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1,4,5,8-Tetrakis(arylamino)anthraquinones/Near IR Dyes (II): Reaction of 4,8-Diaminoanthrarufin with Arylamines

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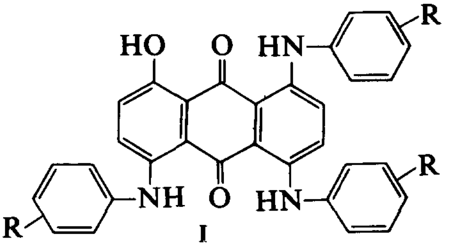
ABSTRACT

Condensation of 4,5-dinitrochrysazin (DNCZ) and 4,8-diaminoanthrarufin (DAAR) with arylamines in the presence of boric acid and phenol gives 8-hydroxy-1,4,5-tris- and 1,4,5,8-tetrakis-(arylamino)anthraquinones, respectively. The dyes absorb in the near infrared at about 750–770 nm and colour polycarbonate (PC) film in green hues of very good light fastness. It is proposed that the initial enol–ketone and amino–imino tautomerism of DAAR facilitates the 1,4,5,8-tetrakis-arylamination.

1 INTRODUCTION

The condensation of DNCZ with excess arylamines in the presence of boric acid and zinc powder to give 1,4,5,8-tetrakisarylamino-anthraquinones, which absorb in the near infrared at about 750–770 nm, has been reported.[1] 1,4,5-Trisarylamino-anthraquinones also result from condensation of 4,5-bisarylamino-chrysazin with excess arylamines in the presence of boric acid and phenol.[2] Low yields and the use of a heavy metal (zinc) are the main disadvantages of these processes. Derivatives of DAAR are some of the most industrially useful anthraquinone dyes for synthetic polymer fibres.[3] Monoalkylation of DAAR (by iodo- and bromo-alkanes) gives a range of blue dyes having excellent dyeing properties and acceptable fastness properties on polyester;[4] bis-alkylation results in dyes of a greener hue, but with poorer colouration properties.[3]

Reaction of 1,5-dimethoxy-4,8-diaminoanthraquinone with excess methylamine gives 1,4,5,8-tetrakis-methylamino-anthraquinone.[5] Little data have been published on the reaction of DNCZ with arylamines in the presence of boric acid and phenol and on the reaction of DAAR with arylamines. The synthesis of a series of 1,4,5-trisarylamino-8-hydroxyanthraquinones (I) from DNCZ and a series of 1,4,5,8-tetrakisarylamino-anthraquinones (II) from DAAR is reported here, and possible mechanisms for the reaction of DAAR with excess arylamine are discussed.



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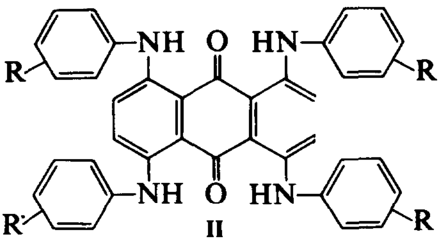

II

2 EXPERIMENTAL

2.1 1,4,5-Trisarylamino-8-hydroxyanthraquinones (I)

DNCZ (1 g) and *o*-toluidine (25 ml) were refluxed for about 5 h (until a blue spot was apparent on TLC); a mixture of phenol (15 g), boric acid (2 g) and *o*-toluidine (8 ml) was added portion-wise and refluxing was continued for 35 h. The liquor was cooled to room temperature, then poured into methanol (50 ml) and left to stand overnight. The crystalline material which separated was filtered and washed with 10% hydrochloric acid and then with water until the washings were neutral and colourless. Recrystallization from 2-methoxyethanol gave 0·45 g (28%) 1,4,5-tris-(2'-methylanilino)-8-hydroxyanthraquinone (**I.1**), m.p. 285°C.

Dyes **I.2–I.6** were synthesized by a similar procedure, as detailed in Table 1.

2.2 1,4,5,8-Tetrakis-arylaminoanthraquinones (II)

The above procedure (Section 2.1) was repeated, except that DNCZ was replaced by DAAR (1 g). Relevant data on yield and m.p. are given in Table 1.

2.3 General

All dyes were homogeneous on TLC (Merck, silica gel 5748) and were analytically pure; molecular weights and the absence of any higher molecular weight impurities were confirmed by mass spectrometry.

TABLE 1
Synthesis and Characterisation Data of Dyes I and II

Dye	*R*	*Amount of arylamines*	*Reaction time (h)*	*m.p. (°C)*	*Weight (g) (yield)*
I.2	3-CH_3	35 ml, *m*-toluidine	43	235–237	0·55 (34%)
I.3	2-OCH_3	30 ml, *o*-anisidine	21	250–252	0·47 (27%)
I.4	3-OCH_3	35 ml, *m*-anisidine	29	255–257	0·71 (40%)
I.5	4-*n*-C_4H_9	25 ml, *p*-(*n*-butyl)aniline	40	230–232	0·70 (35%)
I.6	4-*n*-C_8H_{17}	25 ml, *p*-(*n*-octyl)aniline	42	360–362	0·75 (30%)
I.7	4-CH_3	3 g, *p*-toluidine and 20 ml, nitrobenzene	45	239–241	0·48 (30%)
I.8	H	30 ml, aniline	15	224–226	0·69 (42%)
I.9	4-OC_2H_5	30 ml, *p*-phenetidine	18	262–264	0·78 (41%)
II.1	4-CH_3	3 g, *p*-toluidine and 25 ml, nitrobenzene	44	2310–312	1·40 (60%)*[a]
II.2	3-CH_3	30 ml, *m*-toluidine	40	340–342	1·44 (62%)
II.3	2-CH_3	30 ml, *o*-toluidine	42	325–327	1·51 (66%)
II.4	4-*n*-C_4H_9	25 ml, *n*-butylaniline	22	above 360	2·00 (68%)
II.5	4-OCH_3	2·22 g, *p*-anisidine and 25 ml, nitrobenzene	48	above 360	1·56 (61%)
II.6	2-OCH_3	30 ml, *o*-anisidine	40	350–352	1·40 (65%)*[b]
II.7	4-*n*-C_8H_{17}	35 ml, *p*-*n*-octylaniline	41	above 360	2·28 (60%)*[c]

* Purified by preparative TLC.

[a] 15% **V.1**, 25% **I.7** and 60% **II.1**.

[b] 15% **V.2**, 20% **I.3** and 65% **II.6**.

[c] 18% **V.3**, 22% **I.6** and 60% **II.7**.

Characterisation data were obtained by mass spectrometry (Hitachi M-52), IR (Hitachi 260-50) and ^{1}HNMR (Varian VXR-300) (Table 2). Electronic spectra were recorded on a Shimadzu UV 240 from dye solutions in chloroform and polycarbonate (PC) film (Table 3).

Dyeings on polycarbonate film and evaluations of the light fastness were carried out as for related dyes in a previous investigation[1] (Table 3).

3 RESULTS AND DISCUSSION

3.1 Syntheses

Condensation of DNCZ with excess arylamine in the presence of phenol and boric acid, under stringent conditions gave only 1,4,5-trisarylamino-8-hydroxy-anthraquinones (**I**), a result consistent with the mechanism previously noted.[1] Replacement of the amino groups in DAAR has usually been carried out using iodo- and bromo-alkanes (i.e. mono- and bis-

TABLE 2
Spectroscopic Data

Dye	*R*	*Mass (m/e)*	*IR*[a] *(cm^{-1}, KBr)*	*NMR*[b] *(δ ppm, CDCl$_3$)*
I.1	2-CH$_3$	539 (M$^+$) 269·5 (M^{+2})	3450 (Ar–NH), 2900 (CH$_3$) 2700 (b, OH), 1580, 1550 (C=O) 1340 (Car–N)	13·935 (s, 1H, OH), 11·933 (s, 1H, NH), 11·620 (s, 1H, NH), 11·461 (s, 1H, NH), 7·316–7·124 (m, 16H, Ar and Aq), 2·343 (s, 9H, Ar–CH$_3$)
I.2	3-CH$_3$	539 (M$^+$)	3450, 3350 (Ar–NH), 2900 (CH$_3$), 2750 (b, OH), 1575, 1550 (C=O), 1320 (Car–N)	13·891 (s, 1H, OH), 12·000 (s, 1H, NH), 11·712 (s, 1H, NH), 11·533 (s, 1H, NH), 7·595–6·924 (m, 16H, Ar and Aq), 2·355 (s, 9H, Ar–CH$_3$)
I.3	2-OCH$_3$	587 (M$^+$) 293·5 (M^{+2})	3450 (Ar–NH), 2900 (CH$_3$), 2750 (b, OH), 1590, 1560 (C=O), 1340 (Ar–N), 1250, 1020 (Ar–OCH$_3$)	13·960 (s, 1H, OH), 11·853 (s, 1H, NH), 11·582 (s, 1H, NH), 11·422 (s, 1H, NH), 7·422–6·913 (m, 16H, Ar and Aq), 3·880 (s, 9H, OCH$_3$)
I.4	3-OCH$_3$	587 (M$^+$)	3400 (Ar–NH), 2800 (b, OH), 1590, 1580 (C=O), 1330 (Car–N), 1250 (Ar–OCH$_3$)	13·926 (s, 1H, OH), 11·952 (s, 1H, NH), 11·640 (s, 1H, NH), 11·451 (s, 1H, NH), 7·380–6·840 (m, 16H, Ar and Aq), 3·834 (s, 9H, OCH$_3$)
I.5	4-n-C$_4$H$_9$	665 (M$^+$) 650 (M$^+$–CH$_3$)	3400 (Ar–NH), 2950, 2900 (CH$_3$), 2850 (CH$_2$), 1575 (C=O)	13·939 (s, 1H, OH), 12·016 (s, 1H, HN), 11·726 (s, 1H, NH), 11·542 (s, 1H, NH), 7·557–6·960 (m, 16H, Ar and Aq), 2·632 (m, 6H, Ar–CH$_2$), 1·585 (m, 6H, CH$_2$), 1·362 (m, 6H, CH$_2$) 0·943 (m, 9H, CH$_3$)
I.6	4-n-C$_8$H$_{17}$	833 (M$^+$) 734 (M$^+$–C$_7$H$_{15}$)	3420 (Ar–NH), 2930, 2900 (CH$_3$), 2840 (CH$_2$), 1560 (C=O)	13·9439 (s, 1H, OH), 12·031 (s, 1H, HN), 11·740 (s, 1H, NH), 11·538 (s, 1H, NH), 7·506–7·081 (m, 16H, Ar and Aq), 2·611 (m, 6H, Ar–CH$_2$), 1·621 (m, 6H, CH$_2$), 1·264 (m, 30H, (CH$_2$)$_5$), 0·890 (m, 9H, CH$_3$)

I.7	4-CH_3	539 (M^+) 269·5 (M^{+2})	3450, 3350 (Ar–NH), 2900 (CH_3) 1575, 1555 (C=O) 1320 (Car–N)	13·934 (s, 1H, OH), 12·00 (s, 1H, NH), 11·72 (s, 1H, NH), 11·580 (s, 1H, NH), 7·580–7·080 (m, 16H, Ar and Aq), 2·368 (s, 9H, Ar–CH_3)
I.8	H	497 (M^+) 406 (M^+–NC_6H_5)	3400 (Ar–NH), 1580 (C=O), 1300 (Car–N)	13·923 (s, 1H, OH), 12·010 (s, 1H, NH), 11·725 (s, 1H, NH), 11·586 (s, 1H, NH), 7·398–6·553 (m, 19H, Ar and Aq)
I.9	4-OC_2H_5	629 (M^+)	3310, 3250 (Ar–NH), 2970, 2940 (CH_3), 2870 (CH_2), 1605 (C=O), 1308 (Car–N), 1250, 1060 (Ar–OCH_3)	13·920 (s, 1H, OH), 11·950 (s, 1H, NH), 11·648 (s, 1H, NH), 11·460 (s, 1H, NH), 7·349–6·640 (m, 16H, Ar and Aq), 4·050 (q, 6H, OCH_2), 1·370 (t, 9H, CH_3)
II.1	4-CH_3	628 (M^+) 314 (M^{+2})	3350 (b, Ar–NH), 2900 (CH_3), 1595 (C=O)	11·780 (s, 4H, NH), 7·450–7·169 (m, 2OH, Ar and Aq), 2·358 (s, 12H, Ar–CH_3)
II.2	3-CH_3	628 (M^+) 314 (M^{+2})	3400 (b, Ar–NH), 2900 (CH_3), 1580 (C=O)	11·790 (s, 4H, NH), 7·517–6·190 (m, 2OH, Ar and Aq), 2·367 (s, 12H, Ar–CH_3)
II.3	2-CH_3	628 (M^+) 314 (M^{+2})	3350 (b, Ar–NH), 2900, 2820 (CH_3), 1590 (C=O)	11·790 (s, 4H, NH), 7·300–7·100 (m, 2OH, Ar and Aq), 2·353 (s, 12H, Ar–CH_3)
II.4	4-*n*-C_4H_9	796 (M^+) 398 (M^{+2})	3450 (b, Ar–NH), 2950, 2900 (CH_3), 2850 (CH_2), 1592 (C=O),	11·480 (s, 4H, NH), 7·611–6·914 (m, 2OH, Ar and Aq), 2·650 (m, 8H, Ar–CH_2), 1·585 (m, 8H, CH_2), 1·387 (m, 8H, CH_2), 1·264 (m, 8H, CH_2), 0·944 (t, 12H, CH_3)
II.5	4-OCH_3	692 (M^+) 346 (M^{+2})	3450 (b, Ar–NH), 1595 (C=O 1290 (Car–N), 1240, 1030 (Ar–OCH_3)	11·650 (s, 4H, NH), 7·400–6·921 (m, 2OH, Ar and Aq), 3·841 (s, 12H, OCH_3)
II.6	2-OCH_3	692 (M^+)	3300 (b, Ar–NH), 2900 (CH_3), 1580 (C=O), 1250, 1008 (Ar–OCH_3)	11·780 (s, 4H, NH), 7·560–6·610 (m, 2OH, Ar and Aq), 3·822 (s, 12H, OCH_3)
II.7	4-*n*-C_8H_{17}	1020 (M^+)	3350 (b, Ar–NH), 2940, 2900 (CH_3), 2850 (CH_2), 1595 (C=O)	11·680 (s, 4H, NH), 7·220–7·150 (m, 12H, Ar and Aq), 2·173 (m, 8H, CH_2), 1·336 (m, 8H, CH_2), 1·257 (m, 24H, $(CH_2)_3$), 0·896 (m, 16H, $(CH_2)_2$), 0·864 (m, 12H, CH_3)

(continued)

TABLE 2—*contd*
Spectroscopic Data

Dye	*R*	*Mass (m/e)*	*IR*[a] *(cm*$^{-1}$*, KBr)*	*NMR*[b] *(δ ppm, CDCl*$_3$*)*
III.1	H	420 (M^+)	3400 (Ar–NH), 1580 (C=O), 1305 (Car–N)	12·030 (s, 4H, NH_2), 11·580 (s, 2H, NH), 7·368–6·853 (m, 14H, Ar and Aq)
III.2	4-OC_2H_5	508 (M^+)	3350 (Ar–NH), 2950 (CH_3), 2860 (CH_2), 1605 (C=O) 1305 (Car–N), 1250 (Ar–OCH_3)	12·010 (s, 4H, NH_2), 11·495 (s, 2H, NH), 7·359–6·650 (m, 12H, Ar and Aq), 4·020 (q, 4H, OCH_2), 1·375 (t, 6H, CH_3)
IV.1	H	496 (M^+)	3405 (Ar–NH), 1585 (C=O), 1305 (Car–N)	12·025 (s, 2H, NH_2), 11·910 (s, 1H, NH), 11·750 (s, 1H, NH), 11·520 (s, 1H, NH), 7·378–6·753 (m, 19H, Ar and Aq)
IV.2	4-OC_2H_5	628 (M^+)	3350 (Ar–NH), 2960 (CH_3), 2870 (CH_2), 1605 (C=O), 1305 (Car–N), 1250, 1010 (Ar–OCH_3)	12·005 (s, 2H, NH_2), 11·750 (s, 1H, NH), 11·650 (s, 1H, NH), 11·452 (s, 1H, NH), 7·350–6·645 (m, 16H, Ar and Aq)
V.1	4-CH_3	450 (M^+) 225 (M^{+2})	3405 (Ar–NH), 2905 (CH_3), 1580, 1560 (C=O), 1315 (Car–N)	13·850 (s, 2H, OH), 11·640 (s, 2H, NH), 7·420–7·100 (m, 12H, Ar and Aq), 2·372 (s, 6H, Ar–CH_3)
V.2	2-OCH_3	482 (M^+) 452 (M^+–CH_3–CH_3)	3310 (b, Ar–NH), 2905 (CH_3), 1590 (C=O) 1250, 1010 (Ar–OCH_3)	13·950 (s, 2H, OH), 11·412 (s, 2H, NH) 7·432–6·813 (m, 12H, Ar and Aq), 3·878(s, 6H, OCH_3)
V.3	4-n-C_8H_{17}	646 (M^+) 323 (M^{+2})	3350 (b, Ar–NH), 2950, 2910 (CH_3), 2850 (CH_2), 1595 (C=O)	13·940 (s, 2H, OH), 11·528 (s, 2H, NH) 7·510–7·065 (m, 12H, Ar and Aq), 2·605 (m, 4H, Ar–CH_2), 1·610 (m, 4H, CH_2), 1·254 (m, 2OH, $(CH_2)_5$), 0·880 (m, 6H, CH_3)
V.4	3-OCH_3	482 (M^+)	3330 (Ar–NH), 2900 (CH_3), 1580 (C=O), 1250, 1030 (Ar–OCH_3)	13·930 (s, 2H, OH), 11·400 (s, 2H, NH) 7·450–6·980 (m, 12H, Ar and Aq), 3·875 (s, 6H, OCH_3)

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[a] Ar, aromatic; b, broad.

[b] s, singlet; t, triplet, q, quartet; m, multiplet; Ar, aromatic; Aq, anthraquinone.

TABLE 3
Colour and Fastness Properties

Dye	*R*	λ_{max} *(nm) (log ε) in chloroform*[a]	λ_{max} *(nm) on PC film*[b]	*Light fastness on PC film*[b]	$\Delta\lambda_{1/2}$ *(nm)*[c]
I.1	2-CH_3	718 (4·45), 665s (4·40), 413 (3·82)	720	5–6	140
I.2	3-CH_3	722 (4·46), 665s (4·36), 423 (3·80)	726	6	120
I.3	2-OCH_3	721 (4·47), 670s (4·46), 430 (3·91)	730	5	139
I.4	3-OCH_3	722 (4·49), 685s (4·46), 420 (3·97)	730	5–6	140
I.5	4-n-C_4H_9	724 (4·46), 670 (4·39), 422 (3·81)	732	6–7	126
I.6	4-n-C_8H_{17}	724 (4·51), 670s (4·43), 420 (3·89)	733	6	125
I.7	4-CH_3	725 (4·47), 666s (4·36), 418 (3·80)	729	6	120
I.8	H	721 (4·45), 680* (4·44), 418 (3·70)	722	6	142
I.9	4-OC_2H_5	733 (4·50), 690s (4·43), 422 (3·72)	732	6–7	146
II.1	4-CH_3	756 (4·54), 690s (4·42), 410 (4·01)	765	6–7	136
II.2	3-CH_3	751 (4·53), 685s (4·39), 400 (3·92)	760	6–7	124
II.3	2-CH_3	748 (4·52), 685s (4·41), 405 (3·81)	759	6–7	121
II.4	4-n-C_4H_9	761 (4·57), 695s (4·48), 400 (4·04)	765	7	133
II.5	4-OCH_3	756 (4·63), 718s (4·55), 410 (4·00)	761	6	138
II.6	2-OCH_3	747 (4·54), 686 (4·40), 451 (3·71)	750	6	119
II.7	4-n-C_8H_{17}	761 (4·56), 723s (4·45), 400 (4·04)	768	6–7	119

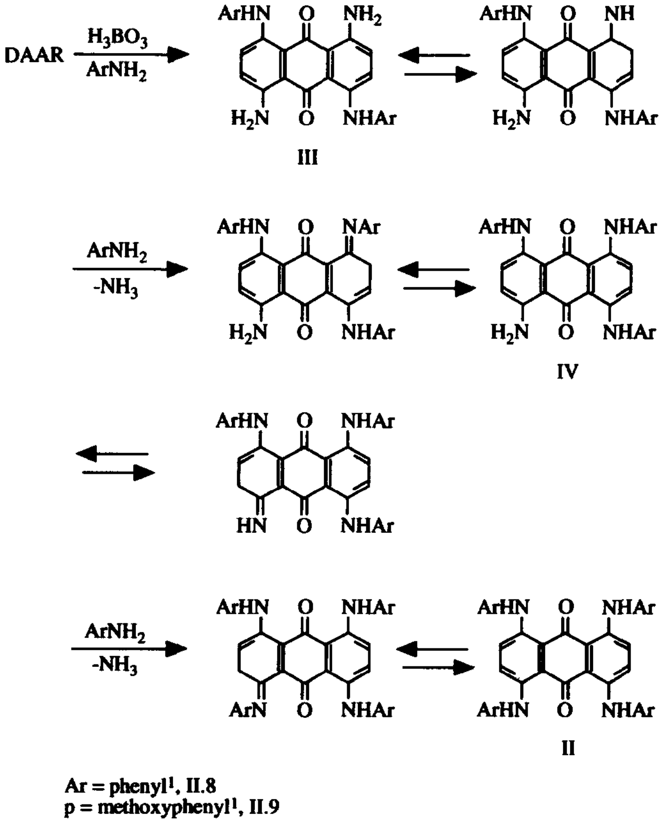
[a] s, shoulder; *, incompletely resolved.

[b] 0·1% o.w.f. and 0·2 mm thick.

[c] $\Delta\lambda_{1/2}$ (nm): half-band width.

alkylation reactions).[3,4] In this present investigation, a mixture of phenol and boric acid was used as reaction medium, with a large excess of arylamine and longer reaction time; replacement of both two amino groups and two hydroxy groups in DAAR occurred. The purity of and yields from this reaction were higher than with the reaction of DNCZ and DCQZ with arylamines in the presence of zinc powder,[1] but for some arylamines, e.g. *p*-toluidine, *p*-anisidine, *p*-*n*-octyl-aniline, aniline and *p*-phenetidine, two by-products were also formed: viz. (a) 4-CH_3 (with nitrobenzene): 15% **V.1**, 25% **I.7** and 60% **II.1**; (b) 4-CH_3 (without nitrobenzene): 35% **III.3**, 45% **II.1**, 20% others; (c) 2-OCH_3: 15% **V.2**, 20% **I.3** and 65% **II.6**; (d) 4-*n*-C_8H_{17}: 18% **V.3**, 22% **I.6** and 60% **II.7**; (e) H: 15% **III.1**, 20% **IV.1** and 65% **II.8**; (f) 4-OC_2H_5: 15% **III.2**, 25% **IV.2** and 60% **II.9**; (g) 3-OCH_3: 35% **V.4**, 30% **I.4**, 35% other components.

Kitao *et al.* have studied the reaction of 5-amino-2,3-dicyano-1,4-naphthoquinone with arylamines and pointed out that the initial quinone–quinoneimine tautomerism facilitates the 8-arylamination.



Ar = phenyl[1], II.8
p = methoxyphenyl[1], II.9

Scheme 1

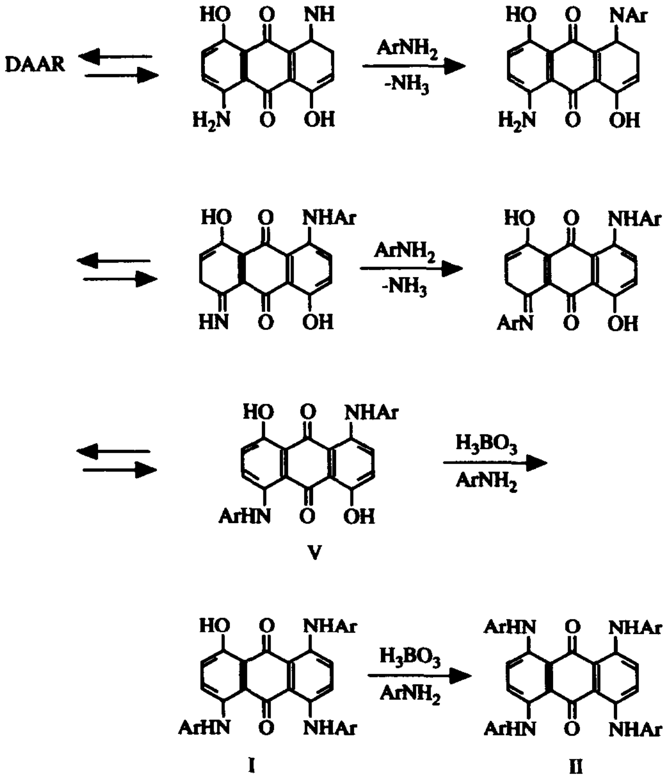
Possible mechanisms for the reactions studied here are shown in Schemes 1 and 2.

3.2 Electronic spectra

Electronic spectra data for dyes **I–II** are shown in Table 3. Comparing the λ_{max} values and molar extinction coefficients of **I.7** and **I.2** with **I.1**; **II.1** and **II.2** with **II.3**; and of **II.5** with **II.6**, hypsochromic shifts (4–9 nm) are apparent and also a hypochromic effect. This is because the 'bulky' groups inhibit intramolecular hydrogen bonding between the arylamino and carbonyl groups.[7]

3.3 Dyeing and fastness properties

All dyes **I** and **II** gave level colouration on PC film, with good fastness to light. The molar extinction coefficients of dyes **II** were larger than those of many anthraquinoid dyes, and the width of the near IR absorption



Scheme 2

band was very narrow (119–138 nm); dyes **II** thus meet possible requirements for use in optical data disks.

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