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Basicity of exceedingly strong non-ionic organic bases in acetonitrile —Verkade's superbase and some related phosphazenes

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The basicity of Verkade's superbase (**12**) in MeCN solution is considered by a quite accurate theoretical model. It is shown that the corresponding pK_a value is 29.0. Hence, its basicity is comparable or higher than that of some other P1 phosphazenes, but it is lower than the basicity of P2 phosphazenes. Structural characteristics of Verkade's superbase and its conjugate acid, as well as the origin of its pronounced basicity, are briefly discussed. Extended Verkade's superbase **13** and some Janus-type phosphazenes are examined too. It is shown that they are very good candidates for even stronger neutral organic superbases. A very useful by-product of the present study are quite accurate estimates of the gas phase proton affinities of some P1, P2, P3 and P4 polyaminophosphazenes obtained by the B3LYP/6-311+G(2df,p)//B3LYP/6-31G* scheme. The latter was successfully tested against G2 results on small molecules. This is of importance, because the experimentally measured gas phase values for phosphazenes are not available, implying that the theoretical data fill this gap with reliable information.

Introduction

Strong organic (super)bases and particularly the "so-called" molecular proton sponges have been the subject matter of continuous research interest for the last three decades. Recent advances in the field have been covered in a number of excellent review articles.[1–7] A lot of attention has been focused on guanidines[8] and phosphazenes.[9] The former compounds were found to be useful in diabetes medication,[8] whereas a class of poly(ethylenimines) was suggested as useful agents in gene therapy.[10,11] Apart from pharmacological applications tremendous progress has been made in their use in organic acid-base reactions. Here the neutral organic (super)bases have some distinct advantages over their inorganic ionic counterparts. The latter exhibit, namely, some unfavorable features, like low solubility in most organic solvents, pronounced sensitivity to moisture and CO_2, *etc.* In contrast, strong neutral organic (super)bases play an outstanding role in organic synthesis,[12] because they permit milder conditions,[13] possess the enhanced reactivity of the more naked anions in the poorly associated ion pairs formed upon deprotonation[14] and show very good stability even at low temperatures.[15] It comes as no surprise that a lot of effort has been devoted to their experimental[9,16–19] and theoretical[20–24] design. The development of a ladder of strong organic bases possessing as many rungs as possible is important because of (at least) three good reasons: (1) their use in preparative laboratory work, (2) their employment in the experimental determination of the basicity of new bases with the bracketing technique and, last but not least, (3) their pivotal role in the interactions with strong mineral (super)acids, which should lead to low barrier hydrogen bonds (LBHB) and to spontaneous proton transfer reactions.[25,26] Continuing our interest in designing potent organic superbases and their characterization by theoretical methods and models, we consider here the basicity of a number of polyaminophosphazenes **1-11** in acetonitrile. By utilizing the experimentally known pK_a values[9,19,27] we shall derive a partly empirical formula enabling theoretical estimates of basicities not measured as yet. In particular, we focus on Verkade's superbase **12** and its extended version **13** (see Fig. 1) not synthesized as yet. Their basicity along with their spatial and electronic structures will be discussed in some detail.

Theoretical and computational method

The theoretical framework for calculating the absolute proton affinity APAs in the gas phase are given by:

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

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

$$(\Delta E_{\mathrm{vib}})_\alpha = E_{\mathrm{vib}}(\mathrm{B}) - E_{\mathrm{vib}}(\mathrm{B}_\alpha\mathrm{H})^+ \qquad (3)$$

The base in question and its conjugate acid are denoted by B and BH^+, respectively, whereas α signifies the site of proton attack. $(\Delta E_{\mathrm{el}})_\alpha$ is the electronic contribution to proton affinity, E_{vib} includes the zero point energy and temperature corrections to the vibrational enthalpy, while $(5/2)RT$ accounts for the translational energy of the proton and the $\Delta(PV)$ term. In selecting a suitable theoretical model, which represents the best compromise between accuracy and feasibility, we shall examine several MP2 (Møller–Plesset perturbation theory of the second order)[28] models and the DFT (density functional theory) procedure at the B3-LYP level.[29] The choice of the optimal theoretical and computational scheme is made by calculating the gas phase APAs of small molecules (containing the P=N group) serving as a calibration set (*vide infra*).

The basicity of organic superbases in a moderately polar aprotic solvent like MeCN is conveniently treated by using a simple theoretical model based on a transparent electrostatic

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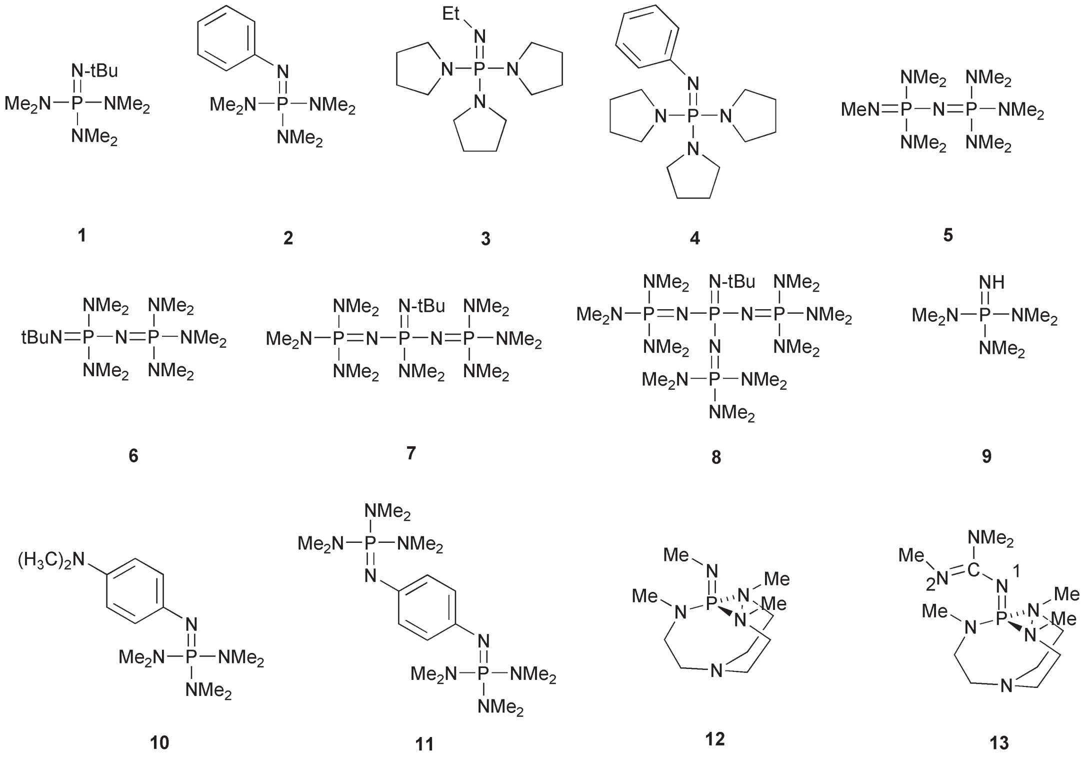


Fig. 1 Schematic representation of the considered phosphazenes and Verkade's proton sponge.

picture of the polarized continuum[30] employing the isodensity criterion in defining the molecular surface.[31] Our approach is similar to that introduced by Peräkylä.[32]

All calculations have been carried out by using GAUSSIAN 98[33] and GAMESS[34] programs.

Results and discussion

The examined molecules are depicted in Fig. 1. They encompass molecules of known basicity in MeCN with some notable exceptions. Systems **10** and **11** are not yet synthesized and serve as test cases, which should help in understanding the role of the phenyl substituent at the most basic imine position. Molecule **11** is a Janus-like system with two identical –N=P(NMe$_2$)$_3$ groups attached at the para positions of the benzene ring. Mutual interaction of these two P1 phosphazene groups is of some interest. Verkade's superbase **12** is of course synthesized, but its experimental basicity in MeCN is not known. Finally, we consider a compound, **13**, not prepared so far, since it may well be significantly more basic than **12** in view of the protonation at the imine position N2 and the concomitant strong resonance effect triggered in conjugate acids along the alternating double and single bonds.[24*c*,35]

In calculating the proton affinities and basicities in the gas phase it is desirable to utilize highly reliable G2[36] or G2(MP2)[37] procedures. Unfortunately, their use is hampered by the size of the studied systems. It is, however, possible to find efficient theoretical models that are computationally feasible with only a small sacrifice in accuracy. Their quantitative appraisal is executed on a set of gauge molecules shown in Fig. 2. The theoretical models tested include: MP2(I) $\equiv$ MP2(fc)/6-311+G**//B3LYP/6-31G*, MP2(II) $\equiv$ MP2(fc)/6-311+G(2df,p)//B3LYP/6-31G*, MP2(III) $\equiv$ MP2(fc)/6-311+G(3df,3pd)//B3LYP/6-31G*, DFT(I) $\equiv$ B3LYP/6-311+G**//B3LYP/6-31G* and DFT(II) $\equiv$ B3LYP/6-311+G(2df,p)//B3LYP/6-31G*.

In all calculations the temperature correction to enthalpy is calculated by the B3LYP/6-31G* method. The performance of various models is checked against the G2 results. Perusal of the results presented in Table 1 clearly indicates that the MP2(I) model is not quite satisfactory. Considerably better performance is provided by model MP2(III), particularly if an off-set correction of 1.6 kcal mol^{-1} is added. In that case a virtually G2-quality of APAs is achieved in a much cheaper way and with a wider range of applicability. However, in spite of the latter, the MP2 formalism based on a large 6-311+G(3df,3pd) set is still not feasible in sizeable phosphazenes like **7** and **8** to be explored. A much more practical procedure is given by the DFT(II) computational scheme, which can be used in very large systems and yet offers APA values of very good quality. Variation in the APAs of small molecules **14**–**21** is very interesting, but they were commented upon in some detail earlier and this will not be repeated here. To epitomize, the DFT(II) scheme will be used in estimating proton affinities of compounds **1**–**13** in the gas phase. The basicity in MeCN is calculated by taking advantage of the fact that the experimental pK_a values for molecules **1**–**8** are known.[9,19,27] Employing DFT(II) calculations for estimating the APA$_{gp}$, where the subscript gp stands for the gas phase, and the isodensity polarized continuum model (IPCM) in order to take into account the energy of solvation ΔE_{solv} at the IPCM(B3LYP/6-311+G**//

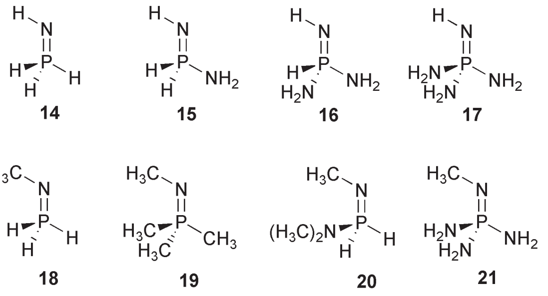


Fig. 2 Schematic representation of small characteristic molecules serving as a test set in developing the theoretical model, which is the best compromise between reliability and practicality.

Table 1 Absolute proton affinities[a] obtained by several computational and theoretical models[b]

	G2	G2(MP2)	MP2(I)	δ	MP2(II)	δ	MP2(III)	δ	DFT(I)	δ	DFT(II)	δ
14	225.5	225.1	230.9	5.4	224.2	−1.3	224.0	−1.5	228.8	3.3	226.0	0.5
15	233.5	233.4	235.9	2.4	231.9	−1.6	231.9	−1.6	235.5	2.0	234.2	0.7
16	240.9	240.8	242.2	1.3	239.0	−1.9	239.3	−1.6	242.2	1.3	241.6	0.7
17	247.8	247.7	248.3	0.5	245.9	−1.9	246.4	−1.4	248.4	0.6	248.1	0.3
18	232.2	232.1	236.1	3.9	229.8	−2.4	230.6	−1.6	234.4	2.2	231.8	−0.4
19	251.3	251.3	253.4	2.1	248.3	−3.0	249.7	−1.6	253.5	2.2	251.9	0.6
20	244.1	244.0	245.1	1.0	241.0	−3.1	242.3	−1.8	245.6	1.5	244.5	0.4
21	252.4	252.4	252.6	0.2	249.7	−2.7	250.8	−1.6	252.6	0.2	252.5	0.1
AAD				2.1		2.2		1.6		1.7		0.5

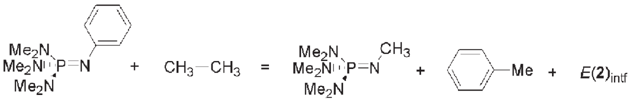
[a] Values in kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}). [b] Theoretical models are abbreviated as: MP2(I) ≡ MP2(fc)/6-311+G**//B3LYP/6-31G*; MP2(II) ≡ MP2(fc)/6-311+G(2df,p)//B3LYP/6-31G*; MP2(III) ≡ MP2(fc)/6-311+G(3df,3pd)//B3LYP/6-31G*; DFT(I) ≡ B3LYP/6-311+G**//B3LYP/6-31G*; DFT(II) ≡ B3LYP/6-311+G(2df,p)//B3LYP/6-31G*. Deviations from the G2 results are denoted by δ = PA(Model) − PA(G2), whereas the average absolute deviation is signified by AAD. In all calculations the temperature correction to enthalpy is calculated by the B3LYP/6-31G* model.

B3LYP/6-31G*) level,[38] one obtains a partly empirical linear relation:

$$\mathrm{p}K_\mathrm{a}(\mathrm{th}) = 0.58684\mathrm{PA}_\mathrm{MeCN} - 145.9 \qquad (4)$$

where $\mathrm{PA}_\mathrm{MeCN}$ is the proton affinity in acetonitrile defined as $\mathrm{PA}_\mathrm{MeCN} = (\mathrm{APA}_\mathrm{gp} + \Delta\Delta E_\mathrm{solv})$. The average absolute deviation AAD is only 0.3, whilst $R^2 = 0.997$ indicates a high correlation of the calculated PA in MeCN and the measured $\mathrm{p}K_\mathrm{a}$(expt) data. This kind of accuracy is quite satisfactory, particularly if one takes into account that 1 $\mathrm{p}K_\mathrm{a}$ unit corresponds to 1.4 kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}). Thus, an AAD of only 0.3 units corresponds to 0.4 kcal mol^{-1}, which is well below the chemical accuracy margin of ±2 kcal mol^{-1}. The very good quality of these results in phosphazenes is achieved due to the use of a large basis in the DFT(II) scheme. The use of the APA_gp values obtained by the DFT(I) model in calculating $\mathrm{PA}_\mathrm{MeCN}$ results in a somewhat worse correlation between the $\mathrm{p}K_\mathrm{a}$ and $\mathrm{PA}_\mathrm{MeCN}$ values, the mean absolute deviation being 0.4 and $R^2 = 0.995$. It should be observed that the empirical parameters in eqn. (4) are different than those found for guanidines earlier.[38] This implies that the linear relations for $\mathrm{p}K_\mathrm{a}$ [eqn. (4)] are valid for each family of compounds separately. In the present case a very large basis set 6-311+G(2df,p) was necessary in order to describe the subtleties of the chemical bonding of the phosphorus atom.

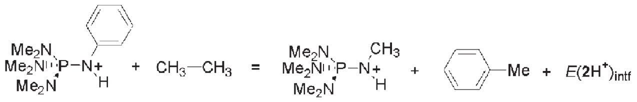
Let us discuss first the gas phase proton affinities, which are important *per se*, because the experimental data are not available. They are presented in Table 2. A most striking finding is that the *t*Bu substituent on the imino nitrogen in **1** increases the PA by 3.3 kcal mol^{-1} with respect to the unsubstituted compound **9**. In contrast, the PA is decreased by 3.9 kcal mol^{-1} compared to **9** upon substitution by a phenyl fragment in **2**. The former result is expected since the alkyl group will decrease the ionization potential of the imine lone pair electrons.[39] The latter result, however, calls for some rationalization. It is found by the corresponding homodesmotic[40] reaction (5):



(5)

where E_intf denotes the interference between the N=P($\mathrm{NMe_2}$)$_3$ framework and the phenyl fragment. Employing the DFT(II) model we find $E(\mathbf{2})_\mathrm{intf} = -10.3$ kcal mol^{-1}, meaning that the phenyl moiety stabilizes the phosphazene moiety. This automatically implies that its PA should be lower. The conclusion obtained from the PAs is corroborated by Löwdin's π-bond order for the N-phenyl bond obtained by the symmetric partitioning of the mixed electron density,[41] which assumes 0.36 and 0.18 in **2** and its protonated form $\mathbf{2}\mathrm{H}^+$, respectively. Obviously, the cationic resonance spurred by protonation is not spread to a large extent to the phenyl ring across the single N–C(aryl) bond, which is in accordance with earlier finding that the N=C double bond acts as a "conductor" of the resonance, whereas the N–C single bond behaves as an "insulator" for the cationic resonance,[35] where N is the protonated center. On the contrary, the conjugative interaction between phenyl and the ($\mathrm{Me_2N}$)$_3$P=N backbone seems to be substantial in the neutral base. Additional evidence is provided by the N–C(aryl) bond distances, which in **2** and $\mathbf{2}\mathrm{H}^+$ are 1.388 and 1.448 Å, respectively. This is a consequence of rehybridization, but it is interesting to point out that the imino N atom becomes practically planar in $\mathbf{2}\mathrm{H}^+$ as evidenced by a very small degree of pyramidalization, DP = 2.1%, thus allowing for an efficient resonance stabilization with the P($\mathrm{NMe_2}$)$_3$ group in the protonated form.

Since the difference between PA(**2**) and PA(**9**) is only −3.9 kcal mol^{-1}, we have to consider the protonated analog of eqn. (5):



(6)

Table 2 Proton affinities of phosphazenes **1**–**13** obtained by the DFT(II) model and comparison of the theoretical $\mathrm{p}K_\mathrm{a}$ values calculated by eqn. (1) with the available experimental data

Molecule	PA_gp[DFT(II)]	PA(MeCN)	$\mathrm{p}K_\mathrm{a}$(th)	$\mathrm{p}K_\mathrm{a}$(expt)
1	260.2	295.0	27.2	26.89
2	253.0	283.9	20.6	21.05
3	265.6	297.8	28.8	28.89
4	258.6	287.6	22.8	22.15
5	274.7	304.0	32.5	32.72
6	274.4	304.8	32.9	33.49
7	288.8	314.5	38.6	38.6
8	297.5	322.0	43.0	42.7
9	256.9	292.4	25.7	–
10	256.0	286.9	22.5	–
11	261.9	285.4	21.6	–
12	265.2	298.2	29.0	–
$\mathbf{13_1}$	257.2	286.9	22.5	–
$\mathbf{13_2}$	272.4	301.4	31.0	–

[a] Values in kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}).

The corresponding interference energy $E(\mathbf{2}H^+)_{intf}$ is −2.0 kcal mol^{-1}, implying that the difference between the proton affinities of **2** and $(Me_2N)_3$ P=NMe (**22**) is −8.3 kcal mol^{-1}. It appears that the methyl group substitution at the imino nitrogen increases PA by 2.3 kcal mol^{-1} as evidenced by comparison of PA(**22**) = 259.2 kcal mol^{-1} with PA(**9**). This chain of considerations indicates that the difference in PA of **2** and **9** should be around −6 kcal mol^{-1}, which comes reasonably close to the value of −3.9 kcal mol^{-1} mentioned above.

One point of considerable importance is that phosphazenes **5**–**8** exhibit superbasic proton affinities ranging from 274.4–297.5 kcal mol^{-1}, exhibiting the maximal value for P$_4$*t*Bu (**8**).

Our next focal point is Verkade's proton sponge **12**. Its PA is comparable to that of **3**, being higher than that of the P1 phosphazenes **1**, **2**, **4** and **9**. It is interesting to identify the origin of its increased basicity. In Fig. 3 we compare the characteristic bond distances of **12** and **12**H$^+$ with the corresponding values in **22** and **22**H$^+$.The general pattern is the same: the N=P double bond is lengthened by 0.11 and 0.10 Å in **12** and **22** upon protonation, respectively. In contrast, the N(sp^3)–P bond distances are shortened by 0.04 Å, which is indicative of the cationic resonance effect. An interesting structural change in **12** is given by a considerable shortening of the nonbonded N(apical)···P distance, which is condensed in **12**H$^+$ by 0.5 Å. This is corroborated by the pyramidalization degrees of the P atom, if only three N(sp^3) nitrogens are taken into account. The corresponding DP values in **12** and **12**H$^+$ are 50.7 and 25.2%, respectively. It is obvious that the angular strain is increased in **12**H$^+$, which is overcome by the apical N lone pair–P atom interaction. This conjecture is substantiated by a comparison with the sum of van der Waals radii[42] r_w. The average van der Waals' radius for singly and doubly bonded N atoms is 1.55 ± 0.04 Å, whereas for the P atom it is 1.80 Å. The corresponding sum $r_w(N) + r_w(P) = 3.35 \pm 0.04$ Å, which compares with an N···P distance of 3.333 Å in **12**. On the other hand, the N···P distance in **12**H$^+$ is 2.835 Å, which is well below the van der Waals contact, thus indicating a strong interaction between the P atom and apical nitrogen. Concomitantly, the prolate apical N atom in **12** assumes an oblate shape in **12**H$^+$ (Fig. 3).

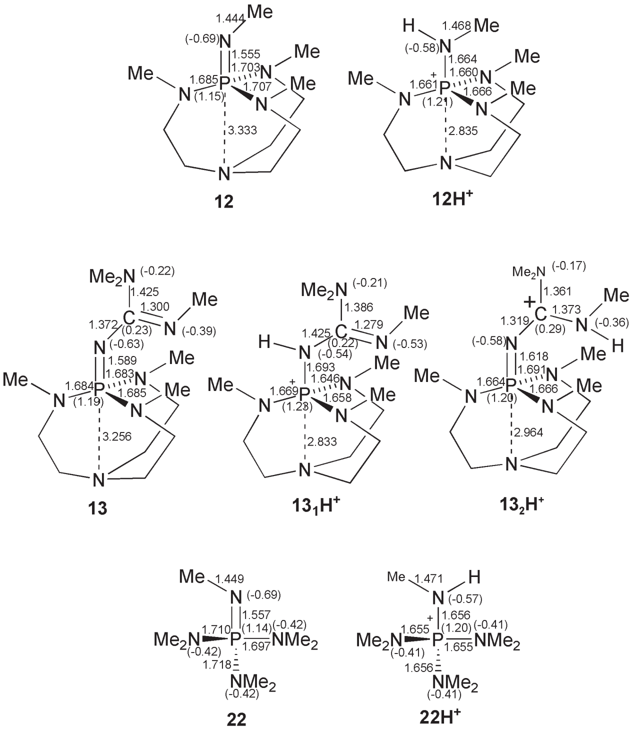


Fig. 3 Some characteristic structural parameters and Löwdin atomic charges (within parentheses).

Finally, a survey of the charge distributions in **12**H$^+$ and **22**H$^+$ reveals that the protonated nitrogen becomes only slightly less negative than in neutral bases, whereas the phosphorus atom increases slightly its positive charge. It appears that the +1 positive charge created by protonation is almost evenly distributed overall the conjugate acids.

Extended Verkade's superbase **13** deserves some more comments. The two most basic positions are at imino nitrogens N1 and N2. It is obvious that N2 will be more basic, because of the cationic resonance effect triggered by protonation. This is evidenced by the bond distances along the N2=C–N1=P fragment, which are enlongated and shortened in an alternating fashion upon protonation in $\mathbf{13}_2$H$^+$ (Fig. 3). In addition, the P–N bonds of the cage are shortened, implying that the resonance effect is spread over the amino nitrogens too. Finally, the "nonbonded" contact between P···N(apical) is 2.964 Å, thus being below the sum of the VdW radii (3.35 ± 0.04 Å). As a consequence of all these effects, $\mathbf{13}_2$ is more basic than **12**. The difference between their APAs is 7.2 kcal mol^{-1}. The protonation at N1 leading to $\mathbf{13}_1$H$^+$ is less profitable than at the N2 position by 15.2 kcal mol^{-1}. The reason behind this is also clear: the cationic resonance effect is not extended over the guanidine building block. On the contrary, the C=N2 double bond is significantly shortened in $\mathbf{13}_1$H$^+$ relative to the parent base **13** (Fig. 3). The structural parameters of $\mathbf{13}_1$H$^+$ are similar to those found in **12**H$^+$, apart from the guanidine moiety. Nevertheless, the protonation at N1 in **13** is less advantageous than in **12** by 8 kcal mol^{-1} *inter alia* because the substituted CH_3 group stabilizes the imino nitrogen, whereas the guanidine fragment destabilizes it.

Finally, let us consider the Janus-like base **11** possessing two equivalent phosphazene groups substituted at para positions of benzene. Its APA is higher by 9 kcal mol^{-1} than that of **2**. Once again the answer is offered by the corresponding homodesmotic reactions:

$$\mathbf{11} + \text{benzene} = 2 \cdot \mathbf{2} + E(\mathbf{11})_{intf} \qquad (7)$$

and

$$\mathbf{11}H^+ + \text{benzene} = 2 \cdot \mathbf{2}H^+ + E(\mathbf{11}H^+)_{intf} \qquad (8)$$

It appears that $E(\mathbf{11})_{intf} = 3.9$ kcal mol^{-1}, indicating a destabilizing interaction between the two phosphazene fragments. In contrast, $E(\mathbf{11}H^+) = -5$ kcal mol^{-1} implies that the cationic resonance is extended to some extent over the unprotonated phosphazene moiety. Examination of the relevant bond distances (not shown here) confirms this conjecture. This is of some interest because **11**H$^+$ represents a rare case where the N–C single bond is not a perfect "insulator" for the cationic resonance.

It is interesting to observe that the basicity in MeCN follows the same hierarchy established in the gas phase (Table 2) with a notable inversion of the basicity in MeCN for compounds **10** and **11**, which is more an exception than the rule. Concomitantly, it is not surprising that the basicity of **12** is practically the same as that of **3** and close to that of the vinamidine proton sponge.[9] It is interesting to notice that the extended Verkade's base **13** is slightly less basic in MeCN than the P2 phosphazene **5**. This is a very important point, since it shows that Verkade's type of cage compounds cannot be used in tailoring very strong superbases. The reason is that the cage is a limiting factor in possible extension of the system. It is well-known by now that very strong bases require large systems capable of a very high cationic resonance, particularly if they are able to form branched isomers. Good examples are given by phosphazenes **7** and **8**. Alternative favorable systems are provided by polyguanides[21*b*] and extended iminopolyenes.[22*b*,24*c*] Finally it should be mentioned that Koppel *et al.*[20] considered some of the bases examined in the present work, including Verkade's proton sponge. They used several theoretical models, the best being B3LYP/6-311+G** applied in a few cases. However, most of the very large phosphazenes are treated at the semiempirical PM3 level, implying that their results are less accurate than the present ones.

Concluding remarks

The proton affinities in the gas phase of some important phosphazenes (**1**–**13**) were calculated by a reliable theoretical procedure, thus filling the gap in the missing experimental data on these strong bases. The pK_a value of Verkade's superbase **12** in MeCN is determined. Finally, both APAs and pK_a values in acetonitrile of the nonexisting systems **11** and **13** are predicted. It is shown that they provide two new useful rungs on the ladder of strong organic (super)bases. However, it should be pointed out that Verkade's cage compounds like **12** and **13** do not provide suitable backbones for the design of potent superbases, because the cage itself is a limiting factor. It is well-known by now that powerful superbases are systems capable of a strong cationic resonance effect, which in turn requires extended π systems in their branched form. Typical examples are provided by phosphazenes,[9] polyguanides[21*b*] and iminopolyenes.[22*b*,24*c*]

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