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Synthesis and Properties of Acid Dyes Derived from 4,4′-Methylene bis(2,5-dichloro aniline)

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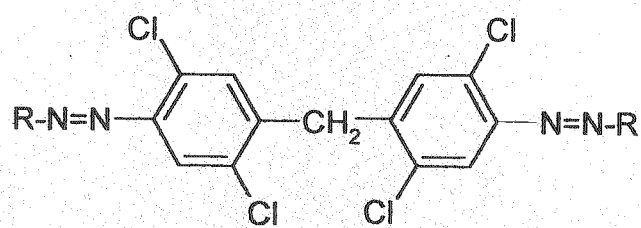
Various acid dyes have been prepared by coupling diazotized 4,4'-methylene-bis-(2,5-dichloro aniline) with various coupling components and their dyeing performance on silk, wool and nylon fibres has been assessed. All the dyes gave a wide range of shades with very good depth and levelness on each fibre. The purity of all the dyes has been checked by thin layer chromatography. The IR spectra showed all characteristic bands and representative dye PMR spectra showed all the signals. The percentage dye-bath exhaustion and fixation on different fibres was reasonably good and acceptable. The dyed fibres showed fair to excellent fastness to light, washing and rubbing.

Key Words: 4,4′-Methylene-bis(2,5-dichloro aniline), Bisazo reactive dyes, Dye, Silk, Wool, Nylon.

INTRODUCTION

Acid dyes are water-soluble anionic dyes that are applied to nitrogenous fibres such as silk, wool and nylon fibred from acid or neutral baths[1, 2]. The acid dyes were probably originally so named because of the presence in their molecules of the one or more sulphonic acid or other acidic groups[3, 4]. Attachment to the fibre is attributed at least partly to salt formation between anionic groups in the dyes and cationic groups in the fibre. The term applies to an application class rather than a chemical class; since acidic groups are also present in many mordant, direct and reactive dyes, their presence is not a distinguishing feature. A number of monoazo dyes and bisazo dyes[5–9] have been reported to give good dyeing and fastness properties.

The present study was focussed on synthesis of acid dyes derived from 4,4′-methylene-bis(2,5-dichloroaniline). The general structure of the dyes investigated is shown below:

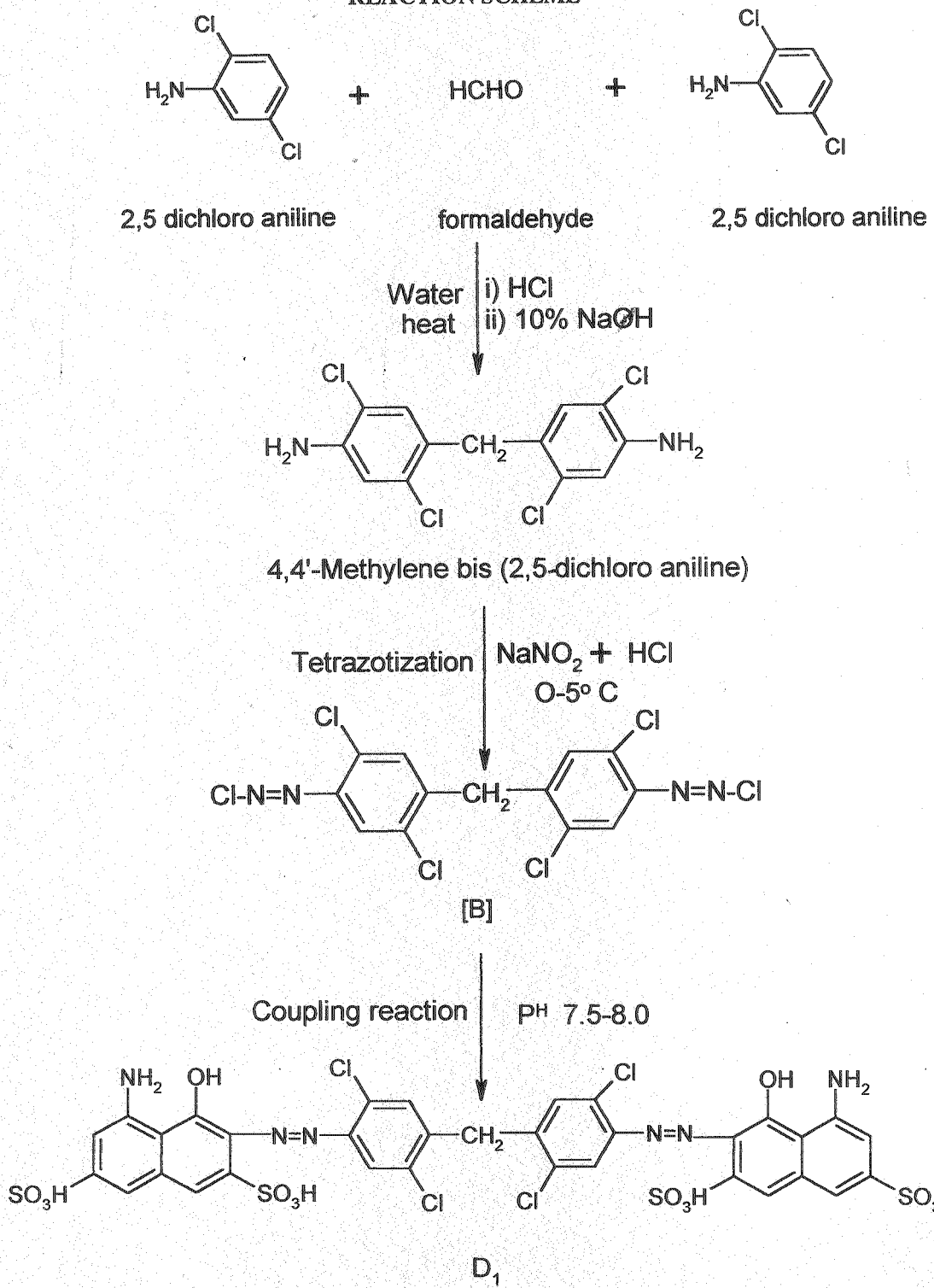


where R = H-acid, R-acid, Schaffer's acid, Peri acid, Bronner's acid, G-acid, gamma acid, N-methyl-J-acid, Koch acid, Tobias acid, Chicago acid, N-phenyl-J-acid, K-acid, J-acid, sulfo-J-acid, Laurent acid and amino-G-acid.

EXPERIMENTAL

Synthesis of 4,4'-methylene-bis-(2,5-dichloro aniline): 2,5-Dichloro aniline (16.2 g, 0.1 mol) was dissolved in 36.5% hydrochloric acid (50 mL, 0.5 mol) and water (100 mL) by warming at 60°C. The solution was cooled to 25°C and 3% aqueous formaldehyde solution (50 mL, 0.05 mol) was added dropwise over

REACTION SCHEME



30 min with constant stirring and the mixture temperature was maintained at 25–30°C for a further 4 h. The pH of the contents was adjusted to 6.5–7.0 with 10% sodium hydroxide solution. The precipitated compound was filtered and washed with water till neutral and dried at 50°C. Yield: 80%; m.p. 140–140°C; Calculated N: 8.33%, Found N: 8.30%. The IR spectrum showed characteristic absorption at 2910 ν(—CH_2—), 1503 ν(—C=C—), 3410 ν(—NH_2), 720 ν(C—Cl) cm^{-1}. The ^1H NMR (DMSO) spectrum showed characteristic peaks at 3.775 (S, 2H, —CH_2), 5.534 (S, 4H, —NH_2), 6.874–6.889 (m, 4H, aromatic proton).

Tetrazotization of 4,4′-methylene bis (2,5-dichloro aniline): 4,4′-Methylene-bis-(2,5-dichloro aniline) (A) (3.36 g, 0.01 mol) was dissolved in 36.5% hydrochloric acid (5 mL, 0.05 mol) and water (60 mL) by warming at 60°C, in order to obtain a clear solution. The clear solution was cooled to 0–5°C in an ice-bath. A solution of $NaNO_2$ (1.38 g, 0.02 mol) in water (10 mL) previously cooled to 0–5°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 with required amount of solution of sulphamic acid; the clear tetrazo solution (B) at 0–5°C was used for subsequent coupling reaction.

Formation of Dyes (D_1): H-acid (6.38 g, 0.02 mol) was dissolved in 10% w/v sodium carbonate solution and water (25 mL). The clear solution was cooled to 0–5°C. The above mentioned tetrazo (B) solution was gradually added to the solution of H-acid and the pH was maintained 7.5–8.0 by the addition of 10% w/v sodium carbonate solution. The contents were stirred for 3 h at 0–5°C. The resulting dye solution was salted out using sodium chloride at 40–50°C. The precipitated dye D_1 was filtered and dried in an oven at 50°C. Yield: 78%. Analysis (%): Calculated: N, 7.74, Found: N, 7.72. IR spectrum showed characteristic absorption at 3449 ν(—OH and —NH), 2922 ν(—CH_2), 1632 ν(N=N), 1384 and 1200 ν(S=O), 1495 ν(C=C). ^1H NMR (DMSO) spectrum showed characteristic peaks at 2.57 (S, 2H, CH_2), 4.80 (S, 2H,—OH) and 6.872–7.671 (aromatic proton and amine).

Dyes D_2 to D_{17} were synthesised by a procedure analogous to that of D_1.

Dyeing of Fabric: All the dyes D_1 to D_{17} were applied on silk, wool and nylon fabrics in 2% shade according to the usual procedure[10] in the dye-bath containing the materials listed as below.

Materials	Dye-Bath		
	For silk	For wool	For nylon
Fabric (g)	2.0	2.0	2.0
Amount of dye (mg)	40.0	40.0	40.0
Glauber salt (20%) (mL)	1.0	1.5	1.0
Soda ash (10%) (mL)	1.0	—	—
pH	3.0	3.0	3.0
MLR	1.4	1.4	1.4
Dyeing time (min)	40.0	60.0	90.0
Dyeing temp. (°C)	85.0	100.0	100.0
Total volume (mL)	80.0	80.0	80.0

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

RESULTS AND DISCUSSION

The absorption spectra of all the dyes were recorded on Beckman DB-GT grafting spectrophotometer. C, H, S contents of dyes sample were estimated using C, H and S analyzer, Carlo Erba, Italy. The IR spectra of dyes were scanned in KBr pellets on a Perkin-Elmer FT-IR Paragon 1000 SPRI S.No. 42825. The NMR spectrum was taken in DMSO-d_6 solution on a Perkin-Elmer Model-32 ^1H NMR spectrometer (200 MHz), with TMS as an internal standard.

All the dye shades varied from light yellowish to violet and obtained in yield 70–82%. The R_f value[11] of all the dyes was checked by thin layer chromatography and they are presented in Table-1.

TABLE-1
CHARACTERIZATION DATA OF ACID DYES

Dye No.	Coupling Components(R)	m.f.	m.w.	Yield (%)	% Nitrogen		R_f
					Calcd.	Found	
D_1	H-acid	$C_{33}H_{18}N_6O_{14}S_4Cl_4Na_4$	1084.56	78	7.74	7.70	0.41
D_2	R-acid	$C_{33}H_{16}N_4O_{14}S_4Cl_4Na_4$	1054.53	84	5.31	5.28	0.40
D_3	Schaffer's acid	$C_{33}H_{18}N_4O_8S_2Cl_4Na_2$	850.44	77	6.58	6.55	0.42
D_4	Peri acid	$C_{33}H_{20}N_6O_6S_2Cl_4Na_2$	848.48	79	9.90	9.85	0.38
D_5	Bronner acid	$C_{33}H_{20}N_6O_6S_2Cl_4Na_2$	848.48	82	9.90	9.86	0.43
D_6	G-acid	$C_{33}H_{18}N_6O_{14}S_4Cl_4Na_4$	1054.53	73	5.31	5.29	0.44
D_7	Gamma acid	$C_{33}H_{20}N_6O_8S_2Cl_4Na_2$	880.47	84	9.54	9.50	0.43
D_8	N-phenyl-J-acid	$C_{35}H_{24}N_6O_8S_2Cl_4Na_4$	908.53	82	9.25	9.21	0.42
D_9	Koch acid	$C_{33}H_{18}N_6O_{18}S_6Cl_4Na_4$	1256.66	73	6.68	6.63	0.39
D_{10}	Tobias acid	$C_{33}H_{22}N_6Cl_4$	644.39	74	13.04	12.99	0.38
D_{11}	Chicago acid	$C_{33}H_{18}N_6O_{14}S_4Cl_4Na_4$	1084.56	74	7.74	7.70	0.38
D_{12}	N-methyl-J-acid	$C_{45}H_{28}N_6O_8S_2Cl_4Na_2$	1032.67	77	8.13	8.10	0.42
D_{13}	K-acid	$C_{33}H_{18}N_6O_{14}S_4Cl_4Na_4$	1084.56	82	7.74	7.71	0.43
D_{14}	J-acid	$C_{33}H_{20}N_6O_8S_2Cl_4Na_4$	880.47	78	9.54	9.51	0.85
D_{15}	Amino-G-acid	$C_{33}H_{18}N_6O_{12}S_4Cl_4Na_4$	1052.57	70	7.98	7.94	0.78
D_{16}	Sulpho-J-acid	$C_{33}H_{18}N_6O_{14}S_4Cl_4Na_4$	1084.56	70	7.74	7.69	0.64
D_{17}	Laurent acid	$C_{33}H_{20}N_6O_6S_2Cl_4Na_2$	848.48	77	9.90	9.86	0.87

The infrared spectra of dyes were scanned in KBr pellets on a Perkin-Elmer FTIR Paragon 1000 SPRI S.No. 42825. IR spectra[12–14] of all the dyes, in general, showed characteristic band at 2915-2925 ν(—CH_2—), 1604-1632 ν(—N=N—),

1449–1973 ν(C=C), 1118–1200 ν(S=O) and 3383–3454 cm^{-1} due to ν(O—H) and ν(N—H) stretching vibrations.

Dyeing and fastness properties: Dyeing was carried out at acidic pH (3.0) on silk, wool and nilon fabrics. The dyes cover almost all the visible ranges and give generally light yellow to blue-violet hues depending on the nature of coupling component used. However, it was found that the shades on silk were deeper than those of wool and nylon. The dyes generally gave satisfactory dying on silk, wool and on nylon.

The percentage exhaustion of 2% dyeing on silk fabric ranges from 31 to 84%, for wool ranges from 55 to 86% and for nylon ranges from 30 to 78%. The percentage fixation of 2% dyeing on silk fabric ranges from 81.4 to 91.8%, for wool ranges from 77.9 to 90.17% and for nylon ranges from 76.3 to 86.1% (Table-2).

TABLE-2
PERCENTAGE EXHAUSTION AND FIXATION OF ACID DYES
ON SILK, WOOL AND NYLON

Dye No.	Shade on dyed fabric	λ_{max}	Exhaustion (%)			Fixation (%)		
			Silk	Wool	Nylon	Silk	Wool	Nylon
D_1	Bluish-Violet	541	73	82	72	89.7	88.4	86.1
D_2	Dull-Orange	493	58	76	57	84.4	90.1	78.9
D_3	Orange	480	53	78	52	83.0	89.1	81.7
D_4	Dull-Red	499	79	80	76	86.0	84.3	85.5
D_5	Orange	467	77	77	72	87.0	88.3	83.3
D_6	Yellowish-Orange	491	97	70	55	87.7	87.8	83.6
D_7	Dull-Red	500	82	80	78	85.3	89.3	85.8
D_8	Yellowish-Red	509	58	75	60	90.5	87.3	76.6
D_9	Light-Red	512	71	70	68	85.9	85.7	79.4
D_{10}	Light-Orange	400	82	82	72	85.3	87.1	76.3
D_{11}	Violet	524	84	84	74	88.0	77.1	83.1
D_{12}	Yellowish-Red	515	83	86	71	89.7	87.2	85.2
D_{13}	Violet	525	83	86	70	87.3	86.0	85.7
D_{14}	Dull-Red	469	81	81	75	81.4	80.8	83.3
D_{15}	Light-Brown	438	31	55	30	83.8	86.3	81.6
D_{16}	Yellowish-Orange	480	65	70	64	83.0	86.4	78.1
D_{17}	Dull-Brown	485	67	83	78	87.7	81.9	83.9
D_{18}	Light-Scarlet	440	55	72	60	91.8	86.8	81.6

All the dyes showed good affinity for silk, wool and nylon and gave moderate to very good lightfastness properties. The washing and rubbing fastness properties range from good to excellent fastness on silk and nylon while washing and rubbing fastness properties of wool range from good to very good (Table-3).

TABLE-3
FASTENESS PROPERTIES OF ACID DYES

Dye No.	Light fastness			Wash fastness			Rubbing fastness					
							Dry			Wet		
	S	W	N	S	W	N	S	W	N	S	W	N
D_1	4	4	3	4	4	3	4–5	3	4	3–4	3	4
D_2	5	5	4	4	4	3	4	2	3	4	5	4
D_3	4–5	5	3–4	4–5	3	3	4	2	5	3	6	3
D_4	4	4–5	3	4–5	4	2–3	4	2	3	4	5	4
D_5	5	4	3–4	3–4	3	4	3	3	3	3	4–5	4
D_6	5	4	2–3	5	4	4	4	3	4–5	3–4	5	3
D_7	4	5	3	3	3–4	2–3	4–5	3	4–3	3	3	3–4
D_8	4–5	4	4	3	5	3	3	3	3	4	4	5
D_9	4	5	2–3	4	4–5	2–3	3	3	4	5	3	4–5
D_{10}	5	4	3	3	3	4	4	2	3	3	4	3
D_{11}	4	4–5	4	3	3–4	3	4	2	3–4	4	5	3–4
D_{12}	4	4	3	4	4	2	4	3	4	3	4	4
D_{13}	5	5	3	3–4	4	4	4	4	3	4–5	3	4
D_{14}	5–6	4–5	4	4	3–4	4	4	3–4	4	4	4	3–4
D_{15}	6	6	5	5	4	4	4	4	4	3–4	4	4
D_{16}	5	4–5	5	4	3–4	4	3–4	3	4	4	4	4
D_{17}	4	4	3–4	3	3	3–4	4	3–4	4	3–4	3–4	3–4

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

REFERENCES

1. P. Jarmila, M. Jiri and K. Peter, *Czech. C.S.*, **269**, 613, *Appl.*, *88/8*, 254; *Chem. Abstr.*, **116**, 237353u (1992).
2. De Giorgi and M. Rita, *J. Soc. Dyers Colours*, **109**, 405 (1993).
3. T. Omura, Y. Kayane, S. Takahashi, T. Miyamoto, A. Takeshita, N. Harada and K. Otake, *Jpn. Kokai Tokyo Koho Jp.*, **60**, 173 (1985); *Chem. Abstr.*, **104**, 90463c (1986).
4. FIAT Fonal Report No. 1331, Vol. III, p. 351 (1948).
5. Y.C. Chao and C.W. Yeh, *Dyes Pigments*, **24**, 285 (1993).
6. I. Sabre and M. Clopotar, *Rev. Roum. Chim.*, **38**, 1083 (1993).
7. P. Wight, PCT Int. Appl. Wo., 9913,008 (CI CO9B 21/08) (1999).; *Chem. Abstr.*, **130**, 253667u (1999).
8. M.S. Patel, S.K. Patel and K.C. Patel, *Orient. J. Chem.*, **13**, 261 (1997).
9. P.S. Patel, R.S. Patel, K.C. Patel and S.K. Patel, *Orient. J. Chem.*, **20**, 263 (2004).
10. V.A. Shenai, Chemistry of Dyes & Principles of Dyeing, Sevak Publication, Bombay (1973).
11. B. Fried and J. Sherma, Thin Layer Chromatography: Techniques and Applications, Marcell-Dekker, Inc., New York-Basel (1982).
12. N.B. Colthup, L.H. Daly and S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York-London (1964).
13. R.M. Silverstein, G.C. Bassler and J.C. Morrill, Spectrophotometric Identification of Organic Compounds, 5th Edn., Wiley, New York (1991).
14. J.A. Dean, *Clin. Chem.*, **14**, 324 (1968).

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