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2,7-Disubstituted proton sponges as borderline systems for investigating barrier-free intramolecular hydrogen bonds. Protonated 2,7-bis(trimethylsilyl)- and 2,7-di(hydroxymethyl)-1,8-bis(dimethylamino)naphthalenes

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ABSTRACT

Protonated 2,7-bis(trimethylsilyl)- and 2,7-di(hydroxymethyl)-1,8-bis(dimethylamino)naphthalenes have been prepared and studied by a combination of X-ray crystallography at room and low temperatures, IR and NMR spectroscopic techniques in conjunction with quantum-chemical calculations. It was demonstrated that the intramolecular $[NHN]^+$ hydrogen bond in the 2,7-bis(trimethylsilyl) system, being sterically compressed, is the shortest among all known aromatic diamine systems. Nevertheless, as it is evidenced by the primary $^1H/^2H$ isotope effect, IR spectra and MP2 calculations, a double minimum potential for the proton motion still exists with a very low barrier estimated to be about 0.7 kcal/mol. An influence of a counter-anion on the NH proton involving the spatially hindered H-bond is also considered.

1. Introduction

Numerous investigations of the cation of naphthalene proton sponge (monoprotonated DMAN, **1**) with its two tertiary amino groups placed in spatial proximity have led to a conclusion that the intramolecular hydrogen bond (IHB) in **1** has a two-well low-barrier potential for the proton motion (Fig. 1b).[1–4] In the NMR time-scale, this corresponds to a symmetrical IHB reflecting in magnetic equivalence of the dimethylamino groups.[2,5,6] At earlier stages of these studies, the symmetry of the IHB has been proved to exist indeed, as it followed from the first X-ray crystallography data.[2] However, as the number of investigated salts (with different anions) grew and additional information based, in particular, on low temperature and time-resolved measurements appeared, the primary impression was changed.[7] The current point of view is that the bridging proton in cation **1** rapidly equilibrates near the symmetry plane with a postulated rate of about 10^{10} s^{-1} (tunnelling mechanism).[8] Thus, the real situation should be expressed as an equilibrium between isoenergetic tautomers **1a** and **1b**.[2,9] As it follows from quantum-chemical estimations, the barrier height for the proton motion in **1** is in the range of 0–4.5 kcal/mol depending on the calculation method.[10]

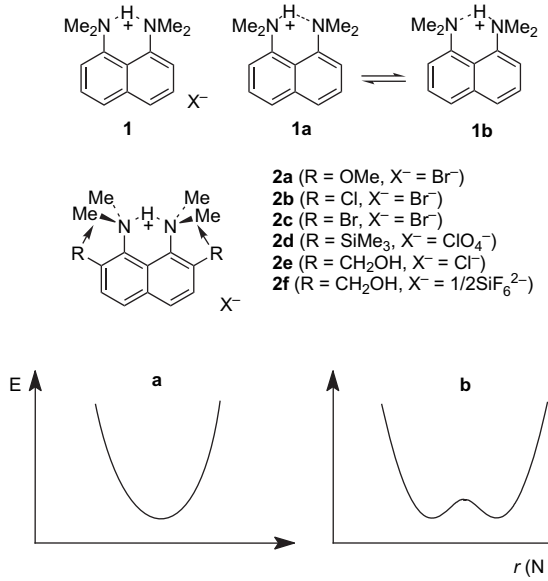

Figure 1. Possible types of IHB potential energy profiles in proton sponge cations.

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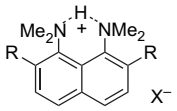
Table 1
X-ray characteristics of N–H···N hydrogen bridge in cations of 2,7-disubstituted proton sponges

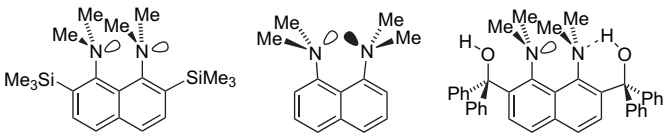


Compound (CCDC refcode)	R	X^-	Temperature (K)	Distances (Å)				Angles (°)		Ref.
				N···N	N–H	H···N	Δ*N*	∠NHN	∑*N*	
1 (EDAFIY)	H	$^1/_2$ $CuCl_4^{2-}$	rt	2.584(8)	1.21	1.43	0.061	158	336.5	12
1 (BUTNOT)	H	Br^-	rt	2.555(4)	1.31(1)	1.31(1)	0.016	153(3)	337.8	13
1[a]	H	—	—	2.595	—	—	—	155	336.4	—
2a (FISLEZ01)	OMe	Br^-	100	2.567(3)	1.30(1)	1.30(1)	0.011	160(3)	340.5	14
2b (CUNWOX)	Cl	Br^-	rt	2.561(3)	1.29(1)	1.29(1)	0.022	165(2)	342.7	15
2c (UNATAE01)	Br	Br^-	100	2.547(3)	0.85(5) (1.73)[b]	1.73(5) (0.85)[b]	0.053	162(4)	342.9	16
2d	$SiMe_3$	ClO_4^-	rt	2.530(4)	1.284	1.284	0.262	160	341.9	[c]
			163	2.524(2)	1.275	1.275	0.264	163	341.6	[c]
2e	CH_2OH	Cl^-	rt	2.568(4)	1.30	1.34	0.061	154	343.0	[c]
			120	2.561(2)	1.16	1.50	0.042	149	342.9	[c]
2f	CH_2OH	$^1/_2$ SiF_6^{2-}	100	2.556(2)	0.87 (1.68)[b]	1.71 (0.89)[b]	0.062	165	342.6	[c]

[a] Average data for about 30 salts **1**·X^- with different X^- anions.
[b] NH proton is equally disordered over two positions.
[c] This work.

An old intriguing question is whether a barrier-free hydrogen bond with a single minimum potential (Fig. 1a) could be possible in protonated DMANs and related systems. Theoretical calculations performed earlier for a model $[H_3N–H\cdots NH_3]^+$ cation[11] showed that at the distance between the N atoms of 2.75 Å, the potential curve has two minima with an energetic barrier of 2.6 kcal/mol, and the barrier disappeared completely when this distance decreased to ~2.50 Å. One can note (Table 1) that the N···N distance for cation **1** is rather small and in some cases reaches 2.555 Å, although its average value for several tens of salts is distinctively larger (2.595 Å). Hence, the theoretical data are in agreement with the opinion testifying moderate asymmetry of the IHB in cation **1**. Is it possible to contract the internitrogen distance in cation **1** significantly? An obvious way to this goal is incorporation of voluminous substituents into the 2 and 7 positions of the naphthalene ring. Many of the compounds of such a type became available only recently.[17] For example, X-ray crystallography studies of 2,7-dimethoxy-,[14] 2,7-dichloro-[15] and 2,7-dibromo-1,8-bis(dimethylamino)naphthalene[16] as hydrobromides **2a–c** have revealed the following changes of their structures if compared to parent salts **1**: (1) 'pressure' of the *ortho*-substituents onto the dimethylamino groups leads to a noticeable planarization of the nitrogen atoms (sum of the CNC angles in all compounds **2** exceeds 340°); (2) the flattening of the NMe_2 groups results in the IHB linearization and enlargement of the N–H···N angle realizing as 'pushing-in' of the NH proton deeper into the internitrogen space exerted by the rising N–Me groups; (3) for dihalides **2b** and **2c** a weak tendency is seen for contraction of both the N···N distance and the N–H bonds as the volume of the substituent grows; (4) the hydrogen bridge in all three cations is symmetrical although some complication is associated with dibromide **2c** with its NH proton being placed into two equivalent positions with the same probability; (5) unlike cation **1**, the presence of bulky *ortho*-substituents in cation **2b** and especially in **2c** restricts the complete release of steric strain, which is habitual for proton sponge bases. For instance, deviation of the nitrogen atoms from the mean ring plane is 0.053 Å for **2c**.

In this context, the molecular structure of 1,8-bis(dimethylamino)-2,7-bis(trimethylsilyl)naphthalene cation **2d** seemed to be of great interest. Firstly, the volume of the $SiMe_3$ group substantially exceeds that of the other substituents in cations **2a–c**. Secondly, some peculiarities are observed just in the structure of trimethylsilyl derivative **3** as free base. As it was established,[17] the lone electron pairs of the NMe_2 groups in **3** have a clear *in*/*out* orientation and are not strictly pre-organized for IHB formation. This is in contrast with the parent base **4** and many other DMAN derivatives whose lone pair axes normally point to the internitrogen space (*in*/*in* orientation).[2] It is noteworthy that an even more pronounced *in*/*out* conformation of the NMe_2 groups was disclosed in the 2,7-di(α-hydroxybenzhydryl) derivative **5**.[18] Therefore, the comparative study of cations of such diols also seemed to be desirable. With these points in mind, in the present work we have conducted an X-ray and spectroscopic investigation of the salt **2d** and its counterparts **2e** and **2f** with *ortho*-hydroxymethyl groups and anions Cl^- and SiF_6^{2-}. The results received are shown in Figures 2 and 3 and in Table 1 and Table1S in Supplementary data.



3 (*in/out*) **4** (*in/in*) **5** (*in/out*)

2. Results and discussion

As expected, the N···N distance in perchlorate **2d** is significantly shorter than that in all other proton sponge cations and protonated aromatic diamines and is 2.530 Å at room temperature and 2.524 Å at 163 K (Table 1).[19] It is even slightly below than the N···N distance (2.526 Å) in the inside protonated 1,6-diazabicyclo[4.4.4]-tetradecane (**6**), whose linear hydrogen bridge was hitherto considered as the shortest one among $[NHN]^+$ systems.[20] The NHN^+ bridge in cation **2d** is perfectly symmetric and this symmetry keeps on lowering the temperature; the N···H bond lengths (1.28 Å) are also the shortest in the aryalmine systems. At the same time, unlike cation **1**, the steric strain in cation **2d** is not fully released and yet remains notable. Thus, the naphthalene system in **2d** is not completely flat and twisted along the C(9)–C(10) bond common for two benzene rings. A torsion angle thus arising between the C(2)–C(3) and C(6)–C(7) bonds is 8° versus 11° and 0° in the base **4** and cation **1**, respectively.[2] Additionally, the nitrogen atoms in **2d** deviate by 0.26 Å in opposite sides of the ring plane that markedly exceeds similar deviation in cations **1** and **2a–c** (compare Δ*N* indices in Table 1). As a consequence, the hydrogen bridge in **2d** crosses the

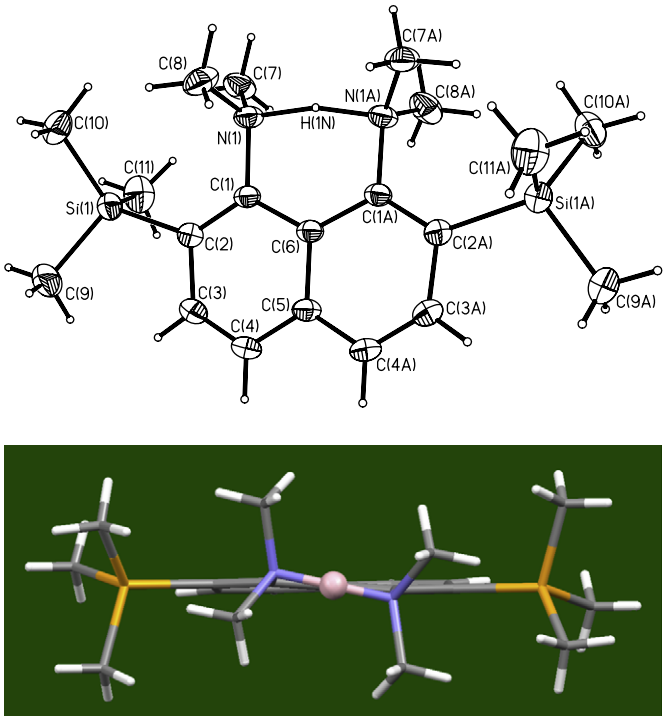
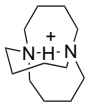


Figure 2. Molecular structure of the cation of 1,8-bis(dimethylamino)-2,7-bis-(trimethylsilyl)naphthalene (**2d**) at 163 K: general view with atom numbering scheme and ellipsoids (30%) of thermal motion (top) and view along the naphthalene ring plane (bottom; the NH proton is drawn as a pink sphere).

mean ring plane at some angle (Fig. 2). The silicon atoms are situated practically in the ring plane but, in turn, are strongly repulsed from the nitrogens: the C(1)–C(2)–Si angle is near 133° versus 123° and 129° for the silicons near inverted and non-inverted NMe_2 groups in compound **3**, respectively.

Contrary to expectation, a linearization of the IHB in the cation **2d**, being rather high (∠NHN=163°), differs little from that in cations **2a–c** (∠NHN=160–165°). The same is true for the flattening of the nitrogen atoms: all cations of 2,7-disubstituted proton sponges by this index, $\sum N$ (the sum of C–N–C angles), supersede considerably other ammonium salts of type $ArAlk_2NH^+$ as it follows from the CCDC data set (see Ref. 17 for details).



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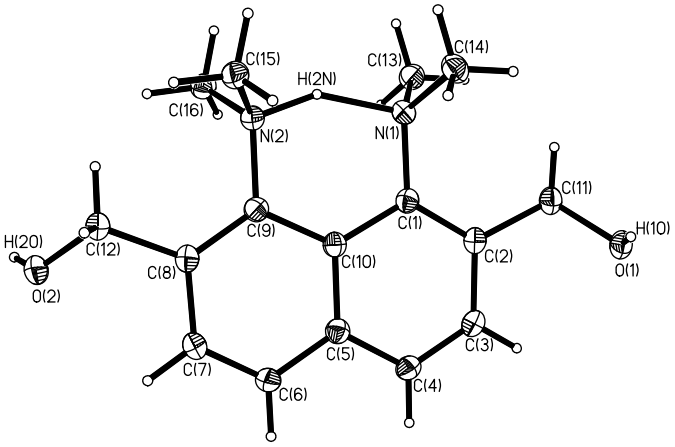
The unusual position of the trimethylsilyl derivative **3** and its salt **2d** among various 2,7-disubstituted DMANs can be understood on the basis of the buttressing effect.[17] This effect, interpreted as an internal pressure, is revealed first of all in shortening of the NHN^+ bridge and as a consequence in the modification of the potential shape for the proton motion. As it has been shown in several papers,[14,21] the IR absorption band for the $\nu_{as}(NHN^+)$ vibrations is characterized by a particularly low frequency at ca. 500 cm^{-1} with an unusual isotope effect ISR=ν_H/ν_D markedly exceeding $\sqrt{2}$ that should be ascribed to a reverse anharmonicity. In usual hydrogen



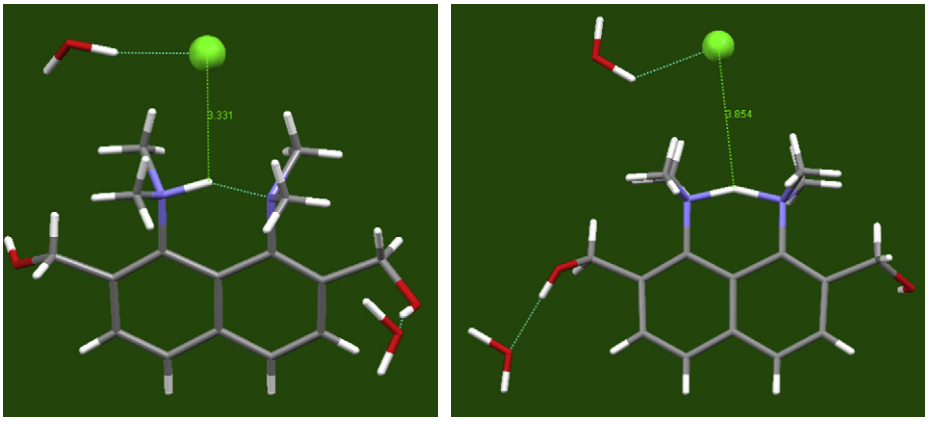


Figure 3. Molecular structure of the cation of 2,7-di(hydroxymethyl)-1,8-bis(dimethylamino)naphthalene (**2e**) at 120 K: general view with atom numbering scheme and ellipsoids (30%) of thermal motion (top) and perspective view from above the naphthalene ring plane (bottom left at 120 K, bottom right at 295 K) showing interaction with chloride ion and water molecules.

Table 2
Characteristic parameters of protonated 2,7-R_2-DMANs

R	r(N···N) (Å)	ν_{as}(NHN$^+$) (cm^{-1})	ISR (ν_H/ν_D)	δ (^{1}H) (ppm)	$\Delta\delta$ (^{1}H/^{2}H) (ppm)
H	2.595[a]	490[a]	1.7–2.0[a]	18.65	0.69
OMe	2.567	488	2.08	19.54	0.31
Cl	2.561	530	1.80	20.10	0.30
Br	2.547	560	1.65	20.27	0.23
$SiMe_3$	2.530	610	1.60	20.63	0.14

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

bonded systems $\nu_H/\nu_D<\sqrt{2}$ and corresponds to a normal anharmonicity.[22] On the other hand, the NMR spectroscopic studies show that the shorter the hydrogen bonds the higher the chemical shifts δ (^{1}H) and the lower the values of the primary isotope effect, $\Delta\delta$ (^{1}H/^{2}H).[23–25] The correlation between these quantities is presented in Table 2.[26] It should be noted that for the true symmetric single minimum potential as in the case of **6**[23] the primary isotope effect is close to zero, although recent DFT calculations have demonstrated that the encapsulated proton of **6** is engaged in a short (2.578 Å)[27] but asymmetric H-bond with very low barrier to the proton transfer.[28] Therefore, the experimental data suggest that in the case of cation **2d** we are dealing with a double minimum but of extremely low barrier so that it is close to a single minimum potential. To get additional arguments, we decided to perform calculations of the potential for the proton motion under adiabatic conditions by using the ab initio MP2 method.[14] The energy was calculated step-by-step as depicted in Figure 4. For the optimized structure with the N···N bridge length equal to 2.509 Å and with the N–H distance of 1.197 Å, the NHN$^+$ bridge is a little bent and the NHN angle value (164°) is in excellent agreement with the experimental one (163°) (Fig. 5). The adiabatic barrier to the proton transfer was estimated to be 0.69 kcal/mol and the distance between the two minima equals only to ca. 0.12 Å.

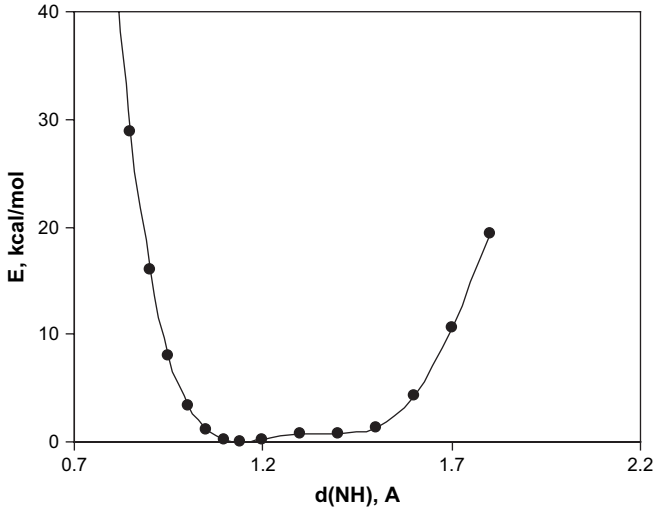


Figure 4. The potential energy curve along proton transfer coordinate for protonated 1,8-bis(dimethylamino)-2,7-bis(trimethylsilyl)naphthalene calculated at MP2/6-31+G-(d,p) level of theory.

In the cation of 2,7-di(hydroxymethyl)-1,8-bis(dimethylamino)naphthalene **2e**, the IHB at ambient temperature is practically symmetrical with the N···N distance of 2.568 Å. This value is less than the average distance for the salts of the parent proton sponge (~2.59 Å), but considerably larger than that in cation **2d**. In another sample of **2e** taken up from MeCN and measured with cooling, the IHB symmetry is lost. Obviously, it is caused by the electric field of the chloride ion in a somewhat rearranged crystal lattice. Indeed, if the NH$^+$···Cl$^-$ distance for the room temperature structure is 3.85 Å, it decreases to 3.33 Å for the structure measured at 120 K. From Figure 3 one can see that the NH proton and the Cl$^-$ anion lie approximately in the ring plane and both on one line with the C(9)–C(10) bond indicating their electrostatic interaction in the crystalline lattice. A noticeable decrease of the NHN angle in the salt **2e** (154° and 149° at 293 K and 120 K, respectively) can be considered as another indirect confirmation of this interaction.[29] Presumably, the hydrogen bond between Cl$^-$ and a water molecule also contributes in the desymmetrisation of the IHB (Fig. 3). Fortunately, the salt **2f** with SiF_6^{2-} dianion instead of Cl$^-$ occasionally had fallen in our hands. In an attempt to prepare the hydrofluoride of 2,7-di(hydroxymethyl)-1,8-bis(dimethylamino)naphthalene by treatment of the base with concd HF in a plastic vessel followed by

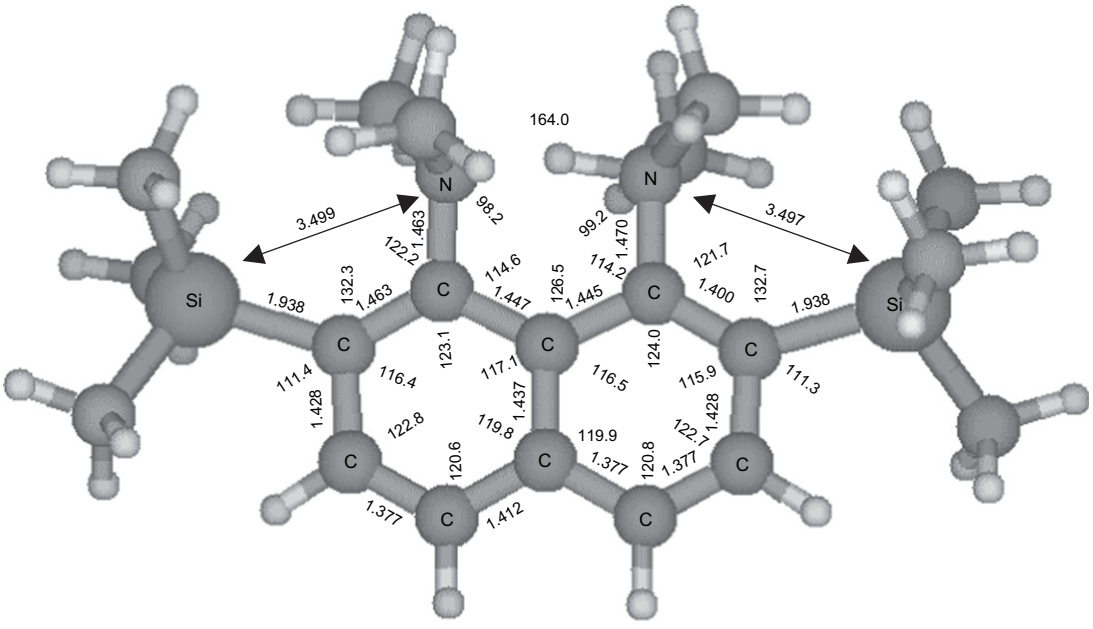


Figure 5. MP2 optimized structure of protonated 1,8-bis(dimethylamino)-2,7-bis(trimethylsilyl)naphthalene.

recrystallization of the initially deposited precipitate in a glass test tube, formation of the hexafluorosilicate **2f** as the dihydrate took place. A low nucleophilicity of this dianion together with its bulkiness gave a chance to test for the first time how the nature of the counter-anion influences the geometry of the compressed IHB in protonated 2,7-disubstituted proton sponges. As expected, the crystal structure of **2f** excludes any interactions between the cationic NHN^+ bridge and the anion leading to a distinct linearization of the H-bridge (165°) although the chelated proton of **2f** is equally disordered over two positions as in the case of **2c** (Table 1). On going from Cl^- to SiF_6^{2-} (**2e**→**2f**) the IHB becomes stronger and the N atoms move closer in space with a separation of only 2.556 Å for **2f**.

In any case, all data obtained testify the two-well low-barrier potential for the proton movement in the cation of chloride **2e** (Fig. 1b). For example, the isotopic ratio was found to be only 1.50, as **2e** (in the form of bromide) and its deuterated analogue gave their IR spectroscopic $\nu(NHN^+)$ and $\nu(NDN^+)$ bands near 510 cm^{-1} and 340 cm^{-1}, respectively.

Unlike the salt **2d**, deviation of the nitrogen atoms from the ring plane in **2e** is insignificant and decreases on cooling. Similarly to all other cations of 2,7-disubstituted DMANs, the NMe_2 groups in **2e** are markedly planarized ($\sum N$=343°) due to a buttressing effect.[17] The non-H-bridge geometries of the cations of salts **2e** and **2f** are virtually the same, differing in part in the mode of interaction between the CH_2OH groups and two water molecules in each single case. Overall, the steric influence of hydroxymethyls on the hydrogen bridge properties, when it is not affected by the anion, is close to that of bromines in cation **2c**.

3. Conclusions

In summary, we have prepared and investigated 1,8-bis(dimethylamino)-2,7-bis(trimethylsilyl)naphthalene salt **2d** having the remarkably short $[NHN]^+$ hydrogen bridge. Actually, a borderline between low-barrier and barrier-free $[NHN]^+$ hydrogen bonds is reached for the first time. This justifies using of proton sponge cations as working and simple models for proton transfer processes in biological systems.

4. Experimental

4.1. General

The NMR spectra for protonated and deuteriated species were recorded at room temperature by using Varian Unity-300 instrument operated at 300 MHz with $SiMe_4$ as the internal standard; *J* values are given in hertz. The IR spectra were recorded at room temperature in Fluorolube and Nujol (low frequency region) suspensions using either KBr or CsI windows on a FT-IR Bruker IFS113V spectrometer. Calculation performed by using Gaussian program[30] with 6-31+G(d,p) basis set.

4.2. 1,8-Bis(dimethylamino)-2,7-bis(trimethylsilyl)-naphthalene perchlorate (2d)

Compound **2d** was prepared from the corresponding base (compound **3**)[17] and 1 equiv of $HClO_4$ in ether solution. Colourless plates with mp 190 °C (dec, from EtOH). For analytical and ^1H NMR data see Ref. 17.

4.3. 2,7-Di(hydroxymethyl)-1,8-bis(dimethylamino)-naphthalene (2e)

The compound was obtained by reduction of 2,7-di(ethoxycarbonyl)-1,8-bis(dimethylamino)naphthalene[17] (0.5 g, 1.4 mmol) with excess of $LiAlH_4$ (0.2 g, 5.6 mmol) in Et_2O or THF (10 mL) at reflux. After careful hydrolysis with water, the ethereal layer was separated and the water layer was extracted with Et_2O (3×3 mL). The combined organic phase was evaporated to dryness and chromatographed on Al_2O_3 with MeCN as eluent. Yield of base **2e** was 0.346 g (90%); yellow crystals with mp 133 °C (from MeCN). Found: C, 69.98; H, 8.07; N, 10.29. Calcd for $C_{16}H_{22}N_2O_2$: C, 70.07; H, 8.03; N, 10.22%. ^1H NMR (DMSO-d_6) δ ppm: 2.89 (12H, s, NMe_2), 4.63 (4H, d, *J* 5.5, CH_2OH), 5.14 (2H, t, *J* 5.5, OH), 7.51 (2H, d, *J* 8.4, 3,6-H), 7.57 (2H, d, *J* 8.4, 4,5-H). ^1H NMR ($CDCl_3$) δ ppm: 2.95 (12H, s, NMe_2), 4.85 (4H, d, *J* 5.5, CH_2OH), 7.44 (2H, d, *J* 8.4, 3,6-H), 7.57 (2H, d, *J* 8.4, 4,5-H), OH is not observed.

4.4. 2,7-Di(hydroxymethyl)-1,8-bis(dimethylamino)-naphthalene hydrochloride (2e)

To a solution of free base **2e** (0.02 g, 0.07 mmol) in ethyl acetate (2 mL), the 33% hydrochloric acid (0.007 mL, 0.07 mmol) was added. After 1 min of standing, the mixture was diluted with ether (3 mL) and the residue formed at this stage was filtered off, washed with ether, dried in vacuum and recrystallized from ethanol. Yield of **2e** is near quantitative; colourless crystals with mp 293 °C (dec, from EtOH). Found: C, 61.96; H, 7.35; Cl, 11.32; N, 9.07. Calcd for $C_{16}H_{23}ClN_2O_2\cdot 2H_2O$: C, 61.83; H, 7.46; Cl, 11.41; N, 9.01%. ^1H NMR (DMSO-d_6) δ ppm: 3.29 (12H, d, $J_{NH,NMe}$ 2.4, NMe_2), 4.87 (4H, d, *J* 5.5, CH_2OH), 5.75 (2H, t, *J* 5.5, OH), 7.82 (2H, d, *J* 8.6, 3,6-H), 8.07 (2H, d, *J* 8.6, 4,5-H), 20.10 (1H, br s, NH).

4.5. 2,7-Di(hydroxymethyl)-1,8-bis(dimethylamino)-naphthalene hexafluorosilicate (2f)

To a solution of 2,7-di(hydroxymethyl)-1,8-bis(dimethylamino)naphthalene as free base (0.02 g, 0.07 mmol) in ethyl acetate (2 mL) placed in a plastic vessel, the 45% aqueous HF (0.002 mL, 0.10 mmol) was added. After 1 min of standing, the mixture was diluted with ether (3 mL) and the precipitate formed was separated, washed with ether and cold ethanol, dried in vacuum and recrystallized from ethanol in a glass test tube. Yield of **2f** is near quantitative; colourless crystals with mp 235–237 °C (from EtOH). Found: C, 50.16; H, 6.11; N, 7.30. Calcd for $C_{16}H_{23}F_3N_2O_2Si_{0.5}\cdot 2H_2O$: C, 50.26; H, 6.02; N, 7.32%. ^1H NMR (DMSO-d_6) δ ppm: 3.26 (12H, d, $J_{NH,NMe}$ 2.2, NMe_2), 4.85 (4H, d, *J* 5.6, CH_2OH), 5.74 (2H, t, *J* 5.6, OH), 7.80 (2H, d, *J* 8.5, 3,6-H), 8.05 (2H, d, *J* 8.5, 4,5-H), 20.08 (1H, br s, NH).

Crystals of **2e**·$2H_2O$ suitable for X-ray studies were grown up by slow evaporation from ethanol or acetonitrile solutions and crystals of **2d** and **2f**·$2H_2O$ were prepared from ethanol. The structures were solved by direct method and refined by the full-matrix least-squares against F^2 in anisotropic (for no-hydrogen atoms) approximation. All hydrogen atoms were located from the difference Fourier syntheses, the H(C) atoms were placed in geometrically calculated positions. All hydrogen atom positions were refined in isotropic approximation in riding model with the U_{iso}(H) parameters equal to $n\cdot U_{eq}(C_i)$ (n=1.2 for CH and CH_2 groups and n=1.5 for CH_3 groups), where $U(C_i)$ are, respectively, the equivalent thermal parameters of the atoms to which corresponding H atoms are bonded. The atomic coordinates, bond lengths, bond angles, and torsion angles for the structures of protonated salts **2d**–**f** were deposited with the Cambridge Structural Database as supplementary publication with CCDC Nos. 248982, 639650–639652, 663348 (see also Table 1S in Supplementary data). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.05.001.

References and notes

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19. Actually, the Cambridge Structural Database reports on several examples of the shorter $[N–H\cdots N]^+$ intramolecular hydrogen bridges in proton sponges, refcodes MUQMUG, FIJVOJ and KAQHIT. However, all of them suffer from bad refinement and other shortcomings. For example, for the MUQMUG entry [**1**, $X^-=B(C_6F_5)\cdot 3H_2O\cdot B(C_6F_5)3OH^-$] the R-factor is rather low, the NH proton is not localized, while in the anionic part [H(O–B) atoms] three protons are localized even including the disordered proton. Furthermore, there are some doubts on geometry of the naphthalene fragment: the C9–N2 bond (1.447 Å) is unbelievably shorter than the C1–N1 1.482 Å; the C1–C2 bond is also unusually short (1.332 Å). Hence, the sharpness and correctness of the MUQMUG structure is questionable and this entry has to be done at low temperature.
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27. This discrepancy between X-ray and calculated values for the length of the $[N\cdots H\cdots N]^+$ bridge in **6** can be attributed to insufficiently precise DFT theoretical methods when they are applied to very strong hydrogen bonds. The results obtained in Ref. 28 should be interpreted that the length 2.578 Å is theoretically overestimated and there should be taken into account an effect of the packing.
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29. Apparently, the greatest closeness of an anion to the chelated proton has been observed for the proton sponge hydrofluoride complex at 293 K: Darabantu, M.; Lequeux, T.; Pommelet, J.-C.; Ple, N.; Turck, A.; Toupet, L. *Tetrahedron Lett.* **2000**, *41*, 6763–6767. For this complex, the $F^-\cdots H^+$ distance reaches 2.760 Å and the NHN angle is as sharp as 142° (the record value among all known proton sponge salts). The situation seems to look as if the counter-ion has already essentially extracted the NH proton from its cavity.
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