Synthesis, characterization and application of novel bisazo reactive dyes on various fibers

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Received: 14 February 2010; revised: 15 February 2011; accepted: 05 May 2011. Available online: 05 September 2011.

ABSTRACT: Ten hot brand bisazo reactive dyes (D₁ to D₁₀) have been synthesized by coupling bis(diazotised), 4,4'-methylene bis(2,6-dichloroaniline) (A) with various 5-sulfo anthranilo cyanurated coupling components (R) and their dyeing performance as reactive dyes has been assessed on silk, wool and cotton fibres. The purity of dyes was checked by TLC. The IR spectra and ¹H-NMR spectra prove the structure of newly reactive dyes. The percentage dye bath exhaustion on different fibres was reasonable good and acceptable. The dyes exhibited high levels of light, washing and rubbing fastness.

Keywords: 4-4'-methylene bis(2,6-dichloroaniline); hot brand bisazo reactive dyes; silk; wool; cotton

Introduction

Reactive dyes are colored compounds which contain one or two groups capable of forming covalent bond between a carbon atom or phosphorus atom of the dyes ion or molecules and an oxygen atom, nitrogen atom or sulfur atom of a hydroxyl, an amino or a mercapto group respectively, of the substrate [1]. These dyes are generally used on higher value clothes, which are normally mercerized [2].

Reactive dyes though late entry in to the field of synthetic dyes, very soon attained a commercial status. Several new reactive systems have been introduced from time to time, which covers the subject of innumerable patents and publication [3]. It was for the first time that dyeing has been done by chemical reaction between the dye and the fibre, enabling one to get 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 it one of the two dye-fibre bonds is hydrolyzed, one is still left for fixation [4, 5]. Reactive dyes are well known and applied for dyeing of different materials [6]. Among them triazine derivatives have an important place [7].

s-Triazine based chemicals have been applied variously in the manufacture of polymers, dyes, drugs, explosives, pesticides and commodity chemicals [8] as a consequence, theoretical and experimental studies on these chemicals have been widely carried out [9, 10] with the result that the s-triazine ring is known as an important conjugated heterocycle whose electronics properties are expected to show suitable differences from those of benzene due to the alternate replacement of -CH- group by nitrogen atoms [11].

s-Triazine plays an important role in synthesized dyes. The key compound of reactive dyes are a cyanuric chloride in synthesized dyestuff have two reactive groups in their structure which give high fixation yields, excellent wet fastness, brilliant shade and simple application techniques in textile printing. The advantage owing to the chloro triazine groups (s-triazine) is that due to the electrophilic property of the cyanuric group, a wide range of chromophores having good fastness to light, perspiration and chlorine.

Hot-Brand reactive dyes have been widely considered due to their fixation yield on various fibers [12].

Various bisazo reactive dyes (Figure 1 and Figure 2) have been reported earlier which shows good dyeing properties on silk, wool and cotton [13, 14].

![Figure 1](image1.png)

**Figure 1.** Cold brand bisazo reactive dyes. Where R = Various cyanurated coupling components.

![Figure 2](image2.png)

**Figure 2.** Hot brand bisazo reactive dyes. Where R = Various m-nitro anilino cyanurated coupling components.

In a continuation of our work we report here the synthesis of some hot-brand reactive dyes with a higher degree of activity synthesis and study of the dyeing
properties of the bisazo reactive dyes base on 4,4’-methylene bis(2,6-dichloroaniline). The reactive dyes of the following structure were prepared (Figure 3).

\[ R - N = N - C H_2 - N = N - R \]

**Figure 3.** Hot brand bisazo reactive dyes. Where R = Various 5-sulfo anthranilo cyanurated coupling components.

### Material and Methods

**General**

All melting points are determined using a DSC 7, Perkin-Elmer (USA) Differential Scanning Caloriate (heating rate 5 °C/min, N$_2$ gas) digital melting apparatus and are uncorrected. IR spectra were recorded in KBr on a Perkin-Elmer model-377 spectrophotometer instrument. Elemental microanalyses were performed on a LECI CHN-932 for C, H and N. Thin Layer chromatography was performed using silica-coated aluminum plates (60-F$_{254}$, Merck) [15]. $^1$H NMR spectra were obtained with a Jeol JNMO-FX 200 at 300 MHz instrument, Using TMS as the internal standard and DMSO-$d_6$ as a solvent. Chemical shifts are given in δ ppm. Absorption spectra were obtained with Becman DB-GT grafting spectrometer instrument. Fastness to light was assessed in accordance with BS 1006-1978 [16]. Rubbing fastness was carried out with an Atlas Crock meter in accordance with AATCC TM 8-1961 [17] and the wash fastness test in accordance with ISO: 765-1979 [18]. The entire regents were purchased from Merck and Renkem, which were of G. R. grade and used without further purification. All crude products were isolated as solids and purified by a combination of column chromatography and recrystallization.

**Chemistry**

**Preparation of 4-4’ methylene bis(2,6-dichloroaniline) [19]**: 2,6-dichloroaniline (14.8 g, 0.1 mole) 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 solution (35 mL). The temperature was maintained at 60 °C and stirred for an hour and neutralized with 10% sodium hydroxide solution, yellow precipitates obtained were filtered, washed with hot water, dried and recrystallised from acetic acid. Yield 84%, m.p. 273 °C. IR (KBr) 3420 cm$^{-1}$, 3300 cm$^{-1}$ (N-H), 2850 cm$^{-1}$ (C-H). $^1$H NMR (DMSO): δ 8.2 (2H, s, NH$_2$), 3.45 (2H, s, CH$_2$), 7.05-7.15 (4H, m, Ar–H). Elemental analysis: Found C-46.40%; H-2.94% N-8.32% C$_{13}$H$_{10}$N$_2$Cl$_4$ (MF require C-46.45%; H-2.99%; N-8.37%).
**Scheme 1.** Preparation of 5-sulfo anthranilo cyanurated H-acid (R).

**Tetrazotisation of 4-4′-methylene bis(2,6-dichloroaniline):** 4-4′-methylene bis(2,6-dichloroaniline) (1.68 g, 0.005 mole) was suspended in H₂O (60 mL). Hydrochloric acid (10 mL) was added drop wise to this well stirred suspension. The mixture was gradually heated up to 70 °C till clear solution obtained. The solution was cooled to 0-5 °C in an ice bath. A solution of NaNO₂ (1.38 g) in H₂O (8 mL) previously cooled to 0 °C, was then added over a period of 5 minutes with stirring. The stirring was continued for an hour maintaining the same temperature, with positive test for nitrous acid with required amount of a solution of a sulphamic acid. The clear tetrazo solution (A) at 0-5 °C was used for subsequent coupling reaction.

**Preparation of 5-sulpho anthranilo cyanurated H-acid (R)**

(i) **Cyanuration of H-acid:** Cyanuric chloride (1.85 g, 0.01 mole) was stirred in acetone (50 mL) at a temperature below 5 °C for a period of an hour. A neutral solution of H-acid (3.19 g, 0.01 mole) aqueous sodium carbonate solution (10% w/v) was then added in small lots in about an hour, the neutral pH was maintained below 5 °C through this reaction. The reaction mass was then stirred at 0-5 °C for further four hours when a clear solution was obtained. The cyanurated H-acid solution thus formed was used for subsequent coupling reaction.

(ii) **Condensation with 5-sulpho anthranilic acid:** The ice-cooled and well-stirred
solution of cyanurated H-acid (4.67 g, 0.01 mole) was heated up to 40-50 ºC for half an hour. To this 5-sulpho anthranilic acid (2.17 g, 0.01 mole) was added dropwise at same temperature during a period of 30 minutes maintaining the pH neutral, by simultaneous addition of sodium carbonate solution (1% w/v). After the addition was completed the stirring was continued for further 3 hours, to prepare a 5-sulpho anthranilo cyanurated H-acid (R). The resulting solution thus obtained was used for further coupling reaction.

\[
\begin{align*}
\text{2,6-dichloro aniline} &+ \text{Formaldehyde} + \text{2,6-dichloro aniline} \\
\triangle &\rightarrow \\
\text{HCl} &\rightarrow \\
\text{10% NaOH} &\rightarrow \\
\text{4,4'-methylene-bis(2,6-dichloro aniline)} &\rightarrow \\
0-5^\circ C &\rightarrow \\
\text{Tetrazosolution (A)} &\rightarrow \\
0-5^\circ C &\rightarrow \\
pH 7.5-8.5 &\rightarrow \\
\text{Coupling with 5-sulfo anthranilo cyanurated H-acid (R) (2 mole)} &\rightarrow \\
\end{align*}
\]

Where R= Various 5-sulfo anthranilo cyanurated coupling components

**Scheme 2.** Synthesis of dye D₁

**Preparation of dye (D₁):** To a well-stirred solution of 5-sulpho anthranilic acid (R) (6.48 g, 0.01 mole), a freshly prepared solution of tetrazo solution (A) (2.155
g, 0.005 mole) was added drop wise over a period of 10-15 minutes. The pH was maintained at 7.5 to 8.5 by simultaneous addition of sodium carbonate solution (10\% w/v). During coupling the purple solution was formed. Stirring was continued for 3-4 hours, maintaining the temperature below 5 °C. The reaction mixture was heated up to 60 °C and sodium chloride (15 g) added until the colouring material was precipitated. It was stirred for an hour, filtered and washed with a small amount of sodium chloride solution (5\% w/v). The solid was dried at 80-90 °C and extracted with DMF. The dye was precipitated by diluting the DMF-extract with excess of chloroform. A purple dye was then filtered, washed with chloroform and dried at 60 °C. Yield 86%.

Following the above procedure other reactive dyes D2 to D10 were synthesized using 5-sulfo anthranilo cyanurated coupling components such as J-acid, N-phenyl-J-acid, Gamma-acid, K-acid, Chicago acid, Peri acid, Bronner acid, Tobias acid and Sulfo tobias acid. All the synthesized dyes were recorded in Table 1.

**Results and Discussion**

**Spectral properties of dyes**

The absorption maxima (\(\lambda_{\text{max}}\)) of the dyes D1 to D10 were recorded in water and conc. H\(_2\)SO\(_4\) and are shown in Table 4. The \(\lambda_{\text{max}}\) values are directly proportional to the electronic power, nature and position of the substituents in the naphthyl ring of the coupler moiety. The values of log\(\varepsilon\) (molar extinction coefficient) are summarized in Table 3. All the values are in the range of 4.19-4.30, which indicates the dyes have high intensity of absorption.

Dye D2 have \(\lambda_{\text{max}}\) is about 462 nm while D3 have \(\lambda_{\text{max}}\) is about 482 nm. Here the introduction of phenyl ring which produce bathochromic effect and shifting the \(\lambda_{\text{max}}\) value. Here 20 nm shifting in absorption is observed. Dye D4 have \(\lambda_{\text{max}}\) is about 458 nm while D7 and D8 have \(\lambda_{\text{max}}\) values are 435 nm and 440 nm respectively. Here the introduction of auxochrome like hydroxyl group which produce bathochromic effect and give rise to the 23 nm and 18 nm \(\lambda_{\text{max}}\) value in D4 with respect to D7 and D8. Dyes D1, D5 and D6 have same groups but the positions of the groups are different so the oscillation of electron is fast in D5 and D6 as compare to D1. So dye D1 possesses higher \(\lambda_{\text{max}}\) value as compare to D5 and D6. The shifting of 20 nm \(\lambda_{\text{max}}\) value in D10 as compare to D9 due to the introduction of auxochrome like sulfonic acid group in D10, which increase the \(\lambda_{\text{max}}\) value in D10 as compare to D9.

**Dyeing properties of dyes**

All the dyes D1 to D10 were applied at 2\% depth on silk, wool and cotton fibres according to usual procedure \[21\] in the dye bath containing materials as listed in Table 2.
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**Table 1.** Characterization data of dyes D₁ to D₁₀

| Dye No. | Various 5-sulfo anthranilic coupling Components (R) | Molecular Formula | Mol. Wt. | Yield (%) | % C Found Req. | % H Found Req. | % N Found Req. | Rf
|---------|-------------------------------------------------|------------------|---------|-----------|---------------|---------------|---------------|------
| D₁      | H-acid                                          | C₅₃H₂₆O₂₅N₁₄S₂Na₄Cl₆ | 1788    | 86        | 35.57         | 1.46           | 10.96         | 0.43
| D₂      | J-acid                                          | C₅₃H₂₆O₂₅N₁₄S₂Na₄Cl₆ | 1577    | 84        | 40.32         | 1.52           | 12.42         | 0.39
| D₃      | N-phenyl J-acid                                 | C₅₃H₂₂O₂₅N₁₄S₂Na₄Cl₆ | 1839    | 84        | 42.41         | 1.74           | 10.65         | 0.40
| D₄      | Gamma-acid                                      | C₅₃H₂₆O₂₅N₁₄S₂Na₄Cl₆ | 1577    | 85        | 40.33         | 1.52           | 12.42         | 0.44
| D₅      | K-acid                                          | C₅₃H₂₆O₂₅N₁₄S₂Na₄Cl₆ | 1788    | 80        | 35.57         | 1.46           | 10.96         | 0.46
| D₆      | Chicago acid                                    | C₅₃H₂₆O₂₅N₁₄S₂Na₄Cl₆ | 1788    | 85        | 35.57         | 1.46           | 10.96         | 0.42
| D₇      | Peri acid                                       | C₅₃H₂₆O₂₅N₁₄S₂Na₄Cl₆ | 1545    | 87        | 41.17         | 1.55           | 12.68         | 0.45
| D₈      | Bronner acid                                    | C₅₃H₂₆O₂₅N₁₄S₂Na₄Cl₆ | 1545    | 83        | 41.17         | 1.55           | 12.68         | 0.40
| D₉      | Tobias acid                                     | C₅₃H₂₆O₂₅N₁₄S₂Na₄Cl₆ | 1545    | 80        | 41.17         | 1.55           | 12.68         | 0.40
| D₁₀     | Sulpho tobias acid                              | C₅₃H₂₆O₂₅N₁₄S₂Na₄Cl₆ | 1749    | 84        | 36.36         | 1.26           | 11.20         | 0.46

* Determined by TLC using Toluene: Ethyl acetate (7.5: 2.5 v/v) solvent system on Silica gel-G F₂₅₄ TLC plate.

**Table 2.** Dye-bath containing materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>For silk</th>
<th>For wool</th>
<th>For cotton</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fabric</td>
<td>2.0 g</td>
<td>2.0 g</td>
<td>2.0 g</td>
</tr>
<tr>
<td>Amount of dye</td>
<td>40 mg</td>
<td>40 mg</td>
<td>40 mg</td>
</tr>
<tr>
<td>Glauber’s salt (20% w/v)</td>
<td>1.0 mL</td>
<td>1.5 mL</td>
<td>1.0 mL</td>
</tr>
<tr>
<td>Soda ash (10% w/v)</td>
<td>-</td>
<td>-</td>
<td>1.0 mL</td>
</tr>
<tr>
<td>Acetic acid (10% w/v)</td>
<td>1.0 mL</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Formic acid (10% w/v)</td>
<td>-</td>
<td>1.5 mL</td>
<td>-</td>
</tr>
<tr>
<td>pH</td>
<td>3</td>
<td>3</td>
<td>8</td>
</tr>
<tr>
<td>MLR</td>
<td>1:40</td>
<td>1:40</td>
<td>1:40</td>
</tr>
<tr>
<td>Dyeing time</td>
<td>40 min</td>
<td>60 min</td>
<td>90 min</td>
</tr>
<tr>
<td>Dyeing temp.</td>
<td>60-80 °C</td>
<td>60-80 °C</td>
<td>60-80 °C</td>
</tr>
<tr>
<td>Total volume</td>
<td>80 mL</td>
<td>80 mL</td>
<td>80 mL</td>
</tr>
</tbody>
</table>

**Infrared spectra of dyes**

IR spectra [20] in general shows characteristic band at 3400-3430 cm⁻¹ indicates the N-H and O-H stretching vibrations. The band at 3050-3085 cm⁻¹ and 2870-2900 cm⁻¹ indicates the C-H stretching vibrations. The strong band observed at 1700-1720 cm⁻¹ indicates the C=O stretching vibration. The band at 1440-1445 cm⁻¹ shows the C-N stretching vibration. The bands at 1180-1192 cm⁻¹ and 1035-1050 cm⁻¹ shows S=O asymmetric and symmetric stretching vibrations. The azo and chloro groups are confirmed at the 1370-1385 cm⁻¹ and 760-780 cm⁻¹ respectively. (IR and ¹H-NMR data
are summarized in Table 3).

**Table 3.** IR and $^1$H-NMR spectra of dyes D$_1$ to D$_{10}$

<table>
<thead>
<tr>
<th>Dye No.</th>
<th>IR (KBr): $v_{max}$ (cm$^{-1}$)</th>
<th>$^1$H-NMR (Chemical shift in δ ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D$_1$</td>
<td>3400$_s$ (O-H &amp; N-H), 3050$_m$, 2890$_m$ (C-H), 1700$_s$ (C=O), 1440$_m$, 1375$_m$ (N=N), 1190$_s$, 1045$_s$ (S=O), 760$_m$, (C-Cl).</td>
<td>3.45 (s, 2H, CH$_2$), 5.07 (s, 2H, 2OH), 9.02 (s, 2H, 2COOH), 9.96 (s, 2H, 2NH), 10.75 (s, 2H, 2NH), 7.82-8.01 (m, 16H, Ar-H).</td>
</tr>
<tr>
<td>D$_2$</td>
<td>3410$_s$ (O-H &amp; N-H), 3060$_m$, 2900$_m$ (C-H), 1710$_s$ (C=O), 1445$_s$, 1370$_m$ (N=N), 1185$_s$, 1042$_s$, (S=O),765$_s$, (C-Cl).</td>
<td>3.45 (s, 2H, CH$_2$), 5.06 (s, 2H, 2OH), 9.05 (s, 2H, 2COOH), 9.92 (s, 2H, 2NH), 10.76 (s, 2H, 2NH), 7.86-8.32 (m, 18H, Ar-H).</td>
</tr>
<tr>
<td>D$_3$</td>
<td>3420$_s$ (O-H &amp; N-H), 3060$_m$, 2900$_m$ (C-H), 1720 (C=O), 1440$_s$, 1375$_m$ (N=N), 1192$_s$, 1050$_s$, (S=O), 760$_m$, (C-Cl).</td>
<td>3.46 (s, 2H, CH$_2$), 5.04 (s, 2H, 2OH), 9.02 (s, 2H, 2COOH), 10.75 (s, 2H, 2NH), 7.79-8.01 (m, 28H, Ar-H).</td>
</tr>
<tr>
<td>D$_4$</td>
<td>3420$_s$ (O-H &amp; N-H), 3070$_m$, 2890$_m$ (C-H), 1725$_s$ (C=O), 1445$_s$, 1380$_m$ (N=N), 1180$_s$, 1035$_s$, (S=O), 780$_m$.</td>
<td>3.44 (s, 2H, CH$_2$), 5.07 (s, 2H, 2OH), 9.02 (s, 2H, 2COOH), 10.02 (s, 2H, 2NH), 10.75 (s, 2H, 2NH), 7.82-8.01 (m,18H, Ar-H).</td>
</tr>
<tr>
<td>D$_5$</td>
<td>3420$_s$ (O-H &amp; N-H), 3085$_m$, 2890$_m$ (C-H), 1700$_s$ (C=O), 1445$_s$, 1385$_m$ (N=N), 1185$_s$, 1035$_s$, (S=O), 780$_m$, (C-Cl).</td>
<td>3.45 (s, 2H, CH$_2$), 5.07 (s, 2H, 2OH), 9.01 (s, 2H, 2COOH), 9.96 (s, 2H, 2NH), 10.79 (s, 2H, 2NH), 7.82-8.01 (m,16H, Ar-H).</td>
</tr>
<tr>
<td>D$_6$</td>
<td>3400$_s$ (O-H &amp; N-H), 3060$_m$, 2870$_m$ (C-H), 1700$_s$ (C=O), 1440$_s$, 1375$_m$ (N=N), 1192$_s$, 1048$_s$, (S=O), 770$_m$, (C-Cl).</td>
<td>3.45 (s, 2H, CH$_2$), 5.08 (s, 2H, 2OH), 9.02 (s, 2H, 2COOH), 9.96 (s, 2H, 2NH), 10.78 (s, 2H, 2NH), 7.86-8.09 (m, 16H, Ar-H).</td>
</tr>
<tr>
<td>D$_7$</td>
<td>3420$_s$ (N-H), 3055$_m$, 2890$_m$ (C-H), 1710$_s$, (C=O), 1440$_s$, 1375$_m$ (N=N), 1195$_s$, 1030$_s$, (S=O), 755$_m$, (C-Cl).</td>
<td>3.45 (s, 2H, CH$_2$), 9.02 (s, 2H, 2COOH), 9.92 (s, 2H, 2NH), 10.62 (s, 2H, 2NH), 7.79-7.97 (m, 20H, Ar-H).</td>
</tr>
<tr>
<td>D$_8$</td>
<td>3420$_s$ (N-H), 3050$_m$, 2890$_m$ (C-H), 1700$_s$, (C=O), 1440$_s$, 1380$_m$ (N=N), 1182$_s$, 1045$_s$, (S=O), 760$_m$, (C-Cl).</td>
<td>3.45 (s, 2H, CH$_2$), 9.03 (s, 2H, 2COOH), 9.92 (s, 2H, 2NH), 10.64 (s, 2H, 2NH), 7.06-8.2 (m, 20H, Ar-H).</td>
</tr>
<tr>
<td>D$_9$</td>
<td>3400$_s$ (N-H), 3080$_m$, 2890$_m$ (C-H), 1710$_s$, (C=O), 1440$_s$, 1375$_m$ (N=N), 1185$_s$, 1035$_s$, (S=O), 765$_s$, (C-Cl).</td>
<td>3.43 (s, 2H, CH$_2$), 9.01 (s, 2H, 2COOH), 9.92 (s, 2H, 2NH), 10.81 (s, 2H, 2NH), 7.82-8.61 (m, 22H, Ar-H).</td>
</tr>
<tr>
<td>D$_{10}$</td>
<td>3430$_s$ (N-H), 3050$_m$, 2870$_m$ (C-H), 1700$_s$, (C=O), 1440$_s$, 1375$_m$ (N=N), 1192$_s$, 1048$_s$, (S=O), 780$_m$, (C-Cl).</td>
<td>3.42 (s, 2H, CH$_2$), 9.00 (s, 2H, 2COOH), 9.96 (s, 2H, 2NH), 10.78 (s, 2H, 2NH), 7.88-8.63 (m, 20H, Ar-H).</td>
</tr>
</tbody>
</table>

Abbreviations: IR: br-broad, m-medium, s-strong
$^1$H NMR: s, singlet; d, doublet; t, triplet; m, multiplet.

**Exhaustion and fixation study**

The percentage exhaustion [22] of 2% dyeing on silk ranges from 67-75%, for wool ranges from 65-72% and for cotton ranges from 65-73%. The percentage fixation [23] of 2% dyeing on silk fabric ranges from 84-92 %, for wool ranges from 85-93% and for cotton ranges from 85-92%.

All the dyes have good exhaustion value may be expected due to the diffusion of the dye molecule within the fabric proceed rapidly under dyeing condition. Also the introduction of triazine molecule in to the dye improves the exhaustion and fixation value (Table 4).

**Fastness properties**

All the dyes show generally fair to very good light fastness properties on cotton and wool and moderate to very good for silk. The washing and rubbing fastness for good to excellent fastness on silk, wool and cotton (Table 5).
### Table 4. Exhaustion and fixation data of the dyes D$_1$ to D$_{10}$

<table>
<thead>
<tr>
<th>Dye No.</th>
<th>Shade on dyed fibre</th>
<th>$\lambda_{\text{max}}$ (H$_2$O)</th>
<th>$\lambda_{\text{max}}$ (H$_2$SO$_4$)</th>
<th>$\log\varepsilon$ (H$_2$O)</th>
<th>% Exhaustion</th>
<th>% Fixation</th>
</tr>
</thead>
<tbody>
<tr>
<td>D$_1$</td>
<td>Purple</td>
<td>535</td>
<td>520</td>
<td>4.30</td>
<td>75.30</td>
<td>70.90</td>
</tr>
<tr>
<td>D$_2$</td>
<td>Yellow</td>
<td>462</td>
<td>455</td>
<td>4.20</td>
<td>73.50</td>
<td>68.82</td>
</tr>
<tr>
<td>D$_3$</td>
<td>Orange</td>
<td>482</td>
<td>472</td>
<td>4.27</td>
<td>70.60</td>
<td>70.47</td>
</tr>
<tr>
<td>D$_4$</td>
<td>Light yellow</td>
<td>458</td>
<td>445</td>
<td>4.21</td>
<td>69.55</td>
<td>65.55</td>
</tr>
<tr>
<td>D$_5$</td>
<td>Light purple</td>
<td>522</td>
<td>512</td>
<td>4.24</td>
<td>67.97</td>
<td>66.12</td>
</tr>
<tr>
<td>D$_6$</td>
<td>Light purple</td>
<td>525</td>
<td>508</td>
<td>4.30</td>
<td>72.60</td>
<td>71.10</td>
</tr>
<tr>
<td>D$_7$</td>
<td>Greenish yellow</td>
<td>435</td>
<td>410</td>
<td>4.30</td>
<td>69.35</td>
<td>68.00</td>
</tr>
<tr>
<td>D$_8$</td>
<td>Light yellow</td>
<td>440</td>
<td>425</td>
<td>4.29</td>
<td>75.45</td>
<td>65.27</td>
</tr>
<tr>
<td>D$_9$</td>
<td>Light yellow</td>
<td>432</td>
<td>418</td>
<td>4.26</td>
<td>69.65</td>
<td>68.40</td>
</tr>
<tr>
<td>D$_{10}$</td>
<td>Reddish yellow</td>
<td>452</td>
<td>420</td>
<td>4.22</td>
<td>71.23</td>
<td>67.23</td>
</tr>
</tbody>
</table>

Abbreviations: S-Silk, W-Wool, C-Cotton.

### Table 5. Fastness properties data of the dyes D$_1$ to D$_{10}$

<table>
<thead>
<tr>
<th>Dyes No.</th>
<th>Light fastness</th>
<th>Wash fastness</th>
<th>Rubbing fastness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S</td>
<td>W</td>
<td>C</td>
</tr>
<tr>
<td>D$_1$</td>
<td>6</td>
<td>5-6</td>
<td>6</td>
</tr>
<tr>
<td>D$_2$</td>
<td>3-4</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>D$_3$</td>
<td>4</td>
<td>5</td>
<td>4-5</td>
</tr>
<tr>
<td>D$_4$</td>
<td>3</td>
<td>4</td>
<td>5-6</td>
</tr>
<tr>
<td>D$_5$</td>
<td>4-5</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>D$_6$</td>
<td>3</td>
<td>5</td>
<td>4-5</td>
</tr>
<tr>
<td>D$_7$</td>
<td>4</td>
<td>5</td>
<td>4-5</td>
</tr>
<tr>
<td>D$_8$</td>
<td>3</td>
<td>5</td>
<td>4-5</td>
</tr>
<tr>
<td>D$_9$</td>
<td>4</td>
<td>5</td>
<td>4-5</td>
</tr>
<tr>
<td>D$_{10}$</td>
<td>5-6</td>
<td>6</td>
<td>3</td>
</tr>
</tbody>
</table>

Abbreviations: S-Silk, W-Wool, C-Cotton.

Light fastness: 1-poor, 2-slight, 3-moderate, 4-fair, 5-good, 6-very good.
Wash & Rubbing fastness: 1-poor, 2-fair, 3-good, 4-very good, 5-excellent.
Conclusion

A series of bisazo reactive dyes containing 4,4’-methylene-bis(2,6-dichloro aniline) coupling moiety have been synthesized by conventional method and their colour properties examined by application on silk, wool and cotton fibres. These dyes give yellow to purple hues depending on the coupling components used. The exhaustion and fixation values of all the dyes are very good and show good fastness properties. These dyes are also used as a substitute for benzidine dyes which shows dangerous carcinogen properties.

Acknowledgments

The authors are thankful to Veer Narmad South Gujarat University, Surat, for research facilities. SAIF, Chandigarh for $^1$H NMR spectra and Atul Limited, Valsad for providing dyeing facilities, fastness tests and important chemicals.

References and Notes


