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1-Alkylamino-4-arylamino-5-nitro-(and 5-amino)-8-hydroxyanthraquinones: Greenish–Blue Dyes for Synthetic-Polymer Fibres

A. T. Peters

Postgraduate School of Chemistry and Chemical Technology, University of Bradford, Bradford, BD7 1DP, UK

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Y. C. Chao

Department of Textile Industries, National Taipei Institute of Technology, Taipei, Taiwan

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ABSTRACT

Whereas reaction of 4-arylamino-5-nitro-1,8-dihydroxyanthraquinones with alkylamines affords, as principal condensation product, the corresponding 5-alkylamino derivative, similar reaction in the presence of boric acid yields 1-alkylamino-4-arylamino-5-nitro-8-hydroxyanthraquinones. These compounds colour polyester in deep greenish–blue hues of good fastness to light and sublimation. Dyes of progressively greener hue are obtained on reduction of the 5-nitro group and by its replacement by a 5-alkylamino substituent, the latter resulting in a shift of the longer-wavelength absorption band into the near-IR. Structure–colour relationships in these compounds are discussed with respect to the nature of the 1-alkylamino and 4-arylamino moieties and also with respect to related dyes containing amino substituents other than in a 1,4-configuration. The bathochromic influence of the 5-nitro group in these, and related, dyes is also demonstrated.

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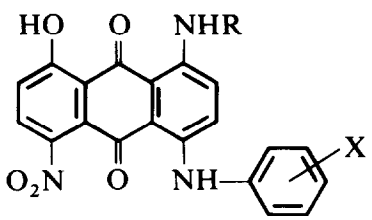
1 INTRODUCTION

Condensation of 4,5-dinitro-1,8-dihydroxyanthraquinone and of 4-amino-5-nitro-1,8-dihydroxyanthraquinone with alkylamines results in replacement of the nitro groups as the principal condensation reaction,[1] although the facility of the reaction is hindered by the formation of by-products due to reduction of the nitro groups. Reaction of 4,5-dinitro-1,8-dihydroxyanthraquinone with arylamines yields 4-arylamino-5-nitro-1,8-dihydroxyanthraquinones,[2] condensation of which with alkylamines, or reduction of which, following by alkylation, affords 4-arylamino-5-alkylamino-1,8-dihydroxyanthraquinones,[3] which colour polyester in deep greenish-blue hues of good fastness.

If, however, the condensation of 4-arylamino-5-nitro-1,8-dihydroxyanthraquinones with alkylamines is effected in the presence of boric acid, the reaction follows a different course, with preferential formation of 1-alkylamino-4-arylamino-5-nitro-8-hydroxyanthraquinones.[4] We report here the synthesis of some of these compounds (**I**), and of the corresponding 5-amino derivatives (**II**) and some 5-alkylamino derivatives (**III**), together with an evaluation of structure–property relationships in these dyes and in related compounds.



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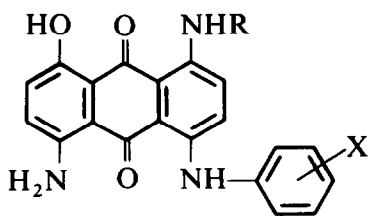

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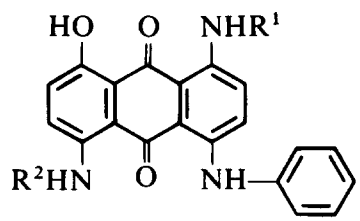


III

2 EXPERIMENTAL

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

Phenol (50 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 was continued for 1 h at 130–135°C, with removal of any evolved water. Butylamine (1·82 g, 0·025 mol) was then added and the reaction continued for 75 min. The liquor was cooled to 50°C, diluted with methanol (30 ml) and water (4 ml) and left to stand overnight. The crystalline material which separated (1·9 g, 44%) was filtered, washed with a little methanol and then with hot water to remove phenolic residues. Recrystallisation from 2-methoxyethanol (Norit) gave dark blue–black prisms, m.p. 224–225°C, of 1-butylamino-4-anilino-5-nitro-8-hydroxyanthraquinone (**I.6**) (P^+ at *m/e* 431) ($C_{24}H_{21}N_3O_5$ requires: C, 66·8; H, 4·9; N, 9·7. Found: C, 66·6; H, 4·8; N, 9·5%).

The mother liquors were stirred into cold 5% aq. potassium hydroxide (400 ml) and the resultant dark blue–black solid (2·2 g) was filtered and washed neutral with warm water. TLC showed it to be essentially **I.6** with several minor blue to blue–green by-products and zero-R_f dark-coloured material. Column chromatography (of 0·5 g) on silica gel (Kieselgel 60, Fluka AG), applying from solution in chlorobenzene and developing with toluene gave, from the principal blue–green zone, 0·33 g of **I.6** (i.e. overall yield, including first fraction, 78%). The principal by-product isolated (0·06 g) from a lower-R_f blue–green zone was 1-butylamino-4-anilino-5-amino-8-hydroxyanthraquinone (**II.3**). Other minor zones and baseline material were not investigated.

Alternatively, the cooled reaction mixture, after dilution with methanol and water as above, was stirred into cold 5% aq. potassium hydroxide (500 ml). After stirring for 1 h and standing overnight, the liquor was filtered and the residue washed with hot water until free of phenol. The resultant product (4·14 g, 96%) had similar purity to the mother liquor crop in the above and afforded pure **I.6** after two recrystallisations from 2-methoxyethanol (Norit).

Other compounds **I** were similarly prepared, using 75 min–3 h reaction time (TLC monitor) and 0·02–0·03 mol alkylamine as appropriate. Conversion to **I** was generally similar to that for **I.6** above and in most cases sufficient **I** for this investigation was obtained as first-crop material after dilution of the reaction mixture with methanol and water. Yields varying from 30 to 60%, depending on the alkylamine, were thus obtained, but yields of 75–85% were readily attainable by addition of the reaction liquor to 5% potassium hydroxide and working up as above. With some amines, e.g. 3-methoxypropylamine and 3-amino-1-propanol, the tendency for reduction side-reactions was more evident and the first-crop material required chromatographic purification to obtain pure **I**. Reduction by-products were formed to an approximate extent of 20% with 3-methoxypropylamine and 35% with 3-amino-1-propanol.

In the case of the 1-amino (**I.1**) and 1-methylamino (**I.2**) derivatives,

TABLE 1
Characterisation Data for 1-Alkylamino-4-arylamino-5-nitro-8-hydroxyanthraquinones (I)

No.	R	*X*	*M.p.* (°C)	λ_{max} (*nm*) (*log* ε) *in chlorobenzene*		*Dyeings on polyester*			
						Light fastness			*Sublimation temp.* (°C)
						0·1%	*0·5%*	*2·5%*	
I.1	H	H	258–259	601 (4·23)	645 (4·26)	4	4	4–5	160
I.2	Me	H	295–296	626 (4·17)	676 (4·22)	5	5	5	170
I.3	Et	H	279–280	625 (4·20)	676 (4·24)	5	5	5	170
I.4	*n*-Pr	H	232–233	625 (4·21)	675 (4·25)	5	5–6	5–6	170
I.5	iso-Pr	H	236–237	625 (4·23)	675 (4·27)	5–6	5–6	6	170
I.6	*n*-Bu	H	224–225	624 (4·25)	674 (4·28)	5	5	5–6	170
I.7	iso-Bu	H	213–214	624 (4·26)	674 (4·28)	5	5	5–6	170
I.8	*sec*-Bu	H	215–216	624 (4·25)	675 (4·28)	5–6	5–6	6	170
I.9	*t*-Bu	H	312–314	625 (4·25)	676 (4·29)	6	6	6	180
I.10	C_3H_6OH	H	205–206	624 (4·23)	675 (4·28)	5–6	5–6	5–6	180

I.11	$C_3H_6OCH_3$	H	186–187	625 (4·21)	674 (4·28)	5–6	6	6	170
I.12	C_6H_{11}	H	240–241	625 (4·27)	676 (4·32)	6	6	6	180
I.13	*sec*-Bu	2-Me	187–188	621 (4·21)	670 (4·28)	5–6	5–6	5–6	170
I.14	*sec*-Bu	3-Me	191–192	625 (4·22)	675 (4·26)	5–6	5–6	5–6	170
I.15	*sec*-Bu	4-Me	169–170	626 (4·21)	675 (4·26)	5–6	5–6	6	170
I.16	*sec*-Bu	2-OMe	170–171	632 (4·18)	667 (4·22)	5–6	5–6	5–6	170
I.17	*sec*-Bu	3-OMe	166–167	626 (4·20)	675 (4·24)	5–6	5–6	6	170
I.18	*sec*-Bu	4-OMe	170–171	626 (4·23)	673 (4·29)	5–6	5–6	6	170
I.19	*sec*-Bu	4-OEt	177–178	626 (4·24)	673 (4·30)	5–6	5–6	6	170
I.20	*sec*-Bu	4-NHCOMe	204–205	627 (4·19)	673 (4·23)	5–6	6	6	180
I.21	*sec*-Bu	4-NHCOPh	187–188	630 (4·18)	676 (4·22)	5–6	6	6	190
I.22	*sec*-Bu	4-C_2H_4OH	207–208	626 (4·18)	677 (4·25)	5–6	5–6	6	180
I.23	*sec*-Bu	$NHC_{10}H_7$-1[a]	161–162	622 (4·08)	667 (4·14)	4–5	4–5	4–5	180
I.24	*sec*-Bu	4-COOEt	232–233	627 (4·22)	681 (4·27)	5–6	6	6	180
I.25	*sec*-Bu	4-COMe	248–249	628 (4·20)	682 (4·24)	5–6	6	6	180
I.26	*sec*-Bu	4-COPh	212–213	627 (4·19)	678 (4·23)	5–6	6	6	190
I.27	*sec*-Bu	4-SO_2NH_2	294–295	625 (4·18)	677 (4·24)	4–5	5	5	190

[a] 4-Substituent is 1-naphthylamino.

gaseous ammonia or methylamine was passed through the reaction liquor until all starting material had reacted. Yields/isolation were as above. The use of ammonium hydroxide (*d* 0·880) did not result in facile reaction. After addition of 10 ml, replacement of the 5-nitro group occurred, but **I.1** was isolated in 24% yield after chromatographic separation of the crude product. Similar reaction at the 5-nitro group occurred with 33% ethanolic methylamine, but after allowing all starting material to react, the 1-methylamino-5-nitro-(**I.2**) and 1-methylamino-5-amino derivatives (**II.1**) were isolated in 32% and 27% yield respectively after chromatographic separation.

Relevant data for **I** with variation in the 1-alkyl substituent (**I.2–I.12**) and with variation in the 4-aryl residue (**I.13–I.27**) are shown in Table 1.

2.2 1-Alkylamino-4-arylamino-5-amino-8-hydroxyanthraquinones (II)

These were prepared by reduction of **I** with hydrated sodium sulphide in ethanol, using established procedures.[2] Products thus obtained were homogeneous by TLC and were recrystallised from 2-methoxyethanol (Norit) prior to recording of electronic spectra. Relevant data are shown in Table 2.

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

1-Propylamino-4-anilino-5-amino-8-hydroxyanthraquinone (**II.2**) (0·5 g) was refluxed in *o*-dichlorobenzene (10 ml) in presence of anhydrous potassium carbonate (0·2 g). A solution of 1-iodopropane (0·75 ml) in *o*-dichlorobenzene (4 ml) was run in over 30 min and refluxing continued for 12 h. Excess iodopropane was distilled off, the liquor was cooled and diluted with a further 20 ml of *o*-dichlorobenzene, and the solution was applied to a column of silica gel (Kieselgel 60, Fluka AG). Elution with toluene gave, from the principal higher-R_f greenish–blue zone, dark greenish–blue prisms, m.p. 160–161°C (ethanol) of 1,5-bis-propylamino-4-anilino-8-hydroxy-anthraquinone (**III.1**) (0·39 g, 71%) P^+ at *m/e* 429) ($C_{26}H_{27}N_3O_3$ requires: C, 72·7; H, 6·3; N, 9·8. Found: C, 72·5; H, 6·2; N, 9·7%); λ_{max}, nm (log *e*) in chlorobenzene, 410 (3·54), 665 (4·36) and 719 (4·39).

Similarly prepared were 1,5-bis-butylamino-4-anilino-8-hydroxy anthraquinone (**III.2**), 67% m.p. 144–145°C (ethanol); λ_{max} (log *e*) in chlorobenzene, 414 (3·55), 665 (4·37) and 722 (4·39); and 1-butylamino-4-anilino-5-propylamino-8-hydroxyanthraquinone (**III.3**); 42%, m.p. 154–155°C (ethanol); λ_{max}, nm (log *e*) in chlorobenzene, 413 (3·56), 665 (4·36) and 721 (4·38).

TABLE 2

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

No.	R	*X*	*M.p.* (°C)	λ_{max} (*nm*) (*log* e) *in chlorobenzene*		*Dyeings on polyester*			
						Light fastness			*Sublimation temp.* (°C)
						0·1%	*0·5%*	*2·5%*	
II.1	Me	H	242–243	640 (4·25)	686 (4·29)	4–5	4–5	4–5	160
II.2	*n*-Pr	H	158–159	640 (4·28)	687 (4·30)	4–5	4–5	4–5	160
II.3	*n*-Bu	H	150–151	640 (4·24)	689 (4·26)	4–5	4–5	4–5	160
II.4	iso-Bu	H	177–178	639 (4·23)	688 (4·25)	4–5	4–5	4–5	160
II.5	*sec*-Bu	H	155–156	640 (4·21)	689 (4·25)	4–5	5	5	160
II.6	*t*-Bu	H	195–196	640 (4·24)	687 (4·27)	4–5	5	5	160
II.7	C_3H_6OMe	H	170–171	638 (4·24)	687 (4·28)	4–5	5	5	160
II.8	C_6H_{11}	H	266–267	640 (4·26)	691 (4·31)	5	5	5	170
II.9	*sec*-Bu	4-CH_3	115–116	642 (4·22)	692 (4·26)	4–5	5	5	160
II.10	*sec*-Bu	3-OMe	126–127	638 (4·19)	690 (4·24)	4–5	4–5	5	160
II.11	*sec*-Bu	4-OMe	153–154	642 (4·23)	690 (4·27)	4–5	4–5	5	160
II.12	*sec*-Bu	4-OEt	137–138	644 (4·21)	692 (4·26)	4–5	5	5	160
II.13	*sec*-Bu	4-C_2H_4OH	165–166	642 (4·24)	688 (4·26)	4–5	4–5	4–5	170
II.14	*sec*-Bu	4-NHCOMe	164–165	642 (4·22)	688 (4·25)	4–5	4–5	5	170
II.15	*sec*-Bu	4-NHCOPh	249–250	643 (4·26)	690 (4·31)	4–5	5	5	180
II.16	*sec*-Bu	$NHC_{10}H_7$-1[a]	128–129	640 (4·16)	687 (4·20)	3	3–4	3–4	180
II.17	*sec*-Bu	4-COMe	240–241	638 (4·20)	688 (4·23)	4–5	5	5	170
II.18	*sec*-Bu	4-COOEt	278–279	638 (4·22)	688 (4·27)	4–5	5	5	180

[a] 4-Substituent is 1-naphthylamino.

The above were also prepared by condensation of the corresponding 5-nitro derivatives **I.4** and **I.6** with propylamine and butylamine respectively, following the procedure previously described for similar condensations with 4-anilino-5-nitro-1,8-dihydroxyanthraquinone.[3] Following column-chromatographic separation, **III.1–III.3** were obtained (from the higher-R_f bands) in 44%, 51% and 56% yields respectively. The other principal reaction products were the 5-amino derivatives.

2.4 1,8-Dihydroxy-4-anilinoanthraquinone

To a stirred solution of 5-amino-4-anilino-1,8-dihydroxyanthraquinone (1 g) in DMF (10 ml) at room temperature was added amyl nitrite (2 ml). After stirring for 20 min, hypophosphorous acid (5 ml) was added and stirring continued for 30 min at room temperature and then at 60–65°C for 20 min. The liquor was cooled, added to ice–water and filtered to give a dark blue solid (0·9 g, 93%) which crystallised from 2-methoxyethanol in dark purple–blue prisms, m.p. 176–177°C, of 1,8-dihydroxy-4-anilino-anthraquinone (P^+ at *m/e* 331) ($C_{20}H_{13}NO_4$ requires: C, 72·5; H, 3·9; N, 4·2. Found: C, 72·3; H, 3·7; N, 4·0%); λ_{max}, nm (log *e*) in chlorobenzene, 576 (4·10) and 597 (4·11).

Similar deamination of 4-amino-5-nitro-1,8-dihydroxyanthraquinone gave 89% of 4-nitro-1,8-dihydroxyanthraquinone, orange-yellow prisms, m.p. 229–230°C (ethanol) (P^+ at *m/e* 285). Condensation of this with aniline in 2-methoxyethanol (cf. Ref. 2) gave 4-anilino-1,8-dihydroxyanthraquinone, identical to the product prepared as above.

5-Amino-4-(4-methoxyanilino)-1,8-dihydroxyanthraquinone was deaminated as above to 4-(4-methoxyanilino)-1,8-dihydroxyanthraquinone, 88%, dark blue-black prisms, m.p. 159–160°C (2-methoxyethanol); λ_{max}, nm (log *e*) in chlorobenzene, 572 s (4·04) and 600 (4·09) and **II.2** by the same process afforded 78% of 1-propylamino-4-anilino-8-hydroxyanthraquinone, bright blue prisms, m.p. 152–154°C (ethanol) ($C_{23}H_{20}N_2O_3$ requires: C, 74·2; H, 5·4; N, 7·5. Found: C, 74·0; H, 5·3; N, 7·3%); λ_{max}, nm (log *e*) in chlorobenzene 606 (4·13) and 654 (4·15).

2.5 General

Electronic spectra were recorded on a Pye–Unicam PU 8800 from dye solutions in chlorobenzene (and, for selected dyes, in 2-methoxyethanol and in absolute ethanol), except for evaluations above 700 nm, for which a PU 8720 was used. Dyeings on polyester and fastness assessments were carried out as for previous investigations.[2]

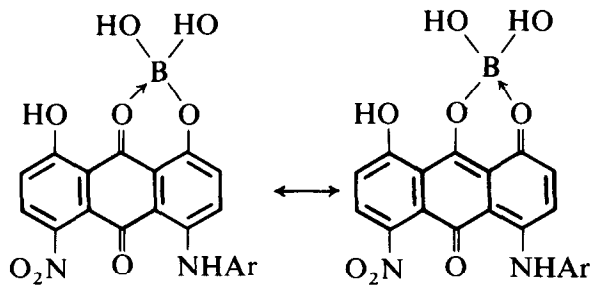
4-Arylamino-5-nitro-1,8-dihydroxyanthraquinones,[2] 4-arylamino-5-

amino-1,8-dihydroxyanthraquinones,[2] and 4-amino-5-nitro-1,8-dihydroxyanthraquinone[1] were prepared as previously described.

3 RESULTS AND DISCUSSION

3.1 Synthesis

Condensation of 4-arylamino-5-nitro-1,8-dihydroxyanthraquinones with alkylamines or arylamines normally results in replacement of the 5-nitro group.[1,2] In the presence of boric acid however, preferential replacement of the 1-hydroxy group ensues,[4] presumably via formation of a boric acid ester **IV**. The reactions of 1,4-dihydroxyanthraquinone and of 1,4,5,8-tetrahydroxyanthraquinone with arylamines under reductive conditions in presence of boric acid have indicated[5] that the arylamination of leuco-α-hydroxyanthraquinones proceeds via a metaborate or an orthoborate intermediate, depending on the conditions used in the reaction with boric acid.



IV

Dyes **I** were obtained in good yield when using phenol as reaction medium, and whilst satisfactory reaction ensued in a lower-volume reaction mixture (cf. Ref. 4), in the small-scale syntheses carried out in this present work the use of larger volumes of phenol gave a cleaner reaction and tended to obviate side-reactions caused by localised temperature differences possible in a more viscous medium. Principal by-products were due to reduction of the 5-nitro group, and whilst these were more evident in reactions with 3-methoxypropylamine and 3-amino-1-propanol, they could be minimised by ensuring a rapid replacement of the 1-hydroxy group and immediate work-up of the reaction liquor. This could be generally effected by using a larger solvent volume and by increasing the amount of alkylamine. Reactions essentially complete within 75–90 min were generally free from significant amounts of by-products, but lowering the amount of alkylamine, the use of a more viscous reaction liquor and of more prolonged

reaction times all favoured increased formation of by-products. By appropriate optimisation of reaction conditions for each reaction, almost quantitative conversion to **I** could be effected. In such cases, maximum product recovery could be obtained by addition of the reaction liquor to excess 5% aq. potassium hydroxide, filtering and recrystallisation(s) or chromatographic separation, as appropriate, of the crude condensate. The use of other solvents was not advantageous. Thus, in alcoholic or aprotic solvents such as DMF, DMSO, 2-methoxyethanol and PEG 400, formation of **I** was negligible, the principal reactions being either reduction or replacement of the 5-nitro group.

Dyes **I** afforded the 5-amino derivatives **II** on conventional reduction with sodium sulphide, and further alkylation of these, or reaction of **I** with alkylamines, yielded the 5-alkylamino derivatives **III**. 5-Amino-4-arylamino-1,8-dihydroxyanthraquinones were deaminated by diazotisation with amyl nitrite in DMF, followed by treatment with hypophosphorous acid (cf. Refs 6, 7). The resultant 4-arylamino-1,8-dihydroxyanthraquinones were also obtained by condensation of arylamines and 4-nitro-1,8-dihydroxyanthraquinone, which was prepared by deamination of 4-amino-5-nitro-1,8-dihydroxyanthraquinone. Dye **II.2**, similarly, afforded 1-propylamino-4-anilino-8-hydroxyanthraquinone.

3.2 Electronic spectra

1-Amino-4-anilino-5-nitro-8-hydroxyanthraquinone (**I.1**) showed principal visible absorption maxima at 601 nm and 645 nm, thus showing similar λ_{max} to 4-amino-5-anilino-1,8-dihydroxyanthraquinone and 8-amino-4-anilino-1,5-dihydroxyanthraquinone.[2]

Replacement of the 1-amino group by 1-methylamino (**I.2**) resulted in bathochromic shifts of 25 nm and 31 nm respectively for the two absorption maxima. These shifts are of a similar general order to those observed on *N*-methylation of amino groups in other chrysazin derivatives, e.g. 4-amino-5-anilino-1,8-dihydroxyanthraquinone, $\Delta\lambda$ 25 nm and 33 nm;[2,3] 4,5-diaminochrysazin, $\Delta\lambda$ 29 nm and 37 nm.[1]

The 1-alkylamino derivatives **I** showed, in monochlorobenzene, two fully resolved maxima in the 625 nm and 675 nm regions. Selected dyes were also evaluated in absolute ethanol and in 2-methoxyethanol, and both maxima were shifted hypsochromically in these solvents. Thus, **I.15** had λ_{max} at 616 nm and 660 nm in ethanol, and at 617 nm and 662 nm in 2-methoxyethanol, and **I.6** showed λ_{max} at 614 nm and 660 nm in ethanol and at 616 nm and 663 nm in 2-methoxyethanol. The hypsochromic shift of 10–15 nm in both visible absorption maxima was apparent in other dyes and is indicative of intermolecular solute–solvent interaction. This is in contrast

to the bathochromic shifts usually observed in simpler substituted amino- and/or hydroxy-anthraquinones (cf. Ref. 8). As the principal colour-contributing polar and hydrogen-bonding interactions in such dyes are enhanced as a result of the introduction of a multiplicity of polar substituents into the dye molecule, the bathochromic influence of ethanolic solvents is generally reversed.

In the following discussion, all λ_{max} values refer to spectra recorded in chlorobenzene, unless stated otherwise. Changes in the nature of the alkyl substituent at the 1-position result in essentially no change in λ_{max} values (**I.2–I.12**, Table 1) and the tendency for slight increase in λ_{max} with increasing chain length noted in the tetra-substituted amino anthraquinones[1,3] is not apparent in dyes **I**. There is additionally little indication of steric influences in the *t*-butyl derivative **I.9**, for which both ε_{max} and λ_{max} values are of a very similar order to those of the isomeric butyl derivatives **I.6–I.8**.

Similarly, introduction of substituents into the 4-arylamino residue dyes **I.13–I.27**) results in only very small shifts in λ_{max} and little significant difference is apparent in dyes thus substituted by electron-donor or acceptor moieties, the latter in fact tending to have the more bathochromic influence, e.g. **I.19**, 4-OEt, 626 and 673 nm; **I.21**, 4-NHCOPh, 630 and 676 nm; **I.24**, 4-COOEt, 627 and 681 nm; **I.25**, 4-COMe, 628 and 682 nm. The effect of such substitution would be expected to result in small bathochromic or hypsochromic shifts commensurate with the donor or acceptor nature respectively of the substituents. Whilst such shifts are apparent in less substituted arylaminoanthraquinones, they are not so apparent in polysubstituted derivatives such as 4-arylamino-5-nitro-(and 5-amino)-1,8-dihydroxyanthraquinones.[2] In the latter, band resolution is incomplete and approximations can be adopted which give a more indicative representation of the polar factors of the substituents in the phenyl ring. In **I**, however, band resolution is good, the twin peaks being fully resolved, but with the exception of steric influences exemplified by the 2-toluidino (**I.13**) and 1-naphthylamino (**I.23**) derivatives, substituent effects are small. The dominating influence in **I** is thus interactions between the donor amino and hydroxy groups and the acceptor carbonyl groups, the resultant polar and intramolecular hydrogen-bonded configurations being relatively insensitive to slight polarity differences resultant from substituent effects in the phenyl ring. A similar conclusion is evident in 4-arylamino-5-nitro-(and amino)-1,8-dihydroxyanthraquinones,[2] in the context of the observed λ_{max} values. In the latter dyes, differences are however apparent in the hue of the dyeings obtained on polyester, and a similar observation is pertinent to **I**. Thus, although showing very similar λ_{max} values, the colour of the chlorobenzene solutions of **I**, and of their dyeings on polyester, were of diverse hues of greenish–blue. For example, the 4-methyl (**I.15**) and 4-(2-hydroxyethyl) (**I.22**)

derivatives were slightly greener than the anilino derivative (**I.19**), the 4-methoxy (**I.21**), 4-ethoxy (**I.19**) and 4-benzamido (**I.21**) derivatives considerably greener, whilst the 4-benzoyl derivative (**I.26**) was somewhat bluer and duller. These differences are relatable to differences in absorption at lower wavelength. Thus, absorption of **I** in the visible region is extensive, and the λ_{max} values in Table 1 are the well-defined maxima of a very broad absorption, showing λ_{min} between 475 nm and 490 nm. From λ_{min} there is gradual absorption to lower wavelengths, with ill-defined maxima in the 360–370 nm region ($\log e$ 3·60–3·80), and an inflexion around 420 nm ($\log e$ 3·40–3·60). The dyes of greener hue tend to exhibit stronger absorption in the 380–420 nm region, hence imparting the greener (i.e. yellower) hue.

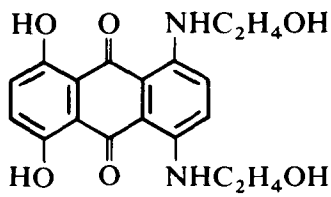
It is of interest to note the bathochromic influence of the 5-nitro group in **I**, despite its strong electron-attracting nature. Thus, 4-anilino-5-nitro-1,8-dihydroxyanthraquinone has λ_{max} at 594 nm and 622 nm and the corresponding 4-(4-methoxy)anilino derivative at 590(s) nm and 622 nm.[2] The respective 4-arylamino-1,8-dihydroxyanthraquinones, obtained by deamination (via the diazonium salt) of the appropriate 5-amino derivatives, have λ_{max} at 576 nm/597 nm and 572s nm/600 nm respectively. A similar bathochromic effect of the 5-nitro group is apparent in comparing **I.4** (λ_{max} 625 nm and 675 nm) with 1-propylamino-4-anilino-8-hydroxyanthraquinone, λ_{max} 606 nm and 654 nm. In the above, the nitro group produces bathochromic shifts of *c.* 20 nm in each of the absorption bands and this is presumably relatable to increase in the interactions involving the 4-aminated residue. Donor–acceptor interaction between the 5-nitro group and the conjugated 8-hydroxy substituent is not significant in this respect, since λ_{max} values of 4,5-dinitro-1,8-dihydroxyanthraquinone and of 4-nitro-1,8-dihydroxyanthraquinone are very similar (436 nm and 437 nm respectively) and neither is significantly different from 1,8-dihydroxyanthraquinone [λ_{max} 432 nm and 444(s) nm].

Reduction of the 5-nitro group in **I** gives, in dyes **II**, bathochromic shifts of 20–25 nm in both visible absorption maxima, commensurate with the replacement of the acceptor nitro substituent by the donor amino substituent. These shifts are of similar order to those observed on the reduction of nitro groups in related dyes, e.g. 4-arylamino-5-nitro-1,8-dihydroxyanthraquinones.[2] Similarly to **I**, substituent effects in both the 4-arylamino and 1-alkylamino groups are small (Table 2), the dominant influences being those involving the basic α-amino and α-hydroxy moieties and the anthraquinone carbonyl groups. Substituent effects in the 4-phenylamino derivative are slightly more in accord with the polar nature of the substituent than in **I** (e.g. anilino, **II.5**, λ_{max} 640 nm and 689 nm; 4-phenetidino, **II.12**, λ_{max} 644 nm and 692 nm; 4-carboethoxy, **II.18**, λ_{max} 638 nm and 688 nm), but the effects are not fully consistent with such factors.

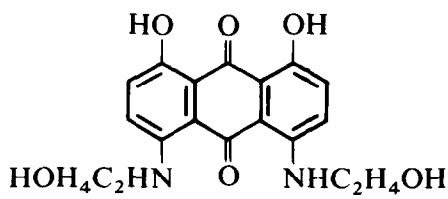
The overall bathochromic shift relative to **I** is additionally indicated by the shift in λ_{min} values to the 450–520 nm region and all dyes **II** showed absorption, with well-defined maxima, in the 410–418 nm area (log e, 3·50–3·70).

Despite the presence of the colour-imparting 1,4-diaminated residue, dyes **I** are hypsochromic with respect to 4.5-bis-alkylamino-1,8-dihydroxy-anthraquinones. Figure 1 indicates some comparative λ_{max} data, taking the propylamino derivatives as illustrative. The overall donor nature of all the substituents, together with the intramolecular hydrogen bonding from two α-hydroxy groups, is thus sufficient to realise the greater colour development in **V** and **VI**. Reduction of the nitro group in **I.4** to the 1,4,5-triaminated derivative **II.2**, whilst giving the expected bathochromic shift, does so only to an extent to yield dyes of similar λ_{max} to **V** and **VI**.

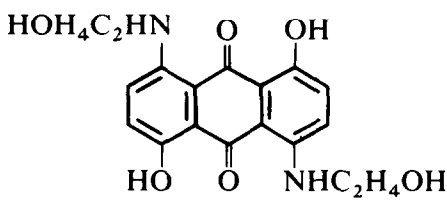
Thus the development of colour in α-donor-substituted anthraquinones, whilst requiring a 1,4-diaminated substitution pattern in simpler derivatives, does not necessarily require such a substitution pattern in 1,4,5,8-tetra-donor-substituted anthraquinones. This is demonstrated by comparison of the isomeric bis-hydroxy-bis-(2-hydroxyethylamino) derivatives **VII–IX**.



VII



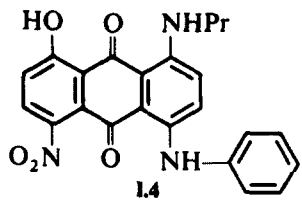
VIII



IX

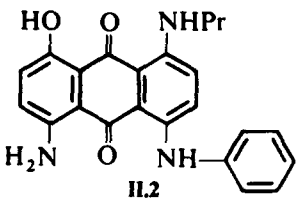
The 1,4-diaminated compound **VII** (principal component of CI62500, CI Disperse Blue 7, isolated by chromatographic separation of the commercial dye) showed λ_{max} 625 nm and 688 nm and is thus not significantly different in colour from the 1,5-isomer **IX**, λ_{max} 631 nm and 687 nm,[9] or from the 1,8-isomer **VIII**, λ_{max} 631 nm and 681 nm[1] (all values in monochlorobenzene). The hypsochromic effect of ethanolic solvents, noted above for **I**, is equally pertinent to **VII**, which showed λ_{max} 619 nm and 672 nm in ethanol.

The bis-hydroxy-bis-arylamino-anthraquinones also show a similar behaviour. Thus, the 1,5-diaminated Toluidine Blue (CI 63340) is, in both



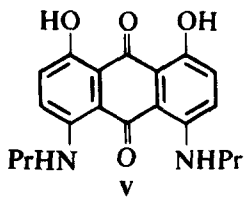
I.4

625 nm and 675 nm



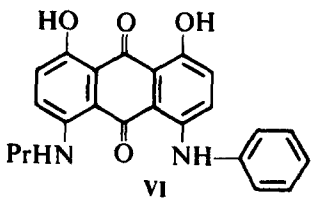
II.2

640 nm and 687 nm



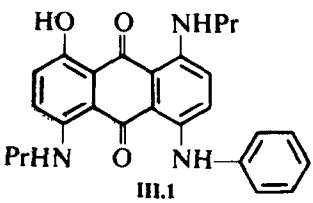
V

640 nm and 688 nm (Ref. 1)



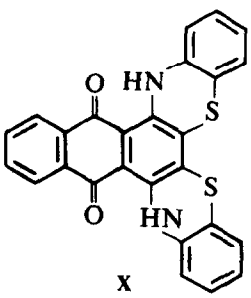
VI

636 nm and 685 nm (Ref. 3)



III.1

665 nm and 719 nm



X

655 nm and 712 nm (in $CHCl_3$; Ref. 12)

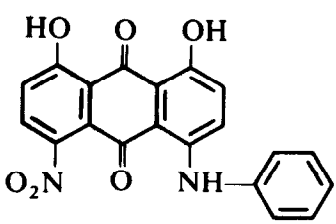
Fig. 1. Absorption maxima of some anthraquinone dyes.

free base and sulphonated forms, more bathochromic in respect of the long-wavelength absorption maxima (>600 nm) than the 1,4-diaminated analogue, Toluidine Green (CI 62560), the greener hue in the latter being due to additional absorption in the 415 nm region.[10]

Alkylation of the 5-amino group in **II** gave the 5-alkylamino derivatives **III**, identical with the compounds obtained on reaction of **I** with alkylamines. The alkylation results in a bathochromic shift of both visible absorption bands of a similar order (25–30 nm) to that obtained on *N*-alkylation of 4-amino-5-alkylamino-1,8-dihydroxyanthraquinones,[1] 4-amino-8-alkylamino-1,5-dihydroxyanthraquinones,[9] 4-amino-8-arylamino-1,5-dihydroxyanthraquinones, and 4-amino-5-arylamino-1,8-dihydroxyanthraquinones.[3] The longer-wavelength absorption of **III** is displaced towards the near-IR, absorption is minimal within the 440–550 nm region, and there is slight blue absorption with a further maximum in the 410–412 nm region (log *e ca.* 3·50). Dyes **III** are thus considerably more bathochromic than 7-hydroxy-14*H*-naphthol[2,3-*a*]-phenothiazine-8,13-dione (λ_{max} 635 nm and 685 nm[11]) and their absorption maxima are of a similar order to that of 11,12-dithia-6*H*,17*H*-6,17-diazadinaphtho[3,2-*a*][2,3-*c*]-5,18-anthraquinone (**X** in Fig. 1) and several of its derivatives,[12] although hypsochromic with respect to the more electron-withdrawing substituted derivatives thereof.

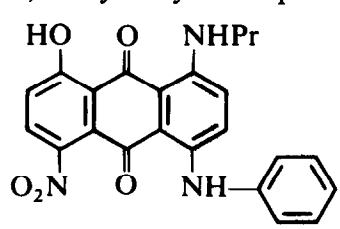
3.3 Dyeing and fastness properties

Colouration properties of **I** on polyester were generally excellent, all dyes building up to deep greenish–blue hues, with hue variation in accord with substituent effects (see above, Section 3.2) in the 4-arylamino residue, and thus not indicative of the very similar long-wavelength absorption maxima of the dyes. Fastness to light was generally good, being of a similar order to those of dyeings of 4-amino-5-arylamino-1,8-dihydroxyanthraquinones[2] and of 4-alkylamino-5-arylamino-1,8-dihydroxyanthraquinones,[3] but lower than those of 4-arylamino-5-nitro-1,8-dihydroxyanthraquinones.[1]



XI

λ_{max} 594 nm and 622 nm
Lightfastness 6–7 (0·1%) 6–7 (0·5%) 6–7 (2·5%)

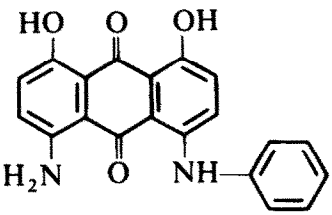


I.4

λ_{max} 625 nm and 675 nm
Lightfastness 5 (0·1%) 5–6 (0·5%) 5–6 (2·5%)

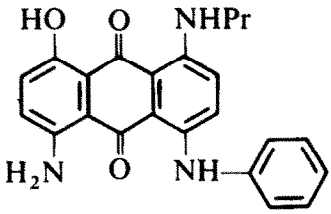
Thus, introduction of an additional amino group into the 1-position (cf. **XI** and **I.4**) whilst giving significant shifts in λ_{max}, also results in a lowering of lightfastness, but not to an unacceptably low order. Sublimation fastness of dyes **I** was generally similar to the values shown by dyes of type **XI**.[2]

The amino derivatives **II** also gave very good colouration of polyester, of a more bluish–green hue compared with **I**, but with lightfastness lower by around 1 unit, viz. a similar order of decrease in lightfastness to that shown on reduction of **X** (cf. **XII** and **II.2**).



XII

λ_{max} 610 nm and 650 nm
Lightfastness 5–6 (0·1%) 5–6 (0·5%) 5–6 (2·5%)



II.2

λ_{max} 640 nm and 687 nm
Lightfastness 4–5 (0·1%) 4–5 (0·5%) 4–5 (2·5%)

The 5-alkylamino derivatives **III.1** gave bright bluish–green hues on polyester of more limited visual build-up than **II**, although dyebath exhaustion was excellent. Alkylation improved the lightfastness to an area midway between **I** and **II**, and sublimation fastness was essentially the same as that of **II**.

CONCLUSIONS

Condensation of 4-arylamino-5-nitro-1,8-dihydroxyanthraquinones with alkylamines in presence of boric acid results in replacement of the 1-hydroxy group, affording a series of dyes which give deep greenish-blue hues of good lightfastness on polyester. Reduction of the 5-nitro group in these dyes gives 1-alkylamino-4-arylamino-5-amino-8-hydroxyanthraquinones, which give greener hues of good build-up but slightly lower lightfastness. The lightfastness is improved, in conjunction with further bathochromic shifts by introduction of an alkylamino substituent into the 5-position.

The presence in di-aminated derivatives of 1,4,5,8-tetra-substituted anthraquinones of a 1,4-diaminated moiety is not totally essential for maximum colour development. The presence of two amino substituents in different rings, in conjunction with other appropriate substitution by hydroxy and/or nitro groups, offers potentially a better combination of bathochromic colour shifts and higher lightfastness. Additional amino groups provide a source of further bathochromic shifts, but at the expense of

lightfastness, which can be improved by *N*-alkylation, such substitution also shifting λ_{max} towards the near-IR.

REFERENCES

1. Peters, A. T., *Dyes and Pigments*, **9** (1988) 167.
2. Peters, A. T. & Chao, Y. C., *J. Soc. Dyers Colourists* (awaiting publication).
3. Lee, C. S. & Peters, A. T., *J. Soc. Dyers Colourists*, **98** (1982) 343.
4. ICI, British Patent 1 341 024 (1970).
5. Shkal'kova, V. I. & Barkov, S. M., *Zhur. Org. Khim.*, **5** (1969) 1274; *Chem. Abstr.*, **71**, 101589).
6. Adams, R. & Kornblum, N., *J. Amer. Chem. Soc.*, **63** (1941) 144.
7. Cadogan, J. I. G. & Molina, G. A., *J. Chem. Soc., Perkin I* (1973) 54.
8. McAlpine, E. & Sinclair, R. S., *J. Soc. Dyers Colourists*, **91** (1975) 399.
9. Fisher, A., Lee, C. S. & Peters, A. T., *J. Chem. Tech. Biotechnol.*, **32** (1982) 532.
10. Allen, C. F. H., Wilson, C. V. & Frame, G. F., *J. Org. Chem.*, **7** (1942) 169.
11. Peters, A. T. & Tenny, B., *Dyes and Pigments*, **1** (1980) 91.
12. Kim, S. H., Matsuoka, M., Kubo, Y., Yodoshi, T. & Kitao, T., *Dyes and Pigments*, **7** (1986) 93.