

Primary $^1\text{H}/^2\text{H}$ isotope effect in the NMR chemical shift of HClO_4 salts of 1,8-bis(dimethylamino)naphthalene derivatives

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ABSTRACT: The primary $^1\text{H}/^2\text{H}$ isotope effect for a number of protonated naphthalene proton sponges (DMAN-s) was measured and correlated with the $\delta(^1\text{H})$ value and IR spectroscopic characteristics of the $[\text{NHN}]^+$ hydrogen bonds. A particular role of the unusual anharmonicity expressed in the isotopic ratio $\text{ISR} \gg \sqrt{2}$ is discussed when the fundamental vibrational levels are close to the barrier top for proton/deuteron motion. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: substituted DMAN; proton sponge; ^1H and ^2H NMR spectroscopy; $[\text{NHN}]^+$ bridge; primary $^1\text{H}/^2\text{H}$ isotope effect

INTRODUCTION

There is a commonly accepted opinion^{1–19} that when there is an asymmetric double-minimum potential for proton motion, the isotope effect in the NMR spectra of hydrogen-bonded systems can be divided into intrinsic and equilibrium parts. The intrinsic part is related to the anharmonicity of the potential, leading to a change in the hydrogen bond length. Several review articles have been published^{1–5,8,13,14} in which the primary isotope effect was analyzed. They were related mostly to $[\text{OHO}]$ bridges. A number of papers were also published on $[\text{OHN}]$ bridges (e.g. Ref. 2), where a substantial role is played by equilibrium effects. Particular attention was paid to the secondary $^1\text{H}/^2\text{H}$ isotope effect reflected in the chemical shifts of atoms other than the bridge atoms.

At the same time, there are limited data on the isotope effects related to the $[\text{NHN}]^+$ hydrogen bonds in protonated proton sponges.^{9–12} This is also characteristic of other chemically symmetric, very short, double-minimum hydrogen bonds. Up to now there has been a lack of systematic data concerning the shortest $[\text{NHN}]^+$ bridges, and the question whether a single minimum can exist in protonated sponges, particularly in solutions, remains open. A probably unique example is the case of protonated 1,6-diazabicyclo[4.4.4]tetradecane with the shortest $[\text{NHN}]^+$ bridge, for which the primary $^1\text{H}/^2\text{H}$ isotope effect is close to zero.²⁰

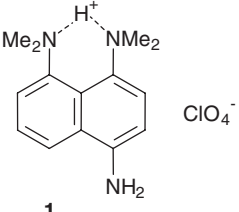
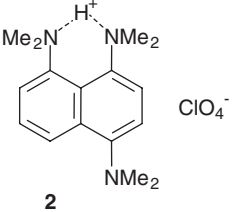
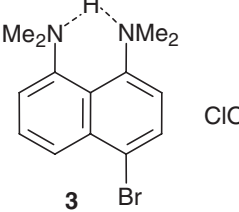
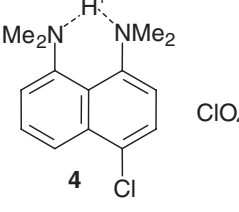
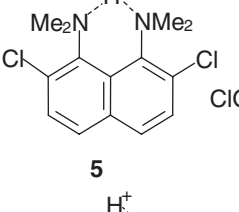
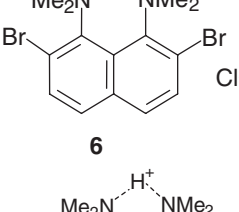
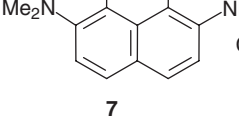
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The aim of the present study was to investigate the primary $^1\text{H}/^2\text{H}$ isotope effect in a regular set of substituted naphthalene proton sponges (DMAN-s), with particular attention to the high $\delta(^1\text{H})(\text{NH})$ chemical shift characteristic of very short $[\text{NHN}]^+$ bridges, especially those affected by the ‘buttressing effect’.²¹ We decided to measure $\Delta\delta(^1\text{H}/^2\text{H})$ for a number of protonated/deuterated sponges under identical conditions, that is, with the same counter-anion and in the same solvent. As follows from the literature data and our own experience, these are the factors which markedly influence the δ value due to modulation of the proton/deuteron potential. Particularly strong is the influence on the potential of the polarity and donor–acceptor properties of the solvent, which should be high enough because of the solubility demands. We assumed in our considerations the isotope effect to be positive when $\delta(^1\text{H}) > \delta(^2\text{H})$, though one can find in the literature a reversed tendency. Finally, acetonitrile was used as the solvent and ClO_4^- was the counter-anion. Acetonitrile is not a fully neutral solvent, but one which guarantees enough solubility and shows limited proton donor–acceptor activity.

RESULTS AND DISCUSSION

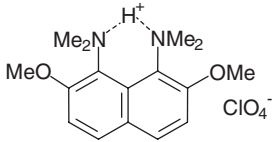
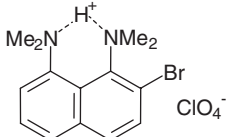
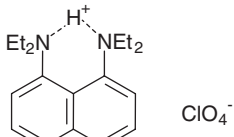
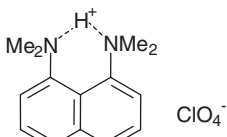
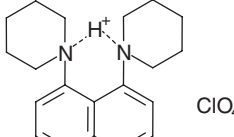
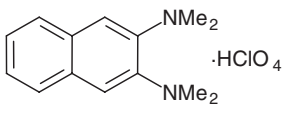
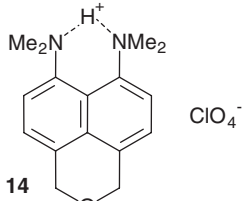
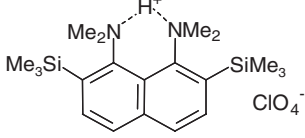
The results of the NMR measurements of the primary $\Delta\delta(^1\text{H}/^2\text{H})$ isotope effect for a set of protonated proton sponges and related compounds are gathered in Table 1, while the correlation between $\Delta\delta(^1\text{H}/^2\text{H})$ (further labeled as $\Delta\delta$) and $\delta(^1\text{H})$ (further labeled as δ) is presented in

Table 1. $^1\text{H}/^2\text{H}$ isotope effect $\Delta\delta = \delta(^1\text{H}) - \delta(^2\text{H})$ for a series of protonated proton sponges

System	$\delta(^1\text{H})$	$\delta(^2\text{H})$	$\Delta\delta$	Substitution ratio ^a
 1	18.59	17.92	0.67	0.53
 2	18.79	18.12	0.67	0.92
 3	18.83	18.17	0.66	0.55
 4	18.80	18.13	0.67	0.30
 5	20.13	19.83	0.30	0.79
 6	20.27	20.04	0.23	0.63
 7	19.97	19.63	0.34	0.06

(Continues)

Table 1. (Continued)

System	$\delta(^1\text{H})$	$\delta(^2\text{H})$	$\Delta\delta$	Substitution ratio ^a
 <p>8</p>	19.54	19.23	0.31	0.04
 <p>9</p>	18.82	18.32	0.50	0.25
 <p>10</p>	17.40	16.68	0.72	0.77
 <p>11</p>	18.65	17.96	0.69	0.67
 <p>12</p>	17.28	16.60	0.68	0.15
 <p>13</p>	10.15	10.01	0.14	0.56
 <p>14</p>	18.52	17.83	0.69	0.18
 <p>15</p>	20.63	20.49	0.14	0.80

^a Based on the relative integral intensity of the ^1H NMR signal of the exchangeable proton referenced to that of the aromatic protons.

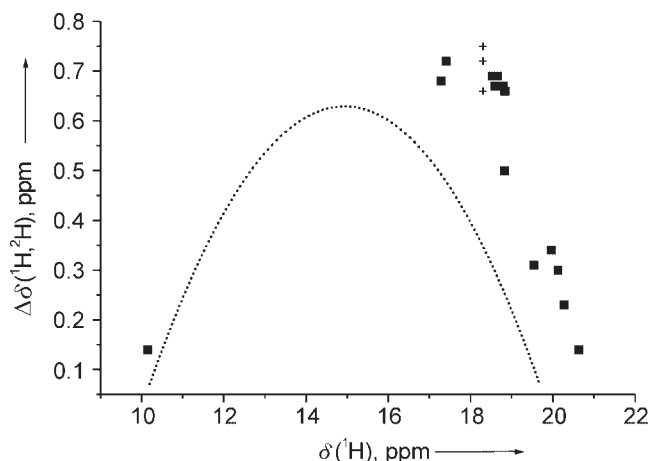


Figure 1. Correlation between $\Delta\delta$ and $\delta(^1\text{H})$ values for protonated DMAN-s against a background of similar relationship for [OHO] hydrogen-bonded systems reported by Gunnarsson *et al.*⁶ The literature data⁹ are included as cross-marks

Fig. 1. Some literature data⁹ are included as well. The majority of points are in the region of $\Delta\delta \approx 0.6\text{--}0.7$ and $\delta \approx 17.3\text{--}18.8$ ppm, thus close to the parameters for the non-substituted $\text{DMAN}\cdot\text{H}^+$ cation with $\delta = 18.65$ and $\Delta\delta = 0.66$ ppm. Among the systems analyzed in this paper are a few salts with asymmetrically substituted DMAN (see: **1–4** and **9**). As can be seen, the asymmetry does not significantly affect either the δ or $\Delta\delta$ values. This is most probably due to a similar electron density distribution on both nitrogen atoms and, simultaneously, similar population of the two potential energy minima. Nevertheless, taking into account all the experimental points around the unsubstituted $\text{DMAN}\cdot\text{H}^+$ cation, the asymmetric bridges are characterized by only slightly higher $\Delta\delta$ values, on the order of *ca.* 0.1 ppm. A marked drop in the $\Delta\delta$ value is characteristic for 2,7-disubstituted DMAN-s and, as can be seen, is related to the ‘buttressing effect’, that is, to the steric hindrance leading to the shortening of the NHN bridge.²¹

We were not able to determine precisely the highest value of $\Delta\delta$ for the protonated DMAN derivatives. It can be estimated as equal to *ca.* 0.7 ppm, that is, close to that of other systems reported so far.^{2,3,6}

The collected experimental data were compared with the correlation between both parameters for chemically symmetric [OHO] bridges published by Gunnarsson *et al.*⁶ Unfortunately, we did not have data at our disposal (except **13**) for [NHN]⁺ hydrogen bonds markedly longer than in DMAN salts; therefore we were able to analyze only the branch of the curve for high values of δ . In the case of compound **13**, a typical isotope effect of medium–strong hydrogen bonds is observed. In our opinion, any correlation searched can be applied to exactly the same type of NHN bridges.

Comparison of our results with the correlation curve for [OHO] bridges shows that the [NHN]⁺ curve

maximum is shifted towards higher values of δ and the isotope effect is somewhat higher. In our considerations we do not compare the obtained results with the correlations presented by Hansen and coworkers³ and Rozwadowski and Dziembowska,² in which various systems are taken into account containing those with the equilibrium effect, that is, corresponding to chemically different bridge atoms described by an asymmetric double-minimum potential for the proton/deuteron motion. As it is known,³ the equilibrium isotope effect can substantially influence the overall effect. The correlation curve reported by Vener¹⁹ for homoconjugated [OHO] hydrogen-bonded systems is similar to that of Gunnarsson *et al.*⁶

The difference between [OHO] and [NHN] hydrogen bonds in protonated DMAN-s, well reflected in Fig. 1, may result from two effects. The first, discussed by Scheiner,²² is due to different covalent radii and a slightly different charge distribution. The second can be ascribed to the diamagnetic field of the naphthalene π -electron system. Comparison of the δ values for DMAN-s, 1,6-diazabicyclo[4.4.4]tetradecane without π -electrons,²⁰ and 1,14-diaza[5]helicene,²³ where the [NHN]⁺ hydrogen bond is strongly affected by the π -electron current and $\delta^1\text{H}$ reaches extremely high value of 23.89 ppm, is remarkable.

The intrinsic NMR primary $^1\text{H}/^2\text{H}$ isotope effects, as commonly accepted, are connected with the potential energy surface for the proton/deuteron motion, so they can be correlated with the spectroscopic isotope effect and, more generally, with the anharmonicity of the potential. For the medium–strong hydrogen bonds, the peak of the square of the wave function for D is located closer to the proton donor than H is, so that the bridge with H is stronger than that with D and, consequently, H is more deshielded than D. Therefore, it seemed interesting to compare the primary isotope effect with spectroscopic features of [NHN] bridges, for which one observes a fast decrease in the $\Delta\delta$ value with an increase in δ . This has been done in Table 2, which contains data connected with the H-bond length, $r(\text{N}\cdots\text{N})$, the $\nu_{\text{as}}(\text{NHN})$ frequency, and the IR isotopic ratio $\text{ISR} = \nu(\text{NHN})/\nu(\text{NDN})$.

Table 2. Properties of protonated 2,7-R₂-DMAN-s

Salt	R	$r(\text{N}\cdots\text{N})$, Å	$\nu(\text{NHN})$, cm^{-1}	ISR	δ , ppm	$\Delta\delta$, ppm
11	H	2.595 ^a	490 ^a	1.7–2.0 ^a	18.65	0.69
8	OMe	2.567 ^b	488 ^b	2.08 ^b	19.54	0.31
5	Cl	2.561 ^c	530 ^c	1.80 ^c	20.10	0.30
6	Br	2.547 ^d	560 ^d	1.65 ^d	20.27	0.23
15	SiMe ₃	2.530 ^e	610 ^e	1.6 ^e	20.63	0.14

^a Average values for various salts of DMAN, strongly dependent on the counter-anion.

^b See Ref. 24.

^c See Ref. 25.

^d See Ref. 26.

^e See Ref. 27.

There are no doubts that the $\Delta\delta$ value correlates with the $\nu(\text{NHN})$ absorption band in the far infrared and with the ISR value. As follows from the analysis performed in Ref. 28, one can expect that on shortening the bridge in the analyzed region, the $\nu(\text{NHN})$ frequency increases and exceeds *ca.* 1000 cm^{-1} after reaching sufficiently short bridges, when the barrier disappears, and ISR is then close to unity. Such a case was found in 1,6-diazabicyclo [4.4.4]tetradecane. Simultaneously, the $\Delta\delta$ value reaches *ca.* zero. A precise quantitative analysis of the correlations between the various parameters is not possible because in many cases they were determined under various experimental conditions. In the solid state, the counter-anion plays a peculiar role, but even in solutions its role as well as that of the solvent activity is important.

Theoretical studies^{24,26} using the *ab initio* MP2 approach for two DMAN·H⁺ derivatives, namely with 2,7-Br₂ and 2,7-(OMe)₂ substituents, confirmed our conclusions. In these cases it was discovered that both the protonic and deuteronic vibrational levels are close to the potential barrier, and this explains the positive anharmonicity expressed by $\nu(\text{NHN})/\nu(\text{NDN})$ being much higher than $\sqrt{2}$. In the case of the usual strong hydrogen bonds, we are dealing with an isotopic ratio ISR of $<\sqrt{2}$. A strong positive anharmonicity means that the amplitudes of the proton and deuteron motions differ much less than in the case of normal anharmonicity. Moreover, the excited vibrational state for the deuteron is much more easily accessible than for the proton.

One should stress here the result obtained for compound **15**, which is characterized by the shortest NHN bridge and lowest $\Delta\delta$ value. In spite of expectations, even in this case the *ab initio* MP2 calculations²⁷ show a double-minimum potential for the proton motion that is consistent with the IR spectroscopic behavior.

Further theoretical calculations for a number of systems are needed on a sufficiently high level for at least a two-dimensional potential surface, but such calculations are, so far, too demanding for CPUs and memory.

CONCLUSIONS

As expected, the results obtained correlate quite well with crystallographic data, IR spectra, and theoretical simulations of the shape of the potential for proton motion. From the presented curve one can see that on increasing the strain exerted by substituents in positions 2,7 (buttressing effect), the $\Delta\delta(^1\text{H}/^2\text{H})$ value approaches zero. However, even for trimethylsilyl substituents, where the shortest bridges were evidenced, the $\Delta\delta$ value is positive (0.14). In this case, the calculated barrier equals 0.69 kJ/mol, so it does not disappear in solution.²⁷ The shape of the correlation curve $\Delta\delta(^1\text{H}/^2\text{H})$ versus $\delta(^1\text{H})$ is similar to that for [OHO] hydrogen-bonded systems, but

the maximum on the correlation curve corresponds to higher values of $\delta^1\text{H}$, which arises most probably from different covalent radii of O and N atoms and somewhat different electron density distributions. An essential role is also played by the π -electron system of the naphthalene ring, as can be deduced from comparisons with systems which do not contain π -electrons.

EXPERIMENTAL

The perchlorates used in this study were prepared and had the same properties as those described in the literature: **1**, **2**,²⁹ **3–6**, **9**, **11**,³⁰ **7**, **8**,³¹ **10**, **13**,³² **14**,³³ **15**,²⁷ **12**: colorless crystals with mp 268–270 °C after treatment of the corresponding base with one equiv. of aqueous HClO₄ in CH₃CN solution.³²

For the preparation of all but one partially deuterated NMR sample the compounds were dissolved in CH₃CN/CH₃OD mixture (70/30 v/v), the solvents were evaporated *in vacuo*, and pure dry CH₃CN was added. In the case of **8**, partial substitution (4%) required 2 days of heating (40 °C) the compound solution in CD₃OD. ²H and ¹H NMR measurements were performed using a Bruker Avance 500 MHz spectrometer. The sample concentrations were about 0.1 M. The chemical shifts were referenced with CH₃CN and CDH₂CN signals, respectively (1.94 ppm).

Acknowledgements

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