J. Org. Chem. 1988, *53*, 5248–5258

was taken up in pH 2.2 citrate buffer and injected onto the 6-mm column of the amino acid analyzer to reveal only asparagine and β-cyanoalanine in the 3:2 ratio seen earlier. No α-aminosuccinimide (retention 69 min; authentic standard made by the procedure of Sondheimer and Holley[38a]) was observed.

Methionine-Enkephalin (H-Tyr-Gly-Gly-Phe-Met-OH). Preformed Fmoc-Met-OPbs **16c** was loaded onto a leucyl-MBHA resin (186 mg, 78 μmol Leu) by the general procedure already stated; amino acid analysis of the resin showed 0.32 mmol of Met/g (77%). The appropriate Fmoc-amino acids were introduced by the general protocol (Table II), and all couplings were found to be ninhydrin negative after 60 min. After the final coupling of Fmoc-Tyr(*t*-Bu)-OH and Fmoc deprotection, a portion of the peptide-resin (150 mg) was cleaved (93% cleavage yield) by the general fluoridolysis procedure already stated. The resultant material was treated with TFA/CH_2Cl_2/dimethyl sulfide (5:4:1) (2 mL) for 30 min to remove the *tert*-butyl protection of the tyrosine phenolic hydroxyl. Solvents were evaporated to provide an oil, which was again washed with diethyl ether (3 × 3 mL). A light tan solid remained, which was taken up in water and lyophilized to yield a white solid (33.9 mg); amino acid analysis: Gly, 1.79; Met, 0.7; Tyr, 1.00; Phe, 1.00. HPLC analysis [C-18 column; eluant 0.01 N aqueous HCl-CH_3CN (3:1), flow 0.9 mL/min; detection 210 nm] revealed desired product (t_R 12.6 min) and the corresponding sulfoxide (t_R 8.2 min), in a ration of $\approx$3:1. Fluoridolytic cleavage in the absence of scavengers gave additional peaks (t_R 10.7 min, $\approx$15%; t_R 19.3 min $\approx$20%). Cleavage of peptide-resin (24 mg) with TFA/CH_2Cl_2/dimethyl sulfide (5:4:1) containing thiophenol (1.2 μL, 12 μmol), 30 min, gave a white solid (4.5 mg, cleavage yield >99% by amino acid analysis of cleaved resin) that was methionine-enkephalin and the corresponding sulfoxide in a ratio of $\approx$3:1, with no other products present.

Methionine-enkephalin and the corresponding sulfoxide were each obtained in pure form from the same preparative MPLC run and matched authentic standards from this laboratory.[6d,44] Methionine-enkephalin FAB MS, *m/e* (relative intensity), positive 574 (MH^+, 21), 185 (43), 136 (48), 120 (100); negative 572 [$(M - H)^-$, 100], 557 [$(M - CH_3)^-$, 20], 153 (64), 127 (50); methionine enkephalin sulfoxide FAB MS, *m/e* (relative intensity), positive: 590 (MH^+, 18), 185 (100), 136 (40), 120 (82); negative 588 [$(M - H)^-$, 42], 573 [$(M - CH_3)^-$, 14], 183 (100), 127 (55).

Fmoc-Glu(*O*-*t*-Bu)-Ala-Tyr(*t*-Bu)-Gly-OH. Preformed Fmoc-Gly-OPbs **16b** was loaded onto a leucyl-MBHA resin (200 mg, 84 μmol of Leu) by the general procedure; amino acid analysis of the resin showed 0.28 mmol of Gly/g (67%). Chain assembly was performed by the general protocol (Table II), and all couplings were ninhydrin negative after 60 min. A sample of resin (34.4 mg) was cleaved by the general procedure (both thiophenol and DIEA were added as scavengers) (cleavage yield 90%) to give a solid, which was dissolved in CH_3CN–water (3:1) and lyophilized. A light tan powder resulted (9.9 mg); amino acid analysis: Glu, 0.93; Gly, 1.00; Ala, 0.95; Tyr, 0.94. HPLC analysis [C-18 column; linear gradient taken from 0.01% aqueous HCl-CH_3CN (9:1) to neat CH_3CN over 40 min, flow 1.5 mL/min; detection 210 nm] of the crude peptide showed one large peak eluting at 23.5 min with small contaminants eluting at 17.6 ($\approx$10%) and 19.3 min (<1%). The peptide was purified by MPLC ($\approx$6 mg crude peptide), eluting with CH_3CN/0.01 N HCl (5:95) (flowrate $\approx$1.75 mL/min) for $\approx$15 min to elute the polar impurities, followed by a gradient to neat CH_3CN over $\approx$6 h. The fractions containing the 23.5 min (HPLC) product were pooled and lyophilized to yield 1.7 mg of a white powder; amino acid analysis: Glu, 0.79; Gly, 1.00; Ala, 0.96; Tyr, 0.95; FAB MS, *m/e* (relative intensity), positive 773 (MH^+, 10), 423 {[Fmoc-Glu(*O*-*t*-Bu)-(CO)NH]$^+$, 10}, 179 [(fluorenyl-$CHCH_2$)$^+$, 100]; negative 807 [$(M + Cl)^-$, 8], 771 (M^-, 15), 715 [$(M - t\text{-Bu})^-$, 6], 549 [$(M - \text{Fmoc})^-$, 51], 107 (100). The impurities were also collected (the 17.6- and 19.3-min impurities eluted together off the MPLC column) and lyophilized to yield 0.7 mg (total recovery from MPLC was 40%) of a white powder; amino acid analysis: Glu, 1.00; Gly, 0.11; Ala, 2.94; Tyr, 0.90.

Acknowledgment. We thank Dr. Fernando Albericio for helpful discussions, Henkel for a graduate fellowship to D.G.M., and the National Institutes of Health (Grant GM 28934) for financial support.

Supplementary Material Available: Discussion and documentation of preliminary studies directed at the preparation and evaluation of the following classes of compounds: silyl esters cleaved by direct fluoridolysis of Si–O bond, 2-silylethyl esters fluoridolyzed by a β-elimination, and a model *p*-siloxybenzyl ester cleaved by a 1,6-elimination (5 pages). Ordering information is given on any current masthead page.

The MM2 Force Field for Silanes and Polysilanes[1]

Manton R. Frierson, Mita R. Imam, Vera B. Zalkow,[†] and Norman L. Allinger*

School of Chemical Sciences, University of Georgia, Athens, Georgia 30602

Received November 27, 1987

The MM2 force field has been extended so as to be able to deal with silanes, alkenyl derivatives of silanes, and polysilanes. Parameters have been chosen so that the available experimental structural and heat of formation data were fit as well as possible. The results are good and make possible molecular mechanics calculations on compounds of these classes.

Introduction

The MM2 force field[1-3] has been extended to include silanes. A large volume of data (both experimental and ab initio) has appeared in the literature since our previous paper was published on silanes,[4] and most of these data have been taken into account in the development and parameterization of this new force field. An improvement in the MM2 force field that is important here was the introduction of the electronegativity correction for bond lengths.[5] Since silicon is electropositive with respect to carbon, when a silicon atom is attached to a C_{sp^3}–C_{sp^3} bond, it causes the bond to stretch out. This elongation of a C_{sp^3}–C_{sp^3} bond due to an attached silicon atom has been

---

[†] Present address: Chemistry Department, Kennesaw College, Marietta, GA 30061.

(1) Most of the material in this paper was taken from the dissertation submitted by Manton R. Frierson to the University of Georgia in partial fulfillment of the requirements for the Ph.D. degree, March 1984.

(2) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982.

(3) The MM2 force field for hydrocarbons was first described by Allinger: Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. Extensions to functionalized molecules and all other sorts of special problems have been described in subsequent papers, which are summarized in ref 2. The original version of the program (MM2(77)) is available from the Quantum Chemistry Program Exchange, University of Indiana, Bloomington, IN 47405, Program 395. The latest version of the MM2 program, which is referred to as MM2(85), is available from the Quantum Chemistry Program Exchange, and also from Molecular Design Limited, 2132 Farallon Drive, San Leandro, CA 94577.

0022-3263/88/1953-5248$01.50/0

taken into account in the MM2 force field by increasing the natural bond length (l_0) of such a C–C bond by 0.015 Å. This electronegativity effect is automatically taken into account by the program.

Results

The van der Waals, stretching, bending, torsional, stretch–bend, dipole, and heat of formation parameters determined for silicon are listed in Table I.

The stretching and bending force constants were taken from the literature where available. Most of these were spectroscopic values. One exception was the stretching force constant for the Si–C_{sp^2} bond, which was an ab initio value.[7] The bending constants were scaled by 0.6.

Bond moments were picked so that the calculated values for the dipole moments of some simple model compounds agreed well with the reported experimental values.

The stretch–bend interaction constants were chosen by adjusting them until the structural parameters (bond lengths and angles) for highly strained compounds were fit as well as possible.

Torsional constants involving silicon were reported earlier.[4] Included in the present work are compounds containing a Si–C_{sp^2} bond. The barriers were assumed to be 3-fold except where it was obviously necessary to include 1- or 2-fold barriers as in angles involving C_{sp^2}. A few important torsional barriers involving Si and C_{sp^2} were determined by crucial spectroscopic measurements of barriers in phenylsilanes,[13] vinylsilane,[14] and methylvinylsilane[15] and the constants were already chosen for the earlier force field.[4] The torsional constants C_{sp^2}–C_{sp^2}–Si–C and C_{sp^2}–C_{sp^2}–Si–H were determined from these measurements and other torsional barriers analogous to these were derived from them. The 3-fold torsional constants for the saturated silanes were derived from experimental measurements of the torsional barriers for methylsilane (defines HSiCH), tetramethylsilane (defines CSiCH), and ethylsilane (defines HSiCC) and the interconversion barrier for silacyclopentane, which determines the torsional constant for the dihedral angle CSiCC.

The silanes constitute the largest group of compounds studied in the present work. They are also important in determining many of the parameters used in the force field. For this set of compounds, we also have the results of independent calculations such as MNDO/3 (for the silanes), as well as the results of earlier force fields.[4,31]

In Table II we present the results of our calculations, compared to experiment, MNDO/3, and earlier force field results. In general there is good agreement between our results and experiment, and we think that with the qualifications listed below, our results offer the best overall fit. At the end of the table we have tabulated average absolute errors for a few key structural features. As can be seen from these numbers and comparison to reported values of experimental errors, MM2 does just about as well as experiment.

Standardization of the Experimental Results. An important feature to note in examining Table II is that many of the experimental structures of the smaller and simpler silanes (especially the methylsilanes) were determined by microwave spectroscopy (MW). In these cases, MM2 calculates what appears to be extremely long SiC bond lengths relative to the experimental values. With MM2 we have tried to duplicate experimental values obtained from electron diffraction (r_g). Since these methods differ in the way they handle vibrational motion, they often arrive at different values for bond lengths. It is not easy to make an accurate correction. Instead, we compare two (or more) experimental results obtained by the different methods in the case of the same (or at least very similar) compounds to arrive at an empirical correction factor. In the case of the SiC bond, this factor has been set at +0.010 Å, which is added to the microwave-determined value (usually r_s) to give a number comparable to ED-determined and molecular mechanics values (r_g). When the correction is added to the MW-determined SiC bond lengths in Table II, we see that the agreement between MM2 and experiment is much improved.

The bond lengths obtained by X-ray crystallography correspond approximately to r_{α_0} values after correction for thermal motion, while the angles are similar to those obtained in electron diffraction. Unfortunately, most X-ray data in the literature was determined at room temperature and have not been corrected for thermal motion. Therefore, the bond lengths tend to be pretty inaccurate, and we have just used them directly from the literature, without attempting corrections.

One might think that the increased C–Si bond lengths in silanes (compared to C–C bond lengths in hydrocarbons) leads to decreased barriers merely because we have moved to a lower energy portion of the repulsive part of the H···H interaction curve. Instead, the kind of distances we are talking about (~3.5 Å) result in attractive forces and we are near the bottom of the van der Waals potential well, as Oulette pointed out in his studies.[31] This leads to some surprising conformational preferences if one is familiar

---

(4) Tribble, M. T.; Allinger, N. L. *Tetrahedron* **1972**, *28*, 2147.

(5) Allinger, N. L.; Imam, M. R.; Frierson, M. R.; Yuh, Y. H.; Schafer, L. *Mathematics and Computational Concepts in Chemistry*; Trinajstic, N., Ed.; E. Horwood, Ltd.: London, 1986; p 8.

(6) Dellepiane, G.; Zerbi, G. *J. Chem. Phys.* **1968**, *48*, 3573.

(7) Ab initio calculated force constant; see: Trinquier, G.; Malrieu, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 6313.

(8) Shimanouchi, T.; Nakagawa, I.; Hiraishi, I.; Ishii, M. *J. Mol. Spect.* **1960**, *19*, 78.

(9) Hengge, E. *Topics in Current Chemistry*; *Silicon Chemistry II. Properties and Preparations of Silicon Linkages*; Springer-Verlag; New York, 1974; Vol. 51.

(10) Burger, H.; Kilian, W. *J. Organomet. Chem.* **1969**, *18*, 299.

(11) Hassler, K.; Kovar, D.; Hengge, E. *Spectrochim. Acta* **1978**, *34A*, 1193. Hengge, E.; Hofler, F.; Bauer, G. *Spectrochim. Acta* **1976**, *32A*, 1435.

(12) These values were previously assigned and discussed. See ref 4.

(13) Schaefer, T.; Parr, W. J. E. *Can. J. Chem.* **1977**, *55*, 2835.

(14) O'Reilly, J. M.; Pierce, L. *J. Chem. Phys.* **1961**, *34*, 1176.

(15) Imachi, M.; Nagayama, A.; Nakagawa, J.; Hayashi, M. *J. Mol. Struct.* **1981**, *77*, 81.

(16) Kilb, R. W.; Pierce, L. *J. Chem. Phys.* **1957**, *27*, 108.

(17) Verwoerd, W. S. *J. Comput. Chem.* **1982**, *3*, 445.

(18) First column: Oullette, R. J. *J. Am. Chem. Soc.* **1972**, *94*, 7674, values in parentheses from ref 4.

(19) Pierce, L. *J. Chem. Phys.* **1959**, *31*, 547.

(20) Pierce, L.; Petersen, D. H. *J. Chem. Phys.* **1960**, *33*, 907.

(21) Beagley, B.; Monaghan, J. J.; Hewitt, T. G. *J. Mol. Struct.* **1971**, *8*, 401.

(22) Durig, J. R.; Craven, S. M.; Bragin, J. *J. Chem. Phys.* **1970**, *52*, 2046. Aston, J. G.; Kennedy, R. M.; Messerly, G. H. *J. Am. Chem. Soc.* **1941**, *63*, 2343.

(23) Hayashi, M.; Matsumura, C. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 732.

(24) Durig, J. R.; Groner, P.; Lopata, A. D. *Chem. Phys.* **1977**, *21*, 401.

(25) Csakvari, B.; Wagner, Z. S.; Hargittai, I. *Acta Chim. Sci. Hung.* **1976**, *90*, 141.

(26) Doun, S. K.; Bartell, L. S. *J. Mol. Struct.* **1980**, *63*, 249.

(27) Beagley, B.; Conrad, A. R.; Freeman, J. M.; Monaghan, J. J.; Norton, B. G.; Halywell, G. C. *J. Mol. Struct.* **1972**, *11*, 371.

(28) Hummel, J. P.; Stackhouse, J.; Mislow, K. *Tetrahedron* **1977**, *33*, 1925.

(29) Yukitoshi, T.; Suga, H.; Seki, S.; Itoh, J. *J. Phys. Soc. Jpn.* **1957**, *12*, 506.

(30) Bartell, L. S.; Clippard, F. B., Jr.; Boates, T. L. *Inorg. Chem.* **1970**, *9*, 2346.

(31) (a) Oullette, R. J. *J. Am. Chem. Soc.* **1974**, *96*, 2421. (b) Oullette, R. J. *Tetrahedron* **1972**, *28*, 2163.

Table I. Force Field Parameters for Silanes and Polysilanes[a]

	van der Waals		bond dipole	
atom	radius	ε(hardness)	bond	μ[b]
Si	2.25	0.147	C–Si	–0.60 (–0.65)

stretching				
bond	l_0	K_s(MM2)	K_s(exptl)	ref
C–Si	1.880	2.97	3.0	6
C(sp^2)Si	1.865	3.50	(3.50)	7
SiH	1.489	2.72	2.75	8
SiSi	2.332	1.85	1.4–2.5	9
SiC[c]	1.860	3.5	–	–
CC[d]	electronegativity correction for silicon = 0.015			

stretch–bend interaction constants

k_{SB} = 0.20 for X–Si–Y (X, Y ≠ H, D); k_{SB} = 0.06 for X–Si–H

bending						bending					
angle	θ	K_θ(MM2)	K_θ(lit.)	type[e]	ref	angle	θ	K_θ(MM2)	K_θ(lit.)	type[e]	ref
CSiSi	110.0	0.75	0.75	1	10	HSiH	104.5	0.380	–	1	12
SiCH	110.8	0.32	–	2	–		108.7			2	
	107.0			3			109.5			3	
SiSiH	111.0	0.378	0.378	all	10	SiSiC(sp^2)	110.2	0.40	–	1	–
SiSiSi	111.3	0.350	0.350	1	11	C(sp^2)SiC(sp^2)	109.5	0.60	–	1	*f*
	110.0			3		C(sp^2)SiH	109.5	0.24	–	all	12
CSiC	110.8	0.48	–	1	12	CSiC(sp^2)	110.2	0.40	–	all	12
	110.4			2		SiC(sp^2)Si	120.0	0.40	–	all	–
	108.5			3		SiC(sp^2)H	120.0	0.40	–	all	–
CCSi	109.0	0.40	–	1	12	C(sp^2)C(sp^2)Si	122.5	0.40	–	all	–
	110.9			2		HSiC[f]	110.2	0.46	–	–	–
SiCSi	112.7	0.40	–	3	12	SiCC[f]	117.5	0.53	–	–	–
	115.0			1		HCSi[f]	123.5	0.24	–	–	–
C(sp^2)CSi	109.5	0.50	–	1	12	CSiC[g]	90.5	0.45	–	1	–
	110.5		–	2			90.5			3	–
	110.5			3		CCSi[g]	94.5	0.30	–	3	–
CSiH	109.3	0.46	–	1	12						
	107.0			2							
	110.2			3							

torsion				torsion			
	V_1	V_2	V_3		V_1	V_2	V_3
CCCSi	0.0	0.0	0.50	C(sp^2)C(sp^2)SiH	0.0	0.0	0.0
C(sp^2)CCSi	0.0	0.0	0.167	HC(sp^2)SiC	0.0	0.0	0.717
HCCSi	0.0	0.0	0.105	HC(sp^2)SiH	0.0	0.0	0.500
SiCCSi	0.0	0.0	0.167	HCSiC(sp^2)	0.0	0.0	0.117
SiCC(sp^2)C(sp^2)	0.0	0.0	0.0	C(sp^2)SiSiC	0.07	0.27	0.093
SiCC(sp^2)H	0.0	0.0	0.717	C(sp^2)SiC(sp^2)H	0.0	0.0	0.600
CCSiC(sp^2)	0.0	0.0	0.167	C(sp^2)CSiC(sp^2)	0.0	0.0	0.400
CCSiC	0.0	0.0	0.167	C(sp^2)SiC(sp^2)C(sp^2)	0.0	0.0	0.400
CCSiH	0.0	0.0	0.272	C(sp^2)SiSiH	0.0	0.0	0.450
C(sp^2)CSiC	0.0	0.0	0.167	C(sp^2)SiSiC(sp^2)	0.0	0.0	0.400
C(sp^2)CSiH	0.0	0.0	0.167	CSiC(sp^2)C	0.0	0.0	0.35
HCSiC	0.0	0.0	0.200	CC(sp^2)SiC(sp^2)	–0.44	–0.24	0.060
HCSiH	0.0	0.0	0.176	SiSiC(sp^2)C(sp^2)	–0.44	–0.24	0.060
SiCSiC	0.0	0.0	0.167	HSiC(sp^2)C(sp^2)	0.0	0.0	0.0
SiCSiH	0.0	0.0	0.167	HC(sp^2)SiH	0.0	0.0	0.520
CCSiSi	0.0	0.0	0.300	SiC(sp^2)C(sp^2)Si	0.0	15.0	0.0
HCSiSi	0.0	0.0	0.270	SiC(sp^2)C(sp^2)C(sp^2)	0.0	15.0	0.0
CSiSiC	0.0	0.0	0.633	C(sp^2)C(sp^2)SiC(sp^2)	0.10	0.0	0.50
CSiSiSi	0.0	0.0	0.300	HSiCH	0.0	0.0	0.50
HSiSiH	0.0	0.0	0.136	HSiCC	0.0	0.0	0.083
HSiSiSi	0.0	0.0	0.070	SiCCC	0.20	0.270	0.093
SiSiSiSi	0.0	0.0	0.100	HCCSi	0.0	0.0	0.120
CC(sp^2)C(sp^2)Si	0.0	15.0	0.0	CCCSi	0.10	0.0	0.90
HC(sp^2)C(sp^2)Si	0.0	15.0	0.0	CCSiC	0.10	0.0	0.90
C(sp^2)C(sp^2)SiC	0.0	0.0	0.0				

[a] Units: distance, Å; *E*, kcal/mol; dipole moments, D; bending angles, deg; stretching constants, mdyne/Å; bending constants, mdyne/rad^2; torsional constants, kcal/mol-deg. [b] Values in parentheses are for sp^2-hybridized carbon (no parentheses, for sp^3-); the sign of the moment is determined as follows: for bond X–Y, the sign of the moment is positive if X is the positive end of the dipole and negative if X is the negative. [c] Silicon–carbon bond where the attached carbon is part of cyclopropyl ring; use the same force constant as for SiC(sp^2). [d] A bond length correction added to the indicated bond due to the attachment of the indicated heteroatom. [e] Type refers to the substitution pattern about the central atom: 1 = X–CR$_2$–Y, 2 = X–CHR–Y, 3 = X–CH$_2$–Y. [f] These values refer to structures in which the indicated carbons are part of and external to a cyclopropyl ring. [g] These values refer to structures in which the indicated atoms are in a four-membered ring.

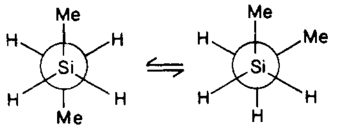
with hydrocarbon conformational analysis. As a good example of one of these kinds of results, let us consider the case of butane and ethylmethylsilane. In the case of butane the anti form is more stable than the gauche form by about 0.9 kcal/mol, while in the case of ethylmethylsilane the gauche conformer is predicted by the MM2 force

Table II. Calculated and Experimental Structural[a] Features of Acyclic Silanes and Polysilanes

compound	structural feature	experimental	MM2(82)	MINDO/3[17]	other FF[18]
methylsilane[16]	SiC	1.867 (MW) (1.877)[b]	1.878	1.834	1.868 (1.873)
	SiH	1.484	1.489	1.476	1.487 (1.484)
	HSiH	108.7	108.7		109.5 (108.3)
	CSiH	110.2	110.3		109.4 (110.6)
	barrier	1.67	1.68		1.66 (1.68)
	dipole moment	0.73	0.60		
dimethylsilane[19]	SiC	1.871 (MW) (1.881)[b]	1.873	1.848	1.868 (1.872)
	SiH	1.483	1.489	1.846	1.484 (1.484)
	HSiH	107.8	107.4		108.7 (108.6)
	CSiH	109.5	109.6		109.5 (109.4)
	CSiC	111.0	111.1	117.0	110.0 (111.0)
	barrier	1.66	1.78		1.66 (1.66)
	dipole moment	0.75	0.679		
trimethylsilane[20]	SiC	1.868 (MW) (1.878)[b]	1.879	1.864	1.867 (1.872)
	SiH	1.489	1.489	1.498	1.484 (1.485)
	CSiH	108.8	109.0	105.6	109.0 (109.1)
	CSiC	110.2	109.0		109.7 (109.8)
	barrier	1.83	1.88		(1.60)
	dipole moment	0.525	0.586		(1.60)
tetramethylsilane[21]	SiC	1.875 (2) (ED)	1.882	1.883	(1.871)
	HCH	109.8 (8)	110.5		
	SiCH	109.2 (8)	108.4		
	CSiC	109.5 (f)	109.5		(109.5)
	barrier	2.00[22]	1.99		(1.56)
ethylsilane[23]	SiC	1.867 (MW) (1.877)[b]	1.887		
	CC	1.540	1.548		
	SiCH	109.5	108.4		
	HSiH	107.8	108.9		
	HSiC	109.5	110.0		
	CCSi	113.2	113.8		113.6
	Me barriers	2.62[24]	2.62		3.78
	SiH_3 barrier	1.98	1.98		1.63
methylethylsilane (t or g)[c,23]	SiC (av)	1.867 (MW) (1.877)[b]	1.878		
	CC	1.540	1.548		
	SiCH(H)	109.2	108.5		
	$SiCH(H_2)$	110.9	108.5		
	HSiH	107.8	107.5		
	HSiC	109.5	109.5		
	CCSi	114.2	114.3		
	CSiC	111.0	111.2		
	Me barrier	1.52	1.82		
	dipole moment	0.758 (5)	0.678		
triethylsilane (C_3)[d]	SiC	1.886 (4) (ED)[25]	1.889		
	CC	1.547 (4)	1.548		
	CSiC	108.7 (19)	108.7		
	SiCC	114.2 (2)	114.3		
tri-*tert*-butylsilane (C_3)[26]	SiC	1.934 (6)	1.926		1.922
	CC	1.548 (3)	1.558		1.535
	SiH	1.49 (F)	1.489		1.491
	HSiC	105.3 (13)	104.7		103.5
	SiCC	115.5 (5)	111.4		111.0
	HSiCC	10.0 (31)	15.2		15.9
	tilt (*tert*-butyl)[e]	2.7 (2.4)	1.1		1.2
disilane[27]	SiSi	2.331 (3)	2.332	2.294	2.343[28]
	SiH	1.492 (3)	1.489	1.476	1.484
	HSiSi	110.3 (4)	110.5		110.2
	HSiH	108.6 (4)	108.4		108.7
	barrier	1.22	1.2		1.2
hexamethyldisilane[21]	SiSi	2.340 (3) (ED)	2.344		2.334[28]
	CSi	1.877 (3)	1.880		1.868
	CSiC	110.5 (4)	109.9		110.2
	SiSiC	108.4	109.0		108.7
	HCSi	108.7 (8)	108.4		107.4
	HCH	110.3 (8)	110.5		111.4
	barrier	5.7 (5)[29]	5.77		1.05[f]
tetrakis(trimethylsilyl)silane[30]	SiSi	2.361 (3) (ED)	2.356		2.346[28]
	SiC	1.889 (3)	1.882		1.869
	SiSiSi		109.5		109.5
	CSiSi	110.9 (6)	109.8		109.9
	SiCH	109.3 (17)	108.5		107.7
	CSiSiSi	11.0 (36)	14.7		15.2
	symmetry	*T*	*T*		*T*

[a] Units: bond lengths, Å; bond angles, deg; dihedral angles, deg; dipole moments, D; "barriers", kcal/mol. MW = microwave, ED = electron diffraction. [b] Vibrationally corrected (approximately) for comparison to ED and MM2. [c] The experimental structure was assumed to be the trans structure; MM2 calculates the gauche as the more stable, but finds no distinguishing differences between the two other than the torsion angle. [d] More than one conformer was found but the C_3 was assumed to be the predominant one. [e] The tilt was taken to be the angle between an imaginary C_3 axis through each *tert*-butyl group and the associated C–Si bond line. [f] Mislow did not mention the experimental measurement in ref 28. absolute average error (calculated): SiC ±0.005 Å; SiSi ±0.003; HSiH ±0.4; CSiC ±0.5; CSiH ±0.3; C–C–Si ± 0.2

Table III.[a] **Ethylmethylsilane (Anti $\rightleftharpoons$ Gauche)**

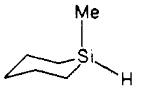


variable	exptl	MM2	Oulette[31b]
K(eq)	2.7	2.3	2.5
ΔG	−0.6	−0.52	−0.56
ΔH	−0.2	−0.10	−0.14
% gauche	73.	70.	71.

[a] All energies in kcal/mol.

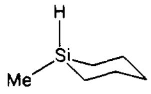
field to be more stable by approximately 0.10 kcal/mol. Using coupling constants and a Karplus-like relation involving Si, Oulette found K (anti $\rightleftharpoons$ gauche) to be 2.7 for ethylmethylsilane.[31] This corresponds to a mixture that is 73% gauche and 27% anti. Oulette also carried out some molecular mechanics calculations that gave similar predictions. The MM2 calculations also predict a similar ratio of 70% gauche and 30% anti. These results are summarized in Table III, along with information on the associated free energies and enthalpies.

An equally interesting case is the equilibrium between 1(a)- and 1(e)-methyl-1-silacyclohexane, 4 and 5. Oulette estimated, on the basis of his calculations on acyclic silanes, that the axial conformer would be more stable than the equatorial one by about 0.30 kcal/mol. Later, full minimization calculations by Oulette confirmed the direction but reduced the magnitude of this difference to about 0.20 kcal/mol. Calculations with our earlier force field[4] gave a value of 0.04 kcal/mol favoring the axial conformer. The MM2 force field predicts the axial conformer to be favored by about 0.13 kcal/mol. In each case, the difference in energy between the two conformers can be ascribed to attractive H···H interactions in the axial conformer that are not present in the equatorial conformer to the same extent. There is also experimental evidence to support the molecular mechanics calculations. Carleer and Anteunis carried out an NMR examination of this equilibrium[32] and arrived at an equilibrium constant of 0.57 kcal/mol favoring the axial form. This amounts to a ΔG value of about 0.34 kcal/mol, which corresponds to 64% of the axial and 36% of the equatorial conformers. In the case of methylcyclohexane the equilibrium constant is found to be 19.0, favoring the equatorial isomer 95% to 5%.[33] The corresponding values calculated by the MM2 force field for 1-methylsilacyclohexane are an equilibrium constant of 0.81 and a mixture that is 55% axial.



4

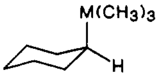
$\rightleftharpoons$



5

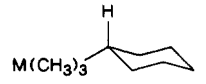
As a final example, let us consider the equilibrium 6 $\rightleftharpoons$ 7. The results of this equilibrium for *tert*-butylcyclohexane and *tert*-butylsilylcyclohexane are shown in Table IV.

In this case, the result for the silane is similar to that for the parent hydrocarbon in that the equatorial conformer is strongly preferred over the axial one. This comes about in spite of the attractive H···H interactions that we have been discussing, because of increased torsional strain as well as angle bending strain in the axial form (from the trimethylsilyl group being bent back away from the ring). The conformational preference of this silane is then determined by a balancing of the van der Waals energy, torsional energy and the bending energy instead of being largely determined by one term as in some of the other compounds discussed above.



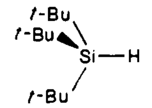
6

$\rightleftharpoons$

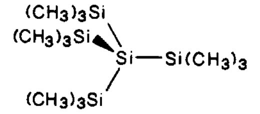


7

Next, let us examine the structure of tri-*tert*-butylsilane and compare it with the parent hydrocarbon. Tri-*tert*-butylmethane is one of the most highly strained hydrocarbons that have been studied experimentally to date.[35] Evidence of its high degree of strain are its extremely long CC bonds (1.611 Å vs 1.534 Å in ethane) and the very small central HCC angles, 101.6°, due to intramolecular repulsions of the three *tert*-butyl groups. For this reason, the reasonably good reproduction of this structure by the MM2 force field was a particularly good test of the program, the potential functions it uses, and the parameters for hydrocarbons. Likewise, two of the more rigorous tests of the parameter set we have generated for silicon compounds have been the reproduction of the known structures of tri-*tert*-butylsilane (8) and tetrakis(trimethylsilyl)silane (9). (The hydrocarbon corresponding to 9 does not yet have a reported structure to our knowledge.)



8



9

In Table V the structures of tri-*tert*-butylsilane and tri-*tert*-butylmethane have been compared. Note that in almost all of the structural features that exhibit the effects of strain in the hydrocarbon, these effects are mirrored in the silane but are somewhat attenuated. For instance, the Si–C bond length increases by about 3% over its equilibrium value compared to about 5% for the C–C bond in the hydrocarbon. The bending of the three *tert*-butyl groups away from each other is indicated by the small CCH and CSiH angles (101.6° and 105.3°, respectively). One way in which both structures seek to alleviate strain is the correlated rotations of the three *tert*-butyl groups away from C_{3v} symmetry. This is seen in the dihedral angles HCCC and HSiCC, both of which are rotated approximately 10° away from the position required for overall C_{3v} symmetry.

Hexamethyldisilane is another interesting compound that we have studied. The parent hydrocarbon (hexamethylethane) is fairly strained and is only a few steps removed from hexaphenylethane.[33b] The central C–C bond length in hexamethylethane is calculated to be 1.571 Å (an MM2 value) compared to 1.534 Å in ethane, and the attached methyl groups are bent back away from the central C–C bond considerably (CCMe = 112.1°) and toward each other (MeCMe = 106.7°). The (MM2) barrier to rotation about the central C–C bond is only 5.3 kcal/mol. This small value is, however, known to be an artifact.[36] The true value, as judged from many substituted derivatives, must lie at approximately 8 kcal/mol. (No experimental

---

(32) Carleer, R.; Anteunis, M. J. O. *Org. Magn. Reson.* **1979**, *12*, 673.

(33) (a) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. *Conformational Analysis*; Interscience: New York, 1965. (b) The structural features of hexamethylethane here are derived from MM2 calculations and are in reasonable agreement with experiment. See: Bartell, L. S.; Boates, T. L. *J. Mol. Struct.* **1976**, *32*, 379.

(34) Kitching, W.; Olszowy, H. A.; Drew, G. M.; Adcock, W. *J. Org. Chem.* **1982**, *47*, 5153.

(35) Burgi, H. B.; Bartell, L. S. *J. Am. Chem. Soc.* **1972**, *94*, 5236, 5239.

(36) Lipkowitz, K. B.; Allinger, N. L. *QCPE Bull.* **1987**, *7*, 19.

Table IV. *tert*-Butylcyclohexane and Trimethylsilylcyclohexane ($6 \rightleftharpoons 7$)

M	axial (%)		equatorial (%)		ΔG, kcal/mol	
	obsd	calcd	obsd	calcd	obsd	calcd
C		0.0		100.0	5.0[33]	4.99
Si	1.7	1.9	98.3	98.1	2.4–2.6[34]	2.44

Table V. Comparison of Tri-*tert*-butylmethane and Tri-*tert*-butylsilane

tri-*tert*-butylsilane[26]	tri-*tert*-butylmethane[35]
CSi = 1.934 (0.054)[b]	C(t)C(q)[c] = 1.611 (0.077)[b]
HSiC = 105.3	HC(t)C(q)[c] = 101.6
HSiCC = 10.8	HC(t)C(q)C(m)[c] = 10.8
steric *E* (MM2) = 12.5	steric *E* = 46.6

[a] Dimensions: bond lengths, Å; bond angles, degrees; and energies, kcal/mol. [b] Values in parentheses are the elongation relative to a typical unstrained bond length.

value was available at the time MM2 was originally developed, and the value chosen proved to be too small.) It is evident from Table II that hexamethyldisilane is much less strained than the parent hydrocarbon, and the strain in this molecule is relieved in a different fashion. The Si–Si bond length is only slightly stretched beyond equilibrium value [2.340 (ED) vs 2.332 (l_0)]. Steric repulsions across the central bond are minimal, while repulsions between methyl groups attached to the same silicon atom are relieved by their bending in toward the central Si–Si bond (SiSiC = 108.4° vs CSiC = 110.5°). This is a consequence of the longer Si–Si bond relative to the Si–C bond (1.880 Å). The barrier to rotation about the central Si–Si bond (5.77 kcal/mol) is large in comparison to the parent hydrocarbon, but this anomaly is largely due to the fact that MM2 calculates the value for the hydrocarbon to be too low. Also, the rotational barrier for the silane was arrived at by NMR studies on the solid compound and the value may differ somewhat from the gas-phase barriers.[37]

Table VI shows the results of the MM2 calculations and the experimental numbers for a variety of structural features of cyclic silanes. In addition, the last column of the table shows the results of the calculations carried out with the MM2 force field but without the stretch–bend interaction terms. The compounds that are important in determining the stretch–bend interaction terms for the two kinds of bond angles involving silicon (X–Si–Y, where X and Y are elements other than hydrogen or deuterium and X–Si–H, where X is some element other than hydrogen or deuterium) are the five- and four-membered rings, especially bicyclic compounds like silanorbornane. The natural bond lengths (l_0) and natural bond angles (θ_0) and their associated force parameters were first fit based on the calculations carried out on the acyclic compounds that have been discussed. We then compared the MM2 results for various trial values of the constants $k_{s,\theta}$ until we found values that gave the best overall fit.

Two independent electron diffraction studies have been reported for both silacyclopentane and silacyclopent-3-ene. Unfortunately, these two studies do not agree on all particulars. However, both of the ED studies gave similar results for the Si–C bond lengths and the CSiC bond angles in silacyclopentane,[39,40] so the stretch–bend constants for the MM2 force field were based on both pieces of data. The radial distribution function obtained in these ED studies only gave accurately the average C–C bond length. These studies cannot distinguish between the C–C bond adjacent to silicon and the other C–C bonds. However, the average C–C bond lengths reported in these studies are in good agreement with each other (1.551[39] and 1.550 Å[40]) and also in good agreement with the average C–C bond length obtained from the MM2 calculations (1.552 Å).

Durig[41] measured the barrier to interconversion of the two mirror image forms of silacyclopentane to be about 3.89 kcal/mol. This is the energy difference between the more stable C_2 (half-chair) form and the C_s (envelope) form. (The latter is the transition state for the interconversion, according to MM2.) Our calculated value is 3.23 kcal/mol, which is somewhat low. It would have been possible to bring the calculated value into better agreement with the experimental barrier by adjusting the torsional constants for the dihedral angles CSiCC and SiCCC, but this would have compromised our good results for a number of acyclic silanes, so we decided not to make this change.

In case of silacyclopent-3-ene, both experiments agree on the value for the CSiC angle and basically also on the value for the Si–C bond length, but they differ on many other important features. For instance, the SiCC angle measured by Cardock et al.[43] is 103.7° whereas Veniaminov et al.[42] report a value of 109.9°. Our calculated value is 103.2° in agreement with Cradock and similar to the value for the SiCC angle in silacyclopentane.

A comparison of the last two columns of Table VI shows that in both silacyclopentane and silacyclopent-3-ene inclusion of the stretch–bend interaction terms significantly improve the calculated values for the Si–C bond lengths but have relatively little effect on the SiCC angle.

1-Methyl-1-silanorbornane was one of the most important compounds in determining the stretch–bend interaction term for the CSiC angle, since the CSiC angle in this compound is quite different from tetrahedral, and the stretch–bend interaction term appears alone (not in conjunction with the CSiH stretch–bend interaction term as occurs in silacyclopentane and silacyclopent-3-ene). The fact that we calculate the structure of this compound fairly well suggests that our stretch–bend interaction term is adequate. Again, a study of the last two columns of Table VI shows that the inclusion of the stretch–bend interaction term causes the Si–C bond length to stretch out by 0.014 Å, thereby bringing it in much closer agreement with the experimental value. With the inclusion of the electronegativity correction, the average C–C bond length is calculated quite accurately while the individual C–C bond lengths deviate severely. Again, the bond lengths are difficult to determine experimentally here, and the MM2 values are probably better.

Silacyclohexane is much less strained than its five-membered ring homologue, so the inclusion of the

---

(37) Yukitoshi, T.; Suga, H.; Siki, S.; Itoh, J. *J. Phys. Soc. Jpn.* **1957**, *12*, 506.

(38) Hilderbrandt, R. L.; Homer, G. D.; Boudjouk, P. *J. Am. Chem. Soc.* **1976**, *98*, 7476.

(39) Mastryukov, V. S.; Golubinskii, A. V.; Atavin, E. G.; Vilkov, L. V.; Cyvin, B. N.; Cyvin, S. J. *Zh. Strukt. Khim.* **1979**, *20*, 726.

(40) Shen, Q.; Hilderbrandt, H. L.; Mastryukov, V. S. *J. Mol. Struct.* **1979**, *54*, 121.

(41) Durig, J. R.; Lafferty, W. J.; Kalasinsky, V. F. *J. Phys. Chem.* **1976**, *80*, 1199.

(42) Veniaminov, N. N.; Alekseev, N. V.; Bashkriova, S. H.; Kamelenkova, N. G.; Chernyskev, E. A. *Zh. Strukt. Khim.* **1975**, *16*, 918.

(43) Cradock, S.; Ebsworth, E. A. V.; Hamill, B. M.; Rankin, D. W. H.; Wilson, J. M.; Whiteford, R. A. *J. Mol. Struct.* **1979**, *57*, 123.

Table VI. Cyclic Silanes and Polysilanes[a]

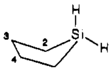
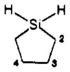
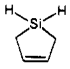
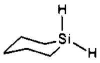
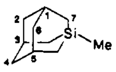
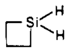
compound	structural feature	experimental	MM2	other[b]
1-methyl-1-silanorbornane[38]	SiC (av)	1.883 (2) (ED)	1.877	1.863
	C(2)C(3)	1.545 (5)	1.563	1.558
	C(4)C(7)	1.564 (4)	1.564	1.553
	C(3)C(4)	1.593 (8)	1.556	1.556
	CC(avg)	1.564 (4)	1.560	1.556
	C(7)SiC(2)	94.7 (5)	95.1	95.8
	C(7)SiC(8)	119.0 (2)	119.7	118.9
	SiCH	119.0 (4)	111.1	111.0
	SiC(2)C(3)	101.4 (4)	99.4	99.3
silacyclopentane[39] (C(2))	SiC	1.891 (4) (ED)	1.890	1.873
	C(2)C(3)	1.564 (9)	1.556	1.553
	C(3)C(4)	1.526 (17)	1.544	1.543
	CC (av)	1.551	1.552	1.548
	SiH	1.478 (F)	1.489	1.489
	CSiC	96.4 (6)	96.1	96.5
	HSiH	108.7 (F)	112.0	111.7
silacyclopentane[40]	SiC	1.892 (2) (ED)	1.890	1.873
	C(2)C(3)	1.535 (5)	1.556	1.553
	C(3)C(4)	1.580 (5)	1.544	1.543
	CC (av)	1.550 (2)	1.552	1.548
	SiH	1.497 (8)	1.498	1.498
	CSiH	113.2 (3)	112.0	112.0
	SiCH	110.1 (8)	110.8	110.8
	CSiC	96.3 (3)	96.1	96.5
	SiCC	103.6 (3)	103.5	103.7
	CCC	108.7 (6)	108.1	108.1
	HSiH	112.3 (29)	112.0	112.0
	barrier	3.89[41]	3.23	
	dipole	0.726 (6)[41]	0.802	
silacyclopent-3-ene[42]	SiC	1.894 (3) (ED)	1.889	1.873
	C(2)C(3)	1.524 (6)	1.524	1.519
	C(3)C(4)	1.326 (11)	1.344	1.343
	SiH	1.49 (F)	1.489	1.489
	CSiC	95.7 (12)	96.2	96.6
	C(2)C(3)C(4)	119.0	118.8	118.5
	SiCC	102.9 (calcd)	103.2	103.2
	HSiH	109.0 (F)	111.9	111.7
silacyclopent-3-ene[43]	SiC	1.885 (3) (ED)	1.882	1.877
	C(2)C(3)	1.533 (4)	1.524	1.519
	C(3)C(4)	1.359 (5)	1.344	1.343
	SiH	1.490 (F)	1.489	1.489
	CSiC	95.8 (5)	96.2	96.6
	C(2)C(3)C(4)	118.4 (2)	118.8	118.5
	SiCC	103.7 (5)	103.2	103.2
	HSiH	109.0 (F)	111.9	111.7
silacyclohexane[40]	SiC	1.885 (3) (ED)	1.882	1.877
	CC (av)	1.550 (3)	1.546	1.548
	SiH	1.465 (22)	1.499	1.489
	CSiH	112.0 (37)	110.8	110.8
	SiCH	110.5 (8)	109.1	109.1
	CSiC	104.2 (14)	104.3	104.3
	SiCC	110.6 (6)	110.9	110.8
	C(2)C(3)C(4)	113.7 (11)	113.0	113.0
	C(3)C(4)C(5)	111.4 (19)	114.0	114.1
	HSiH	105.0 (139)	109.3	109.3
1-methyl-1-silaadamantane[44]	SiC	1.879 (3) (ED)	1.879	1.871
	CC (av)	1.548 (2)	1.548	1.549
	C(10)SiC(7)	115.2 (4)	115.0	114.7
	SiC(7)C(1)	107.4 (4)	107.0	107.0
	SiCH	107.2 (21)	109.4	109.3
cyclopentasilane[45] (C(2)) (Si_5H_{10})	SiSi	2.342 (3) (ED)	2.349	2.330
	SiH	1.496 (6)	1.489	1.489
	SiSiSi	104.2 (7)	104.7	105.1
	HSiH	105.3 (3)	105.5	105.3
cyclohexasilane[46] (Si_6H_{12})	SiSi	2.342 (5) (ED)	2.334	2.330
	SiH	1.484 (8)	1.489	1.489
	HSiH	103.0 (F)	104.6	104.6
	SiSiSi	110.3 (13)	109.1	109.2
	SiSiSiSi	54.8 (3)	60.8	60.7
dodecamethylcyclohexasilane[47] (Si_6Me_{12})	SiSi	2.338 (4) (XR)	2.344	-
	SiC	1.889 (7)	1.882	-
	CSiC	108.1 (5)	108.6	-
	SiSiSi	111.9 (4)	111.4	-
	SiSiSiSi	53.5 (3)	54.9	-

Table VI (Continued)

compound	structural feature	experimental	MM2	other[b]
silacyclobutane[48]	SiC	1.897 (10) (ED)	1.891	1.879
	SiH	1.49	1.489	–
	CC	1.585 (10)	1.557	1.553
	CSiC	80.0 (2)	78.9	79.3
	CCC	100.0 (2)	101.1	101.1
	SiCC	86.0 (2)	84.8	84.9
	barrier	1.27[49]	1.33	–

[a] Units: bond lengths, Å; bond angles, degrees; barriers to rotation ("barrier"), kcal/mol. Experimental methods: MW = microwave, XR = X-ray, ED = electron diffraction. Error limits in parentheses, F = fixed.

[b] Same force field as MM2 but without the stretch–bend interaction parameters.

stretch–bend interaction term does not result in greatly increased Si–C bond lengths. However, the CSiC bond angle is much smaller than the tetrahedral value, presumably because of the longer Si–C bond length relative to the C–C bond length. Again, the average calculated value for the C–C bond length (1.546 Å) is in fairly good agreement with the average experimental value of 1.550 Å,[40] indicating that we have probably picked a good value for the electronegativity correction to a C–C bond attached to a silicon atom.

It is a little surprising to find that the Si–Si bond lengths are identical in the experimental structures of cyclopentasilane and cyclohexasilane. From what we know about silacyclopentane and silacyclohexane, one would expect some differences in strain in these two compounds and some reflection of this strain in the Si–Si bond lengths. There is also an undeniable difference in the SiSiSi bond angles in the two (SiSiSi = 104.2° in cyclopentasilane[45] and 110.3° in cyclohexasilane[46]). Yet there seems to be no coupling of this bending stress to stretching in the experimental structure. However, the calculated value for the Si–Si bond in the five-membered ring compound is about 0.015 Å longer than the calculated value for the Si–Si bond in cyclohexasilane. This error (which is not much beyond experimental error) could be reduced by using a smaller stretch–bend constant for Si–Si–Si than that used for C–Si–C. We have decided to accept the error rather than introduce an additional constant, however.

Silacyclobutane has the most pinched CSiC bond angle that we know of (80°), but we have special bending and torsional parameters for four-membered ring compounds anyway, so it was possible to fit this compound without too much difficulty. This structure is reasonably well calculated and the barrier to interconversion of the two nonplanar forms is calculated to be in good agreement with the reported experimental value. The calculation of a reasonable heat of formation for 1,1-dimethylsilacyclobutane provides further support for the parameters that we have selected for four-membered ring silanes.

Aryl- and Vinylsilanes. This is an interesting subclass of the silanes because of the possibility of (p–d) π-interactions. The question of whether such interactions are important in these compounds has not been resolved.[50] Fortunately, from the work that we have done so far, it appears that we can largely sidestep the issue, since whatever effects exist seem to be relatively constant from structure to structure.

Experimentally determined valence force field parameters were not always available for these compounds. For instance, an ab initio value had to be used for the Si–C$_{sp^2}$ stretching force constant.[57] The fact that this value (3.5 mdyne/Å^2) is somewhat larger than the stretching constant for a Si–C$_{sp^3}$ bond is probably reasonable since the bond contains more s character. Alternatively, one may suggest that there is some (p–d) π-type overlap, which would also strengthen this bond. For the few bending parameters that had not been previously assigned,[4] we chose values based on a similar angle. For example, the value of the force constant for the SiSiC$_{sp^2}$ angle was taken to be the same as the value already picked for the force constant for the CSiC$_{sp^2}$ angle.

Fortunately, a number of the important barriers to rotation had been determined for these compounds. The barriers also tend to be quite small, so that even large errors percentage-wise may not be very significant. The barrier to rotation of the silyl group on vinylsilane is only 1.5 kcal/mol, and the stable conformation was determined to be the one with the HSiCC angle eclipsed. We therefore assigned the 3-fold torsion parameters for HSiC$_{sp^2}$C$_{sp^2}$ 0.0 kcal/mol and for HSiC$_{sp^2}$H 0.5 kcal/mol, which led to a good fit to experiment (Table VII).[14] We also knew that phenylsilane was essentially a free rotor.[51] The methyl rotation barriers in methylvinylsilane allowed an assignment of the torsional parameters for the HC$_{sp^2}$SiC angle.

The most stable conformation in vinylsilane has the C=C eclipsing a hydrogen on the silyl group, analogous to propene, and the barrier to rotation is lower in the silane (1.5 kcal/mol for the silane[57] vs 1.98 kcal/mol for the hydrocarbon[58]).

The most stable conformation for methylvinylsilane was not reported, although the fact that the two conformations cis and skew were structurally determined suggests that the enthalpy difference between them is small.[15] We calculate the cis conformer to be slightly lower in enthalpy (by about 0.12 kcal/mol) than the skew, which is the opposite of what might be expected on the basis of the hydrocarbon analogue 1-butene, where the skew form is lower

---

(44) Shen, Q.; Kapfer, C.; Boudjouk, P.; Hilderbrandt, R. L. *J. Organomet. Chem.* **1979**, *169*, 147.

(45) Smith, Z.; Seip, H. M.; Hengge, E.; Bauer, G. *Acta Chem. Scand. Ser. A* **1976**, *30A*, 697.

(46) Smith, Z.; Almenningen, A.; Hengge, E.; Kovar, D. *J. Am. Chem. Soc.* **1982**, *104*, 4362.

(47) Carrell, H. L.; Donohue, J. *Acta Crystallogr., Sect. B* **1972**, *B28*, 1566.

(48) Vilkov, L. V.; Mastryukov, V. S.; Baurova, Y. V.; Vdovin, W. M.; Grinberg, P. L. *Dokl. Akad Nauk SSSR* **1967**, *177*, 1804. Vilkov, L. V.; Mastryukov, V. S.; Oppenheim, V. D.; Tarasenko, N. A. *Mol. Struct. Vib.*; Cyvin, S. J., ed.; Elsevier: Amsterdam, The Netherlands, 1975; p 310.

(49) Laane, J.; Lord, R. C. *J. Chem. Phys.* **1968**, *48*, 1508.

(50) Oberhammer, H.; Boggs, J. E. *J. Mol. Struct.* **1979**, *57*, 175.

(51) Durig, J. R.; Hellams, K. L.; Mulligan, J. H. *Spectrochim. Acta* **1972**, *28A*, 1039.

(52) Shen, Q.; Hilderbrandt, R. L.; Burns, G.; Barton, T. *J. Organomet. Chem.* **1980**, *195*, 39.

(53) Vidal, P. J. P.; Lapasset, J.; Falgueirettes, J. *Acta Crystallogr., Sect. B* **1972**, *28B*, 3137.

(54) Vidaland, P. J. P.; Falgueirettes, J. *Acta Crystallogr., Sect. B* **1973**, *29B*, 263.

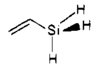
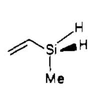
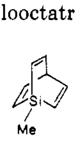
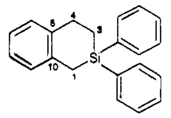
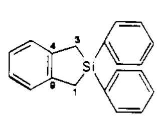
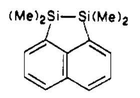
(55) D'yachenko, O. A.; Soboleva, S. V.; Atovmyan, L. O. *J. Struct. Chem.* **1976**, *17*, 300.

(56) Glidewell, G. C.; Sheldrick, G. M. *J. Chem. Soc. A* **1971**, 3127.

(57) Trinquier, G.; Malrieu, J. *J. Am. Chem. Soc.* **1981**, *103*, 6313.

(58) Herschbach, D. R.; Krisher, L. C. *J. Chem. Phys.* **1958**, *28*, 728.

Table VII. Aryl- and Vinylsilanes[a]

compound	structural feature	experimental	MM2
vinylsilane (ecl)[b,14]	SiC	1.853 (3) (MW)	1.868
	SiH	1.457 (3)	1.489
	C=C	1.347 (3)	1.339
	SiCC	122.9 (3)	123.0
	HSiH	108.7 (7)	108.9
	barrier	1.50	1.51
	dipole	0.66	0.65
methylvinylsilane[c,15] (cis)	SiC(sp^2)	1.858 (MW)	1.865
	SiH	1.483	1.489
	C=C	1.351	1.339
	SiC(sp^2)	1.865	1.875
	CCSi	124.5	123.6
	CSiC	111.5	113.9
	HSiH	107.3	105.6
	C(sp^2)SiH	109.0	110.9
	C(sp^2)SiH	109.9	107.9
	barrier (Me, cis)	1.87 (4)	2.05
	barrier (Me, skew)	1.70 (2)	1.53
	dipole (cis)	0.729 (2)	0.689
	dipole (skew)	0.670 (8)	0.707
1-methyl-1-silabicyclooctatriene[52]	SiC (av)	1.875 (10) (ED)	1.866
	SiC(2)	1.885 (8)	1.872
	SiC(Me)	1.844 (30)	1.849
	CC	1.547 (5)	1.526
	C=C	1.348 (3)	1.345
	C=CC	119.4 (7)	119.9
	CSiC	98.8 (3)	98.7
	SiC=C	109.5 (5)	109.7
	C(Me)SiC	118.7 (2)	118.8
2,2-diphenyl-2-silatrihydro-1,3,4-naphthalene[53]	SiC(sp^2)	1.871 (3) (XR)	1.876
	SiC	1.883 (3)	1.890
	C(3)C(4)	1.546 (4)	1.552
	C(4)C(5)	1.511 (5)	1.515
	C(1)C(10)	1.523 (5)	1.524
	SiCC(sp^2)	110.5 (2)	110.6
	SiCC	110.4 (2)	111.3
	C(sp^2)SiC(sp^2)	109.3 (1)	110.6
	CSiC	103.3 (1)	104.0
2,2-diphenyl-2-silaindane[54]	SiC(sp^2)	1.875 (4) (XR)	1.870
	SiC	1.886 (4)	1.893
	CSiC(sp^2)	110.3 (2)	110.4
	CSiC	93.6 (2)	94.8
	CCSi	101.6 (3)	103.2
	C(3)C(4)	1.529 (6)	1.525
	C(1)C(9)	1.515 (6)	1.524
	CC (av)	1.522	1.524
1,1,2,2-tetramethyl-1,2-disilaacenaphthalene[55]	SiC(sp^2)	1.888 (XR)	1.880
	SiC	1.872	1.869
	SiC (av)	1.877	1.873
	SiSi	2.338	2.367
	C(sp^2)SiSi	92.2	93.3
	SiC(sp^2)C(sp^2)	116.9	116.6
	CSiC	109.4	114.2
tetraphenylsilane[56]	SiC	1.872 (5) (XR)	1.880
	CSiC(2X)	107.7 (5)	106.3
	CSiC (4X)	110.3	111.1
	symmetry	S(4)	S(4)

[a] Units: bond lengths, Å; bond angles, deg; barriers to rotation ("barrier"), kcal/mol; error limits (where reported) are given in parentheses. XR = X-ray, MW = microwave, ED = electron diffraction. MW values are uncorrected. [b] The most stable conformation is the one with torsion angle HSiCC = 0°, i.e., eclipsed; "barrier" then refers to energy difference between thiis and HSiCC "staggered". [c] "Cis" and "skew" refer to the conformation associated with CSiCC = 0°, and CSiCC = 119°, respectively. There are methyl rotation barriers reported for each conformation as well as dipole moments; the geometric parameters are reported (here) for the cis only. The conformational enthalpy difference was not reported in ref 15; however, we calculate a difference of 0.12 kcal/mol.

in enthalpy than the cis by about 0.15 kcal/mol.[59]

1-Methyl-1-silabicyclo[2.2.2]octatriene is the only silane in this subclass for which an electron diffraction structure is known. It is also one of the more highly strained compounds, as evidenced by the small CSiC$_{sp^2}$ (98.0°) and SiC$_{sp^2}$C$_{sp^2}$ (109.5°) angles. These are well reproduced by our calculations. Although the calculated value for the average Si–C bond length is much smaller than the experimental value, it is still within the quoted experimental error. In addition, the authors state that they had some problems using a single average Si–C bond length of 1.875 Å in fitting the theoretical radical distribution curves to the experimental one.[52]

Tetraphenylsilane was also studied in this work. The most interesting feature of this compound is its distortion away from T_d symmetry along an S_4 axis (apparently due to nonbonded interactions). The angles bisected by the S_4 axis are pinched from their tetrahedral value to a value of 107.7°. We were not able to duplicate this feature as well as we would have liked. Since the average value for the CSiC bond angle remains at 109.5°, it would appear that merely increasing the force constant for the CSiC bond angle would eventually lead to a fit. While this did result in improvement, still larger values began to seem unreasonable and had less and less effect on the calculated angles. After this work was completed, studies were carried out[60] that indicate the importance of the charge distributions in the benzene ring in determining the conformation in a wide variety of examples. Inclusion of charges in the case at hand might have some effect on the conformations.

Table VIII. Calculated Structures for Hexaphenyldisilane

symmetry	structural feature	MM2 (1982)	Mislow (1977)[61]
D_3	SiSi	2.370	2.369
	CSi	1.878	1.864
	CSiSi	107.8	109.4
	CSiC	111.1	109.5
	CSiSiC	6.1	7.2
	CCSiSi	54.5	48.0
S_6	SiSi	2.364	2.374
	CSi	1.879	1.866
	CSiSi	108.6	109.3
	CSiSiC	58.4	59.9
	CCSiSi	55.6	50.7
	$\Delta E(S_6 - D_3)$	−1.6	0.92

[a] Units: bond lengths, Å; bond angles and torsional angles, deg; energy differences, kcal/mol.

1,1,2,2-Tetramethyl-1,2-disilaacenaphthalene is another strained molecule that we had some problems in fitting. In particular, the SiSiC$_{sp^2}$ angle could not be fit well unless the extremely small natural bond angle (θ_0) of 103.0° was used. However, this value was found to be too small for the compound hexaphenyldisilane (vide infra) to obtain results consistent with the other hexaphenyl dielement compounds in group IV. This value was therefore set at 110.2°, which is the value expected from similar compounds. This also results in a lengthening of the Si–Si bond to 2.367 Å, which seems reasonable for a compound with this degree of strain, while the experimental value of 2.332 Å does not.

Experimental difficulties have prevented the study of hexaphenyldisilane,[61] but structures have been published

---

[59] Kondo, S.; Hirota, E.; Morino, Y. J. Mol. Spect. **1968**, 28, 471.

[60] (a) Allinger, N. L.; Lii, J.-H. J. Comput. Chem. **1987**, 8, 1146. (b) Pettersson, I.; Liljefors, T. J. Comput. Chem. **1987**, 8, 1139.

[61] Hounshell, W. D.; Dougherty, D. A.; Hummel, J. P.; Mislow, K. J. Am. Chem. Soc. **1977**, 99, 1916.

Table IX. Least-Squares Assignment of Bond Enthalpy Increments for Silanes

compound	sum *H*[a]	steric[b]	Pop[c]	Tors[d]	*T*/*R*	wt
A. Data Other Than Experimental Heats Used						
silane	0.0	0.0	0.0	0.0	2.4	5
disilane	0.0	−0.23	0.0	0.36	2.4	5
trisilane	0.0	−.78	0.0	0.72	2.4	5
methylsilane	−9.61	−0.34	0.0	0.0	2.4	5
dimethylsilane	−19.23	−0.53	0.0	0.0	2.4	5
trimethylsilane	−28.84	−1.70	0.0	0.0	2.4	5
tetramethylsilane	−38.46	−2.66	0.0	0.0	2.4	5
diethylsilane	−35.08	0.67	0.21	0.72	2.4	0
triethylsilane	−52.61	−0.26	0.21	1.08	2.4	5
tetraethylsilane	−70.16	−1.36	0.09	1.44	2.4	5
dimethylsilacyclobutane	−38.47	11.70	0.0	0.36	2.4	5
dimethylsilacyclopentane	−44.88	7.56	0.0	0.36	2.4	5
hexamethyldisilane	−57.69	−5.31	0.0	0.36	2.4	5
bis(trimethylsilyl)dimethylsilane	−76.92	−8.47	0.0	0.72	2.4	5
decamethyltetrasilane	−96.15	−11.61	0.30	1.08	2.4	5
tetrakis(trimethylsilyl)silane	−115.38	−18.35	0.0	1.44	2.4	0

	heats of formation, kcal/mol						
		MM2[g]		MINDO/3[17]		EECBA[i]	
compound	exptl[67,k] ΔH_f°	ΔH_f°	diff[h]	ΔH_f°	diff[h]	ΔH_f°	diff[h]
B. Results of Least-Squares Analysis							
silane	8.20	8.91	0.71	8.5	0.30		
disilane	19.10	18.89	−0.21	10.0	−0.10	19.1	0.0
trisilane	28.9	28.59	−0.34	30.2	1.30	28.6	−0.3
methylsilane	−8.0	−7.93	0.07	−11.8	−3.8	−8.1	−0.1
dimethylsilane	−24.3	−24.62	−0.32	−29.8	−5.5	−24.8	−0.5
trimethylsilane	−41.4	−42.3	−0.91	−44.5	−3.10	−41.9	−0.5
tetramethylsilane	−58.7 ± 2.4	−59.8	−1.08	−55.5	3.20	−59.1	0.4
diethylsilane	−43.6 ± 1.4	−26.49	17.1			−30.96	12.6
triethylsilane	−48.0 ± 3.6	−45.57	2.43			−51.1(−48.7)	3.10
tetraethylsilane	−63.4 ± 3.7	−64.9	−1.54			−73.0(−63.4)	8.10
dimethylsilacyclobutane	−33.0 ± 2.7	−33.21	−0.21				
dimethylsilacyclopentane	−43.4 ± 3.0	−43.76	−0.36				
hexamethyldisilane	−86.8 ± 2.0	−85.23	1.57			−85.6	1.20
bis(trimethylsilyl)dimethylsilane	−135.8 ± 5.6	−136.83	−1.03			−139.2	−3.4
decamethyltetrasilane	−112.4 ± 4.1	−111.19	1.21			−112.4	0.0
tetrakis(trimethylsilyl)silane	−133.7 ± 9.5	−166.68	−32.98			−166.7(−133.7)	−33.0
standard deviation[j]	3.60	1.08			3.08		2.98

[a] Sum of bond enthalpy increments that do not contain silicon; stored in MM2 program. [b] Steric energy as calculated by the MM2 program for the molecule in question. [c] Correction term due to the population of higher energy conformations. [d] A correction term due to the torsional vibrational levels. [e] This term accounts for the translational, rotational, and pressure volume work required to convert the internal energy of a molecule to enthalpy (assuming molecule is nonlinear). [f] This factor "weights" the data for any given molecule to take account of large experimental errors or otherwise suspect data; a weight of zero means that compound's data is ignored in the least-squares treatment. [g] These heats calculated by using the "best fit" bond enthalpy increments for silanes; SiH = 1.63; Si–Me = −5.23; Si–Si = 6.60; Si–C = 0.663. [h] The difference "diff" is the calculated minus the experimental value. [i] Electrostatic energy corrected bond additivity scheme, ref 64 and papers cited therein; numbers in parentheses refer to "corrections" for nonbonded interactions; see text. [j] Diethylsilane and tetrakis(trimethylsilyl)silane were omitted (weighted zero) in each column for this calculation; see text. [k] A referee has called our attention to a paper by Szepes and Baer Szepes, L.; Baer, T. *J. Am. Chem. Soc.* **1984**, *106*, 273) that gives a new value for the heat of formation of tetramethylsilane gas as −54.1 ± 1.1 kcal/mol. This is quite different than the value that we used as the experimental value for this compound and also different from that calculated by MM2. It illustrates a problem well known to those who would like to calculate heats of formation, namely that one frequently is confronted with two values, apparently accurate to within some limits, but differing by more than the sum of the experimental errors. And of course, one has to work with the data available at the time the work is done. (The paper quoted did not appear until after the work described in this paper was completed.) Sometimes there are unrecognized systematic experimental errors, which may depend upon the type of experiment carried out, or the laboratory in which it was carried out, etc. The only generalization that seems possible is that experimental errors are sometimes larger than thought or than claimed by the original investigators. We have made an effort to keep MM2 calculations time independent. We have not been wholly successful, but the philosophy is that if systematic errors are uncovered, they can be allowed for. But if the force field keeps changing, it will be difficult for the user to know which things have been allowed for and which have not. Hence we do not ordinarily make any change in the force field once it is established.

for the lead and tin analogues.[62] However, a previous molecular mechanics study[61] has been published for the whole group IV series, including hexaphenylethane, using a modified version of the MM1 force field.[63] If we compare the SiSiC angles reported in Table VIII to the SiSiC angle in hexamethyldisilane reported in Table II, it appears that hexaphenyldisilane is not much more strained than the hexamethyl compound. This is probably due to the long Si–Si equilibrium bond length compared to the C–C bond length in the corresponding hydrocarbon (hexaphenylethane is too strained to exist or at least to have been isolated so far). Our structure for hexaphenyldisilane differs from that of Mislow in some important aspects. We found the S_6 structure to be slightly favored over the D_3 whereas Mislow found the opposite. Another interesting divergence in the two structures is that in our structure, the nonbonded repulsions between phenyl rings on the same silicon atom are apparently larger than the nonbonded repulsions between phenyl rings on different silicon

---

(62) (a) Tin derivative: Haupt, H. J.; Huber, F.; Preut, H. *Z. Anorg. Chem.* **1973**, *396*, 81. (b) Lead derivative: Preut, H.; Huber, F. *Z. Anorg. Chem.* **1970**, *419*, 92.

(63) Andose, J. D.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 2168. The force field was modified to allow for calculation of the structures of the conjugated system of the benzene rings; in addition, the authors used their own silane parameters.

Table X. "Strainless" Silanes Heat Data and Calculations

A. Data Used in Generating Strainless Enthalpy Bond Increments

compound	sum H^a	ΔH^b strainless	Pop	Tors	T/R	wt
silane	0.0	8.91	0.0	0.0	2.4	5
disilane	0.0	18.89	0.0	0.36	2.4	5
trisilane	0.0	28.59	0.0	0.72	2.4	5
methylsilane	−9.38	−7.93	0.0	0.0	2.4	5
dimethylsilane	−18.80	−24.60	0.0	0.0	2.4	5
diethylsilane	−33.40	−26.50	0.21	0.72	2.4	5
triethylsilane	−50.20	−45.60	0.21	1.08	2.4	5

B. Calculated Heats for Strainless Compounds Using Best fit Strainless Bond Enthalpy Increments[c]

compound	ΔH calcd	ΔH strainless	diff (calcd − strainless)	compound	ΔH calcd	ΔH strainless	diff (calcd − strainless)
silane	9.04	8.91	0.13	dimethylsilane	−24.67	−24.60	−0.07
disilane	18.83	18.89	−0.06	diethylsilane	−27.02	−26.50	−0.52
trisilane	28.62	28.59	0.03	triethylsilane	−45.25	−45.60	−0.35
methylsilane	−7.79	−7.93	0.14				

[a] Sum of strainless bond enthalpy increments not containing silicon. [b] Calculated (MM2) $\Delta H_f°$ from Table IX. [c] Best fit values are Si–H = 1.66; Si–Me = −5.80; Si–Si = 6.11; SiC = −0.135.

atoms, as witnessed by the larger CSiC angle compared to the CSiSi angle (110.3° vs 108.6°). This is similar to the case of hexamethyldisilane, as shown by experiment and calculations (see Table II). Associated with this feature, we find that the Si–Si bond length is not quite as long in our calculations as in Mislow's structure where most of the nonbonded repulsions appear across the Si–Si bond.

Heats of Formation of Silanes and Polysilanes. The experimental quantity actually measured in heat of formation determinations is usually a heat of combustion, which in silanes and polysilanes is particularly troublesome because of incomplete combustion and the indeterminate nature of the products.[64] More recently, combustion analyses have been carried out in the presence of HF, which gives a well-defined product, and are apparently more reliable.[64] Another good way to determine heats of formation of silanes is by calorimetric determinations of heats of decomposition, such as Gunn and Green's data on silane, disilane and trisilane.[65] In spite of this, there is some lively debate as to which compilation of data is the most reliable.[64,66] We have chosen to use the Pedley CATCH Tables values,[67] which appear to have an internal consistency that the other compilations lack[64] and are more extensive.

The additivity scheme that we used for the heat of formation calculations is similar to those used by others[68] for compounds of silicon and is identical with that described previously for hydrocarbons[4] with additional bond enthalpy increments for Si–H, Si–C (methyl), Si–C (all others), and Si–Si (all types). In Table IX are presented the results of our calculations of the heats of formation for 16 compounds, along with the heats calculated by two independent and competing methods. The MINDO/3 method[17] is the poorest of the three and will not be further discussed here. Comparing MM2 and the electrostatic energy corrected bond additivity (EECBA) method developed by Benson[69] and used by O'Neal and Ring[64] for silanes, we see very similar results. We find that MM2 and EECBA predict identical heats of formation for tetrakis(trimethylsilyl)silane, and this value deviates considerably from the experimental value. Also, MM2 and EECBA calculate heats of formation for diethylsilane that deviate in the same direction and by similar magnitudes from the experimental value. We feel that there may be considerable error in the reported experimental values for the heats of formation of these two compounds. The MM2 method is a general, reliable method of calculating heats of formation. O'Neal and Ring concede the EECBA method will not reproduce the heats of formation for strained cyclic structures such as 1,1-dimethylsilacyclobutane and 1,1-dimethylsilacyclopentane for which we calculate the heats of formation to within experimental error. Strainless bond enthalpy increments were also generated for the silanes, which permit the calculation of strain energies. A summary of our heat of formation calculations are shown in Tables IX and X.

Acknowledgment. This research was supported in part by grants from the National Science Foundation (Grant CHE 8614548) and from the National Institutes of Health (Grant 5 R24 RR02165).

Registry No. Methylsilane, 992-94-9; dimethylsilane, 1111-74-6; trimethylsilane, 993-07-7; tetramethylsilane, 75-76-3; ethylsilane, 2814-79-1; methylethylsilane, 18230-82-5; triethylsilane, 617-86-7; tri-*tert*-butylsilane, 18159-55-2; disilane, 1590-87-0; hexamethyldisilane, 1450-14-2; tetrakis(trimethylsilyl)silane, 4098-98-0; 1-methyl-1-silanorbornane, 61192-29-8; silacyclopentane, 288-06-2; silacyclopent-3-ene, 7049-25-4; silacyclohexane, 6576-79-0; 1-methyl-1-silaadamantane, 65672-54-0; cyclopentasilane, 289-22-5; cyclohexasilane, 291-59-8; dodecamethylcyclohexasilane, 4098-30-0; silacyclobutane, 287-29-6; vinylsilane, 7291-09-0; methylvinylsilane, 18191-61-2; 1-methyl-1-silabicyclooctatriene, 67754-92-1; 2,2-diphenyl-2-silatrihydro-1,3,4-naphthalene, 20152-03-8; 2,2-diphenyl-2-silaindane, 20151-88-6; 1,1,2,2-tetramethyl-1,2-disilaacenaphthalene, 32538-47-9; tetraphenylsilane, 1048-08-4; hexaphenyldisilane, 1450-23-3; silane, 7803-62-5; trisilane, 7783-26-8; diethylsilane, 542-91-6; tetraethylsilane, 631-36-7; dimethylsilacyclobutane, 2295-12-7; dimethylsilacyclopentane, 1072-54-4; bis(trimethylsilyl)dimethylsilane, 3704-44-7; decamethyltetrasilane, 865-76-9.

---

(64) O'Neal, H. E.; Ring, M. A. *J. Organomet. Chem.* **1981**, *213*, 419.

(65) Gunn, S. R.; Green, L. G. *J. Phys. Chem.* **1961**, *65*, 779; **1964**, *68*, 946.

(66) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

(67) Pedley, J. B.; Iseard, B. S.; Kirk, A.; Seilman, S.; Heath, L. G. *Comput. Anal. Thermochem. Data* **1972**, 1.

(68) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1968.

(69) Benson, S. W. *Angew. Chem.* **1978**, *17*, 812.