

Benzene Dimer: High-Level Wave Function and Density Functional Theory Calculations

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Abstract: High-level OVOS (optimized virtual orbital space) CCSD(T) interaction energy calculations (up to the aug-cc-pVQZ basis set) and various extrapolations toward the complete basis set (CBS) limit are presented for the most important structures on the benzene dimer potential energy surface. The geometries of these structures were obtained via an all-coordinate gradient geometry optimization using the DFT-D/BLYP method, covering the empirical dispersion correction fitted exclusively for this system. The fit was carried out against two estimated CCSD(T)/CBS potential energy curves corresponding to the distance variation between two benzene rings for the parallel-displaced (PD) and T-shaped (T) structures. The effect of the connected quadruple excitations on the interaction energy was estimated using the CCSD(TQ_i) method in a 6-31G*(0.25) basis set, destabilizing the T and T-shaped tilted (TT) structures by ≈ 0.02 kcal/mol and the PD structure by ≈ 0.04 kcal/mol. Our best CCSD(T)/CBS results show, within the error bars of the applied methodology, that the energetically lowest-lying structure is the TT structure, which is nearly 0.1 kcal/mol more stable than the almost isoenergetic PD and T structures. The specifically parametrized DFT-D/BLYP method leads to a correct energy ordering of the structures, with the errors being smaller by 0.2 kcal/mol with respect to the most accurate CCSD(T) values.

Theoretical Background

Throughout the history of computational chemistry, the benzene dimer has been quite extensively studied system for several reasons. First, it is an ideal example of a system bound by π – π interaction, which is in numerous cases present in many biologically relevant systems (stacking interactions in DNA base pairs, aromatic side-chain interactions in proteins) as well as in material and nanoscience.¹ Second, an accurate description of the π – π interaction is in general a challenging task for the methods of quantum

chemistry.² Noncovalent interaction between benzene rings results in a very shallow potential energy surface (PES), where it seems even more problematic to obtain the proper geometry of the global and local minima, saddle points, and barriers than to obtain the accurate, single-point stabilization energies themselves.³ Even the experimentally known values of the stabilization energies of the benzene dimer^{4,5} have rather large error bars, and their correspondence to particular structures has not yet been completely resolved.

The goal of this paper is to provide a benchmark calculation on both the geometry and the electronic component of the stabilization energy of the most important structures on the benzene dimer PES, which will make it possible to identify the “global” minimum and a proper energy ordering of the other important structures.

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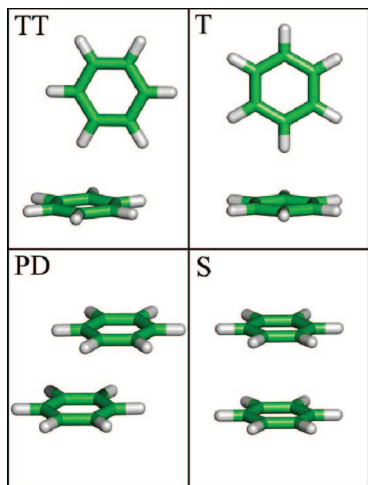


Figure 1. Investigated structures of the benzene dimer: T-shaped tilted c_s (TT), T-shaped c_{2v} (T), parallel-displaced c_{2h} (PD), and sandwich d_{6h} (S).

We are certainly aware of the fact that the transition barriers separating the global and local minima are quite low³ (of an order of magnitude of 0.1 kcal/mol) and that they are likely to disappear once the zero-point vibrational energy is included. This means that the structures populated at various temperatures can be quite different from the minima localized at the PES (see the proceeding paper⁶). An accurate description of the PES is, however, important in order to be able to understand the nature of stabilization in various structures. It must be kept in mind that these structures (T-shaped tilted c_s (TT), T-shaped c_{2v} (T), parallel-displaced c_{2h} (PD), and sandwich d_{6h} (S); see Figure 1) represent the model motifs occurring in biomacromolecules and complex molecular systems. In these cases, the energy barriers will be much higher and might lead to the coexistence of various structures. A dominant role in the stabilization of all benzene dimer structures is played by dispersion energy. Besides this energy, the T-shaped and PD structures are stabilized also by the electrostatic quadrupole–quadrupole term, and the former structure is stabilized additionally by the H-bonding contribution (in this case the blue-shifting H-bond⁷). In the case of the S structure, the electrostatic energy is repulsive. Both the electrostatic and H-bonding terms are properly described already by such low-level quantum mechanical (QM) methods as Hartree–Fock (HF) or density functional theory (DFT) methods. On the other hand, the description of dispersion energy requires the use of the most advanced QM procedures. Within the wave function (WF) theory, the description of the dispersion energy is notorious for its slow convergence with respect to both the level of the applied theory and atomic orbital (AO) basis set size. In the case of the benzene⁸ and uracil⁹ dimer an “oscillatory” convergence of the stabilization energy, manifested by a strong overestimation at the Møller–Plesset second-order perturbation theory (MP2) level and underestimation at the MP3 or CCSD (coupled clusters with single and double excitations) level, is a good example. CCSD energies corrected for the effect of the connected triple excitation treated in either the fully

iterative or perturbative way are in good agreement¹⁰ and bring the results into reasonable agreement with the experiment. However, the question of the importance of the higher connected excitation in the benzene dimer interaction was raised in the past¹¹ but due to the computationally prohibitive size of the system could not be convincingly answered. Calculations on smaller, model systems suggest that the effect could be of an order of magnitude of tenths of kilocalories per mole. Quadruple (and higher) excitations typically gain in importance in cases where the single reference WF begins to acquire a multireference character. This is most likely not the case of dominantly dispersion-bound complexes, where the interaction on the orbital level is practically negligible. The true source of the importance of quadruples originates in the incompleteness of the (in our case) CCSD(T) supermolecular interaction energy, as pointed out by Jeziorski et al.¹²

Another important problem concerns the structures of the dimer. The most investigated structures have been the T, S, and PD structures, with their geometries being determined by point-by-point energy optimization.¹³ However, it has recently^{1,14} been shown that the T structure does not correspond to an energy minimum but is a transition structure. The minimum has a tilted T structure (TT) with lower symmetry (c_s instead of c_{2v}). In this case, the point-by-point optimization becomes difficult and more accurate geometries are provided by a gradient optimization.

The most accurate calculations on the benzene dimer published so far were carried out by Janowski and Pulay.¹³ Their results calculated at the QCISD(T)|CBS level (Helgaker’s extrapolation¹⁵ from Dunning-type aug-cc-pVTZ and aug-cc-pVQZ basis sets)¹⁶ using geometries from the QCISD(T)|aug-cc-pVTZ optimization of the intermolecular distances have led to the following ordering of the stabilization energies: $T(2.68) \geq PD(2.66) > S(1.65)$ (the stabilization energies in parentheses, in kilocalories per mole). Further publications, suggesting that the most stable benzene dimer structure is TT, have recently been issued by Distasio et al.¹⁴ and Lee et al.,¹ in the first of which the stabilization energy was calculated at the estimated CCSD(T)|complete basis set (CBS) level (MP2|CBS + dCCSD(T)|6-311+G(2df,p), see below) leading to the ordering: $TT(2.66) > T(2.54) > PD(2.27)$. The authors of the latter publication, apart from presenting an extensive literature review on this topic, suggested the ordering: $TT(2.84/2.84) > T(-2.77) > PD(2.73/2.62) > S(1.66/1.53)$. The first value in the parentheses was obtained as both a CCSD(T)|CBS (MP2|CBS + dCCSD(T)|aug-cc-pVTZ) geometry optimization and single-point calculation, whereas the second value was obtained as a CCSD(T)|CBS (with the same methodology) on the Boys–Bernardi¹⁷ counterpoise basis set superposition error (BSSE)-corrected RI-MP2|aug-cc-pVDZ optimized geometry. The latter results are almost identical with those published recently by Bludský et al.,¹⁸ who introduced DFT/CCSD(T) correction scheme and applied it for the geometry optimization. Upon the basis of these geometries, they estimated the CCSD(T)|CBS as a Helgaker’s extrapolation of the spin-component-scaled MP2

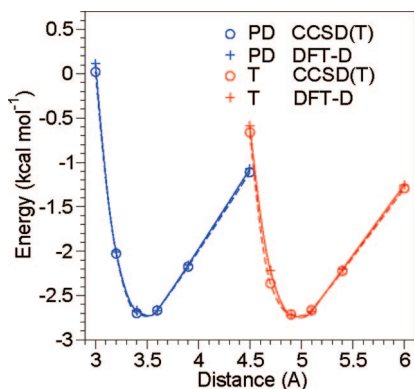


Figure 2. Fitting of the dispersion term for the parallel displaced (PD, blue/left) and T-shaped (T, red/right) benzene dimer; (circles) reference CCSD(T)/CBS values, (lines and crosses) fitted DFT-D energy.

(SCS-MP2)¹⁹ energies from the aug-cc-pVTZ and aug-cc-pVQZ basis sets, corrected with the dCCSD(T)/aug-cc-pVDZ.

In the paper being presented, we will investigate such benzene dimer structures whose geometries have been determined by the all-coordinate gradient optimization based on the DFT-D procedure, which closely mimics the estimated CCSD(T)/CBS results. The energies of the dimer were determined at the highest affordable CCSD(T)/CBS level with various extrapolations adopted.

Methodology

The accurate geometry of the conformers investigated plays an important role in obtaining highly accurate stabilization energies. Since the CCSD(T) gradient optimization for benzene dimer is impractical, typically the intrasystem coordinates are kept frozen, and step-by-step one-dimensional optimization is applied.

Our approach is based on two key elements: (a) the DFT-D/BLYP/TZVP²⁰ procedure containing an empirical dispersion term, which was parametrized specifically for the benzene dimer; the resulting DFT-D method was applied for an all-coordinate geometry optimization; (b) highly accurate single-point energies obtained by BSSE corrected CCSD(T), calculated in truncated optimized virtual orbital space (OVOS).²¹

The OVOS method is a tool for accelerating calculations of the correlation energy (MP2, MP3,..., CCSD, CCSD(T)) via expanding the correlated WF in a subset of unitary transformed HF virtual orbitals (VOs). Optimal unitary transformation is found by maximizing the overlap of the first-order many-body perturbation (MBPT) WF in the full and the truncated virtual orbital space (VOS). For instance, CCSD(T) in OVOS truncated to 70% is the CCSD(T) energy calculated in the unitary transformed HF VOs, from which only lowest 70% were correlated. This energy will also be referred to as the CCSD(T)^{OVOS} 70%.

The dispersion correction in the DFT-D procedure was reoptimized to reproduce the highly accurate CCSD(T)/CBS reference data. Six reference points were calculated for both the T and PD structures; see Figure 2. The BSSE corrected

CCSD(T)/CBS interaction energies were constructed as a sum of the HF/aQZ interaction energies (aXZ refers to Dunning's aug-cc-pVXZ basis set),¹⁶ the MP2/CBS term (Helgaker's extrapolation;¹⁵ see eq 1 from aTZ and aQZ basis sets) and the dCCSD(T)^{OVOS} correction term (i.e., the difference between MP2 and CCSD(T) interaction energies determined with an aTZ basis set in OVOS truncated to 70%). All three parameters in the dispersion formula, i.e. the scaling factor for the van der Waals radii, s_R , the global scaling of the dispersion energy according to Grimme,²² s_6 , and the exponent of the damping function, α , were included in the optimization. For the sake of computational speed, we opted for the B-LYP functional and the relatively small, TZVP basis set. As the main guideline for the fitting, we used the unsigned error of the interaction energy, weighted by the Boltzmann factor (at 50 K), in order to ensure that the energy minimum was described with a higher accuracy than the rest of the PES. Some arbitrariness entered the fitting procedure through the compromise between the minimum weighted error and the requirement that both conformers have the correct relative energy in their minima. The resulting curves corresponding to the parameter set $s_R = 0.88$, $s_6 = 1.503$, and $\alpha = 6$ are compared to the reference data in Figure 2. The agreement between the reference CCSD(T)/CBS and DFT-D values is very good, but note that this is on account of the highly customized dispersion parameters, which differ significantly from the transferable parameters given in Jurečka et al.²⁰

The DFT-D procedure, connected with the all-coordinate gradient optimization, yielded optimal TT, T, PD, and S structures (see section 3.1). For these structures, single-point CCSD(T) or OVOS CCSD(T)₂ (CCSD(T)₂ = MP2^{FullVOS} + dCCSD(T)^{OVOS}) energies were calculated in the aDZ, the aTZ with the OVOS truncated to 70%, the aQZ with the OVOS truncated to 60%, and the MP2 energies calculated in a5Z. These rather demanding calculations were carried out using a new, parallel CCSD(T) code²³ based on Cholesky decomposed two-electron integrals, implemented in the MOLCAS 7²⁴ program package. In all of the calculations, the 10^{-5} threshold was used for the Cholesky decomposition of the two-electron integrals. In the aQZ and a5Z basis set calculations, the 10^{-5} threshold for eliminating the linear-dependent basis functions in the HF-SCF step resulted in the deletion of 50–56 basis functions in the aQZ and 103–114 basis functions in the a5Z basis sets, depending on the particular structure. Those calculations of the stabilization energies using these sets of thresholds lead to errors not larger than 0.03 kcal/mol, which is within the error bars of the CCSD(T) calculations in the truncated OVOS.²⁵

In this work, two CBS extrapolation schemes have been used: (a) Helgaker's scheme¹⁵

$$E_X^{\text{corr}} = E_{\text{CBS}}^{\text{corr}} + k/X^3 \quad (1)$$

where $E_{\text{CBS}}^{\text{corr}}$ is an estimate of the CBS correlation energy and k is an arbitrary constant; (b) Kim's scheme,^{1,27} using both BSSE corrected (ΔE_X^b) and uncorrected (ΔE_X^n) interaction energies

$$\delta_X = \Delta E_X^b - \Delta E_X^n \quad (2)$$

$$\varepsilon_X = \Delta E_X^b + \Delta E_X^n \quad (3)$$

$$\Delta E_{\text{CBS}} = 1/2(\delta_X \varepsilon_{X+1} - \delta_{X+1} \varepsilon_X)/(\delta_X - \delta_{X+1}) \quad (4)$$

in the (typically a Dunning-type) basis set with cardinality X . Use of this pseudointerpolation scheme is justified by the fact that the BSSE corrected and BSSE uncorrected interaction energies converge with increasing of the basis set size to the same CBS value and an observation that (especially the correlation part) the BSSE corrected and BSSE uncorrected values approach the CBS interaction energy from each side.²⁶ Furthermore, this “extrapolation” does not depend on any external parameter(s), contrary to the Helgaker’s scheme and its variants, and is more indulgent to the numerical noise caused by superposition of the several approximations made in our computational scheme.

3. Results and Conclusions

3.1. Geometries Obtained from the DFT-D Optimization. The coordinates of all the optimized structures are summarized in the Supporting Information, and their main internal geometry parameters are presented in Table 1.

3.2. Role of the connected quadruple excitations. The most relevant work on the importance of the connected quadruple excitations in a coupled-cluster framework¹¹ was done on the acetylene dimer with the CCSD(TQ)₂^{28,29} method using the aug-cc-pVDZ basis set, where the largest contribution from quadruples was 0.04 kcal/mol for the T-shaped structure. For larger systems, calculations were feasible only in the 6-31G*(0.25)³⁰ basis set and the authors obtained quite large contributions, i.e. 0.13 kcal/mol for the butadiene in an antiparallel stacked geometry and 0.20 kcal/mol for the furan dimer in the C_{2h} stacked geometry. If similar contributions from the quadruples would arise in the benzene dimer, it could completely change their energy ordering. CCSD(TQ)₂ calculation on our optimized benzene dimer structures were carried out using the ACES II program package,³¹ and the results are shown in Table 2. The accuracy of these results obtained with such a small basis set is, however, questionable. Two effects, directed against each other, might play a role. It is known that the higher-order connected excitations in the coupled-cluster wave operator converge faster with basis set size, but on the other hand, their contribution in small basis sets tends to be artificially large as they try to “imitate” the basis set effect. By looking at the rate of convergence of the CCSD-MP2 and the (T) contributions to

Table 1. Geometry Parameters [Å] of the Investigated Benzene Dimer Structures

structure	lateral disp ^a	distance
T		4.948
TT	0.875 ^b	4.828
S		3.847
PD	1.768 ^c	3.486

^a Displacement with respect to the center of mass of the individual benzene rings. ^b Benzene ring in the plane of the C_2 axis of the “T” structure is rotated clockwise against the axis by 24.07° (see the TT and T structures in Figure 1). ^c Horizontal displacement is in the direction of the C–H bond (unlike the horizontal displacement perpendicular to the C–C bond in Janowski et al.¹³ and Sinnokrot et al.^{32,33}

Table 2. Contribution from the Connected Quadruple Excitation (kcal/mol) to the Stabilization Energy Obtained by the CCSD(TQ)₂/6-31G*(0.25) Method/Basis Set for the Benzene Dimer Structures Shown in Figure 1^a

structure	$\Delta E(Q_i)$
PD	0.043
TT	0.024
T	0.021
S	0.038

^a All contributions are repulsive.

Table 3. Benzene Dimer Stabilization Energies [kcal/mol] Obtained for Various Structures, Basis Sets, Methods, and CBS Extrapolationsⁱ

method/basis set	PD	PD _p	TT	T	S
CCSD(T)/ID	2.15	2.29 (2.30) ^a	2.44	2.28 ^b	1.27 ^c
CCSD(T) ₂ /T 70%	2.49	2.53 (2.55)	2.66	2.57	1.51
CCSD(T) ₂ /Q 60%	2.63	2.64 (2.61)	2.75	2.65	1.61
(T → Q) ^d	2.73	2.72 (2.66)	2.81	2.71	1.68
(T → Q) ^e	2.66	2.65	2.76	2.68	1.63
(Q → 5) ^f	2.74	2.73	2.81	2.71	1.68
(Q → 5) ^g	2.70	2.69	2.78	2.69	1.64
DFT-D/BLYPITZVP	2.88	2.81	2.93	2.80	1.84
DFT-D ^h /BLYPITZVP	2.57	2.51	2.33	2.03	1.45

^a QCISD(T) stabilization energies by Janowski et al.¹³

^b Corresponding QCISD(T)/X and CBS stabilization energies,¹³ obtained in a slightly different, QCISD(T)/T-optimized geometry, are 2.30, 2.57, 2.64, and 2.68 kcal/mol. ^c Corresponding QCISD(T)/X and CBS stabilization energies,¹³ obtained in a slightly different, QCISD(T)/T-optimized geometry, are 1.40, 1.60, 1.64, and 1.65 kcal/mol. ^d (T → Q) extrapolation using Helgaker’s formula in the form: SCFIQ + corr CCSD(T)₂ (T → Q). ^e Kim’s extrapolation scheme using both BSSE corrected and uncorrected CCSD(T)₂ interaction energies in T, Q. ^f (Q → 5) extrapolation using Helgaker’s formula in the form: SCFI5 + corr MP2!(Q → 5) + dCCSD(T)^{OVOSI}(T → Q). ^g Kim’s scheme with interaction energies calculated as SCFI_X + corr MP2!_X + dCCSD(T)^{OVOSI}(X − 1), where X stands for Q, 5 and X − 1 for T, Q. ^h Empirical dispersion term with the original parameters fitted to S22 test set.²⁰ ⁱ X = T, Q, 5 stand for Dunning’s aug-cc-pVXZ basis sets.

the stabilization energy for 6-31G*(0.25) and aug-cc-pVXZ basis sets for the benzene dimer structures under consideration, we believe that the numbers in Table 2 might still be a reasonable estimate of their CBS values, especially in the sense of their relative importance for the different structures. Repulsion is in case of the stacked structures (PD and S) somewhat stronger than in case of the T-shaped structures (TT, T), thus supporting our conclusions (see the next section) that the TT structure is likely to be the most stable one.

3.3. Stabilization Energies of the Dimers. The stabilization energies obtained for the optimized structures in Figure 1 are shown in Table 3.

This table provides DFT-D and CCSD(T) energies as well as CBS extrapolations for the structures obtained as described above and the “PD_p”, the one selected structure optimized by Janowski et al.,¹³ which is equivalent to our PD structure. The PD_p structure serves as a reference for our methodology of geometry optimization, for the accuracy of the single-point calculations and extrapolations. Let us first to compare our results obtained for the PD structure with the values obtained for the PD_p structure, which was point-by-point optimized (with the geometry of the monomers being fixed)

by means of the expensive BSSE corrected QCISD(T)/aTZ method.¹³ So as to provide an estimate of errors of our single-point CCSD(T) energies in the truncated OVOS, we present our values along with their QCISD(T) stabilization energies (in parentheses). The difference between the CCSD(T) and QCISD(T) stabilization energies in this particular case was shown to be very small, as roughly 0.004 kcal/mol overestimated by QCISD(T). The errors with respect to our OVOS CCSD(T) values in the PD_p geometry are −0.01 in the aDZ basis set, −0.02 in the aTZ basis set and 0.03 kcal/mol in the aQZ basis set. An important fact to be emphasized is that our aTZ calculation was carried out with 534 VOs instead of 786 VOs and our aQZ calculation with only 851 VOs instead of 1416 VOs (after the deletion of 54 basis functions due to their linear dependence), which resulted in an almost 1 order of magnitude acceleration in the CPU time. The stabilization energies in aDZ and aTZ slightly underestimate the reference values due to the error introduced by the truncation of the OVOS. The error in the aQZ basis set has the opposite sign as a consequence of the superposition of the errors of the truncation of the OVOS and the error of the elimination of the linear dependent basis functions (which itself has an effect of ≈0.01 kcal/mol). Such an unbalanced error distribution for different basis sets can result in error amplification (by up to 0.06 kcal/mol) when Helgaker's extrapolation scheme (see the footnote of Table 3) is used. However, Kim's extrapolation scheme, due to its more "interpolative" character, seems to be less sensitive, and agrees with the reference data, being within 0.02 kcal/mol. This is the reason that the extrapolation labeled in the table as (Q → 5)^g is, in our opinion, the most reliable and serves as our benchmark data. Concerning the accuracy of the geometries obtained by our parametrized DFT-D/BLYP/TZVP for PD, T, and S structures, our values are within 0.03 kcal/mol error bars on the CCSD(T)/aQZ 60% OVOS level with respect to the reference values, which is quite surprising for a method as cheap as the DFT-D.

The energy ordering of the structures is preserved while increasing the basis set size. The TT structure is the most stable, separated by ≈0.1 kcal/mol from the other structures in all the basis sets and CBS. On the other hand, the S structure is the least stable, separated from the other structures by almost 1 kcal/mol. The energy difference between the PD and T structures decreases, starting from 0.13 kcal/mol in the aDZ basis set, converging to almost zero (−0.01 kcal/mol) in the CBS. The ordering of the stabilization energies obtained in our calculations is TT > T ≥ PD > S. This is in agreement with the thus-far most accurate values, provided by Janowski et al.,¹³ except for the fact that they excluded the "relatively well" separated, most stable TT structure from their considerations. Our fitted DFT-D method leads to the same energy ordering of the structures, with errors being ≈0.2 kcal/mol when compared to our most accurate CCSD(T)/CBS values. DFT-D with the original parameters fitted to S22 test set performs significantly worse and leads to an incorrect ordering of the structures with respect to the energy. Errors for the stacked structures (PD, PD_p, S) are of the same magnitude as with our DFT-D optimized structures for the benzene dimer but are substantially larger for the

T-shaped structures (0.45 kcal/mol for the TT structures and 0.66 kcal/mol for the T structure). This clearly demonstrates that, when high accuracy is desired, use of any "universal" parameters for the empirical dispersion term is not possible (for further discussion, see the proceeding paper on the benzene dimer⁶).

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Supporting Information Available: Animation of all the optimized structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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