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Fluorescent Perylene Dyes for Liquid Crystal Displays

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ABSTRACT

A number of alkyl esters of perylene-3,4,9,10-tetracarboxyl acid have been synthesised. The structure of the dyes obtained was confirmed by ^{1}*H-NMR, mass spectroscopy and elemental analysis. Their fluorescent properties in isotropic and anisotropic (nematic) media have been determined. Absorption and fluorescence order parameters of the dyes in liquid crystal mixtures of the 'quest–host' type have been determined. Liquid crystal displays containing the dyes have been constructed and a strong contrast on the fluorescent background achieved.*

1 INTRODUCTION

Among fluorescent dyes[1] which have been evaluated for use in liquid crystal displays, perylene derivatives are of interest. Previously described diimide derivatives of perylene-3,4,9,10-tetracarboxylic acid[2] exhibited rather poor solubility, but esters of perylene-3,9(or 10)-dicarboxylic acid having good functional parameters have been described.[3–5] Perylene-carboxylic acid derivatives have also been reported as being useful dyes for fluorescent collectors.[6] In this present work, the synthesis of some alkyl esters of perylene-3,4,9,10-tetracarboxylic acid of formula **1** and an

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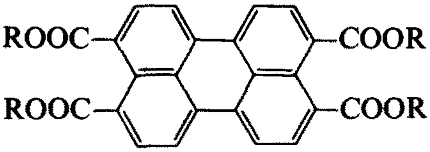
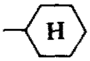
investigation of their properties were made. To ensure good solubility of the dyes in the liquid crystal, esters of alcohols having 5–7 carbon atoms were utilised.



1

1a R = $-(CH_2)_3CH_3$
1b R = $-(CH_2)_4CH_3$
1c R = $-(CH_2)_6CH_3$
1d R =



2 EXPERIMENTAL

2.1 General

Melting points were determined with a Boetius PHMK-05 apparatus and the values were corrected. ^{1}H-NMR spectra were recorded using a JOEL 200 MHz and mass spectra were recorded on an LKB 2091 spectrometer. The absorption spectra of the dyes were recorded on a SPECORD M 40 (Carl Zeiss Jena) at a concentration of 1–4 × 10 mole/dm^3. Fluorescence spectra were measured with standard equipment, using a microcomputer, the detector being placed at an angle of 90° and the plane of the absorption cell at an angle of 40° to the exciting radiation.

The quantum yield of fluorescence was determined by standard method[7] (fluorescein; λ_{exc} = 436 nm); the absorption and emission spectra of the solutions of dyes in liquid crystal (E7 from BDH) were recorded at a concentration of 1×10^{-3}–5×10^{-3} mole/dm^3.

Order parameters can also be calculated from absorption as well as from fluorescence measurements. The order parameters S_A of the dyes dissolved in liquid crystal were estimated from absorbances measured parallel and perpendicular to the direction of the homogeneous layers:

$$S_A = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} - 2A_{\perp}}$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances of light polarised parallel and perpendicular to the direction, respectively.

The fluorescence order parameter (S_F) may be calculated from measurement of the fluorescence intensities by taking into account their parallel ($F_{\|}$) and perpendicular ($F_{\perp}$) components:

$$S_F = \frac{F_{\|} - F_{\perp}}{F_{\|} - 2F_{\perp}}$$

All the liquid crystal samples were placed into cells consisting of front and rear glass plates constructed with a planar homogeneous alignment, using the known rubbing polyimide technique (twisted by 90°). The thickness of the cell was maintained with 10 μm Teflon foil. After filling and hermetic sealing of the cells, they were heated to the isotropic phase and allowed to cool to room temperature before measurements.

The fluorescence intensities of the dyes in the liquid crystal cells were resolved into parallel ($F_{\|}$) and perpendicular ($F_{\perp}$) components with an analyser placed between the sample and the detector. Polarised components of the fluorescence spectra obtained in this way were stored in a computer and then transformed to yield the fluorescence order parameters.

Cells containing the E7 mixture with the dyes ($c = 5 \times 10^{-3}$ mole/dm^3) were irradiated using a HBO-200 lamp placed 300 mm from the cell. After every 5 h, the absorption spectra of the samples were recorded in order to ascertain the influence of UV light on the stability of the dyes.

Solutions of dyes **1** in the liquid crystal E7 were used as active layers in model[8] liquid crystal displays of the twisted nematic type (TN). A conventional mini-fluorescent lamp with removed luminophore layer was used as the source of light. Fluorescence of the display was excited over the whole spectral range emitted by the lamp. The light exciting the fluorescence was invisible to an observer due to the appropriate geometry of the source–display–observer system. As a result, after applying the electric field to the display (about 5 V) the black image on the strongly fluorescent green background appeared. Additionally, after use of a neutral polariser as an analyser of light emitting from the display, further improvement of the display contrast was achieved.

2.2 Tetramethyl ester of perylene-3,4,9,10-tetracarboxylic acid 2

The product was prepared according to literature data[9] in 97% yield; mp 321–322°C (lit., mp 322–323°C).

2.3 Tetra-*n*-butyl ester of the perylene-3,4,9,10-tetracarboxylic acid 1a[10]

Sodium (0·23 g; 0·01M) was dissolved in 200 cm^3 of anhydrous butanol; **2** (4·85 g; 0·01M) was then added and the mixture boiled for 80 h. The reaction was monitored chromatographically (TLC-Kieselgel Merck 5553, cyclohexane : 1,4-dioxane 3 : 1). The reaction was considered complete when the disappearance of the **2** spot and of the three spots of the intermediate products were noted, the plate showing only the spot of the highest R_f component. The mixture was then concentrated under reduced pressure to 20 cm^3 and allowed to crystallise. The product was filtered, washed with methanol and water and again with methanol. After drying 6 g (91%) of dye **1a**, in the form of a yellow powder, was obtained (mp 114–116°C from butanol; mass spectroscopy (M^+) = 652).

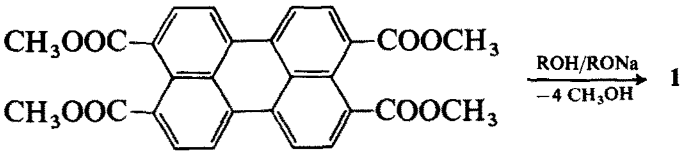
Analysis for $C_{40}H_{44}O_8$: C, found 73·52% (calc. 73·60%); H, found 6·70% (calc. 6·79%).

^{1}H-NMR ($CDCl_3$): δ 1·15, t, CH_3 (12H); δ 1·42–2·55 overlapped multiplets —CH_2—CH_2—CH_2— (24H); δ 7·2–8·4, m, perylene ring (8H).

Dyes **1b–1d** were synthesised in a similar way; results are given in Table 1.

3 RESULTS AND DISCUSSION

Four dyes **1** were synthesised by transesterification of **2** with the appropriate alcohol in the presence of its sodium alcoholate:[9]



2

The yellow dyes **1** were obtained in good yield and had good solubility in most organic solvents. Dye **1c** with four *n*-heptyl residues, and dye **1d** with four cyclohexyl residues, exhibited the best solubility.

The absorption spectra of the solutions of **1** in solvents of different polarity (Table 2) were almost identical. They showed three bands of increasing intensity towards the long wavelength range (0·4 : 0·82 : 1). The intensity of the absorption bands tended to increase with increasing solvent polarity. Figure 1 shows that the first absorption band is usually overlapped by other more intense bands. Spectral data for the second and third bands are given in Table 2.

The emission spectra are the mirror image of the absorption spectra and have high intensity as a result of the high probability of absorption as well as the high quantum yield of fluorescence. The quantum yield of fluorescence increases with increasing polarity of the solvent, and in 96·5% ethanol it varies from 0·82 for **1c** to 0·87 for **1a** (Table 2).

TABLE 1
Results of Transesterification of **2** and Some Properties of **1**

Dye	R	Temperature of reaction (°C)	Time (h)	Yield (%)	Products m.p. (°C)	R_f[a]	Elemental analysis				MS (M^+)
							%C		%H		
							Found	Calc.	Found	Calc.	MS
1a	*n*-Butyl	114–116	80	91	165–166	0·61	73·52	73·60	6·70	6·79	652
1b	*n*-Pentyl	135	64	94	125–126	0·70	77·50	74·55	7·42	7·39	708
1c	*n*-Heptyl	160–165	12	94	67–69	0·73	76·00	76·07	8·52	8·35	—
1d	Cyclohexyl	160	2	76	232·5–234	0·49	76·10	76·16	6·90	6·93	—

[a] TLC Silica gel Merck 5553, cyclohexane : 1,4-dioxane 3 : 1.

TABLE 2
Spectral Properties of **1**

Dye	*Absorption*[a] λ_{max} *(nm)* *(ε (dm^3/mol cm)*						*Fluorescence*[b]				
	Benzene		*1,2-dichloroethane*		*Ethanol 96·5%*		*Main band (nm) in 1,2-dichloroethane*		*Quantum yield, ϕ*		
									Benzene 0·75	*1,2-dichloroethane*	*Ethanol 96·5%*
1a	448 (26 900)	478 (32 800)	445 (28 900)	475 (35 200)	442 (29 800)	472 (36 400)	430	520	0·75	0·78	0·87
1b	448 (29 000)	478 (35 000)	445 (32 400)	475 (38 500)	442 (32 200)	472 (39 300)	492	522	0·70	0·77	0·84
1c	448 (25 400)	478 (31 200)	445 (27 200)	475 (33 500)	442 (28 100)	472 (34 300)	493	518	0·70	0·78	0·82
1d	448 (23 600)	478 (29 800)	445 (26 000)	475 (32 000)	442 (26 500)	472 (32 500)	491	518	0·61	0·78	0·84

[a] $c = 4 \div 5 \times 10^{-6}$ mole/dm^3.

[b] $c = 1 \times 10^{-6}$ mole/dm^3, $\lambda_{exc} = 436$ nm.

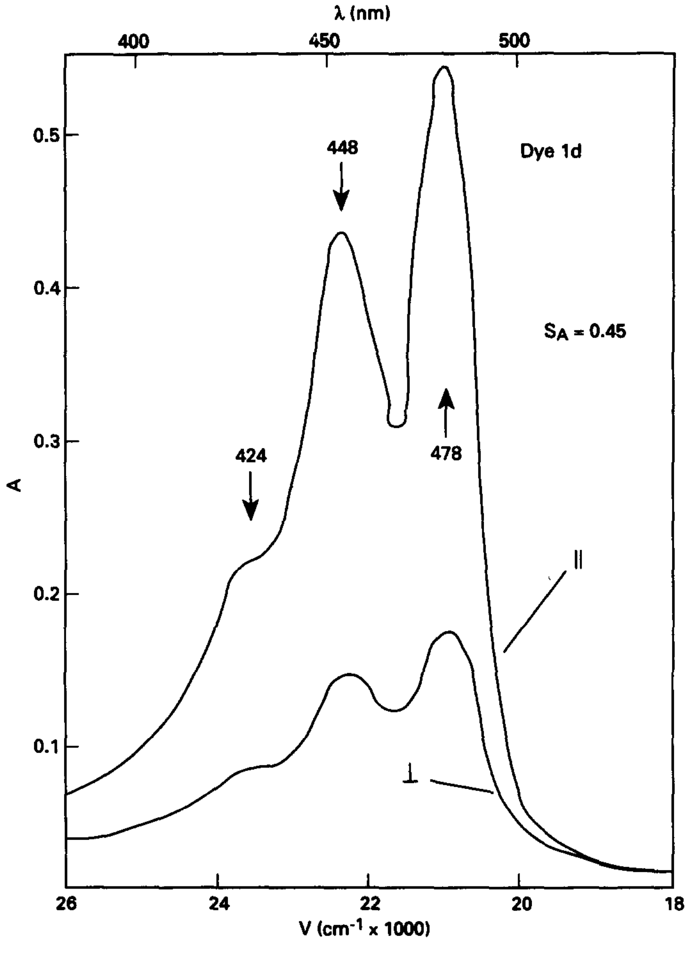


Fig. 1. Polarisation absorbance of solution of dye **1d** in liquid crystal E7.

Measurement of the polarisation components of the absorbance (Fig. 1) and fluorescence (Fig. 2) allows calculation of the order parameters of dyes **1** to be made. The results obtained in nematic media for different concentrations of the dyes are listed in Table 3.

The order parameters for S_A absorptions and S_F fluorescence are not influenced by the length of the alkyl chain in the case of dyes **1a**, **1b** and **1c**. However, the presence of the four cyclohexyl residues in dye **1d** results in an increase of the order parameters S_A and S_F by 35% and 25% respectively (S_A = 0·45 and S_F =0·51 for the highest concentrations of the dye obtained). The observed values may be the result of the increase of the effective length of the dye molecule, caused by the lower rotation possibilities of cyclohexyl residues.

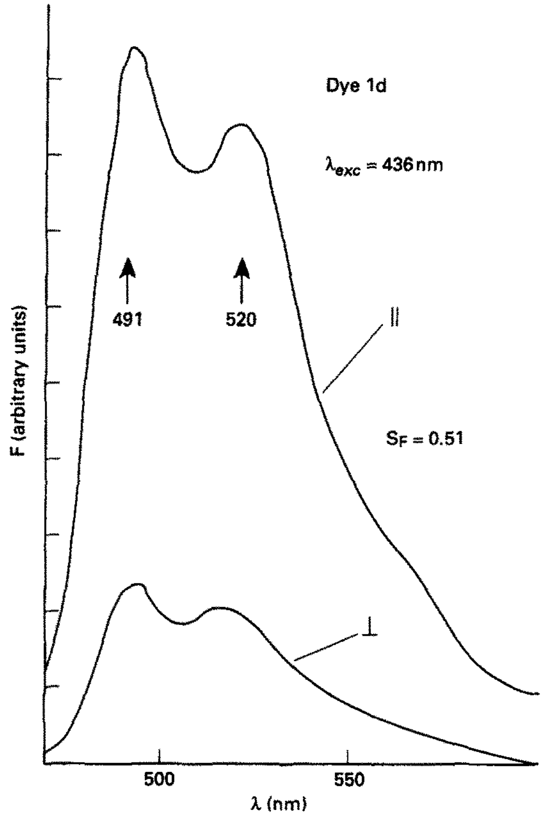


Fig. 2. Polarisation fluorescence of solution of dye **1d** in liquid crystal E7.

Solutions of **1** in the liquid crystal E7 were subjected to testing in order to determine their stability to UV light. Figure 3 shows the results of the UV stability evaluations and it is apparent that dyes **1b** and **1d** exhibit the greatest stability in comparison with **1a** and **1c**. This is unexpected, and may possibly be due to intermolecular interactions of the dyes (and aggregation) in solution.

TABLE 3
Absorption (S_A) and Fluorescence (S_F) Order Parameters of **1** in E7

Dye	S_A			S_F		
	c (mole/dm³)			*c (mole/dm³)*		
	5×10^{-3}	2×10^{-3}	1×10^{-3}	5×10^{-3}	2×10^{-3}	1×10^{-3}
1a	0·35	0·42	0·44	0·39	0·30	0·27
1b	0·33	0·40	0·43	0·40	0·32	0·29
1c	0·32	0·40	0·42	0·43	0·37	0·34
1d	0·45	0·48	0·56	0·51	0·46	0·41

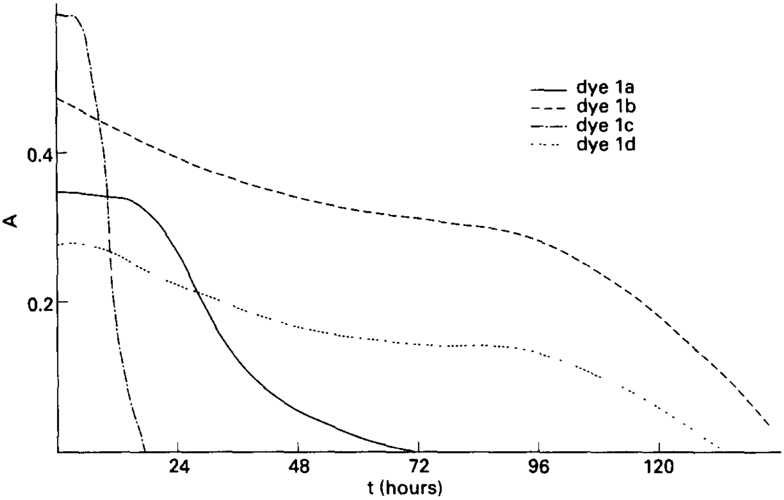


Fig. 3. UV stability in liquid crystal solution of dyes **1a–1d** (*A*, absorbance; *t*, time irradiation).

4 CONCLUSION

Dye **1d** shows the best properties of the dyes prepared. Apart from a smaller colour yield than the others, it is characterised by a high quantum yield of fluorescence, the best order parameters S_A and S_F, high stability to UV light, and good solubility. A constructed fluorescent liquid crystal display made using **1d** meets all the requirements for such devices.

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