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A facile syntheses and absorption characteristics 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

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Abstract

A series of some new bis-hetaryl monoazo dyes derived from different heterocycles has been synthesized from the coupling reactions of diazotized diazo components, polysubstituted 2-aminothiophenes with the corresponding coupling components, 2-pyridone and 5-pyrazolone derivatives, respectively. The structures of these bis-hetaryl azo dyes were confirmed by FT-IR, ^{1}H-NMR and mass spectroscopy and elemental analyses. Their solvatochromic properties in different solvents were also investigated.

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

1. Introduction

Many structural types of heterocyclic aromatic systems can be used as diazo components in azo dyes to enhance colour strength and brilliant shades for synthetic fabrics. There are reports of some azo dyes derived from heterocycles, such as pyridone and pyrazolone derivatives [1–6]. The absorption maxima of these dyes show their visible absorption wavelength mostly in the ranging of yellow to orange [7], due to poorly delocalized electrons in the rings of heterocycles, however, it has also been observed that some types of these types show more deeper colour strength and shades such as red or violet [8–10]. Recent interests have been directed toward azo dyes based on heterocyclens, such as 2-aminothiophene derivatives as diazo components that tend to show bathochromic shift and deep colour strength with high extinction coefficient when compared to analogous dyes derived from carbocyclic aromatic systems [11–13].

The purpose of this study is to investigate some bis-hetaryl monoazo dyes containing two heterocyclic rings in one molecular. Two series of different structural types of these dyes were synthesized and the chemical structures of these bis-hetaryl monoazo dyes are presented by following formulas **9**, **10**

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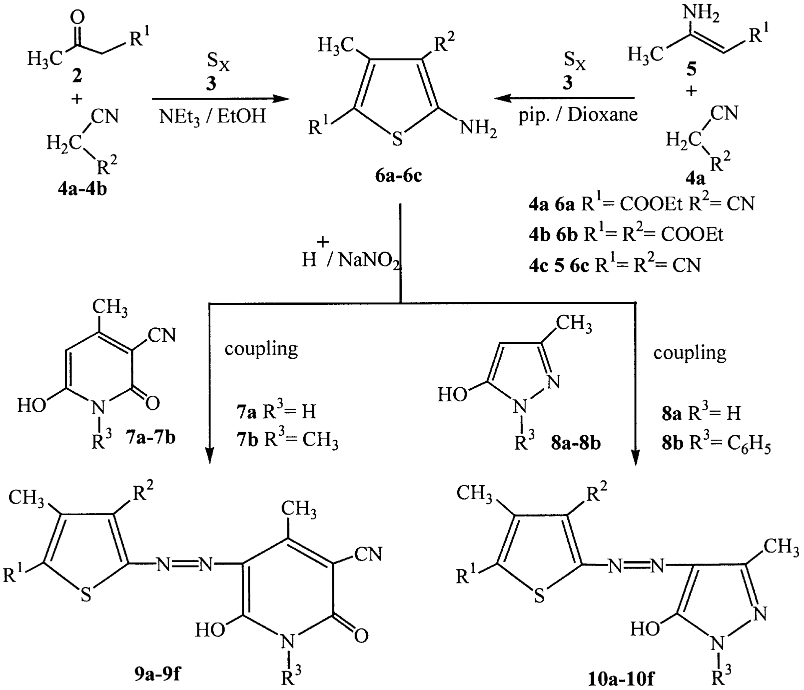
(Scheme 1). The spectral characteristics and the relationship between colour and constitution of these dyes in solvents with different polarities were systematically studied and evaluated.

2. Results and discussion

2.1. Synthesis

The general routes used for the syntheses of intermediates **6**, **7** and **8** and bis-hetaryl monoazo dyes **9** and **10** are outlined in Scheme 1. In this work, intermediates **6a–6c** were obtained using the Gewald's reaction [14,15]. This process were carried out by dissolving ethylacetoacetate or aminocrotononitrile and methylene compounds **4a** and **4b** in dioxane or ethanol in the presence of a base as catalyst and then followed by cyclization with sulfur. Intermediates 2-pyridone derivatives **7a** and **b** were prepared by condensation of the ethylacetoacetate, ethylcyanoacetate and ammonia water or methylamines, respectively. Similarly, the pyrazolone derivatives **8a** and **b** were prepared



Dyes	R^1	R^2	R^3
9a	COOEt	COOEt	H
9b	COOEt	CN	H
9c	CN	CN	H
9d	COOEt	COOEt	CH_3
9e	COOEt	CN	CH_3
9f	CN	CN	CH_3
10a	COOEt	COOEt	H
10b	COOEt	CN	H
10c	CN	CN	H
10d	COOEt	COOEt	C_6H_5
10e	COOEt	CN	C_6H_5
10f	CN	CN	C_6H_5

Scheme 1.

from ethylacetoacetate and hydrazine or phenylhydrazine, respectively [1,8]. Bis-hetaryl monoazo dyes **9** and **10** were readily obtained from diazotised polysubstituted 2-aminothiophenes **6a–c** via coupling reaction with 2-pyridone compounds **7a**,**b** and 5-pyrazolone compounds **8a**,**b**, respectively, in good yield (Scheme 1). The physical properties, ^{1}H-NMR and IR spectra data of the intermediates **6a–c** and the bis-hetaryl monoazo dyes **9** and **10** are listed in Tables 1 and 2.

2.2. *Solvatochromic properties of bis-hetaryl monoazo dyes **9** and **10***

Visible absorption spectra data and the molar extinction coefficients of bis-hetaryl monoazo dyes **9a–f** and **10a–f** in various solvents are listed in Table 3. The solvatochromic behaviour of these dyes in solvents with different dielectric constants (ε_r) was investigated. Table 3 shows that dyes **9a** absorbs at 521 mn in dimethylformamide

Table 1
Characterization data for intermediates and dyes derivatives **6a–c**, **9a–f**, **10a–f**

Compound	M.p.[a] (°C)	Yield[b] (%)	Molecular formula	Elemental analysis (%)			
				Calc./(found)			
				C	H	N	S
6a	120–121	72	$C_{11}H_{15}NSO_4$	51.35	5.88	15.44	12.46
				(51.30)	(5.79)	(15.49)	(12.42)
6b	208–209	78	$C_9H_{10}N_2SO_2$	51.41	4.79	13.32	15.25
				(51.35)	(4.84)	(13.37)	(15.18)
6c	219–220	63	$C_7H_5N_3S$	51.52	3.09	25.75	19.65
				(51.55)	(3.02)	(25.83)	(19.59)
9a	280–282	76	$C_{18}H_{18}N_4O_6S$	51.67	4.34	13.39	7.66
				(51.58)	(4.26)	(13.35)	(7.76)
9b	302–304	80	$C_{16}H_{13}N_5O_4S$	51.75	3.53	18.86	8.63
				(51.70)	(3.51)	(18.82)	(8.75)
9c	358–360	78	$C_{16}H_8N_6O_2S$	51.85	2.49	25.91	9.89
				(51.82)	(2.54)	(25.85)	(9.92)
9d	260–262	80	$C_{19}H_{20}N_4O_6S$	52.77	4.66	12.96	7.41
				(52.86)	(4.60)	(12.92)	(7.47)
9e	308–310	82	$C_{17}H_{15}N_5O_4S$	52.98	3.92	18.17	8.32
				(52.87)	(3.97)	(18.12)	(8.44)
9f	272–274	84	$C_{15}H_{10}N_6O_2S$	53.25	2.98	24.84	9.48
				(53.21)	(2.92)	(24.89)	(9.43)
10a	202–204	83	$C_{15}H_{18}N_4O_5S$	49.17	4.95	15.29	8.75
				(49.24)	(4.99)	(15.18)	(8.71)
10b	162–164	70	$C_{13}H_{13}N_5O_3S$	48.90	4.10	21.93	10.04
				(48.92)	(4.08)	(21.88)	(10.13)
10c	262–264	86	$C_{11}H_8N_6OS$	48.52	2.96	30.86	11.77
				(48.40)	(2.92)	(30.89)	(11.83)
10d	182–184	83	$C_{21}H_{22}N_4O_5S$	57.00	5.01	12.66	7.25
				(57.08)	(4.95)	(12.62)	(7.16)
10e	276–278	72	$C_{19}H_{17}N_5O_3S$	57.71	4.33	17.71	8.11
				(57.63)	(4.42)	(17.73)	(8.16)
10f	240–242	86	$C_{17}H_{12}N_6OS$	58.61	3.47	24.12	9.20
				(58.68)	(3.38)	(24.17)	(9.16)

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

Table 2
Spectral data of intermediates and dyes derivatives **6a–c**, **9a–f**, **10a–f**

Dyes	MS (m/e, M^+)	IR (KBr) ν (cm^{-1})	^1H-NMR (DMSO-d6) δ (ppm)
6a	256	3316 3423 (NH_2) 2209 (C≡N) 1685 (C=O)	1.23 (3H, t, $5\text{-}CO_2CH_2\underline{CH_3}$), 1.28 (3H, t, $3\text{-}CO_2CH_2\underline{CH_3}$), 2.53 (3H, s, CH_3), 4.16 (2H, q, $5\text{-}CO_2\underline{CH_2}CH_3$), 4.22 (2H, q, $3\text{-}CO_2\underline{CH_2}CH_3$), 7.92 (2H, s, NH_2)
6b	210	3312 3405 (NH_2) 2206 (C≡N) 1677 (C=O)	1.23 (3H, t, $CO_2CH_2\underline{CH_3}$), 2.37 (3H, s, CH_3), 4.17 (2H, q, $CO_2CH_2CH_3$), 7.93 (2H, s, NH_2)
6c	163	3302 3411 (NH_2) 2212 (C≡N)	2.35 (3H, s, CH_3), 8.23 (2H, s, NH_2)
9a	418	3436 (N–H) 2212 (C≡N) 1672 (C=O)	1.30 (3H, t, $5\text{-}CO_2CH_2\underline{CH_3}$), 1.38 (3H, t, $3\text{-}CO_2CH_2\underline{CH_3}$), 2.44 (3H, s, pyridone-CH_3) 2.70 (3H, s, CH_3), 4.28 (2H, q, $5\text{-}CO_2\underline{CH_2}CH_3$), 4.39 (2H, q, $3\text{-}CO_2\underline{CH_2}CH_3$), 7.95 (1H, s, NH), 14.26 (1H, s, OH)
9b	371	3414 (N–H) 2414 (C≡N) 1667 (C=O)	1.30 (3H, t, $CO_2CH_2\underline{CH_3}$), 2.42 (3H, s, pyridone-CH_3), 2.51 (3H, s, CH_3), 4.28 (2H, q, $CO_2\underline{CH_2}CH_3$), 7.91 (1H, s, NH), 10.71 (1H, s, OH)
9c	324	3431 (N–H) 2212 (C≡N) 1662 (C=O)	2.39 (3H, s, pyridone-CH_3), 2.45 (3H, s, CH_3), 7.92 (1H, s, NH), 10.81 (1H, s, OH)
9d	432	2220 (C≡N) 1664 (C=O)	1.30 (3H, t, $5\text{-}CO_2CH_2\underline{CH_3}$), 1.37 (3H, t, $3\text{-}CO_2CH_2$ $\underline{CH_3}$), 2.45 (3H, s, pyridone-CH_3), 3.46 (3H, s, N-$\underline{CH_3}$), 4.28 (2H, q, $5\text{-}CO_2\underline{CH_2}CH_3$), 4.38 (2H, q, $3\text{-}CO_2\underline{CH_2}CH_3$), 11.19 (1H, s, OH)
9e	385	2213 (C≡N) 1672 (C=O)	1.29 (3H, t, $CO_2CH_2\underline{CH_3}$), 2.44 (3H, s, pyridone-CH_3), 2.52 (3H, s, CH_3), 3.47 (3H, s, N-$\underline{CH_3}$), 4.27 (2H, q, $CO_2\underline{CH_2}CH_3$), 10.74 (1H, s, OH)
9f	338	2203 (C≡N) 1676 (C=O)	2.43 (3H, s, pyridone-CH_3), 2.54 (3H, s, CH_3), 3.52 (3H, s, N-$\underline{CH_3}$), 10.83 (1H, s, OH)
10a	366	3422 (N–H) 2210 (C≡N) 1682 (C=O)	1.29 (3H, t, $5\text{-}CO_2CH_2\underline{CH_3}$), 1.36 (3H, t, $3\text{-}CO_2CH_2\underline{CH_3}$), 2.13 (3H, s, pyrazolone-CH_3) 2.68 (3H, s, CH_3), 4.26 (2H, q, $5\text{-}CO_2\underline{CH_2}CH_3$), 4.37 (2H, q, $3\text{-}CO_2\underline{CH_2}CH_3$, 11.84 (1H, s, NH)
10b	319	3428 (N–H) 1698 (C=O)	1.29 (3H, t, $5\text{-}CO_2CH_2\underline{CH_3}$), 2.42 (3H, s, 2217 (C=N) pyrazolone-CH_3), 2.53 (3H, s, CH_3), 4.25 (2H, q, $CO_2CH_2CH_3$), 11.45 (1H, s, NH)
10c	272	3328 (N–H) 2210 (C≡N)	2.43 (3H, s, pyrazolone-CH_3), 2.54 (3H, s, CH_3), 11.35 (1H, s, NH)
10d	442	1714 (C=O)	1.29 (3H, t, $5\text{-}CO_2CH_2\underline{CH_3}$), 1.37 (3H, t, $3\text{-}CO_2CH_2\underline{CH_3}$), 2.15 (3H, s, pyrazolone-CH_3) 2.63 (3H, s, CH_3), 4.26 (2H, q, $5\text{-}CO_2\underline{CH_2}CH_3$), 4.36 (2H, q, $3\text{-}CO_2\underline{CH_2}CH_3$), 7.04–7.98 (5H, m, PhH of pyrazolone)
10e	395	2216 (C–N) 1682 (C=O)	1.28 (3H, t, $5\text{-}CO_2CH_2\underline{CH_3}$), 2.40 (3H, s, pyrazolone-CH_3), 2.53 (3H, s, CH_3), 7.36–7.95 (10H, m, PhH of pyrazolone)
10f	348	2206 (C≡N) 1664 (C=O)	2.39 (3H, s, pyrazolone-CH_3), 2.43 (3H, s, CH_3), 7.04–7.98 (5H, m, PhH of pyrazolone)

Table 3
Absorption maxima spectra of dyes derivatives **9a–f**, **10a–f**

Dyes	DMF	CH_3OH		Acetone		$CHCl_3$	
	λ_{max} (log ε)	λ_{max} (log ε)	$\Delta\lambda_{max}$	λ_{max} (log ε)	$\Delta l\lambda^{a}_{max}$	λ_{max} (log ε)	$\Delta\lambda^{a}_{max}$
9a	521 (4.34)	470 (4.27)	−51	465 (4.32)	−56	452 (4.37)	−69
9b	533 (4.37)	513 (4.37)	−20	511 (4.33)	−22	483 (4.32)	−50
9c	536 (4.42)	523 (4.43)	−13	520 (4.45)	−16	486 (4.42)	−50
9d	524 (4.39)	477 (4.30)	−47	468 (4.32)	−56	464 (4.26)	−60
9e	534 (4.43)	520 (4.36)	−14	517 (4.28)	−17	487 (4.27)	−47
9f	537 (4.36)	527 (4.43)	−10	523 (4.22)	−14	497 (4.21)	−40
10a	515 (4.14)	442 (4.18)	−73	439 (4.22)	−76	436 (4.24)	−79
10b	518 (4.22)	487 (4.22)	−31	483 (4.16)	−35	474 (4.12)	−44
10c	522 (4.25)	495 (4.23)	−27	493 (4.24)	−29	476 (4.20)	−46
10d	518 (4.09)	451 (4.03)	−67	441 (4.21)	−77	440 (4.26)	−78
10e	520 (4.13)	502 (4.10)	−18	490 (4.15)	−30	478 (4.17)	−42
10f	528 (4.26)	515 (4.23)	−13	512 (4.19)	−16	488 (4.21)	−40

Note: 1. The ε_r value of solvents: DMF = 36.71, CH_3OH = 32.66, CH_3COCH_3 = 20.56, $CHCl_3$ = 4.81. 2. $\Delta\lambda max^{a}$ relative to corresponding DMF. 3. Unit of λ_{max} and $\Delta\lambda_{max}$: nm.

(ε_r = 36.71), at 470 nm in methanol (ε_r 32.66, $\Delta\lambda_{max}$ = 51 nm), at 465 nm in acetone (ε_r 20.56, $\Delta\lambda_{max}$ = 56 nm) and at 452 nm in chloroform (ε_r 4.81, $\Delta\lambda_{max}$ = 69 nm). The results show that dye **9a** shifted considerably hypsochromic as the solvent polarity is decreased. Similar results were also observed for dye **9d, 10a** and **10d**. The $\Delta\lambda_{max}$ values of these dyes show hypsochromic shift in the range of 47–60 nm for dye **9d**, 73–79 nm for dye **10a** and 67–78 nm for dye **10d** in the solvents with different polarities, whereas dyes **9b**,**c**, **9e**,**f**, **10b**,**c** and **10e**,**f** change hypsochromically in their absorption maxima. The significance is slight in methanol and acetone, but large in chloroform as compared to dimethylformamide, e.g., for dye **9b** $\Delta\lambda_{max}$ is 20 nm in MeOH, 22 nm in acetone and 50 nm in $CHCl_3$. Comparison of absorption maxima of these dyes indicate 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). It can be seen in Table 3 that dyes **10a**,**c**, each with a pyrazolone coupler **8a** attached, absorb hypsochromically and the molar extinction coefficients are lower as compared to dyes **9a**,**c**, each with a pyridone coupler **7a** attached, in solvents with different polarities due to the ring of pyridone residue possesses more π-electron density than that of pyrazolone moiety. The $\Delta\lambda_{max}$ of dyes **10a**,**c** shift hypsochomically in the range of 6–15 nm in dimethylformamide, 25–28 nm in methanol, 26–28 nm in acetone and 9–16 nm in chloroform. Table 4 shows that the shifts of absorption wavelength of dyes in polar protic methanol and in moderately polar acetone are larger than those in polar aprotic dimethylformamide and in lowerly polar chloroform. The effects of substitution in the diazo components and coupling components on the visible absorption maxima of dyes **9** and **10** were also evaluated. Table 5 shows the absorption maxima for the dyes **9a–c** derived from 2-pyridone compound **7a** as a coupling component are in the range of 521 to 536 nm in dimethylformamide, whereas the analogous dyes **9d–f** derived from 2-pyridone compound **7b** as a coupling component show the absorption maxima in the range of 524–537 nm in the same solvent, corresponding to additional bathochromic shifts ranging from 3 to 1 nm when compared to dyes **9a–c**. The result is believed to be caused by an additional electron donating group (methyl) in the N-position of 2-pyridone ring. Replacement of the 2-pyridone compounds **7a**,**b** in dyes **9a–f** 5-pyrazolone compounds **8a**,**b** as coupling components, as in dyes **10a–f**, resulted in a displacement of the absorption maxima from 518 to 528 nm in dimethylformamide. Dyes **10a–c** show the absorption maxima in the range of 515–522 nm. However, additional bathochromic shifts of 2–6 nm were

Table 4
Spectral shifts of coupling components

Dyes	R^1	R^2	R^3	$\Delta\lambda_{max}$ (nm)			
				DMF	Methanol	Acetone	Chloroform
9a(**10a**)	COOEt	COOEt	H(H)	−6	−28	−26	−16
9b(**10b**)	COOEt	CN	H(H)	−15	−25	−28	−9
9c(**10c**)	CN	CN	H(H)	−14	−28	−27	−10

$\Delta\lambda_{max}$; λ_{max} (**10**)−λ_{max} (**9**). λ_{max}: see Table 3.

Table 5
Electronic effect of substituent groups in the coupling component ring

Dyes	R	$\Delta\lambda_{max}$ (nm)			
		DMF	Methanol	Acetone	Chloroform
9d	Me	+3	+7	+3	+12
9e	Me	+1	+7	+6	+4
9f	Me	+1	+7	+3	+11
10d	Ph	+3	+9	+2	+4
10e	Ph	+2	+15	+7	+4
10f	Ph	+6	+20	+19	+2

$\Delta\lambda_{max}$: Relative to R = H **9a–c** to **9d–f**, **10a–c** to **10d–f**, respectively. λ_{max}: see Table 3.

observed for dyes **10a–c** as compared to dyes **10d–f** in the same solvent, which could be attributable to the introduction of an electron-rich phenyl group to the N-position of pyrazolone ring in dyes **10d–f**. Similar results (Δλ) were found in methanol, acetone and chloroform. The absorption maxima of analogoues **9** and **10** dyes have only a little effect owing to the introduction of an additional electron donating group by the methyl group or an electron-rich group by the phenyl group in the coupling components. The electronic effect of substituent in the 3- and 5-position of diazo components **6a–c** for the dyes **9** and **10** has also been investigated. As shown in Table 6, it was observed that introduction of electron accepting group in the diazo component results in a bathochromic shift, which is attributed to more electron delocalization in the thiophene residue. Hence dyes **9c**,**f**, **10c**, and **f** containing two CN groups show the absorption maxima at longer wavelengths in dimethylformamide when compared with the corresponding dyes **9a**,**d**, **10a**, and **d** containing two COOEt groups in the 3,5-position of thiophene diazo components, and result in the bathochromic shifts in the range of 7–15 nm. This is due to the fact that CN substituent is a stronger electron accepting group than the COOEt substituent. Replacement of a COOEt group in the 3-position of thiophene ring by CN group, as in dyes **9b**,**e**, **10b**, and **e**, also results in bathochromic shifts in the range of 2 to 12 nm in the same solvents.

3. Experimental

All melting points are uncorrected and in °C. FT-IR spectra were recorded on a JASCO FTIR-3 spectrometer (KBr). ^{1}H-NMR spectra were obtained on a Jeol-EX-400MHz 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 litre.[1]

3.1. Preparation of the intermediates

Polysubstituented-2-aminothiophene derivatives **6a–c**, N-substituted-3-cyano-4-methyl-6-hydroxy-2-pyridone **7a**,**b** and N-substituted-3-substituted-pyrazol-5-one derivatives **8a**,**b** were prepared from the method described in the literature [1,8,14,16].

Table 6
Electronic effect of substituent groups in the diazo component ring

Dyes	R1	R2	R3	Δ_{max} (nm)			
				DMF	Methanol	Acetone	Chloroform
9a	COOEt	COOEt	H				
9b	COOEt	CN	H	+12	+43	+46	+31
9c	CN	CN	H	+15	+53	+55	+34
9d	COOEt	COOEt	Me				
9e	COOEt	CN	Me	+10	+43	+49	+23
9f	CN	CN	Me	+13	+50	+55	+33
10a	COOEt	COOEt	H				
10b	COOEt	CN	H	+3	+45	+44	+38
10e	CN	CN	H	+7	+53	+54	+40
10d	COOEt	COOEt	Ph				
10e	COOEt	CN	Ph	+2	+51	+49	+38
10f	CN	CN	Ph	+10	+54	+71	+48

$\Delta\lambda_{max}$: Relative to **9a**,**d**, **10a** and **d**, respectively. $R^1 = R^2 =$ COOEt R3 = H. λ_{max}: see Table 3.

3.2. Preparation of the dyes

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

A general preparative procedure is described below for the preparation of dye **9a**.

A finely grounded powder of 5-amino-3-methyl-thiophene-2,4-dicarboxylic acid ethyl ester **6a** (2.57 g, 0.01 mol) 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 mol) was added in portions to 5 ml of concentrated sulfuric acid at 10 °C and stirred for 1 h at 60–65 °C. The solution was cooled to below 5 °C, then the solution of **6a** was slowly added and the mixture was stirred for an additional 1 h at 5–10 °C to give a clear 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 **7a** (1.5 g, 0.01 mol) 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 5-(5-cyano-2-hyhroxy-4-methyl-6-oxo-1,6-dihydro-pyridin-3-ylazo)-3-methyl-thiophene-2,4-dicarboxylic acid ethyl ester (**9a**).

Syntheses of compounds **9b–f** and **10a–f** were carried out by the same method as described for **9a**. The physical properties and spectral data of these dyes are given in Tables 1 and 2, respectively.

4. Conclusion

N-substituted 2-pyridones and N-substituted 5-pyrazolones are used respectively for coupling with 3,5-substituted-4-methyl-2-aminothiophenes to produce red to purple hetarylazo dyes. These dyes are found to exhibit a strong solvent dependence which shows a variation with the dielectric constants of the solvent. The absorption maxima of these dyes showed bathochromic shifts when dissolved in DMF. The spectral shifts of dyes derived from coupler N-substituted pyridones and diazo components 3,5-substituted-4-methyl-2-aminothiophenes are larger than those of coupled with N-substituted pyrazolones. The absorption maxima of dyes containing two CN groups in the 3,5-position of thiophene diazo components as compared with the corresponding dyes containing two COOEt groups illustrate at longer wavelengths in different solvents.

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