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Supporting Information

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

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**SI Table 1.** Experimental (from the NIST compilation, unless otherwise indicated)<sup>i-iv</sup> 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 <sup>i</sup>	--	--
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 <sup>i</sup>	--	-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 <sup>i</sup>	17.9	20.50

1-pentene	$-5.09 \pm 0.24^i$	-5.6	11.19
trans-2-pentene	$-7.90 \pm 0.30$	-7.8	14.00
1,3-pentadiyne	--	98.3	23.67
1-pentyne	$34.50 \pm 0.50$	34.2	13.24
2-pentyne	$30.80 \pm 0.50$	30.3	16.94
n-hexane	$-39.96 \pm 0.19$	-40.3	11.32
1-hexene	$-10.40 \pm 0.38^i$	--	14.35
3-hexene	$-13.00 \pm 0.31^i$	--	16.95
benzene	$19.82 \pm 0.12$	--	64.39
cyclohexane	$-29.43 \pm 0.19$	--	16.53
cyclohexene	$-1.03 \pm 0.23$	--	20.72
1,3-cyclohexadiene	$25.00 \pm 0.15$	--	27.28
1,3,5-hexatriene	$40.1 \pm 0.6$	--	28.88
1-hexyne	$29.23 \pm 0.29^{ii}$	29.14	16.36
1,4-hexadiyne	--	98.1	21.72
1,5-hexadiyne	$99.14 \pm 1.1$	99.3	20.68
1,3,5-hexatriyne	--	163.4	30.7
n-heptane	$-44.89 \pm 0.19$	-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	$148.7 \pm 1.0^{iii}$	145.5	-102.9
dodecahedrane	$18.2 \pm 1.0^{iv}$	--	96.2
norbornane	$-13.13 \pm 0.25$	--	13.82
adamantane	$-32.12 \pm 0.56$	--	42.10
tetramethyladamantane	$-68.0 \pm 1.7$	--	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) computed 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
<i>n</i> -butane	-157.205568	-158.372614	-157.829397	-157.909953
isobutane	-157.206719	-158.374048	-157.833122	-157.913209
<i>n</i> -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	--
tetrahydrane	-153.572683	-154.619329	-154.135315	--
cubane	-307.320405	-309.399868	-308.453517	--
dodecahydrane	-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 <sub>4</sub>	T <sub>d</sub>	-40.19517	-40.51839	-40.14224	-40.33255
C <sub>2</sub> H <sub>6</sub>	D <sub>3d</sub>	-79.22875	-79.83042	-79.13401	-79.49474
C <sub>3</sub> H <sub>6</sub>	D <sub>3h</sub>	-117.05887	-117.89520	-116.92407	-117.05844
C <sub>4</sub> H <sub>8</sub>	D <sub>4h</sub>	-156.09575	-157.21184	-155.92290	-156.61438
C <sub>5</sub> H <sub>10</sub>	D <sub>5h</sub>	-195.15568	-196.54979	-194.94572	-195.80668
C <sub>6</sub> H <sub>12</sub>	D <sub>6h</sub>	-234.16311	-235.83919	-233.91543	-234.94352
C <sub>7</sub> H <sub>14</sub>	D <sub>7h</sub>	-273.14579	-275.10561	-272.85985	-274.05778
C <sub>8</sub> H <sub>16</sub>	D <sub>8h</sub>	-312.11337	-314.36012	-311.79095	-313.15811
C <sub>9</sub> H <sub>18</sub>	D <sub>9h</sub>	-351.06785	-353.60184	-350.70851	-352.24617

C <sub>10</sub> H <sub>20</sub>	D <sub>10h</sub>	-390.01499	-392.83773	-389.61959	-391.32768
SiH <sub>4</sub>	T <sub>d</sub>	-291.22513	-291.88369	-290.94594	-291.30712
Si <sub>2</sub> H <sub>6</sub>	D <sub>3d</sub>	-581.30509	-582.58273	-580.76275	-581.46471
Si <sub>3</sub> H <sub>6</sub>	D <sub>3h</sub>	-870.18218	-872.04390	-869.39068	-870.42320
Si <sub>4</sub> H <sub>8</sub>	D <sub>4h</sub>	-1160.29787	-1162.77559	-1159.24343	-1160.61438
Si <sub>5</sub> H <sub>10</sub>	D <sub>5h</sub>	-1450.39704	-1453.49255	-1449.08093	-1450.79467
Si <sub>6</sub> H <sub>12</sub>	D <sub>6h</sub>	-1740.47369	-1744.18905	-1738.89557	-1740.94972
Si <sub>7</sub> H <sub>14</sub>	D <sub>7h</sub>	-2030.53943	-2034.87617	-2028.70029	-2031.09687
Si <sub>8</sub> H <sub>16</sub>	D <sub>8h</sub>	-2320.59716	-2325.55709	-2318.49864	-2321.23536
Si <sub>9</sub> H <sub>18</sub>	D <sub>9h</sub>	-2610.64957	-2616.23301	-2608.29190	-2611.36992
Si <sub>10</sub> H <sub>20</sub>	D <sub>10h</sub>	-2900.69842	-2906.90645	-2898.08255	-2901.50078

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

<sup>ii</sup> Rogers, D. W.; Dagdagan, O. A.; Allinger, N. L. *J. Am. Chem. Soc.* **1979**, *101*, 671-676.

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

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