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Synthesis and properties of fluorescent 1,8-naphthalimide dyes for application in liquid crystal displays

Ivo Grabchev,[a] Ivanka Moneva,*[a] Vladimir Bojinov[b] and Sylvie Guittonneau[c]

[a]Institute of Polymers, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria.
E-mail: itmoneva@bas.bg
[b]Technical University of Chemical Technology and Metallurgy, Sofia 1756, Bulgaria
[c]Laboratoire de Photochimie Industriele (LACE), UMR 5634, Université C. Bernard, Lyon 1, 69622 Villeurbanne-Cedex, France

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A series of highly fluorescent 1,8-naphthalimide derivatives having an *N*-allylamino group at position 4 of the aromatic structure have been synthesised, and some of their properties for application in liquid crystal displays have been determined. The optical properties of the new substances are studied both in organic solvents and in the nematic liquid crystal ZLI 1840. The utility of the dyes for colouring liquid crystal displays of the "guest–host" type is discussed on the basis of their spectral properties (absorption and emission) and the effect that the dyes have upon the orientation order parameter $\langle P_2 \rangle$ and upon the phase-transition behaviour of the liquid crystal in surface-stabilised display cells.

Introduction

1,8-Naphthalimide derivatives with amino and alkoxy groups at position C-4 usually exhibit fluorescent emission on irradiation.[1] The derivatives with amino groups are of excellent yellow colour enhanced by fluorescence, while those with alkoxy groups are colourless and have a blue emission. Due to their spectral properties, the 1,8-naphthalimide derivatives find use as fluorescent dyes for solar energy collectors,[2] organic light-emitting diodes,[3] markers in molecular biology,[4] in laser active media,[5,6] and so on. The presence of an unsaturated polymerizable double bond enables their use also in copolymerization processes with vinylic monomers forming a covalent bond in the polymer molecule with intense fluorescence and colour resistance to solvents and wet treatment.[7,8]

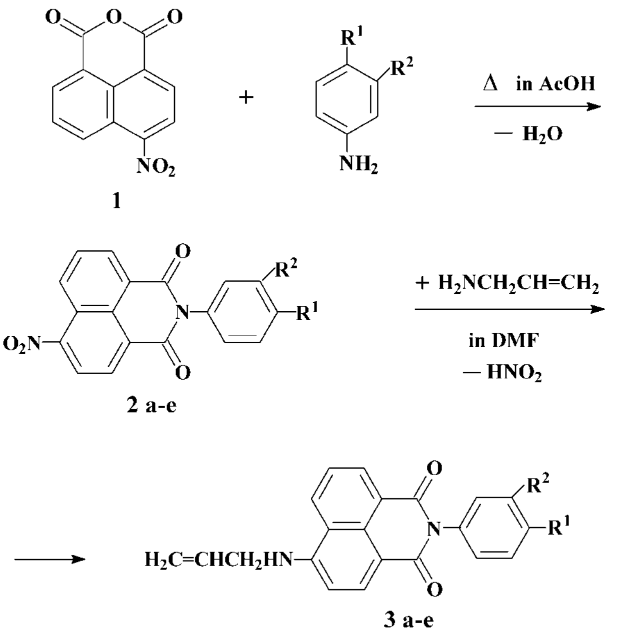
Recently, 1,8-naphthalimide dyes have been intensively examined for use in nematic liquid crystals (LC) for electro-optical displays of the guest–host type.[9–12] Their action is based on the so called "guest–host" effect[13] which consists in orienting the LC molecules under applied voltage accompanied by close alignment of dye molecules, with the resulting selectivity in dye absorption depending upon orientation. Such displays can work both in passive and active modes and need only one polarizer. A number of 1,8-naphthalimide dyes have shown an improving effect on the contrast ratio and viewing angle of the displays.[10] Among the most important problems to be solved at present for the practical utilisation of this type of displays is the choice of suitable fluorescent dyes.

It is known that introduction of primary or secondary amino groups into the naphthalimide moiety drastically increases the quantum yield of fluorescence. Looking for new chromophores having high fluorescence combined with high photostability, we have synthesised a series of highly fluorescent 1,8-naphthalimide derivatives having an *N*-allylamino group at position 4 of the naphthalimide moiety and have studied some of their properties for use in nematic liquid crystal displays. The optical behaviour of the dyes in organic solvents of different polarity and in the commercial liquid crystal ZLI 1840 are studied *via* UV–visible spectroscopy. The utility of the novel substances for colouring LC displays of the guest–host type is discussed on the basis of their spectral properties (absorption and emission), the orientation order parameter $\langle P_2 \rangle$ in surface-stabilised display cells determined by polarised UV–visible absorption spectroscopy, and the influence that the dyes have upon the phase-transition behaviour of LC.

Experimental

Materials

A two-step method was employed in the synthesis of the 4-(*N*-allylamino) derivatives of 1,8-naphthalimide (Scheme 1).



3 a-e

3a $R^1 = H, R^2 = H$
b $R^1 = CH_3, R^2 = H$
c $R^1 = OCH_3, R^2 = H$
d $R^1 = Cl, R^2 = H$
e $R^1 = H, R^2 = OH$

Scheme 1 Synthesis of 4-(*N*-allylamino) derivatives of 1,8-naphthalimide dyes.

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4-Nitro-1,8-naphthalic anhydride, **1**, synthesised according to a method described recently,[4] was reacted in 1 : 1 molar ratio with different aromatic amines in boiling glacial acetic acid for 8 h, giving respective 4-nitro-*N*-phenyl substituted 1,8-naphthalimide derivatives, **2a–e**, in good yields (60–75%). The final products, dyes **3a–e**, were obtained by nucleophilic substitution of the nitro group in **2a–e** with an *N*-allylamino group by reaction with allylamine in DMF for 24 h at room temperature. It is intended to copolymerize them with vinylic monomers and use them as guest components in LC displays.[14] Details of the dye synthesis are given below.

Synthesis of the precursor compounds 2a–c

4-Nitro-*N*-phenyl-1,8-naphthalimide, 2a. 4-Nitro-1,8-naphthalic anhydride **1** (0.01 mol) was dissolved in 50 ml of glacial acetic acid, and aniline (0.01 mol) was added. The solution was refluxed for 8 h and then cooled to room temperature. The product **2a** formed was filtered off, washed with water and dried at 60 °C.

Compounds 2b–e. The synthesis of compounds **2b–e** was carried out in a similar way to that of **2a**, using instead of aniline, respectively, 4-methylaniline (**2b**), 4-methoxyaniline (**2c**), 4-chloroaniline (**2d**), and 3-hydroxyaniline (**2e**).

Synthesis of the dyes 3a–e

4-(*N*-Allylamino)-*N*-phenyl-1,8-naphthalimide, dye 3a. To 1.6 g 4-nitro-*N*-phenyl-1,8-naphthalimide **2a** dissolved in 60 ml of DMF was added 1 ml allylamine at room temperature. After 24 h, 600 ml of water were added into the solution. The precipitate was filtered off and washed with water, then dried under vacuum at 40 °C.

Dyes 3b–e. The dyes **3b–e** were prepared, respectively, from **2b–e** and allylamine following the same procedure as used for the synthesis of **3a**.

The products **3a–e** have been characterised by mp, TLC (R_f), elemental analysis, and ^{1}H NMR spectroscopy. The results obtained are displayed in Table 1.

Throughout the work, the liquid-crystalline mixture ZLI 1840, from Merck (Darmstadt, Germany), was used as host. It exhibits a stable nematic phase over a broad temperature range (−15 to 90 °C[15]). The dyes were initially screened for solubility in the liquid crystal. For further studies, dyes were dissolved at a concentration of 0.5 wt%, which was suitable for spectroscopic evaluation of the order parameter and simultaneously guarantees appropriate constant ratio.[16] Dye–LC mixtures were studied in "sandwich" cells of 20 µm thickness. The mixtures formed thin oriented layers between two glass plates with an area of 2 × 3 cm. The uniform planar orientation of the systems was achieved by coating the cell surfaces with polyvinyl alcohol layers which were additionally rubbed.[9,17] The orientation order parameter of the dyes dissolved in LC was evaluated from the polarised components of absorption spectra.

Methods

^{1}H NMR spectra were recorded on a JEOL JNM-PS spectrometer, operating at 100 MHz in d_6-DMSO and using TMS as internal standard (chemical shifts are given as δ in ppm).

The reaction course and purity of the final products were followed by TLC on silica gel (Fluka F_{60} 254 20 × 20; 0.2 mm), using as eluant the solvent system *n*-heptane–acetone (1 : 1). Melting points were determined by means of a Kofler melting point microscope.

Electronic spectra of the dyes in various media including LC

Table 1 Yield, melting point, R_f (TLC), elemental analysis, and ^{1}H NMR data obtained for 4-allylamine substituted 1,8-naphthalimide dyes **3a–e**

				Analysis			
Dye	Yield (%)	Mp/°C	R_f	C% calcd (found)	H% calcd (found)	N% calcd (found)	^{1}H NMR δ/ppm
3a	88.5	198–200	0.36	76.84 (76.71)	4.84 (4.80)	8.53 (8.50)	7.92–8.48, m, 3H, ArH 7.59–7.80, s, 1H, NH 6.32–7.51, m, 7H, ArH 5.41–6.02, m, 1H, CH= 4.92–5.93, m, 2H, =CH_2 3.80–4.12, d, 2H, NCH_2
3b	77.2	107–108	0.38	77.20 (77.04)	5.26 (5.19)	8.13 (8.09)	7.86–8.62, m, 3H, ArH 7.65–7.91, s, 1H, NH 6.41–7.62, m, 6H, ArH 5.64–5.92, m, 1H, CH= 4.95–5.28, m, 2H, =CH_2 3.83–4.08, d, 2H, NCH_2 2.24–2.40, d, 3H, CH_3
3c	93.0	208–211	0.30	73.76 (73.52)	5.02 (4.90)	7.82 (7.73)	8.00–8.61, m, 3H, ArH 7.75–8.02, s, 1H, NH 6.52–7.68, m, 6H, ArH 5.68–6.16, m, 1H, CH= 5.04–5.20, m, 2H, =CH_2 3.96–4.16, d, 2H, NCH_2 3.28–3.56, s, 3H, OCH_3
3d	92.0	212–215	0.41	69.54 (69.40)	4.14 (4.05)	7.72 (7.60)	8.00–8.86, m, 3H, ArH 7.85–7.96, s, 1H, NH 6.48–7.64, m, 6H, ArH 5.69–6.08, m, 1H, CH= 4.96–5.22, m, 2H, =CH_2 3.94–4.12, d, 2H, NCH_2
3e	69.2	153–154	0.14	73.27 (73.12)	4.65 (4.59)	8.13 (8.04)	7.96–8.83, m, 3H, ArH 7.76–7.92, s, 1H, NH 6.28–7.64, m, 6H, ArH 5.69–6.12, m, 1H, CH= 4.96–5.48, m, 2H, =CH_2 3.92–4.12, d, 2H, NCH_2 3.22–3.42, s, 1H, OH

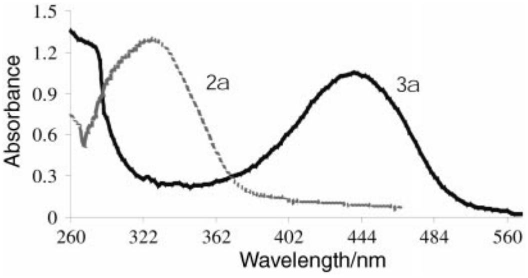

Fig. 1 UV–vis absorption spectra of 4-nitro- (**2a**) and 4-allylamino- (**3a**) *N*-phenyl-1,8-naphthalimide derivatives, recorded in ethanol.

were recorded on a Hewlett Packard 8452A spectrophotometer with 2 nm resolution, at room temperature. For recording the polarised absorption spectra, UV neutral filters were used. The fluorescence quantum yield of the dyes was measured in ethanol solution by comparison with the emission from Rhodamine 6G as standard ($\Phi_o = 0.88$[18]).

The measurements of phase-transition temperatures were performed under the polarising microscope Zetopan Pol, with an accuracy of 0.5 K.

Results and discussion

UV–visible absorption and fluorescence of the 1,8-naphthalimide derivatives measured in different media

The UV–vis absorption properties of the dyes under study are basically related to the polarisation of the naphthalimide molecule on irradiation, resulting from the electron donor–acceptor interaction between the substituents at C-4 and the carbonyl groups from the imide structure of the chromophoric system, and may be influenced by the environmental effect of the media upon this interaction.

First we studied the spectral properties of 1,8-naphthalimide dyes in common solvents and then in LC where interactions are more complex.

Absorption spectra of the dyes **2a–e** and **3a–e** were recorded in solvents of different polarity. A comparison of the absorption spectra reveals the strong influence of the polarisation of the molecule upon the spectral properties. The absorption maxima of the nitro derivatives of 1,8-naphthalimide are in the UV region at $\lambda = 343$–347 nm due to the electron-accepting nature of the nitro group. The replacement of the nitro group by the electron-donating *N*-allylamino group leads to a large bathochromic shift of the absorption maximum. Fig. 1 shows as an example the UV–vis absorption spectra of 4-nitro-*N*-phenyl-1,8-naphthalimide (**2a**) and its allylamine derivative **3a**. The absorption maximum of **3a** is bathochromically shifted, with $\Delta\lambda = 90$ nm. The weak maximum in the UV region at 346 nm (λ_A of dye **2a**) implies that the band $\lambda_A = 436$ nm of dye **3a** is a charge transfer (CT) band, the same being valid also for the other allylamine derivatives.

Table 2 Photophysical characteristics of the 4-allylamino substituted 1,8-naphthalimide dyes **3a–e**, measured in ethanol and in the liquid crystal ZLI 1840 (see text)

Dyes	3a	3b	3c	3d	3e
In ethanol					
λ_A/nm	436	436	436	437	436
log ε	4.176	4.156	4.139	4.217	4.246
λ_F/nm	523	524	524	524	525
λ_{S1}/nm	485	485	486	485	484
E_{S1}/kJ mol^{-1}	247	247	247	247	246
$(\nu_A - \nu_F)$/cm^{-1}	3815	3851	3851	3799	3888
f	0.221	0.210	0.229	0.258	0.246
Φ_F	0.69	0.62	0.58	0.75	0.32
In liquid crystal					
λ_A/nm	430	432	430	432	434
λ_F/nm	503	500	501	503	500
λ_{S1}/nm	474	472	469	475	471
E_{S1}/kJ mol^{-1}	252	253	255	252	254
$(\nu_A - \nu_F)$/cm^{-1}	3375	3148	3296	3265	3041

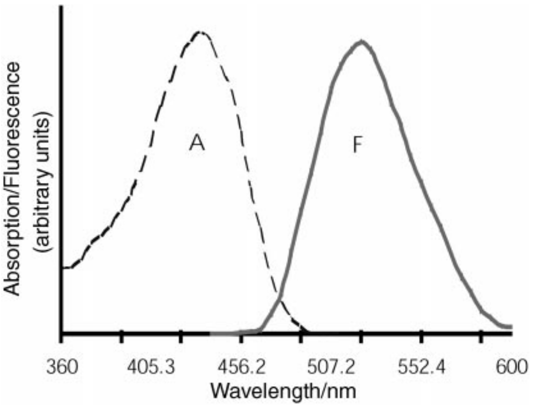

Fig. 2 UV–vis absorption and fluorescence spectra of the 1,8-naphthalimide dye **3b**, recorded in ethanol.

Table 2 presents basic photophysical characteristics of the final dye products **3a–e** measured in ethanol solution: the absorption maximum (λ_A), the molecular extinction coefficient (log ε), the fluorescence maximum (λ_F), the Stokes shift ($\nu_A - \nu_F$), the relevant cross-point λ_{S1} and the energy of the first singlet state (E_{S1}), the oscillator strength (f) for the long-wave absorption band, and the quantum yield of fluorescence Φ_F.

All the dyes **3a–e** exhibit in solution a yellow-green colour and an intense fluorescence, with $\lambda_A = 436$–437 nm and $\lambda_F = 523$–525 nm. Fig. 2 displays the absorption and fluorescence spectra of dye **3b** as a typical example for the spectra of all the dyes. The fluorescence curve is approximately a mirror image of the absorption curve, which is indicative that the molecular structure of the dyes is maintained in the excited state and that emission of fluorescence prevails.[1]

The absorption and fluorescence spectra of the naphthalimide derivatives **3a–e** in ethanol solution are similar. The Stokes shift has values between 3799 and 3888 cm^{-1}, as is common for this class of dyes. On excitation, dyes **3a–e** pass from the ground state S_0 to the first excited singlet state S_1, the energy of the first excited state E_{S1} being 246–247 kJ mol^{-1}. On fluorescence emission, the dye molecules deactivate and pass back to the S_0 state.

Among the important characteristics of dyes is also their oscillator strength, f, showing the effective number of electrons the transition of which from the ground to excited state gives the absorption area in the electron spectrum. Values of the oscillator strength were calculated using eqn. (1),[19]

$$f = 4.32 \times 10^{-9} \Delta\nu_{1/2} \varepsilon_{\max} \qquad (1)$$

where $\Delta\nu_{1/2}$ is the width of the absorption band in cm^{-1} at $\varepsilon_{\max}/$

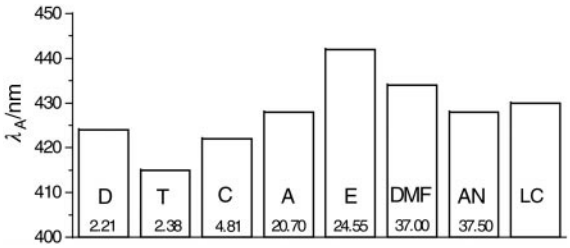

Fig. 3 Visible absorption maxima of the 1,8-naphthalimide dye **3d** measured in solvents of increasing relative permittivity ε(s) (T = toluene, D = 1,4-dioxane, C = chloroform, A = acetone, E = ethanol, DMF = dimethylformamide and AN = acetonitrile) and in the liquid crystal LC ZLI 1840.

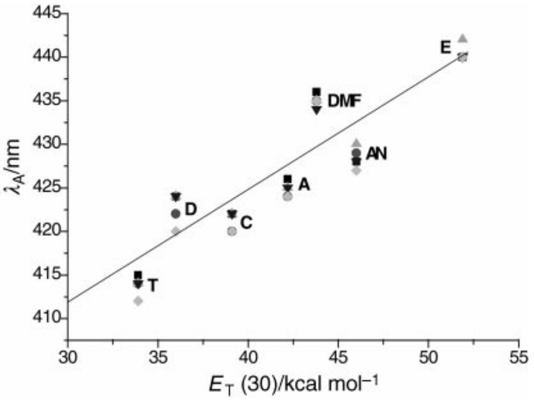

Fig. 4 Dependence of the visible absorption maxima of dyes **3a–e**, measured in organic solvents, upon the empirical solvent polarity parameter $E_T(30)$: D = 1,4-dioxane, T = toluene, C = chloroform, A = acetone, E = ethanol, DMF = dimethylformamide and AN = acetonitrile. The symbols for the dyes are: **3a** ★, **3b** ■, **3c** △, **3d** ◊ and **3e** +.

2. The *f* values of dyes **3a–e** vary from 0.210 to 0.260 in ethanol, being in accord with the change in ε. The slightly larger *f* values for dyes **3d** and **3e** as compared to those for **3a–3c** are related to some increase in their polarisation due to the electron accepting substituent R^1 (dye **3d**) and to H-bonding (dye **3e**). All the data found for dyes **3** show that the substituents at the phenyl moiety have a small effect upon the photophysical characteristics λ_A, λ_F, the Stokes shift, E_{S1}, and *f*, which is indicative of their similar polarisation ability.

The substituents R^1 and R^2 have but a distinct effect upon Φ_F of the dyes, probably related to the possibility for deviation from the plane of the naphthalimide structure. All dyes **3** having a secondary amino group exhibit, in accord with our previous studies,[20,21] a very good quantum yield of fluorescence Φ_F (in ethanol), with the exception of dye **3e**. The lower value of Φ_F for dye **3e** can alternatively be related to the specific interaction of the R^2 (OH group) with ethanol which may fix any deviation of the attached phenyl ring out of plane of the naphthalimide structure.

The large effect that different media have upon the UV–vis absorption of dyes **3** is illustrated in Figs. 3 and 4, which display the absorption maxima of the dyes in media of increasing polarity. The polarity was characterised both by the relative permittivity, ε(s), Lippert's solvent polarity function, Δ*f*,[22] and the empirical solvent polarity parameter $E_T(30)$.[23]

On the histogram Fig. 3 are shown the absorption maxima λ_A of dye **3d** in solvents of increasing relative permittivity as an example. There is no unique dependence of λ_A upon ε(s). A trend to bathochromic shift of λ_A with increasing ε(s) is observed in the series of the less polar solvents: toluene, chloroform and acetone, with the exception of 1,4-dioxane. The absorption maxima in 1,4-dioxane are bathochromically shifted with regard to toluene, a solvent of almost the same ε(s), being close to those of the more polar chloroform and acetone. The anomaly is revealed still more clearly in the series of the more polar solvents: ethanol, DMF, and acetonitrile, where the trend is for decreasing λ_A with increasing ε(s).

The effect of the medium is due not only to the polarity of solvents but also to the possibility of intermolecular interactions that may lead to a change in the polarisation of the molecules. The anomalous behaviour observed in Fig. 3 can be satisfactorily explained with the formation of intermolecular H-bonds between dyes and solvents. The hypsochromic shift of λ_A in the row of increasing ε(s) of solvents: ethanol, DMF, and acetonitrile, is surely connected with the different ability of these solvents to H-bond with the dyes. The proton-donating ethanol forms H-bonds with the carbonyl groups of the dyes thus enhancing the electron donor–acceptor interaction in the chromophoric system. In the case of DMF and acetonitrile, H-bonds can be formed between the H-atom of the allylamino group with the nonshared electron pairs of the hetero atoms of the solvents. The H-bonds decrease the donating ability of the amino group, and consequently, decrease the electron donor–acceptor interaction which leads to the hypsochromic shift of λ_A. This also explains the close positions of λ_A in acetone and chloroform despite the largely different ε values of those solvents.

Table 3 Molecular aspect ratio *l*/*d*, dichroic ratio *N*(λ) (at λ_{max} in LC), and the orientational parameter S_A of 4-allylamine substituted 1,8-naphthalimide dyes **3a–e**

Dyes	3a	3b	3c	3d	3e
l/*d*	3.30	3.62	3.88	3.62	3.30
N(λ)	6.00	6.69	7.20	4.64	3.44
S_A	0.63	0.65	0.67	0.55	0.45

The Lippert's function, Δ*f*, describes the dielectric behaviour of solvents both by its relative permittivity ε(s) and by its refractive index.[22] It was however again not appropriate for the description of the solvatochromic behaviour of the 1,8-naphthalimides under study. The plot of the absorption maxima, in wavenumbers, *vs.* Δ*f* shows only a poor linear correlation (correlation coefficient −0.79), decreasing with increasing polarity Δ*f*. The failure has been explained in terms of the possible H-bonding discussed above, since the underlying Lippert's theory[22] considers dipole–dipole, dipole–polarisation, polarisation–inductive, and dispersion forces but not charge transfer, H-bonding, and related interactions.

In Fig. 4 is shown the dependence of λ_A of **3a–e** on $E_T(30)$, the empirical solvent polarity parameter.[23] $E_T(30)$ values are based on the negatively solvatochromic *N*-phenolate betaine dye as probe. While ε(s) can be related to the solvatochromic properties of the dyes (Fig. 3) only when no interactions occur, the parameter $E_T(30)$ evidently accounts also for the solvating effects discussed. The linear course of the λ_A *vs.* $E_T(30)$ dependence (Fig. 4) implies positive solvatochromism of the dyes under study. The analytical form of the λ_A dependence upon solvent polarity for that class of substituted dyes is given by eqn. (2).

$$\lambda_A = 371.2 + 1.32E_T(30) \qquad (2)$$

It is derived by the least squares method, with a correlation coefficient of $R = 0.91$ and a standard deviation of SD = 3.56 nm, $N = 35$.

In LC, all dyes **3** retain their yellow-green colour, with absorption maxima at 430–432 nm and more intense fluorescence (Table 2). The absorption maxima λ_A of the dyes are hypsochromically shifted with regard to λ_A in the polar solvents ethanol and DMF and bathochromically shifted with regard to the less polar solvents toluene and chloroform. By means of eqn. (2), one can find an $E_T(30)$ value of 45 kcal mol^{-1} for LC ZLI 1840. The fluorescence spectra of the dyes recorded in surface-stabilised LC cells show that the fluorescence maxima λ_F are hypsochromically shifted with regard to λ_F in ethanol and the energy of the first excited state E_{S1} is accordingly higher. The lower Stokes shift in LC with regard to ethanol can be connected with the induced disposition of substituents in the plane of the aromatic structure (by the surface stabilised LC texture). It should be noted that intermolecular H-bonding is also possible in LC ZLI 1840 because of the presence of C≡N and C=O groups.

Ordering in dye–liquid crystal systems

It has been found that substances added to a nematic LC affect its orientation order. Particularly convenient for measuring orientation parameters in LC systems involving dichroic dyes is

Table 4 Influence of the 4-allylamino substituted 1,8-naphthalimide dyes **3a–e** upon the behaviour of liquid crystal ZLI 1840 at the nematic–isotropic phase transition (see text). Temperatures are given in K

System	T_N	T_I	T_I-T_N	ΔT_N	ΔT_I	T_{NI}	ΔT_{NI}
LC	362.5	368.5	6.0	—	—	365.5	—
LC+dye **3a**	361.8	369.1	7.3	−0.7	0.6	365.5	0.0
LC+dye **3b**	362.4	369.3	6.9	−0.1	0.8	365.9	0.4
LC+dye **3c**	362.5	368.7	6.2	0.0	0.2	365.6	0.1
LC+dye **3d**	362.5	368.4	5.9	0.0	−0.1	365.5	0.0
LC+dye **3e**	362.6	368.5	5.9	0.1	0.0	365.6	0.1

the method based on polarised absorption or fluorescence spectra.

The orientation order parameter S_A of a dye in LC can be calculated by use of eqn. (3).[16,24,25]

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

Here, $A_{\parallel}$ and $A_{\perp}$ are the corresponding absorbances in polarised light (at λ_{max}) at parallel and vertical orientations of the polarizer towards the LC director, and β is the angle between the long molecular axis of the dye and the vector of its absorption transition moment.

At $\beta = 0$, eqn. (3) reduces to eqn. (4).

$$S_A = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}} \equiv \frac{N(\lambda) - 1}{N(\lambda) + 2} \quad (4)$$

Here, $N(\lambda) = A_{\parallel}/A_{\perp}$ is the dichroic ratio of the dye molecule in polarised light.

It is accepted that elongation of dye molecules enables their better orientaton in LC. Table 3 displays the values of the ratio of length to width (*l*/*d*) of a dye molecule, the dichroic ratio $N(\lambda)$, and the orientation parameter S_A of dyes **3a–e**. The relative linearity of the molecule is given by its aspect ratio *l*/*d*. The calculation of *l* and *d* values is made by using the bond lengths in the molecule including the end groups.[26] The order parameters S_A determined are of satisfactory values for dyes **3a–c** (0.63–0.67), but however are low for dyes **3d** and **3e**.

It was noted that the results for S_A could be related to the electronic nature of the substituents R^1 and R^2. The dyes **3a–c** with substituents an H-atom or electron-donating methyl or methoxy groups have very good orientation parameters, whereas S_A for dye **3d**, which bears the electron-accepting Cl atom, is small. In the case of dye **3d**, this could arise from repulsive forces between the dye and LC which also has electron-accepting groups. In the case of dye **3e**, the hydroxy group in the *meta*-position decreases the molecular symmetry as evident and, in addition, causes intermolecular H-bonding with the carbonyl and nitrile groups present in LC. Both effects cause a misalignment of the dye and of LC, leading to the much lower value for the orientation parameter S_A (0.45).

The orientation parameters determined for this class of 1,8-naphthalimide derivatives are higher than those for 1,8-naphthalimide derivatives with an aliphatic residue bound to the imide nitrogen atom.[11] It is suggestive that the phenyl residue in most dyes under study stabilises better the planarity of the chromophoric structure thus leading to higher S_A.

Phase transition temperatures of dye–liquid crystal systems

It is well known that addition of a nonmesogenic solute to nematic LC changes its normal nematic–isotropic phase transition temperature, in most cases causing its decrease. Another specific feature of the phase transition is the appearance of two-phase regions predicted by theory and observed experimentally.[27]

The results from the temperature investigations on pure LC and on dye (0.5%)–LC mixtures are given in Table 4. The following temperature characteristics of the nematic–isotropic phase transition are determined: T_N, at which the first drop of the isotropic liquid appears, and T_I, at which the last drop of the nematics disappears. Their difference, $(T_I - T_N)$, is the range of the two-phase region, and ΔT_N and ΔT_I are the shifts of T_N and T_I with respect to the relevant temperatures of pure LC. $T_{NI} = 1/2(T_N + T_I)$ is the average temperature of the nematic–isotropic transition of the dye–LC mixtures and ΔT_N is its shift with respect to pure LC.

The temperature investigations on the binary systems show that the most of dyes **3a–e** either do not, or only very slightly, decrease the phase-transition temperatures T_N and T_I of pure LC and have a minor effect upon the two-phase region of LC.

Concluding remarks

By a two-step synthesis, nitro- and allylamino-substituted 1,8-naphthalimide derivatives are obtained in good yields. The nitro substituted derivatives are colourless, absorbing in the near UV region, whereas the allylamino-substituted derivatives absorb in the visible region exhibiting yellow-green fluorescence, the most of them being of high quantum yield.

There is a large effect of the medium upon the spectral properties of the novel compounds, caused by the polarity of the medium and the possibility of intermolecular solute–solvent interactions. The empirical solvent polarity parameter $E_T(30)$[23] is found to describe satisfactorily the effect of both solvent polarity and hydrogen bonding upon the spectral properties of the dyes. An analytical expression, derived on its basis, allows the determination of the solvatochromic properties of related dyes or of the solvent polarity.

The dyes under study are being investigated for applications in electro-optic liquid crystal displays of the guest–host type. In the nematic liquid crystal ZLI 1840, all the dyes retain their yellow-green fluorescence emission which is even more intense. With the novel substances, orientation order parameters up to 0.67 are attained in surface-stabilised display cells, the values being better than with other 1,8-naphthalimide dyes. It is found that the substituents in the molecules can give rise to large orientation effects and this may alternatively be related to their electronic nature. The dye guests have no influence upon the phase-transition temperature of the liquid crystal host, and very slightly affect the two-phase region specific to the transition. Thus, the high fluorescence of the dyes and their appropriate effect upon the orientation order and the phase-transition behaviour of the liquid crystal make them suitable components of liquid-crystal displays operating both in passive and active modes.

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