Empirically corrected DFT and semi-empirical methods for non-bonding interactions

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Supporting Information

No.	Molecule (symmetry)	Ref. Values	B97-D / TZV(2df,2pd)	BLYP-D / TZV(2df,2pd)	B2PLYP-D/TZVPP
Hydrogen bonded complexes					
1	(NH3)2 (C2h)	-3.17	-3.72	-4.16	-3.65
2	(H2O)2 (Cs)	-5.02	-5.07	-5.80	-5.47
3	Formic acid dimer (C2h)	-18.61	-18.25	-19.34	-19.43
4	Formamide dimer (C2h)	-15.96	-15.28	-16.39	-16.37
5	Uracil dimer (C2h)	-20.65	-19.45	-20.73	-20.88
6	2-Pyridoxine2-aminopyridine (C1)	-16.71	-17.13	-18.05	-17.60
7	Adenine thymine WC (C1)	-16.37	-16.20	-17.19	-16.85
Complexes with predominant dispersion contribution					
8	(CH4)2 (D3d)	-0.53	-0.57	-0.36	-0.40
9	(C2H4)2 (D2d)	-1.51	-1.55	-1.55	-1.50
10	Benzene CH4 (C3)	-1.50	-1.51	-1.37	-1.42
11	Benzene dimer (C2h)	-2.73	-2.67	-2.35	-2.52
12	Pyrazine dimer (Cs)	-4.42	-4.07	-4.05	-4.26
13	Uracil dimer (C2)	-10.12	-10.02	-10.50	-10.14
14	Indole benzene (C1)	-5.22	-4.72	-4.55	-4.69
15	Adenine thymine stack (C1)	-12.23	-12.11	-12.85	-12.52
Mixed complexes					
16	Ethene ethine (C2v)	-1.53	-1.73	-1.62	-1.60
17	Benzene H2O (Cs)	-3.28	-4.14	-4.16	-3.66
18	Benzene NH3 (Cs)	-2.35	-2.75	-2.66	-2.47
19	Benzene HCN (Cs)	-4.46	-4.88	-4.87	-4.96
20	Benzene dimer (C2v)	-2.74	-2.93	-2.76	-2.82
21	Indole benzene T-shape (C1)	-5.73	-6.26	-6.16	-6.04
22	Phenol dimer (C1)	-7.05	-6.60	-7.35	-7.28
	RMSE (Hydrogen bonded)		0.60	0.83	0.58
	RMSE (Dispersion bonded)		0.22	0.40	0.24
	RMSE (Mixed bonded)		0.48	0.43	0.29
	RMSE		0.46	0.58	0.39
	MUE		0.35	0.47	0.31

Table S1: Single-point interaction energies (kcal/mol) at the S22 geometries.

No.	Molecule (symmetry)	Ref. Values	TPSS / LP	TPSS / LP CP	TPSS-D / LP	TPSS-D / LP CP
Hydrogen bonded complexes						
1	(NH3)2 (C2h)	-3.17	-2.3	-2.2	-3.0	-3.1
2	(H2O)2 (Cs)	-5.02	-4.9	-4.4	-5.5	-5.2
3	Formic acid dimer (C2h)	-18.61	-18.3	-17.5	-19.8	-19.2
4	Formamide dimer (C2h)	-15.96	-14.4	-13.9	-16.1	-15.9
5	Uracil dimer (C2h)	-20.65	-18.2	-17.6	-20.5	-20.2
6	2-Pyridoxine2-aminopyridine (C1)	-16.71	-14.6	-14.2	-17.5	-17.5
7	Adenine thymine WC (C1)	-16.37	-13.6	-13.1	-16.7	-16.7
Complexes with predominant dispersion contribution						
8	(CH4)2 (D3d)	-0.53	0.2	0.2	-0.7	-0.7
9	(C2H4)2 (D2d)	-1.51	0.2	0.3	-1.8	-2.5
10	Benzene CH4 (C3)	-1.50	0.1	0.5	-1.7	-1.5
11	Benzene dimer (C2h)	-2.73	2.1	3.0	-3.3	-2.6
12	Pyrazine dimer (Cs)	-4.42	1.3	1.9	-4.2	-3.9
13	Uracil dimer (C2)	-10.12	-2.2	-1.0	-9.8	-9.2
14	Indole benzene (C1)	-5.22	2.4	3.7	-5.4	-4.5
15	Adenine thymine stack (C1)	-12.23	-0.6	0.8	-11.9	-11.4
Mixed complexes						
16	Ethene ethine (C2v)	-1.53	-1.0	-0.8	-1.7	-1.3
17	Benzene H2O (Cs)	-3.28	-2.1	-1.4	-3.6	-3.2
18	Benzene NH3 (Cs)	-2.35	-0.8	-0.3	-2.5	-2.3
19	Benzene HCN (Cs)	-4.46	-2.8	-2.2	-4.4	-4.1
20	Benzene dimer (C2v)	-2.74	0.0	0.6	-2.6	-2.3
21	Indole benzene T-shape (C1)	-5.73	-1.8	-1.0	-5.4	-4.8
22	Phenol dimer (C1)	-7.05	-3.5	-2.9	-6.9	-6.7
	RMSE (Hydrogen bonded)		1.7	2.2	0.6	0.4
	RMSE (Dispersion bonded)		6.3	7.2	0.3	0.6
	RMSE (Mixed bonded)		2.5	3.0	0.2	0.4
	RMSE		4.2	4.8	0.4	0.5
	MUE		3.0	3.7	0.3	0.4

Table 2: Single-point interaction energies (kcal/mol) at the S22 geometries. LP = 6-311++G(3df,3pd).

		Interaction Energies (kcal/mol)		Interaction Distances (Å)		CM-Distances (Å)	
No.	Molecule (symmetry)	Ref. Values	BLYP-D / TZV(2d,2p)	Ref. Values	BLYP-D / TZV(2d,2p)	Ref. Values	BLYP-D / TZV(2d,2p)
Hydrogen bonded complexes							
1	(NH3)2 (C2h)	-3.17	-3.58	2.504	2.595	3.209	3.305
2	(H2O)2 (Cs)	-5.02	-5.98	1.952	1.961	2.909	2.927
3	Formic acid dimer (C2h)	-18.61	-16.62	1.670	1.674	2.993	3.017
4	Formamide dimer (C2h)	-15.96	-14.91	1.841	1.864	3.229	3.267
5	Uracil dimer (C2h)	-20.65	-18.41	1.775	1.789	6.075	6.127
6	2-Pyridoxine2-aminopyridine (C1)	-16.71	-16.20	1.859, 1.874	1.846, 1.851	5.136	5.165
7	Adenine thymine WC (C1)	-16.37	-15.48	1.819, 1.929	1.786, 1.908	5.974	5.99
Complexes with predominant dispersion contribution							
8	(CH4)2 (D3d)	-0.53	-0.32	3.718	3.717	3.718	3.716
9	(C2H4)2 (D2d)	-1.51	-1.39	3.718	3.712	3.718	3.712
10	Benzene CH4 (C3)	-1.50	-0.94	3.716	3.732	3.716	3.732
11	Benzene dimer (C2h)	-2.73	-2.01	3.765	3.775	3.765	3.772
12	Pyrazine dimer (Cs)	-4.42	-3.76	3.479	3.631	3.479	3.628
13	Uracil dimer (C2)	-10.12	-9.01	3.166	2.807	3.166	3.223
14	Indole benzene (C1)	-5.22	-4.20	3.498	3.574	3.498	3.724
15	Adenine thymine stack (C1)	-12.23	-11.20	3.172	3.259	3.172	3.268
Mixed complexes							
16	Ethene ethine (C2v)	-1.53	-1.46	2.752	2.755	4.422	4.428
17	Benzene H2O (Cs)	-3.28	-3.72	2.531	3.330	3.380	3.262
18	Benzene NH3 (Cs)	-2.35	-2.14	3.592	3.628	3.560	3.596
19	Benzene HCN (Cs)	-4.46	-4.08	3.387	3.510	3.950	4.068
20	Benzene dimer (C2v)	-2.74	-2.19	3.513	3.651	4.909	5.053
21	Indole benzene T-shape (C1)	-5.73	-5.09	3.210	3.409	4.884	5.024
22	Phenol dimer (C1)	-7.05	-6.94	1.937, 4.921	1.921, 5.084	4.921	5.084
	RMSE (Hydrogen bonded)		1.32		0.035		0.047
	RMSE (Dispersion bonded)		0.76		0.144		0.104
	RMSE (Mixed bonded)		0.40		0.304		0.117
	RMSE		0.90		0.192		0.095
	MUE		0.72		0.097		0.071

Table 3: Geometry optimized energies (kcal/mol), interaction distances (Angstroms), and CM-distance (Angstroms) for the complexes in the S22 database. The interaction distance is defined as the CM-distance for complexes 11-15 and the 2nd distance reported for complex 22.

		Ref. Values		TPSS / LP		TPSS-D / LP		
No.	Molecule (symmetry)	ΔE	CM Distance	ΔE	CM Distance	ΔE	CM Distance	Interaction Distances (Å)
Hydrogen bonded complexes								
1	(NH3)2 (C2h)	-3.17	3.209	-2.4	3.257	-3.1	3.324	2.635
2	(H2O)2 (Cs)	-5.02	2.909	-5.0	2.891	-5.6	2.897	1.928
3	Formic acid dimer (C2h)	-18.61	2.993	-20.7	2.964	-22.4	2.955	1.608
4	Formamide dimer (C2h)	-15.96	3.229	-15.3	3.210	-17.0	3.205	1.800
5	Uracil dimer (C2h)	-20.65	6.075	-19.1	6.074	-21.5	6.055	1.731
6	2-Pyridoxine2-aminopyridine (C1)	-16.71	5.136	-15.9	5.134	-18.9	5.104	1.804,1.800
7	Adenine thymine WC (C1)	-16.37	5.974	-14.6	5.969	-17.9	5.938	1.752, 1.851
Complexes with predominant dispersion contribution								
8	(CH4)2 (D3d)	-0.53	3.718	0.0	3.923	-0.7	3.719	3.719
9	(C2H4)2 (D2d)	-1.51	3.718	-0.3	4.202	-1.8	3.718	3.735
10	Benzene CH4 (C3)	-1.50	3.716	0.1	3.723	-1.7	3.721	3.721
11	Benzene dimer (C2h)	-2.73	3.765	0.0	4.638	-3.3	3.769	3.769
12	Pyrazine dimer (Cs)	-4.42	3.479	-0.6	4.322	-4.3	3.575	3.575
13	Uracil dimer (C2)	-10.12	3.166	-3.5	3.800	-10.2	3.172	3.172
14	Indole benzene (C1)	-5.22	3.498	-0.7	4.637	-5.4	3.515	3.515
15	Adenine thymine stack (C1)	-12.23	3.172	-6.7	4.525	-12.0	3.224	3.224
Mixed complexes								
16	Ethene ethine (C2v)	-1.53	4.422	-1.0	4.445	-1.6	4.437	2.768
17	Benzene H2O (Cs)	-3.28	3.380	-2.2	3.544	-3.6	3.386	2.531
18	Benzene NH3 (Cs)	-2.35	3.560	-1.0	3.845	-2.5	3.567	3.599
19	Benzene HCN (Cs)	-4.46	3.950	-2.8	3.956	-4.4	3.951	3.395
20	Benzene dimer (C2v)	-2.74	4.909	-0.8	5.411	-2.9	5.134	3.738
21	Indole benzene T-shape (C1)	-5.73	4.884	-2.5	5.279	-5.3	4.891	3.241
22	Phenol dimer (C1)	-7.05	4.921	-4.4	5.420	-7.2	4.983	1.924,4.983
	RMSE (Hydrogen bonded)			1.3	0.023	1.8	0.051	0.070
	RMSE (Dispersion bonded)			3.9	0.812	0.3	0.039	0.040
	RMSE (Mixed bonded)			2.0	0.331	0.2	0.089	0.084
	RMSE			2.7	0.524	1.1	0.062	0.067
	MUE			2.1	0.342	0.6	0.036	0.045

Table 4: Geometry optimized interaction energies (kcal/mol) and CM-distances (Angstroms) for the complexes in the S22 database. LP = 6-311++G(3df,3pd). The

interaction distance is defined as the CM-distance in complexes 11-15 and 2nd value reported for complex 22.

No.	Molecule (symmetry)	Ref. Values	AM1	PM3	AM1-D[a]	AM1-D	PM3-D	PM3-D*
Hydrogen bonded complexes								
1	(NH3)2 (C2h)	-3.17	-0.78	0.77	-2.35	-3.43	-1.77	-0.67
2	(H2O)2 (Cs)	-5.02	-2.89	-2.79	-3.74	-7.29	-5.14	-4.53
3	Formic acid dimer (C2h)	-18.61	1.54	-9.91	-1.24	-15.45	-18.57	-17.46
4	Formamide dimer (C2h)	-15.96	-12.02	-8.08	-8.67	-17.16	-15.37	-10.32
5	Uracil dimer (C2h)	-20.65	-5.79	-11.32	-9.48	-20.15	-20.3	-19.88
6	2-Pyridoxine2-aminopyridine (C1)	-16.71	-4.45	-7.46	-8.84	-16.50	-17.52	-13.50
7	Adenine thymine WC (C1)	-16.37	-4.28	-6.79	-8.95	-16.58	-17.33	-13.89
Complexes with predominant dispersion contribution								
8	(CH4)2 (D3d)	-0.53	0.21	-0.25	-0.70	-0.94	-1.24	-1.00
9	(C2H4)2 (D2d)	-1.51	-0.13	-1.11	-2.48	-3.31	-3.60	-2.44
10	Benzene CH4 (C3)	-1.50	0.40	-0.19	-2.00	-2.12	-2.42	-1.83
11	Benzene dimer (C2h)	-2.73	3.52	2.38	-2.79	-2.90	-4.30	-4.41
12	Pyrazine dimer (Cs)	-4.42	2.49	3.90	-4.38	-4.57	-4.20	-4.83
13	Uracil dimer (C2)	-10.12	0.12	5.80	-9.87	-10.56	-6.78	-10.78
14	Indole benzene (C1)	-5.22	5.39	4.04	-4.04	-4.04	-6.09	-5.68
15	Adenine thymine stack (C1)	-12.23	2.91	7.37	-11.74	-12.20	-10.63	-11.58
Mixed complexes								
16	Ethene ethine (C2v)	-1.53	-0.35	-0.82	-1.45	-1.61	-1.85	-1.41
17	Benzene H2O (Cs)	-3.28	-0.69	-1.47	-3.29	-3.43	-3.65	-2.71
18	Benzene NH3 (Cs)	-2.35	-0.33	-0.59	-2.85	-3.00	-2.96	-1.97
19	Benzene HCN (Cs)	-4.46	-0.81	-1.63	-4.27	-4.44	-4.43	-3.05
20	Benzene dimer (C2v)	-2.74	0.37	-0.43	-3.68	-3.85	-4.15	-2.90
21	Indole benzene T-shape (C1)	-5.73	-1.05	-1.25	-6.96	-7.10	-6.65	-4.60
22	Phenol dimer (C1)	-7.05	-1.36	-1.37	-5.86	-9.76	-7.52	-5.57
	RMSE (Hydrogen bonded)		11.64	7.77	9.25	1.56	0.76	2.85
	RMSE (Dispersion bonded)		8.21	10.13	0.61	0.82	1.68	0.81
	RMSE (Mixed bonded)		3.57	3.22	0.77	1.25	0.72	0.92
	RMSE		8.47	7.73	5.25	1.23	1.18	1.76
	MUE		6.54	5.94	2.77	0.85	0.90	1.23

Table 5: Single-point interaction energies (kcal/mol) at the S22 geometries. [a] AM1-D results without re-parameterization of AM1 method (S_6=1.1 and d=23.0).

No.	Molecule (symmetry)	Ref. Values	AM1	PM3	AM1-D	PM3-D	PM3-D*
Hydrogen bonded complexes							
1	(NH3)2 (C2h)	-3.17	-1.39	-0.71	-3.03	-1.99	-2.12
2	(H2O)2 (Cs)	-5.02	-3.30	-3.55	-7.22	-6.53	-4.04
3	Formic acid dimer (C2h)	-18.61	-6.62	-9.58	-12.45	-16.16	-19.71
4	Formamide dimer (C2h)	-15.96	-2.06	-6.99	-14.64	-14.42	-10.05
5	Uracil dimer (C2h)	-20.65	-10.48	-10.70	-17.80	-18.83	-22.19
6	2-Pyridoxine2-aminopyridine (C1)	-16.71	-6.15	-7.06	-13.06	-18.32	-13.70
7	Adenine thymine WC (C1)	-16.37	-5.06	-6.90	-12.66	-18.66	-16.29
Complexes with predominant dispersion contribution							
8	(CH4)2 (D3d)	-0.53	-0.21	-0.32	-4.10	-2.38	-1.14
9	(C2H4)2 (D2d)	-1.51	-0.13	-1.08	-4.85	-4.11	-2.37
10	Benzene CH4 (C3)	-1.50	0.35	-0.20	-2.93	-2.88	-1.84
11	Benzene dimer (C2h)	-2.73	0.01	-0.02	-3.10	-4.59	-4.82
12	Pyrazine dimer (Cs)	-4.42	-0.34	-0.26	-4.87	-4.45	-6.36
13	Uracil dimer (C2)	-10.12	-6.05	-4.26	-11.25	-7.59	-15.47
14	Indole benzene (C1)	-5.22	-1.33	-1.65	-8.16	-6.26	-5.89
15	Adenine thymine stack (C1)	-12.23	-5.15	-6.50	-15.13	-11.70	-17.13
Mixed complexes							
16	Ethene ethine (C2v)	-1.53	-0.57	-1.23	-2.47	-2.58	-1.36
17	Benzene H2O (Cs)	-3.28	-1.03	-1.63	-3.90	-4.46	-2.94
18	Benzene NH3 (Cs)	-2.35	-0.80	-0.93	-4.04	-3.99	-1.99
19	Benzene HCN (Cs)	-4.46	-0.92	-1.85	-4.28	-4.40	-2.88
20	Benzene dimer (C2v)	-2.74	-0.09	-0.52	-4.22	-4.39	-2.87
21	Indole benzene T-shape (C1)	-5.73	-1.24	-1.67	-7.74	-7.20	-4.87
22	Phenol dimer (C1)	-7.05	-3.39	-4.33	-11.55	-8.95	-5.63
	RMSE (Hydrogen bonded)		9.90	8.04	3.38	1.82	2.66
	RMSE (Dispersion bonded)		3.73	3.65	2.36	1.71	2.79
	RMSE (Mixed bonded)		2.96	2.40	2.09	1.40	0.89
	RMSE		6.25	5.22	2.65	1.65	2.31
	MUE		4.82	4.09	2.16	1.51	1.60

Table 6: Geometry optimized interaction energies (kcal/mol) for the S22 complexes.

No.	Molecule (symmetry)	Ref. Values	AM1	PM3	AM1-D	PM3-D
Hydrogen bonded complexes						
1	(NH3)2 (C2h)	2.504	2.784	3.241	2.646	2.726
2	(H2O)2 (Cs)	1.952	2.094	1.809	1.911	1.769
3	Formic acid dimer (C2h)	1.670	2.101	1.776	1.925	1.737
4	Formamide dimer (C2h)	1.841	2.072	1.807	1.981	1.763
5	Uracil dimer (C2h)	1.775	2.044	1.787	1.946	1.744
6	2-Pyridoxine2-aminopyridine (C1)	1.859, 1.874	2.511, 2.107	1.798, 1.815	1.980, 1.981	1.722,1.768
7	Adenine thymine WC (C1)	1.819, 1.929	2.476, 2.101	1.780, 1.821	1.807, 2.018	1.708,1.769
Complexes with predominant dispersion contribution						
8	(CH4)2 (D3d)	3.718	3.721	3.447	2.881	3.160
9	(C2H4)2 (D2d)	3.718	3.714	3.706	3.305	3.469
10	Benzene CH4 (C3)	3.716	3.746	3.718	3.315	3.450
11	Benzene dimer (C2h)	3.765	6.952	6.096	3.643	3.499
12	Pyrazine dimer (Cs)	3.479	4.848	4.760	3.695	3.437
13	Uracil dimer (C2)	3.166	5.805	6.732	3.097	3.406
14	Indole benzene (C1)	3.498	5.572	5.520	4.448	3.415
15	Adenine thymine stack (C1)	3.172	6.202	5.788	4.320	3.280
Mixed complexes						
16	Ethene ethine (C2v)	2.752	2.468	2.429	2.319	2.366
17	Benzene H2O (Cs)	2.531	4.020	3.746	2.986	2.982
18	Benzene NH3 (Cs)	3.592	4.092	4.025	2.995	3.069
19	Benzene HCN (Cs)	3.387	3.472	3.694	3.228	3.343
20	Benzene dimer (C2v)	3.513	5.225	3.606	3.253	3.370
21	Indole benzene T-shape (C1)	3.210	3.811	3.807	3.010	3.233
22	Phenol dimer (C1)	1.937, 4.921	2.174, 5.925	1.829, 5.712	2.001, 5.040	1.778, 5.265
	RMSE (Hydrogen bonded)		0.387	0.257	0.137	0.134
	RMSE (Dispersion bonded)		2.015	1.962	0.644	0.272
	RMSE (Mixed bonded)		0.929	0.598	0.336	0.315
	RMSE		1.277	1.171	0.419	0.249
	MUE		0.853	0.691	0.301	0.199

Table 7: Geometry optimized interaction distances (Angstroms) for the S22 complexes. The interaction distance is defined as the CM-distance in complexes 11-15 and 2nd value reported for complex 22.