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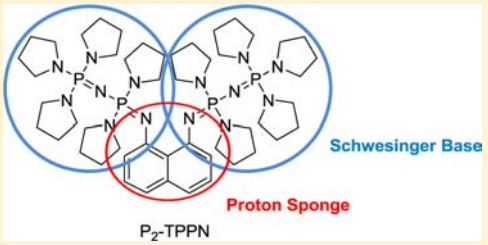
A New Synthetic Pathway to the Second and Third Generation of Superbasic Bisphosphazene Proton Sponges: The Run for the Best Chelating Ligand for a Proton

Julius F. Kögel,[†] Benjamin Oelkers,[†] Borislav Kovačević,[‡] and Jörg Sundermeyer*[,†]

[†]Fachbereich Chemie, Philipps-Universität Marburg Hans-Meerwein-Straße, 35032 Marburg, Germany
[‡]Quantum Chemistry Group, Rudjer Bošković Institute, Bijenička c. 54, 10000 Zagreb-HR, Croatia

Supporting Information

ABSTRACT: We present the up to now strongest chelating neutral pincer ligand for the simplest electrophile of chemistry, the proton. Two novel bisphosphazene proton sponges, 1,8-bis(trispyrrolidinophosphazenyl)naphthalene (TPPN) and its higher homologue P_2-TPPN, were obtained via a Staudinger reaction and investigated concerning their structural features and basic properties by experimental and computational means. They exhibit experimental pK_{BH}^+ values in acetonitrile of 32.3 and 42.1, respectively, exceeding the existing basicitiy record for proton sponges by more than 10 orders of magnitude. We show that Schwesinger's concept of homologization of phosphazene bases and Alder's concept of proton chelation in a constrained geometry regime of basic centers can be combined in the design of highly basic nonionic superbases of pincer type.



INTRODUCTION

Alder discovered the phenomenon of proton sponges in 1968, noticing the unexpectedly high basicity of 1,8-bis(dimethylamino)naphthalene (DMAN).[1] Such strong nonionic organic bases possess two basic nitrogen centers able to act as a chelate ligand for a proton which commonly is ligated in an asymmetric hydrogen bond N−H···N. The superior basicity compared to nonchelating bases can be due to the unfavorable situation in the proton sponge's free base form: the proximity of two nitrogen atoms leads to a repulsion of their lone pairs and distortion of the naphthalene backbone. Protonation is accompanied by strain relief and the formation of a favorable intramolecular hydrogen bridge. Proton sponges typically show a very low kinetic basicity which can be due to the hydrophobic shielding of the two basicity centers hindering another base from approaching this captured proton array. They have found various applications, such as as bases in organic synthesis,[2,3] as model compounds to study [N−H···N] hydrogen bridges,[4−7] as components of frustrated Lewis pairs for the activation of molecular hydrogen[8] or as a matrix in MALDI mass spectrometry.[9] Since Alder's discovery, the phenomenon of proton sponges has fascinated synthetically and theoretically oriented chemists and has been summarized in several reviews.[10−15] Classical DMAN has been modified in manifold ways to investigate the effects on basicity and chemical properties. Apart from the variation of the aromatic skeleton or the substituents at the basicity centers, superbases have been created by hybridizing the class of proton sponges with superbasic building blocks like guanidines,[16−19] amidines,[20] or phosphazenes (Figure 1).[21−25] Two representatives of the latter class with PPh_3 and PPh_2Me moieties were studied in their protonated forms but showed only moderate pK_{BH}^+ values because of the electron-withdrawing effect of the aryl groups (15.6 in water for the triphenylphosphane-substituted compound). A tributyl-substituted analogue recently reported by Dries was not investigated for its basic features.[25] A vinamidine proton sponge reported by Schwesinger exhibits the highest pK_{BH}^+ value for proton sponges so far (30.94 in MeCN).[20] It was suggested to use the term superbase for a neutral organic base exhibiting a gas phase basicity higher than 1000 kJ/mol

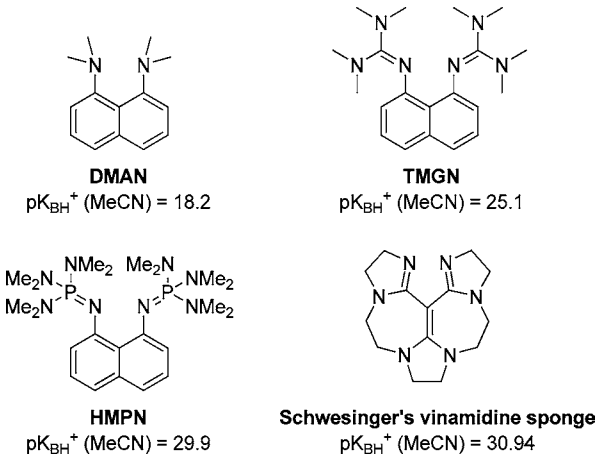


Figure 1. Alder's DMAN and three hybrid proton sponges bearing guanidine, phosphazene, or amidine moieties.

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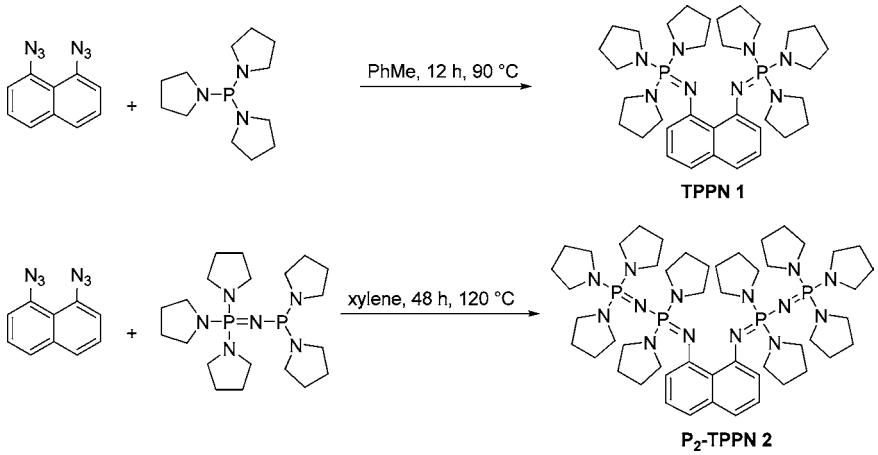
Scheme 1. Synthesis of TPPN and P_2-TPPN via a Staudinger Reaction



and a pK_{BH^+} value (MeCN) higher than 25.[8] In this respect, the amidine DBU would not be a superbase, but pentamethylguanidine would mark the edge of superbasicity.

In 2005, we reported on the synthesis of the first superbasic bisphosphazene proton sponge 1,8-bis(hexamethyltriaminophosphazenyl)naphthalene (HMPN).[26] Adding the chelating effect of proton sponges to a classical phosphazene base led to a tremendous increase in basicity: by chelation, proton affinity in the gas phase rises from 250.5 kcal/mol for monodentate (dma)P_1-1-Naph (dma = NMe_2) to 274.1 kcal/mol for HMPN. As expected, an analogous rise is observed for the corresponding pK_{BH^+} values which increase by more than 8 orders of magnitude from 21.25 for (dma)P_1-Ph[27] (pK_{BH^+} has not been reported for the naphthalene derivative; it is 19.5 at a rough estimate)[28−30] to 29.9 for HMPN.

Aware of the fact that substituting the dimethylamino groups of a Schwesinger base for pyrrolidine moieties leads to a further growth of basicity, we identified 1,8-bis(tris(pyrrolidino)-phosphazenyl)naphthalene (**1**, TPPN) as a promising target compound whose pK_{BH^+} could break the basicity record for proton sponges. Going deeper into Schwesinger's concept of phosphazene bases provoked us to perform a so-called homologization step: the formal insertion of further PN units into TPPN could lead to P_2-TPPN (**2**)—a compound with a pK_{BH^+} value close to those of the strongest nonionic superbases known.

RESULTS

Since the scope of the Kirsanov route, which was used for the synthesis of HMPN, turned out to be limited due to the proximity of the basicity centers and sterically demanding only slightly electrophilic phosphonium synthons, a Staudinger reaction between 1,8-diazidonaphthalene and the corresponding phosphane was chosen as the key step for the synthesis of the new pincer ligands TPPN and P_2-TPPN (Scheme 1). Literature-known $P(pyr)_3$ (pyr = $N(CH_2)_4$)[31] was the reactant in the case of TPPN, and it could be converted to the homologous P_2 phosphane $(pyr)_3P{=}N{-}P(pyr)_2$ in a three-step procedure similar to the synthesis reported for the corresponding dimethylamino-substituted analogue.[32] The Staudinger reaction initially led to the formation of stable bisphosphazides [Ar−N═N−N═PR_3] that lost molecular nitrogen upon heating in toluene or xylene to give the desired bisphosphazene proton sponges.[33] Due to the greater steric demand and the stronger electron-donating nature of the P_2 bisphosphazide, a higher kinetic barrier for nitrogen abstraction was expected for the formation of P_2-TPPN. Thus, a higher temperature and a longer reaction time are required for bisphosphazene formation than in the case of TPPN. TPPN and P_2-TPPN were obtained in their protonated form by reaction with $HN(SO_2CF_3)_2$. The "acidic" protons exhibit chemical shifts of δ_H = 15.02 ppm for TPPN·$HN(SO_2CF_3)_2$ and 15.14 ppm in the case of P_2-TPPN·$HN(SO_2CF_3)_2$ in CD_3CN.

The molecular structures of the two bisphosphazene proton sponges in their free base forms are presented in Figures 2−4. They reveal the typical features of proton sponges: they exhibit long and nearly equal N−N distances (TPPN = 276.6(3) pm, P_2-TPPN = 276.3(2) pm) and a significant distortion of the naphthalene backbone (average twist: TPPN = 8.2(2)°, P_2-TPPN = 6.3(2)°) which can both be due to the repulsion of the nitrogen atoms' lone pairs. The two basicity centers are located slightly above and below the naphthalene plane because of the sterically demanding substituents. The molecular structures of TPPN and P_2-TPPN reveal considerable shorter nonbonding distances between the basicity centers than found in their parent compound HMPN (282.2(3) pm).[26] This indicates a higher energy content for TPPN in its initial free base form and is enforced by the sterically demanding pyrrolidine groups. Comparison with other proton sponges shows that the N−N distance is slightly shorter than in DMAN (279.2(3) pm)[34] and longer than observed for TMGN (271.7(4) pm)[16] or quino[7,8-*h*]quinoline (272.7(2) pm).[35]

Protonation is accompanied by a considerable shortening of the N···N distances from 276.6(3) to 260.0(6) and 262.5(5) pm in the two independent TPPN·$HN(SO_2CF_3)_2$ molecules found in the elementary cell and from 276.3(2) to 257.0(4) pm in the case of P_2-TPPN·$HN(SO_2CF_3)_2$. Similar or slightly shorter values for the corresponding nonbonding distance between the two basic nitrogen atoms have been reported for the monoprotonated forms of DMAN (between 255.3(5) and 265.4(2) pm),[12] HMPN (256.8(3) pm),[26] TMGN (259.3(5) pm),[16] or Schwesinger's vinamidine sponge (254.1(5) pm).[20] The acidic protons could be located on the Fourier map, revealing a hydrogen bond that is nonlinear; angle N11−H1−N12 in TPPN·$HN(SO_2CF_3)_2$ 141(2)°, in P_2-TPPN·$HN(SO_2CF_3)_2$ 146(4)° with unsymmetric NH distances: *d*(N11−H1) in TPPN·$HN(SO_2CF_3)_2$ 85(3) pm,[36] in P_2-TPPN·$HN(SO_2CF_3)_2$ 81(4) pm) (Figure 5).

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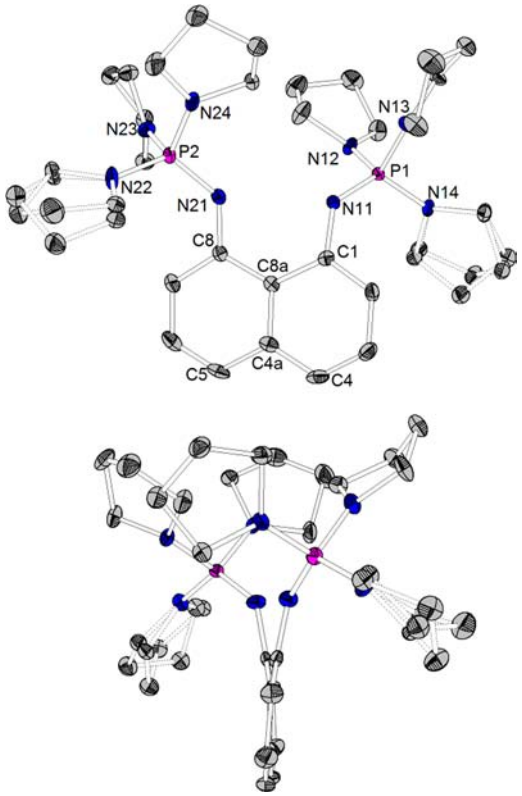

Figure 2. Molecular structure of TPPN (ellipsoids with 50% probability). Hydrogen atoms and the acetonitrile molecules are omitted for clarity. Selected bond lengths (pm) and angles (deg): N11···N12 276.6(3), N11–P1 155.0(2), P1–N12 165.1(2), P1–N13 164.2(2), P1–N14 165.0(2), N21–P2 155.3(2), P2–N22 164.4(2), P2–N23 164.1(2), P2–N24 163.7(2), C1–C8a–C4a–C5 −172.0(2), C8–C8a–C4a–C4 −171.7(2).

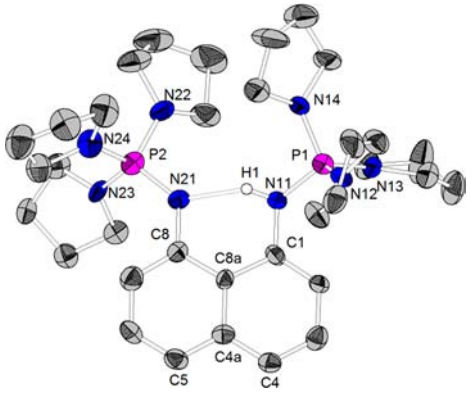

Figure 3. Molecular structure of TPPN·HN$(SO_2CF_3)_2$. Only one of two independent molecules in the asymmetric unit is shown. Carbon-bonded hydrogen atoms and the anion are omitted for clarity. Selected bond lengths (pm) and angles (deg): N11···N12 260.0(6), N11–H1 85(3), N21–H1 188(3), N11–P1 158.7(4), P1–N12 161.1(4), P1–N13 162.7(4), P1–N14 164.3(4), N21–P2 159.7(4), P2–N22 163.1(4), P2–N23 163.6(4), P2–N24 162.5(4), N11–H1–N21 141(2), C1–C8a–C4a–C5 174.3(4), C8–C8a–C4a–C4 175.6(4).

Relaxation of the naphthalene skeletons can be observed to some extent, but the aromatic backbones still exhibit a considerable distortion: average twist in TPPN·HN$(SO_2CF_3)_2$ is 5.1(4)°/2.6(4)°, and in P_2-TPPN·HN$(SO_2CF_3)_2$ it is

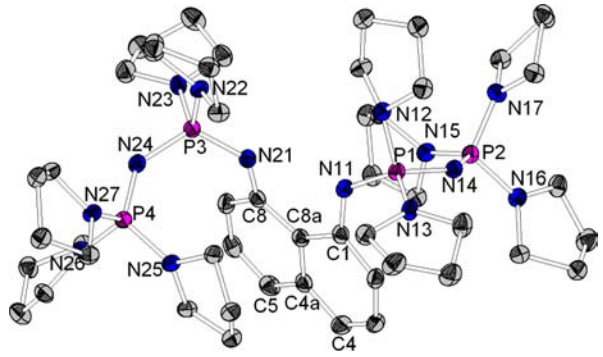

Figure 4. Molecular structure of P_2-TPPN (ellipsoids with 50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (pm) and angles (deg): N11···N12 276.3(2), N11–P1 156.7(2), P1–N12 167.7(2), P1–N13 166.2(2), P1–N14 161.3(2), N14–P2 156.5(2), P2–N15 164.6(2), P2–N16 163.4(2), P2–N17 164.5(2), C1–C8a–C4a–C5 −173.7(2).

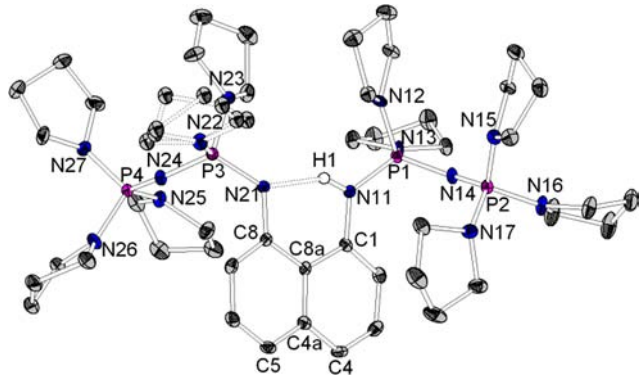

Figure 5. Molecular structure of P_2-TPPN·HN$(SO_2CF_3)_2$ (ellipsoids with 50% probability. Carbon-bonded hydrogen atoms and the anion are omitted for clarity. Selected bond lengths (pm) and angles (deg): N11···N12 257.0(4), N11–H1 81(4), N21–H1 185(4), N11–P1 162.3(3), P1–N12 164.4(2), P1–N13 163.3(2), P1–N14 158.6(2), N14–P2 156.3(2), N21–P3 161.0(2), P3–N22 163.8(2), P3–N23 166.3(2), P3–N24 158.4(2), N24–P4 155.4(2), N11–H1–N21 146(4), C1–C8a–C4a–C5 175.5(3), C8–C8a–C4a–C4 173.3(2).

5.6(3)°. Deviation from planarity can be explained by the bulky pyrrolidine substituents.

The pK_{BH^+} values were determined via NMR titration experiments versus bases with a similar basicity. Compound (dma)P_2-*t*Bu (pK_{BH^+} (MeCN) = 33.5)[37] was used in acetonitrile in the case of TPPN and P_2-TPPN competing with (dma)P_4-*t*Bu (pK_{BH^+} (MeCN) = 42.7)[37] for protons in THF.[38] The titration experiments revealed pK_{BH^+} values of 32.3 for TPPN and 42.1 for P_2-TPPN on the acetonitrile scale. For the evaluation of the effect of proton chelation on the basicity of P_2-TPPN, the "one-armed" analogue (pyr)P_2-1-Naph was synthesized via a Kirsanov reaction between 1-naphthylamine and the corresponding bromophosphonium bromide. NMR titration experiments revealed a pK_{BH^+} value of around 26 on the acetonitrile scale.[39−41]

As already observed for HMPN, both TPPN and P_2-TPPN exhibit a very low kinetic basicity which was investigated via proton self-exchange experiments. Even at 100 °C, no coalescence but two separated sets of signals for the proton sponges in their free base form and their protonated form were observed in the ^1H and ^{31}P NMR spectra when dissolving both species in C_6D_5Br. TPPN turned out to be hydrolytically stable

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and even remains intact after 24 h in 2 M aqueous NaOH at 70 °C.

THEORETICAL SECTION

The calculations were carried out utilizing the Gaussian 03[42] program package. The B3LYP/6-31G(d) method was used to obtain the most stable conformers in the gas phase. The frequency analysis was done at the same level of theory to confirm whether the structure is a minimum or a transition state on the potential energy surface. The structure optimizations were done without any symmetry constraints. However, the most stable conformer in both proton sponges (TPPN and P_2-TPPN) exhibits nearly C_2 symmetry. It turned out that in both sponges C_2 symmetry is lost upon protonation since the proton is attached to only one basic substituent. The C_2-symmetric protonated structure with the proton in the middle between the two basicity centers represents a first-order saddle point with one imaginary frequency that corresponds to the transfer of the proton between the two nitrogen atoms in both sponges. The energy barriers for the proton transfer calculated at the B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d) + ZPVE(B3LYP/6-31G(d) level for TPPN and P_2-TPPN are 0.8 and 1.5 kcal mol^{-1}, respectively, indicating that both molecules can be classified as a sponge with localized proton motion.[43]

The gas phase proton affinities (PA) of TPPN and P_2-TPPN together with their monosubstituted analogues were calculated at the B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d) level taking into account the thermal corrections estimated by the B3LYP/6-31G(d) method. They are presented in Table 1. The PA of P_2-TPPN is 298.0 kcal mol^{-1}, which is only 2 kcal mol^{-1} below the suggested threshold for hyperbasicity.[44] It is interesting that P_2-TPPN exhibits a slightly higher PA than the (dma)P_4-*t*Bu base (297.5 kcal mol^{-1}, calculated at the same level of theory).[45] The proton affinity of TPPN is 283.2 kcal mol^{-1}, thus being higher by 9.1 kcal mol^{-1} than the PA of its dimethylamino-substituted analogue HMPN (PA = 274.1 kcal mol^{-1}).[26] From where does this increase in the basicity of TPPN compared to HMPN come? Let us first consider the difference in the basicity of the basic substituents in TPPN and HMPN. The proton affinity of the $(pyr)_3P{=}NH$ moiety is 262.9 kcal mol^{-1}, which is by 6.0 kcal mol^{-1} higher than the PA of the $(dma)_3P{=}NH$ counterpart. To quantify the influence of the destabilization energy (E_d) in the neutral base and the energy of the intramolecular hydrogen bond (E_{IMHB}) in the conjugate acid, homodesmotic reactions were used analogously to the procedure applied in our previous paper[26] (see Supporting Information Figure S1). It appears that the destabilization energy due to a strain in neutral TPPN is 16.2 kcal mol^{-1}, which is 2.1 kcal mol^{-1} more than that calculated for HMPN. This finding supports the conclusion based on the experimental data for the distance between the basicity centers N(11) and N(21) that TPPN has a higher energy content in its initial base form than HMPN. However, the increase in energy is not substantial. The stabilization energy of the IMHB in TPPN's conjugate acid equals −9.9 kcal mol^{-1}, being 0.4 kcal mol^{-1} larger than in HMPN. The overall effect of the strain relief and the IMHB stabilization contributes to the PA of TPPN by 26.1 kcal mol^{-1}, which is by 2.5 kcal mol^{-1} larger than in HMPN where this contribution is 23.6 kcal mol^{-1}. It should be emphasized that the contribution from the strain relief and the formation of the IMHB corresponds to the difference between the PA of the proton sponge and its monosubstituted (one-armed) analogue, and it can be considered as a contribution from the chelating effect. To conclude, the higher PA of TPPN relative to HMPN is primarily caused by the higher basicity of $Pyr_3P{=}NH$ compared to the $(dma)_3P{=}NH$ fragment, whereas the contribution from the chelating effect is less pronounced. Now we will consider the proton affinity of P_2-TPPN, which is by 23.9 kcal mol^{-1} higher than the PA of HMPN and do the same type of analysis of energy contributions to the PA. The $(pyr)_3P{=}N{-}P(pyr)_2{=}NH$ moiety has a PA of 279.7 kcal mol^{-1}. This is by 22.8 kcal mol^{-1} higher than the PA of the $(dma)_3P{=}NH$ counterpart. Analysis by homodesmotic reactions reveals that the strain energy in neutral P_2-TPPN is 18.3 kcal mol^{-1}, whereas the energy of the IMHB stabilization in the conjugate acid equals −9.5 kcal mol^{-1}. Increase in strain energy is 2.1 kcal mol^{-1} compared to TPPN and 4.2 kcal mol^{-1} compared to HMPN. Consequently, P_2-TPPN has the highest energy content in its initial base form in this series. The stabilization due to the IMHB is exactly the same as in HMPN. The overall effect of strain relief and IMHB stabilization contributes to the PA of P_2-TPPN by 27.8 kcal mol^{-1}, which is by 4.2 kcal mol^{-1} higher than in HMPN. Therefore, the primary contribution to the PA of P_2-TPPN compared HMPN is the much higher proton affinity of $(pyr)_3P{=}N{-}P(pyr)_2{=}NH$ relative to the $(dma)_3P{=}NH$ fragment.

Table 1. Theoretically Obtained Gas Phase Proton Affinities and pK_a Values of Proton Sponges, Their Monosubstituted Analogues and Corresponding Basic Fragments

molecule	PA	pK_{BH^+}
HMPN	274.1[26]	29.1[26]
TPPN	283.2	33.0
P_2-TPPN	298.0	40.2
(dma)P_1-1-Naph	250.5[26]	
(pyr)P_1-1-Naph	257.1	21.3
(pyr)P_2-1-Naph	270.2	26.4
$(dma)_3P{=}NH$	256.9[46]	25.7
$(pyr)_3P{=}NH$	263.0	26.9
$(pyr)_3P{=}NP(pyr)_2{=}NH$	279.7	32.8

Theoretical calculations of the pK_{BH^+} values in acetonitrile were performed using the isodensity polarized continuum model (IPCM; the procedure is described elsewhere).[45] The pK_{BH^+} values for TPPN and P_2-TPPN, together with their monosubstituted (one-armed) analogues, are presented in Table 1. Most of them are in reasonable agreement with the experimental data with discrepancies being smaller than 0.7 pK_{BH^+} units. P_2-TPPN is an exception: the difference between the experimental and the theoretical value is 1.9 units. Thus, the resultant disagreement deserves some rationalization. The gas phase PA of P_2-TPPN is by only 0.5 kcal mol^{-1} higher than in Schwesinger's (dma)P_4-*t*Bu superbase. However, the solvation effect should be less pronounced in P_2-TPPN due to the chelating effect (the proton is less exposed to the solvent molecules in P_2-TPPN than in (dma)P_4-*t*Bu). Consequently, the protonated form of P_2-TPPN is less stabilized by the solvent compared to protonated (dma)P_4-*t*Bu. That would lead to a lower pK_{BH^+} for P_2-TPPN versus (dma)P_4-*t*Bu in acetonitrile. The same effect is observed for HMPN: it has a very similar gas phase PA as (dma)P_2-*t*Bu. However, the pK_{BH^+} of HMPN is lower than the pK_{BH^+} of (dma)P_2-*t*Bu by 4 units.[26] The experimental pK_{BH^+} of P_2-TPPN is indeed lower than

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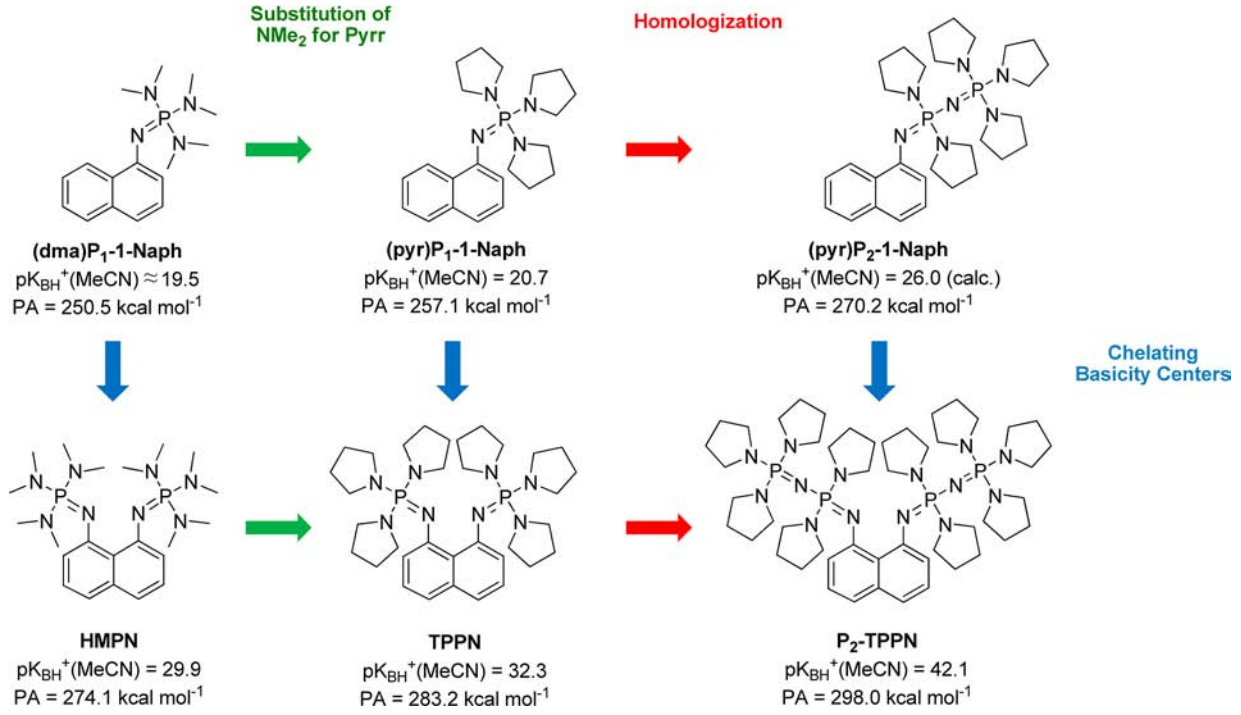
Scheme 2. Stepwise Basicity Enhancement Finally Leading to P2-TPPN



reported for (dma)P_4-*t*Bu, but the difference is only 0.7 units. Since the theoretical pK_{BH}^+ value for P_2-TPPN is by ∼3 units smaller than the theoretical pK_{BH}^+ value for (dma)P_4-*t*Bu, it would be plausible to assume that the theoretical value is more realistic. However, it should be emphasized that the theoretical procedure for calculating the pK_{BH}^+ is based on the fitting between the experimental pK_{BH}^+ and theoretically obtained basicities in the corresponding solvent,[45] and there is a lack of experimental data for compounds with pK_{BH}^+ values in acetonitrile close to or above 40. Consequently, theoretically calculated values in that area of the basicity scale could be less accurate. Regardless of taking into account the theoretical or the experimental data, the estimated pK_{BH}^+ value above 40 makes P_2-TPPN by far the most basic proton sponge synthesized so far.

■ CONCLUSION AND OUTLOOK

Scheme 2 helps to rationalize the particular steps of designing P_2-TPPN and carves out the effects of its attributes on its pK_{BH}^+ value and its proton affinity in the gas phase starting from the simple Schwesinger base (dma)P_1-1-Naph: the substitution of dimethylamino groups for more basic pyrrolidine moieties only brings a minor basicity increase by about 1 order of magnitude in the case of the classical Schwesinger base (dma)P_1-1-Naph and a bit more than 2 orders of magnitude for the corresponding bisphosphazene HMPN. Comparison of the two proton sponges reported herein with classical nonchelating Schwesinger bases highlights the dramatic effect of both homologization and chelation: these two modifications each cause an increase in the pK_{BH}^+ value by more than 10 orders of magnitude. Proton chelation by a second phosphazene increases the pK_{BH}^+ value substantially by nearly 12 orders of magnitude in the case of (pyr)P_1-1-Naph. The influence of two interacting basicity centers becomes even more extreme when it comes to the higher homologue (pyr)P_2-1-Naph, which upon chelation is boosted to a pK_{BH}^+ value 16 orders of magnitude higher. Finally, it is worth mentioning that this pincer effect is much more pronounced in compounds in which the positive charge occurring after protonation is stabilized by means of negative hyperconjugation than in systems relying on conjugative effects. The bisguanidinyl proton sponge TMGN (Figure 1, pK_{BH}^+ (MeCN) = 25.1) is only by less than 5 orders of magnitude more basic than its one-armed analogue (pK_{BH}^+ (MeCN) (calcd) = 20.5).[46]

As a result, connecting two Schwesinger P_1 bases via a 1,8-disubstituted naphthalene backbone yields a bisphosphazene proton sponge with a basicity in the dimension of a classical P_2 base. The forced interaction of two P_2 bases even leads to a compound as basic as a Schwesinger P_4 base and catapults the basicity record of proton sponges into a new dimension: P_2-TPPN is by more than 10 orders of magnitude more basic than the hitherto most basic sponge. It is anticipated that in the future the strongest neutral organic bases will be gained by a combination of kinetic aspects of proton chelation with thermodynamic aspects of the intrinsic superbasicity of the chelating centers, thus overcoming the limits of higher generation monodentate phosphazene bases. We hope that the Staudinger reaction will give rise to more representatives of the class of bisphosphazene proton sponges with outstanding basic properties and to the investigation of their interesting nitrogen-rich bisphosphazide precursors.

■ EXPERIMENTAL SECTION

All reactions were carried out under inert atmosphere using standard Schlenk techniques. Moisture- and air-sensitive substances were stored in a conventional nitrogen-flushed glovebox. Solvents were purified according to literature procedures and kept under an inert atmosphere. 1,8-Diaminonaphthalene (Acros) was purified by recrystallization from toluene followed by sublimation and converted to 1,8-diazidonaphthalene via its diazonium salt.[47] Tris(pyrrolidino)phosphane was accessible by adding phosphorus trichloride to a solution of pyrrolidine in THF.[31] $HN(SO_2CF_3)_2$ was synthesized by protonation of the corresponding lithium salt.[48] The Schwesinger base P_2-*t*Bu used for

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NMR titration experiments was purchased as 2 M solution in THF (Aldrich) and protonated with $HN(SO_2CF_3)_2$ in THF.

Spectra were recorded on the following spectrometers: NMR (Bruker ARX300, Bruker DRX400, Bruker DRX500); IR (ATR-FT-IR); MS (LTQ-FT or QStarPulsar i (finnigan)); elemental analysis (CHN-Rapid (Heraeus)).

Atoms are labeled from 1 to 8a in the naphthalene moiety and from 9 on in the alkyl groups. Labeling is described in detail in the Supporting Information.

1,8-Bis(trispyrrolidinophosphazenyl)naphthalene (TPPN, 1). Tris(pyrrolidino)phosphane (263 mg, 1.09 mmol) in toluene (10 mL) was added dropwise to a solution of 1,8-diazidonaphthalene (111 mg, 0.53 mmol) in the same solvent (10 mL). After 12 h of stirring at 90 °C, the light green solution had changed its color to brown and was evaporated to dryness. The brown residue was extracted with boiling hexane, and crystallization at −30 °C overnight yielded TPPN as a beige crystalline solid. Yield: 221 mg, 0.36 mmol, 68%. ^{1}H NMR (400.0 MHz, CD_3CN, 25 °C): δ = 6.85 (t, 2H, $^3J_{H-H}$ = 7.7 Hz, H(3,6)), 6.69 (d, 2H, $^3J_{H-H}$ = 7.7 Hz, H(4,5)), 6.34 (d, 2H, $^3J_{H-H}$ = 7.7 Hz, H(2,7)), 3.20 (m, 24H, H(9)), 1.76 (m, 24H, H(10)). $^{13}C\{^1H\}$ NMR (100.0 MHz, CD_3CN, 25 °C): δ = 153.2 (d, $^2J_{P-C}$ = 6.8 Hz, C(1,8)), 140.3 (t, $^3J_{P-C}$ = 12.7 Hz, C(4a)), 128.9 (C(8a)), 126.6 (C(3,6)), 117.2 (d, $^3J_{P-C}$ = 10.6 Hz, C(2,7)), 116.1 (C(4,5)), 48.3 (d, $^2J_{P-C}$ = 4.5 Hz, C(9)), 27.9 (d, $^3J_{P-C}$ = 8.2 Hz, C(10)). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3CN, 25 °C): δ = 2.5. IR (cm^{-1}): $\tilde{\nu}$ = 3039 (w), 2957 (m), 2858 (m), 1544 (s), 1430 (s), 1383 (m), 1341 (m), 1290 (m), 1239 (w), 1195 (m), 1125 (s), 1065 (s), 1005 (s), 912 (w), 870 (w), 814 (m), 778 (w), 748 (s), 636 (w), 563 (s), 487 (m), 443 (w). MS (ESI, CH_3CN): $C_{34}H_{55}N_8P_2$ requires m/z 637.4019, accurate mass found 637.4025. MS (ESI, CH_3CN): m/z (%) = 637 (100) $[MH]^+$, 566 (3), 497 (3), 381 (1), 256 (1). Anal. Calcd (%) for $C_{34}H_{54}N_8P_2$ (636.79): C, 64.13; H, 8.55; N, 17.60. Found: C, 64.16; H, 8.42; N, 17.57.

Protonation of TPPN with $HN(SO_2CF_3)_2$ (1·$HN(SO_2CF_3)_2$). A solution of $HN(SO_2CF_3)_2$ (22 mg, 0.079 mmol) in THF (5 mL) was added dropwise to a solution of TPPN (50 mg, 0.079 mmol) in THF (5 mL). The pale blue solution was stirred for 1 h and evaporated to dryness. The gray residue was washed with hexane (20 mL) and dried in vacuo to give TPPN·$HN(SO_2CF_3)_2$ as a gray solid. Yield: 65 mg, 0.071 mmol, 90%. ^{1}H NMR (300.1 MHz, CD_3CN, 25 °C): δ = 15.02 (t, 1H, $^2J_{P-H}$ = 4.9 Hz, −NH), 7.17 (m, 4H, H(3,4,5,6)), 6.66 (t, 2H, $^3J_{H-H}$ = 4.0 Hz, H(2,7)), 3.26−3.21 (m, 24H, H(9)), 1.88−1.83 (m, 24H, H(10)). $^{13}C\{^1H\}$ NMR (100.6 MHz, THF-d_8, 25 °C): δ =144.2 (C(1,8)), 137.8 (C4a), 126.3 (CH_{Ar}), 120.9 (t, $^3J_{P-C}$ = 13.8 Hz, C(8a)) 120.8 (q, $^1J_{F-C}$ = 322.4 Hz, $-CF_3$), 120.1 (CH_{Ar}), 113.9 (d, $^3J_{P-C}$ = 7.2 Hz, C(2,7)), 48.0 (d, $^2J_{P-C}$ = 4.6 Hz, C(9)), 26.9 (d, $^3J_{P-C}$ = 8.2 Hz, C(10)). $^{19}F\{^1H\}$ NMR (282.4 MHz, CD_3CN, 25 °C): −81.0. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3CN, 25 °C): δ = 18.1. IR (cm^{-1}): $\tilde{\nu}$ = 2966 (m), 2870 (m), 1608 (w), 1573 (m), 1513 (w), 1458 (w), 1410 (w), 1354 (w), 1335 (m), 1300 (m), 1259 (w), 1173 (s), 1129 (w), 1073 (s), 1050 (s), 1013 (s), 970 (w), 915 (w), 871 (w), 818 (m), 787 (w), 762 (m), 738 (w), 699 (w), 653 (w), 614 (m), 568 (m), 509 (m), 483 (w), 449 (w). MS (ESI, CH_3CN): $C_{34}H_{55}N_8P_2$ requires m/z 637.4019, accurate mass found 637.3995. MS (ESI, CH_3CN): m/z (%) = 637 (100) $[M]^+$. Anal. Calcd (%) for $C_{36}H_{55}F_6N_9O_4P_2S_2$ (917.32): C, 47.10; H, 6.04; N, 13.73; S, 6.99. Found: C, 47.04; H, 6.07; N, 13.88; S, 6.98.

1,8-Bis[tris(pyrrolidino)phosphazenylbis(pyrrolidino)-phosphazenyl]naphthalene (P_2-TPPN, 2). A solution of [tris-(pyrrolidino)phosphazenyl]bis(pyrrolidino)phosphane (629 mg, 1.475 mmol) in xylene (15 mL) was added dropwise to a solution of 1,8-diazidonaphthalene (148 mg, 0.702 mmol) in xylene (15 mL). The purple reaction mixture changed color to green and was stirred for 48 h at 120 °C. After evaporation of the solvent in vacuo, the green residue was washed twice with pentane (30 mL). P_2-TPPN (**2**) was obtained as a green solid. Yield: 383 mg, 0.380 mmol, 54%. ^{1}H NMR (400.0 MHz, THF-d_8, 25 °C): δ = 6.66 (t, 2H, $^3J_{H-H}$ = 7.6 Hz, H(3,6)), 6.43 (d, 2H, $^3J_{H-H}$ = 7.6 Hz, H(4,5)), 6.30 (d, 2H, $^3J_{H-H}$ = 7.6 Hz, H(2,7)), 3.40 (m, 8H, H(9)), 3.20 (m, 8H, H(9)), 2.97 (m, 24H, H(11)), 1.73 (m, 16H, H(10)), 1.55 (m, 24H, H(12)). $^{13}C\{^1H\}$ NMR (100.6 MHz, THF-d_8, 25 °C): δ = 155.0 (C(1,8)), 139.7 (C(4a)), 129.9 (t, $^3J_{C-P}$ = 23.8 Hz, C(8a)), 124.9 (C(3,6)), 114.9 (d, $^3J_{C-P}$ = 16.1 Hz, C(2,7)), 112.9 (C(4,5)), 47.7 (d, $^2J_{C-P}$ = 4.3 Hz, C(9)), 47.2 (d, $^2J_{C-P}$ = 4.7 Hz, C(11)), 27.4 (d, $^3J_{C-P}$ = 9.0 Hz, C(10)), 27.0 (d, $^3J_{C-P}$ = 8.4 Hz, C(10)). $^{31}P\{^1H\}$ NMR (121.5 MHz, THF-d_8, 25 °C): δ = 1.5 (d, $^2J_{P-P}$ = 41.7 Hz), 5.0 (d, $^2J_{P-P}$ = 41.7 Hz). MS (ESI, CH_3CN): $C_{50}H_{86}N_{14}P_4$ requires m/z 1007.6189, accurate mass found 1007.6183. MS (ESI, CH_3CN): m/z (%) = 1007 (100) $[M]^+$, 796 (23), 441 (8), 356 (28). Anal. Calcd (%) for $C_{50}H_{86}N_{14}P_4$ (1007.21): C, 59.62; H, 8.61; N, 19.47. Found: C, 59.32; H, 8.57; N, 19.48.

Protonation of P_2-TPPN with $HN(SO_2CF_3)_2$ (2·$HN(SO_2CF_3)_2$). A solution of $HN(SO_2CF_3)_2$ (28 mg, 0.099 mmol) in THF (10 mL) was added dropwise to a solution of P_2-TPPN (**2**) (100 mg, 0.099 mmol) in THF (10 mL) at 0 °C. The reaction mixture changed color from green to violet and was stirred at room temperature overnight. After evaporation of the solvent in vacuo, the residue was washed twice with diethylether (15 mL). P_2-TPPN·$HN(SO_2CF_3)_2$ was obtained as a pale violet solid. Yield: 79 mg, 0.061 mmol, 62%. ^{1}H NMR (300.1 MHz, CD_3CN, 25 °C): δ = 15.14 (br m, 1H, −NH), 7.05 (t, 2H, $^3J_{H-H}$ = 7.8 Hz, H(3,6)), 6.95 (d, 2H, $^3J_{H-H}$ = 7.8 Hz, H(4,5)), 6.67 (d, 2H, $^3J_{H-H}$ = 7.8 Hz, H(2,7)), 3.30 (br s, 8H, H(9)), 3.17 (br s, 8H, H(9)), 2.90 (br s, 24 H, H(11)), 1.85 (br s, 16H, H(10)), 1.55 (br s, 24H, H(12)). $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_3CN, 25 °C): δ = 147.5 (C(1,8)), 137.6 (C(4a)), 126.3 (CH_{Ar}), 121.6 (t, $^3J_{P-C}$ = 13.3 Hz, C(8a)), 120.9 (q, $^1J_{F-C}$ = 320.7 Hz, CF_3), 117.7 (CH_{Ar}), 113.1 (d, $^3J_{P-C}$ = 9.5 Hz, C(2,7)), 47.3 (d, $^2J_{P-C}$ = 5.0 Hz, C(9, 11)), 27.1 (d, $^3J_{P-C}$ = 9.4 Hz, C(10)), 26.7 (d, $^3J_{P-C}$ = 8.7 Hz, C(12)). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3CN, 25 °C): δ = 2.0 (d, $^2J_{P-P}$ = 53.7 Hz), −0.6 (d, $^2J_{P-P}$ = 53.7 Hz). $C_{50}H_{86}N_{14}P_4$ requires m/z 1007.6183, accurate mass found 1007.6153. MS (ESI, CH_3CN): m/z (%) = 1007 (100) $[M]^+$. Anal. Calcd (%) for $C_{52}H_{87}F_6N_{15}O_4P_4S_2$ (1288.36): C, 48.48; H, 6.81; N, 16.31; S, 4.98. Found: C, 47.92; H, 6.74; N, 15.90; S, 4.91.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic procedures, crystallographic and computational data, and NMR titration experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

jsu@staff.uni-marburg.de

Notes

The authors declare no competing financial interest.

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■ DEDICATION

This paper is dedicated to the memory of Prof. Zvonimir B. Maksić who recently passed away.

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(39) NMR titration experiments were performed in THF since (pyr)P_2-1-Naph is insoluble in acetonitrile. (pyr)P_2-1-Naph is able to partly deprotonate TMGN (pK_{BH^+} (MeCN) = 25.1, ref 16), but no deprotonation of (dma)P_1-^{t}Bu·HPF_6 (pK_{BH^+} (MeCN) = 26.88, ref 40) is observed. A pK_{BH^+} value around 26 on the acetonitrile scale is in good accordance with the value found for (pyr)P_2-Ph (pK_{BH^+} (MeCN) = 27.55, ref 41) that should be a bit more basic than its naphthalene analogue. A more exact experimental determination of the pK_{BH^+} value was prevented by signal overlay and signal broadening because of proton exchange processes. A pK_{BH^+} of 26.0 was determined computationally (vide infra).
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