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CRYSTAL STRUCTURE OF 1-[*N*-(2-AMINOETHYL)-AMINOPROPYL]SILATRANE*

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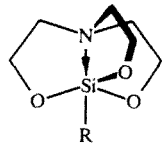
The crystal structure of 1-[N-(2-aminoethyl)aminopropyl]silatrane has been determined by x-ray diffraction at room temperature. The Si←N bond distance (2.165(2) Å) is in the range observed for other 1-X-propylsilatranes (X = CN, OH, SH, Cl and SCN). The structure is partially disordered: the silatrane moiety displays a disorder that is typical for silatranes and the aminoethyl group terminating the planar chain linked to silicon is rotationally disordered.

In 1989 Voronkov et al. reported [1] a study of 1-[*N*-(2-aminoethyl)amino alkyl]silatranes I, II (c.f. scheme) and their 2:1 complexes with $CuCl_2$. The title compound is the building block of one of the complexes characterized in the cited paper. Xe^0 fast atom bombardment spectra indicated that the Si←N bonds in the complexes are stronger than in the parent silatranes. Unfortunately no crystal structure data are available on the complexes, therefore direct comparison of the lengths of the transannular dative bonds, as determined by crystal structure analysis, is not possible. The crystal structures of five other 1-(γ-propyl)silatrane derivatives of the type $X\text{-}(CH_2)_3\text{-}Si(OCH_2CH_2)_3N$, X = CN (III), OH (IV), SH (V), Cl (VI), SCN (VII) was published. In the present paper we report the crystal structure of 1-[*N*-(2-aminoethyl)aminopropyl]silatrane (II).



R = $(CH_2)_n$–X; I n = 1, X = NH–$(CH_2)_2NH_2$;
II n = 3, X = NH–$(CH_2)_2NH_2$;
III n = 3, X = CN;
IV n = 3, X = OH;
V n = 3, X = SH;
VI n = 3, X = Cl;
VII n = 3, X = SCN

A perspective molecular diagram with the numbering of atoms is depicted in Fig. 1a., selected bond lengths and angles are presented in Table 1. The transannular dative-acceptor Si←N bond length is 2.165(2) Å which fits in the range of observations for other (III-VII) 1-(γ-propyl)silatranes (Table 2). The rather long Si←N bond is attributable to the methylene chain (n = 3) separating the electron withdrawing group from the silicon atom.

The disorder in the silatrane moiety (c.f. Fig. 1b) is typical for most disordered silatranes. The disordered carbon atoms (in α-positions to N_5) appear on both sides of an imaginary plane passing through the Si_1, O, C^β, N_5 atoms. This type of disorder may be regarded as a frozen state of the dynamic flapping in solution of the C^α atoms that deviate most from the best plane of the $Si_1-O-C^\beta\cdots N_5$ moiety.

The geometric features, correlated with the length of the transannular bond, are the deviation of the silicon atom from the plane of the equatorial oxygen atoms (ΔSi) and the distance of N_5 from the plane formed by its three substituents (ΔN).

*Dedicated to Professor Dr. Édmund Lukevits on the occasion of his 60th birthday.

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TABLE 1. Selected Bond Lengths (Å) and Angles (°)

Bond	Bond lengths (Å)	Bond	Bond lengths (Å)
$Si_1—O_9$	1,661(2)	$C_6—C_7$	1,509(4)
$Si_1—O_2$	1,668(2)	$C_7—O_8$	1,415(3)
$Si_1—O_8$	1,670(2)	$O_9—C_{10}$	1,414(3)
$Si_1—C_{12}$	1,875(2)	$C_{10}—C_{11}$	1,528(5)
$Si_1—N_5$	2,165(2)	$C_{12}—C_{13}$	1,527(3)
$O_2—C_3$	1,412(3)	$C_{13}—C_{14}$	1,508(3)
$C_3—C_4$	1,523(4)	$C_{14}—N_{15}$	1,456(3)
$C_4—N_5$	1,474(3)	$N_{15}—C_{16}$	1,455(3)
$N_5—C_{11}$	1,464(3)	$C_{16}—C_{17}$	1,448(6)
$N_5—C_6$	1,478(3)	$C_{17}—N_{18}$	1,378(1)
Angles	**Angles (°)**	**Angles**	**Angles (°)**
$O_9—Si_1—O_2$	119,0(1)	$C_{11}—N_5—Si_1$	104,8(2)
$O_9—Si_1—O_8$	117,9(1)	$C_4—N_5—Si_1$	105,1(1)
$O_2—Si_1—O_8$	118,5(1)	$C_6—N_5—Si_1$	105,4(1)
$O_9—Si_1—C_{12}$	97,1(1)	$N_5—C_6—C_7$	105,8(2)
$O_2—Si_1—C_{12}$	96,6(1)	$O_8—C_7—C_6$	110,1(2)
$O_8—Si_1—C_{12}$	97,9(1)	$C_7—O_8—Si_1$	123,3(1)
$O_9—Si_1—N_5$	83,0(1)	$C_{10}—O_9—Si_1$	122,9(2)
$O_2—Si_1—N_5$	82,5(1)	$O_9—C_{10}—C_{11}$	108,8(2)
$O_8—Si_1—N_5$	82,7(1)	$N_5—C_{11}—C_{10}$	105,4(2)
$C_{12}—Si_1—N_5$	179,1(1)	$C_{13}—C_{12}—Si_1$	116,3(1)
$C_3—O_2—Si_1$	123,7(1)	$C_{14}—C_{13}—C_{12}$	114,1(2)
$O_2—C_3—C_4$	109,1(2)	$N_{15}—C_{14}—C_{13}$	112,2(2)
$N_5—C_4—C_3$	105,4(2)	$C_{14}—N_{15}—C_{16}$	113,1(2)
$C_{11}—N_5—C_4$	114,5(2)	$C_{17}—C_{16}—N_{15}$	112,4(3)
$C_{11}—N_5—C_6$	113,5(2)	$N_{18}—C_{17}—C_{16}$	125,0(6)
$C_4—N_5—C_6$	112,3(2)		

TABLE 2. Si←N Distances (Å) in Various 1-(γ-Propyl)silatranes

X	d(N — Si)	Ref.	X	d(N — Si)	Ref.
CN, III	2,164(4)	[2]	SH, V	2,177(4)	[4]
Title compound, II	2,165(2)	This work	Cl, VI	2,181(7)	[5]
OH, IV	2,173(2)	[3]	SCN, VII	2,209(4)	[6]

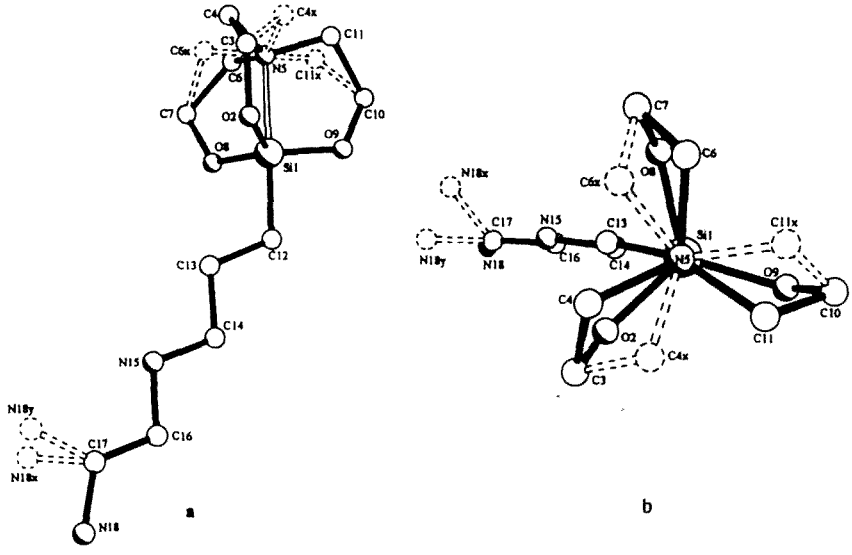

Fig. 1. Molecular diagram with the numbering of atoms (a). View down the N_5→Si bond (b). Minor component disordered atoms are drawn with dashes and hydrogen atoms are omitted for clarity.

TABLE 3. Crystal Data and Structure Refinement

Empirical formula	$C_{11}H_{25}N_3O_3Si$
Formula weight	275,43
Temperature	293(2) K
Wavelength	1,5418 Å
Crystal system	Triclinic
Space group	P_1
Unit cell dimensions	a = 6,814(1) Å, α = 111,68(1)°
	b = 11,101(1) Å, β = 105,21(1)°
	c = 11,337(1) Å, γ = 91,80(1)°
V	761,1(2) Å^3
Z	2
Density (calculated)	1,202 Mg/m^3
Absorption coefficient	1,421 mm^{-1}
F(000)	300
Crystal size	0,250 × 0,20 × 0,18 mm
θ range for data collection	4,33 to 76,12°
Index ranges	$-8 \leqslant h \leqslant 0$, $-13 \leqslant k \leqslant 13$, $-13 \leqslant l \leqslant 14$
Reflections collected	3457
Independent reflections	3181 [R(int) = 0,029]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3102 / 4 / 213
Goodness-of-fit on F^2	1,052
R indices [$I > 2\sigma$ (I)]	R^1 =0,059, wR^2 = 0,163
Largest diff. peak and hole	0,66 and -0,59 e.Å^{-3}

TABLE 4. Atomic Coordinates ($\times 10^4$), Equivalent Isotropic Displacement Parameters (U_{iso} values for the hydrogen atoms) (Å^2 × 10^3). Multiplicities Are Also Given for the Disordered Atoms. U(Eq) is Defined as One Third of the Trace of the Orthogonalized U_{ij} Tensor

	x	y	z	$U(eq)$	Multiplicity
H_{12a}	1615	560	7495	68	
H_{12b}	2795	1086	6744	68	
H_{13a}	1378	2991	7325	72	
H_{13b}	244	2498	8122	72	
H_{14a}	-1713	803	6124	82	
H_{14b}	-651	1369	5346	82	
H_{15}	-3208	2570	6780	86	
H_{16a}	-4934	1022	4830	106	
H_{16b}	-4017	1720	4096	106	
H_{17a}	-5443	3470	4888	166	
H_{17b}	-6338	2906	5719	166	
H_{18a}	-8260	1544	3259	163	0,469(8)
H_{18b}	-8873	2903	3982	163	0,469(8)
H_{18c}	-4490	4230	4887	146	0,276(12)
H_{18d}	-6751	4400	4890	146	0,276(12)
H_{18e}	-5418	4221	6603	210	0,255(13)
H_{18f}	-7472	4204	5583	210	0,255(13)
Si_1	4566(1)	2040(1)	9052(1)	41(1)	
O_2	3207(2)	2468(2)	10134(1)	51(1)	
C_3	4095(4)	2961(3)	11525(2)	61(1)	
C_4	6254(4)	3663(3)	11882(3)	62(1)	0,862(5)
C_{4x}	6306(21)	2630(19)	11805(14)	51(4)	0,138(5)
N_5	7133(3)	2851(2)	10845(2)	49(1)	
C_6	8581(4)	3643(3)	10554(3)	55(1)	0,862(5)
C_{6x}	7606(24)	4170(14)	10998(14)	49(4)	0,138(5)

TABLE 4. (continued)

	x	y	z	$U_{(eq)}$	Multiplicity
C_7	7270(3)	4165(2)	9606(2)	53(1)	
O_8	5588(2)	3206(2)	8701(2)	52(1)	
O_9	5663(2)	690(1)	8832(2)	61(1)	
C_{10}	7613(4)	669(2)	9653(3)	66(1)	
C_{11}	7934(5)	1712(3)	11046(3)	66(1)	0,862(5)
C_{11x}	8688(20)	1961(16)	10467(15)	48(4)	0,138(5)
C_{12}	2316(3)	1334(2)	7514(2)	52(1)	
C_{13}	703(4)	2229(2)	7343(2)	55(1)	
C_{14}	-1114(4)	1596(3)	6121(2)	63(1)	
N_{15}	-2668(3)	2457(2)	6043(2)	66(1)	
C_{16}	-4443(5)	1862(4)	4874(3)	81(1)	
C_{17}	-6062(6)	2678(6)	4880(5)	127(2)	
N_{18}	-7952(7)	2337(9)	3932(6)	109(3)	0,469(8)
N_{18x}	-5718(20)	3914(7)	4894(14)	97(5)	0,276(12)
N_{18y}	-6345(24)	3836(13)	5796(15)	140(9)	0,255(13)
H_{3a}	4136	2252	11820	79	
H_{3b}	3281	3564	11959	79	
H_{4a}	6194	4535	11907	81	0,862(5)
H_{4b}	7030	3726	12747	81	0,862(5)
H_{4xa}	6292	1727	11685	77	0,138(5)
H_{4xb}	7121	3163	12696	77	0,138(5)
H_{6a}	9543	3149	10162	71	0,862(5)
H_{6b}	9337	4354	11363	71	0,862(5)
H_{6xa}	9007	4517	11518	73	0,138(5)
H_{6xb}	6724	4716	11425	73	0,138(5)
H_{7a}	6732	4918	10093	69	
H_{7b}	8079	4427	9141	69	
H_{10a}	8656	845	9287	86	
H_{10b}	7693	-178	9690	86	
H_{11a}	7214	1407	11529	86	0,862(5)
H_{11b}	9369	1928	11530	86	0,862(5)
H_{11xa}	9744	1974	11224	72	0,138(5)
H_{11xb}	9320	2240	9929	72	0,138(5)

For the title compound these data are 0.210(1) and 0.383(3) Å. The calculated values, from a polynomial fit of second order based on data for 41 silatrane structures [7], are: $\Delta Si = -4.557 + 3.706d - 0.697d^2 = 0.199$ Å; $\Delta N = -1.187 + 1.665d - 0.436\,d^2 = 0.374$ Å, where d is the Si←N dative bond distance.

The zigzag chain built up by the Si_1, C_{12}, C_{13}, C_{14}, N_{15}, C_{16}, C_{17} atoms is planar with a mean deviation of 0.052 Å. The major disorder atom N_{18} lies also close to this plane (0.223 Å). The amino group is best described as rotationally disordered, with one of the two minor components (N_{18x}) deviating from the basically planar tail of the molecule.

EXPERIMENTAL

Synthesis. 1-[*N*-(2-aminoethyl)aminopropyl]silatrane was synthesized as described in [1].

X-Ray Structure Analysis. The determination of the unit cell and intensity data collection was performed on an Enraf-Nonius CAD4 diffractometer. Crystal data, data collection, and refinement details are summarized in Table 3. The structure was solved by direct methods using the SHELXS program [8]. At early stages of refinement the apparent disorder was detected. The sum of the multiplicities of the atoms, split by disorder, were constrained to 1. Identical occupancies were assumed for the corresponding disordered atoms in the silatrane moiety. Hydrogen atomic positions were generated from assumed geometry, except the hydrogen atoms bonded to N_{18}, which were located in a difference map (prior to constraining the C−N bond dis-

tance, see below). The atomic positions for H_{17a} and H_{17b} (linked to C_{17}) were generated excluding N_{18x} and N_{18y}. All disordered hydrogen atoms were included in the structure factor calculations with the corresponding occupancy factors. The hydrogen atoms were treated as riding on the nonhydrogen atoms to which they are linked. Isotropic displacement factors for the hydrogen atoms were derived from the atom to which they are bonded as $U_{iso} = nU(eq)$, where $n = 1.3$ and 1.5. The C–N bond distance for the N_{18}, N_{18x}, and N_{18y} atoms were constrained to 1.38 Å to avoid too short (ca. 1.29 Å) bonds (i.e., it is possible that the disorder of amino group could not be entirely resolved). The structure was refined against intensities using the SHELXL-93 program [9]. All disordered nonhydrogen atoms behaved well during anisotropic refinement.

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