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1-(Methylaminomethyl)silatrane: Synthesis, characterization and reactivity

I.V. Sterkhova, I.M. Lazarev, V.I. Smirnov, N.F. Lazareva*

A.E. Favorsky Irkutsk Institute of Chemistry, Siberian Division of The Russian Academy of Science, 1 Favorsky Street, 664033 Irkutsk, Russian Federation

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ABSTRACT

1-(Methylaminomethyl)silatrane $MeNHCH_2Si(OCH_2CH_2)_3N$ **2** was prepared and characterized by elemental analysis, IR, ^1H, ^{13}C, and ^{29}Si NMR spectra. Solvate complex $MeNHCH_2Si(OCH_2CH_2)_3N\cdot C_6H_6$ was isolated after recrystallization of silatrane **2** from benzene and its molecular structure has been determined by X-ray diffraction study. It is the first example of X-ray study of acyclic *N*-(silatranylmethyl) amine. The interaction silatrane **2** with HCl or $CHCl_3$ led to the formation of its hydrochloride $[MeNHCH_2Si(OCH_2CH_2)_3N]\cdot HCl$ **3**. The composition and structure of compound **3** was confirmed by elemental analysis, IR, ^1H, ^{13}C, ^{29}Si NMR spectra and X-ray structure analysis.

Introduction

Silatranes (or 2,8,9-trioxa-5-aza-1-silatricyclo-[3.3.3.01,5] undecanes) $XSi(OCH_2CH_2)_3N$ are cyclic organosilicon ethers of tris(2-oxyalkyl)amines. Silatranes are very important class of pentacoordinate organosilicon compounds, they feature a hypervalent silicon atom with a transannular dative bonding interaction between the silicon and the bridged nitrogen atom and their structure and chemical properties have been the subject of intense study [see, e.g., Refs. [1–4] and references cited therein] since their discovery in 1961 [5]. Several hundreds of such compounds with hydrogen, organyl, organoxy, aminoalkyl, thioorganyl, acyloxy, halogen, pseudohalogen and other groups as substituent X have been synthesized and studied. Among of 1-(aminoalkyl)silatranes $RR'N(CH_2)_nSi(OCH_2CH_2)_3N$ ($n = 1–3$) 1-(3-aminopropyl)silatrane $H_2N(CH_2)_3Si(OCH_2CH_2)_3N$ is one of the best investigated. This compound is precursor for the synthesis of a number of N-derivatives silatranes [see, for example Refs. [6–11]], which exhibit biological activity [12–17]. Of specific interest are the 1-(aminomethyl)silatranes $RR'NCH_2Si(OCH_2CH_2)_3N$ as representatives of acyclic α-silylamines.

The amines $RR'NCH_2SiX_3$ containing the silicon atom in the geminal position to nitrogen have unusual physical and chemical properties and they widely apply as synthons in synthetic organic chemistry [18,19]. Recently, we have found that the 1-(dialkylaminomethyl)silatrane exhibit enhanced reactivity with respect to polychloromethanes CH_nCl_{4-n} [20–23]. They react with alcohols and phenols in inert solvents at room temperature with cleavage of the Si–C bond [24], and reduce salts of some metals [25].

There is little information on the synthesis, reactivity and structure of 1-(aminomethyl)silatranes $RNHCH_2Si(OCH_2CH_2)_3N$ with secondary amino group. Despite the fact that the first representatives of $RR'NCH_2Si(OCH_2CH_2)_3N$ were obtained in the 70s of the last century [26,27] their molecular and crystal structure remains an unknown. In the last year the synthesis of 1-(methylaminomethyl)silatrane $MeNHCH_2Si(OCH_2CH_2)_3N$ and its complexes with transition metal chlorides was described [28]. Data of ^1H NMR spectrum of this silatrane presented by the authors are somewhat surprising. As compared to the spectra of 1-(dialkylaminomethyl)silatrane $RR'NCH_2Si(OCH_2CH_2)_3N$ [22,25,27] the significant downfield shifts of the signals of NCH_3 and NCH_2Si groups in the ^1H NMR spectrum of this compound takes place. What is the cause of this phenomenon? In the first place, this difference may be caused by structural features of the compound and secondly, it may be due to the experimental error. As noted above α-silatranylamines readily react with polychloromethanes CH_nCl_{4-n} ($n = 0–2$) and with chloroform in particular [23]. Unfortunately this important property of α-silylamines was ignored by

* Corresponding author.
E-mail address: nataly_lazareva@irioch.irk.ru (N.F. Lazareva).

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authors [28] and the mixture of chloroform–hexane was used by them for the recrystallization of this silatrane. It is not inconceivable that this procedure gave rise to the formation of hydrochloride 1-(methylaminomethyl)silatrane.

On the basis of present knowledge about chemical properties α-silylamines we expect that 1-(methylaminomethyl)silatrane will exhibit an unusual reactivity which will provide its use in organic synthesis. Herein we report the results of synthesis of 1-(methylaminomethyl)silatrane, the investigation of its structure by NMR and X-ray methods and some evidence on its reactivity.

Experimental section

General

All reactions were performed in the flame dried glassware under an atmosphere of dry argon. The used solvents were purified according to standard procedures [29]. As a further precaution, diethyl ether was dried by filtration through column packed with neutral alumina under a positive pressure of argon. The solvents were stored under argon over molecular sieves. Chloroform was purified just before use. The purification of chloroform involves washing with water to remove the EtOH, drying with K_2CO_3, refluxing with P_2O_5 and distilling. Triethanolamine was purified by low-pressure distillation and stored on molecular sieves. Starting silane $ClCH_2Si(OMe)_3$ was obtained according to Ref. [30]. Methylamine was obtained from water solution 40% (Merck), dried by standing with sodium pellets at 0° during 18 h and was distilled.

IMPORTANT! Compounds **1** and **2** are extremely sensitive to moisture.

*N-[(Methylamino)methyl]trimethoxysilane (**1**)*

A mixture of 8.53 g (50 mmol) (chloromethyl)trimethoxysilane and the excess of methylamine 16 g (~500 mmol) was sealed in glass ampoule. During the 3-h ampoule was kept at temperature 15 °C and then at room temperature for 2 days. After the ampoule was cooled to −10 °C and opened. The excess methylamine was evaporated and freshly distilled Et_2O (150 mL) was added to the residue. The precipitate of $MeNH_2 \cdot HCl$ was filtered off, washed by ether (35 mL × 2) and the solvent removed from the filtrate by distillation on rotary evaporator. Compound **1** as colorless liquid isolated by vacuum distillation of the resulting residue (yield 11.8 g, 72%). Bp 65–67 °C/24 mm Hg. ^{1}H NMR (C_6D_6, δ ppm): 2.27 (s, 2H, $SiCH_2N$), 2.40 (s, 3H, NCH_3), 3.65 (s 9H, OCH_3). 5.8 (broad s, 1H, NH). ^{13}C NMR (C_6D_6, δ ppm): 36.9 ($SiCH_2N$), 42.3 (NCH_3), 51.3 (OCH_3). ^{29}Si NMR (C_6D_6, δ ppm): −48.25.

$$ClCH_2Si(OMe)_3 \xrightarrow[-\,MeNH_2\cdot HCl]{MeNH_2} \underset{\mathbf{1}}{MeNHCH_2Si(OMe)_3} + MeN[CH_2Si(OMe)_3]_2$$

Scheme 1. Synthesis of silane **1**.

*1-(Methylaminomethyl)silatrane (**2**)*

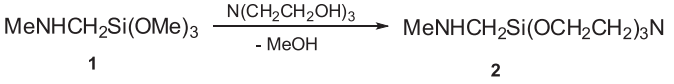
Triethanolamine 1.49 g (10 mmol) was added drop wise to cooled (+15 °C) solution 1.65 (10 mmol) of *N*-[(methylamino) methyl]trimethoxysilane in 10 mL thoroughly dried ether at stirring vigorously. Slight heating of the reaction mixture was observed and the reaction temperature maintained between 15 and 20 °C. Solvent and the released methanol were removed in vacuum immediately after homogenization of reaction mixture. The white solid residue was dried in vacuum and yield is practically quantitative (2.1 g), mp 96–97 °C (in a sealed capillary). IR spectrum, ν, cm^{-1}: 3391, 2939, 2881, 2790, 1622, 1456, 1275, 1087, 914, 794. Anal. Calcd. for $C_8H_{18}N_2O_3Si$: C, 44.01; H, 8.31; N, 12.83, Si, 12.86. Found: C, 44.32; H, 8.55; N, 12.95; Si, 12.24.

Colorless crystals suitable for structural analysis were obtained by the recrystallization from benzene.

Table 1
Crystal data, details of intensity measurements, and structure refinement for compounds **2** and **3**.

Parameter	Compound	
	2·C$_6$H$_6$	**3**
Empirical formula	$C_{14}H_{24}N_2O_3Si$	$C_8H_{19}ClN_2O_3Si$
Formula weight/g mol^{-1}	296.44	254.79
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
Cell dimensions		
a/Å	6.7586(5)	6.8882(12)
b/Å	13.8374(11)	7.6958(15)
c/Å	13.7508(12)	22.533(4)
β/°	98.856(3)	96.742(6)
Volume/Å^3	1270.66(18)	1186.2(4)
Temperature/K	296(2)	296(2)
Z	4	4
Density (calculated)/g cm^{-3}	1.466	1.427
Absorptions coefficient/mm^{-1}	0.192	0.414
Radiation (λ/Å)	MoKα (0.71073)	MoKα (0.71073)
2Θ range/°	5.88–60.03	5.59–60.17
Crystal size/mm	0.12 × 0.13 × 0.50	0.18 × 0.25 × 0.28
F(000)	600	544
Index ranges	$-9 \le h \le 9$, $-19 \le k \le 19$, $-19 \le l \le 19$	$-9 \le h \le 9$, $-10 \le k \le 10$, $-31 \le l \le 28$
Reflections collected	38,775	12,836
Independent reflections	3747 (R_{int} = 0.0652)	3186 (R_{int} = 0.0522)
Max. and min. transmission	0.9100 and 0.9770	0.8930 and 0.9290
Data/restraints/parameters	3747/0/163	3186/0/137
R_1/wR_2 [$I > 2\sigma(I)$][a]	0.0357/0.09733	0.0500/0.1364
R_1/wR_2 (all data)	0.0541/0.1035	0.0655/0.1433
S on F^2	1.066	1.131
Largest diff. peak and hole/e Å^{-3}	0.896 and −0.830	0.498 and −0.504

[a] $w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 16.3125P]$, where $P = (F_o^2 + 2F_c^2)/3$.



Scheme 2. Synthesis of 1-(methylaminomethyl)silatrane **2**.

*1-(Methylaminomethyl)silatrane hydrochloride (**3**)*

HCl (0.0365 g, 1 mmol) dissolved in carefully dried benzene was slow added to benzene solution of compound **2** (0.218 g, 1 mmol) at 10 °C. After 10 min, the reaction mixture was evaporated to remove the solvent. The solid residue was purified by the recrystallization from chloroform/benzene (1:2). Colorless crystals of the compound **3** were isolated (yield 0.13 g, 50%). Mp 195–197 °C (in a sealed capillary). IR spectrum, ν, cm^{-1}: 2930, 2879, 1461, 1272, 1120, 1090, 1020, 940, 916, 815, 793, 688. Anal. Calcd. for $C_8H_{19}ClN_2O_3Si$: C, 37.71; H, 7.52; N, 10.99, Si, 11.02. Found: C, 37.99; H, 7.94; N, 10.95; Si, 11.62.

*Reaction silatrane **2** with $CHCl_3$*

Silatrane **2** (0.44 g, 2 mmol) was dissolved in chloroform (10 mL). After 36 h, the excess of chloroform was removed, the residue was purified by the recrystallization from chloroform/benzene (1:2) mixture and 1-(methylaminomethyl)silatrane hydrochloride (**3**) was isolated, (yield 0.39 g, 75%).

NMR study

The ^1H, ^{13}C and ^{29}Si NMR spectra of 10–20% solutions of compounds **1**–**3** were registered on a Bruker DPX 400 spectrometer (400.1, 100.6 and 79.5 MHz respectively) with tetramethylsilane as an internal standard.

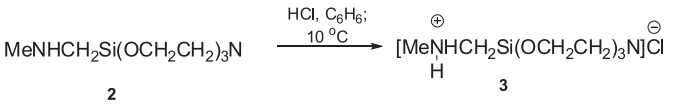
Crystal structure analyses

Suitable single crystals of **2**·C_6H_6 were obtained by crystallization of silatrane **2** from benzene (slow cooling of a boiling saturated solution to room temperature), single crystals of **3** were obtained by crystallization of silatrane from chloroform/benzene (1:1). This operation consisted in slow evaporation of the solvent at room temperature.

Crystal data were collected on a Bruker D8 Venture diffractometer with MoKα radiation ($\lambda = 0.71073$) using the φ and ω scans. The structures were solved and refined by direct methods using the SHELX programs set [31]. Data were corrected for absorption effects using the multi-scan method (SADABS). Non-hydrogen atoms were refined anisotropically using SHELX [31].

The H-atoms (except for H–N of compound **2**) were placed at calculated positions using the instructions AFIX 43, AFIX 137. The coordinates and the isotropic temperature factor for the H23 for compound **2** atom (attached to N1) were refined from the residual electron density map(AFIX 0).

Details of crystallographic data and experimental conditions are presented in Table 1.



Scheme 3. Synthesis of hydrochloride 1-(methylaminomethyl)silatrane **3**.

Table 2
^1H, ^{13}C, ^{29}Si NMR data for compounds **2** and **3**.

Compound	δ, ppm							Solvent
		N–CH_2Si	Me–N	NCH_2	OCH_2	NH	^{29}Si	
2	^1H	1.63 s	2.25 s	2.81 t	3.65 t	2.1 br. s	−75.28	CD_3CN
	^{13}C	40.36	43.45	50.20	56.67			
2·C_6H_6[a]	^1H	1.62 s	2.26 s	2.80 t	3.65 t	1.38 br. s	−75.35	CD_3CN
	^{13}C	40.11	43.32	50.14	56.63			
2[b]	^1H	1.88 s	2.42 s	2.84 t	3.80 t	1.69 br. s	−77.22	$CDCl_3$
	^{13}C	40.54	43.53	48.79	56.21			
2[c]	^1H	2.18	2.70	2.95	3.80		−81.61	$CDCl_3$
	^{13}C	35.83	39.53	51.02	56.91			
2	^1H	1.62	2.24	2.84	3.64	2.23 br. s	−76.09	DMSO-d_6
	^{13}C	40.50	43.47	49.66	56.16			
3	^1H	1.87	2.45	2.99	3.74	1.92 br. s	−83.56	DMSO-d_6
	^{13}C	35.74	39.55	49.01	56.22			
3	^1H	2.15	2.71	2.97	3.84	1.85 br. s	−81.92	$CDCl_3$
	^{13}C	35.87	39.51	51.02	56.93			
3[d]	^1H	2.16	2.73	2.98	3.86	2.34 br. s	−81.92	$CDCl_3$
	^{13}C	35.84	39.53	51.04	56.91			
2 [28]	^1H	2.01	2.64	3.25	4.05		−76.2	DMSO-d_6
	^{13}C	44.19	41.31	50.05	56.57			

[a] Signal of benzene in the ^1H (7.35 ppm) and ^{13}C (129.1 ppm).
[b] Spectrum of compound **2** was recorded immediately after preparation of the solution.
[c] Spectrum of compound **2** was recorded 36 h after preparation of the solution.
[d] Spectrum of compound **3**, which was obtained by interaction of **2** with $CHCl_3$.

Results and discussion

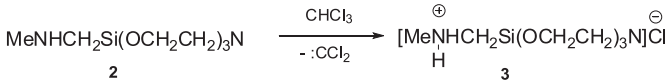
Synthesis

Previously *N*-[(methylamino)methyl]trimethoxysilane **1** was synthesized by interaction of (chloromethyl)trimethoxysilane with methylamine on heating in an autoclave at 120 °C/20 bar for 16 h [32]. We have found that (chloromethyl)trimethoxysilane reacts with methylamine at room temperature in a sealed glass ampoule (Scheme 1). We used the cooling of ampoule by water during the first few hours as a precautionary measure against explosion because this reaction is exothermic. *N*,*N*-Bis[(trimethoxysilyl) methyl]–*N*-methylamine is byproduct of this reaction and the increasing of the ratio of amine/silane reduces its yield. Therefore we used the molar ratio of amine/silane = 10:1.

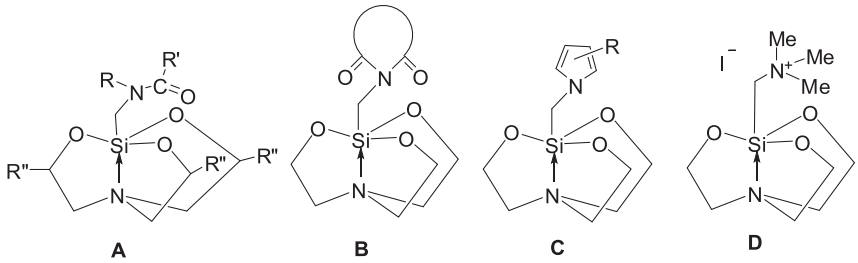
The typical procedure for the synthesis of silatranes $RSi(OCH_2CH_2)_3N$ involves treatment of respective $RSi(OAlk)_3$ with triethanolamine $N(CH_2CH_2OH)_3$ [1–5]. Interaction of *N*-[(methylamino)methyl]trimethoxysilane **1** with triethanolamine led to formation of 1-(methylaminomethyl)silatrane **2** with high yield without the application of any catalyst (Scheme 2), this reaction is exothermic.

Of special note is the ease cleavage of the Si–C bond of formed silatrane **2** by the methanol, as one would expect [24]. We dropped the triethanolamine to the ether solution of compound **1** at the stirring vigorously and cooling as a precautionary measures against this side reaction.

Hydrochloride 1-(methylaminomethyl)silatrane **3** was synthesized by the slowly mixing (drop by drop) of the solution HCl in dry benzene with solution of silatrane **2** in dry benzene at 10 °C (Scheme 3). It is significant that an increasing of the temperature of the reaction leads to the cleavage of the atrane skeleton and the formation of byproducts.



Scheme 4. Reaction silatrane **2** with $CHCl_3$.



Scheme 5. Structural data were obtained for some silatranes with geminal N–C–Si group.

Table 3
Selected bond lengths for silatrane **2**.

Parameter	*l*, Å	Parameter	*l*, Å
Si1–O1	1.667(2)	C4–N1	1.455(9)
Si1–O2	1.670(4)	N1–C6	1.473(8)
Si1–O3	1.675(4)	N1–H23	0.905(7)
Si1–C6	1.889(5)	N2–C8	1.479(9)
Si1–N2	2.159(2)	N2–C9	1.478(8)
O1–C10	1.422(16)	N2–C11	1.477(9)
O2–C12	1.419(16)	C8–C13	1.523(2)
O3–C13	1.422(17)	C9–C12	1.522(2)
C4–H10	0.960(9)	C10–C11	1.520(2)

The NMR monitoring of solution of compound **2** in $CDCl_3$ shows that the spectra recorded the immediately after preparation of the solution essentially differ from the spectra obtained 36 h after preparation of this solution (Table 2). This change is indicative of a chemical reaction (Scheme 4).

At room temperature the reaction of silatrane **2** with excess chloroform was completed after 36 h. The reaction time is increased to 3–4 days at use of equimolar ratio of the reactants in acetonitrile or benzene. The reaction time is reduced to 10–15 min by refluxing the reaction mixture. The dehydrochlorination of chloroform gave rise to dichlorocarbene and this leads to the production of terachloroethylene. The availability of a low intensity signal with δ 120.67 ppm in ^{13}C NMR spectrum of the reaction mixture is indicated on its formation. Early we demonstrated, that chloroform reacts with *N*,*N*-bis(silatranylmethyl)methylamine $MeN[CH_2Si(OCH_2CH_2)_3N]_2$ resulting in its hydrochloride and dichlorocarbene [21]. So, it is not surprising that the silatrane **2** reacts readily with $CHCl_3$ with formation of the hydrochloride 1-(methylaminomethyl)silatrane **3**.

NMR spectroscopic studies

The structure of compounds **1**–**3** was proved by multinuclear NMR spectroscopy. Data of NMR spectra of compound **1** were given in the experimental part, they agree closely with data [30]. Data of NMR spectra of silatranes **2** and **3** are shown in Table 2. The recrystallization of compound **2** from benzene leads to the appear of signal of benzene in the ^1H and ^{13}C NMR spectra. The value of chemical shift of this signal is close to the value of chemical shift of benzene in CD_3CN. The precipitated crystals after the recrystallization were dried under vacuum at room temperature and the increasing the drying time (10 h) at room temperature does not lead to a change in the spectra. Drying the sample of compound **2** under vacuum at the more high temperature results to the removal of benzene, but the crystals were destroyed. These results are indicative of the formation of a complex between the compound **2** and benzene. The complexes the amines with the aromatic compounds (including benzene) are described in the literature [33–39].

The significant downfield shift of the signals of NCH_3 and NCH_2Si groups was observed in the ^1H NMR spectrum of compound **3** with respect to the starting compound **2**. Such changes in the spectra are indicative of quaternization of the exocyclic nitrogen atom and are typical for *N*-(silatranylmethyl)ammonium salts [22,23,25,40].

The chemical shifts of signals of N–Me and $N–CH_2Si$ groups in ^1H, ^{13}C NMR spectra of previously synthesized compound **2** [28] differ radically from our data not only for compound **2**, but for compound **3** as well.

X-ray studies

To date, only crystal structures of *N*-(silatranylmethyl)amides (A) [41,42], -imides (B) [43,44] and *N*-(silatranylmethyl) substituted five-membered aromatic heterocycles (C) (derivatives of pyrrole, indole, pyrazole, imidazole, triazole and carbazole) [45–55] with geminal fragment N–C–Si have been described in the literature. Amongst the *N*-(silatranylmethyl)amines of row $RR'NCH_2Si(OCH_2CH_2)_3N$ (**D**) (R, R′ = H, Alk, Ar) only the single crystal structure of trimethyl(1-silatranylmethyl)ammonium iodide has been studied [56] (Scheme 5).

The molecular structures of 1-(methylaminomethyl)silatrane **2** and its hydrochloride **3** were determined by single-crystal X-ray diffraction. The selected bond lengths and angles are presented in Tables 3–6. 1-(Methylaminomethyl)silatrane **2** exists as solvate complex with benzene $\mathbf{2}\cdot C_6H_6$, which was obtained after the recrystallization of silatrane **2** from benzene. The geometry of the Si

Table 4
Selected bond angles for silatrane **2**.

Parameter	Angle, °	Parameter	Angle, °
O1–Si1–O2	118.41(5)	O3–Si1–N2	83.24(4)
O1–Si1–O3	117.88(5)	C6–Si1–N2	176.59(5)
O2–Si1–O3	119.87(5)	C10–O1–Si1	121.88(7)
O1–Si1–C6	99.58(5)	C12–O2–Si1	122.63(8)
O2–Si1–C6	94.79(5)	C13–O3–Si1	122.63(7)
O3–Si1–C6	95.29(5)	C3–C1–C2	119.72(11)
O1–Si1–N2	83.82(4)	C1–C3–C2	120.28(11)
O2–Si1–N2	83.33(4)	C4–N1–C6	112.37(10)
C4–N1–H23	107.3(11)	C6–N1–H23	110.1(11)

Table 5
Selected bond lengths for silatrane **3**.

Parameter	*l*, Å	Parameter	*l*, Å
Si1–O1	1.667(2)	O2–C5	1.428(4)
Si1–O2	1.675(2)	O3–C7	1.429(3)
Si1–O3	1.669(2)	N2–C4	1.481(3)
Si1–N2	2.078(2)	N2–C8	1.484(3)
Si1–C2	1.921(3)	N2–C6	1.485(3)
N1–C3	1.482(3)	C1–C8	1.512(4)
N1–C2	1.503(4)	N1–H16	0.970(7)
O1–C1	1.441(3)	N1–H17	0.970(7)

Table 6
Selected bond angles for silatrane **3**.

Parameter	Angle, °	Parameter	Angle, °
O3–Si1–O1	118.39(6)	O3–Si1–O2	117.92(5)
O1–Si1–O2	119.85(5)	O3–Si1–C2	99.54(6)
O1–Si1–C2	94.83(6)	O2–Si1–C2	95.27(6)
O3–Si1–N2	83.83(5)	O1–Si1–N2	83.32(5)
O2–Si1–N2	83.26(5)	C2–Si1–N2	176.62(6)
C1–O1–Si1	122.62(9)	C8–O2–Si1	122.59(8)
C10–O3–Si1	121.83(9)	O1–C1–C6	108.70(11)
C9–N2–C6	114.31(11)	C9–N2–C7	113.53(11)
C6–N2–C7	113.23(11)	C9–N2–Si1	104.43(8)
C6–N2–Si1	104.76(8)	C7–N2–Si1	105.29(8)

coordination centers in compounds **2**·C_6H_6 and **3** (Figs. 1 and 2, respectively) is typical for the silatranes. The coordination polyhedron of the silicon atom in these compounds represents a distorted trigonal bipyramid with N atom and C atom in the axial positions and three oxygen atoms occupying the equatorial positions. The angles N → Si–C axial fragment is almost linear in both compounds (176.59° and 176.99° for silatrane **2**·C_6H_6 and **3**, respectively). The displace of the silicon atom relative to the equatorial plane defined by three oxygen atoms towards the apical substituent (ΔSi) approximated 0.19 Å and 0.14 Å for compound **2**·C_6H_6 and **3**, respectively. The deviation of the endocyclic nitrogen atom from the plane of the neighboring carbon atoms (Δ*N*) comprises 0.38 Å and 0.41 Å for compound **2**·C_6H_6 and **3**, respectively. According to the Cambridge Structural Database [31], these values lie within the typical range for silatranes (ΔSi ≈ 0.09–0.24 Å and Δ*N* ≈ 0.34–0.40 Å). The values of Si ← N distance in compounds **2**·C_6H_6 and **3** (2.159 Å and 2.078 Å, respectively) lie within the typical range for silatranes (1.964–2.420 Å) and clearly show the existence of Si ← N coordination bond. The lengths of Si–C bond in silatranes **2**·C_6H_6 and **3** represent 1.889 Å and 1.921 Å, respectively. The length of Si ← N coordination bond of molecule **2**·C_6H_6 is longer than in molecule **3** (Δ*l* = 0.081 Å), but length of Si–C bond is shorter on 0.032 Å. The protonation of the amino group (–NHMe) leads to significant increase of its electron withdrawing effect (σ^* are 0.69 and 3.76 for –NHMe and $-N^+H_2Me$, respectively) [57]. As a rule, the length of Si ← N coordination bond in silatranes

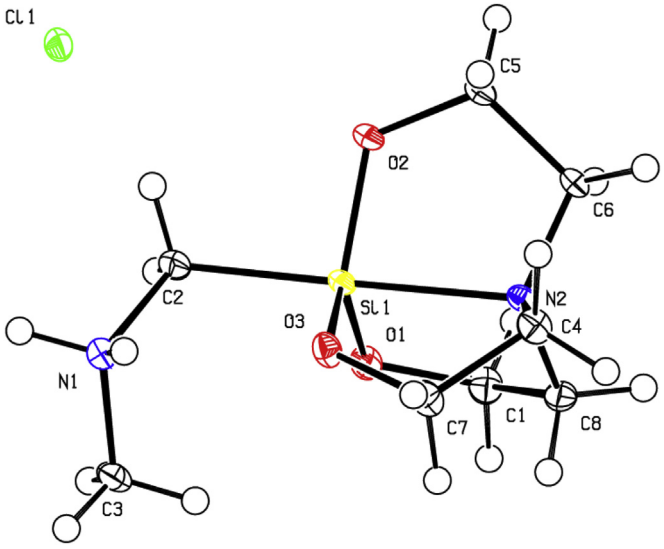


Fig. 2. Thermal ellipsoid plot for silatrane **3** (50% probability contours).

$RSi(OCH_2CH_2)_3N$ decreases on increasing the electron withdrawing effect of the axial substituent R and silatranes **2**·C_6H_6 and **3** follow this rule. Correlations between geometrical parameters (including the Si ← N bond distance) with the σ^* inductive constants of substituent R were found and discussed [58–60]. In particular it was showed that with an increase in the order of the Si ← N bond, the X–Si bond order reduces. The retention of the total order of the axial bonds is one of the fundamental property of silatranes as well as the other compounds with the pentacoordinate silicon atom [61]. The obtained parameters of lengths of axial bonds of silatranes **2**·C_6H_6 and **3** provide support for this view.

Conclusion

1-(Methylaminomethyl)silatrane **2** and its hydrochloride **3** were synthesized and the solvate complex silatrane **2** with benzene was

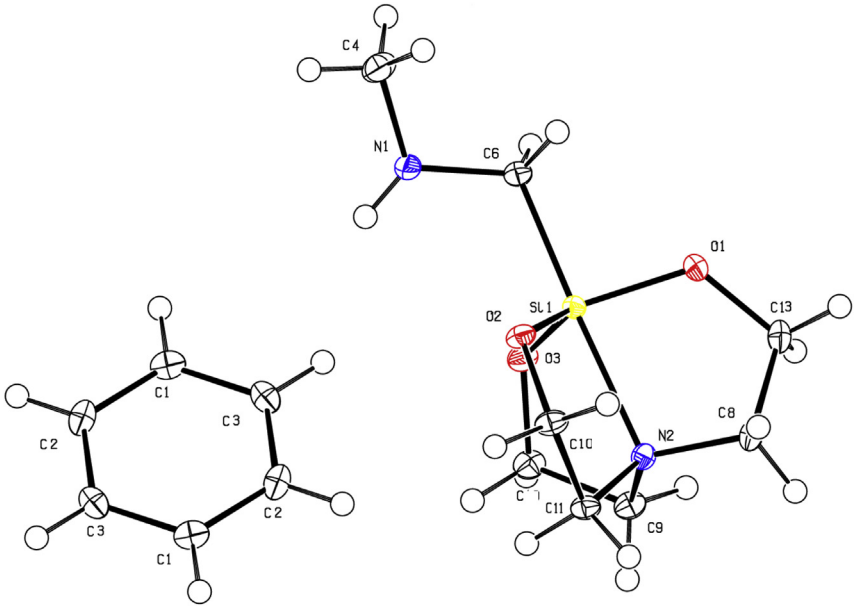


Fig. 1. Thermal ellipsoid plot for silatrane **2** (50% probability contours).

obtained after the recrystallization of compound **2** from benzene. The structures of compounds in solutions and in the solid state were confirmed by multinuclear NMR spectra and X-ray diffraction study.

Appendix A. Supplementary material

CCDC 1020992 (**2**), 991271 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] M.G. Voronkov, V.M. Dyakov, S.V. Kirpichenko, J. Organomet. Chem. 233 (1982) 1–147.
[2] J.G. Verkade, Coord. Chem. Rev. 137 (1994) 233–295.
[3] V.A. Pestunovich, S.V. Kirpichenko, M.G. Voronkov, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organic Silicon Compounds, vol. 2, John Wiley & Sons Ltd., Chichester, 1998, pp. 1447–1537.
[4] J.K. Puri, R. Singh, V.K. Chahal, Chem. Soc. Rev. 40 (2011) 1791–1840.
[5] C.L. Frye, G.E. Vogel, J.A. Hall, J. Am. Chem. Soc. 83 (1961) 996–997.
[6] R. Singh, R. Mutneja, V. Kaur, J. Wagler, E. Kroke, J. Organomet. Chem. 724 (2013) 186–191.
[7] V.V. Semenov, N.F. Cherepennikova, S.Ya. Khorshev, T.G. Mushtina, M.A. Lopatin, G.A. Domrachev, Russ. J. Coord. Chem. 28 (2002) 856–863.
[8] S. Alam, M. Nasim, L.D. Kandpal, G.N. Mathur, Angew. Makromol. Chem. 269 (1999) 1–7.
[9] E.Yu. Ladilina, V.V. Semenov, Yu.A. Kurskii, S.Ya. Khorshev, G.A. Domrachev, Russ. J. Org. Chem. 40 (2004) 1258–1264.
[10] Z. Li, D. Tian, Heterocycl. Commun. 9 (2003) 605–608.
[11] Z. Li, X. Song, Phosphor Sulfur 179 (2004) 1411–1416.
[12] R. Singh, J.K. Puri, V.K. Chahal, R.P. Sharma, S. Kohli, R. Kant, B.S. Gill, Synth. React. Inorg. Met. 42 (2012) 823–832.
[13] N. Jain, S.K. Tripathi, M. Nasim, Int. J. Polym. Mater. 63 (2014) 178–184.
[14] S. Senapati, S. Manna, S. Lindsay, P. Zhang, Langmuir 29 (2013) 14622–14630.
[15] A. Han, L. Li, K. Qing, X. Qi, L. Hou, X. Luo, S. Shi, Bioorg. Med. Chem. Lett. 23 (2013) 1310–1314.
[16] R. Singh, J.K. Puri, V.K. Chahal, R.P. Sharma, P. Venugopalan, J. Organomet. Chem. 695 (2010) 183–188.
[17] A. Grna, N. Ledinko, F. Fazely, S. Darling, J. Hogan, Anticancer Res. 8 (1988) 249–253.
[18] J.-P. Picard, Can. J. Chem. 78 (2000) 1363–1379.
[19] J.-P. Picard, Adv. Organomet. Chem. 52 (2005) 175–375.
[20] N.F. Lazareva, E.I. Brodskaya, V.V. Belyaeva, M.G. Voronkov, Russ. J. Gen. Chem. 70 (2000) 1547–1551.
[21] N.F. Lazareva, I.M. Lazarev, N.G. Dianova, Russ. Chem. Bull. 57 (2008) 2193–2194.
[22] N.F. Lazareva, T.I. Vakul'skaya, I.M. Lazarev, J. Phys. Org. Chem. 22 (2009) 144–154.
[23] N.F. Lazareva, I.M. Lazarev, Russ. Chem. Bull. 60 (2011) 598–600.
[24] N.F. Lazareva, E.I. Brodskaya, Russ. J. Gen. Chem. 71 (2001) 201–205.
[25] N.F. Lazareva, T.I. Vakul'skaya, A.I. Albanov, V.A. Pestunovich, Appl. Organomet. Chem. 20 (2006) 696–705.
[26] J. Czermak, S. Korzistek, J. Stepanek, Jan, Ger. Offen., 1971, DE 2113217 A 19711118.
[27] E. Lukevics, L. Liberts, M.G. Voronkov, Latv. PSR Zinat. Akad. Vestis Kim. Ser. 4 (1972) 451–453.
[28] M.G. Voronkov, Yu.I. Bolgova, V.V. Belyaeva, A.I. Emel'yanov, O.M. Trofimova, G.F. Prozorova, Russ. J. Org. Chem. 49 (2013) 472–474.
[29] A.J. Gordon, R.A. Ford, The Chemist's Companion. A Handbook of Practical Data, Techniques and References, John Wiley & Sons, New York, 1972.
[30] R. Tacke, J. Pikies, H. Linoh, R. Rohr-Aehle, S. Gönne, Liebigs Ann. Chem. (1987) 51–57.
[31] G.M. Sheldrick, Acta Crystallogr. D64 (2008) 112–122.
[32] R. Tacke, R. Bertermann, A. Biller, O. Dannappel, M. Pülm, R. Willeke, Eur. J. Inorg. Chem. (1999) 795–805.
[33] L.A. Strait, Spectr. Lett. 8 (1975) 449–457.
[34] L.M. Salonen, M. Ellermann, F. Diederich, Angew. Chem. Int. Ed. 50 (2011) 4808–4842.
[35] J.-J. An, R.-M. Wu, T. Yang, D.-Y. Wu, X. Wang, Comput. Theor. Chem. 1017 (2013) 144–152.
[36] H. Iga, T. Isozaki, T. Suzuki, T. Ichimura, J. Phys. Chem. A 111 (2007) 5981–5987.
[37] J. Wang, H. Yang, Z. Zuo, X. Yan, Y. Wang, X. Luo, H. Jiang, K. Chen, W. Zhu, J. Phys. Chem. B 114 (2010) 15172–15179.
[38] T. Steiner, G. Koellner, J. Mol. Biol. 305 (2001) 535–557.
[39] A.E. Aliev, J. Moïse, W.B. Motherwell, M. Nič, D. Courtier-Murias, D.A. Tocher, Phys. Chem. Chem. Phys. 11 (2009) 97–100.
[40] V.A. Pestunovich, Yu.Yu. Popelis, E.Ya. Lukevics, M.G. Voronkov, Izv. Akad. Nauk Latv. SSR Ser. Khim. (1973) 365–366.
[41] V.E. Shklover, Yu.E. Ovchinnikov, Yu.T. Struchkov, V.M. Kopylov, T.G. Kovyazina, M.G. Voronkov, Dokl. Akad. Nauk SSSR 284 (1985) 131–135.
[42] V.G. Pukhalskaya, E.P. Kramarova, L.P. Kozaeva, A.A. Korlyukov, A.G. Shipov, S.Yu. Bylikin, V.V. Negrebetsky, G.V. Poryadin, Yu.I. Baukov, Appl. Organomet. Chem. 24 (2010) 162–168.
[43] M.G. Voronkov, A.A. Korlyukov, E.A. Zel'bst, A.A. Kashaev, O.M. Trofimova, Yu.I. Bolgova, M.Yu. Antipin, Dokl. Chem. 420 (2008) 120–122.
[44] M.G. Voronkov, E.A. Zel'bst, A.D. Vasiliev, Yu.I. Bolgova, A.S. Soldatenko, O.M. Trofimova, J. Struct. Chem. 52 (2011) 985–988.
[45] M.G. Voronkov, E.A. Zelbst, V.S. Fundamensky, Yu.V. Katkevich, Yu.I. Bolgova, O.M. Trofimova, N.F. Chernov, J. Struct. Chem. 46 (2005) 1122–1125.
[46] M.G. Voronkov, V.S. Fundamenskii, E.A. Zel'bst, Yu.V. Katkevich, O.M. Trofimova, Yu.I. Bolgova, N.F. Chernov, Dokl. Chem. 401 (2005) 39–41.
[47] M.G. Voronkov, E.A. Zelbst, A.A. Kashaev, Yu.V. Katkevich, V.S. Fundamenskii, Yu.I. Bolgova, O.M. Trofimova, N.F. Chernov, Dokl. Phys. Chem. 397 (2004) 137–140.
[48] M.G. Voronkov, O.M. Trofimova, Yu.I. Bolgova, L.V. Klyba, L.I. Larina, A.I. Albanov, V.A. Pestunovich, N.F. Chernov, K.B. Petrushenko, Chem. Heterocycl. Compd. 39 (2003) 1639–1644.
[49] M.G. Voronkov, O.M. Trofimova, V.K. Turchaninov, E.A. Zel'bst, Yu.I. Bolgova, V.V. Belyaeva, L.I. Larina, T.N. Aksamentova, A.I. Mikhaleva, N.F. Chernov, Russ. J. Org. Chem. 39 (2003) 1458–1466.
[50] M.G. Voronkov, O.M. Trofimova, E.I. Brodskaya, Yu.I. Bolgova, L.I. Larina, L.V. Klyba, E.A. Zelbst, N.F. Chernov, ARKIVOC 13 (2003) 125–136.
[51] M.G. Voronkov, E.A. Zelbst, A.A. Kashaev, Yu.V. Katkevich, V.S. Fundamenskii, V.A. Bruskov, Yu.I. Bolgova, O.M. Trofimova, N.F. Chernov, Dokl. Chem. 391 (2003) 215–218.
[52] M.G. Voronkov, E.A. Zel'bst, A.A. Kashaev, Yu.V. Katkevich, V.S. Fundamenskii, Yu.I. Bolgova, O.M. Trofimova, V.V. Belyaeva, N.F. Chernov, Dokl. Chem. 389 (2003) 69–72.
[53] M.G. Voronkov, E.A. Zelbst, A.A. Kashaev, Yu.V. Katkevich, V.S. Fundamenskii, Yu.I. Bolgova, O.M. Trofimova, N.F. Chernov, Dokl. Chem. 386 (2002) 233–237.
[54] M.G. Voronkov, E.A. Zel'bst, V.S. Fundamenskii, A.A. Kashaev, O.M. Trofimova, Yu.I. Bolgova, N.F. Chernov, Dokl. Akad. Nauk 381 (2001) 348–350.
[55] M.G. Voronkov, E.A. Zel'bst, A.A. Kashaev, O.M. Trofimova, Yu.I. Bolgova, V.S. Fundamenskii, N.F. Chernov, Dokl. Akad. Nauk 376 (2001) 204–206.
[56] M.P. Demidov, V.E. Shklover, Yu.L. Frolov, Yu.A. Lukina, V.M. D'yakov, Yu.T. Struchkov, M.G. Voronkov, Zh. Strukt. Khimii 26 (1985) 103–108.
[57] A.R. Cherkasov, V.I. Galkin, R.A. Cherkasov, Russ. Chem. Rev. 65 (1996) 641–656.
[58] A. Greenberg, G. Wu, Struct. Chem. 1 (1990) 79–85.
[59] P. Hencsei, Struct. Chem. 2 (1991) 21–26.
[60] L. Parkanyi, P. Hencsei, L. Nyulaszi, J. Mol. Struct. 377 (1996) 27–33.
[61] V.A. Pestunovich, V.F. Sidorkin, O.B. Dogaev, M.G. Voronkov, Dokl. Akad. Nauk SSSR 251 (1980) 1140–1143.