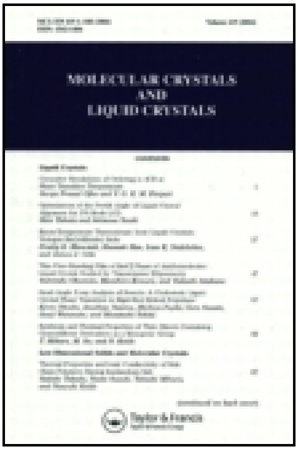

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Refractive Indices, Densities and Optical Anisotropy of Cholesteryl Oleate

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Refractive Indices, Densities and Optical Anisotropy of Cholesteryl Oleate

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

Keywords: birefringence, polarizabilities, optical anisotropy

INTRODUCTION

There have been several studies on cholesteric esters. Earlier investigators[1–2] have carried out X-ray diffraction studies on cholesteryl esters and in particular Albertini *et al.*[3] have studied cholesteryl oleate (CO). Armitage[4] has reported blue phase and four solid phases in CO. Small and co-workers[5] have investigated the presence of cholesteryl esters in alpha and beta serum lipoproteins and in the lipids of the altherosclerosis. The present paper reports the results of measurements on the refractive indices of cholesteryl oleate which exhibits the smectic A and cholesteric phases.

EXPERIMENT

Before doing refractive index and density measurements, we have performed DTA and X-ray diffraction studies of cholesteryl oleate which has a 98% purity. The cholesteryl oleate used here was obtained from M/s E Merck, West Germany. Owing to the limited quantity of the substance available, no further purification of the substance was attempted. DTA recording of cholesteryl oleate indicating solid–isotropic transition (heating curve) was obtained. No 'blue phase' transitions were clearly visible. The obtained transition temperature is slightly lower as compared to reported DSC studies of cholesteryl oleate,[4] as a consequence of lower purity of the sample. ΔH obtained from the above DTA recording and the transition temperatures obtained using Leitz Orthoplan microscope in conjunction with a hot stage are given in Table I along with the values obtained by earlier investigators. A satisfactory agreement exists concerning transition enthalpy and transition temperatures with the earlier reported data.

XRD recordings of the sample (JEOL JAPAN) at various temperatures were obtained and the value of 'd', the Bragg spacing obtained from the lower angle of the present XRD recording in smectic phase is 39.6 Å and the factor $Q(=4\pi \sin \theta/\lambda)$ varies between 0.16 to 0.2 in cholesteric phase with temperture. These are in agreement with the extensive observations made by Albertini *et al.*[3]

The density measurements for the specimen were carried out at different temperatures between 17 and 50°C by the capillary method while the sample was being cooled.[6] The experimental values are correct to ±0.001. The variation of the density as a function of temperature is shown in Figure 1. It is surprising that the values of the densities do not show any discontinuities at the phase transitions. This feature may be explained tentatively by assuming 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

TABLE I

Measured enthalpy and observed transition temperatures of cholesteryl oleate

	Present		Reported (4,5)	
Phase transition	ΔH in Kcal/mole	T in °C	ΔH in Kcal/mole	T in °C
Solid–Isotropic	$6.50 + 0.2$	45.0	6.64 ± 0.33	46.8
Smectic A–Solid	—	17.0	—	—
Cholesteric–Smectic A	—	35.0	0.23 ± 0.02	39.2
Isotropic–Cholesteric	—	45.0	0.13 ± 0.02	44.6

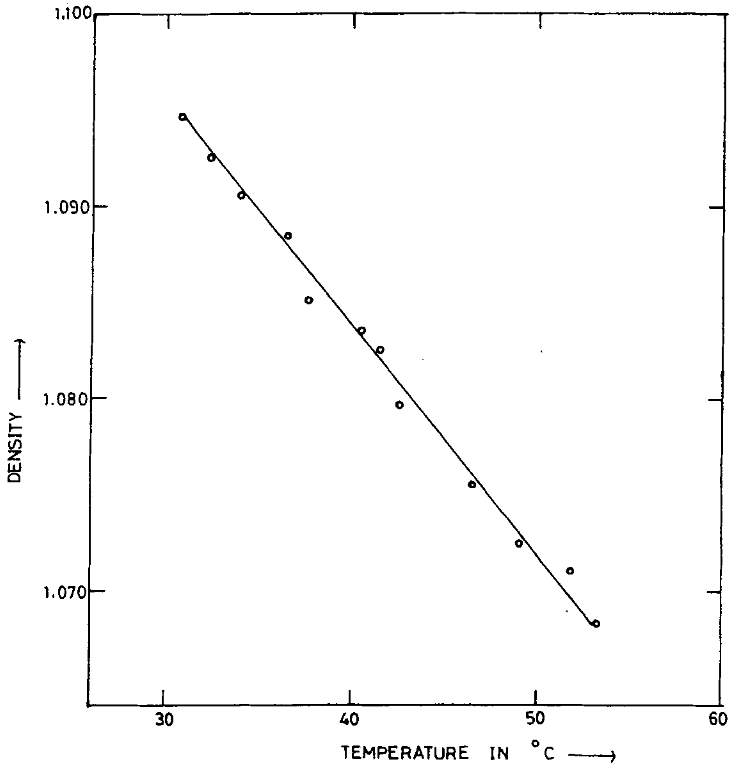

FIGURE 1 Variation of density with temperature.

($\bar{\alpha}$) in Table II, provides indirect support to the genuine nature of the variation of density.

The refractive indices were measured using an Abbe refractometer for various temperatures from 17 to 50°C for 5893 Å the temperature having been controlled by circulation of water.[7] Prior to using the sample for measurements it was melted to isotropic phase and then cooled to room temperature. The measurements of the temperature were carried out using a calibrated thermometer and the values of the temperatures were read correct to ±0.2°C. The method used for orientation of the sample in the smectic phase is the same as described in an earlier paper.[8] In smectic phase we have two indices n_e and n_o ($n_e > n_o$) for electric vector parallel and perpendicular to the mean direction of the long axes of the molecules respectively. In cholesteric phase we have two indices n_1 and n_2 ($n_1 > n_2$) for electric vector perpendicular and parallel to the helical axis. The measured indices are given in Figure 2 for smectic, cholesteric and isotropic phases.

TABLE II

Calculated values of polarizabilities (in units of 10^{-24} cm^3) in Smectic A, Cholesteric and Isotropic phases, using Lorenz–Lorentz relation

Temp in °C	α_e	α_o	$\alpha_e - \alpha_o$	$\bar{\alpha}$
Smectic A				
17.0	71.14	69.08	2.06	69.77
20.0	70.99	69.13	1.86	69.75
22.0	70.93	69.19	1.73	69.78
24.0	70.87	69.27	1.59	69.81
26.0	70.84	69.35	1.49	69.85
28.0	70.84	69.44	1.39	69.90
30.0	70.88	69.59	1.29	70.02
34.0	70.71	69.72	0.99	70.05
Cholesteric				
36.0	70.75	69.73	1.02	70.07
38.0	70.17	69.75	0.43	69.89
40.0	69.96	69.79	0.17	69.84
42.0	69.92	69.85	0.07	69.87
Isotropic				
46.0	—	—	—	69.91
50.0	—	—	—	70.04

The refractive indices are accurate to within ±0.0005. It may be remarked that at temperatures near the smectic–cholesteric transition, the values of the different indices satisfy the following relations viz., $n_2 \approx n_o$, and $n_1 \approx (n_e + n_o)/2$ (see also Ref. 9 and 10).

CALCULATION OF THE POLARIZABILITIES AND DISCUSSION

Subramhanyam *et al.*[11] have shown that the anisotropy of the Lorentz field factors in the case of cholesteryl compounds is very small. Under these circumstances, it is a reasonably good approximation to assume that the Lorenz–Lorentz relations given below are valid for both smectic and cholesteric phases,

$$\alpha_i = 3(n_i^2 - 1)/4\pi N(n_i^2 + 2) \qquad \begin{aligned} i &= e, o \text{ (smectic)} \\ &= 1, 2 \text{ (cholesteric)}, \end{aligned} \qquad (1)$$

where 'N' is the number of molecules per unit volume. Here, α_e and α_o are the effective polarizabilities calculable from n_e and n_o of smectic phase for electric vectors parallel and perpendicular to the optic axis. α_1 and α_2 are the effective polarizabilities calculable from n_1 and n_2

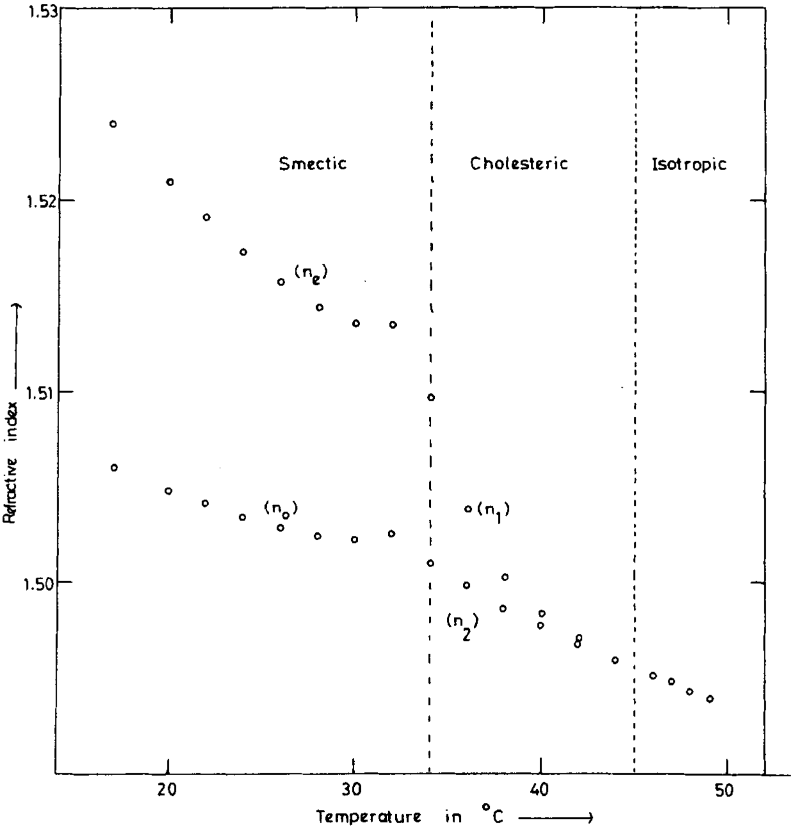

FIGURE 2 Variation of refractive indices with temperature.

of cholesteric phase for electric vector perpendicular and parallel to the helical axis. α_2 is α_o, since the long axes of the molecules are nearly transverse to the helical axis. Therefore the values of α_o and α_2 should be nearly equal. There is a reasonably good agreement between the two sets of values (smectic and cholesteric) as seen from Table II.

Further it is easily proved that

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

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

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 cholesteric phase $\bar{\alpha}$ is calculated using α_1 and α_2. There is a good agreement between the values of $\bar{\alpha}$ in the cholesteric and smectic and also in isotropic phases, as may be seen in Table II. Since α_2 is α_o, α_e in cholesteric phase can be calculated from equation (3). It may be noticed from Table II that $(\alpha_e - \alpha_o)$ decreases with increase of temperature. This feature has its origin in the increase of the thermal fluctuations 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 effective optical anisotropy is determined by the effects arising from the fluctuations in the orientation of the rigid and flexible portions of the molecules. Owing to the flexible nature of the end chains, the values of $\alpha_\parallel$ and $\alpha_\perp$ may depend on temperature. The decrease of α_e in the smectic phase is a noteworthy fact in this context. However, the mean polarizability is constant since it is only a sum of the isotropic bond polarizabilities.

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