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Derivatives of 4-Amino-*N*-Ethylnaphthalimide for Use in Nematic Liquid Crystals

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ABSTRACT

*The order parameters of some dichroic fluorescent dyes {derivatives of 4-amino-*N*-ethylnaphthalimide} in three nematic liquid crystal mixtures (W52, E7 and ZLI 2359) have been determined by means of optical spectroscopy methods and the influence of the dye addition on the nematic–isotropic phase transition temperature has also been investigated. The voltages characterizing the impact of the electric field on the dye–liquid crystal mixtures have been estimated. It was found that the dyes can be utilized in guest–host liquid crystal display devices.*

1 INTRODUCTION

In a guest–host liquid crystal display (GH LCD) a dichroic dye (guest) is dissolved in a liquid crystalline host which acts as an anisotropic matrix to orientate the dye molecules. The electric field applied to the display re-orientates the liquid crystal and dye molecules along the field direction, and induces a change in the selective absorption of the dichroic dye. Such an effect in a nematic liquid crystal was first observed by Heilmeier and co-workers,[1,2] while White and Taylor found it in chiral nematics.[3] Since then, GH LCDs in many configurations have been described.[4,5] In comparison with conventional twisted-nematic displays they have many advantages, such as displaying information in colour, good contrast over a large viewing angle, high brightness and the need for only one, or no external polarizers at all.

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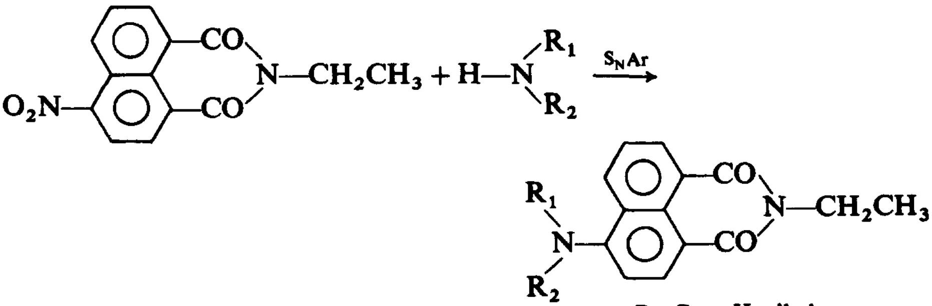
Guest–host displays are available in a variety of colours but in many applications black–white displays are preferred because they have the highest contrast ratio (in terms of luminance) and the neutral colour often harmonizes better with the surrounding area. A black–white GH LCD can be realized if three or more dichroic dyes are simultaneously dissolved in the host matrix.[6,7] These dyes should be chosen in such a way that their absorption spectra cover the whole visible spectral region. Yellow, red and blue dyes are required for black images. If in a GH LCD a dye emitting fluorescent light is used, then not only the absorption of light but also the fluorescence intensity can be controlled by changing the orientation of the guest and host molecules by means of an electric field; some GH LCDs using fluorescent dyes have been reported.[8–12]

With regard to the dyes used in GH LCDs, they should be non-ionic, have good solubility in the liquid crystal host, a high dichroic ratio, good chemical, photochemical and electrochemical stability and have good alignment in the liquid crystal matrix. In the case of fluorescent displays, the quantum fluorescence yield of dyes should be as high as possible. The position of the fluorescence maximum is important and should preferably occur in the visible region.

In this paper we describe the synthesis and properties of some yellow dichroic dyes, derivatives of 4-amino-*N*-ethylnaphthalimide, and discuss their usefulness to application in GH LCDs working both in the passive and active modes.

2 MATERIALS AND METHODS

The alkyl derivatives of 4-amino-*N*-ethylnaphthalimide were obtained using the reported synthesis method[13] according to the following scheme:



R_1, R_2 = H, alkyl

The reaction was carried out in DMSO at 50–80°C using excess amine.

The end of the reaction (2–8 h) was determined using TLC. The dyes were obtained in 90–99% yield, and small amounts of impurities were removed by repeated crystallization to constant melting point. The dyes thus prepared are listed in Table 1.

Three technologically important liquid crystal mixtures: W52 (POCH, Lublin), E7 (BDH) and ZLI 2359 (Merck) were used as host matrices. All these mixtures exhibit a stable broad nematic phase, good chemical stability and high positive dielectric anisotropy. The dyes were initially screened for their solubility in the liquid crystals and were dissolved in these media at a concentration of 0·5% (w/v).

The absorption measurements were performed using a double-beam SPECORD M40 spectrophotometer (Carl Zeiss Jena), and the fluorescence intensity measurements on equipment constructed in our laboratories. In order to obtain the polarized absorption and fluorescence spectra, neutral UV polarizers (Carl Zeiss Jena) were used. The measurements for the dyes dissolved in the liquid crystals were made in 'sandwich' cells of 20 μm thickness. Planar homogeneous molecular orientation of the samples was achieved by coating the cell surfaces with a polyimide layer and by an additional rubbing process. The electro-optical parameters of the dye–liquid crystal mixtures in the thin oriented layers were estimated using an a.c. voltage of 1 kHz.

The quantum fluorescence yield was determined on the basis of the absorption and fluorescence spectra of the dyes dissolved in 1,2-dichloroethane at a concentration of $7{\cdot}5\times10^{-6}$ M using a method described in Ref. 14. Fluorescein at a concentration of 10^{-6} M in 0·1 M NaOH was used as standard.

The fluorescence spectra of the dye–liquid crystal mixtures were measured in the π geometry, i.e. the exciting light beam was perpendicular

TABLE 1
Structure and Molecular Weight of Dyes Studied

Dye code	R_1	R_2	*Mol. wt*
1	—H	$—CH_3$	254
2	—H	$—CH_2CH_3$	268
3	—H	$—(CH_2)_2CH_3$	282
4	—H	$—(CH_2)_3CH_3$	296
5	—H	$—(CH_2)_4CH_3$	310
6	—H	$—(CH_2)_6CH_3$	338
7	—H	$—(CH_2)_{11}CH_3$	407
8	—H	$—(CH_2)_2CH(CH_3)_2$	310
9	$—CH_3$	$—CH_3$	268

to the cell surface, the fluorescence light being emitted perpendicular to the surface from the same side of the cell. The wavelength of the exciting radiation corresponded to the absorption maximum of the dyes.

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 two-month period.

The temperature of the nematic–isotropic phase transition for pure liquid crystals and the dye–liquid crystal mixtures was obtained by means of a polarizing microscope equipped with a heating stage; the accuracy of the temperature determination was ±0·1 K.

3 RESULTS

Table 2 presents some spectral properties of dyes **1**–**9** in 1,2-dichloroethane: the positions of the absorption and fluorescence maxima in the visible region, λ_A^{max} and λ_F^{max}, respectively, the extinction coefficient, ϵ, and the quantum fluorescence yield, Q.

Figure 1 shows the polarized absorption and fluorescence spectra for dye 7 in E7 as an example. The spectra are presented in arbitrary units. The maxima of the parallel components of both the absorbance and the fluorescence intensity are normalized to unity. The absorption and fluorescence spectra for the other dyes in the liquid crystals were similarly measured. On the basis of such spectra, the order parameters for the dyes were calculated. The order parameter of the guest dissolved in a nematic host is defined by eqn (1):[15]

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

TABLE 2
Spectral Properties of the Dyes in 1,2-Dichloroethane ($c = 7{\cdot}5 \times 10^{-6}$ M)

Dye code	*Absorption*		*Fluorescence*	
	λ_A^{max} (nm)	ϵ	λ_F^{max} (nm)	Q
1	426	16 500	487	0·74
2	427	17 000	495	0·76
3	432	17 000	497	0·74
4	429	20 500	495	0·75
5	431	20 600	497	0·71
6	431	19 000	497	0·73
7	433	15 000	491	0·66
8	431	17 150	497	0·73
9	416	10 300	500	0·64

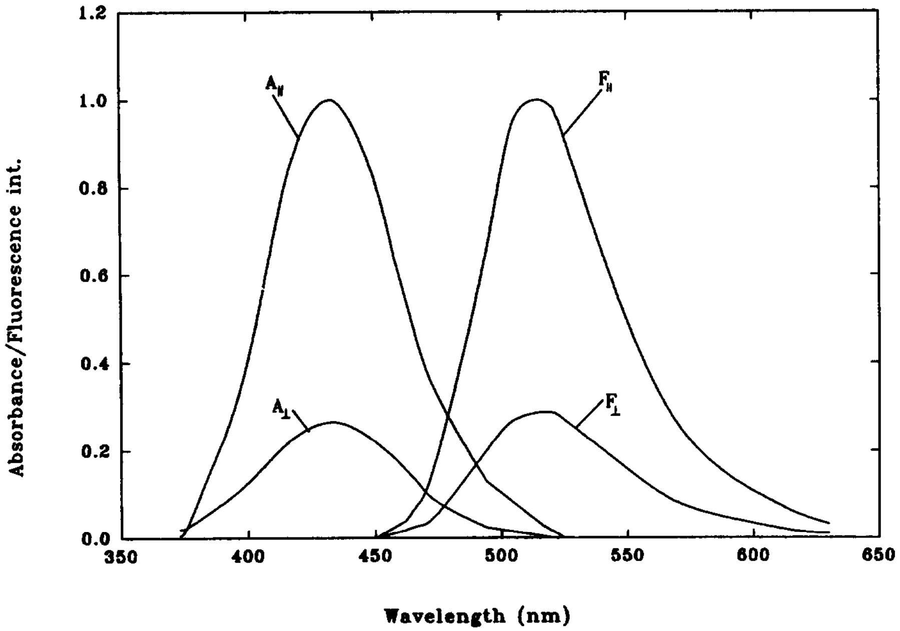


Fig. 1. Polarized components of the absorption and fluorescence spectra for dye 7 in E7.

where θ is the angle between the long axis of the guest molecule and the direction of the host orientation.

If, for guest molecules, it can be assumed that their geometric long axis corresponds to the direction of 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 eqn (2):[3,16]

$$S_A = \frac{D-1}{D+2} = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}} \tag{2}$$

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, respectively, parallel and perpendicular to the orientation axis of the sample.

Analogous 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 by applying eqn (3):[17]

$$S_F = \frac{F_{\parallel} - F_{\perp}}{F_{\parallel} + 2F_{\perp}} \tag{3}$$

where $F_{\parallel}$ and $F_{\perp}$ are the intensities of the fluorescence light polarized parallel and perpendicular, respectively, to the liquid crystal orientation axis. Equation (3) is valid for excitation with unpolarized light and for dyes with absorption and emission transition moments parallel to the long molecular axis.

For calculations of the order parameters, the values of A_k and F_k ($k = \parallel, \perp$) were taken at the wavelength corresponding to the maxima of the absorbance and the fluorescence intensity, respectively, of the given dye–liquid crystal mixtures. The positions of these maxima, as well as the values of the order parameter obtained from eqns (2) and (3) at three various reduced temperatures T^* are shown in Tables 3–5. $T^* = T/\bar{T}_{NI}$, where $\bar{T}_{NI}$ is the average temperature of the nematic–isotropic phase transition. At least three, and usually five, samples were used to determine each order parameter. Tables 3–5 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.

Exact determination of the fluorescence efficiency for a dye dissolved in an oriented matrix is very difficult because many factors, including anisotropy, need to be taken into account. We attempted to estimate this efficiency for the dyes investigated, but the results should be regarded as qualitative rather than quantitative. The values of Q obtained for dyes **1–9** in all the liquid crystals used was very high and similar to the values obtained for the dyes dissolved in 1,2-dichloroethane.

All the liquid crystalline matrices used are mixtures of several com-

TABLE 3

Positions of Absorption and Fluorescence Maxima and Order Parameters of Dyes **1–9** in W52

Dye code	*Absorption*				*Fluorescence*				
	λ_A^{max} *(nm)*	S_A			$\lambda_{F_\parallel}^{max}$ *(nm)*	$\lambda_{F_\perp}^{max}$ *(nm)*	S_F		
		T^* = *0·89*	T^* = *0·94*	T^* = *0·97*			T^* = *0·89*	T^* = *0·94*	T^* = *0·97*
1	427	0·42	0·35	0·26	509	507	0·40	0·36	0·28
2	431	0·38	0·32	0·25	517	515	0·41	0·34	0·28
3	429	0·47	0·43	0·35	511	509	0·40	0·35	0·34
4	431	0·46	0·35	0·27	517	515	0·43	0·37	0·28
5	431	0·44	0·38	0·29	515	513	0·39	0·33	0·27
6	429	0·48	0·43	0·31	514	512	0·43	0·33	0·27
7	431	0·45	0·37	0·29	518	517	0·41	0·37	0·29
8	431	0·39	0·30	0·29	507	504	0·36	0·32	0·26
9	416	0·37	0·33	0·25	522	520	0·41	0·37	0·29

TABLE 4
Positions of Absorption and Fluorescence Maxima and Order Parameters of Dyes 1–9 in E7

Dye code	*Absorption*				*Fluorescence*				
	λ_A^{max} *(nm)*	S_A			$\lambda_{F_\parallel}^{max}$ *(nm)*	$\lambda_{F_\perp}^{max}$ *(nm)*	S_F		
		$T^* =$ *0·89*	$T^* =$ *0·94*	$T^* =$ *0·97*			$T^* =$ *0·89*	$T^* =$ *0·94*	$T^* =$ *0·97*
1	434	0·41	0·37	0·31	520	517	0·40	0·35	0·33
2	433	0·45	0·39	0·32	519	517	0·38	0·33	0·26
3	435	0·44	0·37	0·28	522	520	0·43	0·41	0·33
4	434	0·44	0·38	0·31	517	514	0·39	0·29	0·26
5	434	0·41	0·34	0·26	515	513	0·41	0·34	0·27
6	431	0·46	0·42	0·33	516	514	0·44	0·36	0·26
7	434	0·48	0·45	0·34	520	517	0·45	0·40	0·34
8	434	0·41	0·33	0·28	522	520	0·40	0·30	0·26
9	420	0·40	0·31	0·33	514	511	0·42	0·34	0·27

pounds. Therefore, according to thermodynamic laws and the first-order nature of the nematic–isotropic phase transition,[18] in the vicinity of the clearing point a two-phase region is observed. In this region, both nematic and isotropic phases coexist in equilibrium. It has been shown[11,12,19–22] that a dichroic dye added to a nematic liquid crystal influences the range of the mesophase, causing either a decrease or an

TABLE 5
Positions of Absorption and Fluorescence Maxima and Order Parameters of Dyes 1–9 in ZLI 2359

Dye code	*Absorption*				*Fluorescence*				
	λ_A^{max} *(nm)*	S_A			$\lambda_{F_\parallel}^{max}$ *(nm)*	$\lambda_{F_\perp}^{max}$ *(nm)*	S_F		
		$T^* =$ *0·89*	$T^* =$ *0·94*	$T^* =$ *0·97*			$T^* =$ *0·89*	$T^* =$ *0·94*	$T^* =$ *0·97*
1	427	0·42	0·36	0·29	502	500	0·42	0·28	0·24
2	427	0·39	0·34	0·26	502	499	0·36	0·30	0·24
3	428	0·42	0·35	0·22	507	506	0·40	0·34	0·27
4	427	0·41	0·33	0·24	504	502	0·39	0·33	0·23
5	427	0·41	0·35	0·23	502	500	0·43	0·40	0·24
6	427	0·44	0·38	0·27	503	501	0·38	0·33	0·23
7	427	0·46	0·38	0·30	503	501	0·40	0·39	0·26
8	427	0·42	0·32	0·23	503	501	0·38	0·37	0·29
9	410	0·37	0·30	0·21	506	504	0·39	0·32	0·26

increase in the nematic–isotropic transition temperature of the pure host. Moreover, the addition of a guest to a liquid crystal induces the two-phase region if the matrix is a single-component liquid crystal[20–22] or causes broadening of this region if the matrix is a liquid crystalline mixture.[11,12]

Tables 6–8 present the results of the temperature investigations of the dye–liquid crystal mixtures. T_N is the temperature at which the first drop of the isotropic liquid appears; T_I is the temperature at which the last drop of the nematic disappears on sample heating; $T_I - T_N$ 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 such temperatures of the pure liquid crystal. In Tables 6–8 the values of the average nematic–isotropic transition temperature $\bar{T}_{NI}$ for the mixtures studied and the average shifts $\Delta \bar{T}_{NI} = 1/2(\Delta T_N + \Delta T_I)$ are also given.

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, then the absorbance of the parallel component of the absorption ($A_\parallel$) decreases as the voltage applied rises, whereas the perpendicular component ($A_\perp$) does not change (within experimental uncertainty). At a suitably large voltage, $A_\parallel$ and $A_\perp$ are equal to each other. We have reported the voltage giving x% absorption (for $A = A_\parallel - A_\perp$, normalized to 100% for no applied voltage) in the form

$$V_x(\alpha, t)$$

where α is the angle measured to the cell normal (degrees) and t is the

TABLE 6
Temperature Data for Dye–W52 Mixtures

Substance	$T_N[K]$	$T_I[K]$	$T_I - T_N$	ΔT_N	ΔT_I	$\bar{T}_{NI}$	$\Delta \bar{T}_{NI}$
W52	333·8	335·6	1·8	—	—	334·7	—
1	333·4	335·4	2·0	−0·4	−0·2	334·4	−0·3
2	332·3	334·9	2·6	−1·5	−0·7	333·6	−1·1
3	332·5	335·3	2·8	−1·3	−0·3	333·9	−0·8
4	332·9	335·9	3·0	−0·9	+0·3	334·4	−0·3
5	333·0	334·8	1·8	−0·8	−0·8	333·9	−0·8
6	333·5	336·3	2·8	−0·3	+0·7	334·9	+0·2
7	332·5	335·1	2·6	−1·3	−0·5	333·8	−0·9
8	332·0	335·0	3·0	−1·8	−0·5	333·5	−1·2
9	332·3	335·1	2·8	−1·5	−0·5	333·7	−1·0

TABLE 7
Temperature Data for Dye–E7 Mixtures

Substance	$T_{\mathrm{N}}[K]$	$T_{\mathrm{I}}[K]$	$T_{\mathrm{I}}-T_{\mathrm{N}}$	ΔT_{N}	ΔT_{I}	$\bar{T}_{\mathrm{NI}}$	$\Delta\bar{T}_{\mathrm{NI}}$
E7	331·5	333·3	1·8	—	—	332·4	—
1	331·4	333·2	1·8	−0·1	−0·1	332·3	−0·1
2	331·2	333·4	2·2	−0·3	+0·1	332·3	−0·1
3	330·6	332·6	2·0	−0·9	−0·7	331·6	−0·8
4	331·0	333·4	2·4	−0·5	+0·1	332·2	−0·2
5	330·9	333·3	2·4	−0·6	0·0	332·1	−0·3
6	331·2	333·8	2·6	−0·3	+0·5	332·5	+0·1
7	332·0	333·6	1·6	+0·5	+0·3	332·8	+0·4
8	331·0	333·8	2·8	−0·5	+0·5	332·4	0·0
9	330·6	333·2	2·6	−0·9	−0·1	331·9	−0·5

temperature (°C). As described in Ref. 23, we regarded the display to be completely off if:

$$\text{OFF} \qquad V < V_{90}(0°, t)$$

and fully on if:

$$\text{ON} \qquad V > V_{10}(0°, t)$$

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 $V_{90}(0°, 22°\mathrm{C})$ and $V_{10}(0°, 22°\mathrm{C})$ for all the mixtures studied are listed in Table 9.

The change in 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.

TABLE 8
Temperature Data for Dye–ZLI 2359 Mixtures

Substance	$T_{\mathrm{N}}[K]$	$T_{\mathrm{I}}[K]$	$T_{\mathrm{I}}-T_{\mathrm{N}}$	ΔT_{N}	ΔT_{I}	$\bar{T}_{\mathrm{NI}}$	$\Delta\bar{T}_{\mathrm{NI}}$
ZLI 2359	340·7	342·1	1·4	—	—	341·4	—
1	340·2	341·8	1·6	−0·5	−0·3	341·0	−0·4
2	339·8	341·4	1·6	−0·9	−0·7	340·6	−0·8
3	340·3	341·9	1·5	−0·4	−0·2	341·1	−0·3
4	340·0	341·4	1·4	−0·7	−0·7	340·7	−0·7
5	339·9	341·9	2·0	−0·8	−0·2	340·8	−0·6
6	339·9	341·5	1·6	−0·8	−0·6	340·7	−0·7
7	340·0	341·6	1·6	−0·7	−0·5	340·8	−0·6
8	339·8	341·4	1·6	−0·9	−0·7	340·6	−0·8
9	339·5	341·1	1·6	−1·2	−1·0	340·3	−1·1

TABLE 9
Characteristic Voltages for Liquid Crystals Doped with Dye

Substance	$V_{90}(0°, 22°C)$ [V] $\Delta V = \pm 0{\cdot}1$ V	$V_{10}(0°, 22°C)$ [V] $\Delta V = \pm 0{\cdot}1$ V
W52 + **2**	1·1	2·1
W52 + **7**	1·0	2·2
E7 + **2**	1·0	2·6
E7 + **7**	1·0	3·1
ZLI 2359 + **2**	2·5	4·8
ZLI 2359 + **7**	2·6	5·0

Figure 2 illustrates the voltage dependence of the values of S'_A and S'_F for dyes **2** and **7** in E7 as examples, where S'_A and S'_F are defined, by analogy to eqns (2) and (3), by eqns (4) and (5), respectively.

$$S'_A = \frac{A_{\parallel}(V) - A_{\perp}(V)}{A_{\parallel}(V) + 2A_{\perp}(V)} \tag{4}$$

$$S'_F = \frac{F_{\parallel}(V) - F_{\perp}(V)}{F_{\parallel}(V) + 2F_{\perp}(V)} \tag{5}$$

The changes in S'_A and S'_F for the other dye–liquid crystal mixtures with the voltage applied to the cell are similar to those presented in Fig. 2.

4 DISCUSSION

From the results in Tables 2–5 it is apparent that the absorbance and fluorescence intensity maxima undergo slight shifts in 1,2-dichloroethane and the various liquid crystal matrices due to the different polarities of the solvents. The length of the alkyl chain (R_2) has no significant influence on the position of either the absorption or the fluorescence maxima. However, replacement of the hydrogen by —CH_3 in substituent R_1 results in a shift in the absorption maximum towards shorter wavelength. The maximum positions of the perpendicular components of the fluorescence for the dyes in the liquid crystals are shifted towards shorter wavelength 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) upon the electric permittivity and the refractive index,[24] which have different values when measured parallel and perpendicular to the optical axis of a liquid crystal. The positions of the maxima and the narrow half-bandwidths of the visible absorption and fluorescence bands of the dyes (δ_A between 3180 and 3975 cm^{-1} and δ_F between 2050 and 2990 cm^{-1}) indicate that the derivatives of 4-amino-*N*-ethylnaphthalimide have a brilliant yellow colour with a strong green fluorescence.

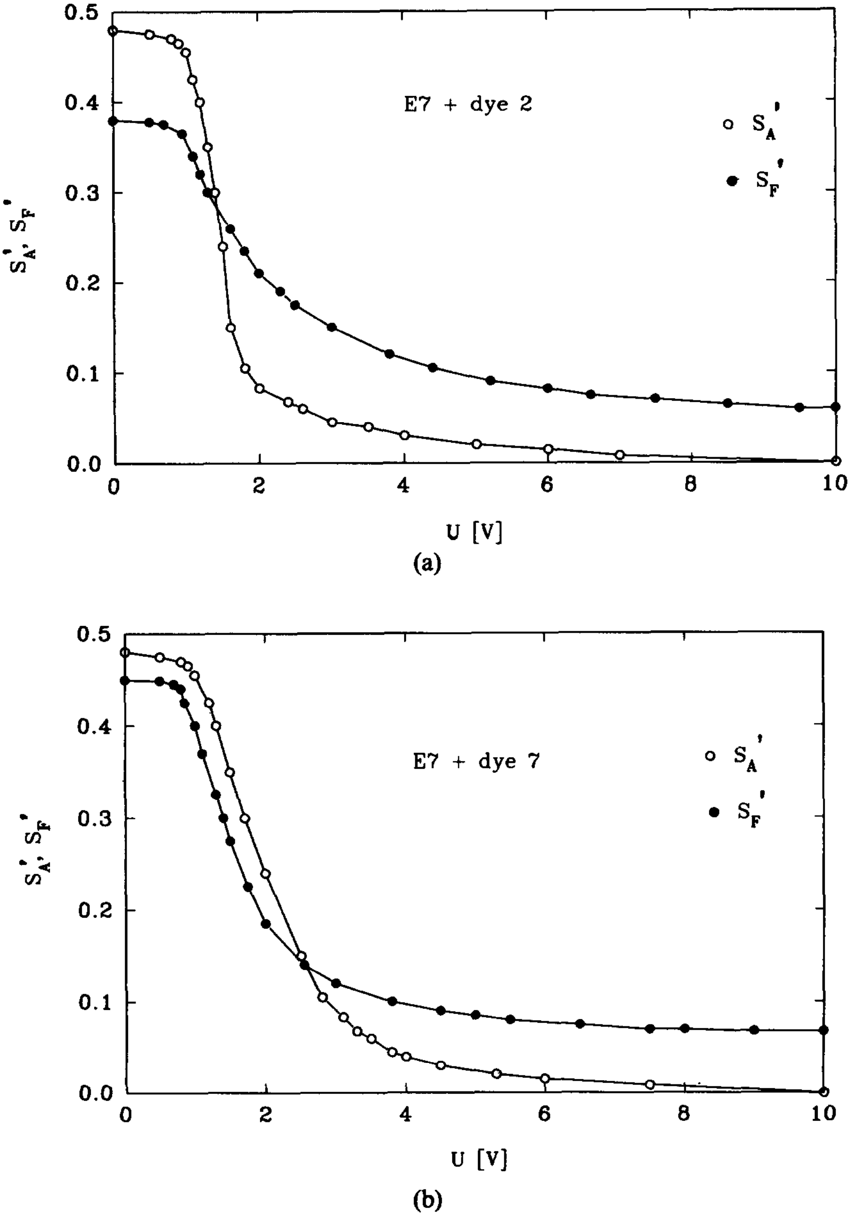


Fig. 2. S'_A and S'_F as a function of voltage for dyes dissolved in E7: (a) dye **2**; (b) dye **7**.

The data in Tables 3–5 indicate that the order parameters of the dye–liquid crystal mixtures are not very high. A low order parameter can arise either from incomplete alignment of the dye molecules in the anisotropic matrix, or from the electronic transition dipole moment not being parallel to the long molecular axis of the dye. Considering the molecular structure of the dyes investigated, it seems that both these factors can contribute to the decreased values of the order parameter. On the one hand, non-zero angles between the absorption and emission transition moments and the long axis of the dye molecules lower the real values of S_A and S_F, and on the other hand the lack of symmetry in the dye structure, and also possible steric effects, reduce the guest–host van der Waals interaction by preventing compatible alignment of the dye with the liquid crystal molecules.

The values of the order parameter 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 factors can be the reason for such differences (1) the existence of non-zero intramolecular angles between the absorption and emission oscillators,[25,26] (2) the intermolecular energy transfer processes, which can depolarize the fluorescence in an unpredictable manner[25,26] and lead to misinterpretation of the results obtained, and (3) the interactions between the liquid crystal molecules and the cell surfaces.[12,27–30] The influence of the latter factor is illustrated in Fig. 2 in which it is seen that S'_F does not become zero even when a large voltage is applied to the cell, whereas S'_A reaches zero at about 9 V. It should also be noted that the order parameter obtained from the absorption measurements (S_A or S'_A) is the value averaged over the whole pathway of the light passing through the cell, whereas in the experimental procedures used in this investigation (π geometry), the fluorescence is emitted mainly from the cell surfaces[29] and therefore, S_F and also S'_F reflect the molecular order in the surface layer rather than in the bulk. The results presented in Fig. 2 suggest that strong surface interactions hinder the re-orientation of the liquid crystal molecules near the glass plates; therefore, even if a large voltage is applied, the orientation at the surfaces is not completely destroyed. This also implies that in a thin layer of a liquid crystal, the molecular alignment in the bulk is different from that at the surfaces, in agreement with previous observations.[28,29] As a result, various values of S_F and S_A for a given dye–liquid crystal mixture can be obtained. Considering these factors, it would appear that the values of S_A are a better reflection of the long orientational order in the nematic phase of the guest–host mixtures 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 the information obtained from S_F and S'_F can be utilized by selection of the appropriate guest–host mixture to GH LCDs working in the active mode.

The order parameters of the dyes are different in the various liquid crystals studied, but the differences are not significant. This effect is connected with various guest–host interactions in the individual dye–liquid crystal mixtures and has been observed previously for many dichroic dyes.[21,31–34] Changes in the order parameters with rise of temperature do not follow the same pattern for all the liquid crystals used, which implies that various guest–host mixtures are differently resistant to thermal fluctuations.

We had expected, for dyes **1–7** dissolved in the liquid crystals, specified changes in the order parameter, i.e. the so-called ‘odd–even’ effect due to the alternation of the interaction between the alkyl chains.[35] The results in Tables 3–5 show, however, that the dyes investigated do not show this effect distinctly; instead, a tendency for an increase in the S_A and S_F values is observed as the length of the alkyl chain increases. The lack of regular alternation in the order parameter values can be attributed either to flexibility of the alkyl chain caused by the rotation of its single bond[36] or to the above-mentioned incomplete alignment of the dyes in the liquid crystals used, as has been observed in Ref. 37.

The data presented in Tables 6–8 indicate that with the same exception, the derivatives of 4-amino-*N*-ethylnaphthalimide decrease the nematic–isotropic transition temperature of the liquid crystal mixtures investigated, which means that after addition of the dye, destabilization of the nematic phase occurs. Moreover, extension of the two-phase region in the vicinity of the clearing point for the dye–liquid crystal mixtures with respect to the pure host matrices is observed. Comparing the results in Tables 3–5 with those in Tables 6–8, it is seen that an indirect correlation between the order parameter of the guest in the liquid crystalline host and the transition temperature T_{NI} can be found. For dyes with higher values of S, a less-negative or even a positive shift in the clearing temperature is observed, for example dye **6** in W52 and E7, and dye **7** in E7. However, the dyes with low order parameters are more effective in destabilizing the nematic phase (dye **2** in W52, dye **9** in W52 and ZLI 2359).

The results in Table 9 show that the threshold voltage and the switching-on voltage depend upon the liquid crystal matrix used, and that the length of the alkyl chain in the dye molecule has little influence on V_{10} and V_{90}.

5 CONCLUSIONS

Some spectral and electro-optical properties, and the orientational ability of dichroic fluorescent dyes dissolved in three commercial liquid crystalline mixtures have been investigated. From the results obtained, the following conclusions can be drawn:

(1) All the dyes investigated had an excellent yellow colour, making them important not only for use as one of the three primary colours but also as components for preparing practically useful black or green colours.
(2) The dyes were characterized by a high fluorescence quantum yield in the visible spectral region.
(3) The orientation of the dyes in the liquid crystal matrices was satisfactory (values of S greater than 0·4 are acceptable, but not optimal, for liquid crystal application).
(4) The dyes did not significantly destabilize the nematic phase of the liquid crystalline host (ΔT_{NI}, is not less than $-1{\cdot}4$ K), and were stable to sunlight.

We conclude that the derivatives of 4-amino-*N*-ethylnaphthalimide studied can be used as dichroic guests in GH LCDs working both in the absorption (passive) and fluorescence (active) modes.

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