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Hydrazone-Azo Tautomerism of Pyridone Azo Dyes. Part II: Relationship Between Structure and pH Values

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ABSTRACT

The absorption spectra of more than thirty pyridone azo dyes have been examined in binary mixtures of water with acetone, ethanol or dimethylsulfoxide (DMSO). The ratio of hydrazone to azo anion isomers has been calculated at different pH values. Each dye has its own specific pK value at which equal amounts of the hydrazone and azo anion isomers exist. The greater the pK values, the higher the hydrazone content. The equilibrium is also related to the structure of the dyes, and is in favour of the hydrazone form for dyes which can form an intramolecular hydrogen bond between the ortho-substituents in the diazo component and the imino group or which contain a 3-carbomoyl group instead of a cyano group in the coupling component. The use of thiadiazoles as diazo components results in a shift of the equilibrium to the azo anion form. Substituents with different Hammett substituent constants (σ) in the diazo component showed an unexpected effect on pK values, but the difference between the absorption maxima showed a linear relationship with σ values.

INTRODUCTION

Pyridone azo dyes give very bright greenish-yellow to orange hues of significantly higher tinctorial strength than those of most arylazonaphthols and have excellent coloration properties. Some of them exhibit a colour change during the application process and this is probably related to the equilibrium of hydrazone–azo anion forms at different pH values. An

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investigation on the influence of structural features of the dyes on this equilibrium is of theoretical and practical significance.

NMR, IR, RAMAN and UV spectroscopy have been used in investigations of substituted arylazonaphthols. A more convenient approach to investigate the quantitative effect of various factors upon the equilibrium is to utilise absorption spectra.[1–8] In previous papers[9,10] the structural characteristics of arylazopyridones have been determined by ^1H- and ^{13}C-NMR spectra in solutions of organic solvents, and a hydrazone–azo anion equilibrium exists in aqueous acid–base media.

In this paper, the absorption spectra of more than 30 dyes have been studied. It has been found that the shift of maximum wavelength (λ_{max}) and molar extinction coefficient (ε_{max}) is related to the pH of the solutions. The relative content of the hydrazone form at different pH values can be calculated from the spectra.

EXPERIMENTAL

The synthesis and purification of the dyes has been previously reported.[10] Deionized water was used to prepare the solutions, and the solvents used were of analytically pure grade. Absorption spectra were recorded immediately the required pH values had been established, this being especially important with solutions which were unstable under strongly acidic conditions.

The absorption spectra were recorded on a Shimazu UV-260 Spectrophotometer using 10 mm matched glass cells at 20 ± 1°C. 7–9 isomolar concentration solutions ($(1{\cdot}5–2{\cdot}5) \times 10^{-5}$M) were prepared and 2N HCl, acetic acid and NaH_2PO_4–NaOH solutions were used to adjust the pH values, which were measured on a PHS-2 meter with error of $\pm 0{\cdot}1$ pH units. The pH meter, with range 0–14 pH and accuracy of 0·02 pH, was made in Shanghai Lei Ci instrument factory, Shanghai, China. Errors of the data are within the range $\pm 0{\cdot}2$ pH for pK values; ± 1 nm for λ_{max} and $+ 10\%$ for ε_{max} in repeated determinations.

RESULTS AND DISCUSSION

It is usually necessary to use the pure hydrazone or azo material as a standard to calculate the ratio of two tautomers.[1,2,6] For pyridone azo dyes, there are some difficulties in establishing suitable standards because of the remarkable change of λ_{max} and ε_{max} with the dye structure. Fortunately, the hydrazone–azo anion equilibrium of most pyridone azo dyes are very

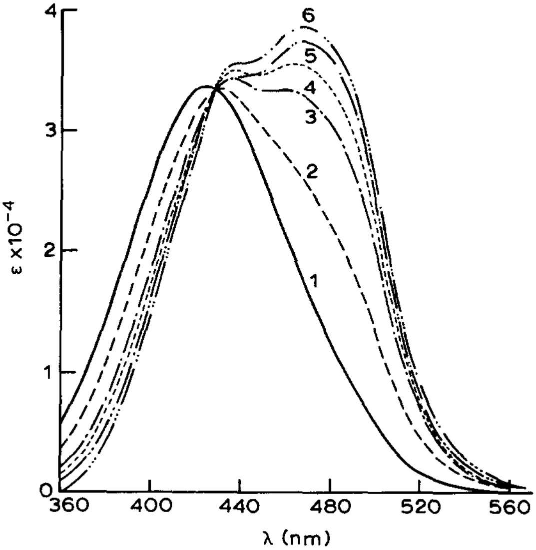


Fig. 1. Absorption spectra of dye **2** in 50 vol% ethanol–water solution at 20 ± 1°C. pH values: 1, 2·5; 2, 3·2; 3, 3·7; 4, 4·0; 5, 5·2; 6, 6·0–12·0.

sensitive to acid or base. The dyes may be transformed completely into the hydrazone form if a small amount of acetic acid or hydrochloric acid is added to the sample solution, or to the azo anion form if a base is added. The ratio of the two isomers at intermediate pH values can be calculated by using both absorption curves as standards.

Dyes **2** and **17** can be used to exemplify the typical absorption curves which are obtained at different pH values (Figs 1 and 2).

There are one or two isosbestic points in each spectrum in the wavelength range 360–560 nm. The changes in the absorption spectra arise from structural transformations in the dyes. Further increase in either acidity or basicity can result in the curves showing deviations from the isosbestic points shown, especially for dyes containing groups which are sensitive to acid or base. Such deviations can arise in strongly basic solutions (pH > 13·5) and also in strongly acidic media, in which amine salts may be formed if the diazo component contains tertiary nitrogen atoms (e.g. dyes **1**–**6**, pH < 1·5). These absorption curves cannot be used as standards for determination of the hydrazone or azo anion forms.

It was also observed (Figs 1 and 2) that whilst, within certain pH ranges, individual dyes did not exhibit any significant change in absorption spectra (e.g. dye **2** in the pH range 5·0–11·0; dye **17**, pH 2·0–7·0), in other pH ranges, the curves were very sensitive to pH (e.g. dye **2**, pH 2·5–5·0; dye **17**, pH 7·0–10·5). The equations introduced by Kishimoto *et al.*[6] can be used to calculate the ratio of the two isomers. The method of Stoyanov and Antonov[5] may

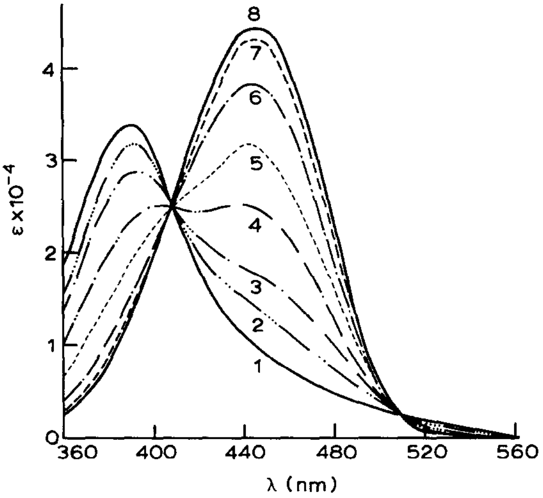


Fig. 2. Absorption spectra of dye **17** in 50 vol% acetone–water solution at 20 ± 1°C. pH values: 1, 11·4; 2, 10·4; 3, 9·4; 4, 9·2; 5, 8·7; 6, 8·4; 7, 6·5; 8, 2·0–5·0.

also be applied. Errors in the measurement depend mainly upon the accuracy of the pH value measurements of the solutions rather than on the curve evaluation. Calculations using the points of λ_{max}^{hyd} and λ_{max}^{anion} were satisfactory for our investigation.

The pH range in which the content of hydrazone form changes between *c.* 5–95% is defined as the colour change range (pH-R) in this paper. The relationship between the content of the hydrazone isomer and the pH values, using dyes **2** and **5** as examples, is shown in Fig. 3.

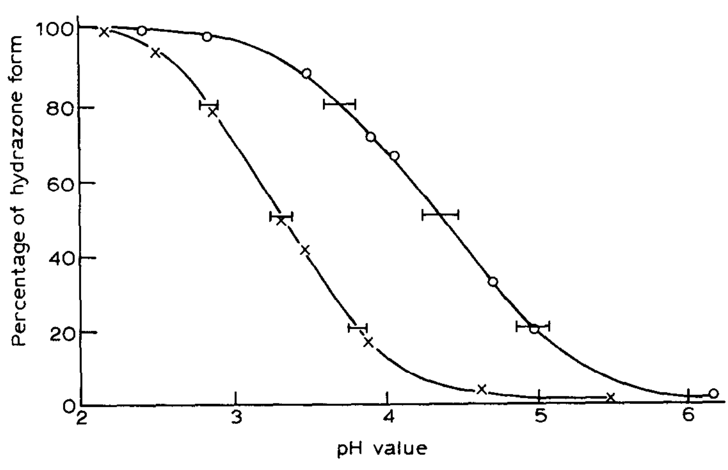


Fig. 3. Relationship between content of hydrazone form and pH values for dyes **2** (×) and **5** (○) in binary mixture of 50 vol% acetone with water, at 20 ± 1°C.

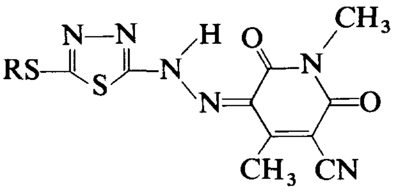
The ratio of hydrazone content to that of azo anion isomers is defined as K_T where

$$K_T = \frac{[\text{Hyd}]}{[\text{Azo anion}]}$$

The relationship between log K_T and pH value is shown in Fig. 4. It is easy to obtain the pK values at which log $K_T = 0$, that is, the ratio of hydrazone to azo anion isomers equals 1·0 pK. Values can be used to define the property of colour change for dyes of different structures in acid-base solutions.

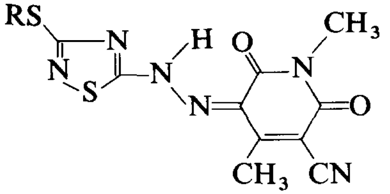
The dyes studied were of the following general formulae:

I



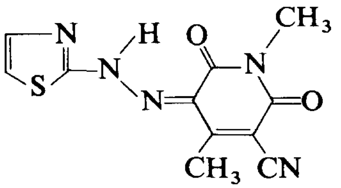
(**1** $R = CH_3$, **2** $R = C_2H_5$, **3** $R = n\text{-}C_4H_9$)

II



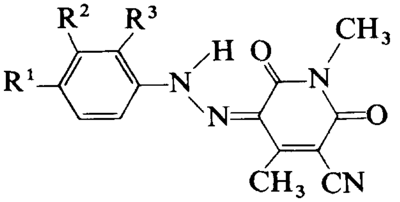
(**4** $R = CH_3$, **5** $R = C_2H_5$)

III



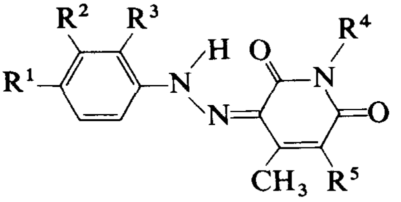
(**6**)

IV



(**7–20**)

V



(**21–32**)

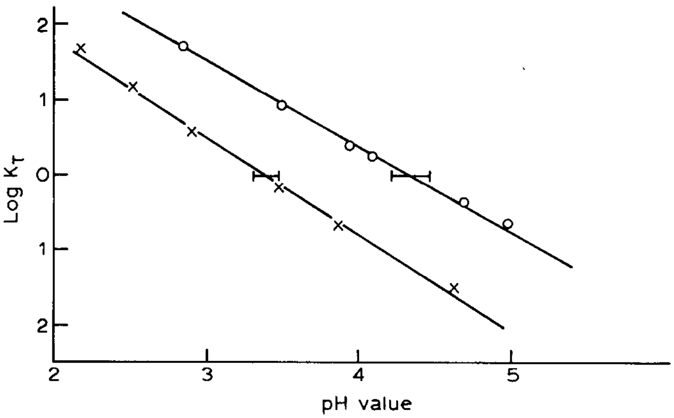


Fig. 4. Relationship between Lg K_T and pH value for dyes **2** (×) and **5** (○) in binary mixture of 50 vol% acetone with water, at 20 ± 1°C.

Typical spectral data for the dyes in 50 vol% water–organic solvents are listed in Tables 1–3. Table 4 gives the influence of concentration of organic solvents on pH-R and on pK values for two typical dyes.

Many arylazopyridones exhibit a different colour at different hydrogen ion concentrations. These colour changes occur because the compounds are quite acidic and can undergo proton transfer reactions. The undissociated

TABLE 1

Spectral Data for Dyes **I**, **II** and **III** (at 20 ± 1°C)

Dye	*Substituent*	*Solution*[a]	λ_{max}^{anion} (*nm*)	$\varepsilon_{max}^{anion}$ ($\times 10^{-4}$)	λ_{max}^{hyd} (*nm*)	ε_{max}^{hyd} ($\times 10^{-4}$)	*pH-R*	*pK*
1	CH_3	Acetone	469	4·5	424	3·8	2·5–5·0	3·4
		Ethanol	468	4·2	426	3·6	2·5–5·0	3·3
		DMSO	472	3·9	427	3·3	2·5–5·0	3·4
2	C_2H_5	Acetone	470	4·5	422	3·8	2·5–5·0	3·4
		Ethanol	468	4·2	425	3·6	2·5–5·0	3·3
		DMSO	473	3·8	427	3·3	2·5–5·0	3·3
3	n-C_4H_9	DMSO	473	3·8	427	3·2	2·5–5·0	3·4
4	CH_3	Acetone	455	4·4	405	2·7	3·0–6·0	4·4
		Ethanol	455	3·5	405	2·2	3·0–6·0	4·2
		DMSO	458	3·2	407	2·1	3·0–6·0	4·3
5	C_2H_5	Acetone	455	3·9	406	2·3	3·0–6·0	4·4
		Ethanol	454	3·6	405	2·2	3·0–6·0	4·3
		DMSO	457	3·1	408	2·1	3·0–6·0	4·4
6	—	Acetone	475	2·9	433	3·3	3·5–6·5	4·8

[a] Aqueous solutions of 50 vol% organic solvents.

TABLE 2
Spectral Data for Dyes **IV** (at 20 ± 1°C)

Dye	R^1	R^2	R^3	*Solution*[a]	λ_{max}^{anion} (*nm*)	$\varepsilon_{max}^{anion}$ ($\times 10^{-4}$)	λ_{max}^{hyd} (*nm*)	ε_{max}^{hyd} ($\times 10^{-4}$)	*pH-R*	*pK*
7	NO_2	H	H	acetone	447	2·9	434	5·6	6·5–10·0	8·5
8	H	NO_2	H	DMSO	402	3·2	425	4·2	6·8–10·0	8·5
9	H	H	NO_2	acetone	408	2·6	441	4·5	7·0–11·0	9·3
				DMSO	406	2·5	446	4·2	7·5–10·5	8·9
10	CN	H	H	DMSO	416	2·9	432	3·8	6·0–9·5	7·8
11	H	CN	H	DMSO	404	2·9	426	3·7	6·0–9·5	7·7
12	H	H	CN	DMSO	418	2·8	426	3·8	5·9–9·3	7·6
13	Cl	H	H	acetone	397	3·6	437	4·5	6·5–9·5	8·0
				ethanol	394	3·4	439	4·4	6·5–9·5	8·0
				DMSO	398	3·3	440	4·4	6·5–9·5	7·9
14	H	Cl	H	acetone	398	3·5	430	4·4	6·5–10·0	8·2
				ethanol	395	[b]	432	[b]	6·4–10·0	8·1
				DMSO	398	3·2	432	4·3	6·4–9·5	7·9
15	H	H	Cl	acetone	401	3·1	435	4·2	7·5–10·7	9·3
				ethanol	402	[b]	436	[b]	7·5–10·5	9·2
				DMSO	400	[b]	438	[b]	7·5–10·5	8·9
16	H	H	H	acetone	389	3·2	435	4·2	7·0–10·5	8·8
				ethanol	388	2·8	437	3·7	7·0–10·5	8·8
				DMSO	390	3·2	436	4·0	6·5–10·0	8·5
17	CH_3	H	H	acetone	389	3·3	444	4·5	7·0–10·5	9·1
				ethanol	388	3·0	447	4·3	7·0–10·5	8·8
				DMSO	390	3·1	448	4·1	7·0–10·5	9·1
18	H	H	CH_3	acetone	391	3·2	444	4·5	7·2–10·6	9·3
				ethanol	390	[b]	445	[b]	7·2–10·6	9·3
				DMSO	394	2·6	446	4·1	7·0–10·5	9·1
19	OCH_3	H	H	acetone	391	3·0	462	4·0	7·0–10·3	8·8
				DMSO	394	3·1	462	4·0	6·5–9·7	8·2
20	H	H	OCH_3	acetone	390	3·0	459	3·9	9·5–12·5	11·3
				ethanol	390	[b]	459	[b]	9·5–12·5	11·3
				DMSO	391	[b]	462	[b]	9·2–12·2	10·7

[a] Aqueous solutions of 50 vol% organic solvents.
[b] Solubility is limited in the solutions.

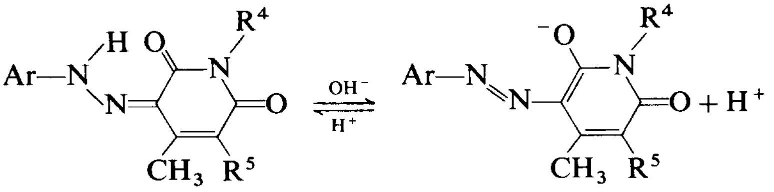
TABLE 3

Spectral Data[a] for Dyes **IV** in Aqueous Solutions of 50 vol% DMSO (at 20 ± 1°C)

Dye	R^1	R^2	R^3	R^4	R^5	λ_{max}^{anion} (*nm*)	λ_{max}^{hyd} (*nm*)	*pH-R*	*pK*
21	SO_3H	H	H	CH_3	CN	401	434	7·0–10·0	8·5
22	H	SO_3H	H	CH_3	CN	398	432	6·6–9·8	8·2
23	H	H	SO_3H	CH_3	CN	390	432	9·0–13·0	11·2
24	CO_2H	H	H	CH_3	CN	402	435	7·0–10·6	8·8
25	H	H	CO_2H	CH_3	CN	382	442	10·7–13·5	12·1
26	H	H	SO_3H	*o*-$CH_3C_6H_4$	CN	392	434	9·0–12·2	10·6
27	H	H	SO_3H	*o*-ClC_6H_4	CN	401	434	9·0–12·2	10·6
28	H	H	SO_3H	*o*-ClC_6H_4	$CONH_2$	416	422	11·0–14·0	>13·0
29	H	H	H	CH	$CONH_2$	400	423	10·0–12·5	11·4
30	SO_3H	H	H	CH_3	$CONH_2$	413	420	10·0–13·5	11·9
31	H	SO_3H	H	CH_3	$CONH_2$	406	418	10·0–13·0	11·3
32	H	H	SO_3H	CH_3	$CONH_2$	419	419	11·0–14·0	>13·0

[a] $\varepsilon_{max}^{anion} = (2–3) \times 10^4$ and $\varepsilon_{max}^{hyd} = (3–4) \times 10^4$ are not listed in the Table.

acid has a different colour to the ionized salts. The hydrogen ion concentration at which the colour change takes place depends on the acid strength of the arylazopyridones and the equilibrium can be represented as:



(Acidic or neutral medium) (Basic medium)

Griffiths[7] has pointed out that 4-phenylazo-1-naphthols can exist in either the hydroxyazo or the hydrazone form in neutral or acidic media. In the presence of alkali, both forms are converted to their common anion form (azo anions rather than hydrazone anions). Trotter,[11] in a study of arylazonaphthols by laser Raman spectroscopy, noted that the hydrazone form in aqueous acid at pH 2 is converted to azo anions at pH 12. Saito *et al.*[12] examined resonance Raman spectra of acid–base indicators and concluded that for hydroxynaphthyl compounds, an azo-type spectrum is obtained in basic solutions and quinoid-type spectra in neutral solutions. For arylazopyridones, as shown in Figs 1 and 2, the absorption spectra change significantly at various pH values, thus implying that there is a change in the

TABLE 4

Spectral Data for Dyes **2** and **21** in Various Solutions (at 20 ± 1°C)

Dye	*Solution*	λ_{max}^{anion} (*nm*)	λ_{max}^{hyd} (*nm*)	*pH-R*	*pK*
2	20% acetone	468	422	2·5–5·0	3·3
	20% ethanol	468	424	2·5–5·0	3·3
	20% DMSO	471	423	2·5–5·0	3·4
	20% dioxane	471	416	2·5–5·0	3·4
21	50% acetone	400	434	7·5–11·0	9·3
	20% acetone	398	432	7·5–11·0	9·2
	50% ethanol	398	434	7·0–10·5	8·7
	20% ethanol	398	432	7·0–10·2	8·5
	25% DMSO	400	436	7·0–10·2	8·7
	10% DMSO	400	432	7·0–10·2	8·6
	20% dioxane	394	434	6·5–11·2	8·7
	water	399	433	6·0–10·0	8·0

conjugated bond system. Therefore, it is reasonable to assume that the contribution of the azo anion structure is predominant in the hydrazone/azo anions in basic solutions. This assumption is confirmed for dye **2** by the ^{13}C chemical shift displacement at different pH in DMSO-water solution.[10] The hydrazone–azo anion equilibrium can also be illustrated by the linear relationship between the absorption frequency and Hammett substituent constants (σ) (Fig. 5). As shown in Fig. 5 and Table 5, ν_{max} (hydrazone)

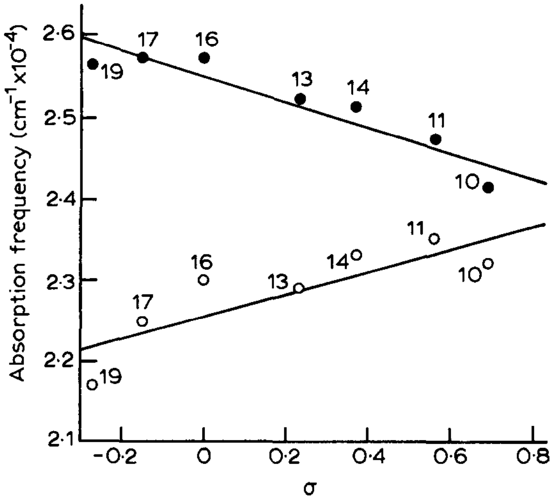


Fig. 5. Absorption frequencies of hydrazone and azo anion versus σ (numbers refer to the dyes in Table 2). ○ Hydrazone, ● azo anion.

TABLE 5

Visible Absorption Maxima (in cm^{-1}) of Some Substituted Phenylazopyridones

Dye	*Substituent*	σ	$\nu_{max} \times 10^{-4}$ (cm^{-1}) azo anion	$\nu_{max} \times 10^{-4}$ (cm^{-1}) hydrazone	$\Delta\nu \times 10^{-3}$ (cm^{-1}) ($\nu_{anion} - \nu_{hydrazone}$)
10	*p*-CN[a]	0·69	2·404	2·315	0·89
11	*m*-CN[a]	0·56	2·475	2·347	1·28
14	*m*-Cl	0·37	2·513	2·326	1·87
13	*p*-Cl	0·23	2·519	2·288	2·31
16	H	0	2·571	2·299	2·72
17	*p*-CH_3	−0·15	2·571	2·252	3·18
19	*p*-OCH_3	−0·27	2·558	2·165	4·23

[a] In aqueous solution of 50 vol% DMSO; others, 50 vol% acetone.

increases with σ, but for ν_{max} (azo anion) it decreases. For phenylazopyridones, it is usually difficult to obtain the pure azo form in aqueous-organic solvents and thus there is no linear relationship between ν_{max} (azo form) and σ.

In acidic or neutral solutions, the arylazopyridones exist largely as the hydrazone isomers. The *p*-NO_2 derivative showed an unusual absorption maximum of this isomer in acetone or DMSO; it may exist in an ionized form in acidic solutions, and its molar extinction coefficient was larger than those of other dyes.[6] Dye **7**, therefore, is not included in Table 5, and Figs 5 and 6. Least-squares analysis of the data afforded the relationships:

$$\nu_{hydrazone} = 1400\sigma + 22\,600\,\text{cm}^{-1} \qquad (r = 0{\cdot}830)$$
$$\nu_{anion} = -1530\sigma + 25\,500\,\text{cm}^{-1} \qquad (r = 0{\cdot}914)$$
$$\nu_{anion} - \nu_{hydrazone} = -3110\sigma + 2990\,\text{cm}^{-1} \qquad (r = 0{\cdot}980)$$

The conjugated system of arylazopyridones is different from that of arylazonaphthols. The 2-carbonyl group may reduce the charge migration from the 6-oxygen anion into the azo group and this may be the reason for the higher absorption frequency of the azo anion compared to the hydrazone, and for the negative slope of the plot of ($\nu_{anion} - \nu_{hydrazone}$) against σ (Fig. 6).

The position of the hydrazone–azo anion equilibrium depends on several factors such as dye structure, pH values, etc. Compared with substituted phenylazopyridones, the pyridone azo dyes containing 2-alkylthio-5-amino-1,3,4-thiadiazole, 3-alkylthio-5-amino-1,2,4-thiadiazole or thiazole residues have an increased acidity (compounds **1**–**6**), because of the electron-withdrawing nature of the hetero residues. The pK values of these dyes are in the range of 3·3–4·8 and the equilibrium is in favour of the azo anion form, especially for dyes **1**–**3** (pK = 3·3–3·4). The pH-R of dyes **1**–**3** (2·5–5·0) are

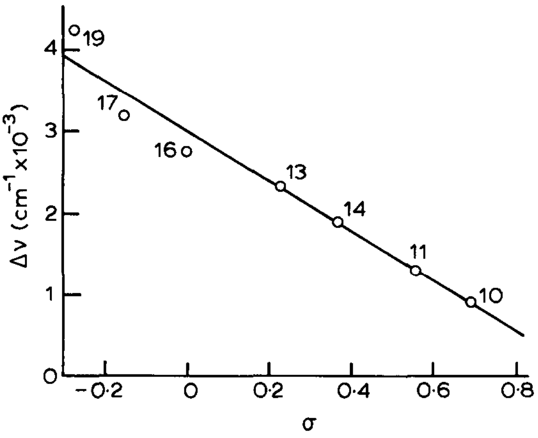


Fig. 6. Azo anion–hydrazone frequency shifts versus σ (numbers refer to the dyes in Table 2).

almost the same as the range of ^{13}C chemical shift changes for dye **2** (pH 3–6).[10] It can therefore be assumed that complete structural transformation takes place in the pH range 2·5–6·0 for dyes **1–3**.

It is interesting to note that substituents in the phenyl ring of the diazo component do not exhibit the expected effect on $\log K_T$, pK, or on the hydrazone–azo anion equilibrium in the solutions. As shown in Table 2, when the substituents on the phenyl ring are *p*-NO_2, *m*-NO_2, *p*-CN, *m*-CN, *m*-Cl, *p*-Cl, H, *p*-CH_3 and *p*-OCH_3, there is no relationship with the measured pK values. Conversely, the pK values for the dyes with electron-donating substituents seem to be larger than those for the dyes with electron-withdrawing substituents. However, when substituents in the coupling component are changed from CN to $CONH_2$, the pK values increase by about 3 pH units (corresponding to about a thousandfold reduction in acid dissociation constants, cf. dyes **28–32** in Table 3).

When the substituents in the *o*-position in the diazo component can form an intramolecular hydrogen bond with the imino group, the pK values are larger than those of the *m*- and *p*- substituted isomers by 0·7–2·5 pH units (Table 2). When the substituent groups are SO_3H or COOH, the pK values increase by more than 3·0 pH units (Table 3). The formation of intramolecular hydrogen bonds has been confirmed[10] by NH chemical shifts. Generally, the stronger the intramolecular hydrogen bond, the greater the δ_{NH} and the larger the increments of pK values. When the substituents in the *o*-position of the azo group cannot form intramolecular hydrogen bond isomers, e.g. CN or CH_3, the dyes do not exhibit such differential pK values compared to the *m*- and *p*-counterparts.

The errors in the measured pK values are in the order of ±0·2 pH unit; it can be seen from Tables 1, 2 and 4 that for dyes **1–5**, the nature and concentration of the organic solvents in the aqueous solutions do not have any significant influence on the pK values. For other dyes, however, the pK values tend to increase with increase in the concentration of the organic solvent. The pK values in water for the water-soluble dyes are lower than those in organic solvent solutions. The nature of the solvent has some influence, e.g., the pK values in acetone solutions are slightly higher than those in DMSO, ethanol and dioxane solutions for some of the dyes, especially dyes **9**, **15** and **20**. This may be related to the effect of the solvents on the strength of the hydrogen bond.

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