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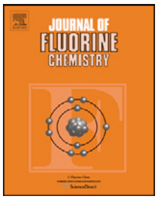

The structure, properties, and nature of C–Br···F halogen bond involving HArF: Substitution, hybridization, and nonadditivity

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ABSTRACT

Quantum chemical calculations have been performed to investigate the halogen bond of HArF with some brominated hydrocarbons at the MP2/aug-cc-pVTZ level. The C–Br bond in F_3CBr–FArH complex is contracted, while it is elongated in other halogen-bonded complexes. However, the C–Br stretch vibration has a small red shift in all complexes. The strength of halogen bond becomes stronger in order of $C^{sp^3}-Br < C^{sp^2}-Br < C^{sp}-Br$. The substitution position in CH_2CHBr has a prominent effect on the strength of halogen bond. With the number of F atom in CH_2CHBr, the halogen bond is stronger and a negative nonadditivity is present for F substitution. The average contribution of each F atom to the interaction energy of halogen bond is estimated to be −4 kJ/mol. Additionally, two hydrogen-bonded complexes of BrCCH–FArH and HCCBr-pi-HArF have also been studied. These complexes have been analyzed with the electrostatic potentials and NBO theory.

1. Introduction

Halogen bonding is an interaction between a halogen-containing molecule (Lewis acid) and a neutral or anionic molecule (Lewis base) [1]. Recently, much interest has been paid to halogen bonding, which exhibits similarities in structures, properties, nature, and applications with hydrogen bonding. The directionality of this interaction is in general greater than that of the hydrogen bonding [2,3]. The formation and direction of halogen bonding can be explained with electrostatic potentials of halogen atoms. The latter has been evidenced to be a good method for predicting and charactering intermolecular interactions [4]. There is a region of positive electrostatic potential (σ-hole) on the outermost portion of the covalently bonded halogen atom [5]. Like that in hydrogen bond, the halogen acceptor is also from lone pair electrons, π electrons [6], sigma electrons [7,8], and single electrons [9]. The electrostatic interaction is a dominant contribution in most halogen-bonded complexes. Of course, other contribution from charge transfer and induction interaction is also important [10].

Upon formation of A–X···B (X = halogen) halogen bonding, the A–X stretch vibration shows a red shift in most cases although the red shift is much smaller than that in hydrogen bonding. Of course, the blue-shifted halogen bonds were also observed in F_3CX–B (X = Cl, Br; B = NH_3, H_2O, Br^-) halogen-boned complex [11,12]. The negative permanent dipole moment derivative of donor molecule is responsible for the blue shift [13].

The strength of halogen bonding is mainly dependent on the nature of halogen donor and acceptor. The fluorine atom seldom forms a halogen bond, while the iodine atom forms the strongest halogen bond. However, when fluorine is bound to residues that can work as particularly strong electron withdrawing groups, fluorine can display a region of positive electrostatic potential [14]. Additionally, the substitution groups adjoined with them also have an effect on its strength. The electron-drawing group in the halogen donor results in an enhancement of halogen bond, while that in the halogen acceptor leads to the weakening of halogen bond [15]. The methyl group in the halogen acceptor plays a positive contribution to the formation of halogen bond, while that in the halogen donor plays a negative contribution [15]. The methyl group in the halogen acceptor exhibits a negative non-additivity in enhancing halogen bonds [16]. The effect of C atom hybridization on the strength of halogen bond follows the order of $C^{sp} > C^{sp^2} > C^{sp^3}$ [17]. Lu et al. [18] performed a systematic study of halogen bonding interactions in three solvents (chloroform, acetone, and water), and found that for charged halogen-bonded complexes the strength of the interactions tends to significantly weaken in solution, while for neutral systems halogen bond distances are shown to shorten and the interaction energies change slightly.

Halogen bonding is close to hydrogen bonding in strength. This property, together with the direction, determines the applications of halogen bonds in molecular recognition [19,20] and crystal

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engineering [21,22]. Halogen bonding can compete with hydrogen bonding [23]. In H_2CO–HOX (X = Cl and Br) system [24], the hydrogen bond is stronger than the halogen bond. The strength difference between them decreases in H_2CS–HOX (X = Cl and Br) system [25], and the Li atom in HLiCS makes the halogen bond stronger than the hydrogen bond. The applications of halogen bonds in materials are related with the cooperativity of halogen bonds. The latter was observed in H_2CO–ClF–ClF trimer [26], and the cooperativity between halogen bond and hydrogen bond has also been reported [27,28].

HArF, a stable Ar-containing molecule, has been identified experimentally in an Ar matrix [29]. Its intrinsic stability was confirmed with high-level ab initio calculations [30,31]. A thermally more stable solid-state configuration of HArF was then detected in an Ar matrix [32]. The stabilization of HArF is mainly from the strong Coulomb attraction between HAr^+ and F^- [33]. Due to the larger dipole moment and polarizability, HArF can form strong hydrogen bonds with some small molecules such as N_2, P_2, H_2, CO, CO_2 [34–39]. In most cases, these hydrogen bonds display a big blue shift of H–Ar stretch frequency. However, a red shift occurs in HArF-P_2 complex. A similar red shift was also observed in dihydrogen-bonded complexes of HArF [40–42]. HArF can form a π hydrogen bond with acetylene [43] and ethylene [44], where the H–Ar stretch vibration presents a red shift. These shifts can be understood with a combination of the electrostatic interaction and charge transfer.

In HArF–XY (XY = ClCl, ClF, BrCl, BrF) complex [45], two isomers were found: a hydrogen bond isomer and a halogen bond one. The fluorine atom of HArF acts as the electron donor in the halogen bond, whereas the hydrogen atom of HArF acts as the proton donor in the hydrogen bond. The halogen bond is much stronger than the hydrogen bond. The H–Ar stretch vibration exhibits a blue shift in both isomers. Followed by this study, we want to study the halogen-bonded complex of HArF with molecules involving with a C–Br bond. The C–Br compounds contain H_3CBr, H_2CCHBr, and HCCBr. The F_3CBr–FArH complex is designed to study if the C–Br bond is contracted and the corresponding blue shift happens. Considering the role of perfluorocarbon compounds in supramolecular assemblies [46], the hydrogen atom in H_2CCHBr is substituted with F atoms. Our aims are to (1) the effect of F atom on the halogen bond, (2) the effect of F atom in different positions on the halogen bond, and (3) the non-additivity of F atom in affecting the halogen bond. Additionally, we also focus on the frequency shift of H–Ar stretch vibration. Finally, the nature of halogen bond in the complexes has been unveiled by means of natural bond orbital (NBO) analyses and electrostatic potentials.

2. Theoretical methods

Calculations were carried out using the Gaussian09 program [47]. The structures of complexes and the respective monomers have been optimized at the MP2/aug-cc-pVTZ level. Then harmonic vibrational frequency was calculated at the same level to confirm the stability of the complexes. All frequencies in the complexes are real. The interaction energy was calculated to the difference between the energy of the complex and the sum of the energies of the monomers. The interaction energy was corrected for the basis set superposition error (BSSE), which was calculated with counterpoise (CP) method proposed by Boys and Bernardi [48]. The natural bond orbital (NBO) analyses were performed using the NBO package [49] included in the Gaussian 09 suite of programs. The electrostatic potentials were calculated at the MP2/aug-cc-pVTZ level using WFA Surface analysis suite [50].

3. Results and discussion

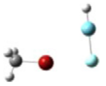
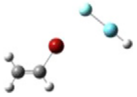
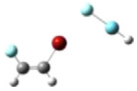
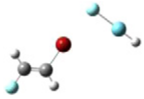
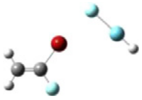
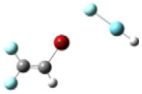
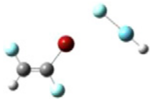
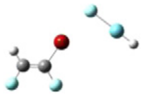
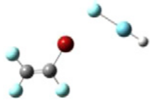
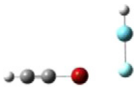
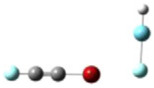
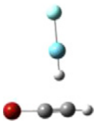
3.1. Geometry and interaction energy

The optimized structures are given in Table 1. An anisotropic distribution has been observed for the electron cloud around the bonded F atom [51,52]. It is smallest on the outermost portion of the bonded F atom. Thus the CH_3Br–FArH complex is not a linear structure. However, the linear and nonlinear structures were found for CF_3Br–FArH complex although the linear one is less stable than the nonlinear one. We only showed in Table 1 the results of linear CF_3Br–FArH complex for comparison with other complexes. With the increase of the number of F atom in the C^{sp^2}–Br complexes, the $\theta_{Br-F-Ar}$ bond angle also increases. This can be attributed to the greater positive electrostatic potential on the Br atom. Although the structures are a little different for the C^{sp^2}–Br and C^{sp}–Br complexes, they have Cs symmetry. For the complex formed of HCCBr and FArH, one halogen bond and two types of hydrogen bonds are considered. The latter contains a C–H$\cdots$F hydrogen bond and an Ar–H$\cdots\pi$ hydrogen bond. It is necessary to point out that the corresponding linear complexes for HCCBr and FCCBr are unstable with an imaginary frequency. The bond angles of halogen bond and hydrogen bond are greater than 170°, and it becomes larger with the increase of F substitution number.

Table 1 presents the interaction energies corrected with BSSE and binding distances in the complexes. One can see from Fig. 1 that there is a good linear relationship between the interaction energy and the binding distance in the halogen-bonded complexes. As the hybridization of C atom in C–Br bond varies from sp^3 to sp, the interaction energy becomes more negative and the binding distance is shorter. The results support the fact that the strength of C–X (X = halogen) halogen bond is related with the hybridization of C atom and it strengthens in order of $C^{sp^3} < C^{sp^2} < C^{sp}$ [17]. The interaction energy in HCCBr–FArH complex is about two times as much as that in CH_2CHBr–FArH complex. This shows that the hybridization of C atom has a great effect on the strength of halogen bond. When the hybridization of C atom in C–Br bond varies from sp^3 to sp, the electronegativity of C is increased. The larger electronegativity can result in an increase of positive electrostatic potential on the Br atom, thus the halogen bond becomes stronger in the order $C^{sp^3} < C^{sp^2} < C^{sp}$.

The interaction energy is calculated to be -10.68 kJ/mol in CH_3Br–FArH complex. However, the corresponding halogen-bonded complex of CH_3Br–FH was not obtained and it is changed to be a hydrogen bond structure with the H atom of FH to combine with the Br atom of CH_3Br as shown in Fig. 2. Relative to the CH_3Br–FArH complex, the interaction energy has a big increase in CF_3Br–FArH complex and the binding distance is shortened by 0.281 Å. Thus the presence of electron-withdrawing group in the halogen donor strengthens the halogen bond. This is consistent with the greater electrostatic potential on the Br atom in the F-substituted complexes. The interaction energy is calculated to be -5.70 kJ/mol in F_3CBr–FH complex, which is much less than that in CF_3Br–FArH complex (-25.19 kJ/mol). The binding distance is decreased from 3.033 Å in the former to 2.639 Å in the latter. The results indicate that the insertion of Ar atom in FH brings out a big change in the strength of halogen bond. One can see from Fig. 2 that the F_3CBr–FH complex is different from the CF_3Br–FArH complex in geometry. The difference in geometry for both complexes in Fig. 2 can be explained with the electrostatic potentials on the Br atom. The presence of F atoms makes the most positive electrostatic potential on the Br atom increased from 5.8 kcal/mol in CH_3Br to 30.0 kcal/mol in F_3CBr, while it causes the most negative electrostatic potential on the Br atom decreased from -15.1 kcal/mol in the former to -0.1 kcal/mol in the latter. Thus the former is inclined to

Table 1
Binding distance (R, Å), bond angle (θ, degree), interaction energy corrected with BSSE (ΔE, kJ/mol), and the most positive electrostatic potential ($V_{S,max}$, kcal/mol) associated with the Br atom in the complexes.

Complexes	Structures	ΔE	R	θ_{C-Br-F}	$\theta_{Br-F-Ar}$	$V_{S,max}$
CH_3Br–FArH		−10.68	2.920	173.7	86.9	5.8
CF_3Br–FArH		−25.19	2.639	173.8	98.7	30.0
CH_2CHBr–FArH		−13.22	2.850	174.0	89.9	11.4
cis-CHFCHBr–FArH		−14.35	2.787	173.2	92.7	15.3
trans-CHFCHBr–FArH		−16.78	2.770	174.5	93.1	17.8
CH_2CFBr–FArH		−21.21	2.738	171.6	92.0	21.4
CF_2CHBr–FArH		−17.28	2.735	173.9	95.0	20.0
2,3-trans-CHFCFBr–FArH		−22.16	2.700	171.2	94.6	24.6
2,3-cis-CHFCFBr–FArH		−24.45	2.688	172.1	94.9	27.1
CF_2CFBr–FArH		−25.16	2.661	171.8	96.5	29.1
HCCBr–FArH		−26.02	2.651	173.5	97.1	30.5
FCCBr–FArH		−26.68	2.631	174.2	97.7	32.3
BrCCH–FArH		−27.97	1.836	179.7	176.8	38.5(H)
HCCBr-pi-HArF		−28.24	0.743	–	–	

form a hydrogen-bonded complex with HF, while the latter is prone to form a halogen-bonded complex with HF.

With the increase of F atom number in the $C^{sp^2}-Br$ complexes, the interaction energy is increased and the binding distance is decreased. As one hydrogen atom in CH_2CHBr is replaced with a F atom, the increase of the interaction energy and the decrease of the binding distance are different for the different position F atom. The CH_2CFBr–FArH complex shows the strongest halogen bond, followed by the trans-CHFCHBr–FArH complex, and the cis-CHFCHBr–FArH complex gives the weakest halogen bond. The difference between trans-CHFCHBr–FArH and cis-CHFCHBr–FArH complexes is −2.43 kJ/mol in the interaction energy and −0.017 Å in the binding distance. Such difference in the strength can be evidenced with the electrostatic potential on the Br atom in the corresponding monomer (Table 1). The most positive electrostatic potential ($V_{S,max}$) associated with the Br atom is 15.3 and 17.8 kcal/mol for cis-CHFCHBr and trans-CHFCHBr, respectively. A similar result is also observed in the $C^{sp^2}-Br$ complex including two F

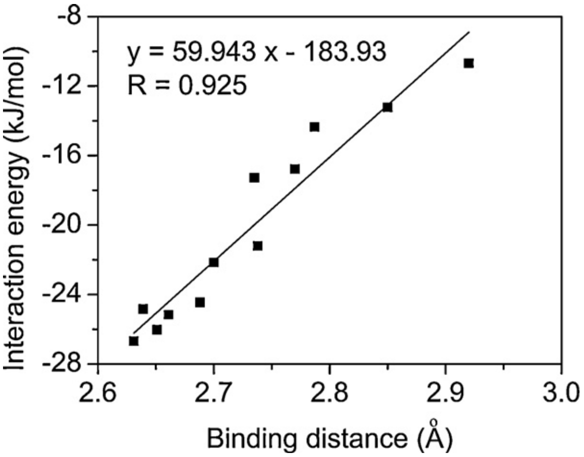


Fig. 1. The relationship of the interaction energy with the binding distance in the halogen-bonded complexes.

atoms in the halogen donor. The electrostatic potential on the Br atom further supports such change.

The average of the interaction energy is −17.45 kJ/mol for the halogen donor with one F substitution and −21.30 kJ/mol for the halogen donor with two F substitution. Thus the difference in the interaction energy between the F substituted C^{sp^2} −Br complex and CH_2CHBr complex is −4.23 kJ/mol for the halogen donor with one F substitution, −8.08 kJ/mol for the halogen donor with two F substitution, and −11.94 kJ/mol for the halogen donor with three F substitution. The interaction energy in the two F-substituted complex is less than twice of that in the one F-substituted complex. The interaction energy in the three F-substituted complex is less than three times of that in the one F-substituted complex. The result indicates that a negative nonadditivity is present for the F atom in the halogen bond. However, a positive nonadditivity is found for the F atom in the Au donor molecule of the Au-bonding [53]. If the above three values are divided by the number of F atom in the halogen donor, the obtained results are −4.23, −4.04, and −3.98 kJ/mol, respectively. This further validates the above conclusion. Of course, the difference in the contribution for the interaction energy is small for each F atom. A about −4 kJ/mol can be considered to be the contribution from one F atom in the C–Br···F halogen bond. According to this, we can have preliminary estimate of the strength of halogen bond involving different number of F atoms.

The interaction energy is increased by −0.66 kJ/mol when the complex is from HCCBr–FArH to FCCBr–FArH. The respective increase is −2.34 kJ/mol when the complex is from CH_2CHBr–FArH to CHFCHBr–FArH. Clearly, the effect of F substitution is related with the hybridization of C atom in the halogen donor. We think that this is due to the easier polarization of π electrons in CH_2CHBr than in HCCBr.

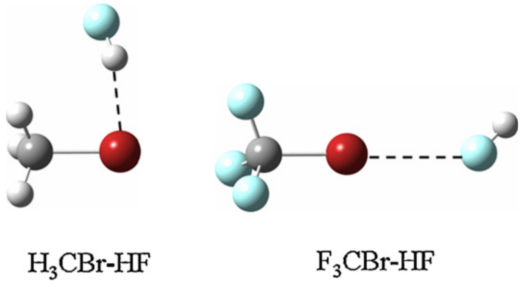


Fig. 2. The optimized structures of H_3CBr–HF and F_3CBr–FH complexes.

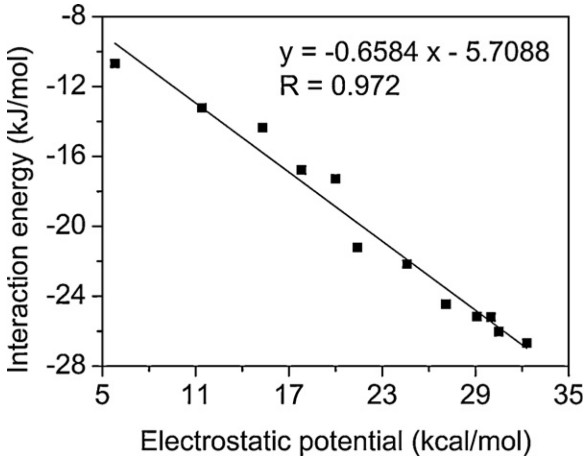


Fig. 3. The relationship of the interaction energy with the most positive electrostatic potential on the Br atom in the halogen-bonded complexes.

When HCCBr interacts with FArH, three modes are found. The F atom in FArH can combine with the H and Br atoms in HCCBr, and forms a hydrogen bond and a halogen bond, respectively. Additionally, the H atom in FArH as the proton donor forms a π hydrogen bond with the HCCBr. Clearly, the halogen bond in HCCBr–FArH system is weaker than the hydrogen bond. This is due to the bigger positive electrostatic potential on the H atom in HCCBr. This is different from that in system of FArH and dihalogen [45]. If the interaction energy is corrected with BSSE and ZVE (zero-point vibrational energy), it is −27.11 kJ/mol in HCCBr-pi-HArF complex and −24.36 kJ/mol in BrCCH–FArH complex. The result indicates that the HCCBr-pi-HArF complex is more stable than the BrCCH–FArH complex. This is different from that in HCCH–FArH complex [43]. We think that the induction and conjugation effect of Br are responsible for it.

Fig. 3 shows the relationship of the interaction energy with the most positive electrostatic potential on the Br atom in the halogen-bonded complexes. A linear relationship with a coefficient of 0.97 is observed for them. This shows that the electrostatic interaction plays a dominant role in halogen bonding.

3.2. Bond lengths and frequency shifts

Table 2 presents the changes in bond lengths and frequency shifts of stretch vibrations in the complexes. Upon complexation, the C–Br bond is elongated in CH_3Br–FArH complex, while it is shortened in CF_3Br–FArH complex. However, the C–Br stretch vibration exhibits a red shift in both complexes although the red shift is very small. The shortening of C–Br bond in CF_3Br–FArH complex is larger than that in CF_3Br–NH_3 complex (−0.001 Å at the M06/6-311++G(d,p) level) [12]. It is necessary to point out that the C–Br bond also presents a prominent lengthening in CF_3Br-X^- (X = F, Cl, and Br) complex [12]. A elongation also occurs for the C–Br bond in the C^{sp^2} −Br complexes except in CH_2CFBr–FArH complex where the C–Br bond is shortened by 0.001 Å. The elongation of C–Br bond in 2,3-trans-CHFCFBr–FArH and 2,3-cis-CHFCFBr–FArH complexes is smaller than that in cis-CHFCHBr–FArH and trans-CHFCHBr–FArH complexes. The elongation in the former two complexes can be seen as a combinative result of the elongation in the latter two complexes and the contraction in CH_2CFBr–FArH complex. The elongation of C–Br bond in HCCBr–FArH and FCCBr–FArH complexes is larger than that in the C^{sp^2} −Br complexes. The distant C–Br bond is elongated in BrCCH–FArH hydrogen-bonded complex, while it is contracted in HCCBr-pi-HArF hydrogen-bonded complex. The C–Br stretch vibration moves to low wavenumber in the C^{sp^2} −Br and C^{sp}–Br halogen-bonded

Table 2
Changes in bond lengths (Δr, Å) and frequency shifts of stretch vibrations ($\Delta \nu$, cm^{-1}) in the complexes.

complexes	Δr_{C-Br}	Δr_{H-Ar}	Δr_{Ar-F}	$\Delta \nu_{C-Br}$	$\Delta \nu_{H-Ar}$	$\Delta \nu_{Ar-F}$
CH_3Br–FArH	0.003	−0.006	0.016	−3	54	−15
CF_3Br–FArH	−0.005	−0.015	0.041	−5	150	−36
CH_2CHBr–FArH	0.002	−0.007	0.020	−1	70	−19
cis-CHFCHBr–FArH	0.005	−0.008	0.022	−6	78	−20
trans-CHFCHBr–FArH	0.005	−0.009	0.025	−5	92	−23
CH_2CFBr–FArH	−0.001	−0.012	0.034	−1	120	−30
CF_2CHBr–FArH	0.007	−0.010	0.026	−5	96	−24
2,3-trans-CHFCFBr–FArH	0.002	−0.013	0.035	−7	126	−31
2,3-cis-CHFCFBr–FArH	0.003	−0.014	0.038	−8	138	−34
CF_2CFBr–FArH	0.004	−0.014	0.039	−9	142	−35
HCCBr–FArH	0.012	−0.014	0.039	−22	143	−35
FCCBr–FArH	0.015	−0.015	0.040	−14	149	−41
BrCCH–FArH	0.005	−0.017	0.035	1	171	−27
HCCBr-pi-HArF	−0.008	0.019	0.097	–	−185	−91

complexes although it is larger in the latter than in the former. The frequency shift of distant C–Br stretch is very small in the hydrogen-bonded complexes.

In the halogen-bonded complexes, the free H–Ar bond is contracted and a blue shift is observed for the corresponding bond stretch vibration. A similar result has also been found in HArF–XY (X = Cl, Br; Y = F, Cl) complexes [45]. However, the blue shift of H–Ar bond is smaller in the C–Br complexes than that in the dihalogen complexes due to the weaker halogen bonding interaction in the former. One can see that the H–Ar blue shift becomes bigger for the stronger halogen bond, depending on the F substitution and C hybridization. In HCCBr-pi-HArF hydrogen-bonded complex, the H–Ar bond is elongated and exhibits a red shift, whereas a reverse result is found for the distant H–Ar bond in BrCCH–FArH hydrogen-bonded complex. The similar result was also observed in the hydrogen-bonded complex of HCCH–FArH [43].

The associated Ar–F bond is elongated in all complexes and its elongation is proportional to the interaction strength. The distant Ar–F bond is also elongated in HCCBr-pi-HArF complex and its elongation is larger than the associated one. The red shift of Ar–F stretch vibration follows a similar pattern with the Ar–F bond elongation.

3.3. NBO analyses

Besides the electrostatic interaction, other factors are also important in the formation of halogen bond. We thus perform NBO analyses in an attempt to render a rationalization of the strength and properties of halogen bonds. There is a main orbital interaction of $n_F \rightarrow \sigma^*_{C-Br}$ in the halogen-bonded complexes. The corresponding stabilization energy is present in Table 3. One can see that the interaction energy has a good relationship with the stabilization energy in the halogen-bonded complexes. Accompanied with the orbital interaction there is charge transfer from the halogen acceptor to donor. Thus the orbital interaction and charge transfer are also important for halogen bonds. The charge transfer is in range of 0.01–0.02 e in the carbon halogen-bonded complexes, which is smaller than that in the corresponding dihalogen-bonded complexes [43]. For hydrogen bonds, the orbital interaction is $n_F \rightarrow \sigma^*_{C-H}$ and $\pi_{C\equiv C} \rightarrow \sigma^*_{Ar-H}$ in BrCCH–FArH and HCCBr-pi-HArF complexes, respectively. The respective stabilization energy and charge transfer in the hydrogen bonds are bigger than those in the halogen bonds.

Table 3 also presents the energy ($E_{\sigma^*(C-Br)}$) and occupation ($n_{\sigma^*(C-Br)}$) of C–Br anti-bonding orbital in the complexes. As summarized in Table 3, the results clearly show that the energy $E_{\sigma^*(C-Br)}$ is increased in order of $C^{sp^3}-Br < C^{sp^2}-Br < C^{sp}-Br$. When the hybridization of C atom is constant, the $E_{\sigma^*(C-Br)}$ becomes smaller due to the F substitution and with the increase of F atom number. When the anti-bonding orbital σ^*(C–Br) is lower in energy, it is rather easy for it to interact with n_F orbital in HArF. Initially, the occupation of $n_{\sigma^*(C-Br)}$ should be zero in the halogen donor. Accompanied with the $n_F \rightarrow \sigma^*_{C-Br}$ orbital interaction, the occupation probability of $n_{\sigma^*(C-Br)}$ in the complex increases. The increase of occupation in $n_{\sigma^*(C-Br)}$ can be used to explain the elongation of C–Br bond in most halogen-bonded complexes.

Table 3
Stabilization energy (E^2, kcal/mol), charge transfer (CT, e), energy (E, eV) and occupation (n, e) of C–Br anti-bonding orbital in the complexes.[a]

Complexes	E^2	CT[b]	$E_{\sigma^*(C-Br)}$	$n_{\sigma^*(C-Br)}$
CH_3Br–FArH	3.14	0.009	0.3010	0.0089
CF_3Br–FArH	8.36	0.020	0.2532	0.0763
CH_2CHBr–FArH	3.91	0.011	0.3403	0.0264
cis-CHFCHBr–FArH	4.93	0.013	0.3237	0.0471
trans-CHFCHBr–FArH	5.23	0.013	0.3182	0.0386
CH_2CFBr–FArH	5.73	0.015	0.3237	0.0471
CF_2CHBr–FArH	5.96	0.015	0.3368	0.0166
2,3-trans-CHFCFBr–FArH	6.58	0.016	0.3237	0.0428
2,3-cis-CHFCFBr–FArH	6.90	0.017	0.3182	0.0386
CF_2CFBr–FArH	7.71	0.018	0.3169	0.0371
HCCBr–FArH	8.19	0.019	0.3789	0.0217
FCCBr–FArH	8.80	0.021	0.3692	0.0194
BrCCH–FArH	12.28	0.020	0.3829	0.0093
HCCBr-pi-HArF	38.18	0.082	0.2875	0.0079

[a] The stabilization energy is due to the $n_F \rightarrow \sigma^*_{C-Br}$ orbital interaction for the halogen-bonded complex, $n_F \rightarrow \sigma^*_{C-H}$ orbital interaction for BrCCH–FArH complex, and $\pi_{C\equiv C} \rightarrow \sigma^*_{Ar-H}$ orbital interaction for HCCBr-pi-HArF complex.

[b] The CT is calculated as the net charge transfer from the electron donor to the electron acceptor.

4. Conclusions

We have investigated the complexes of HArF and some brominated hydrocarbons at the MP2/aug-cc-pVTZ level. HArF can form a halogen bond with the C–Br compounds and two types of hydrogen bonds with HCCBr. The hydrogen-bonded complex is a little more stable than the halogen-bonded one. The F substitution causes the contraction of C–Br bond in F_3CBr–FArH complex, which is reverse to the elongation in H_3CBr–FArH complex. The C–Br stretch vibration exhibits a small red shift in all complexes. With the hybridization of C atom varies from C^{sp3}–Br to C^{sp}–Br, the halogen bond is strengthened. The F substitution in the C–Br compounds enhances the halogen bond and its enhancing effect is related with the substitution position and the hybridization of C atom. The halogen bond in trans-CHFCHBr–FArH complex is stronger than that in cis-CHFCHBr–FArH one. A similar result is found in 2,3-trans-CHFCFBr–FArH and 2,3-cis-CHFCFBr–FArH complexes. The halogen bond becomes stronger with the number of F atom in CH_2CHBr and the F substitution exhibits a negative nonadditivity in enhancing the halogen bond. The average contribution of each F atom to the interaction energy of halogen bond is estimated to be -4 kJ/mol, which is can be used to estimate the strength of halogen bond in perfluorocarbon compounds. The linear relationship between the interaction energy and the electrostatic potential on the Br atom indicates that the electrostatic interaction plays a dominant role in the C–Br halogen bonds.

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