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Novel azo disperse dyes derived from aminothiophenes: Synthesis and UV–visible studies

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Abstract

A number of red to violet thienyl-2-azo and thienyl-5-azo disperse dyes were prepared using Gewald's methodology. Structural characterization of these novel dyes was carried out using IR, NMR and mass spectroscopy. UV–visible studies of these azo dyes in a number of polar solvents showed a considerable difference in the λ_{max}. The introduction of various substituents to these azo dyes as well as the polarity of solvents resulted in absorption in the visible region ranging from 461 to 555 nm.

Keywords: Aminothiophenes; Thienyl-2-azo dyes; Thienyl-5-azo dyes; Absorption spectra

1. Introduction

Interest in the design of azo dyes containing heterocyclic moieties stems from their high degree of brightness compared to azo dyes derived from anilines [1–11]. The 2-aminothiophene based azo dyes are known as disperse dyes with excellent brightness of shade. This class of dyes was established as an alternative to more expensive anthraquinone dyes [12,13]. The thiophene-containing azo dyes have many advantages including a colour deepening effect as an intrinsic property of the thiophene ring and small molecular structure leading to better dyeability. The heterocyclic nature of the thiophene ring has also allowed for excellent sublimation fastness on the dyed fibers [14,15]. Increasing the electron-withdrawing strength of the substituents on the thiophene ring resulted in bathochromic shifts [16]. Additionally, the sulfur atom plays a decisive role by acting as an efficient electron sink as explained by valence band theory [17].

A one-pot procedure by Gewald [18,19] created an efficient route to the synthesis of thiophenes based heterocyclic dyes. A number of researchers studied aminothiophene derivatives as azo disperse dyes in the dyeing of synthetic fibers [20–28], blended polyester/wool fibers [29,30], and more recently in optical data storage devices [31]. This class of compounds also showed semiconducting properties [32].

Our recent research program has been focused on the incorporation of aryl and hetaryl azo dyes in or pendent to the backbone of polynorbornenes, polyether and polythioethers [33–35]. In light of the interesting *cis–trans* photoisomerization behaviour, these materials may have potential optical applications.

In the present work, *o*-acetoacetotoluidide, *o*-acetoacetanisidide, 4′-chloro-acetoacetanilide, and *N*-(2,4-dimethylphenyl)-3-oxobutyramide as 1,3-dicarbonyl derivatives were applied using Gewald's reaction for the synthesis of 2- and 5-aminothiophenes. The resulting aminothiophenes were diazotized and coupled with phenol or naphthol derivatives and/or amine couplers affording a variety of azo dyes based on thiophene moieties. Using the same strategy, the synthesis of aminothiophenes can be further broadened by using

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di- and tri-substituted acetoacetanilide with electron-donating or electron-withdrawing groups to yield a new wider variety of aminothiophenes prepared directly by Gewald's synthesis.

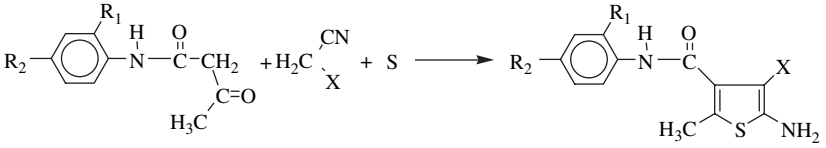
2. Results and discussion

In this study, aminothiophene intermediates **1**–**12** were prepared using Gewald's methodology through the reaction outlined in Scheme 1. This convenient methodology includes the condensation of the 1,3-dicarbonyl compounds, *o*-acetacetotoluidide, *o*-acetoacetanisidide, 4′-chloroacetoacetanilide and *N*-(2,4-dimethylphenyl)-3-oxobutyramide, with the activated nitriles such as malononitrile, ethyl- and methylcyanoacetate in the presence of sulfur in ethanol/basic media.

The aminothiophene intermediates **1**–**12** were characterized using ^{1}H and ^{13}C NMR, IR and mass spectroscopy (Tables 1 and 2). The IR spectra of aminothiophene intermediates **1**, **4**, **7** and **10** showed absorption peaks in the range 2203–2213 cm^{-1} due to the presence of cyano group. The amino group absorption for **1**–**12** appeared in the range of 3555–3262 cm^{-1} while the carbonyl absorption in the range 1630–1664 cm^{-1}. The *m*/*z* fragmentation in Table 1 showed the base peak for compound **1** at 107 ($M^+ - 164$) while compounds **2** and **3** showed base peaks at 212 and 198, respectively, ($M^+ - 106$) due to the cleavage of the amide bond. Further evidence was observed for aminothiophenes **4**–**6** where the base peaks at 165, 212 and 198 ($M^+ - 126$) corresponding to the loss of $M^+ + 2$ peak due to the presence of other isotope of the chloro susbstituents. The mass spectral data for aminothiophenes **7**–**12** are listed in Table 1 and followed the same patterns as compounds **1**–**6**.

The ^{1}H NMR spectrum of aminothiophene **1** showed two singlets at 2.23 and 2.45 ppm due to the two methyl groups, one on the phenyl ring and the other attached to C-2 of the thiophene ring. The presence of a broad singlet at 7.75 ppm was attributed to the presence of NH_2 group on the thiophene ring, while the NH group of the amide linkage is upfield shifted to 9.18 ppm, as compared to the starting *o*-acetoacetotoluidide that showed NH signal at 9.49 ppm. The formation of the thiophene intermediate **1** was evident by the disappearance of the CH_2 peak in the ^{1}H NMR of *o*-acetoacetotoluidide at 3.60 ppm. ^{13}C NMR spectrum of aminothiophene **1** showed resonance at 15.00 and 18.10 ppm for the two methyl groups while the corresponding values for the starting *o*-acetoacetotoluidide appeared at 17.81 and 30.10 ppm as well as the disappearance of the CH_2 peak at 51.63 ppm due to the formation of aminothiophene **1**. Further confirmation of aminothiophene **1** was also indicated by the presence of amide carbonyl linkage at 165.30 ppm, and the disappearance of the acetyl carbonyl of *o*-acetoacetotoluidide that had resonated at 203.07 ppm. As can be seen in Table 2, the signals of the NH groups of aminothiophenes **2**–**12** shifted upfield as compared with their corresponding values for the starting materials (δ NH = 9.49, 10.21, 9.48 and 9.41 ppm for *o*-acetoacetotoluidide, 4′-chloro-acetoacetanilide, *o*-acetoacetanisidide and *N*-(2,4-dimethylphenyl)-3-oxobutyramide, respectively). As an example, the NH group of 4′-chloroacetoacetanilide appeared at 10.21 ppm is shifted to 9.68 ppm upon the formation of aminothiophene **4**. It is also important to note that the inductive effect of the chloro substituent was the main reason for the downfield shift in the NMR values of compounds **4**–**6** from their corresponding aminothiophene derivatives **1**–**3** and **7**–**12**. This is consistent with the assignments of Silverstein et al. [36] where the shifts of the aromatic carbon atom directly attached to the substituent have been correlated with substituent electronegativity after correcting for the magnetic anisotropic effects.

A number of azo dyes were prepared by diazotizing aminothiophene intermediates using nitrosyl sulfuric



1-12

1. $R_1 = CH_3$, $R_2 = H$, X = CN
2. $R_1 = CH_3$, $R_2 = H$, X = $COOCH_2CH_3$
3. $R_1 = CH_3$, $R_2 = H$, X = $COOCH_3$
4. R_1 = H, R_2 = Cl, X = CN
5. R_1 = H, R_2 = Cl, X = $COOCH_2CH_3$
6. R_1 = H, R_2 = Cl, X = $COOCH_3$
7. $R_1 = OCH_3$, $R_2 = H$, X = CN
8. $R_1 = OCH_3$, $R_2 = H$, X = $COOCH_2CH_3$
9. $R_1 = OCH_3$, $R_2 = H$, X = $COOCH_3$
10. $R_1 = CH_3$, $R_2 = CH_3$, X = CN
11. $R_1 = CH_3$, $R_2 = CH_3$, X = $COOCH_2CH_3$
12. $R_1 = CH_3$, $R_2 = CH_3$, X = $COOCH_3$

Scheme 1.

Table 1
Characterization of aminothiophene intermediates

Intermediates	Molecular formula	M.Wt.	Yield (%)	Mp (°C)	Mass *m/z* (%)	IR ν_{max}(cm^{-1}, KBr)
1	$C_{14}H_{13}N_3OS$	271	72	235–237	271 (M^+, 19), 165 (49), 107 (100)	3364, 3323, 3217 (NH), 2203 (CN), 1638 (CO)
2	$C_{16}H_{18}N_2O_3S$	318	70	128–130	318 (M^+, 24), 212 (100)	3396, 3262, 3153 (NH), 1645, 1630 (CO)
3	$C_{15}H_{16}N_2O_3S$	304	69	127–129	304 (M^+, 22), 198 (100)	3396, 3266, 3152 (NH), 1645, 1632 (CO)
4	$C_{13}H_{10}ClN_3OS$	291	73	233[a]	291 (M^+, 24), 293 ($M^+ + 2$, 9), 165 (100)	3378, 3311, 3195 (NH), 2204 (CN), 1638 (CO)
5	$C_{15}H_{15}ClN_2O_3S$	338	74	170	338 (M^+, 15), 340 ($M^+ + 2$, 6), 212 (100)	3481, 3341, 3305 (NH), 1663, 1620 (CO)
6	$C_{14}H_{13}ClN_2O_3S$	324	70	165–167	324 (M^+, 16), 326 ($M^+ + 2$, 5), 198 (100)	3475, 3337, 3303 (NH), 1664, 1620 (CO)
7	$C_{14}H_{13}N_3O_2S$	287	75	212	287 (M^+, 29), 165 (35), 123 (100)	3432, 3360, 3202 (NH), 2213 (CN), 1632 (CO)
8	$C_{16}H_{18}N_2O_4S$	334	71	154–156	334 (M^+, 29), 212 (100), 166 (74)	3396, 3293, 3299 (NH), 1645, 1626 (CO)
9	$C_{15}H_{16}N_2O_4S$	320	68	139–141	320 (M^+, 32), 198 (100)	3439, 3408, 3290 (NH), 1647, 1632 (CO)
10	$C_{15}H_{15}N_3OS$	285	69	234–236	285 (M^+, 22), 165 (35), 121 (100)	3378, 3323, 3214 (NH), 2204 (CN), 1632 (CO)
11	$C_{17}H_{20}N_2O_3S$	332	71	126–128	332 (M^+, 29), 212 (100), 166 (46)	3553, 3427, 3273 (NH), 1661, 1589 (CO)
12	$C_{16}H_{18}N_2O_3S$	318	65	141	318 (M^+, 27), 198 (100)	3555, 3427, 3271 (NH), 1662, 1588 (CO)

[a] Literature value: 226 °C.

acid and coupling with resorcinol (**a**), 2,3-dihydroxynaphthalene (**b**) and/or amine couplers such as: 2-(*N*-methylanilino)ethanol (**c**); 2-(*N*-ethylanilino)ethanol (**d**) and 3-[(2-hydroxyethyl)phenyl-amino]propionitrile (**e**), as shown in Scheme 2.

The IR spectra of the prepared azo dyes showed the characteristic absorption peaks due to stretching frequency of the OH group in the region 3245–3515 cm^{-1} and the stretching frequency of the NH group in the region of 3270–3314 cm^{-1}. An overlap between NH and OH stretching frequencies for the azo dyes **1d**, **5a**, **10c**, **10d**, **10e**, **11a** and **11b**, was also observed as indicated in Table 3. An absorption peak in the region 2222–2228 cm^{-1} due to ν_{CN} was observed for the azo dyes **1d**, **4a**, **4c**, **4d**, **4e**, **10a**, **10c**, **10d** and **10e**, while the aliphatic nitrile appeared in the region 2247–2248 cm^{-1} for the dyes **4e**, **5e**, **10e** and **11e**, indicative to the presence of the terminal $-CH_2CH_2CN$ of the coupling component. The IR spectra of the prepared azo dyes also showed an absorption peak in the region 1445–1521 cm^{-1}, attributed to $\nu_{N=N}$, while the observed peak in the region 1622–1736 cm^{-1} was due to the $\nu_{C=O}$, as outlined in Table 3.

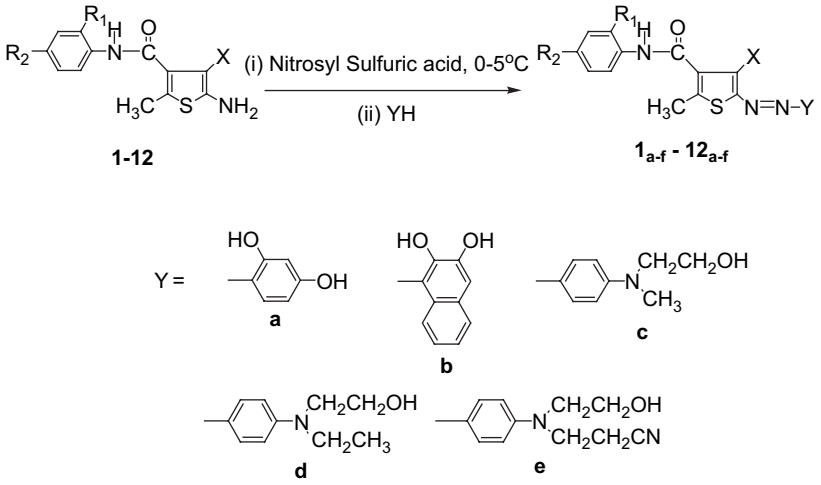
The mass fragmentation for the prepared azo dyes in Table 3 showed the cleavage of the C–C next to the oxygen atom for azo dyes **1d**, **2d**, **4c**, **4d**, **4e**, **5c**, **5e**, **10c**, **10d** and **10e**, where the coupling components are of the amine type. Thus, a peak due to loss of CH_2OH is of general occurrence, which agrees with that previously reported by Chao et al. [37].

The ^1H and ^{13}C NMR data for the prepared azo dyes are given in Table 4. In comparison between the ^1H NMR spectra of the azo dyes and their starting aminothiophene intermediates, it was observed that the NH peaks of azo dyes were shifted downfield relative to their values for aminothiophenes **1**, **2**, **4**, **5**, **10** and **11**. For example, the NH peak for azo dye **1d** appeared at 9.80 ppm while that of aminothiophene **1** was observed at 9.07 ppm. The NH peaks detected at 10.43, 10.35, 10.36 and 10.49 ppm for azo dyes **4a**, **4c**, **4d** and **4e**, respectively, while the NH peak of the starting aminothiophene **4** appeared at 9.68 ppm. It was also observed that most of the methyl groups resonated at downfield values as compared with their starting aminothiophene intermediates. As well, all the aromatic protons for the azo dyes showed downfield values, and in some cases one set of the doublets arising from the coupling site overlapped with the aromatic protons of the diazonium site, as can be seen in the azo dyes **2d**, **4a**, **4c**, **4d**, **5e**, **10e** and **11e**.

The ^{13}C NMR data for the azo dyes as outlined in Table 4 showed the C–CN peak downfield shifted in the region 108.42–109.90 ppm as compared with their starting aminothiophenes **1**, **4**, **7** and **10**, where it resonated in the region 88.13–88.59 ppm. The observed chemical shifts for C–CN are similar to those reported

Table 2
NMR data of aminothiophene intermediates

Intermediates	^{1}H NMR in (DMSO-d_6), δ (ppm)	^{13}C NMR in (DMSO-d_6), δ (ppm)
1	2.23 (3H, s, CH_3); 2.45 (3H, s, CH_3); 7.19−7.44 (4H, m, ArCH); 7.75 (2H, br s, NH_2); 9.07 (1H, s, NH)	15.00, 18.10 (CH_3); 115.61 (CN); 125.73, 125.86, 126.05, 130.34 (ArCH); 133.07, 136.53 (Ar−C); 88.28, 113.36, 140.23,160.60 (Ar−C thiophene); 165.30 (CO amide)
2	1.28 (3H, t, CH_3); 2.21 (3H, s, CH_3); 2.57 (3H, s, CH_3); 4.23 (2H, q, CH_2); 7.40−7.09 (4H, m, ArCH); 7.75 (2H, br s, NH_2); 9.13 (1H, s, NH)	14.27, 16.43, 18.06 (CH_3); 59.27 (CH_2); 125.45, 125.61, 125.93, 130.23 (ArCH); 132.82, 136.69 (Ar−C); 105.59, 112.83, 140.41, 161.40 (Ar−C thiophene); 165.01 (CO ester); 165.12 (CO amide)
3	2.19 (3H, s, CH_3); 2.55 (3H, s, CH_3); 3.74 (3H, s, CH_3); 7.09−7.38 (4H, m, ArCH); 7.73 (2H, br s, NH_2); 9.12 (1H, s, NH)	16.49, 18.12, 50.69 (CH_3); 125.51, 125.66, 125.98, 130.29 (ArCH); 132.88, 136.75 (Ar−C); 105.73, 112.95, 140.52, 161.53 (Ar−C thiophene); 165.13 (CO ester); 165.25 (CO amide)
4	2.31 (3H, s, CH_3); 7.33 (2H, d, $J = 8.2$ Hz, ArCH), 7.64 (2H, d, $J = 8.6$ Hz, ArCH); 7.77 (2H, br s, NH_2); 9.68 (1H, s, NH)	14.98 (CH_3); 115.43 (CN); 121.89, 128.43 (ArCH); 127.17, 137.91 (Ar−C); 88.19, 112.67, 141.01, 160.51 (Ar−C thiophene); 165.30 (CO amide)
5	1.27 (3H, t, CH_3); 3.43 (3H, s, CH_3); 4.22 (2H, q,CH_2); 7.34 (2H, d, $J = 9.0$, ArCH); 7.64 (2H, d, $J = 8.7$, ArCH); 7.76 (2H, br s, NH_2); 9.80 (1H, s, NH)	14.26, 16.54 (CH_3); 59.31 (CH_2); 121.57, 128.42 (ArCH); 126.91, 138.11 (Ar−C); 105.55, 112.48, 140.90, 161.46 (Ar−C thiophene); 164.94 (CO ester); 165.28 (CO amide)
6	2.40 (3H, s, CH_3); 3.65 (3H, s, CH_3); 7.24 (2H, d, $J = 8.6$, ArCH); 7.55 (2H, d, $J = 8.2$, ArCH); 7.67 (2H, br s, NH_2); 9.70 (1H, s, NH)	16.53, 50.67 (CH_3); 121.51, 128.38 (ArCH); 126.96, 138.09 (Ar−C); 105.60, 112.58, 140.94, 161.48 (Ar−C thiophene); 164.84 (CO ester); 165.22 (CO amide)
7	2.42 (3H, s, CH_3); 3.83 (3H, s, OCH_3); 6.86−7.07 (3H, m, ArCH); 7.98 (1H, d, $J = 7.8$, CH); 7.78 (2H, br s, NH_2); 8.46 (1H, s, NH)	14.79 (CH_3); 55.95 (OCH_3); 115.41 (CN); 110.97, 120.43, 121.13, 124.41 (ArCH); 127.27, 139.53 (Ar−C); 88.59, 113.96, 149.38, 159.70 (Ar−C thiophene); 165.56 (CO amide)
8	1.28 (3H, t, CH_3); 2.59 (3H, s, CH_3); 3.84 (3H, s, OCH_3); 4.22 (2H, q, CH_2); 6.92 (1H, t, ArCH); 7.04 (2H, br m, ArCH); 7.99 (1H, d, $J = 7.4$, ArCH); 7.80 (2H, br s, NH_2); 8.50 (1H, s, NH)	14.22, 15.95(CH_3); 55.89 (OCH_3); 59.36 (CH_2); 110.91, 120.37, 120.99, 124.19 (ArCH); 127.43, 149.27 (Ar−C); 105.91, 113.14, 140.45, 160.58 (Ar−C thiophene); 164.91 (CO ester); 165.38 (CO amide)
9	2.59 (3H, s, CH_3); 3.73 (3H, s, CH_3); 3.83 (3H, s, OCH_3); 6.91 (1H, t, ArCH); 7.02 (2H, br m, ArCH); 8.01 (1H, d, $J = 7.6$, ArCH); 7.81 (2H, br s, NH_2); 8.47 (1H, s, NH)	14.23, 50.68 (CH_3); 55.90 (OCH_3); 110.90, 120.37, 120.99, 124.20 (ArCH); 127.43, 149.27 (Ar−C); 105.92, 113.14, 140.46, 160.59 (Ar−C thiophene); 164.92 (CO ester); 165.39 (CO amide)
10	2.14 (3H, s, CH_3); 2.25 (3H, s, CH_3); 2.38 (3H, s, CH_3); 6.94 (1H, s, ArCH); 7.01 (1H, d, $J = 7.8$, ArCH); 7.20 (1H, d, $J = 7.8$, ArCH); 7.68 (2H, br s, NH_2); 8.96 (1H, s, NH)	14.92, 17.98, 20.54 (CH_3); 115.58 (CN); 125.89, 126.51, 130.83 (ArCH); 132.95, 133.88, 134.84 (Ar−C); 88.13, 113.42, 139.93, 160.58 (Ar−C thiophene); 165.93 (CO amide)
11	1.27 (3H, t, CH_3); 2.14 (3H, s, CH_3); 2.24 (3H, s, CH_3); 2.53 (3H, s, CH_3); 4.21 (2H, q, CH_2); 6.95 (1H, d, $J = 8.2$, ArCH); 7.01 (1H, s, ArCH); 7.21 (1H, d, $J = 8.2$, ArCH); 7.70 (2H, br s, NH_2); 9.04 (1H, s, NH)	14.28, 16.42, 18.06, 20.56 (CH_3); 59.30 (CH_2); 125.72, 126.45, 130.79(ArCH); 132.81, 134.82, 136.68 (Ar−C); 105.58, 112.85, 140.40, 161.45 (Ar−C thiophene); 164.98 (CO ester); 165.11 (CO amide)
12	2.15 (3H, s, CH_3); 2.24 (3H, s, CH_3); 2.53 (3H, s, CH_3); 3.73 (3H, s, CH_3); 6.95 (1H, d, $J = 8.2$, ArCH); 7.02 (1H, s, ArCH); 7.21 (1H, d, $J = 7.8$, ArCH); 7.71 (2H, br s, NH_2); 9.06 (1H, s, NH)	14.30, 18.01, 20.51, 50.53 (CH_3); 125.72, 126.45, 130.79(ArCH); 132.78, 134.08, 134.60 (Ar−C); 105.55, 112.96, 140.21, 161.46 (Ar−C thiophene); 164.97 (CO ester); 165.10 (CO amide)



Scheme 2.

previously by Gewald [38] and Hallas [23]. Similarly, the C–COOR signals for the azo dyes were downfield shifted and appeared in the region 127.60–130.11 ppm in comparison to their values in the ^{13}C spectra of the aminothiophenes **2**, **5**, **8** and **11**, where the C–COO signals appeared in the region 105.55–105.91 ppm. On the other hand, the cyano group resonated upfield and appeared at 114.03, 113.55, 113.92, 114.04, and 113.76 ppm for the azo dyes **1d**, **4a**, **4c**, **4d** and **4e**, respectively, while the values for aminothiophenes **1** and **4** were 115.61 and 115.43 ppm, respectively.

2.1. Absorption spectra

Absorption spectra of the azo dyes derived from aminothiophene derivatives were recorded in various solvents and the results are summarized in Table 5. The colour of these azo dyes depends on the nature of both the diazo and the coupling components.

The electronic spectra of these dyes showed an absorption band in the region 469–540 nm in ethanol, 466–546 nm in acetone, 494–555 nm in dimethyl formamide (DMF), 464–546 nm in dichloromethane (DCM), and 461–546 nm in acetonitrile. This band was due to electronic transitions involving the whole conjugate system (both of the phenyl and five-membered sulfur heterocycles and the azo groups are assigned to a transition of $\pi-\pi*$ type).

The introduction of the cyano group as an electron-withdrawing subsituent onto the thiophene ring produces a bathochromic shift of the absorption band, while the replacement of the cyano group by an ethyl ester group exerts a notable hypsochromic shift. This was observed for the azo dye **1d** where the introduction of the cyano group as an electron-acceptor results in a bathochromic shift of 29–31 nm, as compared with the ethyl ester group in the diazo component of azo dye **2d**. This is attributed to more extensive electron delocalization and the smaller steric requirements of the rod-like cyano group [39].

Bathochromic shifts of the visible absorption band were also observed on increasing the solvent polarity as seen in Table 5, where a difference of 7–66 nm in λ_{max} was noticed upon measuring the azo dyes in ethanol and DMF. This is expected for a system in which the excited state is more polar than the ground state [40,41].

The data in Table 5 reveal that the change in the λ_{max} value depends on the nature of the coupling site as well as the nature of the substituents at the terminal amino group. Bathochromic shifts were observed on replacing resorcinol at the coupling site with 2-(methylphenylamino-)ethanol, where a difference of 53–55 nm in λ_{max} was seen upon comparing the azo dyes pairs **4a** and **4c**, and **10a** and **10c** using the same solvent. However, hypsochromic shifts of 14–17 nm in λ_{max} values were found by replacing the CH_3 at the terminal amino group of the coupling site by CH_2CH_2CN, as can be seen for the three pairs of azo dyes **4c** and **4e**, **5c** and **5e**, and **10c** and **10e**. Inductive electron-withdrawal by the CH_2CH_2CN group leads to a reduction in the electron-releasing tendency of the terminal nitrogen atom and a consequent hypsochromic shift of the visible absorption band. This is in agreement with that previously reported by Patel et al. [42]. Meanwhile, the substituents on the phenyl ring of the diazonium site exerted a negligable change in λ_{max} on comparing azo dyes **1d**, **4d** and **10d**.

2.2. Conclusion

Thienyl-2-azo and thienyl-5-azo disperse dyes have been synthesized and their spectral properties investigated. The nature of the coupling components as well as the solvent polarity afforded a bathochromic shift with aminothiophene derivatives. The absorption maxima of the investigated azo dyes showed larger bathochromic

Table 3
Characterization of prepared azo dyes

Dye	Molecular formula	M.Wt.	Yield (%)	Mp (°C)	Appearance	Mass m/z (%)	IR ν_{max}(cm^{-1}, KBr)
1e	$C_{24}H_{25}N_5O_2S$	447	85	172	reddish violet	447 (M^+, 47); 416 (100)	3384 (br s, OH & NH), 2224 (CN), 1640 (CO), 1520 (N=N)
2e	$C_{26}H_{30}N_4O_4S$	494	65	115	reddish brown	494 (M^+, 40); 463 (100)	3428 (OH), 3270 (NH), 1714, 1647 (CO), 1449 (N=N)
4a	$C_{19}H_{13}ClN_4O_3S$	412	70	261	orange	412 (M^+, 30); 414 ($M^+ + 2$, 11); 286 (100)	3515 (OH), 3275 (NH) 2227 (CN), 1700 (CO), 1486 (N=N)
4d	$C_{22}H_{20}ClN_5O_2S$	453	65	205	violet	453 (M^+, 35); 455 ($M^+ + 2$, 12); 422 (100); 296 (75)	3443 (OH), 3309 (NH), 2222 (CN), 1650 (CO), 1520 (N=N)
4e	$C_{23}H_{22}ClN_5O_2S$	467	66	162	violet	467 (M^+, 41); 469 ($M^+ + 2$, 15); 436 (100)	3448 (OH), 3314 (NH), 2222 (CN), 1665 (CO), 1521 (N=N)
4f	$C_{24}H_{21}ClN_6O_2S$	492	70	180	brown	492 (M^+, 28); 494 ($M^+ + 2$, 14) 461 (M^+, 46); 366 (M^+, 15) 165 (M^+, 100)	3474 (OH), 3283 (NH), 2222, 2248 (CN), 1640 (CO), 1490 (N=N)
5a	$C_{21}H_{18}ClN_3O_5S$	459	79	254	orange	459 (M^+, 29); 461 ($M^+ + 2$, 11) 333 (100); 197 (77)	3283 (br s, OH & NH), 1707, 1671 (CO), 1517 (N=N)
5d	$C_{24}H_{25}ClN_4O_4S$	500	78	125	red	500 (M^+, 25); 502 ($M^+ + 2$, 9); 469 (29); 374 (13); 212 (100)	3422 (OH), 3293 (NH), 1710, 1650 (CO), 1518 (N=N)
5f	$C_{26}H_{26}ClN_5O_4S$	539	65	138–140	red	539 (M^+, 27), 541 ($M^+ + 2$, 10), 508 (35), 413 (45), 212 (100)	3448 (OH), 3299 (NH), 2247 (CN), 1707, 1646 (CO), 1518 (N=N)
10a	$C_{21}H_{18}N_4O_3S$	406	84	245–247	reddish orange	406 (M^+, 53), 286 (68), 258 (15), 121 (100)	3445 (OH), 3292 (NH), 2228 (CN), 1622 (CO), 1488 (N=N)
10d	$C_{24}H_{25}N_5O_2S$	447	82	135	reddish brown	447 (M^+, 49), 416 (100), 327 (35), 107 (65)	3425 (br s, OH & NH), 2222 (CN), 1643 (CO), 1445 (N=N)
10e	$C_{25}H_{27}N_5O_2S$	461	79	158–160	reddish violet	461 (M^+, 56), 430 (100), 341 (25), 121 (78)	3375 (br s, OH & NH), 2223 (CN), 1640 (CO), 1518 (N=N)
10f	$C_{26}H_{26}N_6O_2S$	486	85	130	reddish violet	486 (M^+, 30), 455 (45), 366 (20), 121 (100)	3452 (br s, OH & NH), 2222, 2248 (CN), 1642 (CO), 1516 (N=N)
11a	$C_{23}H_{23}N_3O_5S$	453	86	180	orange	453 (M^+, 48), 333 (100), 197 (67), 121 (87)	3242 (br s, OH & NH), 1707, 1618 (CO), 1518 (N=N)
11c	$C_{27}H_{25}N_3O_5S$	503	82	254–255	red	503 (M^+, 44), 383 (100), 212 (28), 121 (19)	3426 (br s, OH & NH), 1711, 1643 (CO), 1493 (N=N)
11f	$C_{28}H_{31}N_5O_4S$	533	79	120	reddish violet	533 (M^+, 40), 413 (100)	3420 (OH), 3300 (NH), 2247 (CN), 1709, 1646 (CO), 1512 (N=N)

shifts in DMF than in other solvents. On changing the substituent on the phenyl ring of the diazo components, there is no significant change in λ_{max}, however, the replacement of the cyano group on the thiophene ring by ethyl ester groups exerts hypsochromic shifts of 29–31 nm in $\lambda_{max.}$

3. Experimental

3.1. Materials and instrumentation

Melting points reported were determined by open capillary method and were uncorrected. The IR analyses were performed on Bomem Grams, Hartmann & Braun (KBr pellet). The ^1H and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively, on a Gemini 200 NMR spectrometer, with chemical shifts calculated in hertz, referenced to solvent residues. Mass spectra were reported on Hewlett Packard 5989 B Mass spectrometer. The electronic spectra were recorded on Shimadzu UV-2501PC, UV–visible recording spectrophotometer. *o*-Acetoacetotoluidide, *o*-acetoacetanisidide, 4′-chloroacetoacetanilide and *N*-(2,4-dimethylphenyl)-3-oxobutyramide were purchased from Aldrich and used without further purification. All other chemicals used were of laboratory grade.

Table 4
NMR data of azo dyes

Azo dyes	^{1}H NMR in (DMSO-d_6), δ (ppm)	^{13}C NMR in (DMSO-d_6), δ (ppm)
1e	1.16 (3H, t, CH_3); 2.23 (3H, s, CH_3); 2.57 (3H, s, CH_3); 3.60 (2H, t, CH_2); 3.80 (4H, m, $2CH_2$); 4.23 (1H, t, OH); 6.93 (2H, d, $J = 9.2$, ArCH); 7.76 (2H, d, $J = 9.4$, ArCH); 7.20–7.37 (4H, m, ArCH); 9.80 (1H, s, NH)	12.08, 14.42, 17.95 (CH_3); 45.65, 52.34, 58.47 (CH_2); 112.47, 126.08, 126.18, 126.29, 130.39 (ArCH's); 108.52, 128.95, 133.40, 160.13 (Ar–C thiophene); 135.78, 140.68, 141.59, 153.05 (Ar–C aromatic); 114.03 (CN); 166.79 (CO amide).
2e	1.29 (3H, t, CH_3); 1.35 (3H, t, CH_3); 2.23 (3H, s, CH_3); 2.63 (3H, s, CH_3); 3.50 (2H, br m, CH_2); 3.57 (2H, br m, CH_2); 4.26 (2H, q, CH_2); 4.38 (2H, q, CH_2); 4.6 (1H, t, OH); 6.86 (2H, d,$J = 9.0$, ArCH); 7.18 (2H, d, $J = 6.4$, ArCH); 7.23 (2H, br m, ArCH); 7.36 (2H, d, $J = 6.2$ ArCH); 7.70 (2H, d, $J = 9.0$ ArCH); 9.77 (1H, s, NH)	12.06, 14.16, 14.35, 18.04 (CH_3); 45.40, 52.25, 58.46, 61.12 (CH_2); 111.90, 126.11, 130.41, 135.67 (ArCH's); 129.94, 132.43, 133.32, 161.01 (Ar–C thiophene); 136.02, 139.00, 141.68, 151.90 (Ar–C aromatic); 162.26 (CO ester); 163.71 (CO amide).
4a	2.53 (3H, s, CH_3); 6.45 (1H, br s, ArCH); 6.47 (2H, d, overlapped ArCH); 7.39 (2H, d, $J = 9.0$, ArCH); 7.67 (4H, doublet overlapped, ArCH); 10.43 (1H, s, NH); 11.13 (1H, br s, OH hydrogen bonded)	14.38 (CH_3); 103.17, 110.62, 121.97, 123.66, 128.61 (ArCH's); 113.55 (CN); 109.68, 121.55, 130.00, 159.92 (Ar–C thiophene); 127.87, 137.34, 133.40, 141.03, 159.72 (Ar–C aromatic); 166.19 (CO amide).
4d	2.53 (3H, s, CH_3); 3.15 (3H, s, CH_3); 3.62 (4H, br m, quartet overlapped, $2CH_2$); 4.24 (1H, t, OH); 6.93 (2H, d, $J = 9.2$ ArCH); 7.40 (2H, d, $J = 8.6$, ArCH); 7.71 (2H, d, $J = 9.0$ ArCH); 7.73 (2H, d, overlapped, ArCH); 10.35 (1H, s, NH)	14.41, 39.33 (CH_3); 54.27, 58.35 (CH_2); 112.58, 121.93, 128.59 (ArCH's); 113.92 (CN); 108.43, 128.47, 141.27, 160.03 (Ar–C thiophene); 127.76, 137.42, 141.70, 154.09 (Ar–C aromatic); 167.15 (CO amide).
4e	1.15 (3H, t, CH_3); 2.53 (3H, s, CH_3); 3.54 (4H, br m, $2CH_2$); 3.75 (2H, q, CH_2); 4.23 (1H, t, OH); 6.95 (2H, d, $J = 8.2$, ArCH); 7.39 (2H, d, $J = 7.2$, ArCH); 7.70 (2H, d, $J = 7.4$ ArCH); 7.70 (2H, d overlapped, ArCH); 10.36 (1H, s, NH)	12.15, 14.51 (CH_3); 45.74, 52.42, 58.56 (CH_2); 112.56, 122.05, 128.66, 128.71 (ArCH's); 114.04 (CN); 108.42, 128.40, 141.42, 160.15 (Ar–C thiophene); 127.87, 137.50, 141.68, 153.19 (Ar–C aromatic); 167.06 (CO amide).
4f	2.54 (3H, s, CH_3); 2.86 (2H, t, CH_2); 3.63 (4H, br m, $2CH_2$); 3.89 (2H, t, CH_2); 4.23 (1H, t, OH); 7.03 (2H, d, $J = 9.0$, ArCH); 7.40 (2H, d, $J = 9.0$, ArCH); 7.71 (2H, d, $J = 9.0$ ArCH); 7.78 (2H, d, $J = 9.4$, ArCH); 10.49 (1H, s, NH)	14.39 (CH_3); 15.33, 46.70, 52.76, 58.27 (CH_2); 112.85, 121.94, 128.61 (ArCH's); 113.76, 119.04 (CN); 109.02, 124.15, 141.27, 159.96 (Ar–C thiophene); 127.82, 137.37, 142.52, 152.53 (Ar–C armatic); 165.73 (CO amide).
5a	1.33 (3H, t, CH_3); 2.51 (3H, s, CH_3); 4.36 (2H, q, CH_2); 6.37 (1H, s, ArCH); 6.56 (2H, d, $J = 8.6$, ArCH); 7.38 (2H, d, $J = 9.0$, ArCH); 7.60 (2H, d, $J = 8.8$, ArCH); 7.71 (2H, d, $J = 8.6$, ArCH); 10.45 (1H, s, NH); 11.08 (OH hydrogen bonded); 12.56 (NH hydrazo form)	14.00, 15.06 (CH_3); 61.34 (CH_2); 103.105, 110.65, 121.76, 128.60, 132.86 (ArCH's); 127.72, 130.75, 140.54, 160.64 (Ar–C thiophene); 128.01, 137.50, 132.61, 156.59, 159.56 (Ar–C aromatic); 162.48 (CO ester); 164.97 (CO amide).
5d	1.36 (3H, t, CH_3); 2.56 (3H, s, CH_3); 3.02 (3H, s, CH_3); 3.40 (4H, br m, $2CH_2$); 4.39 (2H, q, CH_2); 4.49 (1H, t, OH); 6.88 (2H, d, $J = 9.0$, ArCH); 7.40 (2H, d, $J = 9.0$, ArCH); 7.70 (2H, d, $J = 9.0$, ArCH); 7.72 (2H, d, $J = 8.6$, ArCH); 10.37 (1H, s, NH)	14.11, 14.72, 39.30 (CH_3); 54.13, 58.32, 61.09 (CH_2); 112.01, 121.75, 126.05, 128.58 (ArCH's); 127.60, 130.67, 139.46, 160.92 (Ar–C thiophene); 129.58, 137.64, 141.80, 152.98 (Ar–C aromatic); 162.14 (CO ester); 163.57 (CO amide).
5f	1.36 (3H, t, CH_3); 2.46 (3H, s, CH_3); 2.84 (2H, t, CH_2); 3.60 (4H, br m, $2CH_2$); 3.85 (2H, t, CH_2); 4.40 (2H, q, CH_2); 4.74 (1H, t, OH); 6.98 (2H, d, $J = 9.0$, ArCH); 7.40 (2H, d, $J = 8.6$, ArCH); 7.72 (2H, d, $J = 9.0$, ArCH); 7.73 (2H, d, $J = 8.6$, ArCH); 10.40 (1H, s, NH)	14.28, 18.50 (CH_3); 15.31, 46.63, 52.66. 58.15, 61.17 (CH_2); 112.36, 121.75, 125.96, 128.60 (ArCH's); 119.16 (CN); 130.11, 131.38, 139.34, 159.88 (Ar–C thiophene); 127.62, 137.57, 142.28, 151.30 (Ar–C aromatic); 160.83 (CO ester); 163.48 (CO amide).
10a	2.18 (3H, s, CH_3); 2.25 (3H, s, CH_3); 2.55 (3H, s, CH_3); 6.43 (1H, s, ArCH); 6.48 (2H, d, $J = 9.0$, ArCH); 6.99 (2H, d, $J = 8.2$, Ar–CH); 7.04 (1H, s, ArCH); 7.21 (2H, d, $J = 8.2$, ArCH); 7.63 (2H, d, $J = 9.0$, ArCH); 9.74 (1H, s, NH); 11.21 (br s, H-bonded)	14.42, 17.92, 20.56 (CH_3); 103.23, 110.67, 124.69, 126.12, 126.65, 130.96 (ArCH's); 113.64 (CN); 109.90, 130.78, 135.54, 160.06 (Ar–C, thiophene); 133.15, 133.23, 133.34, 140.38, 159.40, 165.50 (Ar–C aromatic); 166.10 (CO amide).
10d	2.19 (3H, s, CH_3); 2.27 (3H, s, CH_3), 2.56 (3H, s, CH_3); 3.15 (3H, s, CH_3); 3.48 (2H, t, CH_2); 3.62 (2H, br m, CH_2); 4.24 (1H, t, OH); 6.92 (2H, d, $J = 8.6$, ArCH); 6.98 (1H, s, ArCH); 7.04 (2H, d, $J = 7.8$, ArCH); 7.22 (2H, d, $J = 7.8$, ArCH); 7.76 (2H, d, $J = 9.4$, ArCH); 9.71 (1H, s, NH).	14.40, 17.87, 20.51, 39.28 (CH_3); 45.15, 58.35 (CH_2); 112.49, 126.08, 126.55, 130.88 (ArCH's); 114.00 (CN); 108.68, 129.99, 140.53, 160.12 (Ar–C thiophene); 133.17, 135.39, 141.69, 153.96 (Ar–C aromatic); 166.65 (CO amide).

Table 4 (*continued*)

Azo dyes	^{1}H NMR in (DMSO-d_6), δ (ppm)	^{13}C NMR in (DMSO-d_6), δ (ppm)
10e	1.16 (3H, t, CH_3); 2.18 (3H, s, CH_3); 2.26 (3H, s, CH_3); 2.55 (3H, s, CH_3); 3.56–3.59 (6H, br m, $3CH_2$); 4.22 (1H, t, OH); 6.92 (2H, d, $J = 8.2$, ArCH); 6.98 (1H, s, ArCH); 7.04 (2H, d, $J = 9.0$, ArCH); 7.21 (2H, d, $J = 7.8$, ArCH); 7.75 (2H, d, $J = 7.8$, ArCH); 9.69 (1H, s, NH).	12.06, 14.38, 17.86, 20.50 (CH_3); 45.63, 52.34, 58.46 (CH_2); 112.41, 126.08, 126.55, 130.87 (ArCH's); 114.01 (CN); 108.56, 129.08, 140.52, 160.13 (Ar–C thiophene); 133.17, 135.37, 141.59, 152.99 (Ar–C aromatic); 166.65 (CO amide).
10f	2.18 (3H, s, CH_3); 2.26 (3H, s, CH_3); 2.56 (3H, s, CH_3); 2.86 (2H, t, CH_2); 3.55–3.73 (4H, br m, $2CH_2$); 3.88 (2H, t, CH_2); 4.24 (1H, t, OH); 6.99–7.06 (3H, br m, ArCH's of the phenyl group attached to thiophene intermediate); 7.22 (2H, d, $J = 7.8$, ArCH); 7.78 (2H, d, $J = 9.0$, ArCH); 9.74 (1H, s, NH).	14.40, 17.88, 20.53 (CH_3); 15.38, 46.75, 52.78, 58.25 (CH_2); 112.79, 126.11, 126.61, 126.82, 130.92 (ArCH's); 113.86, 119.09 (CN); 109.69, 129.96, 140.60, 160.11 (Ar–C thiophene); 133.14, 133.22, 135.49, 142.25, 152.41 (Ar–C aromatic); 166.18 (CO amide).
11a	1.34 (3H, t, CH_3); 2.19 (3H, s, CH_3); 2.25 (3H, s, CH_3); 2.55 (3H, s, CH_3); 4.36 (2H, q, CH_2); 6.37 (1H, s, ArCH); 6.55 (2H, d, $J = 8.8$, ArCH); 6.99 (2H, d, $J = 8.2$, ArCH); 7.05 (1H, s, ArCH); 7.22 (2H, d, $J = 8.0$, ArCH); 7.60 (2H, d, $J = 9.0$, ArCH); 9.76 (1H, s, NH); 11.02 (br s, OH, H-bonded); 12.59 (br s, NH, hydrazo form)	14.03, 15.08, 17.92, 20.53 (CH_3); 61.33 (CH_2); 103.14, 110.61, 126.02, 126.58, 130.92 (ArCH's); 128.11, 131.34, 140.03, 156.48 (Ar–C thiophene); 132.59, 133.09, 133.25, 135.35, 154.32, 160.79 (Ar–C aromatic); 162.55 (CO ester); 164.87 (CO amide).
11f	1.36 (3H, t, CH_3); 2.19 (3H, s, CH_3); 2.26 (3H, s, CH_3); 2.56 (3H, s, CH_3); 2.84 (2H, t, CH_2); 3.61 (4H, br m, $2CH_2$); 3.84 (2H, t, CH_2); 4.40 (2H,q, CH_2); 5.22 (1H, br s, OH); 6.95–7.02 (2H, br m, ArCH); 7.06 (1H, s, ArCH); 7.22 (2CH, d, $J = 8.2$, ArCH); 7.72 (2H, d,$J = 8.6$, ArCH); 9.72 (1H, s, NH)	14.29, 17.90, 20.51 (CH_3); 15.34, 46.64, 52.67, 58.16, 61.16 (CH_2); 112.34, 125.90, 126.05, 126.55, 130.88 (ArCH's); 119.20 (CN); 130.67, 133.12, 142.31, 159.54 (Ar–C thiophene); 131.62, 133.32, 135.27, 138.75, 151.20 (Ar–C aromatic); 160.91 (CO ester); 163.59 (CO amide).

*3.2. Synthesis of thiophene intermediates **1–12***

Aminothiophenes derived from 1,3-dicarbonyl compounds, active α-methylene nitriles, and sulfur were prepared using a "one-pot" Gewald's reaction [43].

*3.2.1. 5-Amino-4-cyano-2-methylthiophene-3-carboxylic acid O-tolylamide (**1**)*

o-Acetoacetotoluidide (20.15 g, 0.1 mol), malononitrile (6.96 g, 0.1 mol), and sulfur (3.37 g, 0.1 mol) in ethanol were stirred in the presence of morpholine (8.97 g, 0.1 mol) at 60–70 °C for 3 h. The resulting thick dark solution was cooled and stored overnight in a refrigerator, followed by filtration, washing with ethanol and then ethanol/water solution and dried. A grey powder was obtained and recrystallization from ethanol afforded a crystalline solid, 72% yield, mp 235–237 °C.

*3.2.2. Ethyl-2-amino-5-methyl-4-O-tolyl carbamoyl-thiophene-3-carboxylate (**2**)*

o-Acetoacetotoluidide (20.22 g, 0.1 mol), ethylcyanoacetate (11.96 g, 0.1 mol), and sulfur (3.39 g, 0.1 mol) were refluxed in ethanol at 55–65 °C for 2 h

Table 5
UV–visible spectra of azo dyes derived from aminothiophenes

Dye	Ethanol		Acetone		DMF		DCM		Acetonitrile	
	λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε
1e	539	4.46	544	4.47	553	4.44	541	4.59	543	4.72
2e	508	4.75	513	4.72	523	4.62	512	4.85	514	4.76
4a	484	4.24	476	4.48	535	4.49	473	4.47	474	4.39
4d	539	4.40	543	4.45	555	4.48	542	4.49	545	4.38
4e	536	4.47	540	4.58	552	4.35	546	4.56	542	4.43
4f	522	4.56	530	4.46	540	4.45	522	4.33	525	4.45
5a	472	4.51	467	4.42	494	4.37	472	4.27	460	4.43
5d	506	4.43	512	4.41	521	4.25	513	4.38	511	4.25
5f	492	4.38	499	4.36	511	4.53	493	4.35	497	4.42
10a	482	4.29	475	4.44	522	4.32	476	4.10	473	4.20
10d	535	4.38	542	4.19	553	4.29	539	4.17	542	4.25
10e	540	4.58	546	4.36	555	4.45	544	4.54	546	4.58
10f	519	4.43	526	4.46	538	4.52	517	4.49	525	4.43
11a	469	4.47	466	4.31	535	4.58	464	4.45	461	4.54
11c	510	4.38	513	4.30	517	4.26	523	4.25	512	4.12
11f	490	4.49	495	4.40	507	4.30	488	4.18	495	4.28

using morpholine (9.0 g, 0.1 mol). The resulting dark solution was cooled and stored overnight in a refrigerator, followed by filtration, washing with a small amount of ethanol, and then ethanol/water mixture and dried. A white powder was obtained and recrystallization from ethanol afforded a crystalline white solid, 70% yield, mp 128–130 °C.

*3.2.3. Methyl-2-amino-5-methyl-4-O-tolylcarbamoyl-thiophene-3-carboxylate (**3**)*

Morpholine (8.92 g, 0.1 mol) was added to a mixture of *o*-acetoacetotoluidide (20.04 g, 0.1 mol), methylcyanoacetate (10.38 g, 0.1 mol), sulfur (3.36 g, 0.1 mol) and ethanol (20 ml) at 50 °C. The mixture was stirred at 70 °C for 3 h. The resulting solution was cooled down by adding crushed ice and placing it in a refrigerator overnight, followed by filtration, washing and drying. A white product was obtained and recrystallization yielded a crystalline product, 69% yield, mp 127–129 °C.

Following the same route for thiophene intermediates **1**–**3**, *o*-acetoacetanisidide, 4′-chloroacetoacetanilide and *N*-(2,4-dimethylphenyl)-3-oxobutyramide were reacted with malononitrile or ethylcyanoacetate and/or methylcyanoacetate and sulfur in ethanol/basic solution and refluxed to afford the aminothiophene intermediates **4**–**12**.

3.3. Preparation of azo dyes

3.3.1. General procedure for diazotization using nitrosylsulfuric acid [23]

Sodium nitrite (2.1 mmol) was added portion wise to 10 ml of sulfuric acid at 10 °C and heated to 60 °C with stirring for 15 min. The solution was cooled to below 5 °C and a mixture of acetic and propionic acids were added at below 30 °C. The finely ground aminothiophene derivatives (**1**–**12**, 2 mmol) were slowly added within 30 min below 5 °C and the whole mixture was stirred at 0–5 °C for 2–4 h.

3.3.2. General procedure for coupling

The coupling components, either resorcinol (**a**) or 2,3-dihydroxynaphthalene (**b**) (2 mmol), were dissolved in 10% sodium hydroxide and then cooled to 0 °C by adding ice. The diazonium solution previously prepared was added drop wise over 30 min with stirring. The mixture was stirred for a further 2 h at 5–10 °C, and the pH of this solution was adjusted to 4–5 by adding acetic or hydrochloric acid slowly prior to filtering, then water-washed until neutral, dried and crystallized from ethanol/DMF (9:1 solvent mixture).

The coupling components, 2-(*N*-methylanilino)ethanol (**c**) or 2-(*N*-ethylanilino)ethanol (**d**) and/or 3-[(2-hydroxyethyl)phenyl-amino]propionitrile (**e**) were dissolved in acetic acid and cooled to 5 °C, following the previous step for the addition of diazonium mixture. This was then stirred for a further 2 h before diluting, raising the pH of the solution to 4–5 using 10% sodium hydroxide or sodium acetate solution if necessary. The resulting product was then filtered off, washed with water until acid-free and then dried. The crude product was purified by Alumina column chromatography using 1:1 hexane:ethyl acetate.

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References

[1] Weaver MA, Shuttleworth L. Heterocyclic diazo components. Dyes and Pigments 1982;3:81–121.
[2] Yen MS, Wang IJ. Synthesis and absorption spectra of hetarylazo dyes derived from coupler 4-aryl-3-cyano-2-aminothiophenes. Dyes and Pigments 2004;61:243–50.
[3] Annen O, Egli R, Hasler R, Henzi B, Jakob H, Matzinger P. Replacement of disperse anthraquinone dyes. Review of Progress in Coloration 1987;17:72–85.
[4] Penchev A, Simov D, Gadjev N. Diazotization of 2-amino-6-methoxybenzothiazole at elevated temperature. Dyes and Pigments 1991;16:77–81.
[5] Peters AT, Gbadamosi NMA. 5,6-(6,7-)Dichlorobenzothiazolylazo dyes for synthetic polymer fibres. Dyes and Pigments 1992; 18:115–23.
[6] Kraska J, Sokolwska-Gajda J. Synthesis and properties of monoazo disperse dyes derived from 3-amino-5-nitro[2,1]benzisothiazole. Dyes and Pigments 1987;8:345–52.
[7] Sokolwska-Gajda J. Synthesis and properties of some disperse dyes derived from 3-amino-5-nitro[2,1]benzisothiazole and alkyl esters of *N*-benzyl-*N*-phenyl-β-alanine. Dyes and Pigments 1991; 15(4):239–45.
[8] Yen MS, Wang IJ. A facile synthesis and absorption characterizatics of some monoazo dyes in bis-heterocyclic aromatic systems. Part I: Syntheses of polysubstituted-5-(2-pyrido-5-yl and 5-pyrazolo-4-yl)azo-thiophene derivatives. Dyes and Pigments 2004;62:173–80.
[9] Stead CV. Developments in azo colorants. Review of Progress in Coloration 1970;1:23–30.
[10] Yen MS, Wang IJ. A facilesynthesis and absorption characterizatics of some monoazo dyes in bis-heterocyclic aromatic systems. Part II: Syntheses of 4-(*p*-substituted)phenyl-2-(2-pyrido-5-yl and 5-pyrazolo-4-yl)azo-thiazole derivatives. Dyes and Pigments 2004;63:1–9.
[11] Griffiths J. Recent developments in the colour and constitution of organic dyes. Review of Progress in Coloration 1981;11:37–57.
[12] Hallas G, Chio J-H. Synthesis and properties of novel aziridinyl azo dyes from 2-aminothiophenes. Part 2: application of some disperse dyes to polyester fibres. Dyes and Pigments 1999; 40:119–29.
[13] Towns AD. Developments in azo disperse dyes derived from heterocyclic diazo components. Dyes and Pigments 1999;42:3–28.
[14] Hallas G, Towns AD. Dyes derived from aminothiophenes. Part 3: application of some disperse dyes derived from 2-aminothiophenes to hydrophobic fibres. Dyes and Pigments 1997; 33:215–28.

[15] Hallas G, Towns AD. Dyes derived from aminothiophenes. Part 6: application of some nitro-substituted thiophene-based azo disperse dyes to hydrophobic fibres. Dyes and Pigments 1997;35:45–55.
[16] Griffiths J. Colour and constitution of organic molecules. London: Academic Press; 1976. p. 186.
[17] Gordon PF, Gregory P. In: Organic chemistry in colour. Berlin: Springer; 1983. p. 139.
[18] Gewald K. Methods for the synthesis of 2-aminothiophenes and their reactions. Chemistry of Heterocyclic Compound (English trans) 1976;12:1077–89. Chemical Abstract 1977;86:55307.
[19] Gewald K. Methods for the synthesis of 2-aminothiophenes and their reactions. Khimiya Geterotsiklicheskikh Soedinenii 1976;1299.
[20] Maradiya HR, Patel VS. Synthesis of novel azo dyes containing the thiophene moiety. Chemistry of Heterocyclic Compounds 2002;38(11):1324–30.
[21] Maradiya HR, Patel VS. Thiophene based monoazo disperse dyes for polyester fabric. Journal of the Serbian Chemical Society 2002;67(1):17–25.
[22] Maradiya HR. Synthesis of azobenzo[*b*]thiophene derivatives and their dyeing performance on polyester fiber. Turkish Journal of Chemistry 2001;25:441–50.
[23] Hallas G, Towns AD. Dyes derived from aminothiophenes. Part 1: synthesis of some heterocyclic disperse dyes using the gewald reaction. Dyes and Pigments 1996;32(3):135–49.
[24] Hallas G, Towns AD. Dyes derived from aminothiophenes. Part 7: synthesis and properties of some benzo[*b*]thiophene-based azo disperse dyes. Dyes and Pigments 1997;35(3):219–37.
[25] Hallas G, Towns AD. Dyes derived from aminothiophenes. Part 4: synthesis of some nitro-substituted thiophene-based azo disperse dyes. Dyes and Pigments 1997;33(4):319–36.
[26] Hallas G, Choi J-H. Synthesis and spectral properties of azo dyes derived from 2-aminothiophenes and 2-aminothiazoles. Dyes and Pigments 1999;42:249–65.
[27] Bhatti HS, Seshadri S. Novel disperse dyes from benzo[*b*]thiophene-3(2*H*)-one-1,1-dioxide and ethylbenzo[*b*]thien-3(2*H*)-ylidenecyanoacetate,*S*,*S*-dioxide:synthesis and properties. Dyes and Pigments 2004;62:83–92.
[28] Sabnis RW, Rangnekar DW. Synthesis of azo benzo[*b*]thiophene derivatives and their application as disperse dyes. Dyes and Pigments 1989;10:295–302.
[29] Afifi TH, Sayed AZ. One-bath dyeing of polyester/wool blend with disperse dyes. Journal of the Society of Dyers and Colourists 1997;113:256–8.
[30] Afifi TH. One-bath dyeing of polyester/wool blend using azo dyes derived from 2-aminothiophenes. Advances in Colour Science and Technology 2003;6(3):63–72.
[31] Astrand P-O, Sommer-Larsen P, Hvilsted S, Ramanujam PS, Bak KL, Saver SPA. Five-membered rings as diazo components in optical data storage devices: an ab initio investigation of the lowest singlet excitation energies. Chemical Physics Letters 2000;325:115–9.
[32] Selim SR, Afifi TH. Electrical properties of some new tetrahydrobenzo[*b*] thiophene-3-carbonitrile-2-azo dyes. Advances in Colour Science and Technology 2001;4(3):82–8.
[33] Abd-El-Aziz AS, Afifi TH, Budakowski WR, Friesen KJ, Todd EK. The first example of cationic iron-coordinated polyaromatic ethers and thioethers with azo dye-functionalized side chains. Macromolecules 2002;35:8929.
[34] Abd-El-Aziz AS, Okasha RM, Afifi TH. Organoiron polynorbornenes with pendent arylazo and hetarylazo dye moieties. Macromolecular Symposia 2004;209:195–205.
[35] Abd-El-Aziz AS, Okasha RM, Todd EK, Afifi TH, Shipman PO, Cooping KMD. Synthesis of iron-containing polymers with azo dyes in the backbones or side chains. Macromolecular Symposia 2004;209:185–203.
[36] Silverstein RM, Clayton BG, Morrill CT. Spectrometric identification of organic compounds. New York: John Wiley & Sons; 1991.
[37] Chao YC, Chen SS. Dyes for polyester microfibres. Dyes and Pigments 1994;24:205–22.
[38] Gewald K, Jeschke T, Gruner M. The Reaction of 2-aminothiophene-3-carbonitriles with heterocumulenes. Journal Fur Praktische Chemie 1991;333(2):229–36.
[39] Hallas G, Choi J-H. Synthesis and properties of novel aziridinyl azo dyes from 2-aminothiophenes. Part 1: synthesis and spectral properties. Dyes and Pigments 1999;40(2–3):99–117.
[40] Hallas G. The effects of terminal groups in 4-aminoazobenzene and disperse dyes related thereto. Journal of the Society of Dyers and Colourists 1979;95:285–94.
[41] Georgiadou KL, Tsatsaroni EG. Hetarylazo disperse dyes derived from substituted *N*,*N*-bis-β-hydroxy- and *N*,*N*-bis-β-acetoxyethylaniline. Dyes and Pigments 2002;53:73–8.
[42] Patel VH, Patel MP, Patel RG. Fused heterocycle 11-amino-13*H*-acenapthol [1,2-*e*] pyridazino [2,3-*b*]quinazoline-13-one based monoazo disperse dyes. Dyes and Pigments 2002;53:191–8.
[43] Sabnis RW, Rangnekar DW, Sonawane ND. 2-Aminothiophenes by the gewald reaction. Journal of Heterocyclic Chemistry 1999;36:333–45.