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Synthesis, Characterization and Fastness Properties of 2-amino 5-methyl-1, 3, 4-thiadiazole

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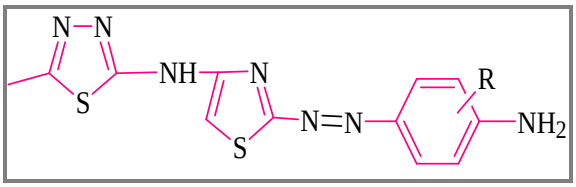
ABSTRACT

Disperse dyes D_1-D_{12} have been synthesized by diazotization of N^4-(5-methyl-1, 3, 4-thiadiazole-2-yl) thiazole-2-4-diamine (Z_1) and coupled with various primary anilines. These were characterized using elemental analysis, UV, IR and NMR spectra. Dyeing performance and fastness properties were evaluated by applying them to polyester fabric. The dye bath exhaustion and fixation on the fabric was also found to be very good. Computer color matching properties (L, a*, b*, C*, H* and K/S) was assessed.*

Graphical Abstract



Synthesis of monoazo disperse dyes.

Keywords: 2-amino 5-methyl-1,3,4-thiadiazole, Chloroacetylchloride, Fastness properties.

INTRODUCTION

Several heterocyclic compounds have been extensively used in disperse dyes chemistry for textile and non-textile applications [**1**]. Recently, the chemistry of 1,3,4-thiadiazole derivatives is highlighted due to their wide spectrum of biological activities including antimicrobial, anti-inflammatory, antioxidant, anti-tumour, anti-cancer and have other pharmacological activities [**2**]. Heterocyclic nitrogenous compounds and their fused analogues exist in numerous natural products, display a wide range of medicinal and biological activities [**3**]. Thiadiazole classes of diazo components have been extensively studied over the last ten years because of their brightness and good light fastness on hydrophobic fabrics [**4-6**]. 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 [**7, 8**]. In the preparation of disperse dyes, heterocyclic amines have been extensively used

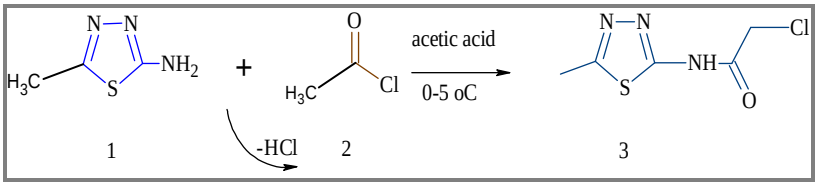
because of their extremely good discharge ability on polyester fibers [9-14]. Dyes derived from 2-amino-1,3,4-thiadiazole are of technical interest for the production of brilliant red shades and 1,3,4-thiadiazoles are very interesting compounds due to their important applications in many pharmaceutical, biological and analytical field [15-17].

The synthesis of 2-amino 5-methyl-1,3,4-thiadiazole which reacted with chloroacetylchloride and cyclized with thiourea to give final compound N^4-(5-methyl-1, 3, 4-thiadiazole-2-yl) thiazole-2-4-diamine. A new series of mono azo disperse dyes D_1-D_{12} were synthesized and applied on polyester fabric. Spectral properties of dyes, their physical properties and a color assessment were evaluated.

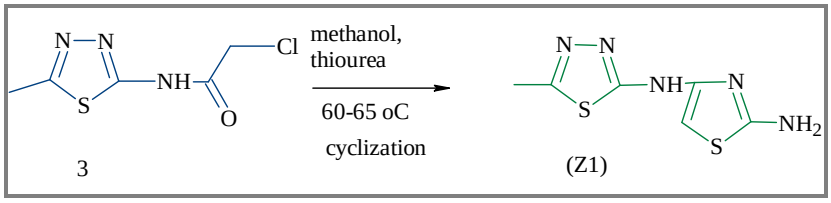
MATERIALS AND METHODS

The purity of the dyes was checked by silica gel-G coated thin layer chromatography (TLC) plates using methanol and toluene (4:1) as the solvent system and spots were visualized under UV light. The disperse dyes D_1-D_{12} were applied at 2% depth on polyester fabric. The dyeing of the polyester fabric samples was carried out by high temperature (130°C) and high pressure (24-30psi) dyeing method. Fastness properties to light, wash, sublimation, perspiration and rubbing were evaluated in accordance with ISO 105 [18,19]. The UV spectra were measured on UV-1800 Shimadzu Spectrophotometer. The visible absorption spectral properties of dyes D_1-D_{12} were recorded in DMF (Table 3). IR spectra were recorded on Perkin-Elmer 1600 FTIR in KBr disc in the range between 4000 cm^{-1} to 400 cm^{-1}. Melting points were taken in open capillary on Stuart SMP 10 melting point apparatus and are uncorrected. ^{1}H NMR spectra were taken on a Bruker avance II 400 NMR MH_Z in DMSO-d_6 as solvent and TMS as internal standard. The dye bath exhaustion (%E) and fixation (%F) of the dyed fabric were determined [20, 21].

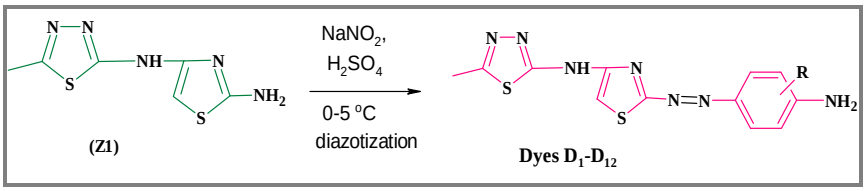
Step-1 Synthesis of 2-chloro-*N*-(5-methyl-1, 3, 4-thiadiazole-2-yl) acetamide (3) [22-24]: In a 250 mL round bottom flask, solution of 2-amino 5-methyl-1,3,4-thiadiazole**(1)** (5 g, 0.04 mol) in acetic acid (80 mL) and chloroacetylchloride **(2)** (7.0 mL, 0.08 mol) was slowly added with continuous stirring and was cooled to 0-5°C. 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. Reaction mixture was dumped into 20% sodium acetate solution to give solid residue 2-chloro-*N*-(5-methyl-1, 3, 4-thiadiazole-2-yl) acetamide (3). It was filtered, washed with cold water, dried and recrystallized from ethanol. Yield: 82.5%; m.p:185-190°C.



Step-2 Synthesis ofN^4-(5-methyl-1, 3, 4-thiadiazole-2-yl) thiazole-2-4-diamine (Z_1) [23]: 2-Chloro-*N*-(5-methyl-1,3,4-thiadiazole-2-yl)acetamide**(3)** (3 g, 0.015 mol) and thiourea (1.6 g, 0.02 mol) in (60 mL) methanol were refluxed for 4 h at 60 to 65°C and the progress was monitored by TLC using methanol: toluene (4:1 v/v) solvent system. The excess of solvent was distilled off to give N^4-(5-methyl-1, 3, 4-thiadiazole-2-yl) thiazole-2-4-diamine.Recrystallization it from ethanol. Yield: 69.89%; m.p.: 205-210°C, Anal.Calcd. for $C_6H_7N_5S_2$: Found: N, 32.84%, Calcd: N, 32.39%.



Step-3 synthesis of dyes[22]: Compound N^4-(5-methyl-1, 3, 4-thiadiazole-2-yl) thiazole-2-4-diamine (2.13 g, 0.01mol) was dissolved in mixture of acetic acid and concentrated sulphuric acid (3.0mL+2.0 mL) and cooled below 5°C in ice-bath. A solution of sodium nitrite (0.69 g, 0.01 mol) in dist. water (4.0 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. Substituted aromatic primary aniline(0.01mol) was dissolved in 3.0 mL sulphuric acid and 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 1hour 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 slid dyes separated out was filtered, washed with cold water and dried it at 50-60°C. The dyes were crystallized from acetone.



R=Substituted primary aromatic anilines

RESULTS AND DISCUSSION

N^4-(5-methyl-1,3,4-thiadiazole-2-yl) thiazole-2-4-diamine was diazotized and its couple with primary aromatic amines to give dyes**D_1-D_{12}**. This synthesized dyes characterized by elemental analysis IR spectra and NMR spectra.

IR and ^{1}H-NMR spectra: IR spectra of synthesized compounds showed the presence of an absorption band at 3476-3410 cm^{-1} for asymmetric and 3345-3300 cm^{-1} for symmetric stretching is due to the -NH_2 group. The -N-H stretching vibrations band is observed at 3260-3240 cm^{-1}. All the compounds showed a characteristic band at 1550-1490 cm^{-1} for the -N=N- group. The asymmetric band at 2995-2900 cm^{-1} and symmetric stretching band at 2850-2810 cm^{-1} is due to the C-H stretching of -CH_3 groups. The aromatic ring of C-H stretching band observed at 3090-3072 cm^{-1} and the stretching vibration bands of the -NO_2 group are present in the range at 1560-1520 cm^{-1} for asymmetric and at 1360-1310 cm^{-1} for symmetric. The C-S-C linkage of the five member ring caused a weak and sharp absorption band at 720-650 cm^{-1} of all dyes.

^{1}H NMR spectra of dye **D_{10}** exhibited one proton present in -NH- group found to resonate as singlet at δ 8.95 ppm, the multiplets in the region at δ 8.06-8.30 ppm for two protons of aromatic ring and singlet in the region at δ 7.39 ppm for two protons of -NH_2 group, one proton present of C-H group of thiazole ring found to resonate as singlet at δ 6.85 ppm and three protons of -CH_3 group are shown singlet in the region at δ 2.68 ppm of thiazole ring.

Fastness properties: The dyes **D_1** to **D_{12}** on polyester fabric (2% depth) gave the colour varying from yellow, orange to lemon yellow with good levelness, brightness and depth. The physical properties of all dyes **D_1** to **D_{12}** have been given in table 1. The purity of the dyes was evaluated by TLC using methanol-toluene (4:1) as the eluting system. The R_f values obtained between 0.81 to 0.94. All the recrystallized dyes exhibited well-defined melting points.

Light fastness of dyes **D_3**, **D_5**, **D_9** and **D_{12}** were fairly good and washing fastness, perspiration and rubbing fastness of all dyes very good to excellent on polyester fabric as shown in table 2. Sublimation fastness of dyes **D_3**, **D_7**, **D_8**, **D_{11}** and **D_{12}** gave good values on polyesterfabric.

Table 1. Physical properties of the dyesD_1-D_{12}

Dye No.	substituent (R)	M. F.	M. W.	Yield (%)	M.P. °C	Nitrogen %	
						Found	Calcd.
D_1	2-NO_2,	$C_{12}H_{10}O_2N_8S_2$	362	74	65-70	30.92	21.71
D_2	3-NO_2	$C_{12}H_{10}O_2N_8S_2$	362	73	120-122	30.92	21.71
D_3	4-NO_2	$C_{12}H_{10}O_2N_8S_2$	362	78	190-195	30.92	21.71
D_4	3-Cl	$C_{12}H_{10}N_7S_2Cl$	351	76	90-95	27.87	29.35
D_5	4-Cl	$C_{12}H_{10}N_7S_2Cl$	351	79	150-154	27.87	27.85
D_6	4-CH_3	$C_{13}H_{13}N_7S_2$	331	80	170-174	29.58	29.55
D_7	H	$C_{12}H_{11}N_7S_2$	317	78	270-275	30.89	30.84
D_8	2,3-$(Cl)_2$	$C_{12}H_9N_7S_2Cl_2$	386	74	70-75	25.38	25.35
D_9	2,5-$(Cl)_2$	$C_{12}H_9N_7S_2Cl_2$	386	72	70-80	25.38	25.35
D_{10}	2-CN, 4-NO_2	$C_{13}H_9O_2N_9S_2$	387	79	260-270	25.02	24.79
D_{11}	2,4-$(NO_2)_2$	$C_{12}H_9N_9S_2O_4$	407	73	260-265	30.94	27.05
D_{12}	2-Cl, 4-NO_2	$C_{12}H_9O_2N_8S_2Cl$	396	76	280-285	28.24	28.22

Table 2. Fastness properties of the dyesD_1-D_{12}

Dye 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
D_1		3	4-5	2	1	4	4	4	4
D_2		3	4-5	1-2	1	4	4	4	4
D_3		4	4-5	3	3	4-5	4	4	4
D_4		3	4-5	2-3	1-2	4	4	4-5	4
D_5		4	4-5	1-2	1-2	4	4-5	4-5	4
D_6		3	4-5	3	1-2	4	4-5	4	4
D_7		3	4-5	3	3	4-5	4	4-5	4
D_8		3	4-5	3	3	4	4-5	4	4
D_9		4	4-5	2	2	4-5	4	4-5	4
D_{10}		3	4-5	2	1-2	4-5	4-5	4	4
D_{11}		3	4-5	3	3	4-5	4	4-5	4
D_{12}		4	4-5	3	3	4	4	4-5	4

Abbreviation

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

Fastness of washing, sublimation, perspiration, rubbing: 1-poor, 2-fair, 3-good, 4-very good, 5-excellent.

Spectral properties: The visible absorption spectra of all dyes were recorded in DMF and observed in the range of 408-482 nm as shown in table 3. The color of the dyes is affected by the substituents in the coupler molecule. Introduction of electron-donating group -CH_3in **D_6**; -NH_2 in all dyes **D_1** to **D_{12}** and electron-withdrawing groups -NO_2 in **D_1-D_3**, **D_{10}**, **D_{11}**; -Cl in **D_4**, **D_5**, **D_8** ,**D_9** and -CN in **D_{10}** 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.

Color measurement: The result of colorimetric data (L*, a*, b*, C*, H* and K/S) on polyester fabric for all dyes are summarized in table 3. The colorimetric data of polyester fabric for all the dyes gave good values. The color of dye on polyester fabric was determined by the CIE Lab coordinates; which were measured for the level Lightness (L*), Chroma (C*), hue angle form 0^o to 360^oC (H*), a* value represent redness (positive) and greenness (negative) and b* value represent yellowness (positive) and blueness (negative) [20, 25]. The *K/S* values given by the reflectance spectrophotometer are calculated at λ_{max} and are directly correlated with the dye concentration on the substrate according to the

Kubelka-Munk equation (Eq.1). A remarkable degree of levelness after washing indicated good penetration and affinity of these dyes to the fabric.

$$K/S = (1-R)^2/2R \text{…….(Eq.1)}$$

Where, K- Absorbance coefficient, *S*- Scattering coefficient and *R*- Reflectance ratio. The color strength (K/S) values of all dyes for polyester fabric were found good. **D_{10}** has high value of (K/S) and **D_2** has low value of (K/S).

Exhaustion and fixation study: Dye bath exhaustion (%) and fixation (%) values were determined according to reported method [20]. The exhaustion values of dyes **D_1-D_{12}** obtained in the range of 69.28 to 79.40 % in which dye **D_{10}** showed maximum exhaustion (79.40%) and dye **D_8** minimum exhaustion (69.28%). The fixation values of dyes **D_1-D_{12}** obtained in the range of 78.30 to 92.93% in which dye **D_3** showed maximum fixation (92.93%) and dye **D_1** showed minimum fixation (78.30 %) shown in table 3. The exhaustion and fixation values depends on the structure of fabric, diffusion rate and dye molecules.

Table 3. UV-Visible spectroscopic data and color coordinates of the dyes D_1-D_{12}

Dye No.	λ max (nm)	R_f	L*	a*	b*	C*	H*	K/S Value	Exhaustion%	Fixation %
D_1	411	0.94	78.64	2.90	30.73	39.66	80.55	2.010	70.23	78.30
D_2	430	0.89	76.35	3.10	23.90	34.88	71.39	1.735	72.69	87.43
D_3	482	0.86	68.53	16.40	68.85	68.35	74.10	7.514	70.45	92.93
D_4	432	0.89	75.79	16.22	77.10	74.53	79.39	3.710	75.28	91.88
D_5	474	0.81	69.50	15.66	35.78	30.49	75.50	3.167	77.23	88.80
D_6	438	0.90	60.87	6.20	28.37	34.72	74.53	3.140	75.26	83.57
D_7	450	0.90	78.30	8.09	67.55	49.40	62.93	2.786	72.34	88.72
D_8	410	0.81	68.70	18.80	50.93	59.78	80.05	2.564	68.28	83.95
D_9	435	0.84	77.45	19.60	35.19	24.27	78.23	6.567	75.84	84.93
D_{10}	408	0.87	70.10	18.77	39.25	34.90	78.14	7.745	79.40	87.85
D_{11}	457	0.86	69.40	14.70	28.29	36.05	66.23	3.760	78.88	83.53
D_{12}	428	0.88	78.14	9.80	20.51	24.44	78.50	1.985	76.89	82.94

APPLICATION

All the synthetic dyes were applied on polyester fibers by HPHT method.

CONCLUSION

A series of mono azo disperse dyes **D_1-D_{12}** were synthesized by HTHP method, these were characterized and their result of dyeing showed that the fastness of disperse dyes on polyester was very good to excellent. Washing, rubbing and perspiration fastness of the dyes for polyester fabric were found to be very good to excellent and light fastness of the dyes was found to be moderate to good. Sublimation fastness of the dyes was found to be poor to very good. These dyes gave mostly the color varying from yellow, orange to golden yellow with good levelness, brightness, depth and shades on polyester fabric with good fastness properties. The variations in the hue of the dyed fabric resulted from, the nature and position of the substituent present on the coupler ring. The colorimetric results of polyester fabric for all the dyes exhibited good values. The exhaustion and fixation of dyes was very good which indicated good solubility.

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