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CONFORMATIONAL ANALYSIS—XV[1]*

FORCE FIELD CALCULATIONS AND NMR DETERMINATION OF CONFORMATIONAL EQUILIBRIA OF ORGANOSILICON COMPOUNDS

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Abstract—Force field calculations of the conformational energies of fifteen silanes are described. The calculated structures of silaethane, 2-silapropane and 2-methyl-2-silapropane are in acceptable agreement with available microwave data. The calculated torsional barriers of silaethane 2-silapropane; 2-methyl-2-silapropane and 1-silapropane are consistent with reported barriers. In 2-silabutane and related compounds, the *gauche* conformation is more stable than the *anti* conformation as a result of attractive van der Waals energy terms. The strain energies of the two eclipsed conformations of 2-silabutane are identical and substantially lower than the strain energies of the two eclipsed conformations of butane which are of unequal energy. The shape of the torsional curve for 2-silabutane differs dramatically from that of butane. 1-Silabutane is stable in the *anti* conformation and the *gauche-anti* energy difference is similar to butane. The two eclipsed conformations of 1-silabutane stand in the same order as those for butane but are of higher energy. A comparison of the torsional curve for 1-silabutane with butane illustrates the steeper barriers for the former compound. Conformational equilibrium constants for 2-silabutane, 1-silabutane, and several compounds containing the 2-silabutane structure are obtained by NMR analysis of vicinal coupling constants and are in agreement with the calculated force field values. The conformational preferences of SiH_3, SiH_2CH_3, $SiH(CH_3)_2$, and $Si(CH_3)_3$ on cyclohexane are calculated. Unique features of silacyclohexane and the conformational preferences of hydrogen, methyl, and *t*-butyl on this ring are discussed.

IN A RECENT PAPER from this laboratory, which reported the use of silanes in demonstrating the effect of internal solvent pressure on conformational equilibria,[2] it was noted that *gauche* conformations about a C—Si bond are unusually stable with respect to *anti* conformations. This observation is in striking contrast to the corresponding hydrocarbon conformations. The C—Si bond is longer than a C—C bond and should allow the attached groups to move apart in *gauche* conformations thus reducing the importance of repulsive interactions. However, consideration of only repulsive interactions clearly does not account for the observed stability of *gauche* conformations. It was suggested that the geometry of silanes allows for nonbonded interactions with energies in the potential minimum of the van der Waals curve. The proposed attractive interactions are calculated by force field approaches and reported in this paper. Attractive interactions between nonbonded atoms whose interatomic distances place the van der Waals energy in or close to the potential well have been observed for the highly polarizable chlorine.[3] Although no force field calculations have been reported, the conformational features of phosphacyclohexane[4] and

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thiacyclohexane[5] are unusual and may be the result of attractive nonbonded interactions. The compounds examined in the internal pressure study involved silicon, another element of the third period, and the observed stability of *gauche* conformations may be the result of attractive nonbonded interactions. The demonstration of such contributions by both calculations and experimental tests should be an important and far reaching feature in understanding the physical and chemical properties of this extensively populated class of compounds.

Force field calculations

The objectives of force field calculations may be structure,[6–8] energies,[8] vibrational spectra,[9] or thermodynamic parameters.[10] The approaches are all based on expedient approximations in order to calculate desired quantities which are now unattainable from total electronic wave functions. The approach used in this paper is derived from the "Westheimer" method.[11,12]

The classical model used involves the calculation of the strain energy, $E(s)$, of the conformation which is defined as the sum of energy terms given in Equation 1.

$$E(s) = E(r) + E(\theta) + E(\phi) + E(nb) \tag{1}$$

The individual terms are the energies associated with bond stretching, bond angle deformations, bond torsions, and van der Waals interactions. The force field can be viewed as two harmonic potentials involving bonded atoms and two nonbonded potentials. The harmonic potentials are given by equations 2 and 3.

$$E(r) = \sum \tfrac{1}{2}k_r(r - r_0)^2 \tag{2}$$

$$E(\theta) = \sum \tfrac{1}{2}k_\theta(\theta - \theta_0)^2 \tag{3}$$

For each bond or bond angle, the r_0 and θ_0 values are selected to represent "strain free" values. The individual force constants k_r and k_θ are calculated or estimated from normal coordinate analysis of the IR and Raman spectra of representative molecules.

The torsional potential is given by equation 4 for the three fold barrier involved in the molecules of interest.

$$E(\phi) = \sum \tfrac{1}{2}k_\phi(1 + \cos 3\phi) \tag{4}$$

The dihedral angle is given by ϕ and the barrier height by k_ϕ.

The Buckingham function given in equation 5 is used to account for the attractive and repulsive van der Waals forces.

$$E(nb) = \sum \{a \exp(-b \cdot d) - c/d^6\} \tag{5}$$

In order to determine the minimized energy structure, the number of terms to be considered is given approximately by $n!/(n - 2)! \cdot 2!$ where n is the number of atoms. Minimization is achieved by utilizing the method of Boyd.[10] The force field is expressed in terms of internal coordinates and the potentials expanded in a Taylor series about the trial geometry. All cross terms are eliminated and the higher order terms are truncated. Since the internal coordinates are not independent, differentiation to solve for the minimum is not possible. Transformation of internal coordinates into Cartesian coordinates followed by application of the conditions for a minimum yield linear equations which may be solved. The solution of the minimum energy structure is not exact due to the neglect of cross and high order terms in the Taylor series. However, the new geometry is used to generate new coordinates and the process is repeated, iteratively until the root mean square deviation of the coordinate position is less than 0·002 Å. The Cartesian coordinates are retransformed into internal coordinates and each term contributing to the strain energy is evaluated and summed.

TABLE 1. PARAMETERS FOR THE CALCULATION OF MOLECULAR GEOMETRIES AND ENERGIES

	van der Waals Constants	
Atom	r	ε
H	1·45	0·100
C	1·65	0·040
Si	2·15	0·310

	Bond stretching constants	
Bond	l_0 (Å)	k (mdyn/A^2)
C—C	1·513	4·50
C—H	1·094	4·80
C—Si	1·870	2·97
H—Si	1·485	2·78

	Angle bending constants	
Angle	θ_0	k (mdyn/rad.^{2})
H-C-H	110·9	0·3194
H-C-C	108·6	0·5486
C-C-C	109·8	0·7986
H-Si-H	108·2	0·236
H-Si-C	109·5	0·403
C-Si-C	110·5	0·570
C-C-Si	112·0	0·684
H-C-Si	110·0	0·476

	Torsional constants
Atoms	V_0 (kcal/mole)
X-C-C-Y	0·5
X-C-Si-Y	0·5

Two additional programs were placed prior to the minimization method in order to decrease the labour of preparing the input data. A molecule builder program calculated the coordinates of the molecules and arranged the structures in the desired geometries. The second program is an atom and parameter inclusion matrix which selects all of the appropriate combinations of atoms and the related parameters for the proper potential functions. All intermediate data was directly accessible on disc. An IBM 360/75 was used for the calculations for molecules containing up to 28 atoms* with a limit of 126 K. For the methyl silane, the times required for the

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* For two conformations of trimethylcyclohexylsilane which contains 32 atoms the program was altered to use 252K.

molecule builder, atom inclusion matrix and minimization steps were 0·5, 1·5 and 3·5 seconds, respectively. For the axial conformation of trimethylcyclohexyl silane the times were 0·8, 5·8 and 137 seconds. The total times per molecule ranging from 6 to 142 seconds represents an efficient approach to the problem of calculating the steric energy of molecules.*

The parameters chosen for carbon and hydrogen structural units are those of Allinger.[13] and are listed in Table 1. Rather than use the complete set of early parameters, the choice was made to adopt V_0(X–C–C–Y) = 0·5 kcal/mole suggested in more recent calculations.[6] For the constants involving silicon selected values available from the limited literature on these compounds were assigned as given in Table 1.

The r and ε values for silicon are chosen to be intuitively consistent with those of the other third row elements, argon, chlorine, and sulfur.[3, 14] As will be shown in the discussion of 2-silabutane, the contribution of van der Waals terms for silicon are small and in fact largely cancel when differences in conformational energies are calculated. For compounds containing the 2-silabutane skeleton a considerable range of r and ε values would be acceptable. In 1-silabutane and related structures the contribution of van der Waals terms for silicon is more substantial and is not cancelled in conformational energies. However, when the ε value is changed to 0·21 for calculations of 1-silabutane, it is shown that the effect on the minimized energies and conformational energy differences is unimportant and does not affect the predictive quality of the force field calculations.

Force constants for C–Si and H–Si stretching as well as H–Si–H bending are available from normal coordinate analysis of methylsilane[15] and silane.[16] The force constant for C–Si–C bending is estimated.[17] By analogy with the ordering of the bending force constants involving carbon as the central atom, the H–Si–C bending force constant is set at a value between those of H–Si–H and C–Si–C. Thus both the bending and stretching force constants for silicon are approximately 30% smaller than those for carbon. The C–C–Si and H–C–Si bending force constants are chosen to be less than the C–C–C and H–C–C values in order to reflect the effect of the ease of deforming an angle when silicon is substituted for carbon.

In order to fit the torsional barrier for silaethane, the torsional parameter V_0(H–C–Si–H) is set at 0·5 kcal/mole. There is insufficient reliable data to assign V_0(X–C–Si–Y) or V_0(Si–C–C–X) for X and Y equal to the other combinations of hydrogen and carbon. However, all of the terms have been assigned identical values as has been done for V_0(X–C–C–Y).[6] The evidence that the estimate is reasonable is the near identity of the torsional barriers of silaethane, 2-silapropane, 2-methyl-2-silapropane, and 1-silapropane. With more accurate redeterminations of these torsional barriers or the study of additional compounds, it may be necessary to change the V_0 terms chosen. However, it is likely that the changes will be no more than 0·1 kcal/mole. For most conformational equilibrium the V_0 terms are relatively unimportant as the dihedral angles are near 60°.

Energy and structures

Each of the compounds studied is described under separate headings and a key number is given for use with the tables. Calculated structures of the simpler com-

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*, In the latter part of this work a few conformations were calculated using an IBM 370/165 which is approximately twice as fast.

pounds are listed in Table 2. Steric energies are given in Table 3. The symbols E_r, E_θ, E_ϕ, E_{nb}, and E_s refer to the energies associated with stretching, bending, torsional, nonbonded, and total steric energies, respectively.

Silaethane 1. In the staggered conformation of CH_3SiH_3 the calculated bond lengths and bond angles are in reasonable agreement with the observed structure.[18c] The principal difference is that the calculated H–Si–H bond angle deviates less from the tetrahedral value than for the observed quantity. However, this difference corresponds to a very small energy. In the eclipsed conformation there is a small elongation of the C—Si bond accompanied by a shortening of the Si—H bonds. The C–Si–H angles increase to move the SiH_3 hydrogens away from the CH_3 hydrogens. As expected the changes at the carbon center are less than at silicon.

The E_s of staggered silaethane is dominated by E_{nb} and both are negative. The nine contributing nonbonded interactions are negative and the six *gauche* H/H interactions are at the minimum energy of the van der Waals curve. For the eclipsed conformation $E_s - E_\phi = -0{\cdot}62$ kcal/mole. A fit of the torsional barrier of 1·67 kcal/mole requires $E_\phi = 1{\cdot}51$ kcal/mole. This quantity is the source of V_0(H–C–Si–H) = 0·5 kcal/mole given in Table 1. Silaethane is markedly different than ethane as the E_s terms are dominated by E_{nb} and are largely self cancelling in the torsional barrier.

Experimental work is in progress on germanium and tin compounds and force field calculations are being undertaken. It is clear from the torsional barriers of CH_3GeH_3, CH_3SnH_3, and $(CH_3)_4Pb$ of 1·24,[18b, 19] 0·65,[20] and 0·18[21] kcal/mole, respectively, that all of the component terms must decrease including E_ϕ. In fact the E_ϕ must be essentially equal to the barrier. Thus V_0(H–C–M–H) are probably in the order C = Si > Ge > Sn > Pb. That V_0 for carbon is not larger than for silicon may be the result of the way in which all of the energy contributions are separated. In the other members of Group IV elements, E_ϕ is the major feature and it may be obtained without having to account for other terms to the degree of certainty required for carbon. A part of E_ϕ for carbon may be contained in the other terms.

1-*Silapropane* 2. Both the staggered and eclipsed conformations about the Si—C bond have been calculated for this compound. While the molecular dimensions are given in Table 2, there is no experimental structure for comparison, although some features of the microwave spectra have been determined.[18g]* A torsional barrier of 1·94 ± 0·04 kcal/mole has been suggested on the basis of doublet spacing of absorptions assigned to the excited torsional state. The splitting of transitions of overall and internal rotation is too small to be resolved in the ground state. If the assignment and torsional barrier is correct and established in other compounds in which H–Si–C–C eclipsing occurs, then a corrected V_0 term would be necessary. However, at this time, there is insufficient experimental evidence to justify this change.*

The energy of the eclipsed conformation about the C—C bond is also given in Table 3. A torsional energy barrier of 3·78 kcal/mole is reasonable as the monosubstituted ethanes all have energy barriers between 2·9 and 3·7 kcal/mole. The closest analog is chloroethane with a barrier of 3·68[22] kcal/mole. Therefore, the assigned V_0(H–C–C–Si) is consistent with the presently available data.

2-*Silapropane* (3). Both the staggered and eclipsed conformations for this compound were calculated. The structural features given in Table 2 are in acceptable agreement

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* Reference 18 g is a short abstract of a report given at the Eleventh Annual Symposium on Spectroscopy in Chicago, June, 1960.

TABLE 2. CALCULATED AND OBSERVED STRUCTURES[a] OF SIMPLE SILANES

		1b			2		3b	4b	5		6	
		stg	ecl	stg	CC-ecl	C-Si-ecl	stg	stg	gauche	anti	gauche	anti
Si–H	Obs	1·484					1·483	1·489				
	Calc	1·487	1·481	1·485	1·486	1·485	1·484	1·484	1·484	1·484	1·484	1·485
Si–C	Obs.	1·867					1·867	1·868				
	Calc	1·868	1·871	1·882	1·893	1·884	1·868	1·867	1·868	1·867	1·878	1·878
H–Si–H	Obs.	108·7					107·8					
	Calc	109·5	108·3	109·2	109·2	108·8[e]	108·7		108·6	108·3	109·3[c]	109·2
C–Si–C	Obs				(C–C–Si)		111·0	110·2			(C C–Si)	
	Calc			113·6	114·4	113·8	110·0	109·7	110·5	111·3	115·8	114·6
H–Si–C	Obs.	110·2					109·5	108·8				
	Calc	109·4	110·6	109·7	109·8	110·1[f]	109·5	109·0	109·4	109·0	109·7[d]	109·7
C–C–Si–C	Calc								59·6	180·0		
C–C–C–Si	Calc										64·1	180·0

[a] Bond lengths in Å, bond angles in degrees. [b] Observed quantities taken from reference 18*c*. [c] 108·3° for one combination. [d] 110·4° for one combination. [e] 109·1 for one combination. [f] 109·8 for one combination.

TABLE 3. CONFORMATIONAL ENERGIES

	Conformation	E_r	E_θ	E_ϕ	E_{nb}	E_s	ΔE_{calc}	ΔE_{obs}
1	stg	0·01	0·08	0·00	−0·87	−0·78	0·00	0·00
	ecl	0·01	0·09	1·50	−0·72	0·88	1·66	1·67
2	stg	0·16	0·40	0·00	−0·36	0·20	0·00	0·00
	ecl H/Si	0·40	1·01	1·50	1·07	3·98	3·78	3·7[a]
	ecl H/C	0·17	0·41	1·50	−0·25	1·83	1·63	1·9[b]
3	stg	0·00	0·11	0·00	−1·97	−1·86	0·00	0·00
	ecl	0·01	0·12	1·50	−1·83	−0·20	1·66	1·66
4	stg	0·01	0·19	0·00	−3·33	−3·13	0·00	0·00
	ecl	0·02	0·20	1·50	−3·19	−1·47	1·66	1·83
5	ecl C/C	0·15	0·64	1·50	−1·63	0·66	1·68	
	gauche	0·13	0·52	0·02	−1·70	−1·02	0·00	0·0
	ecl C/H	0·14	0·49	1·50	−1·45	0·68	1·70	
	anti	0·12	0·51	0·00	−1·52	−0·88	0·14	0·2
6	ecl C/Si	0·83	2·56	1·51	0·96	5·86	5·67	
	gauche	0·34	1·00	0·13	−0·72	0·75	0·56	0·7
	ecl H/Si	0·29	1·34	1·50	0·72	3·85	3·66	
	anti	0·18	0·61	0·00	−0·60	0·19	0·00	0·0
7	ecl C/C	0·42	0·91	1·51	−1·48	1·36	1·85	
	sym	0·38	0·83	0·02	−1·73	−0·49	0·00	0·0
	ecl C/H	0·39	0·78	1·50	−1·38	1·20	1·69	
	asym	0·38	0·80	0·05	−1·54	−0·30	0·19	0·5
8	sym	0·40	0·91	0·12	−3·10	−1·67	0·19	0·2
	asym	0·39	0·96	0·06	−3·28	−1·86	0·00	0·0
9	stg	0·94	1·62	0·46	−5·55	−2·53		
10	anti–anti	0·28	0·84	0·00	−1·08	0·04	0·41	
	anti–gauche	0·29	0·86	0·03	−1·24	−0·07	0·30	
	cis (gauche–gauche)	0·28	1·13	0·90	−1·51	0·80	1·17	
	trans (gauche–gauche)	0·27	0·95	0·03	−1·62	−0·37	0·00	
11	gauche	0·82	2·57	0·77	−4·16	0·00	0·78	1·1
	anti	0·81	2·22	0·17	−3·98	−0·78	0·00	0·00
12	eq.	0·64	0·85	0·04	−0·39	1·14	0·00	
	ax.	0·74	1·84	0·19	−0·37	2·40	1·26	
13	sym eq	0·65	0·96	0·05	−1·90	−0·25	0·00	
	asym eq	0·64	0·91	0·09	−1·75	−0·10	0·15	
	sym ax	0·81	3·31	0·85	−1·65	3·31	3·56	
	asym ax	0·74	1·97	0·23	−1·75	1·19	1·44	
14	sym eq	0·66	1·02	0·16	−3·29	−1·46	0·23	
	asym eq	0·65	1·06	0·09	−3·50	−1·69	0·00	
	sym ax	0·76	2·14	0·29	−3·41	−0·22	1·47	
	asym ax	0·81	3·38	0·82	−3·28	1·74	3·43	
15	eq	0·67	1·24	0·16	−5·32	−3·25	0·00	
	ax	0·84	3·77	0·86	−5·30	0·16	3·41	

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[a] Estimated from chloroethane.[21] [b] See text and refs 18*g* and 20. [c] See text for a treatment of the multi-equilibrium system.

with the microwave structure.[18c] As in silaethane the E_{nb} term, which is made up exclusively of attractive terms, dominates E_s. The E_{nb} term is slightly more than twice that for silaethane. The number of attractive terms between *gauche* protons (H–C–Si–H) increases from six in silaethane to eight in 2-silapropane. In addition there are substantial attractive terms between protons on the methyl groups.

The calculated barrier to rotation for 2-silapropane agrees with the experimental values and is equal to that of silaethane. The identity of the observed torsional barriers is the basis of the choice of the V_0 (H–C–Si–C) term.

2-Methyl-2-silapropane (**4**). The agreement between the calculated and experimental structures[18c] is good. As the third member of a series in which Me groups are successively added to silicon, there is yet another substantial increase in the attractive E_{nb} term. All 56 of the contributing non-bonded terms are negative with terms involving protons on different methyl groups and the six *gauche* H–C–Si–H interactions at the minimum of the van der Waals curve.

The negative E_s of 2-methyl-2-silapropane as well as for the majority of the compounds calculated, when added to E_{bond} terms will yield a more negative ΔH_f°. It is unfortunate that the experimental heats of combustion are suspect because of incomplete combustion.[23] No additive scheme utilizing contributing heat of formation parameters is really justified at this time.

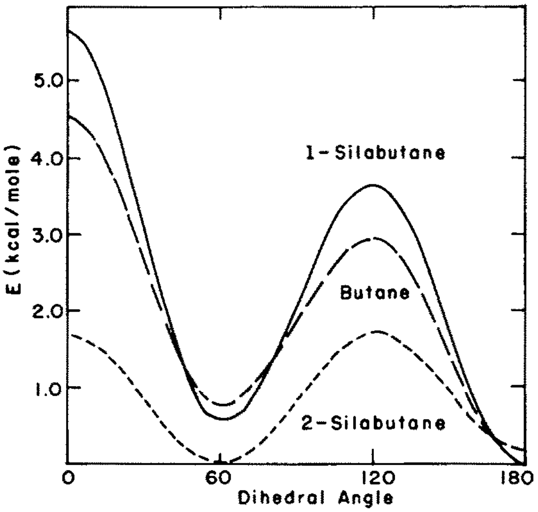

FIG 1. Torsional Coordinate for Butane, 1-Silabutane and 2-Silabutane.

2-Silabutane (**5**). In Fig 1 the E_s values of 2-silabutane as a function of ϕ are depicted One striking feature of the torsional coordinate function is the stability of the *gauche* conformation over that of the *anti* conformation. Taking into account the entropy of mixing term which favors the *gauche* conformation, the predicted equilibrium constant for anti $\rightleftarrows$ gauche is 2·5 at 25°. The E_{nb} term dominates E_s and accounts for the calculated ΔE. The choice of r and ε for silicon is shown to be unimportant to ΔE_{nb}. The only non-bonded terms involving silicon are those with the C-4 hydrogen atoms. A sum of these three terms is 0·40 and 0·37 kcal/mole for the *anti* and *gauche* conformations, respectively. If there were no bond angle differences, the values would obviously be identical. There are small bond angle changes, but the net difference of 0·03 kcal/mole favoring the *gauche* conformation is clearly insignificant and in fact is counterbalanced by differences in E_r, E_θ, and E_ϕ equaling 0·04 kcal/mole favoring the *anti* conformation.

Of the 54 non-bonded terms, 48 are negative in the *gauche* conformation. The hydrogen interactions of H–C–Si–H contribute strongly as the distances are at the minimum of the van der Waals curve. Furthermore, the C—Si bond increases the distance between the ends of the molecule in the *gauche* conformation as compared to butane. Thus the protons of the terminal methyl groups give rise to substantial negative E_{nb} terms.

The dihedral angle between the methyl groups in 2-silabutane is 59·6°, a value which indicates the ease with which these groups can coexist. In butane the dihedral angle is 63·6°, a value which reflects a necessary compromise between the various contributing energy terms in deforming the conformation.

In butane the calculated C—C—C bond angles are 113·0° and 111·8° in the *gauche* and *anti* conformations respectively.* In 2-silabutane the C—C—Si and C—Si—C bond angles undergo smaller changes in spite of the smaller force constants. The C—Si—C bond angles are 110·5° and 111·3° in the *gauche* and *anti* conformations, respectively, while the Si—C—C bond angles are 114·5° and 114·3°, respectively. In Table 2 some of the other calculated structural features are given. While there is no experimental structure for comparison, there are similar features in 2-silapropane which is a reasonable reference structure.

1-Silabutane (**6**). The E_s values as a function of ϕ for 1-silabutane are shown in Fig. 1 and compared to butane and 2-silabutane. There is a similarity to butane in the order of stability of the *anti* and *gauche* conformations rather than to 2-silabutane. This difference is related to the "long" C—Si bond and its placement within the molecule. In 1-silabutane SiH_3 and Me groups are in the gauche relationship. A relatively "short" CH_2CH_2 unit separates the Me group from the "large" SiH_3, which is attached by a "long" bond. Qualitatively, the "long" bond balances the effect of the "large" group. In 2-silabutane there are two "long" C—Si bonds compared to one in 1-silabutane. One of the "long" bonds is in the CH_2SiH_2 unit and serves to separate the two CH_3 groups. Furthermore, one CH_3 group is moved out from the CH_2SiH_2 unit by a "long" bond.

The dihedral angle between SiH_3 and Me in the *gauche* conformation of 1-silabutane is 64·1°. This value is slightly greater than the 63·6° for two Me groups in butane, but is a distinct contrast to the 59·6° in 2-silabutane. Included in the E_θ for 1-silabutane is the bending of the C—C—Si bond angle to 114·6° and 115·8° in the *anti* and *gauche* conformations, respectively.

The higher energy of the eclipsed conformations of 1-silabutane as compared to butane gives rise to a steep torsional coordinate curve. In order to test the possibility that the calculated energies are due to the chosen r and ε values for silicon and may not be realistic, the nonbonded terms were examined. While the contributions of silicon are substantial and differ in the various conformations, a change in ε did not alter the shape of the torsional coordinate. For $\varepsilon = 0{\cdot}21$, a value similar to those

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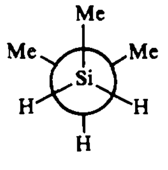
* These values were obtained by the same force field calculations used for the silicon compounds.

TABLE 4. ENERGIES OF 1-SILABUTANE FOR $\varepsilon_{Si} = 0{\cdot}21$

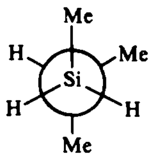
ϕ	E_r	E_θ	E_ϕ	E_{nb}	E_s	ΔE
0°	0·76	2·40	1·50	1·03	5·69	5·58
60°	0·29	0·94	0·15	−0·66	0·72	0·61
120°	0·28	1·21	1·50	0·69	3·69	3·58
180°	0·17	0·56	0·00	−0·62	0·11	0·0

used by Allinger[3] for chlorine and sulphur. The E_s terms given in Table 4 for $\phi = 0°$, 60°, 120°, and 180° are 5·71, 0·72, 3·69 and 0·11 kcal/mole, respectively. Therefore, within a reasonable range of ε values, the torsional coordinate is insensitive to change.

3-*Methyl-2-silabutane* (7). In Table 3 the energies of the two eclipsed conformations as well as the symmetric (**7s**) and asymmetric (**7a**) conformations are given. The symmetric conformation has the C-1 Me group in *gauche* positions with respect to two Me groups whereas there is only one *gauche* methyl-methyl interaction in the asymmetric conformation. The operation of attractive van der Waals forces discussed for 2-silabutane accounts for the order of stabilities. In fact small and subtle changes in E_r, E_θ and E_ϕ contribute to making the difference in energy between *anti* and *gauche* conformations of 2-silabutane less than the energy difference between symmetric and asymmetric conformations of 3-methyl-2-silabutane.



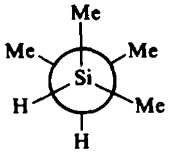
7s



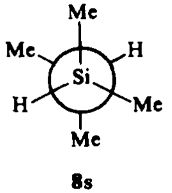
7a

As expected the two eclipsed conformations are of higher energy than the staggered conformations. Although the methyl-methyl eclipsed conformation is of slightly higher energy than the methyl-hydrogen eclipsed conformation, the difference is insignificant compared to the large difference in butane. Overall the ΔE values are very close to those for 2-silabutane. There is little change in the C—Si—C bond angle in achieving the eclipsed conformations. A 111·0° angle is calculated for both the symmetric and asymmetric conformations whereas the angles are 110·3° and 112·3° for the methyl-hydrogen and methyl-methyl eclipsed conformations, respectively.

2,3-*Dimethyl-2-silabutane* (**8**). The asymmetric conformation (**8a**) of this compound contains three sets of methyl-methyl *gauche* interactions compared to two in the



8a



8s

symmetric conformation (**8s**). As in 2-silabutane and 3-methyl-2-silabutane *gauche* interactions stabilize the conformation which contains them.

2,2,3,3-*Tetramethyl*-2-*silabutane* (**9**). Although this compound is of no conformational interest and there are no thermodynamic parameters available for comparison, the presence of six *gauche* methyl-methyl interactions makes this compound uniquely interesting in the light of the stability of *gauche* and *anti* conformations of 2-silabutane derivatives. The E_{nb} term is the most negative of the structures calculated. Although other energy terms counterbalance E_{nb}, the E_s term is still quite negative. Addition of E_s to E_{bond} terms will yield a more negative ΔH_f°. The heat of combustion of this substance would be of great interest.

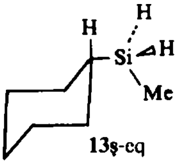
3-*Silapentane* (**10**). The conformational analysis of this compound is complex due to the four nonequivalent staggered conformations. The E_s values for all conformations are given in Table 3. As expected from calculations of simpler compounds incorporating a 2-silabutane structure, a *gauche* arrangement is more stable than an *anti* arrangement of bonds. Therefore, the order of stability *trans* (*gauche-gauche*) > *gauche-anti* > *anti-anti* is consistent with expectations. There is also a *cis* (*gauche*-gauche) conformation in which the terminal Me groups are placed in proximity of each other and the resultant repulsive non-bonded interactions must be minimized by a combination of molecular distortions. In order to calculate the populations of each conformation, the entropy contributions from symmetry numbers and optical activity must be calculated. Combining the enthalpy and the entropy of mixing terms, the mole fractions of *anti-anti*, *anti-gauche*, *cis* (*gauche-gauche*) and *trans* (*gauche-gauche*) are 0·10, 0·51, 0·07 and 0·32, respectively. The ratio of *gauche* to *anti* bonds in the calculated equilibria is 1·8.

4-4-*Dimethyl*-2-*Silapentane* (**11**). The *gauche* conformation of this compound contains a *t*-Bu and a Me group which would be expected to contribute to a decrease in the stability of the *gauche* 2-silabutane parent system. Indeed in the hydrocarbon analog the *gauche* conformer should be much less stable than the *anti* conformer. A first order approximation for the hydrocarbon can be obtained from considering the conformational preference of 4·5 kcal/mole[13] for the *t*-Bu group in *t*-butylcyclohexane. In the axial conformer there are two *gauche* *t*-butyl-methylene interactions whereas the equatorial conformer contains two *anti* *t*-butyl-methylene interactions. Thus the *gauche* conformation of 2,2-dimethylpentane should be less stable than the *anti* conformation by 2·7 kcal/mole. In marked contrast to the estimated hydrocarbon energy difference the *gauche* conformation of 4,4-dimethyl-2-silapentane is only 0·78 kcal/mole less stable than the *anti* conformation.

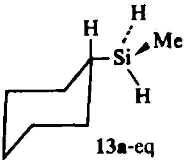
Cyclohexylsilane (**12**). The E_s terms for the equatorial and axial conformations of cyclohexylsilane are 1·14 and 2·40 kcal/mole, respectively. The conformational preference for SiH_3 is 1·26 kcal/mole. This value is entirely consistent with expectations based on the calculations for 1-silabutane. In the equatorial conformation of cyclohexylsilane the SiH_3 group is *anti* with respect to both the C-3 and C-5 methylene units while in the axial conformation, SiH_3 is *gauche* with respect to the two methylene units. Thus the conformational preference of the SiH_3 group should be twice that of the conformational energy difference between *gauche* and *anti* 1-silabutane. This argument is identical to the analysis of methylcyclohexane in terms of butane.

The smaller conformational preference of SiH_3 with respect to Me might not have been expected a priori. The conformational preference of chlorine and fluorine are distinctly in the order Cl > F.[24] Furthermore, the conformational preference SH > OH[24] is also established. However, in the axial conformation of methylcyclohexane the methyl proton directed over the plane of the ring gives rise to repulsive non-bonded terms with the axial protons on the 3 and 5 carbon atoms. For the "over the plane" proton in the axial conformation of cyclohexylsilane the non-bonded term with the two ring axial protons is only 0·02 kcal/mole. The long C—Si and Si—H bonds increase the distance to the two axial ring protons. Somewhat surprisingly, the conformational energy of the SiH_3 is not due to the E_{nb} terms but rather the E_θ terms* (Table 3). In the axial conformation the silicon atom is displaced away from the top of the ring by decreasing the Si—C—H bond angle. The H—C—H bond angles of the 3 and 5 methylene groups are also decreased somewhat. Thus all of the axial atoms on one side of the ring are moved away from each other. In the axial conformer of methylcyclohexane the E_{nb} terms are more severe and the Me–C–H bending force constant is larger. Both factors contribute to the larger conformational preference for the Me group.

Methylcyclohexylsilane (**13**). The symmetric equatorial (**13s**-eq) conformation of this compound is more stable than the asymmetric equatorial (**13a**-eq) conformation. In the symmetric conformation there are two *gauche* methyl-methyl type interactions whereas in the asymmetric conformation there is only one. However, the statistical factor of two favoring the asymmetric equatorial conformation should make it the more populated.

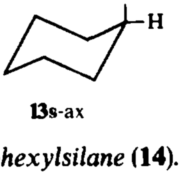


13s-eq

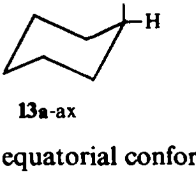


13a-eq

Of the two axial conformers the symmetric conformation (**13s**-ax) is of considerable higher energy than the asymmetric conformation (**13a**-ax). The statistical factor of two favors the conformation of lower enthalpy in this case. Taking into account the entropy of mixing terms, the conformational preference of $—SiH_2CH_3$ is 1·62 kcal/mole. The increase over that of 1·26 kcal/mole for $—SiH_3$ is a consequence of entropy of mixing. The ΔH_{conf} is 1·22 kcal/mole for $—SiH_2CH_3$. A comparison of silicon containing groups and alkyl groups and alkyl groups is given in Table 5.



13s-ax



13a-ax

Dimethylcyclohexylsilane (**14**). The asymmetric equatorial conformational (**14a**-eq) of this compound is more stable than the symmetric equatorial conformer (**14s**-eq)

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* Of course this observation is valid only for the minimized structure. In the initial structure E_{nb} is quite large and is subsequently decreased at the expense of increasing E_θ. A small $\Delta\theta$ in each of several bonds rapidly affects the nonbonded interactions.

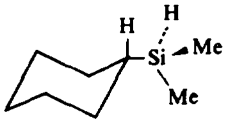
because of enthalpy contributions. In the asymmetric conformation there are three favorable *gauche* interactions whereas there are two in the symmetric conformation. The calculated energy difference is close to that calculated for 2,3-dimethyl-2-silabutane. A statistical factor of two favoring the asymmetric equatorial conformation increases the population still more over that of the alternate conformation.

TABLE 5. CONFORMATIONAL THERMODYNAMIC PARAMETERS FOR EQUATORIAL–AXIAL EQUILIBRIUM AT 298°K

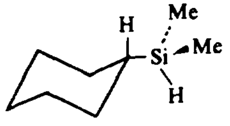
	Me[a]	SiH_3	Et	CH_3SiH_2	$(Me)_2CH$	$(Me)_2SiH$	$(Me)_3C$	$(Me)_3Si$
$\Delta H°$	1·77	1·26	1·69	1·22	1·46	1·61	5·41	3·41
$\Delta S°$	0	0	−0·61	−1·3	−2·18	−1·1	0	0
$\Delta G°$	1·77	1·26	1·87	1·62	2·05	1·94	5·41	3·41

[a] See reference 13 for calculations on the alkyl groups.

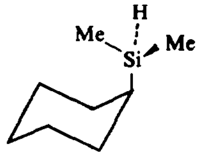
Of the axial conformers the asymmetric conformation (**14a**-ax) is considerably higher in energy than the symmetric (**14s**-ax) and is not significantly populated in spite of a statistical factor of two.



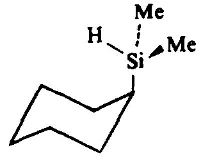
14a-eq



14s-eq



14a-ax

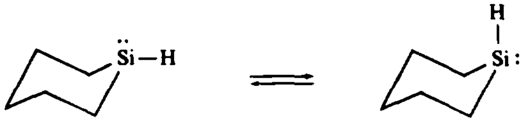


14s-ax

Taking into account the entropy of mixing terms, the conformational preference of the dimethylsilyl group is 1·94 kcal/mole. Part of this value is a consequence of entropy of mixing terms. The ΔH_{conf} is 1·61 kcal/mole.

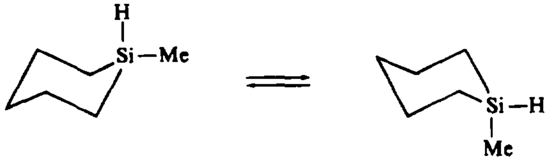
Trimethylcyclohexylsilane (**15**). The difference in the enthalpy values in Table 3 for the equatorial and axial conformers of trimethylcyclohexylsilane is 3·41 kcal/mole. Both the longer bonds of silicon and relative ease of deforming molecules containing silicon account for the smaller conformational preference compared to the 5·4 kcal/mole for *t*-butylcyclohexane.

Silacyclohexane (**16**). Although no calculations were carried out for this heterocyclic compound, some highly interesting conformational predictions can be made on the basis of other calculations. Although the ring will be a flattened chair in the vicinity of silicon, a pseudo axial and pseudo equatorial position can be designated. One question which can be asked involves the conformational preference of a single proton bonded to silicon in a silanion. By considering the nonbonded terms for analogous protons in staggered 1-silapropane, it is found that the axial proton in the anion of silacyclohexane experiences more attractive van der Waals terms in the axial conformation. The estimated conformation preference obtained by this method is 0·25 kcal/mole in favor of the axial conformation.



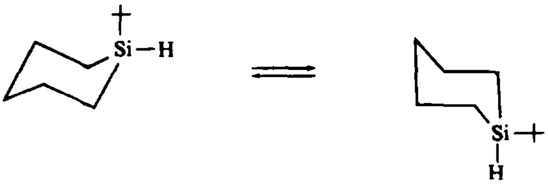
If this prediction is verified, the silacyclohexane anion will join phosphacyclohexane[4] and the sulfur protonated thiacyclohexane[5] as examples of stable axial heterocyclic cyclohexanes of the third period elements.

The conformational preference of a Me group at the 2 position of silacyclohexane can be estimated from the calculated enthalpies of *gauche* and *anti* 2-silabutane. In the axial conformation of 1-methyl-1-silacyclohexane there are two favorable *gauche* 2-silabutane interactions whereas in the equatorial conformation there are two *anti* 2-silabutane structures. Therefore, the axial conformation should be more stable by approximately 0·3 kcal/mole.



From the calculated energies of the *gauche* and *anti* conformations of 4,4-dimethyl-2-silapentane, the conformational preference of a t-Bu group on silacyclohexane can be estimated by the same procedure used for the Me group. In the case of t-Bu the equatorial conformation should be more stable by 1·6 kcal/mole. Thus the conformational preference of the t-Bu group is significantly less than for cyclohexane.

The predictions for hydrogen, Me and t-Bu await experimental tests.



Conformational equilibria

The approach used to calculate conformational equilibrium constants from vicinal coupling constants as a function of dihedral angle follows that described previously.[3] The coupling constants determined in the study are given in Table 6. Assignment of the empirical parameters for the Karplus equation is made from model compounds. The coupling constant for groups such as Me or SiH_3 with a methylene or methine group is given by $(2J_{60} + J_{180})/3$ and is equal to A in equation 6. The B and C terms are estimated.[32]

$$J_\theta = (A + B\cos\phi + C\cos 2\phi)\,(1\text{-}bn) \qquad (6)$$

TABLE 6. COUPLING CONSTANTS[a] OF SILICON COMPOUNDS IN VARIOUS SOLVENTS

Compound	Group	C_7F_{14}	C_5H_{12}	C_6H_{12}	CCl_4	C_6H_6	CS_2	CH_2Cl_2	$CHBr_3$
1	CH_3SiH_3				4·56				
2	CH_3CH_2				7·30				
	CH_2SiH_3				3·71				
3	CH_2SiH_3				4·15				
5	CH_2SiH_2	3·18			3·11		3·11	3·10	3·08
	SiH_2CH_3	4·18			4·16		4·16	4·16	4·16
6	CH_2CH_2	7·53			7·44			7·44	7·40
	CH_2SiH_3	3·90			3·89			3·87	3·88
7	$CHSiH_2$		2·1						1·8
8	$CHSiH$	2·15			1·99	1·92	1·87		
10	CH_2SiH_2		3·46	3·44	3·43		3·42		3·40
11	CH_2SiH_2	3·94				3·84	3·78		

[a] The coupling constants were determined on a Varian 100 MHz instrument. Those coupling constants reported to 0·01 Hz are reproducible to that accuracy. Those value reported to 0·1 Hz are accurate to 0·05 Hz.

In the assignment of vicinal coupling constants as a function of dihedral angle, the effects due to changes in bond length and bond angles are neglected. The differences in bond lengths are quite small. While there are some differences in bond angles between model compounds and the conformationally mobile compounds it is difficult to assess quantitatively the resultant change in J. Nevertheless, it is clear that dihedral angle contributions to J are far more significant than small changes in bond angle.

In order to correct for contributions of attached alkyl groups to the coupling constant a term (1-bn) is used. The proportionality constant b is chosen to represent the factor by which J changes as a function of electronegativity of the alkyl group. The number of the alkyl groups is given by n.

Since the vicinal coupling constants of ethane and propane are 8·0 and 7·26 Hz, respectively, b is chosen to be 0·09 for the Me group. As noted in our previous paper[2] the electronegativity contribution to J of a Me group present in a silane is also 0·09.

The $J_{CH_3CH_2}$ in 1-silapropane is 7·30 Hz. Using this value and the electronegativity contribution of a Me group, the parameterized Karplus equation (7) for 1-silabutane is obtained.

$$J_\theta = 6{\cdot}64 - 0{\cdot}83 \cos\phi + 7{\cdot}47 \cos 2\phi \qquad (7)$$

Therefore, $J_{60} = 2{\cdot}44$ Hz and $J_{180} = 14{\cdot}94$ Hz. The derived coupling constants for the *gauche* and *anti* conformations of 1-silabutane are 5·57 Hz and 8·69 Hz, respectively. Correcting for the effect of internal solvent pressure by using the values given in Table 7, $K = 0{\cdot}61$ at one atmosphere. Accounting for the entropy of mixing $\Delta S = 1{\cdot}4$ cal/mole deg, $\Delta G^\circ = 0{\cdot}3$ kcal/mole and $\Delta H^\circ = 0{\cdot}7$ kcal/mole are obtained. The agreement between the energy difference calculated by the force field method of 0·56 kcal/mole and the ΔH° determined by the analysis of vicinal coupling constant is excellent.

The $J_{CH_2SiH_3}$ in 1-silapropane is 3·71 Hz. Using an electronegativity correction factor for the addition of a Me group to yield 2-silabutane results in equation 8 which is used to calculate the coupling constants of the two conformations of 2-silabutane.

$$J_\theta = 3{\cdot}38 - 0{\cdot}42 \cos \theta + 3{\cdot}80 \cos 2\theta \tag{8}$$

From equation 8 $J_{60} = 1{\cdot}27$ Hz, $J_{180} = 7{\cdot}60$ Hz are obtained which in turn yield $J_{gauche} = 2{\cdot}85$ Hz and $J_{anti} = 4{\cdot}43$ Hz. Correcting for the effect of internal solvent pressure K (*gauche-anti*) $= 2{\cdot}7$ is obtained at 1 atmosphere. Accounting for the entropy of mixing $\Delta S = 1{\cdot}4$ cal/mole deg, $\Delta G^\circ = -0{\cdot}6$ kcal/mole and $\Delta H^\circ = -0{\cdot}2$ kcal/mole. The agreement between the experimentally derived difference in conformational energies and the $-0{\cdot}14$ kcal/mole calculated from force field method is well within the uncertainties of either value.

TABLE 7. INTERNAL SOLVENT PRESSURES AND COHESIVE ENERGY DENSITIES IN ATMOSPHERES AT 34°C

Solvents	P_i^b	c.e.d.^{a}	n	References
$CF_3C_6F_{11}$	2050	1370	1·50	27, 28
$n\text{-}C_5H_{12}$	2090	1950	1·07	27
$c\text{-}C_6H_{12}$	3190	2690	1·19	29, 30
CCl_4	3250	2960	1·10	30, 31
CS_2	3620	3880	0·93	27, 32
CH_2Cl_2	3830	3900	0·98	27, 30
$CHBr_3$	4370	4470	0·98	30, 32

[a] The correction for temperature was made using the equation $d\ln \delta/d\ln V = -1{\cdot}25$ where δ is the solubility parameter such that c.e.d. $= 41{\cdot}3\ \delta^2$ atm. Also the density as a function of temperature was assumed to be linear over a small temperature range.

[b] The correction for temperature was made by interpolating between reported values when necessary. Pentane, CH_2Cl_2 and MeOH had to be corrected by using the same assumptions in *a* and by assuming *n* to be constant over a small temperature range.

In 3-methyl-2-silabutane two Me groups are substituted on the model 1-silapropane used as the basis for calculating coupling constants. Equation 9 is used to calculate $J_{60} = 1{\cdot}14$ Hz and $J_{180} = 6{\cdot}84$ Hz. Therefore, $J_{sym} = 1{\cdot}14$ Hz and $J_{asym} = 3{\cdot}99$ Hz, and K(sym/asym) $= 1{\cdot}3$ at the extrapolated pressure of one atmosphere.

$$J_\theta = 3{\cdot}04 - 0{\cdot}38 \cos \theta + 3{\cdot}42 \cos 2\theta \tag{9}$$

Accounting for the entropy of mixing $\Delta S = -1{\cdot}4$ cal/mole deg, $\Delta G^\circ = -0{\cdot}1$ kcal/mole and $\Delta H^\circ = -0{\cdot}5$ kcal/mole. While the NMR analysis and force field calculations are in agreement in indicating that the symmetric conformation is the more stable in terms of enthalpy, there is a difference of 0·3 kcal/mole between the two values.

In order to analyze 2,3-dimethyl-1,2-silabutane, three Me groups are substituted on the model 1-silapropane compound. Equation 10 is used to calculate $J_{60} = 1{\cdot}00$ Hz and $J_{180} = 6{\cdot}08$ Hz.

$$J_\theta = 2{\cdot}70 - 0{\cdot}34 \cos \theta + 3{\cdot}04 \cos 2\theta \tag{10}$$

Since only a single set of vicinal hydrogens are involved in this compound $J_{asym} = 1{\cdot}00$ Hz and $J_{sym} = 6{\cdot}08$ Hz. At one atmosphere K(asym/sym) $= 2{\cdot}7$. Accounting for the entropy of mixing $\Delta S = +1{\cdot}4$ cal/mole deg, $\Delta G^\circ = -0{\cdot}6$ kcal/mole and $\Delta H^\circ = -0{\cdot}2$ kcal/mole. As is the case for all the compounds studied, there is agreement between the two methods in the prediction of the most stable conformer. The force field method predicts that the asymmetric conformer is more stable than the symmetric conformer by 0·19 kcal/mole.

The analysis of the vicinal coupling constants of 3-silapentane is identical to that of 2-silabutane. The inductive effect of an Et group is assumed to be equal to that of a Me group. Using equation 8 and the coupling constants derived for 2-silabutane it is possible to calculate the ratio of *gauche* bonds/*anti* bonds even though a multi-equilibrium system is involved. At one atmosphere the extrapolated ratio is 1·4. Using the enthalpy terms from the force field calculations and the entropy contributions from symmetry numbers and optical activity, the ratio of *gauche* bonds/*anti* bonds = 1·8. The difference between the two values derived by the two methods corresponding to a difference of only 0·2 kcal/mole and represents a good agreement.

In order to analyze 4,4-dimethyl-2-silapentane, it is only necessary to use equation 8 previously described for 2-silabutane. The additional alkyl groups contained in 4,4-dimethyl-2-silabutane are not directly attached to the atoms involved in the vicinal coupling. At one atmosphere $K(anti/gauche) = 3{\cdot}2$. Accounting for the entropy of mixing $\Delta S = 1{\cdot}4$ kcal/mole deg, $\Delta G^\circ = -0{\cdot}7$ kcal/mole and $\Delta H^\circ = -1{\cdot}1$ kcal/mole. The agreement between the ΔH° and $-0{\cdot}78$ kcal/mole obtained from the force field calculation is fair. However, in the *gauche* conformation, the presence of a *t*-Bu group and a Me group causes a rotation about the carbon-silicon bond which in turn should decrease J_{gauche}. If a smaller value for J_{gauche} is used, then the difference between the values obtained by the two methods will decrease.

Cyclohexane compounds

Attempts were made to experimentally establish the conformational preference of the SiH_3 group. The Eliel method of time averaged chemical shifts[26] was inapplicable as the proton on the C-1 position is contained in a broad absorption of the ring protons. The shielding effect of the SiH_3 group is insufficient to cause a separation of absorptions in either *cis* or *trans*-4-*t*-butylcyclohexylsilane. Furthermore, the chemical shifts of the equatorial and axial SiH_3 groups are apparently identical. A mixture of *cis* and *trans*-4-*t*-butylcyclohexylsilane has a doublet centered at 3·394 ppm downfield from internal TMS. The corresponding group in cyclohexylsilane occurs at 3·402 ppm. Thus neither the Eliel method nor the low temperature methods of Jensen[24] can be applied directly to these compounds. An experimental attempt to employ low temperature methods using cyclohexylsilane in CS_2 containing $CHCl_3$ as an internal reference and TMS as a lock signal was a failure. No separation of the —SiH_3 signal occurred down to the freezing point of MeOH. Thus the chemical shifts of the SiH_3 group in the equatorial and axial positions are identical even in the absence of a *t*-Bu group.

Equilibration of *cis* and *trans*-4-*t*-butyl-cyclohexylsilane at 300° over a 5% Pd–C catalyst* resulted in rupture of the C—Si bond and a complete disappearance of the doublet of the silyl group in the NMR. All attempts to effect equilibration without decomposition failed.

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* In our hands this equilibration procedure has worked well for hydrocarbons. Therefore, it is most likely that the lower bond energies of silicon compounds make this method of less utility.

Attempts were made to experimentally determine the conformational preference of the trimethylsilyl group. The Eliel method is inapplicable as the cyclohexyl proton α to silicon cannot be separated from the other resonances of the cyclohexane ring. The chemical shifts of the trimethylsilyl group in *cis* and *trans*-4-*t*-butylcyclohexyltrimethylsilane occur at 7·327 ± 0·002 ppm and 7·422 ± 0·002 ppm upfield from $CHCl_3$, respectively. However, the corresponding resonance of trimethylcyclohexylsilane occurs at 7·428 ± 0·002 ppm and is not within the range of the reference models. Evidently, there is a small chemical shift contribution of the *t*-Bu group in each isomer with the deshielding contribution in the *cis* isomer being greater than the *trans* isomer. At any rate the small difference between the chemical shifts of the two isomers and the large calculated conformational preference of the trimethylsilyl group would limit the application of the Eliel method.

Attempted equilibrations over 5% Pd/C in sealed tubes at both 289° and 350° led to destruction of the compound and an equilibrium constant could not be obtained. Equilibration by the use of benzoyl peroxide in a degassed benzene solution resulted in only a small change in the initial *cis*/*trans* ratio of compounds.

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