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Synthesis and structure of (O–Si)chloro[1-(1,1-dimethyl-2-trifluoroacetylhydrazonium)methyl]dimethylsilane

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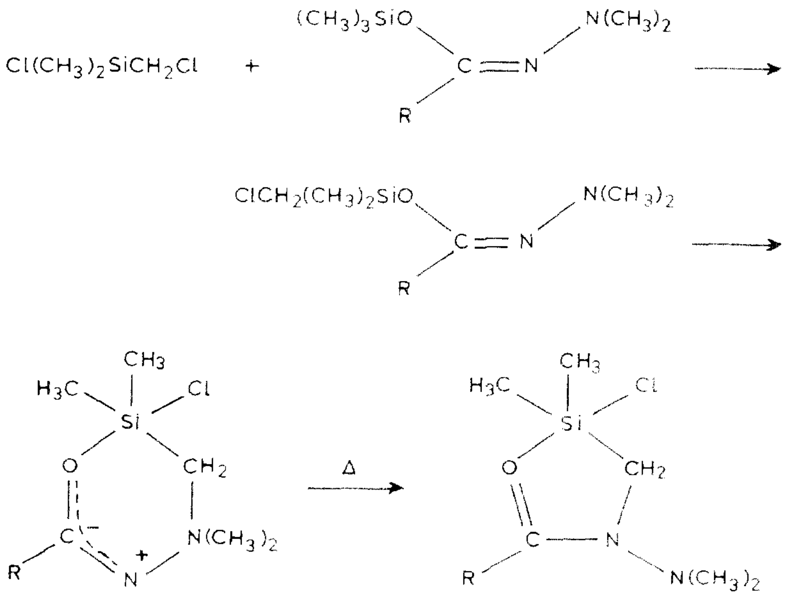
Abstract

(O–Si)Chloro[1-(1,1-dimethyl-2-trifluoroacetylhydrazonium)methyl]dimethylsilane, $Cl(CH_3)_2SiCH_2(CH_3)_2NNC(O)CF_3$ (I), has been prepared and its X-ray structural study ($R = 0.33$ for 2737 reflections with $I \geqslant 2\sigma$) has been carried out. The Si atom has a trigonal-bipyramidal [3 + 2]-coordination with the O and Cl atoms in the axial positions (Si–O 1.879(1), Si–Cl 2.432(1) Å). The hypervalent Cl–Si–O interaction results in the chelate six-membered silacarbofunctional cycle which has for the first time been studied by the use of X-ray crystallography.

A considerable number of organic derivatives of pentacoordinated silicon with a five-membered silacarbofunctional cycle closed by a Si–O coordination bond has been synthesized and studied recently [1,2]. In some of these compounds the Si atom is bonded to such groups as $RC(O)OCH_2$, $RC(O)NRCH_2$, $CH_2(CH_2)_nC(O)NCH_2$, $R_2NC(O)NR'CH_2$ and $RS(O)CH_2$, in addition to being bonded to one or more highly electronegative substituents (Hal, OAc, OSO_2R).

Analogous compounds with the chelate six-membered cycles have only recently been found. These compounds, particularly a number of (O–Si)chloro[1-(1,1-dimethyl-2-acylhydrazonium)methyl]dimethylsilanes of the general formula $Cl(CH_3)_2SiCH_2(CH_3)_2NNC(O)R$, were characterized in solution by multinuclear NMR spectroscopy [3–5]. They are formed in the two-stage reaction of *O*-trimethylsilyl derivatives of carboxylic acid 1,1-dimethylhydrazides (*Z*-isomers) with dimethyl(chloromethyl)chlorosilane. These derivatives of five-coordinated Si atom are remarkable not only in their unusual structure which was unambiguously established by NMR spectroscopy, but also for their surprising ability to undergo thermal isomerization into the five-membered chelate(O–Si)chloro[2-(1,1-dimethyl-2-acylhydrazino)methyl]dimethylsilanes:



The necessary conditions for this rearrangement depend on the nature of the substituent R. The reaction is sometimes sufficiently slow, to allow the isolation of the six-membered (O–Si)-chelate compounds including I in its individual form [5].

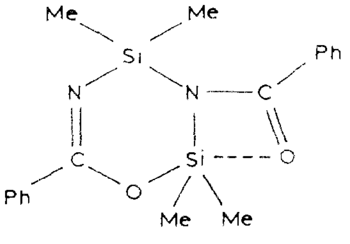
Here we describe the synthesis and structural characterization of one of the representatives of this interesting type of compound, viz. (O–Si)chloro[1-(1,1-dimethyl-1-trifluoroacetylhydrazonium)methyl]dimethylsilane (I).

Results and discussion

The X-ray structural study of I has provided full support for the structure which was previously put forward on the basis of the NMR (^{1}H, ^{13}C, ^{15}N, ^{29}Si) data [4,5].

Compound I is the first derivative of pentacoordinated silicon with the six-membered cycle closed by a Si–O coordination bond, whose structure has been established directly by X-ray diffraction study.

Although in cyclobis(benzamido)dimethylsilane (II), the Si atom is also involved in the six-membered cycle, it is the exocyclic benzamide O atom which takes part in the very weak secondary Si–O interaction (Si–O 2.613(2) Å) whereas the endocyclic Si–O distance of 1.670 Å corresponds to that of a normal covalent bond (see e.g. [6]).



(II)

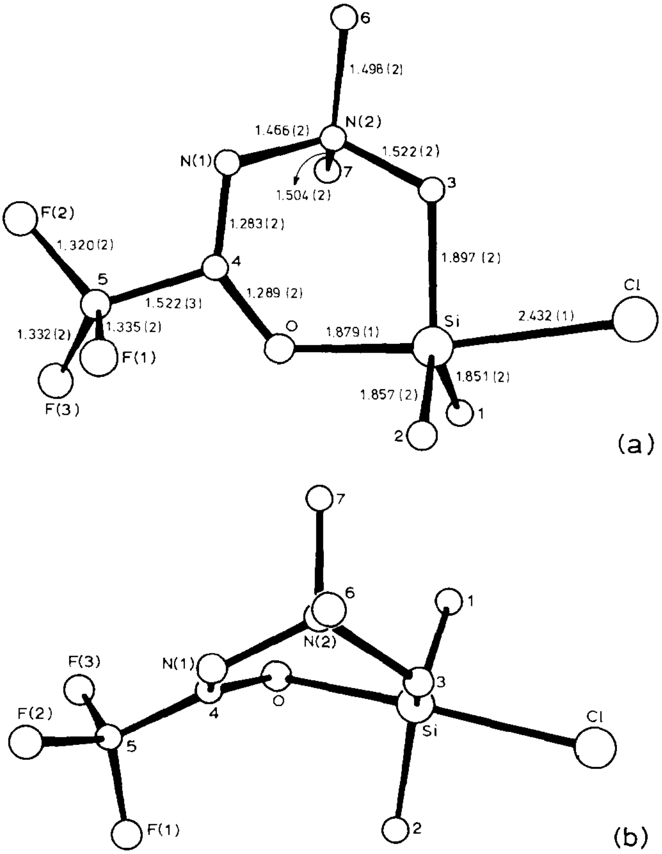


Fig. 1. Structure of molecule 1: (a) projection onto the mean plane of the molecule with bond lengths, H atoms are not shown; (b) projection of molecule normal to the mean plane, and passing through the mid-points of the C(4)–N(1) and Si–C(3) bonds.

The pentacoordinated Si atom in molecule I (Fig. 1, Table 1) has a slightly distorted trigonal-bipyramidal [3 + 2]-coordination with the O and Cl atoms in the axial, and the three carbon atoms in the equatorial positions.

Table 1

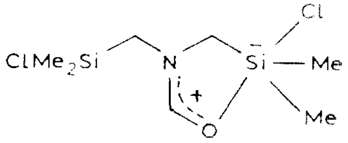
Bond angles ω (°)

ClSiO	172.20(5)	SiOC(4)	122.5(1)	OC(4)N(1)	131.3(2)
ClSiC(1)	91.41(7)	N(2)N(1)C(4)	112.5(1)	OC(4)C(5)	114.1(1)
ClSiC(2)	88.87(7)	N(1)N(2)C(3)	113.0(1)	N(1)C(4)C(5)	114.6(2)
ClSiC(3)	82.46(5)	N(1)N(2)C(6)	106.1(1)	F(1)C(5)F(2)	106.7(2)
OSiC(1)	95.13(8)	N(1)N(2)C(7)	108.8(1)	F(1)C(5)F(3)	106.0(2)
OSiC(2)	91.38(8)	C(3)N(2)C(6)	108.2(1)	F(1)C(5)C(4)	110.4(2)
OSiC(3)	90.73(7)	C(3)N(2)C(7)	111.8(1)	F(2)C(5)F(3)	108.3(2)
C(1)SiC(2)	120.96(9)	C(6)N(2)C(7)	108.8(1)	F(2)C(5)C(4)	114.0(2)
C(1)SiC(3)	117.72(9)	SiC(3)N(2)	117.4(1)	F(3)C(5)C(4)	111.0(2)
C(2)SiC(3)	120.79(9)				

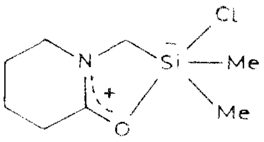
Slight distortions of trigonal-bipyramidal geometry may be caused by the small displacement of the Si atom from the equatorial plane towards the O atom (Si 0.078(1) Å). The axial Si–Cl, 2.432(1) Å, and Si–O, 1.879(1) Å bonds are elongated to somewhat different extents (~ 0.40 Å = 17% and ~ 0.20 Å = 12%) as compared with the corresponding standard bond length values for the tetrahedral silicon atom (Si–Cl 2.048 Å [7] and Si–O 1.68 Å [8]). The OSiCl angle between the axial substituents (172.20(5)°) differs slightly from 180°. The C(1)SiC(3) equatorial angle (117.72(9)°) is somewhat smaller than 120°, whereas the other two equatorial angles are in fact equal to this value (C(1)SiC(2)120.96(9) and C(2)SiC(3) 120.79(9)°).

The C=O and C=N bond lengths of 1.289(2) and 1.283(2) Å lie between the standard values for corresponding double (1.215(5) and 1.255 Å [9]) and single C_{sp^2}–O (1.360 Å [10]) and C_{sp^2}–N (1.43 Å [9]) bonds. From the well-known bond length/bond order correlation [11], their bond orders (n_{CO} = 1.31 and n_{CN} = 1.72) indicate significant π-conjugation in the N=C=O group. The increase of the N(1)C(4)O angle (131.3(2)°) at the planar-trigonally sp^2-hybridized carbon atom, bonded to the CF_3 group, is noteworthy. Such widening of the angle is analogous to the increase in the OCO angle in the structurally related F_3CCOO^- anion (129.5(2)° [12]) and indicates delocalization of the negative charge in the N(1)–C(4)–O fragment. The N(1)–N(2) bond length (1.466(2) Å) in molecule I is close to the corresponding values usually found in hydrazinium cations (e.g. 1.463(3) Å in 1,1,1-trimethylhydrazinium chloride [13]), the N(2)–C distance being characteristic of the bonds involving the ammonium nitrogen atom (1.512 Å [14]).

It is interesting to compare the structure of I and its *N*-amidomethyl (III) [15] and *N*-lactamomethyl (IV) [16] analogues.



(III)



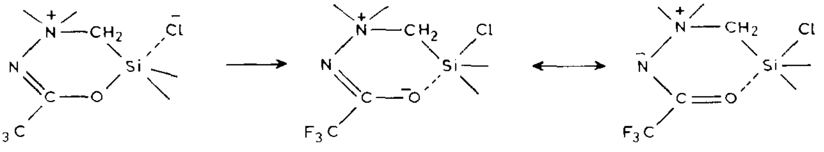
(IV)

In molecules I, III and IV the pentacoordinated Si atom is bonded to the same substituents.

However, in molecule I the negative charge (but not the positive charge as in III and IV) is delocalized over the N=C=O group. It is probably this fact, not the difference in the cycle size, which is responsible for the formation of the stronger Si–O bond in I compared with those in III and IV (1.918 and 1.954 Å respectively). Remarkably, the electron-releasing effect of N=C=O group in molecule I exceeds that of amido fragments in molecules III and IV in spite of the presence of the electron-accepting CF_3 group in the former. Quite naturally, strengthening of the Si–O bond in molecule I is accompanied by weakening of the C=O bond of 1.289(2) Å in length compared with 1.266(3) and 1.269(2) Å in III and IV. By contrast, the Si–Cl bond in I is weaker than in III and IV (2.348(2) and 2.307(2) Å, respectively).

The tendency to elongation of the endocyclic equatorial Si–C(3) bond (1.897(2) Å) in comparison with other equatorial Si–C bonds (1.851(2) and 1.857(2) Å), which is manifested in I, III and IV, is noteworthy. However, whereas in molecules III and IV some elongation of the endocyclic Si–C bond can be attributed to the formation of the strained five-membered cycle, in molecule I this elongation is evidently due to the steric overcrowding in the surroundings of the ammonium N atom.

Thus the bond length distribution in molecule I may be explained by the superposition of resonance forms Ia, Ib, Ic with the predominance of the first two forms.



(Ia) (Ib) (Ic)

The puckering parameters of six-membered heterocycle (Q 1.48 Å, θ 154.9°, ψ_2 258.6°) [17] show that it has a somewhat distorted boat conformation: the O and N(2) atoms are displaced by 0.340(1) and 0.677(1) Å from the N(1)C(4)SiC(3) plane and the dihedral angles formed by the latter with the N(1)N(2)C(3) and C(4)OSi planes are equal to 48.04 and 28.32° respectively (Fig. 1b). The folding angle of the six-membered cycle along the N(2) ··· O line is equal to 40.5°.

There are no shortened intermolecular distances in crystal I.

Thus molecule I provides the first example where the existence of six-membered chelate silacarbofunctional cycles, involving the Si–O coordination bond has been confirmed by a direct structural study. The Si–O and Si–Cl bond lengths were found to be one of the shortest and one of the longest, respectively, in the structurally studied derivatives of the pentacoordinated Si atom with a trigonal-bipyramidal $OSiC_3Cl$ fragment. At the same time NMR data indicate that analogues of I with an aryl or alkyl substituent at the C(4) atom should exhibit in even shorter Si–O bond. The Si–Cl bond in these molecules is possibly greatly weakened, so that it is the Si–Cl, and not the Si–O bond, which is most likely to be the coordinated, i.e. it represents a secondary bond. The results of X-ray structural study of these compounds will be published shortly.

Experimental

Preparation and isolation of I was carried out in evacuated glass ampoules. To a solution of 3.17 g (0.014 mol) of trimethylsiloxy-2,2,2-trifluoroethanone-dimethylhydrazone in 30 ml of dry ether cooled by liquid nitrogen was added 1.99 g (0.14 mol) of dimethylchlorosilane. The temperature of the reaction mixture was gradually increased over 1–2 h to 20 °C and maintained at this temperature for 5 h. Crystallization of needle-shaped colourless crystals I followed. The solvent and the trimethylchlorosilane formed were removed in vacuo (0.5 mmHg). The crystals obtained were washed with dry ether (10 ml) and dried in vacuo (0.5 mmHg) at 20 °C. Yield of I was 2.99 g (82%), m.p. (in the evacuated capillary) 162.5%. Found: C, 32.43; H, 5.68; F, 21.00; N, 10.56; Si, 9.09; Cl, 13.71. $C_7H_{14}F_3N_2OSiCl$ calc: C, 32.00; H, 5.37; F, 21.69; N, 10.66; Si, 10.69; Cl, 13.51%.

The colourless crystals of I are triclinic: a 7.119(3), b 8.581(3), c 10.038(3) Å, α 94.21(3), β 98.51(2), γ 93.16(3)°, V 603.5(3) Å^3, D_c 1.446 g cm^{-3}, $Z = 2$, $C_{17}H_{14}F_3N_2OSiCl$, space group $P\bar{1}$. The unit cell parameters and intensities of 2866

Table 2

Atomic coordinates ($\times 10^5$ for Cl and Si; $\times 10^4$ for F, O, N, C; $\times 10^3$ for H) and equivalent isotropic (isotropic for H atoms) temperature factors (Å^2)

Atom	x	y	z	B_{iso}^{eq}
Cl	22356(7)	30712(5)	58263(5)	2.68(1)
Si	34151(7)	52468(5)	74824(5)	1.71(1)
F(1)	8424(2)	7955(1)	8977(1)	3.62(4)
F(2)	7725(2)	10266(2)	8548(2)	5.30(5)
F(3)	6783(2)	9226(2)	10240(1)	4.28(4)
O	4449(2)	7058(1)	8567(1)	2.07(3)
N(1)	4764(2)	8898(2)	6988(1)	1.83(3)
N(2)	2988(2)	8188(2)	6195(1)	1.63(3)
C(1)	1403(3)	4899(2)	8422(2)	2.85(5)
C(2)	5662(3)	4259(2)	7885(2)	2.81(5)
C(3)	2989(2)	6416(2)	5946(2)	1.72(4)
C(4)	5233(2)	8237(2)	8083(2)	1.83(4)
C(5)	7047(3)	8952(2)	8960(2)	2.55(5)
C(6)	2821(3)	8873(2)	4855(2)	2.23(5)
C(7)	1349(3)	8662(2)	6887(2)	2.18(4)
Atom	x	y	z	B_{iso}
H(1.1)	13(3)	495(3)	780(2)	4.6(5)
H(1.2)	118(3)	990(3)	868(2)	5.4(6)
H(1.3)	139(3)	530(2)	911(2)	4.0(5)
H(2.1)	661(3)	436(3)	728(3)	6.2(6)
H(2.2)	637(3)	454(3)	870(3)	6.2(7)
H(2.3)	536(3)	324(3)	776(3)	6.7(7)
H(3.1)	171(2)	607(2)	538(2)	1.7(4)
H(3.2)	399(3)	627(2)	540(2)	2.8(4)
H(6.1)	146(3)	840(2)	431(2)	2.5(4)
H(6.2)	396(2)	867(2)	446(2)	2.4(4)
H(6.3)	278(3)	997(2)	499(2)	3.4(5)
H(7.1)	134(2)	828(2)	772(2)	2.5(4)
H(7.2)	133(2)	978(2)	698(2)	2.5(4)
H(7.3)	11(2)	823(2)	630(2)	1.7(4)

reflections were measured with a Syntex $P2_1$ four-circle automatic diffractometer at 153 K (Mo-K_α radiation $\theta/2\theta$ scan, θ_{max} 30°). The structure was solved by direct method (using the MULTAN [18] programme) and refined by the block-diagonal least-squares technique to an anisotropic approximation for non-hydrogen atoms. All H atoms were located in the difference Fourier synthesis and refined in the isotropic approximation. The final R factors are $R = 0.033$ and $R_w = 0.033$ for 2737 reflections with $I \geqslant 2\sigma$. All calculations were performed with an "Eclipse S/200" computer using the INEXTL programme package [19]. The atomic coordinates and the temperature factors are listed in Table 2.

Acknowledgments

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