Three Types Halogen Bond Interaction Studied Between Pyrazine And XF

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Abstract

Except σ-type and π-type halogen bond, a new type of the parallel halogen bond interactions between pyrazine ($C_4H_4N_2$) and XF (X=F,Cl,Br and I) have been discovered at the MP2/aug-cc-pVTZ level. Through comparing the calculated interaction energy, we can know that the π-type halogen bonding interactions are weaker than the corresponding σ-type halogen bonding interactions, and parallel halogen-bond interactions are weaker than the corresponding π-type halogen bonding interactions in $C_4H_4N_2$-XF complexes. SAPT analysis shows that the electrostatic energy are the major source of the attraction for the σ-type halogen bonding interactions while the parallel halogen-bond interactions are mainly dispersion energy. For the π-type halogen bonding interactions in $C_4H_4N_2$-XF(X=F and Cl) complexes, electrostatic energy are the major source of the attraction, while in $C_4H_4N_2$-XF(X=Br and I) complexes the electrostatic term, induction and dispersion play equally important role in the total attractive interaction. NBO analysis, AIM theory and Conceptual DFT are also be utilized.

1. Introduction

In recent years, the research of halogen bond has become a hot pot [1–16]. Electrostatic surface potentials is very versatile and powerful tool for discovering the interaction properties of halogen bonds [17–20]. Figure 1 illustrates that the electrostatic surface potentials of pyrazine ($C_4H_4N_2$) and dihalogen molecule XF (X=F, Cl, Br and I). Pyrazine has two nitrogen atoms on the 1,4-position to replace the carbon atom on the benzene ring. Compared with benzene analogues, pyrazine has many functions and reactivity. As can been see from Figure 1 that a blueness region of nitrogen atom represents the most negative electrostatic surface potential, and there are positive electrostatic potentialis on both the upper and lower surfaces of pyrazine ring. For the dihalogen molecule XF (X=F, Cl, Br and I), a red region with σ-hole was discovered on the tip of the X atom is the electropositive potential region. If the dihalogen molecule XF interacts with pyrazine, except σ-type and π-type halogen bond, a new type of the parallel halogen bond interactions between XF (X=F,Cl,Br,I ) and pyrazine have been discovered.

In the present study, we discussed the three types halogen bond interaction between pyrazine and XF (X=F,Cl,Br and I ). The purpose of this work is to explore the bonding nature of the σ-type halogen bond,π-type halogen bond and parallel halogen bonds of the studied dimer. The strength of the σ-type,π-type halogen bond and parallel halogen bond are also compared.

2. Methodology

The geometric structure of the dimers and isolated monomers were fully optimized by MP2 method with the aug-cc-pVTZ (aug-cc-pVTZ-pp for Br and I) basis sets [21, 22] applying the Gaussian 03 [23]. At the same time, the vibration frequency is calculated at the same level to ensure that the optimized structure has real frequency and stability. The interaction energies have been corrected for basis set superposition error (BSSE) using counterpoise method which is put forward by Boys and Bernardi [24]. The single-point computations have been carried out on the MP2/aug-cc-pVTZ optimized geometry at CCSD(T)/aug-cc-
pVTZ level [25]. To understand the interaction of σ-type, π-type and parallel halogen bond of these dimeres, the NBO population analysis [26] was performed at the same level.

The electrostatic surface potentials on the 0.001 au were calculated by WFA-SAS procedure [27]. To further our understanding of the three types halogen bond interaction, the concept of DFT [28–30] is used to study the reaction properties of the interacting molecules in the σ-type, π-type and parallel halogen bond complexes. In addition, the QTAIM (quantum theory of atoms in molecules) [31] has been used to analyze the chemical bond between two adjacent atoms. The QTAIM topological analysis was carried out by the AIMAll program [32]. Furthermore, the SAPT method [33, 34] has been utilized to decompose the interaction energy of σ-type, π-type and parallel halogen bond by the SAPT2016 [35].

3. Results And Discussion

3.1 Interaction Energies of the σ-type, π-type and parallel halogen bond complexes

Figure 2 illustrates the geometry optimizations structures for the minimum energy of σ-type, π-type and parallel halogen bond complexes of the pyrazine and XF (X=F, Cl, Br and I). For all types of halogen atom X=F, Cl, Br and I, σ-type and π-type halogen-bonded minimum was located. However parallel halogen-bonded minima were only found for X = Cl, Br or I. The interaction energies of these parallel halogen bond σ-type and π-type halogen bond complexes are shown in Table 1.
Table 1

ΔE, BSSE and with BSSE correction (ΔE_{CP}) in kcal/mol. V_{s,max} in kcal/mol related with the X of XF and V_{s,min} on the XF surface

| σ-type halogen bond complexes | MP2/aug-cc-pVTZ | CCSD(T)/aug-cc-pVTZ | | | | |
|---|---|---|---|---|---|---|
| | ΔE | BSSE | ΔE_{CP} | ΔE | BSSE | ΔE_{CP} | V_{s,max} |
| C_4H_4N_2-F_2(I) | -2.31 | 0.63 | -1.68 | -2.22 | 0.51 | -1.71 | 8.4 |
| C_4H_4N_2-ClF (I) | -14.14 | 1.52 | -12.62 | -13.78 | 1.21 | -12.57 | 39.4 |
| C_4H_4N_2-BrF(I) | -22.68 | 5.16 | -17.53 | -21.57 | 4.73 | -16.84 | 40.8 |
| C_4H_4N_2-IF(I) | -24.24 | 4.99 | -19.25 | -23.68 | 4.21 | -19.47 | 46.4 |
| π-type halogen bond complexes | ΔE | BSSE | ΔE_{CP} | ΔE | BSSE | ΔE_{CP} | V_{s,min} |
| C_4H_4N_2-F_2 (II) | -1.90 | 0.74 | -1.16 | -1.73 | 0.62 | -1.11 | -2.1 |
| C_4H_4N_2-ClF(II) | -4.22 | 0.97 | -3.25 | -3.94 | 0.76 | -3.18 | -8.6 |
| C_4H_4N_2-BrF(II) | -8.32 | 3.86 | -4.46 | -7.86 | 3.51 | -4.35 | -17.7 |
| C_4H_4N_2-IF(II) | -9.34 | 4.17 | -5.17 | -8.94 | 3.56 | -5.38 | -22.3 |

Parallel halogen Bondcomplexes

| | ΔE | BSSE | ΔE_{CP} | ΔE | BSSE | ΔE_{CP} | V_{s,min} |
|---|---|---|---|---|---|---|---|
| C_4H_4N_2-ClF(Ш) | -3.21 | 0.94 | -2.27 | -2.94 | 0.78 | -2.16 | -8.6 |
| C_4H_4N_2-BrF(Ш) | -5.36 | 2.78 | -2.58 | -5.12 | 2.45 | -2.67 | -17.7 |
| C_4H_4N_2-IF(Ш) | -5.96 | 2.83 | -3.13 | -5.68 | 2.42 | -3.26 | -22.3 |

As shown in the Table 1, the difference of interaction energies corrected for BSSE attained by MP2 and CCSD(T) level has been small. That suggests that MP2/aug-cc-pVTZ provided reliable calculation results for the σ-type, π-type and parallel halogen bond of these investigated dimers. The binding energies of these σ-type, π-type and parallel halogen bond all gradually increased orderly from from X=F to X=I of XF. For σ-type halogen bonded dimers, this order is close association with the maximum positive electrostatic potentials (V_{s,max}) of the σ-hole related with the X of XF, corresponding coefficients is 0.9717. Relative to the corresponding π-type and parallel halogen bond, this order is close association the maximum negative electrostatic potential (V_{s,min}) on the XF surface, corresponding coefficients is 0.9776 and 0.9403, as shown in Figure 3.

A diagrams of the ΔE_{CP} energies of these σ-type, π-type and parallel halogen-bonded minimum structure in Figure 4 reveal that the π-type halogen bonding interactions are weaker than the corresponding σ-type
halogen bonding interactions, and parallel halogen-bond interactions are weaker than the corresponding π-type halogen bonding interactions in C₄H₄N₂-XF complexes.

3.2 NBO population analysis.

We used Natural bond orbital (NBO) to analysis the studied σ-type, π-type and parallel halogen-bonded complexes. The value of $\Delta Q$ (charge transferred from donor to the acceptor) and $\Delta E^2$ (the second-order perturbation energy) is shown in Table 2. For the σ-type halogen-bonded complexes, the charge transfer from the lone electron pair of the N atom of pyrazine was directed mainly at the X-F antibonding orbitals of the XF. For the π-type halogen-bonded complexes, the charge transfer from the bonding orbitals for the C₄⁻C₅ in the C₄H₄N₂ is mainly refers to the C-N antibonding orbitals of the XF. In regard to parallel halogen-bonded complexes, the charge transfer from the lone electron pair of the F and X atom of XF was directed mainly at the C-N antibonding orbitals of in the C₄H₄N₂.
Table 2
The NBO analysis of C₄H₄N₂-XF complexes (ΔQ in au, ΔE² in kcal/mol)

| Complex               | Donor NBOs | Acceptor NBOs | ΔE²  | ΔQ  | ΔEcp |
|-----------------------|------------|---------------|------|-----|------|
| **σ-type halogen bond complexes** |            |               |      |     |      |
| C₄H₄N₂-F₂(I)         | LP N       | BD* F - F     | 4.92 | 0.014 | -1.68 |
| C₄H₄N₂-ClF (I)       | LP N       | BD* Cl- F     | 83.78 | 0.154 | -12.62 |
| C₄H₄N₂-BrF(I)        | LP N       | BD* Br-F      | 98.30 | 0.148 | -17.53 |
| C₄H₄N₂-IF(I)         | LP N       | BD* I- F      | 104.89 | 0.108 | -19.25 |
| **π-type halogen bond complexes** |            |               |      |     |      |
| C₄H₄N₂-F₂ (II)       | BD C4-C5   | BD* F - F     | 2.83  | 0.004 | -1.16 |
| C₄H₄N₂-ClF(II)       | BDC4-C5    | BD*Cl- F      | 10.02 | 0.022 | -3.25 |
| C₄H₄N₂-BrF(II)       | BD C4-C5   | BD*Br- F      | 21.35 | 0.044 | -4.46 |
| C₄H₄N₂-IF(II)        | BD C4-C5   | BD* I- F      | 38.63 | 0.050 | -5.17 |
| **parallel halogen bond complexes** |            |               |      |     |      |
| C₄H₄N₂-ClF(Ш)        | LP Cl      | BD*N3 - C4    | 0.16  | 0.004 | -2.27 |
|                       | LP Cl      | BD* C5 - N6   | 0.16  |       |       |
|                       | LP F       | BD*N3 - C4    | 0.22  |       |       |
|                       | LP F       | BD* C5 - N6   | 0.22  |       |       |
|                       |            |               | 0.22  | (sum 0.76) |       |
| C₄H₄N₂-BrF(Ш)        | LP Br      | BD*N3 - C4    | 0.21  | 0.003 | -2.58 |
|                       | LP Br      | BD* C5 - N6   | 0.21  |       |       |
|                       | LP F       | BD*N3 - C4    | 0.28  |       |       |
|                       | LP F       | BD* C5 - N6   | 0.28  |       |       |
|                       |            |               | 0.28  | (sum 0.98) |       |
| C₄H₄N₂-IF(Ш)         | LP I       | BD*N3 - C4    | 0.24  | 0.002 | -3.13 |
|                       | LP I       | BD* C5 - N6   | 0.24  |       |       |
|                       | LP F       | BD*N3 - C4    | 0.36  |       |       |
|                       | LP F       | BD* C5 - N6   | 0.36  |       |       |
|                       |            |               | 0.36  | (sum 1.20) |       |
From the amount of $\Delta E^2$, $\Delta Q$ and the binding energies $\Delta E_{\text{CP}}$, we discovered that the $\Delta E^2$ are concerned with the binding energies ($\Delta E_{\text{CP}}$) of $\sigma$-type, $\pi$-type and parallel halogen bond complexes (See Figure 5), corresponding coefficients 0.9562, 0.9144 and 0.9873, respectively.

As can be seen in Table 3, $\Delta Q$ has no relevance to the $\Delta E_{\text{CP}}$ for $\sigma$-type and parallel halogen bond complexes. And for the $\pi$-type halogen bond complexes, $\Delta Q$ has relevance to the $\Delta E_{\text{CP}}$, corresponding coefficients is 0.9867 (See Figure 6).

### Table 3

| Molecule | $I$(eV) | $A$(eV) | $S$(eV) | $f_x^+$ | $f_x^-$ | $s_x^+$ | $s_x^-$ |
|----------|---------|---------|---------|---------|---------|---------|---------|
| $F_2$    | 0.055   | -0.670  | 1.379   | -0.500  | -0.500  | -0.690  | -0.690  |
| ClF      | 0.025   | -0.500  | 1.905   | -0.722  | -0.794  | -1.375  | -1.513  |
| BrF      | 0.006   | -0.457  | 2.160   | -0.752  | -0.813  | -1.624  | -1.756  |
| IF       | -0.010  | -0.406  | 2.525   | -0.808  | -0.890  | -2.040  | -2.247  |

### 3.3 Research on the conceptual DFT

In the current study, using these reactivity indices, we have studied the reactivity properties of the interacting molecules in $\sigma$-type, $\pi$-type and parallel halogen bond complexes by the conceptual density functional theory (conceptual DFT). The local softness $s(r)$ is an important factor in quantifying soft-soft interactions (or orbital-controlled reactivity) [36]. It is calculated from $s(r) = f(r) \cdot S$, where $f(r)$ is the Fukui function and $S$ is the global softness of the system. The the global softness $S$ can be approximated as $1/(I-A)$. $I$ is the vertical ionization energies of the system and $A$ is the electron affinity [37].

The pertinent calculated reactivity indices are shown in Table 3 for different lewis bases and acids considered in $\sigma$-type, $\pi$-type and parallel halogen bond complexes. For the lewis acids $XF$ ($X=F, \text{Cl}, \text{Br}$ and $I$) of the $\sigma$-type halogen-bonded complexes, it was revealed that the local softness $s^+$ on the $X$ of $XF$ is linked to the binding energies ($\Delta E_{\text{CP}}$), corresponding coefficients is 0.9752. For the lewis bases $XF$ ($X=F, \text{Cl}, \text{Br}$ and $I$) of $\pi$-type and parallel halogen bond complexes, it was revealed that the local softness $s^-$ on $X$ of $XF$ is linked to the $\Delta E_{\text{CP}}$, corresponding coefficients are 0.9875 and 0.9995 (see Figure 7).

### 3.4 Topological analysis

The topological analysis of the Laplacian function and its electron charge density is a powerful tool for studying the physical nature of halogen bonding [38, 39]. Table 4 displays the topological parameters, including electron density ($\rho_b$) [40] at the $\sigma$-type, $\pi$-type and parallel halogen bond critical points, its Laplacian ($\nabla^2 \rho_b$) and the electron energy density ($H_b$). The types of interaction can be classified
according to the sign of $H_b$ and $\nabla^2 \rho_b$. The halogen bond is generated when the $X$ of $XF$ used as a Lewis acid for the formation of $\sigma$-type halogen bond complex. $H_b$ is negative and $\nabla^2 \rho_b$ is positive, this corresponds to a partial colvalent interaction [41–43]. Nevertheless, the $\pi$-type and parallel halogen bond arises when the $X$ of $XF$ acts as lewis bases, both $H_b$ and $\nabla^2 \rho_b$ are positive, demonstrating a closed-shell molecular interactions [44].

On the base of QTAIM, $\rho_b$ (the electron density) should be a reflection of the bond strength. Normally, the greater of the value of the electron density, the greater bond strength. In the Table 4, the value of $\rho_b$ of the $\sigma$-type halogen bond complex is from 0.0226 to 0.0878. The amount of $\rho_b$ of the $\pi$-type halogen-bonded complexes is from 0.0117 to 0.0241. The amount of the parallel halogen bond complexes is from 0.0075 to 0.0086. The intermolecular forces of $\sigma$-type halogen bond complexes are noticeably stronger than that of appropriate $\pi$-type or parallel halogen bond complexes. The higher electron densities $\rho_b$ and the greater the interaction energy ($\Delta E_{CP}$), the stronger the $\sigma$-type, $\pi$-type or parallel halogen bond. The $\varepsilon$ (ellipticity) can be defined as $\lambda_1/\lambda_2-1$ and measures the extent to which charge is preferentially accumulated [45].

The ellipticity ($\varepsilon$) supplies a measure of the $\pi$ properties of a bond. The larger the ellipticity $\varepsilon$, the more obvious $\pi$ character the bond shows. It can be seen that the $\varepsilon$ of the $\pi$-type and parallel halogen bond

### Table 4

| complexes       | $\rho_b$ | $\lambda_1$ | $\lambda_2$ | $\lambda_3$ | $\nabla^2 \rho_b$ | $\varepsilon$ | $H_b$  |
|-----------------|----------|-------------|-------------|-------------|------------------|---------------|--------|
| $C_4H_4N_2-F_2(I)$ | 0.0226   | -0.0253     | -0.0243     | 0.1774      | 0.1278           | 0.0412        | -0.0017 |
| $C_4H_4N_2-ClF(I)$ | 0.0758   | -0.0784     | -0.0751     | 0.3124      | 0.1588           | 0.0439        | -0.0214 |
| $C_4H_4N_2-BrF(I)$ | 0.0816   | -0.0685     | -0.0652     | 0.2812      | 0.1474           | 0.0506        | -0.0228 |
| $C_4H_4N_2-IF(I)$  | 0.0878   | -0.0512     | -0.0485     | 0.2438      | 0.1440           | 0.0557        | -0.0148 |
| $C_4H_4N_2-F_2(II)$ | 0.0117   | -0.0106     | -0.0040     | 0.0700      | 0.0554           | 1.6500        | 0.0029  |
| $C_4H_4N_2-ClF(II)$ | 0.0169   | -0.0124     | -0.0034     | 0.0732      | 0.0573           | 2.6471        | 0.0013  |
| $C_4H_4N_2-BrF(II)$ | 0.0231   | -0.0164     | -0.0043     | 0.0848      | 0.0641           | 2.8140        | 0.0001  |
| $C_4H_4N_2-IF(II)$  | 0.0241   | -0.0139     | -0.0034     | 0.0710      | 0.0538           | 3.0882        | 0.0004  |
| $C_4H_4N_2-ClF(\Pi)$ | 0.0075   | -0.0052     | -0.0010     | 0.0353      | 0.0291           | 4.2001        | 0.0015  |
| $C_4H_4N_2-BrF(\Pi)$ | 0.0083   | -0.0055     | -0.0011     | 0.0352      | 0.0285           | 4.0000        | 0.0013  |
| $C_4H_4N_2-IF(\Pi)$  | 0.0086   | -0.0050     | -0.0012     | 0.0317      | 0.0255           | 3.1667        | 0.0011  |
complexes are much larger than those of the σ-type halogen bond.

3.5 Energy partition by SAPT

Energy decomposition gives us to have a very useful understanding the nature of the studied three types halogen bond interactions [46, 47]. The interactive energy of the three types complexes can be divided into four items: exchange energy, induced energy dispersion energy and electrostatic energy. The results are listed in table 5.

Table 5. Energy decomposition (kcal·mol⁻¹) for the σ-type, p-type and parallel halogen bond complexes of C₄H₄N₂-XF gained from SAPT
| σ-type halogen bond complexes | $E_{\text{elst}}$ | $E_{\text{ind}}$ | $E_{\text{disp}}$ | $E_{\text{exch}}$ | $E_{\text{int(SAPT2)}}$ | $\Delta E_{\text{CP}}$ | %$E_{\text{elst}}$ | %$E_{\text{ind}}$ | %$E_{\text{disp}}$ |
|-------------------------------|------------------|-----------------|------------------|-----------------|--------------------------|---------------------|------------------|------------------|------------------|
| $C_4H_4N_2-F_2$ (I)           | -6.02            | -3.53           | -3.41            | 11.21           | -1.75                    | -1.68               | 46.5             | 27.2             | 26.3             |
| $C_4H_4N_2-ClF$ (I)           | -45.18           | -32.37          | -13.31           | 78.21           | -12.65                   | -12.62              | 49.7             | 35.6             | 14.6             |
| $C_4H_4N_2-BrF$ (I)           | -54.14           | -31.26          | -13.31           | 81.56           | -17.14                   | -17.53              | 54.8             | 31.7             | 13.5             |
| $C_4H_4N_2-IF$ (I)            | -40.28           | -25.66          | -13.12           | 60.55           | -18.51                   | -19.25              | 50.9             | 32.5             | 16.6             |
| p-type halogen bond complexes | $E_{\text{elst}}$ | $E_{\text{ind}}$ | $E_{\text{disp}}$ | $E_{\text{exch}}$ | $E_{\text{int(SAPT2)}}$ | $\Delta E_{\text{CP}}$ | %$E_{\text{elst}}$ | %$E_{\text{ind}}$ | %$E_{\text{disp}}$ |
| $C_4H_4N_2-F_2$ (II)          | -1.87            | -1.63           | -3.33            | 5.84            | -0.98                    | -1.16               | 27.4             | 23.9             | 48.8             |
| $C_4H_4N_2-ClF$ (II)          | -4.60            | -4.92           | -6.40            | 13.14           | -2.78                    | -3.25               | 28.9             | 30.9             | 40.2             |
| $C_4H_4N_2-BrF$ (II)          | -9.09            | -8.71           | -8.02            | 21.49           | -4.34                    | -4.46               | 35.2             | 33.7             | 31.1             |
| $C_4H_4N_2-IF$ (II)           | -7.30            | -8.45           | -8.87            | 19.76           | -4.86                    | -5.17               | 29.7             | 34.3             | 36.0             |
| parallel halogen bond complexes | $E_{\text{elst}}$ | $E_{\text{ind}}$ | $E_{\text{disp}}$ | $E_{\text{exch}}$ | $E_{\text{int(SAPT2)}}$ | $\Delta E_{\text{CP}}$ | %$E_{\text{elst}}$ | %$E_{\text{ind}}$ | %$E_{\text{disp}}$ |
| $C_4H_4N_2-ClF$ (III)         | -2.51            | -0.57           | -5.06            | 6.05            | -2.08                    | -2.27               | 30.8             | 7.0              | 62.2             |
| $C_4H_4N_2-BrF$ (III)         | -3.48            | -0.70           | -4.89            | 6.31            | -2.76                    | -2.58               | 38.4             | 7.7              | 53.9             |
| $C_4H_4N_2-IF$ (III)          | -4.07            | -0.84           | -5.54            | 7.07            | -3.38                    | -3.13               | 38.9             | 8.0              | 53.0             |

As described in Table 5, the electrostatic energy are the major source of the attraction for the σ-type halogen bonding interactions while the parallel halogen-bond interactions are mainly dispersion energy in $C_4H_4N_2-XF$ complexes. For the π-type halogen bonding interactions in $C_4H_4N_2-XF (X=F and Cl)$ complexes, electrostatic energy are the major source of the attraction, while in $C_4H_4N_2-XF (X=Br and I)$ complexes the electrostatic, induction and dispersion term play equally important role in the total attractive interaction.
4. Conclusions

In present work, the three types halogen bond complexes between pyrazine \((C_4H_4N_2)\) and \(XF (X=F,Cl,Br,I)\) have been investigated at the MP2/aug-cc-pVTZ level. It can been found that the σ-type halogen bonding interactions are stronger than the corresponding π-type halogen bonding interactions, and π-type halogen-bond interactions are stronger than the corresponding parallel halogen bonding interactions in \(C_4H_4N_2-XF\) complexes. It can be see that the \(\Delta E^2\) are concerned with the binding energies \(\Delta E^{CP}\) for all the σ-type, π-type or parallel halogen bond complexes. The σ-type halogen-bonded complexes are stabilized by electrostatics energy, while the parallel halogen bond complexes are stabilized by dispersion energy. For the π-type halogen bonding interactions in \(C_4H_4N_2-XF(X=F \text{ and } Cl)\) complexes, electrostatic term are the major source of the attraction, while in \(C_4H_4N_2-XF(X=Br \text{ and } I)\) complexes the electrostatic, induction and dispersion term play equally important role in the total attractive interaction.

Moreover, this study also indicates that the local softness \(s^+\) or local softness \(s^-\) on the X of XF is related to the binding energies of σ-type, π-type or parallel halogen bond complexes.

Declarations

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Figures
Fig. 1 The electrostatic potentials of pyrazine and \( XF(X=\text{F,Cl,Br and I}) \) on 0.001 au. Color identification: red \( > 18 \) kcal/mol, yellow \( 8-18 \); green \( -3-8 \), blue \( < -3 \); Black dots represent the position of the \( \sigma \)-holes, and the light blue dots are linked with the lone pairs.

**Figure 1**

See image above for figure legend.
Fig. 2 Optimized geometries for the \( \sigma \)-type, \( \pi \)-type, and parallel halogen bond complexes C\( _4 \)H\( _8 \)N\(_2\)-XF (X=F, Cl, Br and I).

Figure 2

See image above for figure legend.
**Figure 3**  Linear relationships between the binding energies versus the $V_{s,\text{max}}$ (most positive electrostatic potentials) related with the X of XF or $V_{s,\text{min}}$ (maximum negative electrostatic potential) on the XF surface.

See image above for figure legend.

**Figure 4**  Comparison of the BSSE corrected interaction energies of the three types halogen bond complexes of $\text{C}_4\text{H}_4\text{N}_2\text{XF}$ (X=F, Cl, Br and I).

See image above for figure legend.
Fig. 5 Correlation between interaction energies and the second-order perturbation energy in the three types halogen bond complexes.

Figure 5

See image above for figure legend.
Fig. 6 Correlation between the $\Delta Q$ (charge transfer) and the interaction energies in the $\pi$-type halogen bond complexes.

See image above for figure legend.
Fig. 7 Correlation between the local softness ($s_x^+$ or $s_x^-$) values in the XF and the interaction energies of the three types halogen bond complexes.

Figure 7

See image above for figure legend.

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