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1,8-Bis(dimethylethyleneguanidino)naphthalene: Tailoring the Basicity of Bisguanidine "Proton Sponges" by Experiment and Theory

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1,8-Bis(dimethylethyleneguanidino)naphthalene (DMEGN), the second example of a peralkyl guanidine "proton sponge" based on the 1,8-naphthalene backbone, was prepared and fully characterized. The crystal structure analysis of monoprotonated DMEGN reveals an unsymmetrical intramolecular hydrogen bridge. A decrease in the basicity with respect to the noncyclic parent 1,8-bis(tetramethylguanidino)naphthalene was found. Nevertheless, a new proton sponge provides a new crossbar in the ladder of highly basic neutral organic compounds. A detailed theoretical study of DMEGN and related cyclic guanidines explains this surprising experimental result. Homodesmotic reactions reveal that the intramolecular hydrogen bond contributes effectively 10 kcal/mol to proton affinity of DMEGN.

Introduction

Since the discovery of the unusual basicity of 1,8-diaminonaphthalene (DMAN) by Alder et al.,[1] the so-called "proton sponges" received continuous interest by a number of research groups.[2] Recently, a combination of the classical 1,8-substituted naphthalene skeleton with two peralkyl guanidine functions, known for their strong intrinsic proton affinity (PA) and basicity,[3] led to the development of 1,8-bis(tetramethylguanidino)naphthalene (TMGN) with an experimental pK_{BH^+} (MeCN) of 25.1 ± 0.2.[4] The thermodynamic basicity of TMGN is nearly 7 orders of magnitude higher than that of DMAN. Furthermore, tetramethylguanidino-substituted TMGN reveals a much higher kinetic activity in comparison with dimethylamino-based DMAN. Theoretical calculations reveal an interplay of two antagonistic factors in determining basicity in a moderately polar solvent like acetonitrile, the intrinsic gas-phase proton affinity and the size effect given by the ratio between the positive charge in the conjugate acid $[TMGN-H]^+$ and the magnitude of the molecular surface.[5] The dramatic increase in proton affinity and basicity by chelating the proton within an asymmetric $[N-H\cdots N]^+$ intramolecular hydrogen bond (IHB) is supported by these calculations: 1-tetramethylguanidino-naphthalene exhibits a $PA(MP2)_{gas}$ of 244.9 kcal mol^{-1} and a pK_{BH^+} (MeCN) of 20.5 (theoretical), while the chelating 1,8-bis(tetramethylguanidino)-naphthalene has a calculated $PA(MP2)_{gas}$ of 257.5 kcal mol^{-1} and a pK_{BH^+} (MeCN) of 25.4 (theoretical).[5]

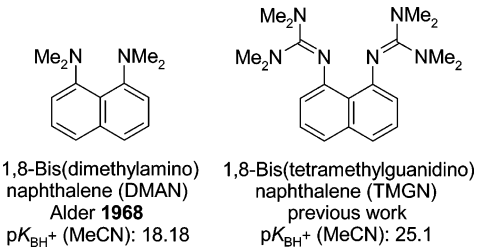

FIGURE 1. Classical "proton sponge" DMAN and bis(guanidine) "proton sponge" TMGN.

Intuitively, one can expect that a better conjugation of the π orbitals within the guanidine moiety of TMGN, consisting of a π double bond and the lone pairs of the NMe_2 groups forming the pseudo π orbitals, might be achieved if a relatively high freedom of rotation of the dimethylamino groups around the C−N bonds is hindered or completely prevented. It turned out, namely, that the steric repulsion between the dimethylamino groups in TMGN has led to a propeller-like conformation.[4,5] Consequently, we were tempted to conclude that, by forcing the guanidine system into a more coplanar five-membered ring system, an increase in the basicity might occur as a result of better conjugation. The pronounced

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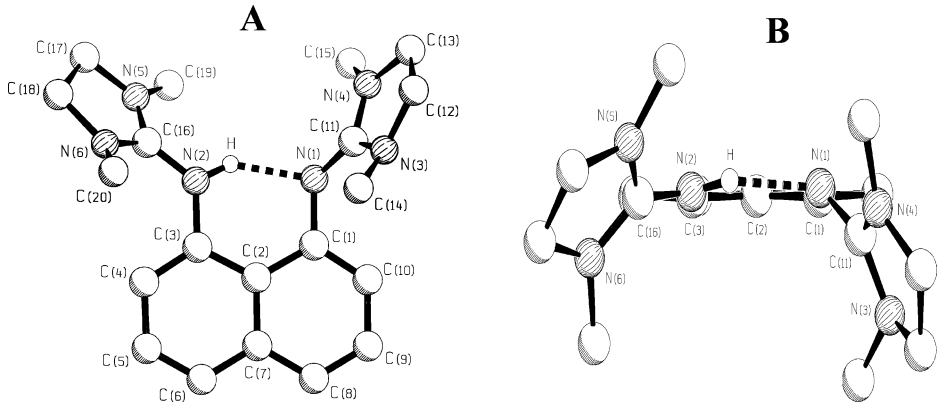
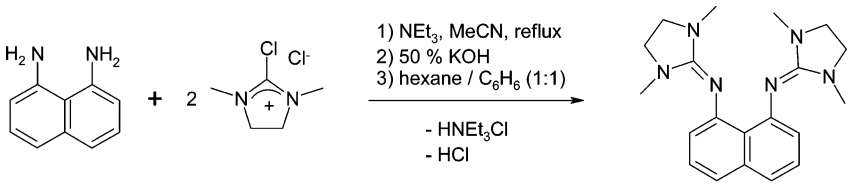


FIGURE 2. Molecular structure of [DMEGN−H][PF_6] (**2**).The anion is omitted for clarity, and the projection is perpendicular to the naphthalene ring plane (A) and along C(2)−C(7) vector (B).

SCHEME 1. Synthesis of DMEGN (1)



DMEGN (**1**)

N basicity of 1,3-dimethyl-1,3-dihydro-imidazole-2-ylideneamine,[6] an unsaturated cyclic guanidine derivative, is an example of this strategy. Thus, our attention was focused on a saturated congener containing two five-membered 1,3-dimethyl-imidazolidine-2-ylideneamine building blocks at the 1,8-positions of the naphthalene backbone aiming at its preparation and characterization. Much to our surprise, it turned out that the new compound was somewhat less basic than TMGN. In the last part of this paper, we theoretically address the problem and consider some properties of the newly prepared compound as well as features of the related unsaturated congener.

Results and Discussion

Synthesis of 1,8-Bis(dimethylethyleneguanidino)-naphthalene, DMEGN (1). The synthetic strategy outlined for TMGN[4] was also applied for DMEGN (Scheme 1). By treatment with phosgene, commercially available *N*,*N*′-dimethylethyleneurea (DMEU) is converted into the corresponding chlorformamidinium chloride. This Vilsmeyer salt is reacted with 1,8-diaminonaphthalene in MeCN in the presence of triethylamine as an auxiliary base. Without isolation, the resulting guanidinium salt is deprotonated with 50% KOH (aq) and extracted into hexane/C_6H_6 (1:1) to yield 78% of DMEGN after purification.

Monoprotonation of DMEGN is best accomplished by reaction of **1** with equimolar amounts of NH_4PF_6 in MeCN. Pure [**1**−H][PF_6] (**2**) is isolated in close to quantitative yield. Similar to acyclic TMGN and Schwesinger's superbasic vinamidine "proton sponge",[7] DMEGN is bisprotonated by strong acids, such as trifluoromethanesulfonic acid, yielding [**1**−H_2][OTf]$_2$ (**3**). This is in contrast to the kinetic inertness of the cation [DMAN−H]$^+$ with respect to further protonation.

Molecular Structure of [DMEGN−H][PF_6] (2). Single crystals were obtained by crystallization from MeCN. The molecular structure is shown in Figure 2, selected bond lengths and angles in Table 1S in Supporting Information (SI). The proton of the hydrogen bridge was located and isotropically refined. It is part of an unsymmetrical, nonlinear intramolecular hydrogen bridge. The angle N(2)−H···N(1), 141.6°, is smaller than that in [TMGN−H][PF_6], 152° (Table 1S), and the distances N(2)−H, 87 pm, and N(1)···H, 185 pm, differ more than those in [TMGN−H][PF_6] (91 and 175 pm). Despite a strong asymmetry, the "partial protonation"[5] occurs as a manifestation of the hydrogen bridge bonding. It can be derived from a new structural parameter ρ (vide infra) and the NMR spectrum of **2**.

Both guanidine CN_3 units are perfectly planar Σ°C(11)/C(16) = 359.98/360.0, but the rings are twisted with respect to the naphthalene ring system. The dihedral angle of planes defined by three atoms N(1)−C(1)−C(10) and N(3)−C(11)−N(4) is 63.5°, whereas planes N(2)−C(3)−C(4) and N(5)−C(16)−N(6) intersect with 51°.

The improvement in overall planarity of the cyclic guanidine **2** in comparison to the propeller-like conformation of the $-NMe_2$ groups in TMGN may be demonstrated by a review of the 12 N−C−N−C torsion angles at both guanidine CN_3 units. However, the closure condition of the five-membered ring leads also to a considerable pyramidalization at the ring amino groups NC_3 at the same time. The average sum of angles Σ°N is 355.8 for [DMEGN−H]$^+$, whereas for the more flexible

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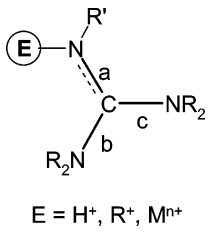

FIGURE 3. C−N bonds a, b, and c for the determination of quotient ρ.

TABLE 1. C−N Bond Lengths and Structural Parameter ρ

compound	C=N (*a*)	C−NR_2 (*b*, *c*)	ρ
TMGN[4]	128.2 ± 0.1	138.4 ± 0.1	0.93
[(TMG_3tren)Cu^{II}Cl]Cl[a]	131.4 ± 0.3	136.4 ± 0.5	0.96
[TMGN−H][PF_6] (N···H)	132.6 ± 0.0	135.8 ± 0.4	0.98
[TMGN−H][PF_6] (N−H)	135.1 ± 0.0	132.6 ± 1.6	1.02
[DMEGN−H][PF_6] (N···H)	130.3 ± 0.0	135.7 ± 1.7	0.96
[DMEGN−H][PF_6] (N−H)	134.5 ± 0.0	132.6 ± 0.2	1.01

[a] TMG_3tren = 1,1,1-tris[N^2-(1,1,3,3-tetramethylguanidino)methyl]ethane.[10]

$[TMGN−H]^+$ it reaches 359.0 (SI Table 1S). The naphthalene backbone of $[DMEGN−H]^+$ is planar and free of steric strain, C(3)−C(2)−C(7)−C(8) = 179.97°. Within the limits of accuracy, the N(1)···N(2) distance of $[DMEGN−H]^+$ (259.0 pm) is the same as that in $[TMGN−H]^+$ (259.3 pm), but it is different to sterically more crowded $[DMAN−H]^+$ (271.7 pm).

Structural Parameter ρ. The structural parameter ρ is defined as the ratio of the doubled C=N distance (*a*) and C−NR_2 distances (*b*, *c*): $\rho = 2a/(b + c)$ in the guanidine moiety (Figure 3). The ρ value reflects the elongation of the C=N double bond of a guanidine by protonation, alkylation, or coordination to a Lewis acid and a concomitant shortening of the average C−NR_2 distance. In structurally characterized guanidine bases such as TMGN, the length of the C−N double bond is 93% of the average C−NR_2 bond lengths, which is documented by a ρ value of 0.93. In symmetrical guanidinium cations $[C(NMe_2)_3]^+$, $\rho = 1.00$.[8] ρ ratios higher than 1.00 are possible, when the electrophile-quenched guanidine nitrogen atom −N(E)R is a weaker donating substituent than −NR_2. Table 1 lists ρ values of TMGN, $[TMGN−H]^+$, and $[DMEGN−H]^+$ along with a representative example for a copper(II) complex of a tripodal pentaalkyl guanidine ligand.[9] Upon full protonation corresponding to the stronger interaction within an unsymmetrical intramolecular hydrogen bridge, the ρ value increases from ≈0.93 to 1.00 ± 0.02. In contrast, the "partial protonation",[5] the weaker interaction within an unsymmetrical intramolecular hydrogen bridge, leads to values slightly lower than 1.00. Guanidine coordination to a Lewis acid leads to C−N double bond elongations ($\rho \approx 0.96$) half as much as full protonation.[10]

The comparison of $[DMEGN−H]^+$ and $[TMGN−H]^+$ reveals analogies as a consequence of the "triggered cationic resonance"[5] within the guanidine fragment not directly attacked by the proton. The structural parameter ρ is nearly identical for each corresponding guanidine function in both molecules. This indicates that the "partial protonation"[5] takes place through the existence of an unsymmetrical intramolecular hydrogen bridge. The corresponding ρ value is closer to the value of a fully protonated rather than to a nonprotonated guanidine species (Table 1).

NMR Spectra. The ^{1}H NMR spectrum of [DMEGN−H][PF_6] (**2**) shows a broad signal at $\delta_{NH} = 14.22$ ppm for the proton of the intramolecular hydrogen bridge (CD_2Cl_2, 400 MHz, 300 K). The *N*-methyl groups are magnetically equivalent under these conditions, which provides further evidence for a true intramolecular hydrogen bridge with a rapidly exchanging proton within the double minimum ground state. Contrastingly, bisprotonated [DMEGN−H_2][OTf]$_2$ (**3**) exhibits a signal at $\delta_{NH} = 9.31$ ppm (CD_2Cl_2, 400 MHz, 300 K). Because of the restricted freedom of C−N bond rotations[4] in comparison with TMGN, cyclic DMEGN does show less complex coalescence phenomena in its vt NMR spectra.[11] Only one regular low-temperature split of the *N*-methyl signal at 200 K was observed (CD_2Cl_2, 400 MHz). From the experimental spectrum and the coalescence temperature, a $\Delta G^{\ddagger}_{T_c}$ (T_c = 200 K) value of 37.9 ± 0.3 kJ mol^{-1} is estimated as barrier to rotation along the C=N bond axis.[12] This value is significantly lower than the corresponding value of TMGN ($\Delta G^{\ddagger}_{200}$ = 49.7 ± 0.1 kJ mol^{-1} [13]), probably due to the sterically less demanding five-ring guanidine substituent.[14]

A determination of the pK_{BH^+} value of **2** via NMR titrations with various bases, including TMGN, failed. Regardless of spectrometer frequency (300−500 MHz), solvent, and temperature applied, only broad signals of rapidly exchanging N donor centers were observed. Therefore we conclude that DMEGN possesses an even higher kinetic activity in proton exchange than TMGN. Figure 4 shows space-filling models of structurally characterized cations $[DMEGN−H]^+$, $[TMGN−H]^+$, and $[DMAN−H]^+$. It is obvious that the proton environment at protonated DMEGN is sterically less crowded than that of TMGN and that the latter is less crowded than the proton environment of DMAN. This trend is in accord with the common view that sterical crowding reduces the kinetic activity of proton exchange.

To our surprise, evidence for a lower basicity of DMEGN compared to TMGN was gained from weakly resolved dynamic NMR proton spectra of the 1:1 mixture of DMEGN/$[TMGN−H]^+$ in CD_3CN. Encouraged by the good agreement for calculated and experimental pK_{BH^+} values for $[TMGN−H]^+$,[4,5] a theoretical study was initiated in order to calculate the intrinsic gas-phase proton affinity (PA) and pK_{BH^+} values in MeCN.

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(11) For spectra, see Supporting Information.
(12) Calculated with: $\Delta G^{\ddagger} = 19.1 \times 10^{-3}(T_c)(9.97 + \log T_c - \log I\nu_A - \nu_B I)$. Hesse, M.; Meier, H.; Zeeh B. In *Spektoskopische Methoden in der organischen Chemie, 4. Aufl.*; Thieme Verlag: Stuttgart, New York, 1991.
(13) Calculated from graphical analysis of rate constants obtained from simulated spectra.[4]
(14) Experimental errors $\Delta\nu = \pm 2$ Hz, $\Delta T = \pm 2$ K, and $\Delta k = \pm 2\%$ (for TMGN) result in an error of $\Delta G^{\ddagger} = \pm 0.3$ kJ mol^{-1} (0.1 kJ mol^{-1} for TMGN).

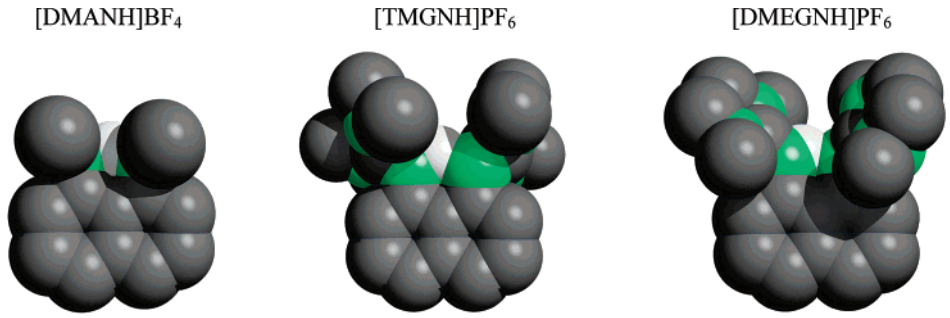

FIGURE 4. Comparative space-filling models of structurally characterized [DMEGN−H]$^+$, [TMGN−H]$^+$, and [DMAN−H]$^+$ salts.

Theoretical Investigation

Theoretical framework for calculating the absolute proton affinities (APAs) is thoroughly discussed elsewhere.[5] Briefly, APAs in the gas phase are given by

$$\mathrm{APA}(\mathrm{B}_\alpha) = (\Delta E_{\mathrm{el}})_\alpha + (\Delta \mathrm{ZPVE})_\alpha \quad (1)$$

$$(\Delta E_{\mathrm{el}})_\alpha = E(\mathrm{B}) - E(\mathrm{B}_\alpha\mathrm{H})^+ \quad (2)$$

$$(\Delta \mathrm{ZPVE})_\alpha = \mathrm{ZPVE}(\mathrm{B}) - \mathrm{ZPVE}(\mathrm{B}_\alpha\mathrm{H})^+ \quad (3)$$

The base in question and its conjugate acid are denoted by B and BH$^+$, respectively, whereas α signifies the site of proton attack. Equations 2 and 3 give the electronic and zero point vibrational (ZPVE) contributions to the proton affinity, respectively. The MP2(fc)/6-311+G**//HF/6-31G* + ZPVE(HF/6-31G*) (MP2) model is selected by comparing the calculated APAs against the experimental measured values at room temperature of some characteristic nitrogen compounds.[15] The Hartree−Fock vibrational frequencies are used to derive the ZPV energies by employing a common weighting factor, 0.89, as customary. The final single point calculations involve a use of the flexible 6-311+G** basis set and MP2 formalism in order to take into account the electron correlation effect.[15] A more efficient, but somewhat less accurate, model is provided by the scaled Hartree−Fock scheme.[15] The corresponding formula for the protonated nitrogen atoms has the following form:[16]

$$\mathrm{APA}(\mathrm{B_N}) = 0.8924\Delta E_{\mathrm{el}}(\mathrm{HF/6\text{-}31G^*})_\mathrm{N} + 10.4 \text{ kcal/mol} \quad (4)$$

Formula 4 is very useful for the pilot calculations in large systems, where a high efficiency is required.

The basicity in moderately polar aprotic solvents such as MeCN can be conveniently studied by using a theoretical model founded on a simple electrostatic picture of the polarized continuum.[16,17] The calculations of pK_{BH^+} values in MeCN (ϵ = 36.64) require several iterations, implying that an economical model is desired. We found that the B3LYP/6-311+G**//HF/6-31G* model, in which the ZPVEs are taken from the gas-phase calculations at the HF/6-31G* level, offers results in good accordance with the experimental data.[17] An excellent least-squares fit was achieved, which put the absolute proton affinities calculated in MeCN by the B3LYP/6-311+G**//HF/6-31G* model in line with the measured pK_{BH^+} values:

$$\mathrm{pK_{BH^+}}\,(\mathrm{MeCN}) = 0.4953\mathrm{APA(MeCN)} - 119.7 \quad (5)$$

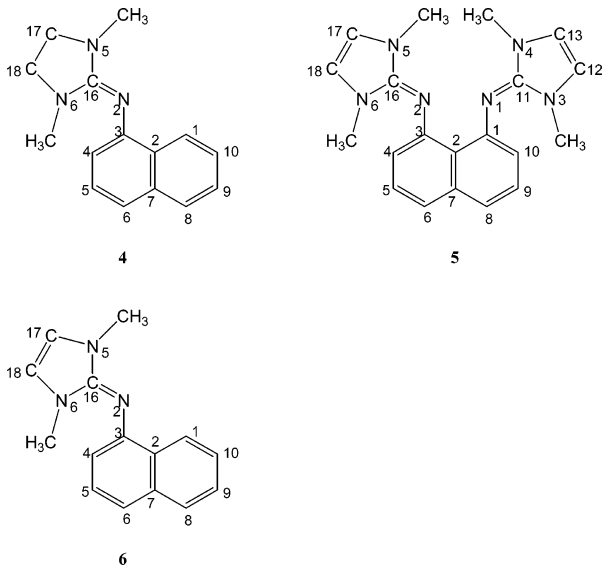

FIGURE 5. Schematic representation and atomic numbering of neutral bases **4**−**6**.

All computations were performed by using Gaussian94 and GAMESS programs.[18,19]

In addition to our target compound DMEGN (**1**) and its protonated form **1H**$^+$, compounds **4**−**6**, depicted in Figure 5, are theoretically studied too. Their structural data are deposited in SI Tables 5S and 6S. The main conclusions are briefly given here. Comparison of the HF/6-31G* structural parameters of **1** with the experimental data presented in SI Table 1S reveals a good agreement despite the fact that computational results are obtained for the gas phase, whereas the measured bond lengths and angles refer to the [DMEGN][PF_5] crystal.

The estimated structural features of **1** and **5** and their comparison indicate that inclusion of a new double bond

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inside the five-membered ring introduces some π conjugation in the latter as evidenced by the increase and decrease in the d(N(1)═C(11)) and d(C(11)─N(3)) bond distances, respectively. A double substitution at the C(1) and C(3) positions on the naphthalene perimeter by imine-nitrogens, attached in turn to five-membered rings in **1** and **5** by double bonds, causes modest but significant changes in the CC bond distances of the aromatic fragment, which deserve some more comments. A careful scrutiny of the bond distances within the naphthalene backbone reveals some resonance between guanidine, 1,3-dimethyl-imidazolidine-2-ylideneamine, and 1,3-dimethyl-1,3-dihydro-imidazole-2-ylideneamine moieties and the aromatic spacer. For this purpose it is helpful to introduce a deformation index Δd, which is given by:

$$\Delta d(\mathbf{n}) = \sum_{i=1}^{10} |d_i(\mathrm{fn}) - d_i(\mathbf{n})|/\text{Å} \qquad (6)$$

where fn and **n** within parentheses denote distances of free naphthalene and its derivative **n**, respectively. The summation is extended over all bond distances in naphthalene fragment. For instance, Δd(**n**) indices for **1**, **4**, **5**, and **6** assume values 0.103, 0.032, 0.110, and 0.041, respectively. Two important conclusions straightforwardly follow: (1) the conjugation effect is larger in **5** than in **1**, and (2) the conjugation in bis-substituted compounds is about three times larger than that in the corresponding monosubstituted naphthalenes. This finding bears some relevance in interpreting the proton affinities as we shall see shortly.

The (non)planarity of molecular fragments is also of some interest. A useful index of nonplanarity of the three-coordinated atoms is given by a degree of pyramidalization DP(%) defined as[20]

$$\mathrm{DP}(\%) = [360 - \sum_{i=1}^{3} \alpha_i]/0.9$$

where the summation goes over three sharp bond angles α_i of the apical three-coordinated atom in question. Degrees of pyramidalization of relevant atoms in **1** and **4**−**6** for the HF structures are given in Table 2.

Conformation of the five-membered rings relative to the naphthalene moiety in systems **1** and **4**−**6** is of importance. The relevant C(16)−N(2)−C(3)−C(4) angles defining this conformation in **1** and **4**−**6** assume values of −82.2, −69.2, −84.4, and −57.2°, respectively, as obtained by the HF model. It appears that a five-membered ring is considerably twisted around the N(2)−C(3) (and around N(1)−C(1)) bond relative to the naphthalene plane in all systems. They become almost perpendicular to this plane in **1** and **5** apparently due to steric requirements and subsequent repulsion of two five-membered rings, which ultimately assume anti positions. Perusal of the results reveals that the guanidine fragment involving N(2), C(16), N(6), and C(18) atoms is approximately planar, as indicated by the dihedral angles N(2)−C(16)−N(6)−C(18) and N(2)−C(16)−N(5)−C(17), which lie within the range of −172.8° to −177.9° and −164.8° to −178.2° in **1** and **4**−**6**, respectively. Apparently planarity of the guanidine moiety is more pronounced in monosubstituted naphthalenes as intuitively expected. Very small pyramidalization values DP(N6) and DP(N5) in **5** and **6** are in harmony with the essential planarity of the 1,3-dimethyl-1,3-dihydro-imidazole-2-ylideneamine fragment. They also indicate that the carbon atoms of the methyl groups are very close to the plane of heavy atoms in these five-membered rings. On the other hand, pyramidalization of N(6) and N(5) nitrogens in **1** (and **4**) is more pronounced, as evidenced by the respective DP(%) values, which assume 14.1, 13.0, 14.0, and 11.5%, correspondingly. This is consistent with appreciable puckering of the 1,3-dimethyl-imidazolidine-2-ylideneamine ring in **1,** which in turn is reflected in the relevant dihedral angles C(16)−N(6)−C(18)−C(17) being 25.1°[24.6°] and N(6)−C(18)−C(17)−N(5) amounting 31.3°[31.0°]. It is noteworthy that there is some deviation from the symmetry in the C(16)−N(6) and C(16)−N(5) bond lengths as well as between the N(6)−C(18) and N(5)−C(17) interatomic distances. They are not a consequence of the steric repulsions in bis-substituted naphthalenes **1** and **5**. This conclusion is derived from a fact that the corresponding bond distances in the five-membered rings are practically equal in compounds **1** and **4**, thus exhibiting the same asymmetry. The same holds for systems **5** and **6**. This finding calls, therefore, for a rationalization. Analysis of the structural parameters shows that it is a consequence of the repulsion between the naphthalene ring and the proximate CH_3 group of the five-membered ring moiety. These structural features have a decisive influence on the basicity of **1** and **5** (see later).

In the discussion of geometric properties of conjugate acids, it is important to realize that in the bis-guanidines **1** and **5**, the protonated forms can assume both syn and anti conformations. The latter are depicted in SI Figure 2S for **1H**$^+$syn and **1H**$^+$ anti isomers. Interestingly, their stability is practically the same. It is noteworthy that the syn conformer becomes more stable in MeCN. The same holds for the solid state (crystal) structure as found by the X-ray analysis (vide supra). Consequently, the structural data for both conformers are given in SI Table 6S, since they can both emerge in the gas phase. It appears

TABLE 2. Degrees of Pyramidalization (%) in Neutral Bases and Their Conjugate Acids[a]

Neutral Bases				
pyramidalization	**1**	**4**	**5**	**6**
DP(N5)	13.0(11.7)	11.5	0.0	0.0
DP(N6)	14.1(13.1)	14.0	2.1	1.7
DP(C17)			0.0	0.0
DP(C18)			0.1	0.0

Conjugate Acids						
pyramidalization	**1H**$^+$ syn	**1H**$^+$ anti	**4H**$^+$	**5H**$^+$ syn	**5H**$^+$ anti	**6H**$^+$
DP(N2)	0.7(0.9)	2.9	0.2	1.9	8.7	3.0
DP(N3)	12.5(12.3)	12.4		0.8	0.8	
DP(N4)	13.8(12.4)	12.8		0.1	0.1	
DP(N5)	0.7(0.7)	7.4	4.3	0.0	0.0	0.0
DP(N6)	0.3(0.4)	5.0	3.8	0.3	0.2	0.3

[a] Results based on B3LYP/6-31G* geometries are given within parentheses.

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that their bond distances are very close. An essential qualitative difference is found only in the sign of the dihedral angles defining both syn and anti conformations.

Changes induced by protonation in $\mathbf{1H}^+$ are instructive. The protonated C(16)−N(2) bond is lengthened due to rehybridization but also due to increased resonance as evidenced by shortening of C(16)−N(6) and C(16)−N(5) bonds. Interestingly, N(1)−C(11) is stretched too, whereas C(11)−N(3) and C(11)−N(4) bonds are contracted in accordance with the partial protonation effect observed earlier.[4,5] The latter is less pronounced than in a directly protonated fragment in harmony with intuition. Further, degrees of pyramidalization reveal considerable planarization of the amino nitrogens of the five-membered ring attached to the protonated imino N atom as evidenced by DP values of N(5) and N(6) (Table 2). Also, the protonated imino-nitrogen is almost planar as well (DP(2)) = 0.7% (0.9%)).

Structural features of the IHB in the protonated forms are of particular interest. The nonlinearity of the IHB is described by angle β. It assumes 125.7° and 135.6° in $\mathbf{1H}^+$ and $\mathbf{5H}^+$, respectively, implying that the IHB is more collinear in the latter compound. It should be also mentioned that the IHB is not perfectly planar in both the syn and anti conformations. Newertheless, it considerably contributes to the basicity of these systems (vide infra).

Energetic data are given in the SI as well. Their examination shows that $\mathbf{1H}^+$ syn and $\mathbf{1H}^+$ anti have the same proton affinities. It is of interest to trace down the origin of the absolute proton affinity of **1**. A useful vehicle in exploring intramolecular interaction between various fragments is provided by homodesmotic reactions.[21] This concept leads to eqs 7 and 8:

$$\mathbf{1} + \text{naphthalene} \rightarrow 2(\mathbf{4}) + \epsilon_1 \qquad (7)$$

and

$$\mathbf{1H}^+ \text{ syn} + \text{naphthalene} \rightarrow \mathbf{4H}^+ + \mathbf{4} + {\epsilon_1}^+ \qquad (8)$$

Calculations at the MP2 level give $\epsilon_1 = -0.7$ kcal/mol and ${\epsilon_1}^+ = -9.9$ kcal/mol. A small negative ϵ_1 value indicates that steric strain and a stabilization of the system **1**, occurring due to conjugative interaction between substituents and naphthalene moiety, practically cancel out. More precisely, the conjugation slightly prevails in magnitude leading to overall stabilization by −0.7 kcal/mol, which will diminish proton affinity by the same amount. A low negative ${\epsilon_1}^+$ value shows that the stabilization in $\mathbf{1H}^+$ syn is about 10 kcal/mol. This will enlarge proton affinity by that amount being the main reason behind an increase in APA of the bis-substituted compound **1** relative to its monosubstituted counterpart **4**. It should be strongly pointed out that ${\epsilon_1}^+$ is a result of an interplay between the IHB and decrease in the conjugative interaction with the naphthalene backbone. This is documented by $\Delta d(\mathbf{1})$ and $\Delta d(\mathbf{1H}^+)$ values 0.103 and 0.078, respectively. It follows as a corollary that a true IHB is higher than 10 kcal/mol. However, it is difficult to delineate individual contributions of the IHB stabilization and a decrease in conjugation effect across the naphthalene perimeter. It is worth noting that a decrease in conjugation between naphthalene and bis-substituted guanidine moieties upon protonation of imine-nitrogen is practically the same in TMGN and DMEGN. Analogous homodesmotic reactions related to **5** read:

$$\mathbf{5} + \text{naphthalene} \rightarrow 2(\mathbf{6}) + \epsilon_3 \qquad (9)$$

and

$$\mathbf{5H}^+ \text{ syn} + \text{naphthalene} \rightarrow \mathbf{6H}^+ + \mathbf{6} + {\epsilon_3}^+ \qquad (10)$$

Here, the ϵ_3 assumed value of −1.6 kcal/mol is implying that the stabilizing interaction of the two five-membered rings mediated by the naphthalene moiety through the conjugation mechanism overwhelms the steric repulsion to a greater extent than that in **1**. The effective IHB energy is 12.2 kcal/mol (${\epsilon_3}^+ = -12.2$ kcal/mol) thus being larger than in **1**. The effective IHB energy includes a decrease in the conjugation interaction with naphthalene upon protonation as evidenced by Δd values. They are $\Delta d(\mathbf{5}) = 0.110$ and $\Delta d(\mathbf{5H}^+) = 0.092$, respectively. It should be noticed that a decreased $\delta(\Delta d) = \Delta d(\mathbf{5}) - \Delta d(\mathbf{5H}^+)$ upon protonation being 0.018 is somewhat smaller than $\delta(\Delta d)$ in **1**, which amounts to 0.025. It is conceivable that a relatively large stabilization ${\epsilon_3}^+$ is at least partly a consequence of a smaller decrease in the conjugative interaction in **5** between five-membered rings and naphthalene compared to that in **1**. Additional arguments in favor of a stronger IHB in $\mathbf{5H}^+$ compared to that in $\mathbf{1H}^+$ are given by the increased collinearity discussed above and smaller N(1)···N(2) distance (2.658 vs 2.681Å). Taking into account that IHB includes a partial protonation of the neighboring guanidine moiety immersed in a five-membered ring, it follows that the IHB is a complex phenomenon, which embraces the whole molecular system. In other words, the effective IHB stabilization is a collective effect, which is not confined only to the X−H···Y bridge. This is consistent with the resonance-assisted hydrogen bonding (RAHB) concept developed by Gilli et al.[22] As a result of a larger IHB stabilization, the corresponding APA(**5**) = 256.0 kcal/mol is higher than the proton affinity of **1** by 4.2 kcal/mol. It follows that inclusion of the endo-double bond in the five-membered rings in **5** increases its proton affinity to relatively large 256.0 kcal/mol. Finally, it is worth noting that **1** has a lower APA than TMGN by 7.2 kcal/mol.[4,5] This difference can be traced down essentially to the greater pyramidalization in the five-membered ring. Additionally, the partial protonation effect in TMGN is larger than that in **1**. This conclusion is supported by ρ values for [TMGN−H][PF_6] (N···H) and [DMEGN−H]-[PF_6] (N···H), which amount 0.98 (0.95) and 0.96 (0.93), respectively. Here the experimental and Hartree−Fock ρ values are given without and within parentheses, respectively. We would like to reiterate that a ρ value closer to 1.00 implies a more pronounced resonance effect induced by partial protonation. It should also be mentioned that $\mathbf{5H}^+$ anti has a slightly higher APA (258.1 kcal/mol) than TMGN (257.5 kcal/mol), which in turn is

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expected in view of a larger cationic resonance effect in unsaturated five-membered ring.

The calculated pK_{BH^+} values are given in SI Table 7S. It appears that $\mathbf{1H}^+$ syn corresponds to a more basic protonated form of **1** compared to $\mathbf{1H}^+$ anti in MeCN. The most basic system is given by **5**, if the $\mathbf{5H}^+$ syn conjugate acid is considered, which has a $pK_{BH^+} = 25.8$.

Conclusion

The structural, spectroscopic, and theoretical results of a detailed study of the second "proton sponge", DMEGN, representing a growing class of 1,8-bis(guanidino)naphthalenes, is presented. The linkage and incorporation of two *N*-methyl groups of the known superbase TMGN into a five-membered imidazoline ring does not increase but decreases the basicity. This surprising result is explained by a crystal structure analysis of protonated $[DMGN-H]^+$ in combination with a theoretical analysis. The main factor influencing the gas-phase proton affinity and the pK_{BH^+} (MeCN) value is the pyramidalization of the peripheral dialkylamino groups. In both "proton sponges" TMGN and DMEGN, the central CN_3 guanidine units are perfectly planar. However, there are important differences in the planarity vs pyramidalization and conjugation of the peripheral amino groups NC_3 with the central CN_3 unit in these two compounds. The constraint imposed by the geometry of the five-membered imidazoline ring of DMEGN leads to a considerable pyramidalization at the peripheral ring nitrogen atoms thus preventing a perfect π conjugation of both amino groups with the central CN_3 unit. In TMGN, although sterically more demanding, at least one of the two dimethylamino groups is conformationally less constrained thus being in better conjugation with the CN_3 unit, whereas the other one is twisted into a propeller-like conformation. Theoretical results reveal that the drawback of pyramidalization in imidazoline-based bis-guanidines can be compensated by involving the peripheral nitrogen atoms into an aromatic planar 1,3-dimethyl imidazole system. This and even more extended conjugated bis-guanidines are fascinating synthetic targets for the development of the next generation of guanidine-based "proton sponges", which will eventually lead to further enrichment of the ladder of strong organic (super)bases. It is important to emphasize that formation of an IHB upon protonation affects the conjugate acid in its entirety, implying that it is justified to talk only about the overall or effective hydrogen bond stabilization energy. This is in harmony with the resonance assisted formation of intra- and intermolecular hydrogen bonds in planar π systems.[22] This finding explains earlier failures in correlating the strength of IHB to structural parameters involving only three N−H···N atoms forming the bridge.[23] The IHB is a rather complex collective phenomenon in protonated species.

Experimental Section

Materials and Methods. All experiments were carried out in hot-assembled and under vacuum-cooled glassware under an inert atmosphere of argon (99.998%) dried with P_4O_{10} granulate. Solvents and triethylamine were purified according to literature procedures and also kept under an inert atmosphere. 1,8-Diaminonaphthalene was purified by distillation from zinc dust.[24] NH_4PF_6 and trifluoromethanesulfonic acid for protonation were used as purchased. Substances sensitive to moisture and air were kept in a nitrogen-flushed glovebox.

Caution! Phosgene is a severe toxic agent that can cause pulmonary embolism and in the case of heavy exposition may be lethal. Use only in a well-ventilated fume hood.

***N,N′*-Dimethylethylenechlorformamidinium Chloride.**[25] According to a general literature method,[26] for 2 h at −20 °C, phosgene was passed through a solution of *N*,*N*'-dimethylethyleneurea, DMEU (Merck, 57.7 g, 61.2 mL, 505 mmol), in toluene (300 mL). The reaction mixture was stirred for 12 h at room temperature and for another 2 h at 50−60 °C under reflux of the phosgene. After the mixture cooled to room temperature, the white precipitate was filtered, washed with dry ether, and dried in vacuo, yield: 83% (71 g, 420 mmol). ^{1}H NMR (200.1 MHz, CD_3CN, RT): $\delta = 4.00-3.87$, (m, 4 H), 3.23−3.04 (m, 6 H) ppm. ^{13}C NMR (50.3 MHz, CD_3CN, RT): $\delta = 50.2$, 34.6 ppm, CN_3, no signal. IR (KBr): $\tilde{\nu} = 3442$ w (b), 2923 s, 2853 s, 1630 s (b), 1541 s (b), 1466 s, 1416 m, 1377 m, 1282 m (b), 1150 w, 1085 w, 988 w, 958 m, 815 w, 721 w, 630 s, 616 s cm^{-1}. MS (FD, MeCN): *m*/*z* (%) = 169 $[M]^+$, 133 $[M - Cl]^+$. Anal. Calcd for $C_5H_{10}N_2Cl_2$ (169.05): C, 35.53; H, 5.96; N, 16.57. Found: C, 35.07; H, 6.19; N, 16.03.

1,8-Bis(dimethylethyleneguanidino)naphthalene, DMEGN (1). 1,8-Diaminonaphthalene (2.39 g, 15.1 mmol) and *N*,*N*′-dimethylethylenechlorformamidium chloride (5.07 g, 30.0 mmol) were dissolved in dry MeCN (75 mL) at 0 °C under inert atmosphere. Triethylamine (3.10 g, 4.20 mL, 30.6 mmol) was slowly added. After 3 h at reflux, 50 wt % KOH (aq, 30 mL) was added and the free base was extracted into the MeCN phase. After MeCN was evaporated under reduced pressure, the crude product was dissolved in warm hexane/C_6H_6 (1:1), stirred over activated charcoal, and filtered. Evaporation of the solvents gave DMEGN as a white powder, yield: 78% (4.1 g, 11.7 mmol). Mp: 159 °C. ^{1}H NMR (200.1 MHz, CD_3CN, RT): $\delta = 7.26-7.05$ (m, 4 H), 6.55−6.43 (m, 2 H), 3.22−3.14 (m, 8 H), 2.54−2.46 (m, 12 H) ppm. ^{1}H NMR (400.1 MHz, CD_2Cl_2, 300 K): $\delta = 7.23$ (dd, $^3J(H_4,H_3) = 8.4$ Hz, $^4J(H_4,H_2) = 1.5$ Hz, 2 H) 7.15 (dd, $^3J(H_3,H_4) \approx {}^3J'(H_3,H_2) \approx 7.3$ Hz, 2 H), 6.57 (dd, $^3J(H_2,H_3) = 6.8$ Hz, $^4J(H_2,H_4) = 1.0$ Hz, 2 H), 3.21 (s, 8 H), 2.55 (s, 12 H) ppm. ^{1}H NMR (400.1 MHz, CD_2Cl_2, 175 K): $\delta = 7.32-7.03$ (m, 4 H), 6.63−6.39 (m, 2 H), 3.12 (s, 8 H), 2.67 (s, 6 H), 2.10 (s, 6 H) ppm. ^{13}C NMR (50.3 MHz, CD_3CN, RT): $\delta = 151.2$, 149.5, 137.2, 125.9, 120.1, 48.5, 34.5 ppm. ^{13}C NMR (100.6 MHz, CD_2Cl_2, 300 K): $\delta = 150.8$, 148.9, 136.8, 125.5, 124.5, 120.1, 117.4, 48.6, 34.7 ppm. IR (KBr): $\tilde{\nu} = 2924$ s, 2854 m, 1685 s, 1637 w, 1561 m, 1462 s, 1377 m, 1284 w, 1011 m, 959 m, 829 m, 763 m cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 350.5 (100) $[M]^+$, 251.3 (14) $[M - C_5H_{11}N_2(ring)]^+$, 99.1 (12) $[C_5H_{11}N_2(ring)]^+$. MS (ESI, MeCN): *m*/*z* (%) = 351 $[M]^+$; MS (FD, MeCN): *m*/*z* (%) = 350 $[M]^+$. Anal. Calcd for $C_{20}H_{26}N_6$ (350.47): C, 68.54; H, 7.48; N, 23.98. Found: C, 68.60; H, 7.56; N, 23.12.

1,8-Bis(dimethylethyleneguanidinium)naphthalene-hexafluorophosphate (2), [1−H][PF$_6$]. DMEGN (**1**) (350 mg, 1.00 mmol) and 1 equiv NH_4PF_6 (160 mg, 0.98 mmol) were dissolved in MeCN (15 mL) and stirred for 1 h at 50 °C. After the addition of activated charcoal at 50 °C, the solution was stirred for 15 minutes and filtered through Celite and volatiles were evaporated. [**1**−H][PF_6] was obtained as pale-yellow crystals by crystallization from hot saturated MeCN solution in 96% yield (469 mg, 0.95 mmol). Mp: 300 °C (dec).

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^{1}H NMR (200.1 MHz, CD_3CN, RT): δ = 7.56−7.23 (m, 4 H), 6.92−6.65 (m, 2 H), 3.69−3.54 (m, 8 H), 2.85−2.70 (m, 12 H) ppm. ^{1}H NMR (400.1 MHz, CD_2Cl_2, 300 K): δ = 14,22 (bs, 1 H), 7.36 (dd, $^3J(H_4,H_3)$ = 8.4 Hz, $^4J(H_4,H_2)$ = 1.0 Hz, 2 H), 7.30 (dd, $^3J(H_3,H_4) \approx {}^3J'(H_3,H_2) \approx$ 7.3 Hz, 2 H), 6.72 (dd, $^3J(H_2,H_3)$ = 7.3 Hz, $^4J(H_2,H_4)$ = 1.0 Hz), 3.69 (s, 8 H), 2.84 (s, 12 H) ppm. ^{1}H NMR (400.1 MHz, CD_2Cl_2, 180 K): δ = 14.52 (s, 1 H), 7.32−7.23 (m, 4 H), 6.67−6.61 (m, 2 H), 3.69−3.54 (m, 8 H), 2.77 (s, 12 H) ppm. ^{13}C NMR (50.3 MHz, CD_3CN, RT): δ = 126.4, 48.8, 35.0 ppm. ^{13}C NMR (100.6 MHz, CD_2Cl_2, 300 K): δ = 158.2, 141.2, 136.6, 126.0, 121.8, 115.0, 48.6, 35.2 ppm. IR (KBr): $\tilde{\nu}$ = 3372 w, 2940 w, 2886 w, 1643 m, 1610 s, 1573 s, 1518 m, 1469 m, 1412 m, 1369 w, 1294 s, 1021 m, 968 m, 837 s, 768 w, 557 s cm^{-1}. MS (FD, MeCN): *m*/*z* (%) = 497 (1) $[M]^+$, 351 (100) $[M - PF_6]^+$. Anal. Calcd for $C_{20}H_{27}N_6PF_6$ (496.44): C, 48.39; H, 5.48; N, 16.93. Found: C, 47.51; H, 5.29; N, 16.59.

1,8-Bis(dimethylethyleneguanidinium)naphthalenebistriflate (3), [1−H$_2$][OTf]$_2$. DMEGN (**1**) (350 mg, 1.00 mmol) dissolved in dry Et_2O (20 mL) was added dropwise to trifluoromethanesulfonic acid (0.9 mL, 10 mmol). A precipitate formed instantly, which, after 1 h stirring at room temperature, was filtered and washed with dry Et_2O. Analytically pure **3** was obtained by dissolving the product in dry MeCN, stirring the solution over activated charcoal (50 °C, 15 min), filtering the solution through Celite, and crystallizing the mixture from a solution of reduced volume. Yield: 93% (605 mg, 0.93 mmol). Mp: 238 °C. ^{1}H NMR (200.1 MHz, CD_3CN, RT): δ = 8.48 (s, 2 H), 8.17−7.97 (m, 2 H), 7.75−7.42 (m, 4 H), 3.81−3.63 (m, 8 H), 2.75−2.57 (m, 12 H) ppm. ^{1}H NMR (400.1 MHz, CD_2Cl_2, 300 K): δ = 9.31 (s, 2 H), 7.98 (d, $^3J(H_4,H_3)$ = 8.4 Hz, 2 H), 7.58 (dd, $^3J(H_3,H_4) \approx {}^3J'(H_3,H_2) \approx$ 8.1 Hz, 2 H), 7.42 (d, $^3J(H_2,H_3)$ = 7.3 Hz, 2 H), 3.92−3.81 (m, 4 H), 3.69−3.58 (m, 4 H), 2.65 (s, 12 H) ppm. ^{1}H NMR (400.1 MHz, CD_2Cl_2, 175 K): δ = 9.20 (s, 2 H), 7.96 (d, $^3J(H_4,H_3)$ = 8.4 Hz, 2 H), 7.55 (dd, $^3J(H_3,H_4) \approx {}^3J'(H_3,H_2) \approx$ 6.8 Hz, 2 H), 7.41 (d, $^3J(H_2,H_3)$ = 7.3 Hz, 2 H), 3.70 (s, 4 H), 3.60 (s, 4 H), 2.52 (s, 12 H) ppm. ^{13}C NMR (50.3 MHz, CD_3CN, RT): δ = 130.5, 49.4, 34.1 ppm. ^{13}C NMR (100.6 MHz, CD_2Cl_2, 300 K): δ = 157.3, 136.1, 130.5, 130.3, 129.0, 127.8, 126.5, 119.0, 49.4, 34.2 ppm. IR (KBr): $\tilde{\nu}$ = 3306 bm, 2943 w, 1640 s, 1602 w, 1572 w, 1485 w, 1416 w, 1373 w, 1295 m, 1265 s, 1239 m, 1223 m, 1161 s, 1031 s, 639 s cm^{-1}. MS (FD, MeCN): *m*/*z* (%) = 501 (45) $[M - (HOTf)]^+$, 351 (100) $[M - (HOTf)_2]^+$. Anal. Calcd for $C_{22}H_{28}N_6O_6S_2F_6$ (650.61): C, 40.61; H, 4.34; N, 12.92. Found: C, 39.47; H, 5.45; N, 13.01.

X-ray Structure Analysis. Crystal data and experimental conditions are listed in SI Table 4S. The molecular structures are illustrated as Schakal[27] plots in Figure 2. Selected bond lengths and angles with standard deviations in parentheses are presented in SI Table 1S. The collected reflections were corrected for Lorentz and polarization effects. All structures were solved by direct methods and refined by full-matrix least-squares methods on F^2.[28] Hydrogen atoms were calculated and refined with fixed isotropic thermal parameters except H(**2**), which was found and isotropically refined.[29] There is a 2-fold disorder of the anion and one of the methyl groups.

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Supporting Information Available: Tables of experimental structure parameters and X-ray crystallographic data for **1**, vt NMR spectra, tables of theoretical structure parameters for **1**−**4** and **1H**$^+$−**4H**$^+$, respectively, tables of total molecular and vibrational energies, and absolute proton affinities. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-194523 (**2**). Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. Fax: (+ 44) 1223 336-033. E-mail: deposit@ccdc.cam.ac.uk.