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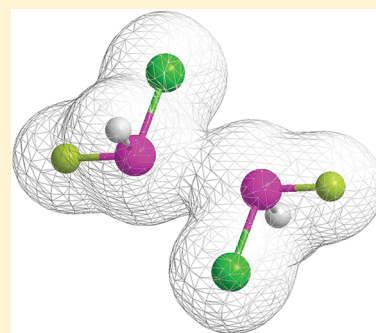
# Structures, Binding Energies, and Spin–Spin Coupling Constants of Geometric Isomers of Pnictogen Homodimers (PHFX)<sub>2</sub>, X = F, Cl, CN, CH<sub>3</sub>, NC

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**ABSTRACT:** Ab initio MP2/aug'-cc-pVTZ calculations have been carried out to determine the structures and binding energies of homodimers (PHFX)<sub>2</sub> for X = F, Cl, CN, CH<sub>3</sub>, and NC. Geometric isomers of these complexes with C<sub>i</sub> symmetry exist, which are differentiated in terms of the nature of the atoms (F–P...P–F, H–P...P–H, or A–P...P–A, with A being the atom of X directly bonded to P), which approach a nearly linear alignment. Of these, isomers having F–P...P–F linear are the most stable. Binding energies, intermolecular distances, and EOM-CCSD spin–spin coupling constants are sensitive to both the nature of X and the atoms that assume the linear alignment.



## ■ INTRODUCTION

The pnictogen bond has been recognized as a new and important type of intermolecular interaction.<sup>1–3</sup> In a recent paper, Hey-Hawkins et al. carried out a high-level theoretical study of the pnictogen P...P bond for a series of complexes, and described this bond as a new molecular linker.<sup>4</sup> Recently, we examined substituent effects in a series of homodimers (PH<sub>2</sub>X)<sub>2</sub>, identified common structural characteristics, and demonstrated that one-bond <sup>31</sup>P–<sup>31</sup>P spin–spin coupling constants could be used to extract intermolecular P–P distances.<sup>5</sup>

Solimannejad et al. described the N...P pnictogen bond involving the interaction of HSN with PH<sub>3</sub> and other phosphines.<sup>6</sup> These studies were further extended by Scheiner, who carried out an examination of the bonding characteristics of complexes formed between substituted PH<sub>3</sub> molecules and NH<sub>3</sub>.<sup>7–9</sup> We also investigated the N...P pnictogen bond in a series of complexes derived from monosubstituted PH<sub>3</sub> and NH<sub>3</sub> molecules, represented as H<sub>2</sub>XP:NXH<sub>2</sub>, for X = H, CH<sub>3</sub>, NH<sub>2</sub>, OH, F, and Cl, and in selected complexes H<sub>2</sub>XP:NXH<sub>2</sub>, which have different X bonded to N and P.<sup>10</sup> 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<sub>2</sub>X)<sub>2</sub>, the substituents X approach a linear A–P...P–A alignment, where A is the atom of X directly bonded to P.

We now turn our attention to the homodimers (PHFX)<sub>2</sub> with P...P pnictogen bonds. When two PHFX molecules form a complex with a P...P bond, dimers of C<sub>2</sub> and C<sub>i</sub> symmetry may be formed. In the present paper, we have elected to limit our discussion to the geometric isomers of (PHFX)<sub>2</sub> of C<sub>i</sub> symmetry, for X = F, Cl, CN, CH<sub>3</sub>, and NC. These can be differentiated by the atoms that approach a linear alignment,

namely, F–P...P–F, H–P...P–H, or A–P...P–A. We report the structures, binding energies, and spin–spin coupling constants of these dimers, compare binding energies as a function of the atoms that assume a linear alignment, analyze the change in binding energies as a function of X when F–P...P–F is linear, and investigate the variation of <sup>1</sup>J(P–P) across the pnictogen bond. In a future paper we will examine similarities and differences between the C<sub>i</sub> and C<sub>2</sub> isomers of (PHFX)<sub>2</sub>.

## ■ METHODS

The structures of the monomers and dimers were optimized at second-order Møller–Plesset perturbation theory (MP2)<sup>11–14</sup> with the aug'-cc-pVTZ basis set,<sup>15</sup> which is the Dunning aug-cc-pVTZ basis<sup>16,17</sup> with diffuse functions removed from H atoms. Frequencies were computed to identify equilibrium and transition structures. These calculations were performed using the Gaussian 09 program.<sup>18</sup>

The symmetry adapted perturbation theory (SAPT)<sup>19</sup> method has been employed to evaluate the electrostatic, exchange, induction, and dispersion components of the interaction energy, using the DFT-SAPT formulation.<sup>20,21</sup> A Hartree–Fock correction term δ(HF), which includes higher-order induction and exchange corrections, has also been included.<sup>22</sup> The DFT-SAPT calculations were performed with the MOLPRO program<sup>23</sup> using the PBE0/aug'-cc-pVTZ computational method.

Coupling constants were evaluated using the equation-of-motion coupled cluster singles and doubles (EOM-CCSD) method in the configuration interaction (CI)-like approximation<sup>24,25</sup> with

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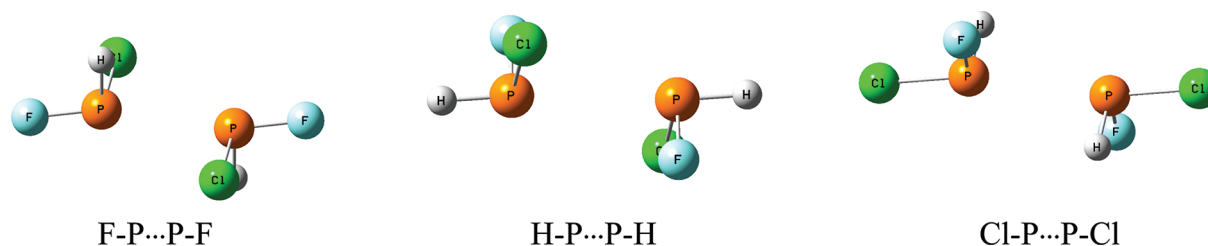


Figure 1. The three isomers of  $(\text{PHFCl})_2$ .

Table 1. P–P Distances [ $R(\text{P}–\text{P})$ , Å], Z–P–P Angles ( $\angle\text{Z}–\text{P}–\text{P}$ , °), Binding Energies ( $\Delta E$ ), and Relative Binding Energies [ $\delta\Delta E$ , kJ/mol], and Values of Imaginary Frequencies ( $\nu$ ,  $\text{cm}^{-1}$ ) of Pnictogen Dimers with  $C_i$  Symmetry

| complex                       | Z–P...P–Z              | $R(\text{P}–\text{P})$ | $\angle\text{Z}–\text{P}–\text{P}$ | $\Delta E^a$ | $\delta\Delta E$ | $\nu$ |
|-------------------------------|------------------------|------------------------|------------------------------------|--------------|------------------|-------|
| $(\text{PHFF})_2$             | F–P...P–F              | 3.180                  | 177                                | 11.78        | 0.00             |       |
|                               | H–P...P–H <sup>b</sup> | 3.481                  | 175                                | 7.47         | 4.31             |       |
| $(\text{PHFCl})_2$            | F–P...P–F              | 3.041                  | 164                                | 17.42        | 0.00             |       |
|                               | Cl–P...P–Cl            | 3.188                  | 167                                | 12.02        | 5.40             |       |
|                               | H–P...P–H              | 3.358                  | 174                                | 12.17        | 5.26             |       |
| $[\text{PHF}(\text{CN})]_2$   | F–P...P–F              | 2.725                  | 166                                | 23.22        | 0.00             |       |
|                               | C–P...P–C              | 3.398                  | 170                                | 6.68         | 16.54            | –4    |
|                               | H–P...P–H              | 3.392                  | 175                                | 12.68        | 10.54            | –12   |
| $[\text{PHF}(\text{CH}_3)]_2$ | F–P...P–F              | 2.800                  | 162                                | 24.36        | 0.00             |       |
|                               | C–P...P–C              | 3.459                  | 174                                | 7.32         | 15.06            | –15   |
|                               | H–P...P–H              | 3.446                  | 173                                | 14.70        | 7.68             | –22   |
| $[\text{PHF}(\text{NC})]_2$   | F–P...P–F              | 2.987                  | 166                                | 16.91        | 0.00             |       |
|                               | N–P...P–N              | 3.314                  | 168                                | 8.24         | 8.67             |       |
|                               | H–P...P–H              | 3.362                  | 176                                | 12.82        | 4.09             | –10   |

<sup>a</sup> $\Delta E$  is the negative of the energy for the reaction  $2 \text{PHFX} \rightarrow (\text{PHFX})_2$ . <sup>b</sup>This dimer has  $C_{2h}$  symmetry and is included for comparison purposes.

all electrons correlated. For these calculations, the Ahlrichs<sup>26</sup> qzp basis set was placed on  $^{13}\text{C}$ ,  $^{15}\text{N}$ , and  $^{19}\text{F}$ , the qz2p basis set on  $^{31}\text{P}$  and  $^{35}\text{Cl}$ , and the Dunning cc-pVDZ basis on  $^1\text{H}$ .<sup>16</sup> Only the one-bond  $^{31}\text{P}–^{31}\text{P}$  coupling constants across the pnictogen 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  $^{1p}J(\text{P}–\text{P})$  in pnictogen dimers  $(\text{PH}_2\text{X})_2$ .<sup>5</sup> That approximation will be further investigated in this paper. The EOM-CCSD calculations were performed using ACES II<sup>27</sup> on the IBM Cluster 1350 (Glenn) at the Ohio Supercomputer Center.

## RESULTS AND DISCUSSION

### Structures and Binding Energies of Complexes $(\text{PHFX})_2$

In a previous study, we observed that complexes  $(\text{PH}_2\text{X})_2$  have a linear or nearly linear A–P...P–A alignment, with A being the atom of X directly bonded to P. Thus, the complexes  $(\text{PHFX})_2$  may in principle have three geometric isomers, distinguished in terms of linear F–P...P–F, H–P...P–H, and A–P...P–A alignments. These are illustrated for  $(\text{PHFCl})_2$  in Figure 1. In this section, we examine the potential energy surfaces to determine whether these are equilibrium or transition structures. We also compare the P–P distances, the P–P–Z angles ( $Z = \text{F}, \text{H}, \text{A}$ ), and the binding energies of these complexes.

Figure 1 illustrates that all isomers of  $(\text{PHFCl})_2$  have a nearly linear Z–P...P–Z arrangement, as measured by the P–P–Z angles, which vary between 162 and 177°. For ease of discussion, this alignment will be referred to as linear. From Figure 1 it can also be seen that substituents not part of the linear Z–P...P–Z alignment are bonded to P in positions that

are close to perpendicular to the P...P bond. The perpendicular arrangement is a consequence of the bond angles around P in the monomers and the trans arrangement of the atoms that are perpendicular to the P...P bond.<sup>5,10</sup>

Table 1 indicates that all complexes  $(\text{PHFX})_2$  with F–P...P–F linear are equilibrium structures on their potential surfaces. Both isomers of  $(\text{PHFF})_2$  and the three isomers of  $(\text{PHFCl})_2$  are equilibrium structures. Isomers of  $[\text{PHF}(\text{CH}_3)]_2$  and  $[\text{PHF}(\text{CN})]_2$  with C–P...P–C linear have one imaginary low-frequency vibration, indicating that the optimized structures are transition structures. The isomers of  $[\text{PHF}(\text{CH}_3)]_2$ ,  $[\text{PHF}(\text{CN})]_2$ , and  $[\text{PHF}(\text{NC})]_2$  with H–P...P–H linear also have one imaginary frequency. We have followed the motion of the imaginary frequencies of  $[\text{PHF}(\text{CH}_3)]_2$  with H–P...P–H and C–P...P–C linear and found equilibrium structures of  $C_i$  symmetry stabilized by intermolecular P...F interactions. We anticipate that other complexes with imaginary frequencies will also optimize to structures that no longer have a pnictogen bond, or perhaps to structures of  $C_i$  symmetry with a pnictogen bond but with two different atoms aligned linearly (Z–P...P–Z'). These will not be further discussed in this paper.

Table 1 reports the P–P distances, Z–P–P angles, binding energies, and relative binding energies for all isomers of  $(\text{PHFX})_2$  with  $C_i$  symmetry. Among these, the most stable are those with F–P...P–F linear. The preference for F–P...P–F linear is consistent with recent studies of pnictogen dimers,<sup>5,7–10</sup> which concluded that the presence of electron-rich groups aligned linearly strengthens the pnictogen bond. Electron-rich substituents such as F have nonbonded electron pairs that can be polarized toward P when F–P...P–F is linear. Mutual polarization results in an increased electron density in the region of the pnictogen bond and increased stability of these

Table 2. Binding Energies ( $\Delta E$ , kJ/mol) of Complexes  $(\text{PH}_2\text{X})_2$  and  $(\text{PHFX})_2$ 

| $(\text{PHFX})_2^a$           | $\Delta E$ | $(\text{PH}_2\text{X})_2^a$    | $\Delta E (\text{A}-\text{P}\cdots\text{P}-\text{A})^b$ | $\Delta E (\text{H}-\text{P}\cdots\text{P}-\text{H})^c$ |
|-------------------------------|------------|--------------------------------|---|---|
| $(\text{PHFF})_2$             | 11.78      | $(\text{PH}_2\text{F})_2$      | 33.97   | 7.54  |
| $(\text{PHFCl})_2$            | 17.42      | $(\text{PH}_2\text{Cl})_2$     | 22.09   | 12.50   |
| $[\text{PHF}(\text{NC})]_2$   | 16.91      | $[\text{PH}_2(\text{NC})]_2$   | 13.76   |   |
| $[\text{PHF}(\text{CH}_3)]_2$ | 24.36      | $[\text{PH}_2(\text{CH}_3)]_2$ | 8.88  | 13.56   |
| $[\text{PHF}(\text{CN})]_2$   | 23.22      | $[\text{PH}_2(\text{CN})]_2$   | 8.37  |   |

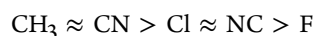
<sup>a</sup>All complexes have F–P⋯P–F linear and H and X in approximately perpendicular positions relative to the P⋯P bond. <sup>b</sup>Data from ref 5. All complexes have A–P⋯P–A linear, with A being the atom of X directly bonded to P. <sup>c</sup>These dimers have H–P⋯P–H linear.

Table 3. Components of the DFT-SAPT Interaction Energies (kJ/mol) for Complexes  $(\text{PHFX})_2$ 

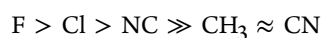
| complex                       | Z–P⋯P–Z   | $E_{\text{el}}^{(1)a}$ | $E_{\text{ex}}^{(1)b}$ | $E_{\text{i}}^{(2)c}$ | $E_{\text{D}}^{(2)d}$ | $\delta(\text{HF})^e$ | $\Delta E^{\text{DFT-SAPT}}$ |
|-------------------------------|-----------|------------------------|------------------------|-----------------------|-----------------------|-----------------------|------------------------------|
| $(\text{PHF}_2)_2$            | F–P⋯P–F   | –24.45                 | 47.54                  | –5.36                 | –17.92                | –7.10                 | –7.29                        |
|                               | H–P⋯P–H   | –11.93                 | 23.54                  | –1.58                 | –12.56                | –2.69                 | –5.22                        |
| $(\text{PHFCl})_2$            | F–P⋯P–F   | –35.38                 | 72.72                  | –9.06                 | –27.53                | –10.50                | –9.74                        |
|                               | Cl–P⋯P–Cl | –23.33                 | 47.77                  | –5.65                 | –19.40                | –7.18                 | –7.78                        |
| $[\text{PHF}(\text{CN})]_2$   | H–P⋯P–H   | –16.01                 | 34.21                  | –2.50                 | –19.49                | –3.82                 | –7.62                        |
|                               | F–P⋯P–F   | –77.94                 | 170.89                 | –34.54                | –45.21                | –22.70                | –9.50                        |
| $[\text{PHF}(\text{CH}_3)]_2$ | C–P⋯P–C   | –8.57                  | 24.64                  | –3.21                 | –13.45                | –3.05                 | –3.64                        |
|                               | H–P⋯P–H   | –12.27                 | 29.71                  | –3.01                 | –18.50                | –3.37                 | –7.44                        |
| $[\text{PHF}(\text{NC})]_2$   | F–P⋯P–F   | –95.66                 | 164.77                 | –28.04                | –43.26                | –15.00                | –17.19                       |
|                               | C–P⋯P–C   | –13.94                 | 25.29                  | –1.45                 | –14.33                | –3.02                 | –6.84                        |
| $[\text{PHF}(\text{NC})]_2$   | H–P⋯P–H   | –21.20                 | 35.12                  | –2.45                 | –20.27                | –3.43                 | –12.23                       |
|                               | F–P⋯P–F   | –37.06                 | 81.64                  | –11.89                | –29.24                | –11.84                | –8.39                        |
| $[\text{PHF}(\text{CN})]_2$   | N–P⋯P–N   | –13.49                 | 31.99                  | –4.04                 | –15.22                | –4.44                 | –5.19                        |
|                               | H–P⋯P–H   | –14.79                 | 32.35                  | –2.86                 | –19.10                | –3.52                 | –7.92                        |

<sup>a</sup>The first-order electrostatic interaction energy. <sup>b</sup>The first-order exchange energy. <sup>c</sup>The second-order induction energy. <sup>d</sup>The second-order dispersion energy. <sup>e</sup>A Hartree–Fock correction that includes higher order induction and exchange corrections.

complexes. The binding energies of these dimers with the F–P⋯P–F alignment decrease with respect to X in the order



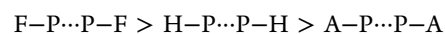
This order is significantly different from that of dimers  $(\text{PH}_2\text{X})_2$  formed from the monosubstituted derivatives, in which case binding energies decrease in the order



The data required for this comparison are given in Table 2.

From Table 2 it can be seen that the binding energy of  $(\text{PH}_2\text{F})_2$  with F–P⋯P–F linear decreases from 34 to 12 kJ/mol in  $(\text{PHF}_2)_2$  upon the introduction of a second F atom in one of the perpendicular positions. This trend continues as substitution of a third F atom in  $(\text{PF}_3)_2$  further reduces the binding energy to 5 kJ/mol. This suggests that in the perpendicular position, electron-rich groups such as F exert their normal electron-withdrawing effect, thus weakening the pnictogen bond. This same effect can also be seen for  $(\text{PH}_2\text{F})_2$  by comparing the binding energy of the isomer with F–P⋯P–F linear (34 kJ/mol) to that with H–P⋯P–H linear (8 kJ/mol). It would follow that substitution of  $\text{CH}_3$  for F in the perpendicular position should lead to a strengthening of the pnictogen bond. This is indeed the case, as the binding energy of 12 kJ/mol for  $(\text{PHFF})_2$  increases to 24 kJ/mol for  $[\text{PHF}(\text{CH}_3)]_2$ . This trend is also evident for the complexes  $(\text{PH}_2\text{X})_2$  with H–P⋯P–H linear, as binding energies increase in the order  $\text{F} < \text{Cl} < \text{CH}_3$ . These data are consistent with the findings of Kirchner and co-workers who noted that the presence of an electron-donating group in the perpendicular position can strengthen the P⋯P pnictogen bond.<sup>4</sup>

It can also be seen from Table 1 that the order of stabilities of dimers  $(\text{PHFX})_2$  for fixed X also depends on the nature of the atoms in the linear alignment. These binding energies decrease in the order



except for  $(\text{PHFCl})_2$ , in which case isomers with H–P⋯P–H and Cl–P⋯P–Cl linear are equienergetic. This order is surprising, since it might have been expected that having the Cl atoms linear should be more stabilizing than having H atoms linear, since Cl is an electron-rich substituent, and  $(\text{PH}_2\text{Cl})_2$  with Cl–P⋯P–Cl linear is more stable than  $(\text{PH}_3)_2$ . Moreover, Table 2 indicates that placing an electron-withdrawing group in a perpendicular position weakens the pnictogen bond. This can be seen by comparing the isomers of  $(\text{PH}_2\text{F})_2$  that have F atoms in linear (34 kJ/mol) and perpendicular (8 kJ/mol) positions.

What then is responsible for this unexpected ordering? Some insight into the answer to this question may be gained by examining the components of the SAPT interaction energies, which are given in Table 3. The term with the largest absolute value is the destabilizing exchange term. However, the remaining terms are stabilizing, and summed together give stability to these complexes. Among the stabilizing terms, the electrostatic interaction is the dominant term for complexes with F–P⋯P–F linear. When H–P⋯P–H and A–P⋯P–A are linear, either the electrostatic or the dispersion term may dominate. A comparison of the exchange and electrostatic terms for these two isomers indicates that as the exchange term increases, the electrostatic term also increases in absolute value, thus having a balancing effect. It is the dispersion interaction that appears to be the term that differentiates these two isomers. Table 4 presents a comparison of the difference

**Table 4. Differences between SAPT Dispersion Energies and MP2 Binding Energies ( $\Delta E$ , kJ/mol) for Complexes with H-P...P-H and A-P...P-A Linear**

| complex                              | $\Delta E(\text{SAPT dispersion})^a$ | $\Delta E(\text{MP2})^b$ |
|--------------------------------------|--------------------------------------|--------------------------|
| (PHFCl) <sub>2</sub>                 | +0.09                                | -0.15                    |
| [PHF(CN)] <sub>2</sub>               | +5.05                                | +6.00                    |
| [PHF(CH <sub>3</sub> )] <sub>2</sub> | +5.94                                | +7.38                    |
| [PHF(NC)] <sub>2</sub>               | +3.88                                | +4.58                    |

<sup>a</sup> $\Delta E = -[E_D^{(2)}(\text{H-P}\cdots\text{P-H}) - E_D^{(2)}(\text{A-P}\cdots\text{P-A})]$ . <sup>b</sup> $\Delta E = \text{BE}(\text{H-P}\cdots\text{P-H}) - \text{BE}(\text{A-P}\cdots\text{P-A})$ . See footnote b of Table 2.

between the SAPT dispersion energies and the difference between the MP2 binding energies of isomers of complexes (PHFX)<sub>2</sub> with H-P...P-H and A-P...P-A linear. This comparison suggests that when H-P...P-H is linear, the groups in the perpendicular positions (F and X) of one molecule have electrons that can be polarized by the electrons of the other, giving rise to a stabilizing London dispersion force. For isomers with A-P...P-A linear, F and H are perpendicular, and the number of electrons that can be polarized is reduced, resulting in a decrease in the dispersion energies, which is reflected by a decrease in the MP2 binding energies.

The binding energies of complexes (PHFX)<sub>2</sub> for a given X with A-P...P-A and H-P...P-H linear do not correlate well with intermolecular P-P distances. For X = Cl and NC, binding energies of the A-P...P-A isomers are 0.2 and 4.6 kJ/mol less than the H-P...P-H isomers, but the P-P distances are 0.17 and 0.04 Å shorter, respectively, in the A-P...P-A isomers. When A is C for CN and CH<sub>3</sub>, isomers with H-P...P-H linear are 6 and 7 kJ/mol more stable, but their P-P distances are only 0.01 Å shorter than the isomers with C-P...P-C linear. Once again, this may arise because of interactions involving the groups in perpendicular positions. When H-P...P-H is linear, the substituents F and X on one P have a greater repulsive interaction with the lone pair on the other P, compared to A-P...P-A, in which F and H are perpendicular. The longer distances in the H-P...P-H isomers reduce these unfavorable interactions.

**Spin-Spin Coupling Constants.** FC and <sup>1</sup>PJ(P-P) values for selected complexes with pnictogen bonds are reported in Table 5. For all dimers except (PH<sub>2</sub>F)<sub>2</sub> with F-P...P-F linear, the FC term is an excellent approximation to <sup>1</sup>PJ(P-P). For (PH<sub>2</sub>F)<sub>2</sub> with F-P...P-F linear, the FC term

**Table 5. FC and <sup>1</sup>PJ(P-P) for Selected Pnictogen Dimers**

| (PH <sub>2</sub> X) <sub>2</sub> <sup>a</sup>                      | FC     | <sup>1</sup> PJ(P-P) |
|--|--------|----------------------|
| [PH <sub>2</sub> (OH)] <sub>2</sub>                                | 641.6  | 644.0                |
| [PH <sub>2</sub> (NC)] <sub>2</sub>                                | 638.2  | 640.3                |
| [PH <sub>2</sub> (NH <sub>2</sub> )] <sub>2</sub> - C <sub>i</sub> | 356.5  | 358.3                |
| [PH <sub>2</sub> (CCH)] <sub>2</sub>                               | 280.8  | 281.9                |
| [PH <sub>2</sub> (CN)] <sub>2</sub>                                | 298.9  | 300.0                |
| [PH <sub>2</sub> (CH <sub>3</sub> )] <sub>2</sub>                  | 160.0  | 160.9                |
| (PH <sub>3</sub> ) <sub>2</sub>                                    | 130.4  | 130.9                |
| (PH <sub>2</sub> F) <sub>2</sub>                                   |        |                      |
| F-P...P-F - C <sub>2h</sub>  | 1007.5 | 998.6                |
| H-P...P-H - C <sub>i</sub>   | 60.2   | 60.5                 |
| (PHF <sub>2</sub> ) <sub>2</sub>                                   |        |                      |
| F-P...P-F - C <sub>i</sub>   | 395.8  | 396.7                |
| H-P...P-H - C <sub>2h</sub>  | 39.3   | 40.1                 |

<sup>a</sup>Have A-P...P-A linear and C<sub>2h</sub> symmetry, except for [PH<sub>2</sub>(NH<sub>2</sub>)]<sub>2</sub>.

underestimates total J by about 10 Hz. However, this difference is a 1% error in view of the very large value (1000 Hz) of this coupling constant. The difference between the FC term and <sup>1</sup>PJ(P-P) is due to a contribution from the PSO term of -19 Hz, which is partially canceled by a 10 Hz contribution from the SD term. On the basis of the data in Table 5, the FC term will be used to approximate <sup>1</sup>PJ(P-P) for complexes (PHFX)<sub>2</sub>. The dominance of the FC terms indicates that P-P coupling is sensitive to s-electron densities both in the ground state and in the excited states which couple to it through the Fermi-contact operator.

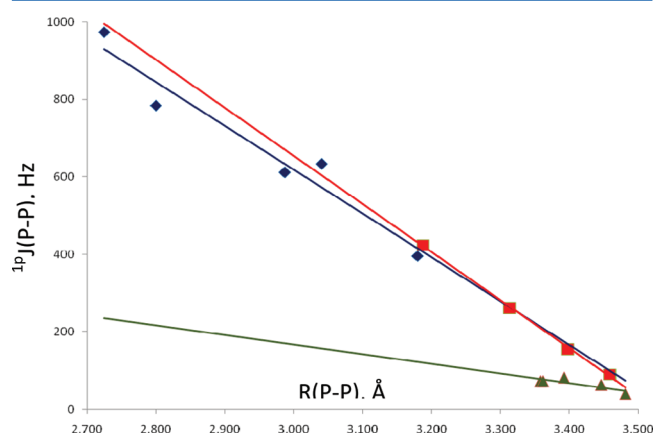
Table 6 presents intermolecular P-P distances and the FC terms for P-P coupling in pnictogen dimers (PHFX)<sub>2</sub> with C<sub>i</sub> symmetry. From Table 6 it can be seen that for a given X,

**Table 6. P-P Distances [R(P-P), Å] and Spin-Spin Coupling Constants [<sup>1</sup>FC(P-P), Hz] for Pnictogen Dimers (PHFX)<sub>2</sub> with C<sub>i</sub> Symmetry**

| complex                              | Z-P...P-Z   | R(P-P) | <sup>1</sup> FC(P-P) <sup>a</sup> |
|--------------------------------------|-------------|--------|-----------------------------------|
| (PHFF) <sub>2</sub>                  | F-P...P-F   | 3.180  | 395.8                             |
|                                      | H-P...P-H   | 3.481  | 39.3                              |
| (PHFCl) <sub>2</sub>                 | F-P...P-F   | 3.041  | 633.2                             |
|                                      | Cl-P...P-Cl | 3.188  | 423.9                             |
| [PHF(CN)] <sub>2</sub>               | H-P...P-H   | 3.358  | 71.7                              |
|                                      | F-P...P-F   | 2.725  | 973.2                             |
| [PHF(CH <sub>3</sub> )] <sub>2</sub> | C-P...P-C   | 3.398  | 153.9                             |
|                                      | H-P...P-H   | 3.392  | 81.6                              |
| [PHF(NC)] <sub>2</sub>               | F-P...P-F   | 2.800  | 783.3                             |
|                                      | C-P...P-C   | 3.459  | 90.0                              |
| [PHF(NC)] <sub>2</sub>               | H-P...P-H   | 3.446  | 62.6                              |
|                                      | F-P...P-F   | 2.987  | 611.7                             |
| [PHF(NC)] <sub>2</sub>               | N-P...P-N   | 3.314  | 260.7                             |
|                                      | H-P...P-H   | 3.362  | 72.1                              |

<sup>a</sup><sup>1</sup>PJ(P-P) approximated by the FC term.

<sup>1</sup>PJ(P-P) decreases in the order F-P...P-F > A-P...P-A > H-P...P-H, which is not the order of decreasing binding energies. Rather, the coupling constants <sup>1</sup>PJ(P-P) are related linearly to the P-P distance, as can be seen in Figure 2. The low correlation coefficient for complexes with H-P...P-H linear is due in part to the clustering of these points at long P-P distances. The single correlation coefficient for the entire set of <sup>1</sup>PJ(P-P) values versus R(P-P) is 0.968. Figure 2

**Figure 2.** <sup>1</sup>PJ(P-P) versus the P-P distance for pnictogen dimers (PHFX)<sub>2</sub>: (◆) F-P...P-F with R<sup>2</sup> = 0.944, (■) A-P...P-A, with R<sup>2</sup> = 0.998, (▲) H-P...P-H, with R<sup>2</sup> = 0.694.



dramatically illustrates that  $^1J(\text{P}-\text{P})$  values are very sensitive to the nature of the atoms that are aligned linearly, as well as to the nature of X.

In ref 5 we reported that  $^1J(\text{P}-\text{P})$  varies quadratically with the P–P distance. However, as is evident from the graph showing this correlation, these variables correlate very well linearly. Since the correlation shown in Figure 2 is linear, it would appear that the distance dependence of  $^1J(\text{P}-\text{P})$  across the P–P pnictogen bond is linear, in contrast to the quadratic correlation usually found between  $^2J(\text{X}-\text{Y})$  and the X–Y distance in complexes with X–H...Y hydrogen bonds.

## CONCLUSIONS

Ab initio MP2/aug'-cc-pVTZ calculations have been carried out to investigate the structures, binding energies, and one-bond  $^{31}\text{P}-^{31}\text{P}$  spin–spin coupling constants of homodimers  $(\text{PHFX})_2$  with  $C_i$  symmetry, for X = F, Cl, CN,  $\text{CH}_3$ , and NC. The results of this study support the following statements.

1. For each complex  $(\text{PHFX})_2$ , the isomer in which the F–P...P–F alignment approaches linearity is the most stable, and is a local minimum on the surface. Geometric isomers with H–P...P–H linear are more stable than those with A–P...P–A linear, with A being the atom of X directly bonded to P. However, these isomers are not always equilibrium structures on their potential surfaces.
2. While dimers  $(\text{PH}_2\text{X})_2$  with electron-rich groups X in a linear alignment have increased stabilities, bonding these same X perpendicular to the P...P bond leads to a decrease in binding energies.
3. Intermolecular P–P distances do not correlate with binding energies.
4. Spin–spin coupling constants  $^1J(\text{P}-\text{P})$  can be approximated by the FC term. A linear correlation exists between  $^1J(\text{P}-\text{P})$  and the P–P distance.
5. Binding energies, intermolecular distances, and coupling constants for complexes  $(\text{PHFX})_2$  are sensitive to both the nature of X and the atoms that assume a linear alignment.

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### Notes

The authors declare no competing financial interest.

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