Organometallics **1992,** *11,* 485–486

Molecular Structure and Conformation of Cyclohexylsilane As Determined by Gas-Phase Electron Diffraction

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Received May 24, 1991

Summary: The molecular structure of cyclohexylsilane has been studied at a nozzle-tip temperature of 75 °C. The molecules exist in the chair conformation as a mixture of equatorial (90 ± 10%) and axial forms.

Molecular mechanics and ab initio calculations[1] show that the steric energy difference between the axial and equatorial forms is smaller in cyclohexylsilane than in methylcyclohexane. This lesser difference between the axial and equatorial forms in cyclohexylsilane is a result of a decrease in the nonbonded energy term betweeen the axial protons and the protons in the silyl group due to the presence of long Si–H and Si–C distances.[2] These calculations are consistent with the reported low-temperature ^{13}C NMR spectroscopic results.[2] For cyclohexylsilane, 2% axial form was observed at −90 °C, and only 0.45–0.5% axial form was observed in methylcyclohexane at −100 °C. However, no gas-phase conformational information is available.

Cyclohexylsilane is an important molecule in the development of a molecular mechanics force field for silicon compounds. It provides a good comparison with methylcyclohexane, which holds an major position in the development and evaluation of a molecular mechanics alkane force field. We have for some time been interested in the gas-phase conformational composition of mono- and disubstituted cyclopentane[3] and cyclohexane[4] and the effect of substituents on the geometry of cyclohexane and the axial/equatorial population ratio. A gas-phase electron diffraction structural investigation on cyclohexylsilane was initiated in our laboratory, and in this article we report our results on the structure and conformational composition of this compound.

Table I. Molecular Structural Parameter Values Obtained from MM3 Calculations and Electron Diffraction Least-Squares Refinement[a]

	MM3		electron diffraction	
param	equatorial	axial	model 1	model 2
r(C–H)	1.114	1.114	1.112 (5)	1.113 (5)
r(Si–H)	1.483	1.483	1.477	1.477
$r(\mathrm{C{-}C})_{\mathrm{av}}$	1.540	1.541	1.542 (2)	
$r(\mathrm{C_1{-}C_2})$[b]	1.550	1.551		1.550 (5)
$r(\mathrm{C_2{-}C_3})$[b]	1.536	1.537		1.535 (3)
$r(\mathrm{C_3{-}C_4})$[b]	1.535	1.535		1.535
r(Si–C)	1.892	1.894	1.882 (6)	1.882 (6)
∠HCC	109.6	109.6	109.5 (9)	109.7 (9)
$\angle \mathrm{C_3C_4C_5}$	111.0	111.3	112.2 (25)	112.6 (26)
$\angle \mathrm{C_2C_3C_4}$	111.3	111.0	111.1 (13)	111.5 (13)
$\angle \mathrm{C_1C_2C_3}$	111.7	112.8	111.1 (13)[c]	112.0 (13)
$\angle \mathrm{C_6C_1C_2}$	109.5	109.2	112.2 (25)[c]	110.9 (25)
$\angle \mathrm{SiC_1C_2}$	112.0	113.6	112.8 (12)	112.4 (12)
t(2345)[d]	−55.3	54.9	−54.9[c]	−53.7[c]
t(6123)	−55.7	53.9	−54.9[c]	−53.6[c]
t(1654)	−56.2	55.4	−54.3[c]	−53.8[c]
t(1234)	56.2	−55.4	54.3[c]	53.8[c]
t(3456)	55.3	−54.9	54.9[c]	53.7[c]
t(2165)	55.7	−53.9	54.9[c]	53.6[c]
t(Si165)	−179.4	73.4	−176[c]	−179[c]
FLAP[e]			130.0 (15)	131.0 (16)
%E[f]			91 (10)	88 (12)

[a] Distances (r_g) in angstroms; angles (∠α) in degrees. Parenthesized values are 2σ, which include estimates of systematic errors. [b] Model 1: all C–C bond distances are identical. Model 2: the C_1–C_6 and C_1–C_2 bonds are assumed to be 0.015 Å longer than the other four C–C bonds. [c] Dependent parameters. [d] Torsional angles, for example t(2345) = C_2–C_3–C_4–C_5 torsional angle. [e] Angle between planes formed by atoms C_1, C_2, C_6 and C_2, C_3, C_6. The FLAP angles at both ends of the six-membered ring are assumed to be the same. [f] Percent of equatorial form found.

Experimental Section

Cyclohexylsilane was prepared by a modification of the method described by Kitching and co-workers.[2] Lithium aluminum hydride (4.62 g, 0.122 mol) was added to 40 mL of dry tetraglyme in a 100-mL flask. The flask was flushed with argon and connected by way of an air condenser to a vacuum line. The mixture was cooled to 0 °C, and a solution of cyclohexyltrichlorosilane (10.0 g, 0.0460 mol) in 30 mL of dry tetraglyme was added dropwise over a period of 2.5 h. The mixture was allowed to stir overnight at room temperature and then distilled at low pressure (0.2 Torr). The product was collected in a liquid-nitrogen trap yielding 2.47 g (47%) of product. No further purification was necessary. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.93–1.08 (m, 1 H), 1.14–1.39 (m, 5 H), 1.63–1.84 (m, 5 H), 3.41 (d, 3 H, $^1J_{\mathrm{SiH}}$ = 190.5 Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 19.0 (C_1, J_{SiC} = 57.1 Hz), 26.5 (C_4), 27.6 (C_3), 30.1 (C_2). Mass spectrum: m/e 114 (M^+, 26), 83 (87), 82 (40), 67 (32), 55 (100), 41 (60), 39 (47), 31 (47), 29 (49), 27 (39), n_{D}^{20} 1.4503.

Electron diffraction patterns were collected on 4 × 5 in. Kodak electron image plates, using the Colgate apparatus equipped with a r^3 sector. The nozzle-tip temperature was kept at 75 °C. The ambient pressure during exposure was maintained below 2.0 × 10^{-5} Torr with the help of a liquid-nitrogen trap. An accelerating voltage of about 41 kEV and a beam current of 3.0 μA were used. Typical exposure times were in the range of 1 min for the long camera plates and 2 min for the short camera plates. Four plates each from the long and short camera distances were selected for the analysis. Wavelength calibration was carried out after each experiment using benzene[5] plates collected under experimental conditions identical with those of the sample plates.

Experimental intensity data were interpolated at integral q units and averaged to form a long camera and a short camera intensity curve. The ranges of the intensity data were $7.0 \le q \le 47.0$ and $28.0 \le q \le 1250$. A least-squares procedure similar to the one outlined by Gundersen and Hedberg[6] was followed.

Data Analysis

Molecular Mechanics Calculations. MM3 calculations[7] were carried out for both the axial and equatorial forms of cyclohexylsilane. The equatorial form was found to be 1.3 kcal/mol lower in energy than the axial form. The entropy difference (axial − equatorial) of −0.62 eu was obtained. Table I summarizes some of the important

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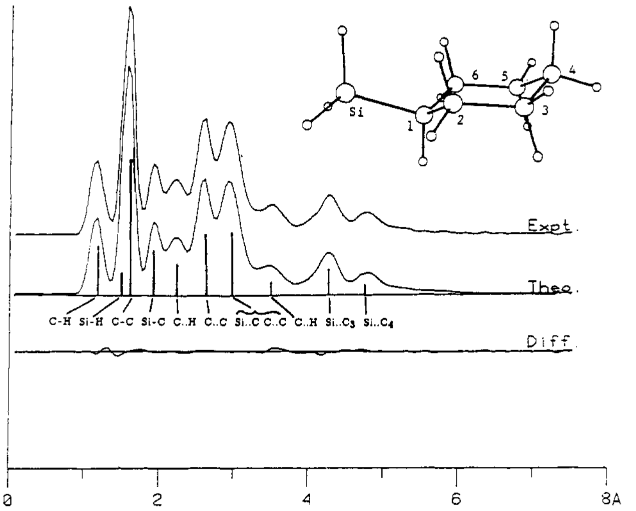

Figure 1. Radial distribution curve for cyclohexylsilane.

geometrical parameter values obtained. Two interesting features can readily be seen. The Si–C_1 bond length (1.892 Å) is longer than the "natural length"[7] of1.876 Å. The C–C bonds C_1–C_2 and C_1–C_6 are longer than the other four by 0.015 Å. It appears that when the silane group is attached to C_1, all the bonds having C_1 as the central atom (i.e. Si–C_1 and C_1–C_2) are lengthened.

Electron Diffraction Analysis. The geometry of the molecule (see Figure 1) for atom numbering) with C_s symmetry was defined using the following selected parameters: r(C–H), r(Si–H), $r\langle$C–C$\rangle_{av}$, r(Si–C), ∠HCC, $\angle C_3C_4C_5$, $\angle C_2C_3C_4$, ∠SiCC, and FLAP (angle between planes formed by atoms C_1, C_2, C_6 and C_2, C_3, C_6). The assumptions made are as follows: (a) all C–C bond lengths are identical; (b) all HCC angles are identical; (c) all HSiC angles are identical, and the SiH_3 group has C_{3v} symmetry; (d) all C–H bond lengths are identical; (e) the FLAP angles on both ends are the same (judging from the calculated torsional angles for the equatorial form (Table I), the FLAP angles on both ends of the cyclohexane are within 2° of each other); (f) $\angle C_1C_6C_5 = \angle C_1C_2C_3$, and $\angle C_2C_3C_4 = \angle C_4C_5C_6$. Amplitudes of vibration were calculated using a force field similar to the ones used in silacyclopentane.[8]

Least-square refinements were first carried out by assuming the presence of only the equatorial form, and good agreement between the theoretical and experimental intensity curves was obtained. The lowest R factor obtained for the long camera data was 3.2%. Since the low-temperature ^{13}C NMR study observed the axial conformer, we proceeded to test the two-conformer model. The axial form was incorporated into the model with the assumption that all the geometrical parameters were identical to the equatorial form except for the location of the silyl group relative to the cyclohexane ring and the FLAP angle. This model also gave an excellent fit to the experimental data. An axial population of 10% (2σ = 10%) was obtained. The R factor for the long camera data was lowered to 2.8%. The radial distribution curves corresponding to this model are shown in Figure 1. Table I shows the geometrical parameter values obtained from least-squares analyses.

A model (model 2) where the C_1–C_2 and C_1–C_6 bonds were assumed to be 0.015 Å longer than the other four C–C bonds, as indicated by the MM3 results, was tested. This model also gave a good fit to the experimental data, and the results are presented in Table I for comparison.

Discussion

The structure of the six-membered ring in cyclohexylsilane is not significantly different from that of cyclohexane. The average C–C bond length (1.542 (3) Å) obtained for cyclohexylsilane is slightly longer than the C–C bond length reported for cyclohexane[9] (1.536 (2) Å). It is interesting to note that MM3 calculations suggested an increase of 0.005 Å in the average C–C bond length in cyclohexylsilane because of the lengthening of the C_1–C_6 and C_1–C_2 bond lengths of 0.015 Å. The averaged CCC valence angle (111.9°) is identical to the CCC angle in cyclohexane of 111.4 (2)°. The Si–C bond length (1.882 (6) Å) in cyclohexylsilane is nearly the same as the one found in cyclopentylsilane (1.874 (4) Å).[10] It is longer than the Si–C bond in methylsilane (1.867 (3) Å)[11] but shorter than the ones in silacyclopentane (1.892 (2) Å).[8] The Si–C bond lengths in tetramethylsilane[12] and trimethylsilane[13] are 1.876 (2) and 1.868 (2) Å, respectively. MM3 calculations also suggested a slightly long Si–C bond.

The presence of both equatorial and axial forms reported by the NMR investigation[2] is supported by our gas-phase electron diffraction work. Unfortunately, the error limits in this study are rather large. Nevertheless, the refined value for the percentage of axial form (10%) at 348 K is not unrealistic. This value corresponds to a Gibb's free energy difference at 348 K of 1.5 kcal/mol. If we include the free energy value obtained from the low-temperature NMR experiment (bearing in mind that the data are from liquid and gas phases, which might not be comparable), a crude estimate of the enthalpy and entropy differences can be obtained. The enthalpy and entropy differences (axial – equatorial) of 1.3 ± 1.3 kcal/mol and –0.62 ± 0.62 eu, respectively, were obtained. These values compared very well with the corresponding values obtained from our MM3 calculations. Earlier MM2 and ab initio calculations gave an energy difference of 1.08 and 1.18 kcal/mol, respectively. It appears that the long Si–C bond length in cyclohexylsilane reduces the steric repulsion of the axial form and diminishes the energy difference between the axial and equatorial forms. It will be interesting to study the axial population of cyclohexylgermane, where the length of the Ge–C bond is even longer than the Si–C bond length.

Registry No. Cyclohexylsilane, 18162-96-4; cyclohexyltrichlorosilane, 98-12-4.

Supplementary Material Available: Listings of the experimental data and the correlation matrix and a figure showing the experimental and theoretical intensity curves (3 pages). Ordering information is given on any current masthead page.

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