Substituent effects on the colour, dyeing and fastness properties of 4-arylamino-5-nitro-(and amino)-1,8-dihydroxyanthraquinone and 4-arylamino-8-nitro-(and amino)-1,5-dihydroxyanthraquinone disperse dyes

A T Peters* and Y C Chao†

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

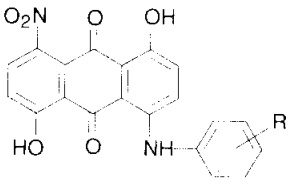
†Dept of Textile Industries, National Taipei Institute of Technology, Taipei, Taiwan (ROC)

Condensation of arylamines with 4,5-dinitro-1,8-dihydroxyanthraquinone and 4,8-dinitro-1,5-dihydroxyanthraquinone afforded the corresponding 4-arylamino derivatives, reduction of which gave 4-arylamino-5-amino-1,8-dihydroxyanthraquinones. The influence of various electron donor and acceptor substituents in the arylamino residue is assessed and dyeing and fastness properties of the dyes on polyester evaluated. Comparison is also made between the bromo-substituted derivatives obtained by bromination of the 4-anilino derivatives with those unambiguously synthesised from condensations with bromoanilines

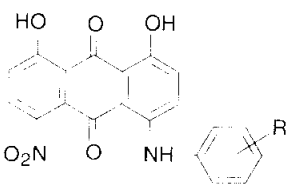
INTRODUCTION

The condensation of 1,8-dihydroxy-4,5-dinitroanthraquinone (DNCZ) and of 1,5-dihydroxy-4,8-dinitroanthraquinone (DNAR) with arylamines gives the respective 4-arylamino derivatives, which are blue dyes of good fastness properties on synthetic-polymer fibres. An extensive range of substituent groups in the arylamino residue have been described in patent specifications and several dyes of this type, or their reduction products, have been introduced as industrial colorants, e.g. 4-amino-8-anilino-1,5-dihydroxyanthraquinone (C.I. 63300), 4-nitro-8-(4-hydroxyethyl)anilino-1,5-dihydroxyanthraquinone (C.I. Disperse Blue 27) and 4-amino-8-(3-sulphonamidoanilino)-1,5-dihydroxyanthraquinone (C.I. Disperse Blue 40).

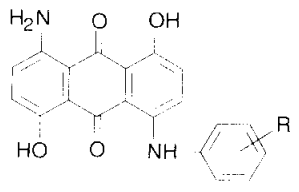
As part of a general study of colour and constitution relationships in dyes derived from DNAR and DNCZ, data for 4-alkylamino-8-anilino-1,5-dihydroxyanthraquinones and 4-alkylamino-5-anilino-1,8-dihydroxyanthraquinones [1], *N*-alkylated-4,8-diamino-1,5-dihydroxyanthraquinones [2] and *N*-alkylated-4-5-diamino-1,8-dihydroxyanthraquinones [3] and of some analogous thioether derivatives [3] have previously been reported. We report here the synthesis of a series of 4-arylamino-8-nitro-1,5-dihydroxyanthraquinones (I), 4-arylamino-5-nitro-1,8-dihydroxyanthraquinones (II) and of the corresponding amino derivatives (III and IV), and an evaluation of the influence of various electron donor and acceptor substituents (R) on the colour of these dyes.



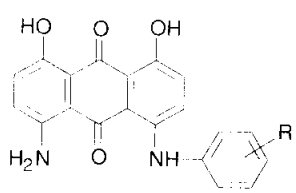
I



II



III



IV

EXPERIMENTAL

Preparation of dyes I and II

Method A

DNAR (3.3 g, 0.01 mol) and aniline (3.72 g, 0.04 mol) were refluxed in 2-methoxyethanol (60 ml) for 5.25 h. The mixture was cooled to room temperature and stirred into ice-cold 5% aqueous hydrochloric acid (200 ml). The blue solid was filtered, washed neutral with warm water (3.5 g, 93%) and recrystallised from 2-methoxyethanol (Norit) in dark brown needles with a metallic lustre, m.p. 222–223°C, of 4-anilino-8-nitro-1,5-dihydroxyanthraquinone (I.1).

From DNAR or DNCZ and the appropriate arylamine were similarly obtained dyes I.2–I.11 (Table 1) and II.1–II.11 (Table 2). Reactions were monitored by t.l.c. and reaction times varied, with DNAR from 1.5 h (4-methoxyaniline) to 16 h (1-naphthylamine) and with DNCZ from 2 h (4-ethoxyaniline) to 30 h (2-toluidine).

Method B

A mixture of DNAR (3.3 g, 0.01 mol) and ethyl-4-aminobenzoate (6.6 g, 0.04 mol) was stirred under reflux in nitrobenzene (45 ml) for 3.5 h. The reaction liquor was cooled, diluted with methanol (200 ml) and filtered. The residue (3.3 g, 73%) was washed with hexane (100 ml), methanol (3 × 10 ml) and warm water and finally recrystallised from 2-methoxethanol in lustrous dark brown plates,

TABLE 1

Characterisation and fastness data for dyes I

Dye	R	M.p. (°C)	λ_{max} (nm) (log ε) in chlorobenzene		Dyeings on polyester				
					λ_{max}(E) (nm)[a]	Light fastness 0.1%	0.5%	2.5%	Sublimation temp. (°C)
I.1	H	222–223	589 (4.10)	620 (4.10)	608	6–7	6–7	6–7	160
I.2	2-Me	240–241	578 (4.09)	618 (4.14)	602	6–7	6–7	6–7	170
I.3	3-Me	231–232	592 (4.12)	622 (4.15)	609	6–7	6–7	6–7	160
I.4	4-Me	250–251	594[b] (4.10)	621 (4.14)	612	6–7	6–7	6–7	170
I.5	2-OMe	286–287	586[b] (4.01)	620 (4.03)	606	6–7	6–7	6–7	160
I.6	3-OMe	214–215	590 (4.11)	621 (4.11)	608	6–7	6–7	6–7	160
I.7	4-OMe	211–212	591[b] (4.09)	622 (4.15)	612	6–7	6–7	6–7	160
I.8	4-OEt	219–220	593[b] (4.10)	622 (4.14)	612	6–7	6–7	6–7	170
I.9	$-NHC_{10}H_7$-1[c]	173–174	576 (4.10)	616 (4.15)	607	5	6	5–6	180
I.10	3-CH(OH)Me	212–213	591 (4.15)	622 (4.17)	611	6	6	6	170
I.11	$4\text{-}C_2H_4OH$	262–263	591[b] (4.13)	624 (4.09)	611	6	6–7	6–7	180
I.12	4-NHCOMe	312–313	592[b] (4.15)	621 (4.21)	618	6–7	6–7	6–7	200
I.13	4-NHCOPh	308–309	590[b] (4.13)	622 (4.17)	616	6–7	6–7	6–7	200
I.14	$4\text{-}N(CH_3)COPh$	295–297	592 (4.12)	618 (4.12)	610	6	6	6–7	210
I.15	4-COOEt	237–238	589 (4.09)	623 (4.08)	603	6–7	6–7	6–7	190
I.16	4-COMe	284–285	590 (4.14)	623 (4.13)	606	6–7	6–7	6–7	190
I.17	4-COPh	260–261	590 (4.15)	623 (4.14)	607	6–7	6–7	6–7	200
I.18	$4\text{-}SO_2NH_2$	292–293	583 (4.16)	620 (4.14)	600	6–7	6–7	6–7	200
I.19	$4\text{-}NO_2$	323–324	580 (4.12)	619 (4.10)	598	5	5–6	5–6	190

(a) λ_{max}(E) – value from extrapolated curves (see text)
(b) 4-substituent is 1-naphthylamino group
(c) λ_{max} values, inflexion

m.p. 237–238°C of 4-(4-carboethoxy)anilino-8-nitro-1,5-dihydroxyanthraquinone (I.15).

By a similar method were obtained, from DNAR, dyes I.12–I.25 (Tables 1 and 3) (reaction times from 2.5 h for 4-chloroaniline to 40 h for 4-nitroaniline) and, from DNCZ, dyes II.12–II.25 (Tables 2 and 5) (reaction times from 5 h for 4-chloroaniline to 60 h for 4-nitroaniline).

Bromination of dyes I.1 and II.1

4-Anilino-5-nitro-1,8-dihyroxyanthraquinone (II.l) (3.76 g, 0.01 mol) was stirred into glacial acetic acid (60 ml) at 50°C and a solution of bromine (1.68 g, 0.0105 mol) in glacial acetic acid (25 ml) was added dropwise over 30 min. The mixture was stirred for 6 h at 75–80°C, cooled and run into ice-water (300 ml). The resultant product (II.26) (4.5 g) contained 18.37% Br (calculated for monobromo derivative, 17.6%). Also obtained from dye II.1 and bromine (0,025 mol) was dye II.27 (after 10 h reaction), containing 27.69% Br (calculated for dibrominated derivative, 29.96% Br). From dye I.1 and bromine (0.0105 mol) dye I.26 was obtained (after 9 h reaction), containing 17.06% Br; while from dye I.1 and bromine (0.025 mol) dye I.27 was obtained (after 14 h reaction), containing 26.59% Br. Characterisation data for these are shown in Table 3.

Preparation of dyes III and IV

A mixture of dye I.1 (2 g) and hydrated sodium sulphide (1.5 g) was stirred at 80°C for 1 h in ethanol (100 ml). The liquor was cooled, diluted with water (50 ml) and filtered to give 4-amino-8-anilino-1,5-dihydroxyanthraquinone (III.1) (1.8 g, 96%) m.p. 257–258°C (2-methoxyethanol).

By using a similar procedure dyes III.2–III.17 (Table 4) and IV.1–IV.17 (Table 5) were obtained.

Spectra and fastness assessment

Electronic spectra were recorded on a Unicam SP800, with solutions of dye in monochlorobenzene at a concentration of 6×10^{-4} mol/l. Dyeing of polyester and assessment of the light and sublimation fastness of the dyeings were carried out as for related dyes in previous investigations [1–3].

RESULTS AND DISCUSSION

Condensation of DNAR and DNCZ with arylamines has been extensively cited in patent specification and various condensation media have been utilised for such condensations, e.g. using arylamines [4] or aqueous arylamine [5] as reactant and reaction medium, or organic solvents such as 2-methoxyethanol [6], 2-ethoxyethanol [7], quinoline [8], 1-pentanol [9], nitrobenzene [10], 2-(2-ethoxyethoxy) ethanol [11], 1-chloronaphthalene [12] and DMF [13]. Whilst for the more reactive arylamines the use of reaction temperatures of 120–125°C (e.g. by refluxing in 2-methoxyethanol) has been concluded to give the best conditions for avoiding the formation of bis-aminated derivatives [14], higher boiling solvents are necessary in attaining a facile monocondensation reaction with elec-

TABLE 2

Characterisation and fastness data for dyes II

Dye	R	M.p. (°C)	λ_{max} (nm) (log ε) in chlorobenzene		λ_{max}(E) (nm)[a]	Dyeings on polyester: Light fastness 0.1%	0.5%	2.5%	Sublimation temp. (°C)
II.1	H	247–248	594 (4.09)	622 (4.09)	610	6–7	6–7	6–7	170
II.2	2-Me	239–240	581 (4.07)	618 (4.11)	604	6–7	6–7	6–7	170
II.3	3-Me	233–234	595[b] (4.11)	620 (4.13)	612	6–7	6–7	6–7	170
II.4	4-Me	242–243	597[b] (4.09)	622 (4.13)	615	6–7	6–7	6–7	170
II.5	2-OMe	243–244	584[b] (4.07)	620 (4.09)	608	6–7	6–7	6–7	180
II.6	3-OMe	218–219	596[b] (4.07)	621 (4.09)	612	6–7	6–7	6–7	170
II.7	4-OMe	219–220	590[b] (4.07)	622 (4.10)	617	6–7	6–7	6–7	180
II.8	4-OEt	230–231	594[b] (4.05)	621 (4.10)	618	6–7	6–7	6–7	170
II.9	$-NHC_{10}H_7$-1[c]	245–246	584[b] (4.06)	617 (4.08)	609	4–5	5	5	180
II.10	3-CH(OH)Me	237–238	592[b] (4.14)	623 (4.15)	612	6	6–7	6–7	170
II.11	$4\text{-}C_2H_4OH$	205–206	598[b] (4.08)	622 (4.09)	614	6	6–7	6	180
II.12	4-NHCOMe	301–302	588[b] (4.06)	621 (4.13)	618	6–7	6–7	6–7	210
II.13	4-NHCOPh	322–324	585[b] (4.04)	622 (4.07)	618	6–7	6–7	6–7	210
II.14	$4\text{-}N(CH_3)COMe$	238–239	592 (4.08)	620[b] (4.07)	610	6	6–7	6–7	190
II.15	4-COOEt	258–259	592 (4.13)	622 (4.13)	606	6–7	6–7	6–7	190
II.16	4-COMe	240–241	592 (4.10)	624 (4.10)	607	6–7	6–7	6–7	190
II.17	4-COPh	286–287	594 (4.11)	623 (4.10)	610	6–7	6–7	6–7	210
II.18	$4\text{-}SO_2NH_2$	296–297	584 (4.08)	619 (4.07)	601	6–7	6–7	6–7	200
II.19	$4\text{-}NO_2$	326–328	580 (4.16)	618 (4.14)	600	5	5–6	5–6	200

(a), (b) and (c) – for key see Table 1

tron acceptor substituted arylamines.

In this present investigation either 2-methoxyethanol or nitrobenzene was used as reaction medium and, with a four molar ratio of arylamine, complete elimination of the DNAR or DNCZ from the mixture was effected in 2.5–60 h, depending on the anthraquinone intermediate used and the arylamine (see Experimental section). Excess arylamine is necessary in view of the elimination, during the nucleophilic replacement of the nitro group, of oxides of nitrogen and possible subsequent reaction of these with arylamine.

A series of condensations of DNAR and DNCZ (0.495 g, 1.5×10^{-3} mol) with varying amounts of aniline (from 1.5×10^{-3} mol to 7.5×10^{-3} mol) in a total volume of 150 ml with 2-methoxyethanol was evaluated, using reaction times of up to 120 h. Assessment of the conversion to dyes I.1 and II.1 was effected spectrophotometrically and also by recovery of the reaction product via column chromatography. With DNAR and 1 mol equivalent of aniline, approx. 50% conversion to dye I.1 was attained in about 20 h and no further reaction occurred after 120 h, thus indicating that about half of the aniline had been inactivated by the liberated nitrogen oxides. Only on increasing the ratio of aniline to 2 mol was a significant increase in the formation of dye I.1 apparent, almost quantitative conversion occurring after 40 h. For effective dye formation in a shorter reaction time, 4 mol aniline was used and this resulted in satisfactory formation of dye I.1 in around 5 h.

Similar reactions with DNCZ were less facile and with 1 mol aniline only 40% conversion to dye II.1 was possible. Even with 2 mol aniline the yield of dye II.1 was only 60–70% after 100 h reaction; use of 4 mol aniline afforded complete reaction of the DNCZ after 6.5 h.

This necessity for greater than stoichiometric amounts of arylamine is in accord with previous studies [15] on the reaction between DNCZ and 3-aminobenzenesulphonamide in nitrobenzene. Monitoring of the reaction chromatographically indicated an optimum requirement of at least a three molar excess of arylamine, principal reaction by-products being 4-5-diaminochrysazin and 2,4,5-trinitrochrysazin.

Electronic spectra data of dyes I and II are shown in Tables 1 and 2 respectively. All the dyes showed a double peak in the principal visible absorption band, generally incompletely resolved. The origin of the twin peak has been the subject of several studies and has been concluded, for 1,4-disubstituted derivatives, to be most probably related to coupling between vibrational modes of the ring system and the electronic charge-transfer transition [16]. Comparison of the anthrarufin (I) and chrysazin derivatives (II) shows the latter to be slightly more bathochromic. This observation is consistent with previous comparisons of analogous anthrarufin and chrysazin derivatives and possible explanations for it have been discussed [3]. Despite the variety of electron donor and acceptor substituents utilised, the absorption maxima of dyes I and II are relatively insensitive to substituent changes. Taking dyes of structure I as illustrative, it might have been assumed that electron delocation structures either enhancing electron availability on the imino nitrogen atom (V, for electron donor substituents) or decreas-

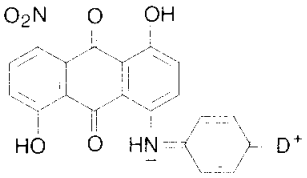
TABLE 3

Characterisation and fastness data for halogenated derivatives of dyes I and II

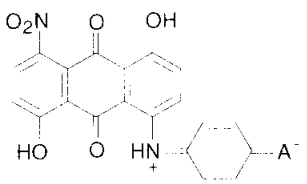
Dye	R	M.p. (°C)	λ_{max} (nm) (log ε) in chlorobenzene		Dyeings on polyester: λ_{max}(E) (nm)[a]	Light fastness 0.1%	Light fastness 0.5%	Light fastness 2.5%	Sublimation temp. (°C)
I.20	2-Cl	255–256	584[b] (4.18)	608[b] (4.19)	595	6–7	6–7	6–7	170
I.21	3-Cl	240–241	618 (4.21)	618 (4.21)	604	6–7	6–7	6–7	160
I.22	4-Cl	275–276	588 (4.21)	618 (4.21)	606	6–7	6–7	6–7	180
I.23	2-Br	279–280	582[b] (4.08)	606 (4.09)	593	6–7	6–7	6–7	180
I.24	3-Br	244–245	584 (4.18)	619 (4.17)	602	6–7	6–7	6–7	170
I.25	4-Br	277–278	589 (4.15)	619 (4.15)	606	6–7	6–7	6–7	180
I.26	(17.06% Br)	259–260	588 (4.16)	618 (4.16)	605	6–7	6–7	6–7	180
I.27	(26.59% Br)	228–229	586[b] (4.10)	607 (4.11)	594	6–7	6–7	6–7	190
II.20	2-Cl	253–254	579[b] (4.08)	607 (4.08)	598	6–7	6–7	6–7	170
II.21	3-Cl	252–253	587 (4.20)	619 (4.19)	605	6–7	6–7	6–7	180
II.22	4-Cl	261–262	596 (4.17)	618 (4.17)	607	6–7	6–7	6–7	180
II.23	2-Br	250–251	580[b] (4.10)	607 (4.12)	597	6–7	6–7	6–7	180
II.24	3-Br	259–260	581 (4.13)	618 (4.11)	605	6–7	6–7	6–7	180
II.25	4-Br	253–254	596 (4.15)	618 (4.15)	609	6–7	6–7	6–7	180
II.26	(18.37% Br)	236–238	594 (4.16)	616 (4.17)	609	6–7	6–7	6–7	180
II.27	(27.69% Br)	262–264	581 (4.12)	606 (4.13)	596	6–7	6–7	6–7	190

(a), (b) and (c) – for key see Table 1

ing it (VI, for electron attracting substituents), with consequent increase or decrease in interactions between the imino nitrogen atom and the adjacent carbonyl oxygen atom, would give bathochromic or hypsochromic shifts respectively in the visible absorption maxima. That such substituents do influence the electron density on the imino nitrogen atom is evidenced by their modifying the reactivity of the imino group to burnt gas fumes, a factor which has been utilised in the synthesis of gas-fast blue colorants for cellulose secondary acetate [4]. Similarly structural changes in the arylamino residue are widely utilised in anthraquinonoid acid dyes to modify the colour range of derivatives of, for example, quinizarin [17] or of 1-amino-4-bromoanthraquinone-2-sulphonic acid [17,18].



V



VI

However, in dye structures I and II bathochromic shifts resulting from the presence of donor substituents in the anilino residue are minimal (dyes I.2–I.14 and II.2–II.14), being of the general order of 0–3 nm for both absorptions, although in some cases slightly larger shifts are apparent, e.g. the 4-toluidino derivatives I.4 and II.4 and the 4-(2-hydroxyethyl)anilino derivatives I.11 and II.11, both of which give slightly larger shifts than the more strongly electron donor 4-acylaminoanilino dyes I.12, I.13, II.12 and II.13. However, several of the electron acceptor substituted dyes also show small bathochromic shifts (I.15–I.17 and II.15–II.17) and it is only with the more strongly acceptor sulphonamido (I.18, II.18) and nitro (I.19, II.19) derivatives that hypsochromic shifts are observed, principally in the lower wavelength absorption. Hypsochromic shifts are also apparent in the 2-toluidino (I.2, II.2) and the 1-naphthylamino derivatives (I.9, II.9) (and also in the 2-halogeno derivatives, see below), and these can be rationalised in terms of steric factors rather than polar effects, originating in twisting around the C–N bond due to steric crowding factors or to repulsion between the 2-substituent and the adjacent CH group of the anthraquinone ring. A similar but less pronounced effect is apparent in the 2-anisidino derivatives (I.5, II.5) in which the methyl group is in a position of freer rotation.

In the reduced derivatives III and IV both absorption bands are shifted to longer wavelengths relative to those in the equivalent structures in the I and II series respectively, commensurate with the introduction of an additional donor function into the dye system. These shifts tend to be slightly greater for the chrysazin derivatives, about 25 nm for the longer wavelength band, than the anthrarufin analogues (approx. 20 nm). Whilst electron acceptor substituents in the phenyl ring give hypsochromic shifts (III.14–III.17, IV.14–IV.17), introduction of electron donor substituents does not give an overall bathochromic effect. Steric factors in the 2-toluidino (III.2, IV.2) and 1-naphthylamino derivatives (III.9, IV.9) are again apparent, hypsochromic shifts resulting, but the general pattern for the alkyl, alkoxy and acylamino substituted dyes is one of a small bathochromic shift in the lower wavelength inflexion and a small hypsochromic shift in the longer wavelength absorption.

The above variable shifts do not follow the more well

TABLE 4

Characterisation and fastness data for dyes III

Dye	R	M.p. (°C)	λ_{max} (nm) (log ε) in chlorobenzene		Dyeings on polyester				
					λ_{max}(E) (nm)[a]	Light fastness 0.1%	0.5%	2.5%	Sublimation temp. (°C)
III.1	H	257–258	605 (4.20)	644 (4.28)	630	5–6	5–6	5–6	160
III.2	2-Me	207–208	600 (4.19)	638 (4.28)	626	5–6	5–6	5–6	160
III.3	3-Me	248–249	606 (4.24)	644 (4.29)	630	5–6	5–6	5–6	160
III.4	4-Me	237–238	608[b] (4.27)	643 (4.31)	634	5–6	5–6	5–6	160
III.5	2-OMe	216–217	602[b] (4.10)	638 (4.24)	629	5–6	5–6	5–6	160
III.6	3-OMe	205–206	606 (4.07)	640 (4.15)	630	5–6	5–6	5–6	160
III.7	4-OMe	208–209	608[b] (4.16)	641 (4.25)	634	5–6	5–6	5–6	170
III.8	4-OEt	228–229	612[b] (4.17)	640 (4.22)	634	5–6	5–6	5–6	160
III.9	$NHC_{10}H_7$-1[c]	257–258	601[b] (4.20)	635 (4.31)	629	4–5	4–5	4–5	180
III.10	3-CH(OH)Me	205–206	605 (4.23)	644 (4.31)	630	5–6	5–6	5–6	170
III.11	4-C_2H_4OH	225–226	606 (4.23)	641 (4.32)	632	5–6	5–6	5–6	170
III.12	4-NHCOMe	328–329	610[b] (4.24)	643 (4.32)	634	5–6	5–6	5–6	200
III.13	4-NHOPh	306–307	610[b] (4.20)	643 (4.29)	636	5–6	5–6	5–6	200
III.14	4-COOEt	285[d]	598 (4.27)	639 (4.37)	628	5–6	5–6	5–6	210
III.15	4-COMe	258–259	603 (4.26)	640 (4.33)	629	5–6	5–6	5–6	180
III.16	4-COPh	285–286	602 (4.29)	639 (4.36)	632	5–6	5–6	5–6	190
III.17	4-SO_2NH_2	295–296	595 (4.30)	635 (4.38)	624	5–6	5–6	5–6	200

(a), (b) and (c) – for key see Table 1
(d) Sublimes

defined pattern observed in simpler substituted arylaminoanthraquinones and related derivatives. Thus, in 1-anilinoanthraquinones, substituent effects in the phenyl ring can modify the absorption maxima of the parent compound (λ_{max} 508 nm, ethanol) from 482 nm with the acceptor substituted 4'-nitroanilino compound to 521 nm for the donor substituted 4-*N*,*N*-dimethylamino derivative [19]. Similar orders of shift for 1-anilinoanthraquinones have also been observed in the relatively non-polar *o*-dichlorobenzene, e.g. 1-anilino, λ_{max} 508 nm; 1,4'-nitroanilino, λ_{max} 487 nm and 1,4'-aminoanilino, λ_{max} 525 nm, and correlations between substituent effects and Hammett σ-constants established in these compounds [20]. Correlations between the shift in λ_{max} and Hammett σ constants (or related parameters) of substituents in the phenyl ring have also been demonstrated for 1-benzoylaminoanthraquinones [21], 7-substituted 3,4-phthaloylacridones [22], 1-amino-4-benzoylaminoanthraquinones [24] and 1,4-bis-benzoylaminoanthraquinones [24,25].

In 1,4,5,8-tetra-donor-substituted anthraquinones there are extensive possibilities for charge transfer interactions [26] and it is feasible to consider that, relative to these, the additional influence of substituent R in structures III and IV (and, by analogy, to some extent in I and II) is not significant enough to produce the range of colour shifts in simpler mono- and di-substituted derivatives. Nonetheless, noticeable colour changes are apparent on application of dyes of structures I–IV to polyester, and the influence of the substituent R has a significant effect. The nitroarylaminochrysazin derivatives II are greener in hue than analogous anthrarufin isomers I and in each series introduction of electron donor substituents (with the exception of the 2-methyl group) results in a greener hue, and of electron acceptor substituents a redder hue, with slight variations within each type depending on the polar character of the substituent. A similar ability to 'fine tune' the hue is apparent in the reduced derivatives III and IV, all of which are considerably greener than analogous derivatives I and II. These colour differences, apparent when the dyes are applied to polyester, are all generally in accord with those anticipated on the basis of the steric and electronic characteristics of the substituent groups R, but are not fully reflected in the λ_{max} values. This clearly demonstrates the difficulties that can ensue in relating λ_{max} values to the visually observed colour on a textile substrate, although the latter can also be influenced by factors other than electronic spectra characteristics, e.g. dye aggregation. Within a series of chemically closely related dyes, however, some relationship might be expected.

In the case of dyes I–IV extinction coefficients, particularly of I and II, are not of a relatively high order (in the region of 15 000) compared to aminoazobenzene-based blue disperse dyes (20 000–60 000). Absorption bands are very broad, and whilst showing incompletely resolved maxima in the 580–620 nm range, the overall absorption extends within the general range of 490–710 nm. At the concentration used in the spectral measurements the dyes I and II had half bandwidths in the 120–130 nm region and in many dyes, whilst shifts in absorption at ε_{max} were very small, somewhat larger displacements in the absorption at $\varepsilon_{max}/2$ were apparent, such displacements tending to be more in accord with the colour shifts concluded on the basis of the polar effects of the substituents R. For

TABLE 5

Characterisation and fastness data for dyes IV

Dye	R	M.p. (°C)	λ_{max} (nm) (log ε) in chlorobenzene		λ_{max}(E) (nm)[a]	Dyeings on polyester: Light fastness 0.1%	0.5%	2.5%	Sublimation temp. (°C)
IV.1	H	243–244	610 (4.22)	650 (4.21)	637	5–6	5–6	5–6	160
IV.2	2-Me	223–224	608[b] (4.20)	643 (4.24)	634	5–6	5–6	5–6	160
IV.3	3-Me	211–212	612[b] (4.22)	648 (4.30)	637	5–6	5–6	5–6	160
IV.4	4-Me	249–250	610[b] (4.21)	649 (4.32)	638	5–6	5–6	5–6	160
IV.5	2-OMe	233–234	612[b] (4.15)	644 (4.19)	635	5–6	5–6	5–6	160
IV.6	3-OMe	213–214	613 (4.22)	647 (4.28)	636	5–6	5–6	5–6	160
IV.7	4-OMe	227–228	614[b] (4.24)	647 (4.34)	638	5–6	5–6	5–6	160
IV.8	4-OEt	236–237	616[b] (4.22)	647 (4.31)	638	5–6	5–6	5–6	160
IV.9	$-NHC_{10}H_7$-1[c]	267–268	613[b] (4.22)	640 (4.29)	636	4–5	4–5	4–5	180
IV.10	3-CH(OH)Me	219–220	613 (4.27)	649 (4.35)	635	5–6	5–6	5–6	160
IV.11	$4\text{-}C_2H_4OH$	222–223	610[b] (4.17)	648 (4.26)	638	5–6	5–6	5–6	160
IV.12	4-NHCOMe	294–295	614[b] (4.22)	648 (4.30)	640	5–6	5–6	5–6	200
IV.13	4-NHCOPh	309–310	614[b] (4.26)	648 (4.34)	640	5–6	5–6	5–6	210
IV.14	4-COOEt	290[d]	606 (4.21)	640 (4.28)	629	5–6	5–6	5–6	210
IV.15	4-COMe	274–275	608[b] (4.25)	640 (4.30)	630	5–6	5–6	5–6	200
IV.16	4-COPh	309–310	606 (4.26)	640 (4.33)	629	5–6	5–6	5–6	200
IV.17	$4\text{-}SO_2NH_2$	289–290	599 (4.20)	638 (4.29)	627	5–6	5–6	5–6	200

(a), (b) and (c) – for key see Table 1
(d) Sublimes

example, dye I.1 shows absorptions in the 535 and 665 nm regions at $\varepsilon_{max}/2$; similar values for the 4-anisidino derivative (I.7) are 550 and 680 nm and for the 4-nitroanilino derivative (I.19) 525 and 650 nm. These bathochromic and hypsochromic shifts in the absorption at $\varepsilon_{max}/2$ show the effect more clearly of electron donor and electron acceptor substituents in the phenyl ring and are more in accord with the expected colour shifts, which are apparent on dyeing but not in the λ_{max} values.

In view of the broad incompletely resolved absorption bands in the region of ε_{max}, the absorption curves were 'approximated' into a single smooth absorption band by extrapolating from the inflexion point into a smooth composite absorption band with more clearly defined maxima, incorporating both the inflexion and maximum of the original spectra. Absorption values thus derived for dyes I–IV are given in Tables 1, 2, 4 and 5 respectively as λ_{max}(E) values and it is apparent that they reflect the relative influence of the polar character of substituents R very well. Thus the chrysazin derivatives II and IV are all bathochromic (2–6 nm for the nitro derivatives I and 3–7 nm for the amino derivatives IV) with respect to analogous anthrarufin isomers I and III. Electron donor substituents R in the phenyl ring are, with the exception of sterically hindered 2-substituted derivatives, all bathochromic, the more strongly donor 4-alkoxy and 4-amino based derivatives giving the largest shifts. All dyes containing electron acceptor substituents R show hypsochromic shifts, in contrast to the values observed in the normal incompletely resolved spectra, and the steric crowding resulting from 2-methyl, and especially the 2-halogeno, substitution is clearly indicated.

Such λ_{max}(E) values can only be regarded as an approximation, but their usefulness in qualitative assessments in cases where the complexity of the normal absorption bands obscures substituent effects is clearly indicated in the dyes I–IV. We have additionally found such values to be helpful in relating substituent effects to colour changes in other related series of anthraquinone disperse dyes [27] and in rationalising anticipated shifts in λ_{max} and hue changes in dyeings in cases where the observed λ_{max} values do not adequately reflect such changes.

Whilst the coloration properties of dyes I and II on cellulose secondary acetate can vary significantly depending on whether they are chrysazin or anthrarufin based and on the nature and orientation of the substituents in the phenyl ring [14], the higher application temperatures used for the coloration of polyester tends to level out such differences. Dyes I and II gave generally good build-up, the weakest dyeings being obtained with the 4-benzamido derivatives I.13 and II.13. The reduced analogues (III and IV) gave deeper dyeings of a much greener hue and dyeing properties were similar to those of related dyes substituted in the primary amino group [2]. Both sublimation and light fastness properties of dyes III and IV were similar to those shown by the alkylaminoanilino derivatives [2] and the higher sublimation fastness values for some dyes in Tables 4 and 5 is relatable to their slightly weaker build-up relative to other dyes in the series. Fastness properties of dyes I and II are generally superior, particularly light fastness; the 4-nitroanilino derivatives I.19 and II.19, whilst having the lowest fastness, are still of an acceptably good order. In general the nitro derivatives I and II have inferior build-up but better fastness while the amino derivatives III and IV

show better build-up and greener hue, but lower fastness.

The halogenated derivatives I.22–I.25 and II–25 gave redder hues, particularly the 2-substituted derivatives, and slightly brighter dyeings than the parent anilino derivatives I.1 and II.1. These dyes, particularly the bromo derivatives, showed an improvement in sublimation fastness, in accordance with the increased molecular weight of the dyes. The use of halogenated derivatives has been described in patent specifications, e.g. by condensation of chloroanilines [28] or halogenomethylanilines [29] with DNAR or DNCZ, and also by bromination of the condensates of DNAR and DNCZ with aniline, toluidines or chloroanilines [30].

Compounds I.26, I.27 and II.26–II.28 (see Experimental section) were obtained by bromination of the anilino derivatives I.1 and II.1 to an extent approximating to mono- and di-bromination. These dyes gave similar hues and build-up to the unambiguously synthesised derivatives. The monobrominated products I.26 and II.26 equated to the 4-bromoanilino derivatives I.25 and II.25 respectively and the dibrominated products I.27 and II.28 coloured the redder hue of the 2-bromoanilino derivatives I.23 and II.23 respectively. Fastness to light and sublimation of the resultant dyeings were identical to those of I.23–I.25 and II.23–II.25. Both λ_{max} and λ_{max}(E) values (Table 3) of the monobrominated compounds were comparable to those of the analogous 4-bromoanilino derivatives, and of the dibrominated compounds to those of analogous 2-bromoanilino derivatives. These colour shifts are indicative of bromination occurring essentially in the phenyl ring, particularly with respect to the hypsochromic shift resultant on introduction of the second bromine atom. This shift is relatable to 2-substitution in the phenyl ring (cf. I.23 and II.23), since bromination of, for example, diaminodihydroxyanthraquinones *ortho* to either the amino or the hydroxy groups in the anthraquinone ring results in bathochromic shifts of up to 14 nm for monobromination and up to 24 nm for dibromination [31]. The mono-condensation products of 2-bromo-DNCZ and 2,7-dibromo-DNCZ with aniline have λ_{max} values at 601/629 and 606/640 nm [27], further demonstrating the bathochromic effect of bromo substitution into the anthraquinone ring.

Dyes of essentially equivalent coloration and fastness properties can thus result from either condensation of DNAR or DNCZ with bromoanilines or by bromination of the DNAR/DNCZ–aniline condensates.

CONCLUSIONS

Condensation of DNAR and of DNCZ with arylamines affords a range of blue dyes having excellent fastness properties on polyester, the condensations preferably being carried out with at least three moles of arylamine. Reduction of these dyes yields a range of deep dyeing more greenish-blue dyes with somewhat lower light fastness. Whilst the dyeings on polyester of all the above dyes reflect the 'fine tuning' of hue resultant from substituent effects in the arylamine residue, these colour changes are not fully indicated by λ_{max} values, most probably due to the very broad and unresolved visible absorption. Extrapolation of the absorption band into a smooth composite curve gives, however, from the resultant λ_{max}(E) values, a more clearly defined relationship between the colour of the dyes and of the steric and electronic effect of the substituents.

The bright reddish-blue dyes obtained by condensation of DNAR and DNAR with bromoanilines can be simulated by further bromination of the DNAR and DNCZ condensates with aniline. Colour shifts in the latter are compatible with bromination proceeding essentially in the phenyl ring.

REFERENCES

1. A Fisher C S Lee and A T Peters, J. Chem. Tech. Biotechnol., **36** (1982) 319.
2. C S Lee and A T Peters, J.S.D.C., **98** (1982) 343.
3. A T Peters, Dyes and Pigments, **9** (1988) 167.
4. ICI, BP 721 885 (1955).
5. USP 2 480 269 (1946); BP 646 459 (1950).
6. BP 928 008 (1960); USP 3 154 568 (1957).
7. BP 894 388 (1954); BP 1 301 745 (1970); USP 3 440 000 (1966).
8. USP 2 641 602 (1953); USP 2 726 251 (1954); French P 1 111 778 (1958).
9. BP 722 367 (1955).
10. German P 1 146 030 (1959); French P 1 205 867 (1958); Netherlands P 6 408 214 (1963).
11. BP 1 173 207 (1966).
12. Italian P 801 436 (1963).
13. German P 1 929 564 (1969).
14. V S Salvin and R A Walker, Amer. Dyestuff Rep., **48** (13 July 1959) 35.
15. F Brodman et al., Rev. Chim. (Bucharest), **24** (1973) 418.
16. R S Sinclair and E McAlpine, J.S.D.C., **91** (1975) 399.
17. W Schoenauer, F Benguerel and J Benz in 'Chemistry of synthetic dyes', Vol. 5, Ed. K Venkataraman (New York: Academic Press, 1971) 59.
18. T Tokumitsu, M Okamoto and T Hayashi, Kogkyo Kagaku Zasshi, **67** (1964) 201.
19. A T Peters and W M Lord, J. Chem. Soc. (Perkin I), (1973) 2305.
20. T Hayashi and M Matsuo, Bull. Chem. Soc. Japan, **35** (1962) 1500.
21. T Hayashi and R Shibata, Bull. Chem. Soc. Japan, **34** (1961) 1116.
22. W Bradley and H Kaiwar, J. Chem. Soc., (1960) 2859.
23. T Hayashi and R Shibata, Kogkyo Kagak Zasshi, **63** (1960) 1241.
24. R H Peters and H H Sumner, J. Chem. Soc., (1953) 2101.
25. T Hayashi and R Shibata, Kogkyo Kagaku Zasshi, **63** (1960) 840.
26. P F Gordon and P Gregory, 'Organic chemistry in colour' (Berlin: Springer-Verlag, 1983) 190.
27. A T Peters, Unpublished results.
28. French P 1 461 238 (1964).
29. German P 2 041 374 (1970).
30. German P 2 050 372 (1970).
31. A T Peters and B A Tenny, J.S.D.C., **93** (1977) 378.