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Trisazo Dyes Derived from 4,4′-Diaminodiphenylsulphide: Substitutes for C.I. Direct Black 38 and C.I. Direct Green 1

Y. C. Chao* & Y. I. Pan

Department of Textiles, National Taipei Institute of Technology, Taipei, Taiwan

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ABSTRACT

The synthesis of a series of trisazo direct dyes obtained by tetrazotization of 4,4′-diaminophenylsulphide and coupling with H-acid and m*-phenylenediamines, phenol or resorcinol is described. These compounds dye cotton in green and black shades with good build-up and levelling properties. It can be concluded that trisazo dyes derived from 4,4′-diaminodiphenylsulphide have superior substantivity and wash fastness on cotton than C.I. Direct Black 38 and C.I. Direct Green 1. Copyright © 1996 Elsevier Science Ltd*

INTRODUCTION

Disazo dyes from 4,4′-diaminodiphenylsulphide (hereinafter referred to as 4,4′-thiodianiline) are useful as acid colours for wool, because the S bridge between the two phenylamino residues decreases the coplanarity of the dye molecule.[1,2] However, some disazo dyes from the less coplanar 4,4′-thiodianiline-2,2′-disulphonic acid give level colours with good washing fastness on cotton.[3] C.I. Direct Black 38 and C.I. Direct Green 1, two benzidine-based trisazo dyes, have many distinguishing characteristics, such as no effect on the hue in the presence of copper and iron, superior substantivity with high tinctorial strength, good printing and dischargeability properties, and good wash fastness on cotton, silk, wool, leather and paper.[4] Some non-benzidine direct dyes have been developed as alternatives to C.I. Direct Black 38 and C.I. Direct Green 1 by Atlantic Chemical Corp,[5] but few data

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*Corresponding author. Present address: Department of Pharmaceutical Chemistry, School of Pharmacy, The University, Bradford BD7 1DP, UK.

have been published concerning the differences between colour, dyeing and fastness properties of nonbenzidine dyes, and C.I. Direct Black 38 and C.I. Direct Green 1. Dyes from 4,4′-thiodianiline generally give similar shades to those from benzidine.[6] We report here the synthesis of a series of trisazo direct dyes derived from 4,4′-thiodianiline, and an evaluation of the influence of the diazo components on the colour and dyeing properties of the dyes is also made.

EXPERIMENTAL

Synthesis of dyes

Twenty-seven trisazo dyes were synthesized by conventional methods.[7] Relevant data are given in Tables 1 and 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.

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 (2 g/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 similar to the AATCC 61-1989-1A test, except that the test conditions described were replaced by 100 ml of wash liquor (5 g/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.

RESULTS AND DISCUSSIONS

Electronic spectra

Electronic spectra data of the dyes synthesized are shown in Table 3. Hydroxyazo dyes of the naphthalene series exist more in the hydrazone form

TABLE 1
Synthesis and Characterization Data of Dyes I (A $\rightarrow_2$ Z[a] $\leftarrow_1$ D $\rightarrow_3$ E)

Dye	*D*/pH used	*A*/pH used	*E*/pH used	Yield (%)
I.1	4,4'-Thiodianiline/2–3	Aniline/9–10	*m*-Phenylene-diamine/7–8	84.5
I.2		*p*-Nitroaniline/9–10		91.5
I.3		*p*-Toluidine/9–10		87.2
I.4		Aniline/9–10	*m*-Phenylene-diamine-4-sulphonic acid/7–8	80.7
I.5		*p*-Nitroaniline/9–10		88.6
I.6		*p*-Toluidine/9–10		83.1
I.7		Aniline/9–10	2,4-Diamino-toluene/7–8	82.4
I.8		*p*-Nitroaniline/9–10		78.3
I.9		*p*-Toluidine/9–10		84.9
I.10		Aniline/9–10	Phenol/9–10	81.4
I.11		*p*-Nitroaniline/9–10		86.9
I.12		Sulphanilic acid/9–10		78.9
I.13		Aniline/9–10	Resorcinol/9–10	83.7
I.14		*p*-Nitroaniline/9–10		89.4
I.15		Sulphanilic acid/9–10		82.2
I.16[b]	Benzidine/2-3	Aniline/9–10	*m*-Phenylene-diamine/7–8	71.3
I.17[c]			Phenol/9–10	80.7

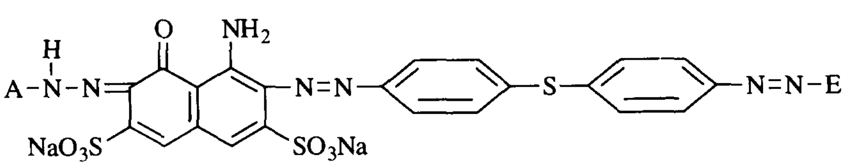
[a] Z: H-acid.
[b] I.16: C.I. Direct Black 38.
[c] I.17: C.I. Direct Green 1.

TABLE 2

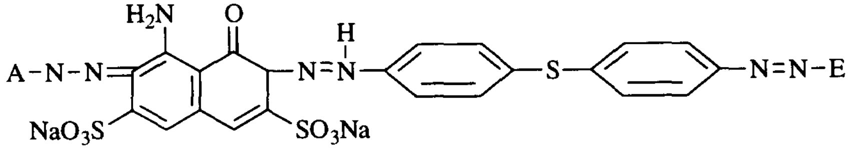
Synthesis and Characterization Data of Dyes II ($A \rightarrow_2 Z^a \leftarrow_1 D \rightarrow_3 E$)

Dye	*A*/pH used	*D*/pH used	*E*/pH used	Yield (%)
II.1	*p*-Nitroaniline/1–2	4,4′-Thiodianiline/8–9	*m*-Phenylene-diamine/9–10	92.4
II.2	Sulphanilic acid/1–2			83.0
II.3	*p*-Nitroaniline/1–2		*m*-Phenylene-diamine-4-sulphonic acid/9–10	84.7
II.4	Sulphanilic acid/1–2			87.7
II.5	*p*-Nitroaniline/1–2		2,4-Diamino-toluene/9–10	98.6
II.6	Sulphanilic acid/1–2			83.1
II.7	*p*-Nitroaniline/1–2		Phenol/9–10	87.3
II.8	Sulphanilic acid/1–2			79.8
II.9	*p*-Nitroaniline/1–2		Resorcinol/9–10	88.9
II.10	Sulphanilic acid/1–2			83.0

[a] Z: H-acid.



(I)



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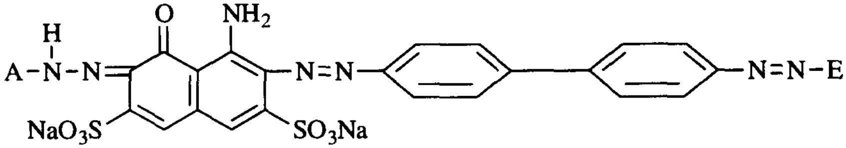

(I.16 and I.17)

than the azo form, by taking into account bond energies and resonance stabilization energy.[9] Unlike their hydroxy analogues, arylazo derivatives of naphthylamines exist totally in the aminoazo form.[10] Therefore, dye of series I exist in the 2-(4′-diphenylsulphideazo)-1-naphthylamine form, and dyes of series II exist in the 2-(4′-diphenylsulphidehydraz)-1-naphthoquinone form.

Introducing electron-accepting groups, especially the powerful *para*-nitro group, generally increases the proportion of the hydrazone form.[11] Usually, the hydrazone form is bathochromic compared to the azo form and has higher tinctorial strength.[12] Hence, the increase in λ max values and molar extinction coefficient can be correlated with the predominance of the hydrazone form, namely; dye II.1 > I. 2, dye II.3 > I.5, dye II.5 > I.8, dye II.7 > I.11, and dye II.9 > I.14, the differences being 46, 14, 26, 20 and 25 nm, respectively. Comparing the λ_{max} values of dye I.2 with I.1 and I.3, dye I.5 with I.4 and I.6, dye I.8 with I.7 and I.9, dye I.11 with I.10 and I.12, dye I.14 with I.13 and I.15, dye II.1 with II.2, dye II.3 with II.4, dye II.5 with II.6, dye II.7 with II.8, and dye II.9 with II.10, a bathochromic effect (4–39 nm) is apparent. This is probably due to the nitro group increasing the proportion

TABLE 3
Dyeing Properties and Colour

Dye	Dye uptake (g/kg fibres)				λ_{max} nm (log ϵ) in water
	0.1% o.w.f.	0.5% o.w.f.	1.0% o.w.f.	2.5% o.w.f.	
I.1	0.819	3.830	6.322	15.248	450 (4.02), 595 (4.40)
I.2	0.825	3.594	7.070	16.362	463 (4.28), 608 (4.24)
I.3	0.827	3.396	5.654	15.376	458 (3.96), 603 (4.12)
I.4	0.759	3.325	5.658	14.919	441 (4.26), 599 (4.36)
I.5	0.895	4.136	5.933	15.335	460 (4.29), 612 (4.27)
I.6	0.815	3.777	6.458	15.194	458 (3.99), 608 (4.17)
I.7	0.906	4.005	5.207	16.758	450 (4.10), 608 (4.06)
I.8	0.908	3.804	5.986	16.342	463 (4.17), 615 (4.11)
I.9	0.813	3.942	6.665	17.126	461 (4.12), 611 (4.02)
I.10	0.819	3.869	6.352	15.285	444 (4.27), 600 (4.22)
I.11	0.855	4.186	6.211	17.236	462 (4.34), 610 (4.35)
I.12	0.752	3.523	5.347	14.108	445 (4.28), 606 (4.33)
I.13	0.706	3.403	4.928	15.541	438 (4.41), 600 (4.10)
I.14	0.781	3.690	5.702	14.079	464 (4.62), 605 (3.82)
I.15	0.813	3.720	5.195	12.785	447 (4.08), 591 (3.99)
I.16	0.847	3.726	5.242	15.138	512 (3.98)
I.17	0.724	3.245	4.831	15.268	680 (4.28)
II.1	0.922	4.103	7.256	18.152	455 (4.00), 654 (4.26)
II.2	0.754	3.249	6.863	17.582	460 (4.23), 615 (4.16)
II.3	0.690	3.472	5.721	17.591	450 (4.20), 626 (4.43)
II.4	0.642	3.040	5.206	12.572	440 (4.24), 605 (4.42)
II.5	0.803	3.637	6.127	17.438	457 (4.05), 636 (4.32)
II.6	0.775	4.061	7.127	16.374	453 (4.28), 612 (4.28)
II.7	0.794	4.220	7.423	18.061	452 (4.24), 630 (4.41)
II.8	0.568	3.147	5.682	14.954	450 (4.22), 604 (4.26)
II.9	0.737	3.392	6.458	17.834	456 (4.58), 630 (4.65)
II.10	0.621	3.028	5.655	14.075	446 (4.35), 594 (4.27)

of the hydrazone form. It can be seen from Table 3 that dyes I.1–I.9 and II.1–II.6 have higher tinctorial strength with similar hue to dye I.16 (C.I. Direct Black 38), and dyes I.10, I.11, I.12, II.7 and II.9 have higher tinctorial strength with similar hue to dye I.17 (C.I. Direct Green 1).

Dyeing and fastness properties

All dyes gave level colouration and good build-up properties on cotton. It can be seen from Table 4 that dye-uptake of the four shades of dyes from 4,4′-thiodianiline is generally higher than that for C.I. Direct Black 38 and C.I. Direct Green 1 (dyes I.16 and I.17). This indicates that dyes from the less sterically hindered 4,4′-thiodianiline have greater coplanarity than those

TABLE 4
Fastness Properties

Dye	o.w.f. (%)											
	Light fastness				Wash fastness[a] (S.W./S.C./C.C.)				Rubbing fastness[b] (D.F./W.F.)			
	0.1	0.5	1.0	2.5	0.1	0.5	1.0	2.5	0.1	0.5	1.0	2.5
I.1	1	2	3	4	5/5/5	4–5/3/4–5	5/3/4–5	4–5/2–3/3–4	5/4	5/3	4–5/2–3	5/1–2
I.2	1	2	3	4	5/5/5	5/3–4/4	5/3/4	5/2–3/3–4	5/4	5/3–4	4–5/3–4	5/2–3
I.3	1	2	3	4	5/5/4–5	5/4/4–5	5/3–4/4–5	4–5/2/3–4	5/5	5/4	4–5/2	5/1–2
I.4	1	2	2	3	5/4–5/4–5	5/3/4–5	5/3/4–5	5/2/3–4	5/4–5	5/3–4	4–5/2	5/1–2
I.5	1	1	2	3	5/5/4–5	5/3–4/4	5/3/4	5/2–3/3–4	5/5	5/3–4	4–5/3–4	4–5/1–2
I.6	1	1	2	3	5/5/5	5/4/4	5/3–4/4	5/2–3/3–4	5/4–5	5/3–4	4–5/2–3	5/1–2
I.7	1	2	2	3	5/5/5	5/4/5	5/4/4–5	5/3–4/3–4	5/4–5	5/4–5	5/2–3	5/2
I.8	1	2	2	3	5/5/5	5/4–5/4	5/3/4	5/3–4/3–4	5/5	5/3–4	5/3–4	4/1–2
I.9	1	2	2	3	5/5/5	5/4–5/4	5/4/4	4–5/3–4/4–5	5/5	5/3	4–5/3	5/1–2
I.10	1	2	2	3	5/4–5/4–5	5/4/4–5	4–5/3–4/4–5	5/3/4–5	5/4–5	5/4	5/3	5/2
I.11	2	2	3	4	4–5/4/4–5	5/3–4/3–4	5/3/3	5/2–3/2–3	5/4	5/3–4	5/2	4–5/1–2
I.12	1	2	2	3	5/3/4–5	5/3/3–4	4–5/2–3/3	5/2/2–3	5/4	5/3	4–5/2	4–5/1–2
I.13	1	2	2	4	5/4–5/5	5/4/4–5	5/3–4/4–5	5/3/4	5/4–5	4–5/4	5/3	4/1–2
I.14	1	2	3	4	5/4–5/4	5/4/4	5/4/4	5/3–4/3	5/4–5	5/4	5/4	5/3
I.15	1	2	3	4	5/5/4–5	5/4/4	5/3–4/3–4	5/3/3	5/4–5	5/3–4	5/3–4	4–5/2
I.16	1	1	2	3	5/4/4	5/3/2	5/2–3/2	5/1–2/1–2	5/3–4	5/3–4	5/3	4–5/2
I.17	1	2	3	4	5/3–4/4	5/3/2–3	5/2/2–3	5/1–2/2	5/4	5/3	5/2–3	4/2

TABLE 4
Fastness Properties—*continued*

Dye	o.w.f. (%)											
	Light fastness				Wash fastness[a] (S.W./S.C./C.C.)				Rubbing fastness[b] (D.F./W.F.)			
	0.1	0.5	1.0	2.5	0.1	0.5	1.0	2.5	0.1	0.5	1.0	2.5
II.1	2	2	3	4	5/4–5/4–5	5/4/3–4	4–5/3–4/3–4	5/3–4/3	5/5	5/4–5	4–5/4	5/3–4
II.2	1	2	2	3	5/4–5/4–5	5/3/3–4	4–5/2–3/3–4	5/2/3	5/4–5	4–5/3–4	4–5/3–4	4/2–3
II.3	2	3	4	5	5/4/4–5	5/4/4	5/3–4/3–4	4–5/3–4/3–4	5/4–5	5/4–5	5/4	4–5/3–4
II.4	1	1	2	3	5/5/4	5/4/3–4	4/3/3–4	4/2–3/2–3	5/4–5	5/4–5	5/4	4–5/3–4
II.5	1	2	3	4	5/4–5/4–5	5/4–5/4	4/3–4/3–4	3–4/2–3/3	5/4–5	5/4–5	4–5/4	4/3–4
II.6	1	1	2	3	5/4–5/4–5	5/4/4	4/3–4/3	3–4/3/2	5/4–5	5/4–5	4–5/4	4–5/3
II.7	2	2	3	4	5/4–5/4–5	4–5/4/4–5	4/4/3–4	4/3–4/3–4	5/4–5	5/4	5/4	4–5/3–4
II.8	1	1	2	3	5/4–5/4–5	4–5/4/4	4–5/3/3–4	4–5/3/3	5/4–5	5/4	5/3–4	4–5/3
II.9	2	3	4	5	5/4–5/4–5	5/4/4	4–5/4/4	4–5/4/3–4	4–5/4	4-5/3–4	4/3–4	4/3
II.10	1	2	3	3	5/4–5/4–5	4–5/4/4–5	4–5/3/3	4/2–3/3	5/4–5	5/3–4	5/3–4	4/3

[a] S.W.: Staining on wool; S.C.: staining on cotton; C.C.: colour change.
[b] D.F.: Dry rubbing fastness; W.F.: wet rubbing fastness.

from benzidine. It can also be seen from Table 4 that dyes with more sulphonic groups have less dye-uptake on cotton, namely dye I.4 < I.1, dye I.12 < I.11, dye II.2 < II.1 and dye II.8 < II.7. It may be concluded that the increase in hydrophilicity by the sulphonic groups causes the decrease in substantivity.[13] Table 4 also shows that the wash fastness and rubbing fastness of all dyes decreases as the depth of dyeing increases. This is consistent with results previously observed.[13,14] Comparison of the wash fastness and the wet rubbing fastness of dye I.10 with I.12, dye II.1 with II.2 and dye II.7 with II.8 shows that the more sulphonic groups present, then the lower is the rating of fastness, despite the substantivity decreasing factor.[13] Dyes from 4,4′-thiodianiline generally have higher wash fastness and rubbing fastness than C.I. Direct Black 38 and C.I. Direct Green 1. It can be seen from Table 4 that the light fastness of all dyes generally increase as the depth of dyeing increases. This is again consistent with previous results.[15] Dyes from 4,4′-thiodianiline have similar or slightly higher light fastness than C.I. Direct Black 38 and C.I. Direct Green 1.

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