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DISPERSE DYES BASED ON 2-AMINO-5-MERCAPTO-1,3,4-THIADIAZOLE AND 2-AMINO-4,6-DIHYDROXYPYRIMIDINE MOIETIES: SYNTHESIS AND APPLICATION ON NYLON 6 FABRICS

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ABSTRACT

The synthesis of azo disperse dyes from the heterocyclic compounds remains one of the best approaches in solving the problem of environmental issues and safety of human health due to their ease of biodegradability. The aim of this study was to synthesize eight azo disperse dyes from 2-amino-4,6-dihydroxy pyrimidine and 2-amino-5-mercapto-1,3,4-thiadiazole, using diazotization-coupling reactions. The dyes were characterized in terms of their spectroscopic studies such as proton (¹H) and ¹³C nuclear magnetic resonance, Fourier transform infrared (FT-IR). The spectroscopic data obtained confirmed the structures of the synthesized dyes. It was also established by these analyses that the dyes existed in the tautomeric form in the solid state and liquid state. The ultraviolet-visible absorption spectra of the dye derivatives were found to show wavelength maxima in the 401-636nm range. The application of the dyes onto nylon 6 fabrics was carried out and their fastness properties in terms of washing, rubbing, light, perspiration and sublimation were studied. It was found that the dyes displayed interesting fastness properties with the following ratings; washing (grade 5), rubbing (grade 3/4 to 4) perspiration (grade 4/5 to 5), light (grade 5 to 5/6) and sublimation (grade 4 to 5). From these results, it can therefore be concluded that the dyes have very good affinity for the nylon 6 fibres. The dyes in solution showed base sensitive function that led to good wet fastness in terms of staining on the adjacent fabrics. Hence, the dyes under study could be commercially important in the dyeing of nylon fibres.

Keywords: Disperse dyes, synthesis, characterization, fastness properties, nylon 6

Introduction

The chemistry of the heterocyclic compounds has achieved considerable success in the dye stuff industry and their importance may even increase further in time to come (Karci, 2005; Deng *et al.*, 2013; Salem *et al.*, 2015) as new areas of dye stuff utility continue to unfold. The huge success

recorded in this regard, is due to the biodegradability of the dyes produced from the heterocycles. In addition, the use of many benzenoid primary amine compounds in the preparation of azo dyes is receiving less attention due to their toxic effect to the environment and

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inability to undergo degradation easily. Based on these facts, more attention is being focused on the heterocycles for the production of dyes.

Many commercially successful disperse monoazo dyes have been produced using the heterocycles (Park *et al.*, 2016). The thiophenes and thiadiazole moieties for instance have been reported to have very good advantage for their use in the production of azo disperse dyes. Some of these advantages include the small molecular size brightness (Qi *et al.*, 2013; Sabnis, 2016) the heterocyclic nature which makes them to exhibit excellent sublimation fastness as well as the fact that they are easily dischargeable.

In an effort to improve the wet fastness of disperse dyes on hydrophobic fibres such as nylon and polyesters, researchers have adopted the strategy of designing the structure of disperse azo dyes to include a base-sensitive function. Also, the phthalimide ring system has been identified as another structural features that imparts a considerable degree of base-sensitive function of disperse dyes on synthetic polymer fibres. The base-sensitive function encourages the disperse dye molecules to go into solution and enables it to diffuse into the textile substrate. This reduces the amount of dye molecules in the dye liquor thereby reducing the extent of staining of adjacent undyed fabrics.

In a previous study, the synthesis and application of disperse dyes containing two hydrazo groups in the molecules derived from 2-amino-5-mercapto-1,3,4-thiadiazole and 2-chloroaniline moieties onto polyester and nylon fabrics have been reported (Otutu *et al.*, 2014). In the present study, the synthesis and application of bisazo dyes derived from 2-amino-5-mercapto-1,3,4-thiadiazole and 6-amino-4,6-dihydroxypyrimidine moieties onto nylon 6 fabrics are described. The dye structures were designed to contain structural features similar to those of the phthalimide structural system. In addition, the colouration

properties in terms of shade and fastness (light, perspiration, wash, rub and sublimation) on nylon 6 fibres were investigated. The dyes were characterized by proton nuclear magnetic resonance (^1H NMR), carbon 13 nuclear magnetic resonance (^{13}C NMR), Fourier transform infrared (FTIR) spectroscopy and ultraviolet-visible (UV-vis) absorption spectrometry.

Materials and methods

Materials

All starting materials including 2-amino-5-mercapto-1,3,4-thiadiazole, 6-amino-4,6-dihydroxypyrimidine, 2-chloroaniline, obtained from Sigma Aldrich (Germany) were used without further purification. All other chemicals used were of pure analytical grade purchased from Merck (Germany). Woven and knitted nylon 6 fabrics was obtained from a local market (Nigeria) and scoured before used in dyeing.

Instrumentation

Melting points were measured in capillary tubes on an gallenkamp apparatus and are uncorrected. Nuclear magnetic resonance ^1H NMR and ^{13}C NMR spectral measurements [$^2\text{H}_6$], were carried out using dimethylsulphoxide (DMSO) and deuterated chloroform (CDCl_3) as solvents and 200BB series instrument at 200 MHz and 50 MHz respectively. The spectra were recorded at room temperature. Chemical shifts (δ) were related to tetramethylsilane (TMS, $\delta = 0.00$) as an internal standard and expressed in ppm. The Fourier Transform Infrared (FTIR) infrared analysis was carried out using Shimadzu 8400S spectrophotometer (Japan) using potassium bromide disc. Measurements of the electronic spectra were performed on a Nicolet Averser (USA) in dimethylformamide (DMF).

General Procedure for Preparing Compound 3

A mixture of 2-amino-5-mercapto-1,3,4-thiadiazole (12.0 g, 0.0090 mol), hydrochloric acid (60 ml) and water (120 ml) was stirred and cooled in an ice bath

at 0 – 5 °C. The heterocyclic aniline diazonium salt was prepared by the slow addition of a solution of sodium nitrite (7.0 g, 0.10 mol) which was dissolved in water. The resulting mixture was stirred for an additional 20 min at 0 – 5 °C. Excess nitrous acid formed was removed by adding a few drops of sulphamic acid. The coupler solution was prepared by dissolving 6-amino-4,6-dihydropyrimidine (11.5 g, 0.090 mol) in acetic acid (25 ml). The cold diazonium salt solution was then run into the coupler solution and the mixture was stirred vigorously for 3 hr. The crude product was isolated by filtration, washed with distilled water recrystallised from toluene/ethanol mixture and air dried to afford a yellow – brown solid. Dyes 5a to 5h were synthesized by diazotising compound 3 as described above and using different coupling components.

Preparation of Dye Dispersion

The synthesized dyes were dissolved in dimethylformamide and then added to a stirred solution of Satemol WS anionic dispersing agent (BASF, Germany). The mixture was stirred and a fine homogenous precipitate appeared.

Dyeing of Nylon 6 Fabrics

The dyeing of nylon 6 fabrics was carried out using an Ahiba laboratory dyeing machine (Data color, USA). A 2% acetic acid was used to adjust the pH of the dye bath from 4-4.5. The dyeing commenced at 40 °C liquor ratio of 50:1 at 2% weight of fibre (owf) and the temperature was raised to boil at a rate of 2 °C min⁻¹. The nylon samples remained in that condition for 1 hr and were then rinsed and were reduction-cleared twice with Iodet T (2 gl⁻¹) in a bath containing water (liquor ratio 1:2) at 40 °C for 15 min. The reduction-cleared samples were thoroughly washed with cold water and air dried (Mohaddes *et al.*, 2016).

Evaluation of Fastness of Dyed Nylon 6 Fabrics

The colour durability of the dyed nylon samples were carried out according to the International

Organization for Standardization (ISO) test methods. The wash fastness properties of the dyed samples were evaluated according to ISO 105 – CO6 (IS), 2010). The samples were washed in a soap solution at 60 °C for 30 min and the degree of staining on the adjacent fabrics was evaluated using a grey scale. The light fastness measurement was assessed using a xenon arc lamp test in accordance with ISO 105-BO2 (ISO, 2013), the nylon 6 samples were tested for the stability to light treatment using Xenon arc lamp for 45 hr. The fastness to rubbing (dry and wet) was assessed according to ISO 105-X12: (ISO, 2001) methods. The sublimation fastness test was carried out using a fixometer at 180 °C in accordance with ISO 105-PO1 (ISO, 2013) protocol. Fastness to perspiration was evaluated according to ISO 105-EO4 test method.

RESULTS

Table 1 shows the UV-Vis absorption data. The results showed that the dyes exhibited a maximum absorption wavelength (λ_{max}) and a shoulder except dyes 4d and 4f.

Table 1: UV-Vis data of synthesized dyes

Compounds	Molecular formula	λ (nm)	Yield (%)	mp (°C)	R _f
4a	C ₁₂ H ₈ N ₉ ClO ₂ S ₂	409, 421	43	183–185	0.62
4b	C ₁₂ H ₈ N ₉ BrO ₂ S ₂	403, 325	54	195–197	0.78
4c	C ₁₀ H ₆ N ₁₀ O ₃ S ₂	402, 431	55	202	0.66
4d	C ₁₅ H ₁₁ N ₈ O ₅ S ₂	435	78	250–252	0.81
4e	C ₁₆ H ₉ N ₉ O ₃ S ₂	401, 404	52	215	0.76
4f	C ₁₅ H ₉ N ₉ O ₃ S ₂	402	56	250	0.56
4g	C ₁₇ H ₁₂ N ₈ O ₄ S ₂	402, 438	65	252–254	0.54
4h	C ₁₃ H ₈ N ₁₀ O ₂ S ₂	440, 636	56	265	0.68

Table 1 showed that the dyes exhibited a maximum absorption wavelength (λ_{\max}) and a shoulder except dyes 4d and 4f without a shoulder. An inspection of the λ_{\max} values indicates that the dyes have a yellow shade and this agrees with the shade shown on the dyed nylon fabrics.

Fastness Properties of the Synthesized Dyes 4a to 4h on Nylon 6 Fabrics

Table 2: Wash and Rub Fastness Values

Compounds	Wash fastness			Rubbing	
	CC	SW	SC	Dry	Wet
4a	5	4/5	5	4	3/4
4b	5	5	5	4	3/4
4c	5	5	5	3/4	3/4
4d	5	5	4/5	3/4	3/4
4e	5	5	5	3/4	4
4f	5	5	5	4	3/4
4g	5	5	5	4	4
5h	5	5	4/5	3/4	4

CC = colour change, SW = staining on wool, SC = staining on cotton. Grey scale of 1-5 was used, where 1 = poor and 5 = excellent

Table 3: Light, Perspiration and Sublimation Fastness Properties of Dyed Nylon Fabric

Compound	Perspiration						Sublimation		180 °C
	Acidic			Alkaline			SW	SC	
	CC	SW	SC	CC	SW	SC			
4a	5	4	5	5	4/5	5	5	4	
4b	5/6	4	5	5	5	5	5	3/4	
4c	5/6	4	5	5	4/5	5	5	3/4	
4d	5	4	4/5	4/5	5	5	5	4	
4e	5	4	4/5	5	5	5	5	4/5	
4f	5	4	5	4/5	5	5	4/5	4/5	
4g	5/6	4	4/5	5	5	5	5	4	
4h	5	4	5	5	5	5	4/5	4	

CC = colour change, SW = Staining of wool, SC = Staining of cotton. Grey scale for light fastness is 1-8 where 1 = poor and 8 = excellent.

4-amino-3-chlorophenylazo-3,5-dihydroxypyrimidylazo-2,4',5'-thiadiazole (5a)

Prepared from compound (3) (2.0 g, 0.012 mol) and 2-chloroaniline (2 ml) using the method described for compound (3). Column chromatography was used to purify the dye, using a solvent system of toluene-chloroform. Yield: 45%; mp: 183 – 185 °C; $^1\text{H NMR } \delta_{\text{H}}$ (ppm) 1.43 (s, 2H, NH₂), 4.50 (s, 1H, OH), 6.92 (s, 1H, 8H), 7.25 (m, 2H, ArH), 8.20 (m, 1H, ArH), 13.22 (s, 1H, NH), $^{13}\text{C NMR } \delta_{\text{C}}$ (ppm): 161.8, 160.9, 142.5, 133.7, 132.9, 115.6, 96.2, 65.7, 41.8, 41.6, 40.9, 40.6, 40.4. IR (KBr) ($\bar{\nu}/\text{cm}^{-1}$): 3494 (OH, NH), 3082, 2931, 2868, 2351, 1672, 1496, 1394, 1265, 1093, 861, 651.

2-amino-5-bromophenylazo-(3,5-dihydroxypyrimidyl)azo-1,3,4-thiadiazole (5b)

Prepared from compound (3) (2.0 g, 0.012 mol) and 4-bromoaniline using the procedure described for compound (3). The crude product was purified by column chromatography toluene/chloroform. Yield: 54%, mp 195 – 197 °C; $^1\text{H NMR } \delta_{\text{H}}$ (ppm): 1.46 (s, 2H, NH₂), 3.90 (s, 3H, OCH₃), 4.62 (s, 1H, OH), 6.88 (s, 1H, 5H), 7.85 – 7.92 (m, 2H, ArH), 8.25 (m, 1H, ArH), 14.12 (s, 1H, NH). $^{13}\text{C NMR } \delta_{\text{C}}$ (ppm): 165.6, 131.5, 130.4, 130.0, 41.5, 40.2, 40.0, 39.7, 39.5, 38.9, 38.7, 38.5. IR (KBr) ($\bar{\nu}/\text{cm}^{-1}$): 3540, 3067, 2931, 2873, 2351, 1673, 1496, 1443, 1393, 1255, 1092, 866, 659, 504.

2,6-dihydroxypyrimidylazo-3,5-dihydroxypyrimidylazo-2',4,5'-thiadiazole (5c)

Prepared from compound (3) (2.0 g, 0.012 mol) and 2,4-dihydroxypyrimidinediol (0.83 g, 0.007 mol). The crude product was purified using column chromatography toluene/chloroform to afford yellow solid. Yield: 55%, mp: 202 °C. $^1\text{H NMR } \delta_{\text{H}}$ (ppm): 4.61 (s, 1H x3, OH), 6.67 (s, 1H, SH), 8.52 (m, 1H ArH), 13.25 (s, 1H, NH).

^{13}C NMR δ_{C} (ppm): 132.6, 130.7, 112.6, 110.5, 41.8, 40.8, 40.7, 40.3, 38.7, 38.5. IR (KBr) $\bar{\nu}/\text{cm}^{-1}$: 3488, 3084, 2932, 2868, 2351, 1671, 1496, 1440, 1255, 1094, 866, 659, 546.

Page | 3362 **2-hydroxy—3-rthoxy-5-oxo-phenylazo-3',5-dihydroxypyrimidylazo-2',4,5'-thiadiazole (5d)**

Prepared from compound 3 (2.0 g, 0.012 mol) and 4-hydroxy-3-ethoxybenzaldehyde (1.23 g, 0.007 mol) using the method described for compound (5c). yield: 78%, mp: 250 – 252 °C. ^1H NMR δ_{H} (ppm): 2.05 (t, 3H, CH_3), 4.26 (s, 1H x2, OH), 5.10, (q, 2H, CH_2), 6.20 (s, 1H, CH), 6.85 (s, 1H, SH), 14.25 (s, 1H, NH). ^{13}C NMR δ_{C} (ppm): 215.8 (C=O), 164.8, 145.6, 133.5, 130.7, 112.8, 110.7, 95.2, 90.5, 57.6, 41.4, 40.8, 39.4, 38.8, 38.5. IR (KBr) ($\bar{\nu}/\text{cm}^{-1}$): 3496, 3036, 2931, 2868, 2352, 1687, 1496, 1440, 1254, 1093, 866, 659, 546.

2-hydroxyquinolylazo-3,5-dihydroxypyrimidylazo-2',4,5'-thiadiazole (5e)

Prepared from compound (3) (2.0 g, 0.012 mol) and 6-hydroxyquinoline (1.16 g, 0.007 mol) as described for compound (3). The crude product was purified using column chromatography to give yellow solid. Yield: 52%, mp: 215 °C. ^1H NMR (200 MHz, CDCl_3), δ_{H} (ppm): 4.52 (s, 1H x2, OH), 6.78 (s, 1H, SH), 6.89 – 7.58 (m, 5H, quinolyl H), 14.10 (s, 1H NH). ^{13}C NMR (50 MHz, CDCl_3) δ_{C} (ppm): 165.8, 145.7, 138.1, 136.5, 132.9, 125.2, 123.8, 113.5, 61.6, 41.8, 41.6, 40.9, 40.7, 39.5, 38.7.

4-hydroxyquinolylazo-3,5-dihydroxypyrimidylazo-2',4,5'-thiadiazole (5f)

Prepared from compound (3) (2.0 g, 0.012 mol) and 8-hydroxyquinoline (1.16 g, 0.007 mol). The crude product was purified using column chromatography to afford a yellow solid. Yield: 56%, mp: 250 °C. ^1H NMR δ_{H} (ppm): 4.52 (s, 1H x2 OH), 6.78 (1H, SH), 6.87 – 7.82 (m, 5H quinolyl H), 13.26 (s, 1H, NH). ^{13}C NMR δ_{C}

(ppm): 165.6, 141.7, 138.2, 135.6, 133.8, 134.7, 122.8, 120.5, 110.8, 41.8, 41.5, 40.3, 38.9, 38.5, 38.4. IR (KBr) ($\bar{\nu}/\text{cm}^{-1}$): 3492, 3054, 2952, 2868, 1394, 1254, 1093, 866, 659, 551.

2-hydroxy-7-methoxynaphthylazo-3,5-dihydroxypyrimidylazo-2',4,5'-thiadiazole (5g)

Prepared from compound (3) (2.0 g 0.12 mol) and 2-hydroxy-7-methoxynaphthalene (1.20 g, 0.007 mol). The crude product was purified as described for compound (5f) to give a yellow brown solid. Yield: 65%, mp: 252 – 254 °C. ^1H NMR δ_{H} (ppm): 3.42 (s, 3H, OCH_3), 4.15 (s, 1H x2, OH), 6.76 (s, 1H, SH), 6.87 – 7.45 (m, 5H, naphthyl H), 13.36 (s, 1H, NH). ^{13}C NMR δ_{C} (ppm): 133.7, 132.6, 132.3, 131.8, 123.5, 110.9, 110.7, 95.8, 41.6, 41.4, 39.7, 39.4, 39.0, 38.7, 38.5, 38.1. IR (KBr) ($\bar{\nu}/\text{cm}^{-1}$): 3492, 2068, 2931, 2873, 2352, 1671, 1495, 1440, 1393, 1254, 1093, 864, 659, 548.

4-amino-3-cyanophenylazo-3,5-dihydroxypyrimidylazo-2,4',5-thaidiazole (5h)

Prepared from compound (3) (2.0 g, 0.12 mol) and 2-cyanoaniline (0.871 g, 0.007 mol) from toluene/ethanol and air dried to afford a brown solid. Yield: 56%, mp: 265 °C. ^1H NMR δ_{H} (ppm): 1.27 (s, 2H, NH_2), 4.26 (s, 1H, OH), 6.69 (s, 1H, SH), 8.10 (m, 2H, ArH), 8.25 (m, 1H, ArH) 13.12 (s, 1H, NH). ^{13}C NMR δ_{C} (ppm): 162.7, 161.4, 151.8, 132.7, 116.6, 62.5, 41.9, 41.7, 41.5, 41.2, 39.8, 39.5, 38.4. IR (KBr) ($\bar{\nu}/\text{cm}^{-1}$): 3483, 3067, 2932, 2873, 2350, 1670, 1496, 1440, 1254, 1094, 864, 659, 556.

Discussion

The disazo disperse dyes were synthesized by diazo coupling reactions of 2-amino-4,6-dihydroxypyrimidylazo-2,3,4-thiadiazole-5-thiol with aryl compounds (Metwally *et al.*, 2013). The structures of the dyes were confirmed by spectroscopic methods (^1H NMR, ^{13}C NMR and FTIR).

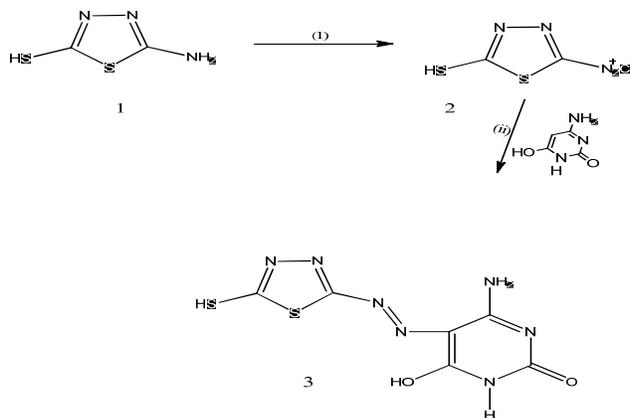
Spectroscopic Studies

The FTIR spectra (in KBr) of the synthesized dyes showed a strong broad band within the range $3483 - 3530 \text{ cm}^{-1}$ corresponding to O-H and NH_2 stretching vibration in dye 5a, 5b and 5h. the medium strength absorption bands of NH were produced in the range $3122 - 3168 \text{ cm}^{-1}$. These stretching vibrations maybe due to the existence of the dyes in the hydrazone form. The absorption of C-H stretch in the FTIR spectra were observed within the range $2931 - 3036 \text{ cm}^{-1}$. Furthermore, the characteristic absorption peak at $2351 - 2352 \text{ cm}^{-1}$ range is due at S-H stretching vibrations. The strong absorption at 1671 cm^{-1} indicates that compound 4d has C=O group. The strong absorption observed around 1496 and 1440 cm^{-1} is due to the presence of benzene rings with C=C stretch (Carey, 2003). The medium absorption bands found in the 1255 and 1254 cm^{-1} region in the FTIR spectra of the dyes indicates the presence of C=N in the dye compounds (Bruice, 2001). The absorption at 1440 cm^{-1} is suggestive of the presence of a methyl group in compound 4d. In addition, the FTIR spectra of the dyes also showed that the absorption bands at 1093 cm^{-1} , attributed to C-O stretching vibrations confirms that there are O-H groups in the compounds (Skoog *et al.*, 1998; Bruice, 2001). The absorption peak at $659 - 804 \text{ cm}^{-1}$ region are due to the C-H bending vibrations.

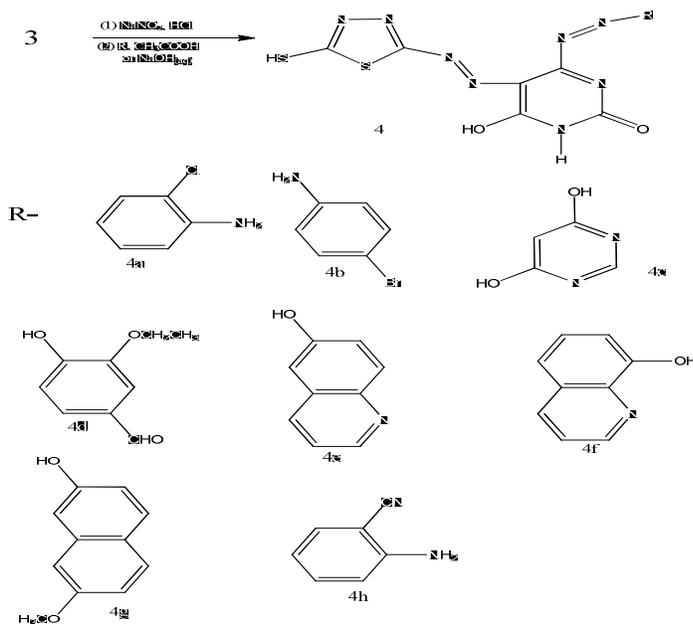
In the ^1H NMR spectra, the signals detected at $\delta = 1.26 - 1.46 \text{ ppm}$ was attributed to the protons of NH_2 in compounds 4a, 4b and 4h. the triplet signals detected at $\delta = 2.05 \text{ ppm}$ and $\delta = 4.81 \text{ ppm}$ are due to the protons of the CH_3 and CH_2 respectively. Moreover, the clear singlet at $\delta = 6.88 \text{ ppm}$ was due to protons of 5H, while the multiplets at $\delta = 7.25 - 8.68 \text{ ppm}$ are attributed to aromatic protons. The strong singlets at $\delta = 11.25 \text{ ppm}$, detected for all the compounds were assigned to secondary amine (NH) protons of the pyrimidine component (Morrison *et al.*, 2011;

Carey, 2003). While the broad absorptions observed at $\delta 1312$ to 14.12 ppm was attributed to the presence of hydrazone tautomeric forms.

Furthermore, the obtained dyes were analysed by ^{13}C NMR spectra and recorded in the solvents $\text{DMSO}-d_6$ and CDCl_3 . The carbon atoms recorded signals at their respective positions to further elucidate their structures.



Scheme 1: Synthetic route of compound 3
(i) NaNO_2/HCl H_2O (ii) $\text{NaOH}_{(\text{aq})}$



Scheme 2: Synthesis and structures of dyes 4a to 4h
(1) $\text{NaNO}_2, \text{HCl}$ (2) $\text{R}, \text{CH}_3\text{COOH}$ or $\text{NaOH}_{(\text{aq})}$

UV-vis Absorption Spectroscopic Analysis

The obtained disazo disperse dyes were also analysed using UV-vis absorption spectra to investigate their colour characteristics in dimethylformamide (DMF).

Fastness Properties

The results of the fastness properties of the dyed nylon fabric are listed in Table 1 and 2. The dyed fabric showed washing fastness rating of 4 to 4/5 when related with the standard grey scale, indicating very good fastness property. Also the fastness ratings of the staining on the adjacent fabric was observed to be 4 to 4/5 which implied very good to excellent performance. The dyes produced yellow shades on the dyed nylon fabrics. The excellent wet fastness results indicates that there was very little staining of the adjacent white textile fabrics. This can be attributed to the inclusion of a base sensitive function in the design of the structure of the disperse dyes. The explanation for this is that, in the solution phase the dyes could exist as either structure A or B (fig 1). The geometry which is called the hydrazone tautomeric form shown by structure B has been observed to be more stable (Metwally *et al.*, 2013; Choudhart *et al.*, 2016). As shown in fig 1, the pyrimidine component of the dyes can exhibit a base-sensitive function which led to the improved dye diffusion into the textile fibre, thus leading to lesser loose dye molecules in the nylon 6 fabric. Thus, there was improvement in wet fastness grade of the dyes compared with previous findings (Otutu *et al.*, 2014).

The rubbing fastness results in Table 2 gave fastness rating of 3/4 to 4, indicating good to very good. This implies that there was relatively good dye diffusion into the fabric. The light fastness results are shown in Table 3. The dyes

gave a light fastness rating of 5 to 5/6 on the blue wool scale,

The light fastness results are shown in Table 3. The dyes gave a light fastness rating of 5 to 5/6 on the blue wool scale, corresponding to moderate to good light fastness property. The fabrics were exposed to xenon arc lamp (artificial light) for 72 h to determine the change in colour shade.

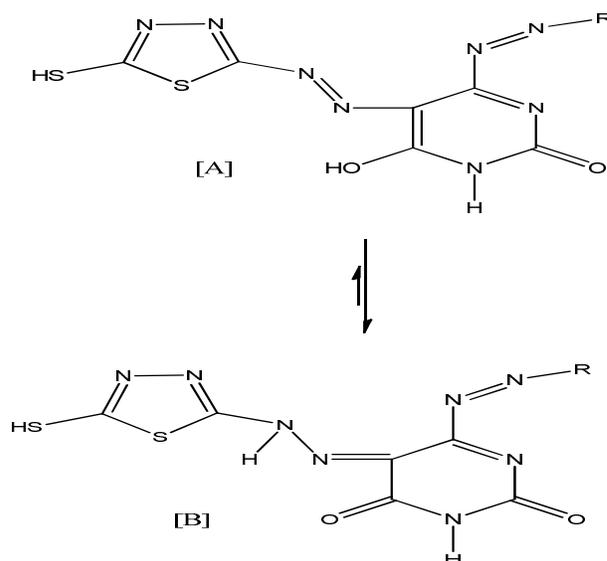


Figure 1: The tautomeric structure of the dyes [A] = azo form [B] hydrazone tautomer

The perspiration fastness rating was observed to be 3/4 (acid perspiration) and 4 to 4/5 for alkaline perspiration on the standard grey scale. This indicates that the dyed fabrics were less stable to acidic perspiration than to alkaline perspiration. The sublimation fastness rating of the dyed fabric is 3/4 to 4/5 corresponding to good to very good fastness property.

Conclusion

Disazo disperse dyes based on 2-amino-4,6-dihydropyrimidine and 2-amino-5-mercapto-1,3,4-thiadiazole were synthesized. The dyed nylon fabrics have high degrees of colour

fastness to washing, rubbing, light and perspiration and good colour fastness to sublimation. Furthermore, dye 4h showed an absorption band at 440nm and a broad shoulder at 635nm in its ultraviolet-visible spectrum. This suggests that it can be used as a near infrared absorber, since it showed absorption in the near infrared region of the electromagnetic spectrum.

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