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Estimates of the Ab Initio Limit for $\pi-\pi$ Interactions: The Benzene Dimer

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Abstract: State-of-the-art electronic structure methods have been applied to the simplest prototype of aromatic $\pi-\pi$ interactions, the benzene dimer. By comparison to results with a large aug-cc-pVTZ basis set, we demonstrate that more modest basis sets such as aug-cc-pVDZ are sufficient for geometry optimizations of intermolecular parameters at the second-order Møller−Plesset perturbation theory (MP2) level. However, basis sets even larger than aug-cc-pVTZ are important for accurate binding energies. The complete basis set MP2 binding energies, estimated by explicitly correlated MP2−R12/A techniques, are significantly larger in magnitude than previous estimates. When corrected for higher-order correlation effects via coupled cluster with singles, doubles, and perturbative triples [CCSD(T)], the binding energies D_e (D_0) for the sandwich, T-shaped, and parallel-displaced configurations are found to be 1.8 (2.0), 2.7 (2.4), and 2.8 (2.7) kcal mol^{-1}, respectively.

1. Introduction

Attractive interactions between π systems are one of the principal noncovalent forces governing molecular recognition. They influence the structures of proteins,[1,2] DNA,[3] host−guest complexes,[4−7] solid materials containing aromatic groups,[8−10] and self-assembled supramolecular architectures.[10,11] These $\pi-\pi$ interactions also control the intercalation of certain drugs into DNA.[12] The conductive properties of molecular wires formed by self-assembly of stacks of aromatic macrocycles are also of recent interest.[13] Although the importance of $\pi-\pi$ interactions is widely recognized, a detailed understanding of their origins, strength, and orientational dependence is not yet available. Hunter and Sanders have presented a simple charge distribution model which attempts to explain the qualitative geometrical preferences for the interactions between aromatic molecules,[8] but it is clear that quantitative predictions of geometries and energies are highly desirable.

In this work, we consider the simplest prototype of $\pi-\pi$ interactions, the benzene dimer. Explicitly correlated (R12) quantum mechanical theories,[14−16] coupled with focal-point analysis,[17,18] yield binding energy estimates of unprecedented accuracy for this system. These results should be a key component in the development of a new generation of molecular mechanics force fields capable of reliably describing $\pi-\pi$ interactions.

The small binding energy (~2−3 kcal mol^{-1}) of gas-phase benzene dimer makes it a challenge for both experiment and theory. The dimer is stable only at low temperatures and is typically prepared in supersonic jet expansions. Because clusters of various sizes are produced, it is necessary to detect their masses. Such challenges are a significant obstacle to a definitive experimental description. Moreover, the diverse experimental techniques employed to date have yielded seemingly contradictory results and are only consistent if there are at least two different low-energy potential energy minima or if the system is highly fluxional with low barriers.[19] The combined experimental and theoretical work to date suggests that the most favorable configurations are the perpendicular T-shaped and parallel-displaced (PD) geometries (see Figure 1), with the eclipsed sandwich (S) configuration somewhat higher in energy. Previous theoretical work[20] indicates that minor variations of these configurations (e.g., the "edge-face" T-shaped configuration, obtained by rotating the top monomer in Figure 1b by

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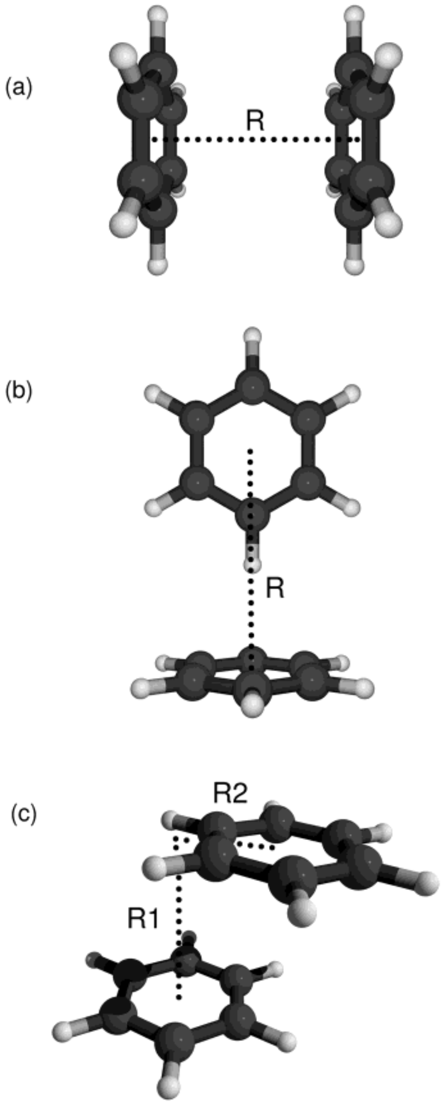

Figure 1. Sandwich, T-shaped, and parallel-displaced configurations of the benzene dimer.

30° about the axis perpendicular to the page, or a rotated C_{6v} sandwich) are very similar in energy. Approximately perpendicular and offset parallel configurations are frequently observed in the crystal structures of simple aromatic compounds,[2,9] and interacting pairs of aromatic side chains in proteins exhibit both orientations, perpendicular arrangements dominating.[1,2] By contrast, directly overlapping rings, as in the S configuration, are rarely observed for these systems.[1,2,9] Neutron diffraction experiments on solid benzene[21] find nearest neighbor orientations that are not quite T-shaped or parallel-displaced.

Early molecular beam electric resonance studies by Klemperer and co-workers[22,23] on the gas-phase benzene dimer provided evidence for the T-shaped configuration, and a subsequent rotational spectrum by Arunan and Gutowsky[24] gave a 4.96 Å separation between the benzene centers of mass. These experiments did not rule out the existence of the parallel-displaced or sandwich configurations, however, since they are only sensitive to molecules with dipole moments. Subsequent mass-selected stimulated Raman spectra of benzene dimer and its isotopomers by Felker et al.[25] were consistent with a dimer composed of monomers not related by a symmetry element (e.g., T-shaped). On the other hand, optical absorption spectra by Bernstein and co-workers[26] and multiphoton ionization studies by Schlag and co-workers[27] support the two monomers being symmetry-equivalent. Additional hole-burning experiments[28] were consistent with the existence of three different dimer configurations. The binding energy of the dimer, obtained from the dissociation energy of the ion and the ionization potentials of the dimer and monomer, was measured as $D_0 = 1.6 \pm 0.2$ kcal mol^{-1} by Krause et al.[29] and as 2.4 ± 0.4 kcal mol^{-1} by Grover et al.[30]

There have been a large number of theoretical studies of benzene dimer.[19,20,31-34] The binding of the dimer is primarily due to London dispersion interactions,[33] which arise from favorable instantaneous multipole/induced multipole charge fluctuations. Since Hartree−Fock molecular orbital theory describes each electron in the *average* field of the other electrons, it is incapable of describing the instantaneous fluctuations giving rise to dispersion forces. Unfortunately, current implementations of Kohn−Sham density functional theory (DFT) rely on essentially local approximations for the density and are also incapable of accurately describing dispersion forces.[34,35] Hence, wave function based correlation methods are required for a qualitatively accurate description of the benzene dimer. Moreover, the need to describe the polarizability of the monomers accurately suggests that very large basis sets—including multiple polarization and diffuse functions—may be necessary.

The importance of using large basis sets has been shown by a number of theoretical studies,[19,31,34] but to date no truly large basis set has been used which can realistically approximate the complete basis limit. The use of multiple diffuse functions, in particular, has received little consideration because of their computational cost. In this study, we consider the large correlation-consistent basis sets augmented by multiple diffuse functions, through aug-cc-pVQZ (1512 basis functions), for second-order perturbation theory (MP2) computations. We explore the effect of basis sets on geometries by obtaining MP2 potential energy curves as a function of the distance between monomers using a much larger basis set (aug-cc-pVTZ, 828 functions) than previously used for dimer geometry optimization. Complete basis set (CBS) limits at the MP2 level have been estimated using the orbital invariant version of the explicitly correlated MP2−R12 method in the standard approximation A (designated as MP2−R12/A)[14] with a custom Gaussian basis set. Key studies by Jaffe and Smith,[19] Hobza et al.,[32] and Tsuzuki

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et al.[33,34] have shown that MP2 overestimates the effect of electron correlation. Moreover, three-body electron correlations, described by triple excitations relative to the reference configuration, are also significant.[33] Hence, coupled-cluster computations with perturbative triples[36] [CCSD(T)] have also been performed and combined with the Hartree−Fock and MP2−R12/A values to estimate complete basis CCSD(T) binding energies for benzene dimer, which should be accurate to a few tenths of a kilocalorie per mole.

2. Theoretical Methods

Most computations were performed using Dunning's augmented correlation-consistent polarized valence basis sets of contracted Gaussian functions,[37] specifically aug-cc-pVDZ (384 functions), aug-cc-pVTZ (828 functions), and aug-cc-pVQZ (1512 functions). The aug- prefix denotes that these basis sets have an extra set of diffuse functions for each angular momentum appearing in the basis. A special fully uncontracted 13s8p5d2f/9s3p1d C/H basis set (provided in the Supporting Information) was constructed for use in MP2−R12/A calculations described below.

The optimum intermonomer distances for the planar sandwich, T-shaped, and parallel-displaced dimer configurations were computed including valence electron correlation via second-order MP2 theory in conjunction with the aug-cc-pVDZ and aug-cc-pVTZ basis sets. For the sandwich and T-shaped geometries, the distance between the center of mass of the two benzene monomers was systematically varied (denoted by R in Figure 1a,b) while the monomer geometries were kept rigid. For the parallel-displaced configuration, both the vertical and horizontal centers of mass distances were varied (denoted by R1 and R2 in Figure 1c) with rigid monomers. Each dimer optimization used a monomer geometry fully optimized at the same level of theory. The counterpoise (CP) correction of Boys and Bernardi[38] was applied to account for basis set superposition error which results from the use of finite basis sets. Full geometry optimization at the MP2/cc-pVDZ level of theory supports the idea that the monomers remain nearly rigid in the dimer; all C−C and C−H distances stay within 0.001 Å of their values in the monomer, except for a 0.003 Å shortening of the C−H bond pointed at the other benzene ring in the T-shaped configuration. Angles did not change significantly in the full optimization.

The optimal aug-cc-pVTZ MP2 intermonomer distances thus determined were coupled with the recommended monomer geometry of Gauss and Stanton[39] (C−C = 1.3915 Å; C−H = 1.0800 Å) to yield our best estimates for the equilibrium geometry of each structure. These geometries were used to study the basis set dependence of Hartree−Fock and MP2 energies (see Figures 6 and 7). They were also used to establish ab initio limits for the binding energies of each configuration. The binding energy limit estimate was composed of three contributions (each counterpoise-corrected): (1) the complete basis set limit at the Hartree−Fock level, approximated with the aug-cc-pVQZ basis; (2) the CBS limit for the MP2 valence correlation contribution, estimated by the MP2−R12/A method; (3) the effect of higher-order electron correlation, estimated as the difference between CCSD(T) and MP2 valence correlation energies evaluated with the aug-cc-pVDZ basis. Although it was not possible to compute the latter ΔCCSD(T) correction in a larger basis, it should be relatively insensitive to basis set improvements, as demonstrated by the success of additive schemes such as those found in focal-point analysis[17,18] or the Gaussian-3 method.[40] Core orbitals were constrained to remain doubly occupied in all correlated computations. The effect of core correlation, estimated at the MP2 level using Dunning's core-valence aug-cc-pCVDZ basis,[41] was found to be negligible (less than 0.03 kcal mol^{-1} for all configurations).

A brief comment is due on the energies obtained with the explicitly correlated MP2−R12/A method. The approximate resolution of the identity utilized in the current form of the linear R12 theories puts certain requirements on the quality of the basis used in such computations. Specifically, the basis has to be complete enough in the one-particle sense that its use in the approximate resolution of the identity will not introduce significant errors. It seems that only through comparison with MP2−R12/A energies computed with larger basis sets may we rigorously evaluate the appropriateness of the custom basis set used here. Computations of such scope will only be possible with a massively parallel implementation of the method, and work along these lines is well underway. However, the difference between the counterpoise-corrected and uncorrected MP2−R12/A interaction energies may also be considered an estimate of the accuracy of our MP2−R12 computations. The computed differences (0.05, 0.23, and 0.13 kcal mol^{-1} for the S, T, and PD configurations, respectively) indicate an accuracy of ~0.2 kcal mol^{-1}, which is the technical limit at the moment.

All MP2 results were obtained using the PSI 3.0[42] and Q-Chem 2.0[43] programs except for the aug-cc-pVQZ MP2 computations, which were performed with Sandia's massively parallel quantum chemistry (MPQC) program[44−47] using 12−15 POWER3-II processors of an IBM SP. CCSD(T) calculations were performed with ACES II[48] and PSI. The MP2−R12/A computations were performed using the orbital invariant version of the method[15] as implemented in the PSI suite.[16] A new, shared-memory parallel MP2−R12/A algorithm based on the direct MP2 transformation scheme of Head-Gordon et al.[49] was implemented for this project and made the current computations feasible. Each MP2−R12/A energy evaluation required approximately 2 weeks running on four processors of the SP.

3. Results and Discussion

Dimer geometry optimizations were performed at the MP2/aug-cc-pVDZ and MP2/aug-cc-pVTZ levels of theory using rigid monomers. The monomer geometries were obtained at these same levels of theory and are displayed in Figure 2. The MP2/aug-cc-pVDZ geometry is in reasonably good agreement with the reference r_e geometry of Gauss and Stanton,[39] with bond length errors of about 1.2%. The larger aug-cc-pVTZ basis yields much better agreement, reducing errors to about 0.2%.

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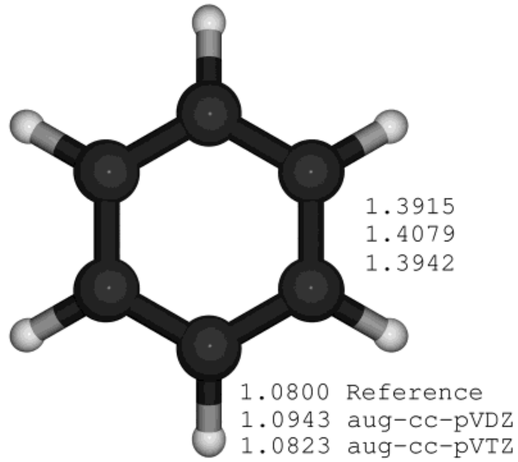

Figure 2. Equilibrium geometry of benzene (bond distances in angstroms).

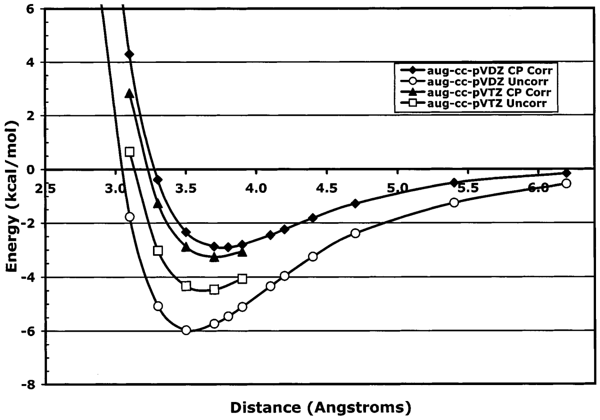

Figure 3. Potential energy curves for the sandwich configuration at the MP2/aug-cc-pVDZ and MP2/aug-cc-pVTZ levels of theory.

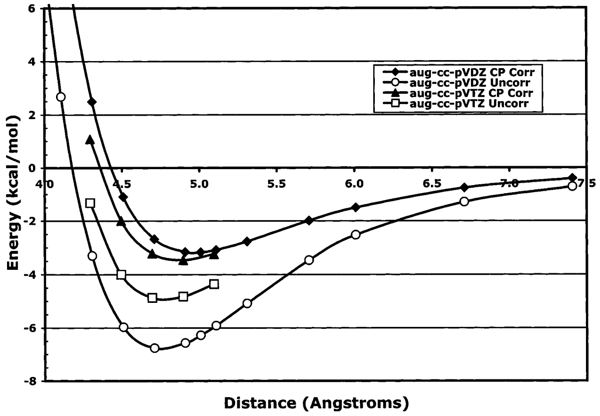

Figure 4. Potential energy curves for the T-shaped configuration at the MP2/aug-cc-pVDZ and MP2/aug-cc-pVTZ levels of theory.

To our knowledge, no previous study has considered the effect of basis sets as large as aug-cc-pVTZ on the geometries of benzene dimer. Potential energy curves for the sandwich, T-shaped, and parallel-displaced configurations were obtained using MP2 with the aug-cc-pVDZ and aug-cc-pVTZ basis sets. These curves, both uncorrected and CP-corrected, are plotted in Figures 3−5 (for clarity, only the CP-corrected aug-cc-pVDZ results are displayed for parallel-displaced). One immediately observes a very large difference between uncorrected and CP-corrected binding energies except near the dissociation limit. Near equilibrium for the T-shaped configuration, this difference is 3−4 kcal mol^{-1} for aug-cc-pVDZ and remains around 1.5 kcal mol^{-1} for aug-cc-pVTZ. Note also that the minima for the uncorrected and CP-corrected curves are significantly different. Although the counterpoise procedure can overcorrect for BSSE, underestimating binding, in this system the CP-corrected values appear to converge faster to the complete basis set limit. The CP-corrected aug-cc-pVDZ and aug-cc-pVTZ curves are nearly parallel and give nearly the same equilibrium intermonomer separations. This suggests that smaller basis sets such as aug-cc-pVDZ may be acceptable for intermonomer geometries, so long as binding energies are counterpoise-corrected. As shown in Figure 5, the sandwich structure represents a potential energy maximum (saddle point) along the displacement coordinate *R*2 which connects two equivalent PD configurations. This behavior agrees with the previous results of Jaffe and Smith.[19] Whether the sandwich structure represents a transition state or a higher-order saddle point cannot be determined with certainty on the basis of the present analysis.

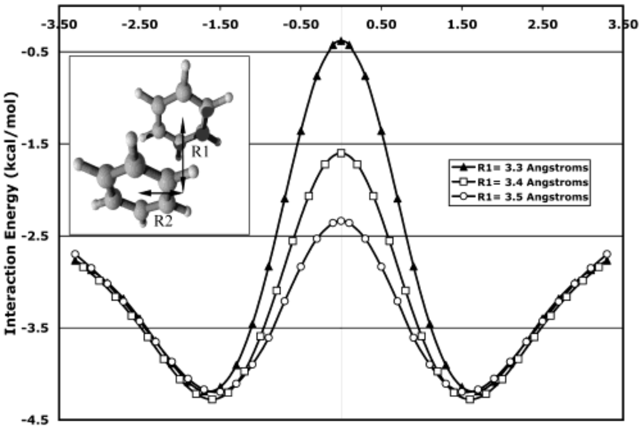

Figure 5. Potential energy curves for the parallel-displaced configuration at the (counterpoise-corrected) MP2/aug-cc-pVDZ level of theory.

The equilibrium dimer intermonomer distances are reported in Table 1. For the sandwich and parallel-displaced configurations, the MP2 optimized geometries are very similar for the aug-cc-pVDZ and aug-cc-pVTZ basis sets. Our value of 3.4 Å for the vertical separation between planes in the PD configuration agrees well with the observation[9] that in crystals many aromatic molecules form stacks with approximately parallel molecular planes separated by 3.3−3.6 Å. For the T-shaped configuration, results with both basis sets are in good agreement with the microwave results of Arunan and Gutowsky,[24] who found a distance of 4.96 Å between the centers of mass for the gas-phase benzene dimer. This value is also similar to the 5.05 Å mean distance between phenyl ring centroids for interacting aromatic side chains in proteins.[1] In agreement with previous work,[19] we found that rotating one monomer with respect to the other made essentially no difference to the interaction energy; at the aug-cc-pVDZ MP2 level, rotating one monomer by 30° about the axes *R* and *R*1 in Figure 1 produced energy changes of less than 0.1 kcal mol^{-1}.

The present aug-cc-pVDZ and aug-cc-pVTZ geometries are in close agreement with the 6-311G(2d,2p) results of Jaffe and Smith,[19] suggesting again that CP-corrected MP2 geometries for benzene dimer are not very sensitive to improvements in the basis set beyond polarized double-ζ with diffuse functions. The CCSD(T) results of Hobza et al.[32] with a modified cc-pVDZ

Table 1. Benzene Dimer Geometries (*R*)[a]

	method	basis	S	T	PD	
					*R*1	*R*2
Hobza et al.[b]	MP2	DZ+2P	3.9	5.0	3.5	1.6
Hobza et al.[c]	CCSD(T)	cc-pVDZ′	4.1	5.1	3.6	1.8
Jaffe and Smith[d]	MP2	6-311G(2d,2p)	4.1	5.1	3.6	1.8
this work	MP2	aug-cc-pVDZ	3.8	5.0[e]	3.4	1.6
		aug-cc-pVTZ	3.7	4.9[f]	3.4	1.6
Arunan and Gutowsky[g]	expt			4.96		

[a] All intermonomer parameters, in angstroms, obtained using rigid monomers. [b] Reference 20 using experimental monomer geometry. [c] Reference 32 using experimental monomer geometry. [d] Reference 19 using MP2/6-311G(2d,2p) monomer geometry. [e] Actual distance used was 5.0079 Å. [f] Actual distance used was 4.8942 Å. [g] Reference 24.

Table 2. Binding Energies (kcal mol^{-1}) for Different Configurations of the Benzene Dimer[a]

	method	basis	S	T	PD
Hobza et al.[b]	MP2	aug-cc-pVDZ	2.56	2.96	3.94
	CCSD(T)	aug-cc-pVDZ	1.12	2.17	2.02
Tsuzuki et al.[c]	MP2	6-311G**	1.30	2.12	
		aug(d)6-311G*	2.58		
	CCSD(T)	6-311G**	−0.02	1.40	
		aug(d)6-311G*	1.02		
Jaffe and Smith[d]	MP2	6-311+G(2d,p)	2.47	2.87	3.79
		6-311G(2df,p)	2.10	2.79	3.36
this work	MP2[e]	aug-cc-pVDZ	2.90	3.16	4.28
	MP2[e]	aug-cc-pVTZ	3.26	3.46	4.67
	MP2[f]	aug-cc-pVQZ	3.37	3.54	4.79
	MP2R12/A[f]	custom	3.64	3.63	4.95
	ΔCCSD(T)	aug-cc-pVDZ	−1.83	−0.89	−2.18
	estd CBS CCSD(T) D_e		1.81	2.74	2.78
	MP2 ΔZPVE	cc-pVDZ	−0.18	−0.35	−0.04
	estd CBS CCSD(T) D_0		1.99	2.39	2.74

[a] All energies are counterpoise-corrected. [b] Reference 32 using MP2/DZ+2P dimer geometry with experimental monomer structure. [c] Reference 33 using MP2/6-31G* monomer geometries. [d] Reference 19 with MP2/6-311G(2d,2p) monomer and dimer geometries. [e] Geometry optimized (monomer kept rigid) at each level of theory (see Table 1). [f] At the MP2/aug-cc-pVTZ optimized dimer geometry using experimentally deduced monomer geometries from ref 39.

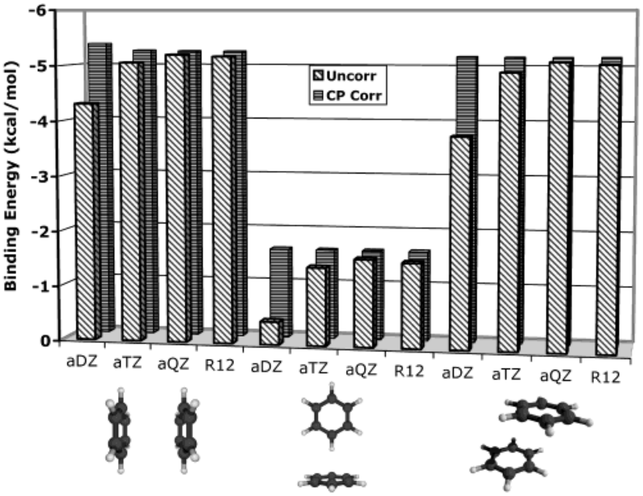

Figure 6. Hartree−Fock binding energies for each dimer structure as a function of basis set. All computations were performed at the same best estimate geometry for each configuration. All energies are negative (repulsive). Labels aXZ denote the aug-cc-pVXZ basis sets.

basis are similar to MP2 results using a similar quality DZ+2P basis,[20] indicating that geometries are also relatively insensitive to improvements in the treatment of electron correlation beyond MP2.

In contrast to optimized geometries, the binding energy is much harder to converge with respect to basis set or theoretical method (as already illustrated in Figures 3 and 4). Several studies have investigated the effect of basis set on the binding energy of benzene dimer. Tsuzuki et al.[31] found that the magnitude of the MP2 interaction energy of the sandwich configuration increased significantly from 6-31G* to 6-311G(3d,3p) as each additional polarization function was added. Hobza et al.[32] and Jaffe and Smith[19] have shown that diffuse functions also have a significant effect on the binding energy. In light of these studies, it is of great interest to estimate the complete basis set limit for binding energies of the benzene dimer. We have examined the basis set dependence of the MP2 binding energy by comparing the previously mentioned aug-cc-pVDZ and aug-cc-pVTZ results to predictions with the even larger aug-cc-pVQZ basis at our best estimates of the geometry for each dimer configuration. Complete basis set estimates were obtained at these same geometries using MP2−R12/A methods and the custom Gaussian basis set described above. These interaction energies are presented in Table 2. The aug-cc-pVTZ basis stabilizes the dimer by 0.3−0.4 kcal mol^{-1} relative to the smaller aug-cc-pVDZ basis, a significant effect in comparison to the overall MP2/aug-cc-pVTZ binding energies of 3.3−4.7 kcal mol^{-1}. Even MP2/aug-cc-pVTZ binding energies are still up to ~0.4 kcal mol^{-1} away from estimated MP2 CBS limit, and improving with the aug-cc-pVQZ basis decreases this gap only to ~0.3 kcal mol^{-1}. As seen in Table 2, the MP2 interaction energies reported in the literature[19,20,32,33] using smaller basis sets are quite far from the CBS limit. The effect of diffuse functions was specifically examined by performing MP2 computations for the S configuration with the cc-pVDZ and cc-pVTZ basis sets (i.e., the diffuse functions were dropped). The resulting binding energies (0.81 and 2.47 kcal mol^{-1}, respectively) show that adding a set of diffuse functions can be more important than going to the next larger basis in the cc-pVXZ series.

To elucidate more clearly the effect of basis set on the MP2 interaction energies, Figures 6 and 7 present the Hartree−Fock and MP2 correlation energy contributions to the interaction energies as a function of basis set. The difference in height between the two bars for each basis represents the counterpoise correction. By splitting the MP2 energies into their Hartree−Fock and correlation contributions, we see that the attraction arises purely from electron correlation at these geometries; the Hartree−Fock binding energies (Figure 6) are all negative (repulsive). The Hatree−Fock energies contain the dominant electrostatic and induction contributions, as well as short-range exchange repulsion. The T-shaped Hartree−Fock energies are the least repulsive because of favorable quadrupole−quadrupole interactions. Basis set superposition error becomes very small

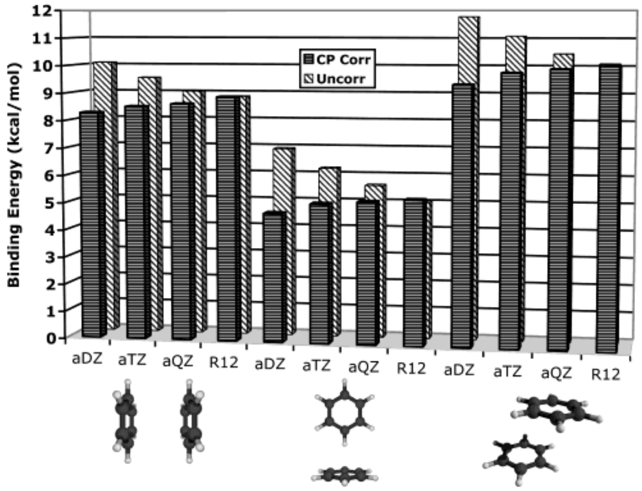

Figure 7. MP2 electron correlation energy contributions to binding energies for each dimer structure as a function of basis set. The total MP2 binding energies are obtained by adding these values to the Hartree−Fock contributions in the previous figure. All computations were performed at the same best estimate geometry for each configuration. Labels aXZ denote the aug-cc-pVXZ basis sets.

for Hartree−Fock with the aug-cc-pVQZ basis, and the CP-corrected values converge rapidly with respect to basis set.

The correlation component of the MP2 interaction energies (Figure 7) includes dispersion effects as well as correlation corrections to the electrostatic and induction contributions. These correlation contributions to the binding energies are all negative (attractive), and, in contrast to the Hartree−Fock components, they do not converge rapidly with respect to basis set; a significant CP correction remains even for the enormous aug-cc-pVQZ basis. Moreover, the aug-cc-pVQZ MP2 results required *more* computer time than the MP2−R12/A values they approach, strongly suggesting that R12 methods can be more affordable than the current CBS extrapolation methods. Correlation favors the S and PD configurations which have larger dispersion energies than the T-shaped. Although one might expect the S configuration to have the largest dispersion interaction, the correlation contribution is actually more favorable for the PD geometry; this remains true even after improvements in the treatment of electron correlation (see below).

Hobza et al.[32] have reported that MP2 significantly overestimates the stabilization energy compared to CCSD(T), with overestimation of 30% for the T-shaped and 92% for the sandwich structure for the largest basis set they considered. Jaffe and Smith[19] also reported that MP2 overestimated the electron correlation energy compared to MP4(SDQ) and MP4(SDTQ). To better account for electron correlation, CCSD(T) computations were performed using the aug-cc-pVDZ basis set. The difference between the CCSD(T) and MP2 binding energies, denoted ΔCCSD(T) in Table 2, was assumed to be relatively insensitive to basis set and was added to the aug-cc-pVQZ Hartree−Fock and MP2−R12/A correlation energy results to estimate the complete basis set limit for CCSD(T). It is clear from the table that ΔCCSD(T) is very large, ranging from -2.2 to -0.9 kcal mol^{-1} for the three benzene dimer configurations studied. The final CBS CCSD(T) estimates of D_e should be within a few tenths of a kilocalorie per mole of the ab initio limit.

To gauge the size of the zero-point vibrational energy (ZPVE) corrections, vibrational frequencies were obtained for fully optimized geometries at the MP2/cc-pVDZ level of theory. At this level, imaginary frequencies are found for each configuration. The sandwich configuration has two imaginary frequencies of $51i$ cm^{-1}, each corresponding to a planar distortion of each benzene ring. The T-shaped configuration has a weak imaginary mode ($24i$ cm^{-1}) corresponding to the rocking of one benzene about the line joining the ring centers of mass. The PD configuration has an imaginary frequency of $79i$ cm^{-1} corresponding to a rotation making the two rings nonparallel. Given the sensitivity of the potential energy surfaces to the theoretical treatment, the MP2/cc-pVDZ level does not seem sufficient to confirm whether these stationary points are actually minima or saddle points. However, the ZPVE corrections should be reasonably well estimated. The ZPVE correction weakens the binding of the T-shaped and parallel-displaced configurations by 0.35 and 0.04 kcal/mol, respectively, while it strengthens the interaction of the sandwich by 0.18 kcal/mol. This result for the T-shaped dimer is consistent with an earlier, lower-level estimate[50] of 0.24 kcal mol^{-1}. The final CBS CCSD(T) estimates of D_e (D_0) predict that the T-shaped and parallel-displaced configurations are isoenergetic within the expected error bars, with binding energies of 2.7 (2.4) and 2.8 (2.7) kcal mol^{-1}, respectively. The sandwich configuration is several tenths of a kilocalorie per mole higher than the other two configurations. Previous CCSD(T) computations with a modified aug-cc-pVDZ basis set found[32] the T-shaped and parallel-displaced configurations to be within 0.15 kcal mol^{-1} of each other, with the T-shaped being more stable ($D_e = 2.17$ kcal mol^{-1}); the sandwich structure at this level was about 1 kcal mol^{-1} less stable. We have shown that these results are qualitatively correct but basis set effects significantly increase the overall binding energy. In light of the present results, it seems clear that the most commonly cited experimental value[29] of $D_0 = 1.6 \pm 0.2$ kcal mol^{-1} is too small. However, an older experimental study by Grover et al.[30] gives $D_0 = 2.4 \pm 0.4$ kcal mol^{-1}, which agrees well with our new theoretical estimates.

This 2.4−2.7 kcal mol^{-1} attraction is appreciable and will significantly influence the interaction of phenyl rings in solution or other environments, in addition to other factors such as solvophobic effects. The rather flat potential energy surface, along with the S configuration being the least favorable, is entirely consistent with the observation that interacting pairs of phenylalanines in proteins are found in mostly T- and PD-like configurations, but they are scattered over a wide variety of conformational space with no strongly preferred single orientation.[2] The benzene dimer itself is expected to be highly fluxional and without a rigid structure, like many van der Waals clusters.[51]

4. Conclusions

In this work we have investigated the basis set and electron correlation effects for the simplest aromatic π-stacking system, the benzene dimer. For constrained geometry optimization, the aug-cc-pVTZ basis set used here is much larger than basis sets employed in previous optimizations. Fortunately, we find the smaller aug-cc-pVDZ basis sufficient to obtain intermonomer distances very near those of aug-cc-pVTZ for the MP2 method,

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(50) Hobza, P.; Selzle, H. L.; Schlag, E. W. *Collect. Czech. Chem. Commun.* **1992**, *57*, 1186.
(51) Sun, S.; Bernstein, E. R. *J. Phys. Chem.* **1996**, *100*, 13348.

so long as energies are counterpoise-corrected. The present theoretical geometries for the T-shaped configuration are in good agreement with experimental data.

The counterpoise correction remains large even for the aug-cc-pVTZ basis, suggesting that even larger basis sets are required for definitive predictions of binding energies in benzene dimer. A new shared memory parallel algorithm has allowed us to perform MP2−R12/A computations for benzene dimer which estimate the MP2 complete basis set limit. Combined with a correction for the difference between CCSD(T) and MP2 determined in a smaller basis, this yields complete basis set CCSD(T) estimates which should be within a few tenths of a kilocalorie per mole of the ab initio limit. Our best estimates indicate that the T-shaped and parallel-displaced configurations are nearly isoenergetic, with D_e (D_0) values of 2.7 (2.4) and 2.8 (2.7) kcal mol^{-1}, respectively. The sandwich structure is somewhat higher, at 1.8 (2.0) kcal mol^{-1}. These results indicate that the experimental binding energy of Krause et al.[29] ($D_0 = 1.6 \pm 0.2$ kcal mol^{-1}) must be too small, but they support the older result of Grover et al.[30] ($D_0 = 2.4 \pm 0.4$ kcal mol^{-1}). The preferred configurations and the rather flat potential energy surface are consistent with a variety of experimental observations of $\pi-\pi$ interactions.

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Supporting Information Available: Custom Gaussian basis for MP2−R12/A computations (TXT). This material is available free of charge via the Internet at http://pubs.acs.org.

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