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

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Ab-initio MP2/aug’-cc-pVTZ calculations have been performed to determine the structures and binding energies of proton-bound complexes stabilized by N−H$^+$−P hydrogen bonds and to investigate the nature of the proton-transfer coordinate in these systems. Double minima are found only when the difference between the protonation energies of the N and P bases is less than about 4 kcal/mol. The isomer in which the protonated nitrogen base is the donor lies lower on the potential surface and also has a greater binding energy relative to the corresponding isolated monomers. Equation-of-motion coupled cluster singles and doubles (EOM-CCSD) calculations have been employed to obtain one- and two-bond spin−spin coupling constants across these hydrogen bonds. Two-bond coupling constants ^{2h}J(N−P) correlate with N−P distances, irrespective of whether the donor ion is N−H$^+$ or P−H$^+$. One-bond coupling constants ^1J(N−H) and ^{1h}J(H−P) for complexes stabilized by N−H$^+$···P hydrogen bonds correlate with corresponding distances, but similar correlations are not found for ^1J(P−H) and ^{1h}J(H−N) for complexes with P−H$^+$···N hydrogen bonds. Negative values of ^{1h}K(H−N) and ^{1h}K(H−P) indicate that the hydrogen bonds in these complexes are traditional. Comparisons are made with complexes stabilized by N−H$^+$−N and P−H$^+$−P hydrogen bonds.

Introduction

In a continuing investigation of proton-bound complexes, we previously examined complexes stabilized by N−H$^+$−N and P−H$^+$−P hydrogen bonds[1,2] and observed interesting differences between these two series. Complexes with N−H$^+$−N hydrogen bonds usually have only a single minimum along the proton-transfer coordinate. The nitrogen base with the greater protonation energy is always protonated and becomes the proton donor ion to the weaker base in the complex. Double minima are found only for protonated homodimers with sp^2 or sp^3 nitrogen atoms, but the barrier to proton transfer in these systems is small. In a related series of complexes, there is a smooth change in hydrogen bond type from proton-shared to traditional as the difference between the protonation energies of the two nitrogen bases increases. Spin−spin coupling constants ^{2h}J(N−N), ^1J(N−H), and ^{1h}J(H−N) vary systematically and are fingerprints of hydrogen-bond type.

The situation is quite different for complexes with P−H$^+$−P hydrogen bonds. First, there are no complexes stabilized by P−H$^+$−P hydrogen bonds involving a simple sp-hybridized P base such as HC≡P or H_3C−C≡P, since these P atoms are extremely weak basic sites. Rather, protonation and hydrogen-bond formation occur through the π system.[3] Complexes formed from sp^2 or sp^3 hybridized P atoms usually have double minima along the proton-transfer coordinate. The complex in which the stronger base is protonated lies lower on the potential surface, but the isomer having the protonated weaker base as the proton donor has the greater binding energy relative to the corresponding isolated monomers. Although all complexes are stabilized by traditional hydrogen bonds, complexes in which the weaker base is protonated have increased proton-shared character, as evident from shorter P−P distances and larger two-bond P−P coupling constants. ^{2h}J(P−P) correlates with the P−P distance, and ^1J(P−H) always increases upon complex formation. However, no correlation is found between changes in P−H distances and changes in ^1J(P−H). ^{1h}J(H−P) is always negative, another indication that the hydrogen bonds in these complexes are traditional hydrogen bonds.

Since the characteristics of complexes with N−H$^+$−N and P−H$^+$−P hydrogen bonds are so different, it is quite natural to ask what properties will mixed complexes with N−H$^+$−P hydrogen bonds exhibit. To answer this question, the structures, binding energies, and spin−spin coupling constants of complexes stabilized by N−H$^+$···P and P−H$^+$···N hydrogen bonds have been investigated. It is the purpose of this paper to (1) report the structures and binding energies of these complexes; (2) describe the nature of the potential surfaces along the proton-transfer coordinate; (3) present and analyze the one- and two-bond spin−spin coupling constants across the N−H$^+$−P hydrogen bonds; and (4) compare the properties of these complexes with those stabilized by N−H$^+$−N and P−H$^+$−P 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)[4−7] with the Dunning aug’-cc-pVTZ basis set,[8−9] which has the aug-cc-pVTZ basis on C, N, 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 some of the complexes containing bases or ions with sp^2 hybridized atoms have one low-frequency imaginary mode corresponding to rotation of the plane of that molecule or ion about the hydrogen-bonding axis. A similar low-frequency vibrational mode was also found for complexes with P−H$^+$−P

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hydrogen bonds containing sp^2-hybridized P bases. However, it was shown in that study that rotation about the P−P axis is essentially free and that the symmetry constraint has little effect on hydrogen-bond geometries and binding energies.[2] The C_s symmetry constraint is required to make the coupling constant calculations feasible. Only complexes with open structures and essentially linear N−H$^+$−P hydrogen bonds have been included in the present study.

The protonation energies for the N and P bases have been obtained at MP2/aug'-cc-pVTZ as the negative electronic energy change ($-\Delta E_e$) for the protonation reaction

$$B + H^+ \rightarrow B{-}H^+ \qquad (1)$$

evaluated as the difference between the electronic energies of B−H$^+$ and B. The proton affinity (PA) is the negative change in the enthalpy ($-\Delta H^{298}$) for the same reaction at 298 K. The electronic binding energy of a hydrogen-bonded complex $-\Delta E_e = -[E_e(D{-}H^+{\cdots}A) - E_e(D{-}H^+) - E_e(A)]$ is the negative energy for the reaction

$$D{-}H^+ + A \rightarrow D{-}H^+{\cdots}A \qquad (2)$$

where D−H$^+$ is the protonated base which acts as the proton donor ion to the acceptor base A.

One- and two-bond ^{15}N, ^{31}P, and ^{1}H spin−spin coupling constants across N−H$^+$−P hydrogen bonds were computed using the equation-of-motion coupled cluster singles and doubles method (EOM-CCSD) in the configuration interaction (CI)-like approximation,[10−13] with all electrons correlated. The Schäfer et al.[14] qzp basis was used on C and N, qz2p was used on P and the hydrogen-bonded H, and the cc-pVDZ basis was used on all other hydrogens. This level of theory has been shown to yield coupling constants in agreement with experimental data[15−20] without any rescaling of computed values. For selected complexes investigated in this study, 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.[21] For most complexes, only the FC term was evaluated and used to approximate total *J*. The justification for this approximation will be given below.

As noted previously, EOM-CCSD t_2 amplitudes for monomers involving sp^2-hybridized N or P atoms may range from 0.1 to 0.15,[1,2] indicating that a second reference state may be important in describing these systems. Similar t_2 amplitudes are also found for some of the complexes involving these same bases. This state usually arises from a two-electron $\pi \rightarrow \pi^*$ excitation, although in three complexes involving an sp^2 nitrogen base and PH$_3$, the state arises from a $\sigma \rightarrow \pi^*$ excitation.

Total coupling constants for (CH$_3$)H$_2$P−H$^+$:NH$_3$ were also evaluated along the proton-transfer coordinate. For this study, the P−H distance was incremented in units of 0.10 Å from 1.50 to 2.20 Å. At each P−H distance, the remaining variables were optimized, and then all terms that contribute to the coupling constants were evaluated for each structure. The optimization and frequency calculations were done using Gaussian 03,[22] and the coupling constant calculations were carried out with ACES II.[23] All calculations were performed at the Ohio Supercomputer Center on the Cray X1 or the Itanium cluster.

Results and Discussion

Table 1 lists the computed electronic protonation energies and computed and experimental[24] proton affinities for the four nitrogen bases [HC≡N, HN=NH (cis and trans), NH$_3$, and H$_2$C=NH, numbers **1**, **2** (**c** and **t**), **3**, and **4**, respectively] and the three phosphorus bases (H$_2$C=PH, PH$_3$, and H$_3$CPH$_2$, numbers **5**, **6**, and **7**, respectively) from which complexes with N−H$^+$−P hydrogen bonds have been formed. The computed proton affinities (PAs) of these bases are in acceptable agreement with the experimental PAs except for a 5 kcal/mol underestimation of the proton affinity of N$_2$H$_2$.

Structures and Binding Energies. Table 2 lists P−N, N−H, and P−H distances and binding energies of proton-bound complexes formed between a nitrogen and a phosphorus base. The complexes are identified as **d**−**a**, where **d** is the proton-

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

		$-\Delta E_e$	$-\Delta H^{298}$ (calcd)	$-\Delta H^{298}$ (exptl)[a]
		Nitrogen Bases		
1	HC≡N	173.8	167.8	170.4
2	HN=NH trans	189.4	182.1	
	HN=NH cis	195.1	187.4	192.
3	NH$_3$	210.6	202.5	204.0
4	H$_2$C=NH	213.1	205.4	203.8
		Phosphorus Bases		
5	H$_2$C=PH	184.3	179.8	
6	PH$_3$	193.1	187.3	188.
7	H$_3$C−PH$_2$	209.3	203.8	203.5

[a] Reference 24.

TABLE 2: Electronic Binding Energies (kcal/mol), P−N, N−H, and P−H Distances (Å), and FC Terms (Hz) for One- and Two-Bond Spin−Spin Coupling Constants for Complexes with Essentially Linear N−H$^+$−P Hydrogen Bonds

Complexes Involving H$_3$CPH$_3^+$ and H$_3$CPH$_2$

ID	Δ*E*	*R*(P−N)	*R*(P−H)	^{2h}J(P−N)	^1J(P−H)	^{1h}J(H−N)
			P−H$^+$···N Hydrogen Bonds			
7−4	15.9	3.265	1.450	−79.6	514.6	9.5
7−3	14.6	3.316	1.446	−65.1	515.1	8.1
7−2t	8.2	3.463	1.419	−45.1	509.2	7.1
7−1	13.3	3.445	1.406	−37.5	521.4	7.1

ID	Δ*E*	*R*(N−P)	*R*(N−H)	^{2h}J(N−P)	^1J(N−H)	^{1h}J(H−P)
			N−H$^+$···P Hydrogen Bonds			
4−7	18.1	3.251	1.064	−86.1	−86.3	−11.7
3−7	18.9	3.273	1.070	−84.5	−67.5	−13.1

Complexes Involving PH$_4^+$ and PH$_3$

ID	Δ*E*	*R*(P−N)	*R*(P−H)	^{2h}J(P−N)	^1J(P−H)	^{1h}J(H−N)
			P−H$^+$···N Hydrogen Bonds			
6−2t	10.5	3.304	1.448	−75.9	524.4	9.2
6−1	15.4	3.355	1.415	−53.8	552.4	9.0

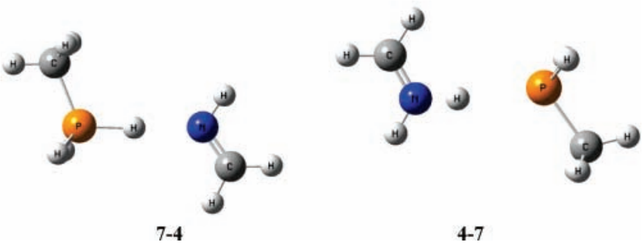
ID	Δ*E*	*R*(N−P)	*R*(N−H)	^{2h}J(N−P)	^1J(N−H)	^{1h}J(H−P)
			N−H$^+$···P Hydrogen Bonds			
4−6	13.8	3.312	1.050	−71.0	−89.4	−17.2
3−6	14.5	3.326	1.056	−69.8	−70.1	−18.3
2c−6	17.5	3.188	1.089	−105.9	−91.9	1.0
2t−6	18.4	3.206	1.081	−92.6	−84.8	−6.8

Complexes Involving H$_2$CPH$_2^+$ and H$_2$C=PH

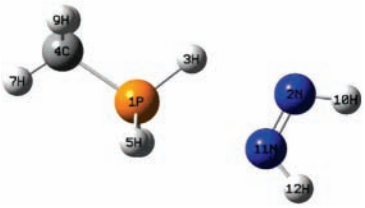
ID	Δ*E*	*R*(P−N)	*R*(P−H)	^{2h}J(P−N)	^1J(P−H)	^{1h}J(H−N)
			P−H$^+$···N Hydrogen Bonds			
5−1	16.2	3.281	1.426	−81.7	692.2	10.4

ID	Δ*E*	*R*(N−P)	*R*(N−H)	^{2h}J(N−P)	^1J(N−H)	^{1h}J(H−P)
			N−H$^+$···P Hydrogen Bonds			
4−5	12.8	3.319	1.044	−70.4	−90.4	−20.3
3−5	13.6	3.333	1.051	−69.2	−70.9	−21.5
2c−5	16.1	3.203	1.075	−105.1	−95.2	−8.1
2t−5	17.0	3.215	1.071	−92.9	−87.3	−13.8

SCHEME 1



SCHEME 2: “Cyclic” 7−2c



donor ion formed by protonation of base **d** in Table 1, and **a** is the proton-acceptor base. Thus, complex **4−7** has $H_2CNH_2^+$ (**4**) as the proton donor and H_3CPH_2 (**7**) as the proton acceptor. Complex **7−4** has $H_3CPH_3^+$ (**7**) as the proton-donor ion and H_2CNH (**4**) as the proton acceptor. In Table 2, the complexes are grouped by phosphorus base according to decreasing protonation energy. Under each base, complexes in which the protonated phosphorus base is the donor ion are listed first. Within this group, the complexes are given in order of decreasing protonation energy of the proton-acceptor nitrogen base. Complexes in which the same phosphorus base is the proton acceptor molecule are listed next, again in order of decreasing protonation energy of the protonated nitrogen base that acts as the proton donor ion.

The first set of complexes reported in Table 2 are those involving the strongest phosphorus base CH_3PH_2 and its protonated ion $CH_3PH_3^+$ (**7**). CH_3PH_2 can be protonated in the presence of all of the nitrogen bases, and it then acts as the proton-donor ion in the resulting complexes. There are several notable features about these complexes, perhaps the most interesting of which is the existence of isomers with open structures along the proton-transfer coordinate on three but only three potential surfaces, namely, **7** with **4**, **7** with **3**, and **6** with **2t**. The isomers **7−4** and **4−7** are shown in Scheme 1. From Table 1, it can be seen that the protonation energy of **7** (209.3 kcal/mol) is similar to the protonation energies of **4** and **3** (213.1 and 210.6 kcal/mol, respectively), differing from both by less than 4 kcal/mol. Similarly, the protonation energies of **6** and **2t** are 193.1 and 189.4 kcal/mol, respectively. Along the proton-transfer coordinate, the isomer with the protonated nitrogen base lies lower in energy on the potential surface than the isomer with the protonated phosphorus base. Thus, **4−7** is 5.9 kcal/mol lower in energy than **7−4**, **3−7** is 5.6 kcal/mol lower in energy than **7−3**, and **2t−6** is 4.2 kcal/mol lower in energy than **6−2t**. Moreover, the more stable isomer which has the protonated nitrogen base as the donor ion also has the greater binding energy relative to the corresponding isolated monomers, as evident from Table 2. This is in contrast to isomers found along the proton-transfer coordinate for complexes with P−H$^+$−P hydrogen bonds. For these, the isomer in which the stronger base is protonated lies lower on the potential surface but is less stable with respect to the isolated monomers. For example, PH_3 and H_3CPH_2 have protonation energies of 193.1 and 209.3 kcal/mol, respectively. The complex $H_3CPH_3^+$:PH_3 in which the stronger base is protonated lies 10.9 kcal/mol lower in energy on the potential surface than the isomer PH_4^+:$PH_2(CH_3)$ in which the weaker base is protonated. However, the binding energy of PH_4^+:$PH_2(CH_3)$ (12.9 kcal/mol) is significantly greater than that of $H_3CPH_3^+$:PH_3 (7.6 kcal/mol).[2] The relative stabilities of the two isomers with P−H$^+$−P hydrogen bonds can be rationalized by noting that the more stable isomer has the stronger conjugate acid as the donor and the stronger base as the acceptor. Obviously, this same explanation does not apply to isomers with N−H$^+$−P hydrogen bonds, for which the isomer with the protonated nitrogen base as the donor is more stable, irrespective of the relative protonation energies of the two bases. This suggests that other factors also play a role in determining the relative stabilities of these complexes.

For complexes with **7** as the proton donor, the binding energies would be expected to decrease in order of decreasing base strength (as measured by the protonation energies) **7−4** > **7−3** > **7−2** > **7−1**. However, **7−2t**, not **7−1**, is the least stable complex. All of these complexes are stabilized by essentially linear P−H$^+$···N hydrogen bonds, but complexes **7−4**, **7−3**, and **7−1** also benefit from a favorable alignment of the P−H bond dipole moment with the dipole moment of the acceptor nitrogen base. Since HN═NH trans (**4t**) has no dipole moment, this additional stabilizing interaction is absent. Complex **7−2t** has a longer P−N distance as well.

Another interesting feature of the set of complexes with **7** as the proton donor ion is the absence of a complex with **2c** as the proton acceptor. During the optimization of this complex, its structure changed from an open structure with one P−H$^+$ bond as the proton donor to a cyclic structure stabilized by distorted nonlinear hydrogen bonds, as illustrated in Scheme 2. Complex **6−2c** is also missing from complexes with PH_4^+ as the proton donor for the same reason.

It is generally accepted that the closer the proton affinities of D (protonated donor base) and A (the acceptor base), the stronger the binding of a complex, with the strongest binding occurring when there is no difference between the proton affinities, that is, when D and A are the same.[25−30] However, it appears that such a generalization is restricted to complexes formed when the atoms involved in hydrogen bonding in D and A are from the second period, and there is only one minimum along the proton-transfer coordinate. Thus, the protonation energies of PH_3 and H_3CPH_2 are 193 and 209 kcal/mol, respectively, but the complex PH_4^+:$PH_2(CH_3)$ has a binding energy of 12.9 kcal/mol and is more stable than the protonated homodimer PH_4^+:PH_3 with a binding energy of 9.3 kcal/mol.[2] Similarly, the protonation energies of PH_3 and NH_3 are 193 and 211 kcal/mol, but the binding energy of NH_4^+:PH_3 is 14.5 kcal/mol, which is again greater than that of the protonated homodimer PH_4^+:PH_3. However, all of these complexes are significantly less stable than the protonated homodimer NH_4^+:NH_3.

Comparisons of Proton-Transfer Coordinates. It is interesting to compare the proton-transfer coordinates for proton-bound complexes with N−H$^+$−N, N−H$^+$−P, and P−H$^+$−P hydrogen bonds and to ask what determines whether or not single or double minima exist along this coordinate. There are two factors which may come into play: the difference between the protonation energies (or PAs) of the two bases and the intermolecular distance. Except for protonated homodimers with two equivalent minima, complexes with N−H$^+$−N hydrogen bonds have a single minimum along the proton-transfer coordinate, irrespective of the difference between the protonation energies of the two bases. They also have relatively short N−N distances, ranging from about 2.5 to 3.1 Å.[1] In contrast,

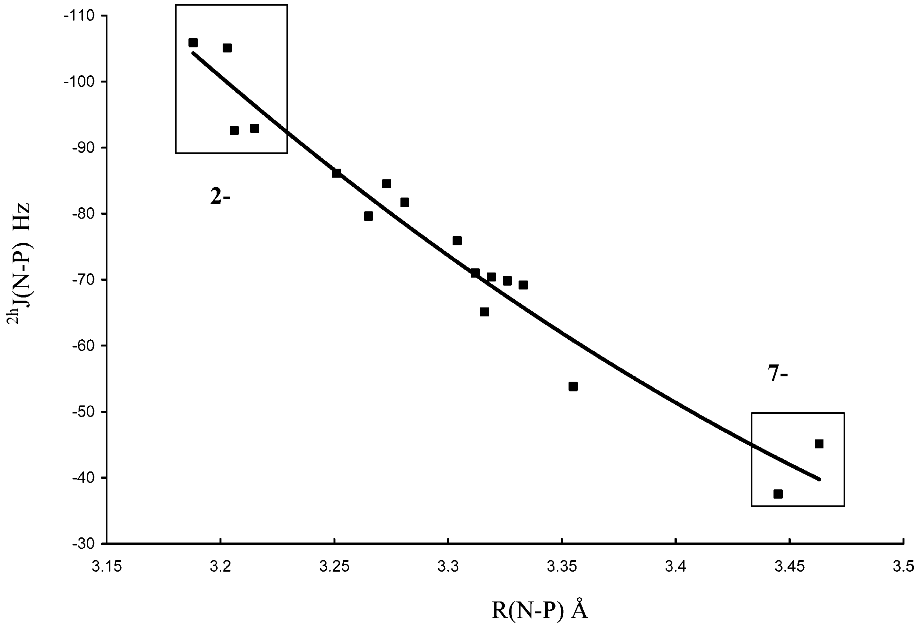


Figure 1. ^{2h}J(N−P) vs the N−P distance for complexes with N−H$^+$−P hydrogen bonds. The box at the upper left contains complexes with **2c** or **2t** as the donor ion; that on the lower right has **7** as the donor ion.

complexes with P−H$^+$−P hydrogen bonds have much longer intermolecular distances, which range from 3.7 to 4.0 Å, undoubtedly a reflection of the larger atomic radius of P compared to N. Double minima are found at the shorter end of this range, even when the protonation energies differ by as much as 16 kcal/mol. However, when the difference in the protonation energies of the two phosphorus bases is 23 kcal/mol, only a single minimum is found along this coordinate.[2] Complexes with N−H$^+$−P hydrogen bonds have intermediate N−P distances which range from 3.2 to 3.5 Å. Double minima are found only when the protonation energies of the nitrogen and phosphorus bases differ by about 4 kcal/mol or less; if the difference is 5 kcal/mol or more, only a single minimum exists. Thus, intermolecular distances and relative protonation energies are factors that determine the nature of the proton-transfer coordinate in proton-bound complexes involving N and P bases.

Spin−Spin Coupling Constants. *FC Term versus J.* Table S1 of the Supporting Information lists the total one- and two-bond spin−spin coupling constants and the components of *J* for complexes **4−6** and **3−6** with N−H$^+\cdots$P hydrogen bonds and for complexes **5−1** and **6−1** with P−H$^+\cdots$N hydrogen bonds. For complexes **4−6** and **3−6**, the FC terms are excellent approximations to ^{2h}J(N−P) and ^{1}J(N−H). Although the FC term overestimates ^{1h}J(H−P) by 2.6 Hz because of the contribution of the SD term, it is nevertheless an adequate approximation to ^{1h}J(H−P). The corresponding FC terms are also excellent approximations to ^{2h}J(N−P), ^{1}J(P−H), and ^{1h}J(H−N) for complexes **5−1** and **6−1**. In the following two sections, total coupling constants will be approximated by the corresponding FC terms.

Two-Bond Spin−Spin Coupling Constants. The two-bond spin−spin coupling constants ^{2h}J(N−P) for the complexes investigated in this study are reported in Table 2 and are always negative. Since the magnetogyric ratio of ^{15}N is negative while that of ^{31}P is positive, all reduced two-bond coupling constants ^{2h}K(N−P) are positive and therefore in agreement with the previously stated generalization concerning the signs of two-bond coupling constants across hydrogen bonds.[31] Within a subgroup of complexes, ^{2h}J(N−P) decreases in absolute value as the N−P distance increases, the single exception being a reversal involving **7−2t** and **7−1**. On the basis of previous studies, a correlation between the hydrogen-bond distance and the two-bond spin−spin coupling constant is expected and is shown graphically in Figure 1. The curve is a second-order curve with a correlation coefficient of 0.95. In Figure 1, the four points found at the shortest N−P distances belong to complexes with the conjugate acid of the weakest nitrogen base that can be protonated as the donor ion (**2c** and **2t** with **5** and **6**), while the two points at the longest distances belong to complexes with the conjugate acid of the strongest base as the proton donor to a weak base (**7−2t** and **7−1**). However, the complexes in-between cannot be similarly grouped only by proton-donor ion. This is in contrast to complexes with P−H$^+$−P hydrogen bonds, in which case the points along this curve are grouped by the proton-donor ion.[2] The binding energies of these complexes do not correlate with either the N−P distance or ^{2}J(N−P).

It is unfortunate that there are no experimental coupling constants available for coupling across N−H$^+$−P hydrogen bonds. However, a three-bond N−P coupling ^{3h}J(N−P) across a N−H$\cdots$O═P hydrogen bond in a protein:nucleotide complex has been measured experimentally by Mishima et al.[32] These investigators observed an appreciable N−P coupling constant for only one of five complexes investigated and speculated that a linear N−H$\cdots$O═P arrangement was required to make ^{3h}J(N−P) observable. We computed values of ^{3h}J(N−P) in models for the experimental systems and confirmed the importance of a linear or nearly linear N−H$\cdots$O═P arrangement.[33]

One-Bond Spin−Spin Coupling Constants. The one-bond spin−spin coupling constants ^{1}J(N−H), ^{1h}J(H−P), ^{1}J(P−H), and ^{1h}J(H−N) are reported in Table 2. ^{1}J(N−H) and ^{1}J(P−H) for the isolated ions are given in Table S2 of the Supporting Information. It is apparent from these data that all one-bond coupling constants ^{1}J(N−H) are negative and that all ^{1}J(P−H) are positive. Since the magnetogyric ratio of ^{1}H is positive, all reduced one-bond coupling constants ^{1}K(X−H) are positive, in agreement with the Dirac vector model[34] and with the previous generalization for ^{1}J(X−H) in hydrogen-bonded complexes.[35]

The one-bond coupling constants in complexes with N−H$^+$−P hydrogen bonds exhibit some patterns that are similar to those

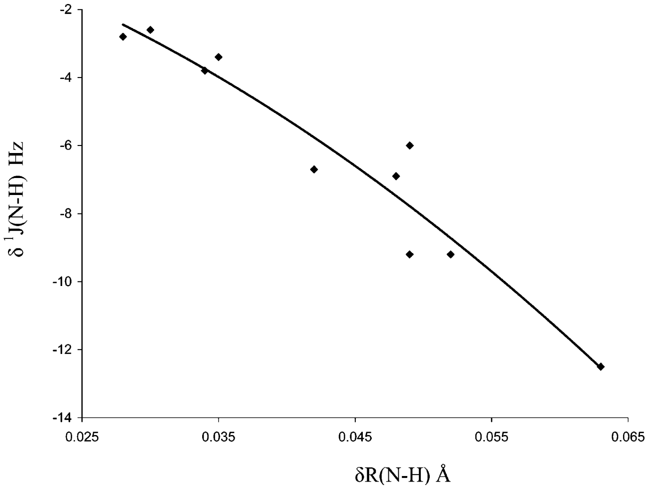


Figure 2. The change in ^{1}J(N−H) versus the change in the N−H distance for complexes with N−H^{+}···P hydrogen bonds.

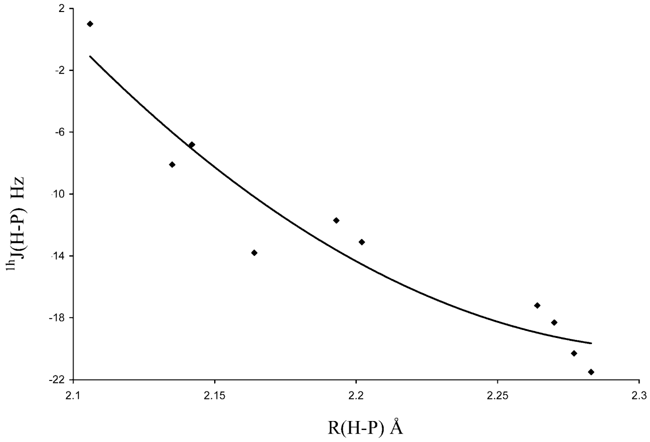


Figure 3. ^{1h}J(H−P) versus the H−P distance for complexes with N−H^{+}···P hydrogen bonds.

observed for complexes with N−H^{+}−N and P−H^{+}−P hydrogen bonds and some patterns that are different. From Tables 2 and S2, it can be seen that ^{1}J(N−H) decreases in absolute value as the N−H distance increases upon formation of N−H^{+}−P hydrogen bonds. The curve describing these changes has a correlation coefficient of 0.93 and is given in Figure 2. The correlation coefficient improves to 0.97 when these variables are plotted only for complexes with sp^{2} hybridized N atoms. Improved correlations between changes in ^{1}J(N−H) and changes in the N−H distance were observed previously for complexes with N−H^{+}−N hydrogen bonds when the complexes were grouped according to the hybridization of the nitrogen donor ion.[1] Insufficient data preclude a similar analysis for complexes with sp^{3} nitrogens that form N−H^{+}−P hydrogen bonds. There is also a correlation between ^{1h}J(H−P) and the H−P distance in these complexes, as illustrated by the curve in Figure 3 which has a correlation coefficient of 0.92. The correlation here is in contrast to the lack of correlation between ^{1h}J(H−P) and the H···P distance for complexes stabilized by P−H^{+}···P hydrogen bonds.[2] Also, the very small but positive value (1 Hz) of ^{1h}J(H−P) for complex **2c−6** indicates that the hydrogen bond in this complex has sufficient proton-shared character to change the sign of this coupling constant. With this exception, the remaining complexes have negative values of ^{1h}J(H−P), ranging from −8.1 to −21.5 Hz, an indication that these N−H^{+}···P hydrogen bonds are traditional.

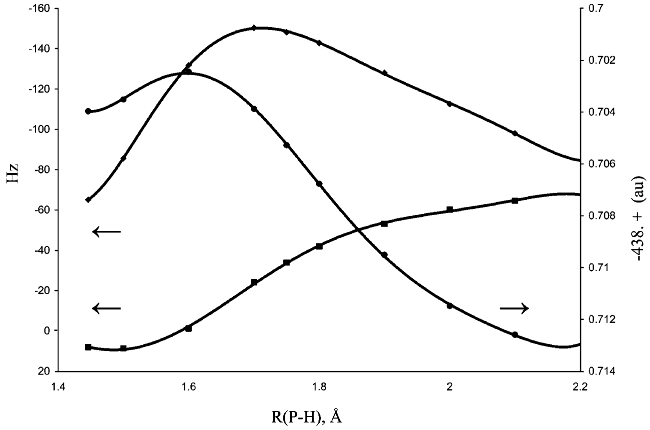


Figure 4. ^{2h}J(P−N) (◆), ^{1h}J(H−N) (■), and total energy E (●) along the proton-transfer coordinate from $(CH_3)H_2P{-}H^{+}\cdots NH_3$ (**7−3**) to $(CH_3)H_2P\cdots{}^{+}H{-}NH_3$ (**3−7**).

The situation is quite different with respect to one-bond coupling constants for complexes with P−H^{+}···N hydrogen bonds. In contrast to ^{1}J(N−H) which always decreases in absolute value as the N−H distance increases in N−H^{+}···P hydrogen bonds, ^{1}J(P−H) increases as the P−H distance increases when P−H^{+}···N hydrogen bonds are formed, although the magnitudes of the changes in these two variables do not appear to correlate. A plausible reason for the lack of correlation will be given below. A similar situation was also observed for complexes stabilized by P−H^{+}···P hydrogen bonds.[2] Moreover, although N−P and H···P distances are obviously correlated, ^{1h}J(H−P) does not appear to correlate with the H···P distance. The negative values for ^{1h}J(H−P) are indicative of traditional hydrogen bonds.[36]

Coupling Constants along the Proton-Transfer Coordinate. As noted above, double minima have been found along the proton-transfer coordinate for protonated complexes formed from CH_3PH_2 (**7**) with $H_2C{=}NH$ (**4**) and NH_3 (**3**) and PH_3 (**6**) with N_2H_2 (**2t**). How do the one- and two-bond coupling constants change along this coordinate? Figure 4 shows the variation of ^{2h}J(P−N) and ^{1h}J(H−N) as a function of the P−H distance for the **7**,**3** pair. As proton transfer occurs, hydrogen-bond type changes from traditional to proton-shared and back to traditional. This change is accompanied by a change in sign of ^{1h}J(H−N) when the P−H and P−N distances are about 1.60 and 3.08 Å, respectively. On the basis of the maximum absolute value of ^{2h}J(P−N), a quasi-symmetric proton-shared hydrogen bond exists when the P−H and P−N distances are about 1.70 and 3.00 Å, respectively. As proton transfer continues, what was ^{1}J(P−H) changes sign at P−H and P−N distances of 2.05 and 3.15 Å, respectively, indicating the formation of a traditional N−H^{+}···P hydrogen bond. ^{1}J(P−H), which is not plotted in Figure 4, spans a large range of values, decreasing from 515 Hz in **7−3** to −13.1 Hz in **3−7**.

In addition to illustrating the changes in coupling constants along the proton-transfer coordinate, Figure 4 also shows the change in the total energy (−438.7*xx* au, right axis) along this coordinate. The transition state for proton transfer from CH_3PH_2 to NH_3 (**7−3** goes to **3−7**) occurs nearer the less stable isomer, as expected, with a barrier to proton transfer of about 1 kcal/mol. The transition structure is found earlier along the proton-transfer coordinate than the structure with the quasi-symmetric proton-shared hydrogen bond.

As noted above, changes in ^{1}J(P−H) along the proton-transfer coordinate are not shown in Figure 4 because of the large range of values. However, if the variation of ^{1}J(P−H) near the equilibrium structure **7−3** is examined, some insight into the lack of correlation between changes in ^{1}J(P−H) and changes in the P−H distance in these complexes can be gained. For the isolated monomer $H_3CPH_3^+$, ^1J(P−H) is 469 Hz at a P−H distance of 1.394 Å. Upon complexation, ^1J(P−H) increases to 515 Hz as the P−H distance increases to 1.446 Å. At a P−H distance of 1.5 Å, ^1J(P−H) then decreases to 493 Hz, but it is still greater than the value for the isolated monomer. Finally, at a P−H distance of 1.6 Å, ^1J(P−H) is less than the monomer value, at 369 Hz. Thus, there is a maximum in the curve for ^1J(P−H) versus the P−H distance for complex **7−3** in the distance interval between 1.4 and 1.5 Å. This implies that within this interval, ^1J(P−H) can have the same value for two different P−H distances. Moreover, since all of these complexes have traditional hydrogen bonds, all P−H distances lie within this range and are so far removed from distances in complexes with proton-shared character that ^1J(P−H) does not decrease below the monomer values in any of these complexes. As a result, a correlation between changes in ^1J(P−H) and changes in P−H distances is not observed.

Conclusions

The calculations carried out in this study of complexes with N−H$^+$−P hydrogen bonds support the following statements.

1. A single minimum is usually found along the proton-transfer coordinate. However, double minima exist when the difference between the protonation energies of the N and P bases is less than 4 kcal/mol. The complex that has the protonated nitrogen base as the donor ion lies lower on the potential surface and also has a greater binding energy than the isomer in which the protonated phosphorus base is the donor ion.

2. With respect to the nature of the proton-transfer coordinate, complexes with N−H$^+$−P hydrogen bonds are intermediate between those with N−H$^+$−N hydrogen bonds which have only a single minimum and those with P−H$^+$−P hydrogen bonds that commonly have double minima. Whether single or double minima exist depends on the intermolecular distance and the difference between the protonation energies of the two proton-bound bases.

3. Values of ^{2h}J(N−P) are always negative [^{2h}K(N−P) is always positive] and are strongly correlated with the N−P distance irrespective of whether the hydrogen bond is N−H$^+$···P or P−H$^+$···N. No correlation is found between coupling constants and binding energies.

4. For complexes with N−H$^+$···P hydrogen bonds, changes in ^1J(N−H) correlate with changes in N−H distances upon complex formation, and values of ^{1h}J(H−P) correlate with H−P distances. These correlations are similar to those found for one-bond coupling constants and corresponding distances for complexes stabilized by N−H$^+$−N hydrogen bonds.

5. For complexes with P−H$^+$···N hydrogen bonds, ^1J(P−H) always increases upon complex formation, but changes in ^1J(P−H) do not correlate with changes in P−H distances. No correlation exists between ^{1h}J(H−N) and H−N distances. Thus, the characteristics of these one-bond coupling constants resemble those for one-bond couplings in complexes with P−H$^+$···P hydrogen bonds.

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Supporting Information Available: Values of PSO, DSO, FC, and SD terms for complexes **4−6**, **3−6**, **5−1**, and **6−1**; N−H and P−H distances, FC terms, and ^1J(X−H) for ions; full references 22 and 23. This material is available free of charge via the Internet at http://pubs.acs.org.

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