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The crystal structure of $(\text{Me}_3\text{Si})_3\text{CSi}(\text{OH})_2(\text{OCOCF}_3)$. Novel hydrogen bonding

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Abstract

Crystals of the title compound are made up of tetrameric units in which the four molecules are linked through both $\text{O}-\text{H}\cdots\text{OH}$ and $\text{O}-\text{H}\cdots\text{O}=\text{C}$ hydrogen bonding.

Introduction

Organosilanols show a strong tendency to undergo self-association in the solid state through $\text{O}-\text{H}\cdots\text{O}$ bonding, and there is a wide range of structures based on such bonding [1,2]. Intermolecular hydrogen bonding between silanols and other hydroxylic species (see for example [3]) and intra- or inter-molecular bonding between silanol groups and either an ether-oxygen [3] or an amino-nitrogen atom [1,4] are also known, but up to now there seems to have been no example of such bonding between a silanol and another element (e.g. the compound ${}^t\text{Bu}_2\text{Si}(\text{OH})\text{F}$ was found not to show the $\text{O}-\text{H}\cdots\text{F}$ interactions that might have been expected [5]) or between a silanol and an oxygen atom in anything other than an OH group, an ether, or a siloxane.

One of the most interesting hydrogen-bonded structures formed by a silanol is that of the triol $\text{TsiSi}(\text{OH})_3$ (where Tsi denotes the bulky group $(\text{Me}_3\text{Si})_3\text{C}$), which forms a remarkably stable hexameric cage in the crystal [6], and one of the types of oxygen atom most able to accept a hydrogen atom in a hydrogen bond is the carbonyl oxygen of a carboxylate group, and we thus thought it of interest to determine the crystal structure of the trifluoroacetate $\text{TsiSi}(\text{OH})_2(\text{OCOCF}_3)$, **1**, the preparation of which was described a few years ago [7].



(1)

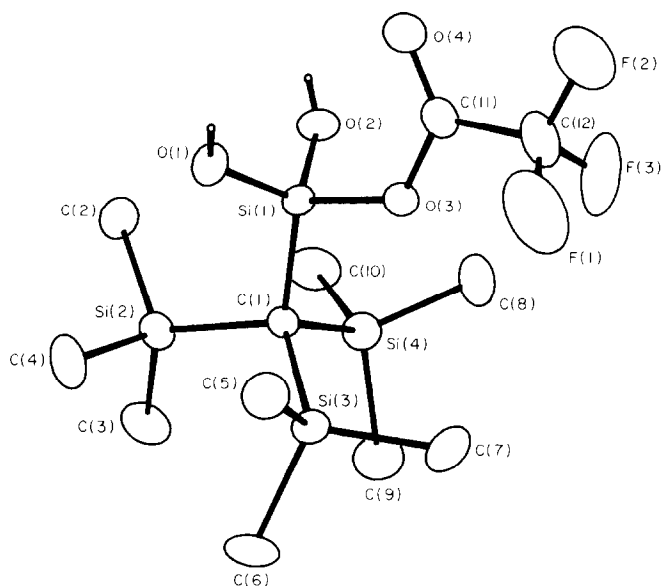


Fig. 1. Structure and atom numbering of molecule A, with hydrogen atoms omitted.

Results and discussion

Crystals of **1** were, indeed, found to show $\text{SiO-H} \cdots \text{O}=\text{C}(\text{O})\text{CF}_3$ interactions. The crystal is made up of tetrameric units containing two types of crystallographically distinct molecules, **A**, containing Si(1), (and the symmetry-related **A'**), the structure and atom-numbering for which are shown in Fig. 1, and **B**, containing Si(1a), (and the symmetry related **B'**). As can be seen from the stereoview in Fig. 2 and from Table 1, each molecule of the first type **A** (or **A'**) is hydrogen bonded

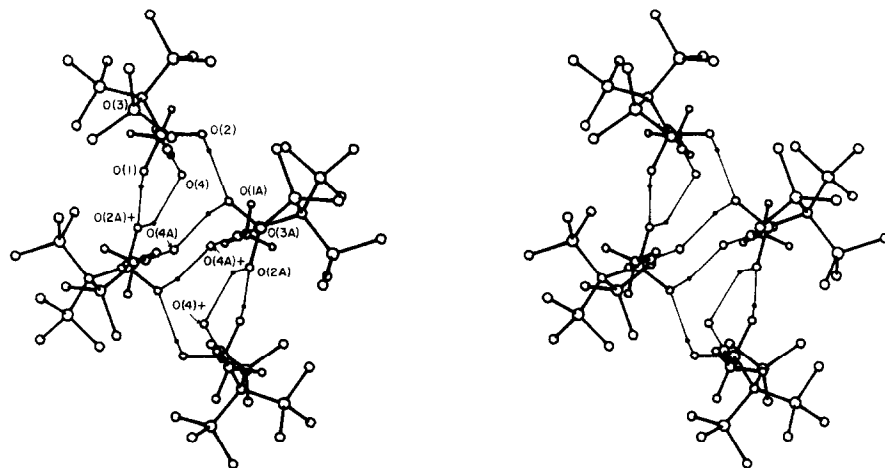


Fig. 2. Stereoview of the tetrameric unit; only hydrogen atoms of OH groups are shown. Narrow lines represent hydrogen bonds. The numbering O(2A), O(2A)+, etc., corresponds to the numbering O(2a), O(2a'), etc., in Fig. 3 and Tables 1 and 2.

Table 1
Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses ^a

	Molecule			Molecule	
	A	B		A	B
<i>(a) Bonds</i>					
Si(1)–O(1)	1.620(4)	1.633(3)	Si(1)–O(2)	1.616(3)	1.624(3)
Si(1)–O(3)	1.719(4)	1.713(3)	Si(1)–C(1)	1.827(5)	1.820(4)
Si(2)–C(1)	1.929(5)	1.920(5)	Si(2)–C(2)	1.873(7)	1.907(7)
Si(2)–C(3)	1.902(8)	1.905(7)	Si(2)–C(4)	1.919(7)	1.976(8)
Si(3)–C(1)	1.927(5)	1.931(5)	Si(3)–C(5)	1.876(6)	1.891(6)
Si(3)–C(6)	1.896(7)	1.928(7)	Si(3)–C(7)	1.916(7)	1.940(7)
Si(4)–C(1)	1.918(5)	1.940(5)	Si(4)–C(8)	1.873(7)	1.867(7)
Si(4)–C(9)	1.909(8)	1.923(6)	Si(4)–C(10)	1.912(7)	1.981(8)
F(1)–C(12)	1.256(9)	1.295(10)	F(2)–C(12)	1.252(9)	1.235(8)
F(3)–C(12)	1.275(9)	1.240(9)	O(1)–H(O1)	0.80(6)	0.92(5)
O(2)–H(O2)	0.69(6)	0.69(5)	O(3)–C(11)	1.304(7)	1.300(5)
O(4)–C(11)	1.199(8)	1.200(5)	C(11)–C(12)	1.512(9)	1.495(8)
H(O1) ··· O(2a)′		2.12(6)	H(O1a) ··· O(4a)′		1.96(5)
H(O2) ··· O(1a)		2.18(6)	H(O2a) ··· O(4)′		2.41(5)
O(1) ··· O(2a)′		2.918(5)	O(2) ··· O(1a)		2.833(5)
<i>(b) Angles</i>					
O(1)–Si(1)–O(2)	112.2(2)	110.6(2)	O(1)–Si(1)–O(3)	105.9(2)	105.4(2)
O(1)–Si(1)–C(1)	113.5(2)	113.7(2)	O(2)–Si(1)–O(3)	106.0(2)	103.3(2)
O(2)–Si(1)–C(1)	110.7(2)	114.4(2)	O(3)–Si(1)–C(1)	108.1(2)	108.5(2)
C(1)–Si(2)–C(2)	112.0(2)	111.9(3)	C(1)–Si(2)–C(3)	111.4(3)	111.8(2)
C(1)–Si(2)–C(4)	111.3(3)	108.8(3)	C(2)–Si(2)–C(3)	106.6(3)	104.7(3)
C(2)–Si(2)–C(4)	106.4(3)	108.8(3)	C(3)–Si(2)–C(4)	109.0(3)	110.7(3)
C(1)–Si(3)–C(5)	111.8(3)	111.1(2)	C(1)–Si(3)–C(6)	113.3(3)	110.7(3)
C(1)–Si(3)–C(7)	111.2(2)	109.7(3)	C(5)–Si(3)–C(6)	105.6(3)	105.2(3)
C(5)–Si(3)–C(7)	106.7(3)	110.0(3)	C(6)–Si(3)–C(7)	107.9(3)	110.1(3)
C(1)–Si(4)–C(8)	112.3(3)	111.4(3)	C(1)–Si(4)–C(9)	110.5(3)	110.7(3)
C(1)–Si(4)–C(10)	111.5(3)	108.2(3)	C(8)–Si(4)–C(9)	106.5(3)	106.4(3)
C(8)–Si(4)–C(10)	107.5(3)	110.6(3)	C(9)–Si(4)–C(10)	108.2(3)	109.6(3)
Si(1)–O(1)–H(O1)	128(4)	110(4)	Si(1)–O(2)–H(O2)	113(4)	122(5)
Si(1)–O(3)–C(11)	124.6(4)	123.8(3)	Si(1)–C(1)–Si(2)	106.6(3)	106.4(2)
Si(1)–C(1)–Si(3)	110.3(2)	110.9(2)	Si(1)–C(1)–Si(4)	108.2(2)	108.1(2)
Si(2)–C(1)–Si(3)	110.3(2)	111.1(2)	Si(2)–C(1)–Si(4)	110.5(2)	110.9(2)
Si(3)–C(1)–Si(4)	110.8(3)	109.4(2)	O(3)–C(11)–O(4)	126.5(5)	127.5(4)
O(3)–C(11)–C(12)	112.1(5)	113.1(4)	O(4)–C(11)–C(12)	121.3(6)	119.4(5)
F(1)–C(12)–F(2)	110.4(6)	103.8(7)	F(1)–C(12)–F(3)	103.4(8)	100.9(7)
F(1)–C(12)–C(11)	112.4(6)	110.0(6)	F(2)–C(12)–F(3)	104.8(6)	111.6(6)
F(2)–C(12)–C(11)	113.8(7)	114.8(5)	F(3)–C(12)–C(11)	111.3(5)	114.3(6)
O(1)–H(O1) ··· O(2a)′		175(6)	O(2)–H(O2) ··· O(1a)		158(6)
O(1a)–H(O1a) ··· O(4a)′		161(6)	O(2a)–H(O2a) ··· O(4)′		137(6)

^a Symmetry element ' is: 0.5 – x, 0.5 – y, 1 – z.

directly to just two molecules, **B** and **B'**, of the second type through both O–H ··· OH bonding and O–H ··· O=C bonding, whereas each molecule of the second type is in addition linked directly to another molecule of its own type solely by O–H ··· O=C bonding. The hydrogen-bonding pattern can be seen more clearly from the diagrammatic representation in Fig. 3 (which is intended only to display the hydrogen-bonding rather than to depict the geometry, which can be seen from the stereoview in Fig. 2).

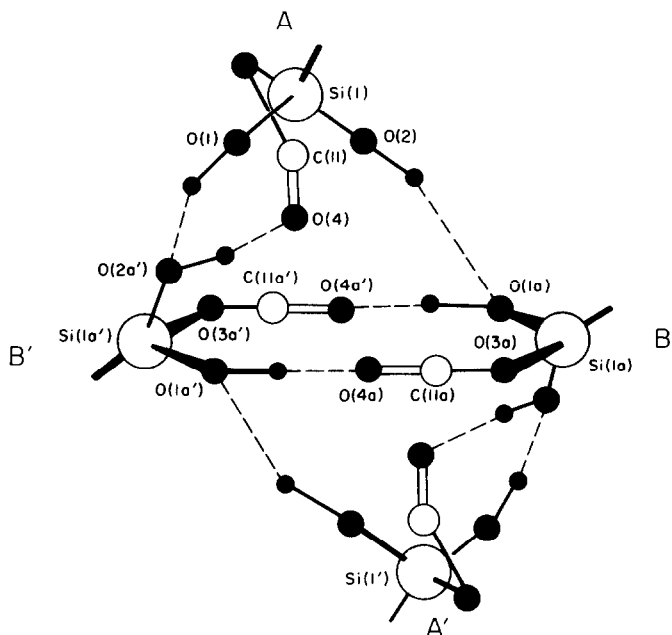
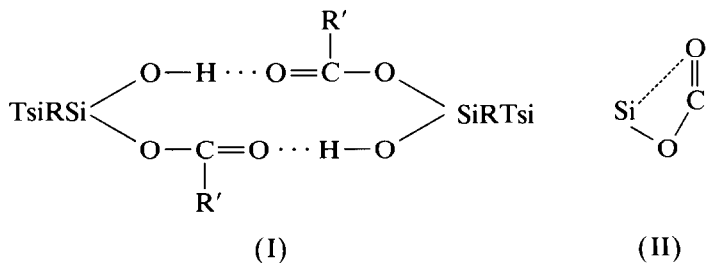


Fig. 3. Diagrammatic representation of the hydrogen bonding in the tetrameric unit of **1**. (This is not intended to depict details of the geometry, which can be seen in Fig. 2.)

The geometry of the O–H \cdots O=C linkage between the two molecules **B** and **B'** of the second type is markedly different from that between molecules of the two types. The former bonding (e.g. between O(1a) and O(4a')) involves an O–H \cdots O angle of 161(6) $^\circ$ and an H \cdots O distance of 1.96(5) Å and the latter type an angle of 137(6) $^\circ$ and a distance of 2.41(5) Å. (It is usual, other things being equal, for a smaller O–H \cdots O angle to be associated with a longer O–H \cdots O distance.) The O–H \cdots OH bonds involve angles of 175(6) $^\circ$ (O(1) \cdots O(2a')) and 158(6) $^\circ$ (O(2) \cdots O(1a)) and corresponding H \cdots O distances of 2.12(6) and 2.18(6) Å, respectively. In view of the magnitudes of the esd's, it cannot be firmly stated that the shortest, and thus strongest, hydrogen bonds are those between the molecules **B** and **B'**, but O–H \cdots O=C could be expected to be stronger than O–H \cdots O(H) bonding provided the O–H \cdots O angles were not too different.

The nature of the bonding between molecules **B** and **B'** suggests that species of the type TsiSiR(OH)(OCOR') would be likely to form dimers of type I.



It is to be expected that hydrogen bonds will be observed between OH groups of silanols and a range of other types of acceptor centres. Species such as $R_2Si(OH)(OCOR')$ or $RSi(OH)_2(OCOR')$ are not normally stable, since the OH group of one molecule would be expected to attack the Si-OCOR bond of another, to give a siloxane linkage, and it is the stabilization provided by the bulk of the Tsi group that makes possible the study of compound **1**. Likewise many other compounds of the types $RSi(OH)_2X$, $RSi(OH)X_2$, and $R_2Si(OH)X$, where X is, e.g. halogen, or any other good leaving group, will not usually be sufficiently stable for study, but again stabilization can be provided by one or more bulky groups R; e.g. TsiSiH(OH)I is a stable solid [8]. However, even without such stabilization there seems no reason why inter- or intra-molecular hydrogen bonding should not be observed between SiOH and appropriate X groups attached to carbon, e.g. in compounds of the type $R_2Si(OH)(CH_2)_nX$.

The silicon atoms within the $(Me_3Si)_3C$ groups were found to be disordered (see Experimental section) in a way frequently observed previously [9], and the consequent uncertainty in the values of the bond lengths and angles within the group rules out detailed discussion of them. There are, however, some features of interest within the molecules of **1** making up the tetramer, as set out below. (Where two values for a parameter are given without explanation they refer to molecules **A** and **B**, respectively.)

(a) In spite of the difficulty mentioned above, it seems safe to conclude that the lengths of the $(Me_3Si)_3C-Si(OH)_2(OCOCF_3)$ bonds (1.827(5), 1.820(4) Å) are significantly shorter than those of the Me_3Si-C bonds (mean 1.925(6), 1.930(10) Å). A similar effect has been noted for other compounds in which the $(Me_3Si)_3C$ group is attached to a silicon atom bearing one or more oxygen atoms [10].

(b) The Si-OH bonds (1.620(4) and 1.616(3) Å in molecule **A**; 1.633(3) and 1.624(3) in **B**) are distinctly shorter than the Si-OCOCF₃ bonds (1.719(4), 1.713(3)). The Si-OCOCF₃ distances are significantly longer than the corresponding distance in tetraacetoxysilane $Si(OCOMe)_4$ (1.625 Å) [11].

(c) The Si-O-CO angles (124.6(4), 123.8(3)°) are similar to those in $Si(OCOMe)_4$ (125.7°) [11] but somewhat larger than those in $H_3SiOCOH$ (116.8°) [12] and $H_2Si(OCOH)_2$ (120.4(4)°) [13] as determined by electron diffraction.

(d) The (non-bonded) distances between the silicon atoms Si(a) and Si(1') and the carbonyl oxygens, O(4) and O(4') of the trifluoroacetoxy groups to which they are attached are 3.029(5) and 3.020(4) Å, respectively. These distances are longer than those in $H_3SiOCOH$ (2.86 Å), $H_2Si(OCOH)_2$ (ca. 2.90 Å), and $Si(OCOMe)_4$ (2.925 Å) that are thought to reflect a weak bonding interaction of type II [1a,11-13] *, but they are still substantially below the sum (3.60 Å) of the relevant van der Waals radii. Any such bonding interaction would be expected to be weaker in the case of **1**, since the coordinating ability of the carbonyl oxygen atom will be reduced by electron-withdrawal by the CF₃ substituent and by the hydrogen bonding to that atom, and yet in the absence of a favourable, though very weak interaction, there seems to be no reason why the carbonyl oxygen in this, as in all

* Similar Si...O=C distances, varying between 2.895 and 2.981 Å, in various amide derivatives of the type $Me_3SiOCONRR'$ have also been interpreted in terms of weak bonding [1]. It is noteworthy that in $Si(OCOMe)_4$ [11] all four carbonyl oxygens appear to be involved in such interaction.

Table 2

Fractional atomic coordinates ($\times 10^4$; except $\times 10^3$ for H) with estimated standard deviations in parentheses

	x	y	z
Si(1)	3373.2(5)	1441.9(12)	3811.1(5)
Si(2)	3882.7(7)	-823.0(16)	3989.1(8)
Si(3)	4412.0(6)	1288.9(16)	3624.1(7)
Si(4)	3508.4(7)	153.2(18)	2876.9(7)
Si(1a)	1671.7(5)	1478.3(11)	4367.7(5)
Si(2a)	1434.3(8)	-928.4(18)	4041.6(10)
Si(3a)	1015.7(8)	1106.4(19)	3296.3(8)
Si(4a)	624.7(7)	717.7(20)	4294.6(9)
F(1)	3744(2)	4984(4)	3566(3)
F(2)	3043(2)	5577(4)	3487(3)
F(3)	3232(2)	4614(4)	2950(2)
F(3a)	1219(2)	4989(4)	4113(3)
F(2a)	1903(2)	5659(3)	4348(2)
F(1a)	1690(3)	4875(5)	3680(2)
O(1)	3484(1)	1510(3)	4427(1)
O(2)	2816(1)	1084(3)	3567(1)
O(3)	3438(1)	2804(3)	3605(1)
O(4)	2869(2)	3666(4)	3930(2)
O(2a)	1679(1)	1526(3)	4972(1)
O(1a)	2213(1)	1178(3)	4278(1)
O(3a)	1566(1)	2863(3)	4178(1)
O(4a)	2201(1)	3671(3)	4715(1)
C(1)	3797(2)	527(4)	3572(2)
C(2)	3298(2)	-1298(5)	4146(2)
C(3)	4110(2)	-2062(5)	3652(3)
C(4)	4333(3)	-564(7)	4627(3)
C(5)	4585(2)	2155(5)	4222(2)
C(6)	4940(2)	277(6)	3642(3)
C(7)	4387(2)	2316(6)	3067(3)
C(8)	3209(3)	1409(7)	2507(2)
C(9)	3994(3)	-370(7)	2537(2)
C(10)	3025(2)	-1009(6)	2830(3)
C(11)	3173(2)	3666(5)	3682(2)
C(12)	3299(3)	4739(5)	3431(3)
C(1a)	1189(1)	600(4)	3995(2)
C(3a)	922(2)	-2020(5)	3931(3)
C(2a)	1815(2)	-1263(5)	4705(3)
C(4a)	1846(2)	-1125(6)	3542(3)
C(6a)	732(3)	-119(7)	2853(2)
C(5a)	1575(2)	1551(5)	3065(2)
C(7a)	561(2)	2366(5)	3234(2)
C(9a)	45(2)	229(6)	3819(3)
C(8a)	514(2)	2219(5)	4463(2)
C(10a)	738(3)	-261(8)	4908(3)
C(11a)	1842(2)	3708(4)	4377(2)
C(12a)	1661(3)	4832(5)	4153(3)
Si(2)*	3563.8(34)	-984.4(82)	3546.4(40)
Si(3)*	4413.2(33)	707.7(86)	4026.2(38)
Si(4)*	3843.9(40)	1025.5(85)	2888.5(36)
Si(2a)*	1188.3(18)	-798.3(42)	4396.8(20)
Si(3a)*	1356.3(16)	202.1(41)	3353.2(17)
Si(4a)*	582.4(15)	1347.6(39)	3881.1(17)

Table 2 (continued)

	x	y	z	
H(O1)	346(2)	204(5)	460(2)	
H(O2)	266(2)	126(5)	371(2)	
H(O1a)	245(2)	133(5)	457(2)	
H(O2a)	189(2)	152(5)	516(2)	
Occupancy for	Si(2),	Si(3),	Si(4)	0.84
	Si(2)*,	Si(3)*,	Si(4)*	0.16
	Si(2a),	Si(3a),	Si(4a)	0.68
	Si(2a)*,	Si(3a)*,	Si(4a)*	0.32

other pertinent structures, should choose to lie so close to the silicon atom when it could move away by rotation about the Si–O bond. It is noteworthy that in spite of the hydrogen-bonding to the carbonyl oxygen and the possible Si ··· O=C interaction, the configuration around the carbonyl carbon is planar, the sum of the bond angles around it being 359.9°.

Experimental

Suitable crystals of **1** [7] were obtained by recrystallization from pentane. A crystal of 0.4 × 0.2 × 0.15 mm was used for the data collection.

Crystal data: C₁₂H₂₉F₃O₄Si₄, *M* = 406.7, monoclinic, space group C₂/c, *a* = 28.149(7), *b* = 11.763(8), *c* = 26.944(6) Å, β = 102.94(2)°, *U* = 8694.9 Å³, *Z* = 16, *D_c* = 1.2 g cm⁻³, *F*(000) = 3456, Mo-K_α radiation, λ = 0.71069 Å, μ = 3.0 cm⁻¹. Data were collected on an Enraf-Nonius CAD4 diffractometer. Intensities of 8169 unique reflections with *hk* ± 1 and 2 < θ < 25° were measured by a θ/2θ scan with Δθ = (0.8 + 0.35 tan θ)° and a maximum scan time of one minute. Correction was made for Lorentz and polarization effects and also for crystal decay of 14% during the data collection; 4200 reflections with |*F*|² > 3σ(*F*²) were used in the structure refinement, where σ(*F*²) = [σ²(*I*) + (0.04*I*)²]^{1/2}/Lp.

Two independent molecules were found with the SHELXS-86 program [14], and all non-hydrogen atoms were refined by full matrix least squares with anisotropic temperature factors. Both (Me₃Si)₃C groups showed a disorder of a type commonly observed [9] of the Si atom between sites in an 84/16 ratio for molecule **A** and a 68/32 ratio for molecule **B**. A difference map was used to locate H(O1), H(O2), H(O1a) and H(O2a), which were refined isotropically with *B* = 6.0 Å². The remaining hydrogen atoms were fixed at calculated positions (C–H = 0.95 Å) corresponding to the geometry defined by the Si sites of major occupancy. Refinement converged at *R* = 0.059, *R*' = 0.071, with weighting scheme *w* = 1/σ²(*F*) and final shift to error ratios of < 0.03. A final difference map had no peaks of > 0.4 e Å⁻³. Atomic coordinates are listed in Table 2. Lists of thermal parameters and structure factors are available from PBH.

The structure solution and refinement were carried out on a Microvax II computer with the Enraf–Nonius Structure Determination Package.

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