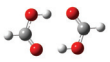
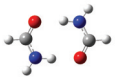
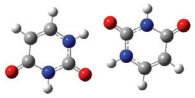
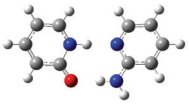
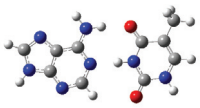
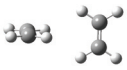
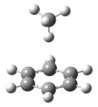
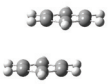
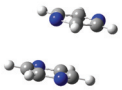
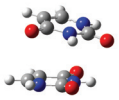
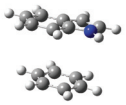
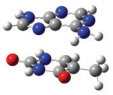
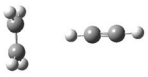
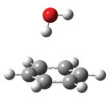
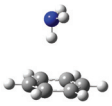
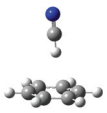
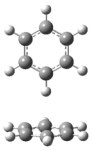
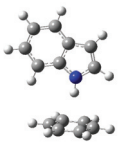
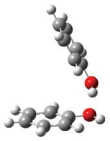
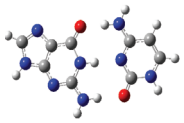
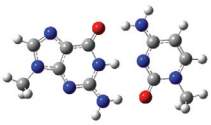
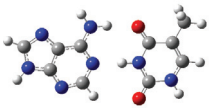
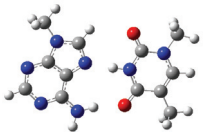
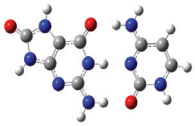
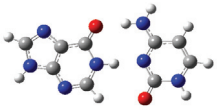
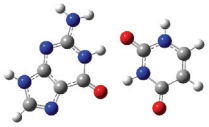
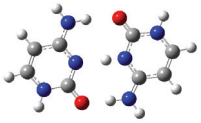
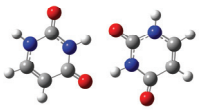
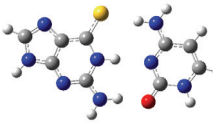
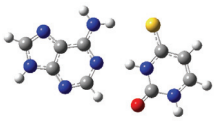
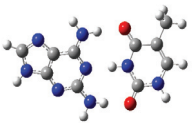
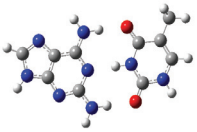
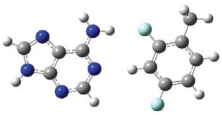
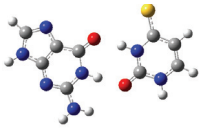
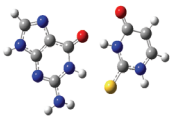
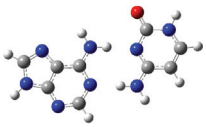
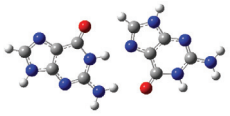
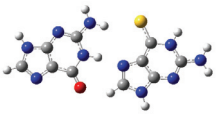
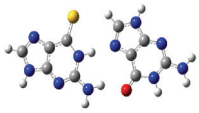
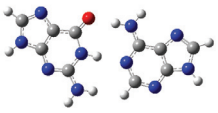
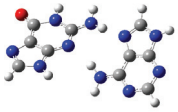
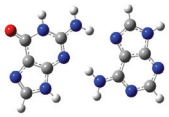
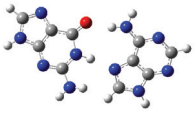
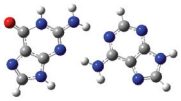
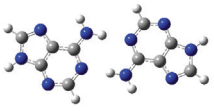
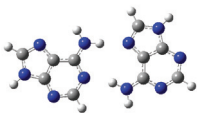
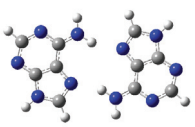
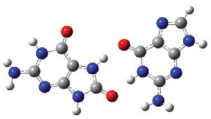
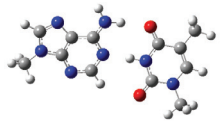
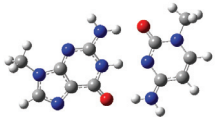
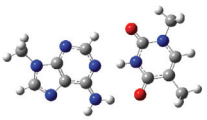
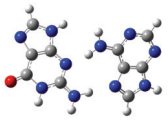
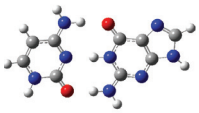
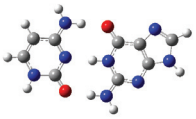
Table S1 Binding structures for the S22 data set [a]

Hydrogen bonded complexes (7)			
			
1. Ammonia_dimer (C_{2h})	2. Water_dimer (C_s)	3. Formic_acid_dimer (C_{2h})	4. Formamide_dimer (C_{2h})
			
5. Uracil_dimer_HB (C_{2h})	6. 2-pyridone_2-amino-pyridine (C_1)	7. Adenine_Thymine_WC (C_1)	
Complexes with predominant dispersion contribution (8)			
			
8. Methane_dimer (D_{3d})	9. Ethene_dimer (D_{2d})	10. Benzene_Methane (C_3)	11. Benzene_dimer (C_{2h})
			
12. Pyrazine_dimer (C_s)	13. Uracil_dimer_stack (C_2)	14. Indole_Benzene_stack (C_1)	15. Adenine_Thymine_stack (C_1)
Mixed complexes (7)			
			
16. Ethene_Ethyne (C_{2v})	17. Benzene_Water (C_s)	18. Benzene_Ammonia (C_s)	19. Benzene_HCN (C_s)
			
20. Benzene_dimer (C_{2v})	21. Indole_Benzene T-shape (C_1)	22. Phenol_dimer (C_1)	

[a] P. Jurečka, J. Šponer, J. Černý, P. Hobza, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1985-1993. Also see http://www.begdb.com

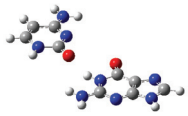
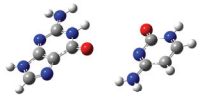
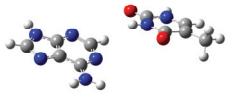
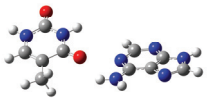
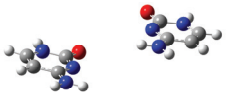
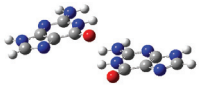
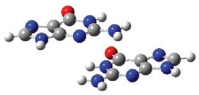
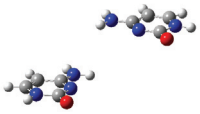
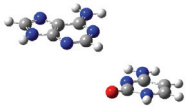
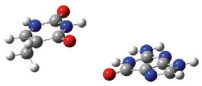
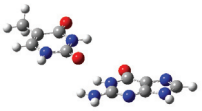
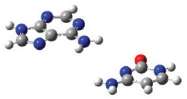
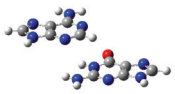
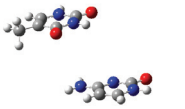
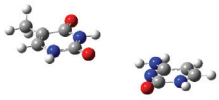
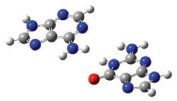
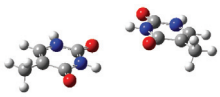
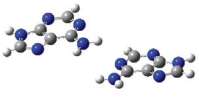
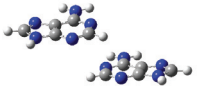
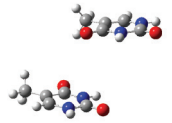
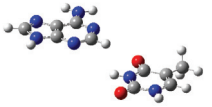
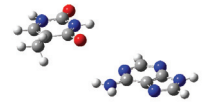
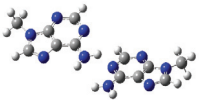
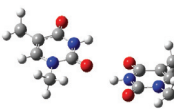
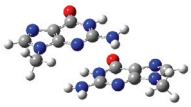
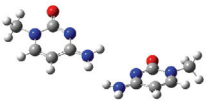
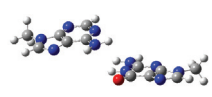
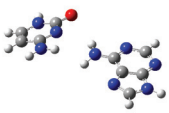
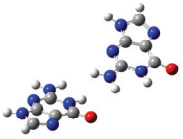
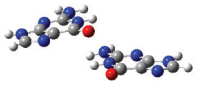
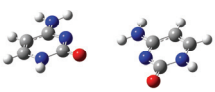
Table S2 Binding structures for 38 Hydrogen-bonded DNA base pairs in the JSCH data set.[a]

Hydrogen-bonded DNA base pairs (38)			
			
1. G...C WC	2. mG...mC WC	3. A...T WC	4. mA...mT H
			
8. 8oG...C WCpl	6. I...C WC pl	7. G...U wobble	8. CCH+
			
9. U...U Calcutta pl	10. U...U pl	11. 6tG...C WC pl	12. A...4tU WC
			
13. 2-aminoA...T	14. 2-aminoA...T pl	15. A...F	16. G...4tU
			
17. G...2tU	18. A...C pl	19. G...G pl	20. G...6tG pl
			
21. 6tG...G pl	22. G...A 1	23. G...A 1 pl	24. G...A 2
			
25. G...A 2 pl	26. G...A 3	27. G...A4	28. A...A 1 pl
			
29. A...A 2 pl	30. A...A 3 pl	31. 8oG...G	32. 2tU...2tU pl

			
33. mA...mT WC	34. mG...mC WC*	35. mA...mT WC	36. G...A HB
			
37. C...G WC	38. G...C WC		

[a] Complexes 33-38 are HB base pairs whose geometries were taken from experiments (P. Jurečka, J. Šponer, J. Černý, P. Hobza, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1985-1993. Also see http://www.begdb.com). For complexes 33-35, the sugar units were replaced by methyl groups, while for complexes 36-38, they are replaced by hydrogen atoms. Therefore, complexes 33-35 are renamed here as mA…mA, mG…mC and mA…mT, respectively.

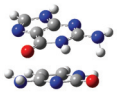
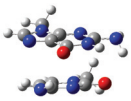
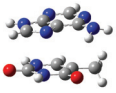
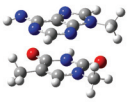
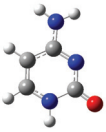
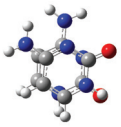
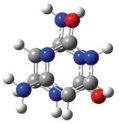
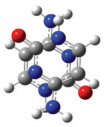
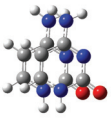
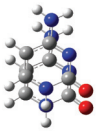
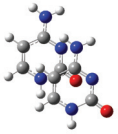
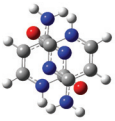
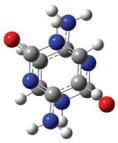
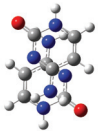
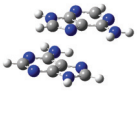
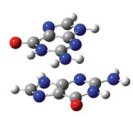
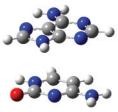
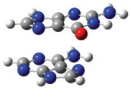
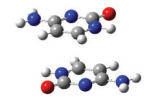
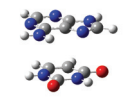
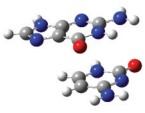
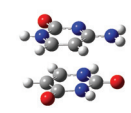
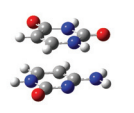
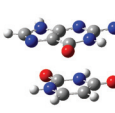
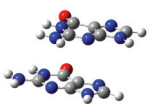
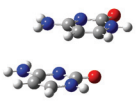
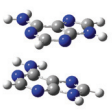
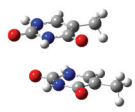
Table S3 Binding structures for 32 interstrand base pairs in the JSCH data set.[a]

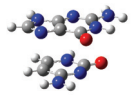
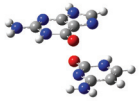
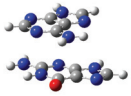
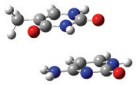
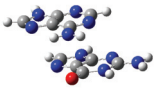
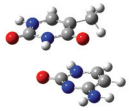
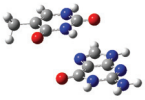
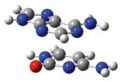
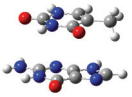
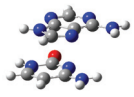
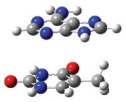
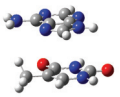
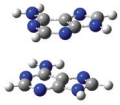
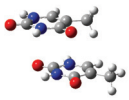
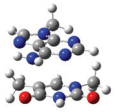
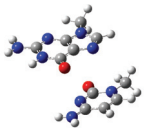
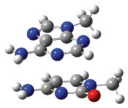
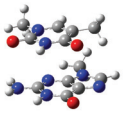
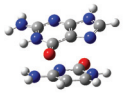
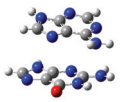
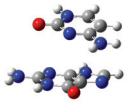
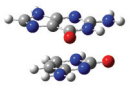
Interstrand base pairs (32)			
			
39. GG0/3.36CGis036	40. GG0/3.36GCis036 (100)	41. AA20/3.05ATis2005 (102)	42. AA20/3.05TAis2005 (41)
			
43. GC0/3.25C//Cis	44. GC0/3.25G//Gis	45. CG0/3.19G//Gis (46)	46. CG0/3.19C//Cis (45)
			
47. GA10/3.15A//Cis	48. GA10/3.15T//Gis	49. AG08/3.19T//Gis	50. AG08/3.19A//Cis
			
51. TG03.19A//Gis	52. TG03.19T//Cis	53. GT10/3.15T//Cis	54. GT10/3.15A//Gis
			
55. AT10/3.26T//Tis	56. AT10/3.26A//Ais	57. TA08/3.16A//Ais	58. TA08/3.16T//Tis
			
59. AA0/3.24A//Tis	60. AA0/3.24T//Ais	61. mA...mA IS	62. mT...mT IS
			
63. mG...mG IS	64. mC...mC IS	65. mA...mG IS	66. mT...mC IS
			
67. C...A IS	68. G...G IS	69. G...G IS	70. C...C IS

[a] P. Jurečka, J. Šponer, J. Černý, P. Hobza, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1985-1993. Also see http://www.begdb.com). As pointed

out by Sherrill and co-workers (L. A. Burns, Á. Vázquez-Mayagoitia, B.G. Sumpter, C. D. Sherrill, J. Chem. Phys., 2011, 134, 084107/1–25), reordering of several systems is necessary to bring the published geometries in line with the original authors' intentions. For example, the geometry provided in the database for complex 40, under the name of 'GG0/3.36 GCis036', actually represents a G…G stack, instead of a G…C interstrand as indicated by this name. Here, we add a parenthesis after the original name as 'GG0/3.36 GCis036 (100)'. Number 100 suggests that the geometry actually associated with complex 40 is that of complex 100 in the database. Similarly, we modify the name of complex 41 as 'AA20/3.05 ATis2005(102)' , meaning that geometry used for calculations of complex 41 should be taken from that in the database under the name of complex 102. Complexes 61-66 are renamed to show explicitly that base pairs are methylated.

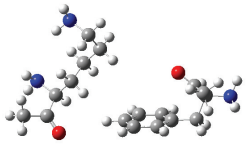
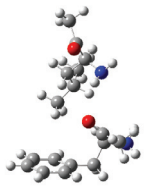
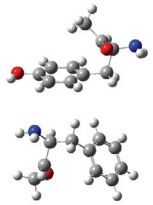
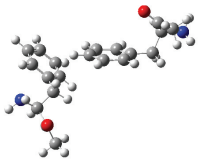
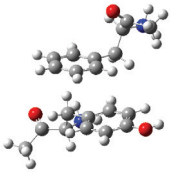
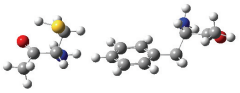
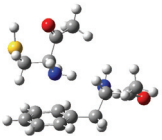
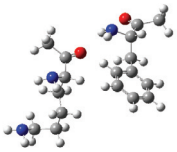
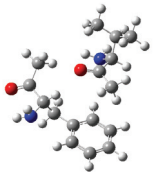
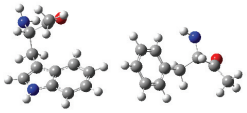
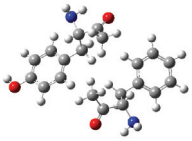
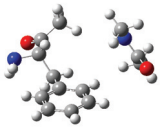
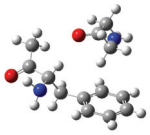
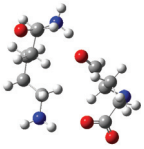
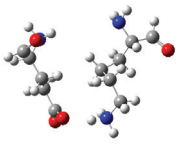
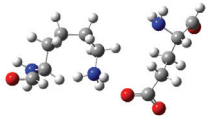
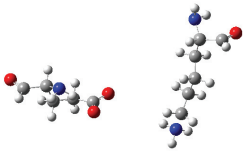
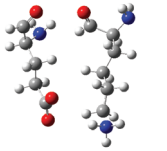
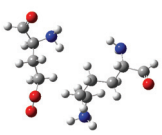
Table S4 Binding structures for 54 stacked base pairs in the JSCH data set.[a]

Stacked base pairs (54)			
			
71. G..C S	72. mG...mC S	73. A...T S	74. mA...mT S
			
75. CC1	76. CC2	77. CC3	78. CC4
			
79. CC5	80. CC6	81. CC7	82. CC8
			
83. CC9	84. CC10	85. CC11	86. CC12
			
87. CC13	88. CC14	89. AAst	90. GGst
			
91. ACst	92. GAst	93. CCst	94. AUst
			
95. GCst	96. CUst	97. UUst	98. GUst
			
99. GG0/3.36GGs036 (40)	100. GG0/3.36CCs036 (99)	101. AA20/3.05AAs2005	102. AA20/3.05ATs2005 (42)

			
103. GC0/3.25G//Cs	104. CG0/3.19G//Cs	105. GA10/3.15A//Gs	106. GA10/3.15T//Cs
			
107. AG08/3.19A//Gs	108. AG08/3.19T//Cs	109. TG03.19T//Gs	110. TG03.19A//Cs
			
111. GT10/3.15T//Gs	112. GT10/3.15A//Cs	113. AT10/3.26A//Ts	114. TA08/3.16A//Ts
			
115. AA0/3.24A//As	116. AA0/3.24T//Ts	117. mA...mT S	118. mG..mC S
			
119. mA...mC S	120. mT...mG S	121. G..C S	122. A...G S
			
123. C...G S	124. G..C S		

[a] P. Jurečka, J. Šponer, J. Černý, P. Hobza, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1985-1993. Also see http://www.begdb.com). Geometry re-ordering is required for complexes 99, 100, and 102. Complexes 117-120 are renamed to show explicitly that base pairs are methylated.

Table S5 Binding structures for 19 amino acid pairs in the JSCH data set.[a]

Amino acid pairs (19)		
		
125. F30-K46	126. F30-L33	127. F30-Y13
		
128. F30-F49	129. F30-Y4	130. F49-C39
		
131. F49-C6	132. F49-K46	133. F49-V5
		
134. F49-W37	135. F49-Y4	136. F49-PB(Y4-V5)
		
137. F49-PB(V5-C6)	138. E47-K6(1IU5)	139. E49-K6(1BQ9)
		
140. E54-K2(1SMM)	141. E50-K30(1BRF)	142. E50-K52(1BRF)
		
143. E49-K6(1BRF)		

[a] P. Jurečka, J. Šponer, J. Černý, P. Hobza, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1985-1993. Also see http://www.begdb.com). As pointed out by Antony and Grimme (J. Antony, S. Grimme, *Phys. Chem. Chem. Phys.*, 2006, 8, 5287-5293), residue 37 of 1RB9 is tryptophan (W), not tyrosine (Y). Complex 134 should be renamed as F49-W37.

Table S6 Comparison of different extrapolated CCSD(T)/CBS reference data: binding energies (kcal/mol) at the equilibrium geometries for the S22 data set

	S22[a]	**S22x5[b]**	S22P[c]	S22A[d,e]	**S22B[f]**
Hydrogen bonded complexes (7)					
1. Ammonia_dimer (C_{2h})	3.17	**3.142**	3.145	3.15	**3.133**
2. Water_dimer (C_s)	5.02	**4.974**	5.004	5.07	**4.989**
3. Formic_acid_dimer (C_{2h})	18.61	**18.586**	18.751	18.81	**18.753**
4. Formamide_dimer (C_{2h})	15.96	**15.947**	16.063	16.11	**16.062**
5. Uracil_dimer_hb (C_{2h})	20.65	**20.460**	20.643	20.69	**20.641**
6. 2-pyridone_2-aminopyridine (C_1) [g]	16.71	**16.702**	16.938	17.00	**16.934**
7. Adenine_Thymine_wc (C_1)	16.37	**16.371**	16.554	16.74	**16.660**
Complexes with predominant dispersion contribution (8)					
8. Methane_dimer (D_{3d})	0.53	**0.529**	0.529	0.53	**0.527**
9. Ethene_dimer (D_{2d})	1.51	**1.484**	1.482	1.48	**1.472**
10. Benzene_Methane (C_3)	1.50	**1.495**	1.448	1.45	**1.448**
11. Benzene_dimer (C_{2h})	2.73	**2.807**	2.655	2.62	**2.654**
12. Pyrazine_dimer (C_s)	4.42	**4.509**	4.256	4.20	**4.255**
13. Uracil_dimer_stack (C_2)	10.12	**9.867**	9.783	9.74	**9.805**
14. Indole_Benzene_stack (C_1)	5.22	**4.682**	4.523	4.59	**4.524**
15. Adenine_Thymine_stack (C_1)	12.23	**12.225**	11.857	11.66	**11.730**
Mixed complexes (7)					
16. Ethene_Ethyne (C_{2v})	1.53	**1.492**	1.503	1.50	**1.496**
17. Benzene_water (C_s)	3.28	**3.274**	3.280	3.29	**3.275**
18. Benzene_Ammonia (C_s)	2.35	**2.348**	2.319	2.32	**2.312**
19. Benzene_HCN (C_s)	4.46	**4.520**	4.540	4.55	**4.541**
20. Benzene_dimer (C_{2v})	2.74	**2.797**	2.717	2.71	**2.717**
21. Indole_Benzene_T-shape (C_1)	5.73	**5.736**	5.627	5.62	**5.627**
22. Phenol_dimer (C_1)	7.05	**7.048**	7.097	7.09	**7.097**

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[c] R. Podeszwa, K. Patkowski, K. Szalewicz, Phys. Chem. Chem. Phys., **2010**, 6, 2365-2376.

[d] T. Takatani, E. G. Hohenstein, M. Malagoli, M. S. Marshall, C. D. Sherrill, J. Chem. Phys., **2010**, 132, 144104.

[e] L. A. Burns, Á. Vázquez-Mayagoitia, B.G. Sumpter, C. D. Sherrill, J. Chem. Phys., **2011**, 134, 084107.

[f] M. S. Marshall, L. A. Burns, C. D. Sherrill, J. Chem. Phys., **2011**, 135, 194102.

[g] The name '2-pyridoxine' is changed to '2-pyridone' to be consistent with its structure.

Table S7 Electronic energy (in au) of XYG3 with basis sets of 6-311+G(d,p) (PP1), and 6-311+G(3df,2p) (PP2).

	PP1 [a]			PP2 [a]		
	Dimers	Mono-A	Mono-B	Dimers	Mono-A	Mono-B
Hydrogen bonded complexes (7)						
1. Ammonia_dimer (C_{2h})	-113.081318	-56.537716	-56.537716	-113.116652	-56.555812	-56.555812
2. Water_dimer (C_s)	-152.821736	-76.405824	-76.405824	-152.863643	-76.427405	-76.427405
3. Formic_acid_dimer (C_{2h})	-379.438721	-189.704747	-189.704747	-379.550565	-189.759907	-189.759907
4. Formamide_dimer (C_{2h})	-339.704638	-169.840032	-169.840032	-339.807249	-169.890842	-169.890842
5. Uracil_dimer_hb (C_{2h})	-829.404628	-414.685839	-414.685839	-829.658088	-414.812628	-414.812628
6. 2-pyridone_2-aminopyridine (C_1)	-626.976416	-323.406982	-303.541763	-627.168571	-323.506095	-303.635456
7. Adenine_Thymine_WC (C_1)	-921.180326	-467.164037	-453.989702	-921.463810	-467.308990	-454.128617
Complexes with predominant dispersion contribution (8)						
8. Methane_dimer (D_{3d})	-80.992330	-40.495978	-40.495978	-81.019590	-40.509559	-40.509559
9. Ethene_dimer (D_{2d})	-157.110042	-78.554082	-78.554082	-157.159235	-78.578679	-78.578679
10. Benzene_Methane (C_3)	-272.657546	-232.159313	-40.496005	-272.742600	-232.230800	-40.509640
11. Benzene_dimer (C_{2h})	-464.323153	-232.159302	-232.159302	-464.465999	-232.230785	-232.230785
12. Pyrazine_dimer (C_s)	-528.445569	-264.219333	-264.219329	-528.606714	-264.299985	-264.299976
13. Uracil_dimer_stack (C_2)	-829.390141	-414.686820	-414.686820	-829.642729	-414.813401	-414.813401
14. Indole_Benzene_stack (C_1)	-595.853129	-232.159304	-363.685922	-596.038197	-232.230765	-363.799738
15. Adenine_Thymine_stack (C_1)	-921.175255	-467.164370	-453.990922	-921.457422	-467.308717	-454.129757
Mixed complexes (7)						
16. Ethene_Ethyne (C_{2v})	-155.862153	-78.554081	-77.305754	-155.910014	-78.578679	-77.328897
17. Benzene_Water (C_s)	-308.570898	-232.159305	-76.405732	-308.663776	-232.230758	-76.427271
18. Benzene_Ammonia (C_s)	-288.700860	-232.159312	-56.537571	-288.790237	-232.230781	-56.555734
19. Benzene_HCN (C_s)	-325.567275	-232.159309	-93.400411	-325.664843	-232.230743	-93.426249
20. Benzene_dimer (C_{2v})	-464.323513	-232.159308	-232.159313	-464.466173	-232.230779	-232.230778
21. Indole_Benzene_T-shape (C_1)	-595.854745	-232.159301	-363.685970	-596.039642	-232.230724	-363.799753
22. Phenol_dimer (C_1)	-614.735265	-307.361078	-307.361099	-614.921880	-307.455109	-307.455140

[a] Spherical basis sets are used (5d, 7f), Keywords as in Gaussian, grid = fine, scf=tight, are used.

Table S8 Electronic energy (in au) of XYG3 with basis sets of aug-cc-pVDZ (aDZ) and aug-cc-pVTZ (aTZ).

	aDZ [a]			aTZ [a]		
	Dimers	Mono-A	Mono-B	Dimers	Mono-A	Mono-B
Hydrogen bonded complexes (7)						
1. Ammonia_dimer (C_{2h})	-113.051452	-56.523093	-56.523093	-113.122507	-56.558725	-56.558725
2. Water_dimer (C_s)	-152.786019	-76.388704	-76.388730	-152.869875	-76.430603	-76.430652
3. Formic_acid_dimer (C_{2h})	-379.347902	-189.658702	-189.658702	-379.554606	-189.761611	-189.761611
4. Formamide_dimer (C_{2h})	-339.621024	-169.797483	-169.797483	-339.811953	-169.892719	-169.892719
5. Uracil_dimer_hb (C_{2h})	-829.202743	-414.584404	-414.584404	-829.664279	-414.814831	-414.814831
6. 2-pyridone_2-aminopyridine (C_1)	-626.811913	-323.322937	-303.460622	-627.178930	-323.510027	-303.640283
7. Adenine_Thymine_WC (C_1)	-920.953302	-467.049294	-453.876278	-921.472746	-467.311689	-454.132775
Complexes with predominant dispersion contribution (8)						
8. Methane_dimer (D_{3d})	-80.960834	-40.479918	-40.479918	-81.025596	-40.512451	-40.512451
9. Ethene_dimer (D_{2d})	-157.059135	-78.528388	-78.528388	-157.165256	-78.581508	-78.581508
10. Benzene_Methane (C_3)	-272.574139	-232.091335	-40.479845	-272.751196	-232.236101	-40.512532
11. Benzene_dimer (C_{2h})	-464.187839	-232.091328	-232.091328	-464.476166	-232.236090	-232.236090
12. Pyrazine_dimer (C_s)	-528.309288	-264.150778	-264.150781	-528.610777	-264.301974	-264.301965
13. Uracil_dimer_stack (C_2)	-829.186900	-414.584893	-414.584893	-829.646943	-414.815523	-414.815523
14. Indole_Benzene_stack (C_1)	-595.686517	-232.091348	-363.586235	-596.049458	-232.236070	-363.806108
15. Adenine_Thymine_stack (C_1)	-920.947515	-467.049130	-453.877133	-921.464719	-467.311442	-454.133916
Mixed complexes (7)						
16. Ethene_Ethyne (C_{2v})	-155.809495	-78.528389	-77.277971	-155.914085	-78.581507	-77.329649
17. Benzene_Water (C_s)	-308.485887	-232.091356	-76.388656	-308.672281	-232.236060	-76.430541
18. Benzene_Ammonia (C_s)	-288.618720	-232.091349	-56.523024	-288.798734	-232.236087	-56.558658
19. Benzene_HCN (C_s)	-325.473567	-232.091378	-93.373725	-325.670604	-232.236045	-93.426058
20. Benzene_dimer (C_{2v})	-464.188585	-232.091347	-232.091356	-464.477259	-232.236083	-232.236068
21. Indole_Benzene_T-shape (C_1)	-595.688466	-232.091385	-363.586306	-596.052210	-232.236021	-363.806114
22. Phenol_dimer (C_1)	-614.569118	-307.278240	-307.278324	-614.934592	-307.461232	-307.461282

[a] Spherical basis sets are used (5d, 7f), Keywords as in Gaussian, grid = fine, scf=tight, are used.

Table S9 Binding energies (kcal/mol) at the equilibrium geometries for the S22 data set: Errors with respect to the S22B reference data for the B3LYP, MC3BB and B2PLYP methods with and without dispersion corrections. Basis set used is def2-QZVP.[a]

	Ref	B3LYP[c]			B2PLYP[c]		
	S22B[b]	-	-D	-D3	-	-D	-D3
Hydrogen bonded complexes (7)							
1. Ammonia_dimer (C_{2h})	3.133	0.823	-0.637	-0.087	0.393	-0.372	-0.087
2. Water_dimer (C_s)	4.989	0.219	-0.600	-0.521	-0.051	-0.480	-0.441
3. Formic_acid_dimer (C_{2h})	18.753	1.263	-1.383	-1.067	0.403	-0.983	-0.827
4. Formamide_dimer (C_{2h})	16.062	1.922	-0.871	-0.648	0.912	-0.551	-0.448
5. Uracil_dimer_hb (C_{2h})	20.641	2.651	-0.846	-0.679	1.271	-0.561	-0.499
6. 2-pyridone_2-aminopyridine (C_1)	16.934	3.084	-1.085	-0.826	1.354	-0.829	-0.686
7. Adenine_Thymine_WC (C_1)	16.660	3.760	-0.692	-0.470	1.890	-0.442	-0.330
Complexes with predominant dispersion contribution (8)							
8. Methane_dimer (D_{3d})	0.527	0.927	0.056	0.007	0.557	0.101	0.137
9. Ethene_dimer (D_{2d})	1.472	1.972	-0.275	-0.148	1.062	-0.115	-0.058
10. Benzene_Methane (C_3)	1.448	2.208	-0.081	-0.032	1.138	-0.061	-0.052
11. Benzene_dimer (C_{2h})	2.654	6.364	0.369	0.324	3.014	-0.127	-0.026
12. Pyrazine_dimer (C_s)	4.255	6.695	0.174	0.425	3.075	-0.341	-0.095
13. Uracil_dimer_stack (C_2)	9.805	8.735	-0.726	-0.425	4.285	-0.671	-0.335
14. Indole_Benzene_stack (C_1)	4.524	9.204	0.237	0.654	4.214	-0.483	-0.136
15. Adenine_Thymine_stack (C_1)	11.730	12.910	-0.971	0.430	6.040	-1.231	-0.330
Mixed complexes (7)							
16. Ethene_Ethyne (C_{2v})	1.496	0.806	-0.234	-0.254	0.396	-0.149	-0.144
17. Benzene_Water (C_s)	3.275	1.805	-0.652	-0.515	0.815	-0.472	-0.345
18. Benzene_Ammonia (C_s)	2.312	2.092	-0.302	-0.268	1.042	-0.212	-0.168
19. Benzene_HCN (C_s)	4.541	2.541	-0.714	-0.199	1.181	-0.524	-0.309
20. Benzene_dimer (C_{2v})	2.717	3.637	-0.185	-0.053	1.757	-0.245	-0.193
21. Indole_Benzene_T-shape (C_1)	5.627	5.027	-0.549	0.097	2.377	-0.544	-0.183
22. Phenol_dimer (C_1)	7.097	4.067	-0.228	-0.193	1.977	-0.273	-0.273
MD[d]		**3.76**	**-0.46**	**-0.20**	**1.78**	**-0.43**	**-0.26**
MAD[d]		**3.76**	**0.54**	**0.38**	**1.78**	**0.44**	**0.28**
RMSD[d]		**4.90**	**0.64**	**0.47**	**2.32**	**0.53**	**0.34**

[a] Calculation data are taken from L. Goerigk, S. Grimme, J. Chem. Theory Comput., **2011**, 7, 291.

[b] M. S. Marshall, L. A. Burns, C. D. Sherrill, J. Chem. Phys., **2011**, 135, 194102.

[c] Errors are calculated by (Ref. – Calc.) in kcal/mol.

[d] Mean deviation (MD), mean absolute deviation (MAD) and root mean square deviation (RMSD).

Table S10 Binding energies (kcal/mol) at the equilibrium geometries for the S22 data set: XYG3 and XYGJ-OS errors with respect to the S22x5 reference data

	Ref	XYG3[b]				XYGJ-OS[b]			
	S22x5[a]	PP1[c]	PP2[d]	aDZ[e]	aTZ[f]	PP1[c]	PP2[d]	aDZ[e]	aTZ[f]
Hydrogen bonded complexes (7)									
1. Ammonia_dimer (C_{2h})	3.142	-0.551	-0.013	-0.170	-0.123	-0.661	-0.101	-0.275	-0.235
2. Water_dimer (C_s)	4.974	**-1.357**	-0.608	-0.411	-0.599	**-1.462**	-0.666	-0.533	**-0.704**
3. Formic_acid_dimer (C_{2h})	18.586	0.246	**-0.710**	-0.559	**-0.641**	0.083	**-0.726**	-0.598	-0.659
4. Formamide_dimer (C_{2h})	15.947	**0.526**	-0.096	-0.410	-0.146	0.323	-0.151	-0.466	-0.214
5. Uracil_dimer_hb (C_{2h})	20.460	-0.216	-0.142	-0.835	-0.333	0.142	0.375	-0.304	0.166
6. 2-pyridone_2-aminopyridine (C_1)	16.702	-0.662	-0.254	-1.095	-0.447	-0.502	0.052	-0.792	-0.172
7. Adenine_Thymine_WC (C_1)	16.371	-0.313	-0.072	-1.032	-0.216	-0.255	0.168	-0.780	-0.015
Complexes with predominant dispersion contribution (8)									
8. Methane_dimer (D_{3d})	0.529	0.294	0.233	-0.102	0.265	0.183	0.154	-0.196	0.174
9. Ethene_dimer (D_{2d})	1.484	0.305	0.307	**0.016**	0.280	0.193	0.231	-0.031	0.231
10. Benzene_Methane (C_3)	1.495	0.098	0.139	-0.373	0.221	0.033	0.097	-0.423	0.173
11. Benzene_dimer (C_{2h})	2.807	-0.048	0.028	-0.457	0.618	0.108	0.279	-0.298	0.802
12. Pyrazine_dimer (C_s)	4.509	0.175	0.271	-0.350	0.615	0.351	0.594	-0.064	0.891
13. Uracil_dimer_stack (C_2)	9.867	-0.487	-0.127	-0.896	0.121	-0.017	0.491	-0.268	0.702
14. Indole_Benzene_stack (C_1)	4.682	-0.277	-0.146	-0.907	0.668	0.147	0.407	-0.421	1.182
15. Adenine_Thymine_stack (C_1)	12.225	-0.302	**0.335**	**-1.128**	**0.937**	**0.414**	**1.256**	-0.190	**1.824**
Mixed complexes (7)									
16. Ethene_Ethyne (C_{2v})	1.492	0.038	-0.038	-0.439	0.027	-0.003	-0.046	-0.446	0.019
17. Benzene_Water (C_s)	3.274	-0.404	-0.332	-0.391	-0.167	-0.497	-0.403	-0.478	-0.238
18. Benzene_Ammonia (C_s)	2.348	-0.148	0.013	-0.389	0.062	-0.221	-0.045	-0.440	0.014
19. Benzene_HCN (C_s)	4.520	-0.221	-0.407	-0.800	-0.152	-0.231	-0.416	-0.782	-0.153
20. Benzene_dimer (C_{2v})	2.797	-0.273	-0.099	-0.886	0.162	-0.194	0.000	-0.799	0.245
21. Indole_Benzene_T-shape (C_1)	5.736	-0.209	-0.015	-1.041	0.303	-0.040	0.178	**-0.849**	0.489
22. Phenol_dimer (C_1)	7.048	-1.165	-0.251	-0.759	-0.192	-1.060	-0.073	-0.633	-0.069
MD		-0.23	-0.09	-0.61	0.06	-0.14	0.08	-0.46	0.20
MAD		0.38	0.21	0.61	0.33	0.32	0.31	0.46	0.43
RMSD		0.50	0.28	0.69	0.41	0.47	0.43	0.52	0.61

[a] L. Gráfová, M. Pitoňák, J. Řezáč, P. Hobza, J. Chem. Theory Comput., **2010**, 6, 2365-2376.

[b] Errors are calculated by (Ref. – Calc.) in kcal/mol.

[c] Pople basis set 1 = 6-311+G(d,p).

[d] Pople basis set 2 = 6-311+G(3df,2p).

[e] Dunning's aug-cc-pVDZ basis set.

[f] Dunning's aug-cc-pVTZ basis set.

Table S11 Binding energies (kcal/mol) at the equilibrium geometries for the S22 data set: Errors with respect to the S22x5 reference data for the B3LYP, MC3BB and B2PLYP methods with and without dispersion corrections. Basis set used is 6-311+G(3df,2p).

	Ref	B3LYP [b]			MC3BB [b,c]		B2PLYP [b]		
	S22x5 [a]	-	-D	-D3	-	-D	-	-D	-D3
Hydrogen bonded complexes (7)									
1. Ammonia_dimer (C_{2h})	3.142	0.880	-0.579	-0.030	0.562	0.215	0.445	-0.320	-0.035
2. Water_dimer (C_s)	4.974	0.153	-0.666	-0.587	0.145	-0.050	-0.170	-0.599	-0.560
3. Formic_acid_dimer (C_{2h})	18.586	0.846	-1.800	-1.484	0.949	0.319	0.213	-1.173	-1.017
4. Formamide_dimer (C_{2h})	15.947	1.706	-1.087	-0.864	1.652	0.987	0.878	-0.585	-0.482
5. Uracil_dimer_hb (C_{2h})	20.460	2.315	-1.181	-1.015	1.781	0.949	1.065	-0.766	-0.705
6. 2-pyridone_2-aminopyridine (C_1)	16.702	2.762	-1.406	-1.148	1.884	0.891	1.104	-1.080	-0.936
7. Adenine_Thymine_WC (C_1)	16.371	3.317	-1.135	-0.913	2.489	1.429	1.528	-0.804	-0.692
Complexes with predominant dispersion contribution (8)									
8. Methane_dimer (D_{3d})	0.529	0.914	0.042	-0.006	0.659	0.452	0.558	0.102	0.138
9. Ethene_dimer (D_{2d})	1.484	1.923	-0.324	-0.197	0.903	0.368	1.070	-0.107	-0.050
10. Benzene_Methane (C_3)	1.495	2.060	-0.229	-0.180	0.701	0.156	0.971	-0.228	-0.219
11. Benzene_dimer (C_{2h})	2.807	5.890	-0.105	-0.150	1.095	-0.333	2.275	-0.865	-0.765
12. Pyrazine_dimer (C_s)	4.509	6.587	0.066	0.317	1.686	0.133	2.702	-0.713	-0.468
13. Uracil_dimer_stack (C_2)	9.867	8.081	-1.379	-1.079	2.308	0.056	3.281	-1.674	-1.339
14. Indole_Benzene_stack (C_1)	4.682	8.501	-0.466	-0.049	1.366	-0.769	3.144	-1.553	-1.206
15. Adenine_Thymine_stack (C_1)	12.225	12.571	-1.310	0.091	2.474	-0.831	5.257	-2.014	-1.113
Mixed complexes (7)									
16. Ethene_Ethyne (C_{2v})	1.492	0.737	-0.302	-0.323	0.493	0.245	0.323	-0.221	-0.217
17. Benzene_Water (C_s)	3.274	1.569	-0.888	-0.751	0.316	-0.269	0.535	-0.752	-0.625
18. Benzene_Ammonia (C_s)	2.348	1.963	-0.431	-0.397	0.578	0.008	0.879	-0.375	-0.331
19. Benzene_HCN (C_s)	4.520	2.137	-1.118	-0.603	0.068	-0.707	0.709	-0.996	-0.781
20. Benzene_dimer (C_{2v})	2.797	3.312	-0.510	-0.378	0.813	-0.097	1.293	-0.709	-0.657
21. Indole_Benzene_T-shape (C_1)	5.736	4.673	-0.902	-0.257	1.206	-0.122	1.901	-1.019	-0.659
22. Phenol_dimer (C_1)	7.048	3.683	-0.612	-0.577	1.181	0.158	1.454	-0.796	-0.796
MD [d]		**3.48**	**-0.74**	**-0.48**	**1.15**	**0.14**	**1.43**	**-0.78**	**-0.61**
MAD [d]		**3.48**	**0.75**	**0.52**	**1.15**	**0.43**	**1.44**	**0.79**	**0.63**
RMSD [d]		**4.62**	**0.90**	**0.66**	**1.35**	**0.58**	**1.88**	**0.93**	**0.72**

[a] L. Gráfová, M. Pitoňák, J. Řezáč, P. Hobza, J. Chem. Theory Comput., **2010**, 6, 2365-2376.

[b] Errors are calculated by (Ref. – Calc.) in kcal/mol.

[c] MP2 calculation was done with 6-31+G(d,p) basis set.

[d] Mean deviation (MD), mean absolute deviation (MAD) and root mean square deviation (RMSD).

Table S12 Binding energies (kcal/mol) at the equilibrium geometries for the S22 data set: Errors with respect to the S22x5 reference data for the B3LYP, and B2PLYP methods with and without dispersion corrections. Basis set used is def2-QZVP. [a]

	Ref	B3LYP [c]			B2PLYP [c]		
	S22x5 [b]	-	-D	-D3	-	-D	-D3
Hydrogen bonded complexes (7)							
1. Ammonia_dimer (C_{2h})	3.142	0.832	-0.628	-0.078	0.402	-0.363	-0.078
2. Water_dimer (C_s)	4.974	0.204	-0.615	-0.536	-0.066	-0.495	-0.456
3. Formic_acid_dimer (C_{2h})	18.586	1.096	-1.550	-1.234	0.236	-1.150	-0.994
4. Formamide_dimer (C_{2h})	15.947	1.807	-0.986	-0.763	0.797	-0.666	-0.563
5. Uracil_dimer_hb (C_{2h})	20.460	2.470	-1.027	-0.860	1.090	-0.742	-0.680
6. 2-pyridone_2-aminopyridine (C_1)	16.702	2.852	-1.317	-1.058	1.122	-1.062	-0.918
7. Adenine_Thymine_WC (C_1)	16.371	3.471	-0.981	-0.759	1.601	-0.731	-0.619
Complexes with predominant dispersion contribution (8)							
8. Methane_dimer (D_{3d})	0.529	0.929	0.058	0.009	0.559	0.103	0.139
9. Ethene_dimer (D_{2d})	1.484	1.984	-0.263	-0.136	1.074	-0.103	-0.046
10. Benzene_Methane (C_3)	1.495	2.255	-0.034	0.015	1.185	-0.014	-0.005
11. Benzene_dimer (C_{2h})	2.807	6.517	0.522	0.477	3.167	0.026	0.127
12. Pyrazine_dimer (C_s)	4.509	6.949	0.429	0.679	3.329	-0.087	0.159
13. Uracil_dimer_stack (C_2)	9.867	8.797	-0.663	-0.363	4.347	-0.608	-0.273
14. Indole_Benzene_stack (C_1)	4.682	9.362	0.395	0.812	4.372	-0.325	0.022
15. Adenine_Thymine_stack (C_1)	12.225	13.405	-0.476	0.925	6.535	-0.736	0.165
Mixed complexes (7)							
16. Ethene_Ethyne (C_{2v})	1.492	0.802	-0.238	-0.258	0.392	-0.153	-0.148
17. Benzene_Water (C_s)	3.274	1.804	-0.653	-0.516	0.814	-0.473	-0.346
18. Benzene_Ammonia (C_s)	2.348	2.128	-0.266	-0.232	1.078	-0.176	-0.132
19. Benzene_HCN (C_s)	4.520	2.520	-0.735	-0.220	1.160	-0.545	-0.330
20. Benzene_dimer (C_{2v})	2.797	3.717	-0.105	0.027	1.837	-0.165	-0.113
21. Indole_Benzene_T-shape (C_1)	5.736	5.136	-0.440	0.206	2.486	-0.435	-0.074
22. Phenol_dimer (C_1)	7.048	4.018	-0.277	-0.242	1.928	-0.322	-0.322
MD [d]		**3.78**	**-0.45**	**-0.19**	**1.79**	**-0.42**	**-0.25**
MAD [d]		**3.78**	**0.58**	**0.47**	**1.80**	**0.43**	**0.30**
RMSD [d]		**4.99**	**0.69**	**0.59**	**2.40**	**0.53**	**0.41**

[a] Calculation data are taken from L. Goerigk, S. Grimme, J. Chem. Theory Comput., **2011**, 7, 291.

[b] L. Gráfová, M. Pitoňák, J. Řezáč, P. Hobza, J. Chem. Theory Comput., **2010**, 6, 2365-2376.

[c] Errors are calculated by (Ref. – Calc.) in kcal/mol.

[d] Mean deviation (MD), mean absolute deviation (MAD) and root mean square deviation (RMSD).

Table S13 Binding energies (kcal/mol) at the 0.9 R_e distorted geometries for the S22 data set: Errors with respect to the S22x5 reference data for the XYG3 and XYGJ-OS methods. Basis sets used are 6-311+G(d,p) (PP1) and 6-311+G(3df,2p) (PP2).

0.9 R_e	Ref	Int.	B3LYP/PP2 [c]		XYG3 [c]		XYGJ-OS [c]	
	S22x5 [a]	Type [b]	-	-D	PP1	PP2	PP1	PP2
Hydrogen bonded complexes (7)								
1. Ammonia_dimer (C_{2h})	2.410	E	1.085	-0.277	-0.684	-0.020	-0.808	-0.119
2. Water_dimer (C_s)	4.319	E	0.206	-0.818	-1.504	-0.696	-1.612	-0.763
3. Formic_acid_dimer (C_{2h})	16.337	E	0.806	-1.954	0.086	-0.960	-0.061	-0.941
4. Formamide_dimer (C_{2h})	14.141	E	1.943	-1.160	0.698	-0.071	0.494	-0.104
5. Uracil_dimer_hb (C_{2h})	18.729	E	2.640	-1.263	-0.106	-0.142	0.382	0.537
6. 2-pyridone_2-aminopyridine (C_1)	15.126	E	3.126	-1.782	-0.693	-0.349	-0.427	0.090
7. Adenine_Thymine_WC (C_1)	15.021	E	3.808	-1.475	-0.274	-0.115	-0.143	0.241
Complexes with predominant dispersion contribution (8)								
8. Methane_dimer (D_{3d})	0.337	D	1.436	-0.194	0.411	0.301	0.250	0.183
9. Ethene_dimer (D_{2d})	0.681	D	2.926	-1.120	0.570	0.427	0.414	0.319
10. Benzene_Methane (C_3)	1.088	D	2.746	-0.607	0.202	0.146	0.135	0.107
11. Benzene_dimer (C_{2h})	0.148	D	8.883	-0.916	0.258	-0.052	0.548	0.371
12. Pyrazine_dimer (C_s)	1.686	D	9.837	-0.185	0.613	0.346	0.926	0.866
13. Uracil_dimer_stack (C_2)	6.763	E	11.962	-1.867	-0.357	-0.251	0.302	0.639
14. Indole_Benzene_stack (C_1)	1.429	D	12.149	-1.397	-0.146	-0.269	0.519	0.557
15. Adenine_Thymine_stack (C_1)	7.991	M	18.300	-1.724	0.233	0.488	1.302	1.845
Mixed complexes (7)								
16. Ethene_Ethyne (C_{2v})	1.174	M	0.956	-0.553	0.124	-0.061	0.077	-0.068
17. Benzene_Water (C_s)	3.007	E	2.140	-1.024	-0.276	-0.360	-0.383	-0.442
18. Benzene_Ammonia (C_s)	2.040	M	2.629	-0.714	-0.042	0.021	-0.125	-0.043
19. Benzene_HCN (C_s)	4.018	E	2.781	-1.232	-0.025	-0.418	-0.019	-0.413
20. Benzene_dimer (C_{2v})	2.204	M	4.383	-0.757	-0.170	-0.087	-0.050	0.052
21. Indole_Benzene_T-shape (C_1)	4.995	M	6.128	-0.614	0.106	0.164	0.334	0.421
22. Phenol_dimer (C_1)	6.422	M	4.377	-0.903	-1.285	-0.318	-1.149	-0.097
MAD [d]-Tot			**4.78**	**1.02**	**0.40**	**0.28**	**0.48**	**0.42**
MAD-E			**3.05**	**1.29**	**0.47**	**0.34**	**0.46**	**0.43**
MAD-D			**6.33**	**0.74**	**0.37**	**0.26**	**0.47**	**0.40**
MAD-M			**6.13**	**0.88**	**0.33**	**0.19**	**0.51**	**0.42**
MARD [e]-Tot			**446.32**	**60.97**	**26.43**	**14.44**	**34.68**	**25.63**
MARD-E			**44.58**	**17.13**	**9.07**	**5.33**	**9.82**	**6.86**
MARD-D			**1424.03**	**167.61**	**74.21**	**12.53**	**101.50**	**75.34**
MARD-M			**138.17**	**27.39**	**7.57**	**4.08**	**9.30**	**7.12**

[a] L. Gráfová, M. Pitoňák, J. Řezáč, P. Hobza, J. Chem. Theory Comput., **2010**, 6, 2365-2376.

[b] Interaction types: E, electrostatics-dominated; D, dispersion-dominated; M, mixed character.

[c] Errors are calculated by (Ref. – Calc.) in kcal/mol.

[d] Mean absolute deviation (MAD)

[e] Mean absolute relative deviation (MARD).

Table S14 Binding energies (kcal/mol) at the 1.0 R_e nondistorted geometries for the S22 data set: Errors with respect to the S22x5 reference data for the XYG3 and XYGJ-OS methods. Basis sets used are 6-311+G(d,p) (PP1) and 6-311+G(3df,2p) (PP2).

1.0 R_e	Ref	Int.	B3LYP/PP2 [c]		XYG3 [c]		XYGJ-OS [c]	
	S22x5 [a]	Type [b]	-	-D	PP1	PP2	PP1	PP2
Hydrogen bonded complexes (7)								
1. Ammonia_dimer (C_{2h})	3.142	E	0.880	-0.575	-0.55	-0.01	-0.66	-0.10
2. Water_dimer (C_s)	4.974	E	0.167	-0.648	-1.36	-0.57	-1.46	-0.64
3. Formic_acid_dimer (C_{2h})	18.586	E	0.846	-1.795	0.25	-0.71	0.08	-0.73
4. Formamide_dimer (C_{2h})	15.947	E	1.706	-1.084	0.53	-0.10	0.32	-0.15
5. Uracil_dimer_hb (C_{2h})	20.460	E	2.315	-1.186	-0.22	-0.14	0.14	0.38
6. 2-pyridone_2-aminopyridine (C_1)	16.702	E	2.762	-1.409	-0.66	-0.25	-0.50	0.05
7. Adenine_Thymine_WC (C_1)	16.371	E	3.317	-1.133	-0.31	-0.07	-0.26	0.17
Complexes with predominant dispersion contribution (8)								
8. Methane_dimer (D_{3d})	0.529	D	0.914	0.046	0.29	0.23	0.18	0.15
9. Ethene_dimer (D_{2d})	1.484	D	1.923	-0.322	0.30	0.31	0.19	0.23
10. Benzene_Methane (C_3)	1.495	D	2.060	-0.230	0.10	0.14	0.03	0.10
11. Benzene_dimer (C_{2h})	2.807	D	5.890	-0.113	-0.05	0.03	0.11	0.28
12. Pyrazine_dimer (C_s)	4.509	D	6.587	0.067	0.17	0.27	0.35	0.59
13. Uracil_dimer_stack (C_2)	9.867	M	8.081	-1.384	-0.49	-0.13	-0.02	0.49
14. Indole_Benzene_stack (C_1)	4.682	D	8.501	-0.459	-0.28	-0.15	0.15	0.41
15. Adenine_Thymine_stack (C_1)	12.225	M	12.571	-1.311	-0.30	0.34	0.41	1.26
Mixed complexes (7)								
16. Ethene_Ethyne (C_{2v})	1.492	M	0.737	-0.309	0.04	-0.04	0.00	-0.05
17. Benzene_Water (C_s)	3.274	M	1.569	-0.887	-0.40	-0.33	-0.50	-0.40
18. Benzene_Ammonia (C_s)	2.348	M	1.963	-0.430	-0.15	0.01	-0.22	-0.04
19. Benzene_HCN (C_s)	4.520	E	2.137	-1.114	-0.22	-0.41	-0.23	-0.42
20. Benzene_dimer (C_{2v})	2.797	D	3.312	-0.519	-0.27	-0.10	-0.19	0.00
21. Indole_Benzene_T-shape (C_1)	5.736	M	4.673	-0.893	-0.21	-0.02	-0.04	0.18
22. Phenol_dimer (C_1)	7.048	M	3.683	-0.606	-1.16	-0.25	-1.06	-0.07
MAD [d]-Tot			**3.48**	**0.75**	**0.38**	**0.21**	**0.32**	**0.31**
MAD-E			**1.77**	**1.12**	**0.51**	**0.28**	**0.46**	**0.33**
MAD-D			**4.17**	**0.25**	**0.21**	**0.17**	**0.17**	**0.25**
MAD-M			**4.75**	**0.83**	**0.39**	**0.16**	**0.32**	**0.36**
MARD [e]-Tot			**78.97**	**13.10**	**9.72**	**6.21**	**8.13**	**6.96**
MARD-E			**17.75**	**11.70**	**7.66**	**3.49**	**7.91**	**4.16**
MARD-D			**156.57**	**11.37**	**14.85**	**12.53**	**10.22**	**11.87**
MARD-M			**71.34**	**16.43**	**6.96**	**3.01**	**6.29**	**5.24**

[a] L. Gráfová, M. Pitoňák, J. Řezáč, P. Hobza, J. Chem. Theory Comput., **2010**, 6, 2365-2376.

[b] Interaction types: E, electrostatics-dominated; D, dispersion-dominated; M, mixed character.

[c] Errors are calculated by (Ref. – Calc.) in kcal/mol.

[d] Mean absolute deviation (MAD)

[e] Mean absolute relative deviation (MARD).

Table S15 Binding energies (kcal/mol) at the 1.2 R_e distorted geometries for the S22 data set: Errors with respect to the S22x5 reference data for the XYG3 and XYGJ-OS methods. Basis sets used are 6-311+G(d,p) (PP1) and 6-311+G(3df,2p) (PP2).

1.2 R_e	Ref	Int.	B3LYP/PP2 [c]		XYG3 [c]		XYGJ-OS [c]	
	S22x5 [a]	Type [b]	-	-D	PP1	PP2	PP1	PP2
Hydrogen bonded complexes (7)								
1. Ammonia_dimer (C_{2h})	2.363	E	0.545	-0.107	-0.296	0.031	-0.370	-0.033
2. Water_dimer (C_s)	4.044	E	0.115	-0.502	-1.074	-0.393	-1.137	-0.437
3. Formic_acid_dimer (C_{2h})	15.624	E	0.635	-1.326	-0.096	-0.586	-0.233	-0.612
4. Formamide_dimer (C_{2h})	13.396	E	1.167	-0.836	0.059	-0.151	-0.106	-0.214
5. Uracil_dimer_hb (C_{2h})	17.158	E	1.685	-0.806	-0.456	-0.114	-0.240	0.210
6. 2-pyridone_2-aminopyridine (C_1)	13.927	E	2.058	-0.822	-0.636	-0.123	-0.582	0.033
7. Adenine_Thymine_WC (C_1)	13.301	E	2.454	-0.615	-0.386	0.004	-0.387	0.120
Complexes with predominant dispersion contribution (8)								
8. Methane_dimer (D_{3d})	0.249	D	0.370	0.084	0.156	0.130	0.108	0.097
9. Ethene_dimer (D_{2d})	0.810	D	0.842	0.116	0.186	0.209	0.129	0.171
10. Benzene_Methane (C_3)	1.128	D	1.146	0.073	0.047	0.132	0.001	0.101
11. Benzene_dimer (C_{2h})	1.917	D	2.580	0.275	-0.173	0.153	-0.112	0.246
12. Pyrazine_dimer (C_s)	3.021	D	2.939	0.373	-0.111	0.249	-0.048	0.375
13. Uracil_dimer_stack (C_2)	6.258	M	3.543	-0.277	-0.471	0.070	-0.221	0.366
14. Indole_Benzene_stack (C_1)	3.312	D	4.126	0.260	-0.281	0.061	-0.077	0.318
15. Adenine_Thymine_stack (C_1)	8.232	M	5.835	-0.051	-0.462	0.326	-0.127	0.745
Mixed complexes (7)								
16. Ethene_Ethyne (C_{2v})	1.084	M	0.417	-0.027	0.011	-0.007	-0.013	-0.014
17. Benzene_Water (C_s)	2.471	M	0.886	-0.300	-0.408	-0.202	-0.475	-0.255
18. Benzene_Ammonia (C_s)	1.746	M	1.108	-0.020	-0.142	0.040	-0.197	-0.003
19. Benzene_HCN (C_s)	3.677	M	1.266	-0.388	-0.300	-0.288	-0.319	-0.307
20. Benzene_dimer (C_{2v})	2.246	D	1.901	-0.051	-0.248	-0.054	-0.216	-0.003
21. Indole_Benzene_T-shape (C_1)	4.877	M	2.849	-0.248	-0.278	-0.001	-0.185	0.112
22. Phenol_dimer (C_1)	5.787	M	2.570	-0.297	-0.904	-0.114	-0.838	0.002
MAD [d]-Tot			**1.87**	**0.36**	**0.33**	**0.16**	**0.28**	**0.22**
MAD-E			**1.24**	**0.72**	**0.43**	**0.20**	**0.43**	**0.24**
MAD-D			**1.99**	**0.18**	**0.17**	**0.14**	**0.10**	**0.19**
MAD-M			**2.31**	**0.20**	**0.37**	**0.13**	**0.30**	**0.23**
MARD [e]-Tot			**58.15**	**8.17**	**10.94**	**6.98**	**8.96**	**7.34**
MARD-E			**11.68**	**6.70**	**7.18**	**2.50**	**7.79**	**2.87**
MARD-D			**113.58**	**13.05**	**17.44**	**15.73**	**11.25**	**14.86**
MARD-M			**50.31**	**5.19**	**8.53**	**3.26**	**7.97**	**4.67**

[a] L. Gráfová, M. Pitoňák, J. Řezáč, P. Hobza, J. Chem. Theory Comput., **2010**, 6, 2365-2376.

[b] Interaction types: E, electrostatics-dominated; D, dispersion-dominated; M, mixed character.

[c] Errors are calculated by (Ref. – Calc.) in kcal/mol.

[d] Mean absolute deviation (MAD)

[e] Mean absolute relative deviation (MARD).

Table S16 Binding energies (kcal/mol) at the 1.5 R_e distorted geometries for the S22 data set: Errors with respect to the S22x5 reference data for the XYG3 and XYGJ-OS methods. Basis sets used are 6-311+G(d,p) (PP1) and 6-311+G(3df,2p) (PP2).

1.5 R_e	Ref	Int.	B3LYP/PP2 [c]		XYG3 [c]		XYGJ-OS [c]	
	S22x5 [a]	Type [b]	-	-D	PP1	PP2	PP1	PP2
Hydrogen bonded complexes (7)								
1. Ammonia_dimer (C_{2h})	1.113	E	0.245	0.053	-0.110	0.046	-0.145	0.015
2. Water_dimer (C_s)	2.294	E	0.086	-0.182	-0.594	-0.171	-0.631	-0.202
3. Formic_acid_dimer (C_{2h})	9.236	E	0.496	-0.871	-0.198	-0.244	-0.281	-0.264
4. Formamide_dimer (C_{2h})	8.104	E	0.673	-0.428	-0.057	-0.014	-0.162	-0.070
5. Uracil_dimer_hb (C_{2h})	10.462	E	0.999	-0.517	-0.418	0.005	-0.301	0.175
6. 2-pyridone_2-aminopyridine (C_1)	8.175	E	1.253	-0.337	-0.458	0.018	-0.451	0.077
7. Adenine_Thymine_WC (C_1)	7.434	E	1.509	-0.200	-0.287	0.103	-0.302	0.143
Complexes with predominant dispersion contribution (8)								
8. Methane_dimer (D_{3d})	0.062	D	0.088	0.015	0.041	0.032	0.033	0.029
9. Ethene_dimer (D_{2d})	0.203	D	0.221	0.044	0.062	0.075	0.053	0.071
10. Benzene_Methane (C_3)	0.484	D	0.493	0.096	0.009	0.109	-0.011	0.097
11. Benzene_dimer (C_{2h})	0.529	D	0.753	0.077	-0.189	0.078	-0.155	0.120
12. Pyrazine_dimer (C_s)	0.982	M	0.875	0.103	-0.208	0.130	-0.171	0.182
13. Uracil_dimer_stack (C_2)	2.421	M	1.020	-0.164	-0.430	0.026	-0.309	0.150
14. Indole_Benzene_stack (C_1)	0.978	D	1.409	0.101	-0.274	0.118	-0.160	0.240
15. Adenine_Thymine_stack (C_1)	3.246	M	1.843	-0.088	-0.510	0.134	-0.367	0.287
Mixed complexes (7)								
16. Ethene_Ethyne (C_{2v})	0.488	M	0.172	0.023	-0.002	0.011	-0.008	0.012
17. Benzene_Water (C_s)	1.298	M	0.362	-0.067	-0.249	-0.094	-0.282	-0.122
18. Benzene_Ammonia (C_s)	0.848	M	0.475	0.061	-0.083	0.056	-0.109	0.036
19. Benzene_HCN (C_s)	2.089	M	0.572	-0.057	-0.206	-0.135	-0.214	-0.145
20. Benzene_dimer (C_{2v})	1.115	D	0.864	0.073	-0.191	0.016	-0.174	0.045
21. Indole_Benzene_T-shape (C_1)	2.802	M	1.371	0.057	-0.290	0.030	-0.249	0.087
22. Phenol_dimer (C_1)	3.407	M	1.482	0.024	-0.529	0.017	-0.493	0.078
MAD [d]-Tot			**0.78**	**0.17**	**0.25**	**0.08**	**0.23**	**0.12**
MAD-E			**0.75**	**0.37**	**0.30**	**0.08**	**0.32**	**0.14**
MAD-D			**0.64**	**0.07**	**0.13**	**0.07**	**0.10**	**0.10**
MAD-M			**0.91**	**0.07**	**0.28**	**0.07**	**0.24**	**0.12**
MARD [e]-Tot			**55.85**	**8.15**	**15.93**	**8.99**	**14.20**	**10.61**
MARD-E			**12.08**	**5.59**	**7.43**	**2.30**	**8.29**	**2.62**
MARD-D			**119.53**	**16.26**	**29.78**	**27.17**	**23.84**	**25.47**
MARD-M			**47.43**	**4.74**	**13.31**	**4.72**	**12.37**	**6.91**

[a] L. Gráfová, M. Pitoňák, J. Řezáč, P. Hobza, J. Chem. Theory Comput., **2010**, 6, 2365-2376.

[b] Interaction types: E, electrostatics-dominated; D, dispersion-dominated; M, mixed character.

[c] Errors are calculated by (Ref. – Calc.) in kcal/mol.

[d] Mean absolute deviation (MAD)

[e] mean absolute relative deviation (MARD).

Table S17 Binding energies (kcal/mol) at the 2.0 R_e distorted geometries for the S22 data set: Errors with respect to the S22x5 reference data for the XYG3 and XYGJ-OS methods. Basis sets used are 6-311+G(d,p) (PP1) and 6-311+G(3df,2p) (PP2).

2.0 Re	Ref	Int.	B3LYP/PP2 [c]		XYG3 [c]		XYGJ-OS [c]	
	S22x5 [a]	Type [b]	-	-D	PP1	PP2	PP1	PP2
Hydrogen bonded complexes (7)								
1. Ammonia_dimer (C_{2h})	0.355	E	0.055	0.016	-0.044	0.009	-0.051	0.004
2. Water_dimer (C_s)	0.961	E	0.054	-0.006	-0.206	-0.031	-0.220	-0.043
3. Formic_acid_dimer (C_{2h})	3.635	E	0.264	-0.126	-0.024	0.001	-0.059	-0.018
4. Formamide_dimer (C_{2h})	3.514	E	0.259	-0.043	-0.004	0.044	-0.051	0.009
5. Uracil_dimer_hb (C_{2h})	4.585	E	0.429	-0.042	-0.130	0.093	-0.075	0.160
6. 2-pyridone_2-aminopyridine (C_1)	3.258	E	0.539	0.050	-0.151	0.083	-0.150	0.097
7. Adenine_Thymine_WC (C_1)	2.592	E	0.656	0.109	-0.135	0.122	-0.141	0.130
Complexes with predominant dispersion contribution (8)								
8. Methane_dimer (D_{3d})	0.010	D	0.011	-0.002	0.009	0.001	0.009	0.002
9. Ethene_dimer (D_{2d})	0.029	M	0.030	0.001	0.018	0.010	0.019	0.013
10. Benzene_Methane (C_3)	0.122	D	0.115	0.013	0.014	0.028	0.017	0.032
11. Benzene_dimer (C_{2h})	0.073	M	0.126	-0.005	-0.002	0.016	0.008	0.028
12. Pyrazine_dimer (C_s)	0.188	M	0.152	-0.003	-0.050	0.015	-0.032	0.035
13. Uracil_dimer_stack (C_2)	0.695	M	0.122	-0.125	-0.196	-0.062	-0.150	-0.017
14. Indole_Benzene_stack (C_1)	0.086	D	0.292	-0.010	-0.045	0.038	0.000	0.086
15. Adenine_Thymine_stack (C_1)	0.923	M	0.311	-0.122	-0.300	-0.049	-0.250	-0.001
Mixed complexes (7)								
16. Ethene_Ethyne (C_{2v})	0.147	M	0.039	0.004	-0.014	-0.002	-0.011	0.003
17. Benzene_Water (C_s)	0.494	M	0.094	-0.013	-0.080	-0.025	-0.083	-0.027
18. Benzene_Ammonia (C_s)	0.277	M	0.116	0.012	-0.009	0.012	-0.010	0.013
19. Benzene_HCN (C_s)	0.849	M	0.146	-0.020	-0.115	-0.058	-0.107	-0.052
20. Benzene_dimer (C_{2v})	0.353	M	0.242	0.012	-0.133	0.002	-0.115	0.021
21. Indole_Benzene_T-shape (C_1)	1.105	M	0.428	0.024	-0.164	0.015	-0.135	0.046
22. Phenol_dimer (C_1)	1.379	M	0.590	0.088	-0.248	0.037	-0.229	0.067
MAD [d]-Tot			**0.23**	**0.04**	**0.10**	**0.03**	**0.09**	**0.04**
MAD-E			**0.32**	**0.06**	**0.06**	**0.05**	**0.07**	**0.07**
MAD-D			**0.14**	**0.01**	**0.02**	**0.02**	**0.02**	**0.04**
MAD-M			**0.20**	**0.04**	**0.11**	**0.03**	**0.09**	**0.03**
MARD [e]-Tot			**58.70**	**5.48**	**21.01**	**8.95**	**18.09**	**13.81**
MARD-E			**12.43**	**2.34**	**6.73**	**2.34**	**7.44**	**2.53**
MARD-D			**180.91**	**12.90**	**50.31**	**26.52**	**33.85**	**49.69**
MARD-M			**55.15**	**5.45**	**22.01**	**8.41**	**20.37**	**11.41**

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