Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION

A critical comparison of CH-π versus π-π interactions in the benzene dimer: obtaining benchmarks at the CCSD(T) level and assessing the accuracy of lower scaling methods

Kristina M. Herman,[a] Edoardo Aprà,[b] and Sotiris S. Xantheas[a, c, *]

[a] Department of Chemistry, University of Washington, Seattle, WA 98195, USA

[b] Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, USA

[c] Advanced Computing, Mathematics and Data Division, Pacific Northwest National Laboratory, 902 Battelle Boulevard, P.O. Box 999, MSIN J7-10, WA 99352, US

[*] Corresponding author. Email: sotiris.xantheas@pnnl.gov and xantheas@uw.edu

Figure S1. Percent error of DFT functionals compared to the CCSD(T)/CBS binding energies for the PD and T(C_{2v}) dimer. The x-axis is ordered based on the total unsigned error for both bonding scenarios.

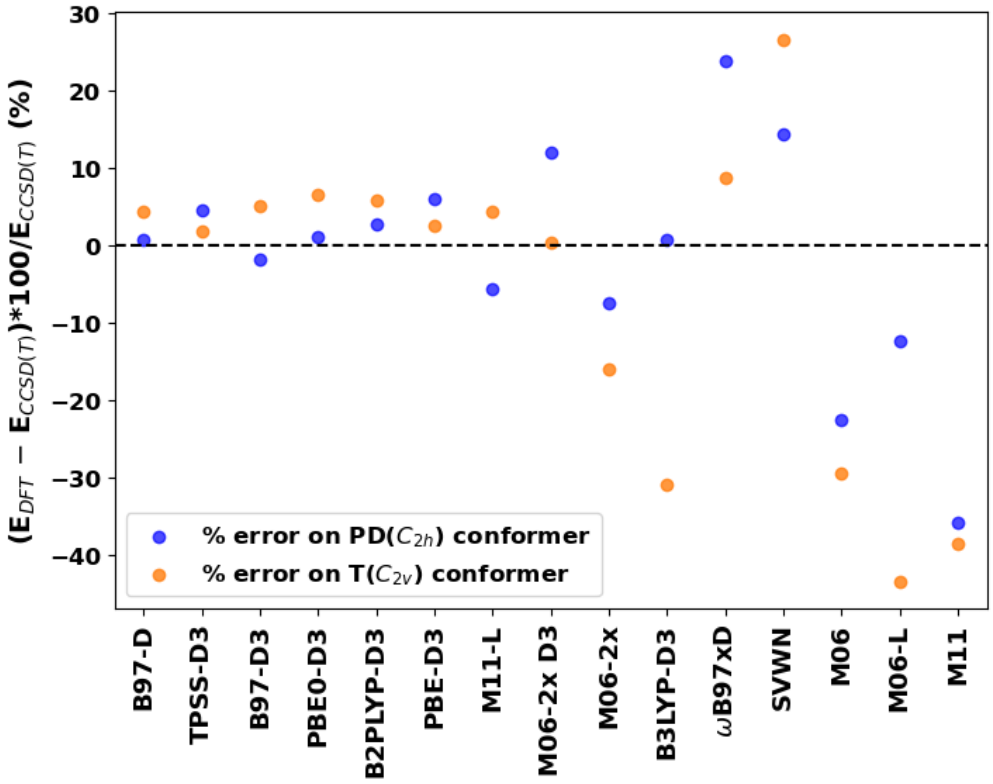

Figure S2. Percent error of DFT functionals compared to the CCSD(T)/CBS structures for the PD and T(C_{2v}) dimer. The x-axis is ordered based on the total unsigned error in the R_{com} for both bonding scenarios.

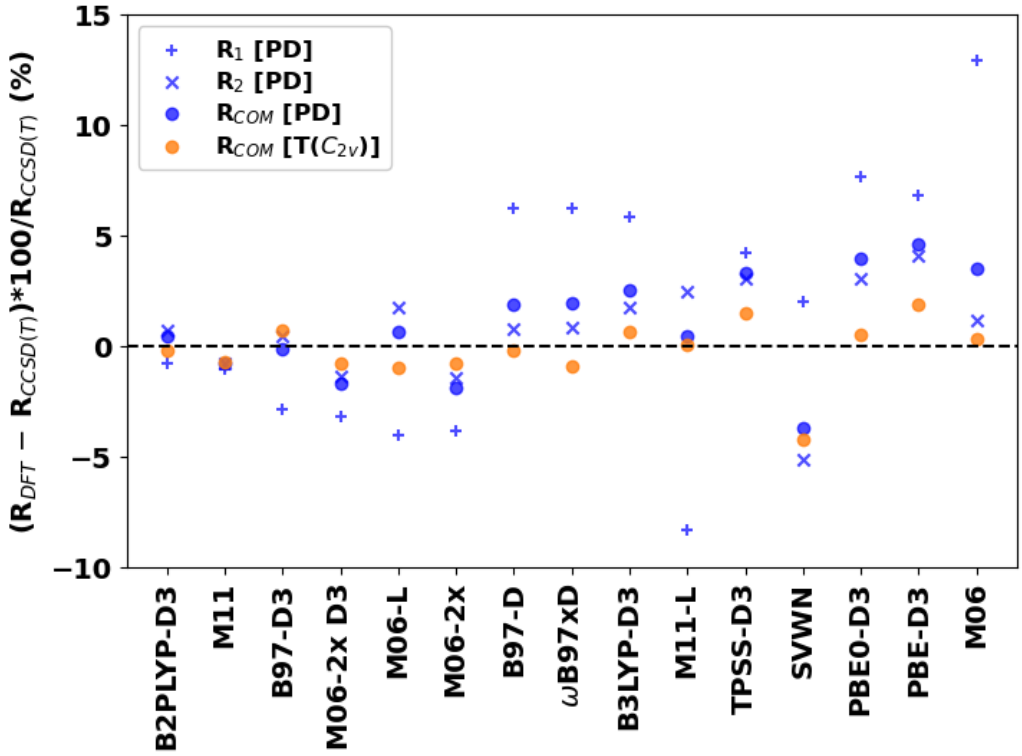

Table S1. A collection of previously reported values at different levels of theory for the various conformations of the benzene dimer studied here. References correspond to the ones in the paper.

	CCSDT(Q)	CCSD(T)	MP2	SCS-MP2	SCS-MI-MP2	SOS-MP2	MP4	QCISDT	SAPT	VMC	DMC	DFT
PD	13	1, 3, 4, 5, 6, 7, 8, 10, 11, 13, a	1, 2, 4, 5, 6, 11, 13, a	6, 11, 13, a	13, a	11, 13, a	1, 2	6	10	12	12	8, 12, a
T		1, 3, 4, 5, 6, 7, 8, 9, 10, a	1, 2, 4, 5, 6, a	6, 9, a	a	a	1, 2	6	10			8, a
TT		8, 10, a	a	a	a	a			10			

1 Hobza et al. 1996
2 Jaffe and Smith 1996
3 Sinnokrot et al. 2002
4 Tsuzuki et al. 2002
5 Park and Lee 2006
6 Janowski and Pulay 2007
7 Lee et al. 2007
8 Pitoňák et al. 2008
9 Hohenstein and Sherrill 2009
10 van der Avoird et al. 2010
11 Miliordos et al. 2014
12 Azadi and Cohen 2015
13 Karton and Martin 2021
a current work

Table S2. The CCSD binding energies (kcal/mol) computed with the cc-pVnZ (n=3, 4, 5) basis sets. The binding energies are not corrected for BSSE.

	PD	$T(C_{2v})$	$TT(C_s)$
	D_e	D_e	D_e
cc-pVTZ	-1.6021	-2.0656	-2.3413
cc-pVQZ	-1.5319	-2.1550	-2.2142
cc-pV5Z	-1.4126	-2.0630	-2.1274

Table S3. The spin-biased MP2 (SCS-MP2, SCS-MI-MP2, SOS-MP2) binding energies *at the MP2 optimized geometries* for the T(C_{2v}) and TT(C_s) conformers.

	SCS-MP2			
	T(C_{2v})		TT(C_s)	
	D_e	D_e^{CP}	D_e	D_e^{CP}
aug-cc-pVDZ	-5.398	-1.390	-5.519	-1.462
aug-cc-pVTZ	-3.663	-1.993	-3.748	-2.082
aug-cc-pVQZ	-2.823	-2.233	-2.918	-2.315
aug-cc-pV5Z[a]	-2.782	-2.365	-2.945	-2.491
CBS	**-2.48 +/- 0.07**		**-2.62 +/- 0.09**	
	SCS-MI-MP2			
	T(C_{2v})		TT(C_s)	
	D_e	D_e^{CP}	D_e	D_e^{CP}
aug-cc-pVDZ	-4.798	-1.937	-4.872	-1.997
aug-cc-pVTZ	-3.339	-2.405	-3.402	-2.478
aug-cc-pVQZ	-2.870	-2.583	-2.943	-2.649
aug-cc-pV5Z[a]	-2.892	-2.676	-3.009	-2.765
CBS	**-2.74 +/- 0.03**		**-2.83 +/- 0.04**	
	SOS-MP2			
	T(C_{2v})		TT(C_s)	
	D_e	D_e^{CP}	D_e	D_e^{CP}
aug-cc-pVDZ	-4.697	-0.662	-4.781	-0.696
aug-cc-pVTZ	-3.014	-1.292	-3.067	-1.349
aug-cc-pVQZ	-2.193	-1.576	-2.252	-1.620
aug-cc-pV5Z[a]	-2.132	-1.703	-2.257	-1.794
CBS	**-1.84 +/- 0.08**		**-1.93 +/- 0.09**	

[a] Computed at the MP2/aug-cc-pVQZ geometry

Table S4. Cartesian coordinates of the T(C_{2v}) conformer optimized at the CCSD(T)/VTZ level of theory. The SCS-MP2 optimized structures were used for the CCSD(T) calculations with larger basis sets.

T(C_{2v}) – CCSD(T)/VTZ			
C	1.39800889	0.00000000	-2.47510742
C	0.69900820	1.21052677	-2.47534190
C	-0.69900820	1.21052677	-2.47534190
C	-1.39800889	0.00000000	-2.47510742
C	-0.69900820	-1.21052677	-2.47534190
C	0.69900820	-1.21052677	-2.47534190
C	0.00000000	-1.20945730	1.77634009
C	0.00000000	-1.21039755	3.17406633
C	0.00000000	0.00000000	3.87317319
C	0.00000000	1.21039755	3.17406633
C	0.00000000	1.20945730	1.77634009
C	0.00000000	0.00000000	1.07595671
H	2.48104878	0.00000000	-2.47120282
H	1.24086727	2.14846348	-2.47399535
H	-1.24086727	2.14846348	-2.47399535
H	-2.48104878	0.00000000	-2.47120282
H	-1.24086727	-2.14846348	-2.47399535
H	1.24086727	-2.14846348	-2.47399535
H	0.00000000	-2.14651893	1.23224816
H	0.00000000	-2.14830744	3.71626399
H	0.00000000	0.00000000	4.95644829
H	0.00000000	2.14830744	3.71626399
H	0.00000000	2.14651893	1.23224816
H	0.00000000	0.00000000	-0.00594289

Table S5. Cartesian coordinates of the PD conformer optimized at the CCSD(T)/VTZ level of theory.[1] The SCS-MP2 optimized structures were used for the CCSD(T) calculations with larger basis sets.

PD – CCSD(T)/VTZ

C	1.275754	-1.235450	0.698770
C	1.275754	-1.235450	-0.698770
C	-1.275754	1.235450	0.698770
C	-1.275754	1.235450	-0.698770
C	0.276643	-1.918543	1.397540
C	0.276643	-1.918543	-1.397540
C	-0.276643	1.918543	1.397540
C	-0.276643	1.918543	-1.397540
C	-0.722468	-2.601635	0.698770
C	-0.722468	-2.601635	-0.698770
C	0.722468	2.601635	0.698770
C	0.722468	2.601635	-0.698770
H	2.050091	-0.706035	1.240335
H	2.050091	-0.706035	-1.240335
H	-2.050091	0.706035	1.240335
H	-2.050091	0.706035	-1.240335
H	0.276643	-1.918543	2.480670
H	0.276643	-1.918543	-2.480670
H	-0.276643	1.918543	2.480670
H	-0.276643	1.918543	-2.480670
H	-1.496806	-3.131050	1.240335
H	-1.496806	-3.131050	-1.240335
H	1.496806	3.131050	1.240335
H	1.496806	3.131050	-1.240335

Table S6. Cartesian coordinates of the TT(C_s) conformer optimized at the SCS-MP2/VTZ level of theory. All CCSD(T) calculations were performed at the SCS-MP2 optimized geometries.

TT(C_s) – SCS-MP2/VTZ			
C	-0.28663524	-1.08763686	0.00000000
C	1.02575096	-1.56219519	0.00000000
C	1.27400133	-2.93513849	0.00000000
C	0.20853093	-3.83641766	0.00000000
C	-1.10422579	-3.36370543	0.00000000
C	-1.35081443	-1.99004829	0.00000000
H	-0.47457010	-0.02300435	0.00000000
H	1.84899825	-0.86010413	0.00000000
H	2.29202738	-3.30196832	0.00000000
H	0.40013837	-4.90131868	0.00000000
H	-1.93036851	-4.06251012	0.00000000
H	-2.36903060	-1.62359755	0.00000000
C	1.22854949	2.24995172	-0.69780597
C	1.22854949	2.24995172	0.69780597
H	2.15074593	2.08570150	-1.23940202
H	2.15074593	2.08570150	1.23940202
C	0.03864978	2.46088433	-1.39566524
C	0.03864978	2.46088433	1.39566524
H	0.03829395	2.45784602	-2.47747037
H	0.03829395	2.45784602	2.47747037
C	-1.15104606	2.67373831	-0.69788169
C	-1.15104606	2.67373831	0.69788169
H	-2.07330175	2.83842147	-1.23911485
H	-2.07330175	2.83842147	1.23911485

References:

(1) Miliordos, E.; Aprà, E.; Xantheas, S. S. Benchmark Theoretical Study of the π–π Binding Energy in the Benzene Dimer. *J. Phys. Chem. A* **2014**, *118* (35), 7568–7578. https://doi.org/10.1021/jp5024235.