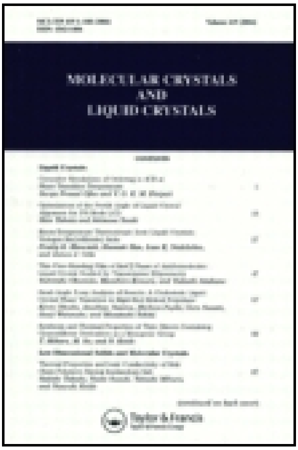

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On the temperature Dependence of the orientational Order Parameter in the Nematic Phase of Cyanophenyl Behzoates

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On the Temperature Dependence of the Orientational Order Parameter in the Nematic Phase of Cyanophenyl Benzoates

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The orientational order parameters for two liquid crystal materials, 4-cyanophenyl 4-butylbenzoate and 4-cyanophenyl 4-pentylbenzoate, have been derived by measuring the change in the refractive index as a function of temperature. The order parameters are compared with Maier-Saupe theory, and the sharpness of the transitions has been shown using the Haller's plot.

INTRODUCTION

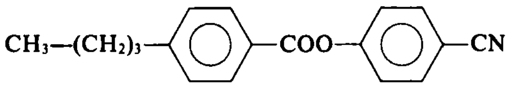
The orientational order parameter in thermotropic liquid crystals changes with temperature and this property has been used to investigate the phase transition phenomenon in liquid crystals.[1,2]

We study the change in the order parameter by measuring the change in the refractive indices of the nematic liquid crystal with respect to temperature. This is most simply done by applying the Vuk's formula and using the Haller's plot to obtain the polarizability ratio for scaling the order parameter. Further, an exponent obtained from this plot can be made available to show the sharpness of the transition.

The two compounds studied here are 4-cyanophenyl 4-alkylbenzoates. They were obtained from Roche[3] under the names RO-CE-1500 and RO-CE-1530 for the butyl and pentyl homologue respectively, and were used as given. They have monotropic nematic transitions; the former melted at 66°C and exhibited the nematic phase at 41.7°C, while the latter had the corresponding temperatures 60°C and 57.4°C. These values are in good agreement with those of the manufacturer.[3]

The transition schemes are shown below.

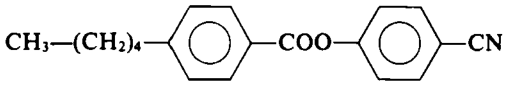
4-CYANOPHENYL-4-*n*-BUTYLBENZOATE (RO-CE-1500)



Crystal $\xrightarrow{66°C}$ Isotropic Liquid

Nematic 41.7°C

4-CYANOPHENYL-4-*n*-PENTYLBENZOATE (RO-CE-1530)



Crystal $\xrightarrow{61°C}$ Isotropic Liquid

Nematic 57.4°C

EXPERIMENTAL

The refractive indices for the ordinary and extraordinary ray were measured by the method of Murthy[4] *et al.* for anisotropic liquids. A thin wedge was formed between two optically flat glass plates using a fused quartz rod as spacer. The wedge was placed vertically in a cylindrical heater with glass windows. The heating was induced electrically. Light ($\lambda = 6328$ A°) obtained from a He-Ne laser was collimated at the edge of the wedge. A screen was attached to a micrometer screw and placed at a distance of about three meters from the wedge. The glass plates were rubbed unidirectionally for the purpose of alignment. The sample under study in the form of solid crystals was introduced at the top of the wedge. The wedge acted as a prism with a small apex angle. The incident laser beam projected two spots on the screen; one for the transmitted direct ray and the other for the emergent ray after the first internal reflection. The distance between the spots was determined as d_1. On heating, the monotropic nematogen melted into the isotropic phase. As the compound cooled back to the nematic phase, the transmitted direct ray deviated due to the presence of the liquid crystalline medium, and split into two, projecting two spots onto the screen, corresponding to the ordinary and extraordinary ray. Their displacements with respect to the spot projected by the transmitted direct ray in the previous case of the empty prism were measured respectively as d_2^o and d_2^e. If the ordinary and extraordinary refractive indices of the liquid crystal are n_o and n_e then

$$n_{o,e} = 1 + 2d_2^{o,e}/d_1$$

The derivation of the above formula is given in Ref. 4. This method, however, does not require the determination of the wedge angle.

OBSERVATIONS AND DISCUSSION

The variation of the ordinary (n_o) and extraordinary (n_e) refractive indices with respect to temperature of both the compounds is shown in Figures 1 and 2. In the proximity of the nematic-isotropic transition, it is seen that the birefringence (n_e—n_o) for cyanophenyl butylbenzoate decreases much faster than that for cyanophenyl pentylbenzoate.

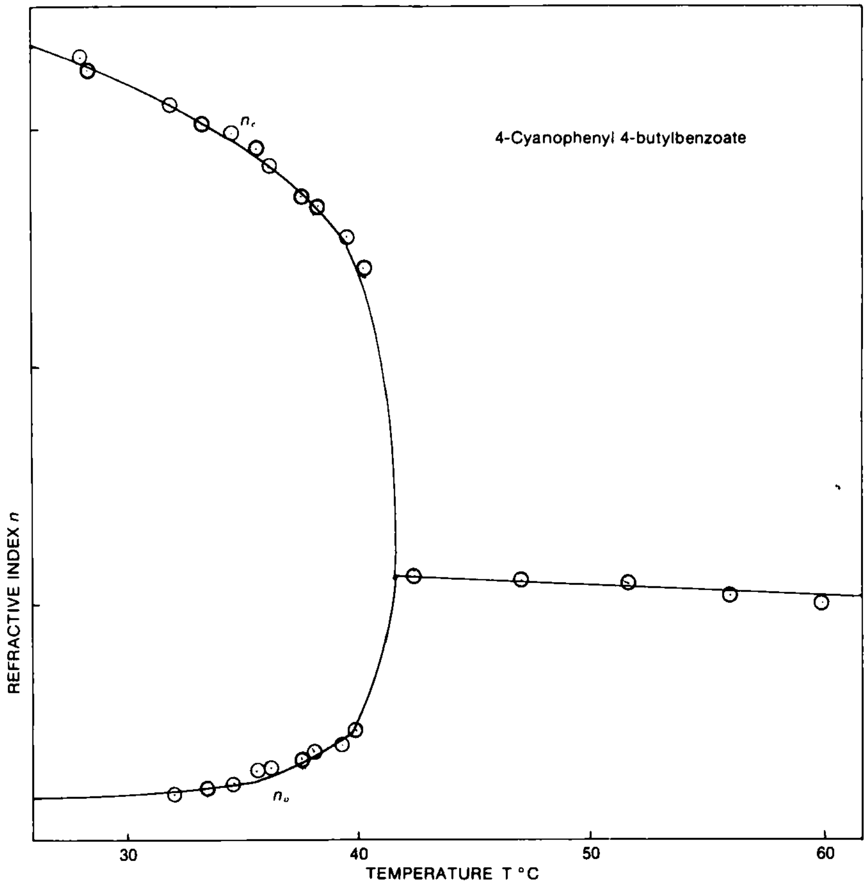


FIGURE 1 Temperature dependence of the refractive indices for 4-cyanophenyl 4-n-butylbenzoate.

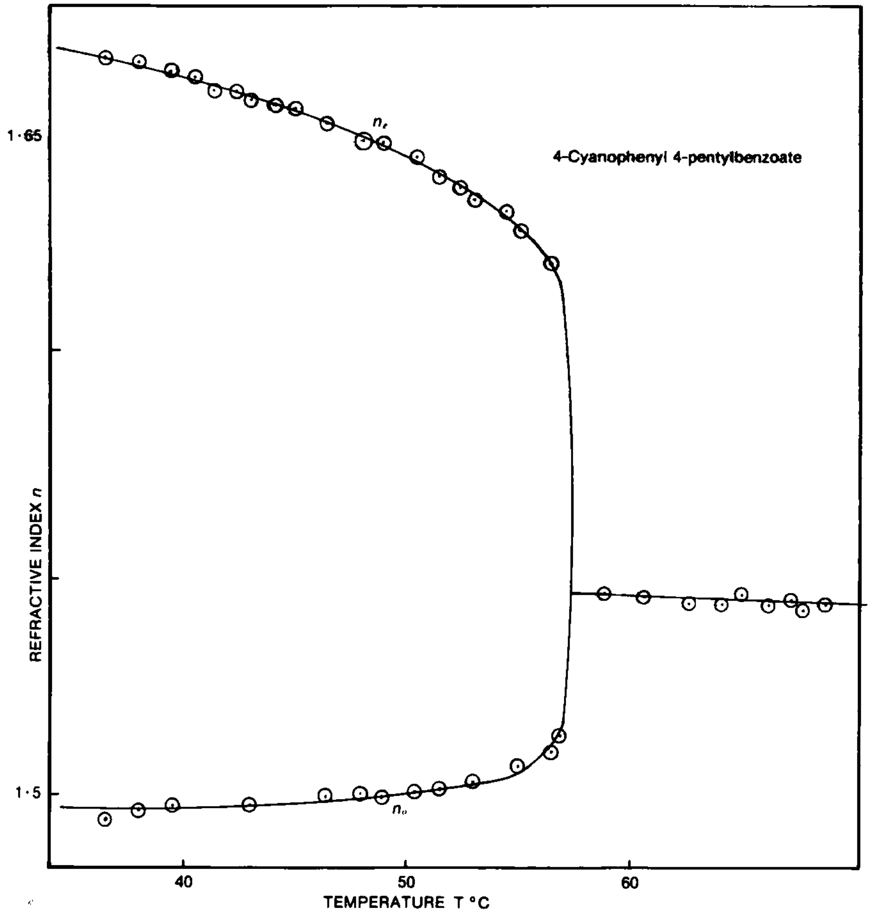


FIGURE 2 Temperature dependence of the refractive indices for 4-cyanophenyl 4-*n*-pentylbenzoate.

The order parameter S has been obtained using Vuk's relation

$$S[(\alpha_{\parallel} - \alpha_{\perp})/\bar{\alpha}] = [(n_e^2 - n_o^2)/(\bar{n}^2 - 1)], \qquad (1)$$

where S is the order parameter, $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the molecular polarizabilities in the directions along and perpendicular to the long axis of the molecule, and $\bar{\alpha}$ is the mean molecular polarizability; $[(\alpha_{\parallel} - \alpha_{\perp})/\bar{\alpha}]$ is the scaling factor.

The scaling factor is obtained from Haller's plot,[5] Log $(1 - T/T_c)$ *vs* Log $[(n_e^2 - n_o^2)/(\bar{n}^2 - 1)]$, as an intercept on the ordinate (Figure 3). The orientational order parameter is plotted in Figure 4 as a function of the reduced temperature.

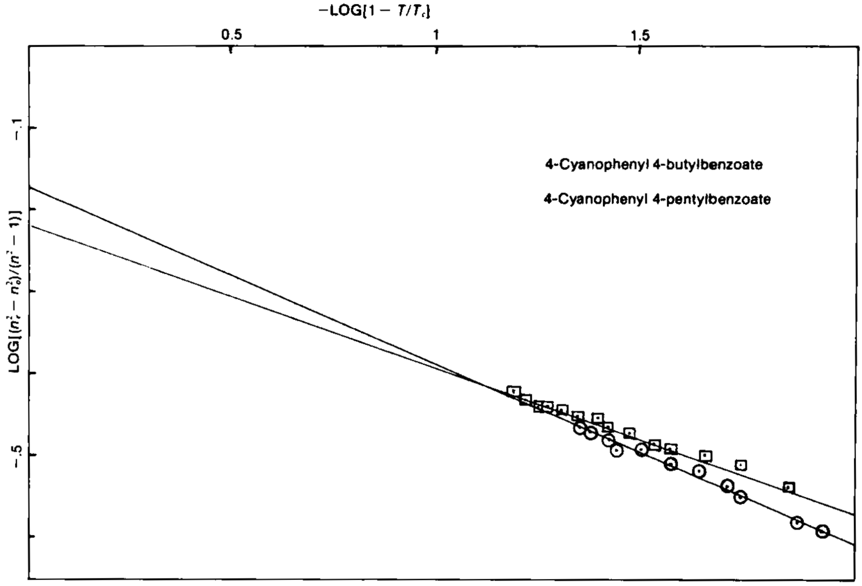


FIGURE 3 Haller plots for the named esters.

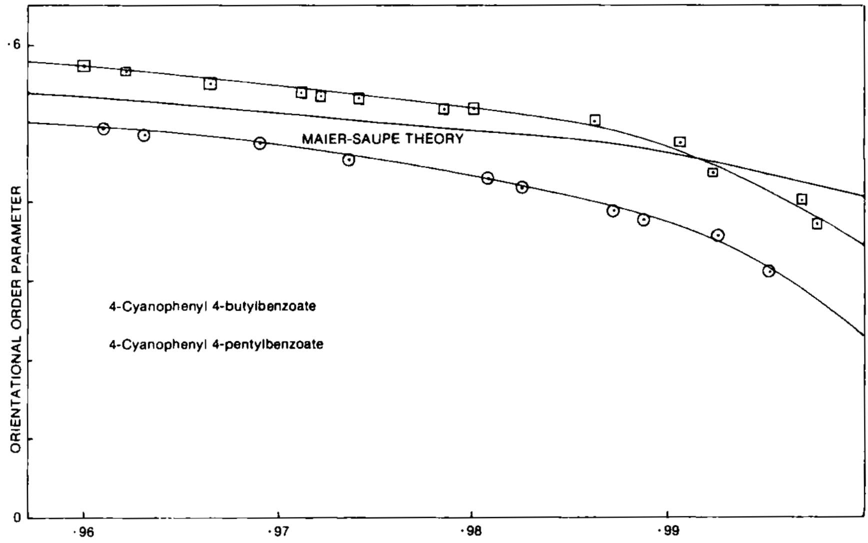


FIGURE 4 Reduced temperature plots of orientational order parameter for the named esters compared with the curve predicted from Maier-Saupe theory.

The Haller's plot in Figure 3 shows straight lines for both the compounds, but their slopes are different, being greater for the higher homologue than for the lower one.

If k is the slope of the straight line in Figure 3,

$$[(n_e^2 - n_o^2)/(\bar{n}^2 - 1)] = \left(\frac{\alpha_{\parallel} - \alpha_{\perp}}{\bar{\alpha}}\right)[1 - T/T_c]^k \tag{2}$$

using (1) and (2)

$$S \sim (1 - T/T_c)^k \tag{3}$$

It is observed that the exponent k is 0.215 for the butyl and 0.172 for the pentyl homologue. The variation of S characterized by equation (3), when plotted against the temperature, shows the rapidity with which S decreases with increasing temperature. The nature of the two curves is distinctively shown in Figure 5. In Figure 4 are shown the orientational order parameter given by Maier-Saupe (MS) theory, and the order parameters of the compounds as studied now. It is found that near the transition region (N—I), the

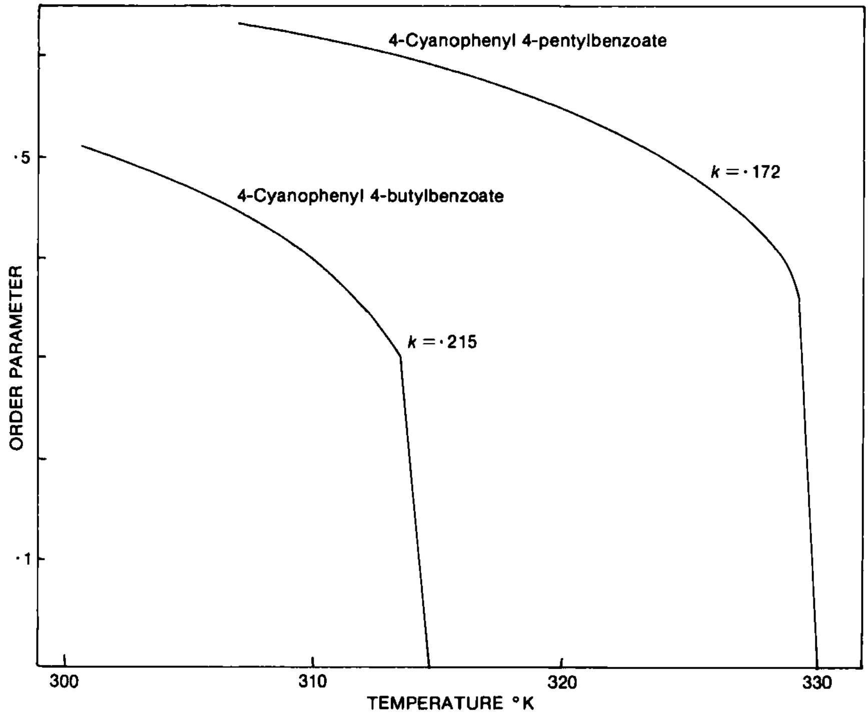


FIGURE 5 Absolute temperature dependence of the order parameter for the two esters named.

experimental curves deviate from the M.S. theory, and S moves faster towards the isotropic phase than predicted. Far away from the transition region, the experimental values of the order parameter are higher for the higher homologue and lower for the lower homologue than those given by theory.

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