Trifluoromethylated Compounds with SiNN and SiON Backbone, and the Crystal Structures of Trimethyl- and Trichloro(trifluoromethyl)silane

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Dedicated to Professor Otto J. Scherer on the occasion of his 75th birthday

The reaction of $(F_3C)Cl_2SiCl_3$ with the lithiated hydrazine $LiN(Me)NMe_2$ gives the compound $(F_3C)Cl_2SiN(Me)NMe_2$ (**1**) and in traces $Cl_3SiN(Me)NMe_2$ (**2**). The reactions with $LiN(SiMe_3)NMe_2$ and $LiONMe_2$ give $(F_3C)Cl_2SiN(SiMe_3)NMe_2$ (**4**) and $(F_3C)Cl_2SiONMe_2$ (**5**), respectively. The compounds were characterised by multinuclear solution NMR, gas-phase IR spectroscopy and mass spectrometry. Information about conformational preferences of **1** and **4** can be extracted by comparing experimental IR spectra with those calculated by quantum chemical methods (B3LYP/6-311G**). The former show the gas phase of the β-donor-acceptor silanes **1** and **4** to be dominated by the *anti* conformations, while the calculations show a preference for the *gauche* conformers. The crystal structure of $Cl_3SiN(Me)NMe_2$ (**2**) has been determined. The solid-state structures of the Ruppert reagent $F_3C–SiMe_3$ (**1**) and its chlorine analogue $F_3C–SiCl_3$ (**2**) have also been determined by X-ray diffraction of single crystals grown by *in situ* techniques.

Key words: Silicon, Trifluoromethylsilanes, Hydroxylamine, Hydrazine, Crystal Structure, Quantum Chemical Calculations

Introduction

Due to the importance of organofunctional silanes in a widespread range of industrial applications [1] the investigation of small model systems is important for an understanding of the nature of bonding in this class of substances. Whereas the gross of organofunctional silanes are those with an alkoxysubstituted silane unit linked to the donor moiety by a propylene spacer [2] [*e. g.* $(MeO)_3SiCH_2CH_2CH_2NMe_2$], in recent years systems with shorter linkers have rapidly gained importance [3]. They are called the α-silanes, and their increased reactivity is said to be due to the α-effect [4], a postulate stemming from the 60'ies, interpreting the increased reactivity at silicon by an intramolecular dative bond between this and the donor atom.

We recently contributed some model studies to this field, which showed that in the ground state compounds with SiCN backbone do not show this type of donor-acceptor interactions [5], but are classical open chain systems. However, they have a very shallow bending potential at the linking carbon atom. In contrast, compounds with longer chains between the Si and N atoms, and even with very weak acceptor ability of the silyl groups, exist in conformations with dative bonds. Examples of such compounds include $H_3SiCH_2CH_2CH_2NMe_2$ [6] and the chlorosilanes $Cl_3SiOCH_2CH_2NMe_2$ and $Cl_2HSiOCH_2CH_2NMe_2$ [7].

While the absence of three-membered rings was demonstrated for SiCN systems in their ground states, the situation is completely different in SiNN [8] and SiON systems [9 – 12], where three-membered rings with dative bonds are a common motif. Depending on the acceptor quality of the silyl group, there can be strong interactions between silicon and geminal nitrogen atoms. The strongest interaction of this type found so far was detected in the solid state and gas phase of the trifluoromethyl compound $(F_3C)F_2SiONMe_2$ [12], which has – in the solid state – an SiON angle of 74.1(1)° and an Si–N distance of 1.904(2) Å. The latter is shorter than the Si–C bond to the CF_3 group at 1.912(2) Å. This proves that CF_3 groups have a strong electron withdrawing effect, but no capability for back-bonding, and thus lead to stronger interactions of the silicon atom with donors than analogous F-substituted systems. For this reason we intended to inves-

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tigate the conformational preference of the F_3C group and the electronic influence of F_3C substitution at otherwise chloro-substituted silicon atoms on their ability to interact with geminal nitrogen atoms.

Here we present some results for compounds with SiNN and SiON backbones and $(F_3C)Cl_2Si$ groups as acceptor sites. The starting material for such $(F_3C)Cl_2Si$ compounds is obviously the silane $F_3C–SiCl_3$. For this reason, we also determined the crystal structures of this reagent and for comparison that of the Ruppert reagent $F_3C–SiMe_3$ [13].

Results and Discussion

A usual complication that occurs in trifluormethylsilane chemistry is the formation of difluorocarbene F_2C: units leaving an Si–F function, which is again reactive towards nucleophilic substitution. The application of low-temperature protocols is therefore advisable.

*Synthesis and characterisation of $(F_3C)Cl_2SiN(Me)NMe_2$ (**1**), $Cl_3SiN(Me)NMe_2$ (**2**), $(F_3C)Cl_2SiN(SiMe_3)NMe_2$ (**3**) and $(F_3C)Cl_2SiONMe_2$ (**4**)*

$(F_3C)Cl_2SiN(Me)NMe_2$ (**1**) and $(F_3C)Cl_2SiN(SiMe_3)NMe_2$ (**3**) were prepared from lithiated *N*,*N′*,*N′*-trimethylhydrazine (Eq. 1) and *N*-trimethylsilyl-*N′*,*N′*-dimethylhydrazine with trifluoromethyltrichlorosilane (**5**) (Eqs. 2 and 3). Small amounts of $SiCl_4$ in the reagent F_3CSiCl_3 (**5**) lead also to the formation of $Cl_3SiN(Me)NMe_2$ (**2**), which could be isolated by extraction of the lithium chloride residue of the reaction described in Eq. 2.

$$\begin{aligned}&\mathrm{HN(R)NMe_2} + n\text{-}\mathrm{BuLi} \rightarrow \\ &\mathrm{LiN(R)NMe_2} + n\text{-}\mathrm{BuH}\ (\mathrm{R} = \mathrm{Me, SiMe_3})\end{aligned} \tag{1}$$

$$\begin{aligned}&\mathrm{F_3CSiCl_3}\ (\mathbf{5}) + \mathrm{LiN(Me)NMe_2} \rightarrow \\ &\mathrm{(F_3C)Cl_2Si–N(Me)NMe_2}\ (\mathbf{1}) \\ &+ \mathrm{LiCl}[+\mathrm{Cl_3SiN(Me)NMe_2}\ (\mathbf{2})]\end{aligned} \tag{2}$$

$$\begin{aligned}&\mathrm{F_3CSiCl_3}\ (\mathbf{5}) + \mathrm{LiN(SiMe_3)NMe_2} \rightarrow \\ &\mathrm{(F_3C)Cl_2SiN(SiMe_3)NMe_2}\ (\mathbf{3}) + \mathrm{LiCl}\end{aligned} \tag{3}$$

Dichloro(trifluoromethyl)(*N*,*N*-dimethylaminoxy)silane (**4**) was synthesised in analogy to **1** and **2** from $LiONMe_2$ and F_3CSiCl_3 in good yields (Eqs. 4, 5)

$$\begin{aligned}&\mathrm{HONMe_2} + n\text{-}\mathrm{BuLi} \rightarrow \\ &\mathrm{LiONMe_2} + n\text{-}\mathrm{BuH}\end{aligned} \tag{4}$$

$$\begin{aligned}&\mathrm{F_3C–SiCl_3}\ (\mathbf{5}) + \mathrm{LiONMe_2} \rightarrow \\ &\mathrm{(F_3C)Cl_2SiONMe_2}\ (\mathbf{4}) + \mathrm{LiCl}\end{aligned} \tag{5}$$

Compounds **1**, **2**, **3**, and **4** are sensitive to hydrolysis. **1** and **2** ignite spontaneously in moist air. Compound **1** was isolated in modest yields (33 %) as a colourless liquid by fractional condensation through a series of cold traps under vacuum. It was retained in a trap at −20 °C and was characterised by gas-phase IR and solution NMR spectroscopy (^{1}H, ^{13}C, ^{19}F, ^{29}Si) and mass spectrometry. We were so far unable to determine a crystal structure of **1**, as crystals deteriorated quickly and never survived mounting, neither under inert perfluoropolyether nor under inert gas in capillaries. Attempts to grow good quality crystals of **1** *via* the *in situ* OHCD technique (a laser-driven microscale zone refinement procedure [14]) were also unsuccessful. The resulting specimen led to a diffraction data quality that did not allow a meaningful structure solution.

The small amounts of **2**, obtained as a side-product, allowed its characterisation by ^{1}H and ^{13}C NMR spectroscopy and by determination of its crystal structure. Compound **3** was purified by vacuum distillation at a temperature of 60 °C at 0.01 mbar, but the yield obtained was low (9 %). It was characterised by solution NMR spectroscopy (^{1}H, ^{13}C, ^{19}F, ^{29}Si) and by mass spectrometry.

Compound **4** could be isolated by fractional condensation through a series of cold traps at a temperature of −40 °C as a colourless liquid, which is extremely sensitive to moisture. The compound also tends to decompose at ambient temperature giving an insoluble product [probably $(CF_2)_\infty$ from CF_2 elimination]. Neither crystallisation in the freezer (cooling the neat substance or solutions in pentane and ether) nor *in situ* techniques made it possible to obtain crystalline material of this compound. It always solidifies in a vitreous style.

NMR spectra

The ^{1}H NMR spectra of **1** and **3** show diagnostic signals for the methylamino groups at δ = 2.51 and 2.66 (**1**) and at 2.51 ppm (**3**). The corresponding signals in the ^{13}C NMR spectra are those at δ = 21.5 and 42.3 ppm, and at 47.6 ppm, and the CF_3 groups in **1** and **3** give rise to quartets at 125 ppm with $^1J_{CF}$ coupling constants of 317 and 315 Hz, respectively. These groups are also detectable in the ^{19}F NMR spectrum at around −66 ppm. Low-field shifted signals are ob-

Compound	1		3		4	
formula	$(F_3C)Cl_2SiN(Me)NMe_2$		$(F_3C)Cl_2SiN(SiMe_3)NMe_2$		$(F_3C)Cl_2SiONMe_2$	
Sp	N		N		O	
	anti	*gauche*	*anti*	*gauche*	*anti*	*gauche*
$\angle$ Si–Sp–N (α)	104.5	101.9	82.4	87.4	101.3	92.5
$\angle$ Si/C–Sp–N (β)	120.9	121.3	127.4	128.1		
$\angle$ Si–Sp–C/Si (γ)	134.6	136.3	146.6	142.2		
$\Sigma(\alpha,\beta,\gamma)$	360.0	359.5	356.4	357.7		
$\angle$ C–N–C	112.2	112.1	112.0	111.8	110.2	111.3
d(Si···N)	2.467	2.421	2.100	2.192	2.417	2.267
d(Sp···N)	1.427	1.427	1.475	1.466	1.473	1.479
d(N–C)	1.461	1.462	1.460	1.459	1.459	1.460
d(Si–C4)	1.923	1.925	1.941	1.940	1.917	1.925
d(Si–Sp)	1.685	1.684	1.703	1.697	1.649	1.656
E_{MP2}	−1774.02713	−1774.02927	−2143.87065	−2143.87232	−1754.68582	−1754.68729
E_{rel}	5.6	0	4.4	0	3.9	0

Table 1. Calculated structural parameters (MP2/6-311G**) of compounds **1**, **2** (Sp = N) and **3** (Sp = O) (angles in deg, distances in Å, absolute energies in Hartrees (E_{MP2}), and relative energies (E_{rel}) in kJ mol^{-1}).

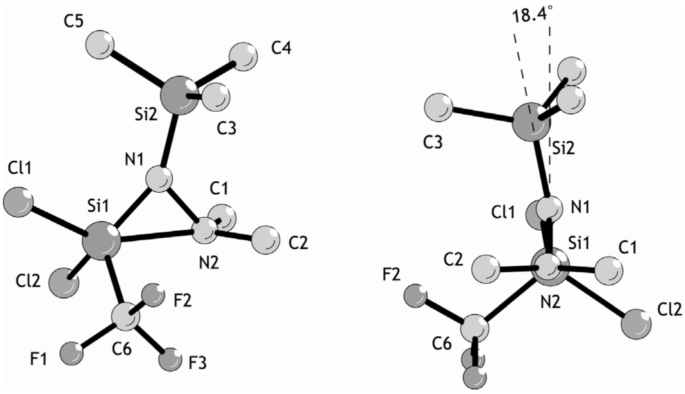

Fig. 1. Calculated structure of the *gauche* conformer of $F_3C–SiCl_2–N(SiMe_3)NMe_2$ (**3**) and a view along the N2–Si1 vector illustrating the geometry at the N spacer. Hydrogen atoms are omitted for clarity.

served in the ^{29}Si NMR spectrum at $\delta = -53.4$ (**1**) and -66.7 ppm (**3**).

The signals for the NMe_2 group of **4** are found in the ^{1}H NMR spectrum at δ = 2.90 ppm and in the ^{13}C NMR spectrum at δ = 49.3 ppm. A quartet at 125 ppm with a coupling constant of 315 Hz ($^1J_{CF}$) proves the presence of a CF_3 group. This group shows a distinguishing shift in the ^{19}F NMR spectrum of −66.6 ppm. The ^{29}Si NMR spectrum contains a low-field shifted signal at $\delta = -66.3$ ppm, to be compared with the value of $(F_3C)F_2SiONMe_2$ [12]: $\delta = -116.8$ ppm.

A further interesting detail for **4** is the ^{15}N NMR resonance of the NMe_2 group at a chemical shift of $\delta = -241.2$ ppm, which is shifted more than 8 ppm to high field compared to the signal for $F_3SiONMe_2$ (−249.2 ppm) [12], and 23 ppm to high field with respect to $(F_3C)F_2SiONMe_2$ (−264.1 ppm) [12].

Quantum chemical calculations

As experimental structure determinations by means of crystal X-ray diffraction failed for compounds **1**, **3** and **4**, we undertook quantum chemical calculations up to the MP2/6-311G** level of theory, which proved earlier to give reliable estimates for these classes of compounds [15]. The structural results are compiled in Table 1, the structures are shown in Fig. 1. For compound **1** an Si···N distance of 2.467 Å and an SiNN angle of 104.5° are predicted for the *anti* conformer. The *gauche* conformer which is calculated to be 5.6 kJ mol^{-1} more stable than the *anti* conformer shows a slightly stronger interaction between the acceptor and the donor function as indicated by an SiNN angle of 101.9° and an Si···N distance of 2.421 Å. It remains unclear whether this is due to a higher apicophilicity [16] of the chlorine substituents or to differences in the repulsion between the CF_3 and Cl groups on one and the methyl groups at nitrogen on the other side. Interestingly, the *gauche* conformation of **1** shows an even stronger interaction between Si and N2 than that found in the crystal structure of $F_3SiN(Me)NMe_2$ (XRD: $\angle$SiNN = 104.1(1)°, d(Si···N) = 2.436(1) Å, MP2/6-311G**: $\angle$SiNN = 106.4°, d(Si···N) = 2.493 Å) [8b]. This may sur-

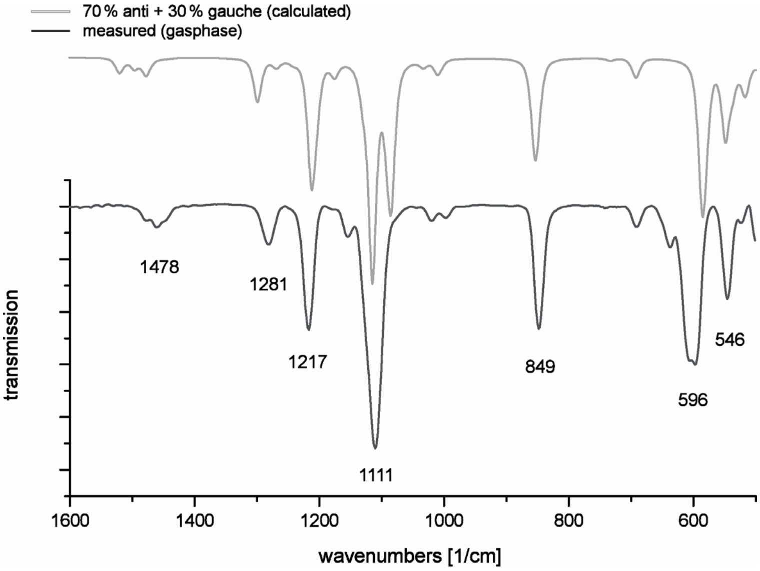

Fig. 2. Measured and calculated IR spectrum of compound **1** in the gas phase. The calculated spectrum (B3LYP/6-31G*) represents a mixture of 70 % *anti* and 30 % *gauche* conformers and represents a best fit to the experimental data.

prise as F is more electronegative than Cl, but due to the limited comparability of free molecule calculations and solid-state experimental results, this should not be overinterpreted.

Consistently predicted for both conformers, the Si···N interaction in **3** is stronger than in **1**, as seen by the more narrow SiNN angles and shorter Si···N distances. The effect, that a $\mathrm{Me_3Si}$ group instead of a $\mathrm{H_3C}$ group bonded to the bridging nitrogen atom in hydrazides leads to a strong enhancement of the attractive interaction between Si and geminal N atoms has already been demonstrated in experiments performed with $\mathrm{F_3Si{-}N(SiMe_3)NMe_2}$ and $\mathrm{F_3Si{-}N(Me)NMe_2}$ [8b]. In contrast to the calculations for **1**, a smaller SiNN angle is predicted for the *anti* than for the *gauche* conformer [82.4° (*anti*) and 87.4° (*gauche*)].

The Si–C distances and Si–N(spacer) distances are almost unaffected by the conformations. The $\mathrm{Si{-}CF_3}$ bonds in **1**, **3** and **4** are very long as is generally found for bonds from silicon atoms to $\mathrm{CF_3}$ groups (see below the structure determinations of $\mathrm{F_3CSiCl_3}$ and $\mathrm{F_3CSiMe_3}$, and lit. [17]). The slightly longer Si–C distance in **1** as compared to **3** corresponds to a smaller SiNN angle in the latter. This confirms the general observation that a stronger Si···N interaction weakens the other bonds at silicon, in particular the apical bond, *i. e.* in this case the $\mathrm{Si{-}CF_3}$ bond becomes longer.

As described in the literature, silylated hydrazines show a planar coordination sphere at the N1 centre [18]. Compound **1** shows the expected planar geometry at N1, but the silylated nitrogen atom in **2** is predicted to be slightly pyramidal (sum of angles at N1 = 356.4 in the *anti* and 357.7° in the *gauche* conformer), despite the presence of two silyl substituents. The trimethylsilyl group in **2** is bent towards the *gauche* positioned trifluoromethyl group (see Fig. 6).

*Experimental and calculated IR spectra of **1** and **2***

The volatility of compound **1** allowed recording the gas-phase IR spectrum shown in Fig. 2. For reasons of assignment and in order to extract conformational information, this spectrum was also quantum chemically calculated at the B3LYP/6-31G* level of theory for two possible conformers, *anti* and *gauche*, defined by their torsional angles: τ(CSiON) = 180° (*anti*), 60° (*gauche*) (Fig. 3).

The broad bands at 546 and 596 $\mathrm{cm^{-1}}$ in the IR spectrum of **1** correspond to the Si–Cl stretching vibrations. The very intense band at 1111 $\mathrm{cm^{-1}}$ results from the asymmetrical valence vibration of the trifluoromethyl group. The spectrum shown in Fig. 2 (grey line) shows a representation of a mixture of 30: 70 % of *gauche* and *anti* conformers of compound **1** in the gas phase, and is the best fit that could be achieved. This shows that *anti* is the dominating conformation in the gas phase. In contrast, the calculations (MP2/6-311G**) favour the *gauche* conformation by 5.6 $\mathrm{kJ\,mol^{-1}}$.

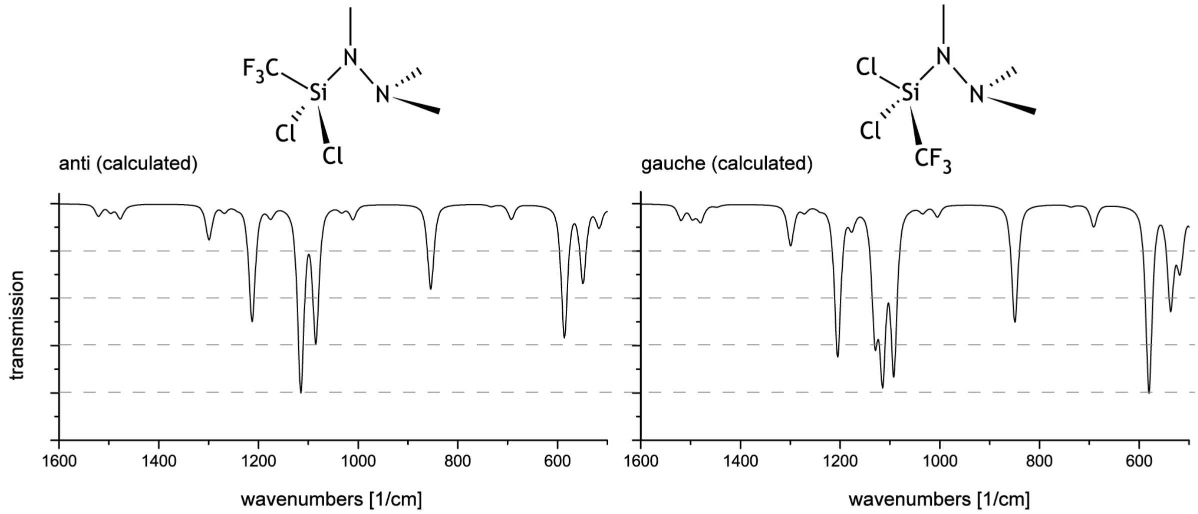

Fig. 3. Calculated IR spectra of the *anti* and *gauche* conformers of compound **1** as obtained at the B3LYP/6-31G* level of theory.

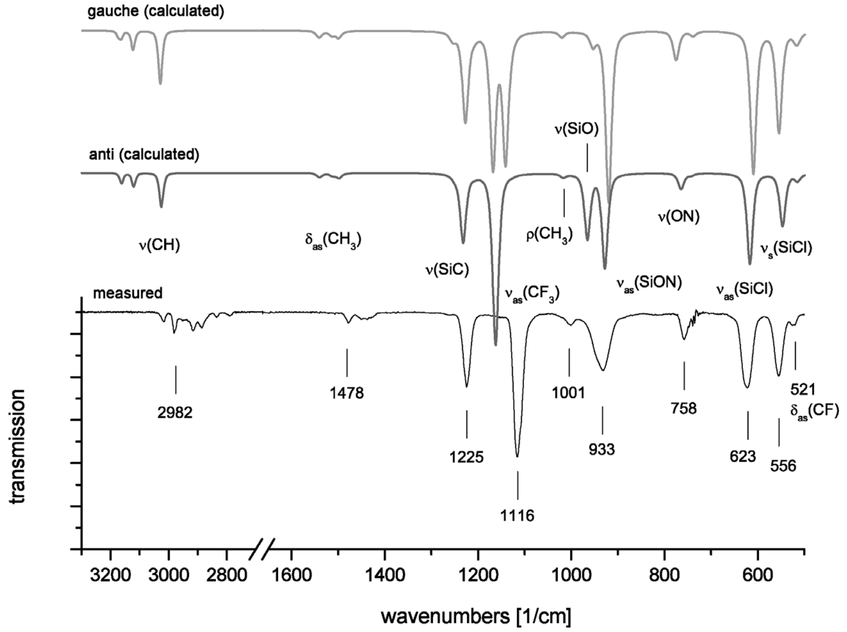

Fig. 4. Measured and calculated IR spectra of compound **4** in the gas phase.

Experimental and calculated IR spectra of 4

As for **1**, a gas-phase IR spectrum of **4** could be recorded, which allows direct comparison with the calculated vibrational spectra of its conformers (Fig. 4). All the important stretching vibrations can be recognised and assigned. The ν_{as}(Si–Cl) stretching vibration mode can be assigned to the band at 556, that of ν(Si–Cl) to the one at 623 cm^{-1}, and the ν(Si–C) vibration is found as a feature at 1225 cm^{-1}. In this case it is not necessary to apply scaling factors to account for the harmonic approximation in the calculations, as these vibrations fit the experimental values well without scaling. However, the asymmetrical stretching vibration of the CF_3 group is computed with a wavenumber about 30 cm^{-1} higher than observed. This is also the case with simple molecules like $F_3C–SiCl_3$ (**6**) (see below). The experimentally observed very broad band at 933 cm^{-1} can be assigned to two weak signals belonging to combined Si–O and O–N vibrations of the three-membered SiON ring of the *anti* conformer.

Distinction between *anti* and *gauche* conformers is possible considering a few details in the spectra. The mentioned broad band of the combined Si–O and O–N vibrations in the *anti* conformer differs from the corresponding ones of the *gauche* conformer (Fig. 4), which are represented by one narrow, strong peak. Moreover, the calculated band of the CF_3 stretching vibration at 1116 cm^{-1} for the *gauche* conformer is split into two signals of equal intensity.

A comparison of the three spectra displayed in Fig. 4 leads to the conclusion that the *anti* conformation is dominating in the gas phase even though the calculations predict the *gauche* conformation to be more stable by 3.9 kJ mol^{-1}. These calculated energy differences are, however, not of a very high precision and thus the experimental observation points to a reverse energetic situation (also taking into account that the *gauche* conformer has two-fold symmetry degeneracy). Moreover, this is consistent with recent observations of the conformer ratio for the Cl/F analogous compound $(F_3C)F_2SiONMe_2$ [12].

*Crystal structure of $Cl_3SiN(Me)NMe_2$ (**2**)*

Compound **2** crystallises in the monoclinic space group $P2_1/n$. Fig. 5 shows the molecular structure and contains structural parameters in its caption. The unit cell comprises four molecules forming Cl···Cl contacts of 3.491 Å length, which is shorter than the sum of van der Waals radii at 2.61 Å [19]. Expectedly, the SiNN angle in **2** at 105.0(1)° is slightly larger than that in the fluorine analogue $F_3SiN(Me)NMe_2$ (104.2(2)° [8b]). Accordingly, the Si···N distance in **2** is larger (2.450(2) Å) than in $F_3SiN(Me)NMe_2$ (2.438(1) Å). Surprisingly, all Si–Cl distances are equal within experimental error, *i. e.* there is no difference between *gauche* and *anti* substituents. Despite this, the angles to the chlorine atoms, N–Si–Cl, are larger for the *gauche* positions [Cl2–Si–N1 114.3(3)°] than for the *anti* positions [108.5(1)°], reflecting a slight trend of the silicon coordination geometry to deform towards a trigonal bipyramid. The N–N distance is about 0.1 Å shorter than in $F_3SiN(Me)NMe_2$, whereas the N–C bonds and CNC angles have very similar values for both compounds. The silylated N atom in **2** is of planar coordination geometry; this configuration is well established for silylated hydrazines [18].

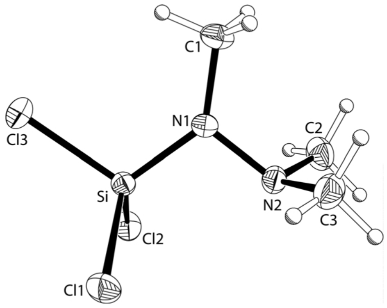

Fig. 5. Molecular structure of $Cl_3SiN(Me)NMe_2$ (**2**) as determined by low-temperature X-ray crystallography (displacement ellipsoids drawn at the 50 % probability level). Selected bond lengths (Å) and angles (deg): Si–N1 1.653(1), Si–Cl1 2.028(1), Si–Cl2 2.026(1), Si–Cl3 2.029(1), N1–N2 1.429(2), N1–C1 1.453(2), N2–C2 1.463(2), N2–C3 1.457(2); N1–Si–Cl1 113.8(1), N1–Si–Cl2 114.8(1), N1–Si–Cl3 108.5(1), C1–Si–Cl2 105.9(1), Cl1–Si–Cl3 107.0(1), N2–N1–Si 105.0(1), C1–N1–Si 134.3(1), C1–N1–N2 120.7(1), N1–N2–C2 111.4(1).

*Crystal structures of the trifluoromethylsilanes $F_3C–SiMe_3$ (**5**) and $F_3C–SiCl_3$ (**6**)*

F_3CSiCl_3 was the starting material for the above described chemistry. We have determined its crystal structure to allow comparison of structural data with other F_3CCl_2Si compounds. Moreover we have undertaken a determination of the crystal structure of the related F_3CSiMe_3, the Ruppert reagent [13] also for reasons to provide a reference. Compound **5** was prepared by the known reaction of $SiCl_4$ with F_3CBr and $P(NEt_2)_3$ in benzonitrile, purified *via* distillation at 41 °C [20, 21], and identified by gas-phase IR spectroscopy.

Single crystals of **5** and **6** were grown by *in situ* crystallisation with the OHCD technique. In the case of **5** the crystal growth experiment was performed at −65 °C and in case of **2** at −83 °C. The results of

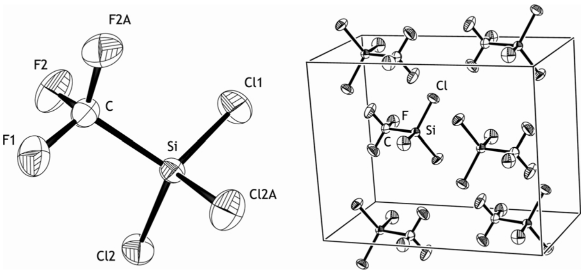

Fig. 6. Molecular and crystal structure of F_3CSiCl_3 (**6**) as determined by low-temperature X-ray crystallography.

Table 2. Experimental [solid-state (XRD) and gas-phase (MW/GED)] and calculated (HF and MP2/TZVPP) structure parameters for compound **5** and **6** (angles are given in deg, distances in Å; the symmetry of the calculated molecules was C_{3v}).

Compound		F_3C–$SiMe_3$ (**5**) X1 = C2, X2 = C3				F_3C–$SiCl_3$ (**6**) X1 = Cl1, X2 = Cl2	
Parameter	XRD	MW/GED	HF	MP2	XRD	HF	MP2
∠Si–C1–F1	113.4(4)	–	112.6	112.5	109.8(2)	111.5	111.4
∠Si–C1–F2	114.4(3)				111.3(2)		
∠F1–C1–F2	103.2(3)	106.4(2)	106.2	106.3	107.8(2)	107.4	107.5
∠F2–C1–F2′	107.0(5)				108.6(3)		
∠C1–Si–X1	105.7(3)	106.2(2)	106.4	106.1	108.1(1)	108.0	107.8
∠C1–Si–X2	105.7(2)				107.5(1)		
∠X1–Si–X1	113.2(2)	–	112.3	112.6	111.1(1)	111.5	111.1
∠X2–Si–X2′	112.6(3)				111.4(1)		
d(Si–C1)	1.917(5)	1.941(3)	1.948	1.937	1.923(3)	1.934	1.928
d(Si–X1)	1.832(5)	1.862(2)	1.876	1.868	2.000(1)	2.024	2.020
d(Si–X2)	1.835(5)				1.997(1)		
d(C1–F1)	1.370(7)	1.356(1)	1.329	1.355	1.338(4)	1.318	1.344
d(C1–F2)	1.335(4)				1.327(3)		

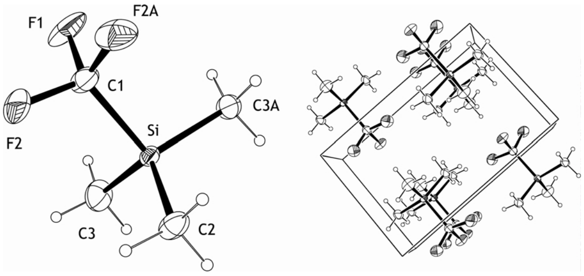

Fig. 7. Molecular and crystal structure of F_3CSiMe_3 (**5**) as determined by low-temperature X-ray crystallography.

the single crystal X-ray diffraction experiments are depicted in Figs. 6 and 7 for **6** and **5**, respectively. Structural data are compiled in Table 2.

In a recent contribution from 2005, the gas-phase structure of F_3C–$SiMe_3$ (**4**) determined by microwave spectroscopy and gas electron diffraction was described [22]. The results of this investigation are also included in Table 2.

Earlier gas-phase structure determinations of the related silylmethanes CH_3SiH_3 [23], CH_3SiF_3 [24], CF_3SiH_3 [25], and CF_3SiF_3 [26] reflect strong effects of fluorination on the Si–C bond length. The Si–C distance is shortened upon fluorination at the silicon atom, but lengthened upon fluorination at the carbon atom [17]. This has been attributed to the strongly electron withdrawing nature of the fluorine atoms, which results in a high positive charge at the carbon atom of the CF_3 group as well as on the silicon atom and leads to a) a reduction of electron density for the central Si–C bond and b) a repulsion between the positive partial charges in the Si^+–C^+ unit. For F_3CSiMe_3, weak force constants of 2.63 and 3.07 N cm^{-1} for the Si–CF_3 and Si–CH_3 bonds, respectively, were also observed [27].

This fact is also confirmed by our new results for the solid-state structures of **1** and **3**, which both show very long Si–C bonds [Si–C = 1.917(5) Å (**5**), 1.929(3) Å (**6**)].

As compared to its gas phase structure (Si–C = 1.941(3) Å) and the calculated values, **5** has a considerably shorter Si–C bond in the solid state, which is in this magnitude of deviation unusual for non-dative bonds. It is further interesting to note that the C–Si–C(H_3) angles in **5** are smaller than the tetrahedral angle, while the Si–C–F angles are wider. A similar observation is made for the respective angles in compound **6**. Surprisingly, there is a difference in the C–F bond lengths (1.370(7) and 1.335(4) Å), but this should not be over-interpreted, as the data have quite large e. s. d.'s.

Experimental Section

General

All reactions were carried out under an atmosphere of dry nitrogen in anhydrous and degassed solvents with standard Schlenk and high-vacuum techniques. NMR spectra were recorded on AC200, Avance 400 or Varian Inova 500 spectrometers in deuteriated solvents, and were referenced relative to residual protio-solvent resonances (^{1}H, ^{13}C) or relative to an external standard (^{19}F: CCl_3F, ^{29}Si; neat $SiMe_4$). Infrared spectra were recorded on a Midac Prospect IR spectrometer. Mass spectra were recorded on a Varian MAT 212, or on a Pfeiffer QMG422/SEM. F_3CSiCl_3 (**5**) was prepared from $P(NEt_2)_3$, F_3CBr and $SiCl_4$ as described in [5].

*$(F_3C)Cl_2SiN(Me)NMe_2$ (**1**) and $Cl_3SiN(Me)NMe_2$ (**2**)*

^{n}BuLi (18.5 mL, 1.8 M solution in hexane) was added to a solution of N,N',N'-trimethylhydrazine (2.22 mL, 30 mmol) in hexane (20 mL) at −60 °C. For completion of the reaction the mixture was warmed to r. t. over a period of 2 h. All volatiles were removed in vacuum at ambient temperature. Dimethyl ether (30 mL liquid, dried through a CaH_2 filled U-shaped tube) and 6.10 g F_3CSiCl_3 (**5**, 30 mmol) were condensed to the flask containing the lithium hydrazide. The reaction was started at −75 °C, and then the mixture was allowed to warm to −35 °C over a period of 2 h. The contents of the flask were passed through a series of cold traps (held at −25, −74 and −196 °C) in vacuum. The product **1** was stopped in the −25 °C trap and further purified by repeated fractionation. Compound **1** can also be separated from the −25 °C trap to prepare a capillary for *in situ* crystallisation.

The residue was washed with dry pentane (40 mL). The liquid was separated from the precipitate through a cannula fitted with a glass wool filter and concentrated under reduced pressure to a volume of about 10 mL. The vessel with this solution was immersed in a 1 L Dewar container (with insulating lid) filled with ethanol at r. t. (serving as a temperature reservoir), and the whole setup was allowed to cool slowly to −25 °C overnight in a freezer. Some colourless crystals of compound **2** precipitated and were isolated.

*Compound **1**:* Yield: 2.4 g, 10 mmol, 33 %. M. p. −17 °C. – ^{1}H NMR ($CDCl_3$; 400 MHz): δ = 2.51 ppm (s, 6 H, $N(CH_3)_2$), 2.66 (s, 3 H, NCH_3). – ^{13}C NMR ($CDCl_3$; 100.6 MHz): δ = 21.5 ppm (s, NCH_3), 42.3 (s, $N(CH_3)_2$), 125.0 (m, CF_3, ^1J(C,F) = 317 Hz). – ^{19}F NMR ($CDCl_3$; 470.3 MHz): δ = −66.4 ppm (s, CF_3, ^2J(Si,F) = 67 Hz). – ^{29}Si DEPT-135 NMR ($CDCl_3$, 79.5 MHz): δ = −53.4 ppm (q, ^2J(Si,F) = 67 Hz, ^3J(Si,H) = 5 Hz). – IR (gas) ν = 500 δ_{as}(CF), 546 ν(SiCl), 596 ν_{as}(SiCl), 849 ν(CN), 1111 $\nu_{as}(CF_3)$, 1217 ν(SiC), 1281 ν(SiN), 1478 $\delta_{as}(CH_3)$. – MS (EI): m/z (%) = 240 (6.9) $[M]^+$, 190 (33) $[M–CF_2]^+$, 98 ($SiCl_2$, 11), 73 (74) $[CH_2NNMe_2]^+$.

*Compound **2**:* M. p. −5 °C. – ^{1}H NMR (C_6D_6; 400 MHz): δ = 2.03 ppm (s, 6 H, $N(CH_3)_2$), 2.13 (s, 3 H, NCH_3). – ^{13}C NMR (C_6D_6; 100.6 MHz): δ = 21.2 ppm (s, NCH_3), 41.9 (s, $N(CH_3)_2$).

*$(F_3C)Cl_2SiN(SiMe_3)NMe_2$ (**3**)*

^{n}BuLi (8.3 mL, 1.8 M solution in hexane) was added to N-trimethylsilyl-N',N'-dimethylhydrazine (1.98 g, 2.58 mL, 15 mmol) at −30 °C. For completion of the reaction the mixture was warmed to r. t. over 2 h. The volatiles were removed *in vacuo* at ambient temperature to yield 2.07 g of $LiN(SiMe_3)NMe_2$ as a waxy solid. Dimethyl ether (30 mL liquid, dried through a CaH_2-filled U-shaped tube) and 3.26 g F_3CSiCl_3 (**5**, 16.0 mmol) were condensed to the flask containing the lithium hydrazide. The reaction was started at −78 °C. Then the mixture was allowed to warm to −30 °C over a period of 2 h. After removing the solvent in a vacuum the residue was washed with 15 mL of dry hexane. The solution was filtered followed by vacuum distillation. Small amounts of **4** were obtained at a temperature of about 60 °C and 0.01 mbar. – Yield: 0.4 g, 1.3 mmol, 9 %. M. p. −12 °C, b. p. (0.01 mbar) 59 – 61 °C. – ^{1}H NMR (C_6D_6; 500 MHz): δ = 0.28 ppm (s, 9 H, $Si(CH_3)_3$), 2.51 (s, 6 H, $N(CH_3)_2$). – ^{13}C NMR (C_6D_6; 125 MHz): δ = 2.87 ppm (s, $Si(CH_3)_3$), 47.6 (s, $N(CH_3)_2$), 125.0 (q, CF_3, ^1J(C,F) = 314 Hz). – ^{19}F NMR (C_6D_6; 470.3 MHz): δ = −65.2 ppm (s, CF_3, ^1J(C,F) = 162 Hz, ^2J(Si,F) = 34 Hz). – ^{29}Si DEPT-135 NMR (C_6D_6; 99.3 MHz): δ = −66.7 ppm (d), 1.4 (m, TMS). – MS (EI): m/z (%) = 298 (4.4) $[M]^+$, 206 (22) $[M–FSi(CH_3)_3]^+$, 156 (83) $[M–Si(CH_3)_3–F_3C]^+$, 73 (100) $[Si(CH_3)_3]^+$, 63 (9) $[SiCl]^+$, 43 (21) $[HN(CH_3)_2]^+$.

*$F_3CSi(Cl)_2–ONMe_2$ (**4**)*

^{n}BuLi (6.25 mL, 1.6 M solution in hexane) was added to N,N-dimethylhydroxylamine (0.61 g, 0.69 mL, 10 mmol) and 20 mL pentane at −45 °C, and the mixture was stirred for 2 h while warming to r. t. The volatiles were removed *in vacuo* at ambient temperature. A 10 mL pentane suspension of this lithium compound was added dropwise *via* a dropping funnel equipped with a magnetic stirrer to a solution of **5** (2.80 g, 13.8 mmol) in dry pentane (20 mL). The temperature was held between −70 and −10 °C for three hours. The contents were distilled through a series of traps (−40, −80 and −196 °C). – Yield: 1.04 g, 4.6 mmol, 46 %. – ^{1}H NMR ($CDCl_3$; 500 MHz, −30 °C): δ = 2.90 ppm (s, 6 H, $(CH_3)_2$). – ^{13}C NMR ($CDCl_3$; 125.7 MHz, −30 °C): δ = 49.3 ppm (s, $N(CH_3)_2$), 125.0 (q, CF_3, ^1J(C,F) = 315 Hz). – ^{15}N NMR ($CDCl_3$, 50.7 MHz, −30 °C): δ = −241.2 ppm. – ^{19}F NMR ($CDCl_3$, 470.3 MHz, −30 °C): δ = −66.6 ppm (s, CF_3, ^1J(C,F) = 57 Hz, ^2J(Si,F) = 34 Hz). – ^{29}Si NMR ($CDCl_3$, 99.3 MHz): δ = −66.3 ppm (q). – IR (gas) ν = 556, 623 ν(SiCl), 758 ν(NO), 933 (br, s), 1001 ρ(CH), 1116 (vs) $\nu_{as}(CF_3)$, 1225 ν(SiC), 1478 $\delta_{as}(CH_3)$. – MS (EI): m/z (%) = 227 (1.4) $[M]^+$, 176 (11) $[M−CF_2]^+$, 158 (4.5) $[M−CF_3]^+$, 98 (5.9) $[SiCl_2]^+$, 69 (14) $[CF_3]^+$, 60 (31) $[ONMe_2]^+$.

Crystal structure determinations

Bruker Apex, Stoe IPDS I and Nonius CAD4 X-ray diffractometers (λ = 0.71073 Å) were used to collect the scattering intensities for the single crystals of **2**, **5** and **6**. Single crystals of **2** were mounted under inert perfluoropolyether at the tip of a glass fibre and cooled in a cryostream of the diffractometer. Single crystals of **5** and **6** were grown by *in situ* methods.

The experimental setup consists of an X-ray diffractometer with an attached low temperature device for cooling the sample. An IR laser source is set up in such a way that the sample can be heated with the focussed laser beam. The intensity and position of the laser focus are controlled by computer routines. The liquid sample was condensed into a thin-walled glass capillary (approximately 0.3 mm diameter) and was then sealed. After placing the capillary on the goniome-

Compound	**2**	**5**	**6**
Formula	$C_3H_9Cl_3N_2Si$	$C_4H_9F_3Si$	CCl_3F_3Si
Formula weight	207.56	142.19	203.45
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/m$	$C2/m$
Diffractometer	Bruker AXS	Stoe IPDS I	Nonius CAD4
a, Å	7.466(1)	6.331(1)	11.664(2)
b, Å	11.451(2)	9.595(2)	9.383(1)
c, Å	10.704(2)	6.472(2)	6.227(1)
β, deg	105.379(4)	103.15(3)	92.72(1)
V, Å^3	882.3(3)	382.8(1)	679.6(2)
ρ_{calc}, g cm^{-3}	1.563	1.737	1.989
Z	4	4	4
μ, mm^{-1}	1.099	0.499	1.477
T, K	123(2)	173(2)	113(2)
Index range	$-10 \le h \le 10$ $-16 \le k \le 16$ $-14 \le l \le 15$	$-7 \le h \le 7$ $-11 \le k \le 11$ $-7 \le l \le 7$	$-14 \le h \le 14$ $-11 \le k \le 11$ $-7 \le l \le 7$
$T_{\text{min / max}}$	0.968 / 0.810	–	–
$2\theta_{\text{max}}$, deg	60.22	51.02	53.86
Measured refl.	9996	4869	2823
Unique refl.	2580	705	783
R_{int}	0.042	0.105	0.073
Observed refl.	2132	705	735
Refined parameters	118	43	43
$R[I \ge 2\sigma(I)]/wR_2$	0.0306 / 0.0702	0.0558 / 0.1343	0.0342 / 0.0856
$\Delta\rho_{\text{fin}}$ (max/min), e Å^{-3}	0.42 / -0.25	0.35 / -0.27	0.79 / -0.31
CCDC no.	701653	693614	693613

Table 3. Summary of crystallographic data and structure refinement for compounds **2**, **5** and **6**.

ter the sample was cooled 20 °C below the melting point, such that the liquid becomes polycrystalline and not glassy. The IR laser was then applied with an intensity sufficient to partially melt the polycrystalline compound. The laser beam was focussed on a very tiny portion of *ca.* 0.2 mm of the capillary and then scanned along the filled length of the capillary very slowly (app. 1 – 3 mm h^{-1} or less). During this procedure the temperature was kept constant. After the first start at the bottom (0 % of the total scan length) of the capillary the next melting scan was started at a position of 10 % higher. The last run was started at 40 % and ended at 100 %. After finishing the crystallisation procedure a suitable single crystal could be chosen by means of a microscope equipped with a polarisation filter.

The structures were solved by Direct Methods and refined with the full-matrix least-squares procedure (SHELXTL) against F^2 with the program SHELXTL 5.01 or SHELXTL 6.10 [28]. Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms isotropically with a riding model (for details see Table 3).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been forwarded to The Cambridge Crystallographic Data Centre as supplementary publications. The deposition numbers are given in Table 3. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

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