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The Next Generation of Phosphorus Bisylide Superbases – Synthesis, Structures, Basicity and Proton Self-Exchange

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Herein we present two phosphorus ylide superbases to enhance the basicity of 1,8-bis (methylylidene (hexamethyltriamino) phosphorane) naphthalene (MHPN) – the first superbase with interacting carbon atoms as basicity centers. Its 1-pyrrolidinyl substituted analog 1,8-bis (methylylidene (tris (1-pyrrolidinyl)) phosphorane) naphthalene (MTPN) and MHPN's theoretically predicted higher homologue P_2-MHPN exhibit extreme pK_{aH} values of 26.0 and 29.5 (experimental) in THF solution and 33.6 and 37.4 (estimated) in acetonitrile solution. The corresponding calculated gas phase basicity values are 281.4 and 284.6 kcal mol^{-1}, respectively. We prepared the neutral free bases together with the corresponding mono- and bisprotonated species which were characterized by NMR spectroscopy, ESI mass spectrometry, IR spectroscopy, elemental analysis and partly XRD analysis. The monoprotonated forms exhibit a rapid proton self-exchange between the two carbon atoms in peri-position and dynamic NMR spectroscopic methods revealed self-exchange rates of 2298 s^{-1} and 300 s^{-1} at 300 K for MTPN and P_2-MHPN, respectively. However, computational studies reveal that the proton chelating effect, which typically considerably contributes to the basicity of proton sponges with basicity centers on nitrogen, is negligible in bisylides, as the 1,8-substitution pattern yields almost the same basicity as the corresponding 2,7- or 1,5-substituted analogues.

Introduction

Uncharged organic superbases have attracted considerable interest in the fields of organic, inorganic and physical chemistry both due to their widespread application as organocatalyst[1] as well as from a fundamental point of view.[2] As one possible threshold for superbasicity, it was suggested to treat 1,8-bis(tetramethylguanidino)naphthalene (TMGN) as a reference compound with a pK_{aH} value of 25 in acetonitrile and 17 in THF solution.[3] The proton sponge 1,8-bis(dimethylamino)naphthalene (DMAN) with a gas phase basicity of 237.8 kcal mol^{-1} is often considered as the reference base for superbasicity in the gas phase.[4] A broad variety of compound classes exhibit superbasicity: The basicity center can be a nitrogen atom (amidines,[1] guanidines,[1] phosphazenes or Schwesinger bases,[5] cyclopropenimines,[6] 2,6-bis(diazaboryl)pyridine[7]), a carbon atom (ylides,[8] carbodiphosphoranes,[9] carbenes[10]) or a phosphorous atom (proazaphosphatrane or Verkade bases,[11] tris(phosphazenyl)phosphanes,[12] tris(guanidinyl)phosphanes[13]). A topical overview on the world of organic superbases has been given in two recent review articles by Hoge and co-workers[14] and Vazdar *et al.*[15] Raczynska and his team shed light on neutral push-pull organic molecules in another very recent review paper.[16]

A prominent strategy for additional basicity enhancement is the structurally enforced interaction of two basicity centers as already demonstrated in Alder's first proton sponge DMAN in 1968.[4] Since Alder's discovery, extreme pK_{aH} values have been achieved by the connection of different highly basic entities such as guanidines,[3a] cyclopropenimines,[17] or phosphazenes[18] being placed at the peri-positions of a naphthalene backbone. In contrast to all these compounds exhibiting nitrogen atoms as basicity centers, we presented the superbasic 1,8-bis(methylylidene(hexamethyltriamino)phosphorane) naphthalene (MHPN) with the carbon atoms of two ylidic entities in close proximity and shed light on the compound's monoprotonated form revealing a fast proton hopping mechanism as the source of increased basicity (Figure 1).[19] In order to further investigate this new class of superbases and its basicity

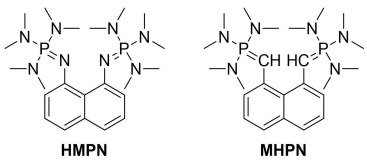

Figure 1. The bisphosphazene proton sponge 1,8-bis(hexamethyltriaminophosphazenyl)naphthalene (HMPN)[18a] and the bisylide MHPN.[19]

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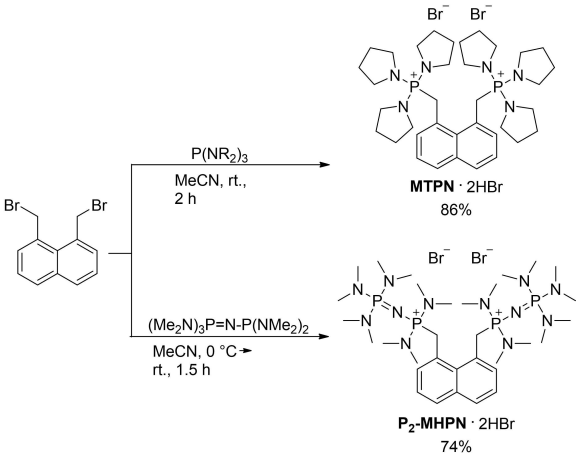
features, we applied two well-known strategies for basicity enhancement: A small increase could be expected for the replacement of the NMe_2 groups by more strongly electron donating 1-pyrrolidinyl substituents resulting in 1,8-bis(methylylidene(tris(1-pyrrolidinyl))phosphorane)naphthalene (MTPN) and a significant enhancement can be achieved by a so-called homologization step leading to MHPN's higher homologue P_2-MHPN.

Results and Discussion

Synthesis

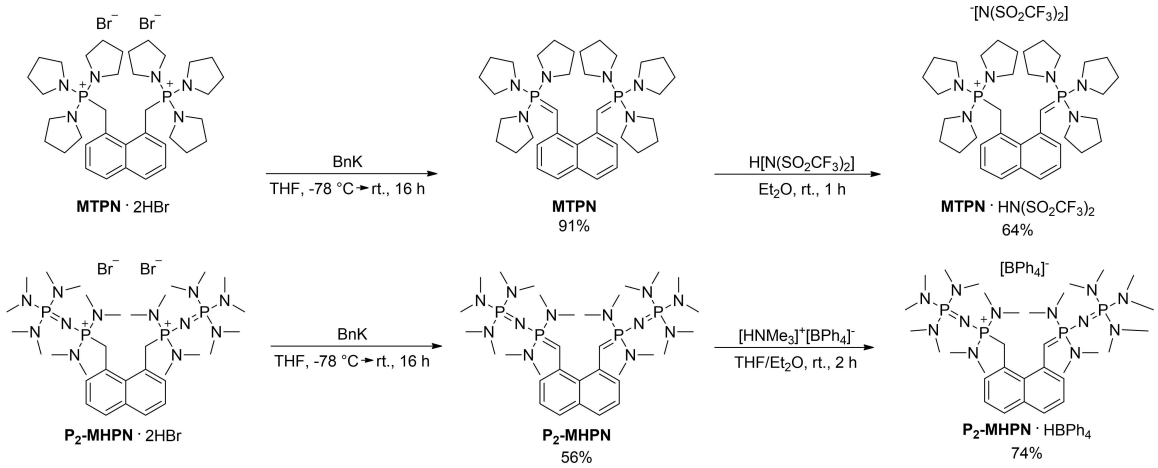
The synthetic routes leading to neutral, mono- and bisprotonated MTPN and P_2-MHPN are analogous to the sequences for the preparation of the parent compound MHPN:[19] In the first step, 1,8-bis(bromomethyl)naphthalene was reacted with the corresponding P-nucleophiles $P(pyr)_3$ (pyr = 1-pyrrolidinyl) or mixed-valent N-phosphazenyl-P(III) base $(Me_2N)_3P^V{=}N{-}P^{III}(NMe_2)_2$ in acetonitrile solution to give the dicationic bisphosphonium species MTPN·2HBr and P_2-MHPN·2HBr, respectively (Scheme 1). A similar procedure was described by Engelhardt *et al.* for the preparation of the related bisphosphonium salt based on trimethylphosphine and 1,8-bis(chloromethyl)naphthalene.[20] In order to obtain the neutral bisylidic form, the dications were deprotonated by benzyl potassium in THF (Scheme 2). The deep yellow free bases could be further purified by extraction with boiling hexane followed by crystallization at −30 °C. Reacting the bisylides with one equivalent of acid yielded the monoprotonated species MTPN·$HN(SO_2CF_3)_2$ and P_2-MHPN·$H(BPh_4)$ in 64% and 74% yield, respectively (Scheme 2). Proton sources resulting in different anions were chosen in order to obtain single crystals for XRD analysis. The identity of all compounds was confirmed by ^1H, ^{13}C and ^{31}P NMR spectroscopy, high resolution ESI mass spectrometry, IR spectroscopy, elemental analysis and partly also x-ray crystallography.



Scheme 1. Synthesis of MTPN·2HBr and P_2-MHPN·2HBr from 1,8-bis(bromomethyl)naphthalene.

Structural Features

Single crystals suitable for X-ray diffraction studies were obtained for the three bisphosphonium salts MHPN·2HBr, MTPN·2HBr and P_2-MHPN·2HBr (Figure 2) and the salts of their monoprotonated forms MHPN·*p*-$TolSO_3H$,[19] MTPN·$HN(SO_2CF_3)_2$ and P_2-MHPN·$HBPh_4$ (Figure 3).[21] The crystal structure of the neutral bisylide MHPN has already been described.[19] Two crucial structural characteristics of naphthalene-based proton sponges and the related bisylide species described herein are the non-bonding distances between the basicity centers in peri-position as well as the distortion of the naphthalene backbone (Table 1).[22] Furthermore, the N–P and C–P distances and the C_{Naph}–N–P and C_{Naph}–C–P angles are notable. In the case of classical proton sponges, the structural features are strongly influenced by the compounds' degree of protonation (*i.e.* free base form vs. mono- and bisprotonation) and can explain their basicity properties.[23] The XRD structures of the bisprotonated species reveal relatively large C–P distances between 1.801(1) and 1.819(3) Å and C–C–P angles slightly higher than the ideal



Scheme 2. Synthetic procedure to obtain MTPN and P_2-MHPN in their neutral and monoprotonated forms.

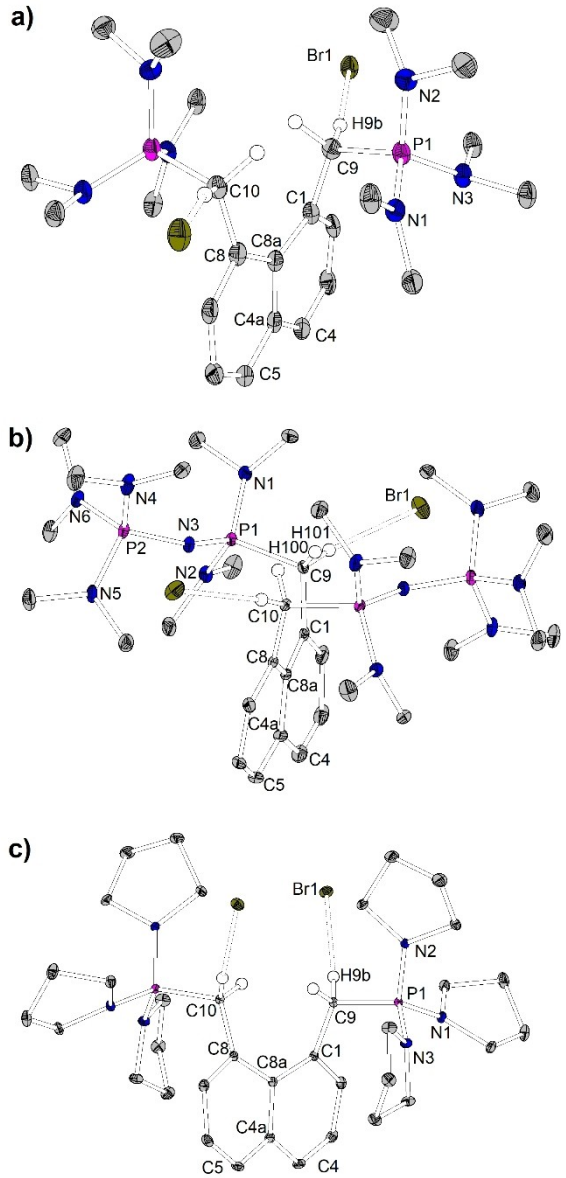


Figure 2. All ellipsoids are displayed with 30% probability. Selected bond lengths/Å and angles/°. **a)** Molecular structure of MHPN·2HBr: C9-P1 1.805(4), P1-N1 1.614(3), P1–N2 1.642(3), P1–N3 1.639(3), H9b–Br1 2.80(4), C9···C10 3.175(6), C1–C9–P1 112.1(3), C1–C8a–C4a–C5 174.1(3); **b)** Molecular structure of P_2-MHPN·2HBr (a second P_2-MHPN·2HBr unit is omitted for clarity): C9–P1 1.819(3), P1–N3 1.568(2), N3–P2 1.580(2), H101···Br1 2.89(3), C9···C10 3.211(4), C9–P3 1.814(3), P3–N9 1.563(3), N9–P4 1.560(3), P4–N10 1.632(3), P4–N11 1.646(3), P4–N12 1.625(3), H200···Br1 2.85(4), C29···C30 3.168(4), C1–C9–P1 110.4(2), P1–N3–P2 141.5(2), C21–C29–P3 110.5(2), P3–N8–P4 150.8(2), C1–C8a–C4a–C5 171.9(3), C21–C28a–C24a–C25 179.4(3); **c)** Molecular structure of MTPN·2HBr (a MeCN molecule is omitted for clarity): C9–P1 1.801(1), P1–N1 1.616(1), P1–N2 1.620(1), P1–N3 1.630(1), H9b···Br 2.67(2), C9···C10 3.036(1), C1–C9–P1 113.93(8), C1–C8a–C4a–C5 165.7(1).

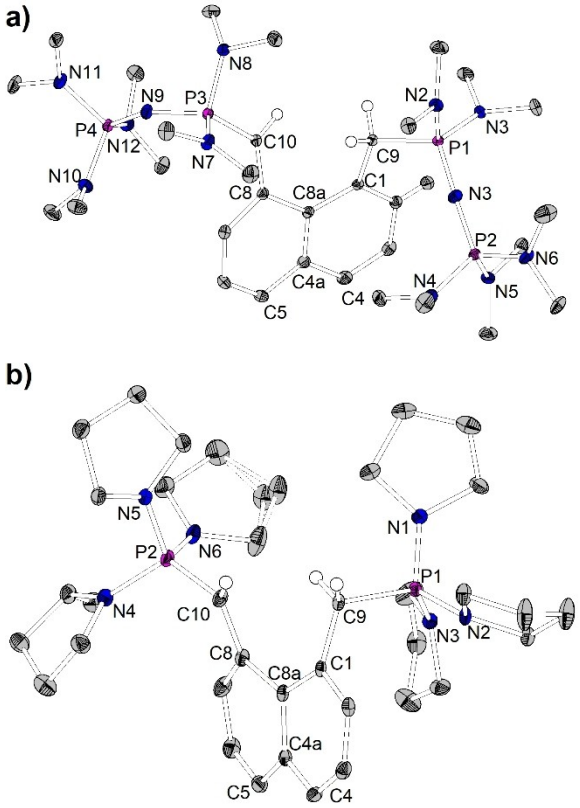


Figure 3. All ellipsoids are displayed with 30% probability and the anions are omitted for clarity. Selected bond lengths/Å and angles/°. **a)** Molecular structure of P_2-MHPN·$HBPh_4$: C9–P1 1.808(2), P1–N3 1.547(2), N3–P2 1.552(2), C10–P3 1.698(2), P3–N9 1.596(2), N9–P4 1.547(2), C9···C10 2.955(3), C1–C9–P1 118.1(1), P1–N3–P2 165.3(1), C8–C10–P3 128.7(2), P3–N9–P4 142.9(1), C1–C8a–C4a–C5 166.9(2), C8–C8a–C4aC4 173.1(2); **b)** Molecular structure of MTPN·$HN(SO_2CF_3)_2$ (a second molecular moiety is omitted for clarity): C9–P1 1.807(3), C10–P2 1.698(3), C9···C10 3.049(4), C109–P3 1.697(3), C110–P4 1.797(3), C109···C110 3.030(4), C1–C9–P1 112.6(2), C8–C10–P2 125.0(2), C101–C109–P3 127.1(2), C108–C110–P4 111.2(2), C1–C8a–C4a–C5 −166.8(2), C8–C8a–C4a–C4 −168.3(2), C101–C18a–C14a–C105 167.5(2), C108–C18a–C14a–C104 168.6(2).

tetrahedral angle (between 110.4(2)° and 113.93(8)°). These findings emphasize the presence of C–P single bonds in the bisphosphonium salts. In the case of P_2-MHPN, the similar and relatively short P–N distances within the P–N–P system (*e.g.* P1–N3: 1.568(2) Å and N3–P2: 1.580(2) Å) suggest an effective delocalization of the positive charge over the P–N–P system. The degree of distortion in the naphthalene backbone shows a large variation for the three compounds between 0.6° (P_2-MHPN·2HBr) and 14.3° (MTPN·2HBr) as well as relatively large differences for the non-bonding distances between the two carbon atoms in peri-position (*e.g.* 3.036(1) Å for MTPN and 3.175(6) Å for MHPN). In contrast to the compounds described herein, classical proton sponges do not readily accept a second proton as the loss of the intramolecular $[N–H···H]^+$ hydrogen bond formed after bisprotonation is highly unfavorable. Bisprotonation has been observed for the bisphosphazene sponge 1,8-bis(trispyrrolidinophosphazenyl)naphthalene (TPPN) by two equivalents of $HN(SO_2CF_3)_2$[18c] and in the case of the bisguanidine $[TMGNH_2]^{2+}$ $[HCl_3]^{2-}$.[3a] The crystal structure of the latter reveals a much lower distance between the two basicity centers (d(N···N): 2.881(3) Å) and a relatively small naphthalene distortion (2.3°) compared to the dicationic bisphosphonium species of this work.

Whereas monoprotonated bisphosphazene proton sponges form an intramolecular $[N–H···H]^+$ hydrogen bond, the molec-

Table 1. Selected distances/Å and angles/° found in the obtained molecular structures.

	d(C9···C10)	d(C–P^+)	d(C=P)	Naphthalene Distortion[a]	<) (C–C–P^+)	<) (C–C=P)
MHPN·2HBr	3.175(6)	1.805(4)	–	5.9	112.1(3)	–
P_2-MHPN·2HBr	3.211(4), 3.168(4)	1.819(3), 1.814(3)	–	8.1, 0.6	110.4(2), 110.5(2)	–
MTPN·2HBr	3.036(1)	1.801(1)	–	14.3	113.93(8)	–
MHPN·*p*-$TolSO_3H$	3.0342(2), 3.0558(2)	1.811(3), 1.809(3)	1.699(3), 1.692(3)	10.6, 10.7	119.7(2), 118.3(2)	128.0(2), 128.3(2)
P_2-MHPN·$HBPh_4$	2.955(3)	1.808(2)	1.698(2)	10.0	118.1(1)	128.7(2)
MTPN·$HN(SO_2CF_3)_2$	3.049(4), 3.030(4)	1.807(3), 1.797(3)	1.698(3), 1.697(3)	12.0, 12.5	112.6(2), 111.2(2)	125.0(2), 127.1(2)
MHPN	3.01(1), 3.02(1)	–	1.673(6), 1.679(7)	12.5, 11.2	–	127.3(5), 128.4(5), 129.9(5), 129.1(5)

[a] The average deviation of the torsion angles C1–C8a–C4a–C5 and C8–C8a–C4a–C4 from 180°.

ular structures of three monocations described herein do not show C–H···C hydrogen bonding between the two basicity centers. Two molecular halves can be distinguished: A neutral Naph–CH=PR_3 side and a Naph–CH_2–P^+R_3 moiety with a positively charged phosphorus atom carrying the additional proton. The structural features on the latter side resemble those found in the structures of the bisphosphonium salts with long C–P distances between 1.797(3) Å (MTPN·$HN(SO_2CF_3)_2$) and 1.811(3) Å (MHPN·*p*-$TolSO_3H$). However, the C–C–P angles (between 112.6(2)° and 119.7(2)°) are slightly larger compared to the dications. The neutral ylidic molecular half stands out due to reduced P–C bond lengths between 1.692(3) and 1.699(3) Å and considerably larger C_{Naph}–C–P angles between 125.0(2)° and 128.7(2)°. These structural features are fully in line with the observations for the neutral bisylid MHPN (d(C–P): 1.673(6) and 1.679(7); <)(C_{Naph}–C–P) between 127.3(5)° and 129.9(5)°).[19] The molecular structure of P_2-MHPN·$HBPh_4$ reveals similar bond lengths in the P–N–P system on the protonated half (d(P1-N3): 1.547(2) Å, d(N3-P2): 1.552(2) Å) whereas the corresponding bond lengths vary on the neutral ylidic side (d(P3-N9): 1.596(2) Å and d(N9-P4): 1.547(2)). The non-bonding distances between the basicity centers are reduced for MHPN·*p*-$TolSO_3H$ (3.0342(2) and 3.0558(2) Å) and P_2-MHPN·$HBPh_4$ (2.955(3) Å), but are similar in case of MTPN·$HN(SO_2CF_3)_2$ (3.049(4) and 3.030(4) Å) compared to the corresponding dications. The naphthalene distortion remains relatively large with dihedral angles between 10.0° and 12.5° and no clear trend is found. In contrast, classical N-based proton sponges usually exhibit a relaxed naphthalene backbone in their monoprotonated form.[18b] No interactions between the 'acidic' proton and the anion can be observed in the salts of the two monoprotonated species. In contrast to that, the XRD structures of the salts of the bisprotonated forms reveal weak hydrogen bonding between the 'acidic' protons to the bromide anions with H···Br distances slightly below the sum of the van der Waals radii (*e.g.* MTPN·2HBr: d(H···Br): 2.67(2) Å).

NMR Spectroscopic Features

Bisprotonated Diphosphonium Salts

Crucial NMR spectroscopic characteristics are summarized in Table 2. As expected, the reaction of the phosphorus (III) amides with 1,8-bis(bromomethyl)naphthalene leads to a strong high field shift in the ^{31}P NMR spectrum (*e.g.* from 103.1 ppm for tris(pyrrolidinyl)phosphane to 41.7 ppm for MTPN·2HBr). The chemical shifts of the hydrogen atoms bound to the carbon atoms in peri-position range from 5.26 ppm for MHPN·2HBr to 4.14 ppm for P_2-MHPN·2HBr. The ^{13}C NMR shifts of the phosphorus bound carbon atoms lie between 33.1 ppm (MTPN) and 36.6 ppm (P_2-MHPN) and ^1J(P,C) coupling constants between 100 Hz (P_2-MHPN·2HBr) and 106.4 Hz (MHPN·2HBr) are observed.

Neutral Bisylides

In agreement with the shortening of the P–C bonds found in the crystal structure of MHPN, double deprotonation of the bisphosphonium salts yielding the neutral bisphosphazenes is accompanied by an increase in the ^1J(P,C) coupling constant (*e.g.* from 106.4 Hz to 185.6 Hz in case of the double deprotonation of MHPN·2HBr to MHPN). The carbon NMR signals of the carbon atoms in peri-position exhibit a slight low field shift. The signals of the hydrogen atoms bound to this carbon atoms are shifted towards higher fields and show similar chemical shifts between 3.61 ppm for MHPN and 3.73 ppm for the other two bisylides. However, the ^{31}P NMR shifts are nearly unaffected by the degree of protonation in case of MHPN and MTPN. Distinct changes concerning the ^{31}P NMR shifts with respect to the degree of protonation are only observed for P_2-MHPN. Furthermore, its ^2J(P,P) coupling constant is increased from 35.5 Hz to 68.4 Hz.

Table 2. Selected chemical shifts/ppm and coupling constants/Hz observed in the NMR spectra of the studied compounds.

	δ_{31P}	^2J(P,P)	δ_{1H}	^2J(P,H)	$\delta_{13C(C-P)}$	^1J(P,C)
MHPN·2HBr[a]	58.2	–	5.26	18.8	33.5	106.4
P_2-MHPN·2HBr[a]	25.2, 21.8	35.5	4.14	17.1	36.6	≈100[d]
MTPN·2HBr[a]	41.7	–	4.83	18.6	33.1	103.6
MHPN·*p*-TolSO$_3$H[b]	59.6, 54.4[c]	–	5.59, 2.41[c]	16.9, 12.6[c]	40.9, 27.0[c]	182.1, 102.0[c]
P_2-MHPN·HBPh$_4$[b]	33.9, 28.5, 20.3, 18.3[c]	71.0, 46.7[c]	4.64, 2.32[c]	16.8, 16.1[c]	49.0, 31.0[c]	173.5, 112.8[c]
MTPN·HN(SO$_2$CF$_3$)$_2$[b]	43.0, 38.5[c]	–	5.20, 2.49[c]	16.2, 10.8[c]	32.9, -[e]	100.8, –[e]
MHPN[b]	58.9	–	3.61	17.7	36.4	185.6
P_2-MHPN[b]	37.7, 17.6	68.4	3.73	22.3	43.7[c]	177.9[c]
MTPN	42.7	–	3.73	17.9	39.0	182.1

[a] in MeCN-d3; [b] in THF-d8; [c] spectra recorded at −43 °C; [d] The exact coupling constant could not be determined due to signal overlay; [e] The corresponding signals are not observed due to low intensity and signal overlay.

Monoprotonated Species

The ^{1}H, ^{13}C and ^{31}P NMR spectra of the monoprotonated compounds P_2-MHPN·HBPh$_4$ and MTPN·HN(SO$_2$CF$_3$)$_2$ exhibit a strong temperature dependence. Only one set of broad signals for the two halves of the molecules is found at room temperature suggesting a rapid exchange of the "acidic" proton between the two carbon atoms in peri-position. Recording the NMR spectra at lower temperatures leads to two different sets of signals for the deprotonated ylidic half and the protonated half with a positively charged phosphorus atom. For instance, the two monoprotonated P_1 compounds MHPN and MTPN reveal two signals in their ^{31}P NMR spectra as well as six signals for the aromatic protons in their proton NMR spectra at −43 °C in THF-d$_8$. Accordingly, P_2-MHPN reveals four signals in its ^{31}P NMR spectrum at −43 °C in THF-d$_8$. The chemical shifts for the two protons bound to C(9) range from 4.64 ppm for P_2-MHPN·HBPh$_4$ to 5.59 ppm for MHPN·*p*-TolSO$_3$H at −43 °C whereas the single protons at the ylidic C(10) are located further in the high field (*e.g.* 2.49 ppm for MTPN). The ^1J(P,C) coupling constants in the respective molecular halves (112.8 Hz on the phosphonium salt side, 173.5 Hz on the ylidic half) found in the ^{13}C NMR spectrum of P_2-MHPN·HBPh$_4$ at −43 °C are similar to the coupling constants observed for the corresponding bisphosphonium (100 Hz) and bisylidic (177.9 Hz) parent compounds.

Temperature Dependent NMR Spectroscopy of the Monoprotonated Species

The dynamic behavior revealed in the NMR spectra of the monoprotonated species corresponds to the exchange of the 'acidic' proton between the two molecular halves and was studied by measuring ^{1}H and ^{31}P NMR spectra at different temperatures. Thereby it was possible to determine the exchange rate as well as the free energy of the activation ΔG‡ on the basis of line shape analysis. As an example, a section of the proton NMR spectra of P_2-MHPN·HBPh$_4$ in THF-d$_8$ between 230 and 330 K is shown in Figure 4. Whereas the signals of the 'acidic' proton and the benzylic CH$_2$ group as well as the six protons belonging to the naphthalene backbone are visible at low temperatures, the two molecular halves cannot be distinguished at room temperature. Further spectra of P_2-MHPN·HBPh$_4$ and MTPN·HN(SO$_2$CF$_3$)$_2$ measured at different temperatures together with the simulated spectra and the resulting Eyring plots are displayed in the supporting information together with a detailed description of the procedure. The monoprotonated P_1 species MHPN·*p*-TolSO$_3$H and MTPN·HN(SO$_2$CF$_3$)$_2$ show similar dynamic behaviors expressed by their proton self-exchange rates (2224 and 2298 s^{-1} at 300 K) and the free energy of the activation ΔG‡(54.1 and 54.3 kJ mol^{-1} at 300 K). A considerably slower exchange is found for P_2-MHPN·HBPh$_4$: The higher homologue of MHPN reveals a proton self-exchange rate of 300 s^{-1} at 300 K accompanied by an increased free activation energy of 59.9 kJ mol^{-1}.

Basicity Measurements and Estimates

For the measurements of the experimental basicity values in acetonitrile and THF, the spectrophotometric titration method similar to pervious works was applied.[8,24–26] Brief description of the method follows. Bases with the known pK_{aH} values from previous works in acetonitrile[27] and THF[8,3b] were used as reference compounds to assign the values for the studied bases.

The pK_{aH} value of MHPN was measured against three reference bases – 4-MeO-C$_6$H$_4$-N=P$_3$(dma)$_7$, Ph-N=P$_1$(tmg)$_3$ and 2-Cl-C$_6$H$_4$-N=P$_3$(pyrr)$_6$NEt$_2$ – and the individually obtained pK_{aH} values were in good agreement: 32.28, 32.29 and 32.34 resulting in an average of 32.3. The three reference bases are linked to the current acetonitrile basicity scale with nine, two and seven measurements, respectively.[28]

Spectrophotometric titration measurements yielded pK_{aH} values of 26.0 and 29.5 for MTPN and P_2-MHPN in THF. It is of interest to have basicity estimates for these highly basic compounds also in acetonitrile. From the correlation Equa-

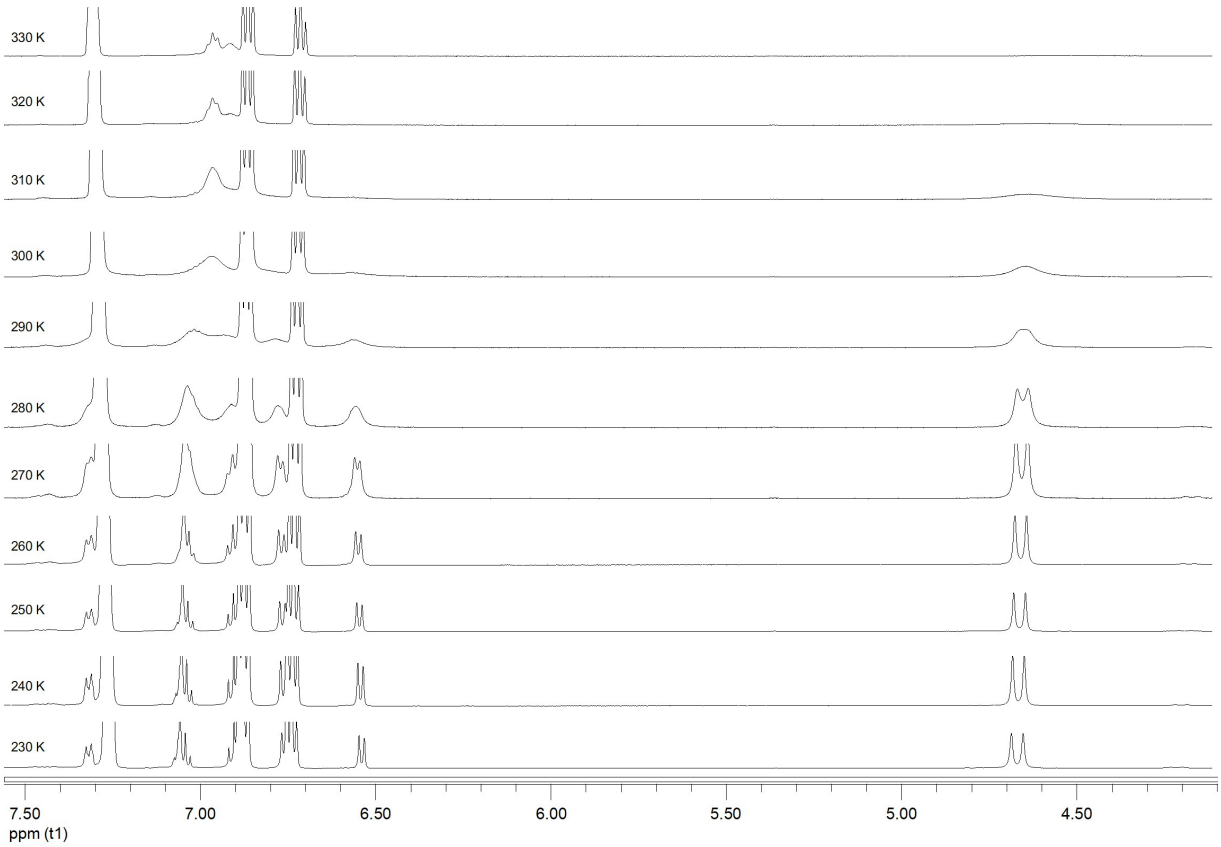


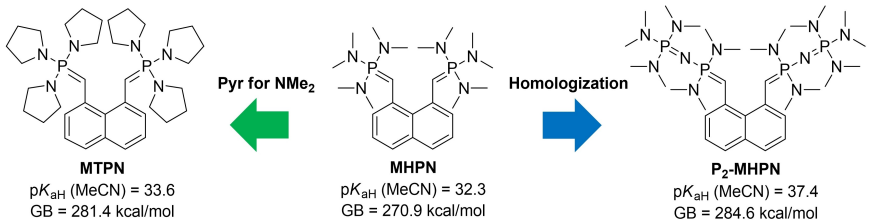
Figure 4. Excerpt from the ^{1}H NMR spectrum of P_2-MHPN·$HBPh_4$ at different temperatures (THF-d_8, 500 MHz).

tions (8) and (10) in ref. [8] and Equation (7) in ref. [27], the following acetonitrile pK_{aH} estimates can be obtained for MTPN and P_2-MHPN, respectively: 33.9, 33.6, 33.7 and 37.7, 37.4, 37.3. The agreement between the different equations is good and we consider the Equation (10) in ref. [8] as the most justified, leading to the estimated pK_{aH} values in acetonitrile of 33.6 and 37.4 for MTPN and P_2-MHPN, respectively (Scheme 3). For comparison, the pK_{aH} values in acetonitrile solution of the corresponding bisphosphazenes HMPN and TPPN are 29.9[18a] and 32.3,[18b] respectively.

In the case of MHPN, the basicity of the corresponding monoprotonated species was also determined in acetonitrile and a pK_{aH2} value of 25.8 was found. This value refers to the basicity of the cationic base $MHPNH^+$ and its value indicates that this compound remains a relatively strong base even in its monoprotonated form.

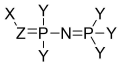
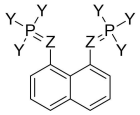
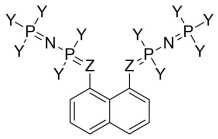
Theoretical Section

Previous studies have established that phosphonium ylides are considerably more basic than phosphazenes (phosphine imides).[2] However, both prior data[19] and experimental results in this paper suggest that phosphonium ylide-based proton sponges exhibit lower-than-expected basicity compared to those based on phosphazene moieties, particularly if P_2-phosphazene and P_2-ylide proton sponges are compared. Relying on chemical reasoning, a possible explanation for the lower-than-expected basicity of ylide proton sponges might



Scheme 3. Increase of MHPN's experimental pK_{aH} value and calculated gas phase basicity by substitution of the dimethylamino groups by 1-pyrrolidinyl entities (MTPN) and by a homologization step resulting in P_2-MHPN.

Table 3. Proton affinity, gas phase basicity and pK_{AH} values of phosphazenes and ylides with different substituents in kcal·mol^{-1}.

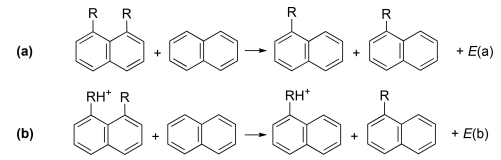
Molecule	X	Y	Z	PA	GB	pK_{aH}(MeCN)	pK_{aH}(THF)
	H	dma	N	258.0	251.3	24.2[25.8]*	18.5[19.7]
	H	dma	C	275.2	268.5	39.1	33.2
	H	pyrr	N	263.7	256.3	25.3[27.0]	19.9[20.8]
	H	pyrr	C	283.2	275.1	40.7	35.1
	napht	dma	N	251.2	245.0	18.0	12.4
	napht	dma	C	272.0	264.5	32.6	26.9
	napht	pyrr	N	260.1	251.2	20.8[20.6]	15.4[14.2]
	napht	pyrr	C	276.9	267.6	33.6	28.2
	H	dma	N	271.2	266.0	29.6	24.3
	H	dma	C	290.5	284.5	44.8	39.4
	H	pyrr	N	280.4	273.1	31.8	27.0
	H	pyrr	C	297.0	290.3	45.3	40.3
	napht	dma	N	265.5	257.3	23.9	18.8
	napht	dma	C	278.0	271.8	33.3	28.1
	napht	pyrr	N	271.5	263.2	25.3	20.5
	napht	pyrr	C	284.7	277.1	35.2	30.3
		dma	N	274.8	267.4	29.9[refn]**	24.8[21.9]
		dma	C	280.1	270.9	32.4[32.3]	27.4
		pyrr	N	283.0	273.9	32.8[32.3]	28.0
		pyrr	C	289.0	281.4	36.8[33.5]	31.8[26.0]
		dma	N	293.0	286.0	38.3	33.8
		dma	C	292.7	284.6	38.2[37.9]	33.6[29.5]
		pyrr	N	298.7	290.2	42.0[42.1]	38.0
		pyrr	C	295.8	289.0	38.4	34.2

[a] * Numbers in square brackets represent experimental results. ** refn. indicates that this was the reference base in pK_a calculations.

originate from a weakened proton chelating effect. To recall, the proton chelating effect refers to the increased basicity of proton sponges arising from two factors: diminishing electron pair repulsion upon protonation of the neutral base and the formation of an intramolecular hydrogen bond in the conjugate acid.[18] As the carbon atoms in the ylides lack a strongly pronounced lone electron pair compared to the (more electronegative) nitrogen atoms of phosphazenes, this could result in weaker electron pair repulsion in the neutral base. Furthermore, using chemical rationale, one might expect that the C–H···C hydrogen bond is significantly weaker compared to the N–H···N hydrogen bond, primarily due to the lower polarization of C–H bond as a consequence of lower electronegativity of the carbon atom. However, a recent computational study by Ganguly et al.[29] concluded that the C–H···C hydrogen bond could exhibit moderate strength. Therefore, motivated by the aforementioned experimental results regarding the lower-than-expected experimental basicity of ylide-based proton sponges, we conducted a direct comparison of the gas- and solution-phase basicities of various phosphorus ylides and their phosphazene counterparts. Additionally, we explored the effect of substituting the aromatic entity (naphthalene) at the basic center on overall basicity, as well as the influence of the proton chelating effect. Computational details are provided in the Supporting Information. Comparison of proton affinity and gas phase basicity values from Table 3 for unsubstituted (X=H) phosphazene/ylide moieties leads to a well-known conclusion that ylides are by 17–19 kcal mol^{-1} more basic in the gas phase than the corresponding phosphazenes.

The substitution of the hydrogen atom by a naphthalene moiety at the basic center (X=napht) decreases the PA and GB values by 3.2–6.8 kcal mol^{-1} in P_1 functionalities. However, in the case of P_2 functionalities, particularly in P_2-ylides, the reduction in basicity is more pronounced, reaching up to 13.2 kcal mol^{-1} for the GB of the P_2pyrr(C) moiety. This suggests that naphthalene stabilizes the neutral base more effectively in the case of P_2 ylides compared to P_1 ylides. This can be attributed to the enhanced delocalization of the electron pair on the carbon atom of the P_2 ylide into the naphthalene entity. Now, let us examine the influence of the proton chelating effect on basicity: Homodesmic reactions, illustrated in Scheme 4, are commonly employed for this purpose.

The energy of the reaction labelled as (a) is typically attributed to the repulsion of electron pairs on substituents,



Scheme 4. Homodesmic reactions of 1,8-substituted naphthalene based phosphazenes and ylides.

which diminishes upon protonation. In contrast, the energy associated with reaction (b) is commonly attributed to the formation of an intramolecular hydrogen bond. This is a simplified picture, as some strain remains present even after protonation, especially if the substituents at the 1,8 positions of naphthalene are bulky. Furthermore, attributing the energy of the homodesmic reaction (b) solely to the intramolecular hydrogen bond is an oversimplification, as it neglects the inductive and mesomeric effects of the substituents on the naphthalene ring. However, even this simplified picture allows getting the first estimate of the proton chelating effect of phosphazene and ylide proton sponges. The corresponding data is presented in Table 4.

Reaction (a) gives generally slightly higher strain energies for phosphazenes than for ylides. This may be due to the greater repulsion of electron lone pairs, which are more pronounced on the nitrogen atom than on the carbon atom. The homodesmic reaction (b) gives more noticeable differences between ylide and phosphazene proton sponges. Stabilization energies in phosphazenes are by around 9–16 kcal mol^{-1} higher than in ylides. At first glance, the significant difference in stabilization energies might support the earlier conclusion that N–H···N intramolecular hydrogen bonds are much stronger than C–H···C bonds. Based on the stabilization energies of reaction (b), these bonds would be expected to be by around 9–16 kcal mol^{-1} stronger, assuming the only contribution arises from the intramolecular hydrogen bond. However, the entire stabilization energy of reaction (b) is not necessarily attributable solely to the intramolecular hydrogen bond. It is expected that there are contributions from the residual strain and from mesomeric and inductive effects. In an attempt to assess the impact of these contributions to basicity, we calculated PA and GB for molecular analogues of the proton sponges, placing the ylide/phosphazene moieties at the 2,7- and 1,5-positions of the naphthalene moiety. The 1,8- and 2,7-positions are of *meta*-type, where substituent interactions are primarily inductive, whereas the 1,5-position is of *para*-type, allowing for both inductive and resonance effects.[30] Results are presented in Table S8. The comparison of PA/GB values for 1,8- and 2,7-substituted naphthalene compounds reveals noteworthy findings. Specifically, 1,8-substituted P_1 phosphazenes exhibit GB values that are 11.7–14.0 kcal mol^{-1} higher than those of their 2,7-substituted counterparts. In the case of P_2 phosphazenes, this difference is even more pronounced, reaching up to 17.7 kcal mol^{-1} for the P_2(dma)N moiety. These differences are lower but still not too distant from energy effects of reaction (b). Conversely, in P_1 ylides, there is virtually no difference between the 1,8- and 2,7- substitutions. Notably, for P_2(dma)C, the basicity of the 2,7-substituted naphthalene is even higher than that of the 1,8-substitution. A similar conclusion can be drawn if we compare 1,8- and 1,5-substituted compounds. In P_1 phosphazenes, the GB of the 1,8-substituted compound is higher by up to 13.9 kcal mol^{-1} (for the P_1(pyrr)N moiety), and in P_2 phosphazenes, this difference goes up to 17.9 kcal mol^{-1} (for the P_2(dma)N moiety). The GB of 1,5-ylides are again almost the same as for 1,8-ylides, with the 1,5 P_2(pyrr)C compound being slightly more basic than the corresponding 1,8-substituted species. Therefore, based on the presented results, we can conclude that the proton chelating effect does not contribute to the gas-phase basicity of ylide proton sponges. However, if we perform the analysis of substituent interaction in 2,7- and 1,5- substituted phosphazenes/ylides through homodesmic reactions, as we did for 1,8-substituted compounds (Schemes S2 and S3; Tables S9 and S10), we can see that even in the former there is a destabilization effect in the neutral base and a stabilization effect in the conjugate acid. Obviously, they can neither be attributed to the repulsion of substituents, nor to the formation of intramolecular hydrogen bonds. They are predominantly caused by the mesomeric and inductive effect. Therefore, when attributing the energy obtained from homodesmic reactions to specific effects, one should be cautious to avoid drawing incorrect conclusions.

Finally, let us examine the computed pK_{aH} values. The computational results reproduce the experimental values relatively well, although a larger discrepancy is observed in the MTPN and P_2-MHPN superbase, but only in THF solution. The reason for these discrepancies remains unclear.

Table 4. Enthalpy values of homodesmic reactions shown in Scheme 4 covering the bisphosphazenes HMPN and TPPN and the bisylides MHPN and MTPN as well as their P_2 homologs in kcal·mol^{-1}.

Molecule	*E*(a)	*E*(b)
R=P_1dma(N); **HMPN**	7.5	−11.8
R=P_1pyrr(N); **TPPN**	7.2	−15.5
R=P_2dma(N); **P_2-HMPN**	8.3	−18.9
R=P_2pyrr(N); **P_2-TPPN**	3.1	−23.7
R=P_1dma(C); **MHPN**	2.2	−5.8
R=P_1pyrr(C); **MTPN**	6.6	−5.4
R=P_2dma(C); **P_2-MHPN**	8.8	−5.8
R=P_2pyrr(C); **P_2-MTPN**	4.3	−6.7

Conclusions

Applying the strategies of pyrrolidinyl substitution and homologization led to the two bisylides MTPN and P_2-MHPN exhibiting basicity values in the gas phase and in solution beyond the ones of the first representative of that compound class MHPN. In-depth characterization of the three superbases by experimental and theoretical methods did not reveal a significant contribution of the spatial proximity of the two basicity centers to the basicity providing a clear separation from

classical nitrogen based proton sponges. Future work on this new compound class could comprise screenings of the compounds' capability to act as organocatalysts in base-catalyzed reactions requiring extremely strong neutral bases to deprotonate weak C–H acids or a study on their coordination chemistry.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Basicity · Ylides · Exchange interactions · Phosphorus · Hydrogen bonds

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