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SYNTHESIS OF 2-AZOBENZO[*b*]THIOPHENE DERIVATIVES AND THEIR APPLICATION ON NYLON FIBRE

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A series of novel monoazo disperse dyes derived from the coupling of diazotized 2-aminobenzo[b]thiophene derivatives with N-arylmaleimides is described. The monoazo disperse dyes applied to nylon fabric and their dyeing performance has been assessed. These dyes have been found to give light yellow to reddish pink color shades with very good depth and levelness on nylon fabric. The dyed fabric shows moderate light fastness and excellent washing, rubbing, perspiration, and sublimation fastness. The percentage dyebath exhaustion on nylon fabric has been found to be good and acceptable.

Keywords: 2-aminobenzo[*b*]thiophene, monoazo disperse dyes, dyeing, nylon fabric, fastness.

Azo dyes with heterocyclic diazo components have been intensively investigated to produce brilliant deep hues ranging from red to greenish blue on synthetic fabrics. These results led to commercial disperse dyes to replace the conventional azobenzene-type reds and anthraquinonoid blues dyes [1]. Before the 1950s, almost all of the disperse dyes available were prepared from either substituted anilines or substituted anthraquinones. The anthraquinone derivatives had the limitations of poor dischargeability and sensitivity to oxides of nitrogen. A major advance was made by the research group of Dickey [2] of Eastman Kodak in the 1950s in heterocyclic azo dyes, and they published a classic paper on thiophene-based disperse dyes in 1958.

The development by Gewald [3] in the 1960s of a simple and versatile synthetic route for various 2-aminothiophenes sparked renewed commercial interest in these compounds as diazo components. The promise of Gewald's discovery signaled a burst of patent activity [4, 5], which was followed by a steady stream of applications concerning thiophene-based azo disperse dyes over the next 20 years [6]. Despite, or perhaps because of, the commercial interest, few papers have been published concerning the synthesis and properties of such dyes. Recently, revival of interest in the synthesis of disperse dyes based upon thiophene derivatives has played a significant role in the technology of disperse dyes [7-9]. Extensive information on the usefulness and technical importance of 2-aminothiophene derivatives as diazo components in the synthesis and application of greenish blue to blue disperse dyes has appeared in the literature [10-13]. The ethyl ester of 2-amino-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylic acid (**1**) is a well-known heterocyclic diazo component. The versatility of this key compound and related analogs in the synthesis of various dyes and fluorescent brighteners has been well demonstrated [14-17].

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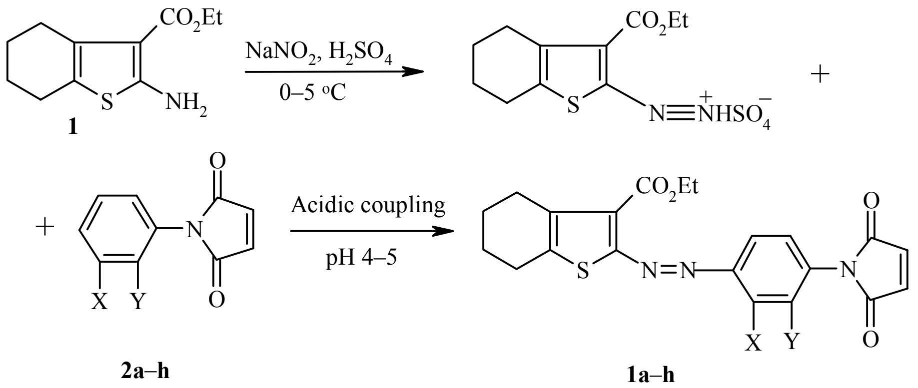
Synthetic route of dyes **1a-h**



2, **3** **a**, **e-h** X = H, **b** X = NO₂, **c** X = Cl, **d** X = Me; **a-d** Y = H, **e** Y = NO₂, **f** Y = Cl, **g** Y = Me, **h** Y = OMe

The structural features of thiophene disperse dyes are unique. The relatively low molecular mass and high molar extinction coefficient of typical azothiophene disperse dyes contribute to their attractive cost effectiveness on fabrics. If an electron-withdrawing group such as cyano, nitro, or methylsulfonyl is introduced into the 3- or 5-position of the 2-aminothiophene system, a bathochromic shift in the wavelength of absorption of the resulting monoazo dyes is possible. The sublimation fastness of such azothiophene disperse dyes is superior to that of azobenzene analogs.

It seems that no report is available on the synthesis of monoazo disperse dyes by coupling various N-arylmaleimides **2a-h** with diazotized ethyl 2-amino-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylate (**1**). The aim of this work was to synthesize a series of such azo compounds **3a-h**, which have been tested successfully as disperse dyes for nylon fabric. In addition to a characterization of the dyes, an evaluation of their technical properties and a color assessment was also performed.

Results and Discussion

Preparation of the Diazo Component. Compound **1** was synthesized by condensation of cyclohexanone, sulfur, and ethyl cyanoacetate following Gewald's elegant method [3]. This synthesis, based on the cyclization of compounds containing an active methylene group to form 2-aminothiophene derivatives, has provided several crucial intermediates used as starting material in various study, particularly those containing an electron-withdrawing substituent at the 3-position. The main advantages of the key compound used here are that the yield is high, the time of reaction 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 the electron-withdrawing carbethoxy group adjacent to the diazotisable 2-amino group has a bathochromic influence on the hue of these dyes on nylon fabric, and the hydrophobic nature of the tetrahydrobenzo structure is useful for better dispersability and dyeability. Two types of nitrosating reagents, nitrosyl chloride from $NaNO_2$/HCl solution and nitrosylsulfuric acid from $NaNO_2$/concentrated H_2SO_4, were used for diazotization. The mild acidity of $NaNO_2$/HCl solution results in a relatively smaller amount of unreacted compound **1** remaining after diazotization.

Because of the lower nucleophilicity of compound **1**, some unreacted compound **1** remained after diaxotization with nitrosyl chloride. Efficient diazotization can only be achieved using nitrosylsulfuric acid obtained from $NaNO_2$ and concentrated H_2SO_4. The acid of choice is concentrated sulfuric acid mixed with glacial AcOH and propionic acid. A particularly important reagent combination is nitrosylsulfuric acid, which is

TABLE 1. Characteristics of Dyes **3a-h**

Dye	Emprical formula	Found, % Calculated, %			mp, °C (DMF)	R_f	λ_{max} (in DMF)	log ε	Exhaustion, %	Yield, %
		C	H	N						
3a	$C_{21}H_{19}N_3O_4S$	61.00 61.61	4.20 4.64	10.00 10.26	152-154	0.91	500	3.39	72	72
3b	$C_{21}H_{18}N_4O_6S$	55.10 55.50	3.50 3.96	12.00 12.33	168-170	0.86	440	3.52	75	81
3c	$C_{21}H_{18}ClN_3O_4S$	56.29 56.82	3.86 4.05	9.30 9.47	180-181	0.93	400	3.69	73	74
3d	$C_{22}H_{21}N_3O_4S$	62.28 62.41	4.80 4.96	9.70 9.92	185-187	0.89	540	4.20	70	71
3e	$C_{21}H_{18}N_4O_6S$	55.20 55.50	3.85 3.96	12.21 12.33	164-165	0.85	400	3.84	68	85
3f	$C_{21}H_{18}ClN_3O_4S$	56.62 56.82	3.81 4.05	9.25 9.47	178-179	0.92	325	3.89	72	75
3g	$C_{22}H_{21}N_3O_4S$	62.25 62.41	4.75 4.96	9.68 9.92	165-166	0.88	520	3.92	78	78
3h	$C_{22}H_{21}N_3O_5S$	60.00 60.13	4.62 4.78	9.41 9.56	178-180	0.87	510	3.74	75	75

used extensively as a nitrosating agent for weakly basic amines. When $NaNO_2$ is added to sulfuric acid of somewhat lower concentration, nitrous fumes are given off. But dry solid $NaNO_2$ can be dissolved in concentrated H_2SO_4 smoothly and without evolution of nitrous fumes to form nitrosylsulfuric acid. Diazotization in nitrosylsulfuric acid is very slow because the concentration of the free amine is exceedingly small.

Compound **1** was diazotized satisfactorily at 0-5°C by nitrosylsulfuric acid in AcOH. In order to determine the end point of diazotization, it was found useful to check for the presence of unreacted diazo component on thin layer chromatography (TLC) plates by sampling the diazotization mixture. Thus, when the unreacted diazo component no longer persisted on TLC plates, the diazotization was finished. The diazonium salt solution was used immediately since it decomposed on standing, even when cold. Subsequent coupling reactions took place readily on adding the resulting diazonium salt continuously to the solution of 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, 71-85% yields of dye were usually obtained. To complete coupling, particularly for reactions using nitrosylsulfuric acid in the previous diazotization, the pH of the reaction mixture was eventually adjusted to approximately 4-5. Thus, an appropriate amount of 10% NaOAc solution was slowly added below 5°C.

Physical Properties of Dyes 3a-h. The purity of the dyes was checked by TLC using EtOAc-benzene (1:4) as the solvent 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.

Visible Spectra of Dyes. The visible absorption spectroscopic properties of dyes **3a-h** were recorded in DMF solution and are mentioned in Table 1. As far as absorption maxima are concerned, the λ_{max} values are directly proportional to the electronic power of the substituents in the ring. The values of the logarithm of the molar extinction coefficient (log ε) of dyes **3a-h** were in the range of 3.39-4.20**,** consistent with their good intensity of absorption. The introduction of electron-donating or electron-attracting groups at suitable positions in the coupler ring affects the absorption characteristics of the dyes. In dyes **3b-d** possessing one substituent *ortho* to the azo linkage, the values of the λ_{max} are consistently higher than in their *meta*-substituted analogues **3e-g**. The extent of this shift is probably accounted for by the steric effects of the coupler substituents. When an electron-donating substituent is present on the coupling moiety of the dyes **3d,g,h**, higher λ_{max} values are observed compared with those of dyes that have electron-attracting substituents on the coupler moiety.

Resonance theory gives the reason for the bathochromism of 2-aminothiophene dyes [18]. The thiophene residue contains sulfur as the π-excessive heteroatom, which has available unoccupied 3*d*-orbitals that can accommodate transferred negative charge and stabilize the excited state, resulting in a bathochromic shift. The 3*d*-orbitals on the sulfur atom may contribute to the first excitation energy [19]. It also increase the diene character of the thiophene ring that is responsible for the higher absorption shift. But, in this dye series, the moderate electron withdrawing CO_2Et group in the thiophene ring is responsible for the comparatively small value of absorption maxima.

Infrared Spectra of Dyes. The unsaturation is indicated by the C–H stretching vibrations, which appear at 3120-3130 and by the one appearing at 825-835 cm^{-1} due to the out-of-plane deformation vibration. The band at 700-730 cm^{-1} is an out-of-plane deformation vibration characteristic of HC=CH. The vibration bands of the skeletal C–C bond appear at 1570 and 1460 cm^{-1}. The band appearing at 1540-1600 cm^{-1} is due to the stretching vibration of C=C, which is conjugated with C=O. The strong bands observed at 1700-1710 cm^{-1} indicate the stretching vibration of the C=O of cyclic maleimide ring. The bands at 630-660 and 570-580 cm^{-1} can be attributed to the in-plane and out-of-plane deformation vibrations of the C=O. The bands at 820-830 cm^{-1} corresponding to a *para*-disubstituted ring, 1370 and 1350 cm^{-1}, are due to the stretching vibration of –C–N–C, the first being asymmetrical and the second symmetrical. The azo and carbethoxy groups are confirmed at 1580-1595 and 1650-1660 cm^{-1} respectively.

TABLE 2. Color Fastness of Dyeing **3a-h** on Nylon Fabric

Dye	Color hue on nylon	Light fastness	Wash fastness	Rubbing fastness		Perspiration fastness		Sublimation fastness
				Dry	Wet	Acid	Alkaline	
3a	Reddish pink	2-3	5	5	5	5	5	5
3b	Light yellow	2-3	5	5	5	5	5	5
3c	Yellow	2-3	5	5	5	5	5	5
3d	Reddish pink	2-3	5	5	5	5	5	5
3e	Yellow	2-3	5	5	5	5	5	5
3f	Reddish pink	2-3	5	5	5	5	5	5
3g	Reddish pink	2-3	5	5	5	5	5	5
3h	Yellow	2-3	5	5	5	5	5	5

Dyeing Properties of Dyes. The disperse dyes **3a-h** were applied at 2% depth on nylon fabric. Their dyeing properties are given in Table 2. These dyes gave light yellow to reddish pink hues with good levelness, brightness, and depth on the fabric. The variation in the hues of the dyed fabric results from both the nature and position of the substituent present on the aryl ring.

The dyeings showed poor fastness to light but excellent fastness to washing, rubbing, perspiration, and sublimation. A remarkable degree of levelness after washing indicates good penetration and affinity of these dyes to the fabric.

Conclusion. A series of tetrahydrobenzo[*b*]thiophene azo disperse dyes containing various N-arylmaleimide coupling moiety have been synthesized by conventional methods and their color properties examined in solution and applied to nylon fabric. This diazo component possesses structural advantages over the conventional substituted aniline diazo components because of the small molecular size, the intrinsic properties of the thiophene ring, the electron-withdrawing character of an appropriately substituted carbethoxy group, and the hydrophobic nature of the tetrahydrobenzo structure which is useful for better dispersability and dyeability.

Color fastness of dyeing **3a-h** on nylon fabric: **3a**,**d**,**f**,**g** – reddish pink, **3b** – light yellow, **3c**,**e**,**h** – yellow; fastness: light – **2-3**, wash – **5**, rubbing gry – **5**, ribbing wet – **5**, perspiration acid – **5**, perspiration alkaline – **5**, sublimation – **5**.

EXPERIMENTAL

Melting points were determined by the open capillary method. The visible absorption spectra were measured on a Carl Zeiss UV/Vis Specord spectrometer. Elemental analysis was carried out on a Carlo Erba Elemental Analyser 1108. IR absorption spectra were recorded in a KBr pellets on Perkin-Elmer model 983 spectrophotometer.

All the chemicals used in the synthesis of dye **1** were of commercial grade. They were further purified by standard methods [20].

Compound 1. The title compound **1** was prepared by the method reported in the literature [3].

N-Arylmaleimides 2a-h were prepared by the method reported in the literature [21].

Preparation of Ethyl 2-(N-Phenylmaleimide)azo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylate (3a). Synthesis of **3a** involves two steps.

(i) Diazotization of **1**.

Dry $NaNO_2$ (1.38 g, 0.02 mol) was slowly added to concentrated H_2SO_4 (1 g, 0.02 mol) with stirring, allowing the temperature to rise to 65°C. The solution was then cooled to 5°C and 20 ml of a mixture of 17 ml of AcOH and 3 ml of propionic acid was added dropwise with stirring, allowing the temperature to rise to 15°C.

The reaction mixture was then cooled to 0-5°C, compound **1** (4.5 g, 0.02 mol) was added portionwise, and stirring was continued at this temperature for 2 h. The excess nitrous acid (its presence tested by 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 (see Scheme 1).

(ii) Coupling with N-phenylmaleimide (**2a**).

Compound **2a** (3.46 g, 0.02 mol) was dissolved in AcOH (10 ml), then cooled in an ice-bath at 0°C. The diazonium solution previously prepared was added dropwise over 1 h with vigorous stirring. The mixture was stirred for a further 2 h at 0-5°C, then 10% NaOAc solution was added slowly dropwise until the pH became 4-5. The product was then filtered off, washed with warm water and with cold water until acid-free, and dried at 50°C in an oven to give azo dye **1a**. It was recrystallized from DMF. All other dyes (**3b-h)** were prepared in a similar manner. The characterization data are given in Table 1.

Dyeing of Nylon Fabric. Dyeing of nylon fabric was carried out with the procedure reported earlier [20].

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 tested in accordance with IS: 765-1979. The details of the various fastness tests are reported in the literature [20].

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