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Exploring the pnicogen bond non-covalent interactions in 4-XPhNH$_2$:PF$_n$H$_{3-n}$ complexes (n = 1–3, X = H, F, CN, CHO, NH$_2$, CH$_3$, NO$_2$ and OCH$_3$)

Hossein Roohi*, Tahereh Tondro

Department of Chemistry, Faculty of Science, University of Guilan, Rasht, Iran

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ABSTRACT

Quantum chemical calculations were carried out to explore the effects of substituents in para position of aniline as well as phosphine on the strength of interactions in pnicogen-bonded (PB) complexes of the **4-XPhNH$_2$:PF$_n$H$_{3-n}$** (n = 1–3 and X = H, F, CN, CHO, NH$_2$, CH$_3$, NO$_2$ and OCH$_3$). The P···N pnicogen bond strength in these complexes was examined at M06-2X/6–311 + +G(d,p), MP2/6–311 + +G(d,p), MP2/cc-pVDZ, CCSD/cc-pVDZ and MP2/aug-cc-pVTZ levels of theory. The dispersion corrected M06-2X-GD3, B2PLYP-GD3 and mPW2PLYP-GD2 functionals were also used to calculate the binding energies. The changes in the pnicogen bond strength due to the change of the substituents were well monitored by the changes in the interaction energy, structural parameters, natural charge, charge transfer, electron density topology, NMR chemical shielding and spin-spin coupling constants. The BSSE-corrected BEs change from 14.5 to 21.4 kJ mol^{-1} for the **4-XPhNH$_2$:PF$_3$**, 21.5 to 30.5 kJ mol^{-1} for the **4-XPhNH$_2$:PF$_2$H** and 24.2 to 33.1 kJ mol^{-1} for the **XPhNH$_2$:PFH$_2$** complex at MP2/aug-cc-pVTZ level and 12.5 to 18.9 kJ mol^{-1} for the **4-XPhNH$_2$:PF$_3$**, 17.4 to 26.5 kJ mol^{-1} for the **4-XPhNH$_2$:PF$_2$H** and 18.9 to 26.5 kJ mol^{-1} for the **XPhNH$_2$:PFH$_2$** complexes at MP2/6–311 + +G(d,p) level. For each PF$_n$H$_{3-n}$ monomer, results demonstrated that the strength of the pnicogen bonds increases by introducimg electron-donating substituents in 4-XPhNH$_2$ molecule, whereas a reverse situation was found upon introducing electron-accepting substituents. Natural bond orbital analysis confirmed that the charge transfer takes place from 4-XPhNH$_2$ to PF$_n$H$_{3-n}$. Electron density properties based on atoms in molecules theory were also utilized to characterize the pnicogen bonds.

1. Introduction

Although non-covalent interactions are not such strong ones, they are of great importance because, they play significant roles in many of the chemical, physical, and biological processes such as bioactive molecular recognition [1,2], crystal engineering [3], proton transfer dynamics [4], formations of molecular clusters [5], designing of materials, molecular self-assembly [6,7,8] and etc.

Non-covalent bond interactions have been subjected to many of the both experimental and theoretical investigations [9–12]. The effect of substituents on the properties of pnicogen–bonded complexes XY:PH$_3$ (XY = ClCl, FCl, and FBr), PH$_3$:N-base (N-base = NCH, NH$_3$, NCF, NCCN, and N$_2$), H$_2$XP:PYH$_2$, (X, Y = F, Cl, OH, NC, CCH, CH$_3$, CN, and H) and H$_2$XP:NXH$_2$ (X = H, CH$_3$, NH$_2$, OH, F, Cl) were explored by Del Bene et al. [13–15]. Several theoretical studies by Scheiner and coworkers have contributed significantly towards the understanding of pnicogen bonding [9,16–18]. Liu and coworkers have investigated the specific set of molecular complexes consisting of the formaldehyde (HCHO) and PH$_2$X (X = H, F, Cl, Br, CH$_3$, C$_6$H$_5$ and NO$_2$) molecules. The nature and electronic structures of these weak interactions were studied using the second-order Møller-Plesset (MP2) theoretical method [19]. The strength of the pnicogen bond in complexes involving N, P, and As elements of group Va was studied by Dani et al. [20]. Shukla et al. have investigated the nature and specifications of P···Se non-covalent interactions by studying the effect of substitution on H$_3$P···SeHX, XH$_2$P···SeH$_2$ and XH$_2$P···SeHX complexes (X = H, F, CH$_3$, CF$_3$, Cl, OH, OCH$_3$, NH$_2$, NHCH$_3$ and CN) [21]. The ternary complexes ML···PyZX$_2$···NH$_3$ (ML = AgCN, CuCl, CuCN and AuCN; X = H and F; Z = P, As, and Sb) have been studied with quantum chemical calculations by Tang and Li [22]. Recently pnicogen and chalcogen bond interactions were studied by Esrafili et al. in the binary XHS:PH$_2$X complexes (X = F, Cl, CCH, COH, CH$_3$, OH, OCH$_3$ and NH$_2$) using quantum chemical computations [23]. The relationship between pnicogen bond and other types of the intermolecular interactions has been propounded by Politzer et al. [24,25].

In the current work, possibility of the pnicogen bond formation

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* Corresponding author.
E-mail addresses: hrouhi@gmail.com, hroohi@guilan.ac.ir (H. Roohi).

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between PF_nH_{3-n} (n = 1–3) and $4\text{-}XPhNH_2$ (X = H, F, CN, CHO, NH_2, CH_3, NO_2 and OCH_3) molecules was investigated by using MP2, CCSD, M06-2X and DFT-GD3 methods in conjunction with the various basis sets. In other words, we have simoltaniously explored the influence of substituents at pnicogen acceptor atom of PF_nH_{3-n} and donor atom of $4\text{-}XPhNH_2$ on the stability of non-covalent pnicogen P⋯N bonded complexes. Optimized geometrical configurations, binding energies, bonding characteristics, charge transfer values, electrostatic potentials, molecular graphes, ^{15}N and ^{31}P chemical shieldings and ^{15}N–^{31}P spin-spin coupling constants of the title complexes were determined and analyzed.

2. Computational details

All monomers and complexes were optimized by using M06-2X [26] and MP2 [27] methods in conjunction with the 6–311 + + G(d,p) basis set [28] and at MP2/aug-cc-pVDZ level of theory. The vibrational frequency calculations were performed to ensure that the optimized structures correspond to the global minima. Binding energies (BEs) of complexes were calculated at M06-2X/6–311 + + G(d,p), MP2/6–311 + + G(d,p), MP2/cc-pVDZ, CCSD/cc-pVDZ and MP2/aug-cc-pVTZ levels of theory and were corrected for basis set superposition error (BSSE) using the counterpoise procedure (CP) of the Boyes and Bernardi [29]. The zero-point corrections to energies are taken into account to improve the BEs. The dispersion corrected M06-2X-GD3, B2PLYP-GD3 and mPW2PLYP-GD2 functionals were also used to calculate the BEs. All of the calculations were carried out by using Gaussian 09 program [30].

Several topological descriptors such as electron densities (ρ_{BCP}), Laplacian of electron densities ($\nabla^2\rho_{BCP}$), the total electron energy density H (H = G + V) and its components are obtained using the theory of atoms in molecules (AIM) [31,32]. For a typical covalent bond between two atoms laplacian of the electron density ($\nabla^2\rho_{BCP}$) and the total electron energy density (H) are negative i.e. $\nabla^2\rho < 0$ and $H < 0$ at the corresponding BCP; the interaction may has partially covalent nature if $\nabla^2\rho > 0$ but $H < 0$ at the corresponding BCP [33,34]; In addition, the interaction is closed-shell if $\nabla^2\rho > 0$ and $H > 0$ at the corresponding BCP. The QTAIM calculations were carried out based on the wave functions obtained at the MP2/6–311 + + G(d,p) level of theory using AIM2000 program package [35]. Electronic properties of the interactions were analyzed with the help of the natural bond orbital (NBO) analysis based on the wave functions obtained at the MP2/6–311 + + G(d,p) level using NBO program package [36].

Absolute ^{31}P and ^{15}N chemical shielding values (σ) in the **4-XPhNH$_2$:PF$_n$H$_{3-n}$** complex configurations and the spin-spin coupling constants including ^{31}P and ^{15}N atoms at all of the isolated monomers and complex configurations were computed at M06-2X/6–311 + + G(d,p) level of theory.

The total coupling constant (J) is consist of the four contributes in the Ramsey approximation [37,38]: the paramagnetic spin-orbit (PSO), the diamagnetic spin-orbit (DSO), the Fermi contact (FC), and the spin-dipole (SD). In the present work, all of the four above mentioned terms which are contributed in nuclear spin-spin coupling constants at non-relativistic theory have been calculated.

3. Results and discussion

The optimized structures of the most stable complexes **4-XPhNH$_2$:PF$_n$H$_{3-n}$** are represented in Fig. 1. A deep analysis of the P-bonded complexes **4-XPhNH$_2$:PF$_n$H$_{3-n}$** (n = 1–3, X = H, F, CN, CHO, NH_2, CH_3, NO_2 and OCH_3) indicates that the PB distances, the ipso angles and ipso-ortho C—C and C—N bond lengths are strongly affected by change in the number of F atoms in PF_nH_{3-n} monomers, the nature of substituents in the para position of the aniline and the location of the PF_nH_{3-n} monomers in the complexes. In addition, PB binding energy, topological properties, charge distribution, vibrational properties, spin-spin coupling constants and electrostatic potentials are influenced by substituents in monomers.

3.1. Binding energy

The binding energies (BE = − ΔE) of the investigated complexes computed according to the model reaction $4\text{-}XPhNH_2 + PF_nH_{3-n} \rightarrow 4\text{-}XPhNH_2\text{:}PF_nH_{3-n}$ are given in Tables 1 and S1 (in Supplementary data). As can be seen from Table 1, the BSSE-corrected BEs range from 14.5 to 21.4 kJ mol^{-1} for the **4-XPhNH$_2$:PF$_3$**, 21.5 to 30.5 kJ mol^{-1} for the **4-XPhNH$_2$:PF$_2$H** and 24.2 to 33.1 kJ mol^{-1} for the **XPhNH$_2$:PFH$_2$** complex at MP2/aug-cc-pVTZ level and 12.5 to 18.9 kJ mol^{-1} for the **4-XPhNH$_2$:PF$_3$**, 17.4 to 26.5 kJ mol^{-1} for the **4-XPhNH$_2$:PF$_2$H** and 18.9 to 26.5 kJ mol^{-1} for the **XPhNH$_2$:PFH$_2$** complexes at MP2/6–311 + + G(d,p) level. From these results, it can be found that the change in the quality of basis set from 6 to 311 + + G(d,p) to aug-cc-pVTZ leads to increase in BE. The BEs computed at M06-2X/6–311 + + G(d,p) level vary from 21.9 to 30.9 kJ mol^{-1}, 25.1 to 37.5 kJ mol^{-1} and 24.1 to 35.2 kJ mol^{-1} for **4-XPhNH$_2$:PF$_3$**, **4-XPhNH$_2$:PF$_2$H** and **4-XPhNH$_2$:PFH$_2$** complexes, respectively. From Table 1, BEs predicted by the M06-2X method are greater than those of found by MP2 one with the 6–311 + + G(d,p) basis set. In other words, at all cases, the M06-2X method tends to overestimate the stability of the **4-XPhNH$_2$:PF$_n$H$_{3-n}$** (n = 1–3) complexes compared to the MP2 approach, which is a feature which appears to be general within the other non-covalent interactions [39,40].

The BSSE corrected BEs calculated at different levels versus Hammett's substituent constant (σ_p) are depicted in Fig. 2. The sum of the total electronic effects which are composed of inductive and resonance effects are represented by Hammett's substituent constant (σ_p) [41]. The sign of the substituent constant (σ_p) is positive/negative when an electron withdrawing/releasing group is attached as a substituent to the phenyl ring. As shown in Fig. 2 the slope of the plot of the BEs versus Hammett's substituent constant is negative, which indicates that the amount of the BE decreases/increases with the increasing/decreasing electron withdrawing ability of the X substituent attached to the para position of the phenyl ring.

Since pnicogen atom P withdraws electrons from the donor N atom of the aniline, it is predicted that the presence of electron-donating and −accepting substituents in the para position of the aniline influences the strength of PB. An accurate inspection of BEs reveals that the influence of substituents in $4\text{-}XPhNH_2$ on the stability of complexes is more sensible than those of substitutions of H atoms by F ones on pnicogen P atom. The effect of substituents in $4\text{-}XPhNH_2$ on stability of complexes is arranged as **4-XPhNH$_2$:PF$_2$H** ≈ **4-XPhNH$_2$:PFH$_2$** > **4-XPhNH$_2$:PF$_3$**. The results show that the electronic BE obtained for all **4-XPhNH$_2$:PF$_n$H$_{3-n}$** (n = 1–3) complexes at all levels decreases in the general order of X = NH_2 > OCH_3 > CH_3 > H > F > CHO > CN > NO_2. The most stable complexes are those with the relatively strong bases NH_2 and OCH_3 bonded to the relatively strong acid PFH_2.

The effects of the method and basis set on the strength of the PB can be understood from Fig. 2a–c. For all three types of PB complexes, the greatest and smallest values of BSSE-corrected BEs correspound to the M06-2X/6–311 + + G(d,p) and MP2/6–311 + + G(d,p) levels, respectively. In comparison with the MP2/aug-cc-pVTZ as a benchmark level of theory, curves given in Fig. 2 show that the M06-2X/6–311 + + G(d,p) level overestimates and MP2/6–311 + + G(d,p), MP2/cc-pVDZ and CCSD/cc-pVDZ levels underestimate BEs. The sequence of the decrease in BE obtained by various levels of theory is M06-2X/6–311 + + G(d,p) > MP2/aug-cc-pVTZ > MP2/6–311 + + G(d,p) > MP2/cc-pVDZ > CCSD/cc-pVDZ.

From Fig. 2, the BE values of the **4-XPhNH$_2$:PF$_n$H$_{3-n}$** complexes are greater for electron donating X substituents compared to the electron-accepting ones. In other words, electron-donating/accepting nature of the X substituent increases/decreases the BE values. An increase in the BE is associated with an immobilization of the lone pair of the nitrogen