ARTICLE

Cooperative and substitution effects in enhancing the strength of fluorine bonds by anion–π interactions

Mehdi D. Esrafili, Fariba Mohammadian-Sabet, and Mohammad Mehdi Baneshi

Abstract: In this work, the cooperative effects between anion–π and fluorine bond interactions are studied by ab initio calculations at the MP2/6-311++G** level. Cooperative effects are observed in complexes in which anion–π and fluorine bond interactions coexist. For each complex, the shortening of the binding distance in the fluorine bond is more prominent than that in the anion–π bond. Favorable cooperativity energies are found with values that range between −0.51 and −0.76 kcal/mol. The atoms in molecules and molecular electrostatic potential analyses are carried out for these complexes to understand the nature of anion–π and fluorine bond interactions and the origin of the cooperativity.

Key words: anion–π, halogen bond, cooperativity, ab initio, molecular electrostatic potential.

Résumé : Dans le cadre des présents travaux, nous avons étudié les effets coopératifs entre les interactions anion–π et les liaisons halogène du fluor par des calculs ab initio au niveau MP2/6-311++G**. Nous avons observé des effets coopératifs dans les complexes dans lesquels existent à la fois des interactions anion–π et des liaisons halogènes avec le fluor. Dans tous les complexes, la réduction de la longueur de la liaison halogène du fluor est plus importante que celle de la liaison anion–π. Nous avons observé des énergies de coopérativité favorables dont les valeurs vont de −,51 à −0,76 kcal/mol. Nous avons modélisé ces complexes selon la théorie quantique des atomes dans les molécules et calculé leur potentiel électrostatique moléculaire afin de comprendre la nature des interactions anion–π et des liaisons halogène du fluor ainsi que l'origine de la coopérativité. [Traduit par la Rédaction]

Mots-clés : anion–π, liaison halogène, coopérativité, ab initio, potentiel électrostatique moléculaire.

Introduction

In recent years, noncovalent interactions have received much attention due to their essential roles in many chemical and biological processes.[1–4] A halogen bond is defined as an attractive R–X⋯Y interaction where the halogen X acts as a Lewis acid and Y is any site with an excess of electron charge density, most often being an atom with the electron lone pair. Since bonded halogens are commonly viewed as being negative in character, the formation and stability of such "negative–negative" interactions were puzzling until Politzer and co-workers[5–7] demonstrated 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. The interpretation given by Politzer and co-workers[8–10] was that when a half-filled p valence orbital of a halogen atom participates in forming a covalent bond, electron density is polarized towards the bond, leaving a region of electron deficiency in the outer lobe of the p orbital along the extension of the covalent bond to X. This electron-deficient region deficiency has been labeled a "σ-hole" because it is opposite a σ bond. If the electron deficiency is sufficient, a positive electrostatic potential is associated with the σ-hole, creating the possibility of an attractive electrostatic interaction with a negative site. Experimental[11–13] and theoretical[14–18] studies have provided support for this idea that, under certain conditions, halogen atoms involved in covalent bonding develop regions of positive electrostatic potential on their molecular surface collinear with their covalent bonds. This explanation also accounts for the remarkable directionality of halogen bonding, which is essentially along the extension of the R–X bond; the angle R–X⋯Y is usually close to 180°.

Since halogen bonds are due to the presence of positive electrostatic potential on the halogen atom, any factor that enhances this potential will strengthen the halogen bond. Extensive quantum chemical calculations[19–22] indicated that σ-holes tend to be more positive as the halogen atom is more polarizable, i.e., F < Cl < Br < I. Another important factor is the electron-withdrawing power of the remainder of the molecule; the greater it is, the more positive is the σ-hole. The strengths of halogen bonding interactions with a given negative site correlate, in general, with the magnitudes of the positive electrostatic potentials associated with the σ-holes.[23,24] As a result of a combination of its high electronegativity and low polarizability, the fluorine atom is frequently deemed to not participate in halogen bonding. However, it has recently been shown that the fluorine atom has the capability of forming halogen bonds and can also affect recognition and self-assembly processes, but only under specific circumstances.[25,26] Hence, in the F_2 molecule, the electron-withdrawing fluorine group is sufficient to create a positive electrostatic potential on the fluorine atom.[10] It is interesting to note that fluorine-centered halogen bonds have been observed experimentally in the gas phase[27] and the solid state as well.[28]
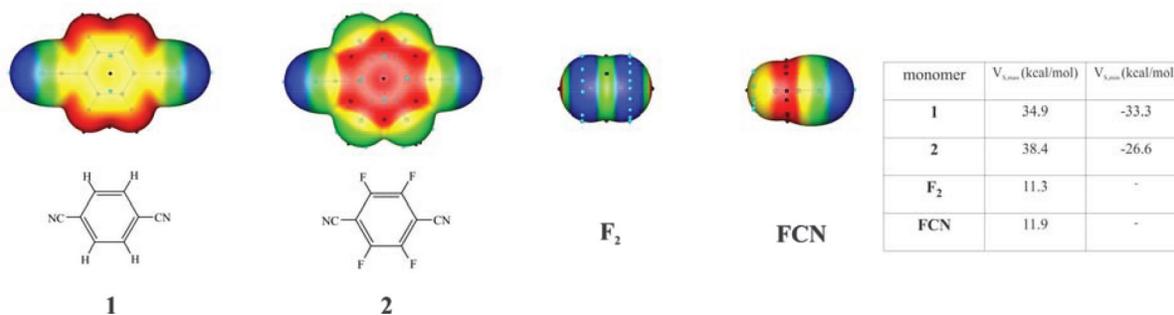
Cooperativity and substituent effects are perhaps the most important properties of noncovalent interactions.[29–33] Like hydrogen bonds, cooperativity and substituent effects are also present among halogen bonds. Recently, the cooperativity between halogen bonds and other types of interactions has been extensively studied.[34–37] For instance, Lu et al.[38] found a strong cooper-

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Fig. 1. Schematic representation and molecular electrostatic potentials of π-acidic heteroaromatic rings **1** and **2** and F_2 and FCN molecules.

monomer	$V_{S,max}$ (kcal/mol)	$V_{S,min}$ (kcal/mol)
1	34.9	–33.3
2	38.4	–26.6
F_2	11.3	-
FCN	11.9	-

ativity between halogen bonds and cation–π interactions in complexes involving aromatic molecules as halogen bond donors. Their results demonstrated that the mutual influence of the two interactions is maintained even when halogen bonds are far away from cation–π interactions in the complexes.

The interactions involving aromatic rings are very important in many fields. For instance, π–π stacking,[39] cation–π,[40] anion–π,[41] and CH–π[42] interactions have a vital role in many important chemical and biological processes including molecular recognition, crystal engineering, and enzymatic mechanisms. In recent years, many studies on the properties and structures of anion–π bonds have been performed. In particular, we recently revealed cooperativity effects when anion–π and pnicogen bond interactions coexist in the same complex.[43] Given the observation that the pnicogen bond has some different features from the fluorine bond (FB), the question arises as to whether a different cooperative effect can be found when anion–π and FB interactions coexist in the same complex.

Accordingly, we selected two π-acidic heteroaromatic rings (**1** and **2**), shown in Fig. 1, that contain substituent groups in the structure that can act as a Lewis base to interact with FCN and F_2. Figure 2 indicates the schematic representation of the isolated anion–π, FB, and anion–π–FB complexes studied here. The aim is to enhance the strength of the FB interaction by means of anion–π interactions. Binding distances, interaction energies, and bonding properties of these complexes will systematically be studied to examine the nature of anion–π and FB interactions in these systems. Also, the cooperativity between them was investigated in the multicomponent systems involving FB and anion–π.

Computational aspects

The geometries of monomers and complexes were fully optimized at the MP2 levels with the 6-311++G** basis set. The harmonic vibrational frequency calculations at the same level were carried out to confirm that the structures obtained corresponded to energy minima. The interaction energies were estimated at the MP2/6-311++G** level with corrections for the basis set superposition error by the counterpoise method of Boys and Bernardi.[44] All ab initio calculations were carried out using the GAMESS package.[45]

Molecular electrostatic potentials (MEPs) were computed on the 0.001 electrons/bohr³ contour of the electronic density using the Wave Function Analysis – Surface Analysis Suite.[46] The topological analysis of the electron charge density[47] was performed by means of the AIM2000 program[48] with the MP2/6-311++G** wave function. Chemical shielding tensors at the site of the fluorine atom in the F_2 and FCN molecules and spin–spin coupling constants across FBs (J_{F-N}) were computed using the gauge-including atomic orbital approach.[49]

Results and discussion

Anion–π and FB complexes

Prior studies have demonstrated the importance of MEPs as an effective method for analyzing and predicting noncovalent interactions.[6–10] Hence, the MEP maps of the isolated monomers are plotted in Fig. 1 to describe the active sites of Lewis acid–base in these molecules. Figure 1 shows that there is a small positive electrostatic potential region associated with the center of the aromatic ring of compounds **1** and **2**, which is surrounded by an electroneutral area. It is this region that favorably interacts with the negative area surrounding the anions F^-, Cl^-, and CN^-. Such an electrostatic attraction is a feature of anion–π bonded complexes (**3–8**), as shown in Fig. 2. From Fig. 1, it is evident that the magnitude of most electrostatic potentials ($V_{S,max}$) of **1** and **2** depends strongly upon the electron-withdrawing power of the fluorine groups. The presence of electron-withdrawing fluorine groups on the ring results in a more positive $V_{S,max}$ value. The representation of the MEP of **1** and **2** also shows a region of negative charge associated with nitrogen atom, with a minimum electrostatic potential ($V_{S,min}$) value of –33.4 and –26.6 kcal/mol for **1** and **2**, respectively. This region is the site of interaction of these structures with potential halogen bond donors. As shown in Fig. 1, the MEP map exhibits the presence of σ-holes (red regions) in the extension of F–F and F–C bonds of F_2 and FCN molecules, respectively. Clearly, the magnitude of the σ-hole on the fluorine atom of both F_2 and FCN is very small. Thus, these molecules are poor acceptors of electron density.

When π-acidic heteroaromatic rings (**1** and **2**) are paired with anion X^- (X = F, Cl, and CN), the negative MEP region associated with X^- is oriented directly to the region of positive MEP on the centroid of the ring (Fig. 2). Table 1 lists the equilibrium distances and interaction energies of isolated anion–π-(**3–8**) and flourine-bonded (**9–12**) complexes at the MP2/6-311++G** level of theory. The anion–π distances are estimated to be in the range of 2.427–3.177 Å and become longer in the order of $F^- < CN^- < Cl^-$, which may be a combination result of the interaction energy and the atomic radius of the interacting atoms. The interaction energies of anion–π complexes are predicted to lie in the range from –10.74 to –28.33 kcal/mol, which compare favorably with the results of previous calculations.[50–52] For example, at the MP2/6-311++G** level, the interaction energies for the anion–π complexes of pyrazine with F^- and Cl^- are estimated to be –16.61 and –12.71 kcal/mol, respectively.[52] Paired with the same ring, F^- forms a stronger anion–π interaction than Cl^- and CN^-, evidenced by the shorter binding distances and more negative interaction energies. Simply, we might ascribe the above trend to the strong polarizing power of F^- compared with the others. In addition, interacting with the same anion, the fluorinated ring (**2**) tends to be a better electron acceptor than **1**, characterized by larger interaction energies in **6–8** complexes than those in **3–5**. For a given FB acceptor,

Fig. 2. Schematic representation of anion–π complexes **3–8**, FB complexes **9–12**, and anion–π–FB complexes **13–24**. The hydrogen atoms of the benzene ring are hidden for simplicity.

3. X=F
4. X=Cl
5. X=CN

6. X=F
7. X=Cl
8. X=CN

9. Y=F
10. Y=CN

11. Y=F
12. Y=CN

13. X=F, Y=F
14. X=Cl, Y=F
15. X=CN, Y=F
16. X=F, Y=CN
17. X=Cl, Y=CN
18. X=CN, Y=CN

19. X=F, Y=F
20. X=Cl, Y=F
21. X=CN, Y=F
22. X=F, Y=CN
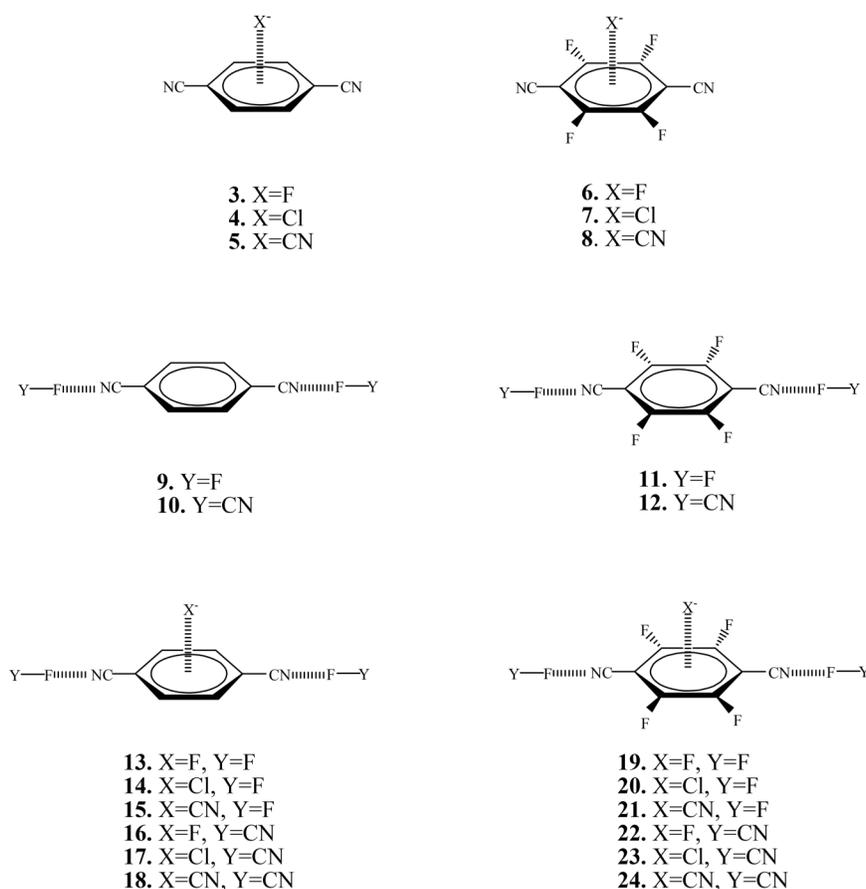**23.** X=Cl, Y=CN
24. X=CN, Y=CN

Table 1. Interaction energies (in kcal/mol), intermolecular distances (in Å), QTAIM properties (in au), ^{19}F chemical shielding isotropy (in ppm), and spin–spin coupling constant across FB (in Hz) for isolated anion–π (**3–8**) and FB (**9–12**) complexes.

Complex	System	E_{int}	$R_{anion-\pi/FB}$	$\rho_{RCP(BCP)}$	$\nabla^2\rho_{RCP(BCP)}$	σ_{iso}	J_{F-N}
3	**1** + F$^-$	−14.26	2.611	0.0197	0.1552		
4	**1** + Cl$^-$	−10.74	3.177	0.0199	0.1556		
5	**1** + CN$^-$	−10.96	2.830	0.0199	0.1551		
6	**2** + F$^-$	−28.33	2.427	0.0177	0.1426		
7	**2** + Cl$^-$	−20.83	2.992	0.0179	0.1429		
8	**2** + CN$^-$	−20.76	2.673	0.0179	0.1424		
9	**1** + 2F$_2$	−1.63	2.748	0.0199 (0.0092)	0.1549 (0.0456)	−374	51
10	**1** + 2FCN	−2.14	2.937	0.0199 (0.0060)	0.1549 (0.0298)	172	57
11	**2** + 2F$_2$	−1.39	2.766	0.0177 (0.0087)	0.1418 (0.0434)	−385	21
12	**2** + 2FCN	−1.74	2.952	0.0177 (0.0057)	0.1418 (0.0286)	173	24

the FCN forms stronger F⋯N interactions than the F$_2$ counterparts, which is consistent with the greater amount of positive electrostatic potential (σ-hole) on the fluorine atom of FCN compared with F$_2$ (Fig. 1). The interaction energies of flourine-bonded complexes **9–12** are modest (less than –1 kcal/mol[1] for each FB interaction) because both rings are not electron donating enough. As the electron donating ability of the nitrogen atom in compounds **1** and **2** decreases, the FB interaction energies become weaker (less negative), which has been demonstrated as well in earlier studies.[4] Thus, the hydrogenated ring forms slightly stronger FBs compared with the fluorinated one.

The topological analysis of the electron density provides helpful information about the existence of anion–π and FB interactions in complexes **3–12**. We used the electron density (ρ) and it's Laplacian ($\nabla^2\rho$) to analyze the topological characteristics at the bond critical points (BCPs) and ring critical points (RCPs). Table 1 lists the results of the above quantities for **3–12** obtained at the MP2/6-311++G** level of theory. It is found that the ρ and $\nabla^2\rho$ values of anion–π RCPs are in the range of 0.0177–0.0199 and 0.1418–0.1549 au, respectively. As expected, the amount of ρ_{RCP} of complex **6** is very small (0.0177 au) due to the strong anion–π interaction between F$^-$ and **2**. The values of ρ at the F⋯N BCPs in complexes **9–12** fall in the generally accepted range of a hydrogen bond, which is in the range of 0.002–0.035 au.[53] Their corresponding Laplacian $\nabla^2\rho$ values fall in the proposed range (0.024–0.139 au) of a hydrogen bond.[53] This suggests that the F⋯N interaction in all complexes is the closed-shell interaction.

Also shown in Table 1 are the ^{19}F chemical shielding isotropy (σ_{iso}) and spin–spin coupling constants (J_{F-N}) for the isolated FB

complexes. The calculated σ_{iso} values of isolated F_2 and FCN monomers are –430 and 228 ppm, respectively. It is typically the case that FB formation is connected with a decrease (downshift) in fluorine's σ_{iso} value.[54] The calculated σ_{iso} values for the fluorine-bonded complexes (**9**–**12**) listed in Table 1 confirm this expectation. In particular, the results indicate that the σ_{iso} parameter at the site of the fluorine atom is reduced by 56 ppm from the free F_2 to the **1** + 2F_2 system. It is interesting that this reduction is considerably greater than the corresponding decrease of 45 ppm in complex **11**. For all FB complexes, the values of J_{F-N} are in the range of 21–57 Hz. It is clear by comparing the interaction energy with the value of the spin–spin coupling constants across FB that the larger J_{F-N} corresponds to the stronger FB interaction.

Cooperative effects in multicomponent anion–π–FB complexes

The representation of anion–π–FB complexes with C_{2v} symmetry are indicated in Fig. 2. These geometries make sense from an electrostatic perspective, matching a positive region of one molecule with a negative area of its partner. As evident, the σ-hole on the fluorine atom of F_2 or FCN interacts with the lone pair of the nitrogen atom and the positive region on the hetroatomic ring is paired with the anion X⁻ simultaneously. The structures of the two molecular pairs of anion–π and FB in the tetramer complexes are similar to those in the optimized isolated complexes, although the anion–π and FB binding distances become a little shorter. This is due to the mutual effects between anion–π and FB interactions when they coexist within the anion–π–FB complexes.

To shed more light on the cooperative phenomenon, let us consider the MEPs of the isolated anion–π and FB complexes. We note that both anion–π and FB interactions have been described as being an electrostatically driven interaction, and therefore, Table 2 compares the computed $V_{S,max}$ and $V_{S,min}$ values of anion–π (**3**–**8**) and FB (**9**–**12**) complexes. One can see that upon anion–π interaction, the $V_{S,min}$ value associated with the nitrogen atom of complexes **3**–**6** becomes more negative. For instance, the nitrogen $V_{S,min}$ is increased from –33.4 kcal/mol in **1** to –92 kcal/mol in the **1** + F⁻ system. Furthermore, there is an approximate relation between the increased percentage of the nitrogen $V_{S,min}$ and the strength of the anion–π interactions in these complexes, namely, the greater the anion–π strength, the larger the increase in the $V_{S,min}$ value. This means that the nitrogen atom in the binary systems **3**–**6** is a better electron donor than that of free **1** and **2** molecules. In other words, the MEP analysis reveals that the formation of each anion–π interaction intrinsically "primes" the nitrogen atom to form stronger FBs. Table 2 also indicates that the calculated $V_{S,max}$ values associated with the aromatic ring of the fluorine-bonded complexes **9**–**12** are more positive than those of compounds **1** and **2**. This increase in the $V_{S,max}$ values explicitly indicates that all anion–π interactions within the multicomponent complexes **13**–**24** should be stronger than those in the isolated anion–π complexes (**3**–**8**).

The geometric and energetic results computed for multicomponent complexes **13**–**24** are listed in Table 3. The binding distances in the multicomponent complexes are always shorter than those in the isolated anion–π or FB complexes. For each complex, the shortening of the binding distance in the flourine bonding is far more prominent than that in the anion–π bonding. For example, it is 0.095 Å in the former and 0.017 Å in the latter for the **1** + F⁻ + 2FCN complex. The total interaction energies of the multicomponent complexes range from –13.25 to –33.91 kcal/mol. One can see that the interaction energies in the F⁻-bonded complexes are more negative than those of the Cl⁻ and CN⁻ counterparts. As the electron-accepting ability of the ring in compounds **1** and **2** increases, the interaction energies become larger (more negative). Hence, the fluorinated ring forms stronger complexes compared with the hydrogenated one. Figure 3 shows the correlation between the interaction energies and anion–π binding distances. A

Table 2. Calculated $V_{S,max}$ and $V_{S,min}$ values for isolated anion–π and FB complexes.

Complex	System	$V_{S,max}$ (kcal/mol)	$V_{S,min}$ (kcal/mol)
3	**1** + F⁻		–92.0
4	**1** + Cl⁻		–87.9
5	**1** + CN⁻		–87.2
6	**2** + F⁻		–85.7
7	**2** + Cl⁻		–82.4
8	**2** + CN⁻		–81.5
9	**1** + 2F_2	48.6	
10	**1** + 2FCN	50.2	
11	**2** + 2F_2	44.0	
12	**2** + 2FCN	45.2	

nice linear relationship is found for X = F, Cl, and CN substituents. The line slope increases in the order X = CN < Cl < F.

The last column of Table 3 shows the cooperativity energy E_{coop} of the multicomponent complexes. This term is intended to provide an estimation of the "extra" energetic stabilization obtained in multicomponent complexes as a result of the interplay of both interactions. It is computed with formulas of

$$(1) \quad E_{coop} = E_{int}(\text{anion–π–FB}) - E_{int}(\text{anion–π}) - E_{int}(\text{FB}) - E_{int}(\text{anion-}F_2/\text{anion-FCN})\lim_{x\to\infty}$$

where $E_{int}(\text{anion–π})$, $E_{int}(\text{FB})$, and $E_{int}(\text{anion–π–FB})$ are the interaction energies of the corresponding optimized anion–π, FB, and anion–π–FB complexes, respectively. $E_{int}(\text{anion–}F_2/\text{anion–FCN})$ is the interaction of the anion–F_2 or anion–FCN fragments in the anion–π–FB complexes. In all anion–π–FB complexes **13**–**24**, a favorable cooperativity is found with values that range between –0.51 and –0.76 kcal/mol. These negative E_{coop} values indicate that a positive cooperative effect is present between the anion–π and FB interactions. That is, the mutual influence of the two interactions is transmitted through the π-bonds from the anion X⁻ to the F_2 or FCN molecule and vice versa. With increasing the interaction energy of anion–π, the cooperative energy between them also grows. From the Table 3 results, one can see that the computed E_{coop} values are modest for complexes **14** and **15** because the anion–π and FB interactions are weak. Nevertheless, cooperative effects between the two interactions contribute 4% of the total interaction energy of the anion–π–FB complexes. For the rest of complexes, the E_{coop} values are significant, especially in complexes **16** and **22**, that is, the compound F⁻ becomes a strong electron donor as a consequence of participation of the aromatic ring in concerted anion–π and FB interactions. On the other hand, for a given X⁻ and π-system, the complexes in which stronger FB donor (FCN) is present exhibit strong cooperativity, while weaker cooperativity occurs in the complexes involving F_2, that is, the stronger FB interaction shows a larger increased percentage of the interaction energy due to anion–π interactions, which has been well documented in previous studies of the interplay between two the different types of interactions.[55] Figure 4 shows the relationship between the cooperative energies E_{coop} and corresponding ΔR_{FB} values. The linear correlation coefficient is 0.946. This reveals that the cooperative effects play a role in the formation and stability of the anion–π–FB complexes.

To further understand the cooperativity between the anion–π and FB interactions in multicomponent complexes, we performed an analysis of many-body decomposition of the interaction energy. Table 4 gives the results of the many-body interaction energy analyses of the multicomponent complexes **13**–**24**. Following the standard notation, the total interaction energy E_{int} of a four-body

Table 3. Binding distances (in Å), their changes relative to isolated anion–π and FB systems (in Å), interaction energies (in kcal/mol), and cooperative energies (in kcal/mol) of anion–π–FB complexes.

Complex	System	$R_{\text{anion–π}}$	R_{FB}	$\Delta R_{\text{anion–π}}$	ΔR_{FB}	E_{int}	E_{coop}
13	$1 + \text{F}^- + 2\text{F}_2$	2.603	2.661	−0.008	−0.087	−16.92	−0.69
14	$1 + \text{Cl}^- + 2\text{F}_2$	3.171	2.674	−0.006	−0.074	−13.25	−0.59
15	$1 + \text{CN}^- + 2\text{F}_2$	2.823	2.680	−0.007	−0.068	−13.41	−0.55
16	$1 + \text{F}^- + 2\text{FCN}$	2.594	2.842	−0.017	−0.095	−20.26	−0.76
17	$1 + \text{Cl}^- + 2\text{FCN}$	3.162	2.848	−0.015	−0.089	−16.32	−0.68
18	$1 + \text{CN}^- + 2\text{FCN}$	2.815	2.858	−0.015	−0.079	−16.47	−0.65
19	$2 + \text{F}^- + 2\text{F}_2$	2.420	2.684	−0.007	−0.082	−30.71	−0.64
20	$2 + \text{Cl}^- + 2\text{F}_2$	2.988	2.698	−0.004	−0.068	−23.09	−0.58
21	$2 + \text{CN}^- + 2\text{F}_2$	2.668	2.707	−0.005	−0.059	−22.94	−0.51
22	$2 + \text{F}^- + 2\text{FCN}$	2.422	2.857	−0.005	−0.095	−33.91	−0.73
23	$2 + \text{Cl}^- + 2\text{FCN}$	2.972	2.862	−0.020	−0.090	−26.12	−0.68
24	$2 + \text{CN}^- + 2\text{FCN}$	2.661	2.872	−0.012	−0.080	−25.89	−0.61

Fig. 3. Correlation between interaction energy and anion–π distances in multicomponents complexes **13–24**.
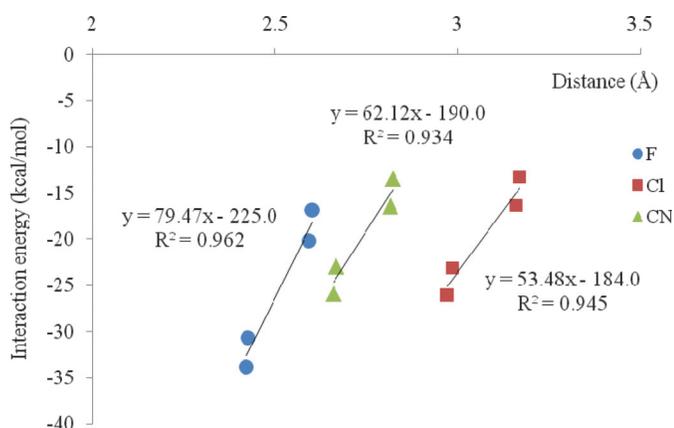
Fig. 4. Correlation between cooperative energies E_{coop} and corresponding ΔR_{FB} values in multicomponents complexes **13–24**.
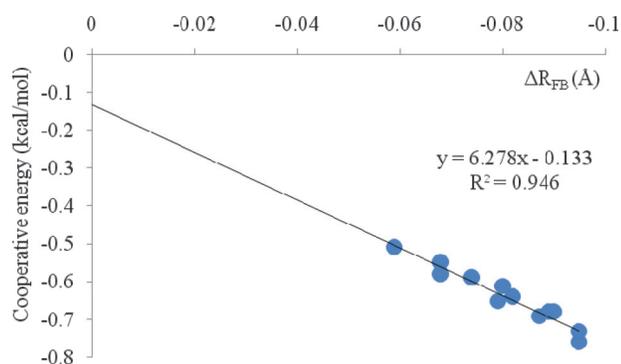
complex may be represented as a sum of the one-, two-, three-, and four-body terms in the following way:[56]

$$(2) \qquad E_{\text{int}} = E_{\text{R}} + E_{\text{2-body}} + E_{\text{3-body}} + E_{\text{4-body}}$$

The one-body term E_{R}, often referred to as the "relaxation" or "deformation" energy, represents the energy penalty for distorting the individual monomers in the equilibrium complex geometries with respect to those in isolation. This term can be quite small, especially for systems with weak interactions. As seen in Table 4, the relaxation energy is positive, that is, it makes a destabilization contribution to the total interaction energy of the complexes. The relaxation energy is largest for the most stable complexes **19** and **22**. The pairwise-additive (two-body) energy for

a given anion–π–FB complex can be estimated as the interaction energy of each molecular pair in the geometry of triad minus the energy sum of the monomers, all of them frozen in the geometry of the complex:

$$(3) \qquad E_{\text{2-body}} = E_{\text{int}}(\text{anion–π}) + E_{\text{int}}(\text{FB}) + 2E_{\text{int}}(\text{anion–F}_2/\text{FCN})$$

whereas the three-body component is defined as

$$(4) \qquad E_{\text{3-body}} = E_{\text{int}}(\text{ABC}) - E_{\text{R}} - E_{\text{2-body}}$$

and so on, following the same logic.

Table 4 lists the calculated $E_{\text{2-body}}$, $E_{\text{3-body}}$, and $E_{\text{4-body}}$ energy terms for the multicomponent complexes **13–24**. It is evident that the two-, three-, and four-body interaction energies are all attractive, indicating a positive contribution to the interaction energy of the complexes. The calculated anion–π interaction energies in the multicomponent complexes are in the range of −10.62 to −28.30 kcal/mol. The corresponding FB and anion–F$_2$/FCN interaction energies range from −0.62 to −1.57 kcal/mol and from −0.14 to −1.56 kcal/mol, respectively. As expected, the fluorinated aromatic ring forms stronger anion–π interactions than the hydrogenated one. Furthermore, all anion–π and FB interactions in the tetramer structure are slightly weaker than those of the isolated binary complexes (Table 1). This is not surprising, since both anion–π and FB distances in the tetramer geometry deviate slightly from their corresponding equilibrium distance in the isolated binary complex. One can see that the most important energy component arises from the two-body interactions, which account for 94%–97% of the total interaction energy. Besides, the three-body term contributes more importantly than the three-body term in the total interaction energy for most of the complexes. An excellent correlation is found between the E_{coop} energies in the ternary complexes and the calculated four-body energies with $R^2 = 0.977$ (Fig. 5). This indicates that the four-body term can be used as a measure of cooperativity between the anion–π and FB interactions in the title systems.

The strong cooperativity between the anion–π and FB interactions is also reflected in the magnitude of the charge density at RCPs and BCPs of the multicomponent systems with respect to the isolated anion–π and FB complexes. The results are listed in Table 5. The values of electron density at the RCPs are in the range of 0.0177–0.0199 au in complexes **21–36**. The corresponding electron density values at the BCPs values are between 0.0070 and 0.0113 au. Clearly, for a given complex, electron density value at the RCP is larger than that in the BCP. However, the difference of the ρ_{RCP} between the multicomponent complexes **13–24** and binary systems **3–8** is very small. This shows that the FB has a negligible effect on the enhancement of the anion–π interaction in

Table 4. Many-body decomposition of anion–π–FB complexes (all energies are in kcal/mol).

Complex	System	E_R	E_{int} (anion–π)	E_{int} (FB)	E_{int} (anion-2F$_2$/FCN)	$E_{2\text{-body}}$	$E_{3\text{-body}}$	$E_{4\text{-body}}$
13	**1** + F$^-$ + 2F$_2$	0.01	−14.22	−0.73	−0.17	−16.04	−0.45	−0.44
14	**1** + Cl$^-$ + 2F$_2$	0.01	−10.70	−0.75	−0.14	−12.49	−0.39	−0.38
15	**1** + CN$^-$ + 2F$_2$	0.01	−10.92	−0.75	−0.14	−12.72	−0.35	−0.35
16	**1** + F$^-$ + 2FCN	0.02	−14.19	−1.00	−1.56	−19.32	−0.48	−0.48
17	**1** + Cl$^-$ + 2FCN	0.01	−10.62	−1.01	−1.42	−15.48	−0.43	−0.42
18	**1** + CN$^-$ + 2FCN	0.01	−10.88	−1.03	−1.37	−15.67	−0.40	−0.41
19	**2** + F$^-$ + 2F$_2$	0.03	−28.30	−0.62	−0.18	−29.93	−0.41	−0.40
20	**2** + Cl$^-$ + 2F$_2$	0.02	−20.80	−0.63	−0.15	−22.40	−0.36	−0.35
21	**2** + CN$^-$ + 2F$_2$	0.01	−20.74	−0.64	−0.14	−22.32	−0.32	−0.31
22	**2** + F$^-$ + 2FCN	0.02	−28.28	−1.57	−0.79	−33.01	−0.46	−0.46
23	**2** + Cl$^-$ + 2FCN	0.02	−20.77	−1.48	−0.80	−25.28	−0.44	−0.42
24	**2** + CN$^-$ + 2FCN	0.01	−20.70	−1.40	−0.81	−25.12	−0.39	−0.39

Fig. 5. Relationship between cooperative energies E_{coop} and four-body energy term in multicomponents complexes **13–24**.

$$y = 1.502x - 0.036$$
$$R^2 = 0.977$$
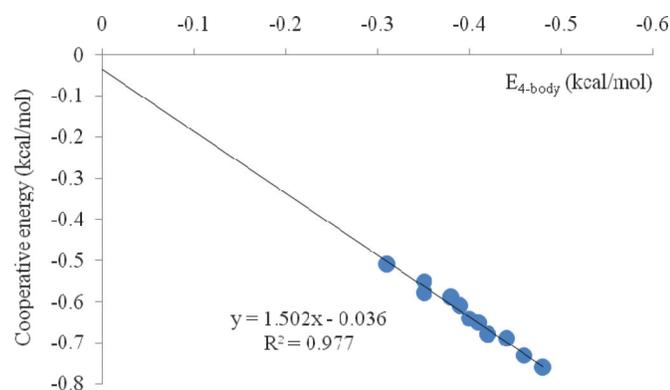
Table 5. Calculated charge density (in au) and the corresponding Laplacian (in au) for RCPs and BCPs of anion–π–FB complexes.

Complex	System	ρ_{RCP}	$\nabla^2\rho_{RCP}$	ρ_{BCP}	$\nabla^2\rho_{BCP}$
13	**1** + F$^-$ + 2F$_2$	0.0197	0.1552	0.0113	0.0573
14	**1** + Cl$^-$ + 2F$_2$	0.0199	0.1554	0.0110	0.0553
15	**1** + CN$^-$ + 2F$_2$	0.0199	0.1550	0.0108	0.0543
16	**1** + F$^-$ + 2FCN	0.0197	0.1552	0.0076	0.0379
17	**1** + Cl$^-$ + 2FCN	0.0199	0.1554	0.0075	0.0373
18	**1** + CN$^-$ + 2FCN	0.0199	0.1551	0.0073	0.0363
19	**2** + F$^-$ + 2F$_2$	0.0177	0.1428	0.0107	0.0537
20	**2** + Cl$^-$ + 2F$_2$	0.0179	0.1432	0.0103	0.0517
21	**2** + CN$^-$ + 2F$_2$	0.0179	0.1423	0.0101	0.0506
22	**2** + F$^-$ + 2FCN	0.0177	0.1426	0.0073	0.0362
23	**2** + Cl$^-$ + 2FCN	0.0179	0.1430	0.0072	0.0358
24	**2** + CN$^-$ + 2FCN	0.0179	0.1423	0.0070	0.0349

Table 6. ^{19}F chemical shielding isotropy (in ppm) and spin–spin coupling constant across FB (in Hz) for RCPs and BCPs of anion–π–FB complexes.

Complex	System	σ_{iso}	J_{F-N}
13	**1** + F$^-$ + 2F$_2$	−259	128
14	**1** + Cl$^-$ + 2F$_2$	−321	95
15	**1** + CN$^-$ + 2F$_2$	−324	80
16	**1** + F$^-$ + 2FCN	165	73
17	**1** + Cl$^-$ + 2FCN	165	71
18	**1** + CN$^-$ + 2FCN	166	70
19	**2** + F$^-$ + 2F$_2$	−321	86
20	**2** + Cl$^-$ + 2F$_2$	−354	78
21	**2** + CN$^-$ + 2F$_2$	−352	72
22	**2** + F$^-$ + 2FCN	166	39
23	**2** + Cl$^-$ + 2FCN	167	38
24	**2** + CN$^-$ + 2FCN	167	35

Table 6 reports the ^{19}F chemical shielding isotropy (σ_{iso}) and spin–spin coupling constant (J_{F-N}) values in the multicomponent systems. Cooperative effects strengthen the anion–π bond and FB interactions and therefore lead to a further shift in fluorine's σ_{iso} values. Obviously, the amount of shift depends on the strength of the anion–π and FB interactions. It is largest in complex **13** and smallest in complex **24**. This is consistent with the fact that the former is bonded more strongly than the latter, which is in agreement with the anion–π and FB strengths in the two systems. For a given FB donor, the absolute value of σ_{iso}(^{19}F) decreases in the order X = CN < Cl < F, which is consistent with the corresponding intermolecular distance and anion–π interaction. Moreover, it is evident from Table 6 that anion–π can cause an increase of the J_{F-N} value, which can be regarded as a good description to quantify the amount of cooperative effects in these systems.

Conclusion

MP2/6-311++G** calculations were carried out to study the interplay between anion–π and FB interactions. The equilibrium distances, interaction energies, electron density, and ^{19}F NMR properties were analyzed. It is found that the ring is able to transmit the cooperative effect from the anion through the conjugated π-system to the F$_2$ or FCN molecule and vice versa. Both anion–π and FB distances in multicomponent complexes are shorter than those in the isolated complexes. The presence of the anion–π interaction strengthens the FB interaction and the enhancement is related to the strength of the FB interaction and the nature of the anion. For each complex, the shortening of the binding distance in the fluorine bonding is more prominent than that in the anion–π bonding. Moreover, stronger anion–π interactions show larger cooperative energies. The calculated charge density values at F···N BCPs of the anion–π–FB systems are slightly greater than

the multicomponent complexes. On the other hand, the Table 5 results reveal that the ρ_{BCP} values in all of the anion–π–CB complexes are slightly larger than those in the isolated FB complexes. This result confirms that the FB interactions in complexes **13–24** are reinforced with respect to the isolated systems. When the anion is F$^-$, greater values of $\Delta\rho_{BCP}$ are predicted, in good agreement with the strong cooperativity found in the complexes involving F$^-$. The increase of the ρ_{BCP} value at the F···N BCP is the largest in complex **13**, which shows a strong cooperativity as noted above. For a given complex, the computed values of $\Delta\rho_{BCP}$ are larger than the corresponding $\Delta\rho_{RCP}$ values, and this is further confirmation that the presence of anion–π influences FB interactions greatly. These results are in agreement with the binding distance changes ΔR in Table 3, indicating that the effect of anion–π on the properties of FB is much larger than that of FB on the properties of anion–π.

those in the isolated complexes, which imply strengthening of the FB interactions. The amount of shift of fluorine's σ_{iso} values depends on the strength of anion–π and FB interactions.

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