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Two-dimensional ^{1}H- and ^{13}C-NMR and ^{15}N-NMR Spectra of Three Azo Dyes Derived from J-Acid and 4-Nitroaniline

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SUMMARY

The ^{1}H-, ^{13}C- *and* ^{15}N-*NMR spectra of three azo dyes prepared by coupling 4-nitrobenzenediazonium chloride with J-acid under both alkaline and acidic conditions have been measured. Two-dimensional H, H-COSY; NOESY; H, C-COSY and one-dimensional selective INEPT have been used in the assignment of the* ^{1}H- *and* ^{13}C-*NMR signals. Using* $\delta(^{13}C)$, $\delta(^{15}N)$ *and* $^{1}J(^{15}N^{15}N)$ *it has been found that the coupling products* ortho *and* para *to the hydroxyl group exist, in hexadeuteriodimethyl sulfoxide solutions, as equilibrium mixtures of the azo and hydrazone tautomers with strongly prevailing naphthoquinone phenylhydrazone configurations, whilst the coupling product* ortho *to the amino group exists almost exclusively as the azo compound.*

1 INTRODUCTION

We have recently published[1] data on the two-dimensional ^{1}H- and ^{13}C-NMR and ^{15}N-NMR spectra of azo dyes prepared by coupling benzenediazonium chloride with J-acid, H-acid and Gamma acid and shown that the above-mentioned aminohydroxynaphthalenesulfonic acids undergo diazo coupling of benzenediazonium chloride *ortho* to the hydroxyl groups under alkaline conditions and that they exist almost completely as naphthoquinone phenylhydrazone derivatives in hexadeuteriodimethyl sulfoxide solutions. It is well known that three azo dyes (Scheme 1) can be prepared by coupling 4-nitrobenzenediazonium chloride with J-acid.[2]

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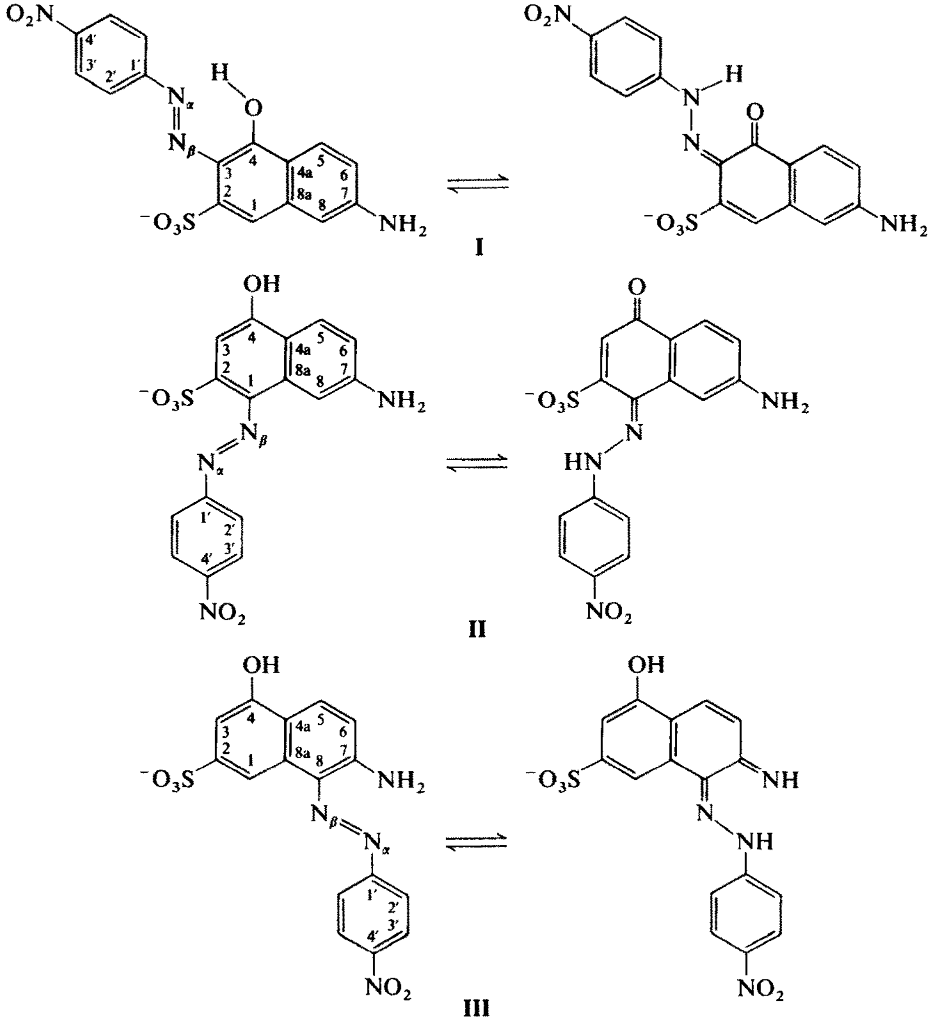
The object of this present work is to measure and assign ^{1}H- and ^{13}C-NMR spectra of the coupling products with J-acid using two-dimensional spectra[3–5] and to interpret ^{13}C- and ^{15}N-NMR spectra in the above-mentioned compounds with respect to azo–hydrazone tautomerism.

2 EXPERIMENTAL

Sodium salts of compounds **I–III** (Scheme 1) were prepared according to ref. 2. ^{15}N-labelled compounds were prepared with 4-nitroaniline ($^{15}NH_2$; 10% ^{15}N) and $Na^{15}NO_2$ (96·2% ^{15}N) obtained from Isocommerz Berlin.

^{1}H and ^{13}C-NMR spectra were measured at 400·13 MHz and



I

II

III

Scheme 1

100·61 MHz, respectively, using a Bruker AM 400 spectrometer. The spectra were measured for saturated solutions in hexadeuteriodimethyl sulfoxide. The deuterated solvent was used as a lock substance. The ^{1}H and ^{13}C chemical shifts were referenced to the signal of solvent ($\delta(^{1}H) = 2{\cdot}55$; $\delta(^{13}C) = 39{\cdot}6$). The measurement conditions of H, H-COSY; NOESY; H, C-COSY and selective INEPT spectra are described in ref.1 (they were slightly modified when necessary).

^{15}N-NMR spectra of ^{15}N-doubly labelled dyes **I**–**III** were measured at 10·095 MHz using a JNM-FX 100 (JEOL) spectrometer equipped with a multinuclear tunable probe and operating in the FT mode. The ^{15}N chemical shifts were referenced to external neat nitromethane (25% ^{15}N; $\delta = 0{\cdot}0$). The temperature of the heating gas was measured with a thermocouple with an accuracy of ± 1K. The measurement conditions are given in ref. 6.

3 RESULTS AND DISCUSSION

The ^{1}H and ^{13}C chemical shifts and the coupling constants $^{n}J(^{15}N_{\beta}{}^{13}C)$ in the compounds **I**–**III** at 300K are given in Tables 1–3.

TABLE 1

^{1}H and ^{13}C Chemical Shifts and Coupling Constants $^{n}J(^{15}N_{\beta}{}^{13}C)$ of Compound **I** in Hexadeuteriodimethyl Sulfoxide at 300K

H/C no.	$\delta(^{1}H)^{a}$	$\delta(^{13}C)$	$^{n}J(^{12}N_{\beta}{}^{15}C)$ (*Hz*; ±0·3)
1	7·35[b]	124·3	4·1
2	—	143·5	9·0
3	—	131·1	4·1
4	—	178·3	
4a	—	119·2	
5	7·95[c]	130·1	
6	6·73[d]	114·2	
7	—	155·3	
8	6·71[e]	111·2	
8a	—	138·2	
1′	—	148·7	7·3
2′	7·85	116·1	2·4
3′	8·30	125·5	
4′	—	142·7	

[a] $\delta(N\underline{H}) = 15{\cdot}63$; $\delta(N\underline{H}_2) = 6{\cdot}68$ (temperature and concentration-dependent).
[b] Broadened singlet.
[c] Broadened doublet; $^{3}J(H(5), H(6)) = 8{\cdot}52$ Hz.
[d] Doublet of doublets; $^{3}J(H(5), H(6)) = 8{\cdot}52$ Hz; $^{4}J(H(6), H(8)) = 2{\cdot}16$ Hz.
[e] Doublet; $^{4}J(H(6), H(8)) = 2{\cdot}16$ Hz.

TABLE 2

^1H and ^{13}C Chemical Shifts and Coupling Constants $^nJ(^{15}N_\beta{}^{13}C)$ of Compound **II** in Hexadeuteriodimethyl Sulfoxide at 300K

H/C no.	$\delta(^1H)^a$	$\delta(^{13}C)$	$^nJ(^{15}N_\beta{}^{13}C)$ (*Hz*; ±0·3)
1	—	128·7	6·2
2	—	145·8[b]	
3	7·01[c]	127·7	
4	—	182·2	
4a	—	122·9	
5	7·86[d]	127·1	
6	7·04[e]	117·7	
7	—	147·0[f]	
8	7·96[g]	111·3	
8a	—	139·4	11·0
1′	—	149·0	6·6
2′	7·48	113·8	
3′	8·27	126·0	
4′	—	141·2	

[a] $\delta(N\underline{H}) = 13{\cdot}90$; $\delta(N\underline{H}_2) = 4{\cdot}49$ (temperature- and concentration-dependent).

[b] Singlet in proton-coupled spectrum.

[c] Singlet.

[d] Doublet; ^3J(H(5), H(6)) = 8·52 Hz.

[e] Doublet of doublets; ^3J(H(5), H(6)) = 8·52; ^4J(H(6), H(8)) = 2·16 Hz.

[f] Doublet in proton-coupled spectrum.

[g] Doublet; ^4J(H(6), H(8)) = 2·16 Hz.

^1H chemical shifts were assigned after analysis of homonuclear shift-COrrelated SpectroscopY (H, H-COSY)[5] spectra. Figure 1 shows the H, H-COSY contour plot of compound **I**, which reveals also weak coupling ^5J(H(1)H(5)). In the NOESY spectrum (Fig. 2), scalar coupling correlations are strongly reduced by random variation of the mixing pulse.[5] Off-diagonal peaks (1, 8) correlate spins which share a dipolar coupling. These cross peaks in the NOESY spectrum indicate the proximity of protons H(1) and H(8), i.e. protons H(1) and H(8) must be in the *peri* position. In the H, H-COSY spectrum of compound **II** (Fig. 3), no correlation between protons H(3) and H(5) was observed and also no cross peaks of proton H(3) and H(8) are present in the NOESY spectrum (Fig. 4) because of their long space separation. NOESY spectra differentiate clearly between the *ortho* and *para* positions of coupling of 4-nitrobenzenediazonium chloride with J-acid and the results obtained are in agreement with those published in our previous paper.[1]

Figure 5 shows the H, H-COSY spectrum of compound **III** in which the

TABLE 3

^{1}H and ^{13}C Chemical Shifts and Coupling Constants $^nJ(^{15}N_\beta{}^{13}C)$ of Compound **III** in Hexadeuteriodimethyl Sulfoxide at 300K

H/C no.	$\delta(^1H)$	$\delta(^{13}C)$	$^nJ(^{15}N_\beta{}^{13}C)$ (*Hz*; ±0·3)
1	8·48[a]	109·3	4·5
2	—	147·9	
3	7·13[b]	105·4	
4	—	153·8	
4a	—	117·3	2·2
5	8·06[c]	130·1	
6	7·11[d]	118·9	
7	—	142·5	
8	—	127·5	
8a	—	135·1	7·9
1′	—	157·4	6·0
2′	8·10	121·9	4·1
3′	8·41	125·3	
4′	—	146·2	

[a] Doublet of doublets; ^4J(H(1), H(3)) = 1·44 Hz; ^5J(H(1), H(5)) = 0·3 Hz.
[b] Doublet; ^4J(H(1), H(3)) = 1·44 Hz.
[c] Doublet of doublets; ^3J(H(5), H(6)) = 9·37 Hz; ^5J(H(1), H(5)) = 0·3 Hz.
[d] Doublet;^{3} J(H(5), H(6)) = 9·37 Hz.

correlation of protons H(1) and H(5) via small ^5J(H(1)H(5)) enables us to distinguish between 'doublets' of H(1), H(3) and H(5), H(6), respectively. ^{1}H chemical shifts and J(H, H) coupling constants in compounds **I–III** were read from ^{1}H-NMR spectra after line narrowing (Line Broadening from −0·5 to −1·5 Hz, Gaussian Broadening = 0·3).

^{13}C chemical shifts of carbons bearing protons were assigned using H, C-COSY spectra, and for assignment of quaternary carbons selective INEPT spectra were used.[1]

The coupling constants $^nJ(^{15}N_\beta{}^{13}C)$ were obtained from the ^{13}C-NMR spectra of ^{15}N-labelled dyes. Of these coupling constants, the values $^2J(^{15}N_\beta{}^{13}C)$ seem to be of great importance. It is well known that $^2J(^{15}N^{13}C)$ are stereochemically dependent.[7] The carbon atoms in the '*cis*' position to the lone pair of the appropriate nitrogen are split into a doublet in ^{15}N-labelled compounds, the value of the coupling constants $^2J(^{15}N^{13}C)$ being about 10 Hz. The values $^2J(^{15}N^{13}C)$ of the carbon atoms in the '*trans*' position to the lone pair of the nitrogen are usually lower than 1·5 Hz.[7] Using these facts and the values of $^2J(^{15}N_\beta{}^{13}C)$ measured in compounds **I–III**, it can be expected that carbons C(2) in **I**, C(8a) in **II** and C(8a) in **III** are in the 'cis' position to the lone pair of the nitrogen N_β as shown in Scheme 1.

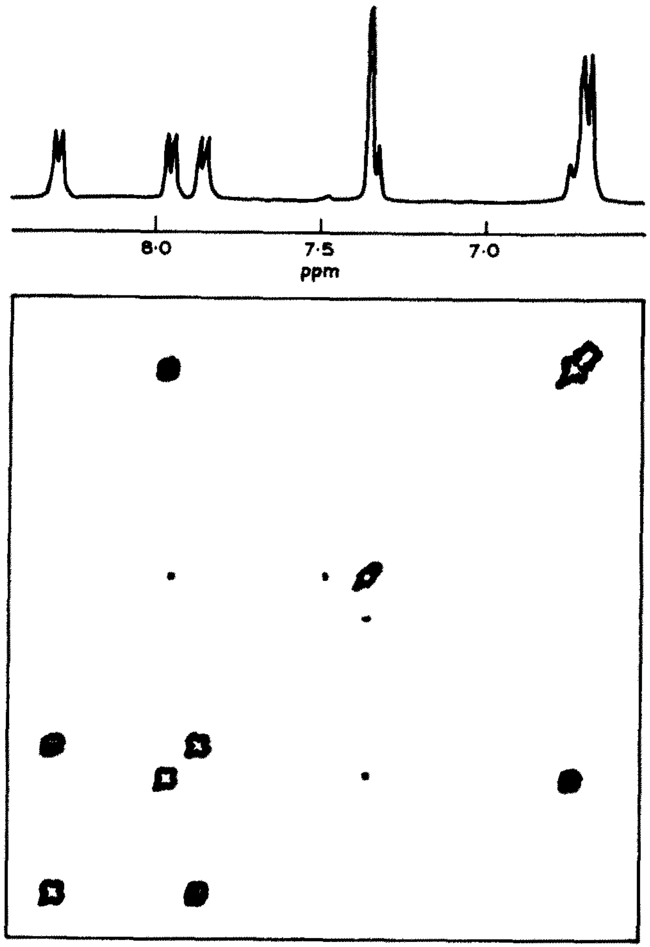


Fig. 1. Contour plot of H, H-COSY spectrum (with a projection) of compound **I**.

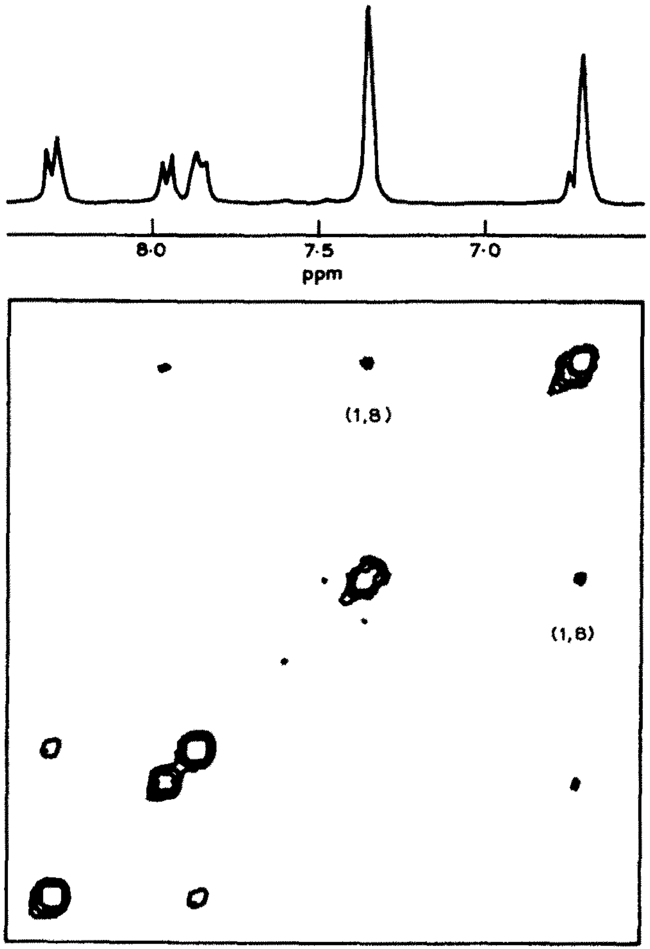


Fig. 2. Contour plot of NOESY spectrum (with a projection) of compound **I**.

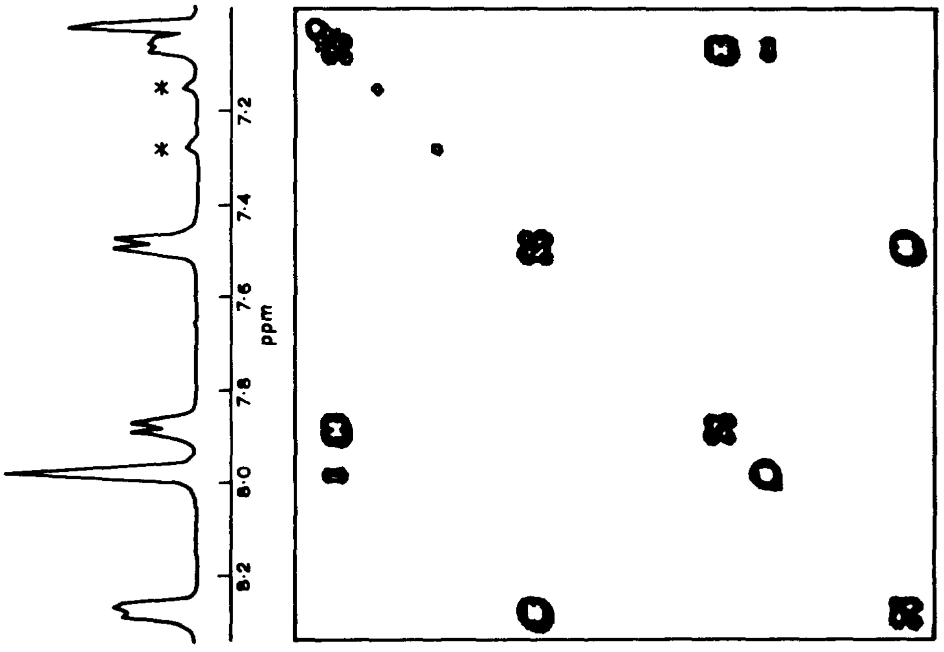


Fig. 3. Contour plot of H, H-COSY spectrum (with a projection) of compound **II**. Asterisks denote two of three signals of NH_4^+ salt formed during separation of compound **II**.

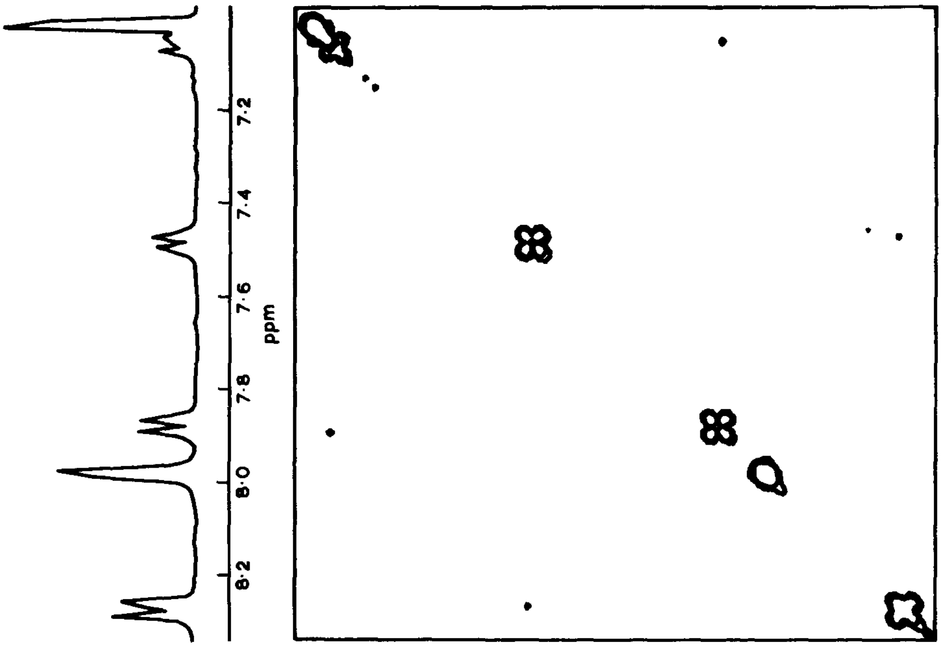


Fig. 4. Contour plot of NOESY spectrum (with a projection) of compound **II**.

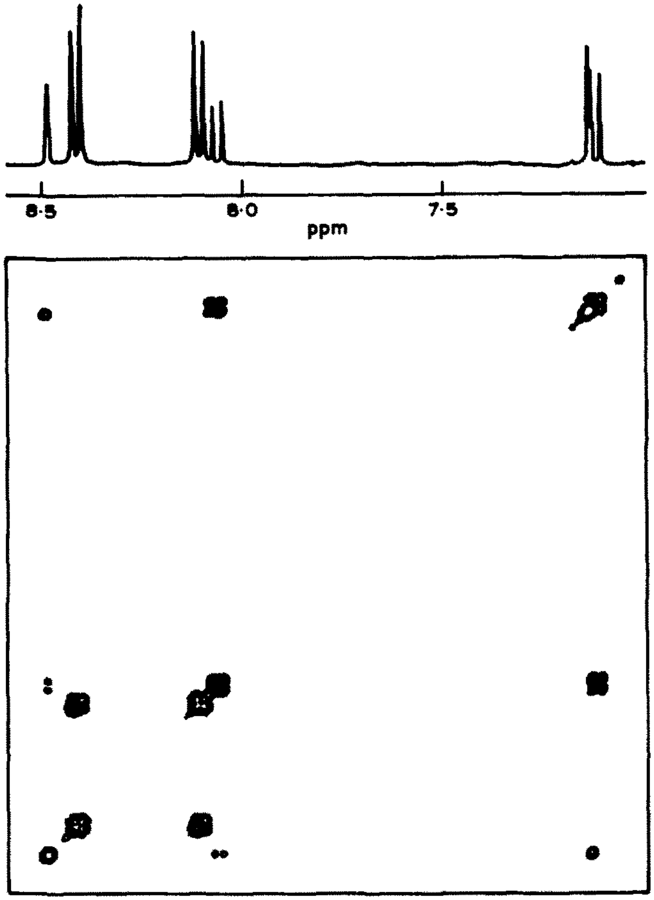


Fig. 5. Contour plot of H,H-COSY spectrum (with ^{1}H-NMR spectrum) of compound **III**.

The ^{13}C chemical shifts of the $O_2N—C_6H_4—$ group in compounds **I** and **II** are similar to those in 3-methyl-1-phenylpyrazole-4,5-dione 4-nitrophenylhydrazone[8] (144·4; 125·7; 115·3; 148·1) and 2-(4-nitrophenylhydrazone)propanodinitrile[9] (144·1; 125·6; 116·9; 147·1). ^{13}C chemical shifts of the same group in compound **III** are similar to the values in 4-nitroazobenzene[10] (148·5; 124·6; 123·3; 155·5). According to Keleman *et al.*[11] the tautomers can best be differentiated by $\delta(^{13}C)$ of C—OH/C=O and C—NH_2/C=NH, respectively. ^{13}C chemical shifts of these carbons support the conclusion that compounds **I** and **II** are best described as hydrazone tautomers and **III** as an azo compound.

The temperature dependence of ^{15}N chemical shifts, coupling constants $^1J(^{15}N^{15}N)$ and hydrazone-form content of compounds **I-III** are collated in Table 4. Different values of the ^{15}N enrichment enables us to assign the ^{15}N

TABLE 4

Temperature Dependence of ^{15}N Chemical Shifts, Coupling Constants $^{1}J(^{15}\mathrm{N}^{15}\mathrm{N})$ and Hydrazone-Form Content of Compounds **I–III** in Hexadeuteriodimethyl Sulfoxide

Compound	*Temperature* (*K*)	$\delta(^{15}N_\alpha)$	*Hydrazone form*[a] (%)	$\delta(^{15}N_\beta)$	*Hydrazone form*[a] (%)	$^{1}J(^{15}N^{15}N)$ (*Hz*; ±0·3)
I	300	−206·8	97·8	−12·6	94·1	11·5
	360	−205·5		−10·0		11·5
II	300	−205·9	91·3	−42·3	94·5	11·3
	360	−207·3		−42·9		11·3
III	300	44·1	<5[b]	118·1	<5[b]	15·4
	360	48·1		121·4		15·4

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

[b] An estimation (see text).

chemical shifts unambiguously. Hydrazone-form content obtained from the $\delta(^{15}\mathrm{N})$ was calculated using the procedure described in ref. 6.

$$\text{Hydrazone (\%)} = \frac{\delta(^{15}\mathrm{N})_\mathrm{A} - \delta(^{15}\mathrm{N})_\mathrm{X}}{\delta(^{15}\mathrm{N})_\mathrm{A} - \delta(^{15}\mathrm{N})_\mathrm{H}} \times 100$$

$\delta(^{15}\mathrm{N})_\mathrm{A}$ and $\delta(^{15}\mathrm{N})_\mathrm{H}$ denote ^{15}N chemical shifts in model azo and hydrazone compounds, respectively, and $\delta(^{15}\mathrm{N})_\mathrm{X}$ refers to the ^{15}N chemical shift of the compound in which the percentage of hydrazone form is being calculated. For compound **I**, ^{15}N chemical shifts in 3-methyl-1-phenylpyrazole-4,5-dione 4-nitrophenylhydrazone[6,8] (model hydrazone compound with an intramolecular hydrogen bond) and ^{15}N chemical shifts in 2-hydroxy-5-*tert*-butylazobenzene[6] corrected with −6·6 (N_α) and 16·5 (N_β) ppm (obtained from $\delta(^{15}\mathrm{N})$ in azobenzene and 4-nitroazobenzene[10]) were used for the calculation. For compound **II**, ^{15}N chemical shifts in 4-hydroxy-4′-nitroazobenzene[10] were used as the model azo compound without an intramolecular hydrogen bond whilst 9,10-anthraquinone 9-phenylhydrazone, the ^{15}N chemical shifts of which were corrected with −2·3 (N_α) and −1·4 (N_3) ppm [obtained from $\delta(^{15}\mathrm{N})$ in 2-phenylhydrazonopropanedinitrile and 2-(4-nitrophenylhydrazono)propanedinitrile[9]], served as a model hydrazone compound. Calculated values of hydrazone-form content are given in Table 4.

We have observed the following $\delta(^{15}\mathrm{N})$ in 1-phenylazo-2-aminonaphthalene[12] in hexadeuteriodimethyl sulfoxide solution: 300K, $\delta(^{15}\mathrm{N}_\beta) = 65{\cdot}9$; $\delta(^{15}\mathrm{N}_\alpha) = 114{\cdot}8$; 370 K, $\delta(^{15}\mathrm{N}_\beta) = 70{\cdot}8$. After correction for NO_2 substitution (−6·6 and 16·5 ppm; see above), the ^{15}N chemical shifts for 1-(4-nitrophenylazo)-2-aminonaphthalene were calculated to be 59·3 and 131·3. ^{15}N chemical shifts in hydrazone forms of azo dyes derived from passive components containing amino groups are not known[12] but it can be expected that these values would not be too different from those for the hydroxy-group-containing analogues. We can conclude therefore that, from a practical point of view, compounds **I** and **II** contain more than 90% of the hydrazone form whilst compound **III** exists almost exclusively (>95%) in the azo form, all in hexadeuteriodimethyl sulfoxide solution. The hydrazone form content in **I** is higher than that in 1-phenylazo-2-naphthol.[6,13] As shown above, compound **II** is mainly in the hydrazone form, contrary to 4-phenylazo-1-naphthol[14] which exists almost completely as a true azo compound under comparable experimental conditions.

The values of the coupling constants $^1J(^{15}N^{15}N)$ in ^{15}N-doubly labelled compounds differ in the azo and hydrazone tautomers[15] and accordingly the values of $^1J(^{15}N^{15}N)$ measured in **I**–**III** corroborate the above-mentioned conclusions.

REFERENCES

1. A. Lyčka and J. Jirman, *Dyes and Pigments*, **8**, 315 (1987).
2. Z. J. Allan and J. Podstata, *Coll. Czech. Chem. Commun.*, **26**, 1862 (1961).
3. A. Bax, *Two-dimensional nuclear magnetic resonance in liquids*. Dordrecht, Reidel (1982).
4. R. Benn and H. Günther, *Angew. Chem., Int. Ed. Engl.*, **22**, 350 (1983).
5. G. A. Morris, *Magn. Reson. Chem.*, **24**, 371 (1986).
6. A. Lyčka, D. Šnobl, V. Macháček and M. Večeřa, *Org. Magn. Reson.*, **16**, 17 (1981).
7. M. Witanowski, L. Stefaniak and G. A. Webb, *Ann. Rep. NMR Spectr.*, **11B**, 122 (1981).
8. A. Lyčka, T. Liptaj and J. Jirman, *Coll. Czech. Chem. Commun.*, **52**, 727 (1987).
9. A. Lyčka, *Coll. Czech. Chem. Commun.*, **49**, 2801 (1984).
10. A. Lyčka, *Coll. Czech. Chem. Commun.*, **47**, 1112 (1982).
11. J. Kelemen, S. Moss, H. Sauter and T. Winkler, *Dyes and Pigments*, **3**, 27 (1982).
12. A. Lyčka, *Coll. Czech. Chem. Commun.*, **48**, 3104 (1983).
13. R. Haessner, H. Mustroph and R. Borsdorf, *Dyes and Pigments*, **6**, 277 (1985).
14. A. Lyčka and V. Macháček, *Dyes and Pigments*, **7**, 171 (1986).
15. A. Lyčka and D. Šnobl, *Coll. Czech. Chem. Commun.*, **46**, 892 (1981).