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Preparation and Structure of 1-(Trifluoromethyl)silatrane

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Summary. 1-(Trifluoromethyl)silatrane, $CF_3Si(OCH_2CH_2)_3N$, was prepared from $CF_3Si(OCH_3)_3$ and triethanolamine and characterized by NMR, vibrational, and mass spectroscopy. The compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 777.2(1)$, $b = 1236.9(2)$, $c = 1002.8(1)$ pm, $\beta = 91.33(1)°$, $Z = 4$. The equatorial Si–O bond lengths of the almost perfect trigonal bipyramid average 165.3(2) pm, the axial Si–C bond length is 94.6(1) pm. The transannular Si–N contact, 202.4(1) pm, is considerably shorter than in other organylsilatranes.

Keywords. Silicon; Silatrane; Trifluoromethyl compounds.

Synthese und Struktur von 1-(Trifluormethyl)silatran

Zusammenfassung. 1-(Trifluoromethyl)silatran, $CF_3Si(OCH_2CH_2)_3N$, wurde aus $CF_3Si(OCH_3)_3$ und Triethanolamin gewonnen und durch NMR-, Schwingungs- und Massenspektroskopie charakterisiert. Die Verbindung kristallisiert in der monoklinen Raumgruppe $P2_1/n$ mit $a = 777.2(1)$, $b = 1236.9(2)$, $c = 1002.8(1)$ pm, $\beta = 91.33(1)°$, $Z = 4$. Die equatorialen Si–O-Abstände der nahezu perfekten trigonalen Bipyramide betragen im Schnitt 165.3(2) pm, der axiale Si–C-Abstand 194.6(1) pm. Der transanulare Si–N-Kontakt, 202.4(1) pm, ist beträchtlich kürzer als in anderen Organylsilatranen.

Introduction

Silatranes and related compounds have attracted great attention over the last decades not only because of their unique structure with pentacoordinated silicon and a transannular N → Si bond but also due to their biological activity. Several review articles covering both structural and biological aspects are available [1–7]. The nature of the Si–N interaction has been the subject of recent theoretical studies [8–11] which agree on the statement that only a very small amount of energy is required to shorten or lengthen the Si–N distance. Thus, the Si–N distances of 1-methylsilatrane and 1-fluorosilatrane have been found to be *ca.* 28 pm shorter in the solid state [12, 13] than in the gas phase [14, 15], and this shortening has been attributed to packing forces [10]. On the other hand, the Si–N bond distance is also

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sensitive to the *Lewis* acidity of the silicon atom and thus reflects the electronic effect of a substituent bonded to silicon. For example, in the solid state the shortest Si–N distance has been found in the 1-(dimethyloxonio)silatranium cation with 196.5 pm, whereas those in the isothiocyanato-[16], fluoro-[13] or chlorosilatrane [17], which slightly exceed 200 pm, are significantly shorter than in organylsilatranes. It is expected that substitution of silicon with the electronegative CF_3 group will result in a similarly short Si–N contact. Earlier attempts to produce the CF_3 substituted silatrane have failed [18]. In the following we report on the synthesis, spectroscopic properties, and structure of 1-(trifluoromethyl)silatrane.

Results and Discussion

1-(Trifluoromethyl)silatrane is readily accessible from $CF_3Si(OCH_3)_3$ and triethanolamine as a white crystalline substance which is stable in air and insoluble in non-polar solvents, but readily dissolves in polar solvents like dimethylformamide, dimethylsulfoxide, or N-methylpyrrolidone.

$$CF_3Si(OCH_3)_3 + N(CH_2CH_2OH)_3 \xrightarrow[-CH_3OH]{THF/RT} CF_3Si(OCH_2CH_2)_3N \qquad (1)$$

Combined calorimetric and thermogravimetric analyses show that the compound decomposes in air at 201°C without melting and without any noticeable thermal effect, but with loss of one third of its weight (33%). Strongly exothermic degradation follows at 285°C with loss of another 18% of weight.

Spectra

The silatrane was characterized by NMR spectroscopy using *DMSO*-d_6 as solvent (^1H: $\delta(OCH_2)$ 3.81 ppm, $\delta(NCH_2)$ 3.09 ppm, $^3J(HH)$ 6.0 Hz; ^{13}C: $\delta(OCH_2)$ 56.6 ppm, $\delta(NCH_2)$ 50.5 ppm, $\delta(CF_3)$ 131.2 ppm, $^1J(CF)$ 325.8 Hz; ^{19}F: $\delta(CF_3)$ −65.1 ppm; ^{29}Si: δ −95.4 ppm, $^2J(SiF)$ 40.8 Hz). The increase of $^1J(CF)$ with simultaneous decrease of $^2J(SiF)$ with respect to the corresponding values of $CF_3Si(OCH_3)_3$ (315.5 and 53.6 Hz, respectively) follows the pattern observed upon increase of the coordination number for other CF_3 substituted silicon compounds [19].

The mass spectrum shows the characteristics of two different fragmentation pathways – both loss of the exocyclic substituent and skeleton fragmentation. Besides the molecular ion ($m/z = 243$, 9%), loss of CF_2 ($m/z = 193$, 68%) and of CF_3 to the silatranyl ion ($m/z = 174$, 100%) dominates – the latter constituting the base peak of most organylsilatranes [20]. In addition, an intense peak is observed at $m/z = 150$ (85%) which is indeed the base fragment ion of 1-fluorosilatrane, $[C_4H_9FNO_2Si]^+$ [13].

The infrared and *Raman* spectra listed in Table 1 show the typical pattern of most silatranes. For the 15 non-hydrogen skeleton atoms $10a_1$, $3a_2$, and $12e$ modes are expected, both a_1 and e being infrared and *Raman* active. The assignment of the a_1 modes is based on a normal coordinate analysis of silatrane [21] and on *Raman* polarization data obtained for molten methylsilatrane [22] which are included in Table 1 for comparison. There have been lots of discussion and attempts to assign

Table 1. Vibrational spectra of polycrystalline 1-(trifluoromethyl)silatrane ($R = \mathrm{CF_3}$) and related silatranes ($\mathrm{cm^{-1}}$)

Raman	IR	*Raman*	Assignment
$R = \mathrm{CF_3}$		$R = \mathrm{H/CH_3}$ [22]	
203 m		184 m/182 m	
233 m-s		(–/242 w)	$e(\rho\ \mathrm{CF_3})$
297 m-s		(–/288 m)	$a_1(\nu\ \mathrm{Si\text{-}CF_3})$
362 m		348 w/354 m,p	a_1[a]
	442 s	–/455 w	e[a]
497 m	492 m	490 w/471 m,p	a_1[a]
526 m			$e(\delta_{as}\ \mathrm{CF_3})$
596 s	596 s	593 s/580 vs,p	a_1[a]
		–/619 vs,p	$a_1\ (\nu\ \mathrm{Si{-}CH_3})$
625 w	625 w		
648 s	648/652 s	630 m/696 m	$a_1(\nu_s\ \mathrm{SiO_3})$
716 m	716 m	–/(718 w)	$a_1(\delta_s\ \mathrm{CF_3})$
767 w	767 w		$\rho\ \mathrm{CH_2}$
813 w	805/811 vs	760 m/769 m	$e\ (\nu_{as}\ \mathrm{SiO_3})$
877 w	871/877 w	864 w/873 w	e[a]
916 m	913 m	911 s/908 m,p	a_1[a]
944 m	938/946 m	942 s/944 m,p	a_1[a]
1028 m	1029 vs		$e(\nu_{as}\mathrm{CF_3})$
1043 m	1048 m	1043 w/1050 m	
1079 m	1086 vs		$a_1(\nu_s\ \mathrm{CF_3})$
1110 m	1115/1118 s	1104 w/1113 m	a_1[a]
1170 m	1167 w	1165 w/1171 m	e[a]
1228 w	1225 m		
1248 m	1245 w	1240 m/1237 w	} $\mathrm{CH_2}$
1274 s	1277 m	1267 m/1278 s	
1353 w		–/1350 w	twisting and
1390 w		–/1381 w	wagging
1460 m-s	1455 m	1455 m/1452 s,p	} $a_1(\delta_s\ \mathrm{CH_2})$
1490 s	1489 m	1486 m/1487 s,p	
2898 s	2891 s	2876 s/2875	} $\nu_s\ \mathrm{CH_2}$
2904 s	2897 s		
2963 s	2958 m	2928 s/2948	$\nu_{as}\mathrm{CH_2}$
3002 s	2998 m	2967 m/2975	$\nu_{as}\mathrm{CH_2}$

[a] Skeleton mode

the Si–N stretching mode although it is evident from the kinetics of the a_1 cage modes that there is no unique Si–N stretch and that an assignment of frequencies to individual internal coordinates is unreasonable. Additionally, the flatness of the calculated potential curves indicates that the contribution of the Si–N stretching force constant to the total potential energy distribution of the a_1 cage modes will be low. In another approximation, the Si–N stretch may be described as a combination of the symmetric $\mathrm{SiO_3}$ and $\mathrm{NC_3}$ deformations. In the $\mathrm{CF_3}$ derivative, these low-energy modes will be further coupled to the Si–CF_3 stretch which appears at 386 cm^{-1} in $CF_3Si(CH_3)_3$ [23] or 402 cm^{-1} in CF_3SiH_3 [24]. The longer Si–C bond in the silatrane implies that the Si–CF_3 stretch should occur at even lower wavenumbers, and an assignment to the *Raman* band at 297 cm^{-1} seems reasonable. Similarly, the $\nu_s(CF_3)$ and $\delta_s(CF_3)$ modes are considerably red-shifted with respect to tetracoordinated CF_3Si compounds. The general increase of almost all other frequencies and especially of those between 350 and 700 cm^{-1} is in accordance with a more rigid skeleton and stronger Si–N interaction.

Crystal structure

No crystallographic symmetry is imposed on the molecule; the structure closely complies with C_3 symmetry with the CF_3 group being rotated about the Si–C bond by 9.4(2)° from an exactly staggered conformation with respect to the SiO_3 entity. The structure is shown in Fig. 1, and selected bond distances and angles are given in Table 2. As found in numerous silatranes [25], the three heterocyclic five-membered rings in this compound adopt an envelope conformation with the C(2), C(4), or C(6) atoms deviating on the average by 51(1) pm from the corresponding plane defined by the other four ring atoms.

A comparison with the structure of the methyl analog [12] shows that fluorination of the methyl group lengthens the Si–C bond by 7.6(6) pm, at the same time leading to a slight but significant shortening (1.3(3) pm) of the average Si–O bond length and to a large contraction (15.1(4) pm) of the transannular Si–N contact. The SiO_3 pyramid is flatter, the average values of both the O–Si–C and O–Si–N angles being closer (4.4(6))° to the perfectly flattened 90° value than are those of the methyl compound.

Whereas the Si–CF_3 bond is significantly longer than the Si–CH_3 bond in the methyl analog, it is not much longer than those found in tetravalent

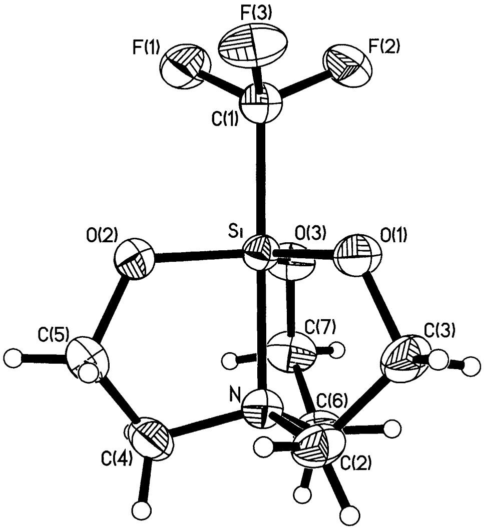

Fig. 1. Perspectivic drawing of 1-(trifluoromethyl)silatrane with 50% probability thermal ellipsoids for the non-hydrogen atoms

Table 2. Selected or average bond lengths (pm) and angles (°) for 1-(trifluoromethyl)silatrane

Si–O(1)	165.17(8)	C(1)–F_{av}	135.9(7)
Si–O(2)	165.29(8)	O–C_{av}	142.7(2)
Si–O(3)	165.42(8)	N–C_{av}	148.1(3)
Si–C(1)	194.61(10)	C–C_{av}	151.4(4)
Si–N	202.42(9)		
C(1)–Si–N	179.54(4)	O–Si–N_{av}	87.1(2)
O(1)–Si–O(2)	119.96(5)	Si–O–C_{av}	119.4(2)
O(1)–Si–O(3)	120.44(5)	C–N–C_{av}	113.5(5)
O(2)–Si–O(3)	118.85(5)	Si–N–C_{av}	105.1(1)
C(1)–Si–O(1)	92.49(4)	F–C–F_{av}	104.3(3)
C(1)–Si–O(2)	93.16(4)	Si–C–F_{av}	114.3(9)
C(1)–Si–O(3)	92.94(4)	N–C–C_{av}	105.9(2)
		O–C–C_{av}	108.1(3)

trifluoromethylsilanes [24, 26–28]. The short transannular Si–N distance, 202.4 pm, is readily associated with the high *Lewis* acidity of the silicon atom induced by the high electronegativity of the CF_3 moiety. The similarity to the values reported for the chloro-and fluorosilatrane (202.3 and 204.2 pm, respectively) clearly demonstrates the pseudohalide character of the CF_3 group despite severe differences in the nature of the Si–CF_3 and Si–X bonding.

Experimental

Chemicals were obtained from commercial sources and used without further purification. (Trifluoromethyl)trimethoxysilane was prepared according to Ref. [29]. *Raman* spectra were obtained on a Cary 82 spectrometer with Kr^+ excitation at 647.1 nm. Infrared spectra were recorded with a Bruker IFS 25 spectrometer as KBr pellets. Combined calorimetric and thermogravimetric analyses (DSC/TGA) were made with a simultaneous DSC/TG instrument, Netzsch STA 409. NMR spectra were recorded with a Bruker AC 250 instrument (^{1}H, 250.13 MHz; ^{19}F, 235.36 MHz; ^{13}C, 62.90 MHz; ^{29}Si, 49.69 MHz) and referenced to internal *DMSO*-d_6 at 2.58 ppm (^{1}H) and 39.50 ppm (^{13}C), external *TMS* (^{29}Si) and $CFCl_3$ (^{19}F), corrections being made for the shift of the lock substance.

1-(Trifluoromethyl)silatrane

To 1.90 g (10 mmol) of $CF_3Si(OCH_3)_3$ in 8 ml of *THF*, 1.49 g of $N(CH_2CH_2OH)_3$ (10 mmol) in 3 ml of *THF* were added dropwise. The reaction mixture was stirred for 2 h at ambient temperature. The white precipitate was filtered off and recrystallized from methanol yielding 1.08 g (44%) of 1-(trifluoromethyl)silatrane.

X-ray structural investigation

Crystals of (trifluoromethyl)silatrane were grown from a solution in methanol, and a specimen with the dimensions 0.23 × 0.32 × 0.50 mm was glued to a glass fiber. X-ray measurements were at 22°C

Table 3. Atomic coordinates and equivalent isotropic displacement parameters (pm^2) for 1-(trifluoromethyl)silatrane

	x	y	z	$U(eq)$[a]
Si	0.05804(3)	0.39859(2)	0.25484(2)	240(1)
F(1)	−0.09707(10)	0.19504(6)	0.23071(8)	450(2)
F(2)	−0.25944(9)	0.32395(6)	0.15832(8)	453(2)
F(3)	−0.22548(10)	0.29782(7)	0.36871(7)	479(2)
O(1)	−0.05849(9)	0.49992(6)	0.31069(8)	352(2)
O(2)	0.17164(10)	0.32319(6)	0.36066(8)	347(2)
O(3)	0.08771(10)	0.38377(7)	0.09304(7)	355(2)
N	0.25984(11)	0.50208(7)	0.25561(8)	279(2)
C(1)	−0.13722(12)	0.30007(8)	0.25372(10)	301(2)
C(2)	0.20777(15)	0.59314(9)	0.34182(13)	370(2)
C(3)	0.0154(2)	0.60531(9)	0.32015(14)	398(2)
C(4)	0.40655(13)	0.43935(10)	0.31259(12)	372(2)
C(5)	0.33100(15)	0.36335(11)	0.41387(13)	394(2)
C(6)	0.2810(2)	0.53248(10)	0.11428(11)	372(2)
C(7)	0.2339(2)	0.43257(11)	0.03384(11)	388(2)

[a] $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

with a Siemens P3 diffractometer equipped with a graphite monochromator and employing MoK_α radiation. The compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 777.2(1)$, $b = 1236.9(2)$, $c = 1002.8(1)$ pm, $\beta = 91.33(1)°$, $Z = 4$, and $D_{calc} = 1.677\ g \cdot cm^{-3}$. The hemisphere of data with $l \geq 0$ and $2.6° \leq \theta \leq 35.1°$ was collected by the θ–2θ scan technique. The intensities were derived by profile analysis, corrected for the small fluctuations (±1%) of the three periodically monitored standards and by integration for absorption (transmission: 0.9221–0.9457), and converted into structure factor amplitudes. Of the 8861 intensities measured, 4274 are unique; 3204 of them have $I > 2\sigma(I)$. The structure was solved by direct methods and refined conventionally with anisotropic and isotropic temperature factors for the non-hydrogen and hydrogen atoms, respectively. The refinement on F^2 of the 185 parameters, which included an extinction correction, converged with a conventional residual $R_1 = 0.034$ for the observed reflections and a weighted residual (F^2) $wR_2 = 0.095$ for all reflections. The final difference density map contains features between 376 and $-236\ e \cdot nm^{-3}$ and confirms the structure. Coordinates of the non-hydrogen atoms are listed in Table 3 [30]. Direct methods, least-squares refinement, and the ORTEP drawing were made with the SHELXTL program package (Version 5.03).

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