New Unsaturated 1,8-Naphthalimide Dyes for Use in Nematic Liquid Crystals

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The properties of new fluorescent dyes (derivatives of unsaturated 1,8-naphthalimide) are studied. Spectral characteristics of the dyes are recorded in both isotropic (ethanol, dioxane) and anisotropic (nematogenic liquid crystal mixture ZLI 1840) media. The optical, electro-optical, and thermodynamical properties of the liquid crystal-dye mixtures are examined. The orientational order parameters are evaluated to be within 0.4 - 0.5, depending upon the dye's molecular structure. Additionally, the influence of chemical bounding of the dyes to polystyrene chains on the phase transition temperature from the nematic to the isotropic state of polymer / liquid crystal mixtures is investigated. The low-molecular-mass dyes do not markedly affect the clearing point of pure liquid crystal, while the dye-styrene copolymers lower the transition temperature and widen the two-phase region at the transition. The electro-optical properties of the dye / liquid crystal systems imply potential utilization of the dyes studied in the so called "guest-host" liquid crystal displays.

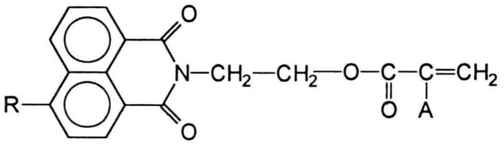
I. Introduction

Fluorescent naphthalimide dyes have bright colour, very good dyeing effect and photostability. They find wide applications in polymer industry, medicine, laser equipment etc. Recently, they have been examined in liquid crystals (LC) for utilization in electro-optical devices, i. e. displays of the so called "guest-host" type [1 - 5]. Such displays can work both in passive and active modes and need only one polarizer. At present, one of the most important problems to be solved for practical utilization of such displays is the synthesis of suitable fluorescent dyes. A number of naphthalene derivatives of bicarboxylic acid have been studied, and they have been shown to have an improving effect on contrast ratio and viewing angle [1 - 5].

In this paper we present some related properties of new fluorescent dichroic dyes of yellow-green colour, i. e. amino-substituted derivatives of unsaturated naphthalimide, and we discuss the possibility of utilizing of these dyes in "guest-host" LC displays. The presence of an unsaturated group in the dye's structure enabled us to obtain their copolymers and to compare the influence of the copolymer on the liquid crystalline matrix with the influence of the low-molecular-mass dyes on the host.

II. Experimental

Derivatives of 4-amino-N-substituted 1,8-naphthalimide (ANI) with the structure



were studied.

The substituents (A and R) and the molecular masses (MM) of the relevant dyes are listed in Table 1. Additionally copolymers of these dyes with styrene were studied.

Table 1. Molecular characteristics of the naphtalimide dyes studied.

Dye	R	A	MM
1		H	378
2		H	380
3		CH_3	394

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The dyes 1 - 3 were obtained by acylization of the hydroxy group from 4-amino-N-(2-hydroxyethyl) 1,8-naphthalimide with methacryloyl or acryloyl chloride; the products were recrystallized and chromatographically purified [6]. Chemical bounding of dyes to polymer chains was accomplished through radical copolymerization of dyes (3 wt %) and styrene in block [6]. Yellow-green copolymers of intense fluorescence were produced and purified by manyfold precipitation from toluene and methanol (of viscosity average molecular mass MM = $2.5 \cdot 10^4$).

The liquid crystalline mixture ZLI 1840 (LC), supplied by MERCK, was used as a host. It exhibits a stable nematic phase over a broad range, from -15°C to about 90°C. The dyes were initially screened for solubility in the liquid crystal. For further studies, ANI dyes were dissolved at a concentration of $1.3 \cdot 10^{-2}$ M (0.5 wt %), which was suitable for spectroscopic evaluation of order parameters and simultaneously guarantee appropriate contrast ratio [7].

The orientational order parameters of the dyes dissolved in LC were evaluated from the polarized components of absorption and fluorescence spectra [8]. The absorption measurements were performed using a double-beam spectrophotometer SPECORD M40 (Carl Zeiss, Jena). Fluorescence intensity measurements were performed on a self-equipped photon counting fluorimeter (Poznań). For excitation, the unpolarized light from a high pressure mercury lamp (436 nm Hg line) was used. The fluorescence spectra were measured in π geometry (exciting light beam perpendicular to the cell surface, detection of the fluorescence light emerging perpendicularly to the surface from the same side of the cell). Both in absorption and fluorescence measurements, neutral UV polarizers were utilized.

The recording of the absorption and the fluorescence spectra, as well as the measurements of the electro-optical parameters of the dye/LC mixtures at 1kHz a. c. voltage, were done in "sandwich" cells of 20 μm thickness. The mixture formed thin oriented layers between two glass plates with an area of 2×3 cm. Uniform planar orientation of the samples was achieved by coating the cell surfaces with polyimide layers and by additional rubbing [9].

Composite films of ZLI 1840 and copolymers having 1.2 wt % ANI attached as side groups were prepared by the s. c. SIPS (solvent induced phase separation) technique [10]. The 60:40 LC-copolymer mixtures are chosen to explore the stabilizing effect of the polymer component upon the system. As a result, the systems have an increased content of dye in comparison of the low molecular dye/LC systems. Films of 20 μm thickness were casted from chloroform solution of both components onto glass plates at room temperature. The films obtained from copolymer/LC systems are noticeably self-supported, which is most suitable for applications to flexible and large area displays [11].

The temperatures of the nematic-isotropic phase transition for the pure liquid crystal and the dye/LC mixtures were determined by means of a polarizing microscope with an accuracy of 0.1 K.

III. Calculations

The quantum fluorescence yield Φ was determined on the basis of absorption and fluorescence spectra of the dyes dissolved in dioxane and ethanol at a concentration of $1 \cdot 10^{-5}$ M using the following expression [12, 13]:

$$\Phi = \Phi_0 \cdot \frac{1 - 10^{-A_0}}{1 - 10^{-A}} \cdot \frac{\int_0^\infty F \, \mathrm{d}\lambda}{\int_0^\infty F_0 \, \mathrm{d}\lambda}, \tag{1}$$

where the pairs A, A_0, and F, F_0 are the absorption and fluorescence intensities of dye and standard, respectively. As standard, rhodamine 6G ($\Phi_0 = 0.88$) was used [12].

Order parameters S_A can be evaluated from the absorption spectra of the dyes dissolved in LC as follows [14 - 16]:

$$S_A = \frac{A_\parallel - A_\perp}{A_\parallel + 2A_\perp} \cdot \left(1 - \frac{3}{2}\sin^2\beta\right)^{-1}, \tag{2}$$

where $A_\parallel$ and $A_\perp$ denote the absorbance of the light polarized parallel and perpendicularly to the orientation axis of liquid crystal, respectively; β is the angle between the vector of absorption transition moment and the long axis of dye molecule.

If $\beta = 0°$, (2) reduces to the expression

$$S_A = \frac{A_\parallel - A_\perp}{A_\parallel + 2A_\perp}. \tag{3}$$

Assuming that the lifetime of the excited state of the fluorescent dyes is greater than the rotational correlation time, Baur at al. [17] showed that the order

Table 2. Spectral characteristics of naphtalimide dyes in dioxane.

Dye	Absorption		Fluorescence	
	$\lambda_{\max}^{\mathrm{A}}$ [nm]	ε [l·(mol·cm)$^{-1}$]	$\lambda_{\max}^{\mathrm{F}}$ [nm]	$\overline{\nu_{\mathrm{A}}} - \overline{\nu_{\mathrm{F}}}$ [cm^{-1}]
1	401	9580	511	5368
2	401	8500	509	5291
3	390	10720	507	5917

Table 3. Spectral characteristics of naphtalimide dyes in ethanol; * using rhodamine 6G as a standard.

Dye	Absorption		Fluorescence		
	$\lambda_{\max}^{\mathrm{A}}$ [nm]	ε [l·(mol·cm)$^{-1}$]	$\lambda_{\max}^{\mathrm{F}}$ [nm]	Φ*	$\overline{\nu_{\mathrm{A}}} - \overline{\nu_{\mathrm{F}}}$ [cm^{-1}]
1	412	15200	526	0.07	5260
2	404	11600	530	0.04	5884
3	400	12000	530	0.04	6132

parameter can also be evaluated from the fluorescence measurements using the formula

$$S_{\mathrm{F}} = \frac{F_{\parallel} - F_{\perp}}{F_{\parallel} + 2F_{\perp}}, \qquad (4)$$

where $F_{\parallel}$ and $F_{\perp}$ are the intensities of the fluorescent light polarized parallel and perpendicularly to LC director, respectively. This equation holds only for $\delta = 0°$, where δ is an angle between the direction of the emission transition moment and the long molecular axis.

IV. Results and Discussion

IV.1. Spectral Characteristics of Dyes in Isotropic and Anisotropic Media

Tables 2 and 3 present spectral characteristics of the dyes 1, 2, and 3 measured in dioxane and ethanol: the absorption ($\lambda_{\mathrm{A}}^{\max}$) and fluorescence maxima ($\lambda_{\mathrm{F}}^{\max}$), the extinction coefficients (ε), the Stokes shifts ($\overline{\nu_{\mathrm{A}}} - \overline{\nu_{\mathrm{F}}}$), and the quantum fluorescence yields (Φ). The data indicate that the polarity of the solvent significantly influences the absorption and fluorescence spectra of the dyes. When ethanol is used instead of dioxane, bathochromic shifts of 3 - 11 nm are observed in the absorption spectra parted by a hyperchromic effect, and considerable bathochromic shifts of 15 - 23 nm are observed for the intensity maxima of fluorescent spectra.

Table 4. Spectral characteristics of naphtalimide dyes in ZLI 1840.

Dye	$\lambda_{\max}^{\mathrm{A}}$ [nm]	$\lambda_{\max}^{\mathrm{F}}$ [nm]	$\overline{\nu_{\mathrm{A}}} - \overline{\nu_{\mathrm{F}}}$ [cm^{-1}]
1	409	512	4930
2	404	511	5293
3	398	520	5869

Table 5. Spectral characteristics of dye-styrene copolymers in solid films.

Coplymer	$\lambda_{\max}^{\mathrm{A}}$ [nm]	$\lambda_{\max}^{\mathrm{F}}$ [nm]	$\overline{\nu_{\mathrm{A}}} - \overline{\nu_{\mathrm{F}}}$ [cm^{-1}]
PS co-dye 1	406	498	4550
PS co-dye 2	404	491	4385
PS co-dye 3	401	501	4977

The values for the quantum fluorescence yield of the dyes measured in ethanol solution are rather low. It was visually observed that the dyes dissolved in ZLI 1840 fluoresce significantly better. The exact determination of the fluorescence efficiency for a dye embedded in an oriented matrix is, however, very difficult because many factors, including anisotropy, must be taken into account. We attempted to estimate this efficiency for the dyes investigated and we obtained $\Phi > 0.1$, but the results should be regarded as qualitative rather then quantitative.

Table 4 presents the spectral characteristics of the dyes 1 - 3 dissolved in ZLI 1840: the absorption ($\lambda_{\mathrm{A}}^{\max}$) and fluorescence ($\lambda_{\mathrm{F}}^{\max}$) maxima and the Stokes shifts ($\overline{\nu_{\mathrm{A}}} - \overline{\nu_{\mathrm{F}}}$). The absorption spectra of all dye/LC mixtures show a bathochromic shift with respect to the spectra of dyes in dioxane. The fluorescence spectra of the dye/LC mixtures studied are hypsochromically shifted only with respect to those taken in ethanol. When using dioxane, there is a shift (of 13 nm) only for the dye 3/LC mixture, while the spectra of the dye 1/LC or dye 2/LC mixtures are almost identical to those taken in dioxane. The results can alternatively be related to conformational states of molecules.

Table 5 displays some spectral characteristics of the dye-styrene copolymers obtained for thin solid films. It is shown that the chemical bounding of the dyes to polymer chains does not markedly affect the positions of the absorption maximum in the solid state with respect to those in organic solvents and LC. However, a considerable shift of the fluorescence spectra is observed. In this case, the maxima are recorded between 490 and 500 nm.

Table 6. Transition temperature data for dye/ZLI 1840 mixtures (Temperatures are given in K).

Substance	T_N	T_I	$T_I - T_N$	ΔT_N	ΔT_I	$\bar{T}_{NI}$	$\Delta\bar{T}_{NI}$
ZLI 1840	362.5	368.5	6.0	—	—	365.5	—
1	360.0	368.0	8.0	−2.5	−0.5	364.0	−1.5
2	359.2	367.7	8.5	−3.3	−0.8	363.5	−2.0
3	359.9	367.6	7.7	−2.6	−0.9	363.8	−1.7

Table 7. Transition temperature data for copolymer/ZLI 1840 mixtures (Temperatures are given in K).

Substance	T_N	T_I	$T_I - T_N$	ΔT_N	ΔT_I	$\bar{T}_{NI}$	$\Delta\bar{T}_{NI}$
ZLI 1840	362.5	368.5	6.0	—	—	365.5	—
PS co-dye 1	356.0	366.0	10.0	−6.5	−2.5	361.0	−4.5
PS co-dye 2	356.3	365.4	9.1	−6.2	−3.1	360.9	−4.6
PS co-dye 3	356.5	364.0	7.5	−6.0	−4.5	360.3	−5.2

IV.2. Phase Transition Temperatures

The results of the temperature investigations of LC doped with the naphtalimide dyes are given in Table 6. Two-phase regions at the phase transition from nematic to isotropic are observed, as was predicted by theory and confirmed experimentally many times [18]. T_N is the temperature at which the first drop of the isotropic liquid appears, whereas T_I is the temperature at which the last drop of the nematic disappears on sample heating. $(T_I - T_N)$ describes the range of the two-phase region. ΔT_N and ΔT_I are the shifts of T_N and T_I with respect to the relevant temperatures of the pure liquid crystal. The average values of the nematic-isotropic transition temperature for the mixtures studied, $\bar{T}_{NI} = (T_N + T_I)/2$, and the shifts with respect to the pure LC, $\Delta\bar{T}_{NI}$, are also presented. These data show that dyes 1 - 3, introduced into the LC host at a concentration of 0.5 wt %, cause a decrease of both T_N and T_I temperatures and additionally widen the two-phase region in comparison to the pure ZLI 1840.

The results from the temperature investigations of LC films doped with dye-styrene copolymers are listed in Table 7. They show a lowering of T_N and T_I with respect to those for the pure LC and simultaneous widening of the two-phase region. This can be related both to the increased concentration of dye and/or to the polymer introduced into the system. If high-molecular-mass substance is used as an LC host, the effect of low-molecular-mass dye molecules upon the LC order is weak [19]. It has been reported that even bounding of up to 40% chromophorous units to a liquid crystalline polymer has not affected its transition temperatures [20]. On the other hand, the introduction of flexible polymer molecules to low-molecular-mass LCs is expected to decrease the LC order and to extend the temperature interval of nematic-isotropic transition according to theoretical predictions (based on Helfand's lattice model) [21]. The LC-copolymer systems under study can seemingly be related to the latter case, showing the wider two-phase region at the LC transition. However, to separate the two effects, that of increased dye concentration and that of the polymer guest, upon the phase transition, further studies should be undertaken.

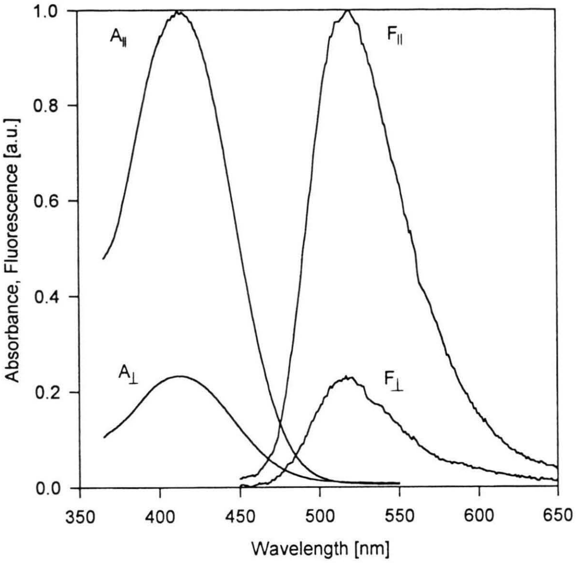

Fig. 1. Polarized components of the absorption and fluorescence spectra of dye 1 in ZLI 1840.

IV.3. Temperature Dependence of Order Parameters for Dye/LC Mixtures

In Fig. 1 the polarized components of the absorption and fluorescence spectra for dye 1 dissolved in ZLI 1840, at $T = 293$ K, are presented, as an example.

Fig. 2 shows the S_A order parameter as a function of temperature for different dye/ZLI 1840 systems. For the new types of fluorescent dyes studied in this paper the angles β and δ are still unknown. However, in first approximation we can use (3) and (4) to estimate the orientation of the dyes in the LC matrix, although the symmetry group of these dyes is not high enough to fix $\beta = \delta = 0°$. For calculations, the values of A_k ($k = \|, \perp$) that correspond to maximum

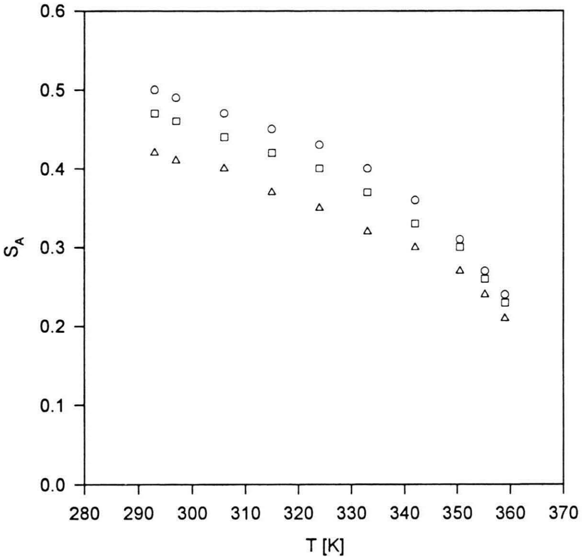

Fig. 2. Order parameters S_A of dye/ZLI 1840 mixtures as a function of temperature T (circles - dye 1, squares - dye 2, triangles - dye 3).

intensity of absorption, were taken. The orientational order parameters of the dyes decrease with increasing temperature, which is connected with the disordering processes of the nematic phase. The highest order parameters are obtained for dye 1 in ZLI 1840 (stabilizing effect of piperidine substituent). Relatively low values of the order parameters for dye 3 can be associated with the different A - substituent.

Table 8 collects the values of the orientational order parameters obtained from the absorption and fluorescence measurements at T = 293 K. It is seen that the S_F order parameters coincide with the S_A ones within experimental uncertainty. These are rather unexpected results, because at least three effects could be the reason for the differences between S_A and S_F: i) the existence of non -zero intramolecular angles between the absorption and emission oscillators [8, 22, 23], ii) the intermolecular energy transfer processes which can depolarize the fluorescence in an unpredictable manner [8, 22, 23] and lead to misinterpretation of the results obtained, and iii) the interactions between the liquid crystal molecules and the cell surfaces [24 - 27]. The factors i) and ii) would decrease the value of S_F, whereas the factor iii) can increase this value. It is possible that in the case of the dyes investigated the influence of all these factors compensates, and as a result S_F is nearly equal to S_A.

Table 8. Absorption and fluorescence order parameters of naphtalimide dyes in ZLI 1840 at T = 293K ($\Delta S_A = \pm 0.01$, $\Delta S_F = \pm 0.02$).

Dye	S_A	S_F
1	0.50	0.51
2	0.47	0.48
3	0.42	0.44

IV.4. Electro-Optical Properties of Dye/LC Mixtures

The reorientation of liquid crystal under applied voltage is very important from technical point of view. This effect can be described by measuring absorption or fluorescence of initially oriented dye/LC mixtures in liquid crystal display.

One of the most important parameters of liquid crystal displays are the switching-on and switching-off voltages. If liquid crystal has a positive dielectric anisotropy, then the parallel component of absorption/fluorescence decreases as the applied voltage is raised, whereas the perpendicular one does not change. At a suitably large voltage, the parallel and perpendicular components should be equal.

Figure 3 presents the dependence of relative absorption anisotropy R_A(V) for the dye 1/LC mixture on the applied voltage:

$$R_A = \frac{A_{\parallel}(V) - A_{\perp}(V)}{A_{\parallel}(0) - A_{\perp}(0)}, \quad (5)$$

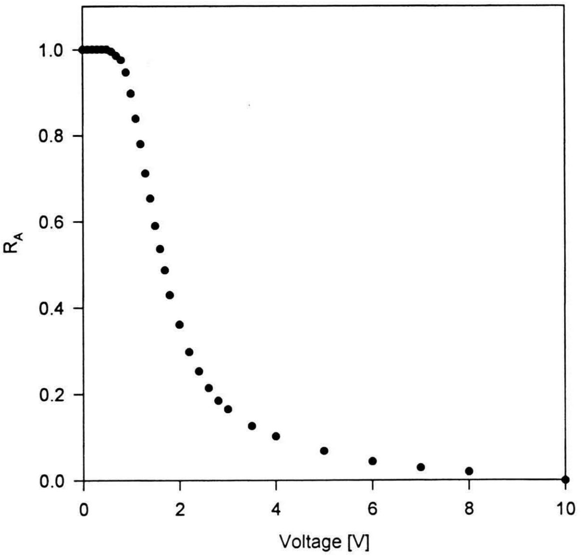

Fig. 3. Absorption relative anisotropy of the dye 1/ZLI 1840 system as a function of applied voltage.

where $A_{||}(V)$ and $A_{\perp}(V)$ are the parallel and perpendicular components of the absorbance when the voltage V is applied to the display.

A threshold effect is observed at about 0.8 V in this case. For the light beam perpendicular to the cell one can introduce the switch-off voltage, $V_{90}(T)$, as that giving 90 % of the relative absorption anisotropy for 0 V and, respectively, the switch-on voltage, $V_{10}(T)$, for 10% relative anisotropy (T is the temperature). The display is regarded to be completely OFF if $V < V_{90}(T)$ and fully ON if $V > V_{10}(T)$. For ZLI 1840 doped with dye 1 these values are equal to 1.0 V and 4.0 V, respectively.

The switch-off and -on voltages were also deduced from fluorescence components of the dye 1/ZLI 1840 layer. The shape of the relative fluorescence anisotropy curve was very close to that for the absorption. As a result, the off and on voltages obtained using both methods are equal in the limits of experimental error. Additional experiments carried out for dye 2 and 3 in ZLI 1840 do not show significant influence of the dopant on the characteristic voltages of ZLI 1840.

V. Conclusions

In this paper we presented the results of optical, electro-optical, and thermodynamical investigations of systems composed of commercial ZLI 1840 nematic liquid crystal and newly synthesized fluorescent dyes, derivatives of 4-amino-N-substituted 1,8-naphthalimide. All these dyes have an excellent yellow color, and emit green light. These low-molar-mass dyes are well oriented in liquid crystalline matrix and have weak destabilizing influence on the nematic phase. Since they are very well soluble in liquid crystals, they can be used as guest species in liquid crystal displays working in passive mode, although the extinction coefficient is not too high. Using ANI concentration of about 0.5 wt % and thickness of 20 μ a good coloration of the display can be obtained. However, because of the relatively low fluorescence efficiency, ANI dyes should not be used in displays working in active mode.

In the case of copolymers having ANI attached as side groups, further investigations should be undertaken. It seems that the main problem here is connected with the orientation of the side groups of the polymer dissolved in liquid crystal.

Acknowledgements

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