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Origin of Attraction and Directionality of the π/π Interaction: Model Chemistry Calculations of Benzene Dimer Interaction

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Abstract: A model chemistry for the evaluation of intermolecular interaction between aromatic molecules (AIMI Model) has been developed. The CCSD(T) interaction energy at the basis set limit has been estimated from the MP2 interaction energy near the basis set limit and the CCSD(T) correction term obtained by using a medium size basis set. The calculated interaction energies of the parallel, T-shaped ,and slipped-parallel benzene dimers are −1.48, −2.46, and −2.48 kcal/mol, respectively. The substantial attractive interaction in benzene dimer, even where the molecules are well separated, shows that the major source of attraction is not short-range interactions such as charge-transfer but long-range interactions such as electrostatic and dispersion. The inclusion of electron correlation increases attraction significantly. The dispersion interaction is found to be the major source of attraction in the benzene dimer. The orientation dependence of the dimer interaction is mainly controlled by long-range interactions. Although electrostatic interaction is considerably weaker than dispersion interaction, it is highly orientation dependent. Dispersion and electrostatic interactions are both important for the directionality of the benzene dimer interaction.

Introduction

The intermolecular interaction of benzene has been studied extensively, especially in the last two decades, both by experimental[1−15] and theoretical[16−41] methods as a prototype for the π/π interaction.[42−62] The importance of the attraction between π systems has been stressed repeatedly in many fields of

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chemistry from molecular biology to material design. The π/π interaction influences the three-dimensional structures of biological systems such as protein and DNA,[43,44,52,56,58,63,64] and is important for the crystal packing of organic molecules containing aromatic rings such as nonlinear optical materials.[62,65,66] This is also important for molecular recognition processes in biological and artificial systems.[50,53,59−61,67−70] Detailed information on the benzene dimer interaction is essential for the understanding of the π/π interaction. An accurate potential energy surface for the benzene dimer is also needed by those who carry out force field simulations of these systems.[5,30,31,35] Although several experimental measurements have been reported on the benzene dimer interaction, it is still difficult to determine accurately the potential energy surface for the benzene dimer from experimental measurements only.

Many ab initio calculations of the benzene dimer have been reported in the literature.[16−27] These calculations were mainly focused on the structure and binding energy. Recent calculations showed that the dimer has two nearly isoenergetic structures (T-shaped and slipped-parallel) and the binding energy is about 2 kcal/mol.[22,26] Despite the extensive studies on the dimer interaction in benzene, there still remain unsettled issues: (1) What is the major source of attraction in the benzene dimer? (2) What is the origin of the directionality of the benzene dimer interaction? The importance of electrostatic interaction in the formation of the benzene dimer has been pointed out repeatedly.[29,71] On the other hand, recent ab initio calculations emphasized the importance of dispersion interaction.[22,26] The directionality of the intermolecular interaction has sometimes been explained by considering the interaction between molecular orbitals,[72] while the importance of electrostatic (quadrupole-quadrupole) interaction in the benzene dimer has also been suggested.[29,71] Unfortunately, however, these issues have not yet been settled. In this paper, we have analyzed the benzene dimer interaction by high-level ab initio calculations and have discussed the roles of electrostatic, dispersion, and charge-transfer interactions in attraction and directionality of the π/π interaction.

Previous ab initio calculations of the benzene dimer show the strong basis set dependence of the calculated interaction energy.[18−27] Small basis sets underestimate the molecular polarizability and thereby the dispersion interaction considerably. The second-order Møller−Plesset perturbation (MP2) method[73,74] was employed for electron correlation correction in early calculations. However, recent coupled cluster calculations with single and double substitutions with noniterative triple excitations (CCSD(T))[75,76] show that the MP2 calculations overestimate the attraction by as much as 30 and 92%, respectively, in the T-shaped and parallel benzene dimers compared to the CCSD(T) results.[22] Similar overestimation of interaction energy at the MP2 level was also reported for naphthalene dimer.[26] Apparently the MP2 method is not appropriate for studying the interaction between aromatic molecules.

The requirement of the computationally demanding CCSD(T) calculation with a very large basis set is the major obstacle of studying intermolecular interaction between aromatic molecules by ab initio methods. It is not an easy task for present computers to obtain the intermolecular interaction energy between aromatic molecules at the CCSD(T) level with use of a very large basis set near saturation. The development of a computationally less demanding model chemistry for the evaluation of the intermolecular interaction energy between aromatic molecules is, therefore, needed. To this end, we have proposed three levels of the model chemistry AIMI (Aromatic Inter-Molecular Interaction) model for this purpose. We have evaluated the accuracy of these proposed models and have shown that the AIMI models provide sufficiently accurate interaction energy of the benzene dimer using moderate size computer resources. We have estimated the interaction energies of parallel, T-shaped, and slipped-parallel benzene dimers at the CCSD(T) level near the basis set limit using the AIMI models.

Computational Method

The Gaussian 98 program[77] was used for the ab initio molecular orbital calculations to evaluate total interaction energies. The basis sets implemented in the Gaussian program and a few modified basis sets were used. Electron correlation was accounted for at the MP2[73,74] and CCSD(T)[75,76] levels. The geometry of an isolated benzene molecule was optimized at the MP2/6-31G* level, and was used for the calculations of dimers. The basis set superposition error (BSSE)[78] was corrected for all calculations with the counterpoise method.[79] The MP2 interaction energies at the basis set limit were estimated by the method proposed by Feller.[80] Distributed multipoles[71,81] were obtained from the MP2/6-311G** wave functions of an isolated benzene with CADPAC version 6.[82] The electrostatic and induction energies of the dimers were calculated with ORIENT version 3.2.[83] The electrostatic energies of the dimers were calculated as interactions between distributed multipoles of monomers. The induction energies were

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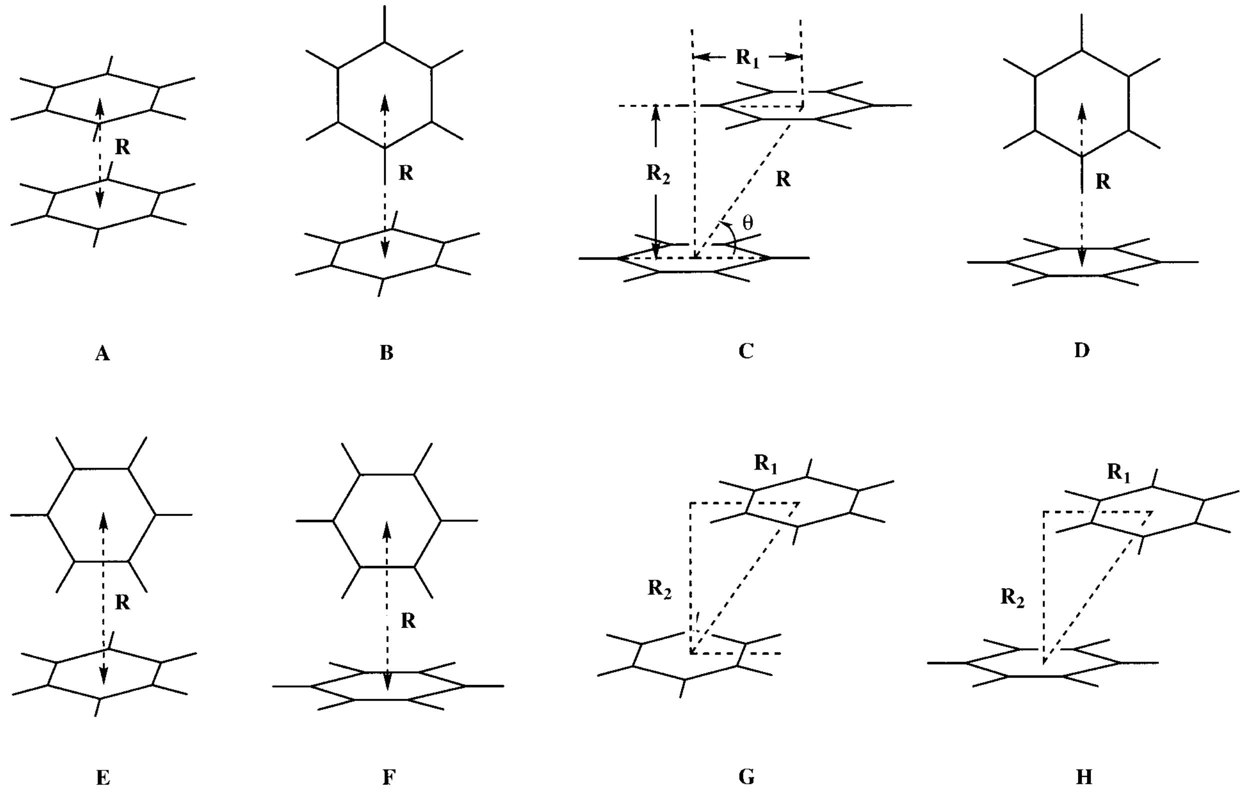

Figure 1. The geometries of the benzene dimers.

calculated as interactions of polarizable sites with the electric field produced by the multipoles of monomers.[84] Anisotropic polarizabilities $\alpha_{xx} = \alpha_{yy} = 14$ and $\alpha_{zz} = 7$ au (the z-axis is parallel to the 6-fold axis) were put on the carbon atoms of benzene.[85] Distributed multipoles and polarizabilities were used only to estimate the electrostatic and induction energies.

Results and Discussion

AIMI (Aromatic Inter-Molecular Interaction) Model. The intermolecular interaction energies of the benzene dimers A, B, and C (Figure 1) were calculated by the Hartree−Fock (HF), MP2, and CCSD(T) methods with several basis sets as summarized in Table 1. The MP2 and CCSD(T) interaction energies depend strongly on the basis set as previously reported,[18−27] while the basis set dependence of the CCSD(T) correction terms (ΔCCSD(T) $= E_{\mathrm{CCSD(T)}} - E_{\mathrm{MP2}}$) is not large, if basis sets larger than 6-311G* are used. The weak basis set dependence of ΔCCSD(T) suggests that the CCSD(T) interaction energy at the basis set limit ($E_{\mathrm{CCSD(T)(limit)}}$) can be estimated sufficiently accurately from the MP2 interaction energy (E_{MP2}) calculated with a large basis set near saturation and the ΔCCSD(T) obtained by using a medium size basis set, according to the equation

$$E_{\mathrm{CCSD(T)(limit)}} = E_{\mathrm{MP2}} + \Delta\mathrm{CCSD(T)}$$

Here we propose three levels of model chemistry, AIMI Models I, II, and III, for the evaluation of intermolecular interaction of aromatic molecules. In Model I, the aug(d)-6-311G* basis set (312 basis functions for the benzene dimer) was used for the calculation of E_{MP2}. 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). The 6-31G* basis set (204 basis functions) was used for the calculation of ΔCCSD(T). In Model II, the aug(d,p)-6-311G** basis set (384 basis functions) was employed for the calculations of E_{MP2}. This basis set is the 6-311G** augmented with the diffuse d functions on carbon atoms and diffuse p functions on hydrogen atoms (α_{p}(H) = 0.1875). The 6-311G* basis set (252 basis functions) was employed for the calculations of ΔCCSD(T). In Model III, estimated E_{MP2} and ΔCCSD(T) values at the basis set limit were used to obtain $E_{\mathrm{CCSD(T)(limit)}}$. The MP2 interaction energies were calculated with the Dunning's correlation consistent basis sets (cc-pVXZ, X = D, T, Q, and 5).[86,87] The MP2 energy at the basis set limit was estimated by the method proposed by Feller.[80] In Feller's method the calculated interaction energies were fitted to the form $a + b\ \exp(-cX)$ (where X is 2 for cc-pVDZ, 3 for cc-pVTZ, etc). The MP2 energy at the basis limit ($E_{\mathrm{MP2(limit)}}$) was then estimated by extrapolation. The ΔCCSD(T) at the basis set limit was estimated from the calculated ΔCCSD(T) by using a modified cc-pVTZ basis set.

Benzene Dimer Interaction Energies Obtained by AIMI Models. The calculated E_{MP2}, ΔCCSD(T), and $E_{\mathrm{CCSD(T)(limit)}}$ of dimers A, B, and C with the AIMI models are summarized in Table 2. It was previously reported that the two benzene dimers

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Table 1. The Calculated HF, MP2, and CCSD(T) Interaction Energies of the Benzene Dimers[a]

basis set	E_{HF}[b]	E_{MP2}[b]	$E_{\mathrm{CCSD(T)}}$[b]	$E_{\mathrm{corr(MP2)}}$[c]	$E_{\mathrm{corr(CCSD(T))}}$[d]	ΔCCSD(T)[e]	ΔCCSD(T)/$E_{\mathrm{corr(MP2)}}$
Dimer A (parallel)							
6-31G	4.66	0.75	1.43	−3.91	−3.23	0.68	−0.17
6-31G*	4.63	0.06	1.10	−4.57	−3.54	1.04	−0.23
6-311G*	4.58	−0.86	0.38	−5.44	−4.20	1.24	−0.23
6-311G**	4.47	−1.30	0.02	−5.76	−4.45	1.32	−0.23
aug(d)-6-311G* [f]	4.45	−2.58	−1.02	−7.03	−5.48	1.56	−0.22
cc-pVDZ	4.49	−0.96	0.34	−5.44	−4.15	1.29	−0.24
cc-pVTZ[g]	4.42	−2.30	−0.71	−6.72	−5.13	1.59	−0.24
basis set limit[h]	4.26[i]	−3.28[j]		−7.54[k]		1.80[l]	
Dimer B (T-shaped)							
6-31G	1.01	−0.69	−0.34	−1.70	−1.35	0.35	−0.21
6-31G*	0.94	−1.41	−0.85	−2.35	−1.78	0.56	−0.24
6-311G*	0.90	−1.99	−1.31	−2.89	−2.21	0.69	−0.24
6-311G**	0.93	−2.12	−1.40	−3.05	−2.33	0.72	−0.24
aug(d)-6-311G* [f]	0.95	−2.92	−2.14	−3.87	−3.09	0.78	−0.20
cc-pVDZ	0.93	−1.94	−1.23	−2.87	−2.16	0.71	−0.25
cc-pVTZ[g]	0.93	−2.87	−2.04	−3.80	−2.97	0.83	−0.22
basis set limit[h]	1.02[i]	−3.45[j]		−4.47[k]		0.99[l]	
Dimer C (slipped-parallel)							
6-31G	4.23	0.45	1.16	−3.78	−3.08	0.71	−0.19
6-31G*	4.20	−0.50	0.63	−4.70	−3.57	1.13	−0.24
6-311G*	3.80	−1.87	−0.48	−5.67	−4.29	1.39	−0.24
6-311G**	3.79	−2.19	−0.73	−5.99	−4.52	1.46	−0.24
aug(d)-6-311G* [f]	3.80	−3.73	−2.00	−7.53	−5.80	1.73	−0.23
cc-pVDZ	3.81	−1.82	−0.39	−5.63	−4.20	1.43	−0.25
cc-pVTZ[g]	3.79	−3.41	−1.62	−7.19	−5.41	1.79	−0.25
basis set limit[h]	3.66[i]	−4.51[j]		−8.17[k]		2.03[l]	

[a] Energies in kcal/mol. The geometries of the dimers are shown in Figure 1. $R = 3.8$ Å for dimer A, $R = 5.0$ Å for dimer B, and R_1 and R_2 are 1.8 and 3.5 Å, respectively, for dimer C. [b] BSSE corrected interaction energies. [c] MP2 correlation interaction energies. Difference between the E_{MP2} and E_{HF}. [d] CCSD(T) correlation interaction energies. Difference between the $E_{\mathrm{CCSD(T)}}$ and E_{HF}. [e] CCSD(T) correction terms. Difference between the $E_{\mathrm{CCSD(T)}}$ and E_{MP2}. [f] 6-311G* basis set augmented with diffuse d functions on carbon atoms ($\alpha_d(\mathrm{C}) = 0.1565$). [g] Modified cc-pVTZ basis set. f functions on carbon atoms and d functions on hydrogen atoms are removed. [h] The estimated values at the basis set limit. [i] HF/cc-pV5Z level interaction energies. See text. [j] Estimated MP2 interaction energies at the basis set limit ($E_{\mathrm{MP2(limit)}}$). See text. [k] Estimated MP2 correlation interaction energy at the basis set limit ($E_{\mathrm{corr(MP2,limit)}}$). Difference between the $E_{\mathrm{MP2(limit)}}$ and HF/cc-pV5Z level interaction energies. [l] Estimated CCSD(T) correction term (ΔCCSD(T)) at the basis set limit. See text.

Table 2. The Calculated MP2 and CCSD(T) Interaction Energies of the Benzene Dimers by AIMI Models I−III[a]

dimer	E_{MP2}	ΔCCSD(T)[b]	$E_{\mathrm{CCSD(T)(limit)}}$[c]
Model I[d]			
A	−2.58	1.04	−1.54
B	−2.92	0.56	−2.36
C	−3.73	1.13	−2.60
Model II[e]			
A	−2.85	1.24	−1.62
B	−3.10	0.69	−2.42
C	−3.98	1.39	−2.59
Model III[f]			
A	−3.28	1.80	−1.48
B	−3.45	0.99	−2.46
C	−4.51	2.03	−2.48

[a] Energies in kcal/mol. BSSE corrected interaction energies. The geometries of the dimers are shown in Figure 1. See footnote *a* of Table 1. [b] CCSD(T) correction terms. See text and footnote *e* of Table 1. [c] Estimated CCSD(T) interaction energies. Sum of E_{MP2} and ΔCCSD(T). [d] E_{MP2} was calculated by using the aug(d)-6-311G* basis set. See footnote *f* of Table 1. ΔCCSD(T) was calculated by using the 6-31G* basis set. [e] E_{MP2} was calculated by using the aug(d,p)-6-311G** basis set. See footnote *f* of Table 2 . ΔCCSD(T) was calculated by using the 6-311G* basis set. [f] E_{MP2} was the estimated MP2 interaction energy at the basis set limit ($E_{\mathrm{MP2(limit)}}$) by the method proposed by Feller (ref 80). ΔCCSD(T) at the basis set limit was estimated from the calculated ΔCCSD(T) by using a modified cc-pVTZ basis set. See text.

Table 3. The Calculated HF and MP2 Interaction Energies of the Benzene Dimers with Several Basis Sets[a]

basis set	E_{HF}[b]	E_{MP2}[b]	$E_{\mathrm{corr(MP2)}}$[c]
Dimer A (parallel)			
aug(d)-6-311G* [d]	4.45	−2.58	−7.03
aug(d,p)-6-311G** [e]	4.40	−2.85	−7.25
cc-pVDZ	4.49	−0.96	−5.44
cc-pVTZ	4.32	−2.48	−6.80
cc-pVQZ	4.29	−2.97	−7.26
cc-pV5Z[f]	4.26	−3.19	−7.45
basis set limit	4.26[g]	−3.28[h]	−7.54
Dimer B (T-shaped)			
aug(d)-6-311G* [d]	0.95	−2.92	−3.87
aug(d,p)-6-311G** [e]	0.97	−3.10	−4.07
cc-pVDZ	0.93	−1.94	−2.87
cc-pVTZ	0.98	−2.97	−3.94
cc-pVQZ	0.99	−3.31	−4.31
cc-pV5Z[f]	1.02	−3.40	−4.41
basis set limit	1.02[g]	−3.45[h]	−4.47
Dimer C (slipped-parallel)			
aug(d)-6-311G* [d]	3.80	−3.73	−7.53
aug(d,p)-6-311G** [e]	3.79	−3.98	−7.77
cc-pVDZ	3.81	−1.82	−5.63
cc-pVTZ	3.71	−3.61	−7.32
cc-pVQZ	3.69	−4.20	−7.88
cc-pV5Z[f]	3.66	−4.42	−8.08
basis set limit	3.66[g]	−4.51[h]	−8.17

[a] Energies in kcal/mol. BSSE corrected interaction energies. The geometries of the dimers are shown in Figure 1. See footnote *a* of Table 1. [b] BSSE corrected interaction energies. [c] Difference between the E_{MP2} and E_{HF}. [d] See footnote *f* of Table 1. [e] 6-311G* basis set augmented with diffuse d functions on carbon atoms ($\alpha_d(\mathrm{C}) = 0.1565$) and p functions on hydrogen atoms ($\alpha_p(\mathrm{H}) = 0.1875$). [f] Modified CC-pV5Z basis set. See text. [g] HF/cc-pV5Z level interaction energies. See text. [h] Estimated MP2 interaction energies at the basis set limit ($E_{\mathrm{MP2(limit)}}$). See text.

(T-shaped and slipped-parallel) are nearly isoenergetic.[22] Our calculations also show that these two dimers are nearly isoenergetic. The previous CCSD(T) interaction energies of the dimers[22] are 10−19% smaller (less negative) than the energies by AIMI Model III.

Table 3 summarizes the MP2 interaction energies calculated with cc-pVXZ basis sets (X = D, T, Q and 5) and the estimated $E_{\mathrm{MP2(limit)}}$ values. The $E_{\mathrm{MP2(limit)}}$ of dimers A, B, and C are close to the interaction energies calculated with the cc-pVQZ and cc-pV5Z basis sets, which indicates that these basis sets are close

Table 4. The Calculated HF, MP2, and CCSD(T) Interaction Energies of the Ethylene Dimer and Benzene−Ethylene Complex[a]

basis set	E_{HF}[b]	E_{MP2}[b]	$E_{CCSD(T)}$[b]	$E_{corr(MP2)}$[c]	$E_{corr(CCSD(T))}$[d]	ΔCCSD(T)[e]	ΔCCSD(T)/$E_{corr(MP2)}$
Ethylene dimer							
6-31G	0.60	0.09	0.10	−0.52	−0.50	0.02	−0.03
6-31G*	0.56	−0.23	−0.14	−0.79	−0.71	0.08	−0.11
6-311G*	0.56	−0.44	−0.33	−1.00	−0.89	0.11	−0.11
6-311G**	0.55	−0.62	−0.50	−1.17	−1.05	0.12	−0.10
aug(d)-6-311G* [f]	0.56	−0.98	−0.88	−1.54	−1.44	0.11	−0.07
aug(d,p)-6-311G** [g]	0.56	−1.23	−1.15	−1.79	−1.71	0.08	−0.04
cc-pVDZ	0.61	−0.51	−0.39	−1.13	−1.00	0.13	−0.11
cc-pVTZ	0.56	−1.16	−1.04	−1.73	−1.60	0.12	−0.07
cc-pVTZ(-f,d)[h]	0.57	−1.08	−0.95	−1.65	−1.52	0.13	−0.08
cc-pVQZ(-g,f)[i]	0.56	−1.39	−1.29	−1.95	−1.85	0.10	−0.05
Benzene−ethylene							
6-31G	1.21	−0.02	0.21	−1.24	−1.00	0.23	−0.19
6-31G*	1.15	−0.61	−0.22	−1.75	−1.37	0.39	−0.22
6-311G*	1.12	−1.08	−0.60	−2.20	−1.72	0.48	−0.22
6-311G**	1.14	−1.27	−0.76	−2.41	−1.89	0.52	−0.21
aug(d)-6-311G*	1.14	−1.92	−1.37	−3.06	−2.51	0.55	−0.18
aug(d,p)-6-311G** [g]	1.16	−2.19	−1.63	−3.35	−2.80	0.56	−0.17
cc-pVDZ	1.14	−1.11	−0.60	−2.25	−1.74	0.51	−0.23
cc-pVTZ(-f,d)[h]	1.12	−1.98	−1.38	−3.11	−2.50	0.61	−0.20

[a] Energies in kcal/mol. The geometries of the dimers are shown in Figure 2. [b] BSSE corrected interaction energies. [c] MP2 correlation interaction energies. Difference between the E_{MP2} and E_{HF}. [d] CCSD(T) correlation interaction energies. Difference between the $E_{CCSD(T)}$ and E_{HF}. [e] CCSD(T) correction terms. Difference between the $E_{CCSD(T)}$ and E_{MP2}. [f] See footnote *f* of Table 1. [g] See footnote *e* of Table 2. [h] Modified cc-pVTZ basis set. f functions on carbon atoms and d functions on hydrogen atoms are removed. [i] Modified cc-pVQZ basis set. g functions on carbon atoms and f functions on hydrogen atoms are removed.

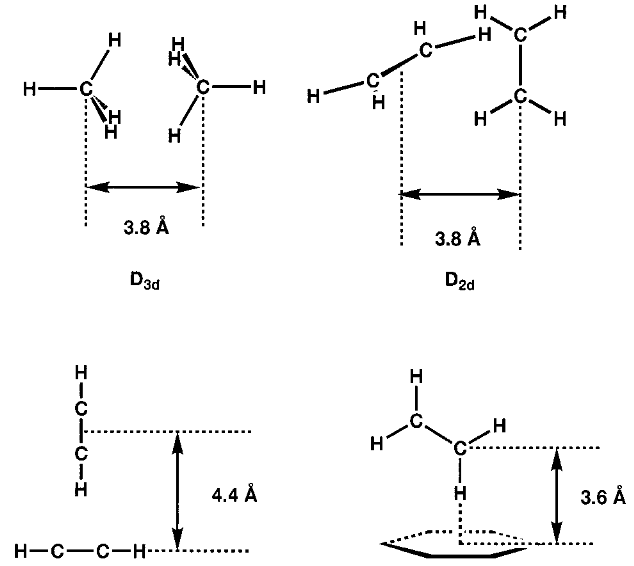

Figure 2. The geometries of the methane, ethylene, and acetylene dimers and the benzene−ethylene complex.

to the saturation limit and that the estimated $E_{MP2(limit)}$ values are reliable. A modified cc-pV5Z basis set [g, h functions on carbon atoms and f, g functions and a set of d functions (α_d(H) = 2.95) on hydrogen atoms were removed] was used for the calculations. The MP2 interaction energies of methane, ethylene, and acetylene dimers (Figure 2) calculated with the modified cc-pV5Z basis set are −0.44, −1.45, and −1.59 kcal/mol, respectively. These values are nearly identical to those calculated with the cc-pV5Z basis set (−0.45, −1.48, and −1.62 kcal/mol, respectively).

The calculated ΔCCSD(T) has a small basis set dependence as shown in Table 1, which suggests that the ΔCCSD(T) at the basis set limit is slightly larger than the calculated values in Table 1. Although both the MP2 correlation interaction energy ($E_{corr(MP2)} = E_{MP2} - E_{HF}$) and the ΔCCSD(T) have basis set dependence, ΔCCSD(T) is always 20−25% of the absolute value of $E_{corr(MP2)}$, if a basis set larger than 6-31G* is used. Table 4 shows the $E_{corr(MP2)}$ and ΔCCSD(T) of ethylene dimer and benzene−ethylene complex (Figure 2) with several basis sets. The ΔCCSD(T) of the ethylene dimer is always 4−11% of the absolute value of $E_{corr(MP2)}$ and that of the benzene−ethylene complex is always 17−23%. The ratio depends on the system, but the ratio of each system is nearly constant. This result suggests that it is reasonable to assume that ΔCCSD(T) of the benzene dimers is about 20−25% of the absolute value of $E_{corr(MP2)}$.

The ΔCCSD(T) of the dimers A, B, and C obtained with a modified cc-pVTZ basis set (f functions on carbon atoms and d functions on hydrogen atoms were removed) are 1.59, 0.83, and 1.79 kcal/mol, respectively. The calculated $E_{corr(MP2)}$ with this basis set are −6.72, −3.80, and −7.19 kcal/mol, respectively. They are respectively 0.82, 0.67, and 0.98 kcal/mol smaller (less negative) than the estimated $E_{corr(MP2)}$ at the basis set limit. Assuming that the ΔCCSD(T) values are approximately 25% of the absolute values of $E_{corr(MP2)}$, we can expect that the modified cc-pVTZ basis set underestimates the ΔCCSD(T) of dimers A, B, and C by as much as 0.21, 0.16, and 0.24 kcal/mol, respectively, compared to the basis set limit (25% of the underestimation of $E_{corr(MP2)}$). From these values we can estimate that the ΔCCSD(T) at the basis set limit are 1.80, 0.99, and 2.03 kcal/mol respectively for dimers A, B, and C.

The $E_{CCSD(T)(limit)}$ of the dimers obtained by Models I and II are not largely different (less than 0.2 kcal/mol) from those obtained by Model III. The E_{MP2} values for dimers A, B, and C by Model I are 0.70, 0.53, and 0.78 kcal/mol smaller (less negative) than those by Model III (the $E_{MP2(limit)}$). The ΔCCSD(T) values by Model I are 0.76, 0.43, and 0.90 kcal/mol smaller than those by Model III. Apparently the error cancellation is a cause of the good performance of Model I.

MP2 and CCSD(T) (AIMI Model II) Potentials of Dimers A, B, and C. Figures 3−5 show the comparison between the CCSD(T) intermolecular interaction potentials of dimers A, B, and C (Model II) and the HF and MP2 interaction potentials

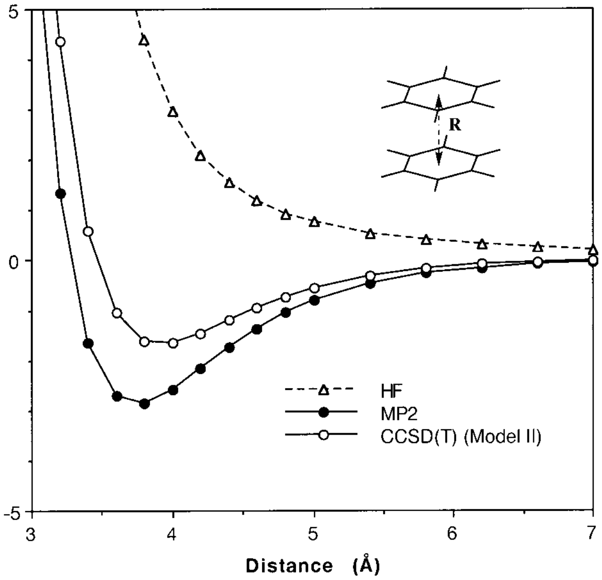

Figure 3. The HF, MP2, and CCSD(T) interaction energies of the benzene dimer A. The HF and MP2 interaction energies were calculated with the aug(d,p)-6-311G** basis set. The CCSD(T) interaction energy was calculated by the AIMI Model II. See text.

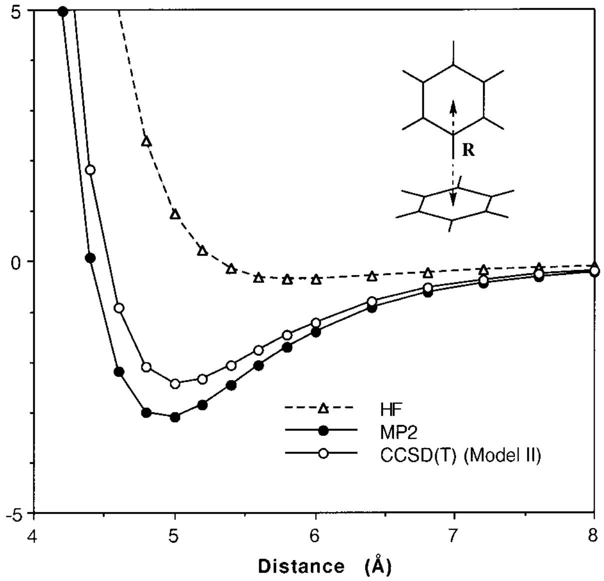

Figure 4. The HF, MP2, and CCSD(T) interaction energies of the benzene dimer B. The HF and MP2 interaction energies were calculated with the aug(d,p)-6-311G** basis set. The CCSD(T) interaction energy was calculated by the AIMI Model II. See text.

calculated with the aug(d,p)-6-311G** basis set. The interaction potential of dimer C was calculated by changing the intermolecular distance R while keeping the angle θ fixed (Figure 5). The MP2 potentials overestimate the attraction considerably compared to the CCSD(T) potentials. The CCSD(T) potentials of the dimers are very shallow near the potential minima. Thus substantial attraction still exists even when the molecules are well separated. This suggests that the major source of attraction in the benzene dimers is not short-range interactions ($E \sim e^{-\alpha R}$) such as charge-transfer but long-range interactions ($E \sim R^{-n}$) such as electrostatic and dispersion. Short-range interactions arise at the distance where the molecular wave functions overlap significantly. The energies of short-range interactions decrease exponentially with distance.[88] The comparison between the

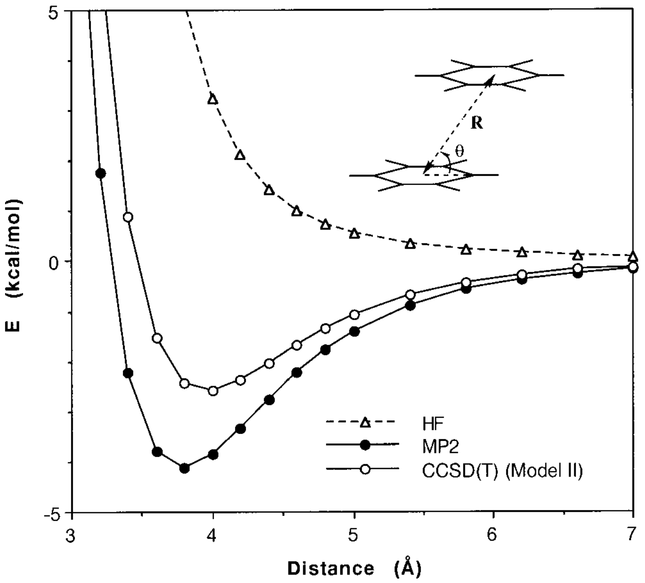

Figure 5. The HF, MP2, and CCSD(T) interaction energies of the benzene dimer C. The HF and MP2 interaction energies were calculated with the aug(d,p)-6-311G** basis set. The CCSD(T) interaction energy was calculated by the AIMI Model II. See text. The angle θ was fixed at 63°. The angle θ is 63° when $R_1 = 1.8$ Å and $R_2 = 3.5$ Å.

CCSD(T) (Model II) and HF potentials shows that the inclusion of electron correlation increases the attraction considerably, which indicates that the dispersion interaction is significantly important for attraction in the benzene dimer.

Intermolecular Interaction Energies of T-Shaped Dimers B, D, E, and F. The calculated CCSD(T) interaction energies of the T-shaped dimers B, D, E, and F by AIMI Model II are summarized in Table 5. The dimers B and D have the largest (most negative) interaction energy when the intermolecular distance (R) is 5.0 Å. The dimers E and F have the largest energy at $R = 5.2$ Å. The dimers B and D have slightly (about 0.3 kcal/mol) larger attraction than E and F. The energy difference between B and D and that between E and F are negligible (less than 0.01 kcal/mol), which shows that the potential energy surface is very flat with respect to the rotation of the benzene ring along the C_2 axis of the dimers.

Intermolecular Interaction Energies of Slipped-Parallel Dimers C, G, and H. The CCSD(T) interaction energies of dimers C, G, and H were calculated by AIMI Model II with changing the horizontal (R_1) and vertical (R_2) displacements as summarized in Table 6. The dimers have the largest (most negative) interaction energy when R_1 and R_2 are 1.8 and 3.5 Å, respectively. The dimer C has the largest interaction energy, but the energy difference among the three dimers is very small (less than 0.04 kcal/mol). The small energy difference indicates that the potential energy surface is very shallow with respect to the rotation of the benzene ring along the C_6 axis of benzene.

Experimental Bonding Energy. Grover et al. reported that the experimental bonding energy (B_0) of the benzene dimer was 2.4 ± 0.4 kcal/mol.[8] Recently Krause et al. reported $B_0 = 1.6 \pm 0.2$ kcal/mol.[9] The calculated bonding energy (B_e) by AIMI

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(88) 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.

Table 5. The Calculated Interaction Energies of the Benzene Dimers A, B, D, E, and F by AIMI Model II[a]

R[a]	$E_{\mathrm{MP2(L)}}$[b]	$E_{\mathrm{MP2(M)}}$[c]	$E_{\mathrm{CCSD(T)(M)}}$[d]	ΔCCSD(T)[e]	$E_{\mathrm{CCSD(T)}}$[f]
Dimer A					
3.4	−1.635	1.010	3.245	2.235	0.600
3.6	−2.712	−0.407	1.252	1.660	−1.052
3.8	−2.852	−0.857	0.379	1.237	−1.616
4.0	−2.578	−0.884	0.043	0.926	−1.652
4.2	−2.162	−0.757	−0.059	0.699	−1.464
Dimer B					
4.6	−2.193	−0.197	1.075	1.273	−0.921
4.8	−3.019	−1.537	−0.608	0.928	−2.090
5.0	−3.103	−1.993	−1.307	0.686	−2.417
5.2	−2.847	−2.009	−1.495	0.515	−2.332
5.4	−2.467	−1.831	−1.438	0.392	−2.074
Dimer D					
4.8	−3.018	−1.536	−0.608	0.927	−2.091
5.0	−3.102	−1.993	−1.308	0.685	−2.417
5.2	−2.846	−2.009	−1.495	0.514	−2.332
5.4	−2.466	−1.831	−1.439	0.392	−2.074
Dimer E					
4.8	−2.502	−1.224	−0.363	0.861	−1.641
5.0	−2.785	−1.810	−1.176	0.634	−2.151
5.2	−2.629	−1.880	−1.405	0.476	−2.153
5.4	−2.304	−1.730	−1.365	0.364	−1.940
Dimer F					
4.8	−2.492	−1.210	−0.348	0.862	−1.630
5.0	−2.781	−1.805	−1.170	0.634	−2.147
5.2	−2.627	−1.879	−1.403	0.476	−2.151
5.4	−2.304	−1.729	−1.365	0.364	−1.940

[a] Energies in kcal/mol. BSSE corrected interaction energies. The geometries of the dimers are shown in Figure 1. [b] MP2 interaction energies calculated with the aug(d,p)-6-311G** basis set. See footnote *e* of Table 2. [c] MP2 interaction energies calculated with the 6-311G* basis set. [d] CCSD(T) interaction energies calculated with the 6-311G* basis set. [e] CCSD(T) correction term. Difference between the $E_{\mathrm{CCSD(T)(M)}}$ and $E_{\mathrm{MP2(M)}}$. [f] Estimated CCSD(T) interaction energy. The sum of $E_{\mathrm{MP2(L)}}$ and ΔCCSD(T).

Model III is about 2.5 kcal/mol. Vibrational zero-point energies (ZPE) of monomer benzene and T-shaped benzene dimer were calculated at the MP2/cc-pVDZ level. The calculated ZPE's were 0.100519 and 0.201625 hartree, respectively. The change of ZPE (ΔZPE) by formation of the dimer is 0.37 kcal/mol. The estimated B_0 ($=B_e - \Delta$ZPE) value of the dimer is about 2.2 kcal/mol. This value is slightly larger than the experimental B_0 value (1.6 ± 0.2 kcal/mol) reported by Krause et al.[9] The reason behind this slight overestimation of the B_0 value is not certain. The choice of electron correlation procedure (MP2 or CCSD(T)) has significant impact on the calculated interaction energy of the benzene dimer. This suggests that further improved treatment of electron correlation beyond the CCSD(T) may slightly change the calculated interaction energy.

Roles of Electrostatic and Dispersion Interactions. Although many ab initio calculations of the benzene dimer have been reported, these calculations focused mainly on the geometry and binding energy. The roles of electrostatic and dispersion interactions for attraction and directionality of the benzene dimer interaction have not yet been confirmed. The electrostatic (E_{es}), repulsion (E_{rep}), and correlation interaction energies (E_{corr}) of the benzene dimers A ($R = 3.8$ Å), B ($R = 5.0$ Å), and C ($R_1 = 1.8$ and $R_2 = 3.5$ Å) are summarized in Table 7. The E_{corr} is the contribution of electron correlation on interaction energy, which is the difference between $E_{\mathrm{CCSD(T)(limit)}}$ by AIMI Model III (E_{total}) and the HF/cc-pV5Z interaction energy (E_{HF}). The E_{rep} ($=E_{\mathrm{HF}} - E_{\mathrm{es}}$) is mainly exchange-repulsion energy, but it also includes other terms such as induction energy. The major part of E_{corr} is the dispersion energy. The significantly large E_{corr} values of the dimers (−5.74, −3.48, and −6.14 kcal/mol, respectively) show that the major source of attraction in the benzene dimer has its origin in the dispersion interaction.

The attractive electrostatic interaction stabilizes the T-shaped dimer B, while E_{es} of this dimer is considerably smaller (less negative) than E_{corr}. The E_{es} of parallel dimer A is 1.24 kcal/mol. The large positive E_{es} shows that repulsive electrostatic interaction destabilizes the parallel dimer considerably. It has been pointed out that the electrostatic interaction stabilizes the T-shaped and slipped-parallel benzene dimers,[29,71] while the calculated E_{es} of the equilibrium slipped-parallel dimer C ($R_1 = 1.8$, $R_2 = 3.5$ Å) is repulsive (0.90 kcal/mol). The E_{es} of dimer C was calculated with changing horizontal displacement (R_1) 0.0−6.0 Å. The vertical displacement (R_2) was fixed at 3.5 Å. The most repulsive (most positive) E_{es} (1.55 kcal/mol) was obtained when R_1 is 0.0 Å (parallel orientation). Although the E_{es} of the slipped-parallel dimer C ($R_1 = 1.8$ Å) is repulsive, it is substantially smaller (less repulsive) than that of the parallel dimer ($R_1 = 0.0$ Å). The most negative E_{es} (−0.28 kcal/mol) was obtained when R_1 was 4.8 Å. Benzene has substantial permanent charge field. However, the calculated induction (polarization) energies of the dimers A, B, and C are only −0.21, −0.17, and −0.25 kcal/mol, respectively, which indicates that induction is not important for attraction in the benzene dimer.

The orientation dependence of the benzene dimer interaction was calculated by AIMI Model II. The intermolecular distance (R) was fixed at 5.0 and 6.0 Å. One benzene was rotated by changing the angle ϕ from 0° to 90° as shown in Figure 6. The calculated CCSD(T) interaction energy (E_{total}) depends strongly on the orientation of the dimer. The calculated E_{total} values show that the dimer is most stable when $\phi = 90°$ (T-shaped) as shown in Figure 7. The calculated interaction energy has strong orientation dependence even when the dimer has a large separation ($R = 6.0$ Å). The orientation dependence is the same as that for small separation ($R = 5.0$ Å). This indicates that the directionality of the benzene dimer interaction is controlled mainly by long-range interactions such as electrostatic and dispersion interactions. If short-range interactions such as charge-transfer are the major source of directionality, the observed directionality at the short separation should disappear at long range.

The orientation dependence of E_{es} and E_{corr} ($R = 5.0$ Å) is compared with that of E_{total}. E_{es} and E_{corr} are most negative (most attractive) when $\phi = 90°$ as of E_{total} (Figure 7). The orientation dependence of E_{es} can be explained as an interaction between two quadrupoles. The quadrupole−quadrupole interaction is repulsive when two quadrupoles have a linear orientation ($\phi = 0°$), while it is attractive when they have a perpendicular orientation ($\phi = 90°$). It is reasonable that E_{corr} is most attractive when $\phi = 90°$. The change of ϕ from 0° to 90° increases the number of short intermolecular C···C contacts and therefore increases dispersion interaction. The shape of the benzene molecule is not close to a sphere. Therefore dispersion interaction of benzene is anisotropic. These results indicate that both the electrostatic and dispersion interactions are responsible for the directionality of the benzene dimer interaction. The absolute value of E_{es} is always considerably smaller than E_{corr}, but E_{es} is highly orientation dependent and, therefore, electrostatic interaction is also important for the directionality.

Buckingham and Fowler have pointed out from simple model calculations that structures of molecular clusters are mainly

Table 6. The Calculated Interaction Energies of the Benzene Dimers C, G, and H by AIMI Model II[a]

R_1[a]	R_2[a]	$E_{MP2(L)}$[b]	$E_{MP2(M)}$[c]	$E_{CCSD(T)(M)}$[d]	ΔCCSD(T)[e]	$E_{CCSD(T)}$[f]
Dimer C						
1.6	3.1	−3.085	0.028	2.775	2.747	−0.338
1.6	3.3	−4.076	−1.456	0.555	2.011	−2.066
1.6	3.5	−4.060	−1.837	−0.353	1.484	−2.576
1.6	3.7	−3.606	−1.726	−0.621	1.105	−2.501
1.6	3.9	−3.011	−1.442	−0.611	0.831	−2.180
1.8	3.1	−3.167	−0.212	2.339	2.551	−0.616
1.8	3.3	−4.040	−1.552	0.321	1.874	−2.167
1.8	3.5	−3.977	−1.869	−0.482	1.387	−2.590
1.8	3.7	−3.514	−1.734	−0.698	1.037	−2.477
1.8	3.9	−2.928	−1.446	−0.664	0.782	−2.146
2.0	3.1	−3.099	−0.330	2.020	2.350	−0.749
2.0	3.3	−3.900	−1.567	0.166	1.734	−2.167
2.0	3.5	−3.825	−1.850	−0.561	1.289	−2.536
2.0	3.7	−3.377	−1.711	−0.744	0.967	−2.410
2.0	3.9	−2.817	−1.430	−0.698	0.732	−2.085
Dimer G						
1.6	3.1	−3.047	0.079	2.845	2.766	−0.281
1.6	3.3	−4.052	−1.427	0.593	2.020	−2.032
1.6	3.5	−4.046	−1.823	−0.335	1.488	−2.558
1.6	3.7	−3.598	−1.721	−0.614	1.107	−2.491
1.6	3.9	−3.007	−1.442	−0.610	0.832	−2.175
1.8	3.1	−3.084	−0.105	2.471	2.576	−0.508
1.8	3.3	−3.993	−1.495	0.391	1.886	−2.107
1.8	3.5	−3.952	−1.843	−0.449	1.394	−2.558
1.8	3.7	−3.501	−1.725	−0.685	1.040	−2.461
1.8	3.9	−2.922	−1.444	−0.660	0.784	−2.138
2.0	3.1	−2.942	−0.138	2.243	2.381	−0.561
2.0	3.3	−3.818	−1.470	0.280	1.750	−2.068
2.0	3.5	−3.784	−1.805	−0.508	1.298	−2.486
2.0	3.7	−3.357	−1.695	−0.724	0.972	−2.386
2.0	3.9	−2.808	−1.427	−0.692	0.735	−2.073
Dimer H						
1.6	3.3	−4.058	−1.436	0.580	2.016	−2.042
1.6	3.5	−4.050	−1.827	−0.342	1.486	−2.564
1.6	3.7	−3.601	−1.722	−0.617	1.106	−2.495
1.8	3.1	−3.119	−0.166	2.399	2.565	−0.554
1.8	3.3	−4.013	−1.529	0.351	1.880	−2.133
1.8	3.5	−3.963	−1.859	−0.469	1.390	−2.572
1.8	3.7	−3.506	−1.732	−0.694	1.038	−2.468
1.8	3.9	−2.925	−1.446	−0.664	0.783	−2.142
2.0	3.3	−3.858	−1.529	0.212	1.741	−2.117
2.0	3.5	−3.803	−1.834	−0.541	1.293	−2.511
2.0	3.7	−3.367	−1.707	−0.738	0.969	−2.398

[a] Energies in kcal/mol. BSSE corrected interaction energies. The geometries of the dimers are shown in Figure 1. [b] MP2 interaction energies calculated with the aug(d,p)-6-311G** basis set. See footnote *e* of Table 2. [c] MP2 interaction energies calculated with the 6-311G* basis set. [d] CCSD(T) interaction energies calculated with the 6-311G* basis set. [e] CCSD(T) correction term. Difference between the $E_{CCSD(T)(M)}$ and $E_{MP2(M)}$. [f] Estimated CCSD(T) interaction energy. The sum of $E_{MP2(L)}$ and ΔCCSD(T).

Table 7. Electrostatic and Dispersion Energies of the Benzene Dimers[a]

energy	A	B	C
E_{total}[b]	−1.48	−2.46	−2.48
E_{es}[c]	1.24	−0.55	0.90
E_{rep}[d]	3.02	1.57	2.76
E_{corr}[e]	−5.74	−3.48	−6.14

[a] Energies in kcal/mol. The geometries of the dimers are shown in Figure 1. See footnote *a* of Table 1. $R = 3.8$ Å for dimer A. $R = 5.0$ Å for dimer B. $R_1 = 1.8$ and $R_2 = 3.5$ Å, respectively, for dimer C. [b] The calculated $E_{CCSD(T)(limit)}$ by AIMI Model III. See text and footnote *c* of Table 4. [c] The electrostatic energy. 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.

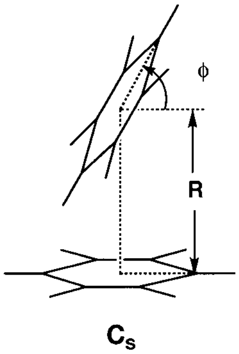

Figure 6. The geometry of the benzene dimer.

determined by exchange-repulsion and electrostatic interactions.[89,90] Ab initio calculations of the interaction of benzene with water, ammonia, and methane indicate that the directionality of the interactions in these systems (OH/π, NH/π, and CH/π interactions) is mainly determined by electrostatic interaction.[91,92] On the other hand the benzene dimer has a strong

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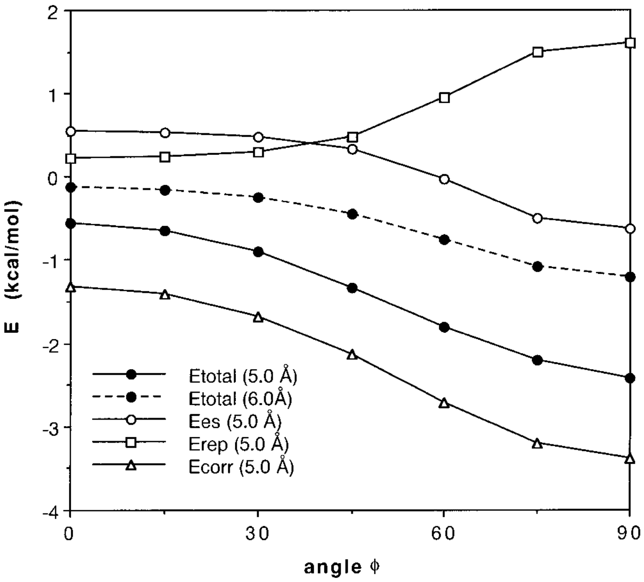

Figure 7. The orientation dependence of the total interaction energy (E_{total}), electrostatic energy (E_{es}), repulsion energy (E_{rep}), and correlation interaction energy (E_{corr}) of the benzene dimer. The geometry of the benzene dimer is shown in Figure 5. The E_{total} was calculated by the Model II. See text.

and anisotropic dispersion interaction. Therefore, both the dispersion and electrostatic interactions are important for the directionality of the benzene dimer interaction.

Conclusions

We have developed a model chemistry for the evaluation of intermolecular interaction between aromatic molecules (AIMI models). The CCSD(T) interaction energy at the basis set limit was estimated from the MP2 interaction energy near saturation and the CCSD(T) correction term obtained by using a medium size basis set. The calculated CCSD(T) interaction energies of the parallel, T-shaped, and slipped-parallel benzene dimers by the most accurate AIMI Model III are −1.48, −2.46, and −2.48 kcal/mol, respectively. The T-shaped and slipped-parallel dimers are nearly isoenergetic. The calculated binding energy is not largely different from the experimental value.

The calculated intermolecular interaction potentials of the T-shaped and slipped-parallel dimers are very shallow near the potential minima. Substantial attraction exists even when the two molecules are well separated, which indicates that the major source of attraction is not the short-range interactions such as charge-transfer, but the long-range interactions such as electrostatic and dispersion. The inclusion of electron correlation greatly increases the attraction. The gain in the attraction due to electron correlation correction (E_{corr}) is considerably larger than the electrostatic energy (E_{es}). This indicates that dispersion interaction is the major source of the attraction in the benzene dimer.

The orientation dependence of the dimer interaction energy for large intermolecular separation is the same as that for small separation, which indicates that the dependence is controlled mainly by long-range interactions. Although electrostatic interaction is smaller than dispersion interaction, it is highly orientation dependent. The orientation dependence of the E_{corr} and E_{es} indicates that both dispersion and electrostatic interactions are responsible for the directionality of the benzene dimer interaction.

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Supporting Information Available: Listing of experimental data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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