

Supporting Information

Effects of basis set and electron correlation correction

Intermolecular interaction energies of the complexes, where the C-H bond points toward the center of benzene ring, (Fig. 1) were calculated at HF and MP2 levels using Dunning' correlation consistent basis sets (cc-pVXZ, X = D, T and Q)^{45,46} to evaluate the basis set effects. The basis set dependence of the HF interaction energies (E_{HF}) is very small. The MP2 interaction energies (E_{MP2}) of the complexes greatly depend on the basis set as summarized in Table 1S. Small cc-pVDZ basis set considerably underestimates the attraction compared with large cc-pVQZ basis set. The significant basis set dependence shows that a very large basis set near saturation is necessary for quantitative evaluation of the CH/ π interaction energy.

Interaction energies of four complexes were calculated by the MP3, CCSD, and CCSD(T) methods using several basis sets to evaluate the effects of electron correlation beyond MP2. The calculated interaction energies are summarized in Table 2S. The MP2 interaction energies are larger (more negative) than the CCSD(T) energies [$E_{\text{CCSD(T)}}$], which shows that CCSD(T) level electron correlation correction is necessary for quantitative evaluation of the CH/ π interactions. The CCSD calculations substantially underestimate the attraction compared with the CCSD(T), which indicates the importance of triple excitation for the attraction

Estimation procedure of CCSD(T) level interaction energy at the basis set limit

The strong basis set dependence and substantial electron correlation effects beyond MP2 show that the estimation of CCSD(T) interaction energy at the basis set limit

[$E_{\text{CCSD(T)}(\text{limit})}$] is necessary for quantitative analysis of the CH/ π interaction.

$E_{\text{CCSD(T)}(\text{limit})}$ was estimated according to

$$E_{\text{CCSD(T)}(\text{limit})} = E_{\text{MP2}(\text{limit})} + \Delta\text{CCSD(T)} \quad (1)$$

where $E_{\text{MP2}(\text{limit})}$ denotes the estimated MP2 interaction energy at the basis set limit and $\Delta\text{CCSD(T)}$ denotes CCSD(T) correction term [$\Delta\text{CCSD(T)} = E_{\text{CCSD(T)}} - E_{\text{MP2}}$], which is the difference between the calculated CCSD(T) and MP2 interaction energies using a medium-size basis set.³

The MP2 interaction energies were calculated with Dunning's correlation consistent basis sets (cc-pVXZ, X = D, T, and Q). The $E_{\text{MP2}(\text{limit})}$ was estimated by the method of Feller.⁴⁷ 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 $E_{\text{MP2}(\text{limit})}$ was then estimated by extrapolation.

The $E_{\text{CCSD(T)}}$ and E_{MP2} of the complexes depend on the basis set greatly, while the basis set dependence of $\Delta\text{CCSD(T)}$ is not large as summarized in Table 2S. The small basis set dependence of $\Delta\text{CCSD(T)}$ suggests that the $E_{\text{CCSD(T)}(\text{limit})}$ can be estimated sufficiently accurately from the $\Delta\text{CCSD(T)}$ calculated with a medium-size basis set. The $\Delta\text{CCSD(T)}$ was calculated using the cc-pVDZ basis set in this work.

It should be noted that the calculated MP2 level interaction energies using the cc-pVTZ basis set are always very close to the estimated $E_{\text{CCSD(T)}(\text{limit})}$ values. The cc-pVTZ basis set underestimates the attraction compared with the basis set limit, while the MP2 method

overestimates the attraction compared with the CCSD(T) method. Apparently error cancellation is the cause of the good performance of the MP2/cc-pVTZ level calculations.

TABLE 1S. Interaction Energies for CH/ π Complexes^a

	R ^b	HF ^c		MP2 ^c		E _{MP2(limit)} ^d	Δ CCSD(T) ^e	E _{CCSD(T)(limit)} ^f
	(Å)	cc-pVQZ	cc-pVDZ	cc-pVTZ	cc-pVQZ			
C ₆ H ₆ -CH ₄ ^g	3.8	0.85	-0.70	-1.42	-1.64	-1.74	0.29	-1.45
C ₆ H ₆ -CH ₃ CH ₃ ^g	3.6	1.80	-0.85	-1.90	-2.20	-2.33	0.51	-1.82
C ₆ H ₆ -CH ₂ CH ₂ ^g	3.6	1.17	-1.11	-2.08	-2.41	-2.57	0.51	-2.06
C ₆ H ₆ -CHCH ₃ ^g	3.6	-0.57	-2.17	-2.96	-3.22	-3.36	0.53	-2.83
C ₆ H ₆ -CH ₃ NH ₂	3.6	1.64	-0.66	-1.81	-2.19	-2.38	0.44	-1.94
C ₆ H ₆ -CH ₃ OH	3.6	1.25	-0.86	-1.88	-2.23	-2.41	0.42	-1.98
C ₆ H ₆ -CH ₃ OCH ₃	3.6	1.29	-1.05	-2.04	-2.36	-2.51	0.45	-2.06
C ₆ H ₆ -CH ₃ F	3.6	0.55	-1.18	-2.15	-2.49	-2.67	0.36	-2.31
C ₆ H ₆ -CH ₃ Cl ^h	3.6	0.38	-1.79	-2.93	-3.32	-3.53	0.54	-2.99
C ₆ H ₆ -CH ₂ CINH ₂	3.4	1.59	-1.81	-3.54	-4.12	-4.41	0.84	-3.57
C ₆ H ₆ -CH ₂ ClOH	3.4	1.19	-1.82	-3.54	-4.14	-4.48	0.77	-3.71
C ₆ H ₆ -CH ₂ Cl ₂ ^h	3.4	0.60	-2.75	-4.53	-5.15	-5.49	0.95	-4.54
C ₆ H ₆ -CH ₂ FCI	3.4	0.51	-2.16	-3.71	-4.27	-4.60	0.71	-3.88
C ₆ H ₆ -CH ₂ F ₂	3.6	-0.53	-1.90	-2.90	-3.29	-3.55	0.33	-3.22
C ₆ H ₆ -CHCl ₃ ^h	3.2	2.21	-3.16	-5.89	-6.80	-7.25	1.61	-5.64
C ₆ H ₆ -CHF ₃ ^h	3.4	-0.76	-2.34	-3.73	-4.28	-4.62	0.44	-4.18

^a Energies in kcal/mol. The geometries of complexes are shown in Fig. 1.

^b Distance between the carbon atom of C-H bond and the centroid of the benzene.

^c BSSE corrected interaction energies of complexes.

^d Estimated MP2 level interaction energy at the basis set limit by Feller's method. See text.

^e CCSD(T) correction term. The difference between the CCSD(T) and MP2 level interaction energies using the cc-pVDZ basis set. See text.

^f Estimated CCSD(T) level interaction energy at the basis set limit by equation (1). See text.

^g Ref. 3.

^h Ref. 7.

TABLE 2S. Effects of Electron Correlation on Calculated Interaction Energies of CH/ π Complexes^a

	E_{HF}	E_{MP2}	E_{MP3}	E_{CCSD}	$E_{\text{CCSD(T)}}$	$\Delta\text{CCSD(T)}^{\text{b}}$
C₆H₆-CH₄^c						
6-31G*	0.85	-0.30	-0.09	0.01	-0.10	0.19
6-311G*	0.83	-0.63	-0.33	-0.23	-0.38	0.25
6-311G**	0.82	-0.83	-0.48	-0.37	-0.54	0.29
cc-pVDZ	0.83	-0.70	-0.35	-0.25	-0.41	0.29
cc-pVTZ	0.84	-1.42	-0.94	-0.79	-1.06	0.35
C₆H₆-CH₂CH₂						
6-31G*	1.15	-0.61	-0.18	-0.04	-0.22	0.39
6-311G*	1.10	-0.77	-0.29	-0.14	-0.35	0.42
6-311G**	1.12	-1.08	-0.52	-0.37	-0.60	0.48
cc-pVDZ ^d	1.14	-1.11	-0.49	-0.35	-0.60	0.51
C₆H₆-CHCH						
6-31G*	-0.65	-1.88	-1.44	-1.34	-1.46	0.43
6-311G*	-0.71	-2.24	-1.69	-1.58	-1.73	0.51
6-311G**	-0.65	-2.25	-1.63	-1.55	-1.73	0.52
cc-pVDZ ^d	-0.66	-2.17	-1.53	-1.47	-1.64	0.53
cc-pVTZ	-0.61	-2.96	-2.20	-2.09	-2.38	0.57
C₆H₆-CH₃Cl						
6-31G*	0.25	-1.43	-1.01	-0.87	-1.03	0.40
6-311G*	0.14	-1.94	-1.40	-1.25	-1.47	0.47
6-311G**	0.18	-2.06	-1.44	-1.30	-1.55	0.51
cc-pVDZ ^d	0.33	-1.79	-1.14	-1.03	-1.25	0.54

^a Energies in kcal/mol. The geometries of complexes are shown in Fig. 1. Distances between the carbon atom of C-H bond and the centroid of the benzene are shown in Table 1S. BSSE corrected interaction energies of complexes.

^b CCSD(T) correction term. The difference between the CCSD(T) and MP2 level interaction energies. See text.

^c Ref. 3.

^d Ref. 7.