High basicity of phosphorus–proton affinity of tris-(tetramethylguanidinyl)phosphine and tris-(hexamethyltriaminophosphazenyl)phosphine by DFT calculations

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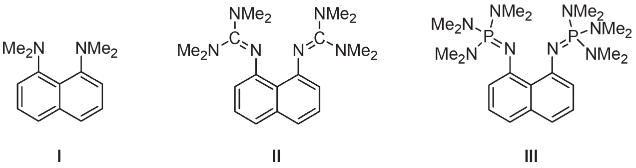
It is shown by approximate but reliable DFT calculations that the title compounds represent very strong superbases in gas phase and MeCN. In particular, tris-(hexamethyltriaminophosphazenyl)phosphine has a proton affinity, PA, of 295.5 kcal mol^{-1} and records a pK_a(MeCN) of 50 ± 1 units.

Neutral organic bases and superbases are useful auxiliary ingredients in organic syntheses, since they require mild reaction conditions and exhibit better solubility at the same time.[1–3] Furthermore, they are very efficient catalysts, if immobilized on appropriate surfaces being also acceptable in green chemistry.[4–6] It is, therefore, not surprising that a lot of efforts have been dedicated to the design of strong organic bases and superbases since the pioneering work of Alder *et al.*[7,8] It is found that superbasicity is exhibited by several families of compounds including guanidines,[9–11] phosphazenes,[12–16] quinoimines and related systems,[17] quinolylboranes,[18] extended 2,5-dihydropyrrolimines.[19] and C$_2$ diamines.[20] The intramolecular hydrogen bonding (IHB) motif can be employed in tailoring superbases too, if it is used in a cooperative way by applying multiple IHB patterns.[21] A useful extension of Alder's fruitful idea, put forward by DMAN(1,8-bis(dimethylamino))naphthalene[7] system **I** and its numerous offspring,[22–24] was given by the recently synthetized TMGN (1,8-bis(tetramethylguanidino)naphthalene)[25,26] **II** and HMPN (1,8-bis(hexamethyltriaminophosphazenyl)naphthalene[27] **III** (Scheme 1) possessing proton affinities of 264.0 and 274.1 kcal mol^{-1} respectively. Interestingly, phosphorus has been utilized in phosphazene compounds only as the central electron donating atom surrounded by highly basic fragments (ligands), which in turn have been protonated. It is the aim of the present work to show that phosphorus itself can play a role as the extremely basic site in some cases, both in the gas phase and acetonitrile (MeCN). For this purpose we consider systems **1–4** depicted in Fig. 1. The reference compound is given by tris(dimethylamino)phosphine **1**. The next is Verkade's proazaphosphatrane[28] **2**, which will serve as a gauge molecule for pK_a values in acetonitrile (*vide infra*).[29] Since replacement of the dimethylamino groups by tetramethylguanidino and hexamethyltriaminophosphazeno fragments significantly affects basicity as evidenced by systems **II** and **III**, it is logical to assume that compounds **3** and **4** should provide strong superbases. It should be mentioned that high basicity of **3** has been speculated already by Schmutzler *et al.*[30]



Scheme 1 Systems **I**, **II** and **III**.

Proton affinities (PAs) were calculated by the B3LYP/6-311 + G(2df,p)//B3LYP/6-31G* method by using a standard procedure described elsewhere.[14] Briefly, the absolute proton affinity is given by:

$$\mathrm{PA}(\mathrm{B}_\alpha) = (\Delta E_{\mathrm{el}})_\alpha + (\Delta E_{\mathrm{vib}})_\alpha + (5/2)\mathrm{RT} \qquad (1)$$

where the base in question and its conjugate acid are denoted by B and BH$^+$, respectively, whereas α signifies the site of proton attack. Further, $(\Delta E_{\mathrm{el}})_\alpha$ is the electronic contribution to proton affinity given by $E(\mathrm{B}) - E(\mathrm{B}_\alpha\mathrm{H})^+$, while $(\Delta E_{\mathrm{vib}})_\alpha = E_{\mathrm{vib}}(\mathrm{B}) - E_{\mathrm{vib}}(\mathrm{B}_\alpha\mathrm{H})^+$ includes both the zero point vibrational energy and temperature corrections to the vibrational enthalpy. The last term (5/2)RT accounts for the translational energy of the proton and Δ(PV) contribution. The adopted density functional theory (DFT) B3LYP method is based on widely used Becke[31] and Lee, Young and Parr[32] functional and parametrization. The final single point calculations are performed with a flexible basis set, which enables a good accuracy. Perusal of the PAs in Table 1 shows that **1** is a moderately basic compound. Verkade's superbase **2** is considerably more basic due to enhanced through-space interaction with the juxtaposed nitrogen particularly in the protonated form. Very strong superbases are given by **3** and **4** as evidenced by PAs of 278.8 and 295.5 (in kcal mol^{-1}), respectively. This is a surprising result, since the inherent basicity of phosphorus is considerably lower than that of nitrogen. To illustrate this fact we give PAs of PH$_3$ and NH$_3$ in Table 1. The corresponding proton affinities are 187.2(188.0) and 203.1(204.0), respectively, where the experimental data[33] are given within parentheses. The origin of a low intrinsic basicity of phosphorus can be easily understood by triadic analysis[34] based on eqn (2), which provides an appealing and useful interpretation of basicity as discussed in great detail by Deakyne:[35]

$$(\mathrm{PA})_\alpha = -(\mathrm{IE})_n^{\mathrm{Koop}} + E(\mathrm{ei})^{(n)}_{\mathrm{rex}} + (\mathrm{BAE})_\alpha^{+} + 313.6\ \mathrm{kcal\ mol}^{-1} \qquad (2)$$

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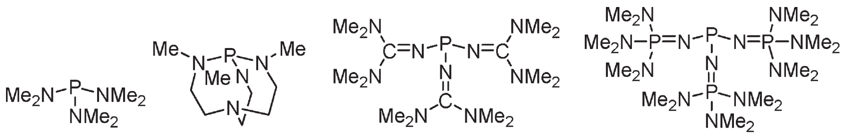

1 **2** **3** **4**

Fig. 1 Systems **1** to **4**.

Table 1 The gas phase proton affinities PA(gp) of compounds **1–4** and their triadic components (in kcal mol^{-1})[a]

Molecule	$PA(gp)_P$	$(IE)_n^{Koop}$	$E(ei)^{(n)}_{rex}$	$(BAE)_P^+$
PH_3	187.2[188.0][b]	$(243.9)_0$	17.3	100.1
NH_3	203.1[204.0][b]	$(271.2)_0$	36.7	123.9
1	242.6[242.5][c]	$(198.2)_0$	46.6	80.5
2	261.0	$(176.8)_0$	34.6	89.3
3	278.8	$(165.8)_0$	49.6	81.3
4	295.5	$(146.9)_0$	46.2	82.5

[a] HOMO is denoted by a subscript zero. [b] The experimental data within square parentheses are taken from ref. 33. [c] (G2MP2) result of this work.

where $-(IE)_n^{Koop}$ refers to the *n*th Hartree–Fock orbital energy ε_n. It gives the negative of the *n*th ionization energy in Koopman's clamped nuclei and frozen electron density approximation. It should be noted that the highest occupied molecular orbital (HOMO) is denoted here by a subscript zero and that lower orbital energies have $n > 0$. The bond association $(BAE)_\alpha^+$ term yields the exothermic energy release upon formation of a new bond between αth atom of the molecular cation and the hydrogen atom. The reorganization of the nuclei and electrons occurring during the ionization of the base is given by the $E(ei)^{(n)}_{rex}$ term. Survey of the results (Table 1) reveals that $\Delta PA = PA(PH_3) - PA(NH_3) = [27,3; -19.4; -23.8] = -15.9$ kcal mol^{-1}, where three entries within square parentheses refer to terms $-\Delta(IE)_0^{Koop}$, $\Delta E(ei)^{(0)}_{rex}$ and $\Delta(BAE)_P^+$, respectively, and the ΔPA is obtained by their summation. It follows that P(sp^3) is less basic than N(sp^3) due to appreciably smaller relaxation and bond association energies. On the other hand, HOMO of PH_3 is higher in orbital energy than its counterpart in NH_3 due to a more peripheral distribution of the electron density which in turn partially remedies a dramatic decrease in basicity by 27.3 kcal mol^{-1}. Further, $(IE)_0^{Koop}$ decreases along the series **1**, **3** and **4** implying that HOMO of the phosphorus atom becomes even less stable in these systems. Consequently, it is easier to ionize these bases implying that the price to be paid in forming a new (P–H) bond is lower. This is the dominating effect, because both $E(ei)^{(0)}_{rex}$ and $(BAE)_\alpha^+$ are fairly constant and do not affect a variation in proton affinities to a significant extent. An exception is given by Verkade's superbase **2**, where triadic components assume lesser and higher $E(ei)^{(0)}_{rex}$ and $(BAE)_P^+$ values, respectively, which is presumably a consequence of the direct through-space interaction of the juxtaposed P and N atoms. Let us examine the influence of triple substitution in molecules **1**, **3** and **4** relative to the parent compound PH_3. One obtains $PA(\mathbf{1})-PA(PH_3) = [45.7; 29.3; -19.6] = 55.4$ kcal mol^{-1} implying that enhancement in basicity induced by NMe_2 substituents is due to the initial state effect reflected by HOMO energies and the intermediate effect given by the relaxation term. Similar but much more dramatic amplifying effect is exerted by $-N{=}C(NMe_2)$ and $-N{=}P(NMe_2)_3$ moieties in **3** and **4**, respectively, as evidenced by $PA(\mathbf{3}) - PA(PH_3) = [78.1; 32.3; -18.8] = 91.6$ kcal mol^{-1} and by $PA(\mathbf{4}) - PA(PH_3) = [97.0; 28.9; -17.6] = 108.3$ kcal mol^{-1}. It is fair to conclude that high basicities of **1**, **3** and **4** are a consequence of the initial state features (high lying HOMOs) of the superbases, which are additionally increased by a combined relaxation and final state effects (*ca.* 10 kcal mol^{-1}).

A point of considerable interest is behavior of the superbases **3** and **4** in acetonitrile. We shall determine pK_a values relative to **2**, since its experimental value is known being pK_a = 32.82 obtained by UV-VIS monitored titration.[29] For this purpose we shall employ several theoretical models as described below. The most common approach is to use a very accurate *ab initio* method for calculation of free energy of solute in gas phase G_{gas}, and then to apply one of the polarized continuum models to estimate the free energy of solvation ΔG_{sol}. If these two values are known, then it is possible to use equations derived from the thermodynamic cycle in obtaining the pK_a data relative to a compound serving as a reference. According to Shields *et al.*[36] basicity of a base B can be calculated relative to the known basicity of base A by eqn (3):

$$\begin{aligned}pK_a(BH^+) = pK_a(AH^+) + \{G_{gas}(B) - G_{gas}(A) -\\ G_{gas}(BH^+) + G_{gas}(AH^+) + \Delta G_{sol}(B) - \Delta G_{sol}(A) -\\ \Delta G_{sol}(BH^+) + \Delta G_{sol}(AH^+)\}/2.303RT\end{aligned} \quad (3)$$

where symbols have their usual meaning. The calculation of free energy in the gas phase was carried out by the B3LYP/6-311 + G(2df,p)//B3LYP/6-31G* method. One of the most successful solvation models is the conductor like polarizable continuum model (CPCM)[37] The CPCM calculations at the HF/6-31G* and HF/6-31 + G* level were performed by employing the B3LYP/6-31G* gas phase geometries. In CPCM, the choice of cavities surrounding the solvated molecule is important because the computed energies and properties depend on their size. In order to examine this dependence we used several different UA0, UAHF, UAKS and Bondi atomic radii in estimating cavities and evaluating the solvation effect using the CPCM approach. All these models are described and implemented in the latest version of GAUSSIAN03.[38] Although different models of solvation are employed, they all indicate that pK_a of **4** in MeCN is in the range

Table 2 pK_a values of compounds **1**, **2** and **4** in acetonitrile

	pK_a							
	HF/6-31G*				HF/6-31 + G*			
Molecule	UA0	UAHF	UAKS	BONDI	UA0	UAHF	UAKS	BONDI
1	22.1	19.8	19.8	20.9	22.2	19.8	19.8	21.0
3	39.1	39.3	39.3	37.4	39.0	39.3	39.3	37.2
4	51.2	51.1	51.1	49.1	51.4	51.2	51.2	49.2

49–51 pK_a units (Table 2). Hence, it is a good candidate for the strongest non-ionic organic superbase provided it is prepared once.

To summarize, it is conclusively shown that the sp^3 phosphorus atom can be an extremely basic atom provided it is flanked by three tetramethylguanidino or hexamethyltriaminophosphazeno groups. The gas phase PAs of **3** and **4** are 278.8 and 295.5 kcal mol^{-1} respectively. The latter compound exhibits enormously high basicity in acetonitrile pK_a(**4**) = 50 ± 1 units! Although this result heavily leans on the experimental value of Verkade's superbase **2** (pK_a = 32.82) and depends on the accuracy of the employed theoretical method, it is safe to conclude that **4** is an extremely strong superbase (several orders of magnitute more basic than Schwesinger's P4-tBu phosphazene[12]) in acetonitrile. Hence, its synthesis is strongly recommended.

We note that basicity of phosphorus was discussed by Kolomeitsev *et al.*[39] quite recently including compound **3**. Their B3LYP/6-311+G** calculations gave PA(**3**) = 276.7 kcal mol^{-1}, which is in good accordance with our result of 278.8 kcal mol^{-1}.

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