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# Structural and conformational analysis of 1-monofluorosilacyclobutane and 1-monochlorosilacyclobutane. A gas-phase electron diffraction and ab initio investigation

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# Abstract

The structures of numerous 1,1-disubstituted silacyclobutanes have been investigated thoroughly, but none of the monosubstituted representatives have been studied as yet. In the present work the geometric structures and conformational equilibria of 1-monofluorosilacyclobutane (MFSCB) and 1-monochlorosilacyclobutane (MCSCB) have been investigated by means of gas-phase electron diffraction and ab initio calculations. The conformational analysis reveals that both molecules are present with both equatorial and axial conformations. Consistent with one another, the electron diffraction data and the ab initio results show that the equatorial conformers of MFSCB and MCSCB are more stable than the higher energy axial forms. The experiments demonstrate that the equatorial conformers of MFSCB and MCSCB are lower in energy than the axial conformers by 4.30 (0.21) kJ/mol (corresponding to eq : ax = 85 : 15 (5)) and 3.92 (0.23) kJ/mol, (eq : ax = 83 : 17 (6)), respectively. For comparison, ab initio calculations at the MP/6-31G(d,p) level predict energy differences of 6.04 and 3.43 kJ/mol, respectively, in favor of the equatorial forms of MFSCB and MCSCB. During the structural refinement it was assumed that all of the structural parameters except the puckering angle  $\theta$  for both the equatorial and axial conformers are equal. This assumption was supported by the ab initio calculations. The major  $(r_a)$  bond distances and bond angles which were obtained from the final refinement of the experimental data are (with uncertainties of  $3\sigma$ ) for MFSC: r(Si-C) = 1.855(1) Å, r(Si-F) = 1.592(2) Å,  $\theta_{eq} = 37.4(20)^{\circ}$  and  $\theta_{ax} = 23.5(70)^{\circ}$ . For MCSCB the following structural parameters were obtained: r(Si-C) = 1.864(2) Å,  $r(\dot{Si}-Cl) = 2.059(3)$  Å, r(Si-H) = 1.470(12) Å, r(C-C) = 1.591(5) Å, r(C-H) = 1.112(4) Å,  $\angle (H-Si-Cl) = 106.0(6)^\circ$ ,  $\angle$ (C-Si-C) = 80.7(14)°,  $\angle$ (C-C-C) = 98.7(22)°. The puckering angles were found to be  $\theta_{eq} = 34.2(25)^{\circ}$  and  $\theta_{ax} = 10^{\circ}$ 21.5(50)°. The observed simultaneous reduction of the Si-C and the Si-F(Cl) bonds can be examined by electrostatic arguments and other concepts such as bond polarity, negative hyperconjugation and  $carbon(2p\pi)$ -silicon(3p\pi) orbital overlap.

By applying various ab initio methods such as HF/6-31G(d,p), MP2/6-31G(d,p) and DFT/b3pw91/6-31G(p) the structures and conformations of mono- and dihalogenated silacyclobutanes of the type  $(CH_2)_3SiY$  (Y = HF, HCl, HBr, HI, H<sub>2</sub>, F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub> and I<sub>2</sub>) have been investigated. Our results show that there is a regular increase of the preferability of the equatorial conformer with the increase of the electronegativity of the halogen atom. This finding is consistent with the correlation which was postulated earlier by Jonvik and Boggs [4–7] for monosubstituted cyclobutanes. In order to gain more insight regarding the influence of the electronegativity of the substituent on the degree of strain in silacyclobutanes and for the purpose of comparison

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of the structures of different mono- and dihalogenated acyclic silanes and silacyclic compounds of larger size, as silacyclopentane and silacyclohexane have been also computed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: 1-Monofluorosilacyclobutane; 1-Monochlorosilacyclobutane; Structural and conformational analysis; Correlation between electronegativity of the susbtituent and conformational stability

# 1. Introduction

As a continuation of our work to clarify the bonding behavior of silicon, we recently prepared some silacyclobutane derivatives of the type: (CH<sub>2</sub>)<sub>3</sub>SiHX (where X = F, Cl, Br) and also  $(CH_2)_3Si(C \equiv CH)_2$  in order to study their structures and dynamical behavior [1-3]. One of the main objectives for studying these novel organosilicon compounds is to investigate the particular sensitivity of the Si-C bond to the effects of substituents and whether the variation of this bond as a result of substitution represents a systematic behavior which can be utilized to predict some chemical and physical properties of molecules containing silicon. Another reason for investigating these compounds is to examine whether the predicted correlations [4-7] between the electronegativity of the substituent in various monosubstituted pure cyclobutanes and the conformational preferability of these molecules are applicable to heterocyclobutanes. According to the ab initio studies by Jonvik and Boggs [4–7], the equatorial conformer becomes increasingly favored with an increase in the electronegativity of the substituent. It is interesting to note that the conformational distribution as well as the geometrical parameters in most of the cyclobutane compounds we have studied [8-14] are in excellent agreement with the rules postulated by Jonvik and Boggs (from now on J + B) [4–7].

A large number of substituted silacyclobutanes are known and some have been the subject of numerous investigations using a variety of experimental methods including thermochemistry [15–18], spectroscopy [3,19–20] and electron diffraction [21–26]. While the structures and dynamics of 1,1-halogenated silacyclobutanes have been studied by applying different experimental techniques, no monosubtituted derivatives have been investigated so far. Therefore, we synthesized the monohalogenated derivatives in order to investigate their structural peculiarities in comparison to the dihalogenated compounds. In this paper, we present the results of the structural and conformational analysis for 1-monofluorosilacyclobutane (MFSCB) and 1-monchlorosilacyclobutane (MCSCB) obtained from electron diffraction and ab initio studies. A comparison of the results of the structural analysis of MFSCB and MCSCB should provide valuable information with respect to the role of electronegativity and size of the substituent by the determining of the conformational stability in these molecules.

The fluorine atom with its pronounced electronegativity and relatively small size (covalent radius of 0.64 Å) is one of the most interesting substituents which gives rise to dramatic changes in structures and energetics of molecules. On the other hand, the chlorine atom is considered to be a moderate  $\pi$ -electron donor and distinct  $\sigma$ -electron acceptor but is larger in size (covalent radius of 0.99 Å). Attaching silicon to fluorine or chlorine leads in most cases to an increase of bond ionicity, i.e. the formation of ionic structures such as  $Y_3Si^+X^-$  and subsequently to a shortening of both the Si-X and Si-Y bonds. In this context, it is of particular interest to investigate the structural consequences of the direct attachment of fluorine or chlorine to silicon when the latter is incorporated in a strained frame such as a four-membered ring. There are reasons to anticipate that the strain energy will be the limiting factor for probable drastic geometrical changes which might be induced by the halogen atom.

It has been long established that the silacyclobutane system is one of the most important precursors for the formation of doubly bonded silicon as in silenes and the silicon analogues of carbenes, silylenes [27]. Moreover, the stability of the halogen–silicon bond has been the focal point of numerous papers. One of the main reasons for the importance of these investigations is to understand the mechanisms of chemical vapor deposition [28,29] and plasma etching [30,31] using systems containing Si–F or Si–Cl [32] fragments.



Fig. 1. Atomic numbering for the equatorial (left) and axial (right) conformers of MFSCB and MCSCB.

### 2. Ab initio calculations

The optimization of the structural parameters of the equatorial and axial conformers of MFSCB and MCSCB (for atomic numbering see Fig. 1) was carried out using several quantum mechanical computational methods, a restricted Hartree–Fock applying 6-31G\*\* [33–35], and density functional (DFT) hybrid b3pw91/6-31G\* [36–38]. All calculations were performed with the GAUSSIAN-98 [39] and SPARTAN 5.0 [40] programs.

In order to calculate the vibrational mean amplitudes we performed a normal coordinate analysis for both conformers of MFSCB and MCSCB. The calculations were based on the force fields provided by the HF/6-31G<sup>\*\*</sup> method. The quadratic force fields in Cartesian displacement coordinates were transferred to the force fields in internal coordinates by applying the method of Zhao and Krimm [41]. The scaling factors applied to the ab initio force field in order to reproduce the experimental frequencies were 0.90 for stretching, 0.80 for bending, and 1.00 for the torsional coordinates.

For the purpose of comparison and for a more reasonable discussion of the reasons leading to the variation of the bond lengths and valence angles associate with the silicon atom within the title compounds we calculated the geometries of a variety of related ring and open chain molecules (see below) using the same methods and basis sets we employed in the case of MFSCB and MCSCB.

# 3. Experimental

Many attempts have been undertaken to synthesize MFSCB by the selective fluorination of only one Si– H linkage using a large variety of mild fluorination agents, but these could not afford the desired product. Finally, the following three-step route has led to MFSCB. Silacyclobutane was prepared by the reduction of 1,1-dichloro-1-silacyclobutane with lithium aluminum hydride according to the method of Laane [42]. A sample of extremely diluted silacyclobutane was then treated with anhydrous  $SnBr_4$  in diethylether at about 0°C provide 1-bromo-1-silacyclobutane. Finally, addition of 1-bromo-1-silacyclobutane to anhydrous  $ZnF_2$  in dibutylether at 5–10°C afforded MFSCB (30%): bp 35.0–35.5°C.

We synthesized MCSCB using a two-steps route, which differs from the method reported earlier by Harthcock et al. [43]. Silacyclobutane was first prepared according to the method of Laane [42]. The resulting silacyclobutane was then diluted with anhydrous *n*-butyl ether and treated with freshly distilled SnCl<sub>4</sub> in *n*-butyl ether at room temperature to provide 1-chloro-1-silacyclobutane (23%): bp 83.5–85°C/711 Torr,  $n_D^{20} = 1.4575$ . The purity of the product was checked by means of IR-spectroscopy and mass spectrometry.

The gas-phase electron diffraction photographs were recorded on Kodak electron image plates using a Balzers KD-G2 diffractometer. Two sets of data for each compound were obtained at approximate camera



Fig. 2. Experimental (  $\times$  ) and calculated (—) reduced molecular intensity curves s<sup>\*</sup>M(s) for MFSCB.



Fig. 3. Experimental (  $\times$  ) and calculated (—) reduced molecular intensity curves s<sup>\*</sup>M(s) for MCSCB.

Experimental geometrical parameters ( $r_a$ -structure) and vibrational amplitudes ( $l_{ij}$ ) of 1-fluorosilacyclobutane (MFSCB)

	Equatorial	Axial		l <sub>ij</sub> (	Å)	
				(eq) <sub>exp</sub>	(eq) <sub>calc.</sub> <sup>a</sup>	
Bond distance	s (Å)					
Si–C Si–F Si–H C–C C–H	$\begin{array}{c} 1.855(1) \\ 1.592(2) \\ 1.472^{b} \\ 1.586^{b} \\ 1.089(3) \end{array}$			0.063(2) 0.051(2) 0.080(14) 0.053 <sup>b</sup> 0.090(5)	0.052 0.040 0.087 0.057 0.077	
Bond angles ( H-Si-F C-Si-C C-C-Si C-C-C H-C-H $\theta^{c}$ $\gamma_{1}^{d}$ $\gamma_{2}^{e}$ $\gamma_{3}^{f}$	°) 106.8(6) 80.8(6) 85.3 <sup>b</sup> 98.6(19) 110.0 <sup>b</sup> 37.4(20) 5.2 <sup>b</sup> 14.6 <sup>b</sup> 6.6 <sup>b</sup>	23.5(70) 14.0 <sup>b</sup> 15.0 <sup>b</sup> 7.0 <sup>b</sup>	$\begin{array}{c} {\rm Si} \cdots {\rm C}_{3} \\ {\rm Si} \cdots {\rm H}_{7,8} \\ {\rm C}_{2,4} \cdots {\rm H}_{5} \\ {\rm C}_{2,4} \cdots {\rm F} \\ {\rm C}_{3,4} \cdots {\rm H}_{7,8} \\ {\rm C}_{3} \cdots {\rm F} \\ {\rm F} \cdots {\rm H}_{9} \\ {\rm F} \cdots {\rm H}_{9} \\ {\rm F} \cdots {\rm H}_{10} \\ {\rm F} \cdots {\rm H}_{7,11} \end{array}$	0.082(6) 0.115(17) $0.160^{b}$ 0.102(5) 0.158(33) 0.076(8) $0.150^{b}$ $0.120^{b}$ $0.202^{b}$	0.067 0.115 0.134 0.099 0.111 0.093 0.177 0.148 0.202	
%(eq)	85(5)		$F \cdots H_{8,12}$	0.135 <sup>b</sup>	0.131	

<sup>a</sup> Ab initio values using HF/6-31G<sup>\*\*</sup>.

<sup>b</sup> Not refined.

<sup>c</sup> Puckering angle.

<sup>d</sup> Rocking angle of the H–Si–F group.

<sup>e</sup> Rocking angle of the  $H-C_2-H$  group.

<sup>f</sup> Rocking angle of the H–C<sub>3</sub>–H group. Uncertainties in parentheses are  $3\sigma$ .

distances of 25 and 50 cm and with an accelerating voltage of 60 kV, yielding a total intensity range from s = 2 to s = 18 Å<sup>-1</sup> for the short camera distance and s = 8 to s = 33 Å<sup>-1</sup> for the long camera distance in intervals of  $\Delta s = 0.2 \text{ Å}^{-1}$ . The samples were kept at -60°C (MFSCB) and -25°C (MCSCB). The inlet system and nozzle were at room temperature. ZnO diffraction patterns were used for the calibration of the electron wavelength providing  $\lambda_{250} = 0.048883$  $\pm 0.000040$  Å,  $\lambda_{500} = 0.048745 \pm 0.000022$  Å in the case of MFSCB and  $\lambda_{250} = 0.048950 \pm 0.000153$  Å,  $\lambda_{500} = 0.048777 \pm 0.000071 \text{ Å}$  in the case of MCSCB. Three plates from each camera distance (MFSCB) and two plates at 25 cm camera distance and three plates from the 50 cm camera distance (MCSCB) were traced on our computercontrolled and modified ELSCAN, E-2500 (Optronics International, Chelmsford, MA, USA) [44] with data being recorded at intervals of 0.1 mm. Data reduction and least-squares refinements were carried out using our usual procedures which have been described elsewhere [45,46]. Figs. 2 and 3 show the molecular intensities for MFSCB and MCSCB in the s range of  $s = 2-33 \text{ Å}^{-1}$ . The atomic scattering amplitudes and phases of Haase [47] were used.

#### 4. Structural analysis and discussion

The experimental results for the structural analysis of MFSCB and MCSCB are displayed in Tables 1 and 2 and the final radial distribution curves resulting from the experiment and the fitted models are shown in Figs. 4 and 5. The present study shows that both MFSCB and MCSCB exist in two stable conformers in the gas-phase with the equatorial conformer being predominant. This finding is consistent with the conformational preferability predicted by all quantum mechanical methods we applied in this study. In the case of MFSCB only eight geometrical parameters

Experimental geometrical parameters ( $r_a$ -structure) and vibrational amplitudes ( $I_{ij}$ ) of 1-chlorosilacyclobutane (MCSCB)

	Equatorial	Axial		l <sub>ij</sub> (A	Å)	
				(eq) <sub>exp</sub>	(eq) <sub>calc.</sub> <sup>a</sup>	
Bond distances	s (Å)					
Si-C	1.864(2)			0.064(1)	0.053	
Si-Cl	2.059(3)			0.059(2)	0.048	
Si-H	1.470(12)			$0.087^{b}$	0.087	
C–C	1.591(5)			$0.056^{b}$	0.056	
C-H	1.112(4)			0.086(5)	0.077	
Bond angles ( <sup>c</sup>	2)					
H-Si-Cl	106.0(6)		Si···C <sub>3</sub>	0.088(5)	0.067	
C-Si-C	80.7(14)		Si····H <sub>7.8</sub>	0.155 <sup>b</sup>	0.117	
C-C-Si	85.0 <sup>b</sup>		$C_{2,4} \cdots H_5$	0.160 <sup>b</sup>	0.135	
C-C-C	98.7(22)		$C_{2,4} \cdots Cl$	0.122(6)	0.107	
H–C–H	110.0 <sup>b</sup>		$C_{2,4} \cdots H_{11,7}$	0.197 <sup>b</sup>	0.197	
$\theta^{c}$	34.2(25)	21.5(50)	$C_3 \cdots Cl$	0.103(11)	0.117	
$\gamma_1^d$	$0.0^{\mathrm{b}}$	9.6 <sup>b</sup>	$Cl \cdots H_9$	0.375 <sup>b</sup>	0.276	
$\gamma_2^e$	10.0 <sup>b</sup>	10.0 <sup>b</sup>	$Cl \cdots H_{10}$	0.246 <sup>b</sup>	0.146	
$\gamma_3^{f}$	$7.9^{\mathrm{b}}$	7.9 <sup>b</sup>	Cl···H <sub>7,11</sub>	0.223 <sup>b</sup>	0.223	
% (eq)	83(6)		$Cl \cdots H_{8,12}$	0.143 <sup>b</sup>	0.143	

<sup>a</sup> Ab initio values using HF/6-31G<sup>\*\*</sup>.

<sup>b</sup> Not refined.

<sup>c</sup> Puckering angle.

<sup>d</sup> Rocking angle of the H–Si–F group. <sup>e</sup> Rocking angle of the H–C<sub>2</sub>–H group.

<sup>f</sup> Rocking angle of the H–C<sub>3</sub>–H group. Uncertainties in parentheses are  $3\sigma$ .



Fig. 4. Experimental (×) and calculated (—) radial distribution curves for MFSCB.

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Fig. 5. Experimental (×) and calculated (—) radial distribution curves for MCSCB.

and nine vibrational mean-amplitudes could be refined whereas for MCSCB ten geometrical parameters and six vibrational mean-amplitudes were fitted. For the purpose of more systematic and reasonable discussion of the structural results we will discuss first the endocyclic bond distances in MFSCB and MCSCB and then the bond angles and exocyclic bond lengths.

# 5. Endocyclic parameters

Comparison between the ring parameters in MFSCB and MCSCB (Tables 1 and 2) reveals that both the Si–C and C–C bonds in the former molecule are shorter by about 0.009 and 0.005 Å, respectively. This slight bond shortening, which is also reproduced by the ab initio calculations (Tables 3 and 4), is less than might be anticipated on the basis of the difference in the electronegativities of fluorine and chlorine. Probably the ring strain and the larger puckering angle of the ring in the case of MFSCB are responsible for this feature. Because of the presence of a Si–C bond in a strained four-membered ring and the attach-

ment of the silicon atom to strong electronegative atoms such as fluorine and chlorine and for reasons pointed out in the introduction, we will focus first on the consideration of the alternation of the Si-C bond in mono and geminally halogenated silacyclobutanes and some related molecules. In accordance with the expectation the Si-C bond in MFSCB and MCSCB (Tables 1 and 2) shortens in comparison to the parent molecule silacyclobutane, SCB, (Table 5). This bond length reduction of 0.040 and 0.031 Å, respectively, is substantial. The experimentally determined value for the Si-C bond in methylsilane is 1.864 Å [48] and it shortens on going to methylmonofluorosilane and dimethyl-difluorosilane by 0.017 Å [49] and 0.028 Å [50], respectively. Although the ab initio calculations at all levels of theory which we employed in this work show the same tendency for the shortening of the Si-C bond on monohalogenation, this bond contraction is significantly smaller (Tables 3 and 4) than provided by the experiment. Another interesting feature which emerges from Tables 3 and 4 is that the Si-C bond distance predicted by the ab initio calculations is always overestimated. In several previous papers, we alluded to this peculiarity and discussed it in detail

	X = Y = H	XY = HCl		XY = HF		X = Y = CL	X = Y = F	$X = Y = CH_3$
		Equatorial	Axial	Equatorial	Axial			
Si-C	1.8957	1.8806	1.8830	1.8750	1.8787	1.8714	1.8612	1.9000
Si-F(Cl)		2.0648	2.0683	1.6224	1.6254	< 2.0559 >	< 1.6122 >	
Si-H	$< 1.4800 > {}^{a}$	1.4752	1.4762	1.4769	1.4783			
Si-C <sub>meth</sub>								< 1.8840 >
C-C	1.5557	1.5591	1.5584	1.5607	1.5599	1.5616	1.5654	1.5557
C-H	< 1.0900 >	< 1.0894 >	< 1.0898 >	< 1.0890 >	< 1.0899 >	< 1.0891 >	< 1.0880 >	
X-Si-X	108.4	106.9	106.4	106.8	106.0	108.4	106.0	109.8
(C-Si-C) <sub>ring</sub>	78.0	79.1	79.1	79.5	79.5	80.4	81.5	77.9
C–C–Si	86.3	85.3	86.4	85.0	86.5	85.5	85.3	86.6
C-C-C	100.2	100.4	100.6	100.4	100.8	101.3	101.8	100.3
H-C <sub>2</sub> -H	108.7	109.1	108.8	109.0	108.5	109.2	108.9	108.4
H-C <sub>3</sub> -H	107.5	107.6	107.8	107.5	107.7	108.1	108.1	107.2
Si-C-C-C	25.1	25.8	22.4	26.2	21.2	22.4	20.5	24.3
C-Si-C-C	20.5	21.2	18.4	21.5	17.5	18.5	17.0	19.8
H,Cl,F-Si(CSiC) <sub>plane</sub>	(131.6) <sub>eq</sub>	131.0	120.0	131.0	121.2	(131.0) <sub>eq</sub>	(131.0) <sub>eq</sub>	(129.8) <sub>eq</sub>
	(120.0) <sub>ax</sub>					(120.7) <sub>ax</sub>	(123.0) <sub>ax</sub>	$(120.3)_{ax}$
$\theta^{\mathrm{b}}$	33.0	34.3	29.6	35.0	28.0	30.0	27.5	32.0
%eq		80.0		92.0				
$\mu_{t}$ (Debye)	0.3	2.2	2.3	1.7	1.8	2.7	2.4	0.56

Table 3 Comparison between bond distances (Å) and bond angles (°) of various mono- and disubstituted silacyclobutanes (CH<sub>2</sub>)<sub>3</sub>SiXY using MP2/6-31G\*\*

<sup>a</sup> <...>: Average values.
<sup>b</sup> Puckering angle.

Comparison between bond distances (Å) and bond angles (°) of various mono- and disubstituted silacyclobutanes  $(CH_2)_3SiXY$  from DFT calculations using  $b3pw91/6-31G^*$ 

	X = Y = H	XY = HCl		XY = HCl		X = Y = CL	X = Y = F
		Equatorial	Axial	Equatorial	Axial		
Si-C	1.9000	1.8854	1.8880	1.8810	1.8841	1.8763	1.8668
Si-F(Cl)		2.0812	2.0834	1.6189	1.6215	< 2.0714 >	< 1.6088 >
Si-H	< 1.4943 > a	1.4885	1.4902	1.4922	1.4944		
C–C	1.5600	1.5630	1.5625	1.5643	1.5643	1.5663	1.5702
C-H	< 1.0950 >	< 1.0930 >	< 1.0950 >	< 1.0950 >	< 1.0960 >	< 1.0930 >	< 1.0930 >
H-Si-H(F,Cl)	107.9	106.1	105.6	106.5	105.6	107.9	105.6
C-Si-C	78.6	79.7	79.8	80.0	80.2	81.2	82.1
C-C-Si	86.7	85.7	87.1	85.5	87.1	86.1	85.9
C-C-C	101.0	101.2	101.7	101.0	101.7	102.4	102.7
$H-C_2-H$	108.4	108.8	108.4	108.7	108.1	108.8	108.5
H-C <sub>3</sub> -H	107.2	107.3	107.5	107.3	107.3	107.8	107.8
Si-C-C-C	21.9	22.7	17.3	23.4	16.5	16.9	15.2
C-Si-C-C	17.9	18.6	14.2	19.3	13.5	13.9	12.5
H,Cl,F-Si(CSiC) <sub>plane</sub>	(131.0) <sub>eq</sub>	130.2	121.8	130.3	122.7	(129.4) <sub>eq</sub>	(129.8) <sub>eq</sub>
· · · ·	(121.0) <sub>ax</sub>					(122.7) <sub>ax</sub>	(124.6) <sub>ax</sub>
$ heta^{ ext{b}}$	28.8	30.2	23.0	31.2	21.7	22.5	20.3
%eq		79.9		92.0			
$\mu_t$ (Debye) <sup>c</sup>	0.6	2.4	2.4	1.7	1.7	2.9	2.4

<sup>a</sup>  $< \cdots >$ : Average values.

<sup>b</sup> Puckering angle.

<sup>c</sup> Total dipole moment.

[51–54]. It is noteworthy that the hybrid DFT method  $b3pw91/6-31G^*$  seems to overestimate the Si–C bond rather more than the perturbation method MP2/6-31G<sup>\*\*</sup>.

As may be anticipated, the replacement of both hydrogen atoms on silicon by fluorine or chlorine atoms leads to an increased contraction of the Si-C bond. Such bonding behavior is apparent from the comparison between the mono and geminally halogenated silacyclobutanes in Tables 3-5. The experimentally determined reduction of the Si-C bond length upon going from MFSCB (the equatorial form has been chosen for comparison since it is prevailing in the conformational equilibrium) to the difluoro derivative is about 0.02 Å. This bond length shortening is predicted by MP2/6-31G(d,p) and DFT/b3pw91/6-31G(d) methods to be about 0.014 Å. Although the Si-C bond in the chlorinated counterpart shows the same tendency, it decreases only slightly (by about 0.004 Å as provided by the experiment and 0.009 Å by the ab initio calculations) upon moving from the

mono to the geminally chlorinated compound. This striking bonding behavior will be discussed more later.

Perhaps the most interesting finding of the present work is the observed correlation between the steadily shortening of the Si–C bond with the increase of the electronegativity of the substituent. Scheme 1 visualizes this systematic behavior of the Si–C bond in correlation with the electronegativity,  $\chi$ , of the substituents. In Scheme 1, the following abbreviations are used: silacyclobutane (SCB), 1,1-dimethylsilacyclobutane (DMSCB), 1,1-diethynylsilacyclobutane (DESCB), 1,1-dichlorosilacyclobutane (DCSCB) and 1,1-difluorosilacyclobutane (DFSCB). The electronegativities of H, CH<sub>3</sub>, -C=C, Cl and F are 2.08 [56], 2.56 [57], 2.66 [57], 3.07 [56], and 4.00 [56], respectively.

When we presented Scheme 1 for the first time at the VIIth European Electron Diffraction Meeting in Prague in 1997 we included the literature value of 1.886(4) Å for the Si–C bond in DCSCB reported

 $(X = Y = CL)^d$  $(X = Y = H)^a$  $(XY = HF)^{b}$  $(XY = HCl)^{b}$  $(X = Y = F)^{c}$  $X = Y = CH_3^e$ Si-Cring 1.895(2)1.855(1)1.864(2)1.836(3) 1.860(3) 1.885(2)1.574(3) Si-F 1.592(2)Si-Cl 2.059(3) 2.040(2)1.496(18) 1.472<sup>f</sup>  $1.470^{f}$ Si-H Si-C<sub>meth</sub> 1.872(2)C-C 1.607(6)1.586<sup>f</sup> 1.591(5) 1.574(8)1.557(4)1.563(4) C-H 1.143(9)1.089(3) 1.112(4) 1.099(6) 1.091(8) 1.115(3) 106.9(5) X-Si-X 115.6(90) 106.8(6) 105.2(8) 109.9(47) 106.0(6) (C-Si-C)<sub>ring</sub> 80.8(5) 80.8(6) 80.7(14) 82.7(6) 81.1(10) 79.2(11) C-C-Si 85.3<sup>g</sup> 86.8<sup>g</sup> 85.1(5) 85.0<sup>g</sup> 86.8(8) 85.7(12) C-C-C98.6(19) 98.7(22) 102.0(15) 99.9<sup>g</sup> 98.6(5) 100.6(8)  $\theta^{h}$ 25.9(26) 29.7(45) 33.6(2.1) 37.4(20) 34.2(22) 25.0(20)

Comparison between some experimental bond distances (Å) and bond angles (°) in various mono- and disubstituted silacyclobutanes  $(CH_{2)3}SiXY$ 

<sup>a</sup> Ref. [21].

<sup>b</sup> This work (equatorial form).

<sup>c</sup> Ref. [24].

<sup>d</sup> Ref. [25].

<sup>e</sup> Ref. [26].

f Not refined value.

<sup>g</sup> Calculated value.

<sup>h</sup> Puckering angle.

by Cyvin et al., in 1986 [22]. We showed that this value did not fit within this systematic behavior and thus it had to be incorrect. Professor Lev Vilkov, who was present in the audience, mentioned that the structure of DCSCB had been reinvestigated, and he provided the new value of 1.860(3) Å for the Si–C bond length. This fits perfectly into Scheme 1. This demonstrates once more the advantage of systematic studies for predicting trends in molecular properties.

In order to obtain as complete a comparison as possible, we optimized the structures of some related unstrained compounds of the types  $R_2SiHX$  and  $R_2SiX_2$  as well as other types of strained silacyclic compounds of the type: (CH<sub>2</sub>)<sub>4</sub>SiHX and (CH<sub>2</sub>)<sub>5</sub>SiX<sub>2</sub>

(where  $R = -CH_3$ ,  $CH_3--CH_2-$  and X = H, Cl, F). These calculations, which have been carried out at the same level of theory as MFSCB and MCSCB, were necessary to gain additional information about the consequences of the incorporation of silicon into four-membered ring systems and the effect of the ring strain on the Si-C bond lengths within the title compounds when compared to unstrained alkyl derivatives and rings of larger size.

Tables 6 and 7 for the monohalogenated silanes demonstrate the following interesting features (i) The HF/6-31G<sup>\*\*</sup> and DFT/b3pw91/6-31G<sup>\*</sup> methods overestimate the Si–C bond more than the MP2/6-31G<sup>\*\*</sup> method. This is also true for the Si–Cl bond.

Scheme 1	l
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S1-C(A) 1.895(2) 1.878(2) 1.874(2) 1.804(2) 1.800(3) 1.855(2) 1.850(3)	SCB > DN Si-C(Å) 1.895(2) <sup>a</sup> 1.8	$MSCB > DESCB  878(2)^{b} 1.874(2)^{b}$	$>$ MCSCB $>$ $1.864(2)^d$	$DCSCB > 1.860(3)^{e}$	• MFSCB > 1.855(2) <sup>d</sup>	DFSCB 1.836(3) <sup>f</sup>
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<sup>&</sup>lt;sup>a</sup> Ref. [21].

<sup>b</sup> Ref. [26].

<sup>c</sup> Ref. [55].

<sup>d</sup> Ref. (this work).

<sup>e</sup> Ref. [25].

<sup>f</sup> Ref. [24].

Table 6 Structural parameters of some dialkylsilanes of the type  $R_2SiHX$  ( $R = CH_3$ ,  $CH_3 - CH_2$  and X = Cl, F) as obtained from ab initio calculations

	$R = CH_3$								R = Cl	H <sub>3</sub> -CH <sub>2</sub>		
		X = F			X = Cl			X = F			X = Cl	
	I <sup>a</sup>	II <sup>b</sup>	III <sup>c</sup>	I <sup>a</sup>	$\mathbf{H}^{\mathbf{p}}$	III <sup>c</sup>	I <sup>a</sup>	$\mathbf{II}^{\mathrm{b}}$	III <sup>c</sup>	I <sup>a</sup>	II <sup>b</sup>	III <sup>c</sup>
Si-C	1.8722	1.8702	1.8670	1.8750	1.8734	1.8701	1.8773	1.8769	1.8714	1.8816	1.8814	1.8760
Si-X	1.6043	1.6238	1.6282	2.0861	2.0892	2.0744	1.6074	1.6274	1.6321	2.0901	2.0950	2.0778
Si-H	1.4766	1.4917	1.4777	1.4731	1.4883	1.4756	1.4788	1.4942	1.4809	1.4753	1.4900	1.4792
X–Si–H	106.9	106.9	107.0	106.0	105.9	106.5	106.4	106.4	106.5	105.6	105.5	106.3
C–Si–C	112.3	112.1	111.6	112.5	112.6	112.0	112.4	112.4	112.6	111.9	112.4	112.7

<sup>a</sup> HF/6-31G\*\*. <sup>b</sup> DFT(b3pw91/6-31G\*). <sup>c</sup> MP2/6-31G\*\*.

Structural parameters of 1-fluorosilacyclopentane (MFSCP), 1-chlorosilacyclopentane (MCSCP), 1-fluorosilacyclohexane (MFSCH) and 1-chlorosilacyclohexane (MCSCH) obtained from ab initio calculations

		MFSCP <sup>a</sup>			<b>MCSCP</b> <sup>a</sup>			$\mathrm{MFSCH}^{\mathrm{b}}$			$\mathrm{MCSCH}^{\mathrm{b}}$	
	I <sup>c</sup>	$\mathrm{II}^{\mathrm{d}}$	III <sup>e</sup>	I <sup>c</sup>	$\mathrm{II}^{\mathrm{d}}$	III <sup>e</sup>	I <sup>c</sup>	$\mathbf{II}^{\mathrm{d}}$	III <sup>e</sup>	I <sup>c</sup>	$\mathrm{II}^{\mathrm{d}}$	III <sup>e</sup>
Si-C	1.8737	1.8759	1.8704	1.8762	1.8787	1.8735	1.8744	1.8746	1.8693	1.8775	1.8779	1.8727
Si-X	1.6017	1.6224	1.6260	2.0790	2.0845	2.0682	1.6037	1.6242	1.6283	2.0831	2.0884	2.0720
Si-H	1.4762	1.4924	1.4783	1.4730	1.4886	1.4765	1.4777	1.4937	1.4799	1.4743	1.4898	1.4779
X–Si–H C–Si–C	106.3 94.7	106.2 94.6	106.6 93.8	105.9 94.6	105.8 94.6	106.8 93.6	106.7 105.6	106.7 105.6	107.0 105.1	106.0 105.6	106.0 105.7	106.8 105.1

<sup>a</sup> C<sub>s</sub>-symmetry (fluorine atom in equatorial position).
 <sup>b</sup> Chair form (fluorine atom in equatorial position).

° HF/6-31G\*\*.

<sup>d</sup> DFT(b3pw91/6-31G<sup>\*</sup>). <sup>e</sup> MP2/6-31G<sup>\*\*</sup>.

Selected structural parameters of various cyclic silanes (SCP = silacyclopentane, MFSCP = 1-monofluorosilacyclopentane, DFSCP = 1,1,difluorosilacyclopentane, MCSCP = 1-monochlorosilacyclopentane, DCSCP = 1,1,-dichlorosilacyclopentane, SCH = silacyclohexane, MFSCH = 1-monofluorosilacyclohexane, DFSCH = 1,1-difluorosilacyclohexane, MCSCH = 1-monochlorosilacyclohexane, DCSCH = 1,1dichlorosilacyclohexane) obtained from ab initio calculations using MP2/6-31G<sup>\*\*</sup>

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$											
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		SCP	MFSCP <sup>a</sup>	DFSCP	<b>MCSP</b> <sup>a</sup>	DCSCP	SCH	MFSCH <sup>b</sup>	DFSCH	MCSCH <sup>b</sup>	DCSCH
Si-H       1.4791       1.4783       1.4765       1.4809       1.4799       1.4779         Si-X       1.6260       1.6156       2.0682       2.0605       1.6283       1.6187       2.0720       2.0653         H-Si-H       108.6       106.6       106.8       107.0       106.8       106.8         X-Si-X       105.7       108.0       106.1       108.3         C-Si-C       92.5       93.8       98.3       93.6       97.6       104.2       105.1       107.5       105.1       106.6	Si-C	1.8860	1.8704	1.8678	1.8735	1.8771	1.8861	1.8693	1.8554	1.8727	1.8633
Si-X       1.6260       1.6156       2.0682       2.0605       1.6283       1.6187       2.0720       2.0653         H-Si-H       108.6       108.2       108.2       107.0       106.8       106.8       107.0       106.8         X-Si-H       105.7       108.0       106.1       108.3       108.3         C-Si-C       92.5       93.8       98.3       93.6       97.6       104.2       105.1       107.5       105.1       106.6	Si-H	1.4791	1.4783		1.4765		1.4809	1.4799		1.4779	
H-Si-H     108.6     108.2       X-Si-H     106.6     106.8     107.0     106.8       X-Si-X     105.7     108.0     106.1     108.3       C-Si-C     92.5     93.8     98.3     93.6     97.6     104.2     105.1     107.5     105.1     106.6	Si-X		1.6260	1.6156	2.0682	2.0605		1.6283	1.6187	2.0720	2.0653
X-Si-H106.6106.8107.0106.8X-Si-X105.7108.0106.1108.3C-Si-C92.593.898.393.697.6104.2105.1107.5105.1106.6	H-Si-H	108.6					108.2				
X-Si-X         105.7         108.0         106.1         108.3           C-Si-C         92.5         93.8         98.3         93.6         97.6         104.2         105.1         107.5         105.1         106.6	X-Si-H		106.6		106.8			107.0		106.8	
C-Si-C 92.5 93.8 98.3 93.6 97.6 104.2 105.1 107.5 105.1 106.6	X-Si-X			105.7		108.0			106.1		108.3
	C-Si-C	92.5	93.8	98.3	93.6	97.6	104.2	105.1	107.5	105.1	106.6

<sup>a</sup>  $C_s$ -Symmetry (halogen atom in equatorial position).

<sup>b</sup> Chair form (halogen atom in equatorial position).

(ii) Despite being overestimated, the values for the Si–F bond lengths produced by the DFT/b3pw91/6-31G<sup>\*\*</sup> and MP2/6-31G<sup>\*\*</sup> calculations are consistent with each other but differ from the values predicted at the HF/6-31G<sup>\*\*</sup> level. (iii) While the HF/6-31 G<sup>\*\*</sup> and MP2/6-31G<sup>\*\*</sup> methods provide consistently similar Si–H bond lengths for all compounds listed in Tables 6 and 7, the DFT/b3pw91/6-31G<sup>\*\*</sup> method, however, produces unreasonably long Si–H bond distances. (iv) There is almost no difference between the values predicted by the various methods for the bond angles around the silicon atom.

From Table 7 it can be seen that all the trends observed for the dialkyl compounds are also present for the monohalogenated cyclic compounds silacyclopentane (SCP) and silacyclohexane (SCH). Table 8 compares the influence of successive halogenation on the geometrical parameters around silicon in the less strained cyclic systems SCP and SCH. The following conclusions can be drawn: (1) The general trend of Si-C and Si-F(Cl) bond reduction upon progressive halogen substitution is present. (2) Except for the SCB series, the C-Si-C valence angle is sensitive to mono- and dihalogenation at silicon. For instance, this angle widens on monofluorination by 1.3° and on difluorination by 5.8°. In SCH this widening amounts to 1.1° and 3.3° on mono and difluorination, respectively. (3) The X-Si-X bond angle reduces simultaneously with the increase of the C-Si-C angle upon progressive halogenation. For example, this angle decreases in SCP by 2°

upon monofluorination and by  $2.9^{\circ}$  upon difluorination. This correlation between the X–Si–X angle and C–Si–C angles at silicon may be interpreted in terms of a large charge withdrawal from the central silicon atom which leads to higher bond polarity and orbital rehybridization. This charge redistribution is also responsible for the shortening of the Si–C and Si–X bonds with the increase of the degree of halogenation.

The values presented in Tables 9 and 10 show the effect of successive chlorination and fluorination on the most prominent structural parameters in silacyclobutane and the unstrained dimethyl- and diethylsilane

#### Table 9

Comparison between some calculated (MP2/6-31G<sup>\*\*</sup>: SCB = silacyclobutane; MCSCB = 1-monochlorosilacyclo-butane; DCSCB = 1,1dichlorosilacyclobutane) bond distances (Å) and bond angles (°) in SCB, MCSCB, DCSCB and various alkylsilanes and their chlorinated derivatives

	Si-C	Si-Cl	X-Si-X	C–Si–C
SCB	1.8957		108.4	78.6
MCSCB	(1.8806) <sub>eq</sub>	2.0648	106.9	79.0
DCSCB	1.8714	$< 2.0559 > {}^{a}$	108.4	80.4
(CH <sub>3</sub> ) <sub>2</sub> SiH <sub>2</sub>	1.8829		107.6	111.0
(CH <sub>3</sub> ) <sub>2</sub> SiHCl	1.8701	2.0744	106.5	112.0
(CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub>	1.8655	2.0693	107.7	114.4
$(C_2H_5)_2SiH_2$	1.8884		107.4	112.4
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SiHCl	1.8760	2.0778	106.3	112.7
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SiCl <sub>2</sub>	1.8736	2.0733	107.4	112.9

<sup>a</sup> Average value.

Comparison between some calculated (MP2/6-31G\*\*: SCB = silacyclobutane; MFSCB = 1-monofluorosilacyclobutane; DFSCB = 1,1difluorosilacyclobutane) bond distances (Å) and bond angles (°) in SCB, MFSCB, DFSCB and various alkylsilanes and their fluorinated derivatives

	Si-C	Si-F	X-Si-X	C-Si-C
SCB	1.8957		108.4	78.6
MFSCB	(1.8750) <sub>eq</sub>	1.6224	106.8	79.5
DFSCB	1.8612	$< 1.6122 > {}^{a}$	106.0	81.5
(CH <sub>3</sub> ) <sub>2</sub> SiH <sub>2</sub>	1.8829		107.6	111.0
(CH <sub>3</sub> ) <sub>2</sub> SiHF	1.8670	1.6280	107.0	111.6
(CH <sub>3</sub> ) <sub>2</sub> SiF <sub>2</sub>	1.8584	1.5916	105.7	115.2
$(C_2H_5)_2SiH_2$	1.8884		107.4	112.4
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SiHF	1.8710	1.6320	106.5	112.6
$(C_2H_5)_2SiF_2$	1.8636	1.5947	105.3	114.9

<sup>a</sup> Average value.

species. From Table 9 it can also be seen that monoand dichlorination lead to a systematic reduction of the Si-C bond length, as expected. However, while the bond shortening in going from mono- to dichlorosilacyclobutane is about 0.0092 Å, this shortening amounts only to 0.0046 and 0.0024 Å in going from the mono- to dichloro derivatives of dimethylsilane (DMS) and diethylsilane (DES), respectively. The contraction of the Si-C bond upon monochlorination of SCB, DMS and DES of 0.015, 0.013 and 0.012 Å is comparable in all these compounds. It is also noteworthy that the Si-C bond in SCB is longer than in DMS and DES by about 0.013 and 0.007 Å, respectively. This bond elongation might be accounted for as being the result of the ring strain. In all compounds shown in Table 9 the Si-Cl bond shortens only slightly in going from the mono- to dichloro derivatives.

As is apparent from Table 10, the shortening of the Si–C bond is more pronounced in the case of the fluorinated derivatives than in their chlorinated counterparts. This bond contraction, which is substantiated by the experiment and parallels the trend found in the chlorinated compounds, might be rationalized by invoking various concepts. Among those which are frequently used in this regard are  $\sigma$ – $\pi$ -hyperconjugation [58–60], negative hyperconjugation (anomeric effect) [61–64] and electronegativity criteria and bond ionicity [65]. Most recent work lends strong

support that the contraction of the Si–C bond results from overlap between  $2p\pi$  orbitals on carbon and  $3p\pi$ orbitals on silicon [66]. This overlap is enhanced by the increase of the positive charge on silicon upon fluorine substitution and the consequent contraction of the  $3p\pi$ (Si) orbital, thus providing a better match to the size of a  $2p\pi$ (C) orbital. Obviously this kind of rationalization explains why the Si–C bond contraction is more pronounced upon fluorination on silicon than upon chlorination.

Table 5 shows that in contrast to the calculated values presented in Tables 3 and 4, the experimentally determined C–C bond lengths in silacyclobutanes are reduced in going from the mono- to the dihalogenated compounds and do not possess any systematic behavior. In contrast, the theoretically predicted values for the C–C bond lengths increase successively with increasing electronegativity of the substituents and thus with increasing positive charge at silicon. The consequence of such charge deficiency at silicon is a charge transfer from the C–C bond region towards silicon and, therefore, the elongation of this bond. Electron releasing substituents such as the methyl groups in dimethylsilacyclobutane (Table 5) seem to have no effect on the ring C–C bond.

## 6. Bond angles and exocyclic bond distances

Because of the well known correlations between the endocyclic and exocyclic angles in silacyclobutanes [67], we will not discuss these angles separately. It is accepted that while the alternation of bond lengths as a result of successively increasing atom or group electronegativity generally shows a systematic behavior and variations of bond angles, however, demonstrate a less regular tendency upon substitution (at least within the group IV) and often defy expectations. The main reasons for this behavior are most likely the rehybridization of the orbitals on the central atom and the subsequent deviation from orthogonality and the increased bond ionicity as a result of the electronegative substituents.

Tables 3–5 demonstrate that endocyclic Si–C–C and C–C–C valence angles are little affected by halogenation at silicon. More intriguing is the alternation of the C–Si–C and X–Si–X (X = H, Cl) bond angles. As found experimentally (Table 5), these angles show almost no variation in going from the mono- to the dihalogenated silacyclobutanes except in the case of the fluoro derivatives. The difluorination widens the C-Si-C angle by about 1.9°. Of particular interest is the behavior of the X-Si-X and C-Si-C bond angles within the series of the compounds shown in Tables 9 and 10. The calculations at MP2/6-31G\*\* level indicate that the X-Si-X angle decreases on monochlorination but increases upon dichlorination to produce almost the H-Si-H angle in the unchlorinated silane. On the other hand, the C-Si-C angle widens on successive chlorination of SCB and DMS but it remains almost unchanged in the case of DES. As can be seen in Table 9, this angle increases by 1.8° upon going from SCB to DCSCB but this widening amounts to 3.4° on dichlorination of DMS. Therefore, the smaller enlargement of the C-Si-C angle in the case of DCSCB might be accounted for by the increase of the strain energy within the ring as a result of the shortening of the Si-C bond.

It should be noted that the experimentally determined [21] H-Si-H angle and C-C bond length in SCB have not been considered by the discussion of the experimental results for the following reasons: The differences between the experimentally determined value for the C–C bond of 1.607 (6) Å [21] and the theoretically predicted one of 1.556 Å is clearly larger than the experimental uncertainty. Another striking feature between the experimental and calculated results is that the values for the Si-C bond within the molecules listed in Tables 3 and 4 are overestimated by the theory on average by 0.017 to 0.020 Å except in the case of SCB where the overestimation amounts only to 0.001 Å. This indicates that the experimental value of 1.895(2) Å is too high. If it can be accepted that the average off-set value which we obtained for MP2/6-31G\*\* method for the Si-C bond of 0.017 Å is also valid for SCB, this would lead to an effective value of 1.878 Å which seems to be reasonable. Further discrepancies between theory and experiment are evident from the values for the H-Si-H and C-Si-C angles. All in all, an experimental reinvestigation of the structure of SCB is warranted and this would benefit from the knowledge of the theoretical values we obtained in this work.

We now consider the behavior of the Si-halogen bond and its variation as a consequence of the geminal halogenation of SCB. Comparison of the electron diffraction and ab initio values for the Si-F bond length in MFSCB (Tables 3-5) reveals that the MP2/6-31G\*\* method overestimates this bond by about 0.030 Å and the DFT/b3pw91/6-31G\* by about 0.027 Å. As is evident from the experimental results (Table 5), this bond shortens by about 0.018 Å upon difluorination. The ab initio methods (Tables 3 and 4) predict a value of about 0.01 Å for this bond reduction. The Si-F bond shortening due to difluorination is appreciably higher, about 0.037 Å, in the acyclic compounds shown in Table 10. Unlike the situation with the Si-F bond, the calculated (MP2/6-31G\*\*) and the experimental values for the Si-Cl bond in MCSCB are in good agreement. The DFT/ b3pw91/6-31G\* method (Table 4), however, overestimates this bond by more than 0.02 Å. The dichlorination leads to an Si-Cl bond contraction of 0.019 Å, which parallels the value for the Si-F bond shortening on difluorination. Although the ab initio methods which have been applied in this work reflect this tendency of bond shortening but they provide a smaller value of about 0.01 Å.

As was the case for the Si–C bond, several explanations may be used to elucidate the Si–F and Si–Cl bond reduction upon dihalogenation. All of these are based on electrostatic considerations, and these simply imply that the increased shrinkage of the silicon atomic radius as a consequence of charge withdrawal by means of the electronegative substituents (F and Cl) result in shortening of all bonds at silicon. Invoking negative hyperconjugation may explain this Si–F(Cl) bond shortening as well.

# 7. Conformational stability of MFSCB and MCSCB

Both the electron diffraction experiments as well as the ab initio calculations carried out in this work have shown that MFSCB and MCSCB occur in both the equatorial and axial forms with the equatorial conformer being more stable. From the experiment we obtained an eq:ax ratio of 85:15(5) for MFSCB and 83:17(6) for MCSCB. These values agree fairly well with those of 84:16(14) [2] and 71:29(21) [1] which we obtained from the microwave spectra some years ago. Both the MP2/6-31G<sup>\*\*</sup> and b3pw91/6-31G<sup>\*</sup> methods predicted 92% and 80%

	XY =	HBr <sup>a</sup>	XY =	= HI <sup>b</sup>	$X = Y = Br^{a}$	$X {=} Y {=} I^b$	
	Equatorial	Axial	Equatorial	Axial			
Si–C	1.8866	1.8890	1.8897	1.8905	1.8785	1.8845	
Si-X	2.2248	2.2269	2.4593	2.4600	< 2.2172 >	< 2.4546 >	
Si-H	1.4891	1.4911	1.4897	1.4915			
C–C	1.5623	1.5617	1.5838	1.5813	1.5637	1.5828	
H-Si-X	106.0	105.8	106.8	106.7			
X-Si-X					110.5	111.4	
C-Si-C	79.4	79.6	80.4	79.9	80.5	80.7	
C-C-Si	85.3	86.9	86.4	86.6	85.3	85.9	
C-C-C	101.0	101.4	100.8	100.3	101.8	101.1	
H-C <sub>2</sub> -H	109.0	108.4	109.5	109.5	109.2	109.8	
$H-C_3-H$	107.4	107.5	108.6	109.1	108.0	109.2	
Si-X <sub>ax</sub> (CSiC) <sub>plane</sub>		122.5		119.6	118.3	118.7	
Si-X <sub>eq</sub> (CSiC) <sub>plane</sub>	132.3		129.6		131.2	130.0	
$\theta^{c}$	32.8	24.7	26.7	27.7	29.2	27.2	
%eq	78.0		56.0				

Comparison between bond distances (Å) and bond angles (°) in monobromo-, monoiodo-, dibromo- and diiodo silacyclobutanes (CH2)3SiXY

<sup>a</sup> DFT (b3pw91/6-31G<sup>\*</sup>).

<sup>b</sup> DFT(b3pw91/3-21G\*).

<sup>c</sup> Puckering angle.

(Tables 3 and 4) for the equatorial form for MFSCB and MCSCB, respectively. The increased stability of the equatorial conformer with the increase of the electronegativity of the substituent is in full agreement with the J + B rules [4,5] which predict a linear relationship between the preferability of the equatorial conformer and the electronegativity of the substituent in monosubstituted cyclobutanes.

The behavior of the puckering angle  $\theta$  is particularly interesting. As is apparent from Tables 1 and 2, the observed puckering angle for the axial conformer  $\theta_{ax}$ is smaller than that for the equatorial conformer  $\theta_{eq}$  by about 12.7° and 13.9° for MCSCB and MFSCB, respectively. Also ab initio calculations (Tables 3 and 4) predict that  $\theta_{ax}$  is smaller than  $\theta_{eq}$  for both molecules (5° and 7° for the chloro and fluoro compounds, respectively). Considering the fairly large uncertainties associated with the experimental values, the agreement is satisfactory. Particularly interesting is the increase of the puckering angle in going from SCB to (MCSCB)<sub>eq</sub> to (MFSCB)<sub>eq</sub> and its subsequent narrowing in going to the dihalogenated derivatives, DCSCB and DFSCB (Table 5). Similarly, the calculated value for the puckering angle reaches its maximum for (MFSCB)eq and then drops down for DCSCB and DFSCB (Tables 3 and 4). While the increase of  $\theta_{eq}$  and the decrease of  $\theta_{ax}$  in going from SCB to MCSCB and MFSCB may be roughly rationalized by invoking the J + B rules, the further decrease of the puckering angle on dihalogenation is surprising. As we saw earlier, the ring Si-C bond shortens uniformly in this series. Thus, the irregular behavior of  $\theta$  is not easy to elucidate. A possible explanation is that the disubstitution at silicon with strong electronegative atoms (chlorine and fluorine) leads to a substantial increase of the positive charge at silicon affecting the Si-C bond polarity. As a result, a charge flow from the carbon atom opposite to silicon towards the highly positive center occurs, and the consequence is an accentuated 1,3-repulsion. To reduce the enhanced Dunitz-Schomaker strain [68-70] the ring flattens and the puckering angle becomes smaller.

For the purpose of more general and complete comparisons we also optimized the geometries of monobromosilacyclobutane (MBSCB), dibromosilacyclobutane (DBSCB), monoiodosilacyclobutane (MISCB) and diiodosilacyclobutane (DISCB) using the DFT/ b3pw91/6-31G<sup>\*</sup> basis set for the bromo derivatives and the same method with the 3-21G<sup>\*</sup> basis set for the

Table 11

iodo compounds. Table 11 summarizes the most important structural results obtained from these calculations. These results, in addition to those which are shown in Table 4 (where the same DFT method was applied), clearly point to the general systematical Si-C bond reduction with increasing electronegativity of the substituent. As can be seen from Table 11, the Si-C bond shortens by 0.0332, 0.0237, 0.0215 and 0.0155 Å in going from SCB to DFSCB, DCSCB, DBSCB and DISCB, respectively. Simultaneously, the Si-Br and Si-I bonds shorten upon dihalogenation. These findings signify once more the role of the electrostatic effects which imply the withdrawal of electrons by means of the electronegative substituents and the subsequent decrease in the silicon atomic radius leading to a shortening of all bonds associated with the central atom. From Tables 4 and 11 it can also be seen that the exocyclic X-Si-X bond angle continues to widen and the endocyclic C-Si-C bond angle continues to decrease in DBSCB and DISCB. Another feature emerges from comparing the puckering angle  $\theta$  in all silacyclobutanes displayed in Tables 4 and 11. Namely, in monohalogenated silacyclobutanes the puckering angle for the equatorial conformers is larger than the puckering angle in the parent molecule SCB but it is appreciably smaller for the axial forms. Additionally, while  $\theta_{eq}$  does not show any systematic behavior in correlation with the increased electronegativity of the substituent, the puckering angle  $\theta_{ax}$ , however, increases uniformly with decreasing electronegativity of the halogen atom. It is also noteworthy that the puckering angle for the dihalogenated compounds drops down drastically in comparison with the corresponding monohalogenated ones. The ring puckering angle, however, increases steadily from DFSCB to DBSCB. This increase of the ring puckering angle is probably due to the decrease of the electronegativity of the substituent (from F to Br) and thus the weakening of the 1,3 repulsion within the ring. It should be pointed out that the values for the iodo compounds which are displayed in Table 11 are not appropriate for the comparisons with the remaining data in Tables 4 and 11 since they have been obtained by using the basis set 3-21G\*. This basis set was used since no higher basis set is available for iodine. Finally, from Tables 4 and 11 it is seen that there is evidently a systematical correlation between the electronegativity of the halogen and the preferability of the equatorial conformer for the silacyclobutanes. The

higher stability of the equatorial conformer with the increase of the electronegativity of the substituent parallels the trend which was reported several years ago by J + B for a variety of monosubstituted cyclobutanes [4,5].

In conclusion, the present electron diffraction study has shown the following. First, the Si-C bond length in MFSCB and MCSCB shortens appreciably (by 0.040 and 0.031 Å, respectively) when compared with the parent molecule SCB. Second, the Si-F(Cl) bond contracts upon dihalogenation. Both of these may be explained using bonding concepts like negative hyperconjugation and  $3p\pi(Si)-2p\pi(C)$  orbital overlap. However, these features are most reasonably explicable by use of electrostatic arguments. Third, the experimental C-C bond length of 1.607(6) Å [21] in SCB is appreciably longer than the theoretically calculated value of 1.556 Å. Furthermore, the Si-C bond of 1.895(2) Å is evidently long. This discrepancy signifies that a reinvestigation of the structure of SCB is recommended. Fourth, the present study has shown that the higher the electronegativity of the substituent the more stable the equatorial conformer is which is in accord with the J + B rules. Fifth and finally, the silacyclobutane ring flattens upon proceeding from the mono- to dihalogenated derivatives and the puckering angle  $\theta$ achieves its minimum for DFSCB. This remarkable behavior is explained by the enhanced Dunitz-Schomaker strain (1,3 repulsion) as a result of the increase of the positive charge on silicon upon difluorination and the subsequent electron flow from the carbon atom opposite to silicon.

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