

## A theoretical study of structure and bonding of chlorinated silaethanes and 1,3-disilapropanes

Heinz Schiffer\* and Reinhart Ahlrichs

Institut für Physikalische Chemie und Elektrochemie, Lehrstuhl für Theoretische Chemie,  
Universität Karlsruhe, Kaiserstrasse 12, D-7500 Karlsruhe, Federal Republic of Germany

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Results of extended basis set treatments on the SCF level of theory are reported for all C-chlorinated, Si-chlorinated, symmetrically C- and Si-chlorinated silaethanes, and some chlorinated 1,3-disilapropanes. These molecules are considered as models for carbosilane compounds in general. Computed geometric structure constants are in good agreement with experiment as far as a comparison is possible. The stability and reactivity of molecules considered is discussed by means of computed bond distances, isodesmic reaction energies, and especially by results of population analysis. Si-chlorination yields a stabilization of the Si-C skeleton in carbosilanes whereas C-chlorination reduces this stability to a large extent.

**Key words:** Carbosilanes — Structure — Bonding — Population analysis

### 1. Introduction

Carbosilanes are compounds in which the molecular framework is exclusively build up by Si-C bonds like those in silicon carbide [1]. 1,3-disilapropane is the simplest member of this class of compounds: two silicon atoms are connected by one carbon atom to form a Si-C-Si arrangement for the molecular skeleton. The chemical behaviour of such compounds is strongly influenced by the substituents at the skeleton atoms [2]. For example, numerous experimental investigations [2] show a weakening of the Si-C bond in C-chlorinated carbosilanes while the Si-C bond in Si-chlorinated carbosilanes are very stable.

\* Present address: Hoechst Aktiengesellschaft, D-6230 Frankfurt am Main 80, FRG

Bond dissociation energies which are directly measured or indirectly derived from experimental standard heats of formation would provide the fundamental information on the strengths of Si-C bonds in carbosilanes. However, in the case of silicon-containing compounds such measurements are either missing or of an unreliable nature [3]. In theoretical treatments of bond dissociation energies one compares energies of a molecule with that of the separated fragments. Since the systems in question have quite different electronic structures, size-consistent CI (configuration interaction) treatments and large basis sets are required to compute bond dissociation energies of chemical accuracy (e.g. see [4]). Therefore, the application of such high level *ab initio* treatments are restricted to relatively small systems like the recently investigated fluorinated and chlorinated monosilanes [5].

In any case the description of a bond by a simple number like the bond dissociation energy is often of little help in getting an idea of the chemical behaviour of molecules. Trends for interatomic distances across a series of molecules are often more reliable indicators for stability and reactivity. Reliable structure constants for a large class of molecules can be obtained by SCF (self consistent field) calculations with basis sets of modest size [6]. Furthermore the SCF method yields at least a qualitatively correct description of the electronic structures for molecules in their electronic ground states in the vicinity of their equilibrium geometries. Hence, a population analysis can provide a very simple but helpful characterization of the electronic structure and yield additional information about covalent bond strengths and atomic charges [6].

In this article we present a systematic theoretical treatment of various chlorinated silaethanes and 1,3-disilapropanes at the SCF level of theory. As a consequence of computer time and above all storage requirements, we have to restrict our investigation mainly to the silaethanes as the simplest stable compounds with only one Si-C bond. Additional computations were performed for some chlorinated 1,3-disilapropanes to make sure that the silaethanes are suitable model systems for investigating substitution effects of chlorine on the Si-C bonds by the molecular skeleton of carbosilanes in general. These effects will be investigated by means of computed structure parameters, energies for isodesmic reactions, and with the aid of results of population analysis.

## 2. Details of computation

All computations were performed at the SCF level of theory with the Karlsruhe version [7] of the Columbus system [8] of programs. Geometry optimizations were carried out by the analytical calculation of the energy gradient together with a quasi-Newton method to find the equilibrium structures [9]. The following CGTO (contracted Gaussian type orbital) basis sets were employed:

Si, Cl	(11s, 7p, 1d)/[6, 4, 1]	$\eta_d(\text{Si}) = 0.40$ , $\eta_d(\text{Cl}) = 0.65$
C	(9s, 5p, 1d)/[5, 3, 1]	$\eta_d = 0.80$
H	(5s, 1p)/[3, 1]	$\eta_p = 0.75(\text{C})$ , $\eta_p = 0.433(\text{Si})$

The contraction pattern for the s-type GTOs of Si and Cl were: (521111). For the H atom a different exponent for the polarization function was used depending

on the type of directly connected neighbour atoms as indicated above. The primitive GTOs were taken from Huzinaga's table [10]. The basis set is of TZP (triple zeta with polarization) quality and yields structure parameters at the SCF level with errors of about  $\pm 1$  pm or  $\pm 1^\circ$  as a consequence of a rather systematic error cancellation, i.e. basis set incompleteness vs. the neglect of electron correlation. For bonds between third row atoms somewhat larger errors of about 2–3 pm may occur (see also [11]). The electronic structure is visualized by means of a population analysis based on occupation numbers [12]. Within this approach the electronic structure is characterized by atomic net charges  $Q(A)$  for atom  $A$  and the shared electron number (SEN)  $\sigma(A-B)$  for the  $A-B$  bond. The SENs have been shown to be reliable measures of covalent bond strengths [12].

### 3. Results and discussion

In Tables 1–4 we have collected the results for computed structure parameters in comparison with available experimental data and the total energies. The results of the population analysis are reported in Table 5–8. For comparison the corresponding data for methylsilane are given in all tables. All molecules considered in this work have equilibrium structures showing staggered conformations although the barriers for rotation about Si–C bonds are relatively small [14, 16, 18, 20].

#### 3.1. Comparison with experimental data

The general agreement between computed and experimental structure constants is quite satisfactory, as expected for the given level of theory and the size of the basis set employed. The computed Si–Cl bond lengths for all molecules considered in this work (Table 2) are about 2 pm longer than the experimental values. A

**Table 1.** Structure constants and total energies for the C-chlorinated silaethanes<sup>a</sup>

Parameter	SiH <sub>3</sub> CH <sub>3</sub> (C <sub>3v</sub> )	SiH <sub>3</sub> CH <sub>2</sub> Cl (C <sub>s</sub> )	SiH <sub>3</sub> CHCl <sub>2</sub> (C <sub>s</sub> )	SiH <sub>3</sub> CCl <sub>3</sub> (C <sub>3v</sub> )
$r(\text{Si}-\text{C})$	188.5 (186.4)	189.7 (188.9)	191.0	192.4
$r(\text{Si}-\text{H}^1)$	148.6 (148.2)	148.6 (147.7)	147.6	147.6
$r(\text{Si}-\text{H}^2)$	—	148.0	148.0	—
$\angle \text{CSiH}^1$	110.6 (110.4)	108.2	108.4	107.4
$\angle \text{CSiH}^2$	—	109.7	107.9	—
$\angle \text{H}^2\text{SiH}^2$	—	110.0 (110.6)	110.1	—
$r(\text{C}-\text{H})$	108.6 (109.5)	108.0 (109.6)	107.5	—
$r(\text{C}-\text{Cl})$	—	180.4 (178.8)	179.0	178.3
$\angle \text{SiCH}$	111.0 (110.4)	11.6 (109.3)	113.2	—
$\angle \text{SiCCl}$	—	110.6 (109.3)	110.2	109.7
$E_{\text{SCF}}$	–330.28462	–789.15040	–1248.01348	–1706.87014

<sup>a</sup> Distances are given in pm, angles in degrees, and energies in a.u. H atoms lying in the symmetry plane in the case of C<sub>s</sub> molecular symmetry are marked by H<sup>1</sup>. Experimental structure constants for SiH<sub>3</sub>CH<sub>3</sub> [13] and SiH<sub>3</sub>CH<sub>2</sub>Cl [14] are given in parentheses

**Table 2.** Structure constants and total energies for the Si-chlorinated silaethanes<sup>a</sup>

Parameter	CH <sub>3</sub> SiH <sub>3</sub> (C <sub>3v</sub> )	CH <sub>3</sub> SiH <sub>2</sub> Cl (C <sub>s</sub> )	CH <sub>3</sub> SiHCl <sub>2</sub> (C <sub>s</sub> )	CH <sub>3</sub> SiCl <sub>3</sub> (C <sub>3v</sub> )
<i>r</i> (Si-C)	188.5 (186.4)	187.1 (186.4)	185.9	185.1 (184.8)
<i>r</i> (C-H <sup>1</sup> )	108.6 (109.5)	108.7	108.4	108.5
<i>r</i> (C-H <sup>2</sup> )	—	108.5	108.5	—
∠SiCH <sup>1</sup>	111.0 (110.4)	110.0	111.0	110.4
∠SiCH <sup>2</sup>	—	111.0	110.4	—
∠H <sup>2</sup> CH <sup>2</sup>	—	108.3	108.5	—
<i>r</i> (Si-H)	148.6 (148.2)	147.8 (147.3)	146.9	—
<i>r</i> (Si-Cl)	—	207.8 (205.5)	206.2 (204.0)	204.8 (202.6)
∠CSiH	110.6 (110.4)	111.5 (111.0)	113.4	—
∠HSiH	—	109.7	—	—
∠CSiCl	—	109.3 (109.2)	109.8 (109.8)	110.5 (110.3)
∠ClSiCl	—	—	108.7 (108.8)	—
<i>E</i> <sub>SCF</sub>	-330.28462	-789.21841	-1248.15127	-1707.08097

<sup>a</sup> Distances are given in pm, angles in degrees, and energies in a.u. H atoms lying in the symmetry plane in the case of C<sub>s</sub> molecular symmetry are marked by H<sup>1</sup>. Experimental structure constants for CH<sub>3</sub>SiH<sub>3</sub> [13], CH<sub>3</sub>SiH<sub>2</sub>Cl [15], CH<sub>3</sub>SiHCl<sub>2</sub> [16], and CH<sub>3</sub>SiCl<sub>3</sub> [17] are given in parentheses

**Table 3.** Structure constants and total energies for the symmetrically C- and Si-chlorinated silaethanes<sup>a</sup>

Parameter	CH <sub>3</sub> SiH <sub>3</sub> (C <sub>3v</sub> )	CH <sub>2</sub> ClSiH <sub>2</sub> Cl (C <sub>s</sub> )	CHCl <sub>2</sub> SiHCl <sub>2</sub> (C <sub>s</sub> )	CCl <sub>3</sub> SiCl <sub>3</sub> (C <sub>3v</sub> )
<i>r</i> (Si-C)	188.5 (186.4)	188.5	189.7	191.9 (193.1)
<i>r</i> (C-H)	108.6 (109.5)	107.9	107.5	—
<i>r</i> (C-Cl)	—	180.2	178.4	177.8 (177.1)
∠SiCH	111.0 (110.4)	111.4	113.0	—
∠HCH	—	109.6	—	—
∠SiCCl	—	109.3	110.0	—
∠ClCCl	—	—	110.9	109.2 (109.9)
<i>r</i> (Si-H)	148.6 (148.2)	147.3	146.2	—
<i>r</i> (Si-Cl)	—	207.4	204.7	202.9 (201.4)
∠CSiH	110.6 (110.4)	110.7	110.6	—
∠HSiH	—	111.4	—	—
∠CSiCl	—	106.9	108.5	—
∠ClSiCl	—	—	108.9	109.9 (110.6)
<i>E</i> <sub>SCF</sub>	-330.28462	-1248.08376	-2165.87355	-3083.65145

<sup>a</sup> Distances are given in pm, angles in degrees, and energies in a.u. H atoms lying in the symmetry plane in the case of C<sub>s</sub> molecular symmetry are marked by H<sup>1</sup>. Experimental structure constants for SiH<sub>3</sub>CH<sub>3</sub> [13] and SiCl<sub>3</sub>CCl<sub>3</sub> [18] are given in parentheses

comparatively large error of about 2 pm is also found for the Si-C bond in methylsilane (see also [11]). With the exception of the SiCSi bond angle in 1,3-disilapropane (Table 4) and the structure constants for the CH<sub>2</sub>Cl moiety in monochloromethylsilane (Table 1) the computed structure parameters show errors of about ±1 pm or ±1° as far as a comparison with experiment is possible.

**Table 4.** Sturcutre constants and total energies for some chlorinated 1,3-disilapropanes<sup>a</sup>

Parameter	(SiH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> <sup>b</sup>	(SiH <sub>3</sub> ) <sub>2</sub> CCl <sub>2</sub>	(SiH <sub>2</sub> Cl) <sub>2</sub> CH <sub>2</sub>	(SiH <sub>2</sub> Cl) <sub>2</sub> CCl <sub>2</sub>
<i>r</i> (Si-C)	188.7 (187.4)	191.3	187.4	191.1
∠SiCSi	116.9 (114.1)	117.9	118.2	114.3
<i>r</i> (C-H)	108.9 (109.1)	—	108.8	—
<i>r</i> (C-Cl)	—	181.0	—	180.3
∠HCH	106.5 (107.3)	—	106.5	—
∠CICCl	—	109.2	—	110.0
∠(Si-H <sup>1</sup> )	148.5 (147.5)	147.6	—	—
<i>r</i> (Si-H <sup>2</sup> )	148.6 (147.7)	148.1	147.7	147.3
<i>r</i> (Si-Cl)	—	—	207.3	204.8
∠CSiH <sup>1</sup>	111.1 (111.2)	108.3	—	—
∠CSiH <sup>2</sup>	110.3 (109.9)	108.3	111.4	108.5
∠H <sup>2</sup> SiH <sup>2</sup>	108.0 (108.6)	109.7	109.7	110.5
∠CSiCl	—	—	109.1	110.7
<i>E</i> <sub>SCF</sub>	-620.36174	-1538.08442	-1538.22768	-2455.94054

<sup>a</sup> All molecules given in this table have equilibrium structures showing C<sub>2v</sub> symmetry. Distances are given in pm, angles in degrees, and energies in a.u. H atoms lying in the symmetry plane are marked by H<sup>1</sup>.

<sup>b</sup> Experimental structure constants [19] are given in parentheses

**Table 5.** Results of the population analysis for the C-chlorinated silaethanes<sup>a</sup>

Parameter	SiH <sub>3</sub> CH <sub>3</sub> (C <sub>3v</sub> )	SiH <sub>3</sub> CH <sub>2</sub> Cl (C <sub>s</sub> )	SiH <sub>3</sub> CHCl <sub>2</sub> (C <sub>s</sub> )	SiH <sub>3</sub> CCl <sub>3</sub> (C <sub>3v</sub> )
σ(Si-C)	1.38	1.31	1.25	1.22
σ(Si-H <sup>1</sup> )	1.41	1.41	1.43	1.42
σ(Si-H <sup>2</sup> )	—	1.42	1.42	—
<i>Q</i> (Si)	+0.51	+0.51	+0.51	+0.51
<i>Q</i> (H <sub>1</sub> )	-0.12	-0.12	-0.10	-0.10
<i>Q</i> (H <sub>2</sub> )	—	-0.11	-0.11	—
σ(C-H)	1.43	1.41	1.39	—
σ(C-Cl)	—	1.05	1.06	1.07
<i>Q</i> (C)	-0.29	-0.16	-0.07	+0.01
<i>Q</i> (H)	+0.05	+0.05	+0.06	—
<i>Q</i> (Cl)	—	-0.11	-0.09	-0.07

<sup>a</sup> *Q*: atomic charge, σ: shared electron number (SEN). H atoms lying in the symmetry plane are marked by H<sup>1</sup>

The experimental values are obtained by different methods such as microwave spectroscopy or electron diffraction and are not directly comparable without further processing. The theoretical values are all computed at the same level of theory and one therefore expects rather systematic errors. Changes in interatomic distances should be predicted with great accuracy although absolute errors be a few pm.

**Table 6.** Results of the population analysis for the Si-chlorinated silaethanes<sup>a</sup>

Parameter	CH <sub>3</sub> SiH <sub>3</sub> (C <sub>3v</sub> )	CH <sub>3</sub> SiH <sub>2</sub> Cl (C <sub>s</sub> )	CH <sub>3</sub> SiHCl <sub>2</sub> (C <sub>s</sub> )	CH <sub>3</sub> SiCl <sub>3</sub> (C <sub>3v</sub> )
$\sigma(\text{Si}-\bar{\text{C}})$	1.38	1.37	1.36	1.33
$\sigma(\text{C}-\text{H}^1)$	1.43	1.42	1.43	1.43
$\sigma(\text{C}-\text{H}^2)$	—	1.43	1.42	—
Q(C)	-0.29	-0.30	-0.30	-0.30
Q(H <sub>1</sub> )	+0.05	+0.04	+0.06	+0.06
Q(H <sub>2</sub> )	—	+0.06	+0.05	—
$\sigma(\text{Si}-\text{H})$	1.41	1.38	1.34	—
$\sigma(\text{Si}-\text{Cl})$	—	1.08	1.08	1.08
Q(Si)	+0.51	+0.65	+0.75	+0.83
Q(H)	-0.12	-0.12	-0.11	—
Q(Cl)	—	-0.27	-0.25	-0.23

<sup>a</sup> Q: atomic charge,  $\sigma$ : shared electron number (SEN). H atoms lying in the symmetry plane are marked by H<sup>1</sup>

**Table 7.** Results of the population analysis for the symmetrically C- and Si-chlorinated silaethanes<sup>a</sup>

Parameter	CH <sub>3</sub> SiH <sub>3</sub> (C <sub>3v</sub> )	CH <sub>2</sub> ClSiH <sub>2</sub> Cl (C <sub>s</sub> )	CHCl <sub>2</sub> SiHCl <sub>2</sub> (C <sub>s</sub> )	CCl <sub>3</sub> SiCl <sub>3</sub> (C <sub>3v</sub> )
$\sigma(\text{Si}-\text{C})$	1.38	1.30	1.21	1.12
$\sigma(\text{C}-\text{H})$	1.43	1.41	1.39	—
$\sigma(\text{C}-\text{Cl})$	—	1.05	1.07	1.09
Q(C)	-0.29	-0.17	-0.10	-0.05
Q(H(C))	+0.05	+0.06	+0.07	—
Q(Cl(C))	—	-0.12	-0.08	-0.05
$\sigma(\text{Si}-\text{H})$	1.41	1.39	1.34	—
$\sigma(\text{Si}-\text{Cl})$	—	1.09	1.12	1.12
Q(Si)	+0.51	+0.64	+0.72	+0.77
Q(H(Si))	-0.12	-0.11	-0.10	—
Q(Cl(Si))	—	-0.26	-0.22	-0.19

<sup>a</sup> Q: atomic charge,  $\sigma$ : shared electron number (SEN). H atoms lying in the symmetry plane are marked by H<sup>1</sup>

### 3.2. The Si-C bond in the C-chlorinated silaethanes

We found a steadily increasing Si-C bond distance in going from methylsilane to trichloromethylsilane (by 3.9 pm) (Table 1). The Si-C bond distance in trichloromethylsilane is nearly exactly the same as in the recently investigated [21] trifluoromethylsilane CF<sub>3</sub>SiH<sub>3</sub> ( $r(\text{Si}-\text{C}) = 192.3$  pm [21]). Longer Si-C bonds are only found in alkyl substituted silicon compounds with considerable steric

**Table 8.** Results of the population analysis for the some chlorinated 1,3-disilapropanes<sup>a</sup>

Parameter	(SiH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub>	(SiH <sub>3</sub> ) <sub>2</sub> CCl <sub>2</sub>	(SiH <sub>2</sub> Cl) <sub>2</sub> CH <sub>2</sub>	(SiH <sub>2</sub> Cl) <sub>2</sub> CCl <sub>2</sub>
$\sigma(\text{Si-C})$	1.37	1.25	1.35	1.23
$\sigma(\text{C-H})$	1.42	—	1.43	—
$\sigma(\text{C-Cl})$	—	1.05	—	1.08
$Q(\text{C})$	-0.46	-0.25	-0.49	-0.30
$Q(\text{H}(\text{C}))$	+0.07	—	-0.08	—
$Q(\text{Cl}(\text{C}))$	—	-0.09	—	-0.06
$\sigma(\text{Si-H}^1)$	1.40	1.42	1.38	1.38
$\sigma(\text{Si-H}^2)$	1.41	1.42	—	—
$\sigma(\text{Si-Cl})$	—	—	1.08	1.13
$Q(\text{Si})$	+0.52	+0.52	+0.65	+0.64
$Q(\text{H}^1(\text{Si}))$	-0.12	-0.09	-0.12	-0.11
$Q(\text{H}^2(\text{Si}))$	-0.12	-0.11	—	—
$Q(\text{Cl}(\text{Si}))$	—	—	-0.25	-0.21

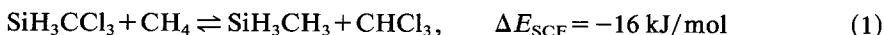
<sup>a</sup>  $Q$ : atomic charge,  $\sigma$ : shared electron number (SEN). H atoms lying in the symmetry plane are marked by H<sup>1</sup>

strain such as Si<sub>2</sub><sup>1</sup>-Bu<sub>6</sub> ( $r(\text{Si-C}) = 199$  pm [22]). Lengthening of the Si-C bond indicates decreasing bond strength and, therefore, reduced stability and enhanced reactivity: neither di- nor tri-chloromethylsilane has yet been synthesized and trifluoromethylsilane has only been synthesized very recently [23].

A similar state of affairs is shown by the results of the population analysis (Table 5). The SENs of the Si-C bonds, which are a measure of covalent contributions to bond strength, decrease slightly from 1.38 for CH<sub>3</sub>SiH<sub>3</sub> to 1.22 for CCl<sub>3</sub>SiH<sub>3</sub> and therefore parallel the trend found for the bond distances. In methylsilane there are stabilizing ionic contributions to the Si-C bond ( $Q(\text{Si}) = +0.51$ ,  $Q(\text{C}) = -0.29$ ) which become slightly destabilizing in trichloromethylsilane ( $Q(\text{Si}) = +0.51$ ,  $Q(\text{C}) = +0.01$ ).

A further indication of the instability of trichloromethylsilane is the short intramolecular non-bonding Cl...Cl distance of 290.7 pm, considerably shorter than the van der Waals distance of 360 pm [24]. One therefore suspects considerable steric repulsion in the CCl<sub>3</sub> group in trichloromethylsilane. This repulsion is reduced in the free CCl<sub>3</sub> radical molecule which has a larger intramolecular non-bonding Cl...Cl distance and a considerably shorter C-Cl bond ( $r(\text{C-Cl}) = 172.4$  pm,  $r(\text{Cl...Cl}) = 292.6$  pm [25]). This reduction in intramolecular Pauli-type repulsion energy for the CCl<sub>3</sub> group on dissociation of the Si-C bond of trichloromethylsilane should provide a further contribution to the relative instability of this molecule or, equivalently, to the weakening of the Si-C bond.

The trends in computed bond distances and the results of the population analysis clearly indicate a weakening of the Si-C bond by C-chlorination of the corresponding silaethanes. Using the reaction energy obtained at the SCF level for the isodesmic reaction, Eq. (1)



one gets at least a rough estimate of the bond dissociation energy for the Si-C bond in trichloromethylsilane. Since all reactants and products have a closed shell structure, and the number and type of the bonds remain constant, the reaction energy can be computed reliably at the SCF level. The SCF energies of  $\text{SiH}_3\text{CCl}_3$  and  $\text{SiH}_3\text{CH}_3$  are taken from Table 1, the corresponding energies for  $\text{CH}_4$  and  $\text{CHCl}_3$  are taken from [26]. The known bond dissociation energies are [27]:  $D(\text{CH}_3\text{-H}) = 440 \text{ kJ/mol}$ ,  $D(\text{CCl}_3\text{-H}) = 401 \text{ kJ/mol}$ , and  $D(\text{SiH}_3\text{-CH}_3) = 369 \text{ kJ/mol}$ . If we neglect the zero point energy contributions we get for the desired bond dissociation energy

$$D(\text{SiH}_3\text{-CCl}_3) \approx 314 \text{ kJ/mol}$$

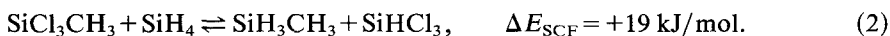
which is 55 kJ/mol lower than for methylsilane.

### 3.3. The Si-C bond in the Si-chlorinated silaethanes

In contrast to the C-chlorinated silaethanes (Sect. 3.2) Si-chlorination of the silaethanes (Table 2) yields a shortening of 3.4 pm in the Si-C bond distance in going from methylsilane to trichlorosilylmethane indicating increased bond strength and stability. Therefore, it is not unexpected that all molecules in Table 2 have been synthesized and are well known. The population analysis (Table 6) shows for the SENs of Si-C bonds a minor decrease of 0.05 in going from methylsilane to trichlorosilylmethane. This indicates roughly constant or even slightly decreasing covalent contributions to Si-C bonds; the computed shortening of bond distances has to be attributed to increasing ionic contributions.

The electron withdrawl by chlorine substituents yields in trichlorosilylmethane a relatively high positive charge of +0.83 on the silicon atom. In order to estimate the ionic contributions we have used the atomic charges obtained from the population analysis to compute the Coulomb-type interactions for the Si-C bond, and all the non-bonding atom pair combinations between the silyl and methyl groups in the silaethanes. These Coulomb-type interactions contribute 62 kJ/mol to the dissociation energy of the Si-C bond in trichlorosilylmethane, 24 kJ/mol more than in methylsilane. We note in passing that the same procedure yields a reduction of only 14 kJ/mol for the Coulomb-type contributions to the Si-C bond dissociation energy in methylsilane compared with that in trichloromethylsilane (Sect. 3.2).

Si-chlorination of silaethanes should result in a strengthening of the Si-C bonds as indicated by trends in computed bond distances and the results of population analysis. As in Sect. 3.2 we can estimate the bond dissociation energy for the Si-C bond in trichlorosilylmethane with the aid of an isodesmic reaction, Eq. (2)



The SCF energies of  $\text{SiCl}_3\text{CH}_3$  and  $\text{SiH}_3\text{CH}_3$  are taken from Table 2, the corresponding energies for  $\text{SiH}_4$  and  $\text{SiHCl}_3$  are taken from [26]. The known bond dissociation energies are:  $D(\text{SiH}_3\text{-H}) = 378 \text{ kJ/mol}$  [28],  $D(\text{SiCl}_3\text{-H}) = 382 \text{ kJ/mol}$  [29], and  $D(\text{SiH}_3\text{-CH}_3)$  as in Sect. 3.2. By neglecting zero point



energy contributions we get

$$D(\text{SiCl}_3\text{-CH}_3) \approx 392 \text{ kJ/mol.}$$

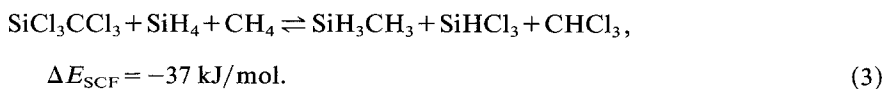
The dissociation energy of the Si-C bond is therefore estimated to be 23 kJ/mol higher for trichlorosilylmethane than for methylsilane, which is close to the estimate for the ionic contributions alone (24 kJ/mol, see above). These results provide evidence for the simple picture that the enhanced ionic contributions in the Si-chlorinated silaethanes are responsible for the higher stability of these compounds compared with methylsilane. Compared with C-chlorinated silaethanes there are only negligible steric repulsions in the chlorinated silylgroups because of considerably larger intramolecular non-bonding Cl...Cl distances ( $r(\text{Cl}\cdots\text{Cl}) = 332.3 \text{ pm}$  for  $\text{SiCl}_3\text{-CH}_3$ ).

### 3.4. The Si-C bond in the symmetrically Si- and C-chlorinated silaethanes

By simultaneous chlorination at the Si and C atoms of silaethanes we found a lengthening of the Si-C bond in going from methylsilane to hexachlorosilaethane (Table 3). The effect is less pronounced than for C-chlorinated silaethanes, the Si-C bond length for 1,2-dichlorosilaethane is the same as for methylsilane, and lengthening just occurs for 1,1,2,2-tetra-chlorosilaethane and further for hexachlorosilaethane.

The population analysis (Table 7) shows the largest decrease for the SENs of the Si-C bonds hitherto found for the molecules of this work: from 1.38 for  $\text{CH}_3\text{SiH}_3$  to 1.12 for  $\text{CCl}_3\text{SiCl}_3$ . This indicates a weakening of covalent bond strength on symmetric chlorination of silaethane. We can only offer the following rationalization for this fact. The change in charges  $Q(\text{C})$  and  $Q(\text{Si})$  on symmetric chlorination ( $Q(\text{C})$  changes from  $-0.29$  to  $-0.05$  and  $Q(\text{Si})$  from  $+0.51$  to  $+0.77$  in going from  $\text{CH}_3\text{SiH}_3$  to  $\text{CCl}_3\text{SiCl}_3$ , Table 7) reduces the attractive Coulomb forces between C and Si. This leads to an increase in the Si-C distance which reduces covalent bond strength since overlap between the atomic orbitals involved in bonding is reduced. In contrast to the C-chlorination of silaethane we now find, however, an almost constant (variation of a few kJ/mol) energetic Coulomb interaction of  $\text{CH}_n\text{Cl}_{3-n}$  and  $\text{SiH}_n\text{Cl}_{3-n}$  for  $n = 0, 1, 2, 3$ . (This is no contradiction to the force argument since force and energy obey different power laws,  $r^{-2}$  and  $r^{-1}$ , respectively.)

In order to get an estimate of Si-C bond strength we use again an isodesmic reaction, Eq. (3)



The corresponding SCF energies are taken from Table 3 and [26]. Equation (3) leads to a dissociation energy in hexachlorosilaethane

$$D(\text{SiCl}_3\text{-CCl}_3) \approx 297 \text{ kJ/mol,}$$

(where zero point energies are again neglected) which is 72 kJ/mol smaller than in methylsilane. In contrast to the isodesmic reactions (1) and (2), we further find for (3) a non-negligible effect of attractive intermolecular dispersion-type (van der Waals) interactions which are, of course, neglected at the SCF-level. An estimate of this van der Waals-type contribution to the reaction energy can be obtained by the method of Slater and Kirkwood [31] and yields for Eqs. (1) and (2)  $\Delta E_{vdw} \approx 0$ , as already indicated above, and for Eq. (3)  $\Delta E_{vdw} = 20$  kJ/mol. By correcting  $\Delta E_{SCF}$  of Eq. (3) using  $\Delta E_{vdw}$  we estimate the dissociation energy of the Si-C bond in hexachlorosilaethane

$$D(\text{SiCl}_3\text{-CCl}_3) \approx 317 \text{ kJ/mol.}$$

Therefore the Si-C bond dissociation energy in hexachlorosilaethane is  $\approx 52$  kJ/mol lower than in methylsilane. This reduction has to be attributed mainly to decreasing covalent bond strength resulting from changes in Coulomb forces.

### 3.5. Comparison with some 1,3-disilapropanes

The investigations of substituents effects by chlorine on the Si-C bond in silaethanes in Sects. 3.2-3.4 were done to get a better understanding of these effects for carbosilanes in general. In the present section we will check the conclusions found for the silaethanes by considering some chlorinated 1,3-disilapropanes.

The computed structure constants (Table 4) show the same trends as found for the silaethanes. C-chlorination yields a lengthening, Si-chlorination a shortening, and simultaneous C- and Si-chlorination again a lengthening of the Si-C bond distances, as found in the corresponding silaethanes. The same picture emerges for trends in results of population analysis (Table 8). In absolute numbers the ionic contributions to bonding for the 1,3-disilapropanes are more pronounced than for the silaethanes. This is demonstrated by the relatively large negative charge of the C atom in 1,3-disilapropane ( $Q(\text{C}) = -0.46$ ) compared with methylsilane ( $Q(\text{C}) = -0.29$ ). Even the charge of C in disilyldichloromethane is comparatively large,  $Q(\text{C}) = -0.25$ .

Due to the relatively pronounced ionic contributions, the Si-C bonds in carbosilanes are quite stable and help to rationalize the high thermodynamic stability of this class of compounds. C-chlorination yields a weakening of Si-C bonds and therefore reduces this stability. On the other hand Si-chlorination increases Si-C bond strengths and therefore stabilizes the Si-C skeleton of carbosilanes.

## 4. Summary

The chlorination of silaethanes has a pronounced influence on the stability and reactivity of the Si-C bond. With the aid of isodesmic reactions we can order the Si-C bonds according to their dissociation energies in the following way:

$$D(\text{SiCl}_3\text{-CH}_3) > D(\text{SiH}_3\text{-CH}_3) > D(\text{SiCl}_3\text{-CCl}_3) \approx D(\text{SiH}_3\text{-CCl}_3).$$

Computed bond distances and results of population analysis give a consistent picture which allows the rationalization of the trends observed.

C-chlorination yields a lengthening of corresponding Si-C bonds and therefore a decrease of covalent bond strength which is also reflected by trends for computed SENs. The lower dissociation energy of the Si-C bond in C-chlorinated silaethanes is in part due to unfavourable intramolecular non-bonding Pauli-type repulsions between Cl atoms connected to C atoms. For the C-chlorinated silaethanes, additional destabilizations arise from ionic contributions.

Si-chlorination yields a shortening of corresponding Si-C bonds; enhanced stabilizing ionic contributions to the bonding are responsible for higher stability of these compounds. Consideration of some chlorinated 1,3-disilapropanes led to the same conclusions as had the silaethanes. Thus the above conclusions about the behaviour of silaethanes can be applied in general to the chlorination of the molecular skeleton of carbosilanes.

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