The Magnitude of the CH/π Interaction between Benzene and Some Model Hydrocarbons

Seiji Tsuzuki,* Kazumasa Honda, Tadafumi Uchimaru, Masuhiro Mikami, and Kazutoshi Tanabe

Contribution from the National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305-8565, Japan

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Abstract: High-level ab initio calculations were carried out to evaluate the interaction between the π face of benzene and hydrocarbon molecules (methane, ethane, ethylene, and acetylene). Intermolecular interaction energies were calculated from extrapolated MP2 interaction energies at the basis set limit and CCSD(T) correction terms. The calculated benzene−methane interaction energy (−1.45 kcal/mol) is considerably smaller than that of the hydrogen bond between waters. The benzene−methane complex prefers a geometry in which the C−H bond points toward the benzene ring. The potential energy surface is very flat near the minimum, which shows that the major source of the attraction is a long-range interaction. The HF interaction energy of the complex (0.85 kcal/mol) is repulsive. The large gain of the attraction energy (−2.30 kcal/mol) by electron correlation correction indicates that dispersion interaction is the major source of the attraction. Although the electrostatic energy (−0.25 kcal/mol) is small, a highly orientation dependent electrostatic interaction determines the orientation of the C−H bond. The calculated charge distributions show that the amount of charge transfer from benzene to methane is very small. The calculated interaction energies of benzene−ethane, benzene−ethylene, and benzene−acetylene complexes are −1.82, −2.06, and −2.83 kcal/mol, respectively. Dispersion interaction is again the major source of the attraction of these complexes. The electrostatic energy (−0.17 kcal/mol) is not large in the benzene−ethane complex, while the large electrostatic energies of benzene−ethylene and benzene−acetylene complexes (−0.65 and −2.01 kcal/mol) show that electrostatic interaction is also important for the attraction between benzene and unsaturated hydrocarbon molecules.

Introduction

Nonbonding interactions play a dominant role in many forefront areas of modern chemistry from molecular biology to material design. Detailed information of the interactions is essential for understanding biological processes and for simulations of materials.[1,2] The attraction between the C−H bond and the π system is called CH/π interaction.[3] It was first proposed by Nishio and co-workers to explain the preference of conformations in which bulky alkyl and phenyl groups had close contact.[4] During these two decades several experimental studies, which support the existence of the attraction, have been reported. The close contact was observed in stable conformations of a lot of molecules.[5−13] Statistical analysis of the crystal structure database indicates that the short contact of the C−H bond and the π system is observed in large numbers of organic crystals.[14−16] The CH/π interaction is believed as a crucial driving force of crystal packing.[14,15] The short contact was also observed in crystals of proteins.[17−23] The importance of the CH/π interaction in molecular recognition was also reported.[17−38] Aoyama et al.

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reported that the interaction is an important driving force of host−guest complexation of cyclic resorcinol derivatives.[27−30] Stoddart et al. reported that self-organization of catenanes was governed by weak nonbonding interactions including the CH/π interaction.[31] Quiocho et al. reported that crystal structures of sugar binding proteins show carbohydrate ligands sandwiched by aromatic side chains and the CH/π interaction is playing an important role in molecular recognition.[17−21]

Despite broad interests in the CH/π interaction in many areas of chemistry and biology, very little is known about the physical origin and scope of the interaction. The physical origin of the interaction is essential for the understanding of conformational preference, crystal packing, and host−guest complexation. Quantitative information on the interaction is also desired by those who carry out force field simulations of these systems. Although a lot of experimental measurements have been reported on the interaction, it is still difficult to determine accurate interaction energy only from experimental measurements.

A few theoretical calculations of model systems were carried out to evaluate the interaction energy of the CH/π interaction.[4,39,40] Takagi et al. reported that main contributions to the attraction were electrostatic and charge-transfer terms from the energy decomposition analysis using the Kitaura−Morokuma scheme.[41] Therefore, charge transfer was believed as an important source for the attraction.[3] Although these early calculations were impressive when they were reported, the basis sets used in these calculations (4-31G and MIDI4*) were too small to evaluate the weak attractive interaction energy quantitatively. Recently reported calculations of small hydrocarbon molecules show that the calculated interaction energies highly depend on basis set[42−45] and electron correlation[46−48] and that a large basis set including multiple polarization functions and appropriate electron correlation correction are necessary to accurately evaluate interaction energies.

In this paper we have provided detailed evaluation of the CH/π interaction of model systems by high-level ab initio calculations. We have calculated MP2 interaction energies of benzene−methane, benzene−ethane, benzene−ethylene, and benzene−acetylene complexes with Dunning's correlation consistent basis sets and estimated MP2 interaction energies at the basis set limit. In addition we have added the CCSD(T) correction to include electron correlation beyond MP2. We discuss the roles of electrostatic, dispersion, and charge-transfer terms for the attraction of these complexes based on the calculated interaction energies.

Computational Method

The Gaussian 94 program[49] was used for the ab initio molecular orbital calculations. 6-311G**[50] and cc-pVXZ (X = D, T and Q)[51,52] basis sets were used. Electron correlation energies were corrected by the second-order Mϕller−Plesset perturbation method (MP2)[53,54] and by the coupled cluster method using single and double substitutions with non-iterative triple excitations (CCSD(T)).[55,56] Geometries of isolated molecules were optimized at the MP2/6-31G* level,[57] and were used for calculations of complexes. Basis set superposition error (BSSE)[58] was corrected by the counterpoise method.[59] MP2 interaction energies at the basis set limit were estimated by the method proposed by Feller.[60] Distributed multipoles[61,62] were obtained from HF/6-311G** wave functions of isolated molecules using CADPAC version 6.[63] Electrostatic and induction energies of complexes were calculated using ORIENT version 3.2.[64] Electrostatic energies of complexes were calculated as interactions between distributed multipoles. Induction energy was calculated as interactions of polarizable sites, which were put on the centers of gravity of monomers, with electric field produced by the multipoles of monomers. Experimental polarizabilities of

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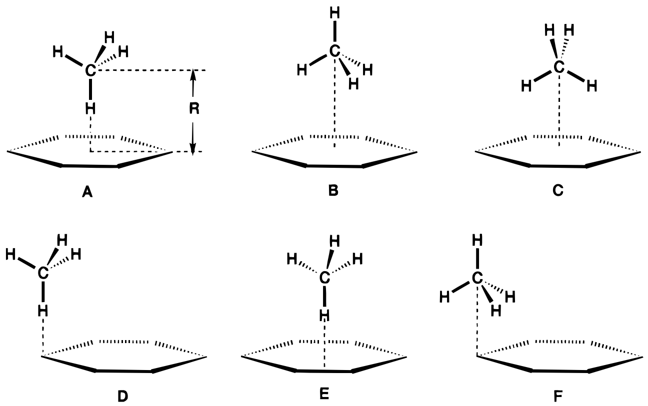

Figure 1. The geometries of the benzene−methane complexes considered in this work. The intermolecular distance *R* is 3.8, 3.6, 3.6, 4,0, 4.0, and 3.6 Å for the complexes A−F, respectively. The MP2/cc-pVTZ level interaction potentials had minima at these intermolecular distances (see Figure 3). The methane is above the center of the benzene ring in complexes A−C. The methane is above one of the carbon atoms of the benzene in complexes D and F. The methane is above the center of a C−C bond of the benzene in complex E.

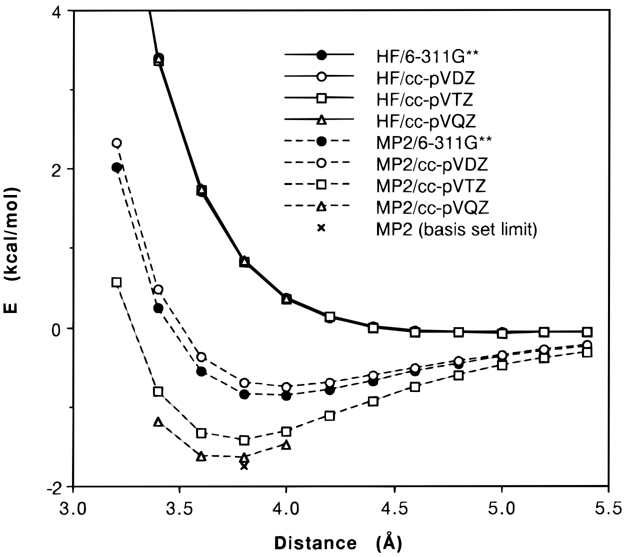

Figure 2. The HF and MP2 intermolecular interaction potentials of complex A calculated with several basis sets.

methane (α = 17.28 au) and benzene ($\alpha_{xx} = \alpha_{yy}$ = 83.07, α_{zz} = 42.85 au) were used for the calculations.[65,66]

Results and Discussion

Basis Set Effects on HF and MP2 Interaction Energies. Intermolecular interaction energies of benzene−methane complex A (Figure 1) were calculated at HF and MP2 levels using 6-311G** and cc-pVXZ (X = D, T, and Q) to evaluate the basis set effect. The basis set dependence of the HF interaction energies is very small as shown in Figure 2. The HF interaction energy is mainly exchange-repulsion and electrostatic energies. But the basis set effect on these interactions is not large.

The MP2 interaction energies of complex A greatly depend on the basis set as shown in Figure 2. The calculated interaction energies of the six complexes (Figure 1) using several basis sets are summarized in Table 1. The intermolecular distances of the complexes shown in Figure 1 correspond to the potential minima calculated at the MP2/cc-pVTZ level (Figure 3). Small cc-pVDZ and 6-311G** basis sets (148 and 186 basis functions for the complex, respectively) considerably underestimate the attraction compared with a large cc-pVQZ basis set (685 basis functions). The MP2/cc-pVDZ interaction energies of complexes A−F are −0.70, −0.43, −0.49, −0.47, −0.52, and −0.40 kcal/mol, respectively. Those calculated at the MP2/cc-pVQZ level are −1.64, −1.41, −1.52, −1.04, −1.11, and −1.21 kcal/mol, respectively. The MP2/cc-pVDZ calculations 53−69% underestimate the interaction energies. It has been reported that small basis sets such as cc-pVDZ and 6-31G* considerably underestimate attractive interactions between small hydrocarbon molecules.[44,45] Small basis sets considerably underestimate molecular polarizabilities and the attractive interactions.[44] A large flexible basis set with multiple polarization functions is necessary to accurately evaluate the attractive interaction between hydrocarbon molecules.[44−46]

Electron correlation gives large effects on the calculated interaction energies of benzene−methane complexes. The HF calculation considerably underestimates the attraction. The HF interaction energies of complexes A−F calculated with cc-pVQZ are 0.85, 1.41, 1.53, 0.61, 0.60, and 1.10 kcal/mol, respectively. The difference between the HF and MP2 interaction energies is mainly attractive dispersion interaction.[46] The large gain of the attraction by electron correlation indicates that the dispersion interaction is significantly important for the attraction between benzene and methane.

Effects of Electron Correlation Beyond MP2. Interaction energies of the benzene−methane complexes were calculated by the MP3, CCSD, and CCSD(T) methods with cc-pVDZ to evaluate the effect of electron correlation beyond MP2. The calculated interaction energies are summarized in Table 2. The MP2 interaction energies are larger (more negative) than the CCSD(T) energies. The MP3 interaction energies are close to the CCSD(T) values. The CCSD calculations substantially underestimate the attraction compared with CCSD(T), which suggests the importance of triple excitation to evaluate the attractive interaction.[67]

Interaction Energies at the Basis Set Limit. The MP2 interaction energies at the basis set limit were estimated by extrapolation of the MP2 interaction energies calculated with Dunning's correlation consistent basis sets using the method proposed by Feller. 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.[60,68] The extrapolated MP2 interaction energies of complexes A−F at the basis set limit (E_{MP2}(limit)) are −1.74, −1.51, −1.64, −1.11, −1.19, and −1.32 kcal/mol, respectively, as summarized in Table 1.[69] These are not largely different from those values calculated with cc-pVQZ, indicating that cc-pVQZ is close to saturation. The MP2/cc-pVQZ interaction energies are only 0.07−0.12 kcal/mol smaller (less negative) than the corresponding estimated MP2 interaction energies at the basis set limit.

The MP2 interaction energy of complex A was also calculated with aug-cc-pVXZ (X = D, T and Q) basis sets. The calculated

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[69] One may claim that the MP2 interaction energies at the basis set limit [$E_{\mathrm{MP2(limit)}}$] should be estimated from the interaction energies calculated with aug-cc-pVXZ, instead of from those with cc-pVXZ. However, the calculations of C_2H_4−CH_4 complexes show that the $E_{\mathrm{MP2(limit)}}$ values estimated from MP2/cc-pVXZ calculations are close to those from MP2/aug-cc-pVXZ calculations. The augmentations of the diffuse functions to cc-pVDZ and cc-pVTZ substantially affected the calculated interaction energies, while the effects of augmentations to cc-pVQZ were very small. See ref 85.

Table 1. Calculated Interaction Energies of the $C_6H_6-CH_4$ Complexes A−F[a]

method	A	B	C	D	E	F
HF/6-311G**	0.82 (0.33)	1.38 (0.37)	1.44 (0.32)	0.57 (0.22)	0.56 (0.23)	1.09 (0.35)
HF/cc-pVDZ	0.83 (0.34)	1.39 (0.38)	1.47 (0.33)	0.59 (0.22)	0.58 (0.23)	1.10 (0.36)
HF/cc-pVTZ	0.84 (0.13)	1.39 (0.15)	1.50 (0.14)	0.60 (0.09)	0.59 (0.09)	1.09 (0.14)
HF/cc-pVQZ	0.85 (0.05)	1.41 (0.06)	1.53 (0.06)	0.61 (0.04)	0.60 (0.04)	1.10 (0.05)
MP2/6-311G**	−0.83 (1.08)	−0.57 (0.81)	−0.67 (0.83)	−0.56 (0.60)	−0.61 (0.64)	−0.52 (0.69)
MP2/cc-pVDZ	−0.70 (0.96)	−0.43 (0.83)	−0.49 (0.88)	−0.47 (0.60)	−0.52 (0.63)	−0.40 (0.73)
MP2/cc-pVTZ	−1.42 (0.42)	−1.18 (0.42)	−1.27 (0.41)	−0.90 (0.28)	−0.96 (0.29)	−1.01 (0.36)
MP2/cc-pVQZ	−1.64 (0.19)	−1.41 (0.18)	−1.52 (0.18)	−1.04 (0.13)	−1.11 (0.14)	−1.21 (0.16)
E_{MP2}(limit)[b]	−1.74	−1.51	−1.64	−1.11	−1.19	−1.32
$\Delta_{CCSD(T)}$[c]	0.29	0.28	0.33	0.18	0.19	0.22
$E_{CCSD(T)}$(limit)[d]	−1.45	−1.23	−1.32	−0.93	−1.00	−1.10

[a] Energies in kcal/mol. BSSE corrected interaction energies. The values in parentheses are BSSE values. The geometries of the complexes are shown in Figure 1. [b] The estimated MP2 interaction energies at the basis set limit. See text. [c] Difference between the interaction energies calculated with the CCSD(T)/cc-pVDZ and MP2/cc-pVDZ methods. [d] The expected CCSD(T) interaction energies at the basis set limit. Sum of E_{MP2}(limit) and $\Delta_{CCSD(T)}$.

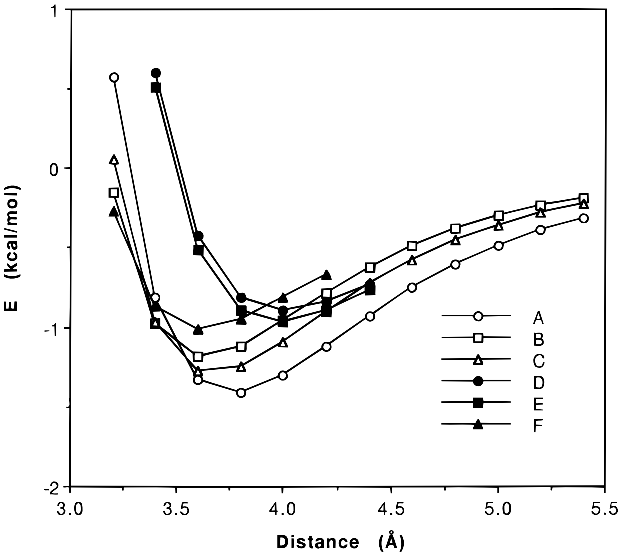

Figure 3. The MP2/cc-pVTZ intermolecular interaction potentials of the six benzene−methane complexes.

Table 2. Interaction Energies of the $C_6H_6-CH_4$ Complexes Calculated with Electron Correlation Correction by Several Methods[a]

complex	HF	MP2	MP3	CCSD	CCSD(T)
A	0.83	−0.70	−0.35	−0.25	−0.41
B	1.39	−0.43	−0.06	0.05	−0.15
C	1.47	−0.49	−0.08	0.05	−0.17
D	0.59	−0.47	−0.26	−0.17	−0.29
E	0.58	−0.52	−0.29	−0.20	−0.33
F	1.10	−0.40	−0.10	−0.01	−0.17

[a] Energies in kcal/mol. BSSE corrected interaction energies. The structures of the complexes are shown in Figure 1. The cc-pVDZ basis set was used.

MP2 interaction energies of the complex with these basis sets are −1.48, −1.69, and −1.74 kcal/mol, respectively. The calculated MP2 interaction energies with cc-pVXZ (X = D, T, and Q) are −0.70, −1.42, and −1.64 kcal/mol, respectively. The augmentations of diffuse functions to the cc-pVDZ and cc-pVTZ basis sets substantially increase the attraction, while the effect of the augmentations to the cc-pVQZ basis set is very small. The estimated E_{MP2}(limit) from the calculated MP2 interaction energies with the aug-cc-pVXZ basis sets is −1.77 kcal/mol. This value is very close to that estimated from the calculated interaction energies with cc-pVXZ basis sets (−1.74 kcal/mol).

The CCSD(T) correction ($\Delta_{CCSD(T)}$) is the difference between the MP2 and CCSD(T) interaction energies using cc-pVDZ. The $\Delta_{CCSD(T)}$ values of the complexes are 0.29, 0.28, 0.33, 0.18, 0.19, and 0.22 kcal/mol, respectively. The CCSD(T) interaction energy of complex A was also calculated using 6-311G*, 6-311G**, cc-pVTZ, aug(d)-6-311G**, and aug(d,p)-6-311G** as shown in Table 3. (See footnotes for Table 3.) The CCSD(T) interaction energies depend on the basis set, while the basis set dependence of $\Delta_{CCSD(T)}$ is not large. The $\Delta_{CCSD(T)}$ values calculated with these basis sets (0.25, 0.29, 0.35, 0.33, and 0.31 kcal/mol, respectively) are close to that calculated with cc-pVDZ (0.29 kcal/mol). The expected CCSD(T) interaction energies of the complexes at the basis set limit (the sum of E_{MP2}(limit) and $\Delta_{CCSD(T)}$) are −1.45, −1.23, −1.32, −0.93, −1.00, and −1.10 kcal/mol, respectively.

Table 3. Basis Set Effects on the Calculated HF, MP2, MP3, CCSD, and CCSD(T) Interaction Energies of the $C_6H_6-CH_4$ Complex A[a]

basis set	HF	MP2	MP3	CCSD	CCSD(T)	ΔCCSD(T)[b]
6-311G*	0.83	−0.63	−0.33	−0.23	−0.38	0.25
6-311G**	0.82	−0.83	−0.48	−0.37	−0.54	0.29
cc-pVDZ	0.83	−0.70	−0.35	−0.25	−0.41	0.29
cc-pVTZ	0.84	−1.42	−0.94	−0.79	−1.06	0.35
cc-pVQZ	0.85	−1.64				
aug(d)-6-311G** [c]	0.80	−1.40	−0.94	−0.81	−1.07	0.33
aug(d,p)-6-311G** [d]	0.84	−1.54	−1.07	−0.93	−1.23	0.31

[a] Energies in kcal/mol. BSSE corrected interaction energies. The geometry of the complex is shown in Figure 1. [b] Difference between the interaction energies calculated with the CCSD(T) and MP2 methods. [c] The aug(d)-6-311G** basis set is the 6-311G** basis set augmented with diffuse d functions on carbon atoms (α_d(C) = 0.1565). [d] The aug(d,p)-6-311G** basis set is the 6-311G** basis set augmented with diffuse d functions on carbon atoms and diffuse p functions on hydrogen atoms (α_d(C) = 0.1565 and α_p(H) = 0.1875).

Complex A has the largest (most negative) interaction energy (−1.45 kcal/mol), which is about 30% of the hydrogen bonding energy of the water dimer.[70−74] The interaction between benzene and methane is substantially weaker than the hydrogen bond between water molecules. Interestingly, the MP2/cc-pVTZ interaction energies of the complexes are −1.42, −1.18, −1.27, −0.90, −0.96, and −1.01 kcal/mol, respectively: these energies

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(74) The vibrational zero-point energies (ZPE) of monomers and a complex were calculated at the MP2/cc-pVDZ level. The calculated ZPE's of benzene and methane monomers and the complex A were 0.100519, 0.045361, and 0.146625 hartree, respectively. The change of the ZPE by the formation of the dimer (ΔZPE) is 0.47 kcal/mol. The estimated $\Delta H°$ of the formation of the dimer A (sum of the $E_{CCSD(T)(limit)}$ and ΔZPE) is −0.98 kcal/mol.

Table 4. Electrostatic and Dispersion Energies of the C_6H_6−CH_4 Complexes A−F[a]

energy	A	B	C	D	E	F
E_{total}[b]	−1.45	−1.23	−1.32	−0.93	−1.00	−1.10
E_{es}[c]	−0.25	0.25	0.05	−0.17	−0.19	0.15
E_{rep}[d]	1.10	1.16	1.48	0.78	0.79	0.96
E_{corr}[e]	−2.30	−2.64	−2.85	−1.54	−1.60	−2.20

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

are not largely different from the estimated CCSD(T) interaction energies at the basis set limit. The good agreement is apparently due to the error cancellation.

Intermolecular Interaction Potentials. Intermolecular interaction energies of the six complexes (Figure 1) were calculated at the MP2/cc-pVTZ level as shown in Figure 3. The calculated intermolecular interaction potentials have minima when intermolecular distances (R) are 3.8, 3.6, 3.6, 4.0, 4.0, and 3.6 Å, respectively. Although the calculated potential of complex A has the deepest minimum, the potential depths of complexes B and C are not largely different from that of A. The calculated potentials show that the potential energy surface is very shallow near the minimum with respect to the rotation of methane and that the bonding between the aliphatic C−H bond and the π system is very loose. The potential of complex A is steeper than those of B and C in the region of short intermolecular distance, apparently due to the short contact of the C−H bond with the benzene ring. The calculated potentials are very flat near the minima. Substantial attraction still exists, even if the intermolecular distance is larger than 4.0 Å, which suggests that the major source of the attraction is not a short-range interaction ($E \sim e^{-\alpha R}$) such as charge transfer, but a long-range interaction ($E \sim R^{-n}$) such as electrostatic and dispersion.[62,75]

The calculated interaction energies of complexes D, E, and F are smaller than those of A, B, and C, which indicates that the methane prefers to locate above the center of the benzene ring. The preference agrees well with results of crystal structure database studies, which show that the carbon atom of the interacting C−H bond prefers to locate near the center of the benzene ring.[14,76]

Roles of Electrostatic and Dispersion Interactions. The electrostatic and correlation interaction energies of benzene−methane complexes were analyzed to understand the details of interactions as summarized in Table 4. The electrostatic energy (E_{es}) was calculated as an interaction between distributed multipoles obtained from the HF/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 the exchange-repulsion and electrostatic energies. The E_{rep} was calculated as the difference between E_{HF} and E_{es}. Although the E_{rep} is mainly the exchange-repulsion energy, it may also include some other energy components. The correlation interaction energy (E_{corr}) was calculated as the difference between the estimated CCSD(T) interaction energy at the basis set limit (E_{total}) and the E_{HF}. The E_{corr} is mainly attractive dispersion energy.[46]

The E_{corr} values of complexes A−F are −1.54 to −2.85 kcal/mol. The very large E_{corr} values indicate that dispersion interaction is significantly important for the attraction. The E_{corr} values of complexes B and C (−2.64 and −2.85 kcal/mol) are substantially larger (more negative) than that of A, apparently due to the shorter intermolecular distances of these complexes (3.6 Å) than that of A (3.8 Å).

The absolute value of E_{es} is always considerably smaller than the E_{corr}, which shows that electrostatic interaction is not essential for the attraction. The E_{es} is highly orientation dependent. The E_{es} of complex B is repulsive (0.25 kcal/mol) and that of C is small (0.05 kcal/mol), while that of A is attractive (−0.25 kcal/mol).[77] The attractive electrostatic interaction of complex A is reasonable. The C−H bonds of benzene have substantial bond dipoles. As a result the region near the center of the aromatic ring is negatively charged. Methane has an octopole moment,[62,78] which means that the C−H bonds have small bond dipoles. The small positive charge on the hydrogen atom of the methane has attraction with the negative charge of the aromatic ring.

The permanent charge field of benzene is substantial. The benzene−methane complex may have large induction (polarization) energy. The induction energy of complex A was calculated. The calculated induction energy (−0.12 kcal/mol) is very small, which suggests that induction is not important for the attraction between benzene and methane.

Complex A has the largest (most negative) interaction energy (−1.45 kcal/mol) among the six complexes. Complexes B and C have slightly smaller interaction energies (−1.23 and −1.32 kcal/mol). It agrees well with experimental observation that the C−H bond prefers to point toward the π system.[14,76] The sum of E_{rep} and E_{corr} (approximately the sum of the exchange-repulsion and dispersion energies) of complexes B and C (−1.48 and −1.37 kcal/mol, respectively) is larger (more negative) than that of A (−1.20 kcal/mol). The smaller repulsion in B and C enables shorter intermolecular distance and gives larger stabilization by attractive dispersion interaction. However, electrostatic interaction increases the relative stability of complex A. As a result, the total interaction energy (E_{total}) of A is larger than those of B and C. These results show that relatively small, but highly orientation dependent electrostatic interaction controls the orientation of the C−H bond. Buckingham and Fowler pointed out from simple model calculations that structures of molecular clusters are mainly determined by exchange-repulsion and electrostatic interactions.[79,80]

The calculated interaction energies of complexes D−F are smaller than those of A−C. The E_{corr} values of D−F are substantially smaller than those of A−C, suggesting that the larger attractive dispersion interaction is mainly responsible for the larger interaction energies of A−C.

The atomic charge distributions of complex A were obtained by the electrostatic potential fitting with the Merz−Singh−

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(75) Nonbonding interactions can be separated into two main types. One is long-range interactions such as electrostatic and dispersion interactions where the energy of interaction behaves as some inverse power of R. Another is short-range interactions such as exchange-repulsion and charge-transfer interactions. Short-range interactions arise at distances where the molecular wave functions overlap significantly. The energies of short-range interactions decrease exponentially with distance.

(76) K. Honda, unpublished work.

(77) Inclusion of electron correlation sometimes has a significant effect on the calculated dipole moment of an isolated molecule. Inclusion of electron correlation may affect largely the E_{es} values of the complexes. The E_{es} values of complexes A and B were calculated from the distributed multipoles obtained from the MP2/6-311G** wave functions of isolated molecules to evaluate the effects of electron correlation. The calculated E_{es} values are −0.22 and 0.26 kcal/mol, respectively. The E_{es} values obtained from the HF/6-311G** distributed multipoles are −0.25 and 0.25 kcal/mol, respectively. The inclusion of the electron correlation affects the E_{es} values only slightly.

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Table 5. Calculated Charges on CH_4 in the $C_6H_6-CH_4$ Complex A[a]

basis set	HF	MP2	basis set	HF	MP2
MIDI![b]	−0.006	−0.008	cc-pVDZ	−0.000	−0.002
6-31G	−0.005	−0.007	cc-pVTZ	−0.000	−0.002
6-31G*	−0.006	−0.008	cc-pVQZ	−0.001	
6-311G*	−0.002	−0.003	cc-pV5Z	−0.000	
6-311G**	−0.002	−0.004			

[a] The geometry of the complex is shown in Figure 1. The total charge of the methane obtained from the atomic charge distributions with the Merz−Singh−Kollman scheme electrostatic potential fitting. [b] Reference 84.

Kollman scheme[81,82] to evaluate the amount of charge transfer from benzene to methane. Takagi et al. reported from the energy decomposition analysis of the ethylene−methane complex using the Kitaura−Morokuma scheme[41] that the main contribution to the attractive CH/π interaction was the electrostatic and charge-transfer terms.[39] Therefore, charge transfer was believed to be an important source for the attraction.[3] However, recently Stone pointed out that the charge-transfer energy obtained by the Kitaura−Morokuma scheme is contaminated by BSSE and this scheme overestimates the charge-transfer energy.[83] The calculated charges on methane (sum of the atomic charges) are summarized in Table 5. The calculated negative charge on methane, which corresponds to the charge transfer from benzene to methane, depends on the basis set. The charge on methane is only −0.001 e (1 e = 1.602×10^{-19} C), if very large cc-pVQZ and cc-pV5Z basis sets are used. The amount of charge transfer is very small. Small basis sets such as MIDI!,[84] 6-31G, and 6-31G* considerably overestimate the charge transfer, and are inappropriate to evaluate it.

The calculated interaction energy of the benzene−methane complex (−1.45 kcal/mol) is about three times as large as that of the ethylene−methane complex (−0.49 kcal/mol).[85] The amount of attraction with an aromatic ring is larger than that with an isolated C═C bond. The considerable difference of the interaction energy is reasonable, if the major part of the attraction has its origin in dispersion interaction. Dispersion energy is approximately proportional to the number of interacting C···C pairs. The benzene−methane complex has six C···C pairs, while the ethylene−methane complex has only two.

Our calculations indicate that the major source of the attraction between benzene and methane is dispersion interaction.[12,86] Relatively small, but highly orientation-dependent electrostatic interaction controls the orientation of the C−H bond of methane. The short contact between the C−H bond and the π system is not the result of unusual attraction between them. The calculated atomic charge distributions and the shape of the intermolecular interaction potential suggest that charge transfer is not important for the attraction. Our finding has proved that careful evaluation of interaction energy by computational methods is very informative and therefore essential to explore the origin of the interaction.

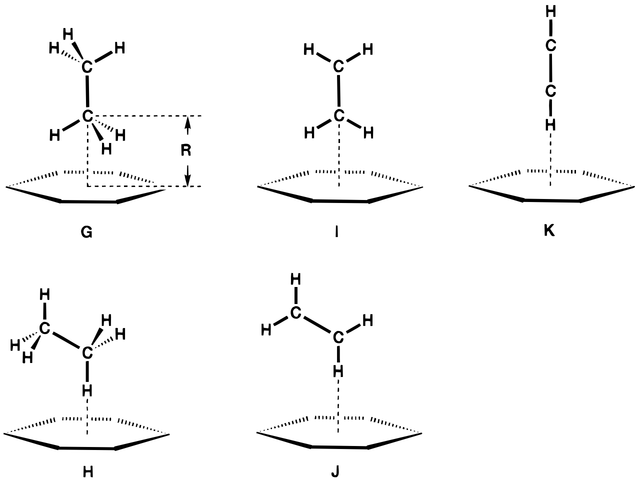

Figure 4. The geometries of the benzene−ethane, benzene−ethylene, and benzene−acetylene complexes considered in this work. The distance *R* (distance between the center of the benzene ring and the carbon atom of ethane, ethylene, and acetylene) is 3.6 Å for the complexes. The MP2/cc-pVTZ level interaction potentials had minima at these intermolecular distances (see Figure 5).

Interaction Energies of Benzene−Ethane, Benzene−Ethylene, and Benzene−Acetylene Complexes. The interaction energies of the five complexes (Figure 4) were calculated with 6-311G** and cc-pVXZ (X = D, T and Q) as summarized in Table 6. The intermolecular distances of the complexes correspond to the potential minima calculated at the MP2/cc-pVTZ level as shown in Figure 5. The basis set effect on the calculated interaction energies is close to that on benzene−methane complexes. The MP2 interaction energies of the complexes greatly depend on basis set. Electron correlation gives a large effect on the calculated interaction energies. The HF/cc-pVQZ interaction energies of the complexes G−K are 1.55, 1.80, 0.87, 1.17, and −0.57 kcal/mol, respectively. On the other hand, the MP2/cc-pVQZ energies of these complexes are −1.54, −2.20, −2.04, −2.41, and −3.22 kcal/mol, respectively. The considerable increase of the attraction by electron correlation indicates that dispersion interaction is again important in the attraction of these complexes. The calculated MP2/cc-pVTZ level potentials of the five complexes (Figure 5) are very flat near the minima as in the case of benzene−methane complexes.

The interaction energies of the complexes were calculated by the MP3, CCSD. and CCSD(T) methods with cc-pVDZ to evaluate the effect of electron correlation beyond MP2. The MP2 interaction energies are substantially larger (more negative) than the CCSD(T) as in the case of benzene−methane complexes (Table 7). The CCSD calculations underestimate the attraction compared with the CCSD(T) calculations.

The extrapolated MP2 interaction energies of the complexes at the basis set limit are −1.64, −2.33, −2.17, −2.57, and −3.36 kcal/mol, respectively. The estimated CCSD(T) energies at the limit are −1.33, −1.82, −1.76, −2.06, and −2.83, respectively. Benzene−ethane and benzene−ethylene complexes in which the C−H bond points toward the center of the benzene ring are more stable than the T-shaped ones. The calculated interaction energies of complexes H and J (−1.82 and −2.06 kcal/mol, respectively) are larger (more negative) than those of G and I (−1.33 and −1.76 kcal/mol, respectively). The correlation interaction energies (E_{corr}) are very large as summarized in Table 8. Dispersion interaction is again the major part of the attractions of these complexes.

The interaction energy of benzene−ethylene complex J (−2.06 kcal/mol) is larger (more negative) than that of benzene−

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Table 6. Calculated Interaction Energies of the $C_6H_6-C_2H_6$, $C_6H_6-C_2H_4$, and $C_6H_6-C_2H_2$ Complexes[a]

	$C_6H_6-C_2H_6$		$C_6H_6-C_2H_4$		$C_6H_6-C_2H_2$
method	G	H	I	J	L
HF/6-311G**	1.51 (0.41)	1.75 (0.51)	0.79 (0.39)	1.14 (0.52)	−0.65 (0.44)
HF/cc-pVDZ	1.52 (0.43)	1.77 (0.55)	0.80 (0.39)	1.14 (0.54)	−0.66 (0.45)
HF/cc-pVTZ	1.53 (0.16)	1.78 (0.20)	0.85 (0.16)	1.16 (0.20)	−0.61 (0.17)
HF/cc-pVQZ	1.55 (0.07)	1.80 (0.09)	0.87 (0.07)	1.17 (0.09)	−0.57 (0.07)
MP2/6-311G**	−0.72 (0.90)	−1.08 (1.59)	−1.23 (0.90)	−1.27 (1.52)	−2.25 (1.39)
MP2/cc-pVDZ	−0.57 (0.96)	−0.85 (1.43)	−1.07 (0.95)	−1.11 (1.38)	−2.17 (1.36)
MP2/cc-pVTZ	−1.32 (0.48)	−1.90 (0.64)	−1.79 (0.47)	−2.08 (0.63)	−2.96 (0.60)
MP2/cc-pVQZ	−1.54 (0.21)	−2.20 (0.29)	−2.04 (0.22)	−2.41 (0.29)	−3.22 (0.28)
E_{MP2}(limit)[b]	−1.64	−2.33	−2.17	−2.57	−3.36
$\Delta_{CCSD(T)}$[c]	0.31	0.51	0.41	0.51	0.53
$E_{CCSD(T)}$(limit)[d]	−1.33	−1.82	−1.76	−2.06	−2.83

[a] Energies in kcal/mol. BSSE corrected interaction energies. The values in parentheses are BSSE's. The geometries of the complexes are shown in Figure 4. [b] The estimated MP2 interaction energies at the basis set limit. See text. [c] Difference between the interaction energies calculated with the CCSD(T)/cc-pVDZ and MP2/cc-pVDZ methods. [d] The expected CCSD(T) interaction energies at the basis set limit. Sum of E_{MP2}(limit) and $\Delta_{CCSD(T)}$.

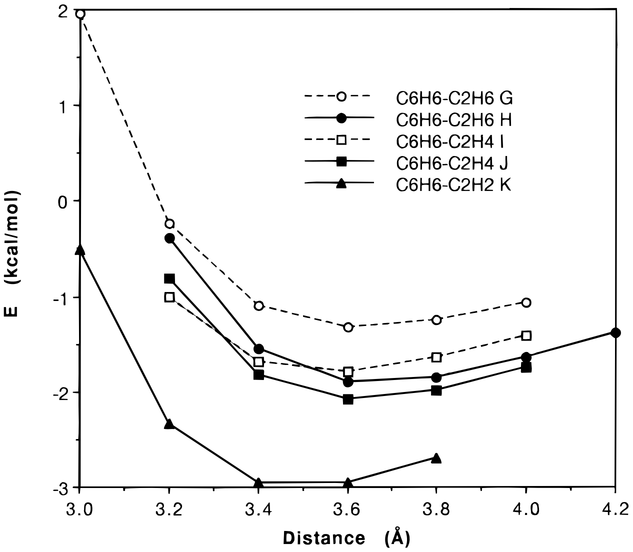

Figure 5. The MP2/cc-pVTZ intermolecular interaction potentials of the benzene−ethane, benzene−ethylene, and benzene−acetylene complexes.

Table 7. Interaction Energies of the $C_6H_6-C_2H_6$, $C_6H_6-C_2H_4$, and $C_6H_6-C_2H_2$ Complexes Calculated with Electron Correlation Correction by Several Methods[a]

complex		HF	MP2	MP3	CCSD	CCSD(T)
$C_6H_6-C_2H_6$	G	1.52	−0.57	−0.15	−0.02	−0.26
	H	1.77	−0.85	−0.21	−0.07	−0.35
$C_6H_6-C_2H_4$	I	0.80	−1.07	−0.56	−0.45	−0.66
	J	1.14	−1.11	−0.49	−0.35	−0.60
$HC_6H_6-C_2H_2$	K	−0.60	−2.17	−1.53	−1.47	−1.64

[a] Energies in kcal/mol. BSSE corrected interaction energies. The structures of the complexes are shown in Figure 4. The cc-pVDZ basis set was used.

Table 8. Electrostatic and Dispersion Energies of the $C_6H_6-C_2H_6$, $C_6H_6-C_2H_4$, and $C_6H_6-C_2H_2$ Complexes[a]

	$C_6H_6-C_2H_6$		$C_6H_6-C_2H_4$		$C_6H_6-C_2H_2$
energy	G	H	I	J	K
E_{total}[b]	−1.33	−1.82	−1.76	−2.06	−2.83
E_{es}[c]	0.34	−0.17	−0.34	−0.65	−2.01
E_{rep}[d]	1.21	1.97	1.21	1.82	1.44
E_{corr}[e]	−2.89	−3.62	−2.63	−3.22	−2.26

[a] Energies in kcal/mol. The geometries of the complexes are shown in Figure 4. [b] The expected CCSD(T) interaction energies at the basis set limit. See text and footnote *d* of Table 6. [c] The electrostatic interaction energies. See text. [d] The difference between the HF/cc-pV5Z interaction energy and E_{es}. [e] The difference between the E_{total} and HF/cc-pV5Z interaction energy.

ethane complex H (−1.82 kcal/mol). The interaction energy of benzene−acetylene complex K (−2.83 kcal/mol) is considerably larger than those of H and J. The larger attractive electrostatic interaction is mainly responsible for the larger attraction in the benzene−acetylene complex. The E_{es} values of complexes H, J, and K are −0.17, −0.65, and −2.01 kcal/mol, respectively. The E_{es} values of benzene−methane and benzene−ethane complexes are about 10% of the E_{corr} values. Dispersion interaction is mainly due to the attraction in these complexes. On the other hand, the large E_{es} values in benzene−ethylene and benzene−acetylene complexes show that electrostatic interaction is also important for the attraction in these complexes. The E_{es} of the benzene−acetylene complex (−2.01 kcal/mol) is comparable to the E_{corr} (−2.26 kcal/mol). The nature of the attraction of the unsaturated hydrocarbon molecules with the benzene is substantially different from that of the saturated hydrocarbon molecules. The C−H bonds of the unsaturated hydrocarbon molecules have larger bond dipoles. They should be the cause of the larger attractive electrostatic interactions. The electrostatic energy should depend on the bond dipole of the C−H bond, which suggests that an aliphatic C−H bond would have large attractive interaction with a benzene, if the bond is activated by electron withdrawing substituents attached to the carbon atom. The enhancement of the attraction by electron withdrawing substituents has been reported from NMR measurements of the formation constants of benzene and chlorinated methanes.[87]

Conclusion

Attraction between benzene and hydrocarbon molecules is considerably weaker than the hydrogen bond between waters. The calculated interaction energy of the benzene−methane complex (−1.45 kcal/mol) is about 30% of the hydrogen bonding energy of the water dimer. The calculated potential energy surface is very flat near the minimum, which indicates that the major source of the attraction is a long-range interaction.

Electron correlation greatly increases the calculated bonding energy, which indicates that dispersion interaction is the major source of the attraction in model complexes studied in this work. Electrostatic interaction is not essential for the attraction in benzene−methane complexes, which is considerably smaller than dispersion interaction. Although electrostatic interaction

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is not essential for the attraction, a highly orientation dependent electrostatic interaction determines the orientation of the C−H bond of methane. The calculated charge distributions and shape of the intermolecular interaction potential suggest that charge transfer is not important for the attraction.

Electrostatic interaction is very weak in benzene−methane and benzene−ethane complexes, while benzene−ethylene and benzene−acetylene complexes have stronger electrostatic interactions. Although dispersion interaction is the major source of the attraction, electrostatic interaction is also important for the attraction of the unsaturated hydrocarbon molecules with benzene.

Our calculations indicate that dispersion interaction is mainly responsible for the attraction between benzene and hydrocarbon molecules. Although the C−H bond prefers to point toward the benzene ring, this preference is not the result of unusual attraction between the C−H bond and the π system. The orientation of the C−H bond is controlled by relatively weak, but highly orientation dependent electrostatic interaction. Existence of a specific attractive interaction is sometimes assumed to explain experimentally observed short contacts in crystals. However, our finding has proved that careful evaluation of interaction energy by computational methods is very informative and therefore essential for exploring the origin of the interaction.

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