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Synthesis and Application of Monoazo Acid Dyes Derived from 5-amino-4-cyano-2-methyl-N-phenylthiophene-3-carboxamide on Chrome Tanned Leather and Nylon 6,6 Substrate

***Magaji I.Y.,[1] Giwa, A,.[2] and Bello, K.A[2]**
[1]Department of Polymer Technology, Nigerian Institute of Leather and Science Technology Zaria
[2]Department of Polymer and Textile Engineering, Ahmadu Bello University, Zaria
Corresponding author's e-mail; ibrahimmagaji63@gmail.com +2348063959910

ABSTRACT

A series of new mono azo dyes have been synthesized in moderate yield from diazotization of thiophene and coupling with R, H, J and ϒ acid. The dyes were characterized by spectral studies. The dyeing potentials were assessed by applying them on chrome tanned leather and nylon 6,6 substrates. The dyes were found to give shade of red dark blue and dark maroon .The synthesized dyes gave a maximum absorption within the UV- visible region with λ_{max}*515-597 nm and molar extinction coefficient ranging from (3.217-4.221 x* 10^4 *l/mol*$^{-1}$ *cm*$^{-1}$*) and the infra-red spectra showed peaks at 1582-1421cm-*^{1} *(due to azo group (N=N) stretching vibration), at 3400 – 3200 cm*$^{-1}$ *due to (OH&NH) medium & broad stretching vibration), at 2830-26-95cm*$^{-1}$ *(due to aromatic group (C-H) stretching vibration) , at 1760-1640 cm*$^{-1}$ *(due to carbonyl group (C=O) stretching vibration), at 1342-1266 cm*$^{-1}$ *(due to aromatic amine group (C-N) stretching vibration) and at 2260-2222 cm*$^{-1}$ *(due to nitrile (C≡N) stretching vibration). The dye exhibited good depth, affinity, levelling and brightness properties on the substrates. The dye gave a good percentage exhaustion on nylon 6.6 and on chrome tanned leather substrates ranging from (78-87%) and (63-75%) respectively. The chrome tanned leather gave a wash fastness rating ranging from (3 -5) good, very good to excellent respectively and nylon 6,6 gave a wash fastness rating ranging from (4-5) very good to excellent fastness properties and the light fastness properties of chrome tanned leather gave a fastness rating (4-7) moderate, good, very good and excellent and rubbing fastness rating (4-5) very good to excellent on both substrates. The good shades observed may be due to better substantivity on chrome tanned leather and nylon 6,6 fabrics.*

Keywords: *Monoazo dyes , Synthesis , Exhaustion , Fastness properties, Diazotization*

INTRODUCTION

Azo-functionalized dyes bearing aromatic heterocyclic components [1] have attracted ever increasing attention in recent years due to their range of colour, brightness, simplicity, ease of manufacturing, good dyeing performance [2]. Azo compounds are a class of chemical components that are continually receiving attention in scientific research [3] [4] [5]. They are usually strong coloured compounds which can be intensely yellow, red, orange, blue and green etc. depending on the exact structure of the molecule. These dyes have characteristically good tinctorial strength as well as stability. Their preparation procedures by the classic diazotization and coupling reactions, are very simple and of low cost. They have found wide application in dyeing of protein fibers such as wool, angora, cashmere, and silk, as well the milk protein fiber called "Silk Latte", the soy protein fiber called "Soy Silk", and the synthetic polyamide fiber nylon [6 -14], As a result of their colour, azo compounds are tremendously important as dyes and as pigments for a long time [13]. Infact, about half of the dyes in industrial use are azo dyes which are mostly prepared from diazonium salt [15-16]. Azo dyes, account for more than half of the dye which contain phenol as intermediates. The aim of the study was to synthesize novel monoazo acid dyes and the assessment of their fastness properties on chrome tanned leather and nylon 6,6 derive from 5-amino-4-cyano-2-methyl-N-phenylthiophene-3-carboxamide using coupling component such as R, H, J and ɣ acid .

MATERIAL AND METHODS

Materials

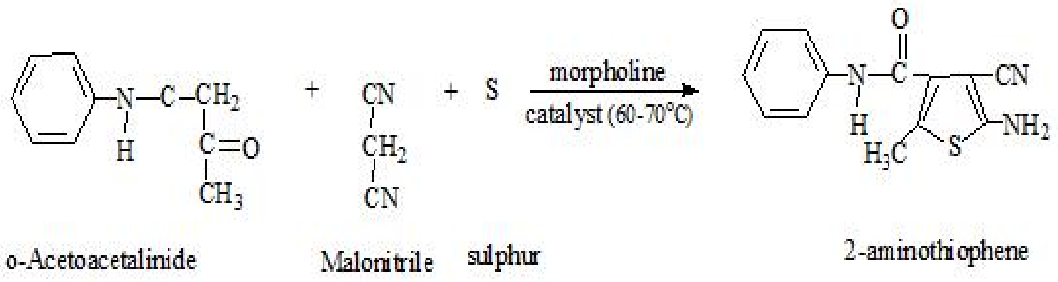
All commercial products were purchased from Sigma-Aldrich. Such as H-acid, R-acid, J-acid. Gamma-acid, acetic acid ,anionic detergent. FT-IR spectrophotometer (Agilent CARRY 630 FT-IR Spectrophotometer), GC-MS spectrometry (7890B GC System),

Synthesis of dye Intermediate (2-Aminothiophene Intermediate)

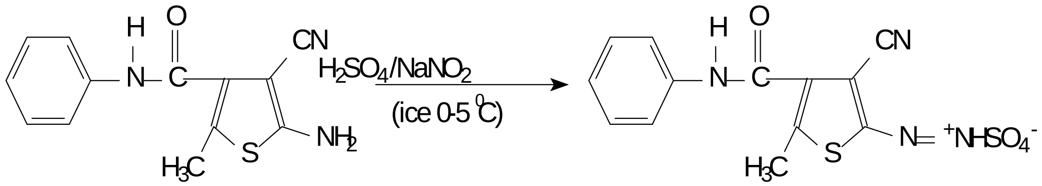
The dye intermediates was synthesized as follows: o-acetoacetanilide (20.0 g, 0.1 mol), Malononitrile (6.50 g, 0.1 mol), Sulphur (3.0 g, 0.1 mol), morpholine (8.50 g, 0.1 mol) were dissolved in 200 cm^3 of ethanol and introduced into a round bottom flask and heated at 60-70 ^{o}C for 3-4 hrs. The resulting thick dark solution is cooled and stored overnight in a refrigerator, The light brown powder obtained was crystallized from ethanol [17]

Synthesis of Diazonium Salt Solution [18]

Sodium nitrite (1.38g, 0.02mol) was added portion wise to mixture 50cm^3 of nitrosyl sulphuric acid added to propionic acid and acetic acid (2:1) cooled to 0-5^{o}C in ice bath and a mixture added to the (2.57g, 0.01) synthesized intermediate. The reaction mixture was then cooled to 0-5^{o}C and then added portion wise and stirring continued for 2 hrs at 0-5^{o}C to avoid excess heat that will destroy the diazonium salt. The resulting diazonium salt solution was obtained.



Equation 1: Schematic route for the synthesis of intermediate (Aminothiophene)



Scheme 1: Schematic route for the synthesis of diazonium salt

Coupling of Diazonium Salt Solution [19]

H-acid (2.0g, 0.01 mol) is dissolved in 10 cm^3 of distilled water and the solution was cool to 0-5^{o}C. To the well stirred solution, the freshly prepared diazonium salt solution was added drop wise over 45 minutes maintaining the temperature below 0-5^{o}C with vigorous stirring. The stirring was done for 1 hour at 0-5 ^{o}C, maintaining pH 4-5 using sodium carbonate solution (10%$^{w}/_{v}$). The resulting dye was collected, wash several times with water to ensure a free acid and dry in an oven at 40 ^{o}C. The result was repeated for R, ,J and ɣ acid .

Structures of Synthesized Dyes

Purification of the Dyes

The dyes were purified through the same process of recrystallization as highlighted above for the intermediate. Some of the dyes required a mixed solvent of ethanol, methanol /DMF (9/1 solvent mixture) according to a procedure suggested by [20]. The purity of each synthesized dyes were confirmed by melting point.

Percentage Yield of Dyes and Intermediate

The percentage yield of the synthesized dyes and intermediates were determined using the formula shown below [21]

$$\%\text{Yield} = \frac{M}{M} \div \frac{M}{M} \times 100$$

where;

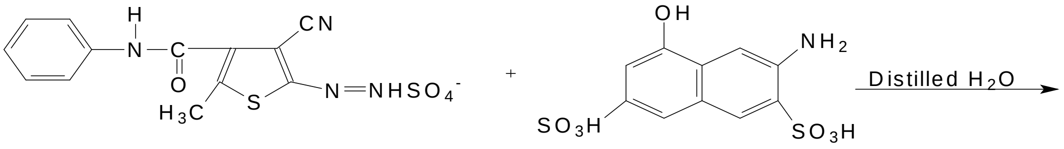
MP is the mass of the product
MMP is the molar mass of the product
MR is the mass of the reactant
MMR is the molar mass of the reactant

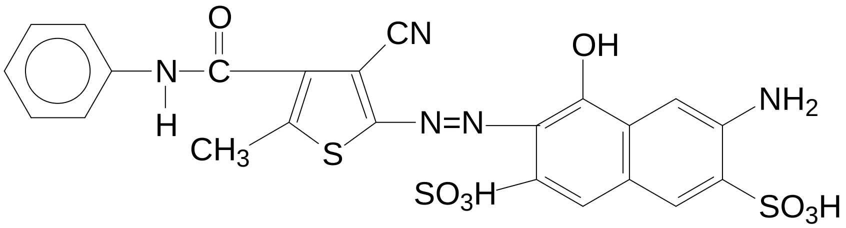
Melting Point of the Dyes

The melting point of each dye was determined using Gallenkamp melting point apparatus. Small amount of each dye was filled into a capillary tube each placed in to the apparatus, the melting point of each dye was obtained by consistently focusing on the apparatus as the apparatus gradually heated the dye in the tube.

Dyeing of Nylon 6, 6 Fabric

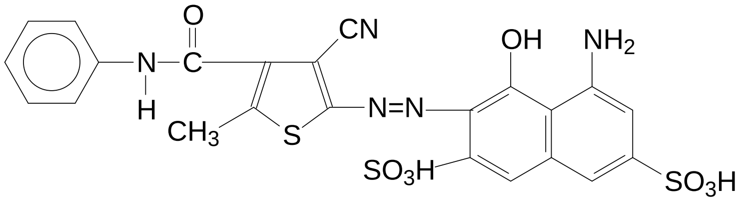
For the nylon 6,6 fibre, a dispersing agent (anionic detergent) was used to facilitate the dyeing process. The fabric was wetted and thoroughly squeezed to remove excess water. It was then immersed into the bath at 70°C and allowed to reach the boil within 15min. Dyeing was carried out for one hour at a temperature of 100°C with agitation. At the end of the dyeing process, the substrate was removed, squeezed and rinsed thoroughly under running tap water and allowed to dry at room temperature [22].





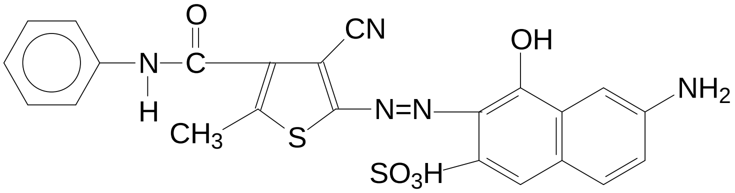
Dye 1a

3-amino-6-((3-cyano-5-methyl-4-(phenylcarbamoyl)thiophen-2-yl)diazenyl)naphthalene-2,7-disulfonic acid



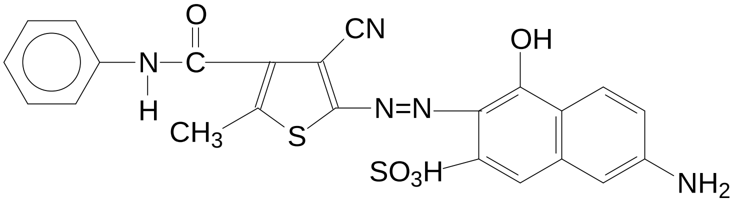
Dye 1b

5-amino-3-((3-cyano-5-methyl-4-(phenylcarbamoyl)thiophen-2-yl)diazenyl)-4-hydroxynaphthalene-2,7-disulfonic acid



Dye 1c

6-amino-3-((3-cyano-5-methyl-4-(phenylcarbamoyl)thiophen-2-yl)diazenyl)-4-hydroxynaphthalene-2-sulfonic acid



Dye 1d

7-amino-3-((3-cyano-5-methyl-4-(phenylcarbamoyl)thiophen-2-yl)diazenyl)-4-hydroxynaphthalene-2-sulfonic acid

Dyeing of Leather

The synthesized dyes were used in dyeing of chrome tanned leather. The standard method of dyeing leather was followed using the recipe.

i. 120 % of water (60 ^{0}C)
ii. 2 % of dye
iii. 0.1 % of formic acid

A solution of the dye sample (2%) was made with distilled water using heating mantle and then was raised to 60 ^{0}C. The pH of the bath was adjusted to 5.5 with formic acid. The leather samples were introduced into the bath and run for 1 hour in a mechanical shaker at a controlled speed [23].

Application of dyes solution

A solution was prepared by dissolving about 1g of dried dye powder in 100mls of distilled water. To determine the qualities required for the experiment the following parameter was utilized.

Number of ml of stock solution required

$$= \frac{W \times P}{C}$$

where W = weight (in g) of sample to be dyed
P = percentage of dye to be used
C = concentration (%) of stock solution [24]

General procedure of dyeing chrome tanned leather:

1 % of dye (on weight of the materials)
50 + 2°C dyeing temperature
0.1 % of formic acid on weight of the dye
Time of dyeing: one hour
Liquor ratio 20:1

Determination of Dye Bath Exhaustion

Dye uptake was determined by measuring the absorbance of diluted dye bath samples at the wavelength of the maximum absorption. The bath was sampled before and after dyeing. A 1ml aliquot was taken from the bath and diluted in 20ml of distilled water. This is to ensure that the absorbance falls within the readable range of 1.5. The percentage dye bath exhaustion (%E) for each substrate was calculated using equation below [25].

$$\%E = \frac{A_0 - A_1}{A_0} \times 100$$

where A_o and A_1 are the absorbance at λ_{max} of the dye bath prior to dyeing and after dyeing respectively.

Light Fastness of Dyed Substrates (Fastness to Sunlight) SLT 401 (IUF 401)

This test was carried out in accordance with the Society of Leather Technology and Chemists (SLTC). The test was carried out on the dyed samples under daylight facing south sloping at an angle 45° from the horizontal. The procedures involved aligning both the eight dyed wool standards together with a 2 cm x 2cm cut pieces of the dyed samples on a card and covering one third of the setup with opaque cover.

Exposure was carried with regular inspection noting when the non-exposed part and exposed part of each dyed sample had contrast equivalent to grade 4 of ISO grey scale after which and opaque cover was placed covering part of the exposed sample part, exposure was continued till the blue standard 7 faded. The rating of the dyed samples was taken to be those equivalents to- that of standard dyed blue wool samples, which faded to the same extent as the specimen at the same time.

Wash Fastness of the Dyed Substrates

This is to assess the dyed leather resistance to prolonged action of water. 2 x 2cm of the dyed leather was dipped into solution made by 5 g (0.5 %) of detergent powder into 200 cm^3 of distilled water. This was placed in water bath and the temperature allowed to rise to 40 °C. This was vigorously stirred for about 30 min and the leather was transferred to 100 cm3 distilled water for washing and rinsing was done five times and dried. The change in colour was assessed by the standard grey scale .

Rubbing Fastness Test of the Dyed Substrates

This method is intended for determining the behaviour of the surface dyed texture of a leather rubbing with felt. The leather to be tested is rubbed with pieces of structure wool felt under a given pressure with a given number of forward and backward motion. 2x2cm piece of the leather sample were cut and dipped on rub fastness tester (Machine Model STM). The number of rub on a fixed position was varied to assess the degree to fastness to rubbing. The change in colour of the felt and leather was assessed with the standard grey scale.

RESULT AND DISCUSSION

Table 1: Physical Properties of the Synthesized Dye Intermediate

Name of Intermediate	Colour	Melting Point (°C)	Percentage Yield (%)	Molecular Weight (g/mol)	Molecular Formula
5-amino-4-cyno-2-methyl-N-phenylthiophene-3-carboxamide	Dark brown	188-194	97	257	$C_{13}H_{11}ON_3S$

Table 2: Physical Properties of the Synthesized Mono Azo Acid Dyes

Dye no	Molecular Formula	Shade Crystal	Molecular Weight(g/mol)	Melting Point (°C)	Percentage Yield (%)
1a	$C_{23}H_{17}O_8S_3N_5$	Red	587	200-202	76
1b	$C_{23}H_{17}O_4$ S_3N_5	Darkblue	587	191-194	62
1c	$C_{26}H_{17}O_5S_2N_5$	Dark maroon	507	120-122	68
1d	$C_{26}H_{17}O_5S_2N_5$	Red	507	212-214	82

Table 3: Spectra Data of the Synthesized Mono Azo Acid Dyes using Dimethylformamide and Ethanol

Dyes no	λ_{max} in (nm) DMF	λ_{max} in (nm) Ethanol	Molar Extinction Coefficient in (DMF) x 10^4 $^{(}$l/mol^{-1}cm$^{-1)}$
1a	530	515	4.181
1b	597	572	4.176
1c	580	577	3.217
1d	565	527	4.145

Table 4 : Infrared Spectra of the Synthesized Intermediate

Functional group	NH cm^{-1}	C-H cm^{-1}	C=O cm^{-1}	C-N cm^{-1}
Types of vibration	Stretching	Stretching	Stretching	Stretching
	3459.0	2967.0	1699.7	2214.0
	3354.6	2870.1	1666.1	
	3205.5		1602	

Table 5: Infrared Spectra of Mono Azo Acid Dyes

Functional group	OH & NH	Aromatic C-H	Carbonyl C-O	Aromatic amine C-N	Azo N=N
Types of vibration	Stretching	Stretching	Stretching	Stretching	Stretching
1a	3347.1		1636.3	1315.8	1488.6
1b	3377.0		1636.3	1367	1499.4 1529.2
1c	3373.2		1703.4 1654.9	1319.5	1468.5
1d	3410.5		1636.3		1535.7 1468.6

Table 6: Gas Chromatography Mass Spectroscopy of Synthesized Intermediate

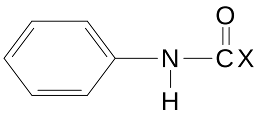
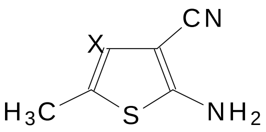
Sample value	Fragmentation (m/z)	Calculated
Intermediate	 $(C_7H_6NO)^+$ =120 but m/z = 123± 3  $(C_6H_5N_2S)^+$=137 but m/z =140±3	257g/mol

Table 7: Percentage Exhaustion the Dyes on Nylon 6,6 and Chrome Tanned Leather Substrate

Dyes No.	% E for Nylon 6,6	% E CTL
1a	80.10	63.10
1b	78.50	68.50
1c	84.00	75.30
1d	87.20	68.20

Table 8: Light and Wash Fastness Properties of Chrome Tanned Dyed Leather

Dyed No.	Light Fastness Rating	Wash Fastness Rating
1a	5-6	4-4
1b	5	4-5
1c	5-6	4-5
1d	3-4	3-4

Table 9: Rubbing Fastness Properties on Chrome Tanned Dyed Leather

Dyed no	Number of Rubs	Fastness Rating	Staining of Adjacent un-dyed Cotton
1a	100	5	4
1b	100	5	4
1c	100	5	3
1d	100	5	3

Table 10: Rubbing Fastness Properties of Dyed Nylon 6.6 Fabric

Dry Treatment	Wet Treatment		Change in Colour	
Dye No.	Change in Colour	Staining		Staining
1a	5	5	5	5
1b	5	5	5	5
1c	5	5	5	5
1d	5	5	5	5

Table 11: Light and Wash Fastness Properties of Nylon 6,6 Fabric.

Dyes	Light Fastness Rating	Wash Fastness Rating	Staining on of Adjacent undyed Fabric
1a	6	3	3
1b	6	3	3
1b	6	4	4
1d	7	4	3

The Spectral Data Analysis of Synthesized Monoazo Acid Dyes

The monoazo acid dye as shown on Table 3: 1a, 1b, 1c and 1d absorbed at 530, 597, 580 and 565 nm respectively in dimethylformamide. Dye 1b for instance is more bathochromic compared with dye 1a, 1c and 1d. Dye 1b was synthesized from the coupling component of 8- amino-1-naphthol 3-6-disulfuric acid. This is followed by dye 1c containing 2, amino–8–naphthol sulfuric acid as coupling component which absorbed at 580nm and is bathochromic compound with dye 1a and 1d which absorbed at 530 and 565 nm containing 2–naphthol–3–6 disulfuric acid and 2-amino-5-naphthol-7-sulfuric acid respectively, The substituent shifts of maximum wavelength (λ_{max}) absorption to shorter wave length, with reduced absorbance energy, intensified the colour of dyes. The colour change observed for each dye is due to the oscillation of electrons and the presence of additional substituents. The higher HOMO energy values show the molecule is a good electron donor, in other hand, the lower HOMO energy values indicate that, a weaker ability of the molecules for donating electron. LUMO energy presents the ability of a molecule for receiving electron.

Maximum absorption moves to longer wavelength as the amount of delocalization increases, therefore the maximum absorption moves to shorter frequency, the absorption needing less energy gap between the bonding and anti-bonding orbitals [24].

Assessment of FT-IR Group Absorption Spectroscopic Properties of Synthesized Intermediate and Acid Dye

It is obvious as shown on Table 4: that dye intermediate which is 2 – aminothiophene gave absorption peaks due to (N –H) group at 3459.0 cm^{-1}, 3354.6 cm^{-1}, and 3205.5 cm^{-1}, (C – H) group at 2967 cm^{-1}, (C = O) group at 1699.7 cm^{-1}, 1666.1 cm^{-1}, and 1602 cm^{-1}, and (C≡ N) group at 2214.0 cm^{-1}, stretching vibration. Dye 1a – d were obtained by diazotization of 2–aminothiophene and coupling with 2–naphthol–3–6 disulfuric acid, 8–amino–1–naphthol-3-6, disulfuric acid, 2–amino–8–naphthol sulfuric acid and 2–amino–5–naphthol–7 sulfuric acids respectively. They absorption peaks due to (O–H and N–H) group at 3347 cm^{-1}, (C=O) at 1636.3 cm^{-1}, (C–N) at 1315.8 cm^{-1}, and (-N=N-) group at 1488.6 cm^{-1}, stretching vibration in dye 1a. dye 1b which is obtained by diazotization of diazonium salt coupling with 8–amino–1-naphthol–3-6–disulfuric acid showed absorption peaks due to (O–H and N–H) group at 3377.0 cm^{-1}, (C=O) group at 1636 cm^{-1}, (C–N) at 1367cm^{-1}, and (-N=N-) group at 1499.4 and 1529.2cm^{-1}, stretching vibration. Dye 1c which is obtained by coupling diazonium salt with 2–amino–8–napthol sulfuric acid gave absorption peak due (O – H)\ and N –H) group at 3373.2cm^{-1}, (C=O) group at 1703.4cm^{-1}, and 1654.9cm^{-1}, (C–N) group at 1319.5cm^{-1}, and (N=N) group at 1468.5cm^{-1} stretching vibration. Dye 1d which obtained by coupling diazonium salt with 2–amino–5–naphthol–sulfuric acid showed absorption peak due to (O –H and N – H) group at 3410.5cm^{-1}, (C = O) group at 1636.3 cm^{-1}, (-N=N-) group at 1535.7 cm^{-1}, and 1468.6 cm^{-1}, stretching vibration.

Molar Extinction Coefficient (€)

From the result indicated on Table 5: it is clear that the dyes possess high molar extinctions coefficient. From the result shown, it can be deduced that majority of the synthesized dyes gave molar extinction coefficient values greater than 4.181×10^{4}mol^{-1}cm^{-1}. The higher molar extinction coefficient value of the synthesized dyes probability for more electronic transition and deepness or tinctorial of the shade on the substrate.

The Gas Chromatography Mass Spectrophotometry of the Synthesize Dye Intermediate

This elucidate structural information of the synthesized intermediate molecular ion of the imtermediate is shown in Table 6; Which underwent fragmentations to produce peaks at 120g/mol but m/z is 123±3 and 137g/mol but m/z is 140±3 corresponding positive charge fragment are $C_6H_7NO^+$ and $C_6H_5N_2S^+$ respectively and its molecular mass is (257g/mol). The difference between the experimental (263g/mol) and the calculated value (257g/mol). May be due to isotropy relative abundance ± 6.The slight difference in numerical value of the molecular weight of the intermediate can be attributed to certain elements with high isotopic abundance [25].

Percentage Exhaustion on Nylon 6, 6 and of Chrome Tanned Leather Substrates

The percentage exhaustion and fixation reported according to [26] of 2% (o.w.f) dyeing of nylon 6.6 and percentage exhaustion on chrome tanned leather substrate is summarized in Table 7. Dye 1a –1d which is monoazo acid dyes is obtained by coupling diazonium salt (2–aminothiophene) with coupling component such as 2–naphthol–3–6-disufonic acid, 8-amino-1-naphthol-3-6 disulfuric acid, 2-amino–8–naphthol sulphonic acid and 2-amino–5–naphthol–7–sulphonic acids. Indicates higher percentage exhaustion values on nylon 6,6 ranges from 78–87 while the percentage exhaustion on chrome tanned leather ranges 75–63% in which dye 1d show maximum exhaustion and dye 1c, 1a, and 1b shows minimum percentage exhaustion values 84, 80, 78% respectively due to the amorphous nature of the fabric. While dye 1c show maximum percentage exhaustion value 75% and dye 1b, 1d, and 1a shows minimum percentage exhaustion values 68, 68 and 63% respectively on chrome tanned leather respectively due to the crystalline nature of the substrate. Which indicate high levelness, penetration, substantivity and affinity due to solubility and high rate of diffusion of dye molecules.

Light Fastness

Light fastness rating of the dyed fabric is shown in Table 8 and 10. The test is carried out by exposing each dyed sample to daylight alongside eight blue wool standards. It was observed that light fastness of dye 1a, 1b, 1c and 1d which is obtained by coupling diazonium salt with 2-naphthol-3-6 difulfonic acid, 8-amino-1-naphthol-3-6 disulfonic acid, 2-amino-8-naphthol sulfonic acid and 2-amino-5-naphthol-7-sulfonic acid to obtained monazo acid dyes gave a light fastness rating (3-5) moderate, good and very good on chrome tanned leather which is attributed to hydrophobic texture of the substrate, while light fastness rating (6-7) very good and excellent on nylon 6,6 is attributed to hydrophilic nature of the fabric.

Washing Fastness

Tables 8 and 10 shows the wash fastness of the dyes coupled with diazoniun salt, 2-naphthol, 3-6 disulfonic acid, 8–amino-1-naphthol; 3-6. Disulphonicacid, 2-amino-8-naphthol sulphonic acid and 2-amino -5- napthol -7- sulphonic acid. These dyes gave purple, brown, pink , deep blue to khaki hues with brighter and deeper shades, high tinctorial strength and excellent levelness on the substrates ranging from good (3), very good (4),to excellent (5) Dye 1a-1d gave a wash fastness rating on chrome tanned leather (3-5) good, very good and excellent which is attributed to dyed in difficult to wash out , while on nylon 6,6 gave a wash fastness rating (3-4) good to very good. It could be seen that chrome tanned leather gave better wash fastness than nylon 6,6. which could be as result of the texture of the fabric which in nylon 6,6 involved high diffusion and penetration and in chrome tanned leather which its interweave involve slow diffusion and penetration.

Colour Fastness to Rubbing of the Synthesized Dyes on Chrome Tanned Leather and Nylon 6,6 Substrates

Rubbing fastness was designed to determine the degree of colour which may transfer from the surface of a colour fabric to a specific test substrate for rubbing. Rubbing fastness of all the dyes was very high ranging from (4-5) and the staining rating of adjacent fabric was (3-4). The results obtained from the rubbing fastness test of the dyed fabric is given in Table 11. All the dyed sample gave a fastness rating (4-5) very good to excellent results. This may be due to the solubilisation of a part of the dye and its migration to the surface of coloured fabric (Clark, 2011) substantivity,penetration,levelness and durability in use.

CONCLUSION

A series of new monoazo dyes have been synthesized in moderate yield from diazotisation of 2 –aminothiophene and coupling with H, R, J and ϒ acids and their different properties examined in solution and applied on chrome tanned leather and nylon 6,6 substrates. The dye gave wide range of fast shade like, red, darkblue and maroon .The chrome tanned leather gave a wash fastness rating ranging from (3-5) good, very good to excellent respectively and nylon 6,6 gave wash fastness rating ranging from (4-5) very good to excellent fastness properties. The light fastness properties of chrome tanned leather gave fastness rating of (4-7) moderate, good, very good and excellent as well as rubbing fastness rating from (4-5) very good to excellent on both substrates.

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