Influence of Substituent Effects on the Formation of (PCl)−C−... Pnicogen Bonds or Halogen Bonds

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Influence of Substituent Effects on the Formation of P···Cl Pnicogen Bonds or Halogen Bonds

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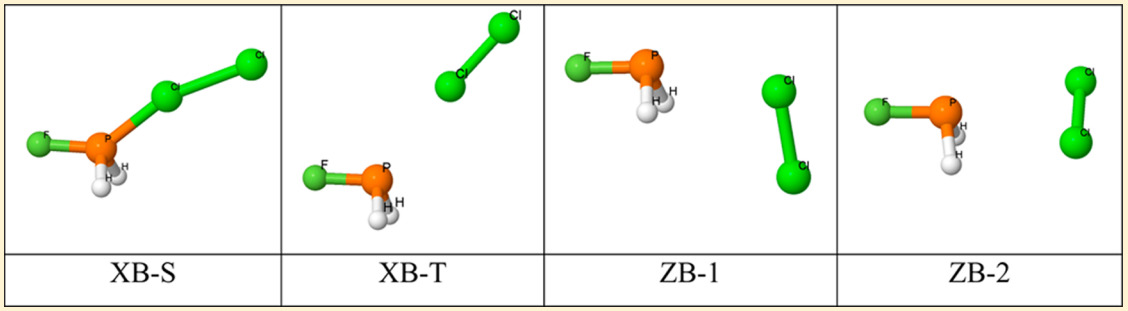
Supporting Information



ABSTRACT: Ab initio MP2/aug′-cc-pVTZ calculations have been carried out in search of equilibrium structures with P···Cl pnicogen bonds or halogen bonds on the potential energy surfaces H_2FP:ClY for Y = F, NC, Cl, CN, CCH, CH_3, and H. Three different types of halogen-bonded complexes with traditional, chlorine-shared, and ion-pair bonds have been identified. Two different pnicogen-bonded complexes have also been found on these surfaces. The most electronegative substituents F and NC form only halogen-bonded complexes, while the most electropositive substituents CH_3 and H form only pnicogen-bonded complexes. The halogen-bonded complexes involving the less electronegative groups Cl and CN are more stable than the corresponding pnicogen-bonded complexes, while the pnicogen-bonded complexes with CCH are more stable than the corresponding halogen-bonded complex. Traditional halogen-bonded complexes are stabilized by charge transfer from the P lone pair to the Cl−A σ^* orbital, where A is the atom of Y directly bonded to Cl. Charge transfer from the Cl lone pair to the P−F σ^* orbital stabilizes pnicogen-bonded complexes. As a result, the H_2FP unit becomes positively charged in halogen-bonded complexes and negatively charged in pnicogen-bonded complexes. Spin−spin coupling constants ^{1X}J(P−Cl) for complexes with traditional halogen bonds increase with decreasing P−Cl distance, reach a maximum value for complexes with chlorine-shared halogen bonds, and then decrease and change sign when the bond is an ion-pair bond. ^{1p}J(P−Cl) coupling constants across pnicogen bonds tend to increase with decreasing P−Cl distance.

INTRODUCTION

Noncovalent interactions play a very important role in supramolecular chemistry, molecular biology, and materials science. Traditionally, research in this field has focused on the most common and well-known noncovalent interaction, the hydrogen bond. However, in the last few decades, interest in the halogen bond[1−3] and more recently, the pnicogen bond[4−7] has increased significantly. Halogen bonds and pnicogen bonds arise when a halogen atom or a pnicogen atom acts as the Lewis acid in a Lewis acid−Lewis base intermolecular interaction.

The molecules involved in the formation of halogen bonds and pnicogen bonds usually have molecular electrostatic potentials (MEPs) at a particular atom in the molecule which exhibit both positive regions or σ-holes[8] and negative regions corresponding to lone pairs or π electrons, as illustrated in Figure 1. If two such molecules interact, then in principle they should be able to form either halogen-bonded or pnicogen-bonded complexes, depending on which molecule is the electron-pair donor and which is the acceptor. Literature describing both kinds of bonds is abundant, and some recent papers have compared these two types of intermolecular interactions.[9−12] However, to our knowledge, the present paper is the first study in which the same monomers compete to form a halogen bond (XB) or a pnicogen bond (ZB). Could substituent effects be used to preferentially select the type of bond formed?

To answer this question, we have investigated a series of complexes involving H_2FP and molecules ClY, with the

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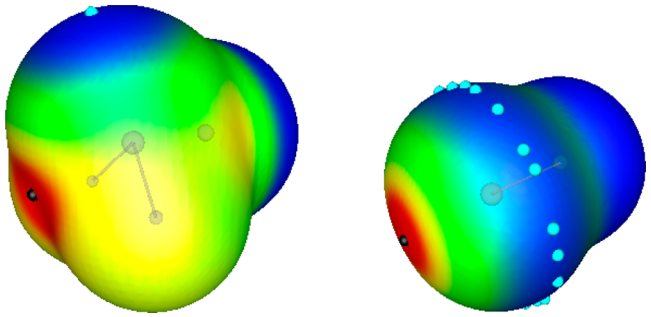

Figure 1. MEPs of H_2FP and ClF. Black dots indicate the position of the σ-holes while light blue dots are associated with the lone pairs.

substituents Y = F, NC, Cl, CN, CCH, CH_3, and H. Because both P and Cl have σ-holes and lone pairs, in principle two types of complexes could be formed, one stabilized by a P···Cl halogen bond, and the other by a P···Cl pnicogen bond. We have examined the H_2FP:ClY potential surfaces in search of these complexes. In this paper we describe the equilibrium halogen-bonded and pnicogen-bonded complexes found on these surfaces and note what circumstances favor one bond over the other. We then present the structures and binding energies of these complexes, their bonding properties, and the one-bond NMR spin−spin coupling constants ^{1X}J(P−Cl) and ^{1p}J(P−Cl) across halogen and pnicogen bonds, respectively.

METHODS

The structures of the isolated monomers and complexes were optimized at second-order Møller−Plesset perturbation theory (MP2)[13−16] with the aug′-cc-pVTZ basis set.[17] This basis set is derived from the Dunning aug-cc-pVTZ basis set[18,19] by removing diffuse functions from H atoms. Frequencies were computed to establish that the optimized structures correspond to equilibrium structures on their potential surfaces. Optimization and frequency calculations were performed using the Gaussian 09 program.[20]

The electron densities of the complexes have been analyzed using the atoms in molecules (AIM) methodology[21−24] employing the AIMAll program.[25] The topological analysis of the electron density produces the molecular graph of each complex. This graph identifies the location of electron density features of interest, including the electron density (ρ) maxima associated with the various nuclei, saddle points which correspond to bond critical points (BCPs), and ring critical points which indicate a minimum electron density within a ring. The zero gradient line which connects a BCP with two nuclei is the bond path. Natural bond order (NBO)[26] MP2/aug′-cc-pVTZ electron populations have been evaluated for monomers and complexes. In addition, the NBO method has also been used to analyze the stabilizing charge-transfer interactions using the NBO-6 program.[27] NBO orbitals have been represented with the Jmol program[28] using the tools developed by Marcel Patek.[29]

Spin−spin coupling constants were evaluated using the equation-of-motion coupled cluster singles and doubles (EOM-CCSD) method in the CI (configuration interaction)-like approximation,[30,31] with all electrons correlated. For these calculations, the Ahlrichs qzp basis set[32] was placed on ^{13}C, ^{15}N, and ^{19}F, and the qz2p basis set on ^{31}P and ^{35}Cl. The Dunning cc-pVDZ basis set was placed on all ^{1}H atoms. Only ^{1X}J(P−Cl) and ^{1p}J(P−Cl) coupling constants for halogen bonds and pnicogen bonds, respectively, are reported in this paper. All terms which contribute to the total coupling constant, namely, the paramagnetic spin orbit (PSO), diamagnetic spin orbit (DSO), Fermi contact (FC), and spin dipole (SD), have been evaluated. The EOM-CCSD calculations were performed using ACES II[33] on the IBM Cluster 1350 (Glenn) at the Ohio Supercomputer Center.

RESULTS AND DISCUSSION

Although there are many minima on the H_2FP:ClY potential surfaces, we have restricted our searches to those regions at which P···Cl pnicogen-bonded and halogen-bonded complexes may exist. Three different types of halogen-bonded complexes have been found: traditional (XB-T), chlorine-shared (XB-S), and ion-pair (XB-IP), all with C_s symmetry. These are differentiated by their P−Cl and Cl−A distances, with A the atom of Y directly bonded to Cl. In addition, two types of pnicogen-bonded complexes have been identified, designated ZB-1 and ZB-2. Complexes ZB-1 have C_s symmetry with the Cl−A bond *cis* to the bisector of the H−P−H angle. Complexes ZB-2 may have either C_s or C_1 symmetry, with the Cl−A bond either *trans* or *gauche*, respectively, to the bisector. These halogen- and pnicogen-bonded complexes are illustrated in Figure 2.

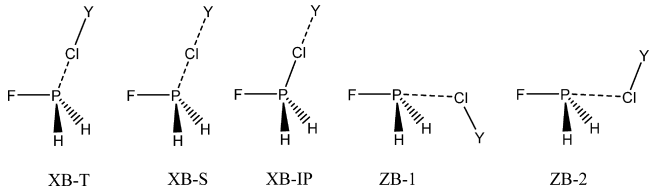

Figure 2. Schematic representation of the halogen-bonded and pnicogen-bonded complexes H_2FP:ClY.

The structures, total energies, and molecular graphs of halogen-bonded and pnicogen-bonded complexes are reported in Table S1 of the Supporting Information. Each graph shows a bond critical point connecting P and Cl. Table 1 presents the binding energies of complexes H_2FP:ClY relative to the isolated monomers H_2FP and ClY, except for the ion-pair complex H_2FPCl^+:NC^-. From the data reported in Table 1, it is possible to answer the question asked in the Introduction. The preferred type of intermolecular bond can be selected by changing the nature of the substituent. When Y of ClY is a very electronegative group such as F or NC, only halogen-bonded

Table 1. MP2/aug′-cc-pVTZ Binding Energies (ΔE, kJ mol^{-1}) of Complexes H_2FP:ClY with Traditional (XB-T), Chlorine-Shared (XB-S), and Ion-Pair (XB-IP) Halogen Bonds and Pnicogen Bonds (ZB-1 and ZB-2)[a]

H_2FP:ClY	XB-T	XB-S	XB-IP	ZB-1	ZB-2
Y = F		−71.1			
NC	−13.6		−381.2[b]		
Cl	−12.9	−15.3		−11.5	−10.8
CN	−8.1			−6.5	−6.3
CCH	−6.2			−11.0	−10.7
CH_3				−15.1	−18.3
H				−10.0	−11.6

[a]See Figure 1 for an identification of the types of complexes and their designations. [b]Binding energy relative to $(H_2FPCl)^+$ and NC^-.

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Table 2. P−Cl Distances (R, Å), F−P−Cl Angles (∠a, °), and P−Cl−A Angles (∠b, °) in Halogen-Bonded and Pnicogen-Bonded Complexes H_2FP:ClY[a]

	XB-T			XB-S			XB-IP		
H_2FP:ClY	R	∠a	∠b	R	∠a	∠b	R	∠a	∠b
Y = F				2.044	119	175			
NC	3.196	113	179				1.970	116	173
Cl	3.061	127	175	2.157	143	158			
CN	3.551	109	178						
CCH	3.542	144	163						

	ZB-1			ZB-2		
H_2FP:ClY	R	∠a	∠b	R	∠a	∠b
Y = Cl	3.169	168	110	3.265	166	89
CN	3.365	165	95	3.437	168	81
CCH	3.295	162	93	3.320	165	85
CH_3	3.157	163	100	3.121	169	90
H	3.280	167	110	3.277	169	80

[a]See Figure 1 for an identification of the types of complexes and their designation.

complexes are formed. This is due to the electron-withdrawing effects of these two substituents, which enhance the σ-hole at Cl so that it becomes a strong electron-pair acceptor for the formation of a P···Cl halogen bond and a poor electron donor for a pnicogen bond. As the electronegativity of Y decreases when the substituents are Cl, CN, and CCH, ClY becomes both an electron-pair donor in a pnicogen-bonded complex and an electron-pair acceptor in a halogen-bonded complex. The halogen-bonded complexes H_2FP:ClCl and H_2FP:ClCN are more stable than the corresponding pnicogen-bonded complexes, but the H_2FP:ClCCH pnicogen-bonded complexes are more stable than the corresponding halogen-bonded complex. When Y is CH_3 or H, only complexes with pnicogen bonds are formed. These electropositive substituents essentially destroy the σ-hole by increasing the electron density on Cl and enhance the electron-pair donating ability of Cl for the formation of P···Cl pnicogen bonds.

Binding Energies. When Y is the most electronegative substituent F, only one equilibrium H_2FP:ClF complex is found on the potential surface. It is stabilized by a chlorine-shared halogen bond, with a binding energy of −71.1 kJ mol^{-1}. As the electronegativity of Y decreases in going from F to NC, two H_2FP:ClNC halogen-bonded complexes exist on the potential surface, one with an ion-pair bond H_2FPCl^+:NC^-, and the other with a traditional halogen bond. The ion-pair complex has a binding energy of −381.2 kJ mol^{-1} relative to the ions H_2FPCl^+ and NC^-, while the value of the binding energy is +9.0 kJ mol^{-1} if the neutral H_2FP and ClNC molecules are considered as the dissociation products. That ClNC forms an ion-pair complex instead of a complex with a chlorine-shared halogen bond as does ClF may be attributed to the ability of NC^- to better accommodate a full negative charge. Neither ClF nor ClNC form pnicogen-bonded complexes. However, as the electronegativity of Y is further reduced, both halogen-bonded and pnicogen-bonded complexes are found on the H_2FP:ClCl surface. The chlorine-shared halogen-bonded complex is more stable than the corresponding complex with a traditional halogen bond, but this is not necessarily always the case. For example, H_2ClP:ClCl also forms complexes with traditional and chlorine-shared halogen bonds, but that with the traditional halogen bond is more stable by 3 kJ mol^{-1}. Both halogen-bonded complexes H_2FP:ClCl are more stable than the corresponding pnicogen-bonded complexes. Only one H_2FP:ClCN halogen-bonded complex with a traditional halogen bond has been found, and its binding energy of −8.1 kJ mol^{-1} is greater than the binding energies of about −6.4 kJ mol^{-1} for the two corresponding pnicogen-bonded complexes. In contrast, both pnicogen-bonded H_2FP:ClCCH complexes are more stable than the corresponding halogen-bonded complex with a traditional halogen bond. Finally, H_2FP:$ClCH_3$ and H_2FP:ClH form only complexes stabilized by pnicogen bonds. The complex H_2FP:$ClCH_3$ ZB-2 has the highest binding energy of −18.3 kJ mol^{-1} among all pnicogen-bonded complexes. Thus, what types of intermolecular bonds are formed and the binding energies of the resulting complexes are determined by the electronegativity of the substituent bonded to Cl. For the halogen-bonded complexes with either chlorine-shared or traditional halogen bonds, the order of decreasing binding energies is

$$F > > NC \approx Cl > CN > CCH$$

For complexes with pnicogen bonds, the order for ZB-1 complexes is

$$CH_3 > Cl \approx CCH > H > CN$$

and for ZB-2 complexes

$$CH_3 > H > Cl \approx CCH > CN$$

Structures. How are halogen-bonded and pnicogen-bonded complexes distinguished? These complexes can be easily differentiated structurally by the values of the F−P−Cl and P−Cl−A angles, where A is the atom of Y directly bonded to Cl. The data of Table 2 indicate that in halogen-bonded complexes, the Cl atom of ClY is located in approximately one of the tetrahedral directions relative to P, with values of the F−P−Cl angle ranging from 109 to 127°, except for values around 144° for the traditional halogen-bonded complex H_2FP:ClCCH and the chlorine-shared complex H_2FP:ClCl. At the same time, the P−Cl−A arrangement approaches linearity, with values of this angle greater than 172°, except for the same two complexes H_2FP:ClCCH and H_2FP:ClCl. The three types of halogen-bonded complexes are differentiated in terms of their P−Cl and Cl−A distances. Traditional halogen bonds have long P−Cl and short Cl−A distances; chlorine-shared halogen bonds have P−Cl and Cl−A bonds of intermediate lengths; ion-pair bonds have short P−Cl and long Cl−A distances. Thus, from Table 2

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it can be seen that the P−Cl distances vary from 3.061 to 3.551 Å in complexes with traditional halogen bonds. The P−Cl distances in the two chlorine-shared halogen-bonded complexes are 2.044 and 2.157 Å, while this distance in the ion-pair complex is 1.970 Å. This distance is similar to the P−Cl distance of 1.930 Å in the cation H_2FPCl^+. The Cl−N distance in the ion-pair complex is 2.246 Å, significantly longer than the distance of 1.624 Å in the ClNC monomer. Cl−A distances in chlorine-shared halogen bonds are longer than the distances in the corresponding monomers, while these distances are similar to the monomer distances when the halogen bonds are traditional.

In contrast to the halogen-bonded complexes, it is the F−P−Cl arrangement which approaches linearity in complexes with pnicogen bonds. The values of this angle are between 162 and 169°, as evident from Table 2. Moreover, the P−Cl−A angles are significantly reduced relative to their values in complexes with halogen bonds. Thus, in ZB-1 complexes the P−Cl−A angle varies between 93 and 110°, while this same angle is reduced to between 81 and 90° in ZB-2. From Table 2 it is also apparent that P−Cl distances do not differentiate between traditional halogen bonds, for which the P−Cl distances vary between 3.061 and 3.551 Å, and pnicogen bonds which have P−Cl distances between 3.121 and 3.437 Å.

NBO Analyses. The NBO analyses indicate that charge transfer stabilizes both halogen-bonded and pnicogen-bonded complexes. The charge-transfer energies for these complexes are reported in Table 3. The dominant charge-transfer interaction in the halogen-bonded complexes XB-T occurs from the lone pair on P of H_2FP to the antibonding σ^* Cl−A orbital of ClY, as illustrated in Figure 3 for H_2FP:ClCl. These energies vary from 3.5 kJ mol^{-1} for H_2FP:ClCCH to 23.5 kJ mol^{-1} for H_2FP:ClCl. In contrast, the dominant charge-transfer interactions in pnicogen-bonded complexes which are also illustrated in Figure 3 occur from the lone pair of Cl to the σ^* P−F orbital of H_2FP. The charge-transfer energies vary from 7.4 to 19.4 kJ mol^{-1} for complexes ZB-1 and from 5.2 to 20.4 kJ mol^{-1} for ZB-2. The weakest charge-transfer interaction in each ZB series occurs in H_2FP:ClCN, and the strongest in H_2FP:ClCH$_3$. The charge-transfer energies do not correlate with the binding energies of halogen-bonded or pnicogen-bonded complexes but do correlate linearly with the P−Cl distances, with correlation coefficients R^2 of 0.994, 0.950, and 0.941 for the complexes XB-T, ZB-1, and ZB-2, respectively. A plot of the charge-transfer energy versus the P−Cl distance for the ZB-1 complexes is shown in Figure 4.

Table 3. P(lp) → σ*Cl−A and Cl(lp) → σ*P−F Charge-Transfer Energies (kJ mol^{-1}) in Complexes H_2FP:ClY with Halogen Bonds[a] and Pnicogen Bonds

H_2FP:ClY	XB-T	ZB-1	ZB-2
	P(lp) → σ*Cl−A	Cl(lp) → σ*P−F	Cl(lp) → σ*P−F
Y = NC	17.9		
Cl	23.5	17.7	13.6
CN	4.8	7.4	5.2
CCH	3.5	9.6	7.9
CH_3		19.4	20.4
H		13.6	13.7

[a]The NBO program treats H_2FP:ClF(XB-S), H_2FP:ClCl (XB-S), and H_2FP:ClNC (XB-IP) as ion-pair complexes with very large charge-transfer energies.

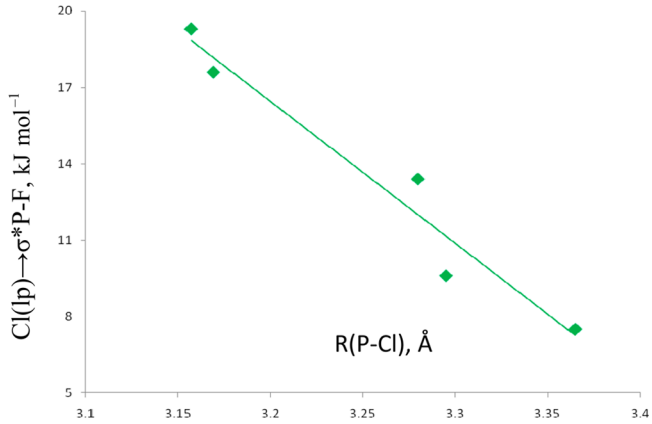

Figure 4. Charge-transfer energy Cl(lp) → σ*P−F versus the P−Cl distance for the pnicogen-bonded complexes ZB-1.

The MP2/aug′-cc-pVTZ charges on the H_2FP unit in complexes H_2FP:ClY are listed in Table 4. The NBO charges are consistent with the nature of the charge-transfer interactions in these complexes. In halogen-bonded complexes, the dominant charge-transfer interaction is P(lp) → σ*Cl−A. As a result, the H_2FP unit in these complexes becomes positively charged, with charges ranging from 0.007e in H_2FP:ClCCH to 0.060e in H_2FP:ClCl for complexes with traditional halogen bonds. Of course, the positive charges on the H_2FP units in chlorine-shared and ion-pair complexes are significantly greater, ranging from 0.462e in H_2FP:ClCl to 0.792e in H_2FP:ClNC. In the pnicogen-bonded complexes ZB-

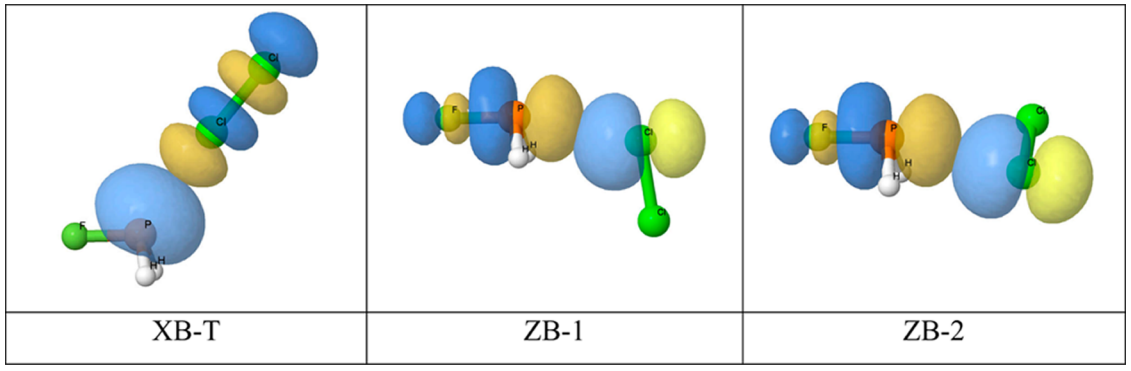

Figure 3. Representation of the orbitals involved in the charge-transfer interactions in H_2ClP:ClCl complexes XB-T, ZB-1, and ZB-2.

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Table 4. NBO MP2/aug′-cc-pVTZ Charges on the H_2FP Unit (au) in Complexes H_2FP:ClY with Halogen Bonds and Pnicogen Bonds

H_2FP:ClY	XB-T	XB-S	XB-IP	ZB-1	ZB-2
Y = F		0.654[a]			
NC	0.038		0.792[a]		
Cl	0.060	0.462[a]		−0.016	−0.016
CN	0.011			−0.006	−0.005
CCH	0.007			−0.011	−0.010
CH_3				−0.023	−0.025
H				−0.014	−0.017

[a]The NBO method treats H_2FP:ClF(XB-S), H_2FP:ClCl (XB-S), and H_2FP:ClNC (XB-IP) as ion-pair complexes.

1 and ZB-2, the dominant charge-transfer interaction is Cl(lp) → σ*P−F. Thus, the H_2FP unit in these complexes becomes negatively charged, with the charges varying from −0.005e in H_2FP:ClCN to −0.025e in H_2FP:$ClCH_3$ ZB-2 complexes.

Electron Densities. The topological analyses of the electron densities of these complexes show the presence of a P−Cl bond critical point (BCP) and the corresponding bond path connecting the BCP with the P and Cl atoms. These features are illustrated in Table S1 of the Supporting Information. The values of the electron density at the BCP are greater for chlorine-shared and ion-pair halogen bonds, ranging from 0.114 to 0.166 au, and are reduced to between 0.007 and 0.020 au for the weaker interactions in the complexes with traditional halogen bonds and pnicogen bonds. The values of the Laplacian and the total energy density at the BCP are negative for the chlorine-shared and ion-pair halogen bonds, indicating their covalent nature,[34] but are positive for the remaining complexes. A good exponential relationship can be found between the electron density at the P−Cl BCP and the P−Cl distance, in agreement with previous reports.[35−42]

It is interesting to compare the relative positions of the P−Cl BCPs in the complexes with weak traditional halogen bonds and pnicogen bonds. For the traditional halogen bonds, the distance between P and the BCP (d1) is longer than that between Cl and the BCP (d2). The ratio d1/d2 in these complexes is between 1.14 and 1.20. In contrast, in the pnicogen-bonded complexes, d1 is shorter than d2, so that the d1/d2 ratio is between 0.88 and 0.95. These ratios are determined by the atom which acts as the electron-pair donor because the BCP path is longer to that atom because of its higher electron density.

Coupling Constants. The one-bond coupling constants ^{1X}J(P−Cl) and ^{1p}J(P−Cl) and their components for coupling across halogen bonds and pnicogen bonds, respectively, in complexes H_2FP:ClY are reported in Table S2 of the Supporting Information. These data show that coupling constants for complexes with traditional halogen bonds XB-T, and those with pnicogen bonds ZB-1 and ZB-2, have FC terms which are positive and dominant and good approximations to total *J*. However, this is not the case for the two complexes XB-S with chlorine-shared halogen bonds. ^{1X}J(P−Cl) for H_2FP:ClCl is dominated by a large positive FC term of 440 Hz, but the PSO term makes a negative contribution of −23 Hz and should not be neglected, although because of the large value of the FC term, neglecting the PSO term introduces an error of only about 4%. H_2FP:ClF also has a chlorine-shared halogen bond but with a shorter P−Cl distance which is approaching the distance in the cation H_2FPCl^+. As a result, the FC term is significantly reduced but remains positive, and the negative PSO term becomes the dominant term. In this complex, ^{1X}J(P−Cl) is reduced to −6. Hz. When the bond becomes an ion−pair bond in H_2FPCl^+:NC^-, the FC term is dominant and negative with a value of −178 Hz, while the PSO term also has a negative value of −41 Hz. The FC term is not a good approximation to total ^{1X}J(P−Cl). This pattern is similar to the pattern observed for the cation H_2FPCl^+.

Table 5 provides values of the coupling constant ^{1X}J(P−Cl) for the halogen-bonded complexes. As can be seen from these

Table 5. Coupling Constants ^{1X}J(P−Cl) for Complexes H_2FP:ClY with Halogen Bonds and ^{1p}J(P−Cl) (Hz) for Complexes with Pnicogen Bonds

H_2FP:ClY	XB-T	XB-S	XB-IP	ZB-1	ZB-2
Y = F		−6.3			
NC	174.8		−217.8[a]		
Cl	245.4	421.0		56.8	20.2
CN	68.5			24.7	15.6
CCH	67.5			26.8	18.5
CH_3				40.6	29.0
H				36.8	22.4

[a]^1J(P−Cl) for H_2FPCl^+ is −153.4 Hz.

data and from the discussion above, the values of this coupling constant span a large range, from −218 Hz in the ion-pair complex to +245 Hz in the H_2FP:ClCl complex with a traditional halogen bond. How can this behavior be understood? The dependence of ^{1X}J(P−Cl) on the P−Cl distance and the nature of the halogen bond is illustrated in Figure 5

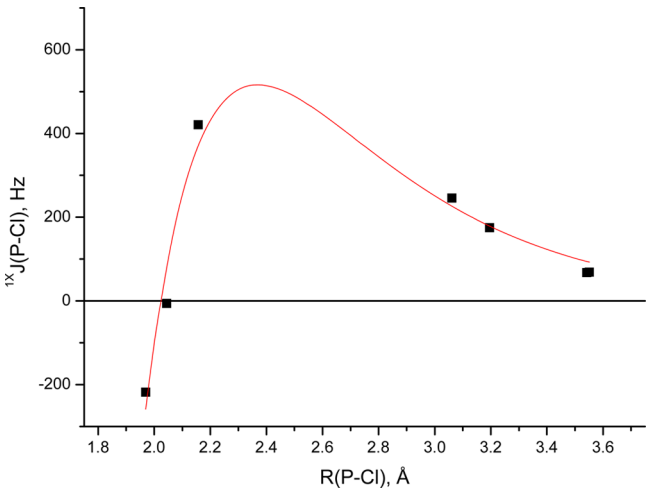

Figure 5. Coupling constant ^{1X}J(P−Cl) versus the P−Cl distance for complexes with halogen bonds.

using a Morse curve. At long distances, ^{1X}J(P−Cl) values for complexes with traditional halogen bonds increase as the P−Cl distance decreases. As this distance decreases further, the curvature changes as the halogen bond changes from traditional to chlorine-shared, and ^{1X}J(P−Cl) attains its maximum values for chlorine-shared halogen bonds. A further decrease in the P−Cl distance leads to a decrease in ^{1X}J(P−Cl) and eventually to a change of sign as the halogen bond changes from chlorine-shared to ion-pair.

^{1p}J(P−Cl) values for the pnicogen-bonded complexes are also reported in Table 5. These values range from 25 to 57 Hz

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for complexes ZB-1 and from 16 to 29 Hz for ZB-2. Values for complexes ZB-1 are always greater than the corresponding ZB-2 values, although the P−Cl distances in ZB-1 complexes are not always shorter than those in ZB-2. The tendency for ^{1p}J(P−Cl) to increase as the P−Cl distance decreases can be seen for all pnicogen-bonded complexes, although the data are definitely scattered. Plotting these data for complexes ZB-1 has a correlation coefficient of only 0.705, but the same plot for the ZB-2 complexes in Figure 6 gives a correlation coefficient R^2 of 0.928.

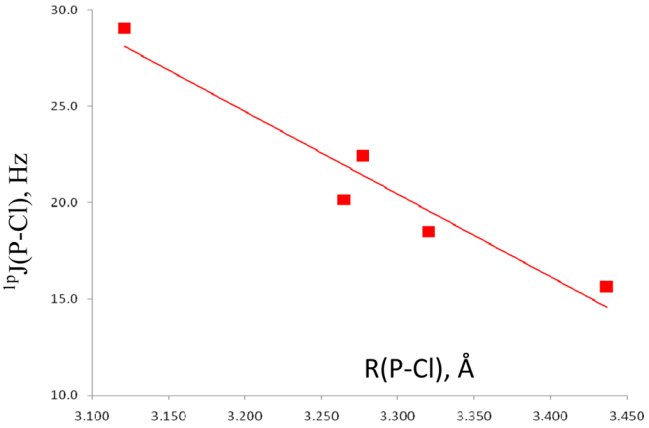

Figure 6. Coupling constant ^{1p}J(P−Cl) versus the P−Cl distance for pnicogen-bonded complexes ZB-2.

CONCLUSIONS

Ab initio MP2/aug′-cc-pVTZ calculations have been carried out on the H_2FP:ClY potential surfaces, for Y = F, NC, Cl, CN, CCH, CH_3, and H, in search of equilibrium complexes with P···Cl pnicogen bonds and halogen bonds. Three different types of halogen-bonded complexes with traditional, chlorine-shared, and ion-pair halogen bonds and two different pnicogen-bonded complexes have been found on these surfaces.

1. The most electronegative substituents F and NC form only halogen-bonded complexes, while the most electropositive substituents CH_3 and H form only pnicogen-bonded complexes. The halogen-bonded complexes involving the more electronegative groups Cl and CN are more stable than the corresponding pnicogen-bonded complexes, while the pnicogen-bonded complexes with CCH are more stable than the corresponding halogen-bonded complex. Thus, changing the substituent Y of ClY can alter the preference for halogen bonds or pnicogen bonds.
2. The substituent F forms only one complex with a chlorine-shared halogen bond; NC forms complexes with traditional and ion-pair bonds; and Cl forms complexes with traditional and chlorine-shared bonds. The substituents CN and CCH form only complexes with traditional halogen bonds. The substituents Cl, CN, CCH, CH_3, and H form two types of pnicogen-bonded complexes: one in which the P−A bond is *cis* to the bisector of the H−P−H angle, and the other in which the P−A bond is either *trans* or *gauche* to the bisector. A is the atom of Y that is directly bonded to Cl.
3. Traditional halogen-bonded complexes are stabilized by charge transfer from the P lone pair to the Cl−A σ^* orbital. Charge transfer from the Cl lone pair to the P−F σ^* orbital stabilizes pnicogen-bonded complexes. As a result, the H_2FP unit becomes positively charged in halogen-bonded complexes and negatively charged in pnicogen-bonded complexes.
4. Spin−spin coupling constants ^{1X}J(P−Cl) for complexes with traditional halogen bonds increase with decreasing P−Cl distance, reach a maximum value for complexes with chlorine-shared halogen bonds, and then decrease and change sign for complexes with ion-pair bonds. ^{1p}J(P−Cl) values for coupling across pnicogen bonds tend to increase with decreasing P−Cl distance.

ASSOCIATED CONTENT

Supporting Information

Geometries, molecular graphs, and total energies of H_2FP:ClY complexes; components of ^{1X}J(P−Cl) and ^{1p}J(P−Cl) for complexes with halogen bonds and pnicogen bonds, respectively, and ^{1}J(P−Cl) for H_2FPCl^+; full refs 20 and 33. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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