

Hydrogen/deuterium isotope effects on the ^{15}N NMR chemical shifts and geometries of low-barrier hydrogen bonds in the solid state¹

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Abstract

In this study, hydrogen/deuterium isotope effects on the geometry and the ^{15}N NMR chemical shifts of strongly hydrogen bonded, solid hydrogen-bisisocyanide salts of the type $[\text{M}-\text{C}\equiv\text{N}\cdots\text{L}\cdots\text{N}\equiv\text{C}-\text{M}]^-\text{X}^+$ **1** ($\text{L} = \text{H}, \text{D}$) are described both experimentally and theoretically. The theoretical studies include MP2/6-31+G(d,p) ab initio calculations of geometries and subsequent calculations of the proton and the deuteron vibrational states in the hydrogen bond of the model compounds $[\text{C}\equiv\text{N}\cdots\text{L}\cdots\text{N}\equiv\text{C}]^-\text{Li}^+$ **1a** ($\text{L} = \text{H}$) and **1b** ($\text{L} = \text{D}$). The Li^+ , at various fixed C–Li distances, represents the external electric field. Furthermore, the ^{15}N NMR chemical shifts were calculated using the Individual Gauge for Localized Orbitals method. The calculated isotope effects depend strongly on the asymmetry of the hydrogen bond caused by the influence of the Li^+ cation. These results are compared with those of a solid state ^{15}N cross polarization, magic angle spinning NMR study of the metal-stabilized salts **1c** and **1d**, where $\text{M} = \text{Cr}(\text{CO})_5$, $\text{X}^+ = \text{AsPh}_4^+$ and $\text{L} = \text{H}$ or D , as well as of those of **1e** and **1f**, $\text{M} = \text{Cr}(\text{CO})_5$, and $\text{X}^+ = \text{NnPr}_4^+$. In the case of **1c** and **1d** the hydrogen bond is symmetric and isotope effects on the ^{15}N NMR chemical shifts are not observed, as predicted theoretically. By contrast, and in agreement with the calculations, large isotope effects are observed for **1e** and **1f**, where the hydrogen bond symmetry is lifted by a strong interaction with the counterion. So far, solid state hydrogen/deuterium isotope effects on the NMR chemical shifts of hydrogen bonded nuclei have, to our knowledge, not been observed and may be used as a promising novel tool in hydrogen bond research.

Keywords: Isotope effect; Solid state NMR spectroscopy; Ab initio calculation; Hydrogen bonding

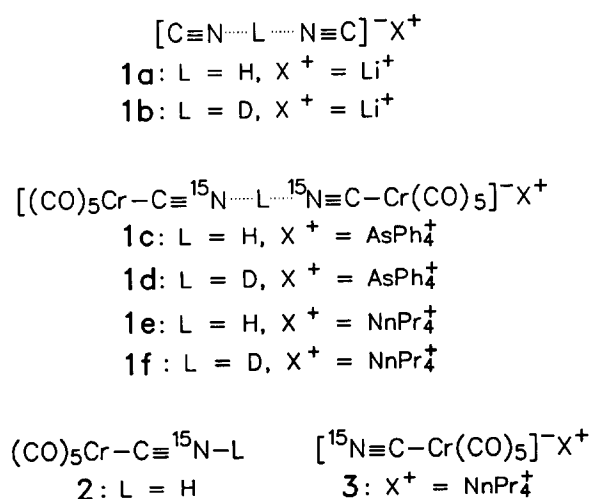
1. Introduction

In recent years, high resolution ^{15}N solid state NMR spectroscopy carried out under the conditions of ^1H – ^{15}N cross polarization (CP), magic angle spinning (MAS) and ^1H decoupling has

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proven to be a useful tool in the study of kinetic hydrogen/deuterium (H/D) isotope effects on solid state proton transfer reactions in weak hydrogen bonds [1]. Here, we show that this method is also capable of giving structural information on very strong hydrogen bonds where proton transfer only involves a low or a vanishingly small barrier [2]. These systems are of special interest because of their role as postulated intermediates in a number of enzymic reactions [3]. The novel information stems from the observation and the interpretation of H/D isotope effects on the isotropic ^{15}N NMR chemical shifts of intermolecular $^{15}\text{N}-\text{H}\cdots^{15}\text{N}$ hydrogen bonds in the solid state. To our knowledge, only intramolecular liquid state isotope effects on chemical shifts have been reported to date [4]. The model hydrogen bonded system considered in this paper is $[\text{M}-\text{C}\equiv\text{N}\cdots\text{L}\cdots\text{N}\equiv\text{C}-\text{M}]^-\text{X}^+$ **1**, with hydron $\text{L} = \text{H}$ or D . ^{15}N CPMAS NMR experiments are presented for the ^{15}N labeled compounds **1c** to **1f** (Scheme 1), as well as for the acid **2** and the base **3**. Some preliminary experimental results concerning the compounds with $\text{L} = \text{H}$ have been reported previously [5]. Ab initio calculations were performed on the simplified systems $[\text{C}\equiv\text{N}\cdots\text{L}\cdots\text{N}\equiv\text{C}]^-\text{Li}^+$ **1a** ($\text{L} = \text{H}$) and **1b** ($\text{L} = \text{D}$). Based on calculated geometries and ^{15}N NMR chemical shifts, a stratagem is proposed in order to estimate the correction arising from the hydron dynamics.



Scheme 1.

2. Results and discussion

In Fig. 1, the experimental ^{15}N CPMAS NMR spectra of **1c** to **1f** are compared with those of the free acid **2** and the salt **3**. Compound **2** contributes a signal at 145 ppm and compound **3** at 283 ppm with respect to external $^{15}\text{NH}_4\text{Cl}$. (The ^{15}N chemical shifts can be converted into the nitromethane scale using the equation $\delta(\text{CH}_3\text{NO}_2) = \delta(\text{NH}_4\text{Cl}) - 352.9$ ppm according to Ref. [6].) By contrast, **1c** gives rise to a single line at 205 ppm [5], indicating that the two nitrogen atoms are equivalent and in agreement with the C_2 symmetry of this bridge observed by X-ray crystallography [5]. The very short N–N distance of 2.569(7) Å indicates the formation of a low-barrier hydrogen bond. As follows from Fig. 1, deuteration of the symmetric bridge leads only to a small shift of the ^{15}N signal to 204 ppm for **1d**.

By contrast, **1e** gives rise to two signals at 219 and 189 ppm [5], indicating that the symmetry of the hydrogen bond, i.e. the equivalence of the two nitrogen atoms, is lifted because of intermolecular interactions. The proton density distribution function is therefore no longer symmetric with respect to the hydrogen bond centre. In other words, replacing one cation X^+ by another leads

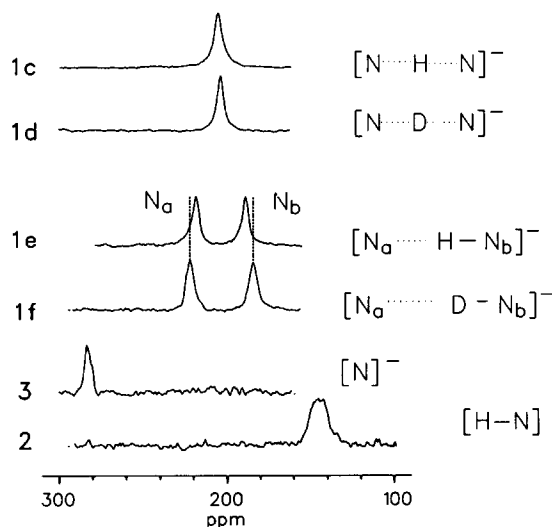


Fig. 1. 9.12 MHz ^{15}N CPMAS NMR spectra of compounds **1c** to **1f**, **2** and **3** at room temperature, 2 kHz spinning speed, 9 μs 90° pulses.

to a proton displacement in the bridge. Deuteration of the asymmetric bridge leading to **1f** has a large effect on the ^{15}N chemical shifts as shown in Fig. 1. For the high-field nitrogen atom involved in the shorter nitrogen–hydron bond we observe an upfield shift of $^1\Delta^{15}\text{N}(\text{D}) = \delta(^{15}\text{N}_a\text{--H}) - \delta(^{15}\text{N}_a\text{--D}) = -3$ ppm. The superscript 1 indicates that the ^{15}N atom experiencing the shift is one bond away from the deuteration site, according to the usual nomenclature [4]. By contrast, for the low-field nitrogen involved in the longer nitrogen–hydron bond, an opposite low-field shift across the hydrogen bond of $^1\Delta^{15}\text{N}(\text{D}) = \delta(^{15}\text{N}_a\cdots\text{H}) - \delta(^{15}\text{N}_b\cdots\text{D}) = 4$ ppm is observed. We note that in our previous studies of high-barrier hydrogen bonded systems, one-bond H/D isotope effects on ^{15}N chemical shifts could never be detected [1]. Therefore, the fact that $^1\Delta^{15}\text{N}(\text{D}) \neq 0$ is a criterion for the formation of a low-barrier hydrogen bond in **1**.

In order to model the above-mentioned results MP2/6-31+G(d,p) ab initio calculations were performed on the linear system $[\text{Cl}\equiv\text{N1}\cdots\text{L}\cdots\text{N2}\equiv\text{C2}]^-\text{Li}^+$ **1a,b** using the GAUSSIAN 92 program package [7]. The anion geometry was optimized at different fixed C2–Li distances.

The dynamic corrections for the interatomic distances N1–L and N1–N2 were performed in the crude adiabatic approximation. This can be justified by the slow N1–N2 motion (275 cm^{-1}) compared with the collinear proton motion (1329 cm^{-1}) in the anion (C2–Li = ∞) of **1a**. The iterative procedure for the dynamically corrected interatomic distances is as follows:

- (1) The potential energy function $V(x)$ for the collinear hydron motion is calculated pointwise at fixed heavy atom positions. The variable x measures the position of the hydron.
- (2) The Schrödinger equation for the anharmonic collinear hydron motion is solved using known methods [8]. For simplicity the masses of the heavy atoms were set to infinity. The expectation value $\langle\Psi_0|x|\Psi_0\rangle$, where $\Psi_0(x)$ represents the anharmonic vibrational ground state wavefunction of the hydron, is used for the dynamic N1–L correction.
- (3) The heavy atom coordinates are reoptimized

keeping C2–Li and the dynamically corrected N1–L distance constant.

This procedure is repeated until self-consistency is achieved; a convergence criterion of 10^{-3} Å was used.

The IGLO (Individual Gauge for Localized Orbitals) method was applied using the basis set II [9] for the calculation of isotropic absolute ^{15}N chemical shifts $\sigma(x)$; the relative chemical shifts $\delta(x)$ are referenced to the calculated absolute shift of the isolated NH_4^+ cation. The values of $\delta(x)$ were calculated traditionally for the optimized minimum geometries as well as for the dynamically corrected structures. In the latter case the ^{15}N chemical shifts were vibrationally averaged by means of $\langle\Psi_0|\delta(x)|\Psi_0\rangle$. Calculated geometries and chemical shifts are summarized in Table 1. The amount of dynamic corrections for interatomic distances, defined by minimum geometries, is maximal for symmetrical H-bonds with low barriers, such as C2–Li = ∞ . Here, the energy barrier from the energy minimum ($C_{\infty v}$) to the transition structure (D_{oh}) for the proton transfer is calculated to be $\Delta E = 0.8\text{ kJ mol}^{-1}$ (see Figs. 2d and 2h); the N1–L corrections are 0.12 Å , and the $\delta(^{15}\text{N})$ corrections are 28 ppm. In going from H to D the N1–N2 distances and ^{15}N chemical shifts, which

Table 1

Results of ab initio MP2/6-31+G(d,p) and IGLO calculations of **1a**. (a) Minimum geometries for fixed C2–Li distances (Å), and IGLO-calculated ^{15}N chemical shifts $\delta = \sigma_{\text{ref}} - \sigma$; $\sigma_{\text{ref}}(^{15}\text{N}) = 244.43$ (NH_4^+). (b) Dynamically corrected interatomic distances (Å) and ^{15}N chemical shifts δ (ppm) for L = H, D

	C2–Li	5	7	9	∞
(a)	N1–L	1.0672	1.0860	1.0977	1.1411
	N1–N2	2.6851	2.6455	2.6257	2.5790
	δN1	201.9	210.0	214.7	229.1
	δN2	305.6	299.1	294.6	281.8
(b)	N1–H	1.1220	1.1813	1.2131	1.2675
	N1–D	1.1001	1.1538	1.1840	1.2675
	N1–N2(H)	2.6378	2.5792	2.5578	2.5350
	N1–N2(D)	2.6572	2.6019	2.5701	2.5350
	$\delta\text{N1(H)}$	213.1	231.2	240.8	257.3
	$\delta\text{N2(H)}$	296.7	281.5	272.7	257.3
	$\delta\text{N1(D)}$	208.3	222.5	234.2	257.3
	$\delta\text{N2(D)}$	300.5	289.0	278.5	257.3

are unchanged in conventional static ab initio calculations, show differences of dynamic origin of up to 0.02 Å and 9 ppm respectively. These are maximal in unsymmetrical H(D) potentials with considerable anharmonicity of the hydron motion.

The influence of the C2–Li distance on the potential for the hydron motion is shown in Fig. 2. For short C2–Li distances an asymmetric H-bond is obtained, with a symmetric single well located close to the nitrogen atom N1 opposite Li⁺, thus minimizing the Coulomb interaction. As C2–Li is increased, the potential well shifts in the direction of the hydrogen bond centre and the asymmetric character of the potential becomes maximal. Further increase of the C2–Li distance leads to a symmetric H-bond with a low-barrier double well potential. The asymmetry of the potential for intermediate C2–Li distances (7 Å, 9 Å) leads to a strong isotope effect on the mean hydron position $\langle x(L) \rangle$ and generally on the geometry of

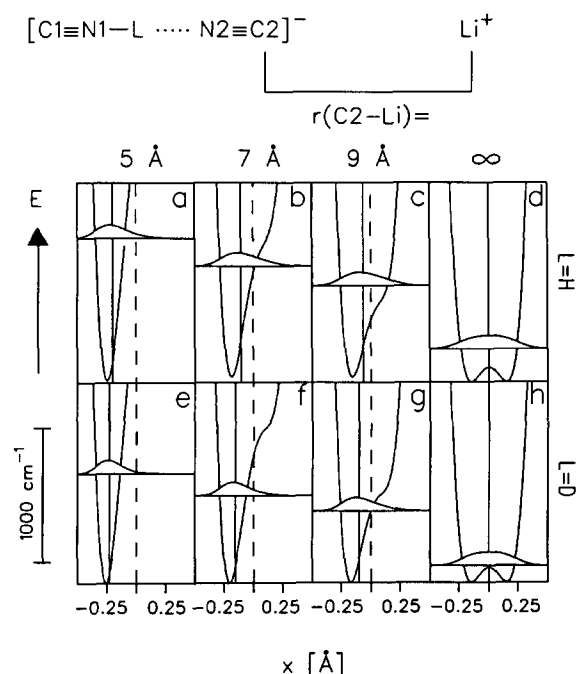


Fig. 2. Calculated potential curves, vibrational states and wavefunctions of the proton (a) to (d) and of the deuteron (e) to (h) motion in **1a** and **1b**, respectively. The abscissa is the distance x between the hydron and the H-bond center which is indicated by the broken vertical line. The mean hydron positions $\langle x(L) \rangle$ are symbolized by the full vertical lines.

the H-bond (Table 1): the length of the H-bond, i.e. the N1–N2 distance, is shorter for the protonated bridge than for the deuterated one. N1–L, the shorter of the two N–L distances, is longer for L = H than for L = D. Consequently, L...N2 is shorter for L = H than for L = D. Such an isotope effect on H-bonds was described by Ubbelohde and Gallagher [10] for a large number of mutually coupled strong H-bonds. To our knowledge, the calculations reported here model the Ubbelohde effect for an isolated low-barrier hydrogen bond for the first time.

The isotope effects on the ^{15}N chemical shift $^1\Delta^{15}\text{N}(\text{D})$ as a function of the chemical shift $\delta^{15}\text{N}(\text{H})$ for the calculated systems **1a,b** and the experimental systems **1c** to **1f** are shown in Fig. 3. Although we did not expect a complete agreement of the experimental and the calculated curves, we note a similar behavior. The shape of the curves can be understood in the following way: Generally the ^{15}N isotropic chemical shift shows a non-linear dependence on the N–L distance. At short distances, N1–L, the nitrogen absorbs at high field. In this case, replacing H by D leads to an upfield shift ($^1\Delta^{15}\text{N}(\text{D}) > 0$) because of the reduction of the N1–L distance mentioned before. However, at long distances, L...N2, the nitrogen absorbs at

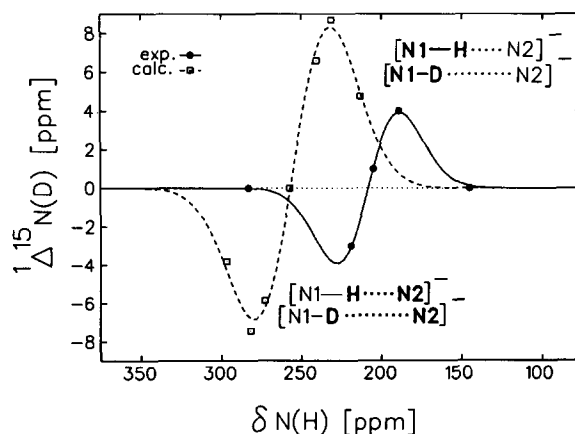


Fig. 3. H/D isotope effects $^1\Delta^{15}\text{N}(\text{D}) = \delta^{15}\text{N}(\text{H}) - \delta^{15}\text{N}(\text{D})$ on the isotropic ^{15}N chemical shifts of **1** as a function of $\delta^{15}\text{N}(\text{H})$. Open squares: calculated vibrationally averaged values for different distances C2–Li in **1a** and **1b**; filled circles: experimental values for the substances **1c** to **1f**, **2** and **3**. The positive values of $^1\Delta^{15}\text{N}(\text{D})$ refer to N1 and the negative to N2 as defined in Fig. 2.

low field and the isotope effect on the chemical shift is reversed ($^1\Delta^{15}\text{N}(\text{D}) < 0$), because now this distance is increased by deuteration. By contrast, the symmetric potentials show no effect. This is the case for the almost separated acid–base pair, as well as for the completely symmetric H-bond. This phenomenon leads to the typical “dispersion-like” form of the function $^1\Delta^{15}\text{N}(\text{D}) = f(\delta^{15}\text{N}(\text{H}))$ in Fig. 3.

3. Conclusions

We have described H/D isotope effects on the ^{15}N chemical shifts of low-barrier H-bonds of the type $[\text{A} \cdots \text{H} \cdots \text{A}]^-$ in the solid state as a function of the counterion X^+ which polarizes the H-bonds. Concomitantly, ab initio calculations of the dynamically corrected H-bond geometries and ^{15}N chemical shifts of a model system have been performed. Very often the geometries of H-bonds cannot easily be measured, but the similar behavior of the H/D isotope effect on the ^{15}N chemical shift in experiment and calculation encourages the use of this effect as a tool for the estimation of such geometries. In the future, we will attempt to directly obtain nitrogen–hydrogen distances by dipolar ^{15}N solid state NMR according to methods described recently [11].

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