High-Level ab Initio Calculations of Interaction Energies of $C_2H_4-CH_4$ and $C_2H_6-CH_4$ Dimers: A Model Study of CH/π Interaction

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Intermolecular interaction energies of five $C_2H_4-CH_4$ dimers and two C_2H_6-CH_4 dimers were calculated. Dunning's correlation consistent basis sets (cc-pVXZ, X = D, T, Q, and 5) were used to estimate the MP2 interaction energies of the dimers at the basis set limit. The dimer in which the C−H bond of CH_4 points to the C=C bond of C_2H_4 has slightly larger bonding energy than the other four $C_2H_4-CH_4$ dimers. The estimated CCSD(T) interaction energy of this dimer at the basis set limit is −0.49 kcal/mol, which is about 10% of the bonding energy of water dimer. The large correlation interaction energy (−0.86 kcal/mol), calculated as the difference between the HF and post-SCF interaction energies, suggests that the dispersion interaction is significantly important for the attraction between C_2H_4 and CH_4. The analysis of the electrostatic interaction using distributed multipoles shows that the attractive electrostatic interaction (−0.24 kcal/mol) is playing important role to stabilize this dimer. On the other hand, the electrostatic interaction is negligible for the $C_2H_6-CH_4$ dimers. The C−H bond of CH_4 does not prefer to point to the C−C bond of C_2H_6.

I. Introduction

The attractive interaction between C−H bond and π-system has attracted much interest in several fields of chemistry.[1] This CH/π interaction was first proposed about 20 years ago to explain the preference of the conformation of benzyl *tert*-butyl sulfoxide in which bulky *tert*-butyl and phenyl groups had a close contact.[2] The close contact of alkyl and phenyl groups was also observed in the stable conformations of other molecules.[3−10] Crystal structure analysis and spectroscopic measurements of supramolecules suggested that the CH/π interaction was important for molecular recognition.[11−14] Recently reported analysis of the crystal structure database showed that more than 35% of organic crystals had a short contact of the C−H bond with the π-system,[15] suggesting that the CH/π interaction is also important for the determination of crystal packing. The close contact of the C−H bond and π-system is also commonly found in crystal structures of proteins.[1] Crystal structures of sugar binding proteins show that carbohydrate ligands are sandwiched by aromatic side chains of protein,[16−20] suggesting that the CH/π interaction is playing an important role for molecular recognition.

The attraction of aromatic, ethylenic, and acetylenic C−H bonds with π-system was explained by the electrostatic interaction between the C−H bonds and π system.[21−24] These sp and sp^2 C−H bonds have substantial bond dipoles. These bond dipoles have attractive electrostatic interactions with the π-system. Stable structures of acetylene dimer and benzene dimer were explained by the favorable configurations of two interacting quadrupoles (T-shape and slipped parallel structures).[23,24] Although the close contact of the aliphatic (sp^3) C−H bond and π-system was also observed,[2−10] the origin of the attraction between aliphatic C−H bond and π-system is still not certain.

The accurate evaluation of the interaction energy of the CH/π interaction is important for the understanding of molecular conformation, crystal packing, and mechanism of molecular recognition. Accurate interaction energy is also desired by those who carry out force field simulations of these systems. Although a lot of experimental measurements have been reported which support the existence of the attraction between the aliphatic C−H bond and π-system, it is still difficult to estimate the accurate interaction energy only from experimental measurements.

A few theoretical calculations were carried out to estimate the interaction energies of model complexes. Kodama et al. reported CNDO/2 calculations of the $C_6H_6-CH_4$ dimer.[2] Takagi et al. reported HF calculations of $C_2H_4-CH_4$ and $C_2H_6-CH_4$ dimers with 4-31G and MIDI4*(*) basis sets.[25] Although these calculations were impressive when they were reported, the basis sets used in these calculations were too small to evaluate the interaction energies quantitatively. Recently reported calculations of small hydrocarbon molecules show that the calculated intermolecular interaction energies considerably depend on the choice of the basis set[26−29] and electron correlation[30−32] and that a large basis set and appropriate electron correlation correction are necessary to accurately evaluate the interaction energies.

In this study, we carried out high-level ab initio calculations of a few orientations of $C_2H_4-CH_4$ and $C_2H_6-CH_4$ dimers to estimate the intermolecular interaction energies. We carried out MP2 calculations with Dunning's correlation consistent basis sets and estimated the interaction energies at the basis set limit. In addition, we carried out CCSD(T) calculations to estimate the effect of electron correlation beyond the MP2 method. We discuss the role of the electrostatic, dispersion, and charge-transfer interactions in the attraction between the aliphatic C−H bond and π-system.

II. Computational Method

The Gaussian 94 program[33] was used for the ab initio molecular orbital calculations. The 6-311G**[34] and cc-pVXZ

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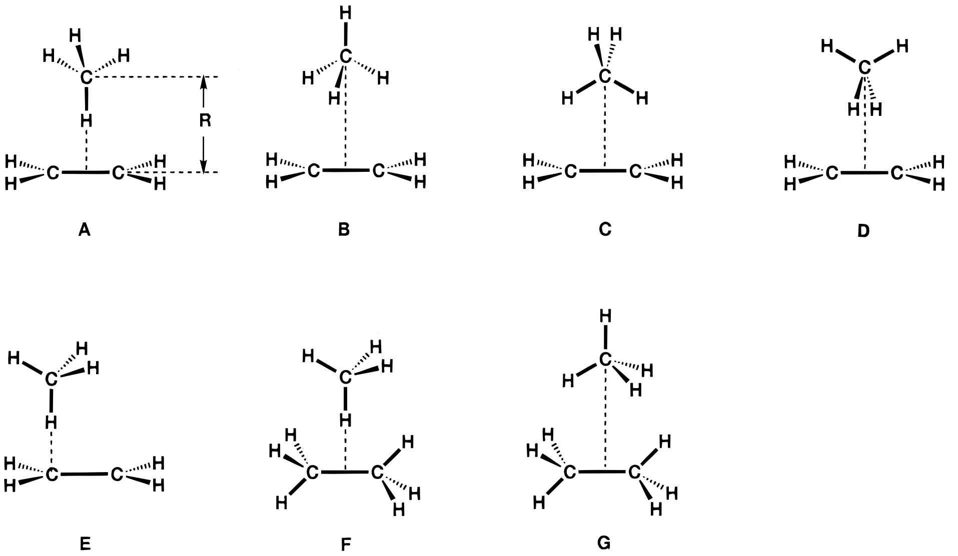

Figure 1. Geometries of the dimers considered in this work. The intermolecular distance $R = 3.8$ Å for the dimers B and G, and 4.2 Å for the other dimers. The MP2/cc-pVQZ level interaction potentials had minima at these intermolecular distances.

TABLE 1: Interaction Energies of the Dimers Calculated with Electron Correlation Correction by Several Methods[a]

dimer	HF	MP2	MP3	CCSD	CCSD(T)
$C_2H_4-CH_4$					
A	0.34	−0.18	−0.14	−0.06	−0.12
B	0.74	0.05	0.09	0.16	0.09
C	0.36	−0.06	−0.05	0.00	−0.04
D	0.35	−0.03	−0.01	0.03	−0.01
E	0.31	−0.18	−0.14	−0.07	−0.13
$C_2H_6-CH_4$					
F	0.50	−0.12	−0.10	−0.03	−0.10
G	0.63	−0.14	−0.11	−0.04	−0.12

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

TABLE 2: MP2/cc-pVQZ Interaction Energies of the Dimers[a]

distance (Å)	$C_2H_4-CH_4$					$C_2H_6-CH_4$	
	A	B	C	D	E	F	G
3.6		−0.279					
3.8	−0.162	−0.377	−0.244	−0.221	−0.223	−0.100	−0.529
4.0	−0.425	−0.373	−0.336	−0.316	−0.426	−0.395	−0.648
4.2	−0.490	−0.329	−0.337	−0.321	−0.467	−0.467	−0.614
4.4	−0.465		−0.301	−0.289	−0.436	−0.442	−0.526

[a] Energies in kcal/mol. BSSE-corrected interaction energies. The structures of the dimers are shown in Figure 1.

(X = D, T, Q, and 5)[35,36] and aug-cc-pVXZ (X = D, T, and Q)[37] basis sets were used. The electron correlation energies were calculated by the second-order Møller−Plesset perturbation method (MP2)[38,39] and by the coupled cluster method using single and double substitutions with noniterative triple excitations (CCSD(T)).[40,41] The geometries of the monomer molecules were optimized at the MP2/6-31G* level[42] and were used for the dimer calculations. The basis set superposition error (BSSE)[43] was corrected by the counterpoise method.[44] The interaction energies at the basis set limit were estimated by the method proposed by Feller.[45] The distributed multipoles[24,46] were obtained from the HF/6-311G** wave functions of isolated molecules using CADPAC version 6.[47] The electrostatic energies of the dimers were calculated as the interactions between the distributed multipoles using ORIENT version 3.2.[48,49]

III. Results and Discussion

A. Effect of Electron Correlation Correction. The interaction energies of the $C_2H_4-CH_4$ and $C_2H_6-CH_4$ dimers (Figure 1, dimers A−G) were calculated by the HF, MP2, MP3, CCSD, and CCSD(T) methods with the cc-pVDZ basis set to evaluate the effect of the electron correlation correction. The calculated interaction energies are summarized in Table 1. The intermolecular distances of the dimers correspond to the potential minima calculated at the MP2/cc-pVQZ level as shown in Table 2. The HF calculations considerably underestimate the attraction compared with the correlated calculations. The correlation interaction energy, corresponding to the difference between the HF and post-SCF interaction energies, is mainly the attractive dispersion interaction.[30] The large correlation interaction energies suggest that the dispersion interaction stabilizes the dimers considerably. The effect of the further improved treatment of the electron correlation corrections beyond the MP2 method is not large. Slightly larger attraction is given by the MP2 calculations compared with the CCSD(T) calculations. The MP3 interaction energies are close to the CCSD(T) ones. The CCSD calculations always underestimate substantially the attraction compared with the CCSD(T) calculations.

B. Effect of Basis Set. The interaction energies of the $C_2H_4-CH_4$ and $C_2H_6-CH_4$ dimers (Figure 1) were calculated with the 6-311G** and Dunning's correlation consistent basis sets to evaluate the effect of basis set. The HF interaction energies of the dimers, which are approximately the sum of the exchange-repulsion and electrostatic energies, are not largely basis set dependent as summarized in Table 3. The HF interaction energies of the dimer A with five different basis sets are very close to each other, as shown in Figure 2. The small basis set dependence of the HF interaction energies has also been reported in the calculations of interaction energies of CH_4, C_2H_6, and C_2H_4 homo dimers.[26,28]

The MP2 interaction energies of the dimers greatly depend on the basis sets. The small cc-pVDZ and 6-311G** basis sets (82 and 102 basis functions for the $C_2H_4-CH_4$ dimer, respectively) considerably underestimate the attraction compared with the large cc-pVQZ and cc-pV5Z basis sets (405 and 713 basis functions, respectively) as shown in Figure 2. The MP2/cc-pVDZ interaction energies of the dimers A−E (Figure 1) are −0.18, 0.05, −0.06, −0.03, and −0.18 kcal/mol, respectively.

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

	$C_2H_4-CH_4$					$C_2H_6-CH_4$	
method	A	B	C	D	E	F	G
HF/6−311G**	0.32 (0.27)	0.75 (0.31)	0.36 (0.26)	0.36 (0.28)	0.29 (0.25)	0.48 (0.03)	0.62 (0.05)
HF/cc−pVDZ	0.34 (0.30)	0.74 (0.36)	0.36 (0.28)	0.35 (0.30)	0.31 (0.28)	0.50 (0.05)	0.63 (0.07)
HF/cc−pVTZ	0.35 (0.10)	0.74 (0.13)	0.35 (0.09)	0.33 (0.10)	0.32 (0.09)	0.50 (0.02)	0.63 (0.03)
HF/cc−pVQZ	0.36 (0.04)	0.74 (0.05)	0.35 (0.03)	0.34 (0.04)	0.33 (0.04)	0.49 (0.00)	0.63 (0.00)
HF/cc−pV5Z	0.37 (0.00)	0.74 (0.00)	0.36 (0.00)	0.34 (0.00)	0.34 (0.00)		
MP2/6−311G**	−0.23 (0.42)	0.00 (0.44)	−0.10 (0.31)	−0.06 (0.34)	−0.22 (0.39)	−0.17 (0.18)	−0.21 (0.26)
MP2/cc−pVDZ	−0.18 (0.49)	0.05 (0.48)	−0.06 (0.35)	−0.03 (0.35)	−0.18 (0.46)	−0.12 (0.25)	−0.14 (0.34)
MP2/cc−pVTZ	−0.41 (0.18)	−0.26 (0.23)	−0.26 (0.13)	−0.24 (0.15)	−0.39 (0.17)	−0.38 (0.09)	−0.51 (0.13)
MP2/cc−pVQZ	−0.49 (0.07)	−0.38 (0.09)	−0.34 (0.05)	−0.32 (0.06)	−0.47 (0.07)	−0.47 (0.04)	−0.65 (0.05)
MP2/cc−pV5Z	−0.53 (0.03)	−0.43 (0.03)	−0.37 (0.02)	−0.36 (0.02)	−0.50 (0.02)		
E_{MP2}(limit)[b]	−0.54	−0.47	−0.39	−0.38	−0.52	−0.52	−0.73
ΔCCSD(T)[c]	0.06	0.03	0.02	0.02	0.05	0.02	0.02
$E_{CCSD(T)}$(limit)[d]	−0.49	−0.43	−0.37	−0.36	−0.47	−0.50	−0.71

[a] Energies in kcal/mol. BSSE-corrected interaction energies. The values in parentheses are BSSE's. The geometries of the dimers are shown in Figure 1. [b] 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] Expected CCSD(T) interaction energies at the basis set limit. Sum of E_{MP2}(limit) and ΔCCSD(T).

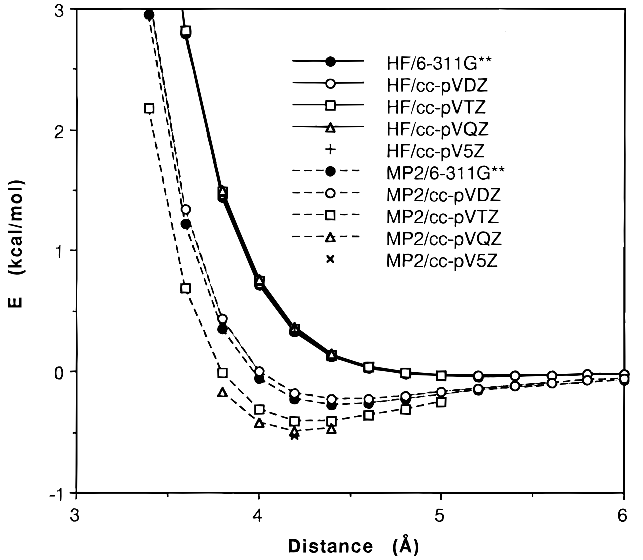

Figure 2. HF and MP2 intermolecular interaction potentials of the $C_2H_4-CH_4$ dimer A calculated with several basis sets.

Those calculated at the MP2/cc-pV5Z level are −0.53, −0.43, −0.37, −0.36 and −0.50 kcal/mol, respectively. The small basis sets also underestimate the attractive interactions in the $C_2H_6-CH_4$ dimers. It has also been reported that small basis sets such as cc-pVDZ and 6-31G* considerably underestimate the attractive interactions of small hydrocarbon molecules.[28,29] Small basis sets considerably underestimate molecular polarizability and attractive interaction.[28] A large flexible basis set with multiple polarization functions is necessary to accurately evaluate attractive interaction of hydrocarbon molecules.[28−30]

We have calculated the interaction energies of the dimers A and B using aug-cc-pVXZ basis sets (X = D, T, and Q)[37] to evaluate the effect of the augmentations of the diffuse functions. The calculated MP2 interaction energies of the dimer A using these basis sets are −0.43, −0.52 and −0.54 kcal/mol, respectively. Those of the dimer B are −0.35, −0.43, and −0.45 kcal/mol, respectively. The MP2 interaction energies of the dimer A with the cc-pVXZ basis sets (X = D, T, and Q) are −0.18, −0.41 and −0.49 kcal/mol, respectively. Those of the dimer B are 0.05, −0.26 and −0.38 kcal/mol, respectively. The augmentation of the diffuse functions to the cc-pVDZ and cc-pVTZ basis sets substantially increases the attraction. On the other hand, the effects of the augmentation to the cc-pVQZ basis set are not significant.

TABLE 4: Basis Set Effects on the Calculated HF, MP2, MP3, CCSD, and CCSD(T) Interaction Energies of the $C_2H_4-CH_4$ Dimer (A)[a]

basis set	HF	MP2	MP3	CCSD	CCSD(T)	ΔCCSD(T)[b]
6-31G*	0.28	−0.11	−0.10	−0.03	−0.07	0.04
6-311G*	0.32	−0.18	−0.16	−0.08	−0.13	0.05
6-311G**	0.32	−0.23	−0.19	−0.10	−0.17	0.06
cc-p-VDZ	0.34	−0.18	−0.14	−0.06	−0.12	0.06
cc-p-VTZ	0.35	−0.41	−0.36	−0.24	−0.34	0.07
cc-p-VQZ	0.36	−0.49				
cc-p-V5Z	0.37	−0.53				
aug(d,p)-6-311G**[c]	0.35	−0.46	−0.42	−0.31	−0.42	0.04
aug(df,pd)-6-311G**[d]	0.36	−0.50	−0.46	−0.34	−0.46	0.04

[a] Energies in kcal/mol. BSSE-corrected interaction energies. The geometry of the C_2H_4-CH_4 dimer A is shown in Figure 1. [b] Difference between the interaction energies calculated with the CCSD(T) and MP2 methods. [c] 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 ($\alpha_d(C) = 0.1565$ and $\alpha_p(H) = 0.1875$). [d] aug(df,pd)-6-311G** basis set is the aug(d,p)-6-311G** basis set further augmented with diffuse f functions on carbon atoms and diffuse d functions on hydrogen atoms ($\alpha_f(C) = 0.2$ and $\alpha_d(H) = 0.25$) .

The electron correlation correction gives a large effect on the calculated interaction energies of the five $C_2H_4-CH_4$ dimers. The HF interaction energies of the dimers A−E calculated with cc-pV5Z are 0.37, 0.74, 0.36, 0.34, and 0.34 kcal/mol, respectively. The MP2 correlation interaction energies, corresponding to the difference between the MP2 and HF interaction energies, of the five dimers calculated with cc-pV5Z are −0.90, −1.17, −0.73, −0.70, and −0.84 kcal/mol, respectively. The large correlation interaction energies suggest the importance of the attractive dispersion interaction.

The basis set effects on the MP3, CCSD, and CCSD(T) interaction energies were also evaluated. The aug(d,p)-6-311G** and aug(df,pd)-6-311G** basis sets[50,51] were also used for the calculations. These basis sets are the 6-311G** basis sets augmented with diffuse polarization function. Although these basis sets employ smaller numbers of basis functions, the calculated MP2 interaction energies of hydrocarbon molecules with these basis sets are close to those with the cc-pVQZ and cc-pV5Z basis sets.[50] The calculated interaction energies of the $C_2H_4-CH_4$ dimer A are summarized in Table 4. The basis set effects on the MP3, CCSD, and CCSD(T) interaction energies are similar to that on the MP2 ones. Small basis sets such as the 6-31G* and cc-pVDZ basis sets considerably underestimate the attraction. The calculations indicate that the CCSD(T) correction (ΔCCSD(T), the difference between the CCSD(T)

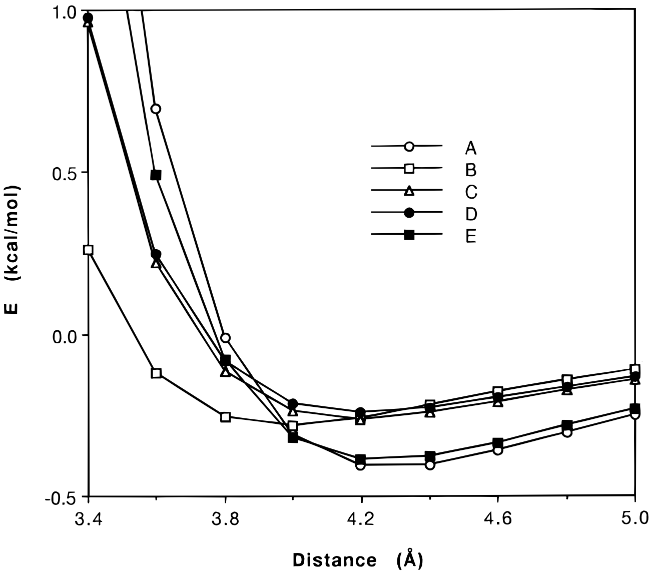

Figure 3. MP2/cc-pVTZ intermolecular interaction potentials of the five $C_2H_4-CH_4$ dimers.

and MP2 interaction energies) has very small basis set dependence. The calculated ΔCCSD(T) are 0.04−0.07 kcal/mol.

C. Interaction Energies at the Basis Set Limit. The MP2 intermolecular interaction energies of the dimers (Figure 1) at the basis set limit were estimated by extrapolating to the basis set limit with fitting to the form $a + b\ \exp(-cX)$ (where X is 2 for cc-pVDZ, 3 for cc-pVTZ, etc).[45] The estimated MP2 interaction energies of the dimers A−E at the basis set limit ($E_{\mathrm{MP2(limit)}}$) are −0.54, −0.47, −0.39, −0.38, and −0.52 kcal/mol, respectively, as summarized in Table 3. These values are not largely different from those calculated with cc-pV5Z, indicating that the cc-pV5Z basis set is close to the saturation.

The MP2 interaction energies at the basis set limit were also estimated from the calculated interaction energies using the augmented basis sets (aug-cc-pVXZ, X = D, T, and Q). The estimated interaction energies of the $C_2H_4-CH_4$ dimers A and B at the basis set limit are −0.55 and −0.47 kcal/mol, respectively. These values are very close to those obtained from the calculated interaction energies using the cc-pVXZ (X = D, T, Q, and 5) basis sets (−0.54 and −0.47 kcal/mol, respectively). Although the augmentation of the diffuse functions to the cc-pVDZ and cc-pVTZ basis sets substantially increases the calculated attractive interaction, the extrapolated values at the basis set limit using the aug-cc-pVXZ basis sets are close to those using the not augmented cc-pVXZ basis sets.

The CCSD(T) corrections (ΔCCSD(T)), corresponding to the difference between the MP2 and CCSD(T) interaction energies calculated with cc-pVDZ are not large. They are 0.06, 0.03, 0.02, 0.02, and 0.05 kcal/mol, respectively. The expected CCSD(T) interaction energies of the dimers at the basis set limit (the sum of the $E_{\mathrm{MP2(limit)}}$ and ΔCCSD(T)) are −0.49, −0.43, −0.37, −0.36 and −0.47 kcal/mol, respectively. The calculated bonding energy (0.49 kcal/mol) is about 10% of the bonding energy of water dimer.[45,52−55] The calculations show that the interaction between aliphatic C−H bond and π-system is very weak.

D. Intermolecular Interaction Potentials of the Dimers. The intermolecular interaction energies of the five $C_2H_4-CH_4$ dimers were calculated at the MP2/cc-pVTZ level with changing the intermolecular distance as shown in Figure 3. The calculated potentials are very flat near the potential minima, showing the looseness of the interaction between the aliphatic C−H bond and π-system. The calculated potentials of the dimers A and E have deeper minima than those of the other dimers. But the potentials of the dimers A and E are steeper in the region of short intermolecular distance, apparently due to shorter contact of the hydrogen atoms with the C=C bonds. The potential of the dimer B has a shorter intermolecular distance at the potential minimum than the other potentials. The CH_4 molecule in the dimers A, B, and E (Figure 1) are rotated 30° along the C−H bond which is perpendicular to the C_2H_4 plane. The HF and MP2 interaction energies of these dimers were calculated with the cc-pVXZ (X = D, T, and Q) basis sets. The rotation of CH_4 has a negligible effect on the calculated interaction energies. The changes are less than 0.01 kcal/mol.

TABLE 5: Electrostatic and Dispersion Energies of the Dimers[a]

	$C_2H_4-CH_4$					$C_2H_6-CH_4$	
energy	A	B	C	D	E	F	G
E_{total}[b]	−0.49	−0.43	−0.37	−0.36	−0.47	−0.50	−0.71
E_{es}[c]	−0.24	0.20	0.08	0.06	−0.17	0.00	−0.04
E_{rep}[d]	0.61	0.54	0.28	0.28	0.51	0.49[f]	0.67[f]
E_{corr}[e]	−0.86	−1.17	−0.73	−0.70	−0.80	−0.99[g]	−1.36[g]

[a] Energies in kcal/mol. The geometries of the dimers are shown in Figure 1. [b] Expected CCSD(T) interaction energies at the basis set limit. See text and footnote *d* of Table 3. [c] Electrostatic interaction energy. See text. [d] The difference between the HF/cc-pV5Z interaction energy and E_{es}. [e] The difference between the $E_{\mathrm{CCSD(T)}}$(limit) and HF/cc-pV5Z interaction energy. [f] The difference between the HF/cc-pVQZ interaction energy and E_{es}. [g] The difference between the $E_{\mathrm{CCSD(T)}}$(limit) and HF/cc-pVQZ interaction energy.

E. Roles of Electrostatic, Dispersion, and Charge-Transfer Interactions. The calculated interaction energies of the five $C_2H_4-CH_4$ dimers A−E (−0.36 to −0.49 kcal/mol) are close to each other. The small difference of the bonding energies of the dimers A−D shows that the CH4 molecule can change the direction of the C−H bond with very small change of the bonding energy. The calculated energy difference between the dimers A and E is only 0.02 kcal/mol, showing that the potential energy surface is very flat with respect to the motion of CH_4 molecule parallel to the C=C bond. These results show the looseness of the interaction between the aliphatic C−H bond and π-system. The calculated bonding energy of the dimer A (0.49 kcal/mol) is slightly larger than those of the dimers B, C, and D (0.36−0.43 kcal/mol). This result agrees well with the experimental observation that the C−H bond prefers to point to the π-system.[15,56]

In order to understand the nature of the interactions between C_2H_4 and CH_4, electrostatic and correlation interaction energies were analyzed as summarized in Table 5. E_{es} is the electrostatic interaction energy calculated with the distributed multipoles obtained from the HF/6-311G** wave functions of isolated molecules. E_{es}'s of the dimer A calculated with distributed multipoles obtained from several HF wave functions are shown in Figure 4. The basis set dependence of the calculated E_{es} is very small.

The inclusion of electron correlation correction on the wave function of an isolated molecule sometimes has significant effect on the calculated dipole moment.[57,58] The inclusion of electron correlation correction may affect largely the E_{es}'s of the dimers. The E_{es}'s of the $C_2H_4-CH_4$ dimers 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 correction. The calculated E_{es}'s are −0.20 and −0.17 kcal/mol, respectively. The E_{es}'s obtained from the HF/6-311G** distributed multipoles are −0.24 and 0.20 kcal/mol, respectively. The inclusion of the electron correlation correction decreases the absolute values of E_{es}'s only slightly.

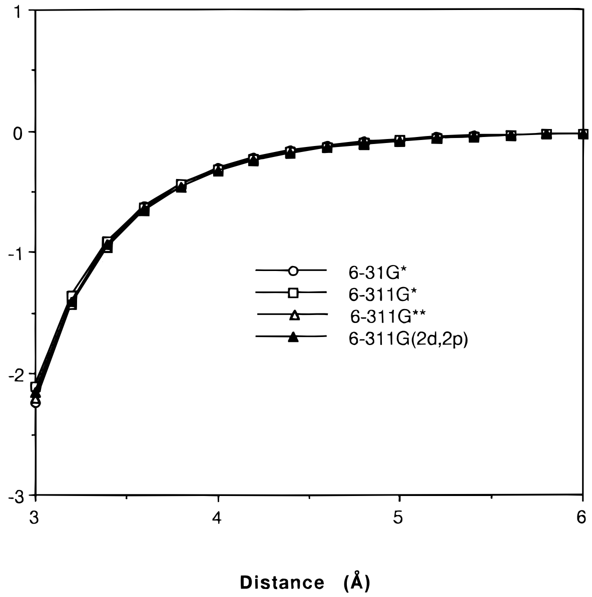

Figure 4. Electrostatic interaction potentials of the $C_2H_4-CH_4$ dimer A calculated with the distributed multipoles obtained from several HF wave functions.

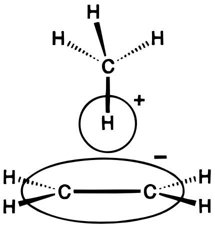

Figure 5. Electrostatic interaction between CH_4 and C_2H_4.

The HF interaction energy is approximately the sum of the exchange-repulsion and electrostatic energies. E_{rep} is the difference between the HF/cc-pV5Z interaction energy and E_{es}. Although E_{rep} is mainly the exchange-repulsion energy, E_{rep} also includes some other energy components. The correlation interaction energy (E_{corr}), the difference between the HF and post-SCF interaction energy, is mainly the attractive dispersion energy. E_{corr} is the difference between the estimated CCSD(T) interaction energy at the basis set limit and the HF/cc-pV5Z interaction energy.

E_{corr}'s of the dimers A−E are −0.70 to −1.17 kcal/mol. The large E_{corr}'s suggest that the stabilization by the attractive dispersion interaction is very large and that the dispersion interaction is playing a significantly important role in the attraction between C_2H_4 and CH_4 molecules. The E_{corr} of the dimer B (−1.17 kcal/mol) is substantially larger (more negative) than those of the other dimers, apparently due to the shorter intermolecular distance (3.8 Å) than those of the other four dimers (4.2 Å). The dimer A has the largest E_{rep} (0.61 kcal/mol), due to the short contact of the hydrogen atom with the C=C bond. The electrostatic energy greatly depends on the orientation of the dimer. E_{es} of the dimer B is repulsive (0.20 kcal/mol) and those of the dimers C and D are small (0.08 and 0.06 kcallmol, respectively) as shown in Table 5. On the other hand, E_{es} of the dimers A and E are attractive (−0.24 and −0.17 kcal/mol, respectively). We can understand why the electrostatic interaction is attractive in the dimer A. The C−H bonds of C_2H_4 have substantial bond dipoles. As a result, the region around the C=C bond is negatively charged as shown in Figure 5. CH_4 has an octopole moment,[24] which means that the C−H bonds have small bond dipoles. The small positive charge on the hydrogen atom has attraction with the negative charge around the C=C bond. E_{es}'s of the dimers F and G ($C_2H_6-CH_4$) are very small, suggesting that the electrostatic interaction is not important for the $C_2H_6-CH_4$ dimer. The calculated E_{es}'s of the $C_2H_4-CH_4$ and $C_2H_6-CH_4$ dimers with different intermolecular distances are shown in Figure 6.

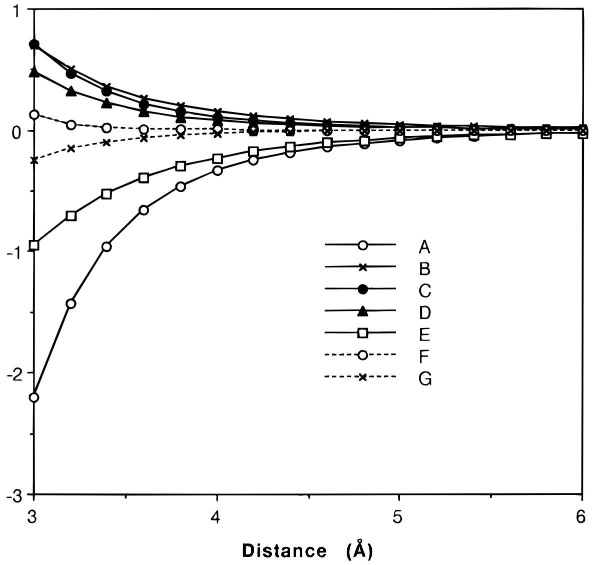

Figure 6. Electrostatic interaction of the dimers calculated with the distributed multipoles obtained from HF/6-311G** wave functions of isolated molecules.

Now we can understand why the $C_2H_4-CH_4$ dimer A, in which the C−H bond points to the C=C bond, is slightly more stable than the dimers B−D. The sum of E_{rep} and E_{corr} (approximately the sum of the exchange-repulsion and dispersion energies) favors the dimer B (−0.63 kcal/mol) to the dimer A (−0.25 kcal/mol). The smaller repulsion of the dimer B enables a shorter intermolecular distance and gives larger stabilization by the attractive dispersion interaction. The interaction energy of the tridentate dimer B is considerably larger (more negative) than that of the dimer A, if there exists no electrostatic interaction. However, the electrostatic interaction increases the relative stability of the dimer A compared with the dimer B. As a result, the total interaction energy (E_{total}) of the dimer A is slightly larger than that of the dimer B. These results show that the electrostatic interaction is playing an important role to determine the orientation of the C−H bond.

The comparison of the calculated interaction energies of the $C_2H_6-CH_4$ dimers F and G shows that the C−H bond of CH_4 does not prefer to point to the C−C bond of C_2H_6 in contrast with the $C_2H_4-CH_4$ dimer. The dimer G is more stable than the dimer F. The electrostatic interaction is negligible in the $C_2H_6-CH_4$ dimers. E_{rep} and E_{corr} determine the relative stability of these dimers. The smaller repulsion in the dimer G enables the shorter intermolecular distance and increases the stabilization by the dispersion interaction. The different conformational preference of the $C_2H_4-CH_4$ and $C_2H_6-CH_4$ dimers also shows that the electrostatic interaction is important to determine the orientation of the C−H bond in the $C_2H_4-CH_4$ dimer.

Charge-transfer interaction may be one of the possible sources of the attraction between the C−H bond and π-system.[1] Atomic charge distributions of the $C_2H_4-CH_4$ dimer A were obtained by Mulliken population analysis[59−61] and by the electrostatic potential (ESP) fitting with the Merz−Singh−Kollman scheme[62,63] to evaluate the amount of charge transfer from ethylene to methane. The calculated charges on CH_4 (sum of the atomic

TABLE 6: Calculated Charges on CH_4 in the $C_2H_4-CH_4$ dimer (A)[a]

basis set	Mulliken[b]		esp[c]	
	HF	MP2	HF	MP2
4-31G	−0.012	−0.012	−0.013	−0.013
6-31G	−0.010	−0.010	−0.011	−0.011
6-31G*	−0.010	−0.010	−0.011	−0.011
6-311G*	−0.007	−0.007	−0.008	−0.008
6-311G**	−0.010	−0.009	−0.008	−0.008
cc-pVDZ	−0.009	−0.009	−0.009	−0.009
cc-pVTZ	−0.006	−0.006	−0.004	−0.005
cc-pVQZ	−0.004	−0.005	−0.003	−0.004
cc-pV5Z	−0.001	−0.001	−0.002	

[a] The geometry of the C_2H_4-CH_4 dimer A is shown in Figure 1. [b] The total charge of methane obtained from the atomic charge distributions with Mulliken population analysis. [c] The total charge of methane obtained from the atomic charge distributions with Merz−Singh−Kollman scheme electrostatic potential fitting.

charges) are summarized in Table 6. The Mulliken and ESP charges are very close. The effects of electron correlation are very small. The calculated negative charge on CH_4, which corresponds to charge transfer from C_2H_4 to CH_4, is highly basis set dependent. The increase of the basis set size from cc-pVDZ to cc-pV5Z considerably decreases the negative charge. The calculated charge on CH_4 is only −0.001 to −0.002, if a very large cc-pV5Z basis set is used. On the other hand, the smaller basis sets in Table 6 overestimate the negative charge. The negative charge calculated with the cc-pVDZ is −0.009. Similar amount of negative charges were also calculated with the Pople's basis sets in Table 6. These calculations indicate that the amount of charge-transfer is very small. The observed considerable overestimation of charge transfer with small basis sets indicates that a very large basis set must be used to study charge transfer.

IV. Conclusion

We have presented high-level ab initio calculations of the bonding energies of $C_2H_4-CH_4$ dimers as a model of CH/π interaction. The calculated bonding energy (0.49 kcal/mol) is only about 10 % of the bonding energy of water dimer. The calculated potential is very shallow near the minimum with respect to the rotation and translation of CH_4, showing the looseness of the CH/π interaction. The calculations show that the geometry in which the C−H bond of CH_4 points to the C═C bond of C_2H_4 (dimer A) has slightly larger bonding energy than the other dimers. The correlation interaction energy, corresponding to the difference between the HF and post-SCF interaction energies, is −0.86 kcal/mol, suggesting that the dispersion interaction is significantly important for the attraction between C_2H_4 and CH_4. Although the electrostatic interaction (−0.24 kcal/mol) is not large, it is playing an important role to stabilize the dimer in which the C−H bond points to the C═C bond. The interaction is negligible in $C_2H_6-CH_4$ dimers. The C−H bond of CH_4 does not prefer to point to the C−C bond of C_2H_6, which also suggests that the electrostatic interaction is important to determine the conformational preference of the $C_2H_4-CH_4$ dimer. The atomic charge distribution of the $C_2H_4-CH_4$ dimer calculated with the cc-pV5Z basis set shows that the charge transfer from C_2H_4 to CH_4 is very small.

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(49) The multipole expansion of electrostatic interaction converges only if the charge distributions are far enough apart. The multipole approximation can be unreliable if the separation between the two interacting molecules is very small. To avoid this problem we have used distributed multipoles model instead of a conventional single site multipole model, in which multipoles is given on the center of gravity of a molecule to represent the charge distribution of the whole molecule. In the distributed multipoles model the molecule is divided into regions, each enclosing a single atom. The charges in each region is represented by the multipoles given on the atom in the region. The distributed multipoles model decreases the convergence sphere significantly, which enables us to obtain accurate electrostatic interaction even in short intermolecular separation. (ref 24).

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