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The molecular structure of 1-(γ-hydroxypropyl)silatrane

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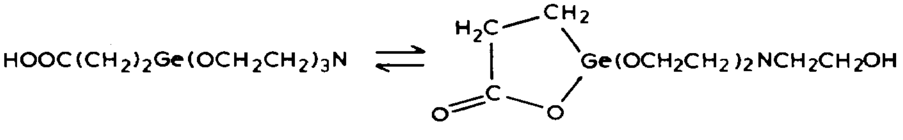
Abstract

The molecular structure of 1-(γ-hydroxypropyl)silatrane $[HO(CH_2)_3\overline{Si(OCH_2CH_2)_3N}$ was determined by X-ray diffraction and investigated by IR spectroscopy. The Si ← N dative bond length is 2.173(2) Å, similar to those observed in other γ-organopropylsilatranes and in methylsilatrane. Two molecules form a dimer about an inversion center in the crystal lattice, linked by an O–H...O hydrogen bond.

Introduction

The crystal structures of three γ-organopropylsilatrane derivatives have been determined so far: $R(CH_2)_3\overline{Si(OCH_2CH_2)_3N}$ (R = Cl, CN and SCN) [1–3]. The γ-substituents in these compounds have only slight effects, if any, on the geometry of the silatrane skeleton. The following rearrangement was, however, noted for a germatrane molecule [4]:



The structure of the cyclic compound was confirmed by X-ray structure determination. The title compound has been synthesized in order to study the capability of silicon of a similar interaction with a γ-OH group. For the study of the

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molecular structure, X-ray structure analysis and IR spectroscopic techniques were applied.

Experimental

Synthesis

Triethoxy(3-trimethylsiloxypropyl)silane (synthesized by a published method [5]) was treated with triethanolamine/sodiummethylate. The precipitate was separated, washed with ether and recrystallized from benzene.

Yield 95%, mp. 124–125°C (Found: C, 46.62; H, 8.00; N, 5.88; Si, 12.31. $C_9H_{19}NO_4Si$ calcd.: C, 46.33; H, 8.21; N, 6.00; Si, 12.04%).

X-ray structure determination

The determination of the unit cell dimensions and the space group and the collection of the intensity data were performed 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 [6] and was refined by full-matrix least-squares for the non-hydrogen atoms. At the end of isotropic refinement an empirical absorption correction [7] was applied (the relative transmission coefficients ranged from 0.904 to 1.174 with an average value of 1.003). Positional parameters of the hydrogen atoms were generated from assumed geome-

Table 1

Crystal data, data collection and least-squares parameters

Empirical formula	$C_9H_{19}O_4NSi$
M (a. m. u)	233.34
$F(000)$	504
Crystal dimensions	0.15 × 0.20 × 0.40 mm
a (Å)	7.819(1)
b (Å)	9.188(1)
c (Å)	16.124(2)
β (deg.)	101.22(2)
V (Å^3)	1136.1(5)
Monoclinic space group	$P2_1/n$
Z	4
D_x (g cm^{-3})	1.364
$\lambda(\text{Cu-}K_{\bar{\alpha}})$ (Å)	1.5418
$\mu(\text{Cu-}K_{\bar{\alpha}})$ (cm^{-1})	18.2
2θ limits (deg.)	3–150
Scan technique	θ–2θ
No. of unique reflexions	2184
Reflexions used in least-squares (NO)	1964 ($I > 3\sigma(I)$)
Number of variables (NV)	136
Weighting scheme	$4\,F_0^{\,2}(\sigma(F_0^{\,2}))^2$
R_0	0.037
R_w	0.054
R_{tot}	0.042
$[\Sigma w(\lvert F_0\rvert - \lvert F_c\rvert)^2(NO - NV)]^{1/2}$	3.41

Table 2

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

Atom	x/z	y/b	z/c	B_{eq}
Si(1)	0.24874(6)	0.16562(5)	0.91299(3)	2.46(1)
O(2)	0.4007(1)	0.1778(1)	0.85427(8)	3.22(4)
O(8)	0.2759(1)	0.0549(1)	0.99571(7)	3.25(4)
O(9)	0.0446(1)	0.2088(1)	0.86581(8)	3.24(4)
O(15)	0.1496(2)	0.5321(1)	1.15335(9)	4.50(5)
N(5)	0.1866(2)	−0.0358(1)	0.84298(9)	3.08(5)
C(3)	0.4410(2)	0.0626(2)	0.8030(1)	4.01(7)
C(4)	0.2773(3)	−0.0247(2)	0.7715(1)	4.17(8)
C(6)	0.2559(3)	−0.1508(2)	0.9039(1)	4.07(7)
C(7)	0.2356(2)	−0.0961(2)	0.9898(1)	3.59(6)
C(10)	−0.0591(2)	0.1201(2)	0.8028(1)	4.08(7)
C(11)	−0.0045(3)	−0.0364(2)	0.8181(1)	4.30(7)
C(12)	0.3026(2)	0.3391(2)	0.9729(1)	2.87(5)
C(13)	0.2084(2)	0.3656(2)	1.0464(1)	3.07(6)
C(14)	0.2424(2)	0.5123(2)	1.0869(1)	3.36(6)

Table 3

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

Atom	x/a	y/b	z/c	B
H(3a)	0.527	0.002	0.835	5.0
H(3b)	0.484	0.101	0.756	5.0
H(4a)	0.306	−0.119	0.754	5.2
H(4b)	0.206	0.024	0.725	5.2
H(6a)	0.375	−0.168	0.903	5.1
H(6b)	0.192	−0.238	0.890	5.1
H(7a)	0.313	−0.147	1.033	4.6
H(7b)	0.119	−0.111	0.997	4.6
H(10a)	−0.043	0.149	0.748	5.1
H(10b)	−0.179	0.130	0.806	5.1
H(11a)	−0.040	−0.092	0.768	5.3
H(11b)	−0.055	−0.076	0.862	5.3
H(12a)	0.424	0.339	0.995	3.9
H(12b)	0.274	0.417	0.934	3.9
H(13a)	0.087	0.356	1.026	4.1
H(13b)	0.245	0.293	1.088	4.1
H(14a)	0.207	0.585	1.045	4.4
H(14b)	0.364	0.522	1.109	4.4
H(15)	0.084	0.609	1.146	4.0

tries, except H(15) which was located in a difference map. No hydrogen parameters were refined. For the scattering factors used see ref. 8. The final atomic parameters are given in Tables 2 and 3 *.

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* Lists of observed and calculated structure factors and anisotropic temperature factors can be obtained from the authors.

Table 4

O–H stretching modes of title compound (cm^{-1})

Phase	Monomer	O–H...O–Si type dimer
Polycrystalline layer	–	3442 vs, rel. sharp
Nujoll mull	–	3434 vs, rel. sharp
Solution in CCl_4	3622 w	3485 m, broad
Solution in $CHCl_3$	3618 s	3458 m, broad

IR spectroscopic measurements

IR spectra were registered on a Perkin–Elmer 225 instrument in Nujol mull, CCl_4 and $CHCl_3$ solutions saturated at room temperature and a polycrystalline thin layer grown from a melt. Wave number reliability is about ± 2 cm^{-1} for sharp bands. Vibrational bands observed in the IR spectrum of the title compound in Nujol mull (cm^{-1}): 3434 vs, 2975 sh, 2932 s, 2878 s, 1487 m, 1479 sh, 1460 sh, 1454 w, 1445 sh, 1410 w, 1385 w, 1381 w, 1351 m, 1299 w, 1294 w, 1279 m, 1272 s, 1260 w, 1250 m, 1179 s, 1173 sh, 1126 vs, 1100 sh, 1085 vs, 1053 s, 1018 vs, 976 s, 939 vs, 909 vs, 876 w, 858 vw, 797 vs, 776 vs, 765 sh, 746 vs, 720 vs, 673 w, 626 s, 618 sh, 580 s, 478 w, 458 sh, 448 m, 353 m, 321 s, 280 m, 275 sh, 236 w, 212 m.

O–H frequencies are shown in Table 4.

Discussion

A molecular diagram with the numbering of atoms is depicted in Fig. 1; bond distances and angles are listed in Table 5. Characteristic features of the molecular

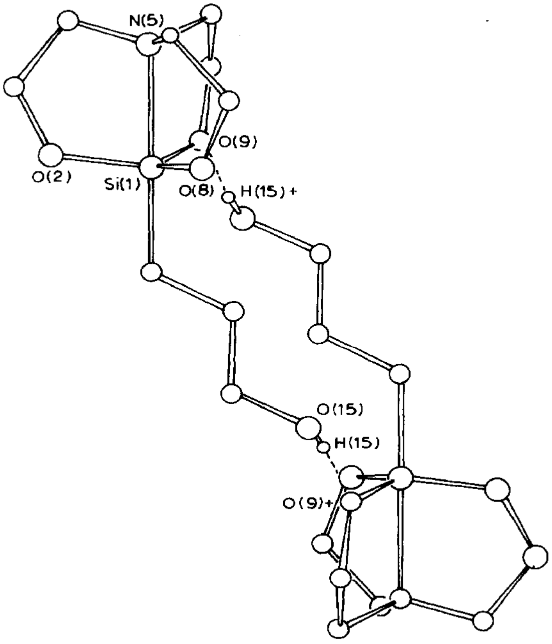

Fig. 1. A diagram of the 1-(γ-hydroxypropyl)silatrane molecule with the numbering of atoms.

Table 5

Bond lengths (Å) and angles (°) with their e.s.d.s

Si(1)–O(2)	1.661(1)	O(2)–C(3)	1.416(3)	N(5)–C(6)	1.472(3)
Si(1)–O(8)	1.658(1)	O(8)–C(7)	1.422(3)	N(5)–C(11)	1.470(2)
Si(1)–O(9)	1.676(1)	O(9)–C(10)	1.426(3)	C(3)–C(4)	1.512(3)
Si(1)–N(5)	2.173(2)	O(15)–C(14)	1.418(2)	C(6)–C(7)	1.512(3)
Si(1)–C(12)	1.869(2)	N(5)–C(4)	1.469(3)	C(10)–C(11)	1.506(3)
				C(12)–C(13)	1.533(3)
				C(13)–C(14)	1.499(3)

O(2)–Si(1)–O(8)	120.4(1)	Si(1)–N(5)–C(6)	104.4(2)
O(2)–Si(1)–O(9)	116.7(1)	Si(1)–N(5)–C(11)	104.9(2)
O(2)–Si(1)–N(5)	82.7(1)	C(4)–N(5)–C(6)	113.6(3)
O(2)–Si(1)–C(12)	97.1(1)	C(4)–N(5)–C(11)	114.0(3)
O(8)–Si(1)–O(9)	118.2(1)	C(6)–N(5)–C(11)	113.7(3)
O(8)–Si(1)–N(5)	82.9(1)	O(2)–C(3)–C(4)	108.8(3)
O(8)–Si(1)–C(12)	97.3(1)	N(5)–C(4)–C(3)	106.2(3)
O(9)–Si(1)–N(5)	82.5(1)	N(5)–C(6)–C(7)	106.4(3)
O(9)–Si(1)–C(12)	97.5(1)	O(8)–C(7)–C(6)	108.9(3)
N(5)–Si(1)–C(12)	179.8(1)	O(9)–C(10)–C(11)	109.0(3)
Si(1)–O(2)–C(3)	123.2(2)	N(5)–C(11)–C(10)	106.4(3)
Si(1)–O(8)–C(7)	123.6(2)	Si(1)–C(12)–C(13)	116.2(2)
Si(1)–O(9)–C(10)	123.2(2)	C(12)–C(13)–C(14)	114.1(3)
Si(1)–N(5)–C(4)	104.8(2)	O(15)–C(14)–C(13)	111.7(3)

geometry correspond to those of γ-organopropylsilatranes and methylsilatrane (cf. Table 6), i.e. the γ-hydroxyl group has no effect on the geometry of the silatrane skeleton. Instead of the expected rearrangement, a dimer is formed around an inversion center by hydrogen bonding (O–H: 0.87 Å, H...O: 1.94 Å, O–H...O: 175°). The Si–O(9) bond is rather long (1.676(1) Å) with respect to the Si–O(2) and Si–O(8) bonds (1.661(1) and 1.658(1) Å). This is attributable to the hydrogen bonding.

The assignment of the IR spectrum is based on [10]. The band observable at 580 cm^{-1} corresponds to the silatrane skeletal deformation vibration (δ_{skel}). Band splittings are also observed in the crystalline state, which indicates that the CH_2–CH_2–O groups in the molecule are not symmetry equivalent. The band observed above 3400 cm^{-1} corroborates the presence of a hydrogen-bonded dimer.

Table 6

Some characteristic geometrical data for γ-organopropylsilatranes and methylsilatrane $R(CH_2)_3\text{-}\overline{Si(OCH_2CH_2)_3N}$

R	Si ← N (Å)	Si–C (Å)	NSiC (°)	$NSiO_{mean}$ (°)	ΔSi (Å)	ΔN (Å)	Lit.
Cl	2.181	1.875	178.2	83.2	0.20		[1]
CN	2.164(4)	1.884(5)	178.9(4)	83.1	0.20	0.37	[2]
SCN	2.209(4)	1.880(5)	179.2(2)	82.3	0.22	0.36	[3]
OH	2.173(2)	1.869(2)	179.8(1)	82.7	0.21	0.37	this work
methyl-silatrane	2.175(4)	1.870(6)	179.4(2)	82.7	0.21	0.38	[9]

In non-polar (CCl_4) and slightly polar ($CHCl_3$) the O–H stretching modes refer to a monomer–dimer equilibrium (cf. Table 4). The relative quantity of the monomer increases in $CHCl_3$ solution.

Acknowledgements

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References

1 A.A. Kemme, Ya. Ya. Bleidelis, V.M. Dyakov and M.G. Voronkov, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 2400.
2 Wang Shoudao and Hu Ninghai, Scientia Sinica B, 26 (1983) 1233.
3 Dai Jinbi, Zhang Jiping, Wu Yexin and Wu Guanli, Jiegou Huaxue, 2 (1983) 101.
4 N.V. Alekseyev, S.N. Gurkova, A.I. Gusev, S.N. Tandura, T.K., Gar, N. Yu. Khromova, N.A. Viktorov and V.F. Mironov, Zh. Obshch. Khim., 52 (1982) 2136.
5 K.A. Andrianov, V.I. Pakhomov and N.E. Lapteva, Dokl. Akad. Nauk SSSR, 151 (1963) 849.
6 P. Main, S.E. Hull, L. Lessinger, G. Germain, J.-P. Declercq and M.M. Woolfson, MULTAN 78, A System of Computer Programmes for the Automatic Solution of Crystal Structures from X-ray Diffraction Data (Univ.'s of York (Great Britain) and Leuven (Belgium))
7 N. Walker and D. Stuart, Acta Crystallogr. A, 39 (1983) 158.
8 L. Párkányi, Á. Szöllósy, L. Bihátsi, P. Hencsei and J. Nagy, J. Organomet. Chem., 256 (1983) 235.
9 L. Párkányi, L. Bihátsi and P. Hencsei, Cryst. Struct. Comm., 7 (1978) 435.
10 M.G. Voronkov, S.G. Shevchenko, E.I. Brodskaya, V.P. Baryshok, P. Reich, D. Kunath and Yu.L. Frolov, Izv. Sibirsk. Otd. Akad. Nauk SSSR, Ser. Khim., 5 (1981) 135.