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DYES and PIGMENTS

Synthesis of some new solvatochromic 1(4)-substituted Pyrazol-5-one Azo derivatives

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Abstract

New 1-(2′-benzthyazolyl)-3-methyl-pyrazol-5-one-4-substituted azo derivatives have been prepared and characterised by elemental analysis, IR, ^{1}H-NMR and UV-VIS. The solvatochromic behaviour was investigated and their ionisation constants were determined. These dyes generally absorb near-infrared light at around 11,000 cm^{-1} and this is the most favourable wavelength region for semiconductor laser optical recording dye medium.

Keywords: Pyrazol-5-one; Azo dyes of 1(4)-substituted Pyrazol-5-ones; IR; UV–VIS; Solvatochromism behaviour; NIR dyes

1. Introduction

It is known that the 4-position of the pyrazol-5-one system is reactive, as it undergoes coupling reactions with aryl diazonium salts to furnish 4-arylazo derivatives [1].

4-Arylazo-pyrazol-5-ones have found extensive applications as textile dyes, food dyes, magenta [2], sensitive reagents used in the spectrophotometric determinations of metal ions [3,4] and as pigments. Methods for obtaining 1-(2′-benzthyazolyl)-3-methyl-pyrazol-5-one have been reported [5–7] and some 4-azomethine derivatives have been described by us [8]. 1-(2-Benzthyazolyl)-3-methyl-pyrazol-5-one has also been prepared [9] by another method than that reported in the literature.

The azo derivatives in this present study have been prepared in order to study their spectral and solvatochromic behaviour with respect to potential application of the compounds as dyes or pigments, and to their exhibiting possible photosensitisation behaviour.

The absorbtion spectra in buffer solution have been utilised for the determination of the acid dissociation constants for some of the compounds in order to permit selection of a suitable pH for the compounds to be applied as photosensitisers.

We have investigated the near-infrared absorbing properties of these dyes, because there is a current interest in the development of near-infrared absorbing dyes which are used as the functional dyes for optical recording media and for protection in the optical filter [10].

2. Results and discussions

In this paper we present six new 4-arylazo-pyrazol-5-ones derivatives. 1-(2′-Benzthyazolyl)-3-

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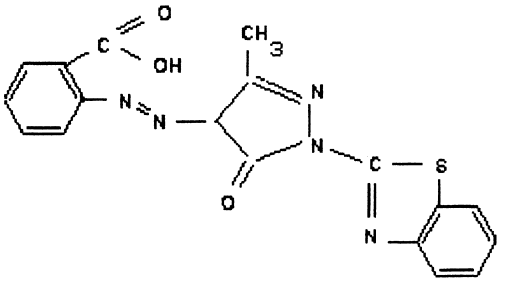
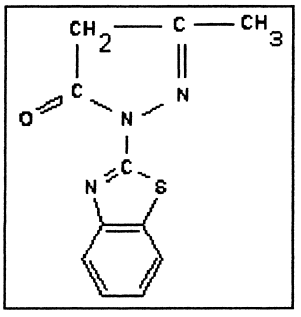
methyl-4-azo-(2″-carboxyphenyl)-pyrazol-5-one (I) has previously been reported [9]. This compound is here characterised by micro analyses, IR, UV–VIS and ^{1}H-NMR data and we have investigated its solvatochromic behaviour and its near-infrared absorbing properties.



(I)

The general reactions for obtaining the other five azo dyes are shown in Scheme 1. 1-(2′-Benzthyazolyl)-3-methyl-pyrazol-5-one **(BMPy)** was used as a coupling component:



BMPy

Compound VI was obtained by replacing 1-(2′-benzthyazolyl)-3-methyl-pyrazol-5-one with m-dimethylamino-phenol in order to compare their properties.

Elemental analysis (Table 1) are in good agreement with the molecular formulae proposed for these compounds.

The IR spectra (Table 2) show characteristic bands for the coupling component (BMPy), which were assigned in accordance with literature data [11,12]. At 1680–1660 cm^{-1} there is a characteristic band for ν(C=O) of the pyrazolone ring, and the intense bands in the range 1615–1605 and 1455–1415 cm^{-1} were assigned to ν(C=N) and ν(N=N) and ν_{as}(N=N). Characteristic bands of the azo derivatives show presence of OH group at around 3550 cm^{-1} νOH phenolic and at around 1225 cm^{-1}, δOH phenolic. The band characteristic for the NO_2 group appear at around 1530–1540 cm^{-1} for $\nu_{asim}NO_2$ and at 1375 cm^{-1} for $\nu_{sim}NO_2$. Characteristic bands for the heterocyclic ring and the aromatic rings are shown in Table 2.

The diffuse reflectance spectra of the azo derivatives (Table 3) show bands due to π–π^* and n–π^* transitions. The other significant bands are those of the >C=O (pyrazole ring) at 265–280 and at 208 nm; –N=N– at around 430, and 320 nm; and –C=N– at around 300 nm. These assignments are in accordance with literature data [13,14].

^{1}H-NMR data are presented in the experimental part for each of the azo derivatives.

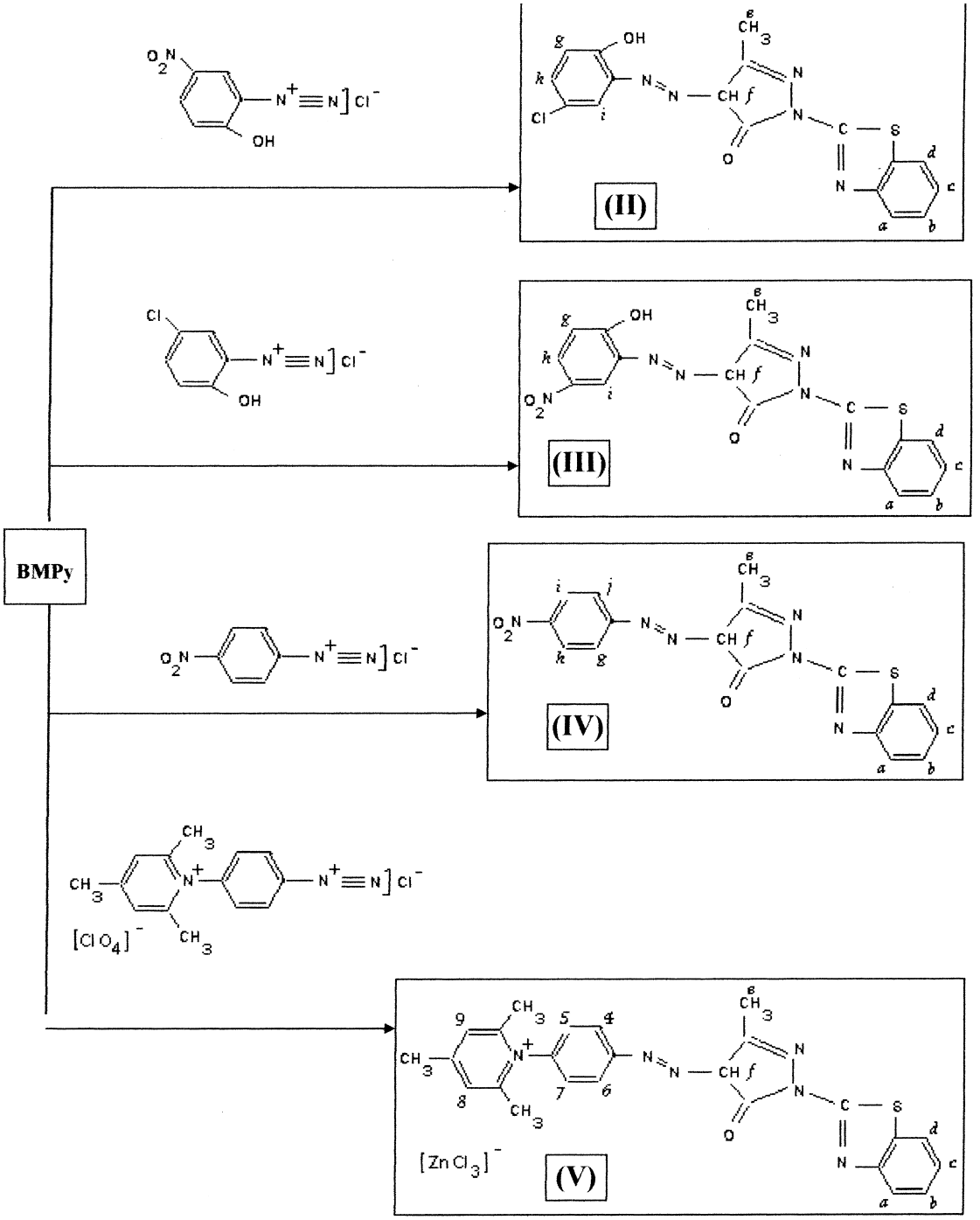
For the NMR data, the atoms are labelled as on Scheme 1.

All data confirmed the expected structure, and also the purity of compounds.

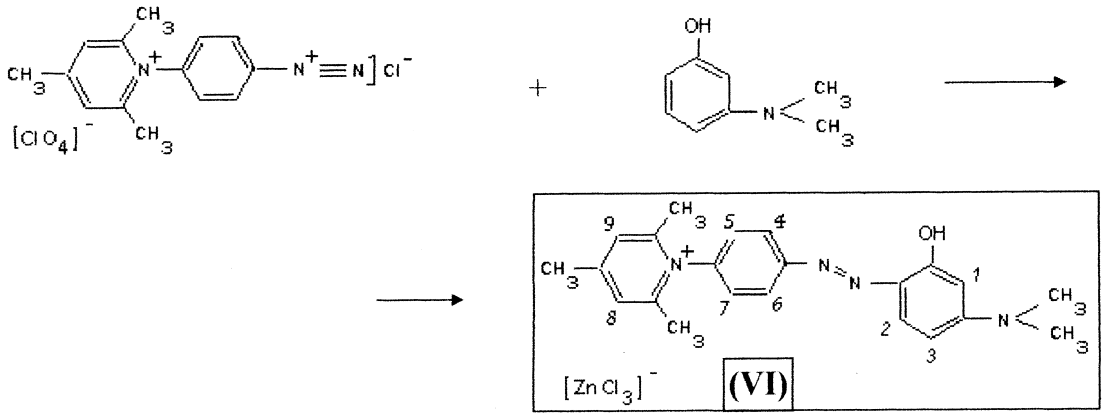
The visible bands observed in the electronic spectra of compounds I, II, III, IV, V and VI in solvents with different dielectric constants can be interpreted as evidence of the possible existence of a mesomeric equilibrium. Generally, the electronic spectra, in solution, of these compounds exhibit three regions [15]. Solvent effects on the visible spectra of the compounds I–VI are shown in Table 4.

Evidence for the existence of these compounds in a mesomeric equilibrium is provided by the well-defined isosbestic points (Fig. 1).

In compound I, the bands corresponding to the >C=O (260–280 nm) and –N=N– (395–435 nm) linkages undergo a red shift when the solvent polarity increases. The electronic spectral behaviour of the –N=N– band is affected by the electronegativity of the substituent and this band is shifted to longer wavelengths with increasing electron-repelling character of the substituent [15]. The mesomeric structures proposed are in good agreement with literature data, because in polar solvents the –COOH group is ionised and the –COO^- anion has an electron-repelling character. For this compound, there are no bands at 450–460 nm attributable to charge transfer over the whole molecule. The CT transition is probably obscured



Scheme 1.



Scheme 1. (Continued)

by the bathochromic shift, and the broadness of the N=N band. This behaviour corresponds to the mesomeric structures (Scheme 2).

Compound II exhibits bands which correspond to the >C=O, N=N linkages, and to CT transitions. The bands corresponding to the –N=N– linkage and to the CT transitions involve a bathochromic shift in aprotic solvents, and a hypsochromic shift in protic solvents. An increase in solvent polarity results in an increase of the –OH repelling character; the mesomeric structures are shown in Scheme 2.

In compound III, the band corresponding to the >C=O linkage is less affected by the polarity of the solvent, and the band corresponding to the CT transition is overlapped by the band corresponding to the –N=N– linkage. The –N=N– band behaves as in compound (II), and four mesomeric structures are proposed (Scheme 2).

Compound IV exhibits both bands for the >C=O and –N=N– linkage and the CT transition band. In this case there is no obvious relation between the –N=N– and CT bands with increase in solvent polarity. This fact is probably due to competition between the polarity of the solvent and the strong electron-attracting character of the NO_2 group. We propose an equilibrium between the mesomeric structures involving the NO_2 electron-attracting character (Scheme 2).

In compounds V and VI there are bands corresponding to the >C=O linkage and the CT transition. The CT band shows a bathochromic shift in aprotic solvents and a hypsochromic shift in protic solvents. Because there is no information about the behaviour of the –N=N– linkage, we have considered the behaviour of the CT transitions in the mesomeric structures (Scheme 2).

Table 1
Characterization data of compounds (I–VI)

Compound no.	Yield %	Molecular formula (M. wt)	Colour of products	Analysis (%) calculated (found)			
				C	H	N	S
I	65	$C_{18}H_{13}N_5SO_3$(379)	Yellow–brown [a]	56.99(56.60)	3.43(3.49)	18.46(18.40)	8.44(8.41)
II	68	$C_{17}H_{12}N_6O_4S$(396)	Yellow–reddish [a]	51.51(51.52)	3.03(3.20)	21.21(21.28)	8.08(8.00)
III	67	$C_{17}H_{12}N_5O_2SCl$(385.5)	Red–brown [a]	52.91(52.87)	3.11(3.18)	18.15(18.12)	8.30(8.34)
IV	72	$C_{17}H_{12}N_6O_3S$(380)	Yellow [a]	53.68(53.61)	3.15(3.19)	22.10(22.14)	8.42(8.40)
V	70	$[C_{25}H_{23}N_6OS]^+[ZnCl_3]^-$(626.8)	Brown–reddish [a]	47.86(47.82)	3.66(3.60)	13.40(13.42)	5.10(5.14)
VI	69	$[C_{22}H_{25}N_4O]^+[ZnCl_3]^-$(532.8)	Brown [a]	49.54(49.60)	4.69(4.70)	10.51(10.49)	–

[a] crystals.

Table 2
IR (cm^{-1}) Assignments of the azo derivatives synthesised

Assignments	(II)	(III)	(IV)	(V)	(VI)
ν(C=O)	1660 s	1675 s	1665 s	1680 s	–
ν(C=N) + ν(N=N)	1605	1615	1615	1610	1610
ν_{as}(N=N)	1415 i	1445 i	1455 i	1455 i	1450 i
ν(C–N=N–C)	920 m	900 m	920 m	900 m	920 m
ν_{OH} phenolic	3550 i	3555 i	3550 i	3555 i	3540 i
δ_{OH} phenolic	1230 s	1225 s	1235 s	1225 s	1220 s
ν $NO_{2\ asim}$	1535–1540 vs	–	1530–1540 vs	–	–
ν $NO_{2\ sim}$	1370 vs		1375 vs		
νC–S (heterociclic)	690 m	692 m	690 m	692 m	–
δC–H (heterociclic)	980 m	982 m	980 m	980 m	–
νCH aromatic	3010 m	3010 m	3010 m	3010 m	3010 m
γCH aromatic	3040 m	3040 m	3040 m	3040 m	3040 m
γCH 1,2,4,6 substituted	800 s 860–900 m	800 s 860–900 m	800 s 860–900 m	800 s 860–900 m	800 s 860–900 m
νC–N aminic					1180–1200 m
νC aliphatic–N aminic					2500 w–3200 m

vs = very strong, s = strong, i = intense, m = medium, w = weak.

From Table 4, a special behaviour of all compounds in the presence of DMF is evident and this indicates that DMF has a greater tendency to form a solvated complex with the solute molecules. This is due to its low ionisation potential and high hydrogen bond-accepting character.

The CT transitions over the whole molecule involve both the quinoid and the polarised pyrazolone ring [15]. The CT nature can be supported by considering the spectral behaviour of these compounds in solutions of varying hydrogen ion concentration (Fig. 2).

The band corresponding to the π–π^* transition of the –N=N– linkage is absent and this conforms to the CT band for compounds I, V, VI, because in these compounds there is no well-defined –N=N– linkage in the resonance structures (Scheme 2).

It has been found that for these compounds the band at longer wavelength showed a shift in alkaline solutions. Compounds II, III, V and VI exhibit a red shift of the CT transition band in alkaline media. These shifts are mainly due to a relatively increased negative charge density on the enolate OH group in these compounds. On the other hand, the longer-wavelength absorbtion band of compounds I and IV showed blue shifts in alkali, due to the high electron-accepting character of the –COOH and $–NO_2$ groups, which inhibit CT from the enolate OH group to the positively heterocyclic quaternary nitrogen. The effectiveness of a compound as photosensitiser increases when it is present in the ionic form in which it has a higher planarity.

The absorbance of the CT band (Fig. 3), (Table 5) increases with increase of pH for com-

Table 3
UV-VIS (nm) Assignments of the azo derivatives synthesised

Assignments		(II)	(III)	(IV)	(V)	(VI)
Aromatic ring		230	235	240	240	240
>C=O pirazolonic	π–π^*	265	270	280	275	–
	n–π^*	208	210	210	208	–
–N=N–	π–π*	396	430	435	435	430
	n–π^*	320	324	320	325	320
–C=N–	π–π^*	~300	295	305	300	290

Table 4
Absorbtion spectra of (I–VI) dyes in different solvents λ_{max} [log ε] (mol^{-1}/cm^{-1})

Compound No.	H_2O	C_2H_5OH	DMSO [a]	CH_3CN	DMF	Dioxan
I [a]	283.3 [4.071]	275.6 [4.166]	278.4 [4.124]	275.8 [4.184]	277 [4.100]	275.5 [4.211]
	–	–	–	–	305.1 sh	–
	–	–	–	–	361.0 sh	–
	413.4 [4.058]	410.2 [4.238]	405.2 [4.176]	404.2 [4.243]	446.4 [4.269]	401.0 [4.260]
II	–	–	284 sh [0.74]	282.6 sh [0.76]	283 sh [0.81]	–
		321.5 [1.18]	326.8 [1.12]	324.3 [1.18]	322.2 [1.20]	322.6 [0.94]
		414.3 [0.535]	438.5 [0.66]	433.7 [0.61]	439 [0.725]	415.6 [0.54]
		485.4 sh [0.44]	530 sh [0.295]	500 sh [0.34]	522 sh [0.36]	–
III		244.7 [0.79]	–	–	–	–
		279 [0.85]	282.6 [0.89]	279.4 [0.85]	281 [0.86]	279.6 [0.93]
		303.7 [0.84]	303 [0.78]	301 [0.72]	302 sh	–
		–	319 [0.71]	319.6 [0.675]	323 [0.75]	–
		407 [0.55]	–	–	–	–
		429.2 [0.58]	444 [0.67]	437 [0.65]	443 [0.72]	437 [0.65]
IV	–	265 [0.16]	264.5 [1.20]	263 [0.73]	268.3 [0.76]	263.7 [1.16]
		330.6 [0.12]	325 [0.61]	330 [0.37]	332 [0.46]	331 [0.66]
		389 sh	394.4 sh	389.4 sh	392.4 sh	329 sh
		410.8 [0.18]	413.2 [1.04]	407.4 [0.95]	412.5 [0.89]	411.5 [1.33]
		432 sh	433 sh	425.8 sh	433.6 sh	432 sh
		–	–	–	494 [0.24]	–
		–	–	–	520.8 [0.28]	–
V	–	269.5 [0.300]	272 [0.285]	269.3 [0.315]	271.2 [0.30]	272.7 [0.295]
		463 [0.60]	479 [0.56]	473 [0.64]	478.5 [0.58]	472.5 [0.62]
VI	266.0 [3.937]	269.1 [3.892]	272.3 [3.928]	269.0 [3.873]	271.7 [3.919]	271.7 [3.928]
	457.0 [4.211]	465.5 [4.193]	481.2 [4.127]	471.7 [4.202]	476.2 [4.202]	471.7 [4.188]

[a] Concentration mole/*l*: I, 5.6×10^{-5}; II, 5×10^{-5}; III, 5×10^{-5}; IV, 3.75×10^{-5}; V, 3.75×10^{-5}; VI, 3.75×10^{-5}.
sh = shoulder.

pounds I, III and VI, which correspond to pyrazol-5-one derivatives. At basic pH, the enolate OH group is deprotonated, hydrogen bonds are broken and charge transfer from the enolate OH group to the positively charged heterocyclic quaternary nitrogen is inhibited.

The optimal pH in the application of these dyes as photosensitisers is an acidic one, and the most suitable compound is III.

An interesting correlation can be made between the light fastness of these compounds and the excitation energy (E_{ex}) of the π-electron-system of the N = N bond (Table 4).

The light fastness is higher with compounds having λ_{max} at shorter wavelengths [15]. For the compounds investigated here, the light fastness is higher in lower polarity aprotic solvents for I–VI, and in higher polarity protic solvents for II–VI (Table 2). This behaviour denotes that the good light fastness properties of the dyes depend on differences in stabilisation of both the ground and excited states by hydrogen bonding interaction with the protic solvents, since there is no difference in the polarity of the ground and exited states of the compounds.

The variation of absorbance with pH can be utilised for the determination of the ionisation constant of organic compounds [16]. By plotting the absorbance at λ_{max} versus pH, S-shaped curves were obtained (Fig. 3). The horizontal portion of the S-curve corresponds to the acidic form of the compound, whilst the upper portion to the right corresponds to the basic form, since the pK_a is defined as the value for which one-half of the compound is in the basic form and the other in the acidic form. This point is determined by the interaction of the curve with a horizontal line midway between the left and right segments. From (Fig. 3) the pK_a values are 3.7 and 11.6 for (I) 2.2, 6.3 and 11.2 for (III) 2.5,11.2 for (V) 4.4 and 6.5 for (VI).

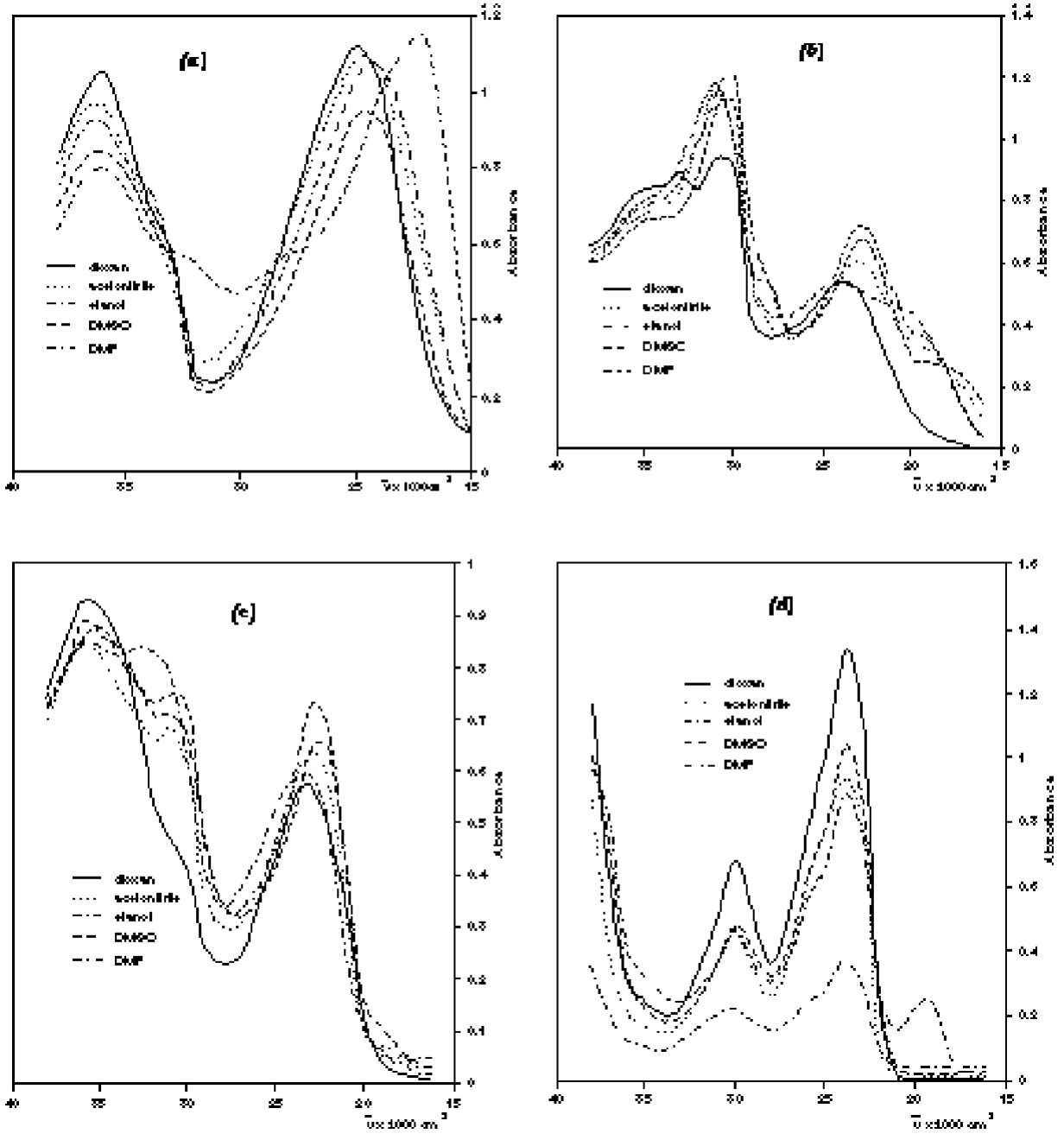

(a)
dioxan
acetonitrile
ethanol
DMSO
DMF
Absorbance
(b)
dioxan
acetonitrile
ethanol
DMSO
DMF
Absorbance
(c)
dioxan
acetonitrile
ethanol
DMSO
DMF
Absorbance
(d)
dioxan
acetonitrile
ethanol
DMSO
DMF
Absorbance

Fig. 1 a–d.

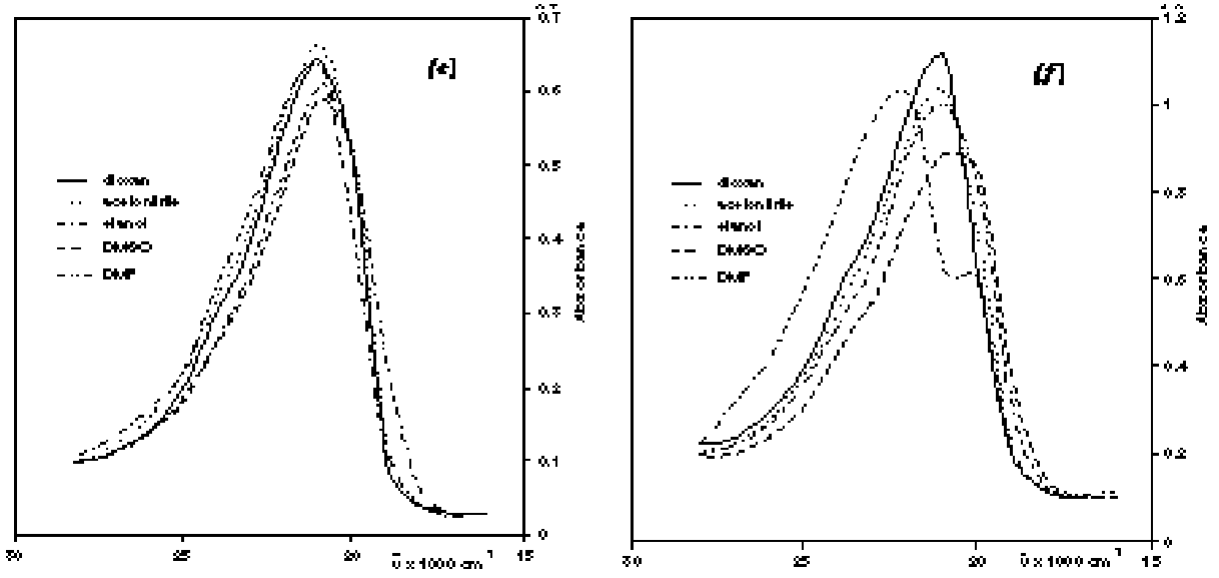


Fig. 1. Electronic absorption spectra of the azo derivatives in different solvents (*a*)-(I); (*b*)-(II); (*c*)-(III); (*d*)-(IV); (*e*)-(V); (*f*)-(VI).

We have found that compounds II, III, IV and V absorb in the near-infrared region and exhibit well-defined bands at:

(II)	900i,	1100i,	1414m,	1670vi,
	1932vi,	2158vi,	2212sh,	2306vi,
(III)	900m,	1134,	1458w,	1664vi,
	1956i,	2150vi,	2266i,	2300sh,
(IV)	−,	1128vw,	−,	1662vi,
	−,	2154vi,	2392i,	2450i,
(V)	900m,	−,	−,	1672i,
	1944i,	2160i,	2282,	2304vi.

where i, intense; vi, very intense; m, medium; w, weak; vw, very weak; sh, shoulder.

Such parameters have been previously noted for dyes which have good properties in dyes medium [17].

3. Experimental

3.1. General

Elemental analysis were obtained by a CARLO ERBA EA 1108. Electronic spectra were obtained by the diffuse–reflectance technique, dispersing the sample in MgO, with a Specord M 400 Carl Zeiss Jena Spectrophotometer and in solution with Specord UV - Carl Zeiss Jena Spectrophotometer ($l = 1$ cm, concentration at around 10^{-5}M). IR spectra were run on a Perkin Elmer FT-IR spectrophotometer in the range 4000–200 cm^{-1} in KBr pellets and in the range 12,000–4,000 cm^{-1} in solid state on a Cary 17 D (NIR), and the ^{1}H-NMR spectra on a VARIA-GEMINI 17KT A-60 (60 MHz, with TMS in d_6-DMSO). All compounds and solvents were pure BDH grade chemicals.

3.2. Synthesis of the Azo derivatives

3.2.1. 1-(2′-Benzothiazolyl)-3-methyl-4-aza-(2″-carboxyphenyl)-pyrazol-5-one.(I) [9]

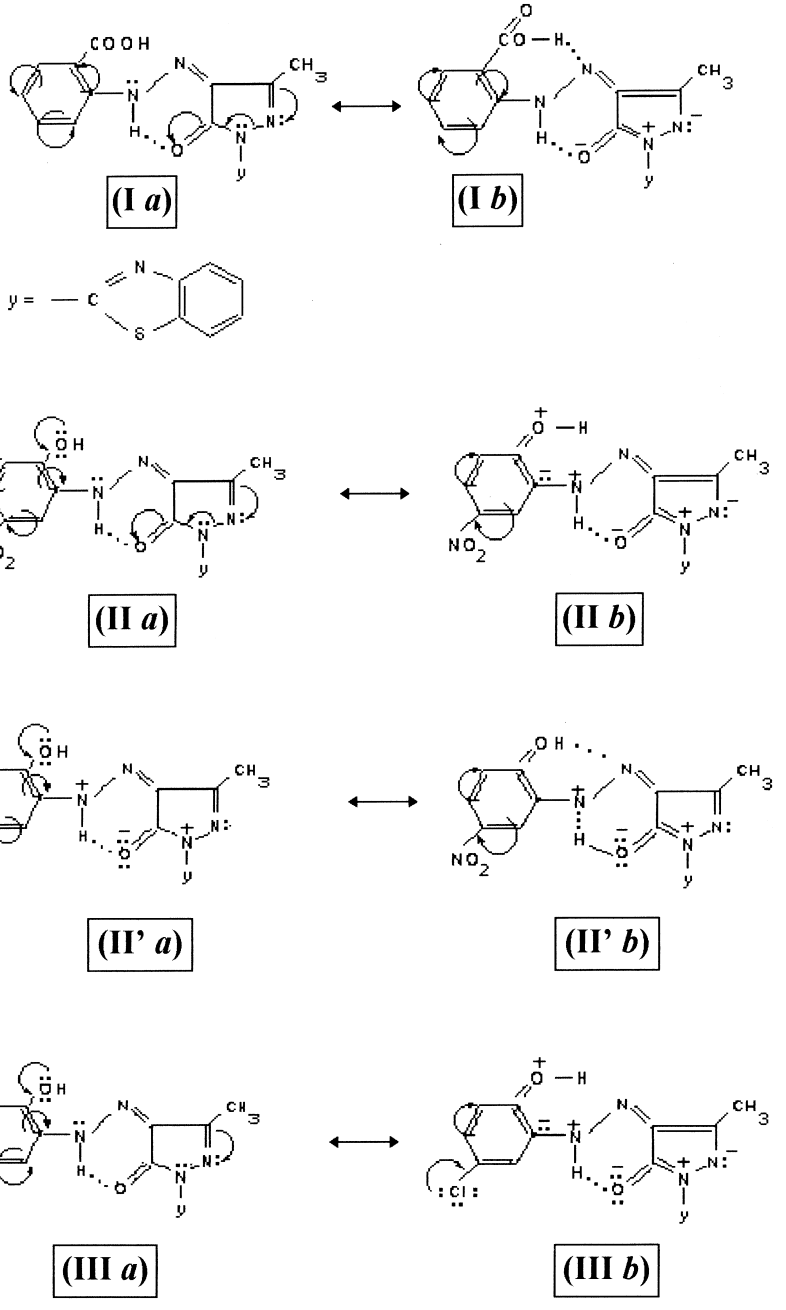
3.2.2. 1-(2′-Benzothiazolyl)-3-methyl-4-aza-(2″-hydroxy-5″-nitrophenyl)-pyrazol-5-one.(II)

2-Amino-4-nitro-1-sodium phenolate (0.01 mol) in 50 ml methanol and 3 ml conc. HCl ($d = 1.19$ g/cm^3) was treated at 0°C with 1.4 g $NaNO_2$ in 5 ml H_2O. The reaction mixture was stirred 1.5 h and the solution of the diazonium salt was then added to 0.01 mol of 1-(2′-benzothiazolyl)-3-methylpyrazol-5-one in 50 ml ethanol and 1 ml NaOH 42% solution. After stirring the reaction mixture 2 h, 5

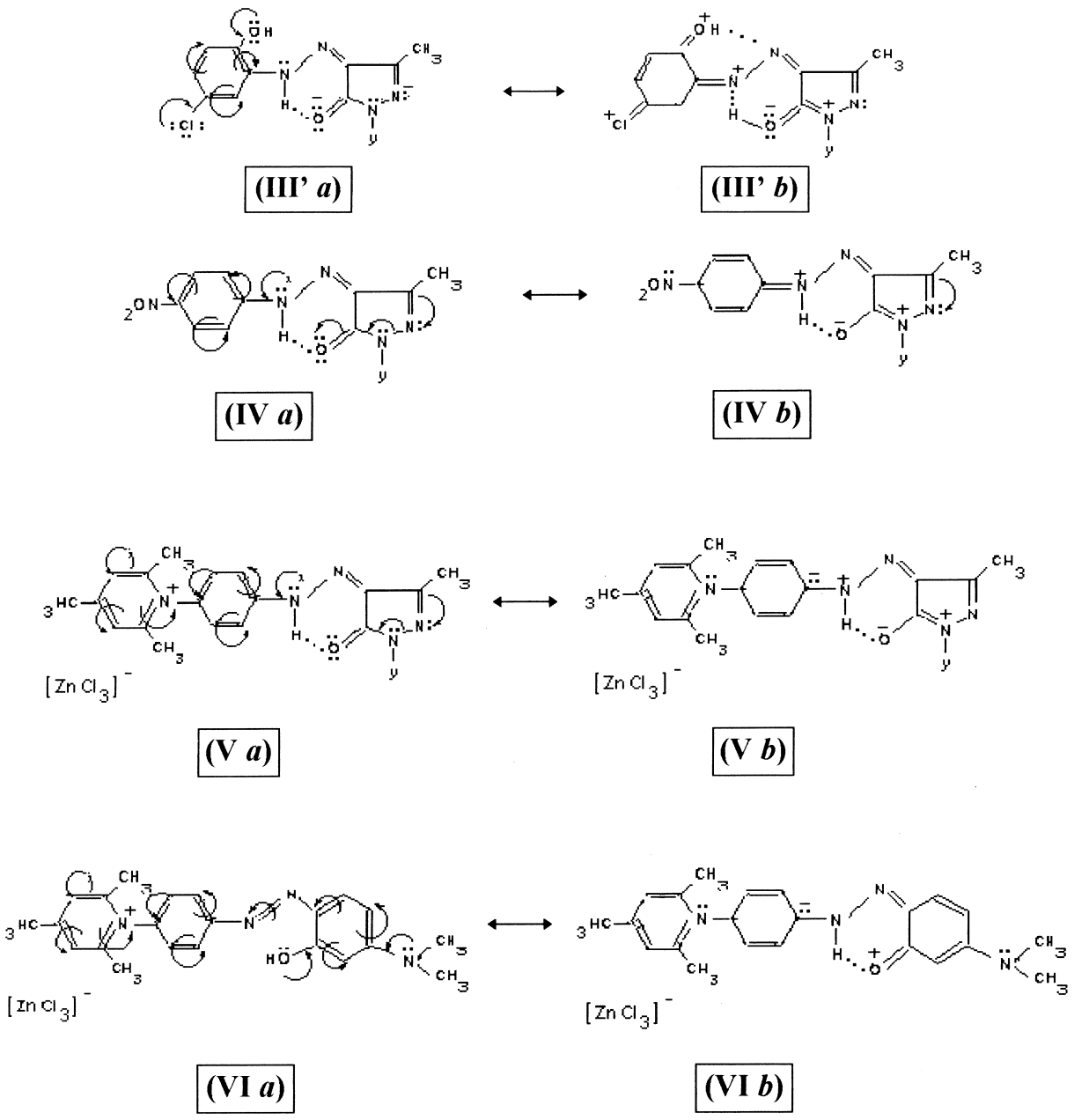
ml ammonia aqueous solution ($d = 0.8$ g/cm^3) was added and after 24 h, the azo compounds were separated with 25 ml aqueous solution HCl/$H_2O = 1/1$ (v/v) and recrystallised from a hot mixture of ethanol/$H_2O = 3/1$ (v/v).

^{1}H-NMR spectra data of the resultant compound was in good agreement with literature data [18,19], viz.,

^{1}H-NMR ($(D_3C)_2SO/TMS_{int}$) $\delta_a = 8.06$ ppm; $\delta_b = 7.52$ ppm; $\delta_c = 7.78$ ppm; $\delta_d = 7.88$ ppm;



Scheme 2.



Scheme 1. (Continued)

$\delta_e = 2.29$ ppm; $\delta_{fg} = 5.96$ ppm; $\delta_g = 7.39$ ppm; $\delta_h = 7.39$ ppm; $\delta_i = 8.06$; $J_{ab} = 7.7$ Hz; $J_{cd} = 8$ Hz; $J_{ac} = 1$ Hz; $J_{bd} = 1$ Hz; $J_{cd} = 7.9$ Hz; $J_{gh} = 7.9$ Hz; $J_{gi} = 0.9$ Hz; $J_{hi} = 0.9$ Hz.

3.2.3. 1-(2′-Benzothiazolyl)-3-methyl-4-aza-(2″-hydroxy-5″-chlorophenyl)-pyrazol-5-one.(III)

A solution of (0.01 mol) 2-amino-4-chlorophenol in 50 ml methanol and 3 ml conc. HCl

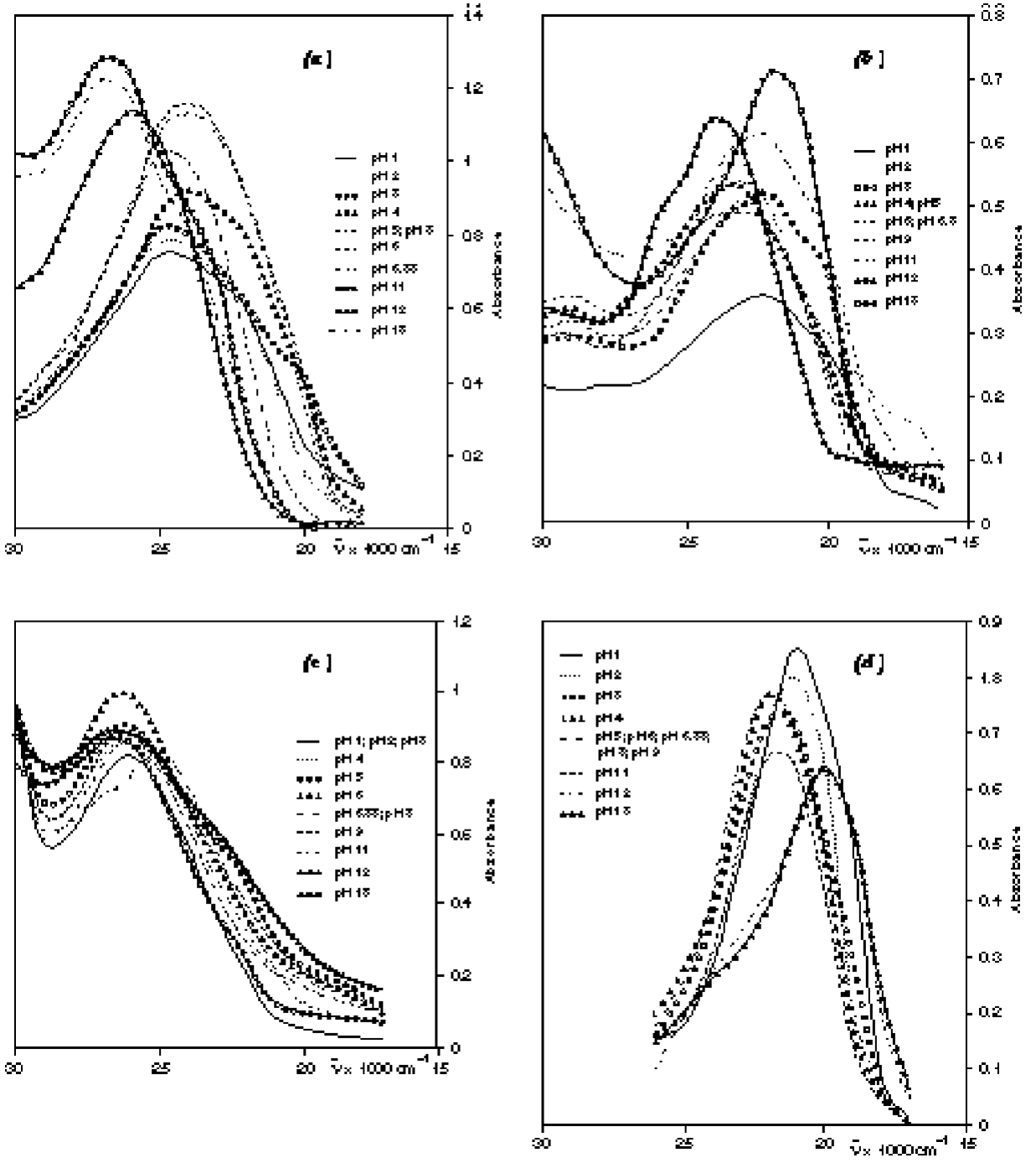


Fig. 2. Electronic absorption spectra of the azo derivatives at different pH (*a*)-(I); (*b*)-(III); (*c*)-(V); (*d*)-(VI).

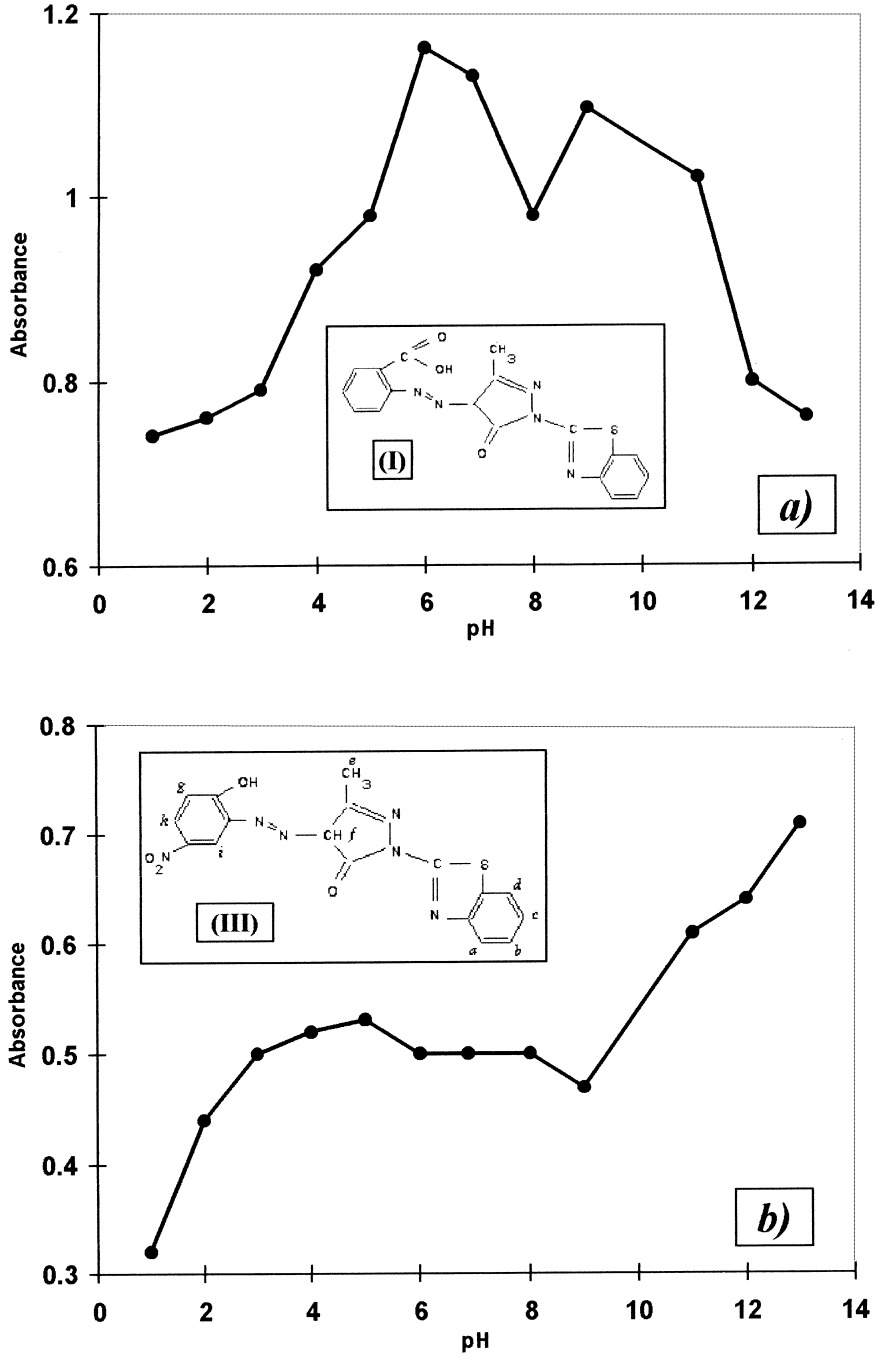


Fig. 3. Electronic absorption spectra of (I), (III), (V), (VI), in universal buffers pH: *a*) 8.17; *b*) 4.24; *c*) 8.17; *d*) 8.17.

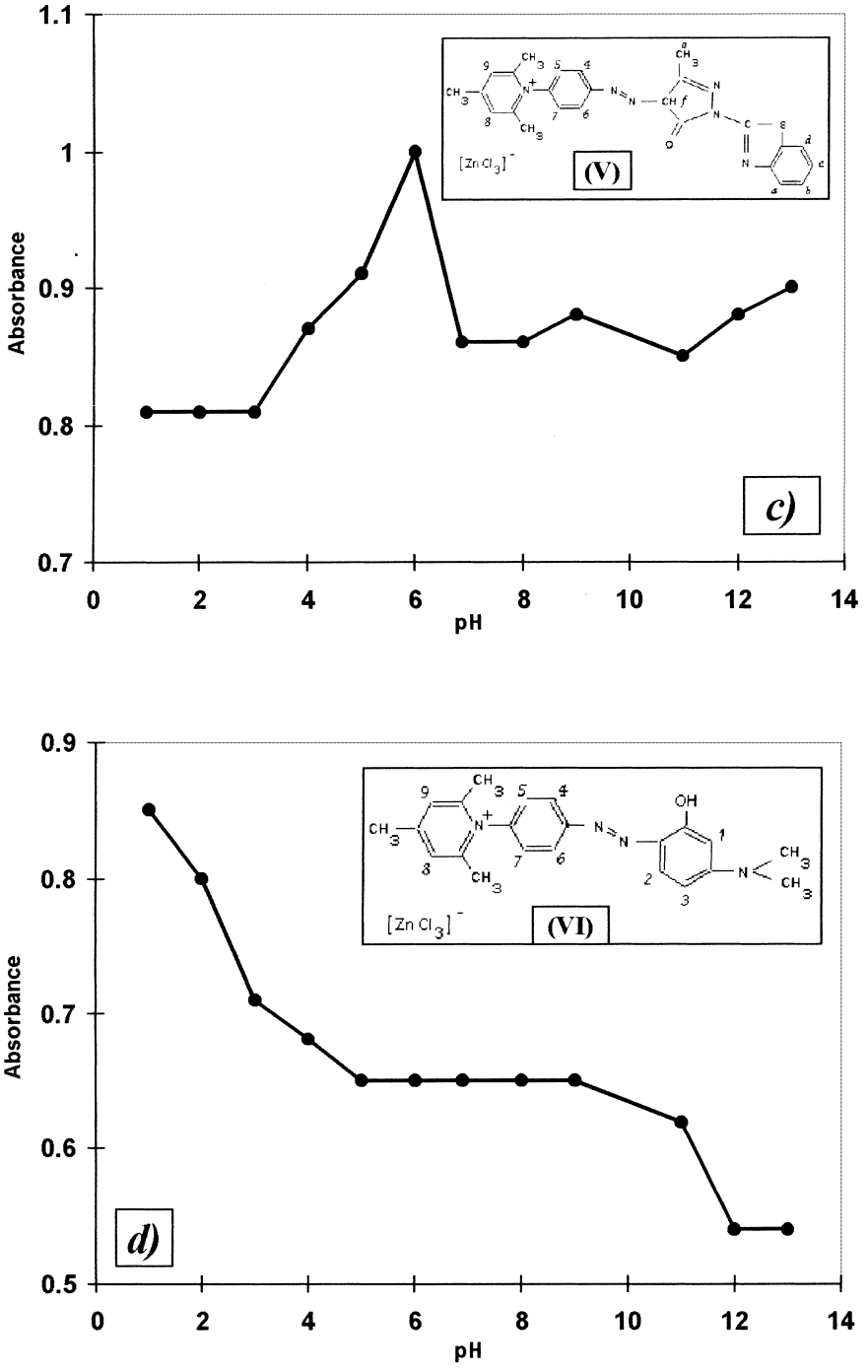


Fig. 3. (Continued)

Table 5
Electronic spectra [a] at different pH for the dyes I–VI

pH	Compound λ_{max} (nm)			
	(VI) 476.2	(V) 386.4	(III) 462	(I) 407.2
1.00	0.85	0.81	0.32	0.74
2.00	0.80	0.81	0.44	0.76
3.00	0.71	0.81	0.50	0.79
4.00	0.68	0.87	0.52	0.92
5.00	0.65	0.91	0.53	0.98
6.00	0.65	1.00	0.50	1.16
6.88	0.65	0.86	0.50	1.13
8.00	0.65	0.86	0.50	0.98
9.00	0.65	0.88	0.47	1.095
11.00	0.62	0.85	0.61	1.02
12.00	0.54	0.88	0.64	0.80
13.00	0.54	0.90	0.71	0.76

[a] Absorbance values at λ_{max}.

was diazotised at 0°C with 1.4 g $NaNO_2$ in 5 ml H_2O. The diazonium liquor was added to a solution of 1-(2′-benzothiazolyl)-3-methyl-pyrazol-5-one prepared in the same manner as in 3.2.1. and 3.2.2.

^{1}H-NMR ($(D_3C)_2SO/TMS_{int}$) $\delta_a = 7.95$ ppm; $\delta_b = 7.28$; $\delta_g = 6.84$ ppm; $\delta_h = 7.03$ ppm; $\delta_i = 7.43$ ppm; $J_{ab} = 7.7$ Hz; $J_{cd} = 7.9$ Hz; $J_{ac} = 1$ Hz; $J_{cb} = 7.6$ Hz; $J_{gh} = 7.2$.

3.2.4. 1-(2′-Benzothiazolyl)-3-methyl-4-azo-(4″-nitrophenyl)-pyrazol-5-one, (IV)

(0.5 mol) 4-Nitroaniline in 25 ml H_2O and 25,2 ml 30% HCl was diazotised with 0.055 mol $NaNO_2$. The diazonium salt solution was coupled with a 1-(2′-benzothiazolyl)-3-methyl-pyrazol-5-one solution obtained as above. The reaction mixture was stirred 2 h at 0°C and at a pH = 8.5, and then the azo compound was separated at pH = 1 and recrystallised from ethanol as a yellow solid.

^{1}H-NMR [$(D_3C)_2SO/TMS_{int}$] $\delta_a = 7.95$ ppm; $\delta_b = 2.28$ ppm; $\delta_c = 7.43$ ppm; $\delta_d = 7.80$ ppm; $\delta_e = 2.40$ ppm; $\delta_f = 5.45$ ppm; $\delta_g = 6.84$ ppm; $\delta_h = 7.14$ ppm; $\delta_i = 7.14$ ppm; $\delta_j = 7.03$ ppm; $J_{ab} = 7.7$ Hz; $J_{cd} = 7.9$ Hz; $J_{ac} = 1$ Hz; $J_{bd} = 1$ Hz; $J_{cb} = 7.6$ Hz; $J_{ij} = 7.5$ Hz; $J_{hg} = 7.9$ Hz.

3.2.5. 1-(2′-Benzothiazolyl)-3-methyl-4-azo-phenyl-[-4″-N(2‴,4‴,6‴-trimethylpyridinium]-pyrazol-5-one chlorozincate (V)

The diazonium liquor was obtained in the same manner as in 3.2.5., and was added to a solution of 1-(2′-benzothiazolyl)-3-methyl-pyrazol-5-one obtained as in 3.2.2., at 0°C. The azo derivative was isolated by the addition of a solution of 2% $ZnCl_2$, and then recrystallised from ethanol as brown-reddish crystals.

^{1}H-NMR [$(D_3C)_2SO/TMS_{int}$ $\delta_a = 7.95$ ppm; $\delta_b = 2.28$ ppm; $\delta_c = 7.43$ ppm; $\delta_d = 7.80$ ppm; $\delta_e = 2.40$ ppm; $\delta_f = 5.45$ ppm; $J_{ab} = 7.7$ Hz; $J_{cd} = 7.9$ Hz; $J_{ac} = 1$ Hz; $J_{bd} = 1$ Hz; $J_{cb} = 7.6$ Hz; δ 5,4,6,7 (7.15–7.61) ppm (m); δ 8,9 (7.46 ppm) (s); δ–CH_3 (2.38 ppm) (s) where s, singlet; m, multiplet.

3.2.6. m-Dimethylaminophenol-ortho-(1-azophenyl-4-N-2′4′6′) trimethylpyridinium chlorozincate (VI)

A suspension of (0.01 mol) N-(4′-aminophenyl)2,4,6-trimethylpyridinium perchlorate in 32 ml H_2O and 5 ml conc. HCl ($d = 1.19$ g/cm^3) at 0°C was diazotised with a solution of 1.3 g $NaNO_2$ in 4 ml H_2O for 2 h. The diazonium solution was added to a solution of 0.01 mol of m-dimethylaminophenol in 50 ml 0.72 M HCl. The reaction

mixture was stirred at 0°C for 2 h and the resulting azo derivative separated after addition of 2% $ZnCl_2$ solution and then recrystallised from a mixture of ether/acetone (1:1) (v/v) as brown crystals.

^{1}H-NMR [$(D_3C)_2SO/TMS_{int}$] δ 1(7.15–7.61) ppm (m*); δ 2,3 (7.15–7.61) ppm (m); δ 5,4,6,7 (7.15–7.61) ppm (m); δ 8,9 (7.46) ppm (s); $-CH_3$ $\delta = 2.38$ ppm (s) where s, singlet; d, doublet; t, triplet; m, multiplet.

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