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THE MOLECULAR STRUCTURES OF 3-SILABICYCLO(3.2.1)OCTANE AND *endo*-3-METHYL-3-SILABICYCLO(3.2.1)OCTANE AS DETERMINED BY GAS PHASE ELECTRON DIFFRACTION

QUANG SHEN,

Department of Chemistry, Colgate University, Hamilton, NY 13346 (U.S.A.)

RICHARD L. HILDERBRANDT,

Department of Chemistry, North Dakota State University, Fargo, ND 58105 (U.S.A.)

C.S. BLANKENSHIP and SHELDON E. CREMER

Department of Chemistry, Marquette University, 535 North 14th Street, Milwaukee, Wisconsin 53233 (U.S.A.)

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Summary

The molecular structures of 3-silabicyclo(3.2.1)octane (SB3210) and *endo*-3-methyl-3-silabicyclo(3.2.1)octane (*endo*-MSB3210) have been determined by gas phase electron diffraction. The average Si—C bond lengths, 1.891(4) Å for SB3210 and 1.883(3) Å for *endo*-MSB3210, are comparable with the observed Si—C bond lengths in silacyclohexane and silacyclopentane. The average C—C bond lengths, 1.552(2) Å for SB3210 and 1.548(2) Å for *endo*-MSB3210, also compare favorably with the corresponding distances in silacyclopentane and silacyclohexane. Observed flap angles at the silicon atom are 145(4)° in SB3210 and 160(5)° in *endo*-MSB3210. Both molecules exhibit considerable flattening at the silicon end of the six-membered ring relative to silacyclohexane which has a flap angle of 139°. The observed structures are compared with the results of molecular mechanics calculations, and with experimental structures for several related compounds.

Introduction

Conformational analysis of six-membered rings containing heteroatoms such as arsenic [1], phosphorus [2], selenium [3], silicon [4], and sulfur [5] have recently received considerable attention in the chemical literature. Compared to cyclohexane, the monosubstituted heteroatom analogues are generally more flattened at the substituent end of the chair conformation with dihedral flap angles significantly greater than the nominal 130° value observed for cyclohexane. It has also been observed that substituents attached to the heteroatom are more generally disposed toward the axial rather than the equatorial position.

Ouellette [6,7] has recently performed molecular mechanics calculations on 1-, 2-, 3- and 4-methylsilacyclohexanes, several tert-butylsilacyclohexanes, 3,5-dimethylsilacyclohexane, and 3-silabicyclo(3.2.1)octane. In 1-methylsilacyclohexane, the methyl group was predicted to favor the axial position by 0.2 kcal/mol. This was rationalized as follows: in the axial conformation two *gauche* 2-silabutane interactions occur whereas in the equatorial conformer two *anti*-2-silabutane interactions occur. This interaction tends to stabilize the axial form relative to the equatorial form since the *gauche* conformer of 2-silabutane is lower in energy than the *anti* conformer which is the reverse of the order found in butane. On the other hand, the more highly substituted 1-tert-butylsilacyclohexane was predicted to prefer the equatorial conformation by 1.28 kcal/mol presumably because of increased steric crowding.

Ouellett's calculations on 3-silabicyclo(3.2.1)octane (SB3210) indicated a slight expansion of the <C—Si—C angle by 1.4° and a compression of the <C(1)—C(8)—C(5) valence angle by 8.7° relative to silacyclohexane. A substantial decrease in the C—Si—C—C torsional angle from 43° in silacyclohexane to 32° in SB3210 and its *exo*-3-methyl derivative (MSB3210) was also observed. In the *endo*-3-methyl derivative, which is predicted to be less stable than the *exo*-3-methyl isomer by 0.6 kcal/mol, a further decrease of the C—Si—C—C torsional angle to 22° was also calculated.

As stated by Ouellette, the *endo*- and *exo*-substituted MSB3210 compounds provide a potentially attractive means of studying reactions at the silicon center since these derivatives fall in the class of geometrical isomers which can be readily separated by chromatographic means. Furthermore, the relative stabilities of the two isomers has recently been determined by Cremer and Blankenship [8], who equilibrated them in the presence of a CsF catalyst in dimethylformamide solvent.

A number of related silicon-containing compounds have recently been studied by gas phase electron diffraction including: silacyclopentane [9], silacyclohexane [9], 1,1-dichloro- and 1,1-dimethoxy-1-silacyclohexane [10], as well as a number of bicyclic silanes [11].

The carbon analogue of SB3210, bicyclo(3.2.1)octane (B3210), has very recently been studied by electron diffraction [12], and a crystal structure of a related compound *exo*-3-*p*-nitrobenzyl-*endo*-3-phenyl-3-phosphabicyclo(3.2.1)-octane bromide (PB3210) has also been determined [13].

Thus, for a variety of reasons, it was felt that a gas phase electron diffraction investigation of the structure of SB3210 and one of its 3-methyl derivatives would provide an interesting conformational study. In addition, an important part of the investigation would involve the confirmation of the tentative stereo-assignment [8] of the *endo*-conformer obtained from the synthesis of the 3-methyl derivative outlined in the experimental section of this paper.

Experimental

SB3210 was prepared by treatment of *cis*-1,3-bis(bromomethyl)cyclopentane with magnesium to give the Grignard reagent which was then allowed to react with $SiCl_4$ to give 3,3-dichloro-4-silabicyclo(3.2.1)octane. The latter was reduced with $LiAlH_4$ in ether to yield SB3210. The product was purified by sublimation (10 mm Hg, 60°C) to give a solid, m.p. 97—100°C. The preparation of the bis(bromomethyl)cyclopentane has been described elsewhere [13]. During the course of our investigation, Anteunis et al. reported [14] on the synthesis of SB3210 using a method essentially identical to ours.

MSB3210 was made by treatment of the Grignard (described above) with methyltrichlorosilane in THF to give 44—50% yield of 3-chloro-3-methyl-3-silabicyclo(3.2.1)octane as an isomer mixture. Treatment of the mixture with sodium methoxide gave the methoxymethyl-SB3210 derivative (isomer mixture). Reduction of the latter with lithium trimethoxyaluminium hydride in ether selectively reduced the *endo*-methyl isomer more rapidly to give the desired *endo*-methyl-SB3210, m.p. 40—42°C (after distillation and sublimation). The *endo*-MSB3210 contained less than 2% of the *exo* isomer as determined by analytical gas chromatography. The synthetic scheme is similar to that used to prepare 1-methyl-4-tert-butyl-1-silacyclohexane [4] and will be described elsewhere [8].

The electron diffraction patterns were obtained using the NDSU diffraction

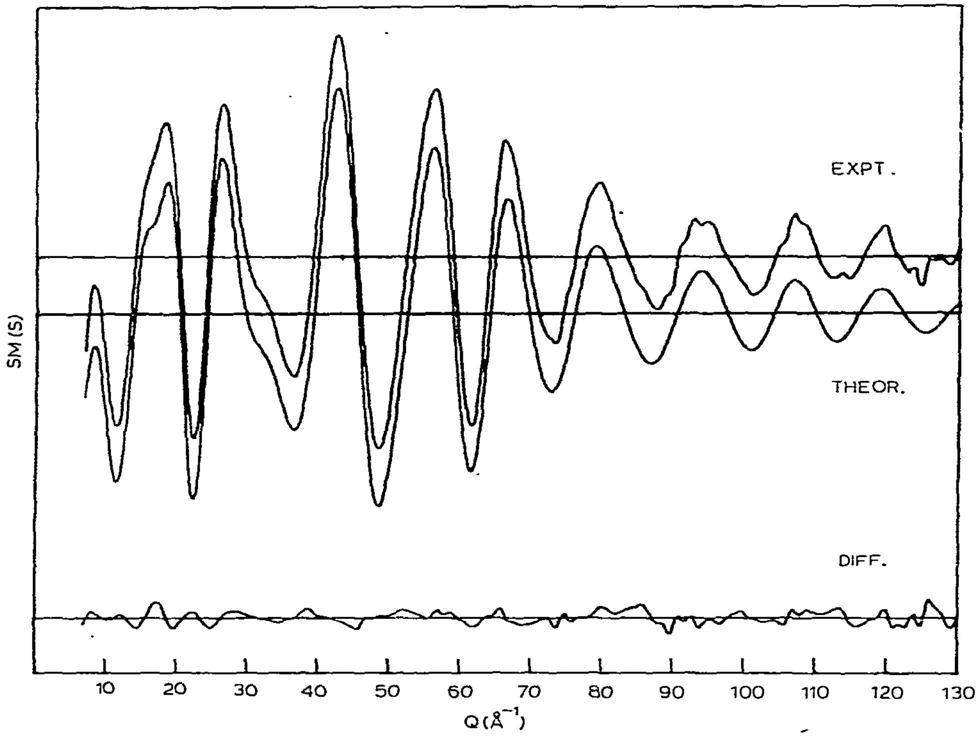

Fig. 1. Levelled experimental intensity curve for 3-silabicyclo(3.2.1)octane.

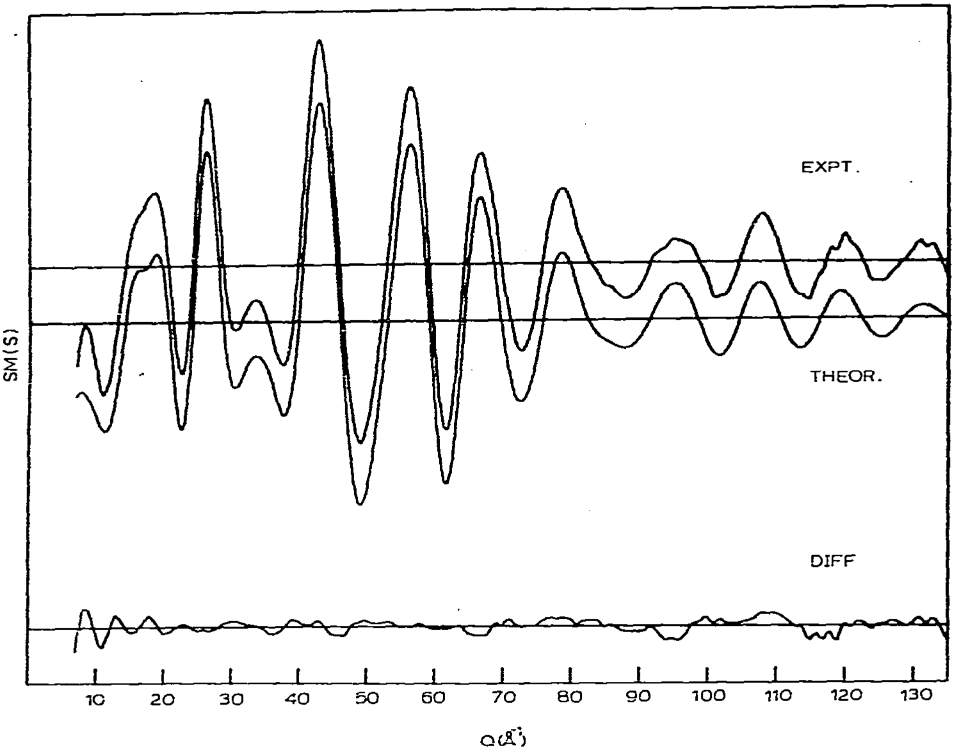

Fig. 2. Levelled experimental intensity curve for *endo*-3-methyl-3-silabicyclo(3.2.1)octane.

instrument. Data were collected at two camera distances (10 and 25 cm) using a 40 keV accelerating potential, and Kodak electron image 4 X 5 inch plates. Nozzle temperatures of 122°C and 134°C were used for SB3210 and MSB3210, respectively. Exposure times for the 0.3 μa electron beam ranged from 60 s for the long distance to 180 s for the short distance exposures. Ambient background pressures were in the range of 0.8 to 1.0 X 10^{-5} Torr during the exposures. Exact voltage and distance calibrations were based on benzene plates which were obtained under conditions identical to those used for each of the samples.

For each sample two long distance plates and three short distance plates were used for the analysis. The averaged intensity data interpolated at integral *q* intervals were analyzed in a way similar to the one outlined by Gundersen et al. [15]. Experimental intensity curves are shown in Figs. 1 and 2 for SB3210 and MSB3210, respectively. Experimental data including intensity and background functions as well as correlation matricies obtained from the least-squares analysis are available as supplementary data *.

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* Supplementary material has been deposited with NAPS. Order from NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance, in U.S. funds only. $5.00 for photocopies or $3.00 for microfiche. Outside the U.S. and Canada add postage of $3 for photocopy and $1 for microfiche.

Molecular mechanics calculations

In parallel with the electron diffraction investigation a series of molecular mechanics calculations were performed on SB3210 and the *exo*- and *endo*-MSB3210 isomers. The force field used is an adaptation of the valence force field for silacyclopentane reported by Philen, Chao and Laane [17]. This model force field has previously been applied, with considerable success, to conformetional analyses of silacyclopentane and silacyclohexane [9] as well as 1-methyl-1-silabicyclo(2.2.2)octane [11]. Although it is similar to the force field used by Ouellette [6,7], it has been optimized to reproduce observed electron diffraction structures rather than equilibrium internuclear bond lengths. The calculations were carried out using the program EMIN [18] which was written in this laboratory. The results are summarized in Table 1, where they are also compared with the earlier calculations by Quellette.

In general the results of the present calculations agree very closely with those reported by Ouellette with one important difference. The present calculations indicate that the *endo*-MSB3210 is slightly lower in energy (0.53 kcal/mol) than the *exo*-MSB3210 isomer. This difference may or may not be significant as will be discussed below. The torsional angles obtained in the present calculation are, nevertheless, very consistent with the values obtained by Ouellette including the rather dramatic ring flattening which occurs in the *endo*-isomer ($\theta 1 = 153°$) relative to the *exo*-isomer ($\theta 1 = 149°$).

TABLE 1

RESULTS OF THE MOLECULAR MECHANICS CALCULATIONS FOR SB3210 AND MSB3210

Parameter	SB3210		*exo*-MSB3210		*endo*-MSB3210	
<123	112.4	109.8	112.4	109.8	113.3	110.5
<234	105.6	106.4	105.7	106.6	106.5	107.3
<218	111.0	109.8	111.0	109.8	111.1	110.0
<217	112.3	110.9	112.3	110.8	112.4	111.0
<817	103.2	104.4	103.2	104.4	103.3	104.5
<185	103.8	103.9	103.8	104.0	103.8	103.9
<176	106.4	106.5	106.4	106.5	106.4	106.5
τ1856	39.7	36.5	39.7	36.4	39.4	36.2
τ8567	24.2	22.2	24.1	22.4	24.3	22.3
τ3456	59.5	56.0	59.6	56.2	63.9	58.5
τ1765	0.1	0.0	0.1	0.0	0.2	0.0
τ1234	32.0	34.8	32.0	34.6	21.5	30.3
τ2185	78.7	82.4	78.7	82.5	79.5	82.9
θ1 [a]	—	146.8	—	147.1	—	151.1
θ2 [b]	—	108.2	—	104.2	—	100.2
θ3 [c]	—	143.1	—	143.2	—	143.4
E(kcal)	—	—	0.0	0.45	0.60	0.0
Ref.	6	this work	6	this work	6	this work

[a] Flap angle between planes 1245 and 234. [b] Flap angle between planes 1245 and 185. [c] Flap angle between planes 1765 and 185.

Structural data analysis

Amplitudes of vibration for both SB3210 and *endo*-MSB3210 were calculated using the valence force field for silacyclopentane reported by Philen, Chao and Laane [17]. This same force field has been previously used in several recent studies of other silicon-containing compounds [9,11]. The calculated values of several bonded and more prominent non-bonded amplitudes are summarized in Table 2.

The atomic numbering used in defining the structural parameters for SB3210 and MSB3210 is illustrated in Fig. 3. In order to reduce the number of structural parameters the following constraints were imposed on the analysis:

1) The molecules were both assumed to have C_s symmetry.
2) All C—H bonds were assumed equal in length.
3) All C—C bonds were initially constrained to be of equal length. In later refinements this constraint was partially released.
4) Methylene hydrogens were constrained to lie in the planes which formed the perpenducular bisector of their respective <CCC valence angles. This was accomplished by refining only one <CCH valence angle for all methylene groups.
5) The two methine hydrogens in the C(1) and C(5) positions were assumed to lie in the C(1)C(8)C(5) plane with a constrained <HCC angle of 112.5°.
6) The <CSiH angles were also fixed at a value of 109.5°.

Within the framework of these six constraints, the molecular model for SB3210 was formulated in terms of the following ten independent parameters: C—H (avg), C—C (avg), Si—H, Si—C, <C(5)C(6)C(7), <C(7)C(1)C(2), <CCH (avg),

TABLE 2

CALCULATED AMPLITUDES OF VIBRATION FOR SB3210 AND *endo*-MSB3210 [a, b]

	SB3210		*endo*-MSB3210	
Distance	Calc.	Refined	Calc.	Refined
C—H	0.0790	0.072(4)	0.0790	0.087(9)
Si—H	0.0899	—	0.0899	—
C—C	0.0528	0.057(1)	0.0530	0.057(1)
Si—C	0.0557	0.063(3)	0.0563	0.059(2)
C(1)C(5)	0.0809	—	0.0774	—
C(8)C(6)	0.0871	—	0.0740	—
C(5)C(7)	0.0746	—	0.0716	—
C(8)C(4)	0.0914	—	0.1280	—
C(6)C(4)	0.0790	—	0.0795	—
SiC(5)	0.0925	—	0.0893	—
C(2)C(4)	0.0877	—	0.0798	—
C(1)C(4)	0.1150	—	0.1080	—
SiC(6)	0.1500	—	0.1420	—
C(4)C(7)	0.1070	—	0.0798	—
C(*m*)C(4)	—	—	0.1040	—
C(*m*)C(1)	—	—	0.1870	—
C(*m*)C(8)	—	—	0.1750	—

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[a] All vibrational amplitudes are expressed in units of Å, [b] Calculated from the force field of Philen, Chao and Laane [17].

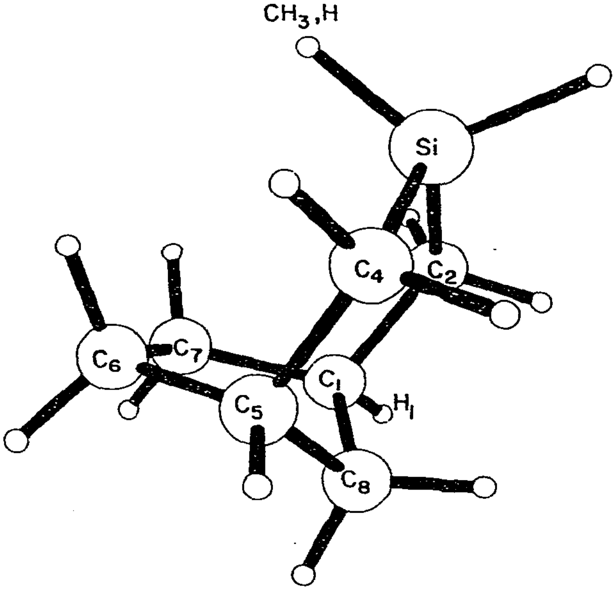


Fig. 3. Atomic numbering used in defining structural parameters for 3-silabicyclo(3.2.1)octane.

τC(4)C(5)C(6)C(7), $\theta 1$ which is the flap angle between the C(1)C(2)C(4)C(5) plane and the C(2)SiC(4) plane, and $\theta 3$ which is the flap angle between the C(1)C(7)C(6)C(5) plane and the C(5)C(8)C(1) plane. In MSB3210 the <CSiC(m) angle was also included in the analysis.

3-Silabicyclo(3.2.1)octane

It was clear from the outset of the analysis that the most stable conformation predicted by molecular mechanics (six-membered ring in the chair conformation) was indeed the correct one. Least-squares refinement of the ten parameter model described above resulted in excellent agreement with the experimental data. The resulting theoretical and experimental intensity curves are shown in Fig. 1 while the corresponding radial distribution functions are illustrated in Fig. 4. The results obtained for the independent and dependent geometrical parameters are listed in Table 3 under the heading Model I.

By symmetry there are four different kinds of carbon—carbon single bonds in SB3210. In an attempt to resolve the various C—C bond lengths two additional models were also tested. In Model II the four C—C distances were placed into three groups by constraining two of them to have the same value. There are a total of six possible ways in which this grouping can be made, and all six possibilities were tested. Of the six models thus tested only two (IIa with C(6)—C(7) = C(5)—C(6) and IIb with C(4)—C(5) = C(1)—C(8)) resulted in a fit which was comparable with or better than Model I. The remaining four models either diverged or resulted in an overall fit which was significantly worse than Model I. Model IIa produced slightly better agreement than Model I while Model IIb resulted in a slightly poorer fit. It should be noted, however, that the

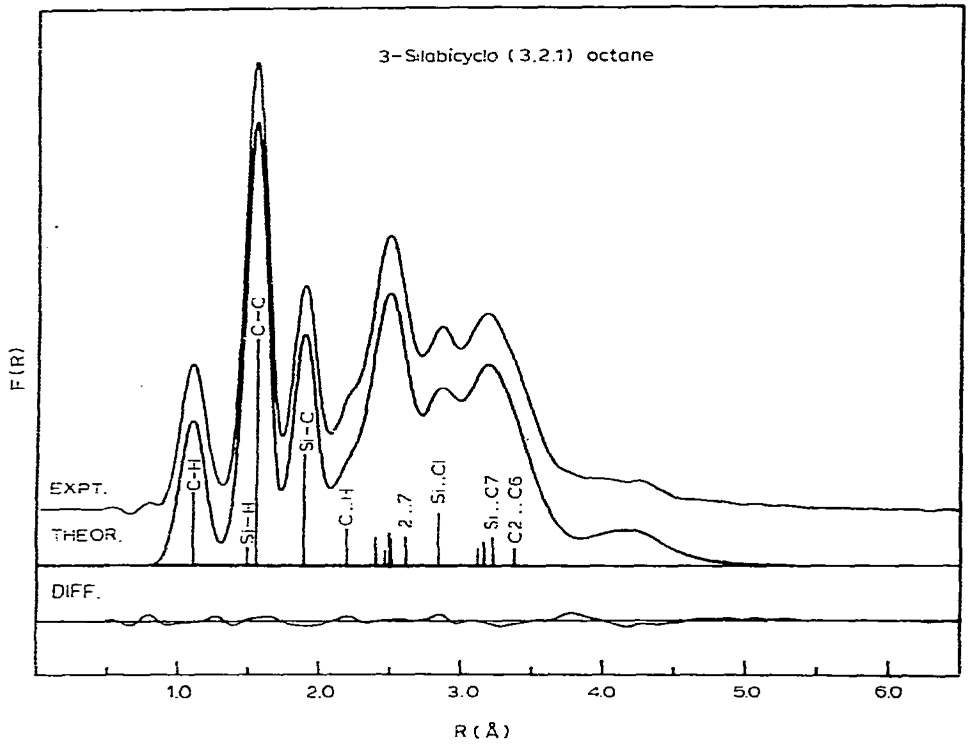


Fig. 4. Experimental and theoretical radial distribution function for 3-silabicyclo(3.2.1)octane.

slight improvement in the fit shown by Model IIa is not statistically significant.

In Model III all four carbon—carbon bond lengths were permitted to vary independently. In this model convergence could only be obtained when the $\theta 3$ and <CCH parameters were constrained. Although the refinement of this model did converge, the overall fit to the experimental data was worse than that obtained for either Model I or II.

The results of these additional tests indicate that, in fact, Model I contains the maximum amount of structural information which can reliably be obtained from the gas phase electron diffraction experiment. Models II and III, while they may provide some crude indications with regard to the relative ordering of the C—C bond lengths, are nevertheless suspect since they are predicated upon a number of constraints and the validity of the calculated vibrational amplitudes. It is interesting to note, however, that the relative ordering of the C—C bond lengths is similar to the ordering reported for bicyclo(3.2.1)octane [12], i.e., C(5)—C(6) > C(4)—C(5) ≈ C(6)—C(7) > C(1)—C(8).

endo-3-Methyl-3-silabicyclo(3.2.1)octane

In Model I for MSB3210 all of the C—C bond lengths were constrained to one average value, and the two Si—C bond lengths were assumed equivalent. Initial tests were performed using Model I in order to verify the actual stereochemical assignment (*endo* vs. *exo*) of the sample used in the experiment.

TABLE 3

MOLECULAR STRUCTURE OF 3-SILABICYCLO(3.2.1)OCTANE OBTAINED FROM LEAST SQUARES REFINEMENT [a]

	Model I	Model IIa	Model IIb	Model III
Independent parameter				
C—H(avg)	1.107(5)	1.107(5)	1.108(5)	1.107(5)
Si—H	1.491	1.491	1.491	1.491
C(1)C(8)	1.552(2)	1.59(1)	1.53(1)	1.53(3)
C(4)C(5)	1.552(2)	1.53(2)	1.53(1)	1.54(4)
C(6)C(7)	1.552(2)	1.59(2)	1.56(4)	1.55(3)
C(5)C(6)	1.552(2)	1.59(2)	1.59(1)	1.59(1)
Si—C	1.891(4)	1.891(4)	1.889(4)	1.889(4)
<C(5)C(6)C(7)	107.3(0.5)	108.5(0.8)	106.6(1.0)	106.6(1.2)
<C(7)C(1)C(2)	114.9(1.1)	117.2(0.8)	114.1(0.9)	113.6(2.3)
<HSiC	109.5	109.5	109.5	109.5
<CCH(avg)	110.5(1.4)	110.5	110.5	110.5
τ 5671	0.0	0.0	0.0	0.0
τ 4567	92.6(1.6)	89.8(1.0)	92.6(1.3)	93.0(3.0)
$\theta 1$ [b]	145.0(4.0)	142.5(2.6)	143.2(3.5)	139.0
$\theta 3$ [b]				
Dependent parameters				
<C(2)SiC(4)	104.2(1.6)	102.9(1.9)	102.5(1.6)	103.1(2.5)
<C(1)C(8)C(5)	105.6(1.9)	105.2(1.2)	107.1(1.7)	107.8(1.5)
<C(1)C(2)Si	111.4(0.8)	112.3(0.8)	111.8(0.8)	111.7(1.7)
$\theta 2$ [b]	107.6(3.0)	104.2(2.0)	110.4(2.0)	110.0(4.0)
τC(7)C(1)C(2)Si	53.0(3.4)	49.1(2.2)	51.9(3.0)	52.6(4.1)
R [c]	8.45	8.34	8.70	8.74

[a] Distances (r_g) are expressed in Ångstroms and angles ($<_\alpha$) in degrees. Estimated errors are three standard deviations as obtained from the least squares analysis. [b] $\theta 1$ is the flap angle between planes C(1)C(2)C(4)C(5) and C(2)SiC(4). $\theta 2$ is the flap angle between planes C(1)C(2)C(4)C(5) and C(5)C(8)C(1). $\theta 3$ is the flap angle between planes C(1)C(7)C(6)C(5) and C(5)C(8)C(1).

[c] $$R = \sqrt{\frac{\sum_i W_i(y_i^{\text{obs}} - y_i^{\text{calc}})^2}{\sum_i W_i(y_i^{\text{obs}})^2}}$$

Separate refinements on MSB3210 were carried out with the methyl group in the *endo* and *exo* positions. Starting values for the geometric parameters were obtained from the analysis of SB3210. The experimental radial distribution curve for MSB3210 along with the difference curves for the best fit *endo* and *exo* models are shown in Fig. 5. The *exo* model clearly exhibits a rather large discrepancy in the 4.0 to 5.0 Å region of the radial distribution curve. This region corresponds to the long C(*m*) ·· C(7) and C(*m*) ·· C(8) non-bonded distances of the *exo* form. These distances are much shorter in the *endo* form. There is little doubt that the *endo* form is the primary product of the above mentioned synthesis.

In Model II the constraint regarding the equivalence of the two Si—C bond lengths was relaxed. Least squares refinement of this model resulted in a cyclic

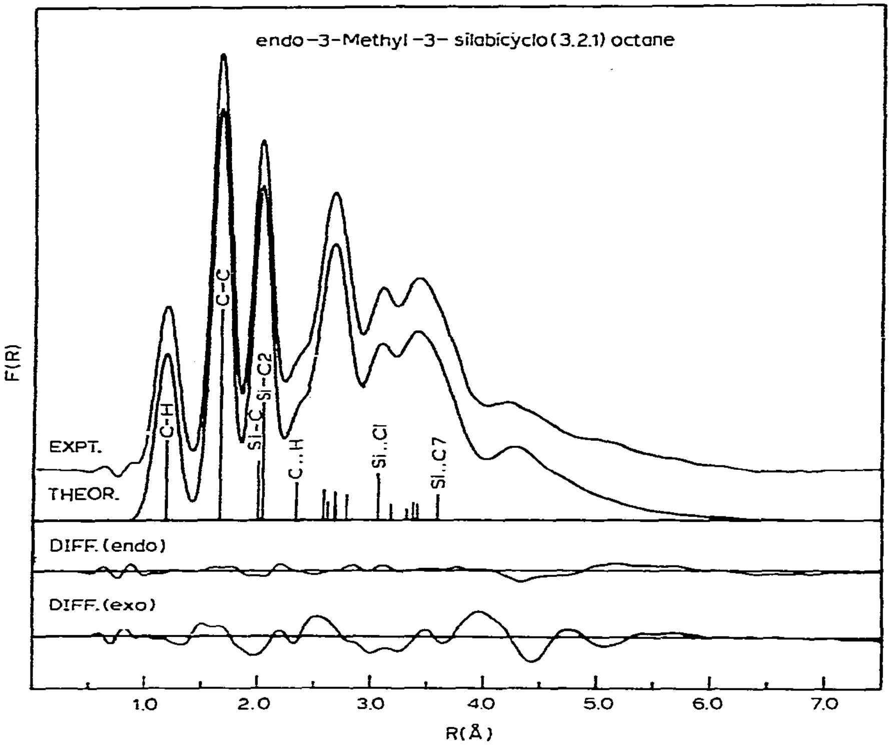


Fig. 5. Experimental and theoretical radial distribution function for 3-methyl-3-silabicyclo(3.2.1)octane. The difference curves labelled *endo*- and *exo*-correspond to those calculated from the best fit *endo*- and *exo*-models for the compound.

Si—C bond (1.900(5) Å) which is longer than the exocyclic one (1.863(8) Å). No appreciable change in any of the other structural parameters was observed. Although the error estimates for these two Si—C distances are relatively small; the improvement in the quality of the fit is not great enough to be statistically significant. The results obtained from the refinements of Models I and II are shown in Table 4, and the intensity curve obtained from Model II is compared with the experimental curve in Fig. 2.

In order to test the possible resolution of the carbon—carbon bond lengths a series of six models in which the four C—C bonds were separated into three groups was again explored. As in the case of SB3210 two models were found to give reasonably good fits to the experimental data. In order to obtain convergence, however, a number of additional parameters had to be constrained as indicated in Table 4. Both models produced a slightly improved fit in the region of the radial distribution curve around 4.0 Å; however, in both cases the overall agreement was poorer than that obtained for either Model I or II. Model IIa for which C(6)—C(7) = C(5)—C(6) and Model IIb for which C(1)—C(8) = C(4)—C(5) are identical to the two models which gave acceptable fits to the data for SB3210. All further attempts to resolve the four distinct C—C bond lengths failed to give converged solutions.

As in the case of SB3210 one must regard Models IIIa and IIIb with some

TABLE 4

MOLECULAR STRUCTURE OF *endo*-3-METHYL-3-SILABICYCLO(3.2.1)OCTANE OBTAINED FROM LEAST SQUARES ANALYSIS [a]

	Model I	Model II	Model IIIa	Model IIIb
Independent parameter				
C—H	1.103(5)	1.102(5)	1.102(5)	1.102(5)
Si—H	1.491	1.491	1.491	1.491
C(1)C(8)	1.548(2)	1.548(2)	1.57(1)	1.536(3)
C(4)C(5)	1.548(2)	1.548(2)	1.55(1)	1.536(3)
C(6)C(7)	1.548(2)	1.548(2)	1.527(5)	1.534(9)
C(5)C(6)	1.548(2)	1.548(2)	1.527(5)	1.579(6)
Si—C	1.888(3)	1.900(5)	1.900(5)	1.897(5)
Si—C(*m*)	1.888(3)	1.863(8)	1.862(8)	1.865(8)
<C(5)C(6)C(7)	108.2(0.4)	108.2(0.4)	109.2(0.3)	108.0(0.3)
<C(7)C(1)C(2)	114.6(1.1)	114.7(1.2)	114.2(1.0)	113.0(1.0)
<HSiC	109.5	109.5	109.5	109.5
<CCH (avg)	110.0	110.0	110.0	110.0
<C(2)SiC(*m*)	113.7(1.8)	113.6(2.0)	113.5	113.5
πC(5)C(6)C(7)C(1)	0.0	0.0	0.0	0.0
τC(4)C(5)C(6)C(7)	94.5(0.9)	94.0(1.0)	94.0	94.0
$\theta 1$ [b]	160.6(5.0)	160.0(5.0)	160.0	160.0
$\theta 3$ [b]	146.1(4.5)	146.7(4.5)	146.0	146.0
<C(2)SiC(4)	109.2(1.6)	109.4(1.5)	111.1(0.6)	110.1(0.6)
<C(1)C(8)C(5)	108.6(1.5)	108.7(1.2)	107.1(0.9)	109.6(1.0)
<C(2)C(2)Si	112.8(0.6)	112.3(0.6)	112.3(0.4)	112.3(0.5)
τC(7)C(1)C(2)Si	62.6(3.3)	62.9(3.6)	65.0(0.4)	67.0(0.5)
$\theta 2$ [b]	101.3(5.0)	100.6(5.0)	102.0(5.0)	103.2(5.2)
R [c]	8.58	8.50	8.67	8.63

[a] Distances (r_g) are expressed in Ångstrom units and angles ($<_\alpha$) in degrees. Estimated errors are three standard deviations as obtained from the least squares refinement. [b] $\theta 1$ is the flap angle between planes C(1)C(2)C(4)C(5) and C(2)SiC(4). $\theta 2$ is the flap angle between planes C(1)C(2)C(4)C(5) and C(5)C(8)C(1). θ_3 is the flap angle between planes C(1)C(7)C(6)C(5) and C(5)C(8)C(1).

[c] $$R = \sqrt{\frac{\sum_i w_i (y_i^{\mathrm{obs}} - y_i^{\mathrm{calc}})^2}{\sum_i w_i (y_i^{\mathrm{obs}})^2}}$$

measure of skepticism. The unambiguous resolution of distances this close together requires additional information from other experimental or theoretical sources.

Discussion

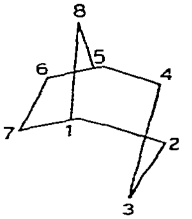
The average C—C and Si—C bond lengths obtained from the two independent structural studies are in excellent agreement with each other. The average C—C bond lengths (1.552(2) Å for SB3210 and 1.548(2) Å in MSB3210) agree well with the average C—C bond lengths in silacyclohexane (1.550(3) Å) and silacyclopentane (1.550(2) Å) [9]. The average Si—C bond lengths (1.891(4) Å in SB3210 and 1.888(3) Å in MSB3210) are also in good agreement with the same parameters obtained for silacyclohexane (1.885(3) Å) and silacyclopentane (1.892(2) Å) [9]. The fact that the average Si—C bond length is slightly shorter in MSB3210 than in SB3210 may be due to the weighted averaging of the endo- and exocyclic Si—C distances. In Model II for MSB3210 these distances are split into an endocyclic Si—C distance of 1.900(5) Å and an exocyclic Si—C bond length of 1.863(8) Å.

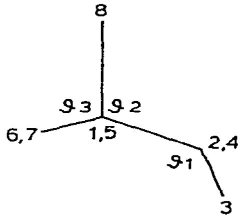
The various attempts to resolve the C—C distances are probably not very useful since in general the uncertainties are too large to draw any definitive conclusions. On the other hand, the indicated relative ordering obtained for model III in SB3210 and Model IIIb for MSB3210 is consistent with that obtained in the analysis of B3210 [12]; i.e. C(1)—C(8) is the shortest bond length and C(1)—C(7) is the longest C—C distance. Although the X-ray structure for PB3210 [13] does not have exact C_s symmetry, the shortest C—C bond length observed in this molecule is the C(5)—C(8) distance, while the longest one is the C(1)—C(7) distance. Thus while the relative ordering of the C—C distances for SB3210 and MSB3210 is not conclusively determined in the present analysis, the indicated trend is similar to related structure determinations.

Table 5 compares a number of the important conformational parameters for cyclohexane, silacyclohexane, PB3210, and B3210 with those obtained from this analysis for SB3210 and *endo*-MSB3210. From the data in Table 5 it is seen that the effect of substitution of a silicon atom in the cyclohexane ring is to: 1) leave <185 unchanged, 2) decrease <234 by 7.2°, 3) increase $\theta 1$ by 8.3°, and 4) decrease $\theta 2$ by 9.1°. The net effect of bridging the cyclohexane ring to form B3210 is to: 1) decrease <185 by 8.6°, 2) decrease <234 by 1.8°, 3)

TABLE 5

CONFORMATIONS OF MOLECULES STRUCTURALLY RELATED TO SB3210 AND MSB3210





Parameter	CHEX [a]	SCHEX [b]	PB3210	B3210	SB3210	MAB3210
<185	111.4	111.4	102.5	102.8	105.6	108.6
<234	111.4	104.2	106.0	109.6	104.2	109.2
$\theta 1$	130.4	138.7	150.7	138.9	145.0	160.6
$\theta 2$	130.4	121.3	111.9	117.4	107.6	101.3
$\theta 3$	—	—	136.9	132.6	139.2	146.1
$R18$	1.536	1.550	1.534	1.543	1.552	1.548
$R23$	1.536	1.885	1.806	1.543	1.891	1.888
$\tau 8123$	54.9	57.3	56.0	—	59.6	48.7
Ref.	20	9	13	12	this work	

[a] CHEX stands for cyclohexane. [b] SCHEX stands for silacyclohexane.

increase $\theta 1$ by 8.5°, and 4) decrease $\theta 2$ by 13.0°. If one assumes that the effects of silicon substitution and bridging are simply additive, then one would predict: 1) an increase in <185 by 8.6° (observed = 5.8°), 2) a decrease in <234 of 9.0° (observed = 7.2°), 3) an increase in $\theta 1$ of 16.8° (observed = 14.6°), and 4) a decrease in $\theta 2$ of 22.1° (observed = 22.8°). Thus all of the changes in the conformation of the six-membered ring are predictable within experimental error as a sum of the individual effects of silicon substitution and bridging.

This simple additivity behavior for SB3210 is in excellent agreement with the qualitative predictions of the simple molecular mechanics calculations. For the most part the additional strain which is introduced by bridging and silicon substitution is alleviated by changes in the torsional dihedral angles which have the smallest force constants, and to a lesser extent by changes in valence angles which have slightly larger force constants. The agreement between the observed structure for SB3210 and the molecular mechanics calculations on this molecule is very good; most of the calculated valence angles and dihedral angles are within two estimated standard deviations of the observed results.

Relative to SB3210, the molecule *endo*-MSB3210 exhibits changes in conformation which may be attributed to the increased steric crowding of the *endo*-methyl group. The largest observed changes are in the $\theta 1$ ($\Delta\theta 1$ = 15.6(5.0)°), $\theta 2$ ($\Delta\theta 2$ = −6.3(5.0)°), $\theta 3$ ($\Delta\theta 3$ = +6.9(4.0)°), <234 (Δ <234 = +5.0(1.6)°), and <185 (Δ < 185 = +3.0(1.5)°). The direction of these changes are correctly predicted by the molecular mechanics calculations, although the observed magnitudes of the changes are substantially larger than predicted. In particular, the increase in $\theta 1$ from 145.0(4.0)° in SB3210 to 160.6(5.0)° in *endo*-MSB3210 indicates a rather severe steric interaction which is not predicted by the molecular mechanics calculations (predicted $\Delta\theta 1$ = +4.3°). It is important to note that, in the analysis of the MSB3210 data, the $\theta 1$ parameter was 86% correlated with the $\tau 4567$ parameter which in turn determines the $\theta 2$ angle. It is possible that the uncertainty in the $\theta 1$ parameter does not accurately reflect this correlation. On the other hand, the value of $\theta 1$ for PB3210, which is also sterically crowded due to substitution on the phosphorus, is also rather large ($\theta 1$ = 150.7°).

The molecular mechanics calculations presented here do not appear to be consistent with the recent experiments of Cremer and Blankenship [8] in which the *endo* and *exo* isomers of MSB3210 were equilibrated in the presence of a CsF catalyst in dimethylformamide solvent. Ouellette's molecular mechanics calculations predict the *exo* isomer to be more stable than the *endo* isomer by 0.6 kcal/mol which seems consistent with the observed equilibrium ratio of 3 : 7 for *endo* : *exo* obtained experimentally. Several important considerations need to be made, however, in comparing the molecular mechanics predictions with these experimental observations. First, there is no way to assess the uncertainty in the calculated energy difference which is very sensitive to the form of the non-bonded potential functions employed. Second, it is the free energy difference which is important in making such comparisons. This would require some estimate of the entropy difference and zero point vibrational energy difference for the two isomers. Third, there is the effect of the polar solvent to consider. In this case the solvent would tend to shift the equilibrium in the direction of the isomer with the higher dipole moment, i.e., the *exo* form.

When one considers these additional uncertainties, all of which could conceivably make contributions comparable in magnitude to the calculated energy difference, the results of the two molecular mechanics calculations are not in fact significantly different.

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