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Syntheses and Properties of Some Deeply Coloured Dichroic Anthraquinone Dyes

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ABSTRACT

The syntheses of some aryl-1,5-diamino-4,8-dihydroxyanthraquinone dyes is described and their properties are discussed on the basis of colour–structure relationships, dichroism and their solubility in liquid crystals. The PPP–MO calculated results agreed well with the observed λ_{max} *values. 2-Aryl-1,5-dihydroxy-4-arylamino-8-aminoanthraquinones had better dichroism and improved solubility compared with their 8-arylamino-4-amino analogues. 2-Aryl-1,5-dihydroxy-4,8-bis(arylamino)anthraquinones also had satisfactory dichroism and solubility. It was found that the presence of 2-aryl- and 4-arylamino groups in deeply coloured anthraquinone dyes resulted in a favourable orientation of the dye molecules in liquid crystals, producing good dichroism and improved solubility, and such compounds can be used practically as deep-blue dichroic dyes.*

1 INTRODUCTION

Some anthraquinone disperse dyes have been developed as dichroic dyes for the guest–host (GH) and twisted nematic (TN) mode liquid-crystal displays.

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Thus a series of red 1,5-bis(arylamino)anthraquinones and blue 1-arylamino-4-hydroxyanthraquinones have been prepared for use as dichroic dyes and have excellent photochemical stability.[1] These dyes which have one or two aryl groups as a rigid substituent at the α-position of the anthraquinone system, give a high dichroic ratio. β-Aryl-1,5-diamino-4,8-dihydroxyanthraquinones were later synthesized as deep-blue dyes with an improved dichroic ratio.[2] The development of β-arylanthraquinones for use as deep-coloured dichroic dyes of potential practical use is thus indicated.

In this present paper, the syntheses and properties of some α- and/or β-aryl-1,5-diamino-4,8-dihydroxyanthraquinone dyes are discussed on the basis of their colour–structure relationship, dichroism and solubility in liquid crystals.

2 RESULTS AND DISCUSSION

2.1 Absorption spectra

The observed absorption spectra together with the calculated results are summarized in Table 1. The value of $\Delta\lambda_{obs-calc}$ which indicates the difference between the observed and calculated λ_{max} values, is in the range 30–40 nm. The MO calculation results are in good agreement with the observed values.

The observed longer-wavelength λ_{max} values were in the order **3a** > **3b** > **3c** > **3f** > **3e** > **3d**, and the calculated values followed a similar

TABLE 1
Absorption Spectra of Anthraquinone Dyes **3**

Dye no.	λ_{max}*(nm)*[a]				$\Delta\lambda$*(nm)*		
	Calc.	*Obs.*	*GR*[b]	*ZLI*[c]	$\Delta\lambda_1$[d]	$\Delta\lambda_2$[e]	$\varepsilon \times 10^{-4}$[a]
3a	650	690	711	701	40	21	3·46
3b	618	656	675	669	38	19	2·88
3c	615	655	675	669	40	20	2·82
3d	583	613	623	619	30	10	1·73
3e	583	619	643	638	38	24	2·65
3f	589	621	644	640	33	23	2·67

[a] measured in chloroform.
[b] GR-41 (biphenyl-type mixed LC).
[c] ZLI-1565 (phenylcyclohexane-type mixed LC).
[d] $\Delta\lambda_1 = \lambda_{obs.} - \lambda_{calc.}$
[e] $\Delta\lambda_2 = \lambda_{GR-41} - \lambda_{obs.}$

order, viz. **3a** > **3b** > **3c** > **3f** > **3e** = **3d**. Introduction of an additional α-arylamino group into the anthraquinone dyes produced a large bathochromic shift (about 35 nm) in chloroform, as shown by comparison of **3a** and **3b** and of **3c** and **3b**, with **3e** and **3f**. An additional α-amino group also produced a 42 nm bathochromic shift, as in **3c** relative to **3d**.

The observed λ_{max} increased in the order GR-41 > ZLI-1565 > $CHCl_3$. Differences of λ_{max} in GR-41 and $CHCl_3$ were in the range 19–24 nm, except for **3d** (10 nm). Dye **3c** absorbed over the region 520–750 nm and **3a** in the range 520–800 nm in GR-41 as shown in Fig. 1. Dye **3a** also absorbed at longer wavelength than the previously reported[3] **3g** (Fig. 2), and its overall absorption in the longer-wavelength range makes it more favourable in obtaining a black colour in liquid crystal displays.

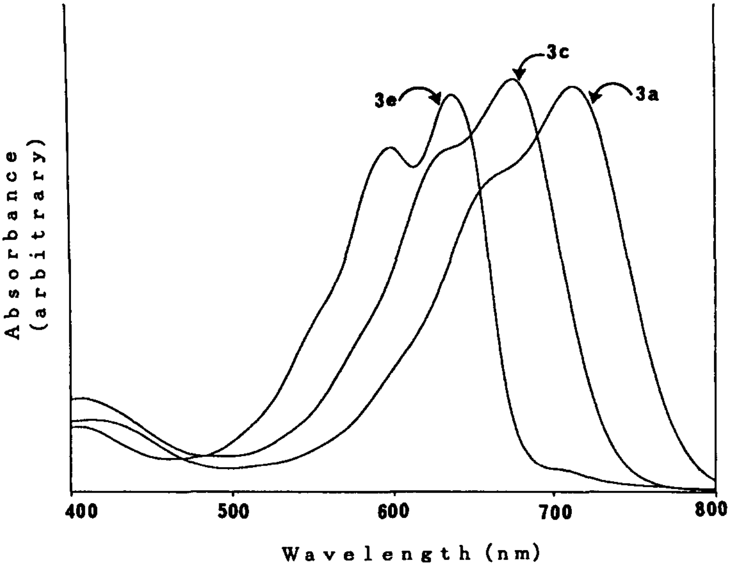
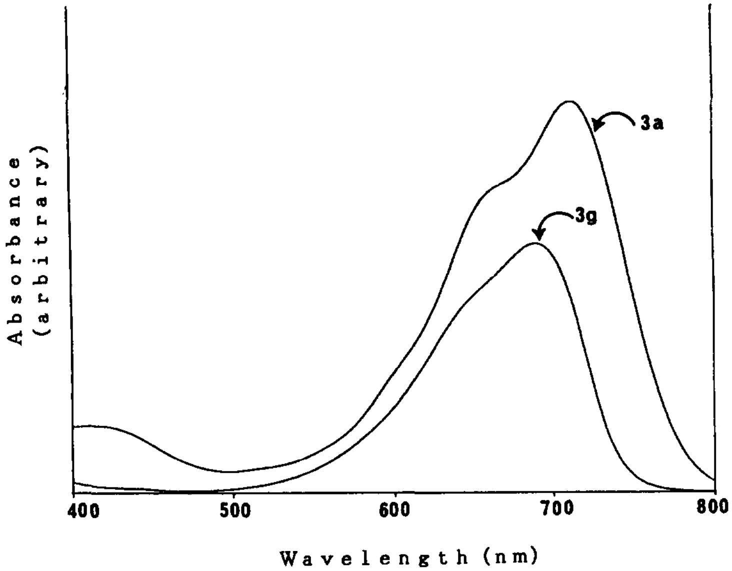


Fig. 1. Absorption spectra of dyes **3a**, **3c** and **3e** in GR-41.

A black-coloured liquid crystal, obtained by mixing dyes **3a** or **3c** with three other components, absorbed over the whole visible region as shown in Fig. 3, and remained black for different types of illumination. This dye mixture is thus able to supply the GH display devices with improved quality, as pointed out by Scheuble *et al.*[4]

The ε values of the dyes increased in the order **3a** > **3b** > **3c** > **3f** > **3e** > **3d**, and this order is in good agreement with the order of the transition moment (*M*) of the dyes as shown in Table 2.



3g

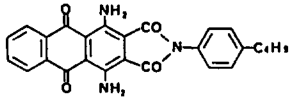


Fig. 2. Absorption spectra of dyes **3a** and **3g** in GR-41.

2.2 Dichroism

One of the parameters which influences the dichroism of a dye is the angle (α) between the direction of the transition moment and the long axis of the molecule and a smaller value for this parameter has been related to a higher dichroic ratio (D).[5,6] The calculated α-values quantitatively were in accord with this relationship for the structural isomeric dyes **3e** and **3f**. Thus the smaller α-value (0·86°) of **3e** gave a larger D-value (9·27) in comparison with **3f** ($\alpha = 5{\cdot}7°$, $D = 7.22$). However, in other dyes, changes in the orientation of the substituents was found to change the D-value slightly, and the smaller differences in the α-value were not relatable to the D-values. Thus, with the isomeric dyes **3b** and **3c**, the α-value of **3c** (9·1°) is larger than that of **3b** (8·5°), but the D-value of **3c** (9·45) is larger than that of **3b** (8·27). The solubility of **3c** is much higher than that of **3b** in GR-41, and the solubility factor must therefore be taken into account in considerations of the D-value.

On the other hand, **3d** has a poor D-value (6·73) in comparison with **3c** (9·45), which has an additional amino group at the 8-position. The difference in α-values for these two dyes is not large (**3c** 9·1°; **3d** 11·6°), and the 8-amino group in **3c** plays a significant role in giving better dichroism and solubility

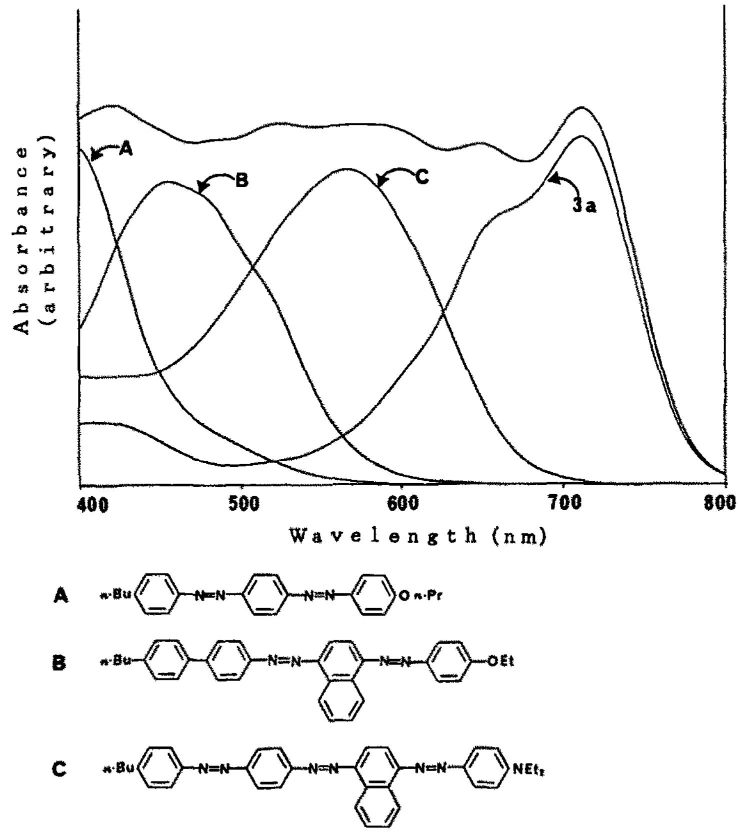


Fig. 3. Absorption spectra of a black colour display obtained by mixing dye **3a** and three other components (**A**–**C**) in GR-41.

TABLE 2
Some properties of Dichroic Dyes **3**

Dye no.	D^a	M^b	α*(deg.)*^{c}	*Solubility (wt%)*^{d}	
				GR	*ZLI*
3a	8·17	2·41	14·2	2·97	1·36
3b	8·27	2·22	8·5	0·70	0·16
3c	9·45	2·15	9·1	2·38	0·93
3d	6·73	1·88	11·6	1·83	0·87
3e	9·27	2·05	0·86	3·91	1·06
3f	7·22	2·10	5·72	3·11	1·40

[a] Dichroic ratio in GR-41.
[b] Calculated transition moment.
[c] Calculated angle.
[d] Measured at 20°C.

in GR-41. The *D*-value is thus influenced by the orientation of the dye in liquid crystals and also by other factors such as solubility, molecular length and transition moment.

2.3 Solubility in liquid crystals

The solubility of the dyes in liquid crystals decreased in the order **3a** > **3c** > **3d** > **3b** as shown in Table 2. Dye **3c** had better solubility than the isomeric **3b**, and sufficient solubility for practical applications. Dye **3a** had better solubility than **3b** despite the presence of an additional aryl group at the 4-position. This suggests that the presence of a 2-aryl group and 4-arylamino substitution imparts better solubility than that resultant from 2-aryl and 8-arylamino substitution. The dyes also have better solubility in GR-41 in comparison with ZLI-1565. This may be caused by the difference in affinity of the dye with the liquid crystal, the biphenyl type (GR-41) having better affinity than the phenylcyclohexane type (ZLI-1565) due to the larger π-conjugated system enhancing van der Waals interaction with the π-conjugated dye molecules. Dye **3a** has better solubility than dye **3g**, which has been previously prepared as a deep-blue dichroic dye for practical use. A comparison of properties between **3a** and **3g** is shown in Table 3.

TABLE 3

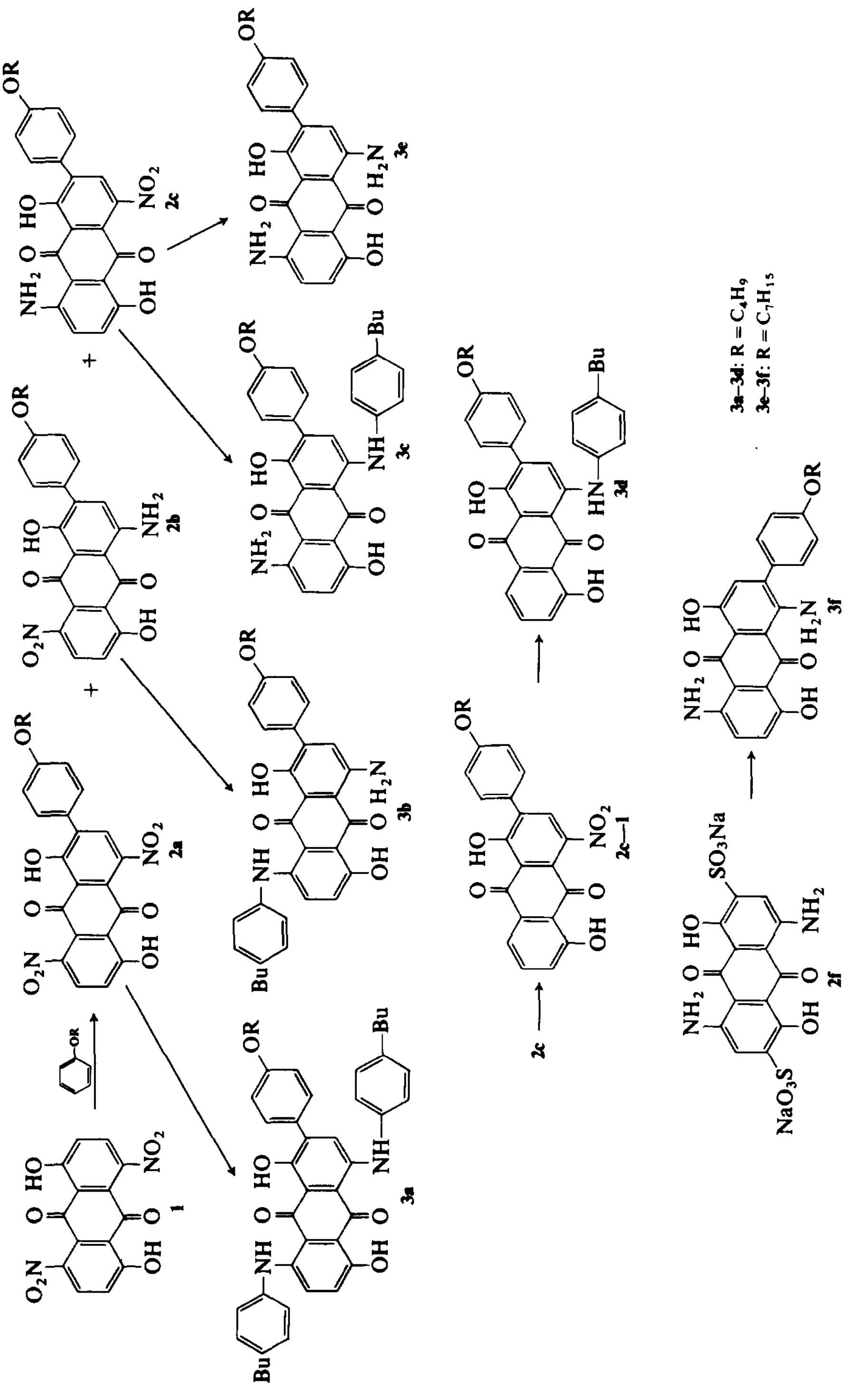
Comparison of Dichroic Property and Solubility of Dyes **3a** and **3g**

Dye no.	λ_{max}*(nm)* *GR-41*	$\varepsilon \times 10^{-4}$	*D* *GR-41*	*Solubility (wt%) (20°C)*	
				GR-41	*ZLI-1565*
3a	711	3·46	8·17	2·97	1·36
3g	690	1·79	9·5[a]	0·75	0·1

[a] Quoted in Ref. 3.

2.4 NMR spectra of dyes

The reaction of 1,5-dihydroxy-4,8-dinitroanthraquinone **1** with alkoxybenzenes in sulphuric acid in the presence of boric acid gave 2-(4-alkoxyphenyl)-4-amino-1,5-dihydroxy-8-nitroanthraquinone **2b** with **2a**,[7] but **2c**, the isomer of **2b**, was also obtained from the reaction mixture as shown in Scheme 1. The alkoxyphenyl group was introduced at the 2-position.[8] The identity of dyes **2b** and **2c** was confirmed by their ^{1}H-NMR



3a–3d: R = C_4H_9
3e–3f: R = C_7H_{15}

Scheme 1. Syntheses of dyes **2** and **3**.

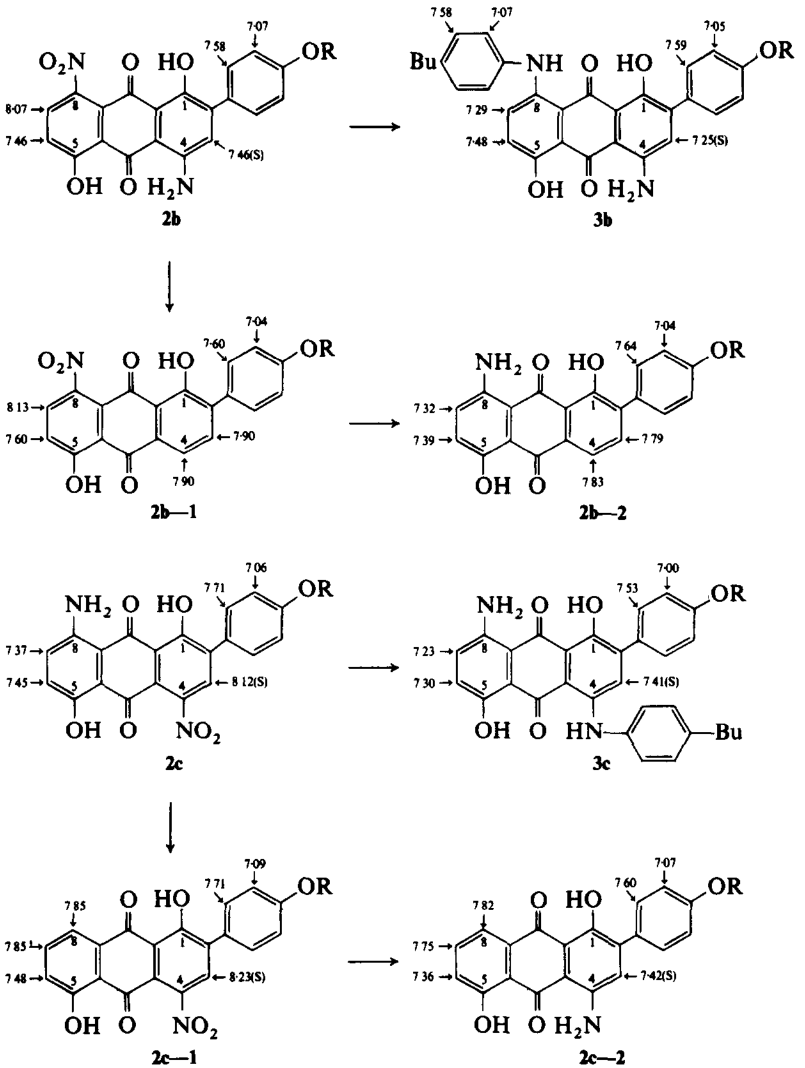


Fig. 4. Identification of isomeric dyes **2b** and **2c** (R = Bu) by means of their ^{1}H-NMR spectra.

spectra, as shown in Fig. 4. Deamination of the 4-amino group of **2b** gave **2b-1**, followed by the reduction of the 8-nitro group giving **2b-2**. Arylamination at the 8-nitro group of **2b** afforded **3b**. Similar reactions of **2c** gave **2c-1**, **2c-2** and **3c**, respectively. Dyes with similar structures were identified by means of their ^{1}H-NMR spectra (270 MHz) in addition to their elemental analyses and infrared spectra. The ^{1}H-NMR spectra and the results of elemental analysis of dyes are summarized in Tables 4 and 5, respectively.

TABLE 4
^{1}H-NMR Spectral Data for Anthraquinone Nucleus in Dyes **2** and **3**

Dye no.	*3H*		*4H*		*6H*		*7H*		*8H*	
	δ[a]	*J*[b]	δ	*J*	δ	*J*	δ	*J*	δ	*J*
2b	7·46 (s)[c]				7·46 (d)	9	8·07 (d)	9		
2b-1	7·85 (d)	9	7·95 (d)	9	7·60 (d)	9	8·13 (d)	9		
2b-2	7·79 (d)	8	7·83 (d)	8	7·39 (d)	9	7·32 (d)	9		
3b	7·25 (s)				7·48 (d)	9	7·29 (d)	9		
2c	8·12 (s)				7·45 (d)	9	7·37 (d)	9		
2c-1	8·23 (s)				7·48 (d)	9	7·85 (m)	—	7·85 (m)	—
2c-2	7·42 (s)				7·36 (d)	9	7·75 (dd)	—	7·82 (d)	9
3c	7·41 (s)				7·30 (d)	9	7·23 (d)	9		

[a] Chemical shifts (ppm).
[b] Coupling constants (Hz).
[c] Abbreviations: s, singlet; d, doublet; dd, double doublet, m, multiplet.

TABLE 5
Characterization Data for Dyes **2** and **3**

Dye no.	*Molecular formula*	*Mol. wt.*	*M.p. (°C)*	*Analysis: Obs. (calc.) %*		
				C	H	N
2a	$C_{24}H_{18}N_2O_9$	478	234	60·36 (60·25)	3·89 (3·77)	5·65 (5·86)
2b	$C_{24}H_{20}N_2O_7$	448	208–209	64·93 (64·29)	4·35 (4·46)	6·42 (6·25)
2b-1	$C_{24}H_{19}NO_7$	433	209	66·99 (66·51)	4·26 (4·39)	3·24 (3·23)
2b-2	$C_{24}H_{21}NO_5$	403	179–180	71·28 (71·46)	5·12 (5·21)	3·47 (3·47)
2c	$C_{24}H_{20}N_2O_7$	448	221–222	64·11 (64·29)	4·28 (4·46)	5·50 (6·25)
2c-1	$C_{24}H_{19}NO_7$	433	188–190	66·85 (66·51)	4·24 (4·39)	3·25 (3·23)
2c-2	$C_{24}H_{21}NO_5$	403	174–175	71·22 (71·46)	4·97 (5·21)	3·82 (3·47)
3a	$C_{44}H_{46}N_2O_5$	682	126–127	77·95 (77·42)	7·22 (6·74)	3·88 (4·11)
3b	$C_{34}H_{34}N_2O_5$	550	219–220	74·80 (74·18)	6·15 (6·18)	5·41 (5·09)
3c	$C_{34}H_{34}N_2O_5$	550	170–171	74·80 (74·18)	6·21 (6·18)	5·37 (5·09)
3d	$C_{34}H_{33}NO_5$	535	129	77·12 (76·26)	6·67 (6·17)	2·45 (2·62)
3e	$C_{27}H_{28}N_2O_5$	460	225–226	70·41 (70·43)	6·07 (6·09)	5·75 (6·09)
3f	$C_{27}H_{28}N_2O_5$	460	186–187	70·78 (70·43)	6·07 (6·09)	6·12 (6·09)

3 EXPERIMENTAL

All melting points are uncorrected. The absorption spectra were measured in chloroform at a concentration of 2×10^{-5} mol litre^{-1} using a Hitachi U-3400 spectrophotometer. Elemental analyses were recorded with a Yanaco CHN recorder MT-2. ^{1}H-NMR spectra were recorded with a Nippon Denshi JNM-GX-270. Dichroic ratios were measured using a 9-μm cell in which GR-41 (Chisso Co. Ltd) was aligned homogeneously. The measurement was made at 20°C. The solubilities were determined spectrophotometrically at 20°C. The modified PPP–MO calculations were carried out by the method described previously.[9]

The dyes used were synthesized in Nippon Kankoh-Shikiso Kenkyusho Co. Ltd and purified by column chromatography on silica gel using chloroform as eluant followed by recrystallization. Dye **2** was synthesized by the method described previously[7,10] and dye **3** by the procedure outlined in Ref. 11. The synthetic routes are shown in Scheme 1.

3.1 Materials

1,5-Dihydroxy-4,8-dinitroanthraquinone **1** was commercial grade material and was used without further purification.

3.2 Separation of dyes 2a, 2b and 2c

The reaction mixtures, which contained three components, were separated by column chromatography on silica gel using chloroform as eluant. The first dye to be eluted was **2a**, followed by **2b**, and **2c**. The results of elemental analysis were consistent with the theoretical values as shown in Table 5.

3.3 Synthesis of dye 2b-1

A suspension of dye **2b** (4·48 g, 0·01 mol) in a mixture of acetic acid (30 ml) and propionic acid (10 ml) was added portionwise with stirring at 0–10°C to nitrosylsulphuric acid (20 ml) prepared by the method described in Ref. 12. The mixture was stirred at 20°C for 3 h, and then poured into cooled diethyl ether (500 ml), and the separated diazonium salt was filtered off. It was dissolved in dimethylformamide (100 ml) and the solution was heated with stirring at 80°C for 30 min, and then poured into water (1 litre). The resultant solid was filtered, washed with water, dried, and purified by column chromatography, followed by recrystallization from ethyl acetate to give **2b-1**.

3.4 Synthesis of dye 2b-2

A solution of 70% sodium hydrosulfide (4·8 g) in water (40 ml) was added to the suspension of dye **2b-1** (4·33 g, 0·01 mol) in ethanol (80 ml) and the mixture was refluxed for 2 h with stirring, and then poured into water (800 ml). The solid was filtered, washed with water and then with methanol, dried and purified by column chromatography, followed by recrystallization from ethyl acetate to give **2b-2**.

3.5 Synthesis of dye 3b

A solution of dye **2b** (4·48 g, 0·01 mol) and 4-butylaniline (4·47 g, 0·03 mol) in nitrobenzene (60 ml) was heated at 200°C for 20 h with stirring. Nitrobenzene was distilled off with steam and the separated product was filtered, and purified by column chromatography, followed by recrystallization from ethyl acetate to give **3b**.

Dyes **2c-1**, **2c-2** and **3c** were synthesized by similar methods.

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