

SYNTHESIS AND PROPERTIES OF SOME HETARYL DISAZO AND TRISAZO DISPERSE DYE DERIVATIVES OF 2-AMINO-5-NITROTHIAZOLE AND 1-NAPHTHYLAMINE

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ABSTRACT

This paper is concerned with the synthesis and evaluation of some hetaryl disazo and trisazo disperse dyes. They were synthesized via diazotization of 2-amino-5-nitrothiazole followed by the coupling with 1-naphthylamine. The monoazo dye obtained was diazotized and coupled with other diazo and coupling components to afford disazo and trisazo dyes respectively. The spectra properties (^1H NMR, ^{13}C NMR, IR and visible spectra) of obtained dyes are reported. The basic fastness properties (light fastness, wet fastness and sublimation or dry heat treatment) of the dyes on polyester fibre and acrylic fibre are also discussed in terms of their chemical structure. The dyes showed good build up, levelling and fastness properties on acrylic fabrics but poor levelling on polyester fabrics. The electronic absorptions in the near infrared region of some of the dyes suggests that they could be potential candidates as organic photoconductors.

Keywords: 2-amino-5-nitrothiazole, acrylic fibre, polyester fibre, fastness, disazo dyes, trisazo dyes.

1. INTRODUCTION

In recent years, several heterocyclic compounds are extensively used in disperse dye chemistry for textile or non-textile applications (Katritzky, 1984). These dyes are now marketed to produce a full range of dispersed dyestuffs without the use of colorants based on heteroaromatic diazo components. Most of the heterocyclic dyes are derived from the diazo components consisting of five-membered rings containing one or more nitrogen heteroatoms, with the rings being fused into another aromatic ring (Towns, 1999; Samieh *et al.*, 2008; Otutu *et al.*, 2011; Griffiths *et al.*, 1984).

The dyes with heterocyclic diazo components have been intensively investigated, to produce bright and strong colour shades ranging from red to greenish blue on synthetic fabrics. These results led to commercial products to replace the conventional azobenzene disperse dyes. The nitrosubstituted aminothiophenes, and aminothiazoles are primarily of importance as diazo components (Seferoglu, 2009; Bradbury *et al.*, 1995). Recently, Towns has summarized the developments in azo disperse dyes derived from heterocyclic diazo components (Towns, 1999). Non-textile uses of heterarylazo disperse dyes have been explored, for example in reprographic technology, functional dye applications, and non-linear optical systems (Zollinger, 2003; Shuttleworth and Weaver, 1990). The monoazo dyes containing heterocyclic rings or carbocyclic rings result in brighter and often deeper shades than their disazo or trisazo analogues. On the other hand, the disazo or trisazo dyes are very important in applications such as disperse dyes for polyester fibres, and as photoconductors. Dyes of these types are usually produced by careful selection of the diazo and coupling components such as to create room for convenient diazotisation and further coupling. Clearly, the large number of possibilities for disazo structures is very large and the choice is increased further in the trisazo and polyazo series. However, very few trisazo disperse dyes have been reported. Recently, our research has reported the synthesis of a series of monoazo disperse dye derivatives of 2-amino-5-nitrothiazole and their application on polyester fibres (Otutu *et al.*, 2011). The results of this gave good to excellent dyeing properties.

In the present study, the synthesis and application of some disazo and trisazo disperse dyes from 2-amino-5-nitrothiazole and 1-naphthylamine on polyester fibre and acrylic fibre are reported. The dyes were characterised by ^1H NMR, ^{13}C NMR, IR and UV-vis analyses.

The fastness properties of the disazo and trisazo disperse dyes on polyester and acrylic fabrics were also evaluated.

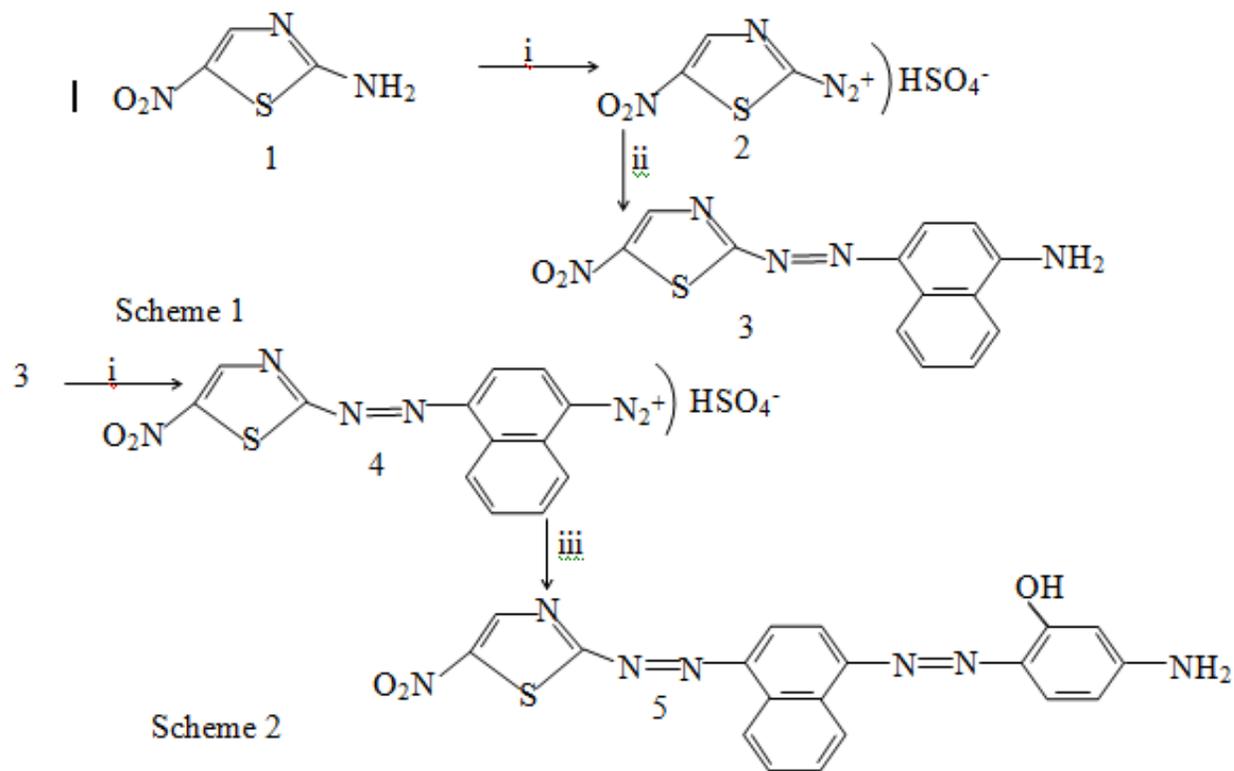
2. EXPERIMENTAL SECTION

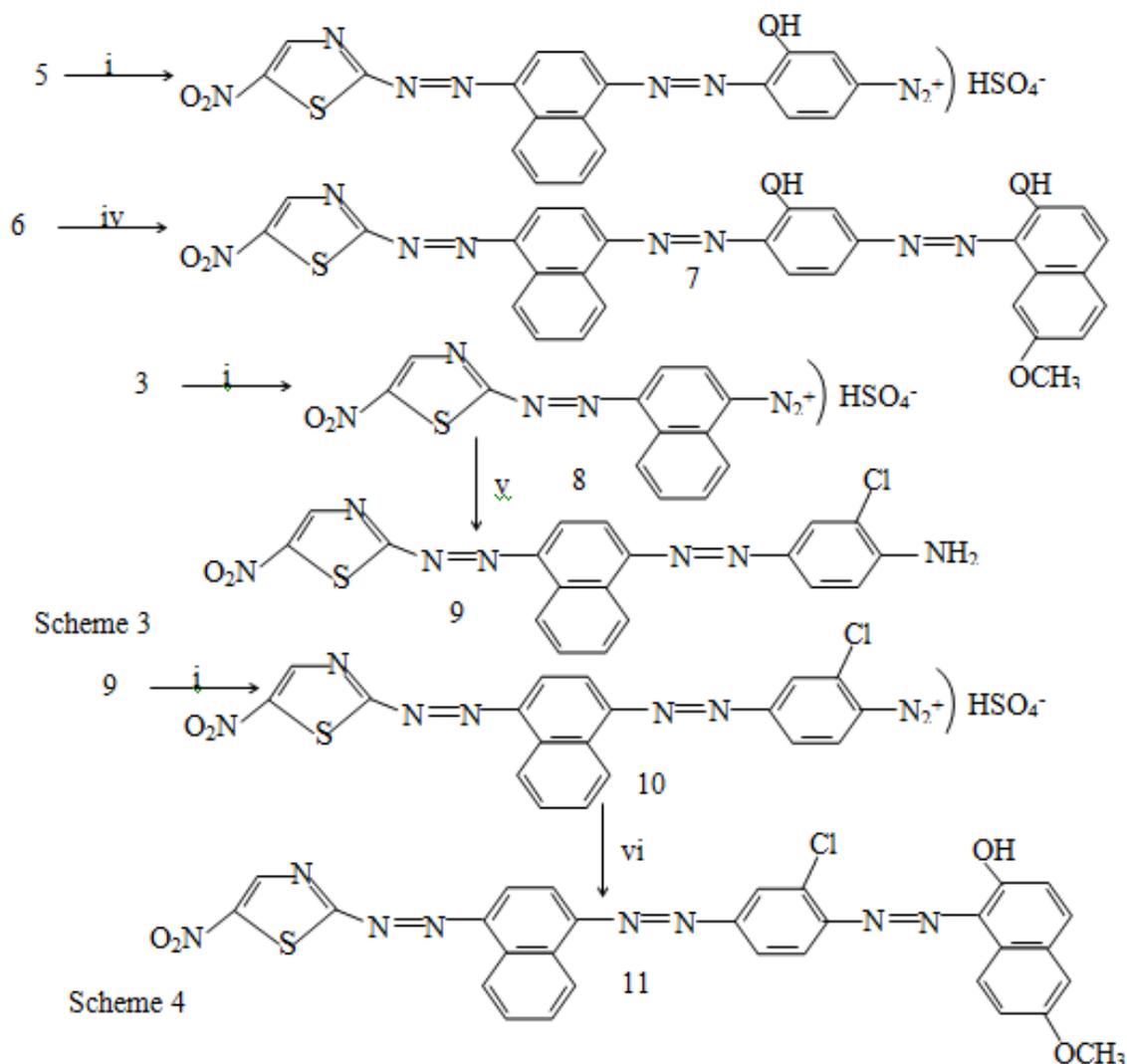
Materials and Methods: The chemicals used in the synthesis of all compounds were obtained from the Aldrich Chemical Company and used without further purification. The solvents used were of spectroscopic grade. IR spectra were recorded on a Shimadzu (8400S) FT-IR in KBr pellets (ν are in cm^{-1}). ^1H NMR and ^{13}C NMR spectra were recorded on Mercury 200BB Series spectrometer in deuterated (CDCl_3). Chemical shifts are expressed in δ units (ppm) downfield from the internal standard, containing 0.03% v/v tetramethylsilane (TMS). Ultraviolet visible

(UV-VIS) absorption spectra were recorded on a Genesys 10S V1.200 series spectrophotometer. Melting points were determined in a Buchi melting point apparatus in glass capillary tubes and are uncorrected.

Synthesis of Compound 3

2-Amino-5-nitrothiazole (4.0 g, 28 mmols) was dissolved in a mixture of 19.0 g ice at 25°C. A solution of 3.50 g NaNO₂ (50.7 mmols) dissolved in 45 g Conc. H₂SO₄ was added drop wise to the aminonitrothiazole solution at -10°C to 0°C with stirring. After 30 minutes of stirring at -10°C to 0°C, the resulting diazonium salt was slowly added to the cooled solution of 1-naphthylamine (4.0 g, 30 mmols) in 8ml of acetic acid. The mixture was stirred at 0-5°C for 1 hour and the precipitate obtained was collected by filtration, washed with water and dried.





Scheme 1, 2, 3, 4: Synthesis of disazo and trisazo disperse dyes using the following amines and phenols.

(i) H_2SO_4 , ice, NaNO_2 (ii) $\text{C}_{10}\text{H}_9\text{N}$, (iii) $\text{C}_6\text{H}_7\text{O}$ (iv) $\text{C}_{11}\text{H}_{10}\text{O}_2$ (7-methoxy), (v) $\text{C}_6\text{H}_6\text{NCl}$ (vi) $\text{C}_{11}\text{H}_{10}\text{O}_2$ (6-methoxy)

The crude product was recrystallized out of hot ethanol to give a brown solid in 96% yield, m.p: $178-180^\circ\text{C}$, ^1H NMR (CDCl_3 , 199.9.7 MHz): 2.46-4.41 (s, 2H, NH_2), 6.85- 8.65 (m, 6H, naphthalene H), 9.00 (m, 1H, thiazole H), ^{13}C NMR (CDCl_3 , 199.97 MHz); 38.81,39.22, 39.64, 40.05, 40.47, 40.89, 41.31, 94.63, 113.72, 114.93,115.72, 128.64, IR (in KBr) vcm^{-1} : 3442 (NH_2), 2920 (C-H_{str}), 1558 (naphthalene- ring), 1525 (NO_2), 1506 (Ar-ring), 1306 (NO_2). UV-Vis, λ_{max} , (nm): 415,630.

Preparation of 4-Amino-2-hydroxyphenylazonaphthylazo- 4¹-nitrothiazole, **5**

Compound **3** (3.25 g, 11 mmoles) was mixed with water 50 ml and concentrated H_2SO_4 (98%, 5 ml) with stirring. This mixture was cooled to $0-10^\circ\text{C}$. Ice- cold nitrosyl H_2SO_4 (10 ml) was added dropwise to the above mixture over a period of 15 minutes. Stirring was continued at this temperature for one hour. The solution was diluted with 5 ml acetic acid. Excess nitrous acid was destroyed using urea (0.15 g, 3 mmole).

The coupling component, 3- aminophenol (2.0 g, 18 mmole) was dissolved in sodium hydroxide solution (1.0g,20ml) was cooled to $0-5^\circ\text{C}$. The diazonium salt solution prepared above was slowly added to the coupler solution with vigorous stirring over a period of 10 minutes stirring was continued further for 2 hours. The precipitated dye was filtered, washed with water and air-dried. The crude product was purified by recrystallization from hot chloroform to give a brown solid in 2.43g (54%) yield m.p: $211-213^\circ\text{C}$, ^1H NMR (CDCl_3 , 199.97 MHz) 2.46-3.,66 (s, 2H, NH_2), 6.76-7.56 (m, 3H, ArH) 7.60-8.63 (m, 6H, naphthalene H), 9.25 (s, 1H thiazole-H), 11.35

(s, 1H, bonded OH), ^{13}C NMR (CDCl_3 199.94 MHz): 38.91, 39.34, 39.95, 41.01, 41.40, 94.61, 112.52, 116.32, 122.61, 130.32, 131.50, 132.67, 133.28. IR (in K Br) vcm^{-1} : 3547 (OH, NH_2) 2929 (C-H_{str}), 1568 (naphthalene -ring), 1528 (NO_2), 1507 (Ar ring), 1305 (NO_2), 1051 (C-O), UV -VIS, λ_{max} (nm): 562, 640.

Preparation of 7-methoxy-2-hydroxynaphthylazo-2¹-hydroxyphenylazo naphthylazo-4- nitrothiazole. 7

Compound 7 was synthesized following a procedure similar to that used for the formation of compound 5 were 7-methoxy-2-naphthol (2.8g, 17 mmole) in 7ml acetic acid was used as the coupling component. The titled compound was obtained in 3.17g, (79%) yield, m.p; 121-123 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 199.97 MHz) 2.45 -3.90 (s, 3H, OCH_3), 6.25-7.25 (m, 6H, naphthalene -H), 7.65-7.70 (m, 2H, Ar- H), 8.40 (b & m, 1H, thiazole - H), 11.25 (s, 1H, bonded DH), ^{13}C NMR (CDCl_3 , 199.97 MHz); 38.99, 39.95, 40.19, 41.03, 41.50, 56.01, 56.20, 94.02, 94.69, 99.27, 116.17, 117.13, 123.05, 123.89, 124.91, 125.49, 130.97, 132.46, 133.03, 146.20, 149.55, 160.43, 161.77. IR (in KBr) vcm^{-1} : 3540 (-OH), 2923 (C-H_{str}), 1569 (naphthalene- ring), 1525 (NO_2), 1506 (Ar- ring), 1302 (NO_2), 1251 (OCH_3) 1025 (C-O), UV - Vis, λ_{max} (nm): 385,650.

Preparation of 4 - Amino-2- chlorophenylazo naphthylazo - 4¹-nitrothiazole, 9

The titled compound was obtained using a procedure similar to that used for preparing compound 5 were 2-chloroaniline was used as the coupling component compared 5 was obtained in 1.4g (70%) yield, m.p: 140-142 $^{\circ}\text{C}$ ^1H NMR (CDCl_3), 199.97 MHz); 2.42-3.63 (s, 2H, NH_2), 6.85-7.42 (m, 6H, naphthalene -H), 7.65-8.63 (m, 3H, Ar-H), 9.45 (m, 1H, thiazol- H); ^{13}C NMR (CDCl_3 199.97 MHz): 39.37 39.79, 40.21, 40.21, 40.62, 41.06, 94.62, 116.22, 116.61, 123.03, 123.16, 124.16, 124.16, 124.36, 25.39, 130.86, 131.57, 132.65; IR (in KBr) vcm^{-1} : 3562 (NH_2), 2921 (C-H_{str}), 1557 -(naphthalene -ring) 1526 (NO_2), 1505 (Ar -ring), 1305 (NO_2); UV-Vis, λ_{max} (nm); 406, 540.

Preparation of 6- Methoxy-2-hydroxynaphthylazo-2¹-Chlorophenylazonaphthylazo-4 -nitrothiazole. 11

As for the procedure used for the formation of compound 9 were 6-methoxy-2-naphthol was used as the coupling component. The titled compound was obtained in 1.2 g (94%) yield, m.p: 191-192 $^{\circ}\text{C}$, ^1H NMR (CDCl_3), 6.28-7.66 (m, 5H, naphthalene-H), 7.85 (m, 3H, Ar-H), 8.42- 8.57 (m, 2H, ArH), 8.87 (m, 1H, thiazole-H) 11.35 (s, 1H, bound OH); ^{13}C NMR (CDCl_3 , 199.97 MHz): 39.35, 39.78, 40.19, 40.61, 41.01, 94.79, 99.38, 99.56, 116.15, 117.23, 123.08, 123.98, 124.81, 125.58, 130.88, 131.94, 132.51, 133.06, 146.30, 149.66, 160.53, 161.66; IR (In K Br) vcm^{-1} : 3546 (O- H_{str}), 2918 (C- H_{str}), 1646 (Ar- ring 15 26 (NO_2), 1245 (OCH_3), 1152 (C-O); UV -Vis, λ_{max} (nm): 510,645.

Dye Application

Acrylic Fabric

Acrylic fabric was dyed at 90 $^{\circ}\text{C}$ for one hour on an Ahiba Texomat dyeing machine using a 3 $^{\circ}\text{C}/\text{min}$ temperature gradient and a dye bath containing 1% owf dye and 2% owf dispersing agent and 1 molar equivalent of N, N-dimethylethylenediamine. The liquor ratio was 60:1 and the pH was 5, adjusted using formic acid. After dyeing, the fabric was removed from the hot dye bath, soaped off, rinsed with cold water and air-dried (Suwanruji *et al.*, 2004).

Polyester fabric

The polyester cloth was dyed in a pressure dyeing machine at a liquor ratio of 20:1. The dye baths were prepared with the synthesized azo dyes using lignosulfonate as the dispersing agent. The pH of the dye liquor was 5, adjusted using acetic acid. Dyeing was carried out and continued for 60 minutes at 130 $^{\circ}$ to 135 $^{\circ}\text{C}$. The dyed fabric was subjected to reduction-rising treatment at 85 $^{\circ}\text{C}$ for 10 minutes in a solution of sodium hydroxide, 2g $^{-1}$, hydrosulfite, 2g $^{-1}$, and a betaine amphoteric surfactant, 2g $^{-1}$ in water, washed with water and dried (Giles, 1974; Burkinshaw, 1994).

Fastness Test

The dyed fabrics were subjected to light fastness Test (AATCC Test method 16-1998), to wash fastness Test method (ISO-105-CO6/C25: 1994) and sublimation test according to ISO, 105-POI 1993 Test Method (ISO,1993). The dyed fabrics were treated in a sublimation testing machine at 177 $^{\circ}\text{C}$ for 30 seconds after heat setting at 180 $^{\circ}\text{C}$ for 60 seconds. The tested fabrics were rated against the standard Grey scales (grade 1-8) where 1 (poor) and 8 (excellent) for light fastness and grade 1-5 where 1 (poor) and 5 (excellent) for wash and sublimation fastness.

3. RESULTS AND DISCUSSION

Characterization of the disazo and trisazo dyes

The hetaryl disazo and trisazo disperse dyes were prepared by coupling 1-naphthlannime with selected diazotized diazo components, first with 2-amino-5-nitrothiazole to give monoazo dye **3**. And this was diazotized and coupled with 3-aminophenol to produce compound **5**. Thus, successive diazotization and coupling gave the hetaryl disazo and trisazo disperse dyes as shown in scheme 1, 2, 3 and 4 (Karci, 2005). The structures of these dyes were verified by spectroscopic methods. (FT-IR, ^1H NMR, ^{13}C NMR and UV-Vis). Physical and spectroscopic data of the prepared dyes are given in the experimental section.

The IR spectra of the dyes (in KBr) showed, bands within the range $3442\text{-}3562\text{ cm}^{-1}$ due to the NH_2 groups of the carbocyclic aromatic rings for dyes **3**, **5** and **9**, and the broad bands at $3540\text{-}3566\text{ cm}^{-1}$ were assigned to hydroxyl (-OH) groups. The peaks appearing at 3547 cm^{-1} in dye **5** is due to -OH stretching vibrations overlapping with the NH_2 groups. The bands at $1525\text{-}1528\text{ cm}^{-1}$ and $1302\text{-}1306\text{ cm}^{-1}$ were attributed to the symmetric and antisymmetric stretching vibrations of NO_2 groups (Carey, 2003). The medium bands observed at $2918\text{-}2029\text{ cm}^{-1}$ region were due to $\nu(\text{C-H}_{\text{str}})$ stretching vibrations of aromatic rings. The presence of the naphthalene rings and aromatic rings were also observed at $1557\text{-}1563\text{ cm}^{-1}$ and $1506\text{-}1646\text{ cm}^{-1}$ regions respectively.

The ^1H NMR spectra measured in deuterated chloroform (CDCl_3) showed peaks at 8.40-9.45 ppm for thiazole protons, 6.25-7.66 ppm for naphthalene protons, 2.46- 3.66 ppm for amino (NH_2) protons for dyes **3**, **5** and **9**. The broad signals which appeared at 11.25-11.35 ppm were those of hydroxyl (-OH) protons in dyes **7** and **11**. The chemical shifts of ^{13}C NMR spectra measured in CDCl_3 are in accordance with the structures of the synthesized compounds. The electronic spectral data of all the dyes showed multiple of absorption bands which indicates the extent of conjugation. Thus, the effect of the substituents in the diazo and coupler component rings on the λ_{max} values was outstanding especially for dyes **3**, **5**, **7** and **11** which gave near infra-red absorptions at 630nm, 640nm, and 645nm respectively.

at 630nm, 640nm, 650nm and 645nm respectively.

Fastness Properties

All the dyeings for the fastness tests were carried out at pH 5 and the dyed fabrics were assessed with the Grey scales. The Grey scale for the change of colour consisted of grades 1-8 for light fastness and 1-5 for other agencies that affect colour.

Wash Fastness

Table I shows the wet fastness test results of the dyes, and they all showed excellent wet fastness ratings of 5. The excellent ratings is due to the large molecular size of the dye molecules and also the nature of the two fabrics used. All the dyes showed a remarkable degree of levelness in surface area after washing, which is an indication of good penetration. However, the dyes showed deeper shades on the acrylic fabrics than on the polyester fabrics. It was also observed that the trisazo dyes showed duller shades than their disazo dye counterparts. This is in agreement with previous findings (Karci, 2005).

Table 1: The wash of fastness of disazo dyes compared to the trisazo dyes on Acrylic fabrics and polyester fabrics

Dye	Type of Dye	Fabric	Change	Staining				
				Acetate	Nylon	Polyester	Cotton	Acrylic
5.	Disazo	Acrylic	5	4/5	4/5	5	5	5
7.	Trisazo	Polyester	5	5	5	5	5	5
9.	Disazo	Acrylic	5	4/5	4/5	4/5	5	5
		Polyester	5	4/5	4/5	4/5	5	5
11.	Trsazo	Acrylic	5	5	5	5	5	5
		Polyester	5	5	5	5	5	5

Table 2: Light and sublimation fastness of dyes 5 – 11 on Acrylic fabrics and polyester fabrics

Dye	Type of Dye	Fabric	Light	Sublimation	Colour on fabric
5.	Disazo	Acrylic	5	5	Brown
		Polyester	5/6	5	Brown
7.	Trisazo	Acrylic	5	5	Yellowish orange
		Polyester	5/6	5	Yellowish orange
9.	Disazo	Acrylic	5	5	Yellowish
		Polyester	5/6	5	Yellowish brown
11.	Trisazo	Acrylic	5	5	Yellowish brown
		Polyester	6	5	Yellowish brown

Light Fastness

The results of the light fastness test of dyes 5-11 on the fibres used in this study are summarized in Table 2. The light fastness varied from grades 5/6 to 6. The light fastness of the dyes on polyester fabric is slightly higher than that of acrylic fabric due probably to the difference in regain of the two substrates (Evans and Stapleton, 1978).

Sublimation Fastness

The sublimation fastness test results in table 2 showed excellent ratings of 5. This performance could be due to the presence of the substituent groups such as $-\text{NO}_2$, $-\text{OH}_2$ and $-\text{Cl}$ which tend to increase the polarity of the azo compounds and hence their sublimation fastness (Giles *et al.*, 1978).

4. CONCLUSIONS

In conclusion, some trisazo and disazo disperse dyes of nitrothiazole azo benzene derivatives were synthesized. Also the spectral properties and fastness properties of these dyes on acrylic fabrics and polyester fabrics were evaluated. The two classes of azo dyes gave excellent sublimation and wet fastness on acrylic fabrics and polyester fabrics. The light fastness of the dyes on polyester fabric is higher than on the acrylic fabric due to the lower regain of the former. As expected the trisazo dyes showed duller shades on the two substrates used for the study than the disazo dyes. However, the near infra-red absorptions of some of the azo disperse dyes suggest that they could find applications in the non- textile areas.

5. REFERENCES

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