3416 *J. Phys. Chem. A* **2007,** *111,* 3416−3422

Probing P−H$^+$−P Hydrogen Bonds: Structures, Binding Energies, and Spin−Spin Coupling Constants

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Received: December 18, 2006; In Final Form: February 14, 2007

Ab initio MP2/aug'-cc-pVTZ calculations have been performed to determine the structures and binding energies of 22 open and 3 cyclic complexes formed from the sp^2 [$H_2C{=}PH$ and HP═PH (cis and trans)] and sp^3 [$PH_2(CH_3)$ and PH_3] hybridized phosphorus bases and their corresponding protonated ions. EOM-CCSD calculations have been carried out to obtain $^{31}P-^{31}P$ and $^{31}P-^{1}H$ coupling constants across P−H$^+$−P hydrogen bonds. Two equilibrium structures with essentially linear hydrogen bonds have been found along the proton-transfer coordinate, except for complexes with $P(CH_3)H_3^+$ as the proton donor to the sp^2 bases. Although the isomer having the conjugate acid of the stronger base as the proton donor lies lower on the potential energy surface, it has a smaller binding energy relative to the corresponding isolated monomers than the isomer with the conjugate acid of the weaker base as the donor. The hydrogen bond of the latter has increased proton-shared character. All of the complexes are stabilized by traditional hydrogen bonds, as indicated by positive values of the reduced coupling constants $^{2h}K_{P-P}$ and $^{1}K_{P-H}$, and negative values of $^{1h}K_{H-P}$. $^{2h}J_{P-P}$ correlates with the P−P distance, a correlation determined primarily by the nature of the proton donor. For open complexes, $^{1}J_{P-H}$ always increases relative to the isolated monomer, while $^{1h}J_{H-P}$ is relatively small and negative. $^{2h}J_{P-P}$ values are quite large in open complexes, but are much smaller in cyclic complexes in which the P−H$^+$−P hydrogen bonds are nonlinear. Thus, experimental measurements of $^{2h}J_{P-P}$ should be able to differentiate between open and cyclic complexes.

Introduction

In a previous paper we reported the structures, binding energies, and coupling constants for a series of cationic complexes stabilized by N−H$^+$−N hydrogen bonds.[1] For that study we chose 11 bases with known proton affinities, and from these formed 66 cationic complexes. When these complexes were arranged in order of increasing base strength of the nitrogen base, and for a given base, increasing base strength of the protonated proton donor base, systematic changes were observed in binding energies, N−N distances, and N−N ($^{2h}J_{N-N}$), N−H ($^{1}J_{N-H}$), and H···N ($^{1h}J_{H-N}$) spin−spin coupling constants across the hydrogen bonds.

We have now extended this study to include a series of analogous cationic complexes stabilized by P−H$^+$−P hydrogen bonds. We are particularly interested in examining one- and two-bond coupling constants across these hydrogen bonds, since it has been noted previously that coupling constants involving ^{31}P can be very large when compared to those involving ^{15}N, even taking into account the difference in the magnetogyric ratios of ^{15}N and ^{31}P.[2−4] As will become evident below, the behavior of complexes with P−H$^+$−P hydrogen bonds is quite different from that found for complexes with N−H$^+$−N hydrogen bonds. We have restricted the present study to an examination of complexes with P−H$^+$−P hydrogen bonds formed from sp^2- and sp^3-hybridized phosphorus bases, since the sp-hybridized P atom in molecules such as HCP and CH_3-CP is an extremely weak base that does not protonate or form hydrogen bonds at P.[5] We have chosen to investigate complexes formed from four phosphorus bases, namely, H_3C-PH_2 and PH_3, which have sp^3 hybridized P atoms, and $H_2C{=}PH$ and HP═PH (cis and trans isomers), which have sp^2 P atoms. From these bases and the corresponding protonated ions, 22 complexes stabilized by essentially linear P−H$^+$−P hydrogen bonds can be formed. In this paper we discuss some features of the potential surfaces of these complexes, their structures and binding energies, and spin−spin coupling constants $^{2h}J_{P-P}$, $^{1}J_{P-H}$, and $^{1h}J_{H-P}$, and examine possible relationships among these properties. In addition, structures, binding energies, and coupling constants are also reported for three "cyclic" complexes stabilized by distorted, nonlinear hydrogen bonds.

Methods

The structures of all complexes were optimized under the constraint of C_s symmetry at second-order Møller−Plesset perturbation theory (MP2)[6−9] with the Dunning aug′-cc-pVTZ basis set,[10−11] which has the aug-cc-pVTZ basis on C and P atoms, and the cc-pVTZ basis on H. Vibrational frequencies were computed to establish whether or not the optimized structures are local minima on the potential surfaces. These frequencies indicate that complexes containing bases and/or ions with sp^2 hybridized P atoms have 1 low imaginary frequency corresponding to rotation of the plane of that molecule or ion about the hydrogen-bonding P−P axis. To evaluate the impact of this constraint, two such complexes were fully optimized in C_1 symmetry. The C_s symmetry constraint is required to make the coupling constant calculations feasible.

Spin−spin coupling constants were computed using the equation-of-motion coupled cluster singles and doubles method

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10.1021/jp068695z CCC: $37.00 © 2007 American Chemical Society
Published on Web 04/11/2007

TABLE 1: Computed Protonation Energies ($-\Delta E_e$, kcal/mol) and Computed and Experimental Proton Affinities ($-\Delta H^{298}$) of Phosphorus Bases

		$-\Delta H^{298}$	
no/monomer	$-\Delta E_e$	computed	experimental[a]
1. CH_3PH_2	209.3	203.8	203.5
2. PH_3	193.1	187.3	188.0
3. H_2CPH	184.3		
4c. HPPH (cis)	186.4		
4t. HPPH (trans)	182.6		

[a] Experimental data from ref 20.

(EOM-CCSD) in the CI(configuration interaction)-like approximation,[12−15] with all electrons correlated. The Ahlrichs[16] qzp basis was used on C, qz2p on P and the hydrogen-bonded H, and the cc-pVDZ basis on all other hydrogens. For selected complexes, all terms that contribute to the total coupling constant, namely, the paramagnetic spin−orbit (PSO), diamagnetic spin−orbit (DSO), Fermi contact (FC), and spin-dipole (SD) were evaluated.[17] For most complexes, only the FC term was evaluated and used to approximate the total coupling constant, J. The justification for this approximation will be given below.

EOM-CCSD t_2 amplitudes for the two bases with double bonds ($H_2C{=}PH$ and HP═PH cis and trans) range from 0.1 to 0.15, indicating that a second reference state may be important for describing these species. This state arises from a two-electron $\pi \rightarrow \pi^*$ excitation, HOMO to LUMO. In the hydrogen-bonded complexes, similar t_2 amplitudes are found, although the π^* orbital may be either the lowest or second-lowest virtual orbital.

Total coupling constants $^{2h}J_{P-P}$, $^{1}J_{P-H}$, and $^{1h}J_{H-P}$ for $H_3P-H^+\cdots PH_3$ were also evaluated along the proton-transfer coordinate. For this study, the P−H distance of the donor ion was incremented in units of 0.05 Å from 1.40 to 1.70 Å. The symmetric structure has a P−H distance of 1.742 Å. At each P−H distance, the remaining variables were fully optimized, and then all terms that contribute to the coupling constants were evaluated for these structures. The optimization and frequency calculations were done using Gaussian 03,[18] and the coupling constant calculations were carried out with ACES II.[19] All calculations were performed at the Ohio Supercomputer Center on the Cray X1 or the Itanium cluster.

Results and Discussion

The phosphorus bases are identified by number in Table 1, and their computed protonation energies and proton affinities are given, along with the available experimental proton affinities for CH_3PH_2 and PH_3.[20] The agreement between the computed and experimental values is excellent. With respect to the computed values, the order of decreasing protonation energy is $CH_3PH_2 > PH_3 >$ HPPH (cis) $> H_2CPH >$ HPPH (trans) (**1** > **2** > **4c** > **3** > **4t**).

In order to facilitate discussion, a numbering scheme will be used to identify complexes based on the numbering given in Table 1. Complexes are denoted **d−a** (donor−acceptor), where **d** is the proton-donor ion derived from protonation of base **d**, and **a** is the acceptor base. When $HPPH_2^+$ is the proton donor ion, **4c** indicates that the non-hydrogen-bonded P−H bonds are cis with respect to the P−P bond of the donor; **4t** indicates that they are trans. The identification scheme is illustrated in Figure 1 which shows the structure of complex **4t−4c**. In the 22 complexes that have linear P−H$^+$−P hydrogen bonds, C═P and/or P═P double bonds are *trans* with respect to the hydrogen-bonding P−P axis.

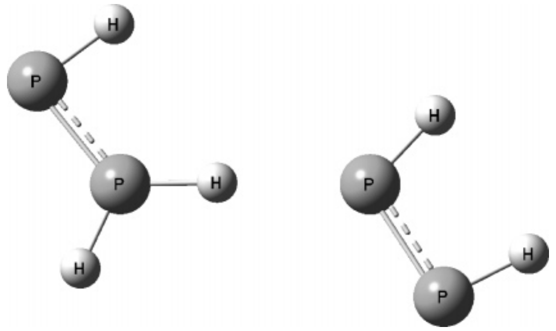

Figure 1. The structure of complex **4t−4c**. The non-hydrogen-bonded P−H bonds of $HPPH_2^+$ are trans with respect to the P═P bond in the proton donor (**4t**); the P−H bonds of the proton acceptor are *cis* with respect to the P═P bond of the acceptor (**4c**). In this open complex, the P═P bonds in the donor and acceptor are trans with respect to the hydrogen-bonding P−P axis.

Potential Surfaces. When two bases compete for a proton, it is generally accepted that the stronger base will be protonated, and that it becomes the proton donor to the weaker base in a hydrogen-bonded complex.[21] This is the situation for complexes stabilized by N−H$^+$−N hydrogen bonds.[1] Along the resulting proton-transfer coordinate, only a single minimum exists except for protonated homo-dimers such as (pyridine)$_2$H$^+$ and $(NH_3)_2H^+$. These complexes are stabilized by proton-shared hydrogen bonds with short N−N distances and relatively small barriers to proton transfer. For (pyridine)$_2$H$^+$ and $(NH_3)_2H^+$, the MP2/6-31+G(d,p) barriers are only 0.5 and 0.9 kcal/mol, respectively. The situation is quite different for complexes stabilized by P−H$^+$−P hydrogen bonds. Specifically, double minima are found along the proton-transfer coordinate for all cationic complexes formed from the bases $H_2C{=}PH$, HP═PH (cis and trans), PH_3, and $(CH_3)PH_2$ and the corresponding protonated ions, except for $(CH_3)PH_3^+$:$H_2C{=}PH$ and $(CH_3)PH_3^+$:HP═PH (cis and trans). That is, only single minima are found for complexes **1−3**, **1−4c**, and **1−4t**. The existence of single minima for these complexes is most probably a consequence of the large difference between the proton affinity of **1** compared to **3**, **4c**, and **4t**.

Of the two complexes found along the proton-transfer coordinate, the complex in which the stronger base is protonated lies lower on the potential surface than the complex that has the protonated weaker base as the proton donor. For example, $(CH_3)H_2PH^+$:PH_3 (**1−2**) lies 10.9 kcal/mol lower in energy than H_3PH^+:$PH_2(CH_3)$ (**2−1**). However, the binding energy of **1−2** relative to $(CH_3)H_2PH^+$ and PH_3 is 7.7 kcal/mol, significantly less than the binding energy of 12.9 kcal/mol for **2−1** relative to PH_4^+ and $PH_2(CH_3)$. That **2−1** has the greater hydrogen bond energy is not unexpected, since PH_4^+ is a better proton donor for hydrogen bonding than $(CH_3)PH_3^+$, and $(CH_3)PH_2$ is a stronger proton acceptor than PH_3.

All of the complexes were constrained to have C_s symmetry, a necessary condition to make the EOM-CCSD calculations feasible. However, for complexes containing an sp^2-hybridized P base ($H_2C{=}PH$ or HP═PH) or corresponding protonated ion, this constraint produces structures with one very low imaginary frequency. This frequency, which varies from −5 to −18 cm^{-1}, corresponds to rotation of the plane of the molecule or ion about the P−P hydrogen bonding axis. To what extent does this constraint influence the structures and binding energies of these complexes? To answer this question, two complexes, **2−4c** and **3−4t**, were fully optimized with no geometric constraints. The **2−4c** (PH_4^+:P_2H_2c) complex of C_1 symmetry has the PH_4^+ ion rotated by 20° relative to the C_s structure; otherwise it is

TABLE 2: Electronic Binding Energies (kcal/mol), P−P and P−H Distances (Å), and FC Terms for Spin−Spin Coupling Constants [$^{2h}J_{P-P}$, $^{1}J_{P-H}$, $^{1h}J_{H-P}$ (Hz)] for Complexes with Linear P−H$^+$−P Hydrogen Bonds[a]

	ID	ΔE	R(P−P)	R(P−H)	$^{2h}J_{P-P}$	$^{1}J_{P-H}$	$^{1h}J_{H-P}$
$CH_3PH_3^+$				1.394		468.9	
Acceptors in Complexes							
CH_3PH_2	**1−1**	10.5	3.903	1.421	375.4	507.7	−40.4
PH_3	**1−2**	7.7	4.002	1.410	265.0	502.7	−32.6
$H_2C{=}PH$	**1−3**	7.3	3.998	1.406	252.4	500.7	−32.9
HP=PH[b]	**1−4c**	7.1	3.982	1.407	254.7	499.5	−33.4
	1−4t	6.2	3.990	1.407	245.2	497.0	−32.6
PH_4^+				1.392		499.3	
Acceptors in Complexes							
H_3CPH_2	**2−1**	12.9	3.755	1.452	613.3	518.8	−42.5
PH_3	**2−2**	9.3	3.871	1.424	413.3	529.8	−41.0
symmetric[c]	**2−2**	4.4	3.484	1.742	1291.8	207.0	207.0
$H_2C{=}PH$	**2−3**	8.8	3.880	1.418	394.1	530.5	−42.8
HP=PH[b]	**2−4c**	8.6	3.870	1.418	382.1	528.7	−42.2
	2−4t	7.6	3.880	1.418	369.3	526.4	−41.4
$H_2CPH_2^+$				1.391		637.2	
Acceptors in Complexes							
PH_3	**3−2**	10.4	3.743	1.447	700.0	652.4	−43.7
$H_2C{=}PH$	**3−3**	9.7	3.780	1.432	625.9	662.8	−48.4
HPPH cis[b]	**3−4c**	9.5	3.755	1.434	632.8	659.5	−49.2
HPPH trans[b]	**3−4t**	8.5	3.760	1.434	616.9	656.0	−49.3
$HP{=}PH_2^{+}$[d]				1.395		551.6	
Acceptors in Complexes							
PH_3	**4c−2**	9.4	3.795	1.438	574.8	589.0	−47.0
$H_2C{=}PH$	**4c−3**	8.8	3.821	1.428	522.6	591.2	−49.6
HPPH cis	**4c−4c**	8.6	3.797	1.429	523.7	588.5	−50.4
HPPH trans	**4c−4t**	7.7	3.806	1.429	506.2	583.3	−50.0
HPPH cis symmetric[c]		5.2	3.444	1.722	1642.1	215.5	215.5
$HP{=}PH_2^{+}$[e]				1.397		561.1	
Acceptors in Complexes							
PH_3	**4t−2**	10.3	3.711	1.462	765.1	580.4	−50.1
H_2CPH	**4t−3**	9.6	3.753	1.442	666.1	594.4	−56.9
HPPH cis	**4t−4c**	9.4	3.729	1.445	672.6	589.8	−57.9
HPPH trans	**4t−4t**	8.5	3.734	1.444	653.3	586.2	−58.3
HPPH trans symmetric[c]		6.5	3.440	1.720	1660.4	198.8	198.8

[a] A linear hydrogen bond implies that the H−P−P angle does not exceed 5°. [b] When HP=PH is the proton acceptor, cis (c) and trans (t) refer to the arrangement of the two non-hydrogen-bonded P−H bonds with respect to the P=P bond. [c] The symmetric structure is not a local minimum on the potential surface. [d] The two non-hydrogen-bonded P−H bonds of the donor are cis with respect to the donor P=P bond. [e] The two non-hydrogen-bonded P−H bonds of the donor are trans.

energetically and structurally equivalent to **2−4c** with C_s symmetry. For the C_1 complex **3−4t** ($H_2CPH_2^+$:P_2H_2t) the ion and molecule lie in nearly perpendicular planes, with a slightly shorter P−P distance (3.755 vs 3.760 Å) and a hydrogen bond that has a slightly greater deviation from linearity (2.3 vs 0.2°) compared to the C_s complex. However, the fully optimized equilibrium C_1 structure is only 0.1 kcal/mol more stable than the C_s structure. Since these data show that the structural and energetic effects of the symmetry constraint are negligible, this study of complexes stabilized by P−H$^+$−P hydrogen bonds has been restricted to complexes that have C_s symmetry.

Structures and Binding Energies. P−P and P−H distances and the binding energies of the 22 complexes investigated in this work are given in Table 2. The complexes are arranged in Table 2 by proton donor ion, beginning with the protonated base that has the highest protonation energy. The conjugate acid of this base is a relatively weak acid. Under a given proton donor, the stronger sp^3 bases, as judged by their protonation energies, are listed first (CH_3PH_2 and then PH_3, **1** and **2**). These are followed by the weaker sp^2 bases $H_2C{=}PH$ and HP=PH, cis and trans (**3**, **4c**, and **4t**). The protonation energies of the sp^2 bases are within 4 kcal/mol in the order HP=PHc > $H_2C{=}PH$ > HP=PHt. Under each acid the complexes are listed in the order **1**, **2**, **3**, **4c**, and **4t**. For a given ion, complexes that have the strongest base as the proton acceptor are the most stable, with the binding energies decreasing in the order **1** > **2** > **3** > **4c** > **4t**. [As noted above, protonated bases **3**, **4c**, and **4t** do not form hydrogen-bonded complexes with CH_3PH_2 (**1**) as the base.] It is interesting to note that although the proton affinities of **3**, **4c**, and **4t** decrease in the order **4c** > **3** > **4t**, **3** always forms a slightly stronger hydrogen bond with a given ion than **4c**, while the hydrogen bond formed by **4t** with the same ion is about 1 kcal/mol less stable.

TABLE 3: Coupling Constants (J) and Components of J (Hz) for Complexes 2−2 and 2−3

	PSO	DSO	FC	SD	J
		Complex **2−2**			
P−P	0.0	0.0	413.3	3.0	416.3
P−H	0.4	0.1	529.8	0.4	530.7
H···P	−0.7	0.7	−41.0	1.8	−39.2
		Complex **2−3**			
P−P	−0.1	0.0	394.1	2.0	396.1
P−H	0.3	0.1	530.5	0.3	531.3
H···P	−0.8	0.7	−42.8	1.5	−41.3

The binding energies (ΔE, kcal/mol from Table 2) of these complexes can be related to four terms:
(i) the protonation energy of the base acting as the proton donor ion (PA_d from Table 1);
(ii) the protonation energy of the proton acceptor base (PA_a);
(iii) the hybridization (sp^2 or sp^3) of the P atom in the proton donor ion;
(iv) the hybridization (sp^2 or sp^3) of the P in the proton acceptor base.

These factors can be related to the binding energies using the equation

$$\Delta E = -0.12\mathrm{PA_d} + 0.17\mathrm{PA_a} + 0.73(\mathrm{sp^3\ donor}) - 0.37(\mathrm{sp^3\ acceptor}) \quad (1)$$

with the last two terms nonzero only if the hybridization is sp^3.

A comparison of the pair of complexes which exist along the proton-transfer coordinate indicates that the complex formed when the weaker base is the proton donor has the shorter P−P distance and the greater binding energy. Thus, the shortest distance for an equilibrium structure is 3.711 Å in complex **4t−2**; complex **2−4t** has a P−P distance of 3.880 Å. The binding energy of **4t−2** is also significantly larger than **2−4t** (10.3 vs 7.6 kcal/mol). These data indicate that although all of the complexes are stabilized by traditional, linear hydrogen bonds, the complex formed from the protonated weaker base as the proton donor has greater proton-shared character.

There is a significant variation in P−P distances, which range from 3.711 to 4.002 Å. Upon complex formation, the proton-donor P−H distance lengthens relative to the isolated protonated monomer. All of these complexes have essentially linear hydrogen bonds, as indicated by the H−P−P angle which does not exceed 5°. Nevertheless, there is no overall correlation between P−P distances and complex binding energies.

Coupling Constants. *Dominance of the FC Term.* Coupling constants $^{2h}J_{P-P}$, $^{1}J_{P-H}$, and $^{1h}J_{H-P}$ and their components are listed in Table 3 for complexes **2−2** and **2−3**. As evident from these data, FC terms for P−P and P−H coupling are very large, being 2 orders of magnitude greater than any other term. The

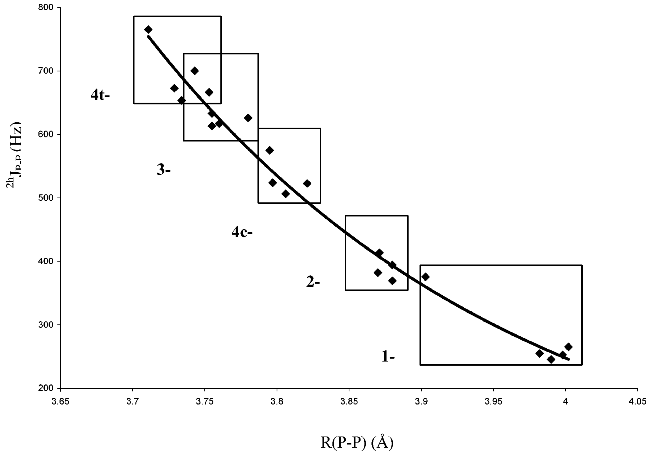

Figure 2. The variation of $^{2h}J_{P-P}$ with the P−P distance for the 22 complexes with linear P−H$^+$−P hydrogen bonds. The blocks identify the proton-donor ions.

FC term is at least 1 order of magnitude greater than the remain terms for H···P coupling. Therefore, the corresponding FC terms can be used to approximate $^{2h}J_{P-P}$, $^{1}J_{P-H}$, and $^{1h}J_{H-P}$.

$^{2h}J_{P-P}$. Table 2 also lists $^{2h}J_{P-P}$, $^{1}J_{P-H}$, and $^{1h}J_{H-P}$ (approximated from the corresponding FC terms) for all of the 22 complexes with essentially linear P−H$^+$−P hydrogen bonds. Values of the two-bond coupling constants $^{2h}J_{P-P}$ for these complexes with traditional hydrogen bonds cover a broad range, from 245 Hz for complex **1**−**4t** to 765 Hz for complex **4t**−**2**. Figure 2 shows a plot of $^{2h}J_{P-P}$ versus the P−P distance. The trendline shown is a decaying exponential, with a correlation coefficient of 0.984. Thus, as observed in previous studies, there is a very good correlation between the P−P coupling constant and the P−P distance, although neither of these properties correlate with the binding energies of the complexes.

Closer examination of Figure 2 shows a grouping of points, which can be identified by the proton donor ion. The first block of points pertains to complexes with protonated **4t** as the proton donor. Since **4t** is the weakest base, its conjugate acid is the strongest acid, and a very good P−H donor for hydrogen bond formation. Points in the second box refer to complexes which have the ion corresponding to the next to the weakest base (**3**) as the donor. There is some overlap between boxes for **4t** and **3**, with the point in the upper left corner of box **3** belonging to **3**, and the point in the lower right corner of **4t** belonging to **4t**. Also found in the box identifying complexes with **3** as the donor is the point for complex **2**−**1**. Relative to other complexes with **2** as the donor, complex **2**−**1** has a very short P−P distance and an unusually large binding energy, most probably reflecting its increased proton-shared character. The remaining boxes do not overlap and are identified by proton donor ion as **4c**, **2**, and **1**. Thus, along the P−P coordinate, the P−P distance of complexes increases with respect to the proton-donor ion in the order **4t** < **3** < **4c** < **2** < **1**, which is the order of weakest base to strongest base. Thus, it is the protonated base acting as a proton donor which is primarily responsible for the correlation between $^{2h}J_{P-P}$ and the P−P distance.

$^{1}J_{P-H}$. Table 2 also reports proton-donor P−H distances and $^{1}J_{P-H}$ for both the isolated ions and these ions as proton donors in complexes. In all cases, the P−H distance increases upon complex formation, but $^{1}J_{P-H}$ also increases. $^{1}J_{N-H}$ was also found to increase with small increases in N−H distances, but eventually $^{1}J_{N-H}$ decreased as the hydrogen bond acquired increased proton-shared character.[1] This suggests that P−H$^+$−P hydrogen bonds have relatively little proton-shared character, most probably due in part to the very long P−P distances. This point will be discussed further below in the section on $^{1h}J_{H-P}$. Moreover, there is no apparent correlation between $^{1}J_{P-H}$ and the P−H distance, or changes in $^{1}J_{P-H}$ and changes in the P−H distance in going from monomer to complex. The only statement that can be made is that $^{1}J_{P-H}$ usually increases by about 20−40 Hz upon complex formation.

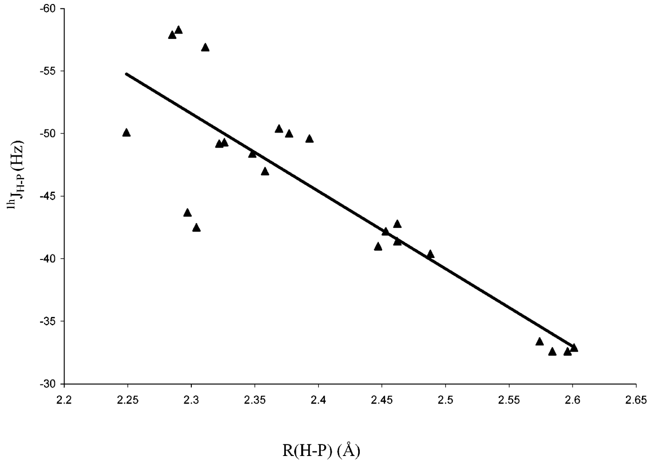

Figure 3. $^{1h}J_{H-P}$ vs the H−P distance for complexes with traditional P−H$^+$−P hydrogen bonds.

$^{1h}J_{H-P}$. Table 2 also presents values of $^{1h}J_{H-P}$ for complexes with linear P−H$^+$−P hydrogen bonds. On the basis of previous studies, generalizations about the signs of coupling constants across hydrogen bonds have been proposed. These state that for traditional X−H···Y hydrogen bonds, reduced two-bond couplings $^{2h}K_{X-Y}$ and one-bond couplings $^{1}K_{X-H}$ are positive,[22,23] while $^{1h}K_{H-Y}$ are negative.[24] Since the magnetogyric ratios of ^{31}P and ^{1}H are both positive, J and K values for P−P and P−H coupling have the same sign. Thus, the signs of $^{2h}J_{P-P}$, $^{1}J_{P-H}$, and $^{1h}J_{H-P}$ indicate that all of these complexes are stabilized by traditional hydrogen bonds. Values of $^{1h}J_{H-P}$ vary from about −30 to −60 Hz. Figure 3 shows a plot of $^{1h}J_{H-P}$ versus the H−P distance. The trendline shown indicates a relatively weak correlation, with a correlation coefficient of 0.76. However, there is a much more disturbing feature of this plot, which suggests that as the H−P distance decreases, $^{1h}J_{H-P}$ becomes more negative. This cannot be the case, since as the proton-shared character of the hydrogen bond increases, $^{1h}J_{H-P}$ changes sign and becomes comparable to $^{1}J_{P-H}$ when the hydrogen bond is a quasi-symmetric proton-shared hydrogen bond. Figure 3 is misleading because it contains no points for proton-shared hydrogen bonds.

A more informative and more realistic curve for the variation of $^{1h}J_{H-P}$ with the H−P distance is presented in Figure 4. The data points included are the same as found in Figure 3, but with the addition of three points for homo-dimers **2**−**2** ($P_2H_7^+$) (D_{3d}), and **4c**−**4c** and **4t**−**4t** ($(HP{=}PH)_2H^+$) (C_{2h}), which were constrained to have symmetric hydrogen bonds. Note that the P−P distances are very short, ranging between 3.44 and 3.48 Å, while the P−H distances are long, at 1.72−1.74 Å. The resulting P−P coupling constants $^{2h}J_{P-P}$ are extremely large, varying between 1300 and 1600 Hz, while $^{1h}J_{H-P}$ has changed sign, and is equal to $^{1}J_{P-H}$ (about 200 Hz). Thus, Figure 3 is misleading because it shows only a relatively small range of $^{1h}J_{H-P}$ values, all of which arise from complexes with traditional hydrogen bonds. These complexes are structurally and spectroscopically very far removed from complexes with proton-shared hydrogen bonds. Thus, the characteristics of coupling constants for complexes with P−H$^+$−P hydrogen bonds are dramatically different from

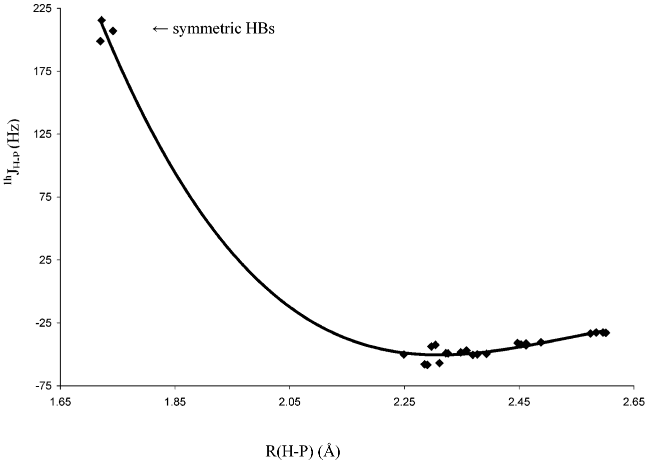

Figure 4. $^{1h}J_{H-P}$ vs the H−P distance for complexes with P−H$^+$−P hydrogen bonds. The data points at short H−P distances are for complexes **2−2**, **4t−4t**, and **4c−4c**.

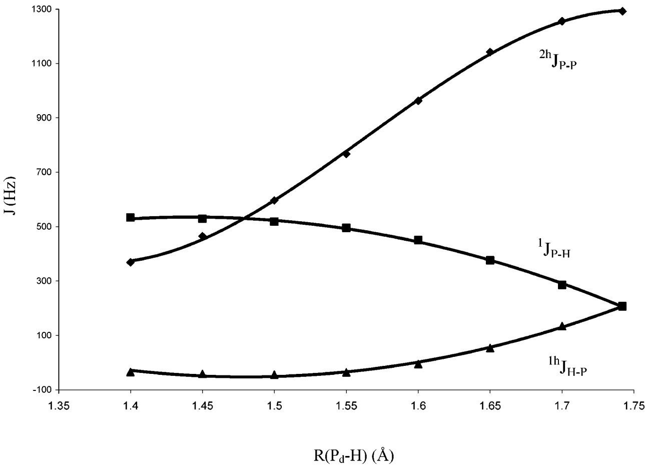

Figure 5. Variation of $^{2h}J_{P-P}$ (◆), $^{1}J_{P-H}$ (■), and $^{1h}J_{H-P}$ (▲) along the proton-transfer coordinate of H_3P_d−H$^+$−PH_3.

those arising from N−H$^+$−N hydrogen bonds. Unfortunately, there are no experimental data for P−P or P−H coupling across P−H$^+$−P hydrogen bonds.

Coupling Constant Curves for $P_2H_7^+$ as a Function of the P−H Distance. Figure 5 shows the variation of $^{2h}J_{P-P}$, $^{1}J_{P-H}$, and $^{1h}J_{H-P}$ as a function of the P−H distance for H_3P−H$^+$−PH_3. Along the proton-transfer coordinate at each P−H distance, the complex was optimized, and coupling constants were computed for each optimized structure. The curves showing the variation of $^{2h}J_{P-P}$, $^{1}J_{P-H}$, and $^{1h}J_{H-P}$ are symmetric about a P−H distance of 1.742 Å. As the P−H distance increases from its equilibrium value, the P−P distance decreases, and $^{2h}J_{P-P}$ increases dramatically, from 368 Hz at a P−H distance of 1.40 Å, to 1292 Hz at a P−H distance of 1.742 Å. Simultaneously, $^{1}J_{P-H}$ decreases, $^{1h}J_{H-P}$ increases and changes sign, and these two coupling constants become equal (207 Hz) when the hydrogen bond is symmetric. While changes in coupling constants as a function of proton position and hydrogen bond type have been reported based on both theoretical and experimental data,[1,25−37] the magnitude of these changes for H_3P−H$^+$−PH_3 is much greater than observed previously. The barrier to proton transfer in this complex is 4.9 kcal/mol.

Coupling Constants for Complexes with Nonlinear Hydrogen Bonds. All of the complexes discussed thus far are stabilized by linear hydrogen bonds, and have the P═P and/or C═P double bonds trans to the P−P hydrogen-bonding axis. When these bonds have a cis arrangement, complexes stabilized by nonlinear P−H$^+$−P hydrogen bonds are formed. Although many of these have been located, only three will be discussed. To differentiate these from complexes formed by the same ion-base pair, the prefix "**cyc**" will be used, which indicates that these complexes have some "cyclic" character. Data for these complexes are reported in Table 4.

The first complex, **cyc-2−4c**, has PH_4^+ acting as a double proton donor to *cis*-HPPH to form two nonequivalent hydrogen bonds, and is illustrated in Figure 6. Hydrogen bond 1−3−2 has a longer P−P distance than hydrogen bond 1−7−5, but the latter has a significantly greater deviation from linearity. The binding energy of 8.8 kcal/mol is only slightly greater than the corresponding open complex **2−4c**, which has a binding energy of 8.6 kcal/mol. However, because of the nonlinearity of these hydrogen bonds, the two-bond coupling constants $^{2h}J_{P-P}$ are significantly less than $^{2h}J_{P-P}$ for **2−4c** (161 and 53 Hz vs 382 Hz). Similarly, $^{1h}J_{H-P}$ values for **cyc-2−4c** are reduced relative to $^{1h}J_{H-P}$ for the open complex **2−4c**, and the two one-bond couplings $^{1}J_{P-H}$, which have been found to increase upon hydrogen-bond formation in the open complexes with linear hydrogen bonds, increase to a lesser extent in this distorted cyclic complex. A complex with C_{2v} symmetry with two equivalent hydrogen bonds was optimized, but has two imaginary frequencies, one corresponding to an out-of-plane rotation similar to that observed for complexes with H_2C═PH and HP═PH and/or their protonated ions, and the other to an in-plane motion that identifies the C_{2v} structure as a transition structure for the interconversion of two equivalent **cyc-2−4c** complexes.

The second cyclic complex, **cyc-4c−4t**, is shown in Figure 7. This complex is an equilibrium structure with no imaginary frequencies, stabilized by two distorted P−H−P hydrogen bonds. The binding energy of this complex is 10.1 kcal/mol, which is significantly higher than the binding energy of 7.7 kcal/mol for **4c−4t**. In **cyc-4c−4t**, *cis*-$HPPH_2^+$ is a proton donor to HPPH forming hydrogen bond 1−3−2, and HPPH is a proton donor to *cis*-$HPPH_2^+$, forming hydrogen bond 5−9−4. Both hydrogen bonds are very nonlinear, but the P−P distance for the 1−3-2 hydrogen bond is remarkably short. As a result, $^{2h}J_{P-P}$ for 1P−2P is 182 Hz, significantly greater than $^{2h}J_{P-P}$ for 4P−5P which is essentially zero. However, both are significantly less than the value of 506 Hz for $^{2h}J_{P-P}$ in the open complex **4c−4t**. Values of $^{1h}J_{H-P}$ for both hydrogen bonds are also very small. Finally, the value of 94 Hz for $^{1}J_{P-H}$ (FC term) for the P−H donor (5−9) is less than the value of 115 Hz for isolated HPPH*t*.

The third cyclic complex, **cyc-4t−4c** has $HPPH_2^+$t acting as a double proton donor to HPPHc to form hydrogen bonds 1−3−2 and 4−7−5. (Relative to complex **cyc-4c−4t** in Figure 7, **cyc-4t−4c** has the 4P−7H bond rotated about the 1P−4P axis by 180°, and the 5P−9H bond rotated by 180° about the 2P−5P axis.) The binding energy of this complex is 10.1 kcal/mol, slightly greater than the value of 9.4 kcal/mol for the open **4t−4c** complex that has the two P═P bonds trans with respect to the hydrogen-bonding axis. The 1P−2P distance in **cyc-4t−4c** is longer than this distance in **4t−4c**, and the hydrogen bond deviates from linearity by 15°, resulting in a value of $^{2h}J_{P-P}$ of 329 Hz, which is significantly less than that found for **4t−4c**. The very long 4P−5P distance and the nonlinearity of the hydrogen bond leads to a very small value of 21 Hz for $^{2h}J_{P-P}$ for 4P−5P. Values of $^{1h}J_{H-P}$ are small and negative, and $^{1}J_{P-H}$ for 4P−7H is slightly reduced (141 vs 135 Hz) relative to the corresponding isolated cation. These data suggest that open and cyclic complexes with P−H$^+$−P hydrogen bonds could be

TABLE 4: Binding Energies (kcal/mol), P−P and P−H Distances (Å), and FC Terms for for Spin−Spin Coupling Constants [$^{2h}J_{P-P}$, $^{1}J_{P-H}$, $^{1h}J_{H-P}$ (Hz)] for Complexes with Nonlinear P−H$^+$−P Hydrogen Bonds[a]

complex/ID	R(P−P)	R(P−H)	R(H−P)	∠H−P−P	ΔE	$^{2h}J_{P-P}$	$^{1}J_{P-H}$	$^{1h}J_{H-P}$
PH_4^+:HPPHc **cyc-2−4c**[b]								
1−3−2	3.815	1.402	2.583	22.9	8.8	160.8	518.1	−24.4
1−7−5	3.730	1.392	3.152	55.3		52.6	506.3	0.8
$HPPH_2^+$:HPPHt **cyc-4c−4t**[c,d]								
1−3−2	3.574	1.394	2.998	54.9	10.1	181.8	581.5	−6.3
5−9−4	4.193	1.423	3.248	40.6		−6.5	94.4	−1.5
$HPPH_2^+$t:HPPHc **cyc-4t−4c**[c]								
1−3−2	3.778	1.415	2.442	15.4	10.1	329.1	578.6	−39.3
4−7−5	4.157	1.427	2.822	16.9		20.8	134.7	−19.6

[a] P_1 is always the proton donor to P_2 for a $P_1-H_3-P_2$ hydrogen bond. [b] PH_4^+ is a double proton donor to HPPHc. [c] P_4 and H_7 are in the protonated ion; P_5 and H_9 are in the neutral base. [d] This complex of C_s symmetry is an equilibrium structure with no imaginary frequencies.

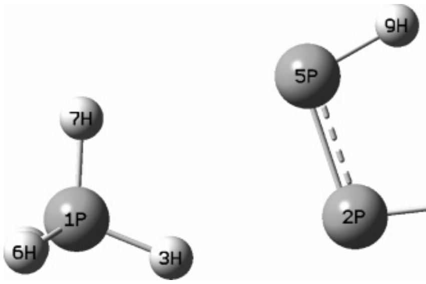

Figure 6. Structure **cyc-2−4c** with nonlinear hydrogen bonds.

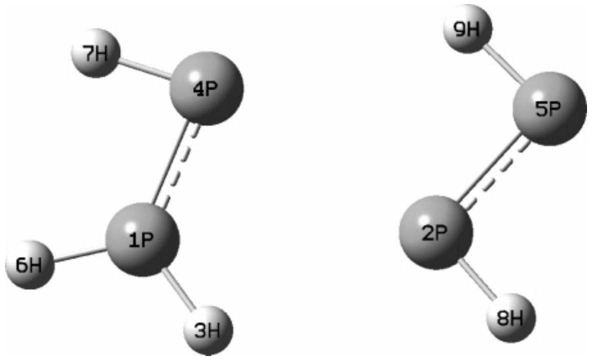

Figure 7. Equilibrium structure of complex **cyc-4c−4t**.

readily differentiated on the basis of experimentally measured coupling constants, particularly $^{2h}J_{P-P}$.

Conclusions

Ab initio MP2/aug′-cc-pVTZ calculations have been performed to determine the structures and binding energies of 22 open complexes with essentially linear P−H$^+$−P hydrogen bonds formed from the sp^2 [$H_2C{=}PH$ and HP═PH (cis and trans)] and sp^3 [$PH_2(CH_3)$ and PH_3] hybridized phosphorus bases and the corresponding protonated ions. Three cyclic complexes stabilized by nonlinear hydrogen bonds have also been included in this study. EOM-CCSD calculations have been carried out to obtain $^{31}P-^{31}P$ and $^{31}P-^{1}H$ coupling constants across P−H$^+$−P hydrogen bonds. The results of these calculations support the following statements.

1. For the open complexes with essentially linear hydrogen bonds, double minima exist along the proton-transfer coordinate for all complexes except those in which $(CH_3)PH_3^+$ is the proton donor to an sp^2-hybridized base.
2. Of the two complexes that exist along the proton-transfer coordinate, the complex in which the stronger base is protonated and acts as the proton donor lies lower on the potential energy surface. However, the binding energy of this complex (relative to the corresponding protonated base and the proton acceptor) is less than the binding energy of the complex in which the weaker base is protonated and is the proton donor. The hydrogen bond in the latter complex has increased proton-shared character.
3. For these complexes, the Fermi-contact terms are excellent approximations to the corresponding total spin−spin coupling constants $^{2h}J_{P-P}$, $^{1}J_{P-H}$, and $^{1h}J_{H-P}$.
4. $^{2h}J_{P-P}$ is always positive and correlates with the P−P distance, but neither of these properties correlate with the binding energies of the complexes. A plot of $^{2h}J_{P-P}$ versus the P−P distance shows a grouping of complexes according to base strength (as measured by proton affinity) with the result that coupling constants corresponding to short P−P distances arise from complexes in which the conjugate acid of the weakest base is the proton donor, while those at long distances correspond to complexes in which the conjugate acid of the strongest base is the proton donor. Thus, it is the protonated base acting as a proton donor which is primarily responsible for the correlation between $^{2h}J_{P-P}$ and the P−P distance.
5. $^{1}J_{P-H}$ values are always positive and increase upon complex formation, while coupling constants $^{1h}J_{H-P}$ are relatively small and negative. Thus, the signs of the reduced coupling constants $^{2h}K_{P-P}$ and $^{1}K_{P-H}$ are positive and $^{1h}K_{H-P}$ is negative, indicating that these complexes are stabilized by traditional hydrogen bonds with little proton-shared character.
6. The potential surfaces, proton-transfer coordinate, and one- and two-bond spin−spin coupling constants for complexes with P−H$^+$−P hydrogen bonds are dramatically different from these same properties for complexes with N−H$^+$−N hydrogen bonds.
7. Cyclic complexes are stabilized by nonlinear P−H$^+$−P hydrogen bonds. In general, $^{2h}J_{P-P}$ values are much smaller for these complexes since the hydrogen bonds tend to have longer P−P distances and are nonlinear. Thus, experimental measurements of $^{2h}J_{P-P}$ could be used to differentiate open from cyclic complexes.

Acknowledgment. The authors wish to thank the Ohio Supercomputer Center for continuing support of this research, and the Spanish Ministry of Science and Education for grant BQU2003-01215.

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