# Investigation of the Substituent Effects on -Type Pnicogen Bond Interaction (Postprint)

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## Abstract

Intermolecular interactions between PH2Cl and Ar–R (R = H, OH, NH2, CH3, Br, Cl, F, CN, NO2) were calculated by using MP2/aug-cc-pVDZ quantum chemical method. It has been shown from our calculations that the aromatic rings with electron-withdrawing groups represent much weaker binding affinities than those with electron-donating groups. The charge-transfer interaction between PH2Cl and Ar–R plays an important role in the formation of pnicogen bond complexes, as revealed by NBO analysis. Nevertheless, AIM analysis shows that the nature of the interactions between PH2Cl and Ar–R is electrostatic, and the interaction energies of the complexes are correlated positively with the electron densities in the bond critical points (BCPs). RDG/ELF graphical analyses were performed to visualize the positions and strengths of the pnicogen bonding, as well as the spatial change of the electron localization upon the formation of complexes. The -type halogen bond was also calculated, and it has been revealed that the -type pnicogen bond systems are more stable than the halogen bond ones.

## Full Text

## Preamble

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## ABSTRACT

Intermolecular interactions between PH Cl and Ar–R (R = H, OH, NH , CH , Br, Cl, F, CN, NO ) were calculated using the MP2/aug-cc-pVDZ quantum chemical method. Our calculations demonstrate that aromatic rings bearing electron-withdrawing groups exhibit significantly weaker binding affinities than those with electron-donating groups. NBO analysis reveals that charge-transfer interaction between PH Cl and Ar–R plays an important role in the formation of pnicogen bond complexes. Nevertheless, AIM analysis shows that the nature of the interactions between PH Cl and Ar–R is electrostatic, and the interaction energies of the complexes correlate positively with the electron densities at the bond critical points (BCPs).

RDG/ELF graphical analyses were performed to visualize the positions and strengths of pnicogen bonding, as well as the spatial changes in electron localization upon complex formation. The  -type halogen bond was also calculated, revealing that  -type pnicogen bond systems are more stable than their halogen bond counterparts.

**Keywords:**  -type pnicogen bonding;  -type halogen bonding; NBO; AIM; RDG/ELF analysis

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## 1. INTRODUCTION

Molecular interactions, which are closely correlated with various physicochemical properties, life phenomena, and material structures, have been of great interest in physics, chemistry, biology, materials science, and other fields [1-5]. The hydrogen bond interaction represents a typical molecular interaction [6], followed by the discovery of halogen bonds [7], lithium bonds [8], and other weak interactions. In 2009, Hey-Hawkins et al. [9] demonstrated the existence of P··· P non-bonded interactions via $^{13}\mathrm{C}\{^{1}\mathrm{H},^{31}\mathrm{P}\}$ NMR experiments. Scheiner [10-15] theoretically calculated the geometrical structures and interaction energies of a series of pnicogen bond systems including P···P, N···P, etc. Since then, research on pnicogen bond interactions has attracted considerable attention from theoretical and experimental chemists [16-20].

Recently, Zukerman-Schepector et al. [21] emphatically discussed the As··· interaction in supramolecular systems, identifying 20 structures involving As··· interactions from the Cambridge Structural Database (CSD) and highlighting the importance of As···  interactions in supramolecular construction. Building upon this work, Frontera' s group [22] calculated the interactions between

ECl (E = As, Sb, Bi) and -electron donors (e.g., benzene, hexafluorobenzene), exploring the significance of -type pnicogen bonds in life sciences. PH is the simplest pnicogen-bond donor molecule, exhibiting weak pnicogen bond interactions. However, when one hydrogen atom is replaced by a chlorine atom (PH Cl), the P $\cdots$ N pnicogen bonding interaction formed between PH Cl and the representative electron donor NH even exceeds the hydrogen bond interaction between water molecules [23]. Consequently, PH Cl is frequently employed as a model molecule in pnicogen bond research [24,25].

In this paper, we calculate the interactions between PH Cl and substituted benzenes (Ar–R, where R = H, OH, NH , CH , Br, Cl, F, CN, NO ) using quantum chemical methods to explore the geometrical structure, electronic structure, and interaction energy of -type pnicogen bonds between PH Cl and aromatic compounds. Furthermore, we examine the effects of substituents on the aromatic ring on the stability of -type pnicogen bond complexes to provide a theoretical basis for understanding the nature of -type pnicogen bonds.

## 2. COMPUTATIONAL METHODS

All structure optimizations and energy calculations were performed using the Gaussian 03 program package [26]. Given the importance of electron correlation for accurately describing interaction energies, structure optimizations of all monomers and complexes were carried out at the MP2 level with the aug-cc-pVDZ basis set, without any symmetry constraints. This method has been proven applicable for pnicogen bond interaction studies [27,28].

The interaction energy (ΔE_int) was obtained by subtracting the sum of two monomer energies from the complex energy, and was corrected for basis set superposition error (BSSE) using the counterpoise (CP) procedure [29] to yield the corrected interaction energy (ΔE_int^CP). To further investigate the geometric and electronic properties of the complex systems, second-order perturbation stabilization energies ($\Delta E^2$) and charge transfer quantities were calculated using the NBO program within Gaussian 03. Meanwhile, topological properties at bond critical points (BCPs) were calculated using the AIM 2000 program, and reduced density gradient (RDG) and electron localization function (ELF) analyses were performed using the Multiwfn software developed by Lu et al. [30].

## 3. RESULTS AND DISCUSSION

### 3.1 Geometrical Structure and Interaction Energy

Stable structures of complexes formed between PH Cl and substituted aromatic compounds were obtained at the MP2/aug-cc-pVDZ level, with geometrical structures shown in Fig. 1 [Figure 1: see original paper].

As evident from these structures, pnicogen bond interactions are generated between the P atom in PH Cl and the -electrons of the aromatic ring. Following our previous definitions [31], the  angle is defined as the angle between the vector from the P atom to the aromatic ring centroid and the P–Cl bond direction (see Fig. 2 [Figure 2: see original paper]). The  values for complexes 1-9 are presented in Table 1 . The  angles for eight complexes are approximately 180°, indicating that the Cl, P, and centroid atoms are nearly collinear. The optimization result for complex 3 shows that one hydrogen atom (H17) in PH Cl is also close to the aromatic ring center, forming a -type hydrogen bond interaction between the PH Cl hydrogen atom and the aromatic -electrons, which causes the decrease in the  angle due to interference from the P(15)-H(17) ⋯  interaction.

The uncorrected interaction energies (ΔE_int) and BSSE-corrected interaction energies (ΔE_int^CP) for the complexes at the MP2/aug-cc-pVDZ level are listed in Table 1. The differences between ΔE_int and ΔE_int^CP range from 2.7 to 3.5 kcal · mol $^{1}$, demonstrating that BSSE correction is necessary for -type pnicogen bond systems. Complex 1, formed between PH Cl and unsubstituted benzene, has a corrected interaction energy of -3.81 kcal · mol $^{1}$. Complexes 2 and 3, bearing electron-donating -OH and -NH substituents, exhibit corrected interaction energies of –7.56 and –9.65 kcal · mol $^{1}$, respectively, which are substantially larger than that of complex 1. These electron-donating groups increase the -electron density in the benzene ring, leading to stronger interactions between PH Cl and the -electrons, greater interaction energies, and more stable complexes. The electron-donating capacity of the -CH group is weaker than that of -OH and -NH , resulting in a smaller interaction energy for complex 4 compared to complexes 2 and 3.

Complexes 7–9, containing electron-withdrawing groups -F, -CN, and -NO , show corrected interaction energies of -3.55, -3.44, and -3.45 kcal · mol $^{1}$, respectively, which are smaller than that of complex 1, indicating reduced stability. This occurs because electron-withdrawing groups decrease the -electron density in the benzene ring, weakening the interaction between P and the -electrons. Notably, complexes 5 and 6, bearing -Br and -Cl substituents, are electron-withdrawing groups but exhibit slightly larger interaction energies than complex 1. This may be attributed to weak hydrogen bond interactions between hydrogen atoms in PH Cl and the halogen atoms of the substituents, as clearly visible in the geometrical structures and confirmed by subsequent NBO analysis.

Halogen bonds represent interactions between electron donors and halogen atoms in halogenated molecules. Discovered earlier than pnicogen bonds, halogen bond research is more mature. In our current system, while -type pnicogen bond interactions can form between PH Cl and aromatic compounds, -type halogen bond complexes can also form between the -electrons of the aromatic ring and the Cl atom in PH Cl. For comparison, molecular structures of nine typical halogen bond complexes were optimized at the MP2/aug-cc-pVDZ level, and their BSSE-corrected interaction energies (ΔE_XB^CP) are presented in Table 1. Comparison of the corrected interaction energies reveals that -type pnicogen bond systems are more stable than the corresponding -type halogen bond systems. This arises from the uneven distribution of positive electrostatic potential in PH Cl, where the positive electrostatic potential at the -hole of the P atom is larger than that at the -hole of the Cl atom when interacting with the same aromatic -electron donor. Representative structures of two halogen bond complexes are shown in Fig. 3 [Figure 3: see original paper].

### 3.2 NBO Analysis

Table 2 presents the donor-acceptor orbitals, second-order perturbation stabilization energies (ΔE²), and charge transfer quantities (Q_CT) for the nine -type pnicogen bond complexes at the MP2/aug-cc-pVTZ level. The second-order perturbation stabilization energy can be obtained from the equation:

$$\Delta E^2 = \Delta E_{ij} = \frac{q_i F_{ij}^2}{\epsilon_j - \epsilon_i}$$

where $q_i$ is the donor orbital occupancy, $\epsilon_i$ and $\epsilon_j$ are diagonal elements (orbital energies), and $F_{ij}$ is the NBO Fock matrix element.

NBO analysis of complexes 1-9 reveals that pnicogen bonding interactions primarily involve the interaction between C-C bonding orbitals and the * anti-bonding orbital of P-Cl in PH Cl monomer. Complexes 3, 5, and 6 additionally involve hydrogen bond interactions. The second-order perturbation stabilization energy values indicate that pnicogen bond interactions, followed by hydrogen bond interactions, play key roles in complex stability. The presence of supportive hydrogen bond interactions explains why complexes 5 and 6 have higher interaction energies than complex 1, and why the angle is smaller in complex 3.

Based on the data in Table 2, the correlation between the second-order perturbation stabilization energy of the C-C bonding orbital and the * anti-bonding orbital of P-Cl and the corrected interaction energy is plotted in Fig. 4(a) [Figure 4: see original paper], yielding the following relationship after fitting:

$$\Delta E_{int}^{CP} = -37.0697 + 21.5691\Delta E^2 - 3.46391(\Delta E^2)^2$$
$$R = 0.956, \mathrm{SD} = 0.527, N = 9$$

The curve in Fig. 4(a) demonstrates a bivariate functional relationship between the second-order perturbation stabilization energy (ΔE²) and the corrected interaction energy (ΔE_int^CP), rather than a traditional linear relationship, highlighting the contribution of pnicogen bond interactions to complex stability. Considering hydrogen bond interactions in three complexes, the combined second-order perturbation stabilization energy (ΔE²) from both -type pnicogen bond and hydrogen bond interactions was correlated with the corrected interaction energy, as shown in Fig. 4(b) [Figure 4: see original paper]. The correlation coefficient (R) of 0.924 indicates that the combined $\Delta E^2$ is linearly related to the interaction energy, demonstrating that weak interaction second-order perturbation stabilization energy is positively correlated with complex stability.

Molecular interactions are always accompanied by charge transfer. The charge transfer quantities for complexes 1-9 are shown in Table 2. Charge transfer from the aromatic compound to PH Cl ranges from 6 to 16 me. These modest charge transfer quantities comply with the soft acid-soft base model (PH Cl as the soft acid and the aromatic compound as the soft base). The relationship between charge transfer quantity and corrected interaction energy is plotted in Fig. 5 [Figure 5: see original paper], yielding the following equation:

$$\Delta E_{int}^{CP} = -11.215 + 1852.819 Q_{CT} - 106824.298 (Q_{CT})^2$$
$$R = 0.954, \mathrm{SD} = 0.540, N = 9$$

Fig. 5 shows that charge transfer quantities decrease with decreasing interaction energies, indicating that charge transfer plays an important role in complex stability.

### 3.3 AIM Analysis

To further analyze the nature of -type pnicogen bond interactions, we employed Bader' s Atoms in Molecules (AIM) theory, which is frequently used in weak interaction research [32-35]. Typical molecular graphs of pnicogen bond complexes (Fig. 6 [Figure 6: see original paper]) show a critical point between the P atom and the aromatic ring, confirming the existence of -type pnicogen bonds. Table 3 presents the electron densities ( _b), Laplacian of electron densities ( ² _b), three eigenvalues ( , , ) of the Hessian matrix, kinetic energy densities (G_b), potential energy densities (V_b), and electronic energy densities (H_b) at the pnicogen bond critical points (BCPs) for the nine complexes at the MP2/aug-cc-pVDZ level.

According to AIM theory, when | + | < and ² _b > 0, charges are dispersed and bond ionicity is dominant; when | + | > and ² _b < 0, charges are concentrated and bond covalency is stronger. The data in Table 3 show that ² _b > 0 and | + | < at the BCPs, indicating that -type pnicogen bonds in complexes 1-9 are primarily ionic. The electronic energy density H_b (sum of kinetic energy density G_b and potential energy density V_b) serves as a reliable index for characterizing weak interactions [36,37]: H_b > 0 indicates electrostatic interactions, while H_b < 0 indicates covalent interactions. All H_b values in Table 3 are positive, confirming that the nine -type pnicogen bond complexes involve electrostatic interactions, consistent with the conclusion that "charges are dispersed and bond ionicity is stronger when | + | < and ² _b > 0."

Electron density ( _b) at BCPs correlates with bond strength, with higher densities indicating stronger bonds. The relationship between electron density at

BCPs and corrected interaction energy is plotted in Fig. 7 [Figure 7: see original paper], showing a correlation coefficient R = 0.915.

### 3.4 RDG/ELF Analysis

Yang Weitao' s group [38] developed a visualization method for weak interaction research, where reduced density gradient (RDG) function values and sign(  (r)) (r) are visualized in RDG isosurface maps. Gradient isosurfaces are colored according to sign(  (r)) (r) values, providing a good indicator of interaction strength. We previously applied this method to analyze hydrogen bonds, halogen bonds, pnicogen bonds, and coordination bonds with promising results [39-41]. The electron localization function (ELF) is an important tool for electronic structure research and is often used to study chemical problems such as molecular interactions [42]. We applied both methods to  -type pnicogen bond interactions to visualize interaction changes.

Fig. 8 [Figure 8: see original paper] shows the combined RDG/ELF isosurface maps for complexes 1 and 2 (Fig. 8a) and the ELF isosurface map of PH Cl (Fig. 8b). These maps reveal the spatial positions of molecular interactions, with interaction strengths indicated by colors in the RDG map (blue for strong interactions, green for weak interactions, and red for repulsion). Comparing the color-filled RDG isosurface maps, complex 2 shows a deeper blue region than complex 1, indicating stronger pnicogen bond interactions. The white column and vacancy ring zones in Fig. 8a represent localization spaces for lone-pair electrons,  -electrons, and valence electrons. The localization space V(P) of the lone-pair electron on the P atom is significantly weakened (Fig. 8b). This occurs because weak interactions shorten the intermolecular distance, generating repulsion between  -electrons and the lone-pair electrons on the P atom. This shortening force is primarily electrostatic, consistent with AIM analysis showing that pnicogen bond interactions are mainly electrostatic forces. In other words, the pnicogen bond interaction weakens the lone-pair electron localization space on the P atom to some extent.

## 4. CONCLUSION

Geometrical structure optimizations, energy calculations, and topological and graphical analyses for various pnicogen bond systems of PH Cl with Ar–R (R = H, OH, NH , CH , Br, Cl, F, CN, NO ) were performed at the MP2/aug-cc-pVDZ level. The results demonstrate that  -type pnicogen bond interactions are strengthened by electron-donating substituents on the benzene ring and weakened by electron-withdrawing substituents. Comparison of interaction energies between  -type pnicogen bond and halogen bond systems reveals that  -type pnicogen bond systems are more stable. NBO analysis of the correlation between second-order perturbation stabilization energy, charge transfer quantity, and interaction energy shows that charge transfer plays an important role in pnicogen bond complex stability. AIM analysis indicates that pnicogen bond interactions are electrostatic in nature, with electron density at BCPs positively correlated with complex interaction energy. RDG analysis visualizes the position and strength of pnicogen bond interactions, while ELF analysis reveals changes in the lone-pair electron localization space on the P atom upon complex formation.

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