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Energetic Effects between Halogen Bonds and Anion-π or Lone Pair-π Interactions: A Theoretical Study

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Ⓢ Supporting Information

ABSTRACT: Energetic effects between halogen bonds and anion-π or lone pair-π interactions have been investigated by means of ab initio MP2 calculations. 1,4-diiodo-perfluorobenzene, a very effective building block for crystal engineering based on halogen bonding, is selected in this work both as electron-deficient π aromatic ring and as halogen bond donor. Additive and diminutive effects are observed when halogen bonds and anion-π/lone pair-π interactions coexist in the same complex, which can be ascribed to the same direction of charge transfer for the two interactions. These effects have been analyzed in detail by the structural, energetic, and AIM properties of the complexes. Finally, experimental evidence of the combination of the interactions has been obtained from the Cambridge Structural Database.
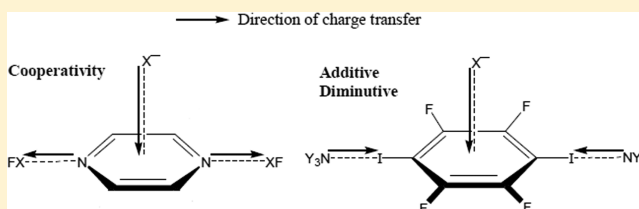
■ INTRODUCTION

Noncovalent interactions play a central role in supramolecular chemistry, molecular biology, crystal engineering, and a host of other fields of chemical sciences. As a result of this broad importance, numerous attempts have been made to elucidate and quantify these interactions, including hydrogen bonding (HB), π−π stacking, cation-π, electrostatic, hydrophobic, and van der Waals forces.[1−5] In recent years, halogen bonding (XB), the noncovalent interaction where halogen atoms function as electrophilic species, has attracted intense interest in chemistry and structural biology.[6−15] Organic halogens display an anisotropic charge distribution, with an equatorial ring of negative charge and a region of positive charge, termed the σ-hole, along the extension of the C−X bonds.[16−20] Therefore, linear attractive interactions, i.e., halogen bonds, can be formed between halogen σ-hole and Lewis bases.

Experimental and theoretical evidence of interesting synergetic effects between anion-π and HB and between anion-π and π−π stacking interactions has been reported recently; the interplay between these interactions can lead to strong cooperativity effects.[21−31] The cooperativity between XB and HB or lithium bond was also studied using ab initio calculations at the post-HF levels.[32,33] Particularly, Frontera and co-workers have revealed cooperativity effects when anion-π interactions and halogen bonds coexist in the same complex.[34] They chose four π-acidic heteroatomic rings that act as acceptors in XB and two dihalogen molecules (FCl and FBr) as halogen bond donors. However, it has been well documented that the chief breakthrough in the application of XB in solid-state supramolecular chemistry was based on the strong, specific, and well-characterized N···I-PFC synthons, where PFC denotes perfluorocarbon moiety and N is either sp[2] (typically

pyridine derivate) or sp[3] (tertiary amine) nitrogen. The excellence of these synthons and the unique advantages of PFC-moieties have been extensively exploited by the group of Metrangolo and Resnati.[6−10] More importantly, certain halogen-bonding receptors based on I-PFCs were developed for tight binding of halide anions in solution.[35,36]

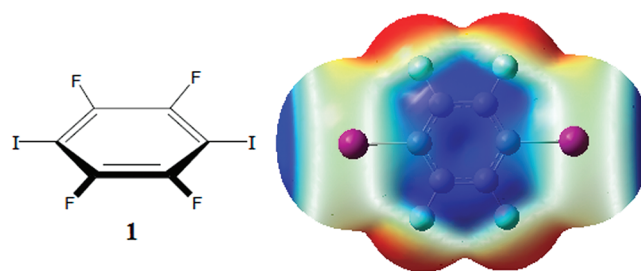In this work, 1,4-diiodo-tetrafluorobenzene (compound **1** in Figure 1), which has been widely used in XB-based

Figure 1. Electrostatic potential surface of compound **1**. The electrostatic potential varies between −0.015 (red) and +0.015 (blue) a.u.

supramolecular architectures,[7] is selected both as electron-deficient π ring and as halogen bond donor. The graphical illustration of electrostatic potential (ESP) surface for compound **1** is depicted in Figure 1. It can be seen that iodine atoms display a region of positive ESP on the outer side of I

along the extension of the C−I bonds, clearly accounting for the directionality of XB. In addition, a large region of positive ESP centered on the aromatic ring is also observed. On the basis of these, the concurrent formation of halogen bonds and anion-π or lone pair (lp)-π interactions in the complexes of **1** can be expected. Two Lewis bases, NF_3 and NH_3, are chosen as halogen bond acceptors to model real systems found within crystal structures.

We first carry out calculations on isolated anion-π/lp-π dimers **2−5** and halogen-bonded complexes **6−9** (see Figure 2).
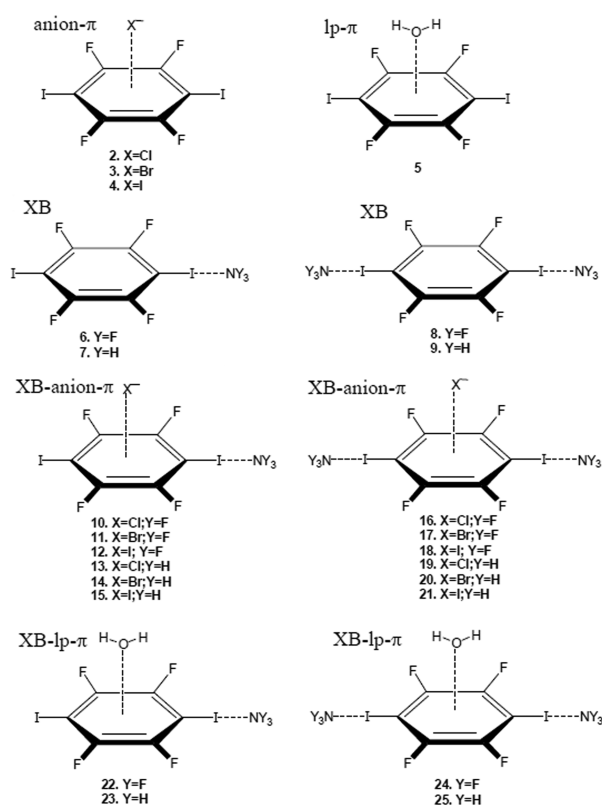

Figure 2. Anion-π dimers **2−4**, lp-π dimer **5**, halogen-bonded complexes **6−9**, XB-anion-π complexes **10−21**, and XB-lp-π complexes **22−25**.

Then, the structural and energetic properties of XB-anion-π complexes **10−21** and XB-lp-π systems **22−25** are computed to explore the mutual influence of the two interactions. Additionally, the quantum theory of atoms in molecules (AIM),[37] which has been successfully applied to characterize various kinds of noncovalent interactions,[22] is employed to analyze additive and diminutive effects in the complexes under investigation. This work would be of great importance in crystal engineering and molecular recognition, considering the fact that I-PFCs have been widely used in the design and synthesis of new functional materials and effective anion receptors based on XB.

■ COMPUTATIONAL DETAILS

The geometries of all the complexes studied in this work were fully optimized at the MP2 level of theory using the *Gaussian 03* and *Gaussian 09* suite of programs.[38,39] The aug-cc-pVDZ-PP basis set, which uses pseudopotentials to describe the inner core orbitals, was employed for iodine, whereas for N, O, Cl, and Br atoms aug-cc-pVDZ was applied and for C, F, H atoms cc-pVDZ was used. During the calculations, geometry constraint, i.e., halogen bond angle $\angle(C-I\cdots N)$ was fixed to be 180° to prevent NH_3 forming $H\cdots X^-$ hydrogen bonds with halide anions, was imposed on the complexes **13−15** and **19−21**. In fact, all halogen bonds in the complexes considered show a strictly linear geometry ($\angle(C-I\cdots N) \approx 180°$). Frequency calculations performed at the same theoretical level indicate that all the structures obtained correspond to energetic minima with the exceptions of **23** and **25** that have one imaginary frequency (18i cm^{-1} and 46i cm^{-1}). In principle, multiple minima are possible for the complexes under study. However, we consider herein only the minima associated with halogen bonds and anion-π/lp-π interactions, because the main purpose of this work is to explore energetic effects between the two interactions.

The interaction energies were counterpoise corrected with the procedure of Boys and Bernardi, in order to account for the basis set superposition error (BSSE).[40] Atomic charges were calculated in terms of the Merz−Kollman (MK) scheme,[41] which has been demonstrated to provide reliable results of charge transfer of noncovalent interactions.[34] The AIM analysis was performed with the help of AIM 2000 software[42] using the wave functions generated at the MP2 level of theory.

For the complexes in which halogen bonds and anion-π or lp-π interactions coexist, the cooperativity energy E_{coop} was evaluated using eq 1

$$E_{coop} = \Delta E(XB + A\pi/lp\pi) - \Delta E(XB) - \Delta E(A\pi/lp\pi)$$
$$- \Delta E(AL/lpL) \quad (1)$$

where $\Delta E(XB)$, $\Delta E(A\pi/lp\pi)$, and $\Delta E(XB + A\pi/lp\pi)$ are the interaction energies of the corresponding optimized XB,

Table 1. Calculated Geometric Parameters, Interaction Energies, AIM Properties, and Amount of Charge Transfer for the Complexes 2−9[a]

complexes	ΔE	R_{XB}	$R_{A\pi/lp\pi}$	ρ_{CCP}	ρ_{BCP}	$Q_{CT}(XB)$	$Q_{CT}(A\pi)$
2 $(1+Cl^-)$	−11.18		3.088	0.668			−0.160
3 $(1+Br^-)$	−10.06		3.248	0.742			−0.134
4 $(1+I^-)$	−8.69		3.501	0.656			−0.128
5 $(1+H_2O)$	−2.39		2.886	0.529			−0.028
6 $(1+NF_3)$	−0.67	3.227			1.002	−0.111	
7 $(1+NH_3)$	−5.07	2.970			1.838	−0.166	
8 $(1+2NF_3)$	−1.35	3.227			1.002	−0.104	
9 $(1+2NH_3)$	−9.68	2.993			1.757	−0.154	

[a]Distances are given in angstroms, energies in kilocalories per mol, and charge transfer in a.u. Electron densities ($10^2\rho$) at cage CPs for the dimers **2−5** and at bond CPs for the complexes **6−9** are given in a.u.

Table 2. Energetic Data and Intermolecular Distances and Their Variations for the Complexes 10−25^a

complexes	ΔE	E_{coop}	E_{syn}	R_{XB}	ΔR_{XB}	$R_{A\pi/lp\pi}$	$\Delta R_{A\pi/lp\pi}$
10 (1+NF$_3$+Cl$^-$)	−11.94	0.22	−0.09	3.287	0.060	3.093	0.005
11 (1+NF$_3$+Br$^-$)	−10.81	0.22	−0.08	3.284	0.057	3.250	0.002
12 (1+NF$_3$+I$^-$)	−9.46	0.19	−0.10	3.277	0.050	3.503	0.002
13 (1+NH$_3$+Cl$^-$)	−12.51	1.96	3.74	3.158	0.188	3.124	0.036
14 (1+NH$_3$+Br$^-$)	−11.52	1.89	3.61	3.134	0.164	3.285	0.037
15 (1+NH$_3$+I$^-$)	−10.41	1.70	3.35	3.114	0.144	3.536	0.035
16 (1+2NF$_3$+Cl$^-$)	−12.69	0.42	−0.16	3.289	0.062	3.089	0.001
17 (1+2NF$_3$+Br$^-$)	−11.57	0.41	−0.16	3.285	0.058	3.249	0.001
18 (1+2NF$_3$+I$^-$)	−10.20	0.41	−0.16	3.285	0.058	3.501	0.000
19 (1+2NH$_3$+Cl$^-$)	−13.52	3.70	7.34	3.160	0.190	3.152	0.064
20 (1+2NH$_3$+Br$^-$)	−12.74	3.52	7.00	3.146	0.176	3.315	0.067
21 (1+2NH$_3$+I$^-$)	−11.93	3.21	6.44	3.138	0.168	3.576	0.075
22 (1+NF$_3$+H$_2$O)	−3.04	0.03	0.02	3.239	0.012	2.881	−0.005
23 (1+NH$_3$+H$_2$O)	−6.98	0.33	0.48	2.999	0.020	2.886	0.000
24 (1+2NF$_3$+H$_2$O)	−3.68	0.08	0.06	3.239	0.012	2.882	−0.004
25 (1+2NH$_3$+H$_2$O)	−11.12	0.63	0.95	3.021	0.051	2.890	0.004

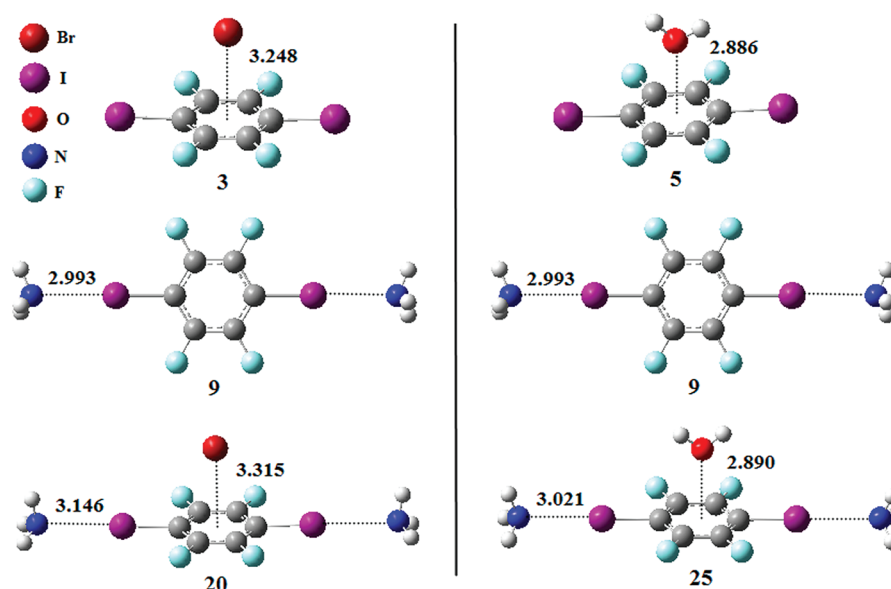^{a}Distances are given in angstroms and energies in kilocalories per mol.

Figure 3. Optimized geometries of the complexes **20** and **25**. Distances are in angstrom.

anion-π/lp-π, and XB-anion-π/lp-π complexes, respectively. The last term is the interactions of Lewis bases (NF$_3$ and NH$_3$) with halide anions or H$_2$O with the coordinates frozen in the geometries of the XB-anion-π/lp-π complexes.

We also computed the synergetic energies using the first three terms of eq 1, as shown in eq 2

$$E_{syn} = \Delta E(XB + A\pi/lp\pi) - \Delta E(XB) - \Delta E(A\pi/lp\pi)$$

(2)

The two interactions in the complexes should be totally additive when the values of E_{syn} are close to zero, whereas positive E_{syn} indicates diminutive effects in the complexes.

■ RESULTS AND DISCUSSION

Structural and Energetic Features of Isolated Anion-π, lp-π, and Halogen-Bonded Complexes. The key geometric parameters and interaction energies for the complexes 2−9 (see Figure 2) are given in Table 1. Anion-π and lp-π interactions have been the subject of a great number of theoretical and

crystallographic data studies over the past few decades.[43−48] It has been accepted that electrostatic forces are the main energetic contributions to anion-π/lp-π complexes of electron-deficient aromatic molecules, while dispersion forces, which are generally important in weak interactions including aromatic rings, play a lesser role in the two interactions. These are consistent with the ESP distribution of compound **1** in which a large region of positive ESP is centered on the aromatic ring, as displayed in Figure 1. Anions and lone pair-possessing atoms thus can reside on the ring and form attractive interactions with **1**. From Table 1, it is seen that the interaction energies for the anion-π/lp-π complexes **2−5** are predicted within the range from −2.39 to −11.18 kcal/mol, which compare favorably well with previous calculation results.[49−51] For example, at the MP2/6-31++G(d,p) level, the interaction energies for the anion-π/lp-π complexes of C$_6$F$_6$ with Cl$^-$, Br$^-$, and H$_2$O are estimated to be −12.88, −12.11, and −3.08 kcal/mol, respectively.[50,51] Topological analysis of the electron density further validates the existence of anion-π/lp-π interactions in the systems **2−5**. Namely, a cage critical point (CCP), which is

Table 3. Amount of Charge Transfer, Electron Densities at the CCPs and BCPs and Their Variations for the Complexes 10−25[a]

| complexes	$Q_{CT}(XB)$	$\Delta Q_{CT}(XB)$	$Q_{CT}(A\pi)$	$\Delta Q_{CT}(A\pi)$	ρ_{BCP}	$\Delta\rho_{BCP}$	ρ_{CCP}	$\Delta\rho_{CCP}$
10 $(1+NF_3+Cl^-)$	−0.078	0.033	−0.163	−0.003	0.900	−0.102	0.661	−0.007
11 $(1+NF_3+Br^-)$	−0.091	0.020	−0.137	−0.003	0.794	−0.208	0.742	0.000
12 $(1+NF_3+I^-)$	−0.090	0.021	−0.131	−0.003	0.802	−0.200	0.656	0.000
13 $(1+NH_3+Cl^-)$	−0.101	0.065	−0.156	0.004	1.279	−0.559	0.634	−0.034
14 $(1+NH_3+Br^-)$	−0.101	0.065	−0.128	0.006	1.171	−0.667	0.710	−0.032
15 $(1+NH_3+I^-)$	−0.097	0.069	−0.122	0.006	1.233	−0.605	0.632	−0.024
16 $(1+2NF_3+Cl^-)$	−0.073	0.031	−0.165	−0.005	0.896	−0.106	0.668	0.000
17 $(1+2NF_3+Br^-)$	−0.093	0.011	−0.141	−0.007	0.902	−0.100	0.636	−0.106
18 $(1+2NF_3+I^-)$	−0.090	0.014	−0.136	−0.008	0.911	−0.091	0.568	−0.088
19 $(1+2NH_3+Cl^-)$	−0.092	0.062	−0.152	0.008	1.271	−0.486	0.620	−0.048
20 $(1+2NH_3+Br^-)$	−0.095	0.059	−0.121	0.013	1.196	−0.561	0.689	−0.053
21 $(1+2NH_3+I^-)$	−0.095	0.059	−0.116	0.012	1.207	−0.550	0.604	−0.052
22 $(1+NF_3+H_2O)$	−0.108	0.003	−0.034	−0.006	0.983	−0.019	0.534	0.005
23 $(1+NH_3+H_2O)$	−0.156	0.010	−0.033	−0.005	1.741	−0.097	0.530	0.001
24 $(1+2NF_3+H_2O)$	−0.105	−0.001	−0.039	−0.011	0.983	−0.019	0.533	0.004
25 $(1+2NH_3+H_2O)$	−0.150	0.004	−0.038	−0.010	1.670	−0.087	0.527	−0.002

[a]All the values are given in a.u.
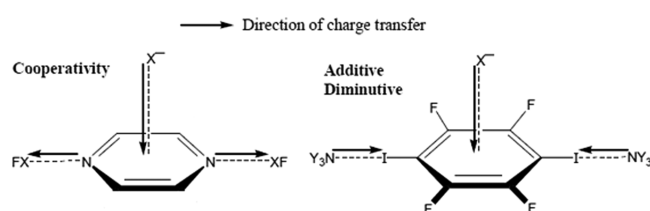
Figure 4. Direction of charge transfer in the complexes in which the two interactions coexist.

a common feature of anion-π/lp-π complexes including aromatic rings,[49,51] is identified for the interactions. It has been demonstrated that the properties at the cage CPs, such as

electron density (ρ) and its Laplacian ($\nabla^2\rho$), are very useful for characterizing and quantifying anion-π and lp-π interactions.[49,51] As anticipated, upon complexation a small amount of charge, ranging from 28 me to 160 me, is transferred from halide anions or H_2O to compound **1** that acts as a Lewis acid.

The optimized equilibrium C−I⋯N contacts in the complexes **6−9** are essentially linear ($\angle(C-I\cdots N) \approx 180°$); all the predicted I⋯N distances are less than the sum of vdW radii of I and N atoms (3.53 Å).[52] These geometric features are concordant with those of conventional halogen bonds that are predominantly electrostatic in character.[16] Not surprisingly, very weak halogen bonds occur in the systems of NF_3 due to its weak electron donor ability, while NH_3 forms much stronger halogen bonds with **1**, as indicated by the shorter I⋯N
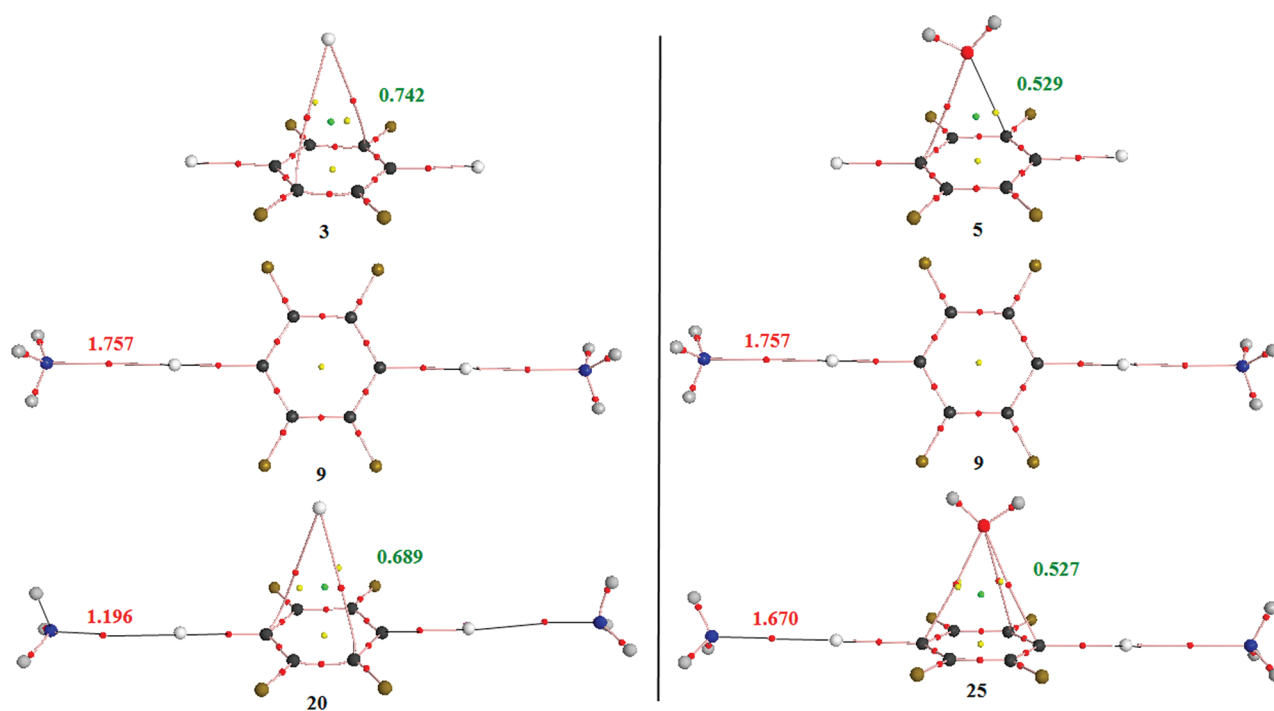
Figure 5. AIM properties of the complexes **20** and **25** (bond CPs in red, ring CPs in yellow, and cage CPs in green). The values of $10^2\rho$ (a.u.) at bond and cage CPs are shown in red and green, respectively.
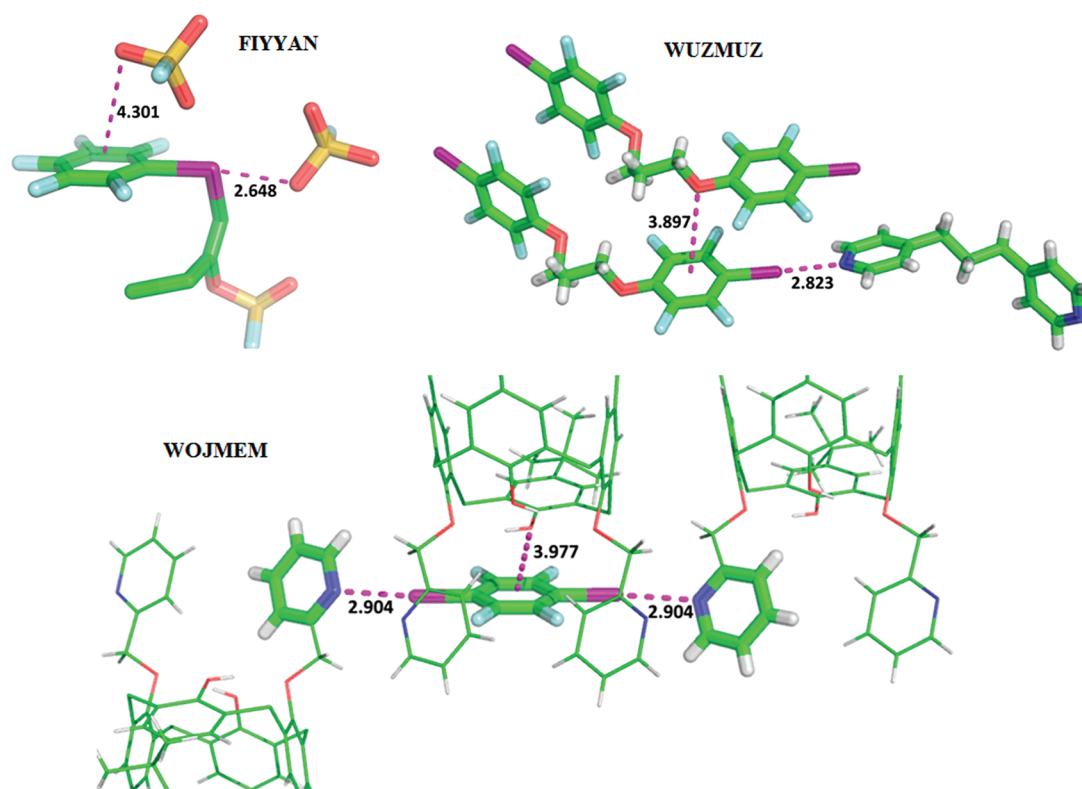
Figure 6. Selected fragments of the crystal structures of FIYYAN, WUZMUZ, and WOJMEM. Distances are in angstrom.

distances and the greater interaction energies of the complexes including NH_3. Table 1 also shows that the interaction energies for the trimers **8** and **9** are almost two times as much as the dimers **6** and **7**; the I···N distances in the trimers remain almost unchanged compared to those in the dimers, thus suggesting the additive behavior of XB. The combined energetic effects of multiple halogen bonds should be very useful in supramolecular architecture and biological design. In addition, upon complex formation there is a magnitude of charge transfer, in the range of 104−166 me, from Lewis bases (NF_3 and NH_3) to aromatic molecule **1** that acts also as a Lewis acid.

Energetic Effects in the XB-Anion-π and XB-lp-π Complexes. The geometric and energetic data for the complexes **10−25** (see Figure 2) are summarized in Table 2. The optimized structures of two representative complexes **20** and **25** are depicted in Figure 3. It can be seen that all of the halogen-bonding distances R_{XB} in these complexes become longer than those in the isolated halogen-bonded systems **6−9**. Clearly, the presence of anion-π or lp-π interactions weakens the I···N interactions. Moreover, relative to the systems involving NF_3, a strikingly pronounced elongation of R_{XB} is observed for the complexes involving NH_3, which indicates that the presence of anion-π/lp-π interactions attenuates strong halogen bonds to a larger degree. However, the variations of $R_{A\pi/lp\pi}$, the distances between halide anions or the oxygen atom on H_2O and the centroid of compound **1**, are relatively limited, and therefore the presence of halogen bonds influences anion-π or lp-π interactions to a less degree. It is worth mentioning that the distances $R_{A\pi}$ in the complexes **13−15** and **19−21** involving NH_3 are somewhat longer than those in the isolated anion-π dimers **2−4**. This, together with the pronounced elongations of R_{XB} mentioned above, implies a strong diminutive effect in these complexes (vide infra).

The calculated cooperativity and synergetic energies (E_{coop} and E_{syn}), which have been widely used in the study of the interplay between two kinds of noncovalent interactions,[21−24,34] are also given in Table 2. It is evident that all the computed values of E_{coop} are positive for the XB-anion-π and XB-lp-π complexes with much larger E_{coop} for the systems involving NH_3. Consequently, the complexes in which strong I···N interactions are presented exhibit a strong anticooperativity, while the interactions in the systems including NF_3 are noncooperative. These results are in accordance with the elongations of the intermolecular distances noted above. Notably, the calculated values of E_{syn} for the complexes involving NF_3 are very close to zero, thereby indicating that the two interactions in these complexes are totally additive. Nevertheless, the systems involving NH_3 exhibit diminutive effects, as indicated by the large positive values of E_{syn}. That said, different energetic effects between halogen bonds and anion-π or lp-π interactions in the studied complexes depend on the strength of halogen bonds. From Table 2, it is also seen that in comparison with the trimers **13−15** that contain one halogen bond, the tetramers **19−21**, in which two I···N interactions are presented, show much larger values of E_{coop} and E_{syn} as well as strikingly pronounced elongations of the intermolecular distances. These imply that diminutive effects between the two interactions would become more and more powerful with the increased number of halogen bonds in the complexes.

The results of charger transfer listed in Table 3 are in good agreement with the geometric and energetic features of the complexes under study. First, the amount of charge transfer from Lewis bases (NF_3 and NH_3) to compound **1** decreases in the XB-anion-π complexes in relation to the isolated halogen-bonded complexes **6−9**, indicating the weakening of

halogen bonds. The magnitude of charge transfer from the anions to **1** changes slightly in these complexes, consistent with the very small values of $\Delta R_{A\pi}$. Second, in the trimers **13−15** and tetramers **19−22** involving NH_3, ΔQ_{CT} is positive for the two interactions, that is, the amount of charge transfer from both the anions and NH_3 to **1** is smaller in the XB-anion-π complexes than in the isolated XB and anion-π systems. These coincide with strong diminutive effects in the complexes **13−15** and **19−22**. Third, the computed ΔQ_{CT} values are very small in the XB-lp-π complexes **22−25**, in accordance with additive and much weak diminutive effects observed in these complexes.

In Frontera's work, strong cooperativity effects are observed when anion-π/lp-π interactions and halogen bonds coexist in the same complex,[34] while the XB-anion-π and XB-lp-π complexes studied in this work exhibit additive and diminutive effects. These different energetic effects can be explained by the direction of charge transfer in the complexes where the two interactions are presented. Frontera et al. selected four π-acidic heteroatomic rings that act as acceptors in XB, whereas the aromatic molecule **1** in this work functions as halogen bond donor. Namely, the heteroatomic rings in the complexes have a dual role: electron acceptors in anion-π/lp-π interactions and electron donors in halogen bonds, while compound **1** in the present complexes acts only as electron acceptors in the two interactions. As shown in Figure 4, the aromatic molecule **1** obtains charge both from halide anions and from Lewis bases in the complexes. The same direction of charge transfer for the two interactions may weaken the interactions and thus lead to a diminutive effect. Nonetheless, the heteroatomic rings in the complexes investigated by Frontera et al. obtain charge from the anions, and simultaneously, they donate charge to the dihalogen molecules. The different direction of charge transfer for the two interactions may strengthen the interactions and hence result in a cooperativity effect.

Electron densities (ρ) at the bond and cage CPs, which characterize halogen bonds and anion-π or lp-π interactions in the studied complexes, are also summarized in Table 3. It can be seen that all the $\Delta\rho_{BCP}$ values are negative, while the values of $\Delta\rho_{CCP}$ are generally very small, consistent with the geometric, energetic and charge transfer results as demonstrated above. Two representative cases that exhibit diminutive effects are illustrated in Figure 5. It is clear that the XB-anion-π complex **20** has a smaller value of $10^2\rho$ at the bond CPs relative to the isolated halogen-bonded system **9** (1.196 vs 1.757), further confirming the weakening of halogen bonds. Also anion-π interaction in this complex becomes weaker compared to the isolated dimer **3**, in view of the negative value of $\Delta\rho_{CCP}$ (-0.053×10^{-2} a.u.). Similar results are observed for the XB-lp-π complex **25** with respect to the isolated systems **5** and **9**. However, the variations of ρ at the bond and cage CPs in this complex are considerably smaller than those in the complex **20**, in good agreement with their corresponding E_{syn} values (0.95 kcal/mol vs 7.00 kcal/mol). Evidently, the XB-anion-π complex **20** exhibits a strong diminutive effect, while a much weaker diminutive effect occurs in the XB-lp-π complex **25**, as demonstrated above.

CSD Analysis. To obtain experimental evidence of the combination of the two interactions, we have performed a survey of the Cambridge Structural Database (CSD, version 5.32).[53] It would be of value to find geometrical information from accurately determined small molecule structures in the CSD. Only crystal structures with no disorder and errors as well as with the R-factor less than 0.1 are considered. Moreover, the contribution of metal organic structures has been included in the survey. Figure 6 displays three selected crystal structures retrieved from the CSD (codes FIYYAN,[54] WUZMUZ,[55] and WOJMEM[56]), in which halogen bonds and anion-π or lp-π interactions coexist and play an important role in crystal packing. In the FIYYAN structure, one fluorosulfonate anion is located above the pentafluorophenyl ring and the other establishes a halogen bond ($d(I\cdots O) = 2.648$ Å, $\angle(C-I\cdots O) = 167°$) with the hypervalent iodine on the same aromatic molecule. The halogen-bonding-driven crystal structure of WUZMUZ determined by the group of Metrangolo and Resnati is very interesting, in which α,ω-di-(2,3,5,6-tetrafluoro-4-iodophenoxy) propane, a very effective halogen bond donor, forms a strong $I\cdots N$ interaction ($d(I\cdots O) = 2.823$ Å) with α,ω-di-(4-pyridyl) propane. In addition, the tetrafluorophenyl ring establishes a lone pair-π interaction with the phenoxy O atom on another donor molecule, although this interaction and its role in the structure have not been realized by the original authors. In the crystal structure of WOJMEM, also determined by Metrangolo and co-workers, 1,4-diiodo-tetrafluorobenzene forms two strong $I\cdots N$ interactions ($d(I\cdots O) = 2.904$ Å) with two 1,3-bis-pyridylmethylcalix[4]arenes, and a phenol O atom on one of the arenes tends to reside on the tetrafluorophenyl ring.

CONCLUSIONS

In this work, we have investigated energetic effects between halogen bonds and anion-π or lone pair-π interactions that coexist in the complexes of 1,4-diiodo-tetrafluorobenzene, a very effective building block for crystal engineering based on halogen bonding. Additive and diminutive effects are observed in these XB-anion-π and XB-lp-π complexes, which can be ascribed to the same direction of charge transfer for the two interactions. The calculated energetic results (E_{coop} and E_{syn}) are in good agreement with the geometric and AIM features of the complexes. Experimental evidence of the combination of the interactions has been obtained from the CSD. This study would be very helpful for understanding the mutual influence of halogen bonds and anion-π/lone pair-π interactions in crystal engineering and molecular recognition.

ASSOCIATED CONTENT

Ⓢ Supporting Information
The complete author list for refs 38 and 39. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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