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REFRACTIVE INDICES AND ORDER PARAMETERS OF TWO LIQUID CRYSTALS

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Résumé. — On a mesuré les indices de réfraction dans toute l'étendue de la phase nématique de 4-n-pentyle-4'-cyanobiphényle (5CB) et des phases smectique A et nématique de 4-n-octyle-4'-cyanobiphényle (8CB). On a comparé les méthodes de calcul du paramètre d'ordre de Vuks et de Neugebauer. On ne peut calculer qu'une quantité proportionnelle au paramètre d'ordre si on ne connaît pas les polarisabilités moléculaires : dans cette limite on trouve que les deux méthodes donnent des résultats identiques. La valeur absolue du paramètre d'ordre est obtenue en utilisant une méthode d'extrapolation suggérée par Haller [14]. On montre enfin, en moyennant de manière particulière les indices de réfraction et en utilisant les données de densité de Gannon et Faber [9], que la relation Lorentz-Lorenz est obéie dans un domaine de densité qui varie d'environ 2 % dans 5CB.

Abstract. — Refractive indices have been measured throughout the nematic phase of 4-n-pentyl-4'-cyanobiphenyl (5CB) and the smectic A and nematic phases of 4-n-octyl-4'-cyanobiphenyl (8CB). The Vuks and Neugebauer methods of calculating the order parameter are compared. Without knowledge of the molecular polarisabilities it is only possible to calculate a quantity proportional to the order parameter, and within this limitation it is found that the two methods give identical results. The order parameter is scaled using the extrapolation method suggested by Haller [14]. Using a suitable average of the refractive indices and the density data of Gannon and Faber [9], it is shown that the Lorentz-Lorenz relation is obeyed over a 2 % density range in 5CB.

The refractive indices of two liquid crystals, 4-n-pentyl-4'-cyanobiphenyl (5CB) and 4-n-octyl-4'-cyanobiphenyl (8CB), have been measured using the method of Pellet and Chatelain [1]. A thin wedge, with an angle A between its faces of about 10° , was formed between two glass slides whose inner surfaces were coated by oblique evaporation of silicon monoxide to promote alignment of the optic axis of the samples parallel to the edge of the wedge [2]. The wedge was arranged so that the incident beam of light from a sodium lamp ($\lambda = 5890 \text{ \AA}$) or a HeNe laser ($\lambda = 6328 \text{ \AA}$) was normal to the first face. In this geometry the beam is split into two components, light polarised parallel to the optic axis (the extraordinary ray) being refracted through a total angle of D_e and light polarised perpendicular to the axis (the ordinary ray) refracted through D_o . These angles are related to the extraordinary and ordinary refractive indices n_e and n_o by :

$$n_j = \frac{\sin(A + D_j)}{\sin A} \quad (j = e, o). \quad (1)$$

The angles D_e and D_o were measured by observing the heights of the refracted spots at a distance of several metres from the wedge, and A was measured by observing the separation between spots reflected from the faces of the empty wedge.

Figure 1 displays the results for 5CB, which has a nematic phase between 21° and 35°C . The error bar indicates the uncertainty in the absolute values due to systematic errors in the measurement of the angles of deviation D_e and D_o and the wedge angle A ; any adjustment would shift all the points by a similar scaling factor.

Measurements on 8CB, which has a smectic A phase between 21° and 33°C and a nematic phase between 33° and 40°C , were made at only one wavelength, 6328 \AA . The results are shown in figure 2. Values for both substances are in excellent agreement with the recent results of Karat and Madhusudana [3].

If the molecules of these liquid crystals are assumed to be rigid and to have cylindrical symmetry about their axes of maximum polarisability, the extent to which they are aligned, given by the order parameter

$$S = \frac{3}{2} \langle \cos^2 \theta \rangle - \frac{1}{2}, \quad (2)$$

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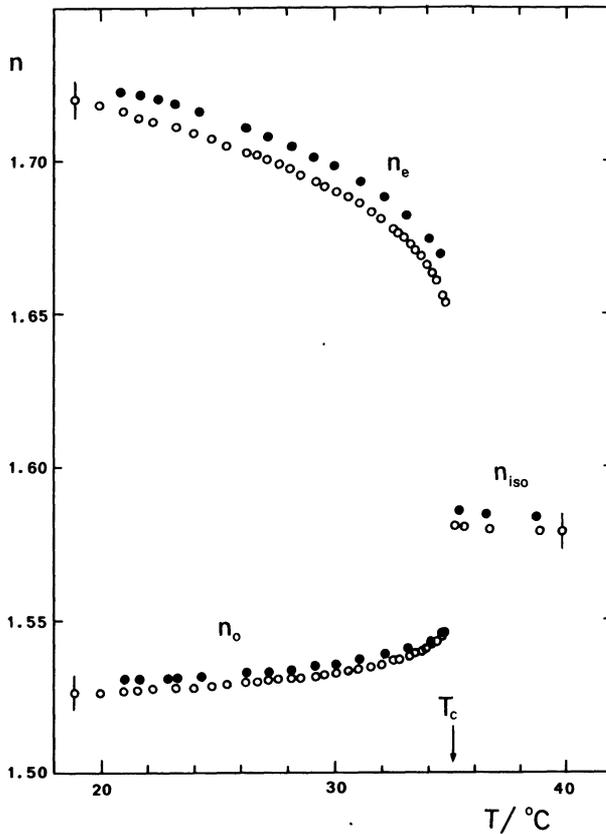


FIG. 1. — Refractive indices of 5CB as a function of temperature (● 5 890 Å, ○ 6 328 Å). T_c is the clearing temperature.

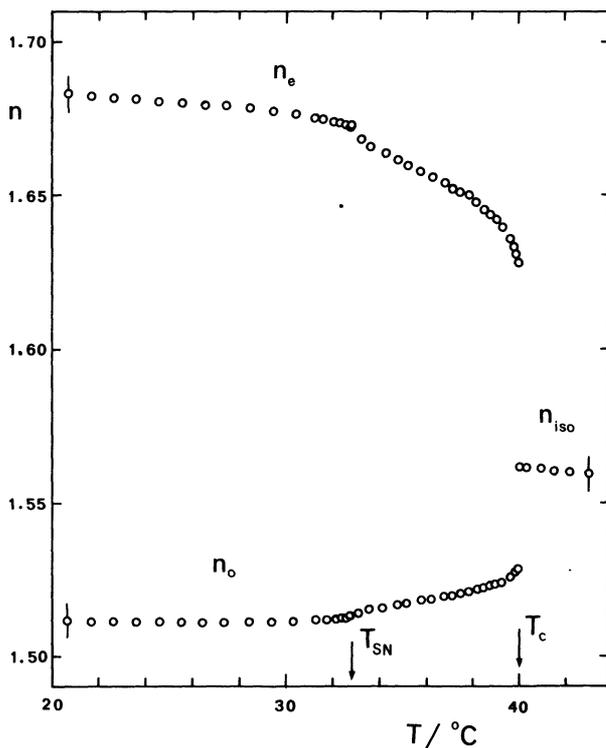


FIG. 2. — Refractive indices of 8CB at 6 328 Å as a function of temperature. T_{SN} is the smectic-nematic transition temperature.

can in principle be calculated from a knowledge of the refractive indices and the molecular polarisabilities α_{\parallel} along the molecular axis and α_{\perp} perpendicular to it. In the above definition θ is the angle between the molecular axis and the optic axis, and the angled brackets denote an average over all the molecules in a macroscopic volume. In practice this calculation can only proceed after assumptions have been made about the nature of the local electric field in the medium.

Two methods for calculating the local field in uniaxial materials are available. The first, due to Neugebauer [4] and applied to liquid crystals by Saupe and Maier [5] and Subramanyam and Krishnamurti [6], includes a correction factor intended to allow for the possibility that around each molecule the distribution of neighbours is anisotropic. This factor may be eliminated, leading to [6]

$$\frac{1}{\alpha_e} + \frac{2}{\alpha_o} = \frac{4\pi N}{3} \left(\frac{n_e^2 + 2}{n_e^2 - 1} + 2 \frac{n_o^2 + 2}{n_o^2 - 1} \right), \quad (3)$$

where N is the number of molecules per unit volume and α_e and α_o are the average components of molecular polarisability parallel and perpendicular to the optic axis. Since the average molecular polarisability

$$\bar{\alpha} = \frac{1}{3}(\alpha_e + 2\alpha_o) = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp}), \quad (4)$$

we can put

$$\alpha_e = \bar{\alpha} + \frac{2}{3}(\alpha_e - \alpha_o)$$

and

$$\alpha_o = \bar{\alpha} - \frac{1}{3}(\alpha_e - \alpha_o)$$

in equation (3), which leads to a quadratic expression in $(\alpha_e - \alpha_o)$.

Taking the positive root ($\alpha_e > \alpha_o$) and using [5] $S = (\alpha_e - \alpha_o)/(\alpha_{\parallel} - \alpha_{\perp})$ gives

$$S = \left(\frac{\bar{\alpha}}{\alpha_{\parallel} - \alpha_{\perp}} \right) \frac{9}{4B} \times \left[\left(B^2 - \frac{10}{3}B + 1 \right)^{1/2} + \frac{B}{3} - 1 \right], \quad (5)$$

where

$$B = \frac{4\pi N}{3} \bar{\alpha} \left(\frac{n_e^2 + 2}{n_e^2 - 1} + 2 \frac{n_o^2 + 2}{n_o^2 - 1} \right). \quad (6)$$

To calculate B it is necessary to know $\bar{\alpha}$, and this is generally obtained by using the Lorentz-Lorenz relation in the isotropic phase :

$$\frac{n_{iso}^2 - 1}{n_{iso}^2 + 2} = \frac{4\pi N_{iso}}{3} \bar{\alpha}. \quad (7)$$

In the second method, first applied to liquid crystals by Chandrasekhar and Madhusudana [7], it is assumed, following Vuks [8], that the local field is isotropic

even in an anisotropic crystal. The Vuks assumption leads to the result

$$S = \left(\frac{\bar{\alpha}}{\alpha_{\parallel} - \alpha_{\perp}} \right) \frac{n_e^2 - n_o^2}{n^2 - 1}, \quad (8)$$

where $\bar{n}^2 = \frac{1}{3}(n_e^2 + 2n_o^2)$. The number density N does not appear in (8) because it has been eliminated using

$$\frac{\bar{n}^2 - 1}{n^2 + 1} = \frac{4\pi N}{3} \bar{\alpha}. \quad (9)$$

This relation follows from the Vuks assumption, although the reverse is not true.

Equation (9) has been tested empirically for 5CB using the present refractive index results and the density data of Gannon and Faber [9]. The results are shown in figure 3, where $(3/4\pi N)(\bar{n}^2 - 1)/(\bar{n}^2 + 1)$ is plotted against the density ρ . It is seen that this quantity remains essentially constant, as it should do if it is equal to $\bar{\alpha}$, throughout the nematic range and across the nematic-isotropic transition (compare equations (7) and (9)). It may decrease a little as ρ increases but the change is certainly less than 0.1 %

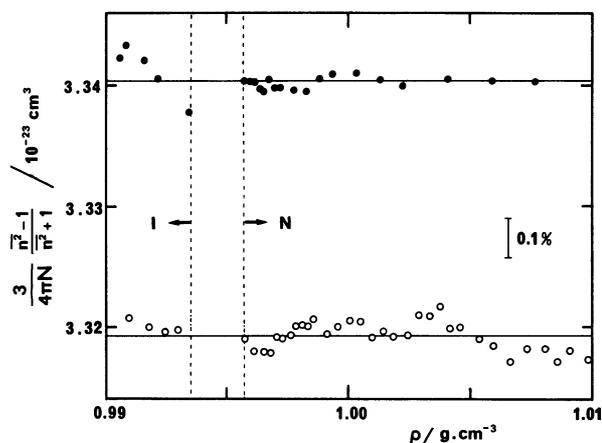


FIG. 3. — Test of the Lorentz-Lorenz relation (9) for 5CB (● 5 890 Å, ○ 6 328 Å; I marks the isotropic phase, N the nematic).

over a density range of 2 %. The relation has not been tested for 8CB because suitable density data are not available, but it is known to be accurate for the familiar nematogens para-azoxyanisole (PAA) [10] and methoxybenzylidene-butylaniline (MBBA) [11]. Since equation (9) is obeyed, it may be used instead of (7) to calculate $\bar{\alpha}$ for use in the Neugebauer method; equation (6) may be replaced by

$$B = \frac{\bar{n}^2 - 1}{n^2 + 2} \left(\frac{n_e^2 + 2}{n_e^2 - 1} + 2 \frac{n_o^2 + 2}{n_o^2 - 1} \right). \quad (10)$$

It is then possible to calculate the Neugebauer result

$$[(\alpha_{\parallel} - \alpha_{\perp}) S / \bar{\alpha}]_N$$

from equation (5), as well as the Vuks result

$$[(\alpha_{\parallel} - \alpha_{\perp}) S / \bar{\alpha}]_V$$

from equation (8), using the refractive indices alone.

Unless the molecular polarisabilities α_{\parallel} and α_{\perp} are known, this is as far as one can get: either method can be used to calculate a quantity proportional to the order parameter. Both methods have been used in the past, although no direct comparison between them has been reported. Haller *et al.* [12] concluded that the assumptions involved in the Vuks method are more sound than those in the Neugebauer method, and Blinov *et al.* [13], who measured the dichroism of dye molecules in a nematic solvent, found that their results were consistent with an isotropic local field, thus giving further support to the Vuks assumption.

Here both methods have been applied to the refractive index data for 5CB and 8CB, and the results are plotted against each other in figure 4. For each substance (including the smectic phase of 8CB) the points lie on an excellent straight line through the origin. The slopes of the lines are not unity (1.237 for 5CB and 1.227 for 8CB) which suggests that the two methods applied to a hypothetical perfectly-ordered liquid crystal ($S = 1$) would give different values for α_{\parallel} and α_{\perp} : at least one of them must be erroneous. However, if the only question at issue is the relative magnitude of S , for example at two different tempe-

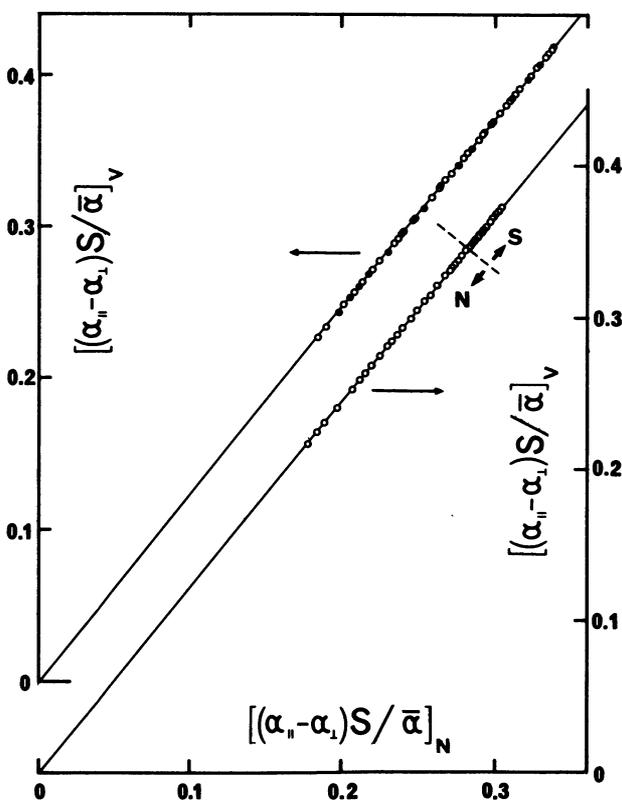


FIG. 4. — Comparison of the Vuks and Neugebauer calculations. Upper line and left-hand scale: 5CB (● 5 890 Å, ○ 6 328 Å); lower line and right-hand scale: 8CB, 6 328 Å. S and N label the smectic and nematic phases of 8CB.

atures, the results of the two methods will be indistinguishable.

Relative values for the order parameter may subsequently be *scaled*, if a reliable value for S is available at just one temperature, e.g. from measurements of some property other than optical birefringence. Here, however, the scaling procedure suggested by Haller [14] has been adopted. This relies on the plausible assumption that if a liquid crystal could be cooled to absolute zero without undergoing any phase transitions, S would become equal to unity. Haller observed that if the logarithm of a quantity proportional to $S(\log[(\alpha_{\parallel} - \alpha_{\perp})S/\bar{\alpha}]_V$ in the present work) is plotted against $\log(1 - T/T_c)$, where T_c is the nematic-isotropic transition temperature, the curve obtained is straight at temperatures away from T_c , and can be extrapolated to $T = 0$ with reasonable confidence. The intercept at $T = 0$ gives the scaling factor required, i.e. $[(\alpha_{\parallel} - \alpha_{\perp})/\bar{\alpha}]_V$. A Haller plot for 5CB is shown in figure 5. While such a long-range extrapolation can never be entirely convincing, we estimate that the intercept on the vertical axis is determined within 0.04, that is an uncertainty of 10 % in scaling the order parameter. If S had been scaled by comparison with other measurements, it would have been subject to an uncertainty of 15-20 % due to the variation which is seen between different experimental results.

The intercepts in figure 5 give $[(\alpha_{\parallel} - \alpha_{\perp})/\bar{\alpha}]_V = 0.676$ at 6 328 Å and 0.697 at 5 890 Å. Equation (9) (see Fig. 3) tells us that $\bar{\alpha}$, in units of Å³, is 33.2 and 33.4 respectively. Thus α_{\parallel} , in the same units, is 48.2 at

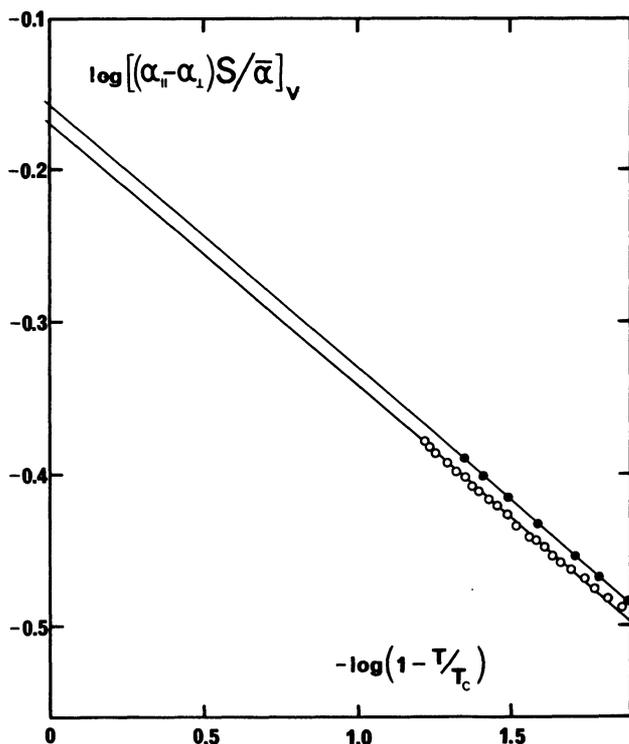


FIG. 5. — Haller plots for 5CB at two wavelengths (● 5 890 Å, ○ 6 328 Å).

6 328 Å and 48.9 at 5 890 Å, while α_{\perp} is 25.7 and 25.6. If the Neugebauer method had been used, the curves in figure 5 would be parallel to those shown but lying lower by a distance $\log 1.237 = 0.092$. The intercepts would then give $[(\alpha_{\parallel} - \alpha_{\perp})/\bar{\alpha}]_N = 0.547$ at 6 328 Å and 0.564 at 5 890 Å, giving values for α_{\parallel} and α_{\perp} of 45.3 and 27.2 at the first wavelength and 46.0 and 27.1 at the second.

A Haller plot is impracticable for 8CB because of the existence of a smectic A phase. However, we can estimate the scaling factor for this substance. Hanson and Shen [15] have recently shown that an increase in the length of the alkyl chain of a nematogen has very little effect on the polarisability anisotropy ($\alpha_{\parallel} - \alpha_{\perp}$), but that it increases the average polarisability $\bar{\alpha}$. Karat and Madhusudana [3] found the same result, showing that $\bar{\alpha}$ increases by 16 % from 5CB to 8CB while ($\alpha_{\parallel} - \alpha_{\perp}$) remains essentially constant. We therefore assume that the scaling factor for 8CB at 6 328 Å is 16 % lower than that for 5CB, i.e. 0.58.

Scaled curves for S for both substances are presented in figure 6. Detailed discussion of the 5CB results will be left to another article in which the author describes extensive measurements of the refractive indices of this substance at high pressures [16]. The most interesting features of the 8CB results are the small discontinuity at the nematic-smectic A transition, and the anomalous behaviour just above this transition where the curve seems to be bending upwards. It is clear that the influence of the smectic phase is present well into the nematic phase. The presence above the smectic-nematic transition of cybotactic groups, in which small clusters of molecules have smectic-like ordering, should affect the relation between the order parameter and the refractive indices because the local field depends on the details of intermolecular correlations. It would be interesting to compare the 8CB curve in figure 6 with measurements of the order parameter by other methods such as NMR or magnetic susceptibilities where the calculation would be independent of the presence of cybotactic groups, to see whether the marked pretransitional

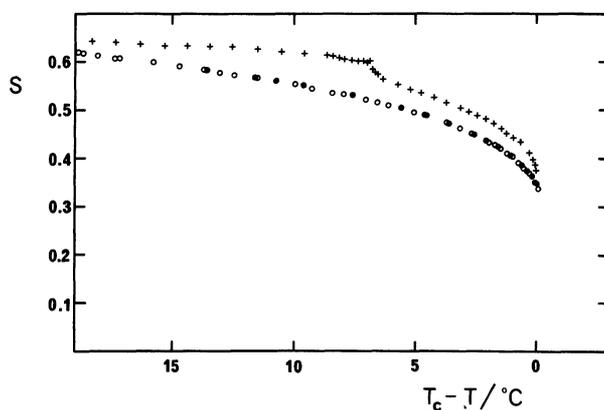


FIG. 6. — Order parameter as a function of $T_c - T$ in 5CB (● from results at 5 890 Å, ○ 6 328 Å) and 8CB (+).

behaviour seen here exists in the order parameter itself or whether it is an artefact of the local field calculations. It would thus be possible to learn more about the sensitivity of these calculations to the molecular environment.

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