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THE STRUCTURE OF 1-METHYL-1-SILAADAMANTANE AS DETERMINED BY GAS PHASE ELECTRON DIFFRACTION

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Summary

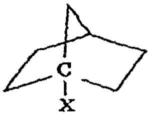
The structure of 1-methyl-1-silaadamantane (MSA) has been determined by gas phase electron diffraction. There appears to be somewhat less ring strain at the silicon bridgehead of MSA than in the previously studied 1-methyl-1-silabicyclo[2.2.1]heptane (MSBH). The average Si—C bond length [1.879(3) Å] is comparable to those found in acyclic organosilicon systems. Also, the average C—C bond length (1.547(2) Å) is only slightly longer than that observed for adamantane (1.540(2) Å). Valence angles at the silicon bridgehead experience only a moderate perturbation away from their unstrained tetrahedral values. On this basis it is expected that MSA should be somewhat less reactive than MSBH under S_N2 conditions according to the reaction mechanism suggested by L.H. Sommer.

Introduction

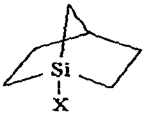
We have recently reported the structure of 1-methyl-1-silabicyclo[2.2.1]-heptane (MSBH) [1] as part of a study of organosilicon compounds containing bridgehead silicon. The purpose of this study is to gather quantitative structural information in support of the proposed mechanism for silicon substitution reactions.

It has been demonstrated that reactivities at silicon centers differ markedly from reactivities at analogous carbon centers. This difference is most dramatically illustrated by the bicyclo[2.2.1] compounds I and II.

Bartlett and coworkers [2] attributed the stability of I to displacement under S_N2 conditions to the fact that the bridgehead carbon atom was protected from backside attack by the cage structure of the bicyclic system. On the other hand, the silicon analogue, II, exhibits extremely high reactivity in substitution reactions. On the basis of this evidence, Sommer [3] has postulated a mechanism,



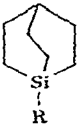
(I)



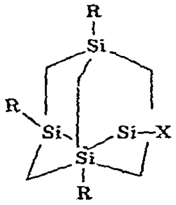
(II)

S_N2-Si, for silicon substitution reactions which involves the formation of a pentacoordinate intermediate with either a square pyramidal or trigonal bipyramidal geometry. Sommer has argued, in support of his mechanism, that the high reactivity of II results from the fact that the molecule already has "built in" much of the requisite geometry of the trigonal bipyramidal transition state as a result of the ring strain. Indeed, our structural study of MSBH [1] indicated ∠C—Si—C valence angles at the silicon center of 94.4° (0.6°) and 116° (2°) whic are very close to the ideal 90° and 120° angles of the proposed intermediate.

As further evidence for the proposed mechanism, Sommer has shown that the reactivity at the bridgehead silicon is strongly correlated with the geometry of the reactive center. For example, 1-silabicyclo[2.2.2]octane (III) is significantly less reactive than the [2.2.1] system and 1,3,5,7-tetrasilaadamantane (I is several orders of magnitude less reactive than either II or III under similar experimental conditions [4]. The implication with regard to the reactivities of III and IV is that as the geometry of the silicon bridgehead departs more signif cantly from that of the transition state, the silicon center becomes less reactiv toward substitution reactions.



(III)



(IV)

The compound 1-methyl-1-silaadamantane (MSA) has recently been synth sized in our laboratory [5], and in light of our above-mentioned interest in bridgehead silicon compounds we felt that a structural study of MSA would provide an interesting comparison with the structure of MSBH. In particular were interested in determining the valence angles at the silicon bridgehead t provide a further test of the structure-reactivity relationship suggested by Sc mer's mechanism. In addition we were interested in determining the effect the increased length of the Si—C bonds relative to the length of the C—C bo would have on the structure of the adamantane cage. The structure of adamantane has previously been studied by gas phase electron diffraction [6].

Experimental

The sample of 1-methyl-1-silaadamantane was prepared by the method of Kapfer and Boudjouk [5], and purified by preparative gas chromatography.

estimated purity, as determined by analytical gas chromatography, was approximately 98%.

The diffraction patterns were recorded at 130° C on the new North Dakota State University gas phase electron diffraction instrument using an r^3 sector and an electrically heated inlet terminating in a nozzle made from a 28 Ga. hypodermic needle. An accelerating voltage of 40 keV was used, and data were collected at 100 mm and 245 mm camera lengths. Voltages were measured to 5 significant digits using a Fluka model 190 digital voltmeter across a calibrated precision resistor. Camera lengths were measured to a precision of 0.02 mm using a Klinger Optical precision cathetometer. Final voltage/distance calibrations were based on benzene calibration plates which were recorded under conditions identical to those used for the sample. Exposure times for the 0.8 u.a. beam ranged from 20 seconds for the long camera length plates to 80 seconds for the short camera length plates. Background pressures during exposure were maintained at 1.2×10^{-5} Torr by employing a liquid nitrogen cold trap situated opposite the nozzle.

Three photographic plates for each camera length were densitometered on the computerized North Dakota State University microdensitometer. The data were corrected for sector imperfections, emulsion saturation and plate flatness, and then interpolated at integral $q(\pi/10\ s)$ intervals for analysis. Preliminary data reductions including division by the atomic scattering function were all performed on the departmental PDP 11/40 computer which produces averaged long and short distance data sets of levelled intensities. These were then analyzed on the campus IBM 370/148 computer.

Least squares calculations were performed in the usual manner [7] using the elastic scattering factors of Schafer, Yates and Bonham [8] together with the inelastic scattering factors of Tavard et al. [9]. Tables of intensity and background data (Table 4) together with correlation and error matrices obtained from the least squares analysis (Tables 5 and 6) are provided.

Analysis

Figure 1 illustrates the numbering system used in defining the structural parameters for MSA. As with any molecule of this complexity, several simplifying assumptions were employed in the analysis in order to reduce the number of independent parameters. The following assumptions or constraints were introduced:

(1) The molecule was assumed to possess C_{3v} symmetry.
(2) The two C—C bond lengths which are permitted by C_{3v} symmetry were both constrained to one geometric parameter.
(3) Both of the Si—C bond lengths allowed by the point group symmetry were constrained to one average geometric parameter.
(4) Only one average C—H bond length was assumed.
(5) All ∠CCH valence angles were constrained to one average value.
(6) All ∠SiCH valence angles including those for the methyl group were constrained to one average parameter.

This somewhat simplified molecular model reduced the number of independent parameters to the eight geometrical parameters listed in the top half of Table 1. The parameter labelled Flap is the dihedral angle which the C(1)—

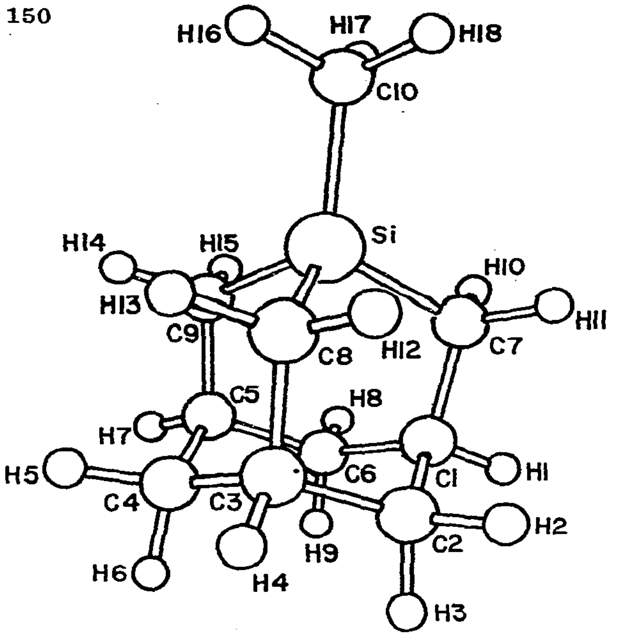


Fig. 1. Atomic numbering scheme used in defining the geometrical parameters for 1-methyl-1-silaadamantan

TABLE 1

STRUCTURAL PARAMETERS OBTAINED FROM LEAST SQUARES ANALYSIS

Independent [a] structural parameters	Value	Amplitude parameters	Value (Å)	Calculated value (Å)
Si—C	1.879(3) Å	Si—C	0.061(3)	0.055
C—C	1.548(2) Å	Si···C(1)	0.075(8)	0.071
C—H	1.112(6) Å	Si···C(2)	0.140(36)	0.085
∠C(10)SiC(7)	115.2(0.4)°	C—C	0.057	0.053
∠SiC(7)C(1)	107.4(0.4)°	C(1)···C(3)	0.072(8)	0.078
∠CCH_{avg}	111.2(0.9)°	C(7)···C(8)	0.089(12)	0.088
∠$SiCH_{avg}$	107.2(2.1)°	C(1)···C(8)	0.091(10)	0.090
Flap [b]	121.9(1.2)°	C(6)···C(8)	0.106(23)	0.090
		C(1)···C(10)	0.131(30)	0.092
		C(4)···C(10)	0.132(33)	0.104
		C—H	0.070(5)	0.079

Dependent structural parameters	Value (°)
∠C(1)C(2)C(3)	112.9(1.8)
∠C(6)C(1)C(2)	107.2(1.2)
∠C(7)SiC(9)	103.2(0.5)
∠C(7)C(1)H(1)	101.7(3.1)
∠H(2)C(2)H(3)	98.4(5.2)
τC(1)C(2)C(3)C(4)	58.6(2.1)
τC(2)C(3)C(4)C(5)	58.6(2.1)
τC(7)C(1)C(2)C(3)	66.2(1.2)
τSiC(7)C(1)C(2)	60.8(1.0)
τC(8)SiC(7)C(1)	53.6(0.4)

[a] Distance parameters are quoted as r_g values with estimated errors of three times the standard deviations obtained from least squares analysis. Angles are quoted as r_α parameters corrected for shrinkage effects.

[b] The Flap angles used is the angle which the C(1)C(2)C(3) plane makes with the C(1)C(3)C(8)C(7) plane.

TABLE 2

FORCE CONSTANTS USED FOR CALCULATION OF VIBRATIONAL AMPLITUDES [a]

Force constant	Value	Force constant	Value
C—C	4.385 mdyne/Å	C—H, Si—C	0.139 mdyne/Å
Si—C	2.780	Si—C, Si—C	0.233
C—H	4.650	$C_\alpha H$, $C_\alpha H$	0.013
∠CCH	0.784 mdyne-Å	$C_\beta H$, $C_\beta H$	−0.013
∠CCSi	0.911	C—C, ∠CCC	0.511 mdyne
∠CSiC	0.759	C—C, ∠HCC	0.198
∠HCH	0.482	C—H, ∠HCC	0.154
∠HCC	0.501	C—H, ∠HCSi	0.154
∠HCSi	0.345	Si—C, ∠HCSi	0.133
C—C, C—C	0.226 mdyne/Å	∠CCC, ∠CCSi	0.069 mdyne-Å
H_t [b]	0.077 mdyne-Å	∠CCC, ∠CCC	0.069

[a] Force field adapted from ref. 11. [b] Only one torsional force constant was used for both Si—C and C—C torsions.

C(2)—C(3) plane makes with the C(1)—C(3)—C(8)—C(7) plane. Note also that the parameter labelled ∠CCH refers to all ∠ CCH valence angles in the molecule except angles ∠C(7)C(1)H(1), ∠C(8)C(3)H(4) and ∠C(9)C(5)H(7). The locations of the three tertiary hydrogens are fixed by the assumption that the other two ∠CCH valence angles are equal, e.g. C(2)C(1)H(1) = C(6)C(1)H(1). The remaining independent parameters should be self explanatory in terms of Fig. 1 and the above six assumptions.

Vibrational amplitudes (l_{ij}'s) and shrinkage parameters (K_{ij}'s) were calculated from the valence force field shown in Table 2. This force field is an adaptation of the valence force field for silacyclopentane determined by Philen, Chao and Laane [11]. The only additional force constant included was the torsional force constant, H_t = 0.077 mdyne-Å, which was assumed for torsions about both the C—C and Si—C bonds. While force constants are not rigorously transferrable between two such unrelated molecules, it was nevertheless felt that they would

TABLE 3

CALCULATED AMPLITUDES AND SHRINKAGE PARAMETERS FOR SELECTED INTERNUCLEAR DISTANCES [a]

Distance	$l_{ij} \times 10^4$	$K_{ij} \times 10^4$
Si—C	552	45
Si···C(1)	710	18
Si···C(2)	849	18
C—C	533	46
C(1)···C(3), C(2)···C(4), C(2)···C(7)	766	34
C(7)···C(8), C(7)···C(10)	879	25
C(1)···C(8)	903	30
C(6)···C(8)	895	19
C(1)···C(10)	916	22
C(4)···C(10)	1041	17
C—H	790	273
$C\cdots H_{gem}$	1731	98
$Si\cdots H_{gem}$	1266	175

[a] Atomic numbering employed is illustrated in Fig. 1.

be sufficiently reliable for the present study. The same set of force constants was successfully employed in our previous analysis of 1-methyl-1-silabicyclo-[2.2.1]heptane [1]. Table 3 lists several of the calculated amplitude and shrinkage parameters for the more prominent peaks in the radial distribution curve for MSA.

One obvious failure of this simplified model is revealed by the significant difference between the calculated Si—C amplitude, 0.0552 Å, and the observed value, 0.061 Å, obtained from the least squares refinement. Such a large difference is strongly indicative of a splitting in the bonded Si—C distances which is to be expected in MSA. Symmetry dictates two different kinds of Si—C bonds with degeneracies of 1 and 3. In the absence of any additional information, such as microwave rotational constants, resolution of these Si—C distances would be highly questionable. Nevertheless, an attempt was made to resolve the two Si—C distances by constraining the vibrational amplitude for both distances to its calculated value, 0.0552 Å, and varying both distances independently. The results obtained were r_g = 1.826(13) Å for the silicon to carbon-methyl bond length and r_g = 1.892(3) Å for the silicon to carbon-ring bond length. All of the other geometrical parameters remained within the error limits quoted in Table 1, and the improvement in the R factor, 6.7% vs. 6.8%, was insignificant. This result is inconclusive on the basis of the usual statistical tests; however, the relative ordering of these two distances agrees with what one would intuitively expect on the basis of ring strain arguments.

Discussion

The results obtained from the least squares refinement of the structure of MSA indicate that there is little, if any, ring strain in the molecule. The average Si—C bond length, 1.879(3) Å, is nearly identical to the unstrained bond lengths found in acyclic systems such as $Si_2(CH_3)_6$ [12] (Si—C = 1.879(3) Å), $Si(CH_3)_4$ [13] (Si—C = 1.876(2) Å) and $(SiH_3)_2CH_2$ [14] (Si—C = 1.874(2) Å).

MSA also appears to be a great deal less strained than MSBH which has an average Si—C bond length of 1.883(2) Å. Further evidence for the lack of ring strain in MSA is the average length of the C—C bond, 1.548(2) Å, which is significantly shorter than the average bond length in MSBH [1], 1.564(4) Å, and only slightly longer than the C—C bond length in adamantane [6] itself, 1.540(2) Å.

MSBH exhibits silicon bridgehead angles which depart significantly from the unstrained tetrahedral values preferred by the silicon atom. The bridgehead geometry in MSBH is very close to the trigonal bipyramidal required by Sommer's mechanistic explanation. MSA, on the other hand, exhibits three ∠CSiC valence angles of 115.2(0.4)° and three ∠CSiS angles with a value of 103.2(0.5)°. These angles are somewhat intermediate between the trigonal bipyramidal values (high reactivity) and pure tetrahedral values (low reactivity) found in 1,3,5,7-tetrasilaadamantane. One would expect that the bridgehead silicon geometry (and therefore its reactivity) in MSA would closely resemble that of 1-silabicyclo-[2.2.2]octane; although no quantitative structural study of this compound has yet been conducted.

As a further investigation of this rather unique structure-reactivity relation-

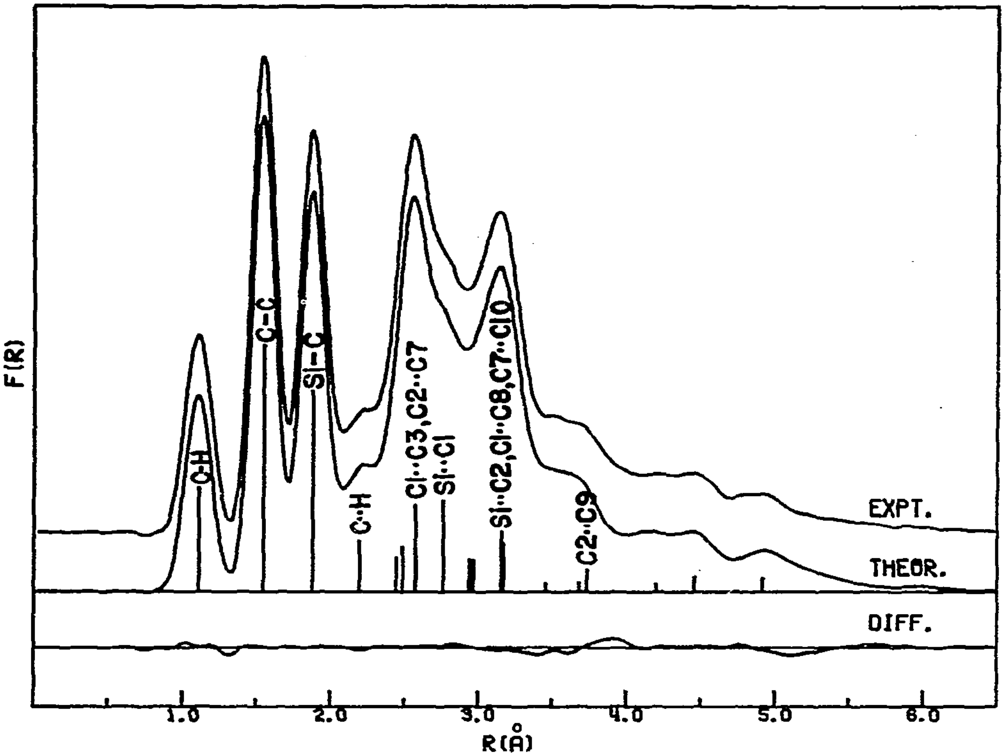


Fig. 2. Experimental and theoretical levelled molecular intensity curves for 1-methyl-1-silaadamantane.

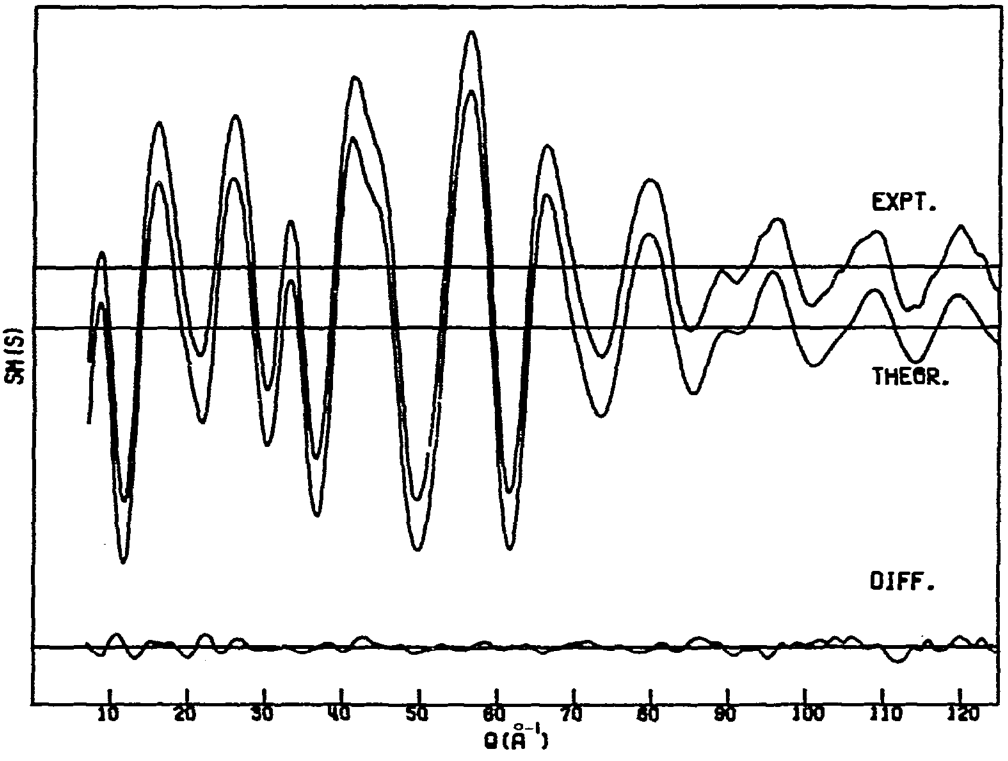


Fig. 3. Experimental and theoretical radial distribution curves for 1-methyl-1-silaadamantane.

ship we plan to investigate the structure of 1-silabicyclo[2.2.2]octane by gas phase electron diffraction. In addition, further competitive reactivity studies involving MSA and other bridgehead silicon systems are currently in progress.

Acknowledgements

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