Influence of Hydrogen Bonds on the P···P Pnicogen Bond

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Ⓢ *Supporting Information*

ABSTRACT: Ab initio MP2/aug'-cc-pVTZ calculations have been carried out to investigate the influence of F—H···F hydrogen bonds on the P···P pnicogen bond in complexes nFH:$(PH_2F)_2$ for $n = 1-3$. The formation of F—H···F hydrogen bonds leads to a shortening of the P—P distance, a lengthening of the P—F distance involved in the hydrogen bond, a strengthening of the P···P interaction, and changes in atomic populations, NMR ^{31}P chemical shieldings, and ^{1p}J(P—P) coupling constants. The magnitude of these changes depends on the number of FH molecules and their positions in the complex and are relatively modest except for complexes 2FH:$(PH_2F)_2$ and 3FH:$(PH_2F)_2$ that have all FH molecules hydrogen bonded to the same F-atom. For these two complexes, ^{1p}J(P—P) decreases as the P—P distance decreases and approaches the value of ^1J(P—P) for P_2H_4. The dramatic changes in these two complexes reflect the changing nature of the hydrogen bonds and the pnicogen bond. Thus, the complex 3FH:$(PH_2F)_2$ acquires ion-pair character represented as $[3(FH)F^-:(H_2P—PH_2F)^+]$, and the P···P pnicogen bond acquires significant covalent character. These changes are observed to a lesser extent in 2FH:$(PH_2F)_2$.

INTRODUCTION

The pnicogen bond has been recognized as a new and important type of intermolecular interaction.[1−3] In a landmark paper, Hey−Hawkins et al. carried out a high-level theoretical study of the pnicogen P···P bond in a series of complexes and described this bond as a new molecular linker.[4] Recently, we examined substituent effects on the structures, binding energies, and spin−spin coupling constants of pnicogen homodimers, $(PH_2X)_2$[5] and $(PHFX)_2$ with C_i symmetry.[6] This latter study was followed by a comparison of these same properties in corresponding homo-(C_i) and heterochiral (C_2) dimers, to determine if these properties would be useful for chiral discrimination.[7]

Solimannejad et al. have described the N···P pnicogen bond involving the interaction of HSN with PH_3 and other phosphines.[8] These studies were further extended by Scheiner, who examined the bonding characteristics of complexes formed between substituted PH_3 and NH_3.[9−11] We also investigated the N···P pnicogen bond in a series of complexes derived from monosubstituted PH_3 and NH_3 molecules, represented as $H_2XP:NXH_2$, for X = H, CH_3, NH_2, OH, F, and Cl, and selected complexes $H_2XP:NX'H_2$, that have different X bonded to N and P.[12] We presented the structures and binding energies of these complexes, examined their bonding characteristics, and characterized selected IR and NMR properties. In all of these complexes as well as in the complexes $(PH_2X)_2$ and $(PHFX)_2$, a nearly linear Z−P···P−Z alignment is found, for Z = H, F, or A, with A the atom of X directly bonded to P. Scheiner has further extended his studies of intermolecular interactions to Cl···N and S···N bonds and examined the effects of substituents bonded to Cl and S on the strengths of these bonds.[13]

In the present article, we turn our attention to pnicogen-bonded complexes nFH:$(PH_2F)_2$ in which the F-atoms of $(PH_2F)_2$ are hydrogen bonded to one or more FH molecules. We ask for the first time what effect hydrogen bond formation has on the structures of these complexes, the strength and nature of the P···P pnicogen bond, ^{31}P chemical shieldings, and ^{31}P−^{31}P spin−spin coupling constants. In this paper, we present our answers to this question.

METHODS

The structures of complexes nFH:PH_2F and nFH:$(PH_2F)_2$ for $n = 1-3$ were optimized at second-order Møller−Plesset perturbation theory (MP2)[14−17] with the aug'-cc-pVTZ basis set,[18] which is the Dunning aug-cc-pVTZ basis set[19,20] with diffuse functions removed from H-atoms. Frequencies were computed to identify equilibrium and transition structures. Two structures needed for energetic comparisons were optimized with constraints, and these will be discussed below. All optimization calculations were performed using the Gaussian 09 program.[21]

The electron densities of these complexes have been analyzed employing the Atoms in Molecules (AIM) methodology[22,23] with the AIMAll program.[24] The Natural Bond Orbital (NBO) method[25] has been employed to obtain atomic charges and to analyze charge-transfer interactions between occupied and virtual orbitals using the NBO-3 program.

Absolute chemical shieldings have been calculated within the GIAO approximation[26] at MP2/aug'-cc-pVTZ. Coupling constants were evaluated using the equation-of-motion coupled

cluster singles and doubles (EOM-CCSD) method in the CI (configuration interaction)-like approximation,[27,28] with all electrons correlated. For these calculations, the Ahlrichs[29] qzp basis set was placed on ^{19}F, and the qz2p basis set on ^{31}P and the hydrogen-bonded [1]H-atoms of FH molecules. The Dunning cc-pVDZ basis set was placed on the H-atoms bonded to P. Only one-bond [31]P−[31]P coupling constants across the pnicogen bond are reported in this paper. It was demonstrated previously that the Fermi-contact term (FC) is by far the dominant term for P−P coupling and is an excellent approximation to total ^{1p}J(P−P) in pnicogen dimers $(PH_2X)_2$[5] and $(PFHX)_2$.[6] The FC term will be used to approximate ^{1p}J(P−P). The EOM-CCSD calculations were performed using ACES II[30] on the IBM Cluster 1350 (Glenn) at the Ohio Supercomputer Center.

RESULTS AND DISCUSSION

The results of this study have been subdivided into four sections. The first section presents a summary of the complexes nFH:PH$_2$F and nFH:(PH$_2$F)$_2$ and their designations. In addition, a brief discussion is included of the attempts to locate equilibrium structures and the problems encountered with two particular structures required as reference structures, which are nonequilibrium structures on their potential surfaces. The second section provides a discussion of the geometries of these complexes and the binding energies of the P···P bond. The third section presents the electronic properties of the complexes as described by AIM and NBO methodologies. In the fourth section computed NMR ^{31}P chemical shieldings and [31]P−[31]P spin−spin coupling constants are discussed. In each section special attention is given to the effect of the presence of one or more F−H···F hydrogen bonds on the properties of the P···P pnicogen bond.

General Description of Complexes and Optimization Challenges. Possible positions of the FH molecule acting as a hydrogen-bond donor to an F-atom of PH$_2$F have been denoted as A, B, and C, as illustrated in Scheme 1. These

Scheme 1
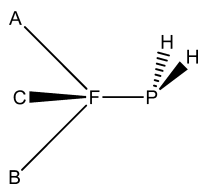
orientations are cis, trans, and essentially perpendicular, respectively, to the bisector of the H−P−H angle. In order to distinguish complexes in which FH molecules are bonded to the same or different PH$_2$F molecules, a prime has been added to the position (A′, B′, C′) when the interaction is with the second PH$_2$F molecule. For complexes having a different number of FH molecules bonded to the two PH$_2$F molecules, (1) indicates the PH$_2$F molecule with the greater number of hydrogen bonds and (2) refers to the molecule with fewer F−H···F bonds.

In addition to the A, B, C designation to indicate the positions of the FH molecules, a second field has been used to indicate the number of molecules in the cluster. Thus, "b", "t", "q", and "p" correspond to binary, ternary, quaternary, and penternary (quinternary) clusters, respectively. For example, pABC′ corresponds to a penternary cluster (two PH$_2$F and
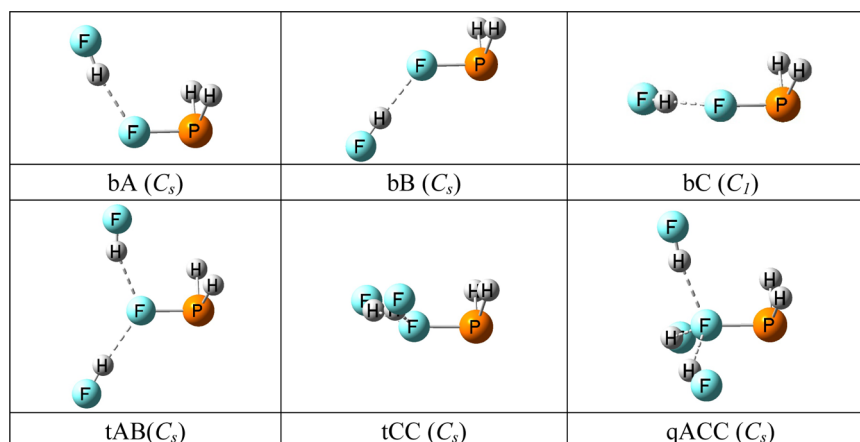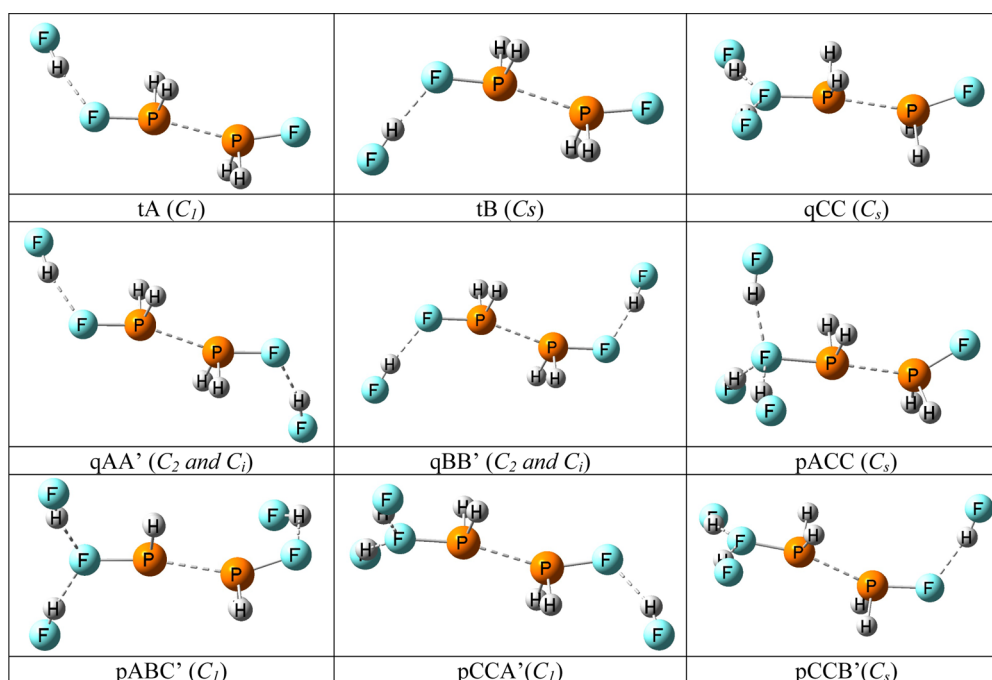
three FH molecules), with two of the FH molecules interacting with PH$_2$F(1) in positions A and B and the third FH molecule interacting with PH$_2$F(2) at position C. qBB′ indicates a complex with one FH molecule bonded to PH$_2$F(1) at position B and the second bonded to PH$_2$F(2) also at position B. qCC indicates a quaternary complex with two FH molecules bonded to the same F at equivalent positions C above and below the symmetry plane of the complex. The structures of all complexes are illustrated in Figures 1 and 2.

Three structures have been optimized for the FH:PH$_2$F binary complex, bA, bB, and bC. bA and bB are equilibrium structures, but bC is not. It was optimized under the constraint that the FH molecule and the P−F bond define a plane which is perpendicular to the plane defined by the P−F bond and the H−P−H bisector. Although bC is not an equilibrium structure, it is needed for comparison purposes with complexes nFH:(PH$_2$F)$_2$ in which an FH molecule occupies position C. Complex bC is one of only two complexes included in this study that is not a minimum-energy equilibrium structure on its potential surface. It has a binding energy of 18.0 kJ mol^{-1}, similar to that of bB (17.9 kJ mol^{-1}) but less than that of bA (19.1 kJ mol^{-1}).

Systematic searches were carried out of the potential surface for complexes 2FH:PH$_2$F with FH molecules located at A, B, C. Only two equilibrium structures, tAB (30.2 kJ mol^{-1}) and tCC (30.1 kJ mol^{-1}), were found. The 2FH:(PH$_2$F)$_2$ surface was searched both with and without symmetry, and ten conformations were identified as stationary points. However, only five of these correspond to equilibrium structures.

All attempts to locate a minimum-energy structure for three FH molecules interacting with a single PH$_2$F failed. However, such a configuration has been found to be an equilibrium structure when the (PH$_2$F)$_2$ dimer is present (pACC). Therefore, for comparison purposes, a quaternary complex qACC (34.9 kJ mol^{-1}) has been generated from pACC by freezing the F−F−P angle to prevent migration of FH to P and then optimizing the remaining coordinates. In addition to pACC, three other equilibrium structures, pABC′, pCCA′, and pCCB′, exist on the 3FH:(PH$_2$F)$_2$ surface.

Structures and Binding Energies. *Structures.* The geometries of complexes nFH:PH$_2$F and nFH:(PH$_2$F)$_2$ with n = 1, 2, or 3 FH molecules are reported in Table S1 of the Supporting Information and illustrated in Figures 1 and 2, respectively, where they are identified by their code. Table 1 reports the P−P distances in these complexes. Hydrogen bond formation of FH with (PH$_2$F)$_2$ leads to a decrease in the P−P distance. Moreover, this distance decreases as the number of F−H···F hydrogen bonds increases. Thus, the P−P distance of 2.47 Å in the parent complex decreases to 2.42 Å in the ternary complexes with one FH molecule. The presence of two hydrogen bonds yields a range of distances between 2.36 and 2.40 Å in the quaternary complexes, and three hydrogen bonds give a range of 2.30 to 2.36 Å in the penternary complexes. Complex qCC with two FH molecules bonded to F(1) has the shortest P−P distance among the quaternary complexes, but the remaining four complexes have similar P−P distances. Likewise, pACC with three FH molecules bonded to F(1) has the shortest P−P distance, and the remaining complexes with two FH bonded to F(1) and one FH bonded to F(2) have similar P−P distances. Thus, the shortest P−P distances among the quaternary and penternary complexes correspond to complexes in which FH molecules are hydrogen bonded only to F(1).

Figure 1. Complexes nHF:PH$_2$F.

Figure 2. Complexes nHF:(PH$_2$F)$_2$.

Although the focus of this article is on the P···P bond, it should be noted that hydrogen bonding has a significant effect on the P(1)–F(1) distance when two or three FH molecules are hydrogen bonded only to F(1). In the complexes qCC and pACC, the P(1)–F(1) distance increases by 0.11 and 0.21 Å, respectively, while in all other complexes the change is less than 0.035 Å. A closer examination of the structure of complex pACC suggests that the three FH molecules hydrogen bonded to F(1) resemble an anionic cluster 3FH:F$^-$ with approximately local C_{3v} symmetry. Consequences of this structure will be discussed below.

Binding Energies. In order to assess the effect of hydrogen bond formation at F on the strength of the P···P pnicogen bond, binding energies of complexes nFH:(PH$_2$F)$_2$ have been computed relative to the energies of the two fragments that form the P···P bond. Using complexes tA and pABC′ as examples,

$$\Delta E(tA) = -[E(tA) - E(bA) - E(PH_2F)] \quad (1)$$

$$\Delta E(pABC') = -[E(pABC') - E(tAB) - E(bC)] \quad (2)$$

That is, the binding energy is the negative of the reaction energy for the formation of the complex. The computed P···P binding energies are also reported in Table 1.

The binding energy of the complex (PH$_2$F)$_2$ is 34.0 kJ mol^{-1}. The addition of one, two, or three FH molecules hydrogen bonded to the same or different F-atoms of (PH$_2$F)$_2$ always increases the strength of the pnicogen bond, but the number and positions of the FH molecules determine the extent of the increase. From Table 1 it can be seen that addition of one FH molecule increases the binding energies of tA and tB to 36.5 and 37.3 kJ mol^{-1}, respectively, with hydrogen bonding at position B slightly favored. If two FH molecules are bonded to the same F as in qCC, the binding energy increases to 44.1 kJ mol^{-1}. In contrast, hydrogen bonding the two FH molecules to two different F-atoms in qAA′ and qBB′ leads to binding energies which are similar to or slightly less than the binding energies of tA and tB. If three FH molecules form hydrogen bonds with the same F-atom as in pACC, the energy of the

Table 1. P−P Distances [R(P−P), Å], Changes in P−P Distances [δR(P−P)], Binding Energies of the P⋯P Pnicogen Bond [ΔE(P⋯P)] (kJ mol^{-1}), and Nonadditivities ($\delta\Delta E$, kJ mol^{-1}) for Complexes nFH:(PH$_2$F)$_2$

complex	R(P−P)	δR(P−P)^a	ΔE(P⋯P)^b	$\delta\Delta E^c$
(PH$_2$F)$_2$	2.471		33.97	
tA	2.425	−0.047	36.45	2.48
tB	2.422	−0.049	37.33	3.36
qCC^d	2.363	−0.108	44.09	4.09
qAA′(C$_2$)	2.401	−0.070	34.74	0.77
qAA′(C$_i$)	2.400	−0.072	34.86	0.89
qBB′(C$_2$)	2.395	−0.076	36.54	2.56
qBB′(C$_i$)	2.395	−0.076	36.54	2.62
pACC	2.301	−0.170	54.59	20.62
pABC′	2.353	−0.118	39.55	5.58
pCCA′	2.356	−0.115	38.74	4.77
pCCB′	2.354	−0.117	39.33	5.36

$^a\delta R$(P−P) = R(P−P) for nFH:(PH$_2$F)$_2$ − R(P−P) for (PH$_2$F)$_2$. $^b\Delta E$(P⋯P) = −[E(complex) − {$E_{(1)}$(nFH:PH$_2$F) + $E_{(2)}$(n′FH:PH$_2$F)}], where n and n′ indicate the number of FH molecules bonded to molecules (1) and (2), respectively, with $n \geq n$′ and $n + n' \leq 3$. $^c\delta\Delta E$ = −{ΔE[nFH:(PH$_2$F)$_2$] − $\Sigma_i\Delta E_i$(binary)}. ^{d}Not an equilibrium structure on the potential surface.

P⋯P bond increases to 54.6 kJ mol^{-1}. Bonding two FH molecules to F(1) and one FH to F(2) leads to complexes with binding energies of about 39 kJ mol^{-1}, which are only 2 kJ mol^{-1} greater than for tA and tB. It is noteworthy that the strength of the P⋯P bond in complexes with FH molecules bonded to both F(1) and F(2) varies from only 35 to 40 kJ mol^{-1}. In contrast, when two or three FH molecules are hydrogen bonded only to F(1), the pnicogen bond energy increases to 44 and 55 kJ mol^{-1}, respectively.

Although the emphasis in this paper is the energy of the P⋯P bond, it is appropriate to examine the nonadditivities of binding energies in these complexes, since there are two different types of relatively weak intermolecular interactions present. The extent to which such intermolecular interactions may be cooperative has been reviewed recently.[31] Table 1 reports the nonadditivities ($\delta\Delta E$), computed in the standard way as

$$\delta\Delta E = -\{\Delta E[n\text{FH: }(\text{PH}_2\text{F})_2] - \Sigma_i\Delta E_i(\text{binary})\} \quad (3)$$

where $\Delta E[n\text{FH:}(\text{PH}_2\text{F})_2]$ is the binding energy of the complex relative to the isolated monomers, and $\Sigma_i\Delta E_i$(binary) is the sum of the binding energies of all binary interactions in the complex. From Table 1 it can be seen that the nonadditivities are positive (synergistic); that is, the binding energy of the complex is greater than the sum of the binding energies of the corresponding binary complexes. Nonadditivities are less than 1 kJ mol^{-1} in the two isomers of qAA′ but are greater than 2.5 kJ mol^{-1} in the remaining complexes. It is interesting to note that the nonadditivity for qCC is less than that found for the penternary complexes, in contrast to the P⋯P bond energy of qCC which is greater than the P⋯P bond energies of penternary complexes pABC′, pCCA′, and pCCB′. However, it is the penternary complex pACC that has a significantly greater nonadditivity (20.6 kJ mol^{-1}) than any other complex. This suggests that there may be a change in the nature of the interactions in this complex relative to the corresponding

binary complexes, a change which will be discussed in detail below.

AIM and NBO Analyses. The topological analysis of the electron density shows the presence of intermolecular bond critical points (BCPs) and corresponding bond paths connecting the pnicogen bonded P⋯P atoms and the hydrogen bonded H⋯F atoms. Electron densities at BCPs (ρ_{BCP}) are reported in Table S2 of the Supporting Information and can be seen to increase as intermolecular distances decrease, in agreement with previously noted tendencies for intermolecular interactions.[32−38]

The values of the Laplacian of the electron density at the BCP ($\nabla^2\rho_{BCP}$), the total energy density at the BCP (H$_{BCP}$), and the ratio of the absolute value of the electron potential energy density to the kinetic energy density ($C = |V|/G$) are also reported in Table S2 and have been used to assess the degree of covalency of the P⋯P interaction.[22,39−42] Negative values of $\nabla^2\rho_{BCP}$ and H and a value of C greater than 2 have been found to be indicative of covalent character. Thus, except for (PH$_2$F)$_2$, the P⋯P bonds in these pnicogen complexes have some covalent character. The variation of $\nabla^2\rho_{BCP}$ with the intermolecular distance is another indication of the degree of covalency,[22] and as illustrated in Figure 3, covalency increases
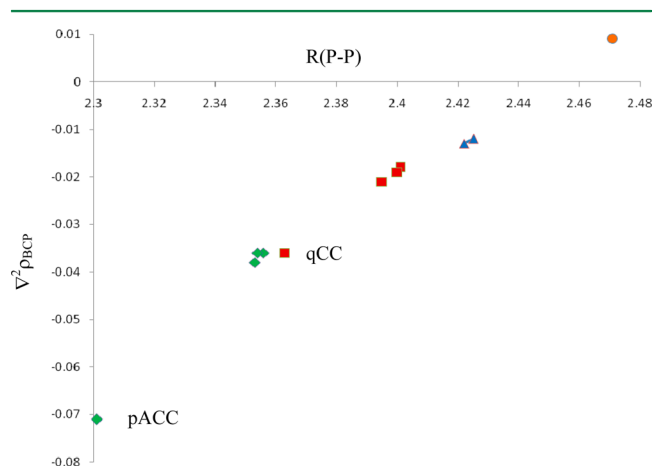
Figure 3. Laplacians of electron densities at bond critical points ($\nabla^2\rho_{BCP}$, au) vs the P−P distance [R(P−P), Å]. (●) (PH$_2$F)$_2$; (▲) FH:(PH$_2$F)$_2$; (■) 2FH:(PH$_2$F)$_2$; (◆) 3FH(PH$_2$F)$_2$. The quadratic trendline has an R^2 value of 0.986.

as the P−P distance decreases and the number of FH molecules increases. Moreover, complexes qCC and pACC which have two and three FH molecules, respectively, bonded to the same F(1) atom, have P⋯P bonds with significantly greater covalent character than the remaining complexes with the same number of hydrogen bonds.

Additional insight into the P⋯P pnicogen bond can be obtained by examining the NBO charges on P(1) and P(2) in Table 2 and the second-order perturbation energies for P lone pair → P−Fσ* charge-transfer transitions across the pnicogen bond in Table 3. The NBO charge on P is +0.673e in the reference complex (PH$_2$F)$_2$. As would be expected, hydrogen bonding of two FH molecules symmetrically in qAA′ and qBB′ produces only slightly lower positive charges on P in these complexes. In contrast, hydrogen bonding of one FH in tA and tB decreases the positive charge on P(1) and increases the positive charge on P(2). That is, upon hydrogen bond formation, charge transfer occurs from the non-hydrogen-

Table 2. NBO Charges (e) on P(1) and P(2) in nFH: $(PH_2F)_2$ Complexes

complex	P(1)	P(2)
$(PH_2F)_2$	0.673	0.673
tA	0.614	0.727
tB	0.617	0.725
qCC	0.535	0.795
qAA′(C_2)	0.666	0.666
qAA′(C_i)	0.665	0.665
qBB′(C_2)	0.667	0.667
qBB′(C_i)	0.667	0.667
pACC	0.438	0.884
pABC′	0.559	0.766
pCCA′	0.591	0.726
pCCB′	0.598	0.723

Table 3. Second-Order Perturbation Energies (kJ mol^{-1}) for P(Lone Pair) → (P−F)σ* Stabilizing Charge-Transfer Transitions across the Pnicogen Bond

Complex	P(1)$_{lp}$ → P(2)−F(2)σ*	P(2)$_{lp}$ → P(1)−F(1)σ*
$(PH_2F)_2$	99.6	99.6
tA	131.7	204.9
tB	132.3	207.1
qCC	117.4	314.5
qAA′ (C_2)	178.3	178.3
qAA′ (C_i)	179.0	179.0
qBB′ (C_2)	181.3	181.3
qBB′ (C_i)	180.9	180.9
pACC	94.9	528.0
pABC′	137.8	295.8
pCCA′	156.6	263.7
pCCB′	163.7	255.7

bonded $PH_2F(2)$ molecule to $PH_2F(1)$. This can also be seen from the second-order perturbation energies for the P lone pair → P−Fσ* excitations in tA and tB, which are 206 ± 1 kJ mol^{-1} for P(2) lone pair → P(1)−F(1)σ* versus 132 kJ mol^{-1} for P(1) lone pair → P(2)−F(2)σ*.

The charges and orbital interaction energies for tA and tB are enhanced in qCC and pACC in which two and three FH molecules, respectively, are hydrogen bonded to $PH_2F(1)$. The positive charges on P(1) are reduced to 0.535 and 0.438e, respectively, while they are increased to 0.795 and 0.884e, respectively, on P(2). Not surprisingly, the P(2) lone pair → P(1)−F(1)σ* energies are 315 and 528 kJ mol^{-1} for qCC and pACC, respectively, versus 117 and 95 kJ mol^{-1}, respectively, for P(1) long pair → P(2)−F(2)σ*.

The patterns observed for the second-order perturbation energies are consistent with the changes in total NBO electron densities in these complexes. In the symmetrically bonded complexes (qAA′ and qBB′) both PH_2F molecules lose electron density which is transferred to the FH molecules. For complexes that are not symmetrically hydrogen bonded, $PH_2F(2)$ loses electron density and becomes positively charged. $PH_2F(1)$ gains some of that density and becomes negatively

charged, even though P(1) remains positively charged, as seen in Table 2. The remainder of the electron density lost by $PH_2F(2)$ is transferred to the FH molecules.

NMR Properties. *Chemical Shieldings.* ^{31}P chemical shieldings are reported in Table 4. The ^{31}P chemical shielding

Table 4. ^{31}P Absolute Chemical Shieldings (σ) and Changes in Shieldings ($\Delta\sigma$, ppm), P−P Distances [R(P−P), Å], and ^{1p}J(P−P) Coupling Constants [^{1p}J(P−P), Hz] for Complexes nFH:$(PH_2F)_2$

complex	P(1)σ^a	P(2)σ^a	$\Delta\sigma$P(1)^b	$\Delta\sigma$P(2)^b	R(P−P)	^{1p}J(P−P)^c
$(PH_2F)_2$	354.0	354.0			2.471	1008
tA	386.1	338.8	32.1	−15.2	2.425	1021
tB	385.4	338.6	31.4	−15.4	2.422	1006
qCC	429.4	324.8	75.4	−29.2	2.363	948
qAA′ (C_2)	362.4	362.4	8.4	8.4	2.401	1080
qAA′ (C_i)	362.5	362.5	8.5	8.5	2.400	1079
qBB′ (C_2)	361.7	361.7	7.7	7.7	2.395	1058
qBB′ (C_i)	361.5	361.5	7.5	7.5	2.395	1058
pACC	484.4	309.3	130.4	−44.7	2.301	782
pABC′	420.1	327.6	66.1	−26.4	2.353	d
pCCA′	398.1	341.9	44.1	−12.1	2.356	d
pCCB′	390.6	345.8	36.6	−8.2	2.354	1072

^{a}The number of hydrogen bonds formed by $PH_2F(1)$ is equal to or greater than the number formed by $PH_2F(2)$. $^b\Delta\sigma P = \sigma P$(complex) − $\sigma P(PH_2F)_2$. ^{c1p}J(P−P) approximated by the FC term. ^{d}EOM-CCSD coupling constants could not be computed for these complexes of C_1 symmetry.

in the reference dimer $(PH_2F)_2$ is 354 ppm, a decrease of 19 ppm relative to PH_2F. In the ternary complexes tA and tB, hydrogen bond formation at F(1) leads to an increase in the shielding of about 32 ppm for P(1) relative to the parent complex and a decrease of 15 ppm for P(2).

The chemical shielding of P(1) in the quaternary complex qCC which has two hydrogen bonds at F(1) increases by 75 ppm, while that of P(2) decreases by 29 ppm. Even more dramatic are the changes in pACC, for which the chemical shielding of P(1) increases by 130 ppm, while that of P(2) decreases by 45 ppm. These shifts reflect the decreasing and increasing positive charges (increasing and decreasing electron densities) on P(1) and P(2), respectively, as indicated by the NBO charges in Table 2. There is a very good correlation between the ^{31}P chemical shielding and the NBO charge, as shown in Figure S1 of the Supporting Information. The second-order trendline has an R^2 value of 0.996.

There are four complexes 2FH:$(PH_2F)_2$ which have the two FH molecules bonded symmetrically to $PH_2F(1)$ and $PH_2F(2)$. For these, the chemical shieldings of both P-atoms still increase relative to $(PH_2F)_2$, although the increase is less than 10 ppm. Penternary complexes pABC′, pCCA′, and pCCB′ have two FH molecules bonded to F(1) and one bonded to F(2). The chemical shieldings of P(1) increase by 37 to 66 ppm and are greater than the P(1) shieldings in tA and tB. However, while the P(2) shielding in pABC′ exhibits a larger decrease than P(2) in tA and tB, the shielding decreases of P(2) in pCCA′ and pCCB′ are less than found those in tA and tB. The chemical shieldings of P(1) and P(2) in the same complex are

related quadratically with a correlation coefficient of 0.906. ^{31}P chemical shifts in these complexes should be quite amenable to experimental study since they arise from a nucleus with spin $I = \frac{1}{2}$ and vary considerably.

Spin−Spin Coupling Constants. $^{31}P−^{31}P$ spin−spin coupling constants are also reported in Table 4. The formation of a single F−H···F hydrogen bond has little effect on $^{1p}J(P−P)$, decreasing its value by 2 Hz for tB and increasing it by 13 Hz for tA relative to its value of 1008 Hz for $(PH_2F)_2$, despite the fact that the P−P distances are shorter by about 0.05 Å in tA and tB. What is observed upon formation of two or three F−H···F hydrogen bonds with only F(1) is even more dramatic. The P−P distance in qCC is 2.363 Å, but $^{1p}J(P−P)$ decreases to 948 Hz. In contrast, the distances in qAA′ and qBB′ are 2.40 Å, and $^{1p}J(P−P)$ increases to 1080 Hz for qAA′ and 1058 Hz for qBB′. The penternary complex pACC has the shortest P−P distance of 2.301 Å, but $^{1p}J(P−P)$ has it smallest value of 782 Hz. The P−P distance in pCCB′ is 2.354 Å, but $^{1p}J(P−P)$ at 1072 Hz lies between the values for qAA′ and qBB′.

The decrease in $^{1p}J(P−P)$ for qCC and pACC as the P−P distance decreases is an unanticipated result, since $^{1p}J(P−P)$ values for dimers $(PH_2X)_2$ and $(PHFX)_2$ increase linearly as the P−P distance decreases.[5,6] Figure 3 provides a plot of $^{1p}J(P−P)$ versus the P−P distance.
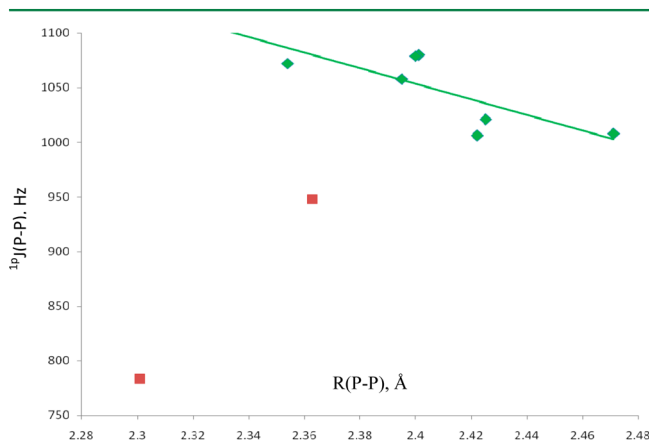
Figure 4. $^{1p}J(P−P)$ vs $R(P−P)$ for complexes nFH:$(PH_2F)_2$. The correlation coefficient of the trendline is 0.584. The red squares represent qCC and pACC.

The trendline for eight of the complexes (excluding qCC and pACC) indicates a linear increase in $^{1p}J(P−P)$ as the P−P distance decreases, but the correlation coefficient is only 0.584. This indicates that $^{1p}J(P−P)$ is less sensitive to the P−P distance when hydrogen bonds are also present, certainly when compared to the distance dependence of $^{1p}J(P−P)$ for $(PH_2X)_2$ and $(PHFX)_2$. This may be attributed in part to the electron density which is lost by $(PH_2F)_2$ and transferred to the FH molecules. Although the operator for the FC term is not distance dependent, the FC term does depend on s electron densities on coupled atoms in the ground state and in the excited states which interact with the ground state.

Why does $^{1p}J(P−P)$ have reduced values for qCC and particularly for pACC, complexes which have the shortest P−P distances? Insight into the answer to this question may be gained by examining pACC in detail. It was noted above that the P(1)−F(1) distance in this complex is very long and that the three FH molecules that are hydrogen bonded to F(1) resemble an anionic cluster 3(FH)F⁻ with approximately local

C_{3v} symmetry. This suggests that pACC is approaching an ion-pair complex, which may be represented as $H_3F_4^-$: $(H_2P:PH_2F)^+$. To examine the effect this structural change has on $^{1p}J(P−P)$, coupling constants were computed for two cationic structures. First, F⁻ was removed from the parent complex $(PH_2F)_2$ to give $(H_2P:PH_2F)^+$, keeping the remaining coordinates in the ion at their values in $(PH_2F)_2$. Then, the three FH molecules and F(1)⁻ were removed from pACC, keeping the remaining cation at its geometry in pACC. $^{1p}J(P−P)$ for these two cations are reported in Table 5. As evident

Table 5. P−P Distances [$R(P−P)$, Å] and $^{31}P−^{31}P$ Coupling Constants [$^{1p}J(P−P)$, Hz] for Neutral Complexes and Corresponding Cations $(H_2P:PH_2F)^+$, and P−P Distances and $^1J(P−P)$ Values for P_2H_4

neutral	$R(P−P)$	$^{1p}J(P−P)^a$	cation	$R(P−P)$	$^{1p}J(P−P)^a$
$(PH_2F)_2$	2.471	1008	$(H_2P:PH_2F)^{+b}$	2.471	160
pACC	2.301	783	$(H_2P:PH_2F)^{+b}$	2.301	−147

P_2H_4	$R(P−P)$	$^1J(P−P)^a$
C_2	2.225	−165
C_{2v}	2.266	−230
C_{2h}	2.238	−45

^{a}Approximated by the FC term. ^{b}At the geometry of the corresponding neutral complex.

from this table, values of $^{1p}J(P−P)$ are dramatically different in the neutral complex and the corresponding cation at the same P−P distance. $^{1p}J(P−P)$ is 1008 Hz for neutral $(PH_2F)_2$ and 160 Hz in its cation. $^{1p}J(P−P)$ for pACC is 783 Hz but changes sign and is reduced to −147 Hz for the corresponding cation. Thus, going from the neutral complex to the corresponding cation $(H_2P:PH_2F)^+$ significantly reduces $^{1p}J(P−P)$ and results in a change of sign for the cation derived from pACC. Why does this occur?

As noted above, the P−P distance in pACC is very short at 2.301 Å and is therefore approaching the P−P covalent bond distance. For comparison purposes, the FC terms for P_2H_4 have been computed for optimized MP2/aug′-cc-pVTZ structures with C_2, C_{2v}, and C_{2h} symmetry, and these data are also reported in Table 5. For these conformations, the FC term is negative and has its largest negative value for the C_{2v} structure of P_2H_4, the one which most closely resembles pACC with its trans arrangement of PH_2 groups. Thus, it appears that the large decrease of $^{1p}J(P−P)$ in pACC is due to the change in the nature of the bonding in 3FH:$(PH_2F)_2$, with the complex acquiring ion-pair character represented as [$H_3F_4^-$: $(H_2P:PH_2F)^+$], and the P···P bond approaching a covalent bond. The decrease in $^{1p}J(P−P)$ for qCC is significantly less, since the degree of ion-pair character of the complex and the covalent character of the P···P bond are reduced relative to pACC. The change in the nature of the bonds in pACC is also the most likely explanation for the large synergistic non-additivity effect for pACC reported in Table 1.

There is one final point that should be mentioned. In the complexes $(PH_2X)_2$ and $(PHFX)_2$ it was demonstrated that the FC term is an excellent approximation to $^{1p}J(P−P)$. However, this may not be the case for qACC with its short P−P distance, since, at short P−P distances in P_2H_4, both the PSO and SD terms make non-negligible contributions to the total coupling constant $^1J(P−P)$.

CONCLUSIONS

Ab initio MP2/aug'-cc-pVTZ calculations have been carried out to investigate the effect of F—H⋯F hydrogen bonds on the P⋯P pnicogen bond in complexes nFH:(PH$_2$F)$_2$ for $n = 1-3$. The following statements are supported by the results of this study.

1. The P—P distance decreases and the strength of the P⋯P pnicogen bond increases upon hydrogen bond formation with FH molecules. The extent of these changes depends on the number of FH molecules and their positions in the complex.

2. The formation of a single hydrogen bond has a relatively small effect on the properties of complexes FH:(PH$_2$F)$_2$. Similarly, hydrogen bonding in complexes 2FH:(PH$_2$F)$_2$ and 3FH:(PH$_2$F)$_2$ which have FH molecules bonded to both F(1) of molecule PH$_2$F(1) and F(2) of molecule PH$_2$F(2) produces only moderate changes in the structures, binding energies, and other properties of these complexes.

3. The effect of hydrogen bonding is dramatic when the two FH molecules in 2FH:(PH$_2$F)$_2$ and the three FH molecules in 3FH:(PH$_2$F)$_2$ are hydrogen bonded to F(1). For these two complexes, respectively,

   a. the P—P distance of 2.471 Å in the parent complex decreases to 2.363 and 2.301A;

   b. the energy of the P⋯P bond increases from 34 kJ mol^{-1} to 44 and 55 kJ mol^{-1};

   c. the positive charge on P(1) decreases dramatically while the positive charge on P(2) increases;

   d. the dominant intermolecular orbital interaction is charge transfer from the lone pair of P(2) to the P(1)—F(1)σ^* orbital;

   e. the NMR ^{31}P chemical shielding of P(1) significantly increases while that of P(2) decreases;

   f. ^{1p}J(P—P) decreases dramatically as the P—P distance decreases.

The dramatic changes in the properties of these two complexes are a consequence of changes in the nature of the hydrogen bonds and the P⋯P pnicogen bond. 3FH:(PH$_2$F)$_2$ acquires ion-pair character $[3(\text{FH})\text{F}^-:(\text{H}_2\text{P}-\text{PH}_2\text{F})^+]$, and the pnicogen bond acquires significant covalent character. These changes are observed to a lesser extent in 2FH:(PH$_2$F)$_2$.

ASSOCIATED CONTENT

ⓢ Supporting Information

for complexes nFH:(PH$_2$F)$_2$ includes MP2/aug'-cc-pVTZ structures, binding energies, and electron density parameters, and a plot of ^{31}P chemical shieldings vs NBO charges on P. This information is available free of charge via the Internet at http://pubs.acs.org

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Notes

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