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## **Synthesis and Application of Disazo Dyes Derived from 2-amino-5-mercapto-1,3, 4-thiadiazole and 2-chloroaniline on Acrylic Fabric and Nylon 66 Fabric**

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### **ABSTRACT**

The dyestuff industry has come under pressure in recent times to minimize the damage to the environment caused by the production process and its effluents. In the present investigation we have synthesized and characterized some disazo dyes from a more environmentally friendly heterocyclic compound, 5-Amino-2-mercapto-1,3,4-thiadiazole as the nucleus of the dyes. In preparation of the dyes, the aforementioned intermediate was diazotized and coupled with 2-chloroaniline to give another intermediate diazo compound, 2-mercapto-1,3,4-thiadiazoleazo-4-amino-3-chlorobenzene. This was subsequently diazotized and coupled with other couplers to afford the disazo dyes. The results of fastness properties of the dyes on acrylic fabric and nylon fabric gave excellent sublimation ratings, excellent washing treatment, perspiration ratings and good light fastness ratings. Thus, all the dyes showed strong affinity for the polymers used for the study as exemplified by the wet fastness and the bright shades on the two fibres. The dyes were characterized using IR, UV-VIS, <sup>1</sup>HNMR and <sup>13</sup>C NMR analyses.

**Key words:** Synthesis, disperse dyes, fastness, acrylic fabric, nylon fabric

### **INTRODUCTION**

The gradual rise in the cost of feedstock, energy for synthesis of dyes and environmental considerations have become some of the major challenges facing the dyestuff industry (Edwards and Freeman, 2005; Gregory, 1994). In this regard, the use of dye intermediates that are relatively less expensive and could at the same time be more environmentally friendly has been advocated (Gregory, 1994). Many heterocycles which show biological activity in both medicinal and pharmaceutical areas as in anti-bacterial, anti-viral, anti-inflammatory and analgesic activities (Seferoglu, 2009; Joseph *et al.*, 2010) could be the best choice for the preparation of dyes. In addition to the aforementioned importance of the heterocycles, they yield dyes that possess high tinctorial strength, improved technical excellence and low cost effectiveness when compared with their counterparts synthesized from the carbocyclic compounds. The heterocycles have also been found to give very brilliant shade dyes that may positively appeal to the consumer when applied on textile fibres (Gregory, 1994; Kidwai and Priya, 2008).

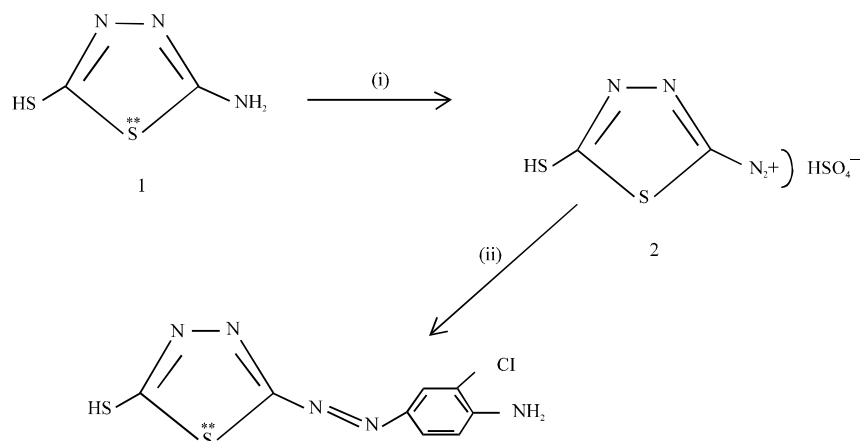


Fig. 1: Synthesis scheme for the preparation of compound 3, (i) H<sub>2</sub>SO<sub>4</sub>/NaNO<sub>2</sub>, 0-5°C (ii) C<sub>6</sub>H<sub>4</sub>Cl

The thiadiazole nucleus, for instance has gained prominence in recent times especially for the synthesis of monoazo dyes of hetaryl origin. Many thiadiazole nucleus, apart from their use in the dyestuff industry have also found use in the inhibition of corrosion of metals especially aluminium, copper, etc. (Al-Juaid, 2007; Ortega-Luom *et al.*, 2007).

The 2-amino-5-mercapto-1,3,4 thiadiazole which is the precursor for this study has been used in the synthesis of monoazo disperse dyes and their fastness properties on polyester fabrics and nylon 66 fabrics were evaluated (Otutu, 2013). In continuation of this research, we report here the synthesis, characterization and fastness properties of disazo disperse dye derivatives of this intermediate on acrylic fabrics and nylon 66 fabrics.

**Synthesis of compound 3:** Figure 1 shows the synthesis of compound 3. Concentrated sulphuric acid (6 mL) was added to a mixture of 2-amino 5-mercapto-1, 3, 4-thiadiazole (8.0 g, 0.045 mole) and sodium nitrite (4.0 g, 0.0579 mole) in water (15 mL) while maintaining the temperature at 0-5°C and stirred for 30 min. Excess nitrous acid was removed by addition of sulfamic acid. The resultant diazonium salt solution was then added to solution of 2-chloroaniline (5 mL) in acetic acid (6 mL) dropwise and stirred for 2 h. The dye was isolated by filtration, washed with water and dried in air. The crude product was recrystallized from hot acetic acid to give orange-yellow crystals in 11.68 g, 92% yield.

**Synthesis of 5-ethyl-2-amino carbazole azo-2-chlorophenylazo-2-mercapto 2",4, 5-thiazole (5a):** Compound 3 (1.23 g, 0.0530 mole) was diazotized in 4 mL of concentrated sulphuric acid and 20 mL water by adding sodium nitrite solution (1.0 g, 0.01449 mole) in 10 mL water at 0-5°C and stirred for 25 min. The diazonium salt solution obtained was added to a solution of 2-amino-9-ethylcarbazole (0.95 g, 0.019 mole) in 5 mL acetic acid and stirred for 2 h. The product was filtered, dried and recrystallized from carbon-tetrachloride to give an orange-green solid. m.p. 164°C yield 65%, IR (KBr):

- $\nu = 3169.15-3315.74 \text{ cm}^{-1}$  (NH<sub>2</sub>),  $2983.34-3063.06 \text{ cm}^{-1}$  (C-H<sub>str</sub>),  $2133.34 \text{ cm}^{-1}$  (S-H<sub>str</sub>),  $1384.94 \text{ cm}^{-1}$  (carbazole ring),  $123855 \text{ cm}^{-1}$  Thiazole ring)  $833.28 \text{ cm}^{-1}$  (C-Cl),  $1591.33 \text{ cm}^{-1}$  (Ar-ring)

- $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta_{\text{H}}$ : 1.25 (2H, s,  $\text{NH}_2$ ), 2.80-3.60 (3H, t,  $\text{CH}_2$ ); 2.65 (1H, s, SH); 4.45 (2H, s,  $\text{CH}_2$ ), 6.80-7.10 (6H, Carbazole-H)
- 7.60 (2H, s, Thiazole-H), 7.90 (2H, m, ArH), 8.20 (1H, m, ArH), 40.99, 40.58, 40.16, 38.75, 38.32, 35.07

**Synthesis of 4-Amino-2-chlorophenyl azo-2'-chlorophenylazo-3-mercapto-2",4,5-Thiadiazole 5b:** Compound 5b was obtained by using the procedure similar to that described for compound 5a to give yellow crystals. m.p  $160^\circ\text{C}$  yield (78%), IR (KBr):

- $\nu = 3471.98\text{-}3591.57\text{ cm}^{-1}$  ( $\text{NH}_2$ ),  $2899.11\text{ cm}^{-1}$  ( $\text{C-H}_{\text{str}}$ ),  $2131.41\text{-}2613.63\text{ cm}^{-1}$  ( $\text{S-H}_{\text{str}}$ ),  $1600.95\text{ cm}^{-1}$  (Ar-ring),  $1168.9\text{ cm}^{-1}$  (Thiazole ring)  $833.28\text{ cm}^{-1}$  ( $\text{C-Cl}_{\text{str}}$ )
- $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta_{\text{H}}$ : 2.24 (2H, s,  $\text{NH}_2$ ), 3.65 (1H, s, SH), 6.40-7.80 (4H, ArH), 7.96 (1H, m, ArH), 8.85(1H, m, ArH)
- $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta_{\text{C}}$ : 131.12, 130.77, 129.96, 128.79, 128.20, 126.77, 126.64, 123.30, 119.27, 41.05, 40.61, 40.20, 39.79, 39.35, 38.93

**Synthesis of 2-hydroxynaphthaleneazo-2-chlorophenyl azo-3-mercapto-2",4,5-thiadiazole 5c:** Compound 3 (1.23 g, 0.0105 mole) mixed with concentrated sulphuric acid (5 mL) and water (20 mL). This mixture was cooled to  $0\text{-}5^\circ\text{C}$  and sodium nitrite (1.0 g, 0.01449 mole) in 10 mL water was added and stirred at  $0^\circ\text{C}$  for 30 min. Excess nitrous acid was removed by adding sulfamic acid. 2-Naphthol (0.65 g, 0.0045 mole) dissolved in sodium hydroxide (0.05 mole) in 20 mL water and the diazonium salt solution was added to this solution and stirred for 1 h. The precipitated compound was isolated by filtration, washed with water and dried in air. The crude product was purified by recrystallization from carbontetrachloride m.p.  $170^\circ\text{C}$ , yield (62%):

- R (KBr)  $\nu = 3180.72\text{-}3296.46\text{ cm}^{-1}$  ( $\text{O-H}_{\text{str}}$ ),  $3070.78\text{ cm}^{-1}$  ( $\text{C-H}_{\text{str}}$ ),  $2362.88\text{ cm}^{-1}$  ( $\text{S-H}_{\text{str}}$ ),  $1620.26\text{ cm}^{-1}$  (Ar-ring),  $1467.88\text{ cm}^{-1}$  (Naphthalene ring),  $1213.19\text{ cm}^{-1}$  (Thiazole ring),  $842.92\text{ cm}^{-1}$  ( $\text{C-Cl}_{\text{str}}$ )
- $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta_{\text{H}}$ : 2.45 (1H, S, SH); 7.05-7.33 (4H, m, ArH), 7.35-7.61 (6H, m, naphthalene-H), 7.75 (1H, m, ArH), 7.85 (1H, m, ArH)
- $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta_{\text{C}}$ : 154.96, 140.93, 134.30, 131.77, 129.96, 123.60, 122.70, 119.82, 118.92, 113.76, 113.64, 41.40, 40.98, 40.56, 40.14, 39.72, 39.31, 38.88

**Synthesis of 4-Amino-2-methoxyphenylazo 2'-chlorophenylazo-3-mercapto-2,4,5-thiadiazole 5d:** A mixture of 4-amino-2-chlorophenylazo-3-mercapto-2,4,5-thiadiazole (1.23 g, 0.0153 mole), water (25 mL) and concentrated sulphuric acid (5 mL) was cooled to  $0\text{-}5^\circ\text{C}$ . Sodium nitrite solution (2.5 g, 0.01449 mole) in 10 mL water was added dropwise and stirred for 20 min. The resultant diazonium salt solution was added to 1.5 mL of m-anisidine in 5 mL of acetic acid and stirred for 2 h. The precipitated product was obtained by filtration, washed with water and air-dried. Recrystallization of the crude product gave orange crystals m.p.  $200^\circ\text{C}$ , yield (72%):

- IR (KBr)  $\nu = 3317.67\text{-}3439.19\text{ cm}^{-1}$  ( $\text{NH}_{2\text{str}}$ ),  $3076.56\text{-}3167.22\text{ cm}^{-1}$  ( $\text{C-H}_{\text{str}}$ ),  $2364.81\text{ cm}^{-1}$  ( $\text{S-H}_{\text{str}}$ ),  $1593.25\text{ cm}^{-1}$  (Ar-ring),  $1219.05\text{ cm}^{-1}$  (Thiazole ring),  $1051.53\text{ cm}^{-1}$  ( $\text{OCH}_3$ ),  $833.28\text{ cm}^{-1}$  ( $\text{C-Cl}_{\text{str}}$ )

- $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta_{\text{H}}$ : 2.45 (3H, s, OCH $_3$ ), 2.67 (2H, s, NH $_2$ ), 3.65 (1H, s, SH), 6.83-7.21 (3H, m, ArH), 7.40 (1H, m, ArH), 7.96 (1H, m, ArH)
- $^{13}\text{C}$  NMR (CDCl $_3$ )  $\delta_{\text{C}}$ : 132.09, 41.45, 41.03, 40.60, 40.19, 39.78, 39.35, 38.94

**Synthesis of 4-Amino-2-hydroxyphenylazo-2'-chlorophenylazo-3-mercapto-2'', 4, 5-Thiadiazole 5e:** Orange crystals of compound 5e was obtained using the procedure similar to that of compound 5c m.p. 175°C yield (75%):

- IR (KBr)  $\nu$  = 3300.31-3439.19  $\text{cm}^{-1}$  (O-H $_{\text{Str}}$ , N-H $_{\text{Str}}$ ), 2872.10-3169.15  $\text{cm}^{-1}$  (C-H $_{\text{Str}}$ ), 2362.88  $\text{cm}^{-1}$  (S-H $_{\text{Str}}$ ), 1593.25  $\text{cm}^{-1}$  (Ar-ring), 1253.77  $\text{cm}^{-1}$  (Thiazole ring), 833.28  $\text{cm}^{-1}$  (C-Cl $_{\text{Str}}$ )
- $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta_{\text{H}}$ : 1.24-2.92 (2H, S, 2NH $_2$ ), 3.65 (1H, S, SH), 6.82-7.25 (4H, m, ArH), 7.60 (1H, m, ArH), 8.02 (1H, m, ArH), 8.95 (1H, S, OH)
- $^{13}\text{C}$  NMR (CDCl $_3$ )  $\delta_{\text{C}}$ : 94.52, 41.40, 40.67, 40.25, 39.84, 39.42, 38.98

**Synthesis of 4-Aminonaphthaleneazo-2-chlorophenylazo-3-mercapto-2',4,5-Thiadiazole 5f:** Compound 5f was obtained using the method described for compound 5a. m.p. 180°C yield (63%):

- IR (KBr)  $\nu$  = 3346.61-3375.54  $\text{cm}^{-1}$  (NH $_{\text{Str}}$ ), 3053.42  $\text{cm}^{-1}$  (C-H $_{\text{Str}}$ ), 2362.88  $\text{cm}^{-1}$  (S-H $_{\text{Str}}$ ), 1595.18  $\text{cm}^{-1}$  (Ar-ring), 1492.95  $\text{cm}^{-1}$  (naphthalene ring), 1267.27  $\text{cm}^{-1}$  (Thiazole ring), 844.85  $\text{cm}^{-1}$  (C-Cl $_{\text{Str}}$ )
- $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta_{\text{H}}$ : 1.20-2.64 (2H, s, 2NH $_2$ ), 3.00 (1H, s, SH), 6.88-7.60 (6H, m, naphthalene H), 7.95 (1H, m, ArH), 8.21 (1H, m, ArH)
- $^{13}\text{C}$  NMR (CDCl $_3$ )  $\delta_{\text{C}}$ : 1451.48, 138.41, 134.74, 131.25, 129.67, 128.52, 126.79, 125.34, 123.86, 116.89, 112.05, 108.91, 57.07, 48.78, 41.49, 40.60, 40.18, 39.76, 39.34, 38.91

## MATERIALS AND METHODS

2-Amino-5-mercapto-1,3,4-thiadiazole, 2-chloroaniline, 2-amino-9-ethylcarbazole, 3-chloroaniline, 2-naphthol, m-anisidine, 3-aminophenol and 1-naphthylamine were purchased from Aldrich Chemical Co (USA) and Fluka Chemical Co (Germany) and used without further purification. All other reagents used were of synthesis grade. This study was a part of the large project on the use of heterocycles in the synthesis of dyes carried out in the Chemistry Laboratory of Delta State University, Abraka (Nigeria) during 2011-2012.

**Chemical and instrumental analysis:** Infrared (IR) spectra (KBr pellets) were recorded using Shimadzu FT-IR model 8400S spectrophotometer. Nuclear magnetic resonance ( $^1\text{H}$  NMR) and Carbon-13 nuclear magnetic resonance ( $^{13}\text{C}$  NMR) were recorded on mercury 200BB (199.97 MHz) series spectrometer with deuterated dimethylsulphoxide (DMSO- $d_6$ ) and chloroform (CDCl $_3$ ) as solvents and Tetramethylsilane (TMS) as internal standard. Chemical shifts are expressed in parts per million (ppm) downfield from the internal standard. Using Thin Layer Chromatography (TLC) we assessed the reactions and the purity of the products using Merck made Precoated Silica gel GF aluminum plates and Toluene: methanol (9.1) as solvent system. Melting points were determined in open capillary tubes and were uncorrected. The (UV-VIS) absorption spectra were recorded on Genesys 10S VI. 200 series spectrophotometer.

### **Dye application**

**Dye dispersions:** Each dye (1.0 g) was dissolved in N, N-dimethyl formamide (DMF) and then added to a solution of dispersing agent (Lignosulfonate-sulphite cellulose liquors) and made up to 100 mL mark.

**Nylon 66 fabric:** The dyebath was prepared by mixing the dye dispersion with an acid buffer pH 5 (Lenacid NL 1.2 mL of 10%). The nylon fabric (2.0 g) was wetted and immersed in the dyebath at 45°C. The bath temperature was then raised to 102°C over 15 min and this was maintained for 30 min. At this temperature, formic acid (1.5 mL of 10%), was added to the dyebath, to achieve good exhaustion. After cooling, the dyed fabric was rinsed and reduction-cleared twice with lodet T (2.0 g L<sup>-1</sup>) in a bath containing water (material to liquor 1: 2) at 46°C for 15 min followed by washing thoroughly with cold water and air-dried.

**Acrylic fabric:** Acrylic fabric was dyed at 100°C for 1 h on an Ahiba Texomat dyeing machine and a dyebath containing 1% of weight of fibre (owf) and 2% of weight of fibre (owf) dispersing agent and 1 molar equivalent of N,N-dimethyl ethylenediamine. The pH of dyebath was adjusted to 5 using formic acid and liquor ratio 60:1. At the end of the dyeing process, the fabric was removed from the hot dyebath, soaped off, rinsed with cold water and air-dried (Giles, 1974).

### **Fastness testing**

**Light fastness:** The light fastness was assessed by exposing the fabrics to the Xenon arc Lamp of an Atlas 3 SUN Weather-Ometer, according to the conditions of AATCC Test Method 1.6 E-1990 (AATCC, 1990; ISO, 1994). The conditions for the test were: Black panel temperature 63°C, dry bulb temperature, 43°C; relative humidity 30%; duration of test is 24 h. After testing, the samples were rated against standard blue wool samples (grade 1-8) and the indications for the Grey Scale for light fastness were 1-2 (poor) and 8 (excellent).

**Wash fastness:** The wash fastness of dyed samples were determined according to the International Standard Organisation (ISO) washing test number 3 (ISO, BO2, ISO, 1989). The composite samples measuring (10×5 cm) were treated with a solution containing 5 g L<sup>-1</sup> soap and 2 g L<sup>-1</sup> sodium carbonate and liquor ratio 50:1 for 30 min at 60°C. The change in colour of the tested specimens and the degree of staining of the adjacent undyed fabrics were rated against the Grey Scales. The indications in this case are 1 to 5 where 1 (poor) and 5 (excellent).

**Perspiration fastness:** Colour fastness to perspiration was evaluated (ISO, 105-E04, ISO, 1994) by treating the dyed fabrics (10×4 cm) in an alkaline solution of freshly prepared 0.5 g L<sup>-1</sup> l-histidine monohydrochloride mono-hydrate, 5 g L<sup>-1</sup> sodium chloride, 2.5 g L<sup>-1</sup> disodium hydrogen orthophosphate and 0.1 M sodium hydroxide liquor ration 50:1. The acid perspiration test solution contains: 0.5 g L<sup>-1</sup> l-histidine mono-hydrochloride mono-hydrate, 5 g L<sup>-1</sup> sodium chloride, 2.2 g L<sup>-1</sup> sodium dihydrogen orthophosphate and 0.1M acetic acid solution. The tested dyed fabrics were then rated against the Grey scales for colour changes (ISO, E04, ISO, 1989).

**Sublimation fastness:** The fastness test to sublimation was assessed according to ISO (1993) methods. The dyed fabrics were treated in a sublimation testing machine at 177°C for 30 sec and then rated against the standard Grey Scales (grade 1-5): 1 (poor), 5 (excellent).

The fading rate of a coloured textile fabric when exposed to various agencies such as sublimation (heat), light, perspiration and so on, is usually evaluated through fastness test. In addition to this, the chemical composition and the crystallinity of the textile fibre also affect the rate of fading.

## RESULTS AND DISCUSSION

The six hetaryl disazo disperse dyes (5a-f) were synthesized by the coupling reactions of the diazonium salt solutions of the azo compound 3 with various coupling compounds as illustrated in Fig. 2. The structures of the synthesized dyes were characterized by IR;  $^1\text{H}$ NMR,  $^{13}\text{C}$  NMR and UV-VIS analyses as shown in the experimental section. The melting points of the compounds are moderate for compounds 5a-c but compounds 5d-f have much higher melting points than the former probably because of the substituent groups and also the benzene nucleus present in the couplers. All the dyes gave moderately high yields except dye 5d which gave relatively high yields.

**Absorption spectra:** Table 1 shows the UV-VIS absorption spectral data of the synthesis dyes 5a-f. The absorption maxima ( $\lambda_{\text{max}}$ ) of dyes did not vary much from each other. However, the absorbance showed slight differences. The value of the molar extinction coefficient ( $\log \epsilon$ ) of the dyes were 4.063, 4.317, 4.416, 4.277, 4.355 and 4.321 and these are consistent with their high absorption intensities. The presence of electron donating or electron withdrawing groups did not bring about any marked increase in the  $\lambda_{\text{max}}$  values. This is as a result of the presence of similar substituent groups in both the diazo and coupler components.

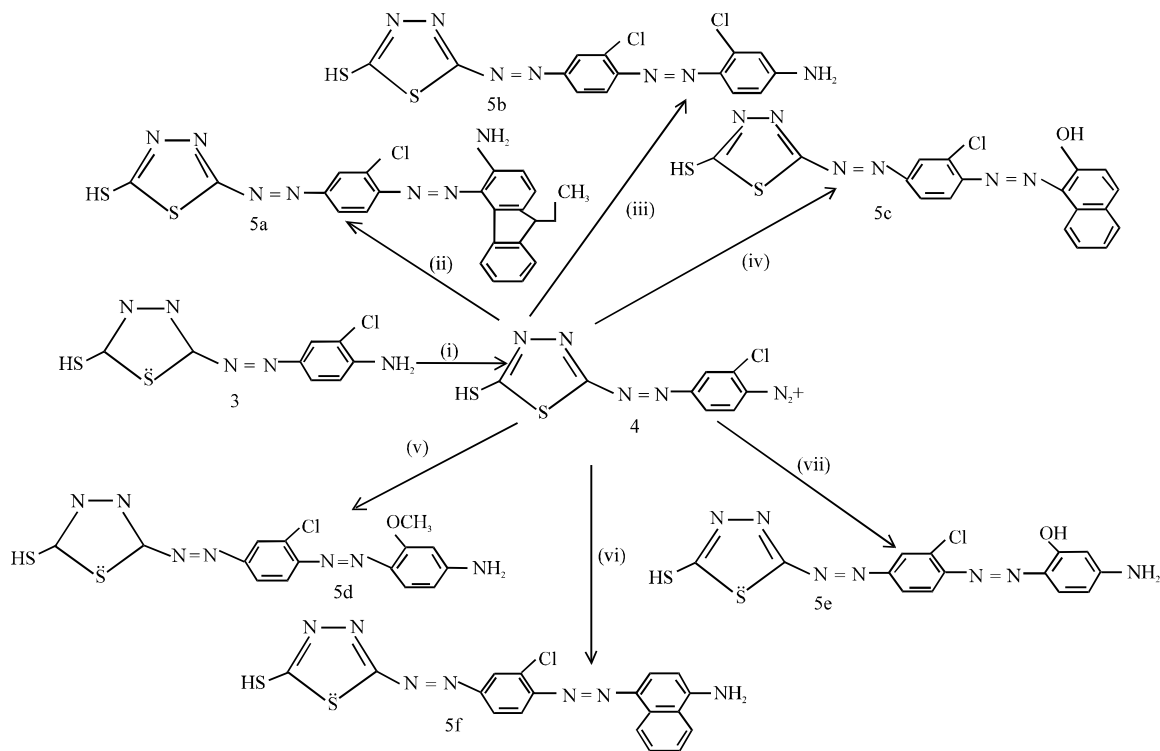


Fig. 2: Synthesis scheme for the preparation of dyes 5a-f, (i) HONO, 0-5°C, (ii)  $\text{C}_{15}\text{H}_{12}\text{N}$ , (iii)  $\text{C}_6\text{H}_6\text{NCl}$ , (iv)  $\text{C}_{10}\text{H}_8\text{O}$ , (v)  $\text{C}_7\text{H}_9\text{NO}$ , (vi)  $\text{C}_{10}\text{H}_9$

**Note:** The reason for the difference in ( $\lambda_{\max}$ ) between 5b and 5f is due to the fact that 5f exhibited higher conjugation than 5b.

In Table 1, the distance that each dye travelled on the TLC plate, expressed as  $R_f$  values are shown. The  $R_f$  value of a compound is the ratio of the distance travelled by the compound to that covered by the solvent, measured from the starting line. Under the same experimental conditions, the  $R_f$  value of a compound is a characteristic value. The position and character of the substituents in the dye structure or aromatic nuclei has considerable influence on the  $R_f$ .

In this study, the dyes have almost the same basic skeleton except for the different substituents on the couplers. For instance, dye 5b and 5d exhibited relatively lower  $R_f$  values of 0.53 and 0.56 due to the presence of the chlorine atoms and  $-\text{OCH}_3$  group, respectively (Moore *et al.*, 1982). On the other hand, dyes 5a-f showed relatively higher  $R_f$  values as a result of the smaller dipole moments in the dye structures.

### Fastness properties

**Wash fastness:** Table 2 shows the results of the wash fastness tests on acrylic fabric and nylon fabric. The wash fastness showed excellent performance on the two substrates used for the study. The high molecular size of the dyes is believed to be responsible for the high wash fastness ratings. This also revealed that the dyes have high affinity for the two fibre substrates (Birds and Boston, 1975) used for the study.

Table 1: Wavelength ( $\lambda_{\max}$ ), molar extinction coefficient ( $\epsilon$ ), Intensity ( $\log \epsilon$ ) of dyes 5a-f

Dye	$\lambda_{\max}$ *(nm)	Absorbance	$\epsilon_{\max}$ *( $1 \text{ mol}^{-1} \text{ cm}^{-1}$ )	Rf	Intensity ( $\log E$ )
5a	431.56	0.94798	11561	0.61	4.063
5b	412.55	2.03530	20768	0.53	4.317
5c	460.75	2.52960	26078	0.82	4.416
5d	446.48	1.87450	18934	0.56	4.277
5e	437.88	1.53920	22635	0.65	4.355
5f	468.87	1.96910	20947	0.72	4.321

\*measured in DMF

Table 2: Wash fastness ratings of the dyes on acrylic and nylon 66 fabrics

Dye	Type of fabric	Staining					
		Change	Acetate	Cotton	Nylon	Polyester	Acrylic
5a	Acrylic	5	5	5	4-5	5	5
	Nylon	5	5	5	5	5	5
5b	Acrylic	5	5	5	5	5	5
	Nylon	5	5	5	5	5	5
5c	Acrylic	5	5	5	4-5	5	5
	Nylon	5	5	5	5	5	5
5d	Acrylic	5	5	5	4-5	5	5
	Nylon	5	5	5	5	5	5
5e	Acrylic	5	5	5	5	5	5
	Nylon	5	5	5	5	5	5
5f	Acrylic	5	5	5	5	5	5
	Nylon	5	5	5	5	5	5

Grey scale for assessing wash fastness is 1-5 where 1 (poor) and 5 (excellent)



Table 3: Light, sublimation and perspiration fastness ratings of the dyes on acrylic nylon 66 fabrics

Dye	Type of fabric	Perspiration				Colour on fabrics
		Light	Sublimation	Acid	Alkaline	
5a	Acrylic	4-5	5	4	5	Greenish orange
	Nylon	5	5	5	5	
5b	Acrylic	4-5	5	4	5	Orange
	Nylon	5	5	5	5	
5c	Acrylic	5	5	5	5	Orange
	Nylon	5	5	5	5	
5d	Acrylic	4-5	5	4	5	Orange
	Nylon	5	5	5	5	
5e	Acrylic	4-5	4	4	5	Orange
	Nylon	5	4	5	5	
5f	Acrylic	5	5	5	5	Yellowish brown
	Nylon	4-5	5	5	5	

Grey scale for assessing light fastness is grade 1-8 where 1 (poor) and 8 (excellent) while the grey scale for other agencies is 1-5

**Light fastness:** The results of the light fastness tests for dyes 5a-f in acrylic fabric and nylon 66 fabric are summarized in Table 3 and they showed good ratings of 4-5 and 5.

However, the photostability of nylon fabric appear to be much higher than that of acrylic fabrics especially for dyes 5a-e. The hydroxyl substituent, ortho to the azo groups in the dye structure is believed to increase the light fastness of the nylon dyeings particularly because there could be hydrogen-bond formation. That is, the amide hydrogen of the nylon could hydrogen bond with the hydroxyl oxygen of the dye thereby increasing photostability. This is quite opposite to the polyester dyeings with disperse dyes (David and Halias, 1994) where -OH and -NH<sub>2</sub> ortho to the azo groups decrease photostability.

The results of the perspiration fastness show that all the dyes exhibited excellent alkaline perspiration fastness on both acrylic fabrics and nylon fabrics whereas the acid perspiration showed good fastness ratings of 4 on acrylic fabrics and excellent fastness ratings of 5 on nylon fabrics.

**Sublimation fastness:** The results of the sublimation fastness tests were summarized in Table 3 and all showed excellent ratings on both acrylic fabrics and nylon fabrics. This is due to the presence of the halogen (chlorine) atom substituent in the dye molecules which usually increase the sublimation fastness ratings of disperse dyes on polymer fibres (Shuttleworth and Weaver, 1990).

## CONCLUSION

Disazo disperse dyes of 2-amino-5-mercapto-1,3,4-thiadiazole and 2-chloroaniline derivatives were synthesized and their application on acrylic fabric and nylon 66 fabric were determined. Their structures were confirmed from their respective spectral data such as IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and UV-VIS studies. Results showed that the presence of electron-withdrawing and electron donating groups in the dye structures had much influence on the yield of the azo compounds.

The results of the fastness tests of the disazo compounds showed that they have affinity for the acrylic and nylon 66 fabrics. The dyes exhibited higher light fastness ratings on nylon fabric than

on the acrylic fabrics. All the dyes, however, showed excellent sublimation and perspiration fastness ratings on nylon fabrics except the acid perspiration fastness of the dyes on acrylic fabric which gave good ratings.

## REFERENCES

- AATCC, 1990. AATCC technical manual, volume 65. American Association of Textile Chemist and Colorist, USA., pp: 33.
- Al-Juaid, S.S., 2007. Mono azo dyes compounds as corrosion inhibitors for dissolution of aluminum in sodium hydroxide solutions. *Portugaliae Electrochem. Acta*, 25: 363-373.
- Birds, C.L. and W.S. Boston, 1975. *The Theory of Coloration of Textiles*. Soc. Dyes and Colourists, Bradford, UK.
- David, R.W. and G. Halias, 1994. *The Chemistry and Application of Dyes*. Plenum Press, New York.
- Edwards, L.C. and H.S. Freeman, 2005. Synthetic dyes based on environmental considerations. Part 3: Aquatic toxicity of iron-complexed azo dyes. *Colorat. Technol.*, 121: 265-270.
- Giles, C.H., 1974. *Laboratory Course Dyeing*. 3rd Edn., Society of Dyers and Colourists (SDC), Bradford, UK.
- Gregory, P., 1994. Application of Dyes. In: *The Chemistry and Application of Dyes*, David, R.W. and H. Geoffery (Eds.). Plenum Press, New York, London.
- ISO, 1989. ISO 105-CO<sub>2</sub>: Textiles-tests for colour fastness-Part CO<sub>2</sub> colour fastness to washing test 3. International Organization for Standardization, Geneva.
- ISO, 1993. Textile test for colour fastness part PO1: Colour fastness to sublimation International Organization for Standardization, Geneva.
- ISO, 1994. ISO 105-E04: Textiles-tests for colour fastness-Part EO4, colour fastness to perspiration. International Organization for Standardization, Geneva.
- Joseph, A., P. Aravinda, K.K. Srinivasan, K. Tukaram, T.T. Angel, E.M. Jessy and K.S. Rajeev, 2010. Synthesis and anticancer activity of some novel 3-(1, 3, 4-thiadiazol-2-yl)-quinazolin-4-(3H)-ones. *Orbital-Electron. J. Chem.*, 2: 158-167.
- Kidwai, M. and Priya, 2008. Synthesis of quinazolinone analogues using sodium perborate as catalyst. *Indian. J. Chem.*, 47B: 1876-1881.
- Moore, A.J., D.L. Dalrymple and O.R. Rodig, 1982. *Experimental Methods in Organic Chemistry*. 3rd Edn., Saunders College Publicher, New York, pp: 64-89.
- Ortega-Luom, P., L. Vera, C. Astudillo, M. Guzman and P. Ortega-Lopez, 2007. Synthesis of metallic Azoderivatives of 2-Amino-5-mercapto-1,3,4-thiadiazole. *J. Chil. Chem. Soc.*, 52: 835-837.
- Otutu, J.O., 2013. Synthesis and application of monoazo disperse dyes derived from 2-Amino-5-mercapto, 1,3,4-thiadiazole on polyester fabric. *Int. J. Res. Rev. Applied Sci.*, (In Press).
- Seferoglu, Z., 2009. A study on tautomeric equilibria of new netarylazo-6-aminouracils. *Arkivoc*, 28: 42-57.
- Shuttleworth, L. and M.A. Weaver, 1990. Dyes for Polyester Fibers. In: *The Chemistry and Application of Dyes*, David, R.W. and G. Halias (Eds.). Plenum Press, New York and London, pp: 107-162.