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Synthesis and tautomeric structures of some novel thiophene-based bis-heterocyclic monoazo dyes

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HIGHLIGHTS

- A series of novel monoazo dyes based on thiophene ring was synthesised.
- The solvatochromic behaviours and tautomeric structures of dyes were evaluated in detail.
- Acid and base effects on λ_{max} of the dyes were also examined in detail.

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ABSTRACT

In this study, ethyl 2-amino-5-methyl-4-(phenylcarbamoyl)thiophene-3-carboxylate (**1**) was prepared using Gewald's methodology. This 2-aminothiophene derivative was diazotised and coupled with, 3-methyl-1H-pyrazolin-5-one, 3-methyl-1-phenylpyrazolin-5-one, 3-amino-5-hydroxy-1H-pyrazole, 3-amino-5-hydroxy-1-phenylpyrazole, 3-cyano-6-hydroxy-4-methyl-2-pyridone, barbituric acid and 4-hydroxycoumarin, respectively (**2**–**8**). The newly synthesized bis-heterocyclic monoazo dyes based on thiophene ring were characterised by elemental analysis and spectral methods. The solvatochromic behaviour and tautomeric structures of these bis-heterocyclic monoazo dyes in various solvents was evaluated. Acid and base effects on the visible absorption maxima of the dyes are also reported.

1. Introduction

In the last four decades, innovations in azo dye chemistry based on heterocyclic systems have been made as a result of intensive studies stimulated by the mounting need for bright blue dyes. Generally speaking, many of the heterocyclic azo dyes show bathochromic shifts combined with brilliance of shade and high tinctorial strength compared with conventional anthraquionone dyes and aminobenzene azo dyes [1–3]. Of most importance are azo dyes derived from 2-aminothiophenes as diazo components. For instance, Hallas et al. [4–8] reported the synthesis of azo dyes derived from 2-aminothiophene derivatives and various heterocyclic coupling components, and their application on polyester fibres gave excellent results. The deep colours of these dyes can be explained by resonance theory; the sulphur atom acts as an electron sink and the thiophene ring system has less resonance stabilisation energy to lose on excitation than benzenoid system [9]. Also, the electron-withdrawing substituents on the thiophene ring resulted in bathochromic shifts [10–12]. Aminothiophenes used as diazo components in the synthesis of thiophene based heterocyclic azo dyes were easily obtained using Gewald's methodology [13,14]. Many papers describe the synthesis, dyeing properties of thiophene based azo dyes for synthetic fibres [15–21] and for blended polyester/wool fibres [22–24]. Also, some dyes derived from thiophene are used in solar cell [25,26].

Although, many papers describe the synthesis and properties of thiophene based monoazo dyes, investigations involved in bis-heterocyclic monoazo dyes based on thiophene ring have been limited [27,28]. In conjunction with our interest in this class of compounds, we have previously reported the synthesis and spectral properties of some heterocyclic azo dyes [29–35]. The purpose of this study is to investigate some bis-heterocyclic monoazo dyes based on thiophene ring. Absorption abilities and tautomeric structures of these dyes were also examined in detail.

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2. Experimental

2.1. General

The chemical used for the synthesis of the compounds were obtained from Aldrich and Merck Chemical Company without further purification. The solvents used were of spectroscopic grade.

IR spectra were determined using a Mattson 1000 Fourier Transform-infrared (FT-IR) spectrophotometer on a KBr disc. Nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker-Spectrospin Avance DPX 400 Ultra-Shield in deuterated dimethylsulphoxide (DMSO-d_6) using tetramethylsilane (TMS) as the internal reference; chemical shifts was (δ) given in ppm. Ultraviolet–visible (UV–vis) absorption spectra were recorded on a Schimadzu UV-1601 double beam spectrophotometer at the wavelength of maximum absorption (λ_{max}) in a range of solvents, i.e. DMSO, DMF, acetonitrile, methanol, acetic acid and chloroform at the various concentrations (1×10^{-6}–10^{-8}). Melting points were determined on an Electrothermal 9100 melting point apparatus and are uncorrected. Elemental analysis was done on a Leco CHNS-932 analyser.

2.2. Synthesis of ethyl 2-amino-4-methyl-5-(phenylcarbamoyl)thiophene-3-carboxylate (**1**)

Acetoacetanilide (1.80 g, 0.01 mol), ethyl cyanoacetate (1.19 g, 0.01 mol) and sulphur (0.33 g, 0.01 mol) were refluxed in ethanol for 3 h using morpholine (0.9 g, 0.01 mol) (Scheme 1). The resulting dark solution was cooled and stored overnight in a refrigerator, followed by filtration, washing with a small amount of ethanol and then ethanol/water (1:1) mixture and dried in air. Recrystallisation from ethanol gave white crystals of the product **1** (Scheme 1) [12–14] (yield 2.19 g, 72%), mp 176–177 °C. IR (KBr): ν (cm^{-1}) = 3381, 3316 (NH_2), 3251 (NH), 3036 (Ar—H), 2973 (Al—H), 1647, 1631 (2 C=O); ^{1}H-NMR (DMSO-d_6): δ = 1.35 (t, 3H, J = 7.02 Hz, CH_3), 2.58 (s, 3H, CH_3), 4.38 (q, 2H, J = 7.00 Hz, OCH_2), 7.12–7.51 (m, 5H, ArH), 7.72 (b, 2H, NH_2), 9.78 (br, 1H, Ph—NH); Anal. Calcd. for $C_{15}H_{16}N_2O_3S$: C: 59.19, H: 5.30, N: 9.20, S: 10.54. Found: C: 59.41, H: 5.14, N: 9.07, S: 10.29.

2.3. Synthesis of 4-[ethyl 4′-methyl-5′-(phenylcarbamoyl)thiophene-3′-carboxylate-2′-ylazo]-3-methyl-1H-pyrazolin-5-one (**2**)

Ethyl 2-amino-5-methyl-4-(phenylcarbamoyl)thiophene-3-carboxylate (3.04 g, 0.01 mol) was dissolved in a mixture of glacial acetic acid and concentrated hydrochloric acid (20 ml, ratio 1:1) and the solution was then cooled to 0–5 °C. Sodium nitrite (0.69 g, 0.01 mol) in water (10 ml) was then added to this solution dropwise with vigorous stirring, during about 1 h, while cooling at 0–5 °C. Then the resulting diazonium solution was added in portions over 30 min to a vigorously stirred solution of 3-methyl-1H-pyrazolin-5-one (0.98 g, 0.01 mol) in KOH (0.56 g, 0.01 mol) and water (10 ml) at between 0–5 °C, maintaining the pH at 7–8 by simultaneous addition of 10% sodium acetate solution. The mixture was then stirred for 2 h. at between 0–5 °C. The precipitated product separated upon dilution with water (50 ml) was filtered off, washed with water several times and dried in air. Recrystallisation from aqueous DMF gave red crystals of the product dye **2** (yield 2.95 g, 71%), mp 306–307 °C. IR (KBr): ν (cm^{-1}) = 3259, 3242, 3230 (3 NH), 3034 (Ar—H), 2982 (Al—H), 1715, 1673, 1645 (3 C=O); ^{1}H-NMR (DMSO-d_6): δ = 1.34 (t, 3H, J = 7.05 Hz, CH_3), 1.89 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 4.31 (q, 2H, J = 7.04 Hz, OCH_2), 7.01–7.69 (m, 5H, ArH), 9.69 (br, tautomeric NH or OH), 9.95 (br, 1H, pyrazole NH), 10.13 (br, tautomeric NH or OH), 10.75 (br, 1H, Ph—NH); Anal. Calcd. for $C_{19}H_{19}N_5O_4S$: C: 55.19, H: 4.63, N: 16.94, S: 7.76. Found: C: 55.43, H: 4.59, N: 16.83, S: 7.65. The above procedure was also used to synthesize dye **3**–**8** (Scheme 2).

2.4. 4-[Ethyl 4′-methyl-5′-(phenylcarbamoyl)thiophene-3′-carboxylate-2′-ylazo]-3-methyl-1-phenylpyrazolin-5-one (**3**)

Red crystals; yield 67%; mp. 263–264 °C (DMF-H_2O); IR (KBr): ν (cm^{-1}) = 3261, 3228 (2NH), 3031 (Ar—H), 2976 (Al—H), 1711, 1681, 1636 (3 C=O); ^{1}H-NMR (DMSO-d_6): δ = 1.42 (t, 3H, J = 6.91 Hz, CH_3), 2.33 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 4.44 (q, 2H, J = 6.90 Hz, OCH_2), 7.10–7.92 (m, 10H, ArH), 9.82 (br, tautomeric NH or OH), 10.19 (br, 1H, Ph—NH), 10.36 (br, tautomeric NH or OH); Anal. Calcd. for $C_{25}H_{23}N_5O_4S$: C: 61.34, H: 4.74, N: 14.31, S: 6.55. Found: C: 61.47, H: 4.62, N: 14.18, S: 6.67.

2.5. 4-[Ethyl 4′-methyl-5′-(phenylcarbamoyl)thiophene-3′-carboxylate-2′-ylazo]-3-amino-5-hydroxy-1H-pyrazole (**4**)

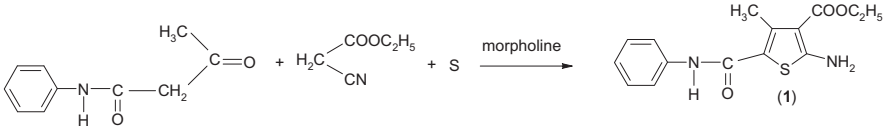
Dark brown crystals; yield 78%; mp. 281–282 °C (DMF-H_2O); IR (KBr): ν (cm^{-1}) = 3477 (OH), 3382 (NH_2), 3266, 3230 (2 NH), 3061 (Ar—H), 2988 (Al—H), 1720, 1638 (2 C=O); ^{1}H-NMR (DMSO-d_6): δ = 1.38 (t, 3H, J = 7.03 Hz, CH_3), 2.57 (s, 3H, CH_3), 4.38 (q, 2H, J = 7.04 Hz, OCH_2), 5.99 (br, 2H, NH_2), 7.08–7.67 (m, 5H, ArH), 10.13 (br, 1H, OH), 10.80 (br, 1H, pyrazole NH), 14.19 (br, 1H, Ph—NH); Anal. Calcd. for $C_{18}H_{18}N_6O_4S$: C: 52.17, H: 4.38, N: 20.28, S: 7.74. Found: C: 52.29, H: 4.21, N: 20.42, S: 7.53.

2.6. 4-[Ethyl 4′-methyl-5′-(phenylcarbamoyl)thiophene-3′-carboxylate-2′-ylazo]-3-amino-5-hydroxy-1-phenylpyrazole (**5**)

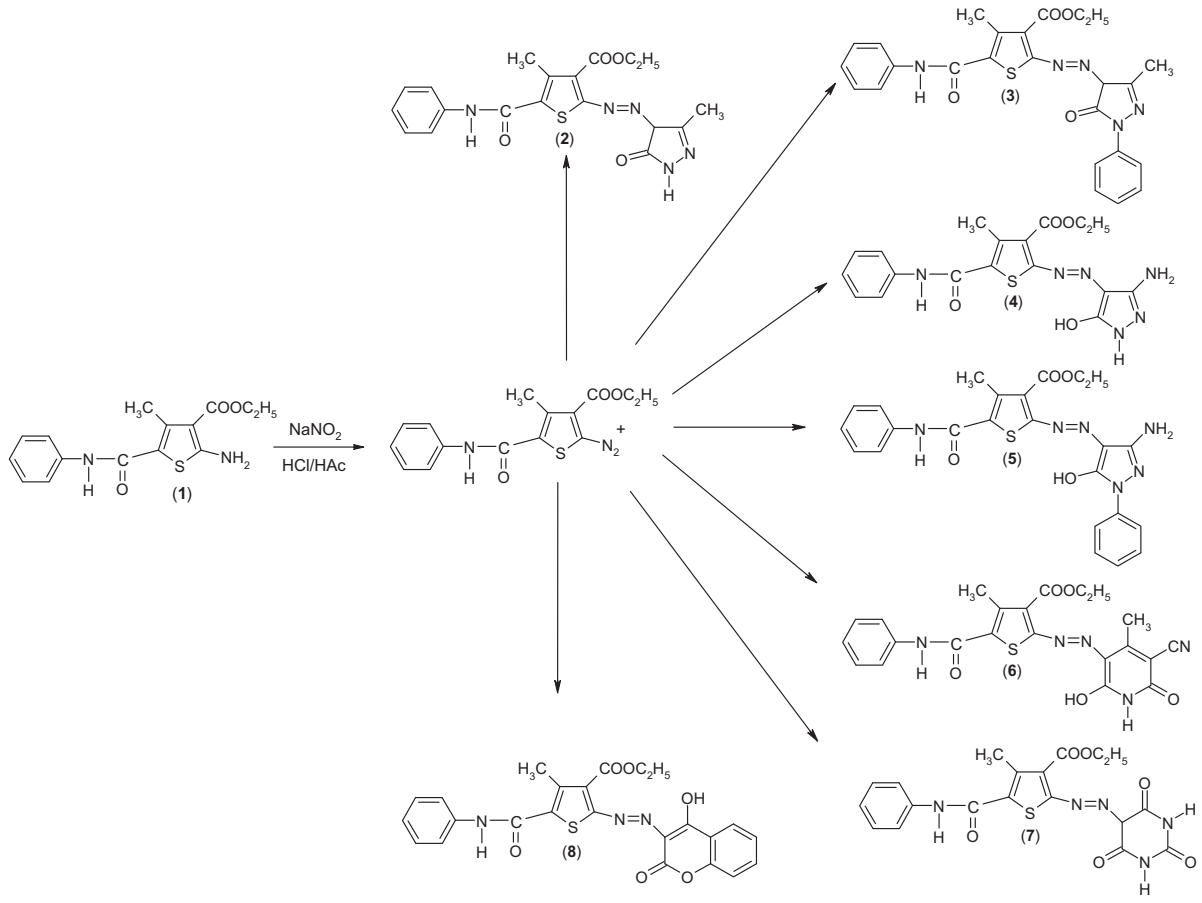
Brown crystals; yield 73%; mp. 253–254 °C (DMF-H_2O); IR (KBr): ν (cm^{-1}) = 3464 (OH), 3391 (NH_2), 3266 (NH), 3055 (Ar—H), 2988 (Al—H), 1673, 1640 (2 C=O); ^{1}H-NMR (DMSO-d_6): δ = 1.42 (t, 3H, J = 7.02 Hz, CH_3), 2.58 (s, 3H, CH_3), 4.43 (q, 2H, J = 7.13 Hz, OCH_2), 6.58 (br, 2H, NH_2), 7.09–7.93 (m, 10H, ArH), 10.18 (br, 1H, OH), 14.31 (br, 1H, Ph—NH); Anal. Calcd. for $C_{24}H_{22}N_6O_4S$: C: 58.76, H: 4.52, N: 17.13, S: 6.54. Found: C: 58.54, H: 4.62, N: 16.92, S: 6.67.

2.7. 5-[Ethyl 4′-methyl-5′-(phenylcarbamoyl)thiophene-3′-carboxylate-2′-ylazo]-3-cyano-6-hydroxy-4-methyl-2-pyridone (**6**)

Red crystals; yield 86%; mp. 320–321 °C (DMF-H_2O); IR (KBr): ν (cm^{-1}) = 3266, 3254, 3247 (3 NH), 3055 (Ar—H), 2988 (Al—H), 2222 (CN), 1716, 1698, 1670, 1645 (4 C=O); ^{1}H-NMR (DMSO-d_6): δ = 1.39 (t, 3H, J = 7.13 Hz, CH_3), 2.58 (s, 3H, CH_3), 2.74 (s, 3H, CH_3), 4.42 (q, 2H, J = 7.02 Hz, OCH_2), 7.10–7.96 (m, 5H, ArH),



Scheme 1. Synthesis of thiophene derivative (**1**).



Scheme 2. Synthesis of dyes **2–8**.

10.21 (br, 1H, OH), 12.26 (br, 1H, pyridone NH), 15.32 (br, 1H, Ph—NH); Anal. Calcd. for $C_{22}H_{19}N_5O_5S$: C: 56.77, H: 4.11, N: 15.05, S: 6.89. Found: C: 56.91, H: 4.05, N: 15.18, S: 6.69.

*2.8. 5-[ethyl 4′-methyl-5′-(phenylcarbamoyl)thiophene-3′-carboxylate-2′-ylazo] barbituric acid (**7**)*

Orange crystals; yield 81%; mp. 323–324 °C (DMF-H_2O); IR (KBr): ν (cm^{-1}) = 3288, 3246, 3163 (3 NH), 3075 (Ar—H), 2990 (Al—H), 1733, 1705, 1696, 1664, 1636 (5 C=O); ^{1}H-NMR (DMSO-d_6): δ = 1.39 (t, 3H, J = 7.14 Hz, CH_3), 2.59 (s, 3H, CH_3), 4.41 (q, 2H, J = 7.01 Hz, OCH_2), 7.09–7.96 (m, 5H, ArH), 10.16 (br, 1H, OH), 11.48 (br, 1H, pyrimidone NH), 11.73 (br, 1H, pyrimidone NH), 15.02 (br, 1H, Ph—NH); Anal. Calcd. for $C_{19}H_{17}N_5O_6S$: C: 51.46, H: 3.86, N: 15.79, S: 7.23. Found: C: 51.22, H: 3.67, N: 15.53, S: 7.08.

*2.9. 3-[Ethyl 4′-methyl-5′-(phenylcarbamoyl)thiophene-3′-carboxylate-2′-ylazo]-4- hydroxycoumarin (**8**)*

Red crystals; yield 63%; mp. 271–272 °C (DMF-H_2O); IR (KBr): ν (cm^{-1}) = 3482 (OH), 3278 (NH), 3081 (Ar—H), 2989 (Al—H), 1749, 1688, 1653 (3 C=O); ^{1}H-NMR (DMSO-d_6): δ = 1.46 (t, 3H, J = 6.88 Hz, CH_3), 2.61 (s, 3H, CH_3), 4.47 (q, 2H, J = 6.80 Hz, OCH_2), 7.11–8.05 (m, 9H, ArH), 10.26 (br, 1H, OH), 16.17 (br, 1H, Ph—NH); Anal. Calcd. for $C_{24}H_{19}N_3O_6S$: C: 60.37, H: 4.01, N: 8.80, S: 6.72. Found: C: 60.44, H: 3.83, N: 8.64, S: 6.87.

3. Results and discussion

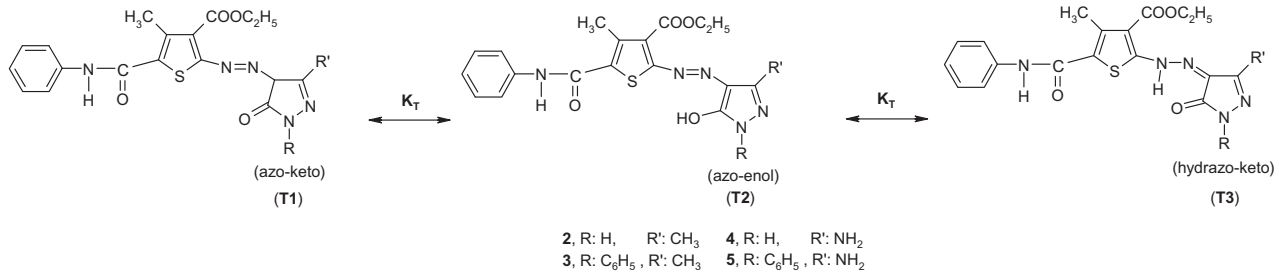
3.1. Spectral characteristics and tautomerism

Dyes **2–8** can exist in three possible tautomeric forms, namely the azo-keto forms (**T1**, **T4**, **T7**, **T10**), the azo-enol forms (**T2**, **T5**, **T8**, **T11**) and the hydrazo-keto forms (**T3**, **T6**, **T9**, **T12**) as shown in Schemes 3–6. The FT-IR spectra of dyes **2** and **3** showed three imino bands (NH) and two imino (NH) bands, respectively. Also, FT-IR spectra of dyes **2** and **3** did not show any broad band for hydroxyl group. These suggest that dyes **2** and **3** are predominantly in hydrazo-keto form (**T3**) as opposed to azo-keto form (**T1**) and azo-enol form (**T2**), in the solid state (Scheme 3).

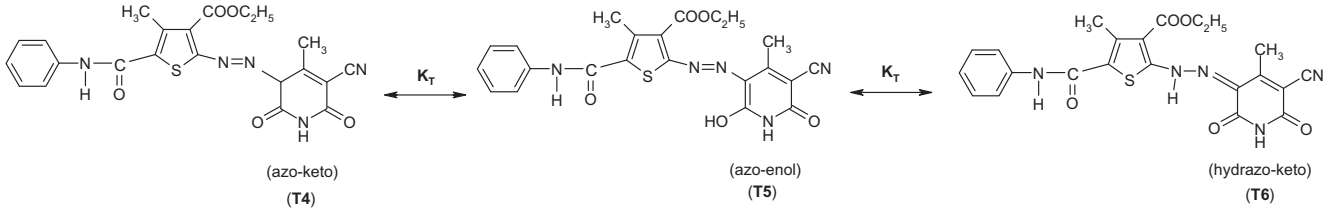
The FT-IR spectra of dyes **4** and **5** showed one broad hydroxyl (OH) band and intense two carbonyl (C=O) bands. These suggest that dyes **4** and **5** are predominantly in azo-enol form (**T2**) as opposed to azo-keto form (**T1**) and hydrazo-keto form (**T3**), in the solid state (Scheme 3).

The FT-IR spectra of dyes **6** and **7** showed three imino (NH) bands. Also, FT-IR spectra of dyes **6** and **7** did not show any broad band for hydroxyl group. These suggest that dye **6** is predominantly in hydrazo-keto form (**T6**) as opposed to azo-keto form (**T4**) and azo-enol form (**T5**) and dye **7** is predominantly in azo-keto form (**T7**) as opposed to azo-enol form (**T8**) and hydrazo-keto form (**T9**) in the solid state (Schemes 4 and 5).

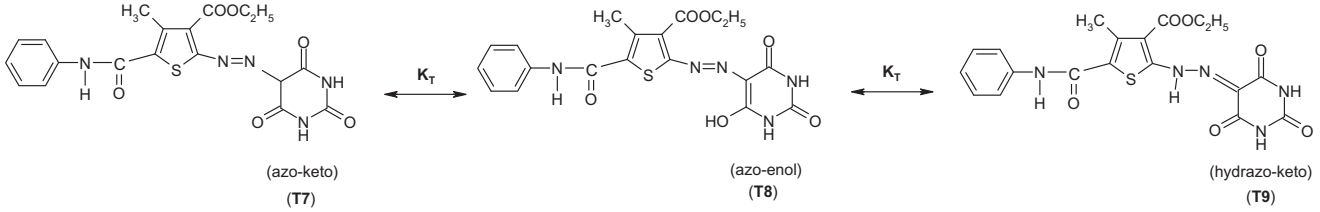
The FT-IR spectra of dye **8** showed one broad hydroxyl (OH) band and one imino (NH) band. These suggest that dye **8** is predominantly in azo-enol form (**T11**) as opposed to azo-keto form (**T10**) and hydrazo-keto form (**T12**), in the solid state (Scheme 6).



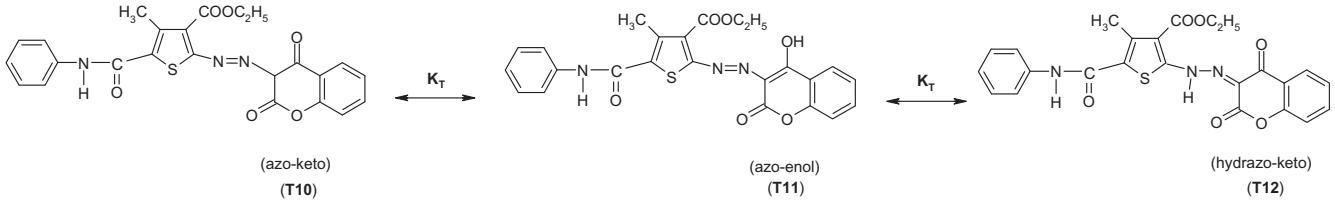
Scheme 3. Tautomeric equilibriums of dyes **2**–**5**.



Scheme 4. Tautomeric equilibriums of dye **6**.



Scheme 5. Tautomeric equilibriums of dye **7**.



Scheme 6. Tautomeric equilibriums of dye **8**.

^{1}H NMR spectra of dyes **2** showed two broad peaks at 9.69 ppm (NH or OH) and 10.13 ppm (NH or OH). Also, ^{1}H NMR spectra of dyes **3** showed two broad peaks at 9.82 ppm (NH or OH) and 10.36 ppm (NH or OH). These results suggest that dyes **2** and **3** were present as a mixture of two tautomeric forms (**T2** and **T3**) in DMSO. ^{1}H NMR spectra of dyes **4**–**8** showed one broad peak within the range of 10.13–10.26 ppm because of OH proton. Also, ^{1}H NMR spectra of dyes **4**–**8** did not show any broad band for tautomeric NH proton. These suggest that dyes **4**–**8** are predominantly in azo-enol form (**T2**, **T5**, T8 and **T11**, respectively) as opposed to azo-keto form (**T1**, **T4**, T7 and **T10**, respectively) and hydrazo-keto form (**T3**, **T6**, T9 and **T12**, respectively) in DMSO.

3.2. Solvent effects on UV–vis. spectra

As the tautomeric equilibria strongly depend on the nature of the media, the behaviour of dyes in various solvents was studied. For this purpose, the UV–vis absorption spectra of dyes **2**–**8** were recorded over the range of λ between 300 and 700 nm, using a variety of solvents in concentrations (10^{-6}–10^{-8} M). Because of solubility problems, these were run at different concentrations and the results are summarised in Table 1. The visible absorption spectra of the dyes did not correlate with the polarity of solvent.

Dyes **2**–**8** gave a maximum absorption peak in all used solvents. This result suggests that dyes **2**–**8** are present in a single tautomeric form in all used solvents.

Table 1
Influence of solvent on λ_{max} (nm) of dyes **2**–**8**.

Dye no	DMSO	DMF	Acetonitrile	Methanol	Acetic acid	Chloroform
2	514	521	452	467	452	452
3	489	514	440	445	438	440
4	471	500	410	427	412	410
5	452	500	430	442	434	433
6	499	515	476	479	479	443
7	431	433	432	442	441	445
8	471	466	468	466	468	470

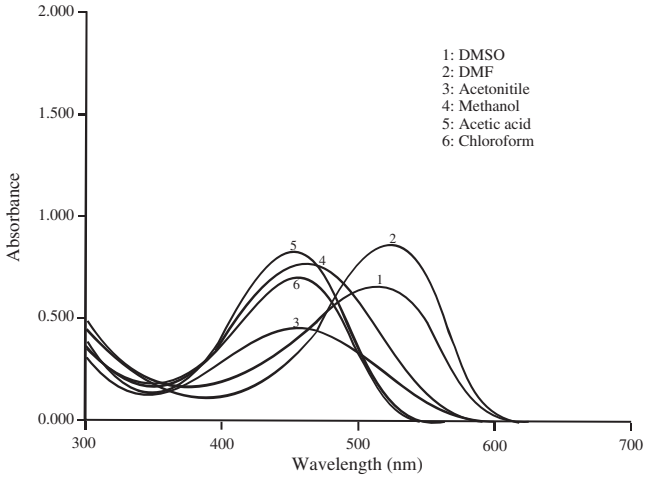


Fig. 1. Absorption spectra of dye **2** in various solvents.

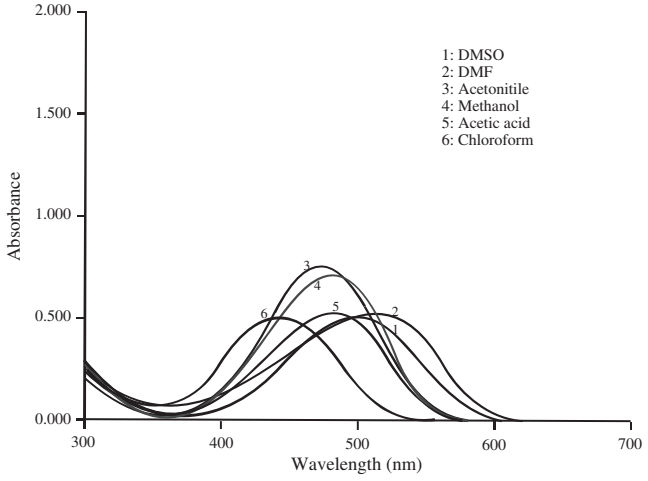


Fig. 2. Absorption spectra of dye **6** in various solvents.

It was observed that the λ_{max} of dyes **2**–**5** in DMSO, DMF and methanol shifted bathochromically with respect to the λ_{max} in chloroform (e.g. for dye **2** λ_{max} is 452 nm in chloroform, 514 nm in DMSO, 521 nm in DMF and 467 nm in methanol) (Fig. 1). But, bathochromic shifts of λ_{max} of dyes **2**–**5** in methanol are less than bathochromic shifts of λ_{max} of dyes **2**–**5** in DMSO and DMF. On the other hand, λ_{max} values of dyes **2**–**5** in acetonitrile and acetic acid did not change significantly with respect to the λ_{max} in chloroform. It was also observed that λ_{max} of dye **6** in DMSO, DMF, acetonitrile, methanol and acetic acid shifted bathochromically with respect to the λ_{max} in chloroform (λ_{max} is 443 nm in chloroform, 499 nm in DMSO, 515 nm in DMF, 476 nm in acetonitrile and 479 nm in methanol and acetic acid) (Fig. 2). Although, λ_{max} of dye **7** in DMSO, DMF, and acetonitrile shifted hypsochromically with respect to the λ_{max} in chloroform, λ_{max} values of dye **7** in methanol, acetic acid and chloroform are similar. λ_{max} values of dye **8** in all used solvents are similar.

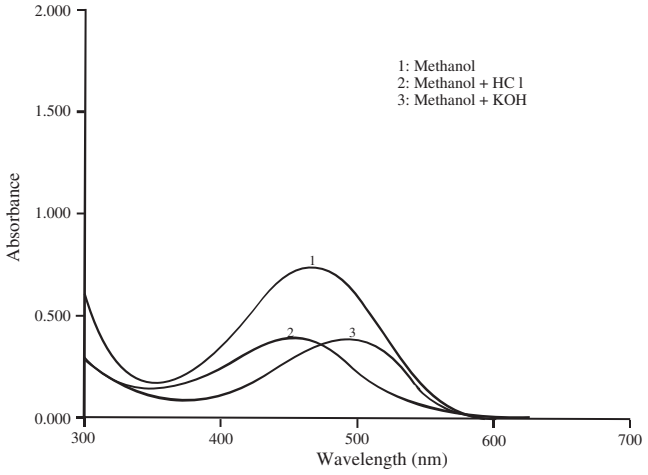


Fig. 3. Absorption spectra of dye **2** in acidic and basic solutions.

3.3. Acid and base effects on UV–vis. spectra

The effects of acid and base on the absorption of dye solutions were investigated and the results are shown in Table 2. The absorption spectra of the dyes **2**–**6** in methanol was quite sensitive to the addition of base (potassium hydroxide, 0.1 M), with λ_{max} of dyes **2**–**6** showing bathochromic shifts and absorption curves of the dyes resembled those in DMSO and DMF (e.g. for dye **2** λ_{max} is 467 nm in methanol, 492 nm in methanol + KOH) (Fig. 3). This result suggests that dyes **2**–**6** are present in a different tautomeric form in methanol + KOH than that in methanol and this tautomeric form resembled those in DMSO and DMF. When base (potassium hydroxide, 0.1 M) was added to dye solutions in methanol, λ_{max} of dye **7** showed slight hypsochromic shift with respect to the λ_{max} in methanol and the absorption spectra of dyes resembled those in DMSO and DMF. It was also observed that when base (potassium hydroxide, 0.1 M) was added to dye solutions in methanol, λ_{max} of dye **8** did not change significantly and absorption curves of the dyes resembled those in DMSO and DMF.

When hydrochloric acid (0.1 M) was added to dye solutions in methanol, λ_{max} of dyes **2**–**5** showed slight hypsochromic shifts with respect to the λ_{max} in methanol and the absorption spectra of dyes resembled those in acetic acid (e.g. for dye **2** λ_{max} is 467 nm in methanol, 452 nm in methanol + HCl) (Fig. 3). Probably, these slight hypsochromic shifts are occured due to solubility of dyes **2**–**5** are different in methanol + HCl than that in methanol and

Table 2
Absorption maxima of dyes **2**–**8** in acidic and basic solutions.

Dye no	λ_{max} (nm)					
	Methanol	Methanol + KOH	Methanol + HCl	Chloroform	Chloroform + piperidine	Acetic acid
2	467	492	452	452	500	452
3	445	492	437	440	501	438
4	427	489	410	410	490	412
5	442	486	430	433	497	434
6	479	523	479	443	502	479
7	442	430	438	445	431	441
8	466	468	469	470	470	468

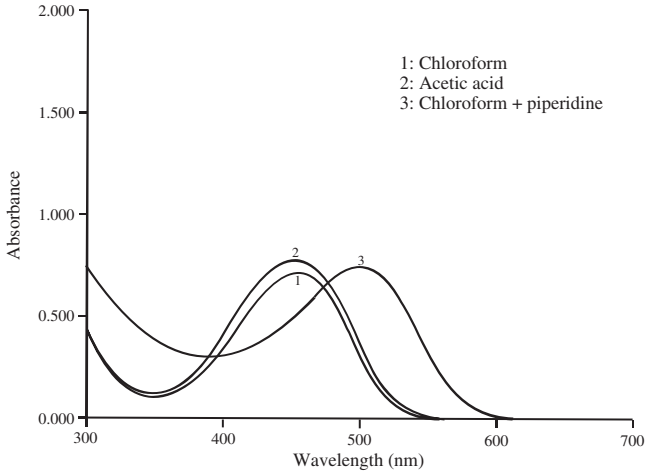


Fig. 4. Absorption spectra of dye **2** in acidic and basic solutions.

solubility resembled those in acetic acid. It was also observed that when hydrochloric acid (0.1 M) was added to dye solutions in methanol, λ_{max} of dyes **6**–**8** did not change significantly.

When piperidine was added to dye solutions in chloroform, λ_{max} of dyes **2**–**6** showed bathochromic shifts and absorption curves of the dyes resembled those in DMSO and DMF (e.g. for dye **2** λ_{max} is 452 nm in chloroform, 500 nm in chloroform + piperidine) (Fig. 4). This result suggests that dyes **2**–**6** are present in a different tautomeric form in chloroform + piperidine than that in chloroform and this tautomeric form resembled those in DMSO and DMF. Although, λ_{max} of the dye **7** showed slight hypsochromic shift when a small amount of piperidine was added to dye **7** solution in chloroform, λ_{max} of the dye **8** did not change significantly.

4. Conclusions

The solvatochromic behaviour and tautomeric structures of newly synthesized bis-heterocyclic monoazo dyes in various solvents was evaluated. Also, acid–base influences on the wavelength of maximum absorption of these dyes have been studied. Dyes **2**–**6** showed bathochromic shifts in most polar solvents, such as DMSO and DMF. It was also observed that the absorption spectra of dyes **2**–**6** in methanol and chloroform were quite sensitive to the addition of base. These results suggest that dyes **2**–**6** are present in a different tautomeric form in basic mediums and DMSO, DMF than that in acetonitrile, methanol, acetic acid and chloroform. Tautomeric forms of dyes **2**–**6** are identical in methanol + KOH, chloroform + piperidine, DMSO and DMF. Also, solubility of dyes **2**–**5** is different in methanol + HCl than that in methanol and solubility resembled those in acetic acid.

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