Carbohydrate-aromatic π interactions: A test of density functionals and the DFT-D method.

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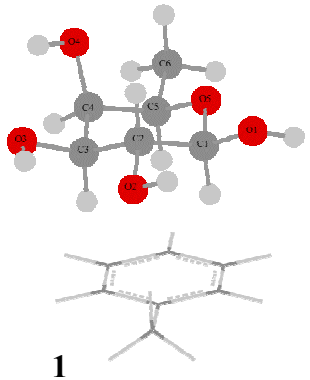
Supplementary Material (ESI) for PCCP



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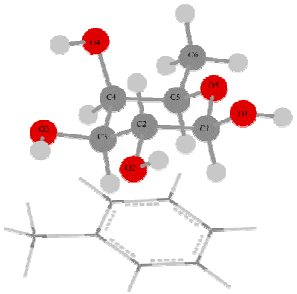

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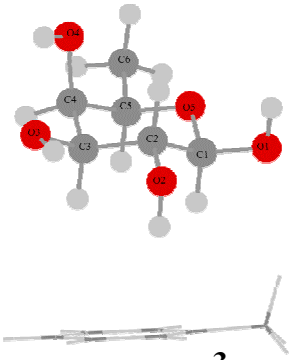

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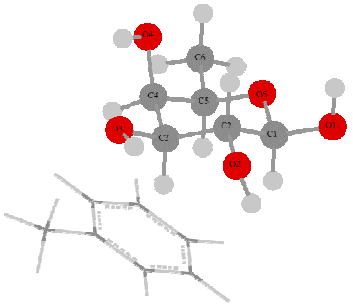

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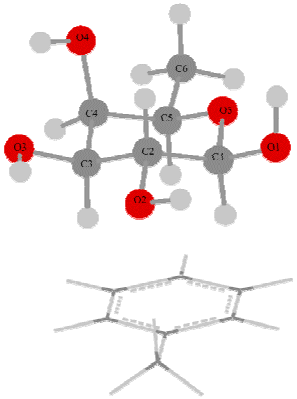

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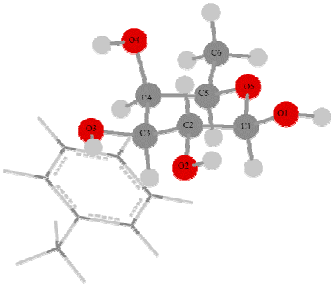

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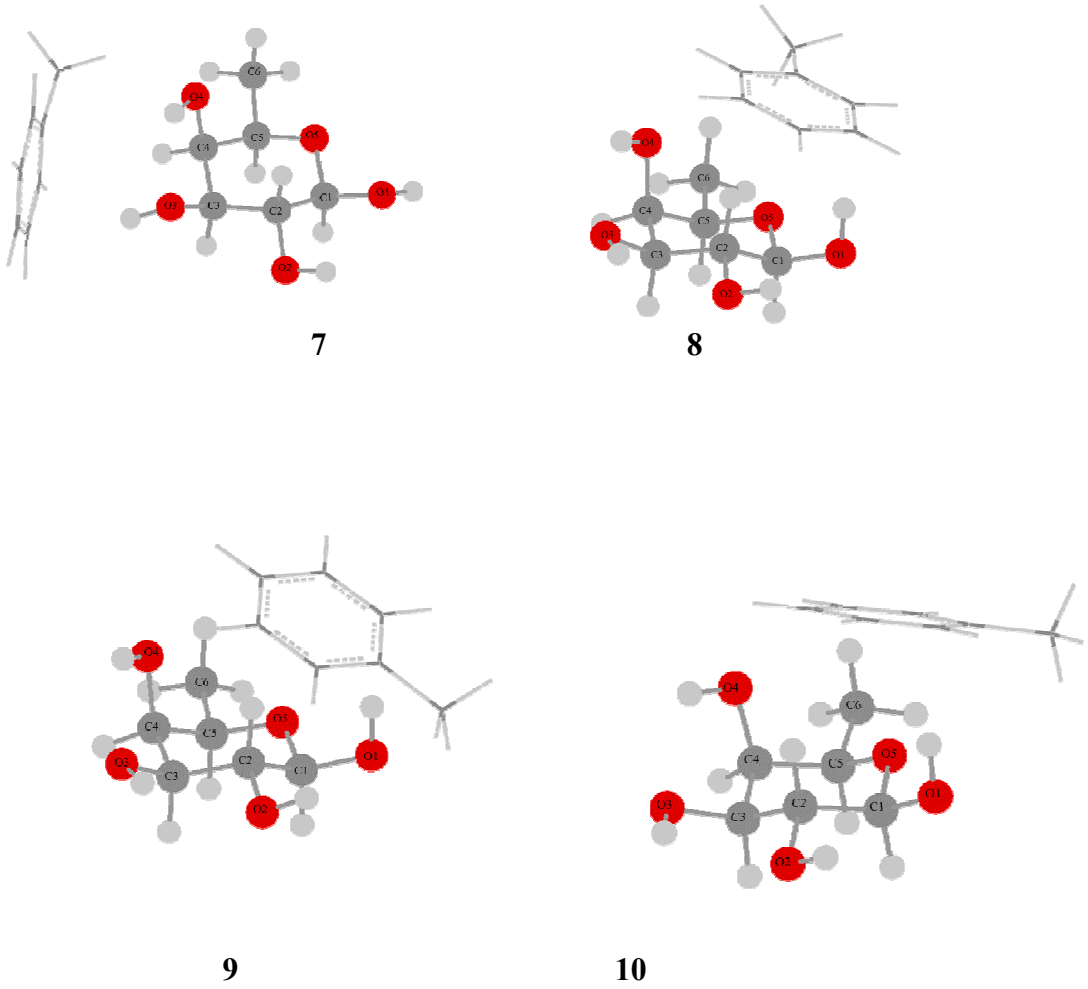
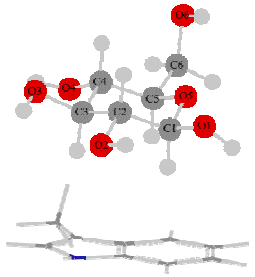


Fig. S1 Optimized structures of fucose-toluene complexes at DFT-D/TZV2D level.



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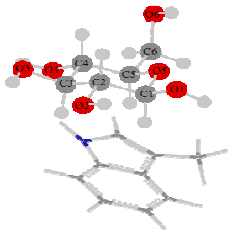

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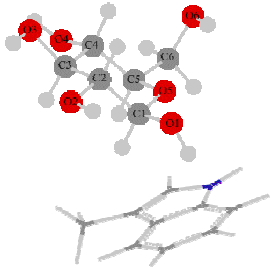

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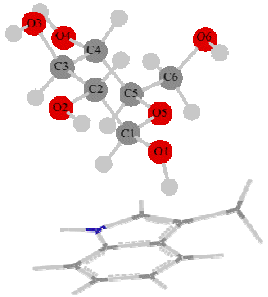

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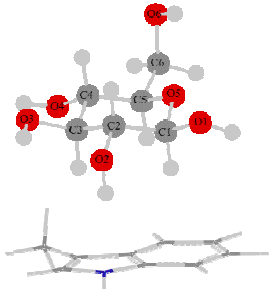

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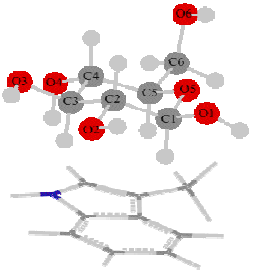

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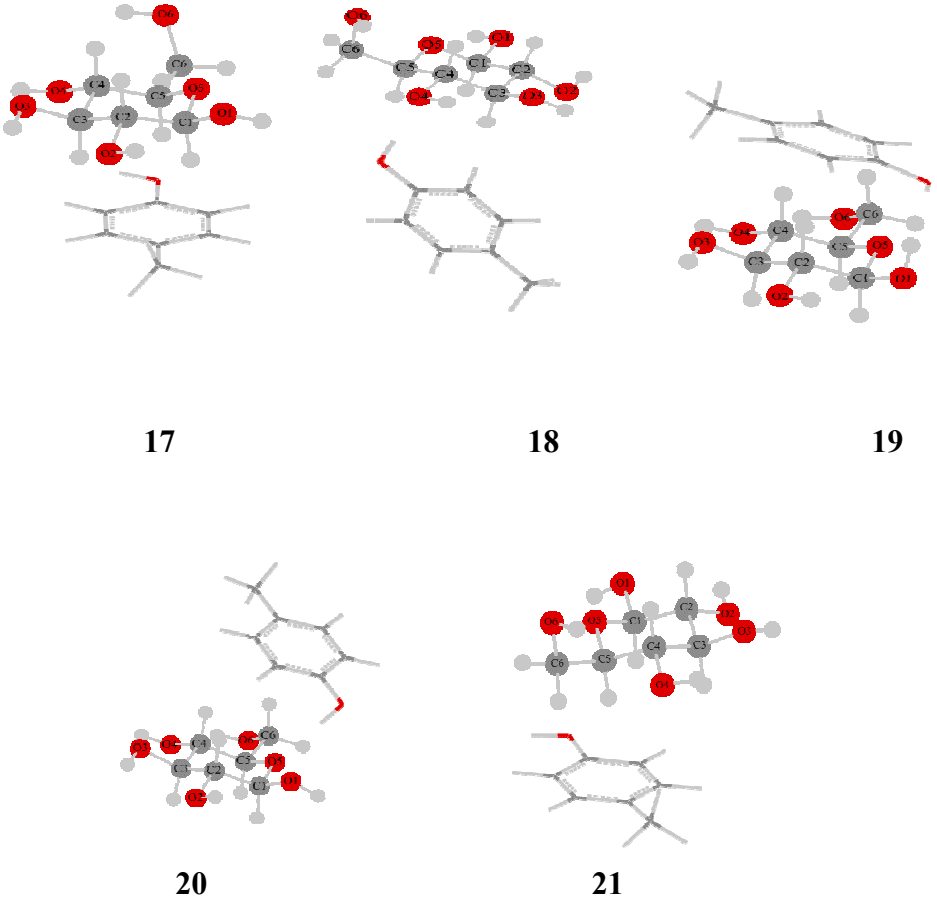

Fig. S2. Optimized structures of glucose–3-methylindole and –*p*-hydroxytoluene complexes

Table S1.
Coordinates(Å) of the structures for which 'benchmark' calculations were carried out.

Benzene/methane: Fig. 1 (d)

6	1.399758	0.026474	-0.662295
6	0.722814	-1.199167	-0.663987
6	-0.677088	-1.225778	-0.664732
6	-1.400043	-0.026694	-0.663711
6	-0.723116	1.198956	-0.662008
6	0.676781	1.225538	-0.661296
1	2.487162	0.047109	-0.658284
1	1.284404	-2.130567	-0.661377
1	-1.202916	-2.177825	-0.662662
1	-2.487452	-0.047338	-0.660847
1	-1.284708	2.130349	-0.657808
1	1.202607	2.177577	-0.656596
6	0.000351	0.000245	3.151023
1	0.499619	0.906243	3.510856
1	-1.030012	-0.017923	3.521994
1	-0.003354	-0.006656	2.057842
1	0.535194	-0.880544	3.522171

Benzene/water: Fig. 1(f)

6	0.713068	-0.624637	-1.213395
6	0.469890	0.754243	-1.213340
6	0.349086	1.443847	0.000334
6	0.468892	0.753984	1.213942
6	0.712102	-0.624890	1.213874
6	0.835524	-1.314031	0.000209
1	0.803713	-1.160673	-2.155057
1	0.371737	1.289024	-2.154966
1	0.162448	2.515382	0.000378
1	0.369903	1.288539	2.155604
1	0.802062	-1.161124	2.155495
1	1.026654	-2.384774	0.000167
8	-2.682516	-0.510858	-0.001195
1	-1.953568	-1.153305	0.003795
1	-2.215121	0.340999	-0.005846

Toluene/Fucose: Fig. 2 (I)

6	0.884848	-0.476453	1.673387
6	0.540867	-1.330203	0.434701
6	1.758637	-1.468225	-0.480760
6	2.330062	-0.088237	-0.848915
6	2.564808	0.735893	0.434112
8	1.367575	0.813824	1.251962
8	0.137457	-2.672479	0.795290
8	1.420887	-2.142556	-1.717114
8	1.445496	0.617976	-1.739042
6	3.030414	2.164148	0.166943
8	-0.230976	-0.288383	2.512339
1	1.643868	-0.985846	2.290107
1	-0.264603	-0.825223	-0.113745
1	2.537706	-2.041039	0.049372
1	3.308280	-0.236063	-1.337761
1	3.346275	0.204143	1.008154
1	-0.658426	-2.592486	1.348305
1	0.832595	-2.879343	-1.475542
1	1.088547	-0.062886	-2.338577
1	3.216715	2.679490	1.114989
1	3.960405	2.148858	-0.413919
1	2.277216	2.718719	-0.400675
1	-0.933854	0.136455	1.979181
6	-3.331721	-0.111511	0.820172
6	-2.634620	1.103108	0.745703
6	-3.361882	-0.972587	-0.282045
6	-1.953506	1.481094	-0.426179
1	-2.630317	1.773902	1.604257
6	-2.703084	-0.600963	-1.460581
1	-3.901930	-1.914680	-0.228517
6	-2.008529	0.611082	-1.529185
1	-3.850539	-0.379904	1.737777
1	-2.725733	-1.259172	-2.326231
1	-1.489079	0.884683	-2.445123
6	-1.137989	2.751436	-0.480586
1	-0.094429	2.524000	-0.229940
1	-1.149636	3.191449	-1.484520
1	-1.506399	3.496398	0.234316

Toluene/Fucose: Fig. 2(II)

6	1.084704	-0.982003	-1.265212
6	2.087747	-0.760831	-0.112747
6	1.487076	0.161673	0.949229
6	1.013367	1.479961	0.312960
6	0.085955	1.177525	-0.880007
8	0.711988	0.269717	-1.839152
8	2.428244	-2.005693	0.543451
8	2.446471	0.496401	1.982244
8	2.129849	2.283622	-0.111777
6	-0.344899	2.418179	-1.652524
8	1.643406	-1.793088	-2.288935
1	0.203206	-1.530924	-0.900725
1	2.990155	-0.288601	-0.532682
1	0.618063	-0.337250	1.402484
1	0.417916	2.029139	1.062047
1	-0.803386	0.679880	-0.469061
1	2.745392	-2.613521	-0.147057
1	2.909691	-0.326978	2.213661
1	2.783034	2.224220	0.608801
1	-1.048266	2.137785	-2.443711
1	-0.844217	3.119612	-0.973575
1	0.520155	2.918722	-2.098126
1	2.295420	-1.240126	-2.758666
6	-2.154372	-0.577130	1.901903
6	-2.925240	0.502865	1.457224
6	-3.504391	0.476856	0.183223
6	-3.303408	-0.636865	-0.640058
6	-2.530660	-1.713370	-0.190745
6	-1.943795	-1.703478	1.087005
1	-2.382345	-2.574786	-0.839980
1	-3.746231	-0.668001	-1.632806
1	-4.104435	1.314341	-0.163812
1	-3.075632	1.362260	2.106776
1	-1.712694	-0.547681	2.896809
6	-1.080902	-2.855661	1.556796
1	-0.030345	-2.706227	1.268669
1	-1.109610	-2.954961	2.648381
1	-1.409748	-3.804129	1.115687

Galactose/benzene: Fig. 2(III)

6	1.457417	-1.081628	-1.059072
6	2.245253	-0.620086	0.178196
6	1.324907	0.199458	1.086407
6	0.667236	1.361830	0.325919
6	0.028465	0.849023	-0.976231
8	0.956746	0.058511	-1.770125
8	2.726457	-1.729985	0.972344
8	2.044089	0.769419	2.205826
8	1.617101	2.408969	0.025735
6	-0.445182	1.979130	-1.911645
8	2.355372	-1.778944	-1.901263
1	0.612784	-1.728493	-0.752890
1	3.080713	0.006079	-0.167659
1	0.526298	-0.461077	1.458229
1	-0.140216	1.765424	0.954425
1	-0.827389	0.222618	-0.691116
1	3.346134	-2.234330	0.418841
1	2.639030	0.073938	2.536362
1	2.166856	2.499981	0.825406
1	0.432037	2.413362	-2.408775
1	-1.104682	1.555036	-2.675388
1	1.850639	-2.154809	-2.642247
6	-2.402927	-0.071098	1.811184
6	-3.052359	0.858826	0.991212
6	-3.566607	0.461131	-0.248680
6	-3.431412	-0.867549	-0.668356
6	-2.775346	-1.797775	0.148926
6	-2.261116	-1.399404	1.389005
1	-1.749847	-2.120238	2.023004
1	-2.666467	-2.829172	-0.178844
1	-3.828560	-1.176314	-1.632645
1	-4.052380	1.191067	-0.890641
1	-3.141613	1.895461	1.304429
1	-1.997105	0.239505	2.771226
8	-1.215675	2.986800	-1.226669
1	-0.583095	3.540472	-0.737572

p-hydroxy-toluene/glucose: Fig. 2 (IV)

6	-2.227820	-1.490429	-0.271481
6	-1.494523	-0.622596	0.730829
6	-0.291335	-1.055927	1.313259
6	-1.962859	0.652948	1.088272
6	0.428809	-0.247499	2.195426
6	-1.260304	1.474775	1.975209
6	-0.051244	1.028390	2.523308
8	0.633309	1.893583	3.359805
6	-0.081128	1.112162	-2.456708
6	0.900017	-0.007169	-2.849784
6	1.817424	-0.348049	-1.669913
6	2.458342	0.921028	-1.101296
6	1.363334	1.943502	-0.747156
6	1.900033	3.236996	-0.122262
8	0.208292	-1.228145	-3.209809
8	2.895688	-1.234736	-2.057218
8	3.230569	0.641212	0.092199
8	0.632768	2.258846	-1.965250
8	3.053196	3.797809	-0.779817
1	1.510082	0.354435	-3.691477
1	-0.331318	-1.032981	-3.994618
1	1.216880	-0.820884	-0.878584
1	2.489488	-2.039992	-2.420072
1	3.109507	1.364075	-1.870176
1	3.802858	-0.114641	-0.128073
1	-0.771817	0.750595	-1.674113
1	0.670659	1.495950	-0.020862
1	1.114081	3.997452	-0.181949
1	2.107176	3.041068	0.939263
1	3.820886	3.261415	-0.520594
1	-1.669855	-1.557340	-1.216532
1	-3.222062	-1.086415	-0.495155
1	-2.355757	-2.513928	0.104289
1	-2.896527	1.018004	0.663284
1	-1.632510	2.462840	2.233448
1	1.376138	-0.597285	2.602350
1	0.102062	-2.039841	1.062967
1	1.470594	1.477178	3.625261
8	-0.785321	1.484291	-3.626561
1	-1.474114	2.123473	-3.376829

Toluene/alpha-methyl-glucose: Fig. 2 (V)

6	4.901750	1.044361	0.468100
6	4.422371	0.516326	-0.744086
6	3.989860	1.416985	-1.732990
6	4.025566	2.798412	-1.517134
6	4.499646	3.309763	-0.302720
6	4.938873	2.425387	0.690323
6	4.320468	-0.977731	-0.962768
8	0.785875	-1.791609	0.107180
6	0.155667	-0.534962	0.444098
6	-0.718847	-0.102292	-0.744131
8	-1.333258	1.193005	-0.448030
6	-0.398347	2.257752	-0.220970
6	0.530884	1.916399	0.964373
6	1.199878	0.547293	0.737580
6	-1.877290	-1.055426	-1.032659
8	-2.649736	-0.640573	-2.175357
8	0.426318	2.531597	-1.348945
6	-0.293793	3.035021	-2.492329
8	1.493569	2.948737	1.231551
8	1.948602	0.113845	1.894613
1	-2.976614	0.253771	-1.977649
1	-2.512616	-1.140340	-0.135156
1	-1.476256	-2.044222	-1.271623
1	-0.095260	-0.013206	-1.644611
1	-0.485058	-0.664227	1.333009
1	1.442921	-1.957921	0.805835
1	1.870656	0.622370	-0.129293
1	2.651775	0.771773	2.036066
1	2.029261	3.071083	0.425000
1	-0.091467	1.861299	1.864774
1	-1.027853	3.129496	0.011319
1	-0.873417	3.932552	-2.224889
1	0.460749	3.296138	-3.239415
1	-0.970326	2.273167	-2.901776
1	3.284126	-1.316582	-0.822076
1	4.617931	-1.252963	-1.982122
1	4.952366	-1.529682	-0.257738
1	3.610947	1.031153	-2.677737

1	3.679814	3.475336	-2.294660
1	4.528434	4.383113	-0.132064
1	5.309796	2.811786	1.636765
1	5.247740	0.364567	1.245175

Table S2. Interaction energies (kcal mol^{-1}) for full dataset, for 18 functionals, DFT-D and MP2, the MUE values compared to the DFT-D values are also given.

Complex	DFT-D	BLYP	B3LYP	B97-2	B98	BMK	BH&H	BH&HLYP	PBE	VSXC
1	-6.25	2.26	0.71	0.75	-1.12	-2.23	-7.43	-0.64	-1.42	-26.84
2	-6.18	2.46	0.87	0.94	-0.97	-2.30	-7.34	-0.54	-1.19	-27.79
3	-8.11	-0.65	-2.12	-1.99	-3.77	-4.34	-10.04	-3.38	-4.12	-23.52
4	-6.19	2.41	0.82	0.88	-1.02	-2.34	-7.36	-0.58	-1.24	-27.88
5 (II)	-6.52	2.09	0.55	0.61	-1.28	-2.37	-7.65	-0.80	-1.61	-27.02
6	-5.92	2.08	0.68	0.84	-1.02	-1.95	-6.93	-0.55	-1.29	-24.63
7	-7.79	-0.57	-1.95	-1.72	-3.54	-4.42	-9.84	-3.19	-4.00	-25.73
8 (I)	-9.28	-0.36	-1.92	-1.58	-3.78	-4.59	-11.05	-3.28	-4.33	-31.88
9	-7.84	0.18	-1.22	-1.08	-2.93	-3.63	-9.28	-2.41	-3.45	-27.16
10	-7.58	-0.76	-2.10	-1.95	-3.61	-3.65	-9.53	-3.28	-4.05	-20.57
α-methyl-glucose - toluene**(V)**	-7.97	0.44	-0.87	-0.61	-2.65	-3.16	-9.04	-1.98	-3.28	-28.10
Galactose-benzene **(III)**	-5.14	2.07	0.67	0.61	-0.99	-1.72	-6.27	-0.57	-1.12	-23.42
Benzene-H_2O	-3.77	-1.33	-1.91	-1.85	-2.70	-2.56	-5.44	-2.44	-2.96	-10.26
Benzene-CH_4	-0.97	0.93	0.44	0.36	-0.28	0.21	-1.98	0.02	-0.32	-5.28
11	-9.78	0.79	-1.01	-0.82	-3.12	-4.41	-10.94	-2.61	-3.57	-36.28
12	-10.55	-1.44	-3.14	-2.74	-4.85	-6.05	-12.52	-4.66	-5.29	-30.05
13	-10.20	-0.66	-2.20	-1.88	-4.02	-4.97	-11.16	-3.49	-4.56	-28.60
14	-10.33	0.07	-1.82	-1.46	-3.76	-5.25	-11.69	-3.32	-4.31	-32.62
15	-11.46	-0.49	-2.60	-2.30	-4.69	-6.54	-13.71	-4.51	-5.09	-36.31
16	-9.96	0.08	-1.84	-1.60	-3.81	-4.98	-11.70	-3.54	-4.04	-30.43
17 (IV)	-7.27	1.91	0.35	0.48	-1.58	-2.35	-8.23	-1.01	-2.00	-29.35
18	-10.56	-4.36	-5.51	-4.81	-6.49	-6.96	-13.15	-6.55	-7.29	-21.19
19	-9.77	-0.57	-2.20	-2.38	-3.91	-4.84	-11.61	-3.66	-4.42	-30.24
20	-9.04	-0.65	-2.02	-1.41	-3.56	-4.83	-10.64	-3.29	-4.17	-29.06
21	-7.16	1.40	-0.14	-0.04	-1.95	-2.43	-8.18	-1.50	-2.32	-26.81
MUE		8.12	6.64	6.83	4.97	4.12	1.48	5.35	4.57	18.62

Complex	MPW1B95	MPWB1K	PWB6K	PW6B95	MP2	M05	M05-2X	M06	M06-L
1	-2.87	-3.29	-4.30	-3.21	-8.71	-2.83	-5.30	-6.08	-5.94
2	-2.89	-3.33	-4.36	-3.25	-8.61	-2.84	-5.27	-6.06	-5.74
3	-4.48	-4.88	-5.86	-4.78	-10.35	-5.32	-7.50	-7.98	-7.22
4	-2.92	-3.37	-4.38	-3.28	-8.66	-2.89	-5.32	-6.12	-5.79
5 (II)	-2.99	-3.41	-4.41	-3.33	-8.94	-2.99	-5.46	-6.26	-6.06
6	-2.46	-2.83	-3.83	-2.83	-8.08	-2.84	-4.78	-5.42	-5.09
7	-4.94	-5.30	-6.25	-5.25	-9.80	-5.24	-7.46	-7.70	-7.30
8 (I)	-5.09	-5.46	-6.62	-5.51	-11.61	-5.81	-8.23	-9.21	-8.72
9	-4.36	-4.70	-5.68	-4.70	-10.06	-4.67	-7.13	-7.72	-7.45
10	-4.36	-4.72	-5.70	-4.67	-9.71	-5.04	-7.09	-6.97	-6.63
α-methyl-glucose - toluene**(V)**	-3.77	-4.04	-5.17	-4.24	-10.02	-4.53	-6.64	-7.41	-7.11
Galactose-benzene **(III)**	-2.59	-2.97	-3.89	-2.93	-7.73	-2.55	-4.77	-5.21	-5.14
Benzene-H_2O	-3.26	-3.38	-3.90	-3.44	-4.18	-3.41	-4.18	-3.56	-3.29
Benzene-CH_4	-0.52	-0.64	-1.10	-0.72	-1.87	-0.81	-1.19	-0.91	-0.80
11	-5.03	-5.50	-6.72	-5.47	-13.65	-5.35	-8.52	-9.45	-9.08
12	-6.18	-6.67	-7.79	-6.54	-13.98	-6.74	-9.42	-10.21	-9.68
13	-5.24	-5.60	-6.74	-5.66	-13.05	-5.99	-8.49	-8.86	-8.42
14	-5.53	-5.97	-7.15	-5.94	-13.37	-5.86	-8.80	-9.28	-8.78
15	-6.53	-7.17	-8.38	-6.86	-15.70	-6.75	-10.42	-11.19	-10.43
16	-4.87	-5.44	-6.65	-5.27	-13.83	-5.81	-8.73	-9.66	-8.76
17 (IV)	-3.08	-3.47	-4.61	-3.52	-9.98	-3.48	-5.96	-6.79	-6.55
18	-7.40	-7.68	-8.54	-7.64	-11.17	-7.81	-9.15	-9.39	-9.43
19	-5.26	-5.67	-6.88	-5.70	-12.44	-5.94	-8.37	-9.23	-8.95
20	-5.14	-5.47	-6.59	-5.57	-11.00	-5.46	-7.51	-8.40	-8.47
21	-3.24	-3.65	-4.76	-3.66	-10.00	-3.70	-6.14	-6.72	-6.54
MUE	3.62	3.24	2.23	3.26	2.44	3.24	1.00	0.40	0.73