

## SYNTHESIS AND CHARACTERISTICS OF SYNTHESIS AND CHARACTERISTICS OF THIOPHENE BASED MONOAZO DISPERSE DYES ON NYLON 6.6 FABRIC

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### ABSTRACT

A series of monoazo disperse dyes has been prepared by diazotizing 2-amino-4-(4-chlorophenylcarbamoyl)-5-methyl-thiophene-3- carboxylic acid ethylester and coupling with N, N-bis (2-cynoethyl) aniline, 3-acetylamino-N,N-diethylaniline and 3-hydroxyl-N,N-dimethyl aniline. The monoazo disperse dyes were characterized by infra red spectra studies. Visible absorption spectra of the dyes were examined in various solvents. The electronic absorption spectra covers a  $\lambda_{max}$  range of 550-650 nm at uniformly high absorption intensity between  $2.3 \times 10^4$  -  $9.2 \times 10^4$  l mol<sup>-1</sup>cm<sup>-1</sup>. These dyes were applied at 5 % depth on nylon 6.6 fabrics and gave bright intense hues of purple and orange. The colour parameters of the dyed fabrics were measured and the dyes have excellent exhaustion between 79-92 % for nylon 6.6 fabrics, more intense and of very good wash fastness property on nylon 6.6 fabrics. The remarkable degree of levelness and brightness after washing is indicative of good penetration and excellent affinity of these dyes for the nylon 6.6 fabric.

**Keywords:** Thiophene, Disperse dye, Exhaustion, Nylon 6.6, Washfastness, Affinity.

### Contribution/ Originality

The study is one of very few studies which have investigated the use of thiophene amino compounds in the synthesis of disperse dyes. The new dyes synthesised showed excellent exhaustion, ranging from 79-92% on nylon 6.6 fabrics. The dyed fabric also showed very good levelness and excellent washfastness and can therefore be exploited for commercial dyeing.

### 1. INTRODUCTION

Heterocycles have been put to much use in disperse dyes chemistry and this was claimed to be the first area to foster the industrial exploitation of heterocyclic amines. Shuttleworth and Weaver [1] Most heterocyclic dyes of technical interest for application to textiles are derived from diazo components consisting of five membered rings containing one sulphur heteroatom and

to which a diazotisable group is directly attached. This type of structure is capable of providing red to blue disperse dyes that meet the rigorous technical and economic requirements demanded of them by both manufacturer and user. Maradiya [2] The colours of hydrophobic monoazo dyes containing thiophene rings were investigated in 1949 by Dann. Maradiya [2] Few papers have been published concerning the synthesis and properties of such dyes.

Interest in the synthesis of disperse dyes based upon thiophene derivative has played a significant role in the technology of disperse dyes. Maradiya [2] A wide variety of information about the usefulness and technical importance of 2-aminothiophene derivatives as diazo components in the synthesis and application of greenish blue to blue disperse dyes have appeared in the literature. Maradiya [2] Synthesis of N-arylmaleimide based 2-aminothiophene dyes were reported. Maradiya [2] These previous works prompted us to study on thiophene moiety. This paper examined the synthesis of thiophene based monoazo disperse dyes 4a-c. In the synthesis, 2-amino-4-(4-chloro-phenylcarbamoyl)-5-methyl-thiophene-3-carboxylic acid ethyl ester was diazotised and coupled with N,N-bis(2-cyanoethyl)aniline, 3-acethylamino-N,N-diethylaniline and 3-hydroxyl-N, N-dimethyl aniline, 3a-c to give the azo disperse dyes 4a-c. In addition to characterization of the dyes, the dyes were applied on nylon 6.6 fabric and their percentage exhaustion and wash fastness property evaluated.

## 2. MATERIALS AND METHODS

### 2.1. Materials

All the chemicals used in the synthesis of the three dyes, 4a-c were of commercial grade. All solvents used were of spectroscopic grade. Melting points were determined by the open capillary method. The visible absorption spectra were measured using JENWAY 6305 Spectrophotometer. Infra red spectra were recorded on FTIR-8400s Fourier Transform Infra Red Spectrophotometer.

### 2.2. Methods

#### 2.2.1. Synthesis of 2-{4[Bis-(2-Cyano-Ethyl) Amino]-Phenylazo-4-Chloro-Phenyl Carbamoyl-5-Methyl-Thiophene-3-Carboxylic Acid Ethyl Ester (4a).

To a solution of cooled concentrated tetraoxosulphate (VI) acid (3 cm<sup>3</sup>), sodium nitrite (0.28 g, 0.004 moles) was added at a rate that brown fumes were not evolved to avoid loss of NO<sub>2</sub> gas. The mixture was warmed gradually on a water bath to temperature between 65-70 °C for the sodium nitrite to go into solution. The solution was cooled to temperature 0-5 °C and mixed with acetic acid (2cm<sup>3</sup>). Thiophene (1.35g, 0.004 moles) was added gradually to the nitrosyl sulphuric acid paste below 5°C with vigorous agitation. The solution was stirred at temperature 0-5° C, the temperature was maintained at 10 °C for 30 minutes.

A solution of equimolar quantities of the coupling component, N,N-bis(2-cyanoethyl) aniline (0.796 g, 0.004 moles) was prepared by dissolving the N,N-bis(2-cyanoethyl) aniline in a mixture of hydrochloric acid (1.5ml) and iced water (40ml). The diazo solution was then added gradually with stirring at pH 4 using acetic acid (10%). The stirring was continued for 2 hours and the

product filtered off, washed with water and dried. Maradiya [2], Maradiya and Patel [3], Sakoma, et al. [4]

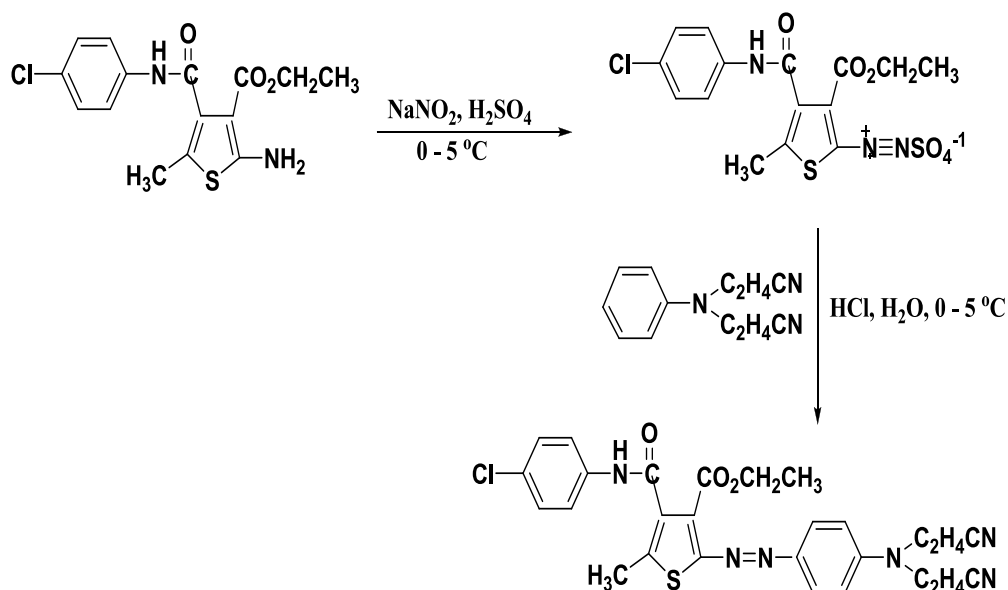
### 2.2.2. Synthesis of 2-(2-Acetylamino-4-Diethylamino-Phenylazo)-4-(4-Chloro-Phenyl Carbamoyl)-5-Methyl-Thiophene-3-Carboxylic Acid Ethyl Ester (4b).

The thiophene derivative (4b) was prepared in a manner similar to 4a, except 3-acetylamino-N,N-dimethyl aniline (0.824 g, 0.004 moles) was used as a coupling component, and was filtered off, washed with water and dried. Maradiya [2], Maradiya and Patel [3], Sakoma, et al. [4]

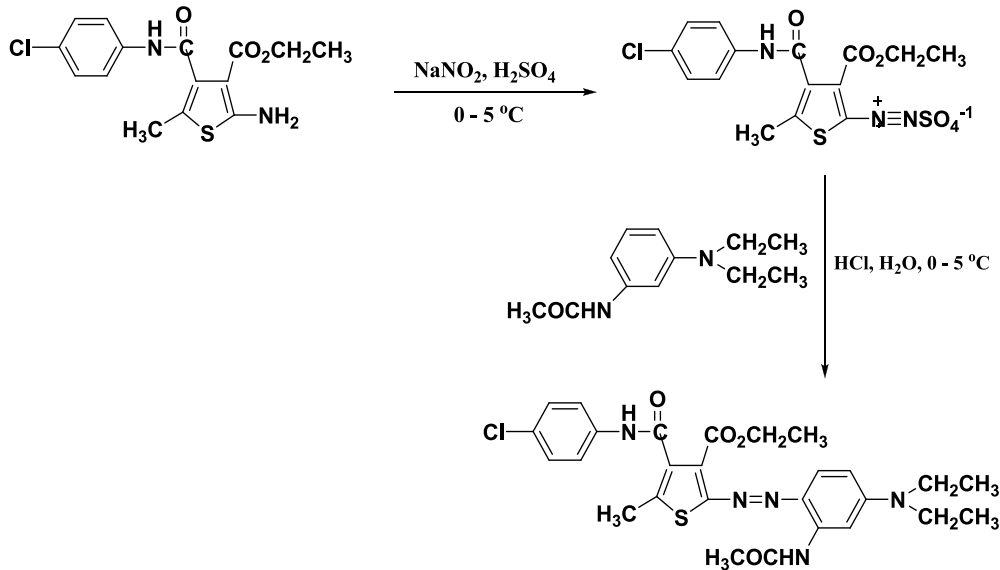
### 2.2.3. Synthesis of 4-(4-Chloro-Phenylcarbomyl)-2-(4-Dimethylamino-2-Hydroxy-Phenylazo)-5-Methyl-Thiophene-3-Carboxylic Acid Ethyl Ester (4c).

The thiophene derivative was prepared in a similar manner to that described above for 4b, except 3-hydroxyl-N,N-dimethyl aniline (0.548 g, 0.004 moles) was used as a coupling component, and was filtered off, washed with water and dried. Maradiya [2], Maradiya and Patel [3], Sakoma, et al. [4] The whole process for the synthesis is shown in schemes 1, 2 and 3.

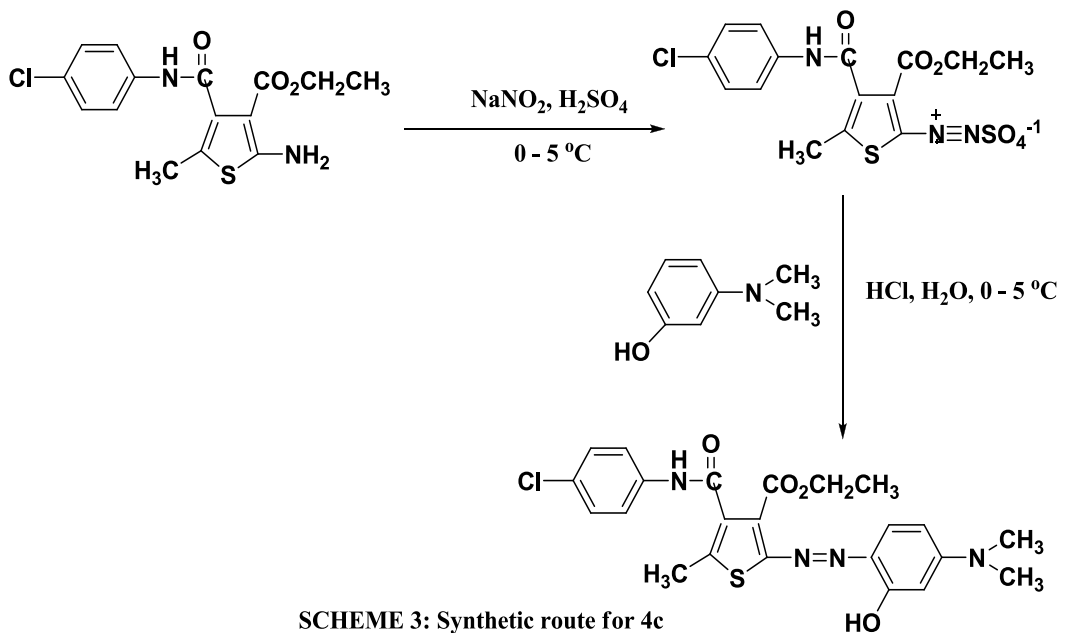
The Physical, Ultraviolet Spectroscopic, Infra Red Spectra, Dyeing and Wash Fastness Characterization Data of Dyes 4a-c are given in Tables 1, 2, 3 and 4 respectively.



SCHEME 1: Synthetic route for 4a



SCHEME 2: Synthetic route for 4b



SCHEME 3: Synthetic route for 4c

#### 2.2.4. Dyeing of Nylon 6.6 Fabric

The dye baths were prepared from the dyes (1.0 % weight of fabric) with a dispersol leveling agent (1.0 g/l) and carrier to a final liquor of 50:1, w/w. The pH of the bath was adjusted to 4-5 with acetic acid (10 %). The nylon fabrics, previously wetted, were placed into the liquor at 25-30 °C. The temperature was raised to 100 °C at the rate of 2 °C/minute and dyeing continued for 90 minutes. After cooling, the dyed fabrics were reduction cleared in sodium hydroxide (6.0 g/l), soap (1.0 g/l) and hydrosulphite (2 g/l) at 75 °C and then washed and dried. The percentage

exhaustion was determined by the methods of Giles. Maradiya [2], Maradiya and Patel [3], Sakoma, et al. [4], Giles [5].

### 2.2.5. Wash Fastness Property of the Dyes

The Wash Fastness was assessed in accordance with I. S. O. Wash Fastness No. 3. Maradiya [2], Maradiya and Patel [3], Sakoma, et al. [4], Giles [5] An undyed sample was attached to each of the dyed sample to form a composite to be used for the assessment. The essence of the undyed sample is to enable the assessment of the degree of staining to be determined. In this method a soap solution containing 5 g/l and 2 g/l soda ash was prepared. The composite was washed in a container containing the appropriate amount of soap solution and soda ash at 60 °C for 30 minutes using liquor ratio 50:1. After washing, the fabric was rinsed, separated and dried. The change in colour and staining of the undyed fabric were assessed with a grey scale. The results are summarized in Table 4.

### 2.3. Results and Discussion

**Table-1.** Physical Characteristics of the Dyes.

Dye No.	M. Pt (°C)	Weight of Dye (g)	% yield	Molar mass	Colour of crystals
4a	192	1.947	88.1	548.5	Orange
4b	163	1.867	96.5	555.5	Purple
4c	171	1.966	90.1	486.5	Purple

**Table-2.** The Ultraviolet Spectroscopic Properties.

Dye No.	Absorption Maxima $\lambda_{\max}$ (nm)				Extinction Coefficient $\epsilon$ (L mol <sup>-1</sup> cm <sup>-1</sup> × 10 <sup>4</sup> )			
	Acetone	Toluene	Ethanol	DMF	Acetone	Toluene	Ethanol	DMF
4a	650	650	600	650	5.8	4.2	6.5	8.0
4b	550	550	550	550	2.4	6.9	7.4	6.9
4c	650	600	550	650	8.5	2.3	9.2	4.7

**Table-3.** Infra-Red Spectral Analysis for the Dyes.

Dye No.	Frequency Absorption (cm <sup>-1</sup> )	Functional Group
4a	1713.81	C=O stretch (ester)
	2968.55	C-H stretch (aromatic)
	2374.45	C-H stretch (sp <sup>3</sup> )
	2247.15	C≡N stretch (nitriles)
	1663.66	C=O stretch (amide)
	1591.33	C=C stretch (arenes)
	3475.84	N-H stretch (amide)
4b	1667.52	C=O stretch (ester)
	2981.08	C-H stretch (aromatic)
	2386.02	C-H stretch (sp <sup>3</sup> )
	1615.44	C=O stretch (amide)
	1517.06	C=O stretch (arenes)
	3466.20	N-H stretch (amide)
	3983.14	N-H

4c	1710	C=O stretch (ester)
	2929	C-H stretch (aromatic)
	2364.81	C-H stretch (sp <sup>3</sup> )
	1603.86	C=O stretch (amide)
	1510.31	C=C stretch (arenes)
	3424.74	O-H stretch (alcohol)

**Table-4.** Dyeing (Exhaustion) and Wash Fastness Properties of the Dyes.

Dye No.	% Exhaustion	Colour Change	Staining of adjacent White
4a	85	4 (very good)	4
4b	92	3 (good)	4-5 (slight staining)
4c	79	4 (very good)	4

### 2.3.1. Synthesis of Dyes

All the dyes were synthesized by diazotizing 2-amino-4-(4-chloro-phenyl carbamoyl-5-methyl-thiophene-3-carboxylic acid ethyl ester using the general method of diazotization of weakly basic amines and coupled to three different coupling components namely: N, N-dimethyl aniline, 3-acetylamino-N,N-diethylaniline and 3-hydroxyl N,N-dimethyl aniline. The weakly basic amines contain an electron withdrawing groups which tend to be soluble in nitrosyl sulphuric acid. [Maradiya and Patel \[3\]](#)

### 2.3.2. Physical Characteristics of the Dyes

The physical characteristics of the Dyes are shown in Table 1. Each of the different dyes synthesized possessed distinct physical characteristics. They exhibited well-defined melting points (192,163 and 171°C) characteristics of pure compounds. The colour of the dye crystals was orange for dye 4a and purple for dyes 4b and 4c respectively. The structures of the dyes are planer thus, can lie flat against the polymer molecules. Their planarity accounts for their good substantivity for hydrophobic fibres. [Fierz-David \[6\]](#), [Bello, et al. \[7\]](#)

### 2.3.3. Visible Absorption Spectra of the Dyes

Visible absorption maxima of the dyes in various solvents are given in Table 2. The visible absorption spectra of the dyes were found to exhibit a strong solvent dependence which did not show a regular variation with the dielectric constants of the solvent. Acetone, N,N-dimethylformamide (DMF), toluene, ethanol were each used as solvents for dissolving the dyes. Dye 4a which was obtained by coupling the diazo component with N,N-bis(2-cyanoethyl) aniline gave a maximum absorption wavelength at 650 nm in acetone, this is however expected to be hypsochromic since the cyano group is an electron withdrawing group incorporating in the electron donor half of the chromogen. [Maradiya \[2\]](#), [Maradiya and Patel \[3\]](#), [Sakoma, et al. \[4\]](#) Coupling the diazo component with 3-hydroxyl-N,N-dimethyl aniline in acetone absorbed at 650nm. When the dye was dissolved in a much more polar solvent such as DMF, dye 4a and 4c each show the highest  $\lambda_{\text{max}}$  at 650 nm as was the case in acetone. Dye 4b also absorbed at the  $\lambda_{\text{max}}$  of 550 nm in DMF.

Dye 4a is orange while dyes 4b and 4c are purple colour respectively. The dyes have absorption maxima between 550 nm and 650 nm. The value of the absorption maximum of the dyes depends on both the nature and position of substitution in the aryl ring system. Maradiya and Patel [3] The values of the molar extinction coefficient ( $\epsilon$ ) of the dyes were in the range of  $2.3 \times 10^4 - 9.2 \times 10^4 \text{ l mol}^{-1}\text{cm}^{-1}$  indicating their good intensity of absorption. One cause of the increased intensity might be attributed to the greater planarity of the dyes, because of the lower steric interaction of a five-membered ring. The resonance theory gives the reason for the bathochromism of 2-aminothiophene dyes. Maradiya and Patel [3], Gordon and Gregory [8] The first concerns the powerful electron withdrawing thiophene residue that contains sulphur as a  $\pi$ -excessive heteroatom. The sulphur atom, which is said to act as an additional electron withdrawing group, has unoccupied 3d orbitals available that can accommodate transferred negative charge and stabilize the excited state, resulting in a bathochromic shift. The 3d orbitals on the sulphur atom may contribute to the first excitation energy. Maradiya and Patel [3], Schulte and Schweig [9] Sulphur also increases the diene character of thiophene ring, so the  $\pi$ -electrons in the thiophene ring are likely to migrate easily. This factor is responsible for the larger absorption shift. Maradiya and Patel [3], Griffiths [10]

#### 2.3.4. Infra-Red Spectral Analysis of the Dyes

The dyes infra red spectra are summarized in Table 3. Dye 4a was obtained by coupling the diazo component with N,N-bis (2-cyanoethyl) aniline gave an absorption peak at  $2247.15 \text{ cm}^{-1}$  due to nitrile ( $\text{C}\equiv\text{N}$ ) group stretching. Dye 4b gave absorption peaks at frequency  $3983.14 \text{ cm}^{-1}$  which was due to N-H stretch.

Dye 4c gave absorption peak at frequency  $3424.74 \text{ cm}^{-1}$ , which was due to an (O-H) stretch. All the dyes shows similar functional groups of C=O (ester), C-H (aromatic), C-H ( $\text{sp}^3$ ), C=O (amide), C=C (arenes), N-H (amide) at different frequencies. These functional groups supported the behaviour of the dyes on nylon 6.6 fabric and this is confirmed by the excellent exhaustions, intensity of colour, and very good wash fastness ratings on nylon 6.6 fabric.

#### 2.3.5. Dyeing and Wash Fastness Properties of the Dyes

Table 4 shows the dyeing and wash fastness properties of the dyes. The level of exhaustion of all the dyes on fabrics ranges from very good to excellent. The exhaustion was excellent ranging from 79-92 %. Dye 4a gave an orange hue while dyes 4b and 4c each gave purple hues with excellent, brightness, levelness and high tinctorial strength. The variation in the hues of the dye fabric results from an alteration in the coupling component. Maradiya and Patel [3].

The wash fastness rating of all the dyes on the fabrics ranges from good to very good. Dyes 4a and 4c having a rating of 4 respectively which is very good, while dye 4b with a rating of 3 indicating good. The staining of the adjacent fabric is also limited with rating of 4-5 indicating slight staining for the dye 4b and 4 each for dyes 4a and 4c. The excellent wash fastness observed in nylon is due to the crystalline structure of the nylon which disallowed the migration of dye out of the fabric when this has entered the fabric. Bello, et al. [7].

The excellent wash fastness of the dyes is also due to their hydrophobic character and the polarity conferred them by the polar substituted groups. The polar substituted groups on the molecules contribute greatly to the strength of the dyed fabric bond. Maradiya and Patel [3], Gordon and Gregory [8], Giles [5], Griffiths [10]

### 3. CONCLUSION

The synthesis of monoazo-disperse dyes based on thiophene was undertaken. Generally, the exhaustion of the dyes was excellent on nylon 6.6 fabrics, with very good wash fastness properties. These dyes have excellent intensity of colour. They also gave deep and bright hues with level dyeings. The bright hue might be attributed to the greater planarity of the thiophene ring, because of the lower steric interaction of a five-membered ring. The remarkable degree of levelness and brightness after washing is an indicative of good penetration and excellent exhaustion of these dyes on nylon 6.6 fabric due to the accumulation of polar substituent groups on the dye moiety, which is an additional property not exhibited by the carbocyclic azo and anthraquinone dye structures.

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