# Molecular Structure of 1-Methyl-1-silabicyclo[2.2.1]heptane by Gas-Phase Electron Diffraction. Structural Support for the Trigonal Bipyramidal Transition State in SN2-Si Reactions

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Abstract: The structure of 1-methyl-1-silabicyclo[2.2.1]heptane has been determined by gas-phase electron diffraction. The molecule appears to be somewhat strained, as evidenced by moderately long average Si–C (1.883 ± 0.002 Å) and C–C (1.564 ± 0.004 Å) bond lengths, where quoted uncertainties are 3σ values obtained from least-squares analysis of the intensity data. The results of this investigation offer convincing structural support for the proposed geometry of the SN2-Si transition state suggested by Sommer.
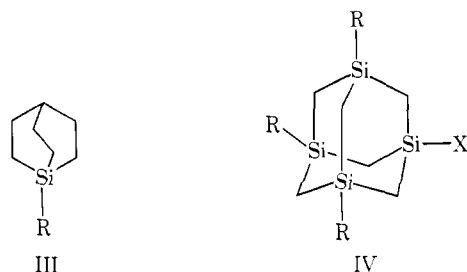
In general, reactivities at silicon centers differ markedly from reactivities at analogous carbon centers with the usual result being that silanes undergo substitution reactions more readily.[1] The generally higher reactivity of organosilicon compounds compared to carbon compounds reflects large differences in the mechanistic pathways accessible to these atoms. The contrast in relative reactivity and mechanism between comparable silicon and carbon atoms is largest in the bicyclic compounds I and II.
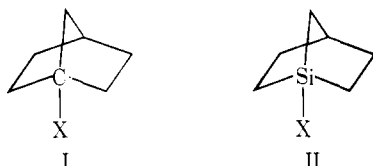
In their classic studies of the bicyclo[2.2.1]heptyl system,[2] Bartlett and co-workers attributed the stability of I to displacement under SN2 conditions to the fact that the bridgehead carbon was protected from backside attack. That the rigidly held bridgehead carbon cannot easily form a planar carbonium ion intermediate explains why SN1 displacements do not occur readily.

On the other hand, the silicon analogue, the 1-silabicyclo[2.2.1]heptyl system (II), exhibits extremely high reactivity in substitution reactions.[3] Sommer has postulated on the basis of scaled models that the ground-state geometry of II has valence angles which closely approximate those for the proposed pentacoordinate transition states illustrated in Figure 1. Only a slight movement of the R groups is required to attain the appropriate transition state geometry; thus greatly facilitating the operation of the proposed SN2-Si mechanism.

Consistent with this proposal is the observation that functionally substituted 1-silabicyclo[2.2.2]octane (III) is significantly less reactive than the [2.2.1] system, presumably be-

cause more energy would be required to form either of the pentacoordinate transition states drawn in Figure 1. It is also noteworthy that functionally substituted 1,3,5,7-tetrasilaadamantane derivatives (IV) are several orders of magnitude less reactive to nucleophilic substitution than II or III under similar conditions.[4] In this case the rigidity of tetrahedral configuration of the silicon atom under attack greatly impedes formation of a pentacoordinate intermediate.

We have initiated a research program directed to the precise determination of the structures of certain key organometallic compounds and present in this paper our results from the gas-phase electron diffraction study of 1-methyl-1-silabicyclo[2.2.1]heptane (MSBH).

We chose this system because it was believed to most closely approximate the SN2-Si transition state and because no quantitative data on its structure are presently available. The methyl derivative was selected because of its ease of handling.

Experimental Section

1-Methyl-1-silabicyclo[2.2.1]heptane. An oven-dried nitrogen-filled 250-ml flask equipped with a thermometer, condenser, and magnetic stirrer was charged with 4.45 g (30.5 mmol) of 1-chloro-1-silabicyclo[2.2.1]heptane[5] dissolved in 75 ml of dry ether (Mallinckrodt). After cooling the solution to 5 °C, 15 ml of 3.0 M methylmagnesium bromide in ether (~45 mmol) was added.

The temperature of the reaction mixture was kept at 5–10 °C during the course of the addition and allowed to warm to room temperature after the addition was complete. Following overnight stirring at room temperature the reaction mixture was cooled to 5 °C and hydrolyzed by dropwise addition of cold dilute HCl. The ether layer was separated, washed with water, and dried over anhydrous $MgSO_4$. After drying the salts were removed by filtration and most of the ether was removed by careful distillation. From the distillation residue 2.10 g (55% yield) of 1-methyl-1-silabicyclo[2.2.1]heptane was obtained by preparative gas chromatography.

Anal. Calcd for $C_7H_{14}Si$: C, 66.58; H, 11.18. Found: C, 66.68; H, 11.08. Molecular weight by peak matching (Varian Model M 66): calcd 126.0861; found 126.0884.

The sample used for this study was analyzed by gas chromatography (6 ft × ⅛ in. 1% UCW-98 on 80/100 M Chromosorb W) and showed less than 1% impurity.

The electron diffraction patterns were obtained using the Indiana University diffraction unit. Data were collected at two distances (12 and 29 cm) using a 40-KeV accelerating potential. The sample was introduced into the scattering chamber through a stainless steel inlet electrically heated so as to maintain a steady temperature of 423 K at the nozzle tip. Carbon dioxide calibration photographs were also taken at each of two nozzle positions using conditions identical with
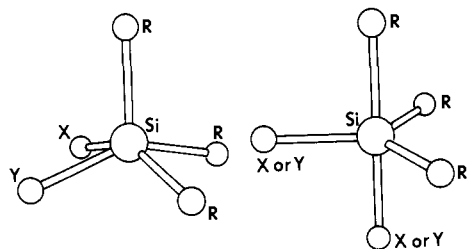
Figure 1. Proposed pentacoordinate transition state geometries for the SN2-Si reaction mechanism. X and Y represent attacking or leaving groups.

those used for the sample. Nozzle to plate distances were measured with a precision cathetometer and the high voltage was monitored with a precision divider network and digital differential voltmeter.

The actual s scale calibrations of the MSBH plates were obtained from the CO_2 calibration data using a new computer program written in this laboratory. This program uses the known spectroscopic structure of CO_2 gas as a primary standard in the following manner. A theoretical intensity curve for CO_2 is generated using the known structure of CO_2. Then, constraining the nozzle to plate distance, L, to its measured value, the wavelength, λ, is adjusted by expanding or contracting the s scale of the CO_2 data so as to produce agreement between the experimental and theoretical curves. For each cycle of refinement the experimental data are reinterpolated, a new background is drawn, the resolution factors are determined, and a comparison based upon the sum of the squares of the residuals is made. This somewhat tedious analysis is greatly facilitated by passing a polynomial background through the calculated correlation background at each step of the refinement. Convergence is usually obtained in 10 cycles or less when the wavelength calculated from the measured voltage is used as a starting point for the analysis. We feel that this calibration procedure, while a great deal more tedious than techniques used previously, is less prone to error and therefore well worth the additional effort. Since the CO_2 plates are obtained and analyzed using procedures identical with those used for the sample, many sources of systematic error are eliminated. Virtually the only source of error is a small displacement of the nozzle tip when the sample being studied is replaced by the CO_2 sample and this may be easily observed and compensated for, if necessary, using the cathetometer.

Two representative plates for each distance were microphotometered on the Indiana University automated microdensitometer.[6] After applying the standard corrections for saturation, plate flatness, and sector imperfections, the data were interpolated at integral q ($(40/\lambda)$ $\sin \theta/2$) intervals and averaged together for analysis. Least-squares analysis of the spliced intensity curves was conducted at N.D.S.U. in the usual manner[7] using the structure factors of Schaffer, Yates, and Bonham[8] along with Tavard's[9] inelastic scattering factors. In the initial stages of analysis polynomial backgrounds were employed with final analysis based on carefully hand drawn backgrounds. Resolution factors of 0.97 and 0.90 for the long and short distance, respectively, were obtained and the crossing points of the long and short distance data in the overlap region agreed within 0.08 q units with no apparent trend.

Tabulations of the intensity data, backgrounds, and correlation and error matricies are available.[10]

Analysis

Because of the relatively low symmetry of MSBH (Figure 2), a detailed specification of its molecular structure would require many more parameters than are typically justified in an electron diffraction experiment. It was therefore decided at the outset of the analysis to impose a number of geometrical constraints and to employ calculated vibrational amplitudes as a means of obtaining the maximum amount of useful information from the experimental data.

The following constraints were imposed throughout the analysis (see Figure 2):

(1) All C–H bond lengths were constrained to one common value.

(2) All methylene hydrogens were constrained to lie in a plane which is the perpendicular bisector of their respective
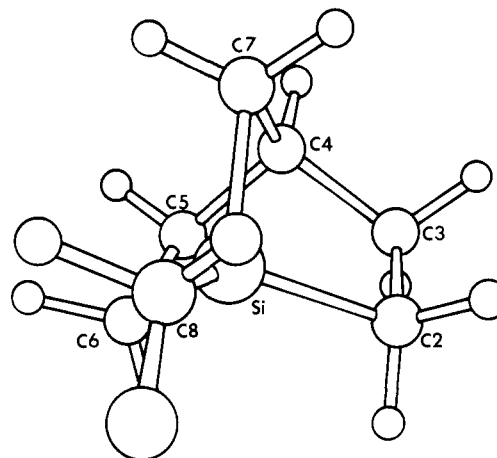

Figure 2. Atomic numbering used in defining structural parameters for 1-methyl-1-silabicyclo[2.2.1]heptane.

$\angle CCC$ or $\angle SiCC$ valence angle. This was done by constraining all $\angle SiCH$ and $\angle CCH$ valence angles to one common value for the methylene hydrogens.

(3) The methyl group was constrained to have C_{3v} symmetry about the axis of its Si–C bond, thus requiring only $\angle SiCH$ valence angle for its geometrical specification.

(4) The methine hydrogen (H_8) was located in the reflection plane of the molecule by the specification of the $\angle C_7C_4H_8$ angle. This parameter was assumed to be 112.5° and constrained throughout the analysis.

(5) The two dihedral angles about the C_2–C_3 and C_5–C_6 bonds were constrained to zero. This constraint, while not required by symmetry, was prompted by the large indeterminancy in the near zero value of this parameter during the initial stages of analysis.

In addition to constraints 1 through 5 various constraints were also placed upon the relative Si–C and C–C bond lengths. These variations constitute the basis for the three models to be discussed below.

Calculated vibrational amplitudes and shrinkage parameters (Table II) were also employed in the analysis in an effort to reduce the number of parameters to be determined and to maximize the use of the experimental data. Since no force field has been determined for MSBH, only approximate vibrational parameters could be calculated by adapting the force field determined for silacyclopentane (Table I) by Philen and Laane.[11] Our previous experience indicates that l_{ij} and K_{ij} parameters calculated in this manner from a transferred force field are adequate, since they are usually well within the uncertainties of the corresponding parameters determined from diffraction data alone.

Model I. As a first attempt at the refinement of the data, a highly idealized model was employed. In addition to constraints 1 through 5 above two more constraints were imposed. It was assumed that all Si–C bonds were equivalent and also that all C–C bonds were equivalent. The obvious utility of such a model is to determine precise values for the average Si–C and C–C bond lengths as well as to obtain a gross average geometry for the entire molecule. In this first analysis nine geometrical parameters were varied in addition to the Si–C and C–C amplitudes of vibration. A variation of the latter two parameters was necessary in order to accommodate this arbitrary grouping of nonequivalent distances.

In spite of the numerous assumptions involved in this grossly simplified model, it was nevertheless found to provide an excellent least-squares parameterization of the experimental data. A plot of the resulting least-squares fit to the molecular intensity curve is shown in Figure 3, while the resulting radial distribution curve is displayed in Figure 4.
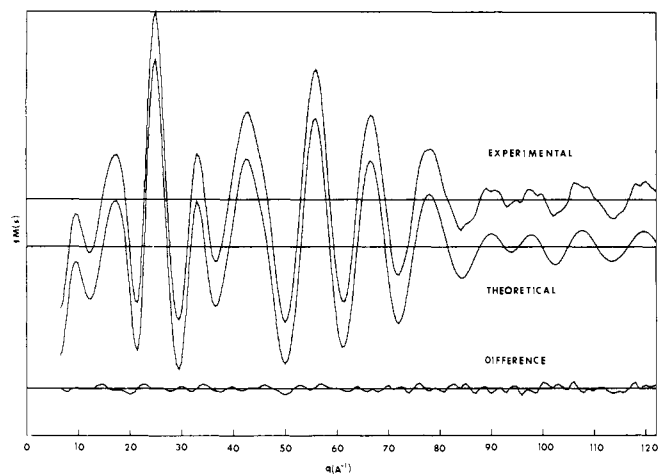
Figure 3. Leveled molecular intensity curve, $sM(s)$, for 1-methyl-1-sila-bicycloheptane. The difference curve shown is for model I.

Figure 4. Radial distribution curve for 1-methyl-1-silabicycloheptane. The difference curve shown is for model I.

Table I. Force Field Used for Calculation of Vibrational Amplitudes[a]

Force constant[b]	Value	Force constant[b]	Value
C–C	4.385 mdyne/Å	$C_\beta H$, $C_\beta H$	0.013
Si–C	2.780	$C_\alpha H$, $C_\alpha H$	–0.013
C–H	4.650	CC, ∠CCC	0.511 mdyn
∠CCH	0.784 mdyne-Å	CC, ∠CCSi	0.484
∠CCSi	0.911	SiC, ∠CSiC	0.083
∠CSiC	0.759	CC, ∠HCC	0.198
∠HCH	0.482	CH, ∠HCC	0.154
∠HCC	0.501	CH, ∠HCSi	0.154
∠HCSi	0.345	SiC, ∠HCSi	0.133
C–C, C–C	0.226 mdyne/Å	∠CCC, ∠CCSi	0.069 mdyne-Å
C–C, Si–C	0.139	∠CCC, ∠CCC	0.069
Si–C, Si–C	0.233	Torsion(Si–C, C–C)	0.077

[a] Force field adapted from D. L. Philen, T. H. Chao, and J. Laane, ref 11, for silacyclopentane. [b] Notation for defining force constants is that used in ref 11.

Table II. Calculted Amplitudes and Shrinkage Parameters[a]

Distance[b]	l_{ij}, Å × 10⁴	K_{ij}, Å × 10⁴
Si–C[c]	556	45
C–C[c]	533	68
C–H[c]	792	293
Si . . C_4	665	19
Si . . C_3	710	29
C_3 . . C_5	791	43
C_2 . . C_4	695	35
C_2 . . C_7	890	30
C_2 . . C_6	1033	33
C_2 . . C_5	1141	24
C_7 . . C_8	996	37
C_6 . . C_8	929	41
C_4 . . C_8	864	14
C_5 . . C_8	901	15

[a] Atom numbering is shown in Figure 2. [b] In the interest of conserving journal space only amplitudes for the major peaks of the radial distribution curve are shown. In the actual analysis calculated amplitude and shrinkage parameters were employed for all internuclear distances and no terms were neglected. [c] l_{ij} and K_{ij} parameters are average values for bonded distances.

The parameters obtained from the refinement of model I are shown in the appropriate column of Table III. The resulting R factor,[12] 6.4%, is surprising when one considers the number of simplifying assumptions involved. It is nevertheless obvious that there is substantial splitting of the Si–C and C–C bond lengths, as evidenced by the rather large amplitude parameters obtained for these two distances. Thus, model I represents an idealized gross conformation of the molecule involving average distances. For many purposes this structure is sufficient. While this model lacks resolution, its parameters are nevertheless unambiguously defined and are precisely determined. This statement cannot be made with regard to model II and model III discussed below, which are attempts at resolving the splittings amongst these parameters.

Model II is an attempt to partially relax the constraints imposed by model I. The symmetry of the molecule dictates three distinct types of Si–C bonds with degeneracies of 2, 1, and 1. The five C–C bonds may also be divided into three groups with degeneracies 2, 2, and 1. Rather than proceeding directly to a complete relaxation of the constraints associated with model I, an intermediate possibility was explored. For the
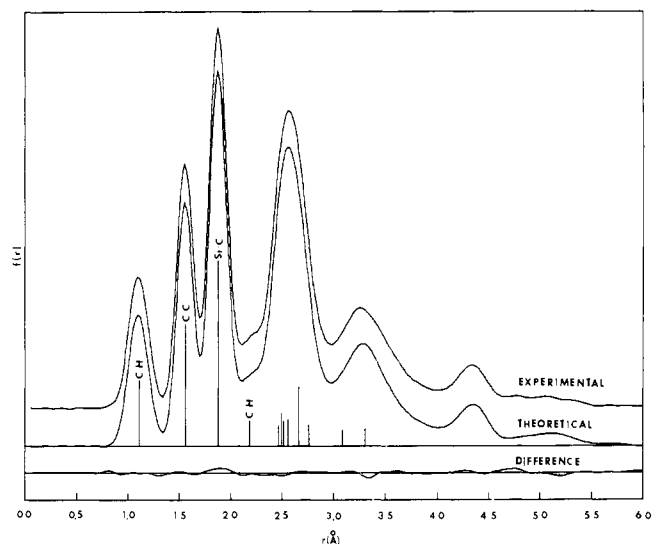
Si–C case the three groups may be categorized into two groups (long Si–C and short Si–C) in three possible ways by combining two of the three distances in the analysis. The same grouping can also be applied to the C–C distances. Combining the groupings for the Si–C distances with those for the C–C distances leads to a total of nine possibilities. Since there is no a priori reason (other than chemical intuition, which can often be misleading) for choosing one of these models in preference to another, refinements of all nine of them were performed. This systematic approach was adopted in hopes of averting convergence to a local least-squares minimum from some assumed starting point. Each of the analyses was started from the same point, i.e., the geometry of model I; however, during these analyses, the vibrational amplitudes were all constrained to their calculated values.

The R factors for the nine models tested ranged from 5.94 to 8.46% and some of the analyses diverged. One model, shown as model II in Table III, gave a substantially better fit than any other. This particular model, which is characterized by long Si–C_2 and long C_3–C_4 bonds, was found to be a significant improvement over model I. According to Hamilton's[12] R test

Table III. Structural Parameters Obtained From Least-Squares Analysis[a]

	Model I	Model II	Model III
Independent Parameters[b]			
Si-C$_7$	1.883 ± 0.002 Å	1.860 ± 0.006 Å	1.84 ± 0.02 Å
Si-C$_8$			1.86 ± 0.02 Å
Si-C$_2$		1.905 ± 0.005 Å	1.905 ± 0.006 Å
C$_2$-C$_3$		1.545 ± 0.005 Å	1.54 ± 0.02 Å
C$_4$-C$_7$	1.564 ± 0.004 Å		1.56 ± 0.05 Å
C$_3$-C$_4$		1.593 ± 0.008 Å	1.59 ± 0.02 Å
C-H$_{avg}$	1.113 ± 0.005 Å	1.113 ± 0.005 Å	1.113 ± 0.005 Å
Si..C$_4$	2.495 ± 0.015 Å	2.486 ± 0.018 Å	2.47 ± 0.02 Å
∠C$_7$SiC$_2$	94.5 ± 0.6°	94.7 ± 0.5°	94.9 ± 0.5°
∠C$_7$SiC$_8$	116 ± 2.°	119 ± 2.°	119 ± 2.°
∠SiCH	121 ± 4.°	119 ± 4.°	120 ± 4.°
∠CCH$_{avg}$	109 ± 1.°	109 ± 1.°	109 ± 1.°
τC$_4$C$_7$SiC$_2$	49.8 ± 0.7°	48.9 ± 0.7°	49.1 ± 0.9°
lSi-C	0.060 ± 0.003 Å		
lC-C	0.058 ± 0.003 Å		
Dependent Parameters[c]			
∠S$_1$C$_2$C$_3$	101.1 ± 0.4°	101.1 ± 0.3°	101.3 ± 0.8°
∠C$_2$C$_3$C$_4$	110.5 ± 0.6°	110.3 ± 0.7°	110.0 ± 0.8°
∠C$_3$C$_4$C$_7$	107.5 ± 0.7°	107.8 ± 0.7°	107.9 ± 0.6°
∠C$_4$C$_7$Si	92.5 ± 0.8°	93.6 ± 0.9°	93.0 ± 2.4°
∠C$_3$C$_4$C$_5$	105.0 ± 1.8°	103.0 ± 1.7°	103.7 ± 2.7°
∠C$_2$SiC$_8$	122.9 ± 1.0°	122.1 ± 1.1°	121.9 ± 1.2°
∠C$_2$SiC$_6$	99.1 ± 1.5°	97.4 ± 1.4°	97.8 ± 1.8°
∠HC$_8$H	95.0 ± 6.0	98.2 ± 4.8°	97.5 ± 4.8°
∠HC$_2$H	118.8 ± 4.1°	119.0 ± 3.8°	118.5 ± 4.3°
∠HC$_3$H	110.9 ± 4.7°	111.3 ± 4.3°	111.1 ± 4.6°
∠C$_3$C$_4$H	112.0 ± 0.8°	112.6 ± 0.9°	112.2 ± 1.3°
∠HC$_7$H	124.2 ± 3.6°	123.8 ± 3.2°	123.8 ± 3.4°
ϕ_1[d]	125.9 ± 0.9°	127.0 ± 0.8°	126.7 ± 1.2°
ϕ_2[e]	108.1 ± 1.8°	106.1 ± 1.7°	106.6 ± 2.5°
R	6.41%	5.94%	5.92%

[a] The distance parameters are reported as $r_g(0)$ values, while the angles are $r\alpha$ parameters which have been corrected for shrinkage effects. Uncertainties quoted are 3σ values. [b] Independent parameters are those which were varied in the least-squares analysis. [c] Dependent parameters were calculated from the geometry specified by the independent parameters. The uncertainties in the dependent parameters were obtained by transforming the error matrix. [d] ϕ_1 is the flap angle between the plane containing atoms Si, C$_7$, and C$_4$ and the plane containing atoms Si, C$_2$, C$_3$, and C$_4$. [e] ϕ_2 is the flap angle between the plane containing atoms Si, C$_2$, C$_3$, and C$_4$ and the plane containing atoms Si, C$_6$, C$_5$, and C$_4$.

the hypothesis that model I is as good as model II may be rejected at the 99% confidence level. The reader should be cautioned, however, that the splittings obtained are contingent upon the precision of the calculated Si-C and C-C vibrational amplitudes. The amplitudes and splittings are highly correlated and could therefore not be varied simultaneously. Separate regression runs, nevertheless, demonstrated that the magnitudes of the parameters remained within the quoted error limits for a reasonable range of values for the amplitudes (±0.02 Å).

Model III was an additional attempt at the relaxation of constraints associated with the relative Si-C and C-C bond lengths. In this model all Si-C and C-C bond lengths were varied independently starting from the geometry of model II. Once again the associated amplitudes were constrained to their calculated values. Although this least-squares analysis did converge, application of Hamilton's statistical test indicates that the improvement obtained relative to model II is not significant even at the 50% confidence level.

Discussion

The results obtained for model I when compared with quoted structures of acyclic silanes suggest a moderate amount of ring strain in MSBH. The average Si-C bond length (1.883 ± 0.002 Å) is slightly longer than that obtained for acyclic systems such as Si$_2$(CH$_3$)$_6$[13] (Si-C = 1.879 ± 0.003 Å), Si(CH$_3$)$_4$[14] (Si-C = 1.876 ± 0.002 Å), and (SiH$_3$)$_2$CH$_2$[15] (Si-C = 1.874 ± 0.002 Å). It is, however, also slightly smaller than the Si-C bond length in Si[Si(CH$_3$)$_3$]$_4$.[16] Still, the ring strain appears to be considerably less than in silacyclobutane[17] (Si-C = 1.897 ± 0.010 Å).

The average C-C bond length seems unusually long (C-C = 1.564 ± 0.004 Å), particularly when compared with the average C-C bond length in norbornane[8] (C-C = 1.549 ± 0.001 Å). This increased length is undoubtedly due to the additional strain introduced into the molecule by the replacement of the C-C bond with the substantially longer Si-C bond.

Models II and III represent a statistically significant improvement compared with model I; however, the reader should be aware that these results are contingent upon many imposed constraints as well as the numerical validity of the calculated mean amplitudes of vibration. A number of other models not shown in Table III resulted in least-squares fits to the experimental data which were only slightly worse than the fit obtained for model II. The pitfalls encountered in attempting to resolve closely spaced distances by electron diffraction are well known to specialists in the area. In the absence of any additional experimental data such as microwave moments of inertia, the most we can say is that the electron diffraction data strongly indicate the relative ordering of distances shown for models II and III.

In spite of the somewhat questionable resolution of the nearly degenerate distances, the results of this analysis reinforce the structure-reactivity relationship suggested by Sommer[1] quite dramatically. The molecular geometry at the silicon center is quite close to that of a trigonal bipyramid with C$_7$ at the apex and atoms C$_2$, C$_6$, and C$_8$ acting as the equatorial groups. It is easy to visualize how, with only a slight distortion of the ∠C$_7$SiC$_8$ valence angle, the attacking group could occupy the other apex of a nearly perfect trigonal bipyramidal transition state. Since the ∠C$_7$SiC$_2$ and ∠C$_7$SiC$_6$ valence angles are already 94.5° in MSBH, a great deal of the requisite transition state geometry is in a sense "built in" as a result of the strained bicyclic nature of the molecule. In conclusion then, we offer this structural evidence in support of the S$_N$2-Si mechanism proposed by Sommer to explain the differences in reactivity for analagous carbon and silicon centers.

Supplementary Material Available: a tabulation of the experimental data, correlation matrices, and error matrices (8 pages). Ordering information is given on any current masthead page.

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Conformational Analysis of Triarylsilanes

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Abstract: Ground-state geometries and relative strain energies of several methyl-substituted triphenylsilanes have been obtained by full relaxation empirical force field calculations. The C–Si–C bond angle in trimesitylsilane is found to be significantly expanded, in parallel with similar previous findings for trimesitylmethane and trimesitylphosphine. The equilibrium conformer population of tris(o-tolyl)silane consists almost entirely of the exo_3 and exo_2 forms, in approximately equal proportion, whereas in the case of tris(m-tolyl)silane all four conformers populate the equilibrium mixture to a significant extent. The experimentally determined dipole moments of the triarylsilanes are in reasonable accord with the quantities calculated by vectorial summation of partial moments based on ground-state geometries and taking into account conformer populations. A marked similarity is noted between the computed geometries and conformational preferences of triarylsilanes and of structurally related phosphine derivatives.

In the course of our work[2] on the stereochemistry of three-bladed molecular propellers of the type Ar_3Z and Ar_3ZX[2] we had occasion to develop an empirical force field program,[3] which proved to be successful in computing the ground-state conformations of triphenylmethane, trimesitylmethane, and congeners.[4] The present study was undertaken in order to use this method as a means for estimating populations of diastereomeric conformers in molecules of this type in which the three aryl groups (Ar) have the same constitution, but lack a local C_2 axis. As a representative system we chose a series of methyl-substituted triphenylsilanes, since a force field had previously been employed to similar ends in a conformational analysis of tetrakis(o-tolyl)silane.[5]

Results and Discussion

Ground-state geometries and energies were computed employing the previously described[3,5] full relaxation empirical force field method, together with the appropriate parameters.[6]

In an exploratory study, ground-state conformations were computed for three molecules of the type Ar_3SiH, in which Ar has a local C_2 axis:[8] triphenylsilane (**1**), tris(p-tolyl)silane (**2**), and trimesitylsilane (**3**). It was found that all three molecules have C_3 symmetry and that **1** and **2** have identical (within the precision of the method) bond angles (C–Si–C = 110.8°) and dihedral angles of twist[9] (H–Si–C–C′ = 32.7°).[10] In contradistinction, the expanded C–Si–C bond angle of 114.9° computed for **3** (H–Si–C–C′ = 42.1°) is a manifestation of significant nonbonded interaction among the three bulky mesityl groups and parallels the expansion of central bond angles found for trimesitylmethane[3,4a] and trimesitylphosphine.[12] The same effect results in a slight lengthening of the Si–C bond in **3** (1.88 Å) as compared to **1** and **2** (1.86 Å).[13]

Tris(o-tolyl)silane and Congeners. Eight conformational stereoisomers (four dl pairs) are possible for molecules of the type Ar_3SiH, in which the three aryl groups are constitutionally the same but lack a local C_2 axis.[14] Tris(o-tolyl)silane

(**4**) is a member of this class. The four diastereomers differ in the number of methyl groups which are proximal or distal to the Si–H hydrogen atom[15] and, by analogy with the corresponding phosphines, they may be designated[16] as $4\text{-}exo_3$, $4\text{-}exo_2$, $4\text{-}exo_1$, and $4\text{-}exo_0$, according as to whether three, two, one, or none of the three methyl groups are proximal (exo). The sense of the propeller (helicity) determines the configuration (P or M) of the enantiomers in each of the four dl pairs.

Structural parameters computed for the four diastereomers are given in Table I. The skeletal structures of $4\text{-}exo_3$ and $4\text{-}exo_0$ closely resemble those of **1** and **3**, respectively. Evidently, the bond stretching and bending suffered by $4\text{-}exo_0$, as compared to $4\text{-}exo_3$, is similar to that suffered by **3**, as compared to **1**, and for the same reason: in $4\text{-}exo_0$, as in **3**, three methyl groups are forced into the endo position of the molecular pyramid[15] and are jammed against the nether face of the benzene rings. The resulting congestion is reflected not only in severe deformation of bond angles and lengths, but also in an increase of 3.63 kcal/mol in strain energy (E_T)[17] for $4\text{-}exo_0$, as compared to $4\text{-}exo_3$. In harmony with this model, it is found (Table I) that structural deformation and strain energy, which are at a minimum in $4\text{-}exo_3$, both increase in direct relation to the number of endo groups.

Whereas $4\text{-}exo_3$ and $4\text{-}exo_0$ both have C_3 symmetry, the isomers with a mixed distribution of exo and endo groups ($4\text{-}exo_2$ and $4\text{-}exo_1$) are asymmetric. Nevertheless, the basic propeller property remains, for although the magnitudes of the three dihedral angles differ appreciably, the sense of twist of each phenyl ring in the triphenylsilane skeleton remains same.

It is instructive to note that in related systems, structures analogous to $4\text{-}exo_3$ have been observed in the solid state. In tris(o-tolyl)phosphine and its oxide, the molecule exhibits virtual C_3 symmetry and all three methyl groups occupy exo positions;[18,19] the torsional angles of the tolyl groups in the phosphine[19] (36.7–49.0°) and its oxide[19] (36.7–53.3°) are comparable in magnitude to those found for $4\text{-}exo_3$ (39.3°).