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A facile syntheses and absorption characteristics 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

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Abstract

The synthesis of 2-amino-4-(*p*-substituted)phenyl-thiazole derivatives has been carried out by treatment of substituted acetophenones with thiourea and iodide as catalyst. Diazotization and coupling with 2-pyridone and 5-pyrazolone derivatives gave a series of bis-hetaryl monoazo dyes. The structures of new azo dyes were confirmed by analytical and spectral data. The solvatochromism of dyes was evaluated with respect to spectroscopic properties in various solvents.

Keywords: 2-Aminothiazole; Pyridone; Pyrazolone; Bis-hetarylazo dyes

1. Introduction

Pyridones and pyrazolones as coupling components have been shown to be important colorants for yellow to orange dyes in industrial applications [1]. Moreover, *N*-substituted pyridone azo disperse dyes, which were derived from benzenoid derivatives as coupling components, show good color strength, luminous colors and excellent light fastness [2–4]. It is further reported that pyrazolone derivatives as coupling component can be used to synthesize yellow 4-arylazo pyrazolone dyes [5]. Both pyridones and pyrazolones have found wide utilization in textile industry for the formation of azo and azamethine dyes [6–10]. The use of heterocyclic aromatic amines for improving tinctorial strength has been well established. It has also been reported that dyes made using 2-aminothiazole compounds which possess different substituents in the 4-position of analogous derivatives as diazo components tend to show bathochromic

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shifts when compared to analogous dyes derived from benzenoid compounds [11–15].

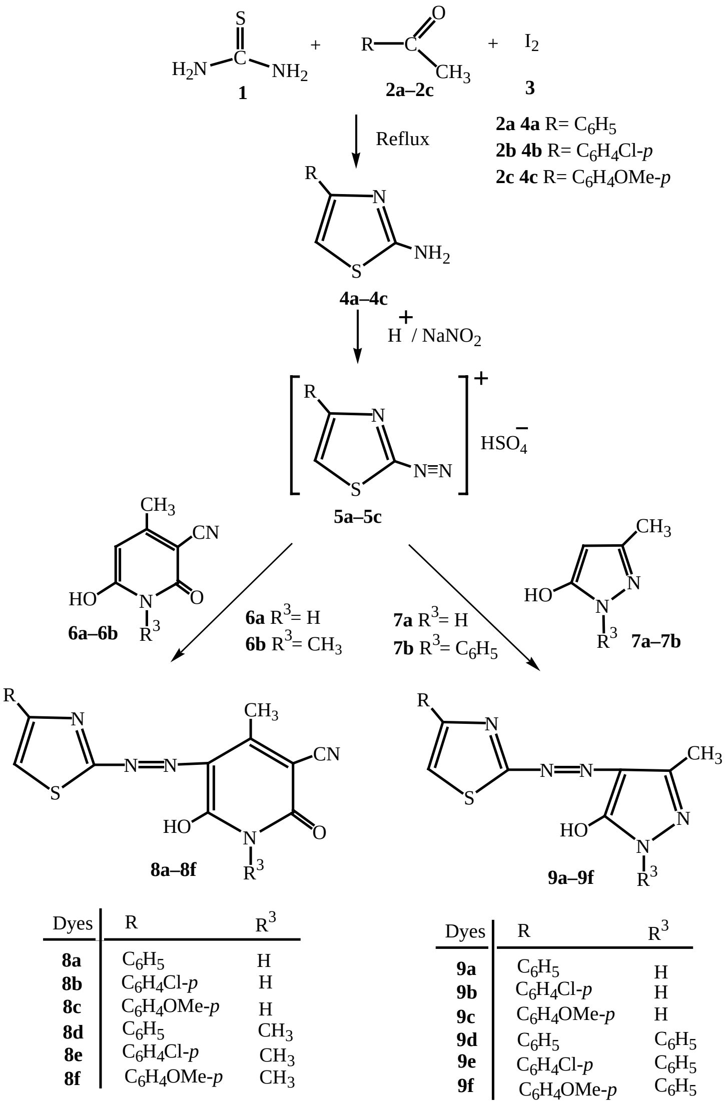
As in the previous study, we report here the syntheses of some new bis-hetaryl monoazo dyes using 4-(*p*-substituted)phenyl-2-aminothiazole compounds as diazo component and evaluate their electronic spectra in various solvents for the color–structure relationships in such dyes. The chemical structures of these dyes are presented in formulas **8**, **9** (Scheme 1).

2. Results and discussion

2.1. Preparation of diazo components *4a–4c* and coupling components *6a*, *6b* and *7a*, *7b*

The routes used for the syntheses of diazo components and bis-hetaryl monoazo dyes are shown in Scheme 1.

The diazo components, 4-phenyl-2-aminothiazole **4a** and its derivatives **4b**, **4c** that were used as



Dyes	R	R^3
8a	C_6H_5	H
8b	C_6H_4Cl-*p*	H
8c	C_6H_4OMe-*p*	H
8d	C_6H_5	CH_3
8e	C_6H_4Cl-*p*	CH_3
8f	C_6H_4OMe-*p*	CH_3

Dyes	R	R^3
9a	C_6H_5	H
9b	C_6H_4Cl-*p*	H
9c	C_6H_4OMe-*p*	H
9d	C_6H_5	C_6H_5
9e	C_6H_4Cl-*p*	C_6H_5
9f	C_6H_4OMe-*p*	C_6H_5

Scheme 1.

starting materials for the syntheses of bis-hetaryl monoazo dyes, were obtained from the cyclization of a mixture of *p*-phenyl-substituted acetophenone **2a**–**2c**, thiourea **1** and iodide **3**. The preparations of the coupling components, both 2-pyridones **6a**, **6b** and 5-pyrazolones **7a**, **7b**, were described in the previous reports [6,1]. 2-Pyridone compounds **6a**, **6b** were obtained directly from the reaction of a mixture of ethyl acetoacetate, ethyl cyanoacetate and ammonia water or methylamines in ethanol with piperidine as catalyst. Similarly, a mixture of 1:1 ratio of ethyl acetoacetate and hydrazine derivatives was refluxed in ethanol in the presence of catalytic amounts of piperidine for 6 h and underwent via β-ketoester intramolecular condensation to give the corresponding 5-pyrazolone compounds **7a**, **7b**. The structures of diazo components **4a**–**4c** were established by elemental analysis and spectral data. The ^{1}H-NMR spectra of diazo components **4a**–**4c** showed a 1H singlet of methine proton in the 5-position of thiazole ring at $\delta = 7.01$, 7.06 and 6.83 ppm, respectively, and a 2H singlet at $\delta = 7.20$, 7.19 and 7.07 ppm for amino protons, respectively [16]. Compound **4a** showed a broad signal of 5H multiplet at $\delta = 7.26$–7.79, attributed to the phenyl protons in the 4-position of thiazole ring; compounds **4b** and **4c** showed 2H doublet signals at $\delta = 7.41$ and 7.72 ppm, attributed to the 2,6 protons of aryl group in 4-position of thiazole, and 2H doublet signals at $\delta = 7.80$ and 6.92 ppm, attributed to the 3,5 protons of aryl group in 4-position of thiazole, respectively. Compound **4c** also showed a 3H singlet signal at $\delta = 3.76$ ppm for methoxy protons. All data confirmed the chemical structure of the thiazole diazo components. Characterization data of 4-aryl-2-aminothiazole derivatives **4a**–**4c** are summarized in Tables 1 and 2. The structure and characterization data of the coupling components 2-pyridone derivatives **6a**, **6b**, and 5-pyrazolone derivatives **7a**, **7b** were found in literature [6,1].

*2.2. Preparation of bis-hetaryl monoazo dyes **8** and **9***

As shown in Scheme 1, two series of some new bis-hetaryl monoazo dyes **8a**–**8f** and **9a**–**9f** based on 4-aryl-2-aminothiazoles as diazo components with both coupling components, 2-pyridone compounds **6a**, **6b** and 5-pyrazolone compounds **7a**, **7b**, were prepared. 4-(*p*-Substituted)phenyl-2-aminothiazoles **4a**–**4c** containing various substituents

Table 1
Characterization data for intermediates and dye derivatives **4a**–**4c**, **8a**–**8f** and **9a**–**9f**

Compound	M.p.[a] (°C)	Yield[b] (%)	Molecular formula	Elemental analysis (%)			
				Calc./(found)			
				C	H	N	S
4a	152–153	65	$C_9H_8N_2S$	61.34 (61.38)	4.58 (4.47)	15.90 (15.98)	18.19 (18.12)
4b	154–155	78	$C_9H_7ClN_2S$	51.31 (51.27)	3.35 (3.39)	13.30 (13.28)	15.22 (15.28)
4c	207–208	85	$C_{10}H_{10}N_6OS$	58.27 (58.21)	4.89 (4.95)	13.58 (13.54)	15.54 (15.59)
8a	312–314	93	$C_{16}H_{11}N_5O_2S$	56.97 (56.92)	3.29 (3.24)	20.76 (20.83)	9.50 (9.53)
8b	265–267	92	$C_{16}H_{10}ClN_5O_2S$	51.69 (51.62)	2.71 (2.78)	18.84 (18.88)	8.62 (8.55)
8c	180–182	72	$C_{17}H_{13}N_5O_3S$	55.58 (55.53)	3.57 (3.59)	19.06 (19.01)	8.73 (8.76)
8d	280–282	86	$C_{17}H_{13}N_5O_2S$	58.11 (58.07)	3.73 (3.67)	19.93 (19.99)	9.12 (9.06)
8e	332–334	94	$C_{17}H_{12}ClN_5O_2S$	52.92 (52.79)	3.13 (3.15)	18.15 (18.07)	8.31 (8.34)
8f	150–152	78	$C_{18}H_{15}N_5O_3S$	56.68 (56.75)	3.96 (3.95)	18.36 (18.27)	8.41 (8.36)
9a	178–180	60	$C_{13}H_{11}N_5OS$	54.73 (54.67)	3.89 (3.85)	24.55 (24.59)	11.24 (11.29)
9b	168–170	62	$C_{13}H_{10}ClN_5OS$	48.83 (48.91)	3.15 (3.11)	21.90 (21.96)	11.09 (11.03)
9c	202–204	55	$C_{14}H_{13}N_5O_2S$	53.32 (53.25)	4.15 (4.19)	22.21 (22.28)	10.17 (10.24)
9d	220–222	62	$C_{19}H_{15}N_5OS$	63.14 (63.06)	4.18 (4.25)	19.38 (19.27)	8.87 (8.81)
9e	184–186	89	$C_{19}H_{14}ClN_5OS$	57.65 (57.60)	3.56 (3.51)	17.69 (17.64)	8.10 (8.14)
9f	152–154	64	$C_{20}H_{17}N_5O_2S$	61.37 (61.33)	4.38 (4.41)	17.89 (17.82)	8.19 (8.24)

[a] Recrystallized from ethanol.

[b] Yield of crude product.

Table 2
Spectral data of intermediates and dye derivatives **4a–4c**, **8a–8f** and **9a–9f**

Dyes	MS (m/e, M$^+$)	IR(KBr) ν (cm^{-1})	^{1}H-NMR (DMSO-d_6) δ (ppm)
4a	175	3325, 3421 (NH$_2$)	7.01 (1H, s, CH), 7.20 (2H, s, NH$_2$), 7.26–7.79 (5H, m, PhH)
4b	210	3319, 3409 (NH$_2$)	7.06 (1H, s, CH), 7.19 (2H, s, NH$_2$), 7.41 (2H, d, 2,6-ArH), 7.80 (2H, d, 3,5-ArH)
4c	206	3318, 3425 (NH$_2$), 1254 (C–O)	3.76 (3H, s, OCH$_3$), 6.83 (1H, s, CH), 6.92 (2H, d, 3,5-ArH), 7.72 (2H, d, 2,6-ArH), 7.07 (2H, s, NH$_2$)
8a	337	3329 (N–H), 2211 (C≡N), 1665 (C=O)	2.73 (3H, s, pyridone-CH$_3$), 7.31–7.99 (5H, m, PhH of thiazole), 7.78 (1H, s, CH), 7.95 (1H, s, NH), 10.56 (1H, s, OH)
8b	372	3352 (N–H), 2210 (C≡N), 1671 (C=O)	2.72 (3H, s, pyridone-CH$_3$), 7.35–7.96 (4H, m, PhH of thiazole), 7.97 (1H, s, CH), 7.96 (1H, s, NH), 10.64 (1H, s, OH)
8c	367	3354 (N–H), 2213 (C≡N), 1663 (C=O)	2.71 (3H, s, pyridone-CH$_3$), 3.82 (3H, s, OCH$_3$), 6.96–7.89 (4H, m, PhH of thiazole), 7.18 (1H, s, CH), 7.85 (1H, s, NH), 10.70 (1H, s, OH)
8d	351	2211 (C≡N), 1658 (C=O)	2.71 (3H, s, pyridone-CH$_3$), 3.65 (3H, s, N-CH_3), 7.33–7.98 (5H, m, PhH of thiazole), 7.78 (1H, s, CH), 10.65 (1H, s, OH)
8e	385	2210 (C≡N), 1666 (C=O)	2.72 (3H, s, pyridone-CH$_3$), 3.63 (3H, s, N-CH_3), 7.31–7.90 (4H, m, PhH of thiazole), 7.65 (1H, s, CH), 10.71 (1H, s, OH)
8f	381	2211 (C≡N), 1658 (C=O)	2.69 (3H, s, pyridone-CH$_3$), 3.70 (3H, s, N-CH_3), 3.82 (3H, s, OCH$_3$), 6.96–7.89 (4H, m, PhH of thiazole), 7.17 (1H, s, CH), 10.72 (1H, s, OH)
9a	285	3315 (N–H)	2.29 (3H, s, pyrazolone-CH$_3$), 7.23–7.93 (5H, m, PhH of thiazole), 7.80 (1H, s, CH), 11.16 (1H, s, NH)
9b	319	3315 (N–H)	2.29 (3H, s, pyrazolone-CH$_3$), 7.44–7.95 (4H, m, PhH of thiazole), 7.87 (1H, s, CH), 11.37 (1H, s, NH)
9c	315	3315 (N–H)	2.30 (3H, s, pyrazolone-CH$_3$), 3.83 (3H, s, OCH$_3$), 7.00–7.95 (4H, m, PhH of thiazole), 7.77 (1H, s, CH), 11.25 (1H, s, NH)
9d	361	1594 (=CH)	2.28 (3H, s, pyrazolone-CH$_3$), 7.22–7.92 (5H, m, PhH of pyrazolone), 7.79 (1H, s, CH)
9e	396	1588 (=CH)	2.28 (3H, s, pyrazolone-CH$_3$), 7.23–7.92 (4H, m, PhH of pyrazolone), 7.80 (1H, s, CH)
9f	391	1593 (=CH)	2.29 (3H, s, pyrazolone-CH$_3$), 3.82 (3H, s, OCH$_3$), 6.96–7.97 (4H, m, PhH of pyrazolone), 7.80 (1H, s, CH)

at the *para*-position of phenyl group in the thiazole ring were diazotized using nitrosyl sulphuric acid at 0–5 °C. Before the end of diazotization, the sulphamic acid was added to diazonium salt solution in order to remove the excess nitrite ion, and the solutions of diazonium salt **5a–5c** were then added to an aqueous diluted sodium carbonate solution of the coupling components **6a** and **6b**. To complete the coupling reaction, the pH value of the mixture was adjusted to about 5–6 by addition of 40% sodium hydroxide solution to improve precipitation of the dyes. The presence of acetic acid prevents an abrupt increase in pH [17]. The dyes **8a–8f** were precipitated after the addition of diazonium solution and filtered, washed and air-dried. The syntheses of dyes **9a–9f** are similar to those for the dyes **8a–8f** except that the coupling components are replaced by 5-pyrazolone intermediates **7a** and **7b**. The physical properties and characterization data for dyes **8a–8f** and **9a–9f** are listed in Tables 1 and 2, respectively.

2.3. Spectral properties of the bis-hetaryl monoazo dyes 8 and 9

The chemical structures of bis-hetaryl monoazo dyes **8** and **9** were established by elemental analysis and spectral data. The IR spectra of the dyes **8a–8f** showed characteristic vibrational absorption bands at 1658–1671 cm^{-1} for the carbonyl group and at 2210–2213 cm^{-1} for the cyano group. No typical absorption bands were observed in the IR spectrum of dyes **9a–9f**. The ^{1}H-NMR spectra of dyes **8a–8f** and **9a–9f** were recorded in

DMSO-d_6. Dyes **8a–8f** and **9a–9f** showed 1H singlet at $\delta = 7.17-7.97$ ppm, which can be attributed to methine proton of thioazole ring at the 5-position, respectively. A multiplet at $\delta = 7.31-7.99$ ppm is due to 5H phenyl protons of dyes **8a**, **8d**, **9a** and **9d** at the 4-position of the thiazole ring. Dyes **8d–8f** showed 3H singlet at $\delta = 3.63-3.70$ ppm, attributed to the 1-methyl protons in the pyridone ring. Dyes **9a–9c** showed 1H singlet at $\delta = 11.16-11.37$ ppm, attributed to the NH proton of the pyrazolone ring at the 1-position. Dyes **9d–9f** showed multiplet at $\delta = 6.96-7.97$ ppm, attributed to the five protons of phenyl group of pyrazolone ring at the 1-position. In the ^{1}H-NMR spectrum of dyes **8c**, **8f**, **9c** and **9f**, a 3H singlet was observed at $\delta = 3.82-3.83$ ppm, which can be attributed to *p*-methoxy protons of phenyl group in the thiazole ring at the 4-position [16,18,19]. All data confirmed the expected structure of the hetaryl monoazo dyes.

*2.4. Solvatochromic properties of the bis-hetaryl monoazo dyes **8** and **9***

Visible absorption spectra data, molar extinction coefficients and electronic effects of substituents in various solvents, viz dimethylformamide, methanol, acetone and chloroform for the bis-hetaryl monoazo dyes **8a–8f** and **9a–9f** are listed in Tables 3–5, respectively. The solvatochromic properties of these dyes in solvents with different polarities were systematically investigated [20]. The absorption spectra of some dyes **8** and **9** in acetone are shown in Figs. 1–3. It can be seen in Fig. 1 and Table 3 that the visible absorption maxima of these dyes very clearly depend on the properties of solvents and increase with increasing polarities of solvents in the order: chloroform < acetone < methanol < dimethylformamide. The influences on the visible absorption maxima of dyes **8** and **9** by substituents at the ring position of coupling components have been evaluated. As shown in Tables 4 and 5, it was found that substituents such as the methyl group at the 1-position of pyridone ring in **8d–8f**, and the phenyl group at the 1-position of pyrazolone ring in **9d–9f** had only a slight influence on the absorption maxima as compared to those of compounds **8a–8c** and **9a–9c**, respectively. It can also be seen in Tables 3 and 5 that dyes **9a–9c**, each with a pyrazolone coupler **7a** attached, absorbed hypsochromically and the molar extinction coefficients were lower as compared to dyes **8a–8c**, each with a pyridone coupler **6a** attached, in solvents with different polarities due to the fact that the ring of pyridone residue possesses more π-electron density than that of pyrazolone moiety.

Table 3
Visible absorption spectra and spectral shifts in various solvents for dyes **8** and **9**

Dyes	DMF (36.71)		MeOH (32.66)			Acetone (20.56)			Chloroform (4.81)		
	λ_{max}	$\varepsilon_{max} \times 10^{-4}$	λ_{max}	$\varepsilon_{max} \times 10^{-4}$	$\Delta\lambda_{max}$	λ_{max}	$\varepsilon_{max} \times 10^{-4}$	$\Delta\lambda_{max}$	λ_{max}	$\varepsilon_{max} \times 10^{-4}$	$\Delta\lambda_{max}$
8a	485	2.14	465	2.39	−20	457	1.91	−28	456	1.95	−29
8b	482	2.45	461	1.82	−21	444	1.99	−38	444	2.19	−38
8c	488	2.34	469	2.39	−19	459	2.19	−29	457	2.09	−31
8d	490	2.24	472	2.09	−18	469	1.95	−21	468	1.86	−22
8e	485	2.69	464	1.95	−21	455	2.04	−30	454	1.74	−31
8f	494	1.95	473	2.29	−21	470	2.09	−24	469	1.95	−25
9a	475	2.09	450	1.86	−25	434	1.82	−41	429	1.66	−46
9b	475	1.66	446	1.91	−29	431	1.74	−44	427	1.51	−48
9c	477	1.86	452	1.74	−25	440	1.82	−37	432	1.58	−45
9d	477	1.47	454	1.66	−23	445	1.58	−32	442	1.62	−35
9e	476	1.38	450	1.35	−26	442	1.78	−34	430	1.45	−46
9f	478	1.45	456	1.74	−22	447	1.86	−31	445	1.69	−33

$\Delta\lambda_{max}$: Solvents relative to dimethylformamide (DMF).
(ε_r): Dielectric constant.

Table 4
Spectral shifts influence by substituents on the ring of diazo components

Dyes	R	R^1	$\Delta\lambda_{max}$ (nm)			
			DMF	Methanol	Acetone	Chloroform
8a	Ph	H	(485)	(465)	(457)	(456)
8b	PhCl-*p*	H	−3	−4	−13	−1
8c	PhOMe-*p*	H	+3	+4	+2	+1
8d	Ph	Me	+5	+7	+12	+12
9a	Ph	H	(475)	(450)	(434)	(429)
9b	PhCl-*p*	H	0	−4	−3	−2
9c	PhOMe-*p*	H	+2	+2	+6	+3
9d	Ph	Ph	+2	+4	+11	+13

$\Delta\lambda_{max}$: Dyes **8b–8d** and **9b–9d** relative to the corresponding dyes **8a** and **9a**, respectively.
(λ_{max}): Values of λ_{max} for **8a** and **9a** in various solvents.
Values of λ_{max}: see Table 3.

The absorption maxima for dyes **8a–8c** were in the range of 482 to 488 nm in dimethylformamide, whereas the analogous dyes **8d–8f**, having an additional electron donating group (methyl) in the 1-position of 2-pyridone ring **6b**, showed the absorption maxima in the range of 485 to 494 nm in the same solvent, that corresponded to bathochromic shifts in the range of positive 3 to 6 nm (Table 5). Replacement of the 2-pyridone ring (compounds **6a**, **6b**) in dyes **8a–8f** by 5-pyrazolone ring (compounds **7a**, **7b**), as in dyes **9a–9f**, resulted in a displacement of the absorption maxima 475–478 nm in dimethylformamide. Dyes **9d–9f**, with the introduction of an electron-rich phenyl group to the 1-position of pyrazolone ring, showed the absorption maxima in the range of 476 to 478 nm, which corresponded to only additional bathochromic shifts of positive 1 nm (Table 5) when compared with analogous dyes **9a–9c**, of which the absorption maxima were in the range of 475 to 477 nm, in the same solvent. Fig. 2 shows the absorption spectra of dyes **8a**, **8d**, **9a** and **9d** in acetone. The absorption maxima of dyes **8** show bathochromic shift compared to dyes **9**. But it was also observed that the $\Delta\lambda_{max}$ values of dyes **8e**, **8f**, **9e** and **9f** showed larger spectral shift in low polar solvents than in high polar solvents, as shown in Table 5. The effects of substituents at the ring of diazo components (compounds **5a–5c**) were also studied. Fig. 3 shows the absorption spectra of dyes **8a–8c** in acetone. The introduction of a methoxy group into the dye **8a** at the *p*-position of phenyl group in the thiazole ring at 4-position giving dye **8c** results in a small bathochromic shift, attributed to the electron donating group (methoxy) that enhance the electron density of phenyl group. Dye **8c** shows the absorption maxima at longer wavelength than the corresponding dye **8a**. The $\Delta\lambda_{max}$ value of dye **8c** is positive 2 nm wavelengths in acetone compared to dye **8a**, but the $\Delta\lambda_{max}$ value of dye **8b** is negative 3 nm wavelengths shorter than dye **8a** in the same solvent; this is thought to be due to weaker effective electron acceptor (chloro), which was presented at the same position as in dye **8c**. Dye **9a** absorbed visible absorption maxima at 485 nm in dimethylformamide (dielectric constant 36.71). Replacement of dimethylformamide by solvents of lower polarities, viz methanol (32.66), acetone (20.56) and chloroform (4.81) [21], led to a hypsochromic shift of absorption maxima. Dye **8a** shows a large hypsochromic shift as the solvent polarity is decreased. Similar results were also observed for dyes **8d**, **9a** and **9d**. The $\Delta\lambda_{max}$ values of these dyes shifted in the range of 18 to 48 nm in solvents with different polarity. It was also observed that dyes **9a–9c**, possessing a pyrazolone coupler **7a**, absorbed hypsochromically as compared to dyes **8a–8c**, involving a pyridone coupler **6a**, in different solvents as

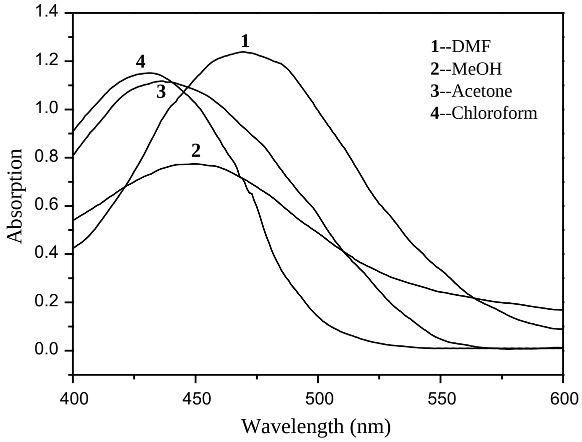


Fig. 1. Absorption spectra of dyes **9a** in various solvents: 1, DMF; 2, Methanol; 3, Acetone; 4, Chloroform ([Dye]: 1×10^{-5} M).

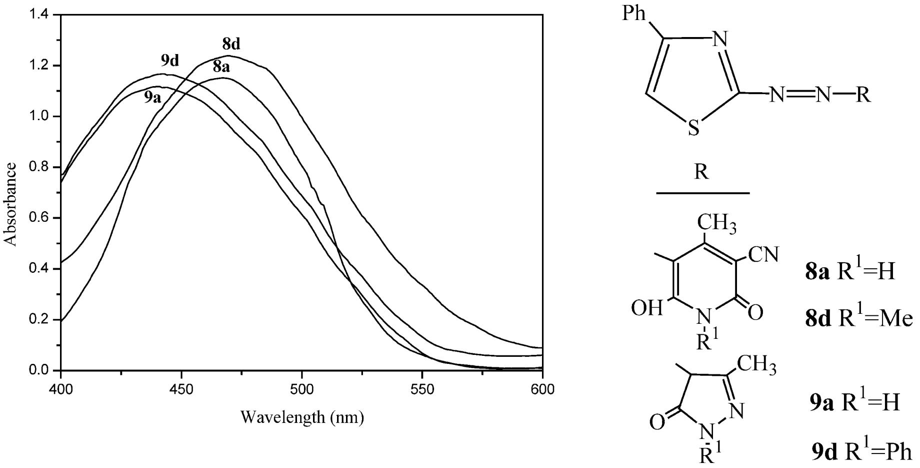


Fig. 2. Absorption spectra of dyes **8a**, **8d**, **9a** and **9d** in acetone (1×10^{-5} M).

shown in Table 5 ($\Delta\lambda_{max}$**8a**(**9a**) = 10–27 nm, $\Delta\lambda_{max}$ **8b**(**9b**) = 7–17 nm, $\Delta\lambda_{max}$ 8c(9c) = 11–25 nm).

3. Experimental

All melting points were 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 dye solutions in DMF, methanol, acetone or chloroform at a concentration of 1×10^{-5} mol l^{-1}.

3.1. Preparation of the intermediates

*3.1.1. Synthesis of the intermediates **4a–4c***

2-Amino-4-phenyl-thiazole (**4a**) was prepared from a mixture of thiourea, acetophenone and

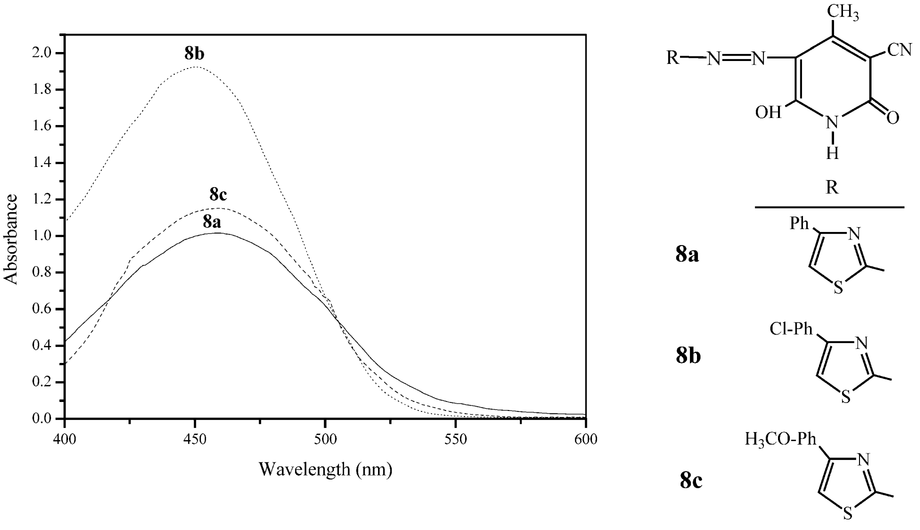


Fig. 3. Absorption spectra of dyes **8a–8c** in acetone.

Table 5
Spectral shifts influence by substituents on the ring of coupling components

Dyes X (Y)	R	R^1	$\Delta\lambda_{max}$ (nm)			
			DMF	Methanol	Acetone	Chloroform
8a (**9a**)	Ph	H(H)	+10	+15	+23	+27
8b (**9b**)	PhCl-*p*	H(H)	+7	+15	+13	+17
8c (**9c**)	PhOMe-*p*	H(H)	+11	+17	+19	+25
8e (**8b**)	PhCl-*p*	Me(H)	+3	+3	+11	+10
8f (**8c**)	PhOMe-*p*	Me(H)	+6	+4	+11	+12
9e (**9b**)	PhCl-*p*	Ph(H)	+1	+4	+11	+3
9f (**9c**)	PhOMe-*p*	Ph(H)	+1	+4	+7	+13
8e (**8d**)	PhCl-*p*	Me(Me)	−5	−8	−4	−14
8f (**8d**)	PhOMe-*p*	Me(Me)	+4	+1	+1	+1
9e (**9d**)	PhCl-*p*	Ph(Ph)	−1	−4	−3	−12
9f (**9d**)	PhOMe-*p*	Ph(Ph)	+1	+2	+2	+3

$\Delta\lambda_{max}$: $\lambda_{max}X - \lambda_{max}(Y)$.
Values of λ_{max}: see Table 3.

iodide using the method previously reported [22]. The synthesis of **4b**, **4c** followed the same method as described for **4a**. The physical and the spectral data of these compounds are given in Tables 1 and 2, respectively.

3.1.2. Synthesis of the intermediates *6a, 6b* and *7a, 7b*

N-substituted-3-cyano-4-methyl-6-hydroxy-2-pyridone **6a**, **6b** were synthesized from a reaction of ethyl acetoacetate, ethyl cyanoacetate and amines in ethanol under refluxing with piperidine as catalyst using the method described previously [6]. Otherwise, *N*-substituted-3-substituted-pyrazol-5-one derivatives **7a**, **7b** were synthesized from 1:1 ratio of ethyl acetoacetate derivatives and hydrazine derivatives in ethanol were refluxed in the presence of catalytic amounts of piperidine for 6 h via β-ketoester intramolecular condensation by the method as previously reported [1].

3.2. Preparation of the dyes

3.2.1. Preparation of the dyes *8a–8f*

A finely ground powder of 4-phenyl-2-amino-thiazole **4a** (2.0 g, 0.01 mole) was added to a mixture of 12 ml of acetic and propionic acids (5:1) and stirred for 20 min. Sodium nitrite (0.72 g, 0.0105 mole) was added portion-wise to 5 ml of concentrated sulphuric acid at 10 °C and stirred for 1 h at 60–65 °C. The solution was cooled to below 5 °C, then the finely ground derivatives were slowly added and the mixture was stirred for an additional 1 h at 5–10 °C to give a solution. The resulting diazonium solution was used immediately in the coupling reaction. A mixture of the coupling component 6-hydroxy-4-methyl-2-oxo-1, 2-dihydro-pyridine-3-carbonitrile **6a** (1.5 g, 0.01 mole) and 10% sodium carbonate was stirred as a clear solution. Addition of the diazonium mixture was made at 0–5 °C and the solution was stirred for at least 2 h before diluting or raising the pH to 7–8 (with aqueous sodium hydroxide or sodium acetate) prior to filtering and water-washing to neutral pH. The resulting product was filtered, washed with water, and recrystallized from ethanol to give 2-(5-cyano-2-hydroxy-4-methyl-6-oxo-1,6-dihydro-pyridin-3-ylazo)-3-phenyl-thioazole (**8a**). The physical and the spectral data of these compounds are given in Tables 1 and 2, respectively.

Synthesis of compounds **8b–8f** was carried out by the same method as the one described for **8a**. The physical and the spectral data of these compounds are given in Tables 1 and 2, respectively.

*3.2.2. Preparation of the dyes **9a–9f***

These dyes were prepared by diazotization of **4a–4c** followed by coupling with **7a** and **7b**. Diazotization and coupling were carried out with the same procedures mentioned above, excepting that the pH value of coupling condition was adjusted to 7–8. The physical and the spectral data of dyes **9a–9f** are given in Tables 1 and 2, respectively.

4. Conclusion

In this work, we have synthesized two series of bis-hetaryl monoazo dyes derived from two different heterocycles. The solvatochromic behaviours and substituent effects in various solvents were evaluated. The results indicated that these dyes were strongly dependent on solvents and show bathochromic shifts as the polarity of solvents was increased. The absorption maxima of dyes shifted bathochromically in the sequence DMF > methanol > acetone > chloroform. The results of substituent effects on the various positions of dyes indicated that the absorption maxima of dyes are only slightly influenced by substituents, but the values of $\Delta\lambda_{max}$ changed more significantly in the low polar solvent than in the high polar solvent.

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