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^{13}C and ^{15}N-NMR Studies of the Azo–Hydrazone Tautomerism of Some Azo Dyes

Antonín Lyčka

Research Institute of Organic Syntheses,
532 18 Pardubice-Rybitví, Czechoslovakia

and

Vladimír Macháček

Department of Organic Chemistry, Institute of Chemical Technology,
532 10 Pardubice, Czechoslovakia

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SUMMARY

The ^{13}C and ^{15}N-NMR spectra of compounds prepared by coupling benzenediazonium ions with 9-hydroxyanthracene, acetylcyclopentadiene, 8-hydroxyquinoline, 3-cyano-1,4-dimethylpyridine-2,6-dione and 1-naphthol have been measured. Using $\delta(^{13}C)$, $\delta(^{15}N)$, $^{1}J(^{15}NH)$ and $^{1}J(^{15}N^{15}N)$ it has been found that the products exist, in deuteriochloroform or in hexadeuteriodimethyl sulfoxide solutions, as 9,10-anthraquinone 9-phenylhydrazone (**I**), *2-acetyl-2,4-cyclopentadienone 1-phenylhydrazone* (**II**), *5-phenylazo-8-hydroxyquinoline* (**III**), *3-cyano-1,4-dimethylpyridine-2,5,6-trione 5-phenylhydrazone* (**IV**) *and 4-phenylazo-1-naphthol* (**V**). *The compounds* **VI** *and* **VII** *have been found to be equilibrium mixtures of the azo and hydrazone tautomers, with prevailing 1,2-naphthoquinone 2-phenylhydrazone* (**VI**) *and 4-phenylazo-1,2-naphthoquinone 2-phenylhydrazone* (**VII**) *configurations.*

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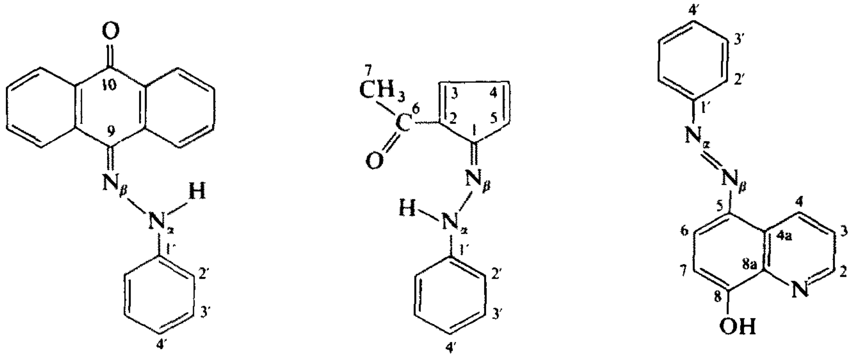
1. INTRODUCTION

Nuclear magnetic resonance spectroscopy is a useful technique for the analysis of azo–hydrazone equilibria. NMR has been applied to the study of these types of equilibria for dyes such as arylazo derivatives derived from hydroxyarenes, pyrazolones, 1,3-dicarbonyls and heterocycles. Papers dealing with such measurements have been reviewed by Kelemen.[1] Several papers have been published recently utilizing ^{13}C-[1-12] and/or ^{15}N-NMR[6,7,12-14] spectral characteristics for the estimation of azo–hydrazone equilibria.

The aim of this communication is the interpretation of the ^{13}C- and ^{15}N-NMR spectra of azo dyes derived from 9-hydroxyanthracene, acetylcyclopentadiene, 3-cyano-1,4-dimethylpyridine-2,6-dione and 1-naphthol with respect to azo–hydrazone tautomerism.

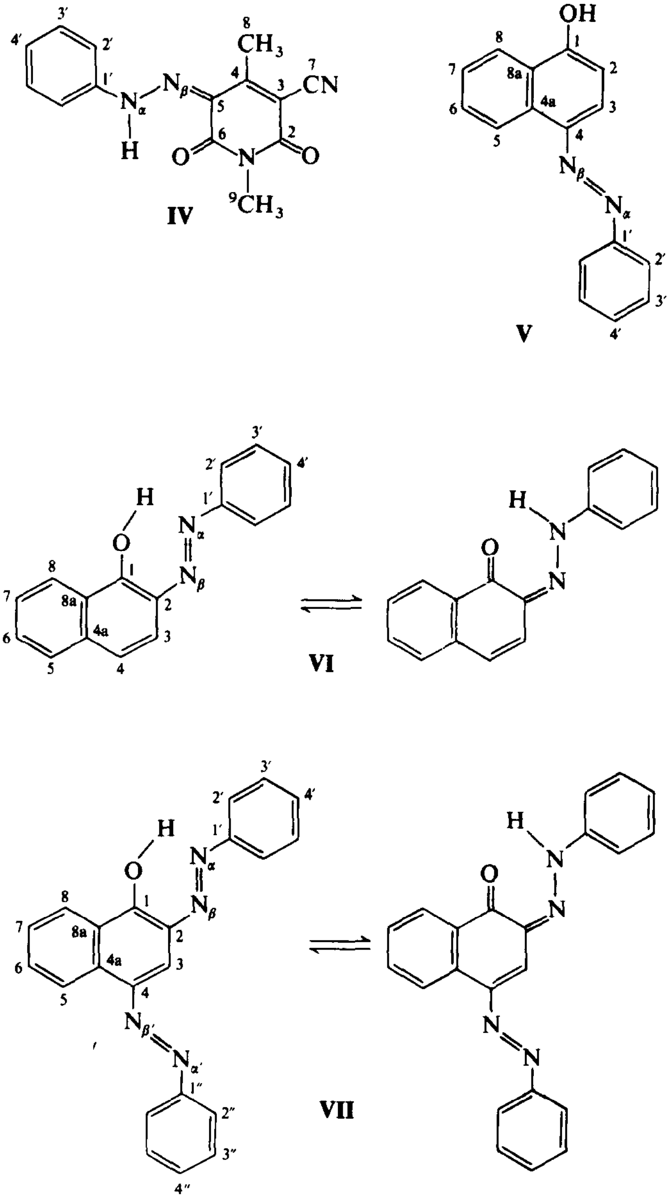
2. EXPERIMENTAL

Compounds **I**, **III**–**V**, **VII**[15] and **VI**[16] (see Scheme 1) were prepared by known methods. Compound **II** was prepared by mixing equimolar amounts of freshly prepared *ca* 10% solutions of benzenediazonium fluoroborate (1·76 g) and the sodium salt of acetylcyclopentadiene (1·4 g) in dimethyl sulfoxide. After *ca* 5 min the mixture was diluted with water and the resultant emulsion was extracted with CCl_4. The solvent was removed *in vacuo* and the residual product purified by chromatography



I **II** **III**

Scheme 1



Scheme 1 (*contd.*)

(silica gel, $CHCl_3$). Crystallization from pentane gave 0·6 g (28 %) of product, m.p. 72–73 °C (ref. 17, 72–73 °C).

^{15}N-Labelled compounds were prepared with ^{15}N-aniline (95 % ^{15}N) and $Na^{15}NO_2$ (96·2 % ^{15}N; Isocommerz, Berlin). 4-Deuterio-2-phenylazo-1-naphthol was prepared by heating 4-sulfo-2-phenylazo-1-naphthol for several hours in a mixture of 15 %(v/v) D_2SO_4 in D_2O. ^2H isotopomers of compounds **II** and **V**–**VII** were prepared using perdeuterioaniline. All compounds were purified by chromatography and their purity was checked by ^1H-NMR spectra.

The ^{13}C-, ^{15}N- and ^1H-NMR spectra were measured at 25·047, 10·095 and 99·602 MHz, respectively, using a JNM-FX 100 (JEOL) spectrometer equipped with a multinuclear tunable probe and operating in the FT mode. The spectra were recorded for *ca* 10 %(w/v) solutions or saturated solutions (for compounds of low solubility) in deuteriochloroform or hexadeuteriodimethyl sulfoxide (DMSO-d_6). The deuterated solvents were used as lock substances. The measurement conditions are given in refs 3 and 13. The ^{13}C chemical shifts were referred to the signal of $CDCl_3$ ($\delta = 77{\cdot}00$) or DMSO-d_6 ($\delta = 39{\cdot}60$). The ^{15}N chemical shifts were related to external neat nitromethane (25 % ^{15}N; $\delta = 0{\cdot}0$). Solvents and temperatures used are reported in the text and in Tables 1–7. The temperature of the cooling or heating gas was measured with a thermocouple with an accuracy of ± 1 °C.

3. RESULTS AND DISCUSSION

^{13}C chemical shifts of the carbon atoms C(2′)–C(4′) were unambiguously assigned owing to the double relative intensity of the C(2′) and C(3′) signals and the typical pattern of the signal for C(4′) in the proton-coupled spectrum. Then δ(C(1′)), depending on azo, hydrazone content, can be estimated according to ref. 3. The assignment was checked by the signal pattern of the proton-coupled spectra and by measuring $^nJ(^{15}N^{13}C)$. In ^2H isotopomers of the compounds **II** and **V**–**VII**, the signals of C(2′)–C(4′) were split into triplets and the relative intensity of the C(1′) signal decreased to *ca* one-fifth of its original value as the result of a change in the relaxation mechanism.[7] When necessary, the ^{15}N-NMR signals were distinguished by measuring the ^{15}N-NMR spectra of ^{15}N enriched compounds (N_α, 15 % ^{15}N; N_β, 96·2 % ^{15}N). Different values of the ^{15}N enrichment makes it possible to measure $\delta(^{15}N_\alpha)$; $\delta(^{15}N_\beta)$ (and to assign them unambigously); ${}^{n}J({}^{15}NH)$, and ${}^{1}J({}^{15}N{}^{15}N)$ and ${}^{n}J({}^{15}N_{\beta}{}^{13}C)$, all in one sample.

9,10-Anthraquinone 9-phenylhydrazone (I)

The ${}^{13}C$ chemical shifts and the coupling constants ${}^{n}J({}^{15}N{}^{13}C)$ in the compound **I** at 300 K are given in Table 1. We observed 18 signals in the ${}^{13}C$-NMR spectrum of the compound **I** in $CDCl_3$ at 300 K. The carbon atoms C(1), C(8); C(2), C(7); etc. are anisochronous due to the hindered rotation around the $C(9) = N_{\beta}$ bond. In DMSO-d_6 the coalescence temperature is about 400 K. The following ${}^{15}N$-NMR characteristics were observed: $\delta({}^{15}N_{\alpha}) = -232{\cdot}8$; $\delta({}^{15}N_{\beta}) = -51{\cdot}4$; ${}^{1}J({}^{15}N{}^{15}N) = (11{\cdot}6 \pm 0{\cdot}3)$ Hz; ${}^{1}J({}^{15}NH) = (89{\cdot}8 \pm 0{\cdot}2)$ Hz (both at 300 and 330 K) and ${}^{2}J({}^{15}NH) = (2{\cdot}20 \pm 0{\cdot}3)$ Hz.

TABLE 1

${}^{13}C$ Chemical Shifts and Coupling Constants ${}^{n}J({}^{15}N_{\alpha}{}^{13}C)$ and ${}^{n}J({}^{15}N_{\beta}{}^{13}C)$ of Compound **I** in Deuteriochloroform at 300 K

Carbon[a]	$\delta({}^{13}C)$	${}^{n}J({}^{15}N_{\alpha}{}^{13}C)$ *(Hz)*	${}^{n}J({}^{15}N_{\beta}{}^{13}C)$ *(Hz)*
1′	144·18	18·6	6·1
2′	114·31	1·8	2·2
3′	129·32	2·0	<0·8
4′	122·07	<0·8	<0·8
9	138·64	2·9	9·5
10	183·40	<0·8	<0·8

[a] The other carbon atoms (see text): 132·87; 132·67; 132·40; 131·43; 129·95; 129·79; 129·01; 128·62; 127·53; 126·32; 125·23; 124·06.

2-Acetyl-2,4-cyclopentadiene 1-phenylhydrazone (II)

The ${}^{13}C$ chemical shifts and the coupling constants ${}^{1}J({}^{13}CH)$ and ${}^{n}J({}^{15}N_{\beta}{}^{13}C)$ in the compound **II** in $CDCl_3$ at 300 K are given in Table 2. The carbon atoms C(1) and C(2) and C(3)–C(5) were assigned on the basis of the ${}^{n}J({}^{15}N_{\beta}{}^{13}C)$ coupling constant values.[3,12,18] The application of selective decoupling enabled us to assign $\delta({}^{1}H)$ of proton signals corresponding to C(3)–C(5) and the same assignment of the proton chemical shifts of these signals described in ref. 19 was achieved. The ${}^{15}N$ chemical shifts ($\delta({}^{15}N_{\alpha}) = -185{\cdot}6$ ($-185{\cdot}5$ at 330 K); $\delta({}^{15}N_{\beta}) = -14{\cdot}1$) and the coupling constant ${}^{1}J({}^{15}NH) = (89{\cdot}6 \pm 0{\cdot}2)$ Hz were measured.

TABLE 2

^{13}C Chemical Shifts and Coupling Constants $^{1}J(^{13}CH)$ and $^{n}J(^{15}N_{\beta}{}^{13}C)$ in Compound **II** in Deuteriochloroform at 300 K

Carbon	$\delta(^{13}C)$	$^{1}J(^{13}CH)$ (Hz)	$^{n}J(^{15}N_{\beta}{}^{13}C)$ (Hz)
1′	142·06	0	5·7
2′	115·94	160·6	2·1
3′	129·09	160·6	<0·8
4′	124·47	161·0	<0·8
1	143·03	0	3·8
2	123·19	0	<0·8
3[a]	144·79	164·8	2·0
4[b]	124·37	170·9	3·3
5[c]	134·74	172·1	11·8
6	192·59	0	<0·8
7	26·18	127·4	<0·8

[a] $\delta(C_3\underline{H}) = 7{\cdot}61$; [b] $\delta(C_4\underline{H}) = 6{\cdot}42$; [c] $\delta(C_5\underline{H}) = 6{\cdot}92$; according to the results of selective decoupling.

5-Phenylazo-8-hydroxyquinoline (III)

The ^{13}C chemical shifts and the coupling constants $^{1}J(^{13}CH)$ and $^{n}J(^{15}N_{\beta}{}^{13}C)$ in compound **III** in DMSO-d_6 at 340 K are given in Table 3. The ^{13}C chemical shifts of the heterocyclic part of the molecule were assigned by application of the ^{13}C chemical shifts in 8-hydroxyquinoline[20] and by selective decoupling ($\delta(C(2)\underline{H}) = 9{\cdot}02$; $\delta(C(4)\underline{H}) = 9{\cdot}33$; $\delta(C(7)\underline{H}) = 7{\cdot}28$). The ^{13}C substituent chemical shifts caused by the phenylazo group (defined as the difference of the ^{13}C chemical shifts in the compound **III** and those in 8-hydroxyquinoline[20]) were determined and they are given in Table 8. The ^{15}N chemical shifts $\delta(^{15}N_{\alpha}) = 110{\cdot}2$; $\delta(^{15}N_{\beta}) = 116{\cdot}8$ and the coupling constant $^{1}J(^{15}N^{15}N) = (15{\cdot}4 \pm 0{\cdot}3)$ Hz were measured.

3-Cyano-1,4-dimethylpyridine-2,5,6-trione 5-phenylhydrazone (IV)

The ^{13}C chemical shifts and the coupling constants $^{1}J(^{13}CH)$ and $^{n}J(^{15}N_{\beta}{}^{13}C)$ in compound **IV** in $CDCl_3$ at 330 K are given in Table 4. The ^{13}C chemical shifts of the carbon atoms C(3) and C(4) were assigned on the basis of the stereospecific behaviour of the coupling constants ^{2}J and

TABLE 3
^{13}C Chemical Shifts and Coupling Constants $^{1}J(^{13}CH)$ and $^{n}J(^{15}N_{\beta}{}^{13}C)$ in Compound **III** in Hexadeuteriodimethyl Sulfoxide at 340 K

Carbon	$\delta(^{13}C)$	$^{1}J(^{13}CH)$ (*Hz*)	$^{n}J(^{15}N_{\beta}{}^{13}C)$ (*Hz*)
1′	152·57	0	5·1
2′	122·26	162·4	4·3
3′	129·23	162·0	<0·8
4′	130·49	161·1	<0·8
2	148·87	180·7	<0·8
3	123·08	166·0	<0·8
4	131·71	167·2	3·4
5	138·22	0	1·6
6	115·19	163·5	<0·8
7	111·44	163·6	<0·8
8	157·30	0	<0·8
4a	127·23	0	6·9
8a	137·90	0	2·6

TABLE 4
^{13}C Chemical Shifts and Coupling Constants $^{1}J(^{13}CH)$ and $^{n}J(^{15}N_{\beta}{}^{13}C)$ of Compound **IV** in Deuteriochloroform at 330 K

Carbon	$\delta(^{13}C)$	$^{1}J(^{13}CH)$ (*Hz*)	$^{n}J(^{15}N_{\beta}{}^{13}C)$ (*Hz*)
1′	140·62	0	6·1
2′	117·06	160·7	2·5
3′	129·92	161·6	<0·8
4′	127·54	160·7	<0·8
2	[a]	0	<0·8
3	101·51	0	3·8
4	158·53	0	10·2
5	122·76	0	4·5
6	[a]	0	<0·8
7	26·27	142·4	<0·8
8	114·33	0	<0·8
9	16·53	130·6	<0·8

[a] 161·75 or 160·13.

${}^3J({}^{15}N{}^{13}C)$.[3,12,18] The following ${}^{15}N$ chemical shifts and coupling constants were found: $\delta({}^{15}N_\alpha) = -189{\cdot}1$; $\delta({}^{15}N_\beta) = -0{\cdot}2$; ${}^1J({}^{15}NH) = (94{\cdot}8 \pm 0{\cdot}2)$ Hz (both at 300 and 330 K); ${}^2J({}^{15}NH) = (2{\cdot}40 \pm 0{\cdot}3)$ Hz and ${}^1J({}^{15}N{}^{15}N) = (10{\cdot}7 \pm 0{\cdot}3)$ Hz.

4-Phenylazo-1-naphthol (V)

The ${}^{13}C$ chemical shifts in compound **V** in DMSO-d_6 at 300 K are reported in Table 5. Compound **V** gives broadened signals in the ${}^{13}C$-NMR spectrum, independent of the type of preparation (by normal coupling methods or by condensation of phenylhydrazine and 1,4-naphthoquinone), temperature (from 300 to 370 K) and addition of trace of acid. Some derivatives of compound **V** substituted in the position 5 (5-Br; 5-OH)[21] showed the same behaviour. The carbon atoms C(2) and C(5) were assigned by selective decoupling ($\delta(C(2)\underline{H}) = 7{\cdot}05$; $\delta(C(5)\underline{H}) = 8{\cdot}88$). The other ${}^{13}C$ chemical shifts of the naphthalene ring were assigned by means of ${}^{13}C$ substituent chemical shifts caused by the phenylazo

TABLE 5

${}^{13}C$ Chemical Shifts (and Coupling Constants ${}^nJ({}^{15}N_\beta{}^{13}C)$) of Compounds **V** (in Hexadeuteriodimethyl Sulfoxide), **VI** and **VII** (in Deuteriochloroform) at 300 K

Carbon	$\delta({}^{13}C)$ *in* **V**	$\delta({}^{13}C)({}^nJ({}^{15}N_\beta{}^{13}C)$ *(Hz))* *in* **VI**	$\delta({}^{13}C)$ *in* **VII**[a]
1′	152·81	143·23 (5·9)	143·09
2′	122·60	117·55 (2·6)	118·08
3′	129·50	129·48 (<0·8)	129·64
4′	129·50	126·70 (<0·8)	127·59
1	157·83	174·18 (<0·8)	174·47
2	108·46	132·76 (2·0)	[b]
3	113·92	128·27 (10·5)	114·04
4	139·61	120·96 (5·0)	141·81
5	122·60	127·54 (<0·8)	123·93
6	127·91	132·22 (<0·8)	132·51
7	125·57	126·18 (<0·8)	126·80
8	122·60	126·70 (<0·8)	126·80
4a	132·78	137·08 (<0·8)	135·39
8a	124·50	130·22 (<0·8)	[b]

[a] δ(C1″) = 153·08; δ(C2″) = 123·06; δ(C3″) = 129·10; δ(C4″) = 130·81.

[b] 131·93 or 130·12.

group (Table 8). The assignment of the ^{13}C chemical shifts of C(1′)–C(4′) was proved by measuring ^{13}C-NMR spectra of the deuterated analogue of compound **V** prepared by coupling of pentadeuteriobenzenediazonium chloride (see above). The ^{15}N chemical shifts $\delta(^{15}N_\alpha) = 108{\cdot}0$; $\delta(^{15}N_\beta) = 119{\cdot}4$, and the coupling constant $^{1}J(^{15}N^{15}N) = (15{\cdot}3 \pm 0{\cdot}3)$ Hz were measured.

2-Phenylazo-1-naphthol (VI)

The ^{13}C chemical shifts and the coupling constants $^{n}J(^{15}N_\beta{}^{13}C)$ in compound **VI** in $CDCl_3$ at 300 K are given in Table 5. The carbon atom C(1) absorbs at the lowest field. The carbon atoms C(4) and C(8) were assigned after selective decoupling ($\delta(C(4)\underline{H}) = 7{\cdot}00$; $\delta(C(8)\underline{H}) = 8{\cdot}43$). In addition, the assignment of C(4) was confirmed by measuring the ^{13}C-NMR spectra of 4-deuterio-2-phenylazo-1-naphthol. The signal corresponding to C(5) gives, in the proton-coupled spectrum, a broadened doublet of quartets because of two coupling constants over three bonds. The ^{13}C chemical shifts of C(6) and C(7) were distinguished after ^{13}C-NMR spectrum measurement of 5-bromo-2-phenylazo-1-naphthol, using substituent chemical shifts caused by bromine[22] ($\delta(C(6)) = 135{\cdot}7$; $\delta(C(7)) = 126{\cdot}5$ (doublet in the proton-coupled spectrum)). The assignment of the signals for C(2); C(4a); and C(8a) was achieved after measurements of proton-coupled spectra by selective excitation (DANTE[23]) because of overlapped signals in the standard proton-coupled spectrum. The signal at 132·76 was assigned to C(2) since it forms a broadened quartet ($J = 9{\cdot}8$ and $7{\cdot}0$ Hz) which changes into a broadened doublet both after selective deuteration in the 4-position ($^{3}J(^{13}C(2)C(4)\underline{H}) = 9{\cdot}8$ Hz) and after selective deuteration of the acidic proton (owing to the lowering of the $^{n}J(XD) = {}^{n}J(XH)/6{\cdot}5$). The signal at 137·08 corresponds to C(4a) since it gives the most complicated multiplet, the pattern of which does not change either after deuteration in the 4-position or deuteration of the acidic proton. The signal at 130·22 was then assigned to C(8a), in agreement with the fact that the multiplet in the proton-coupled spectrum narrowed in 4-deuterio-2-phenylazo-1-naphthol ($^{3}J(^{13}C(8a)C(4)\underline{H}) \sim 6$ Hz). Temperature dependence of the ^{15}N chemical shifts and the coupling constants $^{n}J(^{15}NH)$ and $^{n}J(^{15}N^{15}N)$ in the compound **VI** in $CDCl_3$ are given in Table 6. Hydrazone-form contents obtained from the ^{15}N chemical shifts were calculated using the

TABLE 6

Temperature Dependence of ^{15}N Chemical Shifts, Coupling Constants $^{1}J(^{15}N^{15}N)$ and $^{n}J(^{15}NH)$ and Hydrazone-Form Content of Compound **VI** in Deuteriochloroform

Temperature (K)	$\delta(^{15}N_\alpha)$	*Hydrazone form (%)*[a]	$\delta(^{15}N_\beta)$	*Hydrazone form (%)*[a]	$^{1}J(^{15}N^{15}N)$ *(Hz)*	$^{1}J(^{15}NH)$ *(Hz)*	*Hydrazone form (%)*[a]	$^{2}J(^{15}NH)$ *(Hz)*
330	−137·4	75·3	22·2	73·0	12·2	73·2	76·2	1·6
300	−148·1	79·2	16·3	76·7	12·0	77·3	80·5	1·7
270	−157·1	82·3	11·5	79·6	12·0	81·5	84·9	1·8
240	−169·2	87·0	4·8	84·0	11·7	85·4	89·0	1·8

[a] Calculated from the data in the preceding column (see text).

TABLE 7

Temperature Dependence of ^{15}N Chemical Shifts, Coupling Constants $^{1}J(^{15}N^{15}N)$ and $^{n}J(^{15}NH)$ and Hydrazone-Form Content of Compound **VII** in Deuteriochloroform

Temperature (K)	$\delta(^{15}N_\alpha)$	*Hydrazone form (%)*[a]	$\delta(^{15}N_\beta)$	*Hydrazone form (%)*[a]	$\delta(^{15}N'_\alpha)$	$\delta(^{15}N'_\beta)$	$^{1}J(^{15}N_\alpha{}^{15}N_\beta)$ *(Hz)*	$^{1}J(^{15}N_\alpha H)$ *(Hz)*	*Hydrazone form (%)*[a]	$^{2}J(^{15}N_\beta H)$ *(Hz)*
330	−126·0	71·2	30·7	67·1	121·6	121·6	13·4	71·3	74·2	1·7
300	−135·1	74·5	26·5	69·6	120·1	120·1	12·7	75·5	78·6	1·9
270	−143·3	77·3	21·9	72·4	[b]	[b]	11·9	79·5	82·8	2·0
240	−154·8	81·7	15·5	76·4	[c]	[c]	11·7	84·7	88·2	2·0

[a] Calculated from the data in the preceding column (see text).
[b] 119·5 or 119·0.
[c] 118·8 or 116·9.

procedure described in ref. 13. Hydrazone contents obtained by means of $^1J(^{15}NH)$ were calculated using eqn (1):[14]

$$\text{Percentage of hydrazone} = 100 \times {}^1J(^{15}\text{NH})_{\text{exp}}/{}^1J(^{15}\text{NH}) \qquad (1)$$

using $^1J(^{15}NH) = 96$ Hz.[14]

2,4-Bisphenylazo-1-naphthol (VII)

The ^{13}C chemical shifts in compound **VII** in $CDCl_3$ at 300 K are given in Table 5. By means of selective ^{15}N labelling it was chosen that the phenylazo group in the 2-position takes part in azo–hydrazone tautomerism, whilst the phenylazo group in the 4-position is a true azo group. The assignment of the ^{13}C chemical shifts of C(1′)–C(4′) and C(1″)–C(4″) was proved by the ^{13}C-NMR measurement of compound **VII** prepared by coupling of pentadeuteriobenzenediazonium chloride. The ^{13}C chemical shifts of the naphthalene carbons were assigned on the basis of comparison of measured and calculated ^{13}C chemical shifts, values of $\delta(^{13}C)$ in the compound **VI** and substituent chemical shifts for the phenylazo group (Table 8). The assignments of C(5) and C(8) were verified by selective decoupling ($\delta(C(5)\underline{H}) = 8{\cdot}74$; $\delta(C(8)\underline{H}) = 8{\cdot}53$). The signal at 114·4 gives a doublet in the proton-coupled spectrum and thus corresponds to C(3). Temperature dependence of the ^{15}N chemical shifts and the coupling constants in the compound **VII** in $CDCl_3$ are given in Table 7. Hydrazone-form contents were calculated above in the case of compound **VI**.

The ^{13}C- and ^{15}N-NMR spectral characteristics and both chemical shifts and coupling constants can be used to describe azo–hydrazone equilibria. The ^{13}C chemical shifts of C—OH and C═O,[1,2,10] respectively, those of C(1′), C(2′) and C(4′),[3] the ^{15}N chemical shifts[6,7,13] and the coupling constants $^1J(^{15}N^{15}N)$[7,14] and $^1J(^{15}N^{13}C)$[3] were utilized. Temperature dependences of these characteristics play a significant role.[7,13,14]

In refs 3 and 13, the ^{13}C- and ^{15}N-NMR spectra of four model azo dyes were measured: 3-methyl-1-phenylpyrazole-4,5-dione 4-phenylhydrazone (hydrazone form only with an intramolecular hydrogen bond), 4-hydroxyazobenzene (azo compound without an intramolecular hydrogen bond), 2-hydroxy-5-*tert*-butylazobenzene (azo compound with an intramolecular hydrogen bond) and 1-phenylazo-2-naphthol (equilibrium mixture of azo and hydrazone forms).

In this communication, the ^{13}C- and ^{15}N-NMR spectral characteristics of further model azo dyes were measured and data obtained interpreted with respect to azo–hydrazone tautomerism.

Compound **I** exists in its hydrazone form without an intramolecular hydrogen bond. The ^{15}N chemical shifts of **I** are shifted upfield in comparison with those in hydrazone compounds with an intramolecular hydrogen bond, in agreement with $\delta(^{15}N)$ in benzaldehyde phenylhydrazone ($\delta(^{15}N) = -239{\cdot}0$; $-54{\cdot}0$; ref. 25). Compound **II** exists in its hydrazone form (contrary to literature data[17,19] in which the azo form is preferred), forming a seven-membered ring with an intramolecular hydrogen bond. All ^{13}C- and ^{15}N-NMR characteristics support the hydrazone form in **II**, especially $\delta(^{13}C)$ of the carbonyl group, $\delta(^{15}N)$ and their temperature independence. It is interesting to note that the hydrazone form was expected on the basis of the fragmentation pattern in the mass spectrum of **II**.[19] The ^{13}C chemical shift of C(1) can be compared with $\delta(\underline{C}{=}N) = 145{\cdot}7$ in acetone phenylhydrazone[26] and the ^{13}C chemical shifts of the methyl groups[26] (15·4 and 26·9) differ considerably in acetone phenylhydrazone (compare with $\delta(^{13}C)$ values of C(2) and C(5) in compound **II**). Compound **III** exists in the azo configuration without an intramolecular hydrogen bond. The ^{15}N chemical shifts are similar to those in 4-hydroxyazobenzene (124·2 and 110·2).[13] The unambiguity of the ^{13}C chemical shifts assignment enables the ^{13}C substituent chemical shifts (SCS) caused by the phenylazo group (Table 8) to be ascertained. Very similar SCS can be obtained from the

TABLE 8

^{13}C Substituent Chemical Shifts in 8-Hydroxyquinoline $(SCS)_1$ and 1-Naphthylamine $(SCS)_2$ Caused by Substitution with the Group $N{=}N{-}C_6H_5$ in the 4- and 5-Positions Respectively

Carbon	*$(SCS)_1$*[a]	*$(SCS)_2$*[b]	*Carbon*	*$(SCS)_1$*[a]	*$(SCS)_2$*[b]
1	4·7	4·2	6	1·9	1·4[c]
2	0·7	−0·4	7	1·4	0·6[c]
3	−11·7	−12·4	8	—	−0·2
4	21·0	21·4	4a	−0·9	−1·2
5	−3·7	−4·4	8a	0·1	−1·1

[a] $(SCS)_1 = \delta(Ci)$ (III) − $\delta(Ci)$ (8-hydroxyquinoline).

[b] $(SCS)_2 = \delta(Ci)$ (4-phenylazo-1-naphthylamine) − $\delta(Ci)$(1-naphthylamine).

[c] In the case where $\delta(C6) = 127{\cdot}0$ and $\delta(C7) = 125{\cdot}2$.[7]

^{13}C chemical shifts in 4-phenylazo-1-naphthylamine[7] (Table 8). Compound **IV**, containing a heteroatom in the passive component, exists in the hydrazone form with an intramolecular hydrogen bond. Compound **V** exists in the azo form in DMSO-d_6, the ^{15}N chemical shifts being similar to those in 4-hydroxyazobenzene[13] and in compound **III**. Compound **VI** exists, similarly to 1-phenylazo-2-naphthol,[3,13] as an equilibrium mixture of the azo and hydrazone tautomers. Hydrazone-form content in compound **VI** is, at a given temperature, greater than that in 1-phenylazo-2-naphthol and compound **VI** exists thus mainly as 1,2-naphthoquinone-2-phenylhydrazone. Similarly, compound **VII** exists predominantly as 4-phenylazo-1,2-naphthoquinone 2-phenylhydrazone. Substitution by the phenylazo group in the 4-position causes a small decrease of the hydrazone-form content.

Several NMR criteria for azo–hydrazone equilibria estimation in the coupling products of the benzenediazonium ions have been tested. The measurement of the ^{13}C chemical shifts of C(1′); C(2′) and C(4′)[3,8–10] of the benzene ring originating from the benzenediazonium ion seems to be the simplest method. The ^{13}C chemical shifts found for various phenylhydrazone groups have the values $\delta(C(1')) \sim 141{\cdot}2$; $\delta(C(2')) \sim 115{\cdot}7$; $\delta(C(4')) \sim 125{\cdot}3$, respectively, whereas those for phenylazo groups have the values $\delta(C(1')) \sim 151{\cdot}8$; $\delta(C(2')) \sim 122{\cdot}4$; $\delta(C(4')) \sim 130{\cdot}9$,[3] respectively. These values of $\delta(^{13}C)$ are, to a certain extent, influenced by the existence or non-existence of an intramolecular hydrogen bond and, in addition, the differences in the ^{13}C chemical shifts of the appropriate carbons are not too great between the azo and hydrazone forms. Thus the $\delta(^{13}C)$ of C(1′), C(2′) and C(4′) (see $\delta(^{13}C)$ of phenyl groups in this paper) can be used only for an approximate estimation of azo–hydrazone equilibria. In compounds having a hydroxy group, the ^{13}C chemical shift of $\underline{C}OH$ (or $\underline{C}{=}O$) is of great importance.[1]

The values of the coupling constants $^1J(^{15}N^{15}N)$ in ^{15}N-doubly labelled compounds differ in the azo and hydrazone tautomers and are only slightly affected by structural surroundings. $^1J(^{15}N^{15}N)$ is about 15·5 in the azo compound, whilst $^1J(^{15}N^{15}N)$ in the hydrazone compounds have values 10·5–11·5 Hz.[14] This difference is not too large and a rough estimation of azo–hydrazone content is thus possible.

The ^{15}N chemical shifts of both nitrogen atoms in azo dyes have been shown[13] to be very useful for the analysis of azo–hydrazone equilibria, since both ^{15}N chemical shifts can be used independently for this purpose and appropriate calculations give nearly identical results. The main advantage of this method lies in the fact that the differences in $\delta(^{15}N)$ of model azo and hydrazone compounds[13] are about 270 ppm for N_α and *ca* 150 ppm for N_β, respectively. The values of the hydrazone content (Tables 6 and 7) obtained from ^{15}N-NMR measurements are in agreement with the data obtained from $^1J(^{15}N_\alpha H)$.

Thus, practically all NMR characteristics can be used for estimation of azo–hydrazone equilibria, but it seems that temperature measurements of $\delta(^{15}N_\alpha)$; $\delta(^{15}N_\beta)$ and/or $^1J(^{15}N_\alpha H)$ give the most reliable results obtainable.

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