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Are phosphatetrahedrane and diphosphatetrahedrane phosphorus or carbon bases?

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ABSTRACT: The protonation processes of phosphotetrahedrane (PTH) and diphosphatetrahedrane (DPTH) were studied using density functional theory approaches. The geometries of the neutrals and the protonated species were optimized at the B3LYP/6– 31G(d) level and the final energies were obtained using the B3LYP/6– 311+G(3df,2p) level of theory. Both PTH and DPTH are tetrahedral compounds which behave as carbon bases in the gas phase. In contrast with what was found for other phosphorus-containing cage structures such as tetraphosphacubane, the nature of the basic center does not change when the hydrogen atoms are substituted by bulky substituents. This is a consequence of the fact that both phosphorus and carbon protonation processes lead to C—P bond fission, so that the repulsive interactions between the susbtituents are not significantly different in carbon- or phosphorus-protonated structures. Protonation of DPTH at the P—P bond yields a local minimum with a P—H—P linkage similar to that described before for the most stable protonated form of P_4. This seems to indicate that the existence of P—P linkages in strained structures clearly favors the formation of non-classical protonated species where the proton bridges the two phosphorus atoms. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: phosphatetrahedrane; diphosphatetrahedrane; phosphorus bases; carbon bases

INTRODUCTION

One of the most important characteristics of gas-phase ion chemistry is that the behavior of the system is not masked by solute– solvent interactions. Hence the gas-phase reactivity is usually known as the *intrinsic* reactivity of the system.[1–6] On the other hand, fairly often gas-phase ion– molecule reactions lead to *exotic* non-classical structures which would not be stable in solution but which, in the gas phase, are not only stable but are also the global minimum of the potential energy surface (PES). Some of these non-classical structures are associated with systems which present two or more adjacent basic centers,[7–10] favoring the formation of compounds where the attaching ion bridges two or more of the atoms of the neutral species This is actually what happens in the gas-phase reactions between triazoles, tetrazoles[8] and polyazines[9,10] with alkali metal cations. However, the formation of stable bridged structures is not exclusively associated with reactions involving closed-shell metal monocations, where the ion–molecule interactions are essentially electrostatic, but have been found also to be responsible for the enhanced stability of some protonated species, where the interactions are truly covalent. This is indeed the case with the protonated form of P_4 where the global minimum of the PES corresponds to a side-protonated species, where the proton is bonded simultaneously to two neighboring phosphorus atoms.[11]

The absence of interactions with the solvent also implies that the charge redistributions associated with most ion– molecule reactions cannot be dispersed into the network of solvent molecules. This is particularly important in the protonation processes of highly strained systems or in compounds where the active center is a very electronegative atom. Protonation always implies a large charge transfer from the base to the attaching proton which significantly perturbs the charge density distribution of the base.[12,13] This charge redistribution can result in bond fission processes, which are particularly favored when they lead to alleviation of the strain of the system or to the formation of very stable carbocations. The gas-phase protonation of tetraphosphacubane is a suitable example of the first kind of processes.[14] Tetraphosphacubane behaves as a carbon base rather than as a phosphorus base because, in the gas phase, the attachment of a proton to one of the carbon atoms results in the breaking of one of the C—P linkages of the cube, so that the resulting structure has a much smaller strain than the neutral species. The protonation of fluoro- and chloro-adamantane constitutes a clear illustration of the second kind of processes where the attachment of the proton to

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the basic center leads to the fission of the carbon–halogen bond in a typical dissociative proton attachment process,[15] where the products of the reaction are the adamantyl cation and the corresponding hydrogen halide.

The aim of this work was to investigate the protonation of phosphatetrahedrane (PC_3H_3) (PTH) and diphosphatetrahedrane ($P_2C_2H_2$) (DPTH) as highly strained systems which, like tetraphosphacubane (TPC), can behave as carbon or phosphorus bases. There are, however, two main differences with respect to tetraphosphacubane which should be noted: on the one hand, both tetrahedral structures, PTH and DPTH, are more strained than the cubic TCP structure, and on the other hand, whereas in PTH there are only P—C bonds as in TPC, in DPTH there is also a P—P bond which is not present in TPC. It is also worth mentioning that the behavior of TPC changes dramatically with the size of the substituents. The fission of a C—P bond upon carbon protonation results in a large increase in the repulsion between the substituents, in particular when they are very voluminous, and the corresponding protonated species becomes highly destabilized.[14] Hence we have considered it of interest to investigate the influence of bulky substituents also on the intrinsic basicity of PTH by studying the protonation of the trisubstituted *tert*-butyl derivative. Although information on stereo effects on chemical reactivity is not abundant, in a recent study by Ma *et al.*[16] stereoelectronic effects in phosphorus dichloride cation– pyiridine complexes were investigated from both experimental and theoretical viewpoints. For the particular case of DPTH, we shall try to establish whether the existence of two phosphorus atoms in an environment different to that of the P_4 molecule also favors the formation of side-protonated species.

COMPUTATIONAL DETAILS

All the computations were performed using the Gaussian 94 series of programs.[17] In all cases we used the B3LYP density functional approach, which has been proved to perform very well as far as the description of protonation processes is concerned. The exchange functional B3[18] is a hybrid method proposed by Becke that includes a mixture of Slater functional.[19] Becke's 1988 gradient correction[18] and Hartree–Fock exchange. The correlation part, LYP,[20] is the gradient corrected functional of Lee, Yang and Parr. The geometries of the species under investigation were optimized at the B3LYP/6–31G(d) level, except for the *test*-butyl-substituted derivatives, for which the more economic 3– 21G(d) basis set expansion was used. Harmonic vibrational frequencies were evaluated at the same level employed in the geometry optimization, in order to confirm the nature of the stationary points found and to account for the zero point energy *(ZPE)* corrections, which were scaled by the empirical factor 0.98.[21] The final energies of the unsubstituted parent compounds and their protonated forms were calculated with the 6– 311+G(3df,2p) basis set, which has been found to yield protonation energies in fairly good agreement with the experimental values for first- and second-row bases.[22–24]

To investigate the bonding characteristics of the different species, we used the natural bond orbital (NBO) analysis of Reed *et al.*[25] and the atoms in molecules (AIM) theory of Bader.[26] The first formalism provides values for the atomic natural total charges and describes the bonding in terms of the natural hybrids centered on each atom. Using the second approach, we located the bond critical points (bcps), i.e. points where the electron density function, $\rho(\mathbf{r})$, is minimum along the bond path and maximum in the other two directions. The Laplacian of the density, $\nabla^2\rho(\mathbf{r})$, as has been shown in the literature,[26] identifies regions of the space wherein the electronic charge is locally depleted ($\nabla^2\rho > 0$) or built up ($\nabla^2\rho < 0$). The former situation is typically associated with interactions between closed-shell systems (ionic bonds, hydrogen bonds and van der Waals molecules), whereas the latter characterizes covalent bonds, where the electron density concentrates in the internuclear region. There are, however, significant exceptions to this general rule, mainly when high electronegative atoms are involved in the bonding. Hence we also evaluated the energy density, $H(\mathbf{r})$, which does not present these exceptions.[27] In general, negative values of $H(\mathbf{r})$ are associated with a stabilizing charge concentration within the bonding region. The AIM analysis was performed using the AIMPAC series of programs.[28]

RESULTS AND DISCUSSION

For both PTH and DPTH we considered not only the tetrahedral structures, **1** and **2,** but also the possible bicyclic open structures, **1a** and **2a** and **b** (Fig. 1). For the corresponding protonated species all possibilities were investigated. The optimized geometries are shown schematically in Fig. 1 and the total energies are given in Table 1.

The first conspicuous fact in Table 1 is that for both neutrals, PTH and DPTH, the most stable structure corresponds to a tetrahedral arrangement of the atoms of the system, so that, for the particular case of PTH, the global minimum **1** has C_{3v} symmetry, whereas the four-membered ring structure **1a** lies 8.5 kcal mol^{-1} (1 kcal = 4.184 kJ) higher in energy. For the particular case of DPTH, two possible open structures can be envisaged, one having a C—C bond (**2a**) and the other a P—P bond (**2b**). As mentioned above, both are less stable than the tetrahedral structure **2,** and they are predicted to lie 29.7 and 24.8 kcal mol^{-1}, respectively, above the global minimum (Table 1).

As far as the protonated species are concerned, the

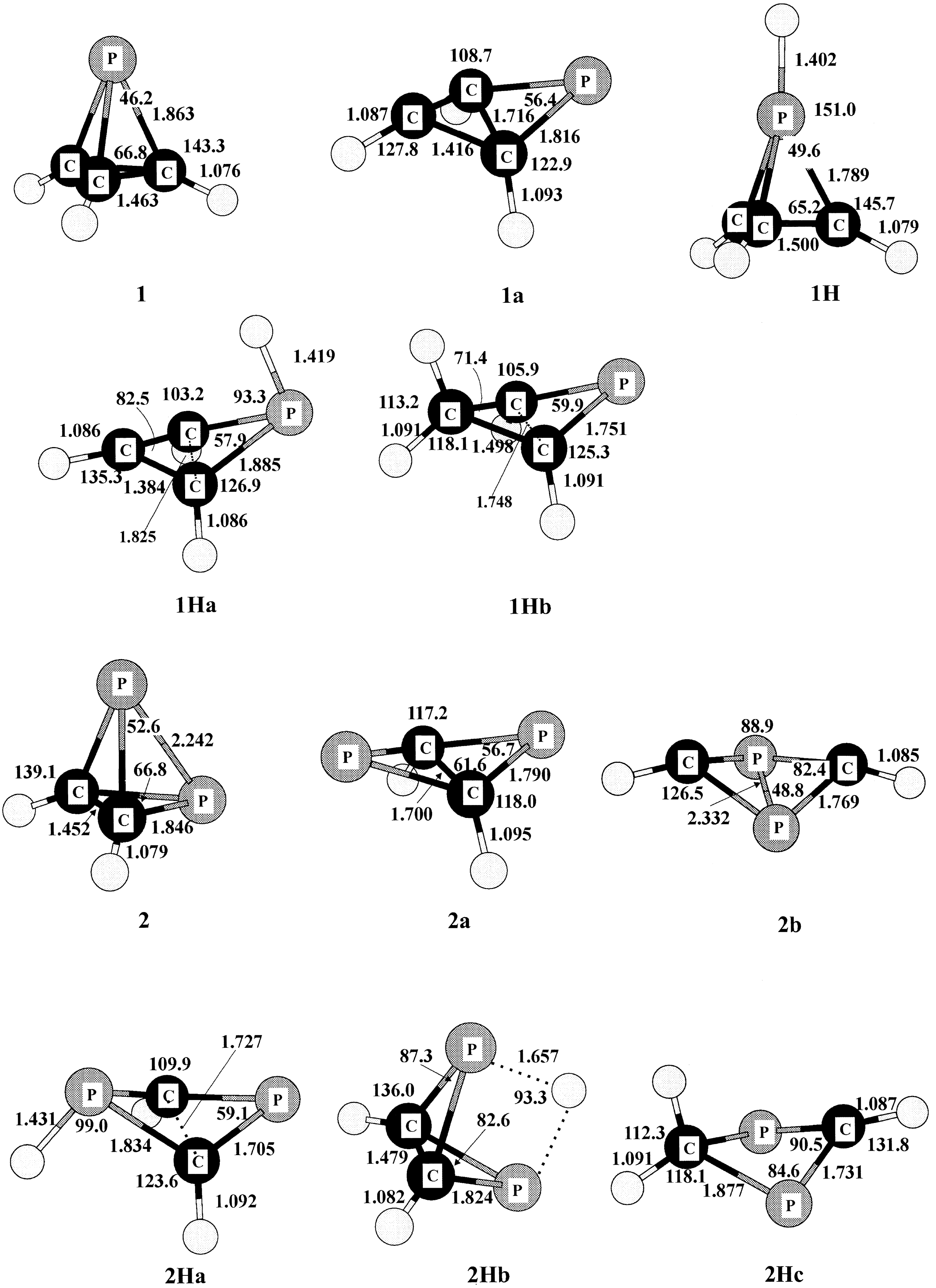

Figure 1. B3LYP/6–31G(d) optimized geometries. Bond lengths in Å and bond angles in degrees. The bond path angles for compound **1** are CPC = 72.1° and CCC = 78.9° and for compound **2** PPC = 72.2° and PCC = 80.7°

Table 1. Total energies (*E*, hartree), zero point energies (*ZPE*, hartree), relative energies (ΔE, kcal mol^{-1}) and proton affinities (*PA*, kcal mol^{-1})

	B3LYP/6–31G(d)					B3LYP/6–311+G(3df,2p)	
Species	*E*	*ZPE*	ΔE	*PA*	*E*	ΔE	*PA*
1	−457.33782	0.046313	0.0	221.4	−457.41216	0.0	217.5
1a	−457.32444	0.046497	8.5		−457.39617	10.1	
1H	−457.58747	0.052426	68.5				
1Ha	−457.68733	0.056909	8.6		−457.75634	8.0	
1Hb	−457.70398	0.059870	0.0		−457.77202	0.0	
2	−760.03632	0.032725	0.0	206.7	−760.12947	0.0	205.6
2a	−759.97960	0.032107	35.2		−760.08153	29.7	
2b	−759.98362	0.030650	32.0		−760.98796	24.8	
2Ha	−760.34440	0.041561	18.8		−760.43611	18.6	
2Hb	−760.34267	0.040338	19.1		−760.44119	14.7	
2Hc	−760.37771	0.044946	0.0		−760.46913	0.0	
3	−924.30290[a]	0.387058		247.5[a]			
3Ha	−924.69529[a]	0.397442	7.7[a]				
3Hb	−924.71038[a]	0.400344	0.0				

[a] Values obtained at the B3LYP/3–21G* level.

situation is very different from that described above for the neutral systems. Protonation of **1** along the C_3 symmetry axis yields a stationary point of the potential energy surface, namely **1H,** which is not a minimum but a saddle point of second order. Actually, the two imaginary frequencies (350i cm^{-1}) associated with a doubly degenerate e-type vibration, correspond to the bending of the P—H bond. When this symmetry constraint is removed, protonation at the phosphorus atom leads to the open structure **1Ha,** where one of the P—C bonds has been broken. A similar bond fission occurs when the protonation takes place at one of the carbon atoms, the resulting open structure **1Hb** being the global minimum. Hence we may conclude that, as has been found before for TPC,[14] PTH is a carbon base in the gas phase.

There are, however, important differences between TPC and PTH in the sense that in the former the phoshorus-protonated species still retains a cubic structure.[14] Actually, one might expect carbon protonation to lead to C—P bond fission, since the carbon atom cannot yield pentacoordinated species. However, tetracoordinated structures are possible when protonation takes place at the phosphorus atom, which has a lone pair of electrons which can interact with the proton. The fact that phosphorus attachment results in C—P bond fission in the case of PTH simply reflects the large strain of this system, which is clearly illustrated by the large difference between bond path angles and geometric angles (Fig. 1). In this respect, it is also worth noting that, in both protonated systems the opening of the tetrahedral structure involves also the fission of one of the carbon–carbon bonds.

In summary, although in TPC the higher stability of the carbon protonated species is partially due to an alleviation of the strain of the system, in PTH this is not the case since both protonated species are open structures. In order to understand the origin of the enhanced stability of the carbon protonated form **1Hb** with respect to the phosphorus-protonated form **1Ha,** we analyzed their electronic structures. In Table 2 we summarize the natural atomic charges and the bonding characteristics of both systems in terms of the charge densities and the energy densities at the bond critical points.

Let us consider first the phosphorus protonation mechanism. In the first step there is a strong charge transfer from the phosphorus lone pair to the proton, which enhances the electronegativity of the former. As a consequence, the basic center recovers part of this charge by depopulating the P—C bond, which dissociates. As mentioned above, the opening of the cage involves a simultaneous C—C bond fission. This leaves the system with three tricoordinated carbon atoms with one *p*-orbital not involved in the σ-bonding. These three orbitals combine to yield three π-MOs, two of which are doubly occupied. The obvious consequence is that in the phosphorus-protonated species the three-membered ring moiety formed by the three CH groups is significantly stabilized by resonance. Consistently, the charge density at the corresponding bcps noticeably increases, the energy density of which becomes more negative and the C—C bonds become considerably shorter.

The protonation at the carbon atom in **1** is also followed by C—P and C—C bond fissions, because the corresponding C—C bonding pair is necessarily involved in the formation of the new C—H covalent bond. This would leave the phosphorus atom with a formal positive charge, as it is indeed the case (Table 2). However, as we have already mentioned, the opening of the cage structure involves also the dissociation of one C—C bond. This favors the interaction between the carbon mono-occupied *p*-orbitals with the P lone pair, forming again a set of three π-MOs, two of which are doubly occupied. Again

Table 2. Charge density [ρ,arbitrary units (au)], Laplacian of the charge density ($\nabla^2\rho$, au) and energy density [$H(\mathbf{r})$,au] evaluated at the bond critical points and atomic natural charges

	Bonding characteristics											
	P— C			C— C			P— P			Atomic natural charges		
System	ρ	$\nabla^2\rho$	$H(\mathbf{r})$	ρ	$\nabla^2\rho$	$H(\mathbf{r})$	ρ	$\nabla^2\rho$	$H(\mathbf{r})$	P	C-1[a]	C-2[b]
1	0.130	−0.100	−0.112	0.258	−0.450	−0.225	—	—	—	+0.538	−0.446	—
1Ha	0.135	−0.037	−0.120	0.315	−0.830	−0.325	—	—	—	+0.724	−0.286	−0.101
1Hb	0.165	0.224[f]	−0.151	0.247	−0.515	−0.211	—	—	—	+1.068	−0.418	−0.468
2	0.138	−0.062	−0.123	0.272	−0.562	−0.248	0.091	−0.025	−0.040	+0.454	−0.730	—
2Ha	0.143[c]	−0.006[c]	−0.129[c]	—	—	—	—	—	—	+0.849	−0.792	—
	0.162	0.224[f]	−0.146							+1.091		
2Hb	0.149	−0.116	−0.142	0.257	−0.483	−0.225	0.098[e]	−0.091[e]	−0.050[e]	+0.960	−0.767	—
2Hc	0.149[d]	−0.234[d]	−0.140[d]	—	—	—	—	—	—	+1.046	−1.000	—
	0.171	0.216[f]	−0.157									

[a] C-1 designates the carbon atom bonded to the phosphorus atom
[b] C-2 designates the carbon atom non-bonded to the phosphorus atom
[c] These sets of values correspond to the bonds involving the non-protonated (first set) and the protonated (second set) phosphorus atom.
[d] These sets of values correspond to the bonds involving the protonated (first set) and the non-protonated (second set) carbon atom.
[e] These values correspond to the P— H linkages which replace the P—P bond of the neutral (see text)
[f] These constitute typical examples of covalent linkages with positive values of the Laplacian. In all cases, however, the energy density, $H(\mathbf{r})$, is negative, indicating a stabilizing charge concentration, typically associated with covalent linkages.

this π-delocalization is reflected in an increase in the charge densities at the C—P bcps, while the energy densities become more negative and the bond lengths shorter. Hence, in the carbon-protonated species the three-membered ring moiety formed by the P atom and the two CH groups is also stabilized by resonance. We can then conclude that similar resonance stabilizations take place in both cases, so that, at least on qualitative grounds, both phosphorus- and carbon-protonated species should be equally stable. It must be noted, however, that there is another factor that contributes to stabilizing more the carbon protonated species. According to our previous arguments, on going from species **1Ha** to **1Hb** we replace a charge delocalization within the CH—CH—P subsystem, by a similar delocalization within the $(CH)_3$ subunit, but we also replace a P— H linkage by a C—H bond, which is more stable. In fact, whereas the typical dissociation energy of the C—H bond is 79.9 kcal mol^{-1},[29] the dissociation energy of a P—H bond is about 8 kcal mol^{-1} lower,[30] and this can be responsible for the observed enhanced stability of species **1Hb.**

It can also be noticed that the substitution of the hydrogen atoms by bulky substituents does not change this situation and the tri-*tert*-butyl-substituted derivative of PTH (**3**) is predicted also to be a carbon base in the gas phase since, as indicated in Table 1, the carbon-protonated species (**3Hb**) is predicted to be 7.7 kcal mol^{-1} more stable than the phosphorus-protonated species (**3Ha**). This is in contrast with what was found for TPC,[14] because in this system only the carbon protonation process is followed by an opening of the cage, leading to a large increase in the repulsion between the substituents. For the particular case of PTH, the repulsive interactions between the substituents are not significantly different in the phosphorus- and the carbon-protonated forms, since both of them are open structures.

Protonation of DPTH **2** yields three different molecular ions. As has been found for PTH, also in this case the protonation at the phosphorus atom results in C—P bond fission, which yields structure **2Ha.** Importantly, the protonation of the P—P bond yields a local minimum of the potential energy surface, **2Hb,** which at the higher level of theory employed in this study is predicted to be *ca* 4 kcal mol^{-1} more stable than the phosphorus-protonated form. This seems to confirm that the existence of P—P linkages favors the formation of non-classical protonated structures, where the proton bridges the two basic centers. As has been found previously[11] for the protonation of P_4, in species **2Hb** the initial P—P bond of the neutral was replaced by two covalent P—H linkages. This is ratified by the fact that a topological analysis of the electron charge density of **2Hb** shows the existence of bcps within the P—H bonding regions whereas no bcp is found between the two phosphorus atoms. One must then conclude that in species **2Hb** a three-centered bonding molecular orbital is formed by the constructive interaction between the *s*-orbital of the hydrogen atom and the *p*-orbitals of the two phosphorus atoms. This MO is occupied by the electron pair which in the neutral was associated with the P—P linkage.

According to the results shown in Table 1, the global minimum is once more the carbon protonated species **2Hc.** It is important to note that in this case the energy gaps between the global minimum and the other minima is almost twice that estimated for PTH. This can be explained if one takes into account that in species **2Hc** the protonated carbon atom is directly attached to two phosphorus atoms, whereas in species **1Hb** it is bonded to two CH groups. Hence the positive charge is better stabilized in the former case, because phosphorus atoms are less electronegative and more polarizable than carbon atoms.

CONCLUSIONS

Both PTH and DPTH behave as carbon bases in the gas phase. In contrast with what was found[14] for phosphorus-containing cage structures such as TPC, the nature of the basic center does not change when the hydrogen atoms are substituted by bulky substituents such as *tert*-butyl groups. This is a consequence of the fact that both phosphorus and carbon protonation processes lead to C—P bond fission, so that the repulsive interactions between the susbtituents are not significantly different in carbon- or phosphorus-protonated structures.

Protonation of DPTH at the P—P bond yields a local minimum with a P—H—P linkage similar to that described before[11] for the most stable protonated form of P_4. This seems to indicate that the existence of P—P linkages in strained structures clearly favors the formation of non-classical protonated species where the proton bridges the two phosphorus atoms. However, this local minimum lies 14.7 kcal mol^{-1} above the corresponding carbon-protonated species.

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