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Synthesis of some hetarylazopyrazolone dyes and solvent effects on their absorption spectra☆

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Abstract

A series of hetarylazopyrazolone dyes were prepared by coupling 3-methyl-1-phenyl-2-pyrazoline-5-one with 11 heterocyclic amines in nitrosyl sulphuric acid. Absorption spectra of the dyes were examined in various solvents and the compounds in solution exhibited hydrazone–common anion equilibrium. The hetarylazopyrazolones readily undergo acid dissociation into the common anion in methanol, DMF and DMSO. Absorption maxima of the dyes showed large bathochromic effects in comparison with analogous dyes containing carbocyclic amine residues in DMF except those containing isoxazolyl and pyridinyl moieties. The pKa values of the compounds have been determined spectrophotometrically in various ethanol–water solutions. The effect of temperature and concentration on the visible absorption spectra are also discussed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Azopyrazolone dyes; Heterocyclic disperse dyes; Azo disperse dyes; Solvent effect; pKa values; Absorption spectra

1. Introduction

Many patents and papers describe the synthesis and technical importance of phenylazopyrazolone dyes [1,2], and several studies have been published with respect to hetarylazopyrazolone dyes. Sabnis et al. [3] reported the synthesis of azo dyes prepared from 2-aminothiophene derivatives and various heterocyclic coupling components, and their application on polyester fibres gave excellent results. On the other hand, the use of heteroaromatic amines as diazo components in the generation of disperse dyes having essentially colour deepening effect is well-established [4,5]. We have recently reported the synthesis of some novel hetarylazopyridone dyes [6], which exhibit a strong solvent dependence in their absorption spectra. In continuation of our work, we report here the synthesis of some hetarylazopyrazolone compounds (**1**–**11**) using 3-methyl-1-phenyl-2-pyrazoline-5-one as coupling component, and an evaluation of their visible absorption spectra with respect to the influence of solvent. The pKa values of the compounds have also been determined in various ethanol–water mixtures. The dye structures are shown in Scheme 1.

2. Experimental

2.1. General

The chemicals used in the synthesis of all dyes were obtained from Aldrich Chemical Company or Sigma Chemical Company and were used

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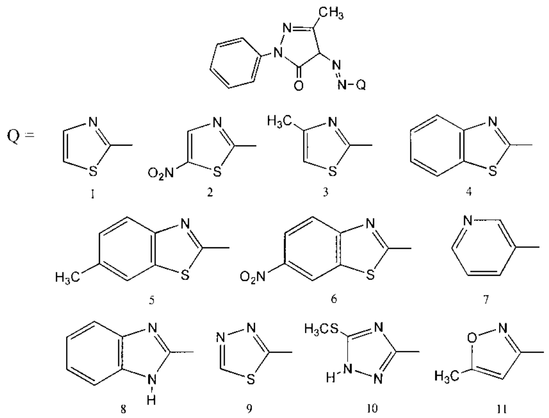


Scheme 1.

without further purification. The solvents used were spectroscopic grade. Ethanol was distilled prior to use.

IR spectra were recorded on a Mattson 1000 FT-IR spectrophotometer in KBr. ^{1}H-NMR spectra were recorded on a Varian EM 360L in TFA/$CDCl_3$ or $CDCL_3$ with TMS as internal reference. Absorption spectra were recorded on an ATI Unicam UV-100 spectrophotometer in various solvents. All melting points were uncorrected. pH measurements were carried out on a Corning M 240 pH meter with a combined glass electrode type 476050. pKa values of the dyes were determined by the previously reported method [7].

2.2. Preparation of hetarylazopyrazolone dyes (1–11)

Diazotisation of the various heterocyclic amines was effected with nitrosyl sulphuric acid. A typical procedure is that described below, used for 2-aminothiazole; all other dyes were prepared in a similar manner. Characterisation data are shown in Tables 1 and 2.

2.2.1. Preparation of 3-methyl-1-phenyl-4-(-2-thiazolylazo)-2-pyrazoline-5-one

2-Aminothiazole (2.0×10^{-3} mol) was dissolved in hot glacial acetic acid (2.5 ml) and was rapidly cooled in an ice–salt bath to −5°C. The liquor was then added in portions during 30 min to a cold solution of nitrosyl sulphuric acid (prepared from sodium nitrite (1 g) and concentrated sulphuric acid (7 ml) at 70°C). The mixture was stirred for an additional 1 h at 0°C. After diazotisation was complete, the diazo liquor was slowly added to a vigorously stirred solution of 3-methyl-1-phenyl-2-pyrazoline-5-one (2.0×10^{-3} mol) in potassium hydroxide (2.0×10^{-3} mol) and water (2 ml). The pH of the reaction mixture was maintained at 7–8 by simultaneous addition of solid sodium carbonate in portions. The mixture was then stirred for 1 h at 0–5°C. The resulting solid was filtered, washed with cold water and dried. Recrystallization from 95% (v/v) ethanol gave orange needles (yield 82%), m.p. 163–164°C.

2.3. Determination of pKa values of the dyes

The acid dissociation constants of the dyes were determined by spectrophotometric titration in various ethanol–water mixtures at 27 ± 0.1 M ionic strength as previously reported [7]. The concentration of the dyes were $\sim1.0\times10^{-6}$ M.

3. Results and discussion

The hetarylazopyrazolone dyes **1**–**11** were prepared by coupling 3-methyl-1-phenyl-2-pyrazoline-5-one with diazotized heterocyclic amines in nitrosyl sulphuric acid. The dyes may exist in four possible tautomeric forms, namely two azo-keto forms A and D, the azo-enol form B and the hydrazone-keto form C, as shown in Scheme 2. The deprotonation of the four tautomers leads to a common anion.

The infrared spectra of all the compounds (in KBr) showed intense carbonyl bands at 1626–1683 cm^{-1} (Table 1). It can be suggested that these compounds do not exist as the azo-enol form in the solid state. Numerous investigations have been carried out to establish the tautomeric structure of arylazo-5-pyrazolones both in the solid state and in solution, and a variety of spectroscopic techniques have been used. The spectral data generally lead to the conclusion that the tautomeric equilibrium of the phenylazopyrazolone dyes is in favour of the hydrazone form in the solid state and in $CHCl_3$, DMSO and pyridine [8–12].

Table 1
Spectral data for dyes **1**–**11**

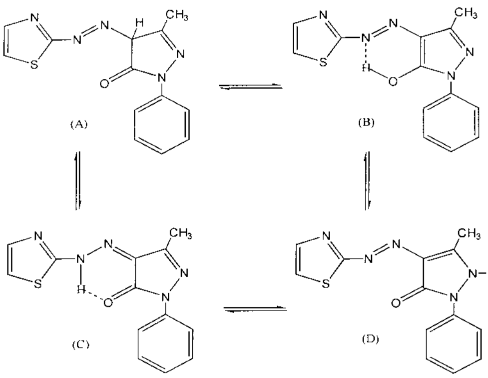
Dye no.	IR (cm^{-1}) in KBr				
	$\nu_{C=O}$	$\nu_{C=N}$	ν_{NH}	$\nu_{C=C(aro)}$	^{1}H-NMR (ppm)
1	1666	1575	3413 3547	1544	2.25 (3H,s), 6.90 (1H,d), 7.5 (1H,d), 7.4–7.9 (5H,m), 12.5 (NH,broad)
2	1683	1591	3415 3545	1531	2.41 (3H,s), 7.2–7.8 (5H,m), 8.3 (1H,s)
3	1665	1579	3200	1545	2.30 (3H,s), 2.4 (3H,s), 6.8 (1H,s), 7.2–7.9 (5H,m)
4	1664	1575	3417 3552	1548	2.25 (3H,s), 7.1–7.5 (5H,m), 7.6–8.1 (4H,m)
5	1658	1581	3425	1600	2.35 (3H,s), 3.85 (3H,s), 7.1–7.6 (5H,m), 7.6–7.9 (3H,m)
6	1660	1548	3462	1525	2.41 (3H,s), 7.1–8.8 (8H,m)
7	1655	1581	3350	1552	2.25 (3H,s), 7.1–7.5 (5H,m), 7.6–8.0 (2H,m), 8.3–8.8 (2H,m)
8	1626	1597	3250	1497	2.35 (3H,s), 7.1–7.9 (9H,m), 5.3 (NH,broad)
9	1658	1575	3438	1543	2.25 (3H,s), 7.1–8.0 (6H,m)
10	1660	1582	3200	1552	2.35 (3H,s), 2.75 (S-CH_3,s), 7.3–7.7 (5H,m), 8.1 (NH,broad)
11	1659	1597	3360	1614	2.30 (3H,s), 2.4 (3H,s), 6.4 (1H,s), 7.2–7.8 (5H,m)

Table 2
Elemental analysis of dyes **1**–**11**

Compound no.	Molecular formula	C %		H %		N %		S %		Melting point (°C)
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
1	$C_{13}H_{11}N_5OS$	54.74	54.74	3.85	3.79	24.56	24.15	11.22	11.31	163–165
2	$C_{13}H_{10}N_6O_3S$	47.27	47.32	3.03	2.99	25.45	25.12	9.70	9.75	241–243
3	$C_{14}H_{13}N_5OS$	56.19	55.73	4.35	4.53	23.41	22.69	10.70	11.35	144(dec)
4	$C_{17}H_{13}N_5OS$	58.12	58.01	3.70	3.65	19.94	19.23	9.12	9.16	206–208
5	$C_{18}H_{15}N_5O_2S$	59.18	59.12	4.11	4.01	19.18	18.96	8.77	8.71	214–216
6	$C_{17}H_{12}N_6O_3S$	53.68	53.98	3.16	3.08	22.11	22.02	8.42	8.51	186–187
7	$C_{15}H_{13}N_5O$	64.52	64.57	4.66	4.87	25.09	24.63	–	–	127–128
8	$C_{17}H_{14}N_6O$	64.15	63.63	4.40	4.65	26.42	23.84	–	–	147–150
9	$C_{12}H_{10}N_6OS$	47.68	47.62	3.31	3.21	27.81	27.26	10.60	10.72	207–209
10	$C_{13}H_{13}N_7OS$	49.52	49.53	4.13	3.99	31.11	30.28	10.16	9.89	222–223
11	$C_{14}H_{13}N_5O_2$	59.36	59.46	4.59	5.01	24.73	24.31	–	–	177–178

Absorption spectra of the dyes **1**–**11** were recorded in various solvents at a concentration of $\sim10^{-6}$–10^{-7} M and the results are summarised in Table 3. Two typical spectra are shown in Figs. 1 and 2. The visible absorption spectra of the dyes were found to exhibit a strong solvent dependence, which did not show a regular variation with the polarity of the solvents. It was observed that although in chloroform, ethyl acetate, acetone and glacial acetic acid the absorption spectra did not change significantly, λ_{max} of the dyes shifted considerably in methanol, 80 (v/v) ethanol–water, DMSO and DMF (e.g. for dye **2** λ_{max} is 409 nm in $CHCl_3$ and 568 nm in DMF; for dye **4** λ_{max} is 404 nm in $CHCl_3$ and 473 nm in DMF).

Strong evidence for the existence of these compound in an equilibrium is provided by the one or two isosbestic points on studying the visible spectra of, for example, dye **1** and dye **2** in different solvents (Figs. 1 and 2). This equilibria depends on the acidity of the solvents used. In proton donating solvents such as glacial acetic acid and



Scheme 2.

chloroform, the dyes give a blue shift of λ_{max} and are basically in the neutral form. In proton accepting solvents, such as alcohols, DMF and DMSO, the dyes give a red shift of λ_{max} and exist mainly in the common anion form. Such an effect of solvents is consistent with the phenomenon of dissociation rather than azo-hydrazone tautomerism. It was also observed that the absorption curves of the dyes (except dye **7** and dye **11**) were very sensitive to acids and bases. λ_{max} of the dyes showed large bathochromic shifts when a small amount of piperidine was added to each of the dye solutions in chloroform and acetone (Table 4) and the absorption curves of the dyes resembled those in DMSO and DMF. A typical example is shown in Fig. 3. There was no significant change in the spectra when a small amount of piperidine was added to dye solutions in DMSO and DMF.

λ_{max} of the dyes in methanol showed large hypsochromic shifts when 0.1 M HCl was added, being nearly the same as those observed in acetic acid. In contrast, addition of a small amount of 0.1 M KOH to the methanolic solutions of the dyes caused a small change in the spectra (Table 4, Fig. 3). This indicates that the hetarylazopyrazolones (**1**–**11**) exist in a dissociated state in methanol, DMSO and DMF. These results are in agreement with those obtained for hetarylazopyridones in our previous work [6]. Peng et al. [13] also reported the same results for thiadiazolylazopyridones. Therefore, the structures of the dyes prepared were assigned to any of the tautomeric forms in acidic medium and to the common anion form in basic medium. The results show that these equilibria exist in solutions of hetarylazopyrazolones and they could be ionized even in proton accepting solvents.

In the next part of the investigation, the pKa values of the dyes were also determined spectrophotometrically in various ethanol–water mixtures. These results are shown in Table 5. Spectra recorded at different pH values in each case showed an isosbestic point. This indicates that two species are in equilibrium. As a typical example, Fig. 4 shows the spectra of dye **1** at different pH values.

The pKa values of the dyes were found to be within the range 2.58–7.68 in 95% (v/v) ethanol–water, 2.95–8.61 in 80% (v/v) ethanol–water and 3.83–8.75 in 50% (v/v) ethanol–water mixtures. As shown in Table 5, the pKa values of the dyes

Table 3
Influence of solvent on λ_{max} (nm) of dyes **1**–**11**

Compound no.	Acetic acid	Chloroform	Ethyl acetate	Acetone	Methanol	80% (v/v) ethanol–water	DMSO	DMF
1	395	404	399	399	452, 400 s[a]	465	442	473
2	403	409	405	406	529	535	569	568
3	402	412	407	407	420	457	460, 420 s[a]	469
4	396	404	399	399	446, 402 s[a]	465	450	473
5	417	430	424	421	467	469	450	477
6	386	347, 405 s[a]	359	370	488	492	453	520
7	371	386	382	381	371	383	382	434
8	371	416	415	423	441	444	469	456
9	350	357	356	356	436	442	522	454
10	354	369	371	371	375, 410 s[a]	424	342	440
11	337	342	340	339	338	342, 410 s[a]	341	410

[a] Shoulder.

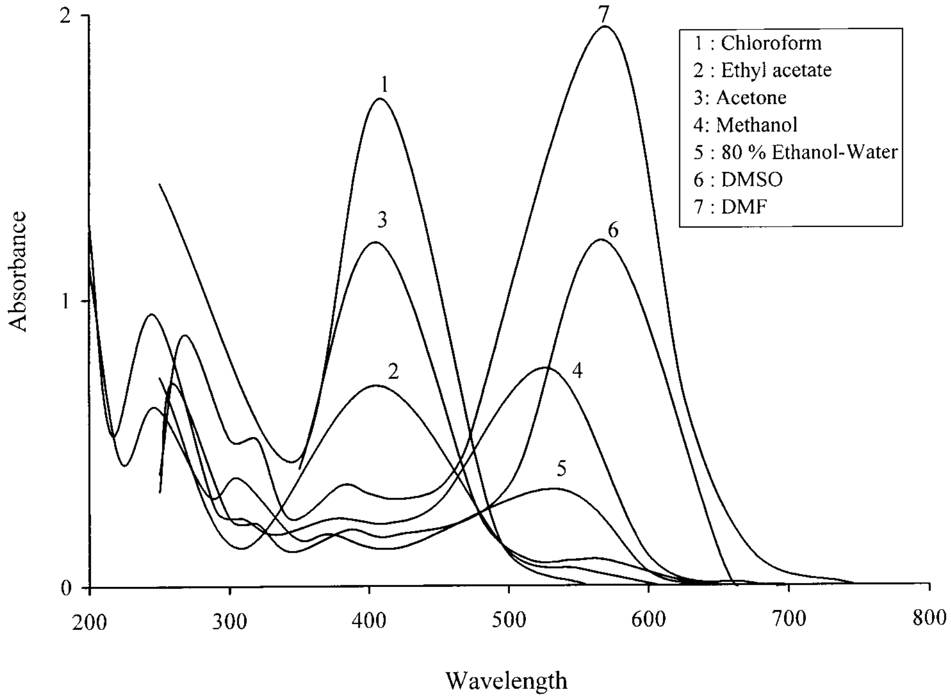


Fig. 1. Absorption spectra of dye **2** in various solvents.

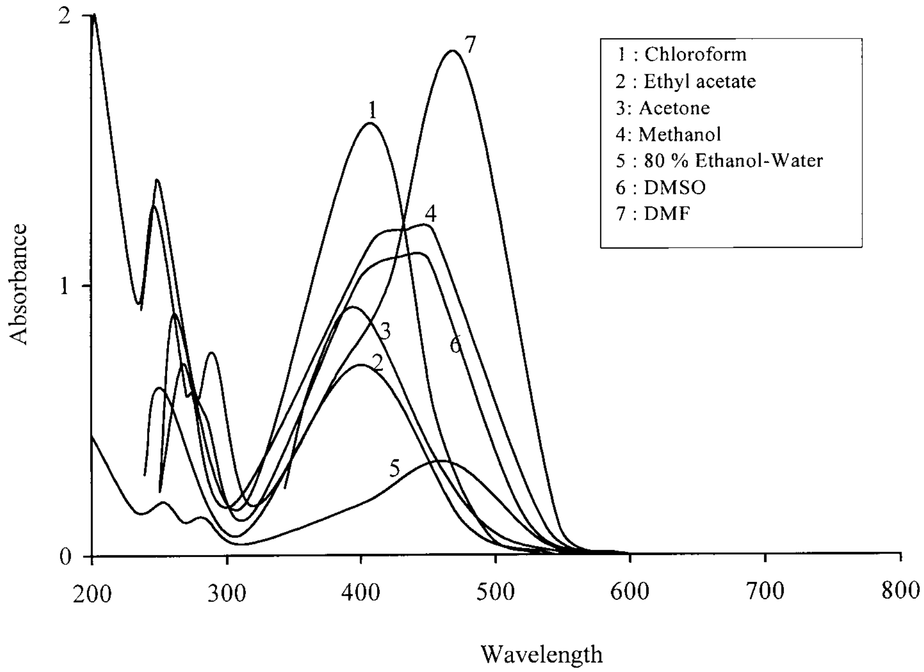


Fig. 2. Absorption spectra of dye **4** in various solvents.

Table 4
Aborption maxima of dyes **1**–**11** in acidic and basic solutions[a]

	λ_{max} (nm)						
Dye no.	Chloroform	Chloroform + piperidine	Acetone	Acetone + piperidine	Methanol	Methanol + HCl	Methanol + KOH
1	404	468	400	468	452	398	461
2	409	530	406	549	529	405	532
3	411	465	408	464	420	401	456
4	403	467	400	466	446	399	462
5	429	475	437	472	467	422	467
6	402	494	371, 496s	500	488	389	488
7	386	386	381	389	371	355	395
8	422	455	434	453	441	360	441
9	357	443	356	446	436	351	441
10	371	429	371	430	375	357	414
11	342	344	347	350	338	336	369

[a] Shoulder.

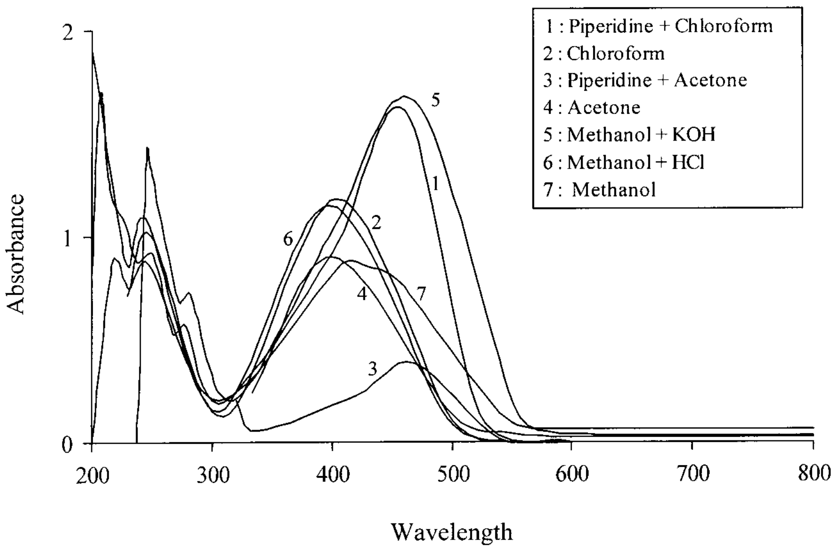


Fig. 3. Absorption spectra of dye **1** in acidic and basic solutions.

decrease as the percentage of ethanol increases. This may be explained on the basis that ethanol acts as proton acceptor, thus facilitating proton dissociation as compared with water.

The strongly electron withdrawing nitro group, in both the thiazole and the benzothiazole series, has a significant influence on the dissociation and decreases the pKa values (e.g. for dye **1** pKa: 4.82, for dye **2** pKa: 2.58 in 95% (v/v) ethanol–water). In contrast, introduction of the donor methyl or methoxy groups in both series of dyes did not significantly change the pKa values of the dyes [e.g. for dye **4** pKa: 4.92, for dye **5** pKa: 4.66 in 95% (v/v) ethanol–water].

The effect of sample concentration on the equilibria was also examined. The results obtained are listed in Table 6. The λ_{max} values of the dyes (**1**–**11**) did not change with dye concentration in chloroform, acetone, DMSO and DMF, but λ_{max} values of some dyes in methanol (e.g. Dyes **1**, **3**,

Table 5
pKa values of the dyes in various ethanol–water mixtures

Dye no.	95% (v/v) ethanol–water	80% (v/v) ethanol–water	50% (v/v) ethanol–water
1	4.82 ± 0.02	5.99 ± 0.01	6.93 ± 0.02
2	2.58 ± 0.03	2.95 ± 0.02	3.83 ± 0.01
3	5.13 ± 0.02	5.28 ± 0.01	6.08 ± 0.02
4	4.92 ± 0.01	5.27 ± 0.03	6.09 ± 0.03
5	4.66 ± 0.03	5.15 ± 0.01	5.56 ± 0.02
6	3.67 ± 0.02	3.95 ± 0.03	4.73 ± 0.01
7	7.68 ± 0.01	8.61 ± 0.02	8.75 ± 0.02
8	5.29 ± 0.02	6.72 ± 0.02	Insoluble
9	3.64 ± 0.02	4.05 ± 0.03	3.93 ± 0.03
10	5.21 ± 0.01	5.76 ± 0.02	6.00 ± 0.02
11	6.12 ± 0.02	6.68 ± 0.12	5.09 ± 0.03

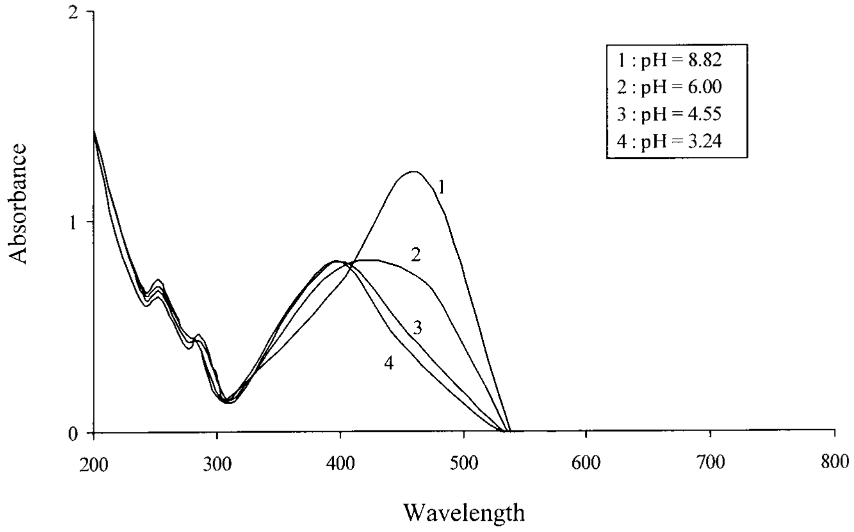


Fig. 4. Absorption spectra of dye **1** at different pH values.

4, **5** and **9**) showed a blue shift and dye **6** showed a red shift with increasing concentrations. This indicates that hetarylazopyrazolones exist in any of the tautomeric forms in chloroform and acetone, in the common anion form in DMF and DMSO, and in a partly dissociated state in methanol.

Solutions of the dyes in chloroform, acetone and methanol were examined in the temperature range 25–50°C (Table 6) and $\lambda_{\max}$ values of the dyes (**1**–**11**) did not change significantly. These results support the dissociation equilibria of hetarylazopyrazolones in proton accepting solvents, which do not involve change of energy.

As is apparent in Table 3, while introduction of nitro groups into the thiazole and benzothiazole moieties results in large bathochromic shifts in methanol, DMSO and DMF (for dye **2** $\Delta\lambda = 95$ nm relative to dye **1**; for dye **6** $\Delta\lambda = 47$ nm relative to dye **4** for spectra in DMF), it produces only a minimal shift in other solvents (for dye **2** $\Delta\lambda = 5$ nm relative to dye **1** for spectra in $CHCl_3$) for the thiazole series. On the other hand, in the benzothiazole series, it produces hypsochromic shifts

Table 6
Influence of temperature and sample concentration on absorption maxima of dyes **1–11**

	$\lambda_{\max}$ (nm)								
Dye no.	Chloroform concentrated, 25°C	Chloroform diluted, 25°C	Chloroform 50°C	Acetone concentrated, 25°C	Acetone diluted, 25°C	Acetone 50°C	Methanol concentrated, 25°C	Methanol diluted, 25°C	Methanol 50°C
1	404	404	400	400	400	401	409	449	449
2	410	409	409	406	406	406	530	531	531
3	411	411	407	408	409	408	410	417	418
4	403	404	403	400	400	401	404	410	410
5	429	430	429	437	438	431	458	463	462
6	402	400	393	371	368	367	357	354	355
7	386	385	384	381	381	381	377	377	377
8	422	427	421	434	434	439	442	443	443
9	357	356	357	356	356	356	354	369	368
10	371	371	369	371	371	371	369	370	371
11	342	342	340	339	337	337	337	337	337

(for dye **6** $\Delta\lambda = 57$ nm relative to dye **4** for spectra in $CHCl_3$). This indicates that the nitro group facilitates dissociation of hetarylazopyrazolone dyes and has little effect on the colour of the neutral form of the dye molecule. The largest bathochromic effect was observed for dye **2** and dye **6** in the series of hetarylazopyrazolone dyes. In contrast, the presence of pyridine and isoxazole rings did not cause any significant variation in the $\lambda_{\max}$ values of the dyes (dye **7** and dye **11**). In conclusion, the dyes prepared are bathochromic in comparison with the analogous phenylazopyrazolone dyes [14,15].

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