Prototypical π-π dimers re-examined by means of high-level CCSDT(Q) composite ab inito methods

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Supporting Information

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Table S1. DSD-PBEP86-D3BJ/Def2-QZVPPD optimized geometries for the species considered in this work (Cartesian coordinates, Å).

Benzene (D6H)

C	0.000000	1.391391	0.000000
C	1.204980	0.695696	0.000000
C	-1.204980	0.695696	0.000000
C	1.204980	-0.695696	0.000000
C	-0.000000	-1.391391	0.000000
C	-1.204980	-0.695696	0.000000
H	0.000000	-2.473869	0.000000
H	-2.142434	-1.236935	0.000000
H	-2.142434	1.236935	0.000000
H	2.142434	-1.236935	0.000000
H	0.000000	2.473869	0.000000
H	2.142434	1.236935	0.000000

Ethene (D2H)

C	0.000000	0.000000	0.664374
H	0.000000	0.922932	1.229685
H	-0.000000	-0.922932	1.229685
C	0.000000	0.000000	-0.664374
H	-0.000000	-0.922932	-1.229685
H	0.000000	0.922932	-1.229685

Ethene•••benzene dimer (C2V)

C	-0.000000	1.391296	-0.948802
H	-0.000000	2.473918	-0.949616
C	1.204371	0.695712	-0.946486
H	2.142127	1.236783	-0.946284
C	1.204371	-0.695712	-0.946486
H	2.142127	-1.236783	-0.946284
C	-0.000000	-1.391296	-0.948802
H	-0.000000	-2.473918	-0.949616
C	-1.204371	-0.695712	-0.946486
H	-2.142127	-1.236783	-0.946284
C	-1.204371	0.695712	-0.946486
H	-2.142127	1.236783	-0.946284
C	0.664307	-0.000000	2.488147
H	1.229538	-0.922870	2.481971
H	1.229538	0.922870	2.481971
C	-0.664307	0.000000	2.488147
H	-1.229538	-0.922870	2.481971
H	-1.229538	0.922870	2.481971

Benzene PD dimer (C2H)

C	1.239940	1.287786	-0.000000
C	0.620172	1.604581	1.204201
C	0.620172	1.604581	-1.204201

C	-0.620172	2.235162	1.204966
C	-1.241671	2.548882	-0.000000
C	-0.620172	2.235162	-1.204966
H	-1.102552	2.480115	-2.142936
H	-2.206901	3.039580	-0.000000
C	1.241671	-2.548882	-0.000000
C	0.620172	-2.235162	1.204966
C	0.620172	-2.235162	-1.204966
C	-0.620172	-1.604581	1.204201
C	-1.239940	-1.287786	-0.000000
C	-0.620172	-1.604581	-1.204201
H	-1.099914	-1.351769	-2.141176
H	-2.196847	-0.782025	0.000000
H	1.099914	1.351769	-2.141176
H	2.196847	0.782025	0.000000
H	1.102552	-2.480115	-2.142936
H	2.206901	-3.039580	-0.000000
H	1.102552	-2.480115	2.142936
H	-1.099914	-1.351769	2.141176
H	1.099914	1.351769	2.141176
H	-1.102552	2.480115	2.142936

Benzene TT dimer (C1)

C	2.720957	1.161166	-0.583167
H	2.942061	2.101127	-1.072550
C	2.582558	1.112223	0.801026
H	2.694810	2.014380	1.388687
C	2.294614	-0.095729	1.429302
H	2.179629	-0.132501	2.504915
C	2.147278	-1.255069	0.673899
H	1.920611	-2.193745	1.163426
C	2.284957	-1.206475	-0.710099
H	2.166488	-2.107364	-1.298734
C	2.570675	0.001926	-1.338852
H	2.673975	0.040561	-2.415680
C	-1.069283	0.306237	-0.165064
H	-0.009368	0.503663	-0.256626
C	-1.527569	-1.006580	-0.108072
H	-0.819024	-1.823796	-0.156180
C	-2.889458	-1.266517	0.011303
H	-3.244726	-2.288387	0.055435
C	-3.795903	-0.212181	0.074356
H	-4.855598	-0.413491	0.167507
C	-3.339245	1.101113	0.017582
H	-4.044186	1.921430	0.066694
C	-1.976776	1.359358	-0.102310
H	-1.621497	2.381292	-0.146323

Table S2. DSD-PBEP86-D3BJ/Def2-QZVPPD optimized geometries for the species considered in this work (Cartesian coordinates, a.u.).

Benzene (D6H)
0.00000000 2.62934773 0.00000000
2.27708202 1.31467481 0.00000000
-2.27708202 1.31467481 0.00000000
2.27708202 -1.31467481 0.00000000
0.00000000 -2.62934773 0.00000000
-2.27708202 -1.31467481 0.00000000
0.00000000 -4.67493454 0.00000000
-4.04861321 -2.33746822 0.00000000
-4.04861321 2.33746822 0.00000000
4.04861321 -2.33746822 0.00000000
0.00000000 4.67493454 0.00000000
4.04861321 2.33746822 0.00000000

Ethene (D2H)
0.00000000 0.00000000 1.25548481
0.00000000 1.74408859 2.32376770
0.00000000 -1.74408859 2.32376770
0.00000000 0.00000000 -1.25548481
0.00000000 -1.74408859 -2.32376770
0.00000000 1.74408859 -2.32376770

Ethene•••benzene dimer (C2V)
0.00000000 2.62916821 -1.79297580
0.00000000 4.67502714 -1.79451403
2.27593118 1.31470505 -1.78859919
4.04803306 2.33718098 -1.78821747
2.27593118 -1.31470505 -1.78859919
4.04803306 -2.33718098 -1.78821747
0.00000000 -2.62916821 -1.79297580
0.00000000 -4.67502714 -1.79451403
-2.27593118 -1.31470505 -1.78859919
-4.04803306 -2.33718098 -1.78821747
-2.27593118 1.31470505 -1.78859919
-4.04803306 2.33718098 -1.78821747
1.25535820 0.00000000 4.70191605
2.32348991 -1.74397142 4.69024510
2.32348991 1.74397142 4.69024510
-1.25535820 0.00000000 4.70191605
-2.32348991 -1.74397142 4.69024510
-2.32348991 1.74397142 4.69024510

Benzene PD dimer (C2H)
2.34314684 2.43356267 0.00000000
1.17195515 3.03221842 2.27560993
1.17195515 3.03221842 -2.27560993

-1.17195515 4.22384372 2.27705557
-2.34641796 4.81668856 0.00000000
-1.17195515 4.22384372 -2.27705557
-2.08352117 4.68673777 -4.04956185
-4.17043817 5.74397332 0.00000000
2.34641796 -4.81668856 0.00000000
1.17195515 -4.22384372 2.27705557
1.17195515 -4.22384372 -2.27705557
-1.17195515 -3.03221842 2.27560993
-2.34314684 -2.43356267 0.00000000
-1.17195515 -3.03221842 -2.27560993
-2.07853607 -2.55447301 -4.04623593
-4.15143887 -1.47781297 0.00000000
2.07853607 2.55447301 -4.04623593
4.15143887 1.47781297 0.00000000
2.08352117 -4.68673777 -4.04956185
4.17043817 -5.74397332 0.00000000
2.08352117 -4.68673777 4.04956185
-2.07853607 -2.55447301 4.04623593
2.07853607 2.55447301 4.04623593
-2.08352117 4.68673777 4.04956185

Benzene TT dimer (C1)
5.14186316 2.19428557 -1.10202584
5.55968913 3.97055430 -2.02682561
4.88032697 2.10179671 1.51371965
5.09245249 3.80662624 2.62423791
4.33619171 -0.18090158 2.70098913
4.11890157 -0.25039058 4.73360297
4.05776704 -2.37173651 1.27348445
3.62942852 -4.14557694 2.19855635
4.31794263 -2.27990716 -1.34189253
4.09406868 -3.98234052 -2.45425139
4.85787136 0.00363961 -2.53006342
5.05308005 0.07664918 -4.56497328
-2.02065187 0.57870402 -0.31192573
-0.01770295 0.95178506 -0.48495282
-2.88668684 -1.90216039 -0.20422647
-1.54773094 -3.44647470 -0.29513740
-5.46028388 -2.39337009 0.02135957
-6.13164305 -4.32442439 0.10475696
-7.17321655 -0.40096395 0.14051247
-9.17574973 -0.78138469 0.31654233
-6.31025806 2.08080185 0.03322516
-7.64240339 3.63097621 0.12603339
-3.73556498 2.56881414 -0.19333787
-3.06418502 4.49998938 -0.27651038

Table S3. Performance of MP*n*-based methods. The tabulated values are deviations from our best CCSDT(Q) binding energies for the benzene•••ethene (BzEt) and benzene•••benzene (Bz_2) π-π dimers (in kcal mol^{-1}).

	BzEt	Bz_2
MP2/A'VDZ	2.006	4.464
MP2/A'VTZ	1.646	3.289
MP2/A'VQZ	1.354	2.634
SCS-MP2/A'VDZ	0.986	2.684
SCS-MP2/A'VTZ	0.560	1.464
SCS-MP2/A'VQZ	0.228	0.756
SCS(MI)-MP2/A'VDZ	0.618	2.126
SCS(MI)-MP2/A'VTZ	0.370	1.177
SCS(MI)-MP2/A'VQZ	0.197	0.771
SCSN-MP2/A'VDZ	0.412	1.810
SCSN-MP2/A'VTZ	0.254	0.996
SCSN-MP2/A'VQZ	0.160	0.742
SCS-MP2-vdW/A'VDZ	1.598	3.735
SCS-MP2-vdW/A'VTZ	1.172	2.487
SCS-MP2-vdW/A'VQZ	0.831	1.748
SOS-MP2/A'VDZ	0.476	1.793
SOS-MP2/A'VTZ	0.016	0.551
SOS-MP2/A'VQZ	-0.335	-0.183
S2-MP2/A'VDZ	1.892	4.251
S2-MP2/A'VTZ	1.494	3.029
S2-MP2/A'VQZ	1.173	2.322
MP2.5/A'VDZ	1.302	2.833
MP2.5/A'VTZ	0.902	1.609
MP2.5/A'VQZ	0.593	0.928
MP3/A'VDZ	0.597	1.203
MP3/A'VTZ	0.159	-0.071
MP3/A'VQZ	-0.169	-0.779
MP3.5/A'VDZ	1.017	2.330
MP3.5/A'VTZ	0.551	0.987
MP3.5/A'VQZ	0.208	0.252
MP4/A'VDZ	1.437	3.458
MP4/A'VTZ	0.944	2.045
MP4/A'VQZ	0.585	1.282

Table S4. Key absolute energies (in Hartree).

		C_6H_6	C_2H_4	BzEt	Bz_2 (PD)
DSD-PBEP86-D3BJ	Def2-QZVPPD	–231.91520640	–78.47012879	–310.38830318	–463.83621423
W1-F12	Escf	–230.79709581	–78.07039850	–308.86222788	–461.58705241
W1-F12	Eccsd	–1.04982989	–0.38532359	–1.44132598	–2.10914438
W1-F12	E(T)	–0.05833424	–0.01703552	–0.07662732	–0.11876688
W1-F12	Ecv	–0.32010363	–0.10657528	–0.42669432	–0.64022255
W1-F12	Erel	–0.08806350	–0.02936762	–0.11743243	–0.17612848
W1-F12	Ew1val	–231.90525994	–78.47275762	–310.38018119	–463.81496367
W1-F12	Ew1all	–232.22536357	–78.57933290	–310.80687550	–464.45518622
W1-F12	Ew1allrel	–232.31342707	–78.60870052	–310.92430793	–464.63131470
SCF	A'VDZ	–230.72722713	–78.04269594	–308.76521750	–461.44876118
SCF	A'VTZ	–230.78135474	–78.06464498	–308.84090285	–461.55586990
SCF	A'VQZ	–230.79462064	–78.06948960	–308.85886633	–461.58214471
SCF	A'V5Z	–230.79749251	–78.07061556	–308.86282004	–461.58781955
SCF	A'V6Z	–230.79788705	–78.07076717	–308.86335730	–461.58859578
MP2 corr	A'VDZ	–0.80594412	–0.28232167	–1.09810636	–1.62871374
MP2 corr	A'VTZ	–0.96092326	–0.33850589	–1.30908664	–1.93794610
MP2 corr	A'VQZ	–1.01429841	–0.35762402	–1.38126616	–2.04392410
MP2 corr	A'V5Z	–1.03412345	–0.36465257	–1.40800234	–2.08332956
MP2 corr	A'V6Z	–1.04333417	–0.36788818	N/A	–2.10163610
CCSD corr	A'VDZ	–0.84245304	–0.31172738	–1.16126921	–1.69647699
CCSD corr	A'VTZ	–0.98352185	–0.36245241	–1.35266856	–1.97761664
CCSD corr	A'VQZ	–1.02568313	–0.37727479	–1.40925296	–2.06106275
CCSD corr	A'V5Z	–1.03872093	–0.38175491	–1.42666869	–2.08691813
(T) corr	A'VDZ	–0.03933156	–0.01085798	–0.05141890	–0.08089683
(T) corr	A'VTZ	–0.05318432	–0.01536134	–0.06979558	–0.10850380
(T) corr	A'VQZ	–0.05643633	–0.01640267	–0.07409556	–0.11498072
CCSD(T)	PVDZNOD	–231.20636310	–78.21371616	–309.42009148	–462.41437514
CCSDT	PVDZNOD	–231.20691936	–78.21405617	–309.42092909	–462.41532766
CCSDT(Q)	PVDZNOD	–231.20837635	–78.21443240	–309.42283245	–462.41836967
CCSD(T)	PVDZnoPonH	–231.52014932	–78.31284536	–309.83405721	–463.04372770
CCSDT	PVDZnoPonH	–231.52056621	–78.31346224	–309.83496361	–463.04426523
CCSDT(Q)	PVDZnoPonH	–231.52318743	–78.31402985	–309.83825629	N/A
CCSD(T)	PVDZ	–231.57979753	–78.35440609	–309.93558987	N/A
CCSDT	PVDZ	–231.58019319	–78.35503392	–309.93648368	N/A
CCSDT(Q)	PVDZ	–231.58290080	–78.35565285	–309.93991009	N/A
CCSD(T)	PVTZNOF1D	–231.64789535	–78.38204561	–310.03169812	–463.30025093
CCSDT	PVTZNOF1D	–231.64766613	–78.38247905	–310.03175721	N/A
CCSD(T)	JunVDZnoPonH	–231.52961732	–78.31690129	–309.84972164	N/A
CCSDT	JunVDZnoPonH	–231.52995652	–78.31751311	–309.85052217	N/A
CCSDT(Q)	JunVDZnoPonH	–231.53264952	–78.31809203	–309.85392326	N/A
CCSD(T)	JunVDZ	–231.58755248	–78.35730689	–309.94744406	N/A
CCSDT	JunVDZ	–231.58787255	–78.35792719	–309.94823731	N/A
CCSDT(Q)	JunVDZ	–231.59064549	–78.35855439	–309.95176149	N/A
CV	W1	–0.29149333	–0.09702951	–0.38855189	–0.58302897
Rel	W1	–0.08821516	–0.02942149	–0.11763935	–0.17643463
DBOC	HF/VDZ	0.01121395	0.00421225	0.01543316	0.02243473
DBOC	CCSD/VDZ	0.01144801	0.00433854	0.01579155	0.02290038
DBOC	HF/AVTZ	0.01121802	0.00422321	0.01544573	0.02244054

Complete references for quantum chemical software

Geometry optimizations and frequency calculations were carried out using the Gaussian 16 rev. A.03 program suite;[1] CCSD(T) calculations were performed using the Molpro 2016.1 program suite;[2,3] post-CCSD(T) calculations were carried out with the MRCC 2019 program suite;[4,5] and DBOC calculations were carried out with the CFOUR program suite.[6,7]

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