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^{15}N CP-MAS NMR Study of Azo–Hydrazone Tautomerism of Some Azo Dyes

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The 20.28 MHz ^{15}N CP-MAS NMR spectra of ^{15}N doubly labelled 3-methyl-1-phenylpyrazole-4,5-dione 4-phenylhydrazone (1), 4-hydroxyazobenzene (2), 2-hydroxy-5-*tert*-butylazobenzene (3) and 1-phenylazo-2-naphthol (4) were measured and the temperature dependence of $\delta(^{15}N)$ was followed. For 4, representing a mixture of the azo and hydrazone forms, the hydrazone content was calculated from the ^{15}N chemical shifts of both nitrogen atoms at various temperatures. The two calculations gave identical results. In comparison with measurements in solution, the hydrazone content in 4 is slightly higher in the solid state. Thermodynamic data were calculated using the temperature dependence of ln *K* (*K* = [hydrazone form]/[azo form]). Some hydrazone content was found in 2 in the solid state, in contrast to the measurements in solution.

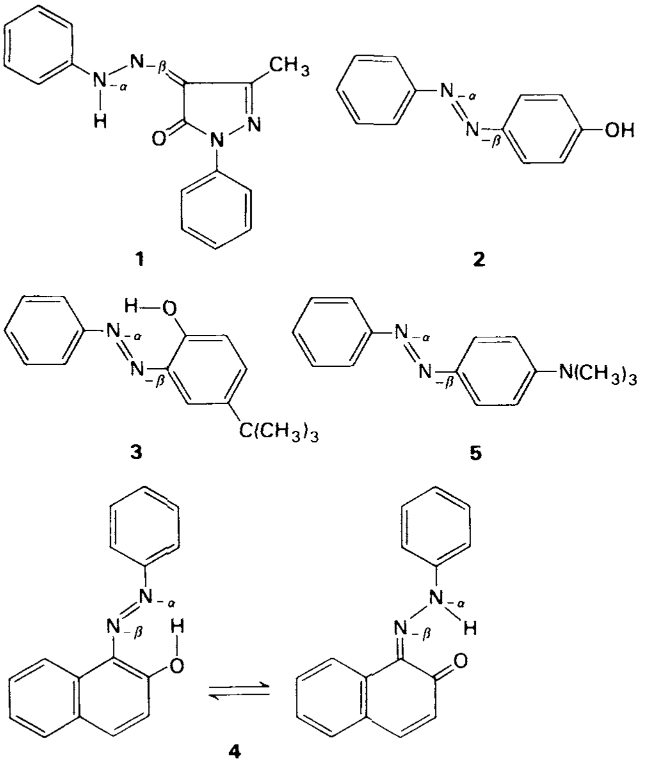
KEY WORDS ^{15}N NMR Solid-state NMR Azo–hydrazone tautomerism

INTRODUCTION

Nuclear magnetic resonance is a powerful technique for the characterization of azo–hydrazone tautomerism.[1,2] The ^{13}C and ^{1}H chemical shifts and the one-bond ^{15}NH coupling constants are the most frequently used values for quantitative purposes.[1,2] In 1981 we described[3] the application of ^{15}N NMR spectra to the determination of the tautomeric ratio in *ortho*-hydroxyazo dyes. Since there are large differences in the nitrogen shieldings between azo and hydrazone compounds, the $\delta(^{15}N)$ values observed for potentially tautomeric systems involving these structures should provide an easy measure of the tautomerization equilibrium constants. The method described[3] employed model compounds that are not simple derivatives of the tautomers concerned. They correspond closely, however, to the hydrogen-bonded structures of the tautomers. The two calculations, from either N-α or N-β, gave almost identical results.[3–6]

It is well known that N-αH ··· N-β $\rightleftharpoons$ N-α ··· N-βH tautomerism exists in the solid state (refs 7 and 8 and references cited therein). For this reason, and because some industrially important groups of azo dyes are insoluble in common solvents, we have investigated the ^{15}N CP-MAS NMR spectra of the model azo dyes studied previously.[3] An application of ^{15}N CP-MAS NMR spectroscopy to the determination of azo–hydrazone tautomerism in monohydrated calcium 1-(2-sulpho-4-methylphenylazo)-2-hydroxynaphthalene-3-carboxylate was published[9] during the preparation of the present manuscript.

The aim of this study was to measure the ^{15}N chemical shifts in compounds **1**–**4** (Scheme 1) in the solid state, to check whether $\delta(^{15}N)$ in **1** and **3** can be used as model data for hydrazone and azo compounds, respectively, in order to calculate the tautomer ratio in the azo coupling product of benzenediazonium chloride with 2-naphthol (**4**) and also to compare the azo–hydrazone tautomeric equilibria for **2** and **4** in the solid state and in solution. The ^{15}N CP-MAS NMR spectrum of 4-(*N*,*N*-dimethylamino)azobenzene (**5**) was measured as a model azo dye which cannot exist in a hydrazone form.



Scheme 1

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EXPERIMENTAL

3-Methyl-1-phenylpyrazole-4,5-dione 4-phenylhydrazone (**1**), 2-hydroxy-5-*tert*-butylazobenzene (**3**) and 1-phenylazo-2-naphthol (**4**) were prepared as described previously[3] using [^{15}N]aniline (20% ^{15}N) and Na^{15}NO$_2$ (20% ^{15}N; Isocommerz, Berlin). 4-Hydroxyazobenzene (**2**) was prepared by coupling in alkaline medium[10] using either [^{15}N]aniline (10% ^{15}N) and Na^{15}NO$_2$ (20% ^{15}N) or unlabelled aniline and Na^{15}NO$_2$ (96% ^{15}N). 4-(*N*,*N*-Dimethylamino)azobenzene (**5**) monolabelled in the β-position (96% ^{15}N) was obtained by coupling in acidic medium.[10] The products were recrystallized from ethanol, and their purities checked by ^{1}H NMR and TLC.

The solid-state ^{15}N NMR spectra were measured at 20.28 MHz on a Bruker MSL 200 spectrometer using the CP-MAS technique.[11] Alternation of the spin temperature in the rotating frame to suppress artifacts[12] and the flip-back pulse[13] was used. The samples were packed in double-bearing Al$_2$O$_3$ rotors supplied by Bruker. The magic angle was adjusted by minimization of the line width of the carbonyl carbon of glycine. Typical measurement conditions were as follows: 90° r.f. pulse, 5.5 μs, contact time 6 ms, pulse repetition time 5 s, MAS frequency 5 kHz, spectral width 20 kHz and acquisition time 51 ms. The ^{15}N chemical shifts were referenced to solid NH$_4$Cl by sample replacement and recalculated to nitromethane using $\delta(\mathrm{NH_4Cl}) = -352.5$.[14] Positive values denote downfield shifts. The temperature measurements were carried out using a Bruker temperature unit. The temperatures of the cooling or heating gas were measured with a thermocouple with an accuracy ±1 K. The absolute temperatures of the samples were not checked during measurements.

RESULTS AND DISCUSSION

The ^{15}N chemical shifts of **1**–**5** are given in Table 1 and their ^{15}N CP-MAS NMR spectra are shown in Figs 1–4.

Compounds **1** and **3** give two signals, one from N-α and the other from N-β, the chemical shifts of which are almost independent of temperature. The ^{15}N chemical shifts were assigned after comparison with data obtained in solution,[3] and are shifted upfield ($\Delta\delta \leqslant 20$ ppm) with respect to the values in ref. 3. This can be caused by the choice of the standard. The value of $\delta(^{15}\mathrm{N}) = -352.5$ for NH$_4$Cl obtained in aqueous solution[14] was used as a standard, but there is probably a slight difference in its ^{15}N chemical shifts in the solid state and in solution. It should be emphasized that the choice of standard does not, in practice, affect the determination of the azo–hydrazone content (see below). Because the above-mentioned differences in $\delta(^{15}\mathrm{N})$ are not constant for **1**–**5**, it is probable that there are almost small changes in their ^{15}N chemical shifts in the liquid and solid state.

The ^{15}N CP-MAS NMR spectra of **4** (Fig. 1) consist of two signals for each nitrogen differing by 3.4–5.8 ppm; these can be ascribed to the existence of two non-equivalent molecules in the unit cell. A similar splitting (*ca.* 3.4 ppm) due to a crystallographic non-equivalence has been reported.[9] The spectra show the typical temperature dependence of $\delta(^{15}\mathrm{N})$ for azo dyes caused by azo–hydrazone tautomerism: the ^{15}N chemical shifts shift downfield with increasing temperature, which corresponds to an increase in the content of the azo form.[3]

Table 1. Temperature dependence of $\delta(^{15}\mathrm{N})$ of 1–5 in the solid state

Compound	Temperature (K)	$\delta(^{15}\mathrm{N}\text{-}\alpha)$	$\delta(^{15}\mathrm{N}\text{-}\beta)$
1	305	−222.9	−37.0
	358	−222.8	−36.9
2	305	94.2[a]	102.9[a]
		57.2[a]	69.0[a]
3	306	53.8	114.4
	323	54.1	114.4
4	194	−185.9[a]	−15.9[a]
		−190.2[a]	−20.3[a]
	203	−183.9[a]	−14.6[a]
		−188.6[a]	−19.1[a]
	243	−172.9[a]	−8.5[a]
		−178.2[a]	−13.0[a]
	305	−156.4[a]	−0.2[a]
		−162.2[a]	−3.7[a]
	358	−144.0[a]	7.0[a]
		−149.7[a]	3.6[a]
5	302	[b]	105.5

[a] Two signals, see text.
[b] Not measured.

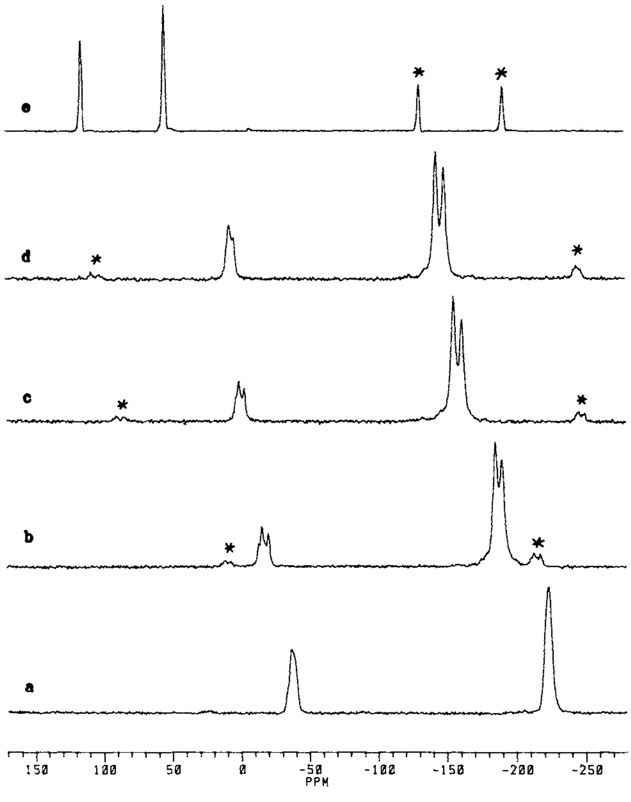

Figure 1. ^{15}N CP-MAS spectra of (a) **1** at 305 K, (b) **4** at 194 K, (c) **4** at 305 K, (d) **4** at 358 K and (e) **3** at 306 K. The asterisks denote spinning side-bands.

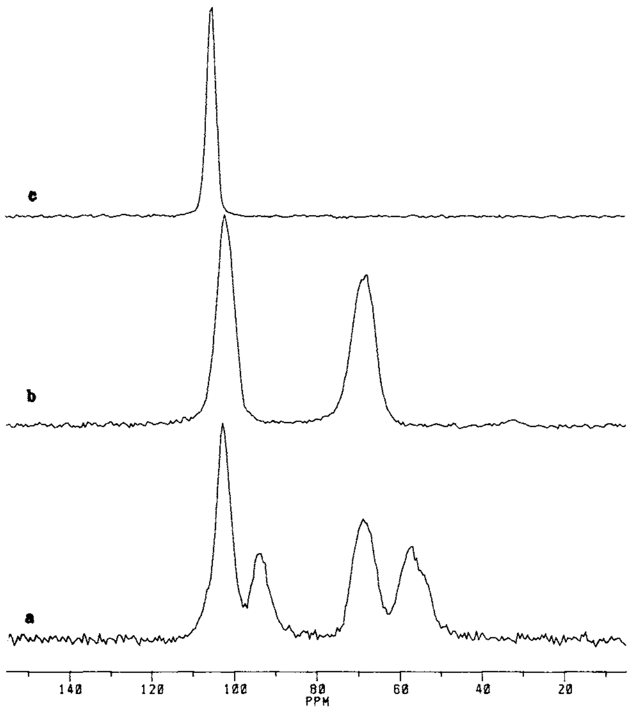

Figure 2. ^{15}N CP-MAS NMR spectra of (a) **2** (10% ^{15}N-α, 20% ^{15}N-β) at 305 K, (b) **2** (96% ^{15}N-β) at 305 K and (c) **5** (96% ^{15}N-β) at 302 K.

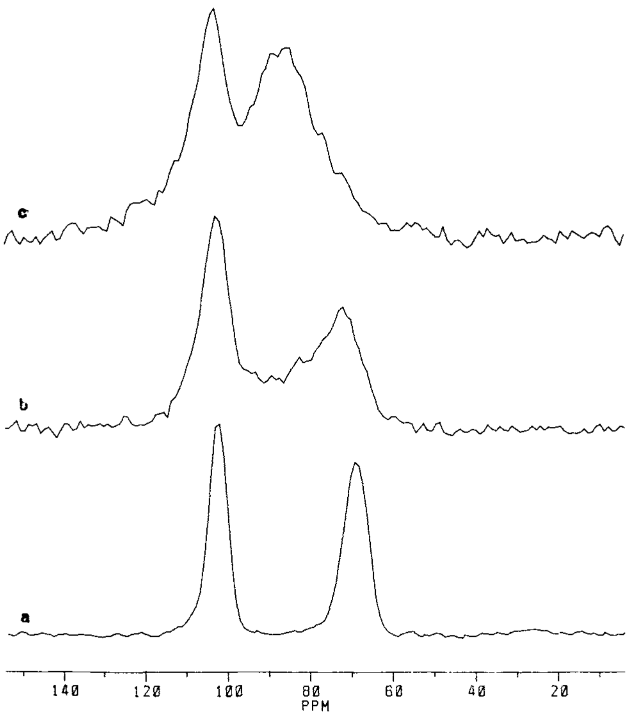

Figure 3. ^{15}N CP-MAS NMR spectra of **2** (96% ^{15}N-β) at (a) 301 K, (b) 341 K and (c) 371 K.

The ^{15}N CP-MAS signals of both N-α and N-β in **4** are relatively narrow at all temperatures and, hence, azo–hydrazone equilibrium formation is fast on the NMR time scale. The hydrazone tautomer content in **4** (i.e. that of 1,2-naphthoquinone 1-phenylhydrazone) was calculated from the equation

$$\text{Hydrazone}(\%) = \frac{\delta[^{15}\text{N}(3)] - \delta[^{15}\text{N}(4)]}{\delta[^{15}\text{N}(3)] - \delta[^{15}\text{N}(1)]} \times 100 \quad (1)$$

as described previously.[3] The hydrazone content was calculated from the $\delta(^{15}\text{N})$ values of both N-α and N-β, and very good agreement (Table 2) was obtained between the two sets of results. The thermodynamic data were calculated according to the equation

$$-\frac{\Delta G}{RT} = \ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (2)$$

where K = [hydrazone form]/[azo form], and are shown in Table 3. The values of ΔH in the liquid state are nearly twice as large as those for the solid state, while the values of ΔS are *ca* ten times larger in the liquid state, ΔS being, as expected, close to zero in the solid state.

The ^{15}N CP-MAS NMR spectrum of 2 (Fig. 2a) recorded at 305 K consists of two sets of signals (δ = 102.9, 94.2, 69.0, 57.2) for two non-equivalent molecules in the unit cell. The ^{15}N chemical shifts differ considerably from those measured in DMSO solution.[3] When the ^{15}N CP-MAS NMR spectrum of the selectively monolabelled (96% ^{15}N-β) compound **2** was measured the two most intensive signals (Fig. 2b) could be assigned to N-β. In 4-(*N*,*N*-dimethylamino)azobenzene (96% ^{15}N-β) (**5**) only one signal was observed (Fig. 2c), although the N(CH$_3$)$_2$ group has a similar electron-donating effect and bulk. The existence of (at least) two non-equivalent molecules in the unit cell in **2** can obviously be connected with azo–hydrazone tautomerism and/or intermolecular hydrogen bond formation. The signals at 102.9 (N-β) and 94.2 ppm could be ascribed to those molecules with a strong preferential azo form content, whereas those at 69.0 (N-β) and 57.2 ppm

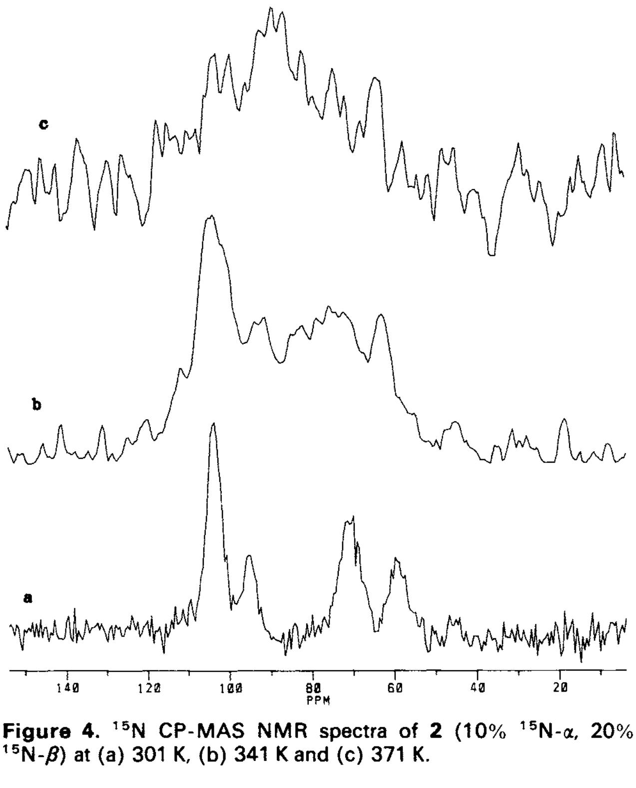

Figure 4. ^{15}N CP-MAS NMR spectra of **2** (10% ^{15}N-α, 20% ^{15}N-β) at (a) 301 K, (b) 341 K and (c) 371 K.

Table 2. Temperature dependence of the hydrazone content and the equilibrium constant K (K = [hydrazone form]/[azo form]) of 4 in the solid state

Temperature (K)	Hydrazone (%)[a]	K[a]	Hydrazone (%)[b]	K[b]
358	71.6[c]	2.52	71.0[c]	2.45
	73.6[d]	2.79	73.2[d]	2.73
305	76.1[c]	3.18	75.7[c]	3.12
	78.1[d]	3.57	78.1[d]	3.57
243	82.0[c]	4.56	81.3[c]	4.35
	83.9[d]	5.21	84.2[d]	5.33
203	86.0[c]	6.14	85.3[c]	5.80
	87.7[d]	7.13	88.2[d]	7.47
194	86.7[c]	6.52	86.1[c]	6.19
	88.3[d]	7.55	89.0[d]	8.09

[a] Calculated from δ(N-α).
[b] Calculated from δ(N-β).
[c] High-frequency signal (see text).
[d] Low-frequency signal.

belong to molecules with an increased hydrazone content.

The ^{15}N signals of **2** (96% ^{15}N-β) are broadened at higher temperatures (Fig. 3) and are shifted downfield. The ^{15}N doubly labelled compound **2** (Fig. 4) gives a more complex spectrum owing to the presence of broadened N-α signals of the azo and hydrazone forms. Azo–hydrazone equilibria in **2** arise from intermolecular interactions of two or more molecules. The broadened ^{15}N signals in **2** at higher temperatures show that proton transfer processes are slower in this compound than those in **4**, where azo–hydrazone equilibrium formation is fast on the NMR time scale and seems to be predominantly intramolecular.

It can be concluded that the model hydrazone compound with an intramolecular hydrogen bond, **1**, and the model azo compound with an intramolecular hydrogen bond, **3**, can be used as standards for the determination of the azo–hydrazone content both in the solid state and in solution. The calculations of the hydrazone content in tautomeric systems similar to that in **4** using both δ(N-α) and δ(N-β) should give almost identical results. The ^{15}N CP-MAS NMR spectra also reveal that the hydrazone contents increase slightly in the solid state with respect to those in solution and, consequently, some hydrazone form can be observed even when it was not detected in the ^{15}N NMR spectra recorded in hexadeuteriodimethyl sulphoxide solution[3] (**2**).

Table 3. Thermodynamic data for the azo–hydrazone tautomerism of 4 in C^2HCl_3 solution and in the solid state calculated according to Eqn (2) (K = [hydrazone form]/[azo form])

Nitrogen	K	ΔG[a] (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	N[b]	r[c]
N-α[d]	2.11[e]	−1.92[e]	(−6.23 ± 0.10)	(−13.88 ± 0.35)	6	0.9995
N-β[d]	2.19[e]	−2.02[e]	(−6.37 ± 0.10)	(−14.00 ± 0.34)	6	0.9995
N-α[f,g]	3.18[h]	−2.93[h]	(−3.35 ± 0.12)	(−1.47 ± 0.48)	5	0.9982
N-α[f,i]	3.57[h]	−3.23[h]	(−3.52 ± 0.13)	(−1.06 ± 0.26)	5	0.9980
N-β[f,g]	3.12[h]	−2.89[h]	(−3.23 ± 0.12)	(−1.33 ± 0.49)	5	0.9980
N-β[f,i]	3.57[h]	−3.23[h]	(−3.81 ± 0.12)	(−2.04 ± 0.50)	5	0.9985

[a] Calculated from Eqn (2). $\Delta G = -RT \ln K$.
[b] Number of temperature measurements.
[c] Correlation coefficient.
[d] C^2HCl_3 solution; data from Ref. 3.
[e] 310 K.
[f] Solid state.
[g] Calculated from high-frequency signals (see text).
[h] 305 K.
[i] Calculated from low-frequency signals.

REFERENCES

1. L. A. Fedorov, *NMR Spectroscopy of Organic and Analytical Reagents and Their Complexes with Metal Ions*, Chap. I. Nauka, Moscow (1987).
2. H. Mustroph, *Z. Chem.* **27**, 281 (1987).
3. A. Lyčka, D. Šnobl, V. Macháček and M. Večeřa, *Org. Magn. Reson.* **16**, 17 (1981).
4. A. Lyčka and V. Macháček, *Dyes Pigments* **7**, 171 (1986).
5. A. Lyčka and J. Jirman, *Dyes Pigments* **8**, 315 (1987).
6. A. Lyčka, J. Jirman and J. Podstata, *Dyes Pigments* **8**, 465 (1987).
7. B. Wehrle, H.-H. Limbach, M.Köcher, O. Ermer and E. Vogel, *Angew. Chem.* **99**, 914 (1987).
8. H.-H. Limbach and B. Wehrle, *Fresenius Z. Anal. Chem.* **327**, 61 (1987).
9. R. K. Harris, P. Jonsen, K. J. Packer and C. D. Campbell, *J. Chem. Soc., Perkin Trans. 2*, 1383 (1987).
10. H. K. Schündenhütte, in *Methoden der Organischen Chemie* (*Houben-Weyl*), edited by R. Stroh, Vol. 10/3. Georg Thieme, Stuttgart (1965).
11. A. Pines, M. G. Gibby and J. S. Waugh, *J. Chem. Phys.* **59**, 569 (1973).
12. E. O. Stejskal and J. Schaefer, *J. Magn. Reson.* **18**, 560 (1975).
13. J. Tegenfeld and U. Haeberlen, *J. Magn. Reson.* **36**, 453 (1979).
14. M. Witanowski, L. Stefaniak and G. A. Webb, *Annu. Rep. NMR Spectrosc.*, edited by G. A. Webb, Academic Press, New York, **11B**, 144 (1981).