

## CONFORMATIONAL ANALYSIS—LXXXIII

### CALCULATION OF THE STRUCTURES AND ENERGIES OF SILANES BY THE METHOD OF MOLECULAR MECHANICS.<sup>1, 2</sup>

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**Abstract**—The structures and energies of a number of silanes have been studied by the method of molecular mechanics, and the results are compared with the available experimental data, and with the hydrocarbon analogs. Torsional barriers are relatively small and gauche interactions are unimportant in the silanes, which leads to several unusual conformational effects. Heats of formation are calculated.

IN RECENT papers we have described a force field to be used for the calculation of the structures and energies of hydrocarbons<sup>3</sup> and of ketones<sup>4</sup> by the methods of molecular mechanics. We have extended these calculations to various other classes of compounds, as will be described in subsequent papers. The present paper describes the extension of the calculations to the silanes. This particular group of compounds is similar to the hydrocarbons in that the Si atom is tetracoordinate and approximately tetrahedral, analogous to the C atom in saturated hydrocarbons. There are no lone pairs or double bonds or other complications, and the calculations follow in a straightforward way from those of hydrocarbons; only the new numerical values of the constants involving silicon need to be determined.

There is only a small amount of experimental structural data concerning the silanes, and we have based the parameterization of our model primarily on the methylsilanes, vinylsilane, and 1,3-disilapropane. The van der Waals, stretching, bending, torsional, and heat of formation parameters used in addition to those required for hydrocarbons<sup>3</sup> are listed in Table 1.

Due to the lack of accurate data concerning nonbonded interactions of silicon, we have chosen to use the same van der Waals radius ( $r^*$ ) and the  $\epsilon$  value used for argon in the Hill equation.<sup>5</sup> Stretching and bending force constants were taken from the literature<sup>6</sup> where available. On the whole, the C–Si stretching constants are found to be approximately two-thirds as large as the corresponding C–C ones, and the silicon-hydrogen constants are about one-half as large as the corresponding C–H ones. In the few cases where no force constants were available, these were estimated by using values two-thirds of the corresponding force constants in the hydrocarbon series.

Bending force constants for C–Si–H, C–Si–C, and H–Si–H angles are slightly larger than those for hydrocarbons. Because of this, silanes tend to stretch more and bend less compared to the hydrocarbons. We have elected not to use stretch-bend interactions for bonds and angles involving silicon, due to the lack of experimental data.

TABLE 1. CONSTANTS FOR CALCULATION OF MOLECULAR GEOMETRIES

van der Waals Constants for the Hill equation <sup>5</sup>		
Atom	$r^*$	$\epsilon$
Si	1.78	0.044
Bond Stretching Constants		
Bond	$l_0(\text{\AA})$	$k(\text{mydn}/\text{\AA}^2)$
$C_{sp^3}-Si$	1.872	2.92
$C_{sp^2}-Si$	1.850	2.97
Si-H	1.484	2.72
Angle Bending Constants		
Angle	$\theta_0$	$k(\text{mdyn}/\text{rad}^2)$
$C_{sp^3}-Si-H$	108.8	0.46
$C_{sp^3}-Si-H$ (C-Si-H)	109.4	0.46
$C_{sp^3}-Si-H$ (C-Si-H)	110.5	0.46
$C_{sp^3}-Si-C_{sp^3}$	109.5	0.48
$C_{sp^3}-Si-C_{sp^2}$ (C-Si-C)	110.3	0.48
$C_{sp^3}-Si-C_{sp^2}$ (C-Si-C)	110.2	0.48
H-Si-H	108.6	0.38
H-Si-H (H-Si-H)	108.4	0.38
C=C-Si	122.5	0.40
Si-C <sub>sp^3</sub> -H	118.4	0.24
Si-C <sub>sp^3</sub> -Si	115.0	0.40

TABLE 1—continued

Torsional Constants (3-fold or 2-fold barrier, as appropriate)	
Angle	$V_0$ (kcal/mole)
$C_{sp^3}-C_{sp^3}-C_{sp^3}-Si$	0.50
$C_{sp^3}-C_{sp^3}-Si-H$	0.69
$Si-C_{sp^3}-C_{sp^3}-H$	0.50
$C_{sp^3}-Si-C_{sp^3}-H$	0.46
$Si-C_{sp^3}-C_{sp^3}-Si$	0.50
$C_{sp^3}-C_{sp^3}-Si-H$	0.00
$H-C_{sp^3}-Si-H$	1.61
$H-C_{sp^3}-C_{sp^3}-Si$	16.25
$C_{sp^3}-C_{sp^3}-Si-C_{sp^3}$	0.00
$C_{sp^3}-Si-C_{sp^3}-H$	0.50
$C_{sp^3}-C_{sp^3}-Si-C_{sp^3}$	0.50
$C_{sp^3}-C_{sp^3}-Si-H$	0.50
$Si-C_{sp^3}-C_{sp^3}-C_{sp^3}$	0.00
$Si-C_{sp^3}-C_{sp^3}-H$	2.15
$C_{sp^3}-C_{sp^3}-C_{sp^3}-Si$	16.25
$C_{sp^3}-C_{sp^3}-C_{sp^3}-Si$	0.50
$C_{sp^3}-Si-C_{sp^3}-H$	2.15
$C_{sp^3}-C_{sp^3}-Si-C_{sp^3}$	0.50
Additional Heat of Formation Parameters	
$C_{sp^3}-Si$	8.08 kcal/mole
$C_{sp^3}-Si$	-10.65
$Si-H$	-2.15

Most of the torsional constants were determined to fit observed data; hydrocarbon values were assumed where data were not available. Comparisons of calculated and experimental geometries for some simple compounds are shown in Table 2.

Since the van der Waals radius of silicon is somewhat larger than that of carbon, steric interactions with this atom could in some cases be severe; we find, however,

TABLE 2. COMPARISON OF CALCULATED AND OBSERVED STRUCTURES OF THE SIMPLE SILANES

	$H^7$	$H^7$	$CH_3^7$	$CH_3^7$
	$CH_3-Si-H$	$CH_3-Si-CH_3$	$CH_3-Si-CH_3$	$CH_3-Si-CH_3$
	$H$	$H$	$H$	$CH_3$
C—Si, obs	1.867 Å	1.867 Å	1.868 Å	
calc	1.873	1.872	1.872	1.871 Å
Si—H, obs	1.484	1.483	1.489	—
calc	1.484	1.484	1.485	—
* H—Si—H, obs	108.7°	107.8°	—	—
calc	108.3	108.6	—	—
* C—Si—H, obs	110.2	109.5	108.8°	—
calc	110.6	109.6	109.1	—
* C—Si—C, obs	—	111.0	110.2	109.5°
calc	—	109.8	109.8	109.5

TABLE 2—continued

Disilapropane <sup>a</sup>		Vinylsilane <sup>b</sup>	
C—Si, obs	1·873	C—Si, obs	1·852
calc	1·872	calc	1·852
Si—H, obs	1·512	Si—H, obs	1·475
calc	1·484	calc	1·484
* Si—C—Si, obs	114·4	C—C, obs	1·347
calc	113·8	calc	1·335
* H—Si—H, obs	108·1	* S—iC=C, obs	127·8
calc	108·5	calc	122·7
* H—C—H, obs	110·0	* C=C—H, obs	118·0
calc	111·7	calc	121·7
* C—Si—H, obs	108·3		
calc	110·7		

that because of the increased bond length of the Si—C bond (1·87 Å) over that of the C—C bond (1·54 Å), interactions with silicon are usually quite minor and of an attractive nature. The hydrogens attached to silicon are also some distance away from most atoms of the hydrocarbon moiety because of the long Si—H bond length (1·48 Å). Bond angles about silicon resemble those about carbon, with the tetrahedral value observed for SiX<sub>4</sub> types of compounds.

It is known experimentally that the barrier to rotation in methylsilane is about 1·7 kcal/mole,<sup>7</sup> a value much smaller than that observed for ethane (2·92 kcal/mole<sup>10</sup>). Unlike the component energies in the eclipsed and staggered forms of ethane, van der Waals interactions in methylsilane are similar in both rotamers, and torsional energy appears to account for most of this barrier. Similarly, the barriers in dimethylsilane (1·66 kcal/mole<sup>7</sup>), trimethylsilane (1·8 kcal/mol<sup>7</sup>), and tetramethylsilane (~ 1·5 kcal/mole<sup>11, 12</sup>) are much lower than those in the hydrocarbon analogs (propane, 3·33; isobutane, 3·9; neopentane, 4·3 kcal/mole<sup>10</sup>). Eclipsing interactions are therefore not as severe in the silanes as in the hydrocarbon series. The energy calculations for all molecules discussed in this paper are shown in Table 3.

TABLE 3. ENERGY CALCULATIONS AND HEATS OF FORMATION

Compound	Steric Energy	$\Delta E$ Calc.	$\Delta E^a$ obs.	Bond Energy	Calc. $\Delta H_f^\circ$	Exp. <sup>b</sup> $\Delta H_f^\circ$
Methylsilane, stg	-0·55	0·00	0·00	-11·78	-12·33	(-12)
ecl	1·13	1·68	1·67			
Dimethylsilane, stg-stg	-1·50	0·00	0·00	-14·96	-16·46	(-17)
stg-ecl	0·17	1·67	1·66			
Ethylsilane, stg	0·61	0·00	0·00	-17·01	-16·40	(-17)
ecl	2·55	1·94	1·90 <sup>14</sup>			
n-Propylsilane, 0°	5·50	4·24				
60°	1·92	0·66				
120°	3·89	2·63				
180°	1·26	0·00		-22·98	-21·72	

TABLE 3—continued

Compound	Steric Energy	$\Delta E$ Calc.	$\Delta E^a$ obs.	Bond Energy	Calc. $\Delta H_f^\circ$	Exp. <sup>b</sup> $\Delta H_f^\circ$
Trimethylsilane, all stg	-2.86	0.00	0.00	-18.14	-21.00	(-21)
stg-stg-ecl	-1.26	1.60	1.83 <sup>7</sup>			
			2.49 <sup>13</sup>			
Tetramethylsilane, all stg	-4.71	0.00	0.00	-21.32	-26.03	(-26)
ecl-stg-stg-stg	-3.15	1.56	1.30 <sup>11</sup>			
			2.00 <sup>12</sup>			
Diethylsilane, all stg	0.71			-25.42	-24.71	(-27)
Triethylsilane, all stg	4.99			-33.83	-28.84	(-36)
Tetraethylsilane, all stg	-1.45			-42.24	-43.69	-44.00
Methyl-isopropylsilane, sym	-1.02	0.00		-25.42	-26.44	
asym	-0.94	0.08				
Methyl ethyl silane, 0°	1.46	1.90				
60°	-0.44	0.00		-20.19	-20.63	
120°	1.48	1.92				
180°	-0.38	0.06				
Trimethyl-t-butylsilane, all stg	-6.12			-38.76	-44.88	
Dimethyl-diethyl-silane	-2.70			-31.78	-34.78	
1,3-Disilapropane, stg	-1.20			-5.68	-6.88	
Silacyclopentane, half chair	8.94	0.00	0.00	-14.99	-6.05	
envelope	12.87	3.93	3.89 <sup>15</sup>			
Silacyclohexane, chair	3.45	0.00		-20.96	-17.51	
boat	9.61	6.16				
twist-boat (1) C <sub>2</sub>	6.55	3.10				
twist-boat (2)	7.79	4.35				
1-Methylsilacyclohexane, eq	2.00	0.04				
ax	1.96	0.00		-24.14	-22.18	
1.1-Dimethylsilacyclohexane, chair	-0.02	0.00	0.00	-27.32	-27.34	
‡ 1234 pl	5.90	5.92				
‡ 2345 pl	11.31	11.33				
‡ 6123 pl	5.44	5.46	5.5 <sup>16</sup>			
1,1,4,4-Tetramethyl-1,4-disilacyclohexane, chair	-8.23	0.00		-18.82	-27.05	
‡ 1234 pl	0.02	8.25				
‡ 2345 pl	-1.27	6.96	<6 <sup>16</sup>			
SiH <sub>3</sub> -cyclohexane, eq	2.80	0.00		-30.46	-27.66	
ax	4.27	1.47				
Si(CH <sub>3</sub> ) <sub>3</sub> -cyclohexane, eq	-1.81	0.00		-40.00	-41.81	
ax	2.07	3.88				
Vinylsilane, ecl to double bond	0.18	0.00	0.0	-1.18	-1.0	-1.0
stg to double bond	1.67	1.49	1.50 <sup>9</sup>			
Silacyclopent-2-ene, planar	9.60			-1.72	7.87	
Silacyclopent-3-ene, planar	5.64			14.11	19.75	
1-Silanorbornane	22.75			-12.97	9.78	
2-Silanorbornane	17.14			-16.50	0.64	
7-Silanorbornane	23.51			-16.50	7.01	
1-Silabicyclo [2.2.2]octane	13.47			-18.94	-5.47	
2-Silabicyclo[2.2.2]octane	11.57			-22.47	-10.90	

<sup>a</sup> Observed energies taken from ref. 7 unless otherwise noted. See also refs. 17 and 18.

<sup>b</sup> Notation used is that of Benson *et al.* (ref. 19). Values in parentheses are extrapolated estimates based on experimental trends.

For both propylsilane and methylethylsilane we have calculated the rotational barrier about the central bond and have compared our results to the rotational barrier about the corresponding bond in butane. This comparison is illustrated in Fig 1.

The results show that *n*-propylsilane has a torsional function very similar to that for *n*-butane, but the numerical values for the energies are slightly smaller. On the other hand, the *gauche* and *anti* forms of methylethylsilane have the same conformational

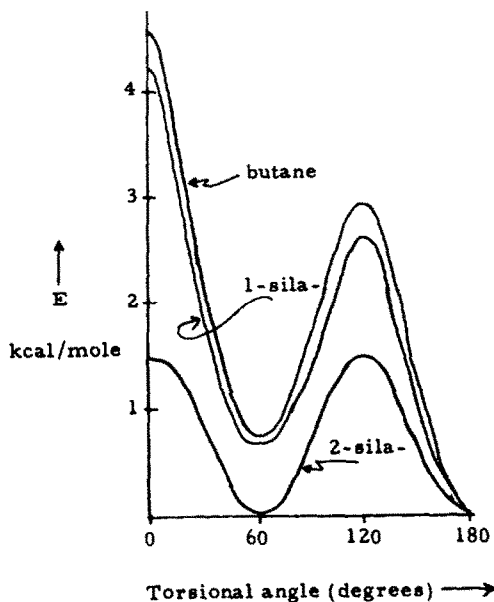


FIG 1. Comparison of the rotational barriers in butane, 1-silabutane, and 2-silabutane

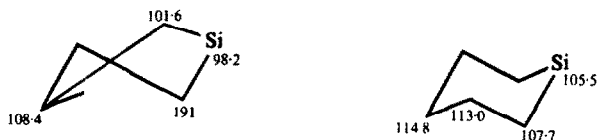
enthalpy to within calculational error. The reason for the difference is that the longer C—Si bond allows the ends of the molecule to move apart in the *gauche* conformation, compared to what is found in *n*-butane. This reduces the repulsions between the nearest hydrogens on atoms 1 and 4, which stabilizes the conformation. The effect is greater with the 2-sila than with the 1-sila compound, because there are two C—Si bonds in the former, and but one in the latter. The longer Si—H bond (compared to a C—H bond) in the latter works against this. In addition, the repulsion between terminal hydrogens causes other deformations in butane and the 1-sila compound. For example, the torsional angles about the 2-3 bond are 63.5 and 63.3°, respectively, as the hydrogens attempt to avoid one another, at the expense of a little unfavourable torsion. With the 2-sila derivative the repulsion is so small (0.06 kcal/mole) that no torsion is needed ( $\omega = 60.0^\circ$ ).

Just as the axial and equatorial conformations of methylcyclohexane can be analyzed in terms of butane interactions, so can we analyze silylcyclohexane in terms of 1-silabutane, and methylsilacyclohexane in terms of 2-silabutane interactions. As one would suppose from the previous discussion, the calculation predicts a lack of preference of the Me substituent in methylsilacyclohexane for either the axial or equatorial position. In addition, the similarity in enthalpies in the two conformers

of methylisopropyl silane further illustrates this trend. The analogous energy difference between the rotamers of isopentane is calculated to be 0.6 kcal/mole favoring the unsymmetrical form.<sup>20</sup>

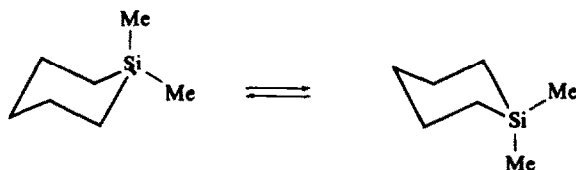
The mid- and far-IR spectra of silacyclopentane have recently been reported<sup>15, 21</sup> and the barrier to pseudorotation (the energy difference between the more stable  $C_2$  half-chair and the  $C_s$  envelope conformations) was estimated<sup>15</sup> to be  $3.89 \pm 0.07$  kcal/mole. Our calculated value for this difference is 3.93 kcal/mole, in excellent agreement with experiment. This unusually high barrier to pseudorotation for a 5-membered ring compound has heretofore been considered anomalous in terms of Pitzer's<sup>22</sup> torsional concepts. This observation is doubly unusual in view of the fact that in cyclopentane, the half-chair and envelope conformers have identical energies. Our calculations for silacyclopentane indicate that all interactions (van der Waals, stretching, bending, and torsional) are larger in the symmetrical envelope than in the half-chair.

For silacyclohexane, we calculate the chair conformer to be lowest in energy, similar to that observed for the cyclohexane system. Because of the rather small torsional barrier about the C—Si bond, the  $C_2$  twist-boat conformer is only 3 kcal higher in energy. We calculate that the internal C—Si—C angle in both silacyclopentane and silacyclohexane is much smaller than for the hydrocarbons. (Corresponding angles in cyclopentane and cyclohexane are  $106.2$  and  $111.1^\circ$ , respectively.



As mentioned previously, we calculate no conformational preference for the Me group in 1-methyl-1-silacyclohexane. When a  $-\text{SiH}_3$  or  $-\text{Si}(\text{CH}_3)_3$  group is substituted on a cyclohexane ring, however, more typical enthalpy differences favoring the equatorial substituent are found. To our knowledge, no experimental conformational free energies for silyl substituents have been reported with the exception of  $-\text{SiCl}_3$ , which was assigned a  $\Delta F$  of 0.61 kcal by NMR methods.<sup>23</sup>

Recently, Jensen<sup>16</sup> has studied the barrier to interconversion of 1,1-dimethyl-1-silacyclohexane and has found a much lower barrier in the heterocycle than for the corresponding carbocycle.



He suggested that the transition state ( $\ddagger$ ) for the interconversion of chair forms to the twist-chair conformation involved an arrangement in which four ring atoms were coplanar. In addition, Murray and Kaplan<sup>24</sup> have studied some 1,1,4,4-tetramethyl-1,4-disilacyclohexanes using a similar NMR method and have suggested that the long bonds and low barriers to rotation about the  $C_{\beta\alpha}$ —Si bonds are responsible for the

low barriers to interconversions in these compounds. We have minimized energies for several methyl substituted silacyclohexanes and the corresponding hydrocarbons in both the lowest energy chair form and in the possible transition states in which four ring atoms are coplanar. Our results are summarized in Fig 2.

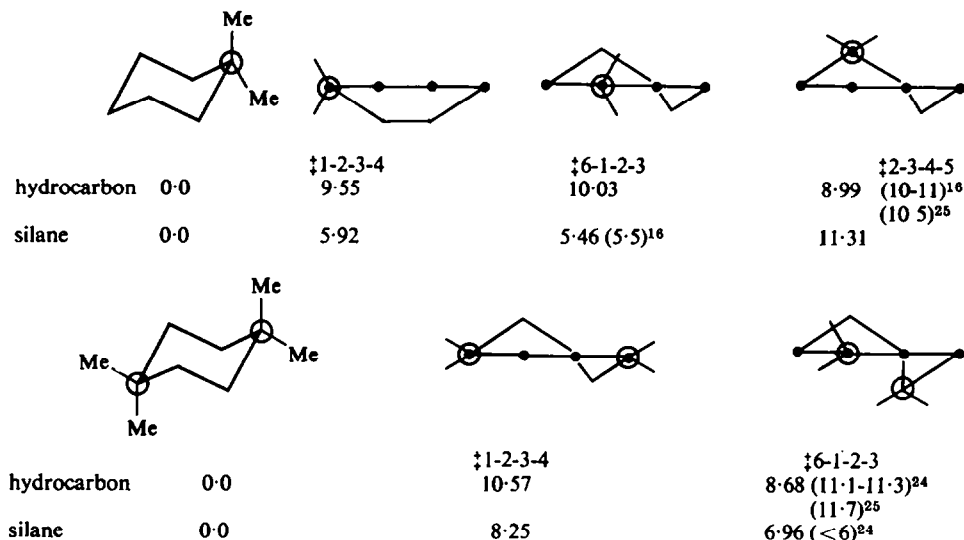


FIG 2. (Experimental values are in parentheses)

1,1-Dimethylcyclohexane and 1,1-dimethyl-1-silacyclohexane prefer different (‡) geometries according to our calculations. The best arrangement of four atoms in a planar system is the 2-3-4-5 set for the hydrocarbon and the 6-1-2-3 set for the silane derivative. In both compounds the 1-2-3-4 system does not minimize to the chair form (even when the minimization is begun with this conformer) but prefers the boat. In both molecules this planar arrangement is higher in energy than other planar combinations. The energy difference between the chair form and the lowest (‡) geometry is a little low for the hydrocarbon (8.99 kcal/mole, calcd; 10.5 kcal/mole, obsd), but is quite good for the silane (5.46 kcal/mole, calcd; 5.5 kcal/mole, obsd.)

Our calculated energy for the transition state of 1,1,4,4-tetramethylcyclohexane (8.65 kcal/mole) is substantially smaller than that determined by NMR (~11.5 kcal/mole), but indicates the distinct preference of this molecule for the 2-3-4-5 transition state geometry. The silane analogue similarly prefers this (‡) conformation and our calculated conformational energy for this state (6.96 kcal/mole) is in good agreement with that determined by NMR (~6 kcal/mole).

Calculations were carried out for the silanorbornanes, and the silabicyclo[2.2.2]-octanes. The former had some very much compressed bond angles, and as we found previously with hydrocarbons, if the bond angles are compressed to values of less than 100°, it is necessary to have included stretch-bend interactions (or something equivalent) in the calculation if the bond lengths are to be satisfactorily predicted. Hence we do not feel our geometries for the silanorbornanes are of sufficient accuracy to warrant reproducing here. On the other hand, the bond angles in the silabicyclo[2.2.2]-



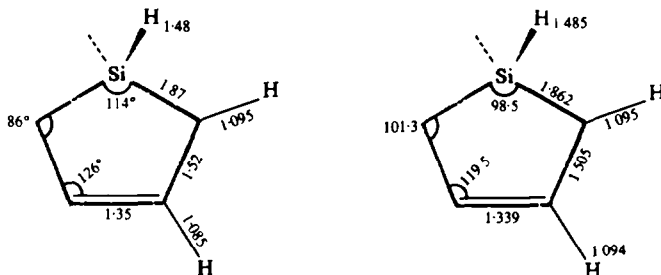
octanes are not so compressed, and we feel these geometries are in fact quite valid, and since they are not known experimentally, they are presented here as predictions of the structures of these interesting molecules.



A study of vinylsilane has recently been reported<sup>9</sup> and our calculated structure is described in Table 2. The barrier to rotation about the  $C_{sp^2}$ —Si bond shows remarkably little difference from the  $C_{sp^3}$ —Si barriers. (The same is true in hydrocarbons; propane and propene have similar rotational barriers.)

Laane has recently studied the far-IR spectra of silacyclopent-2-ene<sup>26</sup> and silacyclopent-3-ene<sup>27, 28</sup> and has shown both molecules to exist in planar conformations. It was suggested that small barriers to rotation about  $C_{sp^2}$ —Si and  $C_{sp^3}$ —Si bonds accounted for the lack of a barrier in these compounds similar to cyclopentene. Our calculations confirm the fact that each of these molecules prefers to be planar; all other conformers of each of these molecules minimized to the planar form.

Laane<sup>27</sup> has estimated a structure for silacyclopent-3-ene which is quite different from that which we calculate. We believe our structure is more reliable.†



**Heats of formation.** Most of the experimental heats of formation for silyl compounds ( $\Delta H_f^\circ$ , gas 25°) are highly suspect due to the difficulty in obtaining complete combustion in the calorimeter. We have taken therefore for completeness and consistency the review by Benson, *et al.*<sup>19</sup> as the most up-to-date set of data available based on modern values for heats of elemental combustion, etc. Most of the data from this work are extrapolated values, however, based on a few accurate thermodynamic pieces of data. While we have attempted to reproduce this body of data as accurately as possible, the calculated and experimental values are probably no better than 1 kcal/mole. The additive scheme which we use for the heat of formation calculation is similar to those used by others<sup>29</sup> for compounds of silicon, and is identical to that described previously for hydrocarbons<sup>3</sup> with the additional quantities for  $C_{sp^2}$ —Si,  $C_{sp^3}$ —Si, and Si—H bonds included. These parameters are listed in Table 3.

†After hearing of our calculations, Dr. Laane informed us that mid-infrared band-types indicated that the molecule is not nearly so squashed as he previously suggested, and a structure very close to the one we have calculated appears to be the correct one. We appreciate Dr. Laane's kindness in furnishing us with this information in advance of publication.

## CONCLUSIONS

From a calculational point of view the silanes are the same as the hydrocarbons in principle, only the numerical values are different. However, since many of the numbers for small molecules are only known approximately, if at all, the number and kinds of conclusions to be drawn, and their degree of reliability, are not as great as with the hydrocarbons. However, as more and better data become available, the calculational methods will be able to better deal with these compounds.

From a chemical point of view, the long C—Si bond length, and the small torsional barrier about the bond lead to differences in properties between the silanes and the analogous hydrocarbons which are far reaching. In general, these differences can be qualitatively estimated from elementary considerations, and as far as can be seen from the present work, quantitative calculations are possible within the limits explored, and can be used for predictive purposes with a fair degree of confidence.

## REFERENCES

- <sup>1</sup> Paper LXXXII N. L. Allinger and M. J. Hickey, *Tetrahedron* **28**, in press (1972)
- <sup>2</sup> This research was supported by a grant from the Eli Lilly Company, which is gratefully acknowledged
- <sup>3</sup> N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Am. Chem. Soc.* **93**, 1637 (1971)
- <sup>4</sup> <sup>a</sup> N. L. Allinger and M. T. Tribble, *Tetrahedron* **27**, in press (1971); <sup>b</sup> N. L. Allinger and M. T. Tribble, *Tetrahedron Letters* 3295 (1971)
- <sup>5</sup> T. L. Hill, *J. Chem. Phys.* **16**, 399 (1948)
- <sup>6</sup> <sup>a</sup> S.-I. Mizushima, *Advances in Molecular Spectroscopy* (Edited by A. Mangini) Vol. 1, pp 60–69. Pergamon Press, New York (1962); <sup>b</sup> J. L. Duncan, *Spectrochim. Acta* **20**, 1807 (1964); <sup>c</sup> T. Shimanouchi, I. Nakagawa, J. Hiraishi, and M. Ishii, *J. Mol. Spectrosc.* **19**, 78 (1966); <sup>d</sup> M. Randic, *Spectrochim. Acta* **18**, 115 (1962)
- <sup>7</sup> L. Pierce and D. H. Petersen, *J. Chem. Phys.* **33**, 907 (1960)
- <sup>8</sup> A. Almenningen, H. M. Seip, and R. Seip, *Acta Chem. Scand.* **24**, 1697 (1970)
- <sup>9</sup> J. M. O'Reilly, L. Pierce and L. C. Krisher, *Spectrochim. Acta* **16**, 1271 (1960)
- <sup>10</sup> J. P. Lowe, *Prog. Phys. Org. Chem.* **6**, 1 (1968)
- <sup>11</sup> J. G. Aston, R. M. Kennedy, and G. H. Messerly, *J. Am. Chem. Soc.* **63**, 2343 (1941)
- <sup>12</sup> J. R. Durig, S. M. Craven, and J. Bragin, *J. Chem. Phys.* **52**, 2046 (1970)
- <sup>13</sup> J. R. Durig, S. M. Craven, and J. Bragin, *Ibid.* **53**, 38 (1970)
- <sup>14</sup> D. H. Petersen and L. Pierce, *Spectrochim Acta* **16**, 1272 (1960)
- <sup>15</sup> J. Laane, *J. Chem. Phys.* **50**, 1946 (1969)
- <sup>16</sup> F. R. Jensen and C. H. Bushweller, *Tetrahedron Letters* 2825 (1968)
- <sup>17</sup> R. W. Kilb and L. Pierce, *J. Chem. Phys.* **27**, 108 (1957)
- <sup>18</sup> L. Pierce, *Ibid.* **34**, 498 (1961)
- <sup>19</sup> S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.* **69**, 279 (1969)
- <sup>20</sup> N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, *J. Am. Chem. Soc.* **90**, 1199 (1968)
- <sup>21</sup> J. R. Durig and J. N. Willis, Jr., *J. Mol. Spectrosc.* **32**, 320 (1969)
- <sup>22</sup> K. S. Pitzer and W. E. Donath, *J. Am. Chem. Soc.* **81**, 3213 (1959)
- <sup>23</sup> F. R. Jensen, C. H. Bushweller, and B. H. Beck, *Ibid.* **91**, 344 (1969)
- <sup>24</sup> R. W. Murray and M. L. Kaplan, *Tetrahedron* **25**, 1651 (1969)
- <sup>25</sup> H. Friebolin, H. G. Schmid, S. Kabuss, and W. Faisst, *Org. Magn. Resonance* **1**, 147 (1969)
- <sup>26</sup> J. Laane, *J. Chem. Phys.* **52**, 358 (1970)
- <sup>27</sup> J. Laane, *Ibid.* **50**, 776 (1969)
- <sup>28</sup> J. F. Blanke, T. H. Chao, and J. Laane, *J. Mol. Spectrosc.* **38**, 483 (1971)
- <sup>29</sup> H. F. O'Neal and M. A. Ring, *Inorg. Chem.* **5**, 435 (1966)