE 1 Variation of the density of cholesteryl oleyl carbonate with temperature.

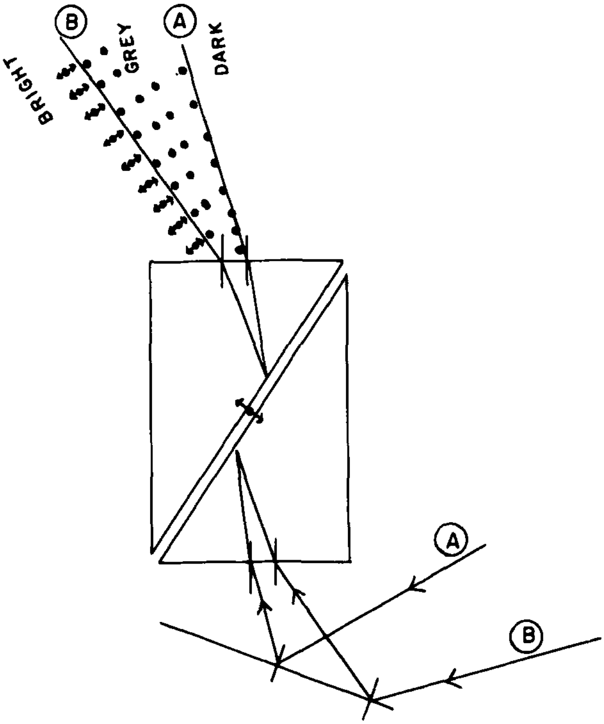

FIGURE 2 Trajectory of the rays close to critical reflection in the Abbe refractometer, when the substance is in the cholesteric phase. The boundaries corresponding to the critical reflections for indices n_1 and n_2 ($n_1 > n_2$), are marked as A and B.

index is a periodic function of Z, varying between n_2 and n_3. The refractive index will be n_3 for propagation along a layer in which the mean direction of the long axes (director) coincides with the direction of the electric vector which lies in the plane of the layer. The index will be n_2 for propagation along a layer in which the director is transverse to the electric vector in the plane of the layer. In general, the thickness of the specimen has a magnitude which is roughly of the order of the pitch of the helical structure. Owing to the rotation of the director in successive layers, the effective refractive index n_1 associated with the propagation of light (with electric vector lying in the plane of the specimen) will have an average value lying between n_2 and n_3, and will involve a combination of $\alpha_{\parallel}$ and $\alpha_{\perp}$ (the principal polarizabilities parallel and perpendicular to the long axis of the molecule). From the foregoing, it is evident that n_1 will be greater than n_2. In fact, the circular field of view of the eye-piece is traversed by two boundaries which respectively separate a relatively dark region from a grey region and the grey region from a bright region as shown in Figure 2. The light emerging out of the grey region was found to be plane polarized with its vibration direction as shown in Figure 2, as could be verified by using an analyzer. This indicated that the boundary between the dark and the grey regions corresponded to the limit at which total internal reflection occurred for polarized light with electric vector lying in the plane of the thin specimen. The measured value of the index corresponds to n_1, the greater of the two indices. On the other hand, the boundary between the bright and the grey region is one which leads to a lower value of the refractive index and corresponds to n_2. Although the polarization effects at the boundaries had been reported by the earlier investigators,[1-4] the interpretation of the effects was not discussed in detail.

In the smectic phase, only one boundary of critical reflection was observable, corresponding to the refractive index n_0 associated with the ordinary vibration. Owing to the formation of textures, it appears that the boundary of critical reflection corresponding to the extraordinary vibration becomes too diffuse to be observable. The values of the refractive indices at different temperatures are shown in Table I. It may be remarked that at temperatures near the smectic-isotropic transition, the values of the different indices satisfy the following relations, viz., $n_2 \approx n_0$ and $n_1 \approx (n_e + n_0)/2$, (see for example, Pelzl and Sackmann[5] and Dreher and Meier[6]).

CALCULATION OF THE POLARIZABILITIES AND DISCUSSION

The mean polarizability of COC in the isotropic phase is calculated from the refractive index for the liquid phase, using the well-known Lorenz-Lorentz relation viz.,

$$\bar{\alpha} = \frac{3}{4\pi N}\left(\frac{n^2 - 1}{n^2 + 2}\right). \tag{1}$$

TABLE I

Refractive indices of cholesteryl oleyl carbonate in smectic, cholesteric and isotropic phases for the wavelength λ 5983 Å

Temperature in °C	Refractive index	
Smectic:		n_o
10		1.4880
12		1.4900
14.5		1.4915
15.5		1.4915
Cholesteric:	n_1	n_2
17	1.5186	1.4910
19	1.5172	1.4905
20.5	1.5150	1.4900
22	1.5109	1.4900
23	1.5098	1.4900
28	1.5090	1.4900
Isotropic:	n	
30	1.5029	

Here, $\bar{\alpha} = (\alpha_{\parallel} + 2\alpha_{\perp})/3$. From the index data of the smectic phase[5] of a number of cholesteryl compounds, it was found by Subramhanyam and Krishnamurti[7] that the anisotropy of the Lorentz field factors in the case of cholesteryl compounds is very small. In the cholesteric phase, the molecules in successive cholesteric layers are not exactly parallel to one another, because of the rotation of the director about the axis of the helical structure. Under the circumstances, it was found by them that for the cholesteric phase, it was a reasonably good approximation to assume that the Lorenz-Lorentz relations given below are valid for the indices n_1 and n_2.

$$\alpha_1 = \frac{3}{4\pi N}\left(\frac{n_1^2 - 1}{n_1^2 + 2}\right) \tag{2}$$

$$\alpha_2 = \frac{3}{4\pi N}\left(\frac{n_2^2 - 1}{n_2^2 + 2}\right). \tag{3}$$

Here, α_1 and α_2 are the effective average polarizabilities calculable from the indices n_1 and n_2 for vibrations in the plane of the cholesteric layer and normal to it respectively and N is the number of molecules per unit volume.

In the smectic phase, it was possible to determine only the ordinary index n_o. Here, the Neugebauer relations, which require data on the extraordinary index also, could not be made use of to calculate the effective polarizability. Therefore, the Lorenz-Lorentz relation viz., $(n_o^2 - 1)/(n_o^2 + 2) = 4\pi N\alpha_o/3$, was applied, assuming that the anisotropy of the Lorentz field factors is small. The effective polarizability calculable from n_o is referred to as α_o here.

In the cholesteric phase, the values of n_2 give the effective polaribility α_2 of the molecules for vibrations along the helical axis of the cholesteric specimen, the long axes of the molecules here being nearly transverse to the helical axis. In the smectic phase, the effective polarizability α_o corresponds to the case where the electric vector is transverse to the optic axis which is the mean direction of the long axes of the molecues. Therefore, the values of α_o and α_2 should be nearly equal. There is reasonably good agreement between the two sets of values as may be seen from column 2 of Table II.

Further, it is easily proved that

$$\alpha_e + 2\alpha_o = \alpha_{\parallel} + 2\alpha_{\perp} = 3\bar{\alpha} \tag{4}$$

and

$$\alpha_2 + 2\alpha_1 = \alpha_{\parallel} + 2\alpha_{\perp} = 3\bar{\alpha}. \tag{5}$$

This is consistent with the requirement that the mean polarizability should remain a constant, so long as there are no changes in the electronic structure of the molecules. In the cholesteric phase, $\bar{\alpha}$ is calculated using the values of α_2 and α_1. There is good agreement between the values of $\bar{\alpha}$ in the cholesteric and isotropic phases as may be seen from Table II. It may be noticed from Table II

TABLE II

Calculated values of polarizabilities in smectic, cholesteric and isotropic phases, using Lorenz-Lorentz relation.

Temperature in °C	Polarizability in units of 10^{-24} cm^3			
Smectic:	α_o	α_e	$\alpha_e - \alpha_o$	
10	75.6	86.2	10.6	
12	76.1	85.1	9.0	
14.5	76.6	84.2	7.6	
15.5	76.7	83.9	7.2	
Cholesteric:	α_2	α_1	$\alpha_1 - \alpha_2$	$\bar{\alpha}$
17	76.6	80.3	3.7	79.1
19	76.7	80.3	3.6	79.1
20.5	76.8	80.1	3.3	79.0
22	77.0	79.8	2.8	78.9
23	77.1	79.8	2.7	78.9
28	77.3	79.9	2.6	79.0
Isotropic:				
30	—	—	—	79.1

Note: α_e is calculated from $\bar{\alpha}$ and α_o using Eq. 4.

that $(\alpha_e - \alpha_o)$ and $(\alpha_1 - \alpha_2)$ decrease with increase of temperature. This feature has its origin in the increase of the thermal fluctuation in the orientation of the molecules with increase of temperature. In our discussion here, we have tacitly assumed that the molecules are rigid. However, the molecules have some flexibility associated with the methylene end-chains in them. The net orientational order and the effective optical anisotropy are determined by the effects arising from the fluctuations in the orientation of the rigid and flexible portions of the molecules. Hence, the calculations of the order parameter also become a complex problem. Owing to the flexible nature of the end-chains, the values of $\alpha_\parallel$ and $\alpha_\perp$ may depend on temperature. The rapid decrease of α_e in the smectic phase is a noteworthy fact in this context. However the mean polarizability is a constant since it is only a sum of the isotropic bond polarizabilities.

Acknowledgments

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