MOLECULAR MECHANICS IN SILICON CHEMISTRY. SOME
APPLICATIONS TO CYCLIC AND POLYCYCLIC SILANES *

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Summary

The MM2 program for molecular mechanics calculations has been applied to
a variety of cyclic and polycyclic silanes. The procedure gives very good repro-
duction of structural parameters for even moderately strained silanes (e.g.
silacyclopent-3-ene), but should be applied with caution for highly strained
silanes (e.g. silacyclobutanes). Conformational energy differences are predicted
at least fairly well in cases where such experimental data exists. This powerful
tool is hence at a level of development for compounds containing Si—C and
Si—H bonds that allows its use for a variety of problems of interest in silicon
chemistry. A correlation of reactivity with calculated bond angle strain at Si
is presented.

Introduction

Molecular mechanics calculations have reached a highly developed state in
applications to hydrocarbons [1,2] and even to some species with relatively
polar functional groups attached to carbon [1]. Structural parameters as well
as energy differences can be reproduced to a high level of accuracy in a calcu-
lation of great speed and relative simplicity. Given a widespread interest in the
effects of molecular strain on structure and reactivity, the calculations can play
an important role in giving a rapid and mostly highly accurate estimate of the
influence of various structural features on overall molecular strain and thus
can serve as a tool for planning experiments as well as analyzing data.

Many studies of strain-reactivity relationships employ cyclic compounds
since they can be tailored to incorporate strain of various types. Cyclic silicon

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compounds have been used in this way by a variety of workers. That fact, plus the rather recent advent of a substantial body of good structural data on simple cyclic silanes, has led us to explore in some detail the applications of molecular mechanics calculations to cyclic silanes. Good benchmarks against which to judge the calculations now exist. We were optimistic about the utility of the calculations in organosilicon chemistry since they have shown themselves to be particularly easily and accurately adaptable to structural and energetic estimates for the nonpolar hydrocarbons. At least in the absence of highly polar functional groups, silanes should have small bond polarities and small overall dipole moments. Furthermore, a number of reports of calculations on simple silanes have appeared [3—6]. Among the early indications of potential utility of the method was the prediction [3b] that the axial conformer of 1-methyl-1-silacyclohexane would be more stable than the equatorial conformational isomer, a prediction which has recently been confirmed by NMR measurements [7] (measured $\Delta G^0 = 0.35$ kcal/mole; ΔE by MM2 calculation $= 0.14$ kcal/mole). Tribble and Allinger [4] reported a number of calculations with acyclic and cyclic silanes using the earlier MM1 force field and prior to the availability of much of the good structural data now in the literature. A particularly notable recent result [6a] was the highly accurate reproduction of the electron diffraction structures of silacyclohexane and -pentane using a force field originally derived for silacyclopentane (I) [8].

Methods and results

Having ourselves an experimental interest in the properties of cyclic silanes, we desired to explore the utility of molecular mechanics in structural prediction and conformational analysis, and we have chosen to employ what we consider to be the most general and highly developed program for structural and energetic estimates, the MM2 program of Allinger [1,9]. That program is probably also the easiest for a novice to begin using, since it is described in some detail in the literature available from QCPE. The program as presently available has a number of built-in parameters for Si, which are described in general as tentative values. The results reported here have used the built-in parameters unchanged, although in several instances involving 4-membered rings additional parameters have been added. The program has not been provided with parameters to afford meaningful heats of formation for silanes.

A common task one would like to do with molecular mechanics calculations is to generate structural parameters for the most stable conformation of a molecule. From a particular set of input coordinates the MM2 program does not in general rapidly find a global minimum energy structure, but rather the nearest local minimum. This is a highly advantageous feature of the program, since it frequently allows the calculation of structures and relative energies of two or more conformers which have the same general symmetry properties. For example, input of coordinates which are reasonably close to those of equatorial-1-methylsilacyclohexane will lead to a minimized structure retaining the equatorial orientation, even though axial placement of the methyl group is more favorable.

One can arrive at a global minimum conformation using MM2 in several ways

which we will illustrate using silacyclopentane (I). A half-chair conformer of the molecule having C_2 symmetry is known to be most stable [6a], and one can start immediately with atomic coordinates derived by making a reasonable guess at bond angle and dihedral values, using for instance values for cyclopentane and intuition about the greater ease of deformation of angles about Si than about C. In the present case there is structural data in the literature to guide the initial choice of coordinates. Once coordinates are supplied, one can ask the program for minimization specifying that C_2 symmetry be retained. In the present case whether one specifies that the initial symmetry be retained or not does not affect the outcome, but in the general case it may do so.

Input coordinates can affect the calculational result dramatically. A more systematic, and in some ways a simpler approach, is to start with coordinates for a flat conformation of I and ask for minimization with restrictions on atomic motions which will retain the flat geometry. One can then use the derived coordinates as input for a series of calculations, in all of which, atoms 1, 2 and 5 are restricted from moving along the y axis, while a specified set of values are imposed on the dihedral angle formed by atoms 2, 3, 4 and 5 using the dihedral driver feature of the program. In the present case calculation was made for every dihedral form 5° to 70° in 5° increments with the minimum

$$C_2 \qquad\qquad\qquad C_{2V} \qquad\qquad\qquad C_S$$
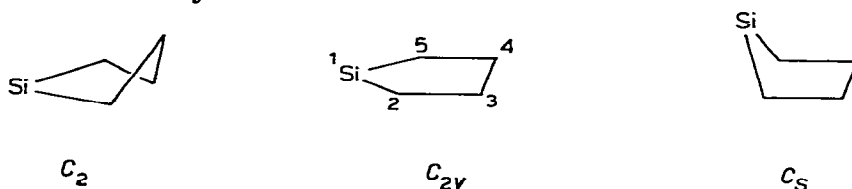
occurring at 50°. The latter coordinates are a close approximation of the best coordinates for the C_2 geometry and may now be used as input for a final refining calculation, which results in a value of 51.6° for the dihedral in question. For I the structure is the same as that obtained by the first method. Since input coordinates can affect the calculational result; and poor input can lead to a poorly minimized structure corresponding to a local minimum, it is highly recommended that several attempts, including a systematic one, be used to attempt to find the global minimum. The lowest energy MM2 conformer having C_s symmetry was found starting from the flat coordinates and restricting motion of C2, C3, C4 and C5 in y while varying the dihedral formed by Si, C2, C3 and C4. The value of that dihedral in the minimum energy structure is 26.0°.

The ring system I is of course a simple example for applying a systematic approach to finding the global minimum. More complex systems require more imagination and patience, and users are urged to make several attempts. Making simple alterations, such as adding methyl groups, may lead to unforeseen complications. Calculations on the *cis*-isomer of 1,2-dimethylsilacyclopentane starting with the coordinates for the minimized C_2 structure of I and substituting methyls *cis* to one another on Si and C2, then carrying out the minimization, results in a structure with a total steric energy almost 1 kcal/mole greater than that for the overall minimum conformer of *cis*-1,2-Me$_2$-I. The latter conformer was found using the dihedral driver as well as alternative sets of input coordinates.

Silacyclopent-anes and -enes

The most accurate structural information available about a simple cyclic silane is the excellent electron diffraction/microwave analysis for I by Hilderbrandt et al. [6a]. The data from that analysis can be compared with the structural parameters generated by MM2 in Table 1, and agreement is excellent. It should be pointed out that the molecular mechanics calculations in ref. 6a are quite comparable to the MM2 results presented here in reproducing the structural parameters. With I we were also interested in the energies of the flat and the envelope (C_s) conformations since the potential energy difference between C_2 and C_s conformers has been estimated to be 3.9—4.0 kcal from infrared/microwave data [10,11], and the barrier to planarity to be 4.5 kcal/mole [11b]. The former value is reproduced reasonably well by MM2, while the latter value is overestimated (see Table 1). The energy data as well as structural parameters for the conformers of I is summarized in Table 1.

We [12] and others [13] have generated considerable experimental data on stereochemistry and reactivity in reactions of the 1,2-dimethylsilacyclopentane ring system, and we were interested in the effects of the added methyl groups on conformation. 1-Methyl-1-silacyclopentane and *cis*- and *trans*-1,2-dimethyl-1-silacyclopentane all prefer the half-chair conformation and have ring dihedral angles very similar to those for the C_2 conformer of I, as indicated in Table 2. In the *cis*-isomer one might have expected a significant interaction of the two substituent methyl groups. The dihedral angle between the methyls is 23°, but the relatively long Si—C bond between makes any interaction very small. Indeed, the *cis*- and *trans*-isomers are calculated to be virtually identical in total energy. That appears to be a reasonable prediction given equilibrium constant data for the 1-halo derivatives of the 1,2-dimethylsilacyclopentane ring system [12], but data is not available for the hydrides.

The unsaturated ring system, 1-silacyclopent-3-ene, has also been the subject of a recent electron diffraction study [14]. Table 3 compares the available structural information with MM2 calculation, and agreement is reasonable. The parameters are somewhat better reproduced in MM2 than in MM1. Both show the molecule to be planar, which is in agreement with results from vibrational spectroscopy [15].

TABLE 1

PARAMETERS FOR CONFORMERS OF SILACYCLOPENTANE (I)

	C_2 e^- diff. [6a]	MM2		
		C_2	C_s	C_{2v}
∠C5—Si—C2	96.3 ± 0.3	96.4	92.8	98.8
∠Si—C2—C3	103.6 ± 0.3	102.3	102.2	105.4
∠C2—C3—C4	108.4 ± 0.7	109.0	113.1	115.3
ϕC2—Si—C5—C4	13.3 ± 0.4	13.2	35.9	0
ϕSi—C2—C3—C4	−36.1 ± 1.0	−37.1	26.1	0
ϕC2—C3—C4—C5	49.7 ± 1.4	51.6	0	0
E_{steric} (kcal/mol)	—	8.42	11.77	14.23

TABLE 2

MM2 PARAMETERS FOR SILACYCLOPENTANE (I) AND METHYL DERIVATIVES

	I	1-Me-I	cis-1,2-Me$_2$-I	trans-1,2-Me$_2$-I
C5—Si—C2	96.4	97.1	97.0	97.1
Si—C2—C3	102.3	102.2	101.8	101.9
C2—C3—C4	109.0	109.0	108.8	108.9
C2—Si—C5—C4	13.2	13.8	10.9	13.3
Si—C2—C3—C4	−37.1	−36.4	−38.6	−36.9
C2—C3—C4—C5	51.6	51.2	51.4	51.6
C6—Si—C2—C7	—	—	22.9	−106.8
steric (kcal/mol)	8.42	7.37	7.84	7.86

TABLE 3

STRUCTURAL PARAMETERS FOR 1-SILACYCLOPENT-3-ENE

	e$^-$ diff. [14]	MM2	MM1 [4]
(C=C)	1.359 ± 0.006	1.343	1.339
(C—C)	1.533 ± 0.004	1.508	1.505
(Si—C)	1.899 ± 0.003	1.901	1.862
C—C=C	118.4 ± 0.2	120.0	119.5
Si—C—C	103.7 ± 0.5	101.4	101.3
C—Si—C	95.8 ± 0.5	97.2	98.5

Silacyclobutanes

A system of particular interest because of the degree of bond angle strain and because some reactivity data are available is the silacyclobutane system. Calculations on silacyclobutanes must be approached with caution, since structural data are not very plentiful or very refined. Preliminary calculational results lead to CSiC bond angles near 75° and Si—C1—C2—C3 dihedrals near 24°. Methyl groups on Si appear to prefer a pseudoaxial position. We have been particularly interested in the 1,2-dimethylsilacyclobutane ring system, but the calculations on those molecules show a tendency to give unreasonably long Si—C bonds (>2.1 Å). The Si—C bond lengths seem to be the main structural parameter that gives problems when MM2 is applied to highly strained Si compounds, whether mono- or poly-cyclic. It is suggested that users look at that parameter first in trying to decide whether a reasonable structure has been achieved in the MM2 program. Work on parameterization of MM2 for silacyclobutanes must be undertaken and will presumably be done when better experimental structural information becomes available.

Polycyclic silanes

A ring compound for which good structural data has recently become available [6b] and one which is of substantial interest with respect to reactivity studies is 1-chloro-1-silabicyclo[2.2.2]octane (II). Calculational results have been generated for the 1-methyl derivative. Starting with reasonable input

coordinates for a structure having a plane of symmetry through Si and C4 leads to a minimum energy conformation in which the dihedral Si—C2—C3—C4 is 0°. Varying that dihedral, however, lowers the energy, and the minimum is
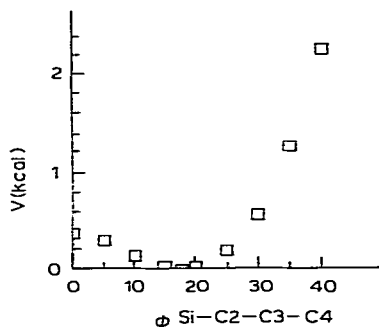

Fig. 1. Variation of potential energy with ring dihedral in 1-methyl-1-silabicyclo[2.2.2]octane.

found at 18.1°. The potential energy is plotted versus dihedral angle in Fig. 1, which may be compared with Fig. 5 in ref. 6b, which shows an experimentally derived twisting function for 1-chloro-1-silabicyclo[2.2.2]octane. That calculated here shows a more shallow potential well for twisting of II. Structural parameters compared with experiment are shown in Table 4.

Structural data is also available for 1-methyl-1-silabicyclo[2.2.1]heptane (III) [16], and agreement with the MM2-generated parameters is much less satisfactory than for II, as seen in Table 4. The unusual feature of the electron diffraction structure is the substantial lengthening of the Si—C2 (1.905 ± 0.005 Å) and C3—C4 (1.593 ± 0.008 Å) bonds, and this feature is not reproduced in the MM2 calculation (r from MM2 equals 1.868 and 1.554 Å, respectively). If one

TABLE 4

STRUCTURAL PARAMETERS FOR 1-X-1-SILABICYCLO[2.2.2]OCTANE (II) AND 1-METHYL-1-SILABICYCLO[2.2.1]HEPTANE (III)

|	II		III	
	e^- diff. [6b] (X = Cl)	MM2 (X = Me)	e^- diff. [16] (X = Me)	MM2 (X = Me)
r(Si—C2)	1.861 ± 0.003	1.869	1.905 ± 0.005	1.868
r(Si—C7)	1.861 ± 0.003	1.869	1.860 ± 0.006	1.871
r(C2—C3)	1.558 ± 0.002	1.541	1.545 ± 0.005	1.545
r(C3—C4)	1.558 ± 0.002	1.549	1.593 ± 0.008	1.554
$\angle$(X—Si—C2)	114.6 ± 0.2	115.2	122.1 ± 1.1	118.4
$\angle$(Si—C2—C3)	105.8 ± 0.4	106.0	101.1 ± 0.3	98.3
$\angle$(C2—C3—C4)	114.2 ± 1.2	114.1	110.3 ± 0.7	110.3
$\angle$C3—C4—C5	111.4 ± 0.8	111.4	103.0 ± 1.7	111.1
$\angle$C2—Si—C6	103.9 ± 0.2	103.2	97.4 ± 1.4	104.6
$\angle$C2—Si—C7	103.9 ± 0.2	103.2	94.7 ± 0.5	96.4
ϕX—Si—C2—C3	171.1 ± 1.2	169.9	159 [a]	159.1
ϕSi—C2—C3—C4	17.5 ± 2.5	18.1	0 [a]	1.4
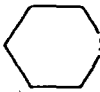
[a] Not explicitly cited in ref. 14, hence no error limits are given.

calculates energies for a structure very close to the electron diffraction structure, the principal differences in energies as compared to the MM2-minimized structure are those associated with the bond stretching of Si—C2, Si—C6, C3—C4 and C4—C5. Coordinates for the electron diffraction structure, as well as several other sets of input coordinates all converge in MM2 on the structure whose parameters are shown in Table 4.

Strain and reactivity

Scattered reactivity data which is interpretable in terms of strain effects is available for cyclic organosilanes. The single reaction for which the widest range of data has been published is base-catalyzed Si—H hydrolysis, a reaction which probably involves front-side nucleophilic attack on all substrates studied. Some of the reactivity data are shown in Table 5. The table also shows the calculated ring angle(s) about Si in the most stable conformation. The MM2 program calculates a bending strain energy for each bond using a Hookes' law kind of relationship (using, one should note, the same standard bond angle except when 4-membered rings are involved). The sum of the calculated strain energies for the ring bonds about Si is shown for each molecule in Table 5, and Fig. 2 gives a linear potential energy plot for silane hydrolysis using the bending strain energies. We think such a plot does in fact faithfully indicate that the

TABLE 5

ANGLE STRAIN AND REACTIVITY

		$\angle$C—Si—C in ring(s)	E_{bend} [a]	$\log k_{rel}$ SiH + OH$^-$
SiMeH	ax. eq.	104.6 104.9	0.4 0.4	0 [c]
SiMeH	'C$_2$'	97.1	1.9	2 [c]
SiH		102.2, 102.2, 102.2	2.1	2 [d]
SiH		94.3, 94.3, 102.2	6.2	4 [e]
SiMeH	ax. eq.	75.0 75.7	10.3 [b] 9.9 [b]	5.5 [e]

[a] Bending strain energy in kcal/mole calculated by MM2 for the angle(s) indicated. [b] An average value is used in the plot shown in Fig. 2. [c] Ref. 17. [d] Ref. 18. [e] Ref. 19.
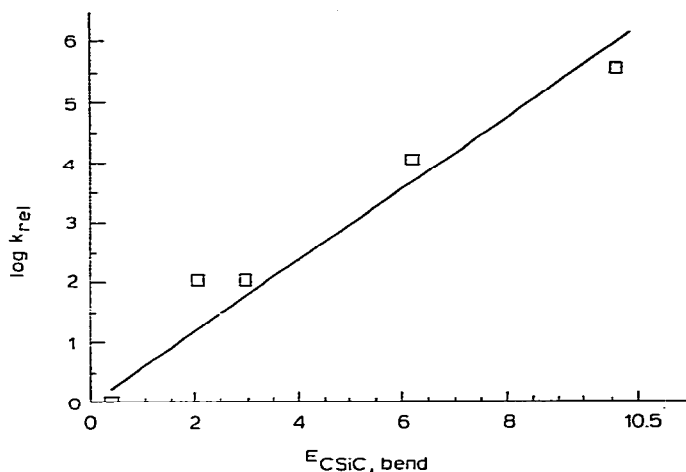
Fig. 2. Log k_{rel} for base-catalyzed SiH hydrolysis versus ring bond angle strain.

principal effect on reactivity in these molecules is one due to bond angle strain. After saying that much, one should demur by admitting that the actual correlation (correlation coefficient = 0.991) is far better than one might have expected. The data for the bicycloheptane and silacyclobutanes is not considered highly reliable (although it is certainly approximately correct). Furthermore, it is clear from West's kinetic results that reactivity in Si—H hydrolysis of cyclic silanes is determined by a mixture of enthalpic and entropic effects.

Two rationalizations of the effects of bond angle strain on reactivity at Si are current. The frontier orbital arguments of Anh [20] concentrate on the effects of angle strain on the amount of s-character in the hydrid orbital used by Si to form the LUMO of interest, the antibonding σ^* between Si and the leaving group. The second rationale, originally from Sommer [6b,14,21], has been applied often to the polycyclic silanes, and finds the reason for reactivity in the closeness of approach of the bond angles about Si to those in a presumed trigonal bipyramidal intermediate or transition state. It is not at all clear that this latter rationale would suggest the relationship in Fig. 2, a relationship which includes both monocyclic and polycyclic silanes.

Attempts to evaluate effects of strain on reactivity must take account of the fact that strain influences both the ground and transition states. Molecular mechanics has not yet been applied to five-coordinate Si species, but estimates of transition state strain are not outside of the realm of possibilities for the method. It is also clear in some cases of displacement reactions at Si that strain can influence the nature of the mechanistic pathway, making an account of strain effects based on a single argument unreasonable. It would obviously be helpful to have much more experimental data.

Conclusions

Molecular mechanics calculations using the MM2 program have been performed on a variety of cyclic and polycyclic silanes. The calculations do a very

good job of reproducing experimental structural parameters as well as affording reasonable structural and conformational energy differences in the cases to which the calculations have been applied. The method should be applied with caution to very highly strained molecules. The calculations can be used to indicate anticipated structural and energetic parameters for molecules which suggest themselves as synthetic targets of theoretical or practical interest.

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