*Asian Journal of Chemistry* Vol. 12, No. 4 (2000), 1193–1198

# Synthesis of 4,4′-Methylene bis *o*-Toluidine Based Bisazo Reactive Dyes and Their Application

R.B. PATEL, NILESH PATEL, S.K. PATEL and K.C. PATEL*
*Department of Chemistry, South Gujarat University, Surat-395 007, India*

Various bisazo reactive dyes have been prepared by coupling diazotised 4,4′-methylene bis *o*-toluidine with various *o*-toluidino cyanurated coupling components such as H-acid, J-acid, K-acid, tobias acid, N-phenyl-J-acid, N-methyl-J-acid, solfo-tobias acid, T-acid and Bronner acid and their dyeing performance as reactive dyes has been assessed on wool, silk and viscose rayon.

## INTRODUCTION

Reactive dyes are becoming increasingly popular for dyeing cellulosic fibres because of their wide shade range, ease of application and excellent wet fastness properties. Several new reactive systems have been introduced from time to time which cover the subject of innumerable patents and publications[1–3]. Improvements 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 dyes[4, 5]. Patel *et al.*[6, 7] have reported fibre reactive dyes for viscose rayon, wool and silk.

## EXPERIMENTAL

**Synthesis of 4,4′-methylene bis *o*-toluidine (A):** *o*-Toluidine (10.7 g, 0.1 mol) was dissolved in water (125 mL) and 36.5% hydrochloric acid (25 mL) at 50°C. The reaction mixture was then treated with 3% aqueous formaldehyde (35 mL) solution at 60°C with stirring for 1 h and neutralized with 10% sodium hydroxide. White precipitate obtained was filtered, washed with hot water, dried and recrystallised from acetic acid. Yield: 84%, m.p.: 273°C, m.f. $C_{15}H_{18}N_2$: Analysis (%), Found, N = 12.37; required, N = 12.39.

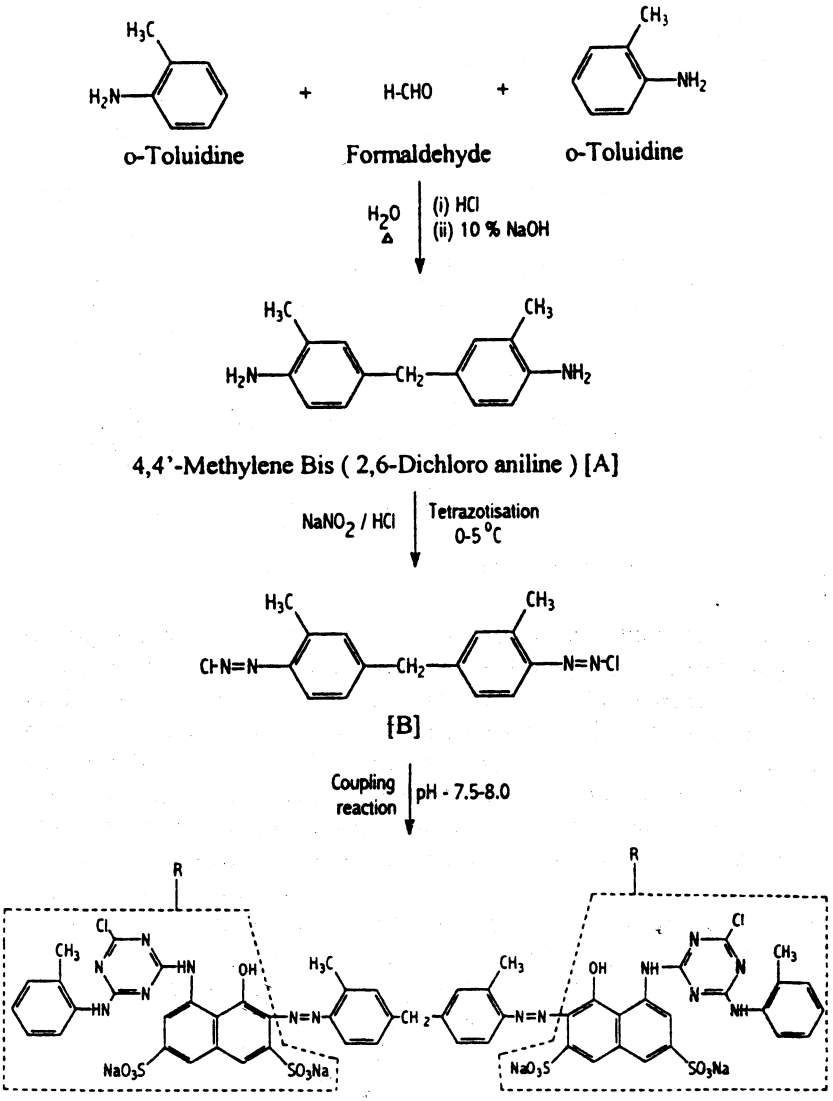
**Tetrazotization of 4,4′-methylene bis *o*-toluidine (B):** 4,4′-Methylene-bis-*o*-toluidine (A) (2.26 g, 0.01 mol) was suspended in $H_2O$ (60 mL); hydrochloric acid (10 mL) was added dropwise to this well stirred suspension. The mixture was gradually heated up to 70°C, till a clear solution was obtained. 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 the required amount of a solution of sulphamic acid, a clear tetraazo solution (B) at 0–5°C was used for subsequent coupling reaction.

**Preparation of *o*-toluidino cyanurated coupling component (R):**

*(a) Cyanuration of coupling component (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 a further 4 h when a clear solution was obtained. The cyanurated coupling component solution (R′) thus formed was used for subsequent coupling reaction.

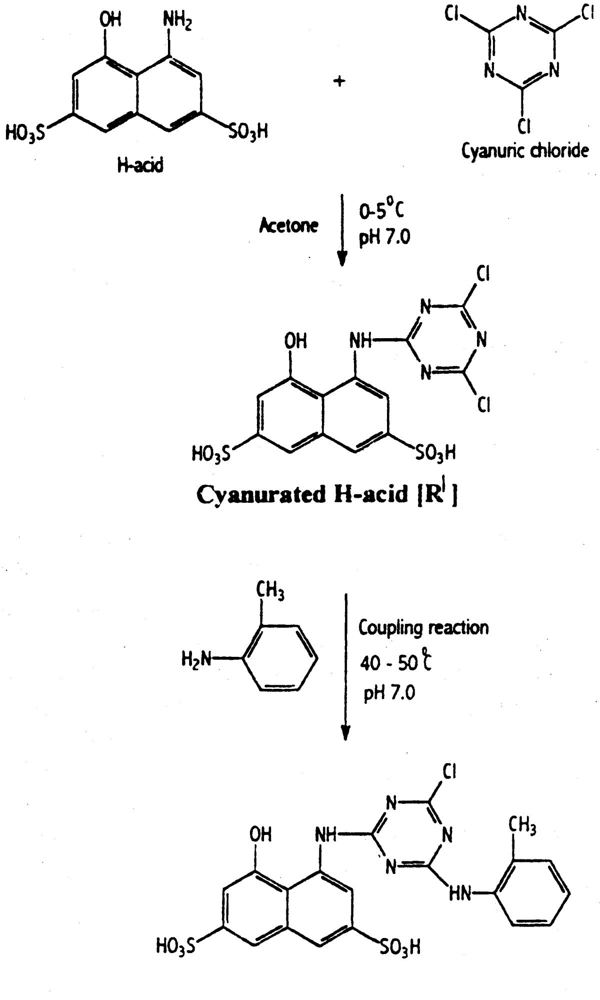
## REACTION SCHEME



$D_1$

*(b) Formation of o-toluidino cyanurated coupling components (R):* To an ice-cooled and well stirred solution of cyanurated coupling component (R′) was heated up to 40–50°C for $\frac{1}{2}$ h. Then *o*-toluidine (2.14 g, 0.02 mol) was added drop-wise at the same temperature, during a period of $\frac{1}{2}$ h., maintaining the pH neutral by simultaneous addition of sodium bicarbonate solution (1% w/v). After the addition was completed stirring was continued for a further 3 h to prepare a *o*-toluidino cyanurated coupling component (R) which was used for further coupling reaction.

## PREPARATION OF *o*-TOLUIDINO CYANURATED H-ACID [R]



o-Toluidino Cyanurated H-acid [R]

**Formation of dyes ($D_1$ to $D_{13}$):** To an ice-cooled and well stirred solution of *o*-toluidino cyanurated coupling compoent (R), a freshly prepared solution of tetraazo solution (B) was added dropwise over a period of 10–15 min. The pH was maintained at 7.5 to 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 *o*-toluidino cyanurated coupling components.

**Dyeing of fibres:** All the dyes $D_1$ to $D_{13}$ were applied on silk, wool and viscose rayon using the reported procedure[8].

**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.

TABLE-1

PHYSICO-CHEMICAL CHARACTERISATION OF VARIOUS DYES

| Dye No. | *o*-Toluidino cyanurated coupling components | m.f. | m.w. | Yield (%) | m.p. (°C) | $R_f$ value | Nitrogen (%) Found (required) |
|---|---|---|---|---|---|---|---|
| $D_1$ | H-acid | $C_{55}H_{40}O_{14}N_{14}Cl_2S_4Na_4$ | 1363 | 78 | 294 | 0.39 | 14.34<br>(14.38) |
| $D_2$ | J-acid | $C_{55}H_{42}O_8N_{14}Cl_2S_2Na_2$ | 1183 | 85 | 298 | 0.36 | 16.54<br>(16.57) |
| $D_3$ | K-acid | $C_{55}H_{40}O_{14}N_{14}Cl_2S_4Na_4$ | 1363 | 83 | 289 | 0.43 | 14.36<br>(14.38) |
| $D_4$ | Tobias acid | $C_{55}H_{44}N_{14}Cl_2$ | 971 | 86 | 310 | 0.46 | 20.15<br>(20.18) |
| $D_5$ | N-phenyl-J-acid | $C_{67}H_{50}O_8N_{14}Cl_2S_2Na_2$ | 1335 | 79 | 296 | 0.41 | 14.65<br>(16.68) |
| $D_6$ | N-methyl-J-acid | $C_{57}H_{46}O_8N_{14}Cl_2S_2Na_2$ | 1211 | 82 | 308 | 0.48 | 16.16<br>(16.18) |
| $D_7$ | Gamma acid | $C_{55}H_{42}O_8N_{14}Cl_2S_2Na_2$ | 1183 | 84 | 292 | 0.42 | 16.52<br>(16.57) |
| $D_8$ | Laurent acid | $C_{55}H_{42}O_6N_{14}Cl_2S_2Na_2$ | 1151 | 79 | 315 | 0.44 | 17.00<br>(17.03) |
| $D_9$ | Chicago acid | $C_{55}H_{40}O_{14}N_{14}Cl_2S_4Na_4$ | 1363 | 76 | 308 | 0.38 | 14.36<br>(14.38) |
| $D_{10}$ | Peri acid | $C_{55}H_{42}O_6N_{14}Cl_2S_2Na_2$ | 1151 | 86 | 314 | 0.45 | 16.98<br>(17.03) |
| $D_{11}$ | Sulfo tobias acid | $C_{55}H_{42}O_6N_{14}Cl_2S_2Na_2$ | 1151 | 82 | 312 | 0.49 | 17.00<br>(17.03) |
| $D_{12}$ | T-acid | $C_{55}H_{38}O_{18}N_{14}Cl_2S_6Na_6$ | 1511 | 81 | 297 | 0.46 | 12.95<br>(12.97) |
| $D_{13}$ | Bronner's acid | $C_{55}H_{42}O_6N_{14}Cl_2S_2Na_2$ | 1151 | 83 | 286 | 0.43 | 17.01<br>(17.03) |

## RESULTS AND DISCUSSION

All the dyes were yellow to red colour and obtained in excellent yield [73 to 86%]. The purity of all dyes has been checked by thin-layer chromatography[9]. The absorption spectra of all the dyes were recorded on Beckmann DB-GT Grafting spectrophotometer. The characterisation data of dyes are given in Table-1 (on previous page).

The IR spectra of dyes $D_1$ to $D_{13}$ were recorded on Perkin-Elmer spectrophotometer (Model 377) using KBr pellets. Dyes $D_1$ to $D_{13}$ showed characteristic band at 2890–2790 ν(—$CH_2$—), 860–790 ν(S-triazine), 630–590 ν(C—Cl), 1680–1590 ν(—NH), 1385–1375 ν(—N=N—), 1150–1050 ν(S=O) and 3450–3400 $cm^{-1}$ due to ν(O—H).

The PMR spectra (300 MHz, $CDCl_3$) of a representative dye showed signals at 1.98–2.02 (12H, —$CH_3$), 2.50 (2H, —$CH_2$—), 7.30–7.96 (aromatic proton), 8.93 (2H, —NH—Ar).

**Fastness properties:** The percentage exhaustion fixation and fastness properties of dyes $D_1$ to $D_{13}$ are given in Table-2 and 3. All the dyes $D_1$ to $D_{13}$ showed good affinity for viscose rayon, wool and silk 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 WOOL, SILK AND VISCOSE RAYON

| Dye No. | Shade on dyed fibre | $\lambda_{max}$ | % Exhaustion | | | % Fixation | | |
|---|---|---|---|---|---|---|---|---|
| | | | S | W | V | S | W | V |
| $D_1$ | Reddish pink | 510 | 74.0 | 65.10 | 44.50 | 90.00 | 79.45 | 61.5 |
| $D_2$ | Brown | 480 | 69.2 | 63.30 | 45.60 | 94.10 | 78.90 | 66.5 |
| $D_3$ | Light yellow | 465 | 76.9 | 64.20 | 49.25 | 89.30 | 76.10 | 64.0 |
| $D_4$ | Reddish pink | 440 | 68.0 | 65.00 | 47.25 | 92.30 | 84.80 | 61.0 |
| $D_5$ | Reddish orange | 475 | 79.1 | 60.15 | 50.50 | 82.70 | 79.80 | 64.5 |
| $D_6$ | Orange | 525 | 79.5 | 64.20 | 50.00 | 93.70 | 76.10 | 61.5 |
| $D_7$ | Reddish pink | 535 | 78.6 | 60.00 | 44.90 | 83.20 | 76.30 | 64.0 |
| $D_8$ | Reddish pink | 490 | 73.2 | 63.85 | 46.55 | 89.70 | 80.25 | 65.0 |
| $D_9$ | Brown | 485 | 67.5 | 65.50 | 50.65 | 94.35 | 78.70 | 61.0 |
| $D_{10}$ | Brown | 470 | 69.5 | 63.70 | 44.50 | 92.15 | 75.30 | 61.5 |
| $D_{11}$ | Light yellow | 505 | 67.8 | 65.30 | 46.10 | 94.20 | 78.55 | 59.5 |
| $D_{12}$ | Light orange | 455 | 70.0 | 64.80 | 46.50 | 92.00 | 80.00 | 65.0 |
| $D_{13}$ | Yellow | 495 | 77.0 | 61.70 | 48.90 | 83.80 | 77.80 | 62.0 |

W = Wool, S = Silk and V = Viscose rayon

TABLE-3
FASTNESS PROPERTIES

| Dye No. | Light fastness | | | Wash fastness | | | Rubbing fastness | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Dry | | | Wet | | |
| | S | W | V | S | W | V | S | W | V | S | W | V |
| $D_1$ | 4 | 5 | 3–4 | 5 | 4 | 3 | 4 | 4 | 3–4 | 4 | 4 | 3 |
| $D_2$ | 5 | 4 | 4 | 4–5 | 4 | 3 | 4 | 4–5 | 3–4 | 5 | 5 | 4 |
| $D_3$ | 5–6 | 6 | 3 | 5 | 4–5 | 2–3 | 5 | 5 | 3 | 4–5 | 5 | 3–4 |
| $D_4$ | 4 | 4–5 | 3–4 | 4 | 5 | 3 | 4–5 | 5 | 4 | 4 | 4–5 | 3 |
| $D_5$ | 5 | 4 | 4 | 4 | 3–4 | 3 | 4 | 4 | 4 | 5 | 4 | 3–4 |
| $D_6$ | 4–5 | 5 | 3 | 4 | 4 | 2–3 | 5 | 4 | 3 | 5 | 4 | 2–3 |
| $D_7$ | 4 | 5 | 3–4 | 5 | 5 | 3 | 4–5 | 4–5 | 3–4 | 4 | 5 | 3 |
| $D_8$ | 5 | 4–5 | 4 | 4–5 | 4 | 3 | 4 | 4 | 4 | 4–5 | 4 | 4 |
| $D_9$ | 4 | 4 | 3 | 4 | 3–4 | 2–3 | 5 | 4 | 3 | 4 | 5 | 2–3 |
| $D_{10}$ | 5 | 5 | 4 | 5 | 4–5 | 4 | 5 | 4 | 4 | 5 | 4 | 4 |
| $D_{11}$ | 4–5 | 5–6 | 3 | 4 | 5 | 3 | 4–5 | 5 | 4 | 4 | 4–5 | 3 |
| $D_{12}$ | 4 | 4 | 4 | 4–5 | 4 | 4 | 4 | 4–5 | 3–4 | 4 | 4 | 4 |
| $D_{13}$ | 4 | 4–5 | 3–4 | 5 | 4 | 2–3 | 4 | 4 | 3 | 5 | 5 | 3 |

W = Wool, S = Silk and V = Viscose rayon

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(*Received:* 13 May 2000; *Accepted:* 17 July 2000) AJC-2075