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Hydrazone-Azo Tautomerism of Pyridone Azo Dyes: Part 1—NMR Spectra of Tautomers

Qinji Peng, Mujie Li, Kunyu Gao & Lubai Cheng

School of Chemical Engineering, Dalian University of Technology,
Dalian 116012, People's Republic of China

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ABSTRACT

The ^{1}H and ^{13}C NMR spectra of 21 pyridone azo dyes in deuterated chloroform and deuterated dimethylsulfoxide were examined. The tautomerism between the hydrazone and azo forms of the dyes was observed when a small amount of piperine or anhydrous sodium carbonate was added to the solutions. The presence of the two tautomers is confirmed both by ^{1}H and ^{13}C NMR spectra.

1 INTRODUCTION

The physical properties of azo dyestuffs are closely related to their tautomerism. Several investigations on substituted aryl-azonaphthols have been carried out and reviewed.[1-6] It has been concluded that the equilibrium between the two tautomers is influenced by the structure of the compounds, the solvents used and by other factors. Few studies on the tautomerism of pyridone azo dyes have been published. Cheng *et al.*[7] and Cee *et al.*[8] reported the structures of some pyridone azo dyes and pointed out that the hydrazone form existed in the crystal form of the dyes or in dye solutions in chloroform.

In this paper, 21 pyridone azo dyes have been prepared and studied using ^{1}H NMR and, for some dyes ^{13}C NMR. It is shown that there is hydrazone–azo tautomerism in these dyes.

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2 EXPERIMENTAL

2-Alkylthio-5-amino-1,3,4- and 3-alkylthio-5-amino-1,2,4-thiadiazole were synthesized and purified according to methods described in the literature.[9-13] The diazonium salts were coupled with 1,4-dimethyl-3-cyano-6-pyridone and 1,4-dimethyl-3-carbamoyl-6-pyridone; commercial products obtained from the Shanghai Dye Company. The dyes were purified by recrystallization from organic solvents. The water soluble dyes were purified by salting out. Purity of the dyes was confirmed by elemental analysis and TLC.

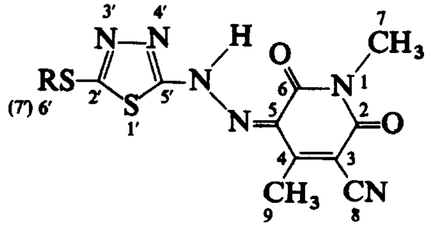
The NMR spectra were recorded on a JEOL FX-90Q spectrometer. ^1H NMR spectra were measured at 25–60°C in $CDCl_3$ and at 45–90°C in DMSO–d_6. Molar concentrations used were 0·03–0·40 M; observed frequency was 89·55 MHz; spectrum width 1800 Hz; data points 8 K; flip angle 60°; and the pulse repeated time 10 s.

The ^{13}C NMR spectra were determined at 45–90°C using a molar concentration 0·12–0·40 M. (Observed frequency 22·49 MHz; spectrum width 5000 Hz; data points 8K; double precision; proton noise decoupling mode; flip angle 60°; pulse repetition time 7 s; number of pulses 1500–5000.) SELINEPT was used to confirm the assignment of the carbon atom peaks.[14] TMS was used as an internal reference for both ^1H and ^{13}C NMR spectra.

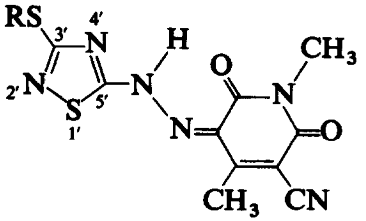
3 RESULTS AND DISCUSSION

3.1 ^1H NMR spectra

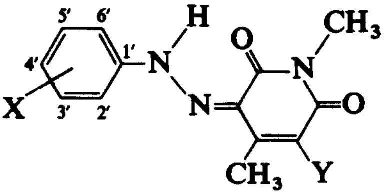
The structures and ring numbering of the atoms within the molecules of dye investigated were as follows.



1 ($R = CH_3$)
2 ($R = C_2H_5$)



3 ($R = CH_3$)
4 ($R = C_2H_5$)



5–21
($X = H, SO_3K, COOK, NO_2, CL, OCH_3, CH_3$)
($Y = CN, CONH_2$)

Dyes **1–4**, in which diazonium salts of substituted thiadiazoles were used as diazo components, showed properties somewhat different to those of dyes **5–21** in which substituted diazotized anilines were used as diazo components. The chemical shifts of the protons for dyes **1–4** are given in Table 1. The spectra of dyes **2** and **4**, as typical examples, are shown in Fig. 1. The peak of the imino group can clearly be seen in $CDCl_3$. When the temperature was raised from 25 to 60°C, the peak shifted to higher field by ~0·05 ppm, this is accompanied by an increase of the half band width ($W_{1/2}$). Values for $W_{1/2}$ at 25 and 60°C were 13·0, 39·6, 12·3, 18·5; 5·3, 7·0 and 4·4, 6·6 Hz for dyes **1** to **4** respectively.

The peak of the imino group of dyes **1–4** cannot be observed in DMSO-d_6. One possible explanation is that a trace amount of the ionic hydrazone

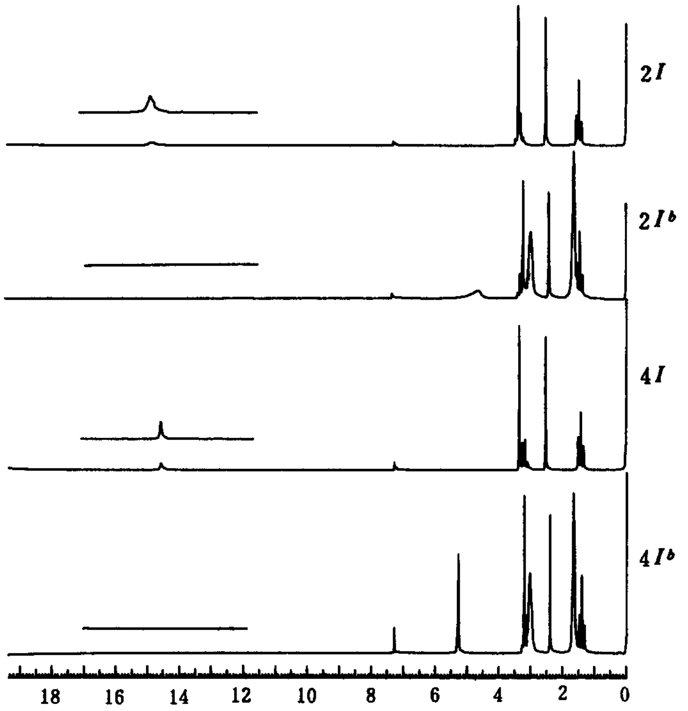


Fig. 1. The ^1H NMR spectra for dyes **2** and **4** (at 45°C). Dyes 2I, 4I in $CDCl_3$; 2Iᵇ, 4Iᵇ–20 μl piperidine was added to 0·5 ml $CDCl_3$.

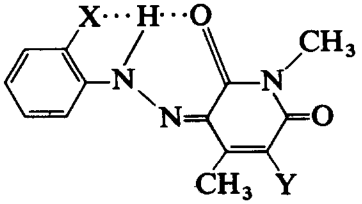
TABLE 1
Chemical Shifts of the Protons for Dyes 1–4[a]

Dyes	*Solvents*[b]	*Chemical shifts (ppm)*					$W_{1/2}$ *(Hz)*
		7	*9*	*6′*	*7′*	*NH*	
1	I	3·36	2·52	2·81	—	14·90	21·1
	I^b	3·22	2·42	2·73	—	—	—
	II	3·18	2·41	2·76	—	—	—
	II^b	3·14	2·40	2·72	—	—	—
2	I	3·36	2·51	3·36	1·48	14·88	18·0
	I^b	3·21	2·41	3·22	1·45	—	—
	II	3·19	2·41	3·22	1·38	—	—
	II^b	3·15	2·40	3·18	1·35	—	—
3	I	3·37	2·54	2·66	—	14·58	6·0
	I^b	3·26	2·52	2·64	—	—	—
	II	3·19	2·42	2·62	—	—	—
	II^b	3·15	2·41	2·58	—	—	—
4	I	3·36	2·53	3·22	1·44	14·58	5·6
	I^b	3·21	2·41	3·17	1·41	—	—
	II	3·19	2·42	3·19	1·36	—	—
	II^b	3·15	2·42	3·16	1·34	—	—

[a] Dye 4 in II and II^b was measured at 60°C, all others at 45°C.
[b] Solvent I is $CDCl_3$, II is DMSO-d$_6$. I^b, II^b–20 μl piperidine was added to 0·5 ml sample solutions.

(structure 2 of Scheme 2, discussed later) catalyzes the exchange rate of NH in the hydrazone form and makes the labile NH peak too wide to be observed.[3]

The peak for the imino group for dyes **5–21** in DMSO-d$_6$ can, however, be observed and perhaps the strength of the NH group in this series of compounds is stronger than that in dyes **1–4**. The chemical shifts of the imino group for dyes **5–21** are given in Table 2. They are within the range 14·3–16·1 ppm. It is interesting to note that when 2′-substituents can form an intramolecular hydrogen bond with the hydrogen atom of the imino group (Scheme 1), the chemical shifts of NH are always larger than those of the imino group of the corresponding 4′- (or 3′-) substituted compounds,



Scheme 1

TABLE 2
Chemical Shifts of the Imino Group for Dyes **5–21**[a]

Dyes	*X*	*Y*	*Temperature (°C)*	δ_{NH} *(ppm)*
5	4'-NO_2	CN	60	14·89
6	2'-NO_2	CN	60	15·51
7	4'-CL	CN	60	14·30
8	3'-CL	CN	60	14·30
9	2'-CL	CN	60	15·05
10	H	CN	90	14·53
11	4'-CH_3	CN	90	14·53
12	2'-CH_3	CN	90	14·94
13	4'-OCH_3	CN	90	14·74
14	2'-OCH_3	CN	90	14·89
15	4'-SO_3K	CN	90	14·55
16	2'-SO_3K	CN	90	15·23
17	4'-CO_2K	CN	90	14·44
18	2'-CO_2K	CN	90	16·09
19	2'-SO_3K, 4'-OCH_3	CN	45	15·30
20	4'-SO_3K	$CONH_2$	45	14·54
21	2'-SO_3K	$CONH_2$	45	14·83

[a] Solvent is DMSO-d_6; molar concentrations are within the range 0·03 to 0·40 M.

especially for groups which can form a strong hydrogen bond, e.g. CO_2K, SO_3K, NO_2, Cl, etc. ($\Delta\delta = 0{\cdot}6$–$1{\cdot}4$ ppm).

The colour change of the solutions (except for dye **21**) was obvious when 20 μl of an organic base (e.g. piperidine) was added to 0·5 ml sample solutions (1:25, v/v). The peak for the imino group at lower field disappeared and moved to higher field (δ 3·6–8·0) and overlapped with the NH proton peak of piperidine in both $CDCl_3$ and DMSO-d_6. A small amount of anhydrous sodium carbonate had the same effect on the tautomerism as piperidine in DMSO-d_6. This phenomenon suggests that perhaps the H atom of the imino group should transfer to a hydroxyl group. The peak of the imino group at δ 14·83 for dye **21** could still be observed after adding sufficient piperidine or Na_2CO_3.

3.2 ^{13}C NMR spectra

The ^{13}C NMR spectra were determined under the same conditions of concentration and temperature as those used for the ^1H NMR spectra. The chemical shifts of corresponding carbon atoms were nearly the same when the samples were measured in $CDCl_3$ and DMSO-d_6. The chemical shifts of the carbon atoms are listed in Table 3 for the dyes, together with two

TABLE 3
Chemical Shifts of the Carbon Atoms for the Dyes

Dye		Chemical shifts (ppm)															
		1	2	3	4	5	6	7	8	9	1′	2′	3′	4′	5′	6′	7′
1	I	—	161·1	106·1	156·9	126·4	159·2	26·7	113·2	16·3	—	163·6	—	—	166·9	16·3	—
	I[b]	—	162·6	92·6	159·3	125·8	156·2	26·3	117·3	17·1	—	163·9	—	—	184·6	16·0	—
	II	—	159·9	102·0	157·4	127·2	159·9	26·1	114·5	16·2	—	163·1	—	—	169·5	16·0	—
	II[b]	—	161·9	89·9	157·6	125·3	155·0	26·0	117·8	17·0	—	162·8	—	—	184·4	15·9	—
2	I	—	161·0	106·1	157·0	126·5	159·2	26·7	113·2	16·4	—	162·6	—	—	167·0	28·8	14·5
	I[b]	—	162·6	92·4	159·3	125·7	156·1	26·3	117·3	17·1	—	163·0	—	—	184·6	28·2	14·6
	II	—	159·7	103·2	157·4	127·2	159·7	26·2	114·4	16·2	—	161·4	—	—	169·2	28·3	14·4
	II[b]	—	162·1	90·2	158·2	125·8	155·4	26·1	118·2	17·4	—	162·4	—	—	184·6	28·3	15·0
3	II	—	159·7	105·9	157·3	128·5	159·4	26·1	113·8	16·0	—	—	169·4	—	183·4	13·9	—
	II[b]	—	161·4	92·6	157·9	125·8	154·9	25·6	116·9	16·9	—	—	169·0	—	200·1	13·8	—
4	I	—	161·0	107·4	156·8	127·5	159·0	26·4	112·9	16·4	—	—	167·9	—	182·9	26·8	14·6
	I[b]	—	162·5	94·5	159·9	126·3	156·3	26·0	116·9	17·2	—	—	168·9	—	199·6	26·3	14·6
	II	—	159·8	105·9	157·3	128·6	159·4	26·2	113·8	16·0	—	—	168·9	—	183·4	25·5	14·4
	II[b]	—	161·4	92·6	157·9	125·8	154·9	25·6	116·8	16·8	—	—	168·4	—	199·9	25·4	14·6
22	I	142·8	127·7	111·5	152·5	111·5	127·7	45·1	12·7	—	—	165·5	—	—	180·8	28·2	14·3
23	I	142·9	128·7	111·8	153·4	111·8	128·7	45·3	12·7	—	—	—	170·9	—	196·3	26·3	14·8
10	II	—	160·3	97·5	158·4	122·6	159·7	25·5	114·5	15·8	140·7	116·9	129·3	126·6	129·3	116·9	—
	II[c]	—	162·2	82·8	157·3	123·5	155·7	25·5	119·3	16·8	154·6	120·6	128·4	126·7	128·4	120·6	—
13	II	—	160·4	98·8	157·9	121·7	159·7	25·2	114·4	15·5	134·1	118·6	114·8	158·4	114·8	118·6	55·2
	II[c]	—	162·2	83·0	153·8	123·9	156·4	25·4	119·1	16·6	148·6	121·9	113·8	158·7	113·8	121·9	55·1
15	II	—	160·3	100·0	158·5	122·9	159·8	25·5	114·6	15·8	140·7	116·3	126·8	146·4	126·8	116·3	—
	II[c]	—	162·4	83·5	155·8	124·5	155·3	25·7	119·2	17·0	154·8	120·1	126·0	145·8	126·0	120·1	—
16	II	—	160·0	100·2	159·0	123·2	159·3	25·5	114·8	16·1	137·5	136·4	127·2	125·5	130·2	116·2	—
	II[c]	—	161·9	84·7	157·7	124·2	155·9	25·7	118·1	16·8	152·1	140·2	127·3	125·6	130·3	121·5	—
21	II	—	161·3	123·6	144·2	125·3	159·8	25·4	160·4	14·2	138·5	135·4	127·4	123·9	130·2	115·6	—
	II[c]	—	161·3	123·7	144·3	125·3	159·8	25·5	166·5	14·2	138·6	135·4	127·4	124·0	130·2	115·7	—

[b] 20 μl Piperdine was added to 0·5 ml solution.

[c] Anhydrous sodium carbonate was added to 0·5 ml DMSO-d_6 solution.

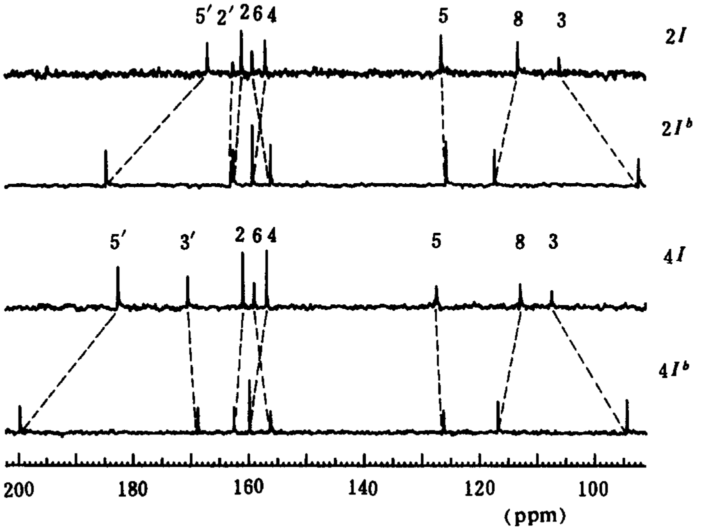
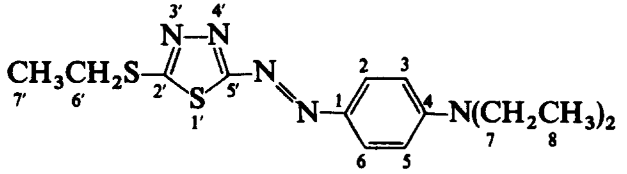


Fig. 2. The partial ^{13}C NMR spectra for dyes **2** and **4** (in $CDCl_3$, at 45°C).

derivatives used as model azo compounds. The partial ^{13}C NMR spectra for dyes **2** and **4**, before and after adding piperidine, are shown in Fig. 2. The assignment of the peaks was confirmed by the SELINEPT technique.[14] Figure 3 may be used as an example illustrating how to assign the peak for each carbon atom.

From Table 3, some remarkable chemical shift displacements merit attention.

1. When 20 μl piperidine is added, the chemical shift displacement of C5′ to lower field is 16·7–17·7 (in $CDCl_3$) and 14·9–15·4 ppm (in DMSO-d_6) for dyes **1**–**4**. The following two model compounds can exist only in the azo form



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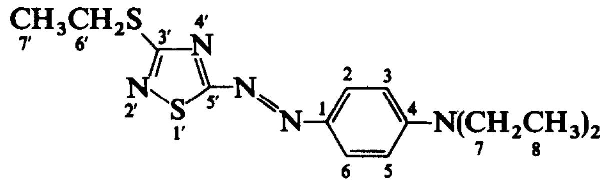


(23)

The chemical shifts of C5′ are 180·8 (for dye **22**) and 196·3 ppm (for dye **23**). The values are similar to those of samples **1**, **2** and **3**, **4** in I^b or II^b

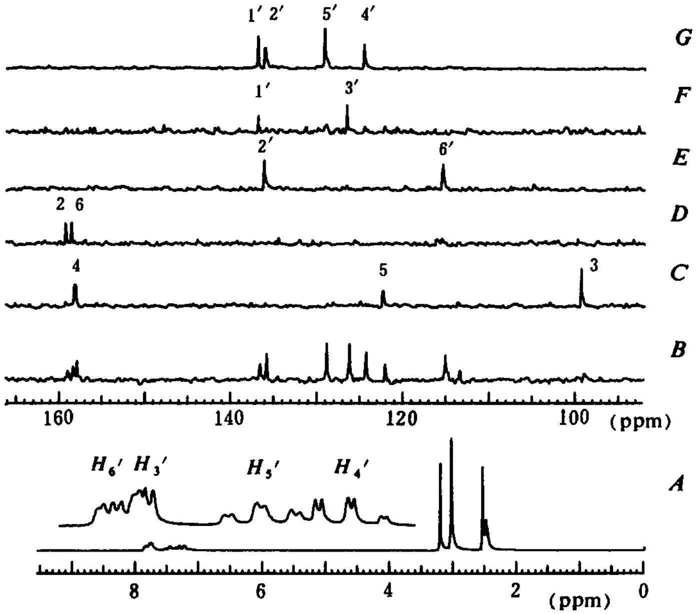


Fig. 3. SELINEPT spectra of dye **16** (in DMSO-d_6). (A) ^1H NMR spectrum (insert is expansion of aromatic hydrogen portion). (B) Proton noise decoupling ^{13}C NMR spectrum. (C)–(G) SELINEPT spectra: (C) Irr 9-CH_3, J = 6 Hz; (D) Irr 7-CH_3, J = 3 Hz; (E) Irr H4′, J = 12 Hz; (F) Irr H5′, J = 12 Hz; (G) Irr H3′, H6′, J = 9 Hz.

respectively, but at a little higher field for 3·3–3·8 ppm, as *N*,*N*-diethylamino is an electron-donating group and the keto group on the pyridone ring is electron-withdrawing.

The chemical shifts of C1′–6′ for dyes **10**, **13**, **15** and **16** in II and II^c have similar regularity. When a small amount of Na_2CO_3 is added to the DMSO-d_6 solutions, the peak of C1′ moves to lower field by 13·9–14·5 ppm, C2′, 6′ by 3·3–5·3 ppm and C3′, 4′ and 5′ are basically unchanged.

Lyčka & Hansen[5] found that the chemical shifts of the carbon atoms which are connected to azo group in the diazo component move to lower field by ~11 ppm (and C2′, 4′ for ~6 ppm) compared with the values for the hydrazone form in investigation on the ^{13}C NMR spectra of arylazonaphthols. The chemical shift displacement of C1′ for the pyridone azo dyes is even larger than that of arylazonaphthols. This suggests the existence of the azo form in I^b, II^b and II^c. At present, this observation cannot reasonably be explained, i.e. why the chemical shift displacements of C2′ and 4′ for this series of compounds are smaller than those of arylazonaphthols.

2. When the dyes are in solution in I and II (Table 1), the chemical shifts of C6 are similar to those of C2, the difference between them being within the range of 0 to 2 ppm; however, it increases to 5·8–6·9 ppm in media I^b, II^b and II^c. The peak of C2 moves to lower field by 0·9–1·9 ppm, the C6 to higher field

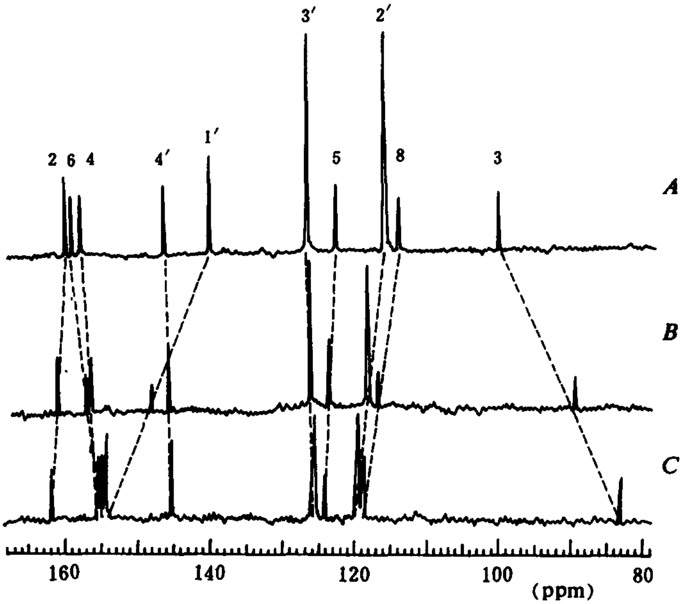


Fig. 4. The ^{13}C NMR spectra of dye **15** (at 90°C). (A) In DMSO-d_6, ~0·4 M; (B) 20 μl piperidine was added to (A); (C) Na_2CO_3 was added to (A).

by 2·7–4·9 ppm, as the functional group on C6 changes from carbonyl to hydroxyl (or hydroxyl anion) group.

3. In media I^b, II^b and II^c, the peak of C3 moves to higher field by 12·1–16·5 ppm. This may be explained by the fact that it is in the *para*-position to the hydroxyl group in the pyridone ring.

4. The above displacements of the carbon atoms are related to the strength of $[H^+]$ or $[OH^-]$ in the solutions. Dye **15** may be used as an example, as shown in Fig. 4. When the sample is in DMSO-d_6 (0·4 M), the chemical shifts of the carbon atoms on the pyridone ring are similar to those reported by Cee *et al.*[8] and, from the ^1H NMR spectra, the dye exists in the hydrazone form (Fig. 4, A). After adding piperidine, the spectrum transfers to B. If Na_2CO_3 is added to the solution, the spectrum would transfer to C. According to the above discussion, the tautomer would be azo form in C. Berrie *et al.*[3] pointed out that the chemical shifts would be the weighted mean values of two tautomers and hence the percentage of the hydrazone form in spectrum B can be calculated according to their chemical shifts. It is shown by Figs 2 and 4 that 20 μl piperidine can only convert dye **15** partly to the azo form (and similarly dyes **5–20**), but can convert dyes **1–4** completely to the azo form. For dye **21**, Na_2CO_3 cannot affect the tautomerism equilibrium.

In order to investigate the relationship between chemical shifts and pH values, a solution of dye **2** in a mixture of DMSO:water = 1:1 (v/v) (molar

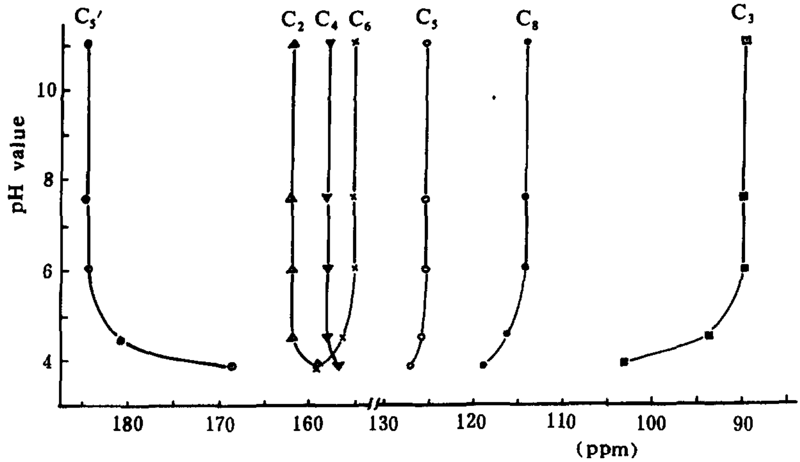
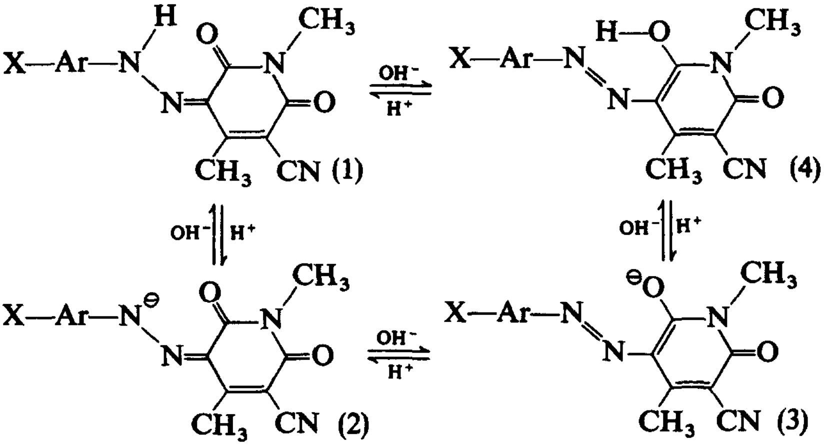


Fig. 5. The relationship between ^{13}C chemical shifts and pH values sample 2 (in the mixture of DMSO : H_2O = 1:1 (v/v) at 45°C).

concentration ~0·2 M) was prepared. As shown in Fig. 5, the chemical shifts change in the range pH 3 to 6, but basically do not change in the range pH 6 to 11. It can be assumed that, for dye **2**, complete transformation of the configuration takes place in the range pH 3 to 6.

4 CONCLUSION

In solutions in $CDCl_3$ and DMSO-d_6 (~10^{-1} M), pyridone azo dyes exist in the hydrazone form. When a small amount of piperidine or Na_2CO_3 is added to the solutions, the tautomeric equilibrium is in favour of the hydroxyazo form (Scheme 2, structure 4).



Scheme 2

In mixtures of organic solvents and water, when a base is added to the solutions, the tautomers may exist in both the hydroxyl anion and hydroxyazo forms (Scheme 2, structures 3 and 4).

The tautomeric equilibrium is related to the structure of the compounds. When the diazo component is 2-alkylthio-5-amino-1,3,4- and 3-alkylthio-5-amino-1,2,4-thiadiazole, the pyridone azo dyes are easily transferred from the hydrazone to the hydroxyazo form. The transformation of tautomers for dyes **5–20** is not as easy as that for dyes **1–4**, especially when the substituents on 2′-position of the phenyl ring can form an intramolecular hydrogen bond and the tautomer is difficult to transfer from the hydrazone to the azo form. If the cyano group on the pyridone ring is hydrolyzed to the carbamoyl group (for dye **21**), the tautomerism equilibrium is not affected by adding Na_2CO_3.

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