



Synthesis and Dyeing Properties of Bi-Functional Reactive Dyes Drive From 2-Aminothiophene on Chrome Tanned Leather and Nylon 6, 6 Substrate

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ABSTRACT

A number of additional bifunctional reactive dyes have been formed in moderate yield from diazotization of 2-aminothiophene -4-carboxylic acid coupling with cyanurated R, H, J and Y acid and condensing with cyanuric chloride and vinyl sulphone. 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 pink, grey and brown. The synthesized dyes gave a maximum absorption within the UV- visible region with λ_{max} 518-581 nm which showed bathochromic effect and molar extinction coefficient ranging from $(3.217-4.221 \times 10^4 \text{ l/mol}^{-1} \text{ cm}^{-1})$ and the infra-red spectra showed peaks at $1582-1421 \text{ cm}^{-1}$ (due to azo group (N=N) stretching vibration), at $3400 - 3200 \text{ cm}^{-1}$ due to (OH&NH) medium & broad stretching vibration), at $2830-26-95 \text{ cm}^{-1}$ (due to aromatic group (C-H) stretching vibration), at $1760-1640 \text{ cm}^{-1}$ (due to carbonyl group (C=O) stretching vibration), at $1342-1266 \text{ cm}^{-1}$ (due to aromatic amine group (C-N) stretching vibration) and at $2260-2222 \text{ cm}^{-1}$ (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 (70-89%) and (69-87%) respectively was successfully synthesized. 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 affinity on chrome tanned leather and nylon 6,6 fabrics.

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INTRODUCTION

Reactive dyes are coloured compounds which contain one or two groups capable of further establishing covalent bond between carbon phosphorus atom of the dyes and oxygen, nitrogen or sulphur atom of the substrate [1]. Such covalent bonds are formed with the hydroxyl group of the cellulosic fibre and with the amino groups of polyamides [2]. Reactive dyes are anionic compounds soluble in water due to the presence of the sulfonic group in the molecule. After dyeing, the dye molecule and the textile macromolecules formed uniquely coloured molecules with very good resistances to wet treatment [3]. Bi-functional reactive dyes are coloured compounds that possess more than one reactive moiety per molecule or groups, capable of forming covalent bonds between dye ions or molecules and the substrate [4]. The covalent bonds that attach reactive dye to natural fibres make them among the most prominent of dyes. They can be applied at

room temperature, they are the best choice for dyeing cotton and other cellulose fibres [2].

They have good fastness properties and exhibit higher fixation yield than those with only one reactive group [5]. With hetero bi-functional dyes such as monochlorotriazine/vinyl sulphone dyes, the difference in reactivity levels between the two functional groups compensates for the variation in dyeing conditions such as temperature/pH and results in the dye being more robust [6]. Chromophores function by altering the energy in the delocalized electron cloud of the dye and thus absorbing radiation from within the visible range [7]. If this change in the wavelength to be absorbed is sufficient to cause any absorption within the visible range, then the compounds will be coloured [1]. These dyes produced have substantial improved dye ability with high percentage exhaustion and fixation properties unlike monofunctional reactive dyes. The aim of this research is to synthesized bi-functional reactive

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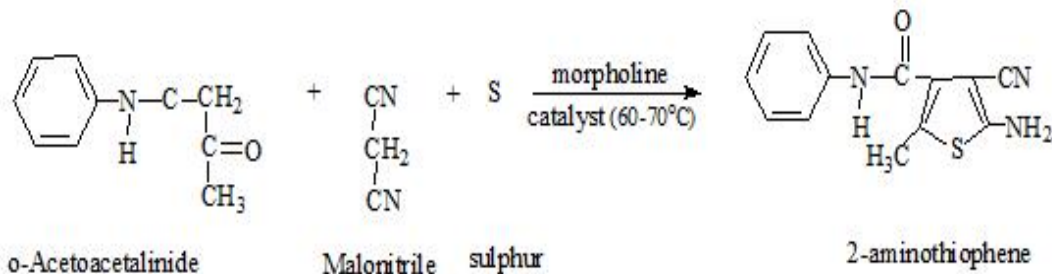
dyes derived from 2-aminothiophene and their application on chrome tanned leather and nylon 6,6 substrates.

MATERIALS AND METHOD

All commercial products were purchased from Sigma-Aldrich. Melting points were determined by the open capillary method using the Gallenkamp melting apparatus. The visible absorption spectra were measured using Agilent CARY 300 UV/Vis spectrophotometer; IR was measured and recorded in KBr pellets using the Agilent CARY 630 Fourier Transform Infra-red Spectrometer.

Synthesis of dye intermediate (Aminothiophene intermediate)

The dye intermediates was synthesized as follows: O-acetoacetanilide (20.0g, 0.1mol), Malononitrile (6.50g, 0.1mol), Sulphur (3.0g, 0.1mol), Morpholine (8.50g, 0.1mol) were combined in the presence of 200 cm³ of ethanol which was introduced into a round bottom flask and place on heating mantle in a stirring condition at 60-70 °C for 3-4 hrs. The resulting thick dark solution was cooled and store overnight in a refrigerator, followed by filtration, washing with ethanol and then ethanol/water (2:1) solution and wash dried at room temperature. The light brown powder obtained was crystallized from ethanol [8].

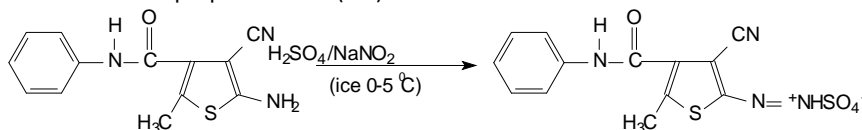


Scheme 1: Schematic route for the synthesis of intermediate (Aminothiophene)

Synthesis of diazonium salt solution [9]

Sodium nitrite (3.0g, 0.02mol) was added portion to 50 cm³ of concentrated sulphuric acid at 10°C and heated to 60°C with stirring for 15min. The solution was then cool to 0-5°C in ice bath and a mixture of acetic and propionic acid (2:1) was

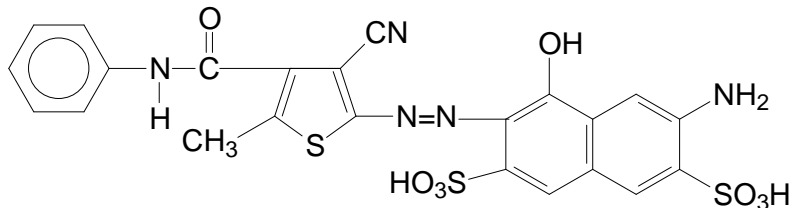
then added to the synthesized intermediate. The reaction mixture was then cooled to 0-5°C and was then added portion wise and stirring was continued for 2 hrs at 0-5°C. The resulting diazonium salt solution was obtained.



Coupling of diazonium salt solution [10]

R-acid (2.0g, 0.01 mole) was dissolved in 10 cm³ of methanol and the solution was cool to 0-5°C. To the well stirred solution, the freshly prepared diazonium salt solution was added drop wise over 45 min maintaining the temperature below 0-5 °C with vigorous stirring. The stirring was done for 1 hour at 0-5°C, maintaining pH 4-5 using

sodium acetate 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 °C. Following the same coupling procedures, controlled condition and reaction some monoazo acid dyes was synthesized using coupling component like H-acid J-acid and Gamma-acid,

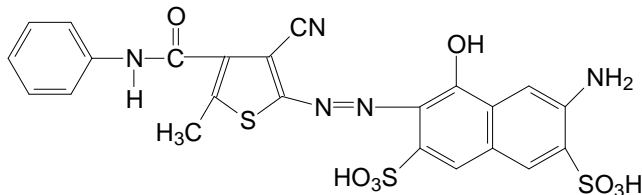


Dye 1a

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

Condensation of 1a Dye with cyanuric chloride to get various dichlorotriazolyl reactive dyes 2a -2d . [11].

Cyanuric chloride (1.20g, 0.01mol) was stirred in acetone (15 cm³) at a temperature below 0-5°C for the period of an hour. A neutral solution of dye 1a- 1d each (2.0g, 0.01mol) was added in



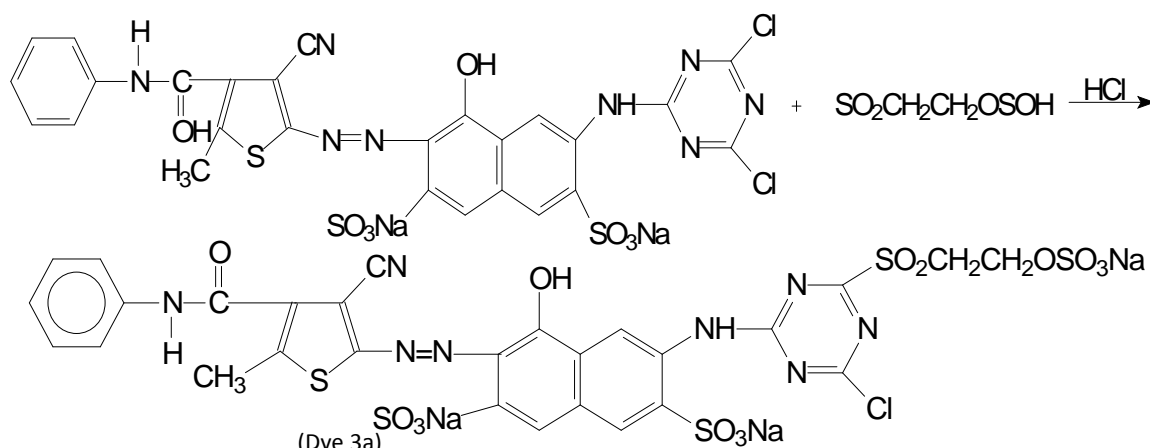
small lots for about an hour, neutral pH was maintained below 0-5°C throughout the reaction. The reaction mass was stirred at 0-5°C for further four hours in order to obtain a clear solution. The cyanurated dye solutions obtained were salted out with 2% NaCl solution, filtered, washed and dried at 70°C.

sodium 3-((3-cyano-5-methyl-4-(phenylcarbamoyl)thiophen-2-yl)diazenyl)-6-((4,6-dichloro-1,3,5-triazin-2-yl)amino)-4-hydroxynaphthalene-2,7-disulfonate

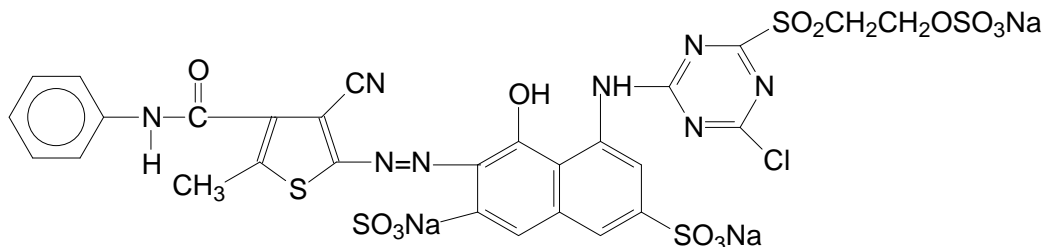
Condensation of dichlorotriazinyl Reactive Dyes (2a-2d) with vinylsulphone to get bifunctional reactive dyes (3a -3d) [11]

To the vigorously stirred aqueous solution of cyanurated dye (2a -2d) each (1.5 g, 0.0016 mol) at room temperature is added to a solution of vinylsulphone (0.80 g, 0.0008 mol) in 15 cm³

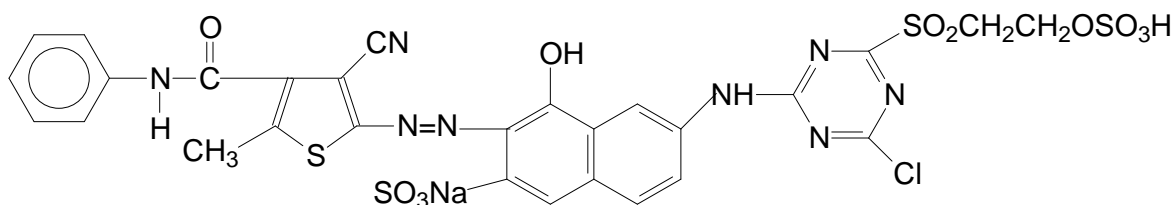
distilled water in acidic medium of HCl. The pH of reaction mixture was kept at 4.0 and continued the stirring for 4 hours for the completion of the reaction mixture. Finally the dye was salted out with 5% solution of NaCl filtered, purified and dried in an oven 70 °C keeping overnight to obtain dye (3a-3d) bifunctional reactive dyes.



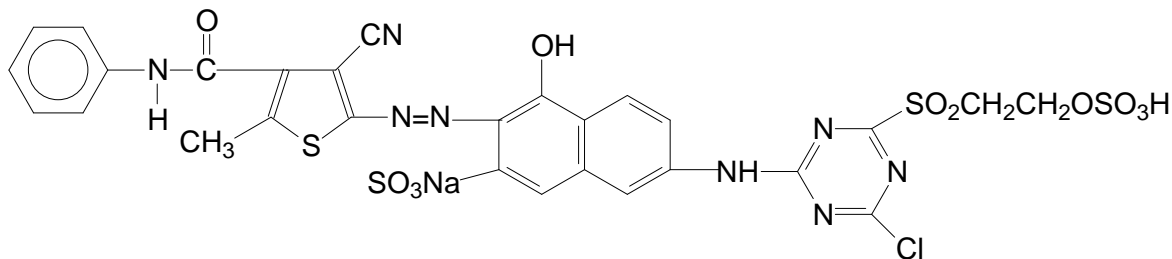
sodium 2-((4-chloro-6-((7-((3-cyano-5-methyl-4-(phenylcarbamoyl)thiophen-2-yl)diazenyl)-8-hydroxy-3,6-disulfonatonaphthalen-2-yl)amino)-1,3,5-triazin-2-yl)sulfonyl)ethyl sulfate



sodium 5-((4-chloro-6-((2-(sulfoxy)ethyl)sulfonyl)-1,3,5-triazin-2-yl)amino)-3-((3-cyano-5-methyl-4-(phenylcarbamoyl)thiophen-2-yl)diazenyl)-4-hydroxynaphthalene-2,7-disulfonate
(Dye 3b)



sodium 6-((4-chloro-6-((2-(sulfoxy)ethyl)sulfonyl)-1,3,5-triazin-2-yl)amino)-3-((3-cyano-5-methyl-4-(phenylcarbamoyl)thiophen-2-yl)diazenyl)-4-hydroxynaphthalene-2-sulfonate (Dye 3c)



sodium 7-((4-chloro-6-((2-(sulfoxy)ethyl)sulfonyl)-1,3,5-triazin-2-yl)amino)-3-((3-cyano-5-methyl-4-(phenylcarbamoyl)thiophen-2-yl)diazenyl)-4-hydroxynaphthalene-2-sulfonate (Dye 3d)

PURIFICATION OF THE DYES

The dyes were purified through the same process of recrystallization as highlighted above for the intermediates. Some of the dyes required the mixed solvent of ethanol, methanol /DMF (9/1 solvent mixture) according to a procedure suggested by [12]. The purity of each synthesized dyes were confirmed by melting point.

Percentage Yield of Dyes and Intermediates

The percentage yield of the synthesized dyes and intermediates were determined using the formula shown below [13].

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

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 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 heat the dye in the tube where the melting point is obtained.

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 [13].

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 °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 the temperature of the medium was raised to 60 °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 [15]

APPLICATION OF DYES SOLUTION

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

Number of ml of stock solution required = $\frac{W \times P}{C}$

C

Where W = weight (in grams) of sample to be dyed

P = percentage of dye to be used

C = concentration (%) of stock solution [16].

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 the equation below [17].

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

Where A_0 and A_1 are the absorbance at λ_{max} of the dye bath prior to dyeing and after dyeing respectively.

Determination of dyed fixation and fixation efficiency

The term fixation ratio refers to the ratio of the amount of dye absorbed (which is covalently bonded to the fibre) to the hydrolyzed dye on the surface of the surface.

$$\text{Percentage fixation} = \frac{OD_1 - OD_2}{OD_1} \times 100$$

Where OD_1 = optical density of the dye before dyeing

OD_2 = optical density of the dye after dyeing

OD_3 = optical density after stripped

Each dyed fabric was stripped in a 25% (w/w) pyridine in water solution (100 °C IR 10:1) for 30 minutes and the part of the solution was taken to the spectrophotometer to give OD_3 ; the optical density after stripping.

Optical overall fixation efficiency value (T) is related to the original amount of dye applied. A simple relationship exist between % T, % F, and % E (dye bath exhaustion) given by:

$$\% T = \frac{\% F \times \% E}{1}$$

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. The test is 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 is 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 an 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 is 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 leather resistance to prolong 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 cm³ of distilled water. This was placed in water bath and the temperature

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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 blue wool scale.

Rubbing fastness test of the dyed substrates

This method is intended for determining the behaviour of the surface 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.

RESULTS 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
2-Aminothiophene-4-carboxylic acid	Darkbrown	188-194	97	257	C ₁₃ H ₁₁ ON ₃ S

Table 2: Physical properties of the synthesized reactive dyes.

Dyes	Molecular formula	Shade crystal	Molecular weight(g/mol)	Melting point (°C)	Percentage yield (%)
3a	C ₃₀ H ₂₅ O ₁₀ S ₄ N ₈ Cl	Pink	820.5	158-160	64
3b	C ₃₀ H ₂₅ O ₁₀ S ₄ N ₈ Cl	Grey	820.5	208-210	72
3c	C ₃₀ H ₂₅ O ₅ S ₂ N ₈ Cl	Pink	739.5	120-122	58
3d	C ₃₀ H ₂₅ O ₅ S ₂ N ₈ Cl	Brownish	739.5	192-194	74

Table 3: λ_{max} and molar extinction coefficient of the synthesized dyes.

Dyes	λ _{max} in (nm) DMF	λ _{max} in (nm) Ethanol	Molar Extinction Coefficient in(DMF) x 10 ⁴ (l/mol ⁻¹ cm ⁻¹)
3a	530	520	4.129
3b	533	532	4.135
3c	581	579	5.221
3d	551	518	4.233

Table 4: Infrared absorption frequency 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.
	3354.6	2870.1	1666.1	
	3205.5		1602	

Table 5: Infrared absorption frequency of reactive 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
3a	3365.8	2832.8	164.0	1313.9	1468.6 1405.2
3b	3358.3	2735.9	1640.0	1313.9	1498.4 1531.9
3c	3343.4 3205.5	2829.0	1632.6	1315.8 1397.8	1453.7
3d	3321.8 3201.8		1751.8 1621.4		1595.8 1513.7

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Table 6: Gas chromatography mass spectroscopy of synthesized intermediate

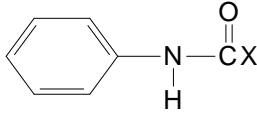
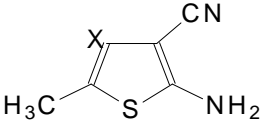
Sample	Fragmentation (m/z)	Calculated value
Intermediate	 $(C_7H_6NO)^+ = 120$ but $m/z = 123 \pm 3$	257g/mol
	 $(C_6H_5N_2S)^+ = 137$ but $m/z = 140 \pm 3$	

Table 7: Percentage exhaustion and fixation of the dyes on nylon 6,6 and chrome tanned leather substrate.

Dyes	% E for Nylon 6,6	% fixation on nylon 6,6	% efficiency on nylon 6,6	% ECTL
3a	76.00	70.04	53.07	74.8
3b	89.61	82.03	73.40	71.0
3c	70.10	74.20	52.00	78.4
3d	80.75	64.01	52.02	69.9

Table 8: Light and wash fastness ratings of chrome tanned dyed leather.

Dyes	Light fastness rating	Wash fastness rating
3a	5	5
3b	5	5
3c	4-5	4-5
3d	4	4-5

Table 9: Rubbing fastness rating of chrome tanned dyed leather

Dyes	number of rubs	Fastness rating	Staining of adjacent undyed cotton
3a	100	5	4
3b	100	5	4
3c	100	4	3
3d	100	4	3

Table 10: Rubbing fastness properties of dyed nylon 6.6 fabric

Dyes	Dry treatment	Change in colour	Wet treatment	Change in colour
		Staining		Staining
3a	4-5	4-5	5	5
3b	4-5	4-5	4-5	4-5
3c	5	5	4-5	4-5
3d	5	5	4-5	4-5

Table 11: Light and wash fastness rating of nylon 6,6 fabric

Dyes	Light fastness rating	Wash fastness rating	Staining on of adjacent undyed fabric
3a	6	5	5
3b	6	4	4
3c	7	4	3
3d	7	4	3

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The spectral data analysis of synthesized bifunctional reactive dyes

Absorbance is a measure of the amount of light absorbed. The higher the value, the more of a particular wavelength is being absorbed. The visible absorption properties of the dyes were measured in dimethylformamide and ethanol respectively and the result are summarized in Table 3: Ultraviolet visible absorption are indicative of electron transition between the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). All the compounds showed absorption in the visible region greater or equal to 400 nm which were characteristic of all compound of the dye studied. From the result in Table 3, Show various wavelength of bifunctional reactive dye 3a, 3b, 3c and 3d is condensed with vinyl sulphone absorbed at 530, 533, 581 and 551 nm respectively in dimethylformamide. Dye 3c shows more bathochromic effect of 30 nm compare to dye 3d, 50 nm compared to 3a, 48 nm compared to 3b in the same way dye 3a, 3b, 3c and 3d absorbed at 520, 532, 479 and 481 nm in ethanol respectively. Dye 3b absorbed at 532 nm which shows more bathochromic effect of 12 nm compared to 3a shows hypsochromic effect. Generally the synthesized dyes exhibit positive solvchromism. The bathochromic effect observed on changing to a more polar solvent such as dimethylformamide suggest that the dye molecule have more polar excited state than ground state, thus lowering the transition energy [18] with increasing polarity of solvent the absorption maximum is shifted to longer wavelength [19]. The energy difference between the ground and excited state is reduced leading to bathochromic shift in the visible absorption band.

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 3a which is obtained by coupling diazonium salt, 2-naphthol-3,6-disulphuric acid and condensing with cyanuric chloride and vinyl sulphuric gave absorption peak, due to (O-H and N-H) group at 3365.8 cm^{-1} , (C-H) group at 2832.8 cm^{-1} , (C=O) group at 164.0 cm^{-1} , (C-N) group at 1313.9 cm^{-1} and (-N=N-) group at 1468.6 cm^{-1} and

1405.2 cm^{-1} stretching vibration. Dye 3b which is obtained by coupling diazonium salt with 8-amino-1-naphthol-3,6-disulphuric acid and condensing with cyanuric chloride and vinyl sulphuric indicates absorption peak, due to (O-H and N-H) group at 3358.8 cm^{-1} , (C-H) group at 2735.9 cm^{-1} , (C=O) group at 1640.0 cm^{-1} , (C-N) group at 1313.9 cm^{-1} and (-N=N-) 1498.4 cm^{-1} and 1531.9 cm^{-1} , stretching vibration. Dye 3c is obtained by coupling diazonium salt with 2-amino-8-naphthol sulphuric acid and condensing with cyanuric chloride and vinyl sulphuric indicates absorption peak, due to (O-H and N-H) group at 3343.4 cm^{-1} and 3205.5 cm^{-1} , (C-N) group at 2829.0 cm^{-1} , (C=O) group at 1632.6 cm^{-1} , (C-N) group at 1315.8 cm^{-1} and (-N=N-) group at 1453.7 cm^{-1} , stretching vibration. Dye 3d is obtained by coupling diazonium salt with 2-amino-5-naphthol-7-sulphuric acid and condensing with cyanuric chloride and vinyl sulphuric gave absorption peak, due to (O-H and N-H) group at 3321.8 cm^{-1} and 3201.8 cm^{-1} , (C-N) group at 2829.0 cm^{-1} , (C=O) group at 1751.8 cm^{-1} and 1621.4 cm^{-1} and (-N=N-) group at 1595.8 cm^{-1} and 1513.7 cm^{-1} stretching vibration.

The gas chromatography mass spectrophotometry of the synthesized dye intermediate

This elucidate structural information of the synthesized intermediate molecular ion of 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 $\text{C}_6\text{H}_7\text{NO}^+$ and $\text{C}_6\text{H}_5\text{N}_2\text{S}^+$ respectively and its molecular mass is (257 g/mol). The difference between the experimental (263g/mol) and the calculated value (257 g/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 [20].

Percentage exhaustion and fixation on nylon 6, 6 and percentage exhaustion of chrome tanned leather substrates

The percentage exhaustion and fixation reported according to [21] of 2% (o.w.f) dyeing of nylon 6.6 and percentage exhaustion on chrome tanned leather substrate is summarized in Table 7: Dye 3a-3d which is bifunctional reactive dyes which is obtained by reaction of each portion of dye 2a-2d and condensation with vinyl sulphuric indicate percentage exhaustion and fixation range from 89-70% and 82-64% respectively on nylon 6,6 substrate. Dye 3b show maximum percentage exhaustion values 80, 76 and 70% respectively on

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nylon fabric. Dye 3 b show maximum percentage fixation values 74, 70 and 64% respectively on nylon 6,6, while dye 3c show maximum percentage exhaustion value 78% and 3a, 3b and 3d shows minimum percentage exhaustion values 74, 71 and 69% respectively on chrome tanned leather.

All the dyes have good exhaustion and fixation values which is expected due to rapid diffusion of the dye molecule within the fabric and good exhaustion and fixation values of dye are in accordance with structure of dye bearing polar groups which establish physical and chemical interaction with fibers.

Reactive component establish covalent linkages with the fibres. Nylon 6,6 gave a better percentage exhaustion and fixation with the same dye sample than chrome tanned leather.

This may be attributed to the amorphous nature of nylon 6,6 when compared with chrome tanned leather. Also chrome tanned leather highly bundles inter weave in various pattern which are made up of fibers composed of fibrolus which could reduce the affinity. Highly bundles interweave also tend to impact hydrophobicity of the fibre even those having polar groups. Nylon 6,6 is semi-crystalline fibre with amorphous region from dye molecule penetration.

Light fastness

Light fastness rating of the dye fabric is shown in Table 8 and 10. The test is carried out by exposing each dyed sample to day light alongside eight blue wool standards. light fastness rating (6-7) very good and excellent on nylon 6,6 fabrics and coupling diazonium salt with dichlorotriazinyl reactive dye to obtained bifunctional reactive dye gave a light fastness rating (4-5) good and very good on chrome tanned leather, while light fastness rating (6-7) very good and excellent on nylon 6,6 fabrics. It was observed that the light fastness of the nylon 6,6 fabric gave higher light fastness than the chrome tanned leather, this may be due to the coarse nature of the chrome tanned leather used. A coarser fibre fade slowly due to the lower surface area to volume ratio, implying that there will be less dye on the surface; the rate of fading will obviously be higher for flat filament and micro fibres [18]. Other dyes gave very good to excellent fastness this, may attributed to the molecular structure of the dyes, planarity and dye substituents that provided shield from radiant energy on azo chromophores, therefore, the this effect conferred good light fastness properties on the dyes.

Washing Fastness

Tables 8 and 10 shows the wash fastness rating of dye 3a-3d which gave a wash fastness rating (4-5) on both substrate. The high ratings of fastness properties could be referred to the covalent binding linkages between the dye and fiber [15]. The wash fastness property of the chrome tanned leather and nylon 6,6 dye fabrics were generally good very good to excellent. The good fastness property of nylon 6,6 dye fabric may be attributed to the difficulty in the dye diffusion into polyactide fibre and the dyes in migration out will be difficult thereby giving dyeing of high fastness to washing. The remarkable degree of levelness and brightness after washing indicate good penetration and excellent affinity of the dyes to the fibres. In addition, the result obtained showed that the dyed nylon 6,6 have excellent fastness level to washing as compared to the dyed chrome tanned leather which may be due to the presence of solubilizing group, which affect solubility and washing ability of the dye-out of the dye substrate. The desire result is a surface fibre reaction that is uniform in colour regardless of whether the colour is deeply tinted or very faint. And this is necessary inspite the fact that the substrate is quite often very uneven in structure [12].

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 solubilisation of a part the dye and its migration to the surface of coloured fabric [15] substantivity, penetration, levelness and durability in use.

CONCLUSION

A series of new bifunctional reactive dyes have been synthesized in moderate yield from diazotisation of 2 -aminothiophene and coupling with H, R, J and Y 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, brown dark blue and maroon. The chrome tanned leather

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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

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