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Study of π Halogen Bonds in Complexes $C_2H_{4-n}F_n-ClF$ ($n = 0-2$)

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The π-halogen bond may be considered, in a broad sense, essentially a π-hydrogen bond. Using the counterpoise-corrected potential energy surface method (interaction energy optimization), the stationary structures of the $C_2H_{4-n}F_n-ClF$ ($n = 0-2$) complexes with all real frequencies have been obtained at the MP2/aug-cc-pVDZ level. For $C_2H_{4-n}F_n-ClF$ ($n = 0-2$), the π-halogen bond has a long distance and is elongated by the F substituent effect. The π-halogen bond length order is 2.661 Å for C_2H_4-ClF < 2.745 Å for C_2H_3F-ClF < 2.766 Å for *g*-$C_2H_2F_2-ClF$ < 2.8076 Å for *trans*-$C_2H_2F_2-ClF$ < 2.8079 Å for *cis*-$C_2H_2F_2-ClF$. For three complexes C_2H_3F-ClF, *g*-$C_2H_2F_2-ClF$, and *cis*-$C_2H_2F_2-ClF$, the π-halogen bonds are further shifted and sloped by the F substituent effect. The F substituent effect reduces also the interaction energy of the π-halogen bond. The interaction energies are respectively −3.7 for C_2H_4-ClF, −2.8 for C_2H_3F-ClF, −2.3 for *g*-$C_2H_2F_2-ClF$, −1.9 for *cis*-$C_2H_2F_2-ClF$, and −1.8 kcal/mol for *trans*-$C_2H_2F_2-ClF$, at the CCSD(T)/aug-cc-pVDZ level. The electron correlation contribution of the interaction energy is large for $C_2H_{4-n}F_n-ClF$ ($n = 0-2$), which shows that the stabilities of the π-halogen bond systems results primarily from the dispersion interaction. In the double F substituent systems, the interaction energy of the π-halogen bond structure with a longer interaction distance is larger than that of the corresponding π-hydrogen bond structure with a shorter interaction distance. This may be because there are the large electron correlation contributions of the interaction energy, and a secondary interaction between lone pairs of Cl atom and some atoms (H, C) with positive charges in the π-halogen bond structure.

1. Introduction

As we know, hydrogen bonds have attracted much attention because of their important roles in chemistry and biology.[1] With progress in the study on the hydrogen bond, a number of unusual hydrogen bonds have been proposed during the past few decades.[2] Recently, although study of weak interaction still focused on hydrogen-bonded interactions,[3−6] a growing system of experimental and theoretical evidence confirms that interactions such as $-X\cdots Y-$ ($X = Cl, Br,$ or I; $Y = N, O, S,$ or π) similarly play important roles in crystal engineering,[7−15] new supramolecular structures, and new high-value materials,[16] drug design, supramolecular chemistry, and physical organic chemistry.[17] The interactions are noncovalent interactions between halogen atoms such as iodine, bromine, chlorine, and even fluorine, which can function as Lewis acids,[18] and Lewis bases such as nitrogen, oxygen, sulfur, halide anions, and a π bond complex, which have attracted particular attention in recent years.[19] Because of the strict analogies of this interaction with the hydrogen bond, the name "halogen bond" has been proposed and is currently used[20] in a study of weak interaction.

The analogies of a halogen bond with the hydrogen bond and the name "halogen bond" as studied by Anthony C. Legon and Duncan W. Bruce et al.[21] are discussed below. A striking parallelism was demonstrated between the properties of $B\cdots XY$ and their $B\cdots HX$ analogues, especially for angular geometries, and the term "halogen bond" was suggested to describe the $B\cdots XY$ interaction. The only significant difference, apart from larger intermolecular distances in $B\cdots XY$, was a noted propensity for the hydrogen bond, but not the $B\cdots XY$ system, to be nonlinear when symmetry allowed. Hassel[22] used also the equivalent term "halogen molecule bridge" to describe conclusions of his pioneering work in the solid state.

Similarly, this interaction is now referred to as halogen bonding, as suggested by Legon,[23] and the topic has recently been reviewed by Resnati.[24] Halogen bonding may involve dihalogens X2 and X−Y as well as organic halides.[18]

The importance of the halogen bond has been indicated by the above statements. Synchronously, many studies on the halogen bond have been reported.[15−18,21,25−29]

As above, a nonaromatic π-halogen bond complex is also an important part in the halogen bond. Some experimental works on nonaromatic π-halogen bond complexes such as C_2H_4-XY ($XY = BrCl, ClF, Cl_2, HBr$) have been completed.[29−33] However, studies of the substituent effect on the nonaromatic π-halogen bonds are few.

It is therefore reasonable to consider, what are the characteristics of structures and π-halogen bonds in fluoroethylene π-halogen bond complexes in comparison with those of C_2H_4-XY? In this paper, we focus attention on the $C_2H_{4-n}F_n-ClF$ ($n = 0-2$) complexes, and the π-halogen bond is found. In the $C_2H_{4-n}F_n-ClF$ ($n = 0-2$) structure, the C_2H_3F, *g*-$C_2H_2F_2$, *cis*-$C_2H_2F_2$, and *trans*-$C_2H_2F_2$ subunits are the unsaturated fluoroethylenes, as the π-electron donors in the π-halogen bond systems. In the $C_2H_{4-n}F_n-ClF$ ($n = 1, 2$) structure, the chemical and physical properties of halogen bond are different from that of C_2H_4-ClF. The halogen bonds are nonlinear for C_2H_3F-ClF, *g*-$C_2H_2F_2-ClF$, and *cis*-$C_2H_2F_2-ClF$, but for C_2H_4-ClF

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TABLE 1: Comparison of Experimental (in Square Brackets) and Theoretical Structural Parameters for the Monomers ($C_2H_{4-n}F_n$ ($n = 1, 2$) and ClF) and Five Complexes ($C_2H_{4-n}F_n-ClF$ ($n = 0-2$)[a]

	$R_{C=C}$	R_{C-F}	R_{C-H}	A_{CCF}	A_{CCH}	A_{FCH}	A_{FCF}	A_{HCH}
C_2H_4-ClF	1.358		1.093		121.2			
	(1.360)		(1.093)		(121.1)			
C_2H_3F-ClF	1.347	1.357	1.092	121.6	118.5	112.4		
	(1.350)	(1.354)	(1.092)	(121.5)	(118.5)	(112.6)		
C_2H_3F	1.339	1.365	1.092	121.7	121.5	111.9		
	[1.333]	[1.348]	[1.076]	[121.0]	[127.7]			
cis-$C_2H_2F_2-ClF$	1.349	1.350	1.090	122.0	122.7	115.3		
	(1.351)	(1.348)	(1.090)	(121.9)	(122.6)	(115.5)		
cis-$C_2H_2F_2$	1.341	1.356	1.089	122.3	122.7	115.0		
	[1.311]	[1.332]	[1.100]	[122.5]	[127.0]	[110.5]		
trans-$C_2H_2F_2-ClF$	1.348	1.357	1.090	119.5	125.5	115.0		
	(1.350)	(1.354)	(1.090)	(119.4)	(125.3)	(115.2)		
trans-$C_2H_2F_2$	1.340	1.363	1.090	119.5	125.8	114.7		
	[1.320]	[1.338]	[1.088]	[119.8]	[125.0]	[115.2]		
g-$C_2H_2F_2-ClF$	1.343	1.330	1.088	124.9	119.1			
	(1.346)	(1.328)	(1.088)	(124.8)	(119.0)			
g-$C_2H_2F_2$	1.335	1.337	1.087	125.2	119.3		109.6	121.5
	[1.311]	[1.321]	[1.07]				[110.0]	[117.0]

[a] The structures of the complexes come from the CP-corrected PES and a standard PES (in parentheses) at the MP2/aug-cc-pVDZ level. Bond lengths are in angstroms and angles in degrees. The experimental values (in square brackets) are taken from refs 35 and 36.

TABLE 2: π Halogen Bonds and Related Structural Parameters in the Five Complexes $C_2H_{4-n}F_n-ClF$ ($n = 0-2$)[a]

	$R_{Cl\cdots C=C}$	$R_{H\cdots C=C}$	R_{Cl-F}	β	d
C_2H_4-ClF	2.661		1.715		
	(2.550)		(1.726)		
	[2.768]				
C_2H_3F-ClF	2.745		1.704	1.6	0.1684
	(2.622)		(1.713)	(1.2)	(0.1667)
g-$C_2H_2F_2-ClF$	2.766		1.700	4.4	0.3133
	(2.642)		(1.708)	(3.6)	(0.3810)
trans-$C_2H_2F_2-ClF$	2.8076		1.695		
	(2.651)		(1.705)		
cis-$C_2H_2F_2-ClF$	2.8079		1.697	9.1	0
	(2.660)		(1.706)	(7.2)	(0)
ClF			1.570		
C_2H_4-HF		2.211			
C_2H_3F-HF		2.264		7.1	0.1690
g-$C_2H_2F_2-HF$		2.274		11.2	0.2859
trans-$C_2H_2F_2-HF$		2.389			
cis-$C_2H_2F_2-HF$		2.411		15.6	0

[a] The structures of the complexes come from the CP-corrected PES and a standard PES (in parentheses) at the MP2/aug-cc-pVDZ level. Bond lengths are in angstrom and angles in degrees. The structural parameters of the five complexes $C_2H_{4-n}F_n-HF$ ($n = 0-2$) of the π-hydrogen bond system are taken from ref 40, and the experimental value of C_2H_4-ClF (in square brackets) is taken from ref 28.

and *trans*-$C_2H_2F_2-ClF$, the halogen bonds are linear. The characteristics of π-halogen bonds come from the different distributions of π-electron densities in $C_2H_{4-n}F_n$ ($n = 1, 2$).

This paper aims at exhibiting characteristics of π-halogen bond complexes between $C_2H_{4-n}F_n$ ($n = 0-2$) and ClF, studying the F substituent effect on the characteristic of the complexes structure and π-halogen bond, spurring further experimental work in this area, enriching the knowledge on novel weak interactions in an exciting part of chemistry.

2. Computational Details

The computations were performed using Dunning's augmented correlation consistent polarized valence basis sets of contracted Gaussian function,[34] aug-cc-pVDZ (160 functions for $C_2H_2F_2-ClF$).

For the complexes C_2H_4-ClF, C_2H_3F-ClF, *cis*-$C_2H_2F_2-ClF$, *trans*-$C_2H_2F_2-ClF$, and *g*-$C_2H_2F_2-ClF$, the optimum configuration, vibration frequencies, and NBO were calculated with MP2 theory in conjunction with the basis set. In geometrical optimization calculations, "standard PES (potential energy surface)" (with Opt keyword) and "CP (counterpoise) corrected PES" (with Counterpoise and Opt keywords) methods are used. To help our comparison, each subunit of $C_2H_{4-n}F_n-ClF$ ($n = 0-2$) has been calculated at the same level (MP2/aug-cc-pVDZ) and the calculated values agree well with the experimental values[28,35,36] (see Tables 1 and 2).

Using the CP procedure,[37] intermolecular interaction energies of the complexes were calculated at the coupled cluster theory with single and double substitutions and perturbatively linked triple excitations CCSD(T)/aug-cc-pVDZ level.

The interaction energies E_{int} have been calculated as the difference between the energy of the complexes and the sum of the energy of the monomers, by the following formula.[38]

$$E_{int} = E_{AB}(X_{AB}) - E_A(X_{AB}) - E_B(X_{AB}) \qquad (1)$$

To eliminate the BSSE effect in the interaction energy given by eq 1, we use the same basis set, X_{AB}, for the monomers calculation as for the complex calculation.

3. Results and Discussion

3.1. Equilibrium Geometry and π Halogen Bond. By the CP-corrected PES method, the optimized geometries of the complexes C_2H_4-ClF, C_2H_3F-ClF, *g*-$C_2H_2F_2-ClF$, *cis*-$C_2H_2F_2-ClF$, and *trans*-$C_2H_2F_2-ClF$ and of related systems have been obtained at the MP2/aug-cc-pVDZ level. These geometric parameters are listed in Tables 1 and 2.

From Tables 1 and 2, each optimized configuration by the standard PES is different from that by the CP-corrected PES method for the five complexes. The intermolecular π-halogen bond length $R_{Cl\cdots C=C}$ from the CP-corrected PES is longer by about 0.1 Å than that from a standard PES for five complexes. The result is similar to that in H-bonded systems.[2,39] From Table 4, we can find that the intermolecular interaction energy E_{int} of the structure from the CP-corrected PES is larger than that from a standard PES for five complexes. It shows that an optimized structure from the CP-corrected PES method is more stable than that from the standard PES method. As follows in the discussion, the accurate structures from the CP-corrected PES are used for C_2H_4-ClF, C_2H_3F-ClF, *g*-$C_2H_2F_2-ClF$, *cis*-$C_2H_2F_2-ClF$, and *trans*-$C_2H_2F_2-ClF$ complexes.

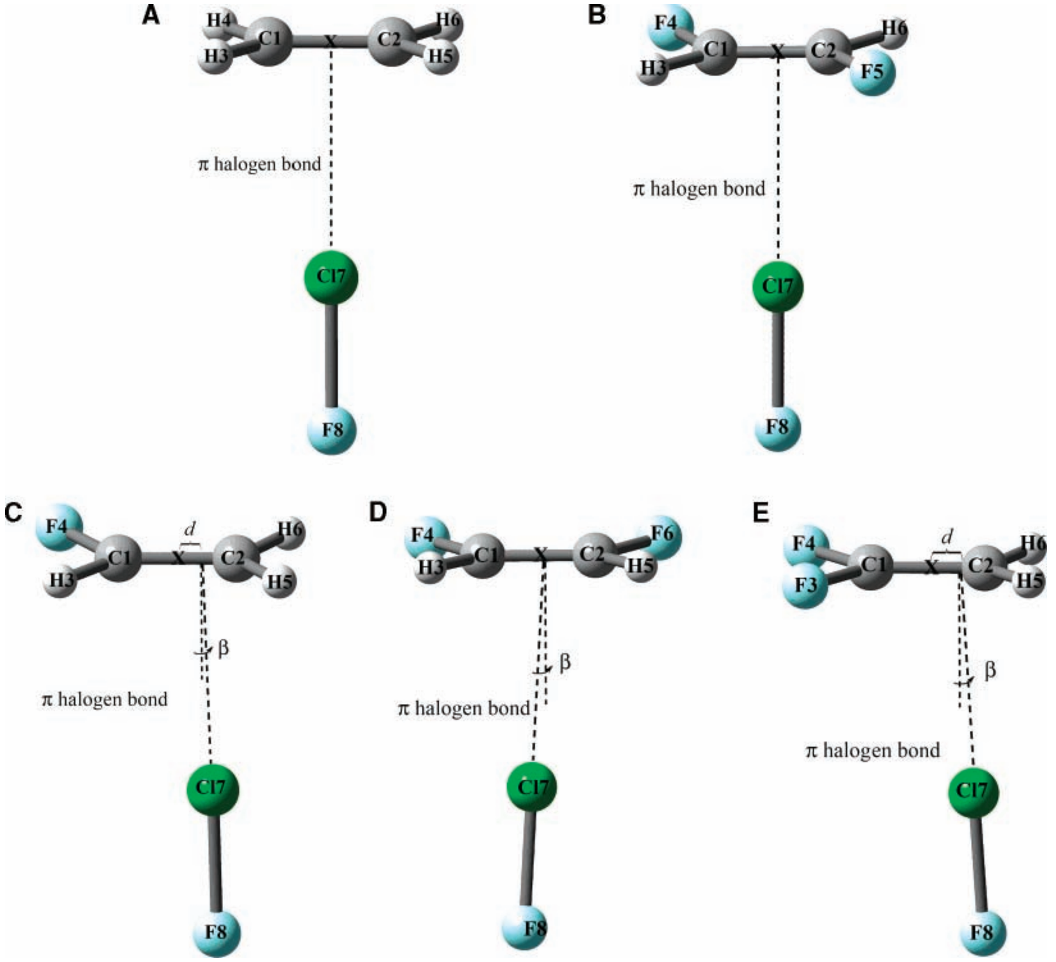

Figure 1. Five complexes' optimized geometries. (A) C_{2v} symmetry T-shaped structure of C_2H_4−ClF. In this, and subsequent figures, the symbol X marks the center of the C−C multiple bond. (B) C_2 symmetry T-shaped structure of *trans*-$C_2H_2F_2$−ClF. (C) C_1 symmetry contorted T-shaped structure of C_2H_3F−ClF. In this, and (E), the symbol d marks the deviate distance of the π-halogen bond. (D) C_s symmetry sloped T-shaped structure of *cis*-C_2H_3F−ClF. (E) C_s symmetry contorted T-shaped structure of g-C_2H_3F−ClF.

TABLE 3: NBO Charges of the Complexes

	C_2H_4−ClF	C_2H_3F−ClF	*g*-$C_2H_2F_2$−ClF	*trans*-$C_2H_2F_2$−ClF	*cis*-$C_2H_2F_2$−ClF
C1	−0.38667	0.32988	0.95432	0.21368	0.21513
C2	−0.38667	−0.51634	−0.62240	0.21368	0.21513
C1 + C2	−0.77334	−0.18646	0.33192	0.42736	0.43026
Cl7 + F8	−0.06133	−0.04214	−0.03535	−0.02842	−0.03234

TABLE 4: Interaction Energies E_{int} (kcal/mol) and Electron Correlation Effect Value of the Five Complexes at Different Levels with the aug-cc-pVDZ Basis Set (EC = CCSD(T)-SCF)

	SCF	MP2	MP3	MP4(SDQ)	CCSD	CCSD(T)	−EC
C_2H_4−ClF	−0.34	−5.88	−3.20	−3.02	−2.65	−3.67	3.3, 91%
	(0.66)	(−6.07)	(−2.60)	(−2.46)	(−2.00)	(−3.24)	
C_2H_4−HF	−3.17	−4.18	−3.93	−3.80	−3.68	−3.88	
C_2H_3F−ClF	0.50	−4.50	−2.32	−2.20	−1.88	−2.77	3.3,118%
	(1.61)	(−4.59)	(−1.70)	(−1.61)	(−1.20)	(−2.33)	
C_2H_3F−HF	−1.86	−3.07	−2.75	−2.67	−2.55	−2.79	
g-$C_2H_2F_2$−ClF	1.13	−3.79	−1.78	−1.75	−1.43	−2.32	3.5,149%
	(2.35)	(−3.96)	(−1.12)	(−1.13)	(−0.73)	(−1.86)	
g-$C_2H_2F_2$−HF	−0.92	−2.46	−2.00	−1.97	−1.83	−2.13	
cis-$C_2H_2F_2$−ClF	1.42	−3.32	−1.45	−1.40	−1.08	−1.91	3.3,174%
	(2.78)	(−3.36)	(−0.73)	(−0.71)	(−0.29)	(−1.40)	
cis-$C_2H_2F_2$−HF	−0.69	−1.80	−1.54	−1.55	−1.40	−1.64	
trans-$C_2H_2F_2$−ClF	1.50	−3.18	−1.34	−1.29	−0.98	−1.79	3.3,184%
	(2.44)	(−3.23)	(−0.59)	(−0.56)	(−0.15)	(−1.25)	
trans-$C_2H_2F_2$−HF	−0.36	−1.49	−1.21	−1.19	−1.08	−1.31	

From Tables 1 and 2 and Figure 1, the structures of five complexes C_2H_4−ClF, *trans*-$C_2H_2F_2$−ClF, C_2H_3F−ClF, *cis*-$C_2H_2F_2$−ClF, and *g*-$C_2H_2F_2$−ClF with all real frequencies are, respectively, C_{2v}, C_2, C_1, C_s, and C_s symmetry. In each structure, the acidic Cl7 atom (as an electron acceptor) of the ClF point to the C═C π bond (as an electron donor with a π electron). And the distances from Cl7 atom to the C═C π bond are 2.66−2.81 Å, which are in the range 2.766−2.957 Å of experimental

π-halogen bond distances.[23a] It shows that the π-halogen bonds between Cl7 and the C═C π bond have formed in the complexes, and its length is longer by about 0.5 Å than that of the corresponding π hydrogen bond[40] (see Table 2). From Table 3, the charge of the subunit ClF is about −0.03 to −0.06, which indicates that there is charge transfer between $C_2H_{4-n}F_n$ (n = 0−2) and ClF in forming of π-halogen bond.

Here, the net charge of C═C (the sum of C1 and C2 charge, C1 + C2 row in Table 3) is used to roughly represent electron donor ability of C═C bond. The order the of net charge of C═C is as follows: −0.773 (C_2H_4) < −0.186 (C_2H_3F) < 0.332 (g-$C_2H_2F_2$) < 0.427 ($trans$-$C_2H_2F_2$) < 0.430 (cis-$C_2H_2F_2$) (see Table 3). Thus, the order of electron donor ability of C═C bond is C_2H_4 > C_2H_3F > g-$C_2H_2F_2$ > $trans$-$C_2H_2F_2$ > cis-$C_2H_2F_2$. Comparing the order of electron donor abilities of the C═C bond with the π-halogen bond $R_{Cl\cdots C=C}$ length in the complexes, we can find that the π-halogen bond $R_{Cl\cdots C=C}$ length increases with the decrease of electron donor abilities of C═C bond. The order also shows that the π-halogen bond length $R_{Cl\cdots C=C}$ in five complexes mainly is affected by the electron donor ability of the C═C bond, and the relationship between the π-halogen bond $R_{Cl\cdots C=C}$ length and electron donor ability of the C═C bond in the complexes is shown.

The structural characteristics of five complexes are shown in Figure 1. The C_2H_4−ClF and $trans$-$C_2H_2F_2$−ClF are T-shaped structure in which the ClF axis is perpendicular to the plane of the C_2H_4 subunit and bisects the carbon−carbon double bond. In experiment, C_2H_4−ClF, C_2H_4−BrCl, and C_2H_4−Cl_2 all are T-shaped C_{2v} symmetry structures.[29−33] For C_2H_4−ClF, the calculated π-halogen bond $R_{Cl\cdots C=C}$ length agrees well with experimental value[28] (see Table 2). The cis-$C_2H_2F_2$−ClF is a sloped T-shaped structure; because the two lobes of the π-electron cloud have been repulsed by two F atoms, the π-halogen bond is sloped from the molecular vertical plane. The C_2H_3F−ClF and g-$C_2H_2F_2$−ClF are contorted T-shaped structures. The π-halogen bond not only is shifted (about 0.2 or 0.3 Å) but also slightly sloped to C2 atom. Thus the shifted and sloped π-halogen bonds are observed in the contorted T-shaped structures.

From Table 1, we can see that the parameters of monomer optimized structures of ClF and $C_2H_{4-n}F_n$ (n = 1, 2) agree well with the experimental results.[35,36] Comparing the structural parameters between monomer and the corresponding subunit in five complexes, we can easily find that the C═C length is increased and C−F is shortened in forming of the π-halogen bond.

For the π-halogen bond, the length order is 2.661 Å for C_2H_4−ClF < 2.745 Å for C_2H_3F−ClF < 2.766 Å for g-$C_2H_2F_2$−ClF, < 2.8076 Å for $trans$-$C_2H_2F_2$−ClF < 2.8079 Å for cis-$C_2H_2F_2$−ClF. And they are longer than the π-hydrogen bond lengths of $C_2H_{4-n}F_n$−HF (n = 0−2).

3.2. π Halogen Bonds and p−π Conjugate Effects. As the π-halogen bond is an attractive interaction between acidic Cl atom and the π-electrons of C═C bond, the σ part of $C_2H_{4-n}F_n$ (n = 0−2) plays no role. The F substituent effect on the π-halogen bonds in $C_2H_{4-n}F_n$−ClF (n = 1, 2) is similar to that on the π-hydrogen bonds in $C_2H_{4-n}F_n$−HF (n = 1, 2).[40] It relates also to the p−π conjugate effect in the subunit $C_2H_{4-n}F_n$ (n = 1, 2), but the induced effect of the F atom is not obviously exhibited. The p−π conjugate effect shows that the p electrons of F atom transfer to the C═C bond direction; thus, the π-halogen bond is also extended, shifted and sloped in the contorted T-shaped structures of the $C_2H_{4-n}F_n$−ClF (n = 1, 2). The summary above shows that due to the F substituent effect through the p−π conjugate, the π-halogen bond is deformed.

3.3. Interaction Energies and π Halogen Bonds. By CP and NCP optimizated geometries at the SCF, MP2, MP3, MP4-(SDQ), CCSD, and CCSD(T) levels with the aug-cc-pVDZ basis set, the interaction energies have been calculated using the CP procedure and listed in Table 4 for the complexes C_2H_4−ClF, C_2H_3F−ClF, cis-$C_2H_2F_2$−ClF, $trans$-$C_2H_2F_2$−ClF, and g-$C_2H_2F_2$−ClF with the π-halogen bond.

The calculated results show that the interaction energies from CP optimized and NCP optimized geometries are different. The CCSD(T) energy difference [E_{int}(CP) − E_{int}(NCP)] between CP and NCP geometries is as follows: −0.43 (11.7%) for C_2H_4−ClF < −0.44 (15.9%) for C_2H_3F−ClF < −0.46 (19.8%) for g-$C_2H_2F_2$−ClF < −0.51 (26.7%) for cis-$C_2H_2F_2$−ClF < −0.54 (30.2%) for $trans$-$C_2H_2F_2$−ClF. The result shows that the interaction from CP is stronger than that from NCP geometry, and the relative difference values are larger in the F substituent systems (see Table 4). Of course, the interaction energies at the different theory levels are different for the CP geometry. Comparing the interaction energy at several levels with that at the CCSD(T) level shows that the SCF interaction energy is too small (positive values for some systems), the MP2 interaction energy is larger, and the MP3 interaction energy is close to the CCSD(T) value, as shown in Table 4.

From Table 4, the interaction energy decreases with increasing π-halogen bond length for the five complexes. The π-halogen bond lengths are, respectively, 2.661 Å for C_2H_4−ClF < 2.745 Å for C_2H_3F−ClF < 2.766 Å for g-$C_2H_2F_2$−ClF < 2.8076 Å for $trans$-$C_2H_2F_2$−ClF < 2.8079Å for cis-$C_2H_2F_2$−ClF. The CCSD(T) interaction energies are, respectively, −3.67 kcal/mol for C_2H_4−ClF > −2.77 kcal/mol for C_2H_3F−ClF > −2.32 kcal/mol for g-$C_2H_2F_2$−ClF > −1.91 kcal/mol for cis-$C_2H_2F_2$−ClF > −1.79 kcal/mol for $trans$-$C_2H_2F_2$−ClF.

Obviously, C_2H_4−ClF is not substituted by the F atom, it has the largest interaction energy. The F substituent complexes have smaller interaction energies. This shows that the F substituent effect decreases the interaction energy in $C_2H_{4-n}F_n$−ClF (n = 1, 2). For the g-$C_2H_2F_2$−ClF, cis-$C_2H_2F_2$−ClF, and $trans$-$C_2H_2F_2$−ClF systems, although they all have two F atoms in the systems, due to the difference of F substitute position in three systems, their π-halogen bond lengths and interaction energies are different. The g-$C_2H_2F_2$−ClF has the shortest π-halogen bond (2.766 Å) and the largest interaction energy (−2.32 kcal/mol).

Comparing the interaction energies and structures between $C_2H_2F_2$−ClF and $C_2H_2F_2$−HF,[40] we can find that although the π-halogen bond length is longer by about 0.4 Å than the corresponding π-hydrogen bond length (see $R_{Cl\cdots C=C}$ and $R_{H\cdots C=C}$ in Table 2), the interaction energy of the π-halogen bond system is larger than that of π-hydrogen bond system (see Table 4). This is because the $C_2H_2F_2$−ClF system has a larger electron correlation contribution than the $C_2H_2F_2$−HF system. For example, the electron correlation contribution of $trans$-$C_2H_2F_2$−ClF is −3.3 kcal/mol (184%), but the electron correlation contribution of $trans$-$C_2H_2F_2$−HF is only −0.95 kcal/mol (72.5%). The result shows that the large electron correlation contribution may cause a large interaction energy in the complex $C_2H_2F_2$−ClF system. This is one reason why the interaction energy ΔE_{int} of $C_2H_2F_2$−ClF is larger than that of $C_2H_2F_2$−HF; the other cause may be the occurrence of the secondary interaction between lone pairs of the acidic Cl7 atom and the H and C atoms with positive charge of $C_2H_2F_2$ for $C_2H_2F_2$−

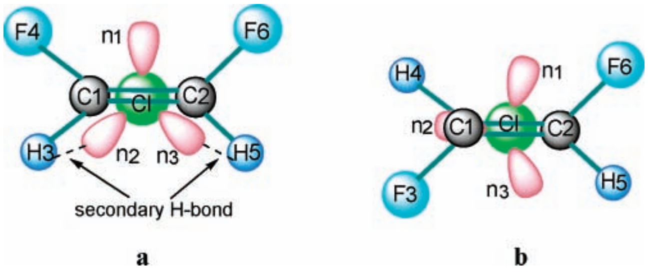

Figure 2. (a) Effective secondary H-bond in the *cis*-$C_2H_2F_2$−ClF. The lone pair n2 points to the H3, and the n3 points to the H5. The effective secondary H-bond is formed and increases the interaction energy. (b) Possible secondary H-bond in the *trans*-$C_2H_2F_2$−ClF. Due to the repulsion action between F6 (F3) and n1 (n2), the n2 is not effective to point to the H4, and n3 is not effective to point to the H5. The effective secondary H-bond is not formed, and the interaction energy is not increased.

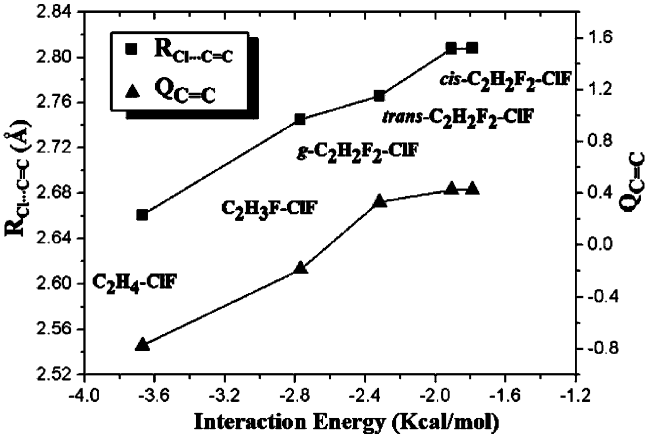

Figure 3. Correlations are between the energy, intermolecular separation, and net charge of the two C atoms in five complexes.

ClF system. But for the $C_2H_{4-n}F_n$−HF system there is not the secondary interaction between acidic H7 atoms and H atoms of $C_2H_2F_2$.

For *cis*-$C_2H_2F_2$−ClF and *trans*-$C_2H_2F_2$−ClF systems, the π-halogen bond length of *cis*-$C_2H_2F_2$−ClF is slightly longer (2.8079Å) than that (2.8076 Å) of *trans*-$C_2H_2F_2$−ClF. The interaction energy of *cis*-$C_2H_2F_2$−ClF should be lower than that of *trans*-$C_2H_2F_2$−ClF, but the calculated result shows that the interaction energy of *cis*-$C_2H_2F_2$−ClF is a little larger (−1.91 kcal/mol) than that (−1.79 kcal/mol) of *trans*-$C_2H_2F_2$−ClF. This reason may be the secondary interaction in the *cis*-$C_2H_2F_2$−ClF system is a little larger than that of *trans*-$C_2H_2F_2$−ClF system (see Figure 2).

The correlation among the interaction energies, intermolecular separation ($R_{Cl\cdots C=C}$), and net charge of C=C (C1 + C2 in Table 3) has been found. These correlations are interesting, and they are exhibited in Figure 3.

For the interaction energy of the complex, the electron correlation contribution is dominant. Electron correlation contributions are −3.3 (91%) for C_2H_4−ClF < −3.3 (118%) for C_2H_3F−ClF < −3.5 (149%) for *g*-$C_2H_2F_2$−ClF < −3.3 (174%) for *cis*-$C_2H_2F_2$−ClF < −3.3 (184%) for *trans*-$C_2H_2F_2$−ClF. In our previous work,[40] the electron correlation contributions are −0.71 (4.4%) for C_2H_4−HF < −0.93 (33.0%) for C_2H_3F−HF < −1.21 (57.6%) for *g*-$C_2H_2F_2$−HF < −0.95 (57.9%) for *cis*-$C_2H_2F_2$−HF < −0.95 (72.5%) for *trans*-$C_2H_2F_2$−HF. It is obvious that the F substituent effect greatly increases the electron correlation contribution of the interaction energy for π-halogen bond and π-hydrogen bond systems. Comparing to the π-hydrogen bond system, it is interesting that the π-halogen bond system has a larger electron correlation effect (about −3.3 to −3.5 kcal/mol for π-halogen bond systems; −0.71 to −1.21 kcal/mol for π-hydrogen bond systems).

According to analyses within a perturbation framework,[41−43] the electron correlation part of interaction energy mainly represents the contribution of the dispersion interaction (and induction effect). The SCF part of interaction energy mainly describes the contribution of the static Coulomb interaction (including static polarization and the secondary effect of back-polarization). It is clear that the interaction energy contribution mainly comes from the dispersion interaction, but the static Coulomb interaction may be small (it is possible to have a very large Coulomb term but have it canceled by a similarly large exchange repulsion) in the complexes with a π-halogen bond (see Table 4). In fact, for F substituent systems, the SCF segments of interaction energy give the repulsion interactions. And with the extending of the π-halogen bond from the F substituent, the repulsion energy of the SCF segment increases (from 0.5 to 1.5 kcal/mol) in the $C_2H_{4-n}F_n$−ClF (n = 1, 2) systems. This shows that those optimized π-halogen bond lengths are in the repulsion area of the SCF interaction potential surfaces.

The ClF molecule interacts mainly through the correlation component; the electron correlation contributions of the interaction energy are attractive interactions, and almost unchangeable to be about −3.3 kcal/mol for different lengths of π-halogen bond in the five complexes.

4. Conclusion

The characteristics of structures and π-halogen bonds of five complexes have been exhibited by an analyzing of the CP-optimized geometries for the C_2H_4−ClF, C_2H_3F−ClF, *cis*-$C_2H_2F_2$−ClF, *trans*-$C_2H_2F_2$−ClF, and *g*-$C_2H_2F_2$−ClF.

In five complexes, the π-halogen bond is longer by about 0.4−0.5 Å than the corresponding π-hydrogen bond in $C_2H_{4-n}F_n$−HF. In the $C_2H_{4-n}F_n$−ClF (n = 1, 2) systems, the π-halogen bond has been extended, shifted, and sloped by F substituent effects. For three $C_2H_2F_2$−ClF structures, the interaction energy is larger by about −0.2 to −0.5 kcal/mol than that of corresponding $C_2H_2F_2$−HF structure. The reason comes from two main factors that are two important characteristics of the π-halogen bond. First, the contribution of the electron correlation of the interaction energy in a $C_2H_2F_2$−ClF structure is greatly increased in comparison with that in the corresponding $C_2H_2F_2$−HF system. Second, there is the secondary interaction between lone pairs on the Cl atom and $C_2H_2F_2$ in $C_2H_2F_2$−ClF (see Figure 2), which mainly includes hydrogen bond interaction between lone pairs on Cl atom and H atom of C=C, and the interaction between lone pairs on the Cl atom and the C atoms with a positive charge of $C_2H_2F_2$.

In *trans*-$C_2H_2F_2$−ClF and *cis*-$C_2H_2F_2$−ClF systems, the π-halogen bond of *cis*-$C_2H_2F_2$−ClF is a little longer than that of *trans*-$C_2H_2F_2$−ClF, but the interaction energy of *cis*-$C_2H_2F_2$−ClF is larger than that of *trans*-$C_2H_2F_2$−ClF. This is due to the secondary hydrogen bond interaction between lone pairs on the Cl atom and the H atom of C=C in *cis*-$C_2H_2F_2$−ClF being stronger than that in *trans*-$C_2H_2F_2$−ClF (see Figure 2).

These results are valuable in the study of halogen bonds for experimental and theoretical development in the future.

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