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The synthesis and solvatochromic properties of some novel heterocyclic disazo dyes derived from barbituric acid

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Abstract

5-Amino-4-arylazo-3-methyl-1*H*-pyrazoles were diazotised and coupled with barbituric acid to provide 13 novel heterocyclic disazo barbituric acid dyes that were characterized by elemental analysis and spectral methods. The effects of varying the pH and solvent on the absorption of the dyes substituted with electron-withdrawing and electron-donating groups at their *o*-, *m*-, *p*-position were examined in detail.

Keywords: Barbituric acid; Azo barbituric acid; Disazo dyes; Pyrazole; Absorption properties; Diazo-coupling reaction

1. Introduction

Recently, metal complex dyes of azo barbituric acids have also attracted increasing attention due to their interesting electronic and geometrical features in connection with their application for molecular memory storages, nonlinear optical elements, printing system, etc. Therefore, several studies have been published on the synthesis and spectral properties of several azo barbituric acids, as well as on their transition metal complexes, so far [1–7].

Nitriles are widely used as intermediates for a large number of heterocyclic compounds [8–11]. Aminopyrazole compounds can be easily obtained by the reaction of nitriles with hydrazine hydrate [12–16]. Pyrazoles are important compounds that have many derivatives with a wide range of interesting properties.

Azo dyes based on heterocyclic amines have been developed, and the resultant dyes give higher tinctorial strength and brighter dyeing than those derived from aniline-based diazo components. For instance, amino-substituted thiazole, isothiazole, thiophene compounds afford highly electronegative diazo components and consequently, provide a pronounced bathochromic effect compared to the corresponding benzenoid compounds [17–25]. Although, many patents and papers describe the synthesis and properties of barbituric acid and monoazo barbituric acid any investigation involved in disazo barbituric acid has not been found. We have previously reported the synthesis of some disazo dyes and solvent effects on their absorption spectra [16,26,27]. In a continuation of our work, we report here the synthesis of a series of new disazo dyes based on barbituric acid. The visible absorption spectra in various solvents of these dyes were also discussed.

2. Experimental

2.1. General

The chemicals used for the synthesis of the compounds were obtained from Aldrich and Sigma Chemical Company

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and used 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 were (δ) given in ppm. Ultraviolet–visible (UV–vis) absorption spectra were recorded on an ATI Unicam UV-100 spectrophotometer at the wavelength of maximum absorption (λ_{max}) in a range of solvents, i.e. DMSO, dimethylformamide

Table 1
Spectral data for dyes **3a–3m**

Dye no.	FT-IR (cm^{-1}, in KBr)				^{1}H NMR[a] (δ, ppm)			
	ν_{N-H}	ν_{Aro-H}	ν_{Al-H}	$\nu_{C=O}$	Aro–H	Alip–H	X–H	Solvent
3a	3182	3082	2984	1737, 1698, 1670	8.00–7.54 (5H, m)	2.60 (3H, s, CH_3)	14.84 (1H, b, barbituric acid OH), 13.27 (1H, b, pyrazole ring NH), 11.64 (1H, b, barbituric acid NH), 11.35 (1H, b, barbituric acid NH)	DMSO-d_6
3b	3191	3077	2982	1726, 1683, 1670	8.43–8.08 (4H, dd)	2.64 (3H, s, CH_3)	14.81 (1H, b, barbituric acid OH), 13.47 (1H, b, pyrazole ring NH), 11.63 (1H, b, barbituric acid NH), 11.34 (1H, b, barbituric acid NH)	DMSO-d_6
3c	3184	3079	2970	1725, 1682, 1669	7.97–7.06 (4H, dd)	2.56 (3H, s, CH_3); 3.85 (3H, s, *p*-OCH_3)	14.80 (1H, b, barbituric acid OH), 13.14 (1H, b, pyrazole ring NH), 11.53 (1H, b, barbituric acid NH), 11.27 (1H, b, barbituric acid NH)	DMSO-d_6
3d	3179	3068	2970	1724, 1712, 1660	7.96–7.59 (4H, dd)	2.58 (3H, s, CH_3)	14.78 (1H, b, barbituric acid OH), 13.28 (1H, b, pyrazole ring NH), 11.59 (1H, b, barbituric acid NH), 11.30 (1H, b, barbituric acid NH)	DMSO-d_6
3e	3175	3096	2992	1718, 1695, 1667	7.91–7.34 (4H, dd)	2.60 (3H, s, CH_3), 2.40 (3H, s, *p*-CH_3)	14.82 (1H, b, barbituric acid OH), 13.20 (1H, b, pyrazole ring NH), 11.55 (1H, b, barbituric acid NH), 11.27 (1H, b, barbituric acid NH)	DMSO-d_6
3f	3180	3053	2964	1723, 1698, 1668	8.59–7.84 (4H, m)	2.63 (3H, s, CH_3)	14.83 (1H, b, barbituric acid OH), 13.42 (1H, b, pyrazole ring NH), 11.62 (1H, b, barbituric acid NH), 11.33 (1H, b, barbituric acid NH)	DMSO-d_6
3g	3184	3071	2994	1726, 1715, 1670	7.60–7.03 (4H, m)	2.60 (3H, s, CH_3), 3.85 (3H, s, *m*-OCH_3)	14.85 (1H, b, barbituric acid OH), 13.24 (1H, b, pyrazole ring NH), 11.56 (1H, b, barbituric acid NH), 11.28 (1H, b, barbituric acid NH)	DMSO-d_6
3h	3181	3053	2994	1723, 1696, 1668	7.96–7.52 (4H, m)	2.61 (3H, s, CH_3)	14.79 (1H, b, barbituric acid OH), 13.32 (1H, b, pyrazole ring NH), 11.58 (1H, b, barbituric acid NH), 11.30 (1H, b, barbituric acid NH)	DMSO-d_6
3i	3184	3066	2982	1710, 1692, 1661	7.88–7.27 (4H, m)	2.62 (3H, s, CH_3), 2.42 (3H, s, *m*-CH_3)	14.84 (1H, b, barbituric acid OH), 13.29 (1H, b, pyrazole ring NH), 11.58 (1H, b, barbituric acid NH), 11.29 (1H, b, barbituric acid NH)	DMSO-d_6
3j	3175	3087	2974	1735, 1695, 1668	8.04–7.63 (4H, m)	2.54 (3H, s, CH_3)	14.60 (1H, b, barbituric acid OH), 13.44 (1H, b, pyrazole ring NH), 11.48 (1H, b, barbituric acid NH), 11.29 (1H, b, barbituric acid NH)	DMSO-d_6
3k	3163	3068	2964	1712, 1692, 1678	7.50–6.99 (4H, m)	2.58 (3H, s, CH_3), 3.92 (3H, s, *o*-OCH_3)	14.48 (1H, b, barbituric acid OH), 13.20 (1H, b, pyrazole ring NH), 11.43 (1H, b, barbituric acid NH), 11.24 (1H, b, barbituric acid NH)	DMSO-d_6
3l	3175	3085	2989	1736, 1695, 1669	7.63–7.43 (4H, m)	2.59 (3H, s, CH_3)	14.50 (1H, b, barbituric acid OH), 13.37 (1H, b, pyrazole ring NH), 11.48 (1H, b, barbituric acid NH), 11.28 (1H, b, barbituric acid NH)	DMSO-d_6
3m	3181	3063	2962	1724, 1696, 1666	7.40–7.27 (4H, m)	2.63 (3H, s, CH_3), 2.58 (3H, s, *o*-CH_3)	14.53 (1H, b, barbituric acid OH), 13.26 (1H, b, pyrazole ring NH), 11.53 (1H, b, barbituric acid NH), 11.29 (1H, b, barbituric acid NH)	DMSO-d_6

[a] Abbreviations: s, singlet; d, doublet; m, multiplet; b, broad.

Table 2
Elemental analysis of dyes **3a–3m**

Dye no.	Molecular formula (m. wt)	M.p.[a] (°C) (colour)	Yield (%)	Elemental analysis: calc. (found)		
				C	H	N
3a	$C_{14}H_{12}N_8O_3$ (340.3)	dec. >340 (orange)	84	49.41 (49.68)	3.55 (3.61)	32.93 (32.77)
3b	$C_{14}H_{11}N_9O_5$ (385.3)	dec. >320 (orange)	86	43.64 (43.89)	2.88 (2.83)	32.72 (32.53)
3c	$C_{15}H_{14}N_8O_4$ (370.3)	dec. >350 (orange)	79	48.65 (48.41)	3.81 (3.70)	30.26 (29.95)
3d	$C_{14}H_{11}ClN_8O_3$ (374.7)	dec. >350 (yellow)	85	44.87 (45.11)	2.96 (2.89)	29.90 (29.78)
3e	$C_{15}H_{14}N_8O_3$ (354.3)	dec. >335 (orange)	74	50.85 (50.67)	3.98 (4.07)	31.62 (31.83)
3f	$C_{14}H_{11}N_9O_5$ (385.3)	dec. >310 (yellow)	91	43.64 (43.81)	2.88 (2.96)	32.72 (32.55)
3g	$C_{15}H_{14}N_8O_4$ (370.3)	dec. >335 (dark yellow)	75	48.65 (48.94)	3.81 (3.89)	30.26 (30.06)
3h	$C_{14}H_{11}ClN_8O_3$ (374.7)	dec. >305 (orange)	87	44.87 (45.16)	2.96 (2.90)	29.90 (29.71)
3i	$C_{15}H_{14}N_8O_3$ (354.3)	dec. >330 (orange)	72	50.85 (50.57)	3.98 (4.13)	31.62 (31.93)
3j	$C_{14}H_{11}N_9O_5$ (385.3)	dec. >310 (red)	85	43.64 (43.81)	2.88 (2.97)	32.72 (33.05)
3k	$C_{15}H_{14}N_8O_4$ (370.3)	dec. >325 (dark yellow)	74	48.65 (48.79)	3.81 (3.92)	30.26 (30.03)
3l	$C_{14}H_{11}ClN_8O_3$ (374.7)	dec. >290 (orange)	82	44.87 (45.16)	2.96 (3.13)	29.90 (29.64)
3m	$C_{15}H_{14}N_8O_3$ (354.3)	dec. >295 (orange)	71	50.85 (50.78)	3.98 (3.87)	31.62 (31.37)

[a] Recrystallized from DMF/H_2O.

(DMF), methanol and acetic acid, at various concentrations ($1\times\ 10^{-6}$–10^{-8}). Change in λ_{max} was also investigated when 0.1 ml base (potassium hydroxide, 0.1 M) and 0.1 ml acid (hydrochloric acid, 0.1 M) were added to dye solutions in methanol (1 ml). Characterization data are shown in Tables 1 and 2.

2.2. Synthesis of 2-arylhydrazone-3-ketiminobutyronitriles and 5-amino-4-arylazo-3-methyl-1H-pyrazoles

2-Arylhydrazone-3-ketiminobutyronitriles (**1a–1m**) and 5-amino-4-arylazo-3-methyl-1*H*-pyrazoles (**2a–2m**) were prepared according to the literature procedures [12,13]. The general route for the synthesis of 2-arylhydrazone-3-ketiminobutyronitriles and 5-amino-4-arylazo-3-methyl-1*H*-pyrazoles is outlined in Scheme 1.

2.3. General synthesis of heterocyclic disazo barbituric acid dyes (3a–3m)

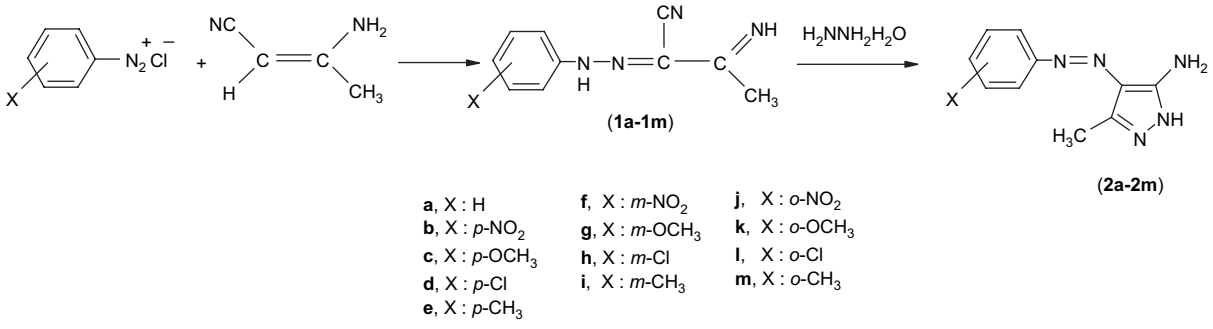
A general preparative procedure is described below for the preparation of dye **3a**. All other dyes (**3b–3m**) were prepared in similar manner.

5-Amino-3-methyl-4-phenylazo-1*H*-pyrazole (2.01 g, 0.01 mol) was dissolved in a mixture of 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, for about 1 h, while cooling at 0–5 °C. The clear diazonium salt solution was then added dropwise to well-cooled (0–5 °C) and stirred solution of barbituric acid (1.28 g, 0.01 mol) in potassium hydroxide (0.56 g, 0.01 mol) and water (10 ml). The pH of the coupling mixture, in each case, was maintained at 5–6 through the coupling process by adding aqueous sodium acetate. Stirring was continued for 4 h at 0–5 °C and the precipitated products separated upon dilution with cold water (50 ml) were filtered off, washed with water several times, dried, and recrystallized from dimethylformamide–water to give 5-(3′-methyl-4′-phenylazo-1′*H*-pyrazole-5′-ylazo) barbituric acid (**3a**) (Scheme 2) as orange crystals, yield 2.86 g (84%), m.p. dec. >340 °C.

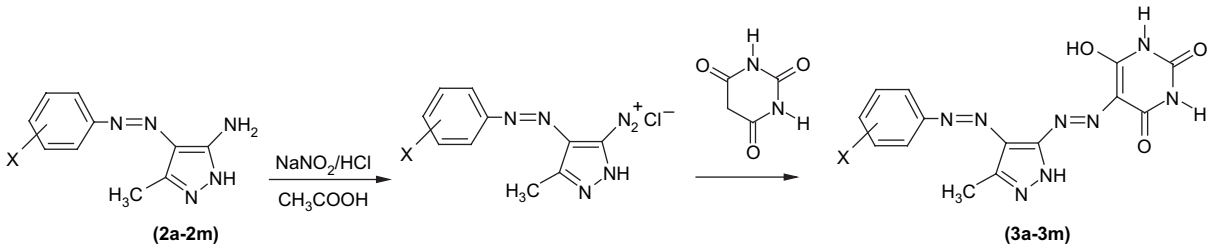
3. Results and discussion

3.1. Spectral characteristics and tautomerism

Tautomerism is not only important to the dyestuff manufacturer but also to other areas of chemistry. Tautomers not



Scheme 1.



Scheme 2.

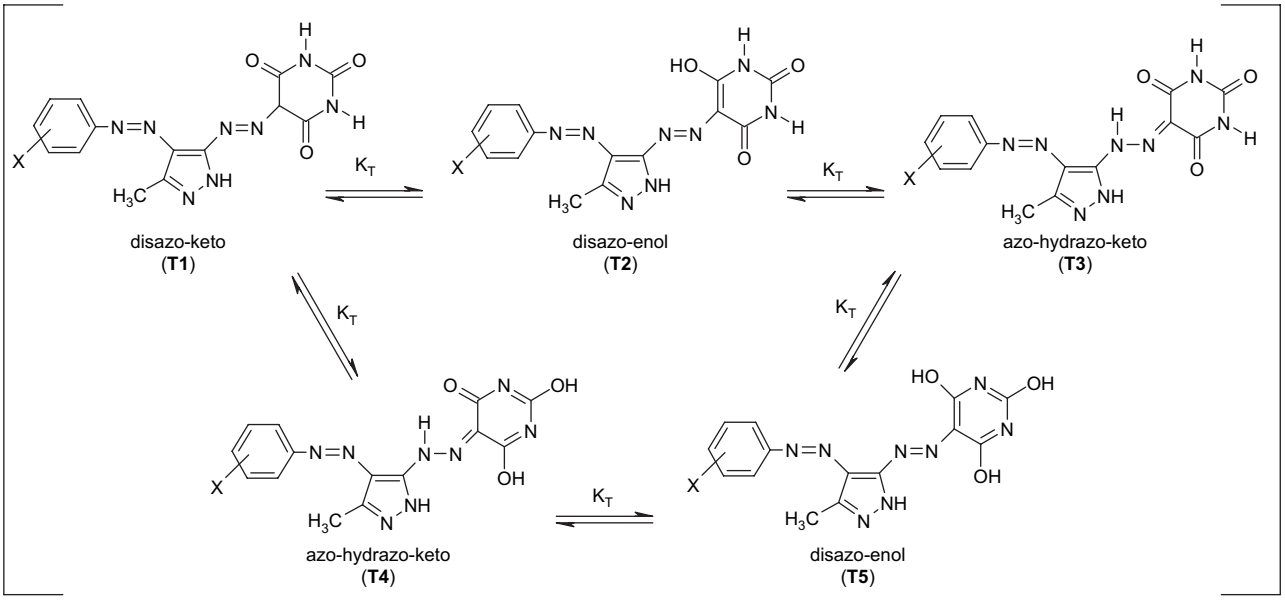
only have different colours, but also have different tinctorial strengths (and hence economics) and different properties, e.g. light fastness. Disazo dyes **3a–3m** can exist in 10 possible tautomeric forms, namely the disazo-keto form **T1**, two disazo-enol forms **T2** and **T5**, two azo-hydrazo-keto forms **T3** and **T4**, the hydrazo-azo-keto form **T6**, two hydrazo-azo-enol forms **T7** and **T10** and two dishydrazo-keto forms **T8** and **T9** as shown in Schemes 3 and 4. The FT-IR spectra of dyes **3a–3m** showed three intense carbonyl (C=O) bands at 1737–1660 cm^{-1} and also did not show any broad band for hydroxyl group. These suggest that these disazo dyes are predominantly in triketo forms (disazo-keto (**T1**), azo-hydrazo-keto (**T3**), hydrazo-azo-keto (**T6**) and dishydrazo-keto (**T8**)) as opposed to the other forms, in the solid state. The FT-IR spectra also showed a band at 3191–3163 cm^{-1}, assigned to imino group (N–H). The other ν_{max} values of 3096–3053 cm^{-1} (aromatic C–H), 2994–2962 cm^{-1} (aliphatic C–H) were recorded. Some investigations were carried out to establish the tautomeric structure of barbituric acid dyes in the solid state using FT-IR. The spectral data generally lead to the conclusion that the tautomeric equilibrium of these dyes is in favour of the triketo form in the solid state [1].

^{1}H NMR spectra of dyes **3a–3m** showed a signal at 14.85–14.48 ppm. These chemical shifts can be attributed to hydrogen bonded OH proton. It is well known that hydrogen bonded OH proton resonance appears at lower field than that of NH proton resonance. Also, in ^{1}H NMR spectra of dyes **3a–3m** two broad signals at 11.64–11.43 and 11.35–11.24 ppm attributed to NH protons at the 1- and 3-position of pyrimidine ring. These results suggest that dyes **3a–3m** are predominantly in the disazo-enol form **T2** or hydrazo-azo-enol form **T7** as opposed to the other forms in DMSO. ^{1}H NMR spectra of dyes **3a–3m** also showed a broad signal at 13.47–13.14 ppm attributed to NH proton at the pyrazole ring or NH proton of hydrazo form of pyrazole ring.

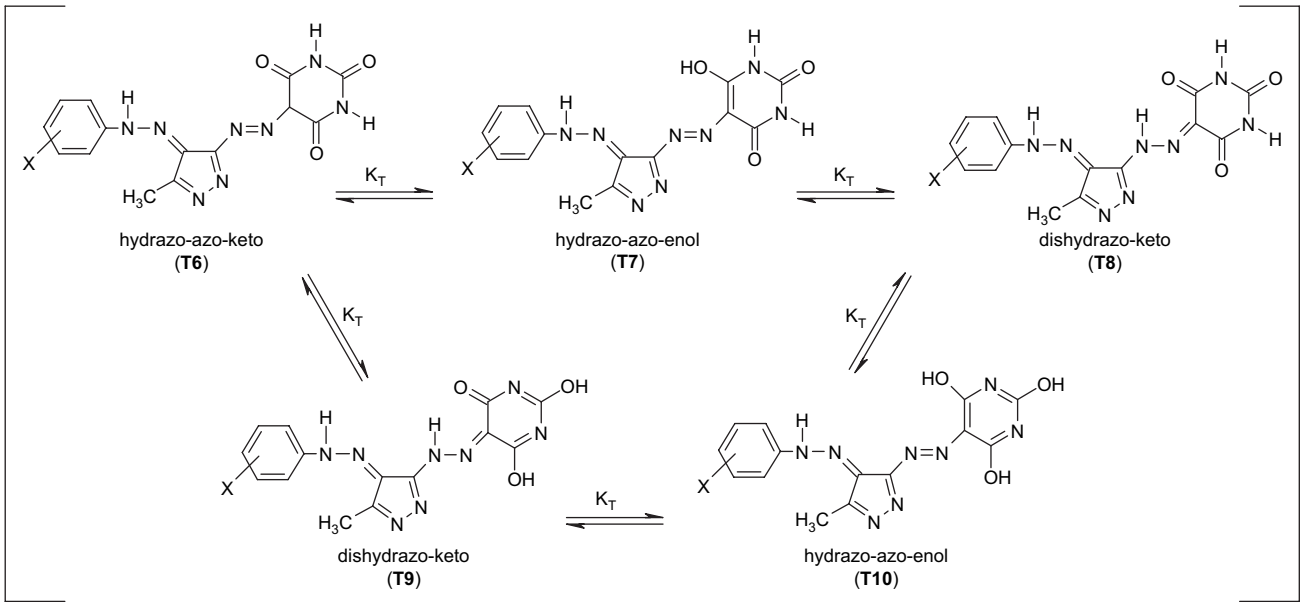
3.2. Solvent effects

The UV–vis absorption spectra of dyes **3a–3m** were recorded over the range of λ between 300 and 700 nm, using a variety of solvents in concentrations (10^{-6}–10^{-8} M) and the results are summarised in Table 3. The visible absorption spectra of the dyes did not correlate with the polarity of solvent. Each of the dyes gave two absorption bands in all the solvents employed.

It was observed that although in DMSO, DMF and methanol the absorption spectra did not change significantly except for dye **3b**, λ_{max} of these dyes shifted hypsochromically in



Scheme 3.



Scheme 4.

acetic acid except for dyes **3a**, **3e**, **3g**, **3k** and **3m**; for example for **3b**, λ_{max} was at 410 nm in acetic acid, but at 437 nm in DMSO, 441 nm in DMF and 430 nm in methanol (Fig. 1). λ_{max} values of dye **3b** in DMSO and DMF were shifted bathochromically with respect to the λ_{max} in methanol and acetic acid. λ_{max} of dyes **3a**, **3e**, **3g**, **3k** and **3m** did not change significantly in all used solvents.

3.3. Acid and base effects

The effects of acid and base on the absorption of dye solutions were investigated and the results are shown in Table 4. The absorption spectra of the dyes in methanol were quite sensitive to the addition of base (potassium hydroxide, 0.1 M), with λ_{max} of dyes **3a**–**3m** showing a bathochromic shift; for example for **3i**, λ_{max} was at 422 nm in methanol, but at 474 nm in methanol + KOH (Fig. 2). This result indicates that tautomeric form in methanol changed with another tautomeric form in basic solution (Schemes 3 and 4).

Table 3
Influence of solvent on λ_{max} (nm) of dyes **3a**–**3m**

Dye no.	DMSO	DMF	Methanol	Acetic acid
3a	415, 329	414, 327	416, 322	414, 321
3b	437, 354	441, 356	430, 343	410, 346
3c	432, 350	431, 348	429, 344	426, 346
3d	419, 333	419, 331	420, 327	414, 326
3e	416, 332	415, 330	421, 336	415, 325
3f	419, 328	422, 327	416, 323	412, 321
3g	416, 330	416, 328	418, 322	414, 321
3h	416, 331	419, 330	418, 325	413, 323
3i	415, 330	415, 328	422, 324	413, 322
3j	415, 328	416, 326	416, 323	409, 323
3k	411, 331	411, 330	412, 332	411, 324
3l	409, 327	408, 325	409, 324	400, 323
3m	408, 327	406, 324	410, 323	406, 321

When hydrochloric acid (0.1 M) was added to dye solutions in methanol, λ_{max} showed slight hypsochromic shifts; for example for **3i**, λ_{max} was at 422 nm in methanol, but at 403 nm in methanol + HCl (Fig. 2). This result indicates that tautomeric forms in methanol changed with the another tautomeric form in acidic solution.

3.4. Substituent effects

As seen in Table 3, the absorption spectra of *p*-nitro derivative (dye **3b**) were shifted bathochromically in DMSO, DMF and methanol when compared with dye **3a**. Moreover, the absorption spectra of *p*-methoxy derivative (dye **3c**) were shifted bathochromically in all used solvents when compared with dye **3a**. On the contrary, the absorption spectra of *o*-methoxy, *o*-chloro and *o*-methyl derivatives (dyes **3k**–**3m**) were shifted hypsochromically in all used solvents when compared with dye **3a**. Generally, the absorption spectra of the other

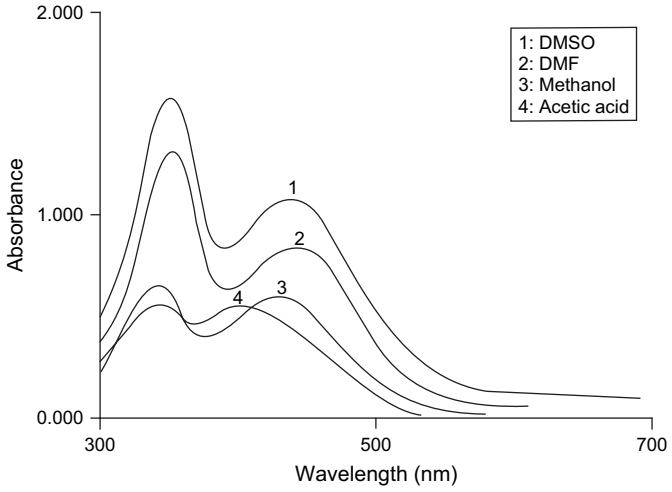


Fig. 1. Absorption spectra of dye **3b** in various solvents.

Table 4
Absorption maxima of dyes **3a–3m** in acidic and basic solutions

Dye no.	Methanol	Methanol + KOH	Methanol + HCl	Acetic acid
3a	416, 322	472, 346	400, 317	414, 321
3b	430, 343	493, 390	374, 351	410, 346
3c	429, 344	477, 350	419, 336	426, 346
3d	420, 327	479, 349	404, 323	414, 326
3e	421, 336	475, 346	405, 323	415, 325
3f	416, 323	479, 349	400, 317	412, 321
3g	418, 322	476, 348	404, 318	414, 321
3h	418, 325	479, 349	403, 317	413, 323
3i	422, 324	474, 346	403, 318	413, 322
3j	416, 323	480, 343	397, 313	409, 323
3k	412, 332	486, 351	404, 317	411, 324
3l	409, 324	459, 350	390, 316	400, 323
3m	410, 323	467, 344	395, 317	406, 321

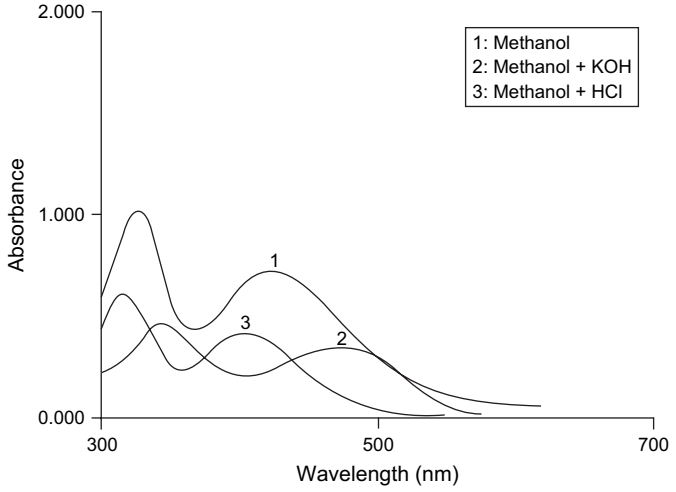


Fig. 2. Absorption spectra of dye **3i** in acidic and basic solutions.

derivatives (dyes **3d–3j**) did not change significantly in all used solvents when compared with dye **3a**.

4. Conclusions

In conclusion, we described the synthesis and solvatochromic properties of a series of 13 novel heterocyclic disazo barbituric acids. Also, acid–base and substituent influence on the wavelength of maximum absorption has been studied. It was found that these disazo dyes exist in triketo forms in solid state, while in azo-enol forms in solvents. It was also observed that the absorption spectra of these disazo dyes in methanol were quite sensitive to the addition of base.

Dyes **3a–3m** can be used as ligand for synthesis of new azo-complex dyes. Dyes **3a–3m** can also be applied to polyester and/or polyamide fibers as disperse dyes.

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