1486 *Organometallics* 1987, *6*, 1486–1490

AM1 Calculations for Compounds Containing Silicon

Michael J. S. Dewar* and Caoxian Jie

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

Received December 30, 1986

AM1 has been parametrized for silicon. Calculations are reported for a number of silicon compounds. The results are generally superior to those from MNDO. AM1 calculations for several reactions are in good agreement with experiment. AM1 should prove useful as a theoretical tool in studies of silicon chemistry.

Introduction

A new parametric SCF MO model (AM1) was recently reported[1] in which the major deficiency of MNDO[2] has been overcome, i.e. the overestimation of repulsive interactions between atoms when at separations greater than about 1.5 times the corresponding covalent bond distance. Extensive tests[1] and applications to a number of chemical problems[3] have given very encouraging results, and it seems clear that AM1 will prove an even more effective aid in organic chemistry than its precursors, MINDO/3[4] and MNDO.[2]

Treatments of this kind are of course restricted to the elements for which parameters are available. In the original paper, parameters were reported for the "organic" elements carbon, hydrogen, oxygen, and nitrogen, and parameters have also been optimized for the halogens[5] and zinc.[6] Here we report the extension of AM1 to silicon, an element of major interest in both organic and inorganic chemistry.

Procedure

The calculations were carried out by using the standard AM1 procedure[7] as implemented in the AMPAC computer program,[8] together with the previously determined parameters for C, H, O, and N[1] and the halogens.[5] The parameters for silicon were determined by a least-squares fit to experiment of the values calculated for various properties of a selected set (basis set) of molecules, using a recently described optimization procedure.[7] This involves the minimization of an error function, SSQ, defined as a sum of the squares of the differences between the individual calculated and experimental values, suitably weighted for different properties. The best values for the weighting factors are found by trial and error, on the basis of the chemical acceptability of the final results. The properties used in the parametrization included heats of formation, ionization energies, dipole moments, and geometries. The minimization of SSQ is affected by a derivative optimization method, based on the Davidon–Fletcher–Powell (DFP) algorithm.[9] The first derivatives of the heats of formation and ionization energies with respect to the various parameters were calculated analytically. The derivatives of the energy with respect to geometry were used as a measure of the deviation of the calculated geometry from the experimental.

Table I. Optimized AM1 and MNDO Parameters for Silicon

optimized parameter	value	MNDO
U_{ss}/eV	−33.953 622	−37.037 533
U_{pp}/eV	−28.934 749	−27.769 678
ζ_s/au	1.830 697	1.315 986
ζ_p/au	1.284 953	1.709 943
β_s/eV	−3.784 852	−9.086 804
β_p/eV	−1.968 123	−1.075 827
α/Å^{-1}	2.257 816	2.205 316
K_1	0.250 000	
K_2	0.061 513	
K_3	0.020 789	
L_1	9.000 000	
L_2	5.000 000	
L_3	5.000 000	
M_1	0.911 453	
M_2	1.995 569	
M_3	2.990 610	

Results and Discussion

Table I shows the final set of parameters obtained for silicon in the usual notation.[1] The corresponding MNDO values[10] are listed for comparison. An anomalous feature of the latter was the apparent inversion of ζ_s and ζ_p. Normally ζ_s is the greater, and this is also true for silicon in AM1. As Table I shows, the reverse was true in MNDO, ζ_p being indeed much greater than ζ_s. As we shall see presently, this is probably the main reason why the AM1 geometries are much better than the MNDO ones. The one-center, two-electron parameters (g and h) were kept constant at their previous values.[9]

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0276-7333/87/2306-1486$01.50/0

Table II. Calculated Heats of Formation, Ionization Potentials, and Dipole Moments for Molecules Containing Silicon[a]

	ΔH_f/kcal mol^{-1}			dipole moment/D			IP/eV		
compd	AM1	obsd	error	AM1	obsd	error	AM1	obsd	error
SiH	89.8	86.4	3.4	0.96			7.43		
SiH_2	67.8	58.6	9.2	1.08			7.76		
SiH_4	4.2	7.3	-3.1				12.35	12.36	-0.01
Si_2H_6	16.2	19.2	-3.0				10.65		
Si_3H_8	24.7	28.9[b]	-4.2	0.11			10.41		
SiH_3SiH	79.9	64.5[c]	15.4	1.17			8.03		
Si_2	139.6	142.0[b]	-2.4				8.91		
SiC_2	151.6	147.0[b]	4.6	3.03			8.71		
SiO_2	-67.5	-77.0[b]	9.5	0.00			11.46		
SiN	83.7	89.0[d]	-5.3	2.81			9.84		
$(CH_3)SiH_3$	-11.1	-7.8	-3.3	0.38	0.74	-0.36	11.62		
$(CH_3)_2SiH_2$	-25.6	-20.0	-5.6	0.45	0.75	-0.30	11.17		
$(CH_3)_3SiH$	-39.3	-37.4	-1.9	0.40	0.52	-0.12	10.94		
$(CH_3)_4Si$	-52.1	-57.1	5.0				10.91	10.29	0.62
$(CH_3)SiH$	45.2	50.9[c]	-5.7	1.81			7.40		
$H_2C{=}CHSiH_3$	11.4	-1.9	13.3	0.54	0.66	-0.12	10.40	10.40	0.00
$(CH_3)Si_2H_5$	1.3	12.6[c]	-11.3	0.60			10.20		
$(CH_3)_6Si_2$	-66.2	-86.8	20.6				8.85		
$(C_2H_5)_2SiH_2$	-36.3	-43.6	7.3	0.36			10.61		
$(C_2H_5)_3SiH$	-54.8	-48.0	-6.8	0.32			10.47		
$(C_2H_5)_4Si$	-71.2	-64.4	-6.8				10.27		
$(CH_3)_3SiOH$	-110.5	-119.4	8.9	1.82			10.82		
1,1-dimethylsilacyclobutane	-35.8	-33.0[e]	-2.8	0.93			10.05		
1,1-dimethylsilacyclopentane	-55.8	-43.4[e]	-12.4	0.34			10.51	9.00[f]	1.51
1,1,3,3-tetramethyl-1,3-disilacyclobutane	-75.3	-72.0[e]	-3.3	0.01			9.98		
$((CH_3)_3Si)_2O$	-167.6	-185.6[e]	18.0	0.01			10.14		
$(CH_3)_3SiNH(CH_3)$	-60.5	-54.2[e]	-6.3	0.31			9.08		
$(CH_3)_3SiN(CH_3)_2$	-55.3	-59.2[e]	3.9	0.16			8.79		
$NH(Si(CH_3)_3)_2$	-117.8	-113.8[e]	-4.0	0.46	0.41	0.05	9.49		
$N(Si(CH_3)_3)_3$	-154.4	-160.1[e]	5.7	0.05			9.56		
$N(CH_3)(Si(CH_3)_3)_2$	-110.7	-107.1[e]	-3.6	0.23			9.17		
SiF	-26.2	1.7	-27.9	0.25			7.17		
SiF_2	-154.6	-147.9	-6.7	0.96	1.23	-0.27	8.19		
SiF_4	-382.0	-385.9	3.9				14.72	16.45	-1.73
SiH_3F	-85.8			1.31	1.27	0.04	11.76		
SiH_2F_2	-181.5	-194.0	12.5	1.56	1.55	0.01	11.62	12.85	-1.23
$SiHF_3$	-280.9	-283.0	2.1	1.55	1.27	0.28	12.31		
SiCl	27.3	45.3	-18.0	0.18			7.53		
$SiCl_2$	-46.7	-39.6	-7.1	0.50			8.61		
$SiCl_3$	-116.0	-96.0[d]	-20.0	0.64			9.26		
$SiCl_4$	-170.9	-157.0	-13.9				12.98	12.03	0.95
SiH_3Cl	-37.7			1.64	1.31	0.33	11.56	11.61	-0.05
SiH_2Cl_2	-80.7			1.73	1.17	0.56	11.56	11.70	-0.14
$SiHCl_3$	-125.1	-122.6	-2.5	1.47	0.86	0.61	11.99	11.94	0.05
$(CH_3)_2SiHCl$	-69.9	-69.9	0.0	2.53			11.17		
$(CH_3)_3SiCl$	-84.8	-84.6	-0.2	2.70			11.14		
$(CH_3)SiHCl_2$	-98.4	-96.0	-2.4	2.45			11.49		
$(CH_3)_2SiCl_2$	-115.3	-107.1	-8.2	3.00			11.49		
$(CH_3)SiCl_3$	-143.9	-136.7	-7.2	2.52			12.06		
SiBr	47.0	50.0	-3.0	0.41			7.79		
$SiBr_2$	-5.9	12.2	-18.1	0.13			8.64		
$SiBr_4$	-94.5	-99.3	4.8				11.78	10.90	0.88
SiH_3Br	-21.1			1.80	1.31	0.49	10.98	11.03[f]	-0.05
$SiHBr_3$	-70.2	-75.9[b]	5.7	1.36			11.38		
$(CH_3)_3SiBr$	-66.4	-70.0	3.6	2.93			10.59		
SiI	80.5	76.4[g]	4.1	0.98			7.97		
SiH_3I				1.43	1.62[h]	-0.19	10.55	10.05[f]	0.50

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A. Heats of Formation, Dipole Moments, and Ionization Potentials. Table II compares with experiment the heats of formation (ΔH_f), dipole moments (μ), and ionization potentials (IP) calculated for a large number of molecules for which experimental data are available, including all those used in the earlier MNDO parametrization.[10] The calculated IPs are vertical ones estimated by using Koopmans' theorem. The average unsigned errors given by AM1 are compared with those from MNDO in Table III. It is clear that AM1 represents a dramatic improvement, the errors all being much less than in the case of MNDO. The average AM1 error in heats of formation is indeed little greater than that for the organic elements (C, H, O, N),[1] and there are now only two silicon

Table III. Comparison of Mean Absolute Errors of AM1 and MNDO

av error in	no. of compds	AM1	MNDO
heat of formatn, kcal/mol	52	7.47	12.81
dipole moment, D	15	0.35	1.00
ionizatn energy, eV	13	0.59	0.86

compounds for which the error is greater than 20 kcal/mol, i.e. $Si_2(CH_3)_6$ (20.6 kcal/mol) and SiF (−27.9 kcal/mol).

While the errors in the calculated IPs are also less than the MNDO ones, they are still rather large in some cases where the HOMOs contain large contributions from silicon. These large errors are probably[10] due mainly to use of the core approximation in AM1, though the neglect of d AOs may also be partly responsible.

The errors in the calculated dipole moments (Table III) are much smaller in AM1 than in MNDO. Indeed, the AM1 results are also much better than those given by MNDO for other third-period elements.[11,12] Since AM1 also gives good geometries for silicon compounds (see below), the fact that it reproduces dipole moments suggests that it is also giving good estimates of electron distributions. The formal charges given by AM1 (Table IV) certainly seem reasonable, unlike some of those from MNDO. Thus the MNDO values for the halogen atoms in SiH_3F (−0.527), SiH_3Cl (−0.537), SiH_3Br (−0.505), and SiH_3I (−0.359) are too large and seem inconsistent with their electronegativities whereas the AM1 values (−0.450, −0.299, −0.223, and −0.101, respectively) are quite reasonable.

The improvement is probably due more to our having located a better minimum on the parameter hypersurface than to superiority of the AM1 model. This indeed is indicated by the more reasonable values for the silicon parameters; see Table I. The situation concerning ζ_s and ζ_p has already been noted, and the AM1 value for β_s is also more reasonable, that in MNDO being unduly large. As we have pointed out elsewhere,[1,7] a major problem in parametrizing treatments such as AM1 is the complexity of the parameter hypersurface and the difficulty of finding the best minimum on it. The one located in the MNDO parametrization was clearly not optimal.

B. Cations and Radicals. Table V shows the heats of formation calculated by AM1 for some silicon-containing cations for which experimental values are available. The agreement is reasonable, whereas the errors in the MNDO values, also listed in Table V, are very large.

C. Molecular Geometries. Table VI shows the geometries calculated by AM1 for 40 molecules for which experimental geometries are available, the experimental values being shown in parentheses. The agreement is again better than it was in MNDO as is shown by the error analysis in Table VII. A major improvement is seen in the case of SiH bonds for which the MNDO values were systematically too small by 0.1–0.15 Å. The errors in the AM1 values are only one-fifth as great.

D. Vibrational Frequencies. Table VIII compares molecular vibration frequencies calculated by AM1 with experiment. The AM1 results are uniformly better than those[10] given by MNDO except for SiH bending vibrations and deformations. Thus the average error for 16 stretching vibrations is now 4.9% compared with 9.5% in MNDO.

Table IV. Calculated Formal Charge

molecule	atom (charge in e)
SiH	Si(+0.307), H (−0.307)
SiH_2	Si (+0.587), H (−0.294)
SiH_4	Si (+0.632), H (−0.158)
$(CH_3)SiH_3$	Si (+0.812), C (−0.528), H (−0.186)
$HC{\equiv}CSiH_3$	Si (+0.971), C (−0.480, −0.143), H (−0.187, +0.214)
Si_2H_6	Si (+0.350), H (−0.117)
$Si_2(CH_3)_6$	Si (+0.755), C (−0.510), H (+0.084)
Si_3H_8	Si (+0.413, −0.038), H (−0.120, −0.075)
SiH_3F	Si (+1.177), H (−0.242), F (−0.450)
SiH_3Cl	Si (+0.810), H (−0.170), Cl (−0.299)
SiH_3Br	Si (+0.635), H (−0.137), Br (−0.223)
SiH_3I	Si (+0.437), H (−0.112), I (−0.101)
$FSiBr_3$	Si (+1.063), F (−0.386), Br (−0.226)
$FSiCl_3$	Si (+1.375), F (−0.410), Cl (−0.392)
SiO	Si (+0.669), C (−0.669)
$(SiH_3)_2O$	Si (+1.190), H (−0.250), O (−0.898)

E. Unsaturated Molecules. Table IX compares the heats of formation and SiC or SiSi bond lengths calculated by AM1 and MNDO for compounds containing single, double, and triple SiC and SiSi bonds. Bond lengths calculated by ab initio procedures are included for comparison, together with an experimental value for methylsilane. AM1 agrees better with the latter and with the ab initio estimates than does MNDO.

Table X compares heats of reaction for some reactions of molecules containing silicon multiple bonds with corresponding ab initio values. Since the corresponding ab initio heats of hydrogenation for ethylene and acetylene are too negative by ca. 10 kcal/mol, it is likely that the same is true for the silicon-containing species. The results in Table X then suggest that AM1 overestimates the stabilities of silenes and disilenes by ca. 20 kcal/mol and that the corresponding errors for silynes and disilynes are very large.

Recent high-level ab initio calculations[13] have indicated that disilene is not planar, having a trans-bent structure. We checked that the planar structure given by AM1 was a minimum, by calculating force constants. The ab initio potential surface was, however, very flat, the difference in energy between the minimum and the planar (D_{2h}) structure being only 2.6 kcal/mol.[13] Experimental studies of heavily substituted disilenes have shown them to be essentially planar.[14] Ab initio calculations agree with AM1 in predicting silene to be planar.[14]

The barrier to rotation calculated for silene by AM1 was 52 kcal/mol. This is probably too large, as would be expected if AM1 does indeed overestimate the strength of the π bond. Experimental estimates and ab initio calculations have led to values close to 40 kcal/mol.[14] However, since the experimental values refer to tetrasubstituted silenes and since the electronic and steric effects of substituents would be expected to lower the barrier, the real value for silene itself may well be greater.

In the case of disilene, the barrier to rotation calculated by AM1 (31 kcal/mol) agrees well with those observed (25–31 kcal/mol) for tetrasubstituted derivatives.[14] The latest ab initio estimate was smaller (22 kcal/mol[14]).

The evidence certainly suggests that AM1 should not be used for compounds containing triply bound silicon. While the situation concerning doubly bound silicon is less

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Table V. Comparison with Experiment of AM1 and MNDO Heats of Formation (kcal/mol) for Cations

ion	heat of formation			error	
	obsd[a]	AM1	MNDO	AM1	MNDO
SiH_3^+	242.3	222.9	190.8	−19.4	−51.5
SiH_4^+	278.4	285.8	245.2	7.4	−33.2
$Si_2H_6^+$	251	241.9	216.9	−9.1	−34.1
SiF_4^+	−34.2	−43.5	b	−9.3	

[a] See footnote b, Table II. [b] Unable to get self-consistence.

Table VI. Calculated and Observed Geometrical Parameters[a]

molecule	bond lengths, Å[f]				bond angles, deg[f]			
SiH	SiH	1.454 (1.520)						
SiH_2	SiH	1.457 (1.516)			HSiH	100.5 (92.1)		
SiH_4	SiH	1.461 (1.481)						
Si_2H_6	SiH	1.466 (1.481)	SiSi	2.417 (2.327)	HSiSi	109.6 (111.1)		
$(CH_3)SiH_3$	SiC	1.806 (1.869)	SiH	1.463	HSiH	108.1 (108.2)	HCH	107.1 (107.7)
$(CH_3)_3SiH$	SiH	1.467 (1.489)	SiC	1.821 (1.868)	CSiH	107.7 (108.7)	HCSi	111.7 (111.0)
$(CH_3)_2SiH_2$	SiH	1.465 (1.483)	SiC	1.814 (1.867)	CSiC	113.2 (110.0)	HSiH	106.9 (107.8)
$H_2C{=}CHSiH_3$	SiH	1.464 (1.475)	SiC	1.764 (1.853)	HSiC	110.0 (110.2)	CCSi	123.3 (120.6)
$HC{-}CSiH_3$	SiH	1.463 (1.488)	SiC	1.703 (1.826)	HSiH	108.0 (110.2)		
SiO	SiO	1.572 (1.510)						
$O(SiH_3)_2$[b]	SiH	1.455 (1.486)	SiO	1.725 (1.634)	HSiO	109.5 (109.9)	SiOSi	154.3 (144.1)
SiN	SiN	1.485 (1.572)						
SiH_3CN	SiH	1.463 (1.488)	SiC	1.703 (1.826)	HSiH	108.0 (110.2)		
$H_3SiN{=}C{=}O$	SiH	1.465 (1.506)	SiN	1.673 (1.699)	HSiH	107.6 (110.4)		
SiF_2	SiF	1.612 (1.59)			FSiF	96.9 (100.8)		
SiH_3F	SiH	1.456 (1.485)	SiF	1.621 (1.593)	HSiF	110.7 (108.4)		
$SiHF_3$	SiH	1.439 (1.447)	SiF	1.610 (1.562)	FSiF	107.0 (108.3)		
$(CH_3)SiH_2F$	SiH	1.459 (1.477)	SiC	1.801 (1.849)	HSiH	107.2 (110.0)	CSiH	109.4 (112.5)
	SiF	1.622 (1.597)			CSiF	111.9 (108.9)		
$(CH_3)SiHF_2$	SiH	1.452 (1.471)	SiF	1.619 (1.580)	FSiF	104.4 (107.1)	CSiH	109.0 (115.5)
	SiC	1.794 (1.840)			CSiF	111.9 (109.4)		
$(CH_3)SiF_3$	SiC	1.783 (1.812)	SiF	1.612 (1.574)	HCSi	112.3 (110.0)		
F_3SiSiH_3	SiSi	2.517 (2.319)	SiH	1.469 (1.480)	SiSiH	109.3 (108.7)	SiSiF	114.1 (112.0)
	SiF	1.612 (1.561)						
$SiCl_3$	SiCl	2.01 (2.02)			ClSiCl	104.8 (110.9)		
SiHCl	SiH	1.459 (1.561)	SiCl	2.021 (2.064)	SSiCl	102.5 (102.8)		
SiH_3Cl	SiH	1.460 (1.485)	SiCl	2.071 (2.049)	HSiCl	109.8 (108.7)		
SiH_2Cl_2	SiH	1.461 (1.480)	SiCl	2.060 (2.033)	ClSiCl	109.7 (109.7)		
$SiHCl_3$	SiH	1.459 (1.470)	SiCl	2.051 (2.021)	ClSiH	109.8 (109.5)		
SiF_3Cl	SiF	1.605 (1.560)	SiCl	2.078 (1.989)				
$SiFCl_3$	SiF	1.612 (1.520)	SiCl	2.054 (2.019)	FSiCl	110.4 (109.5)	ClSiCl	108.6 (109.4)
$(CH_3)SiHCl_2$	SiH	1.461 (1.467)	SiC	1.790 (1.850)	CSiH	110.4 (110.9)	CSiCl	111.1 (109.8)
	SiCl	2.073 (2.040)			ClSiCl	108.1 (108.8)		
$(CH_3)SiCl_3$	SiC	1.785 (1.876)	SiCl	2.061 (2.021)				
$(CH_3)_3SiCl$	SiCl	2.121 (2.022)	SiC	1.811 (1.857)	ClSiC	107.4 (110.5)		
$(C_2H_5)SiH_2Cl$	SiH	1.392 (1.478)	SiCl	2.042 (2.060)	CSiCl	107.5 (109.9)	CSiH	110.3 (113.6)
	SiC	1.834 (1.869)			SiCC	113.4 (111.3)		
SiH_3Br	SiH	1.464 (1.481)	SiBr	2.234 (2.21)	HSiBr	110.3 (107.9)		
$SiHBr_3$	SiH	1.476 (1.494)	SiBr	2.240 (2.17)	BrSiH	108.2 (110.0)		
SiF_3Br	SiBr	2.295 (2.153)	SiF	1.607 (1.560)	FSiF	106.6 (108.5)		
$SiFBr_3$	SiBr	2.266 (2.171)	SiF	1.620	BrSiBr	107.8 (111.6)		
$(CH_3)_3SiBr$	SiBr	2.288 (2.235)	SiC	1.816 (1.856)	CSiBr	107.9 (107.5)		
ISiH	SiI	2.424 (2.451)	SiH	1.453	HSiI	103.2 (102.7)		
$ISiH_3$	SiH	1.466 (1.487)	SiI	2.434 (2.437)	HSiI	109.8 (108.4)		
$ISiF_3$	SiI	2.508 (2.387)	SiF	1.609	FSiI	112.4		

[a] Except where noted, experimental geometries are taken from: Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; et al. *J. Phys. Chem. Ref. Data* **1979**, *8*(3). [b] Almenningen, A.; Bastiansen, O.; Ewing, V.; Hedberg, K.; Traettegerg, M. *Acta Chem. Scand.* **1963**, *17*, 2455. [c] Stull, D. R.; Prophet, H., et al. *JANAF Thermochemical Tables*, 2nd ed.; U.S. Department of Commerce, National Bureau of Standards, 1970. [d] Harmony, M. D.; Strand, M. R. *J. Mol. Spectrosc.* **1980**, *81*, 308–315. [e] Kawley, R.; McKinney, P. M.; Robiette, A. G. *J. Mol. Spectrosc.* **1970**, *34*, 390. [f] Observed geometrical parameters are given in parentheses.

Table VII. Errors in Geometry of AM1 and MNDO

type of parameters in geometry	av error	
	AM1	MNDO
bond length, Å		
Si–H	0.028	0.112
Si–C	0.063	0.062
Si–F	0.043	0.023
Si–Cl	0.040	0.069
Si–Br	0.076	0.031
bond angle, deg		
H–Si–H	1.9	1.2
F–Si–F	2.4	3.8
Cl–Si–Cl	1.5	1.6
H–Si–Cl	0.6	2.2

clear, AM1 does seem to overestimate the stabilities of such species. We have not felt it worth while to try to correct this apparent error because compounds of multiply bound silicon are of limited chemical significance and because no accurate and reliable thermochemical data are available. The only estimates of heats of formation come from indirect inferences of uncertain reliability; see e.g. ref 15. Ab initio calculations do not provide an adequate substitute because the errors in the values given by them are un-

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(15) Olbrich, G.; Potzinger, P.; Reimann, B. *Organometallics* **1984**, *3*, 1267.

Table VIII. Vibration Frequencies

compd	assignt	descriptn	AM1, cm^{-1}	expt, cm^{-1}	% error	ref
$SiHD_3$		Si-H stretch	2254	2187.2	3.1	*a*
$SiHF_3$		Si-H stretch	2267	2316.8	2.1	*a*
$SiHCl_3$		Si-H stretch	2192	2260.3	3.0	*a*
Si_2HD_5		Si-H stretch	2232	2162.5	3.2	*a*
SiH_4	A	symmetric stretch	2258	2185	3.3	*b*
	T	asymmetric stretch	2255	2189	3.0	
	E	asymmetric bend	854	972	12.0	
	T	asymmetric bend	770	913	15.6	
CH_3SiH_3	A1	SiH_3 stretch	2249	2169	3.6	*c*
	E	SiH_3 stretch	2242	2166	3.5	
	E	SiH_3 bend	826	946	12.6	
	A1	SiH_3 deformation	826	946	12.6	
	A1	Si-C stretch	675	701	3.7	
	E	SiH_3 rock	511	545	6.2	
$CH_3C{\equiv}CSiH_3$	A	Si-H stretch	2248	2182	3.0	*d*
	E	Si-H stretch	2243	2182	2.8	
	A	Si-H deformation	821	943	12.9	
	E	Si-H deformation	833	937	11.1	
	E	SiH_3 rock	635	697	8.9	
	A	Si-C stretch	580	523	10.9	
	E	Si-C-C bend	181	132	37.1	
HSiOH (trans)	a′	O-H stretch	3579	3650	1.9	*e*
	a′	Si-H stretch	2228	1872	19.0	
	a′	H-Si-O bend	901	937	3.8	
	a′	Si-O stretch	901	851	5.9	
	a′	Si-O-H bend	661	723	6.6	
	a′	torsion	626	595	5.2	
c-$C_3H_5SiHD_2$		Si-Ha stretch	2241	2162.7	3.6	*f*
		Si-Hs stretch	2248	2157.8	4.1	

[a] McKean, D. C.; Torto, I.; Morrisson, A. R. *J. Phys. Chem.* **1982**, *86*, 307. [b] Kattenberg, H. W.; Oskam, A. *J. Mol. Spectrosc.* **1974**, *49*, 52. [c] Wilde, R. E. *J. Mol. Spectrosc.* **1962**, *8*, 427. [d] Cradock, S.; Koprowski, J.; Rankin, D. W. H. *J. Mol. Struct.* **1981**, *77*, 113. [e] Ismail, Z. K.; Hauge, R. H.; Fredin, L.; Kauffman, J. W.; Margrave, J. L. *J. Chem. Phys.* **1982**, *7*, 1617. [f] McKean, D. C.; Morrisson, A. R.; Dakkouri, M. *Spectrochim. Acta, Part A* **1984**, *40A*, 771.

Table IX. Compounds Containing Multiply Bonded Silicon

	ΔH_f, kcal/mol		Si-X bond length, Å			
compd	AM1	MNDO	AM1	MNDO	ab initio	obsd.
$H_3Si{-}SiH_3$	15.9	22.4	2.417	2.173	2.352[a]	2.327[b]
$H_2Si{=}SiH_2$	54.5	74.9	2.055	1.967	2.19[c]	2.16,[cd] 2.14[cef]
$HSi{\equiv}SiH$	80.8	127.0	1.767	1.806	*g*	
$H_3C{-}SiH_3$	-11.1	-14.0	1.807	1.800	1.882[h]	1.869[b]
$H_2C{=}SiH_2$	21.8	38.0	1.605	1.607	1.70[c]	1.702[c]
$HC{\equiv}SiH$	58.9	101.2	1.489	1.471	1.59[c]	

[a] Glidwell, C. *J. Organomet. Chem.* **1981**, *217*, 11. [b] See Table VI. [c] See Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419 [d] Tetramesityldisilene. [e] Tetrakis(2,6-diethylphenyl)disilene. [f] 1,2-Di-*tert*-butyl-1,2-dimesityldisilene. [g] Not a minimum; see ref c. [h] Magnusson, E. *Tetrahedron* **1985**, *41*, 2945.

Table X. Heats of Reaction (kcal/mol)

reaction	AM1	ab initio
$H_2C{=}SiH_2 \rightarrow H_3CSiH$	23.5	-0.4[a]
$HC{\equiv}SiH \rightarrow H_2C{=}Si$	11.1	-49.1[b]
$H_2Si{=}SiH_2 \rightarrow H_3SiSiH$	25.4	-8.1[a]
$H_2C{=}Si + H_2 \rightarrow H_2C{=}SiH_2$	-43.0	-31.0[c]
$H_2C{=}SiH_2 + H_2 \rightarrow H_3CSiH_3$	-27.7	-56.9[c]
$HC{\equiv}SiH + H_2 \rightarrow H_2C{=}SiH_2$	-31.9	-71.7[c]
$SiO + H_2 \rightarrow H_2Si{=}O$	-11.8	2.5[d]
$H_2Si{=}O \rightarrow$ HSiOH(trans)	-2.6	-3.7[d]
$H_2Si{=}O + H_2O \rightarrow H_2Si(OH)_2$	-61.3	-72.6[d]

[a] Yoshioka, Y.; Goddard, J. D.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1981**, *103*, 2452. [b] Hoffmann, M. R.; Yoshioka, Y.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1983**, *105*, 1084. [c] Gordon, M. S.; Pople, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 2945. [d] Kudo, T.; Nagase, S. *J. Phys. Chem.* **1984**, *88*, 2833.

known. The errors in ab initio values for heats of reaction or activation can be estimated only by comparison with experiment, and here the lack of experimental data makes such comparisons impossible. Preliminary attempts to improve the agreement between the AM1 and ab initio results led moreover to unacceptable errors in the AM1 values for other silicon compounds.

Table XI. Heats of Activation (kcal/mol)

reaction	AM1	obsd[a]
$Si_2H_6 \rightarrow :SiH_2 + SiH_4$	49.0	49.3
$CH_3Si_2H_5 \rightarrow :SiH_2 + CH_3SiH_3$	50.0	50.7
$CH_3Si_2H_5 \rightarrow :SiH(CH_3) + SiH_4$	44.2	49.9
$Si_3H_8 \rightarrow :SiH_2 + Si_2H_6$	51.2	53.0
$Si_3H_8 \rightarrow :SiH(SiH_3) + SiH_4$	48.8	49.2

[a] References 13 and 14.

F. Activation Energies of Some Reactions. Table XI compares activation energies calculated by AM1 for some simple reactions of silicon compounds with those observed in the gas phase.[16,17] The agreement is clearly satisfactory. Further studies of silicon chemistry are in progress.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Grant AF86-0022) and the Robert A. Welch Foundation (F-126).

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(16) Bowery, M.; Purnell, J. H. *Proc. R. Soc. London, A* **1971**, *321*, 341.

(17) Vanderwielen, A. J.; Ring, M. A.; O'Neal, H. E. *J. Am. Chem. Soc.* **1975**, *97*, 993-8.