

# Topological Properties of the Pnicogen Bond Complexes Based on Atoms-in-Molecule Theory: A Way of Supramolecular Materials Construction

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**Abstract.** Pnicogen bond is a Lewis acid-Lewis base intermolecular noncovalent attractive interaction in which a pnicogen atom (N, P, or As) is the Lewis acid. It has been known since 2011. In this paper, the topological properties of the particular set of pnicogen bond complexes formed with formaldehyde (HCHO) and PH<sub>2</sub>X (X=H, F, Cl, Br, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, NO<sub>2</sub>) were studied base on atoms-in-molecules theory so as to present a way of supramolecular materials construction.

## Introduction

For many years long, intermolecular noncovalent interaction has been implicated as an important type of interaction in many different types of physical systems and is especially of great interest within the fields of biochemistry[1–4], material science[5–7], and atmospheric chemistry[8,9]. And now days, intermolecular noncovalent interaction has captured the interest of chemists for a long time and reports about its theory and experiment have been well presented. It has been found that a lot of physical and chemical phenomena are closely related to the intermolecular weak interactions including hydrogen bond,  $\pi$ -cation, halogen bond, *etc.* Among these intermolecular interactions studied, hydrogen bond is the earliest and the most extensive one, and pnicogen bond is a novel interesting weak interaction analogous to hydrogen bond. The pnicogen bond is a Lewis acid-Lewis base intermolecular noncovalent attractive interaction in which a pnicogen atom (N, P, or As) is the Lewis acid. The complexes formed by pnicogen bonds have been known for some time[10–14], but until 2011 this interaction became the subject of intense investigations subsequent to the landmark paper by Hey-Hawking et al. [15]. To date, pnicogen bond has been identified in a variety of systems and the concept of pnicogen bond has become important in noncovalent interaction fields. However, studies on pnicogen bond interaction are still relatively rare. In this paper, the topological properties of the particular set of pnicogen bond complexes formed with formaldehyde (HCHO) and PH<sub>2</sub>X (X=H, F, Cl, Br, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, NO<sub>2</sub>) were studied base on atoms-in-molecules theory.

## Methodology and Computational details

All the wave functions of the pnictogen bond complexes were obtained based on the optimized configurations at the MP2/aug-cc-pvdz level of theory. Harmonic frequency analyses were performed at the same level to confirm that these structures were local minima on the energy surfaces. Atoms-in-molecules (AIM) theory of Bader [16] was employed to analyze the electronic behaviors and electronic density topological properties of the pnictogen bond complexes. AIM 2000 program[17] was used to calculate the topological properties of the pnictogen bond structures. All the other calculations were performed with Gaussian 03 program [18].

## Results and discussions

### *The fundamental theories*

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, namely as eq. (1),

$$\nabla r(r) = i \frac{dr}{dx} + j \frac{dr}{dy} + k \frac{dr}{dz} \rightarrow \begin{cases} =0(\text{at critical points and at } \infty) \\ \text{generally} \neq 0(\text{at any other point}) \end{cases} \quad \text{eq. (1)}$$

According to the critical point's curvature obtained by calculating the second derivative of the  $\rho(r)$ , the type of the critical point can be defined. The Hessian matrix of electron density is composed by nine secondary derivatives of  $\rho(r)$  in three dimensions. The three eigenvalues ( $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$ ) can be acquired by performing a diagonalized operator on Hessian matrix. The sum of the three eigenvalues is equal to Laplacian of the electron density (eq(2)).

$$\nabla^2 \rho(r) = \lambda_1 + \lambda_2 + \lambda_3 \quad \text{eq. (2)}$$

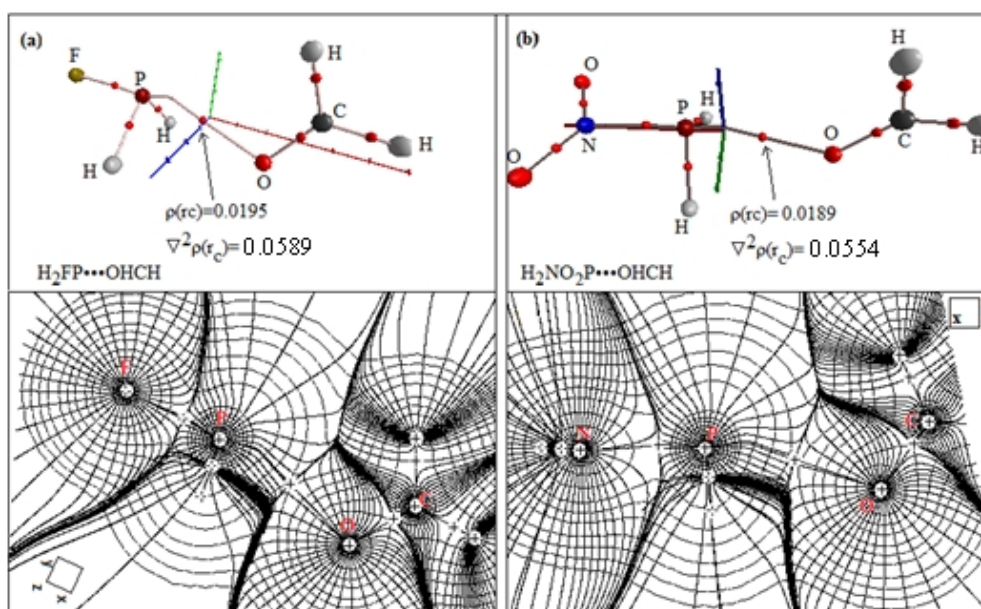
Among the three eigenvalues, if two of them are negative and the other is positive, the corresponding critical point is designated as the bond critical point (BCP) and marked as (3, -1), indicating the linkage between the two atoms; if two of them are positive and the other is negative, the corresponding critical point is designated as the ring critical point (RCP), and marked as (3, +1), indicating the existence of the ring structure. The nuclear position is marked as (3, -3). According to Bader's atoms in molecules (AIM) theory,<sup>46</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 smaller the  $\rho(r_c)$  is, the weaker 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.

Moreover,  $\varepsilon$ , the bond ellipticity, is defined as  $\lambda_1/\lambda_2 - 1$ , 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  $\pi$  character is.

### Topological properties of the pnictogen bond structures

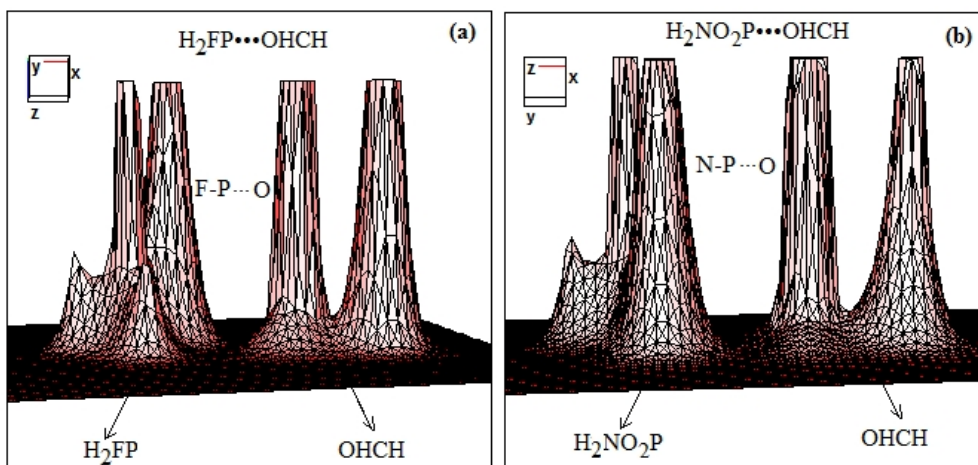
**Table 1** Electron density topological properties of pnictogen bond (P···O) critical points for the seven complexes

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



**Fig. 1** The molecular graphs (upper) and electron density maps (lower) of the HCHO···PH<sub>2</sub>F and HCHO···PH<sub>2</sub>NO<sub>2</sub> complexes

Table 1 lists the electron density topological properties of the pnictogen bond critical points in the seven complexes. It can be seen that the eigenvalues of the electron density Hessian matrix of P···O are both “one positive two negative”. Therefore, the pnictogen bond critical points between the atom pairs of P···O all belong to the type of BCPs. Additionally, 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 on the small scale. 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> are obviously larger than the former three complexes. This indicates that the pnictogen bond interactions in the former three complexes are weak and in the later four are relatively strong, implying that the electron-drawing groups may enhance the strength of the pnictogen bond interaction. The bond ellipticity of pnictogen bonds (not listed in Table 1),  $\varepsilon$ , are basically not more than 0.119, which indicate that pnictogen bonds in the present systems have stronger  $\sigma$  character than  $\pi$  character.



**Fig. 2** The relief maps of the electron density of the  $\text{HCHO}\cdots\text{PH}_2\text{F}$  and  $\text{HCHO}\cdots\text{PH}_2\text{NO}_2$  complexes expressed in the planes of the two PB systems

In Bader's AIM theory, a molecular graph is the intuitionistic expression of the electron density topological properties, and it can reliably describe the bond structures. The electron density gradient,  $\nabla\rho(\mathbf{r})$ , establishes the relationship among the critical points and defines the atom basin in a molecule. For the sake of simplicity, only the molecular graphs and electron density maps of the  $\text{HCHO}\cdots\text{PH}_2\text{F}$  and  $\text{HCHO}\cdots\text{PH}_2\text{NO}_2$  complexes are given in Fig. 1. It shows that there are only one type critical points, BCPs, in the two complexes. Especially, there exist BCPs between the atom pairs of  $\text{O}\cdots\text{P}$ . The electron density maps display three kinds of gradient routes. The first kind starts from infinite distance and ends at the nucleus; the second kind starts from BCPs and ends at two adjacent atoms along the increased  $\rho(\mathbf{r})$  directions, and this gradient route is the sole bond path linking the corresponding atom pair; the third kind also starts from BCPs, but ends at infinite distance along the maximum decreased  $\rho(\mathbf{r})$  directions, and this gradient route forms inter-atomic surface in three dimensions. The case of electron density is much more complicated because, being the fourth dimension, it is the function of three coordinates. Fig. 2(a) and (b) present the relief maps of electronic charge density for the plane passing through the  $\text{HCHO}\cdots\text{PH}_2\text{F}$  and  $\text{HCHO}\cdots\text{PH}_2\text{NO}_2$  complexes, respectively. There are also saddle points between two  $\text{O}\cdots\text{P}$  atom pairs. Because the atoms involved in PB structures are nearly coplanar, as can be seen, all the maxima of electron density corresponding to the positions of atoms are visible. The maxima corresponding to F, N, P, O and C atoms are much "higher" than those of hydrogen atoms.

## Conclusions

In this work, the topological properties of the particular set of pnictogen bond complexes formed with formaldehyde ( $\text{HCHO}$ ) and  $\text{PH}_2\text{X}$  ( $\text{X}=\text{H}, \text{F}, \text{Cl}, \text{Br}, \text{CH}_3, \text{C}_6\text{H}_5, \text{NO}_2$ ) were studied base on atoms-in-molecules theory. The molecular graphs, electron density maps and relief maps of the electron density of the complexes were established to understand the topological properties of pnictogen bonds. The results showed that that the electron-drawing groups may enhance the strength of the pnictogen bond interaction. Additionally, pnictogen bonds in the present systems have stronger  $\sigma$  character than  $\pi$  character.

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