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A Theoretical Survey of Unsaturated or Multiply Bonded and Divalent Silicon Compounds. Comparison with Carbon Analogues

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Abstract: Multiply bonded Si molecules, H_2SiX (X = Be, BH, CH_2, SiH_2, NH, O), HSiY (Y = B, CH, SiH, N), and SiZ (Z = O, O_2), along with their carbon analogues, have been investigated by ab initio methods. All structural parameters were optimized by use of the 3-21G basis set and the higher 3-21G$^{(*)}$ basis set for silicon. In addition, the isomeric substituted silylenes which result from 1,2-hydrogen shifts were also considered. In many cases, the substituted silylene structures were energetically favored. The effect of all first-row substituents on the singlet-triplet energy separation of divalent silicon molecules was assessed and compared with the corresponding carbenes.

Though many molecules involving silicon singly bonded to first- and second-row elements are known,[2] multiply bonded silicon analogues of carbon compounds, until recently, were experimentally elusive. Transient $Si{=}C$ intermediates were first inferred in 1971.[3] Developments have culminated in the recent isolation of molecules containing both $Si{=}C$[4] and $Si{=}Si$ double bonds.[5] In addition, $Me_2Si{=}O$ was postulated from the pyrolysis of octamethylcyclotetrasilanone.[6] $H_2Si{=}O$ was inferred by product analysis to be a reactive intermediate,[7] both SiO and SiO_2 have a significant literature,[8] and SiN was reported to exist in the outer atmosphere.[9] Although these species are unstable, their existence increases interest in other presently unknown multiply bonded silicon molecules. In addition, the reactive nature of the known species makes it difficult to obtain quantitative data, e.g., energies and geometries, experimentally. It is now more practical to carry out systematic studies calculationally. To gain insight into the extent of double and triple bonds in compounds of silicon with elements of the first row, we have undertaken a theoretical investigation of an entire set of H_2SiX (X = Be, BH, CH_2, SiH_2, NH, O), HSiY (Y = B, CH, SiH, N), and SiZ (Z = O, O_2) molecules. Many of these species are presently unknown, but appear to offer good prospects for experimental realization.

In each case, the silicon molecules are compared with the analogous multiply bonded carbon compounds. In addition, the alternative isomers with divalent atoms are considered. While in carbon compounds the classical, tetravalent unsaturated structures (e.g., ethylene, $H_2C{=}CH_2$) are generally much more stable than the divalent isomers (e.g., methylcarbene, CH_3CH),[10] the situation in unsaturated silicon compounds is different.[11,12] The importance of 1,2-hydrogen shifted forms[11] is shown by recent predictions that methylsilylene, CH_3SiH, is similar in energy to silaethylene, $H_2C{=}SiH_2$.[12] The parent silylene, SiH_2, is presented in the companion paper.[2] We consider here the entire first-row set of substituted silylenes, HSiX (X = Li, BeH, BH_2, CH_3, NH_2, OH, F, as well as SiH_3), along with the corresponding carbenes, XCH. The effects of substituents on the triplet-singlet splittings are analyzed.

The companion study dealt with the singlet states of saturated silicon and carbon molecules, SiH_3X and CH_3X.[2] However, in unsaturated systems the lowest energy states may be either triplets or singlets. Hence, we examine here low-lying minima on the potential energy surface of both singlet and triplet states. Since our purpose is to compare the structural differences of unsaturated silicon and carbon molecules, only equilibrium structures will be discussed. The energy barriers either to internal rotation or to 1,2-hydrogen shifts in the silicon molecules are not considered here, the barriers to 1,2-hydrogen shifts for many of the carbon species have already been examined at a higher level of theory.[13]

Computational Methods

All molecular geometries were fully optimized with both the 3-21G[14] and 3-21G$^{(*)}$[15] basis sets. The latter includes a set of six Gaussian *d*-functions on the silicon. Singlet spin states were calculated by using closed-shell spin-restricted Hartree-Fock theory (RHF),[16] while states

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Table I. HF/3-21G, HF/3-21G*, and MP4SDTQ/6-31G* Energies for All Silicon Compounds (in Hartrees)

molecule	sym	state	HF/3-21G	ZPE	HF/3-21G*	MP4SDTQ/6-31G*	RE[a]
HSiLi	C_s	$^3A''$	−295.343 59	4.1	−295.403 14	−296.972 08	0.0
HSiLi	C_s	$^1A'$	−295.306 52	3.9	−295.367 86	−296.956 32	9.7
HSiBeH	C_s (**3**)[b]	$^3A''$	−303.051 57	9.4	−303.115 08	−304.764 17	0.0
HSiBeH	C_s (**3**)	$^1A'$	−303.025 54	9.0	−303.093 35	−304.749 15	9.0
H_2SiBe	C_{2v}	$^3B_1$	−303.026 03	9.6	−303.100 37	−304.734 13	19.0
H_2SiBe	C_s (**4**)	$^1A'$	−302.981 55	9.1	−303.058 33	−304.729 80	21.2
$HSiBH_2$	C_s (**8**)	$^1A'$	−313.590 31	16.7	−313.663 34	−315.424 30	0.0
$HSiBH_2$	C_s (**9**)	$^3A''$	−313.598 10	17.1	−313.668 23	−315.411 80	8.8
H_2SiBH	C_{2v}	$^1A_1$	−313.560 74	16.9	−313.642 58	−315.404 55	12.8
H_3SiB	C_{3v}	$^1A_1$	−313.515 14	15.7	−313.607 71	−315.355 56	42.0
HBSi	$C_{\infty v}$	$^3\Sigma^-$	−312.425 27	7.1	−312.492 79	−314.271 35	0.0
HBSi	$C_{\infty v}$	$^1\Delta$	−312.382 37	7.3	−312.447 02	−314.188 99	51.7
HSiB	C_s	$^1A'$	−312.284 08	4.2	(*c*)	(*c*)	
HSiB	C_s	$^3A''$	−312.358 73	4.6	−312.436 07	−314.154 58	70.5
H_2CSiH_2	C_{2v}	$^1A_1$	−327.301 67	26.8	−327.392 11	−329.286 39	0.0
H_3CSiH	C_s	$^1A'$	−327.325 46	28.2	−327.398 61	−329.285 08	2.2
H_3CSiH	C_s	$^3A''$	−327.315 46	28.7	−327.387 15	−329.254 20	22.0
H_2CSiH_2	C_s (**10**)	$^3A''$	−327.288 37	25.0	−327.376 20	−329.229 69	33.7
H_3SiCH	C_s	$^3A''$	−327.270 95	22.8	−327.372 55	−329.207 74	45.2
H_3SiCH	C_1	^1A	−327.201 71	22.8	−327.302 19	−329.166 84	71.0
H_2SiSiH_2[d]	C_{2h}, D_{2h}	^1A_g	−577.038 61	20.3	−577.203 62	−580.279 10	0.0
H_3SiSiH	C_s (**14**)	$^1A'$	−577.038 72	19.8	−577.203 78	−580.268 24	6.2
H_3SiSiH	C_s (**14**)	$^3A''$	−577.044 78	20.4	−577.209 06	−580.252 91	16.5
H_2SiSiH_2	C_2 (**13**)	^3B	−577.035 85	19.7	−577.201 36	−580.246 78	19.6
H_2CSi	C_{2v}	$^1A_1$	−326.143 18	15.1	−326.213 17	−328.089 39	0.0
H_2CSi	C_{2v}	$^3A_2$	−326.127 97	14.7	−326.192 72	−328.031 96	35.6
HCSiH	C_s[e]	$^3A''$	−326.081 04	11.5	−326.159 99	−327.985 91	61.1
H_2CSi	C_{2v}	$^3B_2$	−326.098 11	15.6	−326.159 75	−327.987 29	64.5
HCSiH	C_s[f]	$^3A'$	−326.057 98	12.1	−326.138 54	−327.965 79	74.3
$Si(H_2)Si$	C_{2v} (**16**)	$^1A_1$	−575.848 27	8.4	−576.012 90	−579.082 54	0.0
HSiSiH	C_2 (**15**)	^1A	−575.848 98	8.1	(*g*)	(*g*)	
H_2SiSi	C_{2v}	$^1A_1$	−575.864 19	9.6	−576.009 87	−579.069 83	9.1
H_2SiSi	C_s	$^3A''$	−575.875 77	9.4	−576.021 86	−579.053 27	19.3
$HSiNH_2$	C_s	$^1A'$	−343.281 59	22.5	−343.360 95	−345.357 15	0.0
H_2SiNH	C_{2v}[h]	$^1A_1$	−343.211 21	19.9[i]	−343.320 30	−345.320 07	20.6
$HSiNH_2$	C_s (**19**)	$^3A''$	−343.238 96	21.8	−343.318 93	−345.291 56	40.3
H_2SiNH	C_s (**20**)	$^3A''$	−343.198 79	17.9	−343.296 69	−345.259 61	56.4
H_3SiN	C_{3v}	$^3A_1$	−343.218 10	16.9	−343.319 97	−345.257 98	56.4
H_2SiNH	C_s (**21**)	$^3A''$	−343.198 79	17.7	−343.392 78	−345.254 61	99.9
HNSi	$C_{\infty v}$	$^1\Sigma^+$	−342.109 70	9.6	−342.194 55	−344.189 31	0.0
HSiN	$C_{\infty v}$	$^1\Sigma^+$	−341.963 32	5.8	−342.050 15	−344.095 27	55.0
HNSi	C_s	$^3A'$	−342.038 63	7.2	−342.108 97	−344.051 91	83.5
HSiN	C_s	$^3A'$	−341.962 06	5.2	−342.037 88	−343.951 26	144.5
H_2SiO	C_{2v}	$^1A_1$	−362.955 89	12.3	−363.076 58	−365.204 11	0.0
HSiOH	C_s[e]	$^1A'$	−362.997 68	13.6	−363.084 07	−365.198 83	4.6
HSiOH	C_s[f]	$^1A'$	−362.997 41	13.3	−363.084 68	−365.197 63	5.1
HSiOH	C_1 (**24**)	^3A	−362.957 72	13.2	−363.044 94	−365.137 36	42.6
H_2SiO	C_s	$^3A''$	−362.936 66	10.9	−363.044 23	−365.091 05	69.3
SiO	$C_{\infty v}$	$^1\Sigma^+$	−361.845 86	1.1	−361.942 12	−364.065 73	0.0
SiO	$C_{\infty v}$	$^3\Sigma^+$	−361.786 14	1.2	−361.859 67	−363.907 75	98.9
SiO	$C_{\infty v}$	$^3\Pi$	−361.738 34	1.2	−361.15 88	−363.890 63	109.6
OSiO	$C_{\infty v}$	$^1\Sigma^+$	−436.228 15	3.8	−436.373 84	−439.096 19	0.0
$Si(O_2)$	C_{2v}	$^1A_1$	−436.212 00	3.8	−436.313 60	−439.013 68	51.5
SiOO	$C_{\infty v}$	$^1\Sigma^+$	−436.148 56	2.8	−436.241 93	−438.911 72	114.4
HSiF	C_s	$^1A'$	−386.881 66	5.6	−386.975 64	−389.196 69	0.0
HSiF	C_s	$^3A''$	−386.843 56	5.7	−386.937 39	−389.136 63	37.8

[a] The relative energy (in kcal mol) is determined by differencing the MP4SDTQ/6-31G* energies and then adding in the differences in the ZPE (obtained from a FREQ/3-12G//HF/3-21G calculation) of the structures. [b] The numbers in parentheses refer to figure numbers in the text. [c] Using the 3-21G$^{(*)}$ basis, this structure went to $^1\Delta$ HBSi. [d] At HF/3-21G, the equilibrium structure was trans-nonplanar (**11**) while at HF/3-21G$^{(*)}$ it was planar (**12**). [e] Trans-planar geometry. [f] Cis-planar geometry. [g] At HF/3-21G$^{(*)}$, this went to $Si(H_2)Si$ structure **16**. [h] At HF/3-21G, this structure was C_s planar. [i] This is the FREQ/3-21G$^{(*)}$//HF/3-21G$^{(*)}$ value.

of higher multiplicity used the Pople–Nesbet spin-unrestricted theory (UHF).[17] Population analyses were based on the Mulliken method.[18] To verify if a minimum or a saddle point on the potential surface has been reached, the 3-21G force constant matrix was constructed; only equilibrium structures (with no negative eigenvalues) are considered here. Extensive comparisons with experiment[19] have shown that corresponding harmonic frequencies are generally 11–12% too large. To include *d*-type polarization functions on first- (as well as second-) row atoms and to determine the relative energy of each species with electron correlation included, full fourth-order Møller–Plesset calculations[20] were performed with the 6-31G* basis set.[21] For silicon molecules, these calculations are denoted MP4SDTQ/6-31G*//HF/3-21G$^{(*)}$, where '//' means 'at the geometry of'. For the carbon analogues, the corresponding calculations are MP4SDTQ/6-31G*//HF/3-21G. The GAUSSIAN 82 program was employed.[22]

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Table II. HF/3-21G and MP4SDTQ/6-31G* Energies for All Carbon Compounds (in Hartrees)

molecule	sym	state	HF/3-21G	ZPE	MP4DTQ/6-31G*	RE[a]
HCLi	$C_{\infty v}$	$^3\Sigma^-$	−45.532 34	6.7	−45.897 19	0.0
HCLi	$C_{\infty v}$	$^1\Delta$	−45.458 00	7.2	−45.842 70	34.7
H_2CBe	C_{2v} (**1**)[b]	$^3B_1$	−53.282 63	14.8	−53.724 34	0.0
HCBeH	$C_{\infty v}$	$^3\Sigma^-$	−53.282 50	12.2	−53.716 01	2.6
H_2CBe	C_{2v} (**1**)	$^1A_1$	−53.199 86	15.0	−53.687 13	23.6
HCBeH	$C_{\infty v}$	$^1\Delta$	−53.204 85	12.8	−53.657 38	39.9
H_2CBH	C_{2v} (**5**)	$^1A_1$	−63.867 88	22.9	−64.446 48	0.0
H_3CB	C_{3v}	$^1A_1$	−63.832 81	23.8	−64.405 42	26.7
$HCBH_2$	C_{2v}	$^1A_1$	−63.811 04	20.7	−64.382 78	37.8
$HCBH_2$	C_s (**7**)	$^3A''$	−63.834 86	20.7	−64.375 83	42.1
H_2CBH	C_s (**6**)	$^3A''$	−63.829 04	22.2	−64.375 13	44.1
HCB	$C_{\infty v}$	$^3\Pi$	−62.605 32	9.5	−63.128 40	0.0
HBC	$C_{\infty v}$	$^3\Sigma$	−62.590 81	7.3	−63.120 38	2.8
HBC	$C_{\infty v}$	$^3\Pi$	−62.598 25	8.1	−63.105 00	13.2
HCB	$C_{\infty v}$	$^3\Sigma^-$	−62.590 31	7.9	−63.103 30	14.1
HBC	$C_{\infty v}$	$^1\Delta$	−62.537 62	8.3	−63.084 35	26.4
HCB	$C_{\infty v}$	$^1\Delta$	−62.514 00	9.1	−63.046 59	50.8
H_2CCH_2	D_{2h}	^1A_g	−77.600 99	34.6	78.318 38	0.0
H_2CCH_2	D_{2d}	^3E	−77.531 60	30.0	−78.211 87	62.1
H_3CCH	C_s	$^3A''$	−77.533 70	31.9	−78.207 75	66.7
H_3CCH	C_1	^1A	−77.485 09	31.5	−78.190 82	77.4
H_2CCH_2	$C_s(D)$	^1A	−77.401 83	41.2	−78.129 65	125.0
HCCH	$D_{\infty h}$	$^1\Sigma_g^+$	−76.395 96	18.9	−77.091 09	0.0
H_2CC	C_{2v}	$^1A_1$	−76.334 50	16.6	−77.020 92	41.7
HCCH	C_{2v}	$^3B_2$	−76.289 25	16.4	−76.951 59	85.0
H_2CC	C_{2v}	$^3B_2$	−76.312 63	16.5	−76.941 85	91.3
HCCH	C_{2h}	^3B_u	−76.277 36	16.6	−76.936 98	94.4
H_2CNH	C_s(A)	$^1A'$	−93.494 78	26.9	−94.343 25	0.0
$HCNH_2$	C_s(A)	$^1A'$	−93.452 52	26.7	−94.279 40	39.9
H_3CN	C_{3v}	$^3A_1$	−93.483 73	25.1	−94.265 80	46.8
H_2CNH	C_s(**17**)	$^3A''$	−93.435 14	23.6	−94.234 34	65.0
$HCNH_2$	C_s	$^3A''$	−93.434 28	24.6	−94.225 55	71.6
H_3CN	C_s (**18**)	$^1A'$	−93.381 48	24.5	−94.194 28	91.1
HCN	$C_{\infty v}$	$^1\Sigma^+$	−92.354 08	11.5	−93.176 93	0.0
HNC	$C_{\infty v}$	$^1\Sigma^+$	−92.339 71	11.0	−93.149 43	16.8
HCN	C_s	$^3A'$	−92.214 51	8.0	−92.989 92	113.5
HNC	C_s	$^3A'$	−92.200 70	8.6	−92.962 44	131.7
CN	$C_{\infty v}$	$^2\Sigma^+$	−91.684 75	2.6	−92.458 77	0.0
CN	$C_{\infty v}$	$^2\Pi$	−91.651 38	2.7	−92.440 72	11.4
H_2CO	C_{2v}	$^1A_1$	−113.221 82	18.2	−114.190 69	0.0
HCOH	C_s[c]	$^1A'$	−113.146 29	17.4	−114.097 15	57.9
HCOH	C_s[d]	$^1A'$	−113.136 25	17.0	−114.088 94	62.7
H_2CO	C_s (**22**)	$^3A''$	−113.166 42	16.0	−114.068 87	74.2
HCOH	C_1 (**23**)	^3A	−113.143 72	16.1	−114.057 92	81.2
CO	$C_{\infty v}$	$^1\Sigma^+$	−112.093 30	3.3	−113.041 70	0.0
CO	$C_{\infty v}$	$^3\Sigma^+$	−119.911 50	1.6	−112.778 07	163.2
OCO	$C_{\infty v}$	$^1\Sigma^+$	−186.561 26	7.4	−188.128 06	0.0
COO	$C_{\infty v}$	$^1\Sigma^+$	−186.369 33	3.8	−187.846 36	172.6
HCF	C_s	$^1A'$	−137.002 06	8.2	−138.056 06	0.0
HCF	C_s	$^3A''$	−137.018 68	8.4	−138.035 88	12.9

[a] The relative energy (in kcal/mol) is determined by differencing the MP4SDTQ/6-31G* energies and then adding in the differences in the ZPE (obtained from a FREQ/3-21G//HF/3-21G calculation) of the structures. [b] The numbers in parentheses refer to figure numbers in the text. [c] Trans-planar structure. [d] Cis-planar structure.

Results

The Hartree–Fock (HF/3-21G and HF/3-21G$^{(*)}$) and the correlated (MP4SDTQ/6-31G*) energies for all of the silicon molecules are listed in Table I. Also included in this Table is the zero-point vibrational energy for each molecule. For each constitution, several equilibrium structures were determined; relative energies also are listed in this table. These are calculated by correcting the relative MP4SDTQ/6-31G*//HF/3-21G$^{(*)}$ energies for differences in the zero-point energies. For comparison, data for the analogous carbon compounds are listed in Table II. All optimized geometries are available in the Carnegie–Mellon Quantum Chemistry Archive.[23] Many of the structures were optimized originally with the minimum STO-3G basis set;[24] these results also are listed in the Archive.

Unless otherwise noted, only the 3-21G$^{(*)}$ geometrical parameters for the silicon molecules will be discussed. In most cases, only minor change in the bond lengths and angles results when *d*-functions are added to the basis set; exceptions will be mentioned. Since we wish to contrast carbon and silicon analgoues, a brief discussion of the low-lying equilibrium structures of the carbon molecules will precede a detailed comparison with the silicon species. Molecules containing divalent carbon and divalent silicon, and the geometries of CH_2 and SiH_2,[2] will also be compared.

HCLi and HSiLi. Lithium is not only more electropositive than hydrogen but has low-lying vacant p-orbitals, allowing for the delocalization of the nonbonding electrons on the carbon through π-bonding. Both σ and π effects result in linear equilibrium

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(23) R. A. Whiteside, M. J. Frisch, and J. A. Pople, Eds., Carnegie-Mellon Quantum Chemistry Archive, Third Edition, 1983, Carnegie-Mellon University.

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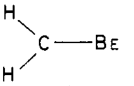
structures for HCLi, akin to the linear structure of LiOH[25] and the planar structure found for $LiNH_2$.[26] Triplet HCLi ($^3\Sigma^-$) is 34.7 kcal/mol lower in energy than the singlet ($^1\Delta$). Mulliken population analysis[18] shows that only 7.7% of the π-electron density resides on the lithium in the $^3\Sigma^-$ molecule, while 15.0% of the π-density is on the lithium in the $^1\Delta$ state. This increase in the π-character is consistent with the shorter C-Li bond in the singlet (1.875 Å) than the triplet (1.893 Å).

In contrast, both singlet and triplet equilibrium structures of HSiLi are bent (C_s symmetry). Unlike the situation in silylene (SiH_2), triplet ($^3A''$) HSiLi is lower in energy than the singlet ($^1A'$) by 9.7 kcal/mol. In the $^3A''$ state, the singly occupied molecular orbitals (SOMO) are the 8a′ and 2a″ orbitals. There is some π-delocalization in the 2a″ orbital onto the lithium (8.9%). The Si-Li separation, 2.406 Å, is smaller than that in H_3SiLi, 2.542 Å, optimized at the same level of theory.[2] The H-Si-Li angle is 140.5°, larger than the 118.0° angle in triplet silylene.

In singlet HSiLi, the nonbonding electrons lie in the plane of the molecule. The Si-Li bond length, 2.635 Å, is longer than that found in H_3SiLi. The H-Si-Li bond angle (94.4°) is only slightly larger than the 93.4° H-Si-H angle in singlet silylene.

H_2CBe and H_2SiBe. HF/3-21G optimization of H_2CBe yields planar equilibrium structures with C_{2v} symmetry, **1**. In agreement with earlier studies,[27-29] Table II shows that the $^3B_1$ form is 23.6 kcal/mol more stable than the $^1A_1$ structure. By use of the polarized 6-31G* basis, DeFrees[23] has shown that the singlet state reoptimizes to a nonplanar C_s structure, **2** (the H-C-H bisector-C-Be angle is 160.4°), though this may be due to mixing with the lower $^1B_1$ structure.[30] At MP4SDTQ/6-311G**//HF/6-31G*, corrected for differences in zero-point energies (HF/6-31G*), the $^1A_1$-$^3B_1$ separation is 16.5 kcal/mol.[30]



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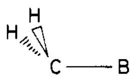
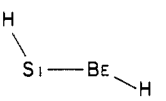


2

Equilibrium structures of HCBeH were found to be linear ($C_{\infty v}$ symmetry) at both the HF/3-21G and HF/6-31G*[30] levels of theory. The results summarized in Table II show the $^3\Sigma^-$ state to be more stable than the $^1\Delta$ by 37.3 kcal/mol; the value is 35.4 kcal/mol at MP4SDTQ/6-311G**.[30] At this higher level, the $^3\Sigma^-$ state of HCBeH is only 2.9 kcal/mol higher in energy than the $^3B_1$ state of H_2CBe, **1**; hence both forms might be experimentally observable.



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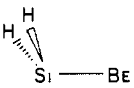


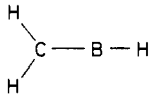
4

Our results, apparently the first on the silicon analogues, indicate definite differences between the bonding preferences of carbon and silicon with beryllium. Of the silicon compounds with composition H_2SiBe, the lowest, energy equilibrium structure is the $^3A''$ state of planar, bent HSiBeH, **3**. The Be-H bond is only 3.9° from linear with the Si-Be axis, but the H-Si-Be angle is 128.6°. The HOMO, the single occupied π-orbital, with 8.0% of the π-electron density residing on the beryllium, is 24.2 kcal/mol higher in energy than the orbital energy of the unpaired electron in the silicon atomic orbital. Singlet ($^1A'$) HSiBeH also has a planar, bent geometry, **3**, and is 9.0 kcal/mol above the triplet. The singlet HOMO is a lone pair on the silicon in the plane of the molecule. The lack of π-electrons causes an increase in the Si-Be bond distance from 2.128 Å in the triplet to 2.256 Å in the singlet. The Si-Be bond length in H_3SiBeH has an intermediate value of 2.204 Å,[2] which suggests a possible delocalization of the Si-H bonding electrons into the vacant p-orbitals on beryllium. Again the Si-Be-H bond angle in singlet HSiBeH is nearly linear (176.6°), but the H-Si-Be bond angle of 94.2° is close to the 93.4° angle found in singlet silylene.[2]

The $^3B_1$ state of H_2SiBe with C_{2v} symmetry, while corresponding to the lowest energy structure of the H_2CBe analogue, is found to lie 19.0 kcal/mol above triplet HSiBeH. The HOMO of H_2SiBe is the singly occupied π-orbital and is 8.4 kcal/mol higher in energy than the SOMO with the nonbonding electron on the beryllium. In the triplet H_2CBe, the π-electron SOMO is 44.9 kcal/mol more stable than the nonbonding SOMO. This difference in the orbital energies 8.4 vs. -44.9 kcal/mol is a good indication of the relative weakness of a silicon-beryllium π-bond. Only 13.0% of the π-electron density was located on beryllium in H_2SiBe, and the charge on this atom, +0.255, is decreased over the carbon species. The H-Si-Be bond angle (124.8°) is only slightly larger than the corresponding angle in H_2CBe (124.0°).

The $^1A_1$ (C_{2v}) state of H_2SiBe has one imaginary frequency and represents a transition structure. The minimum, a $^1A'$ (C_s) state with pyramidal geometry **4**, is found to lie 21.2 kcal/mol above the $^3A''$ state of HSiBeH, or only 3.2 kcal/mol above the $^3B_1$ H_2SiBe structure. The H-Si-Be and H-Si-H bond angles are 91.8° and 96.2°, respectively. The HOMO is a nonbonding orbital on silicon. The hydrogen atoms have a much larger negative charge (-0.111) than silicon (-0.053).

H_3CB and H_3SiB. The lowest energy structure of the H_3CB constitution is singlet ($^1A_1$) $H_2C{=}BH$, with C_{2v} symmetry, **5**. The C-B separation, 1.380 Å (longer than the STO-3G value of 1.339 Å),[31,32] is much shorter than the C-B single bond distance of 1.577 Å found in staggered H_3CBH_2 (both at 3-21G).[2] The π-HOMO of $H_2C{=}BH$ has 41% of the electron density residing on boron. The lowest energy triplet state of H_2CBH is formed by moving an electron from the π-orbital to the nonbonding orbital on the boron. The resulting planar triplet with C_s symmetry, **6**, lies 44.1 kcal/mol above the singlet. The shift of a bonding π-electron to boron (**5** → **6**) has several effects. The remaining π-electron is polarized more towards carbon; in **6** only 16% of the π-density is on boron. There is an increase of 0.148 Å in the C-B bond distance and a decrease in the positive charge on boron.



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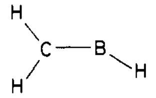
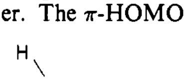


6

H_3CB, produced from the reaction of H_3CBBr_2 with either the liquid alloy NaK or the compound C_8K,[33] is found to be 26.7 kcal/mol above the singlet state of $H_2C{=}BH$, **5**, and has C_{3v} symmetry. The HOMO in H_3CB is the boron lone pair; the C-B bond length, 1.572 Å, is almost the same as the value (1.577 Å) found in H_3CBH_2.[2] Two $HCBH_2$ structures were located. The energy of the more stable form, the $^1A_1$, C_{2v} singlet, was 37.8 kcal/mol above the singlet $H_2C{=}BH$. The planar ($^3A''$) C_s triplet, **7**, lies 4.3 kcal/mol higher. The π-HOMO of singlet $HCBH_2$ has



7

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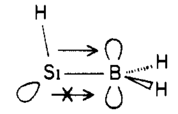
21.1% of the electron density residing on the boron. The triplet state, **7**, is formed by exciting an electron from the π-orbital to a nonbonding orbital on carbon: the H–C–B bond angle bends to 141.1°. Only 13.5% of the π-electron density is found to be on boron. There is also an increase in the C–B bond length from 1.410 Å in the singlet to 1.523 Å in the triplet.

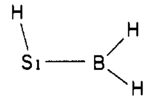
Four stable H_3SiB isomers were located; as with the H_2SiBe compounds, the lowest energy equilibrium structure has divalent silicon. This singlet $HSiBH_2$ molecule **8** has C_s symmetry ($^1A'$).



8

The H–B–H bisector–B–Si angle is 178.6°; the arrangement about boron is virtually planar. This molecule is very different from the corresponding carbon compound, **5**. Singlet $HCBH_2$ has C_{2v} symmetry and a π-HOMO; in **8**, the HOMO is a lone pair on the silicon. The H–Si–B bond angle is only 91.5°, which is 1.9° smaller than the H–Si–H angle in singlet silylene.[2] This possibly indicates that interaction between the Si–H bond and a vacant p-orbital on boron is more important than that involving the silicon lone pair.

The triplet ($^3A''$) state of $HSiBH_2$, **9**, has a planar geometry with C_s symmetry, is 8.8 kcal/mol above the singlet, and has a different ordering of the singly occupied orbitals than the carbon analogue, **7**. In **7**, the carbon-centered SOMO was 14.0 kcal/mol higher in energy than the π-SOMO, while in the silicon species (**9**) the π-SOMO is 25.8 kcal/mol higher in energy than the nonbonding silicon SOMO. The π-electron density in $HSiBH_2$ on boron (14.6%) helps explain the decrease in the Si–B bond length from 1.994 Å in the singlet (**8**) to 1.961 Å in the triplet (**9**). All other bond lengths also decrease on going from singlet to triplet. The H–Si–B bond angle in **9** is 123.1°, which is 18.0° smaller than the H–C–B angle in **7** and 5.1° larger than the bond angle in triplet silylene.[2] This increase in the bond angle compared to silylene is most probably due to steric interactions with the syn-hydrogen on the boron.



9

The singlet ($^1A_1$) C_{2v} structure of $H_2Si{=}BH$ is analogous to **5**, the most stable equilibrium structure of the H_3CB family, but is calculated to be 12.6 kcal/mol higher in energy than singlet $HSiBH_2$ (**8**). As with **5**, the HOMO is the π-orbital with 47.2% of the electron density on boron. This represents an increase in the density on the boron of 6.3% over the carbon species, as expected from electronegativity considerations. The Si–B bond distance in $H_2Si{=}BH$ (1.816 Å) is 0.178 Å shorter than in singlet $HSiBH_2$.

The $^1A_1$ (C_{3v}) state of H_3SiB corresponds to the second most stable structure in the carbon set but is found to be 42.0 kcal/mol above **8**. As with the carbon analogue, the HOMO is the boron lone pair. The Si–B bond length in H_3SiB (2.135 Å) is unusually long, e.g., 0.110 Å longer than the separation found in the lowest energy structure of H_3SiBH_2.[2] The H–Si–B bond angle (109.9°) is much closer to the tetrahedral value than the carbon analogue.

HCB and HSiB. The low-lying states of HCB and CBH, discussed separately,[34] were all found to have linear ($C_{\infty v}$) geometries. The lowest energy equilibrium HCB structure is the $^3\Pi$ state with three π-electrons. The results presented in Table II show that the $^1\Delta$ and $^3\Sigma^-$ states, both with two π-electrons, are higher in energy by 49.2 and 14.2 kcal/mol, respectively. MP4SDTQ/6-311G**//HF/6-31G* total energies, corrected for zero-point differences (HF/6-31G*), reduce the separation between the $^3\Pi$ and $^3\Sigma^-$ forms slightly, to 12.7 kcal/mol. The lowest energy CBH structure has only two π-electrons ($^3\Sigma^-$); the $^1\Delta$ and $^3\Pi$ structures lie 23.6 and 10.5 kcal/mol higher (Table II). At MP4SDTQ/6-311G**//HF/6-31G*, the separation between the triplet states of CBH is a bit less, 9.4 kcal/mol.[34] At this higher level of theory, the $^3\Pi$ state of HCB is only 3.9 kcal/mol lower in energy than $^3\Sigma^-$ CBH; the results in Table II show a slightly smaller separation (2.8 kcal/mol). The barrier to conversion of CBH into HCB is predicted to be 23.7 kcal/mol,[34] suggesting that both triplet species might exist independently.

The linear HBSi molecule with two unpaired π-electrons ($^3\Sigma^-$) is the global energy minimum. As with the carbon species, the orbital energy of the electron residing on the silicon is lower than for the π-electrons with the same spin. In CBH the energy splitting between these orbitals was 19.8 kcal/mol, while in HBSi the splitting increases to 33.4 kcal/mol. This reflects the relative stability of silicon nonbonding and π-orbitals. No other equilibrium structure was found to be within 50 kcal/mol of triplet HBSi. Pairing the π-electrons results in a linear ($^1\Delta$) HBSi molecule which is 51.7 kcal/mol above the triplet. As with the carbon analogues, similar Si–B bond lengths are found for the HBSi molecules with two π-electrons, 1.855 Å in the triplet and 1.875 Å in the singlet.

Attempts to find linear HSiB structures all resulted in species having one or more imaginary frequencies. An optimized bent structure (C_s) for the $^1A'$ state of HSiB was found with the 3-21G basis set and has an H–Si–B bond angle of only 82.9°. Even though a frequency calculation at this geometry yielded no imaginary frequencies, addition of *d*-functions to the silicon atom (3-21G$^{(*)}$ basis set) resulted in the hydrogen atom migrating, with no energy barrier, to the boron atom to form the $^1\Delta$ state of HBSi. A $^3A''$ state, also with C_s symmetry, of HSiB was found; it also had a very small H–Si–B bond angle of only 86.0°. This molecule is 70.5 kcal/mol higher in energy than the ground-state HBSi molecule. The HOMO is the lone π-electron, but it is only 3.3 kcal/mol higher in energy than the MO with the lone electron on silicon. Most (68.6%) of the π-electron density resides on the boron. The relatively long Si–B bond distance, 1.933 Å, is still smaller than for the lowest energy equilibrium structure of $HSiBH_2$.

C_2H_4, $CSiH_4$, and Si_2H_4. The ground state of ethylene has been extensively studied in the past.[10,14a,35–41] The optimized C–C bond distance of 1.315 Å agrees well with the HF/4-31G[37,38] and the HF/6-31G*[10,39] results but is 0.015 Å smaller than the experimental value of 1.330 Å.[42] Better agreement with experiment is obtained at the MP2/6-31G* level of theory.[39] The perpendicular triplet state (^3E) is calculated to be 62.1 kcal/mol higher in energy, in agreement with the results of Buenker and Peyerimhoff[40] and Köhler and Lischka.[41] As expected, this is slightly less than the experimental rotational barrier of singlet ethylene, 65 kcal/mol.[43] The loss of the π-bond results in an increase in the C–C bond distance of 0.159 Å, with virtually no change in the C–H bond lengths or H–C–C bond angles. This C–C "single" bond is still 0.068 Å shorter than the bond length found in ethane, optimized at the same level of theory.[2]

The lowest energy state of ethylidene, H_3CCH, has a staggered C_s conformation and is a triplet ($^3A''$). It is calculated to be 66.7 kcal/mol above the ethylene ground state. The C–C bond length,

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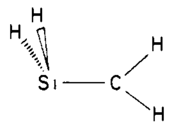
1.496 Å, is longer than in any of the H_2CCH_2 structures but is still shorter than the distance in ethane. A stable singlet state (^1A) was found for H_3CCH, 77.4 kcal/mol above the ground state. This singlet–triplet energy separation of 10.7 kcal/mol in H_3CCH is in good agreement with the CI results of Ha, Nguyen, and Vanquickenborne,[44] though larger than the CEPA results of Köhler and Lischka.[41] A recent theoretical study using a larger basis set[10] argues that this singlet structure does not really exist since there is no barrier for rearrangement into ethylene.

There has been recent interest, both theoretical[12,45-52] and experimental,[3,4,53-55] in the structure and relative energy of silaethylene and methylsilylene and the energy barrier of the 1,2-hydrogen shift in these and related molecules. In agreement with the earlier studies of Schaefer et al.[47-49] and Köhler and Lischka,[41] we calculate very little energy difference between these two molecules. Our results show silaethylene to be more stable by 2.2 kcal/mol, of which 1.4 kcal/mol comes from the difference in zero-point energy, while the previous work indicated methylsilylene to be more stable by 0.4[47,48] and 0.6 kcal/mol.[41] These results are in serious contrast to the recent experimental results of Pau, Pietro, and Hehre,[55a] who contend that 1-methylsilaethylene is 28 kcal/mol more stable than dimethylsilylene. It is unlikely that the replacement of a hydrogen by a methyl group could cause that much of a change in the energies of these compounds;[52d,55b] more study appears to be necessary.[49]

The silaethylene structure agrees well with other theoretical results.[41,45,46,48-52] The HOMO is the π-bond, where 42.1% of the electron density is found to reside on silicon. The atomic charges on the heavy atoms are quite large, −0.771 on carbon and +0.550 on silicon, but the dipole moment is relatively small (0.722 debye). This is due to the compensating charges of the hydrogens. Those bound to the carbon are positively charged (+0.216), while those bound to the silicon have a negative charge (−0.106).

A $^3A''$, C_s structure of silaethylene, 10, was found to be 33.7 kcal/mol higher in energy than the $^1A_1$ structure. In 10, the local geometry at carbon is planar but nonplanar at silicon. The nonbonding orbital on silicon is 38.1 kcal/mol less stable than the carbon atomic p-orbital, as expected from electronegativity considerations. The total electron density in the carbon p-orbital (0.954) demonstrates some interaction with the SiH_2 group. The Si–C bond distance, 1.859 Å, is larger than the double bond length in the ground state but still is shorter than in the other methylsilylene isomers.



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The methylsilylene structure given by Goddard, Yoshioka, and Schaefer[47] (using a double-ζ basis set) has Si-C and Si-H bond distances which are between the 3-21G and the 3-21G$^{(*)}$ optimized values. The HOMO is the lone pair on the silicon atom; this extra electron density causes a decrease in the Si charge to +0.494. As with the other singlet divalent silicon species, the H-Si-C bond angles is quite small (95.8°), only 2.4° larger than the angle in singlet silylene.[2]

The triplet state ($^3A''$) of methylsilylene is calculated to be 22.0 kcal/mol higher in energy than silaethylene. The methylsilylene singlet–triplet splitting of 19.8 kcal/mol agrees very well with a splitting of 18.7 ± 5 kcal/mol predicted earlier[47] and is slightly larger than the splitting of silylene (16.4 kcal/mol) at the same level of theory.[2] The H-Si-C bond angle (118.6°) is only 0.6° larger than the angle found in triplet silylene.[2] The increase in the bond angle between the singlet and triplet structures probably is also responsible for the decrease in the bond lengths to the silicon atom. In the singlet, the Si–C and Si–H bond distances are 1.907 and 1.511 Å, respectively, while in the triplet they are 1.899 and 1.474 Å.

Triplet silylmethylene, H_3SiCH, is calculated to be 45.2 kcal/mol above the lowest energy structure or 23.2 kcal/mol above the triplet state of methylsilylene. Goddard, Yoshioka, and Schaefer[47] calculated triplet methylsilylene to be 25.9 kcal/mol more stable than triplet silylmethylene, while Köhler and Lischka[41] found a difference of 21.3 kcal/mol. All these results agree quite well. The Si-C bond length in H_3SiCH (1.832 Å) is shorter than in the methylsilylene molecules. The highest SOMO is a carbon p-orbital perpendicular to the H–C–Si plane. The population of only 0.957 electrons in this carbon atomic orbital demonstrates some interaction with the Si–H bonds. The positive charge on the silicon atom attains its largest value (+0.743); each hydrogen bound to the silicon has an average charge of −0.137. The H-C-Si bond angle, 150.7°, is much larger than the HF/3-21G angle in triplet methylene (131.0°).[2]

The singlet state of silylmethylene was found to have C_1 symmetry and is 71.0 kcal/mol less stable than silaethylene or 25.8 kcal/mol above triplet H_3SiCH. This singlet–triplet separation is in good agreement with previous theoretical values (20.3[41] and 27.2[47] kcal/mol). The Si-C-H bond angle, 119.2°, is larger than the earlier results, and the Si-C separation, 1.882 Å, is slightly smaller.

There has been much recent theoretical interest in the structures and relative stability of disilene, H_2SiSiH_2, and of silylsilylene, H_3SiSiH.[56-62] We find the lowest energy structure to be the

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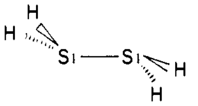
singlet state of disilene. At the 3-21G level of optimization, this structure has a C_{2h} trans, bent configuration, **11**, in accord with



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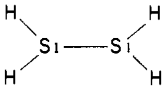
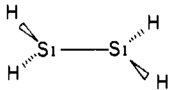


12

the 3-21G results of Poirier and Goddard[56] and the 4-31G results of Snyder and Wasserman.[57] When polarization functions are added to silicon (3-21G$^{(*)}$ basis), a planar equilibrium structure with D_{2h} symmetry, **12**, results instead. This was also found by Lischka and Köhler.[48] This structure has no imaginary frequencies, verifying that it is indeed a minimum at this level. However, recent results using the larger 6-31G* basis[62] favor **11**, though the energy difference between **11** and **12** is small.[63] The presence of a silicon–silicon π-bond results in a bond distance of 2.116 Å, which is 0.226 Å smaller than the bond length in disilane, both optimized at 3-21G$^{(*)}$.[2] Our calculated Si–Si bond length is in excellent agreement with the values of 2.140 and 2.160 Å found in substituted disilenes.[5]

In agreement with the results of Lischka and Köhler,[58] the triplet state (^{3}B) of disilene is found to have C_2 symmetry, **13**.



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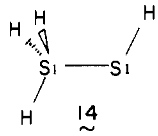

14

However, we find **13** to be 19.6 kcal/mol less stable than the singlet state. This is a significant change from the near degeneracy calculated at the Hartree-Fock level of theory[58] or the valence CI plus Davidson correction (CI + DC) value of 10.6 kcal/mol calculated by Poirer and Goddard.[56] With the loss of the π-bond, the Si–Si bond distance in the triplet increases to 2.325 Å, but this is still 0.017 Å shorter than the bond length in disilane.[2] The H–Si–H bisector makes an angle of 134.1° with the Si–Si bond axis. The partial positive charges on the silicon atoms increase to +0.182.

The ground state of silylsilylene, H_3SiSiH, is a singlet with a C_s staggered geometry, **14**. We find this $^1A'$ state to be 6.2 kcal/mol higher in energy than singlet H_2SiSiH_2. This can be compared with the CI + DC 3-21G result of 10.1 kcal/mol,[56] the Hartree–Fock value of 5.6 kcal/mol using a more extensive basis,[58] or the MP3/6-31G*//HF/6-31G* separation of 5.7 kcal/mol.[62] The silylene hydrogen angle with the Si–Si axis is only 92.0°, 1.4° smaller than the angle found in singlet silylene.[2] The Si–Si bond distance, 2.391 Å, is 0.049 Å longer than in disilane.

The $^3A''$ state of H_3SiSiH, also represented by **14**, is calculated to be 16.5 kcal/mol higher in energy than the ground-state disilene structure. The singlet–triplet energy separation of 10.3 kcal/mol for silylsilylene again is larger than has been reported earlier.[56,58] The hydrogen bound to the divalent silicon makes an angle of 121.6° with the Si–Si bond, which is 3.6° larger than the angle found in triplet silylene.[2] This increased bond angle may be related to the shorter Si–Si bond distance of 2.322 Å. There is also a definite change in the atomic charges when singlet and triplet silylsilylene are compared. The tetravalent silicon has a much larger positive charge in the triplet (+0.382) than in the singlet (+0.256). Conversely, the divalent silicon has a charge of +0.205 in the singlet and is virtually neutral in the triplet. In both molecules, all hydrogens are negatively charged, though the magnitudes are larger in the singlet than in the triplet.

C_2H_2, $CSiH_2$, and Si_2H_2. The linear singlet ground state of acetylene[64,65] has been previously examined at many levels of theory.[14a,37–39,66–68] The triplet prefers a cis geometry ($^3B_2$) with C_{2v} symmetry. This lies 85.0 kcal/mol above linear acetylene but is 9.4 kcal/mol more stable than the C_{2h} trans structure (^3B_u). The CI calculations of Wetmore and Schaefer[69] using a double-ζ basis set indicated the $^3B_2$ and ^3B_u states to be 80.5 and 96.4 kcal/mol, respectively, above the acetylene ground state. We find both cis and trans triplets to have C–C bond lengths of 1.318 Å, 0.130 Å longer than in the singlet state; Wetmore and Schaefer found the trans triplet to have a longer C–C bond than the cis.[69]

The most stable form of vinylidene, H_2CC, is the $^1A_1$ state with C_{2v} symmetry. The π-HOMO is 24.0 kcal/mol higher in energy than the lone-pair orbital on the divalent carbon. The calculated C–C bond length of 1.294 Å agrees well with the SCF results of Hopkinson, Yates, and Csizmadia[70] but is shorter than the correlated distance obtained by Dykstra and Schaefer.[71] As the level of the calculation increases, so does the energy difference between singlet vinylidene and the ground state of acetylene. Including zero-point energies, at the HF/4-31G//HF/STO-3G level[35,36] the separation is 33.5 kcal/mol and is 36.9 kcal/mol at the MP4SDQ/6-31G*//HF/6-31G* level.[66] The results presented here (MP4SDTQ/6-31G*//HF/3-21G) show that the separation increases to 41.7 kcal/mol and is finally 44.1 kcal/mol at the MP4SDTQ/6-311G**//MP2/6-31G* level of theory.[68] At this latter level, the 1,2-hydrogen rearrangement barrier to give acetylene is only 0.9 kcal/mol, and so this vinylidene structure may not be a minimum on the potential surface at the highest level of theory.[72]

The $^3B_2$ state of vinylidene results from the promotion of a lone-pair electron to the in-plane p-orbital. There is an increase in the C–C bond length of 0.052 Å on going from singlet (1.294 Å) to triplet (1.346 Å). There is also an increase in the H–C–C bond angles from 120.7° in the singlet to 121.4° in the triplet. The double-ζ SCF results of Conrad and Schaefer[73] agree, except for a slightly shorter C–C distance. The singlet–triplet separation in vinylidene is calculated to be 49.6 kcal/mol; the GVB-CI value is 46 kcal/mol.[74]

Several theoretical studies have recently examined the $SiCH_2$ molecule[75–79] in an attempt to characterize a silicon–carbon triple bond. First observed by Hopkinson and Lien,[76] and confirmed by later studies,[77–79] linear HSiCH is found to rearrange to methylenesilylene, H_2CSi, without any barrier at the Hartree–Fock level. Gordon and Pople[77] suggested that if electron correlation is included, an equilibrium trans structure of HSiCH can be found in a shallow potential minimum. Such a molecule has been recently found by Hoffmann, Yoshioka, and Schaefer[78] using a

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double-ζ basis with *d*-functions added to carbon and silicon and CI.

All previous studies[75-79] find the lowest energy structure to be the singlet ($^1A_1$) state of methylenesilylene, H_2CSi, with C_{2v} symmetry. The π-HOMO is 39.2 kcal/mol higher in energy than the lone-pair orbital on silicon. Less than half (42.5%) of the π-electron density resides on silicon; the charges are +0.390 on Si and -0.833 on C.

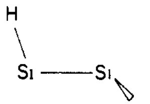
The lowest energy triplet state is also a planar (C_{2v}) structure of H_2CSi ($^3A_2$). This molecule results from promoting an electron from the π-orbital to the nonbonding silicon p-orbital in the plane of the molecule and is 35.6 kcal/mol above the singlet structure. Hopkinson, Lien, and Csizmadia[79] calculate the separation to be slightly smaller (30.3 kcal/mol), but their results suggest that increasing the level of the calculation will increase the separation. The loss of a π-electron lengthens the C-Si bond from 1.696 Å in the singlet to 1.867 Å in the triplet.

A second triplet state of H_2CSi with C_{2v} symmetry is formed by unpairing the nonbonding electrons on the silicon. This molecule is 28.9 kcal/mol less stable than the $^3A_2$ structure. This energy ordering is expected since the π-orbital is higher in energy than the nonbonding orbital in the singlet molecule. Since the $^3B_2$ structure still has two π-electrons, the C-Si separation (1.780 Å) is shorter than in the $^3A_2$ molecule. The π-electrons are almost equally shared between the two heavy atoms (49.8% on silicon). This results in the smallest silicon positive charge in this set (+0.198), although carbon still has a substantial (-0.647) charge.

Two triplet structures of HSiCH were located; *trans*-HSiCH ($^3A''$) is lowest in energy. This molecule, 61.1 kcal/mol less stable than singlet methylenesilylene, has a lone pair on the silicon atom, a single electron in a carbon hybrid orbital, and a single electron in a π-orbital with 86.9% of the electron density on carbon. This structure reflects the ground states of methylene, a triplet, and silylene a singlet. The H-C-Si angle, 143.8°, is 12.8° larger than the H-C-H angle in triplet methylene (HF/3-21G),[2] but the H-Si-C angle, 96.3°, is only 2.9° larger than the H-Si-H angle in singlet silylene at the same level of theory.

The $^3A'$ cis structure of HSiCH, 74.3 kcal/mol above singlet H_2CSi, can be regarded as the combination of triplet methylene and triplet silylene. The H-Si-C bond angle is 121.3°, which is 3.3° larger than the H-Si-H angle in triplet silylene.[2] There are two π-electrons with 47.0% of the density on silicon. This reduces the Si-C bond distance from 1.834 Å in the trans structure to 1.737 Å in the cis form (which only has one π-electron) and also reduces the charge on silicon from +0.470 to +0.342.

At HF/3-21G, the lowest energy H_2Si_2 singlet is the $^1A_1$, C_{2v} H_2SiSi structure. This agrees with the GVB pseudopotential results of Snyder, Wasserman, and Moskowitz.[80] The linear disilyne, HSiSiH, geometry gave two imaginary frequencies and the planar trans geometry one imaginary frequency. Two stable nonplanar singlet structures were located. The lower energy form (3-21G) was the ^1A state with C_2 symmetry, **15**; the less stable $^1A_1$ isomer, **16**, had two bridging hydrogens, which we denote by $Si(H_2)Si$. Addition of silicon *d*-function atoms (3-21G$^{(*)}$ basis) resulted in a complete reordering of the singlet energies. The disilyne species **15** disappeared on optimization, the H-Si-Si bond angle decreased until the $Si(H_2)Si$ structure, **16**, was reached. At HF/3-21G$^{(*)}$, **16** lies lower than the H_2SiSi C_{2v} structure. Further improvement of the basis set and electron correlation corrections caused this energy difference to increase; at MP4SDTQ/6-31G* the $Si(H_2)Si$ isomer is more stable than H_2SiSi by 9.1 kcal/mol. This is in agreement with the results of Morokuma and coworkers,[81] Binkley,[82] and others,[83] who all find **16** to be the lowest energy structure.



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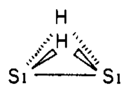


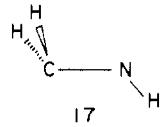
16

The HF/3-21G$^{(*)}$ Si-Si bond distance in **16**, 2.172 Å, is 0.057 Å longer than in the ground-state disilene but is still 0.170 Å shorter than the distance found in disilane.[2] The Si-H distances involving the bridging hydrogens, 1.668 Å, are quite long. The Si-H-Si and H-Si-H bond angles are 81.3° and 72.5°, respectively. The silicon charges are +0.166; the hydrogens have the same negative charge.

A singlet ($^1A_1$) C_{2v} structure of H_2SiSi is 9.1 kcal/mol above $Si(H_2)Si$. The π-HOMO is 47.7 kcal/mol higher in energy than the lone-pair orbital on the terminal silicon. Even with this π-bond, the Si-Si distance elongates to 2.175 Å, which is even longer (0.003 Å) than the separation found in **16**. The H-Si-Si bond angles are 123.5°. The charges on the central and terminal silicons are only +0.039 and +0.097, respectively.

The triplet ($^3A''$) state of H_2SiSi with nonplanar C_s symmetry is calculated to be only 19.3 kcal/mol above **16**. In contrast to the planar singlet, there is only one "π-electron", and this occupies a nonbonding orbital largely on the central silicon atom. The second SOMO is now an atomic p-orbital on the terminal silicon. This electron distribution results in an increase in the Si-Si bond distance to 2.280 Å. The H-Si-H bisector makes an angle of 163.3° with the Si-Si axis; this shows the degree of nonplanarity about the central silicon. The charge on the central silicon (+0.143) is now greater than that on the terminal silicon (+0.032).

H_3CN and H_3SiN. Six equilibrium H_3CN structures have been found; the planar (C_s) singlet H_2CNH molecule ($^1A'$) is lowest in energy. This is in agreement with experiment[84a] and previous calculations.[13,84b] The nitrogen lone-pair HOMO is 25.7 kcal/mol higher in energy than the π-orbital. Triplet H_2CNH, formed by promoting an electron from the π-orbital to the π*-orbital, no longer is planar.[85] The favored trans structure with C_s symmetry, **17** ($^3A''$), exhibits an increase in the C-N bond distance from 1.256 Å in the singlet to 1.427 Å. The bisector of the H-C-H angle makes an angle of 148.2° with the C-N bond (the tetrahedral value is 125.26°). The singlet-triplet energy separation for H_2CNH is calculated to be 65.0 kcal/mol. Demuynck, Fox, Yamaguchi, and Schaefer[85] obtained a splitting of about 64 kcal/mol using CI, while Pople and co-workers[13] calculated an MP4SDTQ/6-31G** plus zero-point correction separation of 65.2 kcal/mol.



17

The $^1A'$ (C_s) state of $HCNH_2$ is 39.9 kcal/mol above the lowest energy equilibrium structure. Like singlet H_2CNH, this molecule also is planar.[36] The HOMO is the lone pair on carbon; the π-orbital is next lower in energy. The C-N bond distance, 1.332 Å, is increased 0.065 Å over the separation in singlet H_2CNH. The $^3A''$, C_s structure of $HCNH_2$ is 31.9 kcal/mol higher than the singlet or 71.8 kcal/mol above $^1A'$ H_2CNH. Similar to **17**, this molecule has a nonplanar trans structure. Here the H-N-H bisector makes an angle of 159.3° with the N-C axis, showing a greater degree of planarity about the nitrogen.

Two stable nitrenes, H_3CN, were found. The more stable triplet ($^3A''$) has C_{3v} symmetry and nearly tetrahedral bond angles. It

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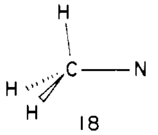
lies 46.8 kcal/mol above the lowest energy H_2CNH structure, in good agreement with previous results.[13,85] The singlet ($^1A'$) structure has C_s symmetry (**18**) and is 44.3 kcal/mol higher in energy than triplet H_3CN. The interaction between the vacant nitrogen p-orbital and the hydrogen in the C_s symmetry plane leads to a Jahn-Teller distortion of one of the H-C-N bond angles to only 98.5°, as opposed to a 115.5° value for the other hydrogens. This molecule is found to have no barrier to rearrangement to the lowest energy structure when correlation is included;[13] therefore, it does not exist.

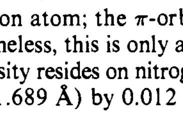


18

The two most stable structures of H_3SiN are similar to their carbon analogues, but the order is reversed. The planar C_s $HSiNH_2$ ($^1A'$) structure is the lowest in energy. The HOMO is the lone pair of the silicon atom; the π-orbital is 73.0 kcal/mol lower in energy. Nevertheless, this is only a partial π-bond, since 86.3% of the electron density resides on nitrogen. This still shortens the Si-N bond length (1.689 Å) by 0.012 Å relative to the separation in silylamine.[2] The H-Si-N bond angle, 95.9°, is 2.5° larger than the H-Si-H angle found in singlet silylene.[2] The nitrogen atom has almost a full negative charge (−0.926); the silicon charge is +0.453.

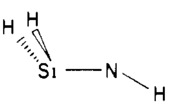
Planar H_2SiNH has C_s symmetry ($^1A'$) and is 20.2 kcal/mol less stable than singlet $HSiNH_2$. The π-MO again is lower in energy than the nonbonding MO, but the separation is only 5.6 kcal/mol. As expected from electronegativity arguments, 67.7% of the π-electron density resides on nitrogen. The π-bond, more fully developed than in $HSiNH_2$, results in a shorter Si-N bond length of 1.531 Å. At the 3-21G level, the Si-N-H bond angle is 132.8°. Addition of *d*-functions to silicon (3-21G$^{(*)}$ basis) increases this angle to 180° and the symmetry to C_{2v}. This molecule had no imaginary frequencies and is an equilibrium structure at this level. Since the optimized structures are so different, the zero-point energy listed in Table I is taken from the 3-21G$^{(*)}$ results. The charge on nitrogen is reduced to −0.772, while the silicon charge increases to +0.710.

The triplet ($^3A''$) state of $HSiNH_2$ is found to be 40.3 kcal/mol above the global minimum and has a nonplanar trans geometry, **19**. Since no π-bonding is present, the Si-N bond length is 1.710 Å, the same distance found in silylamine.[2] The H-Si-N bond angle is 120.7°, 2.7° larger than in triplet silylene.[2] The bisector of the H-N-H angle makes an angle of 177.9° with the Si-N axis. This almost planar arrangement about the nitrogen is very similar to the geometry for the ground state of silylamine at the same level of theory.[2] As expected, the SOMO's on silicon are higher in energy than the lone-pair orbital on nitrogen. There is little change in the atomic charges between the singlet and triplet states of $HSiNH_2$; the greatest difference is found in the hydrogen bound to silicon. This has a −0.200 charge in the singlet and −0.109 in the triplet.



19

The lowest energy triplet state of H_2SiNH ($^3A''$) has a nonplanar trans geometry (**20**) with C_s symmetry and is 36.2 kcal/mol less stable than singlet H_2SiNH. A second H_2SiNH $^3A''$ triplet has a nonplanar cis structure (C_s symmetry) **21** and is 43.5 kcal/mol less stable than **20**. In **20**, the Si-N bond length, 1.757 Å, is 0.047 Å longer than the separation in silylamine.[2] The SOMO on nitrogen is in an atomic p-orbital, and some donation to the SiH_2 group occurs since this orbital population is only 0.963 electrons. In **21**, the Si-N distance is 1.753 Å, very slightly less than in the trans structure. Again the p-orbital on the nitrogen contains only 0.956 electrons, showing some interaction with the SiH_2 group.



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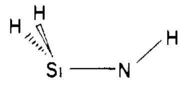

21

Similar to the triplet methylnitrene, the triplet ($^3A_1$) state of H_3SiN has C_{3v} symmetry. This molecule is 56.4 kcal/mol less stable than singlet $HSiNH_2$ thus making it energetically equivalent to triplet *trans*-H_2SiNH, **20**. In triplet H_3SiN there is a very long Si-N bond distance of 1.816 Å. This is analogous to the long C-N separation found in the carbon species, but the H-Si-N bond angles (108.8°) are slightly smaller. The atomic p-orbitals on the nitrogen atom contain only 0.962 electrons, suggesting some interaction with the SiH_3 group. As in the carbon analogue, the charge on the nitrogen atom (−0.345) is smaller than in the other species. The large positive charge on silicon (+0.736) is due to the higher electronegativity of the hydrogen atoms, which have a −0.130 charge.

HCN and HSiN. The energy separation between the $^1\Sigma^+$ states of linear ($C_{\infty v}$) HCN and HNC has been extensively studied, both experimentally[86-88] and theoretically.[89-92] Our 16.8 kcal/mol separation, although larger than the CI or Møller-Plesset[91,92] calculations, does seem to support the 14.8 ± 2 kcal/mol experimental value[88] more than the higher 17.2-26.3 kcal/mol[87] or lower 10.3 kcal/mol[86] experimental alternatives. The ground-state geometry of the HCN molecule has already been given at the HF/3-21G level[14a] and at many other levels of calculation.[14a,36,38,39,68] In all cases, uncorrelated optimizations yield bond distances which are smaller than are found experimentally.[93] The nitrogen lone-pair MO is found to have a lower energy than the π-MO's by 42.6 kcal/mol. The triplet state of HCN is formed through π–π* excitation. The resulting loss of π-bonding produces an equilibrium bent geometry (C_s) with an H-C-N angle of 123.5° and an increase in the C-N separation from 1.137 Å in the singlet to 1.303 Å in the triplet.

In singlet HNC, the lone pair on carbon has a higher energy than the π-MO by 26.9 kcal/mol. The N-C bond distance in HNC, 1.160 Å, is larger than the HF/6-31G* result[39] but still is 0.005 Å smaller than the experimental value.[94] The triplet is formed here by promoting an electron from the σ-lone pair on carbon to a π*-orbital, and a bent (C_s) equilibrium geometry is produced. The presence of nonbonding electrons on the nitrogen results in a H-N-C bond angle of 114.1°; the C-N bond length increases to 1.290 Å.

When carbon is replaced by silicon, the lowest energy structure is linear HNSi ($^1\Sigma^+$). The Si-N and N-H bond lengths (calculated to be 1.528 and 0.991 Å, respectively) are both shorter than the experimental values[95] but agree well with the SCF results of Preuss, Buenker, and Peyerimhoff.[96] In their study, optimization at the multiconfigurational CI level resulted in better agreement in the Si-N bond length with experiment. Unlike HNC, the lone-pair orbital on silicon in HNSi is 6.2 kcal/mol lower than the π-MO's. As expected from electronegativity arguments, 74.1% of the π-electron density resides on nitrogen. The silicon has a substantial positive charge (+0.401), as does the

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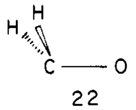
hydrogen (+0.352). Since these atoms are at opposite ends of a linear molecule, the dipole moment is calculated to be only 0.256 debye.

Triplet HNSi is found to be 83.5 kcal/mol higher in energy than the singlet and, as with triplet HNC, has a bent (C_s) geometry with a bond angle of 151.0°. This singlet–triplet energy splitting is 13.2 kcal/mol less than that found in the carbon analogues. The electronic distribution is also found to be different in the triplet states of HNC and of HNSi. In HNC, both unpaired electrons reside in carbon nonbonding orbitals following the n–π^* excitation from the singlet. On the other hand, triplet HNSi is derived from a π–π^* excitation. This results in an increase in the N–Si bond distance to 1.723 Å, a value 0.013 longer than the separation found in H_3SiNH_2.[2] The presence of three nonbonding electrons on the silicon also causes a decrease in its partial positive charge to +0.291.

The singlet ($^1\Sigma^+$) state of HSiN is also linear and is 55.0 kcal/mol higher in energy than singlet HNSi. This separation is less than previously reported values of 68[96] and 74.7[97] kcal/mol. The Si–N bond length is 1.536 Å, 0.008 Å longer than the separation found in the singlet state of HNSi, and is actually 0.005 Å longer than the Si–N distance in singlet H_2SiNH. The nonbonding orbital on nitrogen is 46.3 kcal/mol lower than the π-MO's. Comparison of this energy splitting to that in singlet HCN suggests that there is a destabilization of 3.7 kcal/mol for an electron in a Si–N π-bond relative to one in a C–N π-orbital. As expected, a greater percentage of the π-electron density resides on nitrogen in HSiN (57.1%) than in the corresponding carbon compound (52.6%). The silicon has a significantly large partial positive charge (+0.384), while the hydrogen bound to it has a slight negative charge (−0.023).

Triplet HSiN is also bent and is 89.5 kcal/mol less stable than the singlet. Once again, this splitting is smaller than that found in the HCN species; the electron distribution also is very different. At HF/3-21G, the $^3A'$ state of HSiN with the same valence electron distribution as the HCN analogue was found to rearrange, with no activation barrier, to the HNSi isomer. The stable structure of triplet HSiN is a molecule with unpaired π-electrons and can be thought of as resulting from a π–π^* excitation. The two unpaired electrons are localized on different heavy atoms; 49.3% of the total π-electron density resides on nitrogen. This equal population of π- and π^*-orbitals results in a long Si–N bond distance of 1.843 Å. The H–Si–N bond angle of 118.1° is virtually identical with the H–Si–H angle found in triplet silylene.[2]

H_2CO and H_2SiO. As is typical for the more common carbon compounds, the $^1A_1$ structure of formaldehyde, $H_2C{=}O$, has already been calculated with a variety of basis sets.[14a,36,38,39,98] The 3-21G C–O bond distance of 1.207 Å is only 0.004 Å longer than the experimental value of 1.203 Å.[97] The 3-21G H–C–O bond angle, 122.5°, is slightly larger than experiment, 121.75°.[98] The triplet ($^3A''$) state of formaldehyde is calculated to be 74.2 kcal/mol above the $^1A_1$ state and to have a nonplanar structure, **22**. This state is formed by transferring an electron from the p_π nonbonding orbital to the π^*-orbital. The loss in π-bonding results in an increase in the C–O bond distance to 1.384 Å (this is shorter than was previously calculated with the STO-3G[36] and 4-31G[99] basis sets).



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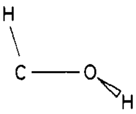
The singlet (C_s) trans structure of hydroxymethylene, HCOH, is calculated to be 57.9 kcal/mol above singlet formaldehyde. This can be compared to 54.7 kcal/mol obtained at MP4SDTQ/6-31G**//MP2/6-31G*[100a] and 53.1 kcal/mol at MP4SDTQ/6-311G**//MP2/6-31G*.[100b] The nonbonding orbital on carbon is higher in energy than the π-orbital, while that on oxygen has a lower orbital energy. This structure would be expected from the ground states of water and of methylene. The H–C–O bond angle, calculated to be 103.1°, is actually 1.6° smaller than in methylene. The (C_s) cis isomer of hydroxymethylene is found to be 4.8 kcal/mol less stable than the trans structure or 62.7 kcal/mol above singlet formaldehyde. In this cis form, both lone-pair orbitals are found to have a higher energy than the π-orbital. Comparing the trans to the cis isomer, one finds that the C–O bond distance is slightly shorter in the cis structure (1.330 vs. 1.335 Å), though both the H–C–O and C–O–H bond angles have increased due to the steric interaction. The H–C–O angle is now 107.6°, 2.9° larger than in singlet methylene.[2] Triplet hydroxymethylene, **23**, has C_1 symmetry with a torsional angle of 99.2°. It is 81.2 kcal/mol above the ground state of formaldehyde. The C–O bond length is 1.370 Å while the H–C–O and C–O–H angles are 124.7° and 113.5°, respectively.



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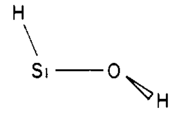

24

$H_2Si{=}O$ has been postulated to be a reactive intermediate[7] and has been considered theoretically by Jaquet, Kutzelnigg, and Staemmler (JKS).[98] The singlet ($^1A_1$) state of $H_2Si{=}O$, with C_{2v} symmetry, is the most stable isomer. The same energy ordering is found for the valence orbitals in this molecule as in formaldehyde. The HOMO is the oxygen lone-pair p-orbital in the plane of the molecule; the π-orbital is lower in energy. Still lower is the other lone pair on the oxygen located in an sp-hybrid orbital. The orbital density shows that 73.1% of the π-charge is located on oxygen, as opposed to only 61.0% in formaldehyde. The oxygen p-orbital in the molecular plane contains only 1.720 electrons, suggesting a definite interaction between the oxygen and the H_2Si group. The Si–O bond length is calculated to be 1.509 Å, nearly the same as JKS.[98] This is significantly shorter than the single bond distance (1.633 Å) found in the ground state of silanol.[2] The H–Si–O bond angle, 124.0°, is larger than the corresponding angle in formaldehyde but is close to that calculated by JKS.[98]

The bond dissociation energy, $H_2SiO \rightarrow H_2Si(^1A_1) + O(^3P)$, is unknown experimentally but was suggested by JKS to lie between values directly calculated (118 kcal/mol) and estimated from heats of hydrogenation (155 kcal/mol). Our directly calculated value, 132.1 kcal/mol, is probably somewhat too low.

The trans structure of hydroxysilylene, HSiOH, only 4.6 kcal/mol higher in energy than the singlet state of H_2SiO, is 0.5 kcal/mol more stable than the cis isomer. Since 89.4% of the π-electron density in both isomers resides on oxygen, the Si–O bond lengths (1.638 Å in the trans and 1.632 Å in the cis isomer) are comparable to the distance in silanol.[2] The trans structure has an H–Si–O bond angle of 97.1°, which is 3.7° larger than the angle in singlet silylene;[2] the cis isomer has a slightly larger H–Si–O angle (99.1°).

In contrast to the carbon analogues discussed above, the triplet state of HSiOH (**24**) is found to be more stable (by 26.7 kcal/mol) than triplet H_2SiO. However, **24** is 42.6 kcal/mol less stable than singlet H_2SiO. Like triplet hydroxymethylene, **24** has C_1 symmetry; the torsional angle is 91.0°. The H–Si–O angle, 118.5°, is very similar to the 118.0° angle found in triplet silylene, while the Si–O bond distance of 1.645 Å is actually 0.012 Å longer than the separation found in silanol.[2]

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Margrave's group[101] has recently reported that the reaction of silicon atoms with water in a solid argon matrix at 15 K produces HSiOH. The trans isomer, indicated to be more stable than the cis, has Si–O, Si–H, and O–H bond lengths of 1.591 ± 0.100, 1.521 ± 0.030, and 0.958 ± 0.005 Å, and H–Si–O and Si–O–H bond angles of 96.6 ± 4° and 114.5 ± 6°, respectively. The agreement with our calculations is not very good. Margrave's thermochemical estimates suggest that HSiOH is roughly 14 ± 15 kcal/mol less stable than H_2SiO; we obtain the same ordering.

The triplet ($^3A''$) state of H_2SiO is calculated to be 69.3 kcal/mol above the singlet, slightly less than the 74.2 kcal/mol singlet–triplet separation found in the carbon analogues. The Si–O bond distance is quite large (1.692 Å), though this increase is comparable to the increase found in comparing singlet and triplet formaldehyde.

CO and SiO. The ground $^1\Sigma^+$ state of carbon monoxide has already been studied with a wide range of basis sets at both the Hartree–Fock level of theory and including electron correlation.[14a,36,39,68,102,103] The HF/3-21G bond length of 1.129 Å[14a] agrees well with the experimental value of 1.128 Å.[104] The HOMO, the lone pair on carbon, lies 57.5 kcal/mol above the π-electron MO's. The $^3\Pi$ state is calculated to be 150.5 kcal/mol above the ground state, which is larger than the 139.2 kcal/mol separation found experimentally.[104] The calculated internuclear separation is 1.248 Å, longer than the experimental value of 1.206 Å, though in better agreement than the previously published STO-3G results of 1.306 Å.[36] A higher $^3\Sigma^+$ state is calculated to be 163.2 kcal/mol above the ground state, which agrees well with the experimental separation of 159.6 kcal/mol.[104] The calculated C–O bond distance (1.402 Å) again is longer than the experimental value of 1.352 Å.

Silicon monoxide, a molecule of astrophysical interest,[105] is similar to CO in having a $^1\Sigma^+$ ground state.[104] The Si–O bond distance, calculated to be 1.496 Å, is only slightly shorter than the experimental value of 1.510 Å[104] and agrees with a prior calculation.[105b] The HOMO is the lone pair on silicon, but the orbital energies show that it is only 23.5 kcal/mol less stable than the π-orbitals. This decrease in the orbital separation from CO results in the $^3\Sigma^+$ being more stable than the $^3\Pi$ state. The energy separation between the $^1\Sigma^+$ and the $^3\Sigma^+$ state is calculated here to be 98.9 kcal/mol. This compares well with a tentative experimental value of 96.2 kcal/mol[104] and is significantly larger than the 79.0 kcal/mol separation estimated by Robbe et al.[105a] from the results of CI calculations. The optimized internuclear separation of 1.714 Å agrees with the rough experimental estimate of 1.70 Å. The $^3\Pi$ state is 10.7 kcal/mol above the $^3\Sigma^+$ state or 109.6 kcal/mol above the ground state. This value is larger than the experimental value of 97.1 kcal/mol[104] and the CI value of 91.0 kcal/mol.[105a] The optimized Si–O bond length, 1.664 Å, is longer than the distance determined experimentally (1.562 Å). The higher singlet states, studied by Langhoff and Arnold,[105b] were not examined here.

The dissociation energy, $SiO(^1\Sigma^+) \rightarrow Si(^3P) + O(^3P)$, is found experimentally to be 190.6 kcal/mol.[104,105b] The MCSCF-CI result of Langhoff and Arnold, 188.0 kcal/mol, is in better agreement than our value, 175.9 kcal/mol, but our basis set is smaller.

CO_2 and SiO_2. The ground ($^1\Sigma_g^+$) state of carbon dioxide is calculated to have a C–O bond distance of 1.156 Å. This compares well with the experimental separation of 1.162 Å,[106] though slightly better agreement is found with the 4-31G basis (1.158 Å).[107] A stable $^1\Sigma^+$ state of a linear C–O–O isomer was also calculated, the energy is 172.6 kcal/mol above the ground state. The C–O bond distance is 1.132 Å, and the O–O separation is long, 1.929 Å.

Feller, Katriel, and Davidson[108] recently performed an MCSCF study with the same 3-21G basis set used here. They found a local minimum for a cyclic CO_2 molecule, though at this level the barrier to conversion to the ground state was only 0.5 kcal/mol. Performing an all single and double excitation CI and correcting the result for quadruple excitations, they found the barrier to increase to 9.04 kcal/mol. In searching for such a cyclic species at the HF/3-21G level, the only stationary point located had one imaginary frequency. Further studies[109] using the 6-31G* basis located this cyclic CO_2 molecule, but the MP4SDTQ/6-31G* barrier to conversion to the lowest energy linear structure was also found to be quite small.

The lowest energy form of molecular silicon dioxide is also a linear ($^1\Sigma_g^+$) O–Si–O structure. The optimized Si–O bond distance, 1.492 Å, is in good agreement with the 1.488-Å separation found by Pacansky and Hermann.[110] The charge on silicon is calculated here to be +1.090, which is smaller than the +1.4 charge found in the earlier study. A cyclic form of SiO_2 was found to lie 51.5 kcal/mol above the ground state. The optimized Si–O distance is 1.653 Å, and the O–Si–O bond angle is only 56.9°. This results in an O–O separation of 1.575 Å, which can be compared to a separation of 1.473 Å in hydrogen peroxide, optimized at the same level of theory.[23] The HOMO, a lone pair on silicon, is 16.7 kcal/mol higher in energy than the out-of-plane π-bond MO between the oxygen atoms. The charge on silicon is +0.802 in this cyclic form. The linear Si–O–O molecule is calculated to be 114.4 kcal/mol above the ground state; the Si–O bond distance, 1.500 Å, is only slightly longer than the separation in O–Si–O. The O–O distance, 1.655 Å, is long but not nearly as long as is found in the carbon analogue. The silicon charge is +0.720, that on the central oxygen is -0.497. The value for the terminal oxygen, which was found to possess virtually no charge in the carbon species, is -0.222.

The MP4SDTQ/6-31G* energy for the ground triplet state of the oxygen atom is -74.89597 hartree. By combining this with the results in Tables I and II, carbon dioxide is indicated to be bound with respect to the ground states of carbon monoxide and oxygen by 115.4 kcal/mol. The experimental value is 125.75 kcal/mol.[111] The linear C–O–O molecule is unbound by 57.8 kcal/mol with respect to the ground states of CO and O. Similarly, both the linear OSiO and the cyclic SiO_2 molecules are calculated to be bound with respect to silicon monoxide and oxygen by 81.7 and 29.9 kcal/mol, respectively. These values probably are underestimated at the level of theory used. As with the carbon analogue, the linear Si–O–O molecule is less stable than SiO and O by 33.1 kcal/mol. The fact that the cyclic form of SiO_2 is bound with respect to the dissociation products is encouraging, and since the MP4SDTQ/6-31G* barrier to conversion to linear OSiO is quite large,[109] isolation of this molecule might be possible.

HCF and HSiF. The lowest energy equilibrium structures of singlet and triplet HCF have bent (C_s) geometries, though in contrast to methylene, the singlet ($^1A'$) is 12.9 kcal/mol more stable than the triplet ($^3A''$). In the singlet, the H–C–F angle is 103.1°, while the triplet has a bond angle of 122.6°. These angles are smaller than those found in the singlet and triplet states of methylene by 1.6° and 8.4°, respectively.[2] In HSiF, the lowest energy singlet and triplet structures also have a bent geometry. As in silylene, the singlet ($^1A'$) is more stable than the triplet ($^3A''$), though the separation has increased to 37.8 kcal/mol. The H–Si–F angle, 98.3°, is 4.9° larger than the angle in singlet silylene,[2] while the angle in triplet HSiF, 116.0°, is smaller than in triplet SiH_2 by 2.0°.[2] A recent experimental estimate of the H–Si–F

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angle in a solid argon matrix is 100 ± 3°; the HSiF species being observed evidently is the singlet.[112a] Replacing a hydrogen by fluorine in either CH_2 or SiH_2 stabilizes the singlet relative to the triplet. In the carbon species, this stabilization is 29.7 kcal/mol, while in the silicon molecules it is 21.4 kcal/mol. Schaefer's group has reported a study comparing HSiF with H_2Si and F_2Si.[112b] Their DZ + P (CISD) results agree well with ours in all respects.

Discussion

Structural and Energetic Comparison. There are often considerable differences in the ordering of states and in the geometries of corresponding unsaturated carbon and silicon molecules. Only ethylene, formaldehyde, carbon monoxide, and carbon dioxide give similar ground-state structures when carbon is replaced by silicon. In the ground states of all other molecules, either the multiplicities and/or the geometries are different. The bond angles of the ground-state silicon molecules imply a certain s,p-hybridization scheme;[113] a pattern emerges which allows the differences between carbon and silicon to be understood. *Silicon prefers to have nonbonding electrons in atomic orbitals with a high percentage of s-character.* This major aspect of silicon chemistry has already been emphasized by Walsh and earlier workers.[114] Thus divalent silicon has relatively small bond angles. Singlet silylene, more stable than the triplet by 16.4 kcal/mol, has a bond angle of only 93.4°.[2] The silicon-to-hydrogen hybrid orbitals are calculated to have only 5.6% s-character; thus the lone pair is in a silicon hybrid orbital with 88.8% s-character. In singlet methylene, the bond angle of 104.7° results in the lone pair residing in an orbital with 59.6% s-character. In the triplet states, the bond angles are larger for both silylene and methylene.[2] In triplet silylene, the silicon-to-hydrogen hybrid orbitals have 31.9% s-character; 36.2% is used in the in-plane SOMO. In triplet methylene, only 20.8% s-character is available for the in-plane SOMO.

For the substituted divalent molecules, the ground triplet state of HSiBeH was found to be 9.0 kcal/mol lower in energy than the singlet, with the stability gained by forming a partial π-bond. The singlet state has an H–Si–Be bond angle of 94.2°, which leaves a large percentage of the s-orbital available for the nonbonding electrons. For the carbon analogues, no structure was determined where nonbonding valence electrons were found on carbon; all were used in bond formation. $HSiBH_2$ is a ground-state singlet; formation of a partial π-bond was not able to stabilize the triplet as much. The H–Si–B bond angle was again very small (91.5°) in the singlet, with virtually all of the s-orbital used for the lone pair. Again in the carbon molecules, the singlet state of $HCBH_2$ was found to be 37.8 kcal/mol above the lowest energy structure, and the HOMO, rather than being a lone pair on carbon, is a π-bond.

The ground state of the molecules with the composition HSiB was the $^3\Sigma^-$ state of HBSi with each π-orbital containing a single electron. This again allowed the silicon atom to have a lone pair of electrons in an orbital with a large percentage of s-character. Silaethylene is found to be virtually degenerate with singlet methylsilylene, where the H–Si–C bond angle also was small (95.8°). The $^1A'$ state of H_3SiSiH is 10.3 kcal/mol more stable than the $^3A''$ structure and is only 6.2 kcal/mol higher than the Si_2H_4 ground state, disilylene.

The $^1A_1$ state of H_2CSi, 61.1 kcal/mol more stable than the $^3A''$ state of silaethyne, again is characterized by a lone pair of electrons on silicon. The H–Si–C angle in the triplet state was only 95.8°, as opposed to 118.0° in the triplet silylene, implying that more of the s-orbital is used for the SOMO on the silicon atom. The unusual structure for the ground state of the H_2Si_2 molecule, **16**, allows nonbonding electrons to reside on each silicon atom. Conversely, in H_2C_2, carbon uses the available valence electrons to form π-bonds, yielding the classical acetylene structure. The $^1A_1$ state of H_2SiSi has a pair of nonbonding electrons on the terminal silicon and is only 6.2 kcal/mol above $Si(H_2)Si$. No other stable structures were located on the singlet potential energy surface.

Table III. Stabilization Energies (kcal/mol) for Singlet and Triplet Silylenes XSiH and Carbenes XCH

	silylenes		carbenes	
substituent, X	singlet[a]	triplet[b]	singlet[c]	triplet[d]
H	0.0	0.0	0.0	0.0
Li	−1.2	25.2	9.2	27.0
BeH	−1.8	23.7	−1.6	18.5
BH_2	7.8	16.1	36.8	15.6
CH_3	0.7	−2.7	12.0	5.4
NH_2	22.3	−1.6	61.5	13.0
OH	15.0	−6.7	51.2	11.0
F	9.3	−12.0	35.0	5.5

[a] Equation 1. [b] Equation 2. [c] Equation 3. [d] Equation 4.

The planar $^1A'$ ground state of $HSiNH_2$, with nonbonding electrons on silicon and a small H–Si–N bond angle (95.9°), is 20.2 kcal/mol more stable than the $^1A'$ state of H_2SiNH, which has nonbonding electrons on nitrogen. Conversely, the $^1A'$ state of $HCNH_2$ is 39.9 kcal/mol higher than the H_2CNH isomer. Another example is provided by the $^1\Sigma^+$ ground states of HAB systems. HCN is found to be 16.8 kcal/mol more stable than HNC, whereas HNSi, with a lone pair on silicon, is 55.0 kcal/mol more stable than HSiN with a lone pair on nitrogen. The $^2\Pi$ state of SiN has a lone pair of electrons on silicon and is 31.7 kcal/mol more stable than the $^2\Sigma^+$ state, which only has a single nonbonding electron on silicon.[23] Conversely, the $^2\Sigma^+$ state of CN is calculated to be 11.4 kcal/mol more stable than the $^2\Pi$ state.[23]

The $^1A'$ state of *trans*-hydroxysilylene and the $^1A_1$ state of H_2SiO are virtually degenerate, whereas *trans*-hydroxymethylene is 57.9 kcal/mol less stable than formaldehyde. Finally, the presence of a pair of nonbonding electrons on silicon could be a factor favoring the cyclic form of SiO_2 relative to the cyclic CO_2 analogue.

While the energy of an electron in a silicon molecule is decreased when it is delocalized, as in forming a π-bond, the energy also is decreased when the electron is in a silicon atomic orbital with a high percentage of s-character. These two effects stabilize different structural types; for this reason the energy separation between different silicon containing isomers is generally much less than between the related carbon analogues.

Substituted Silylenes and Methylenes. The chemistry of the divalent silylenes, the silicon analogues of carbenes, is of much current interest,[55,115,116] but most investigations have been confined to alkyl, aryl, or halogen substituents.[117] With the exception of matrix isolation studies of HSiOH[101] and HSiF,[112a] very little is known experimentally about other silylenes. Most of the theoretical calculations have also concentrated on H_2Si, CH_3SiH, and $(CH_3)_2Si$.[49,118] In contrast, the isovalent substituted carbenes

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(117) Our results for the carbenes are generally in good agreement with previous calculations at similar levels of theory.[116]

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have been examined previously in much greater detail.[116] Our results, summarized in Tables I and II, allow a systematic comparison of a series of substituted silylenes with the corresponding carbenes for the first time.

The effect of substituents, X, on the stabilities of the singlet and triplet silylenes can be evaluated by the isodesmic bond separation equations, (1) and (2). The results are compared in Table III with the stabilization energies for the corresponding carbenes (eq 3 and 4). While most of the substituents stabilize

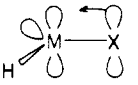
$$\text{XSiH (singlet)} + SiH_4 \rightarrow H_3SiX + H_2Si \text{ (singlet)} \quad (1)$$

$$\text{XSiH (triplet)} + SiH_4 \rightarrow H_3SiX + H_2Si \text{ (triplet)} \quad (2)$$

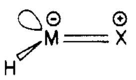
$$\text{XCH (singlet)} + CH_4 \rightarrow H_3CX + H_2C \text{ (singlet)} \quad (3)$$

$$\text{XCH (triplet)} + CH_4 \rightarrow H_3CX + H_2C \text{ (triplet)} \quad (4)$$

the singlet state of the silylenes, Li and BeH are slightly destabilizing and methyl has little effect (0.7 kcal/mol). The influence of BH_2 is moderate (7.8 kcal/mol), but the most effective stabilization is achieved with π-donors and decreases along the series NH_2 (22.3 kcal/mol) > OH (15.0 kcal/mol) > F (9.3 kcal/mol) with the π-donating ability. The importance of the resonance form M=Si (**25b**) for these substituents is indicated by the significant charge that is transferred into the 3p-orbital of the silylene (the populations are: NH_2 (0.215), OH (0.143), and F (0.094)) and by the shortening of the silylene Si–X bond relative to the saturated silyl structure[2] (e.g., the Si–N bond length in $HSiNH_2$ is 1.531 Å compared with 1.710 Å in H_3SiNH_2 at $3\text{-}21G^{(*)}$).

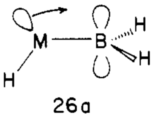


25a

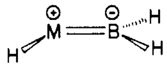


25b

The singlet carbenes behave similarly,[117] but the stabilization energies are usually much greater than for the corresponding silylenes (Table III).[118] For example, the largest stabilizing effects (for an amino group) are 61.5 kcal/mol in the carbene and 22.3 kcal/mol in the silylene. The reduction in substituent effects in the silylenes results mainly from the lower tendency of silicon to form π-bonds. This is attributable to the higher energy of the 3p (Si) acceptor orbital in silylene compared to the 2p (C) orbital in carbene and also to the longer Si–X bonds relative to C–X bonds. Both factors reduce the interaction with the lone pair on X and thus the stabilization. A similarly reduced substituent effect was found in comparing silicenium ions (R_3Si^+) with carbenium ions (R_3C^+).[119] The lower tendency of silicon to form π-bonds also contributes to the lower stabilization of singlet silylenes compared with carbenes by π-acceptor substituents. For example, BH_2 stabilizes singlet methylene significantly (36.8 kcal/mol) due to contributions from the resonance structure M=B (**26b**). This contribution is not nearly as important for the BH_2 substituted silylene, and the stabilization is much smaller (7.8 kcal/mol).



26a



26b

The substituent effects in the triplet silylenes are very different from those in the singlets. The triplet stabilization energies correlate roughly with the electronegativity of X and increase as the electronegativity of the substituent decreases. Li, BeH, and BH_2 are highly stabilizing while OH and F substitutions destabilize the triplet state significantly. Three-electron π-interactions between the lone pair on X and the one electron in the 3p (Si) orbital of the silylene appear to be unimportant. Even NH_2, the most potent π-donor, is slightly destabilizing. On the other hand, all substituents stabilize the triplet carbenes. The three-electron, 2p (C)–2p (X), π-conjugation (**25b**, M=C) is effective, although σ-donors (e.g., Li and BeH) are more stabilizing than π-donors. In conclusion, π-conjugation is more important in the triplet carbenes, but substituent electronegativities dominate with the triplet silylenes.

Table IV. Relative Energies (RE) of the Lowest Lying Singlet and Triplet States of Divalent Silicon Molecules, HSiX, Along with the Si–X Bond Length and H–Si–X Bond Angle

molecule	sym	state	Si–X[a]	H–Si–X[b]	RE[c]
HSiH	C_{2v}	$^1A_1$	1.506	93.4	0.0
	C_{2v}	$^3B_1$	1.471	118.0	16.4
HSiLi	C_s	$^1A'$	2.635	94.4	9.7
	C_s	$^3A''$	2.406	140.5	0.0
HSiBeH	C_s	$^1A'$	2.257	94.2	9.4
	C_s	$^3A''$	2.128	128.6	0.0
$HSiBH_2$	C_s	$^1A'$	1.994	91.5	0.0
	C_s	$^3A''$	1.961	123.1	8.8
$HSiCH_3$	C_s	$^1A'$	1.907	95.8	0.0
	C_s	$^3A''$	1.899	118.6	19.8
$HSiNH_2$	C_s	$^1A'$	1.698	95.9	0.0
	C_s	$^3A''$	1.710	120.7	40.3
HSiOH	C_s	$^1A'$	1.638	97.1	0.0
	C_1	^3A	1.645	118.5	38.0
HSiF	C_s	$^1A'$	1.596	98.3	0.0
	C_s	$^3A''$	1.602	116.0	37.8

[a] Bond lengths are in angstroms. [b] Bond angles are in degrees. [c] Taken from Table I and ref 2; in kcal/mol.

Silicon tends to have nonbonding electrons in atomic orbitals with high s-character. Electropositive substituents transfer charge from the Si–X bonding orbital with much p-character to the partially populated s-type orbital on silicon. With electronegative substituents the effect is reversed; charge is transfered from the s-type orbital on silicon to the Si–X bond. In the singlet silylenes, the s-type orbital on silicon is doubly occupied, and charge donation by electropositive substituents is less favorable.

In the carbenes, the C–X bonding and the carbon lone-pair orbitals both have sp^2-character, and electron transfer from one orbital to the other is not as important. Note, however, that the overall stabilization of triplet silylene and triplet carbene by Li, BeH, and BH_2 groups is similar. The lower σ-inductive stabilization in the carbene series is compensated by additional stabilization due to π-conjugation (as in **25b**, M=C), involving one electron.

Singlet–Triplet (S–T) Energy Differences. Singlet H_2Si is calculated to be more stable than the triplet $^3B_1$ state by 16.4 kcal/mol at MP4/6-31G*.[2] This result is in agreement with other calculations,[112c,118] but somewhat higher than an upper bound of 14 kcal/mol reported by Lineberger and co-workers.[120] For CH_2, the $^3B_1$ triplet is calculated to be 16.8 kcal/mol lower than the $^1A_1$ singlet at MP4/6-31G*.[2] This S–T separation is overestimated, recent experimental results place it at about 9 kcal/mol,[121] and our best theoretical estimate is 8.2 kcal/mol.[2]

However, as we are concerned primarily with the effect of substituents on the S–T separation, this deficiency at MP4/6-31G* is not expected to alter the conclusions. The reason for the reversed spin preference in CH_2 and SiH_2 and a detailed discussion of their structures are presented elsewhere.[2] Table IV lists the calculated energy differences between the lowest energy singlet and triplet silylenes, along with the Si–X bond lengths and the H–Si–X bond angles. Similar data for the carbon analogues are given in Table V. The S–T energy differences in Tables IV and V are determined by the S–T gaps in the parent divalent molecules and by the effects (discussed above) of the various substituents on the stabilities of the two states (Table III).

In the silylene series there is a continual increase in the stabilization of the singlet relative to the triplet as the electronegativity

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Table V. Relative Energies of the Lowest Lying Singlet and Triplet States of Divalent Carbon Molecules, HCX, Along with the C–X Bond Length and H–C–X Bond Angle

molecule	sym	state	C–X[a]	H–C–X[b]	RE[c]
HCH	C_{2v}	$^1A_1$	1.102	104.7	16.8
	C_{2v}	$^3B_1$	1.071	131.0	0.0
HCLi	$C_{\infty v}$	$^1\Delta$	1.875	180.0	34.7
	$C_{\infty v}$	$^3\Sigma^-$	1.893	180.0	0.0
HCBeH	$C_{\infty v}$	$^1\Delta$	1.631	180.0	37.3
	$C_{\infty v}$	$^3\Sigma^-$	1.642	180.0	0.0
$HCBH_2$	C_{2v}	$^1A_1$	1.401	180.0	0.0
	C_s	$^3A'$	1.523	141.1	4.3
$HCCH_3$	C_1	^1A	1.508	107.4	10.7
	C_s	$^3A''$	1.495	130.9	0.0
$HCNH_2$	C_s	$^1A'$	1.322	107.4	0.0
	C_s	$^3A''$	1.385	126.8	31.7
HCOH	C_s	$^1A'$	1.335	103.1	0.0
	C_1	^3A	1.370	124.7	23.3
HCF	C_s	$^1A'$	1.339	103.1	0.0
	C_s	$^3A''$	1.349	122.6	12.9

[a] Bond lengths are in angstroms. [b] Bond angles are in degrees. [c] Taken from Table I and ref 2; in kcal/mol.

Table VI. Comparison of Carbon and Silicon Multiple Bond Energies, Reactions 5 and 6

reaction	ΔH_{rxn}[a]
$H_2CBH(^1A_1) + SiH_2 \rightarrow H_2SiBH(^1A_1) + CH_2$	67.0
$H_2CCH_2(^1A_g) + SiH_2 \rightarrow H_2SiCH_2(^1A_1) + CH_2$	59.6
$H_2CSiH_2(^1A_1) + SiH_2 \rightarrow H_2SiSiH_2(^1A_g) + CH_2$	45.5
$H_2CNH(^1A') + SiH_2 \rightarrow H_2SiNH(^1A_1) + CH_2$	53.9
$H_2CO(^1A_1) + SiH_2 \rightarrow H_2SiO(^1A_1) + CH_2$	33.1
$HCN(^1\Sigma^+) + SiH \rightarrow HSiN(^1\Sigma^+) + CH$	133.1
$HCCH(^1\Sigma_g{}^+) + SiH \rightarrow HSiCH + CH$	130.5[b]

[a] Heats of reaction are in kcal/mol and are calculated from the MP4SDTQ/6-31G* energies, corrected for zero-point energy differences, taken from Tables I and II and ref 2. [b] For this reaction, HSiCH is assumed linear, and since this is not a stable structure, no zero-point corrections were used.

of the atom bound to silicon increases. This result is in agreement with the qualitative predictions made previously by Harrison et al.[116b] The S–T separation is largest in $HSiNH_2$ and decreases slightly in HSiOH and HSiF. Electropositive substituents, on the other hand, stabilize the triplet silylene more effectively than the singlet. For example, the S–T gap in H_2BSiH is smaller than in H_2Si. HSiLi and HSiBeH are predicted to have triplet ground states.[116e] A similar pattern is found for the carbenes (Table V) and agrees with previous conclusions.[116] The triplet is the ground state for HCLi, HCBeH, and $HCCH_3$, but $HCNH_2$, HCOH, and HCF prefer singlet ground states. The $HCBH_2$ singlet state is found to be slightly more stable than the triplet. Both electrons on carbon in the singlet are stabilized by delocalization into the vacant p-orbital on boron; in the triplet, only one electron resides in a similar π-orbital.[116c] Finally, due to the effective stabilization of the singlet CH_2 by π-donors, the decrease in the S–T separation along the series $HCNH_2$, HCOH, and HCF is greater than in the corresponding silicon analogues.

Comparison of Carbon and Silicon Multiple Bond Energies. Prior experimental experience and theoretical investigations have shown that multiple bonds involving silicon are considerably weaker than corresponding carbon linkages. Some quantitative estimates are available, but these have been evaluated somewhat differently.[114] A simple procedure is to compare carbon and silicon multiple bonds directly by means of eq 5 and 6. Equation 5 is the formal replacement of a CH_2 group by SiH_2 in a double bond system. The values in Table VI have been determined by using the energy of triplet CH_2 ($^3B_1$); at the level of theory employed, this form is 16.8 kcal/mol lower in energy than the $^1A_1$ structure. The overestimation from the experimental difference introduces only a small error. The data in Table VI reveal all C=X double bonds to be more stable than their Si=X counterparts. However, the energy differences decrease with the increasing electronegativity of X, reaching their smallest value at X=O. The C=C double bond is 105.1 kcal/mol more stable than the Si=Si linkage.

$$H_2C{=}XH_n + SiH_2(^1A_1) \rightarrow H_2Si{=}XH_n + CH_2(^3B_1) \tag{5}$$

$$HC{-}XH_n + SiH(^2\Pi) \rightarrow HSi{-}XH_n + CH(^2\Pi) \tag{6}$$

Because other states and geometries are favored, the only straightforward triple bond comparison (eq 6) is with nitrogen (X=N). The C–N triple bond is 133.1 kcal/mol more stable than its Si–N analogue. Although linear HSiCH is not a minimum, its energy can be used to evaluate the energy of eq 6 vs. acetylene. On this basis, the Si≡C triple bond is also about 130 kcal/mol less stable than the C≡C triple bond.

Basis Set Comparison. In saturated silyl molecules, the addition of *d*-functions to the second-row atoms resulted in only slight decreases in the bond lengths and atomic charges.[2] For unsaturated molecules, the inclusion of *d*-functions caused greater changes in the bond lengths, and in four cases different structures resulted. In HSiB, a stable (no imaginary frequencies) $^1A'$ state with a very small bond angle (82.4°) was obtained with the 3-21G basis set. When *d*-functions were added to silicon (3-21G$^{(*)}$ basis) and the calculation resumed, this state converted to the $^1\Delta$ state of HBSi. This suggests that the $^1A'$ state is an artifact of the smaller basis and does not exist. In the H_2SiSiH_2 ground state, the 3-21G optimized structure was nonplanar (C_{2h}). With the 3-21G$^{(*)}$ basis, a planar (D_{2h}) structure was obtained. H_2Si_2 at HF/3-21G had a twisted HSiSiH ^1A ground state; the $Si(H_2)Si$ isomer with the hydrogens bridging the silicon atoms was calculated to be 0.4 kcal/mol higher in energy, neglecting zero-point corrections. With *d*-functions, the HSiSiH form collapsed to $Si(H_2)Si$ with no activation barrier. At 3-21G, singlet H_2SiNH preferred a planar C_s structure with a Si–N–H bond angle of 132.8°; the 3-21G$^{(*)}$ basis gave a C_{2v} structure with a linear arrangement about the nitrogen.

In all silicon first-row saturated molecules,[2] the addition of *d*-functions to the silicon resulted in a decrease in the silicon–heavy-atom bond length. If the first-row atom was either Be, B, C, N, or O, this decrease was between 0.014 and 0.010 Å, with the amount of decrease becoming generally larger on moving from beryllium to oxygen. The $^3A''$ states of HSiBeH and H_2SiBe are exceptional, the addition of *d*-functions to silicon increased the Si–Be bond lengths. In all other cases, a decrease in the bond distance was observed, and this generally is greater in magnitude than that for the saturated molecules.[2] Particularly large decreases are found for the $^1A'$ state of H_2SiNH (0.080 Å), the $^2\Pi$ states of SiN (0.090 and 0.077 Å for the states with three and five π-electrons, respectively), the $^3A''$ state of H_2SiO (0.078 Å), and for many of the molecules containing two silicon atoms. In the few cases where experimental structures are available, the HF/3-21G$^{(*)}$ optimized geometries are in better agreement than are the HF/3-21G results.

Conclusion. The structural differences in saturated silyl and methyl compounds are minimal.[2] At the same ab initio level there are often large differences between unsaturated carbon and silicon molecules, both in the ground-state geometries and in the energy separations between various states. The ground state of most of the silicon species has one or more nonbonding electrons on silicon. For the carbon species, forms with π-bonds are favored over those possessing nonbonding electrons.

The energetic separation between various stable species is smaller for most of the silicon molecules than for the carbon analogues. H_2SiO is a notable example. Two other stable structures are within 5.1 kcal/mol of the ground state. Such small energy separations preclude the definite assignment of the ground state; further studies are needed for several of the systems studied.

The singlet state of silylene is stabilized by both π-donors and σ-donors. However, π-donors are less effective in stabilizing silylene than singlet carbene. Triplet silylenes are stabilized by electropositive substituents and destabilized by electronegative groups, including π-donors such as hydroxyl. SiH_2 is a ground-state singlet, and the S–T gap is 16.4 kcal/mol at MP4/6-31G*. The S–T energy separation in HSiX increases as the electronegativity of X increases. The S–T gap reaches a maximum separation in $HSiNH_2$ (40.3 kcal/mol). HSiLi and HSiBeH, on the other hand, are calculated to have triplet ground states.

The effect of *d*-functions on silicon is much greater for the unsaturated than for the saturated silicon molecules.[2] In general, much greater decreases in the silicon bond distances are found in the unsaturated molecules when *d*-functions are added.

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Enantiocontrolled Cycloaddition Approach to (+)-Brefeldin A

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Abstract: The concept of a cycloaddition to form five-membered rings allows a retrosynthetic analysis of the antifungal, antiviral, and antitumor agent (+)-brefeldin A that resolves the problem of relative and absolute stereochemistry. The acetonide of D-glyceraldehyde which provides C-4 of the target transmits its stereochemistry ultimately to C-5, -7, and -9 via a Pd-catalyzed cycloaddition as the key step to form the five-membered ring unit. The last chiral center at C-15 is established by using a microbiological reduction of 1-phenylsulfonyl-5-hexanone with a relatively unknown microorganism *C. guillermonde*. Julia olefination attaches the derived hexanol unit which constitutes the lower side chain to the cyclopentyl unit. Alkylative elimination using the dianion of phenylthioacetic acid introduces the acrylate unit and completes the synthesis of the optically pure natural product.

While the Diels–Alder reaction enjoys unparallel prominence in the formation of six-membered rings for the synthesis of complex natural products, cycloaddition strategy for forming five-membered ring carbocyclic natural products is virtually unknown. The opportunities for selectivity embodied in such a strategy based upon a Pd-catalyzed cycloaddition[1] are revealed in analyzing an approach to (+)-brefeldin A (**1**), a significant target because of its antifungal, antimitotic, antiviral, and antitumor activities.[2,3] This 16-membered macrolide antibiotic, also known as cyanein,[4] decumbin,[5] and ascotoxin, bears a structural resemblance to the prostaglandins. Studies on the biosynthesis of **1**, however, strongly suggest that cyclopentanol formation in **1** does not parallel prostaglandin biosynthesis.[7]

The synthesis[8] of racemic brefeldin A was first reported by Corey and Wollenberg[9] and subsequently by others.[8] Natural (+)-brefeldin A has been prepared by a rather long route from D-mannitol and D-glutamic acid[10] and also more efficiently from an optically active Diels-Alder adduct.[11] Studies directed toward a possibly biomimetic synthesis have also been recently reported.[12]

Previous syntheses of **1** (with one exception[18]) have relied on one of two methods for obtaining the cyclopentanol ring with the correct stereochemistry: one uses *trans* cyclopentanone-3,4-dicarboxylic acid as the starting material; the other uses conjugate addition of an organometallic reagent to a 4-substituted cyclopentenone, giving 3,4-trans substituents.

The approach to (+)-brefeldin A described herein is unique in that the absolute configuration at carbons 4, 5, and 9 (brefeldin numbering) is controlled by the method by which the cyclopentyl ring is constructed.

Scheme I outlines a retrosynthetic analysis. As in almost all previous syntheses,[8] the seco acid **2** was envisioned as the immediate precursor. The concept of alkylative elimination (eq 1)[13,14] allows dissection of the upper side chain between C(2) and C(3) of **3** and requires a leaving group at *pro*-C-3 as exemplified by the epoxide in **4**. Obviously, any vicinal oxygen substitution such as in **5** is easily convertible into an epoxide. At this point, attention turned to the lower side chain which nicely draws upon the Julia olefination[15] which has been shown to be capable of generating (*E*)-olefins with excellent geometrical control.[16] The availability of the requisite *β*-hydroxy sulfone **6** via the *β*-keto sulfone **7** suggested acylation of a sulfone-stabilizing anion with the ester

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