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Triangular Halogen Trimers. A DFT Study of the Structure, Cooperativity, and Vibrational Properties

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Triangular halogen trimers $(RX)_3$, where X = Br, I and R represents H, H_3C, H_2FC, HF_2C, F_3C, $CH_2{=}CH$, $CH{\equiv}C$, and Ph, have been investigated using the density functional theory in the Perdew, Burke, and Ernzerhof method. We report herein the optimized geometries of the stable structures, their vibrational frequencies, and binding energies with the two- and three-body terms. All trimer structures possess a cyclic array of halogen atoms in the type II approach by virtue of the nonspherical atomic charge distribution around the halogens. The Br···Br interactions in trimers are very weak, whereas the I···I interactions in trimers are relatively stronger. While all bromine trimers and most of iodine trimers are predicted to be noncooperative, three of iodine trimers show weak cooperativity. The analysis of vibration modes reveals that all halogen trimers exhibit no especially remarkable frequency shifts. It is also shown that the electrostatic contribution plays a major role in the halogen···halogen interactions in halogen trimers. In contrast to bromine trimers, the relative contribution of charge-transfer component to the halogen···halogen interactions becomes more important for iodine trimers.

Introduction

Triangular halogen···halogen···halogen interactions have attracted substantial interest in recent years since these interactions are of vital importance in crystal engineering. This trimeric alignment of halogen···halogen interactions as a cohesive force in crystal structures was noticed by Desiraju and co-workers in 1998,[1] and shortly after Mak et al. examined the interactions for a series of tris(bromoaryl) triazines and showed that weak hydrogen bonds and heteroatom interactions can be both effectively utilized in the construction of host frameworks.[2] Bosch and Barnes explored the structures and molecular packing of tribromo- and tri-iodomesitylene and concluded that the donor−acceptor halogen···halogen interactions must be regarded as a viable synthon in crystal engineering.[3] More recently, Nangia and co-workers have reported that the hexagonal layer structure of host atoms in chloro, bromo, and iodo derivatives of 2,4,6-tris(4-halophenoxy)-1,3,5-triazine, is stabilized by a cyclic and cooperative triangular halogen trimer (X···X) synthon.[4]

Halogen···halogen and halogen···oxygen (nitrogen or sulfur) interactions have been debated intensively during the past decade.[5−9] There is now general agreement that the attractive nature of these interactions is primarily ascribed to electrostatic effects, but polarization, charge transfer, and dispersion contributions all play an important role. We have previously demonstrated that electrostatic interactions are mainly responsible for binding energies of the complexes formed between hydrogen halide (HX) and carbon-bound halogen molecules and ammonia.[10]

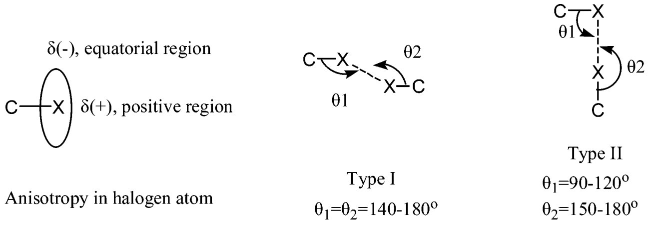

Figure 1. Type I and type II halogen···halogen interactions.

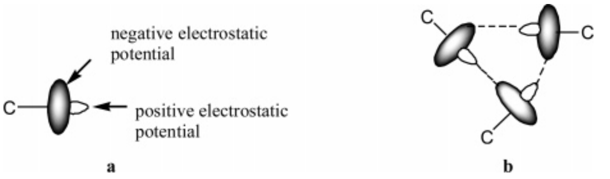

Figure 2. Negative and positive electrostatic potentials of halogen trimers.

There are two distinct types of angular preferences for halogen···halogen interactions as depicted in Figure 1: the nucleophile "head-on" approach, i.e., the positive $\delta(+)$ region along the C−X axis, and the electrophile "side on" approach (the equatorial $\delta(-)$ region). For the halogen···halogen type I and II geometries (see Figure 1),[8] the former is believed to be a result of close packing, whereas the latter is ascribed to the polarization of adjacent halogen atoms for a donor−acceptor interaction. The triangular halogen nonbonding interaction is built up by three halogen···halogen interactions with an orientation of type II. The positive $\delta(+)$ region of one halogen atom points to the equatorial $\delta(-)$ region of an adjacent halogen, with each halogen acting as both a donor and an acceptor.

Indeed, the calculated electrostatic potential of some halogen-containing molecules clearly shows that there is a positive cap at the end region of halogen atoms along the C−X bond vectors (Figure 2a).[3,11,12] Triangular halogen trimers thus involve multiple Coulombic "donor−acceptor" attractions as displayed in Figure 2b. Recent literature on the crystal engineering of halogen···halogen contacts have provided further support that these interactions are of an effective Lewis acid (halogen-

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bonding donors)−Lewis base (halogen-bonding acceptors) pairing type.[13,14]

It is well known that the cooperativity is a crucial factor in determining the crystal structure of compounds containing hydrogen-bonded arrays.[15] And a red shift in the −OH stretching frequencies has been used to identify hydrogen-bonded clusters.[16] Whether the halogen trimers also show cooperativity? What about the vibrational frequency shifts of the halogen trimers? Can the halogen trimers behave like the well-studied hydrogen-bonded clusters? With these questions in mind, the present work aims to conduct a theoretical study on the interactions in bromine trimers $(RBr)_3$ and iodine trimers $(RI)_3$, where R represents H, H_3C, H_2FC, HF_2C, F_3C, $CH_2{=}CH$, $CH{\equiv}C$, and Ph. The purpose of this effort is to explore the geometric changes, the binding energies, including the two- and three-body terms, and some selected vibrational frequency shifts upon the formation of trimers.

Computational Details

All calculations were performed with the Gaussian 98 suite of programs.[17] Optimized geometries of all triangular halogen trimers and isolated monomers were obtained by density functional theory (DFT) in the Perdew, Burke, and Ernzerhof (PBE) generalized gradient approximation.[18] The split-valence triple-ξ 6-311+G(d,p) basis set with polarization functions on all atoms and diffuse orbitals on heavy atoms was used to investigate bromine trimers. For iodine trimers, the Lanl2DZ basis set, augmented by one set of six d polarization functions (Lanl2DZ*) with exponents as follows, $\alpha_C = \alpha_F = 0.8$, $\alpha_{Br} = 0.39$, and $\alpha_I = 0.29$, was employed. This modified effective core potential basis set has been successfully used to describe iodine-containing systems in various theoretical studies.[10,19−21] The Lanl2DZ* basis set was also employed for the calculations of bromine trimers to ascertain that the bromine and iodine trimers are comparable. Frequency calculations were carried out at the same level to ensure that the trimer structures are minimal on the potential-energy surface (PES). The basis-set superposition error (BSSE) was taken into account by means of the Boys−Bernardi counterpoise method.[22]

The binding energy (ΔE) was obtained as the difference between the energy of trimers and the sum energies of the isolated monomers (in fully relaxed geometries)

$$\Delta E = E(123) - (E_1 + E_2 + E_3) \quad (1)$$

This energy was then corrected by the counterpoise technique through calculating the energy of each monomer in the basis set of all three subunits[23,24]

$$\Delta E^{CP} = E(123) - [E_1(123) + E_2(123) + E_3(123)] \quad (2)$$

The additive part of the binding energy, ΔE_2^{CP}, was assessed as the sum of the difference between the energy of a given interacting pair and the energy of the corresponding isolated monomers with all coordinates frozen in the trimer geometry

$$\Delta E_2^{CP} = E_{12}(123) + E_{13}(123) + E_{23}(123) - 2[E_1(123) + E_2(123) + E_3(123)] \quad (3)$$

The three-body nonadditive term or cooperativity, ΔE_3^{CP}, was estimated as the difference between the binding energy and the two-body energy

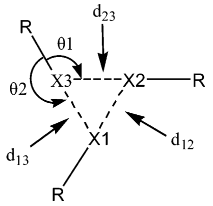
$$\Delta E_3^{CP} = E_{coop}^{CP} = \Delta E^{CP} - \Delta E_2^{CP} \quad (4)$$

TABLE 1: Optimized Geometrical Data and Binding Energies of $(HBr)_3$ and $(HI)_3$ at Various Levels of Theory[a]

$(HBr)_3$	d_{12}	d_{13}	d_{23}	θ_1	θ_2	ΔE
MP2(full)/basis 1	3.898	3.898	3.899	113.0	173.0	−9.15 (−3.45)
PBE/basis 1	3.914	3.917	3.951	110.0	170.0	−6.31 (−5.51)
PBE/basis 3	3.875	3.896	3.911	110.0	170.0	−6.57 (−5.60)
PBE1PBE/basis 1	3.934	3.948	3.968	110.0	170.0	−5.14 (−4.38)
B3P86/basis 1	3.913	3.926	3.927	110.0	170.0	−1.06 (−0.26)
B3LYP/basis 1	4.100	4.143	4.204	110.0	170.0	−0.54 (−0.01)
BHandHLYP/basis 1	4.003	4.016	4.020	110.0	170.0	−2.72 (−2.11)
$(HI)_3$						
MP2(full)/basis 2	4.248	4.251	4.260	109.3	169.3	−9.56 −6.63)
PBE/basis 2	4.007	4.010	4.020	108.6	168.6	−12.77 (−11.75)

[a] Distances are given in Å and angles in degrees. Binding energies are given in kJ mol^{-1}. The BSSE-corrected ΔE are given in parentheses. Basis 1 = 6-311+G(d,p); basis 2 = Lanl2DZ*; basis 3 = 6-311++G-(2d,2p). θ_1 and θ_2 are the average values.

SCHEME 1



Finally, other factors potentially providing valuable information of the interactions were considered.

Results and Discussion

Choice of Theoretical Method. It is well-established that ab initio methods accounting for electron correlation are necessary for an accurate description of nonbonding interactions.[10,25−28] Nevertheless, the correlated methods have to be used to make an accurate description of halogen trimers are computationally very demanding. To solve this problem, it is significant to explore strategies that are computationally less demanding but describe halogen trimers with a similar accuracy as MP2 (or higher levels of theory). A reasonable alternative is offered by DFT methods. Many theoretical studies of nonbonding interactions have shown that the DFT methods provide the best compromise between the accuracy of calculations and computational costs.[29] So in this work, the HBr trimer was investigated using five different DFT methods (PBE, PBE1PBE, B3P86, B3LYP, and BHandHLYP) to determine the optimal one for describing the halogen trimers. Table 1 lists some selected geometrical parameters and binding energies of the HBr trimer with these methods, including the results at the MP2-(full) level. The nonbonding interatomic distances, d_{ij}, and angles, θ_1 and θ_2, are defined in Scheme 1.

As can be seen from these data, the B3LYP and BHandHLYP methods give considerably longer interatomic distances than the MP2(full) method and extremely underestimate the binding energy. The distances calculated by the B3P86 method are close to the MP2(full) results; however, the binding energy obtained by B3P86 is only −1.06 kJ mol^{-1}, which is significantly greater than the MP2 binding energy. The PBE1PBE results are much improved, but they are still inferior to the results of PBE. Geometry parameters and the binding energy with the PBE method are more close to those with MP2(full). It is noteworthy that the BSSE-corrected binding energy at the MP2(full) level is slightly larger than that of PBE and PBE1PBE due to the substantial overcorrection of the CP method at this level. In addition, as is well known, an appropriate basis set for an accurate description of the structures and energies of clusters

TABLE 2: Some Selected Optimized Geometry Parameters of $(RX)_3$ and the Elongations of the R−X Distances upon Trimers Formation

	$(RBr)_3$ (basis 1)				$(RBr)_3$ (basis 2)				$(RI)_3$ (basis 2)			
R=	d_{ij}	Δd(R−Br)	θ_1	θ_2	d_{ij}	Δd(R−B r)	θ_1	θ_2	d_{ij}	Δd(R−I)	θ_1	θ_2
H−	3.914	0.001	110.1	170.0	3.744	0.003	110.3	170.1	4.007	0.005	108.5	169.0
	3.917	0.001	109.8	170.2	3.754	0.003	110.3	170.3	4.010	0.005	108.2	168.7
	3.951	0.001	110.3	170.2	3.757	0.003	110.2	170.5	4.020	0.005	109.0	168.1
H_3C−	3.785	0.003	111.2	178.2	3.704	0.003	109.8	171.1	3.927	0.005	110.7	171.3
	3.934	0.002	114.2	163.2	3.718	0.003	110.7	170.4	3.927	0.006	110.3	170.7
	3.981	0.002	117.6	171.2	3.720	0.003	111.0	170.0	3.931	0.005	111.3	170.3
H_2FC−	3.874	0.001	104.4	170.3	3.724	0.002	115.5	164.6	3.935	0.007	110.0	173.5
	3.876	0.002	108.0	176.7	3.727	0.002	108.2	174.6	3.994	0.005	113.1	166.0
	4.013	0.001	118.1	163.2	3.817	0.002	105.4	169.8	4.012	0.006	105.1	168.8
HF_2C−	3.906	0.002	109.1	172.0	3.702	0.003	107.7	175.3	3.940	0.006	107.2	169.2
	3.914	0.002	105.6	169.5	3.712	0.004	116.0	164.8	3.947	0.006	109.2	168.8
	3.940	0.003	112.2	164.8	3.792	0.003	105.7	169.3	3.950	0.006	109.0	167.2
F_3C−	3.847	0.003	107.7	167.7	3.693	0.007	109.5	169.5	3.832	0.013	104.8	169.6
	3.880	0.004	107.9	168.0	3.698	0.007	109.4	169.3	3.871	0.013	109.3	167.8
	3.882	0.003	107.5	167.3	3.704	0.006	110.1	169.7	3.870	0.013	108.6	165.2
$CH_2{=}CH$−	3.919	0.001	109.1	171.9	3.757	0.002	110.0	171.2	3.970	0.005	112.5	173.0
	3.941	0.001	111.3	173.0	3.760	0.002	112.7	169.7	4.011	0.005	111.5	170.8
	3.969	0.001	113.6	169.1	3.786	0.002	110.7	172.5	4.023	0.005	106.7	167.0
$CH{\equiv}C$−	3.908	0.002	104.6	165.3	3.715	0.003	107.0	167.2	3.895	0.008	107.5	167.7
	3.910	0.002	105.2	164.8	3.716	0.003	107.1	166.8	3.895	0.008	107.7	167.7
	3.912	0.002	104.9	164.6	3.720	0.003	107.0	166.8	3.896	0.008	107.7	167.5
Ph−	3.901	0.001	109.4	170.3	3.730	0.001	109.4	170.0	3.968	0.006	110.1	170.0
	3.905	0.001	111.4	169.3	3.733	0.001	110.3	169.3	3.973	0.006	110.0	170.2
	3.928	0.001	110.0	171.1	3.748	0.002	109.6	170.1	3.978	0.006	110.4	170.1

[a] Distances are given in Å and angles in degrees. Basis 1 = 6-311+G(d,p); basis 2 = Lanl2DZ*. See Scheme 1 for the definitions of d_{ij} and θ_1 and θ_2.

is of pivotal importance. A large basis set is usually required; however, the size of bromine trimers in this work excludes the use of a very large basis set. Table 1 shows that the results obtained with 6-311+G(d,p) are not significantly different from those with the 6-311++G(2d,2p) (Basis 3). On the basis of these comparisons in hand, PBE/6-311+G(d,p) was selected to investigate bromine trimers. Furthermore, we also calculated the HI trimer at the PBE/Lanl2DZ* and MP2(full)/Lanl2DZ* levels. As can be seen from the results, summarized in Table 1, the PBE calculations reproduce the experimental I···I distances reasonably well, even better than the MP2(full) method, which shows that the DFT/PBE method with the Lanl2DZ* basis set describes iodine trimers faithfully.

It has to be pointed out that the DFT/PBE method gives somewhat longer Br···Br intermolecular distances and underestimates the binding energy as compared to the MP(full) method due to failing to consider important dispersion component for bromine trimers. Nevertheless, as part of our systematic study on halogen bond cooperativity, the present theoretical calculations of bromine trimers using the DFT/PBE approach may provide some insights into the nature of halogen bond, at least in a comparable sense.

Geometries of Triangular Halogen Trimers. Table 2 shows the optimized X···X distances, d_{ij}, and angles, θ_1 and θ_2, along with the elongations of R−X distances upon the formation of trimers. The Br···Br distances range from 3.785 to 4.013 Å at the PBE/6-311+G(d,p) level of theory, which are slightly larger than twice the Bondi van der Waals (vdW) radius of bromine (3.70 Å)[30] and close to twice the vdW radius of bromine (3.90 Å) recommended by Pauling.[31] The PBE/Lanl2DZ* calculations systematically give shorter Br···Br distances (3.693−3.817 Å). This provides an initial evidence for very weak Br···Br interactions in bromine trimers. The calculated I···I distances are close to twice the Bondi vdW radius of iodine (3.96 Å) and significantly lower than that of Pauling's definition (4.30 Å). The I···I distances, collected in Table 2 span a range between 3.832 and 4.023 Å. However, which can be ascribed to the close packing, the Br···Br and I···I distances in the crystal structures are shorter than the predicted ones. The C(H)···X···X angles, θ_1 and θ_2, are close to one another for each of the trimers. One interaction is nearly linear with $\theta_2 = 170°$ (±7°), and the other is oblique with $\theta_1 = 110°$ (±6°). This is also consistent with the crystal structures that the halogen···halogen interactions in trimer synthons are of the attractive electrophile-nucleophile pairing type II contact.[2,3,4] All trimer structures have low symmetry, with a dipole moment of 0.0−0.5 D.

The interaction usually causes slight changes in intramolecular geometry. Upon triangular halogen trimers formation, the corresponding R−X bonds undergo a small elongation, for which an increase of 0.001−0.003 Å for bromine trimers at the PBE/6-311+G(d,p) level and an increase of 0.005−0.013 Å for iodine trimers at the PBE/Lanl2DZ* level are observed. This property behaves quite like that of well-studied hydrogen-bonded clusters. Additionally, it has been noticed that the distortions in the molecular geometry caused by the interaction of iodine trimers are more pronounced than those of bromine trimers.

Binding Energies and Cooperativities. The binding energies with their two and three terms of the studied halogen trimers are collected in Table 3. The percentages of cooperativity defined as the ratio $\Delta E_3/\Delta E$ (×100%) are given as well. As can be seen from these data, the binding energies at the PBE/6-311+G(d,p) level of theory are within -6.98 kJ mol^{-1} for all eight bromine trimers under considerations. The PBE/Lanl2DZ* binding energies of bromine trimers range from -7.86 to -5.21 kJ mol^{-1}. This suggests that the Br···Br interactions are reasonably weak, which is consistent with the relatively long Br···Br distances of trimers (vide supra). In previous studies[10,32] of halogen bonding between RX and the electron-donor molecules (e.g., NH_3), it has been shown that the more electron-withdrawing the moiety bound to the halogen is, the stronger is the halogen bonding to which it gives rise. However, there is no general correlation between the binding energy and the electron-withdrawing ability of the group bound

TABLE 3: Binding Energies (ΔE) for $(RX)_3$, the Two-Body (ΔE_2) and Three-Body (ΔE_3) Terms (kJ mol^{-1}), and Percentages of Three-Body Contributions (% coop)[a]

	ΔE	$\Delta E_2(12)$	$\Delta E_2(13)$	$\Delta E_2(23)$	ΔE_2	ΔE_3	% coop
				$(RBr)_3$ (Basis 1)			
H−	−5.52 (−6.32)	−1.97 (−2.24)	−1.97 (−2.24)	−1.97 (−2.24)	−5.91 (−6.72)	0.39 (0.40)	−7.1 (−6.3)
H_3C-	−4.35 (−5.18)	−2.07 (−2.41)	−1.41 (−1.70)	−1.28 (−1.56)	−4.76 (−5.67)	0.41 (0.49)	−9.4 (−9.5)
H_2FC-	−6.98 (−8.30)	−2.65 (−3.14)	−2.19 (−2.63)	−2.82 (−3.31)	−7.66 (−9.08)	0.68 (0.79)	−9.8 (−9.5)
HF_2C-	−6.61 (−8.00)	−2.33 (−2.83)	−2.37 (−2.80)	−2.30 (−2.81)	−7.00 (−8.44)	0.39 (0.45)	−5.9 (−5.6)
F_3C-	−5.94 (−7.60)	−2.06 (−2.68)	−2.07 (−2.65)	−1.95 (−2.58)	−6.08 (−7.91)	0.14 (0.31)	−2.4 (−4.2)
$CH_2{=}CH-$	−5.05 (−5.80)	−1.91 (−2.21)	−1.83 (−2.07)	−1.88 (−2.18)	−5.62 (−6.46)	0.57 (0.66)	−11.3 (−11. 4)
$CH{\equiv}C-$	−6.08 (−7.03)	−2.10 (−2.43)	−2.10 (−2.43)	−2.11 (−2.41)	−6.31 (−7.28)	0.25 (0.27)	−4.1 (−3.9)
Ph−	−6.15 (−8.12)	−2.21 (−2.91)	−2.29 (−3.00)	−2.23 (−2.87)	−6.72 (−8.78)	0.57 (0.66)	−9.3 (−8.1)
				$(RBr)_3$ (Basis 2)			
H−	−7.04 (−9.40)	−2.53 (−3.33)	−2.44 (−3.24)	−2.44 (−3.23)	−7.41 (−9.80)	0.37 (0.40)	−5.3 (−4.3)
H_3C-	−5.21 (−9.26)	−1.76 (−3.17)	−1.94 (−3.32)	−1.88 (−3.26)	−5.60 (−9.75)	0.39 (0.39)	−7.5 (−4.2)
H_2FC-	−7.34 (−10.95)	−2.36 (−3.50)	−2.76 (−4.10)	−2.95 (−4.22)	−8.07 (−11.82)	0.73 (0.87)	−9.9 (−7.9)
HF_2C-	−7.34 (−10.68)	−3.22 (−4.37)	−2.72 (−3.92)	−2.20 (−3.24)	−8.14 (−11.53)	0.80 (0.85)	−10.9 (−8.0)
F_3C-	−7.69 (−10.80)	−2.62 (−3.70)	−2.80 (−3.87)	−2.83 (−3.90)	−8.25 (−11.47)	0.56 (0.67)	−7.3 (−6.2)
$CH_2{=}CH-$	−5.81 (−9.63)	−2.26 (−3.63)	−1.92 (−3.21)	−1.90 (−3.23)	−6.08 (−10.07)	0.27 (0.44)	−4.7 (−4.6)
$CH{\equiv}C-$	−7.86 (−10.96)	−2.61 (−3.68)	−2.61 (−3.68)	−2.62 (−3.69)	−7.84 (−11.05)	−0.02 (0.09)	0.3 (−0.8)
Ph−	−6.00 (−12.00)	−2.16 (−4.28)	−2.20 (−4.31)	−2.11 (−4.16)	−6.47 (−12.75)	0.47 (0.75)	−7.8 (−6.3)
				$(RI)_3$ (Basis 2)			
H−	−11.75 (−12.77)	−3.83 (−4.18)	−3.83 (−4.18)	−3.80 (−4.14)	−11.46 (−12.50)	−0.29 (−0.27)	2.5 (2.1)
H_3C-	−12.38 (−14.35)	−4.09 (−4.81)	−4.05 (−4.83)	−4.00 (−4.77)	−12.14 (−14.41)	−0.24 (0.06)	1.9 (−0.4)
H_2FC-	−12.15 (−14.61)	−4.05 (−4.81)	−4.66 (−5.64)	−4.09 (−4.90)	−12.80 (−15.35)	0.65 (0.74)	−5.3 (−5.1)
HF_2C-	−13.99 (−16.20)	−4.66 (−5.46)	−4.73 (−5.50)	−4.63 (−5.40)	−14.02 (−16.36)	0.03 (0.16)	−0.2 (−1.0)
F_3C-	−14.58 (−17.05)	−4.77 (−5.73)	−4.38 (−5.12)	−4.48 (−5.28)	−13.63 (−16.13)	−0.95 (−0.92)	6.5 (5.4)
$CH_2{=}CH-$	−11.75 (−13.80)	−4.05 (−4.77)	−3.93 (−4.63)	−4.32 (−5.12)	−12.30 (−14.52)	0.55 (0.72)	−4.7 (−5.2)
$CH{\equiv}C-$	−13.26 (−15.91)	−4.24 (−4.94)	−4.24 (−4.94)	−4.24 (−4.94)	−12.72 (−14.82)	−0.54 (−1.09)	4.1 (6.9)
Ph−	−11.13 (−14.64)	−3.68 (−4.85)	−3.74 (−4.92)	−3.71 (−4.86)	−11.13 (−14.63)	0.00 (0.01)	0.0 (0.1)

[a] The uncorrected-BSSE values are given in parentheses. All the energy parameters are calculated by eqs 2−5. Basis 1 = 6-311+G(d,p); basis 2 = Lanl2DZ*.

to the bromine. For example, the $CH_{3-n}F_nBr$ ($n = \sim 1-3$) yield significantly stronger halogen bonding toward NH_3 with progressive fluorine substitution,[10] whereas the binding strengths of the trimers vary in the reverse order $(H_2FBr)_3 > (HF_2Br)_3 > (F_3Br)_3$ at the PBE/6-311+G(d,p) level of theory. This can be rationalized by the distribution of electrostatic potential around the bromine, i.e., although the ability of electrophile in the positive $\delta(+)$ region along the R−Br bond is strengthened by the electron-withdrawing group, the ability of nucleophile in the equatorial $\delta(-)$ region becomes weaker. To gain a quantitative insight into the electrostatic contribution to the Br···Br interactions, the electrostatic potentials at two given sites were calculated for monomers RBr. On the basis of the optimized geometries of bromine trimers, electrostatic potentials at two points to which the distance from the Br atom is 1.95 Å (the vdW radius of bromine, Pauling's definition) and the angles Y−Br−R (Y is the point considered) are 170 and 110°, respectively, were derived. The ESP values calculated at the PBE/6-311+G(d,p) level at the two given sites are listed in Table 4. It can be readily appreciated from these data that the ESP1 and ESP2 values increase with the electron-withdrawing ability of the group bound to the bromine, which clearly shows that the stronger the electrophilic ability of the RBr species, the weaker its nucleophilicity. This provides further support for the major electrostatic contribution to Br···Br interactions. It should be noted that the predicted ESP2 values for F_3CBr and $CH{\equiv}CBr$ are positive. This implies quite weak attractive but not repulsive interactions at these points, and indeed, these electrostatic potential values are significant only in a relative sense.

TABLE 4: Electrostatic Potentials (kJ mol^{-1}) at Two Different Sites of RX[a]

	RBr (6-311+G(d,p))		RI (Lanl2DZ*)	
R	ESP1	ESP2	ESP1	ESP2
H−	71.55	−31.05	141.45	−6.67
H_3C-	41.55	−59.16	102.75	−38.05
H_2FC-	67.03	−19.87	119.66	−3.26
HF_2C-	89.66	−5.10	137.90	−1.03
F_3C-	119.45	13.81	174.00	28.30
$CH_2{=}CH-$	61.60	−34.43	119.08	−14.21
$CH{\equiv}C-$	130.12	15.56	190.73	33.81
Ph−	59.16	−34.77	113.57	−16.25

[a] ESP1 and ESP2: the angles Y−Br(I)−R (Y is the point considered) are 170 and 110°, respectively, and the distance from the Br and I atoms are, respectively, 1.95 and 1.98 Å.

The BSSE-corrected binding energies of iodine trimers span over a reasonably narrow range, from −14.58 to −11.13 kJ mol^{-1}, indicating that the I···I interactions in trimers are relatively stronger as compared to bromine trimers. This is also in consistent with the calculated I···I distances, which are close to or slightly below twice the Bondi vdW radius of iodine (3.96 Å). The binding energies of iodine trimers decrease in the order $(F_3CI)_3 > (HF_2CI)_3 > (CH{\equiv}CI)_3 > (CH_3I)_3 > (H_2FCI)_3 > (CH_2{=}CHI)_3 \approx (HI)_3 > (PhI)_3$. Again, no correlation between the binding strength and the electron-withdrawing ability of the group bound to iodine has been observed. Similarly, we calculated the electrostatic potentials at the two given sites (the definitions are essentially the same as for RBr, except that different Bondi vdW radius, 1.98 Å, was adopted) for various monomers RI. Table 4 presents the ESP values at the PBE/Lanl2DZ* level of theory at the two given sites of RI. From the values, it is seen that both the ESP1 and ESP2 values increase with the electron-withdrawing ability of the substituent group on the iodine atom.

We can see from Table 3 that the two-body interaction energies in all trimers are negative. Nevertheless, the obtained values of ΔE_3 in all bromine trimers are positive, indicating the repulsive three-body energy in these cases. For iodine trimers, the three-body contribution, a description of cooperative effects, is low but not negligible.

TABLE 5: Frequency Shifts (cm^{-1}) of the υ(RX-) Vibrations

R	$\Delta\upsilon$(RBr$-$) (6-311+G(d,p))			$\Delta\upsilon$(RI$-$) (Lanl2DZ*)		
H$-$	-22.0	-12.0	22.0	-31.2	-27.2	-26.2
H_3C-	-2.6	-0.7	-0.2	-7.2	-7.0	-6.7
H_2FC-	-0.9	-0.2	4.3	-4.6	-4.0	-1.5
HF_2C-	-4.0	-2.7	2.4	-6.4	-5.8	-2.4
F_3C-	-0.7	-0.6	1.0	-1.8	-1.5	-1.1
$CH_2{=}CH-$	-5.0	-3.9	-1.8	-4.1	-3.7	-3.4
$CH{\equiv}C-$	-5.2	-4.8	-3.1	-12.0	-12.8	-12.6
Ph$-$	-0.2	1.6	2.0	-4.0	-3.7	-3.6

In fact, the three-body nonadditive contribution to the overall binding energy is up to about 6.5% for $(F_3CI)_3$. According to our present calculations, only the HI, F_3CI, and $CH{\equiv}CI$ trimers show weak cooperativity, indicating the importance of the chemical environment around the halogen atom. Besides, there are many other factors that may influence the cooperative effect of multiple halogen bonded systems, as the hydrogen bonded clusters presented. For instance, in open water trimers, when one H_2O molecule acts as a biacceptor or a bidonor, the cooperativity then becomes positive due to a large destabilizing effect[33,34]

Vibrational Frequencies and NBO Analysis. Some of the vibrational frequencies of individual molecules undergo remarkable shift upon complex formation with other molecules.[35−38] The frequency shift represents an important feature of some weakly bound systems; for instance, a red shift in the $-$OH stretching frequencies has offered one of the most important tools for the identification of hydrogen-bonded clusters. Here, vibrational frequencies for bromine and iodine trimers and their isolated monomers have been calculated. Table 5 shows the frequency shifts (not scaled) of RX$-$ stretching vibration modes with respect to those of isolated monomers. As can be seen, the RBr$-$ stretching frequencies mainly exhibit small red shifting, yet the blue shifts also take place in some trimers. For example, two calculated υ(CBr) stretches of the HF_2CBr trimer are red-shifted by 4.0 and 2.7 cm^{-1}, respectively, whereas the third one is blue-shifted by 2.4 cm^{-1}. Such a blue shift of υ(RBr$-$) stretches were also found in other four bromine trimers. For iodine trimers, the largest red shift is only ca. 13 cm^{-1} if we disregard the shifts of υ(HI$-$) stretching, and no blue-shifting phenomenon was discerned. The intensity of the υ(RX$-$) vibration shows no significant change in trimers relative to that of isolated monomers. In some hydrogen-bonded clusters, the induced shift can be as large as several hundred reciprocal centimeters and the intensity of the bands increases by more than 1 order of magnitude.[39,40] Therefore, the halogen···halogen interactions in trimers are relatively weak. The analysis of other vibration modes also showed no remarkable shift. It must be pointed out that the frequency analysis should be taken cautiously because the approximations in computing harmonic frequencies may result in significant errors, especially for anharmonic and large vibration modes.

NBO analysis has been conducted on all triangular halogen trimers. According to the NBO theory, halogen···halogen interactions can be viewed as a consequence of charge transfer from a lone pair donor orbital on one halogen into a R$-$X σ* acceptor orbital on the other, with each halogen atom in trimers being simultaneously a donor and an acceptor. The energetic stabilization by CT interactions was evaluated using the second-order perturbation analysis and was referred to as E^2. As can be seen from the results, presented in Table 6, the electron density in the R$-$X antibonding orbital is increasing, whereas the occupancy of the halogen lone pair (π) is decreasing from its value in isolated monomers. This clearly manifests that the halogen···halogen interactions involve CT from the halogen lone pair to the R$-$X antibonding orbital, with each halogen atom acting both as a donor and as an acceptor. However, the second-order perturbation energies E^2 of bromine trimers are quite limited (lower than 4 kJ mol^{-1} at the PBE/6-311+G(d,p) level), suggesting that the role of CT is not predominant in Br···Br interactions. The predicted E^2 values of iodine trimers are up to twice higher than those of bromine trimers and the corresponding changes of electron densities for the iodine lone pair and the R$-$I antibonding orbital are somewhat large, which

TABLE 6: Natural Bond Orbital Analysis (E^2 in kJ mol^{-1}) for $(RX)_3$[a]

	$(RBr)_3$ (basis 1)			$(RBr)_3$ (basis 2)			$(RI)_3$ (basis 2)		
R	donor NBOs δ	acceptor NBOs δ	E^2	donor NBOs δ	acceptor NBOs δ	E^2	donor NBOs δ	acceptor NBOs δ	E^2
H$-$	1.994 (1.999)	0.005 (0.000)	3.01	1.991 (2.000)	0.001 (0.000)	3.85	1.983 (2.000)	0.016 (0.000)	6.82
	1.994	0.005	3.10	1.991	0.001	3.97	1.983	0.016	6.57
	1.994	0.005	3.05	1.991	0.001	3.90	1.983	0.016	6.78
H_3C-	1.972 (1.981)	0.008 (0.003)	4.0 2	1.971 (1.983)	0.014 (0.002)	4.77	1.961 (1.986)	0.028 (0.002)	9.50
	1.976	0.011	1.92	1.971	0.014	5.02	1.961	0.027	9.25
	1.975	0.008	2.18	1.971	0.014	4.77	1.960	0.027	9.41
H_2FC-	1.942 (1.950)	0.067 (0.064)	3.10	1.942 (1.947)	0.077 (0.070)	3.05	1.933 (1.955)	0.091 (0.071)	10.17
	1.943	0.069	2.93	1.938	0.075	4.94	1.940	0.094	7.53
	1.945	0.070	1.72	1.943	0.078	3.26	1.938	0.090	8.03
HF_2C-	1.962 (1.965)	0.115 (0.112)	1.05	1.944 (1.950)	0.126 (0.115)	3.35	1.946 (1.957)	0.141 (0.121)	8.62
	1.960	0.116	2.18	1.940	0.122	4.94	1.948	0.149	9.20
	1.962	0.116	1.46	1.950	0.125	5.02	1.946	0.141	8.12
F_3C-	1.951 (1.953)	0.147 (0.139)	2.93	1.943 (1.952)	0.151 (0.140)	5.36	1.931 (1.961)	0.172 (0.142)	13.68
	1.951	0.146	2.97	1.943	0.151	5.44	1.934	0.174	12.13
	1.950	0.147	3.26	1.944	0.151	5.23	1.9340	0.172	12.05
$CH_2{=}CH-$	1.970 (1.974)	0.043 (0.040)	2.13	1.966 (1.975)	0.046 (0.038)	4.40	1.958 (1.978)	0.055 (0.039)	8.20
	1.969	0.042	2.10	1.967	0.046	3.97	1.960	0.058	7.61
	1.970	0.042	2.10	1.966	0.045	4.44	1.975	0.056	5.98
$CH{\equiv}C-$	1.904 (1.907)	0.015 (0.011)	2.34	1.903 (1.908)	0.018 (0.009)	4.18	1.906 (1.918)	0.032 (0.009)	9.96
	1.904	0.015	2.10	1.903	0.020	4.14	1.906	0.032	10.04
	1.904	0.015	2.55	1.903	0.019	4.10	1.906	0.032	10.00
Ph$-$	1.968 (1.974)	0.047 (0.042)	2.51	1.962 (1.971)	0.054 (0.045)	4.48	1.955 (1.974)	0.065 (0.045)	7.70
	1.968	0.047	2.30	1.962	0.054	4.27	1.954	0.065	7.95
	1.968	0.046	2.55	1.962	0.054	4.52	1.955	0.065	7.11

[a] Data in the parenthesis are the occupancy of corresponding NBO of isolated monomers. Donor NBOs are π-type lone pairs of halogens. Basis 1 = 6-311+G(d,p); basis 2 = Lanl2DZ*.

indicates a larger contribution of CT for iodine trimers. As can be seen from Tables 3 and 6, the F_3CI and CH≡CI trimers having great E^2 values show weak but significant cooperative effect except for the HI trimer which exhibits some abnormal properties (including the shifts of υ(HI−) stretching vibration), Thus, we suggest that the CT contributions may be responsible for the cooperativity. Indeed, a very recent study on the bromomethane−water 1:2 complexes has shown that the charge-transfer stabilization energy is proportional to the cooperative effects between hydrogen bonds and between hydrogen bond and halogen bond.[41]

Conclusions

In this work, triangular halogen trimers $(RX)_3$, where X = Br and I and R represents H, H_3C, H_2FC, HF_2C, F_3C, CH_2=CH, CH≡C, and Ph, have been investigated using the DFT/PBE method. We can summarize our conclusions as follows:

1. The DFT/PBE method used to calculate halogen trimers $(RX)_3$ predicts that all trimer structures possess the polarization-induced L-shaped (type II) approach.
2. The Br···Br interactions in trimers are very weak, whereas the I···I interactions in trimers are relatively stronger.
3. While all bromine trimers and most of iodine trimers exhibit noncooperative effects, three of iodine trimers show weak cooperativity.
4. The trimers show no remarkable frequency shifts with respect to the corresponding isolated monomers.
5. The CT from the X lone pair is mainly directed to the R−X antibonding orbital, with each halogen atom behaving both as a donor and as an acceptor. The electrostatic contribution plays a dominant role in the halogen···halogen interactions in halogen trimers. Comparison with bromine trimers, the contribution of CT is larger for iodine trimers.

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