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Molecular Orientation of Perylene-like Dyes in Liquid Crystal 8OCB

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The polarized absorption and fluorescence spectra of some dichroic fluorescent dyes (derivatives of 3,4,9-perylenetricarboxylic acid and 3,4,9,10-perylenetetracarboxylic acid) oriented in liquid crystal 8OCB have been recorded as a function of temperature. On the basis of these spectra the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ and orientational distribution function have been determined. The conclusions about the influence of the molecular structure of the dyes on their orienting properties in uniaxial liquid crystalline phases have been drawn.

Keywords: liquid crystal; dichroic dye; absorption; fluorescence; order parameter

INTRODUCTION

Since discovery of the „guest-host" effect in liquid crystals by Heilmeier and Zanoni [1] there has been much interest on phenomena associated with the addition of the dichroic dyes (guests) to liquid crystalline matrices (hosts). Dye-liquid crystal systems can be used in the optical spectroscopy for obtaining information concerning the electronic spectra of the dyes [2-6] as well as to study the orientational order of liquid crystal matrices [7] and molecular interactions between dye molecules and their anisotropic environment [8-12]. Furthermore, they are utilized in the construction of the guest-host liquid

crystal displays (GH LCDs) used in high performance applications requiring unrestricted viewing angle and harsh environmental conditions. A number of dyes of different chemical classes containing various extended chromophore systems had been examined as guests in liquid crystalline hosts[13] in order to improve the color contrast, brightness and viewing angle of LCDs. Recently, it had been found that perylene-like dyes can be used successfully both in passive and active GH LCD devices[14,15]. These dyes have yellow to orange-red color and emit light with high fluorescence quantum yield in the spectral region advantageous for human eye. Moreover, they have good dichroic properties, are stable to the sunlight and do not significantly destabilize the mesomorphic phase of the liquid crystal hosts.

In this paper we have studied some derivatives of 3,4,9-perylene-tricarboxylic acid and 3,4,9,10-perylenetetracarboxylic acid dissolved in liquid crystal 8OCB by means of optical spectroscopy. The aim of these studies is obtaining information about the ability of the dyes to orientation in liquid crystal in smectic A and nematic phases.

For a uniaxial system containing molecules with an effective cylindrically symmetric form the orientational order can be described by a probability distribution, $f(\beta)$, where β is the angle between the long molecular axis and the major symmetry axis of the system. This distribution can be expressed[16] as a series expansion of even Legendre polynomials, $P_{2L}(\cos\beta)$, each of which is weighted by an order parameter $\langle P_{2L}\rangle$, which is the ensemble average of the corresponding term:

$$f(\beta)=\sum_{L=0}^{\infty}\frac{4L+1}{2}\langle P_{2L}(\cos\beta)\rangle P_{2L}(\cos\beta), \tag{1}$$

This expansion defines the order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ as follows:

$$\langle P_2\rangle=\frac{1}{2}\langle 3\cos^2\beta-1\rangle, \tag{2a}$$

$$< P_4 >= \frac{1}{8} < 35\cos^4\beta - 30\cos^2\beta + 3 >. \quad (2b)$$

The problem of determining the orientational order in uniaxial liquid crystal phases has been approached *via* wide variety of spectroscopic techniques [17]. Doping the liquid crystal with a fluorescent dye and utilizing the guest-host effect, information about the molecular orientation can be obtained using classical methods of optical spectroscopy: polarized absorption and fluorescence measurements. In principle, these methods determine only the degree of order for the guest molecules because the guest-host interaction causes often the perturbation of the orientation. However, in some particular cases, if the dye with the molecular structure similar to that of the liquid crystal molecules is chosen, one can assume that no significant differences between the orientational order of host and guest molecules occur and that the orientation of guest reflects well the orientation of the matrix [11,18].

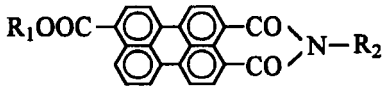
EXPERIMENTAL

The molecular structure of the perylene-like dyes investigated in the paper is presented in Fig.1. The dyes were synthesized and chromatographically purified in the Institute of Dyes at Łódź University of Technology, Poland. The structure of the dyes was confirmed by NMR and MS spectra and their purity was estimated by TLC method.

As host matrix we have used 4-n-octyloxy-4'-cyanobiphenyl (8OCB), which was synthesized in the Laboratory of Professor R. Dąbrowski at the Military Academy of Technology, Warsaw and was used without further purification. The temperatures of the phase transitions were in the agreement with the literature [19,20] and were as follows:

C - 327.7 K - S_A - 340.2 K - N - 353.2 K - I

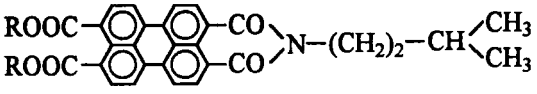
1) DERIVATIVES OF 3,4,9-PERYLENETRICARBOXYLIC ACID:



Dye code	R_1	R_2
1	$-CH_2-CH(CH_2CH_3)-(CH_2)_3CH_3$	$-CH_2CH_3$
2	$-CH_2-CH(CH_2CH_3)-(CH_2)_3CH_3$	$-CH_2CH_2OH$
3	$-(CH_2)_7CH_3$	$-(CH_2)_2CH(CH_3)_2$
4		$-(CH_2)_2CH(CH_3)_2$

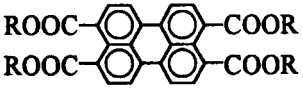
2) DERIVATIVES OF 3,4,9,10-PERYLENETETRACARBOXYLIC ACID:

a)



Dye code	R
5	$-CH_3$
6	$-(CH_2)_3CH_3$

b)



Dye code	R
7	$-(CH_2)_3CH_3$
8	$-(CH_2)_4CH_3$
9	$-(CH_2)_6CH_3$

FIGURE 1 Molecular structure of the dyes investigated.

The dyes were initially screened for their solubility in the liquid crystal and were dissolved in 8OCB at a concentration of $1.5 \cdot 10^{-3}$ M/l.

The polarized absorption spectra were obtained by means of a double beam spectrophotometer SPECORD M40 (Carl Zeiss, Jena). The polarized fluorescence spectra were recorded using a home-made photon-counting fluorimeter in the π geometry, i.e. the exciting light beam was perpendicular to the cell surface and the fluorescence light was monitored perpendicularly from the same side of the cell[21]. Both the spectrophotometer and fluorimeter were equipped with neutral UV polarizers. Corrections for the photomultiplier spectral sensitivity and for the different response of the device set with various directions of polarization were made. The measurements were carried out as a function of temperature using „sandwich" cells of 20 μm thickness. The planar orientation of the liquid crystal and dye molecules was achieved by treating the glass surfaces of the cells with polyimide and by an additional rubbing process. This procedure gives a good homogenous orientation of the molecules in the thin layer, which was controlled with a polarizing microscope. The temperature of the cells was regulated and controlled with an accuracy of ±0.1 K.

RESULTS AND DISCUSSION

Absorption

The absorption of light by the dye in relation to a certain electronic transition is determined by the transition moment μ. If we assume for simplicity that there is a single transition from the ground to the excited state and that the direction of this transition deviates from the direction of the molecular axis at an angle ϕ, the order parameter $\langle P_2 \rangle$ can be obtained from the measured absorbance for the incident polarized light using the following formula:

$$< P_2 >= \frac{A_{||} - A_{\perp}}{A_{||} + 2A_{\perp}} \frac{2}{3\cos^2\phi - 1} = \frac{D-1}{D+2} \frac{2}{3\cos^2\phi - 1}, \quad (3)$$

where $A_{||}$ and $A_{\perp}$ are the absorbances of the light polarized, respectively, parallel and perpendicular to the orientation axis of the liquid crystal, and $D=A_{||}/A_{\perp}$ is the dichroic ratio.

For the perylene molecule, which makes the main part of the molecular structure of the dyes investigated, a point symmetry group D_{2h} is attributed. The presence of the terminal groups causes „the breaking" of the molecular symmetry. In the first approximation the structure of the substituents attached to the planar π system would suggest C_S symmetry. Then the electronic transition as well as the orientation axis, which is approximately correlated with the long molecular axis, lie in the plane of the aromatic skeleton and rotate about an axis perpendicular to the plane. On the basis of the results of the polarized absorption measurements for perylene-like dyes in liquid crystalline mixture ZLI 1695 in the UV and visible spectral region, the computer simulation had been made in order to obtain the angles between the long molecular axis and the moment transitions directions [22], using procedure described in details in ref. [4,5] However, no consistent results for dyes **7**, **8** and **9** had been obtained. It seems, that the alkyl chains because of steric interactions cause that the molecular symmetry of these dyes is lower than C_S. In this case the point symmetry group C_2 can be considered [22], what means that there exists one transition polarized parallel to C_2 rotation axis, whereas others lie in a plane perpendicular to it.

All the dyes investigated in 8OCB have exhibited a broad absorption band with two peaks in the visible spectral region. The position of the maxima are listed in Table I. The values of the absorbance for these maxima have been used to calculation of the dichroic ratio and the order parameter $<P_2>$ from Eq. (3). It has been found that the values of the dichroic ratio for both

maxima are the same within the experimental uncertainty ($\Delta D=\pm 0.01$), what suggests that the two peaks observed in the visible region of the absorption spectra origin from the transition between the same electronic states. The angle ϕ between the direction of this transition moment and the long axis of the molecule for the perylene-like are presented in Table I. These results are obtained by assuming the appropriate symmetry of the dyes molecules and by using data given in [22].

TABLE I Positions of absorption maxima, λ_{max}, angle between transition moment and long molecular axis, ϕ and order parameter $\langle P_2 \rangle$ for dyes in 8OCB.

dye	λ_1^{max}/nm	λ_2^{max}/nm	$\langle P_2 \rangle$	
			$T^*=0.930$	$T^*=0.973$
1	487	514	0.56	0.47
2	485	512	0.62	0.51
3	485	512	0.66	0.56
4	487	514	0.65	0.54
5	480	510	0.67	0.53
6	482	512	0.67	0.49
7	449	478	0.43	0.33
8	449	478	0.51	0.38
9	449	478	0.60	0.47

Knowing the values of D and ϕ, the order parameter $\langle P_2 \rangle$ could be determined from Eq. (3). The results obtained for all the dyes investigated in 8OCB at two reduced temperatures ($T^*=0.930$, the smectic A phase and $T^*=0.973$, the nematic phase) are shown in Table I. $T^*=T/T_{NI}$, where T_{NI} is the clearing temperature for dye-8OCB mixture and T is the temperature of the

measurement in K. At least three, and usually five, samples were used to determine each order parameter. Table I contains the average values.

Figure 2 presents the dependence of the order parameter $<P_2>$ on the reduced temperature for dyes **1** and **6** in 8OCB, as examples. Additionally, in this figure the values of $<P_2>$ for pure 8OCB estimated on the basis of the optical birefringence measurements [11] are shown. It is seen, that the character of the changes of the guest order parameter is similar to that of the host. As the thermal molecular motions counteract parallel orientation, the $<P_2>$ value

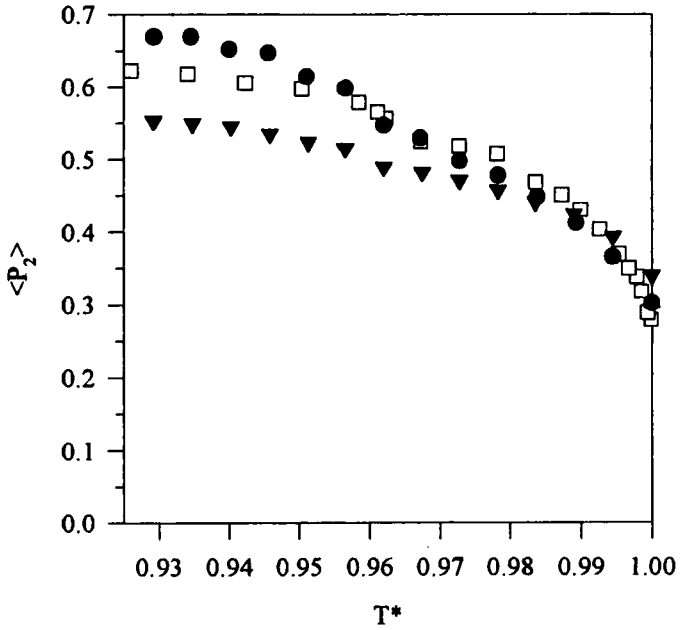


FIGURE 2 Order parameter $<P_2>$ estimated from the absorption measurements for dye **1** (triangles) and dye **6** (circles) in 8OCB. The squares represent the values of $<P_2>$ for pure 8OCB[11].

of 8OCB as well as that of the dissolved substance decreases with increasing temperature. Initially, in the smectic A phase the order parameter weakly depends on the temperature, then at $T^*=0.960$ for the dye-liquid crystal mixture and at $T^*=0.963$ for pure liquid crystal a small discontinuity, corresponding to the smectic A-nematic phase transition, is observed. The shift of the transition point in the presence of the dye indicates, that the guest added to the liquid crystal can change the transition temperatures, what had been observed also previously [9-12]. In the nematic phase $\langle P_2 \rangle$ decreases with the temperature to a certain value and at the clearing point drops discontinuously to zero.

From results presented in Table I and in Fig.2 it is seen, that the order parameter of the dyes investigated depends on the molecular structure of the terminal groups attached to the perylene skeleton. In some cases (dyes **3-6**) its value is larger than $\langle P_2 \rangle$ of the pure host. It happens often when the length of the guest exceeds that of the host [9-13,23,24] and can be explained in term of the tendency of the guest molecules to balance out the more extreme deviations of the smaller host molecules from the direction of orientation. It is worth noting, that for the derivatives of 3,4,9-perylenetricarboxylic acid the molecular structure of the substituent R_2 has a strong influence on the order parameter. If the hydrogen in the methylene group is replaced by -OH group, $\langle P_2 \rangle$ rises significantly. However, the substituent R_1 does not affect the order parameter (compare $\langle P_2 \rangle$ for dye **3** and **4**), changes solely the angle between the long molecular axis and the absorption transition moment. The results for dyes **7**, **8** and **9** indicate, that the length of the alkyl chains strongly affects the molecular orientation: the order parameter rises distinctly together with the rise of the alkyl chain length, instead of the steric interactions and the flexibility of the terminal chains.

Fluorescence

The intensity of the fluorescence excited with the light beam polarized in the i-direction and observed after passing the analyzer with its polarization direction along the j-axis is given by:

$$J_{ij} = < \mathbf{M}_{ai}^2 \mathbf{M}_{ej}^2 >, \tag{4}$$

where $\mathbf{M}_{ai}$ and $\mathbf{M}_{ej}$ are the absorption and emission oscillator components projected onto the axes i and j, respectively. The average extends over all molecules in the illuminated volume and includes all possible angular positions of the absorption and emission oscillators weighted by the appropriate statistical distribution.

From the fluorescence intensity measurements the emission anisotropies R_1 and R_2 for excitation with the light polarized parallel and perpendicularly to the orientation axis, respectively, can be calculated from the formula:

$$R_{1,2} = \frac{J_{||} - J_{\perp}}{J_{||} + 2J_{\perp}}, \tag{5}$$

where $J_{||}$ and $J_{\perp}$ are the intensities of emission polarized parallel and perpendicular to the orientation axis, respectively, measured in the parallel geometry [21,25].

For the special case of $\phi=0^{\circ}$ and assuming that the rotational relaxation time τ_R is much larger than the lifetime τ_F of the excited state of the fluorescent molecule and that the effect of the rotational motions on the fluorescence depolarization can be neglected, R_1 and R_2 are related to the order parameters $<P_2>$ and $<P_4>$ as follows [26]:

$$R_1 = \frac{\left[\frac{2}{5} + \frac{11}{7} < P_2 > + \frac{36}{35} < P_4 >\right] P_2(\cos\delta)}{1 + 2 < P_2 >}, \tag{6}$$

$$R_2 = \frac{\left[< P_2 > - \frac{2}{5} - \frac{21}{35} < P_4 > \right] P_2(\cos\delta)}{1 - < P_2 > + 2\left[\frac{1}{5} - \frac{2}{7} < P_2 > + \frac{3}{35} < P_4 > \right] P_2(\cos\delta)}, \quad (7)$$

where δ is the angle between the absorption and emission oscillators.

If the angle $\phi \neq 0°$ and/or $\tau_F \approx \tau_R$, then the relation between the emission anisotropies and $<P_2>$ and $<P_4>$ parameters is much more complicated [16,26,27].

In the case of the dyes investigated, instead of the high fluorescence quantum yield in the isotropic solvents [15], the fluorescence intensity with the significant efficiency only for dyes **7-9** dissolved in 8OCB have been observed. (for other dyes the intensity of the fluorescence has been hardly measurable and has not allowed to obtain the reliable results). Therefore, the Eqs. (6) and (7) could be used to determine the order parameters $<P_2>$ and $<P_4>$ as for these dyes the angle ϕ is equal to 0°. Moreover, for the dyes dissolved in 8OCB it has been assumed that $\tau << \tau_R$ in the liquid crystalline phases.

The dyes oriented in 8OCB has been excited at λ_{exc}=436 nm (the Hg-line) and for calculation of the emission anisotropies R_1 and R_2 the values of the fluorescence intensities have been taken at the wavelength corresponding to the maximum of the emission band, i.e. at λ=500 nm. The angle δ, which is needed to determine the order parameters from Eqs. (6) and (7) has been estimated on the basis of the absorption and fluorescence measurements of the dyes in 8OCB at the temperature just after crystal-smectic A transition. We have supposed that at the lowest temperature in the smectic state, because of high viscosity, the thermal molecular motions are strongly hindered and have a negligible effect on the emission anisotropy. Therefore, in this case $<P_2>$ obtained from the fluorescence measurement must be equal to that determined

on the basis of the polarized absorption spectra. By knowing $\langle P_2 \rangle$ from absorption measurement, $\langle P_4 \rangle$ and $\cos\delta$ has been determined by solving Eqs. (6) and (7). We have obtained $\delta = 18° \pm 4°$ for dye **7** and $\delta = 20° \pm 4°$ for dyes **8** and **9**. Then the angle δ has been assumed to be constant in our experimental temperature range, and the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ as a function of temperature have been determined from measured fluorescence and Eqs. (6) and (7).

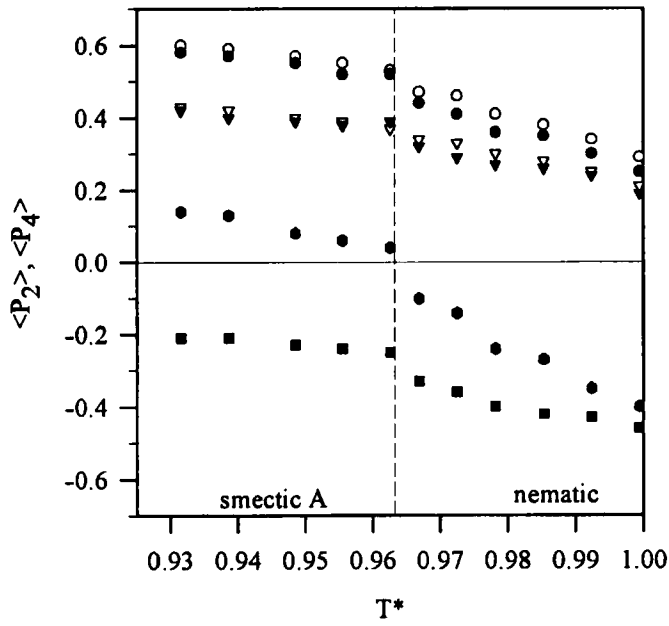


FIGURE 3 Order parameters for dyes 7 and 9 in 8OCB obtained from the absorption (open symbols) and fluorescence (filled symbols) measurements. The triangles and squares represent, respectively, $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values for dye 7; the circles and hexagons represent, respectively, $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values for dye 9.

Fig. 3 shows the order parameter $\langle P_2 \rangle$ obtained from the absorption and fluorescence measurements as well as $\langle P_4 \rangle$ *versus* reduced temperature for dyes **7** and **9** in 8OCB. It is seen, that in the smectic A phase $\langle P_2 \rangle$ values obtained by using both methods are similar within the experimental uncertainty, whereas in the nematic phase the tendency of $\langle P_2 \rangle$ determined from the fluorescence to be lower than that obtained from the absorption is observed. This can be due to the fact, that in the nematic phase the assumption $\tau_F << \tau_R$ is not sufficiently fulfilled.

$\langle P_4 \rangle$ parameter is positive only for 8OCB-dye **9** mixture in the smectic A phase, while it becomes negative after transition to the nematic phase. For 8OCB doped with dyes **7** and **8** $\langle P_4 \rangle$ has been observed to be always negative, even in the smectic A phase. The order parameter $\langle P_4 \rangle$ depends on higher power of the angle β, is therefore more sensitive to the molecular fluctuations and decreases rapidly if the molecular orientation is perturbed, i.e. because of the guest-host interactions. It is worth noting, that the change of $\langle P_4 \rangle$ at the smectic A-nematic transition is more distinct than the change of $\langle P_2 \rangle$, what helps in the determination of this transition temperature.

The negative value of $\langle P_4 \rangle$ influences the breadth of the molecular distribution function, $f(\beta)$, as is illustrated in Fig.4. The solid and dashed curves represent the distribution of the host and guest molecules as a function of the angle β for dye **9**-8OCB mixture in the smectic A and nematic phases, respectively. We can see, that $f(\beta)$ in the nematic phase is significantly broadened with respect to that in the smectic A phase. The maximum occurs not at $\beta=0^\circ$, but at an angle between 0 and $\pi/2$, what indicates the existence of collective molecular tilt. This means, that the dye added to the liquid crystal can be the reason of the strong tendency of the molecules in the guest-host mixture to tip away from the preferred direction of orientation.

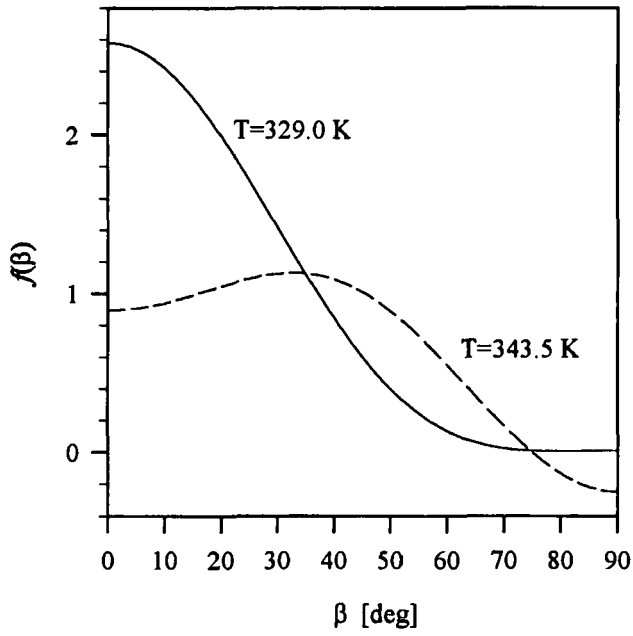


FIGURE 4 Molecular distribution function, $f(\beta)$ in the smectic A (T=329K) and nematic (T=343.5K) phases for dye **9** in 8OCB.

Acknowledgments

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