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Synthesis and absorption spectra of hetarylazo dyes derived from coupler 4-aryl-3-cyano-2-aminothiophenes

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Abstract

A series of hetarylazo dyes was synthesized by coupling reaction of 4-aryl-2-aminothiophenes derivatives with diazotized 4-nitro-aniline, 5-nitro-2-aminothiazole and 6-nitro-2-aminobenzothiazole, respectively, as diazo components. Characterization of these dyes was carried out by spectral and elemental analyze. The solvent effects of dyes in the visible absorption spectra were also evaluated.

Keywords: 2-Aminothiophene; 2-Aminothiazole; 2-Aminobenzothiazole; Azo dyes

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1. Introduction

In recent years, efforts have been made to replace certain anthraquinone dyes with technically equivalent azo dyes for both environmental and economic reasons [1]. In this regard, the use of heterocyclic intermediates in the synthesis of azo disperse dyes is well established, and the resultant dyes exhibit good tinctorial strength and brighter dyeing than those derived from aniline-based diazo components. For instance, amino-substituted thiazole [2,3], benzothiazole [4–7] and benzoisothiazole [8,9], being very electronegative diazo components and produce a pronounced bathochromic shift when compared to the corresponding benzoid compounds [10–12]. Moreover, azo disperse dyes containing 2-aminothiophene as coupling component have also been described as having red-violet colors in literature [13,14].

We report here the synthesis of hetarylazo dyes derived from 4-aryl-2- aminothiophenes as coupling component and 4-nitroaniline, 5-nitro-2-aminothiazole, 6-nitro-2-amino-benzothiazole as diazo components. The visible absorption spectra in various solvents of these dyes were discussed.

2. Results and discussion

2.1. Preparation of 4-aryl-3-cyano-2-aminothiophene derivatives

As shown in scheme 1 Thiophene derivatives **5a**–**5c**, the starting materials for dyes syntheses were obtained according to the method of Gewald et al. [15], which involved the condensation of

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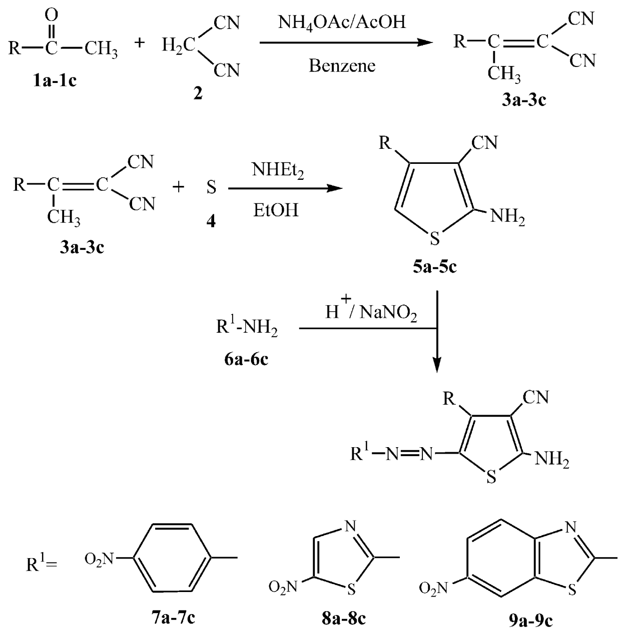

Dyes			R
7a	**8a**	**9a**	C_6H_5
7b	**8b**	**9b**	C_6H_4Cl-p
7c	**8c**	**9c**	C_6H_4OMe-p

Scheme 1.

corresponding ketone and malononitrile in benzene. The reaction mixture was refluxed in the presence of catalytic amount of acetic acid and ammonium acetate to produce the intermediates **3a**–**3c**, followed by the cyclisation with sulphur, using diethylamine as catalysts at 65 °C for 2 h to give the desired thiophene products **5a**–**5c**. The characteristic data of thiophene derivatives were then obtained by elemental and spectral analyze and are presented in experimental. The IR spectra of thiophene derivatives were recorded in KBr; the compound **5a** showed two sharp absorption bands of the amino group at 3308 and 3412 cm^{-1}, and an absorption band of nitrile group at 2210 cm^{-1}, whilst the absorption bands for the other derivatives **5b** and **5c** were observed in the regions 3308–3311 and 3405–3404 cm^{-1} for amino group, and at 2213–2215 cm^{-1} for nitrile group, respectively. The ^{1}H-NMR spectra of thiophene derivatives **5a**–**5c** were recorded in DMSO-d_6. The ^{1}H NMR spectra of aromatic protons of **5a**–**5c** in the thiophene ring appeared at 7.49, 7.62 and 7.41 ppm, and showed a 2H singlet of amino group at 8.35, 8.56 and 8.21 ppm, respectively. Compound **5a** showed a broad signal of 5-H multiplet at 7.47–7.55 ppm, that was attributed to the phenyl protons in the four-position of thiophene ring; compound **5b** showed two 2H doublets at 6.93–7.58 ppm, attributed to 4 protons of *p*-chlorosubstituted phenyl group; compound **5c** showed a 3H singlet of methoxy group at 3.78 ppm and also two doublets at 6.84–7.47 ppm, attributed to the *p*-methoxysubstituted phenyl group in four-position of thiophene ring, respectively. All data confirmed the expected structure of the thiophene compounds.

2.2. Preparations of hetarylazo dyes

Hetarylazo dyes (**7a**–**7c**, **8a**–**8c**, **9a**–**9c**) were obtained by the coupling reactions of the intermediates, 4-nitroaniline **6a**, 5-nitrothiazole **6b**, and

6-nitrobenzothiazole **6c**, respectively, with relevant diazotized 4-aryl-3-cyano-2-aminothiophene products **5a**–**5c**.

The hetarylazo dyes **7a**–**7c** were prepared by coupling 4-aryl-2-aminothiophene **5a**–**5c** with diazotized 4-nitroaniline **6a** in a mixture of acidic solution (15 ml acetic acid: propionic acid = 5:1); the pH value of solution was regulated to 4–5 with aqueous sodium hydroxide or sodium acetate, and the temperature was maintained under 5 °C in an ice bath, the reaction mixture was further stirred for 2–4 h and then to facilitate precipitation of the resulting dyes. In order to remove the remained amine, it was added to urea before the end of diazotization. Subsequent coupling reaction took place readily when adding the resulting diazonium salt continuously to an aqueous dilute ethanol solution of the coupling component **5a**–**5c**. The precipitated dyes **7a**–**7c** were filtered, washed with water and air-dried. The syntheses of the hetarylazo dyes 2-amino-4-aryl-5-(5-nitro-2,3-dihydrothiazol-2-ylazo)-thiophene-3-carbonitrile **8a**–**8c** is followed the similar procedure as that for dyes **7a**–**7c** except that the diazo component was replaced by intermediate 5-nitro-2-aminothiazole **6b**. The pH value of the coupling condition was also adjusted to 4–5. Similarly, the hetarylazo dyes 2-amino-4-aryl-5-(6-nitro- benzothiazol-2-ylazo)-thiophene-3-carbonitrile **9a**–**9c** were synthesized following the procedure for **8a**–**8c** except that the diazo component was replaced by intermediate 6-nitro-2-aminobenzothiazole **6c**.

The physical properties and characteristic data of dyes (**7a**–**7c**, **8a**–**8c** and **9a**–**9c**) are presented in the experimental for each of the azo derivatives.

The IR spectra of the hetarylazo dyes **7a**–**7c** showed bands at 3430–3378 cm^{-1} due to the amino group. The spectra also showed typical cyano absorption at 2201–2204 cm^{-1} and nitro absorption at 1302–1315 and 1505–1530 cm^{-1}. The ^{1}H NMR spectra of dyes **7a** in DMSO-d_6 showed a multiplet at $\delta = 7.33$–7.49 ppm, attributed to the signals of the phenyl group; a 2H doublets at $\delta = 8.13$ ppm, attributed to the proton at the 2,6-position of the benzoid ring; and a 2H doublets at $\delta = 8.26$ ppm, attributed to the proton at the 3,5-position of the benzoid ring. There are also singlet of the amino group at $\delta = 10.09$ ppm.

The IR spectra of the hetarylazo dyes **8a**–**8c** showed absorption bands at 3406–3332 cm^{-1}; due to the amino group. The spectra also showed typical cyano absorption at 2201–2203 cm^{-1} and nitro absorption at 1308–1318, and 1507–1523 cm^{-1}. The ^{1}H NMR spectra of dyes **8a** in DMSO-d_6 showed a multiplet at $\delta = 7.29$–7.53 ppm, attributed to the signals of the phenyl group; a 1H singlet at $\delta = 7.42$ ppm, attributed to the proton at the thiazole ring and a singlet at $\delta = 9.75$ ppm, attributed to the amino group.

The IR spectra of the hetarylazo dyes **9a**–**9c** showed absorption bands at 3414–3436 cm^{-1} due to the amino group; and also showed typical cyano absorptions at 2192–2206 cm^{-1} and nitro absorptions at 1324–1337, and 1511–1531 cm^{-1}. The ^{1}H-NMR spectra of dyes **9a** in DMSO-d_6 showed a multiplet at $\delta = 7.60$–7.78 ppm, attributed to the signals of the phenyl group; a 1H doublet at $\delta = 8.24$ ppm, attributed to the proton at the four-position of the benzothiazole ring; a 1H doublet at $\delta = 8.26$ ppm, attributed to the proton at the five-position of the benzothiazole ring; a 1H doublet at $\delta = 8.93$ ppm, attributed to the proton at the seven-position of the benzothiazole ring and a singlet at $\delta = 9.75$ ppm attributed to the amino group. All data confirmed the expected structure of the hetarylazo dyes.

2.3. *Electronic absorption properties of hetarylazo dyes*

The absorptions maxima of some hetarylazo dyes (**7a**–**7c**, **8a**–**8c**, and **9a**–**9c**) derived from coupling components 3-cyano-4-substituted-2-aminothiophenes **5a**–**5c** in various solvents are given in Table 1. It was found that the electronic absorption properties of these hetarylazo dyes are strongly solvents dependent and vary with the different solvents. These dyes show bathochromic shifts as the polarity of the solvents is increased. The influence of solvents for theses dyes increase in the order DMF > CH_3OH > CH_3COCH_3 > $CHCl_3$. The spectral shifts of dye **9a** in various solvents is shown in Fig. 1. Dye **9a** showed the absorptions maximum at 590 nm in DMF, 554 nm in methanol, 548 nm in acetone, and 545 nm in chloroform, respectively, so that dye **9a** showed significant larger bathochromic shifts in stronger polar solvent (DMF) than the weaker polar solvents, such as methanol, acetone and chloroform. The same results in the various solvents were observed also in the absorption maxima of dyes **7a**–**7c**, **8a**–**8c** and **9b**–**9c**, as shown in Table 1. The spectral shifts of **9a**–**9c** derived from various couplers **5a**–**5c**, respectively, coupled with diazo component 6-nitro-2-aminobenzothiazole **6c** in acetone are shown in Fig. 2. The absorption maxima of dyes **9a**–**9c** ranged from 543 to 552 nm. It was found that dye **9c** contained an electron donor group (methoxy) in the *p*-position of phenylsubstituted on the four-position of the thiophene ring, so that the λ_{max} of dye **9c** showed slight bathochromic shift of + 4 nm relative to dye **9a** in acetone; the dye **9b** showed a hypsochromic shift in comparison with the corresponding dye **9a**, and the absorption maximum of dye **9b** showed at shorter wavelengths than dyes **9a**, due to weaker electron accepter of chloro group in the *p*-position of the phenylsubstituted on the four position the thiophene ring. The λ_{max} of dye **9b** is −5 nm shorter than dye **9a** in acetone. As for the previous series, the spectral shifts of dyes **7a**–**7c** and **8a**–**8c**, derived from diazo component 4-nitro-aniline **6a** and 5-nitro-2-aminothiazole **6b**, respectively, coupled with **5a–5c**, in absorption

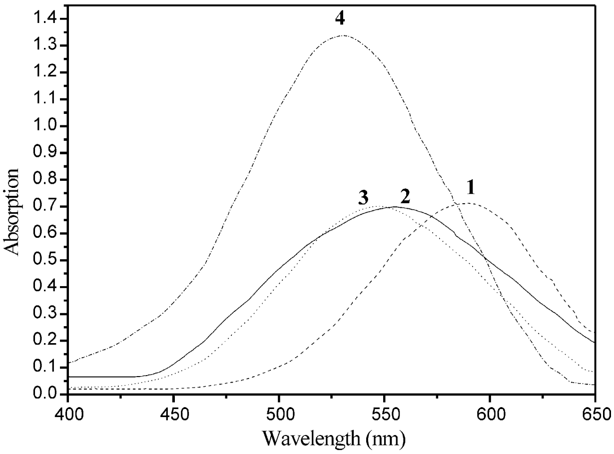

Fig. 1. Absorption spectra of dyes 9a in various solvents: 1.DMF; 2. Methanol; 3.Acetone; 4.Chloroform.

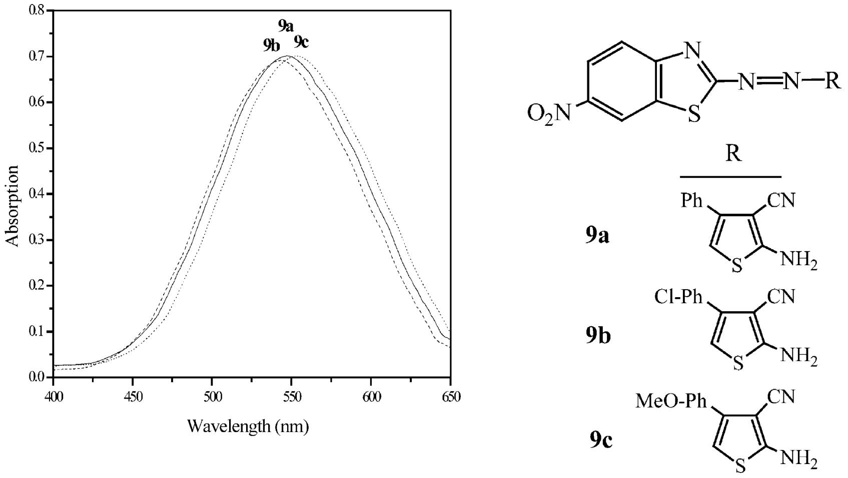

Fig. 2. Absorption spectra of dyes **9a**-**9c** in acetone.

maxima relative to dyes **7a** and **8a**. It was observed that the trend of variation of λ_{max} is similar to **9a**–**9c**. The spectral shifts of dyes **7a**, **8a** and **9a**, derived from coupler **5a**, coupled with diazo component 4-nitro-aniline **6a**, 5-nitro-2-aminothiazole **6b**, and 6-nitro-2-aminobenzothiazole **6c**, respectively in acetone, as shown in Fig. 3. The absorption maxima of **7a**, **8a** and **9a** varied from 512 to 548 nm. It shows that the λ_{max} of dyes **7a** and **8a** are presented more significant hypsochromic effects than dyes 9a owing to the fact that the thiazole ring and benzene ring have poorer resonance stabilization than the benzothiazole ring. The absorption maxima of dyes are in the following order: **9a** > **8a** > **7a**.

3. Experimental

All melting points are uncorrected and in °C. IR spectra were recorded on a JASCO FTIR-3 spectrometer (KBr); ^{1}H NMR spectra were obtained on a Jeol-EX-400 MHz NMR spectrometer, and chemical shifts are expressed in δ ppm using TMS as an internal standard. Mass spectra were obtained from a Finnigan TSQ-700 GC/LC/MS spectrometer. Microanalyses for C, H and N were performed on a Perkin-Elmer 2400 **II** elemental analyzer. Electronic spectra were recorded on a Heliosa UV1 from dyes solutions in DMF, methanol, acetone or chloroform at a concentration of 1×10^{-5} mol l^{-1}.

Table 1
Absorption maxima spectra of hetarylazo dyes **7a**–**7c**, **8a**–**8c**, 9a–**9c**

Dyes	DMF		CH$_3$OH		Acetone		CHCl$_3$	
	λ_{max} (nm)	logε	λ_{max} (nm)	logε	λ_{max} (nm)	logε	λ_{max} (nm)	logε
7a	568	4.37	515	4.38	512	4.35	483	4.31
7b	562	4.35	514	4.37	506	4.34	464	4.27
7c	572	4.42	515	4.33	513	4.35	494	4.22
8a	586	4.25	534	4.34	528	4.24	523	4.25
8b	582	4.29	530	4.35	526	4.20	520	4.26
8c	592	4.36	537	4.35	531	4.32	527	4.31
9a	590	4.35	554	4.41	548	4.32	545	4.34
9b	589	4.36	549	4.38	543	4.32	535	4.38
9c	602	4.47	557	4.43	552	4.36	550	4.41

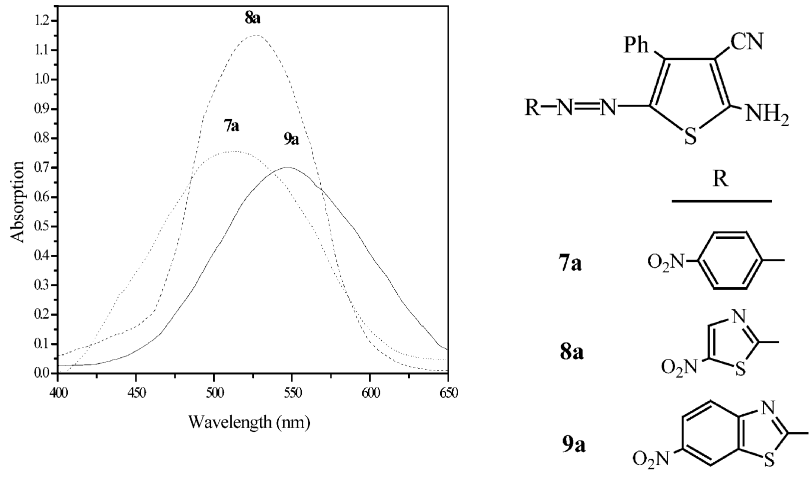

Fig. 3. Absorption spectra of dyes 7a, 8a, 9a in Acetone.

*3.1. Preparation of 2-aminothiophene derivatives **5a–5c***

A mixture of acetophenone (6 g, 0.05 mol), malononitrile (3.36 g, 0.051 mol), acetic acid (2 g) and ammonium acetate (1.85 g, 0.024 mol) was added to 50 ml benzene with a Dean-Stark trap. The reaction mixture was stirred under reflux for 8 h with removal of the condensed water. The excess benzene was evaporated and the resulting product was cooled to room temperature. The separated solid was then filtered, washed with water, and dried to give intermediate 2-(1-phenyl-ethylidene)-malononitrile **3a** (7.14 g, 85%). Synthese of intermediate **3b**–**3c** followed the same method except for the use of substitutes.

*3.1.1. 2-Amino-4-phenyl-thiophene-3-carbonitrile (**5a**)*

A reaction flask was mixed with **3a** (8.4 g, 0.05 mol) and sulphur (1.6 g, 0.05 mol) in 50 ml ethanol. After the mixture was cooled to 15 °C, a solution of diethylamine (3.65 g 0.05 mol) was added dropwise at 15 °C, and stirred for 2 h at 65 °C. Evaporation of ethanol yielded the crude product, which was added to 50 ml ethanol, followed by further stirring for 30 min in the ice bath. The separated solid was filtered, washed with water, dried and recrystallized from ethanol to give a pale orange solid 2-amino-4-phenyl-thiophene-3-carbonitrile (**5a**) (4.3 g, 43%). mp 161–163 °C; FTIR (KBr)/cm^{-1}: 3308 3412 (NH_2), 2210 ($C\equiv N$); ^1H NMR (DMSO-d_6.) δ ppm: 7.47–7.55 (5 H, *m*, 4-PhH), 7.49 (1 H, *s*, 5-ArH), 8.35 (2 H, *s*, NH_2). $C_{11}H_8N_2S$ (200.1) calc.: C, 65.98; H, 4.03; N, 13.99; S, 16.01. Found: C, 65.94; H, 4.06; N, 13.97; S, 16.04.

*3.1.2. 2-Amino-4-(4-chloro-phenyl)-thiophene-3-carbonitrile (**5b**)*

Yield of crude product 67%, light yellow crystals purified by recrystallization (ethanol); mp 102–103 °C; FTIR (KBr)/cm^{-1}: 3308 3433 (NH_2), 2204 ($C\equiv N$); ^1H NMR (DMSO-d_6) δ ppm: 6.93 (2 H, *d*, 2,6-ArH), 7.58 (2 H, *d*, 3,5-ArH), 7.62 (1 H, *s*, 5-H), 8.56 (2 H, *s*, NH_2). $C_{11}H_7N_2SCl$ (234.4). calc.: C, 56.29; H, 3.01; N, 11.94; S, 13.66. Found: C, 56.24; H, 3.05; N, 11.97; S, 13.64.

*3.1.3. 2-Amino-4-(4-methoxy-phenyl)-thiophene-3-carbonitrile (**5c**)*

Yield of crude product 52%, pale yellow crystals purified by recrystallization (ethanol); mp 182–184 °C; FTIR (KBr)/cm^{-1}: 3320 3424 (NH_2), 2201 ($C\equiv N$), 1241 (C–O–C); ^1H NMR (DMSO-d_6) δ ppm: 3.78 (3 H, *s*, OCH_3), 6.84 (2 H, *d*, 3,5-ArH), 7.47 (2 H, *d*, 2,6-ArH), 7.41 (1 H, *s*, 5-H), 8.21 (2 H, *s*, NH_2). $C_{12}H_{10}N_2SO$ (230). calc.: C, 62.59; H, 4.38; N, 12.16; S, 13.92. Found: C, 62.55; H, 4.33; N, 12.19; S, 13.94.

*3.2. Preparation of the hetarylazo dyes **7a–7c**, **8a–8c**, and **9a–9c***

The syntheses of hetarylazo dyes were carried out according to the general preparation of azo dyes and is described in the preparation of dye **7a**.

*3.2.1. 2-Amino-4-phenyl-5-(4-nitrophenylazo)-thiophene-carbonitrile (**7a**)*

4-Nitroaniline **6a** (1.38 g, 0.01 mol) was dissolved in a mixture of acidic solution (12 ml acetic acid: propionic acid = 5:1), sodium nitrite (0.72 g, 0.0105 mol) in 5 ml conc. sulfuric acid was gradually added to this solution within 5 min at 10 °C, the temperature was raised to 60–65 °C and the reaction mixture was then stirred for 1 h while maintaining at this temperature. Excess nitrous acid was destroyed by the addition of urea, and the solution was then cooled to 0–5 °C 2-amino-4-phenyl- thiophene-3-carbonitrile (2.00 g. 0.01 mol) dissolved in the mixture of ethanol and water (1:1, 50 ml) and the solution cooled to 0–5 °C. To the cooled solution, the diazonium salt solution **6a** was added slowly so that the temperature did not rise above 5 °C, while maintaining pH at 4–5 by addition of sodium acetate or 40% sodium hydroxide solution. The mixture was then stirred for 2 h at 0–5 °C. The resulting product was filtered and the pre-cake washed with water, dried, and recrystallized from DMF–ethanol as red crystals.

Yield of crude product 78%; mp 204–206 °C. FTIR (KBr) /cm^{-1}: 3430 (NH), 2201 ($C\equiv N$), 1315 1530 (NO_2); ^1H NMR (DMSO-d_6) δ ppm: 7.33–7.49 (5 H, *m*, PhH), 8.13 (2 H, *d*, 2,6-ArH–NO_2), 8.26 (2 H, *d*, 3,5-ArH–NO_2), 10.09 (2 H, *s*, NH_2).

$C_{16}H_{13}N_5O_4S$ (350.2). calc.: C, 51.75; H, 3.53; N, 18.86; S, 8.63. Found: C, 51.72; H, 3.46; N, 18.91; S, 8.68.

The above procedure was also used to synthesize dyes **7b**, **7c**, **8a**–**8c** and **9a**–**9c**.

*3.2.2. 2-Amino-4-(4-chloro-phenyl)-5-(4-nitro-phenylazo)-thiophene-3-carbonitrile (**7b**)*

Yield of crude product 75%, red crystals purified by recrystallization (DMF–ethanol); mp 222–224 °C. FTIR (KBr)/cm^{-1}: 3378 (NH), 2204 (C≡N), 1302 1505 (NO_2); ^{1}H NMR (DMSO-d_6) δ ppm: 7.39 (2 H, *d*, 2,6-ArH-Cl), 7.51 (2 H, *d*, 3,5-ArH-Cl), 8.02 (2 H, *d*, 2,6-ArH–NO_2), 8.14 (2 H, *d*, 3,5-ArH–NO_2), 10.17 (2 H, *s*, NH_2). $C_{18}H_{18}N_4O_6S$ (384.1). calc.: C, 51.67; H, 4.34; N, 13.39; S, 7.66. Found: C, 51.72; H, 4.30; N, 13.32; S, 7.69.

*3.2.3. 2-Amino-4-(4-methoxy-phenyl)-5-(4-nitro-phenylazo)-thiophene-3-carbonitrile (**7c**)*

Yield of crude product 93%, red crystals purified by recrystallization (DMF–ethanol); mp 226–228 °C. FTIR (KBr)/cm^{-1}: 3423 (NH), 2203 (C≡N), 1315 1506 (NO_2), 1258 (C–O–C); ^{1}H NMR (DMSO-d_6) δ ppm: 3.86 (3 H, *s*, OCH_3), 7.13 (2 H, *d*, 3,5-ArH–OCH_3), 7.65 (2 H, *d*, 2,6-ArH–OCH_3), 7.71 (2 H, *d*, 2,6-ArH–NO_2), 8.26 (2 H, *d*, 3,5-ArH–NO_2), 9.14 (2 H, *s*, NH_2). $C_{16}H_8N_6O_2S$ (380.1). calc.: C, 51.85; H, 2.49; N, 25.91; S, 9.89. Found: C, 51.93; H, 2.43; N, 25.82; S, 9.97.

*3.2.4. 2-Amino-4-phenyl-5-(5-nitro-2,3-dihydrothiaol-2-ylazo)-thiophene-3-carbonitrile (**8a**)*

Yield of crude product 88%; red crystals purified by recrystallization (DMF–ethanol); mp 153–155 °C. FTIR (KBr)/cm^{-1}: 3406 (NH), 2202 (C≡N), 1316 1507 (NO_2); ^{1}H NMR (DMSO-d_6) δ ppm¡G 7.29–7.53 (5 H, *m*, PhH), 7.42 (1 H, *s*, 4-thiazole-H), 9.75 (2 H, *s*, NH_2). $C_{13}H_{13}N_5O_3S$ (357.3). calc.: C, 48.90; H, 4.10; N, 21.93; S, 10.04. Found: C, 48.94; H, 4.05; N, 21.83; S, 10.12.

*3.2.5. 2-Amino-4-(4-chloro-phenyl)-5-(5-nitro-2,3-dihydro-thiazol-2-ylazo)-thiophene-3-carbonitrile (**8b**)*

Yield of crude product 81%, ruby-red crystals purified by recrystallization (DMF–ethanol); mp 142–144 °C. FTIR (KBr)/cm^{-1}: 3371(NH), 2201 (C≡N), 1308 1523 (NO_2); ^{1}H NMR (DMSO-d_6) δ ppm: 7.38 (2 H, *d*, 2,6-ArH–Cl), 7.47 (1 H, *s*, 4-thiazole-H), 7.62 (2 H, *d*, 3,5-ArH–Cl), 9.75 (2 H, *s*, NH_2). $C_{15}H_{18}N_4O_5S$ (391.1). calc.: C, 49.17; H, 4.95; N, 15.29; S, 8.75. Found: C, 49.23; H, 4.85; N, 15.33; S, 8.67.

*3.2.6. 2-Amino-4-(4-methoxy-phenyl)-5-(5-nitro-2,3-dihydro-thiazol-2-ylazo)-thiophene-3-carbonitrile (**8c**)*

Yield of crude product 86%, ruby-red crystals purified by recrystallization (DMF-ethanol); mp 132–134 °C. FTIR (KBr)/cm^{-1}: 3332(NH), 2203 (C≡N), 1318 1512 (NO_2), 1246 (C–O–C); ^{1}H NMR (DMSO-d_6) δ ppm: 3.78 (3 H, *s*, OCH_3), 6.94 (2 H, *d*, 3,5-ArH–OCH_3), 7.21 (2 H, *d*, 2,6-ArH–OCH_3), 7.47 (1 H, *s*, 4-thiazole-H), 9.74 (2 H, *s*, NH_2). $C_{11}H_8N_6OS$ (387.3) calc.: C, 48.52; H, 2.96; N, 30.86; S, 11.77. Found: C, 48.47; H, 2.94; N, 30.96; S, 11.80.

*3.2.7. 2-Amino-4-phenyl-5-(6-nitro-benzothiazol-2-ylazo)-thiophene-3-carbonitrile (**9a**)*

Yield of crude product 93%; violet crystals purified by recrystallization (DMF–ethanol); mp 297–299 °C. FTIR (KBr)/cm^{-1}: 3414 (NH), 2206 (C≡N), 1337 1524 (NO_2); ^{1}H NMR (DMSO-d_6) δ ppm: 7.60–7.78 (5 H, *m*, PhH), 8.24 (1 H, *d*, 4-ArH), 8.26 (1 H, d, 5-ArH), 8.93 (1 H, d, 7-ArH), 9.75 (2 H, s, NH_2). $C_{13}H_{13}N_5O_3S$ (407.1) calc.: C, 48.90; H, 4.10; N, 21.93; S, 10.04. Found: C, 48.92; H, 4.06; N, 21.85; S, 10.12

*3.2.8. 2-Amino-4-(4-chloro-phenyl)-5-(6-nitro-benzothiazol-2-ylazo)-thiophene-3-carbonitrile (**9b**)*

Yield of crude product 80%; violet crystals purified by recrystallization (DMF–ethanol); m.p. 178-180 °C. FTIR (KBr)/cm^{-1}: 3436 (NH), 2192 (C≡N), 1324 1511 (NO_2); ^{1}H-NMR(DMSO-d_6) δ ppm: 7.43 (2 H, d, 2,6-ArH-Cl), 7.62 (2 H, d, 3,5-ArH–Cl), 8.09 (1 H, d, 4-ArH), 8.27 (1 H, d, 5-ArH), 8.69 (1 H, d, 7-ArH), 9.77 (2 H, s, NH_2). $C_{15}H_{18}N_4O_5S$ (441.2) calc.: C, 49.17; H, 4.95; N, 15.29; S, 8.75. Found: C, 49.25; H, 4.87; N, 15.38; S, 8.69.

*3.2.9. 2-Amino-4-(4-methoxy-phenyl)-5-(6-nitro-benzothiazol-2-ylazo)-thiophene-3-carbonitrile (**9c**)*

Yield of crude product 84%; violet crystals purified by recrystallization (DMF–ethanol); mp 220–222 °C. FTIR (KBr)/cm^{-1}: 3427 (NH), 2205 (C≡N), 1330 1531 (NO_2), 1243 (C–O–C); ^1H NMR (DMSO-d_6) δ ppm: 3.90 (3 H, *s*, OCH_3), 7.18 (2 H, *d*, 3,5-ArH–OCH_3), 7.79 (2 H, *d*, 2,6-ArH–OCH_3), 8.23 (1 H, *d*, 4-ArH), 8.25 (1 H, *d*, 5-ArH), 8.89 (1 H, *d*, 7-ArH), 9.76 (2 H, *s*, NH_2). $C_{15}H_{18}N_4O_5S$ (437.2) calc.: C, 49.17; H, 4.95; N, 15.29; S, 8.75 Found: C, 49.25; H, 4.88; N, 15.37; S, 8.70

4. Conclusion

4-Aryl-2-aminothiophenes are used for coupling with 4-nitro-aniline, 5-nitro-2- aminothiazoles and 6-nitro-2-aminobenzothiazoles, respectively, to produce red hetarylazo dyes. The electronic absorption properties of these dyes are found to exhibit a strong solvent dependence that vary with the dielectric constants of the solvents. The absorption maxima of these dyes showed larger bathochromic shifts in DMF than other three solvents The spectral shifts of dyes derived from coupler 4-aryl-2-aminothiophenes and diazo components 6-nitro-2-amino benzothiazoles are larger than these coupled with 4-nitro-aniline and 5-nitro-2-aminothiazoles.

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