Theoretical Study of the C−F/π Interaction: Attractive Interaction between Fluorinated Alkane and an Electron-Deficient π-System

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A molecular interaction between a methane/fluoromethane molecule and a benzene/hexafluorobenzene molecule was theoretically studied. Attractive interaction between the fluorine atom of the fluoromethane and the π-system of the hexafluorobenzene was observed (C−F/π_F interaction, −2.43 kcal/mol in MP2/aug-cc-pVDZ). The attractive C−F/π_F interaction energy was larger than that of the interaction between methane and benzene (C−H/π_H interaction, −1.47kcal/mol). On the other hand, the very weak repulsive interaction was observed between the fluorine atom of the fluoromethane and the benzene (C−F/π_H interaction, +0.12 kcal/mol). The interaction energies between methane and benzene (C−H/π_H interaction, −1.47 kcal/mol) and between methane and hexafluorobenzene (C−H/π_F interaction, −1.36 kcal/mol) were almost the same.

Introduction

A molecular interaction between a π-electron system of aromatics and a hydrogen atom of alkane (C−H/π interaction) is an important topic in supermolecular chemistry.[1] The typical C−H/π interaction is the interaction between a hydrogen atom of methane and an aromatic ring of benzene. From the result of a theoretical study of attractive interaction between alkane and an aromatic compound,[1e,f] a major part of the attractive force is the dispersion term. Weak attractive electrostatic interaction was observed between the weakly positively charged hydrogen atom[2] of the alkane and the π-electron system.[1e,f]

Although the aromaticity of hexafluorobenzene is comparable to that of benzene,[3] the electron densities of these two molecules are substantially different: benzene has an electron-rich π-system while hexafluorobenzene has an electron-deficient π-system.[4] Thus, inverse electrostatic interaction is expected between hexafluorobenzene and the negatively charged fluorine atom in fluoroalkane,[2] comparing the C−H/π interaction. Gallivan and Dougherty[5a] and Danten et al.[5b] independently reported a theoretical study on the water−hexafluorobenzene interaction. They described the attractive interaction between a lone pair of the water and a plane of the hexafluorobenzene (−2.05 kcal/mol in MP2/6-311G**). Besnard et al.[6] reported a remarkable difference between the dynamics of solitary water in benzene and those of hexafluorobenzene, based on the result of IR and Raman study: a proton of the water cannot form a hydrogen bond[7] with the hexafluorobenzene but can form a hydrogen bond with the benzene. Alkorta et al. reported a very weak attractive interaction between the fluorine atom in hydrogen fluoride and a plane of the hexafluorobenzene (−1.23 kcal/mol including BSSE in B3LYP/6-311++G**).[5c] They also reported the interaction between some electron donors,[5d] including anions,[5e] and electron-deficient π-sytems. The interaction between an anion and the π-system was reported by Quiñonero et al.[8a−e] and Mascal et al.[8f] independently. These studies suggest that a hexafluorobenzene acts as a lone pair acceptor. Although perfluoroaromatic compounds are expected as negatively charged fluorine atom acceptors, interaction between the fluorine atom in fluoroalkane and a perfluoroaromatic compound has not been reported.

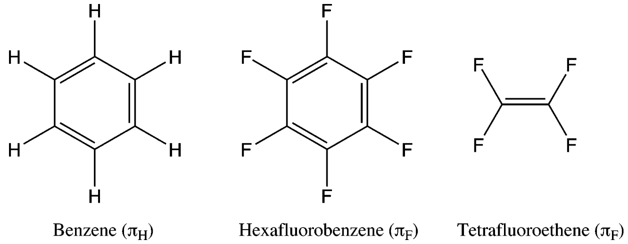

Figure 1. Benzene, hexafluorobenzene, and tetrafluoroethene.

Hydrofluorocarbons and hydrochlorofluorocarbons are widely used in various areas: for example, as refrigerant,[9] foaming agent,[10] detergent,[11] supercritical fluid,[12] oxygen-carrying blood substitutes,[13] and so on. On the other hand, these groups of compounds are considered to bring about destruction of the ozone layer[14,15] and to warm up the earth temperature.[16] Thus, development of technologies for recovery of these groups of compounds is highly demanded. The perfluoroaromatic compounds are promising for this purpose, thus, it is important to investigate the size of the molecular interactions of the compounds in sufficient accuracy.

We report herein the molecular interactions between methane/fluoromethane and benzene/hexafluorobenzene: change in the interaction energies depending on the π-system character.

Computational Methods

Structure optimization and energy estimation calculations were both carried out with the GAUSSIAN 98 program.[17]

We refer to a π-system in benzene as π_H, and a π-system whose hydrogen atoms are fully substituted by a fluorine atom (in tetrafluoroethene and hexafluorobenzene) as π_F (see also Figure 1). The structures of isolated molecules were optimized at the B3LYP/6-311G(d) level of calculation. The potential energy surfaces for intermolecular distance (*R*, Figure 2A) and offset distance (*X*, Figure 2B) were studied. The optimized structures of the monomers were used for the molecular

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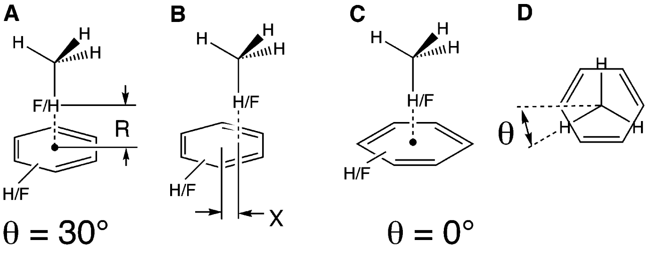

Figure 2. Geometries of the model complexes.

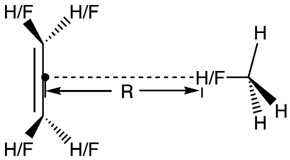

Figure 3. Molecular arrangement for the evaluation of the basis set effect and the electron correlation effect.

interaction study. The rotation angle (θ) in Figure 2D was set at 30° in this study. The difference in total energy between $\theta = 0°$ (Figure 2C) and 30° (Figure 2A) was less than 0.01 kcal/mol for all four interactions, i.e., benzene−methane ($R = 2.7$ Å), benzene−fluoromethane ($R = 3.4$ Å), hexafluorobenzene−methane ($R = 2.7$ Å), and hexafluorobenzene−fluoromethane ($R = 3.0$ Å), using the level of MP2/aug-cc-pVDZ calculation. Thus, change in the molecular interaction properties depending on the change in θ is negligible.

The molecular interaction energy was studied at the MP2/aug-cc-pVDZ level of calculation if not otherwise noted. The molecular interaction energies were evaluated by a supermolecular method. The basis set superposition error (BSSE) for the interaction energies was corrected by using the counterpoise method.[18] Hereafter, we refer to the molecular interaction energy without and with BSSE correction as δE and ΔE, respectively.

The electrostatic energy (E_{ES}) was calculated as the interaction between distributed multipoles of monomers with use of ORIENT.[19] Distributed multipoles were obtained from MP2/cc-pVTZ wave functions of the isolated monomers. GDMA[18] is used to obtain distributed multipoles from the wave functions calculated with the Gaussian program system. The repulsive interaction ($E_{\mathrm{rep}} = \Delta E_{\mathrm{HF}} - E_{\mathrm{ES}}$) is mainly exchange-repulsion energy, but it also includes other terms such as induction energy. The electron correlation energy (E_{corr}) was calculated as the difference between the calculated MP2 interaction energy (ΔE_{MP2}) and the HF interaction energy (ΔE_{HF}) with use of the aug-cc-pVDZ basis set. The major part of E_{corr} is the dispersion energy.

Results and Discussion

Effects of Basis Set and Electron Correlation on the Interaction between Tetrafluoroethene and Fluoromethane. First, the basis set effect for the interaction energies of fluoromethane−tetrafluoroethene, fluoromethane−ethene, and methane−tetrafluoroethene were studied at the MP2 level of theory. Dunning's correlation consistent basis sets without (cc-pVXZ, X = D and T) and with the augmentation (aug-cc-pVXZ) were used. The distance between the fluorine/hydrogen atom of fluoromethane/methane and the center of the two carbon atoms in tetrafluoroethene/ethene was 2.8 Å (Figure 3).

TABLE 1: Basis Set Dependence of the Calculated Interaction Energies (ΔE, BSSE Corrected, kcal/mol) and BSSE (kcal/mol) at the MP2 Level of Theory[a]

interaction model	ΔE (BSSE)			
	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	aug-cc-pVTZ
C−F/π_{F}	+0.22 (+1.94)	−0.55 (+1.03)	**−1.06 (+1.33)**	−1.30 (+0.70)
C−H/π_{F}	+0.18 (+0.57)	−0.23 (+0.47)	**−0.33 (+1.37)**	−0.49 (+0.72)
C−F/π_{H}	+3.11 (+1.85)	+2.42 (+0.92)	**+2.11 (+0.81)**	+1.85 (+0.35)

[a] Intermolecular distance was 2.8 Å. See also Figure 3. The B3LYP/6-311G(d) optimized structure was used for each molecule.

TABLE 2: Electron Correlation Dependence of the Calculated Interaction Energies (kcal/mol) in the aug-cc-pVDZ Basis Set[a]

interaction model	electron correlation effect		
	ΔE_{HF}	ΔE_{MP2} ($\Delta_{\mathrm{MP2}}{}^{b}$)	$\Delta E_{\mathrm{MP4}}{}^{c}$ ($\Delta_{\mathrm{MP4}}{}^{d}$)
C−F/π_{F}	+0.46	**−1.06 (−1.52)**	−1.11 (−0.05)
C−H/π_{F}	+0.94	**−0.34 (−1.28)**	−0.38 (−0.04)
C−F/π_{H}	+4.67	**+2.11 (−2.56)**	+2.02 (−0.09)

[a] The intermolecular distance was 2.8 Å. See also Figure 3. The B3LYP/6-311G(d) optimized structure was used for each molecule. [b] $\Delta_{\mathrm{MP2}} = \Delta E_{\mathrm{MP2}} - \Delta E_{\mathrm{HF}}$. [c] Single, double, triple, and quadruple substitution was considered for the MP4 calculations. [d] $\Delta_{\mathrm{MP4}} = \Delta E_{\mathrm{MP4}} - \Delta E_{\mathrm{MP2}}$.

Table 1 shows the basis set effect for the interaction energies at the MP2 level of theory. In the case of cc-pVXZ basis sets, the attractive interaction energies were underestimated, and the repulsive interaction energy was overestimated compared to that of the corresponding aug-cc-pVXZ basis set. This trend was improved by use of the aug-cc-pVXZ basis sets. The BSSE corrected interaction energies in the aug-cc-pVDZ basis set (−1.06, −0.33, and +2.11 kcal/mol for fluoromethane−tetrafluoroethene, methane−tetrafluoroethene, and fluoromethane−ethene, respectively) were in good agreement with the result of the aug-cc-pVTZ basis set (−1.30, −0.49, and +1.85 kcal/mol as above). These results show that the aug-cc-pVXZ basis sets should be used for the estimation of these interactions. As shown below, the results at the MP2/aug-cc-pVDZ level of calculation for the C−H/π_{H} interaction were in quite good agreement with previously reported higher level calculations.[1e] Although the aug-cc-pVDZ basis set is a small basis set, moderately good performance was observed for the molecular interaction energies.

Next, the effect of the electron correlation was studied (Table 2). In the previous study of the C−H/π_{H} interaction, the MP2-level electron correlation should be considered, but the correlation effect higher than MP2 was small.[1e,f] However, the effect of the higher electron correlation on the other interaction in this study has not been studied. Repulsive interaction was observed at the HF level of theory for all types of the interaction. Although large correlation energy (the difference between the MP2 and HF level interaction energies) was observed, the electron correlation effect higher than the MP2 level of theory was quite small: the difference in interaction energies at the MP2 and the MP4(SDTQ) levels of theory with use of the aug-cc-pVDZ basis set was negligible (less than 0.1 kcal/mol). Therefore, we can evaluate the C−F/$\pi_{\mathrm{H/F}}$ and C−H/$\pi_{\mathrm{H/F}}$ interaction energies sufficiently accurately using the MP2/aug-cc-pVDZ level of calculation.

Interaction between a Methane/Fluoromethane and a Benzene/Hexafluorobenzene. Figure 4 shows the potential energies of hexafluorobenzene−fluoromethane interaction (a model of the C−F/π_{F} interaction), hexafluorobenzene−methane interaction (a model of the C−H/π_{F} interaction), benzene−fluoromethane interaction (a model of the C−F/π_{H}), and benzene−methane interaction (a model of the C−H/π_{H}, interaction). The interaction energies of the complexes were calculated by changing the intermolecular distance R (see Figure 2A). The

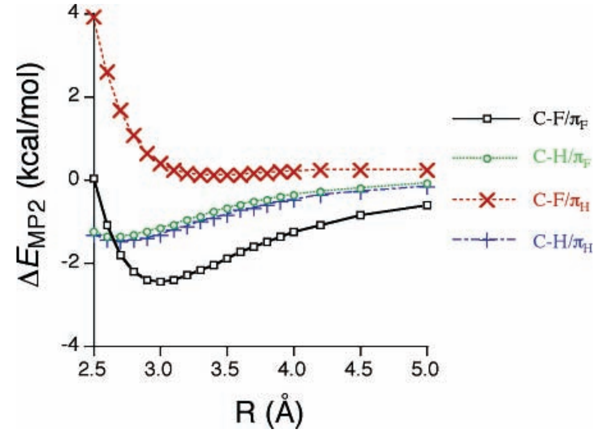

Figure 4. Potential energy for the intermolecular distance (*R*, Å) of C−F/π_F (black), C−H/π_F (green), C−F/π_H (red), and C−F/π_F (blue) interactions.

TABLE 3: BSSE Corrected Interaction Energy (ΔE_{HF} and ΔE_{MP2}, kcal/mol), the Contribution of Each Interaction Term (kcal/mol), and Molecular Distance at the Energetically Minimum (*R*, Å) in the MP2/aug-cc-pVDZ Potential Energy

	C−F/π_F	C−H/π_F	C−F/π_H[a]	C−H/π_H[b]
ΔE_{HF}	−0.73	+1.02	+1.76	+0.90
$BSSE_{HF}$	+0.66	+1.00	+0.17	+0.59
ΔE_{MP2}	**−2.43**	**−1.36**	**+0.12**	**−1.47**
$BSSE_{MP2}$	+1.57	+2.08	+0.72	+1.77
E_{corr}	−1.70	−2.38	−1.63	−2.37
E_{ES}	−1.20	+0.38	+1.20	−0.20
E_{rep}	+0.47	+0.64	+0.56	+1.10
R	3.0	2.7	3.4	2.7

[a] See ref 21. [b] See refs 1e and 22.

potential energies of each component (ΔE_{MP2}, ΔE_{HF}, E_{ES}, E_{corr}, and E_{rep}) of the C−F/π_F, C−H/π_F, C−F/π_H, and C−H/π_H interactions are shown in Figure 5, parts A−D (for *R*). Table 3 summarizes the interaction energies at the potential minimum.[22]

The interaction energy became minimum at $R = 3.0$ Å, and the ΔE_{MP2} was −2.43 kcal/mol at that point for the C−F/π_F interaction. The C−F/π_F interaction energy was the most negative of the four interactions in this study. It was much more negative than the C−H/π_H interaction ($\Delta E_{MP2} = -1.47$ kcal/mol). Only the C−F/π_F interaction was attractive at the HF level of theory (ΔE_{HF}). Comparing the other three interactions, E_{ES} (−1.20 kcal/mol) in the C−F/π_F interaction was strongly attractive. Although both E_{ES} and E_{corr} (−1.70 kcal/mol) had important contributions to the attractive interaction, E_{corr} was more negative than E_{ES}.

The C−H/π_F interaction energy ($\Delta E_{MP2} = -1.36$ kcal/mol) was almost the same as that of the C−H/π_H interaction ($\Delta E_{MP2} = -1.47$ kcal/mol) at the same molecular distance of the potential minimum ($R = 2.7$ Å). Intermolecular distance in these two cases at the potential minimum was smaller than that of the C−F/π_F interaction (3.0 Å). The E_{corr} values in these two interactions (−2.38 and −2.37 kcal/mol for the C−H/π_F and C−H/π_H interactions, respectively) were almost the same. In contrast to the attractive electrostatic interaction in the C−H/π_H interaction ($E_{ES} = -0.20$ kcal/mol), the electrostatic interaction in the C−H/π_F interaction ($E_{ES} = +0.38$ kcal/mol) was repulsive. In both cases, the absolute value of the E_{ES} was small. Though the intermolecular distances of these two interactions were the same (2.7 Å), the E_{rep} in the C−H/π_H interaction (+1.10 kcal/mol) was about twice as large as the E_{rep} in the C−H/π_F interaction (+0.64 kcal/mol). Therefore, the exchange-repulsion between the C−H and the electron-rich π_H system has a larger contribution, comparing the exchange-repulsion between the C−H and the electron-deficient π_F system. It is the first quantitative analysis to show that the π-electron density has a serious effect on the exchange-repulsion: a decrease of the π-electron density causes a decrease of the exchange-repulsion and vice versa. The exchange-repulsion term is considered as the interaction between occupied orbitals of the molecules; thus, it is an acceptable result that the exchange-

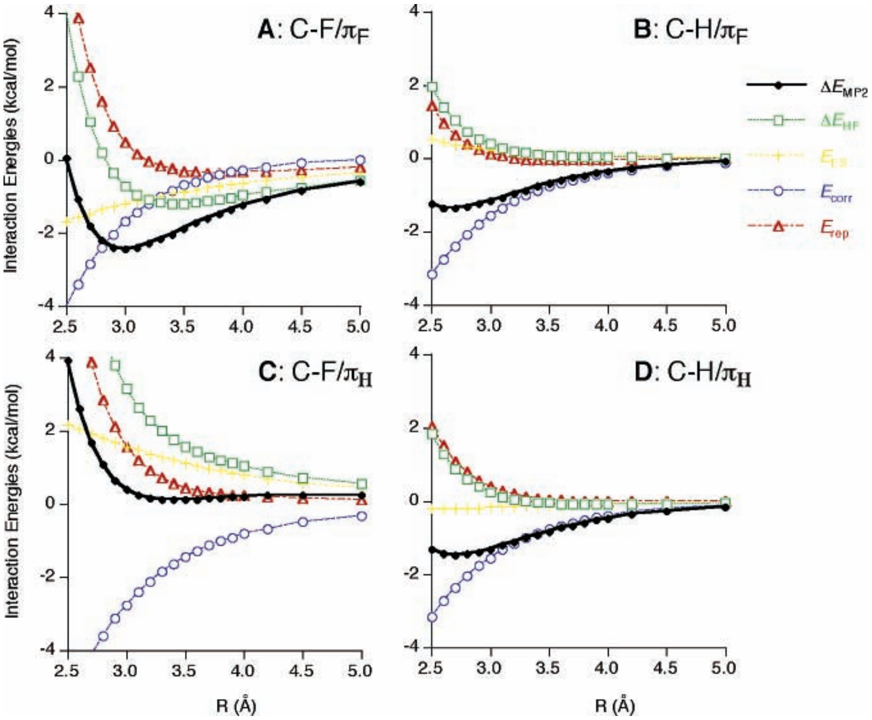

Figure 5. The potential energies for the intermolecular distance (*R*, Å) of each term in C−F/π_F (A), C−H/π_F (B), C−F/π_H (C), and C−F/π_F (D) interactions.

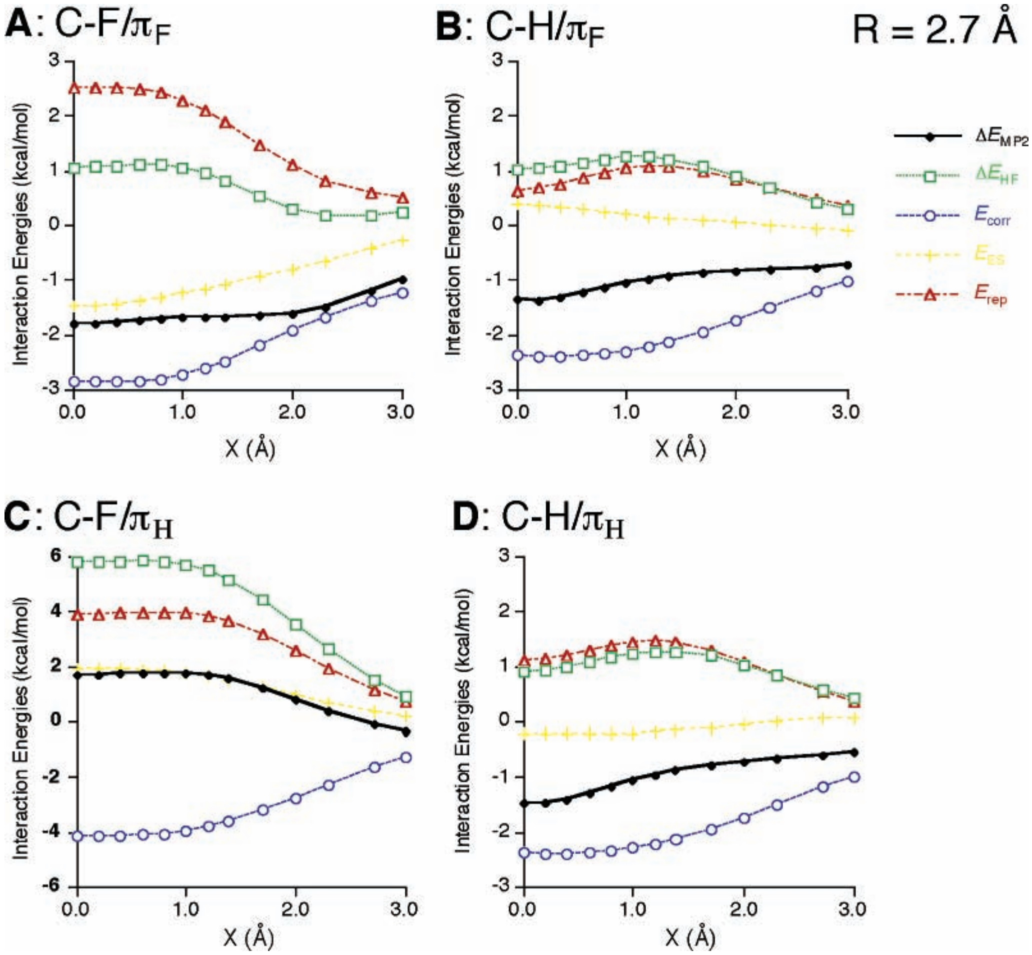

Figure 6. The potential energies for offset distance (X, Å) of each term in C−F/π_F (A), C−H/π_F (B), C−F/π_H (C), and C−F/π_F (D) interactions.

repulsion term in the electron-deficient π_F system is much smaller than that in the electron-rich π_H system.

In contrast to the C−F/π_F interaction ($\Delta E_{MP2} = -2.43$ kcal/mol), the C−F/π_H interaction was repulsive ($\Delta E_{MP2} = +0.12$ kcal/mol). The potential energy of the C−F/π_H interaction for $R > 3.0$Å was flat. E_{rep} and E_{corr} in the C−F/π_H interaction (+0.56 and −1.63 kcal/mol, respectively) were almost the same in the C−F/π_F interaction (+0.47 and −1.70 kcal/mol, respectively). On the other hand, E_{ES} in the C−F/π_H interaction (+1.20 kcal/mol) was strongly repulsive. Similarly for the C−H/$\pi_{H/F}$ interactions, substitution of the hydrogen atoms in the benzene by the fluorine atoms decreases the exchange-repulsion: though the intermolecular distance of the C−F/π_H interaction was larger than that of the C−F/π_F interaction, E_{rep} in the C−F/π_H interaction was much more positive than that in the C−F/π_F interaction.

Figure 6 shows the interaction energies of the four complexes with changing the horizontal displacements (X, Å; see Figure 2B). The R was set at the potential minimum in each interaction (2.7, 3.0, and 3.4 Å, see Table 2). For the total interaction energy (ΔE_{MP2}), the potential minimum was observed when the methane or the fluoromethane was located at the point of the center ($X = 0$), except in the C−F/π_H interaction. On the other hand, the energetic maximum was observed when the fluoromethane was located at the point of the center ($X = 0$) in the case of the C−F/π_H interaction. For all the cases, E_{corr} was always negative.

The potential energies for X in the C−F/π_F and the C−F/π_H interactions were remarkably different. In the case of the C−F/π_F interaction, a large attractive E_{ES} was observed; in contrast, a large repulsive E_{ES} was observed in the case of the C−F/π_H interaction. On the other hand, E_{rep} in the C−F/π_H interaction was much more positive than that in the C−F/π_F interaction.

The potential energies for X in the C−H/π_F and the C−H/π_H interactions were quite similar. Only E_{ES} was opposite, but the absolute values of E_{ES} in the C−H/π_F and the C−H/π_H interactions were very small. In the cases of $R = 2.7$ Å (potential minimum for the C−H/π_F and the C−H/π_H interaction), the ΔE_{HF} and E_{rep} became maximum at the point of $X = 1.2$ Å, which is the point at which the carbon of the aromatic ring and alkane overlap. The ΔE_{HF} was always positive in the C−H/π_F and the C−H/π_H interactions. E_{corr} was negative; thus, the dispersion energy has a dominant role in the attractive interaction in both the C−H/π_F and the C−H/π_H interactions.

Substitution Effect on C−H/π and C−F/π Interactions. We studied the substitution effect from hydrogen atom to fluorine atom on the methyl group (CH_3, CH_2F, CHF_2, and CF_3) for four types of interactions (C−F/π_F, C−H/π_F, C−F/π_H, and C−H/π_H). Parts A−D in Figure 7 show the trends for the substitution effect in the interaction energies. The molecular interaction distances (R, Å) were set on the potential energy minimum, for each interaction. In all cases, the interaction energies varied considerably with the introduction of fluorine atom on the methyl group. The changes in the interaction energies mainly depended on the change in E_{ES}. The change of E_{corr} and E_{rep} were small, though E_{corr} has a dominant role in the attractive interaction in all cases. In the C−F/π_F interaction (Figure 7A), ΔE_{MP2} was negative, but the attractive interaction became less negative by adding the fluorine atom. The same as for the C−F/π_F interaction, the attractive interaction of the C−H/

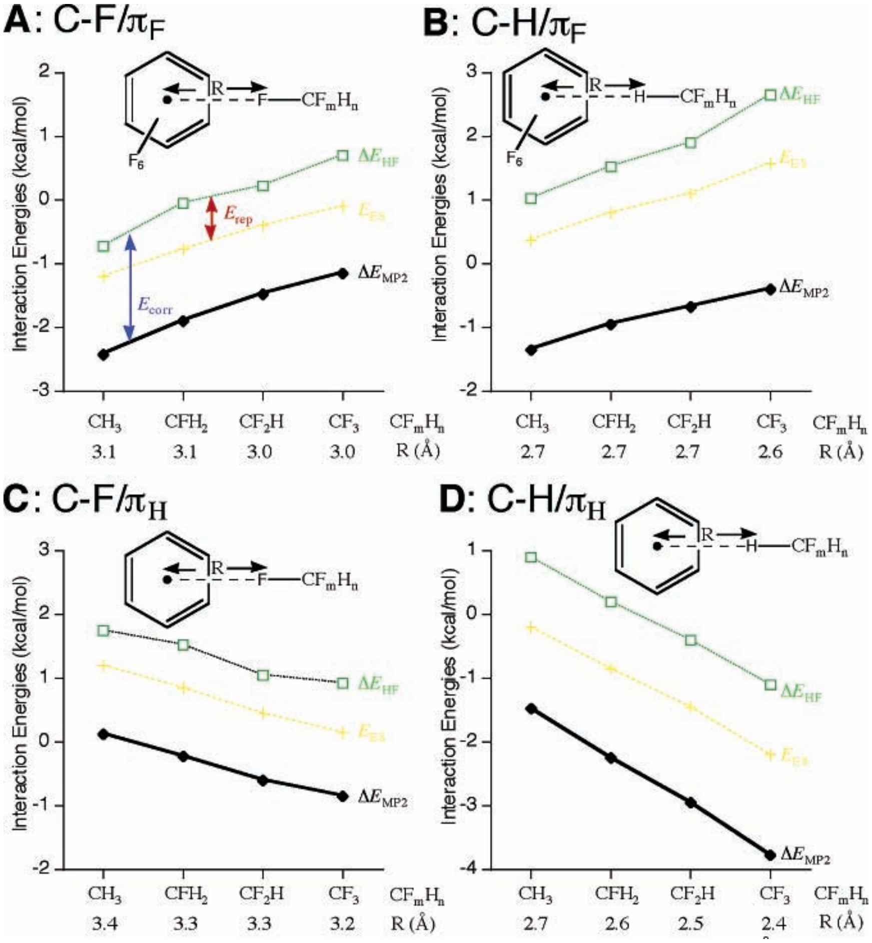

Figure 7. Substitution effect on the molecular interaction distances (*R*, Å) and the interaction energies in C−F/π_F (A), C−H/π_F (B), C−F/π_H (C), and C−H/π_H (D) interactions.

π_F interaction (Figure 7B) became less negative by adding the fluorine atom. As described above, the C−F/π_H interaction was repulsive in the case of H_3C−F/π_H interaction; however, it became attractive with the introduction of one fluorine atom on the methyl group, and the attractive interaction became more negative by adding the fluorine atom (Figure 7C). In contrast to the C−F/π_F interaction, the attractive interaction of the C−H/π_H interaction (Figure 7D) became more negative by adding the fluorine atom.

Conclusion

The molecular interactions between a methane/fluoromethane and a benzene/hexafluorobenzene were theoretically studied. Attractive interaction was observed between a fluoromethane and a hexafluorobenzene (C−F/π_F). On the other hand, weakly repulsive interaction was observed between a fluoromethane and a benzene (C−F/π_H). The interactions between a methane and a hexafluorobenzene (C−H/π_F) and between a methane and a benzene (C−H/π_H) were both attractive, and the interaction energies were almost the same. The C−F/π_F interaction should be attractive for the selective interaction with fluoroalkane.

For all four interactions, the electron-correlation energy had the largest contribution for the attractive interaction. The electrostatic interaction in the C−F/$\pi_{F/H}$ interactions is more important compared with that in the C−H/$\pi_{F/H}$ interactions. The absolute values of the electrostatic interaction in the C−F/$\pi_{F/H}$ interactions were comparable to the electron-correlation energies of the complexes. The exchange-repulsion term in the π_F system was remarkably smaller than that in the π_H system.

The C−H/π_F and the C−F/π_F interactions became less attractive with the introduction of the electron-withdrawing fluorine atom on the methyl group, in contrast, the C−H/π_H and the C−F/π_H interactions became more attractive with the introduction of the fluorine atom. The change in the interaction energies mainly depended on the change of the electrostatic interaction.

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Supporting Information Available: Potential energies with changing the horizontal displacements (*X*) in various *R* (2.7, 3.0, and 3.4 Å), and details of the substitution effect of the interactions (Tables S1−S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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