

## SYNTHESIS OF NOVEL AZO DYES CONTAINING THE THIOPHENE MOIETY

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*A series of disperse dyes have been synthesized by diazotation of 2-aminothiophene derivative and coupling with various N-arylmaleimides. The dyes were characterized by IR spectral studies, visible absorption spectra, and elemental analysis. The dyeing performance of these dyes was assessed on nylon fabric. These dyes were found to give yellowish brown to reddish violet shades on dyeing with very good depth, levelness, and brightness on fabric. The percentage dyebath exhaustion and fixation on fabric was found to be very good. The dyed fabric showed poor light fastness and good to excellent fastness to washing, rubbing, perspiration, and sublimation.*

**Keywords:** 2-aminothiophene, nylon, exhaustion, fixation, monoazo dyes.

Heterocyclic diazo components have long been used in the manufacture of disperse dyes. The original dyes were employed on secondary cellulose acetate and had above average brightness, together with a high tinctorial strength. Most of these dyes were introduced by Eastman Kodak and were usually based on derivatives of 2-aminothiazole and 2-aminothiophene.

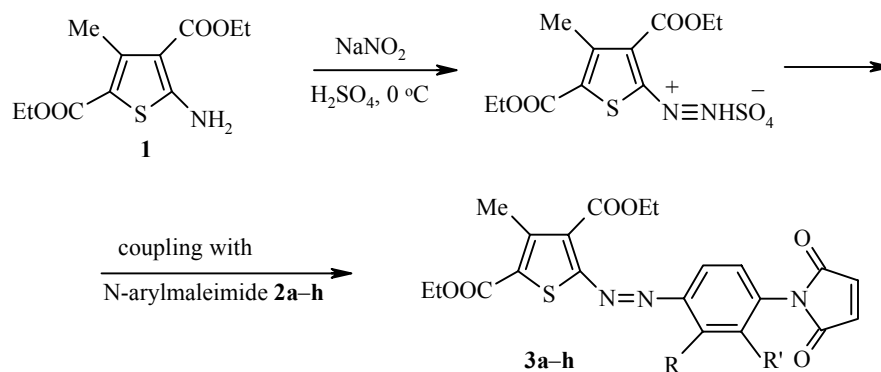
The colors of hydrophobic monoazo dyes containing thiophene rings were investigated as long ago as 1949 [1]. While nitrothiopheneazo disperse dyes have been known for around forty years [2], their commercial exploitation as replacements for blue anthraquinone disperse dyes [3, 4] has occurred only over the last two decades. The first investigations into monoazo dyes based on 2-amino-5-nitrothiazole [5] and 5-acetyl-2-amino-3-nitrothiophene [2] by Eastman Kodak in the 1950s showed that these dyes had rather high bathochromism and performance. A systematic study by Dickey [2] was published which established the better relative bathochromy of thiophene azo dyes over their carbocyclic counterparts and provided qualitative evidence of the higher absorption intensities of the former dye type (Scheme 1).

Gewald discovered in the 1960s a simple and versatile synthetic route for 2-aminothiophenes [6]. A recent important development is the resurgence of interest in dyes derived from 2-aminothiophene derivatives. The technical potential of such dyes for cellulose acetate and for polyester was noted some time ago [2], but their manufacture was not commercialized because of the lack of suitable economic synthetic procedures. Improvement in synthetic approaches to derivatives of 2-aminothiophene, stimulated by the work of Gewald [7], renewed commercial interest. The promise of Gewald's discovery signaled a steady stream of applications concerning thiophene-based azo disperse dyes over the next 20 years [8-10]. Despite, or perhaps because of, the commercial interest, few papers have been published recently [11-20] concerning the synthesis and properties of such dyes.

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Scheme 1



**2, 3 a,e-h** R = H, **b** R = NO<sub>2</sub>, **c** R = Cl, **d** R = Me; **a-d** R' = H, **e** R' = NO<sub>2</sub>, **f** R' = Cl, **g** R' = Me, **f** R' = Me, **h** R' = OMe

Some disperse dye structures dyed on polyester-cellulose blend respond to treatment with hot alkali by superficial removal of the dyes on the surface of polyester and also those cross-stained on cellulose [21]. Thus disperse dye structures having carboxylic acid ester groups as well as those possessing 2-arylazothiophenes respond to such treatment. This phenomenon is known as dischargeability and is commercially important.

Earlier we had studied disperse dyes based on various N-arylmaleimide coupling components [22-24]. The encouraging results prompted us to extend our study on the thiophene moiety. In this paper, we report the synthesis of N-arylmaleimide based 2-aminothiophene dyes. To achieve the synthesis of the above compounds, 2-amino-3,5-bis(ethoxycarbonyl)-4-methylthiophene (**1**) was diazotized and coupled with various N-arylmaleimides **2a-h** to give azo dyes **3a-h**. The dyes have been tested successfully as disperse dyes for nylon fabric. In addition to the characterization of the dye, an evaluation of their technical property and a color assessment were performed.

TABLE 1. Characterization Data and Exhaustion (E) and Fixation (F) Properties of Dyes **3a-h**

Dye	mp (from DMF), °C	Absorption maxima, $\lambda_{\text{max}}$ , nm		log $\epsilon$	E, %	F, %	$R_f$	Yield, %
		DMF	Conc. H <sub>2</sub> SO <sub>4</sub>					
<b>3a</b>	107-108	700	410	4.25	94	85	0.86	76
<b>3b</b>	120-122	650	400	3.91	92	79	0.82	79
<b>3c</b>	103-104	550	415	3.93	85	83	0.89	82
<b>3d</b>	121-122	740	410	4.42	83	80	0.81	70
<b>3e</b>	101-102	565	400	4.14	92	86	0.90	77
<b>3f</b>	139-141	555	425	3.93	78	80	0.92	72
<b>3g</b>	126-127	575	410	4.11	92	85	0.91	80
<b>3h</b>	110-111	570	390	3.53	82	76	0.86	75

TABLE 2. Elemental Analysis of Dyes **3a-h**

Dye	Empirical formula	Molecular weight	Found, %		
			Calculated, %		
			C	H	N
<b>3a</b>	C <sub>21</sub> H <sub>19</sub> N <sub>3</sub> O <sub>6</sub> S	441	57.14	4.30	9.52
			57.00	4.10	9.40
<b>3b</b>	C <sub>21</sub> H <sub>18</sub> N <sub>4</sub> O <sub>8</sub> S	486	51.85	3.70	11.52
			51.78	3.65	11.40
<b>3c</b>	C <sub>21</sub> H <sub>18</sub> ClN <sub>3</sub> O <sub>6</sub> S	475.5	52.94	3.78	8.82
			52.80	3.70	8.70
<b>3d</b>	C <sub>22</sub> H <sub>21</sub> N <sub>3</sub> O <sub>6</sub> S	455	58.02	4.61	9.23
			57.52	4.52	9.10
<b>3e</b>	C <sub>21</sub> H <sub>18</sub> N <sub>4</sub> O <sub>8</sub> S	486	51.85	3.70	11.52
			51.75	3.60	11.40
<b>3f</b>	C <sub>21</sub> H <sub>18</sub> ClN <sub>3</sub> O <sub>6</sub> S	475.5	52.94	3.78	8.82
			52.80	3.65	8.70
<b>3g</b>	C <sub>22</sub> H <sub>21</sub> N <sub>3</sub> O <sub>6</sub> S	455	58.02	4.61	9.23
			57.59	4.50	9.10
<b>3h</b>	C <sub>22</sub> H <sub>21</sub> N <sub>3</sub> O <sub>7</sub> S	471	56.05	4.45	8.91
			55.80	4.30	8.80

TABLE 3. Dyeing Properties of Dyes **3a-h** on Nylon Fabric

Dye	Shade on nylon	Fasteness to*	
		Rubbing dry	Rubbing wet
<b>3a</b>	Reddish violet	4	5
<b>3b</b>	Brown	5	5
<b>3c</b>	Reddish brown	5	4
<b>3d</b>	Reddish violet	5	5
<b>3e</b>	Reddish violet	5	5
<b>3f</b>	Reddish violet	5	5
<b>3g</b>	Reddish violet	5	4
<b>3h</b>	Bronze red	5	5

\* **3a-h** light 2-3; washing 5; perspiration acid 5, alkaline 5; sublimation 5.

## EXPERIMENTAL

The C, H and components of all the dyes were determined using an elemental analyzer made by Carlo Erba, Italy. The IR spectra were scanned in KBr pellets on a Perkin–Elmer 983 spectrophotometer. The visible absorption spectra were recorded on a Carl Zeiss UV-vis Specord spectrophotometer. Melting points were determined by the open capillary method.

The solvents and reagents were obtained from commercial sources. They were further purified by standard methods [25].

The diazo component **1** was prepared by the method reported in the literature [26]. The coupling components **2a-h** were prepared by the method reported in the literature [27].

**Preparation of 2-(N-Phenylmaleimido)azo-3,5-bis(ethoxycarbonyl)-4-methylthiophene (3a).** Synthesis of **3a** involves two steps.

A. Diazotization of compound **1**. Dry sodium nitrite (1.38 g, 0.02 mol) was added in parts over a period of 30 min to 98 % H<sub>2</sub>SO<sub>4</sub> (1.98 g, 0.02 mol) with stirring below 65°C. The resulting solution was then cooled to 5°C and a mixture of 20 ml of EtCOOH and AcOH (3:17) was added dropwise with stirring, allowing the

temperature to rise to 15°C. The resulting mixture was then cooled to 0°C, compound **1** (5.14 g, 0.02 mol) was added in portions, and stirring was continued at this temperature for 2 h. The excess nitrous acid (presence tested by starch-iodide paper) was decomposed using the required amount of urea. The clear diazonium salt solution thus obtained was used for the subsequent coupling reaction (see Scheme 1).

B. Coupling with N-phenylmaleimide (**2a**). Compound **2a** (3.46 g, 0.02 mol) was dissolved in AcOH (10 ml) and cooled to 0°C in an ice-bath. A freshly prepared diazonium salt solution was added at this temperature dropwise over 2 h with vigorous stirring. The pH of the reaction mass was maintained between 4.5-5.0 by addition of 10% AcONa solution. The mixture was stirred for further 1 h at 0-5°C and then heated up to 30°C, diluted with 100 ml water, and further stirred for 15 min. The solid product separated was filtered off, washed with water, and finally dried at room temperature. The crude product was recrystallized in a minimum amount of DMF to give **3a** as a dark brown powder.

The above procedure was used for the preparation of other dyes **3b-h** using various coupling components **2b-h** (see Scheme 1). The characterization data of all the dye **3a-h** are given in Table 1.

**Dyeing Method.** Dyeing of nylon fabric was carried out with the procedure reported earlier [18].

**Fastness Properties.** The fastness to light, sublimation, and perspiration was assessed in accordance with BS: 1006-1978. The rubbing fastness test was carried out using a crockmeter (Atlas) in accordance with AATCC-1961 and the wash fastness test in accordance with IS: 765-1979. The details of various fastness tests are mentioned in the literature [28].

**Determination of the Percentage Exhaustion and Fixation.** The dyebath exhaustion percentage (% E) and fixation percentage (% F) of the dyed fabric were determined according to the known method [29].

## RESULTS AND DISCUSSION

**Diazotization of Diazo Component 1.** The diazo component **1** is a versatile key intermediate in the synthesis of various disperse dyes. The principle advantages of the key compound used here are that the yield is high, the reaction time is short, the procedure involves only one facile step, the work-up is convenient, and thus the starting material can be easily prepared. The presence of an electron withdrawing group such as carboxy adjacent to the diazotizable amino group has a bathochromic influence on the shades of these dyes on fabric and is also useful for better dispersability and dyeability. However, one disadvantage of the ester functionality is that its conjugation with the amino group reduces the basicity of the nitrogen atom and thus efficient diazotation can only be achieved using nitrosylsulfuric acid obtained from NaNO<sub>2</sub> and concentrated H<sub>2</sub>SO<sub>4</sub>. Here, the acid of choice is concentrated H<sub>2</sub>SO<sub>4</sub> used in admixture with AcOH and EtCOOH. When NaNO<sub>2</sub> is added to concentrated H<sub>2</sub>SO<sub>4</sub> of somewhat lower concentration, nitrous fumes are given off. But dry solid NaNO<sub>2</sub> can be dissolved in concentrated H<sub>2</sub>SO<sub>4</sub> smoothly and without evolution of nitrous fumes to form nitrosylsulfuric acid. Diazotation in nitrosylsulfuric acid is very slow because the concentration of the free amine is exceedingly small.

Thus, the thiophene intermediate **1** was diazotized satisfactorily at 0-5°C by nitrosylsulfuric acid in AcOH. In order to determine the end point of diazotation, it was found useful to check for the presence of unreacted diazo component by thin layer chromatography (TLC) by sampling the diazotization mixture and extracting with AcOEt. Thus, when unreacted diazo component no longer persisted on TLC, the diazotation was ended. The diazonium salt solution was used immediately since it decomposed on standing, even when cold. Subsequent coupling reactions took place readily on adding the diazonium salt continuously to the solution of the coupling component in AcOH. Coupling was usually accompanied by some evidence of decomposition; however, by careful addition of the diazonium salt solution at 0-5°C to a solution of the coupling component in AcOH, high yields (70-82%) of the dye were usually obtained. To complete coupling, particularly for reactions using nitrosylsulfuric acid for the diazotation, the pH of the reaction mixture was eventually adjusted to approximately 4-5 by addition of an appropriate amount of 10% AcONa solution below 5°C.

**Physical Properties of the Dyes.** The purity of the dyes was evaluated by TLC using AcOEt–benzene (1:4) as the eluting system. When adsorbed onto silica chromatography plates, the dyes produced yellow-red colors. All the recrystallized dyes exhibited well-defined melting points characteristic of pure compounds. The characterization data are given in Table 1.

**Visible Absorption Spectroscopy.** The visible absorption spectroscopic properties of dyes **3a-h** were recorded in concentrated H<sub>2</sub>SO<sub>4</sub> and DMF solution (Table 1). As far as absorption maxima are concerned,  $\lambda_{\text{max}}$  values are directly proportional to the electronic power of the substituents in the aryl ring. The value of the logarithm of molar extinction coefficient ( $\log \epsilon$ ) of the dyes **3a-h** was in the range 3.53–4.42, consistent with their high intensity of absorption. The introduction of electron-releasing or electron-withdrawing groups at suitable positions in the coupler ring affects the absorption characteristics of the dyes. One cause of the increased intensity might be attributed to the greater planarity of the thiophene dyes, because of the lower steric interaction of a five-membered ring. The bathochromic effect noted on replacement of a phenyl ring with a thiophene unit for this class of dyes is well documented [30] and is a consequence of the less aromatic, more polarizable thiophene system being substituted with a conjugated electron-withdrawing ester function. The sulfur atom is said to act as an additional electron withdrawing group: it has unoccupied 3*d* orbitals available that can accommodate transferred negative charge and stabilize the excited state, resulting in a bathochromic shift.

**Infrared Spectra.** The infrared spectra of dyes reveals that the 1,2-ethylenic bond of the maleimide ring can be identified by the stretching vibration of C–H. The band appearing at 1620 cm<sup>-1</sup> is due to the stretching vibration of C=C, which is conjugated with a C=O group. The unsaturation is indicated by the C–H stretching vibrations, which appears at 3100 and 850 cm<sup>-1</sup> and are due to the out-of-plane-deformation vibration. The band at 680 cm<sup>-1</sup> is an out-of-plane-deformation vibration characteristic of CH=CH. The pair of strong bands observed at 1700 and 1721 cm<sup>-1</sup> is due to the stretching vibration of the C=O unit of the cyclic maleimide ring. The band appearing at 630–680 cm<sup>-1</sup> can be attributed to the in-plane deformation vibration of the C=O, and that at 570–580 cm<sup>-1</sup> to the out-of-plane deformation vibration of the C=O. The bands at 1350 and 1371 cm<sup>-1</sup> are due to the stretching vibration of C–N–C, the first being asymmetrical and the second symmetrical. The band of the skeletal C–C bond appears at 1570 cm<sup>-1</sup>, and that at 1575–1585 cm<sup>-1</sup> is due to the –N=N– stretching vibration. The bands around 1480–1530 cm<sup>-1</sup> are due to the carbethoxy group. The bands at 2850, 640–700, and 1390–1450 cm<sup>-1</sup> are due to the C–H bending vibration of –OCH<sub>3</sub>, C–Cl, and the C–CH<sub>3</sub> stretching vibration, respectively. The band at 1320–1360 cm<sup>-1</sup> is due to the symmetric stretching of the –NO<sub>2</sub> group.

**Dyeing Properties of Dyes.** All the dyes **3a-h** were applied at 2% depth on fabric as disperse dyes. Their dyeing properties are given in Table 3. These dyes gave a narrow range of color varying from brown to reddish violet shades with good levelness, brightness, and depth on the fabric. The variation in the shades of the dyed fabric results from both the nature and position of the substituent present in the aryl ring.

The light fastness of dyes on fabric is found to be similar (2–3). In attempting to trace the relationship between chemical structure and light fastness, it is important to note that there is no absolute value for the light fastness of a dye; the value obtained for a given colorant in any fading test depends on many factors, the most important of which are: the concentration and/or degree of aggregation of dye within the fabric (deep sample shade); the nature of the fabric in which it is dispersed; the characteristics of the incident radiation, molecular structure, molecular size, and substantivity. The substantivity of dyes for nylon fabric is such that they almost conferred similar depths of shade (close fixation values), which had the same rating, implying that the intrinsic photostabilities of dyes on the fabric are similar. This suggests that smaller molecular size and higher substantivity factors are more important than slight differences in the molecular structure of dyes.

Table 1 shows the exhaustion and fixation of all the dyes on fabric. A high exhaustion on the fabric may be expected due to the open structure; consequently, diffusion of the dye within the fabric proceeds rapidly under the dyeing condition. Hence, the rate of diffusion of the dye molecules into the fabric is higher, which increases the exhaustion value. Also the smaller thiophene dye molecule penetrates deeper into the fabric, which

closes easily on fabric after dyeing and so protects it from sublimation. With respect to sublimation fastness, all the dyes exhibit an excellent rating of 5 on fabric. The other fastness properties are found to be good (4) to excellent (5).

## CONCLUSIONS

A series of thiophene-based monoazo disperse dyes containing various N-arylmaleimide residues have been synthesized by conventional methods and their color properties examined both in solution and on application to nylon fabric. The dyes provide brown to reddish violet shades on fabric and offer excellent affinity and intensity of color. Furthermore these dyes show level dyeing and display excellent dispersability. The intrinsic conjugation in the dye structure reduce the basicity of the nitrogen atom of the amino group and thus efficient diazotation can only be achieved using nitrosylsulfuric acid. The conjugations in the dye structure also ensure very good color strength and intensity.

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