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Synthesis and Colour–structure Relationships in 1,4,5-Amino-8-hydroxyanthraquinones

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ABSTRACT

Reaction of N-substituted-1,8-dihydroxy-4,5-diaminoanthraquinones with arylamines in the presence of boric acid affords the pertinent 1-aminated derivatives. Replacement of the α-hydroxy group is dependent, in asymmetric 4,5-diaminated derivatives, on the relative basicity of the different amino substituents. The influence of the relative orientation of amino, alkylamino and arylamino substituents on the colour of the products is reported. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Whilst the condensation of 1,8-dihydroxy-4,5-dinitroanthraquinone with arylamines normally affords initially the 4-arylamino-5-nitro derivatives,[1] and thence the 4,5-bis-arylamino products,[2] in the presence of boric acid reaction with alkylamines[3] or arylamines[4] with either 1,8-dihydroxy-4,5-dinitroanthraquinone or 1,8-dihydroxy-4-nitro-5-arylaminoanthraquinones gives 1-aminated-4-arylamino-5-nitro-8-hydroxy derivatives. These compounds colour polyester fibres in blue–green hues of excellent fastness properties. We report here some further reactions of a series of 4,5-bis-aminated, and of 4-nitro-5-aminoanthraquinones with amines in the presence of boric acid, and an evaluation of the course of the reaction, and of colour–structure parameters of the ensuing products **I**–**III**.

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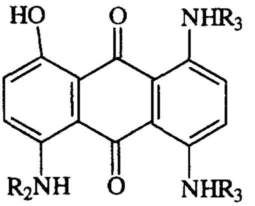
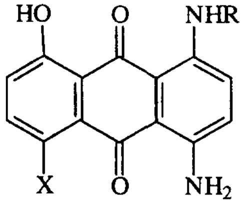


I



II $X = NO_2$

III $X = NH_2$

EXPERIMENTAL

General

Electronic spectra were recorded on a Philips PU 8730 from dye solutions in chlorobenzene and mass spectra (EI) on an AEI MS 902. Column chromatography was carried out on silica gel (for column chromatography, Acros), applying the dyes from solution in toluene or chlorobenzene and eluting with toluene containing up to 10% ethyl acetate as appropriate. TLC monitoring was on Eastman Chromagram Sheets, Type 13181, silica gel, using toluene: ethyl acetate:glacial acetic acid 7:2:1 as eluent.

The anthraquinone derivatives used as start materials were prepared as previously described.[1,5,6]

Syntheses

Phenol (50 g) and boric acid (1.89, 0.93 mol) were stirred for 15 min at 125–130°C, the appropriate anthraquinone derivative (0.01 mol) added and stirring continued at 125–130°C for 40 min. The pertinent alkylamine or arylamine (0.03 mol) was added and reaction continued until all start material had been consumed (TLC monitor, 1–4 h). The liquor was cooled, diluted with methanol (50 ml) and stirred into 5% aq. KOH (400 ml). Stirring was continued until a filterable material resulted (1–4 h) and the product collected and washed with hot water (yields 80–90%). In the case of homogeneous products, final purification was effected by recrystallisation from 2-methoxyethanol; where product mixtures resulted, these were separated using column chromatography.

Reductions, where appropriate, were carried out by standard procedures using sodium sulphide in ethanol.[1]

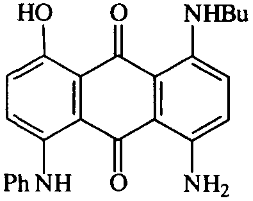
Characterisation data for dyes **I–III** are shown in Table 1, and for dyes **II–III** in Table 2.

RESULTS AND DISCUSSION

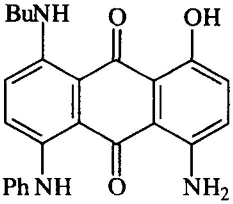
Syntheses

Condensation of the 4,5-diaminated-1,8-dihydroxyanthraquinones with amines proceeded readily in the presence of boric acid, using phenol as reaction medium, following the method previously reported for similar reactions of 4-arylamino-5-nitro-1,8-dihydroxyanthraquinones.[3,4] In the case of symmetrically substituted anthraquinone start materials, the boric acid complexes will be equivalent, irrespective of which hydroxy group is involved, and hence only one mono-condensed product is possible. In general, material recovered from such reactions was homogeneous and could be satisfactorily purified by recrystallisation.

Where the 4- and 5-substituents are dissimilar, reaction can proceed at either the 1- or 8-hydroxy group, with possible resultant formation of isomeric products. It was observed (TLC) that one isomer was usually predominant, with only small amounts of the other isomer; in these cases, column chromatography was used to resolve the mixture. Thus, reaction of 4-anilino-5-amino-1,8-dihydroxyanthraquinone with *sec*-butylamine could yield either **I.4** or **IV**. Column chromatography of the reaction mixture gave, from a higher R_f green zone, 10% of a product showing m/z 401, which was found to be identical to the previously reported compound[3] derived from the condensation of 4-anilino-5-nitro-1,8-dihydroxyanthraquinone with *sec*-butylamine, followed by reduction, viz. **IV**. The major greenish-blue zone gave material also showing m/z 401, and was, therefore, **I.4**. Isomer formation to a similar extent was also observed in the formation of dye **I.3**. Where the reacting amine was an arylamine (dye **I.5**), the minor product was in lower amount (< 5%) and the principal product could be satisfactorily purified by recrystallisation.



I.4



IV

TABLE 1
Characterisation Data for Dyes **I**–**III**

Substituents in the 1,8-dihydroxyanthraquinone starting material 4-	5-	Reacting amine	Dye code	Dyes **I**–**II** R^1	R^2	R^3	m.p. (°C)	% yield[a]	λ_{max} (log ϵ) in chlorobenzene	
NHPr	NHPr	aniline	**I.1**	Pr	Pr	Ph	174–176	82 (R)	672 (4.27)	729 (4.42)
$NHBu^{sec}$	$NHBu^{sec}$	aniline	**I.2**	*sec*-Bu	*sec*-Bu	Ph	163–165	87 (R)	676 (4.25)	730 (4.39)
NH_2	NHPh	propylamine	**I.3**	H	Ph	Pr	223–225	76 (C)	637 (4.31)	686 (4.37)
NH_2	NHPh	*sec*-butylamine	**I.4**	H	Ph	*sec*-Bu	211–213	80 (C)	636 (4.33)	687 (4.38)
NH_2	NHPh	aniline	**I.5**	H	Ph	Ph	301–303	78 (R)	643 (4.30)	693 (4.43)
NHPr	NHPh	propylamine	**I.6**	Pr	Ph	Pr	136–137	80 (C)	664 (4.25)	724 (4.43)
NHPr	NHPh	aniline	**I.7**	Pr	Ph	Ph	166–168	74 (C)	674 (4.31)	723 (4.41)
NHPh	NHPh	propylamine	**I.8**	Ph	Ph	Pr	184–186	72 (R)	665 (4.22)	722 (4.39)
NHPh	NHPh	*sec*-butylamine	**I.9**	Ph	Ph	*sec*-Bu	148–150	76 (R)	666 (4.24)	722 (4.41)

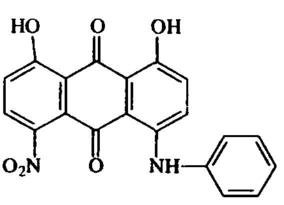
[a] Yields of product from recrystallisation (R) or chromatography (C).

TABLE 2
Characterisation Data for Dyes **II**–**III**

				Dyes **II**–**III** R				
NH_2	NO_2	propylamine	**II.1**	Pr	266–268	87 (R)	599 (4.26)	647 (4.31)
NH_2	NO_2	butylamine	**II.2**	*sec*-Bu	270–271	84 (R)	599 (4.25)	648 (4.33)
NH_2	NO_2	aniline	**II.3**	Ph	282–284	80 (R)	605 (4.23)	649 (4.30)
			III.1	Pr	236–238	89 (R)	615 (4.27)	667 (4.29)
			III.2	*sec*-Bu	196–198	92 (R)	615 (4.26)	667 (4.25)
			III.3	Ph	216–218	90 (R)	622 (4.28)	666 (4.31)

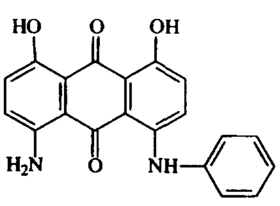
Isomer formation was also minimal in reactions from 4-arylamino-5-alkylaminoanthraquinones; product identity was confirmed by reference to previously reported data.[3,4] Thus, condensation of 4-anilino-5-propylamino-1,8-dihydroxyanthraquinone with aniline gave a product of dissimilar mp and R_f to the known 1,4-bis-anilino-5-propylamino-8-hydroxyanthraquinone.[4] The reaction had, therefore, generated as principal product that resulting from replacement of the 8-hydroxy group, i.e. dye **I.7**.

It is evident, therefore, that when two possible sites for reaction exist, the reaction proceeds preferentially via the OH group in the ring containing the more basic amino substituent. Similar differential reactivity was observed with 4-amino-5-nitro-1,8-dihydroxyanthraquinones, which react in the aminated ring only.[3,4,7–9] Condensation of 4-amino-5-nitro-1,8-dihydroxyanthraquinone occurred selectively in the animated ring, giving good yields of the 1-aminated-4-amino-5-nitro-8-hydroxyanthraquinones (**II**) under the conditions outlined in the section on synthesis. Variations in reaction conditions, such as increase in reaction time and temperature, increased amount of boric acid and reacting amine, and decreased amount of phenol have been shown[8,9] to result in product mixtures containing, e.g. from reaction with aniline, β-phenylamino derivatives.



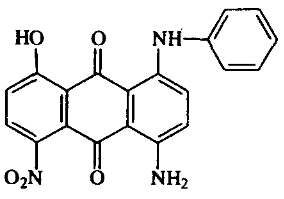
V

λ 594 and 622nm
(Ref 1)



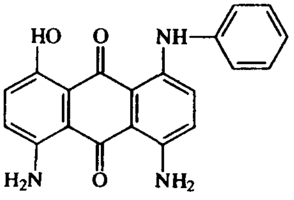
VI

λ 610 and 650nm
(Ref 1)



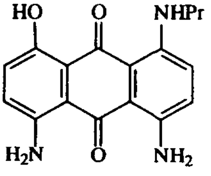
II.3

λ 605 and 648nm



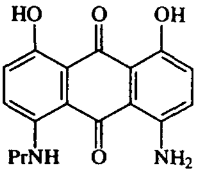
III.3

λ 622 and 666nm



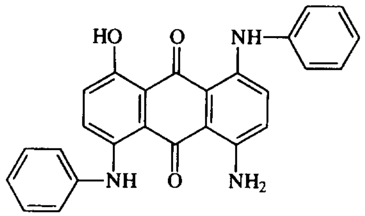
III.1

λ 615 and 667nm



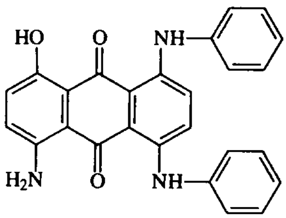
VII

λ 614 and 659nm



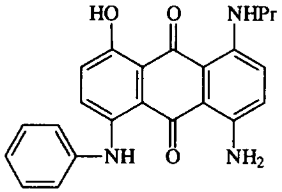
I.5

λ_{max} 643 and 693nm



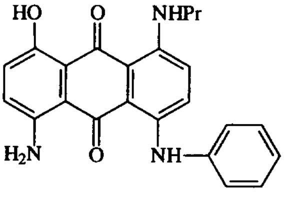
VIII

λ_{max} 646 and 695nm
(Ref 4)



I.3

λ_{max} 637 and 686nm



IX

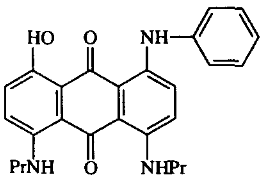
λ_{max} 640 and 687nm
(Ref 3)

Electronic spectra

The nitro derivatives **III** absorb in the general region of 600 and 650 nm, i.e. at somewhat longer wavelength than the monocondensates **V** of 4,5-dinitrochrysazin and arylamines in the absence of boric acid, but of similar wavelength to the reduction products thereof (**VI**). The reduced products **III** show shifts of 15–20 nm for both principal absorption bands relative to **II**, giving values of similar order to those of N-monoalkylated derivatives of 4,5-diaminochrysazin, e.g. **VII**.

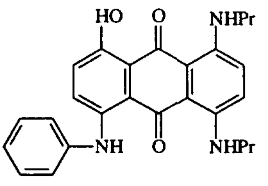
Further N-substitution results in progressive bathochromic shifts. Dyes containing one 1° amino group and two 2° amino groups in a 1,5-orientation (**1.3–1.5**) absorb at similar wavelength to analogues in which the 2° amino groups are in a 1,4-orientation, cf. **I.5** and **VIII**, **I.3** and **IX**.

Interestingly, despite the presence in these dyes of three amino moieties, substituents which usually impart greater colour shifts in anthraquinone dyes than a hydroxy group, the λ_{max} of these derivatives is of a similar order to that of 1,8-dihydroxy-4,5-diaminated dyes, e.g. 1,8-dihydroxy-4-amino-5-propylaminoanthraquinone, λ_{max}, 636 and 685 nm.[5]



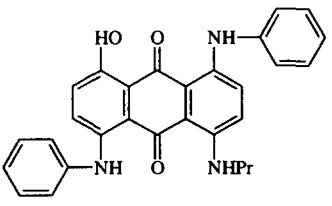
I.1

λ_{max} 672 and 729 nm



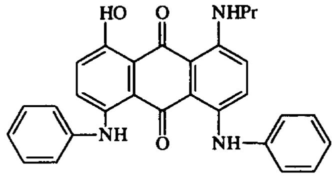
I.6

λ_{max} 664 and 724 nm



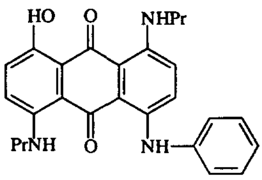
I.7

λ_{max} 674 and 623 nm



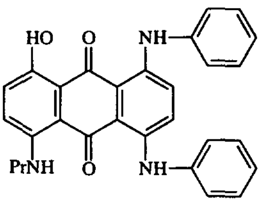
I.8

λ_{max} 665 and 722 nm



X

λ_{max} 665 and 719 nm
(Ref 3)



XI

λ_{max} 668 and 722 nm
(Ref 4)

Significant bathochromic shifts occur on alkylation or arylation of the 1° amino substituent, i.e. dyes **I.1**, **I.2** and **I.6–I.9**. Absorption maxima are of similar order irrespective of whether two alkylamino and one arylamino, or one alkylamino and two arylamino, substituents are present, or on their relative orientation, cf. **I.2**, **I.6–1.8**, **X** and **XI**; 1,4,5-trianilino-8-hydroxyanthraquinone also absorbs in a similar region, viz. 673 and 724 nm.[4]

Whilst the λ_{max} of these triaminated dyes is at longer wavelength than that of 11,12-dithia-6*H*,17*H*,6,17-diazadinaphtho[3,2-*a*][2,3-*c*]5,18-dione (λ_{max} 655 and 712 nm, in $CHCl_3$[10]), the latter compound contains an unsubstituted phenyl ring in the anthraquinone moiety and by appropriate substitution, NIR absorbing colorants can be obtained.[11] Dyes **I** offer more limited possibilities for further extension of λ_{max} to longer wavelength. Only by replacement of the residual hydroxy group by a further amino substituent can further shifts be induced, as in 1,4,5,8-tetra-arylaminoanthraquinones, e.g. 1,4,5,8-tetra-anilinoanthraquinone, λ_{max} 700 and 750 nm.[12]

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