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The Interaction of Benzene with Chloro- and Fluoromethanes: Effects of Halogenation on CH/π Interaction

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High-level ab initio calculations were carried out to evaluate the interaction of C_6H_6 with CH_3Cl, CH_2Cl_2, $CHCl_3$, and CHF_3. Intermolecular interaction energies were calculated from extrapolated MP2 interaction energies at the basis set limit and CCSD(T) correction terms. The calculated interaction energies of the complexes are −3.0, −4.5, −5.6, and −4.2 kcal/mol, respectively. These values are significantly larger than the interaction energy of $C_6H_6-CH_4$ complex (−1.5 kcal/mol). The interaction energy of $C_6H_6-CHCl_3$ is slightly larger than that of the hydrogen bond between waters. The calculated potentials of the complexes are very flat near the minima. Substantial attraction still exists even if the molecules are well-separated. This shows that the major source of attraction in the complexes is not short-range interactions such as charge transfer but long-range interactions such as electrostatic and dispersion. A large gain of attraction by electron correlation indicates that dispersion interaction is the major source of attraction. The size of attraction depends on the substituents of methane considerably. Substitution of hydrogen atoms of methane by chlorine and fluorine atoms increases attractive electrostatic interaction. Substitution by chlorine atoms also increases dispersion interaction significantly. The calculated potentials show that the substitution of methane does not enhance short-range interactions.

Introduction

The attraction between a C−H bond and a π system is called a CH/π interaction.[1] This interaction was first proposed more than 20 years ago to explain the preference of conformation in which bulky alkyl and phenyl groups had a close contact.[2] During these 2 decades, several experimental measurements that support the existence of attraction have been reported.[3−15] The short contact of a C−H bond and a π system is observed in large numbers of crystals of organic molecules and proteins.[16−27] It is believed that the CH/π interaction is important for conformational preference, crystal packing, host−guest complexation, and self-organization processes.[26,28−44] The importance of the CH/π interaction for structures and properties of biological systems has also been reported.[16−20,22−24]

Despite broad interest in the CH/π interaction in many areas of chemistry and biology, very little was known about the origin and magnitude of the interaction. The physical origin and magnitude of the interaction are essential for the understanding of crystal packing and molecular recognition processes of biological and artificial systems. An accurate interaction energy is needed for force field simulations of these systems and for rational design of artificial host molecules. Although many experimental measurements have been reported on the interaction, it is still difficult to determine an accurate interaction energy from experimental measurements only.

A few theoretical calculations of model systems have been carried out to evaluate the interaction energy of the CH/π interaction.[2,45−51] Early calculations using small 4-31G and MIDI4* basis sets concluded that the main contributions to attraction were electrostatic and charge-transfer terms.[45] Therefore, charge transfer was believed to be an important source for attraction.[1] However, recently reported high-level ab initio calculations of benzene−hydrocarbon complexes (C_6H_6−X, X = CH_4, C_2H_6, C_2H_4, and C_2H_2) show that dispersion is the major source of attraction.[47−49] The interaction energies of the complexes are substantially smaller than the hydrogen-bonding energy of water dimer. The calculated bonding energy of the $C_6H_6-CH_4$ complex (−1.5 kcal/mol)[48] is about 30% of the bonding energy of water dimer (about 5 kcal/mol).[52−55] Electrostatic interaction is substantially smaller than dispersion interaction, but highly orientation-dependent electrostatic interaction is mainly responsible for the directionality of interactions in these complexes.

There still remain, however, unsettled issues on the interaction. (1) How greatly do substituents change the magnitude of the CH/π interaction? A few experimental measurements of substituent effects on the CH/π interaction in solution have been reported.[11−15,56] The measurements show that electron-donating substituents on the π system and electron-withdrawing substituents on the CH carbon atom increase attraction. For example, it has been reported that chloroform forms a stable complex with benzene.[57−59] However, the magnitude of substituent effect on the CH/π interaction has not yet been quantitatively confirmed. (2) Another important issue is the origin of substituent effects. The changes of attraction by substituents have often been explained by the change of charge-transfer interaction.[1,12,14] However, recent ab initio calculations show that charge transfer is not the major source of attraction in benzene−

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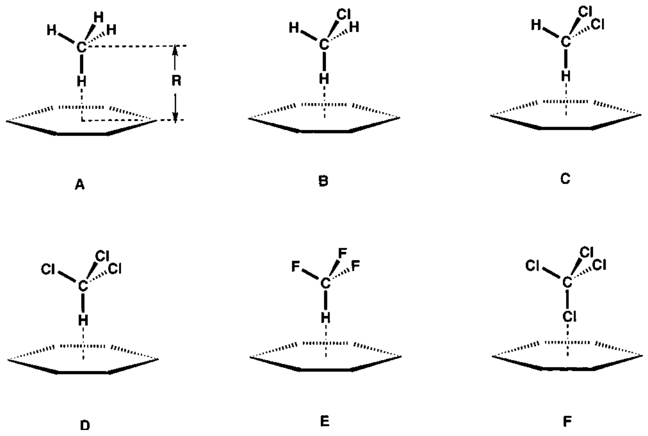

Figure 1. The geometries of complexes considered in this work. The carbon atoms of substituted methanes are above the center of the benzene ring.

hydrocarbon complexes.[47−49] It is still not certain whether substituents enhance charge-transfer interaction or the change of other interactions is mainly responsible for the substituent effects.

In this paper, we have calculated the interaction of benzene with chloro- and fluoromethanes using high-level ab initio method to evaluate the magnitude and origin of the substituent effects on the CH/π interaction. We have calculated MP2 interaction energies of the complexes with Dunning's correlation consistent basis sets and estimated MP2 interaction energies at the basis set limit. We have added CCSD(T) correction to include electron correlation beyond MP2. We have also discussed the roles of electrostatic, dispersion, and charge-transfer terms for the substituent effects.

Computational Method

The Gaussian 98 program[60] was used for the ab initio molecular orbital calculations. The 6-311G**[61] and cc-pVXZ (X = D, T, and Q)[62,63] basis sets were used. Electron correlation energies were corrected by the second-order Møller−Plesset perturbation method (MP2)[64,65] and by the coupled cluster method using single and double substitutions with noniterative triple excitations (CCSD(T)).[66] Geometries of isolated molecules were optimized at the MP2/6-31G* level,[67] and were used for calculations of complexes. Basis set superposition error (BSSE)[68] was corrected with the counterpoise method.[69] MP2 interaction energies at the basis set limit were estimated with the method proposed by Feller.[70] Distributed multipoles[71,72] were obtained from MP2/6-311G** wave functions of isolated molecules using CADPAC, version 6.[73] Electrostatic energies of complexes were calculated as interactions between distributed multipoles using ORIENT, version 3.2.[74]

Results and Discussion

Basis Set Effects. The interaction energy of C_6H_6−$CHCl_3$ complex (Figure 1D) was calculated with HF and MP2 methods using 6-311G** and cc-pVXZ (X = D, T, and Q) basis sets. The basis set dependence of HF interaction energy is very small as shown in Figure 2, while the MP2 interaction energy depends on the basis set greatly (Figure 2). The calculated intermolecular interaction energies of C_6H_6−X complexes (X = CH_3Cl, CH_2Cl_2, $CHCl_3$, and CHF_3, Figure 1) are summarized in Table 1. The intermolecular distances (R) of the complexes correspond to the potential minima calculated at the MP2/cc-pVTZ level (Figure 3). Small 6-311G** and cc-pVDZ basis sets underestimate the attraction considerably compared to large cc-pVTZ and cc-pVQZ basis sets. These small basis sets lead to the underestimation of molecular polarizability and dispersion interaction. The underestimation of dispersion interaction with small basis sets was also observed in other hydrocarbon molecules.[75−79] The HF calculations, which cannot evaluate dispersion interaction, underestimate the attraction greatly compared to the MP2 calculations. The large gain of attraction by electron correlation indicates that dispersion is significantly important for attraction in these complexes.

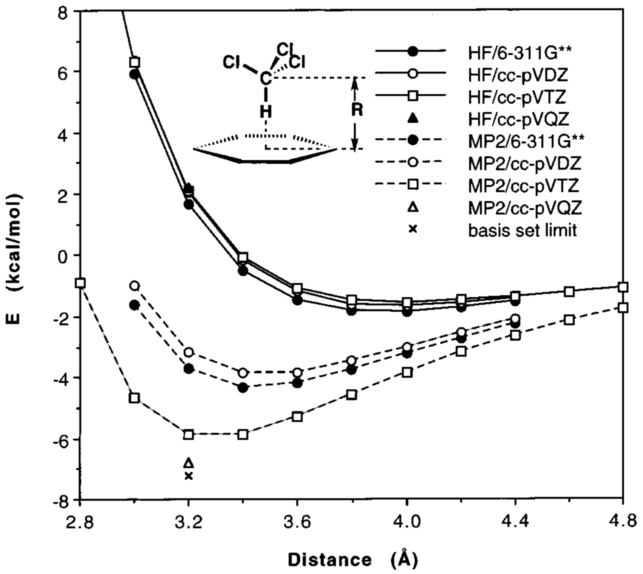

Figure 2. The HF and MP2 intermolecular interaction potentials of the C_6H_6−$CHCl_3$ complex using several basis sets. Intermolecular separation (R) is the distance between the center of benzene and the carbon atom of $CHCl_3$.

Effects of Electron Correlation beyond MP2. The interaction energy of C_6H_6−CH_3Cl complex was calculated with CCSD and CCSD(T) methods to evaluate the effect of electron correlation beyond MP2 as summarized in Table 2. The MP2 interaction energies are larger (more negative) than the CCSD(T) ones. The CCSD calculations slightly underestimate attraction compared to the CCSD(T), which suggests the importance of triple excitation for the evaluation of attractive interaction.[80]

Interaction Energies at the Basis Set Limit. The MP2 interaction energies of the complexes at the basis set limit were estimated by extrapolation of the MP2 interaction energies calculated with Dunning's correlation consistent basis sets (cc-pVXZ, X = D, T, and Q) using the method proposed by Feller.[70,81] The form $a + b\ \exp(-cX)$ (where X is 2 for cc-pVDZ, 3 for cc-pVTZ, etc.) was fitted to the calculated interaction energies. The extrapolated MP2 interaction energies of C_6H_6−X complexes (X = CH_3Cl, CH_2Cl_2, $CHCl_3$, and CHF_3) at the basis set limit ($E_{\mathrm{MP2(limit)}}$) are −3.5, −5.5, −7.2, and −4.6 kcal/mol, respectively, as summarized in Table 1. These values are not largely different from those calculated with cc-pVQZ, indicating that cc-pVQZ is close to saturation. The MP2/cc-pVQZ interaction energies are only 0.2−0.4 kcal/mol smaller (less negative) than the corresponding estimated MP2 interaction energies at the basis set limit.[82]

The MP2 and CCSD(T) interaction energies of C_6H_6−CH_4 and C_6H_6−CH_3Cl complexes depend on the basis set greatly, while the basis set dependence of the CCSD(T) correction term ($\Delta_{\mathrm{CCSD(T)}}$), the difference between MP2 and CCSD(T) interaction energies, is not large as summarized in Table 2. The small basis set dependence of $\Delta_{\mathrm{CCSD(T)}}$ suggests that the CCSD(T)

TABLE 1: Calculated Interaction Energies of Benzene with Substituted Methanes[a]

method	$C_6H_6-CH_4$[b]	$C_6H_6-CH_3Cl$	$C_6H_6-CH_2Cl_2$	$C_6H_6-CHCl_3$	$C_6H_6-CHF_3$	$C_6H_6-CCl_4$
HF/6-311G**	0.8 (0.3)	0.2 (0.5)	0.2 (0.9)	1.7 (1.6)	−0.9 (0.8)	1.7 (0.7)
HF/cc-pVDZ	0.8 (0.3)	0.3 (0.6)	0.5 (0.9)	2.1 (1.5)	−0.8 (0.7)	1.7 (0.4)
HF/cc-pVTZ	0.8 (0.1)	0.4 (0.2)	0.6 (0.4)	2.1 (0.5)	−0.8 (0.4)	1.9 (0.2)
HF/cc-pVQZ	0.9 (0.0)	0.4 (0.0)	0.6 (0.1)	2.2 (0.2)	−0.8 (0.2)	1.9 (0.0)
MP2/6-311G**	−0.8 (1.1)	−2.1 (1.6)	−3.2 (2.4)	−3.7 (3.9)	−2.7 (2.3)	−1.2 1.7)
MP2/cc-pVDZ	−0.7 (1.0)	−1.8 (1.4)	−2.8 (2.2)	−3.2 (3.4)	−2.3 (1.9)	−1.2 (1.2)
MP2/cc-pVTZ	−1.4 (0.4)	−2.9 (0.7)	−4.5 (1.1)	−5.9 (1.7)	−3.7 (1.2)	−2.6 (0.7)
MP2/cc-pVQZ	−1.6 (0.2)	−3.3 (0.3)	−5.2 (0.5)	−6.8 (0.8)	−4.3 (0.6)	−3.2 (0.3)
$E_{MP2(limit)}$[c]	−1.7	−3.5	−5.5	−7.2	−4.6	−3.7
$\Delta_{CCSD(T)}$[d]	0.3	0.5	0.9	1.6	0.4	0.8
$E_{CCSD(T)(limit)}$[e]	−1.5	−3.0	−4.5	−5.6	−4.2	−2.9
R[f], Å	3.8	3.6	3.4	3.2	3.4	5.0

[a] Energies in kcal/mol. BSSE-corrected interaction energies. The values in parentheses are BSSEs. The geometries of complexes are shown in Figure 1. [b] Reference 48. [c] Estimated MP2 interaction energies at the basis set limit. See text. [d] Difference between the interaction energies calculated with CCSD(T)/cc-pVDZ and MP2/cc-pVDZ methods. [e] Expected CCSD(T) interaction energies at the basis set limit. Sum of $E_{MP2(limit)}$ and $\Delta_{CCSD(T)}$. [f] Intermolecular separation (R) is the distance between the center of benzene and the carbon atom of the substituted methane. The MP2/cc-pVTZ level interaction potentials have their minima at these intermolecular distances.

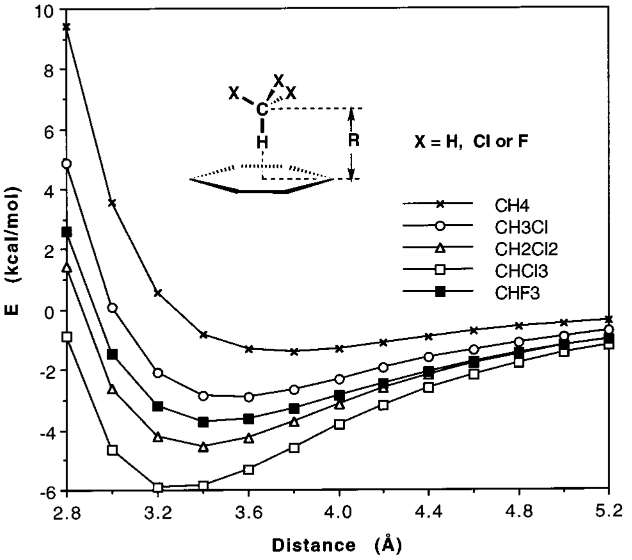

Figure 3. The MP2/cc-pVTZ intermolecular interaction potentials of five complexes. Intermolecular separation (R) is the distance between the center of benzene and the carbon atom of the substituted methane.

TABLE 2: Basis Set Effects on the Calculated HF, MP2, MP3, CCSD, and CCSD(T) Interaction Energies of $C_6H_6-CH_4$ and $C_6H_6-CH_3Cl$ Complexes[a]

basis set	HF	MP2	CCSD	CCSD(T)	$\Delta_{CCSD(T)}$[b]
		$C_6H_6-CH_4$			
6-311G*[c]	0.8	−0.6	−0.2	−0.4	0.2
6-311G**[c]	0.8	−0.8	−0.4	−0.5	0.3
cc-pVDZ[c]	0.8	−0.7	−0.3	−0.4	0.3
cc-pVTZ[c]	0.8	−1.4	−0.8	−1.1	0.4
		$C_6H_6-CH_3Cl$			
6-311G*	0.1	−1.9	−1.3	−1.5	0.5
6-311G**	0.2	−2.1	−1.3	−1.6	0.5
cc-pVDZ	0.3	−1.8	−1.0	−1.3	0.5

[a] Energies in kcal/mol. BSSE-corrected interaction energies. The geometries of complexes are shown in Figure 1. [b] Difference between the interaction energies calculated with CCSD(T) and MP2 methods. [c] Reference 48.

TABLE 3: Calculated Interaction Energies of Benzene with Substituted Methanes by Several Electron Correlation Correction Procedures[a]

complex	HF	MP2	CCSD	CCSD(T)	$\Delta_{CCSD(T)}$[b]
$C_6H_6-CH_3Cl$	0.3	−1.8	−1.0	−1.3	0.5
$C_6H_6-CH_2Cl_2$	0.5	−2.8	−1.5	−1.8	0.9
$C_6H_6-CHCl_3$	2.1	−3.2	−1.0	−1.6	1.6
$C_6H_6-CHF_3$	−0.8	−2.3	−1.7	−1.9	0.4
$C_6H_6-CCl_4$	1.7	−1.2	−0.0	−0.4	0.8

[a] Energies in kcal/mol. BSSE-corrected interaction energies. The geometries of complexes are shown in Figure 1. The cc-pVDZ basis set was used. [b] Difference between the interaction energies calculated with CCSD(T) and MP2 methods.

interaction energy at the basis set limit ($E_{CCSD(T)(limit)}$) can be estimated sufficiently accurately from the sum of $E_{MP2(limit)}$ and $\Delta_{CCSD(T)}$.[46] The $\Delta_{CCSD(T)}$ values obtained using cc-pVDZ basis set (Table 3) were used for the estimation of $E_{CCSD(T)(limit)}$. The estimated $E_{CCSD(T)(limit)}$ values of C_6H_6-X complexes (X = CH_3Cl, CH_2Cl_2, $CHCl_3$ and CHF_3) are −3.0, −4.5, −5.6, and −4.2 kcal/mol, respectively, as shown in Table 1. Recently reported calculations of $C_6H_6-H_2O$, $C_6H_6-NH_3$, and hydrogen-bonded complexes show that the estimated $E_{CCSD(T)(limit)}$ values with this method are very close to experimental bonding energies.[70,83-85] The MP2/cc-pVTZ interaction energies of the complexes are close to the estimated $E_{CCSD(T)(limit)}$. Apparently, error cancellation is a cause of the good performance of MP2/cc-pVTZ calculations.

The interaction energy of the $C_6H_6-CHCl_3$ complex (−5.6 kcal/mol) is about 4 times larger than that of the $C_6H_6-CH_4$ complex (−1.5 kcal/mol).[48] The interaction energy of the $C_6H_6-CHCl_3$ complex is slightly larger than that of water dimer (about −5.0 kcal/mol).[52-55] The large attraction in the $C_6H_6-CHCl_3$ complex indicates that the size of the CH/π interaction depends on the system strongly. Our previous study on the interactions of $C_6H_6-C_2H_4$ and $C_6H_6-C_2H_2$ complexes also shows that the size of the CH/π interaction is not constant.[48] The calculated bonding energies of these complexes (−2.1 and −2.8 kcal/mol, respectively) are considerably larger (more negative) than that of the $C_6H_6-CH_4$ complex (−1.5 kcal/mol).

Intermolecular Interaction Potentials. The HF and MP2 interaction energies of C_6H_6-X complexes (X = CH_3Cl, CH_2Cl_2, $CHCl_3$, and CHF_3) were calculated using cc-pVTZ basis set. The calculated potentials were compared with those of the $C_6H_6-CH_4$ complex as shown in Figures 3 and 4. The order of the depths of HF potentials is $CHF_3 > CHCl_3 > CH_2Cl_2 > CH_3Cl > CH_4$ as shown in Figure 4. The substitution of the hydrogen atoms of methane by chlorine and fluorine atoms increases attraction substantially. The HF interaction energy is mainly exchange−repulsion and electrostatic energies. The observed enhancement of attraction at the HF level suggests that the substitution by chlorine and fluorine atoms increases attractive electrostatic interaction. The electrostatic energies of the complexes were calculated as shown in Figure 5. The order

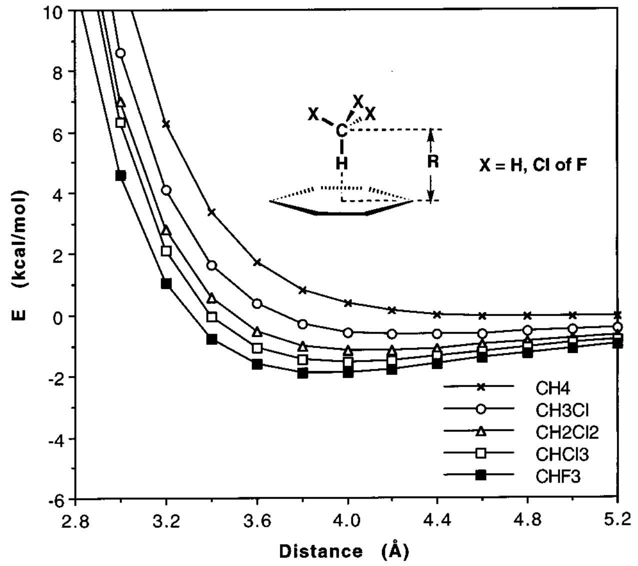

Figure 4. The HF/cc-pVTZ intermolecular interaction potentials of five complexes. Intermolecular separation (*R*) is the distance between the center of benzene and the carbon atom of the substituted methane.

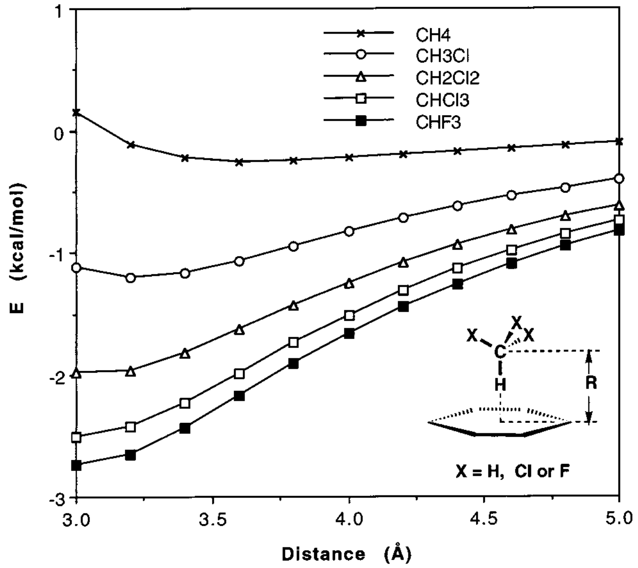

Figure 5. The calculated electrostatic energies of five complexes. Intermolecular separation (*R*) is the distance between the center of benzene and the carbon atom of the substituted methane.

of magnitude of electrostatic interaction agrees well with the order of depths of HF potentials. The increase of the number of chlorine atoms increases attractive electrostatic interaction. The $C_6H_6-CHF_3$ complex, which has more electronegative fluorine atoms, has larger (more negative) electrostatic energy than the $C_6H_6-CHCl_3$ complex.

The substitution by chlorine and fluorine atoms increases the MP2 interaction energies considerably as shown in Figure 3. The change of MP2 interaction energy by the substitution is significantly larger than the corresponding change of HF interaction energy, which indicates that the substitution increases not only attractive electrostatic interaction but also dispersion interaction considerably. There exists substantial dispersion interaction between chlorine atoms and benzene, because dispersion interaction is a long-range interaction. A chlorine atom has a significantly large atomic polarizability (16 au) compared to a hydrogen atom (3.5 au).[86] Therefore, the substitution by chlorine atoms increases dispersion considerably. The order of depths of MP2 potentials is $CHCl_3 > CH_2Cl_2 > CHF_3 > CH_3Cl > CH_4$. Although CHF_3 has larger attraction than $CHCl_3$ at the HF level, the calculated attraction of CHF_3 at the MP2 level is considerably smaller than that of $CHCl_3$. The atomic polarizability of fluorine (3.2 au) is substantially smaller than that of chlorine.[86] The smaller polarizability is the cause of smaller attraction of CHF_3 at the MP2 level.

The MP2/cc-pVTZ potentials of C_6H_6-X complexes ($X = CH_3Cl$, CH_2Cl_2, $CHCl_3$, and CHF_3) have their minima when the intermolecular separations (the distance between the center of benzene and the carbon atom of substituted methane) are 3.6, 3.4, 3.2, and 3.4 Å, respectively. These distances are shorter than that of the $C_6H_6-CH_4$ complex (3.8 Å). The large attraction leads to shorter equilibrium intermolecular separation.

The calculated potentials of these complexes are all very flat near the minima as shown in Figure 3. Substantial attraction still exists even if the intermolecular distance is larger than 4.0 Å, which suggests that the major source of attraction in these complexes is not short-range interactions ($E \approx e^{-\alpha R}$), such as charge-transfer, but long-range interactions ($E \approx R^{-n}$), such as electrostatic and dispersion. Although the substitution of hydrogen atoms of methane by chlorine and fluorine atoms increases the depth of potential considerably, it also increases the attraction when the molecules are well-separated, which suggests that the substitution does not enhance short-range interactions.[72,87] It was sometimes stated that charge-tranfer interaction (delocalization) was important for the CH/π interaction.[49,88] However, high-level ab initio calculations do not indicate that charge transfer is important.[47,48]

Roles of Electrostatic and Dispersion Interactions. The electrostatic and correlation interaction energies (contributions of electron correlation on the interaction energies) of benzene-substituted methane complexes are summarized in Table 4. The electrostatic energy (E_{es}) was calculated as an interaction between distributed multipoles obtained from the MP2/6-311G** wave functions of isolated molecules. The HF interaction energy (E_{HF}) was calculated at the HF/cc-pVQZ level, which is approximately the sum of exchange−repulsion and electrostatic energies. The E_{rep} was calculated as the difference between E_{HF} and E_{es}. Although E_{rep} is mainly exchange−repulsion energy, it may also contain some other energy components. The correlation interaction energy (E_{corr}) was calculated as the difference between $E_{CCSD(T)(limit)}$ (E_{total}) and E_{HF}. E_{corr} is mainly dispersion energy.

The significantly large E_{corr} values of the complexes (−3.4, −5.1, −7.9, and −3.4 kcal/mol) indicate that the major source of attraction in these complexes is dispersion. The E_{corr} of the $C_6H_6-CHCl_3$ complex (−7.9 kcal/mol) is significantly larger than that of the $C_6H_6-CHF_3$ complex (−3.4 kcal/mol), which shows that larger dispersion interaction is the cause of the larger bonding energy of the $C_6H_6-CHCl_3$ complex. Although the E_{es} values of the complexes (−1.1, −1.8, −2.4, and −2.4 kcal/mol, respectively) are not negligible, they are smaller than the E_{corr} values. The E_{es} values of the $C_6H_6-CHCl_3$ and $C_6H_6-CHF_3$ complexes at their potential minima are nearly equal because of the smaller intermolecular separation in the $C_6H_6-CHCl_3$ complex (3.2 Å) than that in the $C_6H_6-CHF_3$ complex (3.4 Å). At the same separation (3.4 Å), the E_{es} value of the $C_6H_6-CHCl_3$ complex (−2.2 kcal/mol) is smaller (less negative) than that of the $C_6H_6-CHF_3$ complex (−2.4 kcal/mol).

Comparison with Experimental Bonding Energy. We have estimated bonding energies of C_6H_6-X complexes ($X = CH_3Cl$, CH_2Cl_2, $CHCl_3$, and CHF_3) with ab initio method. The formation of the complexes in solution have been reported from the observation of an aromatic-solvent-induced shift of ^1H NMR

TABLE 4: Electrostatic and Dispersion Energies of Benzene and Substituted Methane Complexes[a]

energy	$C_6H_6-CH_4$[b]	$C_6H_6-CH_3Cl$	$C_6H_6-CH_2Cl_2$	$C_6H_6-CHCl_3$	$C_6H_6-CHF_3$	$C_6H_6-CCl_4$
E_{total}[c]	−1.5	−3.0	−4.5	−5.6	−4.2	−2.9
E_{es}[d]	−0.2	−1.1	−1.8	−2.4	−2.4	−0.2
E_{rep}[e]	1.1	1.4	2.4	4.6	1.7	2.1
E_{corr}[f]	−2.3	−3.4	−5.1	−7.9	−3.4	−4.9
R (Å)	3.8	3.6	3.4	3.2	3.4	5.0

[a] Energies in kcal/mol. The geometries of complexes are shown in Figure 1. [b] Reference 48. [c] Expected CCSD(T) interaction energies at the basis set limit. See text and footnote e of Table 1. [d] Electrostatic interaction energy. See text. [e] The difference between HF/cc-pV5Z interaction energy and E_{es}. [f] The difference between $E_{CCSD(T)(limit)}$ and HF/cc-pV5Z interaction energy.

spectra.[57−59] The complex formation has been believed to be firm evidence of the CH/π interaction.[1] Although bonding energies of the complexes in the gas phase have not yet been reported, recently, Ehama and co-workers measured the enthalpies of $C_6D_6-CHCl_3$ and $C_6D_6-CH_2Cl_2$ complex formation (−1.89 and −1.59 kcal/mol, respectively) in CCl_4 solution.[15] The experimental values are considerably smaller than the calculated interaction energies of the complexes. The experimental enthalpies of complex formation cannnot be directly compared with the calculated bonding energies, because the solvation energies of the solutes ($CHCl_3$, CH_2Cl_2, and C_6D_6) and the complexes may contribute to the observed enthalpies of complex formation substantially. We would like to show that consideration of interaction between C_6D_6 and CCl_4 is important to explain the small experimental enthalpies of complex formation.

A C_6D_6 molecule would have substantial interaction with solvent (CCl_4). Therefore, the observed enthalpy of $C_6D_6-CHCl_3$ complex formation in CCl_4 solution corresponds to the reaction energy of the following exchange reaction:

$$C_6D_6-CCl_4 + CHCl_3 \rightarrow C_6D_6-CHCl_3 + CCl_4$$

We also have to evaluate solvation energies of the four species ($CHCl_3$, CCl_4, $C_6D_6-CHCl_3$, and $C_6D_6-CCl_4$) to accurately estimate the reaction energy in solution. If we suppose that the sum of the solvation energies of $CHCl_3$ and the $C_6D_6-CCl_4$ complex is equal to that of CCl_4 and the $C_6D_6-CHCl_3$ complex as a very crude approximation, we can roughly estimate the reaction energy from the difference between the interaction energies of the $C_6D_6-CCl_4$ and $C_6D_6-CHCl_3$ complexes.

The interaction energy of the $C_6H_6-CCl_4$ complex (Figure 1, $R = 5.0$ Å) was calculated with the same method used for the calculations of other complexes. The MP2/cc-pVTZ potential of the complex has its minimum at this intermolecular distance. The calculated interaction energies are shown in Tables 1, 3, and 4. The calculated $E_{CCSD(T)(limit)}$ of the $C_6H_6-CCl_4$ complex is −2.9 kcal/mol. The difference between the calculated interaction energies of the $C_6H_6-CHCl_3$ and $C_6H_6-CCl_4$ complexes is −2.7 kcal/mol and that between the $C_6H_6-CH_2Cl_2$ and $C_6H_6-CCl_4$ complexes is −1.6 kcal/mol. The estimated reaction energy of $C_6H_6-CH_2Cl_2$ complex formation in CCl_4 (−1.6 kcal/mol) is very close to the experimental value (−1.59 kcal/mol). Although the estimated reaction energy of $C_6H_6-CHCl_3$ complex formation (−2.7 kcal/mol) is still larger (more negative) than the experimental one (−1.89 kcal/mol), the consideration of the interaction between C_6D_6 and CCl_4 improves the agreement considerably.

Conclusion

The size of the CH/π interaction of benzene with chloro- and fluoromethanes depends on the substituents considerably. Substitution of hydrogen atoms of methane by chlorine and fluorine atoms increases attraction. The calculated bonding energy of the $C_6H_6-CHCl_3$ complex (−5.6 kcal/mol) is slightly larger than that of water dimer (about 5 kcal/mol).

Calculated potentials of the complexes suggest that the major source of attraction in the complexes is not short-range interactions, such as charge transfer, but long-range interactions, such as electrostatic and dispersion. Electron correlation increases attraction greatly, which indicates that dispersion is the major source of attraction in the complexes studied in this work. Electrostatic interaction is also important for attraction, but electrostatic energy is smaller than dispersion energy.

Substitution of hydrogen atoms of methane by chlorine and fluorine atoms changes both electrostatic and dispersion energies considerably. The substitution increases attractive electrostatic interaction. Substitution by chlorine atoms increases dispersion interaction greatly. The substitution increases the depths of potentials significantly, while it also increases the attraction greatly when the molecules are well-separated. This shows that the substitution does not enhance short-range interactions.

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