of BaP and 6-CH_3-BaP as reported above are seen to parallel the behavior of anthracene. The observed cation radical from BaP is found to be the 6-CF_3CO_2-BaP cation radical formed most probably by the following sequence of steps (eq 2). The appearance of a single major product in the HPLC separation of the reaction products,[4] due to the 6-(trifluoroacetoxy)benzo[*a*]pyrene, is further proof of the identity of the observed cation radical. A similar reaction pathway has been previously proposed[18] for the reaction of BaP with manganic acetate in acetic acid in which the major product is 6-acetoxybenzo[*a*]pyrene.

$$\mathrm{BaP} \xrightarrow{-1e^-} \mathrm{BaP}^{+\cdot} \xrightarrow[-e^-]{CF_3CO_2^-} 6\text{-}CF_3CO_2\text{-BaP} \xrightarrow{-1e^-} 6\text{-}CF_3CO_2\text{-BaP}^{+\cdot} \quad (2)$$

6-CH_3-BaP is much less reactive in TTFA/TFA; the substitution of the methyl group in the position of highest electron density considerably retards the substitution reactions, the one-electron oxidation product of 6-CH_3-BaP being relatively stable for several hours at reduced temperatures. Reaction is not, however, completely elminated; the 6-CH_3-$BaP^{+\cdot}$ EPR spectrum decays appreciably at room temperature, and a variety of reaction products consistent with both methyl and ring substitution by trifluoroacetoxy groups are found.[4] These results again parallel the behavior seen by 6-CH_3-BaP in manganic acetate–acetic acid mixtures.[18]

Reactions in H_2SO_4. The reactions of 6-CH_3-BaP and 6-F-BaP observed in H_2SO_4 may be of some significance to proposed metabolic pathways for these compounds. Cavalieri[2] has proposed that cation radicals can be generated from polycyclic hydrocarbons by one-electron oxidation with a Fe(V) form of cytochrome P-450. That such a reaction could occur is evidenced by the one-electron oxidation of methylarenes with tris(phenanthroline)iron(III) complexes in TFA.[19] It was further proposed that the cation radicals would then react with nucleophiles, including DNA, at the positions of highest charge density. The metabolic formation of quinones[2,20] from 6-F-BaP is hypothesized to proceed via a cation radical intermediate which is then attacked by a nucleophilic oxygen atom. Adducts of 6-F-BaP to DNA in model systems have also been identified which are consistent with the reaction at the 6-position of BaP. Circumstantial evidence for the intermediacy of cation radicals in the metabolism of 6-CH_3-BaP comes from the identification of adducts in a variety of systems in which the BaP-6-CH_2 group is bound to the 2-amino group of guanine,[21] and the formation of 6-CH_2OH-BaP as a major product of metabolism.[22]

Our studies seem to have demonstrated rather directly that the formation of a cation radicals from 6-CH_3-BaP and 6-F-BaP could lead to the observed reaction products. In H_2SO_4, the first produced one-electron oxidation products appear to react with residual water to give 6-CH_2OH-$BaP^{+\cdot}$ and 6-OH-$BaP^{+\cdot}$, the former yielding 6-CH_2OH-BaP on workup and the latter autoxidizing on workup to give the three benzo[*a*]pyrenequinones (1,6-, 3,6-, and 6,12-).

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A Theoretical Survey of Singly Bonded Silicon Compounds. Comparison of the Structures and Bond Energies of Silyl and Methyl Derivatives

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Abstract: The silicon hydrides, SiH_n (n = 1–4), and the entire set of H_3SiX (X = Li, BeH, BH_2, CH_3, NH_2, OH, F and Na, MgH, AlH_2, SiH_3, PH_2, SH, Cl) molecules have been investigated by using ab initio methods. All structural parameters were optimized by use of the 3-21G and 3-21G$^{(*)}$ basis sets. The silyl derivatives are compared with the corresponding methyl compounds. In most cases, the equilibrium geometries of the methyl and silyl molecules are similar. The most notable exception is in silylamine, where a planar geometry is found about the nitrogen. Addition of *d*-functions to the second-row atoms results in a decrease in the bond lengths. The relative H_3Si–X and H_3C–X bond energies depend principally on the electronegativity of the group X. Since SiH_3 has a higher electron affinity and a lower ionization potential than CH_3, groups which are very electronegative or very electropositive have stronger bonds to silicon than carbon.

Silicon, although a contiguous group 4 (group 14 in the more recent notation) element,[171] often frustrates chemists in their search for analogues of carbon compounds.[2,3] Difficulties in studying many silicon singly bonded species are often attributed to the

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Table I. HF/3-21G Energy, Zero-Point Energy, ZPE, HF/3-21G$^{(*)}$ and MP4/6-31G* Total Energies, and Relative Energy, RE, for All Silicon Compounds[a]

molecule	sym	state	HF/3-21G	ZPE[b]	HF/3-21G$^{(*)}$	MP4SDTQ/6-31G*	RE[c]
SiH	$C_{\infty v}$	$^2\Pi$	−287.907 21	2.9 [0]	−287.971 42	−289.482 24	0.0
SiH	$C_{\infty v}$	$^4\Sigma^-$	−287.878 56	3.2 [0]	−287.938 14	−289.428 23	34.1
SiH_2	C_{2v}	$^1A_1$	−288.484 29	7.5 [0]	−288.560 28	−290.089 96	0.0
SiH_2	C_{2v}	$^3B_1$	−288.480 90	7.9 [0]	−288.553 63	−290.064 34	16.4
SiH_2	$D_{\infty v}$	$^3\Sigma_u^-$	−288.445 74	6.7 [2]	−288.508 32	−290.023 95	40.5
SiH_2	$D_{\infty v}$	$^1\Delta_u$	−288.374 36	8.1 [1]	−288.436 06	−289.970 92	75.1
SiH_3	C_{3v}	$^2A_1$	−289.080 54	13.8 [0]	−289.166 16	−290.695 72	0.0
SiH_3	D_{3h}	$^2A_2''$	−289.072 49	12.8 [1]	−289.153 99	−290.687 06	4.4
SiH_4	T_d	$^1A_1$	−289.686 98	20.2 [0]	−289.784 26	−291.331 26	
H_3SiLi	C_{3v}	$^1A_1$	−296.509 92	15.1 [0]	−296.590 96	−298.196 80	
H_3SiBeH	C_{3v}	$^1A_1$	−304.231 69	20.7 [0]	−304.318 44	−305.991 75	
H_3SiBH_2	C_s, **1**[d]	$^1A'$	−314.783 31	28.5 [0]	−314.876 68	−316.651 68	0.0
H_3SiBH_2	C_s, **3**[d]	$^1A'$	−314.783 29	28.4 [1]	−314.876 65	−316.651 69	−0.1
H_3SiCH_3	C_{3v}, **4**[d]	$^1A_1$	−328.526 12	40.5 [0]	−328.622 74	−330.524 62	0.0
H_3SiCH_3	C_{3v}, **5**[d]	$^1A_1$	−328.524 32	40.5 []]	−328.620 47	−330.522 22	1.5
H_3SiNH_2	C_s, **3**[d]	$^1A'$	−344.450 39	33.3 [0]	−344.555 48	−346.559 84	0.0
H_3SiNH_2	C_s, **1**[d]	$^1A'$	−344.450 35	33.2 [1]	−344.555 48	−346.559 93	−0.2
H_3SiOH	C_s, **6**[d]	$^1A'$	−364.180 60	25.2 [0]	−364.293 37	−366.414 42	0.0
H_3SiOH	C_s, **7**[d]	$^1A'$	−364.179 80	24.8 [1]	−364.292 64	−366.413 08	0.4
H_3SiF	C_{3v}	$^1A_1$	−388.074 06	18.1 [0]	−388.193 34	−390.422 77	
H_3SiNa	C_{3v}	$^1A_1$	−449.968 32	14.6 [0]	−450.051 28	−452.587 07	
H_3SiMgH	C_{3v}	$^1A_1$	−488.152 40	18.7 [0]	−488.259 54	−490.947 98	
H_3SiAlH_2	C_s, **3**[d]	$^1A'$	−530.845 48	24.0 [0]	−530.990 88	−533.866 63	0.0
H_3SiAlH_2	C_s, **1**[d]	$^1A'$	−530.845 48	24.0 [1]	−530.990 88	−533.866 63	0.0
H_3SiSiH_3	D_{3d}	$^1A_{1g}$	−578.241 21	31.9 [0]	−578.427 52	−581.508 28	0.0
H_3SiSiH_3	D_{3h}	$^1A_1'$	−578.239 93	31.8 [1]	−578.426 09	−581.506 63	0.9
H_3SiPH_2	C_s, **1**[d]	$^1A'$	−629.265 70	27.5 [0]	−629.465 45	−632.760 15	0.0
H_3SiPH_2	C_s, **2**[d]	$^1A'$	−629.264 02	27.4 [1]	−629.463 21	−632.759 85	0.1
H_3SiPH_2	C_s, **3**[d]	$^1A'$	−629.230 71	26.6 [1]	−629.424 52	−632.720 41	24.0
H_3SiSH	C_s, **6**[d]	$^1A'$	−685.277 10	22.0 [0]	−685.487 90	−689.007 45	0.0
H_3SiSH	C_s, **7**[d]	$^1A'$	−685.275 85	21.8 [1]	−685.486 17	−689.005 65	0.9
H_3SiCl	C_{3v}	$^1A_1$	−746.457 79	17.0 [0]	−746.669 85	−750.423 00	

[a] The Hartree–Fock and MP4 total energies are in hartrees while the ZPE and RE are in kcal/mol. [b] The number in brackets is the number of imaginary frequencies. [c] The relative energy is determined by differencing the MP4 total energies and correcting for changes in the ZPE. [d] The bold face numbers refer to figures given in the text.

involvement of Si d-orbitals. These orbitals are low enough in energy to be available for bonding. Pentacoordinate transition states with relatively low activation energies give rise to reaction pathways not accessible to carbon.[4] Some small molecules with singly bonded silicon are known; these include the silicon hydrides SiH_n (n = 1–4), methylsilane, fluoro- and chlorosilane, and the silanols. However, many of the other possible silyl compounds are not known experimentally. In order to explore single bonds involving silicon in a systematic manner, a theoretical examination of the energies and geometries of the full set of silyl compounds H_3SiX (X = Li, BeH, BH_2, CH_3, NH_2 OH, F and Na, MgH, AlH_2, SiH_3, PH_2, SH, Cl) is presented. The silicon hydrides are also examined. Emphasis is laid on a comparison between corresponding silicon and carbon compounds.

An earlier paper investigated the role of d-orbitals on normal valent silicon molecules.[5] When d-functions were added to the minimal STO-3G basis,[6] the structural description of nonhypervalent species was not improved significantly. We now employ the split valence 3-21G and also the 3-21G$^{(*)}$ basis sets.[7,8] The latter includes a set of six Gaussian d-orbitals on all second-row atoms. These results allow the investigation of Si species for which there is insufficient experimental knowledge. Most of the corresponding methyl compounds have been calculated previously at various levels.[7-10] Since our primary goal is to compare the lowest energy equilibrium structures of saturated silyl molecules with those of their methyl counterparts, only the singlet potential energy surfaces were examined. For the lower silicon hydrides, states of different spin multiplicity were calculated. We first determine the most stable equilibrium structure, and then obtain information on the energies of rotation about the silicon–heavy-atom bond.

Computational Method

All molecular geometries were fully optimized by minimization of the Hartree-Fock energy within prescribed symmetry constraints. Singlet states were examined with spin-restricted (RHF) theory,[11] while spin-unrestricted (UHF) theory[12] was used for states of higher multiplicity. Population analyses were based on the Mulliken method.[13] The geometries were determined by using the 3-21G (no d-functions) and the 3-21G$^{(*)}$ (d-functions on all second-row atoms) basis sets.[7,8] The two basis sets are coincident for molecules with only first-row atoms. To determine whether the optimized geometry represents a local minimum on the potential energy surface or a transition structure, the force constant matrix was constructed for all molecules at the 3-21G optimized geometry. Diagonalization of this matrix yields the vibrational frequencies for normal mode harmonic motions. Extensive comparisons with experiment[14] have shown that these harmonic frequencies are generally about 11% too large; the error decreases with correlation.[15] By

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Table II. HF/3-21G Energy, Zero-Point Energy, ZPE, HF/3-21G$^{(*)}$ and MP4/6-31G* Total Energies, and Relative Energy, RE, for All Carbon Compounds^a

molecule	sym	state	HF/3-21G	ZPE^b	HF/3-21G$^{(*)}$	MP4SDTQ/6-31G*	RE^c
CH	$C_{\infty v}$	$^2\Pi$	-38.051 91	4.1 [0]		-38.360 38	0.0
CH	$C_{\infty v}$	$^4\Sigma^-$	-38.070 56	4.8 [0]		-38.344 62	10.6
CH_2	C_{2v}	$^3B_1$	-38.709 07	11.4 [0]		-39.020 89	0.0
CH_2	C_{2v}	$^1A_1$	-38.651 85	11.0 [0]		-38.993 37	16.8
CH_2	$D_{\infty v}$	$^3\Sigma_u{}^-$	-38.651 85	9.9 [2]		-39.009 09	5.9
CH_2	$D_{\infty v}$	$^1\Delta_u$	-38.600 72	12.1 [1]		-38.929 44	57.9
CH_3	D_{3h}	$^2A_2{}''$	-39.342 61	19.5 [0]		-39.689 14	
CH_4	T_d	$^1A_1$	-39.976 88	30.1 [0]		-40.354 50	
H_3CLi	C_{3v}	$^1A_1$	-46.752 48	22.4 [0]		-47.182 96	
H_3CBeH	C_{3v}	$^1A_1$	-54.515 28	28.5 [0]		-55.012 13	
H_3CBH_2	C_s, **1**^{d}	$^1A'$	-65.078 09	37.2 [0]		-65.681 10	0.0
H_3CBH_2	C_s, **3**^{d}	$^1A'$	-65.078 01	37.1 [1]		-65.680 98	0.0
H_3CCH_3	D_{3d}	$^1A_{1g}$	-78.793 95	50.2 [0]		-79.532 15	0.0
H_3CCH_3	D_{3h}	$^1A_1{}'$	-78.789 57	50.0 [1]		-79.527 26	2.9
H_3CNH_2	C_s, **1**^{d}	$^1A'$	-94.681 66	42.7 [0]		-95.537 51	0.0
H_3CNH_2	C_s, **2**^{d}	$^1A'$	-94.678 50	42.1 [1]		-95.532 84	2.3
H_3CNH_2	C_s, **3**^{d}	$^1A'$	-94.677 93	41.6 [1]		-95.528 01	4.8
H_3COH	C_s, **6**^{d}	$^1A'$	-114.398 02	34.2 [0]		-115.372 99	0.0
H_3COH	C_s, **7**^{d}	$^1A'$	-114.395 66	33.7 [1]		-115.370 64	1.0
H_3CF	C_{3v}	$^1A_1$	-138.281 89	26.5 [0]		-139.360 13	
H_3CNa	C_{3v}	$^1A_1$	-200.200 30	21.9 [0]	-200.203 16	-201.569 84	
H_3CMgH	C_{3v}	$^1A_1$	-238.413 16	26.4 [0]	-238.435 20	-239.947 11	
H_3CAlH_2	C_s, **3**^{d}	$^1A'$	-281.126 55	32.1 [0]	-281.182 81	-282.880 95	0.0
H_3CAlH_2	C_s, **1**^{d}	$^1A'$	-281.126 55	32.0 [1]	-281.182 80	-282.880 95	-0.1
H_3CPH_2	C_s, **1**^{d}	$^1A'$	-379.533 74	36.2 [0]	-379.641 09	-381.762 32	0.0
H_3CPH_2	C_s, **2**^{d}	$^1A'$	-379.531 10	36.0 [1]	-379.637 98	-381.759 17	1.8
H_3CPH_2	C_s, **3**^{d}	$^1A'$	-379.479 48	35.2 [1]	-379.575 50	-381.703 98	35.5
H_3CSH	C_s, **6**^{d}	$^1A'$	-435.526 29	30.6 [0]	-435.637 28	-437.990 98	0.0
H_3CSH	C_s, **7**^{d}	$^1A'$	-435.524 56	30.3 [1]	-435.635 12	-437.988 72	-1.1
H_3CCl	C_{3v}	$^1A_1$	-496.689 48	25.3 [0]	-496.795 00	-499.388 17	

[a] The Hartree–Fock and MP4 total energies are in hartrees while the ZPE and RE are in kcal/mol. [b] The number in brackets is the number of imaginary frequencies. [c] The relative energy is determined by differencing the MP4 total energies and correcting for changes in the ZPE. [d] The bold face numbers refer to figures given in the text.

examining the number of negative eigenvalues of this matrix (imaginary frequencies), classification (local minimum or transition structure) of the stationary point is possible. Electron correlation effects are assessed by single-point Møller–Plesset perturbation theory at fourth order,[16] carried out with the 6-31G* basis[17] which includes polarization functions on all heavy atoms. Inner shell orbitals are excluded (frozen core approximation). These calculations will be denoted MP4SDTQ/6-31G*//HF/3-21G$^{(*)}$ where "//" means "at the geometry of". All calculations were carried out with the GAUSSIAN 82 program.[18]

Results

The Hartree–Fock (HF/3-21G and HF/3-21G$^{(*)}$) and correlated (MP4SDTQ/6-31G*) energies for all of the silicon molecules are listed in Table I, together with the zero-point vibrational energies. If more than one structure is calculated for a given molecule, the relative energies also are listed. These are derived from the MP4SDTQ/6-31G*//HF/3-21G$^{(*)}$ energies corrected for the zero-point differences. For comparison, energies for analogous carbon compounds are listed in Table II, calculated in the same manner as in Table I. Optimized geometries are available in the Carnegie–Mellon Quantum Chemistry Archive.[19] Unless otherwise noted, all structural parameters and electron populations for the silicon and carbon second-row molecules quoted below are those obtained with the 3-21G$^{(*)}$ basis set.

CH and SiH. Experimentally, the ground state of CH is known to be $^2\Pi$ (one π-electron).[20] As determined from the photoelectron spectrum of CH^-,[21] the $^4\Sigma^-$ state (two π-electrons) is 17.1 kcal/mol higher in energy. The results summarized in Table II (10.6 kcal/mol) underestimate this splitting. Adding polarization functions to hydrogen (6-31G** basis[17]) results in an MP4SDTQ/6-31G**//HF/3-21G energy separation of 11.1 kcal/mol,[19] after correcting for zero-point energy differences. By use of more extensive 6-311G** basis set[22] to generate MP4SDTQ/6-311G** potential energy surfaces, the energy difference between the $v = 0$ vibrational levels is 12.4 kcal/mol.[23] Extending the basis set and extrapolating the Møller–Plesset series to infinite order result in a 19.5 kcal/mol separation.[24] The HF/3-21G C–H bond distance is 1.119 Å, in good agreement with the experimental value of 1.120 Å.[20] The bond distance is shorter in the quartet (1.072 Å), in agreement with experiment.[20]

Silicon monohydride, SiH, is also known to have a $^2\Pi$ ground state.[20] The $^2\Pi$–$^4\Sigma^-$ energy separation (MP4SDTQ/6-31G**//HF/3-21G$^{(*)}$) is 34.8 kcal/mol, after correcting for zero-point energy differences. By analogy with CH, further theoretical refinements are expected to increase this number. It is noteworthy that Park[25] has used available spectroscopic results to estimate this splitting to be only 14.2 kcal/mol, in serious disagreement with our results. The SCF results of Bozhenko and Charkin[26] yield a separation of 41 kcal/mol, while the CI study of Wirsam[27] produced a splitting of 24.0 kcal/mol. Goddard and Harding[28]

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argued that the GVB Si–H bond strength was greater in the $^2\Pi$ state by 35 kcal/mol, while Mavridis and Harrison found a splitting of approximately 36 kcal/mol.[29] The calculated bond length in the $^2\Pi$ state is 1.511 Å, in good agreement with the experimental value of 1.520 Å,[20] and is longer than the calculated 1.471-Å separation in the $^4\Sigma^-$ state.

CH_2 and SiH_2. The bent $^3B_1$ state of methylene has been thoroughly established by ESR and spectroscopic studies[30,31] to be the lowest energy structure. The lowest singlet ($^1A_1$ with no π-electrons) is higher in energy. Numerous calculations[32–39] agree in predicting a triplet ground state. The singlet–triplet separation in CH_2 has long been a subject of controversy,[40] but it has now been established to be 8.56 ± 0.09 kcal/mol (T_e value),[41] in agreement with theory[40,42] and earlier experiments.[43–46] The energy separation presented in Table II is larger (16.8 kcal/mol). Reoptimizing the structures using the 6-31G* basis set and computing the zero-point energies yield a singlet–triplet separation of 13.1 kcal/mol at the MP4SDTQ/6-31G**//HF/6-31G* level.[19] Again, extending the basis set and extrapolating the Møller–Plesset series yield a splitting of 8.2 kcal/mol.[24] The H–C–H bond angle (HF/3-21G) is 131.0° in the $^3B_1$ state, which is smaller than the experimental values of 136°[47] and 133.9°.[48] In the $^1A_1$ state, the bond angle is only 104.7°, compared to an experimental value of 102.4°;[47] better agreement is obtained at the MP2/6-31G* level of optimization.[49] The bond angle being smaller, the energy difference between the bent and linear structures is larger in the singlet state (41.1 kcal/mol) than in the triplet (5.9 kcal/mol). From experimental data, the barrier to linearity is 5.4 kcal/mol in triplet methylene.[48]

In contrast to methylene, silylene is known to have a singlet ground state.[50] This is in agreement with previous ab initio calculations of Wirsam,[51] Meadows and Schaefer,[35a] and Poirier and Goddard.[52] This $^1A_1$ state is calculated (MP4SDTQ/6-31G*//HF/3-21G$^{(*)}$) to be 16.4 kcal/mol more stable than the $^3B_1$ state of SiH_2. Adding polarization functions to the hydrogen (6-31G** basis) increases the separation to 17.0 kcal/mol at the MP4SDTQ level,[19] after correcting for zero-point energy differences. Assuming that these values again approach the actual energy separation, a conflict could exist between these results and the upper bound value of 14 kcal/mol reported by Lineberger and co-workers.[53] The same conclusion has been reached by Schaefer et al.[35b]

The reversed spin preferences in CH_2 and SiH_2 arise from the magnitude of separation of the highest (a_1) and (b_1) singly occupied orbital energies in the $^3B_1$ state. In methylene, this energy difference (27 kcal/mol) is considerably smaller than that of silylene (52 kcal/mol). The energy gained in forming a triplet is not enough to compensate for this large energy separation in silylene. Hence, in SiH_2, the $5a_1$ orbital is doubly occupied. This singlet character of silylene is also reflected in that of various substituted silylenes.[54]

The calculated SiH_2 bond angle is 93.4° in the singlet, compared to an experimental value of 92.5°,[55] and 118.0° in the triplet. As these angles are smaller than the corresponding angles of CH_2, the energy separations between the bent and linear structures of SiH_2 are larger. The separation in the singlet (75.1 kcal/mol) is much larger than in the triplet (24.1 kcal/mol).

CH_3 and SiH_3. At the HF/3-21G level, the methyl radical is planar (D_{3h}); higher levels agree.[49,56] Experimentally[57] there is some evidence for slight nonplanarity due to thermal agitation; Ellison, Engelking, and Lineberger[58] find a barrier less than one-half of the corresponding zero-point vibrational energy.

There is some doubt about the structure of the silyl radical, as experimental evidence has been presented for both planar[59] and nonplanar[60,61] structures. Early theoretical investigations also were inconclusive.[22,53,62–64] Our results clearly favor a nonplanar pyramidal structure (bond angle 110.9°). The energy of the planar structure (a transition structure for inversion) is 4.4 kcal/mol higher. This value is in good agreement with recent theoretical results of Marynick[65] and Ohta and co-workers.[66]

CH_4 and SiH_4. Both methane and silane are tetrahedral. The calculated bond length in silane (1.475 Å)[8] agrees well with experiment (1.481 Å).[67] The Si–H bond lengths decrease in the

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order SiH > SiH_2 > SiH_3 ~ SiH_4. Such a smooth trend is not found in the carbon series, either theoretically or experimentally.[20,47,68a] These results are the direct consequence of the smoothly increasing s character found in the Si–H bonds with increasing number of hydrogens. The s character in the corresponding carbon series does not exhibit this trend. The factors controlling the degree of hybridization in first- and second-row molecules have been discussed in detail by Kutzelnigg.[68b]

Mulliken populations in the CH_n and SiH_n series reflect the change in polarity in going from carbon to the more electropositive silicon. The partial charge (HF/3-21G) on the hydrogen in CH is +0.127. For the series CH_2, CH_3, CH_4, the charge per hydrogen atom is almost constant (~+0.2), resulting in an increase in the negative charge on the carbon atom, up to –0.80 in CH_4. In the silicon hydride series, the situation is reversed. The hydrogen atoms bound to silicon have a partial negative charge, as would be expected by electronegativity arguments, and vary slightly (HF/3-21G$^{(*)}$): SiH ($^2\Pi$) –0.15, SiH_2 –0.15, SiH_3 –0.11, and SiH_4 –0.13. The silicon atom in SiH_4 has a charge of approximately +0.50.

H_3CLi, H_3SiLi, H_3CNa, and H_3SiNa. Silyllithium, produced from the reaction of disilane with lithium hydride in 1,2-dimethoxymethane,[69] exists as a monomer in solution, in contrast with the tetrameric nature of methyllithium[70] under similar conditions. Examining the atomic charges in both of the monomers shows that in H_3CLi the lithium atom has a charge of +0.48, while the charge on lithium is +0.43 in H_3SiLi. This agrees with the recent study of the ionicity of X–Li bonds using ^7Li chemical shifts,[71] which indicates that the charge transfer in C–Li and Si–Li is similar. As expected, the C–Li bond length of 2.001 Å is considerably shorter than the 2.3 Å found experimentally for the methyllithium tetramer,[70] where each methyl carbon is equidistant to three Li atoms, but agrees well with other calculations.[72-77] The Si–Li bond length (2.542 Å) is shorter than the average separation of 2.68 Å found in crystalline hexameric (trimethylsilyl)lithium.[78] In H_3SiLi, the H–Si–Li bond angle of 115.1° deviates more from the tetrahedral angle than does the 111.9° H–C–Li angle in H_3CLi. Moreover, the C–H and Si–H bonds lengthen in comparison to unsubstituted methane and silane.

Very soluble monomeric silylsodium has been prepared,[79,80] but no experimental structural parameters are available. This is also true of monomeric methylsodium, though the tetrameric solid has been examined.[81] The C–Na bond length in the tetramer is 2.58 Å[81] and in crystalline ethylsodium is 2.6 Å,[82] considerably longer than the calculated bond length of 2.315 Å in isolated H_3CNa. When Na replaces Li in the methyl species, there is an increase in the H–C–H bond angle and a slight decrease in the C–H bond length. For the silyl species, there is virtually no change in the H–Si–H bond angle or the Si–H bond length.

H_3CBeH, H_3SiBeH, H_3CMgH, and H_3SiMgH. Silylberyllium hydride, like its monomeric methyl analogue, has not been described, although methylberyllium hydride is known in a coordinated dimeric form.[83] The C–Be bond length of 1.698 (5) Å[84] found in $(CH_3)_2Be$ is quite close to the 1.713-Å separation calculated for monomeric H_3CBeH. The Si–Be separation found in $Be_3Al_2(SiO_3)_6$ is 2.74 Å,[85] much longer than the 2.204 Å bond length found in H_3SiBeH. However, this comparison involves quite different compounds.

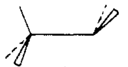
As with methyl- and silyllithium, the direction of charge donation in H_3CBeH and H_3SiBeH is the same. In both molecules there is a loss of electron density on the BeH group, though the charge on the CH_3 group (–0.39) is larger than that on the SiH_3 group (–0.19). The charge on the hydrogen bound to beryllium is approximately the same for both molecules (–0.135), so the drop in electronegativity in replacing carbon with silicon results in a decrease in the positive charge found on beryllium.

Comparison of the results for H_3CLi and H_3CBeH shows that in changing BeH for Li there is a decrease (0.011 Å) in the C–H bond length, with virtually no change in the H–C–H bond angle. In the corresponding silicon compounds, replacing Li with BeH also results in a decrease (0.012 Å) in the Si–H bond length. There is also an increase in the H–Si–H bond angles from 103.3° in H_3SiLi to 107.1° in H_3SiBeH.

Recently, Rosch[86] isolated the first molecule containing a silyl–magnesium bond, bis(trimethylsilyl)magnesium, although there are earlier reports of analogues of silyl Grignard reagents.[87] The experimental dimethylmagnesium dimer bridging distance, 2.24 Å,[88] is longer than the theoretical monomeric single bond length, 2.104 Å. A more pertinent comparison involves the C–Mg bond (2.16 Å)[85] in ethylmagnesium bromide.

There is virtually no change in the C–H bond length or the H–C–H bond angle in H_3CBeH and H_3CMgH, but a decrease in the H–Si–H bond angle to 106.0° is found in H_3SiMgH. As expected, the positive charge on magnesium is larger in H_3CMgH than in H_3SiMgH, but no significant change in the Mg–H bond length results. Both Mg-bound hydrogens are partially negatively charged, but the magnitude is larger in H_3SiMgH.

H_3CBH_2, H_3SiBH_2, H_3CAlH_2, and H_3SiAlH_2. These H_3XYH_2 compounds are considered in three possible C_s conformations: staggered (**1**), eclipsed (**2**), and γ-coplanar (**3**). While methylborane, H_3CBH_2, is only known experimentally as a dimer,[89] the monomer has been examined theoretically.[90] The staggered form **1** is found to be the equilibrium structure (no negative eigenvalues). The conformation around the boron is almost planar, the BH_2 bisector making an angle of 178° with the C–B axis. No stationary point on the potential energy surface is found for the eclipsed conformation **2**. The y-coplanar form **3** is the transition structure for the sixfold rotation barrier. After correcting for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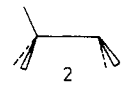
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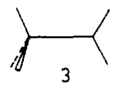
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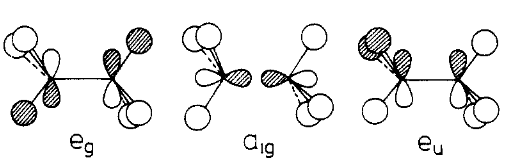
differences in zero-point vibrational energy (Table II), there is no energetic difference between structures **1** and **3**, so rotation about the C-B bond bond should be free.

Silylborane is not known experimentally; the closest analogue is F_3SiBF_2.[91a] The calculated structural features[91b] are similar to methylborane, the staggered form **1** being the equilibrium structure. The BH_2 bisector is less than 2° out of line with the Si-B axis. No eclipsed conformation **2** of H_3SiBH_2 was found, and y-coplanar **3** is energetically equivalent to the staggered structure at the MP4SDTQ/6-31G* level; rotation is free. The Si-B bond length, 2.025 Å, may be compared to an experimental value of 2.32 Å in 1-Br-μ-$(CH_3)_3SiB_5H_7$, but this structure has three-center electron-pair bonds.[92]

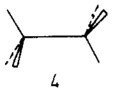
There is a reversal in the direction of charge transfer in H_3CBH_2 and H_3SiBH_2. In methylborane, a charge of −0.31 is donated to the methyl group, whereas in silylborane, the silyl group has a charge of +0.17. This reflects the changes in electronegativity.

The alanes show properties similar to the boranes, with insignificant sixfold rotational barriers. Methylaluminum hydride monomer exists as a colorless gas,[93] but no experimental structure is available. Bridging in dimeric di- and trimethylaluminum compounds has been studied.[94] Experimental C-Al and Al-H distances in these bridged compounds are 1.947 and 1.676 Å, respectively, as compared to the calculated values of 1.974 and 1.591 Å for the monomeric structure **1**. No data appear to be available for silylaluminum hydride. However, the preparation of tris(trimethylsilyl)aluminum,[95] following the earlier work of Wiberg and co-workers,[96] indicates the existence of Si-Al bonds. In both H_3CAlH_2 and H_3SiAlH_2 there is a shift of electron density away from the AlH_2 group. As expected from electronegativity arguments, the charge on the methyl group (−0.35) is larger than the charge on the silyl group (−0.21).

H_3CCH_3, H_3SiCH_3, and H_3SiSiH_3. Several theoretical comparisons of the series H_3CCH_3, H_3SiCH_3, and H_3SiSiH_3 have already been published.[5,97-101] The level of theory presented here yields the same valence orbital energy ordering as that predicted by Liskow and Schaefer,[98] Nicolas,[100] and Topiol and co-workers[101] for several members of the series. In ethane, the a_{1g} orbital is 10 kcal/mol lower in energy than the degenerate e_g orbitals. In methylsilane this order is reversed, with the a_1 orbital 8 kcal/mol higher in energy than the e orbitals. This trend continues in disilane, where the e_g orbitals are considerably lower (43 kcal/mol) in energy than the a_{1g} orbital. This reversal in orbital energy is due to the longer bond lengths involving silicon. The e_g orbitals, antibonding between the two heavy atoms, are bonding to the hydrogens. Increasing the distance between the heavy atoms would tend to stabilize this orbital by decreasing the antibonding contribution. The a_1 orbital involves σ-bonding and becomes considerably destabilized due to loss in orbital overlap. The e_u orbitals which are lower in energy than the a_{1g} and the e_g orbitals also become destabilized at greater heavy atom separations. This is observed in both H_3SiCH_3 and H_3SiSiH_3. These orbitals are pictured below.



A consequence of this increase in heavy atom separations is a decrease in the rotational barriers. In ethane, the energy difference between the staggered, **4** and eclipsed, **5**, forms is 2.9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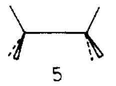
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kcal/mol, in good agreement with the experimental rotational barrier of 2.744 kcal/mol.[102] On passing through the transition structure, C-C bond length increases from 1.542 Å to 1.556 Å and the H-C-C bond angle decreases slightly. In methylsilane, the rotational barrier decreases to 1.5 kcal/mol, in good agreement with the experimental values of 1.7[103,104] and 1.51 kcal/mol.[105] The Si-C bond length increases from 1.883 Å in the staggered form **4**[8] to 1.893 Å in the eclipsed **5**. There are only small changes in the bond angles. In disilane, both theory and experiment predict smaller rotational barriers of 0.9 and 1.2 kcal/mol,[106] respectively. On passing through the transition structure, the Si-S distance decreases by 0.010 Å, from 2.342[8] to 2.352 Å. In each of these molecules, the calculated heavy-atom-heavy-atom separation is slightly larger than the corresponding experimental value.[103,107-113]

H_3CNH_2, H_3SiNH_2, H_3CPH_2, and H_3SiPH_2. Methylamine, H_3CNH_2, has a staggered equilibrium structure, **1**. The C-N bond distance, 1.472 Å, is in good agreement with the experimental values (1.471-1.474 Å).[47,114-116] The calculated C-H (1.082 and 1.090 Å) and N-H (1.004 Å) bond lengths are slightly smaller than the experimental values (1.099 and 1.010 Å, respectively); HF/6-31G* and MP2/6-31G* structures are in better agreement.[49] The H-N-C (113.6°) and H-N-H (111.1°) bond angles are slightly larger than the experimental values which range from 110.3° to 112.2° and from 105.8° to 107.1°, respectively. This results in a more planar geometry about the nitrogen than is observed. The eclipsed form, **2** of methylamine is calculated to be 2.3 kcal/mol higher in energy than the staggered structure. The experimental rotational barrier is 1.96 kcal/mol.[117] There is virtually no change in the C-N bond distance in **1** and **2**, but there is an increase in the bond angles about the nitrogen. In the staggered structure **1**, the NH_2 bisector makes an angle with the C-N axis of 135.1°, while in the eclipsed form **2**, this angle increases to 141.0°. Y-coplanar methylamine, **3**, represents the transition structure for nitrogen inversion. The relative energy is in exact agreement with the experimental inversion barrier of

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4.8 kcal/mol.[117] In **3**, the C–N bond length decreases to 1.450 Å.

Although silylamine, H_3SiNH_2, is not known, both $(CH_3)_3SiNH_2$[118] and $H_3SiN(CH_3)_2$[117] have been studied experimentally. The HF/3-21G and HF/3-21G$^{(*)}$ equilibrium structures of H_3SiNH_2 both predict a planar arrangement about nitrogen, **3**, to be the lowest in energy. In the staggered structure **1**, the angle between the NH_2 bisector and the Si–N axis is 176.7° (HF/3-21G$^{(*)}$), only a slight deviation from planarity. The energies of **1** and **3** are virtually identical, suggesting free rotation about the Si–N axis. Similar results have been recently reported by Glidewell and Thomson;[119] planar arrangements at nitrogen are found in $(SiH_3)_2NH$[120] and in $(SiH_3)_3N$.[121]

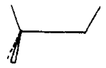
Previous theoretical studies of ammonia[49,122] show that *d*-functions are necessary to accurately determine the geometry and inversion barrier. Reoptimization of silylamine with the 6-31G* basis results in an equilibrium structure with a staggered conformation, **1**.[123] The y-coplanar structure **3** has one imaginary frequency (HF/6-31G*) and represents a transition structure for rotation. These structures differ in energy by only 0.1 kcal/mol (MP4SDTQ/6-31G*//HF/6-31G* plus HF/6-31G* zero-point correction); rotation about the Si–N axis again is virtually free.[123]

Methylphosphine, H_3CPH_2, prefers a staggered geometry, **1**. The calculated C–P bond distance, 1.856 Å,[8] is in good agreement with experiment (1.863 Å).[124] Recent calculations with the 4-31G* basis[125] yield slightly better results (1.861 Å). The C–P–H and H–P–H angles are 98.3° and 94.5°, respectively, compared to experimental values of 97.5° and 93.4°.[124] The long C–P bond distance counteracts the effect of these small phosphorus bond angles; a rotational barrier of 1.8 kcal/mol, slightly smaller than the rotational barrier found in methylamine, results. The experimental barrier in H_3CPH_2 is 1.96 kcal/mol.[104,124] In the eclipsed conformation **2**, the C–P bond distance increases to 1.868 Å. Due to the small bond angles at phosphorus, the inversion barrier (35.5 kcal/mol) is much larger than in H_3CNH_2. In the y-coplanar structure **3**, the C–P bond distance decreases to 1.835 Å.

Silylphosphine, H_3SiPH_2, originally discovered by Jolly and co-workers,[126-128] is the major product of the IR multiphoton-induced decomposition of SiH_4–PH_3 mixtures.[129] Unlike the amines, the structures of methyl- and silylphosphine are similar. In H_3SiPH_2, the equilibrium structure also is staggered **1**. The calculated Si–P bond distance is 2.256 Å, in good agreement with the experimental value, 2.249 Å.[130] The bond angles at phosphorus also are small; the Si–P–H and H–P–H values, 96.8° and 95.1°, respectively, are slightly larger than reported experimentally (92.8° and 93.9°).[131] The larger Si–P distance, compared to the C–P bond length, results in a decrease in the rotational barrier in H_3SiPH_2. The calculated barrier of 0.1 kcal/mol is smaller than the experimental value of 1.51 kcal/mol.[131] In the eclipsed structure **2**, there is the usual increase in the heavy-atom separation (to 2.270 Å). The inversion barrier of silylphosphine, calculated to be 24.0 kcal/mol, is 11.5 kcal/mol smaller than that in methylphosphine. The decrease in the Si–P separation in the planar structure **3** (to 2.183 Å), larger than in the carbon analogue, may contribute to the inversion-barrier-lowering sterically. However, the principal effect is probably the lower electronegativity of silicon. The phosphorus inversion barrier in $LiPH_2$ is even smaller, 6.2 kcal/mol at the same level of theory.[19]

H_3COH, H_3SiOH, H_3CSH, and H_3SiSH. All these H_3XYH molecules have staggered equilibrium structures, **6**. The eclipsed forms, **7**, represent transition structures for X–Y bond rotations.

6



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In methanol, the optimized C–O bond length (1.440 Å) and the C–O–H angle (110.4°) are both slightly larger than the values determined experimentally;[132-139] HF/6-31G* and MP2/6-31G* structures again are in better agreement.[49] The eclipsed form **7** is found to be 1.0 kcal/mol higher in energy; this agrees with the experimental rotational barrier of 1.06 kcal/mol.[132-134] In this structure, the C–O bond length increases to 1.455 Å and the C–O–H bond angle increases to 111.1°.

Silanol, H_3SiOH, is unstable toward disproportionation and has never been isolated experimentally:[140]

$$2H_3SiOH \rightarrow H_3SiOSiH_3 + H_2O$$

The HF/3-21G$^{(*)}$ equilibrium structure of H_3SiOH has been reported recently.[141] The Si–O bond length, 1.633 Å, is in excellent agreement with the experimental distance of 1.63 Å in the diol and triol.[142] The Si–O–H bond angle, 128.8°, is much larger than the C–O–H angle in methanol. This and the longer Si–O bond length help to reduce the rotational barrier to 0.4 kcal/mol. In the eclipsed structure **7**, the Si–O–H bond angle increases to 130.4°.

In agreement with photoelectron spectra,[143] the ordering of the valence orbitals in H_3CSH and H_3SiSH is the same. This is also true of methanol and silanol. The staggered form **6** of methyl mercaptan has a C–S bond distance[8] of 1.822 Å, in good agreement with the experimental values of 1.819[144] and 1.818 Å[145] and the HF/4-31G* separation of 1.815 Å.[125] The C–S–H bond angle is small, 97.6°; experiments give 96.5°[144] and 110.3°.[145] The C–S distance, larger than the C–O bond length, compensates for the smaller angle at sulfur and yields a rotational barrier of 1.1 kcal/mol in H_3CSH, approximately the same as that in methanol. The experimental barrier is 1.27 kcal/mol.[104,144] The eclipsed structure **7** has a C–S bond length of 1.831 Å and a C–S–H angle of 98.0°, both values are slightly larger than in **6**.

Silyl mercaptan, H_3SiSH, characterized calculationally by Glidewell,[146] may result from the reaction of disilyl sulfide with

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Table III. HF/3-21G$^{(*)}$ Optimized Si-H and Si-X Bond Lengths and H-Si-X Bond Angles for All H_3SiXH_n Molecules[a]

XH_n	r(Si-H)[b]	Θ(H-Si-X)[c]	r(Si-X)[b]	Δr(Si-X)[d]
H	1.475	109.5	1.475	0.012
Li	1.495	115.1	2.542	-0.011
BeH	1.483	111.8	2.204	-0.009
BH_2	1.479	110.7	2.025	0.013
CH_3	1.478	110.6	1.883	0.034
NH_2	1.478	111.2	1.710	0.032
OH	1.468	110.5	1.633	0.042
F	1.469	109.1	1.593	0.042
Na	1.496	115.2	2.837	-0.002
MgH	1.486	112.8	2.607	0.005
AlH_2	1.481	111.5	2.467	0.014
SiH_3	1.477	110.3	2.342	0.041
PH_2	1.475	109.8	2.256	0.091
SH	1.471	109.2	2.139	0.116
Cl	1.467	108.5	2.056	0.135

[a] When more than one distinct H-Si-X angle is present, the average value is reported. [b] Distances are in angstroms. [c] Angles are in degrees. [d] This difference is the HF/3-21G optimized bond length minus the HF/3-21G$^{(*)}$ separation (caused by adding *d*-functions to the second-row atoms), in angstroms.

hydrogen sulfide.[147] No experimental structures are available. The staggered form **6** of this molecule has a Si-S bond length of 2.139 Å. The Si-S-H bond angle is 98.2°, slightly larger than the bond angle in H_3CSH. The greater bond length to the sulfur results in a lower rotational barrier in silyl mercaptan (0.9 kcal/mol) than in H_3CSH. The Si-S bond length in eclipsed **7** increases to 2.147 Å; the increase in H_3CSH is virtually the same.

H_3CF, H_3SiF, H_3CCl, and H_3SiCl. The valence orbital ordering, the same in H_3CF, H_3SiF, H_3CCl, and H_3SiCl, agrees with earlier results on silyl chloride[148] and methyl chloride.[149] The degenerate HOMO with e symmetry corresponds to nonbonding halogen orbitals. Orbitals of a_1 symmetry, representing the heavy-atom–heavy-atom bond, are lower in energy. In methyl fluoride, the C-F bond distance (1.404 Å) is longer than the experimental value of 1.385 Å, while the calculated H-C-F bond angle, 109.4°, is slightly larger than experiment (108.3-109.4°).[150-152] In H_3SiF, the Si-F bond distance of 1.593 Å[8,153] is essentially identical with experiment (1.594 Å).[154-156] The H-Si-F bond angle, 109.1°, also is in good agreement. In methyl fluoride, the p-orbitals on the fluorine perpendicular to the C-F axis contain 1.957 electrons, showing only a slight interaction with the C-H bonds. In silyl fluoride, these p-orbitals contain 1.897 electrons, suggesting a larger interaction.

Table IV. HF/3-21G$^{(*)}$ (HF/3-21G for Methyl First-Row Molecules) Optimized C-H and C-X Bond Lengths and H-C-X Bond Angles for All H_3CXH_n Molecules[a]

XH_n	r(C-H)[b]	Θ(H-C-X)[c]	r(C-X)[b]	Δr(C-X)[d]
H	1.083	109.5	1.083	
Li	1.094	111.9	2.001	
BeH	1.090	111.7	1.713	
BH_2	1.089	111.4	1.577	
CH_3	1.084	110.8	1.542	
NH_2	1.085	110.9	1.472	
OH	1.083	110.3	1.440	
F	1.080	109.4	1.404	
Na	1.091	110.6	2.315	0.005
MgH	1.090	111.5	2.104	0.008
AlH_2	1.089	111.4	1.974	0.015
SiH_3	1.087	111.0	1.883	0.034
PH_2	1.084	110.5	1.856	0.053
SH	1.080	109.7	1.822	0.072
Cl	1.076	108.1	1.806	0.086

[a] When more than one distinct H-C-X angle is present, the average value is reported. [b] Distances are in angstroms. [c] Angles are in degrees. [d] This difference is the HF/3-21G optimized bond length minus the HF/3-21G$^{(*)}$ separation (caused by adding *d*-functions to the second-row atoms), in angstroms.

The H-C-Cl angle in H_3CCl is 108.7°, smaller than in H_3CF. The C-Cl bond length, 1.806 Å,[8] is longer than experiment.[157-159] In silyl chloride, the Si-Cl separation, 2.056 Å, is only slightly longer than experiment.[160-162] The H-Si-Cl bond angle, 108.5°, also is smaller than the H-C-Cl angle in the carbon analogue. The atomic charge on the fluorine is -0.41 in H_3CF and -0.43 in H_3SiF. As expected, the negative charge on the chlorine is smaller in H_3CCl (-0.11) than in H_3SiCl (-0.41).

Discussion

Structural Features and Trends. The 3-21G$^{(*)}$ optimized Si-H bond lengths and H-Si-X bond angles for the H_3SiXH_n molecules, listed in Table III, can be compared with the corresponding bond lengths and angles for the H_3CXH_n molecules (Table IV). The Si-H distances and H-Si-X bond angles tend to decrease on moving from left to right across either the first or second row of the periodic table. A similar trend is found for the saturated methyl species. The only definite inconsistency is silylamine; the H-Si-N bond angle is larger than the H-Si-C angle found in the equilibrium structure of methylsilane. This larger H-Si-N angle is most likely due to the unusual structure of silylamine, with a planar arrangement at nitrogen. The H-Si-X bond angles are found to be larger for X = N, O, and F than for the second-row element of the same group. This is also true for the H-C-X bond angles, and indicates the influence of the electronegativity of the substituent.

Table V compares the geometries of the XH_n groups with methyl and silyl substituents. Generally, replacing the methyl group with a silyl group does not change the geometry at the X atom. The only exceptions are for XH_n = NH_2 and OH. As stated above, the equilibrium structure of methylamine has a nonplanar structure at nitrogen, but is planar in silylamine. In the staggered form (**6**) of methanol, the C-O-H bond angle is 110.4°, while in silanol, the Si-O-H angle is 128.8°. Both the N-H and O-H bond lengths are smaller in the silyl than the methyl compounds. An increase in the s-character of the σ-bond orbital involving nitrogen or oxygen due to the lower electronegativity of silicon is responsible.

The last two columns of Tables III and IV list the heavy-atom–heavy-atom bond lengths obtained with the 3-21G$^{(*)}$ basis set and also the change in this distance caused by adding *d*-functions to the second-row atoms. These *d*-functions generally decrease the bond lengths. The only exceptions are Si-Li, Si-Be, and Si-Na; the 3-21G$^{(*)}$ bond lengths are slightly longer than those at 3-21G. The bond length decrease becomes greater as the electronegativity of the atoms increases. The decrease is much larger between two second-row atoms, both of which have *d*-functions added, than between a first- and second-row atom. In the few cases where experimental structures are available, the

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Table V. Optimized Bond Lengths to Hydrogen and Bond Angles Involving the Heavy Atom Bound to Either Carbon or Silicon in the Equilibrium Structures of H_3CXH_n and H_3SiXH_n Molecules[a]

	H_3CXH_n			H_3SiXH_n		
XH_n	r(X-H)[b]	Θ(C-X-H)	Θ(H-X-H)[c]	r(X-H)[b]	Θ(Si-X-H)	Θ(H-X-H)[c]
BeH	1.341	180.0		1.341	180.0	
BH_2	1.192	121.1	117.8	1.191	121.5	117.0
CH_3	1.080	110.8	108.1	1.087	111.0	107.9
NH_2	1.004	113.6	111.1	1.001	123.3	113.4
OH	0.966	110.4		0.959	128.8	
MgH	1.729	180.0		1.726	180.0	
AlH_2	1.592	120.8	118.4	1.590	120.7	118.6
SiH_3	1.478	110.6	108.3	1.477	110.3	108.6
PH_2	1.403	98.3	94.6	1.403	96.8	95.1
SH	1.327	97.6		1.329	98.2	

[a] For the methyl first-row molecules, the 3-21G basis set was used while 3-21G$^{(*)}$ results are listed in all other cases. [b] Distances are in angstroms. [c] Angles are in degrees.

Table VI. Heats of Reaction (ΔH) for the Exchange between H_3Si–X and H_3C–X (Equation 1), Experimental H_3C–X Bond Energies, and Theoretical and Experimental H_3Si–X Bond Strength[a]

X	ΔH_{rxn}[b]	exptl $D°_{298.15}(H_3C\text{–}X)$[c]	theory[d] (exptl) $D(H_3Si\text{–}X)$
H	-14.5	105.1 ± 0.2	90.6 (90.3)[e]
Li	6.2	39.2	45.4
BeH	-14.8		
BH_2	-19.6	[f]	
CH_3	-4.9	90.4 ± 0.3	85.5 (82.1)[g]
NH_2	13.8	84.9 ± 1.1	98.7 (100)[h]
OH	26.6	92.3 ± 1	118.9 (128)[i] (108)[j]
F	37.9	109.9 ± 1	147.8 (135)[j]
Na	8.3		
MgH	-1.6		
AlH_2	-10.7	[f]	
SiH_3	-11.5	82.1 ± 3	70.6 (74)[e] (53)[j]
PH_2	-2.5	[f]	
SH	9.1	74.0 ± 3	83.1 (70?)[j]
Cl	20.3	84.6 ± 0.2	104.9 (113)[i] (91)[j]

[a] All energies are in kcal/mol. [b] Calculated from MP4/6-31G* energies, corrected for zero-point energy differences. [c] Except where noted, data are from D. F. McMillen and D. M. Golden, *Annu. Rev. Phys. Chem.*, **11**, 493 (1982). [d] Calculated by adding the energies of columns 2 and 3. [e] From ref 163a. [f] Average bond strengths for trimethyl compounds are available in A. Pilcher and H. A. Skinner in "The Chemistry of the Carbon-Metal Bond", S. Patai, Ed., Wiley, New York, 1982. [g] From the reference in footnote c. [h] From $(CH_3)_3Si\text{–}NHCH_3$, ref 163a. [i] From $(CH_3)_3Si$-X, ref 163a. [j] From ref 163b.

3-21G$^{(*)}$ results are always found to be in better agreement than the3-21G geometries. This is the general experience.[8]

H_3Si–X Bond Strengths. Reliable bond dissociation energies are essential for the interpretation of the kinetics and mechanisms of the reactions of silicon compounds. Unfortunately, accurate thermodynamic data for silicon molecules are sparse, and only a few Si–X bond energies are known.[163] Furthermore, in most cases the available data are derived from polysubstituted systems (e.g., $(CH_3)_3SiX$),[163] where the effects of the additional substituents complicate the analysis, and not from the parent H_3SiX.

At the level of theory used here, *directly* calculated bond energies are not accurate. Much better values may be obtained indirectly. With the energies in Tables I and II, it is possible to compare the relative Si–X and C–X bond strengths in saturated silyl and methyl species by examining the enthalpy change in the isogyric reaction in which the spin multiplicity is conserved:

$$H_3SiX + CH_3 \rightarrow SiH_3 + H_3CX \qquad (1)$$

These heats of reaction, calculated by using the MP4SDTQ/6-31G* energies, corrected for zero-point vibrational energies, are listed in the second column of Table VI. From the first entry, it is clear that the C–H bond in methane is stronger than the Si–H bond in silane by 14.5 kcal/mol.

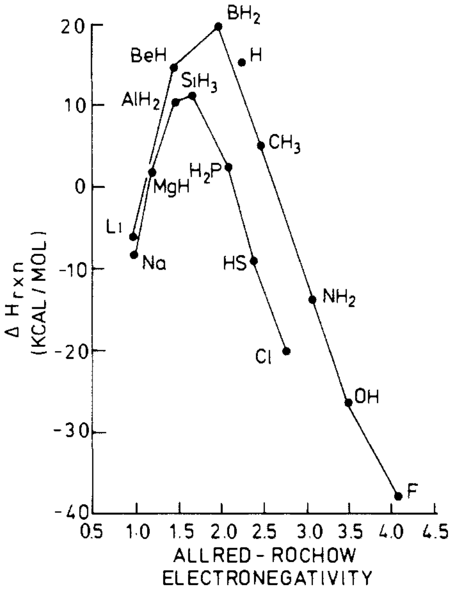

Figure 1. Plot of the heats of reaction for exchange between $H_3Si\text{–}XH_n$ and $H_3C\text{–}XH_n$ vs. the Allred–Rochow electronegativity of atom X. The energies are the negative of the values in Table VI.

Figure 1, a plot of these data against Allred–Rochow electronegativities,[164] reveals that about half of the C–X bonds are stronger than the corresponding Si–X bonds. Two inverted V-shaped curves, one for first-row and the other for second-row substituents, are found, but these merge on the electropositive side. The Si–Li and Si–Na bonds are stronger than their carbon counterparts. The electron affinity of SiH_3 is much greater than CH_3 (which is near zero),[165] and largely ionic bonds involving $SiH_3^-X^+$ ion pairs are better than $CH_3^-X^+$.

Although the bonds are less ionic, the same trend in Si–X vs. C–X bond strengths is found when the substituents contain the more electronegative elements in each period (F, OH, NH_2, as well as Cl and SH). The ionization potential of SiH_3 is less than that of CH_3 by 2.3 eV.[166] Thus, $H_3Si^+\text{–}X^-$ character is favored over $H_3C^+\text{–}X^-$. The ambielectronic nature of SiH_3 is thus responsible for the inverted V's of Figure 1.

The substituents with electronegativities closer to silicon have stronger bonds to carbon. With H, BeH, BH_2, AlH_2, and SiH_3, the differences favoring C–X are in the 10–20 kcal/mol range; the preferences involving X = CH_3 (4.9 kcal/mol) and PH_2 (2.5 kcal/mol) are smaller.

Values of H_3Si–X bond energies can now be determined by using experimental H_3C–X bond strengths. The experimental

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(163) (a) R. Walsh, *Acc. Chem. Res.*, **14**, 246 (1981). (b) J. H. Huheey, "Inorganic Chemistry", 3rd ed., Harper and Row, New York, 1983, Appendix E, p A-29 ff.

(164) A. L. Allred and E. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 264 (1958).

(165) B. K. Janosek and J. I. Brauman, in "Gas Phase Ion Chemistry", Vol. 2, M. T. Bowers, Ed., Academic Press, New York, 1979, Chapter 10; P. S. Drzaic, J. Marks, and J. I. Brauman, *Ibid.*, Vol. 3, 1984, Chapter 21.

(166) W. C. Steele, L. D. Nichols, and F. G. A. Stone, *J. Am. Chem. Soc.*, **84**, 4441 (1962).

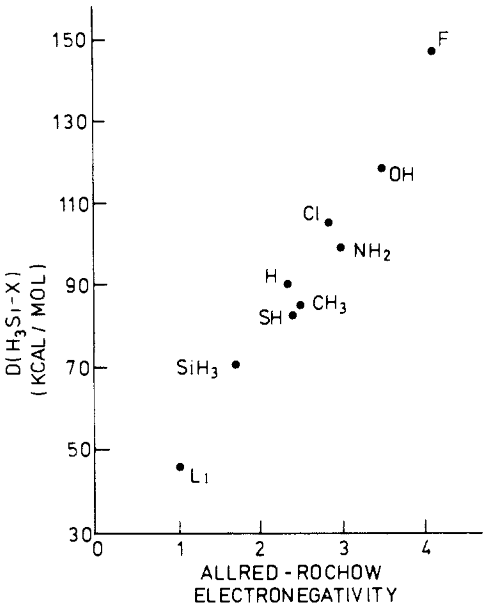

Figure 2. Plot of the calculated H_3Si-XH_n bond strengths vs. the Allred-Rochow electronegativity of atom X.

values are listed in the third column of Table VI, and when combined with the heats of reaction of eq 1 yield the H_3Si-X bond energies listed in the fourth column of Table VI. These results are in fair agreement with the few available experimental bond energies; studies on simple hydrides have shown that both basis set expansion and extrapolation of the Møller-Plesset series to infinite order are necessary to obtain accurate bond strengths.[24] When these values are plotted against Allred-Rochow electronegativities (Figure 2), a correspondence emerges. As the electronegativity of X increases, so does the Si-X bond strength.

It has been argued that d-π conjugation, for example in H_3SiNH_2, involving good π-donor substituents and vacant d-orbitals on silicon might contribute to the strengthening of silicon bonds.[167] On the other hand, the correlation in Figure 2 argues strongly that the major factor determining the strength of single bonds to silicon is the electronegativity of the group X. Stronger bonds are formed with more electronegative groups because of greater contributions from ionic structures of the type $H_3Si^+X^-$. The fact that bonds between silicon and substituents of similar electronegativity but different chemical character have very similar dissociation energies argues against the importance of d-π bonding. Thus $D(H_3Si-SH) \sim D(H_3Si-CH_3)$, although sulfur has lone pairs that can participate in d-π conjugation and the methyl group does not. In addition, Mislow has concluded that (p-d) π conjugation need not be invoked to explain the decrease in amine inversion barriers when silicon-based substituents are present.[168] The isoelectronic $H_3SiCH_2^-$ carbanion is strongly stabilized relative to CH_3^-, but we have shown recently that (p-d) π conjugation can only be a very minor contributor.[169]

We stress, however, in agreement with previous workers,[170] that it is difficult to separate d-π bonding effects from ionic contributions. A more elaborate study is needed to determine the relative importance of various factors such as ionicity, d-π conjugation, and orbital overlap in determining the strength of bonds to silicon.

The BH_2-F and SiH_3-Cl lines of Figure 1 are roughly parallel but are displaced from one another by about 15 kcal/mol Thus, for a given electronegativity, Si-X bonds to first-row groups are generally weaker than C-X bonds by this amount. This may be due to poorer first-row-second-row σ-overlap. Bonds tend to be stronger when they are between elements of the same row.[68b]

Conclusions

There are definite similarities between the structures of silyl and methyl derivativies. The only exceptions are H_3SiNH_2 and H_3SiOH, where greater bond angles are found at nitrogen and oxygen than in the corresponding methyl compounds. The lower hydrides of silicon favor states which have nonbonding electrons in silicon orbitals with a large degree of s-character, more than in the carbon analogues. This results in a greater separation between the $^2\Pi$ and $^4\Sigma^-$ states in SiH than in CH and accounts for a singlet state having the lowest energy in SiH_2, smaller H-Si-H bond angles, and a nonplanar structure of SiH_3. This requirement also plays a major role in the structure of unsaturated silicon molecules.[54]

The addition of *d*-functions to second-row molecules often reduces the bond lengths. In all cases, the optimized 3-21G$^{(*)}$ geometries are in better agreement with available experimental structures than the 3-21G geometries.

The results presented in Figures 1 and 2 show that the relative energies of H_3Si-X and H_3C-X bonds are mainly influenced by the electronegativity of the group X. Groups with either a very high or a very low electronegativity are found to make stronger bonds to silicon than to carbon. There does not appear to be any support to the contention that the bonds to silicon are strengthened or bond angles widened by π-donation into vacant d-orbitals.

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Registry No. SiH, 13774-94-2; SiH_2, 13825-90-6; SiH_3, 13765-44-1; SiH_4, 7803-62-5; H_3SiLi, 14311-51-4; H_3SiBeH, 98921-84-7; H_3SiBH_2, 14809-30-4; H_3SiCH_3, 992-94-9; H_3SiNH_2, 13598-78-2; H_3SiOH, 14475-38-8; H_3SiF, 13537-33-2; H_3SiNa, 16693-29-1; H_3SiMgH, 98921-85-8; H_3SiAlH_2, 56697-79-1; H_3SiSiH_3, 1590-87-0; H_3SiPH_2, 14616-47-8; H_3SiSH, 14044-97-4; H_3SiCl, 13465-78-6; CH, 3315-37-5; CH_2, 2465-56-7; CH_3, 2229-07-4; CH_4, 74-82-8; H_3CLi, 917-54-4; H_3CBeH, 6917-55-1; H_3CBH_2, 12538-96-4; H_3CCH_3, 74-84-0; H_3CNH_2, 74-89-5; H_3COH, 67-56-1; H_3CF, 593-53-3; H_3CNa, 18356-02-0; H_3CMgH, 63533-51-7; H_3CAlH_2, 27140-10-9; H_3CPH_2, 593-54-4; H_3CSH, 74-93-1; H_3CCl, 74-87-3.

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(171) In this paper the periodic group notation is given in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)