A General Database for Main Group Thermochemistry, Kinetics, and Non-Covalent Interactions – Assessment of Common and Reparameterized (meta-)GGA Density Functionals

Supporting Information

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These Supporting Information contains:

- All reference values of the GMTKN24 database (Tab. S1-S24)
- Information about the parameters fit set (Tab. S25)
- All results for the GMTKN24 database (Tab. S26-S36 and Fig. S1)
- All results for the geometry benchmark sets (Tab. S37-39).

Table S1 - Estimated CCSD(T)/CBS reference data for the MB08-165 database in kcal · mol^{-1}.[a]

#	ref. value	#	ref. value	#	ref. value	#	ref. value	#	ref. value
001	129.0	034	−9.7	067	133.7	100	−98.9	133	107.6
002	10.2	035	−4.9	068	103.7	101	20.5	134	−81.9
003	−64.5	036	−34.4	069	201.2	102	−10.5	135	39.5
004	64.2	037	−199.4	070	62.6	103	−171.7	136	49.2
005	103.3	038	41.7	071	95.3	104	−207.9	137	−6.3
006	94.9	039	25.5	072	148.9	105	−107.3	138	47.5
007	−83.8	040	145.0	073	−37.5	106	−100.9	139	−266.7
008	−87.9	041	273.1	074	17.4	107	−124.8	140	25.4
009	101.9	042	316.1	075	32.6	108	−126.0	141	−114.8
010	73.4	043	31.8	076	65.5	109	−8.5	142	−86.3
011	−69.9	044	3.8	077	91.6	110	−187.0	143	−192.4
012	6.3	045	65.5	078	225.2	111	−362.4	144	179.6
013	−7.7	046	36.6	079	139.5	112	−359.8	145	−173.9
014	212.8	047	49.5	080	37.2	113	45.5	146	−55.0
015	167.8	048	96.3	081	86.8	114	−146.9	147	−68.1
016	70.7	049	93.5	082	−120.4	115	−67.9	148	−259.8
017	93.8	050	62.6	083	−169.0	116	275.2	149	−117.0
018	−2.1	051	88.3	084	−18.3	117	−25.5	150	−119.4
019	79.8	052	−12.7	085	−117.7	118	52.6	151	−225.2
020	315.1	053	48.0	086	6.4	119	241.4	152	59.2
021	145.4	054	16.9	087	−54.5	120	45.2	153	301.7
022	82.0	055	433.7	088	−394.9	121	−59.4	154	−312.7
023	33.4	056	248.5	089	−200.2	122	192.9	155	−72.2
024	166.6	057	65.3	090	−109.0	123	−125.6	156	−77.8
025	−34.8	058	13.2	091	37.7	124	−311.4	157	−240.7
026	−53.9	059	49.8	092	−7.8	125	62.6	158	−164.1
027	−64.3	060	282.1	093	17.4	126	60.0	159	180.4
028	228.3	061	96.9	094	44.6	127	−64.1	160	127.8
029	141.5	062	2.2	095	−341.8	128	−62.2	161	−79.4
030	−5.2	063	331.1	096	−87.7	129	−570.6	162	−64.2
031	199.4	064	−45.4	097	−131.5	130	−192.1	163	−42.5
032	346.8	065	185.4	098	181.6	131	−96.0	164	52.3
033	246.8	066	7.9	099	67.9	132	−37.9	165	−136.6

[a]for more details, see: *J. Chem. Theory Comput.* **2009**, *5*, 993-1003.

Table S2 - W4 (or higher) reference data for the W4-08 database in kcal · mol^{-1}.[a]

	ref. value		ref. value		ref. value		ref. value		ref. value
B_2H_6	607.02	OCS	335.75	C_2H	266.16	Cl_2	59.75	BN[b,d]	105.82
BF_2H	410.97	CS_2	280.78	C_2H_2	405.52	Be_2[b]	2.67	CF	132.72
BF_3	470.97	S_2O	208.78	NH_3	298.02	B_2[b]	67.46	BeF_2	309.10
C_2H_6	713.08	S_3[b]	168.36	C_2[b]	147.02	BH	84.99	CH_2C	359.93
H_2CN	343.75	S_4[b]	234.35	N_2	228.48	BH_3	281.29	CH_2CH	446.08
NCCN	502.04	$BeCl_2$	225.27	CO	259.73	BN[b,c]	105.24	C_2H_4	564.10
CH_2NH_2	482.28	CCl_2	177.36	CN	181.35	BF	182.52	CH_2NH	439.44
CH_3NH	474.63	$AlCl_3$	312.65	NO	152.75	NH	83.10	HCO	279.42
CH_3NH_2	582.30	ClCN	285.45	O_2	120.82	NH_2	182.59	CH_2O	374.66
CF_2	258.78	OClO[b]	128.12	OF[b]	53.08	HCN	313.42	CO_2	390.14
N_2H	224.86	ClOO[b]	126.39	F_2[b]	39.04	HOF	158.65	HNO	205.89
N_2H_2	296.53	Cl_2O[b]	101.46	PH_3	242.27	AlH	73.57	NO_2	227.88
N_2H_4	438.28	H_2	109.49	HS	87.73	AlH_3	213.17	N_2O	270.85
FO_2[b]	134.72	OH	107.21	H_2S	183.91	AlF	163.78	O_3[b]	147.43
FOOF[b]	152.37	HF	141.64	HCl	107.50	AlCl	122.62	HOO	175.53
AlF_3	430.97	H_2O	232.97	SO	126.47	SiH	73.92	H_2O_2	269.09
Si_2H_6	535.89	CH	84.22	ClO	65.45	SiH_4	324.95	F_2O[b]	93.78
P_4	290.58	CH_2	190.74	ClF	62.80	SiO	193.05	HOCl	166.23
SO_2	260.62	CH_3	307.87	P_2	117.59	SiF	142.71	SSH	165.13
SO_3	346.94	CH_4	420.42	S_2	104.25	CS	172.22		

[a]for more details, see: *J. Phys. Chem. A* **2008**, *112*, 12868-12886. [b]Multi-reference case (not included in W4-08woMR). [c] $^1\Sigma^+$ state. [d] $^3\Pi$ state.

Table S3 - Exp. reference data for the G21IP database in kcal · mol^{-1}.[a]

	ref. value		ref. value		ref. value
H	314.9	P	241.9	SH	239.3
Li	123.3	S	239.0	HCl	294.5
Be	214.9	Cl	299.1	C_2H_2	264.6
B	190.4	CH_4	296.3	C_2H_4	243.7
C	259.6	NH_3	235.7	CO	323.0
N	335.3	OH	300.9	N_2	359.4
O	313.8	H_2O	292.6	O_2	277.7
F	401.7	HF	371.3	P_2	242.9
Na	118.5	SiH_4	255.4	S_2	215.7
Mg	176.3	PH	234.1	Cl_2	265.1
Al	138.0	PH_2	226.4	ClF	291.7
Si	188.0	PH_3	227.8	Sc	261.2

[a]for more details, see: *J. Chem. Phys.* **1991**, *94*, 7221-7230.

Table S4 - Exp. reference data for the G21EA database in kcal · mol^{-1}.[a]

	ref. value		ref. value		ref. value
C	29.2	CH_3	1.2	SH	54.2
O	33.7	NH	8.3	O_2	9.5
F	78.4	NH_2	16.8	NO	−0.2
Si	32.1	OH	41.7	CN	89.5
P	17.3	SiH	29.3	PO	24.9
S	48.0	SiH_2	25.1	S_2	38.0
Cl	83.5	SiH_3	31.4	Cl_2	54.7
CH	27.9	PH	23.5		
CH_2	13.4	PH_2	28.8		

[a]for more details, see: *J. Chem. Phys.* **1991**, *94*, 7221-7230.

Table S5 - Est. CCSD(T)/CBS[a] and W1[b] reference data for the PA database in kcal · mol^{-1}.

	ref. value		ref. value
C_2H_4	167.8	C_2H_2	157.4
C_4H_6	193.4	SiH_4	156.8
C_6H_8	209.7	PH_3	192.7
C_8H_10	219.7	H_2S	174.2
NH_3	211.9	HCl	137.8
H_2O	171.6	H_2	106.3

[a]For the polyenes: *J. Phys. Chem. A* **2006**, *110*, 10478-10486. [b]For the other molecules: *J. Chem. Phys.* **2001**, *114*, 6014-6029.

Table S6 - Est. CCSD(T)/CBS reference data for the new SIE11 database in kcal · mol^{-1}.

	reaction	ref. value
1	$He_2^+ \rightarrow He + He^+$	57.44
2	$(NH_3)_2^+ \rightarrow NH_3 + NH_3^+$	35.34
3	$(H_2O)_2^+ \rightarrow H_2O + H_2O^+$	37.25
4	$C_4H_{10}^+ \rightarrow C_2H_5 + C_2H_5^+$	35.28
5	$(CH_3)_2CO^+ \rightarrow CH_3 + CH_3CO^+$	22.57
6	$ClFCl \rightarrow ClClF$	−1.01
7	$C_2H_4 \cdots F_2^a \rightarrow C_2H_4 + F_2$	1.08
8	$C_6H_6 \cdots Li^b \rightarrow Li + C_6H_6$	9.50
9	$NH_3 \cdots ClF^c \rightarrow NH_3 + ClF$	10.50
10	$NaoMg \rightarrow MgO + Na$	69.56
11	$FLiF \rightarrow Li + F_2$	94.36

[a]vdW complex with F_2 being perpendicular to the C-C axis of ethene. [b] Benzene-lithium complex. [c]vdW complex with N, Cl and F being linearly aligned.

Table S7 - W1[a] and CBS-QB3[b] reference data for the BHPERI database in kcal · mol^{-1}.

	reaction	ref. value
1	cyclobutene	35.3
2	*cis*-1,3,5-hexatriene	30.9
3	*o*-xylylene	28.3
4	1,3-pentadiene	39.6
5	1,3-cyclopentadiene	28.2
6	1,5-hexadiene	35.6
7	1,3-butadiene + C_2H_4	22.1
8	1,3-cyclopentadiene + C_2H_4	18.3
9	1,3-cyclopentadiene	9.8
10	*cis*-triscyclopropacyclohexane	23.6
11	N_2O + C_2H_4	26.3
12	N_3H + C_2H_4	18.1
13	N_2CH_2 + C_2H_4	12.2
14	HCNO + C_2H_4	11.1
15	HCNNH + C_2H_4	5.3
16	$HCNCH_2$ + C_2H_4	4.0
17	H_2COHN + C_2H_4	11.5
18	H_2CNHNH + C_2H_4	4.0
19	H_2CNHCH_2+ C_2H_4	−1.4
20	1,3-cyclopentadiene + C_2H_4	15.0
21	cyclo-$C_4H_4SiH_2$ + C_2H_4	13.5
22	furane + C_2H_4	19.8
23	pyrrole + C_2H_4	25.4
24	C_4H_4PH + C_2H_4[c]	18.1
25	C_4H_4PH + C_2H_4[d]	18.2
26	thiophene + C_2H_4	28.1

[a]1-8: *J. Phys. Chem. A* **2008**, *112*, 12868-12886. [b]9-10: *J. Phys. Chem. A* **2003**, *107*, 11445-11459; 11-19: *J. Phys. Chem. A* **2006**, *110*, 2583-2586; 20-26: *J. Phys. Chem. A* **2002**, *106*, 1627-1633. [c]TS of the exo-product. [d]TS of the endo-product.

Table S8 - W1 and theor. est. reference data for the BH76 database in kcal · mol^{-1}.[a]

	reaction	ref. val. (forw.)[b]	ref. val. (rev.)[c]
1	$H + N_2O \rightarrow OH + N_2$	18.14	83.22
2	$H + FH \rightarrow HF + H$	42.18	42.18
3	$H + ClH \rightarrow HCl + H$	18.00	18.00
4	$H + CH_3F \rightarrow HF + CH_3$	30.38	57.02
5	$H + F_2 \rightarrow HF + F$	2.27	106.18
6	$CH_3 + ClF \rightarrow CH_3F + Cl$	7.43	60.17
7	$F^- + CH_3F \rightarrow CH_3F + F^-$	−0.34	−0.34
8	$F^- \cdots CH_3F \rightarrow FCH_3 \cdots F^-$	13.38	13.38
9	$Cl^- + CH_3Cl \rightarrow CH_3Cl + Cl^-$	3.10	3.10
10	$Cl^- \cdots CH_3Cl \rightarrow ClCH_3 \cdots Cl^-$	13.61	13.61
11	$F^- + CH_3Cl \rightarrow Cl^- + CH_3F$	−12.54	20.11
12	$F^- \cdots CH_3Cl \rightarrow FCH_3 \cdots Cl^-$	2.89	29.62
13	$OH^- + CH_3F \rightarrow CH_3OH + F^-$	−2.78	17.33
14	$OH^- \cdots CH_3F \rightarrow HOCH_3 \cdots F^-$	10.96	47.20
15	$H + N_2 \rightarrow HN_2$	14.69	10.72
16	$H + CO \rightarrow HCO$	3.17	22.68
17	$F + C_2H_4 \rightarrow C_2H_5$	1.72	41.75
18	$CH_3 + C_2H_4 \rightarrow C_3H_7$	6.85	32.97
19	$HNC \rightarrow HCN$	48.16	33.11
20	$H + HCl \rightarrow H_2 + Cl$	5.7	8.7
21	$OH + H_2 \rightarrow H_2O + H$	5.1	21.2
22	$CH_3 + H_2 \rightarrow CH_4 + H$	12.1	15.3
23	$OH + CH_4 \rightarrow H_2O + CH_3$	6.7	19.6
24	$H + H_2 \rightarrow H_2 + H$	9.6	9.6
25	$OH + NH_3 \rightarrow H_2O + NH_2$	3.2	12.7
26	$HCl + CH_3 \rightarrow Cl + CH_4$	1.7	7.9
27	$OH + C_2H_6 \rightarrow H_2O + C_2H_5$	3.4	19.9
28	$F + H_2 \rightarrow HF + H$	1.8	33.4
29	$O + CH_4 \rightarrow OH + CH_3$	13.7	8.1
30	$H + PH_3 \rightarrow H_2 + PH_2$	3.1	23.2
31	$H + OH \rightarrow H_2 + O$	10.7	13.1
32	$H + H_2S \rightarrow H_2 + HS$	3.5	17.3
33	$O + HCl \rightarrow OH + Cl$	9.8	10.4
34	$NH_2 + CH_3 \rightarrow NH + CH_4$	8.0	22.4
35	$NH_2 + C_2H_5 \rightarrow NH\ C_2H_6$	7.5	18.3
36	$C_2H_6 + NH_2 \rightarrow C_2H_5 + NH_3$	10.4	17.4
37	$NH_2 + CH_4 \rightarrow NH_3 + CH_3$	14.5	17.8
38	$s-$trans$-$cis$-C_5H_8 \rightarrow$ *s-trans-cis*-C_5H_8	38.4	38.4

[a]1-19: *J. Phys. Chem. A* **2005**, *109*, 2012-2018; 20-38: *J. Phys. Chem. A* **2004**, *108*, 2715-2719. [b]Forward barrier height. [c]Reverse barrier height.

Table S9 - W1 and theor. est. reference data for the BH76RC database in kcal · mol^{-1}.[a]

	reaction	ref. value
1	$H + N_2O \rightarrow OH + N_2$	−65.1
2	$H + CH_3F \rightarrow HF + CH_3$	−26.6
3	$H + F_2 \rightarrow HF + F$	−103.9
4	$CH_3 + ClF \rightarrow CH_3F + Cl$	−52.7
5	$F^- + CH_3Cl \rightarrow Cl^- + CH_3F$	−32.7
6	$F^- \cdots CH_3Cl \rightarrow FCH_3 \cdots Cl^-$	−26.7
7	$OH^- + CH_3F \rightarrow CH_3OH + F^-$	−20.1
8	$OH^- \cdots CH_3F \rightarrow HOCH_3 \cdots F^-$	−36.2
9	$H + N_2 \rightarrow HN_2$	4.0
10	$H + CO \rightarrow HCO$	−19.5
11	$F + C_2H_4 \rightarrow C_2H_5$	−40.0
12	$CH_3 + C_2H_4 \rightarrow C_3H_7$	−26.1
13	$HNC \rightarrow HCN$	−15.1
14	$H + HCl \rightarrow H_2 + Cl$	−3.0
15	$OH + H_2 \rightarrow H_2O + H$	−16.1
16	$CH_3 + H_2 \rightarrow CH_4 + H$	−3.2
17	$OH + CH_4 \rightarrow H_2O + CH_3$	−12.9
18	$OH + NH_3 \rightarrow H_2O + NH_2$	−9.5
19	$HCl + CH_3 \rightarrow Cl + CH_4$	−6.2
20	$OH + C_2H_6 \rightarrow H_2O + C_2H_5$	−16.5
21	$F + H_2 \rightarrow HF + H$	−31.6
22	$O + CH_4 \rightarrow OH + CH_3$	5.6
23	$H + PH_3 \rightarrow H_2 + PH_2$	−20.1
24	$H + OH \rightarrow H_2 + O$	−2.4
25	$H + H_2S \rightarrow H_2 + HS$	−13.8
26	$O + HCl \rightarrow OH + Cl$	−0.6
27	$NH_2 + CH_3 \rightarrow NH + CH_4$	−14.4
28	$NH_2 + C_2H_5 \rightarrow NH\ C_2H_6$	−10.8
29	$C_2H_6 + NH_2 \rightarrow C_2H_5 + NH_3$	−7.0
30	$NH_2 + CH_4 \rightarrow NH_3 + CH_3$	−3.3

[a] 1-13: *J. Phys. Chem. A* **2005**, *109*, 2012-2018; 14-30: *J. Phys. Chem. A* **2004**, *108*, 2715-2719.

Table S10 - Est. CCSD(T)/CBS reference data for the RSE43 database in kcal · mol^{-1}.[a]

Radical	ref. value[b]	Radical	ref. value	Radical	ref. value
$(C_6H_5)CH_2$	−15.2	CH_2COOH	−6.4	$PH_3CH_2^+$	0.7
CH_2CCN	1.9	$(CH_2CHCH_2)CH_2$	−3.0	CH_3SCH_2	−10.8
CH_2CF	6.8	CH_2F	−3.9	CH_2SCHO	−8.4
CCl_3CH_2	7.0	CH_2NH_2	−12.0	$CH_2SH_2^+$	2.7
$CH_3CF_2CH_2$	0.1	$CH_2NH_3^+$	4.7	CH_2SH	−9.4
CF_3CH_2	1.4	CH_3NHCH_2	−12.6	$CH_3SO_2CH_2$	0.0
CH_2ClCH_2	−3.2	CH_2NHCHO	−11.1	CH_3SOCH_2	−2.9
CH_2FCH_2	−1.3	CH_2NHOH	−8.6	H_2NCHCN	−22.5
$HOCH_2CH_2$	−1.8	$(CH_3)_2NCH_2$	−12.8	$H_2NCHCONH_2$	−24.1
CH_2CHCH_2	−17.5	CH_2NO_2	−3.3	$H_2NCHCOOH$	−25.4
CH_2CHO	−10.0	CF_3OCH_2	−3.9	H_2CCCH	−13.1
CH_2CN	−8.6	CH_3OCH_2	−2.7	$(CH_3)_3C$	−6.4
CH_2CONH_2	−6.3	CH_2OCHO	−5.9	$(CH_3)_3CCH_2$	−2.3
$CH_3NHCOCH_2$	−6.3	CH_3COOCH_2	−6.2		
CH_2COOCH_3	−6.6	CH_2OH	−4.2		

[a]for more details, see: *J. Chem. Theory Comput.* **2009**, DOI: 10.1021/ct9003299. [b] Radical stabilization energy defined as: RH + CH_3 → R + CH_4.

Table S11 - Est. CCSD(T)/CBS reference data for the O3ADD6 database in kcal · mol^{-1}.[a]

	reaction	ref. value
1	$O_3 + C_2H_2 \rightarrow (O_3\text{-}C_2H_2)^b_{vdW}$	−1.90
2	$O_3 + C_2H_2 \rightarrow (O_3\text{-}C_2H_2)^c_{TS}$	7.74
3	$O_3 + C_2H_2 \rightarrow (O_3\text{-}C_2H_2)^d_{add}$	−63.80
4	$O_3 + C_2H_4 \rightarrow (O_3\text{-}C_2H_4)^b_{vdW}$	−1.94
5	$O_3 + C_2H_4 \rightarrow (O_3\text{-}C_2H_4)^c_{TS}$	3.37
6	$O_3 + C_2H_4 \rightarrow (O_3\text{-}C_2H_4)^d_{add}$	−57.15

[a] *J. Phys. Chem. A* **2009**, *113*, 5786-5799. [b] vdW complex. [c]Transition state. [d]Primary ozonide.

Table S12 - Exp. reference data for the G2RC database in kcal · mol^{-1}.[a]

	reaction	ref. value
1	$(CH_3)_2SO \rightarrow C_2H_4S + H_2O$	−1.0
2	$CO_2 + H_2 \rightarrow HCOOH$	−2.0
3	$CH_3CHO \rightarrow CO + CH_4$	−2.6
4	$Si_2H_6 + H_2 \rightarrow 2SiH_4$	−3.9
5	$CO + H_2O \rightarrow CO_2 + H_2$	−7.0
6	$CH_3COCl + H_2O \rightarrow CH_3COOH + HCl$	−10.0
7	$CH_3CN + H_2O \rightarrow CH_3CONH_2$	−20.1
8	$C_2H_2 + HF \rightarrow CH_2CHF$	−25.4
9	$F_2 + Cl_2 \rightarrow 2ClF$	−26.4
10	$BCl_3 + AlF_3 \rightarrow BF_3 + AlCl_3$	−26.9
11	$SiCl_4 + CF_4 \rightarrow SIF_4 + CCl_4$	−26.3
12	$H_2CO + H_2 \rightarrow CH_3OH$	−29.2
13	$C_2H_2 + C_2H_4 \rightarrow C_4H_8$	−32.7
14	$SiO + 3H_2 \rightarrow SiH_4 + H_2O$	−33.9
15	$N_2 + 3H_2 \rightarrow 2NH_3$	−38.9
16	$CH_4 + 2Cl_2 \rightarrow CH_2Cl_2 + 2HCl$	−47.1
17	$C_2H_2 + H_2 \rightarrow C_2H_4$	−48.4
18	$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O$	−60.5
19	$CO + 3H_2 \rightarrow H_2O + CH_4$	−64.8
20	$OF_2 + H_2 \rightarrow F_2 + H_2O$	−68.7
21	$N_2O + H_2 \rightarrow N_2 + H_2O$	−80.7
22	$C_2H_4 + CH_2 \rightarrow C_3H_6$	−109.1
23	$H_2 + F_2 \rightarrow 2HF$	−134.3
24	$3C_2H_2 \rightarrow C_6H_6$	−151.6
25	$Li_2 + F_2 \rightarrow 2LiF$	−212.7

[a]Systems and data are taken from the G2/97 set: *J. Chem. Phys.* **1997**, *106*, 1063-1079.

Table S13 - Exp. reference data for the AL2X database in kcal · mol^{-1}.[a]

	reaction	ref. value
1	$Al_2H_6 \rightarrow 2AlH_3$	35.8
2	$Al_2F_6 \rightarrow 2AlF_3$	52.6
3	$Al_2Cl_6 \rightarrow 2AlCl_3$	31.4
4	$Al_2Br_6 \rightarrow 2AlBr_3$	28.4
5	$Al_2(CH_3)_4 \rightarrow 2Al(CH_3)_2$	37.8
6	$Al_2(CH_3)_5 \rightarrow Al(CH_3)_2 + Al(CH_3)_3$	30.0
7	$Al_2(CH_3)_6 \rightarrow 2Al(CH_3)_3$	21.4

[a]for more details, see: *J. Chem. Phys.* **2008**, *129*, 204112.

Table S14 - Est. CCSD(T)/CBS reference data for the new NBRC database in kcal · mol^{-1}.

	reaction	ref. value
1	$NH_3 + BH_3 \rightarrow NH_3BH_3$	−31.8
2	$NH_3BH_3 \rightarrow NH_2BH_2 + H_2$	−0.1
3	$NH_2BH_2 \rightarrow NHBH + H_2$	37.3
4	$2NH_2BH_2 \rightarrow (NH_2BH_2)_2$	−18.9
5	$3NH_2BH_2 \rightarrow (NHBH)_3 + 3H_2$	−48.3
6	$3NH_2BH_2 \rightarrow (NH_2BH_2)_3$	−45.1

Table S15 - Exp. reference data for the ISO34 database in kcal · mol^{-1}.[a]

#	ref. value	#	ref. value	#	ref. value	#	ref. value	#	ref. value
1	1.6	8	22.9	15	7.3	22	3.2	29	11.9
2	21.9	9	6.9	16	10.8	23	5.3	30	9.5
3	7.2	10	3.6	17	27.0	24	12.5	31	14.0
4	1.0	11	1.9	18	11.2	25	26.5	32	7.1
5	0.9	12	46.9	19	4.6	26	18.2	33	5.6
6	2.6	13	36.0	20	20.2	27	64.2	34	7.3
7	11.1	14	24.2	21	0.9	28	31.2		

[a]for more details, see: *J. Org. Chem.* **2007**, *72*, 2118-2120.

Table S16 - Reference data for the DC9 database in kcal · mol^{-1}.

	reaction	ref. value
1	2-pyridone → 2-hydroxypyridine[a]	−1.0
2	$(C_{20})_{cage} \rightarrow (C_{20})^b_{bowl}$	−13.3
3	hepta-1,2,3,5,6-hexaene → hepta-1,3,5-triyne[c]	−14.3
4	2 tetramethyl-ethen → octamethylcylobutane[d]	−19.2
5	$(CH)_{12}$ isomerization[e]	−19.5
6	isomerization of carbo-[3]-oxacarbon[f]	−26.9
7	$N_2CH_2 + C_2H_4 \rightarrow (CH_2)_3N^g_2$	−38.1
8	$4Be \rightarrow Be^h_4$	−88.4
9	$4S_2 \rightarrow S^i_8$	−101.0

[a]for more details, see: *J. Comput. Chem.* **2004**, *25*, 83-99. [b]New est. CCSD(T)/CBS. [c]for more details, see: *J. Phys. Chem. A* **2002**, *106*, 11923-11931. [d]SCS-MP2/TZVPP. [e]Isomers '1' and '31' in *Org. Lett.* **2006**, *8*, 3635-3638. [f]Reaction taken from *J. Phys. Chem. A* **2007**, *111*, 136-149. Ref. value calculated for this work: est. QCISD(T)/CBS. [g]for more details, see: *J. Phys. Chem. A* **2006**, *110*, 2583-2586. [h]for more details, see: *J. Phys. Chem. A* **2005**, *109*, 11927-11932. [i]for more details, see: *J. Chem. Phys.* **2006**, *124*, 034108.

Table S17 - Est. CCSD(T)/CBS reference data for the DARC database in kcal · mol^{-1}.[a]

	reaction	ref. value
1	ethene + butadiene	−43.8
2	ethyne + butadiene	−59.3
3	ethene + cyclopentadiene	−30.0
4	ethyne + cyclopentadiene	−33.1
5	ethene + cyclohexadiene	−36.5
6	ethyne + cyclohexadiene	−48.2
7	furane + maleine (endo-product)	−14.4
8	furane + maleine (exo-product)	−16.2
9	furane + maleinimide (endo-product)	−17.2
10	furane + maleinimide (exo-product)	−19.2
11	cyclopentadiene + maleine (endo-product)	−31.6
12	cyclopentadiene + maleine (exo-product)	−32.1
13	cyclopentadiene + maleinimide (endo-product)	−34.1
14	cyclopentadiene + maleinimide (exo-product)	−34.4

[a]for more details, see: *J. Chem. Phys.* **2008**, *129*, 204112.

Table S18 - Reference data for the IDISP database in kcal · mol^{-1}.

	reaction	ref. value
1	2 anthracene → anthracene dimer[a]	−9.0
2	2 *p*-xylene → [2.2]-paracyclophane + $2H_2$[a]	−58.5
3	n-octane → iso-octane[b]	−1.9
4	$(C_{14}H_{30})_{folded} \rightarrow (C_{14}H_{30})^a_{linear}$	9.4
5	$(C_{22}H_{46})_{folded} \rightarrow (C_{22}H_{46})^a_{linear}$	−2.2
6	n-undecane → 2,2,3,3,4,4-hexamethyl-pentane[c]	3.6

[a]for more details, see: *Phys. Chem. Chem. Phys.* **2007**, *9*, 3397-3406. [b]for more details, see: *J. Org. Chem.* **2007**, *72*, 2118-2120. [c]for more details, see: *Angew. Chem. Int. Ed.* **2006**, *45*, 4460-4464.

Table S19 - Est. CCSD(T)/CBS and MP2/CBS reference data for the WATER27 database in kcal · mol^{-1}.[a]

Radical	ref. value[b]	Radical	ref. value	Radical	ref. value
$(H_2O)_2$	5.01	$(H_2O)_{8\ \text{cube}}$ (S_4)	72.6	$H_3O^+(H_2O)_2$ ($2D$)	114.9
$(H_2O)_{3\ \text{cyclic}}$	15.8	$(H_2O)_20_{\ \text{dodecahedron}}$	200.1	$OH^-(H_2O)$	26.6
$(H_2O)_{4\ \text{cyclic}}$	27.4	$(H_2O)_20_{\ \text{fused cubes}}$	212.6	$OH^-(H_2O)_2$	48.4
$(H_2O)_{5\ \text{cyclic}}$	35.9	$(H_2O)_20_{\ \text{face−sharing}}$	215.0	$OH^-(H_2O)_3$	67.6
$(H_2O)_{6\ \text{prism}}$	46.0	$(H_2O)_20_{\ \text{edge−sharing}}$	217.9	$OH^-(H_2O)_4$ (C_4)	84.8
$(H_2O)_{6\ \text{cage}}$	45.8	$H_3O^+(H_2O)$	33.5	$OH^-(H_2O)_4$ (C_s)	84.8
$(H_2O)_{6\ \text{book}}$	45.3	$H_3O^+(H_2O)_2$	56.9	$OH^-(H_2O)_5$	100.7
$(H_2O)_{6\ \text{cyclic}}$	44.3	$H_3O^+(H_2O)_3$	76.5	$OH^-(H_2O)_6$	115.7
$(H_2O)_{8\ \text{cube}}$ (D_{2d})	72.6	$H_3O^+(H_2O)_6$ ($3D$)	117.8	$(H_2O)_{8\ \text{cube}}$ (S_4) − $H_3O^+(H_2O)_6OH^-$	28.5

[a] Decomposition energies into fragments execpt for the last entry; for more details, see: *J. Chem. Theory Comput.* **2009**, *5*, 1016-1026.

Table S20 - Est. CCSD(T)/CBS reference data for the S22 database in kcal · mol^{-1}.[a]

	ref. value		ref. value
$(NH_3)_2$	3.17	pyrazine dimer	4.42
$(H_2O)_2$	5.02	uracil dimer (C_2)	10.12
formic acid dimer	18.61	indole · benzene	5.22
formamide dimer	15.96	adenine · thymine (stack)	12.23
uracil dimer (C_{2h})	20.65	ethene · ethyne	1.53
2-pyridoxine · 2-aminopyridine	16.71	benzene · H_2O	3.28
adenine · thymine	16.37	benzene · NH_3	2.35
$(CH_4)_2$	0.53	benzene · HCN	4.46
$(C_2H_4)_2$	1.51	benzene dimer (C_{2v})	2.74
benzene · CH_4	1.50	indole · benzene (T-shape)	5.73
benzene dimer (C_{2h})	2.73	phenol dimer	7.05

[a]Binding energies; for more details, see: *Phys. Chem. Chem. Phys.* **2006**, *8*, 1985-1993.

Table S21 - Est. CCSD(T)/CBS reference data for the PCONF database in kcal · mol^{-1}.[a]

	ref. value		ref. value
FGG_444	0.14	FGG_114	1.87
FGG_357	0.90	FGG_412	2.37
FGG_366	1.15	FGG_691	2.07
FGG_215	0.79	FGG_470	2.51
FGG_300	1.31	FGG_224	2.04

[a]Relative energies compared to FGG_99 in 'Set 3' of *Chem. Eur. J.* **2005**, *11*, 6803-6817.

Table S22 - W1h-val reference data for the ACONF database in kcal · mol^{-1}.[a]

	ref. value		ref. value
B_g[b]	0.598	H_g+t+g−[d]	1.302
P_tg[c]	0.614	H_ggg[d]	1.250
P_gg[c]	0.961	H_g+x−t+[d]	2.632
P_gx[c]	2.813	H_t+g+x−[d]	2.740
H_gtt[d]	0.595	H_g+x−g−[d]	3.283
H_tgt[d]	0.604	H_x+g−g−[d]	3.083
H_tgg[d]	0.934	H_x+g−x+[d]	4.925
H_gtg[d]	1.178		

[a]B = n-butane; P = n-pentane; H = n-hexane; g = gauche; t = trans ; x = perpendicular; '±' indicates the direction of rotation; for more details, see: *J. Phys. Chem. A* **2009**, DOI: 10.1021/jp903640h. [b]Relative energy compared to B_t. [c]Relative energy compared to P_tt. [d]Relative energy compared to H_ttt.

Table S23 - Est. CCSD(T)/CBS reference data for the SCONF database in kcal · mol^{-1}.

	ref. value		ref. value
C2[a]	0.83	C11[a]	6.08
C3[a]	2.60	C12[a]	6.05
C4[a]	3.37	C13[a]	6.17
C5[a]	4.87	C14[a]	6.75
C6[a]	5.18	C15[a]	6.71
C7[a]	4.47	G2[b]	0.27
C8[a]	4.68	G3[b]	5.92
C9[a]	6.69	G4[b]	5.29
C10[a]	6.75		

[a]Relative energy compared to the C1 conformer of the AnGol15 set (*J. Chem. Theory Comput.* **2009**, *5*, 679-692.); est. CCSD(T)/CBS reference values were recalculated for this work. [b]Relative energy compared to the G1 conformer of the GLC4 set (*J. Chem. Theory Comput.* **2009**, *5*, 679-692.); new est. CCSD(T)/CBS reference values were provided by G. I. Csonka in a private communication.

Table S24 - Est. CCSD(T)/CBS reference data for the CYCONF database in kcal · mol^{-1}.[a]

	ref. value		ref. value
2	1.522	7	1.933
3	1.609	8	2.177
4	1.948	9	2.359
5	1.795	10	2.562
6	2.098	11	2.674

[a]Relative energy compared to conformer '1' in *J. Chem. Theory Comput.* **2009**, *5*, 1511-1523.

Table S25 - All entries of the parameters fit set and their weight factors for the determination of the root mean square deviations.

system	factor	system	factor	system	factor	system	factor
atomization energies[a]		H_2O_2	1.00	**electron affinities**[c]		MB039	1.00
H_2	1.00	F_2	1.00	C→C^-	1.00	MB044	1.00
LiH	1.00	CO_2	1.00	O→O^-	1.00	MB045	1.00
BeH	1.00	Na_2	1.00	F→F^-	1.00	MB046	1.00
CH	1.00	Si_2	1.00	Si→Si^-	1.00	MB047	1.00
CH_2 ($^3B_1$)	1.00	P_2	1.00	P→P^-	1.00	MB049	1.00
CH_2 ($^1A_1$)	1.00	S_2	1.00	S→S^-	1.00	MB055	1.00
CH_3	1.00	Cl_2	1.00	Cl→Cl^-	1.00	MB056	1.00
CH_4	1.00	C_4H_8	1.00	**isomerization energy**[d]		MB062	1.00
NH	1.00	C_6H_6	1.00	iso-octane → n-octane	5.00	MB067	1.00
NH_2	1.00	adamantane	1.00	**non-covalently bound dimers**[e]		MB072	1.00
NH_3	1.00	anthracene	1.00	$(H_2COOH)_2$	20.00	MB074	1.00
OH	1.00	**atomic energies**[b]		$(NH_3)_2$	20.00	MB078	1.00
H_2O	1.00	H	0.50	$(H_2O)_2$	20.00	MB079	1.00
HF	1.00	Li	0.10	$(CH_4)_2$	20.00	MB086	1.00
SiH_2 ($^1A_1$)	1.00	Be	0.10	$(C_2H_4)_2$	30.00	MB087	1.00
SiH_2 ($^3B_1$)	1.00	B	0.10	**decomposition energies**[f]		MB090	1.00
SiH_3	1.00	C	0.50	MB001	1.00	MB098	1.00
SiH_4	1.00	N	0.50	MB003	1.00	MB099	1.00
PH_2	1.00	O	0.50	MB004	1.00	MB100	1.00
PH_3	1.00	F	0.50	MB005	1.00	MB101	1.00
H_2S	1.00	Na	0.05	MB006	1.00	MB105	1.00
HCl	1.00	Mg	.0.05	MB009	1.00	MB109	1.00
Li_2	1.00	Al	0.05	MB010	1.00	MB115	1.00
LiF	1.00	Si	0.05	MB011	1.00	MB117	1.00
C_2H_2	1.00	P	0.05	MB012	1.00	MB118	1.00
C_2H_4	1.00	S	0.05	MB013	1.00	MB120	1.00
C_2H_6	1.00	Cl	0.05	MB015	1.00	MB121	1.00
CN	1.00	**ionization potentials**[c]		MB016	1.00	MB126	1.00
HCN	1.00	C→C^+	1.00	MB018	1.00	MB128	1.00
CO	1.00	N→N^+	1.00	MB019	1.00	MB146	1.00
HCO	1.00	O→O^+	1.00	MB021	1.00	MB151	1.00
H_2CO	1.00	F→F^+	1.00	MB023	1.00	MB158	1.00
H_3COH	1.00	Si→Si^+	1.00	MB031	1.00	MB159	1.00
N_2	1.00	P→P^+	1.00	MB032	1.00	MB161	1.00
N_2H_4	1.00	S→S^+	1.00	MB035	1.00	MB162	1.00
NO	1.00	Cl→Cl^+	1.00	MB036	1.00	MB163	1.00
O_2	1.00			MB037	1.00		

[a]Taken from the G2/97 set (*J. Chem. Phys.* **1997**, *106*, 1063-1079.) and "NIST Standard Reference Database" (http://webbook.nist.gov/chemistry/). [b] *Phys. Rev. A* **1991**, *44*, 7071-7083. [c] Taken from the G2-1 set (*J. Chem. Phys.* **1991**, *94*, 7221-7230.). [d]Taken from the ISO34 set (*J. Org. Chem.* **2007**, *72*, 2118-2126.). [e]Taken from the S22 set (*Phys. Chem. Chem. Phys.* **2006**, *8*, 1985-1993.). [f]Taken from the MB08-165 database (*J. Chem. Theory Comput.* **2009**, *5*, 993-1003.).

Table S26 - Mean absolute deviations of the complete GMTKN24 database for the original and reoptimized BLYP versions with and without dispersion correction. All values are in kcal · mol^{-1} and were obtained with the (aug-)def2-QZVP basis.

	BLYP	BLYP-D^a	oBLYP	oBLYP-D^b
MB08-165	11.1	9.2	9.1	8.2
W4-08	6.9	6.9	8.1	8.1
W4-08woMR	5.8	5.7	6.7	6.7
G21IP	4.7	4.7	4.6	4.6
G21EA	3.3	3.3	3.3	3.3
PA	2.5	2.8	2.3	2.4
SIE11	11.7	12.2	12.3	12.7
BHPERI	5.8	2.5	4.6	2.6
BH76	8.4	9.2	9.2	9.7
BH76RC	3.3	3.1	3.4	3.2
RSE43	3.5	2.9	3.6	3.1
O3ADD6	6.0	6.6	5.5	6.1
G2RC	5.5	5.1	4.5	4.4
AL2X	11.4	5.9	9.3	5.2
NBRC	9.5	5.3	7.2	4.6
ISO34	3.2	2.5	2.9	2.3
DC9	20.3	14.5	18.2	13.8
DARC	22.9	14.0	19.3	13.3
IDISP	20.7	4.7	18.0	4.1
WATER27	9.9	3.8	4.1	6.9
S22	4.81	0.29	3.84	0.45
PCONF	4.84	1.08	4.34	1.24
ACONF	1.08	0.69	0.87	0.43
SCONF	0.89	0.56	0.55	0.52
CYCONF	0.65	0.45	0.59	0.54

^{a} $s_6 = 1.20$; $r_{scal}^{vdW} = 1.1$. ^{b} $s_6 = 1.00$; $r_{scal}^{vdW} = 1.15$.

Table S27 - Root mean square deviations of the complete GMTKN24 database for the original and reoptimized BLYP versions with and without dispersion correction. All values are in kcal · mol^{-1} and were obtained with the (aug-)def2-QZVP basis.

	BLYP	BLYP-D^a	oBLYP	oBLYP-D^b
MB08-165	14.4	12.1	11.9	10.8
W4-08	10.0	10.0	11.4	11.4
W4-08woMR	8.1	8.0	9.1	9.1
G21IP	5.6	5.6	5.5	5.5
G21EA	3.9	3.9	4.0	3.9
PA	3.4	3.8	3.1	3.2
SIE11	15.6	16.0	15.9	16.2
BHPERI	6.8	3.5	5.3	3.4
BH76	9.6	10.3	10.4	10.8
BH76RC	4.5	4.4	4.7	4.7
RSE43	4.1	3.5	4.1	3.6
O3ADD6	7.7	7.7	6.8	6.9
G2RC	6.8	6.3	5.9	5.7
AL2X	12.0	6.2	9.9	5.7
NBRC	11.8	6.3	9.3	5.7
ISO34	4.4	3.5	3.9	3.3
DC9	24.5	17.3	21.2	16.1
DARC	23.3	14.2	19.8	13.5
IDISP	24.1	7.9	21.1	8.3
WATER27	16.0	4.8	7.2	8.8
S22	6.07	0.38	5.08	0.57
PCONF	5.15	1.28	4.58	1.40
ACONF	1.20	0.78	0.98	0.51
SCONF	1.08	0.98	0.68	0.89
CYCONF	0.72	0.50	0.63	0.61

[a] $s_6 = 1.20$; $r_{scal}^{vdW} = 1.1$. [b] $s_6 = 1.00$; $r_{scal}^{vdW} = 1.15$.

Table S28 - Mean absolute deviations of the complete GMTKN24 database for the mPWLYP and oPWLYP methods with and without dispersion correction. All values are in kcal · mol^{-1} and were obtained with the (aug)-def2-QZVP basis.

	mPWLYP	mPWLYP-D^a	oPWLYP	oPWLYP-D^b
MB08-165	8.9	8.0	9.1	8.2
W4-08	8.7	8.8	8.1	8.1
W4-08woMR	7.3	7.4	6.6	6.6
G21IP	4.4	4.4	4.5	4.5
G21EA	3.6	3.6	3.3	3.3
PA	2.5	2.5	2.3	2.4
SIE11	12.4	12.7	12.3	12.7
BHPERI	4.7	2.7	4.5	2.7
BH76	9.3	9.9	9.2	9.7
BH76RC	3.4	3.2	3.3	3.2
RSE43	3.6	3.1	3.6	3.1
O3ADD6	5.9	6.6	5.5	6.1
G2RC	4.8	4.6	4.5	4.4
AL2X	9.5	5.4	9.3	5.2
NBRC	7.9	4.8	7.2	4.6
ISO34	3.1	2.5	2.9	2.3
DC9	19.3	14.9	18.2	13.8
DARC	20.7	14.0	19.3	13.3
IDISP	18.5	4.5	18.00	4.1
WATER27	3.0	9.1	4.1	7.0
S22	3.41	0.60	3.84	0.46
PCONF	4.20	1.38	4.34	1.24
ACONF	0.88	0.45	0.87	0.44
SCONF	0.67	0.47	0.54	0.54
CYCONF	0.59	0.44	0.59	0.54

^{a} $s_6 = 0.90$; $r_{scal}^{vdW} = 1.1$. ^{b} $s_6 = 1.00$; $r_{scal}^{vdW} = 1.15$.

Table S29 - Root mean square deviations of the complete GMTKN24 database for the mPWLYP and oPWLYP methods with and without dispersion correction. All values are in kcal · mol^{-1} and were obtained with the (aug-)def2-QZVP basis.

	mPWLYP	mPWLYP-D^a	oPWLYP	oPWLYP-D^b
MB08-165	11.7	10.5	11.9	10.8
W4-08	12.0	12.0	11.3	11.3
W4-08woMR	9.8	9.9	9.0	9.0
G21IP	5.4	5.4	5.4	5.4
G21EA	4.5	4.5	4.0	4.0
PA	3.1	3.3	3.0	3.2
SIE11	16.2	16.5	15.9	16.2
BHPERI	5.6	3.6	5.3	3.5
BH76	10.5	11.1	10.4	10.8
BH76RC	4.7	4.6	4.7	4.6
RSE43	4.1	3.7	4.1	3.6
O3ADD6	7.1	7.4	6.8	6.9
G2RC	6.1	5.9	5.9	5.7
AL2X	10.1	5.8	9.9	5.7
NBRC	10.0	5.9	9.2	5.6
ISO34	4.2	3.5	3.9	3.3
DC9	22.9	17.5	21.2	16.1
DARC	21.1	14.2	19.7	13.5
IDISP	21.7	8.9	21.1	8.3
WATER27	4.7	12.0	7.1	9.0
S22	4.66	0.72	5.08	0.57
PCONF	4.45	1.50	4.58	1.40
ACONF	0.99	0.52	0.97	0.51
SCONF	0.84	0.84	0.66	0.91
CYCONF	0.63	0.47	0.63	0.62

^{a} $s_6 = 0.90$; $r_{scal}^{vdW} = 1.1$. ^{b} $s_6 = 1.00$; $r_{scal}^{vdW} = 1.15$.

Table S30 - Mean absolute deviations of the complete GMTKN24 database for the original and reoptimized PBE versions with and without dispersion correction. All values are in kcal · mol^{-1} and were obtained with the (aug-)def2-QZVP basis.

	PBE	PBE-D^a	oPBE	oPBE-D^b
MB08-165	9.0	9.9	9.5	9.2
W4-08	12.9	13.0	7.4	7.4
W4-08woMR	11.0	11.2	6.1	6.0
G21IP	3.9	3.9	3.9	3.9
G21EA	3.4	3.4	4.8	4.8
PA	2.1	2.4	3.3	3.6
SIE11	12.0	12.6	10.9	11.4
BHPERI	2.9	5.7	3.9	2.4
BH76	9.2	9.8	7.8	8.3
BH76RC	4.3	4.4	3.2	3.1
RSE43	3.4	3.0	3.1	2.6
O3ADD6	4.4	5.0	5.2	5.4
G2RC	6.2	6.7	4.4	4.7
AL2X	4.2	2.4	7.9	3.9
NBRC	2.6	3.1	5.4	2.8
ISO34	1.8	1.5	2.2	1.7
DC9	10.8	9.9	14.5	10.2
DARC	6.8	2.8	14.2	8.2
IDISP	12.3	2.0	17.9	3.9
WATER27	3.2	10.0	12.1	2.8
S22	2.61	0.66	4.50	0.70
PCONF	3.94	1.59	4.93	1.83
ACONF	0.61	0.50	1.03	0.28
SCONF	0.36	0.80	0.99	0.49
CYCONF	0.86	0.80	0.67	0.64

^{a} $s_6 = 0.75$; $r_{scal}^{vdW} = 1.1$. ^{b} $s_6 = 1.00$; $r_{scal}^{vdW} = 1.15$.

Table S31 - Root mean square deviations of the complete GMTKN24 database for the original and reoptimized PBE versions with and without dispersion correction. All values are in kcal $\cdot$ mol^{-1} and were obtained with the (aug-)def2-QZVP basis.

	PBE	PBE-D^a	oPBE	oPBE-D^b
MB08-165	11.5	12.3	12.8	11.8
W4-08	16.7	16.8	10.3	10.2
W4-08woMR	14.1	14.2	8.2	8.1
G21IP	4.8	4.8	4.9	4.9
G21EA	4.1	4.1	6.7	6.7
PA	2.8	3.1	4.3	4.6
SIE11	14.9	15.4	14.2	14.5
BHPERI	3.7	6.0	4.4	3.3
BH76	10.5	11.0	8.9	9.3
BH76RC	6.3	6.3	4.8	4.7
RSE43	3.7	3.3	3.5	3.0
O3ADD6	5.7	6.4	6.5	6.4
G2RC	7.7	8.2	6.2	6.4
AL2X	4.7	3.1	8.6	5.0
NBRC	3.0	3.2	7.3	3.7
ISO34	2.5	1.9	3.1	2.3
DC9	15.1	14.6	16.0	12.0
DARC	7.9	3.1	14.9	8.6
IDISP	13.8	3.2	20.2	6.1
WATER27	4.0	12.6	19.5	5.1
S22	3.74	0.81	5.70	0.97
PCONF	4.05	1.83	5.16	1.90
ACONF	0.68	0.56	1.15	0.33
SCONF	0.44	1.09	1.19	0.67
CYCONF	0.97	1.00	0.74	0.77

^{a} $s_6 = 0.75$; $r_{scal}^{vdW} = 1.1$. ^{b} $s_6 = 1.00$; $r_{scal}^{vdW} = 1.15$.

Table S32 - Mean absolute deviations of the complete GMTKN24 database for the original and reoptimized TPSS versions with and without dispersion correction. All values are in kcal $\cdot$ mol^{-1} and were obtained with the (aug-)def2-QZVP basis.

	TPSS	TPSS-D[a]	oTPSS	oTPSS-D[b]
MB08-165	10.0	10.0	6.5	7.1
W4-08	5.3	5.5	3.3	3.4
W4-08woMR	4.4	4.7	2.7	2.8
G21IP	4.0	4.0	4.5	4.5
G21EA	3.4	3.4	3.4	3.4
PA	4.6	5.0	3.4	3.7
SIE11	10.7	11.6	9.8	10.2
BHPERI	2.7	4.8	4.6	2.1
BH76	8.6	9.3	7.3	7.8
BH76RC	3.8	3.7	3.2	3.1
RSE43	2.5	1.9	2.5	2.1
O3ADD6	3.7	4.4	4.4	4.3
G2RC	6.4	7.0	3.5	3.5
AL2X	3.9	3.0	5.9	3.0
NBRC	2.3	1.7	5.2	2.6
ISO34	2.4	2.0	2.0	1.5
DC9	12.3	8.7	16.3	11.9
DARC	11.1	3.7	14.4	8.5
IDISP	14.3	4.2	17.3	3.8
WATER27	5.6	6.9	11.4	2.6
S22	3.50	0.56	4.52	0.76
PCONF	4.41	1.35	5.29	2.19
ACONF	0.71	0.77	0.97	0.34
SCONF	0.36	1.22	0.55	0.51
CYCONF	0.83	0.76	0.92	0.93

[a] $s_6 = 1.00$; $r_{scal}^{vdW} = 1.1$. [b] $s_6 = 1.00$; $r_{scal}^{vdW} = 1.15$.

Table S33 - Root mean square deviations of the complete GMTKN24 database for the original and reoptimized TPSS versions with and without dispersion correction. All values are in kcal · mol^{-1} and were obtained with the (aug-)def2-QZVP basis.

	TPSS	TPSS-D^a	oTPSS	oTPSS-D^b
MB08-165	13.7	12.9	8.8	9.1
W4-08	6.9	7.2	4.5	4.6
W4-08woMR	5.5	5.9	3.6	3.8
G21IP	4.8	4.8	5.3	5.3
G21EA	4.1	4.1	4.8	4.8
PA	5.4	5.8	4.4	4.7
SIE11	14.0	14.6	14.6	14.8
BHPERI	3.1	5.2	5.3	2.7
BH76	9.6	10.2	8.1	8.5
BH76RC	5.0	5.0	4.1	4.0
RSE43	2.8	2.2	3.0	2.5
O3ADD6	5.1	6.1	5.1	5.1
G2RC	8.5	8.8	5.2	5.2
AL2X	4.3	3.2	6.4	3.7
NBRC	3.4	1.9	7.1	3.6
ISO34	3.3	2.8	2.8	2.0
DC9	14.3	11.5	18.7	15.1
DARC	11.9	4.3	14.9	8.7
IDISP	16.5	5.0	19.6	5.9
WATER27	9.8	8.4	18.8	4.8
S22	4.71	0.75	5.88	1.14
PCONF	4.57	1.64	5.50	2.30
ACONF	0.79	0.85	1.08	0.38
SCONF	0.43	1.58	0.70	0.75
CYCONF	0.93	0.97	1.02	1.11

^{a} $s_6 = 1.00$; $r_{scal}^{vdW} = 1.1$. ^{b} $s_6 = 1.00$; $r_{scal}^{vdW} = 1.15$.

Table S34 - Mean absolute (MADs) and root mean square deviations (RMSDs) of the complete GMTKN24 database for the modified TPSS variant 'modTPSS'[a] with and without dispersion correction. All values are in kcal · mol^{-1} and were obtained with the (aug-)def2-QZVP basis.

	MADs		RMSDs	
	'modTPSS'	'modTPSS-D'[b]	'modTPSS'	'modTPSS-D'[b]
MB08-165	10.8	10.5	15.0	13.8
W4-08	6.0	6.2	13.7	13.8
W4-08woMR	4.1	4.3	5.2	5.5
G21IP	4.1	4.1	4.9	4.9
G21EA	2.2	2.3	2.7	2.7
PA	4.8	5.3	5.6	6.1
SIE11	10.3	11.2	13.8	14.3
BHPERI	2.9	4.2	3.3	4.7
BH76	8.2	8.9	9.3	9.9
BH76RC	3.9	3.8	5.0	5.0
RSE43	2.5	2.0	3.1	2.6
O3ADD6	3.9	4.4	4.9	5.7
G2RC	6.5	7.0	8.7	9.0
AL2X	7.9	5.4	11.7	8.8
NBRC	2.7	1.1	4.1	1.2
ISO34	2.5	2.0	3.4	2.8
DC9	12.5	8.9	14.4	11.4
DARC	11.7	4.3	12.4	4.9
IDISP	15.4	3.6	17.5	4.6
WATER27	8.3	3.6	14.0	4.3
S22	3.88	0.43	5.08	0.50
PCONF	4.57	1.44	4.76	1.67
ACONF	0.82	0.66	0.92	0.73
SCONF	0.42	0.86	0.54	1.22
CYCONF	0.76	0.69	0.84	0.86

[a]for more details, see: *Phys. Rev. A* **2007**, *76*, 042506. [b] $s_6 = 1.00$; $r_{scal}^{vdW} = 1.1$.

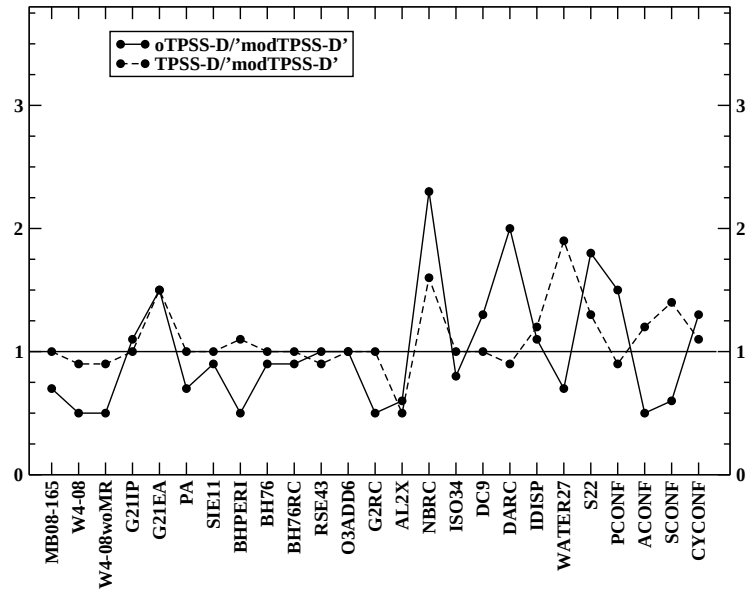

Figure S1 - The ratios MAD(oTPSS-D)/MAD('modTPSS-D') and MAD(TPSS-D)/MAD('modTPSS-D') for the complete GMTKN24 database.

Table S35 - Mean absolute deviations of the complete GMTKN24 database for the B3LYP and B2PLYP methods with and without dispersion correction. All values are in kcal · mol^{-1} and were obtained with the (aug-)def2-QZVP basis.

	B3LYP	B3LYP-D^a	B2PLYP	B2PLYP-D^b
MB08-165	8.2	6.5	5.1	4.1
W4-08	4.4	4.3	2.5	2.5
W4-08woMR	3.6	3.6	2.0	2.0
G21IP	3.6	3.5	2.3	2.3
G21EA	1.8	1.8	1.4	1.4
PA	2.3	2.7	1.4	1.6
SIE11	7.6	8.1	4.7	4.8
BHPERI	5.8	2.0	2.8	1.3
BH76	4.7	5.4	2.2	2.6
BH76RC	2.3	2.3	1.2	1.1
RSE43	2.3	1.7	1.1	0.8
O3ADD6	2.0	2.5	2.3	2.7
G2RC	2.6	2.7	1.7	1.8
AL2X	8.5	3.6	4.0	1.6
NBRC	6.4	3.0	3.2	1.4
ISO34	2.3	1.6	1.4	1.1
DC9	15.1	9.9	7.7	5.0
DARC	15.4	7.6	7.8	3.7
IDISP	18.0	3.7	9.2	1.6
WATER27	6.5	5.5	3.1	3.5
S22	3.8	0.57	1.84	0.41
PCONF	3.97	0.70	1.99	0.35
ACONF	0.96	0.59	0.50	0.31
SCONF	1.03	0.34	0.59	0.17
CYCONF	0.45	0.28	0.22	0.13

^{a} $s_6 = 1.05$; $r_{scal}^{vdW} = 1.1$. ^{b} $s_6 = 0.55$; $r_{scal}^{vdW} = 1.1$.

Table S36 - Root mean square deviations of the complete GMTKN24 database for the B3LYP and B2PLYP methods with and without dispersion correction. All values are in kcal $\cdot$ mol^{-1} and were obtained with the (aug-)def2-QZVP basis.

	B3LYP	B3LYP-D[a]	B2PLYP	B2PLYP-D[b]
MB08-165	10.62	8.75	6.63	5.49
W4-08	6.87	6.78	4.33	4.31
W4-08woMR	5.06	4.96	2.62	2.61
G21IP	4.37	4.37	2.80	2.79
G21EA	2.33	2.34	1.71	1.72
PA	3.44	3.87	2.28	2.48
SIE11	10.40	10.67	6.10	6.07
BHPERI	7.06	2.22	3.37	1.64
BH76	5.41	5.99	2.63	2.94
BH76RC	2.90	2.81	1.70	1.67
RSE43	2.69	2.14	1.32	1.05
O3ADD6	2.33	3.41	2.84	3.05
G2RC	3.18	3.19	2.22	2.26
AL2X	8.98	3.84	4.33	1.78
NBRC	8.44	3.72	4.20	1.74
ISO34	3.27	2.34	1.98	1.57
DC9	18.26	11.97	9.03	6.12
DARC	15.92	7.87	8.15	4.02
IDISP	20.18	5.28	10.21	2.24
WATER27	11.16	6.92	5.75	4.25
S22	5.05	0.69	2.47	0.51
PCONF	4.27	0.85	2.14	0.40
ACONF	1.07	0.66	0.56	0.35
SCONF	1.18	0.65	0.67	0.33
CYCONF	0.55	0.34	0.27	0.16

[a] $s_6 = 1.05$; $r_{scal}^{vdW} = 1.1$. [b] $s_6 = 0.55$; $r_{scal}^{vdW} = 1.1$.

Table S37 - Assessment of the performance of common and reoptimized density functionals for bond lengths of the light element test set. For each method the deviations from experiment are given in pm.[a] The mean (MD), mean absolute (MAD), root mean square (RMSD), maximal (max), and minimal deviations (min) are given. All calculations were carried out with the def2-QZVP basis set.

			Deviation							
Mol.	Bond	Exp.[b]	BLYP-D	oBLYP-D	mPWLYP-D	oPWLYP-D	PBE-D	oPBE-D	TPSS-D	oTPSS-D
B_2	B-B	159.0	2.8	2.6	2.6	2.6	2.8	3.3	2.9	2.9
BF	B-F	126.3	1.1	0.9	0.9	0.9	0.9	1.4	1.0	1.0
BH	B-H	123.2	0.8	0.8	0.7	0.8	1.9	1.8	0.4	0.9
BO	B-O	120.5	0.8	0.7	0.7	0.7	0.8	1.0	0.7	0.3
C_2	C-C	124.3	1.2	1.1	1.1	1.1	1.1	1.4	1.1	0.2
C_2H_2	C-H	106.2	0.5	0.5	0.5	0.5	0.9	0.8	0.3	0.5
	C-C	120.3	0.3	0.2	0.2	0.2	0.4	0.5	−0.1	−0.1
C_2H_4	C-H	108.1	0.8	0.7	0.8	0.7	1.0	1.0	0.6	0.7
	C-C	133.4	0.1	−0.1	0.0	−0.1	−0.1	0.1	−0.3	-0.6
CF	C-F	127.2	2.1	1.9	1.9	1.9	1.3	1.9	1.7	1.8
CH	C-H	112.0	1.2	1.2	1.1	1.2	1.6	1.6	0.9	1.2
CH_2O	C-H	109.9	1.7	1.6	1.6	1.6	1.9	1.9	1.2	1.5
	O-C	120.3	0.8	0.7	0.7	0.7	0.5	0.7	0.4	−0.4
CH_4	C-H	108.6	1.0	0.8	0.9	0.8	1.1	1.0	0.7	0.6
CO	C-O	112.8	0.7	0.7	0.7	0.7	0.7	1.0	0.5	0.2
CO_2	C-O	116.0	1.2	1.1	1.2	1.2	1.1	1.3	0.8	0.0
F_2	F-F	141.2	2.1	1.7	2.0	1.8	0.2	0.9	0.4	3.1
F_2^+	F-F	132.2	1.2	0.9	1.1	0.9	−0.6	0.0	−0.5	1.3
H_2	H-H	74.1	0.4	0.5	0.5	0.5	0.9	0.6	0.1	0.4
H_2O	H-O	95.7	1.3	1.3	1.3	1.3	1.2	1.2	1.0	0.4
HCN	C-H	106.5	0.7	0.7	0.7	0.7	1.0	1.0	0.5	0.7
	N-C	115.3	0.4	0.3	0.3	0.3	0.5	0.6	0.1	0.1
HF	H-F	91.7	1.5	1.5	1.5	1.5	1.3	1.3	1.2	1.1
HOF	O-H	96.6	1.5	1.4	1.5	1.5	1.3	1.4	1.2	0.8
	F-O	143.5	3.3	2.8	3.2	2.9	1.0	1.9	1.5	3.2
N_2	N-N	109.8	0.4	0.3	0.4	0.4	0.4	0.6	0.1	0.0
N_2+	N-N	111.6	−0.1	−0.2	−0.2	−0.2	−0.2	0.0	−0.4	−1.1
NF	N-F	131.7	2.6	2.3	2.5	2.4	1.0	1.7	1.6	1.3
NH	N-H	103.6	1.4	1.4	1.4	1.4	1.3	1.3	0.8	0.3
NH^+	N-H	107.0	2.0	2.0	2.0	2.0	2.1	2.0	1.3	1.6
NH_3	N-H	101.2	0.9	0.8	0.9	0.9	0.9	0.9	0.7	0.5
NO^+	N-O	106.3	0.7	0.6	0.7	0.7	0.6	0.8	0.3	0.0
O_2	O-O	120.8	2.1	1.9	2.1	2.0	1.0	1.5	1.1	0.9
O_2^+	O-O	111.6	1.1	1.0	1.1	1.0	0.5	0.8	0.4	0.0
OH	O-H	97.0	1.4	1.4	1.4	1.4	1.3	1.3	1.1	0.7
OH^+	O-H	102.9	2.1	2.1	2.2	2.1	1.8	1.7	1.0	1.2
MD			1.2	1.1	1.2	1.1	1.0	1.2	0.7	0.8
MAD			1.2	1.1	1.2	1.2	1.0	1.2	0.8	0.9
RMSD			1.4	1.3	1.4	1.3	1.2	1.3	1.0	1.2
min			−0.1	−0.2	−0.2	−0.2	−0.6	0.0	−0.5	−1.1
max			3.3	2.8	3.2	2.9	2.8	3.3	2.9	3.2

[a]Deviations are defined as theory–experiment. The particular s_6 and r_{scal}^{vdW} values for each functional can be found in the footnotes of Tab. S26-S36. [b]Experimental data taken from *Chem. Phys. Lett.* **2004**, *392*, 229-235.

Table S38 - Assessment of the performance of common and reoptimized density functionals for bond lengths of the heavy element test set. For each method the deviations from experiment are given in pm.[a] The mean (MD), mean absolute (MAD), root mean square (RMSD), maximal (max), and minimal deviations (min) are given. All calculations were carried out with the def2-QZVP basis set.

			Deviation							
Mol.	Bond	Exp.[b]	BLYP-D	oBLYP-D	mPWLYP-D	oPWLYP-D	PBE-D	oPBE-D	TPSS-D	oTPSS-D
H_2CS	H-C	108.6	1.0	0.8	0.9	0.9	1.2	1.2	0.7	1.3
	C-S	161.1	1.0	0.8	1.0	0.8	0.3	0.7	0.2	1.2
OCS	C-S	156.1	1.2	1.0	1.1	1.0	0.6	1.0	0.5	1.1
	C-O	115.6	1.4	1.3	1.3	1.3	1.2	1.4	0.9	0.6
HBS	B-S	159.8	1.1	1.0	1.1	1.1	1.0	1.3	0.7	1.7
	H-B	117.0	0.3	0.3	0.2	0.4	1.0	1.0	0.2	1.5
FBS	F-B	127.6	1.7	1.5	1.6	1.5	1.3	1.7	1.2	2.0
	B-S	160.9	1.3	1.2	1.2	1.2	1.1	1.4	0.8	2.1
H_2S	H-S	133.6	1.6	1.5	1.5	1.5	1.6	1.6	0.9	2.0
SO_3	O-S	141.8	3.1	2.8	3.0	2.9	2.4	2.8	2.1	0.8
SO_2	O-S	143.1	2.8	2.7	2.8	2.7	2.3	2.6	2.0	1.4
S_2O	O-S	145.7	2.7	2.5	2.6	2.5	1.9	2.3	1.7	1.5
	S-S	188.7	3.9	3.5	3.8	3.5	2.1	2.7	1.7	3.3
CS	C-S	153.5	1.3	1.1	1.2	1.1	1.1	1.4	0.8	1.5
CS_2	C-S	155.3	1.4	1.2	1.3	1.2	0.9	1.2	0.7	2.2
ClBS	B-S	160.5	1.5	1.4	1.4	1.4	1.3	1.6	1.0	1.5
	Cl-B	168.1	1.2	1.0	1.1	1.0	0.4	1.0	0.5	−0.6
SiS	Si-S	192.9	2.9	2.7	2.8	2.7	2.1	2.5	1.5	3.0
Cl_2S	Cl-S	201.3	5.4	4.8	5.3	4.9	2.1	3.2	2.3	1.4
HOCl	Cl-O	169.1	4.5	4.0	4.4	4.0	1.8	2.8	2.2	0.2
	O-H	96.4	1.3	1.2	1.3	1.2	1.1	1.2	1.0	0.2
HCP	H-C	107.0	0.7	0.6	0.6	0.7	1.0	1.0	0.5	1.4
	C-P	154.0	0.8	0.6	0.7	0.6	0.6	0.8	0.1	0.7
ClNO	Cl-N	197.5	7.6	6.3	7.2	6.4	2.7	4.7	4.5	6.0
	N-O	113.4	0.9	0.8	0.9	0.9	0.8	0.9	0.4	−0.3
HCl	H-Cl	127.5	1.5	1.4	1.5	1.5	1.3	1.3	0.9	−0.3
PH_3	P-H	141.2	1.6	1.6	1.6	1.7	1.8	1.9	0.8	2.1
SiH_4	Si-H	147.4	1.0	1.0	1.0	1.0	1.7	1.6	0.5	1.1
PN	P-N	149.1	0.8	0.7	0.7	0.7	0.6	0.9	0.2	0.6
SiO	Si-O	151.0	1.9	1.8	1.8	1.8	1.6	1.9	1.2	1.3
HSiCl	Si-Cl	207.2	4.4	4.0	4.3	4.1	2.4	3.3	2.2	1.7
SiH_2	H-Si	151.4	2.4	2.4	2.4	2.4	2.9	3.0	1.2	2.6
	H-Si	151.4	1.8	1.8	1.8	1.9	2.3	2.3	0.8	2.7
SiF_2	F-Si	159.0	3.9	3.6	3.7	3.6	3.2	3.7	2.6	3.8
ClF	F-Cl	162.8	4.4	3.9	4.3	4.0	2.2	3.0	2.2	1.9
Cl_2O	O-Cl	169.6	5.0	4.4	4.9	4.5	2.3	3.3	2.7	0.3
CCl−2	C-Cl	171.1	4.3	3.8	4.1	3.8	2.2	3.3	2.6	1.8
BCl	B-Cl	171.6	1.9	1.6	1.7	1.7	1.4	2.2	1.6	−0.2
BCl_3	B-Cl	174.0	2.1	1.6	1.9	1.7	0.9	1.5	1.0	−1.3
P_2	P-P	189.3	1.8	1.6	1.8	1.6	1.1	1.5	0.4	1.6
Cl_2	Cl-Cl	198.8	5.2	4.6	5.1	4.7	1.7	2.8	2.0	−1.6
Cl_2Si	Si-Cl	206.5	5.4	5.0	5.2	5.0	3.4	4.3	3.0	2.3
MD			2.4	2.2	2.3	2.2	1.6	2.0	1.3	1.4
MAD			2.4	2.2	2.3	2.2	1.6	2.0	1.3	1.6
RMSD			2.9	2.6	2.8	2.7	1.8	2.3	1.6	1.9
min			0.3	0.3	0.2	0.4	0.3	0.7	0.1	−1.6
max			7.6	6.3	7.2	6.4	3.4	4.7	4.5	6.0

[a]Deviations are defined as theory–experiment. The particular s_6 and r_{scal}^{vdW} values for each functional can be found in the footnotes of Tab. S26-S36. [b]Experimental data taken from Ref. *J. Chem. Phys.* **2005**, *123*, 184107.

Table S39 - Assessment of the performance of common and reoptimized density functionals for bond lengths of the transition metal test set. For each method the deviations from experiment are given in pm.[a] The mean (MD), mean absolute (MAD), root mean square (RMSD), maximal (max), and minimal deviations (min) are given. All calculations were carried out with the def2-QZVP basis set.

			Deviation							
Mol.	Sate	Exp.[b]	BLYP-D	oBLYP-D	mPWLYP-D	oPWLYP-D	PBE-D	oPBE-D	TPSS-D	oTPSS-D
$Cr(CO)_6$	$^1A_1$	191.4	2.2	1.5	2.0	1.5	−0.9	0.3	0.2	−2.2
CrH	$^6\Sigma^-$	165.5	0.2	0.0	0.2	0.0	−0.2	0.2	0.1	1.5
Cu_2	$^1\Sigma^+$	221.9	5.4	4.5	5.1	4.4	3.4	5.1	1.5	0.9
CuCl	$^1\Sigma$	205.1	3.5	2.8	3.3	2.9	1.0	2.5	1.1	−0.2
$CuCl_2$	$^2\Pi$	203.7	5.6	5.0	5.4	5.0	3.2	4.6	3.1	0.9
CuF	$^1\Sigma$	174.5	2.6	2.1	2.4	2.1	1.4	2.5	0.9	1.8
CuH	$^1\Sigma$	146.3	1.4	1.2	1.3	1.2	1.2	1.6	1.2	0.4
CuO	$^2\Pi$	172.4	1.0	0.6	0.8	0.5	−0.5	0.6	−0.2	−0.9
$Fe(CO)_5$	$^1A_1$	$181.0^{ax.}$	2.0	1.5	1.9	1.5	−0.6	0.5	0.3	−1.4
		$184.2^{eq.}$	−1.2	−1.6	−1.3	−1.6	−3.8	−2.6	−3.2	−4.7
$Mn_2(CO)_{10}$	$^1A_1$	293.0[c]	8.3	9.7	9.1	9.7	−0.7	6.2	−3.6	−3.8
MnH	$^7\Sigma$	173.3	−0.6	−0.8	−0.4	−0.7	−1.9	−1.4	−1.7	−1.3
$Ni(CO)_4$	$^1A_1$	183.8	1.3	1.1	1.2	1.1	−1.3	0.3	−0.9	−3.3
NiH	$^2\Delta$	145.4	1.9	1.6	1.8	1.6	1.6	2.0	1.7	−0.5
ScCl	$^1\Sigma$	222.9	4.8	4.2	4.4	4.2	2.5	4.0	3.9	3.6
ScF	$^1\Sigma$	178.8	3.6	3.2	3.4	3.2	2.1	3.1	2.6	3.5
ScO	$^2\Sigma$	166.8	0.9	0.7	0.9	0.7	−0.5	0.0	0.0	0.5
$TiCl_4$	$^1A_1$	217.0	3.2	2.9	3.0	3.1	1.3	2.6	1.3	0.5
TiF_4	$^1A_1$	174.5	2.6	2.4	2.5	2.4	1.6	2.2	1.4	2.7
VCl_4	^2E	213.7	2.9	2.6	2.8	2.7	0.8	2.1	0.9	−0.2
VF_5	$^1A_1$	170.8	3.1	2.7	2.9	2.7	1.8	2.5	1.6	2.7
		173.4	4.4	3.9	4.2	3.9	3.1	3.8	2.7	3.7
VO	$^4\Sigma$	158.9	0.9	0.6	0.8	0.7	−0.4	0.1	0.0	0.6
$VOCl_3$	$^1A_1$	156.8	1.7	1.5	1.7	1.6	0.5	0.9	0.6	0.7
		213.8	3.2	2.9	3.1	3.0	1.3	2.5	1.2	0.0
VOF_3	$^1A_1$	157.0	1.6	1.5	1.6	1.5	0.5	1.0	0.6	0.6
		172.9	1.7	1.5	1.7	1.5	0.7	1.4	0.4	1.7
ZnH	$^2\Sigma$	159.5	4.1	3.8	4.1	3.9	2.4	2.8	1.5	1.6
MD			2.6	2.3	2.5	2.3	0.7	1.8	0.7	0.3
MAD			2.7	2.4	2.6	2.5	1.5	2.1	1.4	1.7
RMSD			3.2	3.1	3.2	3.1	1.8	2.6	1.8	2.1
min			−1.2	−1.6	−1.3	−1.6	−3.8	−2.6	−3.6	−4.7
max			8.3	9.7	9.1	9.7	3.4	6.2	3.9	3.7

[a]Deviations are defined as theory–experiment. The particular s_6 and r_{scal}^{vdW} values for each functional can be found in the footnotes of Tab. S26-S36. [b]Experimental data taken from *J. Chem. Phys.* **2007**, *126*, 124115. [c] Mn-Mn distance, taken from *Organometallics* **2004**, *23*, 5581-5592.