

Perylene-like Dyes in Liquid Crystalline Media

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The spectral and electrooptical properties of some dichroic fluorescent dyes (derivatives of 3,4,9,10-perylenetetracarboxylic acid and of 3,4,9-perylenetricarboxylic acid) in isotropic solvents and nematic liquid crystals have been studied. The order parameter of the dyes in the anisotropic matrices has been determined by means of optical spectroscopy methods. Moreover, the influence of the dye addition on the nematic-isotropic phase transition temperature of the pure host has been investigated. It was found that some of the dyes studied can be utilized in guest-host liquid crystal display devices.

I. Introduction

Guest-host liquid crystal displays (GH LCDs) are widely used in high performance applications that require unrestricted viewing angle and harsh environmental conditions. Recently, they have found such sophisticated applications as automotive dashboards, multicolour displays, electrophotographic printers and optical storage devices. In GH LCDs a small amount of a dichroic dye (guest) is dissolved in a liquid crystalline host which acts as a matrix to orient the guest molecules. The application of an electric field causes reorientation of the liquid crystal and dye molecules and thereby a change in the colour intensity. The dyes used in GH LCDs must have a very high purity, good solubility in the liquid crystal matrix, low viscosity, a high dichroic ratio and high photostability and electrical resistivity. Dyes of different chemical classes containing various extended chromophore systems have already been examined as solutes in liquid crystalline media [1]. Mainly azo and anthraquinone dyes were employed. However, the azo dyes have often a poor photochemical stability [2], whereas most of the anthraquinone dyes have inadequate solubility [3]. In [4 - 6] it has been shown that the naphthalene derivatives of bicarboxylic acid have properties which qualify them as possible dichroic dyes in GH LCDs. Many of them emit green fluorescence with very high quantum yield, which can be controlled by changing the orientation of guest and host molecules by means of an electric field. In [7]

it was found that also perylene diesters have a high fluorescence intensity and satisfactory dichroic ratio for use in GH LCDs.

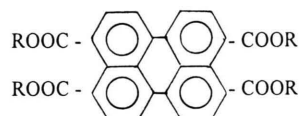
In this paper we describe the properties of some new synthesized perylene-like dyes and discuss the possibility of their application in GH LCDs working both in absorption (passive) and fluorescence (active) modes.

II. Materials and Methods

The following dyes were studied:

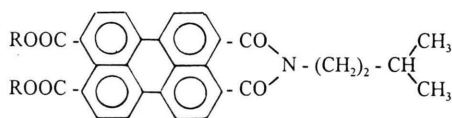
1) derivatives of 3,4,9,10-perylenetetracarboxylic acid:

a)



Dye code	R
1	-CH ₃
2	-(CH ₂) ₃ CH ₃
3	-(CH ₂) ₄ CH ₃
4	-(CH ₂) ₆ CH ₃

b)



Dye code	R
5	-CH ₃
6	-(CH ₂) ₃ CH ₃

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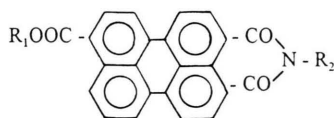
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2) derivatives of 3,4,9-perylenetricarboxylic acid:



Dye code	R ₁	R ₂
7	-CH ₂ -CH-(CH ₂) ₃ CH ₃ CH ₂ CH ₃	-CH ₂ CH ₃
8	-CH ₂ -CH-(CH ₂) ₃ CH ₃ CH ₂ CH ₃	-CH ₂ CH ₂ OH
9	-(CH ₂) ₇ CH ₃	-(CH ₂) ₂ CH(CH ₃) ₂
10		-(CH ₂) ₂ CH(CH ₃) ₂

The dyes were synthesized and chromatographically purified in the Institute of Dyes, Łódź University of Technology, Poland. The structure of the dyes was confirmed by NMR and MS spectra and their purity was estimated by the TLC method.

For isotropic solvents dioxane and acetone were used. The dyes were dissolved in these solvents at a concentration of 10^{-5} M/l.

As host matrices both the one - component liquid crystal 4-n-pentyl-4'-cyanobiphenyl (5CB) or 4-(trans-4'-n-hexylcyclohexyl)isothiocyanatobenzene (6CHBT) and the liquid crystalline mixture 602 were used. 5CB was supplied by Merck, whereas 6CHBT and the mixture 602 were synthesized in the Laboratory of Prof. R. Dąbrowski, Military Academy of Technology, Warsaw. All these liquid crystalline substances exhibit a stable nematic phase, good chemical stability and high positive dielectric anisotropy. The dyes were initially screened for their solubility in liquid crystal, and it has been found that not all of them are sufficiently soluble in the liquid crystals used. Generally, the solubility of the dyes was better in the liquid crystalline mixture 602 than in the one-component liquid crystals. Well soluble were the dyes **3**, **4**, **5**, **6**, **7** and **8**, whose solubility was up to 0.5 - 0.7% wt. in the mixture 602 and 0.3 - 0.4% wt. in 5CB and 6CHBT. Worst soluble was the dye **1**, only up to 0.1% wt. in 5CB and slightly more in 602. In order to compare the behaviour of the dyes, the same concentration, 0.1% wt., for all the dye-liquid crystal mixtures was chosen. Solutions were prepared by dissolving powdered samples of the dye into the liquid crystal host at room temperature. Next, the dye-liquid

crystal mixtures were heated to the isotropic phase and mixed for about one hour. Microscopic examination ensured that complete dissolution of the dye had occurred.

The optical and electrooptical properties of the dye-liquid crystal mixtures were measured in 40 μ m thick "sandwich" cells. A homogenous planar orientation of molecules was obtained by treating the glass surfaces of the cells with polyimide and additional rubbing. The cells filled with the dye-liquid crystal mixtures were tested for photostability by exposure to sunlight: no significant changes in the absorbance and fluorescence intensity were observed over a three-month period.

Absorption and its polarized spectra were recorded on a double beam spectrophotometer Specord M40 (Carl Zeiss Jena, Germany). Fluorescence spectra were measured using a home-made photon counting fluorimeter. The wavelength of the excitation light was chosen to correspond to the absorption maximum of the dyes.

The quantum fluorescence yield of the dyes in isotropic solvents was calculated using the equation [8]

$$Q = Q_r \frac{1 - 10^{-A_r(\lambda)}}{1 - 10^{-A_x(\lambda)}} \frac{\int_0^\infty F_x d\lambda}{\int_0^\infty F_r d\lambda}, \quad (1)$$

where Q_r is the quantum fluorescence yield of a standard, $A(\lambda)$ the absorbance of the solution at the exciting wavelength λ , $\int_0^\infty F d\lambda$ the integrated area under the emission spectrum, and the subscripts x and r refer to the unknown and reference solutions, respectively. As a standard, fluorescein at a concentration of 10^{-6} n NaOH was used. The quantum yield of fluorescein at 20°C is 0.92 [8].

For the absorption and fluorescence measurements of the dye-liquid crystal mixtures both the spectrophotometer and fluorimeter were equipped with neutral UV polarizers. The fluorescence spectra were recorded 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.

From the polarized absorption and fluorescence spectra the order parameter of the dye molecules in a nematic liquid crystal host was determined. This order parameter is defined as [9]

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

where θ is the angle between the long molecular axis of the dye and the direction of the host orientation, and $\langle \cos^2 \theta \rangle$ is the average value of $\cos^2 \theta$ for the dye molecules.

If it can be assumed that the geometric long axis of the dye molecules corresponds to the direction of the absorption polarization, and that the contribution to the absorption caused by molecular polarization in the perpendicular direction is small, then the order parameter can be determined from the polarized absorption spectra of the guest-host mixture by means of the equation [10–12]

$$S_A = \frac{D - 1}{D + 2} = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}}, \quad (3)$$

where $D = A_{\parallel}/A_{\perp}$ is the dichroic ratio of the dye, and A_{\parallel} and A_{\perp} are the absorbances of the light polarized in parallel and perpendicularly to the orientation axis of the sample, respectively.

In analogy to the case of light absorption, the order parameter of a dye in a liquid crystal can be calculated from the polarized components of the fluorescence spectra by applying the equation [12]

$$S_F = \frac{F_{\parallel} - F_{\perp}}{F_{\parallel} + 2F_{\perp}}, \quad (4)$$

where F_{\parallel} and F_{\perp} are the intensities of the fluorescence light polarized parallel and perpendicularly, respectively, to the liquid crystal orientation axis. Equation (4) is valid for excitation with unpolarized light and for dyes with absorption and emission transition moments parallel to the long molecular axis.

The temperature of the nematic-isotropic phase transition for the pure nematics and those doped with the dye was determined by means of a polarizing microscope (PZO, Warsaw) equipped with a heating stage: The accuracy of the temperature determination was ± 0.1 K. The electrooptical parameters were estimated using a c. voltage of 1 kHz.

III. Results and Discussion

III.1. Absorption and Fluorescence Spectra

All perylene-like dyes investigated exhibited a broad absorption band with two peaks in the visible region. In the fluorescence emission spectrum also

Table 1. Positions of absorption and fluorescence maxima and quantum fluorescence yields for the dyes in dioxane.

Dye code	Absorption			Fluorescence		
	λ_1 [nm]	λ_2 [nm]	ε^a	λ_1 [nm]	λ_2 [nm]	Q_x
1	444	473	32000	490	520	0.80
2	444	473	45000	490	520	0.63
3	444	473	39000	490	520	0.74
4	444	473	41000	490	520	0.66
5	468	501	55000	517	555	0.85
6	489	525	90000	532	575	0.68
7	477	506	44000	527	565	0.68
8	477	506	44000	527	565	0.60
9	477	506	33000	527	565	0.84
10	477	506	41000	527	565	0.70

^a for λ_2

Table 2. Positions of absorption and fluorescence maxima and quantum fluorescence yields for the dyes in acetone.

Dye code	Absorption			Fluorescence		
	λ_1 [nm]	λ_2 [nm]	ε^a	λ_1 [nm]	λ_2 [nm]	Q_x
1	439	467	55000	488	515	0.50
2	439	467	49000	488	515	0.58
3	439	467	56000	488	515	0.47
4	439	467	66000	488	515	0.20
5	465	495	58000	521	560	0.43
6	486	521	100000	533	570	0.55
7	472	500	50000	535	570	0.33
8	472	500	44000	535	570	0.38
9	472	500	46000	535	570	0.51
10	472	500	57000	535	570	0.34

^a for λ_2

two distinct peaks appeared. The positions of the absorbance and fluorescence intensity maxima for the dyes in dioxane and acetone are gathered in Tables 1 and 2. In these tables the extinction coefficient, ε , and the quantum fluorescence yield of the dyes, Q_x , are also presented. It is seen that the differences in the molecular structure of the terminal substituents added to the basic perylene structure influence both the absorption and fluorescence spectra. The colour of the dyes varies from yellow to orange-red, and they emit blue-green to green-yellow light. The efficiency of the fluorescence is high (in the dyes **1**, **5**, **9** in dioxane even very high) and depends on the substituent structure, its length and the solvent.

Figure 1 shows the polarized absorption and fluorescence spectra for dye **8** in the mixture 602, as an example. In the liquid crystals also two peaks in

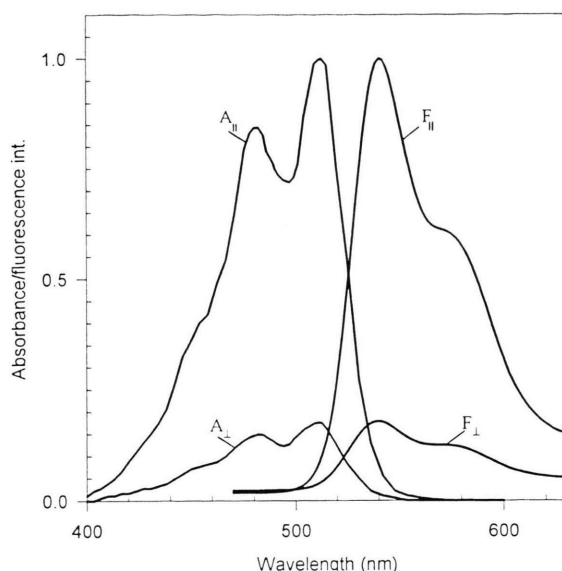


Fig. 1. Polarized components of the absorption and fluorescence spectra for dye **8** in the liquid crystalline mixture 602.

the absorption and fluorescence spectra in the visible region are observed. Longwavelength peak in the fluorescence spectrum is, however, significantly less distinct than in the case of the isotropic solvents, which is probably due to the perturbation of the excited states of the dye molecule by the anisotropic matrix.

For calculation of the order parameter from (3) and (4) the values of A_k and F_k ($k = \parallel, \perp$) were taken at the wavelength corresponding to the higher intensity maximum of absorption and fluorescence, respectively, of the dye-liquid crystal mixture. The positions of these maxima are given in Tables 3 and 4. It is apparent that the absorbance and fluorescence intensity maxima undergo slight shifts in the various liquid crystals due to the different polarities of the hosts. The maximum positions of the perpendicular component of the fluorescence are shifted slightly with respect to those of the parallel components. This results from the dependence of the energy difference between the absorption and emission bands (Stokes shift) on the electric permittivity and the refractive index [13], which are different when measured parallel and perpendicular to the optical axis of a liquid crystal.

An exact determination of the fluorescence quantum yield for dyes dissolved in oriented liquid crystals is very difficult because many factors (also anisotropic) must be taken into account. We tried to

Table 3. Positions of absorption (longwavelength) and fluorescence (shortwavelength) maxima and order parameters of the dyes in one-component liquid crystals.

Dye code	λ [nm]	Absorption			Fluorescence				
		S_A			$\lambda(\parallel)$	$\lambda(\perp)$	S_F		
		$T = 295\text{K}$	$T = 301\text{K}$	$T = 306\text{K}$	[nm]	[nm]	$T = 295\text{K}$	$T = 301\text{K}$	$T = 306\text{K}$
1 ^a	480	0.43	0.35	0.29	500	498	0.42	0.37	0.28
2 ^a	480	0.40	0.33	0.28	500	498	0.38	0.30	0.24
3 ^a	480	0.38	0.32	0.26	500	498	0.35	0.28	0.20
4 ^a	480	0.35	0.31	0.26	500	498	0.30	0.25	0.20
5 ^a	509	0.60	0.55	0.47	535	532	0.57	0.46	0.40
6 ^a	536	0.58	0.54	0.43	552	532	0.54	0.43	0.38
7 ^b	514	0.51	0.41	0.32	541	538	0.50	0.40	0.35
8 ^b	514	0.56	0.48	0.40	541	538	0.58	0.46	0.38
9 ^b	514	0.56	0.50	0.42	541	538	0.58	0.52	0.47
10 ^b	514	0.58	0.49	0.40	541	538	0.54	0.47	0.41

^ain 5CB, ^bin 6CHBT

Table 4. Positions of absorption (longwavelength) and fluorescence (shortwavelength) maxima and order parameters of the dyes in the liquid crystalline mixture 602.

Dye code	λ [nm]	Absorption			Fluorescence				
		S_A			$\lambda(\parallel)$	$\lambda(\perp)$	S_F		
		$T = 295\text{K}$	$T = 318\text{K}$	$T = 338\text{K}$	[nm]	[nm]	$T = 295\text{K}$	$T = 318\text{K}$	$T = 338\text{K}$
1	475	0.55	0.50	0.36	495	493	0.55	0.52	0.38
2	475	0.54	0.48	0.32	495	493	0.52	0.46	0.33
3	475	0.52	0.45	0.38	495	493	0.50	0.43	0.37
4	475	0.52	0.45	0.38	495	493	0.48	0.37	0.31
5	506	0.73	0.66	0.57	525	522	0.69	0.62	0.56
6	531	0.70	0.63	0.54	545	542	0.62	0.55	0.46
7	510	0.55	0.50	0.44	540	538	0.60	0.56	0.47
8	510	0.61	0.54	0.43	540	538	0.61	0.52	0.46
9	510	0.65	0.54	0.44	540	538	0.68	0.58	0.53
10	510	0.68	0.59	0.53	540	538	0.65	0.56	0.52

estimate these yields, but the estimation should be regarded as more qualitative than quantitative. The results indicated that the Q_x values for the dye-liquid crystal mixtures are similar to those obtained for the dyes dissolved in acetone.

III.2. Order Parameter

The order parameters of the dyes dissolved in the liquid crystal, obtained from the absorption and fluorescence measurements at three various temperatures,

are gathered in Tables 3 and 4. At least three, and usually five, samples were used to determine each order parameter. Tables 3 and 4 contain the average values. The uncertainties in the determination of S_A and S_F were estimated to be ± 0.01 and ± 0.03 , respectively. The values of the order parameter determined for the second maximum (at shorter wavelength for the absorption and at longer wavelength for the fluorescence) are within the experimental uncertainty the same as for the maxima given in Tables 3 and 4, which suggests that the two peaks observed in the absorption and fluorescence spectra origin from the transition between the same electronic states.

The order parameters for the dyes investigated are different in the various liquid crystals. This results from the various guest-host interactions in dye-liquid crystal mixtures and has already been observed for many dichroic dyes [14–17]. It must be emphasized, however, that in the liquid crystalline mixture 602 the orientation of the dye by the nematic host at room temperature is generally better than in the liquid crystals 5CB and 6CHBT. Not only the various guest-host interactions, but also the different nematic-isotropic transition temperatures of the liquid crystals used have an influence on this effect. A higher clearing temperature usually results in an increase in the order parameter, which is observed also in our studies. From the data presented in Tables 3 and 4 it is seen that the changes in the order parameter with rise of the temperature do not follow the same pattern for all the dye-liquid crystal mixtures, which implies that the various guest-host mixtures are differently resistant to thermal fluctuations.

The values of the order parameters estimated from the fluorescence measurements (S_F) are somewhat different from those obtained on the basis of the absorption spectra (S_A), and except for a few cases $S_F < S_A$. At least three effects can be the reason for such differences: i) the existence of non-zero intramolecular angles between the absorption and emission oscillators [18, 19], ii) the intermolecular energy transfer processes, which can depolarize the fluorescence in an unpredictable manner [18, 19] and lead to misinterpretation of the results obtained, and iii) the interactions between the liquid crystal molecules and the cell surfaces [20–23]. Many authors [5, 6, 20–23] have found that the molecular orientation in the liquid crystal cell is larger at the glass surfaces than in the bulk, where the flexible mesogenic molecules are more mobile. The order parameter S_A , determined

from the absorption measurements, is the averaged value over the whole optical pathway of the light passing through the cell, whereas the fluorescence in the geometry used in our experiment is emitted mainly from the cell surface. Therefore S_F reflects the molecular order in the surface layer rather than in the bulk. The influence of the surface interaction on the order parameter could be confirmed by the results for dyes **7** and **9**, but one cannot exclude in these cases the second possibility, namely that the direction of the emission transition moment makes a smaller angle with the long axis of the dye molecule than the direction of the transition moment of the absorption. Considering the above mentioned factors, it would appear that the values of S_A reflect better the dye orientation in the nematic host than those of S_F . Determination of the order parameter for fluorescent dyes dissolved in liquid crystals from the polarized fluorescence spectra is, however, not completely inexpedient because information obtained from S_F can be utilized by selection of the appropriate guest-host mixture to GH LCDs working in the active mode.

The molecular structure of the substituent influences the order parameter. The long and symmetric dyes **5** and **6** have the highest order parameter among the dyes investigated. The lack of the terminal group in position 10 of the basic perylene structure (dyes **7**–**10**) causes a somewhat smaller order parameter, which can be due to the fact that in this case the direction of the transition moment is not parallel to the long axis of the dye molecule. It is worth noting that for derivatives of 3,4,9-perylenetricarboxylic acid the molecular structure of the substituent R_1 has a strong influence on the order parameter. If the alkyl chain is replaced by the cyclohexane ring, S rises in both liquid crystals used. For the dyes **1**–**4**, which have the highest symmetry, the order parameter is not very high, especially in 5CB. Since for such molecules (C_{2v} point symmetry group) the symmetry dictates that the direction of the transition moment is parallel to the long molecular axis, the low order parameter can arise only from the incomplete alignment of the dye molecules in the anisotropic matrix. It can be caused by the fact, that the dye molecules are significantly broader than the molecules of the liquid crystals. From the results for dyes **1**–**4** and **5** and **6** it is seen that the alkyl chain length has little effect on the order parameter. The rise of the length of alkyl chain does not necessarily lead to the increase of the length of the whole molecule because the alkyl groups

are flexible and the rigidity of the molecule decreases with increasing chain length. This is reflected by the results presented in Tables 3 and 4: when the length of the alkyl chain rises, the order parameter slightly decreases.

III.3. Nematic-Isotropic Phase Transition Temperature

It is well known that the addition of a dichroic dye to a liquid crystal results in a change of the range of the host mesophase causing either an increase or a decrease of the nematic-isotropic phase transition temperature T_{NI} of the pure liquid crystal [4 - 6, 24 - 27]. As it had been shown in [25], the changes of the clearing point are dependent on the size and shape of the dye molecule, and on the dye concentration as well as on the mutual intermolecular interaction among guest and host molecules. Tables 5 and 6 illustrates the influence of the dyes on the nematic-isotropic transition temperature of the liquid crystal matrices. In the liquid crystalline mixture 602 and in the dye-liquid crystal mixtures there appears a two-phase region, in which both the nematic and isotropic phases coexist in equilibrium [28]. Therefore, in Tables 5 and 6 T_N is the temperature at which the last isotropic drop disappears, and T_I is the temperature at which the first nematic drop appears on cooling the sample. ΔT_N and ΔT_I , respectively, are the shifts of T_N and T_I with respect to such temperatures of the pure host, ($T_I - T_N$) is the range of the two phase region and \bar{T}_{NI} is the average nematic-isotropic transition temperature.

From Tables 5 and 6 it is seen that, although the dyes are added to the liquid crystals at very low concentration, they affect the transition temperature of the pure host, which can be connected with the large size of the dye molecules in comparison to those of liquid crystals. With only two exceptions, the dyes increase T_{NI} of the one-component liquid crystals, which indicates the stabilization of the mesophase by addition of these dyes. The two-phase region for 5CB and 6CHBT doped with the dyes is very narrow (0.1 K), but it is measurable. In the case of the liquid crystalline mixture 602, the dyes cause a distinct broadening of the two-phase region, and the average \bar{T}_{NI} for the dye-liquid crystal mixture is lower (with one exception) than for the pure nematic host, but $\Delta \bar{T}_{NI}$ is not less than -0.5 K. This means that the dyes destabilize slightly the mesophase region of the mixture 602.

Table 5. Temperature data for the dyes dissolved in 5CB or 6CHBT.

Substance	T_N	T_I	ΔT_N	ΔT_I	\bar{T}_{NI}
5CB	308.3	308.3	—	—	308.30
5CB + dye 1	308.0	308.1	-0.3	-0.2	308.05
5CB + dye 2	308.5	308.6	+0.2	+0.3	308.55
5CB + dye 3	308.4	308.5	+0.1	+0.2	308.45
5CB + dye 4	308.5	308.6	+0.2	+0.3	308.55
5CB + dye 5	308.3	308.4	0.0	+0.1	308.35
5CB + dye 6	308.1	308.2	-0.2	-0.1	308.15
6CHBT	316.0	316.0	—	—	316.00
6CHBT + dye 7	316.0	316.1	0.0	+0.1	316.05
6CHBT + dye 8	316.2	316.3	+0.2	+0.3	316.25
6CHBT + dye 9	316.3	316.4	+0.3	+0.4	316.35
6CHBT + dye 10	316.1	316.2	+0.1	+0.2	316.15

Table 6. Temperature data for dyes dissolved in the liquid crystalline mixture 602.

Substance	T_N	T_I	$T_I - T_N$	ΔT_N	ΔT_I	\bar{T}_{NI}
602	349.6	356.2	6.6	—	—	352.90
602 + dye 1	348.9	356.7	7.8	-0.7	+0.5	352.80
602 + dye 2	348.8	356.3	7.5	-0.8	+0.1	352.55
602 + dye 3	348.8	356.2	7.4	-0.8	0.0	352.50
602 + dye 4	348.9	356.3	7.4	-0.7	+0.1	352.60
606 + dye 5	349.0	356.4	7.4	-0.6	+0.2	352.70
602 + dye 6	348.7	356.3	7.6	-0.9	+0.1	352.50
602 + dye 7	349.0	356.6	7.6	-0.6	+0.4	352.80
602 + dye 8	349.3	356.6	7.3	-0.3	+0.4	352.95
602 + dye 9	349.0	356.5	7.5	-0.6	+0.3	352.75
602 + dye 10	348.4	356.3	7.9	-1.2	+0.1	352.35

III.4. Electrooptical Properties

One of the very important parameters of liquid crystal displays is the threshold voltage and the switching-on voltage. The absorption of a dye dissolved in a liquid crystal is strongly dependent upon the voltage applied to the cell. If a liquid crystal has a positive dielectric anisotropy, the parallel component of the absorption ($A_{||}$) decreases as the voltage applied rises, whereas the perpendicular component (A_{\perp}) remains constant (within experimental uncertainty). At a suitable large voltage, $A_{||}$ and A_{\perp} are equal. We have reported the voltage giving x% absorption (for $A = A_{||} - A_{\perp}$, normalized to 100% for no applied voltage) in the form

$$V_x(\alpha, t),$$

where α is the angle to the cell normal and t is the

Table 7. Characteristic voltages for the liquid crystalline mixture 602 doped with dye.

Dye code	$V_{90}(0^\circ, 22^\circ\text{C})$ [V] $\Delta V = \pm 0.1$ V	$V_{10}(0^\circ, 22^\circ\text{C})$ [V] $\Delta V = \pm 0.1$ V
4	2.1	4.2
5	2.1	4.1
8	2.0	4.0

temperature ($^\circ\text{C}$). As described in [29], we regarded the display to be completely *off* if

$$\text{OFF } V < V_{90}(0^\circ, t),$$

and fully *on* if:

$$\text{ON } V < V_{10}(0^\circ, t).$$

V_{90} can be considered as the threshold voltage, and V_{10} as the switching-on voltage of the liquid crystal display. The values of $V_{90}(0^\circ, 22^\circ\text{C})$ and $V_{10}(0^\circ, 22^\circ\text{C})$ for the technologically important liquid crystalline mixture 602 doped with three different dyes are listed in Table 7. The results presented in this table show that both the threshold voltage and the switching-on voltage are not influenced by the molecular structure of the dye substituents.

The change in the light absorption with the voltage applied must influence the intensity of the fluorescence. Similarly, as in the case of the absorption, the intensity of the parallel component of the fluorescence (F_{\parallel}) decreases as the voltage rises, whereas the perpendicular component (F_{\perp}) remains constant.

Figure 2 shows the voltage dependence of the S'_A and S'_F for dye 9 in the mixture 602 as an example, where S'_A and S'_F are defined, by analogy to (3) and (4) as

$$S'_A = \frac{A_{\parallel}(V) - A_{\perp}(V)}{A_{\parallel}(V) + 2A_{\perp}(V)}, \quad (5)$$

$$S'_F = \frac{F_{\parallel}(V) - F_{\perp}(V)}{F_{\parallel}(V) + 2F_{\perp}(V)}. \quad (6)$$

The character of the changes in S'_A and S'_F for the other dye-liquid crystal mixture 602 with the voltage applied to the cell is similar to that presented in Fig. 2.

From the results presented in Fig. 2 it is seen that S'_F does not become zero even at the large values of the

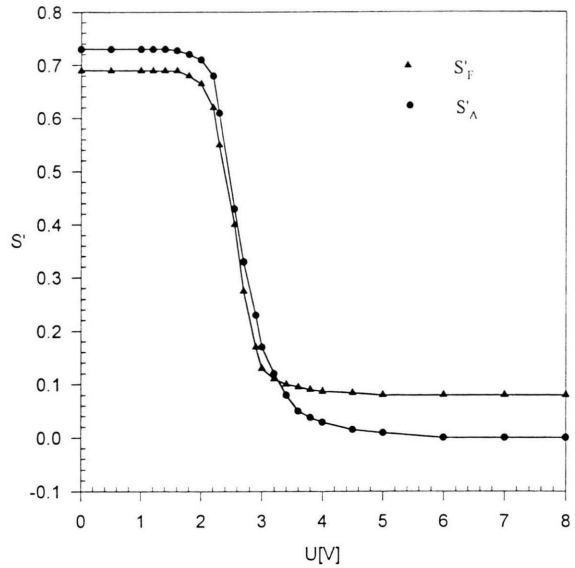


Fig. 2. S'_A and S'_F as a function of voltage for dye 5 in the liquid crystalline mixture 602 ($d = 40 \mu\text{m}$).

applied voltage, whereas S'_A reaches zero at about 6V. This observation confirms the fact that strong surface interactions occur near the glass plates. These interactions hinder the reorientation of the liquid crystal molecules in the surface layers in the electric field, and as a result the ordered state at the surfaces is not completely destroyed. Further, this means that in liquid crystal cells the molecular order in the bulk is different from that at the surfaces, what agrees with observations described in [21, 22].

IV. Conclusions

We have investigated the derivatives of 3,4,9,10-perylenetetracarboxylic acid and 3,4,9-perylenetricarboxylic acid in isotropic solvents and liquid crystal matrices. The dyes used have yellow to orange-red colour and emit fluorescence light in the spectral region advantageous for the human eye. In some cases the quantum fluorescence yield is very high. Moreover, the dyes have good dichroic properties: their order parameter in the liquid crystal, especially in the mixture 602, is high or even very high. They do not destabilize significantly the mesomorphic phase of the nematic host and are stable to sunlight. The disadvantage of the dyes are only the poor solubility of some

of them. However, even at concentration of 0.1% wt. by using a 40 μm thick cell one can obtain the satisfactory coloration and at high quantum fluorescence yield sufficient fluorescence intensity. Therefore, it seems that at least some of the dyes investigated can be used as guest species in GH LCDs working both in passive and active modes.

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