Electron-Diffraction Study of Gaseous Cyclohexasilane

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Abstract: The molecular structure of gaseous cyclohexasilane has beeen investigated by electron diffraction at 130 °C. The molecule was found to exist predominantly in a chair form, but the conformational composition could not be uniquely determined since three models fit the experimental data (100% chair; 63 (8)% chair and 37 (8)% twist; and 62 (7)% chair, 25 (7)% twist, and 13 (8)% boat; the values in parentheses are standard deviations). The values of the bond lengths and bond angles of the chair conformation obtained from these models were essentially identical. They were determined from geometrically consistent r_α refinements, r_a(Si–Si) = 2.342 (5) Å, r_a(Si–H) = 1.484 (8) Å, ∠SiSiSi = 110.3 (4)°, and the dihedral SiSiSiSi angle, 57.9 (9)°. The values in parentheses are 2σ where estimates of data correlation and systematic uncertainties are included. A simple valence force field was constructed by reanalyzing the vibrational spectra of cyclohexasilane, and it was used for the calculation of the amplitudes of vibration and correction terms.

The first cyclic silicon–hydrogen compound, cyclopentasilane, was synthesized[1] and studied by vibrational spectroscopy and electron diffraction.[2] Within the limitations of the methods used, it was shown that, structurally, cyclopentasilane is remarkably similar to cyclopentane.

Cyclohexasilane was later synthesized,[3] and its vibrational spectra in the liquid phase were recorded and assigned.[4] The following is a structural and conformational study of this molecule in the gas phase by the electron-diffraction method.

The lowest energy conformations of cyclohexane are well understood,[5] and at room temperature the molecule exists almost entirely in the chair conformation (D_{3d} symmetry). It is generally agreed that the twist (D_2) and boat (C_{2v}) conformations lie about 5–6 kcal/mol above the chair, with the boat about 0.6 kcal/mol above the twist. The activation energy for returning the twist or boat conformation to the chair is about 5 kcal/mol. From calcualtions it was concluded[5a,b] that cyclohexane is freely pseudorotating in the transition state for the reaction of chair conformers to boat or twist conformers. Furthermore, the twist and boat forms can interconvert by pseudorotation; twist forms are at the minima of the pseudorotation path and the boats are the transition state. Twist-boat is then any form along this path. It is very difficult to study properties of these higher energy conformations; some infrared bands were observed and measured in matrices and were assigned to the twist-boat conformer[6a] and "most likely" to the twist conformer.[6b]

Before cyclohexasilane had been synthesized, the energies of its conformers were calculated by molecular mechanics by Hummel et al.[7] and found to be in the same order as in cyclohexane but with much smaller differences. Namely, the energies of the twist and boat were 1.95 and 2.31 kcal/mol above the chair, respectively. The C_2 conformer was described as a transition state separating the chair and twist forms and calculated to be 4.14 kcal/mol above the chair.

Considering the much smaller predicted energy differences between the conformers in cyclohexasilane in comparison to cyclohexane, one might expect a detectable mixture of different forms to be present in the gas phase.

Experiment and Data Processing

A sample of cyclohexasilane was synthesized as described previously[3] and placed into an ampule directly usable in the electron-diffraction apparatus. The diffraction diagrams were recorded with the Oslo apparatus[8] on Kodak Electron Image plates at a nozzle temperature of about 130 °C. Six plates exposed at a camera distance of 480.94 mm and four at 200.79 mm were selected for the structural analysis. The electron wavelength of 0.06467 Å was determined from the diffraction patterns of gaseous benzene.

The optical densities were recorded with a Joyce-Loebl MK 111 C densitometer (XY recorder), and the experimental intensities were treated in the usual way.[9] They were leveled by using the elastic scattering factors calculated by the partial-wave method[10] based upon the analytical HF potential for a Si atom[11] and by using the best electron density of bonded hydrogen for H.[12] The inelastic scattering factors were those of Tavard et al.[13]

The computer-calculated backgrounds[14] were subtracted separately from each intensity curve on the leveled form, and the average molecular intensities were calculated for each set of plates by using a modification function $s/|f_{Si}'|^2$, where s is the scattering angle parameter and f_{Si}' is the scattering amplitude of Si. The intensities, I, for the first plate-set were in the s range 1.50–19.50 Å^{-1} with the increment of s being 0.125 Å^{-1}; the other set had an s range of 6.5–40.0 Å^{-1}, with the increment being 0.25 Å^{-1} (see Figure 1). The radial distribution function calculated by the Fourier transformation of the composite molecular intensity[9] is show in Figure 2.

Normal Coordinate Analysis

The liquid-phase Raman and infrared data previously measured and assigned[4] for Si_6H_{12} and Si_6D_{12} were used in this work (see Tables I and II). The preliminary calculations of the mean

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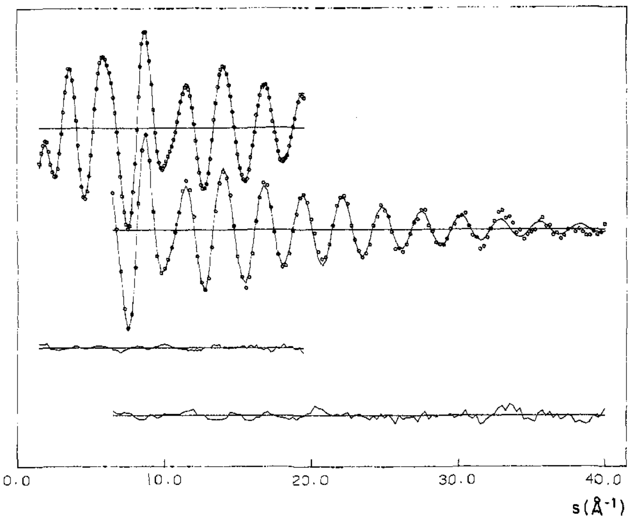

Figure 1. The experimental intensity data for cyclohexasilane from the 48-cm ($\Delta s = 0.125$ Å^{-1}) and the 20-cm ($\Delta s = 0.25$ Å^{-1}) nozzle-to-plate distances. The solid line corresponds to the calculated intensities (using model B), and the lower curves represent the differences between the experimental and calculated intensities.

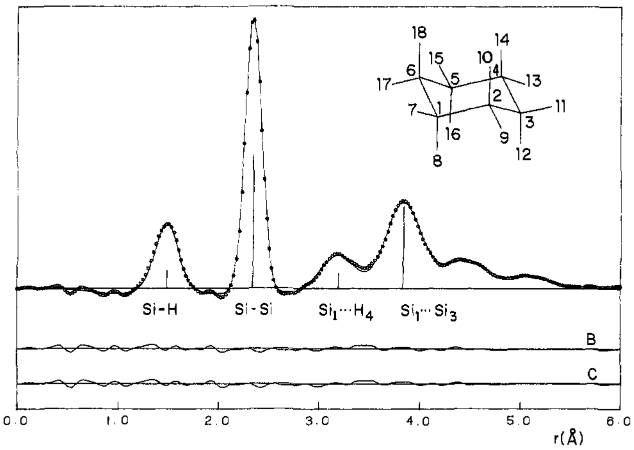

Figure 2. Radial distribution curves for cyclohexasilane. The value 0.0015 was used for the damping constant *b*. The vertical lines indicate the main interatomic distances, which do not depend on the conformation; the length of the lines are proportional to the weights of the distances. The theoretical distribution (solid line) was calculated from model B. The differences between theoretical and radial distribution curves for models B and C are denoted B and C, respectively.

amplitudes of vibration using a simple valence force field[15] strongly suggested that several of the frequencies of cyclohexasilane should be reassigned. In particular, it was predicted that there is a normal mode in the range 850–950 cm^{-1} in each of the Raman- and IR-active symmetry species that is associated with the SiH$_2$ deformation (650–680 cm^{-1} for Si$_6$D$_{12}$). Similar modes were also observed in cyclohexane,[16] but, of course, at higher frequencies.

The very strong lines at 905 and 893 cm^{-1} (IR) were thus taken as e$_u$ and a$_{2u}$ fundamentals, respectively, since a$_{2u}$ came lower in the calculated spectrum. The band at 865 cm^{-1} (IR) may be interpreted as 476 (e$_g$) + 384, (a$_{2u}$) and 519, (e$_u$) + 350, (a$_{1g}$); it was not possible to explain the 330-cm^{-1} (IR) weak line as a sum or difference band.

The only band observed in the Raman spectrum in the 850–950-cm^{-1} region was at 893 cm^{-1}, which was therefore assigned to both the e$_g$ and a$_{1g}$ fundamentals. (Again, in cyclohexane this a$_{1g}$ fundamental is probably very weak and overlapped by a strong nonpolarized line belonging to the e$_g$ species.) The very weak polarized band at 625 cm^{-1} satisfies the product rule for the a$_{1g}$ species better than the weak line at 515 cm^{-1}, but the force field did not reproduce that value very well. The stronger line at 515 cm^{-1} was thus left as a fundamental.

Table I. Observed and Calculated Fundamentals of Cyclohexasilane

		ν, cm^{-1}			
species	no.	ref 4	present	calcd	PED[a]
a$_{1g}$ (R)	1	2128		2134	2 (100)
	2	2128		2118	2 (100)
	3	515	893	914	4 (17), 5 (77)
	4	377	515	561	4 (63)
	5	350		354	1 (94)
	6	114		118	3 (45), 4 (17), 6 (50), 10 (−13)
a$_{2u}$ (IR)	12	2120		2134	2 (100)
	13	2120		2118	2 (100)
	14	384	893	874	4 (18), 5 (85)
	15	330	384	398	4 (102), 7 (10), 8 (12), 11 (−16)
	16	180		176	3 (77), 4 (30), 9 (−18), 10 (22)
e$_g$ (R)	17	2128		2134	2 (100)
	18	2128		2117	2 (100)
	19	893		890	4 (19), 5 (79)
	20	736		721	4 (91), 8 (−11)
	21	655		655	1 (14), 4 (114), 8 (−13), 14 (−10)
	22	476		477	1 (58), 4 (40)
	23	455		413	1 (24), 4 (72)
	24	114		111	3 (80), 4 (34), 9 (−18), 10 (12)
e$_u$ (I)	25	2120		2134	2 (100)
	26	2120		2118	2 (100)
	27	865	905	908	4 (18), 5 (77)
	28	720		712	4 (98), 8 (−12)
	29	625		626	4 (126), 8 (−14), 11 (−13)
	30	519		508	4 (80)
	31	384		394	1 (90)
	32			78	3 (27), 4 (14), 6 (66)

[a] Potential energy distribution ($\delta \ln \lambda/\delta \ln F$). Percent contributions are in parentheses and numbering is given in Table III. Terms below 10% are omitted.

Table II. Observed and Calculated Fundamentals of S$_6$D$_{12}$

		ν, cm^{-1}			
species	no.	ref 4	present	calcd	PED[a]
a$_{1g}$ (R)	1	1561		1543	2 (100)
	2	1543		1521	2 (100)
	3	430	677	665	4 (16), 5 (75)
	4	325	430	446	4 (61)
	5	252	325	327	1 (86)
	6	107		105	3 (45), 4 (15), 6 (53), 10 (−13)
a$_{2u}$ (IR)	12	1552		1543	2 (100)
	13	1530		1520	2 (100)
	14	293	641	629	4 (17), 5 (85)
	15	253	293	299	4 (102), 7 (10), 8 (12), 11 (−18)
	16	153		162	3 (72), 4 (32), 9 (−17), 10 (21)
e$_g$ (R)	17	1561		1544	2 (100)
	18	1543		1521	2 (100)
	19	646		649	4 (20), 5 (70)
	20	575		560	1 (45), 4 (59), 5 (12)
	21	487		505	4 (90), 8 (−10)
	22	402		389	1 (32), 4 (77)
	23			313	4 (89), 11 (−13)
	24	107		107	3 (80), 4 (35), 9 (−18), 10 (12)
e$_u$ (IR)	25	1552		1542	2 (100)
	26	1530		1521	2 (100)
	27	657		662	4 (18), 5 (73)
	28	545		520	4 (95)
	29	463		482	1 (21), 4 (96), 8 (−10), 11 (−12)
	30	370		389	4 (75)
	31	353		352	1 (63), 4 (45)
	32			70	3 (30), 4 (13), 6 (65)

[a] Potential energy distribution ($\delta \ln \lambda/\delta \ln F$). Percent contributions are in parentheses and numbering is given in Table III. Terms below 10% are omitted.

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Table III. Valence Force Constants[a]

stretch	1	K_R	1.723	bend/bend	7	F_γ	−0.039
	2	K_d	2.588		8	$F_{\gamma'}$	0.040
bend	3	H_ω	0.274		9	$F_{\gamma\omega}$	0.031
	4	H_γ	0.390		10	$f^g{}_\omega$	−0.039
	5	H_δ	0.388		11	$f^g{}_\gamma$	0.101
torsion	6	H_τ	0.056		12	$f^t{}_{\gamma\omega}$	−0.029
					13	$f^g{}_{\gamma\omega}$	0.008
					14	$f_{\gamma'}{}^t$	0.036

[a] Snyder and Schachtschneider symbols and definitions are used (see ref 17) where carbon atoms were replaced by silicon. Subscripts R and d refer to Si-Si and Si-H distances, respectively. ω denotes SiSiSi angle, γ SiSiH angle, and δ HSiH angle. Superscript g and t represent gauche and trans, respectively. Stretch constants are in mdyn Å^{-1} and bend, torsion, and bend/bend constants in mdyn Å rad^{-2}.

Table IV. Some Distances[a] and the Mean Amplitudes of Vibration

parameter	r_a	l^{ED}	l^S	K
Si-Si	2.342	0.062	0.062	0.015
Si-H	1.483	0.080	0.090	0.035
		Chair		
$Si_1 \cdots Si_3$	3.824	0.159	0.159	0.007
$Si_1 \cdots Si_4$	4.471	0.184	0.183	0.002
$Si_1 \cdots H_9$	3.179	0.153	0.157	0.032
$Si_1 \cdots H_{12}$ (ax)	4.180	0.296	0.300	0.017
$Si_1 \cdots H_{14}$ (ax)	5.024	0.301	0.305	0.009
$Si_1 \cdots H_{11}$ (e)	5.102	0.175	0.179	0.018
$Si_1 \cdots H_{13}$ (e)	5.812	0.203	0.207	0.010
		Twist		
$Si_1 \cdots Si_3$	3.778	0.162	0.161	0.007
$Si_1 \cdots Si_5$	3.779	0.151	0.150	0.006
$Si_1 \cdots Si_4$	4.006	0.247	0.246	0.002
$Si_3 \cdots Si_6$	4.630	0.170	0.169	0.002
		Boat		
$Si_1 \cdots Si_3$	3.901	0.154	0.153	0.007
$Si_3 \cdots Si_6$	4.195	0.249	0.248	0.002
$Si_1 \cdots Si_4$	4.543	0.200	0.199	0.002

[a] The distances correspond to model C, which is described in the text below. For numbering, see Figure 2. l^{ED} are the mean amplitudes of vibration determined from the electron-diffraction data; l^S are the mean amplitudes calculated from the force field at $T = 130$ °C. The distances r_a, amplitudes l, and perpendicular amplitude correction coefficient K are given in Å.

Table V. Constants of the Weighting Scheme[9]

data	48 cm	20 cm
s_1, Å^{-1}	5.5	16.0
s_2, Å^{-1}	10.0	28.0
w_1	0.2	0.005
w_2	0.05	0.01

Similar changes were considered for Si_6D_{12}. The very strong line at 641 cm^{-1} (IR) (previously taken as a sum band) was reassigned as a fundamental and attributed to a_{2u}. The band at 253 cm^{-1} (previously assigned to a_{2u}) was interpreted as 353 (e_u) − 107 (a_{1g}). The weak, polarized Raman band at 677 cm^{-1} was assigned as a_{1g}. The weak, polarized band at 252 cm^{-1} that was replaced by this band might be due to an impurity.

A simple valence force field was used and was refined by an iterative procedure aimed at minimizing simultaneously the deviations between the calculated and experimental frequencies of vibration of both the parent and Si_6D_{12}. The final force field, consistent with the electron-diffraction structure, is presented in Table III. Other interactive force constants of a similar type as determined in cyclohexane[16,17] were tried but were found to be very small, and since there were not enough experimental frequencies to determine all the force constants, they were assumed to be zero. The newly assigned frequences are shown in Tables I and II together with the calculated ones and the potential-energy distribution. The program used was written by Hilderbrandt.[15a]

The mean amplitudes of vibration (l^S) and the perpendicular amplitude correction coefficients (K) were calculated from the final force field and used in the analysis of the electron-diffraction data. Some of the results are given in Table IV.

Molecular Mechanics Calculations

The MM2[18] program was used for the calculation of the conformational energies of cyclohexasilane in order to better understand the relative importance of the different kinds of energy contributions. Unfortunately, many of the needed constants are not very well determined; therefore, ranges of their values were tested.

Starting values were taken from ref 7 (called here Mislow's constants). The bending force constants for ∠SiSiSi and ∠SiSiH were varied between 0.2 and 0.4 mdyn/rad^2 and 0.3 and 0.4 mdyn/rad^2, respectively, and the strain-free angles were 109.4–111.7° and 109.4–110.3°, respectively. The threefold rotational barrier V° was between 0.9 and 1.2 kcal/mol.

The energy differences between chair and twist were between 1.7 and 2.2 kcal/mol and the twist and boat were between 0.2 and 0.3 kcal/mol. These differences were almost entirely determined by the differences in the torsional energies. For examples, the difference in conformational energy between chair and twist using Mislow's constants was 2.1 and twist and boat 0.3 kcal/mol. Differences in torsional energies were 2.0 and 0.3 kcal/mol, respectively. The ∠SiSiSi in the chair form was 109.8°, and the ring dihedral angle ϕ(Si–Si) was 59.7°. One can get better agreement with electron-diffraction results by using a bending force constant for ∠SiSiSi and ∠SiSiH of 0.25 mdyn/rad^2. Then, ∠SiSiSi was found to be 110.4°, and ϕ(Si–Si) 57.7°. The energy differences in this case were 2.0 and 0.2 kcal/mol ($V^\circ = 1.1$ kcal/mol).

Structural Analysis

The preliminary electron-diffraction analysis determined that the predominant conformer present is the chair. Three types of models were therefore examined by the least-squares analysis of the data.

(A) Chair. The geometry of the chair conformation is determined by four independent parameters, namely, r(Si–Si), r(Si–H), and HSiH and SiSiSi angles.

(B) Chair + Twist. The geometry of the chair was characterized as above. For the twist conformation, the first three parameters were assumed to be the same as in the chair. There are, however, two different SiSiSi angles, which were found to be highly correlated. Furthermore, the relatively small fraction of the twist conformer did not justify using two independent angles; therefore, only the average SiSiSi angle was adjusted. In summary, this model was defined by five geometric parameters and the percentages of the conformers.

(C) Chair + Twist + Boat. Chair and twist were defined as above. The same arguments as for twist apply also to the boat, so that only one independent SiSiSi angle was considered. In some least-squares refinements, that angle was assumed to be the same as in the chair. Because of the low content of the boat it did not make a significant difference.

In all the models, unless specifically stated, the electron-diffraction amplitudes of vibration of nonbonded distances were refined in two groups, one group being all Si⋯Si nonbonded distances and the other Si⋯H distances. The differences within the groups of amplitudes were calculated from the force field described above as well as all the H⋯H amplitudes of vibration, which were kept constant. The shrinkage corrections were also included in all the models, and the least-squares refinements were carried out on a geometrically consistent r_α structure ($r_\alpha = r_a + l^2/r - K$). For definitions of different r values, see ref 19a.

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Table VI. Structural Parameters[a] for Si_6H_{12}

parameters	model C	model B	model A
r_a(Si–Si)	2.342 (5)	2.342 (5)	2.342 (5)
r_a(Si–H)	1.484 (8)	1.484 (8)	1.484 (8)
∠HSiH[b]	[103.0]	[103.0]	[103.0]
l(Si–Si)	0.062 (2)	0.062 (1)	0.062 (2)
l(Si–H)	0.080 (9)	0.080 (9)	0.080 (9)
$l(Si_1 \cdots Si_3)$	0.159 (7)	0.160 (7)	0.160 (8)
$l(Si_1 \cdots Si_4)$	0.184 (7)	0.185 (7)	0.234 (35)
		Chair	
∠SiSiSi	110.3 (1.3)	110.4 (1.4)	110.3 (4)
ϕ(Si–Si)[c]	57.8 (3.3)	57.7 (3.6)	57.9 (9)
percent	62.2 (6.6)	62.6 (7.6)	100.
		Twist	
$\angle SiSiSi_{av}$	108.4 (2.8)	109.2 (2.2)	
$\phi(Si_1–Si_2)$	34.3 (3.0)	32.9 (2.8)	
$\phi(Si_2–Si_3)$	73.7 (8.0)	69.9 (7.0)	
percent	25.3 (6.6)	37.4 (7.6)	
		Boat	
$\angle SiSiSi_{av}$[d]	[113.8]		
$\phi(Si_1–Si_2)$	0.0		
$\phi(Si_2–Si_3)$	47.7		
percent	12.5 (7.8)		
R_W[e]	6.907	6.956	7.038

[a] Distances (r_a) and amplitudes (l) are in angstroms, angles in degrees. Assumed values are in square brackets. The values in parentheses are 2σ, where the standard deviations, σ, include estimates of correlation and of systematic error. For composition they are σ_{LS}. For numbering of the atoms, see Figure 2. [b] Was assumed. For details, see text. [c] ϕ is a ring torsional angle. [d] Adjusted manually. [e] The generalized weighted R factor.[20]

Table VII. Correlation Coefficients Whose Absolute Value is Grater Than 0.5

	model A	model B	model C[a]	model C[b]
l(Si–Si), scale 48 cm	0.62	0.61	0.61	
l(Si–Si), scale 20 cm	0.66	0.66	0.66	
∠SiSiSi (T), ∠SiSiSi (CH)[c]		−0.92	−0.91	
l(Si···Si), ∠SiSiSi (T)				0.61
% B, ∠SiSiSi (T)				−0.58
% B, l (Si···H)				−0.82
l(Si–Si), scale				0.65

[a] The data from two camera distances were refined separately. The percentages were held constant. [b] The data from the two camera distances were combined. [c] T represents the twist, CH the chair, and B the boat.

All structural results quoted were obtained in least-squares refinements by using diagonal weight matrices, and the constants for the weighting scheme are shown in Table V.[9] However, the standard deviations for the distances and the amplitudes obtained in this manner, σ_{LS}, were augmented by a factor F[19b] ($2.0\exp(-0.25r_{ij}^2/2\pi)$, where r_{ij} is a distance between atoms i and j), to account for data correlation. For the bond distances, F was about 1.8. The final standard deviations were calculated by using $\sigma = [F^2\sigma_{LS}^2 + (0.001r_{ij})^2]^{1/2}$, where the term involving r_{ij} provides an estimate of systematic error. The standard deviations for the angles were corrected by $\sigma = 1.5\sigma_{LS}$. The asymmetry constants used were in units of 10^{-6} Å^3: k(Si–Si) = 2.0 and k(Si–H) = 10.0; $k = 0$ for nonbonded distances.

In order to refine the composition and calculate its uncertainty, we used a similar least-squares program that analyzes a composite molecular intensity from the different camera distances and allows the composition to be varied. The resulting percentages and the standard deviations are shown in Table VI. Correlation coefficients whose absolute value is greater than 0.5 are presented in Table VII.

Figure 2 shows the complete radial distribution curve, where the main internuclear distances that do not depend on the conformation are indicated. The curves shown below this curve represent the differences between the experimental radial distribution and the theoretical radial distributions for two models. Figure 3 shows the outer part of the radial distribution curve for some models, which depends on the conformational composition. The main nonbonded distances for all three conformers are indicated there. The curve a1 in Figure 3 shows the difference for model A (100% chair), in which the amplitudes of vibration of the two nonbonded Si···Si distances were refined as a group. Obviously, the agreement is not satisfactory. The difference curve a2 was calculated from model A where $l(Si_1 \cdots Si_4)$ was refined as an independent parameter to 0.234 (35) Å^{-1}. None of the other parameters changed by more than half a standard deviation.

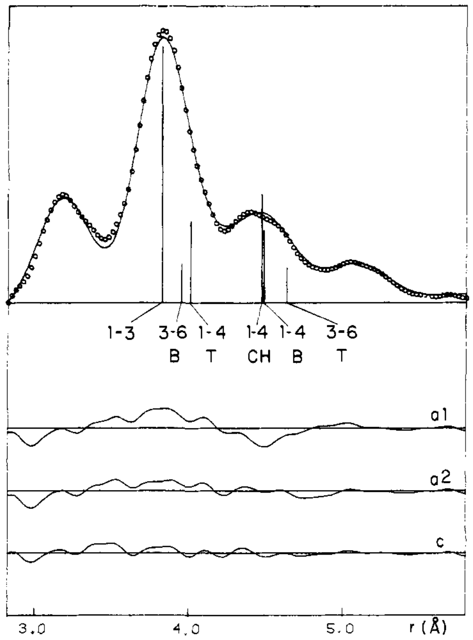

Figure 3. Outer part of the radial distribution curve that depends on conformational composition. The vertical lines indicate the nonbonded distances, and their length is proportional to the weight of the distances in the particular conformer. The theoretical radial distribution curve (solid line) and the difference c are calculated from model C. The difference curve denoted a1 was calculated from model A (100% chair) with Si···Si amplitudes of vibration refined in a group and a2 when these amplitudes are refined separately. CH denotes a chair, T a twist, and B a boat.

The best fit for model B (chair + twist) was achieved with 62.6 (7.6)% chair and 37.4 (7.6)% twist. Again, the parameters of the chair hardly changed. However, in this case the independently refined $l(Si_1 \cdots Si_4)$ parameter was found to be 0.186 (36) Å^{-1}. The parameters for this model are shown in Table VI (l values of Si···Si nonbonded distances were refined in a group), and the difference curve is denoted B in Figure 2.

The best overall fit was achieved with model C (chair + twist + boat), curve C in Figure 2 and c in Figure 3, with relative percentages of 62 (7):25 (7):13 (8), and the parameters used in this model are shown in Table VI. Almost the same fit was obtained when SiSiSi angles in the chair and boat were assumed to be equal. The percentages then weere 62:27:11, and the SiSiSi angle in both the chair and boat was 110.6° and in the twist 109.2°.

The HSiH angle was held constant at the value of 103° in all these final models. Although the other parameters did not change, the fit became rapidly worse when this angle was increased. For example, in going from 103 to 105 to 107.5°, the R_w factor for model C changed from 6.907 to 7.022 to 7.242, respectively, where R_w is the generalized weighted R factor.[20] It is defined as $R_w = [\sum w_i\Delta_i^2/\sum w_iI_i^2(\text{obsd})]^{1/2}$, and $\Delta_i = I_i(\text{obsd} - I_i(\text{theor})$. (At

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HSiH = 107.5° the Si–H bond lengthened by 0.001 Å and the ϕ(Si–Si) angle increased by 0.1°.)

Discussion

The Si–Si distance agrees very well with that in cyclopentasilane, 2.342 (3) Å,[2b] and both are longer than that in disilane[21] 2.331 (3) Å. In hexamethyldisilane,[22] the Si–Si distance was 2.340 (9) Å, and in crystals of dodecamethylcyclohexasilane,[23] 2.338 (4) Å. In hydrocarbons, one observes similar lengthening of the C–C bond between ethane 1.534 (1) Å and cyclopentane 1.546 (1) Å; however, the cyclohexane[5e] C–C bond 1.536 (2) Å has a value close to ethane, not to the cyclopentane value.

The structure of the chair conformation of cyclohexasilane is found to be less flattened than that in cyclohexane,[5e] where the ∠CCC was 111.4 (2)° and the ϕ(C–C) angle was 54.9 (4)° in comparison to 110.3 (4) and 57.9 (9)°, respectively, in cyclohexasilane. This is not surprising since Si–Si bonds are considerably longer than C–C bonds, and therefore the repulsive gauche $SiH_2 \cdots SiH_2$ interactions are smaller than the $CH_2 \cdots CH_2$. In the X-ray study of dodecamethylcyclohexasilane,[23] the six-membered ring was found in a chair conformation only, and the average SiSiSi angle was 111.9 (4)°, very close to the cyclohexane value.

As shown in Figure 2, one can unfortunately obtain a satisfactory agreement with experimental data with at least three reasonable models of different conformational composition. There are two different nonbonded Si···Si distances in the chair conformation. The spectroscopically calculated l values for these distances were 0.159 Å for $Si_1 \cdots Si_3$ and 0.183 Å for $Si_1 \cdots Si_4$, and no "reasonble" change in the force field could make the difference between them much larger. In order to fit the data with only the chair conformation, one must increase the amplitude for $Si_1 \cdots Si_4$ to 0.23 Å, while the electron-diffraction l value for $Si_1 \cdots Si_3$ is 0.160 Å. If this discrepancy is not a result of the presence of another conformer, it might be an indication that the torsion in the cyclohexasilane ring should be treated as a large amplitude motion. In the study of cyclohexane,[5e] the experimental l value for $C_1 \cdots C_4$ agreed well with the calculated value; therefore, we tend to believe that the presence of another conformer in cyclohexasilane is more probable.

There are two plausible models that involve mixtures of conformers. In one case the data were fitted, including about 63% chair and 37% twist conformation. In this model the experimental l values agreed well with calculated ones. Considering that there are six twist conformations available for the two chairs, 37% would correspond to an energy difference of about 1.3 kcal/mol, which is slightly lower than the calculated value but within the estimated error limits. The presence of the twist might be the reason for the difference between the bond lengths in silanes and hydrocarbons that was described above.

The third model is a mixture of 62% chair, 25% twist, and 13% boat, which corresponds to an energy difference of about 1.6 and 2.1 kcal/mol, respectively. The difference in R_w factors is statistically insignificant, as is also suggested from the large uncertainties in the composition parameters. It has been calculated for cyclohexane that the boat conformation is an unstable saddle point, and therefore, one should not expect any boat conformation to be present. With the molecular mechanics models one consistently obtains a rather small energy difference between the twist and boat conformers (0.2–0.3 kcal/mol), which agrees with the pseudorotation path picture.[5a] The better overall fit that is achieved with this model might be simply due to the larger number of independent parameters.

The vibrational spectra did not give any indication of a mixture of conformers. However, they were recorded at lower temperatures and only in the liquid phase, where intermolecular forces may hamper the internal motion.

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Registry No. Cyclohexasilane, 291-59-8.

Supplementary Material Available: Table VIII containing molecular intensity data from each plate (6 pages). Ordering information is given on any current masthead page.

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