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Bis(arylamino)-dihydroxyanthraquinones: Bluish Green Dyes for Synthetic Polymer Fibres

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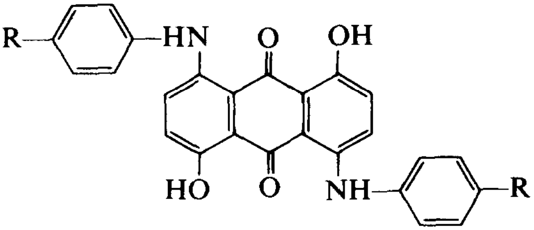
ABSTRACT

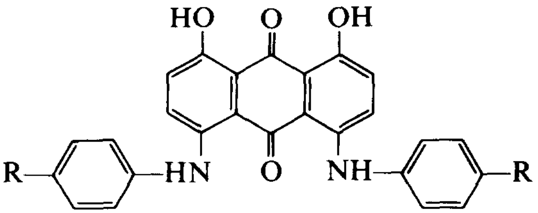
Condensation of arylamines with 4,8-dinitroanthrarufin, 4,5-dinitrochrysazin and 4,8-dichloroquinizarin afforded the corresponding bis(arylamino)-dihydroxyanthraquinones. These compounds dye polyester fibres in deep bluish green hues of very good fastness to light and sublimation. The relationships between visible absorption spectra and the structure of the dyes are discussed.

1 INTRODUCTION

4,5-Dinitrochrysazin (DNCZ) and 4,8-dinitroanthrarufin (DNAR) are widely utilized in the synthesis of blue disperse dyes. Thus, the condensation of DNAR and DNCZ with alkylamines and arylamines affords the corresponding 4-alkylamino, 4,8- and 4,5-bis(alkylamino) and 8-(5-)amino-4-alkylamino derivatives,[1,2] and 4-arylamino-5(8-)nitro-,[3] 4-arylamino-5(8-)amino,[3] 1-alkylamino-4-arylamino-5-nitro (and -5-amino),[4] 1,5-bis(alkylamino)-4-arylamino,[4] 1,4-bis(arylamino)-5-nitro (and -5-amino),[5] 1,4,5-tris(arylamino)[5] and 5-alkylamino-1,4-bis(arylamino)[5] derivatives. Little data have been published on 4,8-, 4,5- and 5,8-bis(arylamino) derivatives. The authors report here the synthesis of a series of 4,8-bis(arylamino)-1,5-



I



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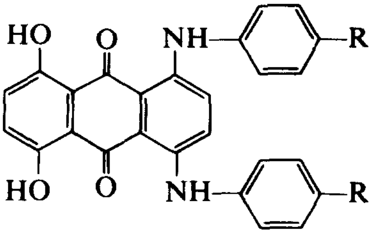


III

dihydroxyanthraquinones (**I**) from DNAR, 4,5-bis(arylamino)-1,8-dihydroxyanthraquinones (**II**) from DNCZ and 5,8-bis(arylamino)-1,4-dihydroxyanthraquinones (**III**), and an evaluation of the influence of various substituents on the colour and dyeing properties of these dyes.

2 EXPERIMENTAL

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

DNAR (3·3 g, 0·01 M) and aniline (7·42 g, 0·08 mol) were refluxed in nitrobenzene (40 ml) for 16 h. The liquor was cooled to room temperature and then diluted with ethanol (60 ml), and left to stand overnight. The crystalline material which separated was filtered and washed with water until the washings were neutral. Recrystallization from 2-methoxyethanol afforded 3·08 g (yield 73%) of 1,5-dianilino-4,8-dihydroxyanthraquinone (dye **I.1**) as small bluish green needles, m.p. 240°C.

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

2.2 4,5-Bis(arylamino)-1,8-dihydroxyanthraquinones (II)

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

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

The same methods to those in·Section 2.1 were used, except that DNAR was replaced by DCQZ and nitrobenzene was replaced by *o*-dichlorobenzene

TABLE 1
Synthesis and Characterization Data of Dyes I–III

Dye	*R*	*M.p. (°C)*	*Amount of arylamines (0·08 mol)*	*Reaction time (h)*	*Weight (yield)*	*Appearance of crystal*
I.2	CH_3	276–277	8·56 g, *p*-toluidine	11	3·37 g (75%)	Bluish green
I.3	OCH_3	262–263	9·84 g, *p*-anisidine	12	3·12 g (65%)	Bluish green
I.4	OC_2H_5	275–276	10·98 g, *p*-ethoxyaniline	13	3·47 g (68%)	Bluish green
I·5	C_2H_4OH	289–290	10·98 g, *p*-hydroxyethylaniline	22	3·76 g (74%)	Bluish green
I.6	$(CH_2)_3CH_3$	298–299	11·92 g, *p*-*n*-butylaniline	12	3·39 g (64%)	Bluish green
II.1	H	242–243	7·42 g, aniline	36	2·20 g (53%)	Bluish green
II.2	OC_2H_5	255–256	10·98 g, *p*-ethoxyaniline	21	2·65 g (52%)	Bluish green
II.3	$(CH_2)_3CH_3$	298–299	11·92 g, *p*-*n*-butylaniline	23	2·85 g (53%)	Bluish green
III.1	H	281–282	7·42 g, aniline	18	2·45 g (58%)	Bluish green
III.2	OC_2H_5	277–278	10·96 g, *p*-ethoxyaniline	22	2·98 g (58%)	Green

and potassium acetate (0·5 g). Characterization data for the products are shown in Table 1.

2.4 General

All dyes were purified by TLC on Kieselgel 60 (Merck). Electronic spectra were recorded on a Shimadzu UV 240 from dye solutions in monochlorobenzene at a concentration of 3×10^{-5} g/ml. Structure and purity were confirmed by mass (Hitachi M-52), infrared (Hitachi 260-50) and NMR (Varian VxR-300) (Table 2).

3 RESULTS AND DISCUSSION

3.1 Syntheses

Condensation of DNAR and DNCZ with alkylamines and arylamines normally results in replacement of one nitro group.[1–3] Under more stringent conditions, i.e. a large excess of arylamine and longer reaction time, replacement of both nitro groups of DNCZ by arylamino occurs.[2] However, little data have been published on the replacement of both nitro groups of DNAR and of both chloro groups of DCQZ by arylamines. In this present investigation, either nitrobenzene or *o*-dichlorobenzene was used as reaction media and, with an eight-molar ratio of arylamines, replacement of both nitro groups of DNAR and DNCZ, and both chloro groups of DCQZ by arylamino, readily occurred. The reaction is one of nucleophilic substitution and the reaction velocity will depend both on the electron availability in the

TABLE 2
Spectroscopic Data of Dyes I–III

Dye	*R*	*Mass* *(m/e)*	*IR*[a] *(KBr)*	*NMR*[b] *(DMSO-d_6)*				
I.1	H	422 (M^+)	1582 C═O 1550, 1470, 1440 ar. 1298, 1240, C—N 1198, 1160 ar. C—H 820, 769, 698 ar. C—H b.o.o.p.	7·600 (d) 7·422 (s)			7.368 | 7·344	
I.2	CH_3	450 (M^+)	3300 —OH st 1600 C═O 1560, 1518, 1470, 1450 ar. 1378 CH_3 1310, 1250 C—N 1200, 1160 ar. C—OH 980, 840, 680 ar. C—H b.o.o.p.	7·610 (d)	13·80 (s)	11·209 (t)	7·254 | 7·245	2·333 (s)
I.3	OCH_3	482 (M^+)	3270 ar. OH 1605 C═O 1570, 1516, 1490, 1460 ar. 1380 CH_3 1318, 1250 C—N 1205, 1160 ar. C—OH 980, 820 ar. C—H b.o.o.p.	7·346 (d) 7·052 | 7·021	13·878 (s)	11·175 (s)	7·319 | 7·291	3·800 (s)
I.4[c]	OC_2H_5	510 (M^+)	3300–3200 ar. OH 1600 C═O 1558, 1518, 1490, 1460 ar. 1382 C_2H_5 1316, 1260 C—N 1202, 1160 ar. C—OH 980, 830 ar. C—H b.o.o.p.	7·196 (t) | 7·143 6·791 | 6·628			7·356 | 7·349	3·900 (s) 1·280 (s)

I.5	C_2H_4OH	510 (M^+)	3250 ar. OH 1605 C═O 1561, 1518, 1480, 1456 ar. 1380 C_2H_4 1310, 1250 C—N 1200, 1164 ar. C—OH 980, 830 ar. C—H b.o.o.p.	7·526 (d) 7·495 (d)	13·805 (s)	11·216 (s)	7·312 | 7·234	4·667 (s) 3·665 (t) 2·774 (t)
I.6[c]	$(CH_2)_3CH_3$	534 (M^+)	2950 CH_3 st 1600 C═O 1560, 1520, 1480, 1460 ar. 1380 CH_3 1316, 1260 C—N 1210, 1170 ar. C—OH 980, 830 ar. C—H b.o.o.p.	7·903 (d) 7·659 (d)			7·383 | 7·321	3·240 2·41 1·82
II.1	H	422 (M^+)	1590 C═O 1560, 1490, 1450 ar. 1318, 1250 C—N 1200, 1178 ar. C—OH 980, 820, 750, 700 ar. C—H b.o.o.p.	7·664 (d) 7·427 (t)	7·331 | 7·280			
II.2[c]	OC_2H_5	510 (M^+)	3000–2900 CH_3 st 1615 C═O 1518, 1490 ar. 1390 C_2H_5 1305, 1270 C—N 1180, 1120 ar. C—OH 920, 820, 756 ar. C—H b.o.o.p.	7·737 (t) 7·670 (t)	7.349 | 7·216	4.100 (t) 1·390 (t)		

(continued)

TABLE 2—*contd.*

Dye	*R*	*Mass* (*m/e*)	*IR*[a] (*KBr*)	*NMR*[b] (*DMSO-d_6*)		
II.3[c]	$(CH_2)_3CH_3$	534 (M^+)	2950–2850 CH_3 st 1615 C═O 1510, 1480 ar. 1380 CH_3 1300, 1250 C—N 1180, 1140 ar. C—OH 830, 810 ar. C—H b.o.o.p.	7·621 (d) 7·476 (t)	7·367 | 7·335	3·009 (d) 1·625 (t) 1·380 (t) 0·930 (t)
III.1	H	422 (M^+)	1620 C═O 1580, 1542, 1460, 1420 ar. 1320, 1240 C—N 1180 ar. C—OH 980, 840, 780, 760, 725 ar. C—H b.o.o.p.	7·600 (d) 7·407 (d)	7·391 | 7·275	
III.2[c]	OC_2H_5	510 (M^+)	2980–2860 CH_3 st 1590 C═O 1560, 1500, 1450 ar. 1340 C_2H_5 1290, 1250 C—N 1180, 1120 ar. C—OH 980, 930, 820 ar. C—H b.o.o.p.	7·203 (d) 6·960 (d)	7·359 | 7·317	4·054 (t) 1·379 (t)

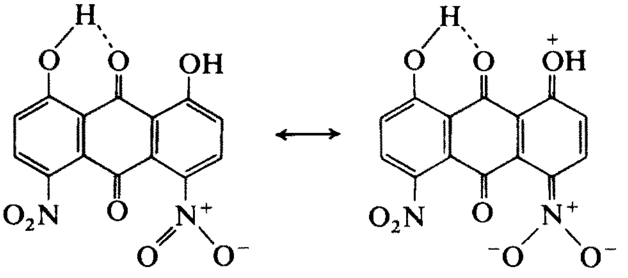
[a] ar., aromatic; b.o.o.p., bending out of plane; st, stretching.

[b] s, singlet; d, doublet; t, triplet.

[c] NMR in acetone-d_6.

arylamines and on the electron attraction exerted within the anthraquinone residue on the reaction centre. Thus, the reactivity of arylamines increases with their nucleophilicity; electron-withdrawing substituents in the anthraquinone nucleus cause activation and electron-donating substituents cause deactivation.

Consideration of the reaction time of dyes in series **I** and **II** (Table 1) shows that the reactivity can be generally correlated with the electron-donating powers of the substituents (R) on the arylamines, i.e. the more electron-donating, the more reactive. Comparing the reaction time and yield of dyes in series **I** (DNAR derivatives) with that of the corresponding dyes in series **II** (DNCZ derivatives) (Table 1), it is apparent that DNAR is more reactive than DNCZ. It can be argued that the two hydrogen bonds formed by two hydroxy groups and their adjacent carbonyl groups in DNAR decrease the electron-donating powers of the hydroxy groups which can deactivate the nitro groups toward nucleophilic substitution because of their electron-donor capacity. Since only one hydroxy group is chelated with its adjacent carbonyl group in DNCZ, the other hydroxy group can increase the electron density of the reaction centre by Scheme 1 and deactivate both nitro groups of DNCZ towards nucleophilic substitution.



more π bond on reactive centre, less reactive

Scheme 1. Resonance structures of DNCZ.

3.2 Electronic spectra

Electronic spectra data of dyes **I–III** are shown in Table 3. All dyes showed a double peak in the principal visible absorption band. The origin of the twin peak 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.[6]

Comparison of the λ_{max} values of dyes **I–III** shows the dyes to be bathochromic in the order **III** > **II** > **I**, differences being 1–3 and 3–8 nm,

TABLE 3
Colour and Dyeing Properties of Dyes I–III

Dye	*Equilibrium dye uptake (g/kg fabrics)*		λ_{max} *(nm)* (log ε) *in chlorobenzene*	*Dyeing on polyester*		
				Light-fastness		*Sublimation temperature (°C)*[b]
	0·5%[a]	*2·0%*[a]		*0·5%*[a]	*2·0%*[a]	
I.1	4·24	14·23	677 (4·31), 642 (4·20)	5	6	190
I.2	4·18	14·53	682 (4.32), 650 (4·23)	6	6	200
I.3	4·33	15·09	678 (4·33), 640_s (4·26)	6	6–7	200
I.4	4·26	14·37	679 (4.35), 645_s (4·28)	6	6–7	200
I.5	3·75	12·35	683 (4.33), 645 (4·25)	6	6–7	190
I.6	4·15	13·75	682 (4·36), 650 (4·27)	6	6–7	190
II.1	3·65	12·35	685 (4·28), 652 (4·19)	6	6	180
II.2	3·53	12·87	686 (4·33), 672[c] (4·33) 430 (4·10)	5	6	200
II.3	3·68	12·70	685 (4·35), 652 (4·30) 410 (3·90)	6	6	180
III.1	3·65	12·67	686 (4·26), 638 (4·19) 422 (3·89)	5	5	180
III.2	3·97	12·91	689 (4·32), 659_s (4·24) 420 (4·02)	5	5	190

[a] o.w.f.
[b] 0·5% (o.w.f.).
[c] Incompletely resolved.
$_s$ Shoulder.

respectively. These differences are in general accord with the known small bathochromicity of chrysazin derivatives compared to anthrarufin analogues, and to the general bathochromic influence of 1,4-diaminated configurations relative to 1,5- and 1,8-isomers. In **I–III**, however, the diverse polar and H-bonding interactions which are possible result in relatively small overall colour differences between the three series. Further substitution by electron-donor substituents into the phenyl rings gives increased conjugation effects, and consequent further small bathochromic shifts. These are typified by the 4′-ethoxy substituent, cf. dyes **I.1** and **I.4** (Δλ 2 nm), **II.1** and **II.2** (Δλ 1 nm), and **III.1** and **III.2** (Δλ 3 nm) (Table 3).

3.3 Dyeing and fastness properties

All dyes in the three series gave level green colouration of polyester fabrics. Comparing the dye uptake of dyes **I** with dyes **II** and **III** indicates that the more symmetrical structure of dyes **I** results in a higher substantivity than that for dyes **II** and **III**. Introduction of the hydrophilic hydroxyethyl group into the phenyl ring (dye **I.5**) causes an apparent decrease in dye uptake (Table 3). Since the deeper the dyeing, the greater the amount of dye which must be destroyed before a visible change in the colour of the material becomes apparent, it is generally found that the deeper the dyeing, the higher is its light-fastness in respect of the visual change in colour on exposure (2% o.w.f. > 0·5% o.w.f.). Comparison of the light-fastness of dyes **I** with dyes **II** and **III** shows that the higher equilibrium dye uptake in the former results in a slightly higher rating for the light-fastness, despite the influence of electron-donating groups in the phenyl ring. Sublimation-fastness, light-fastness and build-up properties of all the dyes in the three series are of an acceptable order to meet commercial requirements.

ACKNOWLEDGEMENT

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