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Determination of the Molecular Arrangement in Liquid Crystals by Polarization of Fluorescence

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Polarized luminescence intensity reading and the polarized absorbance spectra of 4-diethylamino-4′-nitrostilbene "impurity" in the *n*-butyl-*p*/*p*-hexyloxyphenyloxycarbonyl/-phenylcarbonate liquid crystal were measured. Degrees of orientational order, S_1 and S_2, of the nematic liquid were calculated from relative values of the absorbance and luminescence intensity components. A function, which describes the angular molecular distribution with respect to a preferred direction in the liquid crystal, is plotted.

INTRODUCTION

The orientational order of the nematic liquid crystal (LC) is characterized by the function $f(\theta)$ which describes the angular molecular distribution with respect to the preferred direction. Spectrophotometric methods of investigation prevent the defining of $f(\theta)$ and provide only indirect information on $f(\theta)$ through the order parameter S_1 [1],

$$S_1 = \tfrac{1}{2}(3\,\overline{\cos^2\theta} - 1), \tag{1}$$

where θ is the angle between the molecular axis and the preferred direction. Averaging is carried out by the angular molecular distribution function. The angular molecular distribution functions $f(\theta)$ may be significantly different for different substances at one and the same value of the order parameter S_1. Indeed, one can judge more definitively the LC ordering if not only S_1 and consequently $\overline{\cos^2\theta}$, but also if the cosines of higher even degrees are known. In [2, 3] the method has been proposed of simultaneous by determining S_1 and S_2 or S_2' defined by $\overline{\cos^4\theta}$, using the LC polarized luminescence intensity measurements, where

$$S_2 = \tfrac{1}{8}(35\,\overline{\cos^4\theta} - 30\,\overline{\cos^2\theta} + 3), \tag{2}$$

$$S_2' = \tfrac{1}{4}(5\,\overline{\cos^4\theta} - 1), \tag{3}$$

Since most substances do not possess luminescence in the LC state, it is of interest to investigate the possibility of determining S_1 and S_2 by the polarized luminescence intensity of "impurity" molecules dissolved in the nematic LC.

EXPERIMENT

The nematic LC *n*-butyl-*p*/*p*-hexyloxyphenyloxycarbonyl-phenylcarbonate was selected as the system for investigation. The LC samples with homogeneous textures were grown in a thermostatic quartz cell and were $\sim 100\,\mu$m thick for the absorption measurements and $\sim 8\,\mu$m thick for the measurement of polarized luminescence intensities. The 4-diethylamino-4′-nitrostilbene molecule which is close in size to the solvent molecules was chosen as the luminescent "impurity." Its transition dipole moment is parallel to the molecular long axis. The luminescent "impurity" concentration was $\sim$0.1 wt% when measuring the absorption spacetra and $\lesssim$ 0.01 wt% when measuring the luminescence intensities. The absorption and luminescence measurements were carried out using DMR-4 monochromators. Luminescence was excited using a xenon lamp with a DMR-4 monochromator set at 472 nm.

RESULTS AND DISCUSSION

Figure 1 shows the results of the measurement of the polarized luminescence intensity ($\lambda_{\text{lum}} = 645$ nm) of the 4-dietylamino-4′-nitrostilbene dye "impurity" in *n*-butyl-*p*/*p*-hexyloxyphenyloxycarbonyl/-phenylcarbonate (I_{XZ} is the intensity of the luminescence polarized parallel to the optical axis (Z) on excitation with light polarized normal to the optical axis (X), similarly are I_{ZZ}, I_{XX} and I_{ZX}). Figure 2 shows the results of the measurement of the absorbance of the dye in the LC with changing temperature.

Attention is drawn to the redistribution of the luminescence intensities among the various components along with some decrease in the total luminescence intensity as the temperature increases (Figure 1). Relative component intensity is defined by the excitation anisotropy (which remains to

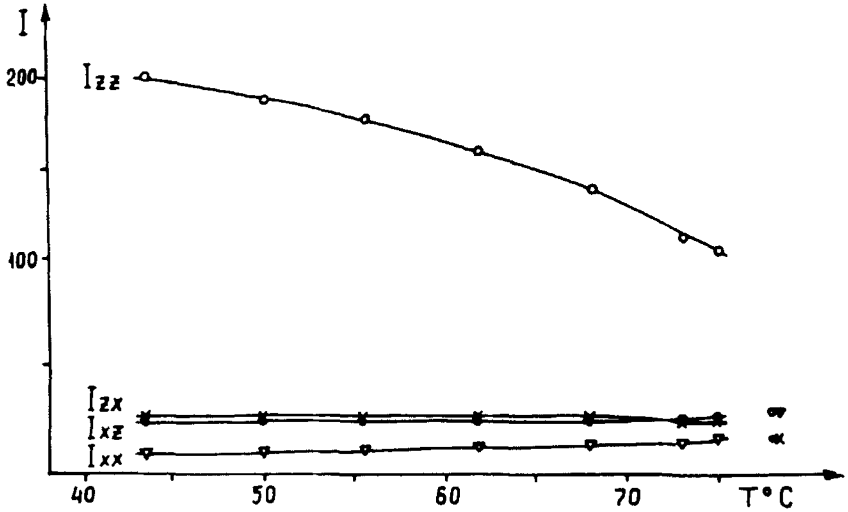

FIGURE 1 Intensity of LC polarized luminescence intensity components. Extreme right points are isotropic liquid measurements.

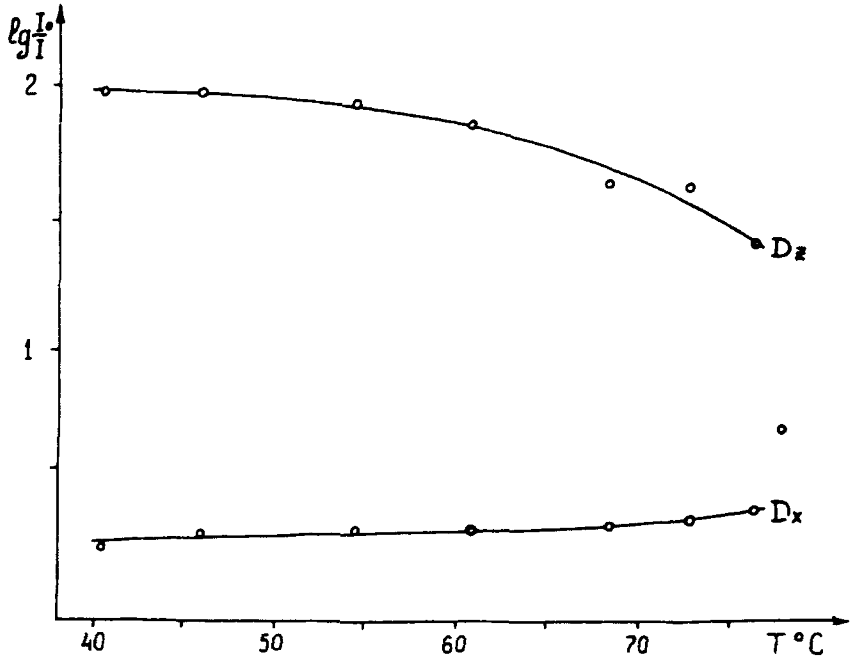

FIGURE 2 Absorbance of LC dye absorption. Z and X relate to light polarization parallel and normal to the optical axis, respectively.

some extent in the isotropic liquid $T \gtrsim 77°C$), due to the ordered arrangement of the LC molecules, as well as by the change of this order with temperature.

In the case where the absorbing and radiating oscillators are parallel to the long molecular axis, the luminescence intensity components are defined by the following expressions:

$$I_{ZZ} = B_Z \overline{\cos^4 \theta}, \tag{4}$$

$$I_{ZX} = B_X \overline{\frac{\cos^2 \theta \cdot \sin^2 \theta}{2}}, \tag{5}$$

$$I_{XZ} = B_Z \overline{\frac{\cos^2 \theta \cdot \sin^2 \theta}{2}}, \tag{6}$$

$$I_{XX} = B_X \tfrac{3}{8} \overline{\sin^4 \theta}. \tag{7}$$

In (4)–(7) averaging over the azimuthal angle φ was carried out. The difference between coefficients B_Z and B_X is due to the different output from the LC of the luminescence which is polarized parallel and normal to the preferred LC direction. It should be emphasized that (4)–(7) are given, as opposed to [2], for weakly absorbing samples, when absorption along the preferred direction and normal to it is proportional to $\overline{\cos^2 \theta}$ and $\overline{\sin^2 \theta}/2$, respectively. $\overline{\text{Cos}^2 \theta}$, $\overline{\cos^4 \theta}$, S_1 and S_2 are calculated from (1)–(7) using the experimental data shown in Figure 1 (Figure 3). Also shown in this picture are the results of S_1 calculated using the absorbance data from Figure 2 and [4].

$$S_1 = \frac{A_Z - A_X}{A_Z + 2A_X}, \tag{8}$$

where A_Z and A_X are the absorbances for the light polarized parallel and normal to the optical LC axis.

Equations (4)–(7) are given for the case when a molecule does not change its spatial orientation during the lifetime of its excited state. The lower values of S_1 determined via $\overline{\cos^2 \theta}$ from the luminescence data, as compared to the S_1 values determined from the absorption data, appears to be due to the fact that the molecule manages, during the lifetime of the excited state, to turn through some angle. However, such an angular relaxation for a molecule turning about its short axis is likely to be insignificant for the LC.

S_1 and S_2 are Fourier coefficients if the function $f(\theta)$ is expanded in terms of Legendre polynomials [5]

$$f(\theta) = \tfrac{1}{2} + \tfrac{5}{2} S_1 P_2(\cos \theta) + \tfrac{9}{2} S_2 P_4(\cos \theta) + \cdots. \tag{9}$$

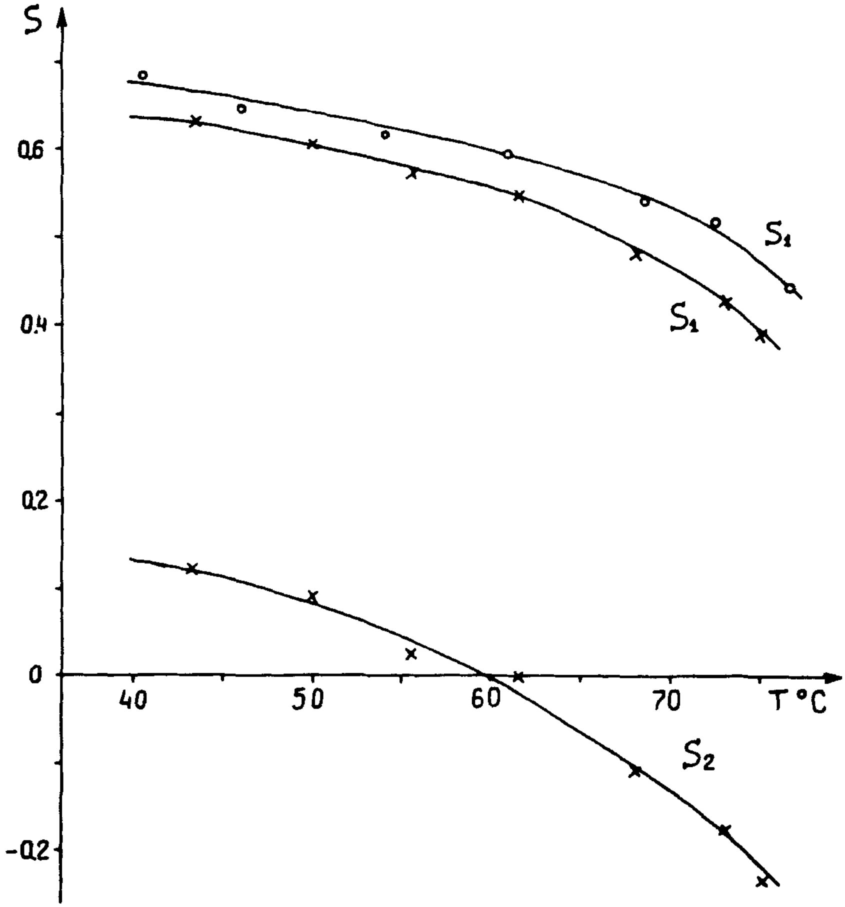

FIGURE 3 Degrees of orientational order S_1 and S_2 calculated from the polarized luminescence (×) and absorption (O) data.

Using S_1 and S_2 the angular molecular distribution function can be plotted in approximation (9). Figure 4 shows the results of the calculation of $f(\theta)$ for at 43.5°C and 61.6°C.

Thus, if absorption data enable one to define only S_1, polarized luminescence provides a greater body of information on the LC state ordering. The relative intensity of polarized luminescence spectrum components can also supply information on the molecular angular relaxation in the LC occurring during the lifetime of molecules in the excited state.

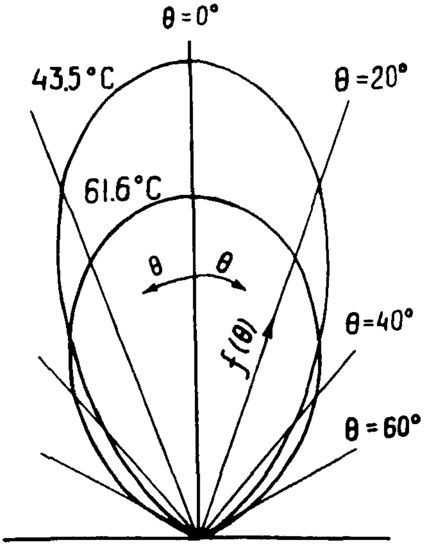

FIGURE 4 The LC molecular angular distribution function at 43.5°C and 61.6°C.

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