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The crystal structure of 1-(γ -mercaptopropyl)silatrane

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Abstract

The crystal structure of 1-(γ -mercaptopropyl)silatrane $\text{HS}(\text{CH}_2)_3\overset{\downarrow}{\text{Si}}(\text{OCH}_2\text{CH}_2)_3\text{N}$ has been determined by X-ray diffraction. The Si←N dative bond length is 2.177(4) Å, similar to those observed in other γ -organopropylsilatranes and in methylsilatrane. In contrast to the corresponding hydroxypropyl compound, no hydrogen-bonded dimers are formed in the lattice.

Introduction

In our previous paper [1] the crystal structure of 1-(γ -hydroxypropyl)silatrane has been described. In this compound the two molecules that form a dimer about an inversion center in the crystal lattice, are linked by an O–H...O hydrogen bond. Here the analogous S–H compound has been studied by X-ray crystallography.

Experimental

Synthesis

The title compound was synthesized by use of the a reesterification reaction [2]. The compound was recrystallized from n-heptane. Yield 82%, m.p. 94–96 °C (lit. 95–96 °C).

Crystal structure determination

The unit cell dimensions and the space group were determined from data collected on a computer-controlled Enraf–Nonius CAD-4 diffractometer at room temperature. Crystal data, data collection and least-squares parameters are listed in Table 1. The structure was solved by the MULTAN program [3] and was refined by full matrix least squares for the non-hydrogen atoms.

Table 1

Crystal data, data collection and least-squares parameters

Empirical formula	C ₉ H ₁₉ NO ₃ Si
<i>M</i> (a.m.u.)	249.41
<i>F</i> (000)	536
Crystal dimensions	0.10 × 0.20 × 0.35 mm
<i>a</i> (Å)	12.809(1)
<i>b</i> (Å)	11.447(1)
<i>c</i> (Å)	8.333(1)
<i>V</i> (Å ³)	1221.8(3)
Orthorhombic space group	<i>Pna</i> 2 ₁
<i>Z</i>	4
<i>D</i> _x (gcm ⁻³)	1.36
λ (Cu-K α) (Å)	1.54184
μ (Cu-K α) (cm ⁻¹)	32.0
2 θ limits (deg.)	3–150
Scan technique	θ –2 θ
No. of unique reflections	1240
Reflections used in least squares (<i>NO</i>)	1085 ($I \geq 3\sigma(I)$)
Number of variables (<i>NV</i>)	136
Weighting scheme	$4F_o^2/(\sigma(F_o^2))^2$
<i>R</i> _o	0.057
<i>R</i> _w	0.070
<i>R</i> _{tot}	0.068
$[\sum w(F_o - F_c)^2 / (NO - NV)]^{1/2}$	6.83

Systematic absences indicated a choice of either *Pna*2₁ or *Pnam* (alt. *Pnma*, no. 62). Parallel refinements showed that *Pna*2₁ was the correct choice of space group. The space group *Pnam* was further rejected from stereochemical considerations (i.e. it requires strictly planar SiOCCN moieties). At the end of isotropic refinements an

Table 2

Atomic coordinates for the non-hydrogen atoms. *B*_{eq} (Å²) is defined as $B_{eq} = 4/3 \text{ trace}(B \times G)$ where *B* is the thermal motion tensor and *G* is the direct metric tensor

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{eq}
Si(1)	0.14537(8)	0.1055(1)	0.0000(0)	3.34(4)
O(2)	0.1974(2)	0.0630(3)	−0.1757(4)	4.4(1)
C(3)	0.2918(5)	0.1004(5)	−0.2329(8)	5.4(3)
C(4)	0.3157(4)	0.2246(6)	−0.1601(9)	5.8(3)
N(5)	0.2803(2)	0.2212(3)	0.003(1)	3.5(1)
C(6)	0.2393(4)	0.3328(5)	0.056(1)	8.3(5)
C(7)	0.1293(4)	0.3403(4)	0.015(1)	6.4(3)
O(8)	0.0804(2)	0.2301(2)	−0.011(1)	6.0(1)
O(9)	0.1970(2)	0.0580(3)	0.1651(5)	4.7(1)
C(10)	0.2895(4)	0.1074(7)	0.2376(8)	5.5(3)
C(11)	0.3532(4)	0.1677(5)	0.1180(8)	4.9(2)
C(12)	0.0278(3)	0.0085(4)	−0.006(1)	4.0(1)
C(13)	0.0483(3)	−0.1203(4)	0.009(1)	4.1(1)
C(14)	−0.0477(3)	−0.1918(5)	−0.003(1)	5.6(2)
S(15)	−0.0276(1)	−0.3468(1)	−0.0006(5)	6.62(7)

Table 3

Atomic coordinates and isotropic B values (\AA) for the hydrogen atoms

Atom	x/a	y/b	z/c	B
H(3a)	0.345	0.047	-0.202	6.4
H(3b)	0.289	0.105	-0.347	6.4
H(4a)	0.389	0.240	-0.164	6.8
H(4b)	0.279	0.283	-0.218	6.8
H(6a)	0.247	0.340	0.169	9.3
H(6b)	0.276	0.394	0.005	9.3
H(7a)	0.094	0.379	0.100	7.4
H(7b)	0.123	0.385	-0.081	7.4
H(10a)	0.269	0.161	0.318	6.5
H(10b)	0.330	0.046	0.285	6.5
H(11a)	0.397	0.114	0.065	5.9
H(11b)	0.394	0.226	0.168	5.9
H(12a)	-0.017	0.031	0.080	5.0
H(12b)	-0.007	0.021	-0.105	5.0
H(13a)	0.095	-0.143	-0.074	5.1
H(13b)	0.080	-0.135	0.111	5.1
H(14a)	-0.092	-0.172	0.084	6.6
H(14b)	-0.081	-0.172	-0.101	6.6
H(15)	-0.084	-0.361	-0.048	7.6

empirical absorption correction [4] was applied (the relative transmission coefficients ranged from 0.505 to 1.533 with an average value of 0.995). Positional parameters of the hydrogen atoms were generated from assumed geometries. No hydrogen parameters were refined. For the scattering factors used see ref. 5. The final atomic parameters are listed in Tables 2 and 3*.

Discussion

The structure and the numbering of atoms is depicted in Fig. 1; bond distances and angles are listed in Table 4. The molecular geometry is consistent with the characteristic structure of silatranes, and is confirmed by the good agreement between the observed and the calculated data. The observed and calculated data, and correlations are listed in Table 5, in which ΔSi is the distance of the silicon atom from the plane of equatorial oxygens, ΔN is the distance of the nitrogen atom from the plane of its substituents.

Four atoms (SiOCN) of the SiOCCN five-membered rings of the silatrane skeleton are nearly planar moieties and the carbon atoms α to the nitrogen atom deviate from the corresponding planes: C(4): 0.480(7); C(6): 0.421(12); C(11): 0.438(7) \AA . The $\text{Si} \leftarrow \text{N}$ bond lengths in various γ -organopropylsilatranes are all similar; $\text{R}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$ R = Cl: 2.181 [10]; CN: 2.164(4) [11]; SCN: 2.209(4) [12]; OH: 2.173(2) [1]; SH: 2.177(4) \AA and in methylsilatrane: 2.175(4) [13] \AA . Other geometric data are also similar in these molecules. It was found that the γ -organyl group has no effect on the geometry of the silatrane skeleton. There are

* Lists of observed and calculated structure factors and anisotropic temperature factors are available from the authors.

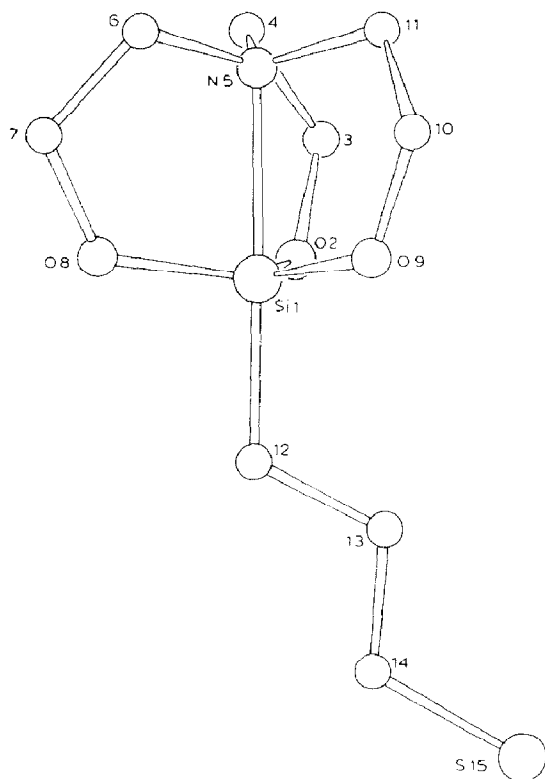


Fig. 1. The structure of 1-(γ -mercaptopropyl)silatrane with the numbering of atoms.

Table 4

Bond lengths (\AA) and angles ($^\circ$) with their esd's

Si(1)–O(2)	1.680(4)	O(2)–C(3)	1.369(8)	C(6)–C(7)	1.454(9)
Si(1)–N(5)	2.177(4)	C(3)–C(4)	1.576(10)	C(7)–O(8)	1.425(6)
Si(1)–O(8)	1.654(3)	C(4)–N(5)	1.435(12)	O(9)–C(10)	1.445(7)
Si(1)–O(9)	1.621(4)	N(5)–C(6)	1.450(8)	C(10)–C(11)	1.461(10)
Si(1)–C(12)	1.872(4)	N(5)–C(11)	1.470(9)	C(12)–C(13)	1.504(7)
				C(13)–C(14)	1.480(7)
				C(14)–S(15)	1.793(6)
O(2)–Si(1)–N(5)	82.7(4)	Si(1)–N(5)–C(6)	104.6(8)		
O(2)–Si(1)–O(8)	113.6(5)	Si(1)–N(5)–C(11)	105.0(7)		
O(2)–Si(1)–O(9)	118.7(4)	C(4)–N(5)–C(6)	112.2(11)		
O(2)–Si(1)–C(12)	97.1(5)	C(4)–N(5)–C(11)	115.3(10)		
N(5)–Si(1)–O(8)	82.9(5)	C(6)–N(5)–C(11)	113.5(10)		
N(5)–Si(1)–O(9)	82.5(4)	N(5)–C(6)–C(7)	109.3(12)		
N(5)–Si(1)–C(12)	178.6(5)	C(6)–C(7)–O(8)	114.2(13)		
O(8)–Si(1)–O(9)	122.9(5)	Si(1)–O(8)–C(7)	122.3(10)		
O(8)–Si(1)–C(12)	96.0(5)	Si(1)–O(9)–C(10)	123.9(7)		
O(9)–Si(1)–C(12)	98.7(5)	O(9)–C(10)–C(11)	111.0(9)		
Si(1)–O(2)–C(3)	124.3(7)	N(5)–C(11)–C(10)	106.6(10)		
O(2)–C(3)–C(4)	108.7(9)	Si(1)–C(12)–C(13)	116.0(9)		
C(3)–C(4)–N(5)	106.2(10)	C(12)–C(13)–C(14)	113.0(11)		
Si(1)–N(5)–C(4)	104.8(8)	C(13)–C(14)–S(15)	115.3(11)		

Table 5

Observed and calculated geometric data for the title compound

	Observed	Calculated	Correlation	Ref.
$d(\text{Si} \leftarrow \text{N})$ (Å)	2.177(4)	2.164 2.172	$d = 302.1 \bar{X}_R \exp(-0.257)$ $d = 0.342 \cdot \Sigma \sigma_i + 2.49$	[6] [7]
ΔSi (Å)	0.210(1)	0.199 0.210 0.199	$\Delta \text{Si} = 0.488d - 0.863$ $\Delta \text{Si} = 0.62d - 1.14$ $\Delta \text{Si} = 0.661d - 1.24$	[6] [8] [7]
ΔN (Å)	0.372(3)	0.363 0.365	$\Delta \text{N} = -0.391d + 1.214$ $\Delta \text{N} = -0.218d + 0.84$	[6] [7]
$\alpha(\text{NSiO})$ (°)	82.7(4)	83.0 83.0	$\alpha = -20.0d + 126.5$ $\alpha = -17.4d + 120.9$	[6] [9]

no $-\text{SH} \dots \text{S}$ close contacts in the structure, thus unlike the hydroxypropyl compound no dimers are formed in the crystal lattice.

Acknowledgements

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