



REGULAR ARTICLE

Substituent effects on the halogen and pnictogen bonds characteristics in ternary complexes 4-YPhNH₂...PH₂F...CIX (Y = H, F, CN, CHO, NH₂, CH₃, NO₂ and OCH₃, and X = F, OH, CN, NC, FCC and NO₂): A theoretical study

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Abstract. The synergistic relationship between pnictogen and halogen non-covalent interactions in 4-YPhNH₂...PH₂F...CIX (Y = H, F, CN, CHO, NH₂, CH₃, NO₂ and OCH₃; X = F, OH, CN, NC, FCC and NO₂) complexes were explored using Aug-ccpVDZ basis set and M06-2X and M06-2X-GD3, B2PLYP-GD3 and mPW2PLYP-GD2 functionals. The effects of the substituents included at pnictogen bond and halogen bond segments on the correlation between BEs and pnictogen as well as halogen bond distances, electron density at both non-covalent interactions, charge transfer energies between components and the NMR properties were evaluated. The energy analysis indicates that the pnictogen bond interaction has a much greater stabilizing effect than the halogen bond one. In addition, the auxiliary effect of a pnictogen bond on a halogen bond is more pronounced than that of a halogen bond on a pnictogen bond.

Keywords. Cooperative effect; pnictogen bond; halogen bond; dispersion; substitution effect.

1. Introduction

The noncovalent interactions play an essential role in intermolecular and intramolecular interactions.^{1–20} The cooperativity between two non-covalent interactions of the same type such as hydrogen bonds,²¹ halogen bonds,^{22–24} pnictogen bonds,²⁵ and different combinations with other σ -hole interactions^{26–31} are the subject of many research works.

The interest in the study of pnictogen bond interactions has grown both experimentally^{32,33} and theoretically.^{5,33–44} Most of the confirmation for pnictogen bonds arose initially from crystal structure analyses.^{45–48} The pnictogen bonds containing phosphorus, in particular, have been an area of increasing interest over the past years due to their potential roles in the medicinal chemistry and biological systems.^{49–52} In addition to expanding scientific knowledge frontiers, the experimental chemists can use the results of theoretical approaches in the wide-ranging interest from the crystal engineering and supermolecular

chemistry,^{53–55} formation of eutectic molecular liquids (EMLs),⁵⁶ interstellar chemistry⁵⁷ to biological recognition processes.^{11,58} The pnictogen and halogen bonds can be verified experimentally by using X-ray diffraction,^{33,47,59,60} terahertz spectroscopy,⁴⁹ IR and Raman,^{47,61} and NMR^{47,62} spectroscopies.

Li *et al.*, have reported significant cooperative effects between non-covalent pnictogen and halogen interactions in XCl...FH₂P...NH₃ complex systems.³ They have also studied the cooperative effects between lithium and halogen bond interactions in MCN...LiCN...XCCH (M = H, Li, and Na; X = Cl, Br, and I) complexes.⁶³ The positive cooperativity between pnictogen bond and anion- π interactions, the cationic- π interactions and pnictogen bonds were studied by Esrafil *et al.*⁶⁴ and Li *et al.*,³⁰ respectively. The substituent effects in cationic pnictogen bonded complexes between XH₃P⁺ and NCY molecules (X = H, F, CN, NH₂ and OH; Y = H, Li, F, Cl) were explored by Esrafil *et al.*⁶⁵ These authors also studied the cooperativity between conventional (Li...N/C) and

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non-conventional (Li... π) lithium interactions in NCLi...NCLi...XCCX and CNLi...CNLi...XCCX (X = H, F, Cl, Br, OH, CH₃, and OCH₃) complexes.⁶⁶ The effect of substituents on the cooperativity between fluorine centered halogen bonds in NCF...NCF...NCX and CNF...CNF...CNX complexes (X = H, F, Cl, CN, OH and NH₂) was investigated by Esrafilı *et al.*⁶⁷ In another study, the cooperative effects between non-covalent interactions of pnictogen and dihydrogen bond types have been propounded by Esrafilı *et al.*, in HMH...HCN...PH₂X (X = H, F, Cl and M = Be, Mg, Zn) complexes.⁶⁸ These authors also examined the cooperativity of pnictogen bonds in XH₂P...NCH₂-P...NCY (X = F, Cl; Y = H, F, CN, OH, NH₂) complexes.⁶⁹ Also, Esrafilı *et al.*,⁷⁰ have investigated the unusual cooperativity effects between halogen bond and donor-acceptor interactions in the C₅H₅-B...NCX...NCY complexes, where X = F, Cl, Br, I, and Y = H, CN, OH, Li.

In the previous work, we have explored the pnictogen bond non-covalent interactions in 4-XPhNH₂:PF_nH_{3-n} complexes (n = 1–3, X = H, F, CN, CHO, NH₂, CH₃, NO₂ and OCH₃).⁷¹ In the current work, the non-covalent pnictogen and halogen bond (PB and HB) interactions in ternary complexes 4-YPhNH₂...PH₂F...CIX (Y = H, F, CN, CHO, NH₂, CH₃, NO₂ and OCH₃ and X = F, OH, CN, NC, FCC and NO₂) were investigated. The substituent effects on cooperativity between pnictogen and halogen bonds were taken into account. Binding energies (BEs), structural characteristics, charge transfer energies, Wiberg bond indexes, electron density properties, ³¹P chemical shielding and ³¹P...¹⁵N spin-spin coupling constants of the ternary complexes were determined and analyzed. To understand the mechanism of synergetic effects and dependence of cooperative effects on substituent, the natural bond orbital (NBO) theory, molecular surface electrostatic potential (MESP) analysis, atoms in molecules (AIM) theory, and energy decomposition analysis (EDA) were utilized. The structures of complexes studied are depicted in Figure 1.

2. Computational methods

All calculations were carried out using the Gaussian package.⁷² The geometries for all of the monomers, dimers and trimers were optimized at M06-2X/aug-cc-pVDZ level of theory. The suitability of the M06-2X density functional method for the study of non-covalent interactions has been described previously.^{73–75}

The interaction energies are corrected for basis set superposition error (BSSE) using the standard counterpoise correction (CP) method proposed by Boys and Bernardi.⁷⁶ The dispersion corrected M06-2X-GD3, B2PLYP-GD3 and mPW2PLYP-GD2 functionals were also used to calculate the BEs.^{77,78}

The topological analyses of the electronic charge density for all complexes were performed using Bader's QTAIM theory⁷⁹ and by mean of AIM2000 software.⁸⁰ The natural bond orbital (NBO) analysis⁸¹ was performed by using the wave functions obtained at the M06-2X/aug-cc-pVDZ level of theory.

The electrophilic and nucleophilic sites in a molecule can be recognized by the molecular electrostatic potential (MESP) topography analysis. The electrostatic potential $V(\mathbf{r})$ is a three-dimensional local property that can be evaluated at any or all points \mathbf{r} in the space of a system by $V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|}$ in terms of atomic units, au. The Z_A is the charge on nucleus A, located at \mathbf{R}_A ; $|\mathbf{R}_A - \mathbf{r}|$ represents its distance from \mathbf{r} , just as $|\mathbf{r}' - \mathbf{r}|$ is the distance of each electronic charge increment $-e\rho(\mathbf{r}')d\mathbf{r}'$ from \mathbf{r} . The $V(\mathbf{r})$ may be either positive or negative in any given region, depending upon whether the effect of the nuclei or the electrons is dominant there.⁸² The MESP on the 0.001 au contours were calculated at the M06-2X/aug-cc-pVDZ level with the Multiwfn program.⁸³

The absolute ³¹P chemical shielding isotropy (σ_{iso}), as well as the spin-spin coupling constant across the pnictogen bond, were calculated at the M06-2X/aug-cc-pVDZ level of theory employing gauge included atomic orbital (GIAO) approach.⁸⁴

The energy decomposition analysis (EDA) was carried out at BP86-D3/TZ2P(ZORA)//M06-2X/aug-cc-pVDZ level using the ADF 2009.01 program package. EDA calculations were carried out in order to analyze the nature of the pnictogen and halogen bonds interactions. Here, the interaction energy between the interacting fragments (4-YPhNH₂, PH₂F and CIX) was divided into four terms as shown in Eq. 1.

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}} + \Delta E_{\text{disp}}, \quad (1)$$

where the ΔE_{elstat} , ΔE_{Pauli} , ΔE_{orb} and ΔE_{disp} are the electrostatic interaction, Pauli repulsion, orbital interaction and the dispersion energy between two interacting fragments, respectively.

Equations 2, 3, 4 and 5 were used for calculation of the $-BE$ (interaction energies) of the pnictogen bonds

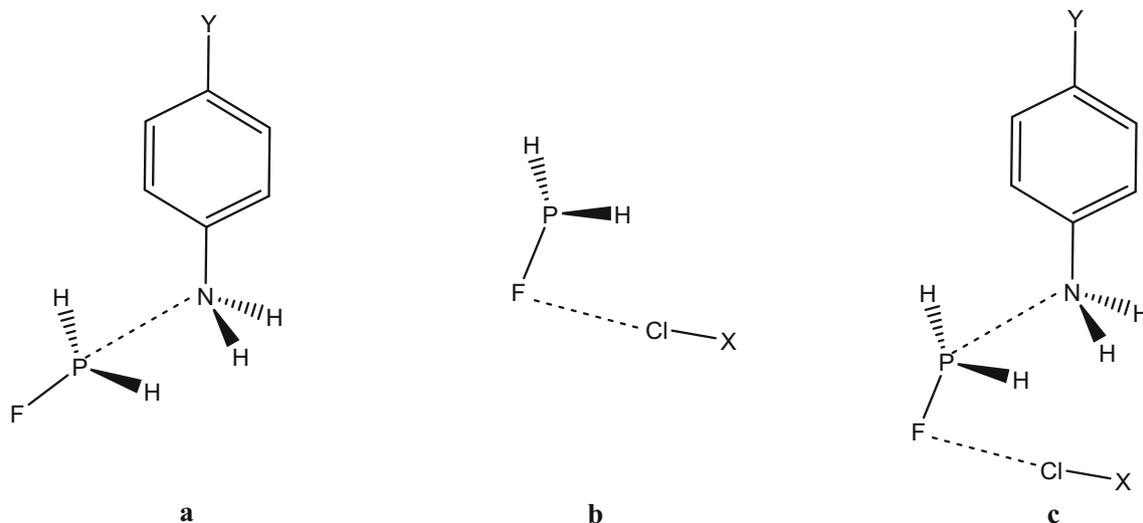


Figure 1. Structures of the studied dimers and trimers. (a) 4-YPhNH₂...PH₂F (b) PH₂F...ClX (c) 4-YPhNH₂...PH₂F...ClX (X = F, OH, CN, NC, FCC and NO₂ and Y = H, F, CN, CHO, NH₂, CH₃, NO₂ and OCH₃).

in dimers ($E_{\text{int,AB}}$), halogen bonds in dimers ($E_{\text{int,BC}}$), pnictogen bonds in trimers ($E_{\text{int,AB(T)}}$) and halogen bonds in trimers ($E_{\text{int,BC(T)}}$), respectively.

$$E_{\text{int,AB}} = E_{\text{AB}} - (E_{\text{A}} + E_{\text{B}}) \quad (2)$$

$$E_{\text{int,BC}} = E_{\text{BC}} - (E_{\text{B}} + E_{\text{C}}) \quad (3)$$

$$E_{\text{int,AB(T)}} = E_{\text{ABC}} - (E_{\text{A}} + E_{\text{BC}} + E_{\text{int,AC(T)}}) \quad (4)$$

$$E_{\text{int,BC(T)}} = E_{\text{ABC}} - (E_{\text{C}} + E_{\text{AB}} + E_{\text{int,AC(T)}}) \quad (5)$$

Where, E_{AB} , E_{BC} , E_{A} , E_{B} , E_{C} are the total energies of the optimized dimers and monomers. In equations 4 and 5, E_{ABC} and $E_{\text{int,AC(T)}}$ are the total energy of optimized trimers and interaction energy between 4-YPhNH₂ and Cl-X monomers at triad geometry. $E_{\text{int,AC(T)}}$ could be calculated using Eq. 6, in which $E_{\text{int,AC(T)}}$ is the energy of 4-YPhNH₂...ClX complex in optimized structure of trimer complex.

$$E_{\text{int,AC(T)}} = E_{\text{AC}} - (E_{\text{A}} + E_{\text{C}}) \quad (6)$$

The total interaction energy of the triads was calculated according to Eq. 7

$$E_{\text{int,ABC}} = E_{\text{ABC}} - (E_{\text{A}} + E_{\text{B}} + E_{\text{C}}) \quad (7)$$

The energy difference of pnictogen bonds and halogen bonds between dimers and trimers was also calculated using the Eqs. 8 and 9.

$$\Delta\Delta E_{\text{PB}} = E_{\text{int,AB(T)}} - E_{\text{int,AB}} \quad (8)$$

$$\Delta\Delta E_{\text{HB}} = E_{\text{int,BC(T)}} - E_{\text{int,BC}} \quad (9)$$

Finally, the cooperative energy in the trimer complexes could be achieved by using the following Eq. 10:

$$E_{\text{coop}} = E_{\text{int,ABC}} - (E_{\text{int,AB}} + E_{\text{int,BC}} + E_{\text{int,AC(T)}}) \quad (10)$$

3. Results and Discussion

3.1 Molecular electrostatic potential (MESP) analysis

MESP is a real physical experimental property that identifies the electron-rich and electron-deficient regions present in monomers and complexes and is valuable for developing bonding theories for intermolecular complex formation induced by lone pair centers.^{85,86} The electrostatic potentials of the ClX, PH₂F and 4-YPhNH₂ monomers and the corresponding binary complexes were calculated at the M06-2X/aug-cc-pVDZ level of theory. Potential surface maxima ($V_{\text{S,max}}$) and potential surface minima ($V_{\text{S,min}}$) are given in Table 1. The MESP maps on the 0.001 au isodensity surface of the electron density of monomers and dimers are depicted in Figure 2. The value of the calculated positive electrostatic potential (σ -hole = $V_{\text{S,max}}$) for ClX range from 21.42 (for ClOH) to 40.56 (ClNC) kcal mol⁻¹ that indicates that the ClNC molecule is better electron acceptor than ClOH. Also, the positive electrostatic potential associated with P atom of PH₂F is calculated to be 37.16 kcal mol⁻¹. There is also a negative potential $V_{\text{S,min}}$ associated with the F atom of PH₂F molecule ($V_{\text{S,min}} = -19.71$ kcal mol⁻¹) which interacts with the ClX to form the

Table 1. The MEP values of N atom in 4-YPhNH₂, V_{s,min}(N), and F atom in 4-YPhNH₂...PH₂F, V_{s,min}(F) (Y = H, F, CN, CHO, NH₂, CH₃, NO₂ and OCH₃) at the M06-2X/aug-cc-pVDZ level (all in kcal mol⁻¹).

Compound	V _{S,max}	V _{S,min}
4-HPhNH ₂	–	– 26.65 (N atom)
4-NH ₂ PhNH ₂	–	– 30.99
4-OMePhNH ₂	–	– 29.48
4-CH ₃ PhNH ₂	–	– 28.26
4-FPhNH ₂	–	– 24.65
4-CHOPhNH ₂	–	– 16.05
4-CNPhNH ₂	–	– 13.69
4-NO ₂ PhNH ₂	–	– 11.07
PH ₂ F	37.16 (P atom)	– 19.71(F atom)
ClF	39.02 (Cl atom)	–
ClOH	21.42	–
ClCN	35.99	–
ClCCF	21.80	–
CINC	40.56	–
CINO ₂	23.02	–
4-HPhNH ₂ ...PH ₂ F	–	– 30.01(F atom)
4-NH ₂ PhNH ₂ ...PH ₂ F	–	– 32.56
4-OMePhNH ₂ ...PH ₂ F	–	– 31.30
4-CH ₃ PhNH ₂ ...PH ₂ F	–	– 30.83
4-FPhNH ₂ ...PH ₂ F	–	– 28.76
4-CHOPhNH ₂ ...PH ₂ F	–	– 25.76
4-CNPhNH ₂ ...PH ₂ F	–	– 24.13
4-NO ₂ PhNH ₂ ...PH ₂ F	–	– 23.42
PH ₂ F...ClF	43.60 (P)/3.13(Cl)	–
PH ₂ F...ClOH	37.03/4.65	–
PH ₂ F...ClCN	44.50/12.46	–
PH ₂ F...ClCCF	39.53/1.03	–
PH ₂ F...CINC	44.56/10.06	–
PH ₂ F...CINO ₂	40.98/16.06	–

σ -hole complexes. The V_{S,min} on the N atom of 4-YPhNH₂ molecules range from -11.07 (for 4-NO₂-PhNH₂) to -30.99 (for 4-NH₂PhNH₂) kcal mol⁻¹ that indicates the involvement of lone pair electrons in the aromatic-conjugation is different and depend on the substituents in para position of benzene ring. The results show that the presence of the electron-donating groups (NH₂ and OCH₃) in the 4-YPhNH₂ molecule causes an increase of the V_{S,min}, whereas, the electron-accepting groups (NO₂ and CN) lead to a decrease of the negative potential.

The calculated V_{S,max} and V_{S,min} values of the binary complexes are also given in Table 1. It is interesting to note that upon halogen bond formation, the V_{S,max} values associated with the P atom of ClX...PH₂F complexes become more positive, with the exception of that found in ClOH...PH₂F (37.0 kcal mol⁻¹), indicating that the inductive electron-withdrawing nature of groups improves the electron-acceptor character of P atom. The tendency of PH₂F

for the formation of the pnictogen bonded 4-YPhNH₂...PH₂F complexes increases in the presence of ClX. The greatest and lowest tendency is predicted in ClCN(NC)...PH₂F and ClOH...PH₂F dimers.

On the other hand, when 4-YPhNH₂ interacts with PH₂F monomer to form the 4-YPhNH₂...PH₂F dyad, the V_{S,min} on the F atom of PH₂F in dimer becomes more negative than that of free PH₂F in the order of Y = NH₂ > OCH₃ > CH₃ > H > F > CHO > CN > NO₂. Depending on the nature of Y, the negative electrostatic potential on the F atom surface of PH₂F in the 4-YPhNH₂...PH₂F complexes is greater than that of monomer (-19.7 kcal mol⁻¹) and is in the range of -23.42 to -32.56 kcal mol⁻¹. This reveals that the F atom in the 4-YPhNH₂...PH₂F dyad is a stronger electron donor than that of free PH₂F molecule, which increases the attraction between the 4-YPhNH₂...PH₂F dyad and the ClX molecule in the ClX...PH₂F...4-YPhNH₂ complex and leads to stronger halogen bond.

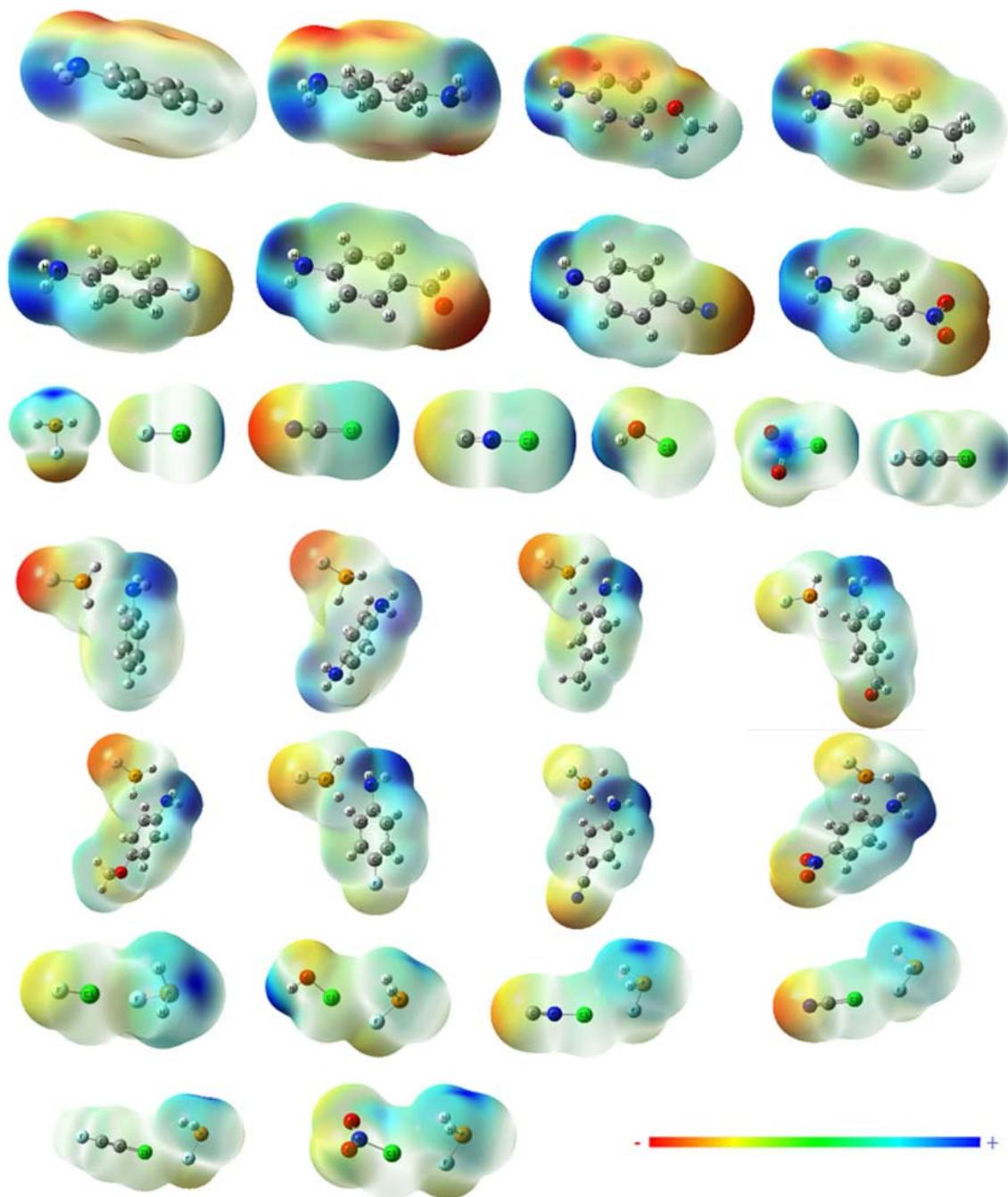


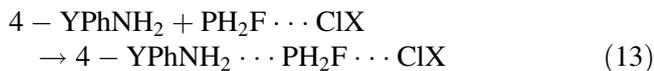
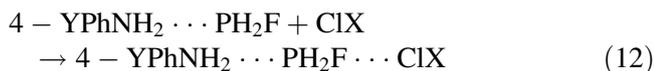
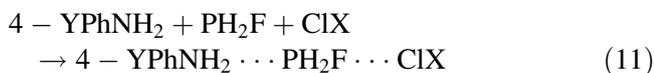
Figure 2. Electrostatic potential maps on the 0.001 au isodensity surface of 4-YPhNH₂, PH₂F, ClX monomers, 4-YPhNH₂⋯PH₂F and PH₂F⋯ClX (X = F, OH, CN, NC, FCC and NO₂ and Y = H, F, CN, CHO, NH₂, CH₃, NO₂ and OCH₃) dimers.

Therefore, one could expect that the dimer systems of 4-YPhNH₂⋯PH₂F with electron donor Y substituents show a good cooperative effect and higher interaction energies than such systems with electron-withdrawing Y substituents during combination with Cl⋯X molecules in the trimer. Thus, it can be predicted that there is a correlation between the V values and binding energies that will be discussed in the next section.

3.2 Binding energy

The binding energy (BE = $-\Delta E$) as a most conclusive measure of the strength of an intermolecular interaction has been widely used in the study of the mutual influence between non-covalent interactions. Three types of interactions may be considered between 4-YPhNH₂, PH₂F and ClX monomers. The binding energies computed according to the following model

reactions are given in Table S1 (Supplementary Information).



As can be seen from Table S1 (Supplementary Information), the BSSE-corrected BEs of the complexes range from 7.38 to 13.31 kcal mol⁻¹ for reaction (11), 2.81 to 6.42 kcal mol⁻¹ for reaction (12), and 5.88 to 10.01 kcal mol⁻¹ for reaction (13). Thus, PB complexes have binding energies varying from 5.88 to 10.01 kcal mol⁻¹, while HB complexes have BE between 2.81 and 6.42 kcal mol⁻¹. Comparison of BEs corresponding to the PBs and HBs reveals that the halogen bonding in trimers is weaker than pnictogen one.

As can be seen from Table S2 (Supplementary Information), the pnictogen binding energies (BE = $-\Delta E$) of dimers (4-YPhNH₂⋯PH₂F) are estimated to be in the range of 5.4 to 7.9 kcal mol⁻¹ and is greater for electron-donating Y substituents than the electron-withdrawing ones. Thus, the electron-donating nature of the Y substituent in the 4-YPhNH₂ fragment leads to an increase in the PB strength, while substitution of electron-withdrawing groups results in a decrease of its strength. The smallest and greatest pnictogen bond energies correspond to the Y = NH₂ and NO₂, respectively. These types of complexes were studied in our previous work.⁴⁰

Although, the aim of this study not to be the study of H-bonding, nevertheless we calculated and compared H-bonding energy in PH₂F⋯HNHPh complex with pnictogen bonding energy in H₂FP⋯NH₂Ph one. The results showed that pnictogen bonding is stronger than H-bonding formed between PH₂F and aniline by 6.1 kcal mol⁻¹, in good agreement with stronger interaction estimated for H₃P⋯NH₃ PB than H₂-PH⋯NH₃ HB in the PH₃-NH₃ complexes.⁶ In addition, for model systems PH₂F – NH₃ and FPH₂ – NH₃, our calculations showed that PB (H₂FP⋯NH₃) complex is more stable than H-bonding (H₂PF⋯HNH₂ and FPH₂⋯NH₃) complexes by 6.9 and 4.1 kcal/mol, respectively.

The binding energies of halogen bonded dimers PH₂F⋯ClX₁₋₆ (X₁₋₆ = F, OH, CN, FCC NC, and NO₂) are computed to be in the range of 1.75 to 3.65 kcal

mol⁻¹. The halogen bond energies follow a descending order of X₁ > X₅ > X₂ > X₃ > X₆ > X₄. The smallest and greatest halogen bond energies in dimer PH₂F⋯ClX correspond to the X = CCF and F, respectively. The trend observed for halogen bonds is in good agreement with those reported for XCl⋯FH₂P⋯NH₃ (X = F, OH, CN, NC, and FCC) and XBr⋯OFH₂P⋯NH₃ (X = F, Cl, CN, NC, OH, and NO₂).^{32,87} Comparison of binding energies reveal that the pnictogen bonds in the studied systems are stronger than halogen bonds, in good agreement with the results given scientific literature.^{32,54}

BEs correspond to the dimers in the trimers were computed. At first, it can be seen that the strongest and weakest pnictogen bond interactions in trimers were obtained in the 4-NH₂PhNH₂⋯PH₂F and 4-NO₂-PhNH₂⋯PH₂F dimers, respectively, as found in dimers. For halogen bonds, these trends were observed for PH₂F⋯ClF and PH₂F⋯ClCCF dimers, respectively. From the halogen binding energies in the ternary complexes listed in Table S2 (Supplementary Information), it can be found that the addition of the 4-YPhNH₂ molecule to the PH₂F⋯ClX dimer complexes leads to an increase in the BE of halogen bond by 1.97 (Y = H and X = F) to 0.55 (Y = H and X = CCF), 2.28 (Y = NH₂ and X = F) to 0.84 (Y = NH₂ and X = CCF), 2.18 (Y = OCH₃ and X = NC) to 0.55 (Y = OCH₃ and X = CCF), 2.10 (Y = CH₃ and X = F) to 0.61 (Y = CH₃ and X = CCF), 1.76 (Y = F and X = F) to 0.64 (Y = F and X = CCF), 1.34 (Y = CHO and X = F) to 0.51 (Y = CHO and X = CCF), 1.11 (Y = CN and X = F) to 0.40 (Y = CN and X = CCF), 1.12 (Y = NO₂ and X = F) to 0.31 (Y = NO₂ and X = OH). From results given in Table S2 (Supplementary Information), the increase of halogen BE ongoing from dimer to trimers in the presence of pnictogen bonding is in the range of 79% for (Y = OCH₃ and X = CN) to 13% for (Y = NO₂ and X = OH). Similarly, the presence of the ClX molecules in the 4-YPhNH₂⋯PH₂F⋯ClX trimers results in increasing pnictogen BE by 35% in 4-NH₂PhNH₂⋯PH₂F⋯ClF to 5% in 4-NO₂PhNH₂⋯PH₂F⋯ClOH.

The results show that the complexes with higher interaction energies display strong cooperativity in the ternary systems. For example, the strongest (4-NH₂-PhNH₂⋯PH₂F) and weakest (4-NO₂PhNH₂⋯PH₂F) pnictogen bonded dimers represent the highest and the lowest cooperativity when they make a trimer by coupling with the Cl-X molecule. However, the energy analysis indicates that the two types of interactions have a synergetic effect on the stability of complexes so that the pnictogen bond interaction has a much greater stabilizing effect than the halogen bond one.

From the comparison of BEs obtained for reactions 12 and 13 (Table S1, Supplementary Information), it can be concluded that the reaction between dimers and a third molecule is energetically favorable. The BEs of pnictogen bonding obtained for reaction $\text{PH}_2\text{F}\cdots\text{ClX} + 4\text{-YPhNH}_2$ are in the range of 6.21 ($\text{X} = \text{NO}_2$, $\text{Y} = \text{NO}_2$) to 10.01 ($\text{X} = \text{NC}$, $\text{Y} = \text{NH}_2$) kcal mol^{-1} and those of halogen bonding calculated based on reaction $\text{ClX} + \text{PH}_2\text{F}\cdots 4\text{-YPhNH}_2$ are in the range of 2.81 ($\text{X} = \text{CCF}$, $\text{Y} = \text{NO}_2$) to 6.42 ($\text{X} = \text{F}$, $\text{Y} = \text{NH}_2$) kcal mol^{-1} . This confirms that pnictogen bonds in trimers are much stronger than halogen bonds.

The calculated BEs based on equation 11 is in the range of 7.38 kcal mol^{-1} in the $4\text{-NO}_2\text{PhNH}_2\cdots\text{PH}_2\text{F}\cdots\text{Cl-CCF}$ trimer up to a maximum of 13.31 kcal mol^{-1} in the $4\text{-NH}_2\text{PhNH}_2\cdots\text{PH}_2\text{F}\cdots\text{Cl-F}$ trimer, as shown in Table S2 (Supplementary Information). The results also show that the amount of the BEs for a given Y substitution in the ternary complexes increases in the order of $\text{X} = \text{CCF} < \text{OH} < \text{NO}_2 < \text{CN} < \text{NC} < \text{F}$ and for a given X substitution increases in the order of $\text{Y} = \text{NO}_2 < \text{CN} < \text{CHO} < \text{F} < \text{H} < \text{CH}_3 < \text{OCH}_3 < \text{NH}_2$.

The BE in the $\text{PH}_2\text{F}\cdots\text{ClX}$ dimer was also much smaller than that in the $4\text{-YPhNH}_2\cdots\text{PH}_2\text{F}$ dimer. This demonstrates that the pnictogen bond is stronger than the halogen bond in these complexes. Upon trimerization, the BE becomes more positive for both the pnictogen bond and the halogen bond. The increased value of the halogen bonding interaction energy for all Y substitutions varies in the order of $\text{CCF} < \text{OH} < \text{NO}_2 < \text{CN} < \text{NC} < \text{F}$. The same trend is also observed for the pnictogen bond. The increased percentage is more noticeable for the BE of the halogen bond than pnictogen one. It is 13–79% for the halogen bond and 5–35% for the pnictogen bond. Thus, auxiliary effect of a pnictogen bond on a halogen bond is more pronounced than that of a halogen bond on a pnictogen bond. However, a strong synergy is predicted between halogen and pnictogen interactions in systems studied here. This is consistent with those reported for hydrogen bonds, halogen bonds, lithium bonds, and cation– π interactions.^{88–101}

The synergy between pnictogen bonding and halogen bonding can also be estimated by calculation of the cooperative energy. The cooperative energy values collected in Table S2 (Supplementary Information) could be used as a valuable quantity to evaluate the pnictogen bonds and halogen bonds interplay within the trimer complexes. The total interaction energy values of the trimer complexes are higher than those of the sum of the interaction energies of the

corresponding dimers $4\text{-YPhNH}_2\cdots\text{PH}_2\text{F}$ and $\text{PH}_2\text{F}\cdots\text{ClX}$, as could be seen in Table S2 (Supplementary Information), all of the calculated cooperative energies are negative, indicating that there is an enhancing synergistic effect between pnictogen bonding and halogen bonding in the $4\text{-YPhNH}_2\cdots\text{PH}_2\text{F}\cdots\text{ClX}$ ($\text{X} = \text{F}$, OH , CN , NC , FCC and NO_2 and $\text{Y} = \text{H}$, F , CN , CHO , NH_2 , CH_3 , NO_2 and OCH_3) trimers. The cooperative energies range from $-1.77 \text{ kcal mol}^{-1}$ in $4\text{-NH}_2\text{PhNH}_2\cdots\text{PH}_2\text{F}\cdots\text{Cl-F}$ to $-0.18 \text{ kcal mol}^{-1}$ in $4\text{-NO}_2\text{PhNH}_2\cdots\text{PH}_2\text{F}\cdots\text{Cl-OH}$. The E_{Coop} value in $4\text{-Y}_{1-4}\text{PhNH}_2\cdots\text{PH}_2\text{F}\cdots\text{ClX}$ complexes becomes more negative in the order: $\text{CCF} < \text{OH} < \text{NO}_2 < \text{CN} < \text{NC} < \text{F}$ and for those of $4\text{-Y}_{5-8}\text{PhNH}_2\cdots\text{PH}_2\text{F}\cdots\text{ClX}$ do not follow a certain trend. The E_{Coop} values and their order are comparable with those calculated by Li *et al.*, for $\text{H}_3\text{N}\cdots\text{XY}\cdots\text{HF}$ complexes (X , $\text{Y} = \text{F}$, Cl , Br).⁶⁴ For the same X substituent, E_{Coop} value increases as the electron-donating property of Y substituent increases.

The relation between total interaction energy and cooperative energy of the trimer complexes are plotted in Figure 3a. The linear correlation coefficients for this dependence are 0.955, 0.778, 0.921, 0.954, 0.940, 0.772 for $\text{X} = \text{F}$, OH , CN , CCF , NC and NO_2 , which shows that the cooperativity causes an increase in the stability of complexes. The linear correlation between cooperative energies in the studied trimer complexes (obtained at M06-2X/aug-cc-pVDZ level of theory) and Hammett's substituent constants (σ_p)¹⁰² is depicted in Figure 3b. As can be seen, E_{Coop} increases when the X changes from OH to F and from positive σ_p (for the electron-accepting group) to negative one (for the electron-donating group).

Dispersion interactions can be important for non-covalent complexes. Thus, dispersion corrected binding energies were calculated by using M06-2X-GD3, B2PLYP-GD3 and mPW2PLYP-GD2 functionals^{45,103,104} on the geometry obtained at M06-2X/aug-cc-pVDZ level of theory. Comparison of BEs obtained at M06-2X/aug-cc-pVDZ and M06-2X-GD3/aug-cc-pVDZ levels in Table S3 (Supplementary Information) shows that the dispersion corrected BEs are slightly greater than the uncorrected ones. It has been concluded that double hybrid functionals that combine both types of correlations (long-range and short-range correlations) are better than either conventional DFTs or MP2 methods.^{67,105} Accordingly, effects of the dispersion correction on the BEs were also investigated by double hybrid functionals B2PLYP-GD3 and mPW2PLYP-GD2 in conjunction with the aug-cc-pVDZ basis set. The results in Table S3 (Supplementary Information) indicate that the dispersion

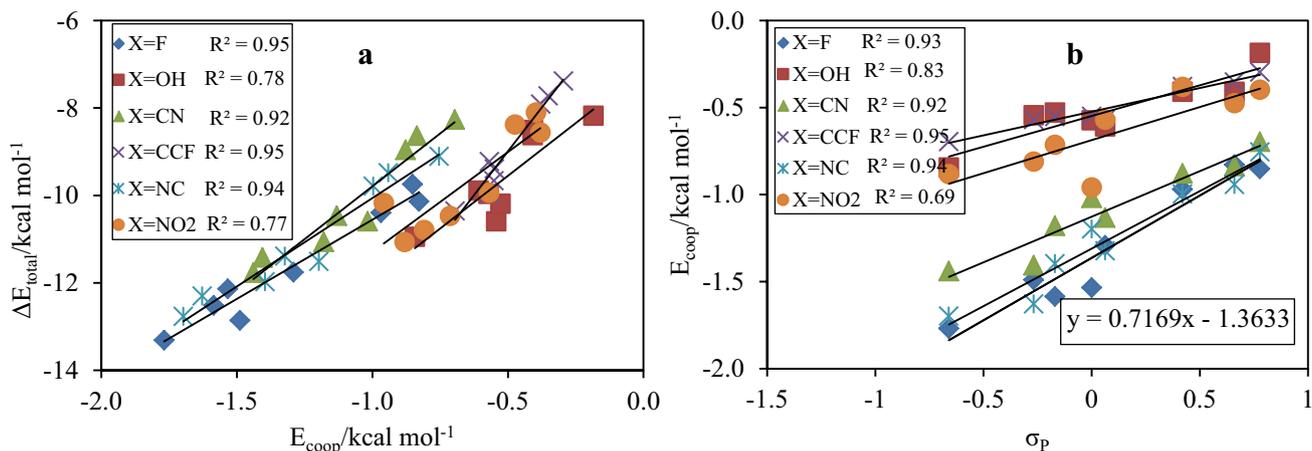


Figure 3. (a) Relationship between total interaction energy of trimers and cooperative energies (b) Correlation between cooperative energies with Hammett's constants (σ_p).

corrected BEs are about 1.78–3.06 kcal mol⁻¹ higher than uncorrected dispersion energies when B2PLYP-GD3 and mPW2PLYP-GD2 double hybrid density functionals are used. The difference between dispersion-corrected and dispersion-uncorrected BEs at M06-2X-GD3 level is lower than those obtained by employing double hybrid density functionals.

A correlation is predicted between V_{min} of N atom involved in pnictogen bond as a donor atom and pnictogen binding energy as shown in Figure 4a. From this figure, it could be concluded that with the higher negative electrostatic potentials for the N atom, the more stable pnictogen bonded complexes could be formed.

Depending on the nature of Y, the negative electrostatic potential on the F atom surface of PH₂F at 4-YPhNH₂...PH₂F is in the range from -23.42 to -32.56 kcal mol⁻¹. The electron-donating and electron-withdrawing Y substituents cause an increase or decrease in the negative electrostatic potential on the F atom surface and as a result the strength of interaction of the F atom with Cl during halogen bonding of the F...Cl type increases and decreases, respectively. Therefore, one could expect that the dimer systems of 4-YPhNH₂...PH₂F with electron donor Y substituents show the good cooperative effect and higher interaction energies than such systems with electron-withdrawing Y substituents during combination with Cl...X molecules in the trimers.

Correlations between cooperative energy as well as the total interaction energy of trimers and V_{min} values of the F atom surface of PH₂F at 4-YPhNH₂...PH₂F dimers are shown in Figure 4b and 4c, respectively. It is obvious that both types of energies increase as the V_{min} values increases. The strong linear correlation observed between V_{min} and BEs suggests that V_{min}

value may be taken as a good measure of the strength of the lone pair of N and F atoms involved in non-covalent pnictogen and halogen bonding interactions, respectively.

3.3 Structural parameters

The optimized structures of the 4-YPhNH₂...PH₂F...ClX (X = F, OH, CN, NC, FCC and NO₂ and Y = H, F, CN, CHO, NH₂, CH₃, NO₂ and OCH₃) trimers are illustrated in Figure 5. One can see that the Cl atom of ClX interacts with F atom of 4-YPhNH₂...PH₂F dimer. The binding distances of pnictogen bonds and halogen bonds in dimers and trimers, their variations and bonding angles are collected in Table S4 (Supplementary Information).

The pnictogen bond distances in the trimer complexes are in the range 2.446 Å (X = F and Y = NH₂)–2.782 Å (X = OH and Y = NO₂) whereas the halogen bond (Cl...F) distance range from 2.491 Å (X = F and Y = NH₂) to 2.833 Å (X = CCF and Y = NH₂), in good agreement with the BEs obtained for pnictogen and halogen bonded complexes. As can be seen, pnictogen bonds are shorter than halogen bonds in good agreement with those observed for similar systems reported in the literature.³²

The van der Waals radii of atoms involved in pnictogen and halogen bonds are 1.80, 1.55, 1.75 and 1.47 Å for P, N, Cl and F, respectively. As can be seen, the PB and halogen bond distances are smaller than the sum of the related van der Waals radii of atoms (3.35 Å for PB and 3.22 Å for halogen bond) involved in interactions. The difference between interaction distance and the sum of the van der Waals radii of atoms for PB interactions (0.904–0.568 Å) is greater than

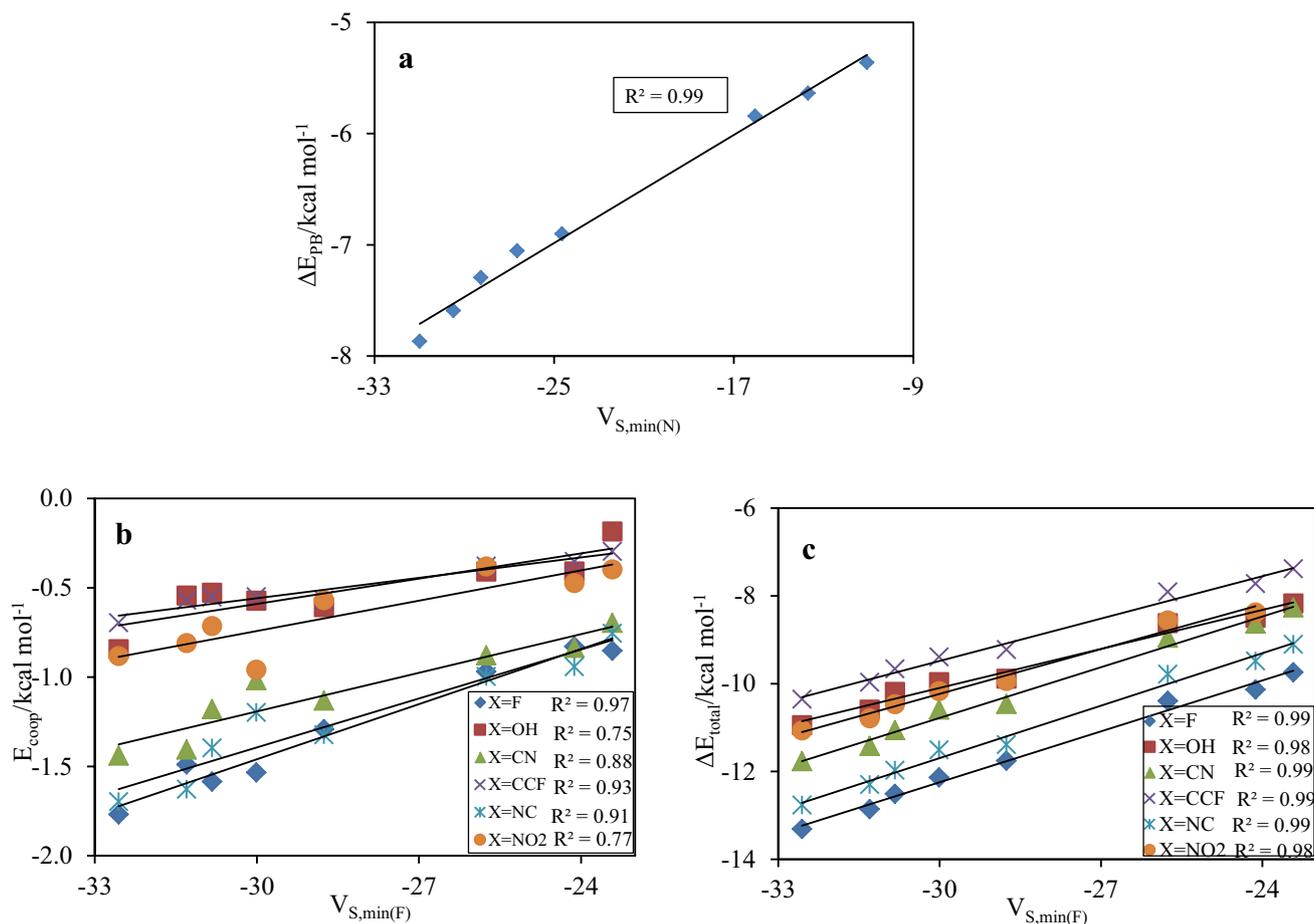


Figure 4. (a) Correlation between interaction energy of 4-YPhNH₂⋯PH₂F and V_{S,min} of N atom of 4-YPhNH₂ (b) Correlation between cooperative energy and (c) total interaction energy of trimers with negative electrostatic potential values on the F atom surface of PH₂F at 4-YPhNH₂⋯PH₂F dimers.

that of halogen bond interactions (0.729–0.517 Å), in good agreement with the stronger interaction predicted for PBs than halogen bonds.

The results also show that the pnictogen bonding distances in the trimers are shorter than those of the respective dimers (2.634–2.806 Å) which imply that the interactions in trimers are stronger than the corresponding dimers. In other words, Cl⋯F halogen bond formation decreases the P⋯N pnictogen bond distance and *vice versa*. The differences between pnictogen bond distances in the trimer (in the presence of halogen bonding) and dimer systems range from 0.035 (X = OH and Y = CN) to 0.201 Å (X = F and Y = OCH₃). For all X substituents, the greatest decrease in the P⋯N distance is found for Y = OCH₃ and smallest decrease is predicted for Y = NO₂ and CN. For a given Y, the greatest decrease in the P⋯N distance appears for X = F and smallest decrease is found for X = OH. Accordingly, there is a good consistency between the decrease in the P⋯N pnictogen bond distance and the increase in pnictogen BE ongoing from dimer to trimer, as can be seen in

Figure 6a. The greater decrease in P⋯N pnictogen bond distance is accompanied by a greater increase in pnictogen BE.

Similar behavior is observed for the effect of pnictogen bond formation on the halogen bond distance. The results show that the pnictogen P⋯N bond formation leads to a contraction of the Cl⋯F halogen bond distance, but amounts of decreasing for Cl⋯F is smaller than those observed for P⋯N bond, in good agreement with the magnitude of increase in corresponding BE that for pnictogen bond formation was greater than halogen bond one. Figure 6b shows the correlation between the decrease in Cl⋯F halogen bond distance and increase in Cl⋯F BE.

We have also found a correlation between cooperative energies and change in Cl⋯F as well as P⋯N bond distances. These correlations are displayed in Figures 6c and 6d. As can be seen, a decrease in both non-covalent Cl⋯F and P⋯N bond distances results in the increase in cooperative energy.

There are two different non-covalent interactions that stabilize the complexes namely, the halogen bond

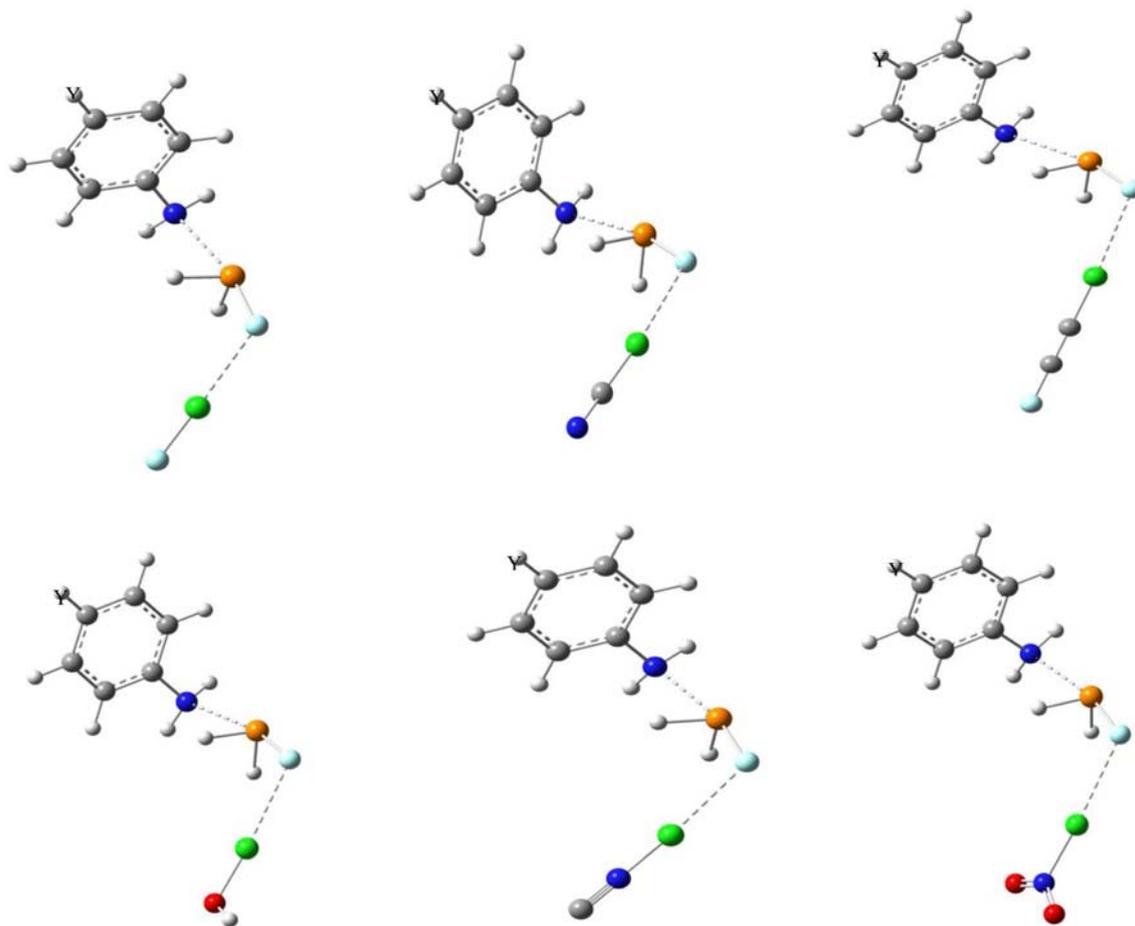


Figure 5. Optimized structures of the investigated trimers ($Y = \text{H, F, CN, CHO, NH}_2, \text{CH}_3, \text{NO}_2$ and OCH_3).

and the pnictogen bond. In all of the studied complexes, P and Cl atoms act as the electron acceptors, and N and F atoms act as electron donor atoms in pnictogen bond and halogen bond interactions, respectively. The nature of the X and Y substituents affect the extent of pnictogen and halogen bond distances. One sees that the interplay between the halogen bond and the pnictogen bond results in a considerable change in the binding distances. Generally, the change of the $\text{P}\cdots\text{N}$ distance is larger than that of the $\text{Cl}\cdots\text{F}$ distance in the trimers.

The $\theta_{\text{F-P}\cdots\text{N}}$ pnictogen bond angle ranges from 164.8° for $4\text{-CHOPhNH}_2\cdots\text{PH}_2\text{F}\cdots\text{Cl-F}$ to 168.0° for $4\text{-FPhNH}_2\cdots\text{PH}_2\text{F}\cdots\text{Cl-F}$ and the $\theta_{\text{X-Cl}\cdots\text{F}}$ halogen bond angle range from 166.0° for $4\text{-NO}_2\text{PhNH}_2\cdots\text{PH}_2\text{F}\cdots\text{Cl-NO}_2$ to 179.1° for $4\text{-NH}_2\text{PhNH}_2\cdots\text{PH}_2\text{F}\cdots\text{Cl-F}$.

3.4 AIM analysis

In order to gain a deep insight into the origin and nature of $\text{P}\cdots\text{N}$ pnictogen and $\text{Cl}\cdots\text{F}$ halogen bonding interactions, atoms in molecules analysis¹⁰⁶ (AIM) are

performed. The values of the electron density $\rho(r)$, Laplacian of the electron density $\nabla^2\rho(r)$, and the electronic energy density $H(r)$ at the bond critical points (BCPs) calculated at the M06-2X/aug-ccpVDZ level of theory are given in Table S5 (Supplementary Information). Generally, the electron density $\rho(r)$ value of a BCP is related to the strength of the bond: the larger the $\rho(r)$ is, the stronger the bond will be. The $\nabla^2\rho(r)$ of a BCP reflects the nature of the bond. If $\nabla^2\rho(r) < 0$, BCP charges will be concentrated, if $\nabla^2\rho(r) > 0$, BCP charges will be dispersed.

The calculated ρ_{BCP} values in $\text{P}\cdots\text{N}$ and $\text{Cl}\cdots\text{F}$ bonds are predicted to be in the range of the 0.0195 au ($X = \text{OH}$ and $Y = \text{NO}_2$) to 0.0406 au ($X = \text{F}$ and $Y = \text{NH}_2$) and 0.0124 au ($X = \text{CCF}$ and $Y = \text{CN}$) to 0.0236 au ($X = \text{F}$ and $Y = \text{NH}_2$), whereas, the values of $\nabla^2\rho_{\text{BCP}}$ are all positive, ranging from 0.0511 au ($X = \text{OH}$ and $Y = \text{NO}_2$) to 0.0664 au ($X = \text{F}$ and $Y = \text{NH}_2$) and 0.0540 au ($X = \text{CCF}$ and $Y = \text{CN}$) to 0.1025 au ($X = \text{F}$ and $Y = \text{NH}_2$), respectively. As can be seen, the ρ_{BCP} values at the both $\text{P}\cdots\text{N}$ and $\text{Cl}\cdots\text{F}$ bonds for $X = \text{F}$ and $Y = \text{NH}_2$ are greater than those found for other substituents, in good agreement with

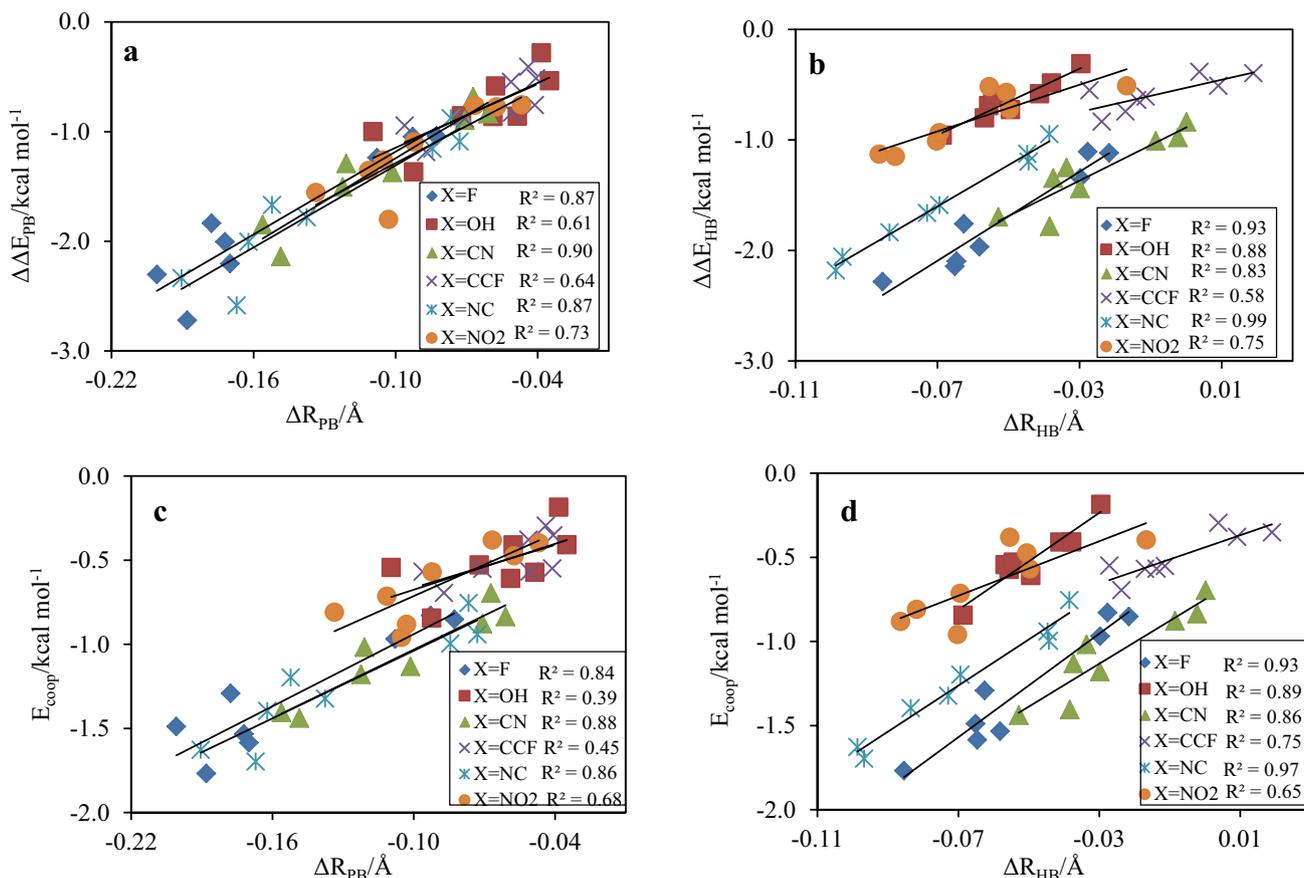


Figure 6. Plots of energy differences and cooperative energy versus the difference in interaction distance between dimers and trimmers for (a) and (c) pnicogen bond, and (b) and (d) halogen bond interactions.

the calculated corresponding BEs. Figures 7a, b show the relationship between the pnicogen BE and the electron density at the P...N and Cl...F bond critical points in the 4-YPhNH₂...PH₂F...CIX (X = F, OH, CN, NC, FCC and NO₂ and Y = H, F, CN, CHO, NH₂, CH₃, NO₂ and OCH₃) trimers, respectively. For all Y,

values of ρ at P...N BCPs increase as BEs increase. Similarly, for all X substituents, values of ρ at Cl...F BCPs increase as BEs increase.

The electronic energy density, H, can also offer deeper insight into the nature of the interactions. For positive H values, a purely closed-shell interaction

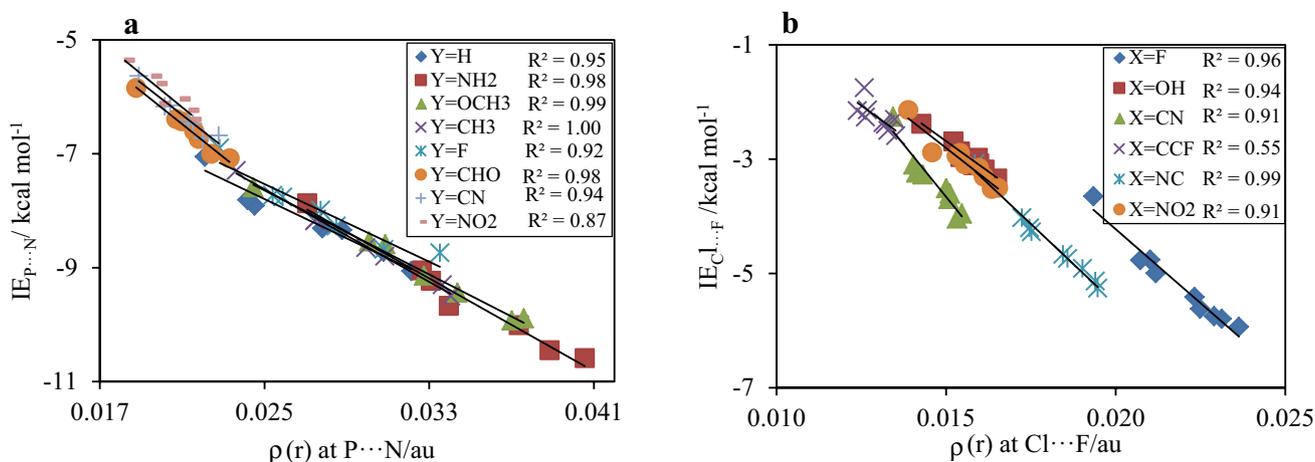


Figure 7. Relationship between the interaction energy (-BE) and the electron density at the P...N (a) and F...Cl (b) bond critical points in the 4-YPhNH₂...PH₂F...CIX (X = F, OH, CN, NC, FCC and NO₂ and Y = H, F, CN, CHO, NH₂, CH₃, NO₂ and OCH₃) trimers.

(electrostatic) is expected.¹⁰⁷ Otherwise, the negative H indicates that the interactions correspond to some degree of covalent character. Since H_{BCP} values computed at the P...N bond critical points are negative (with the exception of those found for $X = \text{NO}_2$ and $Y = \text{OH}$, CN and NO_2), so the pnictogen bonds in our studied complexes are partially covalent in nature. On the contrary, H_{BCP} values at the Cl...F bond critical points are positive, indicating the electrostatic nature of halogen bonds in all complexes studied here.

The values shown in Table S5 (Supplementary Information) indicate that the ρ_{BCP} and $\nabla^2\rho_{\text{BCP}}$ values at the P...N and Cl...F critical points in the triad are slightly greater than that in the corresponding dyad. This result confirms that the P...N and Cl...F interactions in the triad are reinforced with respect to the binary systems. Correlation between cooperative energy E_{coop} and electron density change at the P...N and Cl...F critical points in the 4-YPhNH₂...PH₂F...ClX complexes are shown in Figures 8a and 8b.

3.5 NBO analysis

The natural bond orbital analysis provides a deeper understanding of the synergy between the pnictogen bonds and halogen bonds in 4-YPhNH₂...PH₂F...ClX complexes. The NBO analysis was carried out at M06-2X/aug-cc-pVDZ level. To study the role of charge transfer in cooperative effects, NBO analysis was performed for the dyad and triad complexes and the results are summarized in Tables S6 and S7 (Supplementary Information).

The main pnictogen bond and halogen bond orbital interactions within the trimer complexes studied are $\text{LP}(\text{N}) \rightarrow \text{LP}^*(\text{P})$ and $\text{LP}(\text{F}) \rightarrow \sigma^*(\text{Cl-X})$, respectively. One can see that the formation of P...N and Cl...F interactions in each ternary system is accompanied by electronic charge transfer from the lone pair of the electron donor to the σ^* antibonding orbitals of the Lewis acids. The nature of these interactions can be affected by substituents inserted in the para position of aniline.

An analysis of NBO data of dyads and triads to examine cooperative effects indicates the significant cooperativity between the pnictogen and halogen bonds in these complexes. By comparison of the charge transfer energies, $E^{(2)}$, in dyads and triads, a positive cooperativity could be expected because of the higher values of the charge transfer energies for triads than those of dyads. For instance, the sum of the $E^{(2)}$ value for P...N interaction of 4-YPhNH₂...PH₂F...ClX is in the range of 15.77–49.94 kcal mol⁻¹, which is 2.18–24.65 kcal mol⁻¹ larger than those of found for binary 4-YPhNH₂...PH₂F complexes. As expected, the largest increase of the $E^{(2)}$ value associated with $\text{LP}(\text{N}) \rightarrow \text{LP}^*(\text{P})$ interaction is found for the complex 4-NH₂PhNH₂...PH₂F...Cl-F (49.94 kcal mol⁻¹), consistent with its greater pnictogen BE (10.59 kcal mol⁻¹). Also, the smallest value of $E^{(2)}$ (15.77 kcal mol⁻¹) corresponds to the 4-NO₂PhNH₂...PH₂F...Cl-OH with smallest pnictogen BE in trimer. Figure 9a shows correlation from dimer to trimer systems. For a given X substituent, as the electron attracting power of the Y substituent increases the

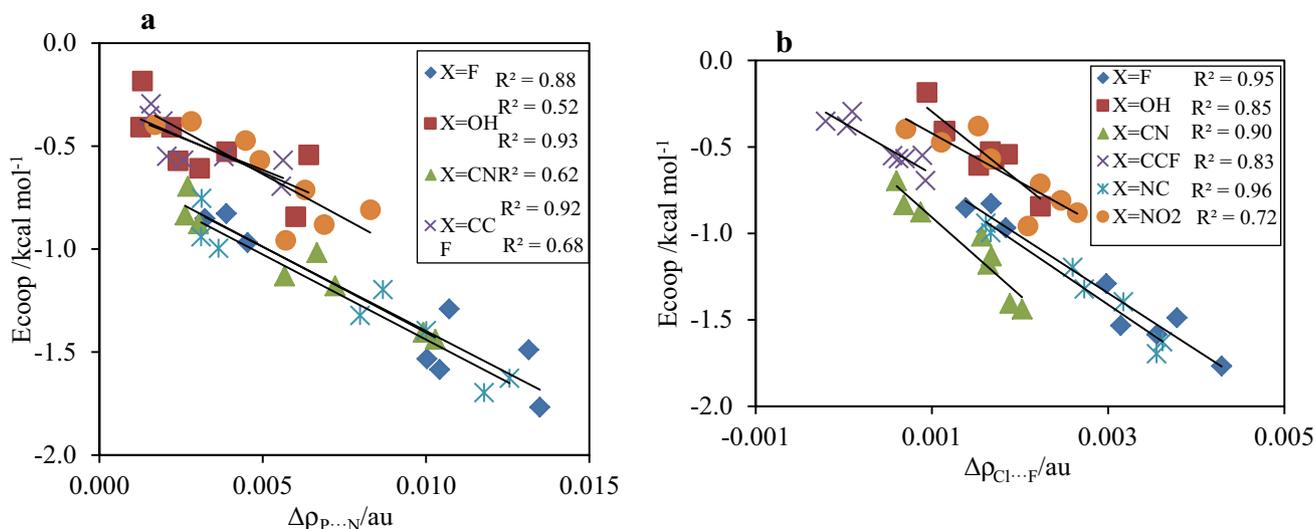


Figure 8. Correlation between cooperative energy E_{coop} and electron density change at the (a) P...N and (b) Cl...F critical points in ongoing from dimers to 4-YPhNH₂...PH₂F...ClX trimers.

values of the charge transfer energy of $LP(N) \rightarrow LP^*(P)$ interaction decrease.

In addition, comparison of the $\sum E^{(2)}$ values correspond to the $LP(F) \rightarrow \sigma^*(Cl-X)$ halogen bonding interaction in dimers $PH_2F \cdots ClX$ and trimers $4-YPhNH_2 \cdots PH_2F \cdots ClX$ reveals that the $Cl \cdots F$ interaction in $4-YPhNH_2 \cdots PH_2F \cdots ClX$ triads is strengthened with respect to the $PH_2F \cdots ClX$ dyads. The presence of pnictogen bond increases the value of the charge transfer energy corresponds to the $LP(F) \rightarrow \sigma^*(Cl-X)$ interaction and, in turn, the strength of the $Cl \cdots F$ interaction. The estimated $E^{(2)}$ value for $LP(F) \rightarrow \sigma^*(Cl-X)$ halogen bond interaction in the $4-YPhNH_2 \cdots PH_2F \cdots ClX$ complexes is in the range of $1.73\text{--}8.98 \text{ kcal mol}^{-1}$, which is $0.09\text{--}2.61 \text{ kcal mol}^{-1}$ greater than those of found for binary $PH_2F \cdots ClX$ complexes. These results show that $E^{(2)}$ values correspond to the $LP(F) \rightarrow \sigma^*(Cl-X)$ interaction are smaller than those of $LP(N) \rightarrow LP^*(P)$ interaction but existence of pnictogen bond significantly increases the $LP(F) \rightarrow \sigma^*(Cl-X)$ interaction energy, as reported for similar systems.³² Figure 9b shows correlation between $\sum E^{(2)}$ and halogen BE in triads. The BE increases when the charge transfer energy increases. The results show an increase in $\sum E^{(2)}$ and BE on going from dyads to triads. For a given Y substituent, as the electron attracting power of the X substituent increases the values of the charge transfer energy of $LP(F) \rightarrow \sigma^*(Cl-X)$ interaction increase. Besides, for a given X, because of increase in electron density of F atom, when the Y changes from the electron-accepting group to electron-donating one, the charge transfer energy of $LP(F) \rightarrow \sigma^*(Cl-X)$ interaction increases.

Interrelation of changes in pnictogen and halogen bond distances on going from dyads to triads with changes in charge transfer energies $E^{(2)}$ and charge transfer values (CT) are depicted in Figure 10.

As can be seen, the amount of decrease in bond distances for interactions with larger $E^{(2)}$ and CT is greater than those of with smaller ones. In other words, interaction energy and charge transfer value increases as the amount of non-covalent bond distances decrease.

The Wiberg bond index (WBI) provides a relative scale for the strength of bond interaction between two atoms and could be useful to estimate the strength of different types of non-covalent bond interactions such as pnictogen bond, halogen bond, etc.¹⁰⁸ One sees from Table S7 (Supplementary Information) that the WBI at the $P \cdots N$ bond (0.075–0.177) is far larger than that at the $Cl \cdots F$ bond (0.008–0.045). This confirms that the pnictogen bond in triads is stronger than the halogen bond.

It is apparent from the Table S7 (Supplementary Information) that the WBI at the $P \cdots N$ bond of $4-YPhNH_2 \cdots PH_2F \cdots ClX$ complex is greater for an electron-donating substituent Y than an electron-withdrawing one, in good agreement with the BEs and charge transfer energies $E^{(2)}$. In addition, the data in Table S7 (Supplementary Information) show that the WBI values for both of $P \cdots N$ and $Cl \cdots F$ bonds in the trimer complexes are greater than those values in the dimers. These findings are in agreement with the observed positive cooperativity within trimer systems. The correlation between the WBI of $P \cdots N$ pnictogen bonds and WBI of $Cl \cdots F$ halogen bonds of trimer systems is depicted in Figure 11. From the positive slope of this plot, it is clear that positive cooperativity exists between the two titled interactions.

3.6 NMR analysis

Main parameters, measured in NMR spectroscopy, are chemical shifts and scalar spin-spin couplings between

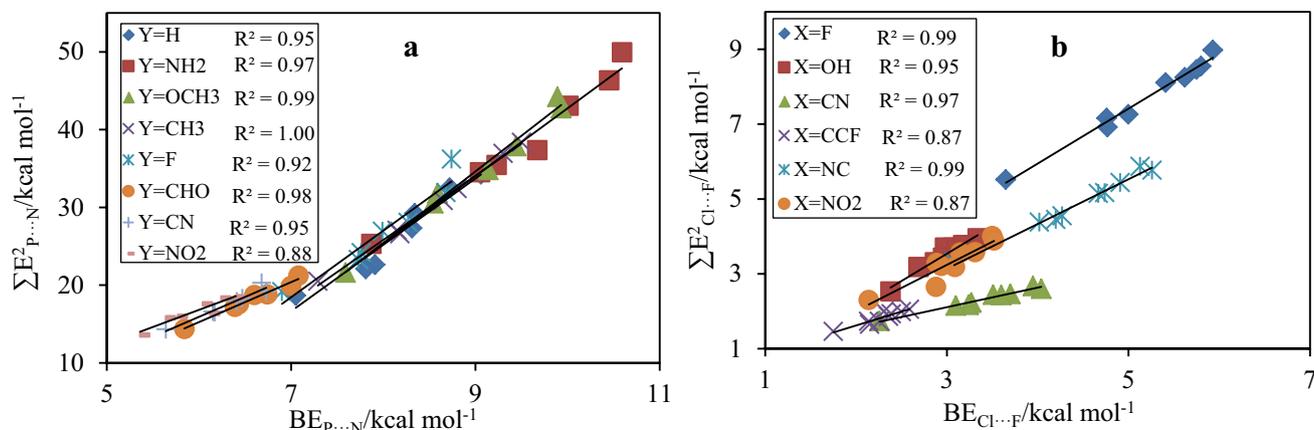


Figure 9. Correlation between $\sum E^{(2)}$ values and (a) Pnictogen BEs (b) Halogen BEs. The values for dyads are also included.

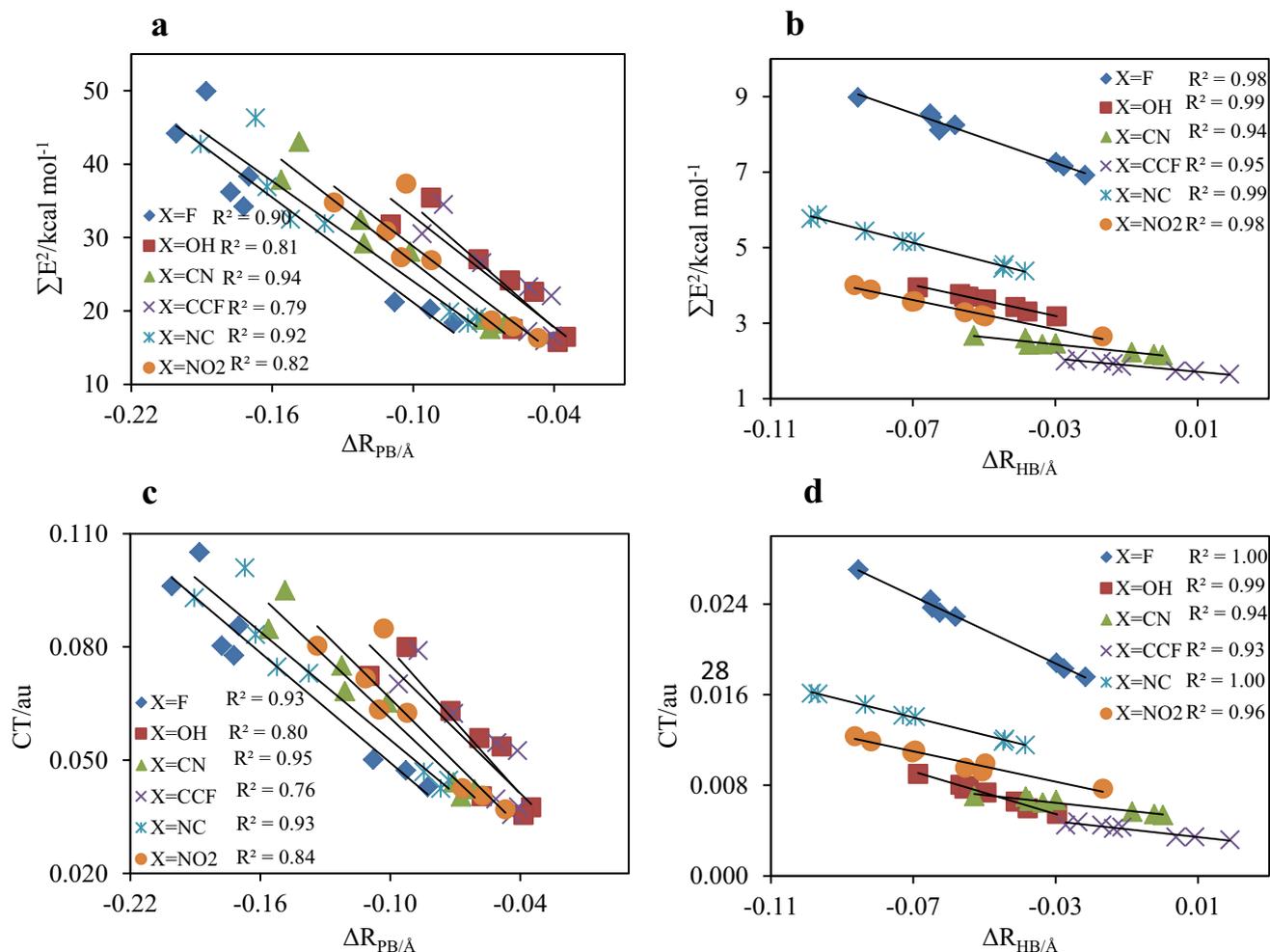


Figure 10. Correlation of ΔR with second order stabilization energy ($E^{(2)}$) and charge transfer (CT) for pnictogen bonds (PB) and halogen bonds (HB) in the 4-YPhNH₂...PH₂F...CIX (X = F, OH, CN, NC, FCC and NO₂ and Y = H, F, CN, CHO, NH₂, CH₃, NO₂ and OCH₃) complexes.

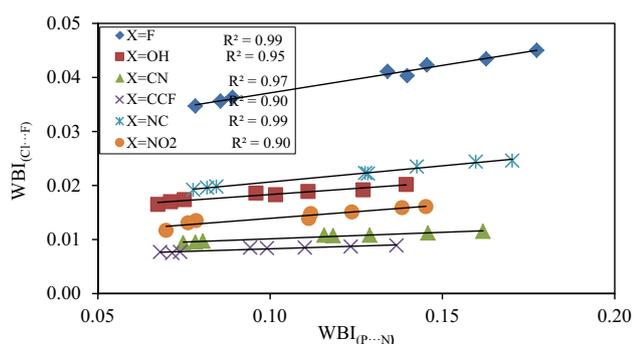


Figure 11. Correlation between WBI of P...N pnictogen bonds and WBI of Cl...F halogen bonds of trimer systems.

adjacent or closely located nuclei. The chemical shift is a characteristic of magnetic shielding of a nucleus by electron shell of a molecule; it is a specific characteristic of a given atom in a molecule. Scalar spin-spin coupling constant J is a characteristic of indirect interaction energy of the magnetic moments of non-

equivalent nuclei through electron shell of a molecule. Scalar spin-spin couplings between nuclei of donor and acceptor groups give valuable information about the overlapping of electron clouds of partner groups upon formation of non-covalent bonding.^{109–111}

Table S8 (Supplementary Information) shows the chemical shielding and spin-spin coupling constants ${}^{15}\text{N}$ across the pnictogen interaction in the ternary complexes obtained at M06-2X/aug-cc-pVDZ level of theory. As noted above, the formation of the P...N bond is expected to strongly affect the electronic environment at the pnictogen bonded nuclei. Thus, the cooperative effects in electronic structure induced by Cl...F bond formation can influence the ${}^{31}\text{P}$ NMR properties in the ternary complexes.

The ${}^{31}\text{P}$ chemical shielding in trimers varies from 316.5 ppm in the 4-NO₂PhNH₂...PH₂F...ClOH to 374.1 ppm in the 4-NH₂PhNH₂...PH₂F...ClCN. For all trimers investigated in this work, the ${}^{31}\text{P}$ chemical shielding exhibits a linear correlation with the

intermolecular P...N distance. Figure 12a shows a plot of the ^{31}P chemical shielding as a function of the P...N distance for these complexes. The trend for ^{31}P chemical shielding shows a correlation with pnictogen BE, $\sum E^{(2)}$ values correspond to the LP(N) \rightarrow LP*(P) and electron density at P...N BCPs as shown in Figures 12b, c and d.

The spin-spin coupling constants $^{1}\text{P}J$ across the PB in the ternary complexes range from -4.39 in 4-NH₂-PhNH₂...PH₂F...Cl-F to -30.43 in 4-NO₂PhNH₂...PH₂F...Cl-OH. The correlation between the spin-spin coupling constant $^{1}\text{P}J$ and, BE, P...N distance, electron density at P...N BCPs and $\sum E^{(2)}$ value are depicted in Figure 13. Formation of Cl...F interaction tends to change σ_{iso} (^{31}P) values in the 4-YPhNH₂...PH₂F...Cl-X complexes. The largest change is seen for the 4-YPhNH₂...PH₂F...Cl-OH complex, while the smallest change occurs for 4-YPhNH₂...PH₂F...Cl-F. On the other hand, cooperative effects in the ternary complexes make a decrease in the total $^{1}\text{PB}J(^{31}\text{P}\dots^{15}\text{N})$ coupling constants. This is another proof of the reinforcement of P...N bonds in the ternary complexes with respect to the binary systems. For Y = H, NH₂, OCH₃ and CH₃, $^{1}\text{PB}J(^{31}\text{P}\dots^{15}\text{N})$ increases in the order

X = OH < CCF < NO₂ < CN < NC < F, which is in line with the calculated total interaction energies.

3.7 Energy decomposition analysis (EDA)

The energy decomposition analysis gives the best measurement of the origin and nature of intermolecular interactions. In order to understand the synergetic mechanism of the pnictogen and halogen bonds in the trimer, energy decomposition analysis (EDA) was carried out. The results for the ΔE_{int} values for the 4-YPhNH₂...PH₂F...Cl-X (X = F, OH and NC; Y = H, F, CN, CHO, NH₂, CH₃, NO₂ and OCH₃) complexes are close to those obtained at M062X/aug-cc-pVDZ. The interaction energy was partitioned into four parts: electrostatic interaction (ΔE_{elstat}), orbital interaction (ΔE_{orb}), Pauli repulsion (ΔE_{Pauli}) and the dispersion energy between two fragments (ΔE_{disp}), suggesting that in the 4-YPhNH₂...PH₂F...Cl-X complexes, the main portion is attributed to ΔE_{elstat} (about 44–51% for pnictogen bond and 47–54% for halogen bond), followed by ΔE_{orb} , with 37–42% for pnictogen bond and 30–42% for halogen bond (Table S9, SI). The

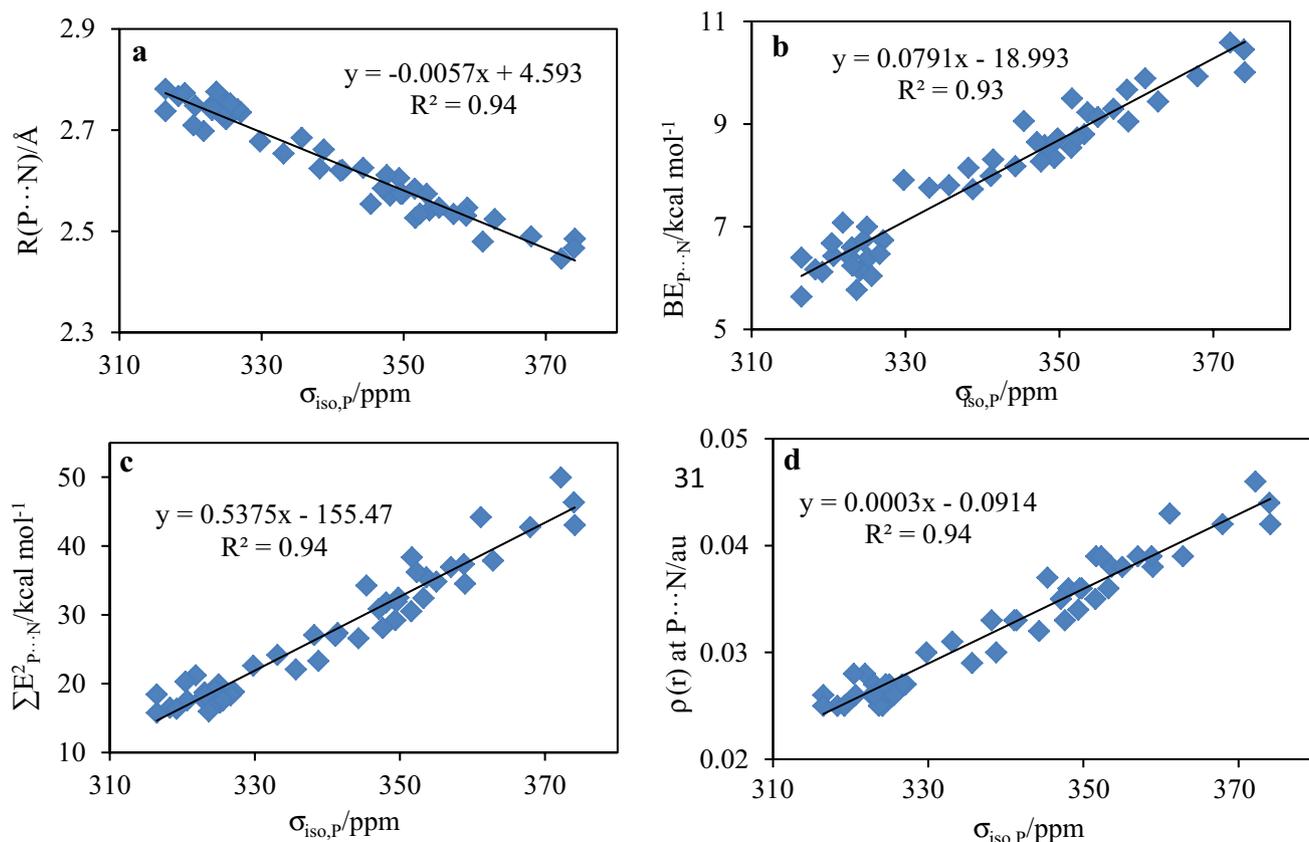


Figure 12. Correlation of ^{31}P chemical shielding with $R(\text{P}\dots\text{N})$, pnictogen BE, $\sum E^{(2)}$ and electron density at P...N BCPs in trimers.

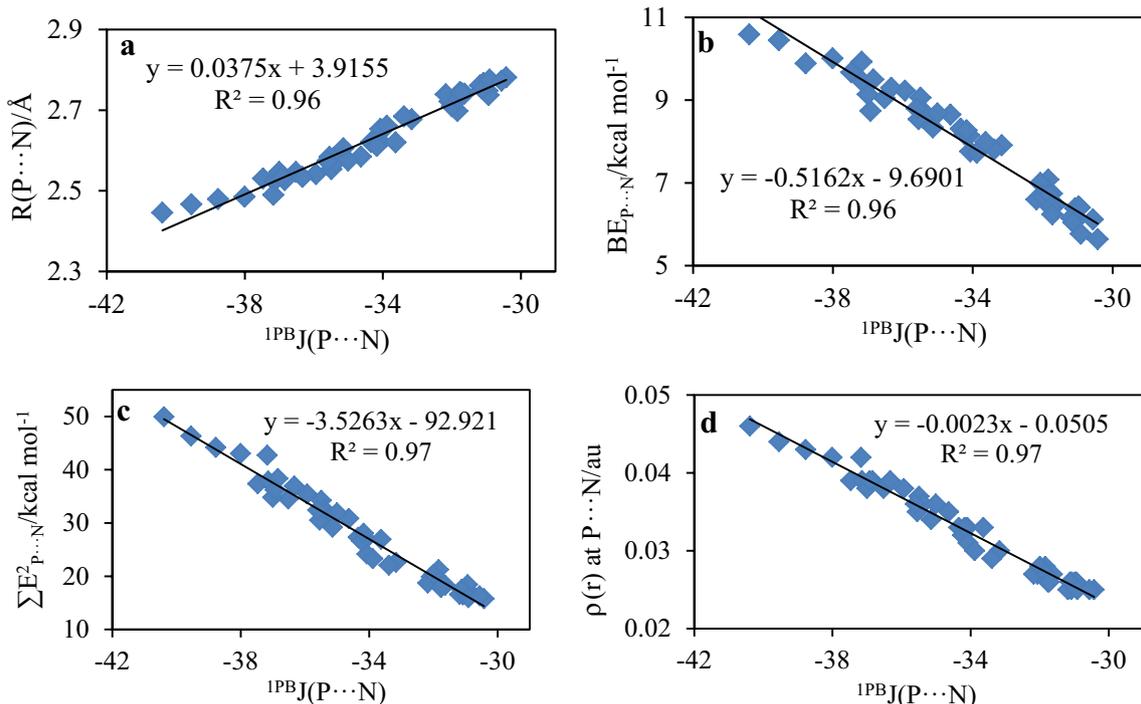


Figure 13. Correlation between the spin–spin coupling constant 1P_J with $R(P\cdots N)$, pnictogen BE, $\sum E^{(2)}$ and electron density at $P\cdots N$ BCPs in trimers.

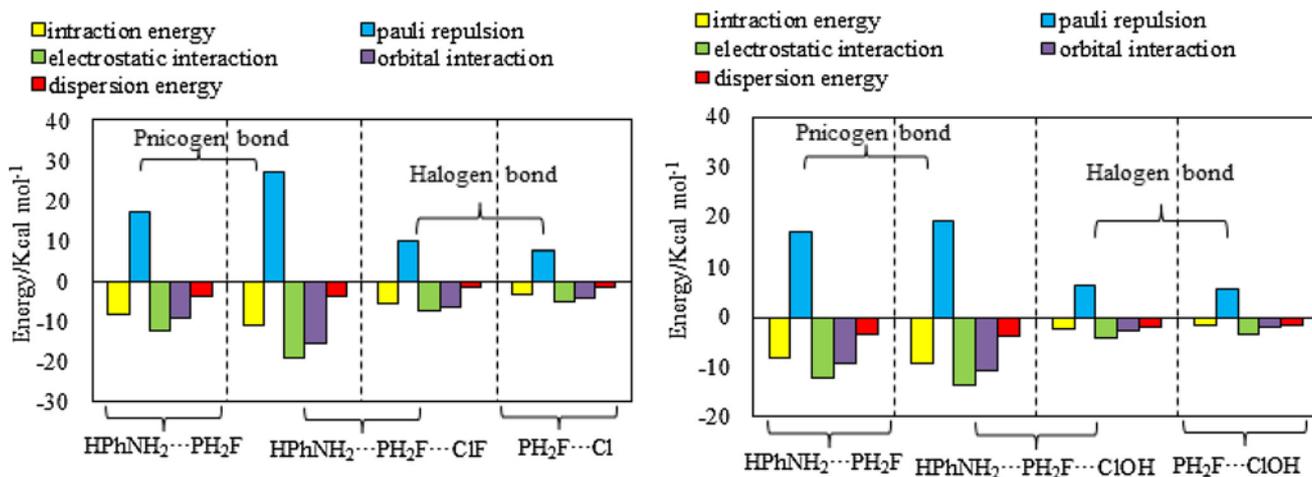


Figure 14. Bar graph illustrating the EDA of the total interaction energy of the $PH_2F\cdots ClF$, $HPhNH_2\cdots PH_2F\cdots ClF$ and $HPhNH_2\cdots PH_2F$; $PH_2F\cdots ClOH$, $HPhNH_2\cdots PH_2F\cdots ClOH$ and $HPhNH_2\cdots PH_2F$ complexes at the M06-2X/aug-cc-pVDZ level.

results confirm that ΔE_{disp} , which arises from the instantaneous dipole–induced dipole forces between two fragments ($4-YPhNH_2$ and PH_2F/PH_2F and ClX), has a significant effect (about 7–18% for pnictogen bond and 9–23% for halogen bond) in ΔE_{int} . The EDA results also indicate that the greatest and smallest interaction energies correspond to $4-NH_2PhNH_2\cdots PH_2F\cdots Cl-F$ and $4-NO_2PhNH_2\cdots PH_2F\cdots Cl-OH$ for

both types of interactions in the trimers, respectively. As shown in Figure 14 for the $4-HPhNH_2\cdots PH_2F\cdots Cl-F$ and $4-HPhNH_2\cdots PH_2F\cdots Cl-OH$ trimers, all terms have an increase in magnitude for pnictogen bond and halogen bond interactions. In all trimers, the ES term has the biggest increase; hence, the ES term is also of greater importance in reinforcing the halogen bond with the pnictogen bond.

4. Conclusions

In the present study, the interplay between pnictogen and halogen bonds in the 4-YPhNH₂...PH₂F...Cl-X (Y = H, F, CN, CHO, NH₂, CH₃, NO₂ and OCH₃; X = F, OH, CN, NC, FCC and NO₂) complexes were studied using DFT calculations at the M06-2X/aug-cc-pVDZ level. Our results verified that both types of interactions have a synergetic effect on each other. The existence of a positive cooperativity between pnictogen and halogen bonds type interactions is confirmed by geometric and energetic parameters, MESP, NMR, NBO and AIM analyses. Comparison of BE obtained at M06-2X, B2PLYP and mPW2PLYP levels with M06-2X-GD3, B2PLYP-GD3 and mPW2PLYP-GD2 levels show that the dispersion corrected BEs are slightly greater than uncorrected ones. For same X substituent, E_{Coop} value increases as the electron-donating property of Y substituent increases. A correlation is predicted between V_{min} of N atom involved in pnictogen bond as a donor atom and pnictogen binding energy. The results show that the pnictogen bonds are shorter than halogen bonds. In addition, the pnictogen bonding distances in the trimers are shorter than those of the respective dimers, indicating that the interactions in trimers are stronger than the corresponding dimers. The AIM results show that halogen bonds have the character of closed-shell interactions while pnictogen bonds are partially covalent in nature. A correlation between cooperative energy E_{coop} and electron density change at the P...N and Cl...F critical points was found in the 4-YPhNH₂...PH₂F...ClX complexes. The BE triads increase as the charge transfer energy increases. For a given X substituent, as the electron attracting the power of the Y substituent increases the values of the charge transfer energy of LP(N) → LP*(P) interaction decrease. The presence of pnictogen bond increases the value of the charge transfer energy corresponds to the LP(F) → σ*(Cl-X) halogen bonding interaction and, in turn, the strength of the Cl...F interaction. The results show that E⁽²⁾ values correspond to the LP(F) → σ*(Cl-X) interaction are smaller than those of LP(N) → LP*(P) interaction but existence of pnictogen bond significantly increases the LP(F) → σ*(Cl-X) interaction energy and *vice versa*. A correlation was found between the ³¹P chemical shielding and intermolecular P...N distance. The results of EDA calculations suggest that in the studied complexes, the attractive interactions are mainly electrostatic (about 44–51% for pnictogen bond and 47–54% for halogen bond), followed by orbital interactions (with a percentage in the range 37–42% for pnictogen bond and 30–42% for halogen bond).

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary Information (SI)

Tables S1–S9 are available at www.ias.ac.in/chemsci.

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