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THE MOLECULAR STRUCTURE OF 1-METHYL-1-SILABICYCLO[2.2.2]OCTATRIENE AS DETERMINED BY GAS PHASE ELECTRON DIFFRACTION

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Summary

The molecular structure of 1-methyl-1-silabicyclo[2.2.2]octatriene has been determined by gas phase electron diffraction. The molecule was found to exhibit a great deal of angular distortion at the silicon bridgehead while the valence angles at the carbon bridgehead appear to be relatively normal. The observed valence angles at the carbon bridgehead, $\angle$C=C—C (119.4(0.7)°) and $\angle$C—C—C (108.3(0.6)°), appear to be unaffected by the ring strain in the molecule. The angles at the silicon bridgehead, $\angle$C—Si—C (98.8(0.3)°), $\angle$Si—C=C (109.9(0.5)°), and $\angle C_m$—Si—C (188.7(0.2)°), are very unusual compared with the typical sp^3 and sp^2 values. These distortions can be qualitatively explained in terms of the relative magnitudes of the bending force constants and in terms of hybridization on the silicon and carbon atoms involved.

Introduction

We have recently been investigating the structures of strained ring compounds containing bridgehead silicon. A portion of our interest in these systems results from the structure-reactivity relationship implied by the S_N2-Si mechanism proposed by Sommer [1]. According to Sommer's proposal the rate of reaction at a substituted bridgehead silicon under S_N2 conditions should depend strongly on the similarity between the bridgehead geometry and that of the trigonal bipyramidal transition state proposed for the mechanism. In conjunction with this study, we have recently investigated the structures of 1-methyl-1-silabicyclo[2.2.1]heptane (MSBH) [2], 1-methyl-1-silaadamantane

(MSA) [3], 1-methyl-silatrane [4], and 1-chloro-1-silabicyclo[2.2.2]octane (CSBO) [5]. The experimental evidence thus far collected appears to support the proposed structure-reactivity relationship.

The molecule 1-methyl-1-silabicyclo[2.2.2]octatriene (MSBAR) has recently been prepared by Barton and Burns [6] as a product in the pyrolysis of 1-methyl-1-allyl-1-silacyclohexa-2,4-diene in a vertical quartz tube heated to about 430°C with acetylene serving as both a reactant and as the carrier gas. At the present time, little is known of the chemistry or the structure of this newly synthesized compound. In view of the unusual structural nature of this molecule, and our interest in compounds containing bridgehead silicon, we decided to undertake an investigation of the structure of this novel compound.

Experimental

The sample of MSBAR was purified by preparative gas chromatography using a 12 ft, column of 20% SE-30 at 100°C. Estimated purity of the sample used in the determination was approximately 98%. Diffraction photographs were recorded on Kodak Electron Image plates (4 × 5 in) with the NDSU electron diffraction unit using an r^3 sector. The sample was heated to 60°C while the inlet and nozzle tip were maintained at approximately 100°C. An accelerating potential of 40 keV was used for the experiment and data were collected at camera distances of 94.357 mm and 245.79 mm. Wavelength calibrations were based on benzene photographs taken under experimental conditions identical to those used for the sample. Exposure times of 70 seconds for the 245 mm photographs, and 200 seconds for the 94 mm plates were needed for an incident beam current of 0.3 microamps. Background pressures with the sample

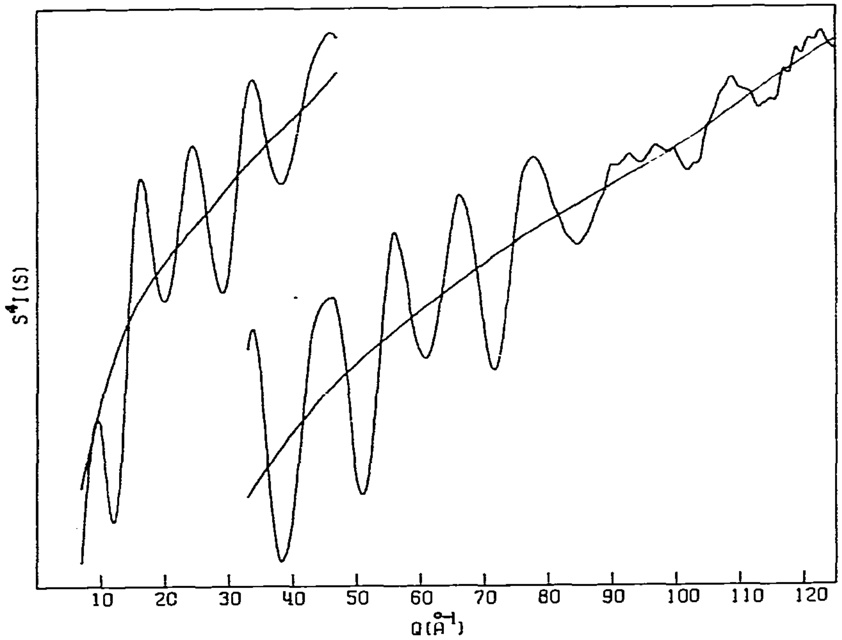

Fig. 1. Raw intensity data and backgrounds for MSBAR.

flowing were in the range of 0.9 to 1.5×10^{-5} Torr.

Optical densities from two photographic plates from each of the two camera positions were recorded on the NDSU microprocessor controlled densitometer. Standard corrections for sector imperfections, emulsion saturated and plate flatness were applied to the data which were then interpolated at unit q ($10\ s/\pi$) intervals for final analysis. Averaged intensity curves for each of the camera distances were analyzed according to procedures outlined by Gundersen and Hedberg [7] using elastic scattering factors calculated by Schaffer, Yates, and Bonham [8]. Plots of the experimental intensity data and backgrounds are shown in Fig. 1, and tables of these data as well as correlation and error matrices obtained from least squares analysis are available from NAPS *.

Analysis

Fig. 2 indicates the atomic numbering scheme used in defining the structural parameters for MSBAR. The following assumptions were made regarding the molecular model in order to reduce the number of geometrical parameters:

1) The molecule was assumed to have C_{3v} symmetry.
2) All C—H bond lengths were assumed to be equal to one average value.
3) The $\angle SiC_9H$ angles were assumed to be tetrahedral.
4) The $\angle HC_3C_2$ angles were assumed to be 120°.
5) The orientation of the methyl group was assumed to be staggered relative to the carbon atoms C_2, C_6 and C_7.

The set of geometrical parameters chosen are shown in Table 1. In the process of formulating the Cartesian coordinate calculation for MSBAR, it became apparent that closure of the bicyclic rings depended critically on the values used for $\angle C_9SiC_2$ and $\angle SiC_2C_3$. For example, if "normal" values of 110° and 120° were used for these two angles, ring closure was found to be impossible for any reasonable values of the bond length parameters involved. If, on the other hand, normal values of the Si—C_2 (1.88 Å) and C=C (1.34 Å) bond lengths were used in the coordinate calculation, ring closure was found to require highly strained values for $\angle C_9SiC_2$ (118°) and $\angle SiC_2C_3$ (110°). While these values seem a little unusual, they are nevertheless required by simple geometrical considerations in order to insure closure of the rings in this very strained molecule.

Vibrational amplitudes (l_{ij}'s) and shrinkage correction parameters (K_{ij}'s) were calculated from a crude diagonal adaption of the valence force fields reported for silacyclopent-3-ene [9], and silacyclopentane [10]. An average force constant of 2.78 mdyne/Å was assumed for the two different types of Si—C bonds in the molecule. All of the amplitude parameters except the seven shown in Table 1 were constrained to calculated values during the course of the refinement.

At the start of the analysis both Si—C bond lengths were constrained to one average parameter for which a value of 1.875(10) Å was obtained. Radial dis-

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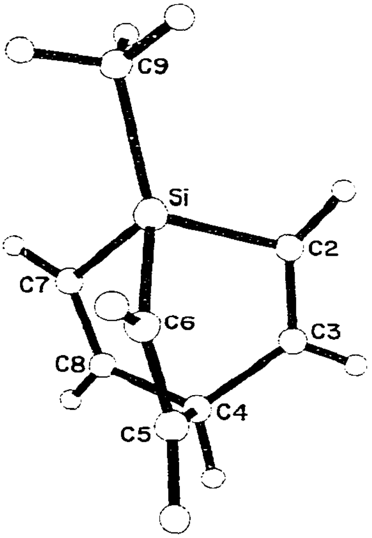

Fig. 2. Atomic numbering scheme used in defining parameters for MSBAR.

tribution curves obtained when this constraint was imposed, however, consistently showed systematic errors in the region between 2.70 and 3.80 Å. This region of the curve was found to correspond to a number of overlapping peaks contributed by various non-bonded distances such as $C_3 \cdots C_6$ and $C_2 \cdots C_9$. A

TABLE 1.

STRUCTURAL PARAMETERS FOR 1-METHYL-1-SILABICYCLO[2.2.2]OCTATRIENE OBTAINED FROM LEAST SQUARES ANALYSIS [a]

Independent parameter	Value (Å or °)	Amplitude parameter	Value (Å or °)
$C—H_{avg}$	1.091(7)	$Si—C_{avg}$	0.053(6)
C=C	1.348(3)	$Si.C_3$	0.066(6)
C—C	1.547(5)	C=C	0.046(3)
$Si—C_{avg}$ [b]	1.865(10)	$C_2.C_8$	0.093(17)
$\Delta Si—C$ [c]	0.021(18)	$C_2.C_9$	0.125(46)
$\angle C_9SiC_2$	118.7(0.2)	$C_3.C_9$	0.114(34)
$\angle SiC_2=C_3$	109.9(0.5)	C—H	0.060(6)
$\angle HC_2Si$	119.6(6.5)		
$\angle HC_3C_2$	120.0		
$\angle HC_9Si$	109.5		

Dependent parameter	Value (Å or °)
$Si—C_9$	1.844(30)
$Si—C_2$	1.885(8)
$\angle C_2SiC_6$	98.8(0.3)
$\angle C_2C_3C_4$	119.4(0.7)
$\angle C_3C_4C_5$	108.3(0.6)

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[a] Distances are reported as r_g values and angles are reported as r_α parameters. Reported errors are 3 values obtained from least squares analysis. [b] $Si—C_{avg}$ is the average value of $Si—C_2$ and $Si—C_9$. [c] Si—C is defined such that $Si—C_2 = Si—C_{avg} + \Delta Si—C$, and $Si—C_9 = Si—C_{avg} - \Delta Si—C$.

statistically significant improvement resulted when a splitting parameter ΔSi—C was included in the refinement. The splitting parameter used corresponds to half the difference between the Si—C_2 and Si—C_9 distances. Thus, Si—C_2 = Si—C_{avg} + ΔSi—C, and Si—C_9 = Si—C_{avg} — ΔSi—C. While the introduction of this additional parameter resulted in a significant improvement of the least squares fit to the experimental data, it had little or no effect on the values obtained for the other structural parameters. A positive value of 0.21(18) Å was obtained for the splitting parameter regardless of whether the starting value used was positive or negative.

A further test of the assumption involving C_{3v} symmetry was also conducted. In 1-chloro-1-silabicyclo[2.2.2]octane [5] a twisted model having C_3 symmetry was observed. For a saturated system this might be expected because of the extensive eclipsing which occurs in a C_{3v} model. In MSBAR, on the other hand, the reduction of the symmetry from C_{3v} to C_3 requires twisting about the 3 double bonds in the molecule. Although this model seems very unlikely, it was nevertheless tested. Release of the C_{3v} constraint resulted in a twist angle about the three double bonds of 176(2)° accompanied by a statistically insignificant improvement in the fit to the experimental data. A twist angle this close to 180° can easily be accounted for by imperfections in the corrections for shrinkage effects observed in molecular structures determined by electron diffraction.

Table 1 summarizes the final results obtained from the least squares refinement of the experimental data. Theoretical and experimental intensity and radial distribution curves are shown in Figs. 3 and 4, respectively.

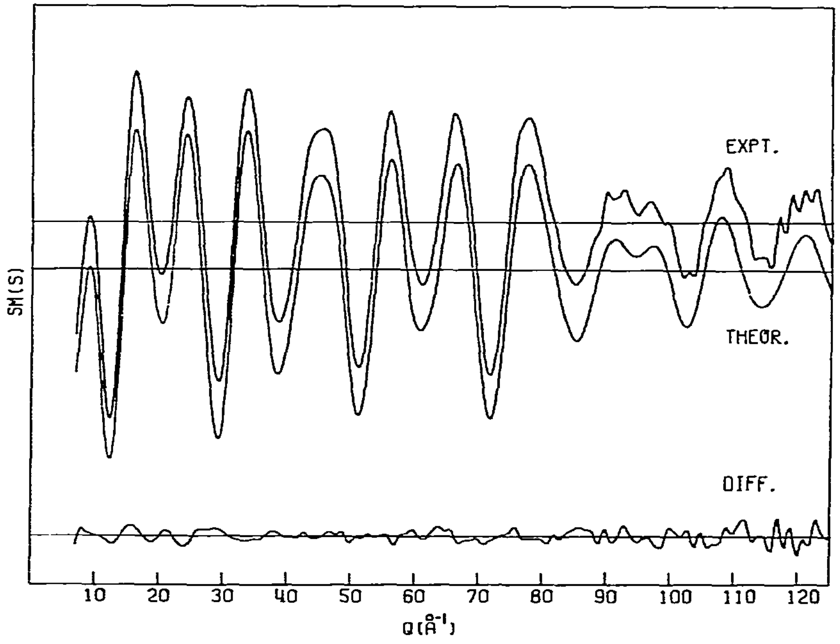

Fig. 3. Levelled molecular intensity curves for MSBAR.

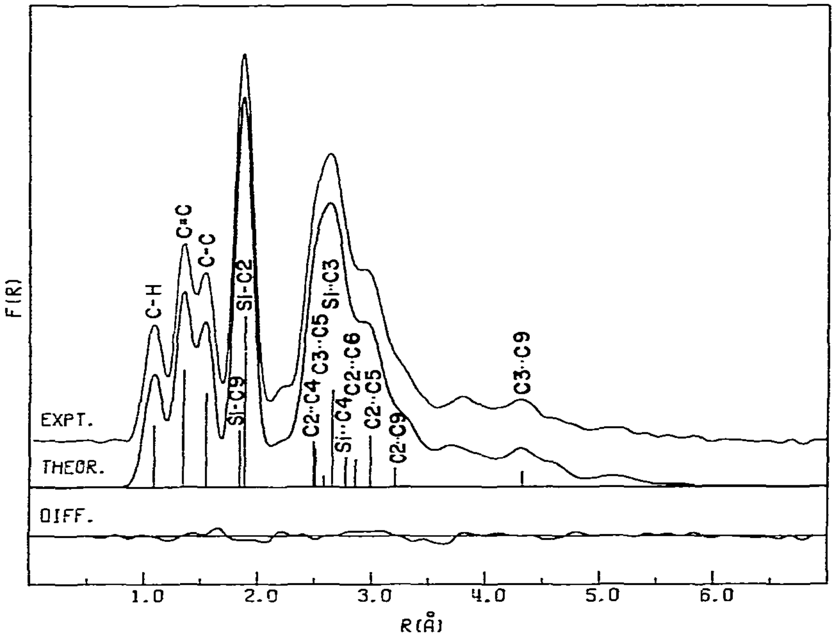

Fig. 4. Experimental and theoretical radial distribution curves for MSBAR.

Discussion

The results shown in Table 1 indicate a rather significant amount of distortion in MSBAR, most of which appears to be localized at the silicon end of the molecule. It is easiest to rationalize the observed geometry by considering the consequences of replacing one of the bridgehead carbon atoms in bicyclo-[2.2.2]octatriene with a larger silicon atom. The resulting perturbation (the lengthening of the three bonds at one apex of the cage) must be alleviated by angular deformations in the remainder of the molecule. The angular distortions which appear in the observed geometry of MSBAR are thus a direct consequence of the relative magnitudes of the valence angle bending force constants. Since the ∠CCC and ∠CC=C bending force constants are quite a bit larger than the ∠CSiC and ∠SiC=C bending force constants, it is not surprising that the largest distortion occurs at the silicon bridgehead. Indeed, the carbon bridgehead of the molecule exhibits relatively little distortion. The values obtained for $\angle C_2C_3{=}C_4$ (119.4(0.7)°) and $\angle C_3C_4C_5$ (108.3(0.6)°) are very close to the respective sp^2 and sp^3 values expected for these parameters.

Since the carbon bridgehead is relatively rigid and is for the most part unaffected by the introduction of the larger silicon atom, almost all of the resulting strain must be alleviated at the silicon bridgehead. The net result is an upward displacement of the silicon atom along the three-fold axis of the molecule thus causing the valence angles at the silicon bridgehead to exhibit large departures from their normal sp^3 values of 109.5°. The ∠SiC=C valence angles (109.9(0.5)°) also show large departures from their normal sp^2 values of 120°. Note, however, that the ∠SiC=C angles can only increase in value by a further upward displacement of the silicon atom which would in turn cause an even greater distortion of the silicon bridgehead.

The unusual Si—C bond lengths which occur at the silicon bridgehead may qualitatively be rationalized on the basis of hybridization arguments. The large angular distortions at the silicon bridgehead also lead to significant changes in the localized bonding description for the silicon atom and for the carbon atoms which are symmetrically equivalent to atom C_2. If one makes the rather gross assumption that the localized bonds on the silicon atom do indeed point in the directions of the atoms to which it is bonded, then the localized hybrids on the silicon atom would be quite different from sp^3 due to the large changes in the valence angles. From the observed valence angles one obtains a localized orbital on silicon directed toward the C_9 atom of the methyl group which is 60% *s* and 40% *p* character while the three equivalent localized hybrids directed toward C_2, C_6 and C_7 atoms are found to contain 13.4% *s* and 86.6% *p* character. Thus relative to the normal sp^3 hybrids, there is a large shift of *s* character out of the bonds to C_2, C_6 and C_7 and into the bond between Si and C_9. At the same time localized orbitals on C_2, C_6 and C_7 also show a decreased *s* character (25.4%) relative to the normal sp^2 value of 33.3%. Thus within the framework of a few crude assumptions regarding localized orbitals on the atoms involved, it seems reasonable to expect a lengthening of the Si—C_2 bond relative to what might be expected for an sp^3 to sp^2 Si—C bond. At the same time this picture appears to be consistent with the observed shortening of the Si—C_9 bond relative to a normal sp^3 to sp^3 Si—C bond length.

According to the observed structure obtained for MSBAR, the silicon bridgehead in silabicyclo[2.2.2]octatriene should be relatively inert to nucleophilic attack under S_N2 conditions. The root mean square deviation of the observed angles in MSBAR from those of the trigonal bipyramidal transition state geometry is 15.46°. This is nearly as large as the rms deviation at a tetrahedral center, 15.65°, and is substantially larger than the 13.96° rms deviation observed for MSBH which is the most reactive bridgehead silicon. This compound would, in fact, provide an interesting test of Sommer's proposed S_N2-Si mechanism and the implied structure reactivity relationship.

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