

SYNTHESIS AND DYEING PERFORMANCE OF 5-METHYL 2-AMINO THIAZOLE BASED MONOAZO DISPERSE DYES

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ABSTRACT

Different substituted monoazo disperse dyes from N⁴-(5-methyl-1,3-thiazol-2-yl)-1,3-thiazole-2,4-diamine have been synthesized, the condensation of 5-methyl 2-amino thiazole with chloroacetylchloride with suitable solvent in the presence of anhydrous potassium carbonate yielded 2-(2-chloroacetyl amino) 5-methyl thiazole which was reacted with thiourea at reflux temperature with methanol and cyclized to yield N⁴-(5-methyl-1,3-thiazol-2-yl)-1,3-thiazole-2,4-diamine which was diazotized and coupled with various 3^o amines to give new series of disperse dyes, these were characterized using elemental analysis, UV, IR and ¹H NMR spectra. Dyeing performance and fastness properties were evaluated by applying them to polyester fiber.

KEYWORDS: 2-AMINO THIAZOLE, N⁴-(5-METHYL-1,3-THIAZOL-2-YL)-1,3-THIAZOLE-2,4-DIAMINE, CHLOROACETYLCHLORIDE, 3^o AMINE, FASTNESS PROPERTIES

1. INTRODUCTION

Development of disperse dyes was led by British Celanese Ltd. These dyes were used on cellulose di and triacetate, polyester, polyamide fibers and to some extent on acrylic fibers^{1, 2}. In the preparation of disperse dyes heterocyclic amines have been extensively used because of their extremely good discharge ability on polyester fibers³⁻⁸. 2-amino thiazole and their derivatives have been found very useful on a large scale for synthesis of disperse dyes as intermediates for dyestuffs and even used for pharmaceutical products⁹⁻¹⁶. The term “disperse dyes” has been applied to organic coloring substances, which are free from ionizing groups, low water solubility and suitable for dyeing hydrophobic fibers from colloidal dispersion¹⁷.

Through an azo coupling reaction with an activated aniline derivative, 2-amino thiazoles can produce a wide range of dye colors.

2-amino thiazoles can be synthesized cleanly and in high yield from α -haloketone and thiourea via the Hantzsch thiazole synthesis¹⁸. In the last decades a major work has been reported on aminothiazole based dyes⁷. In this paper we used 2-amino 5-methyl thiazole reacted with chloroacetylchloride and cyclized with thiourea to give final compound *N*⁴-(5-methyl-1, 3-thiazol-2-yl)-1, 3-thiazole-2, 4-diamine¹⁹⁻²¹ (compound 2). Azo dyes of this type are classified as donor-acceptor chromogen. A red shift is observed by introduction of electron withdrawing substituent in the coupler. An interesting anomaly is the large bathochromic shift produced by *m*-acetamido group in the coupler.

The thiazole derivatives gave bright strong color shades and fastness properties because of sulfur heterocyclic azo dyes that range from pink, orange to red^{11, 22}. A series of mono azo disperse dyes (**D₁-D₁₂**) was synthesized and applied as disperse dyes on polyester fabric. Spectral data of dyes, their physical properties and a color assessment was evaluated. Here we report the synthesis of 5-methyl 2-amino thiazole and its applications for dyeing polyester fabric.

2. EXPERIMENTAL

2.1 General information

Melting points were measured using Stuart SMP 10 melting point apparatus and are uncorrected. Purity of compounds was checked by silica gel-G coated TLC plates and spots were visualized under UV radiation. IR spectra were recorded on Perkin – Elmer 1600 FTIR in KBr disc. ¹H NMR spectra were taken on a Bruker Avance II 400 NMR MHz in DMSO and CDCl₃ as solvent and TMS as internal standard. All chemicals used were analytical grade reagent and were used without further purification. The dyeing of the polyester fabric samples was carried out by HTHP dyeing method⁹ and fastness properties to light, wash, perspiration, sublimation and rubbing was evaluated in accordance with ISO 150.

2.2 Synthesis of 2-chloro-N- (5-methyl-1, 3-Thiazol-2-yl) acetamide (1)

In a 250 mL round bottom flask, chloroacetylchloride (7.0 mL, 0.08 mol) and solution of 5-methyl 2-amino thiazole (5 g, 0.04 mol) in dichloromethane (80 mL) reacted and was cooled to 0-5°C and 8 g potassium carbonate was added as a base

catalyst^{8,9}. The reaction mixture was stirred in ice-bath for 30 min and further stirred for 1 h at 15 to 20°C then stirred for 6-8 h at room temperature. Excess of dichloromethane was distilled out. The solid residue thus obtained was washed with cold water, filtered and dried. Recrystallization from ethanol gave white solid of 2-chloro-*N*-(5-methyl-1, 3-thiazole-2-yl) acetamide (**1**).

2.2a 2-chloro-*N*-(5-methyl-1, 3-Thiazol-2-yl) acetamide (1): Yield (82.5%); mp 185-190°C (Scheme 1).

2.3 General procedure for the synthesis of preparation N⁴(5-Methyl-1, 3-Thiazole-2-yl) 1-3-Thiazole-2-4-diamine (2)

2-chloro-*N*-(5-methyl-1, 3-thiazole-2-yl) acetamide (3 g, 0.015 mol) and thiourea (1.6 g, 0.02 mol) in 60 mL methanol was refluxed for 4 h. The excess of solvent was distilled off and the solid obtained. Recrystallization from ethanol gave Yellow crystals of N⁴(5-Methyl-1, 3-Thiazole-2-yl) 1-3-Thiazole-2-4-diamine (**2**) (Scheme 2).

2.3a N⁴(5-Methyl-1, 3-Thiazole-2-yl)1-3-Thiazole-2-4-diamine (2): Yield (65.86%); mp 210-215°C; IR (KBr) cm⁻¹: 3406, 3225 (-NH₂, NH), 2998 (C-H str.), 639 (C-S); ¹H-NMR (400 MHz, DMSO-d₆/TMS): δ 2.25(s, 3H, -CH₃), 3.29-3.40 (1H, -NH), 6.98-7.14 (s, 2H, CH of thiazole ring), 9.30 (s, 2H, NH₂); Anal.Calcd. for C₇H₈N₄S₂: N, 29.50. Found N, 29.39.

2.4 General procedure for the Diazotization of N⁴(5-Methyl-1, 3-Thiazole-2-yl) 1-3-Thiazole-2-4-diamine (2)

Compound **2** (2.12 g, 0.01mol) was dissolved in mixture of sulphuric acid and glacial acetic acid (3 mL+2 mL). It was cooled below 5°C in ice-bath. A solution of sodium nitrite (0.69 g, 0.01mol) in dist. water (4 mL) previously cooled to 0°C was added over a period of 5 min with stirring and maintained the temperature at 0-5°C. Stirring was continued, maintaining the same temperature 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. This clear diazonium salt solution was used for coupling reaction (Scheme-3).

2.5 General procedure for the Coupling with N, N- di methyl aniline (D₁-D₁₂)

N, N- dimethyl aniline (1.21 g 0.01mol) was dissolved in 10 mL acetic acid. It was cooled below 5°C in an ice-bath. To this well stirred solution, above mentioned

diazonium salt solution was added dropwise over a period of 1h maintaining the pH 7.0 to 8.0 by simultaneous addition of aqueous sodium acetate (20% w/v). The stirring was continued for 3 h at 0-5°C. The colored material was obtained, it was filtered, washed with cold water and dried at 50-60°C in an oven to give azo dye **D₁**. It was crystallized from acetone. The dye (**D₂-D₁₂**) was prepared as same procedure (Scheme-3). Practical yielded and physicochemical parameter are reported:

(Z)-N-(2-((4-(dimethylamino)phenyl)diazenyl)thiazol-4-yl)-5-methylthiazol-2-amine (D₁)

Orange crystals, yield 66%; mp 195-197°C; IR (KBr): 3065.93 (N-H str.), 2918 (C-H str.), 1555 (N=N), 1367 (C-N), 821 (C-H of sub. benzene), 629 (C-S) (cm⁻¹); ¹H NMR (400MHz, CDCl₃/TMS): δ 1.15-1.19 (s, 6H, -CH₃), 2.25 (s, 3H, -CH₃), 3.29-3.40 (1H, -NH), 6.51-6.53 (2H, Ar.), 7.67-7.70 (1H, CH of thiazole), 8.02-8.04 (2H, Ar.), 8.27-8.29 (1H, CH of thiazole); Anal. Calcd for: C₁₅H₁₆N₆S₂; N, 24.40. Found. N, 24.21.

(Z)-N-(2-((4-(diethylamino)phenyl)diazenyl)thiazol-4-yl)-5-methylthiazol-2-amine (D₂)

Orange crystals, yield 71%; mp 110-115 °C; IR (KBr): 3249 (N-H str.), 2938(-CH str.), 1521 (N=N), 1452 (CH₂), 1366 (C-N), 815 (C-H of Sub. benzene), 678 (C-S) (cm⁻¹); ¹H NMR (400MHz, CDCl₃/TMS): δ 1.18 (t, 6H, -CH₃), 2.40 (s, 3H, -CH₃), 3.39 (1H,-NH), 3.47 (qt, 4H, -CH₂), 6.61 (2H, Ar.), 7.93 (2H, Ar.), 7.70 (1H, CH of thiazole), 8.15 (1H, CH of thiazole); Anal. Calcd for: C₁₇H₂₀N₆S₂; N, 22.42. Found: N, 22.56.

(Z)-N-(2-((4-(diethylamino)-2-methylphenyl)diazenyl)thiazol-4-yl)-5methylthiazol -2-amine (D₃)

Dark Orange crystals, yield 76%; mp 108-111°C; IR (KBr): 3244 (N-H str.), 2969 (-CH₃), 1528 (N=N), 1444 (CH₂), 1351 (C-N), 838 (C-H of Sub. benzene), 687 (C-S) (cm⁻¹); ¹H NMR (400MHz, DMSO-d₆/TMS): δ 1.15-1.19 (t, 6H, -CH₃), 2.44-2.60 (s, 6H, -CH₃), 3.37 (1H,-NH), 3.45-3.47 (qt, 4H, -CH₂), 6.58-6.63 (2H, Ar.), 7.55 (1H, CH of thiazole), 7.71-7.73 (1H, Ar.), 8.27 (1H, CH of thiazole); Anal. Calcd for: C₁₈H₂₂N₆S₂; N, 21.68. Found. N, 21.74.

(Z)-N-(5-(bis(2-hydroxyethyl)amino)-2-((4-((5-methylthiazol-2-yl)amino)thiazol-2-yl) diazenyl) phenyl) acetamide (D₄)

Red crystals, yield 72%; mp 118-120°C; IR (KBr) cm^{-1} : 3415 (-NHCO), 3230 (N-H str.), 2979 (-CH₃), 2935 (COCH₃), 1680 (C=O), 1506 (N=N), 1323 (C-N), 815 (C-H of Sub. benzene), 692 (C-S); ¹H NMR (400MHz, DMSO-d₆/TMS): δ 1.18 (t, 6H, -CH₃), 1.98 (s, 3H, -CH₃), 2.33 (s, 3H, -CH₃), 3.35 (1H,-NH), 3.47 (qt, 4H, -CH₂), 6.61 (1H, Ar.), 7.73 (2H, Ar.), 7.55 (1H, CH of thiazole), 8.10 (1H, CH of thiazole), 9.48 (1H,-NH); Anal. Calcd for: C₁₉H₂₃N₇OS₂: N, 22.83. Found. N, 22.82.

(Z)-N-(5-(bis(2-hydroxyethyl)amino)-2-((4-((5-methylthiazol-2-yl)amino)thiazol-2-yl) diazenyl) phenyl)acetamide (D₅)

Red crystals, yield 62%; mp 100°C; IR (KBr) cm^{-1} : 3248 (N-H str.), 2928(-CH₃), 1511 (N=N), 1362 (C-N), 1154 (-SO₂), 815 (C-H of Sub. benzene), 685 (C-S); ¹H NMR (400MHz, DMSO-d₆/TMS): δ 1.18 (t, 6H, -CH₃), 1.78 (s, 3H, -CH₃), 2.33 (s, 3H, -CH₃), 3.35 (1H,-NH), 3.47 (qt, 4H, -CH₂), 6.61 (1H, Ar.), 7.73 (2H, Ar.), 7.49 (1H, CH of thiazole), 8.04 (1H, CH of thiazole), 9.42 (1H,-NH); Anal. Calcd for: C₁₈H₂₃N₇O₂S₃: N, 21.06. Found. N, 21.02.

(Z)-N-(5-(bis(2-hydroxyethyl)amino)-2-((4-((5-methylthiazol-2-yl)amino)thiazol-2-yl) diazenyl) phenyl)acetamide (D₆)

Light Orange crystals, yield 65%; mp 138-140°C; IR (KBr) cm^{-1} : 3238(N-H str.), 2978(-CH₃), 2251(-CN), 1518 (N=N), 1452 (-CH₂), 1346 (C-N), 815 (C-H str. of aromatic ring), 765 (C-S); ¹H NMR (400MHz, DMSO-d₆/TMS): δ 1.19-1.23 (t, 3H, -CH₃), 2.49-2.53 (s, 3H, -CH₃), 2.79-2.82 (t, 2H, -CH₂), 3.33 (1H,-NH), 3.55-3.60 (qt, 2H, -CH₂), 3.78-3.81 (t, 2H, -CH₂), 6.89-6.91 (2H, Ar.), 7.61 (1H, CH of thiazole), 7.78-7.80 (2H, Ar.), 8.18 (1H, CH of thiazole); Anal. Calcd for: C₁₈H₁₉N₇S₂: N, 24.48. Found. N, 24.66.

(Z)-N-(5-(bis(2-hydroxyethyl)amino)-2-((4-((5-methylthiazol-2-yl)amino)thiazol-2-yl) diazenyl) phenyl)acetamide (D₇)

Light Orange crystals, yield 78%; mp 98-100°C; IR (KBr) cm^{-1} : 3250 (N-H str.), 2921(-CH₃), 1738 (C=O), 1531 (N=N), 1350 (C-N), 815 (C-H of Sub. benzene), 745 (C-S); ¹H NMR (400MHz, DMSO-d₆/TMS): δ 1.33 (s, 6H, -CH₃), 2.49 (s, 3H, -CH₃), 3.33 (1H,-NH), 3.66 (t, 4H, -CH₂), 4.24 (t, 4H, -CH₂), 6.89 (2H, Ar.), 7.8 (2H, Ar.), 7.6 (1H, CH of thiazole), 8.15 (1H, CH of thiazole); Anal. Calcd for: C₂₁H₂₄N₆O₄S₂: N, 17.32. Found. N, 17.20.

(Z)-N-(5-(bis(2-hydroxyethyl)amino)-2-((4-((5-methylthiazol-2-yl)amino)thiazol-2-yl) diazenyl) phenyl)acetamide (D₈)

Dark Red crystals, yield 68%; mp 87-90°C; IR (KBr) cm⁻¹: 3425 (-NHCO), 3248 (N-H str.), 2955(-CH₃), 2935 (COCH₃), 1680 (C=O), 1520 (N=N), 1352 (C-N), 815 (C-H of Sub. benzene), 765 (C-S); ¹H NMR (400MHz, DMSO-d₆/TMS): δ 1.33 (s, 6H, -CH₃), 1.98 (s, 3H, -CH₃), 2.49 (s, 3H, -CH₃), 3.33 (1H,-NH), 3.66 (t, 4H, -CH₂), 4.24 (t, 4H, -CH₂), 6.61 (1H, Ar.), 7.73 (2H, Ar.), 7.6 (1H, CH of thiazole), 8.15 (1H, CH of thiazole), 9.4 (1H,-NH); Anal. Calcd for: C₂₃H₂₇N₇O₅S₂: N, 17.79. Found. N, 17.97.

(Z)-N-(5-(bis(2-hydroxyethyl)amino)-2-((4-((5-methylthiazol-2-yl)amino)thiazol-2-yl) diazenyl) phenyl)acetamide (D₉)

Light pink crystals, yield 68%; mp 90°C; IR (KBr) cm⁻¹: 3438 (-NHCO), 3255 (N-H str.), 2954(-CH₃), 2837 (OCH₃), 1741 (C=O), 1517(N=N), 1356 (C-N), 815 (C-H of Sub. benzene), 755 (C-S); ¹H NMR (400MHz, DMSO-d₆/TMS): δ 1.33 (s, 6H, -CH₃), 1.98 (s, 3H, -CH₃), 2.49 (s, 3H, -CH₃), 3.33 (1H,-NH), 3.66 (t, 4H, -CH₂), 3.31 (s, 3H, -CH₃), 4.24 (t, 4H, -CH₂), 6.61 (1H, Ar.), 7.73 (1H, Ar.), 7.6 (1H, CH of thiazole), 8.15 (1H, CH of thiazole), 9.4 (1H,-NH); Anal. Calcd for: C₂₄H₂₉N₇O₆S₂: N, 17.12. Found. N, 17.03.

(Z)-N-(5-(bis(2-hydroxyethyl)amino)-2-((4-((5-methylthiazol-2-yl)amino)thiazol-2-yl) diazenyl) phenyl)acetamide (D₁₀)

Pink crystals, yield 70%; mp 150-155°C; IR (KBr) cm⁻¹: 3240 (N-H str.), 2951(-CH₃), 1738 (C=O), 1530 (N=N), 1339 (C-N), 815 (C-H of Sub. benzene), 752 (C-S), 712 (C-Cl); ¹H NMR (400MHz, DMSO-d₆/TMS): δ 1.33 (s, 6H, -CH₃), 2.49 (s, 3H, -CH₃), 3.33 (1H,-NH), 3.66 (t, 4H, -CH₂), 4.24 (t, 4H, -CH₂), 6.61 (1H, Ar.), 7.73 (2H, Ar.), 7.6 (1H, CH of thiazole), 8.15 (1H, CH of thiazole); Anal. Calcd for: C₂₁H₂₃ClN₆O₄S₂: N, 16.12. Found. N, 16.07.

(Z)-N-(5-(bis(2-hydroxyethyl)amino)-2-((4-((5-methylthiazol-2-yl)amino)thiazol-2-yl) diazenyl) phenyl)acetamide (D₁₁)

Yellow crystals, yield 76%; mp 70-73°C; IR (KBr) cm⁻¹: 3255 (N-H str.), 2914(-CH₃), 2245 (CN), 1597 (N-H), 1506 (N=N), 1454 (C-H), 1359 (C-N), 815 (C-H of Sub. benzene), 761 (C-S); ¹H NMR (400MHz, DMSO-d₆/TMS): δ 2.49 (s, 3H, -CH₃), 3.33 (1H,-NH), 3.56 (t, 4H, -CH₂), 3.64 (t, 4H, -CH₂), 6.89 (2H, Ar.), 7.8 (2H,

Ar.), 7.6 (1H, CH of thiazole), 8.22 (1H, CH of thiazole); Anal. Calcd for: C₁₉H₁₈N₈S₂: N, 26.38. Found. N, 26.52.

(Z)-N-(5-(bis(2-hydroxyethyl)amino)-2-((4-((5-methylthiazol-2-yl)amino)thiazol-2-yl) diazenyl) phenyl)acetamide (D₁₂)

Pink crystals, yield 78%; mp 125-130°C; IR (KBr) cm⁻¹: 3635 (-OH), 3468 (-NHCO), 3258 (N-H str.), 2952 (COCH₃), 2978(-CH₃), 1680 (C=O), 1521 (N=N), 1346 (C-N), 815 (C-H of Sub. benzene), 786 (C-S); ¹H NMR (400MHz, DMSO-d₆/TMS): δ 1.98 (s, 3H, -CH₃), 2.33 (s, 3H, -CH₃), 3.35 (1H, -NH), 3.56 (t, 4H, -CH₂), 3.64 (t, 4H, -CH₂), 5.8 (2H, -OH), 6.61 (1H, Ar.), 7.73 (2H, Ar.), 7.55 (1H, CH of thiazole), 8.10 (1H, CH of thiazole), 9.48 (1H, -NH); Anal. Calcd for: C₁₉H₂₃N₇O₃S₂: N, 21.24. Found. N, 21.24.

2.6 Dyeing method

Dyeing of polyester fabric was carried out according to the following procedure. Dyeing was assessed by HTHP method⁹. High temperature (130°C-135°C) and high pressure is a convenient method for dyeing polyester fibers in the laboratory glycerin-bath high temperature beaker dyeing machine was used. 5 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 percent Setamol WS as anionic dispersing agent of BASF. 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 increasing the dyebath temperature to 130°C at a rate of 3 °C/min at this temperature was maintained for 1 h, under (24-30 psi) pressure. After completion of process it was cooled to 50°C, the dyed fabric pieces were rinsed with cold water and reduction cleared properly (1 g/L sodium hydroxide, 1 g/L sodium hydrosulphite, 10 min and 80°C). The dyed sample was rinsed with hot and cold water and finally the samples were air-dried.

2.7 Determination of the percentage exhaustion

Determination of percentage exhaustion of azo disperse dyes **D₁-D₁₂** on polyester fibres were determined according to the known method²³.

2.8 Color Fastness Properties

All fastness properties included light, washing, rubbing, sublimation, perspiration carried out by standard method²⁴.

2.9 Fastness to light

Fastness to light was measured by Microsal light fastness tester. The dyed sample was exposed to light along with standard dye. Assessed by comparing change in color of specimen with respect to ISO Blue Wool Standard scale (1-8). The rating is high so light fastness is good.

2.10 Fastness to washing

Fastness to washing was measured by a wash fastness tester (ISO 105 CO3). A specimen of dyed polyester sample (10cm x 4cm) was stitched by same size of cotton and wool. Multifibre fabric can also be used as adjacent fabric. In the test 5 g/L soap, 2 g/L anhydrous sodium carbonate used, then washed at 50°C for 30 min and rinsed and air dried at temperature not exceeding 60°C; changes in color of the specimen and staining on adjacent fabric are assessed with Grey scales: 1-poor, 2-fair, 3-moderate, 4-good, 5-excellent.

2.11 Fastness to sublimation

Fastness to sublimation was determined by iron tester. The dyes sample were sandwiched between two undyed cotton and polyester pieces, all are equal length and temperature is applied on sample at 150°C, 180°C, 210°C each for 30 sec. Any staining on the un-dyed adjacent fabrics or change in tone was assessed according to the following grey scale: 1-poor, 2-fair, 3-moderate, 4-good, 5-excellent.

2.12 Fastness to rubbing

Determination of the resistance of the color to rubbing off and staining other materials was used by Crockmeter. Dry rubbing specimen (14cm x 5cm) sample is rubbed with a dry rubbing cloth (5cm x 5cm) (mounted on rubber finger) to and in a straight line for 10 times in 10 sec. Wet rubbing specimen (14cm x 5cm) sample is rubbed with a wet rubbing cloth. Staining is assessed on rubbing using Grey Scale: 1-poor, 2-fair, 3-moderate, 4-good, 5-excellent.

2.13 Fastness to perspiration (Acidic and Alkaline)

Determination of the resistance of the color was done by perspirometer. The composite specimen smooth dyed sample sandwiched by multifibre in a flat bottomed dish and cover with solution then immersed in the acid or alkaline solution for 30 min. change in color of the specimen and staining on adjacent fabric assessed with Grey Scales. Acidic perspiration (pH=5.5) 0.5 g/L histidine monohydrochloride monohydrate, 5 g/L sodium chloride, 2.2 g/L sodium dihydrogen orthophosphate dehydrate, 0.1 mol/L sodium hydroxide. The Alkaline perspiration (pH=8.0) 0.5 g/L histidine monohydrochloride monohydrate, 5 g/L sodium chloride, 2.5 g/L disodium hydrogen orthophosphate dodecahydrate, 0.1 mol/L sodium hydroxide. The staining on the undyed adjacent fabric was assessed according to the following grey scale: 1-poor, 2-fair, 3-moderate, 4-good, 5-excellent.

2.14 Color assessment

The colorimetric parameters determined by CCM on polyester fabric of each dye samples. The color of dye on polyester fabric was determined by the CIELAB (**Table-II**). CIELAB coordinates were measured for the level Lightness (L^*), Chroma (C^*), hue angle from 0 to 360 (H), a^* value represent redness (positive) and greenness (negative) and b^* value represent yellowness (positive) and blueness (negative). Colorimetric data of dyes was measured by a reflectance spectrophotometer. The K/S value was calculated at λ_{max} and directly correlated with the dye concentration on the substrate according to the Kubelka-Munk equation²⁵⁻²⁷.

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

Where K- Absorbance coefficient, S- scattering coefficient and R- reflectance ratio.

3. RESULT AND DISCUSSION

3.1 Chemistry

2-amino-5-methyl-thiazole reacted with chloroacetylchloride in the presence of potassium carbonate at 0-5°C gave solid 2-chloro-*N*-(5-methyl-1,3-thiazol-2-yl)acetamide (**1**) which reacted with thiourea resulting in the formation of N^4 -(5-methyl-1,3-thiazole-2-yl)-1,3-thiazole-2,4-diamine (compound **2**) in the presence of

methanol^{23, 28}. Diazotization of above compound **2** was carried out and the resulting diazonium salt solution was coupled with various *N, N*-dialkylaniline derivatives to prepare azo disperse dyes **D₁-D₁₂**. The new compounds were confirmed by elemental analysis, IR, ¹H NMR and UV spectral data.

3.2 Spectral properties of dyes

The spectra of visible absorption of dyes were performed in acetic acid and shown in **Table- II**. Their absorption maxima were in the range of 459-588 nm. The color of the dyes is affected by the substituents in the coupler molecule. The introduction of electron-donating groups in dyes **D₁**, **D₃-CH₃**, **D₂** to **D₆-C₂H₅**, **D₄**, **D₈**, **D₉** - **NHCOCH₃**, **D₇** to **D₁₀**, **D₁₁-OCOCH₃**, **D₉-OCH₃**, **D₁₂-OH** or electron-withdrawing groups in dyes **D₆**, **D₁₁-CN**, **D₁₀-Cl**, **D₅-NHSO₂CH₃** at respective positions in the coupling components affect the absorption characteristics of the dyes. Electron withdrawing groups activate the substitution at the ortho and para carbons. Bathochromic shift can be obtained by enhancing electron donor properties as mentioned above of the couplers. Bathochromic shift of absorption to a longer wavelength due to substitution (a red shift) and hypsochromic shift of absorption to a shorter wavelength due to substitution (a blue shift). It is clear that the value of λ_{\max} depends on the electron-donor or electron-accepter nature and position (ortho or para) at of coupling component used. The color change observed for each dye is due to the alternation of electrons and the presence of additional substituent.

3.3 IR and NMR Spectra

The IR spectra of dyes showed the presence of a peak at 3200-3350 cm⁻¹ and 1300-1362 cm⁻¹ corresponding to the amino group and the dimethyl group respectively. Compound **2** was further confirmed by its ¹H NMR spectra recorded in DMSO. The IR spectra of the dye showed the stretching vibration of alkyl group appeared at 2926-2960 cm⁻¹ and C-H stretching vibration of the aromatic ring appearing at 700-820 cm⁻¹. The azo group stretching vibration band appeared at 1500-1530 cm⁻¹. Further, ¹H NMR spectra exhibited singlet in the region at δ 1.18 ppm for six protons of dimethyl amine group of dye **D₁**. Three protons present in dye **D₁** of -CH₃ group of thiazole is found to resonate as singlet at δ 2.49 ppm respectively.

3.4 Dyeing properties of dyes

The series of disperse dyes **D₁** to **D₁₂** was applied on (2% depth) polyester fabric by HTHP dyeing method. These dyes on fabric gave a colour varying from pink, orange to red with good levelness, brightness and depth. The dyed fabric was exposed to light along with the standard dye patterns of specific ratings of the grade 1-8. Light fastness of all dyes was moderate to good and washing fastness, perspiration fastness very good to excellent on polyester fabric. The sublimation fastness was assessed by keeping a composite specimen of dyed polyester between two undyed polyester pieces in a precision press at 210°C for 30 seconds. The fastness to sublimation of all dyes gave rating 1-4, showing sublimation fastness of all dyes average to very good (**Table-I**). The rubbing fastness (Dry and Wet) of synthesized dyes on polyester fibers was found very good to excellent due to more electrostatic interaction. Thus most of these dyes showed very good dyeing properties. Vander Waals interactions affect the affinity of dyes to polyester fabric. It gives K/S values and is directly correlated with the dye concentration on the substrate according to the Kubelka-Munk equation. A remarkable degree of levelness after washing indicated good penetration and affinity of these dyes to the fabric shown in **Table-I** and **Table-II**.

3.5 Exhaustion of dyes

The exhaustion values of dyes **D₁**-**D₁₂** obtained in the range of 68.24–84.26% (**Table-II**). The exhaustion values depends on the structure of fabric, diffusion rate and dye molecules.

4. CONCLUSION

A series of mono azo disperse dyes containing substituted 3° amines as a coupling compound have been synthesized by conventional method and their color fastness properties exhibited in solution and applied on polyester fabric. These mono azo disperse dyes (**D₁**-**D₁₂**) resulting from 2-amino 5-methyl thiazole gave red, orange, dark red, pink with level dyeing colors shades with fair to excellent washing, light, perspiration, rubbing fastness properties. With little variation in the poor to very good sublimation fastness on polyester fabric and loss of color under high temperature exhaust dyeing conditions. The bright dark color might be attributed to the greater planarity of the thiazole dyes, because of the lower steric interaction on of a five member ring.

5. ACKNOWLEDGEMENT

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TABLE CAPTIONS

TABLE I. Fastness properties of the dyes.

TABLE II. UV-Visible spectroscopic data and color coordinates of the dyes **D₁-D₁₂**.

TABLE I. Fastness properties of the dyes.

Dyes No.	Shade on Polyester	Fastness to		Sublimation on polyester		Perspiration		Rubbing	
		Light	Washing	Staining at 180 ^o C	Staining at 210 ^o C	Acid	Basic	Dry	Wet
		D₁	Orange	4	4-5	2	1	4-5	4-5
D₂	Orange	4	4-5	2	1	4-5	4-5	4-5	4
D₃	Dark orange	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	Red	4	4-5	3	1-2	4-5	4-5	4-5	4
D₆	Light orange	4	4-5	3	1-2	4-5	4-5	4-5	4
D₇	Light orange	4-5	4-5	3	2	4-5	4-5	4-5	4
D₈	Cream	3-4	4-5	2-3	2	4-5	4-5	4-5	4
D₉	Light pink	4-5	4-5	2-3	2	4	4	4-5	4
D₁₀	Pink	3-4	4-5	3	1-2	4-5	4-5	4-5	4
D₁₁	Yellow	4	4-5	3-4	2-3	4-5	4-5	4-5	4
D₁₂	Pink	4	4-5	3-4	2-3	4	4	4-5	4

Abbreviation:

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

Washing, Sublimation, Perspiration, Rubbing: 1-poor, 2-fair, 3-good, 4-very good, 5-excellent.

TABLE II. Uv-visible spectroscopic data and color coordinates of the dyes **d₁-d₁₂**

Dyes	λ max (nm)	L*	a*	b*	C*	H*	K/S Value	% Exhaustion
D₁	461	53.71	55.53	58.70	80.81	46.59	17.54	73.24
D₂	588	50.50	55.22	51.46	75.49	42.98	17.40	76.67
D₃	588	44.69	57.44	42.48	71.44	36.49	18.08	74.12
D₄	523	39.28	54.44	27.13	60.83	26.49	18.44	71.24
D₅	517	43.61	49.42	27.79	56.70	29.35	15.89	78.23
D₆	483	59.67	49.09	68.35	84.15	54.32	16.92	84.26
D₇	492	45.67	50.69	53.99	74.05	67.78	15.64	81.34
D₈	525	55.60	57.43	51.45	55.67	56.55	16.23	68.24
D₉	532	58.45	47.55	38.56	68.57	45.56	14.34	78.24

D₁₀	500	59.10	50.69	57.45	74.05	46.81	12.34	72.24
D₁₁	459	58.45	54.46	45.67	67.56	56.66	15.67	70.38
D₁₂	515	67.14	41.82	11.74	43.44	15.69	19.51	72.89

SCHEME CAPTIONS

Scheme I. Synthesis of 2-chloro- *N*- (5-methylthiazol-2- yl) acetamide.

Scheme II. Synthesis of *N*⁴-(5-methylthiazol-2- yl) 1, 3-thiazole-2,4-diamine.

Scheme III. Synthesis of disperse dyes (**D₁-D₁₂**)

