Synthesis and Application of 5-Arylazothiophene Derivatives

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Synopsis. Synthesis of 5-(hetoarylazo or arylazo)thiophene derivatives (**6a**—**g**) was achieved by diazotization of ethyl 5-amino-2,4-bis(ethoxycarbonyl)-3-thiopheneacetate (**3**) using nitrosyl hydrogensulfate, coupling with suitable heterocyclic hydroxy and *N,N*-dialkyl-substituted arylamines which resulted in thiophene azo dyes. The key intermediate **3**, used as the diazonium component, was synthesized in one pot and in excellent yield from diethyl 3-oxopentanedioate, sulfur and ethyl cyanoacetate following the Gewald Synthesis. The dyes when applied as disperse dyes on polyester fibres gave excellent results.

Several patents[1—6] describe the synthesis and technical importance of azo thiophene disperse dyes. We have recently reported the synthesis of novel heterocyclic dyes and fluorescent brighteners such as benzo[*b*]thiophenes,[7] thiophenes,[8] 1,2,3-triazoles,[9] pyrimidines,[10] quinoxalines,[11] thiazoles,[12] and their application on synthetic fibres, which gave encouraging results. Thiophene moiety has been extensively studied in the field of medicine[13] and fungicides.[14]

In the present study, we report the synthesis of model compounds of azo dyes derived from novel diazonium component, 5-aminothiophene derivative synthesized by the Gewald Synthesis[15] and their use as disperse dyes for polyester fibres. Azo disperse dyes derived from thiophene have many advantages, such as color deepening effect as an intrinsic property of thiophene ring, small molecular structure leading to better dyeability and heterocyclic structure of thiophene ring resulting in good sublimation fastness of dyed fibres.

Ethyl 5-amino-2,4-bis(ethoxycarbonyl)-3-thiopheneacetate (**3**) is a versatile intermediate in the synthesis of heterocyclic systems. The principle advantages of the key intermediate used here are that the yields are high, time of the 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 diazotizable amino group adjacent to electron-withdrawing groups results in deepening of the dye hues on the polyester fibres.

Results and Discussion

The thiophene intermediate, ethyl 5-amino-2,4-bis(ethoxycarbonyl)-3-thiopheneacetate (**3**), was synthesized from diethyl 3-oxopentanedioate (**1**), sulfur, and ethyl cyanoacetate (**2**) with diethylamine as a catalyst, using the Gewald Synthesis. Compound **3** was diazotized using nitrosyl hydrogensulfate in the cold and coupled with a variety of heterocyclic hydroxy couplers such as 3-methyl-1-phenyl-1*H*-pyrazol-5-ol (**5a**), 3-cyano-4-methylpyridine-2,6-diol (**5b**), 4-hydroxy-1-methylquinolin-2(1*H*)-one (**5c**), 2,4,6-pyrimidinetriol (barbituric acid) (**5d**), and *N,N*-dialkyl-substituted arylamines such as *N,N*-dimethylaniline (**5e**), *N,N*-bis(2-cyanoethyl)aniline (**5f**), 3-chloro-*N,N*-bis(2-hydroxyethyl)aniline (**5g**) to yield ethyl 5-(hetoarylazo or arylazo)-2,4-bis(ethoxycarbonyl)-3-thiopheneacetate (**6a**—**g**).

The absorption maxima of these dyes recorded in their DMF solution are shown in Table 1. Their absorption maxima were in the range of 472—588 nm. The absorption maxima of the dyes **6a**—**d** derived from heterocyclic hydroxy-coupling components, were in the range of 472—502 nm, whereas dyes **6e**—**g**, derived from *N,N*-dialkylsubstituted arylamines, showed absorption maxima in the range of 576—588 nm.

Dyes **6a**—**g** were applied on polyester fibres as 1% shade. The hues of the polyester dyed fibres were golden yellow, orange, red, pink, violet, and blue and are shown in Table 1. The pickup values of the dyed polyester fibres varied from two to three, with most of them having a pickup value of three. The light fastness of these dyes varied from three to six, thus the dye **6d** had poor light fastness (three), dyes **6e**, **6g** had fair

Table 1. Absorption Spectra and Dyeing Properties of 5-Arylazothiophene Derivatives

Dye	Color on dyed polyester fibres	Absorption maxima nm	log ε	Pick-up	Light fastness	Sublimation fastness
6a	Brilliant golden yellow	472	4.34	3	6	5
6b	Brilliant orange	484	4.39	3	5	4
6c	Brilliant red	498	4.28	3	5	4
6d	Pink	502	4.19	2	3	3
6e	Blue	588	4.64	2	4	4
6f	Blue	582	4.61	3	5	5
6g	Violet	576	4.57	3	4	4

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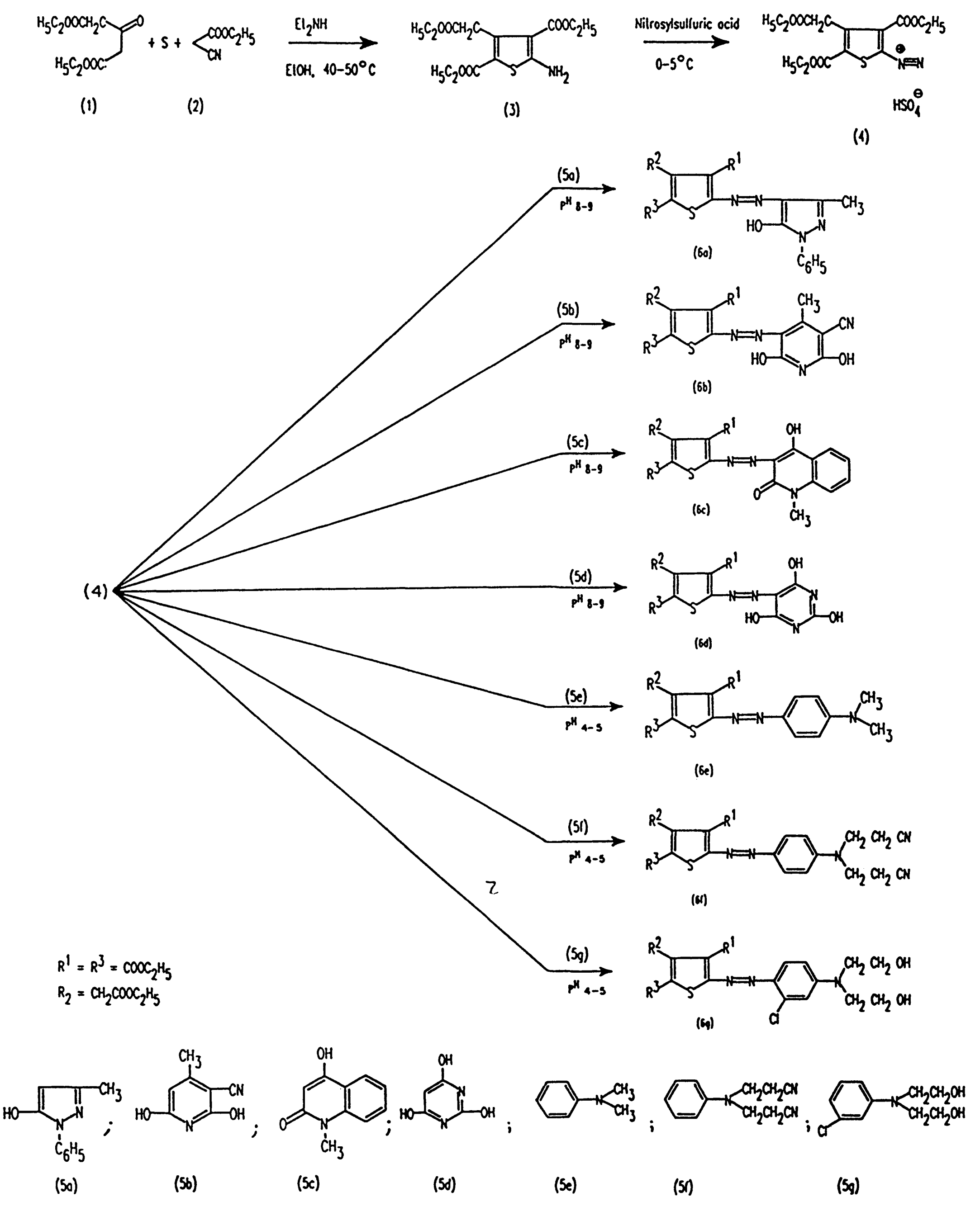

light fastness (four), dyes **6b**, **6c**, **6f** had good light fastness (five) and dye **6a** had very good light fastness (six). The sublimation fastness of these dyes was in the range of three to five, thus the dye **6d** showed good sublimation fastness (three), dyes **6b**, **6c**, **6e**, **6g** showed very good sublimation fastness (four), dyes **6a**, **6f** showed excellent sublimation fastness (five). Dyes **6a**—**c**, **6f**, and **6g** among these dyes thus showed good fastness properties on polyester fibres.

Experimental

All melting points are uncorrected. The IR spectra were recorded on a Perkin-Elmer Model 397 spectrophotometer in Nujol mull. The ^{1}H NMR spectra were recorded on a Varian-60 MHz instrument EM-360L using TMS as internal standard and the chemical shifts are given in ppm. Mass spectra were recorded on a Varian Mat-311 instrument (70 eV). Absorption spectra in DMF solution were recorded on a Beckman Model-25 spectrophotometer.

Ethyl 5-Amino-2,4-bis(ethoxycarbonyl)-3-thiopheneacetate (3). In a 100 ml round bottomed flask, were placed a mixture of diethyl 3-oxopentanedioate (**1**) (20.2 ml, 0.1 mol), sulfur (3.2 g, 0.1 mol), ethyl cyanoacetate (**2**) (11.3 ml, 0.1 mol), ethanol (20 ml), and diethylamine (10 ml). The reaction mixture was stirred on a waterbath for 2 h at 40—50 °C. At the end of the reaction, a reddish brown solid was separated. After cooling to room temperature, the reaction mixture was filtered, washed with cold ethanol and dried. The product was recrystallized from ethanol as shiny white needles. Yield: 87%, mp 179 °C. Anal. Calcd for $C_{14}H_{19}NO_6S$: C, 51.06; H, 5.77; N, 4.25; S, 9.72%. Found: C, 51.11; H, 5.57; N, 4.27; S, 9.74%. IR (Nujol mull) 3330, 3430 (NH_2), 1675 (COOEt), 1720 (CH_2COOEt) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ=1.34 (t, 9H, $3CH_3$), 3.5—4.8 (m, 8H, $4\text{-}CH_2$)), 5.5—6.1 (s, 2H, NH_2).

MS m/z 329.

Ethyl 5-[(5-Hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)azo]-2,4-bis(ethoxycarbonyl)-3-thiopheneacetate (6a). Ethyl 5-amino-2,4-bis(ethoxycarbonyl)-3-thiopheneacetate (**3**) (1.64 g, 0.005 mol) was added in portions during 1 h to a cooled mixture of nitrosyl hydrogensulfate prepared from sodium nitrite (0.38 g, 0.0055 mol) and concentrated sulfuric acid (10 ml) at 0 °C. The mixture was stirred for an additional 1 h at 0 °C, then added to an ice-water mixture under stirring, excess of nitrous acid was destroyed by the addition of urea (1 g) and the solution was filtered to obtain a clear diazonium salt solution **4**. 3-Methyl-1-phenyl-1*H*-pyrazol-5-ol (**5a**) (0.87 g, 0.005 mol) was dissolved in dilute sodium hydroxide. The solution was cooled by external cooling so that the temperature was at 0—5 °C. To this cooled solution, the prepared diazonium salt **4** was added slowly so that the temperature did not rise above 5 °C. The pH of the reaction mixture was maintained alkaline throughout the coupling period (1 h) by the addition of solid sodium carbonate in portions. After the addition of the diazonium salt was completed, the reaction mixture was stirred for 4 h at 0 °C, when the dye which partially separated was neutralized with dilute hydrochloric acid (5%), filtered, thoroughly washed with water and dried. The product was recrystallized from methanol. Yield: 89%, mp 246 °C. Anal. Calcd for $C_{24}H_{26}N_4O_7S$: C, 56.03; H, 5.05; N, 10.89; S, 6.22%. Found: C, 56.08; H, 5.11; N, 10.82; S, 6.19%. IR (Nujol mull) 3200—3400 (OH), 1680—1700 (COOEt) cm^{-1}.

Ethyl 5-[(2,6-Dihydroxy-5-cyano-4-methyl-3-pyridyl)azo]-2,4-bis(ethoxycarbonyl)-3-thiopheneacetate (6b). the dye was synthesized in the same manner as given for dye **6a**, except that instead of **5a**, 3-cyano-4-methylpyridine-2,6-diol (**5b**) (0.75 g, 0.005 mol) was used. The product was recrystallized from methanol. Yield: 92%, mp 230 °C. Anal. Calcd for $C_{21}H_{22}N_4O_8S$: C, 51.42; H, 4.48; N, 11.42; S, 6.53%. Found: C, 51.39; H, 4.51; N, 11.46; S, 6.58%. IR (Nujol mull) 3380—3440 (OH), 1660—1700 (COOEt), 2210 (CN) cm^{-1}.

Ethyl 5-[(4-Hydroxy-1-methyl-2-oxo-1,2-dihydro-3-quinolyl)azo-2,4-bis(ethoxycarbonyl)-3-thiopheneacetate (6c). The dye was synthesized in the same manner as given for dye **6a** except instead of **5a**, 4-hydroxyl-1-methylquinolin-2(1*H*)-one (**5c**) (0.87 g, 0.005 mol) was used. The product was recrystallized from chloroform. Yield: 81%, mp 144 °C. Calcd for $C_{24}H_{25}N_3O_8S$: C, 55.92; H, 4.85; N, 8.15; S, 6.21%. Found: C, 55.93; H, 4.87; N, 8.18; S, 6.23%. IR (Nujol mull) 3310—3400 (OH), 1675—1720 (COOEt), 1680 (CO) cm^{-1}.

Ethyl 5-[(2,4,6-Trihydroxy-5-pyrimidinyl)azo]-2,4-bis(ethoxycarbonyl)-3-thiopheneacetate (6d). The dye was synthesized in the same manner as given for dye **6a**, except instead of **5a**, 2,4,6-pyrimidinetriol (barbituric acid) (**5d**) (0.64 g, 0.005 mol) was used. The product was recrystallized from ethanol. Yield: 74%, mp 152 °C. Anal. Calcd for $C_{18}H_{20}N_4O_9S$: C, 46.15; H, 4.27; N, 11.96; S, 6.83%. Found: C, 46.08; H, 4.22; N, 11.93; S, 6.81%. IR (Nujol mull) 3200—3400 (OH), 1680—1700 (COOEt) cm^{-1}.

Ethyl 5-[4-(Dimethylamino)phenylazo]-2,4-bis(ethoxycarbonyl)-3-thiopheneacetate (6e). Ethyl 5-amino-2,4-bis(ethoxycarbonyl)-3-thiopheneacetate (**3**) (1.64 g, 0.005 mol) was added in portions during 1 h to a cooled mixture of nitrosyl hydrogensulfate prepared from sodium nitrite (0.38 g, 0.0055 mol) and concentrated sulfuric acid (10 ml) at 0 °C. The mixture was stirred for an additional 1 h at 0 °C, then added to an ice-water mixture under stirring, excess of nitrous acid was destroyed by the addition of urea (1 g) and the solution was filtered to obtain a clear diazonium salt solution **4**. *N,N*-Dimethylaniline (**5e**) (0.60 g, 0.005 mol) was dissolved in acetic acid. The solution was cooled by external cooling so that the temperature was 0—5 °C. To this cooled solution, the prepared diazonium salt **4** was added slowly so that the temperature did not rise above 5 °C. The pH of the reaction mixture was maintained acidic throughout the coupling period (1 h). After the addition of the diazonium salt was completed, the reaction mixture was stirred for 4 h, when the dye which partially separated was neutrallized with sodium carbonate, filtered, thoroughly washed with water and dried. The product was recrystallized from ethyl acetate. Yield: 76%, mp 296 °C. Anal. Calcd for $C_{22}H_{27}N_3O_6S$: C, 57.26; H, 5.85; N, 9.11; S, 6.94%. Found: C, 57.29; H, 5.88; N, 9.16; S, 6.92%. IR (Nujol mull) 1680—1710 (COOEt) cm^{-1}.

Ethyl 5-[4-[Bis(2-cyanoethyl)amino]phenylazo]-2,4-bis(ethoxycarbonyl)-3-thiopheneacetate (6f). The dye was synthesized in the same manner as given for the dye **6e** except that instead of **5e**, *N,N*-bis(2-cyanoethyl)aniline (**5f**) (0.99 g, 0.005 mol) was used. The product was recrystallized from DMF. Yield: 68%, mp 324 °C. Anal. Calcd for $C_{26}H_{29}N_5O_6S$: C, 57.88; H, 5.38; N, 12.98; S, 5.93%. Found: C, 57.81; H, 5.34; H, 12.92; S, 5.96%. IR (Nujol mull): 1660—1680 (COOEt), 2220 (CN) cm^{-1}.

Ethyl 5-[2-Chloro-4-[bis(2-hydroxyethyl)amino]phenylazo]-2,4-bis(ethoxycarbonyl)-3-thiopheneacetate (6g). The dye was synthesized in the same manner as given for the dye **6e**, except that instead of **5e**, 3-chloro-*N,N*-bis(2-hydroxyethyl)aniline (**5g**) (1.07 g, 0.005 mol) was used. The product was recrystallized from DMF. Yield: 62%, mp >360 °C. Anal. $C_{24}H_{30}ClN_3O_8S$: C, 51.89; H, 5.40; Cl, 6.30; N, 7.56; S, 5.76%. Found: C, 51.81; H, 5.42; Cl, 6.27; N, 7.59; S, 5.72%. IR (Nujol mull) 3320—3400 (OH), 1680—1700 (COOEt) cm^{-1}.

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