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Synthesis and Characterization of Some Cold Brand Reactive Dyes and Their Application on Various Fibres

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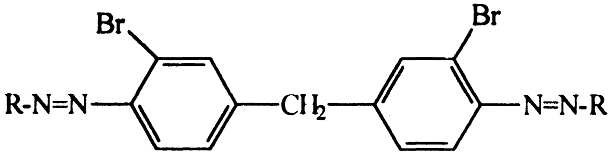
Various reactive dyes have been prepared by coupling diazotised 4,4′-methylene-bis-*o*-bromo aniline with cyanurated coupling components and their dyeing performance as reactive dyes has been assessed on silk, wool and cotton fibre. All the dyes gave yellow to maroon shades with good to very good light fastness on each fibre. The purity of dyes was checked by thin layer chromatography. The IR spectra showed all characteristic bands and a representative dye's PMR spectra showed all the signals. The percentage dye-bath exhaustion on different fibres was reasonably good and acceptable. The dyed fibres showed moderate to very good fastness to light, washing and rubbing.

INTRODUCTION

The most recent technological contribution to textile has been the development of reactive dyes. Several new reactive systems have been introduced from time to time, which covers the subject of innumerable patents and publications[1–3]. It is for the first time that dyeing has been by chemical reaction between the dye and the fibre, enabling one to get an assortment of bright, attractive shades of adequate fastness with considerable ease of dyeing. It can also be easily understood that dyes with two reactive groups give a higher fixation yield than dyes with one reactive group for if one of the two dye-fibre bonds is hydrolyzed, one is still left for fixation[4, 5]. Patel *et al.* has synthesized bis-azo reactive dyes based on 4,4′-methylene-bis-anthranilic acid[6].

We report here the synthesis and study of the dyeing properties of the cold-brand reactive dyes based on 4,4′-methylene-bis-*o*-bromo aniline. The cold-brand reactive dyes of the following structure were prepared.



where R = cyanurated coupling components such as H-acid, Chicago acid, N-methyl-J-acid, T-acid, sulpho tobias acid, Bronner acid, gamma acid, Tobias acid, Cleve acid and J-acid.

EXPERIMENTAL

Preparation of 4.4′-methylene-bis-*o*-bromo aniline (A)

(i) Synthesis of 4,4′-diaceto-amido diphenyl methane: A mixture of acetic anhydride (36 mL) and glacial acetic acid (60 mL) and 4.4′-methylene-bis-aniline (17.2 g, 0.1 mole) was refluxed for 30 min on a hot water bath. The product was precipitated by pouring the mixture into cold water and crystallized from 75% acetic acid; yield 80%, m.p. 236–237°C, m.f. $C_{17}H_{18}N_2O_2$. Analysis (%): N, found (calcd) 9.90 (9.92).

(ii) Synthesis of 3,3′-dibromo-4,4′-diaceto-amido diphenyl methane: 4,4′-Diaceto-amido diphenyl methane (0.282 g, 0.001 mole) was dissolved in acetic acid (30 mL) and bromine in acetic acid (2 mL, 10%) was slowly added to it. Th reaction mixture was kept for 4 h in a water bath. Then it was treated with ice water. The solid separated was filtered, washed with sodium thiosulphate solution and then with water, dried and crystallized from absolute alcohol; yield 80%, m.p. 193°C., m.f. $C_{17}H_{16}O_2N_2Br_2$: Analysis (%): N, found (calcd.) 6.34 (6.36).

(iii) Synthesis of 3,3′-dibromo-4,4′-diamino-diphenyl methane [4,4′-methylene-bis-*o*-bromo aniline (A)]: 3,3′-Dibromo-4,4′-diaceto-amido diphenyl methane (4.40 g, 0.01 mole) and 70% of H_2SO_4 was refluxed for 30 min on hot water bath. Poured the clear hot solution into icecold water and precipitated by adding excess of 10% NaOH solution and crystallized from alcohol yield 60%, m.p. 110°C, m.f. $C_{13}H_{12}N_2Br_2$. Analysis (%): N, found (calcd.) 7.84 (7.86).

Tetrazotisation of 4,4′-methylene-bis-*o*-bromo aniline (B)

4,4′-Methylene-bis-*o*-bromo aniline (A) (1.78 g, 0.005 mole) was suspended in water (60 mL). Hydrochloric acid (10 mL) 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 mole) in water (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) at 0–5°C was used for subsequent coupling reaction.

Preparation of cyanuration coupling components (R)

Cyanuric chloride (1.85 g, 0.01 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 (0.01 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 the reaction. The reaction mass was then stirred at 0–5°C for further 4 h; then a clear solution was obtained. The cyanurated coupling component (R′) thus formed was used for subsequent coupling reaction.

Formation of dyes (D_1 to D_{10})

To an ice-cold 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; 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.

Dyeing of fibres: All the dyes were applied on silk, wool and cotton fibres using the reported procedure[7].

Fastness test: Fastness to light was assessed in accordance with BS: 1006–1978. The rubbing fastness test was carried out with a crockmeter (Atlas) in accordance with AATCC-1961, and the wash-fastness test in accordance with IS: 765–1979.

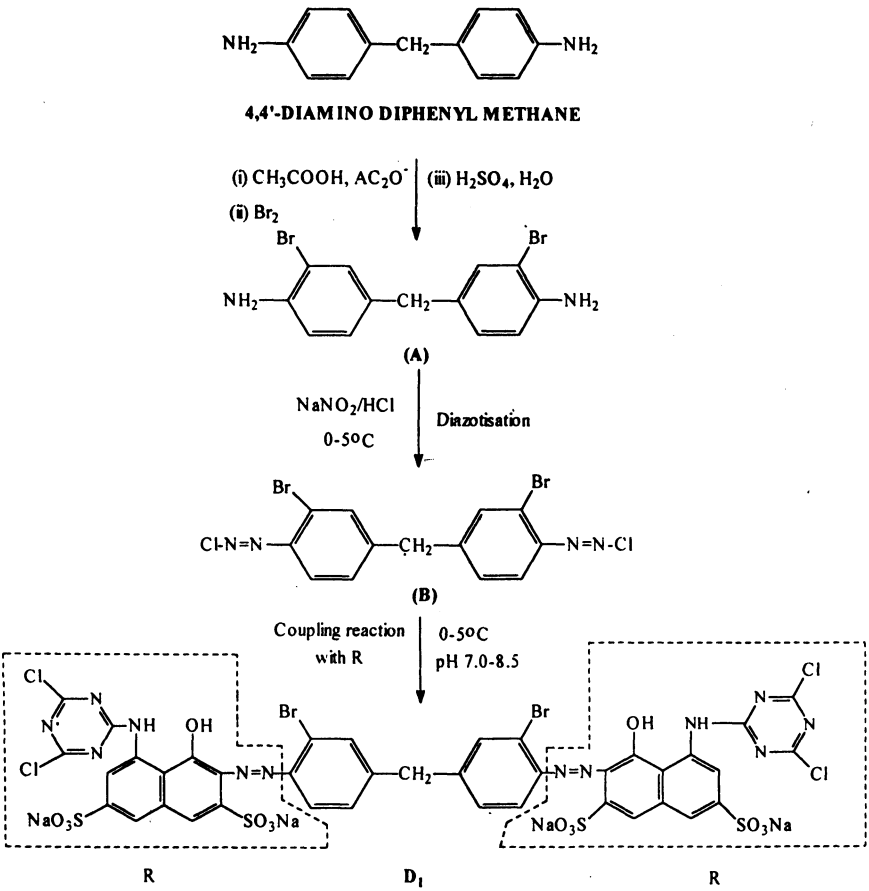
RESULTS AND DISCUSSION

All the dyes were yellow to maroon in colour and obtained in excellent yield (75 to 86%). The purity of all dyes was checked by thin-layer chromatography[8]. The absorption spectra of all the dyes were recorded on Beckmann DB-GT grafting spectrophotometer. The characterization data of dyes are given in Table-1.

TABLE-1
CHARACTERIZATION

Dye No.	Coupling component	m.f.	m.w.	Yield (%)	Nitrogen (%) Found (Req.)	R_f value
D_1	H-acid	$C_{39}H_{18}O_{14}N_{12}Cl_4S_4Na_4Br_2$	1400	86	12.00 (12.00)	0.41
D_2	Chicago acid	$C_{39}H_{18}O_{14}N_{12}Cl_4S_4Na_4Br_2$	1400	75	12.00 (12.00)	0.42
D_3	N-methyl J-acid	$C_{41}H_{24}O_{18}N_{12}Cl_4S_2Na_2Br_2$	1384	81	12.11 (12.13)	0.44
D_4	T-acid	$C_{39}H_{16}O_{18}N_{12}Cl_4S_6Na_6Br_2$	1572	82	10.67 (10.68)	0.37
D_5	Sulfo tobias acid	$C_{39}H_{20}O_6N_{12}Cl_4S_2Na_2Br_2$	1164	85	14.40 (14.43)	0.39
D_6	Bronner acid	$C_{39}H_{20}O_6N_{12}Cl_4S_2Na_2Br_2$	1194	81	14.40 (14.43)	0.43
D_7	Gamma acid	$C_{39}H_{18}O_8N_{12}Cl_4S_2Na_2Br_2$	1196	87	14.03 (14.04)	0.40
D_8	Tobias acid	$C_{39}H_{22}N_{12}Cl_4Br_2$	960	84	17.50 (17.50)	0.41
D_9	Cleve acid	$C_{39}H_{20}O_6N_{12}Cl_4S_2Na_2Br_2$	1164	79	14.42 (14.43)	0.42
D_{10}	J-acid	$C_{39}H_{20}O_8N_{12}Cl_4S_2Na_2Br_2$	1196	78	14.00 (14.04)	0.36

REACTION SCHEME



Infrared spectra

The IR spectra of the dyes D_1 to D_{10} were recorded on Perkin-Elmer spectrophotometer (Model 830) using KRr pellets. Dyes D_1 to D_{10} showed characteristic bands at 2910–2890 (—CH$_2$—)[9], 830–800 (S-triazine), 560–510 (C—Br), 1635–1580 (—NH—), 1390–1360 (—N=N—), 1270–1110 (S=O) and 3420–3410 cm^{-1} due to (O—H) stretching vibration.

PMR spectra

The PMR spectra (300 MHz, CDCl$_3$) of a representative dye showed signals at 2.10 (—CH$_2$—), 3.61 (—OH), 8.10–6.84 (aromatic proton) and 9.2 (—NH—).

Fastness properties

The percentage exhaustion, fixation and fastness properties of dyes D_1 to

D_{10} are given in Tables 2 and 3. All the dyes D_1 to D_{10} showed good affinity for silk, wool and cotton and gave moderate to very good light, washing and rubbing fastness and good to very good exhaustion and fixation.

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

Dye No.	Shade on dyed fibre	% Exhaustion			% Fixation		
		Silk	Wool	Cotton	Silk	Wool	Cotton
D_1	Maroon	76.90	64.60	48.15	83.87	75.85	68.53
D_2	Dark pink	68.20	61.70	53.35	91.67	77.02	66.54
D_3	Dark orange	74.00	64.55	54.00	83.78	83.65	65.74
D_4	Light yellow	69.20	63.05	53.65	91.76	77.71	61.50
D_5	Yellow	78.60	65.35	55.50	82.72	79.57	63.10
D_6	Light orange	67.80	64.70	49.75	95.13	73.45	68.59
D_7	Pink	77.35	65.25	54.55	85.32	79.69	65.07
D_8	Yellowish brown	74.60	58.90	50.75	85.79	77.24	69.01
D_9	Brown	67.95	64.15	51.75	74.92	74.82	62.85
D_{10}	Reddish orange	68.15	63.70	51.85	92.44	80.84	68.40

TABLE-3
FASTNESS PROPERTIES OF REACTIVE DYES ON SILK, WOOL AND COTTON

Dye No.	Light fastness			Wash fastness			Rubbing fastness					
							Dry			Wet		
	S	W	C	S	W	C	S	W	C	S	W	C
D_1	4–5	4	2	5	3–4	2	4	4–5	2	3	4	1–2
D_2	3	3	3	3	3	3	3	3	3	3	3	3
D_3	4	6	3	4	4–5	3	4–5	4–5	2–3	4	4	2–3
D_4	4–5	3–4	3	4	4	3–4	4–5	4	3–4	4–5	4	3
D_5	5	4	3–4	5	4	4	5	4	3	5	4	2–3
D_6	3–4	4–5	2–3	4	4	3	4	4–5	3	4	4	2–3
D_7	3	4	3–4	3	3–4	3–4	3	4	3	3	3	3
D_8	4–5	3–4	1–2	4–5	3	2	4–5	3	2	4	3	2
D_9	4–5	5–6	3–4	3	3	3	4	4	3–4	4–5	4–5	3
D_{10}	4	4	4	4	3–4	3	4–5	4	3	4	4	2

REFERENCES

1. Detiz Rolf and Tzikas Athanassios (Ciba-Geigy A-G), Eur. Pat., Appl., EP., 581, 733 (CI, COg B 62/03), 1994; *Chem. Abstr.*, **121**, 85707a (1994).
2. Ebenerer and Warren James (BASF A-G Germany) PCT Int. Appl. WO 99 05, 223; *Chem. Abstr.*, **130**, 154985 g (1999).
3. E. Seigel, K. Venkataraman in: (Ed.), The Chemistry of Synthetic Dyes, Academic Press, New York Vol. 6, p. 1, (1972).
4. K. Bredereck and C. Schumacher, *Dyes and Pigments*, **21**, 23 (1993).
5. M. Masak, U. Meyer and H. Zollinger, *J. Soc. Dyers Colour*, **104**, 425 (1988).
6. R.B. Patel, N.B. Patel, S.K. Patel and K.C. Patel, *Asian J. Chem.*, **12**, 1193 (2000).
7. V.A. Shenai, Chemistry of Dyes and Principles of Dyeing, Sevak Publications, Bombay (1973).
8. Bernard Fried and Joseph Sherma, Thin Layer Chromatography: Technique and Application, Marcel-Dekker, New York-Basel (1982).
9. N.B. Colthup, L.H. Daly and E.W. Stephen, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York-San Francisco-London (1975).

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