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Tetraphosphacubane: An Unexpectedly Strong Base in the Gas Phase[†]

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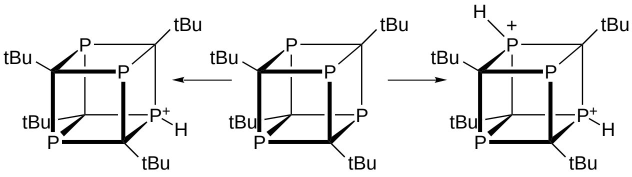
The experimental determination of physical properties of tetra-*tert*-butylphosphocubane (TtBuPC) is of paramount importance for understanding the reactivity of this fascinating molecule.The gas-phase basicity of TtBuPC measured by FT-ICR spectroscopy (GB = 221.8 kcal mol^{-1}, PA = 230.5 kcal mol^{-1}) is surprisingly high although protonation in solution is only achieved under drastic conditions. A molecular orbital treatment, including electron correlation effects, predicts the unsubstituted parent compound phosphacubane (PC) to be a carbon base. Carbon protonation implies a P−C bond fission which alleviates the strain of the system. A similar behavior is also predicted for the tetramethyl derivative. However, TtBuPC is found to be a phosphorus base, because the strong repulsive interactions which appear between the *tert*-butyl substituents destabilize significantly the C-protonated form. These effects decrease dramatically when just one *tert*-butyl group is removed and both P- and C-protonated species become almost degenerate. As for other strained systems, the PAs of PC and TtBuPC are only adequately reproduced when G2-type [6-311+G(3df,2p)] basis sets are used.

Introduction

The 1,3,5,7-tetraphosphacubane (PC) ring system has been discovered by one of us (M.R.) who thoroughly studied its properties often using as substrate its most common derivative, 2,4,6,8-tetra-*tert*-butyl-1,3,5,7-tetraphosphacubane, TtBuPC.[1−3] Of these studies, those that are relevant for the present paper will be briefly summarized here. For the neutral TtBuPC molecule, the ^{13}C NMR signal of the cage carbon appears at $\delta = -29.1$ ppm and the ^{31}P NMR signal at $\delta = 257.4$ ppm; these unusually high- and low-field positions correspond to the unusual electronic structure of TtBuPC and have been assigned to the presence of a positive net charge at phosphorus and a negative net charge at the cage carbon atoms.[4] This conclusion implies that the phosphorus atoms in TtBuPC should be only slightly nucleophilic (or basic). Actually, normal acids are not able to protonate TtBuPC and only superacids can achieve this: FSO_3H in liquid SO_2 for the monoprotonation and FSO_3H/SbF_5 (magic acid) in liquid SO_2 for the diprotonation (quaternary salts, studied by MS, have a phosphonium structure).[5,6] Concerning the structure of the cations resulting from the protonation of TtBuPC, ^{13}C, and ^{31}P NMR results and the reversibility of the protonation proved that they are mono- and diprotonated on the phosphorus atoms:



TtBuPCH$^+$ (**1**) TtBuPC TtBuPCH$_2^{2+}$

We decided to study the basicity of TtBuPC in the gas phase to separate intrinsic properties from the solvent dependent behavior.

Experimental Section

A sample of TtBuPC (CAS Registry numbers (supplied by author): PC, 1,3,5,7-tetraphosphapentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]-octane, 121869-04-3; TtBuPC, 2,4,6,8-tetrakis(1,1-dimethyl-

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[†] Dedicated to Prof. Robert W. Taft. In Memoriam.

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S0022-3263(95)01629-X CCC: $12.00

Table 1. Experimental Determination of the Gas-Phase Basicity of Tetra-*tert*-butylphosphocubane (TtBuPC)

B_{ref}	$GB(B_{ref})^{a,b}$	$\Delta G_{H^+}(g)^a$	$GB(TtBuPC)^a$	av $GB(TtBuPC)^a$
piperidine	219.2	3.03	222.2_3	
4-methylimidazole	220.0	1.67	221.6_7	221.8 (sd = 0.4)
$(CH_3)_2NC_2H_5$	221.4	0.05	222.4_5	

[a] All values in kcal mol^{-1}. [b] From ref 9b.

Table 2. MP2/6-31G//MP2/6-31G** total energies (in hartrees) and proton affinities (in kcal mol^{-1})[a].**

compd	neutral	protonated	PA
PH_3	−342.578 58	−342.89361	190.7
PH_2CH_3	−381.763 80	−382.10307	206.3
$PH(CH_3)_2$	−420.951 64	−421.31087	218.9
$P(CH_3)_3$	−460.141 98	−460.51775	229.3
PC	−1517.550 19	−1517.888 99 (P)[b]	208.6[c]
		−1517.868 63 (P, open form)[b]	196.3[c]
		−1517.904 17 (C)[b]	218.8[c]

[a] These values include the corresponding ZPE correction. [b] The protonation site is given in parentheses. [c] These values include the thermal corrections evaluated at 333 K.

ethyl)-1,3,5,7-tetraphosphapentacyclo[$4.2.0.0^{2,5}.0^{3,8}.0^{4,7}$]-octane, *121097*−72−1) of high purity was used.[1]

FTICR Experiments. The experimental determination of the gas-phase basicity of TtBuPC, GB(TtBuPC) (defined as the Gibbs energy change for reaction 1) was carried out by means of Fourier transform ion cyclotron resonance spectroscopy[7] on a modified Bruker CMS-47 mass spectrometer used in previous studies.[8]

$$TtBuPCH^+(g) \rightarrow TtBuPC(g) + H^+(g) \tag{1}$$

The FTICR experiments provided the standard Gibbs energy changes, $\Delta G_{H^+}(g)$, pertaining to the proton exchange reaction between TtBuPC and several reference bases, B_{ref} (reaction 2):

$$TtBuPCH^+(g) + B_{ref}(g) \rightleftharpoons TtBuPC(g) + B_{ref}H^+(g),\ \Delta G_{H^+}(g) \tag{2}$$

Table 1 summarizes the results of the experimental study. The gas-phase basicities of the reference compounds were determined in Prof. Taft's laboratory and have been published in an important compilation.[9] We have anchored them to the most recent value of $GB(NH_3)$, namely, 195.4 kcal mol^{-1}.[10]

GB(TtBuPC) is given by eq 3:

$$GB(TtBuPC) = GB(B_{ref}) + \Delta G_{H^+}(g) \tag{3}$$

Using the data from Table 1 we obtain GB(TtBuPC) = 221.8 ± 0.4 kcal mol^{-1}. Double-resonance experiments using ion-selection techniques were performed. They allowed us to observe proton transfer from $TtBuPCH^+$ to B_{ref} and from $B_{ref}H^+$ to TtBuPC. Constant ratios of ion intensities were observed in both cases after reaction times of 10−20 s. They led to essentially the same values for the equilibrium constants for reaction 2.

We have carried out several MS/MS[11] experiments on $TtBuPCH^+$ (**1**). To this end, a 1:1 mixture of TtBuPC and a reference base (e.g., piperidine) with a nominal pressure of $\sim 2 \times 10^{-7}$ mbar was subject to electron ionization (nominal ionization energies of ~15 eV). **1** was formed by chemical ionization, the fragments of the reference base acting as proton sources. After reaction times of 3−5 s, all ions except **1** were ejected by means of radiofrequency chirps. **1** was then excited for variable periods of time (up to 50 μs) by irradiation at the appropriate radiofrequency. Thus, energies of up to 25 eV (center of mass) were reached. Argon (Alphagaz, purity > 99.99%), used as the inert collision gas, was then introduced in the ICR cell by means of a piezoelectric valve ("bursts" of up to 0.2 s). This raised the pressure up to $\sim 1 \times 10^{-3}$ mbar. All these experiments were extremely clean, and *within the range of energies indicated above, no fragmentation of **1** was observed.*

Computational Details. To rationalize the unexpected high gas-phase basicity of TtBuPC as well as to determine the site of protonation of this molecule, we have carried out a parallel *ab initio* molecular orbital study. The corresponding calculations have been performed using the Gaussian-92 and Gaussian-94 series of programs.[12]

Results and Discussion

It is well-known that a reliable prediction of gas-phase basicities requires the use of flexible enough basis sets, as well as to incorporate electron correlation effects into the theoretical treatment. In this respect, a good option would be the MP2/6-31G** method. To confirm the reliability of this approach, we have taken as suitable model the set of phosphorus bases formed by phosphamine and its methyl derivatives. To do so, the geometries of the different neutrals and those of their protonated species were optimized at the HF/6-31G** level. For each equilibrium geometry, we have also evaluated the corresponding harmonic vibrational frequencies to estimate the zero-point energy (ZPE) correction to the protonation energies. Then, the HF geometries were refined at the MP2/6-31G** level. The proton affinities were obtained as the MP2/6-31G** energy difference between protonated and neutral species, plus the corresponding ZPE correction scaled by the empirical factor 0.893, to account for the overestimation of this magnitude at the HF level of the theory. The agreement between these calculated proton affinities (see Table 2) and the experimental values taken from ref 9 is apparent (Figure 1).

Unfortunately, this approach is prohibitively expensive for treatment of molecules of the size of TtBuPC. There-

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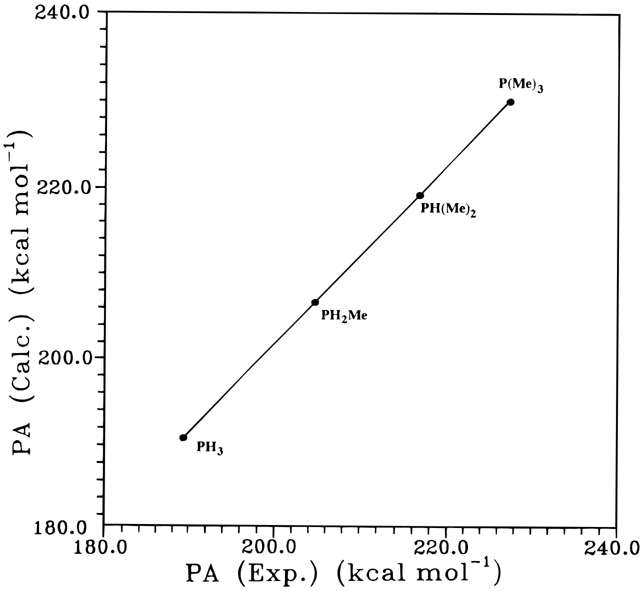

Figure 1. Linear correlation between MP2/6-31G** calculated proton affinities and experimental values for phosphine and its methyl derivatives. This linear relationship obeys the equation PA(calc.) = 1.009PA(exp.) + 0.31(kcal mol^{-1}), r = 0.9998.

fore, we have considered, as a reasonable compromise, evaluating the gas-phase basicity of tetraphosphacubane (PC) at the MP2/6-31G** level, while the effect of the four *tert*-butyl substituents on the proton affinity would be estimated in the framework of the density functional theory. Actually it has been shown[13] that, in general, different functionals yield reliable proton affinities for a great variety of compounds. The advantage of these formalisms is that it is possible to account for electron correlation effects at a reasonably low cost, which permit the study of very large systems such as TtBuPC. For this purpose we have chosen the hybrid functional B3-LYP, which has been shown[14] to perform particularly well in evaluating proton affinities. These DFT calculations will be carried out on a 3-21G* basis set, which has a moderate size but enough flexibility to describe substituent effects.[15] Hence, in a first step the geometries of TtBuPC and PC and those of their phosphorus-protonated species were fully optimized at the B3-LYP/3-21G* level. The total energies so obtained indicate (see Table 3) that the former is 16.2 kcal mol^{-1} more basic than the latter. Accordingly, this value was taken as a reasonably good estimation of the effect of the four *tert*-butyl groups on the gas-phase basicity of PC.

It must be noted, however, that while our theoretical estimations refer to proton affinities of the neutral species under consideration, *i.e.*, to the enthalpies of the protonation processes [PA = ΔH for reaction 1], the experimental measurement corresponds to gas-phase basicities, *i.e.*, to changes in the free energy in the corresponding protonation processes (GB = ΔG). To compare the experimental GB value of the gas-phase basicity of TtBuPC reported above (221.8 kcal mol^{-1}) with the PA values of Table 2, we have to calculate the entropic change corresponding to eq 4:

Table 3. B3-LYP Calculated Proton Affinities (PA, kcal mol^{-1}) for PC and TtBuPC (Total Energies Are in hartrees)

	neutral	protonated[a]	PA[b]
B3-LYP/3-21G*			
PC	−1512.784 85	−1513.122 72 (P)	208.1
		−1513.132 33 (C)	214.7
TtBuPC	−2138.445 07	−2138.808 73 (P)	224.3
		−2138.796 30 (C)	217.1
B3-LYP/6-31+G(d)//B3-LYP/3-21G*			
PC	−1520.142 98	−1520.479 56 (P)	207.3
		−1520.497 55 (C)	219.2
TtBuPC	−2149.191 54	−2149.549 75 (P)	221.0
		−2149.541 29 (C)	216.2
B3-LYP/6-311+G(3df,2p)//MP2/6-31G**			
PC	−1520.315 75	−1520.660 93 (P)	212.8
		−1520.674 72 (C)	221.9

[a] The protonation site is given in parenthesis. [b] These values include the thermal corrections evaluated at 333 K.

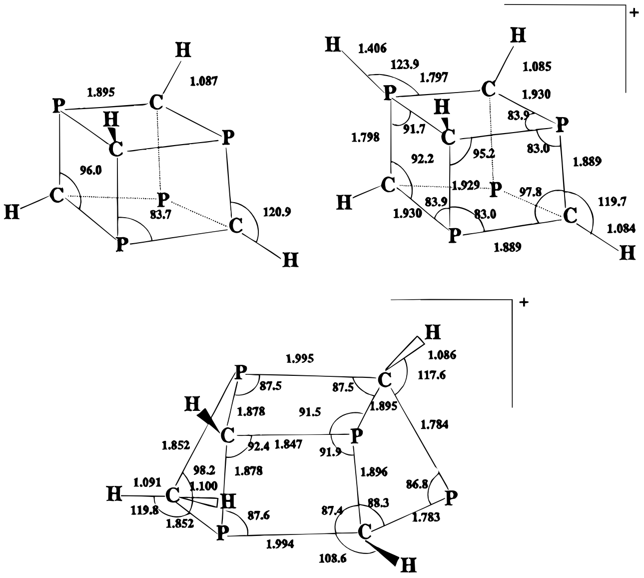

Figure 2. MP2/6-31G** optimized geometries of phosphacubane (PC) and its phosphorus- and carbon-protonated species. Bond lengths in Å and bond angles in degrees.

$$\mathrm{PC} + \mathrm{H}^+ \rightarrow \mathrm{PCH}^+ \qquad (4)$$

We have estimated the corresponding entropy changes from our *ab initio* calculations. Protonation of PC at the phosphorus atom implies an increase of the entropy of the system of 0.4 cal mol^{-1} K^{-1}. Considering that the translational entropy of the proton is 26.5 cal mol^{-1} K^{-1},[9] the entropic balance of eq 4 is −26.5 + 0.4 = −26.1 cal mol^{-1} K^{-1}. At the temperature of the experiments, 333 K, this corresponds to $T\Delta S$ = 8.7 kcal mol^{-1}. Then, PA(TtBuPC) = 221.8 + 8.7 = 230.5 kcal mol^{-1}.

The geometries of PC and its phosphorus-protonated cation were reoptimized at the HF/6-31G** level. To check whether the protonated species was a minimum of the potential energy surface (PES), the HF/6-31G** harmonic vibrational frequencies were calculated and the ZPE correction obtained. These geometries were refined, in a further step, at the MP2/6-31G** level and are presented in Figure 2. The corresponding total energies, as well as the proton affinities, are given in Table 2. It

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can be seen that PC is predicted to be a phosphorus base of similar strength (208.6 kcal mol^{-1}) as methylphosphine (206.3 kcal mol^{-1}) and therefore, according to the linear correlation of Figure 1, only slightly (~2.4 kcal mol^{-1}) more basic than ammonia.

Taking into account the effect of the *tert*-butyl groups (+16.2 kcal mol^{-1}), TtBuPC should have a PA of 208.6 + 16.2 = 224.8 kcal mol^{-1} instead of 230.5 kcal mol^{-1}. The gap is even greater considering that according to the equation defined in Figure 1, to a calculated value of 224.8 kcal mol^{-1} should correspond an "experimental" value of 222.5 kcal mol^{-1}. This clear disagreement with the experimental estimated value prompted us to investigate alternative structures for the phosphorus-protonated species. By similarity with the protonation of P_4[8c] which takes place at the tetrahedral side rather than at the tetrahedral corner, we have investigated whether protonation at the PC side was more favorable than corner protonation, *i.e.*, the initial structure tested corresponded to a proton bridging a phosphorus atom and one of the carbon atoms directly bonded to it. However, this structure was not stable as it collapsed to the corner-protonated species. The possibility that protonation at the phosphorus atom would involve a P−C bond fission was also explored, since this would involve a certain alleviation of the strain present in the neutral. We have actually found a stationary point corresponding to this possibility. Further analysis of the corresponding harmonic vibrational frequencies confirmed it to be a minimum of the PES. Nevertheless, it was found to be 12.2 kcal mol^{-1} less stable than the corner protonated species (see Table 2). Furthermore, when the same possibility was investigated for TtBuPC, at the 3-21G* level, it was found that the energy gap between close and open cations increases. Hence, the hypothesis that *tert*-butyl substituents would eventually stabilize preferentially the open structure corresponding to P-protonation was found to be unsound.

The following step of our survey of the potential energy surface corresponding to the protonation of PC was to consider the protonation at one of the carbon atoms. As before, the geometry of this cation was initially optimized at the HF/6-31G** level. The structure so obtained involves the fission of one of the P−C bonds in which the protonated carbon atom participates. In other words, the protonated carbon retains its tetracoordination by breaking one of the C−P linkages. What is more important, an inspection of the corresponding harmonic vibrational frequencies showed it to be a minimum of the PES of $C_4P_4H_5^+$. The refinement of the geometry of this carbon-protonated species at the MP2/6-31G** level did not introduce any significant structural changes (see, Figure 2, note that the structure has a C_s symmetry with the mirror plane going through P^+ and CH_2, the small differences in bond lengths and angles of Figure 2 came from not imposing any restriction during the geometry optimization; the positive charge of the phosphenium cation, -P^+-, is delocalized in the four-membered ring). The most significant result however is that this new minimum is predicted to be 9.6 kcal mol^{-1} lower than that of the phosphorus-protonated isomer (see Table 2). As mentioned above carbon protonation implies a C−P bond fission, which results in a sizeable increase (5.0 cal mol^{-1} K^{-1}) of the entropy of the system. This would imply that under the hypothesis of carbon protonation the entropy contribution to the PA of the system should be smaller than that estimated above for protonation at the phosphorus atom. From our ab initio results a $T\Delta S$ value of 7.2 kcal mol^{-1} is obtained, so that the experimental PA of TtBuPC would be 221.8 + 7.2 = 229.0 kcal mol^{-1}, provided that protonation takes place at the carbon atom.

Going back to our theoretical estimations, from the 218.8 kcal mol^{-1} obtained for the PA of PC (protonated on carbon) (see Table 2), the estimated proton affinity of TtBuPC should be 218.8 + 16.2 = 235.0 kcal mol^{-1}, assuming that the effect of *tert*-butyl groups is independent of the protonation site. The correction based on the Figure 1 equation leads to PA(exp.) = 233.0 kcal mol^{-1} which is in reasonably good agreement with the experimental value (229.0 kcal mol^{-1}).

However it is not clear that the *tert*-butyl substituents must stabilize to the same degree both protonated species, among other reasons because carbon protonation leads to a open cation and we have mentioned above that the *tert*-butyl substituents seem to destabilize the P-protonated open form. Hence it seems crucial to investigate the effect of the *tert*-butyl substituents on the carbon-protonated species. For this purpose we shall follow the same strategy as before, *i.e.*, we will estimate this effect by fully optimizing the carbon-protonated species of both PC and TtBuPC, at the B3-LYP/3-21G* level. The final energies are presented in Table 3.

Two things are important. In the first place, also at the B3-LYP/3-21G* level the carbon-protonated species of PC is found to be more stable than the P-protonated one, in agreement with our MP2/6-31G** calculations. Second, this stability order is reversed when the four hydrogens are replaced by *tert*-butyl groups. As shown in Table 3, the C-protonated species of TtBuPC is 7.8 kcal mol^{-1} less stable than the P-protonated one. To check whether this result might be affected by the lack of flexibility of the basis set used, we have carried out single-point B3-LYP/6-31+G(d) calculations at the B3-LYP/3-21G* optimized geometries. As illustrated in Table 3, the enlargement of the basis set has no dramatic effects although it tends to stabilize more the C-protonated species. As a consequence, for PC the gap between C- and P-protonated forms increases favoring the former, while for TtBuPC the gap decreases, but the P-protonated structure is still clearly favored by 5.3 kcal mol^{-1}.

One question arises immediately: why does the *tert*-butyl substituent destabilize rather than stabilize the C-protonated species? Steric interactions might be at the origin of this effect. Actually, we must remember that C protonation is followed by a C−P bond fission, and as a consequence the *tert*-butyl group attached to the carbon atom which undergoes protonation moves closer to the nearest *tert*-butyl group. This can be verified by looking at some significant interatomic distances. In the neutral TtBuPC as well as in the P-protonated species the average distance between the two closest hydrogen atoms of two neighbor *tert*-butyl groups is 3.0 Å. Similarly, the distance between the two closest carbon atoms is 3.8 Å and the distance between the central carbon atoms of the substituents is 5.1 Å. In the C-protonated species these distances decrease dramatically as far as the aforementioned *tert*-butyl groups are concerned (see Figure 3) and become 2.2, 3.4, and 4.6 Å, respectively. This seems to indicate that the substantial increase in the repulsion between the substituents is what explains the higher stability of the P-protonated system with respect to the C-protonated one.

To ratify this conclusion from an energetic point of view we have performed some model calculations. We have

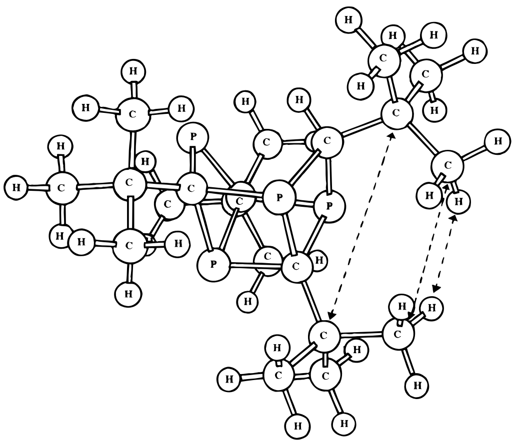

Figure 3. B3-LYP/3-21G* optimized structure of the C-protonated form of TtBuPC. The arrows indicate the nearest hydrogen and carbon atoms as well as the central carbon atoms of the *tert*-butyl substituents which present a stronger repulsive interaction (see text).

Table 4. B3-LYP Calculations on the Protonation of Tri-tBuPC and TMePC (Total Energies in hartrees and Proton Affinities in kcal mol^{-1})

	neutral	protonated[a]	PA[b]
B3-LYP/3-21G*			
Tri-tBuPC		−1982.390 26 (P)	
		−1982.385 03 (C)	
B3-LYP/6-31+G(d)//B3-LYP/3-21G*			
Tri-tBuPC		−1992.285 89 (P)	
		−1992.284 14 (C)	
B3-LYP/3-21G*			
TMePC	−1669.20217	−1669.552 21 (P)	211.7
		−1669.555 43 (C)	218.4
B3-LYP/6-31+G(d)//B3-LYP/3-21G*			
TMePC	−1677.41705	−1677.763 63 (P)	213.7
		−1677.770 76 (C)	218.7

[a] The protonation site is given in parentheses. [b] These values include the thermal corrections evaluated at 333 K.

evaluated the relative stabilities of both P- and C-protonated forms when the *tert*-butyl group which is nearest to that bonded to the protonated carbon is replaced by a H atom (hereafter this trisubstituted derivative will be designated as Tri-tBuPC). This would necessarily alleviate the repulsions while maintaining the possible stabilization effect associated with the *tert*-butyl group which remains attached to the basic carbon. Hence, this should bring the C-protonated species of Tri-tBuPC closer in energy to the P-protonated one. The corresponding results are given in Table 4. In agreement with our expectations, our B3-LYP/6-31+G(d)//B3-LYP/3-21G* results show that the C-protonated species is only about 1 kcal mol^{-1} less stable than the P-protonated one. In summary, these calculations indicate that the unsubstituted parent compound should be a C base, but due to the appearance of strong steric effects, the tetra-*tert*-butyl-substituted derivative behaves as a phosphorus base.

At this point it would be interesting to know what the behavior of the system would be if the substituents were less voluminous. To answer this question we have decided to investigate, at the same level of theory, the intrinsic basicity of the tetramethyl derivative (TMePC) either as a phosphorus or as a carbon base.

The results are presented also in Table 4. The first conspicuous fact is that the C-protonated species is more stable than the P-protonated one. It may be also observed that the energy gap between both structures (4.5 kcal mol^{-1}) is smaller than that estimated, at the same level of theory (11.3 kcal mol^{-1}), for the unsubstituted compound. This reveals that the repulsive interactions between the methyl groups in the C-protonated species play also a significant role, although they are not large enough to reverse the stability order of both species. As was found before, the enlargement of the basis set stabilizes preferentially the C-protonated form.

We have checked whether the cation **1** experimentally generated was stable, to rule out possible "nonclassical" structures like a π complex between isobutene and the remaining protonated base (Tri-tBuPCH$^+$).

The stability of **1** is consistent with a recent experiment of Laali *et al.*[16] in which it is reported that the quaternary salt TtBPCMe$^+$ (the methyl group on one of the P atoms) submitted to high-energy collisionally activated decomposition (CAD) never losses isobutene, due to the fact that endocyclic P−C bonds are broken more easily than exocyclic C−C bonds. Our own experiments (MS/MS) indicate that **1** is an ion of substantial stability with respect to fragmentation

Once the existence of "nonclassical" structures has been ruled out, one may consider that the disagreement between the experimental PA (230.5 kcal mol^{-1}) and the theoretically estimated value (222.5 kcal mol^{-1}) might indicate that higher levels of theory would be necessary. This is not surprising if one takes into account that for other strained compounds containing second row atoms, as is the case for dithiete and dithioglyoxal, the correct stability order of the systems is only attained,[17] at the correlated level, when the basis set includes polarization functions of high angular momentum, *i.e.*, when the basis includes at least *f* functions. Similarly, we have recently shown,[8c] for another strained phosphorus base, as is the case of the P_4 molecule, that its experimental proton affinity can only be correctly reproduced when G2 high-level *ab initio* calculations are carried out. Unfortunately, G2 calculations are prohibitive for molecules of the size of the PC and its derivatives. However, it was also shown[14] that B3-LYP functionals yield proton affinities in fairly good agreement with the G2 and the experimental values, provided a 6-311+G(3df,2p) basis set is used. Accodingly, we have estimated the basicity of the unsubstituted parent compound PC at this level of accuracy, using the corresponding MP2/6-31G** optimized structures for the neutral and its P- and C-protonated species. The results obtained have been included in Table 3.

It may be observed that our previous conclusions do not change at this higher level, in the sense that PC is predicted to be a carbon base, the C-protonated species being 8.6 kcal mol^{-1} more stable than the P-protonated form. However, the use of a G2-type basis set implies a significant stabilization of both protonated species, with an increment of the intinsic basicities of about 5.4 kcal mol^{-1}. This would imply that our estimated value for the PA of the tetra-*tert*-butyl-substituted derivative should increase in the same amount. More especifically, since the PA of PC is 212.8 kcal mol^{-1} the estimated PA of TtBuPC should be 16.2 kcal mol^{-1} higher, *i.e.*, about 229.0 kcal mol^{-1}, and therefore quite close to the experimental value (230.5 kcal mol^{-1}).

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(16) Laali, K. K.; Wesdemiotis, C.; Polce, M.; Berenová, S. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1191.

(17) Jonas, V.; Frenking, G. *Chem. Phys. Lett.* **1991**, *117*, 175.

Concluding Remarks

From the results discussed in preceding sections we can conclude that TtBuPC is a rather strong base in the gas phase, since it was found to be about 26 kcal mol^{-1} more basic than ammonia. From the molecular orbital studies carried out we can also conclude that the unsubstituted parent compound and the tetramethyl substituted derivatives are carbon bases in the gas phase rather than phosphorus bases. Carbon protonation involves a C−P bond fission which results in an enhancement of the basicity of these systems, due to a significant decrease in their strain. However, when the substituents are more bulky than the methyl groups, as it is the case for the *tert*-butyl groups, the C−P bond fission which takes place upon C protonation results in a considerable increase of the repulsive interactions between the substituents, which counterbalances the stability gain due to the loss of strain. The consequence is that the P-protonated form becomes more stable than the C-protonated one. Quite importantly, when only one of the *tert*-butyl substituents is removed this effect decreases dramatically and both C- and P-protonated species are almost degenerate.

Phosphacubane and their protonated species constitute new examples of strained systems whose proper description requires the inclusion of high angular momentum polarization functions in the basis set. Only when the PA of this system is estimated using a quite flexible G2-type basis set is a good agreement with the experimental value attained. Something similar has been recently reported[8c] for the gas-phase protonation of P_4.

In tautomerism studies it is usual to describe two prototropic tautomers by putting the proton on one side or the other of the compound name. Thus we could consider that HPC^+ (protonated on P) and PCH^+ (protonated on C) are two cations in equilibrium (K_T is the tautomeric equilibrium constant) [eq 5]:

$$\begin{tikzcd}
& PC \arrow[dl, "H^+"'] \arrow[dr, "H^+"] & \\
HPC^+ \arrow[rr, shift left, "K_T"'] & & PCH^+ \arrow[ll, shift left]
\end{tikzcd} \qquad (5)$$

According to our calculations (same level), depending on the number and the nature of the substituents on PC, the equilibrium is shifted toward one or the other tautomer: compound HHHH (PC itself) −11.3 kcal mol^{-1}, compound MeMeMeMe (TMePC) −4.5 kcal mol^{-1}, compound HtButButBu (Tri-tBuPC) 1.0 kcal mol^{-1}, and compound tButButButBu (TtBuPC) 5.3 kcal mol^{-1}. Using ΣE_s (E_s being Taft's steric parameter: H 1.24, Me 0.00, tBu −1.54),[18] a linear relationship, eq 6, is obtained between $\Delta H_{(5)}$ and ΣE_s (4.96, 0.00, −4.62, and −6.16):

$$\Delta H_{(5)} = (-4.4 \pm 0.6) - (1.4 \pm 0.1)\sum E_s \qquad n = 4 \quad r^2 = 0.985 \quad (6)$$

The synthesis of the tetramethyl derivative or at least some *tert*-butyl derivative with a smaller number of substituents and the characterization of their basicities in the gas phase would be, according to the previous arguments, of great importance to verify that PC is a strained system which behaves as a carbon or as phosphorus base depending on the existence of steric hyndrance between the substituents.

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