



ORIGINAL ARTICLE

Synthesis and dyeing properties of new disazo disperse dyes for polyester and nylon fabrics



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Fastness properties

Abstract Diazotized aryl amines were coupled with two stenhouse salt namely, *N*-(5-phenylamino-penta-4-ol-2,4-diene-1-ylidene)anilines hydrochloride [**S**₁ (R=H) or **S**₂ (R=OH)] to furnish two series of disazo disperse dyes (**S**₁**D**_{1–10} and **S**₂**D**_{1–10}). The structure of all the dyes was established by estimating number of azo groups, elemental analysis and spectral studies (IR, ¹H-NMR, UV/Visible). The structure–property relationship was discussed by using electronic absorption spectra of the dyes. These dyes were applied to polyester and nylon fabrics as disperse dyes by using temperature exhaust dyeing method. The relevant dyeing characteristics, such as dyeability on fabrics, wash-fastness and light-fastness were evaluated. Fabrics dyed with these dyes furnished generally deep and bright intense hues ranging from light yellow to orange to reddish brown. The color fastness of the dyed fabric was assessed by determining wash-fastness and light-fastness properties.

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1. Introduction

Among the various organic crystalline salts, stenhouse salts are well known compounds like Schiff's bases. Lewis and co-worker reported a reaction of 2-furfuraldehyde with two moles of aryl amines in the presence of acid (HCl or HClO₄) under-

going furan ring opening to yield crystalline colored stenhouse salt having a conjugated double bond open-chain structure. Literature survey reported a number of analytical applications of such stenhouse salts as a reagent to detect furfural in oil, inhibitor for corrosion of steel and as a reagent in spectrometry (Sze-Wan and Robert, 2007; Matsunaga and Suzuki, 1997; Sato and Washiyama, 1999; Podobav and Kopach, 1994). Recently P. Miladinova et al. mentioned in the report that the combination of unsaturated functional group and a stabilizer residue in the dye molecules improves the dyeability, fastness properties and possibility of dyeing synthetic fibers (Bojinov and Konstantinova, 2000, 2002; Konstantinova et al., 2003; Bojinov, 2004; Bojinov et al., 2004; Miladinov and Konstantinova, 2004, 2005). In view of this, it was thought

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to use a bifunctional stenhouse salt as dye precursors for the synthesis of disazo disperse dyes.

The introduction of the synthetic fibers like nylon, polyester, polyacrylonitrile produced significant challenge to dyeability of hydrophobic fibers to dyestuff chemists. Consequently in the last three decades, the research trends focused their efforts on the synthesis of dyes for these fibers. Polyester is the most hydrophobic of all common fibers and usually dyed with disperse dyes because of their high tinctorial strength and good fastness properties. From the chemical point of view more than 50% of disperse dyes are simple azo compounds because of the ease with which a number of molecular combinations can be achieved by varying diazonium and coupling components, simple manufacturing process and providing very wide color gamut of high color strength (Hamprecht and Westerkamp 2003; Christi et al., 2000). As a result the success has been achieved with the discovery of several new coupling and diazonium components designed to give disperse azo dyes especially for dyeing polyester and nylon fibers. Such disperse dyes include azo disperse dyes, triphenyldioxazinone azo dyes, polycyclic aromatic carbonyl dyes, benzodifuranones dyes and dihydrophenophosphazine dyes (Zhi-Gang et al., 2009). Technically important disperse azo dyes used for polyester are normally monoazo compounds but a few disazo compounds have also received commercial status since disazo dyes with two groups provide excellent properties (James et al., 1982; Oyewale et al., 2001; Otutu et al., 2007, 2008).

On the basis of these reports, in the present paper we are reporting two new bifunctional stenhouse salts as coupling component with a view to incorporate conjugated double bond system into disazo disperse dyes. These novel couplers were synthesized by the reaction of 2-furfuraldehyde respectively with two moles of aniline and *p*-aminophenol in the presence of acid catalyst to form crystalline red color stenhouse salts, **S₁** and **S₂**. In the subsequent coupling reaction, **S₁** and **S₂** were reacted with a variety of 10 diazonium salt of aromatic amines to yield corresponding two series of disazo disperse dyes **S₁D₁₋₁₀** and **S₂D₁₋₁₀**, respectively. These dyes were used as disperse dyes for dyeing polyester and nylon fabrics using high temperature exhaust dyeing method. The dye performance on the resultant dyeing was evaluated by studying the dyeing characteristics and fastness properties on both fabrics.

2. Experimental

2.1. Materials

Reagent grade 2-furfuraldehyde and aniline derivatives were used after purification. Perchloric acid (72%) was purchased from S.D. Fine Chemicals Ltd., Mumbai, India, and was used as received. All the solvents and chemicals were used of analytical reagent grade without further purification. Spectroscopic grade solvents (Merck-India, Ltd.) were used for UV-Visible, ¹H-NMR spectroscopy and TLC plates were used also from Merck-India, Ltd. Nylon and polyester materials were used commercially and the nylon fabrics was purchased from Sapana Fabrics Ltd., Surat, while polyester fabrics was purchased from Rustam Fabrics Ltd., Ahmedabad.

2.2. Methods and instruments

Melting points were determined by open capillary method (uncorrected). Elemental analysis was performed on Carlo Erba Elemental Analyzer (Italy). Azo group estimation of the dye was carried out by the method reported in the literature (Vogel, 1989). IR spectra were recorded on a Nicolet 400-D IR Spectrophotometer (in KBr pellets). ¹H-NMR spectra were obtained with a Bruker 400 MHz in DMSO-*d*₆ solvent at room temperature with TMS as an internal standard (chemical shifts δ in ppm). UV-Visible absorption spectra were scanned on Shimadzu A-20 Spectrophotometer using dye concentration of 1×10^{-3} mg/ml in spectroscopic grade DMF.

2.3. General procedure for the synthesis of stenhouse salts (**S₁** and **S₂**)

Stenhouse salts **S₁** and **S₂** were prepared by the method reported in the literature (Lewis and Mulquiney, 1970, 1979). Accordingly, an equimolar amount of perchloric acid (72%) was added dropwise to the methanolic solution of aniline (0.1 mol) with continuous stirring at room temperature during 30 min. The resulting solution was cooled to below 5 °C and 2-furfuraldehyde (0.1 mol) was added gradually with stirring, followed by the addition of a second portion of methanolic solution of aniline (0.1 mol) containing HCl as catalyst over a period of 20 min. The resultant reaction mixture was stirred for half an hour below 5 °C. The red product precipitated was filtered off, washed several times with water and dried in air giving red color stenhouse salts **S₁** (76%). Two moles of *p*-aminophenol were used in a similar manner for the synthesis of stenhouse salts **S₂** (88%).

2.4. Synthesis of disazo disperse dyes **S₁D₁₋₁₀** and **S₂D₁₋₁₀**

Diazotization of aromatic amine was carried out by the procedure reported in literature (Townes, 1999). The general procedure followed is typically given for aniline.

A solution of aniline (0.1 mol) in HCl (2 N, 2.5 mol) was cooled to 0–2 °C. To this cooled solution of aniline, aqueous solution of NaNO₂ (1 N, 1.0 mol) was added dropwise during half an hour by maintaining the temperature of the reaction mixture below 2 °C. The resulting solution of diazonium salt was immediately used in coupling reaction of disazo dye synthesis.

For coupling reaction, in the above prepared diazonium salt solution, a cooled solution of stenhouse salt **S₁** (0.05 mol) was added under stirring over a period of 20 min. by maintaining temperature below 5 °C. Stirring was continued for 30 min. to give clear solution by maintaining pH and subsequently sodium chloride was added to precipitate out the dye. The precipitated dye **S₁D₁** was filtered, washed several times with water until washings were neutral and dried in air. Salt removal and dye purification for all dyes were conducted by dissolution and reprecipitation using DMF-ether solvent. The purity of the resultant dyes was checked by TLC using butanol-water-DMF solvent system (2:1:2).

In the ¹H-NMR spectrum of **S₁**, four signals were observed at δ 5.51, 5.74, 6.36 and 6.77 ppm integrating for four protons of C₁, C₂, C₃ and C₄ of aliphatic chain. The spectral data for all the compounds are given below:

S₁: ¹H-NMR (400 MHz, DMSO): δ = 4.90 (s, 1H, NH), 5.28 (s, 1H, OH), 5.51 (d, 1H), 5.74 (t, 1H), 6.36 (s, 1H), 6.77 (s, 1H), 6.94–9.03 (m, 10H), 9.86 (s, 1H, ⁺NH). IR (KBr) cm^{-1} : ν = 3202 (OH & NH), 1326 & 1228 (OH), 1110 (CO), 1555 (NH), 753 (NH), 2992 (conjugated alkene), 1623 (C=C of aromatic ring).

S₂: ¹H-NMR (400 MHz, DMSO): δ = 4.90 (s, 1H, NH), 5.28 (s, 1H, OH), 5.49 (d, 1H), 5.83 (t, 1H), 6.35 (s, 1H), 6.86 (s, 1H), 7.01–8.94 (m, 8H), 9.90 (s, 1H, ⁺NH), 10.36 (s, 2H, OH). IR (KBr) cm^{-1} : ν = 3066 (OH & NH), 1300 & 1252 (OH), 1110 (CO), 1521 (NH), 580 (NH), 2992 (conjugated alkene), 1623 (C=C of aromatic ring).

S_{1D₁}: ¹H-NMR (400 MHz, DMSO): δ = 4.92 (s, 1H, NH), 5.30 (s, 1H, OH), 5.50 (d, 1H), 5.83 (t, 1H), 6.36 (s, 1H), 6.88 (s, 1H), 7.16–9.32 (m, 18H), 9.88 (s, 1H, ⁺NH). IR (KBr) cm^{-1} : ν = 3200 (OH & NH), 1326 & 1228 (OH), 1553 (NH), 1308 (C–N), 1608 (N=N).

S_{1D₂}: ¹H-NMR (400 MHz, DMSO): δ = 2.27 (s, 6H), 4.91 (s, 1H, NH), 5.28 (s, 1H, OH), 5.58 (d, 1H), 5.88 (t, 1H), 6.46 (s, 1H), 6.92 (s, 1H), 7.21–9.39 (m, 16H), 9.88 (s, 1H, ⁺NH). IR (KBr) cm^{-1} : ν = 3180 (OH & NH), 1327 & 1226 (OH), 1527 (NH), 1327 (C–N), 1612 (N=N).

S_{1D₃}: ¹H-NMR (400 MHz, DMSO): δ = 4.96 (s, 1H, NH), 5.32 (s, 1H, OH), 5.49 (d, 1H), 5.72 (t, 1H), 6.30 (s, 1H), 6.74 (s, 1H), 7.39–9.31 (m, 16H), 9.95 (s, 1H, ⁺NH). IR (KBr) cm^{-1} : ν = 3202 (OH & NH), 1328 & 1226 (OH), 1528 (NH), 1324 (C–N), 1624 (N=N).

S_{1D₄}: ¹H-NMR (400 MHz, DMSO): δ = 4.92 (s, 1H, NH), 5.28 (s, 1H, OH), 5.51 (d, 1H), 5.83 (t, 1H), 6.36 (s, 1H), 6.88 (s, 1H), 7.12–9.03 (m, 16H), 9.89 (s, 1H, ⁺NH). IR (KBr) cm^{-1} : ν = 3160 (OH & NH), 1390 & 1280 (OH), 1550 (NH), 1310 (C–N), 1622 (N=N).

S_{1D₅}: ¹H-NMR (400 MHz, DMSO): δ = 4.92 (s, 1H, NH), 5.29 (s, 1H, OH), 5.48 (d, 1H), 5.75 (t, 1H), 6.39 (s, 1H), 6.82 (s, 1H), 7.18–8.97 (m, 22H), 9.84 (s, 1H, ⁺NH). IR (KBr) cm^{-1} : ν = 3361 (OH & NH), 1310 & 1219 (OH), 1514 (NH), 1380 (C–N), 1629 (N=N).

S_{1D₆}: ¹H-NMR (400 MHz, DMSO): δ = 4.01 (s, 6H), 4.96 (s, 1H, NH), 5.32 (s, 1H, OH), 5.44 (d, 1H), 5.78 (t, 1H), 6.24 (s, 1H), 6.87 (s, 1H), 7.20–8.96 (m, 16H), 9.87 (s, 1H, ⁺NH). IR (KBr) cm^{-1} : ν = 3355 (OH & NH), 1395 & 1250 (OH), 1501 (NH), 1395 (C–N), 1608 (N=N).

S_{1D₇}: ¹H-NMR (400 MHz, DMSO): δ = 3.94 (s, 6H), 4.92 (s, 1H, NH), 5.28 (s, 1H, OH), 5.51 (d, 1H), 5.83 (t, 1H), 6.36 (s, 1H), 6.88 (s, 1H), 7.12–9.03 (m, 16H), 9.89 (s, 1H, ⁺NH). IR (KBr) cm^{-1} : ν = 3348 (OH & NH), 1333 & 1252 (OH), 1508 (NH), 1333 (C–N), 1608 (N=N).

S_{1D₈}: ¹H-NMR (400 MHz, DMSO): δ = 4.92 (s, 1H, NH), 5.29 (s, 1H, OH), 5.48 (d, 1H), 5.75 (t, 1H), 6.39 (s, 1H), 6.82 (s, 1H), 7.18–8.97 (m, 14H), 9.84 (s, 1H, ⁺NH). IR (KBr) cm^{-1} : ν = 3388 (OH & NH), 1390 & 1279 (OH), 1501 (NH), 1300 (C–N), 1602 (N=N).

S_{1D₉}: ¹H-NMR (400 MHz, DMSO): δ = 2.78 (s, 12H), 4.96 (s, 1H, NH), 5.32 (s, 1H, OH), 5.44 (d, 1H), 5.78 (t, 1H), 6.24 (s, 1H), 6.87 (s, 1H), 7.20–8.96 (m, 16H), 9.87 (s, 1H, ⁺NH). IR (KBr) cm^{-1} : ν = 3375 (OH & NH), 1395 & 1252 (OH), 1501 (NH), 1395 (C–N), 1602 (N=N).

S_{1D₁₀}: ¹H-NMR (400 MHz, DMSO): δ = 2.24 (s, 12H), 4.92 (s, 1H, NH), 5.28 (s, 1H, OH), 5.51 (d, 1H), 5.83 (t, 1H), 6.36 (s, 1H), 6.88 (s, 1H), 7.12–9.03 (m, 14H), 9.89 (s, 1H, ⁺NH). IR (KBr) cm^{-1} : ν = 3449 (OH & NH), 1360 & 1232 (OH), 1501 (NH), 1360 (C–N), 1629 (N=N).

S_{2D₁}: ¹H-NMR (400 MHz, DMSO): δ = 4.92 (s, 1H, NH), 5.30 (s, 1H, OH), 5.50 (d, 1H), 5.83 (t, 1H), 6.36 (s, 1H), 6.88 (s, 1H), 7.16–9.32 (m, 16H), 9.88 (s, 1H, ⁺NH), 10.80 (s, 2H, OH). IR (KBr) cm^{-1} : ν = 3456 (OH & NH), 1313 & 1220 (OH), 1535 (NH), 1313 (C–N), 1602 (N=N).

S_{2D₂}: ¹H-NMR (400 MHz, DMSO): δ = 2.27 (s, 6H), 4.91 (s, 1H, NH), 5.28 (s, 1H, OH), 5.58 (d, 1H), 5.88 (t, 1H), 6.46 (s, 1H), 6.92 (s, 1H), 7.21–9.39 (m, 14H), 9.88 (s, 1H, ⁺NH), 10.78 (s, 2H, OH). IR (KBr) cm^{-1} : ν = 3375 (OH & NH), 1380 & 1266 (OH), 1500 (NH), 1380 (C–N), 1609 (N=N).

S_{2D₃}: ¹H-NMR (400 MHz, DMSO): δ = 4.96 (s, 1H, NH), 5.32 (s, 1H, OH), 5.49 (d, 1H), 5.72 (t, 1H), 6.30 (s, 1H), 6.74 (s, 1H), 7.39–9.31 (m, 14H), 9.95 (s, 1H, ⁺NH), 10.86 (s, 2H, OH). IR (KBr) cm^{-1} : ν = 3200 (OH & NH), 1326 & 1228 (OH), 1553 (NH), 1308 (C–N), 1608 (N=N).

S_{2D₄}: ¹H-NMR (400 MHz, DMSO): δ = 4.92 (s, 1H, NH), 5.28 (s, 1H, OH), 5.51 (d, 1H), 5.83 (t, 1H), 6.36 (s, 1H), 6.88 (s, 1H), 7.12–9.03 (m, 14H), 9.89 (s, 1H, ⁺NH), 10.82 (s, 2H, OH). IR (KBr) cm^{-1} : ν = 3180 (OH & NH), 1332 & 1224 (OH), 1529 (NH), 1342 (C–N), 1612 (N=N).

S_{2D₅}: ¹H-NMR (400 MHz, DMSO): δ = 4.92 (s, 1H, NH), 5.29 (s, 1H, OH), 5.48 (d, 1H), 5.75 (t, 1H), 6.39 (s, 1H), 6.82 (s, 1H), 7.18–8.97 (m, 20H), 9.84 (s, 1H, ⁺NH), 10.80 (s, 2H, OH). IR (KBr) cm^{-1} : ν = 3202 (OH & NH), 1329 & 1222 (NH), 1528 (NH), 1321 (C–N), 1626 (N=N).

S_{2D₆}: ¹H-NMR (400 MHz, DMSO): δ = 4.10 (s, 6H), 4.96 (s, 1H, NH), 5.32 (s, 1H, OH), 5.44 (d, 1H), 5.78 (t, 1H), 6.24 (s, 1H), 6.87 (s, 1H), 7.20–8.96 (m, 14H), 9.87 (s, 1H, ⁺NH), 10.86 (s, 2H, OH). IR (KBr) cm^{-1} : ν = 3166 (OH & NH), 1386 & 1278 (OH), 1550 (NH), 1310 (C–N), 1622 (N=N).

S_{2D₇}: ¹H-NMR (400 MHz, DMSO): δ = 3.89 (s, 6H), 4.92 (s, 1H, NH), 5.28 (s, 1H, OH), 5.51 (d, 1H), 5.83 (t, 1H), 6.36 (s, 1H), 6.88 (s, 1H), 7.12–9.03 (m, 14H), 9.89 (s, 1H, ⁺NH), 10.82 (s, 2H, OH). IR (KBr) cm^{-1} : ν = 3341 (OH & NH), 1320 & 1219 (OH), 1525 (NH), 1372 (C–N), 1624 (N=N).

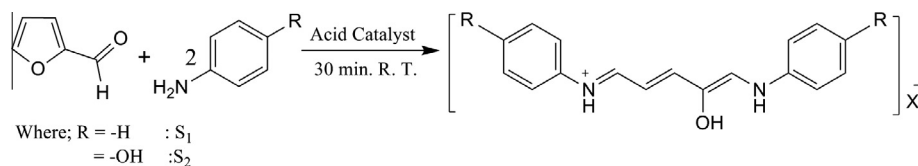
S_{2D₈}: ¹H-NMR (400 MHz, DMSO): δ = 4.92 (s, 1H, NH), 5.29 (s, 1H, OH), 5.48 (d, 1H), 5.75 (t, 1H), 6.39 (s, 1H), 6.82 (s, 1H), 7.18–8.97 (m, 12H), 9.84 (s, 1H, ⁺NH), 10.80 (s, 2H, OH). IR (KBr) cm^{-1} : ν = 3388 (OH & NH), 1390 & 1276 (OH), 1509 (NH), 1308 (C–N), 1612 (N=N).

S_{2D₉}: ¹H-NMR (400 MHz, DMSO): δ = 2.81 (s, 12H), 4.96 (s, 1H, NH), 5.32 (s, 1H, OH), 5.44 (d, 1H), 5.78 (t, 1H), 6.24 (s, 1H), 6.87 (s, 1H), 7.20–8.96 (m, 14H), 9.87 (s, 1H, ⁺NH), 10.86 (s, 2H, OH). IR (KBr) cm^{-1} : ν = 3378 (OH & NH), 1388 & 1242 (OH), 1519 (NH), 1369 (C–N), 1610 (N=N).

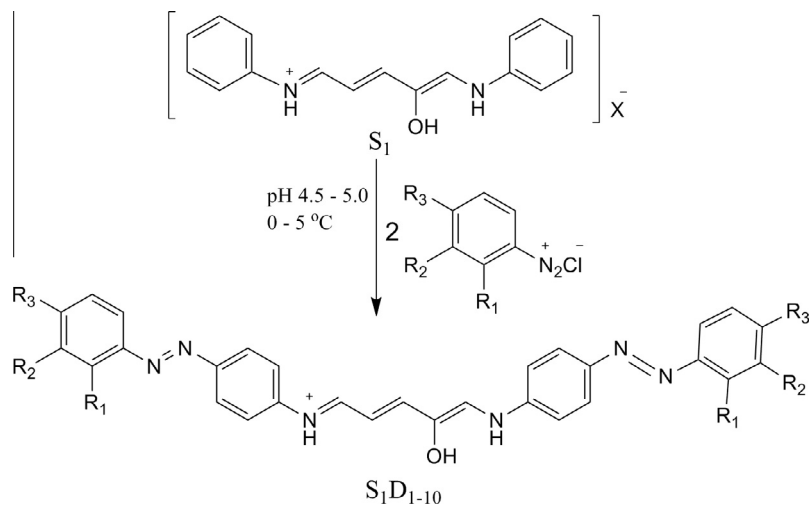
S_{2D₁₀}: ¹H-NMR (400 MHz, DMSO): δ = 2.27 (s, 12H), 4.92 (s, 1H, NH), 5.28 (s, 1H, OH), 5.51 (s, 1H), 5.83 (s, 1H), 6.36 (s, 1H), 6.88 (s, 1H), 7.12–9.03 (m, 12H), 9.89 (s, 1H, ⁺NH), 10.82 (s, 2H, OH). IR (KBr) cm^{-1} : ν = 3446 (OH & NH), 1353 & 1232 (OH), 1519 (NH), 1349 (C–N), 1632 (N=N).

2.5. Dyeing method

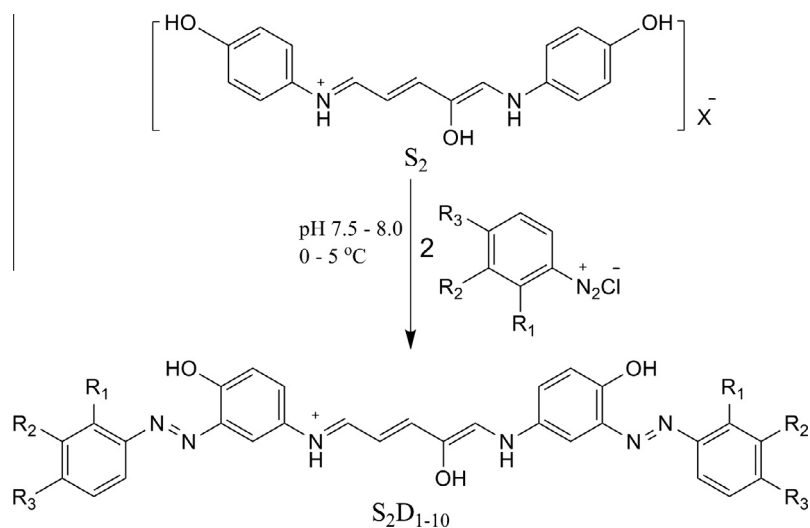
Dyeing on polyester and nylon was carried out by reported dyeing procedure (Hallas and Choi, 1999; Bello, 1995). The polyester and nylon fabrics were treated at pH 5–6 (adjusted with acetic acid) for 15 min at 60 °C. A laboratory model glycerin bath of metallic beaker-dyeing machine was used. A paste of dye (4×10^{-5} kg) was prepared with dispersing agent Doda-



Scheme 1 Synthetic route for preparation of stenhouse salts.



Scheme 2 Synthetic route for preparation of S₁-series dyes (S₁D₁₋₁₀).



Scheme 3 Synthetic route for preparation of S₂-series dyes (S₂D₁₋₁₀).

mol (80×10^{-5} kg), wetting agent Tween-80 (5×10^{-6} kg) (in case of polyester) and water (1×10^{-3} dm³) in a beaker. To this paste, 160×10^{-3} dm³ water was added under stirring and the pH was adjusted to 4 using acetic acid to give the dyeing solution. This solution was then transferred to a metallic beaker provided with a lid and a screw cap. Before closing the lid and tightening the metal cap over the beaker, a pretreated patch of polyester or nylon fabric (2×10^{-6} kg) of was rolled into the beaker. The beaker was then placed vertically on the rotatory carrier inside the tank and the clamp plate was firmly

tightened. The rotatory carrier was then allowed to rotate in the glycerin bath. The temperature of the bath was raised to 110 and 95 °C, respectively, for polyester and nylon fabrics at the rate of 2 °C/min. The dyeing was continued for 60 min. under pressure. After cooling for an hour, the beaker was removed from the bath and washed thoroughly with water. The mother liquor after dyeing was collected and used further for exhaustion study. The dyed pattern was washed several times with cold water followed by detergent (2×10^{-7} kg) and sodium carbonate (1×10^{-7} kg) in

$100 \times 10^{-3} \text{ dm}^3$ water at 80°C for 30 min. Finally, it was washed thoroughly with water and dried at room temperature. The dyeing behavior of these dyes was examined by studying the percentage dye-bath exhaustion and fixation of the dye on fabric according to a standard method (Kochergin, 1956; Ma, 2009). The dyed polyester and nylon fabrics were tested for wash-fastness according to ISO-105 test (Shah et al., 2009; Ullmann's, 1984) using detergent and 2% sodium carbonate. The change in shade and staining of adjacent fabrics were assessed using gray scales. A light-fastness was carried out in accordance with the ISO-105 test (Ullmann's, 1984).

3. Results and discussion

3.1. Synthesis and characterization of stenhouse salts

Scheme 1 shows the synthesis of stenhouse salts (S_1 and S_2) by the reaction of 2-furfuraldehyde with two moles of aniline and *p*-aminophenol respectively in the presence of mineral acid (HCl or HClO_4) to form crystalline red color products. Both of these salts were obtained in good yields (75% and 88%). The structure of these salts was established by elemental analysis and spectral studies (IR, $^1\text{H-NMR}$). The analytical data of C, H and N were in close agreement with the proposed structure. It was further confirmed by preparing the acetyl derivatives of S_1 and S_2 (m.p. above 250°C decompose). The IR spectra of the salts exhibit the characteristic absorption bands at $1650\text{--}1600 \text{ cm}^{-1}$ (C=C conjugated), $1400\text{--}1350 \text{ cm}^{-1}$ (C=N) and $1350\text{--}1280 \text{ cm}^{-1}$ (aryl sec. -NH-). $^1\text{H-NMR}$ spectra of S_1 and S_2 salts were in good agreement with the proposed structure (Scheme 1). In the $^1\text{H-NMR}$ spectra of stenhouse salts, the signal due to 1H of secondary -NH- stenhouse salts appeared at δ value of a 9–10 ppm was resulted from the reaction of aniline and furfural, and showed the

absence of corresponding 2H signal of primary -NH₂ of aniline. Analogously, signals of 3H of furfural ring at 7.51, 6.67 and 6.49 δ ppm (Abeysekera et al., 2008; AL-Showiman et al., 1987) were also absent in the spectra of S_1 and S_2 indicating the ring opening reaction of furfural.

3.2. Synthesis and characterization of disazo disperse dyes S_1D_{1-10} and S_2D_{1-10}

Ten diazonium salts of aryl amines were used in the coupling reaction respectively with S_1 and S_2 yielded two series of disazo dispersed dyes S_1D_{1-10} and S_2D_{1-10} . Usually, disazo dyes were synthesized by multi step procedure using mono functional coupling component (Karci and Karci, 2008a; Karci and Karci, 2008b) but we report here the synthesis of dyes in two steps (Schemes 2 and 3). The first step was the diazotization of aromatic amine using HCl and sodium nitrite to yield diazonium salt which was immediately coupled with stenhouse salt (2:1 M ratio) to form disazo dye. Most of these dyes were obtained in good yields (70–85%) and characterized for number of azo groups, elemental analysis (Table 1) and spectral studies with a view to confirm their structure. The estimated value of number of azo groups was ~ 2 and analytical data of C, H and N content were in good agreement with the proposed structure shown in Schemes 2 and 3. The IR spectra of the dyes showed the characteristic absorption band of azo group -N = N- (1610 cm^{-1}) and that of corresponding substituent such as -CH₃ (3048 & 1469 cm^{-1}), -OCH₃ (1226 cm^{-1}), -Cl (749 cm^{-1}), -NO₂ (1333 cm^{-1}) etc. in aryl amino diazonium component. $^1\text{H-NMR}$ spectrum of the disazo disperse dyes shows two singlet in the range of 5.51–6.77 δ ppm and 9.86 δ ppm corresponding to two aliphatic and -NH- protons, a multiplet in the region of 7.0–7.5 δ ppm due to aromatic protons and a singlet at 14.43 δ ppm of O-H proton.

Table 1 Dye designation and physicochemical properties^a.

Sr. No.	Molecular formula	Substitution			% Yield	Elemental analysis: calc. (found)		
		R ₁	R ₂	R ₃		% C	% H	% N
S_1D_1	C ₂₉ H ₂₅ N ₆ O	H	H	H	78	73.55 (73.41)	5.32 (5.13)	17.75 (17.56)
S_1D_2	C ₃₁ H ₂₉ N ₆ O	H	H	CH ₃	75	74.23 (74.01)	5.83 (5.96)	16.75 (16.57)
S_1D_3	C ₂₉ H ₂₃ Cl ₂ N ₆ O	H	H	Cl	79	64.21 (64.42)	4.27 (4.12)	15.49 (15.33)
S_1D_4	C ₂₉ H ₂₃ N ₈ O ₅	H	H	NO ₂	75	61.81 (61.93)	4.11 (4.23)	19.88 (19.70)
S_1D_5	C ₃₇ H ₂₉ N ₆ O	Fused Phenyl		H	80	77.47 (77.14)	5.10 (5.01)	14.65 (14.56)
S_1D_6	C ₃₃ H ₂₉ N ₆ O ₅	H	H	COOCH ₃	73	67.22 (67.01)	4.96 (5.05)	14.25 (14.49)
S_1D_7	C ₃₁ H ₂₉ N ₆ O ₃	H	H	OCH ₃	78	69.78 (69.61)	5.48 (5.56)	15.75 (15.58)
S_1D_8	C ₂₉ H ₂₁ Cl ₄ N ₆ O	Cl	H	Cl	75	56.98 (56.54)	3.46 (3.40)	13.75 (13.64)
S_1D_9	C ₃₃ H ₃₅ N ₈ O	H	H	N(CH ₃) ₂	82	70.82 (71.14)	6.30 (6.19)	20.02 (19.88)
S_1D_{10}	C ₃₃ H ₃₃ N ₆ O	H	CH ₃	CH ₃	73	74.83 (74.55)	6.28 (6.41)	15.87 (15.79)
S_2D_1	C ₂₉ H ₂₅ N ₆ O ₃	H	H	H	69	68.90 (69.47)	4.98 (4.87)	16.62 (16.51)
S_2D_2	C ₃₁ H ₂₉ N ₆ O ₃	H	H	CH ₃	80	69.78 (70.11)	5.48 (5.37)	15.75 (15.60)
S_2D_3	C ₂₉ H ₂₃ Cl ₂ N ₆ O ₃	H	H	Cl	84	60.64 (61.02)	4.04 (4.15)	14.63 (14.76)
S_2D_4	C ₂₉ H ₂₃ N ₈ O ₇	H	H	NO ₂	77	58.49 (57.97)	3.89 (3.76)	18.82 (18.95)
S_2D_5	C ₃₇ H ₂₉ N ₆ O ₃	Fused Phenyl		H	73	73.37 (72.88)	4.83 (4.95)	13.88 (13.76)
S_2D_6	C ₃₃ H ₂₉ N ₆ O ₇	H	H	COOCH ₃	82	63.76 (64.13)	4.70 (4.84)	13.52 (13.69)
S_2D_7	C ₃₁ H ₂₉ N ₆ O ₅	H	H	OCH ₃	85	65.83 (66.28)	5.17 (5.26)	14.86 (14.72)
S_2D_8	C ₂₉ H ₂₁ Cl ₄ N ₆ O ₃	Cl	H	Cl	78	54.14 (53.72)	3.29 (3.36)	13.06 (13.24)
S_2D_9	C ₃₃ H ₃₅ N ₈ O ₃	H	H	N(CH ₃) ₂	74	66.99 (66.50)	5.96 (6.12)	18.94 (18.72)
S_2D_{10}	C ₃₃ H ₃₃ N ₆ O ₃	H	CH ₃	CH ₃	76	70.57 (70.12)	5.92 (5.84)	14.96 (15.09)

^a Melting point of all dyes: decomposed above 250°C .

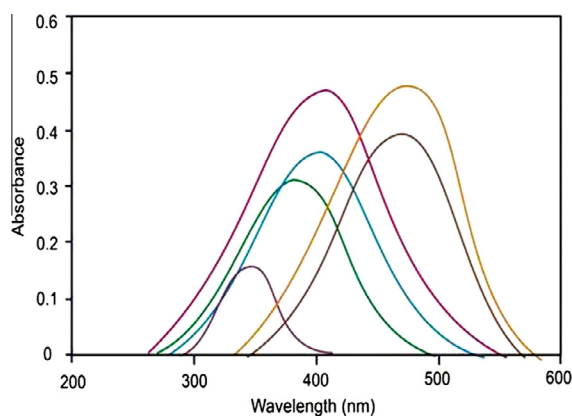


Figure 1 UV-visible absorption spectra for selected dyes of S_1 -series dyes.

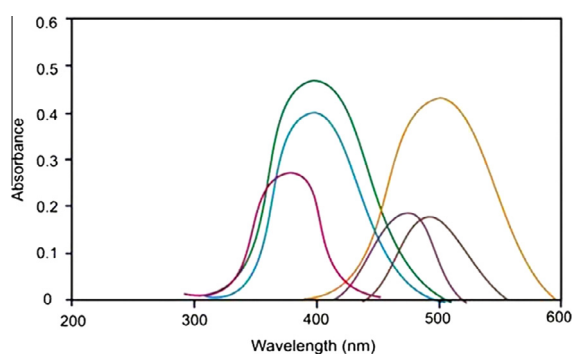


Figure 2 UV-visible absorption spectra for selected dyes of S_2 -series dyes.

The electronic spectra of the disazo disperse dyes were recorded in DMF and selected scans are given in Figs. 1 and

2. The data reported in Table 2 show the value of extinction coefficient (ϵ) 10^4 for all of the dyes indicating the high color strength. Further, it is observed that all the dyes have λ_{\max} value in the region of 350–530 nm. The variation of λ_{\max} and high absorbance value of the dyes can be correlated in terms of substituent effect (Ghoneim et al., 2008) of the group present in disazo dyes by comparing with the spectra of dye derived from anilines. Bathochromic shift was observed in the disperse azo dyes consisting of $-\text{OCH}_3$, $-\text{Cl}$, $-\text{CH}_3$ and $-\text{N}(\text{CH}_3)_2$ group at the *p*-position to the azo group of dyes of series S_1 and S_2 . This is as expected due to the auxochromic effect of corresponding auxochromes in the dye. Analogously, the bathochromic effect observed in dyes derived from α -naphthylamine is explicable on the basis of higher aromaticity of naphthalene moiety. Finally, the conjugated system with three double bonds may have contributed to hyperchromic effect in disperse azo dyes. Dyeing behavior of these disperse azo dyes envisages the percentage dye-bath exhaustion in the range of 60–90%. Whereas percentage fixation of the dye on fabrics was in the range of 70–90% calculated on the basis of the dye exhausted and data showed in Table 2. The dyed fabrics exhibit very good to excellent washing fastness properties and with a little variation in the good to excellent light-fastness. The nature of the substituent in the diazonium components has a little influence on the visible absorption. The data in Table 3 gives a color gamut range from light yellow to orange to reddish brown by visual observations of the dyed patterns mounted in the shade.

4. Conclusion

A series of twenty disazo disperse dyes (S_1D_{1-10} and S_2D_{1-10}) were synthesized by using stenhouse salts as new coupling component. All of them were investigated for their dyeing behavior on polyester and nylon fabrics. Dyeing with disperse dyes gave bright hues from light yellow to orange to reddish

Table 2 Absorption maxima (λ_{\max}), intensity, exhaustion and fixation of disazo disperse dyes.

Dye designation	λ_{\max} (nm)	$\log \epsilon$	Polyester fabrics		Nylon fabrics	
			% E	% F	% E	% F
S_1D_1	352	0.180	71	86	78	77
S_1D_2	384	0.311	70	82	75	78
S_1D_3	406	0.370	70	84	79	76
S_1D_4	412	0.400	73	88	82	79
S_1D_5	476	0.486	69	82	75	75
S_1D_6	482	0.500	72	87	76	70
S_1D_7	490	0.446	71	85	78	71
S_1D_8	492	0.432	65	83	74	72
S_1D_9	501	0.400	68	87	75	72
S_1D_{10}	508	0.364	65	89	78	76
S_2D_1	381	0.275	73	88	78	76
S_2D_2	400	0.400	71	84	76	80
S_2D_3	409	0.482	72	84	80	78
S_2D_4	473	0.425	75	89	84	80
S_2D_5	484	0.188	70	85	75	76
S_2D_6	508	0.175	76	89	78	72
S_2D_7	510	0.280	74	88	79	76
S_2D_8	492	0.310	68	85	75	77
S_2D_9	488	0.440	70	89	77	73
S_2D_{10}	496	0.260	67	90	78	79

Table 3 Fastness properties of disazo disperse dyes.

Dye designation	Polyester fabrics			Nylon fabrics		
	Color shade	Light fastness ^a	Washing fastness ^b	Color shade	Light fastness ^a	Washing fastness ^b
S ₁ D ₁	Creamish yellow	4	3	Light brown	3	5
S ₁ D ₂	Light yellow	5	4	Light brown	3	4
S ₁ D ₃	Light orange	5	4	Dark brown	4	4
S ₁ D ₄	Wooden	4	2	Wooden	3	4
S ₁ D ₅	Reddish brown	4	3	Reddish brown	4	4
S ₁ D ₆	Light brown	5	4	Light brown	4	5
S ₁ D ₇	Dark brown	5	3	Dark brown	3	4
S ₁ D ₈	Brown	4	4	Brown	4	5
S ₁ D ₉	Light brown	5	3	Light brown	4	5
S ₁ D ₁₀	Brown	4	3	Brown	3	4
S ₂ D ₁	Yellow	4	3	Light brown	3	5
S ₂ D ₂	Yellow	4	4	Light brown	3	4
S ₂ D ₃	Orange	5	4	Dark brown	4	5
S ₂ D ₄	Wooden	4	3	Wooden	3	4
S ₂ D ₅	Reddish brown	4	4	Reddish brown	3	4
S ₂ D ₆	Light brown	4	4	Light brown	4	5
S ₂ D ₇	Dark brown	5	3	Dark brown	3	4
S ₂ D ₈	Brown	4	4	Brown	4	5
S ₂ D ₉	Light brown	5	3	Light brown	4	5
S ₂ D ₁₀	Brown	4	3	Brown	3	4

Grading:

^a 8 – maximum, 7 – excellent, 6 – very good, 5 – good, 4 – fairly good, 3 – moderate, 2 – poor, 1 – very poor.^b 5 – excellent, 4 – very good, 3 – good, 2 – fair, 1 – poor.

brown on polyester and nylon fabrics. The dyed fabrics exhibit very good to excellent washing fastness properties and with a little variation in the good to excellent light fastness. The nature of the substituent in the diazonium components has a little influence on the visible absorption. The striking feature of the dyeing behavior of disazo disperse dyes envisages good dye-bath exhaustion and fixation with major amount of dye exhausted from dye-bath in case of polyester with compare to nylon. In general, all the dyes have shown good to moderate fastness properties, however S₂D_{1–10} disazo dyes have shown very good fastness properties than S₁D_{1–10}. The fastness properties of all the dyes on polyester fabric are much more higher than on nylon fabric, especially light fastness was good on polyester fabrics while wash-fastness was batter on nylon fabrics.

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