Gas Phase Structures and Conformational Properties of 1-Silabutane and 2-Silabutane

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Received: June 13, 2002; In Final Form: August 16, 2002

The molecular structures of 1-silabutane **1** and 2-silabutane **2** have been determined by gas electron diffraction (GED). The conformational equilibrium of **1** and **2** was studied experimentally in the gas phase (GED) and by quantum chemical (QC) calculations (HF with 6-31G* basis sets, MP2 with 6-31G* and cc-pVTZ basis sets, and B3LYP with 6-311G* basis sets). The potential function for internal rotation around the central C−C bond in **1** resembles that for *n*-butane, whereas the rotation around the Si−C bond in **2** has much lower energy barriers. The experimental relative enthalpies $\Delta H°$ (gauche−anti) are 0.76(10) and 0.14(18) kcal mol^{-1} for **1** and **2**, respectively. The enthalpy difference for **2** is reproduced within the experimental uncertainties by all four QC methods. Only the MP2 method with a large basis set reproduces the enthalpy difference for **1** correctly. Taking the different multiplicities of anti and gauche conformers into account, the conformational composition of **1** was found to be 65(5)% anti and 35(5)% gauche. The conformational composition of **2** was found to be 43(9)% anti and 57(9)% gauche.

Introduction

Because *n*-butane is the simplest alkane, which exists as two different rotamers, its conformational properties and those of butanelike molecules have attracted continuous interest for several decades. The enthalpy difference between the anti (dihedral angle $\phi = 180°$) and the gauche form (dihedral angle $\phi \sim 60°$) of *n*-butane has been the subject of numerous experimental and theoretical investigations.[1] The most accurate value, $\Delta H° = 0.71(2)$ kcal mol^{-1}, was derived from a laser spectroscopic study of rotational transitions,[2] and a value of $\Delta H° = 0.67(10)$ kcal mol^{-1} was obtained from vibrational spectra of gaseous *n*-butane.[1] This experimental value is reproduced very well by some but not by all theoretical calculations.[3] The highest level quantum chemical (QC) calculation (CCSD(T)/cc-pVTZ//MP2/6-311G(2df,p)) results in $\Delta H° = 0.64$ kcal mol^{-1}.[4] Very similar conformational properties ($\Delta H° = 0.7$ kcal mol^{-1}) have been derived for 1-silabutane (propylsilane) **1** from vicinal coupling constants using a Karplus-like relation[5] and from vibrational spectra of the liquid ($\Delta H° = 0.60-0.65$ kcal mol^{-1}).[6] Molecular mechanics (MM) calculations with different parametrizations predict $\Delta H°$ values between -0.35 and $+0.60$ kcal mol^{-1}.[7,8] In the microwave spectra, only the anti form was observed,[9] although calculations (B3LYP/6-311G*) predict very similar dipole moments in the a direction for both conformers. For 2-silabutane (ethylmethylsilane) **2**, contradicting results have been reported in the literature. Ouellette et al. found a preference of the gauche form (73% gauche and $\Delta H° = -0.2$ kcal mol^{-1}) from NMR spectra.[5] This unexpected result, which was reproduced by several MM calculations ($\Delta H°$ between -0.14 and $+0.01$ kcal mol^{-1}),[5,8,10-12] has been rationalized by attractive interactions between hydrogen atoms linked to the carbon atoms at positions 1 and 4. Such interactions are possible only in the gauche form. On the other

SCHEME 1: Equatorial and Axial Conformers of 3 Showing the Relation to Anti and Gauche Conformers of 2, Respectively
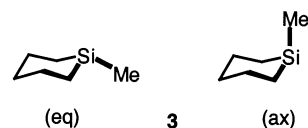

hand, vibrational spectra of the liquid were assigned to the anti conformer with a small amount of the gauche form.[13] Only the anti form was observed in the microwave spectra of the vapor.[14] The calculated μ_b dipole moment component in the anti conformer is about twice as large as the μ_a and μ_b components in the gauche form. Only the strongest rotational transitions in the generally weak microwave spectra, which belonged to the anti conformer, were assigned. The rotational constants of the parent isotopic species and some deuterated species of compounds **1** and **2** did not allow complete structure determinations, and several geometric parameters had to be transferred from analogous compounds.

The conformational properties of **2** are closely related to those of 1-methyl-1-silacyclohexane **3**. Two anti conformations occur in the equatorial form of **3**, and two gauche conformations occur in the axial form (Scheme 1). Earlier results based on NMR data[15] and MM calculations,[11,16] which favored the axial position of the methyl group, were rationalized with the same type of attractive interactions between hydrogen atoms as in gauche 2-silabutane. In a recent investigation using low-temperature ^{13}C NMR, gas electron diffraction (GED), and QC calculations, however, we demonstrated that the methyl group on silacyclohexane definitely prefers the equatorial position.[17] Our results suggest that the above-mentioned attractive hydrogen−hydrogen interactions are not of major importance for the conformational properties of **3**; therefore, one may question results for **2**, which favor the gauche conformation. In the present paper, we report conformational analyses for 1- and 2-silabutanes using GED and QC calculations.

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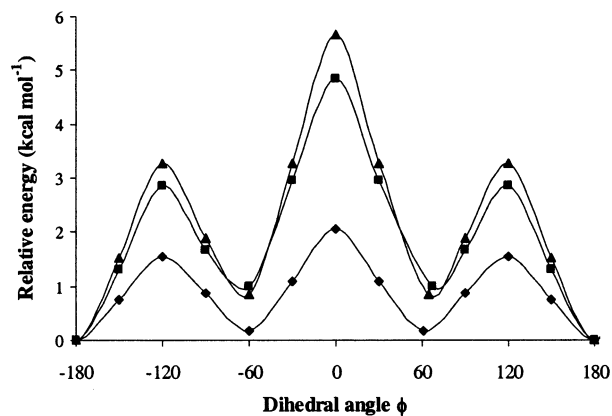
Figure 1. Calculated potential functions (B3LYP/6-311G*) for internal rotation around central bond in ▲, *n*-butane; ■, 1-silabutane **1**; and ◆, 2-silabutane **2**.

In the context with conformational properties of butane and butanelike molecules, it should be mentioned that in the presence of bulky substituents the possible existence of additional conformers, transoid ($\phi \sim 165°$), deviant ($\phi \sim 145°$), ortho ($\phi \sim 90°$), cisoid ($\phi \sim 40°$), and syn ($\phi = 0°$), has been predicted.[18−21] In the case of 1- and 2-silabutanes, however, only stable anti and gauche forms are expected.

QC Calculations

The geometries of the anti and gauche conformers of **1** and **2** were fully optimized with the HF approximation (6-31G* basis sets), with the MP2 approximation (6-31G* and cc-pVTZ basis sets), and with the hybrid method B3LYP (6-311G* basis sets). The potential functions for internal rotation around the central C−C bond in *n*-butane and **1** and around the Si−C bond in **2** were derived by geometry optimizations at fixed torsional angles Φ with the B3LYP method (Figure 1). Furthermore, vibrational frequencies for **1** and **2** were calculated with the B3LYP method. Cartesian force constants were transformed to symmetry force constants, scaled with a factor of 0.95, and used for calculating vibrational amplitudes for both conformers of **1** and **2**. All QC calculations were performed with the GAUSSIAN 98 program suite,[22] and the vibrational amplitudes were derived with the program ASYM40.[23]

Electron Diffraction Analysis

Experimental radial distribution functions (RDF) were calculated by Fourier transformation of the averaged molecular intensities. Figures 2 and 3 show the experimental curves together with the calculated RDFs for anti and gauche conformers. The calculated functions for **1** differ appreciably in the range $r > 3$ Å (Figure 2). The Si⋯C4 distance produces separate peaks around 3.48 Å in the gauche form and around 4.24 Å in the anti form. Obviously, both conformers contribute to the experimental RDF. In **2**, the contributions of the C1⋯C4 distances at 3.57 and 4.49 Å, which are characteristic for the two conformers, are considerably weaker. Preliminary molecular models and conformational compositions, which were derived from the RDFs, were refined by least-squares fitting of the molecular intensities. The following assumptions, which are justified by the QC calculations, were made in these refinements. (i) CH$_3$ and SiH$_3$ groups were constrained to C_{3v} symmetry and −CH$_2$− and −SiH$_2$− groups to C_{2v} symmetry. According to calculations, the individual bond lengths and bond angles in these groups differ by less than 0.003 Å and 0.6°, respectively. (ii) C−H bond lengths in CH$_3$ and CH$_2$ groups were set equal.
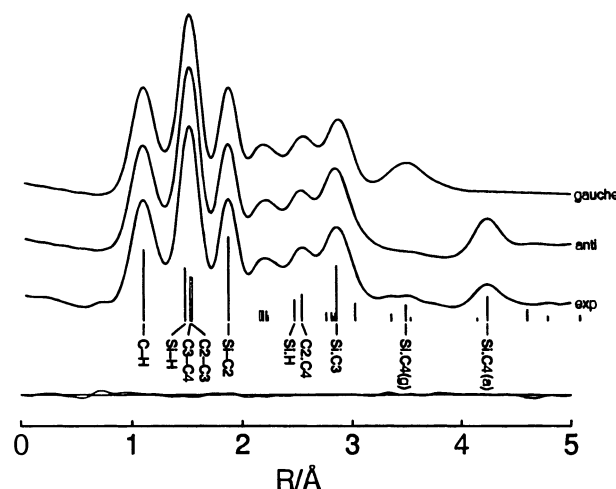
Figure 2. 1-Silabutane: experimental and calculated RDFs for gauche and anti isomers and difference curve for mixture. Interatomic distances for prevailing anti form and Si⋯C4 distance for gauche conformer are indicated by vertical bars.
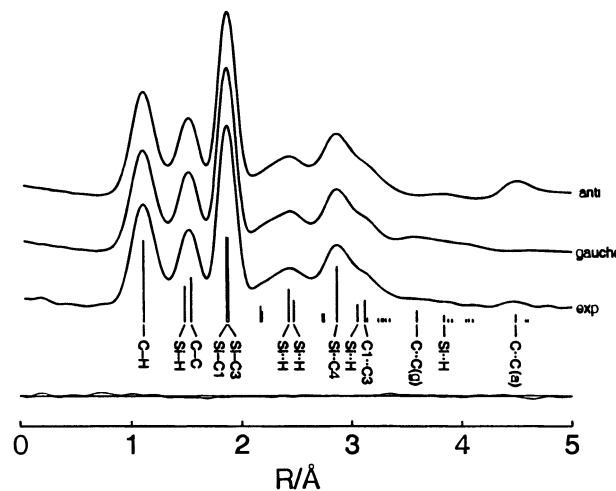
Figure 3. 2-Silabutane: experimental and calculated RDFs for anti and gauche isomers and difference curve for mixture. Interatomic distances for prevailing gauche form and C⋯C distance for anti conformer are indicated by vertical bars.

(iii) The differences between the C−C bond lengths in **1**, (C2−C3)−(C3−C4), and between the Si−C bond lengths in **2**, (Si−C3)−(Si−C1), were set to calculated values. (iv) The H−C−H angle of the CH$_2$ groups in **1** and likewise the H−C−H angles of the CH$_3$ groups in **2** were assumed to be equal, and the angles in CH$_2$ and SiH$_2$ groups in **2** were constrained to calculated angles. (v) The geometric parameters of the less abundant conformer, i.e., the gauche form in **1** and the anti form in **2**, were tied to the respective parameters of the predominant form using the calculated differences. (vi) Vibrational amplitudes of the predominant form, which either caused large correlations between geometric parameters or which are poorly determined in the GED analysis, and all vibrational amplitudes of the less abundant form are set to calculated values. Attempts to refine such amplitudes resulted either in high correlations or in very large uncertainties. With these assumptions, nine geometric parameters were refined for **1**, eight for the anti form and the dihedral angle $\phi(\text{Si}−\text{C}−\text{C}−\text{C})$ for the gauche conformer, and nine geometric parameters for the gauche form of **2**. For both compounds, five vibrational amplitudes were refined. The following correlation coefficients had values greater than |0.5|: $p2/p3 = -0.68$ and $p5/p7 = -0.72$ for compound

Conformations of Silabutanes

J. Phys. Chem. A, Vol. 107, No. 2, 2003 **245**

TABLE 1: 1-Silabutane: Experimental and Calculated Bond Lengths and Bond Angles for the Anti Conformer, Dihedral Angle for the Gauche Conformer, and Conformational Composition

	GED[a]		MP2/ cc-PVTZ	B3LYP/ 6-311G*
(C−H)$_{mean}$	1.106(3)	p1	1.091	1.095
(Si−H)$_{mean}$	1.480(8)	p2	1.482	1.488
C2−C3	1.539(3)	p3	1.531	1.539
C3−C4	1.532(3)[b]		1.524	1.533
Si−C	1.874(2)	p4	1.883	1.892
Si−C−C	113.0(6)	p5	113.4	114.8
C−C−C	111.6(6)	p6	112.4	113.1
H−Si−H	105.7(31)	p7	108.5	108.3
H−C4−H	109.2(18)	p8	109.4	109.5
H−C2−H = H−C3−H	106.0[c]		106.0	105.9
ϕ(Si−C−C−C)$_{gauche}$	73.7(26)	p9	63.3	67.2
% gauche	35(5)		36	26

[a] r_a values in Ångstroms and degrees. Uncertainties are 3σ values. For atom numbering, see Figure 4. [b] (C2−C3)−(C3−C4) constrained to 0.007 Å. [c] Not refined.

TABLE 2: 2-Silabutane: Experimental and Calculated Bond Lengths and Bond Angles for the Gauche Conformer and Conformational Properties

	GED[a]		MP2/ cc-PVTZ	B3LYP/ 6-311G*
(C−H)$_{mean}$	1.114(3)	p1	1.090	1.095
(Si−H)$_{mean}$	1.482(9)	p2	1.485	1.491
C3−C4	1.543(4)	p3	1.532	1.539
Si−C1	1.867(2)	p4	1.880	1.888
Si−C3	1.872(2)[b]		1.885	1.894
C−Si−C	113.0(8)	p5	111.1	112.3
Si−C−C	113.7(5)	p6	113.1	115.1
H−C1−H = H−C4−H	110.3(16)	p7	108.4	107.6
H−C3−H	106.0[c]	p8	106.0	105.7
H−Si−H	107.1[c]		107.1	107.6
ϕ(C−Si−C−C)	58.2(34)	p9	59.2	61.0
% gauche	57(9)		61	56

[a] r_a values in Ångstroms and degrees. Uncertainties are 3σ values. For atom numbering, see Figure 5. [b] (Si−C3)−(Si−C1) constrained to 0.005 Å. [c] Not refined.

TABLE 3: 1-Silabutane: Interatomic Distances and Experimental and Calculated Vibrational Amplitudes for the Anti Conformer (without Nonbonded Distances Involving Hydrogen Atoms)

|	distance[a]	exp amplitude[a]		calcd amplitude[b]
C−H	1.11	0.081(3)	l1	0.078
Si−H	1.48	0.090[c]		0.090
C−C	1.54	0.054(2)	l2	0.053
Si−C	1.87	0.054(2)	l2	0.054
C2···C4	2.54	0.068(8)	l3	0.076
Si···C3	2.85	0.091(6)	l4	0.092
Si···C4	4.24	0.097(8)	l5	0.083

[a] Values in Ångstroms, uncertainties are 3σ values. For atom numbering, see Figure 4. [b] B3LYP/6-311G*. [c] Not refined.

1 and $p2/p3 = -0.59$ for compound **2**. Least squares refinements were performed for different fixed conformational compositions. The minimum of the agreement factor R occurred for 35(5) and 57(9)% gauche in **1** and **2**, respectively. The uncertainty was obtained by Hamilton's test at 1% significance level.[24] Least squares refinement of the conformational ratio lead to high correlations with some vibrational amplitudes. The results of the GED analyses are listed together with the calculated values in Tables 1 and 2 (geometric parameters) and in Tables 3 and 4 (vibrational amplitudes). Molecular models of both conformers are shown in Figures 4 and 5.

TABLE 4: 2-Silabutane: Interatomic Distances and Experimental and Calculated Vibrational Amplitudes for the Gauche Conformer (without Nonbonded Distances Involving Hydrogen Atoms)

	distance[a]	exp amplitude[a]		calcd amplitude[b]
C−H	1.11	0.081(3)	l1	0.078
Si−H	1.48	0.090[c]		0.090
C−C	1.54	0.053(2)	l2	0.053
Si−C	1.87	0.053(2)	l2	0.054
Si···C4	2.87	0.087(6)	l3	0.091
C1···C3	3.13	0.093(13)	l4	0.107
C1···C	3.57	0.145(23)	l5	0.232

[a] Values in Ångstroms, uncertainties are 3σ values. For atom numbering, see Figure 5. [b] B3LYP/6-311G*. [c] Not refined.
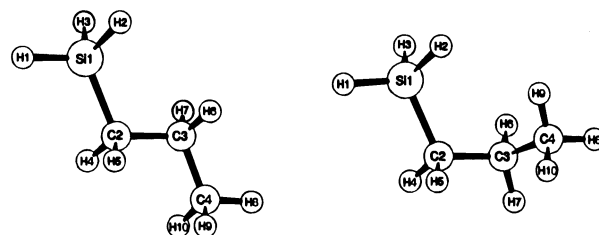
Figure 4. 1-Silabutane: molecular models for anti and gauche isomers.
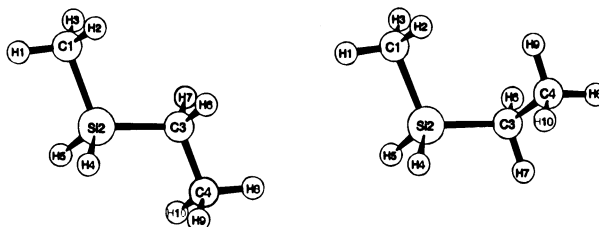
Figure 5. 2-Silabutane: molecular models for anti and gauche isomers.

Discussion

The geometric parameters in **1** and **2** (Tables 1 and 2) are very similar to those in analogous compounds. Bond lengths and bond angles are reproduced very well with the MP2 and B3LYP method. Only the Si−C bond lengths are predicted slightly too long by both methods, even more so if we consider that experimental r_a distances are systematically longer by about 0.005−0.010 Å than equilibrium r_e distances derived from calculations. The same observation has been made in the case of silicon-containing ring systems as well.[17,25] The calculated dihedral angles (r_e values) in the gauche form of **1** are about 10 or 6° smaller than the experimental r_a value. This difference is most likely due to the low-amplitude torsional vibration (79 cm^{-1} from B3LYP/6-311G* calculation). The calculated vibrational amplitude for the C1···C4 distance in **2** (Table 4) is appreciably larger (0.232 Å) than the experimental value (0.145(23) Å). This amplitude depends mainly on the torsional frequency around the Si2−C3 bond, which appears to be predicted too low by the B3LYP method. If this amplitude is fixed at the calculated value, the agreement factor increases very slightly, and the conformer ratio changes by less than the experimental uncertainty.

The main interest in these studies was the conformational composition of the two silabutanes. The calculated energy, enthalpy, and Gibbs free energy differences are compared with the experimental results in Tables 5 and 6. The corrections between ΔE and $\Delta H°$ and the entropy differences $\Delta S°$ were derived with the B3LYP/6-311G* method and applied to all computational methods. The predicted entropy differences between the two isomers are very small (−0.10 and −0.38 cal

TABLE 5: 1-Silabutane: Calculated and Experimental Relative Energies $\Delta E = E(\text{Gauche}) - E(\text{Anti})$, Relative Enthalpies $\Delta H°$, and Relative Gibbs Free Energies $\Delta G°$ in kcal mol^{-1}

method	ΔE	$\Delta H°$	$\Delta G°$ ^{a}
HF/6-31G*	1.09	1.16	0.77
MP2/6-31G*	0.84	0.91	0.52
MP2/cc-PVTZ	0.66	0.73	0.34
B3LYP/6-311G*	0.93	1.00	0.61
GED		0.76(10)	0.37(10)

^{a} $\Delta G° = \Delta H° - T\Delta S° - RT\ln 2$.

TABLE 6: 2-Silabutane: Calculated and Experimental Relative Energies $\Delta E = E(\text{Gauche}) - E(\text{Anti})$, Relative Enthalpies $\Delta H°$, and Relative Gibbs Free Energies $\Delta G°$ in kcal mol^{-1}

method	ΔE	$\Delta H°$	$\Delta G°$ ^{a}
HF/6-31G*	0.22	0.23	−0.08
MP2/6-31G*	0.04	0.05	−0.26
MP2/cc-PVTZ	0.04	0.05	−0.26
B3LYP/6-311G*	0.16	0.17	−0.14
GED	- - -	0.14(18)	−0.17(18)

^{a} $\Delta G° = \Delta H° - T\Delta S° - RT\ln 2$.

mol^{-1} K^{-1} in **1** and **2**, respectively). The difference between $\Delta H°$ and $\Delta G°$ takes the different multiplicities of anti and gauche conformers into account. In **1**, the enthalpy difference $\Delta H° = 0.76(10)$ kcal mol^{-1} from the GED experiment agrees with the value derived from NMR spectra of the liquid (0.7 kcal mol^{-1})[5] and is within experimental uncertainties equal to that in *n*-butane (0.71(2) kcal mol^{-1}).[2] Only the MP2 method with a large basis set (cc-PVTZ) reproduces the experimental enthalpy difference correctly. Also, the calculated potential function for internal rotation around the central C—C bond in **1** is very similar to that in *n*-butane (Figure 1). The energy barriers are slightly higher in *n*-butane, however. The very similar conformational properties of *n*-butane and **1** are consistent with the similar enthalpy differences between axial and equatorial conformers of methyl- and silylcyclohexane.[26,27]

In **2**, the enthalpy difference $\Delta H°$ between anti and gauche form is very small (0.14(18) kcal mol^{-1}) but still positive. This value is reproduced correctly by all four QC methods, which also predict slightly positive values. Although this seems to be in contrast to the result derived from room temperature NMR spectra ($\Delta H° = -0.2$ kcal mol^{-1}),[5] both values are rather similar if we consider the experimental uncertainties of both experiments (no estimate of the uncertainty is given in the NMR analysis). Because of the different multiplicities of anti and gauche conformers, $\Delta G°$ is negative in all cases. The slightly positive value for $\Delta H°$ in **2** correlates very well with the recently determined conformational properties of **3**[17] where the equatorial conformer with two anti arrangements of 2-silabutane is slightly favored over the axial form with two gauche arrangements.

The enthalpy differences between anti and gauche forms of *n*-butane or butanelike compounds result from several effects, such as steric interactions between atoms (repulsive or attractive), repulsion between bonds, angle strain, donor–acceptor interactions between bonding and antibonding orbitals, etc. At present, it is not possible to derive quantitative values for these individual contributions. We want to point out that interactions between hydrogen atoms at the terminal carbon or silicon atoms, which can occur only in the gauche conformer, do not explain the results for *n*-butane, **1** and **2**. The shortest H···H contacts in the gauche forms (H2···H9) occur at 2.39, 2.67, and 2.79 Å in butane, **1**, and **2**, respectively, and do not correlate with the
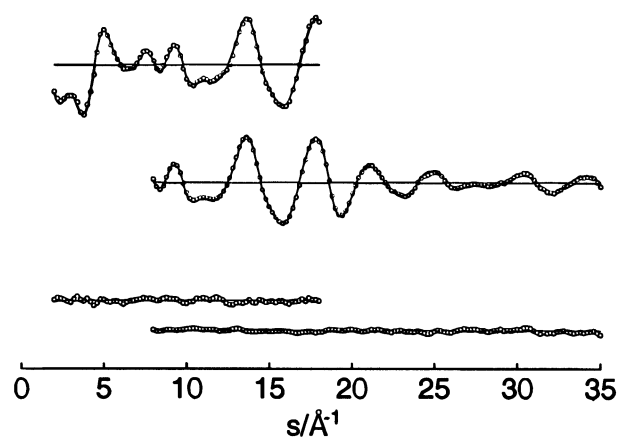
Figure 6. 1-Silabutane: averaged experimental (dots) and calculated (full line) molecular intensities for 50 (above) and 25 cm (below) nozzle-to-plate distances and residuals.
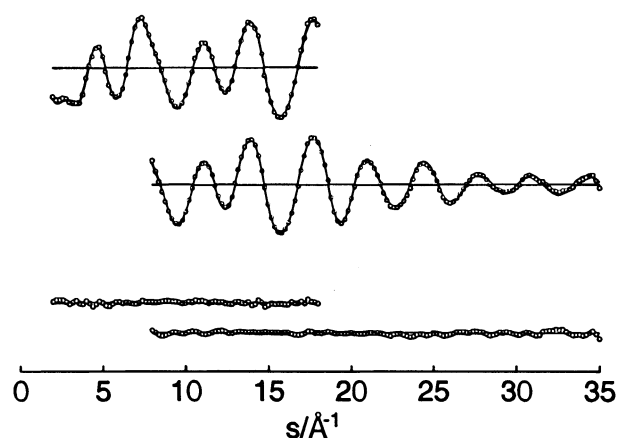
Figure 7. 2-Silabutane: averaged experimental (dots) and calculated (full line) molecular intensities for 50 (above) and 25 cm (below) nozzle-to-plate distances and residuals.

enthalpy differences of this series (0.71(2), 0.76(10), and 0.14(18) kcal mol^{-1}, respectively).

Experimental Section

Samples of **1** and **2** were prepared from the corresponding Si-chlorinated organosilanes by hydrogenation with LiAlH$_4$ in di-*n*-butyl ether as solvent. A solution of the silane in (*n*-Bu)$_2$O was added slowly to a suspension of LiAlH$_4$ in (*n*-Bu)$_2$O at 0 °C. The reaction mixture was stirred for 1 h at room temperature, and then, the volatile product was condensed into a N$_2$(l) cooled trap. The product was purified by fractionated condensation on the vacuum line. The fraction that passed a −63 °C bath and was held at −95 °C was collected. After repeated fractionation, **1** and **2** were recovered in 49 and 50% yield, respectively. The purity of the samples was 95% or better.

The electron diffraction intensities were recorded with a KD-G2 Diffractograph[28] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of about 60 kV. Both compounds were kept at −48 °C during the GED experiment, and the inlet nozzle was at room temperature. Possible higher volatile impurities were pumped off for several minutes before recording the diffraction intensities. The photographic plates (Kodak Electron Image Plates 18 cm × 13 cm) were analyzed with the usual procedures.[29] Averaged molecular intensities in the *s* ranges 2−18 and 8−35 Å^{-1} in steps of $\Delta s = 0.2$ Å^{-1} ($s = (4\pi/\lambda)\sin\theta/2$, λ = electron wavelength, θ = scattering angle) are shown in Figures 6 and 7.

Conformations of Silabutanes

J. Phys. Chem. A, Vol. 107, No. 2, 2003 **247**

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