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Hydrazone–Azo Tautomerism of Pyridone Azo Dyes. Part III—Effect of Dye Structure and Solvents on the Dissociation of Pyridone Azo Dyes

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ABSTRACT

It has been shown by electronic spectra that hydrazone–azo anion equilibria of arylazopyridones exist in various solvents. The thiadiazoleazopyridones more easily undergo acid dissociation into the azo anion than substituted phenylazopyridones in polar solvents. In alcohols, dimethylformamide, dimethylsulfoxide (DMSO), pyridine, etc., the azo anion predominates, in glacial acetic acid and chloroform the hydrazone predominates; and in acetone, cyclohexanone and benzene the hydrazone and azo anion structures of dyes 1–4 are present in different proportions. Substituted phenylazopyridones (dyes 5–48) favour the hydrazone form in all the solvents used. The concentration of the samples in solutions of ethanol, acetone, cyclohexanone, DMSO, etc. influences the equilibria to a certain extent. The equilibria tend to be shifted to the azo anion side on decreasing the concentration from 10^{-4} *M to* 10^{-6} *M. Temperature changes within the range 20–80°C do not exert any obvious influence on the dissociation equilibria. The nature of 3-substituents on the pyridone ring have an effect on pK values,* ν_{max}^{hyd} *and* ν_{max}^{anion}*; the correlation between these parameters and the Hammett* σ *constant of the substituent is discussed.*

1 INTRODUCTION

Arylazopyridones usually exist in the hydrazone form in the solid state or in solutions.[1,2] When a small amount of organic base (e.g. piperidine) is added to the solutions, the dyes may dissociate to their azo anions. Previously, on the basis of ^{13}C-NMR spectra, we assigned the equilibria in solution for the arylazopyridones to hydrazone–azo tautomerism.[3] Subsequent work[4] has

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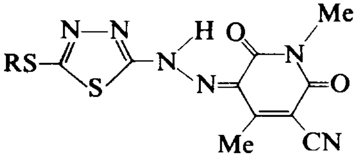
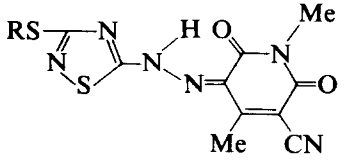
shown that the equilibrium is mainly a dissociative process, in which the hydrazone form corresponds to the azo anion form. This point of view is supported by the influence of dye structure, concentration, solvents and temperature on the dissociation equilibria reported in this paper. It is necessary, therefore, to have a correct understanding of the colour change in acid-base solutions for arylazopyridones.

2 RESULTS AND DISCUSSION

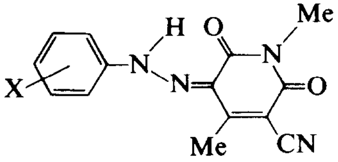
The structures of the dyes are as follows.



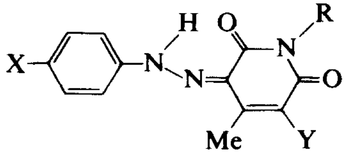
1, R = Me; 2, R = Et



3, R = Me; 4, R = Et



5–18, X = NO_2, CN, Cl, H, Me, OMe



19–33, X = SO_3K {R = H, Me, Et, Ph
34–48, X = OMe {Y = H, $CONH_2$, CN, NO_2

The effect of solvents on hydrazone–azo anion equilibria

The absorption spectra of the dyes were determined in various solvents at a concentration of $(1{\cdot}5\text{–}2{\cdot}1) \times 10^{-5}$ M. Two typical spectra are shown in Fig. 1. The spectra of dyes 1–4 are influenced by the solvent properties. Changes in the spectra of other dyes were not so evident as those of dyes 1–4. In order to estimate the ratio of the two forms quantitatively, spectra for the hydrazone form were obtained in glacial acetic acid or chloroform. Differences in the λ_{max} and ε_{max} of the curves in these solvents are to be expected because of the differences in the solvating power of the media. The best way to obtain the absorption curves of the hydrazone form is to add 20 μl glacial acetic acid

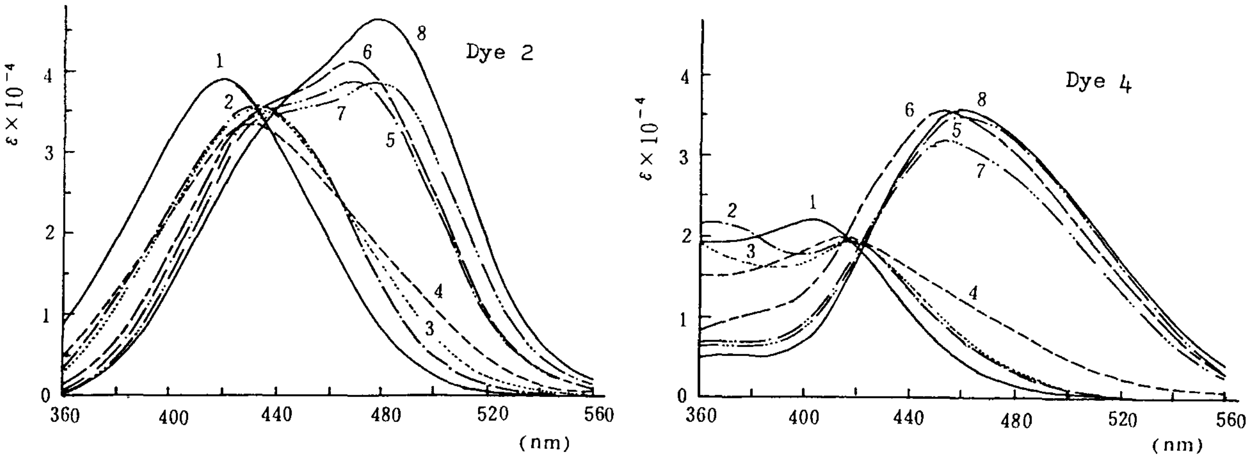


Fig. 1. Typical absorption spectra of the dyes, conc. (1·7–2·0) × 10^{-5} M, at 20 ± 1 C. Solvents: 1, glacial acetic acid; 2, chloroform; 3, benzene; 4, acetone; 5, absolute ethanol; 6, methanol; 7, DMSO; 8, pyridine.

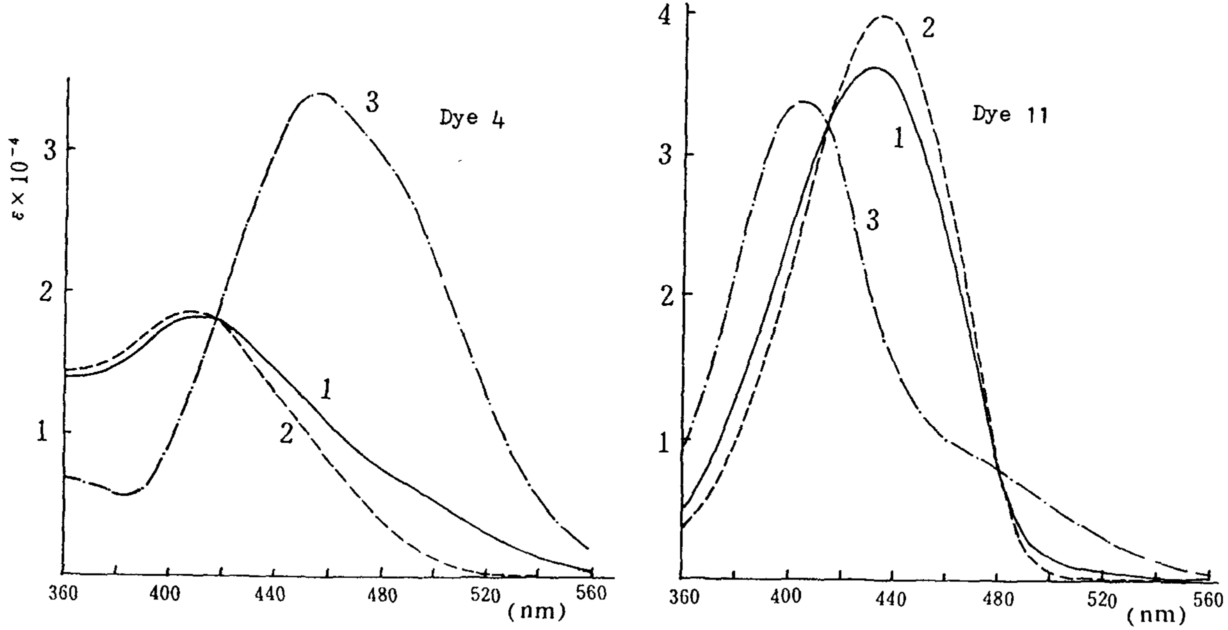


Fig. 2. Absorption spectra of dye 4 in acetone ($1{\cdot}7 \times 10^{-5}$ M) and dye 11 in DMSO ($1{\cdot}8 \times 10^{-5}$ M), at 20 ± 1°C. Curves: 1, in neutral solutions; 2, 20 *μl* glacial acetic acid and 6N HCl was added to the 5-ml solutions of dyes 4 and 11, respectively; 3, 20 *μl* piperidine was added to 5-ml solutions.

into 5-ml sample solutions of chloroform, benzene, acetone, cyclohexanone, alcohols, etc., or the same amount of 6N hydrochloric acid to dimethylformamide (DMF) dimethylsulfoxide (DMSO) solution. In this way the influence of solvents on the spectra can be avoided. In alcohols, DMF, DMSO and pyridine, the azo anion structure of the dyes 1–4 predominates. There was no significant change in the spectra when $20\,\mu$l piperidine was added to the above solutions. This indicates that the acidic thiadiazoleazopyridones are in a dissociated state in these solvents. The absorption curves of dye solutions in chloroform, benzene, acetone and cyclohexanone for dyes 1–4 show apparent changes when piperidine is added. The new curves are quite similar to the spectra in methanol, pyridine, etc. Therefore, it is reasonable to assume that only the azo anion structure is present in solutions of all solvents with a small amount of piperidine added (except in acetic acid for all dyes, and in chloroform for dyes 5–48) for the arylazopyridones studied in this paper. Dyes 4 and 11 may be used as examples (Fig. 2); curve 2 arises from the hydrazone form and curve 3 from the azo anion form. The equations to calculate the ratio of two colorants are the same as those used in the previous literature.[4–6] The estimated results for dyes 1–4 are listed in Table 1 and those for dyes 5–18 in Table 2.

It can be seen from Fig. 1 and Tables 1 and 2 that:

(1) For dyes 1–4, the hydrazone–azo anion equilibria depends on the properties of the solvents used. In proton-donating solvents, such as glacial acetic acid and chloroform, the dyes give a blue shift of λ_{max} and exist basically in the hydrazone form. In proton-accepting solvents, such as alcohols, DMF, DMSO and pyridine, the dyes give a red shift of λ_{max} and exist mainly in the azo anion structure. The percentage of the azo anion

TABLE 1

Content of Hydrazone Structure of Dyes 1–4 in Various Solvents (conc. (1·7–2·0) × 10^{-5}M, at 20 ± 1°C)

Solvent	λ_{max} *(nm)*				ε_{max} (× 10^{-4})				*Hyd (%)*			
Dye	*1*	*2*	*3*	*4*	*1*	*2*	*3*	*4*	*1*	*2*	*3*	*4*
Acetic acid	420	420	402	404	3·9	3·9	2·4	2·2	100	100	100	100
Chloroform	433	433	415	418	3·7	3·6	1·8	1·8	99	98	99	98
Benzene	435	432	417	419	3·4	3·5	1·8	1·8	89	90	96	94
Acetone	428	428	412	413	3·3	3·3	1·8	2·0	82	82	81	81
Cyclohexanone	—	431	—	419	—	3·3	—	2·0	—	79	—	78
Ethanol	468	469	453	453	3·8	3·8	3·3	3·2	2	3	2	2
Methanol	—	469	—	453	—	4·2	—	3·6	—	0	—	0
DMSO	476	476	459	459	4·0	3·9	3·4	3·4	1	2	1	2
DMF	—	474	—	458	—	4·3	—	3·9	—	0	—	0
Pyridine	476	476	465	459	4·3	4·5	3·4	3·6	0	0	0	0

TABLE 2

Content of Hydrazone Structure of Dyes 5–18 in Various Solvents (conc. (1·6–2·1) × 10^{-5}M, at 20 ± 1°C)

Dye	*Substituent X*	*Parameter*	*Solvent*					
			Chloroform	*Acetone*	*Methanol*	*Ethanol*	*DMSO*	*DMF*
5	*p*-NO_2	λ_{max}(nm)	433	429	431	430	444	447
		$\varepsilon(\times 10^{-4})$	5·7	4·8	4·6	—[a]	3·8	4·0
		Hyd(%)	100	96	83	84	61	44
6	*m*-NO_2	λ_{max}(nm)	421	416	416	417	418	419
		$\varepsilon(\times 10^{-4})$	4·2	4·1	3·9	4·0	3·5	3·6
		Hyd(%)	100	94	77	88	12	35
7	*p*-CN	λ_{max}(nm)	429	423	423	425	436	431
		$\varepsilon(\times 10^{-4})$	5·1	5·3	5·2	5·0	4·4	4·8
		Hyd(%)	100	97	84	95	12	58
8	*m*-CN	λ_{max}(nm)	422	418	416	416	418	422
		$\varepsilon(\times 10^{-4})$	4·0	3·7	3·8	3·3	3·2	3·5
		Hyd (%)	100	34	70	83	3	29
9	*m*-Cl	λ_{max}(nm)	431	422	423	425	423	422
		$\varepsilon(\times 10^{-4})$	4·4	4·2	3·7	—[a]	3·8	3·6
		Hyd(%)	100	97	86	97	58	37
10	*p*-Cl	λ_{max}(nm)	439	427	432	433	420	427
		$\varepsilon(\times 10^{-4})$	4·2	4·1	3·9	3·9	3·6	3·6
		Hyd(%)	100	85	88	96	46	66
11	H	λ_{max}(nm)	435	427	430	431	430	432
		$\varepsilon(\times 10^{-4})$	4·1	4·0	4·3	4·0	3·6	3·9
		Hyd(%)	100	99	96	98	79	91
12	*p*-Me	λ_{max}(nm)	446	438	440	440	443	442
		$\varepsilon(\times 10^{-4})$	4·4	4·4	4·3	4·2	3·8	4·4
		Hyd(%)	100	100	93	99	80	92
13	*p*-OMe	λ_{max}(nm)	463	455	457	455	460	460
		$\varepsilon(\times 10^{-4})$	4·4	4·3	4·2	4·2	3·8	4·0
		Hyd(%)	100	98	94	100	71	94
14	*o*-Me	λ_{max}(nm)	435	426	439	436	424	442
		$\varepsilon(\times 10^{-4})$	4·5	4·2	4·4	—[a]	3·6	4·4
		Hyd(%)	100	100	99	99	75	95
15	*o*-CN	λ_{max}(nm)	425	417	418	419	429	428
		$\varepsilon(\times 10^{-4})$	4·2	4·2	3·8	—[a]	3·3	3·6
		Hyd(%)	100	95	70	92	14	20
16	*o*-Cl	λ_{max}(nm)	435	426	428	426	424	430
		$\varepsilon(\times 10^{-4})$	4·4	4·2	4·3	—[a]	3·6	3·8
		Hyd(%)	100	100	100	100	75	84
17	*o*-NO_2	λ_{max}(nm)	437	433	434	433	442	439
		$\varepsilon(\times 10^{-4})$	4·3	4·3	4·3	4·0	3·6	3·8
		Hyd(%)	100	100	99	98	88	77
18	*o*-OMe	λ_{max}(nm)	458	451	453	450	458	456
		$\varepsilon(\times 10^{+4})$	4·1	4·0	4·2	—[a]	3·9	3·9
		Hyd(%)	100	100	100	100	99	100

[a] The solubility is limited.

increases in different solvents according to the order: acetic acid < chloroform < benzene < acetone ≈ cyclohexanone < ethanol < DMSO ≈ methanol ≈ DMF ≈ pyridine.

The effect of solvents on the equilibria is somewhat different from that of solvents on hydrazone–azo tautomerism.[6,7] It is evident that the acidity of the solvents decreases in order from acetic acid to pyridine. Such an order of the effect of solvents is consistent with the phenomenon of dissociation.

(2) For dyes 5–18, the equilibria are in favour of the hydrazone structure in all the solvents used, the nature of the solvent not showing any obvious effect on the equilibria. If the substituents in the ortho-position to the imino group, e.g. *o*-Cl, *o*-NO_2 and *o*-OMe, in the phenyl hydrazone structure can form an intramolecular hydrogen bond, the percentage of the hydrazone form in proton-accepting solvents is higher than that of the corresponding *p*- and *m*-analogues. The results are in good agreement with the chemical shifts of the imino group which shift to lower field by 0·6–1·4 ppm[3]. Methyl and cyano substituents do not exert any effect on the equilibria.

When the ortho-substituents are SO_3H or CO_2H (i.e. they can form strong intramolecular hydrogen bonds), the dyes exist completely in the hydrazone form in various solvents (these results are not listed in Table 2).

(3) For dyes 6–13, the hydrazone–azo anion equilibria can be illustrated by the linear correlations between the maximum absorption frequencies and Hammett constants (σ), as shown in Fig. 3. Least-squares analysis of the data gives the relations:

in acetone $\nu_{hyd} = 1803\sigma + 22900\ \text{cm}^{-1}$ $(r = 0{\cdot}928)$
$\nu_{anion} = -653\sigma + 24400\ \text{cm}^{-1}$ $(r = 0{\cdot}937)$
in methanol $\nu_{hyd} = 1779\sigma + 22800\ \text{cm}^{-1}$ $(r = 0{\cdot}926)$
$\nu_{anion} = -820\sigma + 25400\ \text{cm}^{-1}$ $(r = 0{\cdot}915)$
in DMF $\nu_{hyd} = 1837\sigma + 22700\ \text{cm}^{-1}$ $(r = 0{\cdot}917)$
$\nu_{anion} = -797\sigma + 24700\ \text{cm}^{-1}$ $(r = 0{\cdot}932)$
in DMSO $\nu_{hyd} = 1901\sigma + 22600\ \text{cm}^{-1}$ $(r = 0{\cdot}933)$
$\nu_{anion} = -903\sigma + 24500\ \text{cm}^{-1}$ $(r = 0{\cdot}914)$

The negative slope of the azo anion structure plots indicates that electron-donating substituents in the phenyl ring shift the visible band to shorter wavelength, the reverse of the effect observed in the hydrazone structure. The results are similar to those reported by Griffiths[8] and in our previous study.[4] Absorption frequencies of the azo anion structures of the dyes in methanol are higher than those in acetone, DMF and DMSO. This may arise from the difference in solvating power of the solvents.

In this report, dyes 19–48 with different substituents in the coupling component were evaluated by using the same procedure[4] to obtain the pK values, λ_{max}^{hyd} and λ_{max}^{anion}. The results are listed in Table 3. It can be seen

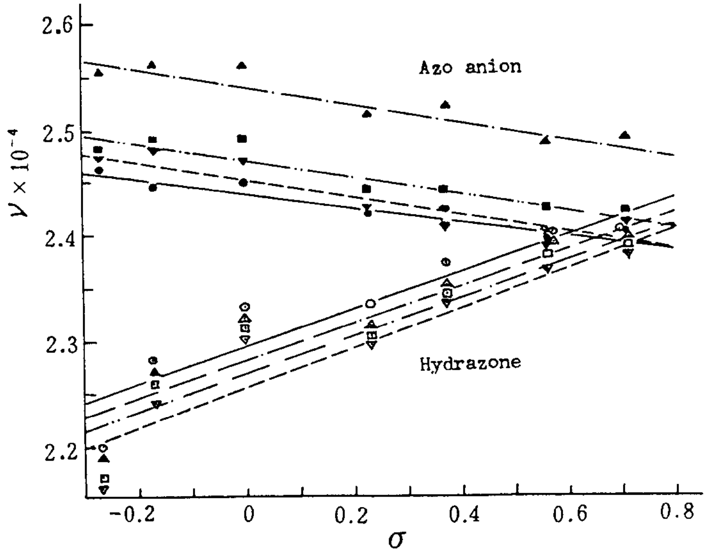


Fig. 3. Correlation between absorption maxima (cm^{-1}) of two colorants and substituent Hammett constants (σ) in different solvents. ○, ● —— in acetone; △, ▲— — in methanol; ⊡, ■— — in DMF; ▽, ▼---- in DMSO.

from the Table 3 that the substituents on the nitrogen atom do not significantly affect λ_{max}^{hyd} and λ_{max}^{anion} (about ± 2 nm), and the pK values of the NH series of compounds seem to be a little lower than those of homologues with NMe, NEt and NPh substituents by about 0·5 pH unit. However, the 3-substituents on the pyridone ring (which can be considered as *meta*-substituents of the hydrazone or azo group) show a significant influence on the spectral data. As shown in Figs 4 and 5, ν_{max}^{hyd} decreases with increasing σ, whereas the ν_{max}^{anion} and $\Delta\nu(\nu_{max}^{anion} - \nu_{max}^{hyd})$ increase. The linear equations are expressed as follows:

For dyes 19–33 $\nu_{hyd} = -1348\sigma + 23900\,\mathrm{cm}^{-1}$ $(r = 0{\cdot}9251)$

$\nu_{anion} = 2039\sigma + 23800\,\mathrm{cm}^{-1}$ $(r = 0{\cdot}9683)$

$\Delta\nu_{(anion\text{-}hyd)} = 3387\sigma - 137\,\mathrm{cm}^{-1}$ $(r = 0{\cdot}9747)$

$\mathrm{pK} = -5{\cdot}85\sigma + 12{\cdot}2$ $(r = 0{\cdot}9340)$

For dyes 34–48 $\nu_{hyd} = -1384\sigma + 22500\,\mathrm{cm}^{-1}$ $(r = 0{\cdot}9125)$

$\nu_{anion} = 1740\sigma + 24400\,\mathrm{cm}^{-1}$ $(r = 0{\cdot}9822)$

$\Delta\nu_{(anion\text{-}hyd)} = 3125\sigma + 1910\,\mathrm{cm}^{-1}$ $(r = 0{\cdot}9893)$

$\mathrm{pK} = -5{\cdot}63\sigma + 11{\cdot}9$ $(r = 0{\cdot}9269)$

(r = Linear correlation coefficient)

The influence of 3-substituents in the coupling component is opposite to that in the diazo component. This can be explained by electron migration

TABLE 3

Spectral Data and pK Values for Dyes 19–33

Dye	*R*	*Y*	λ_{max}^{anion} (*nm*)	λ_{max}^{hyd} (*nm*)	*pK*	*Dye*	*R*	*Y*	λ_{max}^{anion} (*nm*)	λ_{max}^{hyd} (*nm*)	*pK*
19	H	H	417	418	11·5	34	H	H	410	444	11·2
20	Me	H	419	419	12·1	35	Me	H	407	443	11·9
21	Et	H	420	419	12·3	36	Et	H	407	443	12·0
22	Ph	H	419	420	12·1	37	Ph	H	408	445	11·7
23	H	$CONH_2$	416	423	10·7	38	H	$CONH_2$	402	448	10·8
24	Me	$CONH_2$	414	422	11·4	39	Me	$CONH_2$	400	446	11·2
25	Et	$CONH_2$	415	422	11·6	40	Et	$CONH_2$	401	447	11·3
26	Ph	$CONH_2$	414	424	11·3	41	Ph	$CONH_2$	401	448	11·0
27	H	CN	401	437	7·7	42	H	CN	393	466	7·8
28	Me	CN	401	435	8·1	43	Me	CN	395	463	8·0
29	Et	CN	403	436	8·4	44	Et	CN	396	464	8·0
30	Ph	CN	402	437	8·0	45	Ph	CN	395	466	7·8
31	H	NO_2	424[b]	432	8·0	46	H	NO_2	385	462	7·9
32	Me	NO_2	393	432	8·6	47	Me	NO_2	386	460	8·4
33	Et	NO_2	396	433	8·9	48	Et	NO_2	390	460	8·8

[a] $\varepsilon_{max}^{anion} = (2{\cdot}2–3{\cdot}3) \times 10^{-4}$ and $\varepsilon_{max}^{hyd} = (3{\cdot}5–4{\cdot}3) \times 10^{-4}$ are not listed in the table. The substituent of X is SO_3K for dyes 19–33 and OMe for dyes 34–48.

[b] The dye may not be completely dissociated into its azo anion structure.

from the diazo to the coupling component, since the pyridone ring is an electron-withdrawing system. Any substituents which may increase the electron density on the diazo ring or decrease the electron density on the coupling component, will produce a red shift of the absorption wavelength for the hydrazone form and an enhancement of the absorption frequency difference between the hydrazone and azo anion forms. It is also interesting to note that the pK values of dyes 19–33 decrease with the σ-constant of the 3-substituents, as shown in Fig. 6. Substituents such as CN and NO_2, which are strongly electron-withdrawing, and which are in the *para*-position to the oxygen-carrying negative charge, may stabilise the azo anion structures and make their pK values lower than those of the anions with H and $CONH_2$ groups at the same position.

Influence of sample concentration on the equilibria

It has been noted the dyes 1–4 in neutral DMSO-d_6 exist in the hydrazone form ($\sim 10^{-1}$ M), but the data in this report indicate that the dyes in DMSO, alcohols, etc. ($\sim 10^{-5}$ M) exist predominantly in the azo anion structure

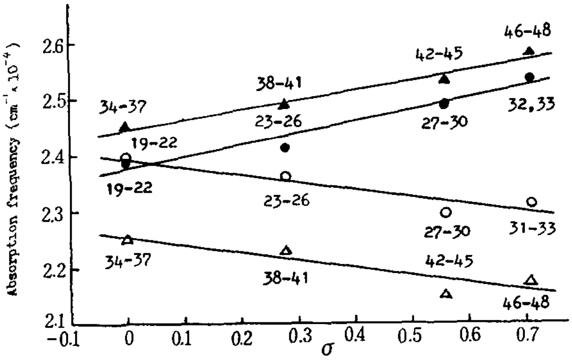


Fig. 4. Absorption frequencies of hydrazone and azo anion versus σ of 3-substituents on coupling component (Numbers in Figs 4–6 refer to the dyes in Table 3). ○, △-hydrazone, ●, ▲-azo anion.

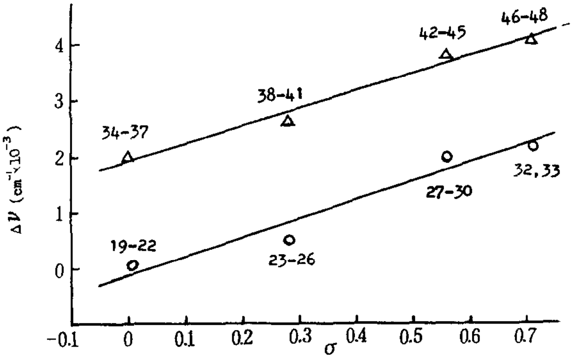


Fig. 5. Azo anion–hydrazone frequency shifts versus σ of 3-substituents on coupling component.

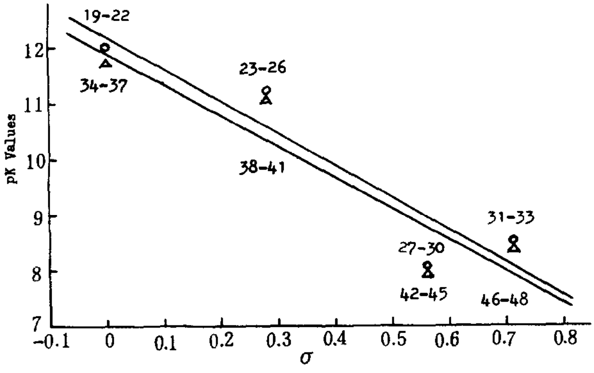


Fig. 6. pK values versus σ of 3-substituents.

(Table 1). Therefore, it was necessary to investigate the concentration range in which the equilibria move from one side to the other. Typical spectra are shown in Fig. 7.

The results obtained are listed in Table 4. The structure of dyes 1–4 in ethanol is mainly in the azo anion form when the concentration is in the range of 10^{-6}–10^{-5} M, whereas the equilibria are in favour of the hydrazone form when the concentration is increased to ~ 10^{-4} M. The effect of sample concentration on the equilibria for dyes 1–4 can also be observed in acetone and cyclohexanone, but not in chloroform in the concentration range determined. For dyes 5–48, a concentration of ~ 10^{-6} M is not dilute enough to cause the dyes to dissociate to azo anion structure completely.

The hydrazone–azo anion equilibrium is a first-order dissociation, so it should not be strongly concentration-dependent. The experiments can not absolutely exclude the action of trace impurity in the solvents as a base, which at low concentration of the dyes becomes very important to the ionisation. However, when the solvents (DMSO, methanol, ethanol) were dried with 4A sieve sorbent and redistilled, the results were basically reproduceable. The electrostatic interaction and hydrogen bonding are

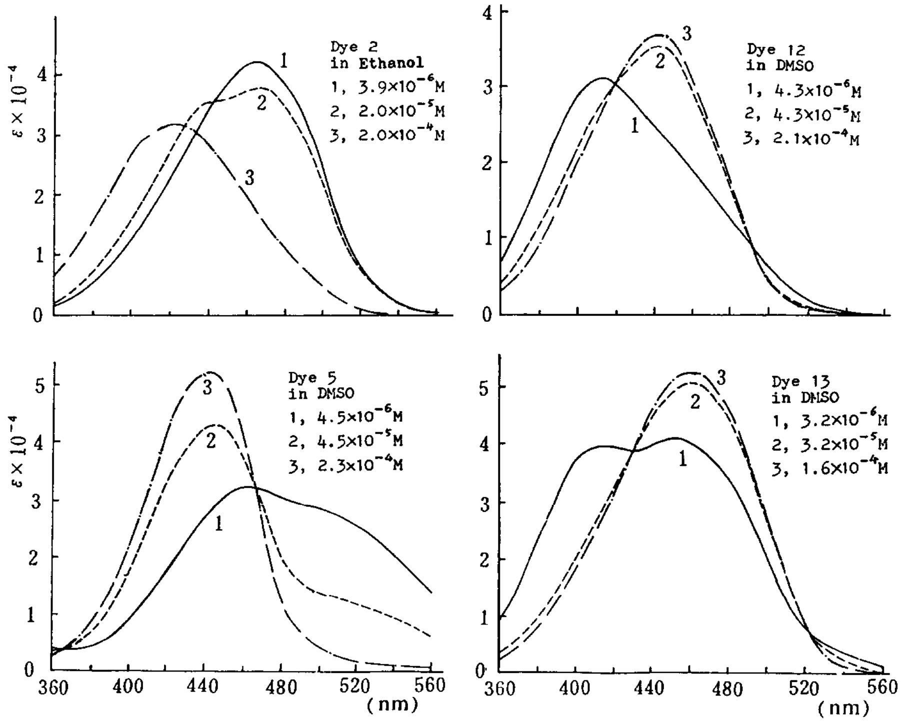


Fig. 7. The influence of concentration on absorption spectra (dye 2 in ethanol; dyes 5, 12 and 13 in DMSO, at 20 ± 1°C).

TABLE 4
Content of Hydrazone Structure in Different Concentrations (at 20 ± 1°C)

Dye	*Solvent*	$C \times 10^5$ (*mol/litre*)	λ_{max}(*nm*)	$\varepsilon \times 10^{-4}$	*Hyd* (%)
1	Ethanol	0·39	469	3·9	1
		1·96	468	3·8	2
		19·6	426	3·3	79
2	Ethanol	0·51	467	4·0	0
		2·54	466	3·8	6
		25·4	423	3·2	84
	Acetone	0·32	439	3·4	28
		1·58	428	3·3	82
		15·8	422	3·2	96
	Cyclohexanone	0·63	440	3·3	50
		1·90	431	3·3	79
		19·0	427	3·2	93
3	Ethanol	0·34	455	3·4	0
		1·71	453	3·3	2
		17·1	405	2·4	94
4	Ethanol	0·40	453	3·3	0
		2·00	453	3·2	2
		20·0	408	1·8	86
	Acetone	0·45	449	2·6	41
		2·23	413	2·0	81
		22·3	405	2·1	94
	Cyclohexanone	0·66	420	1·9	75
		1·99	419	2·0	78
		19·9	409	1·8	97
5	DMSO	0·45	468	3·5	12
		1·70	442	3·8	61
		23·0	440	4·7	92
9	DMSO	0·34	415	3·7	20
		1·70	422	3·8	59
		3·40	423	4·0	65
		17·0	426	4·3	73
10	DMSO	0·40	415	3·6	25
		1·70	419	3·7	46
		20·0	419	4·1	73
11	DMSO	0·46	407	3·5	11
		1·80	430	3·6	79
		23·0	433	3·7	87
12	DMSO	0·43	412	3·6	34
		1·70	443	3·8	80
		21·0	445	4·0	92
13	DMSO	0·32	451	3·7	42
		1·70	460	3·8	71
		16·0	461	4·2	90

probably stronger for hydrazone dimer formation relative to azo dimer formation, the more concentrated solution (10^{-4}M) favouring the hydrazone form, as noticed by Monahan *et al.*[9] Of course, the influence of concentration of arylazopyridones on the absorption spectra cannot be explained by simple aggregation:[10-12]

(1) Solutions of the dyes in ethanol, acetone, cyclohexanone or DMSO at room temperature follow Beer's law over the concentration range 10^{-6}–10^{-4}M. The λ_{max} of some dyes (e.g. dyes 2 and 5) show a blue shift and others (e.g. dyes 12 and 13) shows a red shift with increasing concentrations. Additionally, dye 2 exhibits a reduction of ε_{max}, but dyes 5, 12 and 13, etc., show an enhancement of the ε_{max} of the new bands.

(2) Over the range of concentrations, one or two isosbestic points appear in the absorption curves, this usually being relatable to the presence of two-coloured species in equilibrium. The persistence of the bands in more concentrated solutions ($\sim 10^{-4}$M) shows that one of these species is the hydrazone, and the other is the azo anion structure obtained in dilute solutions ($\sim 10^{-6}$M). The influence of concentration on the absorption curves of arylazopyridones indicates that change of the spectra may be caused by the shift of the equilibria.

Effect of temperature on the equilibria

Many authors[7,13,14] have examined the effect of temperature on the tautomeric equilibria of arylazonaphthols in the solutions and found that

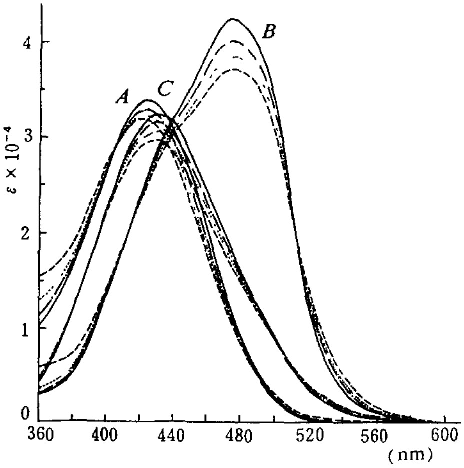
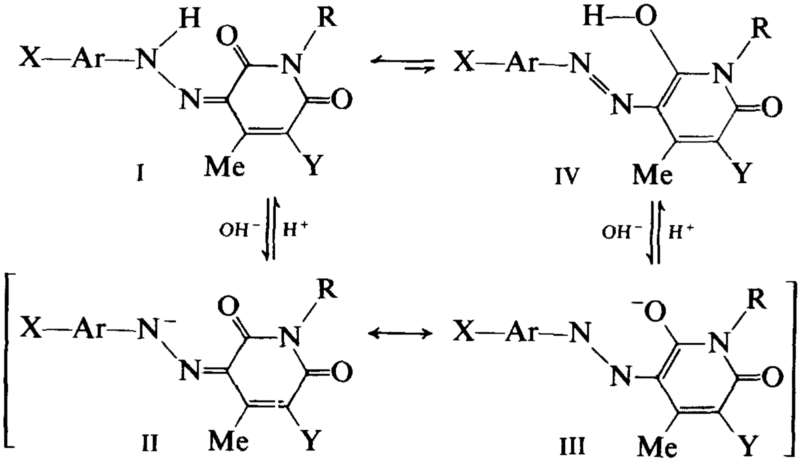


Fig. 8. The effect of temperature on the dissociation equilibria of dye 2 in cyclohexanone (conc. 1·9 × 10^{-5}M). C, in neutral cyclohexanone; A, 20 μl glacial acetic acid was added into 5 ml C solution; B, 20 μl piperidine was added into 5 ml C solution. ———, 20 ± 1°C; — —, 40 ± 1°C; ...., 60 ± 1°C; - - - -, 80 ± 1°C.

the equilibria shift to the hydrazone side with decreasing temperature. The data suggest that the process of shifting from azo to hydrazone is exothermic. In this study, solutions of dye 1–4 and dyes 5, 7, 11–13 in cyclohexanone and DMF were examined in the temperature range 20–80°C. Typical spectra for dye 2 in cyclohexanone are shown in Fig. 8; λ_{max} does not basically shift, but ε_{max} decreased somewhat with increasing temperature. It is of interest to note that the reference curves of both structures are also affected by temperature. This may arise from expansion of the solutions with increasing temperature. The estimated content of the hydrazone form does not change significantly. These results support the acid-base equilibria of arylazopyridones which do not involve change of energy.

3 CONCLUSIONS

Hydrazone–azo anion equilibria exist in the solutions of arylazopyridones. The strong acidic dyes 1–4 could be ionised by traces of piperidine or even in neutral polar solvents. The other dyes may be dissociated to their azo anion structure in more strongly basic conditions. The equilibrium scheme can be illustrated as follows, in which II and III are resonance hybrids and III is the major form in basic conditions.[8,15]



Dye structure has a significant effect on the equilibria. Dyes 1–4 are more readily transformed to the azo anion in solutions, because of their specific electronic induction and p-π conjugation system, and perhaps also the proton-accepting property of the diazonium components. The hydrazone structure is predominant in organic solvents for substituted phenylazopyridones. If the substituents in the *o*-position of the phenyl ring can form an intramolecular hydrogen bond with the imino group, the dyes are more difficult to be dissociated to the azo anion structure, even in proton-accepting solvents. The 3-substituents on pyridone ring have a significant influence on the dissociation. Strongly electron-withdrawing groups decrease the pK values of the dyes.

Substituents with increasing electron density in the diazo component, or 3-substituents with decreasing electron density in the coupling residue, will produce a red shift for the hydrazone form and a blue shift for the azo anions.

The equilibria are affected by sample concentration. In proton-accepting solvents the equilibria may shift to the azo anion side with decreasing concentration.

Variance of temperature in the range 20–80°C does not have a noticeable influence on the equilibria of arylazopyridones.

4 EXPERIMENTAL

The solvents were analytical pure; they were dried with 4A sieve sorbent for 48 h and redistilled. The pH values of the solvents (acetone, ethanol, methanol, DMSO and DMF) were tested before use in aqueous solutions (organic solvents:water = 1·0:1·0, v/v) and equalled 7·0 ± 0·2 pH.

Absorption spectra were recorded on a Shimaru UV-260 Spectrophotometer using 0·1, 0·5, 1·0, 3·0 and 5·0 cm matched glass cells at 20°C ± 1°C. The temperature experiments were carried out at 20, 40, 60 and 80°C ± 1°C. The percent error of ε_{max} and estimated content of the hydrazone form are presumed to be within the range of ±10% and that of the maximum absorption frequencies, ±1 nm, over repeated determinations.

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