ELSEVIER

Dyes and Pigments 55 (2002) 99–108

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Hetarylazo disperse dyes derived from 3-methyl-1-(3′,5′-dipiperidino-*s*-triazinyl)-5-pyrazolone as coupling component

Fikret Karcı[a], Nermin Ertan[b,*]

[a]*Department of Chemistry, Pamukkale University, Kínikli 20017, Denizli, Turkey*
[b]*Department of Chemistry, Gazi University, Teknikokullar 06500, Ankara, Turkey*

Received 8 April 2002; received in revised form 19 April 2002; accepted 28 August 2002

Abstract

The synthesis of some novel, hetarylazopyrazolone dyes was achieved by diazotisation of five heterocyclic amines using nitrosyl sulphuric acid, coupling with 3-methyl-1-(3′,5′-dipiperidino-*s*-triazinyl)-5-pyrazolone. Visible absorption spectra of the dyes were examined in various solvents and the compounds in solution exhibited several equilibria. The hetarylazopyrazolones readily undergo acidic dissociation into the respective common anion in both DMF and DMSO. The absorption maxima of the dyes showed large bathochromic effects in comparison with analogue dyes containing carbocyclic amine residues and *N*-phenylpyrazolone derivatives. The colour of the dyes is discussed with respect to the nature of the heterocyclic ring and substituents therein. The affects of temperature, concentration as well as acid and base on the visible absorption maxima of the dyes are also reported.

Keywords: Azopyrazolone dyes; Heterocyclic disperse dyes; Thiazolylazo dyes; Benzothiazolylazo dyes; Solvent effect; Substituent effect

1. Introduction

Many patents and papers describe the synthesis and dyeing properties of phenylazopyrazolone disperse dyes [1–3]. In recent years, the synthesis and comparative tinctorial behaviour of some *N*-hetaryl substituted pyrazolone derivatives have been reported [4,5]. However, very few comparable investigations have been made using hetarylazo dyes derived from the pyrazole-5-one system [6]. We have previously reported the synthesis of some hetarylazopyrazolones and solvent effects on their absorption spectra [7]. In a continuation of our work, we report here the synthesis of some hetarylazopyrazolone dyes **4**–**8** resulting from the use of 3-methyl-1-(3′,5′-dipiperidino-*s*-triazinyl)-5-pyrazolone as coupling component and an evaluation of their visible absorption spectra with respect to the influences of solvent and 1-substitution on the pyrazolone residue. Also, the λ_{max} of the dyes

* Corresponding author. Tel.: +90-312-2126030/2771; fax: +90-312-2122279.
E-mail addresses: karcifikret72@hotmail.com (F. Karcı), nertan@gazi.edu.tr (N. Ertan).

0143-7208/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0143-7208(02)00102-X

were examined in comparison with *N*-phenyl and *N*-hetaroylphenylazo derivatives.

2. Experimental

2.1. General

The chemicals used in the synthesis of the dyes were obtained from Aldrich or Sigma and were used 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 Bruker-Spectrospin Avance DTX 400 Ultra-Shield in $CDCl_3$ or DMSO with TMS as internal reference. Absorption spectra were recorded on a ATI Unicam UV-100 spectrophotometer in various solvents. All melting points were uncorrected.

2.2. The synthesis of 3-methyl-1-(3′,5′-dipiperidino-s-triazinyl)-5-pyrazolone (**3**)

Cyanuric chloride was condensed with piperidine at 40–45 °C to yield 6-chloro-2,4-dipiperidino-*s*-triazine **1** and then 6-hydrazino-2,4-dipiperidino-*s*-triazine **2** was obtained by treating 6-chloro-2,4-dipiperidino-*s*-triazine with hydrazine hydrate [5].

A mixture of 6-hydrazino-2,4-dipiperidino-*s*-triazine (0.01 mol) and ethyl acetoacetate (0.011 mol) in ethanol was refluxed for 4 h. The mixture was cooled and sodium hydroxide solution (5 ml, 10%) was added dropwise with stirring over a period of 30 min. The reaction mixture was further refluxed for 4 h. Ethanol was removed by distillaton and the precipitated product was dissolved in a minimum amount of glacial acetic acid. On dilution with water, the product separated out and was filtered, washed with water, dried and recrystallised from ethyl acetate [5]. (Yield: 88.8%, mp: 204–205 °C.) Synthesis of coupling component are shown in Scheme 1.

2.3. Preparation of hetarylazopyrazolone dyes (**4–8**)

Diazotisation of the various heterocyclic amines was effected with nitrosyl sulphuric acid. A typical procedure is that described later used for 2-aminothiazole; all other dyes were prepared in a similar manner. The pure yield of the dyes was in the range of 55–75%. Characterisation data are shown in Tables 1 and 2.

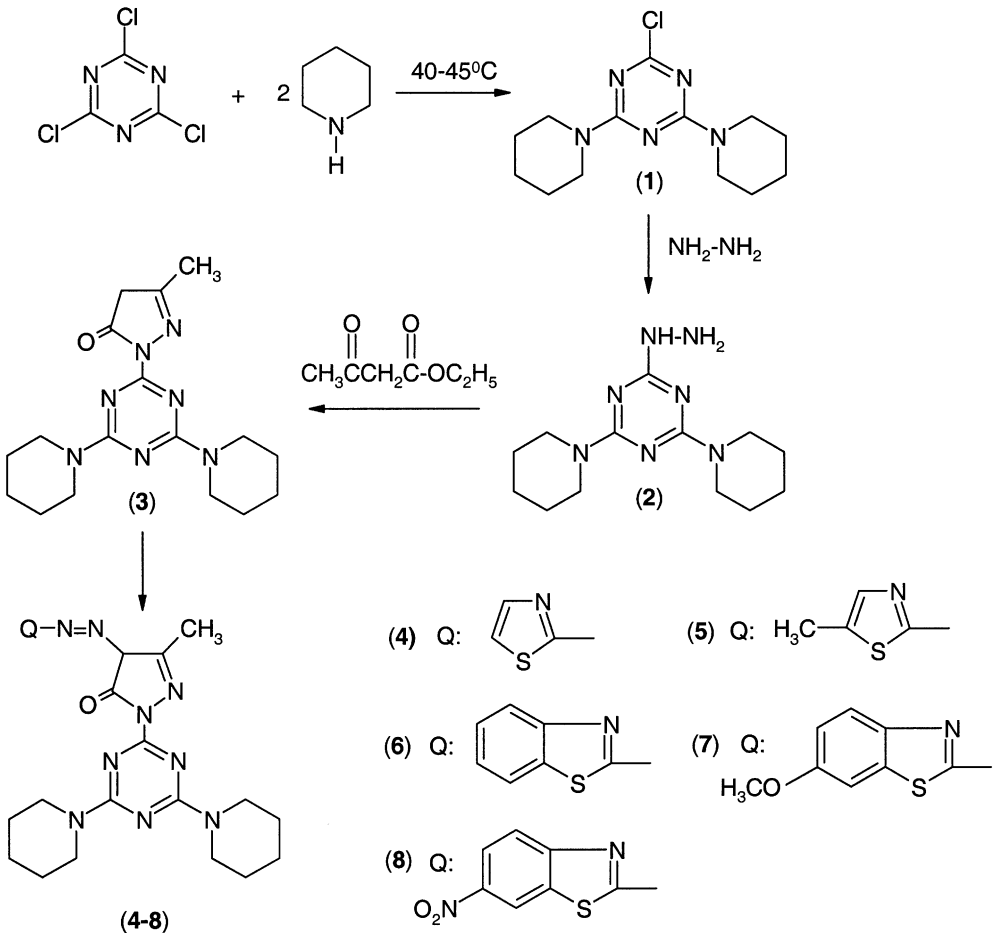
2.3.1. Preparation of 3-methyl-1-(3′,5′-dipiperidino-s-triazinyl)-4-(2′-thiazolylazo)-5-pyrazolone (**4**)

2-Aminothiazole (2.0×10^{-3} mol) was dissolved in hot glacial acetic acid (2.5 ml) and rapidly cooled in an ice–salt bath to −5 °C. The liquor was then added in portions over 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-(3′,5′-dipiperidino-*s*-triazinyl)-5-pyrazolone (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 the simultaneous addition of solid sodium carbonate in portions. The mixture was then stirred for 1 h at 0–5 °C. The progress of the reaction was followed by TLC using a DMF–water mixture (5/2 by volume) as the developing solvent and silica gel TLC plates as the stationary phase. The resulting solid was filtered, washed with cold water and dried. Recrystallisation from DMF–H_2O mixture gave greenish yellow product (yield: 60%, mp: 257–258 °C).

3. Result and discussion

The hetarylazopyrazolone dyes **4–8** were prepared by coupling 3-methyl-1-(3′,5′-dipiperidino-*s*-triazinyl)-5-pyrazolone with the appropriate diazotized heterocyclic amine in nitrosyl sulphuric acid (Scheme 1). 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 1651–1709 cm^{-1} (Table 1). It can be suggested that these



Scheme 1.

compounds do not exist as the azo-enol form in the solid state. Numerous investigations were carried out to establish the tautomeric structure of arylazo-5-pyrazolone both in the solid state and in solution using a variety of spectroscopic techniques. 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 also in $CHCl_3$, DMSO and pyridine [3–8].

The ^1H NMR spectra of compounds **3**–**7** in $CDCl_3$ showed broad bands at δ 13.9 which were attirubuted to OH or NH protons except for the nitro derivative (Table 1). Its ^1H NMR spectrum exhibits two broad bands at δ 13.9 and δ 15.1. These findings show that the compounds are predominantly in the single tautomeric form in $CDCl_3$ except for the nitro derivative **8**, which may exist a mixture of several tautomeric forms in $CDCl_3$.

3.1. Solvent effects

The absorption spectra of dyes **4**–**8** were recorded in various solvents at a concentration of $\sim 10^{-6}$ to 10^{-8} M; the results are summarised in Table 3. Figs. 1 and 2 illustrate the effect of solvents on the shape and the position of the λ_{max} of dye **5** and dye **8**, respectively. The visible absorption spectra of the dyes were found to exhibit a strong solvent dependency, which did not show a regular variation with the polarity of the solvents.

Table 1
Spectral data for compound **1-8**

Compound no.	IR z(cm^{-1}) in KBr						^{1}H NMR (ppm)
	ν_{O-H}	$\nu_{C=O}$	$\nu_{C=N}$	ν_{NH}	$\nu_{C-H(aro)}$	$\nu_{C-H(alip)}$	
1	–	–	1574	–	–	2936	3.7(8H,*t*), 1.6(12H,*m*)
2	–	–	1528	3397	–	2999	5.9(1H,NH,*b*), 4.0(2H,NH_2,*b*), 3.7(8H,*t*), 1.6(12H,*m*)
				3393		2932	
3	3442	1651	1596	–	3011	2934	13.2(OH,*b*), 5.4(*b*), 3.7(8H,*t*), 2.3(3H,*s*), 2.2(2H,*s*), 1.6(12H,*m*)
			1560			2852	
4	–	1709	1586	3446	3196	2931	13.9(1H,NH,*b*), 7.6(1H,*d*), 7.0(1H,*d*), 3.9(8H,*t*), 2.3(3H,*s*), 1.8(12H,*m*)
			1510		3001	2852	
5	–	1651	1593	3442	3064	2925	13.9(1H,NH,*b*), 7.1(1H,*s*), 3.9(8H,*t*), 2.4(3H,*s*), 2.3(3H,*s*), 1.8(12H,*m*)
			1531			2851	
6	–	1696	1587	3423	3001	2934	13.9(1H,NH,*b*), 7.7(2H,*m*), 74(1H,*m*), 7.3(1H,*m*), 3.9(8H,*t*), 2.4(3H,*s*)1.8(12H,*m*)
						2854	
7	–	1696	1587	3442	2999	2938	13.9(1H,NH,*b*), 7.7(1H,*m*), 7.3(1H,*m*), 7.0(1H,*m*), 3.9(3H,*s*), 3.8(8H,*t*), 2.4(3H,*s*), 1.8(12H,*m*)
						2854	
8	–	1696	1587	3435	2998	2931	15.1(OH,*b*), 13.9(NH,*b*), 8.7(1H,*m*), 8.3(1H,*m*), 7.8(1H,*m*), 3.9(8H,*t*), 2.4(3H,*s*), 1.8(12H,*m*)
						2851	

s: singlet, *t*: triplet, *m*: multiplet, *b*: broad

Table 2
Element analysis of dyes **4**–**8**

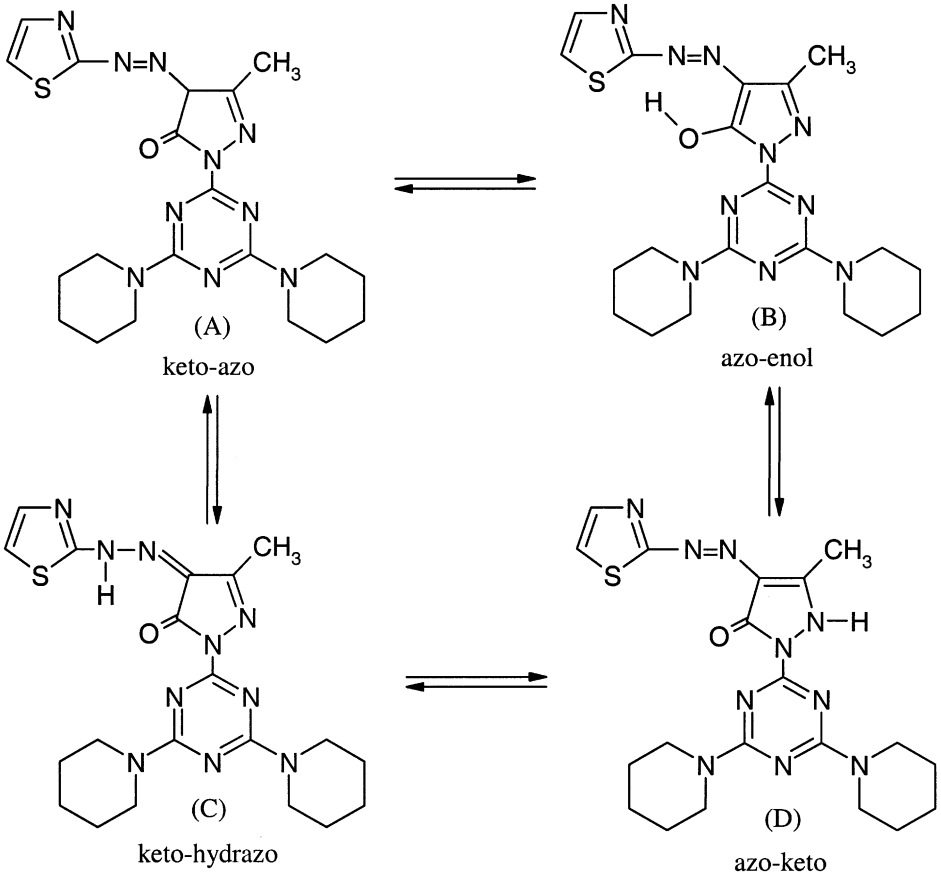
Dye no.	Molecular formula	C%		H%		N%		S%		Melting point (°C)
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
4	$C_{20}H_{26}N_{10}OS$	52.85	53.07	5.76	5.54	30.81	30.58	7.05	7.11	257–258
5	$C_{21}H_{28}N_{10}OS$	53.83	54.35	6.02	6.21	29.89	29.65	6.84	6.86	271–272
6	$C_{24}H_{28}N_{10}OS$	57.12	56.87	5.60	5.41	27.76	27.34	6.35	6.11	279–280
7	$C_{25}H_{30}N_{10}O_2S$	56.16	55.78	5.66	5.79	26.19	25.88	5.99	5.61	277–278
8	$C_{24}H_{27}N_{11}O_3S$	52.45	52.72	4.95	5.09	28.03	27.76	5.83	5.95	283–284

It was observed that the absorption spectra of the compounds in acetonitrile did not significantly change with respect to the absorption spectra in chloroform, with the exception of compound **8**. In contrast, the λ_{max} of the dyes shifted considerably in DMSO and DMF (e.g. for dye **4** λ_{max} is 411 nm in $CHCl_3$, 467 nm in DMF and 436 nm in DMSO; for dye **6** is 413 nm in $CHCl_3$, 471 nm in DMF and 472 nm in DMSO; for dye **8** is 412 nm in $CHCl_3$ and 528 nm both in DMF and in DMSO). The λ_{max} values of the nitro derivative (dye **8**) has a large bathochromic shifts in all solvents.

Heterocyclic based azo disperse dyes tend to show larger solvatochromic effects than azobenzene based dyes because of the increased polarity of the dye system, especially in the excited

state. Similar effects for dyes containing a benzothiazolyl, thiazolyl and thienyl moieties have been reported for some derivatives of *N*-β-cyanoethyl-*N*-β-hydroxyethyl aniline [9–13]. On the other hand, in hetarylazopyrazolone dyes, their tautomeric equilibria need to be considered.

Strong evidence for the existence of these compounds existing in an equilibrium is provided by the single or twin isosbestic points in the visible spectra of, for example, dye **4** and dye **8**, in different solvents (Figs. 1 and 2). This equilibrium may exist between tautomeric forms or between acidic



Scheme 2.

Table 3
Influence of solvent on λ_{max}(nm) of dyes **4**–**8**

Dye no	DMSO	DMF	Acetonitrile	Methanol	Acetic acid	Chloroform
4	436	467	409	444, 422 s[a]	427	411
5	470	467	414	435, 422 s[a]	450	428
6	472, 485 s[a]	471, 489 s[a]	416	423	432	413
7	462	475	444	457, 421 s[a]	456	444
8	528, 500 s[a]	528, 506 s[a]	475, 436 s[a]	484, 510 s[a]	434, 466 s[a]	412, 477 s[a]

[a] Shoulder.

and basic forms, or between both. The equilibrium depends on the acidity of the solvents used; in proton accepting solvents such as DMSO and DMF, the dyes displayed a red shift of λ_{max} and exist therefore mainly in the common anion form. In a proton donating solvent such as acetic acid, the dyes also displayed a red shift of λ_{max}, probably due to the cationic form of the dye formed through protonation of the piperidine rings. In the weak proton accepting solvent, acetonitrile, the λ_{max} of the dyes did not change significantly. In methanol, which is both proton accepting and proton donating, the dyes displayed a red shift in λ_{max}, which may be attributed to the presence of both anionic or cationic species. Such a solvent effect is consistent with the phenomenon of dissociation rather than azo-hydrazone tautomerism. It was also observed that the absorption curves of the dyes were very sensitive to acid and base. The 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 (Table 4) and the absorption curves of the dyes resembled those in 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 solutions of the dyes in DMSO and DMF (Table 4). The λ_{max} of the dyes in methanol also showed bathochromic shifts when 0.1 M HCl and 0.1 M KOH were added and these shifts were especially large in the case of KOH solution (Fig. 4). This indicates that the hetarylazopyrazolones **4**–**8** exist in a dissociated state in methanol, DMSO and DMF. These results are in agreement with those obtained previously for both hetarylazopyridones [14] and hetarylazopyrazolones [7]. Therefore, the structures of the dyes prepared were assigned to the tautomeric form in acidic medium and the common anion form in basic medium.

The effects of dye concentration and temperature on absorption maxima was examined

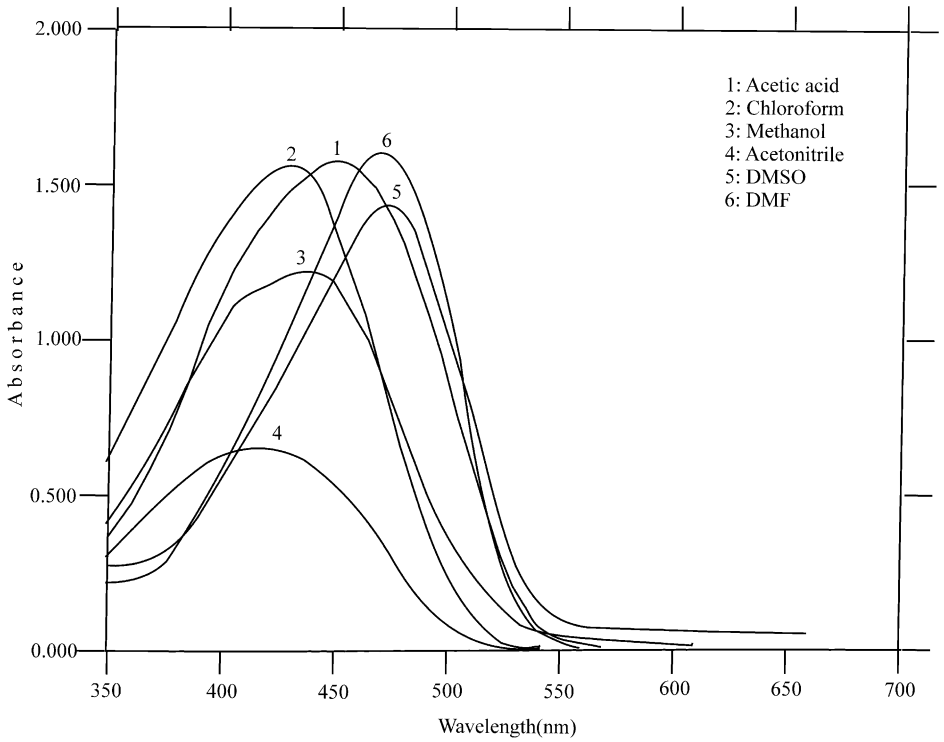


Fig. 1. Absorption spectra of dye **5** in various solvents.

(Table 5). Although the λ_{max} values of the dyes **4–8** did not change with dye concentration in chloroform, acetonitrile, DMSO and DMF, the λ_{max} values of some dyes in methanol and acetic acid (e.g. dyes **4–6**) showed a blue shift with increasing concentration. This also indicates that the hetarylazopyrazolones exist in the tautomeric form in chloroform and acetonitrile, in the common anion form in DMF and DMSO and in a partly dissociated state in both methanol and acetic acid.

When solutions of the dyes in DMSO and DMF were examined over the temperature range 25–70 °C (Table 5), the λ_{max} values of the dyes **4–8** did not change significantly. These findings support the dissociation equilibria of hetarylazopyrazolones in proton-accepting solvents, which do not involve a change in energy.

3.2. Substituent effects

As Table 3 shows, the introduction of electron-donating methyl and methoxy groups into the thiazole and benzothiazole rings results in bathochromic shifts in chloroform, acetic acid and acetonitrile (for dye **5** $\Delta\lambda = 17$ nm relative to dye **4**; for dye **7** $\Delta\lambda = 27$ nm relative to dye **6** for spectra in $CHCl_3$), the strong electron-accepting nitro group did not change the λ_{max} values in $CHCl_3$ and acetic acid but did produce a large bathochromic shift in acetonitrile. Similar effects were apparent in dyes derived from 3-methyl-1-phenyl-2-pyrazoline-5-one as coupling component in which the nitro group resulted in a large hypsochromic shift in both $CHCl_3$ and acetic acid [13]. The unsubstituted dyes (**4** and **6**) also showed large bathohromic shifts in comparison with their *N*-phenyl [5,13] and *N*-hetaroyl analogues [4,5]. In methanol, the introduction of the donor methoxy substitute in the 6-position of the benzothiazole ring (dye **7**) gave a large bathochromic shift (34 nm), in contrast to similar substitution in the thiazole ring (dye **5**), for which a small (9 nm) hypsochromic shift resulted. However, the introduction of the electron-attracting nitro substituent at the same position in the benzothiazole ring, caused a very

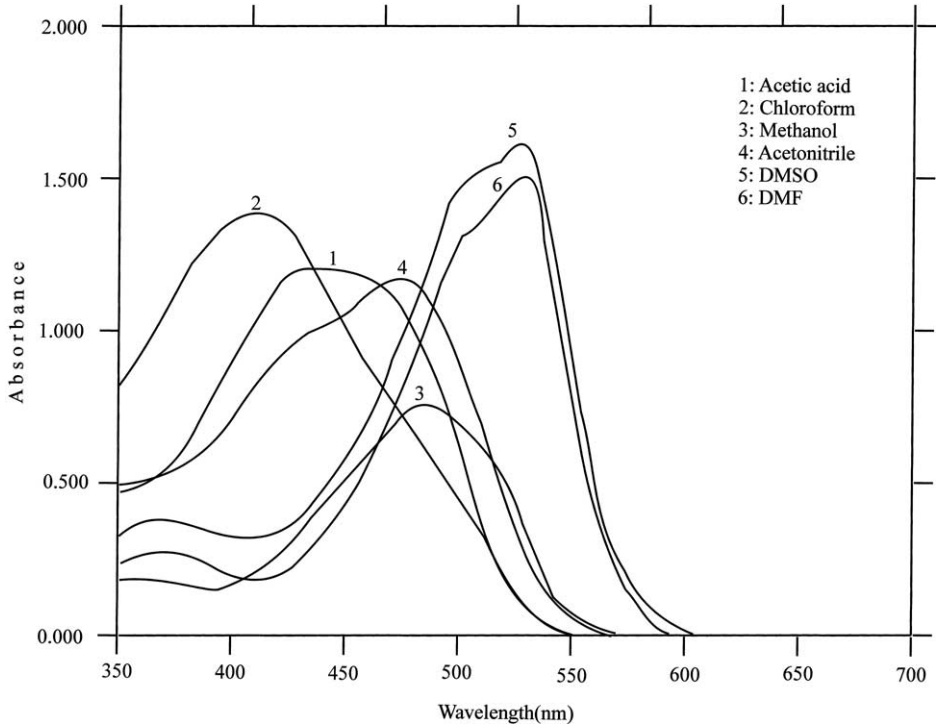


Fig. 2. Absorption spectra of dye **8** in various solvents.

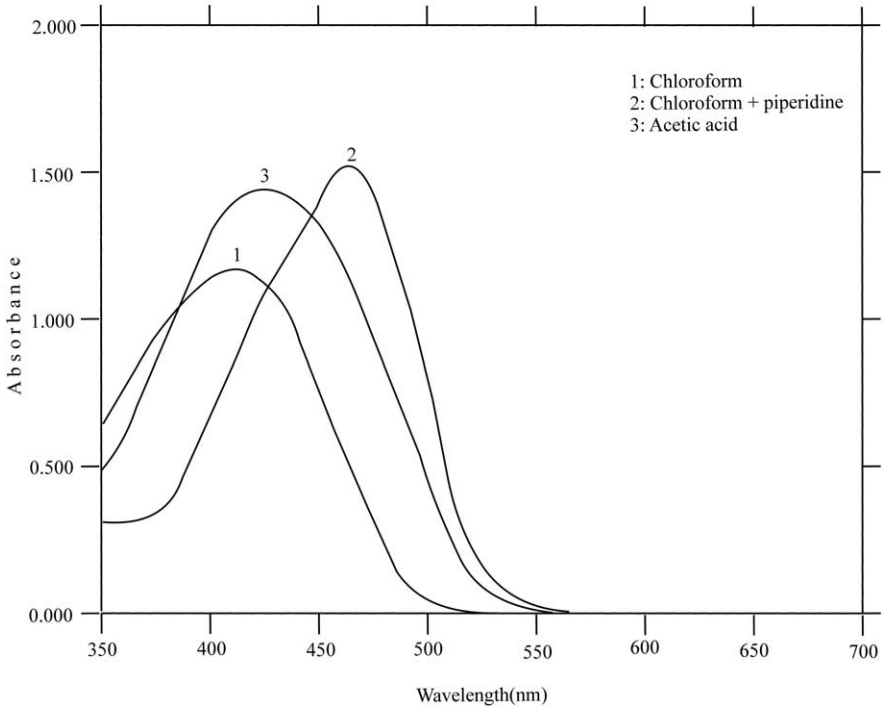


Fig. 3. Absorption spectra of dye **4** in acidic and basic solutions.

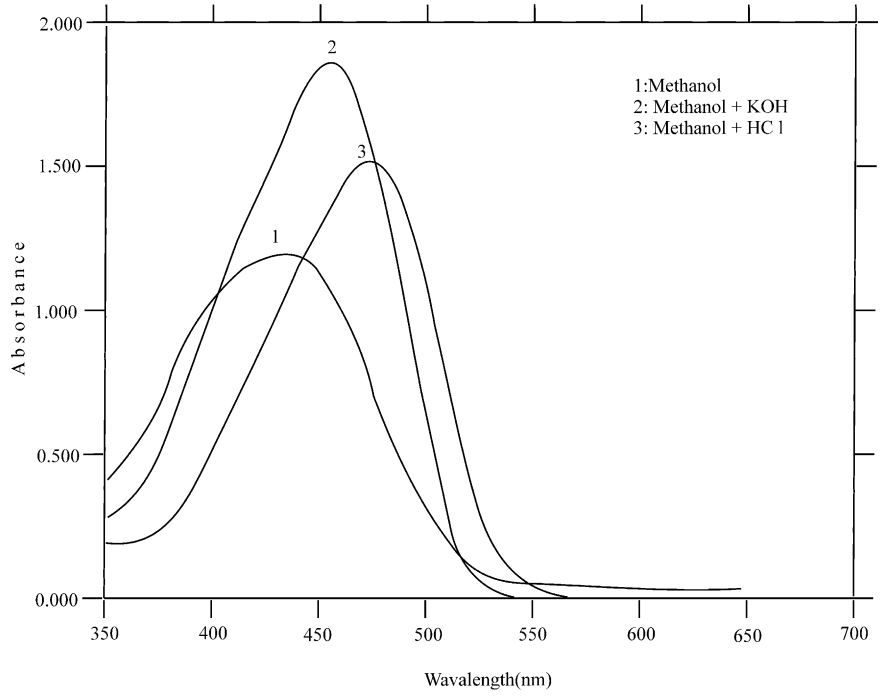


Fig. 4. Absorption spectra of dye **5** in acidic and basic solutions.

Table 4
Absorption maxima of dyes **4**–**8** in acidic and basic solutions

Dye no.	λ_{max} (nm)								
	DMSO	DMSO + piperidine	DMF	DMF + piperidine	Methanol	Methanol + KOH	Methanol + HCl	Chloroform	Chloroform + piperidine
4	436	440	467	465	444	453	467	411	463
5	470	470	467	468	435	455	473	428	467
6	472, 485 s[a]	472	471, 489 s[a]	471	423	462	470	413	470
7	462	472	475	476	457, 421 s[a]	467	490	444	478
8	528, 500 s[a]	528, 500 s[a]	528, 506 s[a]	527, 500 s[a]	484, 510 s[a]	488	446	412, 477 s[a]	493

[a] Shoulder.

Table 5
Influence of temperature and sample concentration on absorption maxima of dyes **4**–**8**

Dye no.	λ_{max} (nm)													
	DMSO conc. 25 °C	DMSO dil. 25 °C	DMSO 70 °C	DMF conc. 25 °C	DMF dil. 25 °C	DMF 70 °C	A. nitrile conc. 25 °C	A. nitrile dil. 25 °C	Meth. conc. 25 °C	Meth. dil. 25 °C	A. acid conc. 25 °C	A. acid dil. 25 °C	Chl. Conc 25 °C	Chl. dil. 25 °C
4	436	437	436	467	467	465	409	408	444	447	427	433	411	410
5	470	467	463	467	468	467	414	416	435	442	450	458	428	427
6	472, 485 s[a]	473, 485 s[a]	473	471, 489 s[a]	471, 485 s[a]	471	416	416	423	437	432	433	413	417
7	462	462	466	475	476	476	444	445	457, 421 s[a]	457, 423 s[a]	456	457	444	444
8	528, 500 s[a]	526, 506 s[a]	527, 500 s[a]	528, 506 s[a]	528, 500 s[a]	527, 500 s[a]	475, 436 s[a]	476, 436 s[a]	484, 510 s[a]	485, 510 s[a]	434, 466 s[a]	433, 463 s[a]	412, 477 s[a]	413, 466 s[a]

Chl., Chloroform; Meth., Methanol; A. acid, Acetic acid, A. nitrile, Acetonitrile; conc., concentrated; dil., diluted.
[a] Shoulder.

large bathochromic shift (61 nm). The same effects for *N*-phenyl derivatives are showed in ethanol, 32 nm hypsochromic shift for methyl group and 21 nm bathochromic shifts for methoxy and nitro groups [15].

The introduction of a nitro group into the benzothiazole ring resulted in large bathochromic shifts in DMSO (56 nm, dye **8**) and in DMF (55 nm, dye **8**) whereas substitution, into dye **6**, of methyl and methoxy groups did not change the λ_{max} values in DMF. In DMSO, whereas substitution of a methyl group in the thiazole ring caused a bathochromic shift of 34 nm, substitution into the benzothiazole ring produced little hypsochromic shift; similar effects for *N*-phenyl derivatives were observed in DMF and DMSO.

These results indicate that the electron-donor methyl and methoxy groups stabilised the excited state of the neutral form of the dyes whereas the strong electron-accepting nitro group stabilised the excited state of the common anion form of the dyes.

4. Conclusions

The influence of the heteroring moiety on the pyrazolone ring in the 1-position of hetarylazopyrazolone dyes resulted in bathochromic shifts in DMF. Similar effects were apparent in dyes derived from 1-(2′-benzothiazolyl)-3-methylpyrazolone-5-one as coupling component and which were reported as near-infrared absorbing dyes [16].

Acknowledgements

The authors are grateful to Research Foundation of Gazi University for supporting this study.

References

[1] Schwander HR. Dyes and Pigments 1982;3:133.
[2] Whitaker A. J Soc Dyers and Colour 1995;111:66.
[3] Abdel-Negeed MR. Spec Lett 1987;20(4):291.
[4] Hanna MA, Girges MM, Fadda AA. J Chem Tech Biotechnol 1992;55:9.
[5] Ayyangar NR, Lahoti RJ, Lugade AG, Otiv SR. J So Dyers Colour 1986;102:176.
[6] Sabnis RW, Kazem G, Rangnekar DW. Bull Chem Soc Jpn 1991;64:3768.
[7] Ertan N. Dyes and Pigments 2000;44:41.
[8] Yasuda H, Midorikawa H. J Org Chem 1966;3:1722.
[9] Snavely FA, Yoder CH. J Org Chem 1968;33(2):513.
[10] Lycka A, Mustrop H. J Prak Chem 1989;331(1):11.
[11] Lestina GJ, Regan TH. J Org Chem 1969;34(6):1685.
[12] Nikolov P, Fratev F, Stoyanov S, Polansky OE. Z Naturforsch 1981;36:191.
[13] Peters AT, Gbadamosi A. J Chem Tech Biotech 1992; 53:301.
[14] Ertan N, Eyduran F. Dyes and Pigments 1995;27:313.
[15] Yasuda H. Bull Chem Soc Jpn 1967;40:1239.
[16] Emandi A, Serban I, Bandula R. Dyes and Pigments 1999; 41:63.