Electronic supplementary information (ESI)

Geometry optimizations of complexes. Estimation procedure of the MP2 and CCSD(T) level interaction energies for the complexes at the basis set limit.

Geometry optimizations of complexes

MP2 level calculations overestimate the attraction compared with CCSD(T) calculations as shown in Figure 1. Therefore, the MP2 level geometry optimization of the benzene-*p*-benzoquinone complex using a large basis set near basis set limit underestimates the equilibrium intermolecular distance compared with the CCSD(T) calculations with the large basis set. On the other hand, the equilibrium intermolecular distance obtained by the MP2/6-311G* level geometry optimization is close to that of the CCSD(T) level potential at the basis set limit as shown in Figure 1S. Error cancellation is the cause of the good performance of the MP2/6-311G* level geometry optimization. Medium size 6-311G* basis set underestimates the attraction by the dispersion interactions compared with a large basis set near saturation and therefore overestimates the equilibrium intermolecular distance. The MP2 calculations underestimate the equilibrium intermolecular distance compared with the CCSD(T) calculations owing to the overestimation of the attraction.

Estimation procedure of MP2 level interaction energy at the basis set limit

The MP2 level interaction energy at the basis set limit [$E_{MP2(limit)}$] for the complex was obtained by Helgaker et al.'s method from the MP2 interaction energies (E_{MP2}) obtained using the aug-cc-pVDZ and aug-cc-pVTZ basis sets. In Helgaker et al.'s method the calculated E_{MP2} were fitted to a form $a + b X^{-3}$ (where X is 2 for aug-cc-pVDZ and 3 for aug-cc-pVTZ). The $E_{MP2(limit)}$ was then calculated by an extrapolation. Helgaker et al.'s method was originally proposed for calculating the electron correlation contribution at the basis set limit. But we used this method to calculate the $E_{MP2(limit)}$, since the basis set dependence of HF level interaction energy (E_{HF}) is small. The E_{MP2} calculated for the complexes using the aug-cc-pVDZ and aug-cc-pVTZ basis set and the $E_{MP2(limit)}$ obtained by Helgaker et al.'s method are summarized in Table 1S.

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

The CCSD(T) level interaction energy at the basis set limit [$E_{CCSD(T)(limit)}$] for the complex was obtained according to equation (1)

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

where ΔCCSD(T)(limit) denotes the CCSD(T) correction term [ΔCCSD(T)] at the basis set limit. The ΔCCSD(T) [= $E_{CCSD(T)} - E_{MP2}$] is the difference between the CCSD(T) level interaction energy [$E_{CCSD(T)}$] and the MP2 level interaction energy (E_{MP2}). The ΔCCSD(T)(limit) was obtained by equation (2)

$$\Delta CCSD(T)(limit) = \Delta CCSD(T)(M) + \Delta(M)\Delta CCSD(T), \quad (2)$$

where ΔCCSD(T)(M) denotes ΔCCSD(T) obtained using a Medium size basis set. The cc-pVDZ basis set was used for the Medium size basis set in this work. The ΔCCSD(T) has a weak basis set dependence. Δ(M)ΔCCSD(T) is a correction term for slight underestimation of the ΔCCSD(T) by the Medium size basis set. The Δ(M)ΔCCSD(T) corresponds to a difference between the ΔCCSD(T)(limit) and ΔCCSD(T)(M).

We can calculate the Δ(M)ΔCCSD(T), if we know the value of $F_{corr(M)}$, which is defined by equation (3)

$$F_{corr(M)} = \Delta CCSD(T)(M)/\Delta CCSD(T)(limit) \quad (3).$$

From equations (2) and (3) we can obtained equation (4)

$$\Delta(M)\Delta CCSD(T) = \Delta CCSD(T)(M) \times (1 - F_{corr(M)})/F_{corr(M)} \quad (4).$$

We calculated the $F_{corr(M)}$ value by equation (5) in this work

$$F_{corr(M)} = E_{corr(MP2)(M)}/E_{corr(MP2)(limit)} \quad (5),$$

where the $E_{corr(MP2)(M)}$ denotes the MP2 level electron correlation effect on the calculated interaction energy ($E_{corr(MP2)} = E_{MP2} - E_{HF}$) using the medium size basis set. The $E_{corr(MP2)(limit)}$ denotes the MP2 level electron correlation effect at the basis set limit (= $E_{MP2(limit)} - E_{HF(limit)}$). We can obtain sufficiently accurate $F_{corr(M)}$ value by equation (5), if the basis set dependence of the CCSD(T) level electron correlation effect is close to that of $E_{corr(MP2)}$. The E_{HF} calculated using the aug-cc-pVTZ basis set was used as the $E_{HF(limit)}$,

since the basis set dependence of the E_{HF} beyond the aug-cc-pVTZ basis set is small. The energy terms used for calculating the $E_{CCSD(T)(limit)}$ are summarized in Table 2S.

TABLE 1S. HF and MP2 Interaction Energies and MP2 Interaction Energies at the Basis Set Limit Calculated for Complexes[a]

	E_{HF}[b]		E_{MP2}[b]		$E_{MP2(limit)}$[c]
	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVDZ	aug-cc-pVTZ	
benzene-*p*-benzoquinone	2.716	2.775	-7.244	-7.772	-7.995
p-hydroquinone-*p*-benzoquinone	2.112	2.173	-12.355	-13.390	-13.826
benzene-tetracyanoethylene	0.773	0.920	-12.115	-13.065	-13.465
benzene-Br_2	0.513	0.877	-4.513	-5.009	-5.218

[a] Energies in kcal mol^{-1}.

[b] BSSE corrected HF and MP2 level interaction energies.

[c] MP2 interaction energies at the basis set limit obtained by Helgaker et al.'s method.

TABLE 2S. Some Energy Terms Used for Calculating CCSD(T) Interaction Energies at the Basis Set Limit for Complexes[a]

	$E_{HF(limit)}$[b]	$E_{MP2(limit)}$[c]	$E_{corr(MP2)(limit)}$[d]	$E_{HF(M)}$[e]	$E_{MP2(M)}$[e]	$E_{CCSD(T)(M)}$[e]
benzene-*p*-benzoquinone	2.775	-7.995	-10.770	2.752	-4.233	-2.212
p-hydroquinone-*p*-benzoquinone	2.173	-13.826	-15.999	2.243	-7.9941	-4.8593
benzene-tetracyanoethylene	0.920	-13.465	-14.385	0.859	-8.273	-4.826
benzene-Br_2	0.877	-5.218	-6.095	0.407	-2.846	-1.513

	$\Delta CCSD(T)(M)$[f]	$E_{corr(MP2)(M)}$[g]	$\Delta(M)E_{corr(MP2)}$[h]	$\Delta(M)\Delta CCSD(T)$[i]	$\Delta CCSD(T)_{(limit)}$[j]	$E_{CCSD(T)(limit)}$[k]
benzene-*p*-benzoquinone	2.021	-6.985	-3.785	1.095	3.117	-4.878
p-hydroquinone-*p*-benzoquinone	3.135	-10.237	-5.762	1.764	4.899	-8.927
benzene-tetracyanoethylene	3.447	-9.132	-5.253	1.983	5.429	-8.036
benzene-Br_2	1.333	-3.253	-2.843	1.165	2.498	-2.720

[a] Energies in kcal mol^{-1}.

[b] HF interaction energies at the basis set limit. HF/aug-cc-pVTZ interaction energies were used. See text.

[c] MP2 interaction energies at the basis set limit obtained by Helgaker et al.'s method. See text.

[d] MP2 correlation interaction energies at the basis set limit [= $E_{MP2(limit)} - E_{HF(limit)}$]. See text.

[e] HF, MP2 and CCSD(T) interaction energies calculated using the Medium size basis sets (cc-pVDZ basis set). See text.

[f] CCSD(T) correction terms calculated using the Medium size basis set [= $E_{CCSD(T)(M)} - E_{MP2(M)}$]. See text.

[g] MP2 correlation interaction energies calculated using the Medium size basis set [= $E_{MP2(M)} - E_{HF(M)}$]. See text.

[h] Underestimation of MP2 correlation interaction energies by the Medium size basis set [= $E_{corr(MP2)(limit)} - E_{corr(MP2)(M)}$]. See text.

[i] Underestimation of CCSD(T) correction terms by the Medium size basis set. See text.

[j] Calculated CCSD(T) correction terms at the basis set limit [= $\Delta CCSD(T)(M) + \Delta(M)\Delta CCSD(T)$]. See text.

[k] Calculated CCSD(T) interaction energies at the basis set limit [= $E_{MP2(limit)}$ + ΔCCSD(T)(limit)]. See text.

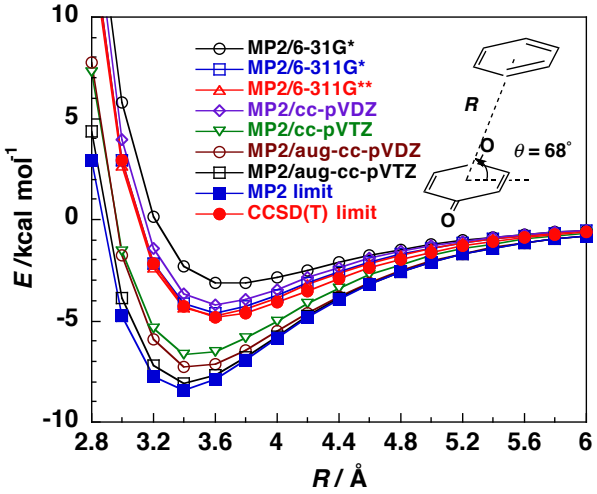

Figure 1S. MP2 level interaction energies calculated for benzene-*p*-benzoquinone complex using several basis sets and MP2 and CCSD(T) level interaction energies at the basis set limit.