How do DFT-DCP, DFT-NL, and DFT-D3 compare for the description of London-dispersion effects in conformers and general thermochemistry?

Supporting Information

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- The weighted total mean absolute deviations (WTMADs) for the reaction energies are explained in detail in the GMTKN30 publications. The MAD for each test set is weighted by its size and "difficulty" and the average over these weighted MADs is taken. For some test sets, the weight factors differ from their original values, because of their size had to be reduced due to the limitation to H,C,N, and O. The final formula reads:

$$\begin{aligned}\text{WTMAD} = [&51.0 \cdot \text{MAD(BH76(RC)} + 37.2 \cdot \text{MAD(G2RC)} + 98.0 \cdot \text{MAD(RSE43)}+ \\ &+ 86.8 \cdot \text{MAD(DARC)} + 222.75 \cdot \text{MAD(BSR36)} \\ &+ 98.6 \cdot \text{MAD(ISO34)} + 46.2 \cdot \text{MAD(ISOL22)}]/640.55\end{aligned}$$

- Tables S1- S21 contain all results for the 21 test sets studied herein. Please refer to the original publications (see main paper) for more details about each test set and an explanation of the used nomenclature.

Table S1 – Reference values, deviations (ΔE^a) and statistical values[b] (kcal mol^{-1}) for all tested methods for the binding energies in the S22 test set.

		ΔE(6-31+G(2d,2p))					ΔE(def2-QZVP)			
system	ref	B3LYP	-DCP	-DCP*	-NL	-D3	B3LYP	-DCP (CP[c])	-DCP (non-CP[d])	-D3
$(NH_3)_2$	3.17	−0.77	−0.04	−0.04	0.20	0.12	−0.86	−0.35	−0.13	0.02
$(H_2O)_2$	5.02	0.03	0.32	0.32	0.92	0.67	−0.25	0.32	0.04	0.39
formic acid dimer	18.80	−1.00	−0.51	−0.38	2.11	1.45	−1.31	0.77	−0.77	1.15
formamide dimer	16.12	−1.88	−0.43	−0.40	1.03	0.68	−1.98	−0.15	−0.50	0.58
uracil dimer (C_{2h})	20.69	−2.41	−0.86	−0.74	1.30	0.95	−2.70	−0.37	−1.07	0.66
2-pyridoxine · 2-aminopyridine	17.00	−2.94	−0.21	−0.33	1.12	1.06	−3.15	−0.27	−0.49	0.85
adenine · thymine	16.74	−3.48	−0.58	−0.68	0.97	0.80	−3.84	−0.56	−0.90	0.45
$(CH_4)_2$	0.53	−0.91	−0.15	−0.10	−0.20	−0.04	−0.93	−0.11	−0.16	−0.06
$(C_2H_4)_2$	1.50	−1.96	−0.19	−0.24	−0.36	0.06	−2.00	−0.08	−0.24	0.02
benzene · CH_4	1.45	−2.07	0.05	0.14	−0.15	0.12	−2.21	0.13	−0.10	−0.02
benzene dimer (C_{2h})	2.62	−5.82	0.22	0.24	−0.02	0.87	−6.33	0.65	−0.22	0.37
pyrazine dimer	4.20	−6.29	−0.41	−0.45	−0.22	0.53	−6.64	−0.19	−0.70	0.19
uracil dimer (C_2)	9.74	−7.89	−0.02	−0.36	0.98	1.37	−8.67	0.07	−0.54	0.59
indole · benzene	4.59	−8.49	0.00	−0.09	−0.01	1.00	−9.27	0.47	−0.62	0.21
adenine · thymine (stack)	11.66	−12.05	−0.68	−1.12	0.61	0.96	−12.84	0.24	−0.69	0.17
ethene · ethyne	1.51	−0.61	0.11	0.29	0.21	0.42	−0.82	0.04	−0.10	0.21
benzene · H_2O	3.29	−1.66	0.25	0.13	0.19	0.49	−1.82	0.12	0.09	0.33
benzene · NH_3	2.32	−2.00	−0.03	−0.05	−0.10	0.22	−2.10	−0.01	−0.14	0.12
benzene · HCN	4.55	−2.30	0.01	0.09	−0.03	0.54	−2.55	0.07	−0.25	0.28
benzene dimer (C_{2v})	2.71	−3.25	0.06	0.05	0.03	0.48	−3.63	0.13	−0.29	0.10
indole · benzene (T-shape)	5.62	−4.57	−0.28	−0.50	−0.09	0.46	−5.02	−0.41	−0.73	0.01
phenol dimer	7.09	−3.46	−0.35	−0.58	0.55	0.61	−4.06	−0.28	−0.94	0.01
MD		−3.44	−0.17	−0.22	0.41	0.63	−3.77	0.01	−0.43	0.30
MAD		3.45	0.26	0.33	0.52	0.63	3.77	0.26	0.44	0.31
RMSD		4.52	0.35	0.42	0.75	0.74	4.90	0.33	0.54	0.43

[a] $\Delta E = E(method) - E(reference)$. [b] Mean (MD), mean absolute (MAD), and root-mean-square deviations (RMSD). [c] The DCP parameters have been fitted to counter-poise corrected results. These DCP parameters are used throughout this study for B3LYP-DCP/def2-QZVP. [d] The DCP parameters have not been fitted to counter-poise corrected results. The higher deviations show that they should not be used in combination with def2-QZVP, which is practically BSSE-free.

Table S2 – Reference values, deviations (ΔE^a) and statistical values[b] (kcal mol^{-1}) for all tested methods for the binding energies in the ADIM6 test set.

		ΔE(6-31+G(2d,2p))					ΔE(def2-QZVP)		
system	ref	B3LYP	-DCP	-DCP*	-NL	-D3	B3LYP	-DCP	-D3
(n-ethane)$_2$	1.30	−1.90	−0.13	−0.09	−0.22	0.05	−1.96	−0.01	−0.01
(n-propane)$_2$	1.97	−2.86	−0.12	−0.07	−0.17	0.14	−2.96	0.07	0.04
(n-butane)$_2$	2.79	−4.11	−0.15	−0.07	−0.08	0.30	−4.24	0.28	0.17
(n-pentane)$_2$	3.68	−5.38	−0.23	−0.16	−0.05	0.37	−5.54	0.44	0.20
(n-hexane)$_2$	4.61	−6.78	−0.33	−0.23	−0.04	0.42	−6.97	0.70	0.24
(n-heptane)$_2$	5.60	−8.24	−0.42	−0.40	−0.10	0.36	−8.47	0.75	0.12
MD		−4.88	−0.23	−0.17	−0.11	0.27	−5.02	0.37	0.13
MAD		4.88	0.23	0.17	0.11	0.27	5.02	0.38	0.13
RMSD		5.35	0.25	0.21	0.13	0.30	5.50	0.47	0.16

[a] $\Delta E = E(method) - E(reference)$. [b] Mean (MD), mean absolute (MAD), and root-mean-square deviations (RMSD).

Table S3 – Reference values, deviations (ΔE^a) and statistical values[b] (kcal mol^{-1}) for all tested methods for the binding energies in the WATER27 test set.

		ΔE(6-31+G(2d,2p))				ΔE(aug'-def2-QZVP)		
system	ref	B3LYP	-DCP	-NL	-D3	B3LYP	-DCP	-D3
$(H_2O)_2$	5.01	0.1	0.4	1.0	0.7	−0.4	0.2	0.2
$(H_2O)_{3\ \text{cyclic}}$	15.8	−0.3	0.4	2.8	1.8	−1.4	0.5	0.6
$(H_2O)_{4\ \text{cyclic}}$	27.4	0.7	1.9	5.6	4.1	−1.4	1.6	1.9
$(H_2O)_{5\ \text{cyclic}}$	35.9	1.3	2.6	7.4	5.4	−1.5	2.4	2.7
$(H_2O)_{6\ \text{prism}}$	46.0	−1.3	2.4	8.9	6.2	−5.0	2.5	2.6
$(H_2O)_{6\ \text{cage}}$	45.8	−0.9	2.5	8.9	6.3	−4.5	2.5	2.8
$(H_2O)_{6\ \text{book}}$	45.3	0.7	3.1	9.2	6.7	−2.9	2.7	3.2
$(H_2O)_{6\ \text{cyclic}}$	44.3	1.7	3.1	9.0	6.5	−1.6	2.8	3.2
$(H_2O)_{8\ \text{cube}}$ (D_{2d})	72.6	−1.0	4.7	14.5	10.5	−6.7	5.2	4.8
$(H_2O)_{8\ \text{cube}}$ (S_4)	72.6	−1.0	4.6	14.5	10.5	−6.8	5.1	4.8
$(H_2O)_{20\ \text{dodecahedron}}$	200.1	−0.6	12.7	38.9	28.0	−16.2	17.1	12.4
$(H_2O)_{20\ \text{fused cubes}}$	212.6	−14.1	6.2	34.8	23.2	−30.1	11.5	7.2
$(H_2O)_{20\ \text{face-sharing}}$	215.0	−14.3	4.8	33.2	21.6	−30.6	12.3	5.3
$(H_2O)_{20\ \text{edge-sharing}}$	217.9	−14.3	4.1	32.4	20.7	−30.5	8.1	4.6
$H_3O^+(H_2O)$	33.5	2.4	2.0	3.9	3.4	1.5	2.3	2.5
$H_3O^+(H_2O)_2$	56.9	2.7	2.4	5.4	4.5	1.3	2.9	3.1
$H_3O^+(H_2O)_3$	76.5	2.6	2.6	6.5	5.3	0.7	3.4	3.5
$H_3O^+(H_2O)_6$ $(3D)$	117.8	1.3	4.4	12.4	9.6	−3.3	5.7	5.0
$H_3O^+(H_2O)_2$ $(2D)$	114.9	2.7	4.2	11.4	8.9	−1.3	4.7	4.9
$OH^-(H_2O)$	26.6	2.6	2.3	4.3	3.2	0.5	1.1	1.2
$OH^-(H_2O)_2$	48.4	3.1	3.0	6.2	4.6	0.1	1.5	1.6
$OH^-(H_2O)_3$	67.6	2.8	3.4	7.5	5.5	−1.0	1.4	1.6
$OH^-(H_2O)_4$ (C_4)	84.8	0.5	2.6	8.0	5.5	−4.4	−0.1	0.7
$OH^-(H_2O)_4$ (C_s)	84.8	1.1	3.4	9.7	6.9	−3.8	1.5	2.0
$OH^-(H_2O)_5$	100.7	−0.7	3.0	10.8	7.4	−6.4	0.8	1.6
$OH^-(H_2O)_6$	115.7	−0.9	4.0	13.1	9.2	−7.6	1.6	2.5
$(H_2O)_{8\ \text{cube}}$ (S_4) − $H_3O^+(H_2O)_6OH^-$	28.5	−5.5	−2.1	−5.3	−4.1	−4.7	−3.4	−3.4
MD		−1.1	3.3	11.7	8.2	−6.2	3.6	3.1
MAD		3.0	3.4	12.1	8.5	6.5	3.9	3.3
RMSD		5.1	4.1	15.7	10.9	11.2	5.6	4.1

[a] $\Delta E = E(method) - E(reference)$. [b] Mean (MD), mean absolute (MAD), and root-mean-square deviations (RMSD).

Table S4 – Reference values, deviations (ΔE^a) and statistical values[b] (kcal mol^{-1}) for all tested methods for the relative conformational energies[c] in the ACONF test set.

		ΔE(6-31+G(2d,2p))					ΔE(def2-QZVP)		
conformer	ref	B3LYP	B3LYP-DCP	B3LYP-DCP*	B3LYP-NL	B3LYP-D3	B3LYP	B3LYP-DCP	B3LYP-D3
B_g	0.60	0.38	−0.04	0.02	0.08	0.04	0.34	−0.07	0.00
P_tg	0.61	0.40	−0.02	0.01	0.06	0.03	0.36	−0.05	−0.01
P_gg	0.96	1.11	−0.22	0.04	0.21	0.12	1.04	−0.29	0.05
P_gx	2.81	0.89	0.28	0.09	0.10	−0.01	0.85	0.16	−0.05
H_gtt	0.60	0.41	−0.04	0.00	0.04	0.01	0.38	−0.06	−0.02
H_tgt	0.60	0.43	−0.02	0.01	0.05	0.02	0.41	−0.04	−0.00
H_tgg	0.93	1.20	−0.23	0.02	0.18	0.10	1.15	−0.29	0.05
H_gtg	1.18	0.89	−0.05	0.02	0.12	0.06	0.83	−0.11	0.01
H_g+t+g−	1.30	0.76	−0.09	−0.01	0.08	0.01	0.70	−0.15	−0.05
H_ggg	1.25	1.91	−0.35	0.08	0.32	0.20	1.84	−0.44	0.12
H_g+x−t+	2.63	1.03	0.24	0.07	0.09	−0.00	0.98	0.12	−0.05
H_t+g+x−	2.74	0.95	0.27	0.06	0.06	−0.03	0.93	0.16	−0.06
H_g+x−g−	3.28	1.36	0.34	0.10	0.15	0.04	1.30	0.18	−0.03
H_x+g−g−	3.08	1.70	0.07	0.06	0.14	−0.05	1.64	−0.13	−0.11
H_x+g−x+	4.93	1.65	0.36	0.11	0.07	−0.13	1.61	0.13	−0.16
MD		1.01	0.03	0.05	0.12	0.03	0.96	−0.06	−0.02
MAD		1.01	0.18	0.05	0.12	0.06	0.96	0.16	0.05
RMSD		1.11	0.22	0.06	0.14	0.08	1.07	0.19	0.07

[a] $\Delta E = E(method) - E(reference)$. [b] Mean (MD), mean absolute (MAD), and root-mean-square deviations (RMSD).
[c] With respect to the most stable conformers in each case (B_t, P_tt, H_ttt).

Table S5 – Reference values, deviations (ΔE^a) and statistical values[b] (kcal mol^{-1}) for all tested methods for the relative conformational energies[c] in the SCONF test set.

		ΔE(6-31+G(2d,2p))					ΔE(def2-QZVP)		
conformer	ref	B3LYP	-DCP	-DCP*	-NL	B-D3	B3LYP	-DCP	-D3
C2	0.83	0.04	0.02	−0.02	−0.08	−0.08	0.05	0.01	−0.07
C3	2.60	−0.73	−0.53	−0.36	0.10	0.09	−0.79	−0.10	0.02
C4	3.37	−0.66	−0.52	−0.40	0.03	0.02	−0.72	−0.10	−0.04
C5	4.87	−1.08	−1.79	−0.85	0.12	−0.31	−1.17	−0.94	−0.41
C6	5.18	−1.11	−1.62	−0.84	0.17	−0.22	−1.31	−0.94	−0.41
C7	4.47	−0.26	−0.82	−0.52	0.47	0.17	−0.38	−0.30	0.05
C8	4.68	−0.36	−0.84	−0.57	0.42	0.09	−0.52	−0.37	−0.07
C9	6.69	−1.81	−2.15	−1.33	0.17	−0.56	−1.89	−0.92	−0.64
C10	6.75	−1.65	−2.03	−1.35	0.22	−0.48	−1.76	−0.90	−0.58
C11	6.08	−0.93	−1.00	−0.74	0.30	−0.14	−1.08	−0.45	−0.29
C12	6.05	−0.85	−0.94	−0.67	0.35	−0.07	−0.96	−0.37	−0.18
C13	6.17	−0.80	−1.34	−0.81	0.17	−0.35	−0.83	−0.26	−0.38
C14	6.75	−1.27	−1.63	−1.09	0.26	−0.35	−1.39	−0.69	−0.46
C15	6.71	−1.27	−1.68	−1.16	0.26	−0.56	−1.31	−0.52	−0.61
G2	0.27	−0.00	0.06	−0.06	−0.26	−0.21	0.05	0.04	−0.16
G3	5.92	2.00	0.92	0.48	−1.08	−0.67	2.17	−0.35	−0.49
G4	5.29	1.06	−0.36	−0.35	−1.95	−1.63	1.05	−2.24	−1.63
MD		−0.57	−0.96	−0.62	−0.02	−0.31	−0.63	−0.55	−0.37
MAD		0.93	1.07	0.68	0.38	0.35	1.03	0.56	0.38
RMSD		1.09	1.25	0.78	0.59	0.51	1.18	0.76	0.53

[a] $\Delta E = E(method) - E(reference)$. [b] Mean (MD), mean absolute (MAD), and root-mean-square deviations (RMSD).
[c] With respect to the most stable conformers in each case (C1, G1).

Table S6 – Reference values, deviations (ΔE^a) and statistical values[b] (kcal mol^{-1}) for all tested methods for the relative conformational energies[c] in the PCONF test set.

		ΔE(6-31+G(2d,2p))					ΔE(def2-QZVP)		
conformer	ref	B3LYP	-DCP	-DCP*	-D3	-NL	B3LYP	-DCP	-D3
FGG_444	0.14	−4.45	−0.44	−0.45	−0.81	−0.80	−4.54	−0.01	−0.89
FGG_357	0.90	−2.07	−0.56	−0.37	−0.68	−0.08	−2.22	−0.36	−0.83
FGG_366	1.15	−5.85	−0.71	−1.01	0.46	0.28	−6.19	0.22	0.13
FGG_215	0.79	−3.47	−0.07	−0.12	−0.59	−0.51	−3.56	0.07	−0.68
FGG_300	1.31	−5.27	−0.48	−0.81	0.43	0.23	−5.65	0.18	0.05
FGG_114	1.87	−1.88	−1.12	−0.47	−0.68	−0.06	−2.04	−0.72	−0.83
FGG_412	2.37	−1.46	−0.72	−0.63	−0.46	−0.30	−1.47	−0.25	−0.47
FGG_691	2.07	−5.47	−0.79	−0.97	0.17	0.07	−5.69	0.13	−0.05
FGG_470	2.51	−4.34	−1.68	−1.00	−0.55	−0.29	−4.53	−0.70	−0.74
FGG_224	2.04	−3.77	−0.94	−0.67	−1.08	−1.02	−3.79	−0.58	−1.10
MD		−3.80	−0.75	−0.65	−0.38	−0.25	−3.97	−0.20	−0.54
MAD		3.80	0.75	0.65	0.59	0.37	3.97	0.32	0.58
RMSD		4.09	0.86	0.71	0.63	0.48	4.27	0.40	0.68

[a] $\Delta E = E(method) - E(reference)$. [b] Mean (MD), mean absolute (MAD), and root-mean-square deviations (RMSD).
[c] With respect to the most stable conformer (FGG_99).

Table S7 – Reference values, deviations (ΔE^a) and statistical values[b] (kcal mol^{-1}) for all tested methods for the relative conformational energies[c] in the TPCONF test set.

		ΔE(6-31+G(2d,2p))					ΔE(def2-QZVP)		
conformer	ref	B3LYP	-DCP	-DCP*	-NL	-D3	B3LYP	-DCP	-D3
GLY_aR	0.57	6.22	1.52	1.15	−0.09	0.15	6.58	1.34	0.51
GLY_pII	1.05	2.09	1.35	0.69	0.66	0.63	2.31	1.45	0.85
GLY_aL	1.91	6.89	2.13	1.51	0.06	0.56	7.21	1.60	0.89
GLY_b	2.03	−0.18	−0.22	−0.37	−0.12	−0.26	−0.16	−0.34	−0.23
SER_aR	1.05	6.10	1.15	1.19	−0.13	0.16	6.50	1.22	0.55
SER_pII	2.63	2.42	1.11	0.86	0.61	0.64	2.59	1.21	0.80
SER_aL	1.79	7.16	1.94	1.67	0.13	0.80	7.56	1.51	1.20
SER_b	2.65	−0.17	−0.11	−0.26	−0.00	−0.12	−0.20	−0.11	−0.15
MD		3.82	1.11	0.81	0.14	0.32	4.05	0.99	0.55
MAD		3.90	1.19	0.96	0.22	0.41	4.14	1.10	0.65
RMSD		4.81	1.37	1.08	0.33	0.49	5.08	1.21	0.73

[a] $\Delta E = E(method) - E(reference)$. [b] Mean (MD), mean absolute (MAD), and root-mean-square deviations (RMSD).
[c] With respect to the most stable conformers in each case (GLY_ab, SER_ab).

Table S8 – Reference values, deviations (ΔE^a) and statistical values[b] (kcal mol^{-1}) for all tested methods for the relative conformational energies[c] in the MCONF test set.

		ΔE(6-31+G(2d,2p))					ΔE(def2-QZVP)		
conformer	ref	B3LYP	-DCP	-DCP*	-NL	-D3	B3LYP	-DCP	-D3
2	0.593	−2.39	−0.03	0.06	0.11	0.49	−2.58	0.15	0.30
3	1.87	−1.12	−0.14	−0.21	−0.14	−0.17	−1.16	−0.12	−0.21
4	1.40	−2.52	−0.26	−0.20	0.06	0.21	−2.70	−0.19	0.03
5	2.07	0.43	−0.16	-0.12	−0.1488	−0.16	0.47	−0.16	−0.12
6	2.36	−1.25	−0.14	−0.18	−0.24	−0.25	−1.20	0.23	−0.20
7	2.68	−0.05	−0.39	−0.36	−0.47	−0.61	0.07	−0.17	−0.48
8	2.80	0.12	−0.21	−0.26	−0.25	−0.30	0.09	−0.22	−0.32
9	2.48	−2.76	−0.30	−0.33	−0.07	0.04	−3.00	−0.41	−0.20
10	2.88	−0.75	−0.65	−0.69	−0.25	−0.47	−0.59	−0.41	−0.32
11	4.13	0.22	1.06	−0.12	−0.03	−0.17	0.35	1.26	−0.04
12	4.33	0.43	1.10	−0.06	−0.01	−0.16	0.51	1.14	−0.08
13	3.87	−2.59	1.03	−0.17	0.18	0.19	−2.69	1.09	0.10
14	2.55	−3.75	−0.43	−0.31	0.07	0.28	−4.03	−0.27	−0.01
15	4.09	−2.63	1.02	−0.17	0.18	0.19	−2.73	1.10	0.09
16	5.17	−1.41	1.01	−0.14	−0.13	−0.29	−1.30	1.49	−0.17
17	5.11	0.15	1.02	−0.26	−0.26	−0.51	0.36	1.36	−0.30
18	3.47	−3.40	−0.24	−0.20	−0.00	0.21	−3.66	−0.12	−0.05
19	3.84	−1.07	−0.71	−0.83	−0.39	−0.68	−0.93	−0.50	−0.54
20	4.08	−2.79	−0.63	−0.61	−0.11	−0.25	−2.83	−0.30	−0.29
21	3.41	−4.04	−0.48	−0.45	−0.07	0.09	−4.34	−0.49	−0.22
22	5.32	−0.86	0.62	−0.67	−0.12	−0.47	−0.63	1.01	−0.24
23	5.36	−0.83	0.61	−0.66	−0.13	−0.47	−0.62	0.96	−0.26
24	4.81	−3.86	0.84	−0.30	0.18	0.26	−4.05	1.16	0.07
25	4.22	−3.71	−1.18	−0.44	−0.06	0.09	−4.02	−1.13	−0.22
26	4.88	−3.87	0.83	−0.30	0.17	0.24	−4.04	1.15	0.07
27	5.04	−3.09	−0.68	−0.74	−0.24	−0.44	−3.16	−0.39	−0.51
28	4.66	−3.00	−0.73	−0.67	−0.16	−0.32	−3.12	−0.42	−0.44
29	5.65	−3.51	0.19	−0.27	0.22	0.28	−3.70	0.42	0.09
30	5.68	−0.75	−0.57	−0.58	−0.53	−0.78	−0.70	−0.57	−0.72
31	5.19	−3.73	−0.82	−0.73	−0.13	−0.23	−3.89	−0.49	−0.39
32	6.53	−2.91	0.65	−0.58	0.02	−0.27	−2.85	1.11	−0.22
33	6.54	−2.90	0.65	−0.58	0.02	−0.28	−2.85	1.10	−0.22
34	6.08	−2.40	−0.44	−0.50	−0.35	−0.54	−2.43	−0.46	−0.57
35	5.67	−3.43	−1.35	−0.06	−0.08	−0.07	−3.57	−0.87	−0.21
36	5.85	−3.62	−0.81	−0.84	−0.30	−0.50	−3.77	−0.69	−0.65
37	7.59	−0.72	0.75	−0.43	−0.26	−0.55	−0.59	1.10	−0.42
38	6.21	−4.05	−0.88	−0.88	−0.28	−0.43	−4.23	−0.75	−0.61
39	5.96	−3.84	−1.32	-0.73	−0.07	−0.10	−4.02	−0.94	−0.27
40	7.31	−3.40	0.52	−0.67	−0.04	−0.30	−3.45	0.95	−0.35
41	7.38	−3.40	0.52	−0.67	−0.05	−0.32	−3.43	0.93	−0.36
42	6.73	−3.68	−1.42	−0.69	−0.22	−0.26	−3.87	−1.16	−0.45
43	7.67	−3.86	0.46	−0.71	−0.01	−0.25	−3.93	0.91	−0.32
44	7.72	−3.85	0.46	−0.71	−0.01	−0.25	−3.92	0.90	−0.32
45	6.55	−4.23	−1.51	-0.74	−0.07	−0.03	−4.40	−1.03	−0.20
46	8.17	−3.51	−0.05	−0.51	0.06	−0.09	−3.55	0.57	−0.14
47	8.25	−3.50	−0.07	−0.51	0.06	−0.09	−3.56	0.54	−0.14
48	7.14	−4.14	−1.38	−0.85	−0.22	−0.31	−4.34	−1.21	−0.51
49	8.58	−3.95	−0.02	−0.70	0.05	−0.14	−4.02	0.50	−0.20
50	8.59	−3.94	−0.02	−0.70	0.05	−0.12	−4.02	0.50	−0.20
51	7.67	−4.51	−1.58	−0.80	−0.22	−0.25	−4.70	−1.31	−0.44
52	9.14	−4.32	−0.22	−0.66	0.04	−0.06	−4.38	0.39	−0.12
MD		−2.60	−0.13	−0.48	−0.09	−0.18	−2.66	0.14	−0.25
MAD		2.65	0.65	0.48	0.15	0.28	2.73	0.72	0.27
RMSD		2.99	0.77	0.54	0.19	0.33	3.10	0.82	0.32

[a] $\Delta E = E(method) - E(reference)$. [b] Mean (MD), mean absolute (MAD), and root-mean-square deviations (RMSD).
[c] With respect to the most stable conformer (1).

Table S9 – Reference values, deviations (ΔE^a) and statistical values[b] (kcal mol^{-1}) for all tested methods for the total atomization energies in the W4-08 and W4-11 test sets. The W4-11 systems are marked with an asterisk.

		ΔE(6-31+G(2d,2p))					ΔE(def2-QZVP)		
system	ref	B3LYP	-DCP	-DCP*	-D3	-NL	B3LYP	-DCP	-D3
C_2H_6	713.08	0.8	67.1	13.9	4.2	8.1	−2.6	68.8	0.8
H_2CN	343.75	3.1	31.3	7.9	4.5	7.0	3.9	35.3	5.3
NCCN	502.04	−10.1	51.2	1.8	−7.5	−3.4	−1.3	66.7	1.3
CH_2NH_2	482.28	5.1	33.9	9.2	7.4	10.9	4.0	35.8	6.3
CH_3NH	474.63	6.3	38.0	11.6	8.5	11.9	4.2	38.9	6.4
CH_3NH_2	582.30	3.2	35.0	8.1	6.0	9.9	0.5	35.5	3.3
N_2H	224.86	4.5	1.5	1.5	5.4	7.8	6.4	6.1	7.2
N_2H_2	296.53	3.1	0.1	0.1	4.3	7.2	3.0	2.4	4.3
N_2H_4	438.28	5.9	2.6	2.6	8.0	12.0	4.0	2.9	6.2
H_2	109.49	1.7	1.6	1.6	1.8	1.9	0.1	0.1	0.2
OH	107.21	1.2	−0.1	−0.1	1.4	2.0	0.5	−0.1	0.7
H_2O	232.97	−1.3	−4.0	−4.0	−1.0	0.3	−2.9	−4.2	−2.5
CH	84.22	1.3	7.9	2.4	1.6	1.9	0.9	8.2	1.2
CH_2	190.74	2.1	22.4	4.7	2.6	3.5	1.3	23.0	1.8
CH_3	307.87	3.2	28.0	6.7	4.0	5.3	1.8	29.0	2.6
CH_4	420.42	2.4	32.4	6.9	3.6	5.4	0.0	33.2	1.2
C_2H	266.16	−8.5	45.6	1.2	−7.4	−5.6	−4.2	53.1	−3.1
C_2H_2	405.52	−6.9	47.9	3.8	−5.5	−3.2	−3.3	56.3	−1.9
NH_3	298.02	3.8	1.3	1.3	4.5	6.2	2.1	1.3	2.8
C_2[b]	147.02	−32.0	6.7	−24.1	−31.2	−29.9	−28.2	12.9	−27.4
N_2	228.48	−5.0	−8.5	8.5	−4.5	−2.7	−0.6	−0.6	−0.1
CO	259.73	−8.2	4.1	−7.8	−7.8	−6.1	−5.3	10.6	−4.8
CN	181.35	−7.0	15.5	−4.1	−6.4	−4.8	−3.0	22.0	−2.4
NO	152.75	−0.7	−5.9	−5.9	−0.4	1.6	1.3	0.1	1.6
O_2	120.82	1.5	−6.2	−6.2	1.7	3.9	1.9	0.2	2.2
NH	83.10	5.0	4.3	4.3	5.2	5.7	4.5	4.3	4.7
NH_2	182.59	5.6	4.0	4.0	6.0	7.1	4.6	4.1	5.1
HCN	313.42	−5.1	20.5	−1.2	−4.2	−2.1	−1.3	28.1	−0.4
CH_2C	359.93	−2.6	39.6	6.9	−1.0	1.1	−1.1	45.4	0.5
CH_2CH	446.08	−0.3	55.0	10.7	1.7	4.4	0.4	59.8	2.3
C_2H_4	564.10	−1.4	58.2	10.6	1.0	4.1	−1.8	62.6	0.6
CH_2NH	439.44	1.3	29.5	5.7	3.1	6.1	1.0	32.5	2.9
HCO	279.42	−1.3	20.4	0.4	−0.5	1.8	0.1	25.2	0.9
CH_2O	374.66	−2.2	23.8	0.3	−1.1	1.6	−2.1	27.5	−1.0
CO_2	390.14	−8.6	21.6	−7.9	−7.6	−4.1	−3.9	32.3	−2.8
HNO	205.89	−1.2	−6.2	−6.2	−0.5	2.1	−0.9	−2.1	−0.2
NO_2	227.88	1.0	−8.7	−8.7	1.9	6.2	3.0	1.7	4.0
N_2O	270.85	−1.5	−8.3	−8.3	−0.4	3.5	3.1	2.2	4.3
O_3[b]	147.43	−9.5	−24.0	−24.0	−8.7	−4.1	−8.9	−10.8	−8.1
HOO	175.53	1.5	−6.1	−6.1	2.0	4.8	1.2	−0.5	1.7
H_2O_2	269.09	−2.2	−10.0	−10.0	−1.4	2.0	−3.3	−5.0	−2.4
propane*	1007.909	−1.7	101.4	4.5	21.0	10.7	−6.2	104.0	0.0
ch2 ($^1A_1$)*	181.456	−0.2	13.6	2.0	0.3	1.1	−1.1	14.1	−0.6
propene*	861.578	−3.0	93.9	18.4	2.0	7.3	−4.5	99.3	0.5
ethanol*	811.241	−2.9	62.6	8.8	1.4	7.7	−6.3	65.7	−1.9
methanol*	513.501	−0.9	28.6	1.9	1.0	4.8	−3.2	30.4	−1.2
propyne*	705.605	−7.2	86.1	12.5	−3.7	0.7	−4.6	95.5	−1.0
acetaldehyde*	677.864	−2.9	58.6	8.1	0.4	5.4	−4.0	63.9	−0.6
allene*	704.100	−3.2	89.3	16.8	0.5	4.8	−1.3	98.0	2.4
oxirane*	651.526	−5.1	59.5	6.0	−2.0	4.1	−5.6	65.0	−2.4
acetic*	804.017	−7.1	56.3	2.1	−2.7	4.7	−7.9	65.2	−3.5
trans-HCOH*	322.477	−2.2	14.9	−1.2	−1.1	1.8	−2.6	17.7	−1.5
cis-HCOH*	317.647	−2.4	14.4	−1.4	−1.2	1.6	−2.4	17.6	−1.3
ketene*	533.462	−4.4	56.6	6.0	−2.1	1.9	−1.1	65.9	1.2
formic acid*	501.899	−5.3	21.8	−5.2	−3.4	1.5	−4.8	29.0	−2.9
HCNH*	336.249	2.7	26.8	6.1	4.1	6.7	3.8	30.9	5.1
glyoxal*	635.101	−7.6	49.0	1.2	−4.2	1.6	−6.4	57.6	−3.1
hnc*	298.203	−3.0	12.3	−1.3	−1.9	0.1	0.1	18.8	1.1
oxirene*	456.072	−8.7	50.2	1.5	−6.5	−1.6	−5.5	58.9	−3.3
HOCN*	410.066	−6.6	24.4	−3.9	−5.0	−1.1	−2.4	33.7	−0.8
HNCO*	434.737	−2.7	27.6	−0.3	−1.0	2.9	1.5	36.8	3.2
cis-N_2H_2*	291.135	2.9	−0.1	−0.1	4.1	7.0	3.2	2.5	4.4
dioxirane*	410.029	−7.1	17.7	−8.8	−5.4	0.3	−6.3	27.2	−4.5
HCNO*	364.971	−1.8	24.4	−0.8	−0.2	3.9	2.5	34.4	4.1
HONC*	350.149	−4.1	8.7	−5.5	−2.4	1.7	−1.1	17.5	0.6
cis-HONO*	312.219	−2.2	−12.0	−12.0	−0.8	4.2	−1.3	−2.7	0.1
trans-HONO*	312.649	−2.0	−11.7	−11.7	−0.7	4.2	−1.1	−2.5	0.2
HNNN*	331.785	3.3	−0.9	−0.9	5.1	9.3	8.0	7.5	9.7
cis-HOOO*	233.089	−0.1	−13.6	−13.6	1.0	6.1	0.1	−1.4	1.2
trans-HOOO*	233.297	−0.3	−13.3	−13.3	0.8	5.7	−0.2	−1.5	0.9
MD (W4-08)		−1.3	16.2	−0.12	−0.2	2.2	−0.5	20.6	0.6
MAD (W4-08)		4.4	20.5	6.4	4.6	5.4	3.1	21.7	3.4
RMSD (W4-08)		6.7	27.4	8.3	6.7	6.4	5.4	30.4	5.5
MD (new W4-11 systems)		−3.0	32.6	1.1	−0.7	3.8	−2.1	39.6	0.2
MAD (new W4-11 systems)		3.6	36.2	6.6	2.4	4.0	3.4	40.2	2.2
RMSD (new W4-11 systems)		4.3	46.4	8.9	3.0	4.8	4.1	51.2	3.0
MD (complete W4-11)		−2.0	23.0	0.4	−0.4	2.9	−1.2	28.5	0.5
MAD (complete W4-11)		4.0	27.0	6.5	3.7	4.8	3.3	29.4	2.9
RMSD (complete W4-11)		5.8	36.5	8.5	5.5	6.4	4.9	40.4	4.6

[a] $\Delta E = E(method) - E(reference)$. [b] Mean (MD), mean absolute (MAD), and root-mean-square deviations (RMSD).

Table S10 – Reference values, deviations (ΔE^a) and statistical values[b] (kcal mol^{-1}) for all tested methods for the electron affinities in the G21EA test set.

		ΔE(6-31+G(2d,2p))					ΔE(def2-QZVP)		
system	ref	B3LYP	-DCP	-DCP*	-D3	-NL	B3LYP	-DCP	-D3
C	29.2	0.2	6.9	1.4	0.2	-2.3	0.6	7.9	0.6
O	33.7	1.4	0.6	0.6	1.4	−1.3	2.7	2.5	2.7
CH	27.9	0.8	7.4	2.0	0.8	−1.6	1.4	8.5	1.4
CH_2	13.4	0.8	0.5	1.5	0.9	−1.5	1.4	1.5	1.4
CH_3	1.2	−2.6	−0.3	−1.7	−2.6	−4.8	−2.1	0.4	−2.1
NH	8.3	−1.0	−1.4	−1.4	−1.0	−3.5	1.0	1.0	1.0
NH_2	16.8	−3.5	−3.8	−3.8	−3.5	−5.8	−1.7	−1.7	−1.7
OH	41.7	−3.1	−3.9	−3.9	−3.1	−5.7	−1.5	−1.6	−1.5
O_2	9.5	0.4	1.3	1.3	0.4	−2.2	0.6	0.8	0.6
NO	−0.2	6.4	7.0	7.0	6.4	3.9	1.2	5.8	1.2
CN	89.5	1.6	−2.4	−2.4	1.6	−0.8	1.6	−1.1	1.6
MD		0.1	1.1	0.1	0.1	−2.3	0.5	2.2	0.5
MAD		2.0	3.2	2.5	2.0	3.1	1.4	3.0	1.4
RMSD		2.6	4.2	3.0	2.6	3.5	1.5	4.1	1.5

[a] $\Delta E = E(method) - E(reference)$. [b] Mean (MD), mean absolute (MAD), and root-mean-square deviations (RMSD).

Table S11 – Reference values, deviations (ΔE^a) and statistical values[b] (kcal mol^{-1}) for all tested methods for the ionization potentials in the G21IP test set.

		ΔE(6-31+G(2d,2p))					ΔE(def2-QZVP)		
system	ref	B3LYP	-DCP	-DCP*	-D3	-NL	B3LYP	-DCP	-D3
H	314.9	−3.1	−3.2	−3.2	−3.1	-7.0	−1.7	−1.8	−1.7
C	259.6	4.6	14.7	6.2	4.6	1.5	4.6	15.8	4.6
N	335.3	1.9	1.2	1.2	1.9	−1.1	0.7	0.9	0.7
O	313.8	10.2	9.1	9.1	10.2	7.1	9.6	9.3	9.6
CH_4	296.3	−6.3	5.1	5.2	−6.3	−9.2	−5.7	0.7	−5.7
NH_3	235.7	−2.4	−2.8	−2.8	−2.4	−5.1	−2.3	−2.2	−2.2
OH	300.9	4.0	3.0	3.0	4.0	1.0	3.5	3.2	3.5
H_2O	292.6	−2.5	−3.6	−3.6	−2.5	−5.37	−3.0	−3.3	−3.0
C_2H_2	264.6	−8.9	3.2	−6.4	−8.9	−11.3	−6.9	6.6	−6.9
C_2H_4	243.7	−8.7	1.6	−6.5	−8.7	−10.9	−7.2	4.1	−7.2
CO	323.0	2.7	−7.9	2.3	2.7	−0.1	1.3	−7.4	1.3
N_2	359.4	3.9	3.1	3.1	3.9	1.2	3.0	3.3	3.0
O_2	277.7	11.3	11.4	11.4	11.3	8.6	8.5	9.0	8.5
MD		0.5	2.2	0.7	0.5	−2.4	0.4	2.9	0.4
MAD		5.4	5.0	4.9	5.4	5.3	4.5	5.2	4.5
RMSD		6.3	6.5	5.7	6.3	6.6	5.3	6.7	5.3

[a] $\Delta E = E(method) - E(reference)$. [b] Mean (MD), mean absolute (MAD), and root-mean-square deviations (RMSD).

Table S12 – Reference values, deviations (ΔE^a) and statistical values[b] (kcal mol^{-1}) for all tested methods for the proton affinities in the PA test set.

		ΔE(6-31+G(2d,2p))					ΔE(def2-QZVP)		
system	ref	B3LYP	-DCP	-DCP*	-D3	-NL	B3LYP	-DCP	-D3
C_2H_4	167.8	1.4	−0.7	0.9	1.7	1.0	0.7	−1.9	1.0
C_4H_6	193.4	6.4	1.1	5.3	6.9	5.5	5.2	−0.3	5.7
C_6H_8	209.7	7.9	2.4	6.7	8.5	6.9	6.7	1.1	7.2
C_8H_10	219.7	9.3	3.7	8.1	9.8	8.1	8.0	2.5	8.6
NH_3	211.9	−0.7	−1.2	−1.2	−0.3	−1.1	−0.4	−0.8	−0.0
H_2O	171.6	−1.1	−1.7	−1.7	−0.8	−1.3	−0.1	−0.6	0.2
C_2H_2	157.4	2.1	−0.1	1.6	2.5	1.7	1.2	−1.5	1.7
H_2	106.3	−1.8	−1.9	−1.9	−1.6	−1.9	−1.4	−1.5	−1.2
MD		2.9	0.2	3.3	2.2	2.4	2.5	−0.4	2.9
MAD		3.8	1.6	4.0	3.4	3.4	3.0	1.3	3.2
RMSD		5.0	1.9	5.4	4.3	4.4	4.2	1.5	4.5

[a] $\Delta E = E(method) - E(reference)$. [b] Mean (MD), mean absolute (MAD), and root-mean-square deviations (RMSD).

Table S13 – Reference values, deviations (ΔE^a) and statistical values[b] (kcal mol^{-1}) for all tested methods for the barrier heights[c] in the BH76 test set.

		ΔE(6-31+G(2d,2p))					ΔE(def2-QZVP)		
system	ref	B3LYP	-DCP	-DCP*	-D3	-NL	B3LYP	-DCP	-D3
H + N_2O → OH + N_2	18.14	−7.4	−7.4	−7.4	−8.1	−8.6	−6.7	−6.7	−7.3
H + N_2O ← OH + N_2	83.22	−9.9	−7.8	−7.8	−11.0	−13.0	−10.2	−9.9	−11.3
H + N_2 → HN_2	14.69	−8.3	−8.8	−8.8	−8.8	−9.3	−7.2	−7.1	−7.8
H + N_2 ← HN_2	10.72	1.6	1.5	1.5	1.4	1.6	0.0	−0.2	−0.2
H + CO → HCO	3.17	−4.6	−7.1	−5.3	−5.2	−5.4	−3.9	−6.2	−4.5
H + CO ← HCO	22.68	2.5	9.4	3.0	2.2	2.6	1.7	8.6	1.4
H + C_2H_4 → C_2H_5	1.72	−2.8	−3.0	−3.2	−3.7	−3.7	−2.0	−2.1	−2.9
H + C_2H_4 → C_2H_5	41.75	1.1	2.8	0.7	0.7	1.1	−0.0	1.5	−0.5
CH_3 + C_2H_4 → C_3H_7	6.85	−1.3	−6.0	−4.7	−3.8	−4.0	−0.6	−5.1	−3.1
CH_3 + C_2H_4 ← C_3H_7	32.97	−2.7	6.1	−0.2	−2.8	−1.7	−3.6	4.6	−3.8
HNC → HCN	48.16	−1.8	3.6	−1.3	−1.8	−2.1	−0.7	5.3	−0.7
HNC ← HCN	33.11	0.1	−4.7	−1.6	0.2	−0.1	0.4	−4.1	0.5
OH + H_2 → H_2O + H	5.1	−4.3	−3.6	−3.6	−4.7	−5.5	−4.2	−3.9	−4.7
OH + H_2 ← H_2O + H	21.2	−9.0	−9.6	−9.6	−9.4	−9.5	−8.2	−8.5	−8.6
CH_3 + H_2 → CH_4 + H	12.1	−3.2	−6.0	−4.2	−4.1	−4.5	−3.2	−6.2	−4.0
CH_3 + H_2 ← CH_4 + H	15.3	−6.5	−3.9	−6.4	−7.1	−7.1	−5.9	−2.9	−6.5
OH + CH_4 → H_2O + CH_3	6.7	−4.9	−3.0	−4.6	−5.9	−6.7	−4.2	−2.6	−5.2
OH + CH_4 ← H_2O + CH_3	19.6	−6.4	−11.0	−8.4	−7.5	−8.1	−5.5	−10.6	−6.7
H + H_2 → H_2 + H	9.6	−5.6	−5.5	−5.5	−6.0	−6.0	−5.4	−5.4	−5.9
H + H_2 ← H_2 + H	9.6	−5.6	−5.5	−5.5	−6.0	−6.0	−5.4	−5.4	−5.9
OH + NH_3 → H_2O + NH_2	3.2	−6.1	−5.9	−5.9	−7.0	−8.0	−5.4	−5.6	−6.3
OH + NH_3 ← H_2O + NH_2	12.7	−5.9	−6.2	−6.2	−7.0	−7.9	−5.4	−6.1	−6.4
OH + C_2H_6 → H_2O + C_2H_5	3.4	−4.6	−3.2	−4.7	−5.9	−6.6	−3.9	−2.8	−5.1
OH + C_2H_6 ← H_2O + C_2H_5	19.9	−5.1	−9.8	−7.6	−6.7	−7.2	−4.2	−9.1	−5.7
O + CH_4 → OH + CH_3	13.7	−6.8	−3.9	−6.2	−7.5	−8.3	−6.0	−3.3	−6.7
O + CH_4 ← OH + CH_3	8.1	−4.6	−8.2	−6.2	−5.5	−6.2	−3.5	−7.5	−4.4
H + OH → H_2 + O	10.7	−7.9	−8.2	−8.2	−8.2	−8.4	−6.9	−7.0	−7.2
H + OH ← H_2 + O	13.1	−6.8	−6.0	−6.0	−7.2	−8.0	−6.6	−6.3	−7.0
NH_2 + CH_3 → NH + CH_4	8.0	−2.8	−6.8	−4.8	−4.0	−4.5	−1.8	−5.7	−3.0
NH_2 + CH_3 ← NH + CH_4	22.4	−5.4	−3.5	−5.7	−6.6	−7.2	−5.0	−2.6	−6.2
NH_2 + C_2H_5 → NH C_2H_6	7.5	−0.3	−4.5	−2.8	−2.0	−2.5	0.9	−3.0	−0.8
NH_2 + C_2H_5 ← NH C_2H_6	18.3	−3.9	−2.5	−4.6	−5.4	−6.0	−3.4	−1.8	−4.8
C_2H_6 + NH_2 → C_2H_5 + NH_3	10.4	−2.1	−1.4	−3.0	−3.7	−4.4	−1.4	−0.5	−3.1
C_2H_6 + NH_2 ← C_2H_5 + NH_3	17.4	−2.7	−7.7	−5.7	−4.5	−5.1	−1.7	−6.3	−3.5
NH_2 + CH_4 → NH_3 + CH_3	14.5	−3.6	−2.4	−4.2	−5.0	−5.6	−3.0	−1.4	−4.3
NH_2 + CH_4 ← NH_3 + CH_3	17.8	−5.1	−10.0	−7.6	−6.5	−7.0	−4.2	−8.9	−5.5
s−trans−cis−C_5H_8 → *s-trans-cis*-C_5H_8	38.4	−0.3	−2.4	−2.4	−1.5	−2.4	0.5	−1.1	−0.7
s−trans−cis−C_5H_8 ← *s-trans-cis*-C_5H_8	38.4	−0.3	−2.4	−2.4	−1.5	−2.4	0.5	−1.1	−0.7
MD		−4.0	−4.3	−4.7	−4.9	−5.4	−3.6	−3.9	−4.5
MAD		4.3	5.6	4.9	5.2	5.6	3.8	4.9	4.6
RMSD		5.0	6.2	5.5	5.8	6.3	4.5	5.6	5.2

[a] $\Delta E = E(method) - E(reference)$. [b] Mean (MD), mean absolute (MAD), and root-mean-square deviations (RMSD). [c] forward and their respective backward reactions.

Table S14 – Reference values, deviations (ΔE^a) and statistical values[b] (kcal mol^{-1}) for all tested methods for the barrier heights in the BHPERI test set.

		ΔE(6-31+G(2d,2p))					ΔE(def2-QZVP)		
system	ref	B3LYP	-DCP	-DCP*	-D3	-NL	B3LYP	-DCP	-D3
cyclobutene	35.3	−2.0	5.6	−0.3	−2.5	-1.8	−2.3	5.0	−2.7
cis-1,3,5-hexatriene	30.9	−0.6	−3.9	−3.5	−2.6	−3.0	0.3	−2.5	−1.7
o-xylylene	28.3	−0.7	−2.9	−2.2	−0.9	−1.7	0.0	−1.3	−0.2
1,3-pentadiene	39.6	−1.4	−3.3	−3.5	−2.7	−3.5	−0.6	−2.0	−1.9
1,3-cyclopentadiene	28.2	−0.8	−4.7	−1.6	−0.5	−1.4	−1.0	−4.4	−0.7
1,5-hexadiene	35.6	−0.5	−1.8	−4.0	−2.9	−3.7	0.4	−0.4	−2.1
1,3-butadiene + C_2H_4	22.1	2.6	−8.3	−5.8	−4.1	−4.2	4.3	−5.9	−2.4
1,3-cyclopentadiene + C_2H_4	18.3	4.2	−6.5	−5.5	−2.9	−3.6	6.1	−3.8	−1.0
1,3-cyclopentadiene	9.8	11.7	−2.1	−1.1	2.1	0.7	14.1	0.5	4.5
cis-triscyclopropacyclohexane	23.6	−1.5	10.5	1.3	−1.2	−1.0	−1.7	10.3	−1.4
N_2O + C_2H_4	26.3	−0.3	−4.2	−4.2	−3.7	−5.6	2.7	−0.9	−0.7
N_3H + C_2H_4	18.1	1.7	−3.8	−3.3	−2.3	−3.7	4.5	0.6	0.5
N_2CH_2 + C_2H_4	12.2	3.7	0.3	−1.7	−0.6	−1.4	6.2	3.8	1.9
HCNO + C_2H_4	11.1	2.0	0.7	−2.4	−1.8	−2.8	4.5	3.3	0.7
HCNNH + C_2H_4	5.3	3.4	−0.8	−1.7	−0.7	−1.4	5.1	1.8	1.0
$HCNCH_2$ + C_2H_4	4.0	4.5	−0.3	−1.1	0.1	−0.3	5.8	1.5	1.4
H_2COHN + C_2H_4	11.5	3.5	−2.5	−2.1	−0.9	−2.1	5.1	−0.5	0.7
H_2CNHNH + C_2H_4	4.0	4.9	−2.0	−1.3	−0.2	−0.8	6.4	0.8	1.4
H_2CNHCH_2+ C_2H_4	−1.4	5.2	−0.3	−0.7	0.2	0.0	6.4	1.5	1.4
1,3-cyclopentadiene + C_2H_4	15.0	7.4	−3.5	−2.3	0.3	−0.4	9.6	−0.5	2.5
furane + C_2H_4	19.8	7.6	−1.5	−1.4	1.7	0.0	10.0	1.5	4.0
pyrrole + C_2H_4	25.4	8.1	−1.4	−1.8	1.7	0.1	10.7	2.6	4.3
MD		2.9	−1.7	−2.3	−1.1	−1.9	4.4	0.5	0.4
MAD		3.6	3.2	2.4	1.7	2.0	4.9	2.5	1.8
RMSD		4.6	4.1	2.8	2.0	2.5	6.1	3.4	2.1

[a] $\Delta E = E(method) - E(reference)$. [b] Mean (MD), mean absolute (MAD), and root-mean-square deviations (RMSD).

Table S15 – Reference values, deviations (ΔE^a) and statistical values[b] (kcal mol^{-1}) for all tested methods for the reaction energies in the BH76RC test set.

		ΔE(6-31+G(2d,2p))					ΔE(def2-QZVP)		
reaction	ref	B3LYP	-DCP	-DCP*	-NL	-D3	B3LYP	-DCP	-D3
H + N_2O → OH + N_2	−65.1	2.5	0.4	0.4	4.4	3.0	3.5	3.2	4.0
H + N_2 → HN_2	4.0	−9.9	−10.3	−10.3	−10.9	−10.3	−7.2	−6.9	−7.6
H + CO → HCO	−19.5	−7.1	−16.5	−8.4	−8.0	−7.4	−5.6	−14.8	−5.8
H + C_2H_4 → C_2H_5	−40.0	−3.9	−5.8	−3.9	−4.7	−4.3	−2.0	−3.6	−2.4
CH_3 + C_2H_4 → C_3H_7	−26.1	1.3	−12.1	−4.5	−2.3	−1.0	3.0	−9.7	0.7
HNC → HCN	−15.1	1.9	−8.3	−0.3	2.1	2.0	1.1	−9.4	1.2
OH + H_2 → H_2O + H	−16.1	4.7	6.0	6.0	4.0	4.6	4.0	4.7	3.9
CH_3 + H_2 → CH_4 + H	−3.2	3.3	−2.0	2.2	2.6	3.0	2.7	−3.3	2.5
OH + CH_4 → H_2O + CH_3	−12.9	1.5	8.0	3.8	1.4	1.6	1.3	8.0	1.4
OH + NH_3 → H_2O + NH_2	−9.5	−0.1	0.3	0.3	−0.1	−0.0	0.0	0.4	0.1
OH + C_2H_6 → H_2O + C_2H_5	−16.5	0.5	6.7	3.0	0.6	0.8	0.3	6.3	0.5
O + CH_4 → OH + CH_3	5.6	−2.2	4.3	0.0	−2.1	−2.0	−2.5	4.1	−2.3
H + OH → H_2 + O	−2.4	−1.0	−2.2	−2.2	−0.5	−1.0	−0.2	−0.8	−0.2
NH_2 + CH_3 → NH + CH_4	−14.4	2.7	−3.3	0.9	2.6	2.6	3.2	−3.0	3.1
NH_2 + C_2H_5 → NH C_2H_6	−10.8	3.6	−2.0	1.8	3.5	3.4	4.2	−1.3	4.0
C_2H_6 + NH_2 → C_2H_5 + NH_3	−7.0	0.6	6.4	2.6	0.7	0.8	0.2	5.8	0.4
NH_2 + CH_4 → NH_3 + CH_3	−3.3	1.5	7.6	3.4	1.4	1.5	1.2	7.5	1.2
MD		−0.0	−1.3	−0.31	−0.31	−0.2	0.4	−0.8	0.3
MAD		2.8	6.0	3.2	3.1	2.9	2.5	5.5	2.4
RMSD		3.8	7.3	4.2	4.1	3.9	3.2	6.5	3.2

[a] $\Delta E = E(method) - E(reference)$. [b] Mean (MD), mean absolute (MAD), and root-mean-square deviations (RMSD).

Table S16 – Reference values, deviations (ΔE^a) and statistical values[b] (kcal mol^{-1}) for all tested methods for the reaction energies in the G2RC test set.

		ΔE(6-31+G(2d,2p))					ΔE(def2-QZVP)		
reaction	ref	B3LYP	-DCP	-DCP*	-NL	-D3	B3LYP	-DCP	-D3
$CO_2 + H_2 \rightarrow HCOOH$	−2.0	−1.2	1.7	−0.8	−3.3	−2.0	1.6	3.8	0.8
$CH_3CHO \rightarrow CO + CH_4$	−2.6	3.2	22.4	9.3	6.4	4.9	1.5	20.2	3.2
$CO + H_2O \rightarrow CO_2 + H_2$	−7.0	−3.2	−23.5	−6.0	−4.1	−3.5	−5.0	−26.4	−5.3
$CH_3CN + H_2O \rightarrow CH_3CONH_2$	−20.1	−3.3	−8.6	−5.0	−7.4	−5.3	−0.8	−6.5	−2.8
$H_2CO + H_2 \rightarrow CH_3OH$	−29.2	0.9	−2.6	0.5	−0.8	0.2	1.8	−2.2	1.1
$C_2H_2 + C_2H_4 \rightarrow C_4H_8$	−32.7	1.0	−21.7	−9.7	−4.6	−2.0	5.2	−15.1	2.2
$N_2 + 3H_2 \rightarrow 2NH_3$	−38.9	−5.9	−4.7	−4.7	−7.9	−6.7	−2.3	−1.0	−3.1
$C_2H_2 + H_2 \rightarrow C_2H_4$	−48.4	−3.9	−8.8	−5.3	−5.5	−4.9	−1.2	−6.1	−2.2
$CO + 3H_2 \rightarrow H_2O + CH_4$	−64.8	−2.7	−17.9	−4.4	−4.7	−3.6	−0.3	−16.3	−1.1
$N_2O + H_2 \rightarrow N_2 + H_2O$	−80.7	6.8	6.1	8.0	6.1	7.2	7.0	7.3	7.4
$C_2H_4 + CH_2 \rightarrow C_3H_6$	−109.1	3.5	−29.3	−6.0	−0.9	1.6	3.7	−28.5	1.8
$3C_2H_2 \rightarrow C_6H_6$	−151.6	−9.0	−48.5	−29.2	−20.0	−16.6	0.5	−37.0	−7.1
MD		−1.2	−11.3	−4.6	−3.8	−2.6	1.0	−9.0	−0.4
MAD		3.7	16.3	7.3	6.2	4.9	2.6	14.2	3.2
RMSD		4.4	21.0	10.2	7.8	6.4	3.3	18.1	3.8

[a] $\Delta E = E(method) - E(reference)$. [b] Mean (MD), mean absolute (MAD), and root-mean-square deviations (RMSD).

Table S17 – Reference values, deviations (ΔE^a) and statistical values[b] (kcal mol^{-1}) for all tested methods for the radical-stabilization energies in RSE43 test set.

		ΔE(6-31+G(2d,2p))					ΔE(def2-QZVP)		
system	ref	B3LYP	-DCP	-DCP*	-NL	-D3	B3LYP	-DCP	-D3
$(C_6H_5)CH_2$	−15.2	−1.9	−2.6	−1.8	−1.7	−1.7	−2.1	−3.1	−1.9
CH_2CCN	1.9	−4.3	−7.8	−4.2	−4.0	−3.8	−4.6	−8.5	−4.1
$HOCH_2CH_2$	−1.8	−1.3	−1.6	−1.1	−1.1	−1.1	−1.4	−2.1	−1.2
CH_2CHCH_2	−17.5	−2.3	−3.0	−2.3	−2.2	−2.2	−2.4	−3.4	−2.2
CH_2CHO	−10.0	−2.2	−3.0	−2.3	−2.1	−2.0	−2.1	−3.3	−2.0
CH_2CN	−8.6	−2.5	−3.7	−2.7	−2.4	−2.4	−2.5	−4.0	−2.3
CH_2CONH_2	−6.3	−1.7	−2.0	−1.6	−1.5	−1.5	−1.7	−2.2	−1.5
$CH_3NHCOCH_2$	−6.3	−1.8	−2.2	−1.8	−1.6	−1.6	−1.8	−2.5	−1.6
CH_2COOCH_3	−6.6	−1.8	−2.1	−1.7	−1.6	−1.6	−1.7	−2.3	−1.5
CH_2COOH	−6.4	−1.8	−2.1	−1.7	−1.6	−1.6	−1.8	−2.3	−1.6
$(CH_2CHCH_2)CH_2$	−3.0	−1.4	−1.2	−1.0	−1.1	−1.1	−1.4	−1.5	−1.1
CH_2NH_2	−12.0	−1.7	−3.9	−1.8	−1.6	−1.5	−2.3	−5.2	−2.1
$CH_2NH_3^+$	4.7	−0.7	−1.7	−0.7	−0.6	−0.5	−0.8	−2.0	−0.6
CH_3NHCH_2	−12.6	−2.0	−4.2	−2.0	−1.8	−1.8	−2.6	−5.5	−2.4
CH_2NHCHO	−11.1	−1.7	−3.9	−1.9	−1.6	−1.6	−2.2	−4.9	−2.0
CH_2NHOH	−8.6	−2.4	−4.8	−2.6	−2.2	−2.2	−3.0	−6.1	−2.8
$(CH_3)_2NCH_2$	−12.8	−2.3	−4.6	−2.1	−1.9	−1.9	−2.8	−5.8	−2.4
CH_2NO_2	−3.3	−2.1	−2.9	−3.0	−2.0	−2.0	−2.0	35.6	−1.8
CH_3OCH_2	−2.7	−1.4	−2.7	−1.3	−1.1	−1.2	−1.8	−3.4	−1.6
CH_2OCHO	−5.9	−1.2	−3.3	−1.3	−1.1	−1.1	−1.7	−4.0	−1.5
CH_3COOCH_2	−6.2	−1.6	−3.7	−1.6	−1.4	−1.4	−2.1	−4.5	−1.8
CH_2OH	−4.2	−0.9	−2.6	−1.1	−0.9	−0.8	−1.4	−3.3	−1.3
H_2NCHCN	−22.5	−4.6	−9.0	−5.0	−4.4	−4.3	−5.2	−10.4	−5.0
$H_2NCHCONH_2$	−24.1	−4.2	−7.9	−4.5	−4.0	−3.9	−4.8	−9.4	−4.5
$H_2NCHCOOH$	−25.4	−4.6	−8.5	−4.9	−4.4	−4.3	−5.4	−10.1	−5.1
H_2CCCH	−13.1	−3.2	−3.7	−3.2	−3.1	−3.1	−3.1	−3.9	−3.0
$(CH_3)_3C$	−6.4	−3.7	−5.5	−3.2	−2.8	−3.0	−3.9	−6.3	−3.2
$(CH_3)_3CCH_2$	−2.3	−1.4	−1.0	−0.8	−0.9	−0.9	−1.4	−1.3	−1.0
MD		−2.2	−3.8	−2.3	−2.0	−2.0	−2.5	−3.1	−2.3
MAD		2.2	3.8	2.3	2.0	2.0	2.5	5.6	2.3
RMSD		2.5	4.3	2.6	2.3	2.3	2.8	8.4	2.5

[a] $\Delta E = E(method) - E(reference)$. [b] Mean (MD), mean absolute (MAD), and root-mean-square deviations (RMSD).

Table S18 – Reference values, deviations (ΔE^a) and statistical values[b] (kcal mol^{-1}) for all tested methods for the reaction energies in the DARC test set.

		ΔE(6-31+G(2d,2p))					ΔE(def2-QZVP)		
reaction	ref	B3LYP	-DCP	-DCP*	-NL	-D3	B3LYP	-DCP	-D3
ethene + butadiene	−43.8	6.6	−21.6	−6.9	−1.8	1.2	10.1	−16.5	4.6
ethyne + butadiene	−59.3	1.7	−25.9	−11.4	−5.7	−3.2	6.2	−19.9	1.3
ethene + cyclopentadiene	−30.0	11.4	−12.6	−3.1	1.8	5.2	14.8	−7.3	8.7
ethyne + cyclopentadiene	−33.1	7.0	−14.5	−6.7	−1.7	1.4	11.5	−8.0	5.9
ethene + cyclohexadiene	−36.5	10.4	−15.8	−5.3	−0.04	3.4	14.1	−10.7	7.1
ethyne + cyclohexadiene	−48.2	6.7	−17.8	−8.5	−2.9	0.2	11.3	−11.6	4.8
furane + maleine (endo-product)	−14.4	14.0	−5.4	−0.8	1.9	5.1	18.6	−1.8	9.7
furane + maleine (exo-product)	−16.2	13.5	−5.1	−0.6	1.9	5.4	18.0	−1.4	9.9
furane + maleinimide (endo-product)	−17.2	14.2	−5.8	−0.9	1.9	5.1	18.7	−2.1	9.6
furane + maleinimide (exo-product)	−19.2	13.6	−5.6	−0.8	1.8	5.3	18.1	−2.8	9.8
cyclopentadiene + maleine (endo-product)	−31.6	14.6	−10.8	−2.4	1.6	4.9	18.7	−6.5	9.0
cyclopentadiene + maleine (exo-product)	−32.1	14.3	−11.0	−2.4	1.7	5.1	18.4	−6.8	9.2
cyclopentadiene + maleinimide (endo-product)	−34.1	14.9	−11.2	−2.5	1.7	5.0	18.9	−6.8	9.0
cyclopentadiene + maleinimide (exo-product)	−34.4	14.5	−11.4	−2.6	1.7	5.0	18.4	−7.3	9.0
MD		11.2	−12.5	−.3.9	0.3	3.5	15.4	−7.8	7.7
MAD		11.2	12.5	3.9	2.0	4.0	15.4	7.8	7.7
RMSD		11.9	13.9	5.1	2.3	4.3	15.9	9.4	8.1

[a] $\Delta E = E(method) - E(reference)$. [b] Mean (MD), mean absolute (MAD), and root-mean-square deviations (RMSD).

Table S19 – Reference values, deviations (ΔE^a) and statistical values[b] (kcal mol^{-1}) for all tested methods for the bond-separation reaction energies in BSR36 test set.

		ΔE(6-31+G(2d,2p))					ΔE(def2-QZVP)		
reaction	ref	B3LYP	-DCP	-DCP*	-NL	-D3	B3LYP	-DCP	-D3
h1	9.8	−6.7	−1.5	0.9	−0.8	−1.3	−7.6	−1.5	−2.2
h2	9.7	−5.1	−1.6	0.7	−0.5	−1.0	−5.8	−1.6	−1.8
h3	11.4	−7.3	−1.7	1.2	−1.0	−1.6	−8.4	−1.9	−2.7
h4	9.0	−5.5	−1.4	0.7	−0.6	−1.0	−6.3	−1.5	−1.8
h5	8.7	−3.6	−1.3	0.6	−0.3	−0.7	−4.3	−1.3	−1.3
h6	10.9	−4.6	−1.6	0.7	−0.4	−0.8	−5.4	−1.6	−1.7
h7	13.6	−7.7	−2.0	1.0	−0.9	−1.5	−8.8	−2.1	−2.6
h8	11.9	−6.1	−1.9	0.8	−0.6	−1.2	−7.0	−1.9	−2.1
h9	13.5	−8.4	−2.1	1.2	−1.0	−1.8	−9.6	−2.3	−3.0
h10	11.4	−8.3	−1.8	1.0	−0.9	−1.5	−9.3	−1.8	−2.6
h11	13.0	−10.4	−2.3	1.2	−1.4	−2.3	−11.8	−2.5	−3.6
h12	12.8	−9.7	−1.7	1.1	−1.2	−1.9	−10.9	−1.9	−3.2
h13	11.2	−6.5	−1.8	0.8	−0.7	−1.2	−7.5	−1.8	−2.1
h14	10.2	−7.0	−1.9	0.8	−0.6	−1.2	−7.9	−1.8	−2.1
h15	15.1	−14.9	−3.4	1.2	−2.3	−3.6	−16.8	−3.9	−5.5
r1	2.4	−3.0	−3.8	−0.2	−1.2	−1.7	−3.2	−3.4	−1.9
r2	10.7	−4.5	−1.8	0.8	−0.7	−1.3	−5.1	−1.5	−1.9
r3	6.4	−4.5	−3.9	0.3	−1.3	−1.9	−5.1	−3.5	−2.5
r4	14.9	−6.5	−2.3	1.1	−0.8	−1.7	−7.4	−2.0	−2.6
r5	10.7	−8.0	−4.3	0.8	−1.7	−2.7	−9.1	−4.0	−3.7
r6	10.1	−6.2	−4.1	0.7	−1.3	−2.1	−7.0	−3.6	−2.9
r7	9.1	−7.6	−4.2	0.5	−1.7	−2.5	−8.5	−3.7	−3.3
r8	10.5	−6.6	−4.0	0.7	−1.4	−2.2	−7.5	−3.5	−3.0
r9	9.8	−6.2	−4.3	0.7	−1.3	−2.1	−7.0	−3.8	−2.9
r10	19.3	−13.0	−5.6	1.2	−2.2	−3.8	−14.6	−4.7	−5.4
r11	9.7	−13.0	−3.7	1.8	−1.1	−2.3	−14.7	−2.4	−4.0
r12	15.2	−11.2	−5.7	1.2	−1.6	−2.9	−12.7	−4.7	−4.4
r13	26.1	−11.6	−3.8	1.6	−1.4	−3.0	−13.3	−3.1	−4.7
r14	23.5	−12.5	−3.4	1.7	−1.6	−3.0	−14.2	−2.6	−4.6
r15	28.0	−15.2	−4.6	1.7	−1.8	−3.5	−17.1	−3.8	−5.5
r16	25.4	−12.1	−3.9	1.5	−1.3	−2.6	−13.8	−3.5	−4.4
c1	27.6	−13.9	−5.0	1.8	−2.6	−4.7	−15.5	−3.5	−6.3
c2	39.6	−19.7	−5.7	3.0	−2.9	−5.6	−22.5	−4.2	−8.5
c3	32.4	−21.1	−6.3	2.0	−3.4	−6.0	−23.8	−4.7	−8.7
c4	51.4	−25.7	−6.4	4.0	−3.1	−6.6	−29.4	−4.9	−10.3
c5	47.1	−23.3	−8.0	2.5	−4.0	−7.5	−26.2	−4.7	−10.4
MD		−9.9	−3.4	1.2	−1.4	−2.6	−11.3	−2.9	−3.9
MAD		9.9	3.4	1.2	1.4	2.6	11.3	2.9	3.9
RMSD		11.3	3.8	1.4	1.7	3.0	12.9	3.1	4.5

[a] $\Delta E = E(method) - E(reference)$. [b] Mean (MD), mean absolute (MAD), and root-mean-square deviations (RMSD).

Table S20 – Reference values, deviations (ΔE^a) and statistical values[b] (kcal mol^{-1}) for all tested methods for the isomerization energies in the ISO34 test set.

		ΔE(6-31+G(2d,2p))					ΔE(def2-QZVP)		
reaction	ref	B3LYP	-DCP	-DCP*	-NL	-D3	B3LYP	-DCP	-D3
1	1.6	−4.1	−3.5	−4.5	−4.2	−4.3	−3.5	−2.7	−3.6
2	21.9	1.0	−6.7	−1.6	0.0	0.8	2.1	−3.8	1.9
3	7.2	1.9	−7.5	−0.4	0.9	2.0	1.9	−6.2	2.1
4	1.0	0.3	−0.4	0.0	0.1	0.1	0.3	−0.4	0.0
5	0.9	−0.5	0.2	0.6	0.1	0.1	−0.6	0.1	−0.0
6	2.6	0.6	1.2	0.4	0.3	0.3	0.5	1.3	0.3
7	11.2	3.3	−6.6	−0.5	1.6	3.2	4.3	−3.9	4.2
8	22.9	−2.0	−1.0	0.3	−0.5	−1.0	−3.2	−2.1	−2.2
9	6.9	1.3	2.1	1.2	1.0	1.0	1.2	2.1	0.9
10	3.6	−2.4	−0.5	0.8	−0.3	−0.6	−2.8	−0.8	−1.0
11	1.9	−9.0	−2.0	0.2	−1.8	−2.4	−9.9	−2.3	−3.4
12	47.0	9.5	5.3	4.7	6.1	8.4	10.2	8.2	9.1
13	36.0	3.2	5.0	3.7	2.9	2.4	3.0	4.8	2.2
14	24.2	−1.7	11.2	1.5	−2.0	−1.9	−0.6	13.1	−0.8
15	7.3	0.1	1.6	0.9	0.0	0.2	0.1	2.1	0.2
16	10.8	1.8	−5.1	−0.2	1.0	1.9	1.6	−4.2	1.7
17	27.0	−1.1	3.9	1.5	−0.9	−0.5	−1.2	3.7	−0.6
18	11.2	0.5	−0.8	0.1	1.2	0.8	0.2	−1.3	0.5
19	4.6	−0.6	−0.7	−0.8	−0.6	−0.6	−0.5	−0.5	−0.5
20	20.2	−1.8	−0.0	−1.5	−1.8	−1.9	−1.9	−0.9	−1.9
21	0.9	0.2	−0.3	−0.1	0.2	0.1	0.3	−0.3	0.1
22	3.2	−0.5	1.8	0.6	−0.3	−0.1	0.6	2.9	1.0
23	5.3	−0.6	1.7	0.8	−0.6	−0.3	−0.6	2.0	−0.3
24	12.5	−1.5	1.6	0.6	−1.6	−1.3	−1.9	0.8	−1.7
25	26.5	2.0	−1.0	2.0	1.1	2.3	1.4	−1.2	1.7
26	18.2	−1.6	1.8	0.6	−1.7	−1.5	−2.2	1.2	−2.1
27	64.2	−2.5	6.1	3.7	−2.0	−1.5	−3.1	1.1	−2.2
28	31.2	2.1	−0.7	1.8	0.5	2.2	2.3	0.1	2.4
29	11.9	−1.3	6.0	2.7	0.8	−0.9	−3.2	3.2	−2.7
30	9.5	0.1	0.9	0.2	−0.3	−0.2	0.2	1.9	−0.2
31	14.1	−1.5	8.1	3.4	1.0	−0.2	−3.3	5.1	−2.0
32	7.1	−3.9	3.8	−3.1	−1.1	−3.2	−4.0	4.8	−3.3
33	5.6	4.6	7.1	4.4	2.2	3.2	4.7	5.8	3.3
34	7.3	−0.4	2.4	−0.1	0.0	−0.2	−0.4	3.1	−0.2
MD		−0.1	1.0	0.7	0.1	0.2	−0.2	1.1	0.1
MAD		2.1	3.2	1.5	1.2	1.5	2.3	2.9	1.8
RMSD		3.0	4.3	2.0	1.7	2.2	3.3	3.9	2.5

[a] $\Delta E = E(method) - E(reference)$. [b] Mean (MD), mean absolute (MAD), and root-mean-square deviations (RMSD).

Table S21 – Reference values, deviations (ΔE^a) and statistical values[b] (kcal mol^{-1}) for all tested methods for the isomerization energies in the ISOL22 test set.

		ΔE(6-31+G(2d,2p))					ΔE(def2-QZVP)		
reaction	ref	B3LYP	-DCP	-DCP*	-NL	-D3	B3LYP	-DCP	-D3
2	40.6	−20.1	10.5	−0.2	−4.1	−8.7	−24.0	6.1	−12.5
3	11.7	−3.6	0.3	−2.8	−1.3	−3.7	−4.4	0.6	−4.5
5	34.9	−10.4	14.6	1.7	−2.6	−6.1	−13.5	10.4	−9.3
6	25.9	−4.2	6.1	—[c]	—[c]	−4.3	−3.0	6.8	−3.1
7	18.8	−10.8	5.2	−0.2	−2.4	−4.8	−12.7	3.4	−6.8
8	18.3	29.2	−2.0	10.1	14.3	18.6	33.4	1.7	22.8
9	22.3	−3.4	3.2	1.5	0.1	−0.3	−4.5	3.2	−1.3
10	7.9	−4.5	2.3	0.4	−3.3	−2.5	−5.2	−0.0	−3.2
11	38.1	−2.8	−1.8	−3.5	−4.1	−2.4	−1.7	−0.3	−1.3
13	35.1	−4.4	3.4	−0.3	−3.9	−3.1	−4.8	3.4	−3.5
14	5.2	0.0	4.0	4.5	1.6	1.8	−1.4	0.7	0.4
15	3.9	−1.2	−7.8	3.2	2.1	1.3	−6.2	−11.9	−3.7
16	22.6	0.8	3.1	4.9	0.9	0.3	1.5	6.4	1.0
17	11.1	−11.5	7.8	−2.5	−5.9	−10.0	−13.0	4.6	−11.6
MD		−3.4	3.5	1.3	−0.7	−1.7	−4.3	2.5	−2.6
MAD		7.6	5.2	2.7	3.6	4.9	9.2	4.2	6.1
RMSD		11.0	6.4	3.8	5.0	6.8	12.9	5.5	8.5

[a] $\Delta E = E(method) - E(reference)$. [b] Mean (MD), mean absolute (MAD), and root-mean-square deviations (RMSD).
[c] Convergence problems with ORCA and various convergence techniques.