

Synthesis of Non-benzidine Reactive Dyes and Their Application on Various Fibres

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Various bisazo reactive dyes have been prepared by coupling diazotised 4,4'-diaminodiphenylsulphonamide with various cyanurated coupling components such as H-acid, Peri acid, Bronner's acid, J-acid, Tobias acid, N-methyl-J-acid, Gamma acid, Laurent acid, Chicago acid and T-acid and their dyeing performance as reactive dyes has been assessed on silk, wool and cotton fibres.

Key words: 4,4'-Diaminodiphenylsulphonamide, bisazo reactive dyes, dyeing, silk, wool and cotton.

INTRODUCTION

The introduction of reactive dyes is an important landmark in the history of synthetic dyes¹. These dyes are the only textile coloration products designed to furnish covalent bonds between dye and substrate during dyeing. Although many different reactions can be used for fixation, two main types are exploited commercially, *i.e.* heteroaromatic nucleophilic substitution and addition to an activated alkene²⁻⁵. Improvement in the structure of reactive dye chromogens and in the structure, selection and number of reactive groups have led to an increased use of reactive dyes⁶⁻⁸. Patel *et al.*^{9,10} have reported fibre reactive dyes for cellulosic fibres.

Reactive dyes are coloured compounds which contain one or two groups capable of forming covalent bonds between a carbon or phosphorus atom of the dye ion or molecule and an oxygen, nitrogen or sulphur atom of a hydroxy, an amino or a mercapto group of the substrate. Such covalent bonds are formed with the hydroxyl groups of cellulosic fibres, with the amino, hydroxyl and mercapto groups of protein fibres and with the amino groups of polyamides¹¹.

EXPERIMENTAL

Synthesis of 4,4'-diaminodiphenylsulphonamide (A)¹²

***p*-Acetamidobenzenesulphonyl chloride:** Chlorosulphonic acid (14.5 g, 0.125 mol) was added to a 250 mL three-necked flask equipped with a stirrer, a thermometer and a reflux condenser. The reagent was cooled to 5°C in an ice-bath, and acetanilide (3.38 g, 0.025 mol) was added slowly at 5°C. The mixture was heated to 60°C and kept for 2 h. Added 100 g of ice with stirring; the precipitate

of *p*-acetamidobenzenesulphonyl chloride was collected by filtration, washed with cold water until neutral and dried. Yield 80%, m.p. 148–149°C, m.f. $C_8H_8NO_3S$; Analysis (%): N = 5.98 (found), 5.99 (required).

4,4'-Diacetamidodiphenylsulphonamide: *p*-Aminoacetanilide (5.0 g, 0.033 mol) in acetone (20 mL) was stirred with *p*-acetamidobenzenesulphonyl chloride (8.5 g, 0.036 mol) in acetone (15 mL) at room temperature. Pyridine was added after 1 h to this reaction mixture. Reaction progress was assessed after 5 h. When the reaction was completed, acetone was decanted and water (20 mL) was added with stirring. The product mixture was filtered, washed, dried and recrystallised from benzene. Yield 84%, m.f. $C_{16}H_{17}N_3O_4S$; Analysis (%): N = 12.09 (found), 12.10 (required).

4,4'-Diaminodiphenylsulphonamide: 4,4'-Diacetamidodiphenylsulphonamide was added to water (20 mL). Sodium hydroxide (15 mL, 20%) was added slowly with stirring. The mixture was refluxed for 2 h and cooled. The precipitate collected by filtration was recrystallised from alcohol and water. Yield 72%, m.p. 136.6–137.5°C, m.f. $C_{12}H_{13}N_3O_2S$; Analysis (%): N = 15.96 (found), 15.97 (required).

Tetrazotisation of 4,4'-diaminodiphenylsulphonamide (B): 4,4'-Diaminodiphenylsulphonamide (2.63 g, 0.01 mol) was suspended in H_2O (60 mL). Hydrochloric acid (0.86 g) was added dropwise to this well stirred suspension. The mixture was gradually heated up to 70°C, till clear solution was obtained. The solution was cooled to 0–5°C in an ice-bath. A solution of $NaNO_2$ (1.2 g, 0.02 mol) in H_2O (8 mL) previously cooled to 0°C was then added over a period of 5 min with stirring. The stirring was continued for 1 h, maintaining the same temperature, with positive test for nitrous acid on starch iodide paper. After just destroying excess of nitrous acid with required amount of a solution of sulphamic acid, the clear tetrazo solution (B) obtained at 0–5°C was used for subsequent coupling reaction.

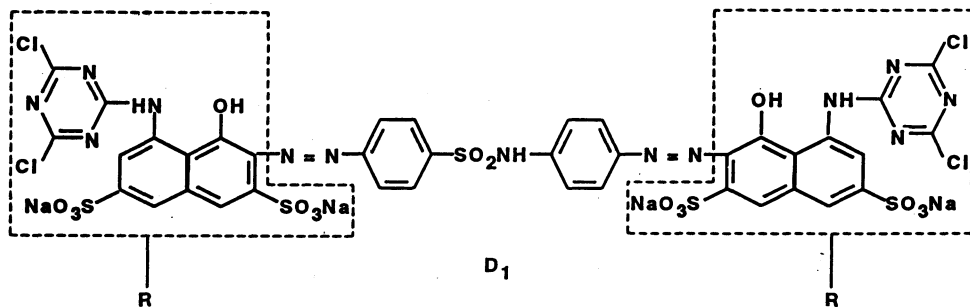
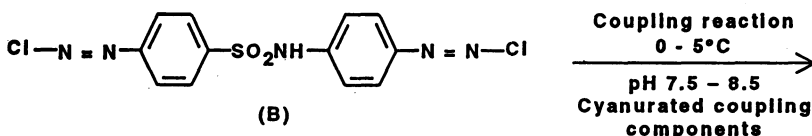
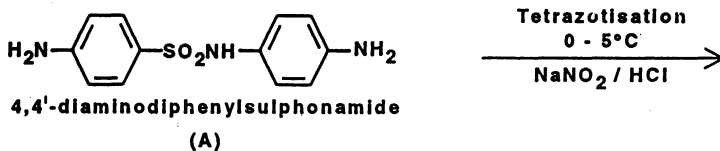
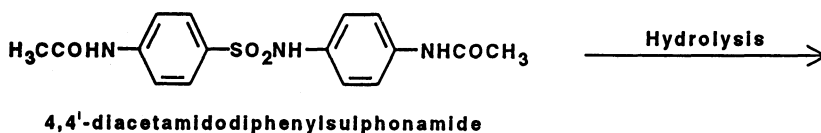
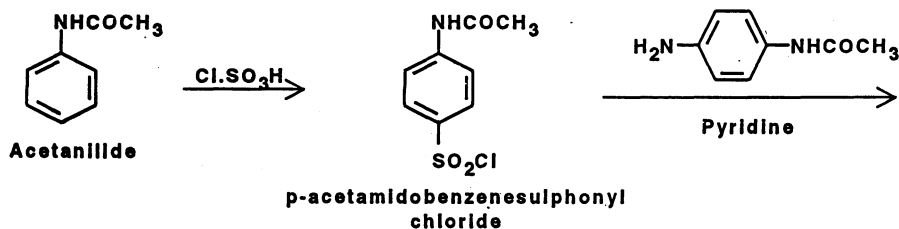
Cyanuration of coupling components (R): Cyanuric chloride (3.7 g, 0.02 mol) was stirred in acetone (25 mL) at a temperature below 5°C for a period of 1 h. A neutral solution of coupling component (0.02 mol) in aqueous sodium carbonate solution (10% w/v) was then added in small lots in about 1 h. The pH was maintained neutral by simultaneous addition of sodium carbonate solution (1% w/v). The temperature was maintained below 5°C throughout this reaction. The reaction was then stirred at 0–5°C for further 4 h; then a clear solution was obtained. The cyanurated coupling component solution (R) thus formed was used for subsequent coupling reactions.

Coupling of tetrazo solution (B) with cyanurated coupling components (R)

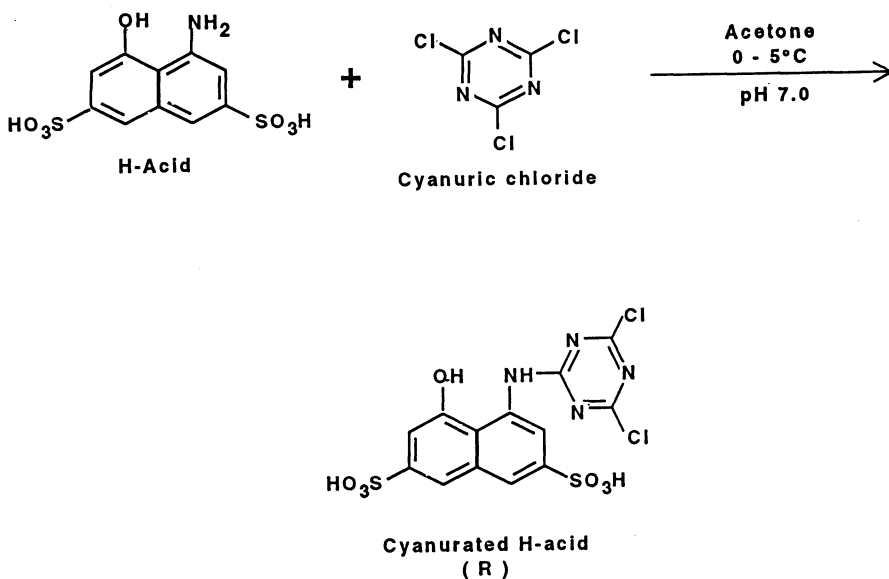
Formation of dyes (D₁ to D₁₀): To an ice-cooled and well stirred solution of cyanurated coupling component (R), a freshly prepared solution of tetrazo solution (B) was added dropwise over a period of 10–15 min. The pH was maintained at 7.5–8.5 during addition and stirring was continued for 4 h, maintaining the temperature below 5°C. Sodium chloride (12 g) was then added and the mixture was stirred for 1 h. The solid dye separated out was filtered, washed with minimum amount of acetone and dried at room temperature. The

same procedure was used to prepare other dyes using, different cyanurated coupling components

REACTION SCHEME



where, R = various cyanurated coupling components for the formation of D₁ to D₁₀ (Table-1).

Preparation of cyanurated H-acid (R):

The purity of all the dyes was checked by TLC¹³. The IR spectra were recorded on a Perkin-Elmer Model-377 spectrophotometer and PMR spectra on a Varian 60 MHz instrument using TMS as internal standard and $\text{CDCl}_3 + \text{DMSO}$ as solvent. UV-visible spectra were recorded on Beckman DB-GT grafting spectrophotometer.

Dyeing of fibres: All the dyes D_1 to D_{10} were applied on silk, wool and cotton fibres by using standard procedure¹⁴.

RESULTS AND DISCUSSION

From the data reported in Tables 1 and 2, it is apparent that the value of λ_{max} depends on the coupling components used. The colour change observed for each dye is due to the oscillation of electrons and the presence of additional substituents. In D_1 there is more place for the oscillation of electrons and also the presence of both $-\text{OH}$ and $-\text{NH}_2$ groups. Thus, $\lambda_{\text{max}} = 520 \text{ nm}$. In D_2 to D_{10} slight lower effect is produced due to the lesser number of electrons and thus the oscillation is fast. Therefore, λ_{max} becomes less than λ_{max} of D_1 . All the dyes, in general, showed (O—H) and (N—H) stretching vibrations at $3520\text{--}3300 \text{ cm}^{-1}$, $-\text{NH}$ bending vibrations at 1500 cm^{-1} , (C=C) stretching vibrations at 1580 cm^{-1} , (N=N) stretching vibrations at $1620\text{--}1600 \text{ cm}^{-1}$, (C—N) stretching vibrations at $1560\text{--}860 \text{ cm}^{-1}$, (S=O) stretching vibrations at $1150\text{--}1050 \text{ cm}^{-1}$, (C—Cl) stretching vibrations at $780\text{--}770 \text{ cm}^{-1}$ (Fig. 1).

The PMR spectra of dye D_1 showed signals at δ 2.49 (6H, DMSO, solvent), δ 3.39 (1H, $-\text{OH}$ and water) and δ 7.0–7.90 (14H, aromatic protons), δ 8.44 (2H, $-\text{NH}-$) (Fig. 2).

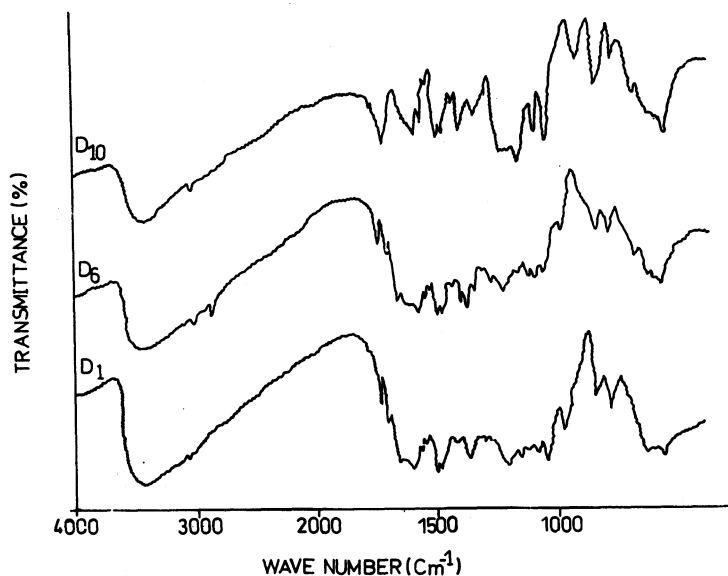


Fig. 1. IR spectra of D_1 , D_6 and D_{10} dyes

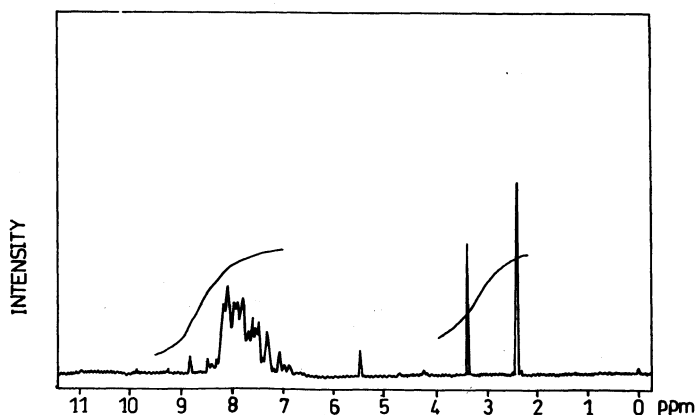


Fig. 2. PMR spectra of D_1 dye

Exhaustion study: The percentage exhaustion of 2% dyeing on silk ranges from 67 to 77%, for wool ranges from 64 to 71% and for cotton ranges from 67 to 71%. The data regarding the fixation on silk ranges from 82 to 93%, for wool ranges from 81 to 92% and for cotton ranges from 85 to 90%. (Table-2).

Fastness properties: Fastness to light was assessed in accordance with BS:1006-1978. The rubbing fastness test was carried out by using Crockmeter (Atlas) in accordance with AATCC-1961 and the wash fastness in accordance with IS:765-1979. All the dyes show generally moderate to very good light fastness properties. The washing and rubbing fastness properties range from good to excellent on silk, wool and cotton (Table-3).

TABLE-1: CHARACTERISATION

Dye No.	Cyanurated coupling components	m.f.	m.w.	Yield (%)	Nitrogen (%)		R _f value
					Found	Reqd.	
D ₁	H-acid	C ₃₈ H ₁₉ O ₁₆ N ₁₃ Cl ₄ S ₅ Na ₄	1307	79	13.91	13.93	0.41
D ₂	Peri acid	C ₃₈ H ₂₁ O ₈ N ₁₃ Cl ₄ S ₃ Na ₂	1071	83	16.98	16.99	0.39
D ₃	Bronner's acid	C ₃₈ H ₂₁ O ₈ N ₁₃ Cl ₄ S ₃ Na ₂	1071	86	16.97	16.99	0.40
D ₄	J-acid	C ₃₈ H ₂₁ O ₁₀ N ₁₃ Cl ₄ S ₃ Na ₂	1103	88	16.48	16.50	0.39
D ₅	Tobias acid	C ₃₈ H ₂₃ O ₂ N ₁₃ Cl ₄ S	867	79	20.98	20.99	0.42
D ₆	N-methyl-J-acid	C ₄₀ H ₂₅ O ₁₀ N ₁₃ Cl ₄ S ₃ Na ₂	1131	83	16.07	16.09	0.46
D ₇	Gamma acid	C ₃₈ H ₂₁ O ₁₀ N ₁₃ Cl ₄ S ₃ Na ₂	1103	77	16.49	16.50	0.41
D ₈	Laurent acid	C ₃₈ H ₂₁ O ₈ N ₁₃ Cl ₄ S ₃ Na ₂	1071	80	16.98	16.99	0.40
D ₉	Chicago acid	C ₃₈ H ₁₉ O ₁₆ N ₁₃ Cl ₄ S ₅ Na ₄	1307	74	13.91	13.93	0.41
D ₁₀	T-acid	C ₃₈ H ₁₇ O ₂₀ N ₁₃ Cl ₄ S ₇ Na ₆	1479	79	12.28	12.30	0.38

TABLE-2: SHADE, PERCENTAGE EXHAUSTION AND FIXATION OF REACTIVE DYES ON SILK, WOOL AND COTTON

Dye No.	Shade on dyed fibre	λ _{max}	% Exhaustion			% Fixation		
			Silk	Wool	Cotton	Silk	Wool	Cotton
D ₁	Violet	520	68.25	69.15	69.60	91.57	85.32	89.05
D ₂	Light brown	490	71.45	66.35	68.55	83.97	90.42	86.40
D ₃	Orange	480	75.45	68.90	71.00	90.12	89.26	90.44
D ₄	Reddish orange	490	75.25	71.85	68.15	85.71	89.77	86.57
D ₅	Light yellow	465	71.80	67.85	70.55	83.56	92.85	85.34
D ₆	Orange	485	75.35	64.45	67.80	92.23	86.11	85.00
D ₇	Reddish brown	510	67.70	69.40	69.05	93.06	86.46	87.32
D ₈	Orange	490	73.70	68.45	69.40	82.09	81.81	88.46
D ₉	Brown	485	68.20	66.55	71.80	87.24	85.65	87.74
D ₁₀	Light orange	485	77.80	65.60	67.00	86.12	87.65	86.20

TABLE-3: FASTNESS PROPERTIES OF REACTIVE DYES

Dye No.	Light fastness			Wash fastness			Rubbing fastness					
							Dry			Wet		
	Silk	Wool	Cotton	Silk	Wool	Cotton	Silk	Wool	Cotton	Silk	Wool	Cotton
D ₁	5	5-6	3-4	4-5	5	4-5	5	3-4	4	4	3-4	3
D ₂	5	4	4	5	5	4	5	4	3-4	3	3	4
D ₃	5-6	4-5	6	3	4	3-4	4-5	4	3	4-5	3	4-5
D ₄	5	6	3	4	4-5	3	3-4	4	3	4	3-4	3
D ₅	3	3	4	4	4	4	4-5	4-5	4-5	3-4	4-5	3-4
D ₆	6	5	5-6	4-5	3	3-4	3	4	4	3-4	4	3-4
D ₇	5-6	4	4	4	3	4-5	4	3-4	4	4	3	3-4
D ₈	4	5	3-4	4	4	3	4-5	3	3-4	4-5	4	4-5
D ₉	5	3-4	6	3	3	4-5	5	4	3-4	3	4-5	3
D ₁₀	4	3	3	3	5	4	3	4	4	4	3	3-4

Light fastness: 1: poor, 2: slight, 3: moderate, 4: fair, 5: good, 6: very good.

Wash and rubbing fastness: 1: poor, 2: fair, 3: good, 4: very good, 5: excellent.

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