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### **ORIGINAL ARTICLE**

# **Colorimetric studies of some newly synthesized bisazo reactive dyes**



Divyesh R. Patel, Amit L. Patel, Keshav C. Patel\*

Department of Chemistry, Veer Narmad South Gujarat University, Surat, 395007 Gujarat, India

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#### KEYWORDS

4,4'-Methylene-bis(2-methyl-5-nitro aniline); Exhaustion; Fixation; Colorimetric data **Abstract** A series of cold brand bisazo reactive dyes (4a–h) were obtained by the coupling of tetrazotised 4,4'-methylene-bis(2-methyl-5-nitro aniline) (2) with various cyanurated coupling components (3a–h) in good yield. Their dyeing performances as reactive dyes have been assessed on silk, wool and cotton fabrics. These dyes were characterized by UV–Vis, FTIR, <sup>1</sup>H NMR spectroscopic techniques elemental analysis. The percentage dye bath exhaustion and fixation on different fibers were found to be very good. The dyed fabric showed moderate to very good light fastness and good to excellent washing and rubbing fastness properties. Spectral properties and colorimetric data ( $L^*$ ,  $a^*$ ,  $b^*$ ,  $C^*$ ,  $H^*$ , K/S) have also been studied in detail.

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#### 1. Introduction

For the last 50 years many fibre reactive dyes have been developed which form covalent bond between dye and fibre particularly cellulosic fibre (Renfrew, 1999). Reactive dyes containing the triazine ring have an electrophilic site which undergoes nucleophilic substitution reaction by react with hydroxyl group of cellulose unit. Reactive dyes are mainly applied to cotton fibre for achieving high wash fastness properties. The high wash fastness is obtained by the covalent

E-mail address: divyeshpatel\_905@yahoo.com (Keshav C. Patel). Peer review under responsibility of King Saud University.



bond formation between dye and fibre in the fixation step (Waring, 1990).

The advantage of bisazo reactive dyes over monoazo reactive dyes is that they possess two reactive groups which give higher fixation yield then monoazo dyes which possess one reactive group because if one of the two dye fibre bonds is hydrolyzed, another is still left for fixation (Bredereck and Schumacher, 1993; Matsi et al., 1988). Additionally, most of the reactive dyes used in exhaust dyeing employ at least two reactive groups in order to maximize fixation (Taylor, 2000).

In continuation of our previous studies (Patel et al., 2009, 2010a,b,c) on the synthesis of a variety of bisazo reactive dyes, we now report on the successful synthesis of several new cold brand bisazo reactive dyes based on 4,4'-methylene-bis(2-methyl-5-nitro aniline) and their application as reactive dyes for dyeing silk, wool and cotton fabrics. The fastness properties, spectral properties and colorimetric data  $(L^*, a^*, b^*, C^*, H^*, K/S)$  were also discussed. The general structure of these dyes (4a-h) is shown in Fig. 1.

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<sup>\*</sup> Corresponding author. Tel.: +91 0261 2258384; fax: +91 0261 2256012.



Where R = various cyanurated coupling components (3a-h) (Table-1)

Figure 1 General structure of reactive dyes (4a-h).

#### 2. Experimental

#### 2.1. General

All the chemicals used in the dye synthesis were of commercial grade and were further purified by crystallization and distillation. Melting points were determined by the open capillary method. The purity of all the dyes was checked by TLC (Fried and Sharma, 1982). The visible absorption spectra were measured using a Shimadzu UV-1700 spectrophotometer. A Perkin-Elmer model 881 recording infrared spectrophotometer was used for recording the FTIR spectra of the dyes as KBr pellets in the range between 4000 and 400 cm<sup>-1</sup> and <sup>1</sup>H NMR spectra on a Bruker Avance II 400 instrument using TMS as internal standard and DMSO as solvent. Elemental analysis of C, H and N were carried on Carlo Erba 1108 instrument. The light fastness was assessed in accordance with

BS: 1006-1978 (Standard Test Method, 1978). The rubbing fastness test was carried out with a Crockmeter (Atlas) in accordance with AATCC-1961 (AATCC Test Method, 1961) and the wash fastness test in accordance with IS: 765-1979 (Indian Standard, 1979). Colorimetric data  $(L^*, a^*, b^*, C^*, H^*, K/S)$  were recorded on Reflectance Spectrophotometer Gretag Macbeth CE: 7000.

## 2.2. Synthesis of 4,4'-methylene-bis(2-methyl-5-nitroaniline) (1) (Patel and Patel, 2011)

2-Methyl-5-nitroaniline (15.2 g, 0.1 mol) was first mixed with sufficient HCl to reach pH 4 of the medium. Then, the pale vellow, colored solution was put into a three-necked flask fitted with a stirrer and was mixed at 50 °C temperature. Formaldehvde (35 ml, 3%, v/v) was added at interval of 10 min over a period of 1 h and the stirring was continued for a further 10 h maintaining temperature at 60 °C. Then, the stirring was stopped and the product was washed with NaOH (2%, w/v) first and then with water till the mixture became neutral. Finally, the yellowish colored product (1) was dried in an oven at 90 °C for about 4 h (13.61 g, 86.04%). Yellow powder, m.p. 202 °C (recrystallized from acetic acid).  $R_{\rm f} = 0.75$  (PhMe:EtOAc, 3:1, v/v). IR (KBr):  $v_{\rm max}$  (cm<sup>-1</sup>): 3455, 3363 (N-H), 2925, 2845 (C-H), 1568, 1356 (N=O). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ ppm: 2.58 (2H, s, CH<sub>2</sub>), 2.75 (6H, s, N-CH<sub>3</sub>), 6.67 (4H, s, NH<sub>2</sub>), 6.95-7.25 (4H, m, Ar-H). Anal. Calcd. for C<sub>15</sub>H<sub>16</sub>O<sub>4</sub>N<sub>4</sub> (316.31 g/mol): C, 56.96; H, 5.10; N, 17.71%. Found: C, 56.78; H, 4.93; N, 17.60% (Scheme 1).



Where R = Various cyanurated coupling components (3a-h)

Scheme 1 Synthesis of reactive dye 4a by using cyanurated H-acid (3a) as coupling component.

#### 2.3. Tetrazotisation of 4,4'-methylene bis(2-methyl-5nitroaniline) (2)

4,4'-Methylene-bis(2-methyl-5-nitroaniline) (1) (1.58 g, 0.005 mol) was stirred in a mixture of water (25 ml), conc. HCl (1.88 ml, 0.015 mol) and ice (10 g). The reaction mixture was cooled to 0-5 °C using an ice bath. NaNO<sub>2</sub> (0.35 g, 0.005 mol) dissolved in water (10 ml) was then added dropwise. The solution was stirred for 30 min and excess HNO<sub>2</sub> was decomposed by adding sulphamic acid. Activated carbon was added with stirring and the mixture was filtered at 0-5 °C to give the clear yellow solution (2) (Scheme 1).

#### 2.4. Cyanuration of H-acid (3a)

H-acid (3.19 g, 0.01 mol) was dissolved in water (15 ml) at pH 7.5, using 20% (w/v) Na<sub>2</sub>CO<sub>3</sub>. A solution of cyanuric chloride (1.85 g, 0.01 mol) in acetone (20 ml) was cooled to 0–5 °C and added dropwise to the stirred H-acid solution at 0–5 °C. After 10 min, the solution was adjusted to pH 7 by adding 20% (w/v) Na<sub>2</sub>CO<sub>3</sub>, and the reaction was continued for 1 h at 0–5 °C. The reaction progress was followed by TLC using *n*-PrOH:*n*-BuOH:EtOAc:H<sub>2</sub>O (2:4:1:3, v/v), in which the product **3a** had  $R_f = 0.70$  (Scheme 2).

#### 2.5. General method for the synthesis of dye 4a

Freshly prepared tetrazonium salt solution (0.005 mol) (2) was added dropwise to a well-stirred solution of cyanurated H-acid (3a) (0.01 mol). The solutions were maintained at pH 9 by adding 20% (w/v) Na<sub>2</sub>CO<sub>3</sub> 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 dyes were isolated by salting out of solution using NaCl (12 g). The pH was adjusted to 7 using HCl (6%, w/v) and stirring was continued for 2 h. The dye was collected by filtration and washed with NaCl (5%, w/v). Salt was removed by stirring the crude dyes with dimethylformamide (DMF), followed by the dye precipitation by adding EtOAc to the filtrate. The dye 4a was collected, washed with EtOAc and dried in oven at 45 °C for 12 h (5.71 g, 84.0%). The eluent system for TLC was 2-BuOH:EtOH:NH<sub>4</sub>OH:pyridine (4:1:3:2, v/v). Dye 4a had  $R_{\rm f} = 0.43$ , with minor impurities at  $R_{\rm f} = 0.23$  (Scheme 1).

Following the above procedure other reactive dyes **4b–h** were synthesized using various cyanurated coupling components such as K-acid (**3b**), Gamma acid (**3c**), N-methyl-Gamma acid (**3d**), J-acid (**3e**), N-methyl-J-acid (**3f**), N-phenyl-J-acid (**3g**) and Chicago acid (**3h**). The structures of all the cyanurated coupling components are shown in Table 1 and the

characterization data of all the synthesized dyes are recorded in Table 2.

#### 3. Results and discussion

#### 3.1. Spectral data of dyes

The structures of dyes 4a-h were confirmed by various spectroscopic techniques including FTIR (Colthup et al., 1991) and <sup>1</sup>H NMR (Bassler et al., 1991) spectral data. Dves 4d, 4f and 4g showed broad band at 3455–3522 due to the O-H stretching vibration. Dyes 4a-c, 4e and 4h showed overlapped absorption band at 3360-3490 cm<sup>-1</sup> region corresponding to the O-H and N-H stretching vibration. Two medium absorption bands at 2920-2945 cm<sup>-1</sup> and 2850-2860 cm<sup>-1</sup> showed C-H stretching vibration of methyl and methylene groups. The absorption band at  $1560-1570 \text{ cm}^{-1}$  confirmed the presence of azo group. All the dyes showed two bands at  $1190-1200 \text{ cm}^{-1}$  and 1040- $1050 \text{ cm}^{-1}$  which showed asymmetric and symmetric S=O stretching vibration of sulfonic acid group. Dyes 4a-h showed bands at 1520-1530 cm<sup>-1</sup> and 1340-1360 cm<sup>-1</sup> showed asymmetric and symmetric N=O stretching vibration of nitro group. The chloro group was confirmed by the band at 765- $775 \text{ cm}^{-1}$ . The IR spectral data are summarized in Table 3.

The <sup>1</sup>H NMR spectra of dyes **4a–h** displayed two signals at 1.32–1.48  $\delta$  ppm and 2.22–2.34  $\delta$  ppm was due to the methyl and methylene proton. Dye **4d** and **4f** showed signals at 2.52  $\delta$  ppm and 2.58  $\delta$  ppm were due to the N–CH<sub>3</sub> proton. All the dyes showed broad signals at 3.62–3.78  $\delta$  ppm due to the OH proton. All the dyes except **4d**, **4f** and **4g** showed singlet at 4.02–4.18  $\delta$  ppm due to the secondary amino group. The aromatic protons were showed signal at 6.58–7.88  $\delta$  ppm as multiplet. The <sup>1</sup>H NMR spectral data are summarized in Table 3.

#### 3.2. Visible absorption spectra of dyes

Absorption maxima ( $\lambda_{max}$ ) of all the dyes (**4a–h**) were recorded in water (10<sup>-6</sup> M) and are shown in Table 2. The absorption maxima values ( $\lambda_{max}$ ) are directly proportional to the electronic power of the substituents in the coupler ring system. The values of molar extinction coefficient maxima ( $\varepsilon_{max}$ ) are shown in Table 2. Dye **4a** has the highest  $\varepsilon_{max}$  value 28,248.80 l mol<sup>-1</sup> cm<sup>-1</sup> which is due to the greater co-planarity of dye **3a**.

The introduction of electron donating or electron attracting group in the coupler moiety results in additional color shifts, i.e. shifting of  $\lambda_{max}$  towards higher wavelength (bathochromic shift) or lower wavelength (hypsochromic shift). Thus the



Scheme 2 Preparation of cyanurated H-acid (3a).



introduction of methyl group in the dye **4d** ( $\lambda_{max} = 485$  nm) resulted in bathochromic shift of 10 nm compared to the dye **4c** ( $\lambda_{max} = 475$  nm), the same effect is observed by the introduction of methyl group in the dye **4f** ( $\lambda_{max} = 490$  nm) resulted in bathochromic shift of 12 nm compared to the dye **4e** ( $\lambda_{max} = 478$  nm) and the introduction of phenyl ring in the dye **4g** resulted in bathochromic shift of 22 nm compared to the dye **4e** ( $\lambda_{max} = 478$  nm). Dye **4a** ( $\lambda_{max} = 530$  nm), **4b** ( $\lambda_{max} = 465$  nm) and **4h** ( $\lambda_{max} = 468$  nm) have the same substituents but the position is different, hence in dye **4a** there is more place for NH and SO<sub>3</sub>Na groups, which cause faster elec-

tron oscillation and hence neutralization of electron is faster than dye **4b** and **4h**, this effect is responsible for higher  $\lambda_{max}$  of dye **4a**. The visible absorption spectra of all the dyes **4a-h** are shown in Fig. 2.

#### 3.3. Dyeing of fibres

All the dyes (4a-h) were applied on hydrophilic fibres such as silk, wool and cotton in 2% (owf) shade according to the following procedure. These dyes are given yellow to purple hues with brighter and deeper shades with excellent levelness on the

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Jye No.	R	Dye color	Molecular formula	Mol. wt. (g)	Yield (%)	$\lambda_{\max}^{a}$ (nm)	$arepsilon^{\mathrm{b}}_{\mathrm{max}}$ (1 mol <sup>-1</sup> cm <sup>-1</sup> )	%C (Found/Req.)	%H (Found/Req.)	%N (Found/Req.)	$R_{ m f}^{ m c}$
â	H-acid (3a)	Dark Purple	$C_{41}H_{22}O_{18}N_{14}Cl_4S_4Na_4$	1360.73	84	530	28,248.80	36.11/36.19	1.58/1.63	14.35/14.41	0.43
ą	K-acid (3b)	Pale yellow	$C_{41}H_{22}O_{18}N_{14}Cl_4S_4Na_4$	1360.73	82	465	16,710.91	36.13/36.19	1.56/1.63	14.36/14.41	0.42
ç	Gamma acid (3c)	Dark yellow	$C_{41}H_{24}O_{12}N_{14}Cl_4S_2Na_2$	1156.63	80	475	15,417.00	42.52/42.58	2.02/2.09	16.90/16.95	0.39
p	N-methyl Gamma acid (3d)	Pale Orange	$C_{43}H_{28}O_{12}N_{14}Cl_4S_2Na_2$	1184.69	82	485	21,183.61	43.52/43.59	2.33/2.38	16.48/16.55	0.36
e	J-acid (3e)	Dark yellow	$C_{41}H_{24}O_{12}N_{14}Cl_4S_2Na_2$	1156.63	78	478	18,030.18	42.50/42.58	2.04/2.09	16.88/16.95	0.41
بو	N-methyl J-acid (3f)	Dark orange	$C_{43}H_{28}O_{12}N_{14}Cl_4S_2Na_2$	1184.69	75	490	16,032.45	43.53/43.59	2.35/2.38	16.50/16.55	0.42
50	N-phenyl J-acid (3g)	Dark red	C <sub>53</sub> H <sub>32</sub> O <sub>12</sub> N <sub>14</sub> Cl <sub>4</sub> S <sub>2</sub> Na <sub>2</sub>	1308.83	84	500	13,335.21	48.58/48.64	2.41/2.46	14.92/14.98	0.40
ų	Chicago acid ( <b>3h</b> )	Pale yellow	$C_{41}H_{22}O_{18}N_{14}Cl_4S_4Na_4$	1360.73	80	468	23,014.42	36.12/36.19	1.54/1.63	14.34/14.41	0.36
<sup>a</sup> Detern	uined in water at 28 °C at $4 \times 10^{-11}$	) <sup>-6</sup> M dye concer	tration.								Ì
<sup>b</sup> Detern	uined by Lambert-Beer's law.										

 Table 2
 Characterization data of reactive dyes (4a-h)

Determined by TLC using 2-BuOH:EtOH:NH4OH:pyridine (4:1:3:2, v/v) solvent system on Silica gel-G F<sub>254</sub> TLC plate.

0.9 1: 4a 0.8 2:4b 3: 4c 0.7 4: 4d 5:4e 0.6 6: 4f 7:4g Absorbance 0.5 8:4h 0.4 0.3 0.2 0.1 550 400 450 500 600 Wavelength (nm)

Figure 2 Visible absorption spectra of reactive dyes (4a-h).

fabric. The variation in the hues (yellow to purple) of the dyed fabric is due to the alteration in the coupling components, e.g. when H-acid is used as coupling component it gives purple hue, J-acid gives yellow color, N-methyl-J-acid gives orange color and N-phenyl-J-acid gives red color.

#### 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 min. 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 min more and then the dyed material was washed with cold water and soap 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 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 into the dyebath at 30 °C and the temperature was raised up to 40 °C over 20 min. Sulphuric acid (0.4 ml of 10%, v/v) was then added and the dyeing was continued for 40 min more at the same temperature. The material was then removed, rinsed with cold water and soap and dried.

#### 3.3.3. Dyeing of cotton

The 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 min. Soda ash (Na<sub>2</sub>CO<sub>3</sub>) solution (0.4 ml of 10%, v/v) was then added to bring about fixation and the dyeing was continued for

Dye	FTIR (KBr): $v_{max}$ (cm <sup>-1</sup> )	<sup>1</sup> H NMR (DMSO- $d_6$ ) (chemical shift in $\delta$ ppm)
4a	3360–3485 (O–H & N–H), 2925, 2855 (C–H), 1525,	2.24 (2H, s, CH <sub>2</sub> ), 1.35 (6H, s, CH <sub>3</sub> ), 3.68
	1405, 805 (C–N), 1565 (N $\equiv$ N), 1190, 1040 (S $\equiv$ O),	(2H, s, OH), 4.02 (2H, s, NH), 6.62–7.80
	1525, 1340 (N=O), 765 (C-Cl)	(10H, m, Ar–H)
4b	3365–3475 (О–Н & N–Н), 2945, 2850 (С–Н), 1530,	2.28 (2H, s, CH <sub>2</sub> ), 1.32 (6H, s, CH <sub>3</sub> ), 3.62
	1415, 800 (C–N), 1562 (N=N), 1195, 1045 (S=O),	(2H, s, OH), 4.10 (2H, s, NH), 6.65–7.85
	1522, 1350 (N=O), 770 (C-Cl)	(10H, m, Ar–H)
4c	3365–3485 (О–Н & N–Н), 2920, 2850 (С–Н), 1535,	2.25 (2H, s, CH <sub>2</sub> ), 1.42 (6H, s, CH <sub>3</sub> ), 3.68
	1412, 805 (C–N), 1570 (N=N), 1195, 1042 (S=O),	(2H, s, OH), 4.12 (2H, s, NH), 6.68-7.82
	1520, 1345 (N==O), 765 (C-Cl)	(12H, m, Ar–H)
4d	3455–3520 (О–Н), 2930, 2855 (С–Н), 1540, 1422, 802	2.22 (2H, s, CH <sub>2</sub> ), 1.40 (6H, s, CH <sub>3</sub> ), 2.52
	(C-N), 1562 (N=N), 1195, 1040 (S=O), 1525, 1355	(6H, s, N-CH <sub>3</sub> ), 3.78 (2H, s, OH), 6.70-
	(N==O), 765 (C-Cl)	7.85 (12H, m, Ar–H)
4e	3370-3490 (O-H & N-H), 2945, 2850 (C-H), 1540,	2.32 (2H, s, CH <sub>2</sub> ), 1.48 (6H, s, CH <sub>3</sub> ), 3.62
	1415, 805 (C–N), 1565 (N=N), 1190, 1045 (S=O),	(2H, s, OH), 4.18 (2H, s, NH), 6.62-7.85
	1525, 1360 (N=O), 770 (C-Cl)	(12H, m, Ar–H)
4f	3460-3515 (O-H), 2940, 2860 (C-H), 1530, 1410, 800	2.26 (2H, s, CH <sub>2</sub> ), 1.45 (6H, s, CH <sub>3</sub> ), 2.58
	(C-N), 1560 (N=N), 1200, 1050 (S=O), 1530, 1350	(6H, s, N-CH <sub>3</sub> ), 3.72 (2H, s, OH), 6.82-
	(N=O), 765 (C-Cl)	7.80 (12H, m, Ar–H)
4g	3468-3522 (O-H), 2935, 2852 (C-H), 1540, 1424, 805	2.30 (2H, s, CH <sub>2</sub> ), 1.38 (6H, s, CH <sub>3</sub> ), 3.62
0	(C–N), 1570 (N=N), 1192, 1050 (S=O), 1530, 1360	(2H, s, OH), 6.60–7.85 (22H, m, Ar–H)
	(N=O), 775 (C-Cl)	
4h	3372–3485 (O–H & N–H), 2935, 2852 (C–H). 1532.	2.34 (2H, s, CH <sub>2</sub> ), 1.42 (6H, s, CH <sub>3</sub> ), 3.62
	1420, 810 (C–N), 1565 (N $\equiv$ N), 1195, 1042 (S $\equiv$ O),	(2H, s, OH), 4.12 (2H, s, NH), 6.58–7.86
	1530, 1352 (N=O), 770 (C-Cl)	(10H  m Ar-H)

Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet.

40 min more at the same temperature. The material was then removed, rinsed with cold water and soap and dried.

#### 3.4. Wash-off process

The dyed fabrics (silk, wool and cotton) were rinsed in warm water, scoured with 2 g/l Lissapol detergent at 90 °C for 5 min 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 fibre surface. The amount of the hydrolyzed dye has low substantivity released easily from the substrate after two or three washes.

#### 3.5. Exhaustion and fixation study

The percentage exhaustion and fixation data are calculated according to the known method (Patel and Patel, 2005) and are summarized in Table 4.

The percentage exhaustion of 2% (owf) dyeing on silk fabric ranges from 67% to 78%, in which dye **4a** shows maximum exhaustion (77.18%) while dye **4h** shows minimum exhaustion (67.20%); for wool percentage exhaustion ranges from 64% to 77%, in which dye **4c** shows maximum exhaustion (76.10%) while dye **4h** shows minimum exhaustion (64.22%) and for cotton fabric the percentage exhaustion ranges from 67% to 76%,

Table 4	Exhaustio	on, fixatio	on and f	fastness	propert	ies data	of the	e react	ive dye	es ( <b>4a</b> -l	h).							
Dye No.	% Exha	austion		% Fix	ation		Ligh	t fastne	ss	Wasł	n fastne	ess	Rub	bing fa	astness			
	S	W	С	S	W	С	S	W	С	S	W	С	Dry			Wet		
													S	W	С	S	W	С
<b>4</b> a	77.18	68.20	72.55	85.54	90.04	89.59	5	4	4–5	5	4	3–4	5	3–4	5	4–5	4	4
4b	75.90	74.10	69.00	82.34	80.97	87.30	3–4	5	5	4–5	3–4	3	3–4	4	3	4–5	3–4	4–5
4c	68.70	76.10	67.15	90.84	88.84	89.35	5	4–5	5	4	4	4	4	4–5	3–4	4	4	3–4
4d	76.80	65.90	75.10	86.58	84.97	90.20	4–5	4	4	3–4	5	4–5	3–4	3–4	4	3–4	3–4	3
<b>4</b> e	71.37	67.00	69.00	82.66	84.32	88.40	5	5	4–5	3–4	4–5	3–4	3–4	3	4–5	3	4	4
4f	73.93	67.88	74.10	87.92	85.77	86.62	4–5	5	3–4	4	4	3	4	3–4	4	4–5	4	5
4g	73.22	74.40	71.57	83.98	81.98	91.46	4	3	3	3	3–4	4	3–4	3–4	3–4	3–4	3	3–4
4h	67.20	64.22	74.32	87.98	82.07	87.45	4	4	4–5	3–4	3	4	4–5	3–4	3	3	5	5

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.

Abbreviations: S, silk; W, wool; C, cotton.

Dye No.	$L^*$			a*	<i>a</i> *					$C^*$			$H^{*}$			K/S		
	S	W	С	S	W	С	S	W	С	S	W	С	S	W	С	S	W	С
<b>4</b> a	75.15	65.78	66.40	25.12	22.65	30.22	11.20	-3.80	-6.50	35.12	30.12	30.52	38.25	247.40	284.69	10.14	14.10	09.70
4b	78.10	75.80	78.43	22.45	16.15	18.40	-9.20	-6.56	12.30	42.18	26.10	21.44	310.25	235.25	50.14	02.15	07.78	04.53
4c	68.28	62.64	72.25	25.35	23.15	26.09	18.54	27.15	18.23	38.66	38.23	29.75	28.25	36.44	44.60	04.10	09.11	05.48
4d	66.20	66.08	68.04	20.12	30.12	22.65	12.44	22.80	11.80	30.40	30.15	36.08	20.07	30.20	30.28	05.10	08.45	06.65
<b>4</b> e	90.45	72.15	83.50	10.24	18.20	11.54	15.80	26.58	19.25	12.78	25.11	26.68	39.86	39.15	50.20	04.44	07.14	07.55
4f	82.10	76.22	78.10	22.23	11.24	12.06	11.75	35.60	11.38	28.55	26.68	22.65	26.60	45.12	43.14	06.10	10.34	07.65
4g	85.32	75.04	86.60	12.56	19.80	15.53	22.15	40.74	25.85	21.90	31.90	32.10	55.36	55.27	50.15	09.06	15.88	07.68
4h	85.56	80.20	75.12	08.14	12.50	12.72	23.18	30.52	19.88	32.54	39.55	33.09	52.34	59.23	45.19	02.45	07.06	04.21

 Table 5
 Colorimetric (CIE lab) data of the reactive dyes (4a-h).

Abbreviations: S, silk; W, wool; C, cotton.

in which dye **4d** shows maximum exhaustion (75.10%) while dye **4c** shows minimum exhaustion (67.15%).

The percentage fixation of 2% (owf) dyeing on silk fabric ranges from 82% to 91%, in which dye **4c** shows maximum fixation (90.84%) while dye **4b** shows minimum fixation (82.34%); for wool fabric the percentage fixation values ranges from 81% to 91%, in which dye **4a** shows maximum value of fixation (90.04%) while dye **4b** shows minimum value of fixation (80.97%) and for cotton fabric the percentage fixation ranges from 87% to 92%, in which dye **4g** shows maximum exhaustion (91.46%) while dye **4b** shows minimum value of fixation (87.30%).

The data summarized in Table 4 show that the exhaustion and fixation values are very good. This is due to the fact that the diffusion of the dye molecule within the fabric is rapid, so the rate of diffusion is high. The lower exhaustion is due to the lower substantivity due to the lower hydrophobicity (Dawson, 1991). The introduction of reactive group like s-triazine ring to the dye molecule improves the exhaustion value.

#### 3.6. Fastness properties

The light fastness property of all the dyes rating 3–6 (Grey scale) for silk, wool and cotton shows that it ranges from moderate to very good. The wash fastness and rubbing fastness properties of all the dyes rating 3–5 for silk, wool and cotton show that these properties of all the dyes range from good to excellent. The good wash fastness properties may be due to the better dye penetration and good covalent fixation with fabrics (Samanta and Das, 1992). The solubility of the dyes and rate of movement of the dyes out of the fibre during washing depends on the size of the dye molecule and also on the nature and position of the substituent present on the coupler ring. The data of light, wash and rubbing fastness properties of all the dyes (**4a–h**) are shown in Table 4.

#### 3.7. Colorimetric data (CIE lab data)

The color of a dye on silk, wool and cotton fibres is expressed in terms of CIE lab value (Table 5) and the following CIE lab coordinates were measured, lightness ( $L^*$ ), chroma ( $C^*$ ), hue angle form 0° to 360° (H),  $a^*$  value represents the degree of redness (positive) and greenness (negative) and  $b^*$  represents the degree of yellowness (positive) and blueness (negative). A reflectance spectrophotometer was used for the colorimetric measurements on the dyed samples. K/S values given by the reflectance spectrophotometer are calculated at  $\lambda_{max}$  and are directly correlated with the dye concentration on the substrate according to the Kubelka–Munk equation (Billmeyer and Saltzman, 1981):

$$K/S = (1-R)^2/2R,$$

where K is the absorbance coefficient, S the scattering coefficient and R is the reflectance ratio.

The color coordinates (Table 5) indicate that the dyes have good affinity to silk, wool and cotton fibres.

For silk fibre, Table 5 showed that the hue obtained using dye 4b was greener, lighter and brighter than dye 4a, while dye obtained using dye 4d was greener, darker and duller than dye 4c. The dyeing obtained using dye 4f was redder, darker and brighter than dye 4e, while the dyeing obtained using dye 4g was redder, darker and brighter than dye 4e. Dye 4a has the highest value of color strength (K/S) of 10.14. The K/S value for silk fibre follows the order,

#### 4a>4g>4f>4d>4e>4c>4h>4b

For wool fibre, Table 5 showed that the dye obtained using dye **4b** was greener, lighter and duller than dye **4a**, the dyeing obtained using dye **4d** was redder, lighter and duller than dye **4c**. The dyeing obtained using dye **4f** was greener, lighter and brighter than dye **4e**. The dyeing obtained using dye **4g** was redder, lighter and brighter than dye **4e**. Dye **4g** has the highest value of color strength (K/S) of 15.88. The K/S value for wool fibre follows the order,

#### 4g>4a>4f>4c>4d>4b>4e>4h

And for cotton fibre, Table 5 showed that dyeing obtained using dye **4b** was greener, lighter, duller than dye **4a**, and the dyeing obtained using dye **4d** was greener, darker and brighter than dye **4c**. The dyeing obtained using dye **4f** was redder, dar-



**Figure 3** CIE lab graph of  $b^*$  vs.  $a^*$  for silk fibre.



**Figure 4** CIE lab graph of  $b^*$  vs.  $a^*$  for wool fibre.



**Figure 5** CIE lab graph of  $b^*$  vs.  $a^*$  for cotton fibre.



Figure 6 Graph of K/S value for dyes 4a-h.

ker and duller than dye **4e** while the dyeing obtained using dye **4g** was redder, lighter and brighter than dye **4e**. The dye **4a** has the highest value of color strength (K/S) of 9.70. Wool fibres possess higher K/S value than silk and cotton due to the high substantivity of the dyes with wool fibre. The K/S value for cotton fibre follows the order,

#### 4a>4g>4f>4e>4d>4c>4b>4h

CIE lab graph of  $b^*$  vs.  $a^*$  for silk, wool and cotton fibre are shown in Figs. 3–5, respectively. The graph of K/S value of all the dyes for silk, wool and cotton fibres are shown in Fig. 6.

#### 4. Conclusion

A new series of cold brand bisazo reactive dyes (4a-h) were synthesized by the process of direct diazotization and coupling in good yields. These dyes were applied on hydrophilic fibres like silk, wool and cotton which gave yellow to purple hues with good depth and levelness. Percentage exhaustion and fixation of these dyes were very good which showed that these dyes have good compatibility with the fabrics. The light, wash and rubbing fastness properties of these dyes are good, this indicates that these dyes have good substantivity with the fabrics. Colorimetric data showed that dye **4a** showed highest K/Svalue on silk and cotton fibres and dye **4g** for wool fibre.

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