

Synthesis and Application of Hetaryl Disazo Disperse Dyes Derived from 2-Amino-5-Mercapto-1,3,4-Thiadiazole and 3-Chloroaniline on Synthetic Polymer-Fibres

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Abstract

The use of polyester fabrics in automotive upholstery has created a need for disperse dyes of exceptionally high sublimation and light fastness to withstand extended exposure to light and heat. Thus, in an attempt to find new disperse dyes of high fastness to sublimation and light, we report here the synthesis and evaluation of their fastness properties on polyester fabrics and nylon 66 fabrics. The synthesis of the dyes was carried out by diazotisation of the 2-amino-5-mercapto-1,3,4-thiadiazole in an acid medium and coupling with 3-chloroaniline to afford an intermediate. This intermediate was also subjected to diazotisation and coupling reactions with various couplers to give disazo disperse dyes. All the dyes exhibited outstanding washing, sublimation, perspiration and good to very good light fastness ratings on polyester and nylon 66 fabrics. The dye structures were characterized, using proton and carbon-13 nuclear magnetic resonance (¹H NMR and ¹³C NMR) IR, and ultraviolet – visible analyses.

Keywords: Hetaryl azo dyes, spectral properties, dye application, fastness properties

INTRODUCTION

The Chemistry of heterocyclic sulphur and nitrogen containing compounds has been an interesting field of study. The 1,3,4-thiadiazoles for instance, has gained more importance in recent times. They have been used in varieties of applications, which cover the fields of agriculture, medicine and many technological fields (Katritzky, 1992; Rajiv et al., 2011). Many of these includes dyes, lubricants, optically active crystals, photographic materials, epoxy resins, and so on (Joseph *et al.*, 2010; Ortega *et al.*, 2007; Fozoonlet *et al.*, 2008).

In the area of dye manufacture, the heterocyclic azo dyes, as the disazo components which contain sulphur, either alone or in combination with nitrogen, provide commercially important azo dyes. The sulphur or sulphur/nitrogen heterocyclic monoazo dyes provide bright strong shades that range from red, through blue to green and therefore complement the yellow/orange colours of the nitrogen heterocyclic azo dyes in providing a complete coverage of the entire shade gamut (Townes, 1999; Bradbury, 1995; Seferoglu, 2009). Azo dyes, as a class are cost effective and they cover the whole shades and possess good all-round fastness properties on synthetic fibres (Otutu *et al.*, 2008; Samiehet *et al.*, 2008).

Recently, monoazo disperse dyes derived from 2-amino-1,3,4-thiadiazole were synthesized and their structures and spectroscopic properties evaluated (Otutu, 2013). As a continuation of this research, the synthesis of disazo dyes of 2-amino-5-mercapto-1,3,4-thiadiazole derivatives is reported and their applications on polyester fabrics and nylon 66 fabrics were evaluated. The fastness properties of the dyes on these substrates were also assessed and discussed in relation to the nature of the hetarylazo dye rings and the substituents.

MATERIALS AND METHODS

The starting compound, 2-amino-5-mercapto-1,3,4-thiadiazole obtained from Aldrich Chemical Company was used without further purification. All other chemicals were of synthesis grade purchased from BDH Chemical Company.

Synthesis of Compound (3)

Compound 1 (8.0 g, 60 mmol) was mixed with 50 ml of water, 8 ml of sulphuric acid, cooled to 0 °C and diazotized by drop-wise addition of sodium nitrite (5.0 g, 72 mmol) in 10 ml of water. An excess of sodium nitrite was detected using starch iodide paper which showed a blue colour indicating excess nitrous acid and this inferred the formation of the diazonium salt. 3-chloroaniline (7 ml) was dissolved in acetic acid (5 ml) and a little of methanol was added. The diazotised amine was added drop-wise to the 3-chloroaniline solution at 0 °C and stirred at room temperature for 1 hour. The precipitate obtained was isolated by filtration and washed with water. The crude product was recrystallized from hot acetic acid to give yellow-orange coloured crystals of compound 3 in 19.7 g (98%) yield. M.P 180°C; ¹H NMR (199.97 MHz) δ: 1.25 (2H, s, NH₂); 6.85 (1H, s, SH); 7.17 (1H, m, ArH), 7.43 (1H, m, ArH), 7.85 (1H, m, ArH). ¹³C NMR (199.97 MHz) δ: 135.41, 133.41, 133.38,

41.35, 40.98, 40.56, 40.14, 39.92; IRK Br pellets $\nu(\text{cm}^{-1})$: 3421.81 – 3443.05 (NH_2), 3095.85 ($\text{C} - \text{H}_{\text{str}}$), 2133.34 – 2297.30 ($\text{S} - \text{H}_{\text{str}}$), 1541.18 – 1637.95 (Aromatic skeleton), 1338.14 – 1396.51 (Thiazole ring), 896.92 ($\text{C} - \text{Cl}_{\text{str}}$).

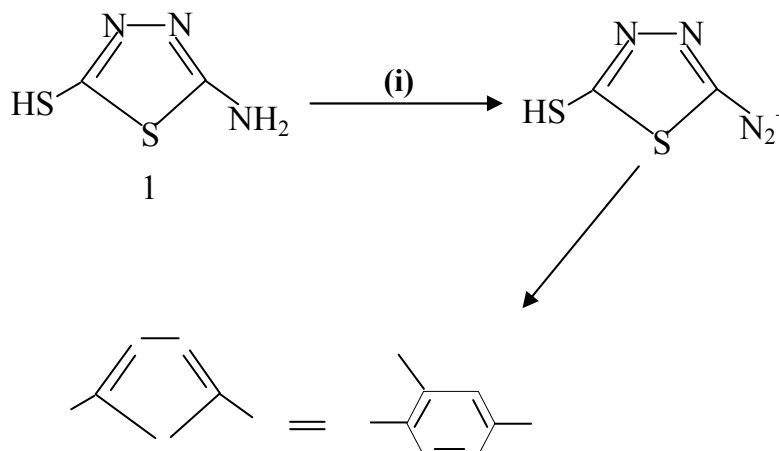


Figure 1: Synthesis scheme for the preparation of compound 3.
(i) $\text{H}_2\text{SO}_4/\text{NaNO}_2$, $0 - 5^\circ\text{C}$ (ii) $\text{C}_6\text{H}_6\text{Cl}$

Synthesis of dye (5a)

Compound 3a (4.0 g, 15 mmol) was mixed with 50 ml of water and diazotised in 6 ml of sulphuric acid with sodium nitrite (4.0 g, 57 mmol) in 10 ml of water at 0°C with stirring for 15 mins. 7-methoxy-2-naphthol (2.56 g, 15 mmol) was dissolved in 10 ml of acetic acid. The diazotised compound 3 was added slowly and stirred at room temperature for 2 hours. The precipitate obtained was isolated by filtration, washed with water and dried. The product was purified by recrystallization from CCl_4 in 58% yield, m.p: 240°C , ^1H NMR, δ : 4.41 (1H, s, OH), 6.23 (1H, s, SH), 6.86 – 7.15 (2H, m, ArH), 7.40 (1H, m, ArH), 7.60 – 8.20 (5H, m, naphthalene-H), ^{13}C NMR, δ : 161.73, 160.83, 145.90, 133.01, 132.48, 130.98, 116.16, 99.16, 97.09, 56.20, 41.37, 40.95, 40.54, 40.12, 39.70, 39.28, 38.86. IR (KBr pellets) $\nu(\text{cm}^{-1})$: 3425.69 (OH_{str}) 2943.47 – 3076.56 ($\text{C} - \text{H}_{\text{str}}$), 2135.27 – 2362.88 ($\text{S} - \text{H}_{\text{str}}$), 1593.25 – 1693.56 (Aromatic skeleton), 1527.67 – 1552.75 (naphthalene skeleton), 1230.63 – 1274.99 (Thiazole ring), 1058.96 – 1205 (OCH_3), 842.92 ($\text{C} - \text{Cl}_{\text{str}}$).

Synthesis of dye (5b)

Compound (5b) was prepared using the method similar to that described for compound (5a) to give orange crystals m.p: 120°C , yield (52%). ^1H NMR δ : 2.40 – 2.80 (2H, m, ArH), 8.15 (1H, m, ArH); ^{13}C NMR (CDCl_3) δ : 163.03, 131.53, 41.40, 40.99, 40.57, 40.16, 39.74, 39.32, 38.91, 36.49, 5.06, 31.46. IR (K Br pellets) $\nu(\text{cm}^{-1})$: 3290.67 – 3396.76 (NH_2_{str}), 3074.63 – 3188.44 ($\text{C} - \text{H}_{\text{str}}$), 2133.34 – 2362.88 ($\text{S} - \text{H}_{\text{str}}$), 1593.60 – 1691.61 (Aromatic Skeleton), 1045.45 – 1344.43 (Thiazole ring) 833.28 – 885.36 ($\text{C} - \text{Cl}_{\text{str}}$).

Synthesis of dye (5c)

Compound (5c) was synthesised as described for compound (5a). Orange crystals m.p: 160°C , yield (73%). ^1H NMR δ : 1.21 – 3.80 (2H, s, HN_2), 6.92 – 7.60 (6H, m, naphthalene H), 7.83 – 8.40 (2H, m, ArH), 8.93 (1H, m, ArH); ^{13}C NMR (CDCl_3) δ : 160.75, 145.82, 133.07, 132.48, 136.87, 116.18, 99.14, 98.16, 56.17, 41.38, 40.86, 40.45, 40.16, 39.18, 38.76. IR (KBr pellets) $\nu(\text{cm}^{-1})$: 3439.19 (NH_2_{str}), 2970.48 – 3068.83 ($\text{C} - \text{H}_{\text{str}}$), 2133.34 – 2364.81 ($\text{S} - \text{H}_{\text{str}}$), 1593.20 – 1693.56 (Aromatic Skeleton), 1546.96 (naphthalene skeleton), 1091.75 – 1346.36 (Thiazole ring) 877.64 ($\text{C} - \text{Cl}_{\text{str}}$).

Synthesis of dye (5d)

Compound (3) (4.0 g, 15 mmol) was mixed with 50 ml of water and diazotised in 6 ml conc. H_2SO_4 with sodium nitrite (57 mmol) in 10 ml of water at $0 - 5^\circ\text{C}$. 1, 3-dihydroxybenzene was dissolved in sodium hydroxide (1.5 g, 14 mmol) in 20 ml of water. The diazonium salt solution was added slowly to the 1, 3 - dihydroxybenzene solution and stirred for 1 hour. The precipitated coloured product was separated by filtration, washed with water and dried in air. The crude product was recrystallized out of N, N-dimethyl formamide-water (1:2) mixture to give orange crystals in 70% yield, m.p: $270 - 272^\circ\text{C}$, ^1H NMR δ : 6.40 (1H, s, SH), 6.65 – 7.20 (2H, m, ArH), 10.40 (1H, s, OH). ^{13}C NMR δ : 131.83, 130.56, 121.88, 94.63, 94.59, 41.42, 40.57, 40.10, 39.74, 39.32, 38.90. IR (KBr pellets) $\nu(\text{cm}^{-1})$: 3464.47 – 3520.21 (OH_{str}), 2818.09 – 3165.29 ($\text{C} - \text{H}_{\text{str}}$), 2133.34 ($\text{S} - \text{H}_{\text{str}}$), 1597.69 – 1695.25 (Aromatic Skeleton), 1132.25 – 1313.57 (Thiazole ring), 846.78 ($\text{C} - \text{Cl}_{\text{str}}$).

Synthesis of dye (5e)

Compound (5e) was prepared using a method similar to that described for compound (5d). m.p 187 °C, yield (59%), ¹H NMR δ: 6.27 (1H, s, SH), 6.65 – 7.43(6H, m, naphthalene H), 7.61 – 7.80 (2H, m, ArH), 7.85 (1H, m, ArH), 10.26 (1H, s, OH), ¹³C NMR (CDCl₃) δ: 132.01, 131.07, 123.82, 94.78, 94.48, 41.32, 40.56, 39.64, 39.33, 38.9, 38.62, 38.52. IR (KBr pellets) ν(cm⁻¹): 3417.98 – 3443.05 (O – H_{str}), 2864.39 – 3074.63 (C – H_{str}), 2135.27 – 2617.49 (S – H_{str}), 1593.25 – 1627.50 (Aromatic Skeleton), 1068.60 – 1284.63 (Thiazole ring), 850.64 – 887.28 (C-Cl_{str}).

Synthesis of dye (5f)

Compound (5f) was obtained in 53% yield using the procedure described for compound (5e), m.p 280 – 282 °C, ¹H NMR δ: 1.25 (2H, s, NH₂), 6.40 (1H, s, SH), 6.45 – 6.88 (2H, m, ArH), 7.10 – 7.40 (2H, m, ArH), 7.60 – 7.82 (2H, m, ArH), 10.17 (1H, s, OH). ¹³C NMR δ: 131.84, 130.13, 122.98, 94.70, 74.60, 41.42, IR (KBr pellets) ν(cm⁻¹): 3252.09 – 3441.12 (OH_{str}NH_{str}), 3063.06 – 3171.08 (ArC – H_{str}), 2133.34 (S – H_{str}), 1593.25 – 1691.63 (Aromatic Skeleton), 1116.82 – 1323.21 (Thiazole ring), 842.92 (C – Cl_{str}).

Chemical and instrumental analyses

Melting points were determined using a Buchi SMP – 20 melting point apparatus and are uncorrected. Infrared spectra were recorded on a Shimadzu (8400S) FTIR spectrometer using KBr discs. Proton nuclear magnetic resonance (¹H NMR) and carbon – 13 nuclear magnetic resonance (¹³C NMR) were recorded with mercury 200 BB 199.97 MHz series spectrophotometer. Dimethylsulphoxide (DMSO-d₆) and deuterated Chloroform (CDCl₃) were used as NMR solvents and containing 0.03% v/v tetramethylsilane as internal standard. The dye purity was monitored by Thin Layer Chromatography (TLC) using silica gel 60 coated plates, F₂₃₄ (Merck aluminium sheets). The visible spectra were measured using a Genesys 10S V1.200 series.

Dye Application

Preparation of Dye Dispersion

The dye dispersion was prepared by dissolving 1.0 g of each dye in 5 ml of N, N-dimethyl formamide (DMF) and finally made up to 100 ml mark with a dispersing agent (A Lignosulphonate).

Nylon

Nylon 66 fabrics was wetted and immersed in the dyebath containing the dispersed dye liquor at P^H 4-5 at 45 °C. The temperature of the dyebath was then raised to 102 °C over 15 minutes and maintained for 30 minutes. Formic acid (1.5 ml of 10%) was then added to the dyebath at this temperature in order to achieve good exhaustion. The temperature of the dyebath was then cooled, and the dyed fabrics were rinsed and reduction – cleared twice with iodet T (2gl⁻¹) in a bath containing water (material to Liquor 1:2) at 46 °C for 15 minutes followed by rinsing thoroughly with water and drying in air (Giles, 1974; Burkinshaw, 1990).

Polyester (100% terylene)

The polyester (PET) fabrics (15 x 10cm) were immersed in a prepared dyebath dispersion, stirred for 5 minutes and the fabric was passed through a mangle in a padding unit where it is squeezed to about 100% expression and dried for 30 – 60 secs. Each dried fabric sample was passed to the even unit where it was heated to a temperature of 180 – 220 °C for 1 – 2 minutes. At this temperature, the dye sublimates and the dye vapour was absorbed by the polyester fabric. The dyed samples were cooled and then reduction cleared by treating them with a solution containing 3 ml of sodium hydrosulphite, 6 ml of caustic soda, and 3 ml of machaesil for 15 minutes. The dyed reduction – cleared fabric was soaped off, rinsed and dried. The thermofixation process is depicted in Figure 2 (Burkinshaw, 1990; Giles, 1974).

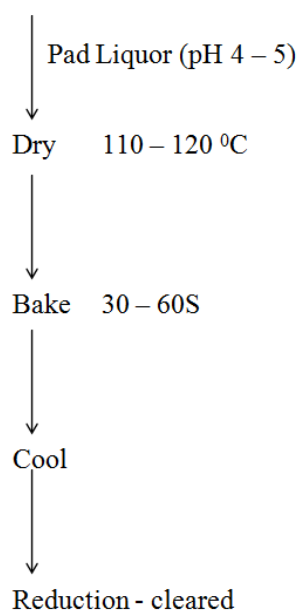


Figure 2: Thermofixation dyeing method

Fastness testing

Wash Fastness

The dyed samples were tested for fastness to washing treatment according to the international standard organisation (ISO) washing test number 3 (ISO, 1989). The composite samples were treated with a solution containing 5 gl^{-1} detergent, and 2 gl^{-1} sodium carbonate and liquor ratio 50:1 for 30 minutes at 60 $^{\circ}\text{C}$. The change in colour of the tested samples and the degree of staining of the adjacent undyed fabrics were rated against the Grey scales. The indication for the Grey scales is 1 to 5, where 1 (poor) and 5 (excellent).

Light Fastness

The photosability was evaluated by exposing the dyed fabric samples to a xenom arc lamp of an Atlas 3 SUN Weather – 0meter according to the conditions of AATCC Test Method (AATCC, 1990). The conditions for the test were: Black panel temperature 60 $^{\circ}\text{C}$, dry bulb temperature, 43 $^{\circ}\text{C}$, relative humidity 30%, duration of test is 24 h. After testing, the tested samples were rated against standard blue wool samples (grade 1 – 8) and the indications in this case are 1 – 2 (poor) and 8 (excellent).

Sublimation Fastness

The fastness to sublimation was determined according to ISO, 105 – PO1, 1993 Method (ISO, 1993). The dyed fabrics were treated in a sublimation testing machine at 177 $^{\circ}\text{C}$ for 30 secs. and then rated against the Standard Grey Scales (grade 1 – 5).

Perspiration Fastness

Colour fastness to perspiration was assessed (ISO 105 – EO4, 1994) by treating the dyed fabrics (10 x 4cm) in an alkaline solution of freshly prepared 0.5 gl^{-1} 1-Histidine monohydrochloride mono-hydrate, 5 gl^{-1} sodium chloride, 2.5 gl^{-1} disodium hydrogen orthophosphate and 0.1M sodium hydroxide liquor ratio 50:1. The acid perspiration test solution contains: 0.5 gl^{-1} 1-Histidine mono-hydrochloride mono-hydrate, 5 gl^{-1} sodium chloride, 2.2 gl^{-1} sodium dihydrogen orthophosphate and 0.1M acetic acid solution. The tested fabrics were rinsed, dried and then rated against the Grey scales for colour changes.

Rubbing Fastness

The rubbing fastness test of the dyed fabrics was determined according to ISO 105 – X12, 2001 Method (ISO 105 – X12, 2001). The tested samples were rated against the Grey scales for colour changes.

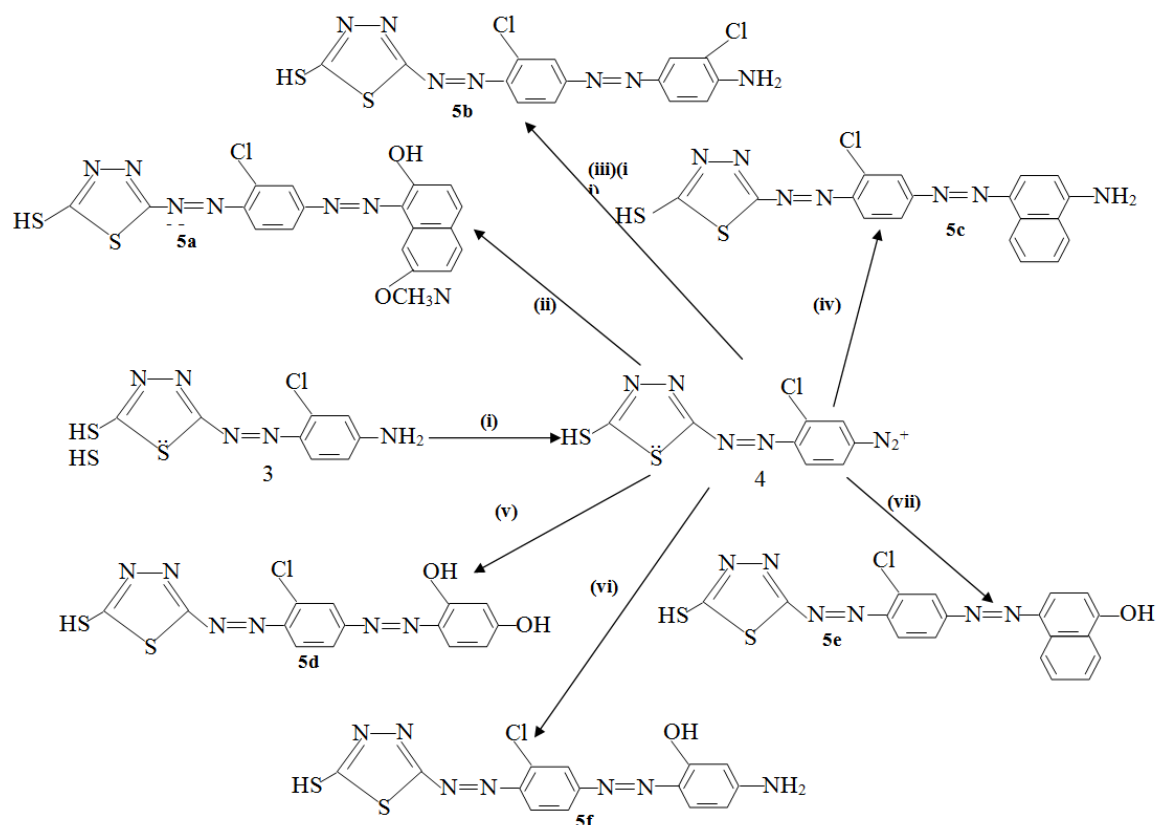


Figure 3: Synthesis Scheme for the Preparation of dyes 5a – 5f

(i) $\text{H}_2\text{SO}_4/\text{NaNO}_2$, $0 - 5^\circ\text{C}$ (ii) $\text{C}_{11}\text{H}_{10}\text{O}_2$ (iii) $\text{C}_6\text{H}_6\text{Cl}$ (iv) $\text{C}_{10}\text{H}_9\text{N}$ (v) $\text{C}_6\text{H}_6\text{O}_2$ (vi) $\text{C}_6\text{H}_7\text{NO}$

RESULTS

The synthesis of hetaryl disazo disperse dye derivatives of 2-amino-5mercapto-1,3,4-thiadiazole and 3-chloroaniline (5a-5e) was carried out according to schemes 1 and 2. The characterization data of the disazo disperse dyes are given in the materials and method section and their physical properties are shown in table 1.

Table 1: Physiochemical properties of synthesized disazo disperse dyes.

Dye compound	Molecular formula	M.Wt (gmol^{-1})	Yield (%)	M.pt ($^\circ\text{C}$)
5a	$\text{C}_{19}\text{H}_{13}\text{N}_6\text{S}_2\text{ClO}_2$	456.5	58	240
5b	$\text{C}_{14}\text{H}_9\text{N}_7\text{S}_2\text{Cl}_2$	410	52	120
5c	$\text{C}_{15}\text{H}_{12}\text{N}_7\text{S}_2\text{Cl}$	389.5	73	160
5e	$\text{C}_{14}\text{H}_9\text{N}_6\text{S}_2\text{ClO}_2$	392.5	70	270-272
5d	$\text{C}_{18}\text{H}_{11}\text{N}_6\text{S}_2\text{ClO}$	426.5	59	187
5f	$\text{C}_{14}\text{H}_{10}\text{N}_7\text{S}_2\text{ClO}$	391.5	53	280-282

Table 1 shows the physiochemical properties of the disazo disperse dyes. Indeed the melting points of the dyes are relatively quite high except for dye 5a which gave a melting point of 120°C . The yield of the dyes 5c and 5e are 73% and 70% which were found to be higher than the other dyes, which tend to be in the range of 53% to 59%.

Table 2: Wavelength (λ_{\max}) Molar Extinction Coefficient (ϵ), Intensity ($\log \epsilon$) of dyes 5a – 5f

Dye	λ_{\max}^x	Absorbance	ϵ_{\max} ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)	R _f	Intensity ($\log \epsilon$)
5a	427	0.680	77,272	0.32	4.89
5b	417	1.760	17,959	0.46	4.25
5c	537	0.927	98,617	0.28	4.99
5d	406	3.130	30,694	0.39	4.49
5e	567	0.367	39,074	0.42	4.59
5f	426	3.5238	34,547	0.30	4.54

* measured in N,N-dimethylformamide (DMF)

Table 2 shows the wavelength maxima of the dyes ranging from 406nm to 567nm. This is within the yellow coloured range of the spectra. Also presented in Table 2 are the molar extinction coefficients of the dyes, in which dye 5c and 5a gave the highest ϵ_{\max} of 98, 617^{dm³mol⁻¹cm⁻¹} and 77,272^{dm³mol⁻¹cm⁻¹} respectively. Dye 5b gave the lowest ϵ_{\max} value compared to the others.

The retention factor (R_f) values as indicated in table 2 are for dyes 5a-5f are 0.46, 0.28, 0.39, 0.42, and 0.30 respectively. The highest R_f values are those recorded by dye 5b and 5d, the smallest R_f values are those of dye 5c and 5e.

Table 3: Colour Fastness values to washing of the dyed samples according to ISO washing test number 3 (30 mins at 60°C)

Dye	Type of Fabric	Colour Change	Staining					
			PET	Co	PA	PAN	WO	CA
5a	polyester	5	5	5	5	5	5	5
	nylon	5	4-5	5	4-5	4-5	5	5
5b	polyester	5	5	5	5	5	5	5
	nylon	5	4-5	5	5	5	5	5
5c	polyester	5	5	5	5	5	5	5
	nylon	5	4-5	5	5	4-5	5	5
5d	polyester	5	5	5	5	5	5	5
	nylon	5	5	5	5	5	5	5
5e	polyester	5	5	5	5	5	5	5
	nylon	5	5	5	5	4-5	5	5
5f	polyester	5	5	5	5	5	5	5
	nylon	5	5	5	5	5	5	5

PET, Polyester, Co, Cotton; PA, Polyamide; PAN, acrylic; WO, Wool, CA, Cellulose acetate

Table 4: Colour Fastness to Light, Sublimation Rubbing, and Perspiration

Dye	Type of Fabric	Light	Sublimation	Rubbing		Perspiration	
				Dry	Wet	Acid	Alkaline
5a	polyester	6/7	5	4/5	4/5	5	5
	nylon	5	5	4	4/5	5	5
5b	polyester	5/6	5	4	4	4/5	5
	nylon	5	5	4	4/5	4/5	5
5c	polyester	6	5	4	4/5	5	5
	nylon	5	5	4/5	4/5	5	4/5
5d	polyester	5/6	5	4	4	5	5
	nylon	5	5	4	4	5	4/5
5e	polyester	6	5	4	4/5	5	5
	nylon	5	5	4	4/5	5	4/5
5f	polyester	6/7	5	4	4	5	5
	nylon	5	5	4	4/5	4/5	5

PET, Polyester, Co, Cotton; PA, Polyamide; PAN, acrylic; WO, Wool, CA, Cellulose acetate

Table 3 shows the colour fastness test results to washing. The wash fastness properties were found to be grade 5 and staining of adjacent multi-fibre fabrics is up to 4-5%. In table 4, the higher fastness properties that were obtained with the disazo disperse dyes was good to very good being grade 5/6 to 6/7 in general on the blue wool reference scale. Also in table 4, the sublimation fastness of the dyed polyester samples gave excellent values of grade 5. The rubbing fastness test results, as indicated in table 4, showed a colour change of grade 4 to 4/5 in general for both wet and dry rubbing. The perspiration test results, as indicated in table 4, showed values of 4/5 to 5 generally for both acid and alkaline perspiration.

DISCUSSION

The application of colour is the main purpose of many dye products, and now more than ever, these products have to be environmentally friendly while continuing to provide an effective product. The heterocyclic compounds have long been embraced as a field of great potential by dye chemist and by the textile industry (Gregory, 1994; Edward and freeman, 2005; Choi et al, 2003).

The compound (3) was obtained by diazotization of 2-amino-5-mercapto-1,3,4-thiadiazole in conc. Sulphuric acid followed by coupling reaction with 3-chloroaniline to give a yellow-orange crystals in good yield as shown in Figure 1. The disazo disperse dyes were synthesized by the coupling reactions between the diazonium salt solutions of compound (3) and other coupling agents as illustrated in Figure 2. (Alexis et al, 2004. Karci; 2003, kirkan and Gup, 2008; Metwally et al; 2013. Luan et al., 2013; Yildiz and Boztepe, 2001)

The melting points of the disazo compounds are quite high for compounds 5a, 5d, 5e, and 5f. Compounds 5a and 5e however, gave relatively lower melting points than the formers. The reason for the lower melting points of compounds 5b and 5e is not immediately understood, but it is believed that the substituents on the coupling components nucleus are responsible. For this, although there are other factors that could affect the melting points of the compounds apart from the aforementioned reason (Lee et al., 2004). The yield of compound (3) is quite high (97%), however, those of the disazo dyes were relatively moderate except that of dye 5f with a relatively higher yield (70%) than the others.

The absorption maxima of the dyes are in the range of 406 nm to 567 nm with orange shades. Comparing the λ_{\max} values and the molar extinction coefficients of dyes 5c and 5e with those of 5a, 5b, 5d, and 5f, a bathochromic effect (110 nm- 140 nm) and a hyperchromic effect (increased in ϵ_{\max}) were observed. However, the values of the extinction coefficient ($\log \epsilon$) of the dyes were 4.89, 4.99, 4.49, 4.59, and 4.54 respectively, and these consistently correspond with their absorption intensities. The electron-donating or electron-withdrawing groups present in the different positions on the dye structures with respect to the azo groups are responsible for the different λ_{\max} values observed.

Fastness properties

From the colour fastness evaluations of the disazo disperse dyes on the polyester and nylon fabrics were observed that the dyes exhibited excellent wash fastness ratings of grade 5. This indicates high wash fastness performance of the dyes on the two substrates used for the study. This is attributed to the large molecular size of the dyes as well as the crystalline nature of the fabrics. The multifibre stripes composited with the dyed fabrics showed no significant staining of the fibre which indicates that the dyes have very good affinity for the polymer-fibres.

In general, the high fastness ratings of the dyes of 5 to 6/7 were observed for the two types of fibres. However, it is observed that the photo stability values of the dyes on nylon 66 fabric is lower than those of the polyester fabric. This is quite contrary to previous findings (venkataraman, 1997, Friskovec et al, 2003) that disperse dyes having -OH and -NH₂ groups ortho to the azo groups, lower light fastness on polyester fibre, especially for dyes 5a, 5d, and 5f. The reason for the high light fastness of the dyes on polyester fibre could be due to the method used for dyeing the polyester fabrics as well as the regain of the polyester fibre.

All the dyes showed excellent perspiration on the two substrates except that slight changes in colour were observed for dye 5b on polyester and nylon in acid perspiration. However, slight colour changes were also observed for dyes 5c, 5d, and 5e on nylon fabric in alkaline perspiration (Hou et al, 2013).

The heat (sublimation) fastness properties of the dyes on both polyester and nylon fibres showed excellent ratings of grade 5. This is attributed to the presence of the halogen group in the dye structures (Shuttle worth and Weaver, 1994, Kahatric et al., 2013)

The rubbing fastness test results obtained are in the range 4-5 which is acceptable for the two textile fibres used for the study. Colour fastness of a dye to any fibre is actually a function of the particular dye-fibre system. Thus, a given dye will often possess different fastness properties on different textile fibres.

Conclusions

The hetaryl azo compounds remain one of the most attractively coloured group of azo compounds in recent times. The six disazo disperse dyes prepared in this study are bright orange dyes which exhibited good to excellent dyeing properties on polyester and nylon 6,6 fabrics. From fastness evaluations, the azo disperse dyes generally showed better fastness properties on polyester than on the polyamide (nylon) fabrics, especially as the former was dyed using the vapour phase method (Thermosol process). Thus, from a commercial standpoint, the best of the disazo disperse dyes will be very useful in the textile and automobile industries.

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Nuclear Magnetic Resonance Measurements.

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