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Synthesis, crystal and molecular structure of *N*,*N*-dimethyl-3-[tris(trimethylsiloxanyl)silyl]pyrrolinium chloride

R. Rudert and G. Schmaucks

Max-Planck-Institut für Kolloid- und Grenzflächenforschung, D-12484 Berlin (Germany)

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Abstract

The synthesis of *N*,*N*-dimethyl-3-[tris(trimethylsiloxanyl)silyl]pyrrolinium chloride was carried out by hydrosilylation of 1,4-dichlorobut-2-yne with tris(trimethylsiloxanyl)silane followed by the reaction of the product with dimethylamine. The structure of the crystalline white solid was determined by an X-ray diffraction study. The Si–O–Si angles range from 145.8(3)° to 161.4(4)°. The molecules are packed in bilayers with a head–head arrangement.

Key words: Silicon; Siloxane; Hydrosilylation; Crystal structure

1. Introduction

The synthesis of new functionalized siloxanes was carried out in order to throw light on their extraordinary surface activity. The relations between structure and adsorption behaviour are of particular interest. The special properties of siloxane amphiphiles in comparison to those of structurally similar hydrocarbon surfactants can be attributed to the remarkable flexibility of the siloxanyl groups.

The determination of the X-ray crystal structure of siloxane surfactants is difficult because of the high thermal motion of the siloxane backbone and the problems of obtaining suitable crystalline material.

We report the first X-ray crystal structure of a surface active tetrasiloxane.

2. Experimental section

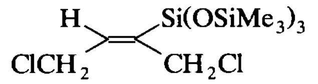
2.1. Synthesis

The hydrosilylation of 1,4-dichlorobut-2-yne (**1**) with tris(trimethylsiloxanyl)silane (**2**) was carried out under anhydrous conditions without solvent under nitrogen in the presence of a platinum catalyst (eqn. (1)). The concentration of the catalyst was about 20 ppm platinum per mole of triple bond. After 8 h at 120°C the conversion was about 80% complete. The yield of 1,4-dichloro-2-[tris(trimethylsiloxanyl)silyl]but-2-ene (**3**) was 70% after distillation. The product was a colourless liquid, which was treated with dimethylamine (**4**) in diethyl ether at − 10°C and the mixture was allowed to warm to room temperature in about 5 h. A white precipitate was formed, and was separated by filtration and shown by analysis to be the by-product dimethylamine hydrochloride (**6**) (eqn. 2).

The *N*,*N*-dimethyl-3-[tris(trimethylsiloxanyl)silyl] pyrrolinium chloride (**5**) was isolated by removing the diethyl ether under reduced pressure. It was characterized by ^{13}C-NMR spectroscopy and elemental analysis.

$ClCH_2C{\equiv}CCH_2Cl + (Me_3SiO)_3SiH \longrightarrow$

(**1**) (**2**)

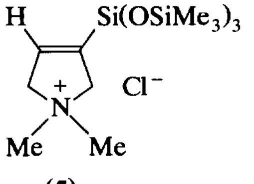


(1)

(**3**)

$(3) + 2\,Me_2NH \xrightarrow{\text{Diethylether}}$

(**4**)



$+ Me_2NH \times HCl$ (2)

(**6**)

(**5**)

Correspondence to: Dr. R. Rudert.

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N,N-dimethyl-3-[tris(trimethylsiloxanyl)silyl]pyrrolinium chloride (**5**): Anal. found: C 42.10, H 8.97, N 3.25. $C_{15}H_{38}NO_3Si_4Cl$ (428.27 g/mole) calcd.: C 42.06, H 8.94, N 3.27%. ^{13}C-NMR [$CDCl_3$]: (Me_3SiO) 1.625; N–Me 53.493; CH_2 73.024, 75.558; =CH 134.568; C= 135.260 ppm.

2.2. Crystal data

$C_{15}H_{38}N^+Si_4O_3Cl^- \cdot H_2O$, M = 446.3, monoclinic, space group $P2_1/c$, $a = 6.953(3)$, $b = 36.385(5)$, $c = 11.214(2)$ Å, $\beta = 105.33(3)°$, $V = 2736(1)$ Å^3, $Z = 4$, $D_x = 1.082$ g cm^{-1}, $\mu = 3.11$ mm^{-1} (Cu Kα radiation).

2.3. Data collection and structure determination

A crystal of approximate size 0.31 × 0.07 × 0.02 mm was mounted on a CAD4 diffractometer. The cell constants were determined by 25 reflections with $16° < \theta < 21°$. 3277 reflections of which 2601 were unique were measured by ω-2θ step scans. Of the unique reflections 2114 were treated as observed ($I > \sigma(I)$). Standard reflections were measured every 30 min. During the measurement the intensities fell by 40%. Corrections were made for Lorentz and polarization effects and for the decay. Equivalent reflections were merged. The internal R based on use of all reflections was 0.028.

The program used for structure solution and refinement was MOLEN [1]. One fragment of the asymmetric unit was found by direct methods. During refinement of this fragment all other non-H atoms were found by difference Fourier synthesis. All non-H atoms were refined with anisotropic displacement parameters minimizing $\Sigma w(|F_o| - |F_c|)^2$, $w = 1/\sigma(F_o)^2$. The H atoms bonded to C atoms were placed at a fixed distance of 0.95 Å assuming trigonal, tetrahedral or staggered tetrahedral conformations. The H atoms of the ring atoms and of the ammonium methyl groups were refined with isotropic displacement parameters and all others were kept fixed. Finally hydrogen atoms of the water were found by difference Fourier synthesis. Of these only H(11W) could be refined and the other was kept fixed. The total number of variables was 274. The final R was 0.063, the weighted R 0.048, and the goodness of fit 3.5.

Empirical absorption correction did not improve the R-values. A full list of bond lengths and angles and a table of thermal parameters has been deposited with the Cambridge Crystallographic Data Centre.

3. Discussion

The final atomic parameters are listed in Table 1. Bond distances and angles are in Table 2 and Table 3. The atomic numbering scheme is shown in Fig. 1. As

TABLE 1. Atomic parameters of non-H atoms and equivalent isotropic displacement parameters (Å^2)

	x	y	z	B_{eq}
Cl	0.9954(3)	0.25023(5)	0.5073(1)	6.55(5)
Si(1)	0.8606(3)	0.11658(5)	0.7339(2)	5.43(5)
Si(2)	0.6675(4)	0.04133(6)	0.7719(2)	8.81(8)
Si(3)	1.1345(3)	0.12723(5)	0.9973(2)	5.95(5)
Si(4)	0.9210(3)	0.11099(6)	0.4658(2)	6.50(6)
O(1W)	0.1693(7)	0.2804(2)	0.7828(4)	11.2(2)
O(12)	0.7303(7)	0.0821(1)	0.7494(4)	8.4(2)
O(13)	1.0530(6)	0.1202(1)	0.8490(3)	6.6(1)
O(14)	0.9393(7)	0.1129(1)	0.6129(3)	7.6(1)
N(1)	0.5882(7)	0.2190(1)	0.6740(4)	4.5(1)
C(2)	0.7772(9)	0.1963(2)	0.7091(5)	4.7(2)
C(3)	0.7078(9)	0.1582(2)	0.7244(5)	5.0(2)
C(4)	0.528(1)	0.1605(2)	0.7381(5)	6.4(2)
C(5)	0.4455(9)	0.1992(2)	0.7316(6)	6.2(2)
C(11)	0.6217(9)	0.2579(2)	0.7159(5)	6.2(2)
C(12)	0.5063(9)	0.2197(2)	0.5361(5)	6.0(2)
C(21)	0.826(2)	0.0088(3)	0.724(1)	20.8(4)
C(22)	0.703(2)	0.0334(3)	0.9387(9)	17.6(4)
C(23)	0.410(2)	0.0361(3)	0.689(2)	27.1(7)
C(31)	0.928(1)	0.1421(2)	1.0602(6)	8.8(2)
C(32)	1.323(1)	0.1635(2)	1.0249(6)	8.3(2)
C(33)	1.245(1)	0.0834(2)	1.0697(8)	12.1(3)
C(41)	1.167(1)	0.1197(4)	0.4443(8)	15.8(4)
C(42)	0.848(2)	0.0652(2)	0.4111(8)	15.7(4)
C(43)	0.743(1)	0.1449(3)	0.3818(6)	12.5(3)

TABLE 2. Bond distances (Å)

Si(1)–O(12)	1.583(5)	Si(3)–O(13)	1.629(4)	N(1)–C(2)	1.514(7)
Si(1)–O(13)	1.598(4)	Si(3)–C(31)	1.842(8)	N(1)–C(5)	1.504(8)
Si(1)–O(14)	1.598(5)	Si(3)–C(32)	1.827(7)	N(1)–C(11)	1.491(8)
Si(1)–C(3)	1.836(6)	Si(3)–C(33)	1.860(8)	N(1)–C(12)	1.500(7)
Si(2)–O(12)	1.588(5)	Si(4)–O(14)	1.622(4)	C(2)–C(3)	1.495(8)
Si(2)–O(21)	1.80(1)	Si(4)–C(41)	1.81(1)	C(3)–C(4)	1.30(1)
Si(2)–O(22)	1.84(1)	Si(4)–C(42)	1.802(9)	C(4)–C(5)	1.514(9)
Si(2)–O(23)	1.79(1)	Si(4)–C(43)	1.823(9)		

TABLE 3. Bond angles (°)

O(12)–Si(1)–O(13)	110.9(2)	O(14)–Si(4)–C(42)	108.9(4)
O(12)–Si(1)–O(14)	111.2(3)	O(14)–Si(4)–C(43)	110.9(3)
O(12)–Si(1)–C(3)	108.7(3)	C(41)–Si(4)–C(42)	107.9(6)
O(13)–Si(1)–O(14)	106.9(3)	C(41)–Si(4)–C(43)	110.2(5)
O(13)–Si(1)–C(3)	109.1(2)	C(42)–Si(4)–C(43)	111.1(4)
O(14)–Si(1)–C(3)	110.1(3)	Si(1)–O(12)–Si(2)	161.4(4)
O(12)–Si(2)–C(21)	110.7(4)	Si(1)–O(13)–Si(3)	145.8(3)
O(12)–Si(2)–C(22)	109.8(4)	Si(1)–O(14)–Si(4)	156.3(3)
O(12)–Si(2)–C(23)	107.2(4)	C(2)–N(1)–C(5)	104.5(4)
C(21)–Si(2)–C(22)	105.9(5)	C(2)–N(1)–C(11)	112.7(4)
C(21)–Si(2)–C(23)	112.5(6)	C(2)–N(1)–C(12)	110.0(4)
C(22)–Si(2)–C(23)	110.7(7)	C(5)–N(1)–C(11)	112.8(5)
O(13)–Si(3)–C(31)	110.0(3)	C(5)–N(1)–C(12)	109.7(4)
O(13)–Si(3)–C(32)	109.1(3)	C(11)–N(1)–C(12)	107.2(4)
O(13)–Si(3)–C(33)	107.5(3)	N(1)–C(2)–C(3)	104.7(5)
C(31)–Si(3)–C(32)	108.7(4)	Si(1)–C(3)–C(2)	125.0(5)
C(31)–Si(3)–C(33)	110.9(4)	Si(1)–C(3)–C(4)	127.3(5)
C(32)–Si(3)–C(33)	110.5(4)	C(2)–C(3)–C(4)	107.5(5)
O(14)–Si(4)–C(41)	107.8(3)	C(3)–C(4)–C(5)	114.7(6)

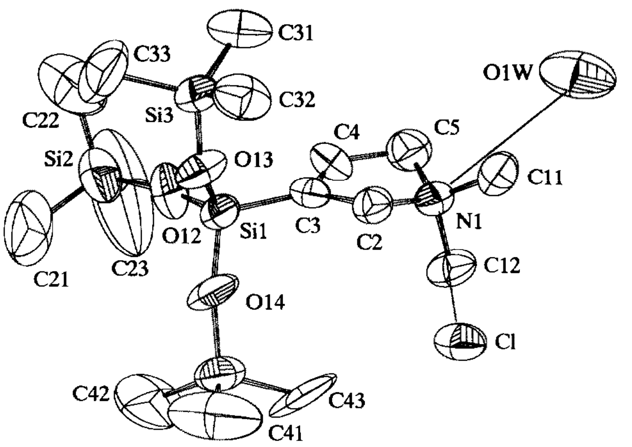

Fig. 1. Structure of the compound with thermal ellipsoids at 50% level. Drawing by PLATON92 [7].

TABLE 4. Selected interatomic distances (Å)

X ··· Y		symm (Y)
O(1W) ··· Cl	3.200(5)	−1+x, y, z
N(1) ··· Cl	3.949(5)	x, y, z
N(1) ··· Cl	4.200(5)	x, 1/2−y, 1/2+z
N(1) ··· Cl	4.207(6)	−1+x, y, z
N(1) ··· O(1W)	4.104(7)	x, 1/2−y, 1/2+z
N(1) ··· O(1W)	4.494(7)	1+x, 1/2−y, 1/2+z
C(32) ··· C(4)	3.846(9)	1+x, y, z
C(32) ··· C(5)	3.84(1)	1+x, y, z
C(32) ··· C(11)	3.836(9)	x, 1/2−y, 3/2+z
C(41) ··· C(4)	3.87(1)	1+x, y, z
C(43) ··· C(11)	3.98(1)	x, 1/2−y, −1/2+z

reported in many other publications (eight examples are listed in [2]), the Si–O–Si angle in siloxane compounds is very flexible, ranging from 140° to 180°. Gibbs [3] found by quantum chemical calculations that the minimum energy angle for $H_6Si_2O_7$ is 140°, but the angle can be deformed to 180° by supplying energy of 3 kT at room temperature. This is confirmed by this work: despite their chemical equivalence all three Si–O–Si angles are different, ranging from 145.8(3)° to 161.4(4)°. A relationship can be seen between the Si–O–Si angle and thermal motion: the larger the thermal vibrations of an $-OSiMe_3$ group, the larger the Si–O–Si angle. A similar relationship has been noted previously [4]. The bond Si–O distances to the central Si atom (Si(1)) are shorter than those to the outer Si atoms. This effect was also seen in some branched trisiloxane compounds [5,6]. The reason may be that the partial positive charge on Si(1) will be larger than those on the other Si atoms. Of the outer O–Si bond distances the bond O(12)–Si(2) appears to be shorter than the others, presumably because of the high thermal motion of Si(2).

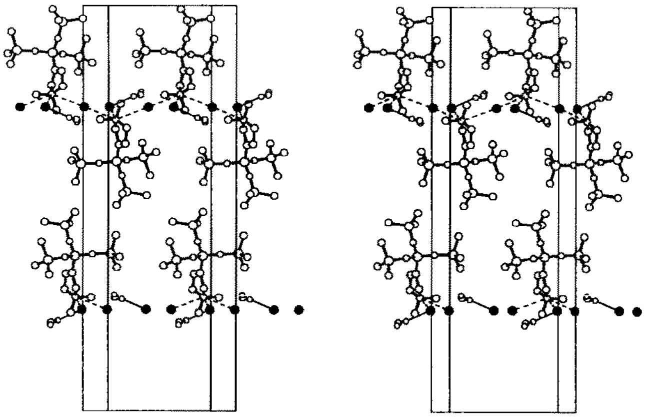

Fig. 2. Crystal packing viewed in the (0, 0, 1) direction. Cl–N contacts are shown by dotted lines, the hydrogen bond by a thin line. Cl atoms are symbolized by filled circles. Drawing by SCHAKAL92 [8].

The 4 ring carbon atoms C(2), C(3), C(4), C(5) and the silicon atom Si(1) are planar, the maximum deviation from the least squares plane being 0.03(3) Å. The distance between this plane and the nitrogen atom is 0.40(3) Å. A similar but planar pyrroline ring is found in N-ethyl-3-(heptamethyltrisiloxan-3-yl) pyrroline hydrochloride [6].

The molecules are packed in double layers in a head–head arrangement parallel to the (010) crystal plane (Fig. 2). There are 3 short Cl–N contacts of between 3.9 and 4.3 Å (Table 4). The two ammonium methyl groups prevent the chloride ion getting closer to the nitrogen atom. The Cl–N interactions form a two-dimensional network parallel to the double layers. The Cl^- ion takes part in a hydrogen bond with H(11W) of the water molecule. The oxygen atoms of the water molecules are near the nitrogen atoms.

The methyl group carbon atoms at Si(3) have three intermolecular contacts and two intramolecular contacts shorter than 4 Å to other carbon atoms. All these contacts involve ring atoms or ammonium methyl group atoms. The methyl group carbon atoms at Si(4) have four such contacts, but those at Si(2) have no short C–C contact. This explains why the thermal motion is small for Si(3) and Si(4) and large for Si(2).

The area required by one molecule in each layer is $a \cdot c \cdot \sin \beta = 75.2$ Å^2. The average of the four previously mentioned amphiphilic trisiloxanes is 60.0 Å^2. The angle between the plane through N(1), C(11) and C(12) and the layer plane is 87.6(5)°, and the angle between least-squares plane of the pyrrolinium ring and the layer plane is 77.1(2)°.

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