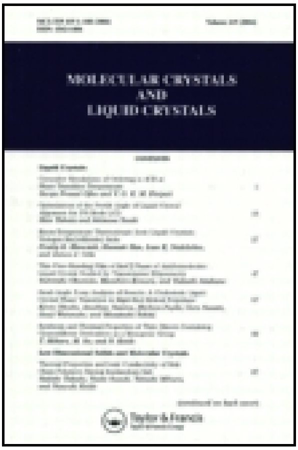

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Measurement of the Refractive Index and Estimate of the Order Parameter in Oriented Liquid Crystals

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Measurement of the Refractive Index and Estimate of the Order Parameter in Oriented Liquid Crystals

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The refractive indices of a cholesteric liquid crystal, cholesteryl dodecyl carbonate (CDC), and a smectic liquid crystal, *p*-*n*-octoxybenzilidene-*p*-*n*-butylaniline (OOBBA), have been measured as a function of temperature in the transition temperature regions. The measurements were made on oriented liquid crystals with an Abbe refractometer. By combining the data on ordinary and extraordinary refractive indices, the relative order parameter, $\alpha_a S/\alpha$, is plotted as a function of temperature. The behavior of the order parameter near the cholesteric to isotropic transition of CDC is similar to a nematic liquid crystal, whereas, the order parameter in OOBBA shows only a slight temperature variation like many solids.

INTRODUCTION

The study of liquid crystal indices has been of interest since the order parameter can be deduced from such measurements and compared with theoretical predictions. The refractive indices of a number of nematic liquid crystals have been investigated by previous authors.[1–3] This paper reports the extension of refractive index measurements to cover a cholesteric and a smectic liquid crystal.

EXPERIMENTAL

The index of refraction measurements were made with a modified high range Abbe refractometer ($n_d = 1.956$). The ground glass roof prism was replaced by a polished piece of high index ($n_d = 1.7$) glass to facilitate sample orientation. A Haake circulating oil bath provided temperature control to ±0.1°C. A sodium light source was used for all measurements.

The cholesteryl dodecyl carbonate (CDC) sample was obtained from Eastman Kodak (#10053) and used without further purification. Using a Mettler hot stage, the transition temperatures were determined to be 51°C-cholesteric-76°C. The smectic liquid crystal, *p*-*n*-octoxybenzylidene-*p*-*n*-butylaniline (OOBBA), sample was synthesized as described in the literature.[4] After recrystallization from ethanol the transition ranges were found to be 40°C(?)-smectic B-65°C-smectic C-68°C-smectic A-81°C.[5]

The samples were oriented with the optic axis normal to the Abbe prism surface by the shear forces resulting from a small sidewise displacement of the cover glass. The alignment was verified by the polarization and extinguishability of both the ordinary and extraordinary rays. All lines were sharp except the extraordinary ray of OOBBA which was slightly broadened. The estimated measurement errors were ±0.0002 for CDC and the ordinary index of OOBBA, and ±0.001 for the extraordinary index of OOBBA.

RESULTS

The relationships between the principal polarizabilities and the refractive index are taken to be

Lorentz-Lorentz
$$\frac{n^2-1}{n^2+2}=\frac{4\pi}{3}N\alpha$$

Vuks
$$\frac{n_e^2-1}{n^2+2}=\frac{4\pi}{3}N\alpha_e$$

$$\frac{n_o^2-1}{n^2+2}=\frac{4\pi}{3}N\alpha_o$$

where $n^2=(n_o^2+n_o^2+n_e^2)/3$ and $\alpha=(\alpha_o+\alpha_o+\alpha_e)/3$ are the mean refractive index and polarizability. The validity of the Vuks formula was demonstrated for a nematic liquid crystal[7] and we assume we can use it in the present instances. The normalized polarizabilities $\alpha_o/\alpha=(n_o^2-1)/(n^2-1)$ and $\alpha_e/\alpha=(n_e^2-1)/(n^2-1)$ found from the previous equations are independent of the density and reduce to unity in the isotropic phase. Figure 1 shows the temperature dependence of the refractive indices of CDC. The normalized polarizabilities for CDC (Figure 2) are similar to those of nematic liquid crystals. The normalized polarizabilities for OOBBA (Figure 3) are weakly temperature dependent within each phase and discontinuous across the phase transitions. The behavior near the smectic-C to smectic-A transition shows the persistence of the smectic-C phase when heating the oriented sample and the persistence of the smectic-A phase upon cooling.

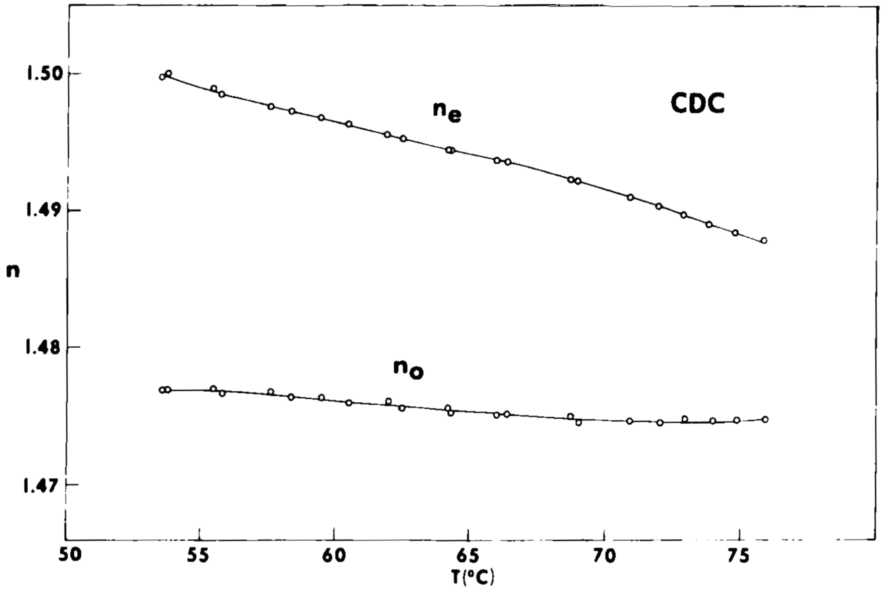

FIGURE 1 The refractive indices of CDC versus temperature at λ = 589.6 nm.

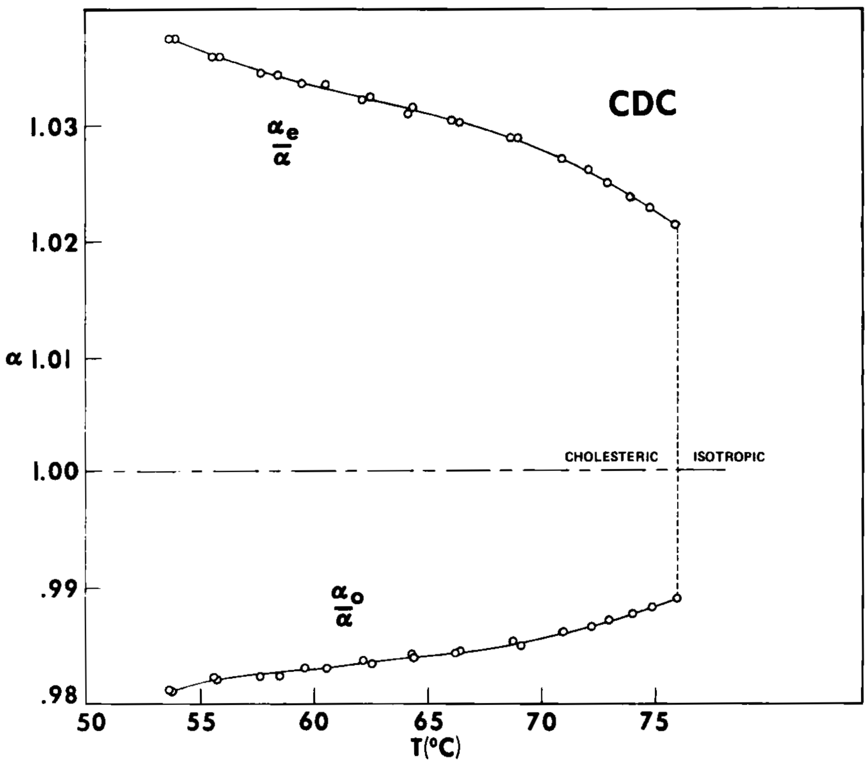

FIGURE 2 The normalized polarizabilities of CDC as a function of temperature.

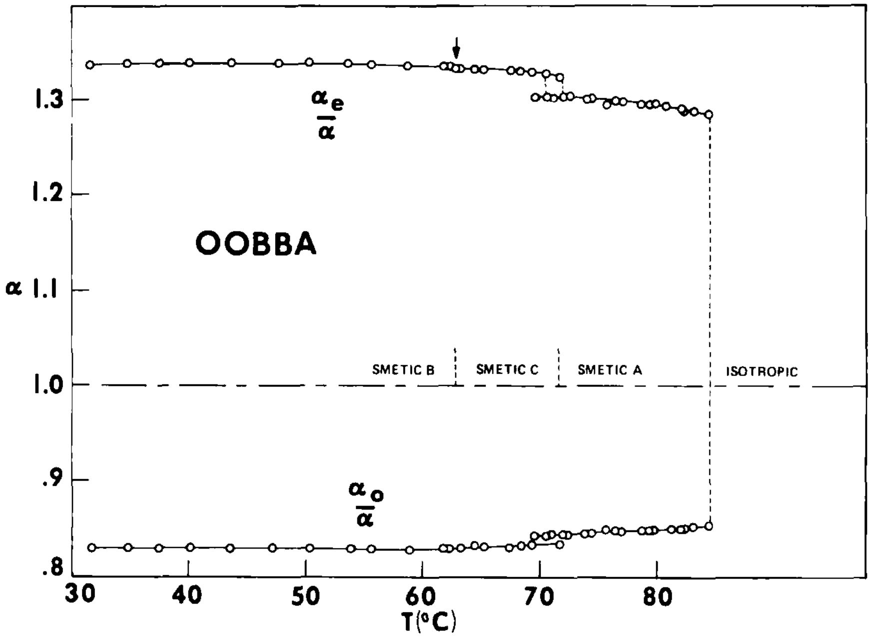

FIGURE 3 The normalized polarizabilities of OOBBA as a function of temperature.

The orientational order parameter, S, is defined by $S = \overline{(3\cos^2\theta - \frac{1}{2})/2}$ where θ is the angle between the macroscopic optic axis and the major axis of the molecule. The principal polarizabilities are related to the order parameter by[8] $\alpha_o = \alpha - \frac{1}{3}\alpha_a S$ and $\alpha_e = \alpha + \frac{2}{3}\alpha_a S$ where $\alpha_a = \alpha_e^m - \alpha_o^m$ is the molecular polarizability anisotropy. The order parameter is then given by $\alpha_a S/\alpha = \alpha_e/\alpha - \alpha_o/\alpha = (n_e^2 - n_o^2)/(n^2 - 1)$ up to the temperature independent factor α_a/α. In the case of nematic crystals, it is possible to obtain a value for the scaling parameter α/α_a by finding the $T = T_c$ intercept of a plot of $\log(n_e^2 - n_o^2)/(n^2 - 1)$ as a function of $\log(1 - T/T_c)$ as was done by Yakhmi, *et al.*[9] The plot for the CDC sample has no linear region that would allow a reasonable extrapolation. While the equation $S = (1 - T/T_c)^\gamma$ describes the behavior of the order parameter in nematic crystals, apparently this is not the case for the entire cholesteric range of CDC. The applicability of the exponential law for the smectic OOBBA, which has no nematic phase, is moot. Figures 4 and 5 show the temperature dependence of the relative order parameter for CDC and OOBBA. The behavior of the order parameter near the cholesteric to isotropic transition of CDC is similar to that of a nematic liquid crystal. In contrast the order parameter for OOBBA shows only a slight temperature variation like many solids. The phase transitions are, however, marked by discontinuities in the order parameter.

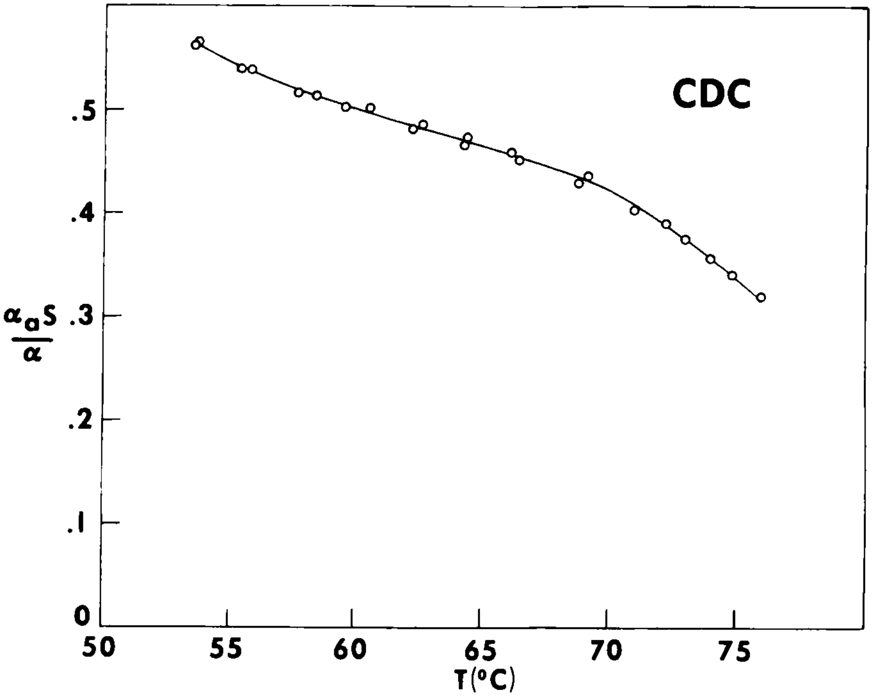

FIGURE 4 The temperature dependence of the relative order parameter of CDC.

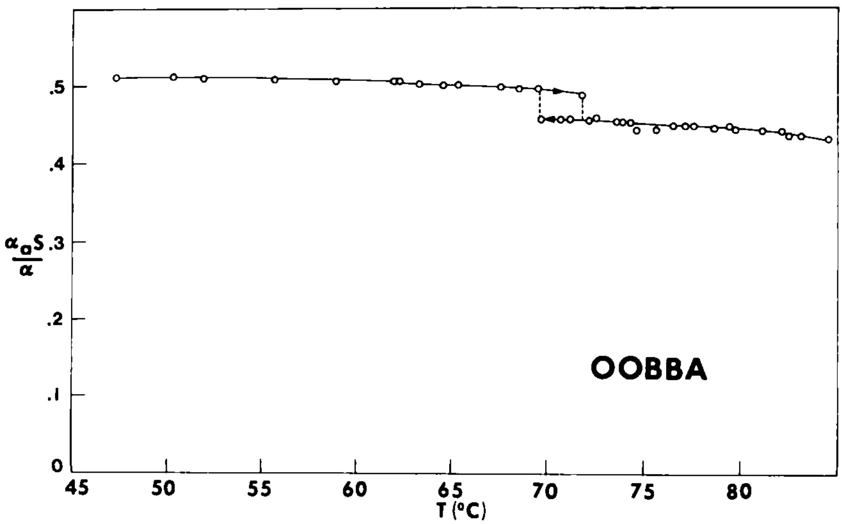

FIGURE 5 The temperature dependence of the relative order parameter of OOBBA.

CONCLUSIONS

We have found that the refractometer method of measuring liquid crystal indices provides accurate results when the problem of obtaining oriented samples can be solved. The results for the order parameter reflect the close relationship between cholesteric and nematic liquid crystals and between smectic liquid crystals and solids. In addition, we find that oriented samples of the smectic OOBBA have an unusual degree of thermal stability beyond their normal transition temperatures.

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