

# SYNTHESIS AND APPLICATION OF AZO DYES DERIVED FROM 2-AMINO-1, 3,4-THIADIAZOLE-2-THIOL ON POLYESTER FIBRE

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## ABSTRACT

The synthesis and application of azo dyes derived from 2-Amino-1, 3,4-thiadiazole-2-thiol on polyester fibre are described. The absorption maxima of the dyes were dependent upon the substituents in the diazo and coupling components and varied from 351 to 777 nm in DMF. Polyester fabric was successfully dyed with the synthesized dyes. The dyes showed good to excellent fastness properties on polyester fabrics, indicating that they have affinity for it. The spectral properties (IR, <sup>1</sup>HNMR, <sup>13</sup>CNMR and visible spectra) of obtained dyes are reported. The results of the electronic absorption spectra of dyes obtained from heterocyclic diazo and coupling components showed that they could act as organic photoconductors.

**Keywords:** *Thiadiazole dyes; Disperse dyes, polyester fibre, light fastness, washing and rubbing fastness.*

## 1. INTRODUCTION

Azo compounds are a class of chemical compounds that are continuously receiving attention in scientific research (Kirkan, 2008; Otutu *et al.*, 2011; Seferoglu, 2009). They are usually strongly coloured compounds which can be intensely yellow, red, orange, blue or even green, depending on the exact structure of the molecule. As a result of their colour, azo compounds are tremendous importance as dyes and also as pigments for a long time (Ebenso *et al.*, 2008). Infact, about half of the dyes in industrial use today are azo dyes, which are mostly prepared from diazonium salts (Robert, 2011; Zollinger, 2003). The structural features in organic compounds, that usually produce colour are >C=C<, -N=O, -N=N-, aromatic rings, >C=O and -NO<sub>2</sub>. Most importantly, the groups that invariably confer colour are the azo (-N=N-) and nitroso (-N=O) while the other groups actually do so under certain circumstances (Abrahart, 1977). Furthermore, azo dyes have been studied widely because of their excellent thermal and optical properties in applications such as optical recording medium (Samichet *et al.*, 2008), toner (Kirkan and Gup, 2008), ink-jet printing (Gregory, 1990), and oil-soluble light fast dyes. Recently, azo compounds as organic dyes have also attracted attention due to their interesting electronic features in connection with their application for molecular memory storage, nonlinear optical elements and organic photoconductors (Yildiz and Boztese, 2002).

A survey of the literature reveals that the intermediate for this study, 2-amino-1, 3, 4-thiadiazole-2-thiol has recently been used to synthesize two organic dyes and their metal complexes, using carbocyclic coupling components (Ortega-Luoniet *et al.*, 2007). This intermediate has also been used to prepare some complexes as corrosion inhibitors (Ebenso *et al.*, 2008).

The present paper reports on the synthesis of three new heterocyclic azo compounds. Three carbocyclic compounds such as resorcinol, 2-aminobenzonitrile and 2-naphthol were also used as coupling compounds with 2-amino-1, 3, 4-thiadiazole-2-thiol as the diazo component to synthesise three other azo dyes for comparison purposes. The chemical structures of the azo dyes were studied using spectral methods. The azo dyes were also applied on polyester fibres and their fastness properties were evaluated.

## Chemical and Instrumental Analysis

All the melting points were uncorrected and determined in a Kofler apparatus. Infrared spectra were recorded using Shimadzu (8400) FT-IR Spectrometer. <sup>1</sup>HNMR (199.96 MHz) and <sup>13</sup>CNMR (199.96 MHz) were recorded on a mercury 200BB series spectrometer. DMSO-d<sub>6</sub> was used as NMR solvent. Chemical shifts were reported in δ units in parts per million (ppm) downfield from internal tetramethylsilane (TMS). Ultraviolet-visible (UV-VIS) absorption spectra were recorded on genesis 10S, VI. 200 series spectrophotometer.

## Washing Fastness

Fastness to washing was assessed by washing the reduction-cleared dyed fabrics according to the ISO C06/C2S, wash test using soap solution (5g, liquor ratio 50:1) for 45 minutes at 60°C. The change in shade and staining of adjacent fabrics were assessed according to Society of Dyers and Colourists grey scale (ISO, 1994).

## Rubbing Fastness

Rubbing fastness was determined according to ISO, 2001 Test Method (ISO, 2001).

## 2. MATERIALS AND METHODS

This study was conducted in the Chemistry Laboratory of Delta State University, Abraka (Nigeria) during 2010-2011.

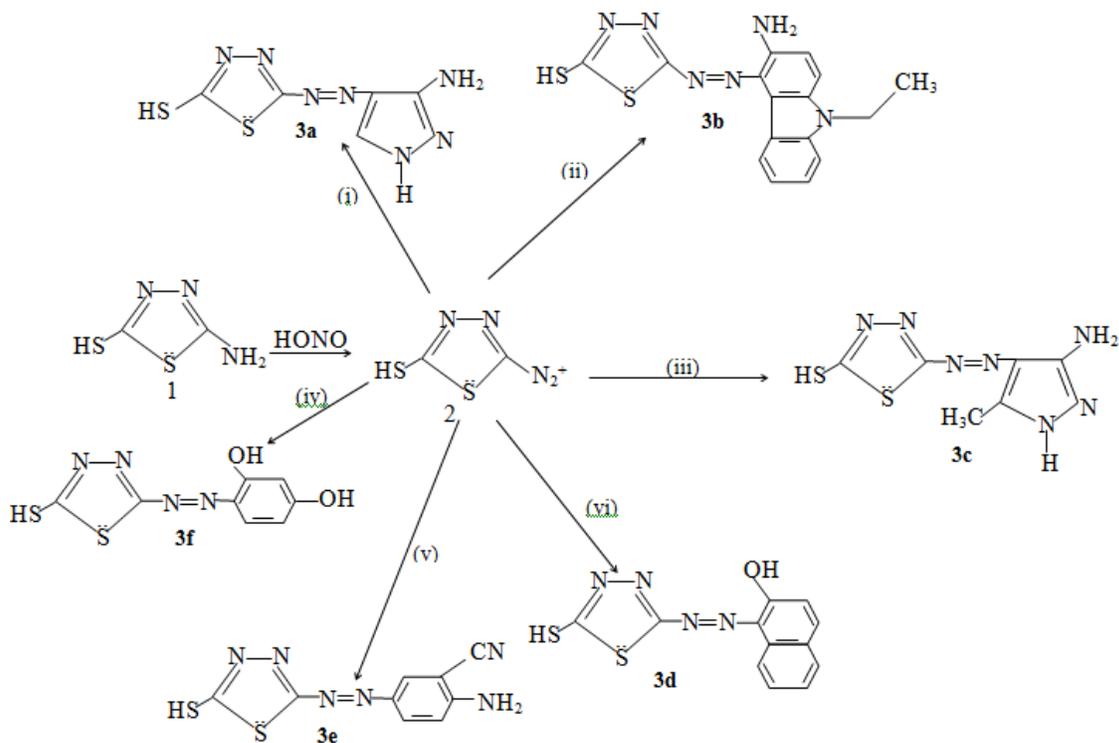
**Materials:** 2-Amino-1, 3, 4-thiadiazole-2-thiol, 3-Amino pyrazole, 3-amino-9-ethyl carbazole, 3-amino-5-methylpyrazole, 2-naphthol, 2-amino-benzonitrile and resorcinol were obtained from Aldrich Chemical Company and were used without further purification. All other chemicals used in the preparation and characterization were Laboratory reagent and analytical grades.

### Methods

#### Preparation of Dyes

##### 3-Aminopyrazoleazo -4-thiol-2,3,5-thiadiazole 3a

5-Amino-1,3,4-thiadiazole-2-thiol (2.0 g 0.0119 mole) was mixed with water. The amine was diazotized in 5 ml of concentrated sulphuric acid by adding sodium nitrite (2.0 g, 0.0289 mole) solution in 10 ml of water dropwise at 0 – 5°C. And stirred for 20 minutes at this temperature. Excess nitrous acid was destroyed by the addition of urea (approximately, 0.1g). The diazo liquor obtained was added slowly to a vigorously stirred solution of 3-aminopyrazole (1.5g, 0.0181 mole) in glacial acetic acid (5 ml). The reaction mixture was then stirred for 2 hours and the resulting product was filtered, washed with water, dried and recrystallized from ethanol to give the titled compound as reddish brown solid crystals in 50% yield, m.p. 198 – 200°C, <sup>1</sup>HNMR (DMSO-d<sub>6</sub>): 8.01 (m, 1H, NH); 7.16 (s, 1H, SH); 5.17 (s, 1H, CH), 2.45 (s, 2H, NH<sub>2</sub>), <sup>13</sup>CNMR (DMSO-d<sub>6</sub>): 41.02, 40.60, 39.77, 38.94, 37.89; FT-IR(KBr), 3276cm<sup>-1</sup>(v NH), 3062 cm<sup>-1</sup>(v CH), 1585 cm<sup>-1</sup>(v-N=N-); UV(λ<sub>max</sub>, nm, DMF): 605, 779.



**Scheme 1**

Synthesis scheme for the preparation of azo disperse dyes 3a – f by diazotization of 2-amino-1,3,4-thiadiazole-2-thiol and coupling with the following amines and phenols:

(i) C<sub>4</sub>H<sub>5</sub>N<sub>3</sub> (ii) C<sub>15</sub>H<sub>14</sub>N<sub>2</sub> (iii) C<sub>5</sub>H<sub>7</sub>N<sub>3</sub> (iv) C<sub>10</sub>H<sub>8</sub>O (v) C<sub>7</sub>H<sub>6</sub>N<sub>2</sub> (vi) C<sub>6</sub>H<sub>6</sub>O<sub>2</sub>

**2-Amino-5-ethylcarbazoleazo-4-thiol-2,3,5-Thiadiazole3b**

Compound **3b** was obtained following the procedure similar to that used for synthesizing compound **3a**, producing a dark green compound after crystallization from ethanol in 69% yield, m.p = 225 – 227<sup>o</sup>C, <sup>1</sup>HNMR (DMSO-d<sub>6</sub>): 7.60 (m, 6H, ArH), 7.20 (m, 2H, CH<sub>2</sub>), 7.10 (t, 3H, CH<sub>3</sub>), 7.00 (s, 1H, SH), 1.26 – 2.45 (s, 2H, NH<sub>2</sub>); <sup>13</sup>CNMR(DMSO-d<sub>6</sub>): 140.93, 139.32, 127.38, 123.27, 123.05, 122.09, 121.40, 119.93, 115.56, 110.78, 41.45, 40.50, 39.76, 38.93, 37.87. FT-IR(KBr), 3564 cm<sup>-1</sup>(v NH), 3074 cm<sup>-1</sup> (v C-H), 1589 cm<sup>-1</sup>(v-N=N-), 1208 cm<sup>-1</sup> (v SH); UV(λ<sub>max</sub>, nm, DMF): 578, 750.

**3-Amino-4-methylpyrazoleazo-4-thiol-2,3, 5-Thiadiazole3c**

Compound **3c** was obtained following the procedure similar to that used for the preparation of compound **3a** producing a brown solid in 49% yield, m.p = 178 – 180<sup>o</sup>C, <sup>1</sup>HNMR (DMSO-d<sub>6</sub>): 7.15 (s, 1H, NH), 4.45 (s, 3H, CH<sub>3</sub>), 2.46 (s, 1H, NH), 2.20 (s, 2H, NH<sub>2</sub>), <sup>13</sup>CNMR(DMSO-d<sub>6</sub>): 41.84, 41.44, 40.60, 40.19, 39.77, 39.36, FT-IR(KBr):3602cm<sup>-1</sup>(v NH), 3037 cm<sup>-1</sup> (v C-H), 1580 cm<sup>-1</sup>(v-N=N-), 1073 cm<sup>-1</sup> (v S-H); UV(λ<sub>max</sub>, nm, DMF): 583, 777.

**2-Hydroxynaphtholazo-4-thiol-2,3,5-thiadiazole3d**

Compound **I** (2.0 g, 0.003 mole) was mixed with water and diazotized in 50% V/V HCl (25 ml) by treatment with sodium nitrite solution (1.0 g, 0.0145 mole) in 10 ml water at 0<sup>o</sup>C. Excess of nitrous acid was destroyed by the addition of approximately 0.1 g of urea. The diazonium salt solution obtained was added portionwise to the coupling component solution, 2-naphthol (2.20 g, 0.003 mole) which was prepared by adding sodium hydroxide solution (1.25 g, 0.031 mole) in 25 ml water. 25 ml more sodium hydroxide solution was added to the reaction mixture and allowed to react for 2 hours to give a dark brown solid, after recrystallization from N-N-dimethylformamide – water (2:1) mixture (1.62 g, 54%) yield, m.p. = 218 – 220<sup>o</sup>C, <sup>1</sup>HNMR (DMSO-d<sub>6</sub>): 8.45 (s, 1H, naphthalene-H) 6.85 – 8.20 (m, 6H, naphthalene-H), 3.95 (s, 1H, SH); <sup>13</sup>CNMR (DMSO-d<sub>6</sub>): 155.94, 133.95, 130.96, 129.96, 126.85, 124.23, 123.32, 119.28, 109.31, 41.41, 38.90, 38.80, FT-IR(KBr): 3706 cm<sup>-1</sup> (v OH), 3061 cm<sup>-1</sup> (v C-H), 1585 cm<sup>-1</sup> (v-N=N-), 1073 cm<sup>-1</sup> (v S-H); UV (λ<sub>max</sub>, nm, DMF): 515.

**4-Amino-3-benzonitrileazo-4-thiol-2,3,5-thiadiazole3e**

As for the procedure used for the preparation of **3a**, where the coupling component was 2-aminobenzonitrile. The titled compound was obtained in 30% yield, m.p = 208 – 210<sup>o</sup>C, <sup>1</sup>HNMR (DMSO-d<sub>6</sub>): 10.10 (S, 1H, ArH), 9.45 (S, 1H, SH), 6.85 – 7.41 (m, 2H, ArH), 3.60 (s, 2H, NH<sub>2</sub>); <sup>13</sup>CNMR (DMSO-d<sub>6</sub>): 180.25, 147.85, 145.63, 135.69, 127.42, 127.24, 125.40, 40.68, 39.43, 38.60. FT-IR(KBr) 3567 cm<sup>-1</sup> (v NH<sub>2</sub>), 3080 cm<sup>-1</sup> (v C-H), 1536 cm<sup>-1</sup> (v-N=N-), 1073 cm<sup>-1</sup> (v S-H); UV (λ<sub>max</sub>, nm, DMF): 351.

**2, 4-Dihydroxybenzeneazo-4-thiol 1-2, 3,5-thiadiazole3f**

Compound **3f** was obtained following the procedure described for compound **3d** as brown solid (1.6 g, 42%) yield; m.p = 198<sup>o</sup>C; <sup>1</sup>HNMR (DMSO-d<sub>6</sub>): 6.40 – 7.82 (m, 3H, ArH), 4.92(s, 1H, OH), 2.62 (s, 1H, SH), <sup>13</sup>CNMR (DMSO-d<sub>6</sub>): 167.43, 134.27, 122.50, 111.15, 109.84, 58.78, 41.38, 39.28, 38.87, FT-IR(KBr) 3547 cm<sup>-1</sup> (vOH), 3012cm<sup>-1</sup> (v C-H), 1539 cm<sup>-1</sup> (v-N=N-), 1079 cm<sup>-1</sup> (v S-H); UV (λ<sub>max</sub>, nm, DMF): 489.

**Dye Application**

Polyester fabrics were dipped in a dyebath containing the azo dye solution. The azo dye solution was prepared by dissolving it (1.0 g of azo dye) in 5 ml of DMF and making up to 100 ml with a detergent. The pH of the dispersed dye solution was adjusted to 5 by adding acetic acid. Dyeing was carried out for 60 minutes at 130<sup>o</sup> to 135<sup>o</sup>c under increased pressures. The dyed polyester fabric was subjected to reduction-rinsing treatment according to a standard method (Giles, 1974; Burkinshaw, 1994).

**Light Fastness**

The light fastness of the dyed fabrics was tested by exposing them to the Xenon Lamp of an Atlas 3 SUN Weather – O meter, according to the conditions of AATC Test method 16E – 1993 (AATCC, 1993).

**Washing Fastness**

Fastness to washing was assessed by washing the reduction – cleared dyed fabrics according to the ISO C06/C2S, wash-test using soap solution (5 g/l, liquor ratio 50:1) for 45 minutes at 60<sup>o</sup>C). The change in shade and staining of adjacent fabrics were assessed according to Society of Dyers and Colourists grey scale (ISO, 1994).

### Rubbing Fastness

Rubbing fastness was determined according to ISO, 2001 Test Method (ISO, 2001).

### 3. RESULTS AND DISCUSSION

5- Amino -1,3,4-thiazole-2-thiol<sub>1</sub> was used as the diazo component. The synthetic pathway (Carey, 2003; David and Geoffrey, 1994), for the diazotization reaction and subsequent coupling with heterocyclic and carboxylic components is shown in scheme 1. The structures of the six azo disperse dyes were characterized by FT-IR, <sup>1</sup>HNMR, <sup>13</sup>CNMR and UV- visible analyses. The melting points of the azo compounds were relatively close to each other and ranged between 178-227<sup>0</sup>C. Thus they are relatively high melting point azo dyes.

The FT-IR spectra showed the absence of bands representing NH<sub>3</sub> groups but showed NH<sub>2</sub> groups at 3567cm<sup>-1</sup>, in compounds 3b, 3c and 3e respectively. The Thione-hydrogen (-SH) group stretching vibrations was also observed at 1073cm<sup>-1</sup>. The presence of N = N group was observed at 1539 – 1580cm<sup>-1</sup> region. The bands at 3547 – 3706cm<sup>-1</sup> region were assignable to the – OH groups in compounds 3d and 3f.

The <sup>1</sup>HNMR spectral analysis showed the presence of the proton environments which are in agreement with those reported earlier in literatures (Paula, 1995; Otutu *et al.*, 2008).

The <sup>13</sup>CNMR spectral data provided evidence of carbon atoms in heterocyclic rings in compounds 3a and 3c, however, the presence of carbon atoms in carbocyclic rings in compounds 3b, 3d, 3e and 3f (Katritzky and Rees, 1984) were also shown. Thus, information obtained through <sup>13</sup>CNMR analysis clearly provided enough evidence of purely heterocyclic azo dye compounds and those having heterocyclic and carbocyclic azo dye compounds.

The electronic spectral data for azo dyes 3a, 3b and 3c showed multiplet of absorption bands corresponding to bands in the region 605-779, 578-770 and 583-777nm. Thus, the presence of the nitrogen atoms in the heterocyclic coupling components resulted in a significant shift in the position of these bands compared to those compounds having carbocyclic coupling components.

This is in agreement with previous findings (Karci, 2005; James *et al.*, 1982).

### Fastness Properties

All the dyeing for the fastness test were carried out at pH5 which has been demonstrated to be the optimum. The results of the wash fastness tests for dyes 3a-f on polyester are summarized in Table 1 and showed good to excellent wash fastness. This suggests that the azo dyes have affinity for the polyester fibre. Table 2 gives the results of the light and rubbing fastness tests. The rubbing fastness test results were good and light fastness was moderate to good. The results of dyes 3a and 3e (Table 1) also showed the staining of adjacent white acrylic fabrics and adjacent nylon fabrics (for dyes 3e and 3f).

**Table 1: The Wash Fastness of Dyes 3a – f (1% owf) on Polyester fabric**

Dye	Change	Staining			
		Cotton	Nylon	Acrylic	Polyester
3a	4/5	5	5	4/5	5
3b	5	5	5	4/5	5
3c	5	5	5	4/5	5
3d	5	5	5	4/5	5
3e	4/5	5	4/5	4/5	5
3f	5	5	4/5	4/5	5

**Table 2: The Light and Rubbing Fastness of Dyes 3a – f (1% owf) on Polyester fabric**

Dye	Light	Rubbing	
		Staining	
		Dry	Wet
3a	4	3/4	4/5
3b	4/5	4/5	4/5
3c	4	4	4/5
3d	5	4	4
3e	5	3/4	4/5
3f	4/5	4/5	4/5

## CONCLUSIONS

This paper describes the synthesis and application of azo disperse dye compounds derived from 2-amino-1,3,4-thiadiazole-2-thiol on polyester fibre. And from fastness evaluations, the heterocyclic couplers produced dyes which gave brighter hues on polyester fabric and also gave multiplet absorption bands. The carbocyclic couplers, however, gave dyes with duller hues on polyester fabric and without multiplet absorption bands. The six azo disperse dyes prepared in this study are reddish brown dyes which exhibited good to excellent dyeing properties on polyester fabric. The results of the washing fastness, suggests that the azo disperse dyes have affinity for the polyester fibres. And from the commercial perspective, the dyes can be very important. The very high electronic absorptions of dyes 3a, 3b and 3c in the near infrared region could make them potential candidates to act as organic photoconductors.

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