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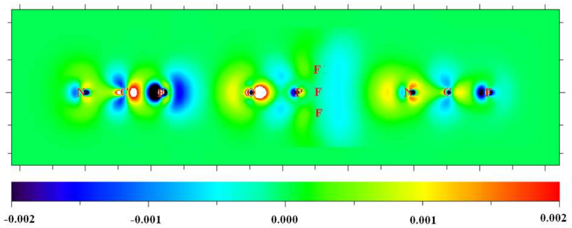

The group V σ-hole interactions have the enhancing effects on the F···O halogen bond and vice versa.

The Enhancing Effects of Group V σ-hole Interactions on the F···O Halogen Bond

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The σ-hole interaction, which is between the covalent IV-VII atoms and nucleophilic substances, has become a hot issue of the weak interaction. In this work, the $NCF\cdots O=PX_3\cdots(NCF)_n$ (X = F, Cl, Br, H, CH_3; n = 0, 1, 2) complexes were constructed and studied based on the second-order Møller–Plesset perturbation theory (MP2) calculations, to investigate the enhancing effects of group V σ-hole interactions on the F···O halogen bond. With the number of n increases, the F···O halogen bond becomes stronger, indicating that the group V σ-hole interactions could enhance the F···O halogen bond. With the capacity of donating electrons of X becomes greater and greater, the most negative electrostatic potentials outside the oxygen atom of $O=PX_3\cdots(NCX)_n$ (n = 0, 1, 2) becomes more and more negative, resulting in stronger F···O halogen bond. In the formation of F···O halogen bond, along the sequence of X = F, Cl, Br, H, CH_3 of the negative sites $O=PX_3$, the electric field of lone pair of oxygen becomes greater and causes more decrease of electron density outside the fluorine atom. On the other hand, with n increases from 0 to 2, the group V σ-hole interactions also make electric field of lone pair of oxygen become greater and results in more decrease of electron density outside the fluorine atom.

1. Introduction

Recently, halogen bonding has drawn more and more attention because of its potential applications in molecular recognition [1-4], crystal engineering [4-7], and biological systems [4, 8-11]. It is well-established that the halogen bonding interactions are between some covalently-bonded halogens and negative sites of other molecules, e.g., lone pairs of Lewis bases [12-15]. It could also be explained as the electrostatic attraction between the positive potential of the halogen atom and the negative site of the other molecule. Halogen bonding typically involves X (X = Cl, Br, I) and a Lewis base; it increases in likelihood and in strength in going from Cl, Br, I. There is now computational evidence that it can sometimes also take place when X = F, although rarely [16-17]. However F has a positive electrostatic potential region (σ-hole) and could form halogen bonds when it is linked to a very electron-withdrawing group, for examples: F_2 and F-CN [18]. These were viewed as "negative-negative" interactions and were puzzling until Brinck et al. [19] and subsequently others [8,20] showed that the halogen atoms X in some molecules RX have regions of positive electrostatic potential on their outer surfaces, on the extensions of the R-X bonds [14]. The region of positive electrostatic potential outside the X atom is called a σ-hole, the interaction between a region of positive electrostatic potential on a covalently bonded halogen and a negative site, such as the lone pair of a Lewis base is calls the σ-hole interaction. In recent years, it has also been pointed out that σ-hole interactions are not limited to halogens, but can also involve covalently bonded atoms of Groups IV-VI[21]. The strengths of these Groups IV-VI interactions are governed by the polarizability and electronegativity of the Groups IV-VI atom and the electron-withdrawing power of the remainder of the covalently-bonded molecule [22].

The applications of halogen bonding in molecular recognition, crystal engineering, and biological systems are affected mainly by the strength of halogen bond [4]. One of the most important and interesting issues on halogen bond is how to strengthen it [4]. The previous studies on the cooperativity [4,23-28] have demonstrated the halogen bonds can display cooperative effect with other types of intermolecular interactions.

In 1969, Olie and Mijlhoff [21,29] noted some unusual short intermolecular Br···O separations in crystalline $POBr_3$, which they ascribed to a bonding interaction. The study of Murray and Politzer et al [14] has demonstrated that the most positive electrostatic potential ($V_{S,\ max}$) and the most negative electrostatic potential ($V_{S,\ min}$) are present in one phosphorus derivative, $O=PCl_3$, they also demonstrated that the positions of $V_{S,\ max}$ and $V_{S,\ min}$ are present in one phosphorus derivative, $O=PBr_3$ [21].

In this work, based on the analysis of the positive and negative electrostatic potential regions POX_3 (X = F, Cl, Br, H, CH_3), the complexes of $NCF\cdots O=PX_3\cdots(NCF)_n$ (X = F, Cl, Br, H, CH_3; n = 0, 1, 2) were constructed, to investigate (1) the F···O halogen-bonging interaction in the bimolecular complexes $NCF\cdots O=PX_3$; (2) the group V σ-hole interactions in the bimolecular complexes between $O=PX_3\cdots(NCF)_n$; (3) the enhancing effects of group V σ-hole interactions on the F···O halogen Bond in the termolecular and tetramolecular complexes $NCF\cdots O=PX_3\cdots(NCF)_n$ (n = 1, 2); (4) the affecting effects of the substituents X to the halogen-bonging interaction and group V σ-hole interactions; and (5) the affecting effects of the number n of NCF to the interactions.

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2. Theoretical methods

The electrostatic potentials, $V(\mathrm{r})$, is a well-established tool for studying the noncovalent interactions [30,31-32,33-39], it has been useful in predicting the directionality of many noncovalent interactions, including hydrogen bonding[33,40-41] and halogen bonding [7-8,15,19,30,33]. In this work, the molecular electrostatic potentials were computed to investigate the possibility of the possible types of directional noncovalent interaction: the region of the most positive electrostatic potentials for fluorine of NCF and the most negative electrostatic potentials for oxygen of $O{=}PX_3$ (X = F, Cl, Br, H, CH_3); the σ-hole outside the group V atoms of $O{=}PX_3$ and the most negative electrostatic potentials region for nitrogen of NCF. The electrostatic potentials were calculated on the 0.001 a.u. (electrons/bohr^3) contour of the molecule's electronic density [32] at the MP2/aug-cc-pVDZ level with the WFA surface analysis suite [42].

The geometries of the monomers and the complexes were optimized by the MP2 method combined with the aug-cc-pVDZ [43-45] basis set. The same procedure was done to compute the frequencies to ensure that the equilibrium geometries were real minima on the potential energy surfaces. The counterpoise procedure proposed by Boys and Bernardi [46] was used to correct the interaction energies while excluding the inherent basis set superposition error (BSSE). The above calculations were performed with the Gaussian 03 program package [47]. The density difference of molecular formation were analyzed using multiwfn software [48].

3. Results and Discussion

3.1 Molecular ESPs of $O{=}PX_3\cdots(NCX)_n$ (X = F, Cl, Br, H,CH_3; n = 0, 1, 2)

Figure 1 shows the contour maps of molecular electrostatic potentials (ESP) of NCF (1a), $O{=}PF_3$ (1b), $O{=}PF_3\cdots NCF$ (1c), and $O{=}PF_3\cdots NCF\cdots NCF$ (1d). As anticipated, the fluorine atom of NCF has a large region of positive ESP ($V_{S,\,max}$ = 14.08 kcal/mol) on its outer side along the extension of the C—F bond, the oxygen atom of $O{=}PF_3$ has a large region of negative ESP on its outer side along the extension of the O—P bond. Therefore, the $NCF\cdots O{=}PF_3$ bimolecular complex could be formed by the F···O halogen bond. Moreover, for $O{=}PF_3$, a positive region of ESP (σ-hole) exists outside the phosphorus atom along the extension of O—P bond; for NCF, the negative region of ESP ($V_{S,\,min}$ = -28.41kcal/mol) exists outside the nitrogen atom along the extension of N—C bond. Therefore, the group V σ-hole interactions could be formed between $O{=}PF_3$ and NCF.

Figure 1 (here)

From Figure 1b, 1c to 1d, with the formation of σ-hole interaction of $O{=}PF_3\cdots NCF$ and $O{=}PF_3\cdots NCF\cdots NCF$, the negative ESP regions outside the oxygen atom of $O{=}PF_3$ become larger and larger. From Table 1, the $V_{S,\,min}$ values outside the oxygen atom of $O{=}PF_3$ (Figure 1b), $O{=}PF_3\cdots NCF$ (Figure 1c), and $O{=}PF_3\cdots NCF\cdots NCF$ (Figure 1d) are -27.13, -32.19, and -33.70 kcal/mol, respectively. This trend is not only for X = F, but also for X = Cl, Br, H, CH_3.

From Table 1, the $V_{S,\,min}$ values of $O{=}PX_3$ become more and more negative along the sequence of X = F, Cl, Br, H, CH_3. This trend is not only for the $V_{S,\,min}$ values of $O{=}PX_3$, but also for the $V_{S,\,min}$ values of $O{=}PX_3\cdots NCF$ and $O{=}PF_3\cdots NCF\cdots NCF$. With the sequence of X = F, Cl, Br, H, CH_3, the capacity of donating electrons of X becomes greater and greater, and the negative ESP outside the oxygen atom become more and more negative, the $V_{S,\,min}$ values become more and more negative.

Table 1 (here)

3.2 Equilibrium geometries and interaction energy

Based on the analysis of molecular ESP of Figure 1, the bimolecular, termolecular, and tetramolecular complexes $NCF\cdots O{=}PX_3$, $NCF\cdots O{=}PX_3\cdots NCF$, $NCF\cdots O{=}PX_3\cdots NCF\cdots NCF$ (X = F, Cl, Br, H, CH_3) were constructed and optimized. As the representative examples, Figure 2 shows optimized geometries of $NCF\cdots O{=}PF_3$, $NCF\cdots O{=}PF_3\cdots NCF$, $NCF\cdots O{=}PF_3\cdots NCF\cdots NCF$. All of the above optimized bimolecular, termolecular, and tetramolecular complexes belong to C_{3v} symmetry.

Figure 2 (here)

Table 2 presents the F···O halogen bond lengths in the $NCF\cdots O{=}PX_3\cdots(NCF)_n$ (X = F, Cl, Br, H,CH_3; n = 0, 1, 2). For n=0, the F···O halogen bond lengths range from 2.9180 to 2.7997 Å along the sequence of X = F, Cl, Br, H, CH_3. When n=1 and n=2, the halogen bond lengths are still in sequence of X = F, Cl, Br, H, CH_3. As the value of n increases, the F···O interaction distance decreases. That is to say, when n=1, the $O{=}PF_3\cdots NCF$ σ-hole interactions show the enhancing effects on F···O halogen Bond. Moreover, when n=2, the addition of NCF can more strengthen the $O{=}PF_3\cdots NCF$ σ-hole interaction, and then make the F···O halogen bond stronger than the n=1.

Table 2 (here)

Table 3 shows the halogen-bonded interaction energies ΔE (in kJ/mol) in the bimolecular, termolecular, and tetramolecular complexes. All the ΔE values become greater in the sequence X=F, Cl, Br, H, CH_3, which are accordant with the $V_{S,\,min}$ values of $O{=}PX_3\cdots(NCX)_n$ (n = 0, 1, 2).

Table 3 (here)

The ΔE values range from -3.41 kJ/mol to -8.40 kJ/mol the bimolecular complexes, from -4.20 kJ/mol to -9.19 kJ/mol in the termolecular complexes, and from -4.45 kJ/mol to -9.71 kJ/mol in the tetramolecular complexes. That is to say, when NCF is added to $O{=}PX_3$ (X = F, Cl, Br, H, CH_3) to form the $O{=}PX_3\cdots NCF$ σ-hole interaction, the F···O halogen-bonded interaction energies, $\Delta E_{(A\text{-}BC)}$, in the termolecular complexes become distinctly greater than those ($\Delta E_{(A\text{-}B)}$) in the bimolecular complexes. For example, the F···O halogen-bonded interaction energy is -3.41 kJ/mol in the bimolecular complex $NCF\cdots O{=}PF_3$ and becomes -4.20 kJ/mol in the termolecular complex $NCF\cdots O{=}PF_3\cdots NCF$, with an increase of 23.08%. For the tetramolecular complexes $NCF\cdots O{=}PX_3\cdots NCF\cdots NCF$ (X = F, Cl, Br, H, CH_3), the F···O halogen-bonded interaction energies $\Delta E_{(A\text{-}BCD)}$ become greater as the addition of latter NCF. For example, the $\Delta E_{(A\text{-}BCD)}$ becomes -4.45 kJ/mol in the $NCF\cdots O{=}PF_3\cdots NCF\cdots NCF$ termolecular complexes, with an increase of 6.05% compared with that of the $NCF\cdots O{=}PF_3\cdots NCF$ termolecular complex, the addition of latter NCF has a positive effect for the σ-hole interactions $O{=}PF_3\cdots NCF$, and further has a positive effect on the F···O halogen bond. In a word, the F···O halogen-bonded interaction energies become greater with n increases. The group V σ-hole interactions have enhancing effects on the halogen-bonding interaction.

Comparing the F···O halogen-bonded interaction energies of $NCF\cdots O{=}PX_3\cdots(NCX)_n$ (n = 0, 1, 2) with respective $V_{S,\,min}$ values of $O{=}PX_3\cdots(NCX)_n$ (n = 0, 1, 2), the linear relationships were found and shown in Figure 3(a), with the correlation coefficients 0.9928 for n=0, 0.9933 for n=1, and 0.9939 for n=2. For comparison of the substituents X = F, Cl, Br, H, CH_3, Figure 3(b) shows the relations between the F···O halogen-bonded interaction energies of

$NCF\cdots O{=}PF_3\cdots(NCF)_n$ and respective $V_{S,\ min}$ values of $O{=}PX_3\cdots(NCX)_n$, the linear correlation coefficients are 1.0000, 1.0000, 1.0000, 0.9927, and 0.9863 for X = F, Cl, Br, H, and CH_3, respectively. These relations indicate that the halogen bond strength of $NCF\cdots O{=}PX_3\cdots(NCF)_n$ (X = F, Cl, Br, H, CH_3, n = 0, 1, 2) are greatly determined by $V_{S,\ min}$ values of $O{=}PX_3\cdots(NCF)_n$ (X = F, Cl, Br, H, CH_3, n = 0, 1, 2).

Figure 3 (here)

3.3 The density difference of molecular formation (MFDD) analys1is

The idea of density difference functions by Daudel and Roux was put forward more than 50 years ago[49-51], which was later applied in the studies of the formation of the molecules and weak interaction systems[52-54]. For a super molecule A-B model, the MFDD can be described as:

$$\rho_d(r) = \rho_{complex}(r) - (\rho_{molA}(r) + \rho_{molB}(r))$$

A more detailed picture of polarization can be obtained by plotting the difference between the electronic density of the complex and the sum of the electronic densities of free molecules A and B[54]. To obtain the density difference between the complexes $NCF\cdots O{=}PX_3$ (X = F, Cl, Br, H, CH_3) and the monomers NCF and $O{=}PX_3$, the free monomers NCF and $O{=}PX_3$ were placed at the same positions as they occupy in the complexes $NCF\cdots O{=}PX_3$. The computed density difference plots for the complexes $NCF\cdots O{=}PF_3$, $NCF\cdots O{=}PCl_3$, $NCF\cdots O{=}PBr_3$, $NCF\cdots O{=}PH_3$, and $NCF\cdots O{=}P(CH_3)_3$ are presented in Figure 4a to 4c, respectively.

Figure 4 (here)

From Figure 4, the density difference plots show how the charge redistributions of NCF and $O{=}PX_3$ when they interact to form $NCF\cdots O{=}PX_3$. The electric field of lone pair of oxygen atom of $O{=}PX_3$ causes a decrease of electron density outside the fluorine atom facing the oxygen lone pair and an increase in the fluorine-carbon internuclear region. At the same time, the electric field of the positive σ-hole of the fluorine atom of NCF also produces a rearrangement of electronic charge within the $O{=}PX_3$ molecule, with an increase near the oxygen atom and a decrease near the phosphor atom.

In this work, we focus on the region of density difference outside the fluorine atom. For the negative sites $O{=}PX_3$, from X = F, Cl, Br, H, and CH_3, the $V_{S,\ min}$ values are -27.13, -35.00, -36.26, -50.56, and -59.25kcal/mol, respectively. According to the sequence of X = F, Cl, Br, H, and CH_3, the electric field of lone pair of oxygen causes more decrease of electron density outside the fluorine atom, these are consistent with the interaction energies of the $NCF\cdots O{=}PX_3$ bimolecular complexes.

The most negative density difference values outside the fluorine atom in the $NCF\cdots O{=}PX_3$ bimolecular complexes are collected in Table 4. For X = F, Cl, Br, H, and CH_3 of the negative sites $O{=}PX_3$, the most negative density difference values are -0.0014, -0.0018, -0.0019, -0.0028, and -0.0034 e/bohr^3. From the fluorine atom to the oxygen atom, we choose a cube to integrate the total charge of the density difference, and obtain negative charge values outside the fluorine atom and positive charge values outside the oxygen atom. The negative integral charges of the density difference region outside the fluorine atom are collected in Table 5. For the $NCF\cdots O{=}PX_3$ bimolecular complexes, when X = F, Cl, Br, H, and CH_3 of $O{=}PX_3$, the integral charges of this region are -0.0112, -0.0147, -0.0154, -0.0217, and -0.0260 e. These are consistent with the $V_{S,\ min}$ value of $O{=}PX_3$ and the interaction energies of the $NCF\cdots O{=}PX_3$ bimolecular complexes.

Table 4 (here)

Table 5 (here)

As the representative complexes $NCF\cdots O{=}PX_3\cdots(NCF)_n$ (n=0, 1, 2), the density difference plots of $NCF\cdots O{=}PF_3$, $NCF\cdots O{=}PF_3\cdots NCF$, and $NCF\cdots O{=}PF_3\cdots NCF\cdots NCF$ are displayed in Figure 5a-5c. With the formation of σ-hole interaction of $O{=}PF_3\cdots NCF$ and $O{=}PF_3\cdots NCF\cdots NCF$, the negative ESP regions outside the oxygen atom of $O{=}PF_3$ become larger and larger, the $V_{S,\ min}$ values outside the oxygen atom become smaller and smaller, thus the electric field of lone pair of oxygen causes more decrease of electron density outside the fluorine atom.

Figure 5 (here)

For the complexes $NCF\cdots O{=}PX_3\cdots(NCF)_n$ (n=0, 1, 2), the most negative density difference values outside the fluorine atom, and the integral charges of the density difference region outside the fluorine atom are also shown in Table 4 and Table 5, respectively. From n = 0, to 1, and 2, both the two kinds of values become more and more negative, which are consistent with the sequence of the interaction energies of $NCF\cdots O{=}PX_3\cdots(NCF)_n$ (n=0, 1, 2).

Comparing the integral charges of the density difference region outside the fluorine atom in Table 5 with respective $V_{S,\ min}$ values in Table 1, linear correlations were found and shown in Figure 6. The relations for comparison of n = 0, 1, 2 are shown in Figure 6(a), with the linear correlation coefficients are 0.9998, 0.9945, and 0.9977 for n = 0, 1, and 2, respectively. The relations for comparison of X = F, Cl, Br, H, and CH_3 are shown in Figure 6(b), with the linear correlation coefficients are 0.9990, 0.9986, 0.9991, 0.9899, and 0.9962 for X = F, Cl, Br, H, and CH_3, respectively.

The above relations show that with the sequence of X = F, Cl, Br, H, CH_3 of the negative sites $O{=}PX_3$, the electric field of lone pair of oxygen becomes greater, and causes more decrease of electron density outside the fluorine atom. On the other hand, with n increases from 0 to 2, the group V σ-hole interactions also make electric field of lone pair of oxygen become greater and results in more decrease of electron density outside the fluorine atom in the formation of $F\cdots O$ halogen bond.

Figure 6 (here)

4. Conclusions

MP2/aug-cc-pVDZ calculations have been carried out for studying the $F\cdots O$ halogen bond in the $NCF\cdots O{=}PX_3\cdots(NCF)_n$ (X = F, Cl, Br, H, CH_3; n = 0, 1, 2) complexes. The enhancing effects of Group V σ-hole interactions on the $F\cdots O$ halogen bond has been investigated. The following conclusions have been drawn:

(1) The positive ESP outside the fluorine atom along the extension of C—F bond in NCF and the negative ESP outside the oxygen atom along the extension of the O—P bond in $O{=}PX_3$ could form the $F\cdots O$ halogen-bonging interaction of $NCF\cdots O{=}PX_3$.

(2) The positive ESP outside the phosphorus atom along the extension of the O—P bond in $O{=}PX_3$ and the negative ESP outside the nitrogen atom along the extension of N—C bond could form the group V σ-hole interactions of $O{=}PX_3\cdots NCF$.

(3) For comparison of n, the $F\cdots O$ halogen bond becomes stronger with n increases in the $NCF\cdots O{=}PX_3\cdots(NCF)_n$ (n = 0, 1, 2) complexes, indicating that the group V σ-hole interactions could enhance the $F\cdots O$ halogen bond.

(4) For comparison of substituents X, the F···O halogen bond becomes stronger along the sequence of X = F, Cl, Br, H, and CH_3. With the capacity of donating electrons of X becomes greater and greater, the $V_{S,\ min}$ values outside the oxygen atom of $O{=}PX_3\cdots(NCX)_n$ (n = 0, 1, 2) becomes more and more negative, which results in stronger F···O halogen bond.

(5) In the formation of F···O halogen bond, along the sequence of X = F, Cl, Br, H, CH_3 of the negative sites $O{=}PX_3$, the electric field of lone pair of oxygen becomes greater, and causes more decrease of electron density outside the fluorine atom. On the other hand, with n increases from 0 to 2, the group V σ-hole interactions also make electric field of lone pair of oxygen become greater and results in more decrease of electron density outside the fluorine atom.

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Table 1 The most negative electrostatic potentials ($V_{S,min}$, in kcal/mol) on the 0.001 a.u. contour of molecular electron density

Species	$V_{S,min}$	Species	$V_{S,min}$	Species	$V_{S,min}$
$O=PF_3$	-27.13	$O=PF_3\cdots NCF$	-32.19	$O=PF_3\cdots NCF\cdots NCF$	-33.70
$O=PCl_3$	-35.00	$O=PCl_3\cdots NCF$	-39.42	$O=PCl_3\cdots NCF\cdots NCF$	-40.90
$O=PBr_3$	-36.26	$O=PBr_3\cdots NCF$	-40.52	$O=PBr_3\cdots NCF\cdots NCF$	-41.97
$O=PH_3$	-50.56	$O=PH_3\cdots NCF$	-58.26	$O=PH_3\cdots NCF\cdots NCF$	-58.58
$O=P(CH_3)_3$	-59.25	$O=P(CH_3)_3\cdots NCF$	-63.62	$O=P(CH_3)_3\cdots NCF\cdots NCF$	-65.08

Table 2 The F···O halogen bond lengths (Å) in the NCF···O=PX_3···$(NCF)_n$ (X = F, Cl, Br, H,CH_3; n = 0, 1, 2) complexes

	n=0	n=1	n=2	n=0→n=1	n=1→n=2
NCF···O=PF_3···$(NCF)_n$	2.9180	2.8964	2.8932	-0.0216	-0.0032
NCF···O=PCl_3···$(NCF)_n$	2.8768	2.8544	2.8568	-0.0224	0.0024
NCF···O=PBr_3···$(NCF)_n$	2.8658	2.8506	2.8486	-0.0152	-0.0162
NCF···O=PH_3···$(NCF)_n$	2.8284	2.8074	2.8058	-0.0201	-0.0016
NCF···O=$P(CH_3)_3$···$(NCF)_n$	2.7997	2.7847	2.7828	-0.0150	-0.0019

Table 3 The F···O halogen-bonded interaction energies (in kJ/mol) in the bimolecular, termolecular, and tetramolecular complexes, as well as their changes

A···B···C···D	$\Delta E_{(A\text{-}B)}$[a]	$\Delta E_{(A\text{-}BC)}$[b]	$\Delta E_{(A\text{-}BCD)}$[c]	$\%E_{A\text{-}BC}$[d]	$\%E_{A\text{-}BCD}$[e]
NCF···O=PF_3···$(NCF)_n$	-3.41	-4.20	-4.45	23.08	6.05
NCF···O=PCl_3···$(NCF)_n$	-4.73	-5.51	-5.78	16.67	4.76
NCF···O=PBr_3···$(NCF)_n$	-4.99	-5.78	-6.04	15.79	4.55
NCF···O=PH_3···$(NCF)_n$	-6.56	-7.88	-8.141	20.00	3.33
NCF···O=$P(CH_3)_3$···$(NCF)_n$	-8.40	-9.19	-9.71	9.38	5.71

[a] $\Delta E_{(AB)}=E_{AB}-E_{A}-E_{B}$; [b] $\Delta E_{(A\text{-}BC)}=E_{ABC}-E_{A}-E_{BC}$; [c] $\Delta E_{(A\text{-}BCD)}=E_{ABCD}-E_{A}-E_{BCD}$; [d] $\%E_{A\text{-}BC}=(\Delta E_{(A\text{-}BC)}-\Delta E_{(A\text{-}B)})/\Delta E_{(A\text{-}B)}$; [e] $\%E_{A\text{-}BCD}=(\Delta E_{(A\text{-}BCD)}-\Delta E_{(A\text{-}BC)})/\Delta E_{(A\text{-}BC)}$;

Table 4 Most negative density difference values (e/bohr^3) outside the F atom in the halogen-bonded bimolecular, termolecular, and tetramolecular complexes

	n=0	n=1	n=2
NCF···O=PF_3···$(NCF)_n$	-0.0014	-0.0016	-0.0017
NCF···O=PCl_3···$(NCF)_n$	-0.0018	-0.0021	-0.0021
NCF···O=PBr_3···$(NCF)_n$	-0.0019	-0.0021	-0.0022
NCF···O=PH_3···$(NCF)_n$	-0.0028	-0.0031	-0.0032
NCF···O=$P(CH_3)_3$···$(NCF)_n$	-0.0034	-0.0036	-0.0036

Table 5 Integral charges (e) of the density difference region outside the F atom in the halogen-bonded bimolecular, termolecular, and tetramolecular complexes

	n=0	n=1	n=2
$NCF\cdots O{=}PF_3\cdots(NCF)_n$	-0.0112	-0.0125	-0.0128
$NCF\cdots O{=}PCl_3\cdots(NCF)_n$	-0.0147	-0.0159	-0.0162
$NCF\cdots O{=}PBr_3\cdots(NCF)_n$	-0.0154	-0.0165	-0.0168
$NCF\cdots O{=}PH_3\cdots(NCF)_n$	-0.0217	-0.0230	-0.0233
$NCF\cdots O{=}P(CH_3)_3\cdots(NCF)_n$	-0.0260	-0.0271	-0.0272

Figure Captions

Fig. 1 Electrostatic potentials on the 0.001 a.u. contour of molecular electron density: (a) NCF; (b) $O=PF_3$; (c) $O=PF_3\cdots NCF$; (d) $O=PF_3\cdots NCF\cdots NCF$. Color ranges, in $kcal\cdot mol^{-1}$: red, more positive than 30; yellow, 10-30; green, -10-10; blue, more negative than -10. Positions of $V_{S,max}$ and $V_{S,min}$ are indicated in black arrows.

Fig. 2 The optimized geometries of $NCF\cdots O=PF_3$(a), $NCF\cdots O=PF_3\cdots NCF$(b), and $NCF\cdots O=PF_3\cdots NCF\cdots NCF$(c)

Fig. 3 Linear correlations between $F\cdots O$ interaction energies in $NCF\cdots O=PX_3\cdots(NCF)_n$ and respective $V_{S,min}$ values of $O=PX_3\cdots(NCF)_n$: (a) Comparison of n= 0, 1, 2; (b) Comparison of X = F, Cl, Br, H CH_3.

Fig. 4 Computed density difference plots for the complexes (a) $NCF\cdots O=PF_3$, (b) $NCF\cdots O=PCl_3$, (c) $NCF\cdots O=PBr_3$, (d) $NCF\cdots O=PH_3$, $NCF\cdots O=P(CH_3)_3$.

Fig. 5 Computed density difference plots for the complexes (a) $NCF\cdots O=PF_3$, (b) $NCF\cdots O=PF_3\cdots NCF$, and (c) $NCF\cdots O=PF_3\cdots NCF\cdots NCF$

Fig 6 Linear correlations between integral charges of the density difference region outside the fluorine atom in $NCF\cdots O=PX_3\cdots(NCF)_n$ and the $V_{S,min}$ values of $O=PX_3\cdots(NCF)_n$: (a) Comparison of n = 0, 1, 2; (b) Comparison of X = F, Cl, Br, H CH_3.