On the T-shaped structures of the benzene dimer
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Abstract
We report the geometries of two distorted T-shaped benzene dimer structures optimized at the RI-MP2/aug-cc-pVTZ level of theory. At the extrapolated RI-MP2/aug-cc-pV(TQ)Z level, the C$_s$ over atom and C$_s$ over bond configurations were found to be lower in energy than the conventionally accepted C$_{2v}$ T-shaped structure by 0.146 and 0.163 kcal/mol, respectively. When DCCSD(T)/6-311+G(2df,p) corrections were included, these structures remained lower in energy than the C$_{2v}$ reference by 0.127 and 0.132 kcal/mol, respectively, with C$_s$ over bond as the minimum energy T-shaped structure. While not the focus of this Letter, we also report that the C$_{2v}$ T-shaped configuration is stabilized by 0.31 kcal/mol over the C$_{2h}$ parallel-displaced configuration at the DCCSD(T)/aug-cc-pVTZ approximation to the CCSD(T)/CBS limit.

1. Introduction
The structures and energetics of the benzene dimer, the simplest model for weak noncovalent interactions of the aromatic π–π type, have posed a substantial challenge for both theoreticians and experimentalists alike. Despite the relatively small binding energy of the benzene dimer, approximately 1–3 kcal/mol, the importance of aromatic π–π interactions as stabilizing forces has been demonstrated in protein structure [1], DNA base-pair stacking [2], host–guest complexes [3], supramolecular self-assembly [4], and molecular recognition [5]. As such, it is not surprising that a more complete theoretical understanding of the strength and directionality of this fundamental and ubiquitous molecular interaction is still highly desired today.

Over the past 30 years, there has been great experimental and theoretical progress in a joint effort to characterize the structures and energetics of the global minimum of the benzene dimer. Despite significant progress, definitive characterization of the structures and particularly the relative energetics that comprise this soft, subtle, and complex potential energy landscape has not been completely accomplished. Among the numerous experimental studies [6–15] performed on the benzene dimer, microwave spectroscopy experiments indicate the presence of a dipole moment [13], and Raman [14] as well as infrared [15] experiments show that the benzene monomers are symmetrically inequivalent and further, that they do not interchange on an experimental (i.e., nanosecond) timescale. These experiments therefore indicate the presence of a T-shaped structure, but cannot unambiguously determine the existence of several other minima and the relative energetics amongst such isomers. High-level quantum mechanical calculations strongly support the existence of either a T-shaped (C$_{2v}$) or parallel-displaced (C$_{2h}$) structure as the global minimum but were unable to agree on definitive relative energetics despite remarkable computational effort [16–22]. Nevertheless, the theoretical literature does concord that the origin of the intermolecular interactions in benzene dimer are predominantly due to dispersive interactions resulting from transient multipole fluctuations that can only be captured by high-level quantum mechanical treatment with relatively large and diffuse atomic orbital (AO) basis sets.

Preliminary computational results on the C$_{2v}$ T-shaped structure performed at the MP2 level using a small basis...
set yielded imaginary frequencies in the normal mode analysis and gave a distorted C\textsubscript{s} structure as the minimum energy conformation [23]. Spurred on by these findings, here we report fully relaxed geometries (using the analytical gradient of resolution-of-the-identity second-order Møller-Plesset perturbation theory (RI-MP2) [24–27]) of two distorted (C\textsubscript{s}) and one alternative (C\textsubscript{2v}) T-shaped structures of benzene dimer that appear to be more stable than the aforementioned C\textsubscript{2v} T-shaped structure. Energetics describing the binding energies of these new configurations, including a full comparison to the conventionally accepted T-shaped (C\textsubscript{2v}) and parallel-displaced (C\textsubscript{2h}) minimum energy configurations, are reported at an approximated MP2 complete basis set (CBS) limit and with additional higher-level coupled-cluster (CCSD(T)) level corrections at the triple-\(f\) level. While this work was in the final stages of preparation, we noticed a report describing structures that are very similar to the Cs structures examined herein, obtained by an exhaustive sampling of the benzene dimer potential energy surface using the SAPT(DFT) methodology [28]. We hope that this Letter not only serves as a validation of these findings, but also as an extension of our theoretical insight into the benzene dimer system by reporting these fully relaxed \textit{ab initio} structures and the corresponding high-level CCSD(T) energetics.

2. Results and discussion

2.1. Structures

Using the newest release of the Q-CHEM [29] program, five benzene dimer structures (in addition to the D\textsubscript{6h} monomer) were fully optimized at the RI-MP2 level of theory (employing the aug-cc-pVTZ [30] atomic orbital (AO) and complementary aux-aug-cc-pVTZ auxiliary (AUX) basis sets) [24,31]. All geometry optimizations utilized 828 [1824] AO [AUX] basis functions and were considered converged when two of the following three criteria were met: a maximum energy change of \(1.0 \times 10^{-6}\) hartrees, a maximum force/gradient component of \(3.0 \times 10^{-4}\) hartrees/bohr, and/or a maximum displacement of \(1.2 \times 10^{-3}\) bohr. For reference, the value of the DIIS error vector utilized in determining SCF convergence was set to \(10^{-8}\) a.u. accompanied by an integral thresholding value of \(10^{-11}\) a.u. All geometry optimizations utilized the frozen core approximation and preserved the initial point group symmetry that was applied. The converged structures reported herein are only minima within the symmetry constraints applied. The structures resulting from the RI-MP2/aug-cc-pVTZ level geometry optimizations included two distorted (Cs) and one alternative (C\textsubscript{2v}) T-shaped configurations in addition to the well-known C\textsubscript{2v} T-shaped dimer (which will be referred to as the C\textsubscript{2v} over bond structure from here on). These new structures were named according to their respective point group and the main characteristics describing the dimeric binding motifs within. The first of the distorted configurations, which we have termed C\textsubscript{s} over atom, features a binding motif in which a C–C bond on one monomer straddles a C atom on the other monomer (Fig. 1). The Cs over atom configuration can be thought of as a rotation by \(30^\circ\) around the C\textsubscript{2} axis coupled with a forward rotation within the \(\sigma_v\) mirror plane of one monomer in the C\textsubscript{2v} over bond reference. The second of these configurations, which we have similarly termed C\textsubscript{s} over bond, results from a forward rotation within the \(\sigma_v\) mirror plane of one monomer in the C\textsubscript{2v} over bond reference. In this configuration, a C–C
bond on one monomer perpendicularly straddles a C–C bond on the other monomer (Fig. 1). The relative energetics of these structures with respect to the C$_{2v}$ over bond reference configuration will be described in some detail in the following section.

The center-to-center distance observed in the RI-MP2/aug-cc-pVTZ optimized C$_{2v}$ over bond reference was 4.8 Å, which is in fair agreement with that of Sherrill and co-workers [20], 4.9 Å, obtained using frozen monomers at the same level of theory, and that of Tsuzuki and co-workers [19], 5.0 Å. An alternative C$_{2v}$ T-shaped structure was also found, named C$_{2v}$ over atom, and is very similar to the reference C$_{2v}$ over bond structure, with one monomer rotated by 30° along the C$_2$ axis and a center-to-center distance of 4.8 Å. This alternative C$_{2v}$ over atom structure was also considered by Tsuzuki et al. [19], who found the separation to be just larger at 5.0 Å and the structure isoenergetic to C$_{2v}$ over bond. Additional C$_{2h}$ structures, in which one monomer is rotated by 30° within the σ$_v$ mirror plane, were found to be higher in energy than the C$_{2v}$ over bond and C$_{2v}$ over atom structures [19], and therefore were not considered in this work.

While not the focus of this Letter, a C$_{2h}$ parallel-displaced structure was also obtained from a full geometry optimization at the RI-MP2/aug-cc-pVTZ level. To date, there are at least two unique C$_{2h}$ parallel-displaced configurations reported in the literature, originating from both the Sherrill and Tsuzuki research groups—their differences first illustrated by Park and Lee [22]. The C$_{2h}$ parallel-displaced configuration discussed in this Letter more closely resembles that of Sherrill and co-workers (see Fig. 1 of Ref. [20]) with fair agreement between the $R_1 = 3.3$ Å and $R_2 = 1.6$ Å; Ref. [20]: $R_1 = 3.4$ Å and $R_2 = 1.6$ Å). Again, we must stress that the key difference between our C$_{2v}$ centered and C$_{2h}$ parallel-displaced structures and that of others reported in the literature, is that we have chosen to perform full analytical geometry optimizations (i.e., no frozen monomers were used).

The D$_{6h}$ monomer, also optimized at the same level of theory, was found with C–C and C–H bond lengths of 1.394 Å and 1.082 Å, respectively. These bond lengths are in excellent agreement with the most accurate theoretical values available of 1.3915 Å and 1.0800 Å computed at the CCSD(T)/cc-pVQZ level of theory [32]. For future reference, the Cartesian coordinates for each of these optimized configurations as well as the D$_{6h}$ monomer are provided in Supplementary Material.

### 2.2. Energetics

To characterize the energetic differences between these configurations, we computed the RI-MP2 binding energy for each configuration using the aug-cc-pVXZ (X = D, T, and Q) [30] AO basis set series and their complementary AUX basis sets [24,31]. During all single-point energy evaluations, SCF wavefunctions were considered converged when the DIIS error vector was less than 10$^{-15}$ a.u. accompanied by a slightly stricter AO integral drop threshold of 10$^{-12}$ a.u. Like the geometry optimizations described above, all energy computations throughout this work employed the frozen core approximation. The MP2/CBS limit was then approximated by extrapolation to the RI-MP2/aug-cc-pV(TQ)Z level using the following prescription [33]

$$E_{XY} = E_{SCF,Y} + \frac{X^3 E_{CORR,X} - Y^3 E_{CORR,Y}}{X^3 - Y^3}; \quad Y > X$$  \hspace{1cm} (1)

where $X = 3$ and $Y = 4$ for the T → Q extrapolation discussed in this work.

Binding energies ($\Delta E_{\text{bind}}$) were corrected for basis set superposition error (BSSE) using the counterpoise correction of Boys and Bernardi [34], accounting for deformation of the monomer geometry within the dimer complex, i.e.,

$$\Delta E_{\text{bind}} = E_{(A-B)} - [E_{(A-X)} - E_{(A-0)}] - [E_{(X-B)} - E_{(0-B)}] - E_{(A)} - E_{(B)}$$  \hspace{1cm} (2)

where $E_{(A-B)}$ is the energy of the dimer (A–B), $E_{(A-X)}$ is the energy of A using both the optimized dimer geometry and basis set with ghost atoms replacing monomer B, $E_{(A-0)}$ is the energy of A using the optimized dimer geometry without monomer B, and $E_{(A)}$ is the energy of A at the monomer geometry optimized at the same level of theory. Using structures optimized at the RI-MP2/aug-cc-pVTZ level, the counterpoise-corrected RI-MP2 binding energies and corresponding absolute BSSE measurements for each of the aforementioned configurations are given in Table 1.

From the data in Table 1, it is clear that both the C$_s$ over atom and C$_s$ over bond configurations are lower in energy than the C$_{2v}$ over bond configurations. The Cartesian coordinates for each of these optimized configurations are provided in Table 1.

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<th>Binding energies (in kcal/mol)</th>
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<tr>
<td></td>
<td></td>
<td>D</td>
<td>T</td>
<td>Q</td>
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<tr>
<td>C$_{2v}$</td>
<td>over bond</td>
<td>−2.992 [3.838]</td>
<td>−3.404 [1.542]</td>
<td>−3.516 [0.511]</td>
</tr>
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</table>

Based on the counterpoise correction scheme given in Eq. (2), the corresponding amount of BSSE in kcal/mol is given in adjacent [square brackets].
than the reference C\textsubscript{2v} \textit{over bond} structure, with the C\textsubscript{2v} \textit{over bond} configuration the lowest amongst the three at all levels of theory. At the RI-MP2/aug-cc-pVTZ level, i.e., the level at which the optimizations were performed, the C\textsubscript{2v} \textit{over bond} and C\textsubscript{2h} \textit{over atom} structures were more stable than the C\textsubscript{2v} \textit{over bond} reference by 0.149 and 0.133 kcal/mol, respectively. At this level of theory, the separation between the C\textsubscript{2v} \textit{over bond} and C\textsubscript{2h} \textit{over atom} structures is very small, namely, 0.016 kcal/mol. Interestingly, this slight separation stays relatively constant at 0.017 kcal/mol as the quality of the basis set employed was increased to aug-cc-pVQZ and extrapolations to the RI-MP2/aug-cc-pV(TQ)Z level were made. On the other hand, the energetic gap between these distorted T-shaped structures and the reference C\textsubscript{2v} \textit{over bond} configuration only slightly increased as the RI-MP2/CBS limit was approached. At the aug-cc-pVQZ level, we found a systematic increase of approximately 0.010 kcal/mol in these gaps, yielding separations of 0.159 [C\textsubscript{2v} \textit{over bond}] and 0.142 [C\textsubscript{2h} \textit{over atom}] kcal/mol with respect to the C\textsubscript{2v} \textit{over bond} structure. Extrapolation to the aug-cc-pV(TQ)Z level provided us with no further resolution, as energetic separations of 0.163 [C\textsubscript{2v} \textit{over bond}] and 0.146 [C\textsubscript{2h} \textit{over atom}] kcal/mol were observed at the approximated MP2/CBS limit.

Among the C\textsubscript{2v} T-shaped structures, the C\textsubscript{2v} \textit{over atom} structure was found to be negligibly more stable than the reference C\textsubscript{2v} \textit{over bond} structure at the RI-MP2/aug-cc-pVTZ level of theory. In fact, these structures were nearly isoenergetic, with an energetic separation of only 0.002 kcal/mol. This finding is consistent with the work of Tsuzuki and co-workers [19], and was reproduced at both the aug-cc-pVQZ level and the T \textrightarrow Q extrapolation to the MP2/CBS limit.

Considering the extrapolated RI-MP2/aug-cc-pV(TQ)Z data as our best MP2 numbers, we report the energetic difference between the traditionally accepted minima of benzene dimer, namely, the C\textsubscript{2v} \textit{over bond} and C\textsubscript{2h} \textit{parallel-displaced} structures, as 1.37 kcal/mol. This number is in fairly close agreement to the MP2-R12/A CBS limit energetic gap provided by Sherrill and co-workers [20], 1.32 kcal/mol, which was obtained from dimer geometries optimized at the MP2/aug-cc-pVTZ level of theory using the frozen monomers of Gauss and Stanton [32]. Based on the findings above, it is clear that the alternative T-shaped structures are slightly closer in energy to the C\textsubscript{2h} \textit{parallel-displaced} structure, with energetic separations of 1.20 [C\textsubscript{2v} \textit{over bond}] and 1.22 [C\textsubscript{2h} \textit{over atom}] kcal/mol at the approximated MP2/CBS limit.

Previous theoretical work has demonstrated that higher-order post-MP2 correlation plays a significant role in the description of the intermolecular interactions in benzene dimer, firstly due to the fact that double excitations first introduced into the perturbative expansion of the HF wavefunction via MP2 theory tend to overestimate \( \pi \)–\( \pi \) interactions. Additionally, three-body correlation (as described by the perturbative triples contribution in the CCSD(T) model) should be included for a quantitative physical description of the dispersion interactions present in this system (i.e., to ensure sub-kcal/mol accuracy). Because of the prohibitive cost associated with CCSD(T) energy computations and nearly complete AO basis sets, the CCSD(T)/CBS binding energies \( \Delta E_{\text{CCSD(T)}}/\text{CBS} \) were approximated via the following \( \Delta \text{CCSD(T)} \) correction scheme:

\[
\Delta E_{\text{CCSD(T)}}/\text{CBS} = \Delta E_{\text{RI-MP2}/\text{CBS}} + \left( \Delta E_{\text{CCSD(T)}} - \Delta E_{\text{MP2}} \right) /\text{FBS},
\]

where \( \Delta E_{\text{RI-MP2}}/\text{CBS} \) is the counterpoise-corrected RI-MP2/aug-cc-pV(TQ)Z binding energy and \( \Delta E_{\text{CCSD(T)}} - \Delta E_{\text{MP2}} /\text{FBS} \) is the difference between the CCSD(T) and MP2 binding energies using a finite basis set (FBS), denoted as CCSD(T)/FBS. Eq. (3) is based heavily upon the assumption that the difference between the CCSD(T) and MP2 methodologies can be captured using a small-to-medium basis set and basis set effects like BSSE have been removed via extrapolation to the MP2/CBS limit. In this work, we first utilized the 6-31G(d) AO basis to approximate the CCSD(T)/CBS limit, but then refined our energetics with \( \Delta \text{CCSD(T)} \) computations using the 6-311+G(2df,p) AO basis set for all of the aforementioned configurations and the aug-cc-pVTZ AO basis set for the higher-symmetry C\textsubscript{2v} and C\textsubscript{2h} structures. The approximated CCSD(T)/CBS binding energies using these AO basis sets are given in Table 2.

Inclusion of higher-level treatment of electron correlation via the CCSD(T) formalism supports our earlier findings in that the C\textsubscript{2h} \textit{over bond} and C\textsubscript{2v} \textit{over bond} configurations are both lower in energy than the C\textsubscript{2v} \textit{over bond} structure. Although the C\textsubscript{2v} \textit{over bond} configuration

<table>
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<th>Configuration</th>
<th>CBS binding (in kcal/mol)</th>
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<td></td>
<td>MP2 6-31G(d) 6-311+G(2df,p) aug-cc-pVTZ</td>
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<tr>
<td>C\textsubscript{2v} \textit{over atom}</td>
<td>-3.749 -2.887 [0.862] -2.658 [1.091] - [ ]</td>
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<tr>
<td>C\textsubscript{2v} \textit{over bond}</td>
<td>-3.766 -2.893 [0.873] -2.663 [1.103] - [ ]</td>
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<tr>
<td>C\textsubscript{2h} \textit{over atom}</td>
<td>-3.605 -2.751 [0.854] -2.543 [1.061] -2.448 [1.156]</td>
</tr>
<tr>
<td>C\textsubscript{2h} \textit{over bond}</td>
<td>-3.603 -2.740 [0.863] -2.531 [1.072] -2.438 [1.165]</td>
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Higher-order correlation effects from \( \Delta \text{CCSD(T)} \) computations are given in kcal/mol in the respective adjacent [square brackets].
represents the minimum amongst the T-shaped configurations, the energy separation between the low-lying distorted T-shaped structures is marginal. For instance, at the ∆CCSD(T)/6-31G(d) and ∆CCSD(T)/6-31+G(2df,p) approximations to the CCSD/CBS limit, the C₄ over bond configuration was stabilized by only 0.006 kcal/mol and 0.005 kcal/mol, respectively, over the C₄ over atom structure. These energetic differences are well below the resolution afforded by the CCSD(T) methodology and strongly suggest that these distorted T-shaped structures are nearly isoenergetic. We are not terribly surprised by this result, as even the most trivial difference in higher-order correlation contributions could easily resolve or entangle the already slight energetic difference of 0.017 kcal/mol at the MP2/CBS limit. We also note that these findings are in excellent agreement with that of Szalewicz and co-workers [28], who found two distorted C₄ T-shaped structures using SAPT(DFT), labeled M2 and S1, that are very similar to our C₄ over bond and C₄ over atom configurations, respectively, with an energetic separation of 0.013 kcal/mol (computed by augmenting MP2/aug-cc-pVTZ binding energies with ∆CCSD(T)/aug-cc-pVDZ corrections).

At the CCSD(T) level, the energetic separations between these distorted T-shaped configurations and the reference C₂ᵥ over bond structure remained very similar to the aforementioned RI-MP2/CBS limit results. At the ∆CCSD(T)/6-31G(d) approximation to the CCSD(T)/CBS limit, these relative energy gaps were found as 0.153 [C₄ over bond] and 0.147 [C₄ over atom] kcal/mol, which are very similar to the MP2/CBS limit results of 0.163 and 0.146 kcal/mol, respectively. With the use of the more complete 6-311+G(2df,p) AO basis set, these relative energetic separations decreased to 0.132 [C₄ over bond] and 0.127 [C₄ over atom] kcal/mol. Indeed, CCSD(T) computations at the triple-ζ level have confirmed the relatively important finding that these distorted C₄ T-shaped structures are lower in energy than the conventionally accepted C₂ᵥ configuration. This finding is echoed in the work of Szalewicz et al. [28] in which the energetic separation between S3 (the structure corresponding to our reference C₂ᵥ configuration) and their analogs to C₄ over bond (M2) and C₄ over atom (S1) were computed at 0.112 and 0.099 kcal/mol, respectively, using ∆CCSD(T)/aug-cc-pVDZ corrections to MP2/aug-cc-pVTZ binding energies.

Among the C₂ᵥ T-shaped structures, we found that the almost negligible energetic separation of 0.002 kcal/mol at the extrapolated MP2/CBS limit slightly increased as the triples were perturbatively introduced in the ∆CCSD(T) correction. In fact, the C₂ᵥ over atom structure was stabilized by approximately 0.010 kcal/mol when ∆CCSD(T) corrections at the 6-31G(d), 6-31+G(2df,p), and aug-cc-pVTZ levels were included. Although this energetic separation is only a fraction of kT under ambient conditions, such a finding does suggest that the C₂ᵥ over atom structure should be considered along with the C₂ᵥ over bond structure during any future theoretical investigations of the lowest-lying C₂ᵥ T-shaped configurations of the benzene dimer.

Based on the approximated CCSD(T)/CBS data in Table 2, we also report some interesting findings regarding the highly contested energetic difference between the conventionally accepted minima of the benzene dimer: the C₂ᵥ over bond and C₂ᵥ parallel-displaced configurations. Based on the ∆CCSD(T)/6-31G(d) corrected binding energies, we found the C₂ᵥ parallel-displaced structure stabilized by 0.29 kcal/mol over the C₂ᵥ over bond structure. However, as the quality of the AO basis set was increased, this relative energetic ordering becomes completely inverted: the C₂ᵥ over bond configuration is now stabilized by 0.26 [∆CCSD(T)/6-31G(2df,p)] and 0.31 [∆CCSD(T)/aug-cc-pVTZ] kcal/mol with respect to the C₂ᵥ parallel-displaced configuration. These findings are in fairly close agreement to the work of Hobza and co-workers [17], who reported the T-shaped structure (C₂ᵥ over bond) as the minimum energy benzene dimer configuration, stabilized by 0.2–0.3 kcal/mol over the C₂ᵥ parallel-displaced structure. Less satisfactory agreement was found when comparing our energetic separation with that of Sherrill and co-workers [20], where the C₂ᵥ parallel-displaced structure was found to be lower in energy by 0.04 kcal/mol over the C₂ᵥ over bond T-shaped structure. This energetic gap represents the MP2-R12/ACBS limit estimate corrected for higher-order correlation effects via the ∆CCSD(T)/aug-cc-pVDZ correction using similar T-shaped and parallel-displaced structures to that reported herein (i.e., structures that were optimized at the MP2/aug-cc-pVTZ level using frozen monomers). Unfortunately, a fair comparison with the work of Tsuzuki and co-workers [19] and Park and Lee [22] cannot be done in this Letter, since both of these groups focused their research efforts on an alternative C₂ᵥ parallel-displaced structure to that reported herein. Interestingly, the recent work of Szalewicz et al. [28] reports a parallel-displaced configuration (M1) that appears to be a mixture of both of these aforementioned C₂ᵥ parallel-displaced structures and predicts it to be more stable than the conventionally accepted C₂ᵥ T-shaped configuration by approximately 0.016 kcal/mol.

Such a comparison, while not the focus of this Letter, was included in an attempt to provide another perspective to the aforementioned discrepancies existing in the literature. These reported differences appear to be the result of limitations of the treatment of electron correlation in the benzene dimer system at the MP2 level of theory. As the AO basis set quality is increased in the ∆CCSD(T) computations, we observed a complete inversion of the relative ordering among the C₂ᵥ over bond and C₂ᵥ parallel-displaced configurations. In all cases, the contributions from CCSD(T) are almost double the BSSE at the RI-MP2/aug-cc-pVQZ level, a finding which strongly supports the claim that even MP2 computations using large, diffuse AO basis sets are not nearly converged with respect to the true benzene dimer binding energy. These findings indicate limitations of the ∆CCSD(T) correction with overly small finite AO basis sets, and perhaps even the use of MP2 theory in the geometry optimization of these
configurations. It seems evident that still further computational research, in particular, high-level CCSD(T) computations for refinement of all energetic quantities and an exhaustive comparison of the two known parallel-displaced structures, will be necessary to further resolve the relative energetics between and within the multiple C2v T-shaped and C2h parallel-displaced structures. In the same breath, we must concede that our findings do suggest that complete resolution of the complex PES of the benzene dimer might also require geometry optimizations utilizing large, diffuse AO basis sets with CCSD(T).

At this point, we should discuss the possible character of the four T-shaped stationary points located. At the RI-MP2/aug-cc-pVTZ level, it is very likely that at most one of these four points is a local minimum (the C2v over bond structure). The Cs over atom structure is presumably a first-order saddle point interconnecting equivalent C2v over bond structures. The higher-energy, nearly isoenergetic, C2v over bond and C2v over atom structures are then likely to be second-order saddle points (e.g., interconnecting Cs over atom structures). Our MP2/CBS level single-point energy calculations appear generally consistent with these conclusions, but, as we have already seen, the already small energy difference between the two Cs structures diminishes even further once ΔCCSD(T) corrections were applied. To further test this hypothesis, Hessians must be computed at the RI-MP2/aug-cc-pVTZ level of theory to determine the number of imaginary frequencies in each of these configurations. Since the vibrational motifs that would interconnect these dimer configurations closely resemble frustrated translations and rotations, we feel that the accuracy associated with numerical RI-MP2 Hessian computations will not provide us with definitive answers.

3. Conclusions

In addition to the well-known C2v over bond and C2h parallel-displaced configurations, two distorted Cs T-shaped benzene dimer structures, C4h over atom and C4v over bond, and one alternative C2x structure, C2x over atom, were optimized at the RI-MP2/aug-cc-pVTZ level of theory. Counterpoise-corrected single-point energy evaluations were performed using RI-MP2 theory and the aug-cc-pVXZ series (X = D, T, and Q) and the MP2/CBS limit was approximated by T → Q extrapolation to the RI-MP2/aug-cc-pV(TQ)Z level.

At all levels of MP2 theory, the Cs over atom and Cs over bond configurations were found to be lower in energy than the reference C2v over bond structure, with the Cs over bond configuration the minimum amongst the T-shaped structures at all levels of theory. At the extrapolated RI-MP2/aug-cc-pV(TQ)Z level, the Cs over bond configuration was slightly stabilized with respect to the Cs over atom by 0.017 kcal/mol, and the relative energy gaps between these distorted T-shaped structures and the reference C2v over bond structure were found as 0.163 kcal/mol and 0.146 kcal/mol, respectively. The alternative C2v, configuration, C2v over atom, was found to be negligibly more stable (~0.002 kcal/mol) than the reference C2v over bond structure at the extrapolated RI-MP2/aug-cc-pV(TQ)Z level of theory.

Higher-level correlation effects were included by approximating the CCSD(T)/CBS limit via ΔCCSD(T) corrections at the 6-31G*, 6-31+G(2df,p), and aug-cc-pVTZ levels. At the ΔCCSD(T)/6-31+G(2df,p) approximation to the CCSD(T)/CBS limit, the C2v over bond and C4v over atom structures, while nearly isoenergetic and separated by only 0.005 kcal/mol, still remained lower in energy with respect to the reference C2v over bond structure by 0.132 kcal/mol and 0.127 kcal/mol, respectively, confirming that these distorted Cs T-shaped structures are indeed lower in energy than the conventionally accepted C2v configuration. While not the focus of this Letter, we also report that the conventionally accepted C2v configuration (C2v over bond) was found to be more stable than the parallel-displaced configuration (C2h parallel-displaced) by 0.31 kcal/mol at the ΔCCSD(T)/aug-cc-pVTZ approximation to the CCSD(T)/CBS limit. Interestingly, this relative energetic ordering was completely inverted from the ΔCCSD(T)/6-31G(d) findings and most of the literature on the topic, to date.

Acknowledgments

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Appendix A. Supplementary material

Cartesian coordinates for four T-shaped benzene dimer configurations, one parallel-displaced benzene dimer configuration, and the benzene monomer optimized at the RI-MP2/aug-cc-pVTZ level of theory. Supplementary material associated with this Letter can be found, in the online version, at doi:10.1016/j.cplett.2007.02.034.

References