^{13}C CPMAS NMR Study of Solid Arylazonaphthols. Evidence of ^{13}C,^{14}N Self-decoupling Induced by a Solid-state Proton Transfer Reaction

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Variable-field ^{13}C CPMAS NMR spectra for several solid arylazonaphthols are discussed. In compounds existing in the pure hydrazone form, spectral changes observed in lowering the magnetic field can be satisfactorily explained as arising from incompletely averaged ^{13}C,^{14}N dipolar coupling interactions. Similar structures which are however known to exist in the solid state as rapidly interconverting mixtures of keto–hydrazone and enol–azo tautomers do not show significant effects from the nitrogen involved in the proton transfer. This result is ascribed to ^{13}C,^{14}N self-decoupling due to a fast quadrupole relaxation of this latter nitrogen, induced by jumps in its electric field gradient which accompany the solid-state proton exchange. This information helps to establish the existence of a double minimum potential for the proton motion in these intramolecularly hydrogen bonded compounds.

Solid-state proton transfer reactions have received considerable attention in recent years.[1,2] Several cases of rapid exchange of protons across O ··· O, N ··· N and N ··· O hydrogen bonds have been shown to occur in crystals of a variety of organic compounds. In cases where exchange broadening and coalescence phenomena could be detected, variable-temperature line-shape analyses of both ^{13}C and ^{15}N CPMAS NMR spectra has led to the unambiguous characterization of this type of processes. Pertinent examples are porphyrins and related materials,[3a,b] and other nitrogen-containing heterocycles.[3c] This method is however not applicable when solid-state proton transfer rates are too fast as compared with ^{13}C chemical shift differences between exchanging tautomers. In the latter case, the problem has been approached through relaxation studies, as in carboxylic acid dimers,[4] or by correlating the changes in ^{13}C CPMAS chemical shifts and X-ray derived geometrical data with temperature, as in arylazonaphthols.[5] In these and other cases, the key question is whether the potential energy surface for the labile proton has one or two minima.

Recently, it has been suggested that a phenomenon known as self-decoupling of the ^{13}C,^{14}N residual dipolar coupling could occur in solid where a fast equilibrium is present between =N–H and =N– groups.[6,7] Self-decoupling effects have been previously invoked to account for the lack of significant dipolar coupling in ^{1}H and ^{31}P solid-state NMR spectra containing ^{1}H,^{127}I[8] and ^{31}P,^{35}Cl[9] spin pairs respectively, in both cases due to molecular motions. In the cases discussed in the present work, the self-decoupling would be caused by changes in the electronic environment around a nitrogen atom due to intramolecular proton jumps, and could be used in support of the double-minimum nature of the proton potential energy profile.[6] High-resolution ^{13}C NMR spectra of ^{14}N-containing substrates are known to display ^{13}C, ^{14}N splittings, especially when recorded at low fields.[10] This effect is seen, in general, when an (observed) spin-$\frac{1}{2}$ nucleus is adjacent to a quadrupolar one.[11] The resulting asymmetric (2:1) doublets are detected, however, provided the spin–lattice relaxation time (T_1) of the ^{14}N nuclei is sufficiently long. It has been shown that proton transfer in solids can be accompanied by corresponding jumps in the ^{14}N electric field gradient (EFG) main axis, which in turn are able to shorten the T_1(^{14}N) to a point where the expected splittings will collapse.[6] Recently, NQR measurements on solid 3,5-dimethylpyrazole where both nitrogens are involved in a triple proton transfer have shown that both ^{14}N sites possess a very short spin–lattice relaxation time.[3c] In the present work, variable-field ^{13}C CPMAS spectra are discussed for a series of proton-exchanging arylazonaphthols, where a rapid solid-state interconversion between keto–hydrazone and enol–azo tautomers takes place. The lack of significant ^{13}C,^{14}N splittings in these spectra is ascribed to self-decoupling produced by the proton transfer. In contrast, related compounds which are known to exist as only the keto–hydrazone tautomer in crystals do reveal the expected partitions. A detailed discussion is presented concerning 1-*p*-nitrophenylazo-2-naphthol in light of available ^{14}N quadrupole parameters and X-ray determined molecular geometries. The partitions are calculated using the well-tested first-order perturbative eqn. (1),[11] where S is the ^{13}C,^{14}N splitting

$$S = (9D\chi/20\nu_N)(3\cos^2\beta^D - 1 + \eta\sin^2\beta^D\cos2\alpha^D) \quad (1)$$

(defined in such a way that it is positive if the smallest peak appears at higher frequencies), D is the ^{13}C,^{14}N dipolar coupling constant, χ and η are the ^{14}N quadrupole coupling constant and the asymmetry parameter of the EFG at the nitrogen site, and β^D and α^D are the polar angles which define the orientation of the line joining the carbon and the nitrogen in the principal axis system of the EFG tensor.

Experimental

All compounds were synthesized according to known procedures. High-resolution ^{13}C CPMAS NMR spectra were recorded at 50.3 MHz on a Chemagnetics A-200 spectrometer (at Purdue University, USA) and at 25.2 MHz on a Bruker MSL-100 (at BP Research, UK). Typical spectral conditions at 50.3 MHz were: SW, 15 kHz; 90° ^{1}H pulse, 5–6 μs; recycle delay, 2 s; number of acquisitions, 5000–6000; NQS delay, 50 μs; spinning rate, 5.5 kHz (Zr rotors). At 25.2 MHz: SW, 10 kHz; 90° ^{1}H pulse, 3.3 μs; recycle delay, 5 s; number of acquisitions, 300–600; NQS delay, 50 μs; spinning rate, 4 kHz (Zr rotors). In all cases chemical shifts were referenced against hexamethylbenzene as a secondary standard (Me signal at 17.4 ppm) and then converted to the Me$_4$Si scale.

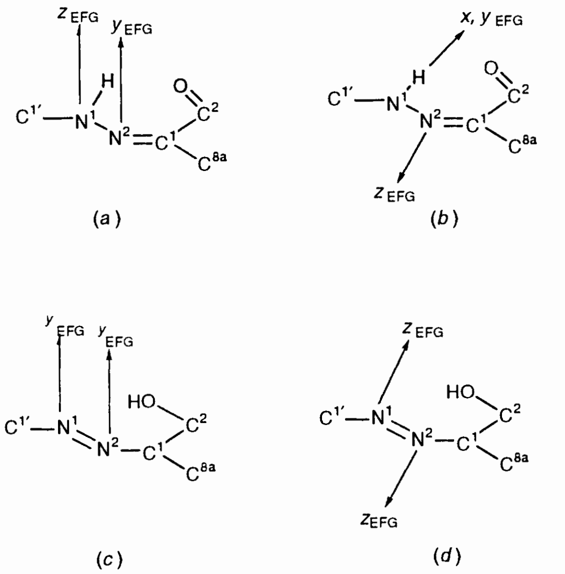
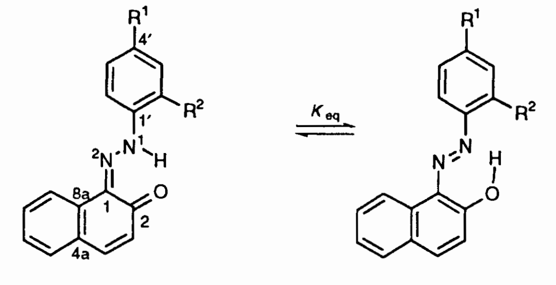


Fig. 1 Assumed orientations of the principal axes of the EFG at both nitrogen sites in keto–hydrazone (*a*, *b*) and enol–azo (*c*, *d*) tautomeric structures. The components perpendicular to the molecular plane are shown in *a*, *c* whereas those in-plane are shown in *b*, *d*.

Results and Discussion

Evidence in support of self-decoupling of ^{13}C,^{14}N residual dipolar coupling requires the study of ^{13}C CPMAS spectra at different fields for proton exchanging solids. Further, related compounds where fast tautomerism is absent are also necessary for comparison purposes. In our case suitable models are compounds existing as pure keto–hydrazone or enol–azo forms. Previous ^{13}C CPMAS reports of azo structures at low fields showed no significant ^{13}C,^{14}N effects other than an increased broadening in carbons that are both directly bonded or two bonds apart from the azo link.[12] However, the lack of significant ^{13}C,^{14}N splittings in theses cases is not due to a small ^{14}N quadrupole coupling constant (in fact, the reported value of χ in azobenzene is *ca.* -5 MHz)[13] but to an unfavourable angle β^D. The z axis of the EFG at both azo nitrogens is likely to coincide with the direction of the lone pair of electrons [Fig. 1(*d*)], so that β^D is close to 120° for the directly bonded carbons, making the factor $(3\cos^2\beta^D - 1)$ close to zero [see eqn. (1)]. The y_{EFG} axis, on the other hand, is generally believed to be perpendicular to the molecular plane [Fig. 1(*c*)]. Angles β^D for long-range positioned carbons may be more favourable, but in this case the ^{13}C,^{14}N dipolar coupling constant D is significantly reduced as it depends on r_{CN}^{-3}. In the case of hydrazones, on the other hand, two types of nitrogen occur. Quadrupole parameters in phenyl hydrazones have been previously reported as $\chi = 4.7$ MHz, $\eta = 0.3$ for N(1), and $\chi = 4.9$, $\eta = 0.5$ for N(2).[14] At the =N–H site [N(1) in **a**] one would expect the z_{EFG} axis to point in the direction of the lone pair, which in these nearly planar molecules is likely to be perpendicular to the mean molecular plane, so that $\beta^D = 90°$ for C(1′) [Fig. 1(*a*)]. Since asymmetry parameters are significant for this nitrogen atom, the use of eqn. (1) requires knowledge of α^D, *i.e.* the position of the x and y EFG axes. Two alternatives have been proposed for hydrogen bonded N–H nitrogens,[15] depending on whether the x_{EFG} or y_{EFG} axis points in the direction of the N–H bond [Fig. 1(*b*)]. Regarding nitrogen N(2), the direction of the EFG axes is assumed to be similar to azo nitrogens [Fig. 1(*c*) and (*d*)]. It is therefore apparent that 90° jumps in the direction of the z_{EFG} axis at N(1) are induced by the proton transfer reaction in the solid state, whereas no change in the direction of the quadrupolar main axis for N(2) is implied. Assuming values of χ and η for N(1) and N(2) similar to those reported for phenyl hydrazones[15] and a typical X-ray derived molecular geometry,[16] Table 1 shows the expected partitions that can be computed from eqn. (1) for the quaternary carbons of a hydrazone structure at 22.6 MHz (these values decrease by a factor of 22.6–25.2 in going to the bottom spectra of Fig. 3). The largest effect is seen to correspond to C(1′), and is due to residual coupling to N(1). Other less affected carbons are C(1) and C(2), in the latter case due to a long range effect combined with a favourable β^D angle. Reported experimental data for **4**–**6** at 22.6 MHz seem to show partitions on C(1′) which are in good agreement with that given in Table 1 when the y_{EFG} is directed along the N–H bond (+165 Hz in **4**; +174 Hz in **5** and evidences of similar effects in **6**).[17] However, the experimental results could also correspond to the alternative selection of EFG axes if the quadrupole coupling constant χ for N(1) were significantly decreased with respect to phenyl hydrazones due to strong intramolecular hydrogen bonding. The latter effect has been previously proposed to occur in a variety of hydrogen bonded compounds.[15] In any case, both Table 1 and reported results agree in showing large partitions for C(1′) at 22.6 MHz. The most clear spectrum is that of compound **4**, which is reproduced in Fig. 2 along with that recorded at 50.3 MHz. In agreement with the predictions of Table 1, a negative ^{13}C,^{14}N splitting of -90 Hz is seen in the signal corresponding to C(2). Furthermore, the changes in the region 130–150 ppm on lowering the field can be satisfactorily explained (as shown in Fig. 2) by a combination of a positive splitting at C(1′) of +165 Hz with a negative one at C(4′) of -120 Hz. The latter arises from the presence of the nitro group attached to C(4′), and can be compared with the predictions from eqn. (1) by assuming a typical value of χ for aromatic nitro groups (*i.e.* about -1.5 MHz),[18] collinearity between r_{CN} and the z_{EFG} axis (leading to $\beta^D = 0$), and $r_{CN} = 1.45$ Å.[16] In this case eqn. (1) predicts a negative splitting of -140 Hz, again in good agreement with the experimental results. Since the two partitions at C(1′) and C(4′) are of opposite sign and asymmetric (2:1), the appearance of the spectrum would consist of three lines with ratio 1:4:1, close to that observed (Fig. 2). A combination of small effects both from N(1) and N(2) produces a broadening on C(1) which is also apparent in the 22.6 MHz spectrum of Fig. 2. Thus, all major changes in the variable-field spectra of **4** can be satisfactorily explained on the basis of the influence of N(1), N(2) and the NO$_2$ group.



a **b**

1 R^1 = N=N-Ph, R^2 = H
2 R^1 = R^2 = H
3 R^1 = MeO, R^2 = H
4 R^1 = NO$_2$, R^2 = H
5 R^1 = Me, R^2 = NO$_2$
6 R^1 = Cl, R^2 = NO$_2$

We now discuss the corresponding results for related compounds which undergo fast proton transfer between tautomers **a** and **b**. Fig. 3 (top) shows ^{13}C CPMAS NMR spectra for compounds **1**–**3** recorded at 50.3 MHz using the NQS technique, which distinguishes the quaternary carbons. Complete

Table 1 Calculated $^{13}C,^{14}N$ splittings according to eqn. (1) for a typical hydrazone structure such as **a** at 22.6 MHz[a]

	N(1)				N(2)			
C	r_{CN}/Å	β^D	α^D	S/Hz	r_{CN}/Å	β^D	α^D	S/Hz
1′[b]	1.41	90	60	+291	2.39	90	0	+27
1[b]	1.41	90	30	+215				
2[c]	2.31	90	90	+75	1.32	60	0	−40
8a[c]	2.31	90	0	+30				
	—	—	—	—	2.40	30	0	−74
	—	—	—	—	2.40	90	0	+27

[a] In all cases, $\chi(N1) = -4.7$ MHz, $\eta = 0.3$; $\chi(N2) = -4.9$ MHz, $\eta = 0.5$, and the molecular geometry is approximated from the reported X-ray crystal strucutres. [b] Two values are given corresponding to the different selection of EFG axes: x_{EFG} (top) or y_{EFG} (bottom) pointing along the N–H bond [Fig. 1(*b*)]. [c] These carbons are too far from N(1).

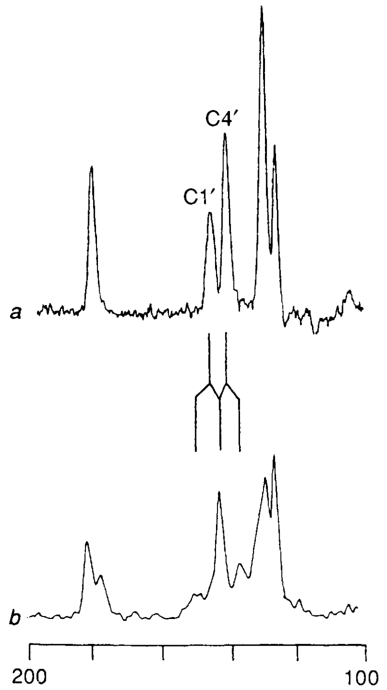


Fig. 2 ^{13}C CPMAS spectra of the quaternary carbons of solid 1-*p*-nitrophenylazo-2-naphthol **4** at the following frequencies: (*a*) 50.3, (*b*) 22.6 MHz (this latter spectrum has been reproduced, with permission, from ref. 17, ©1986, John Wiley & Sons, Ltd.). The signals assigned to carbons C(1′) and C(4′) are indicated, as well as the corresponding partitions in going to the lower field (see text). Horizontal scale is in ppm from Me_4Si.

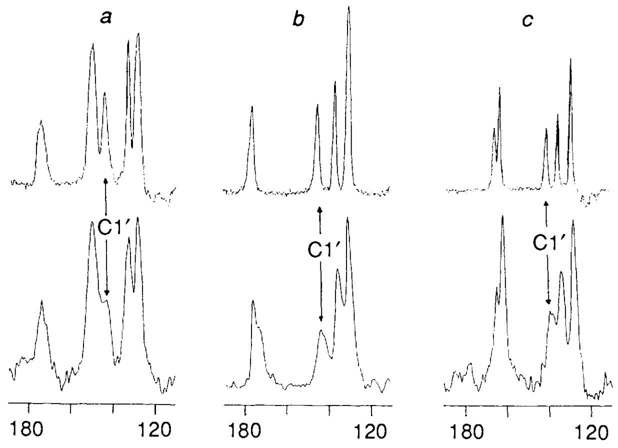


Fig. 3 ^{13}C CPMAS NMR spectra of the quaternary carbons of solid arylazonaphthols: (*a*) compound **1**; (*b*) compound **2**; (*c*) compound **3**. Spectra shown on the top have been recorded at 50.3 MHz whereas those on the bottom at 25.2 MHz. In all cases the signal assigned to C(1′) has been marked with an arrow. Horizontal scales are in ppm from Me_4Si.

assignment of ^{13}C signals of both protonated and quaternary carbons of **2** and **3** has been previously made both in $CDCl_3$ solution and in the solid state.[5] Solution data for **1** have also been reported.[19] As discussed in a previous work,[5] the chemical shift of C(2) is able to monitor the position of the equilibrium between tautomers **a** and **b**, covering a range of *ca.* 30 ppm [*i.e.* $\delta(C2) \approx 180$ in **a** and 150 in **b**]. According to the values observed for **1**–**3** in the solid state (Table 2), all three compounds occur in crystals as rapidly interconverting mixtures of **a** and **b** tautomers, though **a** seems to be the preferred form in **1** and **2**. The comparison of both sets of spectra presented in Fig. 3 reveals a close similarity at the two fields. In view of the fact that carbons bonded to =N–H groups are normally split at low fields,[7] it is noteworthy that $^{13}C,^{14}N$ effects on the signal ascribed to C(1′) are only reduced to a distinct broadening. This is especially so in view of the large ^{14}N quadrupole coupling constants reported for N(1) in phenyl hydrazones (about 4.5 MHz).[14] The only clearly visible partition is that of C(2) in **2** (−60 Hz; with hints of similar effects in **1** and **3**), and is due to a long range effect from N(2), as explained above both in magnitude and sign. Indeed, we also ascribe the small broadening effects noticed at 25.2 MHz in the signals corresponding to C(1′) in **1**–**3** to long range coupling to N(2). The effects due to N(1), on the other hand, are likely to be collapsed by self-decoupling induced by the proton exchange. If self-decoupling were not invoked, then all partitions on C(1′) should be seen as averages of those occurring in the extreme hydrazone and azo tautomers, *i.e.* $S_{av} = p_aS_a + p_bS_b$.[6] Since S_b for C(1′) is very small (see above), one would expect a somewhat reduced S_{av} in comparison with a pure hydrazone such as **4**. This reduction in S_{av} should be more noticeable as we proceed in the order **1**–**3**, since this is the order of increasing azo content at equilibrium. However, all three bottom spectra in Fig. 3 show similar broadening effects on C(1′), consistent with the presently discussed picture that this is due to a long range effect due to C(1′), N(2) coupling, which is independent of the hydrazone/azo ratio.

In conclusion, it has been shown that variable-field ^{13}C CPMAS spectra of solid-state proton-exchanging compounds such as arylazonaphthols show evidence of the existence of a self-decoupling of residual $^{13}C,^{14}N$ dipolar coupling effects due to fast ^{14}N spin–lattice relaxation induced by the proton jumps. In comparison, compounds existing as only hydrazone tautomers do show the expected partitions, as can be calculated from reported quadrupole coupling constants, X-ray determined molecular geometries, and using a simple first-order perturbative equation to calculate the residual dipolar effects.

The presently discussed evidence for self-decoupling provides additional support to the idea of a double-minimum potential energy profile for the proton motion in the studied compounds.

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Table 2 ^{13}C CPMAS NMR chemical shifts of quaternary carbons in compounds **1**–**4** at both studied fields[a]

	1		**2**		**3**		**4**	
C	50.3[b]	25.2[b]	50.3[b]	25.2[b]	50.3[b]	25.2[b]	50.3[b]	22.6[b,c]
1	128.4	127.7	128.2	128.2	128.8	128.1	131.5	130.9
2	175.1	175.1	174.1	175.7 173.3	163.5	164.1	181.6	182.5 178.4
4a	128.4	127.7	128.2	128.2	128.8	128.1	128.8	128.1
8a	133.1	132.1	134.2	133.8	134.3	134.1	128.0	129.4
1′	144.6	144.5	143.0	142.8	139.5	139.5	147.2	150.7 143.4
4′	150.0	150.1			161.2	161.0	142.6	143.4 138.0

[a] All chemical shifts are reported in ppm downfield from Me_4Si. [b] ^{13}C Resonance frequency/MHz. [c] From ref. 17.

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