SUPPORTING INFORMATION

Benchmark thermochemistry of the C_nH_{2n+2} alkane isomers (n=2–8) and performance of DFT and composite ab initio methods for dispersion-driven isomeric equilibria

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Table S 1: Diagnostics for importance of nondynamical correlation

	%TAE$_e$ [SCF][a]	%TAE$_e$ [(T)][a]	%TAE$_e$ [post-(T)][a]	%TAE$_e$ [(Q)][a]	$\mathcal{T}_1$ diagnostic	D_1	Largest T_2 amplitudes
					— CCSD/cc-pVTZ —		
methane	79.09	0.70	-0.01	0.02	0.007	0.011	0.037
ethane	78.51	0.90	-0.01	0.03	0.008	0.013	0.032
propane	78.18	1.02	-0.01	0.04	0.008	0.014	0.016
n-butane	78.01	1.08	-0.02	0.04	0.008	0.015	0.017
isobutane	77.95	1.09	-0.02	0.04	0.008	0.015	0.019
n-pentane	77.89	1.12	-0.02	0.05	0.008	0.015	0.013
isopentane	77.72	1.13			0.008	0.016	
neopentane	77.72	1.15	-0.02	0.05	0.008	0.016	0.017
n-hexane	77.74	1.14			0.008	0.016	
isohexane	77.65	1.16			0.008	0.016	
3-methylpentane	77.61	1.16			0.008	0.016	
neohexane	77.52	1.18			0.008	0.016	
diisopropyl	77.53	1.18			0.008	0.017	
n-heptane	77.68	1.16			0.008	0.016	
isoheptane	77.60	1.17			0.008	0.016	
neoheptane	77.48	1.20			0.008	0.017	
n-octane	77.64	1.17			0.008	0.016	
hexamethylethane	77.15	1.26			0.009	0.017	

[a] Percentages of the W1h total atomization energy relate to nonrelativistic, clamped-nuclei values with inner-shell electrons constrained to be doubly occupied; methane, ethane, propane, *n*-butane, isobutane, *n*-pentane, and neopentane from W3.2lite theory, and all the rest from W1h theory.

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Table S 2: Component breakdown of the final W1h total atomization energies and from hypohomodesmotic and isodesmic reactions involving linear alkanes (in kcal/mol).

	SCF	valence CCSD	valence (T)	inner shell	relativ.	spin orbit	DBOC[a]	TAE_e	ZPVE[b]	TAE_0
methane	331.53	85.15	2.93	1.21	-0.19	-0.08	0.10	420.54	27.57	392.97
ethane	557.99	146.92	6.44	2.34	-0.39	-0.17	0.14	713.12	45.98	667.14
propane	785.20	209.78	10.20	3.45	-0.58	-0.25	0.20	1007.80	63.69	944.11
n-butane	1012.62	272.62	13.93	4.63	-0.77	-0.34	0.25	1302.69	81.26	1221.42
n-pentane	1239.85	335.54	17.71	5.78	-0.97	-0.42	0.30	1597.48	98.88	1498.61
n-hexane	1467.07	398.49	21.49	6.92	-1.16	-0.51	0.36	1892.31	116.39	1775.91
n-heptane	1694.32	461.43	25.27	8.07	-1.35	-0.59		2187.14	134.00	2053.14
n-octane	1921.55	524.39	29.05	9.21	-1.54	-0.68		2481.98	151.51	2330.46
isobutane	1012.93	273.55	14.12	4.63	-0.77	-0.34	0.26	1304.13	81.01	1223.13
isopentane	1238.93	337.07	18.01	5.77	-0.96	-0.42	0.31	1598.40	98.57	1499.83
neopentane	1240.06	338.44	18.30	5.77	-0.95	-0.42	0.32	1601.19	98.56	1502.63
isohexane	1466.05	400.07	21.81	6.92	-1.16	-0.51	0.36	1893.19	116.20	1776.99
neohexane	1464.71	402.54	22.31	6.91	-1.15	-0.51	0.38	1894.81	115.77	1779.04
3-methylpentane	1464.71	400.66	21.92	6.91	-1.16	-0.51		1892.54	116.16	1776.38
diisopropyl	1463.86	402.07	22.22	6.90	-1.15	-0.51	0.37	1893.39	115.96	1777.43
isoheptane	1693.28	463.05	25.60	8.06	-1.35	-0.59		2188.05	133.66	2054.40
neoheptane	1691.72	465.62	26.13	8.05	-1.34	-0.59		2189.59	133.21	2056.38
hexamethylethane	1910.54	534.68	31.21	9.13	-1.53	-0.68		2483.36	150.37	2332.98
isooctane[c]	1915.48	530.52	30.32	9.17	-1.53	-0.68		2483.28	150.63	2332.64
Hypohomodesmotic reactions, Eq. (5) of the main text										
n-butane	0.20	-0.02	-0.03	0.06	0.00	[0]	0.00	0.21	0.13	0.34
n-pentane	0.22	0.04	-0.02	0.10	0.00	[0]	-0.01	0.33	0.22	0.55
n-hexane	0.22	0.13	-0.01	0.13	0.00	[0]	-0.01	0.48	0.41	0.89
n-heptane	0.25	0.21	0.01	0.16	0.01	[0]		0.64	0.50	1.14
n-octane	0.27	0.30	0.03	0.20	0.01	[0]		0.80	0.70	1.50
Isodesmic reactions, Eq. (6) of the main text										
n-butane	1.71	2.17	0.48	0.03	0.01	[0]	0.02	4.39	1.55	5.94
n-pentane	2.48	3.32	0.74	0.05	0.02	[0]	0.03	6.61	2.34	8.95
n-hexane	3.24	4.51	1.02	0.06	0.02	[0]	0.04	8.85	3.24	12.08
n-heptane	4.02	5.68	1.29	0.08	0.03	[0]		11.10	4.04	15.14
n-octane	4.79	6.87	1.56	0.09	0.03	[0]		13.35	4.94	18.29

[a] DBOCs are not included in the final TAEs.
[b] B3LYP/pc-2 harmonic frequencies scaled by 0.985
[c] First order saddle point (C_s symmetry).

Table S 3: W1h Component breakdown from isodesmic reaction energies involving branched alkanes (in kcal/mol).

Reaction	valence SCF	valence CCSD	valence (T)	inner shell	relativ.	DBOC	RE_e	ZPVE	RE_0	TAE_0[a]	uncert.[a]
Isodesmic reactions, Eq. (5) of the main text											
isobutane+C_2H_6→2C_3H_8	0.52	0.91	0.16	0.07	0.01	0.00	1.66	0.39	2.04	1221.76	0.39
isopentane+2C_2H_6→3C_3H_8	-0.70	1.56	0.28	0.10	0.01	0.00	1.25	0.53	1.78	1498.27	0.60
isohexane+3C_2H_6→4C_3H_8	-0.79	1.71	0.31	0.13	0.01	0.00	1.36	0.60	1.96	1775.22	0.82
isoheptane+4C_2H_6→5C_3H_8	-0.78	1.83	0.34	0.16	0.01		1.55	0.85	2.40	2052.43	1.04
neopentane+2C_2H_6→3C_3H_8	0.42	2.94	0.57	0.09	0.02	0.02	4.04	0.53	4.57	1501.06	0.60
neohexane+3C_2H_6→4C_3H_8	-2.13	4.18	0.81	0.12	0.01	0.01	2.98	1.03	4.01	1777.27	0.82
neoheptane+4C_2H_6→5C_3H_8	-2.34	4.40	0.87	0.14	0.01		3.09	1.30	4.38	2054.41	1.04
3-methylpentane+3C_2H_6→4C_3H_8	-2.14	2.29	0.43	0.12	0.01		0.71	0.64	1.35	1774.61	0.82
diisopropyl+3C_2H_6→4C_3H_8	-2.99	3.71	0.72	0.11	0.01	0.01	1.57	0.84	2.41	1775.67	0.82
hexamethylmethane+5C_2H_6→6C_3H_8	-10.74	10.60	2.19	0.11	0.02		2.18	1.83	4.01	2330.81	1.26
Isodesmic reactions, Eq. (6) of the main text											
isobutane+2CH_4→3C_2H_6	2.03	3.10	0.67	0.03	0.02	0.03	5.84	1.80	7.64	1221.23	0.60
isopentane+3CH_4→4C_2H_6	1.56	4.85	1.05	0.04	0.02	0.04	7.52	2.65	10.17	1497.47	0.82
isohexane+4CH_4→5C_2H_6	2.22	6.09	1.34	0.06	0.02	0.05	9.73	3.43	13.16	1774.16	1.04
isoheptane+5CH_4→6C_2H_6	2.99	7.30	1.62	0.07	0.03		12.01	4.39	16.40	2051.10	1.26
neopentane+3CH_4→4C_2H_6	2.69	6.23	1.34	0.04	0.03	0.05	10.31	2.65	12.97	1500.27	0.82
neohexane+4CH_4→5C_2H_6	0.88	8.56	1.84	0.05	0.03	0.06	11.35	3.86	15.21	1776.21	1.04
neoheptane+5CH_4→6C_2H_6	1.43	9.87	2.15	0.06	0.03		13.54	4.84	18.38	2053.08	1.26
3-methylpentane+4CH_4→5C_2H_6	0.88	6.67	1.45	0.05	0.02		9.07	3.47	12.55	1773.55	1.04
diisopropyl+4CH_4→5C_2H_6	0.03	8.09	1.74	0.04	0.03	0.06	9.93	3.67	13.60	1774.60	1.04
hexamethylmethane+6CH_4→7C_2H_6	-6.21	17.17	3.72	0.01	0.04		14.73	6.08	20.81	2329.22	1.48
Isodesmic reactions balance the number of 1,3-interactions on both sides											
isobutane+3C_2H_6→CH_4+3C_3H_8	-0.24	-0.18	-0.10	0.08	0.00	-0.01	-0.43	-0.32	-0.76	1222.03	0.72
isopentane+4C_2H_6→CH_4+4C_3H_8	-1.45	0.47	0.02	0.11	0.00	-0.01	-0.85	-0.18	-1.02	1498.53	0.93
isohexane+5C_2H_6→CH_4+5C_3H_8	-1.55	0.61	0.06	0.14	0.00	-0.01	-0.73	-0.11	-0.84	1775.49	1.15
isoheptane+6C_2H_6→CH_4+6C_3H_8	-1.53	0.73	0.08	0.18	0.01		-0.54	+0.14	-0.40	2052.70	1.38
neopentane+8C_2H_6→3CH_4+6C_3H_8	-1.84	-0.34	-0.20	0.14	0.00	-0.02	-2.23	-1.59	-3.82	1501.86	1.68
neohexane+9C_2H_6→3CH_4+7C_3H_8	-4.40	0.89	0.05	0.17	0.00	-0.02	-3.29	-1.09	-4.38	1778.07	1.89
neoheptane+10C_2H_6→3CH_4+8C_3H_8	-4.60	1.11	0.10	0.20	0.00		-3.19	-0.83	-4.01	2055.21	2.11
3-methylpentane+5C_2H_6→CH_4+5C_3H_8	-2.89	1.20	0.17	0.14	0.00		-1.38	-0.06	-1.45	1774.88	1.15
diisopropyl+7C_2H_6→2CH_4+6C_3H_8	-4.49	1.52	0.21	0.15	0.00	-0.01	-2.62	-0.58	-3.19	1776.20	1.52
hexamethylmethane+17C_2H_6→6CH_4+12C_3H_8	-15.26	4.03	0.65	0.22	0.00		-10.37	-2.41	-12.78	2332.41	3.47
Isodesmic reactions balance the number of CH_2 groups on both sides											
isopentane+2CH_4→2C_2H_6+C_3H_8	0.81	3.75	0.79	0.06	0.02	0.03	5.43	1.94	7.37	1497.73	0.51
isohexane+2CH_4→C_2H_6+2C_3H_8	0.72	3.90	0.82	0.09	0.02	0.02	5.55	2.01	7.56	1774.69	0.51
isoheptane+2CH_4→3C_3H_8	0.73	4.01	0.85	0.12	0.02		5.73	2.26	8.00	2051.90	0.55
neohexane+3CH_4→3C_2H_6+C_3H_8	0.13	7.46	1.58	0.06	0.03	0.05	9.26	3.15	12.41	1776.48	0.72
neoheptane+3CH_4→2C_2H_6+2C_3H_8	-0.08	7.68	1.64	0.09	0.03		9.36	3.42	12.78	2053.62	0.68
3-methylpentane+2CH_4→C_2H_6+2C_3H_8	-0.63	4.48	0.94	0.09	0.01		4.89	2.06	6.95	1774.08	0.51
Isodesmic reactions balance the number of CH_3 groups on both sides											
2isobutane+CH_4→3C_3H_8	1.79	2.92	0.57	0.11	0.02	0.02	5.41	1.48	6.88	1221.63	0.27
2isopentane+CH_4+2C_2H_6→5C_3H_8	-0.65	4.22	0.81	0.17	0.02	0.02	4.58	1.77	6.35	1498.13	0.45
2isohexane+CH_4+4C_2H_6→7C_3H_8	-0.83	4.51	0.88	0.23	0.02	0.01	4.82	1.90	6.72	1775.09	0.65
2isoheptane+CH_4+6C_2H_6→9C_3H_8	-0.80	4.75	0.93	0.30	0.02		5.19	2.41	7.60	2052.30	0.87
neopentane+CH_4→2C_3H_8	1.18	4.04	0.83	0.07	0.02	0.03	6.13	1.24	7.37	1500.80	0.39
neohexane+CH_4+C_2H_6→3C_3H_8	-1.38	5.27	1.07	0.10	0.02	0.03	5.07	1.74	6.81	1777.01	0.55
neoheptane+CH_4+2C_2H_6→4C_3H_8	-1.59	5.49	1.13	0.13	0.02		5.18	2.01	7.18	2054.15	0.75
3-methylpentane+CH_4+4C_2H_6→7C_3H_8	-3.52	5.68	1.11	0.23	0.02		3.51	1.99	5.50	1774.48	0.65
diisopropyl+CH_4+C_2H_6→3C_3H_8	-2.23	4.80	0.98	0.09	0.01	0.02	3.66	1.55	5.20	1775.40	0.55
hexamethylmethane+2CH_4+C_2H_6→4C_3H_8	-9.23	12.79	2.70	0.08	0.03		6.36	3.25	9.61	2330.28	0.75

[a] TAE_0 of the branched alkane in the first column obtained by assuming that the isodesmic reaction energy stay constant at the W1h and W4 levels, and using the W4 TAE_0 for methane, ethane and propane from Table I of the main text.

Table S 4: Basis set convergence of Hypohomodesmotic and isodesmic reaction components[a] (in kcal/mol).

	SCF				CCSD				(T)	
	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV{D,T}Z	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV{D,T}Z	cc-pVDZ	cc-pVTZ
Hypohomodesmitic reactions, Eq. (5) of the main text										
n-butane+C_2H_6→$2C_3H_8$	-0.22	-0.03	-0.01	0.00	-0.31	-0.05	-0.02	0.05	0.01	0.00
n-pentane+$2C_2H_6$→$3C_3H_8$	-0.33	-0.04	-0.01	0.00	-0.49	-0.07	-0.03	0.09	0.02	0.01
n-hexane+$3C_2H_6$→$4C_3H_8$	-0.42	-0.05	-0.01	0.00	-0.66	-0.08	-0.03	0.13	0.02	0.01
n-heptane+$4C_2H_6$→$5C_3H_8$	-0.54	-0.07	-0.02	0.00	-0.86	-0.10	-0.04	0.18	0.02	0.01
n-octane+$5C_2H_6$→$6C_3H_8$	-0.65	-0.08	-0.02	0.00	-1.06	-0.12	-0.05	0.23	0.02	0.01
Isodesmic reactions, Eq. (5) of the main text										
isobutane+C_2H_6→$2C_3H_8$	-0.25	-0.02	-0.01	0.01	-0.33	-0.08	-0.03	0.01	0.00	0.00
isopentane+$2C_2H_6$→$3C_3H_8$	-0.30	-0.03	-0.01	0.01	-0.60	-0.07	-0.03	0.12	-0.03	-0.01
isohexane+$3C_2H_6$→$4C_3H_8$	-0.40	-0.04	-0.01	0.01	-0.73	-0.07	-0.03	0.17	-0.02	-0.01
isoheptane+$4C_2H_6$→$5C_3H_8$	-0.50	-0.06	-0.01	0.01	-0.91	-0.09	-0.03	0.22	-0.02	-0.01
neopentane+$2C_2H_6$→$3C_3H_8$	-0.31	-0.02	0.00	0.03	-0.38	-0.04	-0.01	0.09	0.00	0.00
neohexane+$3C_2H_6$→$4C_3H_8$	-0.31	-0.02	0.00	0.03	-0.73	0.02	0.01	0.30	-0.06	-0.02
neoheptane+$4C_2H_6$→$5C_3H_8$	-0.40	-0.03	-0.01	0.03	-0.83	0.03	0.01	0.35	-0.05	-0.01
3-methylpentane+$3C_2H_6$→$4C_3H_8$	-0.35	-0.03	-0.01	0.01	-0.88	-0.06	-0.02	0.25	-0.07	-0.02
diisopropyl+$3C_2H_6$→$4C_3H_8$	-0.37	-0.03	-0.01	0.02	-0.90	-0.05	-0.02	0.26	-0.11	-0.03
hexamethylmethane+$5C_2H_6$→$6C_3H_8$	-0.26	-0.03	-0.01	0.01	-1.28	0.39	0.15	1.01	-0.28	-0.08
Isodesmic reactions, Eq. (6) of the main text										
isobutane+$2CH_4$→$3C_2H_6$	-0.08	0.02	0.01	0.04	-0.39	-0.23	-0.09	-0.17	-0.08	-0.02
isopentane+$3CH_4$→$4C_2H_6$	-0.05	0.04	0.01	0.05	-0.70	-0.30	-0.12	-0.15	-0.16	-0.04
isohexane+$4CH_4$→$5C_2H_6$	-0.06	0.05	0.01	0.06	-0.87	-0.37	-0.15	-0.19	-0.19	-0.05
isoheptane+$5CH_4$→$6C_2H_6$	-0.07	0.05	0.01	0.07	-1.08	-0.46	-0.18	-0.23	-0.23	-0.06
neopentane+$3CH_4$→$4C_2H_6$	-0.06	0.05	0.01	0.06	-0.48	-0.26	-0.10	-0.18	-0.13	-0.03
neohexane+$4CH_4$→$5C_2H_6$	0.04	0.07	0.02	0.08	-0.86	-0.28	-0.11	-0.06	-0.23	-0.06
neoheptane+$5CH_4$→$6C_2H_6$	0.03	0.08	0.02	0.09	-0.99	-0.34	-0.14	-0.10	-0.27	-0.07
3-methylpentane+$4CH_4$→$5C_2H_6$	-0.01	0.05	0.01	0.06	-1.01	-0.36	-0.14	-0.11	-0.24	-0.06
diisopropyl+$4CH_4$→$5C_2H_6$	-0.02	0.05	0.01	0.07	-1.03	-0.35	-0.14	-0.10	-0.28	-0.08
hexamethylmethane+$6CH_4$→$7C_2H_6$	0.26	0.11	0.03	0.08	-1.48	-0.06	-0.02	0.47	-0.54	-0.15
Isodesmic reactions balance the number of 1,3-interactions on both sides										
isobutane+$3C_2H_6$→CH_4+$3C_3H_8$	-0.34	-0.04	-0.01	0.00	-0.29	0.00	0.00	0.10	0.04	0.01
isopentane+$4C_2H_6$→CH_4+$4C_3H_8$	-0.39	-0.05	-0.01	0.00	-0.57	0.00	0.00	0.21	0.01	0.00
isohexane+$5C_2H_6$→CH_4+$5C_3H_8$	-0.49	-0.06	-0.01	0.00	-0.70	0.00	0.00	0.26	0.02	0.01
isoheptane+$6C_2H_6$→CH_4+$6C_3H_8$	-0.59	-0.08	-0.02	0.00	-0.88	-0.01	0.00	0.31	0.02	0.01
neopentane+$8C_2H_6$→$3CH_4$+$6C_3H_8$	-0.57	-0.08	-0.02	-0.01	-0.28	0.19	0.07	0.36	0.13	0.04
neohexane+$9C_2H_6$→$3CH_4$+$7C_3H_8$	-0.56	-0.08	-0.02	-0.01	-0.63	0.25	0.10	0.57	0.07	0.02
neoheptane+$10C_2H_6$→$3CH_4$+$8C_3H_8$	-0.66	-0.09	-0.02	-0.01	-0.73	0.26	0.10	0.62	0.08	0.02
3-methylpentane+$5C_2H_6$→CH_4+$5C_3H_8$	-0.44	-0.06	-0.01	0.00	-0.84	0.02	0.01	0.34	-0.02	-0.01
diisopropyl+$7C_2H_6$→$2CH_4$+$6C_3H_8$	-0.54	-0.08	-0.02	-0.01	-0.83	0.10	0.04	0.44	-0.02	-0.01
hexamethylmethane+$17C_2H_6$→$6CH_4$+$12C_3H_8$	-0.77	-0.16	-0.04	-0.06	-1.08	0.84	0.33	1.56	-0.03	-0.01
Isodesmic reactions balance the number of CH_2 groups on both sides										
isopentane+$2CH_4$→$2C_2H_6$+C_3H_8	-0.13	0.02	0.00	0.04	-0.67	-0.22	-0.09	-0.06	-0.12	-0.03
isohexane+$2CH_4$→C_2H_6+$2C_3H_8$	-0.23	0.00	0.00	0.04	-0.80	-0.22	-0.09	-0.01	-0.11	-0.03
isoheptane+$2CH_4$→$3C_3H_8$	-0.33	-0.01	0.00	0.04	-0.98	-0.24	-0.09	0.04	-0.11	-0.03
neohexane+$3CH_4$→$3C_2H_6$+C_3H_8	-0.05	0.05	0.01	0.06	-0.83	-0.20	-0.08	0.03	-0.19	-0.05
neoheptane+$3CH_4$→$2C_2H_6$+$2C_3H_8$	-0.14	0.04	0.01	0.07	-0.93	-0.19	-0.08	0.08	-0.18	-0.05
3-methylpentane+$2CH_4$→C_2H_6+$2C_3H_8$	-0.18	0.01	0.00	0.04	-0.94	-0.21	-0.08	0.07	-0.15	-0.04
Isodesmic reactions balance the number of CH_3 groups on both sides										
2isobutane+CH_4→$3C_3H_8$	-0.42	-0.02	-0.01	0.04	-0.69	-0.23	-0.09	-0.07	-0.04	-0.01
2isopentane+CH_4+$2C_2H_6$→$5C_3H_8$	-0.52	-0.03	-0.01	0.04	-1.23	-0.22	-0.09	0.16	-0.10	-0.03
2isohexane+CH_4+$4C_2H_6$→$7C_3H_8$	-0.72	-0.06	-0.01	0.04	-1.50	-0.22	-0.09	0.26	-0.09	-0.02
2isoheptane+CH_4+$6C_2H_6$→$9C_3H_8$	-0.92	-0.09	-0.02	0.04	-1.86	-0.25	-0.10	0.35	-0.08	-0.02
neopentane+CH_4→$2C_3H_8$	-0.23	0.01	0.00	0.04	-0.41	-0.11	-0.04	0.00	-0.04	-0.01
neohexane+CH_4+C_2H_6→$3C_3H_8$	-0.22	0.01	0.00	0.04	-0.77	-0.05	-0.02	0.21	-0.10	-0.03
neoheptane+CH_4+$2C_2H_6$→$4C_3H_8$	-0.31	-0.01	0.00	0.04	-0.86	-0.04	-0.02	0.26	-0.09	-0.03
3-methylpentane+CH_4+$4C_2H_6$→$7C_3H_8$	-0.62	-0.05	-0.01	0.04	-1.79	-0.19	-0.07	0.41	-0.18	-0.05
diisopropyl+CH_4+C_2H_6→$3C_3H_8$	-0.28	-0.01	0.00	0.03	-0.93	-0.13	-0.05	0.17	-0.15	-0.04
hexamethylmethane+$2CH_4$+C_2H_6→$4C_3H_8$	-0.08	0.02	0.00	0.03	-1.35	0.24	0.10	0.83	-0.37	-0.10

[a] The numbers given are the difference from the basis set limit results: SCF/cc-pV{T,Q}Z, CCSD/cc-pV{T,Q}Z, and (T)/cc-pV{D,T}Z.

Table S 5: Root mean square deviations for the S22 weak interactions reference data and recommended s_6 values for different DFT functionals.

		uncorrected			corrected			
Functional	recommended s_6	raw	CP	avg.	raw	CP	avg.	ref.
HF-SCF	1.20	6.04	6.31	6.18	0.78	0.82	0.79	[3]
SVWN5	(-0.25)	3.56	3.21	3.38	3.23	3.02	3.13	present work
PBE	0.75	3.53	3.90	3.71	1.06	0.77	0.89	[4]
HCTH407	1.10	5.19	5.76	5.47	0.95	0.89	0.86	[3]
BLYP	1.20	5.80	6.24	6.02	0.59	0.41	0.43	[4]
TPSS	1.00	4.54	4.87	4.70	0.97	0.64	0.79	[4]
TPSSh	0.95	4.54	4.87	4.70	0.86	0.63	0.72	present work
M06-L	0.20	0.91	1.26	1.08	0.47	0.43	0.40	[5]
PBE0	0.70	3.37	3.65	3.51	1.10	0.89	0.98	[5]
B3PW91	1.10	5.19	5.50	5.34	0.75	0.53	0.62	[5]
X3LYP	0.85	4.15	4.49	4.32	1.03	0.82	0.90	[5]
B3LYP	1.05	4.77	5.12	4.95	0.81	0.51	0.66	[4]
B97-1	0.65	3.28	3.59	3.43	0.84	0.72	0.76	present work
B97-2	1.05	5.00	5.33	5.16	0.60	0.42	0.48	present work
B97-3	0.90	4.42	4.73	4.57	0.46	0.41	0.39	present work
TPSSh	0.90	4.38	4.69	4.54	0.86	0.68	0.75	present work
TPSS1KCIS	0.90	4.38	4.71	4.55	0.84	0.66	0.72	present work
PW6B95	0.50	2.38	2.73	2.55	0.52	0.47	0.45	present work
BMK	0.65	2.99	3.34	3.16	0.69	0.55	0.59	[5]
M06-2X	(0.06)	0.50	0.63	0.54	0.48	0.43	0.45	[5]
M06	0.25	1.12	1.58	1.35	0.40	0.44	0.33	[5]
B1B95	0.75	3.73	4.07	3.90	0.52	0.63	0.54	present work
B2K-PLYP	0.30	1.09	1.95	1.50	0.72	0.50	0.36	[5]
B2GP-PLYP	0.40	1.53	2.35	1.92	0.75	0.42	0.38	[5]
B2T-PLYP	0.48	1.90	2.67	2.28	0.78	0.38	0.43	[5]
B2-PLYP	0.55	1.67	2.36	2.00	0.72	0.39	0.39	[6]
mPW2-PLYP	0.40	1.77	2.42	2.08	0.88	0.63	0.64	[6]
mPW2GP-PLYP	0.28	1.11	1.84	1.44	0.83	0.56	0.52	[5]
mPW1PW91	0.85	4.24	4.54	4.39	0.89	0.76	0.80	[3]
MP2	(-0.16)	1.59	0.90	1.06	(0.89)	(1.15)	(0.71)	[5]
MP2@CBS limit	(-0.22)	1.22	1.22	1.22	(0.53)	(0.53)	(0.53)	[5]
SCS-MP2	(0.17)	0.76	1.94	1.27	(1.01)	(1.34)	(0.92)	[5]

Table S 6: Component breakdown of the theoretical $H_{298}-H_0$ and comparison between final theoretical and experimental $H_{298}-H_0$ (in kcal/mol).

				$H_{298}-H_0$		
				Theor.	Expt.	
	RRHO	conformer	Int.Rot.	Total	USBM[1]	CCCBDB[2]
ethane	2.78	0.00	0.05	2.83	2.84	2.84
propane	3.45	0.00	0.09	3.54	3.52	3.52
n-butane	4.23	0.25	0.13	4.62	4.71	4.61
n-pentane	5.05	0.46	0.19	5.70	5.78	5.78
n-hexane	5.88	0.67	0.24	6.79	6.86	6.86
n-heptane	6.72	0.87	0.28	7.87	7.94	N/A
n-octane	7.57	1.05	0.35	8.97	9.03	N/A
isobutane	4.18	0.00	0.11	4.29	4.30	4.29
isopentane	5.02	0.09	0.19	5.30	5.26	5.26
neopentane	4.78	0.00	0.06	4.84	5.54	5.54
isohexane	5.82	0.24	0.21	6.28	6.29	6.29
3-methylpentane	5.87	0.26	0.24	6.37	6.23	6.23
diisopropyl	5.81	0.04	0.22	6.07	5.85	5.85
neohexane	5.78	0.00	0.20	5.98	6.01	6.01
isoheptane	6.71	0.44	0.29	7.44	7.39	N/A
neoheptane	6.65	0.15	0.21	7.01	6.98	N/A
hexamethylethane	7.29	0.00	0.22	7.52	7.53	N/A
isooctane	7.39	0.16	0.22	7.77	7.69	N/A

Table S 7: Benchmark zero-point exclusive, clamped-nuclei, non-relativistic atomization energies and individual errors for different DFT functionals (in kcal/mol).

		methane	ethane	propane	n-butane	n-pentane	n-hexane	n-heptane	n-octane	isobutane	iso-pentane	iso-hexane	iso-octane	iso-heptane	neo-pentane	neo-hexane	neo-heptane	diiso-propyl	3-methyl-pentane	hexamethyl-ethane
	Reference	420.43	713.06	1007.89	1302.86	1597.78	1892.73	2187.68	2482.64	1304.30	1598.69	1893.61	2484.26	2188.59	1601.48	1895.22	2190.12	1893.81	1892.95	2484.01
pc-2	SCS-MP2	-4.52	-7.44	-10.67	-13.98	-17.24	-20.52	-23.80	-27.07	-14.06	-17.37	-20.62	-27.14	-23.89	-17.31	-20.64	-23.84	-20.80	-20.70	-27.10
pc-3	SCS-MP2	-0.83	-0.97	-1.34	-1.81	-2.24	-2.70	-3.16	-3.61	-1.87	-2.41	-2.85	-4.07	-3.31	-2.28	-2.89	-3.33	-3.06	-2.96	-4.19
pc-2	MP2-CBS10	-2.81	-0.81	1.32	3.46	5.57	7.74	9.84	12.03	3.77	6.02	8.21	13.99	10.36	6.70	9.11	11.33	8.69	8.27	15.38
pc-2	MP2	-8.26	-10.60	-12.87	-15.18	-17.46	-19.74	-22.01	-24.29	-14.93	-17.11	-19.34	-22.54	-21.61	-16.52	-18.58	-20.76	-18.96	-19.29	-21.34
pc-3	MP2	-5.15	-5.11	-4.90	-4.76	-4.59	-4.43	-4.27	-4.11	-4.46	-4.25	-4.06	-2.65	-3.90	-3.56	-3.28	-3.07	-3.67	-4.03	-1.56
pc-2	PW6B95	-0.58	-0.94	-2.02	-3.29	-4.56	-5.85	-7.14	-8.43	-3.92	-5.34	-6.65	-11.52	-7.99	-6.38	-8.01	-9.43	-7.53	-6.75	-12.81
pc-2	SVWN5	41.94	81.09	120.48	159.72	198.90	238.11	277.26	316.46	159.87	199.25	238.43	317.17	277.57	199.27	238.71	277.76	238.89	238.66	318.02
pc-2	BLYP	-3.78	-9.03	-15.36	-21.93	-28.51	-35.10	-41.72	-48.32	-22.96	-30.04	-36.66	-54.63	-43.32	-31.75	-39.42	-46.18	-38.63	-37.09	-58.85
pc-2	PBE	-0.59	3.35	6.59	9.64	12.66	15.69	18.67	21.69	8.95	11.70	14.69	17.58	17.65	10.53	12.90	15.75	13.47	14.47	14.98
pc-2	TPSS	4.82	5.91	5.89	5.67	5.45	5.23	4.97	4.73	4.71	4.17	3.92	-0.35	3.63	2.64	1.73	1.36	2.45	3.66	-2.99
pc-2	TPSSh	4.65	5.58	5.42	5.08	4.73	4.38	4.00	3.64	4.15	3.48	3.10	-1.35	2.69	2.02	1.00	0.50	1.67	2.84	-3.91
pc-2	TPSS1KCIS	0.74	0.81	-0.18	-1.38	-2.57	-3.78	-5.01	-6.23	-2.33	-3.89	-5.13	-11.60	-6.40	-5.44	-7.42	-8.79	-6.71	-5.43	-14.68
pc-2	HCTH407	-3.00	-5.79	-9.50	-13.47	-17.43	-21.43	-25.43	-29.44	-14.52	-19.16	-23.21	-36.74	-27.26	-20.87	-26.35	-30.55	-25.67	-23.82	-42.49
pc-2	B1B95	-2.21	-3.33	-5.29	-7.43	-9.57	-11.73	-13.90	-16.05	-8.16	-10.52	-12.69	-19.74	-14.91	-11.68	-14.25	-16.56	-13.74	-12.85	-21.24
pc-2	B3LYP	0.47	-1.59	-4.64	-7.90	-11.17	-14.45	-17.75	-21.05	-8.81	-12.52	-15.84	-26.70	-19.18	-14.01	-18.23	-21.68	-17.56	-16.22	-30.31
pc-2	X3LYP	0.37	-1.17	-3.58	-6.21	-8.85	-11.51	-14.18	-16.84	-7.03	-10.07	-12.76	-22.02	-15.47	-11.43	-14.95	-17.77	-14.33	-13.11	-25.35
pc-2	B3PW91	-0.86	-0.69	-1.54	-2.57	-3.60	-4.65	-5.72	-6.77	-3.50	-4.94	-6.03	-12.31	-7.13	-6.40	-8.29	-9.52	-7.66	-6.37	-15.45
pc-2	B971	-5.51	-7.46	-10.26	-13.26	-16.26	-19.27	-22.30	-25.32	-14.01	-17.30	-20.34	-29.70	-23.42	-18.58	-22.22	-25.39	-21.67	-20.59	-32.46
pc-2	B972	-3.84	-5.14	-7.46	-9.98	-12.50	-15.04	-17.60	-20.14	-10.96	-13.94	-16.52	-26.09	-19.12	-15.48	-18.98	-21.70	-18.35	-16.93	-29.80
pc-2	B973	-2.39	-3.70	-6.06	-8.61	-11.15	-13.72	-16.28	-18.87	-9.57	-12.47	-15.08	-24.35	-17.68	-13.99	-17.40	-20.10	-16.79	-15.38	-27.89
pc-2	BMK	-1.53	-1.87	-2.95	-4.18	-5.43	-6.66	-7.95	-9.14	-4.61	-6.00	-7.19	-11.42	-8.57	-6.87	-8.01	-9.45	-7.86	-7.40	-12.42
pc-2	M06	-1.50	-2.43	-3.71	-5.14	-6.46	-7.93	-9.26	-10.72	-5.23	-6.47	-7.90	-10.60	-9.34	-6.22	-7.49	-9.06	-7.91	-7.77	-10.10
pc-2	M062X	-2.72	-3.41	-4.32	-5.41	-6.44	-7.56	-8.60	-9.72	-5.54	-6.58	-7.69	-10.14	-8.80	-6.55	-7.72	-8.93	-7.72	-7.65	-9.89
pc-2	M06L	-2.97	-4.11	-6.00	-8.05	-9.98	-12.06	-14.01	-16.07	-8.68	-10.46	-12.50	-17.86	-14.56	-11.55	-13.18	-15.37	-12.82	-12.23	-17.49
pc-2	PBE0	-2.60	-0.92	0.04	0.82	1.58	2.34	3.07	3.82	0.15	0.64	1.35	-0.25	2.05	-0.44	-0.30	0.28	0.18	1.12	-2.57
pc-2-CBS10	B2-PLYP	-0.76	-1.96	-3.72	-5.62	-7.52	-9.43	-11.36	-13.27	-6.07	-8.20	-10.11	-16.05	-12.06	-8.87	-11.26	-13.25	-11.00	-10.33	-17.76
pc-3-CBS15	B2-PLYP	-0.41	-1.33	-2.79	-4.41	-6.02	-7.64	-9.28	-10.91	-4.86	-6.72	-8.36	-13.88	-10.02	-7.40	-9.55	-11.27	-9.27	-8.59	-15.69
pc-2-CBS10	B2GP-PLYP	-0.89	-1.58	-2.71	-3.97	-5.23	-6.49	-7.77	-9.02	-4.29	-5.71	-6.97	-11.02	-8.26	-6.15	-7.76	-9.08	-7.62	-7.14	-12.17
pc-3-CBS15	B2GP-PLYP	-0.55	-0.96	-1.79	-2.76	-3.73	-4.70	-5.69	-6.66	-3.09	-4.25	-5.24	-8.91	-6.24	-4.70	-6.08	-7.13	-5.92	-5.42	-10.19
pc-2-CBS10	B2T-PLYP	-0.97	-2.05	-3.65	-5.38	-7.11	-8.84	-10.59	-12.32	-5.76	-7.69	-9.43	-14.73	-11.19	-8.25	-10.40	-12.20	-10.19	-9.62	-16.17
pc-3-CBS15	B2T-PLYP	-0.63	-1.44	-2.74	-4.19	-5.63	-7.09	-8.55	-10.01	-4.58	-6.25	-7.72	-12.64	-9.20	-6.81	-8.74	-10.28	-8.52	-7.92	-14.19
pc-2-CBS10	B2K-PLYP	-1.14	-1.61	-2.46	-3.42	-4.38	-5.34	-6.32	-7.27	-3.66	-4.75	-5.71	-8.80	-6.69	-5.05	-6.29	-7.28	-6.21	-5.85	-9.62
pc-3-CBS15	B2K-PLYP	-0.80	-0.99	-1.53	-2.20	-2.87	-3.54	-4.23	-4.89	-2.45	-3.28	-3.96	-6.70	-4.66	-3.59	-4.60	-5.34	-4.50	-4.12	-7.67
pc-2-CBS10	mPw2-PLYP	-1.36	-3.17	-5.57	-8.11	-10.66	-13.21	-15.78	-18.33	-8.58	-11.36	-13.92	-21.26	-16.51	-12.07	-15.12	-17.75	-14.85	-14.15	-23.04
pc-3-CBS15	mPw2-PLYP	-1.04	-2.58	-4.69	-6.97	-9.24	-11.52	-13.81	-16.09	-7.44	-9.97	-12.27	-19.22	-14.59	-10.68	-13.51	-15.89	-13.22	-12.51	-21.10
		Dispersion corrected																		
pc-2	MP2-SCS-D	-4.42	-7.09	-9.93	-12.81	-15.66	-18.52	-21.37	-24.22	-12.76	-15.54	-18.35	-23.26	-21.19	-15.27	-17.96	-20.71	-18.22	-18.33	-22.52
pc-3	MP2-SCS-D	-0.73	-0.61	-0.59	-0.65	-0.66	-0.70	-0.73	-0.76	-0.57	-0.58	-0.58	-0.18	-0.61	-0.24	-0.21	-0.20	-0.47	-0.59	0.39
pc-2	MP2-CBS10	-2.93	-1.23	0.45	2.09	3.71	5.38	6.98	8.67	2.24	3.87	5.54	9.42	7.18	4.30	5.95	7.64	5.64	5.48	9.99
pc-2	MP2-D	-8.35	-10.91	-13.53	-16.21	-18.85	-21.51	-24.16	-26.81	-16.08	-18.72	-21.35	-25.97	-23.99	-18.32	-20.95	-23.52	-21.24	-21.38	-25.38
pc-3	MP2-D	-5.24	-5.42	-5.56	-5.78	-5.98	-6.20	-6.42	-6.63	-5.61	-5.86	-6.06	-6.08	-6.28	-5.36	-5.64	-5.84	-5.96	-6.13	-5.60
pc-2	PW6B95-D	-0.28	0.09	0.17	0.12	0.09	0.05	0.01	-0.04	-0.09	0.04	0.02	-0.08	-0.05	-0.38	-0.13	-0.21	0.08	0.22	0.66
pc-2	SVWN5-D	41.79	80.58	119.38	158.01	196.58	235.16	273.68	312.26	157.95	196.56	235.09	311.45	273.60	196.27	234.77	273.15	235.09	235.17	311.28
pc-2	BLYP-D	-3.05	-6.55	-10.11	-13.73	-17.34	-20.94	-24.56	-28.17	-13.77	-17.12	-20.65	-27.19	-24.27	-17.36	-20.51	-24.05	-20.38	-20.37	-26.51
pc-2	PBE-D	-0.13	4.90	9.87	14.76	19.64	24.54	29.40	34.28	14.70	19.77	24.70	34.72	29.56	19.52	24.72	29.58	24.88	24.93	35.20
pc-2	TPSS-D	5.44	7.98	10.27	12.50	14.76	17.02	19.27	21.53	12.36	14.93	17.27	22.52	19.50	14.64	17.49	19.81	17.66	17.60	23.96
pc-2	TPSSh-D	5.21	7.43	9.36	11.22	13.11	15.00	16.87	18.75	11.04	13.17	15.11	19.22	16.98	12.82	15.18	17.10	15.36	15.39	20.34
pc-2	TPSS1KCIS-D	1.30	2.67	3.76	4.77	5.81	6.84	7.86	8.89	4.56	5.80	6.88	8.97	7.89	5.35	6.76	7.81	6.98	7.11	9.57
pc-2	HCTH407-D	-2.33	-3.51	-4.69	-5.96	-7.20	-8.45	-9.70	-10.97	-6.10	-7.32	-8.53	-11.59	-9.80	-7.68	-9.02	-10.26	-8.94	-8.49	-12.85
pc-2	B1B95-D	-1.75	-1.78	-2.01	-2.31	-2.59	-2.88	-3.17	-3.45	-2.42	-2.44	-2.69	-2.59	-3.00	-2.68	-2.44	-2.72	-2.33	-2.40	-1.03
pc-2	B3LYP-D	1.11	0.57	-0.04	-0.73	-1.40	-2.06	-2.74	-3.41	-0.77	-1.21	-1.83	-2.70	-2.51	-1.42	-1.68	-2.31	-1.59	-1.58	-2.02
pc-2	X3LYP-D	0.89	0.59	0.14	-0.41	-0.94	-1.48	-2.02	-2.56	-0.52	-0.92	-1.42	-2.58	-1.98	-1.24	-1.56	-2.09	-1.40	-1.26	-2.45
pc-2	B3PW91-D	-0.19	1.58	3.28	4.94	6.63	8.33	10.01	11.71	4.92	6.90	8.65	12.84	10.33	6.80	9.04	10.77	9.07	8.96	14.19
pc-2	B971-D	-5.11	-6.12	-7.42	-8.82	-10.21	-11.60	-13.01	-14.40	-9.03	-10.31	-11.67	-14.84	-13.10	-10.79	-11.97	-13.40	-11.78	-11.53	-14.94
pc-2	B972-D	-3.20	-2.97	-2.86	-2.81	-2.73	-2.65	-2.59	-2.51	-2.92	-2.64	-2.51	-2.09	-2.45	-2.89	-2.43	-2.33	-2.38	-2.29	-1.50
pc-2	B973-D	-1.84	-1.84	-2.13	-2.46	-2.77	-3.10	-3.41	-3.75	-2.67	-2.78	-3.07	-3.78	-3.39	-3.20	-3.21	-3.50	-3.10	-2.83	-3.64
pc-2	BMK-D	-1.13	-0.53	-0.11	0.26	0.62	1.01	1.34	1.78	0.37	1.00	1.48	3.44	1.75	0.93	2.24	2.54	2.03	1.66	5.10
pc-2	M06-D	-1.35	-1.91	-2.62	-3.43	-4.14	-4.98	-5.69	-6.52	-3.32	-3.78	-4.56	-4.88	-5.37	-3.23	-3.55	-4.45	-4.11	-4.29	-3.36
pc-2	M062X-D	-2.68	-3.28	-4.05	-5.00	-5.88	-6.85	-7.74	-8.71	-5.08	-5.93	-6.89	-8.77	-7.85	-5.84	-6.78	-7.82	-6.81	-6.82	-8.27
pc-2	M06L-D	-2.85	-3.69	-5.13	-6.68	-8.12	-9.70	-11.15	-12.71	-7.15	-8.31	-9.83	-13.28	-11.38	-9.15	-10.02	-11.68	-9.78	-9.45	-12.10
pc-2	PBE0-D	-2.17	0.53	3.10	5.60	8.10	10.60	13.08	15.58	5.51	8.17	10.69	15.75	13.17	7.95	10.73	13.19	10.83	10.87	16.30
pc-2-CBS10	B2-PLYP-D	-0.43	-0.82	-1.31	-1.86	-2.41	-2.94	-3.50	-4.03	-1.85	-2.28	-2.77	-3.48	-3.33	-2.27	-2.59	-3.10	-2.63	-2.66	-2.94
pc-3-CBS15	B2-PLYP-D	-0.07	-0.19	-0.38	-0.65	-0.90	-1.15	-1.42	-1.67	-0.65	-0.80	-1.02	-1.31	-1.29	-0.80	-0.88	-1.12	-0.91	-0.93	-0.87
pc-2-CBS10	B2GP-PLYP-D	-0.65	-0.76	-0.96	-1.24	-1.51	-1.77	-2.05	-2.30	-1.22	-1.41	-1.64	-1.88	-1.91	-1.35	-1.46	-1.70	-1.53	-1.57	-1.39
pc-3-CBS15	B2GP-PLYP-D	-0.31	-0.13	-0.04	-0.03	-0.01	0.02	0.03	0.05	-0.02	0.06	0.10	0.24	0.11	0.10	0.23	0.25	0.16	0.16	0.59
pc-2-CBS10	B2T-PLYP-D	-0.67	-1.06	-1.55	-2.10	-2.64	-3.17	-3.73	-4.26	-2.08	-2.52	-3.02	-3.76	-3.57	-2.49	-2.83	-3.34	-2.89	-2.93	-3.23
pc-3-CBS15	B2T-PLYP-D	-0.34	-0.45	-0.64	-0.91	-1.17	-1.42	-1.69	-1.95	-0.90	-1.08	-1.31	-1.66	-1.58	-1.06	-1.17	-1.42	-1.22	-1.23	-1.25
pc-2-CBS10	B2K-PLYP-D	-0.95	-0.99	-1.15	-1.37	-1.59	-1.80	-2.03	-2.23	-1.36	-1.52	-1.70	-1.94	-1.93	-1.45	-1.56	-1.75	-1.65	-1.67	-1.54
pc-3-CBS15	B2K-PLYP-D	-0.61	-0.37	-0.22	-0.15	-0.08	0.00	0.06	0.15	-0.15	-0.05	0.04	0.16	0.10	0.01	0.13	0.20	0.06	0.06	0.42
pc-2-CBS10	mPw2-PLYP-D	-1.12	-2.35	-3.82	-5.38	-6.94	-8.49	-10.06	-11.61	-5.52	-7.06	-8.59	-12.12	-10.16	-7.27	-8.82	-10.38	-8.76	-8.58	-12.26
pc-3-CBS15	mPw2-PLYP-D	-0.79	-1.76	-2.94	-4.24	-5.52	-6.80	-8.09	-9.38	-4.38	-5.66	-6.93	-10.07	-8.24	-5.89	-7.20	-8.51	-7.13	-6.93	-10.32

Table S 8: Benchmark zero-point exclusive, clamped-nuclei, non-relativistic isomerization reaction energies and individual errors for different DFT functionals (in kcal/mol).

		n-butane→ isobutane	n-pentane→ isopentane	n-pentane→ neopentane	n-hexane→ isohexane	n-hexane→ neohexane	n-hexane→ diisopropyl	n-hexane→ 3-methyl-pentane	n-hptane→ isoheptane	n-heptane→ neoheptane	n-octane→ hexamethyl-ethane	n-octane→ isooctane
	Reference	-1.441	-0.909	-3.695	-0.879	-2.494	-1.080	-0.226	-0.908	-2.437	-1.367	-1.621
pc-2	SCS-MP2	0.08	0.13	0.07	0.09	0.11	0.28	0.18	0.09	0.04	0.02	0.07
pc-3	SCS-MP2	0.06	0.16	0.04	0.15	0.19	0.36	0.26	0.15	0.18	0.58	0.46
pc-2	MP2-CBS10	-0.32	-0.45	-1.13	-0.47	-1.36	-0.94	-0.53	-0.52	-1.49	-3.35	-1.96
pc-2	MP2	-0.25	-0.35	-0.93	-0.40	-1.16	-0.78	-0.45	-0.41	-1.26	-2.95	-1.76
pc-3	MP2	-0.29	-0.34	-1.02	-0.37	-1.15	-0.76	-0.40	-0.37	-1.20	-2.56	-1.46
pc-2	PW6B95	0.63	0.78	1.82	0.80	2.16	1.68	0.90	0.85	2.29	4.38	3.08
pc-2	SVWN5	-0.14	-0.34	-0.37	-0.32	-0.60	-0.78	-0.55	-0.31	-0.50	-1.56	-0.71
pc-2	BLYP	1.03	1.53	3.24	1.56	4.32	3.53	2.00	1.60	4.46	10.52	6.31
pc-2	PBE	0.68	0.96	2.13	1.00	2.79	2.22	1.22	1.02	2.92	6.70	4.11
pc-2	TPSS	0.96	1.29	2.81	1.30	3.50	2.77	1.56	1.34	3.61	7.72	5.08
pc-2	TPSSh	0.93	1.25	2.71	1.27	3.38	2.70	1.53	1.31	3.50	7.55	4.99
pc-2	TPSS1KCIS	0.95	1.32	2.87	1.35	3.64	2.93	1.65	1.39	3.78	8.46	5.38
pc-2	HCTH407	1.05	1.73	3.43	1.78	4.92	4.24	2.39	1.83	5.12	13.05	7.29
pc-2	B1B95	0.73	0.94	2.10	0.97	2.53	2.02	1.13	1.01	2.66	5.19	3.69
pc-2	B3LYP	0.91	1.35	2.84	1.38	3.77	3.11	1.77	1.43	3.93	9.27	5.65
pc-2	X3LYP	0.82	1.22	2.59	1.25	3.45	2.82	1.60	1.29	3.60	8.51	5.18
pc-2	B3PW91	0.93	1.34	2.80	1.38	3.64	3.01	1.72	1.42	3.80	8.68	5.54
pc-2	B971	0.75	1.05	2.32	1.08	2.95	2.40	1.33	1.11	3.08	7.14	4.38
pc-2	B972	0.98	1.44	2.98	1.48	3.93	3.30	1.89	1.52	4.10	9.65	5.95
pc-2	B973	0.96	1.32	2.85	1.36	3.68	3.07	1.66	1.40	3.82	9.02	5.49
pc-2	BMK	0.43	0.57	1.44	0.53	1.35	1.20	0.75	0.62	1.49	3.28	2.28
pc-2	M06	0.10	0.00	-0.24	-0.03	-0.43	-0.02	-0.15	0.07	-0.21	-0.63	-0.12
pc-2	M062X	0.13	0.14	0.12	0.13	0.16	0.16	0.09	0.20	0.34	0.17	0.42
pc-2	M06L	0.63	0.48	1.57	0.44	1.12	0.76	0.18	0.55	1.36	1.42	1.78
pc-2	PBE0	0.66	0.95	2.02	0.98	2.64	2.16	1.22	1.02	2.79	6.39	4.07
pc-2-CBS10	B2-PLYP	0.45	0.67	1.34	0.68	1.83	1.57	0.90	0.70	1.89	4.50	2.79
pc-3-CBS15	B2-PLYP	0.45	0.70	1.38	0.72	1.90	1.63	0.95	0.74	1.98	4.78	2.97
pc-2-CBS10	B2GP-PLYP	0.32	0.48	0.92	0.49	1.28	1.13	0.66	0.49	1.31	3.15	2.00
pc-3-CBS15	B2GP-PLYP	0.32	0.52	0.97	0.53	1.38	1.22	0.72	0.55	1.44	3.52	2.24
pc-2-CBS10	B2T-PLYP	0.38	0.58	1.14	0.59	1.56	1.36	0.78	0.60	1.61	3.85	2.42
pc-3-CBS15	B2T-PLYP	0.39	0.61	1.18	0.63	1.65	1.43	0.84	0.65	1.72	4.18	2.63
pc-2-CBS10	B2K-PLYP	0.24	0.37	0.67	0.37	0.95	0.87	0.51	0.37	0.96	2.36	1.53
pc-3-CBS15	B2K-PLYP	0.25	0.41	0.72	0.42	1.06	0.97	0.58	0.43	1.11	2.78	1.80
pc-2-CBS10	mPw2-PLYP	0.47	0.70	1.41	0.72	1.91	1.64	0.94	0.73	1.98	4.72	2.94
pc-3-CBS15	mPw2-PLYP	0.47	0.73	1.45	0.75	1.99	1.70	0.99	0.78	2.08	5.00	3.12
		Dispersion corrected										
pc-3	MP2-SCS-D	-0.06	-0.12	-0.39	-0.17	-0.56	-0.30	-0.19	-0.18	-0.66	-1.70	-0.96
pc-2-CBS10	MP2-D	-0.08	-0.08	-0.42	-0.12	-0.48	-0.22	-0.11	-0.12	-0.53	-1.15	-0.57
pc-3-CBS15	MP2-D	-0.15	-0.16	-0.59	-0.16	-0.57	-0.26	-0.10	-0.20	-0.66	-1.32	-0.75
pc-2	MP2-D	-0.13	-0.13	-0.53	-0.16	-0.56	-0.27	-0.13	-0.17	-0.64	-1.43	-0.85
pc-3	MP2-D	-0.17	-0.12	-0.62	-0.14	-0.56	-0.25	-0.08	-0.13	-0.57	-1.03	-0.55
pc-2	PW6B95-D	0.21	0.05	0.47	0.03	0.18	-0.03	-0.17	0.06	0.21	-0.70	0.05
pc-2	SVWN5-D	0.06	0.02	0.31	0.07	0.39	0.07	-0.01	0.08	0.53	0.98	0.81
pc-2	BLYP-D	0.04	-0.22	0.01	-0.29	-0.43	-0.56	-0.57	-0.29	-0.51	-1.66	-0.98
pc-2	PBE-D	0.06	-0.13	0.12	-0.16	-0.18	-0.34	-0.39	-0.16	-0.19	-0.91	-0.44
pc-2	TPSS-D	0.14	-0.17	0.12	-0.24	-0.46	-0.64	-0.58	-0.24	-0.54	-2.43	-0.99
pc-2	TPSSh-D	0.18	-0.06	0.29	-0.12	-0.18	-0.36	-0.39	-0.11	-0.23	-1.59	-0.47
pc-2	TPSS1KCIS-D	0.21	0.01	0.45	-0.04	0.08	-0.14	-0.28	-0.03	0.05	-0.68	-0.08
pc-2	HCTH407-D	0.14	0.12	0.48	0.08	0.57	0.49	0.04	0.09	0.56	1.88	0.62
pc-2	B1B95-D	0.11	-0.15	0.09	-0.19	-0.44	-0.54	-0.48	-0.18	-0.45	-2.43	-0.86
pc-2	B3LYP-D	0.04	-0.18	0.02	-0.24	-0.38	-0.47	-0.48	-0.23	-0.43	-1.40	-0.72
pc-2	X3LYP-D	0.11	-0.02	0.30	-0.06	0.08	-0.08	-0.22	-0.05	0.07	-0.12	0.02
pc-2	B3PW91-D	0.02	-0.27	-0.16	-0.32	-0.71	-0.74	-0.63	-0.32	-0.76	-2.49	-1.14
pc-2	B971-D	0.22	0.10	0.58	0.07	0.38	0.18	-0.06	0.09	0.39	0.54	0.44
pc-2	B972-D	0.11	-0.09	0.16	-0.14	-0.22	-0.28	-0.36	-0.14	-0.25	-1.01	-0.42
pc-2	B973-D	0.21	0.01	0.43	-0.03	0.12	0.00	-0.26	-0.02	0.09	-0.11	0.03
pc-2	BMK-D	-0.11	-0.38	-0.31	-0.47	-1.22	-1.01	-0.64	-0.41	-1.20	-3.32	-1.66
pc-2	M06-D	-0.11	-0.36	-0.91	-0.42	-1.42	-0.87	-0.69	-0.32	-1.24	-3.17	-1.64
pc-2	M062X-D	0.08	0.05	-0.04	0.04	-0.07	-0.04	-0.03	0.11	0.09	-0.44	0.05
pc-2	M06L-D	0.46	0.19	1.03	0.13	0.33	0.08	-0.25	0.23	0.53	-0.61	0.57
pc-2	PBE0-D	0.08	-0.07	0.14	-0.10	-0.13	-0.23	-0.28	-0.09	-0.11	-0.72	-0.17
pc-2-CBS10	B2-PLYP-D	-0.01	-0.13	-0.13	-0.17	-0.35	-0.31	-0.28	-0.17	-0.40	-1.09	-0.55
pc-3-CBS15	B2-PLYP-D	0.00	-0.10	-0.10	-0.13	-0.27	-0.25	-0.23	-0.13	-0.30	-0.80	-0.36
pc-2-CBS10	B2GP-PLYP-D	-0.02	-0.10	-0.15	-0.13	-0.31	-0.23	-0.20	-0.14	-0.35	-0.91	-0.42
pc-3-CBS15	B2GP-PLYP-D	-0.01	-0.07	-0.11	-0.08	-0.21	-0.15	-0.14	-0.08	-0.22	-0.54	-0.19
pc-2-CBS10	B2T-PLYP-D	-0.02	-0.12	-0.15	-0.15	-0.34	-0.28	-0.24	-0.16	-0.38	-1.02	-0.50
pc-3-CBS15	B2T-PLYP-D	-0.01	-0.09	-0.11	-0.11	-0.25	-0.21	-0.19	-0.11	-0.27	-0.69	-0.28
pc-2-CBS10	B2K-PLYP-D	-0.01	-0.07	-0.14	-0.09	-0.24	-0.15	-0.13	-0.10	-0.28	-0.69	-0.29
pc-3-CBS15	B2K-PLYP-D	0.00	-0.03	-0.08	-0.04	-0.13	-0.06	-0.06	-0.04	-0.13	-0.27	-0.02
pc-2-CBS10	mPw2-PLYP-D	0.13	0.12	0.33	0.10	0.33	0.27	0.09	0.10	0.32	0.66	0.51
pc-3-CBS15	mPw2-PLYP-D	0.14	0.15	0.37	0.13	0.40	0.34	0.13	0.14	0.42	0.94	0.70

Table S 9: Benchmark zero-point exclusive, clamped-nuclei, non-relativistic reaction energies for the $C_mH_{2m+2} + (m-2)CH_4 \rightarrow (m-1)C_2H_6$ isodesmic reaction and individual errors for different DFT functionals (in kcal/mol).

		propane	n-butane	n-pentane	n-hexane	n-heptane	n-octane	isobutane	isopentane	isohexane	isoheptane	isooctane	neopentane	neohexane	neoheptane
	Reference	2.20	4.54	6.82	9.13	11.45	13.78	5.98	7.73	10.01	12.36	15.40	10.52	11.63	13.89
pc-2	MP2-SCS	-0.31	-0.69	-1.04	-1.40	-1.75	-2.11	-0.78	-1.17	-1.49	-1.84	-2.18	-1.11	-1.51	-1.79
pc-3	MP2-SCS	-0.24	-0.58	-0.88	-1.21	-1.53	-1.85	-0.64	-1.04	-1.35	-1.68	-2.31	-0.92	-1.40	-1.71
pc-2-CBS10	MP2	0.13	0.27	0.38	0.56	0.66	0.85	0.59	0.83	1.02	1.17	2.81	1.52	1.92	2.15
pc-2	MP2	0.08	0.11	0.18	0.24	0.31	0.38	0.36	0.53	0.64	0.72	2.13	1.11	1.40	1.57
pc-3	MP2	0.17	0.27	0.41	0.52	0.64	0.76	0.57	0.74	0.89	1.01	2.23	1.43	1.68	1.84
pc-2	PW6B95	-0.73	-1.65	-2.56	-3.49	-4.43	-5.37	-2.27	-3.34	-4.29	-5.28	-8.45	-4.38	-5.65	-6.72
pc-2	SVWN5	0.23	0.33	0.36	0.42	0.42	0.47	0.47	0.70	0.73	0.73	1.17	0.73	1.02	0.92
pc-2	BLYP	-1.08	-2.40	-3.74	-5.08	-6.45	-7.81	-3.44	-5.27	-6.64	-8.05	-14.11	-6.97	-9.40	-10.91
pc-2	PBE	-0.69	-1.58	-2.49	-3.39	-4.34	-5.27	-2.26	-3.45	-4.39	-5.37	-9.38	-4.62	-6.18	-7.27
pc-2	TPSS	-1.11	-2.42	-3.72	-5.04	-6.38	-7.71	-3.38	-5.01	-6.34	-7.72	-12.78	-6.53	-8.53	-9.99
pc-2	TPSSh	-1.07	-2.34	-3.61	-4.89	-6.19	-7.48	-3.27	-4.86	-6.16	-7.50	-12.47	-6.32	-8.27	-9.69
pc-2	TPSS1KCIS	-1.06	-2.32	-3.58	-4.86	-6.15	-7.44	-3.28	-4.90	-6.20	-7.54	-12.81	-6.45	-8.50	-9.93
pc-2	HCTH407	-0.93	-2.11	-3.29	-4.50	-5.72	-6.94	-3.17	-5.02	-6.28	-7.54	-14.24	-6.73	-9.43	-10.84
pc-2	B1B95	-0.85	-1.87	-2.90	-3.93	-4.99	-6.02	-2.60	-3.84	-4.90	-6.00	-9.72	-5.00	-6.46	-7.65
pc-2	B3LYP	-0.98	-2.18	-3.38	-4.61	-5.84	-7.07	-3.09	-4.73	-5.99	-7.27	-12.73	-6.23	-8.38	-9.77
pc-2	X3LYP	-0.88	-1.98	-3.09	-4.21	-5.35	-6.48	-2.80	-4.30	-5.46	-6.64	-11.65	-5.67	-7.65	-8.94
pc-2	B3PW91	-1.01	-2.20	-3.40	-4.62	-5.85	-7.07	-3.14	-4.74	-5.99	-7.27	-12.61	-6.20	-8.26	-9.65
pc-2	B971	-0.85	-1.89	-2.95	-4.00	-5.09	-6.15	-2.65	-3.99	-5.08	-6.20	-10.54	-5.27	-6.95	-8.17
pc-2	B972	-1.03	-2.26	-3.49	-4.74	-6.01	-7.26	-3.24	-4.93	-6.22	-7.53	-13.21	-6.47	-8.68	-10.11
pc-2	B973	-1.04	-2.27	-3.50	-4.75	-6.00	-7.27	-3.23	-4.82	-6.11	-7.40	-12.76	-6.34	-8.43	-9.82
pc-2	BMK	-0.73	-1.62	-2.52	-3.40	-4.36	-5.20	-2.05	-3.09	-3.94	-4.97	-7.48	-3.96	-4.75	-5.85
pc-2	M06	-0.36	-0.86	-1.26	-1.80	-2.21	-2.75	-0.96	-1.27	-1.77	-2.28	-2.62	-1.02	-1.37	-2.01
pc-2	M062X	-0.22	-0.62	-0.96	-1.39	-1.74	-2.17	-0.75	-1.10	-1.52	-1.94	-2.59	-1.08	-1.55	-2.07
pc-2	M06L	-0.75	-1.66	-2.46	-3.40	-4.21	-5.14	-2.29	-2.94	-3.84	-4.76	-6.92	-4.03	-4.52	-5.57
pc-2	PBE0	-0.71	-1.61	-2.52	-3.44	-4.39	-5.31	-2.28	-3.47	-4.43	-5.40	-9.38	-4.55	-6.09	-7.17
pc-2-CBS10	B2-PLYP	-0.56	-1.27	-1.98	-2.69	-3.43	-4.14	-1.72	-2.65	-3.37	-4.12	-6.92	-3.32	-4.52	-5.31
pc-3-CBS15	B2-PLYP	-0.54	-1.25	-1.94	-2.65	-3.37	-4.08	-1.70	-2.64	-3.37	-4.11	-7.06	-3.32	-4.55	-5.36
pc-2-CBS10	B2GP-PLYP	-0.44	-1.01	-1.58	-2.15	-2.74	-3.30	-1.33	-2.06	-2.63	-3.23	-5.30	-2.50	-3.42	-4.05
pc-3-CBS15	B2GP-PLYP	-0.43	-0.99	-1.55	-2.11	-2.70	-3.26	-1.31	-2.07	-2.65	-3.25	-5.50	-2.52	-3.49	-4.13
pc-2-CBS10	B2T-PLYP	-0.50	-1.15	-1.79	-2.43	-3.10	-3.73	-1.53	-2.37	-3.02	-3.70	-6.15	-2.93	-3.99	-4.70
pc-3-CBS15	B2T-PLYP	-0.49	-1.13	-1.76	-2.40	-3.06	-3.70	-1.52	-2.37	-3.03	-3.70	-6.33	-2.94	-4.05	-4.78
pc-2-CBS10	B2K-PLYP	-0.37	-0.86	-1.34	-1.82	-2.33	-2.80	-1.09	-1.71	-2.19	-2.70	-4.33	-2.01	-2.77	-3.29
pc-3-CBS15	B2K-PLYP	-0.35	-0.84	-1.31	-1.79	-2.29	-2.77	-1.08	-1.72	-2.21	-2.72	-4.57	-2.04	-2.85	-3.40
pc-2-CBS10	mPw2-PLYP	-0.58	-1.31	-2.05	-2.78	-3.54	-4.28	-1.78	-2.75	-3.50	-4.28	-7.21	-3.46	-4.70	-5.52
pc-3-CBS15	mPw2-PLYP	-0.57	-1.30	-2.02	-2.76	-3.51	-4.25	-1.77	-2.75	-3.51	-4.28	-7.37	-3.47	-4.75	-5.58
		Dispersion corrected													
pc-2	MP2-SCS-D	-0.16	-0.37	-0.55	-0.73	-0.90	-1.08	-0.32	-0.43	-0.56	-0.73	-0.12	-0.16	-0.17	-0.24
pc-3	MP2-SCS-D	-0.09	-0.26	-0.39	-0.54	-0.68	-0.83	-0.18	-0.31	-0.42	-0.57	-0.25	0.03	-0.06	-0.15
pc-2-CBS10	MP2-D	-0.04	-0.10	-0.19	-0.23	-0.34	-0.36	0.05	-0.04	-0.07	-0.14	0.39	0.40	0.34	0.32
pc-2	MP2-D	-0.05	-0.17	-0.25	-0.35	-0.43	-0.53	-0.04	-0.12	-0.18	-0.26	0.32	0.28	0.22	0.20
pc-3	MP2-D	0.04	-0.01	-0.03	-0.07	-0.10	-0.14	0.16	0.09	0.07	0.03	0.41	0.59	0.49	0.47
pc-2	PW6B95-D	-0.30	-0.72	-1.12	-1.53	-1.95	-2.36	-0.93	-1.17	-1.56	-2.01	-2.41	-1.59	-1.71	-2.16
pc-2	SVWN5-D	0.02	-0.14	-0.36	-0.56	-0.83	-1.04	-0.20	-0.38	-0.63	-0.91	-1.85	-0.66	-0.95	-1.36
pc-2	BLYP-D	-0.05	-0.17	-0.28	-0.36	-0.48	-0.59	-0.21	-0.06	-0.08	-0.19	0.39	-0.29	0.07	0.03
pc-2	PBE-D	-0.05	-0.18	-0.32	-0.45	-0.62	-0.75	-0.25	-0.19	-0.29	-0.46	-0.31	-0.44	-0.27	-0.43
pc-2	TPSS-D	-0.25	-0.56	-0.84	-1.11	-1.41	-1.69	-0.69	-0.67	-0.87	-1.17	-0.70	-0.96	-0.65	-0.87
pc-2	TPSSh-D	-0.30	-0.67	-1.02	-1.36	-1.72	-2.06	-0.85	-0.96	-1.24	-1.61	-1.59	-1.31	-1.18	-1.49
pc-2	TPSS1KCIS-D	-0.28	-0.65	-0.98	-1.33	-1.68	-2.02	-0.86	-0.99	-1.28	-1.64	-1.94	-1.44	-1.40	-1.72
pc-2	HCTH407-D	0.02	-0.07	-0.12	-0.18	-0.25	-0.32	-0.21	-0.24	-0.27	-0.34	-0.94	-0.60	-0.75	-0.81
pc-2	B1B95-D	-0.20	-0.47	-0.73	-0.99	-1.26	-1.51	-0.59	-0.58	-0.80	-1.08	-0.65	-0.82	-0.55	-0.81
pc-2	B3LYP-D	-0.08	-0.23	-0.36	-0.48	-0.62	-0.75	-0.27	-0.17	-0.24	-0.39	-0.04	-0.38	-0.10	-0.19
pc-2	X3LYP-D	-0.15	-0.40	-0.63	-0.87	-1.12	-1.36	-0.51	-0.61	-0.81	-1.07	-1.38	-0.94	-0.95	-1.19
pc-2	B3PW91-D	-0.06	-0.16	-0.23	-0.30	-0.38	-0.45	-0.18	0.03	0.02	-0.06	0.69	-0.07	0.41	0.38
pc-2	B971-D	-0.29	-0.69	-1.07	-1.45	-1.86	-2.24	-0.90	-1.17	-1.52	-1.95	-2.68	-1.65	-1.83	-2.24
pc-2	B972-D	-0.13	-0.31	-0.46	-0.62	-0.79	-0.94	-0.42	-0.37	-0.48	-0.65	-0.52	-0.62	-0.40	-0.53
pc-2	B973-D	-0.27	-0.60	-0.90	-1.22	-1.52	-1.85	-0.81	-0.91	-1.19	-1.50	-1.88	-1.33	-1.33	-1.61
pc-2	BMK-D	-0.18	-0.41	-0.65	-0.85	-1.12	-1.29	-0.30	-0.27	-0.38	-0.72	0.37	-0.34	0.37	0.08
pc-2	M06-D	-0.14	-0.40	-0.54	-0.82	-0.97	-1.24	-0.28	-0.18	-0.40	-0.65	0.40	0.37	0.60	0.27
pc-2	M062X-D	-0.17	-0.51	-0.78	-1.16	-1.44	-1.81	-0.59	-0.84	-1.20	-1.55	-1.86	-0.74	-1.08	-1.52
pc-2	M06L-D	-0.58	-1.29	-1.88	-2.61	-3.22	-3.93	-1.76	-2.07	-2.74	-3.45	-4.50	-2.92	-2.94	-3.75
pc-2	PBE0-D	-0.11	-0.31	-0.51	-0.70	-0.91	-1.10	-0.40	-0.43	-0.60	-0.82	-0.92	-0.65	-0.57	-0.79
pc-2-CBS10	B2-PLYP-D	-0.09	-0.25	-0.39	-0.53	-0.69	-0.83	-0.24	-0.26	-0.36	-0.52	-0.28	-0.26	-0.18	-0.30
pc-3-CBS15	B2-PLYP-D	-0.07	-0.22	-0.36	-0.49	-0.64	-0.77	-0.22	-0.26	-0.36	-0.51	-0.41	-0.26	-0.22	-0.34
pc-2-CBS10	B2GP-PLYP-D	-0.10	-0.27	-0.43	-0.58	-0.75	-0.89	-0.25	-0.32	-0.44	-0.61	-0.47	-0.27	-0.27	-0.40
pc-3-CBS15	B2GP-PLYP-D	-0.08	-0.25	-0.40	-0.54	-0.71	-0.85	-0.24	-0.33	-0.46	-0.63	-0.67	-0.29	-0.34	-0.49
pc-2-CBS10	B2T-PLYP-D	-0.09	-0.25	-0.40	-0.55	-0.71	-0.85	-0.24	-0.28	-0.39	-0.55	-0.35	-0.25	-0.21	-0.33
pc-3-CBS15	B2T-PLYP-D	-0.08	-0.23	-0.37	-0.51	-0.67	-0.81	-0.23	-0.29	-0.40	-0.56	-0.53	-0.26	-0.26	-0.40
pc-2-CBS10	B2K-PLYP-D	-0.12	-0.30	-0.48	-0.64	-0.84	-0.99	-0.29	-0.41	-0.55	-0.74	-0.71	-0.34	-0.40	-0.56
pc-3-CBS15	B2K-PLYP-D	-0.10	-0.28	-0.45	-0.61	-0.80	-0.96	-0.28	-0.42	-0.57	-0.76	-0.95	-0.36	-0.49	-0.67
pc-2-CBS10	mPw2-PLYP-D	-0.24	-0.57	-0.89	-1.21	-1.55	-1.87	-0.70	-1.01	-1.31	-1.66	-2.38	-1.23	-1.54	-1.87
pc-3-CBS15	mPw2-PLYP-D	-0.22	-0.55	-0.87	-1.19	-1.52	-1.84	-0.69	-1.02	-1.32	-1.66	-2.53	-1.24	-1.59	-1.94

A. CCSD(T)/cc-pVQZ optimized geometries (in au)

Methane

H	1.678580536	0.000000000	1.186935680
H	-1.678580536	0.000000000	1.186935680
H	0.000000000	-1.678580536	-1.186935680
H	0.000000000	1.678580536	-1.186935680
C	0.000000000	0.000000000	0.000000000

Ethane

C	0.000000000	0.000000000	-1.442348942
C	0.000000000	0.000000000	1.442348942
H	1.921715694	0.000000000	-2.188005755
H	-1.921715694	0.000000000	2.188005755
H	-0.960857847	1.664254610	-2.188005755
H	-0.960857847	-1.664254610	-2.188005755
H	0.960857847	1.664254610	2.188005755
H	0.960857847	-1.664254610	2.188005755

Propane

C	0.000000000	2.391996497	-0.490920727
C	0.000000000	-2.391996497	-0.490920727
H	-1.665758360	2.454327488	-1.708464791
H	1.665758360	2.454327488	-1.708464791
H	1.665758360	-2.454327488	-1.708464791
H	-1.665758360	-2.454327488	-1.708464791
H	0.000000000	4.094090643	0.672375839
H	0.000000000	-4.094090643	0.672375839
C	0.000000000	0.000000000	1.120448235
H	1.654440658	0.000000000	2.357886921
H	-1.654440658	0.000000000	2.357886921

B. B3LYP/pc-2 optimized geometries (in Å)

Methane

H	0.628202	0.628202	0.628202
C	0.000000	0.000000	0.000000
H	-0.628202	-0.628202	0.628202
H	-0.628202	0.628202	-0.628202
H	0.628202	-0.628202	-0.628202

Ethane

C	0.000000	0.000000	0.763841
C	0.000000	0.000000	-0.763841
H	0.000000	1.015959	1.160838
H	-0.879847	-0.507980	1.160838
H	0.879847	-0.507980	1.160838
H	0.000000	-1.015959	-1.160838
H	-0.879847	0.507980	-1.160838
H	0.879847	0.507980	-1.160838

Propane

C	0.000000	1.273530	-0.259115
H	-0.880531	1.317689	-0.903353
H	0.880531	1.317689	-0.903353
H	0.000000	2.168280	0.364795
C	0.000000	0.000000	0.584794
H	0.873349	0.000000	1.242219
H	-0.873349	0.000000	1.242219
C	0.000000	-1.273530	-0.259115
H	0.880531	-1.317689	-0.903353
H	0.000000	-2.168280	0.364795
H	-0.880531	-1.317689	-0.903353

n-Butane

C	0.702083	1.829968	0.000000
C	0.702083	0.302433	0.000000
C	-0.702083	-0.302433	0.000000
C	-0.702083	-1.829968	0.000000
H	1.716982	2.230009	0.000000
H	-1.716982	-2.230009	0.000000
H	0.190262	2.223197	0.880885
H	0.190262	2.223197	-0.880885
H	-0.190262	-2.223197	0.880885
H	-0.190262	-2.223197	-0.880885

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   H     1.249626   -0.063080   -0.874233
   H     1.249626   -0.063080    0.874233
   H    -1.249626    0.063080   -0.874233
   H    -1.249626    0.063080    0.874233

n-Pentane
   C     0.000000    1.280505   -0.521590
   C     0.000000    0.000000    0.313568
   C     0.000000   -1.280505   -0.521590
   C     0.000000   -2.553050    0.323507
   C     0.000000    2.553050    0.323507
   H     0.000000   -3.447725   -0.300528
   H    -0.873925    1.280001   -1.179957
   H     0.873925    1.280001   -1.179957
   H    -0.880562   -2.598122    0.967492
   H     0.880562   -2.598122    0.967492
   H     0.874444    0.000000    0.973249
   H    -0.874444    0.000000    0.973249
   H     0.873925   -1.280001   -1.179957
   H    -0.873925   -1.280001   -1.179957
   H     0.000000    3.447725   -0.300528
   H    -0.880562    2.598122    0.967492
   H     0.880562    2.598122    0.967492

n-Hexane
   C     1.410334    2.896387    0.000000
   H     2.425113    3.296971    0.000000
   H     0.898446    3.290030    0.880632
   H     0.898446    3.290030   -0.880632
   C     1.410334    1.368805    0.000000
   H     1.958703    1.004405   -0.873957
   H     1.958703    1.004405    0.873957
   C     0.006006    0.764276    0.000000
   H    -0.542834    1.129954   -0.874559
   H    -0.542834    1.129954    0.874559
   C    -0.006006   -0.764276    0.000000
   H     0.542834   -1.129954    0.874559
   H     0.542834   -1.129954   -0.874559
   C    -1.410334   -1.368805    0.000000
   H    -1.958703   -1.004405   -0.873957
   H    -1.958703   -1.004405    0.873957
   C    -1.410334   -2.896387    0.000000
   H    -0.898446   -3.290030    0.880632
   H    -2.425113   -3.296971    0.000000
   H    -0.898446   -3.290030   -0.880632

n-Heptane
   C     0.000000    2.560476    0.492753
   H     0.873840    2.560193    1.151200
   H    -0.873840    2.560193    1.151200
   C     0.000000    1.279634   -0.342089
   H    -0.874383    1.280292   -1.001574
   H     0.874383    1.280292   -1.001574
   C     0.000000    0.000000    0.494405
   H    -0.874475    0.000000    1.153543
   H     0.874475    0.000000    1.153543
   C     0.000000   -1.279634   -0.342089
   H     0.874383   -1.280292   -1.001574
   H    -0.874383   -1.280292   -1.001574
   C     0.000000   -2.560476    0.492753
   H    -0.873840   -2.560193    1.151200
   H     0.873840   -2.560193    1.151200
   C     0.000000   -3.832739   -0.352911
   H     0.880601   -3.877290   -0.996775
   H     0.000000   -4.727394    0.271023
   H    -0.880601   -3.877290   -0.996775
   C     0.000000    3.832739   -0.352911
   H    -0.880601    3.877290   -0.996775
   H     0.000000    4.727394    0.271023
   H     0.880601    3.877290   -0.996775

n-Octane
   C    -0.162804    1.957862    0.000000
   H    -0.816690    2.044788    0.874380
   H    -0.816690    2.044788   -0.874380
   C     0.498460    0.579577    0.000000
   H     1.151912    0.493203   -0.874479
   H     1.151912    0.493203    0.874479
   C    -0.498460   -0.579577    0.000000
   H    -1.151912   -0.493203   -0.874479
   H    -1.151912   -0.493203    0.874479
   C     0.162804   -1.957862    0.000000
   H     0.816690   -2.044788    0.874380
```

```
   H     0.816690   -2.044788   -0.874380
   C    -0.832656   -3.117803    0.000000
   H    -1.485721   -3.031747   -0.873746
   H    -1.485721   -3.031747    0.873746
   C    -0.162804   -4.490823    0.000000
   H     0.469428   -4.621287    0.880573
   H    -0.900043   -5.294738    0.000000
   H     0.469428   -4.621287   -0.880573
   C     0.832656    3.117803    0.000000
   H     1.485721    3.031747   -0.873746
   H     1.485721    3.031747    0.873746
   C     0.162804    4.490823    0.000000
   H    -0.469428    4.621287    0.880573
   H     0.900043    5.294738    0.000000
   H    -0.469428    4.621287   -0.880573

Isobutane
   C     0.000000    0.000000    0.370815
   C     0.000000    1.457967   -0.095417
   C    -1.262636   -0.728983   -0.095417
   C     1.262636   -0.728983   -0.095417
   H     0.000000    0.000000    1.466177
   H     0.882018    1.990404    0.264493
   H     0.000000    1.516083   -1.186841
   H    -0.882018    1.990404    0.264493
   H    -1.282732   -1.759052    0.264493
   H    -2.164750   -0.231352    0.264493
   H    -1.312966   -0.758041   -1.186841
   H     1.282732   -1.759052    0.264493
   H     1.312966   -0.758041   -1.186841
   H     2.164750   -0.231352    0.264493

Isopentane
   C    -1.732561   -0.825763   -0.019573
   H    -1.634022   -1.847963   -0.388664
   H    -1.910585   -0.877524    1.057549
   H    -2.619809   -0.387861   -0.479742
   C    -0.481047    0.001802   -0.325076
   H    -0.346660    0.016402   -1.413094
   C     0.765467   -0.658847    0.284090
   H     0.771313   -1.714000   -0.003579
   H     0.673736   -0.644495    1.375467
   C     2.096588   -0.029981   -0.125945
   H     2.188143    0.999337    0.221366
   H     2.935948   -0.588872    0.289776
   H     2.210369   -0.024444   -1.212155
   C    -0.666253    1.447818    0.144287
   H    -0.783205    1.489362    1.230411
   H     0.180584    2.079436   -0.123564
   H    -1.558971    1.890444   -0.300470



Isohexane
   C    -2.838120   -0.209882    0.152002
   H    -2.896148   -0.249524    1.241592
   H    -3.670588    0.399865   -0.201618
   H    -2.988193   -1.224742   -0.221784
   C    -1.495339    0.355665   -0.308552
   H    -1.479272    0.408770   -1.401580
   H    -1.399777    1.383821    0.047454
   C    -0.304682   -0.476954    0.169743
   H    -0.294057   -0.497566    1.265784
   H    -0.456996   -1.513351   -0.148561
   C     1.071597   -0.012684   -0.331543
   H     1.021720    0.045380   -1.425132
   C     2.149851   -1.037663    0.031745
   H     3.126013   -0.740836   -0.355390
   H     2.241113   -1.138157    1.116153
   H     1.914393   -2.023189   -0.373477
   C     1.452161    1.374681    0.195238
   H     0.743197    2.141842   -0.115442
   H     1.488476    1.376314    1.287838
   H     2.437312    1.672395   -0.167637

Isoheptane
   C    -2.223705   -0.502453    0.272279
   H    -2.190337   -0.604336    1.361136
   H    -2.255742   -1.521228   -0.125243
   C    -0.943981    0.184455   -0.207392
   H    -0.975338    0.278518   -1.298374
   H    -0.923943    1.204745    0.184773
   C     0.329089   -0.560430    0.197503
   H     0.387904   -0.611004    1.290959
```

```
   H     0.249780   -1.596374   -0.147579
   C     1.640954    0.031158   -0.341575
   H     1.542887    0.113641   -1.430328
   C     2.814476   -0.908266   -0.049403
   H     3.747342   -0.516604   -0.458362
   H     2.952773   -1.034196    1.027404
   H     2.649082   -1.897312   -0.479868
   C     1.924764    1.431454    0.210945
   H     1.137158    2.140379   -0.043141
   H     2.012998    1.406435    1.300317
   H     2.861787    1.825040   -0.186558
   C    -3.495641    0.241443   -0.130289
   H    -4.389290   -0.273924    0.224158
   H    -3.509538    1.251503    0.284060
   H    -3.573259    0.330556   -1.215766

Isooctane (C1 symmetry, local minimum)
   C    -1.200687   -0.028771    0.007671
   C    -2.273346   -0.248326    1.087568
   C     0.182279   -0.297097    0.654957
   C    -1.454121   -1.017252   -1.142640
   C    -1.322182    1.407830   -0.522100
   C     1.452281   -0.051738   -0.194287
   H     0.254992    0.298575    1.570707
   H     0.175173   -1.340627    0.982210
   C     2.500712   -1.138840    0.069348
   C     2.063900    1.332151    0.055805
   H     1.183502   -0.111786   -1.252620
   H     3.402044   -0.973208   -0.523611
   H     2.794336   -1.147215    1.122076
   H     2.115331   -2.129956   -0.174813
   H     2.933104    1.497521   -0.583514
   H     1.355045    2.136927   -0.132826
   H     2.395617    1.420092    1.093411
   H    -0.727093   -0.901939   -1.947210
   H    -1.402898   -2.049646   -0.790840
   H    -2.445183   -0.861284   -1.573045
   H    -3.275119   -0.097774    0.680391
   H    -2.225399   -1.261970    1.490186
   H    -2.142335    0.447858    1.918207
   H    -0.614171    1.604273   -1.327631
   H    -2.324333    1.583688   -0.918149
   H    -1.145629    2.138724    0.269136


Isooctane* (first order saddle point, Cs symmetry)
   C     0.504417   -1.532859    1.256293
   C    -0.300648   -1.164711    0.000000
   C     0.504417   -1.532859   -1.256293
   C    -1.610642   -1.969030    0.000000
   C    -0.662960    0.341394    0.000000
   C     0.511500    1.355135    0.000000
   C     0.504417    2.229136    1.258917
   C     0.504417    2.229136   -1.258917
   H    -1.296680    0.528696   -0.871445
   H    -1.296680    0.528696    0.871445
   H     1.452054    0.798491    0.000000
   H    -0.056133   -1.298953   -2.163523
   H     1.453990   -0.998755   -1.302716
   H     0.728820   -2.601144   -1.270264
   H    -2.212004   -1.741548   -0.882289
   H    -1.411450   -3.042580    0.000000
   H    -2.212004   -1.741548    0.882289
   H     0.728820   -2.601144    1.270264
   H     1.453990   -0.998755    1.302716
   H    -0.056133   -1.298953    2.163523
   H     1.352796    2.915969    1.269945
   H    -0.408042    2.828471    1.308986
   H     0.552201    1.623285    2.164906
   H     1.352796    2.915969   -1.269945
   H     0.552201    1.623285   -2.164906
   H    -0.408042    2.828471   -1.308986

Neopentane
   C     0.000000    0.000000    0.000000
   C     0.886824    0.886824    0.886824
   C    -0.886824   -0.886824    0.886824
   C    -0.886824    0.886824   -0.886824
   C     0.886824   -0.886824   -0.886824
   H     1.529595    1.529595    0.281953
   H     0.281953    1.529595    1.529595
   H     1.529595    0.281953    1.529595
   H    -1.529595   -1.529595    0.281953
```

```
   H    -0.281953   -1.529595    1.529595
   H    -1.529595   -0.281953    1.529595
   H    -1.529595    0.281953   -1.529595
   H    -1.529595    1.529595   -0.281953
   H    -0.281953    1.529595   -1.529595
   H     0.281953   -1.529595   -1.529595
   H     1.529595   -0.281953   -1.529595
   H     1.529595   -1.529595   -0.281953

Neohexane
   C     1.909156   -1.067526    0.000000
   H     1.674119   -1.665532    0.880957
   H     2.987449   -0.902580    0.000000
   H     1.674119   -1.665532   -0.880957
   C     1.169434    0.270366    0.000000
   H     1.486859    0.848202   -0.873462
   H     1.486859    0.848202    0.873462
   C    -0.377218    0.217601    0.000000
   C    -0.899338   -0.498861   -1.255087
   H    -1.990228   -0.472266   -1.287758
   H    -0.597231   -1.546197   -1.280560
   H    -0.528045   -0.020073   -2.163675
   C    -0.899338    1.663145    0.000000
   H    -0.553880    2.206371    0.881918
   H    -1.990778    1.686390    0.000000
   H    -0.553880    2.206371   -0.881918
   C    -0.899338   -0.498861    1.255087
   H    -1.990228   -0.472266    1.287758
   H    -0.528045   -0.020073    2.163675
   H    -0.597231   -1.546197    1.280560



Neoheptane
   C     1.382083    1.004589    0.000000
   H     1.838156    0.534367    0.874097
   H     1.838156    0.534367   -0.874097
   C    -0.128744    0.758657    0.000000
   H    -0.560865    1.258825   -0.873638
   H    -0.560865    1.258825    0.873638
   C    -0.616963   -0.709861    0.000000
   C    -0.128744   -1.449918   -1.255413
   H    -0.536699   -2.462012   -1.288109
   H     0.957932   -1.533995   -1.280986
   H    -0.446893   -0.934416   -2.164084
   C    -2.154131   -0.696002    0.000000
   H    -2.542626   -0.183102    0.882098
   H    -2.554912   -1.711469    0.000000
   H    -2.542626   -0.183102   -0.882098
   C    -0.128744   -1.449918    1.255413
   H    -0.536699   -2.462012    1.288109
   H    -0.446893   -0.934416    2.164084
   H     0.957932   -1.533995    1.280986
   C     1.725331    2.494198    0.000000
   H     1.316043    2.993582    0.880457
   H     2.804289    2.654502    0.000000
   H     1.316043    2.993582   -0.880457

3-Methylpentane (diethylmethylmethane)
   C    -0.332728   -0.121350    2.575521
   H    -1.063912   -0.932242    2.551099
   H     0.640901   -0.559786    2.794486
   H    -0.590828    0.528927    3.412444
   C    -0.332728    0.658684    1.260911
   H    -1.299837    1.157066    1.150568
   H     0.414324    1.458052    1.310992
   C    -0.075942   -0.183404    0.000000
   H    -0.804036   -1.004805    0.000000
   C    -0.332728    0.658684   -1.260911
   H     0.414324    1.458052   -1.310992
   H    -1.299837    1.157066   -1.150568
   C    -0.332728   -0.121350   -2.575521
   H    -0.590828    0.528927   -3.412444
   H     0.640901   -0.559786   -2.794486
   H    -1.063912   -0.932242   -2.551099
   C     1.327529   -0.797769    0.000000
   H     2.089957   -0.013988    0.000000
   H     1.494365   -1.423101    0.876573
   H     1.494365   -1.423101   -0.876573

Diisopropyl
   C     0.341702   -0.695133    0.000000
   H     1.424935   -0.520295    0.000000
   C    -0.341702    0.695133    0.000000
```

```
   H    -1.424935    0.520295    0.000000
   C     0.000000    1.513924    1.250811
   H    -0.342372    1.037017    2.167609
   H     1.079758    1.663618    1.333715
   H    -0.464798    2.499792    1.202345
   C     0.000000    1.513924   -1.250811
   H    -0.342372    1.037017   -2.167609
   H    -0.464798    2.499792   -1.202345
   H     1.079758    1.663618   -1.333715
   C     0.000000   -1.513924   -1.250811
   H    -1.079758   -1.663618   -1.333715
   H     0.342372   -1.037017   -2.167609
   H     0.464798   -2.499792   -1.202345
   C     0.000000   -1.513924    1.250811
   H     0.342372   -1.037017    2.167609
   H    -1.079758   -1.663618    1.333715
   H     0.464798   -2.499792    1.202345


Hexamethylethane
   C     0.000000    0.000000    0.794386
   C     0.000000    0.000000   -0.794386
   C     0.829563    1.172031    1.355274
   C    -0.829563    1.172031   -1.355274
   C    -0.600227   -1.304438   -1.355274
   C     0.600227   -1.304438    1.355274
   C    -1.429791    0.132407    1.355274
   C     1.429791    0.132407   -1.355274
   H    -1.410270    0.023506    2.440955
   H     0.725492    1.209576    2.440955
   H     0.684778   -1.233082    2.440955
   H    -0.725492    1.209576   -2.440955
   H    -0.684778   -1.233082   -2.440955
   H     1.410270    0.023506   -2.440955
   H     0.500327    2.135132    0.965123
   H     1.598915   -1.500862    0.965123
   H    -2.099242   -0.634270    0.965123
   H    -0.500327    2.135132   -0.965123
   H    -1.598915   -1.500862   -0.965123
   H     2.099242   -0.634270   -0.965123
   H     1.890712    1.063129    1.134862
   H    -0.024659   -2.168969    1.134862
   H    -1.866053    1.105840    1.134862
   H     1.866053    1.105840   -1.134862
   H    -1.890712    1.063129   -1.134862
   H     0.024659   -2.168969   -1.134862
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