CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

The Concept of Protobranching and its Many Paradigm Shifting Implications for Energy Evaluations

Matthew D. Wodrich, Chaitanya S. Wannere, Yirong Mo, Peter D. Jarowski, Kendall N. Houk, and Paul von Ragué Schleyer*

SI Table 1. Experimental (from the NIST compilation, unless otherwise indicated)[i-iv] and G3(MP2) computed heats of formation; Pople bond separation energies of relevant alkanes, alkenes, and alkynes. All data in kcal/mol.

Compound	Heat of Formation (Experimental)	Heat of Formation (G3(MP2)	Pople Bond Separation Energy
methane	-17.89	--	--
ethane	-20.04 ± 0.07	--	--
ethylene	12.55 ± 0.17[i]	--	--
acetylene	54.19 ± 0.19	--	--
propane	-25.02 ± 0.12	-25.1	2.83
cyclopropane	12.74 ± 0.14	--	-19.19
propene	4.87 ± 0.19	--	5.62
propyne	44.32 ± 0.21	43.9	7.72
n-butane	-30.03 ± 0.16	-30.2	5.69
isobutane	-32.07 ± 0.15	--	7.73
cyclobutane	6.78 ± 0.14[i]	--	-15.38
1-butene	-0.15 ± 0.19	--	8.40
trans-2-butene	-2.58 ± 0.24	--	10.83
2-methyl-1-propene	-4.29 ± 0.26	--	12.54
anti-1,3-butadiene	26.00 ± 0.19	24.9	14.84
syn-1,3-butadiene	--	27.9	12.94
1-butyne	39.48 ± 0.21	39.4	10.41
2-butyne	34.68 ± 0.24	34.9	15.21
1,3-butadiyne	[111.0]	109.0	15.12
n-pentane	-35.08 ± 0.14	-35.2	8.59
isopentane	-36.73 ± 0.14	--	10.24
neo-pentane	-40.14 ± 0.15	--	13.65
cyclopentane	-18.26 ± 0.19	--	7.51
trans-1,3-pentadiene	18.19 ± 0.22[i]	17.9	20.50

1-pentene	-5.09 ± 0.24[i]	-5.6	11.19
trans-2-pentene	-7.90 ± 0.30	-7.8	14.00
1,3-pentadiyne	--	98.3	23.67
1-pentyne	34.50 ± 0.50	34.2	13.24
2-pentyne	30.80 ± 0.50	30.3	16.94
n-hexane	-39.96 ± 0.19	-40.3	11.32
1-hexene	-10.40 ± 0.38[i]	--	14.35
3-hexene	-13.00 ± 0.31[i]	--	16.95
benzene	19.82 ± 0.12	--	64.39
cyclohexane	-29.43 ± 0.19	--	16.53
cyclohexene	-1.03 ± 0.23	--	20.72
1,3-cyclohexadiene	25.00 ± 0.15	--	27.28
1,3,5-hexatriene	40.1 ± 0.6	--	28.88
1-hexyne	29.23 ± 0.29[ii]	29.14	16.36
1,4-hexadiyne	--	98.1	21.72
1,5-hexadiyne	99.14 ± 1.1	99.3	20.68
1,3,5-hexatriyne	--	163.4	30.7
n-heptane	-44.89 ± 0.19	-45.4	14.10
3-heptyne	--	20.4	23.0
1,3-heptadiyne	--	88.3	29.4
1,3,6-heptatriyne	--	162.4	29.5
tetrahedrane	--	128.3	-105.4
cubane	148.7 ± 1.0[iii]	145.5	-102.9
dodecahedrane	18.2 ± 1.0[iv]	--	96.2
norbornane	-13.13 ± 0.25	--	13.82
adamantane	-32.12 ± 0.56	--	42.10
tetramethyladamantane	-68.0 ± 1.7	--	69.38

SI Table 2. Computed values for relevant hydrocarbons using various functionals. All calculations computed using the 6-311++G(d,p) basis and include scaled zero-point and thermal corrections. CCSD(T) computated at MP2/6-311++G(2d,2p) geometries and include MP2 zero-point and thermal corrections. Scaling factors used are HF=0.92, B3LYP=0.96, MP2=0.95. All values in hartrees.

	HF	B3LYP	MP2	CCSD(T)
methane	-40.162166	-40.487382	-40.332685	-40.359303
ethane	-79.175191	-79.780752	-79.495239	-79.540113
propane	-118.190445	-119.076760	-118.662318	-118.725033
n-butane	-157.205568	-158.372614	-157.829397	-157.909953
isobutane	-157.206719	-158.374048	-157.833122	-157.913209
n-pentane	-196.220595	-197.668303	-197.004148	-197.102559
neopentane	-196.222776	-197.670950	-197.006566	-197.103491
cyclopropane	-117.005651	-117.848890	-117.455984	--
cyclobutane	-156.022362	-157.146178	-156.625822	--
tetrahedrane	-153.572683	-154.619329	-154.135315	--
cubane	-307.320405	-309.399868	-308.453517	--
dodecahedrane	-768.836281	-774.007885	--	--
norbornane	-271.944704	-273.864680	-272.992257	--
adamantane	-387.867662	-390.583172	-389.357773	--
tetramethyladamantane	-543.939966	-547.779708	-545.670649	--
ethene	-78.002459	-78.562770	-78.294173	--
propene	-117.022248	-117.864402	-117.465293	--

SI Table 3. Electronic energies for planar cycloalkanes and cyclosilanes using various functionals. Calculations computed with 6-31G(d) basis set. All value in hartree.

Molecule	**Point Group**	**HF**	**B3LYP**	**BHandH**	**MP2**
CH_4	T_d	-40.19517	-40.51839	-40.14224	-40.33255
C_2H_6	D_{3d}	-79.22875	-79.83042	-79.13401	-79.49474
C_3H_6	D_{3h}	-117.05887	-117.89520	-116.92407	-117.05844
C_4H_8	D_{4h}	-156.09575	-157.21184	-155.92290	-156.61438
C_5H_{10}	D_{5h}	-195.15568	-196.54979	-194.94572	-195.80668
C_6H_{12}	D_{6h}	-234.16311	-235.83919	-233.91543	-234.94352
C_7H_{14}	D_{7h}	-273.14579	-275.10561	-272.85985	-274.05778
C_8H_{16}	D_{8h}	-312.11337	-314.36012	-311.79095	-313.15811
C_9H_{18}	D_{9h}	-351.06785	-353.60184	-350.70851	-352.24617

$C_{10}H_{20}$	D_{10h}	-390.01499	-392.83773	-389.61959	-391.32768
SiH_4	T_d	-291.22513	-291.88369	-290.94594	-291.30712
Si_2H_6	D_{3d}	-581.30509	-582.58273	-580.76275	-581.46471
Si_3H_6	D_{3h}	-870.18218	-872.04390	-869.39068	-870.42320
Si_4H_8	D_{4h}	-1160.29787	-1162.77559	-1159.24343	-1160.61438
Si_5H_{10}	D_{5h}	-1450.39704	-1453.49255	-1449.08093	-1450.79467
Si_6H_{12}	D_{6h}	-1740.47369	-1744.18905	-1738.89557	-1740.94972
Si_7H_{14}	D_{7h}	-2030.53943	-2034.87617	-2028.70029	-2031.09687
Si_8H_{16}	D_{8h}	-2320.59716	-2325.55709	-2318.49864	-2321.23536
Si_9H_{18}	D_{9h}	-2610.64957	-2616.23301	-2608.29190	-2611.36992
$Si_{10}H_{20}$	D_{10h}	-2900.69842	-2906.90645	-2898.08255	-2901.50078

---

[i] Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: London, 1986.

[ii] Rogers, D. W.; Dagdagan, O. A.; Allinger, N. L. *J. Am. Chem. Soc.* **1979**, *101*, 671-676.

[iii] Kybett, B. D.; Carroll, S.; Natalis, P.; Bonnell, D. W.; Margrave, J. L.; Franklin, J. L. *J. Am. Chem. Soc.* **1966**, *88*, 626.

[iv] Beckhaus, H. D.; Rückhardt, C.; Lagerwall, D. R.; Paquette, L. A.; Wahl, F.; Prinzbach, H. *J. Am. Chem. Soc.* **1994**, *116*, 11775.