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Intermolecular Interaction between Hexafluorobenzene and Benzene: Ab Initio Calculations Including CCSD(T) Level Electron Correlation Correction

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The intermolecular interaction energy of hexafluorobenzene−benzene has been calculated with the ARS-E model (a model chemistry for the evaluation of the intermolecular interaction energy between aromatic systems using extrapolation), which was formerly called the AIMI model. The CCSD(T) interaction energy at the basis-set limit has been estimated from the MP2 interaction energy at the basis-set limit and the CCSD(T) correction term obtained using a medium-sized basis set. The slipped-parallel (C_s) complex has the largest (most negative) interaction energy (−5.38 kcal/mol). The sandwich (C_{6v}) complex is slightly less stable (−5.07 kcal/mol). The interaction energies of two T-shaped (C_{2v}) complexes are very small (−1.74 and −0.88 kcal/mol). The calculated interaction energy of the slipped-parallel complex is about twice as large as that of the benzene dimer. The dispersion interaction is found to be the major source of attraction in the complex, although electrostatic interaction also contributes to the attraction. The dispersion interaction increases the relative stability of the slipped-parallel benzene dimer and the hexafluorobenzene−benzene complex compared to T-shaped ones. The electrostatic interaction is repulsive in the slipped-parallel benzene dimer, whereas it stabilizes the slipped-parallel hexafluorobenzene−benzene complex. Both electrostatic and dispersion interactions stabilize the slipped-parallel hexafluorobenzene−benzene complex, which is the cause of the preference of the slipped-parallel orientation and the larger interaction energy of the complex compared to the benzene dimer.

Introduction

Intermolecular interaction between π systems (π/π interaction) plays an important role in determining the crystal structures and molecular recognition processes in biological and artificial systems.[1−4] One of the most interesting systems is the hexafluorobenzene−benzene complex. The strong attraction in this complex has been reported in the 1960s. The melting point of the crystal from an equimolar mixture is substantially higher than that of either of the two components.[5] This motif is suggested as a valuable supramolecular synthon and is used widely for designing structures of crystals and molecular assemblies.[6−17]

Many experimental studies were reported on the hexafluorobenzene−benzene interaction.[5−36] The crystals of hexafluorobenzene and benzene have herringbone structures,[37,38] whereas the molecules are stacked in columns of alternating hexafluorobenzene and benzene in the crystal of a 1:1 mixture.[6,19] Molecular beam studies of the hexafluorobenzene−benzene complex in the gas phase also show that the molecular planes are very nearly parallel.[18] Neutron diffraction studies in the liquid phase also show a similar structure.[20]

Although these experimental measurements provide useful information for understanding the hexafluorobenzene−benzene interaction, it is still difficult to reveal the details of the interaction (size of the interaction, orientation dependence, etc.) by experimental measurements alone. A few molecular orbital calculations of the hexafluorobenzene−benzene complex have been reported.[39−43] MP2 calculations show that a sandwich structure is stable and a T-shaped structure is unstable.[39] A more recently reported MP2/6-31G* level geometry optimization suggests that a slipped-parallel structure is an equilibrium structure.[41]

The stability of the sandwich structure was explained by the quadrupole−quadrupole interaction.[2,3,44] The quadrupole moments of benzene and hexaflurobenzene are nearly equal in magnitude but opposite in sign. The quadrupole−quadrupole interaction between benzene and hexaflurobenzene stabilizes the sandwich structure. Therefore, electrostatic interaction was believed to be an important source of the attraction in the complex. Although recent ab initio calculations suggest that dispersion is important for the attraction, an HF calculation significantly underestimates the attraction compared to the calculations including the electron correlation correction.[39−42]

Recently, high-level ab initio calculations of dimer interaction energies of a few aromatic molecules (benzene, naphthalene, toluene, thiophene, etc.) were reported.[45−50] These calculations indicate that a very large basis set and a CCSD(T) level electron correlation correction are necessary for accurate evaluation of the interaction energies of aromatic molecules. The MP2 method considerably overestimates the attraction compared to the more reliable CCSD(T) method.[45−50] The MP2 calculations overestimate the attraction in the benzene dimer as much as 30−90%.[45] Small basis sets underestimate the attraction because small basis sets underestimate dispersion energy.[45−50] These results suggest that CCSD(T) calculations with a large basis set are necessary for the quantitative evaluation of the interaction energy of the hexafluorobenzene−benzene complex. Unfortunately, however, CCSD(T) calculation of the complex has not yet been reported.

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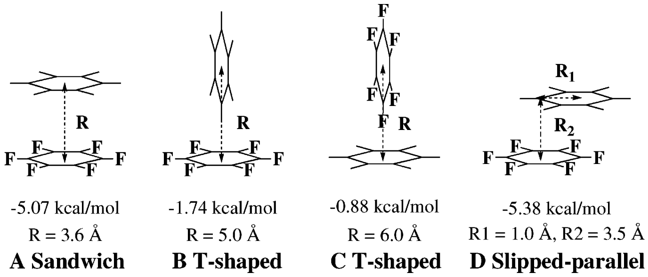
Despite many previous experimental and theoretical studies of the hexafluorobenzene−benzene complex, fundamental unsettled issues still remain: (1) The size of the intermolecular interaction energy of the hexafluorobenzene−benzene complex has not yet been confirmed. CCSD(T) calculations of the interaction energy of the complex are necessary. (2) Recent ab initio calculations suggest the importance of dispersion for the attraction in the complex, whereas the importance of the quadrupole−quadrupole interaction has been stressed repeatedly. Quantitative analysis of electrostatic and dispersion energies is necessary to reveal the origin of the attraction in the complex. (3) Detailed information on the orientation dependence of the hexafluorobenzene−benzene interaction is important for designing the structures of crystals and molecular assemblies using the interaction. But the details of the directionality and the roles of electrostatic and dispersion interactions for the directionality are not well understood.

In this paper we have analyzed the interaction energy of the hexafluorobenzene−benzene complex by high-level ab initio calculations. We have estimated the CCSD(T) level interaction energy of the complex at the basis-set limit ($E_{\mathrm{CCSD(T)(limit)}}$) for studying the size of the interaction energy and its directionality. We have also discussed the roles of electrostatic and dispersion interactions for the attraction and its directionality.

Computational Method

The Gaussian 98 and 03 programs[51,52] were used for the ab initio molecular orbital calculations. The geometries of hexafluorobenzene and benzene monomers were optimized at the MP2/6-311G** level[53] and were used for the calculations of the hexafluorobenzene−benzene complexes. Dunning's correlation consistent basis sets (cc-pVXZ and aug-cc-pVXZ, X = D, T, and Q)[54,55] and modified 6-311G* basis sets were used. The aug(d)-6-311G* basis set is the 6-311G* basis set augmented with diffuse d functions ($\alpha_d(\mathrm{C}) = 0.1565$ and $\alpha_d(\mathrm{F}) = 0.4375$) on heavy atoms. The aug(d,p)-6-311G** basis set is the 6-311G** basis set augmented with the diffuse d functions on heavy atoms and diffuse p functions ($\alpha_p(\mathrm{H}) = 0.1875$) on hydrogen atoms.[56] Electron correlation was accounted for by the MP2[57,58] and CCSD(T) methods.[59] The basis-set superposition error (BSSE)[60] was corrected for all calculations by using the counterpoise method.[61] $E_{\mathrm{CCSD(T)(limit)}}$ was estimated with the ARS model. Feller's method[62] and Helgater's method[63] were used for obtaining the MP2 interaction energy at the basis-set limit ($E_{\mathrm{MP2(limit)}}$). The HF and MP2 interaction energies were calculated with the Dunning's correlation consistent basis sets (cc-pVXZ, X = D, T, and Q and aug-cc-pVXZ, X = D and T). In Feller's method, the calculated HF interaction energies were fitted to the form $a + b\exp(-cX)$ (where X is 2 for cc-pVDZ, 3 for cc-pVTZ, etc.). The HF interaction energy at the basis-set limit ($E_{\mathrm{HF(limit)}}$) was then estimated by extrapolation. In Helgakers's method, the calculated MP2 level correlation interaction energies ($E_{\mathrm{corr(MP2)}}$, the difference between the MP2 and HF interaction energies) using the aug-cc-pVXZ, (X = D and T) were fitted to the form $a + bX^{-3}$. The $E_{\mathrm{corr(MP2)}}$ at the basis-set limit ($E_{\mathrm{corr(MP2)(limit)}}$) was then estimated by extrapolation. The $E_{\mathrm{MP2(limit)}}$ was obtained as the sum of the estimated $E_{\mathrm{HF(limit)}}$ and $E_{\mathrm{corr(MP2)(limit)}}$. The electrostatic and induction energies of the complexes were calculated with ORIENT version 3.2.[64] The electrostatic energy was obtained from the interactions between distributed multipoles of monomers. Distributed multipoles[65,66] up to hexadecapole on all atoms were obtained from the MP2/6-311G** wave functions of isolated monomers using CADPAC version 6.[67] The induction energy was calculated from the electric field produced by the distributed multipoles of monomers and polarizabilities.[68] The atomic polarizabilities of carbon ($\alpha = 10$ au) and fluorine ($\alpha = 3$ au) were used for the calculations.[69]



-5.07 kcal/mol
R = 3.6 Å
A Sandwich

-1.74 kcal/mol
R = 5.0 Å
B T-shaped

-0.88 kcal/mol
R = 6.0 Å
C T-shaped

-5.38 kcal/mol
R1 = 1.0 Å, R2 = 3.5 Å
D Slipped-parallel

Figure 1. Structures of the hexafluorobenzene−benzene complexes. The intermolecular distances in complexes **A**−**C** and horizontal and vertical displacements in complex **D** at the potential minima are shown. The CCSD(T) interaction energies of the complexes at the basis-set limit ($E_{\mathrm{CCSD(T)(limit)}}$) estimated by the ARS-E model are also shown. See the text and footnote d of Table 2.

Results and Discussion

Effects of Basis-Set and Electron Correlation. The intermolecular interaction energies of hexafluorobenzene−benzene complex **A** (Figure 1) were calculated using several basis sets. The calculated HF level interaction energy (E_{HF}) of the complex is not largely dependent on the basis set, whereas the MP2 interaction energy (E_{MP2}) has a strong basis-set dependence, as shown in Table 1 and Figure 2. The 6-31G, 6-31G*, and 6-311G** basis sets underestimate the attraction considerably as in the cases of the interactions of benzene, naphthalene, toluene, and thiophene dimers.[45−50] The calculated MP2- and CCSD(T) level interaction energies ($E_{\mathrm{CCSD(T)}}$) show that the MP2 calculations largely overestimate the attraction compared to the corresponding CCSD(T) calculations (Supporting Information Table 1S and 2S) as in the cases of other aromatic molecules.[45−50]

Estimation of CCSD(T) Interaction Energies at the Basis-Set Limit ($E_{\mathrm{CCSD(T)(limit)}}$). The $E_{\mathrm{CCSD(T)(limit)}}$ of the hexafluorobenzene−benzene complex was estimated with the ARS model[46,49] in this work. In this model the $E_{\mathrm{CCSD(T)(limit)}}$ was estimated according to eq 1

$$E_{\mathrm{CCSD(T)(limit)}} = E_{\mathrm{MP2(limit)}} + \Delta\mathrm{CCSD(T)(limit)} \qquad (1)$$

where ΔCCSD(T)(limit) denotes the CCSD(T) correction term ($\Delta\mathrm{CCSD(T)} = E_{\mathrm{CCSD(T)}} - E_{\mathrm{MP2}}$) at the basis-set limit. E_{MP2} and $E_{\mathrm{CCSD(T)}}$ denote the MP2 and CCSD(T) interaction energies.

$E_{\mathrm{MP2(limit)}}$ is obtained by extrapolation in the ARS-E model, whereas it was obtained by eq 2 in the ARS model

$$E_{\mathrm{MP2(limit)}} = E_{\mathrm{HF(limit)}} + E_{\mathrm{corr(MP2)(limit)}} \qquad (2)$$

where $E_{\mathrm{HF(limit)}}$ and $E_{\mathrm{corrMP2(limit)}}$ denote the HF interaction energy (E_{HF}) and MP2 level correlation interaction energy ($E_{\mathrm{corr(MP2)}} = E_{\mathrm{MP2}} - E_{\mathrm{HF}}$) at the basis-set limit.

The estimation of $E_{\mathrm{MP2(limit)}}$ by extrapolation requires a large CPU time. Therefore, the $E_{\mathrm{MP2(limit)}}$ value obtained by eq 2 was used in this work for the evaluation of the potential energy surface. The E_{HF} value obtained using a large basis set ($E_{\mathrm{HF(L)}}$) was used as the $E_{\mathrm{HF(limit)}}$ value because the basis-set dependence of the E_{HF} is small, if sufficiently large basis sets are used, as shown in Table 1.

$E_{\mathrm{corr(MP2)(limit)}}$ was obtained by eq 3

$$E_{\mathrm{corr(MP2)(limit)}} = E_{\mathrm{corr(MP2)(L)}}/F_{\mathrm{corr(MP2)}} \qquad (3)$$

where $E_{\mathrm{corr(MP2)(L)}}$ denotes the $E_{\mathrm{corr(MP2)}}$ obtained using the large

TABLE 1: HF and MP2 Interaction Energies of Hexafluorobenzene−Benzene Complexes A−D[a]

basis set	Bf[b]	E_{HF}[c]	E_{MP2}[c]	$E_{corr(MP2)}$[d]
complex **A**				
6-31G	174	0.39	−2.80	−3.19
6-31G*	282	1.62	−3.62	−5.24
6-311G**	360	1.16	−4.70	−5.86
aug(d)-6-311G*[e]	432	1.70	−6.41	−8.11
aug(d,p)-6-311G**[f]	468	1.73	−6.42	−8.15
cc-pVDZ	282	1.41	−4.07	−5.47
cc-pVTZ	624	1.53	−6.08	−7.61
cc-pVQZ	1170	1.54	−6.89	−8.43
aug-cc-pVDZ	468	1.45	−6.83	−8.28
aug-cc-pVTZ	966	1.55	−7.22	−8.76
basis-set limit		1.54[g]	−7.42[h]	−8.96[i]
complex **B**				
aug(d)-6-311G*[e]	432	1.94	−2.19	−4.12
cc-pVDZ	282	2.31	−0.96	−3.27
cc-pVTZ	624	2.16	−2.00	−4.15
cc-pVQZ	1170	2.07	−2.41	−4.49
aug-cc-pVDZ	468	2.09	−2.29	−4.37
aug-cc-pVTZ	966	2.07	−2.54	−4.61
basis-set limit		1.98[g]	−2.73[h]	−4.71[i]
complex **C**				
aug(d)-6-311G*[e]	432	0.96	−1.08	−2.04
cc-pVDZ	282	1.02	−0.33	−1.35
cc-pVTZ	624	0.97	−0.90	−1.87
cc-pVQZ	1170	0.96	−1.16	−2.12
aug-cc-pVDZ	468	0.95	−1.20	−2.14
aug-cc-pVTZ	966	0.94	−1.32	−2.27
basis-set limit		0.95[g]	−1.37[h]	−2.32[i]
complex **D**				
aug(d)-6-311G*[e]	432	1.68	−6.82	−8.50
cc-pVDZ	282	1.32	−4.36	−5.68
cc-pVTZ	624	1.54	−6.46	−7.99
cc-pVQZ	1170	1.56	−7.31	−8.86
aug-cc-pVDZ	468	1.49	−7.19	−8.68
aug-cc-pVTZ	966	1.57	−7.64	−9.20
basis-set limit		1.56[g]	−7.87[h]	−9.43[i]

[a] $R = 3.6$, 5.0, and 6.0 Å, respectively, in complexes **A**−**C**. $R_1 = 1.0$ Å and $R_2 = 3.5$ Å in complex **D**. See Figure 1 and the text. [b] Number of basis functions used for calculation of the complex. [c] BSSE-corrected interaction energies. [d] MP2 correlation interaction energy ($=E_{MP2} - E_{HF}$). [e] 6-311G* basis set augmented with diffuse d functions on carbon and fluorine atoms. See the text. [f] 6-311G** basis set augmented with diffuse d functions on carbon and fluorine atoms and diffuse p functions on hydrogen atoms. See the text. [g] Estimated HF level interaction energy at the basis-set limit ($E_{HF(limit)}$) by Feller's method from the calculated E_{HF} using cc-pVXZ (X = D, T, and Q) basis sets. See the text. [h] Estimated MP2 level interaction energy at the basis-set limit ($E_{MP2(limit)}$). Sum of $E_{HF(limit)}$ and $E_{corr(MP2)(limit)}$. [i] Estimated MP2 correlation interaction energy at the basis-set limit ($E_{corr(MP2)(limit)}$) by Helgaker's method from the calculated $E_{corr(MP2)}$ using aug-cc-pVDZ and aug-cc-pVTZ basis sets. See the text.

basis set near saturation. $F_{corr(MP2)}$ is a correction factor to estimate the $E_{corr(MP2)(limit)}$ value from the $E_{corr(MP2)(L)}$ value. The aug(d)-6-311G* basis set[56] was used for the large basis set in this work.

Although the aug(d)-6-311G* basis set employs a relatively small number of basis functions (432 basis functions are used for the hexafluorobenzene−benzene complex), the calculated E_{MP2} of complex **A** with this basis set (−6.41 kcal/mol) is close to those calculated using very large cc-pVTZ (624 base functions, −6.08 kcal/mol) and cc-pVQZ basis sets (1170 basis functions, −6.89 kcal/mol) and the estimated $E_{MP2(limit)}$ of the complex by the extrapolation (−7.42 kcal/mol), as shown in Table 1. Similar good performance of the aug(d)-6-311G* basis set for the calculations of complexes B−D is also shown in Table 1. These results show that the aug(d)-6-311G* basis set is close to saturation.

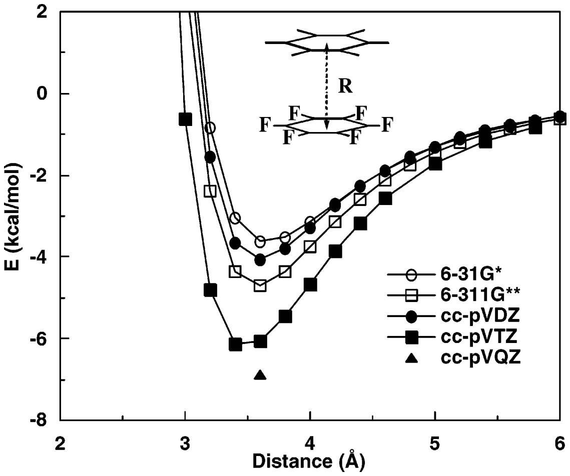


Figure 2. MP2 interaction energies of sandwich hexafluorobenzene−benzene complex **A** calculated using several basis sets.

The $E_{corr(MP2)(L)}$ of complex **A** is −8.11 kcal/mol. The $E_{corr(MP2)(limit)}$ value obtained from the extrapolaton is −8.96 kcal/mol. The $E_{corr(MP2)(L)}$ value of complex **A** is 90.5% of the $E_{corr(MP2)(limit)}$. A very close ratio (90.2%) was obtained for complex **D**.[70] Therefore, $F_{corr(MP2)} = 0.90$ was used for the estimation of $E_{corr(MP2)(limit)}$ by eq 3 in this work.

The ΔCCSD(T)(limit) value was estimated by eq 4

$$\Delta\text{CCSD(T)(limit)} = \Delta\text{CCSD(T)(M)} + \Delta\text{(M)}\Delta\text{CCSD(T)} \quad (4)$$

where ΔCCSD(T)(M) denotes the ΔCCSD(T) obtained using a medium-sized basis set. The ΔCCSD(T) has a weak basis-set dependence. Δ(M)ΔCCSD(T) is the correction term for the slight underestimation of ΔCCSD(T) by the medium-sized basis set. Δ(M)ΔCCSD(T) corresponds to the difference between the ΔCCSD(T) at the basis-set limit (ΔCCSD(T)(limit)) and the ΔCCSD(T)(M).

The ΔCCSD(T)(M) was obtained using the 6-31G basis set as the medium-sized basis set in this work, if not otherwise noted. The Δ(M)ΔCCSD(T) was estimated according to eq 5

$$\Delta\text{(M)}\Delta\text{CCSD(T)} = F_{\Delta\text{CCSD(T)}} \times \Delta\text{(M)}E_{corr(MP2)} = F_{\Delta\text{CCSD(T)}} \times (E_{corr(MP2)(limit)} - E_{corr(MP2)(M)}) \quad (5)$$

where $E_{corr(MP2)(M)}$ denotes the $E_{corr(MP2)}$ obtained using the medium-sized basis set. $\Delta(M)E_{corr(MP2)}$ ($=E_{corr(MP2)(limit)} - E_{corr(MP2)(M)}$) is the underestimation of the $E_{corr(MP2)}$ by the medium-sized basis set. $F_{\Delta CCSD(T)}$ is a parameter used for the estimation of Δ(M)ΔCCSD(T). The CCSD(T) interaction energies of benzene, thiophene, and naphthalene dimers using several basis sets (6-31G*, 6−311*, 6-311G**, cc-pVDZ, and a modified cc-pVTZ basis sets) show that ΔCCSD(T) is always 20−29% of the absolute value of $E_{corr(MP2)}$.[45−50] These results suggest that we can assume that Δ(M)ΔCCSD(T) is approximately 25 ± 5% of the absolute value of $\Delta(M)E_{corr(MP2)}$. Therefore, $F_{\Delta CCSD(T)} = -0.25$ was used for the estimation of Δ(M)ΔCCSD(T) using eq 5 in this work.

Interaction Energy of the Hexafluorobenzene−Benzene Complex. The interaction energies ($E_{CCSD(T)(limit)}$) of hexafluorobenzene−benzene complexes **A**−**D** were calculated by the ARS model with changing intermolecular geometrical parameters, as summarized in Table 2. The calculated interaction

TABLE 2: Estimated MP2 and CCSD(T) Interaction Energies of Benzene−Hexafluorobenzene Complexes A−D at the Basis-Set Limit by the ARS Model[a]

dimer	R_1[b]	R or R_2[b]	$E_{\mathrm{MP2(limit)}}$[c]	$E_{\mathrm{CCSD(T)(limit)}}$[d]
A		3.0	−3.09	2.16
		3.2	−6.82	−2.89
		3.4	−7.72	−4.76
		3.6	−7.31	−5.08 (−5.07)
		3.8	−6.41	−4.70
		4.0	−5.38	−4.07
		4.2	−4.42	−3.41
		4.4	−3.58	−2.80
		4.6	−2.88	−2.28
B		4.8	−2.52	−1.35
		5.0	−2.64	−1.78 (−1.74)
		5.2	−2.41	−1.76
		5.4	−2.04	−1.56
C		5.8	−1.41	−0.86
		6.0	−1.31	−0.89 (−0.88)
		6.2	−1.13	−0.80
		6.4	−0.93	−0.68
D	0.6	3.3	−8.07	−4.76
	0.6	3.5	−7.79	−5.30
	0.6	3.7	−6.89	−5.00
	0.8	3.3	−8.29	−5.06
	0.8	3.5	−7.82	−5.39
	0.8	3.7	−6.84	−4.99
	1.0	3.3	−8.37	−5.25
	1.0	3.5	−7.76	−5.41 (−5.38)
	1.0	3.7	−6.73	−4.94
	1.2	3.3	−8.29	−5.29
	1.2	3.5	−7.60	−5.34
	1.2	3.7	−6.56	−4.84

[a] Energies in kcal/mol. The geometries are shown in Figure 1. [b] Distance in Å. See Figure 1. [c] MP2 interaction energies at the basis-set limit estimated by eq 2 using the aug(d)-6-311G* basis set. See the text. [d] CCSD(T) interaction energy at the basis-set limit estimated by the ARS model using the aug(d)-6-311G* basis set as the large basis set and the 6-31G basis set as the medium-sized basis set. The estimated value by the ARS-E model using the 6-31G* basis set as the medium-sized basis set is shown in parentheses. $E_{\mathrm{MP2(limit)}}$ was estimated from the estimated $E_{\mathrm{HF(limit)}}$ by Feller's method using the cc-pVXZ (X = D, T, and Q) and the estimated $E_{\mathrm{corr(MP2)(limit)}}$ by Helgaker's method using the aug-cc-pVXZ (X = D and T) in this model. See the text.

TABLE 3: Estimated HF and MP2 Interaction Energies of Benzene−Hexafluorobenzene Complexes A−D at the Basis-Set Limit ($E_{\mathrm{HF(limit)}}$ and $E_{\mathrm{MP2(limit)}}$)[a]

	A	B	C	D
estimated values using the cc-pVXZ basis sets				
$E_{\mathrm{HF(limit)}}$				
Helgaker DT[b]	1.5850	2.0903	0.9519	1.6286
Helgaker TQ[c]	1.5467	2.0113	0.9469	1.5694
Feller DTQ[d]	1.5410	1.9756	0.9512	1.5571
$E_{\mathrm{corr(MP2)(limit)}}$[e]				
Helgaker DT[b]	−8.5064	−4.5256	−2.0874	−8.9652
Helgaker TQ[c]	−9.0291	−4.7270	−2.3037	−9.4975
Feller DTQ[d]	−8.9437	−4.6841	−2.3572	−9.3876
$E_{\mathrm{MP2(limit)}}$				
Helgaker DT[b,f]	−6.9214	−2.4353	−1.1355	−7.3366
Helgaker TQ[c,f]	−7.4824	−2.7157	−1.3568	−7.9281
Feller DTQ[d,f]	−7.4421	−2.6887	−1.3984	−7.8906
$E_{\mathrm{HF(limit)}} + E_{\mathrm{corr(MP2)(limit)}}$[g]	−7.4881	−2.7513	−1.3525	−7.9404
estimated values using the aug-cc-pVXZ basis sets				
$E_{\mathrm{HF(limit)}}$[h]	1.5856	2.0595	0.9410	1.5981
$E_{\mathrm{corr(MP2)(limit)}}$[h]	−8.9646	−4.7100	−2.3187	−9.4255
$E_{\mathrm{MP2(limit)}}$[f,h]	−7.3791	−2.6504	−1.3778	−7.8274
$E_{\mathrm{MP2(limit)}}$[i]	−7.4236	−2.7343	−1.3675	−7.8685

[a] Energies in kcal/mol. The geometries are shown in Figure 1. [b] Estimated values by Helgaker's method using the cc-pVDZ and cc-pVTZ basis sets. [c] Estimated values by Helgaker's method using the cc-pVTZ and cc-pVQZ basis sets. [d] Estimated values by Feller's method using the cc-pVXZ (X = D, T and Q) basis sets. [e] MP2 correlation interaction energy at the basis-set limit estimated from $E_{\mathrm{corr(MP2)}}$ (=$E_{\mathrm{MP2}} - E_{\mathrm{HF}}$). [f] Estimated directly from the calculated E_{MP2} value. [g] Sum of the $E_{\mathrm{HF(limit)}}$ obtained by Feller's method and the $E_{\mathrm{corr(MP2)(limit)}}$ obtained by Helgaker's method using the cc-pVTZ and cc-pVQZ basis sets. [h] Estimated values by Helgaker's method using the aug-cc-pVDZ and aug-cc-pVTZ basis sets. [i] Sum of the $E_{\mathrm{HF(limit)}}$ obtained by Feller's method using cc-pVXZ (X = D, T, and Q) basis sets and the $E_{\mathrm{corr(MP2)(limit)}}$ obtained by Helgaker's method using the aug-cc-pVDZ and aug-cc-pVTZ basis sets.

energy potentials of complexes **A** (sandwich), **B**, and **C** (T-shaped) have their minima when their intermolecular separations, R, are 3.6, 5.0, and 6.0 Å, respectively. Complex **D** (slipped-parallel) has the largest (most negative) interaction energy when R_1 and R_2 are 1.0 and 3.5 Å. The calculated interaction energies ($E_{\mathrm{CCSD(T)(limit)}}$) of complexes **A**−**D** at the potential minima are −5.08, −1.78, −0.89, and −5.41 kcal/mol, respectively.

The $E_{\mathrm{CCSD(T)(limit)}}$ of complexes **A**−**D** at the potential minima were also calculated using the ARS-E model. In this model, the $E_{\mathrm{MP2(limit)}}$ values estimated by the extrapolation shown in Table 3 were used. $E_{\mathrm{HF(limit)}}$ was estimated by Feller's method from the calculated HF interaction energies using the cc-pVXZ (X = D, T, and Q) basis sets. The estimated $E_{\mathrm{HF(limit)}}$ of the complexes are 1.54, 1.98, 0.95, and 1.56 kcal/mol, respectively. $E_{\mathrm{MP2(corr)(limit)}}$ was estimated by Helgaker's method from the MP2 calculations using the aug-cc-pVXZ (X = D and T) basis sets. The estimated $E_{\mathrm{MP2(corr)(limit)}}$ values are −8.96, −4.71, −2.32, and −9.42 kcal/mol, respectively. (The $E_{\mathrm{MP2(corr)(limit)}}$ obtained by Helgeker's method using the cc-pVXZ (X = T and Q) (−9.02, −4.73, −2.30 and −9.50 kcal/mol) and those obtained by Feller's method using the cc-pVXZ (X = D, T and Q) (−8.94, −4.68, −2.36 and −9.39 kcal/mol) are close to these values.) The estimated $E_{\mathrm{MP2(limit)}}$ values (sum of $E_{\mathrm{HF(limit)}}$ and $E_{\mathrm{MP2(corr)(limit)}}$) of the complexes are −7.42, −2.73, −1.37, and −7.87 kcal/mol, respectively. The estimated ΔCCSD(T)(limit) of the complexes using the 6-31G* basis set as the medium-sized basis sets (Table 2S) are 2.35, 0.99, 0.49, and 2.49 kcal/mol, respectively. The estimated $E_{\mathrm{CCSD(T)(limit)}}$ (sum of $E_{\mathrm{MP2(limit)}}$ and ΔCCSD(T)(limit)) are −5.07, −1.74, −0.88, and −5.38 kcal/mol, respectively (Table 2 and Table 2S). The $E_{\mathrm{CCSD(T)(limit)}}$ values obtained using the 6-31G basis set as the medium-sized basis set (−5.20, −1.84, −0.94, and −5.52 kcal/mol) are not largely different from those obtained using the 6-31G* basis set as the medium-sized basis set (Table 2S). The differences are less than 0.14 kcal/mol. The good agreement suggests that further improvement of the medium-sized basis set does not largely change the ΔCCSD(T)(limit).

The estimated $E_{\mathrm{HF(limit)}}$ values are very close to the calculated HF interaction energies using the cc-pVQZ basis set as shown in Tables 1 and 3. The difference is less than 0.1 kcal/mol, which suggests that the errors associated with the estimation of $E_{\mathrm{HF(limit)}}$ are less than 0.1 kcal/mol. The estimated $E_{\mathrm{corr(MP2)(limit)}}$ values are close to the calculated $E_{\mathrm{corr(MP2)}}$ using the aug-cc-pVTZ basis set, which shows that the aug-cc-pVTZ basis set is close to saturation. The differences are less than 0.2 kcal/mol. The errors of $E_{\mathrm{corr(MP2)(limit)}}$ values associated with extrapolation are probably less than 0.1 kcal/mol. Therefore, we can expect that the errors associated with the estimation of $E_{\mathrm{MP2(limit)}}$ (=$E_{\mathrm{HF(limit)}} + E_{\mathrm{corr(MP2)(limit)}}$) are less than 0.2 kcal/mol. The ΔCCSD(T)(limit) was estimated from the ΔCCSD(T)(M) obtained using the medium-sized basis set and the Δ(M)ΔCCSD(T) (estimated error of ΔCCSD(T)). It was assumed that the Δ(M)ΔCCSD(T) was 25 ± 5% of $\Delta(\text{M})E_{\text{corr(MP2)}}$. The $\Delta(\text{M})E_{\text{corr(MP2)}}$ values of the four complexes using the 6-31G* basis set as the medium-sized basis set are 0.9 to 4.1 kcal/mol. Five percent of the $\Delta(\text{M})E_{\text{corr(MP2)}}$ values are 0.05 to 0.20 kcal/mol. Therefore, we can expect that the errors of the estimated ΔCCSD(T)(limit) are less than 0.2 kcal/mol. From these evaluations, we can conclude that the errors of the estimated $E_{\text{CCSD(T)(limit)}}$ values by the ARS-E model in this work are less than 0.4 kcal/mol.

The error of the relative value of the $E_{\text{CCSD(T)(limit)}}$ of complexes **A** and **D** is smaller than the errors of the $E_{\text{CCSD(T)(limit)}}$ values. The estimated $E_{\text{HF(limit)}}$ values of complexes **A** and **D** are 1.541 and 1.557 kcal/mol, respectively. The $E_{\text{HF(limit)}}$ of complex **D** is 0.016 kcal/mol larger than that of A. Nearly the same difference (0.015 kcal/mol) was obtained from the HF/cc-pVQZ level calculations, which shows that the error of the relative E_{HF} associated with the extrapolation is negligible (less than 0.001 kcal/mol). The difference between the estimated $E_{\text{corr(MP2)(limit)}}$ values of complexes **A** and **D** is 0.461 kcal/mol. The difference of the $E_{\text{corr(MP2)}}$ obtained using the aug-cc-pVTZ basis set is 0.423 kcal/mol. The change of the difference by the extrapolation is only 0.038 kcal/mol. Therefore, we can expect that the error of the relative value of $E_{\text{MP2(limit)}}$ of the two complexes is less than 0.04 kcal/mol. The ΔCCSD(T)(M) (ΔCCSD(T) values calculated using the 6-31G* basis set as the medium-sized basis set) of complexes **A** and **D** are 1.422 and 1.478 kcal/mol. The difference is 0.056 kcal/mol. The estimated ΔCCSD(T)(limit) of the complexes are 2.365 and 2.491 kcal/mol. The difference of the ΔCCSD(T)(limit) is 0.126 kcal/mol. The change of the difference between the ΔCCSD(T) of two complexes by the estimation at the basis-set limit is only 0.070 kcal/mol. Therefore, we can assume that the error of relative energy of two complexes associated with the estimation of ΔCCSD(T)(limit) is less than 0.07 kcal/mol. From these evaluations, we can conclude that the error of the calculated energy difference ($E_{\text{CCSD(T)(limit)}}$) of complexes **A** and **D** by the ARS-E model is less than 0.11 kcal/mol (=0.04 + 0.07 kcal/mol).

In the above calculations, the fixed monomer geometries were used. Full optimization of the complex may largely change the calculated interaction energy of the complex. The geometry of complex **D** was fully optimized at the MP2/6-311G* level with counterpoise correction for evaluating the effect of geometry optimization. The changes of bond distances and valence angles by the optimization are less than 0.003 Å and 0.1°. The interaction energy of the fully optimized complex calculated at the MP2/cc-pVTZ level was −6.68 kcal/mol. The geometry of complex **D** was also optimized at the MP2/6-311G* level using the fixed monomer geometries with changing R_1 and R_2 (horizontal displacement and vertical separation). The optized R_1 and R_2 values are 0.92 and 3.45 Å. The calculated interaction energy of the optimized geometry at the MP2/cc-pVTZ level was −6.59 kcal/mol, which is only 0.09 kcal/mol smaller (less negative) than that of the fully optimized complex. The small difference shows that the effect of geometry changes upon complex formation is very small.

Our calculations show that slipped-parallel complex **D** is considerably more stable than T-shaped complexes **B** and **C**. Sandwich complex **A** is slightly less stable than slipped-parallel complex **D**. The energy difference between complexes **A** and **D** (0.31 kcal/mol) is considerably smaller than that between the slipped-parallel and sandwich benzene dimers (1.00 kcal/mol).[46]

Hernandez-Trujillo et al. reported that the sandwich structure is stable and the T-shaped structure is repulsive.[39] The calculated MP2 level interaction energy of the sandwich structure is −4.33 kcal/mol. More recently, Vanspeybrouck et al. reported that a slipped-parallel equilibrium geometry was obtained from the MP2/6-31G* level geometry optimization.[41] The calculated interaction energy of the sipped-parallel structure is −4.02 kcal/mol. The MP2 level interaction energies reported by these groups are not largely different from the $E_{\text{CCSD(T)(limit)}}$ of complex **D** estimated in this work (−5.38 kcal/mol). They used considerably smaller basis sets than those used this work, which leads the underestimation of the attraction, while the MP2 method overestimates the attraction compared to the CCSD(T) method. The error cancellation would be the cause of the fairly good performance of their MP2 calculations.

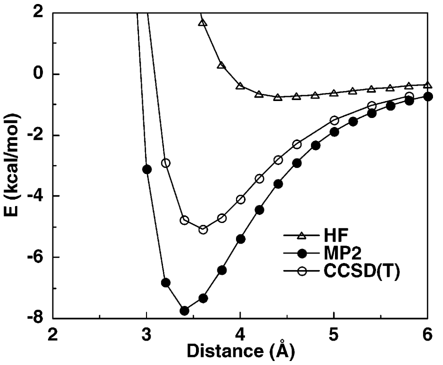


Figure 3. HF, MP2, and CCSD(T) interaction energies of sandwich hexafluorobenzene−benzene complex **A**. The HF interaction energies were calculated with the aug(d)-6-311G* basis set. The MP2 and CCSD(T) interaction energies were the estimated values at the basis-set limit. See the text.

Molecular beam studies show that hexafluorobeznene and benzene are nearly parallel in the gas phase.[18] A similar parallel structure was also observed in the liquid phase by neutron diffraction measurements.[20] The calculated interaction energies show that the complex prefers the parallel structures, which agrees well with the experimental observation. The slipped-parallel structure was also found in the crystal of a 1:1 mixture. The observed interplanar distance (ca 3.4 Å) is close to the calculated vertical separation (3.5 Å) in the most stable slipped-parallel complex, **D**.

Source of Attraction and Directionality. The electrostatic and induction energies (E_{es} and E_{ind}) of hexafluorobenzene−benzene complexes **A**−**D** at the potential minima are summarized in Table 3. E_{total} is the estimated $E_{\text{CCSD(T)(limit)}}$ by the ARS-E model. E_{corr} is the effect of electron correlation on the calculated total interaction energy, which is the difference between E_{total} and E_{HF}. The dispersion interaction is the major contributor to E_{corr}. E_{rep} (= $E_{\text{HF}} - E_{\text{es}} - E_{\text{ind}}$) is mainly exchange-repulsion energy, but it also includes some other terms.

The absolute value of E_{corr} is always considerably greater than that of E_{es}, which indicates that dispersion is the major source of attraction in the hexafluorobenzene−benzene complex. E_{ind} is always small (less than 0.5 kcal/mol). The calculated interaction energy potential of complex **A** (Figure 3) also shows the importance of dispersion because electron correlation considerably increases the attraction. The complex has substantial attraction even when the molecules are well separated, which shows that short-range interactions such as charge transfer are not the major source of attraction in the hexafluorobenzene−benzene complex.

Comparison with Benzene Dimer. Slipped-parallel and T-shaped benzene dimers are nearly isoenergetic,[45−47] whereas the slipped-parallel hexafluorobenzene−benzene complex is considerably more stable than the T-shaped ones. Electrostatic

TABLE 4: Electrostatic, Induction, and Dispersion Energies of Hexafluorobenzene−Benzene Complexes and Benzene Dimers[a]

complex	$E_{\mathrm{total}}{}^{b}$	$E_{\mathrm{es}}{}^{c}$	$E_{\mathrm{ind}}{}^{d}$	$E_{\mathrm{rep}}{}^{e}$	$E_{\mathrm{corr}}{}^{f}$
hexafluorobenzene-benzene					
sandwich (**A**)	−5.07	−1.15	−0.46	3.14	−6.61
slipped-paralell (**D**)	−5.38	−1.12	−0.47	3.15	−6.94
T-shaped (**B**)	−1.74	0.60	−0.08	1.45	−3.72
T-shaped (**C**)	−0.88	0.41	−0.05	0.59	−1.83
benzene dimer					
slipped-parallel[g]	−2.48	0.90	−0.25	3.01	−6.14
T-shaped[g]	−2.46	−0.55	−0.17	1.74	−3.48

[a] Energies in kcal/mol. [b] Estimated CCSD(T) interaction energies at the basis-set limit ($E_{\mathrm{CCSD(T)(limit)}}$) by the ARS-E model. See the text. [c] Electrostatic energies. See the text. [d] Induction energies. See the text. [e] Repulsion energies ($=E_{\mathrm{HF}} - E_{\mathrm{es}} - E_{\mathrm{ind}}$). E_{HF} was calculated using the aug(d)-6-311G* basis set. [f] Correlation interaction energies ($=E_{\mathrm{total}} - E_{\mathrm{HF}}$). See the text. [g] References 46 and 50.

interaction (quadrupole−quadrupole inetraction) stabilizes the T-shaped benzene dimer, whereas dispersion interaction increases the relative stability of the slipped-parallel benzene dimer.[45−47] Because of the balance of the two interactions, the T-shaped and slipped-parallel benzene dimers are nearly isoenergetic. However, the quadrupole−quadrupole interaction is attractive in the slipped-parallel hexafluorobenzene-benzene complex because the quadrupole moments of benzene and hexafluorobenzene are opposite in sign. Both electrostatic and dispersion interactions enhance the relative stability of the slipped-parallel hexafluorobenzene−benzene complex. Therefore, the interaction energy of slipped-parallel hexafluorobenzene−benzene complex **D** (−5.38 kcal/mol) is considerably larger than those of T-shaped complexes **B** and **C** (−1.74 and −0.88 kcal/mol, respectively).

The E_{total} value of slipped-parallel hexafluorobenzene−benzene complex **D** is 2.2 times larger than that of the slipped-parallel benzene dimer (−2.48 kcal/mol).[46] The large E_{corr} (−6.94 and −6.14 kcal/mol) values indicate that dispersion is the major source of the attraction in both systems.[46] The E_{corr} of the slipped-parallel hexafluorobenzene−benzene complex is only 13% larger than that of the benzene dimer. The difference of electrostatic energies (−1.12 and 0.90 kcal/mol) is the major cause of the considerably larger E_{total} of slipped-parallel hexafluorobenzene−benzene complex **D** than that of the benzene dimer.

Slipped-parallel hexafluorobenzene−benzene complex **D** is slightly (0.31 kcal/mol) more stable than sandwich complex **A**. The E_{es}, E_{ind}, and E_{rep} values of complex **D** are nearly equal to those of the complex **A**, whereas the E_{corr} of **D** is 0.33 kcal/mol larger (more negative) than that of **A**, which shows that the larger dispersion interaction is the cause of the greater stability of slipped-parallel complex **D**. The smaller vertical separation in complex **D** (3.5 Å) than that in complex **A** (3.6 Å) would be the cause of the larger dispersion energy.

Conclusions

The estimated CCSD(T) interaction energies of the benzene-hexafluorobenzene complexes at the basis-set limit show that the slipped-parallel (C_s) structure has the largest (most negative) interaction energy (−5.38 kcal/mol). The sandwich (C_{6v}) structure is slightly less stable (−5.07 kcal/mol). The interaction energies of the two T-shaped structures (C_{2v}) are very small. The electrostatic interaction is substantially smaller than the dispersion interaction. The dispersion interaction is the major source of the attraction. But both dispersion and electrostatic interaction play important roles for the directionality of the interaction.

Although the T-shaped and slipped-parallel benzene dimer are nearly isoenergetic, the slipped-parallel hexafluorobenzene−benzene complex is substantially more stable than the T-shaped ones. The electrostatic interaction stabilizes the T-shaped benzene dimer, whereas it destabilizes the T-shaped hexafluorobenzene−benzene complex. The dispersion interaction enhances the relative stability of the slipped-parallel benzene dimer and the hexafluorobenzene−benzene complex. The stabilization of the slipped-parallel hexafluorobenzene−benzene complex by both electrostatic and dispersion interactions is the cause of the preference of this structure and larger interaction energy compared to the benzene dimer.

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Supporting Information Available: Table 1S shows the estimated MP2 and CCSD(T) interaction energies of the hexafluorobenzene−benzene complex at the basis-set limit by the ARS model using the 6-31G basis set as the medium-sized basis set, and Table 2S shows the estimated MP2 and CCSD(T) interaction energies of the hexafluorobenzene−benzene complex at the absis-set limit by the ARS-E model using the 6-31G and 6-31G* basis sets as the medium-sized basis set. This material is available free of charge via the Internet at http://pubs.acs.org.

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(70) The ratio obtained for complexes **B** and **C** (87.6% and 88.0%) are slightly (about 3%) smaller. The use of $F_{\text{corr(MP2)}} = 0.90$ for complexes **B** and **C** slightly underestimates the $E_{\text{corr(MP2)(limit)}}$ value. The underestimation is less than 0.15 kcal/mol, as the absolute values of $E_{\text{corr(MP2)(limit)}}$ of complexes **B** and **C** are less than 5 kcal/mol.