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Disazo Direct Dyes Derived from 4,4'-Diamino Derivatives of Benzanilide, Diphenylamine-2-Sulfonic Acid and Stilbene-2,2'-Disulfonic Acid

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ABSTRACT

4-4'-Diamino derivatives of diphenylamine-2-sulfonic acid, stilbene-2,2'-disulfonic acid and benzanilide were used as potential substitutes for benzidine in the synthesis of disazo direct dyes. The relationship between structure and colour, dyeing and fastness properties of non-benzidine and benzidine disazo direct dyes has been studied. It can be concluded that dyes derived from benzanilide have superior substantivity and wash fastness on cotton compared to the other dyes studied. It was also found that dyes derived from diphenylamine-2-sulfonic acid and stilbene-2,2'-disulfonic acid have a similar colour on cotton to benzidine based dyes.

1 INTRODUCTION

It is many years since awareness of the carcinogenicity of benzidine and certain azo dyes derived therefrom was recognised, and since then there has been considerable interest in the synthesis of non-benzidine-based azo dyes. Introducing certain substituents into the phenyl rings of the benzidine reduces the affinity of dyes towards cellulose, because the two phenyl rings of the benzidine moiety can then no longer be coplanar. However, when two phenyl-amino residues are linked via groups which maintain the coplanarity of the two rings, this gives rise to diamines suitable for use as diazo components for direct dyes.[1] When diamines are

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arranged in order of increasing bathochromic effect, it is seen that the dominant factor in the final shade is the degree of insulation between the two phenyl rings. Dyes from 4,4'-diamino derivatives of diphenylamine and stilbene generally give deeper shades than those from benzidine. However, dyes from 4,4'-diaminobenzanilide are usually lighter in shade than those from benzidine.[2] 4,4'-Diamines of diphenylamine-2-sulfonic acid and stilbene-2,2'-disulfonic acid have been used for the preparation of disazo and trisazo direct dyes.[3] More recently, 4,4'-diamino derivatives of benzanilide, diphenylamine-2-sulfonic acid and stilbene-2,2'-disulfonic acid have been investigated as alternatives to benzidine,[4,5] but few data have been published concerning the relationship between structure, colour, dyeing and fastness properties of non-benzidine and benzidine dyes. The synthesis of a series of disazo direct dyes obtained by tetrazotisation of 4,4'-diaminobenzanilide (I), 4,4'-diaminodiphenylamine-2-sulfonic acid (II), 4,4'-diaminostilbene-2,2'-disulfonic acid (III) and benzidine (IV), and coupling with naphthalene sulfonic acids is here reported. An evaluation of the influence of the diazo components on the colour and dyeing properties of the dyes is also made.

2 EXPERIMENTAL

2.1 Synthesis of dyes

Thirty-five disazo dyes (series I, II, III and IV) and four trisazo dyes (series V) were synthesised by conventional method.[6,7] Relevant data are given in Tables 1 and 2.

2.2 General

All dyes were chromatographically purified on Kieselgel 60 (Merck). Electronic spectra were recorded on a Shimadzu UV 240 from dye solutions in water and *N*,*N*-dimethylformamide (DMF).

Dyeing of cotton was carried out in 20% aq. NaCl (liquor ratio 30:1) at 100°C for 30 min; the dyed samples were washed with an aqueous solution of detergent (2g/litre) at 40°C for 20 min. The dye uptake was evaluated by extracting the dye from a known weight of dyed material with water and determining the absorbance of the solution. Dye uptake was calculated from the calibration curve of absorbance vs concentration of dye.

The wash fastness was tested according to CNS 1494-A2, which is

TABLE 1
Synthesis and Characterisation Data of Dyes I–IV

Dye	*E_1/pH used*	*E_2/pH used*	*Weight, g (yield, %)*	*Rf/colour (TLC)*[a]
I.1	H acid/8–9	H acid/8–9	7·08 (73·5)	0·73/violet
I.2	R acid/8–9	R acid/8–9	8·27 (89·4)	0·48/red
I.3	Chromotropic acid/ 8–9	Chromotropic acid/ 8–9	7·97 (83·4)	0·58/purple
I.4	N.W. acid/8–9	N.W. acid/8–9	6·09 (84·6)	0·80/red
I.5	Naphthionic acid/ 2–3	Naphthionic acid/ 2–3	5·89 (87·3)	0·88/red
I.6	Gamma acid/2–3	Gamma acid/2–3	6·11 (86·6)	0·75/reddish purple
I.7	H acid/7·5–8·5	Gamma acid/8·5–9·5	6·85 (78·8)	0·63/violet
I.8	Salicylic acid/7·5–8·5	Gamma acid/8·5–9·5	4·85 (80·2)	0·83/brown
I.9	Gamma acid/7·5–8·5	J acid/8·5–9·5	6·42 (91·0)	0·73/reddish purple
II.1	H acid/8–9	H acid/8–9	7·25 (71·4)	0·70/blue
II.2	R acid/8–9	R acid/8–9	8·04 (82·3)	0·45/blue
II.3	Chromotropic acid/ 8–9	Chromotropic acid/ 8–9	7·91 (78·5)	0·42/blue
II.4	N.W. acid/8–9	N.W. acid/8–9	6·56 (85·0)	0·75/dark blue
II.5	Naphthionic acid/ 2–3	Naphthionic acid/ 2–3	6·13 (84·3)	0·85/red
II.6	Gamma acid/2–3	Gamma acid/2–3	6·17 (81·4)	0·65/blue
II.7	H acid/7·5–8·5	Gamma acid/8·5–9·5	7·69 (86·7)	0·58/blue
II.8	Gamma acid/7·5–8·5	J acid/8·5–9·5	5·71 (76·4)	0·67/blue
III.1	H acid/8–9	H acid/8–9	7·68 (69·4)	0·62/blue
III.2	R acid/8–9	R acid/8–9	9·10 (85·3)	0·33/blue
III.3	Chromotropic acid/ 8–9	Chromotropic acid/ 8–9	7·76 (70·7)	0·23/blue
III.4	N.W. acid/8–9	N.W. acid/8–9	6·75 (78·2)	0·67/purple
III.5	Naphthionic acid/ 2–3	Naphthionic acid/ 2–3	5·91 (72·4)	0·75/red
III.6	Gamma acid/2–3	Gamma acid/2–3	6·72 (79·2)	0·58/blue
III.7	H acid/7·5–8·5	Gamma acid/8·5–9·5	7·42 (75·9)	0·49/blue
III.8	Salicylic acid/7·5–8·5	Gamma acid/8·5–9·5	5·71 (76·4)	0·52/brown
III.9	Gamma acid/7·5–8·5	J acid/8·5–9·5	7·05 (83·1)	0·47/purple
IV.1	H acid/8–9	H acid/8–9	7·18 (72·4)	0·57/blue
IV.2	R acid/8–9	R acid/8–9	7·52 (78·8)	0·47/blue
IV.3	Chromotropic acid/ 8–9	Chromotropic acid/ 8–9	7·13 (72·4)	0·62/blue
IV.4	N.W. acid/8–9	N.W. acid/8–9	5·83 (77·8)	0·70/purple
IV.5	Naphthionic acid/ 2–3	Naphthionic acid/ 2–3	5·72 (81·3)	0·62/red
IV.6	Gamma acid/2–3	Gamma acid/2–3	5·71 (77·6)	0·60/violet
IV.7	H acid/7·5–8·5	Gamma acid/8·5–9·5	6·48 (75·0)	0·50/blue
IV.8	Salicylic acid/7·5–8·5	Gamma acid/8·5–9·5	4·96 (78·2)	0·78/brown
IV.9	Gamma acid/7·5–8·5	J acid/8·5–9·5	5·43 (73·8)	0·55/purple

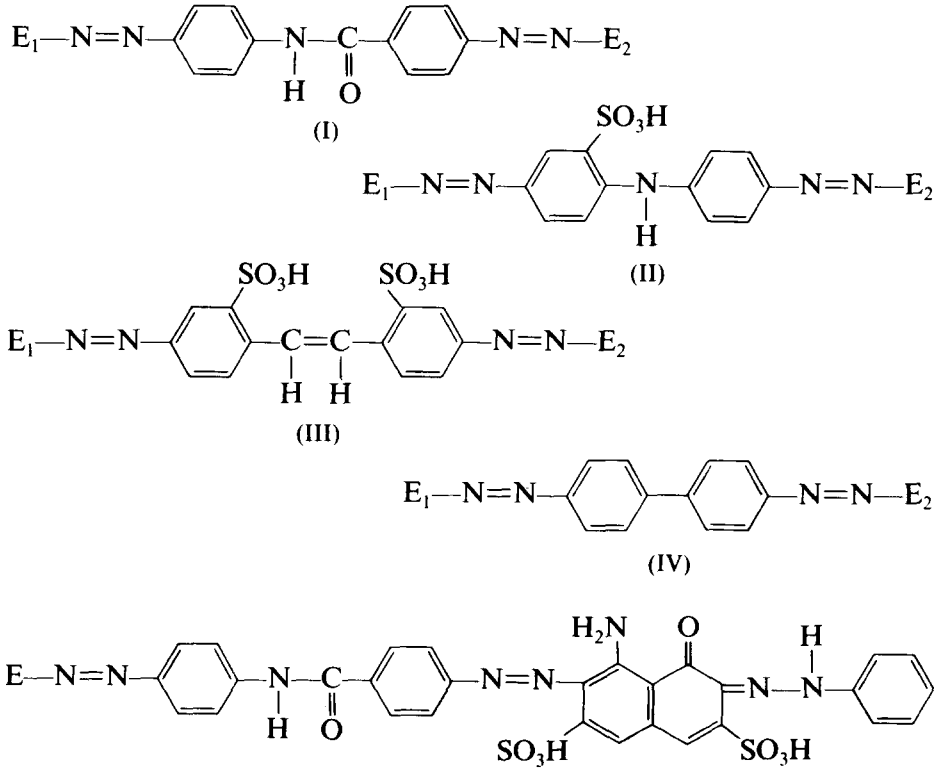
[a] Eluent: n-butanol/pyridine/0·880 ammonia/water = 50/50/20/20.

TABLE 2
Synthesis and Characterisation Data of Dyes V (E ← D $\overset{1}{\rightarrow}$ Z $\overset{2}{\leftarrow}$ A)

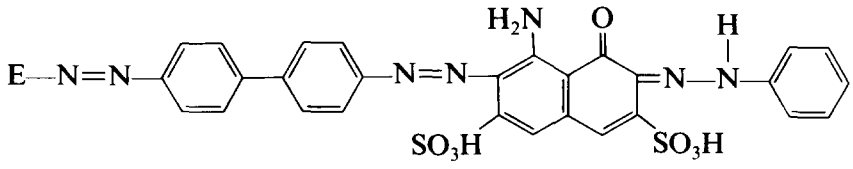
Dye	*A*	*Z/pH used*	*E/pH used*	*Weight, g (yield, %)*	*Rf/colour (TLC)*[a]
V.1	Aniline	H acid/1. 2–3 2. 8–8·5	Phenol/8·5–9·5	6·23 (79·6)	0·75/green
V.2	Ibid.	Ibid.	m-Phenylenediamine/8·5–9·5	5·92 (74·3)	0·78/black
V.3	Ibid.	Ibid.	Phenol/8·5–9·5	5·79 (71·3)	0·52/green
V.4	Ibid.	Ibid.	m-Phenylenediamine/8·5–9·5	6·67 (80·7)	0·53/black

[a] Eluent: n-butanol/pyridine/0·880 ammonia/water = 50/50/20/20.

similar to the AATCC 61-1989-1A test, except that the test conditions described were replaced by 100 ml of wash liquor (5g/litre soap) at 50°C (±2°C) for 30 min. Light fastness assessments were carried out as for a previous investigation.[8] Rubbing fastness was tested according to CNS 1499, similar to AATCC 8-1989, except that those test conditions were replaced by 50 complete turns.



E = 4'-hydroxyphenyl (V.1) or 2',4'-diaminophenyl (V.2)



E = 4'-hydroxyphenyl (V.3) or 2',4'-diaminophenyl (V.4).

3 RESULTS AND DISCUSSIONS

3.1 Electronic spectra

Electronic spectral data of the dyes synthesised are shown in Table 3. Comparison of the λ_{max} values of dyes I (and V.1, V.2), III and IV (and V.3, V.4) shows the dyes to be bathochromic in the order, III > IV (and V.3) > I (and V.1), differences being 2–16 and 8–54 nm respectively, consistent with previously reported data.[2] Comparison of series III with series II shows a bathochromic effect of 6–24 nm (III → II), which might be due to the enhancement of electron donation from the NH group of diphenylamine-2-sulfonic acid. Steric crowding between the amino group and sulfonic group is minimised by appropriate rotating out of the molecular plane, thus increasing the electron density on the amino group.

3.2 Dyeing and fastness properties

All dyes gave level dyeings and good build-up on cotton. From Table 3, it is apparent that dye-uptake of the three depths of shade of dyes I–V is in the order I (and V.1, V.2) > IV (and V.3, V.4) > III > II. The increase in substantivity can be interpreted in terms of relative coplanarity, intermolecular hydrogen bonding factors (with cotton) and the presence of less hydrophilic groups (e.g. SO_3H); viz; (a) dyes I: greater coplanarity and intermolecular hydrogen bonds; (b) dyes III; more hydrophilic groups; (c) dyes II: lowered coplanarity and more hydrophilic groups.

It can be seen from Table 4 that both the wash and rubbing fastnesses of all the dyes decrease as the depth of dyeing increases. This is in accord with the established fact that the greater the amount of dye present the more likely it is that, during treatments sufficient to cause staining, it will be removed from the fabric.[7] It may be seen from Table 4 that on cotton fibres, dyes II and III have inferior washing and rubbing fastness to dyes I, IV and V, since they contain more hydrophilic groups and have a lower degree of coplanarity.

In dyeings of greater depth, a larger amount of dye must be eliminated

TABLE 3
Dyeing Properties and Colour

Dye	*Dye uptake (g/kg fibres)*			λ_{max} *(nm) in water*	λ_{max} *(nm) in DMF*
	0·1% o.w.f.	*0·5% o.w.f.*	*2·5% o.w.f.*		
I.1	0·82	4·01	16·65	556	552
I.2	0·90	3·94	15·88	521	510
I.3	0·87	3·55	15·76	513	510
I.4	0·93	4·43	15·32	520	518
I.5	0·74	3·47	15·05	496	492
I.6	0·82	4·03	17·13	504	500
I.7	0·84	4·09	18·35	525	522
I.8	0·82	3·25	17·44	510	510
I·9	0·82	4·01	17·31	520	520
II.1	0·54	2·64	12·32	587	580
II.2	0·62	2·25	13·25	578	570
II.3	0·52	2·71	11·57	584	575
II.4	0·54	3·19	12·02	571	566
II.5	0·54	2·45	12·53	518	510
II.6	0·62	3·02	13·26	580	572
II.7	0·52	2·42	10·64	596	578
II.8	0·65	3·15	14·22	566	560
III.1	0·69	3·03	13·65	572	566
III.2	0·71	2·84	14·45	554	550
III.3	0·73	3·03	12·29	578	570
III.4	0·63	3·61	13·73	562	556
III.5	0·58	2·95	13·64	510	506
III.6	0·73	3·58	14·38	564	558
III.7	0·63	3·04	13·31	578	570
III.8	0·74	3·49	15·74	542	542
III.9	0·78	3·58	15·84	550	550
IV.1	0·75	3·58	15·78	568	564
IV.2	0·87	3·83	15·25	550	548
IV.3	0·80	3·31	13·24	562	550
IV.4	0·84	3·98	14·34	556	548
IV.5	0·69	3·22	14·53	508	502
IV.6	0·77	3·80	15·23	558	552
IV.7	0·79	3·89	16·54	569	568
IV.8	0·80	3·75	16·84	541	541
IV.9	0·80	3·72	16·21	538	535
V.1	0·75	3·68	15·37	602	584
V.2	0·84	4·00	16·43	380; 700	380; 700
V.3	0·72	3·25	15·07	608	590
V.4	0·85	4·06	16·54	380; 700	380; 700

TABLE 4
Fastness Properties

Dye o.w.f. (%)	*Light fastness*			*Wash fastness[a] (S.C./C.C.)*			*Rubbing fastness[b] (W.R./D.R.)*		
	0·1%	*0·5%*	*2·5%*	*0·1%*	*0·5%*	*2·5%*	*0·1%*	*0·5%*	*2·5%*
I.1	1	2	3	3–4/4	3/3–4	2–3/3	3–4/5	3/5	2/5
I.2	1	1	2	3–4/2–3	3/2	2/1–2	4/5	3–4/5	2/4
I.3	1	2	3	3–4/3–4	3/3	2/2	4/5	3/4–5	2/4
I.4	1	2	3	3–4/3	3/2	2–3/2	3–4/5	3/4–5	2–3/4
I.5	1	2	2	4/3–4	3–4/3	2–3/2	4/5	3–4/4–5	2–3/4
I.6	2	3	5	3/3–4	2–3/3	2/2–3	4/5	3–4/5	3/4–5
I.7	2	2	4	4/3–4	3/3	2–3/2–3	4/5	3–4/5	3/5
I.8	2	3	5	4/4	3–4/3	3/2–3	3–4/5	3/5	2–3/4–5
I.9	2	2	3	3–4/3	3/2–3	2–3/2–3	3–4/5	3/4–5	2–3/4–5
II.1	1	2	2	3–4/2–3	3/2	2/1–2	3/4–5	2–3/4	2/3–4
II.2	1	1	2	3/2	2–3/2	1–2/1–2	3–4/4–5	3/4	2/3–4
II.3	1	1	2	3/2–3	2–3/2	2/2	3–4/4–5	3/4	2/3–4
II.4	1	1	3	3–4/2–3	3/2–3	2–3/2	3/4	2–3/3	2/2–3
II.5	1	1	2	3–4/3–4	2–3/2	2/2	3–4/4–5	3/4	2–3/3
II.6	1	2	4	3/3	2–3/2–3	2/2	3–4/4–5	3/4	2–3/3
II.7	2	2	3	3–4/2–3	2–3/2–3	2/2	3–4/4–5	3/4	2–3/3–4
II.8	2	2	5	3–4/3–4	3/2–3	2–3/2	3/4	2–3/3	2/2–3
III.1	1	1	3	3–4/2–3	3/2	2/1–2	3/4	2–3/3–4	2/3
III.2	1	1	2	3/2	2–3/2	2/1–2	3–4/4	3/3–4	2/3
III.3	1	1	3	3/2	2–3/2	2/1–2	3–4/4–5	2–3/3	2/2–3
III.4	1	2	4	3–4/2–3	3/2–3	2–3/2	3/4	2–3/3	2/2–3
III.5	1	2	3	3–4/3	3/2–3	2/2	3/4	2–3/3–4	2/2–3
III.6	2	3	5	3/3–4	2–3/3	2/2	3–4/4	2–3/3	2/2–3
III.7	1	2	3	3/2–3	2–3/2	2/2	3/4	2–3/3	2/2–3
III.8	2	2	3	3/2–3	2–3/2	2/1–2	3/4	3/3–4	2/3
III.9	1	2	4	3/2–3	2–3/2	2/1–2	3/4–5	2–3/3–4	2/3
IV.1	1	3	5	3–4/3–4	3/3	2–3/2	3–4/5	3/5	2/4–5
IV.2	1	2	4	3/2–3	2–3/3	2/1–2	4/5	3–4/5	3/4–5
IV.3	1	2	4	3/3–4	2–3/3	2/2–3	3–4/5	3/4–5	2/4
IV.4	2	2	3	3/3	2–3/2–3	2/1–2	3–4/5	3/4–5	2–3/4
IV.5	1	2	3	3–4/4	3/3–4	2–3/2–3	4/5	3–4/4–5	3/4
IV.6	2	3	4	3–4/4	3/3–4	2/2–3	3–4/5	3/4–5	2–3/4
IV.7	2	3	5	3–4/3	2–3/2–3	2/2	3–4/5	3/5	2–3/4–5
IV.8	2	3	5	4/4	3/3–4	2–3/3	4/5	3/5	2/5
IV.9	3	4	5	4/3–4	3/3	2–3/2	3–4/5	3/4–5	2–3/4
V.1	1	1	4	3–4/3	2–3/2	2/1–2	4/5	3/5	2/4–5
V.2	1	2	3	4/3–4	3/2–3	2/1–2	4/5	3–4/5	2/5
V.3	1	1	3	4/4	3/2	1–2/1–2	4/5	3–4/5	2/4–5
V.4	2	3	4	3–4/4	3/2–3	1–2/2	4/5	3/5	2/4

[a] S.C.: Staining on cotton; C.C.: Colour change.
[b] W.R.: Wet rubbing fastness; D.R.: Dry rubbing fastness.

before a visible change in the colour of the material becomes apparent, and it is generally found that the deeper the dyeing, the higher is its light fastness with respect to the visual change in colour on exposure.[9] Comparison of the light fastnesses of dyes I, IV and V with those of dyes II and III shows that the higher dye uptake in the former results in a slightly higher light fastness rating (Table 4).

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