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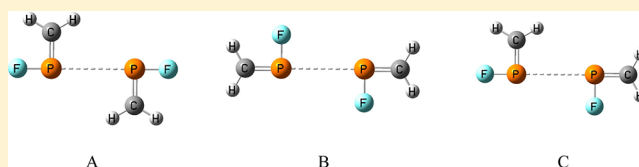
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Characterizing Complexes with Pnictogen Bonds Involving sp^2 Hybridized Phosphorus Atoms: $(H_2C=PX)_2$ with $X = F, Cl, OH, CN, NC, CCH, H, CH_3$, and BH_2 Janet E. Del Bene,^{*,†} Ibon Alkorta,^{*,‡} and José Elguero[‡][†]Department of Chemistry, Youngstown State University, Youngstown, Ohio 44555, United States[‡]Instituto de Química Médica (IQM-CSIC), Juan de la Cierva, 3, E-28006 Madrid, Spain

S Supporting Information

ABSTRACT: Ab initio MP2/aug'-cc-pVTZ searches of the potential surfaces of $(H_2C=PX)_2$ complexes, with $X = F, Cl, OH, CN, NC, CCH, H, CH_3$, and BH_2 , have been carried out to identify and characterize the properties of complexes with $P\cdots P$ pnictogen bonds. All $(H_2C=PX)_2$ form equilibrium conformation A dimers with C_{2h} symmetry in which A—P—P—A approaches a linear alignment, with A the atom of X directly bonded to P. Conformation A dimers containing the more electronegative substituents are stabilized by a $P\cdots P$ pnictogen bond, have shorter P—P distances, and have binding energies which correlate with the P—P distance. Dimers stabilized by a $P\cdots P$ pnictogen bond and two $P\cdots H_b$ interactions consist of those with the more electropositive substituents, have shorter P— H_b distances, and have binding energies which are too high for their P—P distances. Conformation A complexes with $P\cdots H_b$ interactions in addition to the $P\cdots P$ bond are more stable than the corresponding $(PH_2X)_2$ complexes, while with only one exception, complexes stabilized by only a $P\cdots P$ bond are less stable than the corresponding $(PH_2X)_2$ complexes. In the region of the potential surfaces with C—P—P—C approaching linearity (conformation B), the only planar equilibrium complex is $(H_2C=POH)_2$, which is stabilized primarily by two O—H—P hydrogen bonds. The remaining $(H_2C=PX)_2$ complexes are not stabilized by pnictogen bonds, but by π interactions between the two $H_2C=PX$ monomers which are in parallel planes. When A—P—P—C approaches linearity, two types of equilibrium structures with $P\cdots P$ bonds exist. Of the conformation C dimers, $(H_2C=POH)_2$ is planar and the most stable, with a $P\cdots P$ pnictogen bond and an O—H—P hydrogen bond. $(H_2C=PH)_2$ and $(H_2C=PCH_3)_2$ are also planar, and stabilized by a $P\cdots P$ pnictogen bond and a $P\cdots H_b$ interaction. The absence of a $P\cdots H_b$ interaction results in nonplanar C' conformations with structures in which the monomers essentially retain their symmetry plane, but the plane of one molecule is rotated about the $P\cdots P$ bond relative to the other. C and C' dimers are less stable than the corresponding A dimers, except for $(H_2C=PCH_3)_2$. ^{31}P chemical shielding patterns are consistent with the changing nature of the interactions which stabilize $(H_2C=PX)_2$ complexes. EOM-CCSD ^{31}P — ^{31}P spin—spin coupling constants increase quadratically as the P—P distance decreases.



■ INTRODUCTION

The pnictogen bond is a Lewis acid–Lewis base interaction in which a pnictogen atom (N, P, As) serves as the Lewis acid. Although the pnictogen bond has been recognized for several decades,^{1–5} it was the landmark paper by Hey-Hawking et al.⁶ which sparked a resurgence of interest in this type of intermolecular interaction,^{7–35} particularly when the pnictogen atom is a phosphorus atom. Previous papers on pnictogen bonding have focused on complexes involving one or two sp^3 hybridized P atoms. This led us to ask whether an sp^2 hybridized P could also form complexes stabilized by $P\cdots P$ pnictogen bonds. To answer this question, we have investigated a series of complexes $(H_2C=PX)_2$, for $X = F, Cl, OH, CN, NC, CCH, H, CH_3$, and BH_2 .

Since $(H_2C=PX)_2$ potential surfaces may have many local minima, we decided to focus our searches of these surfaces on complexes stabilized by $P\cdots P$ pnictogen bonds with structural characteristics found in previous studies. These potential

surfaces were searched initially in regions in which there exists a linear or nearly linear arrangement of atoms across the pnictogen bond, as illustrated in Figure 1 using $(H_2C=PF)_2$ as an example. Structures A and B have C_{2h} symmetry, with F—P—P—F approaching linearity in A and C—P—P—C in B. Structure C has only C_s symmetry with F—P—P—C linear.

In this paper we present the equilibrium dimers which were found on the $(H_2C=PX)_2$ potential surfaces. We will characterize these complexes in terms of their structures, binding energies, bonding properties, charge-transfer energies, ^{31}P chemical shieldings, and ^{31}P — ^{31}P spin—spin coupling constants. We will also compare these complexes with the dimers $(PH_2X)_2$ with $P\cdots P$ pnictogen bonds involving sp^3 hybridized P atoms.

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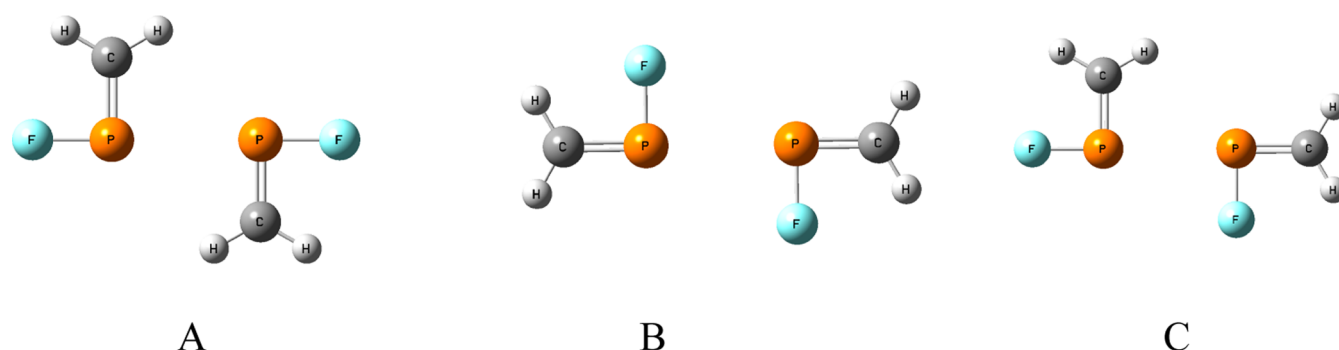


Figure 1. Structures A, B, and C illustrating linear F–P...P and C–P...P arrangements.

Table 1. Computed and Experimental Geometries and Dipole Moments of $\text{H}_2\text{C}=\text{PH}^a$

	R(P–H)	R(C–P)	R(C–H)	<HCP(Z)	<HCP(E)	<CPH	μ
expt ^b	1.425	1.671	1.082	124.5	119.1	95.5	0.860
calcd	1.419	1.674	1.082	124.4	118.9	97.1	0.867

^aDistances (R) in Å; angles (<) in degrees; dipole moments (μ) in Debyes. ^bExperimental data from ref.⁵⁸

COMPUTATIONAL METHODS

The structures of the monomers and complexes were optimized at second-order Møller–Plesset perturbation theory (MP2)^{36–39} with the aug'-cc-pVTZ basis set,⁴⁰ which is the Dunning aug-cc-pVTZ basis set^{41,42} with diffuse functions removed from H atoms. Because some complexes with structures B and C are not equilibrium structures, further optimizations were carried out under relaxed symmetry constraints. Frequencies were computed to identify local minima and transition structures. Optimization and frequency calculations were performed using the Gaussian 09 program.⁴³

Electron densities of complexes were analyzed employing the Atoms in Molecules (AIM) methodology^{44,45} with the AIMAll program.⁴⁶ The Natural Bond Orbital (NBO) method⁴⁷ was used to obtain atomic charges and analyze charge-transfer interactions between occupied and virtual orbitals using the NBO-5 program⁴⁸ within the Gamess program.⁴⁹ The molecular electrostatic potential (MEP) was calculated and represented on the 0.001 au electron density isosurface using the WFA program.⁵⁰ This isosurface has been shown to resemble the van der Waals surface.⁵¹

MP2/aug'-cc-pVTZ absolute chemical shieldings have been calculated within the GIAO approximation.⁵² Coupling constants were evaluated using the equation-of-motion coupled cluster singles and doubles (EOM-CCSD) method in the CI (conformation interaction)-like approximation,^{53,54} with all electrons correlated. For these calculations, the Ahlrichs⁵⁵ qzp basis set was placed on ¹³C, ¹⁵N, ¹⁷O, and ¹⁹F, and the qz2p basis set on ³¹P, ³⁵Cl, and ¹H of a hydrogen-bonded O–H group. The Dunning cc-pVDZ basis set was placed on the remaining H atoms. A previously developed basis set with the same number of functions as the qzp basis was used for ¹¹B.⁵⁶ The EOM-CCSD calculations were performed using ACES II⁵⁵ on the IBM Cluster 1350 (Glenn) at the Ohio Supercomputer Center.

RESULTS AND DISCUSSION

This section has been divided into five subsections. The first compares the experimental and computed structures of $\text{H}_2\text{C}=\text{PH}$ and examines the MEP of $\text{H}_2\text{C}=\text{PF}$. Section II presents equilibrium complexes with structure A. Section III presents

equilibrium complexes resulting from optimizations of structure B, and section IV reports those arising from structure C. Finally, section V presents a comparison of the equilibrium conformations for the series of complexes $(\text{H}_2\text{C}=\text{PX})_2$. Structures, total energies, and molecular graphs are reported in Table S1 of the Supporting Information.

I. Monomers $\text{H}_2\text{C}=\text{PH}$ and $\text{H}_2\text{C}=\text{PF}$. The experimental geometry and dipole moment of the parent molecule $\text{H}_2\text{C}=\text{PH}$ have been derived from its microwave spectrum⁵⁸ and are reported in Table 1 along with the corresponding MP2/aug'-cc-pVTZ data. As evident from this Table, the computed and experimental geometries and dipole moments are in very good agreement.

The molecular electrostatic potential (MEP) on the 0.001 au electron density isosurface of one of the monomers, $\text{H}_2\text{C}=\text{PF}$, is illustrated in Figure 2. This surface clearly shows the P lone pair and the σ -hole. The MEP suggests that the P atom may simultaneously act as an electron-pair donor and an electron-pair acceptor, a necessary condition for the formation of a P...P pnictogen bond.

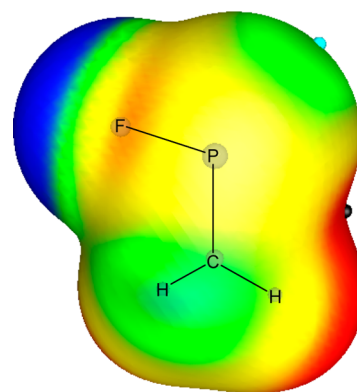


Figure 2. The MEP on the 0.001 au electron density isosurface of $\text{H}_2\text{C}=\text{PF}$. Color code: red > 0.02 > yellow > 0.0 > green > -0.01 > blue. Blue and red indicate the most negative and most positive values, respectively, of the MEP. Black and light blue dots indicate the σ -hole and the lone pair of the P atom, respectively.

II. Complexes with Structure A. All conformation A complexes have C_{2h} symmetry with an A–P···P–A arrangement which approaches linearity, with A the atom of X directly bonded to P. All C_{2h} conformations are equilibrium structures on their potential surfaces, with no imaginary frequencies. Binding energies and selected structural parameters of conformation A complexes are given in Table 2. Binding

Table 2. Binding Energies (ΔE), Charge-Transfer Energies [$P(1)_{ip} \rightarrow \sigma^*P-A(2)$, kJ mol^{-1}], P–P and P–H_b Distances (R , Å), and P–P–C angles (\angle , deg) of Conformation A Complexes ($\text{H}_2\text{C}=\text{PX}$)₂ with C_{2h} Symmetry

($\text{H}_2\text{C}=\text{PX}$) ₂ X =	ΔE	$R(\text{P}-\text{P})$	$R(\text{P}-\text{H}_b)^a$	\angle	$P(1)_{ip} \rightarrow \sigma^*P-A(2)$
CCH	13.87	3.510	3.230	87	5.4
BH ₂	13.52	3.779	3.136	78	1.0
Cl	13.33	3.373	3.305	92	8.7
CN	11.61	3.456	3.293	90	6.9
H	11.16	3.618	3.220	84	3.6
NC	11.06	3.422	3.362	92	9.4
CH ₃	10.81	3.701	3.217	83	1.8
F	10.41	3.477	3.406	93	6.0
OH	9.45	3.583	3.370	90	4.1

^aH_b is the H atom of the CH₂ group of one molecule which is closer to the P atom of the other.

energies are defined as the negative energy for the reaction which forms the dimer from the isolated monomers. The structures and molecular graphs of these complexes are given in Table S1 of the Supporting Information. Representative complexes ($\text{H}_2\text{C}=\text{PH}$)₂ and ($\text{H}_2\text{C}=\text{PF}$)₂ are illustrated in Figure 3.

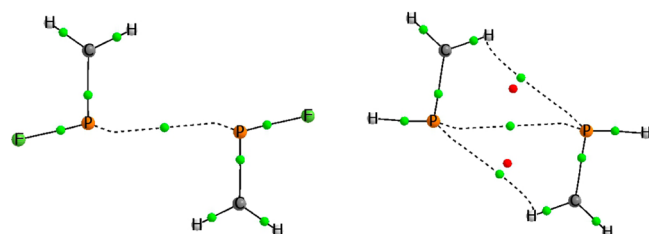


Figure 3. Structures and molecular graphs for ($\text{H}_2\text{C}=\text{PF}$)₂ and ($\text{H}_2\text{C}=\text{PH}$)₂ illustrating the two types of conformation A dimers. ($\text{H}_2\text{C}=\text{PF}$)₂ has only a P···P pnictogen bond; ($\text{H}_2\text{C}=\text{PH}$)₂ has a pnictogen bond and two P···H_b interactions.

The structures and binding energies of complexes ($\text{H}_2\text{C}=\text{PX}$)₂ with conformation A exhibit many interesting features. As evident from Table 2, the range of binding energies is relatively narrow, from 9.5 to 13.9 kJ mol^{-1} . This may be compared with the binding energies of complexes (PH_2X)₂, which range from 7.0 kJ mol^{-1} for (PH_2BH_2)₂ to 34.0 kJ mol^{-1} for (PH_2F)₂. Moreover, among complexes (PH_2X)₂, (PH_2BH_2)₂ has the smallest binding energy, but ($\text{H}_2\text{C}=\text{PBH}_2$)₂ has one of the highest binding energies among ($\text{H}_2\text{C}=\text{PX}$)₂ complexes. F as the substituent produces the strongest P···P bond in the (PH_2X)₂ series, but a relatively weak P···P bond among complexes ($\text{H}_2\text{C}=\text{PX}$)₂.

Another interesting feature is the lack of correlation between the binding energies of these complexes and the intermolecular P–P distances, as evident from Figure 4. On the basis of Figure 3, Figure 4, and the molecular graphs in Table S1, it appears

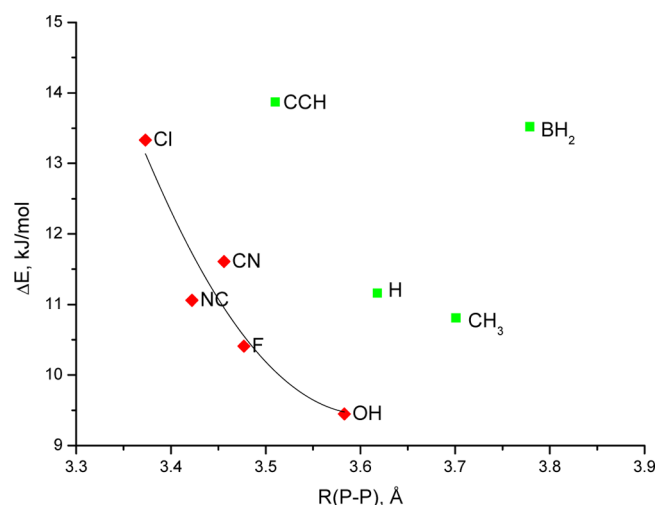


Figure 4. Binding energies of complexes ($\text{H}_2\text{C}=\text{PH}$)₂ versus the P–P distance. (Red diamonds) Complexes with P···P pnictogen bonds; (green squares) complexes involving two P···H_b interactions in addition to a P···P bond.

that conformation A complexes can be subdivided into two types: those which are stabilized by the pnictogen bond, and those which are stabilized by the P···P pnictogen bond and in addition by two significant P···H_b interactions, where H_b is the H atom of the CH₂ group of one molecule which is closer to the P atom of the other. The complexes stabilized by pnictogen bonds tend to have shorter P–P distances. In Figure 4 they are indicated by red diamonds, and consist of complexes with X = Cl, CN, NC, F, and OH, which are the more electronegative substituents. Structurally, these complexes have P–H_b distances of 3.29 Å or greater, and P–P–C angles between 90 and 93°. This group is typified by ($\text{H}_2\text{C}=\text{PF}$)₂ in Figure 3. The complexes represented by green squares in Figure 4 have binding energies which appear to be too high for their P–P distances, and consist of complexes with X = CCH, BH₂, H, and CH₃, which are the more electropositive substituents. Complexes in this group have shorter P–H_b distances between 3.13 and 3.23 Å, and P–P–C angles which range from 78 to 87°. ($\text{H}_2\text{C}=\text{PH}$)₂ which is illustrated in Figure 3, is representative of this group. Although the molecular graph for ($\text{H}_2\text{C}=\text{PCCH}$)₂ does not indicate a bond path for P···H_b interactions, its structural parameters and its relationship to the other complexes in this group in Figure 4 suggest that it should be included. Since there is a second stabilizing interaction in some of these complexes in addition to the P···P pnictogen bond, it should not be surprising that the binding energies of configuration A complexes do not correlate with P–P distances. However, a correlation does exist for the subset of complexes stabilized only by a pnictogen bond, as evident from Figure 4.

A comparison of the binding energies of complexes ($\text{H}_2\text{C}=\text{PX}$)₂ and (PH_2X)₂ shows that when X = Cl, NC, F, and OH, the binding energy of (PH_2X)₂ is greater than the binding energy of the corresponding ($\text{H}_2\text{C}=\text{PX}$)₂. Both series of complexes are stabilized by P···P pnictogen bonds. In contrast, when X = CCH, BH₂, H, and CH₃, the binding energy of ($\text{H}_2\text{C}=\text{PX}$)₂ is greater than the corresponding complex (PH_2X)₂. These complexes ($\text{H}_2\text{C}=\text{PX}$)₂ are stabilized by a pnictogen bond and two P···H_b interactions. The only complexes that do not fit this pattern are (PH_2CN)₂ and

$(\text{H}_2\text{C}=\text{PCN})_2$, in which case $(\text{H}_2\text{C}=\text{PCN})_2$ is more stable by 3.2 kJ mol^{-1} .

To further illustrate the importance of the $\text{P}\cdots\text{H}_\text{b}$ interaction, the ELF 0.08 au isosurface of $(\text{H}_2\text{C}=\text{PH})_2$ is illustrated in Figure 5. This surface shows that the smaller value of the $\text{P}-\text{P}$

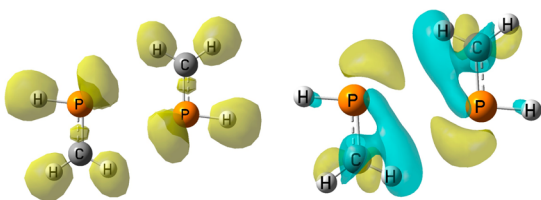


Figure 5. The ELF 0.08 au isosurface of $(\text{H}_2\text{C}=\text{PH})_2$ (left). The lone pair on one P is directed toward the $\text{C}-\text{H}_\text{b}$ bond and the positive region of the MEP around the P of the other molecule. Electron density shifts upon complexation at the $\pm 0.0002 \text{ au}$ isosurface (right). Blue and yellow indicate gain and loss of electron density, respectively.

C angle for a complex with a $\text{P}\cdots\text{H}_\text{b}$ interaction directs the lone pair on P of one monomer toward the $\text{C}-\text{H}_\text{b}$ bond of the other, and simultaneously, toward the positive MEP region associated with the P atom of the second molecule. The electron density shifts upon complex formation at the $\pm 0.0002 \text{ au}$ isosurface are also illustrated in Figure 5. These shifts show the gain of electron density in the region of the $\text{C}-\text{H}_\text{b}$ bond and the positive MEP, and the loss of density in the lone pair region of P.

Table 2 also presents $\text{P}(1)_\text{p} \rightarrow \sigma^*\text{P}-\text{A}(2)$ charge-transfer energies for complexes $(\text{H}_2\text{C}=\text{PX})_2$ with conformation A. Charge transfer stabilizes these complexes, but charge-transfer energies are relatively small, ranging from 1.0 to 9.4 kJ mol^{-1} , compared to 100 kJ mol^{-1} for $(\text{PH}_2\text{F})_2$ with $\text{F}-\text{P}\cdots\text{P}-\text{F}$ being linear. Thus, they reflect the weaker pnictogen bonds in $(\text{H}_2\text{C}=\text{PX})_2$. Charge transfer energies tend to be greater in complexes stabilized by the pnictogen bond compared to those with both a pnictogen bond and two $\text{P}\cdots\text{H}_\text{b}$ interactions, although there is an overlap involving complexes with $\text{X} = \text{OH}$ and CCH . Thus, these data also support the existence of two types of conformation A complexes, and the importance of the $\text{P}\cdots\text{H}_\text{b}$ interaction in one of these.

Are there other factors which influence the differences between the binding energies of complexes $(\text{H}_2\text{C}=\text{PX})_2$ and $(\text{PH}_2\text{X})_2$? Insight into the answer to this question can be obtained by comparing values of the MEP minima and maxima on the 0.001 au electron density isosurfaces which are reported in Table 3 for the two sets of monomers. It is well-known that part of the stabilization of complexes with pnictogen bonds is due to the electrostatic interaction between the negative lone pair on one atom and the positive σ -hole on the other. It is apparent from Table 3 that $V(\text{S},\text{max})$ for PH_2X is more positive than $V(\text{S},\text{max})$ for the corresponding $\text{H}_2\text{C}=\text{PX}$ monomer. Similarly, $V(\text{S},\text{min})$ for PH_2X is more negative than $V(\text{S},\text{min})$ for $\text{H}_2\text{C}=\text{PX}$. Since the $\text{P}-\text{P}$ distance in $(\text{PH}_2\text{X})_2$ is also shorter than the $\text{P}-\text{P}$ distance in the corresponding $(\text{H}_2\text{C}=\text{PX})_2$ complex, the electrostatic attraction between the two P atoms in $(\text{PH}_2\text{X})_2$ is greater.

Another interesting observation from Table 3 is the absence of a $V(\text{S},\text{max})$ value on the 0.001 au electron density isosurfaces for monomers $\text{H}_2\text{C}=\text{PH}$, $\text{H}_2\text{C}=\text{PCCH}$, $\text{H}_2\text{C}=\text{PBH}_2$, and $\text{H}_2\text{C}=\text{PCH}_3$. These are the monomers which give rise to the four configuration A complexes which are stabilized by two $\text{P}\cdots\text{H}_\text{b}$ interactions in addition to the $\text{P}\cdots\text{P}$ pnictogen bond. It

Table 3. MEP Maxima and Minima [$V(\text{S},\text{max})$] and [$V(\text{S},\text{min})$, au] around the P Atom on the 0.001 au Electron Density Isosurfaces of $\text{H}_2\text{C}=\text{PX}$ and PH_2X ^a

X =	$\text{H}_2\text{C}=\text{PX}$		PH_2X	
	$V(\text{S},\text{max})$	$V(\text{S},\text{min})$	$V(\text{S},\text{max})$	$V(\text{S},\text{min})$
F	0.0356	−0.0076	0.0597	−0.0191
Cl	0.0352	−0.0057	0.0534	−0.0148
OH	0.0197	−0.0138	0.0395	−0.0240
NC	0.0474	0.0268	0.0682	−0.0047
CN	0.0439	0.0018	0.0577	−0.0029
H	<i>b</i>	−0.0209	0.0205	−0.0257
CCH	<i>b</i>	−0.0174	0.0341	−0.0222
BH ₂	<i>b</i>	−0.0263	0.0044	−0.0312
CH ₃	<i>b</i>	−0.0274	0.0128	−0.0343

^aMinima are associated with lone pairs and maxima with σ -holes. ^bNo $V(\text{S},\text{max})$ found on these surfaces.

may well be that $\text{P}\cdots\text{H}_\text{b}$ interactions are the more important interactions in these complexes, and that the σ -holes on P are not well-defined in these monomers.

Table 4 reports ^{31}P chemical shieldings for monomers $\text{H}_2\text{C}=\text{PX}$ and corresponding dimers $(\text{H}_2\text{C}=\text{PX})_2$ with

Table 4. NMR ^{31}P Chemical Shieldings (ppm) and $^{1\text{p}}\text{J}(\text{P}-\text{P})$ Spin–spin Coupling Constants (Hz) for Dimers $(\text{H}_2\text{C}=\text{PX})_2$ with Conformation A

$(\text{H}_2\text{C}=\text{PX})_2$, X =	^{31}P shielding		$^{1\text{p}}\text{J}(\text{P}-\text{P})$
	monomer	dimer	
CCH	166.9	171.6	140.3
BH ₂	88.0	93.7	31.2
Cl	65.3	73.0	330.1
CN	192.7	198.5	187.3
H	155.2	161.4	74.7
NC	135.9	141.1	264.1
CH ₃	90.1	94.9	58.5
F	13.8	17.0	247.9
OH	44.8	45.3	134.3

conformation A. The region in the NMR spectra in which the NMR signals appear is determined by the substituent X. From Table 4 it can be seen that ^{31}P shieldings increase in going from the monomer to the dimer. This is consistent with the decrease in the positive charge on P, since dimer formation leads to an increase in electron density on P. Although a graph of these variables shows a tendency for the shielding to increase as the electron density increases upon dimer formation, the correlation coefficient R^2 between these two variables is only 0.4.

Table 4 also reports the $^{31}\text{P}-^{31}\text{P}$ spin–spin coupling constants for the dimers $(\text{H}_2\text{C}=\text{PX})_2$. The values reported are the Fermi-contact (FC) terms, since it has been demonstrated that FC terms are excellent approximations to total $^{1\text{p}}\text{J}(\text{P}-\text{P})$ in complexes with pnictogen bonds. This approximation has been checked for $(\text{H}_2\text{C}=\text{PH})_2$ which has $\text{FC} = 74.7 \text{ Hz}$ and $^{1\text{p}}\text{J}(\text{P}-\text{P}) = 74.6 \text{ Hz}$, and for $(\text{H}_2\text{C}=\text{PF})_2$ which has corresponding values of 247.9 and 248.9 Hz , respectively.

$^{1\text{p}}\text{J}(\text{P}-\text{P})$ values in $(\text{H}_2\text{C}=\text{PX})_2$ range from 31 Hz for $(\text{H}_2\text{C}=\text{PBH}_2)_2$ to 330 Hz for $(\text{H}_2\text{C}=\text{PCl})_2$. Consistent with binding energies and charge transfer energies, this range is much smaller than that observed for the dimers $(\text{PH}_2\text{X})_2$, for

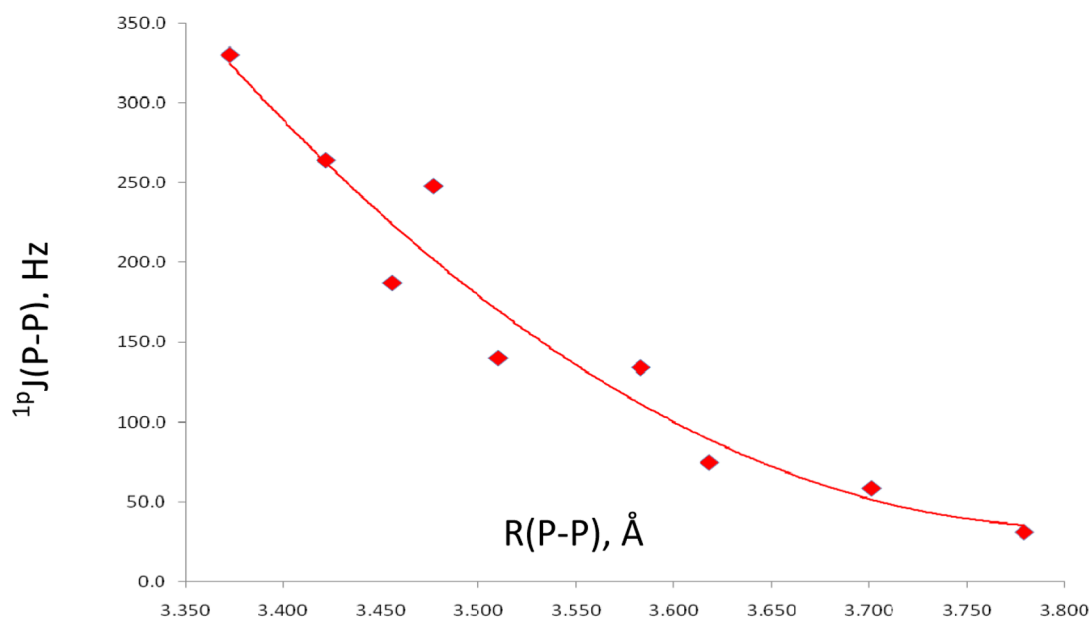


Figure 6. $^1\text{pJ}(\text{P}-\text{P})$ versus the P–P distance in complexes $(\text{H}_2\text{C}=\text{PX})_2$. The correlation coefficient $R^2 = 0.937$.

which $^1\text{pJ}(\text{P}-\text{P})$ ranges from 46 Hz for $(\text{PH}_2\text{BH}_2)_2$ to 1120 Hz for $(\text{PH}_2\text{Cl})_2$. $^1\text{pJ}(\text{P}-\text{P})$ values for $(\text{H}_2\text{C}=\text{PX})_2$ correlate quadratically with the P–P distance, as seen in Figure 6. This correlation includes both types of configuration A complexes.

III. Complexes Derived from Structure B. Searches were carried out of the potential surfaces to identify complexes with P...P pnictogen bonds with C–P...P–C linear and C_{2h} symmetry. These are type B complexes if the optimized structure has C_{2h} symmetry, or B' if the optimized structure has a lower symmetry. With one exception, all of the optimized complexes with C_{2h} symmetry have one or more imaginary frequencies. The single exception is $(\text{H}_2\text{C}=\text{POH})_2$, which is illustrated in Figure 7. $(\text{H}_2\text{C}=\text{POH})_2$ conformation B is

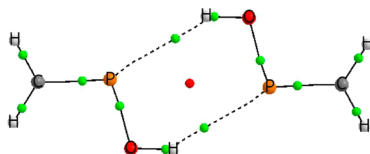


Figure 7. The equilibrium structure and molecular graph of $(\text{H}_2\text{C}=\text{POH})_2$, type B.

stabilized primarily by two distorted O–H...P hydrogen bonds. The H–O–P angle is 26° , the O–P distance is 3.462 Å, and the P...P–C alignment approaches linearity with a P–P–C angle of 175° . Although there is no bond path for a P...P interaction, the P–P distance of 3.644 Å suggests that a pnictogen bond contributes to some extent to the stability of this complex. The binding energy of $(\text{H}_2\text{C}=\text{POH})_2$ is 24.8 kJ mol $^{-1}$, which makes it 15.4 kJ mol $^{-1}$ more stable than the corresponding conformation A dimer, and the most stable complex found on any potential surface examined in this study.

The NBO analysis of charge transfer energies in $(\text{H}_2\text{C}=\text{POH})_2$ indicates that charge transfer $\text{P}(1)_{\text{lp}} \rightarrow \sigma^*\text{O}-\text{H}(2)$ across the hydrogen bond is much more important than charge transfer $\text{P}(1)_{\text{lp}} \rightarrow \sigma^*\text{P}-\text{C}(2)$ across the pnictogen bond. The charge-transfer energies are 13.9 kJ mol $^{-1}$ and 2.0 kJ mol $^{-1}$, respectively.

The ^{31}P chemical shielding for $(\text{H}_2\text{C}=\text{POH})_2$ is 64.4 ppm, an increase of 19.6 ppm relative to the isolated monomer. This is a much larger change upon dimer formation than observed for dimer A. $^1\text{pJ}(\text{P}-\text{P})$ for $(\text{H}_2\text{C}=\text{POH})_2$ has a value of 32.4 Hz. The point for this complex on the $^1\text{pJ}(\text{P}-\text{P})$ versus $R(\text{P}-\text{P})$ graph in Figure 6 lies a bit below the trendline. The FC term for O–P coupling across the O–H...P hydrogen bond is –9.9 Hz. For comparison, the FC term and $^{2h}\text{J}(\text{O}-\text{P})$ for the

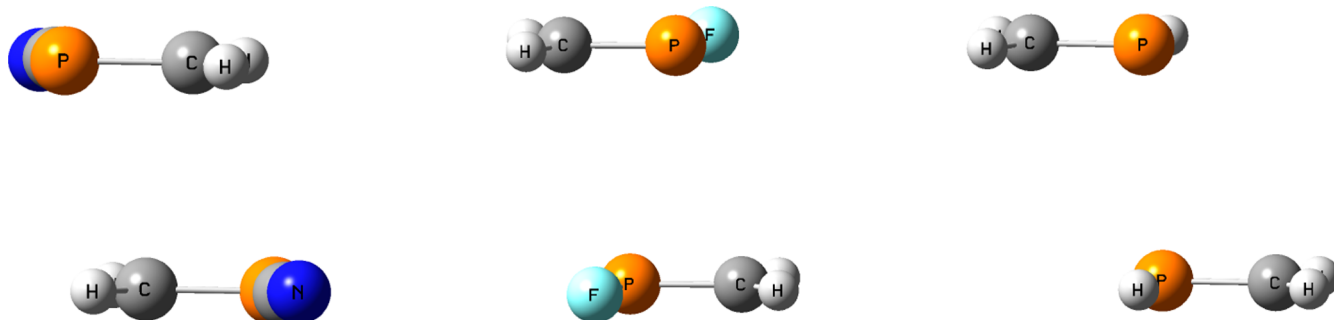
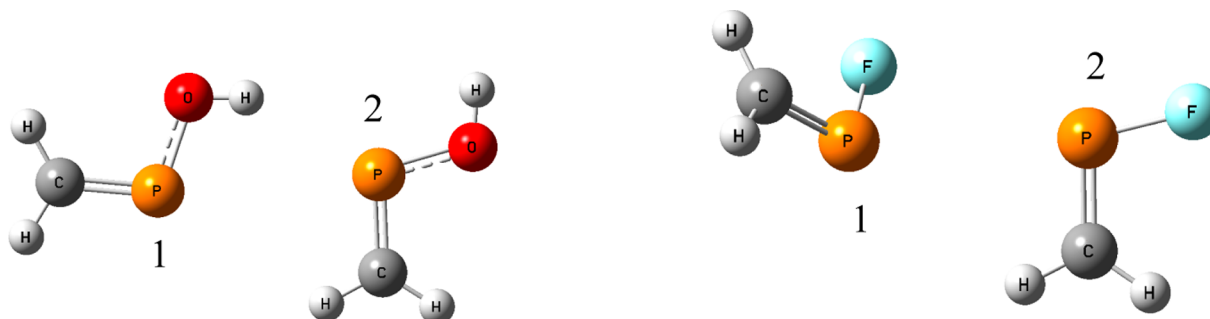


Figure 8. B' complexes $(\text{H}_2\text{C}=\text{PCN})_2$, $(\text{H}_2\text{C}=\text{PF})_2$, and $(\text{H}_2\text{C}=\text{PH})_2$ with C_i symmetry.

Table 5. P–P Distances [$R(\text{P}–\text{P})$, Å], Binding Energies (ΔE , kJ mol^{−1}), ³¹P Chemical Shieldings [$\sigma\text{P}(1)$ and $\sigma\text{P}(2)$, ppm], and ³¹P–³¹P Spin–Spin Coupling Constants [$^1J(\text{P}–\text{P})$, Hz] of Equilibrium ($\text{H}_2\text{C}=\text{PX})_2$ Conformations C and C'

complex	type	symmetry	$R(\text{P}–\text{P})$	ΔE	$\sigma\text{P}(1)^a$	$\sigma\text{P}(2)^a$	$^1J(\text{P}–\text{P})$
($\text{H}_2\text{C}=\text{POH}$) ₂	C	C _s	3.738	16.39	54.9	57.3	43.5
($\text{H}_2\text{C}=\text{PCl}$) ₂	C'	C ₁	3.457	11.55	71.1	66.0	
($\text{H}_2\text{C}=\text{PCH}_3$) ₂	C'	C ₁	3.696	11.40	90.8	95.4	
	C	C _s	3.712	11.35			66.1
($\text{H}_2\text{C}=\text{PCN}$) ₂	C'	C ₁	3.519	10.99	193.9	191.7	
($\text{H}_2\text{C}=\text{PNC}$) ₂	C'	C ₁	3.254	9.95	139.9	135.8	
($\text{H}_2\text{C}=\text{PH}$) ₂	C	C _s	3.657	8.89	152.6	159.6	99.3
($\text{H}_2\text{C}=\text{PF}$) ₂	C'	C ₁	3.579	7.67	20.0	12.4	95.9

^aThe arrangement which approaches linearity is C–P(1)⋯P(2)–A.

**Figure 9.** Complexes with conformations C ($\text{H}_2\text{C}=\text{POH}$)₂ and C' ($\text{H}_2\text{C}=\text{PF}$)₂. Labels identify P(1) and P(2).

hydrogen-bonded complex $\text{HOH}\cdots\text{PH}_3$ are -13.2 and -13.5 Hz, respectively. Since O–H coupling constants have non-negligible contributions from PSO terms, O–H coupling constants for ($\text{H}_2\text{C}=\text{POH}$)₂ are not reported.

Relaxing the C_{2h} symmetry constraint yielded five equilibrium structures with C_i symmetry and no imaginary frequencies. However, one of these, ($\text{H}_2\text{C}=\text{PBH}_2$)₂, is really not a complex, but a molecule $\text{C}_2\text{H}_4\text{B}_2\text{P}_2$ with a six-member ring and P–B bonds. The remaining optimized complexes, ($\text{H}_2\text{C}=\text{PCN}$)₂, ($\text{H}_2\text{C}=\text{PH}$)₂, ($\text{H}_2\text{C}=\text{PCH}_3$)₂, and ($\text{H}_2\text{C}=\text{PF}$)₂ also have C_i symmetry and will be referred to as B' conformations. In these conformations, the monomers remain essentially planar, and the planes of the two monomers are parallel, as illustrated in Figure 8 for ($\text{H}_2\text{C}=\text{PCN}$)₂, ($\text{H}_2\text{C}=\text{PF}$)₂, and ($\text{H}_2\text{C}=\text{PH}$)₂. Although the molecular graphs indicate a P–P interaction, B' complexes are not stabilized by pnictogen bonds, but by π interactions. However, these complexes have binding energies comparable to or even greater than the corresponding A dimers. For example, ($\text{H}_2\text{C}=\text{PCN}$)₂ has a binding energy of 20.4 kJ mol^{−1}, which is 8.8 kJ mol^{−1} greater than that of conformation A. Since type B' complexes are not stabilized by pnictogen bonds, they will not be discussed further in this paper. Given the absence of pnictogen bonds in these complexes, no further searches of potential surfaces were done in C_1 symmetry.

$^1J(\text{P}–\text{P})$ coupling constants have been computed for ($\text{H}_2\text{C}=\text{PCN}$)₂, ($\text{H}_2\text{C}=\text{PF}$)₂, and ($\text{H}_2\text{C}=\text{PH}$)₂. $^1J(\text{P}–\text{P})$ values are relatively small at 1.1, 6.3, and 12.7 Hz, at P–P distances of 3.894, 3.777, and 3.656 Å, respectively. These small coupling constants also support the absence of P⋯P pnictogen bonds.

IV. Complexes Derived from Structure C. Complexes in this group were obtained starting with structure C with C_s symmetry, and the carbon of the CH_2 group of one molecule and atom A of the substituent X of the other approaching a

linear C–P⋯P–A arrangement across the P⋯P bond. However, only two equilibrium structures of this type with no imaginary frequencies were found, namely, ($\text{H}_2\text{C}=\text{POH}$)₂ and ($\text{H}_2\text{C}=\text{PH}$)₂. These have C_s symmetry and will be referred to as conformation C complexes. Other equilibrium complexes found on the potential surfaces include ($\text{H}_2\text{C}=\text{PCl}$)₂, ($\text{H}_2\text{C}=\text{PCH}_3$)₂, ($\text{H}_2\text{C}=\text{PCN}$)₂, ($\text{H}_2\text{C}=\text{PNC}$)₂, and ($\text{H}_2\text{C}=\text{PF}$)₂. These complexes belong to point group C_1 , and are designated C' conformations. However, it should be noted that ($\text{H}_2\text{C}=\text{PCH}_3$)₂ with C_s symmetry is essentially identical structurally and energetically to the C_1 dimer. The C_s structure has one imaginary frequency of -4 cm^{−1} corresponding to a small displacement of methyl groups, and a binding energy only 0.05 kJ mol^{−1} less than the equilibrium C_1 conformation. The complex with BH_2 as X optimizes to a molecule with P–B bonds, while that with CCH as X optimizes to a structure in which the two monomers approach a parallel alignment similar to that found for complexes B'. Structural and energetic data for equilibrium C and C' complexes with pnictogen bonds are given in Table 5. Their structures and molecular graphs are reported in Table S1 of the Supporting Information. Figure 9 illustrates the structures of ($\text{H}_2\text{C}=\text{POH}$)₂ and ($\text{H}_2\text{C}=\text{PF}$)₂.

Except for ($\text{H}_2\text{C}=\text{PCH}_3$)₂, complexes with C and C' conformations have interestingly different structures. Complexes with conformation C have planar C_s symmetry. ($\text{H}_2\text{C}=\text{POH}$)₂ is stabilized by a P⋯P pnictogen bond, as well as an O–H⋯P hydrogen bond. The pnictogen bond has a P–P distance of 3.738 Å; the O–H⋯P hydrogen bond has an O–P distance of 3.461 Å and an H–O–P angle of 22° . The binding energy of this complex is 16.4 kJ mol^{−1}. The NBO analysis shows that the hydrogen bonding charge-transfer $\text{P}(2)_{\text{lp}} \rightarrow \sigma^* \text{O}–\text{H}(1)$ energy of 15.8 kJ mol^{−1} is more stabilizing than the $\text{P}(1)_{\text{lp}} \rightarrow \sigma^* \text{P}–\text{O}(2)$ energy of 2.3 kJ mol^{−1}.

($\text{H}_2\text{C}=\text{PH}$)₂ conformation C is stabilized by a pnictogen bond with a P–P distance of 3.657 Å, and one P⋯H_b

interaction with a P–H_b distance of 3.187 Å. Its binding energy is 8.89 kJ mol^{−1}. The NBO analysis shows that both molecules are involved as lone pair donors and acceptors for the pnictogen interaction with P(1)_{lp}→σ*P–H(2) and P(2)_{lp}→σ*P–C(1) energies of 3.6 kJ mol^{−1} in both cases. The values are the same as those found for conformation A.

The five equilibrium complexes with conformation C' are (H₂C=PCl)₂, (H₂C=PCH₃)₂, (H₂C=PCN)₂, (H₂C=PNC)₂, and (H₂C=PF)₂. The monomers that make up these dimers essentially retain their plane of symmetry, but the plane of one molecule is rotated about the P···P bond relative to the other, as illustrated in Figure 9 for (H₂C=PF)₂. The exception is (H₂C=PCH₃)₂. The binding energies of these complexes decrease in the order (H₂C=PCl)₂ > (H₂C=PCH₃)₂ > (H₂C=PCN)₂ > (H₂C=PNC)₂ > (H₂C=PF)₂. Except for (H₂C=PCH₃)₂, this is the same order found for corresponding complexes with conformation A. (H₂C=PCH₃)₂ is the second complex in the order of stability among the C' complexes, but among the A complexes, it is only more stable than (H₂C=PF)₂. The increased relative stability of (H₂C=PCH₃)₂ among the C' conformations may be attributed to the retention of the P···H_b interaction in its essentially planar structure.

The AIM molecular graphs indicate that conformation C' complexes are stabilized by P···P pnictogen bonds. Table 6

Table 6. NBO Charge-Transfer Stabilization Energies (kJ mol^{−1}) for Conformation C' Complexes

complex	P(1) _{lp} →σ*P–A(2)	P(2) _{lp} →σ*P–C(1)
(H ₂ C=PCl) ₂	5.2	4.9
(H ₂ C=PCH ₃) ₂ ^a	2.1	1.5
(H ₂ C=PCN) ₂	3.9	4.2
(H ₂ C=PNC) ₂	5.6	4.0
(H ₂ C=PF) ₂	4.0	3.3

^a(H₂C=PCH₃)₂ also has a stabilizing P···H_b interaction.

reports the energies of the two charge-transfer interactions which stabilize these complexes. The two charge transfer energies are similar, and except for (H₂C=PCN)₂, P(1)_{lp}→σ*P–A(2) is slightly more stabilizing than P(2)_{lp}→σ*P–C(1).

The NMR properties of absolute ³¹P chemical shieldings and ³¹P–³¹P spin–spin coupling constants have been computed for complexes with conformations C and C', and are reported in Table 5. Chemical shieldings are reported for P(1) and P(2), which are distinguished by the alignment across the pnictogen bond which approaches linearity as C–P(1)···P(2)–A, as illustrated in Figure 9.

The largest change in the chemical shielding relative to the corresponding monomer is found for (H₂C=POH)₂ conformation C, in which case both σ(P1) and σ(P2) increase by 10.1 and 12.5 ppm, respectively. The two complexes, (H₂C=PH)₂ and (H₂C=PCH₃)₂, which are stabilized by a P···P pnictogen bond and a P···H_b interaction show a pattern in which the chemical shielding of the phosphorus P(1) which interacts with H_b decreases slightly or remains the same, while the chemical shielding of P(2) increases by 4.4 and 5.3 ppm, respectively. The remaining conformation C' complexes exhibit a different pattern, with σ(P2) decreasing or remaining essentially the same, and σ(P1) increasing. Thus, the chemical shieldings in these dimers are sensitive to the different interactions which stabilize these complexes.

¹PJ(P–P) coupling constants for conformation C complexes (H₂C=POH)₂, (H₂C=PH)₂, and (H₂C=PCH₃)₂, and the C' complex (H₂C=PF)₂ are also reported in Table 5. Coupling constants have not been computed for the remaining C' complexes because of the computational expense of EOM-CCSD calculations for dimers with C₁ symmetry. Figure 10 presents a plot of ¹PJ(P–P) versus the P–P distance for complexes with conformations A, C, and C'. The points for the C and C' complexes fit nicely with the points for the conformation A complexes. The trendline in Figure 10 refers to all complexes, and has a correlation coefficient R² of 0.938.

V. Comparison of Different Equilibrium Complexes of (H₂C=PX)₂. The potential surfaces of complexes (H₂C=PX)₂

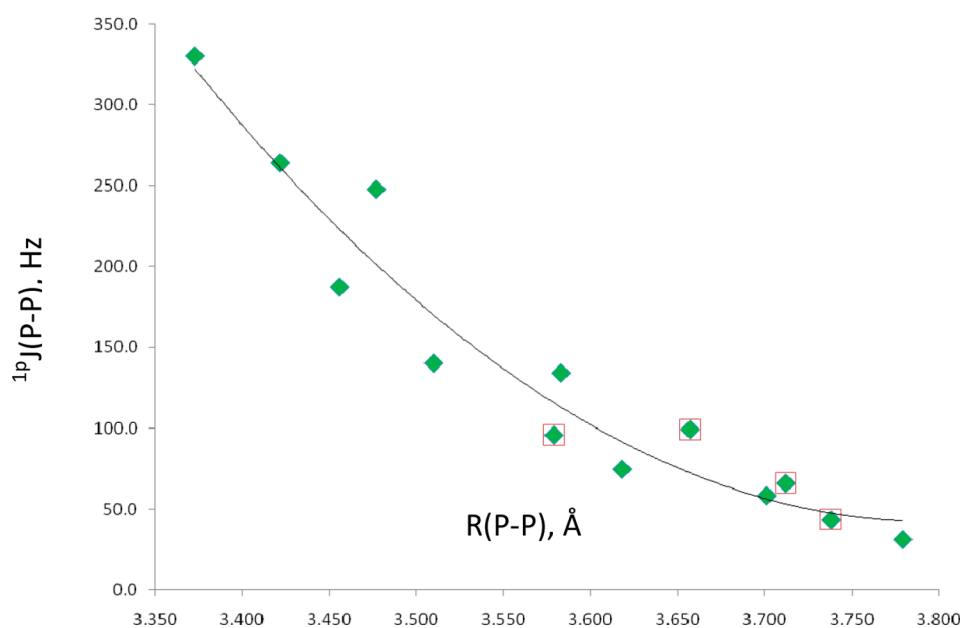


Figure 10. ¹PJ(P–P) versus the P–P distance for complexes A (green diamond), C and C' (red square).

which are stabilized at least in part by P...P pnictogen bonds have very different features, as evident by comparing the data in Table 7. While (H₂C=PCCH)₂ has the highest binding energy

Table 7. Conformations, Symmetries, Binding Energies (ΔE), Relative Binding Energies ($\delta\Delta E$, kJ mol⁻¹), and P–P Distances [$R(P-P)$, Å] for Equilibrium Structures on (H₂C=PX)₂ Potential Surfaces

(H ₂ C=PX) ₂ , X =	conf.	symmetry	ΔE	$\delta\Delta E^a$	$R(P-P)$
CCH	A	C _{2h}	13.87	0.0	3.510
BH ₂	A	C _{2h}	13.52	0.0	3.779
Cl	A	C _{2h}	13.33	0.0	3.373
	C'	C ₁	11.55	-1.78	3.479
CN	A	C _{2h}	11.61	0.0	3.456
	C'	C ₁	10.99	-0.62	3.519
H	A	C _{2h}	11.16	0.0	3.618
	C	C _s	8.89	-2.27	3.657
NC	A	C _{2h}	11.06	0.0	3.422
	C'	C ₁	9.95	-1.11	3.254
CH ₃	A	C _{2h}	10.81	0.0	3.701
	C'	C ₁	11.40	+0.59	3.696
	C ^b	C _s	11.35	+0.54	3.712
F	A	C _{2h}	10.41	0.0	3.477
	C'	C ₁	7.67	-2.74	3.579
OH	A	C _{2h}	9.45	0.0	3.583
	B	C _{2h}	24.80	+15.35	3.644
	C	C _s	16.38	+6.94	3.738

^aBinding energy relative to conformation A. ^bHas one imaginary frequency of -4 cm⁻¹.

among complexes with conformation A, no other equilibrium structures of this complex with P...P bonds were found on this potential surface. Similarly, on the (H₂C=PBH₂)₂ surface, only one equilibrium dimer with conformation A was found, since optimization of other structures led to cyclic molecules with P–B bonds. It is noteworthy that both (H₂C=PCCH)₂ and (H₂C=PBH₂)₂ conformation A complexes are stabilized not only by P...P bonds, but also by P...H_b interactions.

Only on the (H₂C=POH)₂ potential surface do three equilibrium structures exist with conformations A, B, and C. These are ordered according to stability as B > C > A. That is, the complex with two O–H...P hydrogen bonds and a weak P...P pnictogen bond is the most stable. In fact, its binding energy of 24.8 kJ mol⁻¹ makes it the most stable dimer among the entire series (H₂C=PX)₂. Next in stability comes conformation C, which is stabilized by one O–H...P hydrogen bond and a P...P pnictogen bond. The least stable conformation is A with only a P...P pnictogen bond. This ordering is another indication of the reduced tendency for sp² hybridized P atoms to form pnictogen bonds.

(H₂C=PH)₂ has two equilibrium structures which are planar. Conformation A with H–P...P–H linear is more stable with a binding energy of 11.2 kJ mol⁻¹. It is stabilized by a pnictogen bond and two P...H_b interactions. Conformation C, which has a binding energy of 8.9 kJ mol⁻¹, is stabilized by a P...P pnictogen bonds and one P...H_b interaction. It is interesting to note that the tilt of the molecule which provides H_b for the P...H_b interaction in C is similar (83°) to that in A, and that the P–H_b distance of 3.187 Å is slightly shorter than the corresponding distance in A.

Although the equilibrium (H₂C=PCH₃)₂ complex C' has C₁ symmetry, conformation C with C_s symmetry is structurally and

energetically essentially identical to C', both being stabilized by one P...P bond and one P...H_b interaction. Thus, conformation A complexes (H₂C=PH)₂ and (H₂C=PCH₃)₂ which are stabilized by this interaction, have corresponding planar C equilibrium conformations with C_s symmetry due to this same interaction. This reinforces the importance of the P...H_b interaction. In contrast, (H₂C=PCl)₂, (H₂C=PCN)₂, (H₂C=PNC)₂, and (H₂C=PF)₂ conformation A complexes are not stabilized to any appreciable extent by a P...H_b interaction. Without this interaction, their equilibrium structures derived from structure C are nonplanar.

The relative binding energies of the equilibrium structures of complexes (H₂C=PX)₂ are also reported in Table 7. (H₂C=POH)₂ is unique among the (H₂C=PX)₂ complexes, since there is a significant difference among the binding energies of its A, B, and C conformations. This difference can be attributed to the number of hydrogen bonds and to the preference for hydrogen bonding over pnictogen bonding. For the remaining complexes, the binding energy differences between the two equilibrium conformations, A and either C or C', are relatively small, ranging between 0.5 and 2.7 kJ mol⁻¹. For these, conformation A is more stable than conformation C or C', except for (H₂C=PCH₃)₂.

Conformation A complexes (H₂C=PX)₂ for X = CCH, BH₂, H, and CH₃, which are stabilized by P...H_b interactions in addition to a relatively weak P...P pnictogen bond, are more stable than the corresponding complexes (PH₂X)₂ with A–P...P–A linear. In contrast, (PH₂X)₂ complexes with X = F, Cl, and OH tend to be significantly more stable than the corresponding (H₂C=PX)₂ conformation A complexes which lack a strong P...H_b interaction. (PH₂NC)₂ is also more stable than (H₂C=PNC)₂, but by only 2.7 kJ mol⁻¹. The only exception to the relationship between the relative stabilities of these two sets of complexes occurs with X = CN, in which case (H₂C=PCN)₂ is more stable than (PH₂CN)₂ by 3.2 kJ mol⁻¹.

CONCLUSIONS

Ab initio MP2/aug'-cc-pVTZ searches of three regions of the potential surfaces of (H₂C=PX)₂, with X = F, Cl, OH, CN, NC, CCH, H, CH₃, and BH₂, have been carried out to identify and then to characterize the structures and binding energies of complexes with P...P pnictogen bonds. The first region has A–P...P–A approaching a linear arrangement, with the A the atom of X directly bonded to P. The second region has a C–P...P–C linear arrangement, with C being the carbon of the CH₂ group. The third region has C–P...P–A approaching a linear arrangement.

1. Complexes in region one are conformation A dimers with C_{2h} symmetry.

- All surfaces have equilibrium conformation A complexes. These can be subdivided into two types: those stabilized by a P...P pnictogen bond, and those stabilized by a P...P pnictogen bond and two P...H_b interactions, with H_b the atom of the CH₂ group of one molecule which is closer to the P atom of the other. The first group includes those complexes with the more electronegative substituents F, Cl, OH, CN, and NC. These complexes have shorter P–P distances and binding energies which correlate with P–P distances. Complexes in the second group have the more electropositive substituents CCH, H, CH₃, and BH₂. These have shorter P–H_b distances and binding

energies which appear to be too high for their P–P distances.

- b. The range of binding energies for conformation A complexes is 9.5 to 13.9 kJ mol^{−1}, which is relatively narrow compared to the range of 7.0 to 34.0 kJ mol^{−1} for complexes (PH₂X)₂ with A–P...P–A linear. Conformation A complexes with P...H_b interactions in addition to the P...P bond are more stable than the corresponding (PH₂X)₂ complexes, while with only one exception, complexes stabilized by only a P...P bond are less stable than the corresponding (PH₂X)₂ complexes.
 - c. Charge-transfer stabilization energies in conformation A complexes are less than 10 kJ mol^{−1}, while they reach 100 kJ mol^{−1} for complexes (PH₂X)₂. In addition, the electrostatic interaction energies in conformation A complexes are less than those in the corresponding (PH₂X)₂ complexes. Thus, with A–P...P–A linear, P...P pnictogen bonds involving sp² hybridized P atoms in (H₂C=PX)₂ are weaker than P...P pnictogen bonds involving sp³ hybridized P atoms in corresponding (PH₂X)₂.
2. In the region of the potential surfaces with C–P...P–C approaching linearity, the only equilibrium complex with C_{2h} symmetry is (H₂C=POH)₂. However, this complex is not stabilized primarily by a P...P pnictogen bond, but by two O–H...P hydrogen bonds. It has the highest binding energy of 24.8 kJ mol^{−1} among all complexes (H₂C=PX)₂. The remaining complexes found in this region are not stabilized by P...P pnictogen bonds, but by π interactions between the two H₂C=PX monomers which lie in parallel planes.
 3. In the region of the potential surfaces with C–P...P–A approaching linearity, equilibrium structures with P...P bonds exist with two different types of structures, designated conformations C and C'.
 - a. There are two equilibrium conformation C complexes with C_s symmetry, namely, (H₂C=POH)₂ and (H₂C=PH)₂. (H₂C=POH)₂ has a P...P pnictogen bond and an O–H...P hydrogen bond, with a binding energy of 16.4 kJ mol^{−1}. (H₂C=PH)₂ is stabilized by a P...P pnictogen bond and a P...H_b interaction, with a binding energy of 8.9 kJ mol^{−1}. Although (H₂C=PCH₃)₂ with C_s symmetry has one imaginary frequency of −4 cm^{−1}, it is structurally and energetically essentially identical to the equilibrium C₁ structure. Both are stabilized by a P...P pnictogen bond and a P...H_b interaction.
 - b. Conformation C' complexes have structures in which the monomers essentially retain their symmetry plane, but the plane of one monomer is rotated about the P...P bond relative to the other. With the exception of (H₂C=PCH₃)₂, the order of decreasing binding energies of C' complexes is the same as the order for the corresponding A complexes.
 4. The potential surfaces of (H₂C=PX)₂ complexes are very different, depending on the nature of X.
 - a. Only (H₂C=POH)₂ has equilibrium conformation A, B, and C complexes. The order of stability is B > C > A, indicative of the preference for hydrogen bonding over pnictogen bonding.
 - b. (H₂C=PCCH)₂ and (H₂C=PBH₂)₂ form only conformation A complexes.
 - c. The remaining complexes (H₂C=PCl)₂, (H₂C=PCN)₂, (H₂C=PH)₂, (H₂C=PNC)₂, (H₂C=PCH₃)₂,

and (H₂C=PF)₂ have conformers A and either C or C'. The binding energy differences between A and C are relatively small. Conformation A is more stable than C or C', except for (H₂C=PCH₃)₂.

5. Changes in ³¹P chemical shieldings in dimers A, C, and C' exhibit patterns which are consistent with the interactions that stabilize these complexes. ³¹P–³¹P spin–spin coupling constants ¹J(P–P) for conformations A and C dimers and one C' dimer increase quadratically as the P–P distance decreases.

■ ASSOCIATED CONTENT

§ Supporting Information

MP2/aug'ccpVTZ structures, energies, and molecular graphs of complexes (H₂C=PX)₂; full references 43, 49, and 57. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The authors declare no competing financial interest.

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