

# Theoretical exploration of pnicoen bond noncovalent interactions in $\text{HCHO} \cdots \text{PH}_2\text{X}$ ( $\text{X}=\text{CH}_3, \text{H}, \text{C}_6\text{H}_5, \text{F}, \text{Cl}, \text{Br}, \text{and NO}_2$ ) complexes

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**Abstract.** Pnicoen bond (ZB) is a new kind of intermolecular weak interaction, which would be an important strategy for the construction of supramolecular materials. In this paper, *ab initio* MP2/aug-cc-pvDZ calculations have been carried out to characterize the  $\text{X-P} \cdots \text{O}$  ZB interactions between  $\text{HCHO}$  and  $\text{PH}_2\text{X}$  ( $\text{X}=\text{CH}_3, \text{H}, \text{C}_6\text{H}_5, \text{F}, \text{Cl}, \text{Br}, \text{and NO}_2$ ). The calculated interaction energies with basis set super-position error (BSSE) corrections in seven ZB complexes are between  $-7.51$  and  $-20.36 \text{ kJ}\cdot\text{mol}^{-1}$ . The relative stabilities of the seven complexes increase in the order:  $\text{HCHO} \cdots \text{PH}_2\text{CH}_3 < \text{HCHO} \cdots \text{PH}_3 < \text{HCHO} \cdots \text{PH}_2\text{C}_6\text{H}_5 < \text{HCHO} \cdots \text{PH}_2\text{Br} < \text{HCHO} \cdots \text{PH}_2\text{Cl} < \text{HCHO} \cdots \text{PH}_2\text{F} < \text{HCHO} \cdots \text{PH}_2\text{NO}_2$ . The natural bond orbital (NBO) and natural resonance theory (NRT) analysis were employed to investigate the electron behavior and nature of the ZBs. The natural bond orbital interactions in the ZBs are mainly  $\text{LP}^{1,2}(\text{O}) \rightarrow \sigma^*(\text{P-X})$ . The P-X ( $\text{X}=\text{Br}, \text{Cl}, \text{F}$  and  $\text{NO}_2$ ) are more suitable for acting as ZB donors than the P-X ( $\text{X}=\text{H}, \text{CH}_3$  and  $\text{C}_6\text{H}_5$ ) groups. The electron density topology properties based on atoms-inmolecules (AIM) theory showed that the ZB interactions in the  $\text{HCHO} \cdots \text{PH}_2\text{X}$  ( $\text{X}=\text{Br}, \text{Cl}, \text{F}$  and  $\text{NO}_2$ ) are stronger than those of  $\text{HCHO} \cdots \text{PH}_2\text{X}$  ( $\text{X}=\text{CH}_3, \text{H}$  and  $\text{C}_6\text{H}_5$ ) complexes, indicating that the electron withdrawing of X benefits for the stability of ZB structure.

**Keywords.** Noncovalent interaction; pnicoen bond; natural bond orbital theory; natural resonance theory; electron density topological property.

## 1. Introduction

Most of the intermolecular noncovalent interactions have important roles in the field of bio-molecular recognition,<sup>1–3</sup> molecular and crystal engineering,<sup>4</sup> formations of molecular clusters,<sup>5,6</sup> proton transfer dynamics,<sup>7</sup> materials design and molecular self-assembly,<sup>8–13</sup> etc. The classical intermolecular noncovalent interactions reported in literature are hydrogen bond,<sup>14</sup> dihydrogen bonds,<sup>15</sup> halogen bonds,<sup>16</sup> single-electron sodium bond,<sup>17</sup> lithium bond,<sup>18,19</sup> and pseudohydrogen bond,<sup>20</sup> etc. These interactions have captured the interest of chemists over decades, and the studies both in theory and experiments have been well reported,<sup>21–23</sup> among which hydrogen bond was the most investigated. A hydrogen atom attracted by a highly electronegative atom tends to bond to some other nearby highly electronegative atom, which is the

so-called the hydrogen bond,<sup>24</sup> a common noncovalent weak interaction besides van der Waals force. Pauling<sup>25</sup> pointed out that in a hydrogen bond system, the hydrogen atom is situated only between the most electronegative atoms and it usually interacts more strongly with one of them. In other words, the interaction between hydrogen and the other electronegative atom is much weaker and mostly electrostatic in nature. However, it is interesting to see if the “pnicoen bond” which is similar to a hydrogen bond, when a pnicoen atom covalently binds to non-metallic atoms locating itself in the middle of two electropositive atoms, or even between a weak electropositive atom and an electronegative atom. Besides answering the question, what will be the nature and the electronic behavior of the interaction, we are also interested in whether there is any noncovalent weak interaction in “pnicoen bond” and how the interaction takes place.

Specially, noncovalent weak interaction involving pnicoen is a new field of intermolecular interactions, but it has been recognized as a potentially important

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type of intermolecular contact. Scheiner<sup>26</sup> fundamentally studied a different sort of noncovalent weak interaction between a phosphorus atom and a nitrogen atom on different molecules, without an intervening H atom. For example, in the  $\text{PH}_3 \cdots \text{NH}_3$  heterodimer system,<sup>27,28</sup> a direct noncovalent bond between the electronegative P and N atoms is formed. Different from any kind of N-H $\cdots$ P or P-H $\cdots$ N H-bond, this binding is rather weak, less than  $2 \text{ kcal}\cdot\text{mol}^{-1}$ , which will be enhanced if the H atom on the phosphine is replaced by a more electronegative group. The stability of this complex relies on the charge transfer from the N lone pair into the  $\sigma^*$  anti-bond of the P-H bond in which the participating H atom is rotated directly away from the N lone pair, so that the charge is transferred into another lobe of the  $\sigma^*$  orbital on the P end of the P-H bond. Recently, Scheiner<sup>29</sup> investigated the effect of different electron donors (D, D=  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{CO}$ ,  $\text{H}_2\text{CS}$  and  $\text{CH}_3\text{OH}$ ) on the  $\text{H}_2\text{FP}\cdots\text{D}$  noncovalent interaction at MP2/aug-cc-pvdz theoretical level, and the result showed that the  $\text{P}\cdots\text{D}$  binding energy diminishes in the order of  $\text{NH}_3 > \text{H}_2\text{CO} > \text{H}_2\text{CS} > \text{H}_2\text{O} > \text{H}_2\text{S}$ , different from the patterns observed in both hydrogen bonds and halogen bonds.

In the conventional concept of the H-bond systems (Z-H $\cdots$ Y, Z=O, S, N; Y=O, S, N,  $\pi$  electron), the charge transfer could be shown as scheme 1(a), that is, the charge of the Y lone pair is transferred into the  $\sigma^*$  (H-Z). When the P atom replaces the H atom of the H-bond systems (Z-H $\cdots$ Y), and if the charge transfer behavior is similar to that of the H-bond systems, then the noncovalent interaction system shown in scheme 1(b) could be defined as “pnico-gen bond”. In fact, the “pnico-gen bond” concept has been proposed by Hey-Hawkins in 2011,<sup>30</sup> which is evidenced by a number of papers published since then, and some latest experimental<sup>31</sup> and theoretical studies<sup>32–37</sup> on pnico-gen bonds have been reported. For example, Scheiner accounted the pnico-gen bond in detail, and stated its relation to the hydrogen bond, halogen bond and other noncovalent bonds.<sup>32</sup> Furthermore, the sensitivity of the pnico-gen bond to angular distortions was also investigated by Scheiner *et al.*<sup>38</sup> A theoretical study of the complexes between dihydrogen,  $\text{H}_2$ , and a series of amines, phosphines, and arsine derivatives ( $\text{ZH}_3$  and  $\text{ZH}_2\text{X}$ , with Z = N, P, or As and X = F, Cl, CN, or  $\text{CH}_3$ ) has been carried out by Grabowski and Alkorta *et al.*<sup>35</sup> using *ab initio* methods (MP2/aug-cc-pVTZ), and they

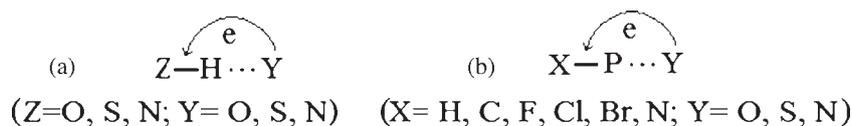
pointed out that, among all involved complexes, only those configurations of which the  $\sigma$ -electrons of  $\text{H}_2$  interact with  $\sigma$ -hole region of the pnico-gen atom generated by the of X–Z bond can be ascribed as pnico-gen bond.

Very recently, much attention has been paid to pnico-gen bond in theoretical studies.<sup>39–46</sup> By employing the block-localized wave function (BLW) based energy decomposition scheme, Guan and Mo<sup>39</sup> investigated thoroughly the pnico-gen bond nature and the corresponding electron transfer in a series of substituted phosphines complexed with ammonia. Moreover, some novel pnico-gen bond with special electronic structures are reported, such as single electron pnico-gen bond<sup>47</sup> and cation pnico-gen bond.<sup>48,49</sup> Although much progress on theoretical study of pnico-gen bond has been made, as a new kind of intermolecular weak interaction, it is far from sufficiency.

In the current work, a particular set of molecular complexes formed with formaldehyde (HCHO) and  $\text{PH}_2\text{X}$  (X=H, F, Cl, Br,  $\text{CH}_3$ ,  $\text{C}_6\text{H}_5$ ,  $\text{NO}_2$ ) were studied, and the ability of the different electron acceptors,  $\text{PH}_2\text{X}$ , to get involved in the  $\text{HCHO}\cdots\text{PH}_2\text{X}$  noncovalent interaction is discussed. The nature and electronic structures of these weak interactions were investigated and characterized using the second-order Møller–Plesset (MP2) theoretical method.

## 2. Computational Details

All the monomers and complexes were optimized using the MP2 method. Harmonic frequency analyses were performed at the same level to confirm that these structures were local minima on the energy surfaces. The interaction energies were corrected with the basis set superposition error (BSSE). The BSSE was evaluated using the counterpoise method of Boys and Bernardi.<sup>50</sup> According to the essence of intermolecular interactions, the accuracy of the calculation results exhibits a close relationship with primary functions. The choice of basis sets must include polarized function and dispersion function. Previous studies have demonstrated that the introduction of polarized function and dispersion function could decrease BSSE significantly,<sup>51</sup> therefore, the aug-cc-pvdz basis set was adopted for all atoms. If the basis set applied is enlarged, and within the limits of the complete basis set, BSSE tends to zero.<sup>52,53</sup>



**Scheme 1.** The charge transfers of the H-bond (a) and P-bond (b).

Natural bond orbital (NBO) theory<sup>54</sup> and atoms-in-molecules (AIM) theory of Bader<sup>55</sup> were employed to analyze the electronic behaviors and electronic density topological properties, respectively. Natural resonance theory (NRT),<sup>56–58</sup> was used to investigate the natural bond order of the ZBs. NBO and NRT calculations were carried out with the NBO 5.0 package.<sup>59</sup> All the other calculations were performed with Gaussian 03 program.<sup>60</sup>

### 3. Results and Discussion

#### 3.1 Geometric configuration and frequency analysis

The optimized geometric configurations on the potential surfaces of the monomers and  $\text{HCHO} \cdots \text{PH}_2\text{X}$  ( $\text{X}=\text{CH}_3, \text{H}, \text{C}_6\text{H}_5, \text{F}, \text{Cl}, \text{Br}, \text{NO}_2$ ) complexes at MP2/aug-cc-pvdz computational level are shown in figure 1, in which some important bond length and bond angle parameters are also presented. The frequencies analysis shows that all the configurations are local

minima on the potential surfaces of the complexes or monomers. As shown in figure 1 within the seven complexes,  $\text{O} \cdots \text{P-X}$  ZB structures were formed via the P-X groups (ZB donors, electron acceptors) of the  $\text{PH}_2\text{X}$  moiety interacting directly with O atom (ZB acceptors, electron donors) of the HCHO moiety. The van der Waals radius and covalent radius are two important factors in investigating the geometric structure of the noncovalent weak interaction systems. If the distance between two atoms is much less than the sum of their van der Waals radius but larger than the sum of their covalent radius, a weak interaction exists between the two atoms to a certain extent, which is stronger than van der Waals forces, such as hydrogen bond or halogen bond, etc. Here, the  $\text{P} \cdots \text{O}$  distances in the seven complexes are in the range of 0.2670~0.3214 nm. The experimental values of van der Waals radius and covalent radius of P atom are 0.180 and 0.110 nm, respectively; these of O atom are 0.152 and 0.066 nm, respectively. It is thus clear that the distances of the two directly involved in the formation of ZB atom pairs are all less than the sum of their van der Waals radius but

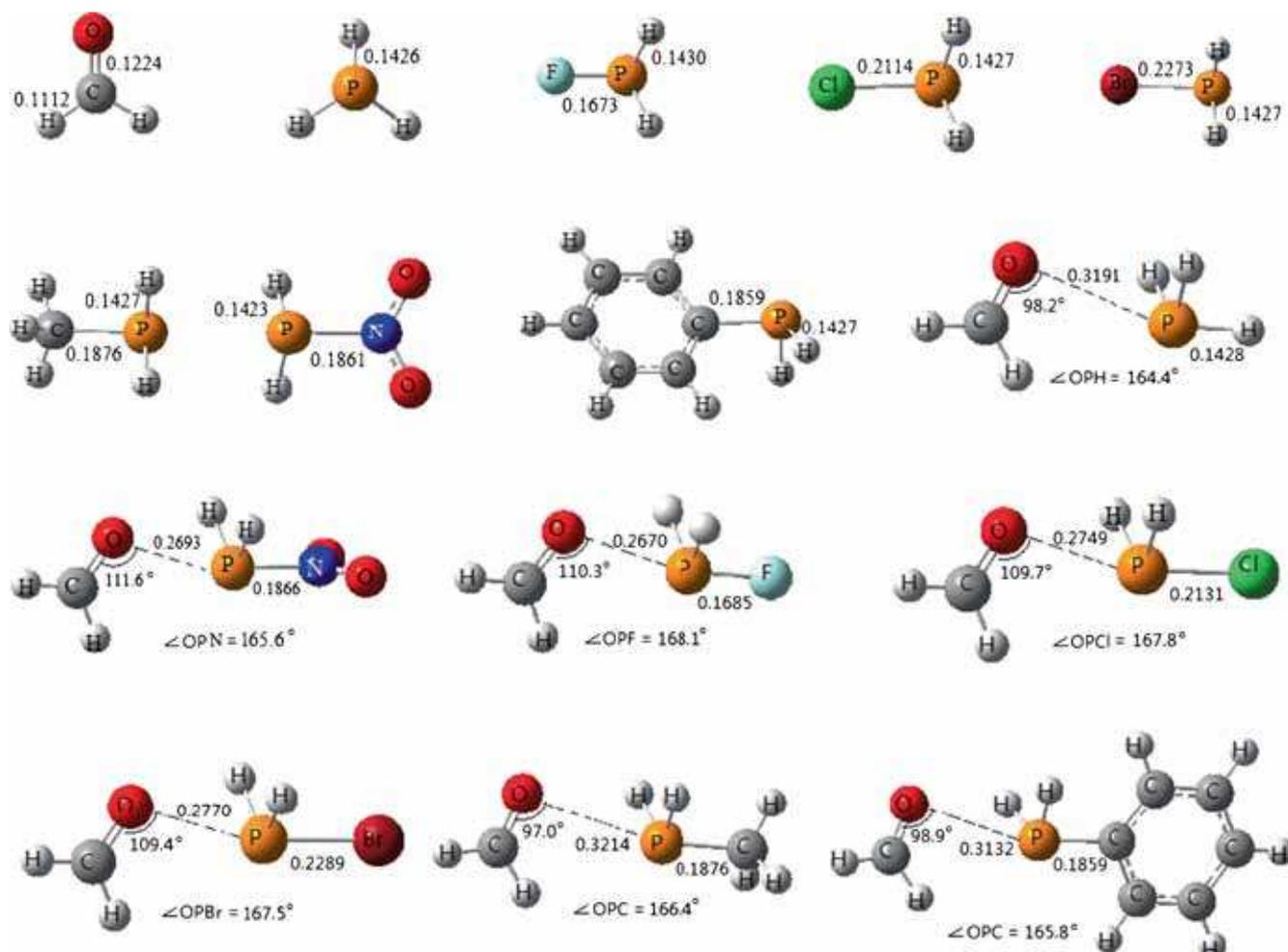


Figure 1. Geometries (nm, °) of the monomers and complexes calculated at MP2/aug-cc-pvdz level.

larger than the sum of their covalent radius. It can be concluded that there is a certain degree of weak interaction which is stronger than van der Waals forces existing between the atom pair of P...O.

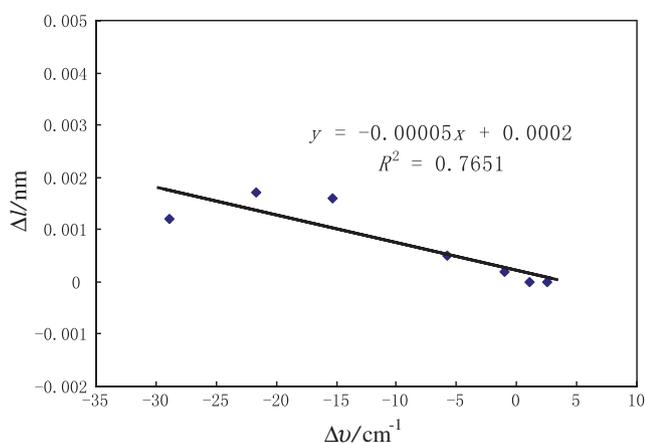
Additionally, in a conventional red-shifted HB structure, it is known that the bond length of hydrogen bond donor (X-H, X=N, O, S, etc.), the electron acceptor, often increases to a certain degree. Comparing parameters of the monomers with those of the complexes given in figure 1, it can be found that the P-H and P-N bond lengths slightly increase upon formations of HCHO...PH<sub>3</sub> and HCHO...PH<sub>2</sub>NO<sub>2</sub> complexes, respectively; the P-C bond lengths have no changes after formations of HCHO...PH<sub>2</sub>CH<sub>3</sub> and HCHO...PH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> complexes, and P-X (X= F, Cl and Br) present obviously increasing upon the formations of the HCHO...PH<sub>2</sub>X (X= F, Cl and Br) complexes. This observation is probably related to electronic effect before and after formation of ZB structures, which will be discussed in the following section. The change potential of bond length of ZB donors (electron acceptors) does not always agree with that of the HB donors in the typical red-shifted HB systems. Furthermore, the bond angle of O...P-X (X=H, F, Cl, Br, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, and NO<sub>2</sub>) is another characteristic parameter that need to be investigated. Generally, in a typical hydrogen bond system(Z-H...Y, Z=O, S, and N; Y= O, S, and N), the angle of Z-H...Y often has a linear structural potential in geometric configuration, which is decided by the n→σ\* electron behavior of the hydrogen bonds. Therefore, the stronger the hydrogen bond is, the closer to 180° bond angle is. For example, the Z-H...Y bond angle is about 175–180° in a strong hydrogen bond, 130–180° in a moderate hydrogen bond and 90–180° in

a weak hydrogen bond.<sup>24</sup> Here, in the O...P-X systems, the O...P-X pnictogen bond angles (O...P-X) are in the range of 164.4~168.1°, which is probably close to that in a strong hydrogen bond.

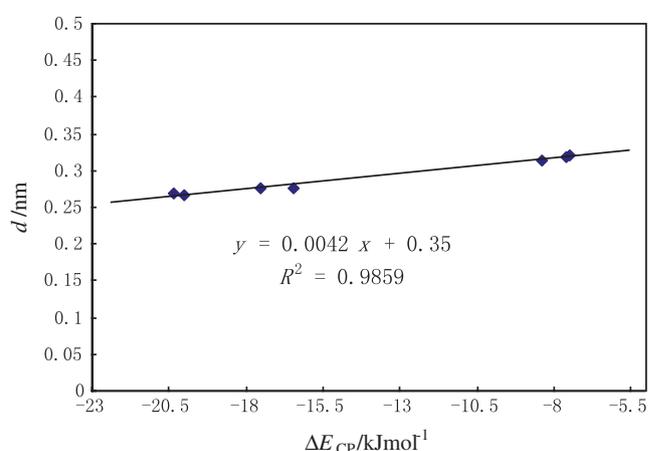
To help possible experimental identification of the ZBs complexes described in this work, table 1 showed the stretch vibrational frequency ( $\nu$ ), frequency shift ( $\Delta\nu$ ), IR intensity ( $I$ ) and bond length change ( $\Delta l$ ) of the P-X (X=CH<sub>3</sub>, H, C<sub>6</sub>H<sub>5</sub>, Br, Cl, F and NO<sub>2</sub>) bond. It is found that the stretching frequencies of the P-X bonds in the complexes of HCHO...PH<sub>2</sub>CH<sub>3</sub> and HCHO...PH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> undergo a slightly blue-shift; and these of HCHO...PH<sub>3</sub> and HCHO...PH<sub>2</sub>NO<sub>2</sub> complexes present a slightly red-shift. On the other hand, the stretching frequencies of the P-X bonds in the complexes of HCHO...PH<sub>2</sub>X (X= F, Cl and Br) show an obvious red-shift with the values of -15.31, -21.66 and -28.9 cm<sup>-1</sup>, respectively. This is well consistent with the significant increase of P-X (X= F, Cl and Br) bond lengths. As shown in figure 2, the frequency-shift values ( $\Delta\nu$ ) of the stretch vibrational frequencies of P-X bonds have a linear correlation to the variation of P-X bond length ( $\Delta l$ ), where the relevant equation is  $y = -0.00005x + 0.00002$  ( $R^2 = 0.7651$ ). It is worth noting that the IR intensity ( $I$ ) of P-X bonds on the PH<sub>2</sub>X moieties increases upon the formation of the complexes. Since the IR intensity ( $I$ ) is in a direct proportion to the square of the partial derivative of the correlative atoms displacement ( $r$ ) to the electric dipole moment ( $\mu$ ), which can be described as  $I \propto |d\mu/d r_{X-H}|^2$ , and the ZBs in the complexes cause further polarization of the P-X bonds with larger dipole moment, the IR intensity increase remarkably, which is consistent with that of the red-shift HB systems.<sup>61</sup>

**Table 1.** Stretch vibrational frequency ( $\nu$ , cm<sup>-1</sup>), frequency shift ( $\Delta\nu$ , cm<sup>-1</sup>), IR intensity ( $I$ , km·mol<sup>-1</sup>) and bond length change ( $\Delta l$ , nm) of the P-X (X=CH<sub>3</sub>, H, C<sub>6</sub>H<sub>5</sub>, Br, Cl, F and NO<sub>2</sub>) bonds.

Compound	$\nu_{P-X}$	$\Delta\nu$	$I$	$\Delta l$
H <sub>2</sub> C <sub>6</sub> H <sub>5</sub> P	684.74	–	1.00	–
H <sub>2</sub> CH <sub>3</sub> P	681.95	–	8.48	–
H <sub>3</sub> P	2451.93	–	33.76	–
H <sub>2</sub> BrP	396.51	–	25.73	–
H <sub>2</sub> ClP	501.07	–	52.69	–
H <sub>2</sub> FP	778.5	–	120.01	–
H <sub>2</sub> NO <sub>2</sub> P	433.88	–	10.42	–
HCHO...PH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	685.49	1.02	1.99	0.000
HCHO...PH <sub>2</sub> CH <sub>3</sub>	684.49	2.54	15.09	0.000
HCHO...PH <sub>3</sub>	2450.87	-1.06	65.46	0.0002
HCHO...PH <sub>2</sub> Br	381.2	-15.31	67.61	0.0016
HCHO...PH <sub>2</sub> Cl	479.41	-21.66	108.19	0.0017
HCHO...PH <sub>2</sub> F	749.6	-28.9	198.30	0.0012
HCHO...PH <sub>2</sub> NO <sub>2</sub>	428.07	-5.81	47.55	0.0005



**Figure 2.** The relationships between frequency shifts ( $\Delta\nu$ ,  $\text{cm}^{-1}$ ) and bond length changes ( $\Delta l$ , nm) of the P-X ( $X=\text{CH}_3$ , H,  $\text{C}_6\text{H}_5$ , Br, Cl, F and N) bonds.



**Figure 3.** The relationship between the  $\Delta E_{\text{CP}}$  and P $\cdots$ O distance ( $d$ ).

### 3.2 Interaction energies and stability

Interaction energy is an important parameter to show the strength and stability of a weak bond. The ZB noncovalent interaction energies of the  $\text{HCHO}\cdots\text{PH}_2\text{X}$  complexes at MP2/aug-cc-pvdz level are listed in table 2. The correction of BSSE is used for calculation because it is a necessary step to depict the energies of intermolecular interaction systems. As shown in table 2, the BSSE of the seven complexes, ranging from 3.06 to 6.09  $\text{kJ}\cdot\text{mol}^{-1}$ , are all relatively large and non-ignorable relative to the raw interaction energies ( $\Delta E$ ), and they accounts for about 22–37% of the absolute value of the  $\Delta E$  in the seven complexes. Apparently, it is necessary to perform a BSSE correction via the CP method in order to obtain the accurate interaction. The BSSE corrected ZB interaction energies ( $\Delta E_{\text{CP}}$ ) of the  $\text{HCHO}\cdots\text{PH}_2\text{CH}_3$ ,  $\text{HCHO}\cdots\text{PH}_3$  and  $\text{HCHO}\cdots\text{PH}_2\text{C}_6\text{H}_5$  complexes are  $-7.51$ ,  $-7.62$  and  $-8.36$   $\text{kJ}\cdot\text{mol}^{-1}$ , respectively, which are obviously smaller than these of  $\text{HCHO}\cdots\text{PH}_2\text{Br}$ ,  $\text{HCHO}\cdots\text{PH}_2\text{Cl}$ ,  $\text{HCHO}\cdots\text{PH}_2\text{F}$  and  $\text{HCHO}\cdots\text{PH}_2\text{NO}_2$  complexes ( $-16.48$ ,  $-17.51$ ,

$-20.01$  and  $-20.36$   $\text{kJ}\cdot\text{mol}^{-1}$ , respectively). This suggests that the electron withdrawing groups ( $X=\text{F}$ ,  $\text{NO}_2$ , Cl, Br) could probably enhance the ZB interaction strength. Additionally, comparing the BSSE corrected interaction energies ( $\Delta E_{\text{CP}}$ ) of the seven ZB complexes, it can be easily found that the relative stabilities of the seven complexes increase in the order of  $\text{HCHO}\cdots\text{PH}_2\text{CH}_3 < \text{HCHO}\cdots\text{PH}_3 < \text{HCHO}\cdots\text{PH}_2\text{C}_6\text{H}_5 < \text{HCHO}\cdots\text{PH}_2\text{Br} < \text{HCHO}\cdots\text{PH}_2\text{Cl} < \text{HCHO}\cdots\text{PH}_2\text{F} < \text{HCHO}\cdots\text{PH}_2\text{NO}_2$ . Moreover, comparing the present system with Scheiner's work ( $\text{H}_2\text{FP}\cdots\text{D}$ ,  $\text{D}=\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{CO}$ ,  $\text{H}_2\text{CS}$  and  $\text{CH}_3\text{OH}$ ),<sup>29</sup> it can be found that the  $\Delta E$  of two systems are similar, suggesting their stabilities are close.

Interestingly, it is found that the BSSE corrected interaction energies ( $\Delta E_{\text{CP}}$ ) are mirrored by the contractions of the P $\cdots$ O interaction distances ( $d$ ) listed in table 2. Figure 3 shows the plot of the  $\Delta E_{\text{CP}}$  against the  $d$ . A good linear relation is observed between  $\Delta E_{\text{CP}}$  and  $d$  with the equation of  $y = 0.0042x + 0.35$  ( $R^2 = 0.9859$ ), which suggests that the shorter the P $\cdots$ O distance ( $d$ ) is, the larger the BSSE corrected interaction energy ( $\Delta E_{\text{CP}}$ ) is and the stronger the ZB strength is.

**Table 2.** With and without BSSE corrected interaction energy ( $\Delta E$  and  $\Delta E_{\text{CP}}$ ,  $\text{kJ}\cdot\text{mol}^{-1}$ ) and P $\cdots$ O distance ( $d$ , nm) of the seven complexes calculated at MP2/aug-cc-pvdz.

Complexes	$\Delta E$	BSSE	$\Delta E_{\text{CP}}$	$d$
$\text{HCHO}\cdots\text{PH}_2\text{CH}_3$	$-11.38$	3.87	$-7.51$	0.3214
$\text{HCHO}\cdots\text{PH}_3$	$-10.68$	3.06	$-7.62$	0.3191
$\text{HCHO}\cdots\text{PH}_2\text{C}_6\text{H}_5$	$-13.26$	4.90	$-8.36$	0.3132
$\text{HCHO}\cdots\text{PH}_2\text{Br}$	$-22.57$	6.09	$-16.48$	0.2770
$\text{HCHO}\cdots\text{PH}_2\text{Cl}$	$-23.42$	5.91	$-17.51$	0.2749
$\text{HCHO}\cdots\text{PH}_2\text{F}$	$-25.78$	5.77	$-20.01$	0.2670
$\text{HCHO}\cdots\text{PH}_2\text{NO}_2$	$-26.36$	6.00	$-20.36$	0.2693

### 3.3 NBO and NRT analysis

For a better understanding on the formation mechanism of the ZBs complexes, natural bond orbital theory (NBO) analysis was performed for the monomers and complexes based on the wave functions obtained at MP2/aug-cc-pVDZ level, and the corresponding results are listed in table 3. The interaction strength between monomers could be clarified according to the second-order stabilization energy,  $E_{ij}^{(2)}$ , obtained from the NBO analysis.<sup>16</sup> Generally, the larger the stabilization energy  $E_{ij}^{(2)}$  is, the stronger the interaction of donor and acceptor orbital will be. For the HCHO moiety, there are two different lone electron pairs in O atom (electron donor). The first pair is with  $sp^{0.6}$  hybridization type, and the second pair is close to pure  $p$  type orbital. As shown in table 3 there are two kinds of charge transfer behaviors between the natural bonds orbital in the seven ZB complexes namely,  $LP^1(O) \rightarrow \sigma^*(P-X)$  and  $LP^2(O) \rightarrow \sigma^*(P-X)$ , respectively. However, the  $E_{ij}^{(2)}$  of the  $LP^2(O) \rightarrow \sigma^*(P-X)$  are all obviously larger than these of the  $LP^1(O) \rightarrow \sigma^*(P-X)$  in the seven complexes. Namely, the  $LP^2(O) \rightarrow \sigma^*(P-X)$  is the main natural bonds orbital behavior. The total  $E_{ij}^{(2)}$  of the two kinds of natural bonds orbital ( $E_{ij}^{(2)} LP^{\text{total}}(O) \rightarrow \sigma^*(P-X)$ ) are also listed in table 3. It is noted that with strength of the electron withdrawing of X increasing, the  $E_{ij}^{(2)}$  of the  $LP^{\text{total}}(O) \rightarrow \sigma^*(P-X)$  increase, implying much larger polarity of ZB donor is advantage for charge transfer.

For completeness and simplicity, figure 4 shows the 3D images of the  $LP^1(O) \rightarrow \sigma^*(P-X)$  (upper),  $LP^2(O) \rightarrow \sigma^*(P-X)$  (middle) and  $LP^{\text{total}}(O) \rightarrow \sigma^*(P-X)$  (lower) interactions in  $H_3P \cdots OHCH$  (a),  $H_2FP \cdots OHCH$  (b) and  $H_2NO_2P \cdots OHCH$  (c) complexes. It clearly shows that the overlaps between  $LP^2(O)$  and  $\sigma^*(P-X)$  are more apparent and efficient than those of  $LP^1(O) \rightarrow \sigma^*(P-X)$  interaction. The total results of the two kinds of charge transfers make the

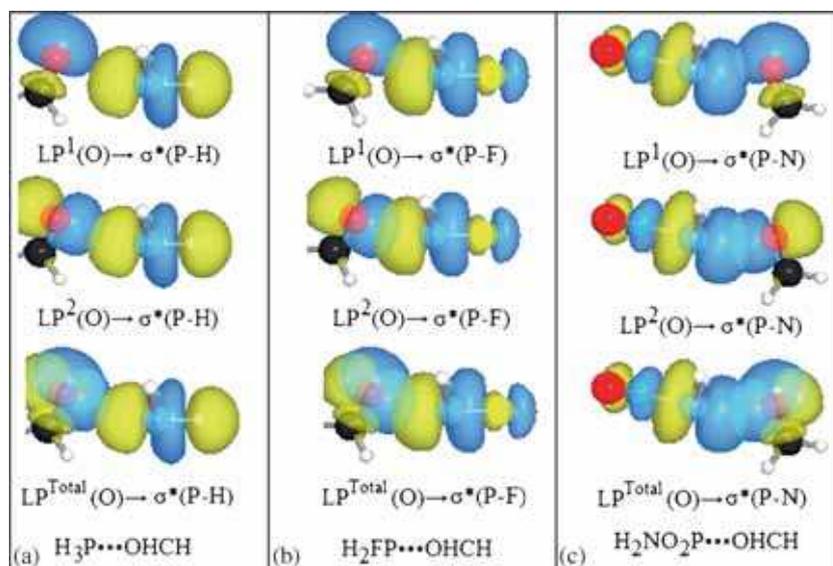
natural population of the  $\sigma^*(P-X)$  sequence increase 3.83, 3.59, 4.76, 19.63, 20.03, 22.65 and 16.76 me in the seven  $HCHO \cdots PH_2X$  complexes, respectively. Especially, the natural populations of the  $\sigma^*(P-X)$  ( $X = Br, Cl, F, NO_2$ ) increase dramatically indicating that P-X ( $X = Br, Cl, F, NO_2$ ) are better ZB donor (electron acceptor) groups than P-X ( $X = H, CH_3$  and  $C_6H_5$ ), corresponding to the related P-X bonds length elongation and the red-shift of stretch vibrational frequency, which was mentioned in the frequency analysis section.

It is noted that the  $E_{ij}^{(2)}$  of the  $LP^{\text{total}}(O) \rightarrow \sigma^*(P-X)$  in the seven complexes are well linearly correlated to the  $\Delta E_{CP}$ , and the relevant equation is  $y = -0.3303x - 5.7562$  ( $R^2 = 0.9956$ ) (figure 5), suggesting that the  $E_{ij}^{(2)}$  of the larger the  $LP^{\text{total}}(O) \rightarrow \sigma^*(P-X)$  is, the greater the BSSE corrected interaction energies ( $\Delta E_{CP}$ ) is and the stronger the ZB strength is. However, it is not found that any correlation between  $\Delta q_{\sigma^*(P-X)}$  and  $\Delta E_{CP}$  or  $\Delta q_{\sigma^*(P-X)}$  and  $E_{ij}^{(2)}$  of the  $LP^{\text{total}}(O) \rightarrow \sigma^*(P-X)$ , which indicates that the amount of the charge transfers between the donor and acceptor in the ZB system is not the determining factor for the strength of the weak interaction, and the amount of the charge transfer is also not corresponding to the  $E_{ij}^{(2)}$ . For example, the  $\Delta q_{\sigma^*(P-X)}$  of the  $HCHO \cdots PH_2NO_2$  and  $HCHO \cdots PH_2F$  complexes are 16.76 and 22.65 me, respectively, but the  $\Delta E_{CP}$  of the related complexes are 20.36 and 20.01  $\text{kJ} \cdot \text{mol}^{-1}$ , and the  $E_{ij}^{(2)}$  of the related  $LP^{\text{total}}(O) \rightarrow \sigma^*(P-X)$  are 32.73 and 28.88  $\text{kJ} \cdot \text{mol}^{-1}$ , respectively. The  $\Delta q_{\sigma^*(P-X)}$  in the ZB interaction systems derives from not only the  $LP^{\text{total}}(O) \rightarrow \sigma^*(P-X)$ , but also the charge redistribution of the intra-moiety after the formation of the complex. For the  $PH_2NO_2$  moiety of the  $HCHO \cdots PH_2NO_2$  complex, the inner charge transferring from the two lone pairs on O atom of the  $-NO_2$  group to  $\sigma^*(P-N)$  is weaker than that in the  $PH_2NO_2$  monomer. So, the  $\Delta q_{\sigma^*(P-N)}$  in the  $H_2NO_2P \cdots OHCH$  is smaller than those in  $HCHO \cdots PH_2X$  ( $X = F, Cl$  and  $Br$ ) complexes.

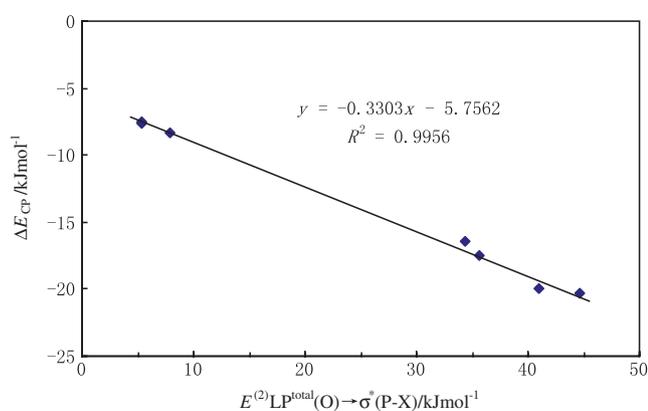
**Table 3.** NBO analysis for  $O \cdots P-X$  ( $X = CH_3, H, C_6H_5, F, Cl, Br$  and  $NO_2$ ).

Complexes	HCHO... PH <sub>2</sub> CH <sub>3</sub>	HCHO... PH <sub>3</sub>	HCHO... PH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	HCHO... PH <sub>2</sub> Br	HCHO... PH <sub>2</sub> Cl	HCHO... PH <sub>2</sub> F	HCHO... PH <sub>2</sub> NO <sub>2</sub>
$E_{ij}^{(2)} LP^1(O) \rightarrow \sigma^*(P-X)$ kJ/mol <sup>a</sup>	1.25	1.42	2.25	10.03	10.41	12.16	12.92
$E_{ij}^{(2)} LP^2(O) \rightarrow \sigma^*(P-X)$ kJ/mol	4.26	3.89	5.64	24.37	25.25	28.88	32.73
$E_{ij}^{(2)} LP^{\text{total}}(O) \rightarrow \sigma^*(P-X)$ kJ/mol	5.51	5.31	7.89	34.40	35.66	41.04	44.65
$\Delta q_{\sigma^*(P-X)}$ /me <sup>b</sup>	3.83	3.59	4.76	19.63	20.03	22.65	16.76
Total bond order of $O \cdots P$	0.00211	0.00011	0.00051	0.0089	0.00571	0.0126	0.00551
Covalent bond order of $O \cdots P$	0.00001	0.00001	0.00001	0.0001	0.00001	0.0001	0.00001
Ionic bond order of $O \cdots P$	0.0021	0.0001	0.0005	0.0088	0.0057	0.0125	0.0055

<sup>a</sup> $LP^i$  ( $i=1, 2$ ) presents the first or second lone electron of the O atom; <sup>b</sup> $\Delta q_{\sigma^*(P-X)}$  presents the charge population difference between  $PH_2X$  and  $HCHO \cdots PH_2X$  complexes.



**Figure 4.** 3D images of the interactions between the natural bond orbitals in HCHO...PH<sub>3</sub> (a), HCHO...PH<sub>2</sub>F (b) and HCHO...PH<sub>2</sub>NO<sub>2</sub> (c) complexes.



**Figure 5.** The relationship between the  $\Delta E_{CP}$  and  $E_{ij}^{(2)}LP^{total}(O) \rightarrow \sigma^*(P-X)$ .

The natural resonance theory (NRT)<sup>56–58</sup> module provides an analysis of molecular electron density (correlated or uncorrelated) in terms of resonance structures and weights, which could confirm the bond order and valency that are closely related to classical resonance theory concepts. The natural bond order is evaluated as eq. (1).

$$b_{AB} = \sum_{\alpha} \omega_{\alpha} b_{AB}^{(\alpha)} \quad (1)$$

where  $b_{AB}^{(\alpha)}$  is the integer number of bonds connecting centers A, B in resonance structure,  $\omega_{\alpha}$  is the final weighting of each resonance structure. The ionic bond order ( $b_{AB}^{(ion)}$ ) and covalent bond order ( $b_{AB}^{(cov)}$ ) of A-B are given as eq. (2) and eq. (3), respectively.

$$b_{AB}^{(ion)} = b_{AB} i_{AB} \quad (2)$$

$$b_{AB}^{(cov)} = b_{AB}(1 - i_{AB}) \quad (3)$$

where  $i_{AB}$  is the ionic character of A-B bond, and  $i_{AB} = \sum_{\alpha} \omega_{\alpha} i_{AB}^{(\alpha)} / b_{AB}$ , where  $i_{AB}^{(\alpha)}$  is the ionicity of the A-B bond in the resonance structure, and determined from NBO polarization coefficients  $c_A$  and  $c_B$  as eq. (4).

$$i_{AB}^{(\alpha)} = \left| \frac{c_A^2 - c_B^2}{c_A^2 + c_B^2} \right| \quad (4)$$

The covalent bond orders, ionic bond orders and total bond orders of P...O are listed in table 3. It is easily found that the ionic bond orders are all larger than the covalent bond orders of the P...O ZB weak bond in each complex. The  $b_{AB}^{(ion)}$  is the main contribution to the total bond order of P...O, suggesting that the P...O ZB weak bond is mainly with electrostatic characteristic and slightly with covalent in nature. Here the NRT analysis for the nature of HCHO...PH<sub>2</sub>X (X=CH<sub>3</sub>, H, C<sub>6</sub>H<sub>5</sub>, F, Cl, Br, NO<sub>2</sub>) pnicogen bonds agrees with Scheiner's report<sup>29</sup> based on energy decomposition analysis for the H<sub>2</sub>FP...D (D=NH<sub>3</sub>, H<sub>2</sub>O, H<sub>2</sub>S, H<sub>2</sub>CO, H<sub>2</sub>CS and CH<sub>3</sub>OH) systems. Nevertheless, it is not noted that the value of the total bond orders of P...O and  $\Delta q_{\sigma^*(P-X)}$  has the same variation trend in the seven complexes. The minimum and maximum values of the total bond orders of P...O correspond to the complexes of HCHO...PH<sub>3</sub> and HCHO...PH<sub>2</sub>F, respectively, and those of  $\Delta q_{\sigma^*(P-X)}$  locating in the same complexes, which indicates that the charge transfer would be helpful to increase the total bond order.

**Table 4.** Electron density topological properties of bond critical points for the seven complexes.

Complexes	Atom pair	$\rho(r_c)$ /a.u.	$\lambda_1$	$\lambda_2$	$\lambda_3$	$\nabla^2\rho(r_c)$ /a.u.	$\varepsilon$
HCHO...PH <sub>2</sub> CH <sub>3</sub>	P...O	0.0057	-0.0040	-0.0032	0.0256	0.0184	0.2374
HCHO...PH <sub>3</sub>	P...O	0.0079	-0.0048	-0.0046	0.0366	0.0272	0.0483
HCHO...PH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	P...O	0.0086	-0.0051	-0.0047	0.0396	0.0298	0.0608
HCHO...PH <sub>2</sub> Br	P...O	0.0167	-0.0119	-0.0110	0.0738	0.0509	0.0853
HCHO...PH <sub>2</sub> Cl	P...O	0.0172	-0.0124	-0.0113	0.0763	0.0526	0.0929
HCHO...PH <sub>2</sub> F	P...O	0.0195	-0.0145	-0.0130	0.0864	0.0589	0.1190
HCHO...PH <sub>2</sub> NO <sub>2</sub>	P...O	0.0189	-0.0139	-0.0126	0.0819	0.0554	0.1071

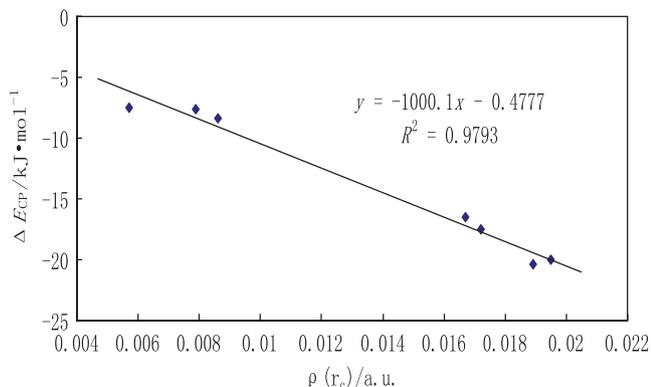
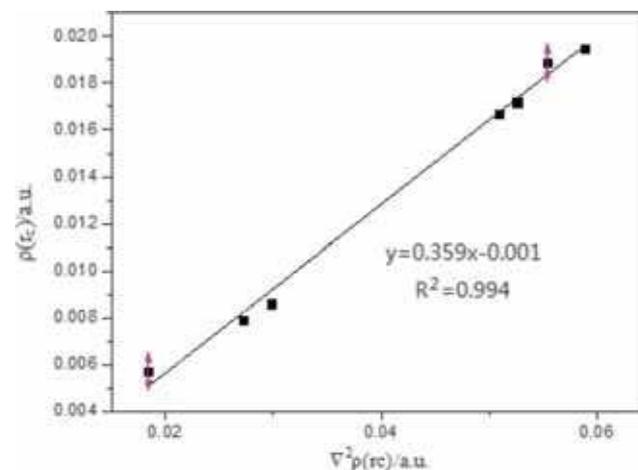
### 3.4 The topological properties and AIM theory analysis

The topological properties of the scalar field electron density ( $\rho(r)$ ) can be described by the numbers and the categories of the critical points. There are special points of the considered electron density; these are critical points (CPs), for which the gradient of electron density vanishes. According to Bader's atoms-in-molecules (AIM) theory,<sup>62</sup> the electron density topological properties of a molecule depend on electron density gradient vector field and  $\nabla^2\rho(r)$ . In general, the electron density of a BCP ( $\rho(r_c)$ ) is related to the strength of the bond: the larger the  $\rho(r_c)$  is, the stronger the bond will be. The  $\nabla^2\rho(r)$  of a BCP reflects the characteristic of the bond. If  $\nabla^2\rho(r_c) < 0$ , BCP charges will be concentrated, if  $\nabla^2\rho(r_c) > 0$ , BCP charges will be dispersed.

Table 4 lists the electron density topological properties of the ZB critical points in the seven complexes. The eigenvalues of the electron density Hessian matrix of P...O are both "one positive two negative". Therefore, the critical points between the atom pairs of P...O all belong to the type of BCPs. The  $\rho(r)$  of P...O in HCHO...PH<sub>2</sub>CH<sub>3</sub>, HCHO...PH<sub>3</sub> and HCHO...PH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> are pretty small with values of only 0.0057, 0.0079 and 0.0086 a.u., respectively. However, the  $\rho(r)$  of P...O in

HCHO...PH<sub>2</sub>Br, HCHO...PH<sub>2</sub>Cl, HCHO...PH<sub>2</sub>F and HCHO...PH<sub>2</sub>NO<sub>2</sub>, ranging from 0.0167–0.0195 a.u., are obviously larger than the former three complexes, indicating that the ZB interactions in the former three complexes are much weaker than those in the other four, which is in good agreement with the result of the interaction energies described previously. Additionally, figure 6 plots the linear relationship between the  $\rho(r_c)$  of the P...O atom pairs and  $\Delta E_{CP}$  of the seven complexes, and the relevant equation is  $y = -100.1 \times -0.4777$  ( $R^2 = 0.9793$ ).

In addition, the  $\nabla^2\rho(r)$  of the corresponding critical points of the P...O are all very small positive values (0.018 ~ 0.059 a.u.), revealing that lowering the potential energy dominates the total energy within the P...O region of space where electronic charge density is dispersed. Especially, the  $\nabla^2\rho(r)$  of the critical points of the P...O in HCHO...PH<sub>2</sub>Br, HCHO...PH<sub>2</sub>Cl, HCHO...PH<sub>2</sub>F and HCHO...PH<sub>2</sub>NO<sub>2</sub> are relatively large (more positive), meaning that P...O PBs mainly present a characteristic of polarized weak bond. Furthermore, it is interesting to find that the  $\rho(r_c)$  are well linearly correlated to the  $\nabla^2\rho(r_c)$  of the P...O atom pairs of the seven complexes, and the relevant equation is  $y = 0.3593x - 0.0015$  ( $R^2 = 0.9944$ ) (figure 7). Moreover,  $\varepsilon$ , the bond ellipticity, is defined as  $\lambda_1/\lambda_2 - 1$ ,

**Figure 6.** The relationships between  $\rho(r_c)$  of the P...O atom pairs and  $\Delta E_{CP}$  of the seven complexes.**Figure 7.** The relationships between  $\rho(r_c)$  and  $\nabla^2\rho(r_c)$  of the P...O atom pairs of the seven complexes.

in which  $\lambda_1$  and  $\lambda_2$  are the two eigenvalues of the Hessian matrix of the electron density. The  $\varepsilon$  provides a measure for the  $\sigma$  or  $\pi$  character of a bond. In general, the less the  $\varepsilon$  is, the stronger the  $\sigma$  character is; contrariwise, the stronger the  $\pi$  character is. Here, except for the bond ellipticity of P $\cdots$ O in HCHO $\cdots$ PH<sub>2</sub>CH<sub>3</sub>, the other  $\varepsilon$  values are not more than 0.1190, revealing that PBs have stronger  $\sigma$  character than  $\pi$  character. In other word, X-P $\cdots$ O PBs have higher symmetry of orbital “bond axe”, which can also be proved from the 3D images of the interactions between the natural bond orbital (figure 4).

#### 4. Conclusions

In the present study, the pnicogen bond (ZB) intermolecular interaction in the HCHO $\cdots$ PH<sub>2</sub>X (X=CH<sub>3</sub>, H, C<sub>6</sub>H<sub>5</sub>, F, Cl, Br, NO<sub>2</sub>) systems have been studied at the MP2/aug-cc-pvdz computational level, which is very useful in the supramolecular system or material design based on the pnicogen bond interaction. According to the theoretical investigations and characterizations, the following conclusions can be drawn:

- (1) In the seven complexes, the O $\cdots$ P-X ZB structures formed via the X-P group of PH<sub>2</sub>X as ZB donor (electron acceptor is anti-bond orbital of P-X sigma bond) and the O atom of HCHO as ZB acceptor (electron donor is the two lone pairs on O atom), which is similar to hydrogen bond systems (Z-H $\cdots$ Y, Z=O, S, N; Y= O, S, N).
- (2) Comparing the BSSE corrected interaction energies ( $\Delta E_{\text{CP}}$ ) of the seven ZB complexes, it can be easily found that the relative stabilities of the seven complexes increase in the order: HCHO $\cdots$ PH<sub>2</sub>CH<sub>3</sub> < HCHO $\cdots$ PH<sub>3</sub> < HCHO $\cdots$ PH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> < HCHO $\cdots$ PH<sub>2</sub>Br < HCHO $\cdots$ PH<sub>2</sub>Cl < HCHO $\cdots$ PH<sub>2</sub>F < HCHO $\cdots$ PH<sub>2</sub>NO<sub>2</sub>.
- (3) As shown by NBO analysis, there are two kinds of charge transfer behaviors between the natural bond orbital in the seven ZB complexes. They are LP<sup>1</sup>(O) $\rightarrow$   $\sigma^*$ (P-X) and LP<sup>2</sup>(O) $\rightarrow$   $\sigma^*$ (P-X), respectively. However, the  $E_{ij}^{(2)}$  of all the second charge transfer are obviously larger than those of the first charge transfers in the seven complexes. The LP<sup>2</sup>(O) $\rightarrow$   $\sigma^*$ (P-X) is the main natural bond orbital behavior. Moreover, P-X (X= Br, Cl, F, NO<sub>2</sub>) are better ZB donors (electron acceptors) than P-X (X=H, CH<sub>3</sub> and C<sub>6</sub>H<sub>5</sub>) groups. NRT calculation indicates that the O $\cdots$ P-X ZB weak bond is mainly with electrostatic and slightly with covalent nature, and the charge transfer benefits

increasing the total bond order of P $\cdots$ O ZB weak bond.

- (4) The topology properties were analyzed *via* AIM theory, and the results showed that the ZB interactions in the HCHO $\cdots$ PH<sub>2</sub>CH<sub>3</sub>, HCHO $\cdots$ PH<sub>3</sub> and HCHO $\cdots$ PH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> complexes are weaker than those in the HCHO $\cdots$ PH<sub>2</sub>Br, HCHO $\cdots$ PH<sub>2</sub>Cl, HCHO $\cdots$ PH<sub>2</sub>F and HCHO $\cdots$ PH<sub>2</sub>NO<sub>2</sub> complexes, which is well consistent with the result of the interaction energies analysis.

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