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^{13}C Detected Scalar Nitrogen−Nitrogen Couplings Across the Intramolecular Symmetric NHN Hydrogen Bond of Proton Sponge

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The discovery of scalar couplings across hydrogen bonds A−H···B has substantially increased the potential of NMR spectroscopy in the area of hydrogen bond research.[1−19] Such couplings can only be observed in the slow hydrogen bond exchange range. This range is often realized in biomolecules, whereas in the case of small hydrogen-bonded complexes special low-temperature NMR-techniques need to be employed.[17,18] One of the most puzzling effects observed was that $^{2h}J_{AB}$ couplings tend to be larger than $^{1h}J_{HB}$ couplings, a phenomenon which we have attributed to a negative contribution to this coupling.[19] Whereas $^{2h}J_{FF}$ couplings and $^{2h}J_{NF}$ couplings ($N \equiv {}^{15}N$) are about 100 Hz and larger,[1,2] $^{2h}J_{NN}$ couplings have been observed in nucleic acid base pairs up to 10 Hz.[1,2,5] These values depend in a very sensitive way on the hydrogen bond geometry. Recently, we have proposed—on the basis of DFT calculations—that the maximum coupling constant $^{2h}J_{NN}$ of about 25 Hz should be found in the case of a symmetric, and hence shortest, NHN hydrogen bond.[19,20] In our search for such couplings our interest turned to the well-known proton sponge 1,8-bis(dimethylamino)-naphthalene-H^+ ($DMANH^+$, Figure 1) which contains an already classical intramolecular low-barrier $[N\cdots H\cdots N]^+$ hydrogen bond.[21] In this paper we demonstrate that this molecule is also characterized by a large $^{2h}J_{NN}$ coupling across the hydrogen bond mediated by the proton. For this purpose, two problems had to be solved. The problem of the measurement of scalar couplings between the two chemically equivalent ^{15}N atoms was solved by synthesis of the ^{15}N doubly labeled material and by measuring the ^{13}C signals of the neighboring carbon atoms (which destroy the nuclear spin

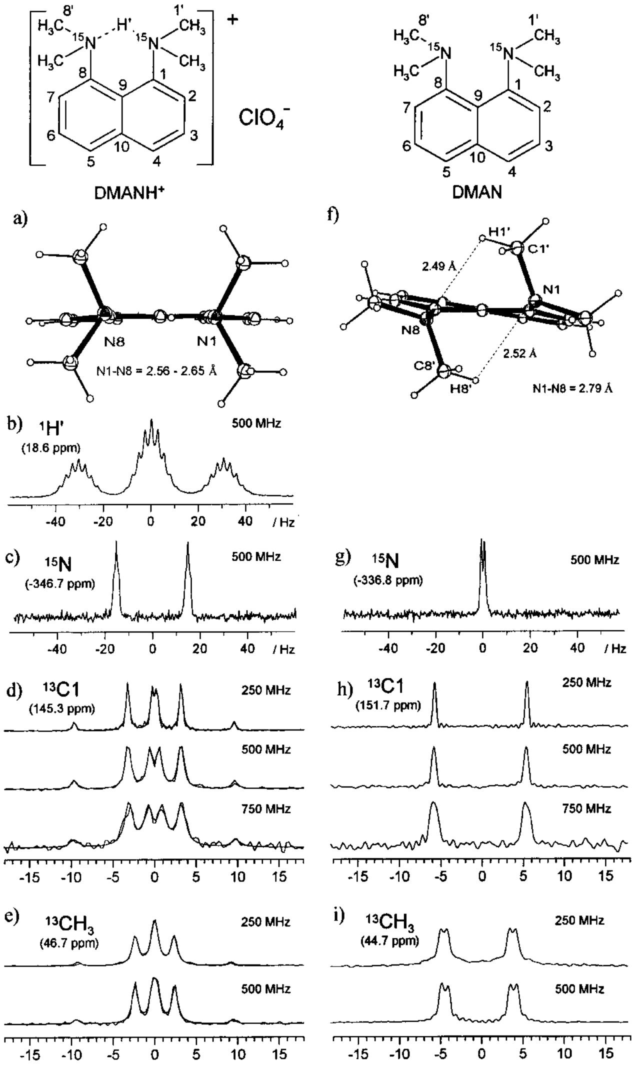

Figure 1. NMR spectra of ^{15}N doubly labeled $DMANH^+ClO_4^-$ (left) and DMAN (right) dissolved in acetonitrile-d_3. The X-ray crystal structures of $DMANH^+BF_4^-$ [23] (a) and DMAN[24] (f) are depicted for comparison. The N−N distances listed in (a) refer to a variety of counterions.[25] (b) ^1H signal of the bridging proton. (c) and (g) ^{15}N spectra, (d) and (h) $^{13}C\{^1H\}$ spectra of C1 at three different magnetic fields (250, 500, and 750 MHz), (e) and (i) $^{13}C\{^1H\}$ spectra of C1′ at two different magnetic fields (250 and 500 MHz). All NMR scales are in Hz.

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Table 1. Observable Parameters from $^{13}C\{^{1}H\}$ for C1 and CH_3 Atoms for $DMANH^+$ at Different Magnetic Fields

carbon nucleus	^{1}H Larmor frequency/ MHz	$\Delta\nu^{A}$/Hz	$\Delta\nu^{B}$/Hz	$\Delta\nu^{C}$/Hz
C1	250	19.15	6.41	0.60
	500	19.35	6.40	1.12
	750	19.68	6.34	1.48
CH_3	250	18.17	4.72	~0.3
	500	18.30	4.74	~0.5

Table 2. NMR Data of DMAN and Its Protonated Form, Obtained Directly from the Spectra or Indirectly from the Simulation

	DMAN	DMAN * $HClO_4$
δ N/ppm vs CH_3NO_2	−336.8	−346.7
δ H/ppm	-	+18.6
J(C1−N1) = J(C8−N8)/Hz	−11.1	−7.4 (±0.5)[a]
J(C1−N8) = J(C8−N1)/Hz	0 (±0.5)	+1.0 (±0.5)[a]
J(C1′−N1) = J(C8′−N8)/Hz	−8.3	−5.8 (±0.5)[b]
J(C1′−N8) = J(C8′−N1)/Hz	0.8	+1.0 (±0.5)[b]
J(H1′−H′) = J(H8′−H′)/Hz	-	+2.6
J(N1−H′) = J(N8−H′)/Hz	-	−30.4
J(N1−N8)/Hz	0 (±0.5)	+8.7 (±0.5)[a,b]
$\|\Delta^{15}N\{^{13}C1\}\|$/ppb	-	2.6 (±0.8)[a]
$\|\Delta^{15}N\{^{13}C1'\}\|$/ppb	-	1.6 (±0.8)[b]

[a] Results obtained from the analysis of the C1 signal (Figure 1d). [b] Results obtained from the analysis of the C1′ signal (Figure 1e).

symmetry) at different magnetic fields. The second problem was the proof of a coupling pathway across the hydrogen bond in $DMANH^+{-}^{15}N_2$, in view of a possible intramolecular contribution $^{4}J_{NN}$. This problem was solved by comparison with nonprotonated $DMAN{-}^{15}N_2$.[22]

The results of our NMR measurements are illustrated in Figure 1. To show the structural differences between the not-protonated and protonated form of proton sponge the crystal structures[23,24] of DMAN and $DMANH^+BF_4^-$ are included in Figure 1a,f.

Figure 1b shows the well-known low-field triplet of the hydrogen-bonded proton of $DMANH^+ClO_4^-{-}^{15}N_2$ which is coupled to both ^{15}N nuclei, exhibiting a coupling constant of 30.5 Hz. Each line component is additionally split into 13 subcomponents because of three-bond couplings to 12 magnetically equivalent methyl protons, with a coupling constant of 2.7 Hz.[26] The bridging proton gives rise to a doublet in the ^{15}N spectrum at −346.7 ppm (Figure 1c).[27]

Figure 1d,e shows a superposition of the experimental and calculated $^{13}C\{^{1}H\}$ signals of the carbon in position 1 and 1′, respectively, at different magnetic fields, 17.7, 11.8, and 5.9 T. Each ^{13}C signal in Figure 1d consists of three line pairs with the separations $\Delta\nu^{A}$, $\Delta\nu^{B}$, and $\Delta\nu^{C}$ (outer, intermediate, and inner lines respectively; Table 1), indicating the presence of a high-order spin system of the ABX type.[28] The degeneracy between the two nitrogen atoms A and B is removed by the different isotopic substitution leading to the chemical shift difference $\Delta^{15}N\{^{13}C\}$. This parameter, as well as the NN and the CN coupling constants including their relative signs, can be directly calculated from these line separations or line shapes obtained in at least at two different magnetic fields.[29] The results obtained are assembled in Table 2, where it was assumed that the one-bond $^{1}H{-}^{13}C$ couplings are negative.[30] We note that within the margin of error, the simulation of both ^{13}C signals (C1 and CH_3) independently gave the same value of $^{2h}J_{NN} = 8.7 \pm 0.5$ Hz which demonstrates that the method used gives consistent results.

By contrast, as shown in the right column of Figure 1, the ^{13}C NMR signals of $DMAN{-}^{15}N$ are of the first-order type, indicating already a NN coupling which is smaller than about 0.5 Hz. Figure 1g shows the ^{15}N spectrum, consisting of a doublet with the coupling 1.4 Hz arising from the adjacent proton H2(H7) of the naphthalene ring. Figure 1, parts h and i, depict the $^{13}C\{^{1}H\}$ signals of carbon 1 and 1′, respectively, at different magnetic fields. In the first case we observe a doublet with the splitting of 11.1 Hz, which is independent of magnetic field, corresponding to the one-bond coupling to the nitrogen atom. In the second case a doublet of doublets is observed with the splittings assigned as $^{1}J_{C1'-N1} = 8.3$ Hz and $J_{C1'-N8} = 0.8$ Hz. Attempts to simulate the signal pattern in terms of the ABX spin system theory with a substantial NN coupling were not successful. Therefore, we speculate that $J_{C1'-N8}$ is caused by a very weak C−H···N hydrogen bond in DMAN, that is, that $J_{C1'-N8} = {}^{2h}J_{C1'-N8}$ which seems to be consistent with the crystal structure in Figure 1f.

The NN coupling in $DMANH^+$ is not particularly large if compared to other values found for asymmetric NHN hydrogen bonds,[1,2,5] which supports the existence of a double well for the proton motion in this molecule, as postulated previously.[21c] However, the value obtained here is the first example of an N−N coupling constant across a symmetric NHN hydrogen-bonded system up to date. Moreover, we showed that this coupling is indeed mediated by the addition of a bare proton forming the intramolecular hydrogen bond, and only to a minor extent by a coupling pathway along the molecular skeleton. The addition of the proton enables a better overlap of the two nitrogen sp^3-orbitals with the 1s orbital of the proton, as discussed previously for the sp-case of $CNHNC^-$.[19] This result could not have been obtained in the case of an intermolecular hydrogen bond as the removal of the proton destroys the bridge.

In conclusion, we have shown an efficient stratagem for the determination of $^{2h}J_{NN}$ coupling constants of symmetric hydrogen bridges and have reported the first example of such coupling with the value of about 8.7 Hz. Currently, we are trying to measure similar couplings in systems exhibiting shorter and stronger NHN hydrogen bonds. The method is limited to compounds exhibiting sufficiently large ^{13}C isotope effects $\Delta^{15}N\{^{13}C\}$ on the nitrogen chemical shifts which should be larger than about 0.02 ppm as the spectral X-part of AA′X spin systems is field-independent.

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Supporting Information Available: A detailed description of the simulation of the spectra of Figure 1 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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