Gas-Phase Structures of 1,3-Disilacyclobutane and 1,1-Difluorosilacyclobutane

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The molecular structures of 1,3-disilacyclobutane (**1**) and 1,1-difluorosilacyclobutane (**2**) were studied by gas phase electron diffraction and *ab initio* calculations. Large amplitude models were applied in the experimental analyses. The molecular intensities are rather insensitive to the ring inversion barriers. For **1**, the spectroscopic value from the literature (0.96 kJ mol^{-1}) was assumed and for **2**, a value with large uncertainties was determined ($V_0 = 5.0 ^{+3.3}_{-2.5} \text{ kJ mol}^{-1}$). Rocking angles for the CH_2, SiH_2 and SiF_2 groups were constrained to *ab initio* values. The following skeletal parameters (r_a values with 3 σ uncertainties) were derived for **1**: $Si-C = 1.888$ (2) Å, $CSiC = 90.6$ (3)°, $SiCSi = 86.8$ (3)°, puckering angle $\theta = 25(2)$°. The transannular $Si \cdots Si$ contact [2.592(8) Å] is shorter than the $C \cdots C$ contact [2.684(8) Å]. This unexpected ring distortion is confirmed by the *ab initio* calculations. A possible explanation is attempted on the basis of a Mulliken population analysis. The skeletal parameters for **2** are: $Si-C = 1.836$ (3), $C-C = 1.574(8)$, $Si-F = 1.574(3)$ Å, $CSiC = 82.7(6)$, $SiCC = 86.8(8)$, $CCC = 100.6(8)$, $FSiF = 106.9(5)$ and $\theta = 25(2)$°.

Dedicated to Professor Otto Bastiansen on his 70th birthday

The degree of puckering and the barrier to inversion in saturated four-membered rings is generally discussed in terms of a balance between various types of strain energies: (1) angle strain (Baeyer strain) and (2) 1,3 repulsion (Dunitz-Schomaker strain) favor a planar configuration, whereas (3) torsional strain (Pitzer strain) favors puckering of the ring. For cyclobutane [experimental values[1] for the puckering angle and the inversion barrier are $27.9(16)$° and $6.10(8)$ kJ mol^{-1}, *ab initio* values[2] 25.0° and 4.02 kJ mol^{-1}, respectively] these individual contributions to the overall strain energy[3] of 111.0 kJ mol^{-1} have been estimated from *ab initio* calculations.[2] For cyclotetrasilane a slightly larger value for the puckering angle (28.7°) but smaller values for the overall strain energy and inversion barrier (71.1 and 2.22 kJ mol^{-1}, respectively) have been obtained from *ab initio* calculations.[4]

In this context, geometric structures of four-membered rings containing carbon *and* silicon appear to be of great interest. 1,1,3,3-tetrachloro-1,3-disilacyclobutane, whose gas phase structure has been determined by electron diffraction[5] [$\theta = 14(3)$°] does not allow a direct comparison with cyclobutane or cyclotetrasilane, since the substituents may have a strong effect on the ring conformation. We therefore report here a structure analysis for the unsubstituted 1,3-disilacyclobutane (**1**). Its FIR and Raman spectra have been analyzed using a three-dimensional potential function,[6] resulting in an inversion barrier of 0.96 kJ mol^{-1} and a puckering angle of 24.2°.

Electron diffraction analyses for silacyclobutane[7] and 1,1-dichlorosilacyclobutane[8] result in strongly puckered rings [$\theta = 33.6(21)$° and 31.7 (10)°, respectively]. The large value for the puck-

ering angle in silacyclobutane is confirmed by FIR[9] ($\theta = 36°$) and microwave data[10] ($\theta = 28°$). A comparison with 1,1-difluorosilacyclobutane (2), whose structure is also reported in this work, reveals the effects of fluorine on the ring geometry. The experimental studies have been supplemented by *ab initio* calculations, and some of these results have been used as constraints in the experimental analyses.

Ab initio calculations

The geometries of the title compounds and of silacyclobutane were fully optimized with the program TEXAS,[11] using 4-21 basis sets[12] for C and F and a 3-3-21 basis set[13] for Si. The calculated puckering angle in 1 depends very strongly on polarization functions at the ring atoms. Without any such functions the optimized ring structure is planar, with polarization functions for Si only ($\alpha = 0.45$) the ring is very slightly puckered

($\theta = 6°$), and the puckering angle increases with polarization functions on carbon ($\alpha = 0.8$) and with two sets of d functions on Si ($\alpha = 0.7$ and 0.2) to 15°. The results corresponding to the latter basis sets are compared with experimental values in Tables 1 and 2.

Electron diffraction analyses

The radial distribution functions are shown in Figs. 1 and 2. Whereas the bonded distances in 1 (C−H, Si−H and Si−C) are well separated, the Si−F and C−C bond lengths in 2 overlap strongly. Preliminary structural models were refined by least-squares analyses based on the modified molecular intensities (Figs. 3 and 4). Diagonal weight matrices[14] were applied to the in-

Table 1. Results of the structure determination for 1,3-disilacyclobutane.

Geometric parameters/Å or °

	e.d.[a]	ab initio
Si−C	1.888(2)	1.899
Si−H	1.504(6)	1.476
C−H	1.092(10)	1.087
C−Si−C	90.6(3)	91.0
Si−C−Si[b]	86.8(3)	88.0
H−Si−H	108.5[c]	108.5
H−C−H	108.3[c]	108.3
θ_e	25(2)	15
$\varrho(SiH_2)$[d]	3.7[c]	2.2
$\varrho(CH_2)$[d]	6.7[c]	4.0

Vibrational amplitudes/Å

C−H	0.098(10)	Si···Si	0.052(3)
Si−H	0.087(6)	C···C	
Si−C	0.057(1)	C2···H5	0.153(27)
Si1···H7	0.196(18)	C4···H7	0.110[c]
		Si1···H9	0.140[c]

[a]r_a values and angles from electron diffraction analysis with non-rigid model ($V_0 = 0.96$ kJ mol⁻¹). Error limits are 3 σ values. [b]Dependent parameter. [c]Not refined. [d]Rocking angle at the potential minimum. A positive value implies that the axial hydrogen atoms approach each other, i.e. leads to a more staggered configuration of the vicinal hydrogens.

Table 2. Results of the structure determination for 1,1-difluorosilacyclobutane.

Geometric parameters/Å or °

	e.d.[a]	ab initio
Si−C	1.836(3)	1.855
C−C	1.574(8)	1.577
Si−F	1.574(3)	1.566
C−H	1.099(6)	1.085
C−Si−C	82.7(6)	82.4
Si−C−C[b]	86.8(8)	86.3
C−C−C[b]	100.6(8)	101.7
F−Si−F	106.9(5)	106.4
H−C−H	111.3(34)	108.6
θ_e	25(2)	20
$\varrho(SiF_2)$[d]	3.1[c]	2.5
$\varrho(CH_2)$ at C2[d]	5.5[c]	4.4
$\varrho(CH_2)$ at C3[d]	3.8[c]	3.0
V_0/kJ mol⁻¹	$5.0^{+3.3}_{-2.5}$	1.3

Vibrational amplitudes/Å

C−H	0.072(6)	C2···F	0.102(5)
C−C	0.050[c]	Si···H9	0.145[c]
Si−F	0.047(1)	C2···H11	
Si−C	0.060(3)	F5···H7	0.23(11)
Si···C3	0.067[c]	C3···F5	0.120[c]
C2···C4		C3···F6	0.090[c]
Si···H7	0.133(32)	F5···H8	0.140[c]
C2···H9		F5···H9	0.160[c]
F···F	0.067(9)		

[a]r_a values and angles from electron diffraction analysis with non-rigid model; error limits are 3 σ values. [b-d]See footnotes to Table 1.

Fig. 1. 1,3-Disilacyclobutane. Experimental radial distribution function and difference curve.
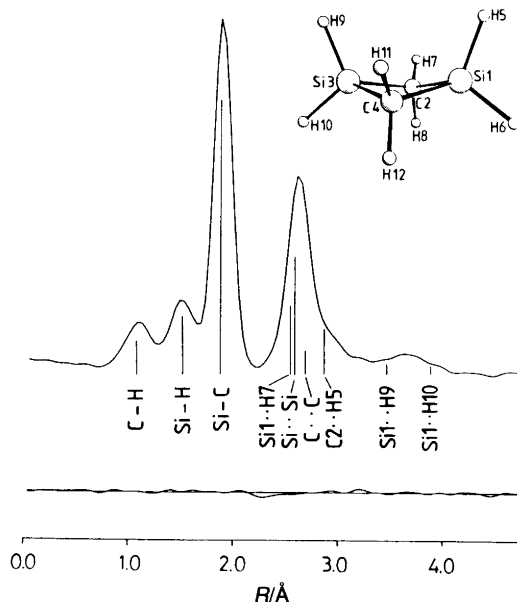

Fig. 2. 1,1-Difluorosilacyclobutane. Experimental radial distribution function and difference curve.

tensities and scattering amplitudes, and phases from Ref. 15 were used. For both compounds, the experimental intensities were fitted with rigid and large amplitude models. In the latter, the puckering potential was expressed by:

$$V = V_0[(\theta/\theta_e)^2 - 1]^2$$

with θ_e corresponding to the potential minimum (equilibrium value) and V_0 to the inversion barrier. The puckering angle is defined as the angle between the CSiC planes in 1, and between the CSiC and CCC planes in 2. In going from the planar to puckered conformations all endocyclic angles were assumed to decrease by the same amount. This assumption is justified by the ab initio calculations. All endocyclic bond angles decrease by 0.5° in 1 and by 0.7° in 2. Variations of the bond lengths between the planar and puckered conformations are predicted to be smaller than 0.002 Å in all cases. The rocking angles ϱ for CH_2, SiH_2 groups (angles between the bisectors of adjacent exo- and endocyclic angles) were assumed to increase linearly with the puckering angle ($\varrho = \delta \cdot \theta$). Such a linear relation was shown to be a good approximation for cyclobutane.[1] Since in the rigid and large amplitude
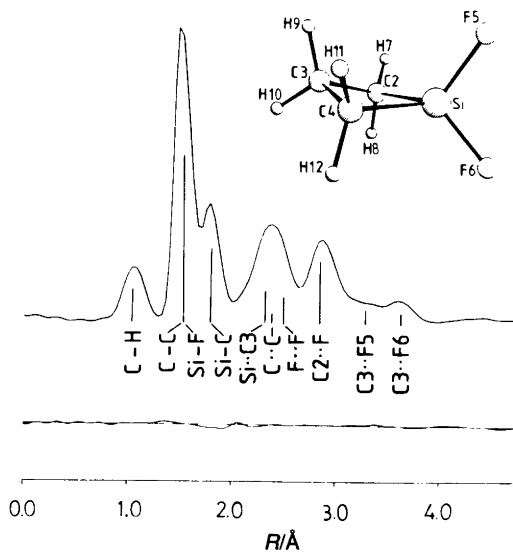
analyses the rocking angles correlate strongly with the puckering and CSiC angles, the coefficients of coupling, δ, were constrained to the ab initio values. Vibrational amplitudes, which are derived with a large amplitude model, correspond to framework values and do not include contributions from the puckering and rocking vibrations.

1,3-Disilacyclobutane. In the refinement of a rigid model, the HCH and HSiH angles converged towards unreasonably small values (~100°) and were therefore constrained to the ab initio results. Constraints for the vibrational amplitudes are evident from Table 1. With these assumptions, five geometric parameters and six vibrational amplitudes were refined simultaneously. Only one correlation coefficient had a value larger than $|0.7|$: CSiC/θ = -0.98. The puckering angle derived from the rigid model is $\theta_0 = 23(3)°$.

A series of refinements based on large amplitude models with different but fixed values for the barrier height V_0 demonstrates that the electron diffraction intensities are very insensitive towards this parameter. Therefore, V_0 was fixed at the spectroscopic value (0.96 kJ mol^{-1}).[6] The geometric parameters corresponding to this barrier height (Table 1) agree within their standard

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deviations with those derived with the rigid model. The puckering angle for the potential minimum [θ_e = 25(2)°] corresponds to a thermal average angle of 20(2)°, in agreement with the value obtained for the rigid model.

1.1-Difluorosilacyclobutane. In the analysis based on the rigid model, all geometric parameters (with the exception of the rocking angles) and seven vibrational amplitudes were refined simultaneously. The *ab initio* calculations predict twisting and wagging angles at the carbon atoms adjacent to Si (C2 and C4 in Fig. 1) of 2.1 and 4.4°. Least-squares analyses with these angles fixed at the calculated values or at zero demonstrate that the other geometric parameters do not depend on these assumptions. Therefore, these distortions were set to zero in the final analysis. The following correlation coefficients had values larger than |0.7|: CC/SiF = −0.97, CC/CSiC = 0.80, SiF/CSiC = 0.80, SiF/l(F5···H7) = 0.70, FSiF/l(F5···H7) = −0.70 and HCH/l(C2···F) = 0.70. This refinement results in a puckering angle, θ_0 of 20(2)°.

For the large amplitude model, various refinements with different but fixed barrier heights resulted in the lowest R factors for V_0 = 5.0 kJ mol⁻¹. From the dependence of the R factors on the barrier height, error limits of (+3.3/−2.5) kJ mol⁻¹ are estimated. The geometric parameters for rigid and large amplitude models agree within their standard deviations (Table 2). The θ_e value [25(2)°] derived from this analysis, which corresponds to a thermal average value of 21(2)°, is again in agreement with the rigid model value.

Discussion

1,3-Disilacyclobutane. The electron diffraction analysis of **1** results in a puckering angle θ_e = 25(2)°, in very good agreement with the spectroscopic value (24.2°),[6] whereas the *ab initio* calculations predict a value of only 15°. The Si−C bonds in the four-membered ring [1.888(2) Å] are slightly longer than those in the unstrained dimethylsilane [1.860(4) Å][16] or disilymethane [1.873(2) Å].[17] Although the puckering angles in cyclobutane[1] and in **1** are very similar [θ_e = 27.9 (16)° vs. 25(2)°], the barrier to ring inversion decreases drastically (from 6.10 to 0.96 kJ mol⁻¹) when two carbon atoms in the ring are replaced by silicon. *Ab initio* calculations for cyclobutane,[2]

1 and cyclotetrasilane[4], which use different basis sets, but of DZ + P quality in all cases, indicate that the barrier in **1** is by far the lowest in these four-membered rings (4.02, 0.33 and 2.22 kJ mol⁻¹, respectively). For cyclobutane and for **1**, the absolute values are strongly underestimated by these calculations.

The most remarkable results of this structure investigation are the endocyclic bond angles: the CSiC angles are larger [90.6(3)°] than the SiCSi angles [86.8(3)°, resulting in a transannular Si···Si distance (2.592 Å) which is shorter than the C···C distance (2.684 Å). This trend (CSiC > SiCSi) is confirmed by the *ab initio* calculations for **1** and also by low-temperature X-ray analyses of 1,1,3,3-tetrafluoro-1,3-disilacyclobutane and the analogous chlorinated compound (planar rings with CSiC = 93.5° and 92.9°).[18] In the gas phase, the chlorinated ring is slightly puckered [θ = 14(3)°] and the endocyclic angles are equal within their error limits [CSiC = 89.0(10)° and SiCSi = 90.1(10)°]. The observation of CSiC > SiCSi contradicts common intuition, which would predict the opposite trend, because one would expect (a) that deformation of CSiC angles requires less strain energy relative to SiCSi angles and (b) that Si···Si repulsion would be stronger than C···C repulsion. The nonbonded Si···Si distances in these rings are shorter than Si−Si bonds in disilanes containing bulky substituents (e.g. Si−Si = 2.697 Å in Si₂Bu'₆[19]) and are only slightly longer than in the parent disilane [Si−Si = 2.332(2) Å].[20] Even shorter Si···Si contacts have been observed for cyclodisiloxanes [2.306 (3) Å] in tetramesitylcyclodisiloxane.[21,22]

The Mulliken overlap populations for nonbonded distances in **1** can possibly explain this counter-intuitive effect. These overlap populations indicate that the transannular Si···Si interaction is much more strongly repulsive than the C···C interaction (−0.55 vs. −0.16 a.u.; for comparison, the Si−C bonding overlap population is +0.70 a.u.). On the other hand, the interactions between Si and the opposite hydrogens are more strongly attractive (Si1···H9 = +0.16 and Si1···H10 = +0.13 a.u.) than those between C and the opposite hydrogens (+0.004 a.u. for both C···H distances). These attractive Si···H interactions compensate for the strong Si···Si repulsion, resulting in a slightly attractive overall interaction between the two SiH₂ groups (+0.04 a.u.), whereas the interaction between the CH₂ groups

is close to zero (-0.01 a.u.). We are aware of the deficiencies of our *ab initio* calculations (HF approximation and limited basis sets) and of the Mulliken population analysis, but for the time being we are unable to present a better explanation for these short Si$\cdots$Si contacts. Our interpretation excludes a Si$\cdots$Si bonding interaction as has been suggested by Tandura *et al.*[23] Very recently, Grev and Schaefer[24] suggested a new model for bonding in 1,3-disubstituted four-membered rings which explains the short non-bonded Si$\cdots$Si distance by the presence of an "unsupported π-bond" in the ring plane.

1.1-Difluorosilacyclobutane. Fluorination at silicon leads to a considerable shortening of the Si$-$C bonds [1.836(3) Å in **2** vs. 1.895(2) Å[7] in the unsubstituted and 1.886(4) Å[8] in the dichlorinated rings]. This effect is larger than that ob-served for unstrained compounds [1.836(2) Å in $(CH_3)_2SiF_2$[25] and 1.860(4) Å in $(CH_3)_2SiH_2$[16]]. Furthermore, the fluorinated ring is less puckered [$\theta_0 = 20(2)°$] than the parent [$\theta_0 = 34(2)°$] and the dichlorinated compound [$\theta_0 = 32(1)°$]. These two effects of fluorination on the geometric parameters are reproduced qualitatively by our *ab initio* calculations, which predict shortening of the Si$-$C bonds from 1.887 to 1.855 Å and a decrease of the puckering angle from 27° to 20°. Due to the large error limits, no conclusion about the effect of fluorination on the inversion barrier can be made: $V_0 = 5.28(4)$ kJ mol^{-1} for silacyclobutane[9] and $V_0 = 5.0 ^{+3.3}_{-2.5}$ kJ mol^{-1} in **2**. Our *ab initio* calculations predict a decrease of this barrier from $V_0 = 3.35$ to 1.30 kJ mol^{-1} upon fluorination. In the case of silacyclobutane the calculated barrier is again strongly underestimated.
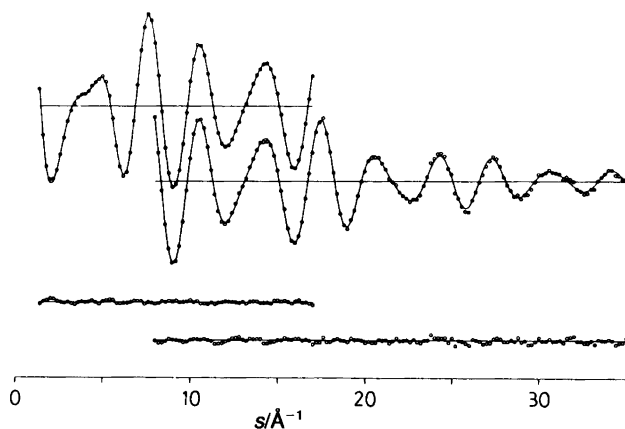

Fig. 3. 1,3-Disilacyclobutane. Experimental (dots) and calculated (full line) molecular intensities $s\,M\,(s)$ and differences.
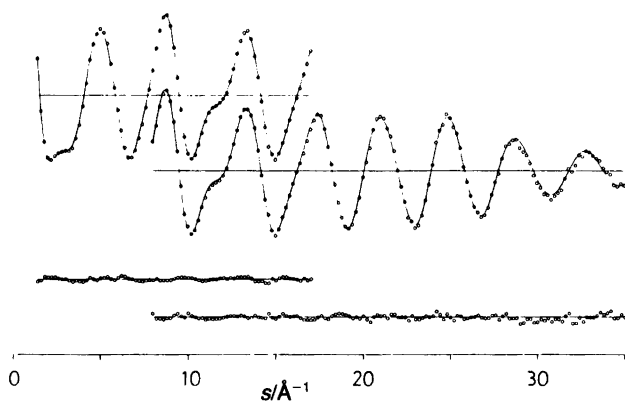

Fig. 4. 1,1-Difluorosilacyclobutane. Experimental (dots) and calculated (full line) molecular intensities $s\,M\,(s)$ and differences.

Experimental

1,3-disilacyclobutane (**1**) and difluorosilacyclo-butane (**2**) were prepared according to literature methods.[26,27] Both compounds were fully charac-terized by spectroscopic measurements; the re-sults agree with known data.[26,27] The purity of the compounds was checked by gas chromatography.

The electron diffraction intensities were re-corded with a Balzers Gas Diffractograph[28] at two camera distances (25 and 50 cm), using an accelerating voltage of about 60 kV. The electron wavelength was calibrated with the use of ZnO diffraction patterns. The samples were kept at $-22\,°C$ and $-33\,°C$ for **1** and **2**, respectively, and inlet system and nozzle were at room temper-ature. Two photographic plates for each com-pound and for each camera distance were ana-lyzed by the usual procedures.[14] The averaged modified molecular intensities are presented in Figs. 3 and 4.

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