Supporting Information

What is special about aromatic-aromatic interactions? Significant attraction at large horizontal displacement.

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■ METHODOLOGY

The benzene–benzene interaction energies were previously calculated in the ORCA (version 2.8) program[1] using the B2PLYP-D[2] method and the def2-TZVP[3] basis set. The B2PLYP-D method, without correction for basis-set superposition error, gives results that are in excellent agreement with the very accurate CCSD(T) data for benzene interactions.[4] and the CCSD(T) interaction energy for orientation B at the offset value of 5.0 Å (−1.98 kcal mol^{-1}) is consistent with the B2PLYP-D interaction energy (−1.92 kcal mol^{-1}). In our previous work we used MP2 method, with the def2-TZVP basis set built in Gaussian09 (version D.01) program for the potential energy surface of cyclohexane-benzene interactions. The MP2/def2-TZVP method, with correction for the basis-set superposition error, gives results that are in good agreement with the accurate CCSD(T) data.[5] Namely, calculated energies for cyclohexane–benzene interactions at the CCSD(T)/CBS level for offset values *r* 0.0, 1.5, and 4.0 Å, are −3.05, −3.27 and −1.19 kcal mol^{-1} respectively, while the MP2/def2-TZVP energies for the same geometries are −3.17, −3.34 and −1.19 kcal mol^{-1}, respectively. We investigated three different geometries between two parallel-align benzenes and cyclohexane-benzene pair (Figure **S1**). The monomer geometries were kept rigid, while for various offset values (r) the normal distance (R) was systematically varied to find the normal distance *R* with the strongest interaction. The calculated energies (Δ*E*) of interaction are plotted in Figures S2, respectively, as a function of the offset value *r*.

In this paper we calculated the CCSD(T)/CBS (using Gaussian09 (version D.01)[6] program) and DF-SAPT2+3[7] with def2-tzvppd basis set (using PSI4 program[8]) for the chosen offsets at geometries A, B, and C for and benzene-benzene and cyclohexane-benzene the data are presented in tables S1-S6.

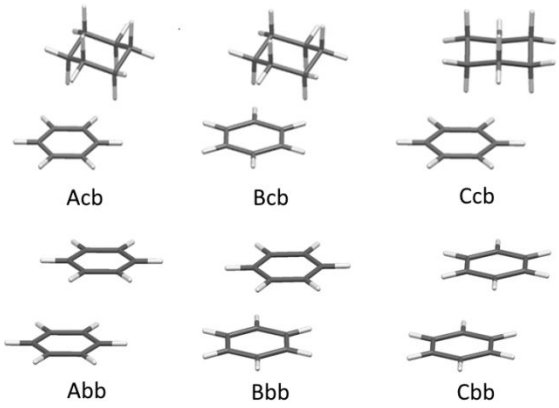

Figure S1. Side view of cyclohexane/benzene and benzene/benzene dimers at displesment (offset) of 1.5 Å along A, B and C directions

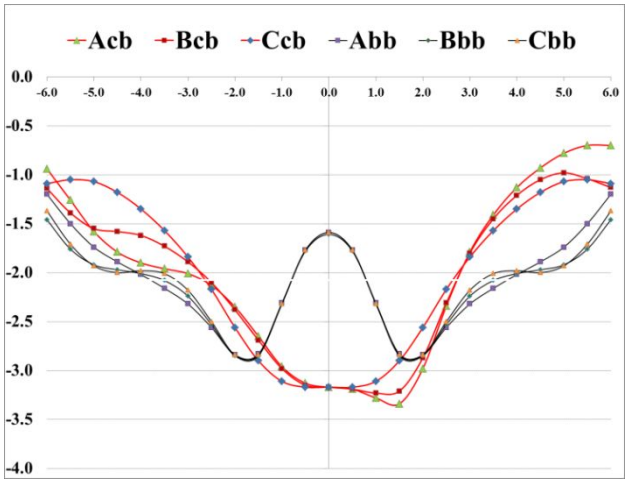

Figure S2. Calculated interaction energies for three different orientations of cyclohexane–benzene (cb)[5] and benzene–benzene (bb)[4] (Figure S1) plotted as a function of the dispasment (Figure 1).

Benzene-Bezene A

Table S1. The results of SAPT analysis of bezene -bezene interactions at several offset values along A direction (Figures 1, S1 and S2). Offset and normal distance values are given in Å. Total interaction energies and energy components are given in kcal/mol.

Offset	r=0.0	r=1.5	r=4.0	r=5.0
Normal distance	3.9	3.5	3.2	2.8
Electrostatics	0.09	-1.49	-1.29	-1.14
Exchange	3.28	6.55	3.05	2.22
Induction	-0.22	-0.69	-0.36	-0.27
Dispersion	-5.00	-7.20	-3.45	-2.57
Net dispersion	-1.72	-0.65	-0.39	-0.35
Total SAPT2+3	-1.84	-2.83	-2.05	-1.77
CCSD(T)/CBS	-1.75	-2.79	-2.01	-1.73
% of the most stable interaction	63	100	72	62

Benzene-Bezene B

Table S2. The results of SAPT analysis of bezene -bezene interactions at several offset values along B direction (Figures 1, 2 and 3). Offset and normal distance values are given in Å. Total interaction energies and energy components are given in kcal/mol.

Offset	r=0.0	r=1.5	r=4.0	r=5.0
Normal distance	3.9	3.5	3.2	2.6
Electrostatics	0.10	-1.51	-1.30	-1.43
Exchange	3.27	6.59	3.08	2.96
Induction	-0.22	-0.70	-0.35	-0.33
Dispersion	-5.00	-7.21	-3.47	-3.13
Net dispersion	-1.73	-0.62	-0.39	-0.17
Total SAPT2+3	-1.86	-2.83	-2.03	-1.94
CCSD(T)/CBS	-1.75	-2.78	-2.00	-1.89
% of the most stable interaction	63	100	72	68

Benzene-Bezene C

Table S3. The results of SAPT analysis of bezene -bezene interactions at several offset values along C direction (Figures 1, 2 and 3). Offset and normal distance values are given in Å. Total interaction energies and energy components are given in kcal/mol.

Offset	r=0.0	r=1.5	r=4.0	r=5.0
Normal distance	3.9	3.5	3.2	2.6
Electrostatics	0.09	-1.51	-1.32	-1.35
Exchange	3.28	6.60	3.16	2.83
Induction	-0.22	-0.71	-0.35	-0.30
Dispersion	-5.00	-7.21	-3.50	-3.13
Net dispersion	-1.72	-0.61	-0.35	-0.30
Total SAPT2+3	-1.84	-2.82	-2.01	-1.95
CCSD(T)/CBS	-1.75	-2.79	-1.98	-1.91
% of the most stable interaction	63	100	71	68

Cyclohexane-Bezene A

Table S4. The results of SAPT analysis of cyclohexane-benzene interactions at several offset values along A direction (Figures 1, S1 and S2). Offset and normal distance values are given in Å and energies are given in kcal/mol.

Offset	-5.0	-4.0	-1.5	0.0	1.5	4.0	5.0
Normal distance	2.7	3.3	4.1	4.2	3.9	3.9	3.5
Electro-statics	-0.88	-0.96	-1.65	-1.84	-2.14	-0.48	-0.23
Exchange	2.74	3.19	4.64	4.91	5.90	1.80	1.23
Induction	-0.31	-0.31	-0.54	-0.61	-0.61	-0.21	-0.13
Dispersion	-3.35	-4.07	-5.19	-5.65	-6.59	-2.35	-1.78
Net dispersion	-0,61	-0.88	-0.55	-0.74	-0.69	-0.55	-0.56
Total SAPT2+3	-1.80	-2.15	-2.73	-3.20	-3.44	-1.25	-0.91
CCSD(T)/CBS	-1.76	-2.10	-2.59	-3.05	-3.27	-1.24	-0.89
% of the most stable interactions	54	64	79	93	100	38	27

Cyclohexane-Bezene B

Table S5. The results of SAPT analysis of cyclohexane-benzene interactions at several offset values along B direction (Figures 1, 2 and 3). Offset and normal distance values are given in Å and energies are given in kcal/mol.

Offset	-5.0	-4.0	-1.5	0.0	1.5	4.0	5.0
Normal distance	2.7	3.5	4.1	4.2	3.9	3.8	3.1
Electro-statics	-0.86	-0.67	-1.62	-1.70	-2.23	-0.59	-0.50
Exchange	2.71	2.44	4.53	4.46	6.26	2.13	2.05
Induction	-0.30	-0.26	-0.52	-0.55	-0.67	-0.24	-0.18
Dispersion	-3.37	-3.35	-5.15	-5.40	-6.69	-2.61	-2.55
Net dispersion	-0.66	-0.91	-0.62	-0.94	-0.44	-0.48	-0.51
Total SAPT2+3	-1.82	-1.83	-2.76	-3.20	-3.33	-1.31	-1.18
CCSD(T)/CBS	-1.79	-1.78	-2.62	-3.20	-3.15	-1.27	-1.18
% of the most stable interactions	55	54	80	98	96	39	36

Cyclohexane-Bezene C

Table S6. The results of SAPT analysis of cyclohexane-bezene interactions at several offset values along C direction (Figures 1, 2 and 3). Offset and normal distance values are given in Å and energies are given in kcal/mol.

Offset	0.0	1.5	4.0	5.0
Normal distance	4.2	4.0	3.7	3.1
Electrostatics	-1.70	-1.28	-0.59	-0.43
Exchange	4.46	5.57	2.11	1.78
Induction	-0.55	-1.11	-0.23	-0.18
Dispersion	-5.40	-6.11	-2.79	-2.45
Net dispersion	-0.94	-0.54	-0.67	-0.67
Total SAPT2+3	-3.20	-2.93	-1.49	-1.28
CCSD(T)/CBS	-3.20	-2.82	-1.45	-1.26
% of the most stable interactions	98	86	44	39

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