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1,4-Bis(arylamino)-5-nitro-(and 5-amino-)-8-hydroxyanthraquinones: Bluish-Green Dyes for Synthetic Polymer Fibres

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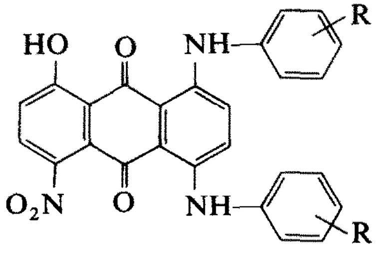
ABSTRACT

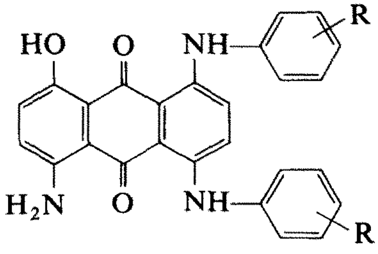
Condensation of 4-arylamino-5-nitro-1,8-dihydroxyanthraquinone with arylamines in presence of boric acid affords 1,4-bis(arylamino)-5-nitro-8-hydroxyanthraquinones. These compounds colour polyester fibres in deep blue–green hues of good fastness to light and sublimation. On reduction they yield the corresponding 5-amino derivatives, which can be alkylated to the 5-alkylamino derivatives, the amino compounds dyeing polyesters in much greener hues than the nitro analogues. The 5-nitro derivatives also result from condensation of 4,5-dinitro-1,8-dihydroxyanthraquinone with arylamines, although with more reactive arylamines the formation of 1,4,5-tris(arylamino)-8-hydroxyanthraquinones also occurs as major by-product. The tris(arylamino) derivatives are more readily obtained by condensation of 4,5-bis(arylamino)-1,8-dihydroxyanthraquinones with arylamines. Structure–colour relationships in the dyes are discussed.

1 INTRODUCTION

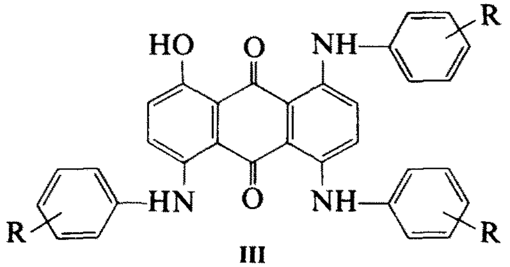
Condensation of 4,5-dinitro-1,8-dihydroxyanthraquinone (DNCZ) with arylamines in organic solvents results initially in the formation of 4-arylamino-5-nitro-1,8-dihydroxyanthraquinones.[1] Under more stringent conditions, replacement of both nitro groups by arylamino occurs.[2] In the presence of boric acid, 4-arylamino-5-nitro-1,8-dihydroxyanthraquinones react with alkylamines by preferential replacement of the 1-hydroxy group,[3] and we have previously reported colour–structure relationships in such dyes.[4] Similar condensation of DNCZ or of 4-arylamino-5-nitro-1,8-dihydroxyanthraquinone with arylamines in presence of boric acid yields 1,4-bis(arylamino)-5-nitro-8-hydroxyanthraquinones (**I**).[5]



I



II



III

We report here the synthesis of a series of dyes **I**, together with some analogous 5-amino (**II**) and 5-arylamino derivatives (**III**), and an evaluation of colour–structure relationships in these dyes.

2 EXPERIMENTAL

2.1 1,4-Bis(arylamino)-5-nitro-8-hydroxyanthraquinones (I)

Method A

Phenol (30 g) and boric acid (2·32 g) were stirred for 30 min at 125–130°C. 4-Anilino-5-nitro-1,8-dihydroxyanthraquinone (3·76 g, 0·01 mol) was added and stirring continued for 1 h at 125–130°C. Aniline (2·8 g, 0·03 mol) was then added and the mixture stirred at 140°C for 3·5 h. The liquor was cooled, diluted with ethanol (50 ml) and steam-distilled. The residual liquor was treated with potassium hydroxide (15 g) and after stirring and standing overnight was filtered to give a dark blue material (4·4 g). This (0·5 g) was purified by column chromatography on silica gel (see Section 2·5), affording, from a major blue–green zone, 0·38 g of 1,4-bisanilino-5-nitro-8-hydroxyanthraquinone (**I.1**), m.p. 310–312°C (with sublimation) ($C_{26}H_{17}N_3O_5$ requires C, 69·2; H, 3·8; N, 9·3. Found: C, 69·0; H, 3·7; N, 9·0%) (P^+ at m/e 451). From a higher R_t green zone was isolated 0·07 g of 1,4,5-trisanilino-8-hydroxyanthraquinone (**III.1**), identical to the product prepared as below (see Section 2.3).

Starting from the appropriate 4-arylamino-5-nitro-1,8-dihydroxyanthraquinone, other dyes **I** were similarly prepared. Reaction times were 2·5–3 h and products were isolated, as appropriate, as above or by addition of the ethanol-diluted reaction liquor to 20% aq. potassium hydroxide (250 ml), filtering and warming the residue at 60–65°C for 30 min in 10% aq. hydrochloric acid (100 ml). The resultant products were purified by recrystallisation (R) from 2-methoxyethanol or by column chromatography (C). Thus obtained were **I.2**, 74%, C; **I.3**, 81%, R; **I.4**, 70%, R; **I.5**, 62%, C; **I.6**, 70%, R; **I.7**, 74%, R; **I.8**, 81%, R; **I.9**, 57%, C; **I.10**, 58%, C; **I.11**, 88%, R; **I.12**, 51%, C. Relevant m.p. and λ_{max} data are shown in Table 1.

Method B

A mixture of DNCZ (2 g), boric acid (0·25 g) and *o*-toluidine (10 ml) were stirred at 150–155°C for 12 h. The mixture was diluted with methanol (20 ml), stirred for 2 h and filtered, to give 2·6 g of a dark greenish-black residue. Two recrystallisations from 2-methoxyethanol (Norit) gave 1·8 g (62%) of 1,4-bis(*o*-toluidino)-5-nitro-8-hydroxyanthraquinone (**I.2**), m.p. 232–233°C (P^+ at m/e 479) ($C_{28}H_{21}N_3O_5$ requires: C, 70·15; H, 4·4; N, 8·8. Found: C, 69·9; H, 4·2; N, 8·5%).

Similar reaction with 4-aminobenzophenone (15 h) gave, as first crop material after dilution with methanol, 2·5 g of a dark blue solid, TLC of which indicated several dark blue components in addition to the expected green product. Column chromatography (of 0·5 g) afforded 0·24 g of 1,4-bis(4-benzoylanilino)-5-nitro-8-hydroxyanthraquinone (**I.12**), m.p. 271–273°C (P^+ at m/e 659) ($C_{40}H_{25}N_3O_7$ requires: C, 72·8; H, 3·8; N, 6·4. Found: C, 71·9; H, 3·6; N, 6·1%).

Similar reaction with aniline, *p*-toluidine, *p*-anisidine and *p*-phenetidine gave products containing dyes **I** and triarylamino derivatives **III** (see Section 3.1). DNCZ (2 g), boric acid (0·2 g) and aniline (10 g) heated at 145°C for 3 h gave a crude product which, separated by column chromatography, yielded 80% of 1,4-bisanilino-5-nitro-8-hydroxyanthraquinone (**I.1**).

2.2 5-Amino-1,4-bis(arylamino)-8-hydroxyanthraquinones (II)

The 5-nitro derivatives **I** were reduced with sodium sulphide in ethanol using established procedures.[4] The products, obtained in generally quantitative

TABLE 1

Characterisation Data for 1,4-Bis(arylamino)-5-nitro-8-hydroxyanthraquinones (I)

Dye no.	*R*	*M.p.* (°*C*)	λ_{max} (*nm*) (*log e*) *in chlorobenzene*			*Dyeings on polyester*			
						Light fastness			*Sublimation* (°*C*)
						0·1%	*0·5%*	*2·5%*	
I.1	H	310–312 (sub 1.)	394 (3·81)	630 (4·20)	680 (4·25)	6–7	6–7	6–7	180
I.2	2-Me	232–233	393 (3·79)	632^b (4·22)	673 (4·29)	6–7	6–7	6–7	180
I.3	3-Me	238–239	394 (3·84)	637 (4·27)	682 (4·30)	6–7	6–7	6–7	180
I.4	4-Me	254–255	395 (3·80)	638 (4·26)	684 (4·29)	6	6–7	6–7	180
I.5	2-OMe	241–242	386 (3·81)		677 (4·25)	6–7	6–7	6–7	170
I.6	3-OMe	232–233	395 (3·79)	639 (4·19)	682 (4·28)	6–7	6–7	7	180
I.7	4-OMe	269–270	394 (3·74)	638^b (4·18)	680 (4·24)	6–7	7	7	180
I.8	4-OEt	228–229	394 (3·82)	639^b (4·27)	679 (4·30)	6–7	7	7	190
I.9	4-NHAc	204–205	411 (3·84)	644^b (4·27)	685 (4·31)	6–7	6–7	7	190
I.10	$NHC_{10}H_7$-1[a]	303–304	408 (3·74)	614^b (4·09)	661 (4·18)	5–6	5–6	5–6	180
I.11	4-COOEt	258–259	417 (4·07)	630 (4·24)	684 (4·27)	7	7	7	190
I.12	4-COPh	271–273	426 (4·12)	636^b (4·17)	680 (4·23)	7	7	7	190

[a] 1,4-substituents are 1-naphthylamino.

[b] Incompletely resolved inflexion.

TABLE 2

Characterisation Data for 1,4-Bis(arylamino)-5-amino-8-hydroxyanthraquinones (**II**)

Dye no.	*R*	*M.p.* (°*C*)	λ_{max}*(nm) (log e) in chlorobenzene*			*Dyeings on polyester*			
						Lightfastness			*Sublimation* (°*C*)
						0·1%	*0·5%*	*2·5%*	
II.1	H	321–323	415 (3·80)	646[b] (4·23)	695 (4·28)	5	5	5–6	160
II.2	2-Me	290–291	415 (3·68)	640[b] (4·18)	694 (4·25)	5	5	5–6	160
II.3	4-Me	248–249	416 (3·78)	650[b] (4·22)	700 (4·29)	5	5	5–6	170
II.4	2-OMe	156–158	420 (3·80)		690 (4·23)	5	5	5–6	160
II.5	4-OMe	253–254	418 (3·72)	660[b] (4·22)	700 (4·30)	5	5–6	5–6	170
II.6	4-OEt	222–223	418 (3·73)	660[b] (4·23)	700 (4·30)	5	5–6	5–6	180
II.7	$NHC_{10}H_7$-1[a]	252–253	420 (3·87)		689 (4·18)	4	4	4–5	180

[a] 1,4-Substituents are 1-naphthylamino.

[b] Incompletely resolved inflexion.

TABLE 3

Characterisation Data for 1,4,5-Tri(arylamino)-8-hydroxyanthraquinones (**III**)

Dye no.	*R*	*M.p.* (°*C*)	λ_{max} (*nm*) (*log e*) *in chlorobenzene*			*Dyeings on polyester*			
						Lightfastness			*Sublimation* (°*C*)
						0·1%	*0·5%*	*2·5%*	
III.1	H	223–224	421 (3·73)	673 (4·29)	725 (4·43)	6	6	6–7	190
III.2	4-Me	175–177	421 (3·75)	684^a (4·32)	727 (4·44)	6	6	6–7	190
III.3	2-OMe	133–135	424 (3·79)	686^a (4·34)	728 (4·42)	6	6–7	6–7	190
III.4	4-OMe	187–188	420 (3·77)	686^a (4·36)	731 (4·46)	6	6	6–7	190
III.5	3-OEt	170–171	426 (3·72)	686^a (4·33)	732 (4·42)	6	6	6–7	200

[a] Incompletely resolved shoulder.

yield, were homogeneous by TLC and were recrystallised from 2-methoxyethanol. Relevant characterisation data are shown in Table 2.

2.3 1,4,5-Tris(arylamino)-8-hydroxyanthraquinones (III)

4,5-Bisanilino-1,8-dihydroxyanthraquinone (4·22 g, 0·01 mol) was reacted with aniline (3·72 g, 0·04 mol) following a similar procedure to Method A in Section 2.1. After 4 h of reaction the liquor was diluted with ethanol (20 ml) and worked up as above to give 4·72 g of a dark greenish-black residue. Column chromatography (of 0·5 g) gave, from a high-R_f green zone, 0·38 g (76%) of 1,4,5-trisanilino-8- hydroxyanthraquinone (**III.1**), m.p. 223–224°C (P^+ at *m/e* 497) ($C_{32}H_{23}N_2O_3$ requires: C, 77·3; H, 4·6; N, 8·45. Found: C, 77·1; H, 4·4; N, 8·2%).

Similarly prepared were **III.2**, 63%; **III.3**, 72%; and **III.4**, 76%. Characterisation data are shown in Table 3.

2.4 5-Propylamino-1,4-bisanilino-8-hydroxyanthraquinone (IV)

The 5-amino derivative **II.1** was reacted with 1-iodopropane in *o*-dichlorobenzene following the procedure used for alkylation of 1-alkylamino-4-anilino-5-amino-8-hydroxyanthraquinone.[4] Chromatographic purification of the crude product gave 68% of **IV**, m.p. 180–181°C. (P^+ at *m/e* 463) ($C_{27}H_{25}N_3O_3$ requires: C, 75·1; H, 5·4; N, 9·1. Found: C, 75·0; H, 5·3; N, 8·95%); λ_{max} (log *e*) in chlorobenzene, 418 nm (3·79), 668 nm (4·28) and 722 nm (4·41).

2.5 General

4-Arylamino-5-nitro-1,8-dihydroxyanthraquinones[1] and 4,5-bis(arylamino)-1,8-dihydroxyanthraquinones[2] were prepared as previously described. Electronic spectra were recorded on a Pye–Unicam PU 8720 from dye solutions in chlorobenzene. Dyeings on polyester and fastness assessments were carried out as in previous studies.[1,2]

3 RESULTS AND DISCUSSION

3.1 Syntheses

The selective replacement of the 1-hydroxy group during reaction of 4-arylamino-5-nitro-1,8-dihydroxyanthraquinones with alkylamines in presence of boric acid gives the 1-alkylamino derivatives which colour polyester fibre in deep greenish-blue hues of good fastness properties.[2] 1,4-Bis(arylamino) analogues have also been described[5] as green dyes of excellent fastness properties on synthetic polymer fibres and the related 5-acylamino-1,4-bis(arylamino)-8-hydroxyanthraquinones also give green hues of good fastness on cotton and cotton–polyester blends.[6]

Whilst condensation of DNCZ with arylamines in presence of boric acid gave satisfactory formation of **I** with less reactive amines such as *o*-toluidine (cf. Ref. 6, Example 1) and 4-aminobenzophenone, the reaction was difficult to control with more basic amines such as aniline, *p*-phenetidine and *p*-anisidine, due to the additionally relatively facile formation of 1,4,5-tris(arylamino) derivatives (**III**). Thus, condensation of DNCZ with aniline (cf. Ref. 5, Example 1) for 6 h gave a product containing approx. 60% **I.1** and 40% **III.1.** The formation of **III.1** was apparent to a slight extent after 90 min of reaction (the major product then being a monoanilino derivative) and optimum yield of **I.1** (80%) was obtained after 3 h of reaction.

Dyes **I** were readily obtained from the partially arylaminated derivatives, viz. 4-arylamino-5-nitro-1,8-dihydroxyanthraquinones, using a modification of the method previously used for the synthesis of 1-alkylamino-4-arylamino-5-nitro-8-hydroxyanthraquinones.[4] Condensation with arylamines in phenol and boric acid gave good yields of **I**, principal by-products being the reduced analogues **II**. Little formation of **III** was apparent and compounds **III** were obtained in excellent yield from the corresponding 4,5-bis(arylamino)-1,8-dihydroxyanthraquinones using a similar procedure. Reduction of **I** to the 5-amino derivatives **II** and further alkylation to the 5-alkylamino derivatives were effected as previously described[4] for analogous 1-alkylamino derivatives.

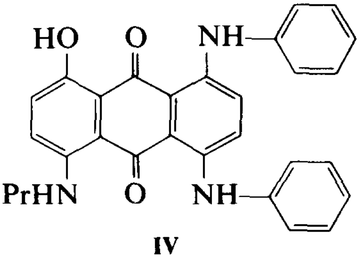
3.2 Electronic spectra

Replacement of the alkylamino group in 1-methylamino-4-anilino-5-nitro-8-hydroxyanthraquinone (λ_{max}626 nm and 676 nm)[4] by the anilino group results (for dye **I.1**) in a shift of absorption maxima to 634 nm and 680 nm. The larger shift in the lower-wavelength band is similar to that observed in other tetra-substituted dyes, e.g. 4-methylamino-5-anilino-1,8-dihydroxyanthraquinone, λ_{max} 635 nm and 683 nm; 4,5-bisanilino-1,8-dihydroxyanthraquinone, λ_{max} 642 nm and 684 nm.[7]

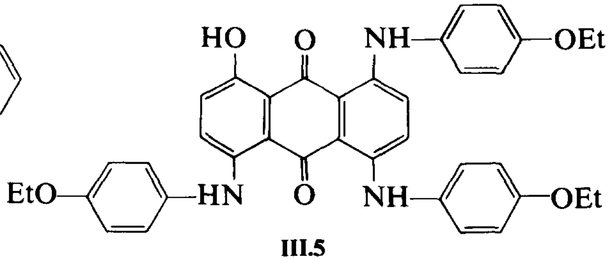
Substitution into the phenyl ring by the electron donor alkyl (**I.2–I.4**), alkoxy (**I.5–I.8**) and acylamino substituents (**I.9**) give only small colour shifts in the longer-wavelength absorption band (up to 5 nm), and similar bathochromic shifts tend to result also with substitution by electron-acceptor groups (**I.11**, **I.12**). The shifts in λ_{max} are thus not substantially relatable to the polar nature of the substituent and further exemplify the more limited influence of substituent effects in polysubstituted anthraquinone dyes[1,2] compared with less substituted derivatives. The most significant colour shifts are resultant from steric factors, as in the 2′-methyl (**I.2**) and 1-naphthylamino derivatives (**I.10**).

The bright greenish hue of **I** is due in part to the contribution of a very broad blue absorption centred around 400 nm, and the colour shift to green is further apparent in the 5-amino derivatives **II**. These show bathochromic shifts of 15 nm to 20 nm in both of the long-wavelength absorption bands compared with **I**. This shift is somewhat lower than observed on reduction of the 1-alkylamino analogues,[4] but is sufficient to shift the overall absorption towards the 700 nm region, the green hue of the dyes being due to a well defined blue absorption around 420 nm. The influence of this blue absorption is apparent in comparing **II.1** with the isomeric 1,5-bisanilino-4-amino-8-hydroxyanthraquinone, which shows λ_{max} at 645 nm and 692 nm (in chlorobenzene) but has no green hue since little absorption in the 420 nm region occurs (Giesse, R. & Peters, A. T., unpublished).

Alkylation of **II.1** with 1-iodopropane yielded the 5-propylamino derivative **IV**, which showed principal absorption maxima at 668 nm and 722 nm, viz. a shift of 22 nm and 27 nm respectively compared with **II.1**. The absorption at 420 nm also imparts an intense greenish hue.



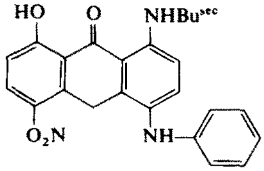
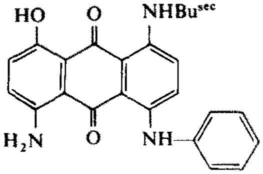
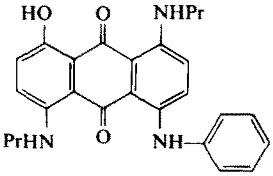
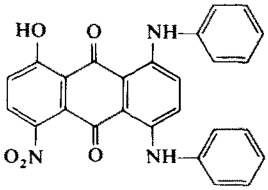
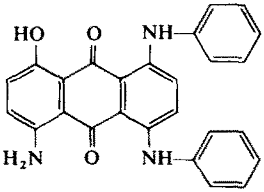
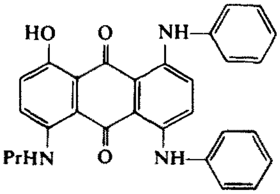
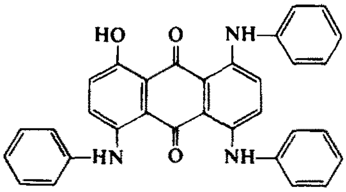
IV



III.5

Phenylation of the 5-amino substituent gives further slight bathochromic shifts, the 1,4,5-trisanilino-8-hydroxy derivative (**III.1**) showing shifts of 2–5 nm compared with the 5-propylamino derivative **IV**. Introduction of electron-donor substituents in the phenyl rings gives further shifts, typified by the tris(4-ethoxyanilino) derivative **III.5**, which has λ_{max} at 686 nm and 732 nm. The influence of the progressive phenylation of the amino groups is exemplified by comparison of **III.5** with 1-propylamino-4-anilino-5-amino-8-hydroxyanthraquinone, the longer-wavelength absorption of which (687 nm)[4] is in the same region as the lower wavelength absorption of **III.5** (686 nm).

TABLE 4
Absorption Maxima and Fastness of Some Anthraquinone Dyes

		λ_{max} (nm) in chlorobenzene	*Lightfastness*			*Sublimation (°C)*
			0·1%	*0·5%*	*2·5%*	
V		624 and 675	5–6	5–6	6	170
VI		640 and 689	4–5	5	5	160
VII		665 and 719	5	5	5–6	160
I.1		634 and 680	6–7	6–7	6–7	180
II.1		647[a] and 695	5	5	5–6	160
IV		668 and 722	5–6	5–6	5–6	170
III.1		673[a] and 724	6	6	6–7	190

3.3 Dyeing and fastness properties

Coloration properties of **I** on polyester were generally good, the dyes building up to greyish-green hue, the alkoxy derivatives **I.6–I.8** and the ester derivative **I.11** having the best build-up of the dyes investigated. Fastness to light was excellent, being in the order of one point better than the 1-alkylamino-4-arylamino analogues.[4] Increased mass effects resulted also in a slightly improved sublimation fastness. The amino derivatives **II** showed better build-up than **I**, yielding deep bluish-green dyeings. Whilst light and sublimation fastness of these dyes were lower than those of **I**, the fastness properties of **II** were of a similar order to those of 1-alkylamino-4-arylamino-5-nitro-8-hydroxyanthraquinones, e.g. **V**, and lightfastness was better than that of the 1-alkylamino-4-arylamino-5-amino-8-hydroxy derivatives, e.g. **VI** (see Table 4).

Alkylation of the amino group of **II** resulted in similar bathochromic shifts and improvement in both light and sublimation fastness to similar alkylations in the 1-alkylamino analogues, cf. **VI** and **VII**, **IV** and **II.1** (Fig. 1) and dye **IV** gave deep green colorations on polyester, build-up being similar to that of **II**. The good overall fastness of the triaminated derivatives is further shown in dyes **III**, these giving clear green hues with build-up lower than those of **II** and **IV**, but of a similar order to **I**.

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