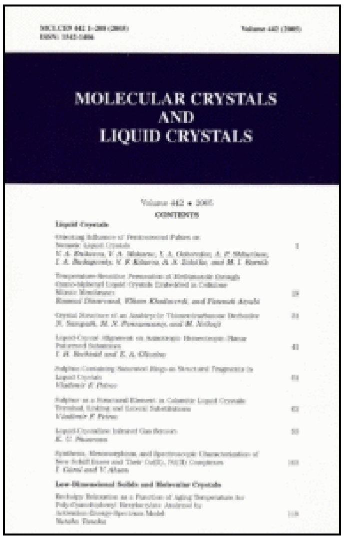

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N. V. Madhusudana[a]; K. P. L. Moodithaya[a]; K. A. Suresh[a]
[a] Raman Research Institute, Bangalore, India

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Effect of Skew Cybotactic Structure on the optical Properties of a Nematogen with a Lateral Cyano Substituent†

N. V. MADHUSUDANA, K. P. L. MOODITHAYA and K. A. SURESH
Raman Research Institute, Bangalore 560 080, India

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We report an unusual thermal variation of the ordinary refractive index (n_0) of the nematogenic compound 2-cyano-4-heptyl-phenyl-4′-pentyl-4-biphenyl carboxylate, which has a cyano group making a large angle (~60°) with the molecular axis. As the sample is cooled from the NI transition point, n_0 initially decreases as usual, but on further cooling it shows an increasing trend after reaching a broad minimum. On the other hand, the extraordinary index n_e shows the normal temperature variation. X-ray investigations of a monodomain sample show that the nematic has a skewed cybotactic type of short-range order, the tilt angle increasing considerably as the temperature is lowered from the NI transition point. We have made a model calculation to explain the temperature variation of n_0 in terms of the variation of the tilt angle.

INTRODUCTION

It is relatively easy to measure the principal refractive indices of nematic liquid crystals accurately, and the birefringence is a good measure of the orientational order in the medium. Consequently, there have been a large number of measurements of the refractive indices of liquid crystals. As the temperature is lowered in the nematic phase, the extraordinary index (n_e) monotonically increases while the ordinary index (n_0) decreases. All the mesogenic compounds with rod-like molecules are characterized by a fairly strong positive polarizability anisotropy $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$ where $\parallel$ and $\perp$ refer to directions in relation to a suitably defined long axis of the molecule.

†Presented at the Ninth International Liquid Crystal Conference, Bangalore, 1982.

As the temperature is lowered, the orientational order parameter S monotonically increases. Assuming that the contribution of each molecule to the polarizabilities of the medium can be added independently, it is easily shown that

$$\alpha_e = \bar{\alpha} + \frac{2}{3} S \Delta\alpha$$

$$\alpha_0 = \bar{\alpha} - \frac{1}{3} S \Delta\alpha \qquad (1)$$

where α_e and α_0 are the principal polarizabilities of the nematic medium and $\bar{\alpha}$ is the average polarizability $[=(\alpha_e + 2\alpha_0)/3]$ which is supposed to be independent of temperature. In a strongly anisotropic medium like the nematic liquid crystal, there is no exact relation between α_e and α_0 on the one hand and n_e and n_0 which are the measured parameters on the other. A few different procedures have been suggested to connect the polarizabilities with the refractive indices,[1–4] and they appear to lead to practically the same values of S.[5] In any case, they would also lead to the result that the temperature variations of n_e and n_0 should have trends similar to those of α_e and α_0 respectively, a result which is in general accord with observations on a number of systems.

In this paper, we will present results on a nematogenic compound which shows an unusual variation of n_0 with temperature. In this case, as the sample is cooled from the nematic-isotropic transition temperature, n_0 decreases at first, attains a broad minimum and then starts *increasing* with further cooling. Our X-ray studies on this compound showed that the nematic phase has a skew cybotactic structure,[6] the tilt angle decreasing considerably with increase of temperature. It is clear that the variation of the structure of the short-range ordered groups has a significant influence on the optical properties of the medium. We have made a model calculation incorporating the effect of the skew cybotactic structure on the refractive indices of the nematic. The calculated trends of n_e and n_0 are in agreement with those found by experiment.

EXPERIMENTAL

The compound used in our studies is 2-cyano-4-heptylphenyl-4′-pentyl-4-biphenyl carboxylate [7P(2CN)5BC] whose structural formula is shown in Figure 1. It was supplied by Merck Co. and was mostly used without further purification. The transition temperatures of the compound are

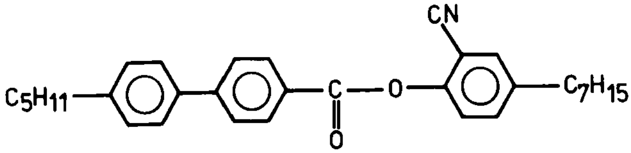

FIGURE 1 Structural formula of 2-cyano-4-heptylphenyl-4′-pentyl-4-biphenyl carboxylate.

K45N102I. Further, the nematic can be easily supercooled to room temperature. Thus we can perform experiments in a temperature range ≃70 °.

The refractive indices were determined using a monodomain sample taken in a small angled (~5°) hollow prism, using a He-Ne laser as the source of light of wavelength 6328 Å. The details of the experimental setup can be found elsewhere.[7] The X-ray studies were made on a sample taken in a Lindemann capillary tube and aligned in a magnetic field of strength ≃8 K Gauss which was acting along the capillary axis. Nickel filtered copper K-α radiation was used for this purpose and the diffracted beams were recorded photographically.

RESULTS AND DISCUSSION

The refractive indices are shown in Figure 2. n_e varies in the expected manner, increasing continuously as the temperature is lowered. However

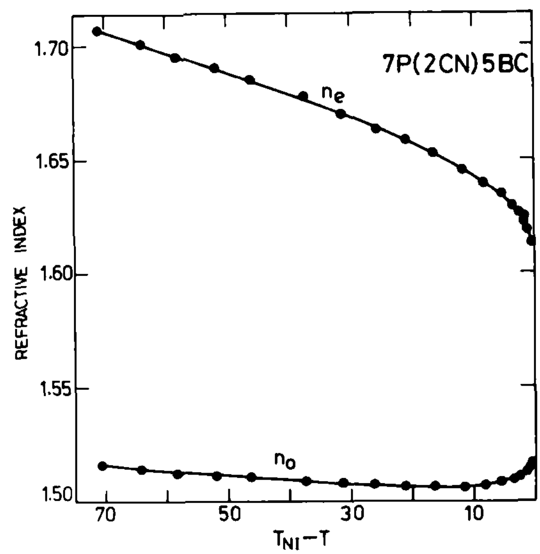

FIGURE 2 Temperature variations of the principal refractive indices in the nematic phase of 2-cyano-4-heptylphenyl-4′-pentyl-4-biphenyl carboxylate.

n_0 shows an unusual trend, exhibiting a broad minimum at $T_{NI} - T \simeq 12°$ or so.

The X-ray diffraction patterns at two temperatures are shown in Figure 3. The pattern is characteristic of a nematic with skewed cybotactic structure,[6] with four well-defined diffracted spots which are reasonably sharp at low temperatures. As the temperature is increased, the sharpness decreases, and further, the spots move closer, indicating that the tilt angle of the skewed cybotactic structure is decreasing, in agreement with the trend which is found in some other compounds.[6,8] We measured the tilt angle directly by joining the centers of diagonally opposite spots of the pattern. The angle between the lines in quadrants containing the direction of the magnetic field is twice the tilt angle (θ) of the cybotactic structure. The temperature dependence of θ is shown in Figure 4. $\theta \simeq 48°$ at 25°C and decreases to ~40° at 90°C, the rate or variation increasing with increase of temperature. We shall now develop a model of the local field in the skewed cybotactic nematic to explain the temperature variations of the refractive indices in terms of that of θ.

A model for the internal field

We shall use an idealized model of the cybotactic structure in order to be able to make some calculations. Firstly, we assume that the molecules are cylindrically symmetric rods. Most of the earlier models used for evaluating the local field in the nematic phase have assumed that the molecules

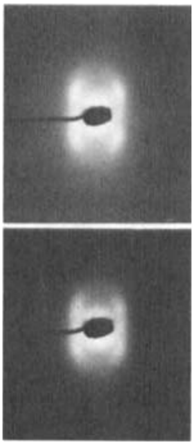

FIGURE 3 X-ray photographs of a monodomain sample of 2-cyano-4-heptylphenyl-4'-pentyl-4-biphenyl carboxylate at (a) 40°C and (b) 60°C.

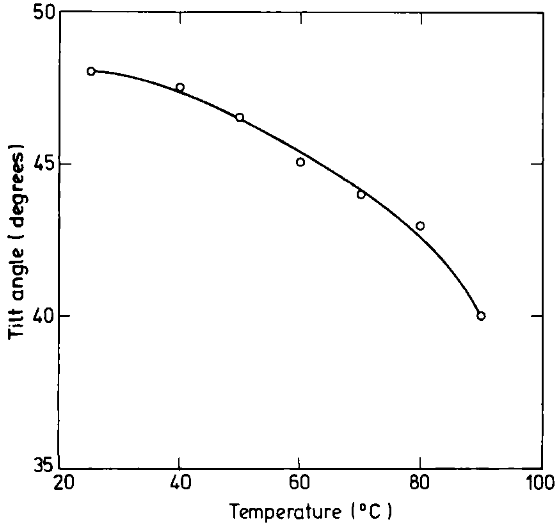

FIGURE 4 Temperature variation of the tilt angle of the skewed cybotactic structure of 2-cyano-4-heptyl phenyl-4′-pentyl-4-biphenyl carboxylate.

have anisotropic *point* polarizabilities. This assumption is not justified in view of (a) the high density of the medium, and (b) the strong conjugation that exists in the aromatic core. We assume that each rod can be replaced by five polarizable centers which are symmetrically located along the length of the molecule. We now construct the skewed cybotactic structure in the following fashion. We first assume that the molecules have their long axes normal to the layers (as in a smectic A), but in a hexagonal close packed arrangement (Figure 5a). The molecules are now allowed to slide parallel to their long axes such that a tilted arrangement as in Figure 5b is obtained. We define the $\xi\eta\zeta$ coordinate system fixed with a given cybotactic cluster (Figure 5) such that (a) the ζ-axis is along the long axis of the molecule and (b) the ξ-axis is in the plane containing the layer normal L and the ζ-axis. The tilt angle θ is the angle between the layer normal and the ζ-axis. For calculating the local field E_l at any *polarizable center,* we consider a spherical region of radius R around that center. The contribution to E_l from the cybotactic structure within the spherical region is exactly calculated. The medium outside R is treated as a continuum. We will write the explicit expressions for the components of the local fields along ξ, η and ζ axes. The local field along the ξ-direction of the j^{th} ($j = 1 \ldots 5$) center can be written as (see for instance, Ref. 9)

$$E_{l\xi j} = E_\xi + \frac{4\pi}{3}\sum_{i=1}^{5} P_{\xi i} + \frac{1}{N}\sum_{i=1}^{5} K(\xi\xi ji)P_{\xi i} + \frac{1}{N}\sum_{i=1}^{5} K(\xi\zeta ji)P_{\zeta i} \qquad (2)$$

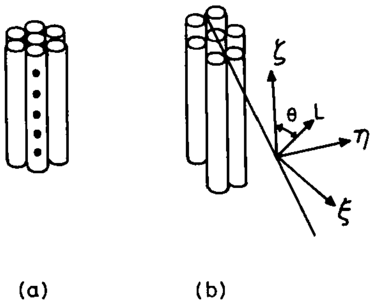

FIGURE 5 Schematic diagram of cybotactic groups. (a) Tilt angle $\theta = 0$. The dots on one of the rods represent centers of polarizability. (b) A skewed cybotactic group with tilt angle $\theta \neq 0$. L is the layer normal.

where E_ξ is the external field along the ξ-axis, $P_{\xi i}$ is the polarization at the i^{th} centers of the molecules along the ξ-axis, i.e.

$$P_{\xi i} = N\alpha_{\xi i}E_{l\xi i}, \tag{3}$$

$\alpha_{\xi i}$ being the component of the polarizability of the i^{th} center along the ξ-direction, N the number of molecules per unit volume,

$$K(\xi\xi ji) = \sum_R \frac{3\xi_{ij}^2 - r_{ij}^2}{r_{ij}^5}$$

where Σ_R stands for a summation over all polarizable centers (except the one at the given point) within a radius R from that point, and

$$K(\xi\zeta ji) = \sum_R \frac{3\xi_{ij}\zeta_{ij}}{r_{ij}^5}.$$

Notice that $P_{\zeta i}$ contributes to $E_{l\xi j}$ due to the skewed cybotactic nature of the structure. Similarly,

$$E_{l\zeta j} = E_\zeta + \frac{4\pi}{3}\sum_{i=1}^{5} P_{\zeta i} + \frac{1}{N}\sum_{i=1}^{5} K(\zeta\zeta ji)P_{\zeta i} + \frac{1}{N}\sum_{i=1}^{5} K(\xi\zeta ji)P_{\xi i} \tag{4}$$

and

$$E_{l\eta j} = E_\eta + \frac{4\pi}{3}\sum_{i=1}^{5} P_{\eta i} + \frac{1}{N}\sum_{i=1}^{5} K(\eta\eta ji)P_{\eta i} \tag{5}$$

The ten equations implied in Eqs. (2) and (4) can be solved to get

$$E_{l\xi j} = A_j E_\xi + B_j E_\zeta, \qquad \text{say} \tag{6}$$

and

$$E_{l\zeta j} = D_j E_\zeta + G_j E_\xi, \qquad \text{say} \tag{7}$$

Similarly, from the five equations implied in Eq. (5), we get

$$E_{l\eta j} = J_j E_\eta, \qquad \text{say} \tag{8}$$

We now assume a space-fixed coordinate system XYZ such that the Z-axis coincides with the director. We can then define the Eulerean angles between the XYZ and $\xi\eta\zeta$ systems in the usual manner (see for instance, Ref. 10). For the sake of simplicity, we assume that the cybotactic groups can freely rotate about the ζ-axis. Further, since the medium is uniaxial, we define a single order parameter

$$S = \left\langle \frac{3\cos^2\beta - 1}{2} \right\rangle \tag{9}$$

where β is the angle between ζ and Z axes and the angular brackets signify a statistical average. We then find that the B and G terms of Eq. (6) and (7) do not contribute to the results.

Again, for the sake of simplicity, we assume that all the five centers of polarizability in each molecule have *equal* and *isotropic* polarizabilities, i.e. $\alpha_\xi = \alpha_\eta = \alpha_\zeta = \alpha$, say. (The mutual disposition of these centers would of course lead to the anisotropy of the polarizability of the molecules.) With these assumptions, it is easy to show that

$$n_e^2 = n_z^2 = 1 + \frac{4\pi}{3} N\alpha \left[(A + J + D) + 2S\left\{ D - \frac{(A + J)}{2} \right\} \right] \tag{10}$$

and

$$n_0^2 = n_x^2 (= n_y^2) = 1 + \frac{4\pi}{3} N\alpha \left[(A + J + D) - S\left\{ D - \frac{(A + J)}{2} \right\} \right] \tag{11}$$

where

$$A = \sum_{j=1}^{5} A_j, \qquad J = \sum_{j=1}^{5} J_i \quad \text{and} \quad D = \sum_{j=1}^{5} D_j$$

are functions of the tilt angle θ of the skewed cybotactic structure.

For the purpose of making calculations, we have assumed that the molecules have a diameter of 5 Å, a length of 20 Å and that the five centers are

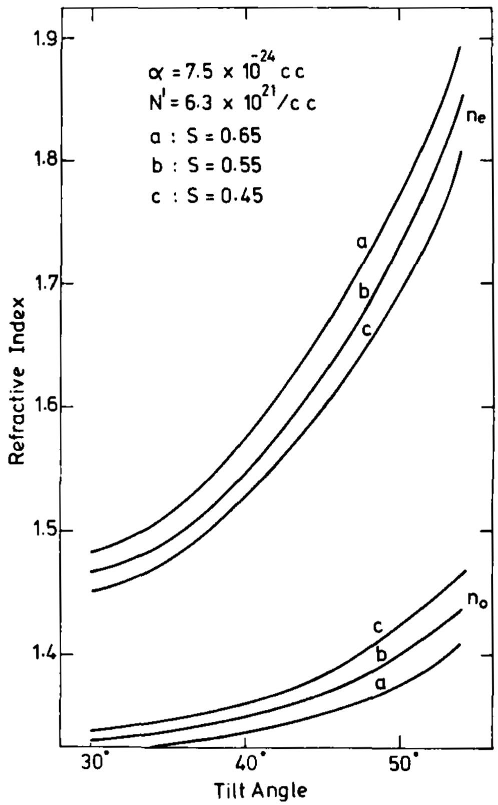

FIGURE 6 Calculated values of extraordinary and ordinary indices of the medium as functions of the tilt angle of the skewed cybotactic groups, with $N' = 4\pi N/3 = 6.30 \times 10^{21}$/cc.

symmetrically situated in the molecule with a mutual separation of 3 Å (see Figure 5). This means that a length of 4 Å is left free on either side and may be regarded as the region occupied by chains which do not contribute much to the polarizability anisotropy of the molecules. The calculations were made on a computer, with $R = 25$ Å and for various values of α, θ, N and S. Some results are shown in Figure 6 for $\alpha = 7.4 \times 10^{-24}$ cc, which leads to reasonable values for the parallel and perpendicular components of the polarizability of the molecules and also to the right order of magnitude of birefrigence in the nematic phase.

It is seen from Figure 6 that both n_e and n_0 *decrease* as θ decreases, for any given value of S. Further, the rate of decrease of the indices is lower for lower values of θ. Calculations with the density increased from $N' = 6.3 \times 10^{21}$/cc to 6.35×10^{21}/cc leads to a small increase in n_e and

n_0 as is to be exepcted, without changing the Θ dependence significantly.

We can now easily understand the experimental results shown in Figure 2. At low temperatures, S varies slowly with temperature and the variation of n_0 is mainly determined by that of θ, i.e. n_0 can *decrease* with increase of temperature. As the temperature is increased, the dependence of n_0 on θ decreases (Figure 6), and at the same time, the temperature variation of S increases. Hence, as can be seen from Figure 6, n_0 starts increasing with temperature as we approach the nematic-isotropic transition point, in accordance with the observation (Figure 2). Indeed, using the temperature variation of S as given by the Maier and Saupe theory, and that of θ from Figure 3, and including a density variation or $\sim 2\%$ over the nematic range, one can reproduce the trend of n_0 shown in Figure 2.

The tilt angle variation has no such dramatic effect on n_e, but as can be easily seen from Figure 6, it leads to a relatively rapid decease of the extraordinary index with temperature.

In conclusion, we have observed a strong influence of the temperature dependence of the tilt angle of skewed cybotactic groups on that of the ordinary refractive index. We have given a simple model to explain it on the basis of the dependence of the local field on the structure.

We may also mention that if the structure of the short range ordered groups does not change significantly with temperature, the models that we referred to in the introduction connecting the principal polarizabilities of the medium with the refractive indices are satisfactory.

Acknowledgment

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