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Accurate ab Initio Binding Energies of the Benzene Dimer

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Accurate binding energies of the benzene dimer at the T and parallel displaced (PD) configurations were determined using the single- and double-coupled cluster method with perturbative triple correction (CCSD(T)) with correlation-consistent basis sets and an effective basis set extrapolation scheme recently devised. The difference between the estimated CCSD(T) basis set limit electronic binding energies for the T and PD shapes appears to amount to more than 0.3 kcal/mol, indicating the PD shape is a more stable configuration than the T shape for this dimer in the gas phase. This conclusion is further strengthened when a vibrational zero-point correction to the electronic binding energies of this dimer is made, which increases the difference between the two configurations to 0.4−0.5 kcal/mol. The binding energies of 2.4 and 2.8 kcal/mol for the T and PD configurations are in good accord with the previous experimental result from ionization potential measurement.

I. Introduction

Noncovalent interactions such as aromatic $\pi-\pi$, $\pi-$cation, and $\pi-$hydrogen bonding interactions play an important role in stabilizing the structures of various organic and biological molecules. They are key elements in understanding the tertiary structures of proteins, base−base interactions in DNA, and also influence the packing architecture in a self-assembled aromatic crystal and binding energetics in host−guest molecules. Among the various molecular systems studied thus far, the benzene dimer is of fundamental importance and provides a prototype for weak $\pi-\pi$ interaction. As a result, there have been a great number of experimental and theoretical studies on this dimer.[1−34] On the experimental side, although the early molecular beam study by Klemperer and co-workers[1] as well as a subsequent microwave study by Arunan and Gutowsky[11] and mass-selected Raman study by Felker and co-workers[12] provided the evidence for the T-shaped configuration as the stable structure of the benzene dimer, these studies could not rule out the existence of other stable isomeric structures such as sandwiched or parallel-displaced (PD) structures for this dimer as these configurations do not exhibit a permanent dipole moment. In fact, a recent mass-selected hole burning experiment by Scherzer[13] as well as the previous optical absorption spectroscopic study by Bernstein and co-workers[4] and multiphoton ionization studies by Schlag and co-workers[5] supported the existence of more than one isomeric structure for this dimer. Similarly, all the theoretical studies thus far seem to converge to the general conclusion that two almost isoenergetic isomeric structures appear to exist,[15−29,30−33] possibly within 0.1 kcal/mol of T-shaped and PD-shaped configurations for this dimer. Recent studies[30−33] also indicate the importance of using large basis sets and a proper correlation method; the second-order Moller−Plesset perturbation theory (MP2) method[35] significantly overestimates the attractive interaction in this dimer compared with the more accurate single- and double-coupled cluster method with perturbative triples correction (CCSD(T)), and diffuse functions are necessary to describe the dispersion interaction in this dimer.

Among various previous studies, recent works by Tsuzuki et al.[32] and Sinnokrot et al.[33] appear most extensive in the usage of the basis set at correlated levels and need to be discussed here in relation to our investigation. First, Tsuzuki et al.[32] examined the various structures and binding energies of this dimer at the MP2 and CCSD(T) levels using the correlation-consistent basis set cc-pVXZ (X = D, T, Q, 5)[37] as well as the 6-31G and 6-311G type basis sets. The CCSD(T) binding energies were computed using AIMI (aromatic intermolecular interaction) model chemistry, which assumes that the additional correlation contribution to the binding energy beyond the MP2 level (denoted as “ΔCCSD(T)” hereafter) could be well approximated using the calculation with medium size basis sets, provided the basis set limit binding energies at the MP2 level could be accurately obtained. In one of their model chemistries (the highest one), these authors estimated the CCSD(T) binding energies of the benzene dimer at the basis set limit to be 2.46 (T shape) and 2.48 (PD shape) kcal/mol, respectively, based on the MP2 basis set limit binding energies obtained by extrapolating the interaction energies with the correlation-consistent basis set cc-pVXZ (X = D, T, Q) using the exponential formula proposed by Feller[38] and the ΔCCSD(T) value with the modified cc-pVTZ set. While their approach could be generally considered as an effective method to reduce the significant computational demand required for the highly correlated CCSD(T) calculations, the accuracy of the adopted values for the MP2 binding energies at the basis set limit and the additional correlation contribution beyond the MP2 level are not clear considering the approximate nature inherent in the extrapolation scheme and the choice of the basis set which did not include enough diffuse functions.

In the relevant study on the same topic, Sherrill and co-workers[33] performed the optimization of this dimer for the T- and PD-shaped structures at the MP2 level using the aug-cc-pVDZ and aug-cc-pVTZ basis sets[39] which include multiple diffuse functions. It was found that the intermolecular geometries optimized with the aug-cc-pVDZ and aug-cc-pVTZ sets at the

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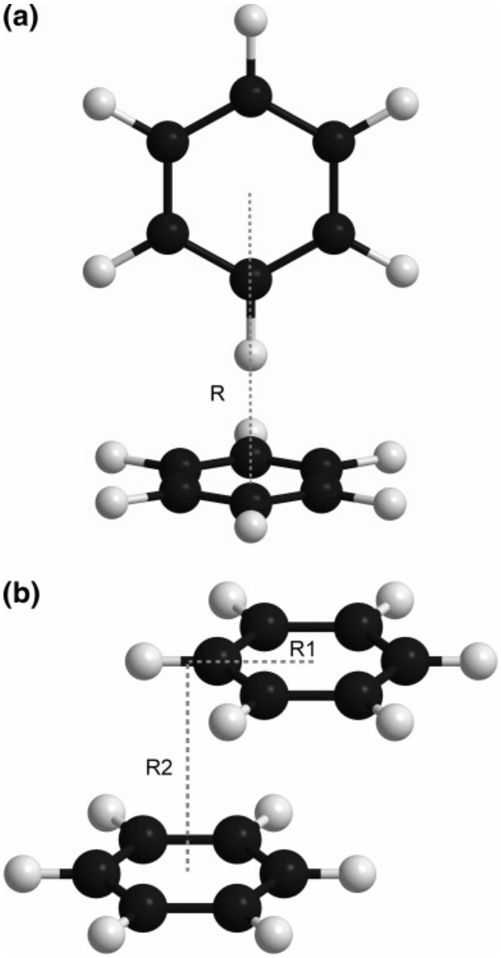

Figure 1. Benzene dimer geometries by Tsuzuki et al. (ref 32) examined in this work: (a) T shape ($R = 5.0$ Å) and (b) parallel-displaced (PD) shape ($R1 = 1.8$ Å, $R2 = 3.5$ Å). Bond distances in the monomers are the same for both configurations ($R_{\mathrm{C-C}} = 1.395$ Å, $R_{\mathrm{C-H}} = 1.087$ Å).

MP2 level were similar and, at the MP2/aug-cc-pVTZ optimized geometries, these authors computed the binding energies for the T- and PD-shaped structures using the MP2-R12 method,[40] which appear to be the closest values to the MP2 basis set limits for the two structures at the present time. By adding the MP2-R12 binding energies to the ΔCCSD(T) value computed with the aug-cc-pVDZ basis set, the binding energies of 2.74 and 2.78 kcal/mol were obtained for the T and PD shapes, respectively. Thus, both studies point toward the isoenergetic structures for the T and PD shapes of the benzene dimer. One major difference between the geometries adopted by Tsuzuki et al. and Sinnokrot et al. is in the way the monomers are oriented with each other in the PD configuration of the dimer as represented in Figures 1 and 2.

In this article, we carefully reexamine the relative stability of the T- and PD-shaped configurations of the benzene dimer by utilizing the previous MP2-R12 binding energies of the benzene diner[33] and employing an effective basis set extrapolation method to derive the accurate basis set limit binding energy estimates at the CCSD(T) level for each configuration. It will be shown that the careful analysis of the extended basis set and correlation effect on the stability of this dimer would lead to a substantially larger difference in binding between the T and PD structures than previously known for this dimer.

This paper is organized as follows: In section II, we explain the theoretical approach and computational procedures employed in this study. The results and discussion are presented in section III. The conclusion is in section IV.

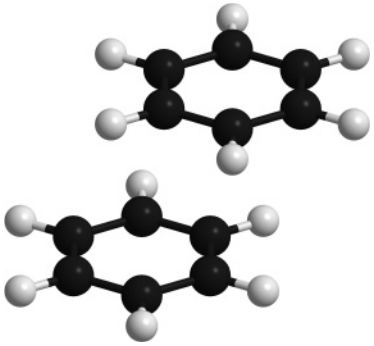

Figure 2. PD-shaped configuration adopted by Sinnokrot et al. (ref 33).

II. Theoretical Approach

The basic theoretical approach adopted here to obtain the basis set limit binding energy of the benzene dimer at the CCSD(T) level is to divide the total binding energy into the MP2 binding energy (which is computationally much more feasible than the CCSD(T) calculation) and the additional correlation contribution beyond the MP2 level

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

Here, $\Delta E_{\mathrm{CCSD(T)}}^{\mathrm{TOT}}(\infty)$ and $\Delta E_{\mathrm{MP2}}^{\mathrm{TOT}}(\infty)$ represent the CBS (complete basis set) limit binding energies at the CCSD(T) and MP2 levels, and $\Delta\mathrm{CCSD(T)}(\infty)$ is the additional correlation contribution beyond the MP2 level at the basis set limit which should be the difference between the MP2 and CCSD(T) binding energies.

$$\Delta\mathrm{CCSD(T)}(\infty) = \Delta E_{\mathrm{CCSD(T)}}^{\mathrm{TOT}}(\infty) - \Delta E_{\mathrm{MP2}}^{\mathrm{TOT}}(\infty) \qquad (2)$$

Also, $\Delta E_{\mathrm{MP2}}^{\mathrm{TOT}}(\infty)$ can be divided into the Hartree−Fock ($\Delta E_{\mathrm{HF}}(\infty)$) and MP2 correlation binding energies ($\Delta E_{\mathrm{MP2}}^{\mathrm{CORR}}(\infty)$).

$$\Delta E_{\mathrm{MP2}}^{\mathrm{TOT}}(\infty) = \Delta E_{\mathrm{HF}}(\infty) + \Delta E_{\mathrm{MP2}}^{\mathrm{CORR}}(\infty) \qquad (3)$$

Although this kind of approach has often been used to estimate the accurate binding energies of various weakly bound complexes,[32,33,41,42] its success relies strongly on the choice of $\Delta E_{\mathrm{MP2}}^{\mathrm{TOT}}(\infty)$ and $\Delta\mathrm{CCSD(T)}(\infty)$ as they are often approximated by the results with basis sets of limited size due to the computational difficulty. One of the distinct features of this study compared with previous studies on the benzene dimer is that highly reliable values for $\Delta E_{\mathrm{MP2}}^{\mathrm{TOT}}(\infty)$ and $\Delta\mathrm{CCSD(T)}(\infty)$ are employed here to ensure the accuracy of $\Delta E_{\mathrm{CCSD(T)}}^{\mathrm{TOT}}(\infty)$ obtained through eq 1. In the next section, a detailed explanation of how one can deduce a reliable and accurate estimate for $\Delta E_{\mathrm{MP2}}^{\mathrm{TOT}}(\infty)$ and $\Delta\mathrm{CCSD(T)}(\infty)$ will be presented. All computed binding energies were corrected by the counterpoise (CP) method[43] for the removal of basis set superposition error and the core electrons were frozen in all correlated calculations. All ab initio computations were performed with the Gaussian 98[44] program package.

III. Results and Discussion

In this study, the determination of an accurate CCSD(T) basis set limit binding energy and the true equilibrium structure of the benzene dimer has been carried out in three separate steps. First, among the various geometries used for investigating the

TABLE 1: Binding Energies (in kcal/mol) for the Different Geometries of the Benzene Dimer

		MP2		CCSD(T)	
		T	PD	T	PD
Sinnokrot geometries[a]	cc-pVDZ	1.98	1.63	1.24	−0.21
	aug′-cc-pVDZ[b]	3.10	4.16	2.27	1.88
	aug-cc-pVDZ[c]	3.16	4.28	2.27	2.10
	aug-cc-pVTZ[c]	3.46	4.67		
Tsuzuki[d] geometry	cc-pVDZ	1.94	1.82	1.23	0.39
	aug′-cc-pVDZ[b]	3.03	4.02	2.24	2.22
	aug-cc-pVDZ	3.11	4.10	2.31	2.33
	aug-cc-pVTZ	3.40	4.65		

[a] MP2/aug-cc-pVDZ optimized intermolecular geometries in ref 33 except the aug-cc-pVTZ results. Monomers are fixed at the MP2/aug-cc-pVDZ optimized geometries for the cc-pVDZ and aug′-cc-pVDZ results. [b] Aug-cc-pVDZ basis set without diffuse functions on hydrogen atoms. [c] Results from ref 33. [d] Results at the geometries adopted by Tsuzuki et al. in ref 32 (see Figure 1).

relative stability of the T and PD configurations for this dimer previously,[24−27,32,33] the geometry which yields the largest CCSD(T) binding energies with the aug-cc-pVDZ basis set is chosen as the equilibrium structure of this dimer. Second, at the chosen geometry, we determine the MP2 basis set limit binding energies through application of an effective extrapolation method to the recent MP2-R12 results by Sinnokrot et al.[33] Finally, the additional correlation contributions beyond the MP2 level (ΔCCSD(T)(∞)) are evaluated using two distinct procedures.

Although there exists several stationary geometries of the benzene dimer optimized at various levels of theory,[24−27,32,33,45] all calculations in this study were performed at the geometry adopted by Tsuzuki et al.[32] (which is shown schematically in Figure 1 and will be called “Tsuzuki geometry” hereafter). The Tsuzuki geometry appears to be close to the true minimum geometry at each configuration of the benzene dimer as the intermonomer distance in the T configuration at the Tsuzuki geometry is the same as the intermonomer distance optimized at the estimated CCSD(T)/aug-cc-pVQZ level by Sinnokrot and Sherrill,[45] and the intermonomer distances in the PD configuration at the Tsuzuki geometry are very similar to the optimized values at the CCSD(T) level by Tsuzuki and co-workers.[48] In Table 1, we compare the binding energies of the benzene dimer with the basis set and correlation level at the geometries adopted by Sinnokrot et al. and Tsuzuki et al., at which extensive ab initio studies have been performed in recent years and larger bindings were observed compared with other geometries of the benzene dimer, especially in the case of Tsuzuki geometry.[24−27,32,33] From Table 1, while it is shown that the binding energies at the T-shaped configuration for the Tsuzuki and Sinnokrot geometries are very similar, the PD-shaped binding energies at the Tsuzuki geometries are shown to be significantly larger than the corresponding values at the Sinnokrot geometries. This appears to be related to the finding that the PD configuration adopted by Sinnokrot et al. differs in monomer arrangement from the PD configuration adopted by Tsuzuki et al. as shown in Figures 1 and 2.[32,33]

The results in Table 1 clearly manifest the importance of employing an appropriate basis set including diffuse functions in combination with the higher electron correlation method beyond the MP2 level for accurate prediction of the binding energies for this complex. Deficiency in either the basis set or correlation treatment (such as MP2/aug-cc-pVTZ or CCSD(T)/cc-pVDZ) would lead to a quite different conclusion about the relative stability of the T and PD configurations for this dimer. The importance of diffuse functions in the basis set for this complex is best exemplified when one compares the binding energies with the cc-pVDZ (or cc-pVTZ) and aug′-cc-pVDZ (or aug-cc-pVDZ) sets at the CCSD(T) level. It is interesting to note that while the CCSD(T) binding energies with the cc-pVDZ (or cc-pVTZ set at the Tsuzuki geometry) are pointing toward more stability for the T-shaped than the PD-shaped configuration, the differences between the CCSD(T) binding energies for the two configurations tend to decrease upon the addition of the diffuse functions as shown in the results with the aug′-cc-pVDZ and aug-cc-pVDZ sets. Therefore, one could expect the order of stability between the two (T and PD shapes) configurations might be reversed at the basis set limit.

Recent studies by Sinnokrot et al.[33] have shown that the MP2 binding energy of the benzene dimer converges to the basis set limit very slowly, which is also confirmed by the results in Table 1. Even for the calculations with a basis set as large as the aug-cc-pVQZ, the results were found to be different from the more accurate MP2-R12 results by about 0.1 kcal/mol for both the T and PD configurations. Here, we exploit the MP2-R12 results by Sinnokrot et al. to deduce the corresponding MP2-R12 results at the Tsuzuki geometry.

In Table 2, we compare the convergence of the Hartree−Fock and MP2 correlation contribution to binding energy (correlation binding energy) with the basis set at the Tsuzuki geometry and at the geometries adopted by Sinnokrot et al. The basis set convergence of the MP2 correlation binding energies of the benzene dimer at the geometries adopted by Tsuzuki et al. and Sinnokrot et al. manifest a very similar tendency toward the corresponding CBS limits which enables one to deduce the R12 results at the Tsuzuki geometry corresponding to the R12 results by Sinnokrot et al. Table 2 also shows that the MP2-R12 results by Sinnokrot et al. are very close to the extrapolated results of the corresponding correlation binding energies with the aug-cc-pVDZ and aug-cc-pVTZ basis sets by $(X + 1)^{-3}$ ($X = 2$ for DZ and 3 for TZ).[46] This extrapolation formula was found to yield accurate estimates to the CBS limit binding energies at the MP2 level for various weakly bound complexes.

TABLE 2: Basis Set Convergence of the Hartree−Fock (in parentheses) and MP2 Correlation Binding Energies (in kcal/mol) of the Benzene Dimer

	Sinnokrot et al.[a]		this work[b]	
	T	PD	T	PD
aug-cc-pVDZ	4.69(−1.63)	9.39(−5.17)	4.11(−1.00)	7.78(−3.68)
aug-cc-pVTZ	5.06(−1.62)	9.81(−5.16)	4.42(−1.02)	8.30(−3.65)
aug-cc-pVQZ	5.16(−1.62)	9.95(−5.16)	(−1.02)	8.44(−3.65)
DZ-TZ[c]	5.33	10.12	4.63	8.68
CBS limit estimate	5.26[d]	10.12[d]	4.56[e]	8.68[e]
$\Delta E^{\text{TOTAL}}_{\text{MP2}}(\infty)$[f]	3.64	4.96	3.54	5.03

[a] From ref 33 and 49. [b] Results at the Tsuzuki geometry (see the text). [c] Aug-cc-pVDZ ∼ aug-cc-pVTZ extrapolated results by $(X + 1)^{-3}$, $X = 2, 3$. [d] MP2-R12 results from ref 33. [e] MP2-R12 results derived from the DZ-TZ extrapolation estimates (see the text). [f] MP2 CBS limit total binding energies including the Hartree−Fock contributions.

TABLE 3: Change of ΔCCSD(T) (in units of kcal/mol) and Ratio β^a

	T		PD	
	ΔCCSD(T)[a]	β	ΔCCSD(T)[a]	β
6-311G*[b]	−0.72	−0.24	−1.39	−0.24
cc-pVDZ[b]	−0.71	−0.25	−1.43	−0.25
cc-pVTZ	−0.82	−0.20	−1.83	−0.25
aug(d)-6-311G*[b]	−0.78	−0.20	−1.73	−0.23
aug′-cc-pVDZ[c]	−0.80	−0.20	−1.80	−0.23
aug-cc-pVDZ	−0.78	−0.19	−1.79	−0.23

[a] $\beta = \Delta\mathrm{CCSD(T)}/\Delta E^{\mathrm{CORR}}_{\mathrm{MP2}}$. [b] Results from ref 32. [c] Aug-cc-pVDZ basis set without diffuse functions on the hydrogen atom.

TABLE 4: Binding Energies (kcal/mol) of the Benzene Dimer at the CCSD(T) Level

		T	PD
this work	CBS1[a]	2.67 (2.37)[c]	3.03 (2.84)[c]
	CBS2[b]	2.66 (2.36)[c]	3.03 (2.84)[c]
theoretical	Tsuzuki et al.[d]	2.46	2.48
	Sinnokrot et al.[e]	2.74 (2.39)[c]	2.78 (2.74)[c]
	Hobza et al.[f]	2.17	2.01
experimental	Grover et al.[g]	2.4 ± 0.4	
	Krause et al.[h]	1.6 ± 0.4	

[a] Binding energies obtained by eq 4 in the text. [b] Binding energies obtained by eq 5 in the text. [c] Values in parentheses are the binding energies with zero-point energy corrections. [d] From ref 32. [e] From ref 33. [f] From ref 27. [g] From ref 6. [h] From ref 8.

Therefore, if one assumes that the difference between the R12 and extrapolated results for correlation binding energy would be same at the geometries adopted by Tsuzukiet al. and Sinnokrot et al., then the R12 results at the Tsuzuki geometry could be deduced from the DZ-TZ extrapolated value at the Tsuzuki geometry and the difference between the R12 and DZ-TZ extrapolated values at the geometries adopted by Sinnokrot et al. Interestingly, the CBS limit correlation binding energies of 4.56 (T shape) and 8.68 (PD shape) kcal/mol thus obtained are already 0.1 and 0.5 kcal/mol larger than the previous CBS limits (estimated) of 4.47 and 8.17 kcal/mol by Tsuzuki et al.[32] at the same geometry. One cautionary reminder for the estimated CBS limit binding energies by this method: It must be remembered that the accuracy of our estimates to the CBS limit correlation binding energies for each configuration of the benzene dimer by this way is dependent on the accuracy of the original R12 results by Sinnokrot et al. which were computed through the utilization of the approximate resolution of the identity with basis set of limited size. The error bounds of the R12 results, however, appear not to exceed 0.2 kcal/mol.[33]

The next element to be determined accurately for the correct estimate of the CBS limit binding energies at the CCSD(T) level according to eq 1 is the difference between the MP2 and CCSD(T) binding energies (ΔCCSD(T)(∞)). Although this term has often been assumed to be relatively insensitive to basis set increase, thereby justifying the computation of this contribution with relatively small or medium basis sets, its convergence behavior with a basis set close to the basis set limit has not been known yet. Table 3 shows the convergence behavior of this contribution with a series of basis sets (with and without diffuse functions) for the T and PD configurations. From these results, one can see that, although ΔCCSD(T) values with basis sets containing diffuse functions appear to be close to the converged results, in view of the nonmonotonic behavior of ΔCCSD(T) with basis set, it is difficult to tell how close they are to the basis set limits, especially considering the small magnitudes of the binding energies. A similar behavior of ΔCCSD(T) with basis set has been observed in previous studies of the benzene dimer.[32,45] Therefore, we use a somewhat different approach to deduce ΔCCSD(T)(∞) from our computed results. It was suggested previously[32] that the ratio (β) between ΔCCSD(T) and $\Delta E^{\mathrm{CORR}}_{\mathrm{MP2}}(\infty)$ appears to be rather insensitive to basis set increase once the basis set contains appropriate polarization and diffuse functions. For the basis sets shown in Table 3, we also note that the ratio between ΔCCSD(T) and $\Delta E^{\mathrm{CORR}}_{\mathrm{MP2}}$ changes very little with the basis set once the basis set contains diffuse functions. This again exemplifies the importance of diffuse functions to describe the interaction in this dimer. In this respect, it is interesting to note that the binding energies or the ratio (β) with the aug′-cc-pVDZ set (which contains diffuse functions on C atoms in addition to the cc-pVDZ set with 336 functions) are closer to the corresponding results with the aug-cc-pVDZ (which should be considered as the closest values to the basis set limit among the results in Table 3) than the corresponding value with the cc-pVTZ set (largest basis set here with 512 contracted functions). By exploiting the ratio with the aug-cc-pVDZ set ($\beta_{a\mathrm{DZ}}$), which is expected to be close to the basis set limit value and the MP2-R12 results deduced in Table 2, we can obtain an accurate estimate to the exact ΔCCSD(T)(∞) and, accordingly, $\Delta E^{\mathrm{TOT}}_{\mathrm{CCSD(T)}}(\infty)$ according to eq 1.

$$\Delta E^{\mathrm{TOT}}_{\mathrm{CCSD(T)}}(\infty) = \Delta E^{\mathrm{TOT}}_{\mathrm{MP2}}(\infty) + \beta_{a\mathrm{DZ}}\Delta E^{\mathrm{CORR}}_{\mathrm{MP2}}(\infty) \qquad (4)$$

Alternatively, one may estimate ΔCCSD(T)(∞) by the X^{-3} extrapolation of ΔCCSD(T)(X) with the cc-pVDZ ($X = 2$) and cc-pVTZ ($X = 3$) sets, which was found to yield an accurate estimate to the basis set limit interaction energies in the case of rare gas dimers.[42] Table 4 presents the CCSD(T) binding energy

$$\Delta\mathrm{CCSD(T)}(X) = \Delta\mathrm{CCSD(T)}(\infty) + aX^{-3}, \quad X = 2, 3 \qquad (5)$$

estimates to the basis set limits ($\Delta E^{\mathrm{TOT}}_{\mathrm{CCSD(T)}}(\infty)$) obtained by these procedures along with the results of previous studies by other workers. Remarkably, both procedures yield virtually the same binding energies, clearly pointing toward the PD-shaped structure rather than the T-shaped as the equilibrium structure of this dimer (~0.4 kcal/mol difference). If one adopts a different β value other than $\beta_{a\mathrm{DZ}}$ in eq 4 such as the β value for the cc-pVTZ or aug′-cc-pVDZ basis set in Table 3, then the difference between the two configurations would still amount to about 0.2−0.4 kcal/mol. Furthermore, for a more meaningful comparison between the PD- and T-shaped structures relevant to the experimental results, we added the vibrational zero-point corrections of −0.30 (T shape) and −0.19 kcal/mol (PD shape) performed at the MP2/aug′-cc-pVDZ level to the electronic binding energies obtained according to eqs 4 or 5. This led to further stabilization for the PD-shaped configuration compared to the T-shaped configuration, with the binding energy difference between the two shapes amounting to ~0.5 kcal/mol in this case. Although a similar conclusion suggesting a more stable PD-shaped configuration than T-shaped configuration of the benzene dimer despite the similar interaction energies at the two configurations could be obtained by exploiting the large difference in the vibrational zero-point corrections between the two configurations computed at the MP2/cc-pVDZ level (−0.35 for T, −0.04 for PD, in kcal/mol),[33] if one presumes that the vibrational zero-point corrections at the MP2/aug′-cc-pVDZ level would be more accurate than the vibrational zero-point corrections at the MP2/cc-pVDZ level, it could be considered a fortuitous result caused by a cancellation of errors. Table 4 summarizes the results of the present study along with the previous study results on the benzene dimer. In short, while our results are in contrast with the previous theoretical studies on the benzene dimer which suggested almost the same interaction energies for the PD and T shapes[32,33] or more stabilization energy for the T than PD shape,[27] they are in accord with the experimental result by Grover et al.,[6] with our theoretical PD-shaped binding energy being very close to the upper bound of the experimental value.

IV. Conclusion

The determination of the true equilibrium structure and binding energies of the benzene dimer has long been an intriguing issue for the last 30 years. By incorporating high-quality ab initio results with effective procedures of estimating the CCSD(T) CBS limit binding energies of weakly bound complexes, we were able to establish that the PD shape is a more stable configuration than the T shape by -0.5 kcal/mol which is in contrast to the previous findings on this dimer. This result, however, is in line with the recent finding of more stable PD-shaped structures than T-shaped in the larger $\pi-\pi$ interaction clusters involving polycyclic aromatic hydrocarbons such as the naphthalene dimer and naphthalene−anthracene complex.[34,47] Although it was recently shown[48] that the binding energy of the T shape may be slightly increased (∼0.1 kcal/mol) by adjusting the tilt angle between the two monomers in the T configuration, this would not affect the relative stability between the two configurations. Therefore, the PD shape generally appears to be the more favorable configuration than the T shape in $\pi-\pi$ interaction clusters involving aromatic hydrocarbons, primarily due to the increased dispersion interaction in the PD shape than T shape.[34,47] Our theoretical binding energies of 2.4 and 2.8 kcal/mol for the T and PD shapes of the benzene dimer are in good accord with the experimental results of 2.4 ± 0.4 kcal/mol by Grover et al.[6] Although other factors remain (such as errors in the MP2-R12 results, higher electron correlation effect beyond the CCSD(T) level, and core-correlation effect, etc.), which could affect our estimated results for the binding energies of the benzene dimer, the reported electronic binding energies in Table 4 appear to be very close to the ab initio limits for the benzene dimer considering the reliability of approximations adopted in this study and would serve as the benchmark results for further refinement of the stabilization energies of this important complex.

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