Ab Initio Calculations of Intermolecular Interaction of CHF_3 Dimer: Origin of Attraction and Magnitude of CH/F Interaction

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Intermolecular interaction energies of 14 orientation CHF_3 dimers were calculated with electron correlation correction by the MP2 method. The cyclic C_{2h} dimer, which has two H/F contacts, has the largest interaction energy (−1.63 kcal/mol). Electron correlation correction increases the attraction considerably, which indicates that the dispersion interaction is important for the attraction. The effects of electron correlation beyond MP2 are not large. Electrostatic interaction stabilizes the C_{2h} dimer significantly. The electrostatic energy (E_{es}) and the effect of electron correlation on the interaction energy (E_{corr}), which is mainly dispersion energy, of the cyclic C_{2h} dimer at the potential minimum are −0.94 and −0.74 kcal/mol, respectively. The electrostatic interaction is highly orientation dependent, and thereby it mainly determines the orientation of the stable dimer. The dimers, which have short H/H contact, have large repulsive electrostatic interaction, and therefore the interaction energy potentials of these dimers do not have minima. The H/H contact considerably destabilizes the dimer, while the short F/F contacts do not greatly destabilize the dimers. The calculated interaction energy of the CHF_3 dimer is significantly larger than those of the CH_4 and CF_4 dimers (−0.44 and −0.69 kcal/mol, respectively). The large attractive electrostatic interaction is the cause of the substantially larger binding energy of the CHF_3 dimer than the CH_4 and CF_4 dimers.

Introduction

Intermolecular interaction of fluoroform (CHF_3) is important in many fields of chemistry. CHF_3 is one of the commonly used solvents for supercritical fluid due to its conveniently located critical point and nontoxicity.[1−5] The intermolecular interaction controls its thermodynamic properties. CHF_3 is one of the simplest hydrofluorocarbons (HFCs). Therefore detailed information of the intermolecular interaction of CHF_3 is also important to understanding the properties of other HFCs. Recently HFCs are replacing chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), which were widely used as refrigerants, blowing agents, and cleaning solvents in industry.[6−9] In contrast to CFCs and HCFCs, HFCs have no ozone depletion potential. Fluorine-containing compounds are also used for battery materials, enzyme substrate analogues, and solvents in organic syntheses.[10−17] Accurate intermolecular interaction energy potential of the CHF_3 dimer is important for the improvement of the force field used for the condensed phase simulations of HFCs. The accurate interaction energy of the CHF_3 dimer is also important to understanding the CH/F interaction (attraction between CH bond and F atom).[18−20] The hydrogen bond acceptor capability of the CF group was reported in the early 1980s.[21] More recently, Desiraju and co-workers reported that the CH/F interaction is important for crystal packing.[18,22] However, the magnitude of the CH/F interaction and the origin of the attraction were not clearly understood.

Experimental measurements provide some useful information on the intermolecular interaction. Unfortunately, however, it is still very difficult to accurate determine the potential energy surface of the CHF_3 dimer by experimental measurements only. Especially it is very difficult to determine the size of the interaction energy and its direction. A few ab initio calculations of the CHF_3 dimer have been reported. In 1981 Popwicz and Ishida reported HF/STO-3G level ab initio calculations of the CHF_3 dimer.[23] They reported that the tilted end-to-end linear dimer had the largest binding energy. On the other hand, Buckingham and Rabb suggested the possible existence of an antiparallel cyclic orientation dimer in the gas phase from the measurement of the polarizability of gaseous CHF_3.[24] More recently Palmer and Anchell calculated the interaction energies of 10 orientations of CHF_3 dimers at the MP2/6-31+G* level and fitted force field parameters based on the calculated interaction energies.[25] Unfortunately, however, they did not report the calculated interaction energies and their orientation dependence.

Ab initio molecular orbital calculation is becoming a powerful tool to study intermolecular interaction.[26−28] Ab initio calculation provides sufficiently accurate interaction energy, if a reasonably large basis set is used and electron correlation is properly corrected. However, recently reported calculations of weak intermolecular interactions (CH/O, CH/π, π/π, etc.) indicate that the calculated interaction energies of the weak interactions depend significantly on the basis set and electron correlation procedure.[29−33] Therefore, careful evaluation of the basis set and electron correlation effects is necessary for quantitative evaluation of the intermolecular interaction of the CHF_3 dimer. Although the HF/STO-3G calculations were impressive when they were published, the minimal basis set is too small to

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accurately evaluate the interaction energy of the CHF_3 dimer. There still remain several fundamental unsettled issues on the intermolecular interaction of the CHF_3 dimer. (1) The stable geometry of the CHF_3 dimer has not yet been confirmed. Is the stable geometry linear of cyclic? (2) The size of the binding energy of the CHF_3 dimer is not known. The binding energy of the CHF_3 dimer is important to estimate the size of the CH/F interaction. (3) The role of electrostatic interaction for the attraction in the CHF_3 dimer is not yet clearly understood. The boiling point of CHF_3 (191 K) is considerably lower than that of water.[34] This suggests that the intermolecular interaction of CHF_3 is substantially smaller than that of water. On the other hand, CHF_3 has substantially large dipole moment (1.6 D), which is 84% of the dipole moment of water (1.9 D).[35] It is not clear why the intermolecular interaction of CHF_3 is small despite its substantial dipole moment. Quantitative evaluation of electrostatic interaction is essential to confirm the role of electrostatic interaction. (4) Is dispersion also important for the attraction in the CHF_3 dimer as in the case of the CF_4 dimer? The boiling point of CHF_3 is substantially higher than that of CF_4 (145 K),[34] which indicates that the CHF_3 dimer has larger interaction energy. Electrostatic interaction in the CHF_3 dimer would be the cause of the larger interaction energy. However, it is not certain whether dispersion is also important for the attraction in the CHF_3 dimer or not. In this paper we have carried out high level ab initio calculations of the interaction energies of CHF_3 dimers to settle these issues.

Computational Method

The Gaussian 98 program[36] was used for the ab initio molecular orbital calculations. Dunning's correlation consistent basis sets (cc-pVXZ and aug-cc-pVXZ, X = D, T, Q and 5)[37−39] and modified 6-311G* basis sets were used. The aug(d,p)-6-311G* basis set is 6-311G** basis set[40] augmented with diffuse d functions ($\alpha_d(C) = 0.1565$ and $\alpha_d(F) = 0.4375$) on heavy atoms and diffuse p functions ($\alpha_p(H) = 0.1875$) on hydrogen atoms. The aug(df,pd)-6-311G** basis set is 6-311G** basis set augmented with the diffuse d functions and diffuse f functions ($\alpha_f(C) = 0.2$ and $\alpha_f(F) = 0.4625$) on heavy atoms and the diffuse p functions and diffuse d functions ($\alpha_d(H) = 0.25$) on hydrogen atoms.[41−44] Electron correlation was accounted for by the MP2[45,46] and CCSD(T) methods.[47] Basis set superposition error (BSSE)[48] was corrected for all calculations by using the counterpoise method.[49] The MP2 interaction energy at the basis set limit was estimated by the method proposed by Feller.[50] Distributed multipoles[51,52] up to hexadecapole on all atoms were obtained from MP2/cc-pVTZ wave functions of isolated molecules using CADPAC version 6.[53] Electrostatic and induction energies of dimers were calculated using ORIENT version 3.2.[54] Electrostatic energy was calculated as the interaction between the distributed multipoles. Induction energy was calculated as interaction of polarizable sites with electric field produced by the multipoles of monomers.[55] Atomic polarizabilities of carbon (α = 10 au) and fluorine (α = 3 au) were used for the calculations.[56]

Results and Discussion

Geometry of Dimers. Intermolecular interaction energies of 14 orientation dimers (Figure 1) were calculated with changing the intermolecular distance. Geometry of CHF_3 monomer was optimized at the MP2/6-31G* level.[57] The optimized C−H and C−F bond distances are 1.089 and 1.344 Å, respectively. The optimized H−C−F and F−C−F angles are 110.47° and 108.45°, respectively. The optimized geometry of the monomer was used for the calculations of dimers. In this paper we have compared the interaction energies of the CHF_3 dimers with those of the CH_4 and CF_4 dimers. We have selected the 14 orientation CHF_3 dimers based on the orientations of the CH_4 and CF_4 dimers in our earlier papers. In the 13 orientations (dimers A−M) a C−H (or C−F) bond of one molecule and a C−H (or C−F) bond of another molecule are linear. In the orientation N, which corresponds to the experimentally suggested cyclic dimer, a bisector of a F−C−F angle of one molecule and that of another molecule are linear. The Cartesian coordinates of the 14 dimers are summarized in Table S1 in Supporting Information for detailed information of the dimer geometries. In addition, the geometry of the dimer N was fully optimized at the MP2/6-31G* level. The optimized bond distances and angles were very close to those obtained from the optimization of monomer. The differences of the bond distances are less than 0.01 Å. The differences of the angles are less than 0.6°. The effects of the dimer formation on the geometry of CHF_3 are negligible. Therefore, we have calculated the distance dependence of the interaction energies of the dimers without further optimization of the dimer geometries.

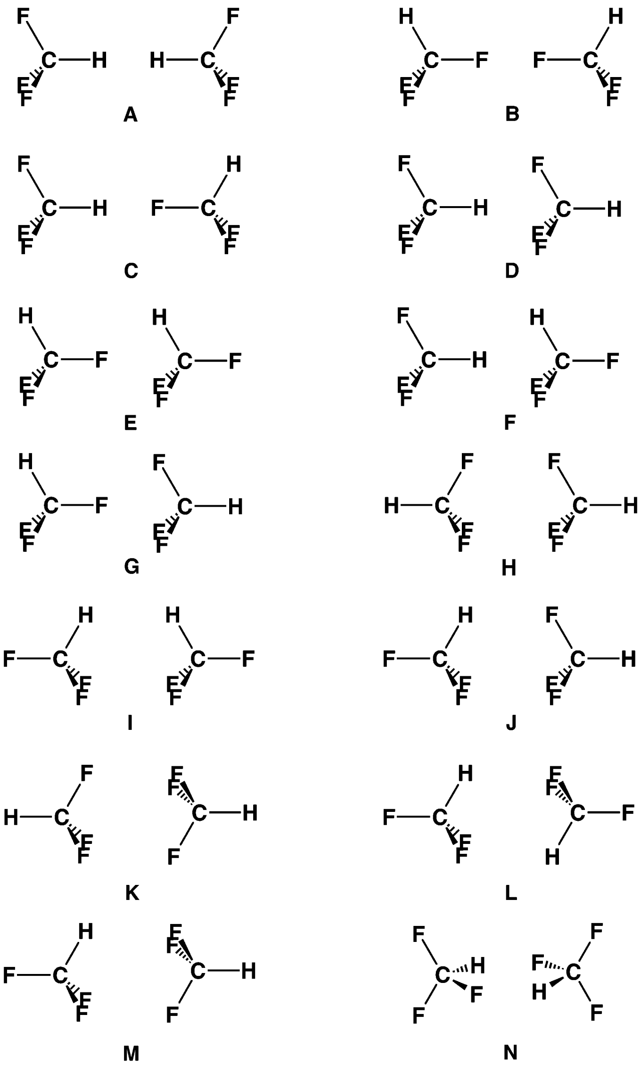

Figure 1. Geometries of CHF_3 dimers. Interaction energies of the dimers were calculated with changing the carbon−carbon distance (R).

Effects of Basis Set and Electron Correlation. Interaction energy of the cyclic C_{2h} CHF_3 dimer (Figure 1, dimer N) was calculated at the HF and MP2 levels using six basis sets as shown in Figure 2. The basis set dependence of the HF

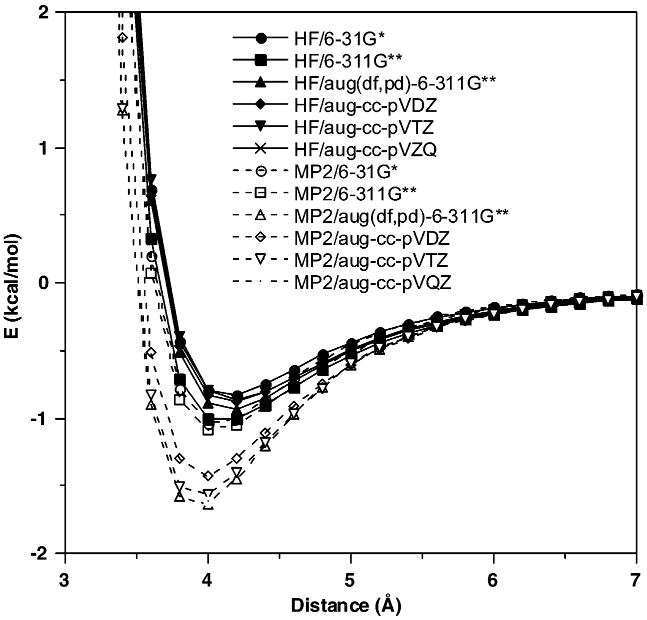

Figure 2. Calculated HF and MP2 interaction energies of C_{2h} CHF_3 dimer N using six basis sets with changing the carbon−carbon distance. The geometry of the dimer is shown in Figure 1.

TABLE 1: Effects of Electron Correlation on the Calculated Interaction Energies of CHF_3 Dimer[a]

basis set	HF	MP2	MP3	CCSD	CCSD(T)
6-31G*	−0.79	−1.04	−1.11	−1.05	−1.08
6-311G*	−1.00	−1.09	−1.17	−1.12	−1.14
cc-pVDZ	−0.95	−0.97	−1.05	−1.00	−1.02
cc-pVTZ	−0.82	−1.31	−1.36	−1.31	−1.38
aug-cc-pVDZ	−0.83	−1.42	−1.46	−1.43	−1.54
aug(d,p)−6-311G**[b]	−0.91	−1.53	−1.56	−1.52	−1.63
aug(df,pd)−6-311G**[c]	−0.89	−1.63	−1.68	−1.65	−1.77

[a] Energy in kcal/mol. BSSE corrected interaction energies. Geometry of the dimer N is shown in Figure 1. The carbon−carbon distance is 4.0 Å. [b] The 6-311G** basis set augmented with diffuse d functions on carbon and fluorine atoms and diffuse p functions on hydrogen atoms. See text. [c] The 6-311G** basis set augmented with diffuse d and f functions on carbon and fluorine atoms and diffuse p and d functions on hydrogen atoms. See text.

interaction energy is not large. On the other hand, the MP2 interaction energy depends strongly on the basis set. Small basis sets (6-31G* and 6-311G*) greatly underestimate the attraction. Similar basis set dependence has been reported in the calculations of the CF_4 and C_2F_6 dimers.[41]

Interaction energy of the dimer was also calculated with electron correlation correction by the MP3, CCSD, and CCSD(T) methods. The effects of electron correlation correction beyond MP2 are small, as summarized in Table 1. The calculated MP2 interaction energies are always slightly smaller (less negative) than the corresponding CCSD(T) interaction energies. But the difference is always very small (0.04 to 0.14 kcal/mol). The HF calculations underestimate the attraction. The electron correlation correction increases the attraction considerably, indicating that dispersion interaction is significantly important for the attraction.

TABLE 2: Effects of Basis Set on the Calculated Interaction Energies of CHF_3 Dimers[a]

basis set	bf[b]	HF	MP2
6-31G*	124	−0.79	−1.04
6-311G**	156	−1.00	−1.09
6-311G(2d,2p)	202	−0.93	−1.34
6-311G(3d,3p)	248	−0.90	−1.53
6-31+G*	156	−0.86	−1.24
aug(d,p)−6-311G**[c]	202	−0.91	−1.53
aug(df,pd)−6-311G**[d]	268	−0.89	−1.63
cc-pVDZ	122	−0.95	−0.97
cc-pVTZ	268	−0.82	−1.31
cc-pVQZ	500	−0.78	−1.48
aug-cc-pVDZ	202	−0.83	−1.42
aug-cc-pVTZ	414	−0.79	−1.57
aug-cc-pVQZ	732	−0.79	−1.62
Basis set limit			−1.64

[a] Energy in kcal/mol. BSSE corrected interaction energies. Geometry of the dimer N is shown in Figure 1. The carbon−carbon distance is 4.0 Å. [b] Number of basis functions used for the calculations. [c] The 6-311G** basis set augmented with diffuse d functions on carbon and fluorine atoms and diffuse p functions on hydrogen atoms. See text. [d] The 6-311G** basis set augmented with diffuse d and f functions on carbon and fluorine atoms and diffuse p and d functions on hydrogen atoms. See text.

MP2 interaction energy of the dimer N was calculated using several basis sets, as summarized in Table 2. The distance between carbon atoms (R) is 4.0 Å. The MP2 level interaction energy at the basis set limit was estimated by the Feller's method from the calculated MP2 interaction energies using the aug-cc-pVXZ (X = D, T and Q) basis sets. The estimated MP2 interaction energy at the basis set limit was −1.64 kcal/mol. Small 6-31G*, 6-311G**, and 6-31+G* basis sets considerably underestimate the attraction. The interaction energy calculated with the 6-31+G* basis set is −1.24 kcal/mol. This value is 24% smaller than the estimated value at the basis set limit. Palmer and Anchell used the 6-31+G* basis set for the calculations of the interaction energies of dimers.[25] These results indicate that their calculations substantially underestimate the attraction of the CHF_3 dimers.

Although the aug(df,pd)-6-311G** basis set employs only 268 basis functions for the calculation of the CHF_3 dimer, the calculated interaction energy with this basis set (−1.63 kcal/mol) is close to the calculated interaction energies (−1.57 and −1.62 kcal/mol, respectively) obtained using large aug-cc-pVTZ and aug-cc-pVQZ basis sets (414 and 732 basis functions, respectively) and the estimated value at the basis set limit (−1.64 kcal/mol). The calculated interaction energy (−1.53 kcal/mol) with the aug(d,p)-6-311G** basis set (202 basis functions) is not largely different from the value at the basis set limit. On the other hand, the Dunning's basis set without diffuse functions (cc-pVDZ and cc-pVTZ) substantially underestimates the attraction. Due to the good performance of aug(df,pd)-6-311G** basis set, we decided to study the potential energy surface of the CHF_3 dimer using this basis set with the MP2 level electron correlation correction.

Dimer Interaction Energy. The calculated interaction energy profiles of the 14 dimers (Figure 1) are shown in Figures 3 and 4. The calculated potential of the cyclic dimer N has the deepest minimum (−1.63 kcal/mol) when $R = 4.0$ Å. The dimer L has the next deepest potential minimum (−1.47 kcal/mol, $R = 3.6$ Å). The potentials of the dimers A and I are repulsive. Other dimers have shallower potential minima.

The calculated potentials of the dimers L and N show that substantial attraction still exists even if the molecules are well separated. This indicates that short-range interactions such as charge-transfer are not the major source of the attraction, because short-range interactions arise at distances where the molecular wave functions overlap significantly and decrease exponentially with distance.[52] The calculated potential of the dimer A shows that substantial repulsion exists when molecules are well separated. This indicates that the electrostatic interaction (long-range interaction) is the cause of the repulsive potential of the dimer A.

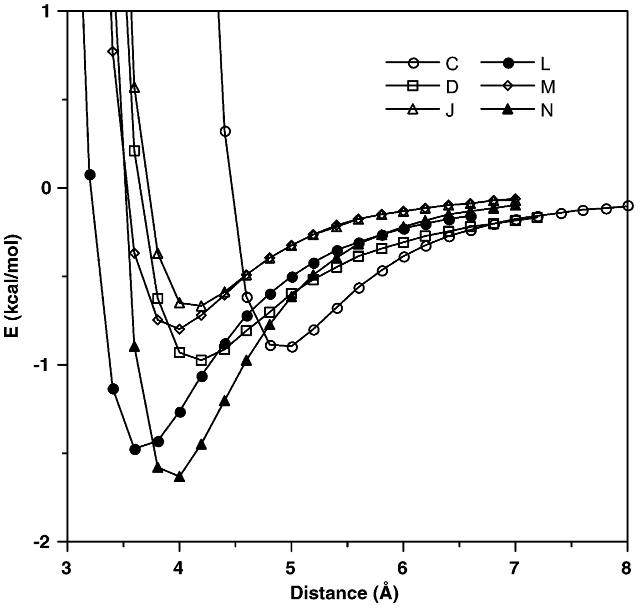

Figure 3. Calculated MP2 interaction energies of the group I and II CHF_3 dimers with changing the carbon−carbon distance. The aug(df,-pd)-6-311G* basis set was used for the calculations. The geometries of the dimers are shown in Figure 1. See text.

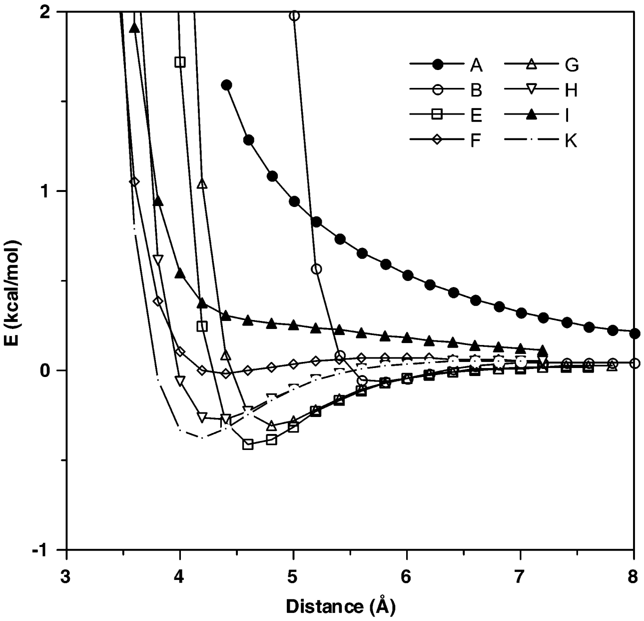

Figure 4. Calculated MP2 interaction energies of the group III and IV CHF_3 dimers with changing the carbon−carbon distance. The aug-(df,pd)-6-311G* basis set was used for the calculations. The geometries of the dimers are shown in Figure 1. See text.

TABLE 3: Calculated Interaction Energies of CHF_3 Dimers[a]

dimer	distance (Å)[b]	E_{total}[c]	E_{es}[d]	E_{rep}[e]	E_{corr}[f]
group I					
L	3.6	−1.47	−0.65	0.50	−1.32
N	4.0	−1.63	−0.94	0.05	−0.74
group II					
C	5.0	−0.89	−0.54	−0.13	−0.22
D	4.2	−0.97	−0.33	0.07	−0.72
J	4.2	−0.66	−0.04	0.16	−0.78
M	4.0	−0.80	−0.05	0.25	−0.99
group III					
B	5.8	−0.06	0.23	0.16	−0.45
E	4.6	−0.42	0.08	0.22	−0.72
F	4.4	−0.01	0.52	0.13	−0.66
G	4.8	−0.31	0.13	0.23	−0.67
H	4.4	−0.28	0.37	0.15	−0.80
K	4.2	−0.38	0.38	0.22	−0.98
group IV					
A	5.6	0.66	0.85	0.16	−0.35
I	4.2	0.37	0.99	0.38	−0.99

[a] Energies in kcal/mol. BSSE corrected interaction energies. The geometries of the dimers are shown in Figure 1. The Cartesian coordinates of the dimers are summarized in Table S1. [b] The intermolecular separations (carbon−carbon distance) at the potential minima. See Figures 2 and 3. [c] The calculated MP2 interaction energies using the aug(df,pd)-6-311G** basis set. [d] Electrostatic energies. See text. [e] Repulsion energies. Difference between the E_{HF} [HF/aug(df,pd)-6-311G** interaction energy] and E_{es}. [f] Correlation interaction energies. Difference between the E_{MP2} [MP2 interaction energies using the aug(df,pd)-6-311G** basis set] and E_{HF}.

Popowicz and Ishida reported that the tilted end-to-end linear dimer had the largest (most negative) interaction energy (−0.68 kcal/mol) and that the tilt to +45° or −45° changes the interaction energy only slightly (less than 0.1 kcal/mol).[23] They reported that the cyclic dimer (dimer N) was slightly less stable (−0.60 kcal/mol). On the other hand our calculations show that the cyclic dimer N is the most stable (−1.63 kcal/mol) and that the dimer C is substantially less stable (−0.89 kcal/mol). (The geometry of the tilted end-to-end linear dimer is close to the dimer C, but the right-hand molecule in the dimer C is tilted.) Our calculations support the cyclic geometry suggested by Buckingham and Raab.[24] The calculated dimer interaction energy in this work (−1.63 kcal/mol) is considerably larger than the HF/STO-3G level interaction energy (−0.68 kcal/mol) reported by Popowicz and Ishida.[23]

Source of Attraction and Directionality. Electrostatic (E_{es}), repulsive (E_{rep}), and correlation interaction (E_{corr}) energies of the dimers at the potential minima were calculated as summarized in Table 3. E_{total} is the calculated MP2 level interaction energy. The correlation interaction energy ($E_{corr} = E_{total} - E_{HF}$), which is the effect of electron correlation on the calculated interaction energy, is mainly dispersion energy. The repulsion energy ($E_{rep} = E_{HF} - E_{es}$) is mainly exchange-repulsion energy, but E_{rep} also includes some other terms such as induction. The calculated energy terms for the dimers A ($R = 5.6$ Å) and I ($R = 4.2$ Å) are also summarized in Table 3.

The eleven dimers D−N have substantially large E_{corr} (−0.66 to −1.32 kcal/mol). The three dimmers A−C have smaller (less negative) E_{corr} (−0.22 to −0.45 kcal/mol) due to the large intermolecular separations (5.0 to 5.8 Å). In most dimers the E_{corr} values are larger (more negative) than the E_{es} values. The only exceptions are dimers C and N. The large E_{corr} values of the dimers show that the dispersion interaction is significantly important for the attraction in the CHF_3 dimer.

The 14 orientation dimers can be classified into four groups. The group I dimers (L and N) have large interaction energies (E_{total} are −1.47 and −1.63 kcal/mol, respectively). These dimers have strong attractive electrostatic interaction (E_{es} are −0.65 and −0.94 kcal/mol, respectively). The electrostatic interaction enhances the stability of these dimers. The group II dimers (C, D, J, and M) have medium size interaction energies (E_{total} are −0.66 to −0.97 kcal/mol). These dimers have weak attractive electrostatic interaction (E_{es} are −0.04 to −0.54 kcal/mol). The group III dimers (B, E, F, G, H, and K) have small interaction energies (E_{total} are −0.06 to −0.42 kcal/mol). These dimers have weak repulsive electrostatic interaction (E_{es} are 0.08 to 0.52 kcal/mol). The intermolecular interaction potentials of the group IV dimers (A and I) are repulsive, as shown in Figure 4. The group IV dimers have strong repulsive electrostatic interaction. The electrostatic interaction is highly orientation dependent, as shown

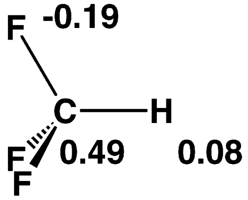

Figure 5. Calculated charge distributions of CHF_3 monomer obtained by electrostatic potential fitting from the MP2/cc-pVTZ wave functions.

in Table 3. The electrostatic interaction is mainly responsible for the relative stability of the 14 dimers.

The group I dimers (L and N) have short H/F contacts. The short contacts between negatively charged fluorine atoms and positively charged hydrogen atoms (3.02 and 2.63 Å, respectively) is the cause of the substantial attractive electrostatic interaction in these dimers (−0.65 and −0.94 kcal/mol, respectively). The calculated atomic charge distributions of the CHF_3 monomer with the Merz−Singh−Kollman scheme electrostatic potential fitting[58] using the MP2/cc-pVTZ wave functions are shown in Figure 5. These dimers are also stabilized considerably by the dispersion interaction. The E_{corr} values of these dimers are −1.32 and −0.74 kcal/mol, respectively.

The dimer C (group II) also has a short H/F contact and therefore has large attractive electrostatic interaction (−0.54 kcal/mol). However, the dispersion interaction in the dimer C is not large ($E_{corr} = -0.22$ kcal/mol) due to the large intermolecular distance ($R = 5.0$ Å), and therefore the dimer C has smaller E_{total} of −0.89 kcal/mol than those of the dimers L and N (−1.47 and −1.63 kcal/mol, respectively). The E_{es} values of the other group II dimers D, J, and M (−0.33, −0.04 and −0.05 kcal/mol, respectively) are substantially smaller than the E_{corr} values (−0.72, −0.78, and −0.99 kcal/mol, respectively). The dispersion interaction is mainly responsible for the attraction in these group II dimers. The electrostatic interaction in the dimers J and M is very small. These dimers have short H/F contacts and short F/F contacts. The repulsive electrostatic interaction between fluorine atoms cancels the attractive electrostatic interaction between hydrogen and fluorine atoms.

The electrostatic interaction is repulsive in the group III and IV dimers. The dispersion interaction is the source of the attraction in the group III dimers. The dimers A, F, and I have large repulsive electrostatic interaction (0.85, 0.52, and 0.99 kcal/mol, respectively). These dimers have short H/H contacts. The other group III dimers (B, E, G, H, and K) have substantially smaller electrostatic interactions (0.08 to 0.38 kcal/mol). Although these dimers have short F/F contacts, they do not have short H/H contacts. This indicates that the short F/F contacts do not largely increase the repulsive electrostatic interaction, but the short H/H contacts greatly enhance the repulsive electrostatic interaction.

Comparison with CH_4 and CF_4 Dimers. CHF_3 has higher boiling point (191 K) and larger heat of vaprization (4.0 kcal/mol) than CF_4 (145 K and 2.8 kcal/mol, respectively),[34] which indicates that the interaction between CHF_3 molecules is substantially larger than that of CF_4. The calculated intermolecular interaction energy potential of the most stable CHF_3 dimer N is compared with those of the most stable D_{3d} CH_4 and CF_4 dimers,[41,59] as shown in Figure 6. The interaction energies of the CH_4 and CF_4 dimers were calculated using the same aug(df,pd)-6-311G** basis set. The calculations also show that the CHF_3 dimer has substantially larger (more negative) interaction energy (−1.63 kcal/mol) than the CH_4 and CF_4 dimers (−0.44 and −0.69 kcal/mol, respectively).[41,44] The calculated energy terms of the dimers at the potential minima are shown in Table 4. The E_{corr} values of the CH_4, CF_4, and CHF_3 dimers are −0.72, −1.22, and −0.74 kcal/mol, respectively. The dispersion interaction is important for the attraction in the three dimers. The E_{es} values of the CH_4 and CF_4 dimers (0.04 and 0.17 kcal/mol, respectively) are very small, which shows that the dispersion interaction is the major source of the attraction in the CH_4 and CF_4 dimers. On the other hand, the CHF_3 dimer N has significantly large attractive electrostatic interaction. The E_{es} of the CHF_3 dimer (−0.94 kcal/mol) is larger than the E_{corr} (−0.74 kcal/mol). The electrostatic and dispersion interactions are both important for the attraction in the CHF_3 dimer N. The large attractive electrostatic interaction is the cause of the larger E_{total} of the CHF_3 dimer than the CF_4 dimer. The E_{es} and E_{corr} of the CHF_3 dimer N was calculated with changing the intermolecular separation as shown in Figure 7. The calculated E_{es} and E_{corr} show that dispersion interaction is also important for the attraction at the potential minimum ($R = 4.0$ Å). But the E_{es} is substantially larger than the E_{corr} when molecules are well separated.

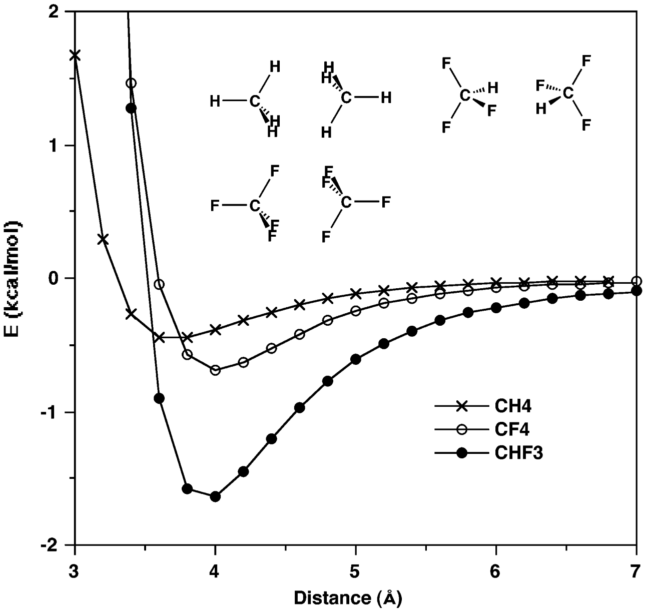

Figure 6. Calculated MP2 interaction energies of the D_{3d} CH_4, CF_4 dimers and the C_{2h} CHF_3 dimer N with changing the carbon−carbon distance. The aug(df,pd)-6-311G* basis set was used for the calculations. See text.

TABLE 4: Calculated Interaction Energies of CH_4, CF_4 and CHF_3 Dimers[a]

dimer	distance (Å)[b]	E_{total}[c]	E_{es}[d]	E_{rep}[e]	E_{corr}[f]
CH_4[g]	3.8	−0.44	0.04	0.24	−0.72
CF_4[h]	4.0	−0.69	0.17	0.36	−1.22
CHF_3[i]	4.0	−1.63	−0.94	0.05	−0.74

[a] Energies in kcal/mol. BSSE corrected interaction energies. [b] The intermolecular separations (carbon−carbon distance) at the potential minima. See Figures 2 and 3. [c] The calculated MP2 interaction energies using the aug(df,pd)-6-311G** basis set. [d] Electrostatic energies. See text. [e] Repulsion energies. Difference between the HF/aug(df,pd)-6-311G** interaction energy and E_{es}. [f] Correlation interaction energies. Difference between the HF and MP2 interaction energies using the aug(df,pd)-6-311G** basis set. [g] The dimer has D_{3d} symmetry. Reference 44. [h] The dimer has D_{3d} symmetry. Reference 41. [i] The most stable cyclic dimer N. The geometry is shown in Figure 1.

CH/F Interaction. Glusker and co-workers have reported that the CF group has hydrogen bond acceptor capability.[21,60] The CH group is known to be a hydrogen bond donor, which can interact with oxygen, nitrogen, or chloride.[61,62] They concluded that, though CH/F interactions are weak, they make a contribu-

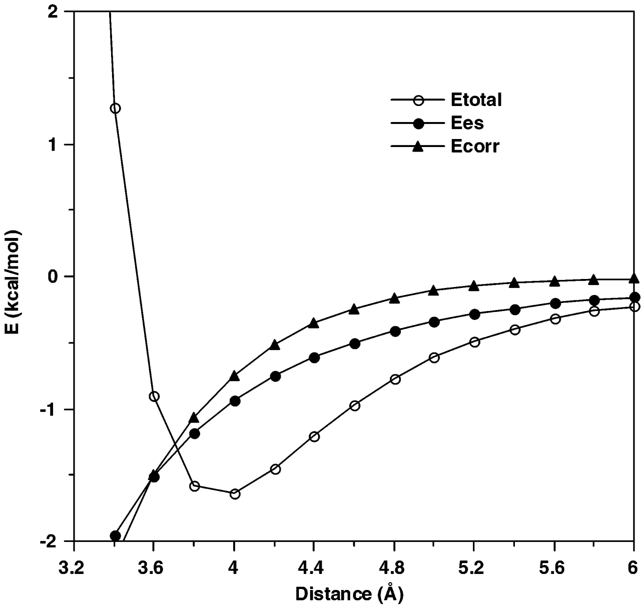

Figure 7. Calculated electrostatic (E_{es}), correlation (E_{corr}), and total interaction (E_{total}) energies of the C_{2h} CHF_3 dimer N with changing the carbon−carbon distance. The geometry is shown in Figure 1. See text.

tion to crystal packing. Desiraju and co-workers reported that the CH/F interaction has hydrogen-bond nature when the acidity of CH bond is enhanced.[18,22] Recently other groups also have reported the importance of the CH/F interaction in the crystal structure.[19,20,63] However, the magnitude of the CH/F interaction and the origin of the attraction were not well understood.

The most stable cyclic dimer N has two CH/F contacts. The dimer C has one CH/F contact. The calculated interaction energies of the dimers N and C are −1.63 and −0.89 kcal/mol, respectively. It might be possible to postulate that the size of one CH/F interaction in the dimers C and N is about −0.8 kcal/mol. The size of attraction of the CH/F interaction is similar to the size of other weak intermolecular interactions such as CH/O and CH/π interactions.[29,30] Scheiner and co-workers have reported that the size of the CH/O interaction is 1 to 2 kcal/mol from their high level ab initio calculations of some model systems.[29] The interaction energies of the benzene with some model hydrocarbons have been calculated by ab initio methods as models of the CH/π interaction. The calculated interaction energies of benzene with methane, ethane, ethylene, and acetylene are −1.45, −1.82, −2.06, and −2.83 kcal/mol, respectively.[30] These calculations of the weak intermolecular interactions show that dispersion in the major source of the attraction of these weak interactions and weak electrostatic interaction also contributes to the attraction. Our calculations (Table 3) indicate that the CHF_3 dimers N and C are stabilized by both electrostatic and dispersion interactions, as in the cases of the other weak intermolecular interactions. Ab initio calculations of the interaction energies of benzene with chloro- and fluoromethanes (models of CH/π interaction) show that the halogenation increases the positive charge on hydrogen atom and thereby increases the attractive electrostatic interaction.[31] It is expected that the fluorine atoms of CHF_3 enhance the attraction. Desiraju and co-workers also have suggested that the strength of the CH/F interaction depends on the CH group acidity.[18,22]

CHF_3 has considerably lower boiling point (191 K) and smaller heat of vaporization (4.0 kcal/mol) than water (373 K and 9.7 kcal/mol, respectively).[34] These differences indicate that the CH/F interaction in the CHF_3 dimer is considerably smaller than the interaction in the water dimer. Our calculations also show that the interaction energy of the CHF_3 dimer N (−1.63 kcal/mol) is considerably smaller (less negative) than that of water (about −5 kcal/mol).[64,65] The weak electrostatic interaction in the CHF_3 dimer is the cause of the small interaction energy. The electrostatic energy of the CHF_3 dimer N (−0.94 kcal/mol) is significantly smaller than that of the water dimer (−6.17 kcal/mol).[65] On the other hand, the dipole moment of CHF_3 (1.6 D) is not largely different from that of water (1.9 D).[35] The considerably small electrostatic energy of the CHF_3 dimer shows that we cannot estimate the size of the electrostatic interaction only from the size of the dipole moment. The dipole−dipole interaction, which is the leading term of the electrostatic interaction between neutral molecules, is the dominant term if the molecules are well separated. In the short separation, however, the contributions of higher terms (dipole−quadrupole, quadrupole−quadrupole, etc.) are sometimes significant and we cannot neglect these terms.

Although the dimers D and L have three and four CH/F contacts, the calculated interaction energies of these dimers (−0.97 and −1.47 kcal/mol, respectively) are not larger than that of the dimer N (−1.63 kcal/mol), which has two CH/F contacts. This indicates that the orientations of the CH/F contacts in these dimers are not suitable to enhance the dimer interaction energy. The relatively small electrostatic energies (−0.33 and −0.65) of these dimers are the causes of the small total interaction energies.

Our calculations indicate that the CHF_3 dimer does not prefer the orientations that have short F/F contacts such as the dimers B, G, H, and K. The repulsive electrostatic interaction destabilizes the dimers having short F/F contacts. Desiraju and Parthasarathy also reported that the CF group does not favor the formation of F/F contacts in the crystal on the basis of Cambridge Structural Database studies.[18]

Conclusion

The calculated interaction energies of the CHF_3 dimers depend on the basis set strongly. An electron correlation correction increases attraction considerably, which indicates that the dispersion interaction is important for the attraction of the CHF_3 dimer. The effects of electron correlation correction beyond MP2 are small. The MP2 interaction energies are not largely different from the CCSD(T) ones. Our calculations show that the cyclic C_{2h} dimer, which has two H/F contacts, (dimer N) has the largest (most negative) interaction energy (−1.63 kcal/mol).

The correlation interaction energy (E_{corr}), which is the difference between the MP2 and HF interaction energies, is larger (more negative) than the electrostatic energy (E_{es}) in most of the dimers. The electrostatic interaction is highly orientation dependent and thereby it mainly determines the stable dimer orientation. The E_{es} and E_{corr} of the most stable dimer N are −0.94 and −0.74 kcal/mol, respectively. The electrostatic and dispersion interactions are both important for the attraction in the CHF_3 dimer.

The two dimers, which have short H/H contacts (dimer A and I), have large repulsive electrostatic interaction. This shows that the short H/H contacts increase the repulsive electrostatic interaction considerably, and thereby significantly destabilize the dimers. The interaction energy potentials of these dimers do not have minima. On the other hand the dimers, which have short F/F contacts, (dimers B, G, H, and K) have shallow potential minima. This indicates that the short F/F contacts do not greatly destabilize the dimers.

The calculated interaction energy of the CHF_3 dimer (−1.63 kcal/mol) is significantly larger than those of the CH_4 and CF_4 dimers (−0.44 and −0.69 kcal/mol, respectively). The CHF_3 dimer has large attractive electrostatic interaction, while the electrostatic energies of the CH_4 and CF_4 dimers are negligible (less than 0.2 kcal/mol). The dispersion interaction is mainly responsible for the attraction in the CH_4 and CF_4 dimers. On the other hand, both dispersion and electrostatic interactions are important for the attraction in the CHF_3 dimer. The large attractive electrostatic interaction is the cause of the larger binding energy of the CHF_3 dimer than the CH_4 and CF_4 dimers.

Although the interaction energy of the CHF_3 dimer is larger than those of CH_4 and CF_4 dimers, the CH/F interaction is considerably smaller than the interaction in the water dimer. The electrostatic interaction in the CHF_3 dimer is considerably smaller than that in the water dimer. The small electrostatic interaction is the cause of the small interaction energy of the CHF_3 dimer.

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Supporting Information Available: Table S1: cartesian coordinates of CHF3 dimers. This material is available free of charge via the Internet at http://pubs.acs.org.

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