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A New Bond from an Old Molecule: Formation, Stability, and Structure of P_4H^+

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Abstract: The hitherto unknown gas-phase basicity of the tetraphosphorus molecule, P_4, has been determined by means of Fourier transform ion cyclotron resonance mass spectrometry using proton transfer equilibrium techniques. A quantum mechanical treatment of P_4 and P_4H^+ in the framework of the G2 level of theory leads to a proton affinity agreeing nicely with the experimental value and, most important, reveals the existence of a novel kind of chemical bond in P_4H^+: the symmetrical and essentially covalent (P···H···P) linkage.

Introduction

Our laboratories are currently involved in a joint systematic study of the gas-phase basicities, GB, of less common species,[1] one of our main goals being the discovery of new reactions and chemical bonds.[1a,c] In this respect, the molecule P_4 is appealing because of (i) the complete lack of quantitative basicity data for P_4, both in the gas phase and in solution, (ii) the fact that, to the best of our knowledge, neither theoretical nor experimental studies have been reported on the structure and vibrational frequencies of P_4H^+ while a wealth of information is available on P_4,[2−11] and (iii) the predictable competition between corner- and side-protonations, respectively, favored by the presence of the electron lone pairs and the relief of internal strain.

Experimental Section

The gas-phase basicity of P_4, GB(P_4) is formally defined as the standard Gibbs energy change for reaction 1, the corresponding proton affinity, PA (P_4) being the standard enthalpy change for the same reaction

$$P_4H^+(g) \rightarrow P_4(g) + H^+(g) \qquad (1)$$

In what follows, all basicities are referred to that of ammonia (GB(NH_3) = 819.2 kJ/Mol, according to the most recent experimental determination[12]), as defined in reaction 2

$$P_4H^+(g) + NH_3(g) \rightleftarrows NH_4^+(g) + P_4(g) \quad \Delta GB(P_4) \qquad (2)$$

The equilibrium constants K_p for the proton exchange between P_4(g) and a series of reference bases B_{ref}, reaction 3

$$P_4H^+(g) + B_{ref}(g) \rightleftarrows P_4(g) + B_{ref}H^+(g) \quad K_p \qquad (3)$$

were determined in a modified Bruker CMS-47 FTICR mass spectrometer[13] used in previous studies.[1,14]

A detailed description of the main features of this instrument is given in ref 12. Here we mention that the substantial field strength of its superconducting magnet, 4.7 T allows the monitoring of ion−molecule reactions for relatively long periods of time.

With respect to the standard instrument,[13] the main modifications are as follows.

1. The insertion of a Balzers BVB063H butterfly valve between the high vacuum turbomolecular pump and the section containing the ion-trapping cell and the head of the Bayard−Alpert ionization gauge. This allows the efficient reduction of the gas flow, thus minimizing the pressure gradient between the cell and the ionization gauge.
2. The insertion, in the same section of the vacuum system and close to the head of the ionization gauge, of an MKS capacitance manometer.
3. The installation in the foreline of a 40 l/s Balzers DIF 040W diffusion pump (lower pressure limit $\approx 10^{-7}$ mbar) for the purpose of thoroughly degassing the samples.

As in our previous studies[1a,b,14] equilibrium constants K_p for reaction 3 were determined by means of an experimental technique based on that used in Prof. Taft's laboratory.[15,16] Briefly stated, mixtures of B_{ref}(g) and P_4(g) of known partial pressures (total pressures generally in the range 5×10^{-7}−3×10^{-6} mbar) were ionized by electron impact (nominal ionization energies in the range 12−14 eV). P_4H^+(g) and

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$B_{ref}H^+$(g) were generated by chemical ionization, the proton sources being the ionic fragments of B_{ref} except in the case of Cl_2CS, where water was used for this purpose. These ionic fragments were deprotonated in 2−3 s, the system being monitored for an extra 10−15 s. A constant ratio of the ion intensities was reached after ca. 5 s and remained constant until the end of the experiment. During the first few seconds, samplings were carried out every 0.2−0.3 s and, afterwards, every 0.5 s.

The fact that the constant ratio of the ion intensities corresponds to the attainment of equilibrium (3) was proven by means of the following double-resonance-like experiments: 2−3 s after ionization, one of the ions, for instance P_4H^+ was isolated by ejecting all other ions by means of radiofrequency "chirps" (broad band). A "safety belt" (an option of the Bruker software that strictly prevents the irradiation of a preselected frequency range around the frequency of the selected ion) was applied around the resonance frequency of P_4H^+ in order to avoid its accidental excitation. The system was then allowed to evolve. The signal of $B_{ref}H^+$ appeared, grew up, and leveled off after 5−10 s, the ratio of the ion intensities ($P_4H^+/B_{ref}H^+$) remaining constant henceforth. The ratio was found to agree very satisfactorily with the ratio obtained without ion ejection. The same method was applied to $B_{ref}H^+$, the outcome of the experiment being the same.

Equilibrium constants, K_p, defined through eq 3a were obtained by combining

$$K_P = [P(P_4)/P(B_{ref})]\cdot[P(B_{ref}H^+)/P(P_4H^+)] \qquad (3a)$$

the ratio of the intensities of $B_{ref}H^+$ to P_4H^+ (taken as a measure of the ratio of the partial pressures of these ions) with the ratio of the partial pressures of the neutral reagents.

The corresponding values of the latter, as determined by the Bayard−Alpert gauge, were corrected by means of the appropriate calibration coefficients obtained for each and every reagent by plotting the readings of the ion gauge against the absolute pressures provided by the capacitance manometer. Routinely, three calibration runs were performed on each reagent.

Because of the high accuracy of the ratios of ion intensities it provides, the McIver−Gaumann[13,17] fast sweep/cross-correlation method was used, as in our previous studies.[1a,14]

Extreme caution was exercised when handling the samples of yellow phosphorous.

Experimental Results

For each reference base, $\Delta GB(P_4)$ is obtained through eq 4

$$\Delta GB(P_4) = \Delta GB(B_{ref}) + \delta\Delta G_{H^+} \qquad (4)$$

wherein

$$\delta\Delta G_{H^+} = -RT \ln K_P$$

The experimental results are summarized in Table 1. Whenever possible, and for the sake of maximal self-consistency, GB(B_{ref}) values were from Prof. Taft's laboratory (also reported in ref 16). Each equilibrium constant is the average of at least six runs at different total pressures. Also, the ratios of the pressures were varied as widely as possible.

In this work, we can formally estimate the uncertainties on K_p values at ca. 20%, part of it originating in the reproducibility (15%) and the rest in the experimental correction of the ion gauge data. This amounts to 0.5 kJ/mol[18] in Gibbs energy. This does not take into account the uncertainty on $\Delta GB(B_{ref})$ for each of the reference bases. Because of the multiple overlap method used to link GB values,[16] these uncertainties are generally fairly small, mostly in the range 0.5−1.0 kJ/mol. A reasonable estimate of the uncertainty on each $\Delta GB(P_4)$ is thus 1.0−1.5 kJ/mol. Slightly higher values can be expected when using $\Delta GB(B_{ref})$ values originating in different laboratories, as we have done here. In this work, the most important source of uncertainty seems to be the adsorption of some of reagents onto the inner surface of the high vacuum section, this phenomenon being most noteworthy in the case of thiophosgene.

Table 1. Experimental Results Pertaining to the Determination of $\Delta GB(P_4)^{a,e}$

refs	$\Delta GB(B_{ref})$	$\delta\Delta G_{H}{}^+(g)$	$\Delta GB(P_4)$	$\Delta GB(P_4)$(av)
CCl_3CH_2OH	108.8[b]	−9.37	99.43	98.6 (sd = 1.8)
$CF_3CO_2CH_3$	99.6[c]	0.08	99.68	
Cl_2CS	92.9[d]	3.43	96.33	
c-C_3H_6	91.2[c]	5.77	96.97	
C_6H_5Cl	90.4[c]	10.00	100.40	

[a] Values of $\delta\Delta G_H{}^+$(g) and $\Delta GB(P_4)$ (both related through eq 4) are given with two decimal figures in order to avoid round-off errors. $\Delta GB(P_4)$ is the gas phase basicity of P_4 relative to ammonia. [b] Measured in this work: found to be 9.20 kJ/mol less basic than $CF_3CO_2CH_3$ (ΔGB = 99.6 kJ/mol) and 6.28 kJ/mol more basic than CCl_3CN (ΔGB = 115.1 kJ/mol). [c] From ref 16. [d] From ref 1a. [e] All values in kJ/mol.

From the data given above, an average value of 98.6 kJ/mol is obtained for $\Delta GB(P_4)$, the standard deviation being 1.8 kJ/mol. According to the IUPAC criterion,[19−21] the latter measures the precision of $\Delta GB(P_4)$. The accuracy of the $\Delta GB(P_4)$ value at the 95% level can be estimated at ±2.1 kJ/mol.[22,23] Combining this results with the experimental value of GB(NH_3) and the entropy change for reaction 1 of 94.1 J mol^{-1} K^{-1} computed at the MP2/6-31+G(d,p) level, we obtain a proton affinity of 748.6 ± 2.1 kJ/mol for P_4.

Computational Techniques

Ab initio molecular orbital calculations were performed using the Gaussian-90 and Gaussian-92 series of programs.[24,25] The geometries of P_4 and of the different protonated species were fully optimized at the MP2/6-31G(d,p) level of theory.

The harmonic vibrational frequencies were calculated using analytical second derivative techniques in order to check whether the optimized structures are minima or saddle points on the potential energy surface and to evaluate the corresponding zero

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(22) Accuracy "relates to the difference between a result (or mean) and the true value".[23] At the 95% significance level this difference can be estimated at 2.1 kJ/mol and is given by $t_4{}^{0.05}$ $(1.8/\sqrt{5})$ kJ/mol wherein $t_4{}^{0.05}$ is the value of the Student t for four degrees of freedom and a 95% level of significance; 1.8 is the standard deviation and 5 originates in the number of experimental values being averaged. See ref 19.

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point energies (ZPE), which were scaled by the empirical factor 0.93.[26]

For the neutral species as well as for the most stable protonated form these geometries were refined at the MP2/6-31+G(d,p) level, which has been shown to be more reliable,[27] in particular when the description of protonated species is intended. For these two systems the harmonic vibrational frequencies were also recalculated at the MP2/6-31+G(d,p) level.

As we shall discuss in forthcoming sections, the most stable protonated form of P_4 corresponds to a nonclassical structure. Hence, we have considered it important to have as reliable energetics as possible as well as a reliable estimation of the intrinsic basicity of P_4 to be compared with the corresponding experimental value reported in this work. For this purpose, the total energies of the neutral and the most stable protonated species, were obtained in the framework of G2 theory,[28] which has been demonstrated[28−30] to yield ionization energies, atomization energies, proton affinities, and heats of formation in agreement with the experimental values within ±0.1 eV. G2 theory[28] is a composite procedure based on Møller−Plesset perturbation theory at second and fourth orders (MP2 and MP4) and on quadratic configuration interaction theory including single, double, and triple excitations (QCISD(T)). In the G2 procedure a total energy effectively of QCISD(T)/6-311+G-(3df,2p) quality is obtained by assuming additivity of different basis set enhancements at the MP4 level and additivity of basis set and correlation effects between MP4 and QCISD(T). It should be noted, however, that the G2 scheme is based in MP2/6-31G(d) optimized structures and that the ZPE corrections are evaluated at the HF/6-31G(d) level of theory, while in the present study, both geometries and ZPE corrections were obtained, as mentioned above, at the MP2/6-31+G(d,p) level. In what follows this approach shall be designed G2+.

Since proton affinities are generally measured at 298 K, we have included in our estimates the corresponding thermal corrections. These thermal corrections include $^1/_2RT$ for each translational and rotational degree of freedom, plus changes in the vibrational energy due to thermal population of the excited vibrational modes.

The nature of the bonding in the nonclassical protonated species **2** was investigated by means of a topological analysis of the electronic charge density, ρ, and its Laplacian, $\nabla^2\rho$. As has been shown by Bader and co-workers,[31−33] $\nabla^2\rho$ identifies regions of space where 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), while the latter characterizes covalent bonds, where the electronic charge concentrates between the nuclei. Here, the location of the bond critical points (bcp) is particularly important, since it has been shown that the existence of a bond critical point between two atomic basins indicates the existence of a bond. Furthermore, the value of the charge density at the bcp is a relative measure of the strength of the corresponding linkage. The bond critical points correspond to stationary points of the electronic charge density where $\rho(\mathbf{r})$ is minimum along the bond path and maximum in the other two directions.

Table 2. Harmonic Vibrational Frequencies (cm^{-1}) of P_4 and its Side-Protonated Species[b]

P_4		
calcd	exptl[a]	P_4H^+ (**2**)
		1719 P−H−P *s*-stretching
		767 P−H−P *a*-stretching
		755 H bending out of the P−H−P plane
625 (a_1)	600.51	606
471 (t_2)	466.925	496
		452
		446
362 (*e*)	360.813	377
		368

[a] Values taken from ref 11. [b] Values obtained at the MP2/6-31+G(d,p) level.

This topological analysis was carried out on MP2 densities evaluated at the 6-31+G(d,p) level, in order to explicitly account for electronic correlation effects. For this purpose we have used the AIMPAC series of programs.[34]

Geometries and Relative Stabilities

The P_4 molecule is known to possess tetrahedral symmetry. The MP2/6-31+G(d,p) optimized bond length (2.199 Å) is very close to previously computed values[7,9,10] and to the experimental value (2.21 Å).[35] It must be mentioned, however, that the harmonic vibrational frequencies evaluated at this level of accuracy (see Table 2) are in better agreement with the experimental values[2,3,8,11] than previous calculations at the MP2/6-31G(d,p) level,[9] thus confirming the reliability of the MP2/6-31+G(d,p) scheme. This is also corroborated by the fact that the corresponding rotational constant (3367 MHz) is only 2% greater than the experimental value.[8]

The first protonated species investigated (**1**) was obviously the one corresponding to the protonation along the C_3 axis of the neutral molecule. However, this species yields a proton affinity substantially smaller than the experimental value determined in our FTICR study. This initial disagreement prompted us to investigate alternative conformations for the protonated species (see Figure 1). In particular, we have considered two subsets of protonated systems, those which retain the tetrahedral structure of the neutral and those wherein one or several P−P linkages are broken. In the first set there are only three possibilities, the corner protonated species (**1**), the side protonated form (**2**), and the face protonated one (**3**). Species **4**, **5**, and **8** are the result of a single bond fission, while in species **6** and **7**, more than one P−P bond is broken. This survey of the P_4H^+ potential energy surface shows that the side protonated species is the global minimum. As shown in Table 3, the global minimum lies some 45 kJ/mol below the corner protonated one (**1**) and about 58 kJ/mol below species **4**. It is worth noting that species **4**, where one P−P bond has been broken, is only 17 kJ/mol less stable than the corner protonated species **1**, where all P−P bonds remain intact. This reflects a significant relief of the strain of the system, which is not sufficient, however, to compensate the energetic cost associated

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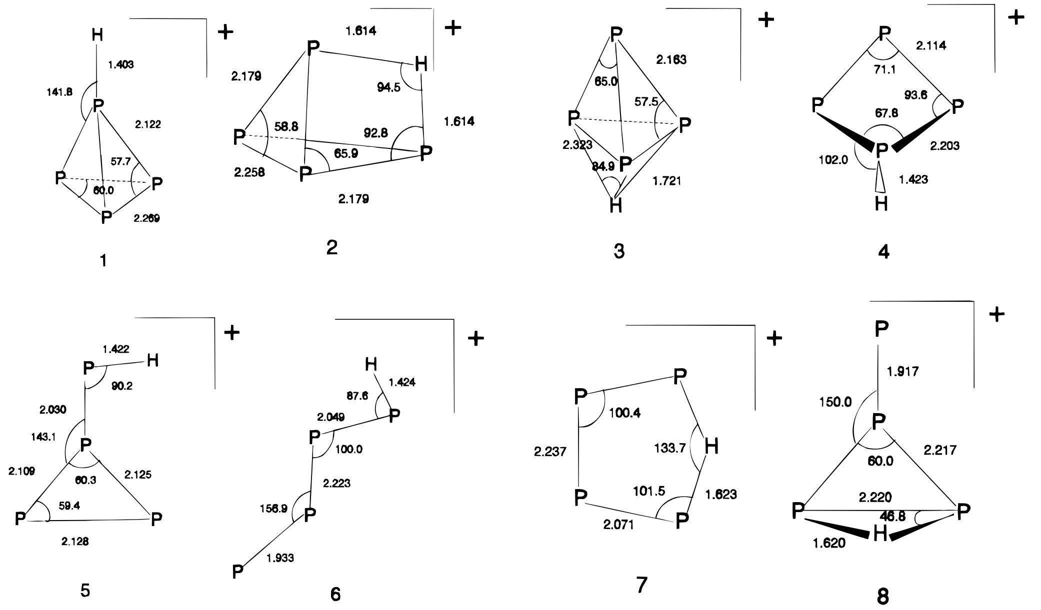

Figure 1. MP2/6-31G(d,p) optimized structures of the protonated species of P_4. Bond lengths in Å and bond angles in deg. The geometry of species **2** was obtained at the MP2/6-31+G(d,p) level.

with the P−P bond fission. As we show below, the situation is different for the side protonated species **2**, where one P−P bond is replaced by two P−H linkages.This leads to a significant stabilization of the system. The remaining protonated forms are much less stable. It must be mentioned that the face protonated species (**3**) is not a minimum but a transition state on the potential energy surface. Actually, it was found that when the proton is not forced to be along the C_3 symmetry axis of the system, this structure collapses, without activation barrier, to the global minimum (**2**). Similarly, species **7** is found to be a saddle point (with two imaginary frequencies) on the PES. If the symmetry constraints are eliminated, the structure evolves to yield species **6**.

Proton Affinity and Bonding Characteristics

In order to establish that the experimentally observed P_4H^+ cation corresponds to the nonclassical side-protonated species **2**, we have built up a theoretical basicity scale based on G2 calculations. For this purpose, a set of 12 standard bases, namely, HCl, CH_4, CS_2, H_2S, C_3H_6, MeOH, H_2CS, Me_2O, PH_3, Me_2S, NH_3, and Me_2NH, was chosen.The corresponding G2 proton affinities at 298 K were taken from ref 36, while the experimental values were taken from ref 15, as were the GB-(B_{ref}) used in this work. In order to achieve an optimal level of statistical reliability[37] this scale spans a very wide range of basicities (ca. 400 kJ/mol) and is centered at 737 kJ/mol, very close to the G2 computed value. Of the 12 experimental values, six are for molecules in which the basic center is a second row atom.

When the theoretical values are plotted against the corresponding experimental results, an excellent linear relationship is obtained (Figure 2), the correlation equation being (5):

$$PA(G2) = -19.2\ (sd = 6.1) + 1.0172\ (sd = 0.0081)\ PA\ (exp) \quad (5)$$

$$\text{in kJ/mol},\ n = 12,\ sd = 3.0\ \text{kJ/mol},\ R = 0.9997$$

The experimental and calculated PAs for cyclopropane, fall nicely on the line defined by eq 5. This suggests that the G2 method performs quite satisfactorily even in the case of significantly strained species.

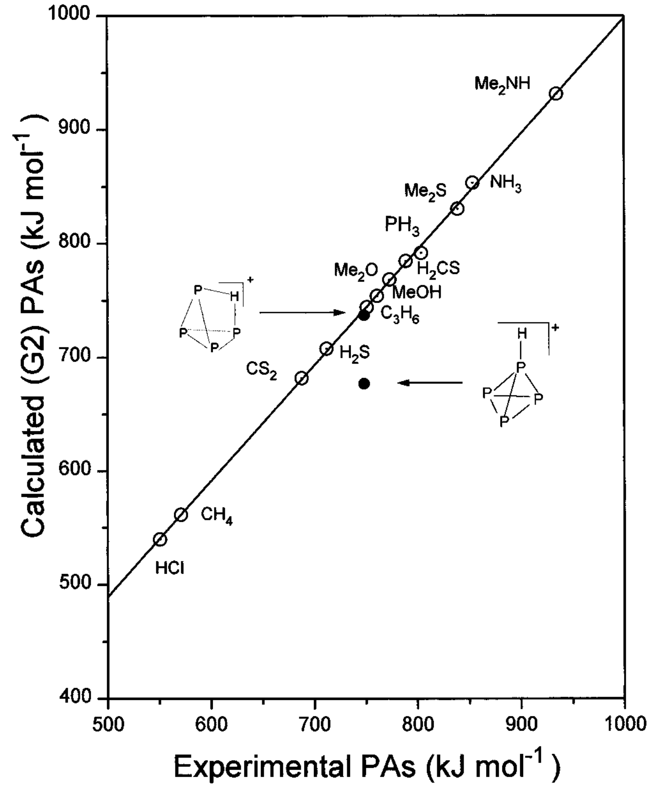

Figure 2. Linear correlation between G2 calculated proton affinities and experimental values which illustrates that the P_4H^+ species corresponds to a side-protonated structure.

The computed PA values at the G2 and G2+ levels for structure **2** are practically indistinguishable. The G2 value is equal to 736.9 kJ/mol. Using the experimental value of 748.6 ± 2.2 kJ/mol, eq 5 predicts a G2 value of PA (P_4) of 742.2 ± 7.9 kJ/mol at the 95% significance level.[37] The computed PA for structure **2** is seen to fall well within these limits. The computed (G2 and G2+) proton affinities for **1** are also extremely close. The G2 value, 676.5 kJ/mol, is 60.4 kJ/mol smaller than that for structure **2**. *The difference from the*

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Table 3. MP2/6-31G(d,p) Total Energies (E, in hartrees) and Relative Energies (ΔE in kJ/mol) of the Protonated Forms of P_4

protonated species	E	ΔE^a
1	−1363.63405	45.2
	−1363.97537^b	60.4^b
	−1363.97541^c	61.9^c
2	−1363.65124	0.0
	−1363.99836^b	
	−1363.99901^c	
3	−1363.61395	87.4
4	−1363.62978	57.7
5	−1363.61242	101.7
6	−1363.60138	128.9
7	−1363.53793	289.5
8	−1363.49714	399.6

[a] These values include the corresponding ZPE correction. [b] G2 values. The G2 total energy for the neutral species is −1363.71962 hartrees. [c] G2+ values. The G2+ total energy for the neutral species is −1363.72013 hartrees.

expected value (742.2 kJ/mol) is 65.6 kJ/mol and hence so large that structure ***1*** *can be rejected well beyond the 99.9% level of significance (the range of acceptable values at this level is 725.7−758.7 kJ/mol).*

It is worth noting that the computed stability of structure **2** with respect to structure **1** is considerably (ca. 15 kJ/mol) enhanced at both the G2 and G2+ levels with respect to the MP2/6-31G(d,p) values (see Table 3). This seems to indicate that these species are sensitive to higher order correlation corrections, possibly as a consequence of their compactness and to the bridged structure of **2**.

In **2**, the global minimum, the incoming proton is located symmetrically between the two phosphorus atoms, which raises interesting questions about the nature of the bonding. To gain some insight into this problem, as we have indicated in previous sections, we have carried out a topological analysis[31−33] of the electronic charge density, $\rho(\mathbf{r})$, of this species and its Laplacian, $\nabla^2\rho(\mathbf{r})$. Only five P−P bond critical points were found for the P_4H^+ species, while the sixth one (that corresponding to the two protonated phosphorus atoms) is replaced by two P−H bond critical points. However, the most significant result is that these P−H bond critical points have electron densities (0.11 e.au^{-3}) of the same order found in typical P−H covalent linkages (~0.15 e.au^{-3}). Furthermore, as illustrated in Figure 3, the Laplacian of the charge density, evaluated in the plane defined by the P−H−P fragment, is negative between the proton and both phosphorus atoms. This reflects a typical covalent interaction, where the electronic charge is concentrated in the interatomic region. In contrast, the Laplacian between both phosphorus atoms is positive, as a result of the depletion of bonding charge density within that region. In other words the initial P−P bond has been replaced by a three-center delocalized bond. This picture is also confirmed by a natural bond orbital analysis[38,39] which shows that the positive charge is strongly delocalized in P_4H^+. Actually, the positive net charge at the hydrogen atom is close to zero, which is consistent with the covalent nature of the P−H linkages and with the strong charge redistribution that is apparent in Figure 3. The corresponding bond orbitals are the result of a combination of sp hybrids of phosphorus (with a very small contribution from the s orbitals) and the 1s orbital of hydrogen. This implies that the P−H−P linkage in the side-protonated species of P_4 has similar characteristics to those found for the first time in diborane, where only a delocalized molecular orbital involving sp hybrids of two boron atoms and the 1s orbital of the hydrogen atom, could account for its structure.

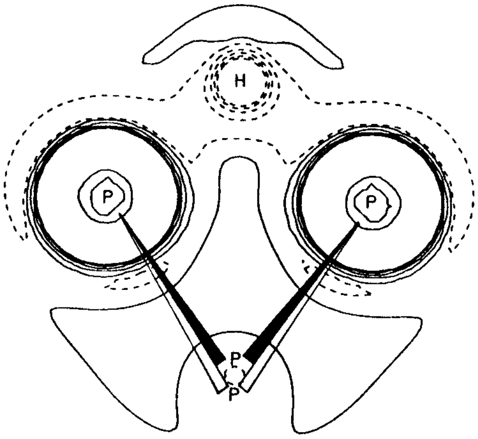

Figure 3. Contour maps of the Laplacian of the charge density of side-protonated P_4. Positive values of $\nabla^2\rho$ are denoted by solid lines and negative values by dashed lines. Contour values in au are ±0.05, ±0.12, ±0.25, ±0.37, ±0.50, ±0.62, ±0.75, ±0.80, ±0.95, ±1.00, and ±1.05. The negative values of the Laplacian in the P−H−P region denotes the existence of a covalent interaction between the three atoms.

These bonding characteristics are also consistent with the calculated harmonic vibrational frequencies (see Table 2). Our results show that the highest vibrational frequency corresponds to a symmetric stretching of the P−H linkages. This stretching frequency is large, since it is only about 700 cm^{-1} smaller than the P−H stretching for the corner protonated species. The next two highest vibrational frequencies correspond to the assymmetric stretching of the P−H linkages and to the bending of the proton out of the plane defined by the PHP moiety. The large force constant associated with the latter harmonic motion is in agreement with the P−H−P bonding described above, in the sense that a displacement of the proton out of the P−H−P plane will significantly weaken the P−H−P bonding.

Due to the breaking of the symmetry undergone by the system upon pro-tonation, the degenerate e and t_2 vibrational modes of the neutral molecule are split into two and three nondegenerate vibrational modes in the side-protonated system (**2**). Similarly, the a_1 vibrational mode of the neutral undergoes a slight red-shifting (19 cm^{-1}). It must also be noticed that while in the neutral species only the t_2 vibrational mode is infrared-active, in the protonated species all of them, with the exception of the 377 cm^{-1} vibrational mode, are active although the predicted intensities for those which originate from the a_1 and e vibrational modes are very small.

Conclusions

From the results discussed in this paper we can conclude that P_4 is moderately basic in the gas-phase. Most important, side protonation is the most favorable process from the thermodynamic point of view. The corresponding protonated species presents a three-center delocalized bond with characteristics similar to those found before for diborane. This seems to be the first time in which such a kind of delocalized bond is found in species involving only second row atoms. It is also noteworthy that it is formed upon the interaction of P_4 with a proton, i.e., it appears in a stable cation as in the case of $C_2H_5^+$.

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