Application of newly synthesized bisazo dichloro-s-triazinyl reactive dyes bearing 1,3,4-oxadiazole molecule

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Abstract Novel bisazo dichloro-s-triazinyl (DCT) reactive dyes (5a-h) containing 1,3,4-oxadiazole molecule as a tetrazo component were synthesized and applied on silk, wool and cotton fibers by exhaust dyeing method. The structures of these dyes were confirmed by UV–vis, FT-IR, 1H and 13C NMR and elemental analyses. The exhaustion, fixation and fastness properties of the dyed fabric were assessed and the results demonstrated that these dyes showed moderate to very good light and good to excellent washing and rubbing fastness properties. The colorimetric data (L*, a*, b*, C*, H*, K/S) of these dyes have also been studied in detail.

1. Introduction

Reactive dyes are textile colorants applied by exhaust and continuous dyeing method to achieve relatively high wash fastness on different fibers due to the formation of a covalent bond during the fixation step (Waring, 1990; Aspland, 1997). The bisazo reactive dyes are more valuable than monoazo reactive dyes, as they are tinctorially more stable and potentially more economic than monoazo reactive dyes (Ayyangar et al., 1987, 1991) furthermore the bisazo dyes possess two reactive groups which give higher fixation efficiency than monoazo dyes because if one dye fiber bond is hydrolyzed, another bond is available for fixation (Bredereck and Schumacher, 1993; Masaki et al., 1988).

The use of heterocyclic intermediates in the dyes synthesis is well established and the resultant molecule exhibits remarkable tinctorial strength and brighter dyeing properties than those derived from aniline based diazo components (Penchev et al., 1991; Peters and Gbadamosi, 1992; Kraska and Sokolwska-Gajda, 1987, 1991, 1992). The 1,3,4-oxadiazole molecule is widely used in the synthesis of drugs, polymers, dyes and also in photography as light screening agents. Also, it has an outstanding capability of transporting electrons, especially its good thermostability and antioxidation given by its special structure (Chen et al., 2002). Bisazo dyes containing...
1,3,4-oxadiazole molecule give brilliant yellowish red hue with fairly to moderate light fastness and very good to excellent wash fastness and sublimation fastness on polyester and nylon fabric (Palekar et al., 2010).

We now report the synthesis and evaluation of some novel hetero bisazo reactive dyes, containing a dichloro- s-triazinyl (DCT) reactive group. These dyes were synthesized by coupling the tetrazonium salt derived from the bisazo intermediate 2,5-bis(3'-amino-4'-chlorophenyl)-1,3,4-oxadiazole (2) with different cyanurated coupling components (4a–h). Visible absorption spectra, fastness properties and colorimetric data are also examined.

2. Experimental

2.1. Materials and methods

All the chemicals used in the dyes synthesis were of commercial grade and were further purified by crystallization and distillation. Melting points were determined by the open capillary method. Thin layer chromatography (TLC) (Fried and Sherlock, 1982) used for monitoring reactions includes aluminum plates coated with silica gel G F254 (Merck) as stationary phase and a mobile phase consisting of toluene:ethyl acetate (7.5:2.5 v/v) solvent system. The developed plates were visualized under both short and long wavelength ultraviolet light (254 nm, 365 nm).

IR spectra were recorded on a Perkin-Elmer model 377 system using the KBr pellet. Both 1H NMR (400 MHz) and 13C NMR (100 MHz) spectra were determined on Bruker Avance II spectrophotometer in DMSO-d6 solvent using TMS as internal standard, the chemical shifts were expressed in δ values compared to Me4Si. UV–vis absorption spectra were recorded using Laboratory Rota Dyer instrument containing stain-der both short and long wavelength ultraviolet light (254 nm, 365 nm).

2.2. Synthesis of 1,2-Bis(3'-amino-4'-chlorobenzoyl)-hydrazine (Qian et al., 2007) (1)

A mixture of 3-amino-4-chlorobenzoic acid (17.2 g, 0.1 mol), polyphosphoric acid (50 mL) and hydrazine hydrate (5 g, 0.05 mol) was stirred for 10 h at 130 °C temperature under nitrogen atmosphere. The mixture was poured into ice water. This was then neutralized, filtered and washed with dilute sodium carbonate (10% w/v) solution to give compound 1 (13.69 g, 80.52%) as yellowish white crystal, M.p. 230 °C (recrystallized from absolute ethanol). Anal. Calcd. for C14H12O2N4Cl2 (339.18 g/mol): C, 49.45; H, 3.43; N, 16.40; IR (KBr, cm−1): 3482, 3455 (N–H), 1665 (C=O), 1101, 1150 (C–Cl); 1H NMR (400 MHz, DMSO-d6) δH ppm: 3.83 (s, 4H, NH2), 7.10-7.94 (m, 6H, Ar–H); 13C NMR (100 MHz, DMSO-d6) δC ppm: 169.44 (C–O), 110.17, 115.36, 120.66, 125.85, 134.71, 145.12 (C–Ar) (Scheme 1).

Compound 1 (17.0 g, 0.05 mol) and POCl3 (150 mL) were added to a flask and refluxed for 8 h under nitrogen atmosphere; this was then cooled to room temperature. The reaction mixture was slowly poured into ice water and neutralized with dilute sodium carbonate solution (10% w/v). Then the precipitate was filtered and dried after washing with water to give compound 2 (10.57 g, 65.83%) as reddish brown needles, M.p. 322 °C (recrystallized from chloroform: methanol). Anal. Calcd. for C14H10ON4Cl2 (321.16 g/mol): C, 52.36; H, 3.14; N, 17.45. Found: C, 52.25; H, 3.04; N, 17.32; IR (KBr, cm−1): 3485, 3450 (C–O), 1278 (C–O–C), 775 (C–Cl); 1H NMR (400 MHz, DMSO-d6) δH ppm: 3.83 (s, 4H, NH2), 7.10-7.94 (m, 6H, Ar–H); 13C NMR (100 MHz, DMSO-d6) δC ppm: 110.09, 115.36, 120.66, 125.85, 134.71, 145.12 (C–Ar) (Scheme 1).

Where R = Different cyanurated coupling components (4a–h) (Table 1)

Scheme 1 Synthesis of monochloro-s-triazine bisazo reactive dyes 5a.

2.3. Synthesis of 2,5-bis(3'-amino-4'-chlorophenyl)-1,3,4-oxadiazole (Qian et al., 2007) (2)

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2.4. Tetrazotization 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole (3)

Compound 2 (3.21 g, 0.01 mol) was suspended in H2O (60 mL). Hydrochloric acid (0.38 mL, 0.03 mol) was added drop wise 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 NaNO2 (0.7 g, 0.01 mol) in water (4 mL) previously cooled to 0 °C, was then added over a period of 5 minutes with stirring. The solution was stirred for 30 min and excess HNO2 was decomposed by adding sulfamic acid. Activated carbon was added with stirring and the mixture was filtered at 0–5 °C to give the clear yellow solution (4) (Scheme 1).

2.5. Cyanuration of H-acid (4a)

Cyanuric chloride (1.85 g, 0.01 mol) was stirred in acetone (25 mL) at a temperature 0–5 °C for a period of an hour. A neutral solution of H-acid (3.19 g, 0.01 mol) in aqueous sodium carbonate solution (10% w/v) was then added in small lots in about an hour. The pH was maintained neutral by simultaneous addition of sodium carbonate solution (1% w/v). The reaction mass was then stirred at 0–5 °C for further 4 h. The clear solution of cyanurated H-acid (4a) thus formed was used for subsequent coupling reaction (Scheme 2).

2.6. Synthesis of reactive dye (5a)

Freshly prepared tetrazonium salt solution (0.005 mol) (3) was added dropwise to well-stirred solution of cyanurated H-acid (4a) (0.005 mol). The solution was maintained at pH 9 by adding 20% (w/v) Na2CO3 and the coupling step was continued for 4 h at 0–5 °C. Then, 10% (w/v) urea was added (Ravikumar et al., 1998) and the dye was isolated by salting out of sodium carbonate solution (1% w/v). The reaction mass was then stirred at 0–5 °C for further 4 h. The clear solution of cyanurated H-acid (4a) thus formed was used for subsequent coupling reaction (Scheme 2).

Dye 5a was synthesized by using H acid as coupling component (5.46 g, 80.04%) as purple powder; M.p. > 300 °C (DMF: EtOAc); Rf = 0.40; UV/vis (Water) λmax (εmax) = 350 nm (28540.12 mol−1 cm−1); IR (KBr, cm−1): 3475–3580 (O–H and N–H), 3016 (C–H), 1525 (N–H bend.), 1612 (N=–N), 1540, 1416, 822 (C–N), 1586, 1479 (C=C), 1338, 1194 (S=–O), 1270 (C–O–C), 783 (C–Cl); 1H NMR (400 MHz, DMSO-d6) δH ppm: 3.36 (2H, s, OH), 4.70 (2H, s, NH), 7.00–8.18 (12H, m, Ar–H); 13C NMR (100 MHz, DMSO-d6) δC ppm: 109.12, 112.70, 115.25, 120.62, 122.85, 125.75, 129.72, 130.09, 132.68, 135.80, 136.77, 140.66, 142.15, 145.65, 152.15, 164.77, 166.34, 169.10; Anal. Calcd. for C40H16O15N14S4Cl6Na4 (1365.58 g/mol): C, 35.18; H, 1.18; N, 14.36. Found: C, 35.03; H, 1.04; N, 14.22.

The characterization data of the synthesized dyes are as follows:

2.6.1. Dye 5a

Dye 5a was synthesized by using H acid as coupling component (5.46 g, 80.04%) as purple powder; M.p. > 300 °C (DMF: EtOAc); Rf = 0.36; UV/vis (Water) λmax (εmax) = 470 nm (23747.35 mol−1 cm−1); IR (KBr, cm−1): 3462–3570 (O–H and N–H), 3010 (C–H), 1528 (N–H bend.), 1456.65, 1512, 1674.77, 166.34, 169.10; Anal. Calcd. for C20H12N12S4Cl6Na4 (965.58 g/mol): C, 34.65; H, 2.04; N, 14.12.

2.6.2. Dye 5b

Dye 5b was synthesized by using Gamma acid (4.57 g, 78.60%) as yellow powder; M.p. > 300 °C (DMF: EtOAc); Rf = 0.36; UV/vis (Water) λmax (εmax) = 470 nm (23747.35 mol−1 cm−1); IR (KBr, cm−1): 3462–3570 (O–H and N–H), 3010 (C–H), 1528 (N–H bend.), 1620 (N=–N), 1565,1422, 825 (C–N), 1592, 1484 (C=C), 1341, 1185 (S=–O), 1268 (C–O–C), 780 (C–Cl); 1H NMR (400 MHz, DMSO-d6) δH ppm: 3.42 (2H, s, OH), 6.95–8.12 (12H, m, Ar–H); 13C NMR (100 MHz, DMSO-d6) δC ppm: 109.12, 112.70, 115.25, 120.62, 122.85, 125.75, 129.72, 130.09, 132.68, 135.80, 136.77, 140.66, 142.15, 145.65, 152.15, 164.77, 166.34, 169.10; Anal. Calcd. for C20H12N12S4Cl6Na4 (965.58 g/mol): C, 34.65; H, 2.04; N, 14.12.

2.6.3. Dye 5c

Dye 5c was synthesized by using Gamma acid as coupling component (4.57 g, 73.2%) as orange powder; M.p. > 300 °C (DMF: EtOAc); Rf = 0.37; UV/vis (Water) λmax (εmax) = 495 nm (26866.42 mol−1 cm−1); IR (KBr, cm−1): 3465–3584 (O–H), 3005 (C–H), 1535 (N–H bend.), 1622 (N=–N), 1562,1430, 828 (C–N), 1595, 1480 (C=C), 1355, 1176 (S=–O), 1260 (C–O–C), 775 (C–Cl); 1H NMR (400 MHz, DMSO-d6) δH ppm: 3.46 (2H, s, OH), 6.95–8.12 (24H, m, Ar–H); 13C NMR (100 MHz, DMSO-d6) δC ppm:

![Scheme 2 Preparation of cyanurated H-acid (4a).](image-url)
Table 1  Different cyanurated coupling components (4a–j) (Arrow indicate the coupling position).

<table>
<thead>
<tr>
<th>No.</th>
<th>Structure</th>
<th>Chemical Formula</th>
<th>UV/vis (Water)</th>
<th>IR (KBr, cm⁻¹)</th>
<th>NMR (DMSO-d₆) ppm</th>
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<tbody>
<tr>
<td>4a</td>
<td><img src="image" alt="4a" /></td>
<td>C₅₂H₂₆O₉N₁₄S₂Cl₆Na₂</td>
<td>λ max (λₘₐₓ) = 475 nm (22832.65 l mol⁻¹ cm⁻¹); 1R (KBr, cm⁻¹) 3462–3580 (O–H and N–H), 3012 (C–H), 1536 (N–H bend.), 1610 (N’N), 1558, 1426, 821 (C–N), 1590, 1477 (C=C), 1359, 1168 (S=O), 1272 (C=O–C).</td>
<td>Anal. Calcd. for C₅₂H₂₆O₉N₁₄S₂Cl₆Na₂ (1313.68 g/mol): C, 47.54; H, 1.99; N, 14.93. Found: C, 47.40; H, 1.86; N, 14.80.</td>
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<tr>
<td>4b</td>
<td><img src="image" alt="4b" /></td>
<td>C₄₀H₁₈O₉N₁₄S₂Cl₆Na₂</td>
<td>λ max (λₘₐₓ) = 475 nm (22832.65 l mol⁻¹ cm⁻¹); 1R (KBr, cm⁻¹) 3462–3580 (O–H and N–H), 3012 (C–H), 1536 (N–H bend.), 1610 (N’N), 1558, 1426, 821 (C–N), 1590, 1477 (C=C), 1359, 1168 (S=O), 1272 (C=O–C).</td>
<td>Anal. Calcd. for C₄₀H₁₈O₉N₁₄S₂Cl₆Na₂ (1161.49 g/mol): C, 41.36; H, 1.56; N, 16.88. Found: C, 41.26; H, 1.42; N, 16.80.</td>
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2.6.4. Dye 5d

Dye 5d was synthesized by using J-acid as coupling component (4.77 g, 82.15%) as yellow powder; M.p. >300 °C (DMF: EtOAc); Rf = 0.42; UV/vis (Water) λ max (λₘₐₓ) = 475 nm (22832.65 l mol⁻¹ cm⁻¹); 1R (KBr, cm⁻¹) 3462–3580 (O–H and N–H), 3012 (C–H), 1536 (N–H bend.), 1610 (N’N), 1558, 1426, 821 (C–N), 1590, 1477 (C=C), 1359, 1168 (S=O), 1272 (C=O–C). | 1H NMR (400 MHz, DMSO-d₆) δ ppm: 3.51 (2H, s, OH), 4.48 (2H, s, NH), 6.98–7.92 (14H, m, Ar–H). 13C NMR (100 MHz, DMSO-d₆) δ ppm: 109.17, 112.44, 116.27, 120.30, 122.94, 125.82, 128.34, 130.57, 132.44, 133.48, 137.38, 141.12, 143.25, 145.23, 155.29, 162.64, 165.33, 169.72; Anal. Calcd. for C₅₂H₂₆O₉N₁₄S₂Cl₆Na₂ (1313.68 g/mol): C, 47.54; H, 1.99; N, 14.93. Found: C, 47.40; H, 1.86; N, 14.80. |

2.6.5. Dye 5e

Dye 5e was synthesized by using N-methyl-J-acid as coupling component (5.01 g, 84.24%) as orange powder; M.p. >300 °C (DMF: EtOAc); Rf = 0.40; UV/vis (Water) λ max
2.6.6. Dye 5f

Dye 5f was synthesized by using N-phenyl-J-acid as coupling component (5.26 g, 80.06 g) as red powder; M.p. >300 °C (DMF: EtOAc); \( R_f = 0.38 \); UV/vis (Water) \( \lambda_{max} (\epsilon_{max}) = 497 \text{ nm (27422.30 l mol}^{-1} \text{ cm}^{-1}) \); IR (KBr, cm\(^{-1}\)) 3482–3575 (O−H), 3022 (C−H), 1542 (N−H bend.), 1620 (N=O), 1556,1430, 823 (C−N), 1586, 1474 (C=C), 1368, 1180 (S=O), 1262 (C−O−C), 776 (Cl−C); \( ^1 \text{H NMR (400 MHz, DMSO-}d_6 \text{)} \delta \text{ ppm: 3.58 (2H, s, OH), 7.07–8.10 (2H, m, Ar−H); } ^{13} \text{C NMR (100 MHz, DMSO-}d_6 \text{)} \delta \text{ ppm: 109.11, 110.55, 112.72, 115.35, 118.53, 120.74, 122.10, 123.25, 126.02, 128.93, 130.73, 132.94, 135.10, 136.55, 138.56, 141.33, 145.80, 147.58, 154.58, 162.90, 165.38, 169.22; Anal. Calcd. for C_{52}H_{26}O_{9}N_{14}S_{2}Cl_{6}Na_{2} (1313.68 g/mol): C, 47.54; H, 1.99; N, 14.93. Found: C, 47.43; H, 1.88; N, 14.84.

2.6.7. Dye 5g

Dye 5g was synthesized by using Chicago acid as coupling component (5.33 g, 78.10%) as yellow powder; M.p. >300 °C (DMF: EtOAc); \( R_f = 0.37 \); UV/vis (Water) \( \lambda_{max} (\epsilon_{max}) = 465 \text{ nm (20249.11 l mol}^{-1} \text{ cm}^{-1}) \); IR (KBr, cm\(^{-1}\)) 3465–3578 (O−H and N−H), 3025 (C−H), 1522 (N−H bend.), 1626 (N=O), 1537, 1411, 826 (C−N), 1580, 1482 (C=C), 772 (Cl−C); \( ^1 \text{H NMR (400 MHz, DMSO-}d_6 \text{)} \delta \text{ ppm: 3.58 (2H, s, OH), 7.07–8.10 (2H, m, Ar−H); } ^{13} \text{C NMR (100 MHz, DMSO-}d_6 \text{)} \delta \text{ ppm: 109.11, 110.55, 112.72, 115.35, 118.53, 120.74, 122.10, 123.25, 126.02, 128.93, 130.73, 132.94, 135.10, 136.55, 138.56, 141.33, 145.80, 147.58, 154.58, 162.90, 165.38, 169.22; Anal. Calcd. for C_{52}H_{26}O_{9}N_{14}S_{2}Cl_{6}Na_{2} (1313.68 g/mol): C, 47.54; H, 1.99; N, 14.93. Found: C, 47.43; H, 1.88; N, 14.84.
1345, 1175 (S–O), 1270 (C–O–C), 780 (C–Cl); 1H NMR (400 MHz, DMSO-d$_6$) δ ppm: 3.44 (2H, s, OH), 4.65 (2H, s, NH), 7.10–8.15 (12H, m, Ar–H); 13C NMR (100 MHz, DMSO-d$_6$) δC ppm: 108.95, 112.42, 115.09, 120.66, 123.15, 125.32, 128.45, 130.67, 132.82, 135.49, 138.02, 140.44, 142.10, 145.15, 155.32, 162.70, 165.30, 169.46; Anal. Calcd. for C$_{40}$H$_{16}$O$_{15}$N$_{14}$S$_4$Cl$_6$Na$_4$ (1365.58 g/mol): C, 35.18; H, 1.18; N, 14.36. Found: C, 35.05; H, 1.06; N, 14.25.

2.6.8. Dye 5h
Dye 5h was synthesized by using K-acid as coupling component (5.28 g, 77.28%) as yellow powder: M.p. >300°C (DMF: EtOAc); R$_f$ = 0.40; UV/vis (Water) $\lambda_{max}$ ($e_{max}$) = 460 nm (21335.28 l mol$^{-1}$ cm$^{-1}$); IR (KBr, cm$^{-1}$) 3480–3575 (O–H and N–H), 3012 (C–H), 1527 (N–H bend.), 1611 (N=N), 1547,1410, 829 (C–N), 1588, 1471 (C=C), 1355, 1180 (S=O), 1265 (C–O–C), 780 (C–Cl); 1H NMR (400 MHz, DMSO-d$_6$) δ ppm: 3.40 (2H, s, OH), 4.77 (2H, s, NH), 7.04–8.11 (12H, m, Ar–H); 13C NMR (100 MHz, DMSO-d$_6$) δC ppm: 109.04, 111.75, 114.20, 120.15, 122.65, 125.79, 129.72, 131.05, 132.37, 135.81, 140.55, 142.17, 145.39, 155.22, 162.47, 166.68, 169.02; Anal. Calcd. for C$_{40}$H$_{16}$O$_{15}$N$_{14}$S$_4$Cl$_6$Na$_4$ (1365.58 g/mol): C, 35.18; H, 1.18; N, 14.36. Found: C, 35.09; H, 1.07; N, 14.24.

3. Results and discussions
3.1. Spectral characteristics
The assumed structures of the synthesized dyes 5a–h were confirmed by IR, 1H NMR and 13C NMR spectra.

The IR spectra (Colthup et al., 1991) showed overlapping band at 3462–3584 cm$^{-1}$ indicating the O–H and N–H stretching vibrations. The medium band observed at 3005–3025 cm$^{-1}$ indicates the C–H stretching vibration. The C–O–C ring of 1,3,4-oxadiazole molecule was confirmed by the presence of band at 1260–1272 cm$^{-1}$. The bands at 1540–1565 cm$^{-1}$, 1410–1433 cm$^{-1}$ and 821–829 cm$^{-1}$ correspond to C–N stretching vibration. The azo group is confirmed by the presence of band at 1610–1626 cm$^{-1}$. Two bands at 1338–1368 cm$^{-1}$ and 1168–1194 cm$^{-1}$ confirmed the presence of S=O stretching vibration. The chloro group showed band at 770–780 cm$^{-1}$.

The 1H NMR (Bassler et al., 1991) spectrum showed signal (singlet) at 3.36–3.58 δ ppm confirmed the presence of hydroxyl (OH) proton. Dyes 5a, 5b, 5d, 5g and 5h showed signal (singlet) at 4.48–4.77 δ ppm due to the secondary amino (NH) proton. Dye 5e showed signal (singlet) at 2.52 δ ppm due to the methyl (CH$_3$) proton. The aromatic protons of all the dyes showed signal (multiplet) at 6.95–8.18 δ ppm.

The 13C NMR (Bassler et al., 1991) spectra of dye 5e showed signal at 22.40–22.52 δ ppm due to the presence of N–CH$_3$ carbon. The aromatic carbons of all the dyes (5a–h) showed signals between 108.52 and 169.72 δ ppm.

IR, 1H NMR and 13C NMR spectra of dye 5a are shown in Figs. 1–3, respectively.

![Figure 3](image-url) **Figure 3** 13C NMR spectra of dye 5a.

![Figure 4](image-url) **Figure 4** Visible absorption spectra of dyes 5a–h.
3.2. Visible absorption spectra

Absorption maxima ($\lambda_{\text{max}}$) of the synthesized dyes ($5a$–$h$) were recorded in water (10$^{-3}$ M) and were found to be in the range of 460–530 nm. The values of molar extinction coefficient ($\varepsilon$) that were determined by Lambert–Beer’s law in the range of 20249.11–28540.12 l mol$^{-1}$ cm$^{-1}$. The presence of electron donating or electron attracting group at the suitable position of the coupler ring affects the absorption characteristics of the dyes. The visible absorption spectra of dyes $5a$–$h$ are shown in Fig. 4.

Dye $5b$ shows $\lambda_{\text{max}}$ at 470 nm and dye $5c$ shows $\lambda_{\text{max}}$ at 495 nm, thus there is a bathochromic shift of 25 nm in the $\lambda_{\text{max}}$ of dye $5b$ ($\lambda_{\text{max}} = 470$ nm) due to the introduction of phenyl group. Same effect is observed by the introduction of methyl group in dye $5c$ ($\lambda_{\text{max}} = 488$ nm) resulting in bathochromic shift of 13 nm compared to dye $5d$ ($\lambda_{\text{max}} = 475$ nm) and the introduction of phenyl group in dye $5f$ ($\lambda_{\text{max}} = 497$ nm) resulted in bathochromic shift of 22 nm compared to the same dye $5d$ ($\lambda_{\text{max}} = 475$ nm). Dyes $5a$, $5g$ and $5h$ are having the same groups but the position is different, hence in dye $5a$ there is more place for NH and SO$_3$Na groups which cause faster electron oscillation and hence neutralization of electron faster than dyes $5g$ and $5h$. Thus dye $5a$ is having a higher absorption maxima value ($\lambda_{\text{max}} = 530$ nm) than dye $5g$ ($\lambda_{\text{max}} = 465$ nm) and $5h$ ($\lambda_{\text{max}} = 460$ nm).

3.3. Dyeing of fibers

The synthesized dichloro-s-triazine reactive dyes $5a$–$h$ were applied on silk, wool and cotton fiber by exhaust dyeing process. These dyes were applied at 2% (owf) depth gives yellow, orange, red and purple hue with good levelness on fabric. The use of different coupling components in the synthesis of dyes gives different shades, i.e. J-acid gives yellow shade while H-acid gives purple shade.

3.3.1. Dyeing of silk

The dye (0.2 g) was pasted with a drop of cold water and then about 80 ml of cold water was added and stirred well to give a clear solution. The resulting dye solution was made up to 100 ml with the dye solution (20 ml), acetic acid (2 ml of 10% v/v) and water 18 ml. The dye bath temperature was maintained at 30°C and silk fabric (2 g) was entered, and the temperature was raised to 40°C over 20 minutes. At this temperature formic acid (1.5 ml of 40% v/v) was added to the dye bath to achieve good exhaustion. The dyeing was continued for 40 minutes more and then the dyed material was washed with cold water, soaped and dried.

3.3.2. Dyeing of wool

Dye (0.2 g) was pasted with a few drops of cold water, then about 80 ml cold water was added, and the mixture was stirred and made up to 100 ml with a dye solution (20 ml), acetic acid (1.5 ml of 10% v/v), glaubers’s salt solution (4 ml of 10% w/v) and water (14.4 ml). A wool fabric (2 g) was introduced in to the dyebath at 30°C and the temperature was raised up to 40°C over 20 minutes. Sulfuric acid (0.4 ml of 10% v/v) was then added and the dyeing was continued for 40 minutes more at the same temperature. The material was then removed, rinsed with cold water, soaping and dried.

3.3.3. Dyeing of cotton

Dye (0.2 g) was pasted with a few drops of cold water, then about 80 ml cold water was added, and the mixture was stirred and made up to 100 ml with dye solution (20 ml), glaubers’s salt solution (4 ml of 10% w/v) and water (14.4 ml). A cotton fabric (2 g) was introduced into the dyebath at 30°C and the temperature was raised up to 40°C over 20 minutes. Soda ash (Na$_2$CO$_3$) solution (0.4 ml of 10% v/v) was then added to bring about fixation and the dyeing was continued for 40 minutes more at the same temperature. The material was then removed, rinsed with cold water, soaped and dried.

3.3.4. Wash-off process

After dyeing process the fabrics were rinsed in warm water, scoured with 2 g/l Lissapol detergent at 100°C for 15 minutes and rinsed again in warm water. The dyed fabrics afforded color in the first warm water rinse, less color in the scouring bath and practically no color in the second water rinse. This indicated that the unfixed dyes were easily removed from the fiber surface. The hydrolyzed dye having low substantivity released easily from the dyed fiber after two or three hot water washes.

### Table 2 Exhaustion, fixation and fastness properties data of reactive dyes $5a$–$h$ on silk, wool and cotton fibers.

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<thead>
<tr>
<th>Dye no.</th>
<th>Exhaustion (%)</th>
<th>Fixation (%)</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>
<td>S</td>
<td>W</td>
</tr>
<tr>
<td>$5a$</td>
<td>73.25</td>
<td>73.11</td>
<td>75.18</td>
<td>86.68</td>
<td>82.76</td>
</tr>
<tr>
<td>$5b$</td>
<td>67.95</td>
<td>64.85</td>
<td>74.85</td>
<td>88.30</td>
<td>85.58</td>
</tr>
<tr>
<td>$5c$</td>
<td>65.10</td>
<td>68.75</td>
<td>71.85</td>
<td>90.62</td>
<td>80.00</td>
</tr>
<tr>
<td>$5d$</td>
<td>66.90</td>
<td>64.85</td>
<td>68.22</td>
<td>90.43</td>
<td>81.73</td>
</tr>
<tr>
<td>$5e$</td>
<td>71.80</td>
<td>65.35</td>
<td>71.00</td>
<td>89.13</td>
<td>79.57</td>
</tr>
<tr>
<td>$5f$</td>
<td>74.00</td>
<td>70.95</td>
<td>69.62</td>
<td>89.18</td>
<td>82.09</td>
</tr>
<tr>
<td>$5g$</td>
<td>71.85</td>
<td>68.93</td>
<td>76.80</td>
<td>86.29</td>
<td>84.47</td>
</tr>
<tr>
<td>$5h$</td>
<td>75.50</td>
<td>64.50</td>
<td>77.83</td>
<td>89.40</td>
<td>84.49</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 and rubbing fastness: 1-poor, 2-fair, 3-good, 4-very good, 5-excellent.
3.4. Exhaustion and fixation study

The percentage exhaustion and fixation data are calculated according to the previously described method (Patel and Patel, 2005) and are summarized in Table 2.

The percentage exhaustion of 2% (owf) dyeing on silk fiber ranges from 65% to 76%, in which dye 5h shows maximum exhaustion (75.50%) and dye 5c shows minimum exhaustion (65.10%); for wool fiber, the percentage exhaustion ranges from 64% to 74%, in which dye 5a shows maximum exhaustion (73.11%) and dye 5h shows minimum exhaustion (64.50%); and for cotton fabric, the percentage exhaustion ranges from 68% to 78%, in which dye 5h shows maximum exhaustion (77.83%) and dye 5d shows minimum exhaustion (68.22%).

The percentage fixation of 2% (owf) dyeing on silk fabric ranges from 86% to 91%, in which dye 5c shows maximum fixation (90.62%) and dye 5g shows minimum fixation (86.29%); for wool fabric, the percentage fixation values ranges from 79% to 86%, in which dye 5b shows maximum value of fixation (85.58%) and dye 5e shows minimum value of fixation (79.57%); and for cotton fabric, the percentage fixation ranges from 79% to 91%, in which dye 5d shows maximum exhaustion (90.87%) and dye 5b shows minimum value of fixation (79.49%).

The introduction of a triazine group into the dye molecule improves the degree of exhaustion and fixation value by increase in substantivity toward fibers. Furthermore exhaustion and fixation of these dyes are very good; this indicates the dyes have good compatibility with the fabrics. The high exhaustion and fixation observed are due to the increase in the rate of diffusion which will allow the dye to penetrate deeper further into the fiber (Beech, 1970).

3.5. Fastness properties

The fastness to light was assessed in accordance with BS: 1006-1978 (Standard Test Method, 1978). The rubbing fastness test was carried out using a Crockmeter (Atlas) in accordance with AATCC-1961 (AATCC Test Method, 1961) and the wash fastness test in accordance with IS: 65-1979 (Indian Standard ISO, 1979). Fastness properties data of the dyes 5a–h are summarized in Table 2.

All the reactive dyes showed generally moderate to very good (rating 3–6 on gray scale) light fastness property and good to excellent (rating 3–5 on gray scale) washing and rubbing fastness properties on silk, wool and cotton fibers. This is attributed to good penetration and excellent affinity of these reactive dyes to the fibers.

3.6. Computer color matching data (CIELab data)

Color measurements are assessed quantitatively and are expressed in terms of CIELab ($L^*, a^*, b^*$, $C^*$, $H^*$, $K/S$) values.

### Table 3  Color measurement (CIELab) of reactive dyes 5a–h on silk, wool and cotton fibers.

<table>
<thead>
<tr>
<th>Dye no.</th>
<th>$L^*$</th>
<th>$a^*$</th>
<th>$b^*$</th>
<th>$C^*$</th>
<th>$H^*$</th>
<th>$K/S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>W</td>
<td>C</td>
<td>S</td>
<td>W</td>
<td>C</td>
<td>S</td>
</tr>
<tr>
<td>5a</td>
<td>45.76</td>
<td>40.15</td>
<td>52.70</td>
<td>35.10</td>
<td>38.09</td>
<td>30.52</td>
</tr>
<tr>
<td>5b</td>
<td>40.12</td>
<td>47.76</td>
<td>57.44</td>
<td>38.14</td>
<td>36.54</td>
<td>28.15</td>
</tr>
<tr>
<td>5c</td>
<td>42.55</td>
<td>47.96</td>
<td>50.41</td>
<td>36.82</td>
<td>32.11</td>
<td>25.35</td>
</tr>
<tr>
<td>5d</td>
<td>50.76</td>
<td>43.11</td>
<td>52.35</td>
<td>34.44</td>
<td>33.65</td>
<td>24.19</td>
</tr>
<tr>
<td>5e</td>
<td>49.09</td>
<td>41.58</td>
<td>52.88</td>
<td>30.58</td>
<td>37.12</td>
<td>21.35</td>
</tr>
<tr>
<td>5f</td>
<td>44.37</td>
<td>40.12</td>
<td>55.68</td>
<td>29.15</td>
<td>38.25</td>
<td>19.38</td>
</tr>
<tr>
<td>5g</td>
<td>38.80</td>
<td>44.33</td>
<td>48.62</td>
<td>22.30</td>
<td>31.62</td>
<td>22.66</td>
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<tr>
<td>5h</td>
<td>39.75</td>
<td>42.22</td>
<td>41.48</td>
<td>25.15</td>
<td>33.15</td>
<td>23.36</td>
</tr>
</tbody>
</table>

**Abbreviations:** S-silk, W-wool, C-cotton.

**Figure 5**  Color strength ($K/S$) graph of dyes 5a–h.

**Figure 6**  Graph of $b^*$ vs. $a^*$ for silk fiber.
by using continuous scanning reflectance spectrocolourimeter in the visible region (400–700 nm). The CIELab coordinates were measured are lightness (L*), chroma (C*), hue angle (H) form 0° to 360°, a* value represent the degree of redness (positive) and greenness (negative) and b* represents the degree of yellowness (positive) and blueness (negative). 

$K/S$ values are calculated at maximum wavelength ($\lambda_{max}$) and are directly correlated with the dye concentration on the substrate according to the Kubelka–Munk equation (Billmeyer and Saltman, 1981; Volz, 1995):

$$K = \frac{(1 - R)^2}{2R}$$  


The CIELab data for silk, wool and cotton fibers are summarized in Table 3. For silk fiber, the data showed that, on going from dye $5b$ to $5c$, the dye becomes lighter, greener, bluer, duller and increasing value of $K/S$, while on going from dye $5d$ to $5e$, the dye becomes darker, greener, yellowish, duller and decreasing value of $K/S$. For wool fiber and on going from dye $5g$ to $5h$, the dye becomes darker, redder, bluer, duller and increasing value of $K/S$ and on going from dye $5g$ to $5h$, the dye becomes darker, redder, bluer, duller and decreasing value of $K/S$.

Results for dyes $5a$–$h$ are presented in Figs. 7–9. Chromaticity diagram of dye $5a$ for silk, wool and cotton fibers is shown in Fig. 9.

**4. Conclusion**

A series of some new bisazo dichloro-s-triazinyl reactive dyes ($5a$–$h$) having 1,3,4-oxadiazole moiety were synthesized and their dyeing performance has been assessed on silk, wool and cotton fibers. The dyed fabric showed moderate to very good light fastness and good to excellent washing and rubbing fastness properties. For visible absorption spectra, these dyes showed maximum absorption ($\lambda_{max}$) in the range of 460–530 nm. The colorimetric data showed dye $5a$ having a higher...
$K/S$ value on silk and cotton fiber while dye 5f having higher $K/S$ value for wool fiber.

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References