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Stabilities of Carbenes: Independent Measures for Singlets and Triplets [*Journal of the American Chemical Society* **2011**, *133*, 3381–3389 DOI: 10.1021/ja1071493]. Scott Gronert* James R. Keeffe and Rory A. More O'Ferrall

Page 3382−3383. In Table 1, computational values were erroneously listed as experimental for the singlet−triplet gaps of several species. The actual experimental values are as follow: CCl_2, −20.8 kcal/mol;[1] FCH, −14.9 kcal/mol;[2] ClCH, −4.2 kcal/mol;[2] and CF_2, −54 kcal/mol.[3] The corrected table is presented below. In addition, some key references to earlier work on heterocyclic carbenes were omitted.[4]

Table 1. G3MP2 Singlet−Triplet Energy Gaps for Selected Carbenes and Carbene Stabilization Enthalpies for Singlet and Triplet Carbenes at 298 K[a]

carbene	ΔE_{ST} (G3MP2), kcal/mol	ΔE_{ST} (lit.),[b] kcal/mol	CSE (singlet), kcal/mol	CSE (triplet), kcal/mol
		Type 1: Alkyl, Alkenyl, and Alkynyl Carbenes[18]		
1 CH_2	9.4	9.0 (exp)	0	0
2 CH_3CH	3.0	2.3	12.1	5.6
3 $(CH_3)_2CH-CH$	0.6		13.2	4.4
4 $(CH_3)_2C$	−1.0	−2.5	21.0	9.7
5 $H_2C=CH-CH$	8.2	6.4	18.0	16.8
6 $HC\equiv C-CH$	11.8		22.0	24.0
7 $(HC\equiv C)_2-C$[19]	13.5		39.5	42.7
8 cyclopropylidene	−16.8	−12.9,[20] −13.8,[21] − 14.1[22]	21.0	−5.1
9 cyclobutylidene	−10.5	−5.9[21]	26.5	6.7
10 cyclopentylidene	−10.0	−8.7[23]	27.6	8.3
11 cyclopropenylidene	−71.6	−70,[24] −52.3[22]	69.1	−12.0
12 cyclopropylcarbinylidene	−6.5		23.0	7.1
13 cyclobut-1-en-3-ylidene	−24.1	25[25]	45.6	12.1
14 cyclopent-1-en-1-ylidene	−7.6		31.5	14.5
15 2,4-cyclohexadienylidene	3.2	3.0	34.7	28.5
16 2,5-cyclohexadienylidene	3.2	3.1	32.4	26.2
17 6,6-dimethylcyclohexa-2,4-dienylidene	5.3		30.7	26.6
18 spiro[2.5]octa-4,6-dien-8-ylidene	−7.3		46.6	29.8
19 spiro[2.5]octa-4,7-dien-6-ylidene	0.9		37.0	27.9
		Type 2: Selected Aryl Carbenes[26]		
20 PhCH	2.32	2.3 (kinetic estimate), 5.4[17]	18.7	11.4
21 $PhCCH_3$	1.0	2.0 (kinetic estimate)[27]	24.9	16.3
22 3-nitrophenyl	3.58	7.8	15.7	9.7
23 4-nitrophenyl	5.10	10.3	15.1	10.7
24 3-hydroxyphenyl	1.91	5.3	19.0	11.3
25 4-hydroxyphenyl	−1.33	1.7	19.6	11.5
26 3-aminophenyl	1.73	5.2	19.2	11.3
27 4-aminophenyl	−3.51	0.7	25.6	12.1
28 3-oxyphenyl$^-$	−8.02		30.9	13.3
29 4-oxyphenyl$^-$	−24.10		53.6	19.9
		Type 3: Acyclic Heteroatom and Cyano Carbenes		
30 H_2NCH	−40.8		58.1	14.2
31 $(NH_2)_2C$	−57.1	−52.6, −53.2[22]	82.9	16.1
32 HOCH (anti)	−25.4	−28.0[28]	46.3	11.2
33 CH_3OCH	−27.8		47.9	10.4
34 CH_3OCCH_3	−32.6		53.5	11.4
35 $(CH_3O)_2C$[29]	−59.8	−53.0	77.3	8.1
36 FCH	−14.6	−14.9 (exp)[d]	28.5	4.5

Table 1. Continued

carbene	ΔE_{ST} (G3MP2), kcal/mol	ΔE_{ST} (lit.),[b] kcal/mol	CSE (singlet), kcal/mol	CSE (triplet), kcal/mol
37 F_2C	−56.2	−54 (exp)[e]	58.7	−6.9
38 SiH_3CH	18.1	18.1[30]	0.7	9.4
39 $(SiH_3)_2C$	22.1	24.7[31]	4.4[31]	17.0[31]
40 H_2PCH	−13.3	−6.6[32]	34.2	11.4
41 HSCH (anti)	−20.4	−13.8[32]	42.7	12.7
42 CH_3SCH	−24.8		48.4	14.1
43 ClCH	−6.9	−4.2 (exp)[d]	24.4	8.1
44 Cl_2C	−21.7	−20.8 (exp)[f]	43.7	12.5
45 $(NH_2)_2CCH^+$	11.9	14.1[33]	−2.0	0.7
46 cyanocarbene	10.0	17.0[34]	11.5	12.0
47 dicyanocarbene	12.2	16.4[35]	23.6	25.9
48 nitrocarbene[36]	NA	NA	NA	0.7
49 dinitrocarbene[37]	−20.0		25.0	−4.1
50 aminocyanocarbene	−31.9		65.3	23.5
51 aminonitrocarbene	−41.5		60.1	9.2
Type 4: Five-Membered, Cyclic 1,3-Diheteroatom Carbenes[c]				
52 imidazol-2-ylidene	−85.5	−84.5	103.1	8.0
53 4,5-dihydroimidazol-2-ylidene	−72.3	−69.4	81.9	2.3
54 *N*,*N*′-dimethylimidazol-2-ylidene	−87.5		103.2	6.2
55 4,5-dimethylimidazol-2-ylidene	−83.5		101.4	8.4
56 4,5,*N*,*N*′-tetramethylimidazol-2-ylidene	−86.1		103.6	7.9
57 imidazol-5-ylidene	−64.9		114.3	39.6
58 1,3-dioxol-2-ylidene	−86.1		84.4	−11.6
59 1,3-dioxolan-2-ylidene	−72.5		80.0	−2.1
60 oxazol-2-ylidene	−86.3		91.8	−4.4
61 4,5-dihydrooxazol-2-ylidene	−70.2		81.9	2.3
62 4,5,*N*,*N*′-tetrasilylimidazol-2-ylidene	−82.4		101.2	8.8
63 1,3-diphosphole-2-ylidene	−26.2		48.1	12.6
64 1,3-diphospholan-2-ylidene	−21.1		43.2	11.8
65 1,3-dithiol-2-ylidene	−56.5		82.5	16.2
66 1,3-thiolan-2-ylidene[38]	−47.0		71.2	14.6
Type 5: Small-Ring Aza- and Diazacarbenes[c]				
67 diazirene-3-ylidene	−33.1	−32.3[22]	56.5	14.0
68 diazirane-3-ylidene	−55.1	−67.0[22]	63.1	−10.8
69 1,3-diazetidin-2-ylidene	−63.0		79.4	7.2
70 azet-2-ylidene	−39.0		46.8	−1.9
71 azetidin-2-ylidene	−46.9		64.3	8.0

[a] A negative value for ΔE_{ST} indicates the singlet is more stable. Where there are several stable conformations, the most stable is used. Calculated values for ΔE_{ST} and ΔH_{ST} are extremely well correlated, with the former averaging 0.2 kcal/mol more positive: $\Delta E_{ST} = 1.00\Delta H_{ST} + 0.18$, $r^2 = 1.00$. [b] Literature values for ΔE_{ST} are found a number of sources. Most values listed here are computational and were obtained by a variety of methods. Experimental results (exp) are noted. Unless otherwise noted literature values, both experimental and computational, were taken from the recent compilations listed in refs 1c, 1e, 17, and especially 1f. [referring to the reference numbering of the original full article] [c] Where cis and trans isomers exist, the more stable of the two is used for the ΔH calculations. [d] Gilles, M. K.; Ervin, K. M.; Ho, J.; Lineberger, W. C. *J. Phys. Chem.* **1992**, *96*, 1130. [e] Schwartz, R.L.; Davicvo, G. E.; Ramond, T. M., Lineberger, W. C. *J. Phys. Chem. A* **1999**, *103*, 8213. [f] Wren, S. W.; Vogelhuber, K. M.; Ervin, K. M.; Lineberger, W. C. *Phys. Chem. Chem. Phys.* **2009**, *11*, 4745.

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