



CHEMISTRY & BIOLOGY INTERFACE

An official Journal of ISCB, Journal homepage; www.cbijournal.com

Synthesis, characterization, dyeing performance and fastness properties of 2-amino 4-phenyl thiazole based bisazo disperse dyes having different tertiary amine as a coupling component

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Received 29 February 2016; Accepted 1 April 2016

Abstract: 2-amino-4-(4'-chlorophenyl) 1, 3-thiazole was coupled with diazotized p-toluidine which yielded mono azo dye. This monoazo dye was further diazotized and coupled with various substituted 3°-amines to give corresponding bisazo dyes (D₁-D₁₀). The synthesized dyes were characterized by elemental analysis, UV, IR and ¹H NMR spectra. These bis azo dyes were applied on polyester fabric and their dyeing performance as well as fastness properties were evaluated.

Keywords: 2-amino 4-(4'-chlorophenyl) 1, 3-thiazole, p-toluidine, nitrosyl sulfuric acid, 3°amine, dyeing performance, fastness properties

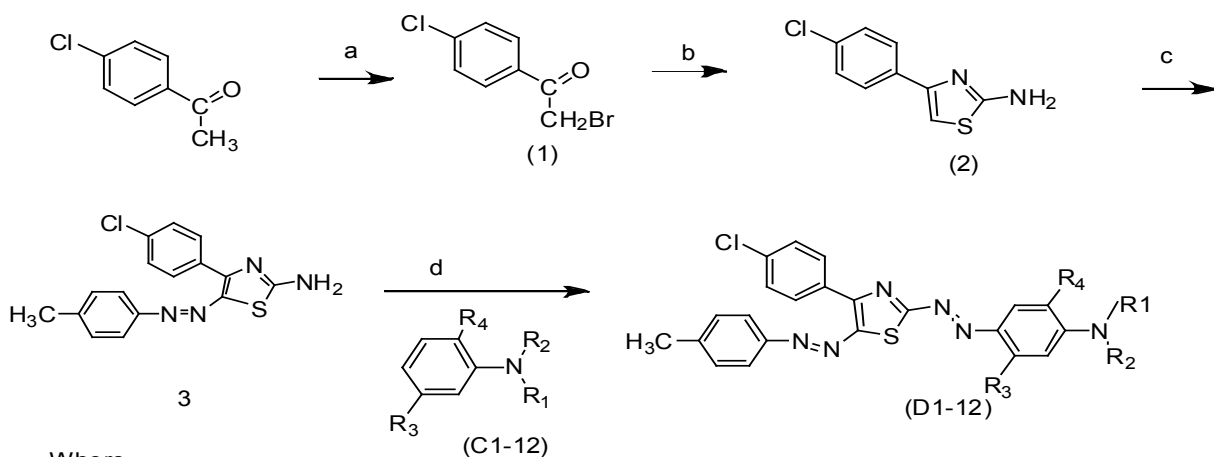
Introduction

The disperse dyes are insoluble in water and applied on fabric as colloidal solution of dyes. Disperse dyes are used for nylon, polyester etc. fibers. Phenyl thiazole and its different substituents are used in dyestuff having good properties of fastness. We synthesized 2-amino 4-(4'-chlorophenyl) 1, 3-thiazole by condensation of 2-bromo 1-(4-chlorophenyl) ethanone and thiourea. The main purpose of our work was to synthesize bis azo dyes having thiazole with two azo substituent. At first mono azo dyes were synthesized using 2-amino 4-(4'-chlorophenyl) 1, 3-thiazole as

coupling component and diazotized p-toluidine. The synthesized monoazo dyes were further diazotized by nitrosyl sulfuric acid and coupled with different substituted 3°amine. They exhibited moderate to good light and washing fastness. The fastness of sublimation gave average to good and rubbing fastness very good to excellent results on polyester fabrics.

Materials and Methods

All the chemicals and solvents used were of AR grade and were used without any further purification. Purity of compounds was checked by silica gel-G coated TLC plates and spots were



Where,
 a= Bromine, Acetic acid,
 b= Thiourea, Methanol,
 c= p-Toluidine, Sodium nitrite, Water, Conc. Sulfuric acid,
 d = Sodium nitrite, Conc. Sulfuric acid.
 (C1-12)= different substituted tertiary amine.

visualized under UV radiation. Melting points were taken in open capillary using Stuart SMP 10 melting point apparatus and are uncorrected IR spectra were recorded on Perkin – Elmer 1600 FTIR in KBr pellet. ^1H NMR spectra were taken on a Bruker avance II 400 MHz in $\text{DMSO}-d_6$ and CDCl_3 as solvent and TMS as internal standard. The dyeing of the polyester fabric samples was carried out by HTHP dyeing method and fastness properties were evaluated.

Experimental work

Synthesis of 2-bromo 1-(4-chlorophenyl) ethanone. (1)

In 250 ml RBF mixture of p-chloroacetophenone (2.10 gm, 0.01 mole) and acetic acid (2 mL) was taken, then bromine and acetic acid mixture (1:1) 5 mL was added drop wise with continuous stirring at 10°C . When addition was completed the reaction mixture was further stirred at room temperature for 3 hours. The reaction mixture was poured in to ice cold water (200mL). Solid thus separated was filtered, dried and recrystallized from methanol. M. P. 79°C . Yield 93%; Anal. Calcd for: $\text{C}_8\text{H}_8\text{BrClO}$ (231.93); Calculated (C, 41.15; H, 2.59; Br, 34.22; Cl,

15.18; O, 6.85%).

Synthesis of 2-amino-4-(4-chlorophenyl) 1, 3-thiazole. (2)

Mixture of 2-bromo 1-(4-chlorophenyl) ethanone (1) (2.39gm, 0.01 mole) in 5 mL methanol and thiourea (9.75gm, 0.125 mole) was refluxed in water bath for 8 hours, completion of reaction was checked by TLC. The excess of solvent was distilled off to obtain solid product. It was recrystallized from ethanol and dried to give the compound (2). M. P. 154°C . Yield 93%; Anal. Calcd for: $\text{C}_9\text{H}_7\text{ClN}_2\text{S}$ (210.68) Calculated (C, 51.31; H, 3.35; Cl, 16.83; N, 13.36; S, 15.22 %); found (C, 48.58; H, 4.42; N, 25.19; %). MS (EI) m/z : 222.26 (M^+), 223.8 ($\text{M}+1$). IR (KBr, cm^{-1}): $\nu = 3459\text{--}3464$ ($-\text{NH}_2$), 3268 (N-H str.), 2998 (C-H str.), 1498 (C-S-C), 723 (C-Cl); ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 7.34 (s, CH of thiazole), 7.50 (2H, Ar), 7.78 (2H, Ar), 9.01 (2H, NH_2).

Synthesis of 4-(4-Chlorophenyl)-5-(p-tolyl)thiazole(3).

p-toluidine (1.37 gm, 0.01 mole) was dissolved in 5 mL concentrated HCl and cooled to

0-5°C. A previously cooled solution of sodium nitrite (0.69g, 0.01mol) in distilled water (4mL) was added keeping temperature at 0-5 °C. Stirring was continued for an hour, with positive test for nitrous acid on starch iodide paper, excess of nitrous acid was removed by adding required amount of sulfamic acid and was used for coupling reaction. 2-amino-4-(4-chlorophenyl)1,3-thiazole(**2**) taken in mixture of acetic acid(1mL)-sulfuric acid(2mL) and cooled below 0-5°C. To this well stirred solution diazotized salt of p-toluidine was added drop wise. Maintaining the pH 5.5 to 6.0 by adding solution of sodium acetate (20% w/v). It was further stirred for 3 hours at 0-5°C. Solid product thus obtained was filtered, washed with cold water and dried. M. P.178-184°C. Yield 83%. Anal. Calcd for: C₁₆H₁₃ClN₄S (328.82) Calculated:(C, 51.31; H, 3.35; Cl, 16.83; N, 13.36; S,15.22 %); found (C, 48.58; H, 4.42; N, 25.19; %). MS (EI) *m/z*: 222.26 (M⁺), 223.8 (M+1).IR (KBr, cm⁻¹): ν= 3462-3469 (-NH₂), 3268(N-H str.), 2998 (C-H str.), 1498 (C-S-C), 723 (C-Cl)

Synthesis of 4-((E)-4-chlorophenyl)-5-((E)-p-tolyldiazenyl)thiazol-2-yl)-N,N-dimethylaniline (**5a**).

The solution of compound (**3**) (0.01mol) in sulfuric acid (3mL) was cooled below 5 °C in ice-bath. A solution of sodium nitrite (0.01mol, 0.69g) in concentrated sulfuric acid (2mL) heated up to 60 °C till all solid dissolved and then rapidly cooled at 0-5 °C. Previously cooled solution of compound (**3**) was added in to sodium nitrite solution at 0-5 °C with continuous stirring and continued for an hour, with positive test for nitrous acid on starch iodide paper, excess of nitrous acid was removed by adding required amount of sulfamic acid and was used for coupling reaction. N, N-dimethyl aniline (0.01mol) dissolved in solution of acetic acid and cooled below 5 °C in an ice-bath. To this well stirred solution, above mentioned diazonium salt solution was drop

wise added over a period of 1 hour. Maintaining the pH 5.5 to 6.0 by simultaneous addition of aqueous sodium acetate (20% w/v). The stirring was continued for 3 hours at 0-5 °C to yield (**5a**). The termuric yellow coloured dye was filtered off, dried at 60-70 °C and recrystallized from acetone. M.P.178-184°C. Yield 84%; Anal. Calcd for: C₂₄H₂₁ClN₆S(460.98); Calculation (C, 62.53; H, 4.59; Cl, 7.69; N,18.23 ;S, 6.96 %); found (C, 62.58; H, 4.42; N, 18.19;S, 6.99 %). MS (EI) *m/z*: 460.12 (M⁺), 461.13 (M+1).IR (KBr, cm⁻¹): ν= 3056-3061 (C-H), 1514 (N=N), 1477 (C-S-C), 815 (C-H str. of aromatic ring), 723(C-Cl). ¹H NMR (400 MHz, DMSO-*d*₆) δ: 1.13 (s, 6H,-CH₃), 2.25 (s,3H,-CH₃),6.63-6.73(4H,Ar), 7.50-7.56(4H,Ar), 7.78-7.82(4H,Ar).

4-((E)-4-chlorophenyl)-5-((E)-p-tolyldiazenyl)thiazol-2-yl)-N,N-diethylaniline (**5b**).

The Brown coloured dye was filtered off, dried at 60-70 °C and recrystallized from acetone. M.P. 195-197 °C. Yield 89%. Anal. Calcd for: C₂₆H₂₅ClN₆S (489.03) Calculated (C, 63.86; H, 5.15; Cl, 7.25; N,17.18 ;S,6.56 %); found (C, 63.80; H, 5.12;Cl, 7.22 N, 7.25;S,6.59; %). MS (EI) *m/z*: 488.12 (M⁺), 490.13 (M+1).IR (KBr, cm⁻¹): ν= 3064-3067 (C-H), 1517 (N=N), 1492 (C-S-C), 812 (C-H str. of aromatic ring), 721(C-Cl). ¹H NMR (400 MHz, DMSO-*d*₆) δ: 1.14 (s, 6H,-CH₃), 2.27 (s,3H,-CH₃), 3.52 (qt, 4H,-CH₂), 6.57- 6.69 (4H, Ar.), 7.52-7.59(4H, Ar), 7.74-7.77(4H, Ar)

N-(2-((E)-4-chlorophenyl)-((E)-p-tolyldiazenyl)thiazol-2-yl)diazonyl)-5-(diethylamino) phenyl) acetamide(**5c**).

The marron coloured dye was filtered off, dried at 60-70 °C and recrystallized from acetone. M.P. 110-115°C. Yield 84%; Anal. Calcd for: C₂₈H₂₈ClN₇OS (546.18) Calculated (C, 61.86; H, 5.17; Cl, 6.49; N,17.95 ;O, 2.93; S,5.87 %); found (C, 61.88; H, 5.17; Cl, 6.33; N, 17.99;O,2.97; S, 6.51%). MS (EI) *m/z*: 488.12

(M⁺), 490.13 (M+1). IR (KBr, cm⁻¹): 3061-3067 (C-H), 2830-2832 (OCH₃), 1645-1649(C=O), 1518 (N=N), 1486(C-S-C), 816 (C-H str. of aromatic ring), 723(C-Cl). ¹H NMR (400 MHz, DMSO-*d*₆) δ: 1.11-1.14 (s, 6H, -CH₃), 1.32-1.35(s, 3H, -CO CH₃), 2.29 (s, 3H, -CH₃), 2.80 (1H, -NH) 3.54 (qt, 4H, -CH₂), 6.59 (4H, Ar.), 7.58(4H, Ar), 7.82(3H, Ar).

N-(2-((E)-4-chlorophenyl)-((E)-p-tolydiazenyl)-thiazol-2-yl)-diazenyl)-5-((2-cynoethyl)2-hydroxyethyl)amino)phenyl)acetamide(5d).

The reddish brown coloured dye was filtered off, dried at 60-70 °C and recrystallized from acetone. M.P. 178-184°C. Yield 84%; Anal. Calcd for: C₂₉H₂₇ClN₈O₂S(587.10) Calculated (C, 59.33; H, 4.64; Cl, 6.04; N, 19.68 ;O, 5.46; S, 5.46 %); found (C, 59.38; H, 4.63; N, 19.71; O, 5.47; S, 5.42 %). MS (EI) *m/z*: 488.12 (M⁺), 490.13 (M+1). IR (KBr, cm⁻¹): ν=3628-3634 (OH), 3340 (N-H), 3056-3664(C-H), 2232(CN), 1645(C=O), 1511 (N=N), 1491 (C-S-C), 816 (C-H str. of aromatic ring), 729(C-Cl). ¹H NMR (400 MHz, DMSO-*d*₆) δ: 1.26-1.32(s, 3H, -CO CH₃), 2.24 (s, 3H, -CH₃), 3.63 (t, 4H, -CH₂), 4.36-4.37 (t, 2H, -CH₂), 4.56-4.61(t, 2H, -CH₂), 5.69(1H, -OH) 6.63-6.64 (4H, Ar.), 7.49-7.54(4H, Ar), 7.77(3H, Ar) , 9.42 (1H, -NH).

N-(2-((E)-4-chlorophenyl)-((E)-p-tolydiazenyl)thiazol-2-yl)diazenyl)-5-(diethylamino)-4-methoxyphenyl)acetamide(5e).

The dark brown coloured dye was filtered off, dried at 60-70 °C and recrystallized from acetone. M.P. 178-184°C. Yield 84%; Anal. Calcd for: C₃₀H₂₉ClN₈O₃S(617.12) Calculated (C, 58.39; H, 4.74; Cl, 5.74; N, 18.16; O, 7.78 ;S, 5.20 %); found (C, 58.47; H, 4.72; Cl, 5.73; N, 18.19; O, 7.76; S, 5.16%). MS (EI) *m/z*: 488.12 (M⁺), 490.13 (M+1). IR (KBr, cm⁻¹): 3062-3667 (C-H), 2827 (OCH₃), 1641(C=O), 1517 (N=N), 1501 (C-S-C), 810 (C-H str. of

aromatic ring), 724(C-Cl). ¹H NMR (400 MHz, DMSO-*d*₆) δ: 1.13-1.16 (s, 6H, -CH₃), 1.79-1.82(s, 3H, -CH₃), 3.25 (s, 3H, O-CH₃), 3.51 (qt, 4H, -CH₂), 6.60-6.63 (4H, Ar.), 6.80 (1H, -NH), 7.54-7.57(4H, Ar), 7.74-7.82(3H, Ar).

2,2'-((3-chloro-4-((E)-(4-(4-chlorophenyl)-5-((E)-p-tolydiazenylthiazol-2yl)diazenyl)phenyl) azanediyl)diethanol(5f).

The tomato red coloured dye was filtered off, dried at 60-70 °C and recrystallized from acetone. M.P. 178-184°C. Yield 84%; Anal. Calcd for: C₂₆H₂₄Cl₂N₆O₂S (555.48) Calculated (C, 56.22; H, 4.55; Cl, 12.76; N, 15.13; O, 5.76 ; S, 5.77 %); found (C, 56.28; H, 4.62; Cl, 12.71; N, 15.38; O, 5.73; S, 5.69%). MS (EI) *m/z*: 488.12 (M⁺), 490.13 (M+1). IR (KBr, cm⁻¹): 3636 (OH), 3339 (N-H), 3061 (C-H), 1515 (N=N), 1489(C-S-C), 818(C-H str. of aromatic ring), 722(C-Cl). ¹H NMR (400 MHz, DMSO-*d*₆) δ: 2.25 (s, 3H, -CH₃), 3.57 (qt, 4H, -CH₂), 3.91 (qt, 4H, -CH₂), 5.86-5.88(2H, -OH), 6.64-6.70 (4H, Ar.), 7.59-7.63(4H, Ar), 7.98-8.01(3H, Ar).

3-3'-((4((E)-(4-(4-chlorophenyl)-5-((E)-p-tolydiazenyl)thiazole-2yl)diazenyl)phenyl) azanediyl)dirpropanenitrile(5g).

The dark red coloured dye was filtered off, dried at 60-70 °C and recrystallized from acetone. M.P. 178-184°C. Yield 84%; Anal. Calcd for: C₂₈H₂₃ClN₈S(539.05) Calculated (C, 62.34; H, 4.30; Cl, 6.56; N, 20.79 ;S, 5.95 %); found (C, 62.39; H, 4.29; N, 20.79; S, 5.92 %). IR (KBr, cm⁻¹): 3056 -3062(C-H), 2232(CN), 1507 (N=N), 1487 (C-S-C), 809 (C-H str. of aromatic ring), 726(C-Cl). ¹H NMR (400 MHz, DMSO-*d*₆) δ: 2.31(s, 3H, -CH₃), 4.54- 4.72 (m, 8H, -CH₂), 6.63 (4H, Ar.), 7.59(4H, Ar), 7.84(4H, Ar)

((4-((E)-(4-(4-chlorophenyl)-5-((E)-p-tolyldiazenyl)thiazol-2yl)diazenyl)phenyl) azanediyl)bis (ethane-2,1-diyl)diacetate(5h).

The marron coloured dye was filtered off, dried at 60-70 °C and recrystallized from

acetone. M.P. 178-184°C. Yield 84%; Anal. Calcd for: $C_{30}H_{29}ClN_6O_4S$ (605.11) Calculated (C, 59.55; H, 4.83; Cl, 5.86; N, 13.89; O, 10.58; S, 5.30 %); found (C, 59.58; H, 4.82; Cl, 5.84; N, 13.93; O, 10.56; S, 5.27 %). MS (EI) m/z : 488.12 (M^+), 490.13 ($M+1$). IR (KBr, cm^{-1}): $\nu=3637$ (OH), 3343 (N-H), 3052-3054 (C-H), 1511 (N=N), 1494 (C-S-C), 813 (C-H str. of aromatic ring), 724(C-Cl). ^1H NMR (400 MHz, DMSO- d_6) δ : 2.08-2.14 (s, 6H, -OCOCH₃), 2.26 (s, 3H, -CH₃), 2.47 (s, 3H, -CH₃), 3.45 (qt, 4H, -CH₂), 3.93 (qt, 2H, -CH₂), 6.60 (4H, Ar), 7.54 (4H, Ar), 7.79 (3H, Ar)

3-((4-((E)-(4-(4-chlorophenyl)-5-((E)-p-tolyldiazenyl)diazenyl)phenyl)ethanimino)propanenitrile(5i).

The maroon coloured dye was filtered off, dried at 60-70 °C and recrystallized from acetone. M.P. 178-184°C. Yield 84%; Anal. Calcd for: $C_{27}H_{24}ClN_7S$ (514.04) Calculated (C, 63.09; H, 9.71; Cl, 6.90; N, 19.07; S, 6.24 %); found (C, 63.12; H, 9.77; Cl, 6.82; N, 19.08; S, 6.20 %). MS (EI) m/z : 488.12 (M^+), 490.13 ($M+1$). IR (KBr, cm^{-1}): $\nu=3061$ -3065 (C-H), 2237(CN), 1518 (N=N), 1498 (C-S-C), 815 (C-H str. of aromatic ring), 723(C-Cl). ^1H NMR (400 MHz, DMSO- d_6) δ : 1.29-1.34 (s, 3H, CH₂-CH₃), 2.25 (s, 3H, -CH₃), 3.34- 3.57 (m, 6H, -CH₂), 6.63 (4H, Ar), 7.50 (4H, Ar), 7.78 (4H, Ar)

((3-acetamido-4-((E)-(4-(4-chlorophenyl)-5-((E)-p-tolyldiazenyl)thiazole-2-yl) diazenyl)phenyl)azanenyl)bis(ethane-2,1-diyl) diacetate(5j).

The maroon coloured dye was filtered off, dried at 60-70 °C and recrystallized from acetone. M.P. 178-184°C. Yield 84%; Anal. Calcd for: $C_{32}H_{32}ClN_7O_5S$ (662.18) Calculated (C, 58.04; H, 4.87; Cl, 5.35; N, 14.81; O, 12.08; S, 6.24 %); found (C, 58.01; H, 4.89; Cl, 5.31; N, 15.19; O, 12.12; S, 6.21 %). MS (EI) m/z : 488.12 (M^+), 490.13 ($M+1$). IR (KBr, cm^{-1}): $\nu=3340$ (N-H), 3067 (C-H), 1649-1657 (C=O), 1519-1524 (N=N), 1492 (C-S-C), 811 (C-H str. of

aromatic ring), 723(C-Cl). ^1H NMR (400 MHz, DMSO- d_6) δ : 1.32 (s, 3H, NHCO-CH₃), 2.08-2.14 (s, 6H, -OCOCH₃), 2.25 (s, 3H, -CH₃), 3.5 (qt, 4H, -CH₂), 3.97 (qt, 4H, -CH₂), 4.47 (1H, -NH), 6.63 (4H, Ar), 7.50 (4H, Ar), 7.68 (3H, Ar).

((3-chloro-4-((E)-(4-(4-chlorophenyl)-5-((E)-p-tolyldiazenyl)thiazole-2-yl)diazenyl)phenyl)azanenyl)bis(ethane-2,1-diyl)diacetate(5k).

The maroon coloured dye was filtered off, dried at 60-70 °C and recrystallized from acetone. M.P. 178-184°C. Yield 84%; Anal. Calcd for: $C_{30}H_{28}Cl_2N_6O_4S$ (639.55) Calculated (C, 56.34; H, 4.41; Cl, 11.09; N, 13.14; O, 10.01; S, 5.01 %); found (C, 56.38; H, 4.39; Cl, 11.14; N, 13.19; O, 10.06; S, 4.96 %). MS (EI) m/z : 488.12 (M^+), 490.13 ($M+1$). IR (KBr, cm^{-1}): $\nu=3348$ (N-H), 3059-3063 (C-H), 1645 (C=O), 1510-1517 (N=N), 1467 (C-S-C), 819 (C-H str. of aromatic ring), 723(C-Cl). ^1H NMR (400 MHz, DMSO- d_6) δ : 2.08-2.14 (s, 6H, -OCOCH₃), 2.25 (s, 3H, -CH₃), 3.51-3.58 (qt, 4H, -CH₂), 3.85-3.92 (qt, 4H, -CH₂), 6.63-6.68 (4H, Ar), 7.4-7.49 (4H, Ar), 7.78-7.83 (3H, Ar).

N-(5-(bis(2-hydroxyethylamino)-2-((E)-(4-(4-chlorophenyl)-5-((E)-p-tolyldiazenyl)thiazole-2-yl)diazenyl)phenyl)acetamido(5l).

The tomato red coloured dye was filtered off, dried at 60-70 °C and recrystallized from acetone. M.P. 178-184°C. Yield 84%; Anal. Calcd for: $C_{26}H_{24}Cl_2N_6O_2S$ (555.48) Calculated (C, 56.22; H, 4.55; Cl, 12.76; N, 15.13; O, 5.76; S, 5.77 %); found (C, 56.28; H, 4.62; Cl, 12.71; N, 15.38; O, 5.73; S, 5.69%). MS (EI) m/z : 488.12 (M^+), 490.13 ($M+1$). IR (KBr, cm^{-1}): 3630 (OH), 3345 (N-H), 3051-3058 (C-H), 1514 (N=N), 1498 (C-S-C), 817 (C-H str. of aromatic ring), 723(C-Cl). ^1H NMR (400 MHz, DMSO- d_6) δ : 1.29-1.34 (s, 3H, NHCO-CH₃), 2.25 (s, 3H, -CH₃), 3.5 (qt, 4H, -CH₂), 3.90 (qt, 4H, -CH₂), 3.97 (1H, -NH), 5.86 (2H, -OH), 6.63 (4H, Ar), 7.50 (4H, Ar), 7.78 (3H, Ar).

Dyeing procedure

Table-1: Shade, Fastness properties of the dyes

Dyes No.	Shade on Polyester	Fastness to		Sublimation on polyester		Perspiration		Rubbing	
		Light	Washing	Staining at 180° C	Staining at 210° C	Acid	Basic	Dry	Wet
3 (monoazo)	yellow	3	4-5	2	1	4	4	4-5	4
D₁	Turmeric Yellow	4	4-5	2	1	4-5	4-5	4-5	4
D₂	Brown	4	4-5	2	1	4-5	4-5	4-5	4
D₃	Dark Brown	3-4	4-5	2	1	4	4	4-5	4
D₄	Red	3-4	4-5	2-3	1-2	4	4	4-5	4
D₅	Dark orange	4	4-5	3	1-2	4-5	4-5	4-5	4
D₆	Dark maroon	4-5	4-5	3	2	4-5	4-5	4-5	4
D₇	Dark Brown	3-4	4-5	2-3	2	4-5	4-5	4-5	4
D₈	Reddish brown	3-4	4-5	3	1-2	4-5	4-5	4-5	4
D₉	Green	4	4-5	3-4	2-3	4-5	4-5	4-5	4
D₁₀	Khakhi	4	4-5	3-4	2-3	4	4	4-5	4
D₁₁	maroon	4	4-5	3-4	2-3	4-5	4	4-5	4
D₁₂	Dark marron	4	4-5	3-4	2-3	4-5	4	4-5	4

Light fastness: 1- poor, 2- slight, 3- moderate, 4- fair, 5- good, 6- very good, 7-excellent.

Sublimation, rubbing and wash: 1-poor, 2-fair, 3-good, 4-very good, 5-excellent.

All the synthesized dyes D₁-D₁₂ were applied on polyester fabric in 2% depth by HTHP method. High temperature (130 °C) and high pressure is a convenient method for dyeing polyester fabric in the laboratory. Glycerin-bath high temperature beaker dyeing machine was used. 10 ml DMF was added and dispersion of the dye was produced by dissolving the appropriate amount of dye (2% depth) and then added dropwise with continuous stirring to the dyebath (liquor ratio 20:1) containing 1% Setamol WS (BASF) as anionic dispersing agent. The pH of dye solution was adjusted to 4 to 5 using aqueous acetic acid. Already wetted-out polyester fabric pieces were added. Dyeing was kept continue by raising the dyebath temperature upto 130

°C at a rate of 2 °C per minute, maintaining this temperature for 1 hour, under (24-30 psi) pressure. After completion of process cooling upto 50 °C was done, the dyed fabric pieces were rinsed with cold water and reduction was cleared properly (1 g/L sodium hydroxide, 1 g/L sodium hydrosulphite, 10 minutes and 80 °C). The dyed sample was rinsed with hot water first and then with cold water and finally dried in air.

Light fastness

The light fastness study was carried out using a xenon light fastness tester having a xenon lamp. The dyed fiber sample was exposed to light along with standard dye patterns of specific

rating (1 to 8). The higher the rating, the better is the light fastness.

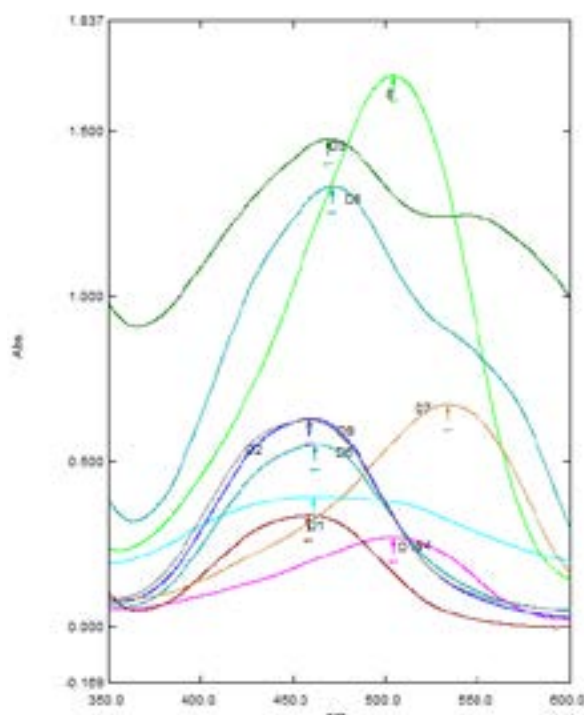
Wash fastness

Fastness to washing was assessed using an automatic Lander-O-meter maintaining the following condition. The washing solution

contained neutral soap at 5g/L and soda ash 2g/L, washing temperature was 95°C, the duration of washing was 30 minutes; the material to liquor ratio was 1:50. After washing, the specimen was removed and rinsed with warm water (35°C) until the rinsed water showed no alkalinity. It was squeezed and air dried. The effect of the colour was expressed and defined by reference

Table-2: UV-Visible spectroscopic data of the dyes D₁-D₁₂ & Graph of Abs. → $\lambda_{\max}$ (nm)

Dyes	$\lambda_{\max}$ (nm)	Abs.
3	461.0	0.330
D ₁	458.4	0.338
D ₂	460.5	0.627
D ₃	468.8	1.478
D ₄	457.8	0.784
D ₅	498.4	1.325
D ₆	492.3	1.063
D ₇	534.0	0.673
D ₈	471.4	1.334
D ₉	459.4	0.632
D ₁₀	504.4	1.478
D ₁₁	489.3	0.968
D ₁₂	495.6	1.204



to the international geometric grey scale.

Sublimation fastness

The dyed fabric was stitched to undyed cotton on one side and the other side undyed polyester fabric. The composite specimens were placed in a heating device (Sublimation tester) equipped with two heating plates with an electrical heating system and kept there for 30 seconds at 180°C. The dried fabric was removed and kept in air for 4 hours. The effect of dyed fabric to other cotton and polyester fabric was measured

and assessed with grey scales.

Effect of different substituent on $\lambda_{\max}$ of synthesized Dyes (D₁-D₁₂)

The absorption spectra of the synthesized dyes D₁-D₁₂ was measured in DMF solvent. Electron donating group -NHCOCH₃ present in coupling component is at ortho position to azolinkage which promotes Bathochromic shift in D₃, D₄, D₅, D₁₀ and D₁₂ which deepen the colour; but electron withdrawing group -Cl present in coupling component is also in ortho position to

azo linkage induces hypsochromic shift. This effect lightens the original colour. (Table-2). –Cl lighter the shade.

Result and Discussion

Chemistry

Bromination of p-chloro acetophenone in acetic acid yielded compound **(1)** which reacted with thiourea in methanol yielded compound **(2)** by cyclization. Then diazotized p-toluidine was coupled with compound **(2)** resulted monoazo dyes **(3)**; which on again diazotized by nitrosyl sulfuric acid and coupled with compound **(4a-l)** gives a series of bis azo disperse dyes of **(5a-l)** respectively. The newly synthesized compounds were confirmed by elemental analysis, IR, ^1H NMR, UV-absorbance and mass spectral data.

Physical properties

All the solid dyes are yellow, dark orange, dark red and dark brown in colour but they gave different shade on polyester fabric. The purity of the dyes was checked by TLC using methanol–toluene (4:6, v/v) as the solvent system. When adsorbed onto silica chromatography plates, each dye produced a reddish-yellowish colour spot. All the dyes recrystallized from ethyl alcohol and exhibited well-defined melting points characteristic of pure compounds. The purified dyes were all found to have satisfactory elemental analysis.

Spectral properties

Visible absorption spectrum of dyes is presented in Table -II. It is illustrated that the value of λ_{max} depends on the different substituted coupling component. The shade of the dye change with changed in different substituent of coupling component. Electron donating group like $-\text{NHCOCH}_3$ which present at ortho to the azo group gives more brighter shade while on the other hand electron withdrawing group like

IR and NMR spectra

The IR spectra of dyes showed the presence of a peak at $3459\text{--}3464\text{ cm}^{-1}$ and $1300\text{--}1362\text{ cm}^{-1}$ corresponding to the amino group respectively. The IR spectra of the dye showed the stretching vibration of alkyl group appeared at $2973\text{--}2998\text{ cm}^{-1}$ and C-H stretching vibration of the aromatic ring appearing at $790\text{--}820\text{ cm}^{-1}$. The azo group stretching vibration band appeared at $1500\text{--}1530\text{ cm}^{-1}$. Further, ^1H NMR spectra exhibited singlet in the region at δ 3.12 ppm for two protons of $-\text{COCH}_2$ group of dye C1, two protons present in dye C1 of NH and $-\text{CONH}$ group is found to resonate as singlet at δ 4.12 ppm and 6.69 ppm and 14 protons of aromatic ring at 6.95–8.12 respectively.

Dyeing properties

All the synthesized dyes **(5a-l)** were applied on polyester fabric in 2% shade according to the literature procedure by HTHP dyeing method. The variation in the hues of the dyed fabric results from the alternation in the coupling components. The remarkable degree of levelness and brightness after washing indicates fair to good light fastness penetration and excellent affinity of these dyes to the fabric.

Acknowledgement

The authors are grateful to Dr. A. S. Patel, principal of Navyug Science College, Surat for providing research laboratory facility and also grateful to Atul Limited, Atul for providing of dyeing facilities.

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