Electron Transfer in Pnicogen Bond

Liangyu Guan

Western Michigan University, liangyuguan50@gmail.com

Follow this and additional works at: http://scholarworks.wmich.edu/masters_theses

Part of the Chemistry Commons

Recommended Citation

http://scholarworks.wmich.edu/masters_theses/524

This Masters Thesis-Open Access is brought to you for free and open access by the Graduate College at ScholarWorks at WMU. It has been accepted for inclusion in Master's Theses by an authorized administrator of ScholarWorks at WMU. For more information, please contact maira.bundza@wmich.edu.
ELECTRON TRANSFER IN PNICOGEN BOND

by

Liangyu Guan

A thesis submitted to the Graduate College in partial fulfillment of the requirements for the degree of Master of Arts Chemistry Western Michigan University August 2014

Thesis Committee:

Yirong Mo, Ph.D., Chair
Ramakrishna Guda, Ph.D.
Gellert Mezei, Ph.D.
Non-covalent bonds and covalent bonds fall into two different categories in chemistry. Studies on non-covalent bonds were growing rapidly in the 20th century. Other than hydrogen bonds, many other kinds of non-covalent bonds have also been discovered and discussed. One of them is halogen bond, which is a non-covalent interaction between a halogen atom and a Lewis base. Similar to halogen bond, pnicogen bond is also a non-covalent interaction. In pnicogen-bond complex, pnicogen atoms (Group VA elements) act as Lewis acid, which can accept electrons from electron donor groups. In this research we applied the block-localized wave function method (BLW method) to the study of a series of substituted phosphines \( X_n PH_3-n \). The advantage of BLW method is that it can define the electron localization state in monomers and complex, which means that electrons can be restricted in individual monomer. It makes the examination of charge transfer effect during the formation of a pnicogen bond feasible.

Also we have developed the orbital correlation diagram based on BLW, which helps us in identifying a new charge transfer pathway from the lone pair of \( NH_3 \) to phosphines. This charge transfer pathway is \( n \rightarrow d\pi^* \). \( d\pi^* \) orbital is formed by the interaction between \( d \) orbitals in pnicogen atom and \( \pi^* \) orbitals in nitro or cyano group. But for pnicogen bond, this explanation may still be oversimplified. The electron density difference (EDD) map shows that electron density only increases at one side of pnicogen atom, which is the \( \sigma \)-hole region.
ACKNOWLEDGMENTS

First, I am so thankful for the support of my advisor Prof. Yirong Mo. This thesis would not be finished without his patience, carefulness and immense knowledge. His guidance helped me all the time in my research and study for master’s degree.

Besides my advisor, I would like to thank Dr. Guda and Dr. Mezei for their encouragement and help with my master’s thesis. I would also want to extend my gratitude to Dr. Sinn and Dr. Schoffers for their interesting and insightful courses and recommendations, to Ms. Hyder for her help when I was a teaching assistant, and to the Chemistry Department of WMU for giving me this precious opportunity of studying chemistry.

I am also deeply indebted to my family: my parents Jianhua Guan and Sujun Wang, and especially my grandmother Aiyun Chen, who takes care of me and brings me up.

Last but not least, my great thanks would go to a special person to me Yufei Wang, thank you for your warm love.

Liangyu Guan
TABLE OF CONTENTS

ACKNOWLEDGMENTS ........................................................................................................... ii
LIST OF TABLES.......................................................................................................................... iv
LIST OF FIGURES....................................................................................................................... v
INTRODUCTION............................................................................................................................. 1
    Non-covalent bond and Hydrogen bond ................................................................................. 1
    Halogen bond and σ-hole concept ......................................................................................... 2
    Brief description of pnicogen bond ....................................................................................... 2
METHODOLOGY............................................................................................................................ 5
    Block-localized wave function (BLW) method ......................................................................... 5
    Energy decomposition analysis .............................................................................................. 6
    Orbital correlation diagram based BLW .............................................................................. 7
    Map of electron density difference (EDD) ........................................................................... 9
COMPUTATIONAL DETAILS........................................................................................................ 10
GENERAL TREND AND DISCUSSION OF RESULTS................................................................. 11
    Structure description ............................................................................................................. 11
    Energy decomposition analysis and binding energy trend .................................................... 12
DISCUSSION OF MONO-SUBSTITUTED PHOSPHINES........................................................... 15
    Hydroxyl-substituted phosphine .......................................................................................... 16
    Nitro-substituted phosphine ................................................................................................. 18
    Cyano-substituted phosphine ............................................................................................... 20
DISCUSSION OF MULTI-SUBSTITUTED PHOSPHINES.......................................................... 23
    Tri-fluoro-substituted phosphine .......................................................................................... 25
    Tri-cyano-substituted phosphine .......................................................................................... 26
CONCLUSION............................................................................................................................... 30
REFERENCES............................................................................................................................... 32
LIST OF TABLES

1. Structure description of 15 pnicogen bond complexes ................................................. 12

2. Result of BLW energy decomposition analysis ................................................................ 13

3. Result of BLW energy decomposition analysis for mono-substituted phosphine series of complexes ............................................................... 15

4. HOMO-LUMO energy gap of mono-substituted phosphines in BLW state and DFT state .............................................................. 17

5. Result of BLW energy decomposition analysis for multi-substituted phosphine series of complexes ..................................................... 23

6. HOMO-LUMO energy gap of multi-substituted phosphines in BLW state and DFT state .............................................................. 28
LIST OF FIGURES

1. Orbital correlation diagram of FPH2...NH3 complex.................................8

2. Electron density difference map of FPH2...NH3 complex..........................8

3. Optimum structures of 15 pnicogen bond complexes...............................11

4. Relationship between bond length and binding energy of mono-substituted phosphines-ammonia complexes..............................16

5. Optimum molecular structure of OHPH2...NH3........................................18

6. Orbital correlation diagram of NO2PH2...NH3 complex............................19

7. Electron density difference map of NO2PH2...NH3 complex......................20

8. Orbital correlation diagram of CNPH2...NH3 complex...............................20

9. Electron density difference map of CNPH2...NH3 complex.........................21

10. Relationship between bond length and charge transfer energy of mono-substituted phosphines-ammonia complexes..........................22

11. Orbital correlation diagram of F3P...NH3 complex..................................25

12. Orbital correlation diagram of (CN)3P...NH3 complex..............................27

13. Electron density difference map of (CN)3P...NH3 complex.........................28
INTRODUCTION

Non-covalent bond and hydrogen bond

Non-covalent bonds broadly exist in complexes and biomolecules\(^1\)-\(^3\). Different from a covalent bond, which is formed by the transferring or sharing of electron pairs, a non-covalent bond involves no direct sharing of electron pairs between two or more different moieties\(^4\). The bond energy ranges from several kcal/mol to over ten kcal/mol. In the 20th century, an increasing number of researchers turned to this field and made a lot of significant achievements, especially in the last decade\(^5\)-\(^10\). Although non-covalent bonds are not such strong interactions, they play critical roles in supermolecules, biomolecules and self-assembly systems\(^5\),\(^8\),\(^11\)-\(^15\). Protein’s tertiary and quaternary structures are also built by these weak interactions\(^16\)-\(^19\).

Among several types of non-covalent interactions, hydrogen bond is the most typical one, and has been studied since the 19\(^{th}\) century\(^20\)-\(^25\). Hydrogen bond was first clearly mentioned in 1912 by T. S. Moore and T. F. Winmill\(^26\). But this term “hydrogen bond” was first introduced in a book written by Pauling in 1931\(^27\). A hydrogen bond is usually expressed as A-H…D, indicating the interaction between a positively charged H and a negatively charged electron donor D, which can be F, O, N or \(\pi\) system\(^21\). As for the hydrogen bond, electrostatic force is assumed to be predominant, while electron transfer from D to A-H antibonding orbital is also believed to be important and responsible for the directionality of the bonding\(^28\)-\(^31\). With the formation of hydrogen bond, A-H bond can be lengthened and thus its stretching vibration frequency reduced (“red-shift”), or shortened and thus its stretching vibration frequency increased (“blue-shift”). Many groups try to elucidate this phenomenon\(^32\)-\(^38\). A general consensus is that blue-shift and red-shift effects have no fundamental distinctions\(^39\)-\(^45\). The researches on hydrogen bond can be a helpful experience and provide a strong reference for research in other types of non-covalent interactions, such as halogen bond (A-X...D, where X is halogen atom, like F, Cl, Br),
chalcogen bond (halogen atom is replaced by chalcogen atom, like O, S, Se),

pnicogen bond (halogen atom is replaced by pnicogen atom, like N, P, As).

Halogen bond and σ-hole concept

Other than hydrogen bond, halogen bond has also caught lots of attentions. Halogen bond has been observed since the 19th century\(^9,46\) (in complex of Cl\(_2\), Br\(_2\), I\(_2\) and NH\(_3\)). Dumas et al. defined this kind of non-covalent interaction by the term “halogen bond” at the first time\(^47\). Another important discovery was made by Murray-Rust et al., who did the crystallographic surveys\(^46,48\). They mentioned a highly directional binding pattern between a halogen atom and both nucleophiles and electrophiles\(^9,48\). This important character was also supported by the research of Auffinger et al. In their survey of structures in the Protein Data Bank, halogen bond was reported commonly existing in biology system\(^16\). Thus halogen bonds can be applied in predictable self-assembly system and drug design\(^13\).

Generally, halogen atoms in molecular are believed to be negatively charged. Why can they accept electrons and work as Lewis acid? Considerable efforts had been devoted to this area before it was resolved by Clark et al. using the concept “σ-hole”, a positively charged region in halogen atom\(^46,48-52\). When a covalent bond forms between a halogen atom and other atom, electrons will accumulate in bond area due to polarization, leading to a decrease in electron density in the outer region, which can accordingly become positively charged and highly anisotropic. This phenomenon also has been reported in chalcogen bond\(^10,51,53-60\).

Brief description of pnicogen bond

With extensive studies conducted on both halogen bond and chalcogen bond, the possibility of interaction between Group VA atoms and Lewis base also attracts researchers’ attention. This kind of non-covalent interaction, called “pnicogen bond”\(^61,62\), was first recognized at the beginning of the 1990s, but it didn’t catch too
much attention until a landmark paper by Hey-Hawking et al. was published in 2011. They reported P…P interaction in a $^{13}$C $^{1}$H-NMR spectrum of ortho-carbaborane derivative, and thus pnicogen bond comes into researchers’ sight again.

Pnicogen bond is unlike hydrogen bond but similar to halogen or chalcogen bond. The structure of pnicogen bond can be expressed by (X)A(H)…D. X is any substituent. A is a pnicogen atom. (X)A(H) acts as a Lewis acid and accepts electrons. H is the hydrogen atom that bonds with A but has no direct interaction with D, the Lewis base and electron donor. Bond angle r(X-A…D) is always close to but never becomes a straight one. In the past several years, Scheiner and Alkortu did lots of works in revealing the nature and property of pnicogen bonds. Now it has been known that the strength of pnicogen bond relates to the electronegativity of substituent which is bonding to pnicogen. For instance, when different substituents bond with the center atom, the strength of pnicogen bond will increase following the order of $\text{CH}_3 < H < \text{NH}_2 < \text{CF}_3 < \text{OH} < \text{Cl} < F < \text{NO}_2$. In the strong pnicogen bond complex, NO$_2$PH$_2$…NH$_3$, binding energy is close to 7 kcal/mol. While in the complex CH$_3$PH$_2$…NH$_3$, binding energy is no more than 1 kcal/mol. $\pi$ bond system can also be electron donors, like FPH$_2$…C$_2$H$_4$. In this kind of pnicogen bonds, F-P is perpendicular to H$_2$C=CH$_2$ plane.

Considerable efforts have been made in the study of pnicogen bonds, by adopting both computational methods and experimental methods. The existence of pnicogen bonds has been confirmed, but the consensus about the nature of it has still not been reached. Scheiner points out that the charge transfer from electron donor (Lewis base) to $\sigma^*$ (X-A) antibonding orbital might be the main cause for the formation of pnicogen bonds, with no apparent $\sigma$-hole in this process. Politzer et al. suggest that 2 $\sigma$-holes can be detected in the pnicogen bond complex ClH$_2$P…PH$_2$Cl. In addition, Del Bene et al. focus on the complex H$_2$C=(X)P…PXH$_2$, and demonstrate not only a charge transfer from the $\pi$ bond of
H$_2$C=(X)P to the $\sigma$-hole of PXH$_2$, but also a charge transfer from the lone pair of PXH$_2$ to the $\pi$-hole of H$_2$C=(X)P$^{52,66}$. This synergistic action makes a very strong pnicogen bond form within it$^{48}$. Another difference between halogen bonds and pnicogen bonds lies in the substitution effect. When more than one electronegativity substituent bonds with a pnicogen atom, the strength of the pnicogen bond will not increase, which means bi- or tri-substitution will not bring extra stability. This interesting property makes it significantly distinct from hydrogen bonds$^{70}$.

To better understand various energy constitutions and the nature of pnicogen bonds, here we applied block-localized wave function (BLW) method and combined it with orbital correlation diagram based on BLW, to study the interaction between NH$_3$ and PH$_3$ with different substituents.
As a new branch of chemistry, computational chemistry is a powerful research method which uses computer simulation in solving problems in chemistry. Based on different simulation philosophies, computation method can be divide into two types, ab initio method and semi-empirical method. ab initio method is based on quantum mechanics and basic physics, while semi-empirical method employs additional parameters. Theoretical calculation in chemistry can date back to 1927, when Walter Heitler and Fritz London finished the first calculation. Computational chemistry developed rapidly in the second half of the 20th century.

Block-localized wave function (BLW) method

All the ab initio theories which are employed in computational chemistry originate from two approaches. One of them results in molecular orbital (MO) theory and the other results in valence bond (VB) theory. In MO theory, electrons are not assigned to certain chemical bond but delocalized in the whole molecular space. Orbitals in the whole space are constrained to be orthogonal, which makes calculation efficient. This advantage attracts lots of computational chemists and increases the number of models or methods established in the past decades. Electrons delocalization also brings an disadvantage to MO theory, that is, it is not applicable in the study of reasonable structures, when electrons are assigned to different chemical bonds of molecule. The other theory is VB theory. In VB theory, electrons are regarded as restricted in each chemical bond, forming a good model for studying resonance structures. But the problem is that orbitals in the whole molecule are non-orthogonal, thus the calculation could be a huge challenge and the efficiency is low.

Block-localized wave function (BLW) method is the simplest and most efficient ab initio VB theory. Different from the two classical models above, the fundamental assumption in BLW method is that all electrons and primitive basis functions can be divided into different subgroups. In each subgroup, orbitals are constrained to be
orthogonal, while orbitals in different subgroups are non-orthogonal. According to BLW method, each subgroup corresponds to one monomer of complex, and electrons will be restricted and localized in different monomers. Based on BLW method, studies of electron transfer across molecule will be feasible without significant increase in computation cost. These characters also make it an especially powerful tool in the study of charge transfer during the formation of complex.

Energy decomposition analysis

It is meaningful to separate the total binding energy into different energy terms, and each energy term can be interpreted by certain physical meaning. This method is called energy decomposition analysis, and can give us the insight of the nature of chemical bond. The advantage of BLW method is in defining the electron localization state. With this definition, intermolecular interaction can be divided into several energy terms.

First, a geometric deformation occurs in monomers, which will distort monomers from their optimal structures to deformed structures, which are parts of optimal supermolecule. The changed energy in this stage is defined as deformation energy ($\Delta E_{\text{def}}$). Then, monomers are brought together with no change in their electron distribution, which means only electrostatic energy ($\Delta E_{\text{elec}}$) is changed. And then, electron exchange is allowed but electrons and orbitals are still frozen. Here the changed energy is named exchange energy ($\Delta E_{\text{ex}}$), as a result of Pauli exchange. In DFT calculation, electrostatic energy ($\Delta E_{\text{elec}}$) and exchange energy ($\Delta E_{\text{ex}}$) are combined together as Heitler-London energy ($\Delta E_{\text{H-L}}$).

After that, molecular orbitals are optimized, but electrons are still restricted in their orbitals. This is an energy decreasing step and the changed energy involved in the accompanying is defined as polarization energy ($\Delta E_{\text{pol}}$), then BLW state complexes are formed. Finally, we delocalized all electrons, which will transfer
between different monomers and lower the total energy in this system, and this change of energy is represented by charge transfer energy ($\Delta E_{\text{ct}}$). Basis set superposition error was also included in the charge transfer term.

To better evaluate dispersion interaction between monomers, Grimme’s dispersion correction is often applied in DFT method\textsuperscript{78}. In energy decomposition analysis, it can be listed as an individual energy term, that is, dispersion correction energy term ($\Delta E_{\text{c}}$). Following the above steps, the energy decomposition is finished, and the total binding energy can be decomposed into different energy terms:

$$\Delta E_b = \Delta E_{\text{H-L}} + \Delta E_{\text{pol}} + \Delta E_{\text{def}} + \Delta E_{\text{ct}} + \Delta E_{\text{c}}$$

Orbital correlation diagram based on BLW

The mechanism of chemical reaction can be explained as molecular orbitals’ interaction between each reagent. In Frontier molecular orbital (FMO) theory, formation of chemical bond is explained as the charge transfer between HOMO of one molecule and LUMO of another one\textsuperscript{90,91}. Here we can combine BLW-ED analysis with HOMO-LUMO theory together, to see how molecular orbital step by step changes during chemical reaction. As we have discussed above, a reaction can be divided into several stages: deformation stage, “Coulomb” stage, polarization stage and charge transfer stage. In the first three stages, every molecular orbital of one fragment will be affected by all other fragments, the energy level for each MO will change either decreasing or increasing, and get well prepared for charge transfer. Finally, in charge transfer stage, electrons will be redistributed among the whole complex, and only relative MO will be affected by charge transfer. Thus, by inspecting the change in MO’s energy level during charge transfer stage, we can see electrons’ transfer pattern. Figure 1 is the example of FPH\textsubscript{2}...NH\textsubscript{3}. 
Figure 1: Orbital correlation diagram and change of molecular orbital’s energy in the formation of FPH$_2$...NH$_3$ complex. BL- and d- denote the block-localized and deformed monomers. Unit of the energy level value is hartree.

Here it shows how MO’s energy level changes. To simplify the map, only relative MOs are listed. Also some MOs, which have no interaction between each other, are omitted. In stage I, the energy level for each MO changes due to external electronic field, which is generated by other fragments. Then electrons in HOMO of monomer NH$_3$ (BLW state) are transferred to LUMO of fluorophosphine. After charge transfer, the HOMO-LUMO energy gap is increased by 0.38 eV. This change can be used to indicate phosphines’ electron transfer capability or charge transfer stability.

Figure 2: Electron density change in polarization stage (a) and charge transfer stage (b) in FPH$_2$...NH$_3$ complex (contour isodensity value=0.0004 a.u.). Red color represents gain in electron density and blue color represents loss of electron density.
Map of electron density difference (EDD)

The map of electron density difference (EDD) can show us the difference of electron density between two states of certain molecule. Based on BLW-ED analysis, electron density will change during polarization and charge transfer stages. In the first stage, electron will be redistributed inside each monomer, while in the second stage, electron will be redistributed among the whole molecule. As electron density change relates to the charge transfer between different molecular orbitals, EDD map can give us a clear picture of overall charge transfer. In the following figures, section in red color is where electron density increases, while section in blue color is where electron density decreases. In the example of FPH$_2$...NH$_3$, during polarization stage, electrons are concentrated from hydrogen atoms to lone pair of nitrogen atom in monomer NH$_3$. In the fluorophosphine, electrons move toward fluorine atom, and electrons in phosphorus atom are also transferred from NH$_3$ group side to F-P bond region. During charge transfer stage, electron densities around the region of three hydrogen atoms of NH$_3$ still keep decreasing, so does that in lone pair region of nitrogen atom. In fluorophosphine, electron density around fluorine atom also keeps increasing, while around phosphorus atom on the side near NH$_3$, electron density increases during charge transfer stage. Roughly, electrons are transferred from NH$_3$ to fluorine atom during the formation of pnicogen bond.
A series of $X_nPH_3\ldotsNH_3$ complexes has been studied in our research. Their geometries were optimized under MP2/aug-cc-pVDZ level of theory. BLW energy decomposition was achieved by our modified version of quantum mechanical software GAMESS at the DFT(wB97x-D)/cc-pVTZ level. Grimme’s dispersion correction was applied in calculation, in order to better describe pnicogen bond interaction. The change of dispersion energy is calculated by subtracting all the monomers’ dispersion energy from dimer’s dispersion energy:

$$\Delta E_c = E_{\text{DFT}}^{\text{disp}} - \sum_{i=1}^{k} E_i^{\text{disp}}$$

Electron density difference was calculated by Mulitiwfn, and the figures were drawn by GaussView software. In the orbital correlation diagram, the pictures of corresponding molecular orbitals were obtained from MacMolPlt, and the whole figures were completed by both Excel and ChemBiodraw.
After optimization, we have got the structures of 15 pnicogen-bond complexes. In the complexes CH₃PH₂...NH₃ and PH₃...NH₅, which don't have the electron withdrawing substituent, the lone pair of NH₃ points to the middle region between two phosphine’s hydrogen atoms. While for other complexes, the lone pair of NH₃ roughly
points to the σ-hole region near phosphorus atom. σ-hole is formed due to the existence of electron withdrawing substituent. Pnicogen bond angles are represented by the bond angle r(X-P...N). A collection of pnicogen bond angles in 15 complexes are listed in Table 1. The bond angles are around 165 degree, especially for relatively strong pnicogen bonds.

Table 1:. Structure description of 15 pnicogen- bond complexes

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>R_PN</th>
<th>r(X-P...N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BrPH₂</td>
<td>2.709</td>
<td>166.6</td>
</tr>
<tr>
<td>CF₃PH₂</td>
<td>3.034</td>
<td>162.1</td>
</tr>
<tr>
<td>CH₃PH₂</td>
<td>3.320</td>
<td>172.2</td>
</tr>
<tr>
<td>Cl₂PH</td>
<td>2.748</td>
<td>168.0</td>
</tr>
<tr>
<td>Cl₃P</td>
<td>2.769</td>
<td>177.3</td>
</tr>
<tr>
<td>ClPH₂</td>
<td>2.694</td>
<td>166.9</td>
</tr>
<tr>
<td>(CN)₂PH</td>
<td>2.860</td>
<td>163.0</td>
</tr>
<tr>
<td>(CN)₃P</td>
<td>2.735</td>
<td>164.8</td>
</tr>
<tr>
<td>CNPH₂</td>
<td>2.988</td>
<td>163.4</td>
</tr>
<tr>
<td>F₂PH</td>
<td>2.697</td>
<td>165.8</td>
</tr>
<tr>
<td>F₃P</td>
<td>2.780</td>
<td>168.5</td>
</tr>
<tr>
<td>FPH₂</td>
<td>2.624</td>
<td>167.2</td>
</tr>
<tr>
<td>NO₂PH₂</td>
<td>2.645</td>
<td>165.0</td>
</tr>
<tr>
<td>OHPH₂</td>
<td>2.870</td>
<td>165.8</td>
</tr>
<tr>
<td>PH₃</td>
<td>3.302</td>
<td>167.6</td>
</tr>
</tbody>
</table>

Energy decomposition analysis and trend of binding energy trend

Calculation results are listed in Table 2. Deformation energy indicates how much the energy cost is when the structure changes from optimum one to well-prepared monomer one. Large value in this term represents large structure change in this
process. According to those data, the structure of NH₃ does not change too much in this process. Deformation energy terms of NH₃ are usually around 0.01 kcal/mol. The largest deformation energy of NH₃ occurs when it interacts with (CN)₃P and they form the complex (CN)₃P...NH₃ (0.04 kcal/mol), which is also the strongest pnicogen bond among all complexes studied in this research. Among the phosphine monomers, deformation energy terms range from 0.02 kcal/mol to 1.6 kcal/mol. It is more notable than that of ammonia, thus the deformation energy of phosphines dominates the total deformation energy.

Table 2: Result of BLW energy decomposition analysis (phosphines are Lewis acid and NH₃ is Lewis base. The unit of energy terms is kcal/mol, and unit of bond length is Å.)

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>ΔE_{def}^P</th>
<th>ΔE_{def}^N</th>
<th>ΔE_{HL}</th>
<th>ΔE_{pol}</th>
<th>ΔE_{ct}</th>
<th>ΔE_c</th>
<th>ΔE_b</th>
<th>R_{PN}</th>
</tr>
</thead>
<tbody>
<tr>
<td>BrPH₂</td>
<td>0.78</td>
<td>0.01</td>
<td>1.11</td>
<td>-2.33</td>
<td>-4.07</td>
<td>-0.93</td>
<td>-5.45</td>
<td>2.709</td>
</tr>
<tr>
<td>CF₃PH₂</td>
<td>0.27</td>
<td>0.01</td>
<td>-1.30</td>
<td>-0.91</td>
<td>-1.14</td>
<td>-0.80</td>
<td>-3.88</td>
<td>3.034</td>
</tr>
<tr>
<td>CH₃PH₂</td>
<td>0.00</td>
<td>0.01</td>
<td>-0.13</td>
<td>-0.24</td>
<td>-0.39</td>
<td>-0.72</td>
<td>-1.47</td>
<td>3.320</td>
</tr>
<tr>
<td>Cl₂PH</td>
<td>1.16</td>
<td>0.02</td>
<td>1.19</td>
<td>-2.37</td>
<td>-3.84</td>
<td>-1.11</td>
<td>-4.95</td>
<td>2.748</td>
</tr>
<tr>
<td>Cl₃P</td>
<td>1.33</td>
<td>0.02</td>
<td>2.50</td>
<td>-2.46</td>
<td>-3.89</td>
<td>-1.29</td>
<td>-3.77</td>
<td>2.769</td>
</tr>
<tr>
<td>CIPH₂</td>
<td>0.92</td>
<td>0.01</td>
<td>0.78</td>
<td>-2.34</td>
<td>-4.18</td>
<td>-0.92</td>
<td>-5.73</td>
<td>2.694</td>
</tr>
<tr>
<td>(CN)₂PH₂</td>
<td>0.57</td>
<td>0.03</td>
<td>-2.17</td>
<td>-2.10</td>
<td>-2.88</td>
<td>-1.28</td>
<td>-7.83</td>
<td>2.860</td>
</tr>
<tr>
<td>(CN)₃P</td>
<td>0.64</td>
<td>0.04</td>
<td>-0.86</td>
<td>-3.46</td>
<td>-5.16</td>
<td>-1.68</td>
<td>-10.47</td>
<td>2.735</td>
</tr>
<tr>
<td>CNPH₂</td>
<td>0.25</td>
<td>0.01</td>
<td>-2.06</td>
<td>-1.06</td>
<td>-1.33</td>
<td>-0.81</td>
<td>-5.00</td>
<td>2.988</td>
</tr>
<tr>
<td>F₂PH</td>
<td>1.53</td>
<td>0.01</td>
<td>0.33</td>
<td>-2.28</td>
<td>-4.07</td>
<td>-1.01</td>
<td>-5.48</td>
<td>2.697</td>
</tr>
<tr>
<td>F₂P</td>
<td>1.60</td>
<td>0.01</td>
<td>0.19</td>
<td>-1.88</td>
<td>-3.19</td>
<td>-1.08</td>
<td>-4.35</td>
<td>2.780</td>
</tr>
<tr>
<td>FPH₂</td>
<td>1.13</td>
<td>0.00</td>
<td>0.91</td>
<td>-2.62</td>
<td>-4.87</td>
<td>-0.92</td>
<td>-6.37</td>
<td>2.624</td>
</tr>
<tr>
<td>NO₂PH₂</td>
<td>0.84</td>
<td>0.01</td>
<td>0.48</td>
<td>-3.05</td>
<td>-4.94</td>
<td>-0.94</td>
<td>-7.60</td>
<td>2.645</td>
</tr>
<tr>
<td>OHPH₂</td>
<td>0.49</td>
<td>0.00</td>
<td>-0.23</td>
<td>-1.19</td>
<td>-1.95</td>
<td>-0.85</td>
<td>-3.74</td>
<td>2.870</td>
</tr>
<tr>
<td>PH₃</td>
<td>0.02</td>
<td>0.01</td>
<td>-0.32</td>
<td>-0.27</td>
<td>-0.40</td>
<td>-0.67</td>
<td>-1.63</td>
<td>3.302</td>
</tr>
</tbody>
</table>

Heitler-London energy (ΔE_{HL}) term represents the electrostatic interaction.
Unlike in halogen bond, where electrostatic energy terms play a key role in the formation of halogen-bond complex\textsuperscript{92}, the roles of electrostatic interaction in pnicogen-bond complexes are not uniform in our study. Electrostatic energy terms can be either positive value or negative value, which means they can either help to stabilize pnicogen bond or perform the counteraction. While on the other hand, the absolute value of $\Delta E_{\text{H-L}}$ is usually not larger than polarization energy and charge transfer energy. These results imply the fact that electrostatic interaction does not contribute too much to the formation of pnicogen bond.

In pnicogen bond, polarization energy and charge transfer energy are the most important energy components. High polarization energy is usually accompanied by high charge transfer energy. This phenomenon is reasonable, as polarization process is the charge redistribution inside the monomer when it is affected by the electric field which is generated by adjacent monomers, and charge transfer process is the charge redistribution in the whole complex. These two processes have intrinsic relationship.

In mono-substituted phosphine, the strength of pnicogen bonds is largely affected by the electron withdrawing ability of substituent. When hydrogen atom in phosphine is substituted by more electronegative groups, the pnicogen bond will be strengthened, and the total binding energy will increase, along with relatively larger polarization energy terms and charge transfer energy terms. But in multi-substituted phosphine, things are quite different. We will discuss it in the following chapters. When more than one hydrogen in phosphine are substituted by electron withdrawing group, the total binding energy can either increase or decrease.
DISCUSSION OF MONO-SUBSTITUTED PHOSPHINES

We studied a series of mono-substituted phosphines, the general form of the target mono-substituted phosphines is XPH₂, with X= CH₃, OH, CF₃, CN, Br, Cl, F. and NO₂. NH₃ is the Lewis base. The results, similar to the one from Scheiner, are listed in Table 3. As we have showed before, the deformation of phosphines is the major cause of deformation energy. When the bond length between P and N in the dimer is less than 2.8 Å, the Heitler-London energy is positive. For complexes in which the bond length is longer than 2.8 Å, the Heitler-London energy is negative. This result implies that electrostatic interaction can be attractive when the distance between monomers is large, and repulsive when the distance between monomers is small, with the transition point standing at around 2.8 Å. Among halogenated phosphines, the polarization energy and charge transfer energy decrease from F to Br, resulting in a decrease in the total binding energy.

Table 3: Result of BLW energy decomposition analysis for mono-substituted phosphine series of complexes (unit of energy terms is kcal/mol, and unit of bond length is Å.)

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>( R_{PN} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃PH₂</td>
<td>0.01</td>
</tr>
<tr>
<td>PH₃</td>
<td>0.03</td>
</tr>
<tr>
<td>CF₃PH₂</td>
<td>0.28</td>
</tr>
<tr>
<td>CNPH₂</td>
<td>0.26</td>
</tr>
<tr>
<td>HOPH₂</td>
<td>0.49</td>
</tr>
<tr>
<td>BrPH₂</td>
<td>0.79</td>
</tr>
<tr>
<td>ClPH₂</td>
<td>0.93</td>
</tr>
<tr>
<td>NO₂PH₂</td>
<td>0.85</td>
</tr>
<tr>
<td>FPH₂</td>
<td>1.13</td>
</tr>
</tbody>
</table>

Roughly, binding energy increases linearly along with the decrease in bond
length. More electronegativity groups can lead to a stronger pnicogen bond, while less electronegativity groups will lead to a weaker pnicogen bond. According to the Figure 4, some substituents make the relationship between bond length and binding energy in complexes deviate from the line. Hydroxyl substitution makes the complex’s binding energy relatively lower than that of its neighbor, under the regression line. On the other side of the regression line, cyano and nitro substitutions make the pnicogen bond have relatively higher binding energy than the neighbor. This phenomenon indicates different binding patterns of those deviating points.

Figure 4: Relationship between bond length and binding energy of mono-substituted phosphines-ammonia complexes.

Hydroxyl-substituted phosphine

For hydroxyl substituent, the binding energy is obviously lower than its neighbor. Energy decomposition analysis indicates the deformation energy is relatively higher than nearby complexes. During the complex formation process, geometric distortion is a preparation for the following steps, namely, polarization and charge transfer. Roughly, deformation energy ($\Delta E_{\text{def}}$) should corresponding to $\Delta E_{\text{pol}}$ and $\Delta E_{\text{ct}}$. In order to explore the reason, we checked the structure of HOPH₂, and found that this phenomenon can account for the existence of intramolecular hydrogen bond between
one hydrogen atom and the lone pair of phosphorus atom. In equilibrium configuration, the bond angle between P-O and O-H is 107.43° (P-O-H=107.43°), while in the distorted geometry of monomer, the bond angel narrows to 107.34°, indicating that the hydrogen bond is strengthened after charge transfer stage.

Table 4: HOMO-LUMO energy gap of mono-substituted phosphines in BLW state and DFT state.

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>BLW</th>
<th></th>
<th></th>
<th>DFT</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HOMO</td>
<td>LUMO</td>
<td>gap</td>
<td>HOMO</td>
<td>LUMO</td>
<td>gap</td>
</tr>
<tr>
<td>CH₃PH₂</td>
<td>-0.350</td>
<td>0.090</td>
<td>11.97</td>
<td>-0.352</td>
<td>0.090</td>
<td>12.03</td>
</tr>
<tr>
<td>PH₃</td>
<td>-0.354</td>
<td>0.107</td>
<td>12.54</td>
<td>-0.359</td>
<td>0.096</td>
<td>12.38</td>
</tr>
<tr>
<td>CF₃PH₂</td>
<td>-0.376</td>
<td>0.084</td>
<td>12.52</td>
<td>-0.384</td>
<td>0.081</td>
<td>12.65</td>
</tr>
<tr>
<td>CNPH₂</td>
<td>-0.384</td>
<td>0.069</td>
<td>12.33</td>
<td>-0.388</td>
<td>0.077</td>
<td>12.65</td>
</tr>
<tr>
<td>HOPH₂</td>
<td>-0.370</td>
<td>0.088</td>
<td>12.46</td>
<td>-0.376</td>
<td>0.083</td>
<td>12.49</td>
</tr>
<tr>
<td>BrPH₂</td>
<td>-0.387</td>
<td>0.045</td>
<td>11.76</td>
<td>-0.409</td>
<td>0.043</td>
<td>12.30</td>
</tr>
<tr>
<td>ClPH₂</td>
<td>-0.388</td>
<td>0.063</td>
<td>12.27</td>
<td>-0.417</td>
<td>0.069</td>
<td>13.22</td>
</tr>
<tr>
<td>NO₂PH₂</td>
<td>-0.402</td>
<td>0.007</td>
<td>11.13</td>
<td>-0.422</td>
<td>0.012</td>
<td>11.81</td>
</tr>
<tr>
<td>FPH₂</td>
<td>-0.389</td>
<td>0.091</td>
<td>13.06</td>
<td>-0.395</td>
<td>0.099</td>
<td>13.44</td>
</tr>
</tbody>
</table>

In order to further demonstrate the existence of intramolecular hydrogen bond, we also obtained the HOMO-LUMO gaps of the electron-localized diabatic state of mono-substituted phosphines, and listed the results in Table 4. By examining the data, we can find that the HOMO-LUMO gap of electron-localized diabatic state of phosphinous acid (12.46 eV) is high and close to that of (trifluoromethyl) phosphine (12.52 eV), much higher than that of nearby bromophosphine (11.76 eV). Thus the electron transfer ability of phosphinous acid can be poorer than expected. The likely structure and position of intramolecular hydrogen bond are shown in Figure 5.
Nitro-substituted phosphine

The interaction between nitrophosphine and ammonia, which has the highest binding energy as shown in Table 3, also can give us some clues. The relatively higher binding energy shows high electron transfer stability of nitrophosphine. It also can be justified in the HOMO-LUMO energy gap table, the HOMO-LUMO gap of nitrophosphine is the lowest with a value of 11.13eV. On the other hand, the pnicogen bond length in complex NO$_2$PH$_2$...NH$_3$ is between the length of the pnicogen bond in FPH$_2$...NH$_3$ and that in ClPH$_2$...NH$_3$, but its Heitler-London energy (0.48 kcal/mol) is lower, and its polarization energy and charge transfer energy are higher, than both of the other two neighbors.

To find out the reason why NO$_2$PH$_2$...NH$_3$ behaves differently from others, we made the orbital correlation diagram and checked the change of molecular orbital during the formation of NO$_2$PH$_2$...NH$_3$, and discovered a new way of charge transfer in this complex other than charge transfer from nitrogen n$_{lp}$ to d$\pi^*$ orbital. This new pathway is the charge transfer from nitrogen n$_{lp}$ to d orbital. d orbital is formed by overlap of d orbital of phosphorus with $\pi^*$ orbital on nitro group. Comparing to FPH$_2$...NH$_3$, whose LUMO is $\sigma^*$ bond, the d$\pi^*$ orbital on NO$_2$PH$_2$ has a lower energy level than $\sigma^*$ orbital and acts as LUMO in this molecule. In all, there are two unoccupied MOs in nitrophosphine which can interact with HOMO of NH$_3$. Thus in this complex, the electrons from the lone pair of NH$_3$ can transfer to both $\sigma^*$ and d$\pi^*$ orbitals of nitrophosphine, HOMO-LUMO energy gap in this BLW state dimer is 11.13 eV. The much lower energy gap makes the electron transfer energy barrier easy.
to overcome. More MOs involved in charge transfer give nitrophosphine a larger electron transfer capability or higher charge transfer stability. These two factors work together and finally make $\text{NO}_2\text{PH}_2...\text{NH}_3$ have a strong pnicogen bond and bond strength/bond length ratio.

Figure 6: Orbital correlation diagram and change of molecular orbital’s energy in the formation of $\text{NO}_2\text{PH}_2...\text{NH}_3$ complex. BL- and d- denote the block-localized and deformed monomers. Unit of the energy level value is hartree.

In the EDD map, during the polarization stage, electrons in nitrophosphine are moving from the right side of phosphorus atom to nitro group. In ammonia part, electrons are concentrated in the lone pair region. During the charge transfer stage, electron move mainly occurs in the pnicogen bond region between the nitrogen atom and the phosphorus atom, leading to an increase in electron density in the $\sigma$-hole region.
Figure 7: Electron density change in polarization stage (a) and charge transfer stage (b) in NO$_2$PH$_2$...NH$_3$ complex (contour isodensity value=0.0004 a.u.). Red color represents gain in electron density and blue color represents loss of electron density.

Cyano-substituted phosphine

Figure 8: Orbital correlation diagram and change of molecular orbital’s energy in the formation of CNPH$_2$...NH$_3$ complex. BL- and d- denote the block-localized and deformed monomers. Unit of the energy level value is hartree.

Similar binding pattern is also found in CNPH$_2$...NH$_3$. Those data in Table 3 shows that the Heitler-London energy term is a considerable one in total binding energy of cyanide-ammonia dimer, which means there is considerable electrostatic attraction between CNPH$_2$ and NH$_3$. Still the charge transfer energy and polarization energy dominated the pnicogen bond. Figure 8 is the orbital correlation diagram of
CNPH$_2$...NH$_3$, and charge transfer from the lone pair of nitrogen n$_{lp}$ to $\sigma^*(C-P)$ can also be found. The d$\pi^*$ orbital in cyano-substituted phosphines is formed by the combination of $\pi^*$ antibonding orbital in cyano group and d orbital in phosphorus atom. During the charge transfer stage, $\sigma^*(C-P)$ energy level increases drastically, indicating that it is a poor electron acceptor. Energy gap of the BLW state is 12.33 eV.

EDD maps for both the polarization process and electron transfer process are shown in Figure 9. Similar to the situation in the EDD map of nitrophosphine-ammonia complex showed above, electrons are moving across each monomer during the polarization stage, and moving mainly in pnicogen bond region in charge transfer stage. A notable character in the electron density change in charge transfer process is that here the charge transfer pattern can be described as from the lone pair on nitrogen to the $\sigma$-hole instead of to antibonding orbital. It is also supported by the considerable Heitler-London energy term in total binding energy.

![Figure 9: Electron density change in polarization stage (a) and charge transfer stage (b) in CNPH$_2$...NH$_3$ complex (contour isodensity value=0.0004 a.u.). Red color represents gain in electron density and blue color represents loss of electron density.](image)

After general survey, a significant finding is that the binding energy of pnicogen bond is dominated by charge transfer and polarization. In phosphine, a complex with a relatively strong pnicogen bond, hydrogen atom is substituted by strong electronegative group, with the binding energy higher than 4 kcal/mol. In these situations, charge transfer energy contributes more than a half of the total binding energy and is further supplemented by polarization effect. Strong binding energy
shortens P-N distance, which also increases repulsive Pauli exchange energy and the cost of deformation energy. EDD maps show the electron transfer during the formation of pnicogen bond. The region with increased electron density during charge transfer period supports the existence of -hole in mono-substituted phosphine.

To further analyze the correlation between charge transfer energy and bond length, we made Figure 10, on which X-axis indicates bond length and y-axis indicates charge transfer energy. This correlation has been discussed—that charge transfer energy decreases exponentially as the distance enlarges\textsuperscript{28,86}. Our results are also consistent with this rule.

![Figure 10](image-url)

Figure 10: Relationship between bond length and charge transfer energy of mono-substituted phosphines-ammonia complexes.
DISCUSSION OF MULTI-SUBSTITUTED PHOSPHINES

We also studied the interaction between multi-substituted phosphine, represented by $X_nPH_{3-n}$ (n=1-3, X=F, Cl and CN), and NH$_3$. Actually, multi-substituted phosphines have different chemical properties, one of which is that they can interact with more than one Lewis base. For example, diflorophosphine can interact with two NH$_3$ molecules. In this aspect, diflorophosphine is similar to F$_2$S, which is often used in the study of chalcogen bond. In addition, triflorophosphine can interact with three NH$_3$ molecules. If we study those complexes, the result may be interesting. But in this research, we only focus on the studies of interaction between multi-substituted phosphine and single NH$_3$.

Table 5: Result of BLW energy decomposition analysis for multi-substituted phosphine series of complexes (unit of energy terms is kcal/mol, and unit of bond length is Å.)

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>R$_{PN}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FH$_3$P</td>
<td>2.624</td>
</tr>
<tr>
<td>F$_2$PH</td>
<td>2.697</td>
</tr>
<tr>
<td>F$_3$P</td>
<td>2.780</td>
</tr>
<tr>
<td>ClPH$_2$</td>
<td>2.694</td>
</tr>
<tr>
<td>Cl$_2$PH</td>
<td>2.748</td>
</tr>
<tr>
<td>Cl$_3$P</td>
<td>2.769</td>
</tr>
<tr>
<td>CNH$_3$P</td>
<td>2.988</td>
</tr>
<tr>
<td>(CN)$_2$PH</td>
<td>2.860</td>
</tr>
<tr>
<td>(CN)$_3$P</td>
<td>2.735</td>
</tr>
</tbody>
</table>

In Table 5, all results about series of multi-substituted phosphine are listed. In the previous section, we have shown that more electronegative substituents can increase the binding energy of pnicongen bond. It is reasonable to infer that if more than one hydrogen atom in phosphine is substituted by electronegative group, the
binding energy between phosphine and ammonia shall be stronger, as a result of much positive \( \sigma \)-hole or larger weight of antibonding orbital. But in our research, the results are different from that inference. Multi-halogenation of phosphines will weaken rather than strengthen the pnictogen bond. On the other hand, multi-cyanosubstitution can increase the binding energy.

The electrostatic energy term changes in different trends in three series of complexes. When the substituent group is fluorine, multi-substitution can decrease the repulsive electrostatic interaction, while the other two substituents have the opposite effect. To explain this interesting phenomenon, we will turn back to the EDA method. In the energy decomposition analysis method, the interaction we studied is actually the interaction between two monomers, not only the pnictogen bond between phosphorus and nitrogen atoms. Thus the electrostatic energy term here can be a combination of two kinds of electrostatic interactions. One of them is between phosphorus and nitrogen atoms, and the other can be between nitrogen atom and adjacent substituent. Multi-substitution can lead to a more positive \( \sigma \)-hole region, that is why the repulsive electrostatic interaction will decrease when more fluorines bond with phosphine. For the other two substituents, their radii are larger than fluorine atom, making the repulsive electrostatic interaction between nitrogen and them stronger than that between nitrogen and fluorine. This repulsive effect is strong enough to override the increasing attractive effect which results from more positive \( \sigma \)-hole region. After all, the electrostatic interaction appears more repulsive in these two series of multi-substituted phosphines.

As we have mentioned in the previous section, charge transfer and polarization energy dominate the total binding energy. Table 5 shows a notable increase in charge transfer energy and polarization energy when more cyano substitutes are applied to phosphine, but a decrease in these two energy terms when more fluorine substitutes are applied to phosphine. To reveal the reason, we also drew the orbital correlation diagram for those two systems.
Comparing this orbital correlation diagram with the diagram of FPH$_2$...NH$_3$, it can be found that the antibonding orbital energy level here is higher than that in FPH$_2$.NH$_3$. A recent study of halogen bond shows the tunability of halogen bond, that is, the property of halogen bond can be affected by its adjacent groups. The adjacent electron withdrawing group, like fluorine atom, can lead to an increasing electrostatic interaction and a decreasing polarization interaction among total binding energy$^{92,93}$, when more than one of them get involved. More adjacent electron withdrawing groups can make the $\sigma$-hole more positive, while also weakening the halogen atom polarization ability. It may show clue for explaining the behavior of pnicogen bond in F$_3$P...NH$_3$.

When two more fluorines substitute hydrogen in phosphine, the phosphorus atom also becomes more positive but less polarizable than that in fluorophosphine. It
can account for the result that electrostatic energy value decreases in positive and polarization energy term decreases in negative. Based on above discussion, pnicogen bond is dominated by polarization and charge transfer. Thus the small decrease in repulsive electrostatic interaction is countered by a remarkable decrease in attractive polarization and charge transfer effect, leading to the weakening of the total binding interaction.

In orbital correlation diagram, the poor charge transfer stability is represented by a large energy-level change of $\sigma^*(F-P)$ orbital between BLW state (before charge transfer) and DFT state (after charge transfer)

**Tri-cyano-substituted phosphine**

One of the interesting results comes from the series of cyano-substituted phosphine. In this kind of complexes, more substituents can strengthen the pnicogen bond $[(CN)_3P...NH_3 > (CN)_2PH...NH_3 > CNPH_2...NH_3]$. It is remarkably different from halogenated phosphines. This special trend can be attributed to more $\pi^*$ antibonding involvements in $d\pi^*$ orbital. $d\pi^*$ orbital in $(CN)_3P...NH_3$ complex has lower energy level than $\sigma^*(C-P)$ orbital, and also, $d\pi^*$ orbital is more delocalized, thus having higher electron transfer capacity and stability.

Orbital correlation diagram was developed for this complex, enabling us to see the energy level change of molecular orbitals during polarization and charge transfer stage. All of the three orbitals from cyano group are involved in the formation of $d\pi^*$ orbital, and the energy gap between $n_{lp}$ and $d$ is smaller than pervious complexes. Both $d\pi^*$ and $\sigma^*$ (which is similar to that in $CHPH_2...NH_3$) orbitals are assisted by $\pi^*(C-N)$ (which is in the other two substituents), making them have lower energy level, as these two antibonding orbitals can expand to more atoms. The map also shows energy gap between these orbitals: the energy gaps are 0.399 a.u. and 0.432 a.u.. The
HOMO-LUMO gap between two BLW state monomers is the lowest, making it the highest binding energy in this article. During the charger transfer process, the energy level of $d\pi^*$ only changes by 0.004 a.u. (from -0.006 a.u. to -0.002 a.u.), which also shows the high charger transfer stability of $d\pi^*$ orbital in (CN)$_3$P.

The EDD map of (CN)$_3$P...NH$_3$ gives us a clear picture about charge transfer. The shape of EDD surface looks like a combination of the shapes of three orbitals in cyano group and d orbitals in phosphorus atom. Electrons are transferred from ammonia to all three cyano groups. It also shows us the function of $\pi^*$ (C-N) orbital to help stabilize the complex. Polarization and charge transfer in this complex are more drastic as a result of its high binding energy. The EDD map of charge transfer stage also shows a great increase in electron density in $\sigma$-hole region and supports the $\sigma$-hole theory.
Figure 13: Electron density change in polarization stage (a) and charge transfer stage (b) in (CN)$_3$P...NH$_3$ complex (contour isodensity value=0.0004 a.u.). Red color represents gain in electron density and blue color represents loss of electron density.

Table 6: HOMO-LUMO energy gap of multi-substituted phosphines in BLW state and DFT state.

| Phosphine | BLW | | DFT | | 
| --- | --- | --- | --- | --- | --- |
|  | HOMO | LUMO | gap | HOMO | LUMO | gap |
| FH$_2$P | -0.389 | 0.091 | 13.06 | -0.395 | 0.099 | 13.44 |
| F$_2$PH | -0.384 | 0.065 | 12.21 | -0.393 | 0.065 | 12.46 |
| F$_3$P | -0.379 | 0.087 | 12.68 | -0.418 | 0.109 | 14.34 |
| ClPH$_2$ | -0.388 | 0.063 | 12.27 | -0.417 | 0.069 | 13.22 |
| Cl$_2$PH | -0.383 | 0.022 | 11.02 | -0.403 | 0.049 | 12.30 |
| Cl$_3$P | -0.379 | 0.017 | 10.78 | -0.404 | 0.040 | 12.08 |
| CNPH$_2$ | -0.384 | 0.069 | 12.33 | -0.388 | 0.077 | 12.65 |
| (CN)$_2$PH | -0.394 | 0.033 | 11.62 | -0.403 | 0.035 | 11.92 |
| (CN)$_3$P | -0.405 | -0.006 | 10.86 | -0.421 | -0.002 | 11.40 |

To better explain the multi-substitution effects on phosphine, we listed HOMO-LUMO energy gap for these multi-substituted phosphines. In this table, (CN)$_3$P has not only the lowest energy gap, but also the strongest electron transfer stability. In other words, the difference in energy gap between BLW state (before charge transfer) and DFT state (after charge transfer) is the smallest, only 0.54eV,
while for $\text{F}_3\text{P}$, HOMO-LUMO energy gap change is 1.66eV. Thus for cyano substituted phosphine, the fact that more molecular orbitals are involved in the formation can both decrease the HOMO-LUMO energy gap and increase the electron transfer capability, leading to the strongest pnicogen bond in this research.
CONCLUSION

Pnicogen bonds are the non-covalent interactions between Group VA atoms, which act as Lewis acid, and Lewis base. Studies have revealed that electrostatic interaction is dominant in some other similar non-covalent interactions, like hydrogen bond and halogen bond. Although this kind of non-covalent interactions look similar to halogen bonds and the σ-hole region can also be found in many substituted phosphines, our BLW energy decomposition analysis shows that pnicogen bond energy is dominated by polarization energy and charge transfer energy. Electrostatic interaction term here may be a combination of two kinds of intermolecular electrostatic interactions, which makes its trend not so clear.

Orbital correlation diagram is a useful tool, which can help us understand the charge transfer process. By examining the correlations between molecular orbitals during charge transfer process, a new kind of charge transfer way has been identified, that is, n→dπ* hyperconjugation. dπ* hyperconjugation is formed by the interaction between d orbital of phosphorus atom and π* antibonding orbital of conjugate substituent. Thus d orbital have lower energy level than σ* orbital. Other than the well-recognized n to σ*(X-P) hyperconjugation, which is the LUMO in most mono-substituted phosphines XPH₂, when nitro or cyano group works as substituent, d will be formed by π* orbital in substituents and d orbital in pnicogen atoms and then works as LUMO. By the assistance of d orbital, these kinds of pnicogen bonds can be stronger than others. Also, the strong electron transfer effect in pnicogen bond results in its high degree of anisotropy.

HOMO-LUMO energy gap and the difference in energy gap between BLW state and DFT state also help us reveal the nature of pnicogen bond. Energy gap will increase when monomers get more electrons. Thus charge transfer energy can be decided by energy gap value, which indicates the energy barrier during charge transfers process, and the change of energy gap in this step, which represents the
charge transfer stability.

By applying BLW energy decomposition analysis method, we can divide the total binding energy to different energy terms, and the polarization effects and charge transfer effect can be visualized on electron density difference (EDD) maps. The explanation that the formation of pnicogen bond is the charge transfer from lone pair of ammonia to $s^*$ or d antibonding orbital is oversimplified. In EDD map of the charge transfer process, the electron density only increases at one side of phosphorus atom which is the pnicogen bond region adjacent to phosphorus atom. This picture is consistent with $\sigma$-hole theory.
REFERENCES


(9) Politzer, P.; Lane, P.; Concha, M. C.; Ma, Y.; Murray, J. S. J. Mol. Model. 2007, 13, 305.


