

Synthesis And Application Of Heterocyclic Disperse And Acid Dyes Derived From 2-Aminothiophene And Conventional Amines As The Diazo Components

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ABSTRACT: Heterocyclic disperse and acid dyes of low molecular weights derived from 2-aminothiophene and conventional amines as diazo components were successfully synthesized. The identity of these dyes and intermediate were investigated using spectroscopic analysis such as Uv-visible spectrometry, Fourier Transform Infrared Spectrometry and GC-MS. The 2-aminothiophene intermediate and heterocyclic disperse dyes were synthesized using the method of Alaa and Tarek (2006) and the molar mass of the synthesized intermediate was 257 while that of the synthesized dyes ranges from 305 to 586 respectively. All the synthesized dyes absorbed within the visible region of the electromagnetic spectrum but the heterocyclic disperse dyes were more bathochromic than those of the conventional azo acid dyes. The dyes gave good exhaustion ranging from 70 % to 85 % on polyester fibre and chrome tanned leather. The dyes gave deep pink to orange shades on dyed substrates and exhibited good to excellent wash fastness properties and moderate to good light fastness on the dyed substrates.

Keywords: Synthesis, 2-Aminothiophene, Heterocyclic Disperse dyes, Acid dyes.

1 INTRODUCTION

Dyes play an indispensable role in human history since ancient time. Dyeing processes are often considered as an important characteristic of a particular civilisation or culture. Dyes are used in almost every commercial product such as food, clothing, pigments and paints, etc. There are many different classes of dyes in which azo dyes are certainly one of the most important classes. About half of the dyes used in industry are azo dyes. Azo dyes have the basic structure, $Ar-N=N-Ar'$, where Ar and Ar' are two aromatic groups. Synthetic azodyes are extensively used in textile dyeing, paper printing, color photography, pharmaceutical, food, cosmetics and other industries [1, 2]. Among them the textile industry is a major consumer. These dyes have characteristically good tinctorial strength as well as stability. Their preparation procedure is by the classic diazotization and coupling reactions, are very simple and of low cost. They have found wide application in dyeing of protein fibres such as leather, wool, angora, cashmere, and silk, as well the milk protein fibre called "Silk Latte", the soy protein fibre called "Soy Silk", and the synthetic polyamide fibre nylon [3, 4] prints inks, and toners, dyes for food [5] and cosmetics. In recent years, several heterocyclic and non

heterocyclic compounds are extensively used in azo dye chemistry for textile and non-textile applications [6]. These dyes are now marketed to produce a full range of azo dyestuffs without the use of colorants based on hetero-aromatic diazo components. Most of the heterocyclic dyes are derived from the diazo components consisting of five-membered rings containing one or more nitrogen heteroatoms, with the rings being fused into another aromatic ring [7, 8]. The dyes with heterocyclic diazo components have been intensively investigated, to produce bright and strong colour shades ranging from red to greenish blue on synthetic and natural fibres. These results led to commercial products to replace the conventional azobenzene dyestuffs.

2 EXPERIMENTAL

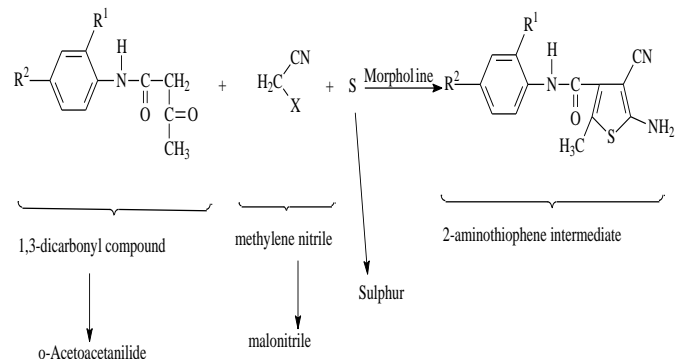
2.1 MATERIALS

Analytical grade reagents and chemicals from Sigma Aldrich were used for this research work. These include N,N-diethylaniline, sulphanilic acid, N,N-dimethylaniline, dodecylpyridon, hydrochloric acid, sodium hydroxide, conc. sulphuric acid, ethanol, methanol, acetone, o-Acetoacetanilide, malononitrile, sulphur, morpholine,

acetic acid, propionic acid, sodium nitrite, dimethylformamide (DMF), dimethylsulphoxide (DMSO), polyester fibre and chrome tanned leather.

2.2 Synthesis of Aminothiophene Intermediate 1

The aminothiophene intermediates were synthesized following methods reported in the literature, as shown in the scheme below [9].



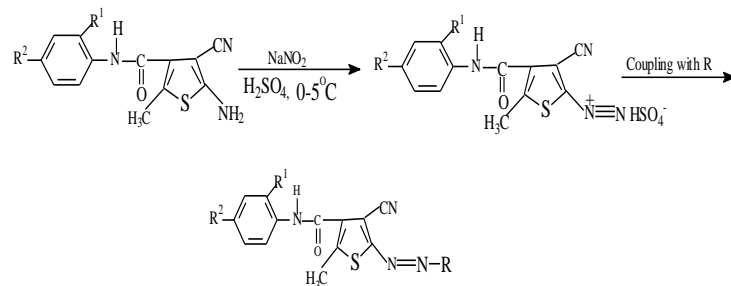
Scheme 1: Synthesis of aminothiophene intermediate

o-Acetoacetanilide (21.16 g, 0.1 mol), malononitrile (6.96 g, 0.1 mol) and sulphur (3.37 g, 0.1 mol) in 30 ml ethanol were stirred in the presence of morpholine (8.97 g, 0.1 mol) at 60-70 °C for 3 hours. The resulting thick dark solution was cooled and stored overnight in a refrigerator, followed by filtration, washing with ethanol and then ethanol/water (1:1) solution and dried. The grey powder was then recrystallized from ethanol.

2.3 Procedure for Diazotization and Coupling Reaction

2.3.1 Diazotization of Intermediate 1

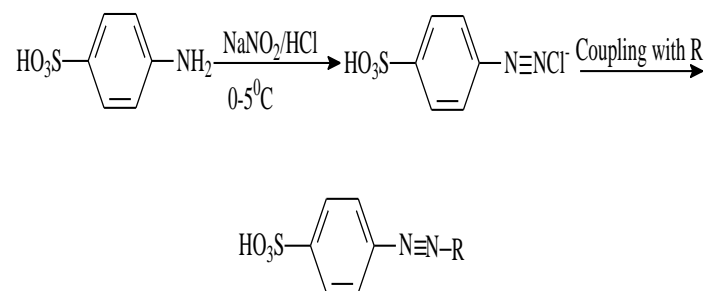
Sodium nitrite (1.38 g, 0.02 mol) was added dropwise to 10 ml of concentrated sulphuric acid at 10 °C and heated to 60 °C with stirring for 15 min. The solution was cooled to 5 °C and a mixture of acetic acid and propionic acid (17:3) was added to the mixture below 30 °C. The finely ground aminothiophene intermediate 1 (4.90 g, 0.02 mol) was slowly added within 30 minutes below 5 °C and the whole mixture was stirred at 0-5 °C for 2-4 hours. The excess nitrous acid (tested for, using starch iodide paper) was decomposed with the required amount of urea. The clear diazonium salt solution thus obtained was used immediately in the coupling reaction. The associated steps are illustrated in the reaction scheme below:



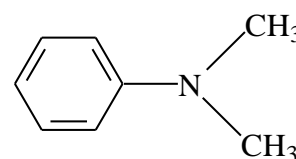
2.3.2 Diazotization of Intermediate 2

Sulphanilic acid (3.5 g, 0.02 M) was dissolved in 30 ml of 2 M solution of NaOH. The solution was then cooled in an

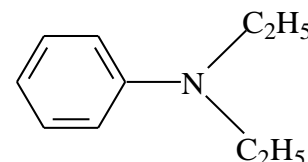
ice bath. A solution of sodium nitrite (50 ml of 1 M) and 10 ml cold solution of conc. HCl was added drop-wise with continuous stirring for 30 min to form the diazonium salt solution. The associated steps are illustrated in the reaction scheme below:



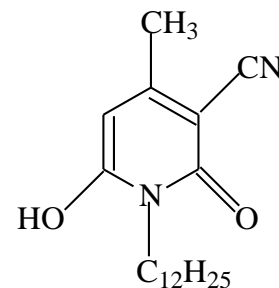
Where R is the coupling component



N, N-Dimethylaniline (a)



N, N-Diethylaniline (b)



Dodecylpyridone (c)

2.4 Coupling Reaction

The coupling components, N, N-dimethylaniline, N, N-diethylaniline and dodecylpyridone were dissolved in acetic acid and cooled to 0 °C, by addition of ice. The diazonium salt solution previously prepared was added over 30-40 minutes with vigorous stirring [10]. The mixture was stirred for further 2-3 hours, under a temperature of 5 °C and the pH of the solution was adjusted to 4-5 using 10 % sodium hydroxide solution. The resulting product was then collected by filtration, washed with water and dried. The crude products were purified by recrystallizing it from ethanol.

2.5 Purification of the Intermediate and Dyes

The aminothiophenes intermediate was purified by three to four recrystallizations from ethanol. A known weight of the intermediate was dissolved in small quantity of ethanol and heated up with constant stirring. It was then filtered off while hot using a Buchner funnel with a suction pump.

The crystals were collected, washed several times with water and dried. After the recrystallization, the purity of the heterocyclic amine was checked by spotting on a TLC plate using Hexane : ethyl acetate (2:1) as the eluent [11].

2.6 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 acetic acid/DMF (9/1 solvent mixture) according to a procedure suggested by Alaa and Tarek (2006). The purity of each synthesized dyes were confirmed on TLC.

2.7 Percentage Yield of Dyes and Intermediates

The percentage yield of the synthesized dyes and intermediates were determined using the formula shown below [12]

$$\% \text{ Yield} = \frac{\text{MP}}{\text{MMP}} \div \frac{\text{MR}}{\text{MMR}} \times 100$$

where;

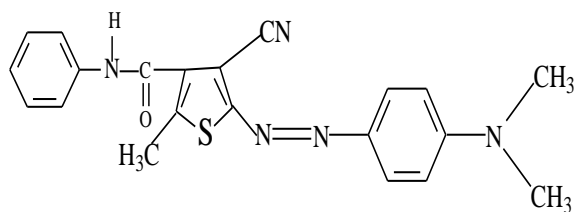
MP is the mass of the product

MMP is the molar mass of the product

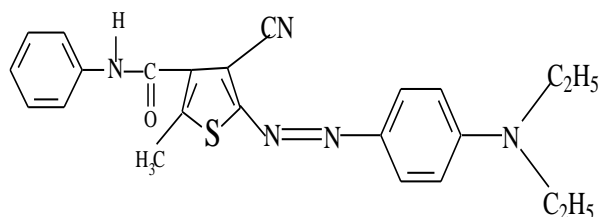
MR is the mass of the reactant

MMR is the molar mass of the reactant

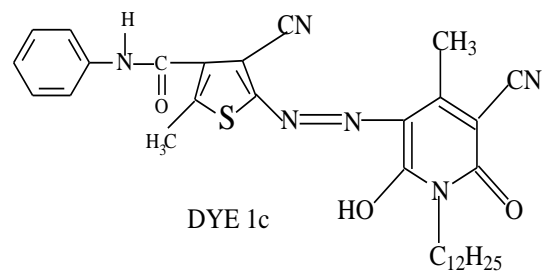
2.8 Structures of the Synthesized Dyes:



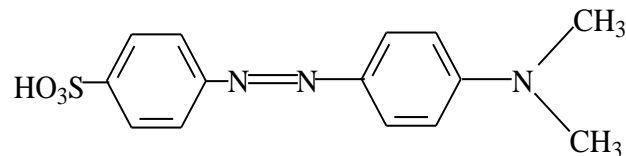
DYE 1a



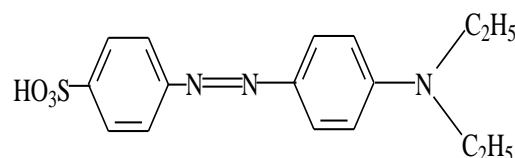
DYE 1b



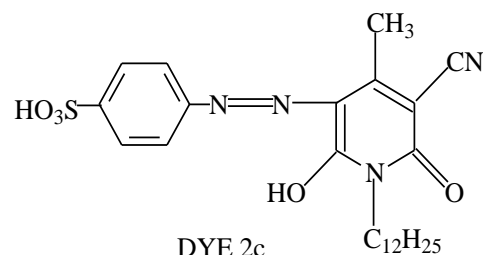
DYE 1c



DYE 2a



DYE 2b



DYE 2c

2.9 Characterization of the Synthesised Dyes and Intermediates.

The intermediate and the synthesized dyes were characterized using gas chromatography – mass spectrophotometer with model number 7890B GC System, FT-IR using Agilent Technologies CARY 630 FT-IR spectrophotometer, UV-visible spectrophotometry on CARY 300 UV-VISIBLE spectrophotometer and melting point using Gallenkamp melting point apparatus [13].

2.10 Molar Extinction Coefficient

The molar extinction coefficient (ϵ), which is a constant for each molecule at any given wavelength, represents the absorbance of a 1cm thickness of a medium containing 1 mole of the absorbing substance per litre [14]. ϵ was calculated using the relation: $\text{Log}_{10} (I_0/I)$ absorbance A or optical density:

$$A = \epsilon CL$$

where

ϵ = Extinction coefficient

A = Absorbance at λ_{max}

C = Concentration of dye in mol/dm³

L = Path length in cm

2.11 Application of Dyes

1 % stock solution of each dye was prepared, a liquor ratio of 50:1 was used, 2 % shade on weight of fabric (o.w.f) and 1 g of fabric each of polyester and chrome tanned leather. The volume required from each stock solution was calculated based on the formula;

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

where:

P = percentage shade

W = weight of fabric

C = percentage concentration of stock solution.

2.11.1 Dyeing of polyester

For the polyester fibre, a carrier (phenol) and dispersing agent (anionic detergent) were 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 40 °C and allowed to reach the boil within 15 minutes. 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 [14, 15].

2.11.2 Dyeing of leather

The synthesised 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 [16].

2.12 Determination of Dyebath Exhaustion

Dye uptake was determined by measuring the absorbance of diluted dyebath 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 20 ml acetone. This is to ensure that the absorbance falls within the readable range of 1.5. The percentage dyebath exhaustion (% E) for each substrate was calculated using the equation below [17, 18]

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

where A_0 and A_1 are the absorbance at λ_{max} of the dyebath prior to dyeing and after dyeing respectively.

2.13 Assessment of Fastness Properties

2.13.1 Wash Fastness Test

The dyed samples were subjected to I.S.O.3 wash fastness test by the following procedures: The specimens were prepared by cutting the dyed fibres into 5 cm x 2 cm dimensions; they were then made into composites by stitching the test specimen made of the dyed sample placed in between white cotton of dimensions 10 cm x 4 cm. The composite was agitated in the solution made up of the following [15];

Soap solution 5 g/l
Sodium carbonate 2 g/l
Liquor ratio 50:1

The washing was maintained at 50 °C for 45 minutes with continuous agitation. At the end of the washing test the composite specimen was removed, rinsed in cold water and the components separated and dried at room temperature. The change in colour of the dyed samples and the staining of adjacent undyed cloths were assessed using the appropriate grey scale.

2.13.2 Light Fastness Test

The dyed samples and blue wool standard were exposed facing due south and inclined at an angle to the horizontal approximately equal to the latitude of the place where the exposure is being made. Adequate ventilation of the samples during exposure was ensured. The partly covered samples were exposed to UV radiation. As exposure proceeded for 7 days, the samples under test and the blue wool standards were examined at intervals and the change in colour of the samples compared visually with the changes that occur in the standards. The light fastness of the sample is the number of the standard that shows a similar visual contrast between the exposed and unexposed part of the samples. The exposure was terminated when the blue wool standard 7 fades or when fully exposed and non-exposed test samples is equivalent to grade 3 on the grey scale [19]. Light fastness values for each material was obtained by comparing the degree of fading with that observed with Blue wool standard. Rating is given according to the Wool standard with which the dyed material fading is comparable.

3.0 RESULTS AND DISCUSSION

3.1 Synthetic Route for the 2-Aminothiophene Intermediates

The synthesis of the aminothiophene intermediate 1 was achieved using the Gewald's methodology as outlined in Scheme 1 above. This convenient methodology includes the condensation of the 1,3-dicarbonyl compound (o-Acetoacetanilide) with the activated nitrile (i.e. malononitrile) in the presence of sulphur in ethanol.

3.2 Physical Properties of 2-aminothiophene Intermediate and Dyes

The molecular formula, molar mass, melting point, percentage yield and colour of the synthesized intermediate and dyes are presented in table 1 below.

Table 1: Physical Properties of the synthesized Intermediate and Dyes

Intermediate/Dyes	Molecular formula	Molecular weight (g/mol)	Melting point (°C)	Percentage yield (%)	Retention factor (R_f)	Appearance of dyes crystals
Intermediate 1	$C_{13}H_{11}N_5OS$	257	201-208	48	0.46	Brown
Dye 1a	$C_{21}H_{19}N_5OS$	389	204-210	57.82	0.48	Magenta
Dye 1b	$C_{23}H_{23}N_5OS$	417	209-213	43.00	0.43	Ash
Dye 1c	$C_{32}H_{38}N_6O_3S$	586	198-206	60.40	0.56	Brown
Dye 2a	$C_{14}H_{13}N_5O_3S$	305	184-190	80.26	0.55	Red
Dye 2b	$C_{16}H_{19}N_5$	333	180-	69.22	0.53	Purple

Dye 2c	${}^3\text{O}_3\text{S}$	503	187	73.00	0.63	Cream
	$\text{C}_{25}\text{H}_{35}\text{N}$		164-			
	${}^4\text{O}_3\text{S}$		168			

The colour of the synthesized heterocyclic diazo component and dyes ranges from brown to deep purple. The molecular mass of the intermediate and dyes is from 257-586 g/mol while the melting point is from 164-213 °C as shown in the Table 1 above. The yield of the 2-aminothiophene intermediate and dyes can also be described as fair to very good. The yield of aminothiophene intermediate is not surprising in view of the result from previous and similar works [20]. Sabnis et al, (1999) reported the fact that 1, 3-dicarbonyl compound generally poses a problem of low yield and difficult purification process when compared to other ketones and aldehydes. One of the methods mentioned as a way of overcoming this is a prolonged reaction time. This was also supported by Jack, (2005), who reported that generally ketones starting materials produced far poorer result than aldehydes. They suggested that the use of a precondensed Knoevenagel intermediate may be

preferred. Equally, Victor et al, (2006) reported that aryl ketones appear generally unreactive in the direct one-spot Gewald synthesis. All the purified dyes exhibited fairly well-defined melting points characteristics of a pure compound as shown above. Whilst it would be unwise to attempt to explain in detail their relative value because of the complex dependence of the melting points on a number of factors (e.g. polarity, size geometry and interaction), a few general trends can be accounted for. The dyes from low-melting diazo components tended to have low melting points themselves and the factors determining high melting points were generally preserved in the dyes from high-melting heteroarylamines as shown in Table 1 above.

3.3 Visible absorption Spectroscopy of Dyes

The visible absorption spectra of the dyes were measured in DMSO and methanol and their molar extinction coefficients calculated using their λ_{max} in DMSO. The results are presented in the Table 2 below.

Table 2: Visible absorption Spectroscopy of Dyes

Dye No	ϵ_{max} (in DMSO) (L/mol cm^{-1})	DMSO λ_{max} (nm)	Methanol λ_{max} (nm)
Dye 1a	27133.33	554	464
Dye 1b	20866.67	524	461
Dye 1c	36400.00	569	529
Dye 2a	41333.33	431	420
Dye 2b	28266.67	440	433
Dye 2c	20333.33	439	453

Some of the dyes show considerable increase in wavelength of absorption when compared generally with their six membered rings as observed by various researchers. Dyes having a thiophene diazo component generally exhibit high bathochromic shift. It is to be noted that coupling components with strong powerful electron donor groups also show similar effect. These bathochromic shifts afforded by five membered ring sulphur heterocycles have been mentioned by several authors [21, 22] indicating that these system are useful in providing blue to greenish blue dyes. The origin of the large shift peculiar to this heterocyclic system could not be explained only in terms of greater stabilization of the excited state, but probably is correlated with the increased diene character of the heterocycles. Most of the shifts in wavelength of maximum absorption observed were bathochromic for majority of the dyes where measurements were done in solvent of higher polarity. The wavelengths of maximum absorption values shifted to longer wavelengths when the solvent is changed from methanol to dimethylsulphoxide (DMSO), e.g. dye 1a, 1b and 1c absorbs at wavelengths of 464 nm, 461 nm and 529 nm in methanol and 554 nm, 524 nm and 569 nm in DMSO respectively. The molar extinction coefficient was calculated based on the concentrations of the dyes in DMSO as a solvent. The molar extinction coefficient, also a measure of the amount of light absorbed by a compound in solution, was calculated for each dye. From the results

in Table 2, it could be seen that dye 2a has the highest molar extinction coefficient. This may be attributed to the fact that the dye transmits more light in comparison to others and therefore has narrow absorption bands with sharp peaks as compared to others.

3.4 The Infra-Red Spectra of the Intermediate and Dyes

The FTIR peaks observed with the corresponding group present for the synthesized intermediates and dyes are shown in Table 3 below.

Table 3: The Infra-Red Spectra of the Intermediate and Dyes

Intermediate/Dyes	Vibrational frequencies (cm^{-1})
Intermediate 1	3421.7, 3276.3 (NH), 2199.1 (CN), 1695.9, 1662.4 (C=O), 3302.4, 3350.9, 3459.0 (NH), 2214.0 (CN), 1695.9, 1662.4, 1602.8 (C=O), 1453.7, 1505.8 (N=N), 2959.9, 2870.1 (C-H), 3302.4, 3347.1, 3459.0 (NH), 2214.0 (CN), 1695.9, 1662.4, 1602.8 (C=O), 1453.7, 1505.8 (N=N), 2873.8, 2967.0 (C-H), 3429.2 (NH), 2273.7 (CN), 1613.9, 1722.0 (C=O), 1509.6, 1569.2 (N=N), 2944.6 (C-H), 3388.2 (NH), 2836.5 (C-H), 1487.2, 1595.3, 1543.1 (N=N)
Dye 1a	3421.7, 3276.3 (NH), 2199.1 (CN), 1695.9, 1662.4 (C=O), 3302.4, 3350.9, 3459.0 (NH), 2214.0 (CN), 1695.9, 1662.4, 1602.8 (C=O), 1453.7, 1505.8 (N=N), 2959.9, 2870.1 (C-H), 3302.4, 3347.1, 3459.0 (NH), 2214.0 (CN), 1695.9, 1662.4, 1602.8 (C=O), 1453.7, 1505.8 (N=N), 2873.8, 2967.0 (C-H), 3429.2 (NH), 2273.7 (CN), 1613.9, 1722.0 (C=O), 1509.6, 1569.2 (N=N), 2944.6 (C-H), 3388.2 (NH), 2836.5 (C-H), 1487.2, 1595.3, 1543.1 (N=N)
Dye 1b	3421.7, 3276.3 (NH), 2199.1 (CN), 1695.9, 1662.4 (C=O), 3302.4, 3350.9, 3459.0 (NH), 2214.0 (CN), 1695.9, 1662.4, 1602.8 (C=O), 1453.7, 1505.8 (N=N), 2959.9, 2870.1 (C-H), 3302.4, 3347.1, 3459.0 (NH), 2214.0 (CN), 1695.9, 1662.4, 1602.8 (C=O), 1453.7, 1505.8 (N=N), 2873.8, 2967.0 (C-H), 3429.2 (NH), 2273.7 (CN), 1613.9, 1722.0 (C=O), 1509.6, 1569.2 (N=N), 2944.6 (C-H), 3388.2 (NH), 2836.5 (C-H), 1487.2, 1595.3, 1543.1 (N=N)
Dye 1c	3421.7, 3276.3 (NH), 2199.1 (CN), 1695.9, 1662.4 (C=O), 3302.4, 3350.9, 3459.0 (NH), 2214.0 (CN), 1695.9, 1662.4, 1602.8 (C=O), 1453.7, 1505.8 (N=N), 2959.9, 2870.1 (C-H), 3302.4, 3347.1, 3459.0 (NH), 2214.0 (CN), 1695.9, 1662.4, 1602.8 (C=O), 1453.7, 1505.8 (N=N), 2873.8, 2967.0 (C-H), 3429.2 (NH), 2273.7 (CN), 1613.9, 1722.0 (C=O), 1509.6, 1569.2 (N=N), 2944.6 (C-H), 3388.2 (NH), 2836.5 (C-H), 1487.2, 1595.3, 1543.1 (N=N)
Dye 2a	3421.7, 3276.3 (NH), 2199.1 (CN), 1695.9, 1662.4 (C=O), 3302.4, 3350.9, 3459.0 (NH), 2214.0 (CN), 1695.9, 1662.4, 1602.8 (C=O), 1453.7, 1505.8 (N=N), 2959.9, 2870.1 (C-H), 3302.4, 3347.1, 3459.0 (NH), 2214.0 (CN), 1695.9, 1662.4, 1602.8 (C=O), 1453.7, 1505.8 (N=N), 2873.8, 2967.0 (C-H), 3429.2 (NH), 2273.7 (CN), 1613.9, 1722.0 (C=O), 1509.6, 1569.2 (N=N), 2944.6 (C-H), 3388.2 (NH), 2836.5 (C-H), 1487.2, 1595.3, 1543.1 (N=N)

Dye 2b	3473.9, 3552.2 (NH), 2993.1 (C-H), 1543.1, 1595.3, 1431.3 (N=N)
Dye 2c	3317.3 (NH), 2847.7, 2918.5, 2959.5 (C-H), 2281.1 (CN), 1699.7, 1632.6 (C=O), 1509.6, 1569.2, 1442.5 (N=N)

From the results in Table 3, the IR spectra of aminothiophene intermediate 1 showed absorption peaks in the region 2199.1 cm^{-1} due to the presence of the cyano group. The amino group absorption for the intermediate appeared in the range $3276.3\text{--}3421.7\text{ cm}^{-1}$ while the carbonyl absorption is seen in the range $1662.4\text{--}1695\text{ cm}^{-1}$. As seen from the IR spectra of the synthesized dyes in Table 3, all the dyes gave absorption peaks due to azo group -N=N- stretching vibration at the range of $1431.3\text{--}1595.3\text{ cm}^{-1}$ and the C-H stretching vibration band at $2993.1\text{--}2836.5\text{ cm}^{-1}$. An absorption peak in the region $2281.1\text{--}2214.0\text{ cm}^{-1}$ due to V_{CN} was observed for the synthesized azo dyes 1a, 1b, 1c, and 2c, and NH stretching vibration was observed at the frequency range of $3552.2\text{--}3302.4\text{ cm}^{-1}$ for all the synthesized azo dyes. The IR spectra of some of the synthesized azo dyes also showed an absorption peak in the region of $1722.0\text{--}1602.8\text{ cm}^{-1}$, attributed to C=O stretching vibration for azo dyes 1a, 1b, 1c and 2c respectively.

3.5 GC-MS Fragments of Intermediate and Dyes

The GC-MS Spectra and fragments of the 2-aminothiophene intermediate and one of the dyes are presented in Fig 1-3 and Table 4 below.

Table 4: GC-MS Fragments of Intermediate and Dyes

Intermediate/Dyes	Mass (m/z)
Intermediate 1	$[\text{C}_6\text{H}_5\text{SN}_2]^+ = 140$, $[\text{C}_7\text{H}_6\text{NO}]^+ = 123$ $[\text{C}_6\text{H}_5\text{SO}_3]^+ = 153$, $[\text{N}_2]^+ = 29$,
Dye 2a	$[\text{C}_8\text{H}_{10}\text{N}]^+ = 125$
Dye 1b	$[\text{C}_{13}\text{H}_9\text{N}_2\text{OS}]^+ = 239$, $[\text{N}_2]^+ = 29$, $[\text{C}_{10}\text{H}_{14}\text{N}]^+ = 141$

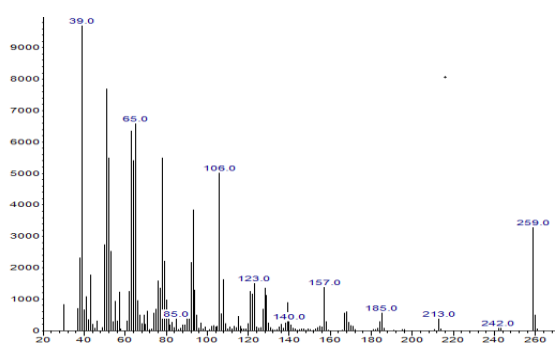


Fig. 1: GC-MS Spectra of Intermediate 1

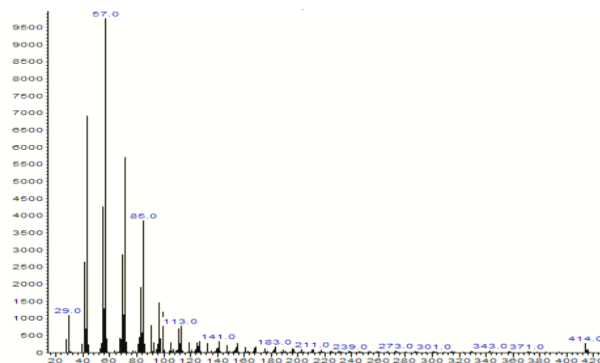


Fig. 2: GC-MS Spectra of Dye 1b

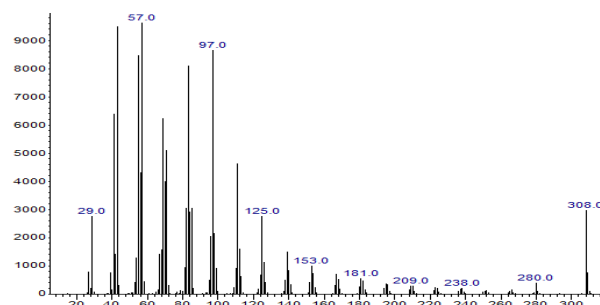


Fig. 3: GC-MS Spectra of Dye 2a

The results in Table 4 showed the fragmentation of the intermediate, dyes and their respective mass (m/z). The mass spectrum of the intermediate 1 is fully consistent with the assigned structures: In most cases, intense molecular ion peaks were observed. Thus intermediate 1 showed intense molecular ion peaks at $m/z\ 259\pm 2$ consistent with the molecular formulae $\text{C}_{13}\text{H}_{11}\text{N}_3\text{OS}$ respectively. The molecular ion of the intermediate 1 shown in Table 4 underwent fragmentations to produce peaks at $m/z\ 123\pm 3$ and 140 ± 3 corresponding to its molecular mass. Dyes 1b and 2a showed molecular ion peaks at $m/z\ 414\pm 3$ and 308 ± 3 respectively which is consistent with the molecular formula of the dyes. The molecular ion in dye 1b underwent fragmentation to produce peaks at 239 ± 2 , 29 ± 1 and 141 ± 7 while the molecular ion in dye 2a underwent fragmentation to produce peaks at 153 ± 4 , 29 ± 1 and 125 ± 5 respectively. Thus, the observed fragmentations for dye 1b and 2a corresponds to the molecular weight of the dyes. The slight difference in numerical value of the molecular weight of the intermediate and dyes can be attributed to certain elements with high isotopic abundance [23].

3.6 Dyeing Exhaustion of the Synthesized Dyes

The results of the dye exhaustion of the synthesized dyes on polyester fabric and chrome tanned leather are shown in Table 5 below.

Table 5: Dye Exhaustion on Polyester Fabric and Chrome Tanned Leather

Dye No.	% Exhaustion on Polyester Fibre	% Exhaustion on Chrome Tanned Leather
1a	75	-
1b	70	-
1c	78	-
2a	-	80

2b	-	85
2c	-	84

From the results in Table 5, dyes 1a, 1b and 1c applied on polyester fibre have percentage exhaustion of 75 %, 70 % and 78 % respectively while dyes 2a, 2b and 2c applied on chrome tanned leather have percentage exhaustion of 80 %, 85 % and 84 % respectively. The levels of exhaustion ranged from high to moderate upon application with wide variation of colour yield obtained. The acid dyes on chrome tanned leather gave high exhaustion as compared to the heterocyclic disperse dyes on polyester fibre. This is probably due to the solubility of the dyes, high rate of diffusion of the dye molecules into the fibre and greater accessibility of the pore structure in chrome tanned leather.

3.7: Wash Fastness.

The resistance of dyed materials to laundry treatment such as washing is referred to as washing fastness and this was achieved using the general procedure recommended by the International Standard Organization, number 3 (I.S.O 3) was adapted and the results are presented in Table 6 below.

Table 6: Wash Fastness Test Using ISO 3 Standard.

Dye No.	Change in Colour	Staining of Fabric	of Adjacent Fabric	Colour on Substrate
1a	5	-	4-5	Deep pink
1b	4	-	4	Light purple
1c	4-5	-	4-5	Brown
2a	-	3-4	-	Golden yellow
2b	-	4-5	-	Orange
2c	-	5	-	Grey

Change in shade

Staining

5 = Excellent

4 = Very good

3 = Good

2 = fair

1 = poor

5 = no staining

4 = very slight staining

3 = moderate staining

2 = significant staining

1 = deep staining

The Table 6 shows that the wash fastnesses of the heterocyclic disperse dyes 1a, 1b and 1c applied at 2 % shade on polyester fibre gave a better wash fastness as compared to the acid dyes 2a, 2b and 2c which was applied on chrome tanned leather. These dyes gave deep pink to orange hues with brighter and deeper shades, high tinctorial strength and excellent levelness on the substrates. Thus from Table 6, all the heterocyclic disperse dyes exhibited good to excellent fastness to washing on

polyester fabric while the acid dyes showed fair to excellent fastness to washing on chrome tanned leather respectively and this may be due to the presence of solubilising group, which affect solubility and washing ability of the dye-out of the dyed chrome tanned leather.

3.8 Light Fastness

The results of light fastness test obtained using 8 blue wool standards for each of the dyed substrates are shown in Table 7

Table 7: Light Fastness Test of Dyed Substrates

Dye No.	Polyester Fabric	Chrome Tanned Leather
1a	6	-
1b	5	-
1c	5	-
2a	-	5
2b	-	5
2c	-	4

Fastness grade	Degree of fading	Fastness
8	none	4
7	appreciable	3
6	very slight	2
5	significant	1
	slight	
	extensive	
	moderate	
	very extensive	

The light fastness results indicate moderate to very good light fastness. The light fastness observed for both disperse and acid dyes ranges from 4-6 which could be ascribed to the coupling components used. The synthesized dyes 1a value of light fastness can be attributed to the introduction of the thiophene ring ortho to the azo group resulting in a significant improvement in light fastness as compared to dyes 3a [4]. It was also observed that the synthesized dyes containing dodecylpyridon as coupling component gave a moderate fastness property on leather. Other dyes gave a good to very good fastness. This may be attributed to the molecular structure of the dyes, planarity and dye substituents that provided shield from radiant energy on azo chromophores, and which conferred good light fastness properties on the dyed substrates [24].

4 CONCLUSION

A series of heterocyclic disperse and acid dyes based on 2-aminothiophene and conventional amines have been synthesized. Their structural characteristics were elucidated using spectroscopic techniques and their application properties were accessed on polyester fibre and chrome tanned leather with dye exhaustion values ranging from 70 % to 78 % on polyester fabric and 80 % to 85 % on chrome tanned leather. The dyeings show very good to excellent fastness to washing and moderate to good light fastness properties. The remarkable degrees of levelness after washing indicate good penetration and affinity of these dyes for the dyed substrates.

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