2. Photodecolorization of the merocyanine form of SPP is also observed together with dark decolorization.

3. The lower boundaries of the extinction coefficients of the photoinduced merocyanine forms and the upper limits of the quantum yields of photocoloration were estimated.

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^{13}C NMR SPECTRA AND AZOQUINONE HYDRAZONE TAUTOMERISM OF AZO-2-NAPHTHOLS AND AZO-1-NAPHTHOLS

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Since the discovery of azoquinone hydrazone tautomerism in hydroxyazo compounds this problem has frequently been studied [1, 2] although fewer tautomeric systems have been found than initially expected. The majority of these compounds exist in solution in the ground state chiefly in the one, thermodynamically more stable azo- or quinone hydrazone form.

Monoazo-2-naphthols (I)/(II) and monoazo-1-naphthols (III)/(IV) are convenient models for studying the general aspects of tautomerism because of the wide variation in properties with change in the structure of the diazo component [1, 2].

The tautomerism of arylazonaphthols has been widely studied using optical [3] and, starting with [4], NMR spectroscopic techniques. In the latter case, its information content has increased with the discovery of new methodology, e.g., ^{1}H and ^{14}N NMR and the NMR of ^{1}H nuclei at high magnetic field and of ^{15}N, ^{13}C, and ^{17}O [5-11].

This report concerns a ^{13}C NMR spectroscopic study of the effect of structural factors on the position of the azoquinone hydrazone tautomeric equilibria [(1) and (2)] and the data obtained is correlated in Table 1. Preliminary results have been given in [9, 10].

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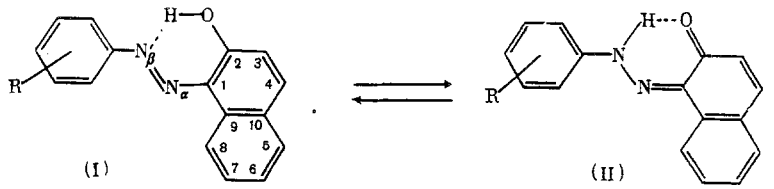
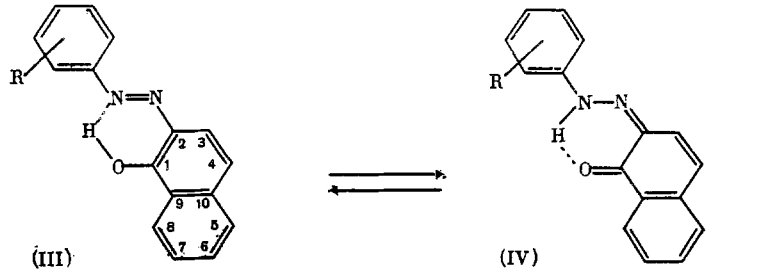


(1)



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DISCUSSION

Analysis of the ^{13}C NMR data needs to take into account certain features of the method. First, the spectra of each of the studied compounds do not show separate tautomer signals for (I) and (II) or (III) and (IV) as is the case for the keto-enol tautomers of acetylacetone derivatives. The NMR spectra of each of the tautomer pairs (I)/(II) and (III)/(IV) shows only a time-averaged picture and the tautomer composition has to be calculated from the position of this signal in the spectrum rather than by signal integration.

Second, it is important to assign uniquely the ^{13}C NMR signals for the naphthalene skeletal signals of (I)-(IV). This problem has generally been resolved for naphthalenes but for tautomeric systems like (1) and (2) some ambiguities still remain. From [5, 11] assignments for the ^{13}C NMR signals of the naphthalene skeleton in (I, II) have been made, including signals C^4 and C^5 which are important for analysis of the tautomeric composition [5, 9, 11].

Third, is the very important choice of NMR parameters appropriate to calculation of the tautomeric equilibrium. A review of the qualitative and quantitative NMR analysis of the equilibrium in 1-phenylazo-2-naphthols [5] shows that they all require a value for the measured parameter in the pure azo- and quinone hydrazone forms and that they assume the existence of a linear dependence of the parameter on the tautomer content in the equilibrium.

The ^{13}C NMR method is particularly successful in determining the tautomer ratio for (I, II) [5, 11] because the carbon chemical shifts are virtually independent of the change in magnetic anisotropy of the naphthalene ring and arise from the effect of the substituent or the medium in process (1) (in the case of ^1H NMR ignoring this effect may not be justified). In our work we have used this method to specify ^{13}C NMR signals [7, 8] (Table 1) in agreement with [5, 11]. The ^{14}N chemical shifts were also suitable after refinement of reference data [12].

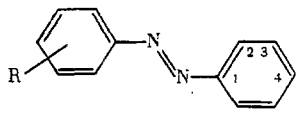
The greatest changes in naphthalene carbon ring shielding when varying the electronic properties of the R substituent were observed for C^2 and $C^{1,3-6}$ (see Table 1). The overall range of this change was: C^2 ~ 22, C^4 ~ 8, C^3 ~ 5, and C^6 and C^1 ~ 3 ppm. While there was less data for (III, IV) (not all the signals being conclusively assigned) the overall picture was similar with the greatest change being observed for the C^1 nucleus.

There may be at least two sources of the observed spectral changes, viz. a direct effect of the RC_6H_4 group on the distribution of electron density in the naphthalene ring (with retention of the overall compound structure, for example, the azo structure) and an indirect effect of this group on a shift of the tautomeric equilibria (1) and (2). ^{13}C NMR data permit measurement of the magnitude of the direct substituent effect on the shielding of C^4 and C^2 in the tautomers (I) and (II) through an analysis of the isostructural series of compounds like (V) and (VI) in which tautomerism is known to be absent. For azo compound (V) the overall change in C^4 shielding does not exceed 2 ppm and 1-1.5 ppm for C^2 [13]. The same result is associated with the naphthalene compounds (VI) [14].

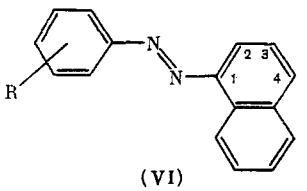
TABLE 1. ^{13}C NMR Chemical Shifts in the Naphthalene Fragment of (I)-(IV) (Solvent $CDCl_3$)

Compound	R	$\delta^{13}C$, ppm, from TMS									
		C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}
(I), (II)	*p*-NH_2	120,2	157,7	121,3	135,0	128,0	124,3	127,6	121,5	133,0	128,6
	p-CH_3O *	129,6	160,8	122,1	136,7	128,2	124,8	128,3	121,6	133,4	128,2
	p-F *	129,9	165,9	123,2	138,6	128,5	125,3	128,6	121,7	133,4	128,2
	p-*n*-C_4H_9	129,6	167,9	123,7	138,4	128,3	125,0	128,2	121,4	133,3	127,8
	p-CH_3 *	129,9	167,9	123,9	138,6	128,6	125,3	128,5	121,7	133,6	128,1
	p-Cl *	130,3	170,1	124,3	139,9	128,9	125,8	128,7	121,8	133,2	128,3
	H	129,9	171,5	124,6	139,8	128,6	125,5	128,4	121,6	133,4	127,9
	m-CH_3	129,9	171,6	124,7	139,7	128,7 †	125,5	128,5 †	121,6	133,5	127,9
	m-Cl	130,4	172,8	124,7	140,7	129,0 †	126,0	128,6 †	121,8	133,2	128,1
	m-NO_2	131,0	174,3	124,9	141,8	129,4 †	126,7	128,8 †	122,1	133,1	128,4
	p-C_6H_5-N=N *	130,8	175,5	125,4	141,4	128,7	126,3	129,1	121,9	133,3	128,2
	p-COOH ‡	130,2	175,6	125,4	142,1	129,5	126,8	129,2	121,7	132,7	128,1
	p-CN *	131,6	178,9	126,1	143,0	129,6	127,3	129,1	122,3	133,2	128,6
	p-CH_3SO_2	131,6	179,0	126,1	142,9	129,6	127,2	129,2	122,3	133,1	128,5
	p-NO_2	131,9	180,0	126,3	143,4	129,7	127,5	129,1	122,4	133,0	128,5
(III), (IV)	*p*-CH_3	170,9	132,4	128,2	120,3	127,4	131,5	125,9	126,3	129,7	137,4
	H	173,8	132,7	128,2	120,9	127,5	132,1	126,6	126,1	130,1	137,0
	p-NO_2	180,0	134,7	127,9 †	120,5	127,6	133,9	127,1 †	124,3	130,7	137,1

*^{13}C NMR data from [5, 7, 8] used with cross-reference of individual signals.
†Signals may be interchanged.
‡Solvent DMSO.



(V)



(VI)

The observed range of the effect of substituent R on the shielding of the ^{13}C naphthalene nuclei in the tautomeric systems (1) and (2) is much greater than that of a pure electronic effect. Thus, the ^{13}C shielding changes observed experimentally in the naphthalene fragment of azo compounds (I), (II) and (III), (IV) are due mainly to the R substituent effect on the azoquinone hydrazone equilibrium. All of the C^{1-4} nuclei of one naphthalene ring and $C^{5,6}$ of the other show a shift to low field with a change in the equilibria of (1) and (2) toward the quinone hydrazone tautomer. Evidently, this has a common derivation and is caused by dearomatization of one of the naphthalene ring systems with a change in the tautomeric equilibria of (1) and (2) to the right.

The $C^{2-4,6}$ nuclei in (I), (II) can be treated as examples and changes in their chemical shifts used for qualitative and quantitative calculation of the equlibrium position for (1) [5, 9]. The C^4 and C^6 nuclei are sufficiently far from the source of the perturbation and are most suitable (although the range of change of chemical shifts is not as great as for C^2). Nucleus C^1 can be used as the model nucleus for the change in equilibrium of (2).

The substituent effect for the equilibria (1) and (2) is such that an electron donating R shifts it to the side of the azo form (I) or (III) and an electron acceptor substituent has the opposite effect (Table 2). This result is in agreement with previous correlations for azo compounds [2].

The quinone hydrazone form (II) content depends on the p-substituent and increases in the series

$$\begin{gathered} NH_2 < CH_3O < F \leqslant n\text{-Alk} \leqslant Cl < H < C_6H_5{-}N{=}N, \\ COOH < CH_3SO_2, CN < NO_2 \end{gathered} \qquad (3)$$

Considering the variation in the shielding of C^1 in Table 1 the effect of the p-substituent in the tautomeric system (2) is similar.

$$CH_3 < H < NO_2 \qquad (4)$$

However, the range of change of C^1 chemical shifts is slightly less in (4) (~9 ppm) than in system (1) (~12 ppm).

For m-substituents, with only an inductive effect, the substituent effect in the tautomer system (1) was similar to series (3) with $CH_3 < Cl < NO_2$. As expected, the change in chemical shift for an individual carbon nucleus in the latter case was strongly attenuated.

	$\Delta\delta$, C^n, ppm	
C^n	p-CH_3 → p-NO_2	m-CH_3 → m-NO_2
C^2	12.1	2.7
C^3	2.4	0.2
C^4	4.8	2.1
C^6	2.2	1.2

It is known that the powerfully electron accepting p-NO_2 group can shift the equilibrium (1) completely to the right [3, 5, 9] and the electron donor NH_2 group almost completely to the left [3]. In the ^{13}C NMR spectrum the same shielding of the C^2-C^4 signals is observed as for the compound with an o-OH substituent which shifts (1) almost fully to the left [9]. A somewhat smaller substituent effect is seen for the compound with p-CH_3O in [7].

Thus, having determined the limits of the structural effect on the position of (1) and with the use of method [9] it is possible to use the ^{13}C shielding data to determine the tautomer composition of the investigated compounds with satisfactory accuracy. The values derived from the C^2 and C^4 atoms are given in Table 2.

TABLE 2. ^{13}C, ^{14}N, and ^{1}H NMR Derived Data for the Tautomer Content of (I) and (II) (%) and Tautomer Equilibrium Constant K_T = [II]/[I] for Process (1)

R	σ	^{13}C NMR						^{14}N NMR						^{1}H NMR [15]		
		C^2			C^4			according to [12]			refined data*					
		(I)	(II)	K_T	(I)	(II)	K_T	(I)	(II)	K_T	(I)	(II)	K_T	(I)	(II)	K_T
p-NH_2	0,66	100	0	0	100	0	0							74	26	0,35
p-CH_3O	0,268	86	14	0,2	80	20	0,25	48	52	1,1	93	7	0,1	64	36	0,55
p-F	0,062	63	37	0,6	57	43	0,75							48	52	1,09
p-C_4H_9-*n*	0,161	54	46	0,85	59	41	0,7									
p-CH_3	0,170	54	46	0,85	57	43	0,75	31	69	2,2	61	39	0,6	44	56	1,26
p-Cl	0,227	44	56	1,3	42	58	1,4	22	78	3,5	44	56	1,3	32	68	2,11
H	0	38	62	1,6	43	57	1,3	21	79	3,8	42	58	2,4	33	67	2,00
m-CH_3	−0,069	38	62	1,6	44	56	1,3	20	80	4	39	61	1,6	35	65	1,85
m-Cl	0,373	32	68	2,1	32	68	2,1	9	91	10	37	63	1,7	24	76	3,18
m-NO_2	0,710	26	74	2,9	19	81	4,3							20	80	3,94
p-C_6H_5−N=N	0,64	20	80	4	24	76	3,2									
p-COOH	0,265	20	80	4	15	85	5,7									
p-CN	0,66	5	95	19	5	95	19	3	97	32	6	94	16	3		28
p-CH_3SO_2	0,728	4	96	24	6	94	16									
p-NO_2	0,778	0	100	–	0	100	–									

*Recalculated with the other reference position for the pure azo form of (I).

There are various possible methods for determining the tautomer equilibrium constant K_T = [II]/[I]. The difficulty of quantitative calculation by IR and UV spectroscopy has already been repeatedly described [7, 12]. NMR chemical shifts have been used successfully for this calculation with the correct choice of reference points. Values of K_T obtained from the chemical shifts of C^2 and C^4 are given in Table 2 and it is apparent that they are in very satisfactory agreement. However, the values of K_T obtained by ^{13}C and ^{14}N NMR [12] are different. These differences have a common origin: In [12] a value for the ^{14}N chemical shift for the pure azo form (I) of −129 ppm was used instead of +20 ppm. A linear connection between the ^{14}N and $^{13}C^2$ chemical shifts [5] permits a more rigorous determination of $\delta^{14}N$ for the pure azo form (I) and recalculation of K_T from [12] which then proved to be in good agreement with the ^{13}C NMR data (Table 2).

As already mentioned the observed ^{13}C chemical shift changes reflect the two effects of redistribution of electron density and change in tautomeric equilibrium (1). It has been found that the chemical shifts are linearly correlated with substituent σ-constants according to the equations

$$\delta C^2 = 13.56\sigma + 168.5;\ r = 0.91$$
$$\delta C^3 = 2.92\sigma + 123.8;\ r = 0.89$$
$$\delta C^4 = 5.21\sigma + 139.1;\ r = 0.94$$
$$\delta C^5 = 1.24\sigma + 128.6;\ r = 0.90$$
$$\delta C^6 = 2.10\sigma + 125.5;\ r = 0.94$$
$$\delta C^1 = 1.76\sigma + 130.0;\ r = 0.94$$

Hence the chemical shift changes in compounds (I), (II) prove to be fully acceptable criteria for the quantitative analysis of the tautomeric equilibrium (1).

EXPERIMENTAL

^{13}C NMR and ^{13}C-{^1H} NMR spectra were recorded for 1000-2500 accumulations on a Bruker AC-250 Fourier spectrometer. The pulse delay was 0.6 sec, the concentration 0.05-0.1 M, and the temperature ~30°C. Chemical shifts were measured from the solvent signal and recalculated to TMS with an accuracy of 0.01 ppm.

The authors thank M. V. Gorelika for submitting samples for investigation and for an interesting discussion.

CONCLUSIONS

The ^{13}C NMR spectra of 1-phenylazo-2-naphthols and 2-phenylazo-1-naphthols have been investigated. For both classes the azoquinone hydrazone tautomeric equilibrium is shifted as a result of the nature of the substituent in the benzene ring and a qualitative series of effects has been established. A quantitative measurement of the tautomer composition has been obtained for the arylazo-2-naphthols.

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