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1,8-Bis(hexamethyltriaminophosphazenyl)naphthalene, HMPN: A Superbasic Bisphosphazene "Proton Sponge"

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Abstract: It is shown that a combination of Schwesinger's phosphazene base concept and the idea of the disubstituted 1,8-naphthalene spacer, first introduced by Alder in paradigmatic 1,8-bis(dimethylamino)-naphthalene (DMAN), yields a new superbase, HMPN, which represents the up to date most basic representative of this class of "proton sponges", as evidenced by the theoretically estimated proton affinity PA = 274 kcal/mol and the measured pK_{BH^+} (MeCN) 29.9 ± 0.2. HMPN is by nearly 12 orders of magnitude more basic than Alder's classical 1,8-bis(dimethylamino)naphthalene (DMAN). The title compound, HMPN, is prepared and fully characterized. The spatial structure of HMPN and its conjugate acid is determined by X-ray technique and theoretical DFT calculations. It is found that monoprotonated HMPN has an unsymmetrical intramolecular hydrogen bridge (IHB). This cooperative proton chelating effect renders the bisphosphazene more basic than Schwesinger's set of "monodentate" P₁ phosphazene bases. The density functional calculations are in good accordance with the experimental results, providing some complementary information. They conclusively show that the high basicity of HMPN is a consequence of the high energy content of the base in its initial neutral state and the intramolecular hydrogen bonding in the resulting conjugate acid with contributions to proton affinity of 14.1 and 9.5 kcal/mol, respectively.

Introduction

Neutral organic bases and superbases play an important role in the organic syntheses as useful auxiliaries.[1,2] They are efficient catalysts particularly if immobilized on appropriate surfaces.[3−8] It should be mentioned that they can greatly contribute to green chemistry because they are recyclable, thus being economical at the same time. Another aspect of importance is given by their chiral derivatives, which have found useful applications in both catalytic and stoichiometric asymmetric syntheses.[9] As an example of a general usefulness of strong bases in pharmacology, we shall single out recent application in some gene therapeutic procedures.[10,11]

Particular interest has been focused on neutral organic bases with chelating proton acceptor functionalities exhibiting en-

hanced basicity, known as "proton sponges". The prototypal compound of this type, 1,8-bis(dimethylamino)naphthalene (DMAN), was introduced by Alder et al. some 35 years ago.[12] The design of more basic proton sponges received unabated attention by an increasing number of research groups[13−21] ever since. Compared to ordinary alkyl and arylamines, amidines, and guanidines, such proton chelators lead to a dramatic increase in basicity on account of the following: (i) destabilization of the initial base as a consequence of strong repulsion of the unshared electron pairs; (ii) formation of an intramolecular hydrogen bond (IHB) in the protonated form; and (iii) relief of

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the steric strain upon protonation in the final state. Although (i) and (iii) are two sides of the same coin, they belong, strictly speaking, to the initial and final state effects, respectively, which is generally useful to distinguish. Two general concepts to raise the intrinsic thermodynamic proton affinity and basicity have been followed in the past. One is to replace the naphthalene skeleton by other aromatic spacers, thus varying the N···N distance of the proton pincers.[22−25] The other concept focuses on the variation of the substituents at the basic nitrogen atoms[26−28] or at the spacer, thus leading to the "buttressing effect" (Figure 1).[16,29,30]

Among strongly basic proton sponges, which are not based on aromatic skeletons, one should single out Schwesinger's vinamidines,[31] Verkade compounds,[32−34] and Alder's aliphatic C2-chiral diamines described recently.[35]

There is a tendency, however, that sterically demanding proton sponges with high thermodynamic basicity with strongly protected protonation sites often have a low kinetic basicity. Typically, the captured proton does not take part in rapid proton exchange reactions, which would enable such neutral superbases to serve as catalysts in salt-free base-catalyzed reactions. A successful strategy to overcome the kinetic inertness of most amino-based proton sponges is to lower the steric congestion in close proximity to the N···H···N IHB. This can be accomplished by designing proton sponges with sp^2 N-donor functionalities as part of an extended π-system instead of the "classical" $N(sp^3)···H···N(sp^3)$ bridge. Recently, we have prepared such a system possessing high thermodynamic basicity in combination with large kinetic activity in 1,8-bis(tetramethylguanidino)naphthalene (TMGN),[36−38] a proton sponge with an experimental pK_{BH^+} (MeCN) of 25.1 ± 0.2, 7 orders of magnitude higher than that of DMAN (Figure 2). The large scale access of TMGN and related 1,8-bis(dimethylethyleneguanidi-
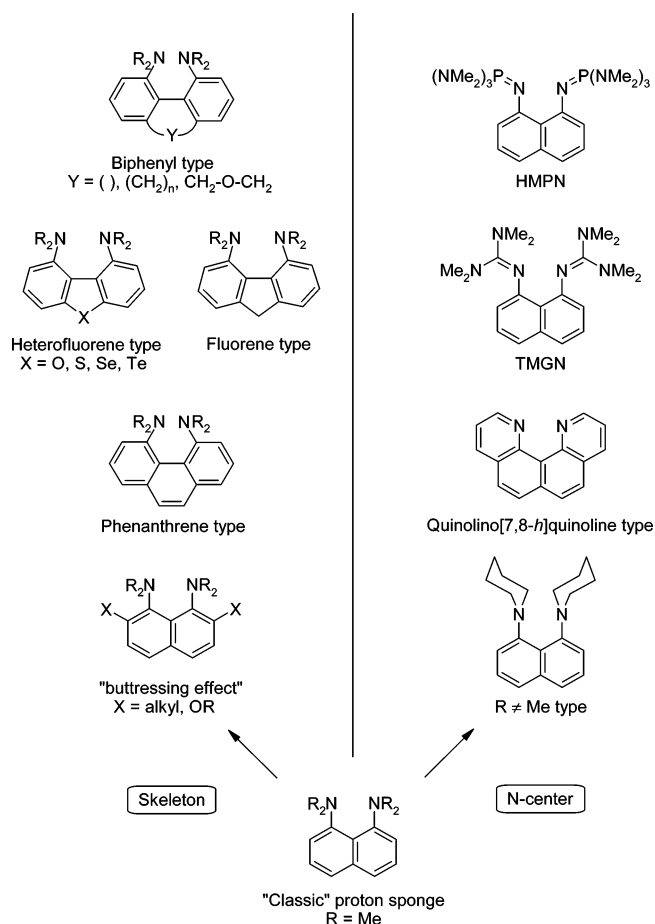

Figure 1. Survey of the strategies to affect and increase the basicity of proton sponges.

no)naphthalene (DMEGN)[39] is a precondition for their application as catalysts or proton scavengers in organic or inorganic synthesis. In this respect, as well as in their relative stability against hydrolysis and oxidation, bisguanidines have some distinct advantages over other chelating superbases, such as bisamidines.[31] Tetramethylguanidino-substituted TMGN reveals a much higher kinetic activity in comparison with that of dimethylamino-based DMAN.

An extension of our previous work[36,38−40] is given by replacement of the guanidine groups in **2** by phosphazene fragments, such as in HMPN **3**. In view of the high basicity of monodentate phosphazenes "Schwesinger bases",[41] it is expected that **3** would exhibit considerably higher basicity compared to that of **2**. The present work vindicates this conjecture. The synthesis of N=PPh₃-substituted proton sponges has been previously reported by Llamas-Saiz et al.[42] However, the free base could not be isolated, and only the monoprotonated salts were presented along with their crystal structure. Determination of their pK_{BH^+} values proved to be difficult due to decomposition of the sponge.[42] Here we report the synthesis of HMPN **3**, its X-ray structure determination, pK_{BH^+} measurements by NMR

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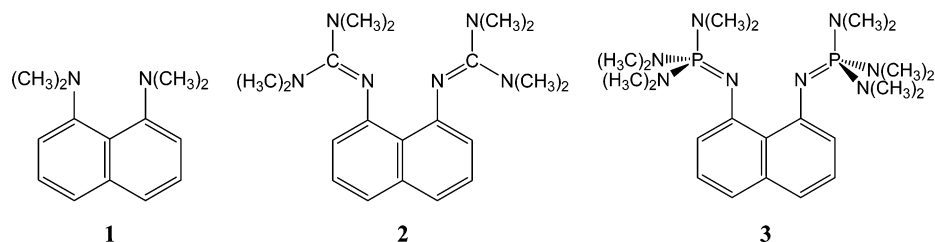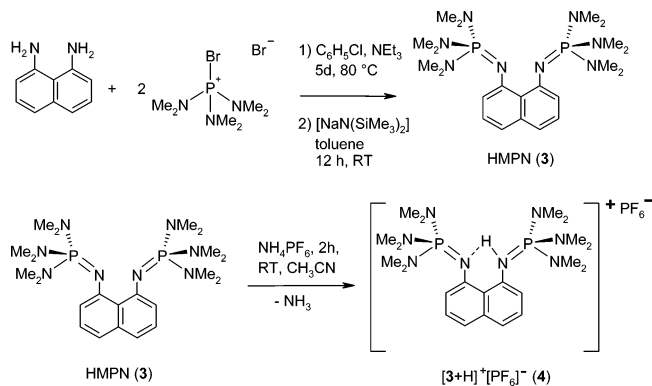
Figure 2. "Classical" proton sponge DMAN **1**, bis(guanidine) TMGN **2**, and bis(phosphazene) HMPN **3**.

Scheme 1. Synthesis of HMPN (**3**) and Its Protonated Form (**4**)

technique, and the results of the density functional (DFT) B3LYP calculations. Although HMPN does not exhibit a record basicity, it is an important rung on the superbasicity scale. It has some advantageous properties as described below.

Results and Discussion

Synthesis of 1,8-Bis(hexamethyltriaminophosphazenyl)-naphthalene, HMPN (3). 1,8-Diaminonaphthalene is reacted with [P(NMe$_2$)$_3$Br]Br in chlorobenzene, whereas triethylamine participates as an auxiliary base. After stirring at elevated temperature, protonated HMPN intermediate is deprotonated by addition of [NaN(SiMe$_3$)$_2$] in toluene followed by extraction into hot hexane to yield 43% HMPN (**3**) in the form of slightly yellow prisms after crystallization. Monoprotonation of **3** was realized by reaction with NH$_4$PF$_6$ in MeCN and [**3** + H]$^+$[PF$_6$]$^-$ (**4**) then crystallized by layering with ether.

Molecular Structure of the Free Base HMPN (3). Single crystals were obtained by crystallization from hexane. The molecular structure is shown in Figure 3, while selected bond lengths and angles are given in Table 1S of the Supporting Information. Theoretical B3LYP/6-31G* results are presented in Table 4S.

The molecular structure of **1** is close to C_2 symmetric with only small deviations from ideal symmetry as a consequence of the steric repulsion between the P(NMe$_2$)$_3$ groups. Interestingly, and in contrast to the guanidine proton sponges, TMGN and DMEGN, the P(NMe$_2$)$_3$ groups are only slightly out of plane from the naphthalene ring. Within the geometry of a distorted

tetrahedron, the P atoms exhibit a significantly shorter bonding distance by ∼10 pm to the sp^2 hybridized N atoms (N1; 155.5 ± 0.1 pm) than to the terminal N atoms of the NMe$_2$ groups (N2, N3, N4; average 165.8 ± 0.1 pm). The naphthalene backbone of **3** is twisted by ∼6°, reflecting the steric strain induced by the large P(NMe$_2$)$_3$ groups: C(1/1_2)−C(6)−C(5)−C(4_2/4) = 173.89°. Compared to other proton sponges previously discussed,[36] HMPN reveals a quite large nonbonding distance of 282.3 pm between the N acceptor atoms N(1)⋯N(1_2), which is close to that in DMAN (DMAN = 279.2 pm;[43] TMGN = 271.7 pm; 1,8-diaminonaphthalene = 272 pm[13c]). The structural resemblance of the naphthalene moiety in HMPN and DMAN is further reflected in the C(1)−C(6)−C(1_2) angle of 125.94° (DMAN = 125.8°; TMGN = 122.6°) and the nonbonding C(1)−C(1_2) distance of 259.5 pm (DMAN = 256.2 pm; TMGN = 251.9 pm).

Molecular Structure of [HMPN + H]$^+$[PF$_6$]$^-$ (4). Single crystals were obtained by crystallization from MeCN. The molecular structure is shown in Figure 4, and selected bond lengths and angles are summarized in Table 1S. Theoretical B3LYP/6-31G* prediction of the structure is given in Table 4S.

Analysis of the X-ray data of the monoprotonated HMPN reveals a strongly unsymmetrical, nonlinear intramolecular hydrogen bridge (IHB) (N(2)−H(1) = 88 ± 3 pm; N(1)−H(1) = 176 ± 3 pm; N(1)−H(1)−N(2) = 150 ± 3°). In [**3** + H]$^+$[PF$_6$]$^-$, the C_2 symmetry of the corresponding base structure is not preserved. The NMe$_2$ groups of the P(1) atom adopt a staggered conformation relative to those at the P(2) atom. In comparison with the geometry of the P atoms in HMPN, it is interesting to observe that the arrangement of the corresponding bonds in [HMPN + H]$^+$ is closer to the ideal tetrahedron.

To describe a degree of the tetrahedral deformation, it is useful to introduce the deformation index TD:

$$TD\ (\%) = 0.944 \left[\sum_{i=1}^{6} |(a_i - 109.5)| \right] (\%)$$

where a_i (given in degrees) denotes one of the six bond angles of the tetrahedral atom. A factor 0.944 is obtained by defining the most distorted tetrahedron, TD$_{max}$, as the one possessing three equivalent bonds forming the bond angles of 90°. It appears that the P atoms in the initial HMPN base have a substantial tetrahedral distortion of 41.4%. In contrast, the phosphorus atom in the protonated HMPN belonging to the directly attacked phosphazene fragment has a TD value of only 13.7%. Its phosphazene counterpart (partially protonated through an intramolecular hydrogen bond) is deformed twice as much

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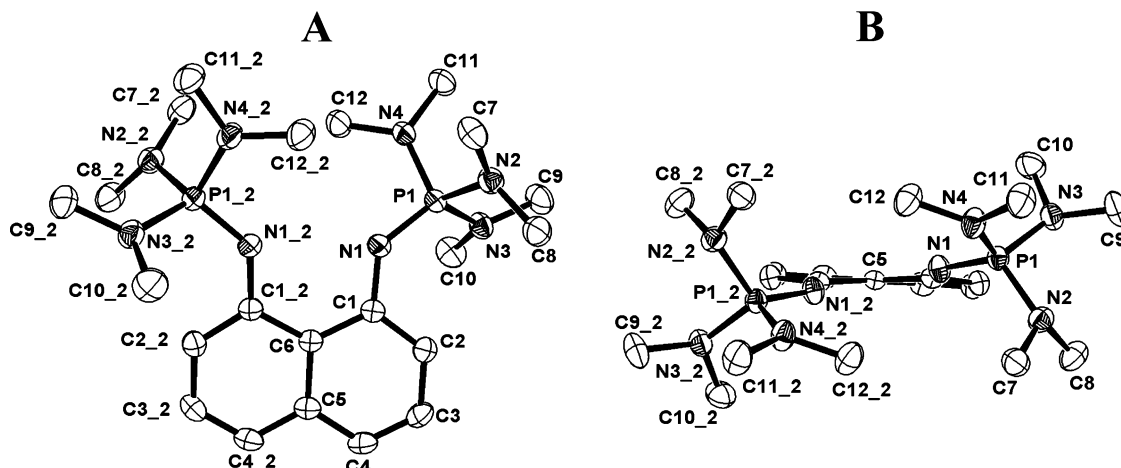
Figure 3. Molecular structure of HMPN (**3**). Hydrogen atoms were omitted for clarity. Projection is perpendicular to the naphthalene ring plane (A) and along the C(6)−C(5) vector (B).
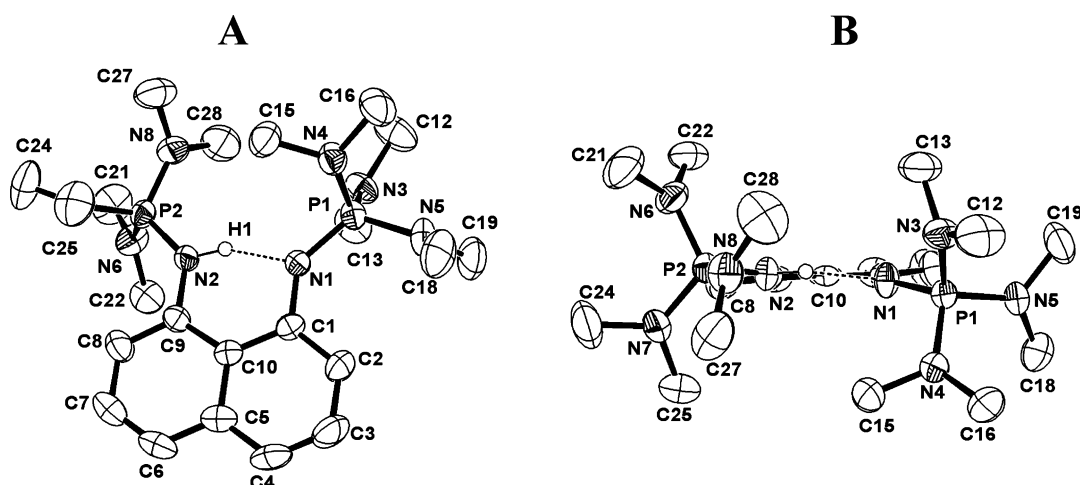

Figure 4. Molecular structure of [HMPN + H]⁺[PF₆]⁻ (**4**). Hydrogen atoms and PF₆⁻ anion were omitted for clarity. Projection is perpendicular to the naphthalene ring plane (A) and along the C(6)−C(5) vector (B).

as reflected in a TD value of 26.9%. It is interesting to observe that the latter denotes an intermediate distortion between the neutral (41.4%) and directly protonated phosphazene (13.7%) value. This is a signature of the partial protonation effect observed earlier in the protonated TMGN and related proton sponges.[36,38,39]

By influence of the IHB, the nonbonding distance between the nitrogen atoms N(1) and N(2) is reduced to 256.8(3) pm, and the naphthalene ring becomes close to planar.

NMR Studies and pK_{BH^+} Value. The ¹H NMR spectrum of the IHB of [HMPN + H]⁺[PF₆]⁻ (**4**) exhibits a triplet at δ_{NH} = 15.0 ppm (CD₃CN) with $^2J_{H-P}$ = 4.9 Hz. Furthermore, the ³¹P{¹H} NMR spectrum of **4** reveals a singlet for equivalent nuclei, due to a rapid intramolecular proton exchange between both nitrogen atoms. As expected, protonation of **3** to **4** is accompanied with deshielding of their ³¹P NMR signals (17.8 ppm in **3** vs 33.9 ppm in **4**).

The experimental pK_{BH^+} value of **3** was determined from the corresponding ¹H and ³¹P{¹H} NMR spectra in transprotonation reactions.[44−46] As reference base, the phosphazene [(CH₂)₄N)₃P= NtBu] (**P₁**) with a pK_{BH^+} value of 28.35 was used.[47] The signals of HMPN (**3**) and [HMPN + H]⁺[PF₆]⁻ (**4**) are sufficiently

separated in the ¹H and ³¹P{¹H} NMR spectra already at room temperature and can be used for an estimation of the pK_{BH^+} value. Even at high temperatures (75 °C, CD₃CN, 500 MHz), no intermolecular proton exchange is observed between **3** and **4**, indicating low kinetic basicity of **3**. After addition of the reference base **P₁** and its protonated form [**P₁** + H]⁺[PF₆]⁻, the signals of **3** and **4** are still separated at room temperature. The experimental pK_{BH^+} value of HMPN could be estimated to 29.9 ± 0.2 from integration of the separated individual aromatic resonance signals of **4** and **3**, which is in accord with the integrals from ³¹P NMR signals of **3** and **4** (for details, see Supporting Information, Table 3S).

HMPN (**3**) and **P₁** both form stable hydrates with excess of D₂O, namely, [**3** + D]⁺ₐq[OD]⁻ₐq and [**P₁** + D]⁺ₐq[OD]⁻ₐq. Hydration is accompanied with characteristic deshielding of the ³¹P NMR signals of the deuterated species. Protonated forms of **3** and **P₁** do not show any hydrolysis or decomposition with

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D_2O, even at the elevated temperature of 70 °C. However, under very basic conditions ($KOH/D_2O/DMSO$-d_6), HMPN slowly decomposes to several unidentified products with a conversion of approximately 50% after 4 days at 70 °C. Exposure of HMPN to an excess of NH_4Cl/CD_3CN does not lead to bis-protonated **3**, whereas DCl/D_2O, 37 wt %, leads to the bis-protonated sponge $[HMPN + 2 D]^{2+}[Cl]^-_2$. After 7 days at 70 °C, nearly complete decomposition to an unidentified mixture of products was recorded by ^{31}P NMR.

The nucleophilic character of **3** was examined by addition of excess C_2H_5I (ca. 15 equiv). **3** was completely converted to a 1:4 mixture of protonated $[3 + H]^+[I]^-$ and monoalkylated $[3 + Et]^+[I]^-$ after 2 days at room temperature. NMR experiments clearly show that only one of the two imino nitrogen atoms is prone to alkylation under these conditions (see Supporting Information). In the same experiment, P_1 reacts more slowly with C_2H_5I to a 3:2 mixture of protonated/alkylated product.

Theoretical Calculations

The density functional calculations at the B3LYP/6-311+G-(2df,p)//B3LYP/6-31G* level indicate the cationic resonance assisted intramolecular hydrogen bonding observed earlier.[36,38,39] It is reflected in a partial protonation of the N(1)=P(1) bond as revealed by changes in the bond distance and bonding parameters, which are similar to that occurring in the directly protonated N(2)=P(2) bond, albeit to a smaller extent. This cooperative proton chelating effect renders the bisphosphazene more basic than Schwesinger's set of P_1 phosphazene bases. The proton affinity of HMPN in the gas phase is 274.1 kcal/mol according to B3LYP/6-311+G(2df,p)//B3LYP/6-31G* calculations taking into account thermal corrections estimated by the B3LYP/6-31G* method. This is 13.9 kcal/mol higher than PA of P_1-tBu and almost the same as PA of P_2-tBu (being 274.4 kcal/mol).[48] The NMR titration experiments yield pK_{BH^+}-(MeCN) = 29.9 ± 0.1 (vide supra), implying that HMPN is the most basic representative of this class of proton sponges. Theoretical calculation of pK_{BH^+} in acetonitrile performed using the isodensity polarized continuum model[49,50] and procedure described elsewhere[48,51] yields pK_{BH^+}(MeCN) = 29.1, in reasonable agreement with measurements. Although the PA values in the gas phase for HMPN and P2-tBu are almost the same, HMPN is, by 4 pK_a units, less basic than P_2-tBu. This is presumably because of a chelating effect and the inability of solvent to approach the protonated part of the molecule, which results in smaller energy of solvation of the protonated form, thus leading to smaller pK_a.

It is of interest to examine the interplay of the steric strain in HMPN and the intramolecular hydrogen bonding in its conjugate acid HMPN$^+$ in order to compare it with that in DMAN and TMGN. For that purpose, we shall make use of the following homodesmotic[52] reactions, where **5** represents for free naphthalene:

$$E(\mathbf{1}) + E(\mathbf{5}) = 2E(\mathbf{1a}) + E_{intf}(\mathbf{1}) \qquad (1a)$$

$$E(\mathbf{1} + H)^+ + E(\mathbf{5}) = \\ E(\mathbf{1a} + H)^+ + E(\mathbf{1a}) + E_{IHB}(\mathbf{1} + H)^+ \quad (1b)$$

$$E(\mathbf{2}) + E(\mathbf{5}) = 2E(\mathbf{2a}) + E_{intf}(\mathbf{2}) \qquad (2a)$$

$$E(\mathbf{2} + H)^+ + E(\mathbf{5}) = \\ E(\mathbf{2a} + H)^+ + E(\mathbf{2a}) + E_{IHB}(\mathbf{2} + H)^+ \quad (2b)$$

$$E(\mathbf{3}) + E(\mathbf{5}) = 2E(\mathbf{3a}) + E_{intf}(\mathbf{3}) \qquad (3a)$$

$$E(\mathbf{3} + H)^+ + E(\mathbf{5}) = \\ E(\mathbf{3a} + H)^+ + E(\mathbf{3a}) + E_{IHB}(\mathbf{3} + H)^+ \quad (3b)$$

Here $E_{intf}(\mathbf{n})$ denotes the steric interference of two basic groupings in **1**, **2**, and **3**, whereas $E_{IHB}(\mathbf{n} + H)^+$ ($\mathbf{n}$ = **1**, **2**, or **3**) denotes the energy of the intramolecular hydrogen bonds. Energies are calculated by the B3LYP/6-311+G(2df,p)//B3LYP/6-31G* model. It appears that the interference destabilization energies in the initial bases $E_{intf}(\mathbf{1})$, $E_{intf}(\mathbf{2})$, and $E_{intf}(\mathbf{3})$ are 6.1, 5.6, and 14.1 kcal/mol, respectively, implying that steric strain in HMPN is by far the largest. The IHB stabilization in conjugate acids $E_{IHB}(\mathbf{1} + H)^+$, $E_{IHB}(\mathbf{2} + H)^+$, $E_{IHB}(\mathbf{3} + H)^+$ are −12.8, −9.7, and −9.5 kcal/mol, respectively. Proton affinities of monosubstituted naphthalenes are PA(**1a**) = 226.4, PA(**2a**) = 248.6, and PA(**3a**) = 250.5 kcal/mol. To estimate the influence of the naphthalene spacer on the PA of the basic functionalities, we have calculated proton affinities of Me_2NH, $(Me_2N)_2C=NH$, and $(Me_2N)_3P=NH$. They are 221.0, 248.6, and 256.9 kcal/mol in the same order. It appears that naphthalene substitution increases basicity of Me_2NH, leaves it unchanged in $(Me_2N)_2C=NH$, and decreases it in $(Me_2N)_3P=NH$, which is an interesting finding. The increase in proton affinity of the disubstituted bases **1**−**3** relative to the corresponding reference monoderivatives **1a**−**3a** is given by $E_{intf}(\mathbf{n}) - E_{IHB}(\mathbf{n} + H)^+$, where $\mathbf{n}$ = **1**, **2**, and **3**. They are 18.9, 15.3, and 23.6 kcal/mol, respectively. It follows that the high basicity of the title compound, HMPN, is a consequence of the appreciable intrinsic basicity of its monoderivative (PA(**3a**) = 250.5 kcal/mol)—despite a decrease of 6.4 kcal/mol caused by naphthalene itself—and a large steric strain in **3** (14.1 kcal/mol) combined with a moderately strong intramolecular hydrogen bond in $[3 + H]^+$ (9.5 kcal/mol).

Conclusion

HMPN, a new 1,8-diaminonaphthalene-based bisphosphazene proton sponge, with the highest thermodynamic basicity reported so far, has been synthesized and fully characterized by hybridizing Alder's concept of proton chelators with Schwesinger's phosphazene basic unit. The structure of this superbase and its protonated form has been investigated by X-ray crystallographic analyses and theoretical B3LYP calculations. The estimated proton affinity by the B3LYP/6-311+G(2df,p)//B3LYP/6-31G* method is 274.1 kcal/mol, and the predicted pK_a value in MeCN is 29.1. The latter is corroborated by the NMR measurements of transprotonation reactions, which gave a pK_a(MeCN) = 29.9. The origin of superbasicity is identified as a combined effect of a large strain inherent in the base (14.1 kcal/mol) and the intramolecular H-bond strength in the final conjugate acid (9.5 kcal/mol).

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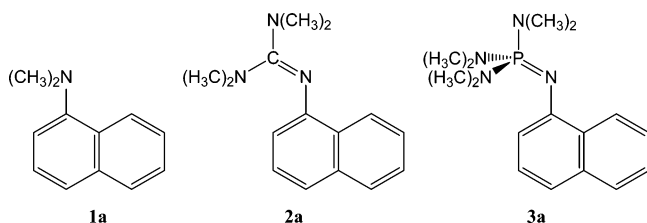
Figure 5. Monosubstituted naphthalene counterparts **1a**, **2a**, and **3a**, which serve as reference compounds.

Experimental Section

General. All reactions and manipulations were carried out under argon using standard Schlenk techniques or in a conventional nitrogen-filled glovebox. Solvents were purified according to literature procedures and kept under inert atmosphere. 1,8-Diaminonaphthalene was purified by sublimation. NH_4PF_6 and NH_4I (Acros), $\mathbf{P_1}$ (Fluka), and DCl/D_2O (Aldrich) were used as purchased.

Analytical data were collected on the following apparatus: melting points, Büchi MP B-540 (uncorrected); NMR, Bruker ARX 200 and DRX 500 (chemical shifts referenced to ^1H (δ 1.94) and ^{13}C (δ 1.32) residual signals of CD_3CN); IR, Bruker IFS 88 FT; MS, Varian MAT CH-7a (EI, 70 eV) and Finnigan MAT 95S (70 eV); elemental analysis, Heraeus CHN-Rapid.

Tris(dimethylamino)bromophosphoniumbromide, [P(NMe₂)₃Br]-Br.[53] Tris(dimethylamino)phosphine (4.94 g, 30 mmol) in dry benzene (30 mL) was slowly added to a stirred solution of bromine (4.80 g, 30 mmol) in the same solvent (40 mL) under cooling in an ice bath. After 1 h of stirring at room temperature, a yellow precipitate was collected. The precipitate was washed with dry ether and dried in vacuo to give 95% (9.2 g, 26 mmol) [P(NMe₂)₃Br]Br in the form of a white powder. ^1H NMR (200.1 MHz, CD_3CN, 25 °C): δ = 2.79 (d, $^3J_{H-P}$ = 13.5 Hz, 18H, CH_3). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_3CN, 25 °C): δ = 53.5.

1,8-Bis[tris(dimethylamino)phosphoranylideneamino]naphthalene, HMPN (3). 1,8-Diaminonaphthalene (317 mg, 2.00 mmol) and [P(NMe₂)₃Br]Br (1280 mg, 3.96 mmol) were suspended in dry chlorobenzene (30 mL). After addition of triethylamine (800 mg, 1.10 mL, 8.00 mmol), a clear beige solution and a yellowish residue developed. The reaction mixture was stirred for 5 days at 80 °C, then cooled to room temperature. For deprotonation, a solution of sodium bis(trimethylsilyl)amide ([NaN(SiMe₃)₂]; 1541 mg, 8.40 mmol, 4.2 equiv) in toluene was slowly added with subsequent stirring for 12 h at room temperature. After filtration, the brown solution was evaporated to dryness. Extraction with hot hexane followed by crystallization yielded 43% (410 mg 0.25 mmol) **3** as slightly yellow prisms. Mp 156 °C. ^1H NMR (500.1 MHz, CD_3CN, 25 °C): δ = 6.89 (dd, $^3J_{H-H}$ = 7.8 Hz, $^3J'_{H-H}$ = 7.4 Hz, 2H, H_{aromat}), 6.75 (d, $^3J_{H-H}$ = 7.8 Hz, 2H, H_{aromat}), 6.33 (d, $^3J_{H-H}$ = 7.4 Hz, 2H, H_{aromat}), 2.68 (d, $^3J_{H-P}$ = 9.3 Hz, 36H, CH_3). $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_3CN, 25 °C): δ = 151.6 (d, $^2J_{C-P}$ = 5.0 Hz, C_{aromat}), 139.6, 126.1, 116.3, 116.2, 115.9 (s, C_{aromat}), 37.9 (d, $^2J_{C-P}$ = 4.0 Hz, CH_3). $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_3CN, 25 °C): δ = 17.8. IR (KBr, cm^{-1}): ν = 2879 (m), 2837 (m), 2792 (m), 1549 (s), 1451 (s), 1435 (s), 1392 (s), 1366 (m), 1352 (m), 1293 (s), 1196 (s), 1133 (m), 1060 (m), 981 (vs), 816 (m), 753 (m). MS (EI): $C_{22}H_{42}N_8P_2$ requires m/z 480.3008, accurate mass found 480.3001. MS (EI, 70 eV): m/z (%) = 480 (89) [M]$^+$, 393 (93), 348 (32), 319 (9), 186 (13), 119 (100). Elemental analysis calcd (%) for $C_{22}H_{42}N_8P_2$ (480.58): C 54.98, H 8.81, N 23.32; found: C 55.23, H 8.97, N 22.36.

1,8-Bis[tris(dimethylamino)phosphoranylideneammonium]-naphthalene hexafluorophosphate, [3 + H]$^+$[PF₆]$^-$ (4). HMPN (**3**) (230 mg, 0.48 mmol) and NH_4PF_6 (77 mg, 0.48 mmol) were dissolved in CH_3CN (20 mL) and stirred for 2 h at room temperature. After evaporation of the solvent, [3 + H]$^+$[PF₆]$^-$ was obtained as colorless needles by layering CH_3CN solution with ether in 95% yield (219 mg, 0.45 mmol). Mp 195−196 °C. ^1H NMR (500.1 MHz, CD_3CN, 25 °C): δ = 15.0 (t, $^2J_{H-P}$ = 4.9 Hz, 1H, $H-N{=}P$), 7.24−7.20 (m, 4H, H_{aromat}), 6.65−6.61 (m, 2H, H_{aromat}), 2.74 (d, $^3J_{H-P}$ = 9.9 Hz, 36 H, CH_3). $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_3CN, 25 °C): δ = 144.5, 137.9, 127.2, 120.6, 114.5, 114.4 (s, C_{aromat}), 37.8 (d, $^2J_{C-P}$ = 3.2 Hz, CH_3). $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_3CN, 25 °C): δ = 33.9 (s, $P{=}N$), −143.2 (sept, $^1J_{P-F}$ = 706 Hz, PF_6^-). IR (KBr, cm^{-1}): ν = 3299 (w), 1606 (w), 1577 (m), 1516 (w), 1338 (m), 1299 (m), 1182 (m), 1132 (w), 1098 (w), 1066 (w), 1052 (w), 991 (s), 875 (w), 849 (s), 780 (w), 765 (m), 750 (w), 739 (w), 669 (w), 596 (w), 557 (m). MS (EI, 70 eV): m/z (%) = 480 (20) [**3**]$^+$, 393 (2), 348 (2), 186 (6), 119 (28), 44 (100). Elemental analysis calcd (%) for $C_{22}H_{43}N_8F_6P_3$ (626.55): C 42.17, H 6.92, N 17.88; found, C 41.51, H 6.68, N 17.37.

X-ray Structure Analyses. Crystal data and experimental conditions are listed in Table 2S. The molecular structures are illustrated as ORTEP[54] plots in Figures 3 and 4. Selected bond lengths and angles with standard deviations in parentheses are presented in Table 1S.

The reflections were collected with a STOE IPDS2 area detector and corrected for Lorentz, polarization, and absorption effects. Both structures were solved by direct methods and refined by full-matrix least-squares methods on F^2.[55] **3**: Hydrogen atoms were located and refined with isotropic thermal parameters. **4**: Hydrogen atoms have been calculated and refined with fixed isotropic thermal parameters except H(**1**), which was found and isotropically refined. The PF_6 ion adopts a 2-fold disorder.[56]

Supporting Information Available: Tables of experimental structure parameters, X-ray crystallographic data for **3** and **4**, and NMR calculation data from transprotonation, hydrolysis, and nucleophilicity NMR experiments. The last Tables 4S and 5S contain selected distances, bond and dihedral angles calculated by the B3LYP/6-31G* method and the corresponding Cartesian coordinates. Reference 41a is given in its complete form. This material is available free of charge via the Internet at http://pubs.acs.org.

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(56) 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-265684 (**3**) and CCDC-265685 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223 336−033; email: deposit@ccdc.cam.ac.uk).