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# Synthesis and solvent characteristics of bishetaryl monoazo dyes derived from polysubstituted-2-aminothiophene derivatives

Ming Shien Yen[a], Ing Jing Wang[b,*]

[a]Department of Polymer Materials, Kun Shan University of Technology, Yung Kang, Tainan 71003, Taiwan, ROC
[b]Department of Polymer Engineering, National Taiwan University of Science and Technology, Taipei 10772, Taiwan, ROC

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**Abstract**

The synthesis of two series of some new bishetaryl monoazo dyes from diazotized 3,5-disubstituted-4-methyl-2-aminothiophene derivatives and 4-aryl-2-aminothiazole and 4-aryl-3-cyano-2-aminothiophene derivatives as coupling components, respectively, is described. Characterization of these dyes was carried out by spectral and elemental analyses. The visible absorption maxima of dyes shift large bathochromic in basic organic solvent with high polarity (dimethylformamide) relative to corresponding solvent with low polarity (chloroform). The behavior of acid–base properties of these dyes in various organic solvents via visible absorption spectra characteristics was also evaluated.

*Keywords:* 2-Aminothiazole; 2-Aminothiophene; Bishetarylazo dyes; Solvent effect

## 1. Introduction

Dyes based on heterocyclic compounds as diazo components tend most to produce brilliant shade, high tinctorial strength and hue ranging from violet to greenish blue [1–5]. In our earlier works, we reported the synthesis of some bishetaryl monoazo dyes derived from both heterocycles 2-pyridones and 5-pyrazolones, as coupling components [6,7]. The obtained dyes exhibit their colour hue in the range from yellow to red. The purpose of this study presents here further the preparation of some new bishetaryl monoazo dyes using 3,5-disubstituted-4-methyl-2-aminothiophene derivatives as diazo components, which were diazotized and coupled with 2-aminothiophenes and 4-aryl-2-aminothiazoles, respectively. The obtained dyes show deep red–blue to blue colour hue.

The visible absorption maxima of dyes in different polarity solvents were measured and the halochromic behaviors of dyes in solution of various pH values via spectral characteristics were discussed.

## 2. Experimental

All melting points were measured on a gallenkamp apparatus and are given uncorrected. IR spectra were recorded on KBr pellets on a JASCO FTIR-3 spectrometer; $^1$H NMR spectra were obtained on a Jeol-EX-400 MHz NMR spectrometer with DMSO–$d_6$ as solvent and using TMS as an internal standard. Chemical shifts are expressed in $\delta$ units (ppm). Mass spectra were obtained from a Finnigan TSQ-700 GC/LC/MS spectrometer. Microanalytical data for C, H and N were performed on a Perkin–Elmer 2400 (II) elemental

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* Corresponding author. Tel.: +886 6 2050349; fax: +886 6 2720964.
*E-mail address:* iwang@tx.ntust.edu.tw (I.J. Wang).

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analyzer. UV–visible spectra were recorded on a Heliosa UV1 spectrophotometer using DMF, methanol, acetone and chloroform as solvents at a concentration of $1 \times 10^{-5}\ \mathrm{mol\,l^{-1}}$.

### *2.1. Synthesis of starting materials*

3,5-Disubstituted-4-methyl-2-aminothiophens **3a–3c**, 4-aryl-2-aminothiazoles **4a–4c** and 4-aryl-3-cyano-2-aminothiophes **5a–5c** are used as starting materials for the synthesis of the corresponding bishetaryl monoazo dyes **I** and **II** according to the described method in the literature [8–11].

### *2.2. General synthesis of bishetaryl monoazo dyes **I** and **II***

A general preparative procedure is described below for the preparation of dye **Ia**.

5-Amino-3-methyl-thiophene-2,4-dicarboxylic acid ethyl ester (2.56 g, 0.01 mol) was dissolved in a mixture of acetic acid and propionic acid (12 ml, ratio 5:1) and stirred for 20 min. The solution was then added gradually in portion to a cold solution of sodium nitrite (0.72 g, 0.0105 mol) in the presence of conc. sulfuric acid (5 ml). The diazo liquor was stirred for further 1 h at temperature 5–10 °C to give a clear solution, and then slowly added to a strong stirred cold solution of 2-amino-4-phenylthiazole (1.75 g, 0.01 mol) in water (50 ml) and acetic acid (10 ml). The mixture was stirred further for 2–3 h and neutralized with aqueous sodium hydroxide or sodium acetate. The pH value was maintained at 4–5. The resulting solid was filtered, washed with water, and dried. The crude product was recrystallized from dimethylformamide–ethanol to give violet needles in very good yield. All the other dyes **Ib–Ii** and **IIa–IIi** were prepared in a similar manner. Characterization data are listed in Tables 1 and 2.

## 3. Results and discussion

### *3.1. Preparation of dyes **I** and **II***

Synthesis of bishetaryl monoazo dyes **I** and **II** is shown in Scheme 1. Polysubstituted thiophene amines were diazotized using sodium nitrite in the presence of sulfuric acid, followed by coupling with 4-aryl-2-amino-thizoles and 4-aryl-3-cyano-2-amino-thiophenes. The physical and spectral characterizations are given in Tables 1 and 2.

### *3.2. Electronic absorption properties of dyes*

The solvatochromic behavior of bishetaryl monoazo dyes **I** and **II** was investigated in solvents with different dielectric constants. The visible absorption maxima of these dyes were recorded in various solvents and are listed in Table 3. It was found that the absorption maximum of dyes **I** and **II** in solvent with high dielectric constant showed larger bathochromic shift than that of low dielectric constant. The absorption maximum of

Table 1
Characterization data for dye derivatives **I** and **II**

| Compound | M.p.[a] (°C) | Yield[b] (%) | Appearance | Molecular formula | Elemental analysis (%) | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Calc. (found) | | | |
| | | | | | C | H | N | S |
| **Ia** | 168–170 | 90 | Violet | $C_{20}H_{20}N_4O_4S_2$ | 54.04 (54.10) | 4.53 (4.48) | 12.60 (12.50) | 13.42 (13.39) |
| **Ib** | 170–172 | 84 | Deep violet | $C_{18}H_{15}N_5O_2S_2$ | 54.39 (54.28) | 3.80 (3.84) | 17.62 (17.55) | 16.13 (16.12) |
| **Ic** | 180–182 | 82 | Deep violet | $C_{16}H_{10}N_6S_2$ | 54.84 (54.91) | 2.88 (2.85) | 23.98 (23.84) | 18.30 (18.25) |
| **Id** | 140–142 | 58 | Violet | $C_{20}H_{19}Cl\ N_4O_4S_2$ | 50.15 (50.17) | 4.00 (3.94) | 11.70 (11.77) | 13.39 (13.25) |
| **Ie** | 166–168 | 77 | Deep violet | $C_{18}H_{14}Cl\ N_5O_2S_2$ | 50.06 (50.11) | 3.27 (3.24) | 16.21 (16.27) | 14.85 (14.82) |
| **If** | 183–185 | 73 | Deep violet | $C_{16}H_9Cl\ N_6S_2$ | 49.93 (49.90) | 2.36 (2.39) | 21.84 (21.78) | 16.66 (16.61) |
| **Ig** | 223–225 | 93 | Deep violet | $C_{21}H_{22}N_4O_5S_2$ | 53.15 (53.21) | 4.67 (4.62) | 11.81 (11.78) | 13.51 (13.54) |
| **Ih** | 274–276 | 92 | Deep violet | $C_{19}H_{17}N_4O_3S_2$ | 53.38 (53.29) | 4.01 (4.05) | 16.38 (16.42) | 15.00 (15.05) |
| **Ii** | 264–266 | 94 | Deep violet | $C_{17}H_{12}N_6OS_2$ | 53.67 (53.62) | 3.18 (3.15) | 22.09 (22.13) | 16.85 (16.89) |
| **IIa** | 160–162 | 80 | Violet | $C_{22}H_{20}N_4O_4S_2$ | 56.40 (56.32) | 4.30 (4.33) | 11.96 (11.92) | 13.68 (13.75) |
| **IIb** | 278–280 | 84 | Deep violet | $C_{20}H_{15}N_5O_2S_2$ | 56.99 (56.87) | 3.59 (3.63) | 16.62 (16.65) | 15.21 (15.27) |
| **IIc** | 280–282 | 87 | Deep violet | $C_{18}H_{10}N_6S_2$ | 57.74 (57.68) | 2.69 (2.73) | 22.44 (22.50) | 17.12 (17.16) |
| **IId** | 160–162 | 72 | Violet | $C_{22}H_{19}Cl\ N_4O_4S_2$ | 52.53 (52.61) | 3.81 (3.85) | 11.14 (11.07) | 12.75 (12.79) |
| **IIe** | 290–292 | 75 | Deep violet | $C_{20}H_{14}Cl\ N_5O_2S_2$ | 52.69 (52.76) | 3.09 (3.04) | 15.36 (15.27) | 14.06 (14.14) |
| **IIf** | 308–310 | 81 | Deep violet | $C_{18}H_9Cl\ N_6S_2$ | 52.88 (52.93) | 2.22 (2.18) | 20.55 (20.61) | 15.68 (15.54) |
| **IIg** | 178–180 | 85 | Deep violet | $C_{23}H_{22}N_4O_5S_2$ | 55.41 (55.46) | 4.45 (4.40) | 11.24 (11.35) | 12.86 (12.79) |
| **IIh** | 180–182 | 88 | Deep violet | $C_{21}H_{17}N_4O_3S_2$ | 55.86 (55.74) | 3.79 (3.75) | 15.51 (15.58) | 14.20 (14.22) |
| **IIi** | 280–282 | 92 | Deep violet | $C_{19}H_{12}N_6OS_2$ | 56.42 (56.46) | 2.99 (2.94) | 20.78 (20.85) | 15.85 (15.95) |

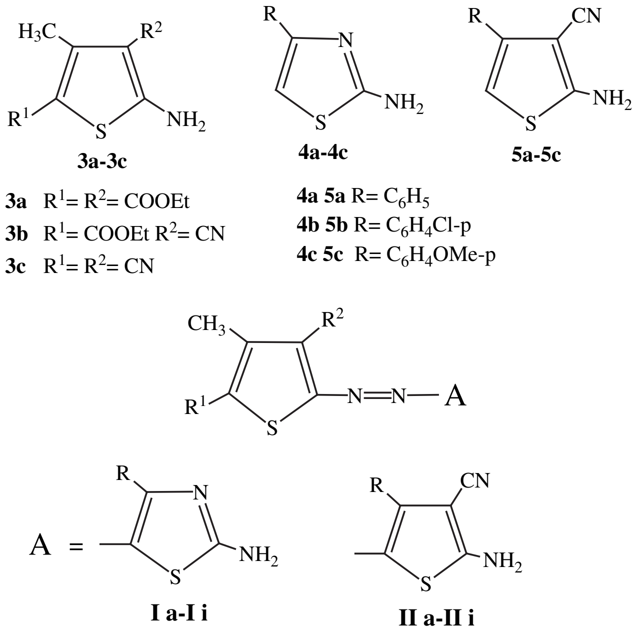
[a] Recrystallized from DMF/ethanol.
[b] Yield of crude product.

Table 2
Spectral data of dye derivatives **I** and **II**

| Dyes | MS ($m/e$, $M^+$) | IR (KBr) $\nu$(cm$^{-1}$) | $^1$H NMR (DMSO$-d_6$) $\delta$ (ppm) |
|---|---|---|---|
| **Ia** | 444 | 3415 (N–H), 1707 (C=O) | 1.30 (3H, t, 5-$\mathrm{CO_2CH_2}\mathit{CH_3}$), 1.36 (3H, t, 3-$\mathrm{CO_2CH_2}\mathit{CH_3}$) 2.53 (3H, s, $CH_3$), 4.28 (2H, q, 5-$\mathrm{CO_2}\mathit{CH_2}\mathrm{CH_3}$), 4.32 (2H, q, 3-$\mathrm{CO_2}\mathit{CH_2}\mathrm{CH_3}$), 7.54–7.57 (3H, m, 3,4, 5-PhH), 8.17 (2H, d, 2,6-PhH), 9.14 (2H, s, $NH_2$) |
| **Ib** | 396 | 3300 (N–H), 2207 (C≡N), 1712 (C=O) | 1.30 (3H, t, $\mathrm{CO_2CH_2}\mathit{CH_3}$), 2.63 (3H, s, $CH_3$), 4.30 (2H, q, $\mathrm{CO_2}\mathit{CH_2}\mathrm{CH_3}$), 7.56–7.58 (3H, m, 3,4,5-PhH), 8.18 (2H, d, 2,6-PhH), 8.78 (2H, s, $NH_2$) |
| **Ic** | 351 | 3432 (N–H), 2217 (C≡N) | 2.89 (3H, s, $CH_3$), 7.48 (2H, t, 3,5-PhH), 7.95 (H, d, 4-PhH), 8.11 (2H, d, 2,6-PhH), 8.82 (2H, s, $NH_2$) |
| **Id** | 478 | 3436 (N–H), 1675 (C=O) | 1.30 (3H, t, 5-$\mathrm{CO_2CH_2}\mathit{CH_3}$), 1.36 (3H, t, 3-$\mathrm{CO_2\ CH_2}\mathit{CH_3}$), 2.89 (3H, s, $CH_3$), 4.28 (2H, q, 5-$\mathrm{CO_2}\mathit{CH_2}\mathrm{CH_3}$), 4.32 (2H, q, 3-$\mathrm{CO_2}\mathit{CH_2}\mathrm{CH_3}$), 7.62 (2H, d, 2,6-ArH), 8.16 (2H, d, 3,5-ArH), 9.13 (2H, s, $NH_2$) |
| **Ie** | 431 | 3302 (N–H), 2208 (C≡N), 1687 (C=O) | 1.30 (3H, t, $\mathrm{CO_2CH_2}\mathit{CH_3}$), 2.57 (3H, s, $CH_3$), 4.31 (2H, q, $\mathrm{CO_2}\mathit{CH_2}\mathrm{CH_3}$), 7.42 (2H, d, 2,6-ArH), 7.80 (2H, d, 3,5-ArH), 8.77 (2H, s, $NH_2$) |
| **If** | 384 | 3394 (N–H), 2203 (C≡N) | 2.89 (3H, s, $CH_3$), 7.66 (2H, t, 2,6-ArH), 7.95 (2H, s, $NH_2$), 8.19 (2H, d, 3,5-ArH) |
| **Ig** | 474 | 3386 (N–H), 1662 (C=O) | 1.30 (3H, t, 5-$\mathrm{CO_2CH_2}\mathit{CH_3}$), 1.36 (3H, t, 3-$\mathrm{CO_2CH_2}\mathit{CH_3}$), 2.52 (3H, s, $CH_3$), 3.87 (3H, s, $OCH_3$), 4.27 (2H, q, 5-$\mathrm{CO_2}\mathit{CH_2}\mathrm{CH_3}$), 4.31 (2H, q, 3-$\mathrm{CO_2}\mathit{CH_2}\mathrm{CH_3}$), 7.11 (2H, d, 3,5-ArH), 8.22 (2H, d, 2,6-ArH), 9.11 (2H, s, $NH_2$) |
| **Ih** | 427 | 3315 (N–H), 2215 (C≡N), 1716 (C=O) | 1.30 (3H, t, $\mathrm{CO_2CH_2}\mathit{CH_3}$), 2.89 (3H, s, $CH_3$), 3.87 (3H, s, $OCH_3$), 4.28 (2H, q, $\mathrm{CO_2}\mathit{CH_2}\mathrm{CH_3}$), 7.13 (2H, d, 3,5-ArH), 8.25 (2H, d, 2,6-ArH), 9.51 (2H, s, $NH_2$) |
| **Ii** | 380 | 3335 (N–H), 2203 (C≡N) | 2.89 (3H, s, $CH_3$), 3.87 (3H, s, $OCH_3$), 7.19 (2H, d, 3,5-ArH), 8.28 (2H, d, 2,6-ArH), 9.22 (2H, s, $NH_2$) |
| **IIa** | 468 | 3386 (N–H), 2202 (C≡N), 1656 (C=O) | 1.28 (3H, t, 5-$\mathrm{CO_2CH_2}\mathit{CH_3}$), 1.35 (3H, t, 3-$\mathrm{CO_2CH_2}\mathit{CH_3}$), 2.69 (3H, s, $CH_3$), 4.25 (2H, q, 5-$\mathrm{CO_2}\mathit{CH_2}\mathrm{CH_3}$), 4.31 (2H, q, 3-$\mathrm{CO_2}\mathit{CH_2}\mathrm{CH_3}$), 7.38–7.55(5H, m, PhH), 9.29 (2 H, s, $NH_2$) |
| **IIb** | 421 | 3384 (N–H), 2203 (C≡N), 1662 (C=O) | 1.26 (3H, t, $\mathrm{CO_2CH_2}\mathit{CH_3}$), 2.63 (3H, s, $CH_3$), 4.26 (2H, q, $\mathrm{CO_2}\mathit{CH_2}\mathrm{CH_3}$), 7.57–7.72(5H, m, PhH), 9.75 (2H, s, $NH_2$) |
| **IIc** | 374 | 3383 (N–H), 2204 (C≡N) | 2.46 (3H, s, $CH_3$), 7.56–7.72(5H, m, PhH), 9.51 (2H, s, $NH_2$) |
| **IId** | 502 | 3411 (N–H), 2202 (C≡N), 1652 (C=O) | 1.27 (3H, t, 5-$\mathrm{CO_2CH_2}\mathit{CH_3}$), 1.29 (3H, t, 3-$\mathrm{CO_2\ CH_2}\mathit{CH_3}$), 2.56 (3H, s, $CH_3$), 4.24 (2H, q, 5-$\mathrm{CO_2}\mathit{CH_2}\mathrm{CH_3}$), 4.27 (2H, q, 3-$\mathrm{CO_2}\mathit{CH_2}\mathrm{CH_3}$), 7.52 (2H, d, 2,6-ArH-Cl), 7.63 (2H, d, 3,5-ArH-Cl), 9.14 (2H, s, $NH_2$) |
| **IIe** | 455 | 3394 (N–H), 2203 (C≡N), 1667 (C=O) | 1.28 (3H, t, $\mathrm{CO_2CH_2}\mathit{CH_3}$), 2.57 (3H, s, $CH_3$), 4.29 (2H, q, $\mathrm{CO_2}\mathit{CH_2}\mathrm{CH_3}$), 7.65 (2H, d, 2,6-ArH-Cl), 7.71 (2H, d, 3,5-ArH-Cl), 9.75 (2H, s, $NH_2$) |
| **IIf** | 408 | 3422 (N–H), 2206 (C≡N) | 2.46 (3H, s, $CH_3$), 7.65 (2H, t, 2,6-ArH-Cl), 7.71 (2H, d, 3,5-ArH-Cl), 9.53 (2H, s, $NH_2$) |
| **IIg** | 498 | 3422 (N–H), 2205 (C≡N), 1695 (C=O) | 1.27 (3H, t, 5-$\mathrm{CO_2CH_2}\mathit{CH_3}$), 1.35 (3H, t, 3-$\mathrm{CO_2CH_2}\mathit{CH_3}$), 2.69 (3H, s, $CH_3$), 3.85 (3H, s, $OCH_3$), 4.25 (2H, q, 5-$\mathrm{CO_2}\mathit{CH_2}\mathrm{CH_3}$), 4.31 (2H, q, 3-$\mathrm{CO_2}\mathit{CH_2}\mathrm{CH_3}$), 7.11 (2H, d, 3,5-ArH-$OCH_3$), 7.66 (2H, d, 2,6-ArH-$OCH_3$), 9.25 (2H, s, $NH_2$) |
| **IIh** | 451 | 3392 (N–H), 2210 (C≡N), 1656 (C=O) | 1.26 (3H, t, $\mathrm{CO_2CH_2}\mathit{CH_3}$), 2.58 (3H, s, $CH_3$), 3.86 (3H, s, $OCH_3$), 4.25 (3H, t, $\mathrm{CO_2}\mathit{CH_2}\mathrm{CH_3}$), 7.14 (2H, d, 3,5-ArH-$OCH_3$), 7.70(2H, t, 2,6-ArH-$OCH_3$), 9.25 (2H, s, $NH_2$) |
| **IIi** | 404 | 3431 (N–H), 2203 (C≡N) | 2.53 (3H, s, $CH_3$), 3.86 (3H, s, $OCH_3$), 7.69 (2H, d, 3,5-ArH-$OCH_3$), 7.73 (2H, d, 2,6-ArH-$OCH_3$), 9.49 (2H, s, $NH_2$) |

dye **I** is in the range 568 nm–583 nm in dimetylforamide, and in the range 516 nm–559 nm in $CHCl_3$. The absorption maxima of dyes **I** and **II** shifted apparently in dimethylforamide larger bathochromic than that of dye **Ia**, which is caused by less steric hindrance of the carboxylic acid ethyl ester group in the 3 position of the thiophene ring with phenyl group in the 4 position of the thiazole ring. By the way, the absorption maxima of dye **Ic** shifted apparently in $CHCl_3$ bigger 42 nm than that of dye **Ia**, but in dimetylforamide only shifted increase 13 nm, that might be the induced effect of both of acceptor cyano group in the 3 and 5 positions of the thiophene ring of dye **Ic**. Otherwise, Table 3 reveals that the $\Delta\lambda_{max}$ of absorption spectra of dye **Ib** shifted longer, 8 nm, in dimetylforamide than dyes **Ia** which results from the weak acceptor electric cyano group in the 3 position of the thiophene ring probably. It also reveals that the spectral shifts of dyes derived from coupler 2-amino-4-phenyl-thiophene, coupled with diazo components polysubstituted 2-aminothiophenes. It shows that dye **IIc**, due to an additional acceptor cyano group in the 3 and 5 positions of diazo components, result in more extensive electron delocalization of the thiophene ring. Table 3 shows that the $\Delta\lambda_{max}$ of absorption spectra is positive 20 nm in DMF. But the dye **IIb** have absorption maxima at longer wavelengths than dye **IIa** due to acceptor electric cyano group both in the 3 positions. The $\Delta\lambda_{max}$ of absorption spectra is positive 9 nm in DMF.

It was also observed that the absorption spectra of dyes **I** and **II** changed significantly in solvents with different polarity. Table 3 shows that dye **Ia** absorbs at 568 nm in dimethylformamide with dielectric constant (36.71). Replacement of solvent with lower polarity for



| Dyes | | R | $R^1$ | $R^2$ |
|---|---|---|---|---|
| I a | II a | $C_6H_5$ | $COOC_2H_5$ | $COOC_2H_5$ |
| I b | II b | $C_6H_5$ | $COOC_2H_5$ | CN |
| I c | II c | $C_6H_5$ | CN | CN |
| I d | II d | $C_6H_4Cl$-p | $COOC_2H_5$ | $COOC_2H_5$ |
| I e | II e | $C_6H_4Cl$-p | $COOC_2H_5$ | CN |
| I f | II f | $C_6H_4Cl$-p | CN | CN |
| I g | II g | $C_6H_4OMe$-p | $COOC_2H_5$ | $COOC_2H_5$ |
| I h | II h | $C_6H_4OMe$-p | $COOC_2H_5$ | CN |
| I i | II i | $C_6H_4OMe$-p | CN | CN |

Scheme 1.

Table 3
Absorption maxima spectra of dye derivatives **I** and **II**

| Dyes | DMF | $CH_3OH$ | | Acetone | | $CHCl_3$ | |
|---|---|---|---|---|---|---|---|
| | $\lambda_{max}$ (log $\varepsilon$) | $\lambda_{max}$ (log $\varepsilon$) | $\Delta\lambda_{max}$ [a] | $\lambda_{max}$ (log $\varepsilon$) | $\Delta\lambda_{max}$ [a] | $\lambda_{max}$ (log $\varepsilon$) | $\Delta\lambda_{max}$ [a] |
| **Ia** | 568(4.62) | 534(4.42) | −34 | 532(4.32) | −36 | 516(4.34) | −52 |
| **Ib** | 576(4.81) | 547(4.63) | −29 | 545(4.50) | −31 | 536(4.47) | −40 |
| **Ic** | 581(4.88) | 564(4.70) | −17 | 562(4.65) | −19 | 558(4.31) | −23 |
| **Id** | 557(4.49) | 529(4.48) | −28 | 526(4.35) | −31 | 511(4.29) | −43 |
| **Ie** | 571(4.75) | 542(4.46) | −29 | 542(4.45) | −29 | 526(4.44) | −45 |
| **If** | 579(4.56) | 555(4.35) | −28 | 551(4.36) | −24 | 550(4.22) | −29 |
| **Ig** | 570(4.62) | 542(4.41) | −28 | 540(4.38) | −30 | 528(4.41) | −42 |
| **Ih** | 577(4.67) | 558(4.43) | −19 | 554(4.42) | −23 | 547(4.40) | −30 |
| **Ii** | 583(4.56) | 565(4.53) | −18 | 562(4.45) | −21 | 559(4.38) | −24 |
| **IIa** | 600(4.64) | 535(4.56) | −65 | 533(4.54) | −67 | 523(4.57) | −77 |
| **IIb** | 609(4.75) | 555(4.63) | −54 | 552(4.57) | −57 | 538(4.66) | −71 |
| **IIc** | 620(4.70) | 565(4.59) | −55 | 563(4.53) | −57 | 559(4.55) | −61 |
| **IId** | 596(4.58) | 560(4.54) | −36 | 531(4.48) | −65 | 529(4.36) | −67 |
| **IIe** | 606(4.67) | 563(4.58) | −43 | 550(4.55) | −56 | 541(4.44) | −65 |
| **IIf** | 619(4.46) | 566(4.50) | −53 | 555(4.46) | −64 | 552(4.34) | −67 |
| **IIg** | 607(4.56) | 561(4.36) | −46 | 542(4.36) | −65 | 529(4.38) | −78 |
| **IIh** | 611(4.47) | 564(4.45) | −47 | 560(4.33) | −51 | 559(4.36) | −52 |
| **IIi** | 619(4.58) | 571(4.53) | −48 | 566(4.51) | −53 | 560(4.34) | −59 |

Note: (1) The $\varepsilon_r$ value of solvents: DMF = 36.71, $CH_3OH$ = 32.66, $CH_3COCH_3$=20.56, $CHCl_3$ = 4.81. (2) Unit of $\lambda_{max}$ and $\Delta\lambda_{max}$: nm.

[a] Relative to corresponding DMF.

Table 4
Spectral shifts of coupling components

| Dyes | $R^1$ | $R^2$ | $R^3$ | $\Delta\lambda_{max}$ (nm) | | | |
|---|---|---|---|---|---|---|---|
| | | | | DMF | Methanol | Acetone | Chloroform |
| **Ia(IIa)** | COOEt | COOEt | Ph | −32 | −1 | −1 | −7 |
| **Ib(IIb)** | COOEt | CN | Ph | −33 | −8 | −7 | −2 |
| **Ic(IIc)** | CN | CN | Ph | −39 | −1 | −1 | −1 |
| **Id(IId)** | COOEt | COOEt | Ph-Cl | −29 | −31 | −5 | −15 |
| **Ie(IIe)** | COOEt | CN | Ph-Cl | −35 | −21 | −8 | −15 |
| **If(IIf)** | CN | CN | Ph-Cl | −40 | −11 | −4 | −2 |
| **Ig(IIg)** | COOEt | COOEt | Ph-OMe | −37 | −19 | −2 | −1 |
| **Ih(IIh)** | COOEt | CN | Ph-OMe | −34 | −6 | −6 | −12 |
| **Ii(IIi)** | CN | CN | Ph-OMe | −36 | −6 | −4 | −1 |

$\Delta\lambda_{max}$: $\lambda_{max}$ (**I**)−$\lambda_{max}$ (**II**). $\lambda_{max}$: see Table 3.

dye **Ia**, leads to a hypsochromic shift of $\Delta\lambda_{max} = 34$ nm in methanol (32.66), $\Delta\lambda_{max} = 36$ nm in acetone (20.56) and $\Delta\lambda_{max} = 52$ nm in chloroform (4.81). Dye **Ia** shows a large hypsochromic shift as the solvent polarity is decreased. Similar result is also observed for dyes **Id**, **Ig**, **IIa**, **IId** and **IIg**. The $\Delta\lambda_{max}$ values of these dyes shifted in the range from 17 nm to 78 nm in solvents with different polarity. It was also observed from Table 4 that dyes **Ia**–**Ic** possessing a thiazole coupler, absorb hypsochromically compared to the dyes **IIa**–**IIc** involving a thiophene coupler, in different solvent. Especially, the variation of spectral shifts dyes **Ia** relative to **IIa** in DMF reveals apparently large shift result in the induced effect of thiophene derivatives is obvious than thiazole derivatives probably. The electronic spectra of these dyes were found to be strongly solvent dependent and increased a regular variation with the dielectric constants of the solvents in the sequence DMF (36.71) > $CH_3OH$ (32.66) > $CH_3COCH_3$ (20.56) > $CHCl_3$ (4.81).

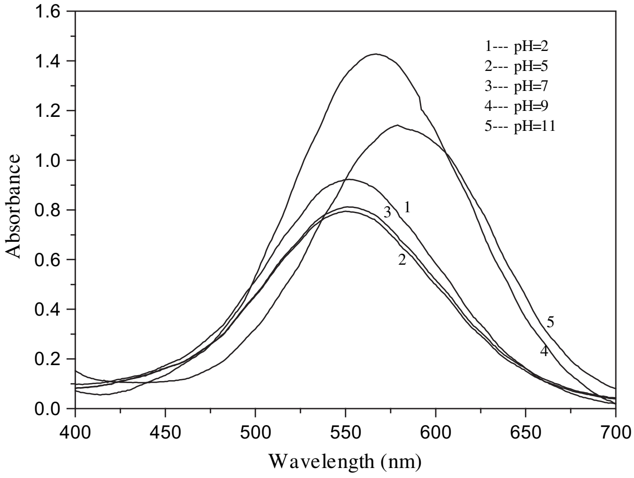


Fig. 1. Absorption spectra of dye **Ib** in solution of different pH (methanol).

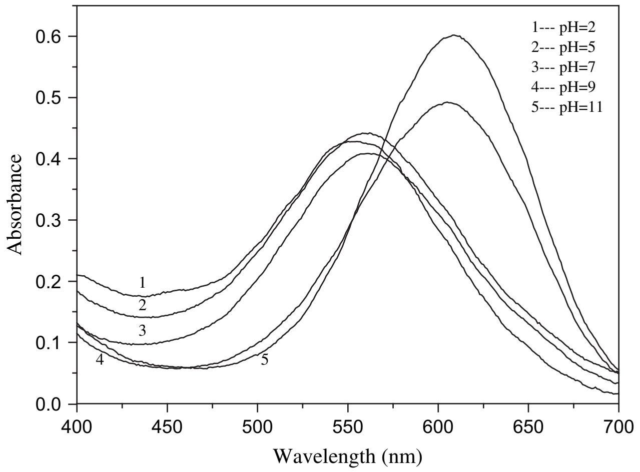


Fig. 2. Absorption spectra of dye **IIb** in solution of different pH (methanol).

The absorption spectra of dyes **Ia**–**Ic**, **IIa**–**IIc**, **Ie**, **IIe**, **Ih**, and **IIh** were recorded in different pH; the results are summarized in Tables 3 and 4. Figs. 1 and 2 show the effect of pH on the shape and the $\lambda_{max}$ of dyes **Ib** and **IIb**, respectively. The visible absorption spectra of the dyes were dependent on pH slightly, which illustrate a regular variation with different acid and base, respectively. The $\lambda_{max}$ of the dyes showed large bathochromic shifts when a small amount of base was added to each of the dye solutions in methanol. It also showed that the maximum visible absorptions of dyes **Ia**–**Ic** below pH = 7.0 (adjusted with 10% aqueous hydrochloric acid or acetic acid) with a slightly variation; but the absorption maxima of pH between 9.0 and 11.0 (adjusted with 10% aqueous sodium hydroxide or sodium acetate) result in large bathochromic shifs ($\Delta\lambda = 21–23$ nm) corresponding to the absorption maxima of pH = 2.0, which was caused by amino group protonation of dyes **Ia**–**Ic** probably. In the meanwhile, the trend of absorption spectral variation of dyes **IIa**–**IIc** in different pH is similar to that of dyes **Ia**–**Ic**. In comparison to dyes **Ia**, **Ib** and **Ic** with variation of pH as shown in Table 5, we observe the following order of absorption maxima of dyes: **Ic** (560) > **Ib** (551) > **Ic** (535) in pH = 7.0, which was caused by the both of the electron acceptor cyano groups in the 2 and 4 positions of the diazo moiety. As can be seen from Table 6, the order of absorption maxima of dyes: **Ih** (556) > **Ib** (551) > **Ie** (550) in pH = 7.0, was caused by the different substitute of phenyl group in the 4 position of the coupling moiety. Table 7 demonstrates that the spectral shifts of dyes **IIa**–**IIc** were more bathochromic than dyes **Ia**–**Ic** ($\Delta\lambda = 2–39$ nm) which may be the result of the thophene ring nature of dyes **IIa**–**IIc** and the acceptor cyano group present in the 3 position of the coupling moiety. Moreover, the trend of variation of $\lambda_{max}$ for dyes **IIb**, **IIe**, and **IIh** is similar to dyes **Ib**, **Ie**, and **Ih**; the variation of $\lambda_{max}$ of those dyes with pH below 7.0 was slightly changed and apparently changed in pH range 9.0–11.0 under the different substitutes effect in those of dyes. Also, the spectral shifts of dyes **Ib**, **Ie**, and **Ih** and **IIb**, **IIe**, and **IIh** reveal that dyes **IIb**, **IIe**, and **IIh** were more bathochromic than dyes **Ib**, **Ie**, and **Ih** ($\Delta\lambda = 3–46$ nm) as shown in Table 8.

Table 5
Absorption maxima of dyes **Ia**–**Ic** and **IIa**–**IIc** in methanolic solution of different pHs

| Dyes | pH | | | | |
|---|---|---|---|---|---|
| | 2.0 | 5.0 | 7.0 | 9.0 | 11.0 |
| **Ia** | 533 | 533 | 535 | 554 | 557 |
| **Ib** | 552 | 550 | 551 | 567 | 569 |
| **Ic** | 558 | 558 | 560 | 574 | 579 |
| **IIa** | 536 | 540 | 540 | 578 | 579 |
| **IIb** | 555 | 562 | 561 | 605 | 608 |
| **IIc** | 560 | 566 | 567 | 611 | 612 |

Table 6
Absorption maxima of dyes **Ib**, **Ie**, **Ih** and **IIb**, **IIe**, **IIh** in methanolic solution of different pHs

| Dyes | pH | | | | |
|---|---|---|---|---|---|
| | 2.0 | 5.0 | 7.0 | 9.0 | 11.0 |
| **Ib** | 552 | 550 | 551 | 567 | 569 |
| **Ie** | 547 | 548 | 550 | 564 | 565 |
| **Ih** | 553 | 554 | 556 | 573 | 575 |
| **IIb** | 555 | 562 | 561 | 605 | 608 |
| **IIe** | 553 | 555 | 559 | 606 | 606 |
| **IIh** | 567 | 565 | 563 | 610 | 611 |

## 4. Conclusion

3,5-Substituted-4-methyl-2-aminothiophenes were diazotized and coupled with 4-aryl-2-aminothiazoles and 4-aryl-2-aminothiophenes, respectively, to produce red to blue hetarylazo dyes. The absorption spectra of these dyes are found to exhibit a strong solvent dependence that varies with the dielectric constants of the solvents. The absorption maxima of these dyes showed bathochromic effects when dissolved in DMF. The spectral

Table 7
Spectral shifts of dyes **Ia**–**Ic** and **IIa**–**IIc** in different pHs

| Dyes | $\Delta\lambda$ | | | | |
|---|---|---|---|---|---|
| pH | 2.0 | 5.0 | 7.0 | 9.0 | 11.0 |
| **Ia IIa** | +3 | +7 | +5 | +24 | +22 |
| **Ib IIb** | +3 | +12 | +10 | +38 | +39 |
| **Ic IIc** | +2 | +8 | +7 | +37 | +33 |

$\Delta\lambda$: $\lambda_{max}$ (**II**)−$\lambda_{max}$ (**I**).

Table 8
Spectral shifts of dyes **Ib**, **Ie**, **Ih** and **IIb**, **IIe**, **IIh** in different pHs

| Dyes | $\Delta\lambda$ | | | | |
|---|---|---|---|---|---|
| pH | 2.0 | 5.0 | 7.0 | 9.0 | 11.0 |
| **Ib IIb** | +3 | +12 | +10 | +38 | +39 |
| **Ie IIe** | +6 | +7 | +9 | +42 | +41 |
| **Ih IIh** | +14 | +11 | +7 | +37 | +46 |

$\Delta\lambda$: $\lambda_{\max}$ (**II**)−$\lambda_{\max}$ (**I**).

shifts of dyes derived from coupler 4-aryl-2-aminothiophenes and diazo components 3,5-substituted-4-methyl-2-aminothiophenes were larger than those of coupled 4-aryl-2-aminothiazoles. The maximum visible absorptions of dyes **I** and **II** below pH = 7.0 reveal slight variation; but the absorption maxima of pH between 9.0 and 11.0 result in large bathochromic shifts, which may be caused by amino group protonation of dyes **I** and **II**.

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