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N-Methyl-N,N-bis(Silatranylmethyl)amine: Structure and reactivity

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A B S T R A C T

Trimethylsilylacetonitrile Me_3SiCH_2CN and N-methyl-N,N-bis(silatranylmethyl)amine hygrohalogenide were obtained by the interaction of N-methyl-N,N-bis(silatranylmethyl)amine $MeN[CH_2Si(OCH_2CH_2)_3N]_2$ **1** with $MeCN/Me_3SiX$ (X = Cl, I). The key stage of this reaction is the formation of the intermolecular complexes between amine **1** and Me_3SiX. The alkylation of amine **1** by ICH_2SiX_3 (SiX_3 = $SiMe_3$, $Si(OMe)_3$ and $Si(OCH_2CH_2)_3N$) give rise to the generation of the corresponding ammonium salts $\{(X_3SiCH_2)MeN[CH_2Si(OCH_2CH_2)_3N]_2\}^{+}I^{-}$. The molecular structures of N-methyl-N,N-bis(silatranylmethyl)amine (**1**), N-methyl-N-[(trimethylsilyl)methyl]-N,N-bis(silatranylmethyl)ammonium iodide (**4**) and N-methyl-N-N,N-tris(silatranylmethyl)ammonium iodide (**6**) were determined by single-crystal X-ray diffraction. Compound **1** exists as mix of the conformers **1A** (values $l_{N\rightarrow Si}$ are equal 2.212 Å and 2.274 Å), **1B** (values of $l_{N\rightarrow Si}$ are equal 2.252 Å and 2.272 Å) and **1C** (values $l_{N\rightarrow Si}$ are equal 2.273 Å and 2.291 Å). The length of dative bond N→Si of molecules **1A-1C** is longer than in molecules **4** and **6** (Δl lie between 0.105 Å and 0.199 Å), but length of $Si-CH_2$ bond is shorter on 0.001–0.034 Å.

1. Introduction

Silatranes (2,8,9-trioxa-5-aza-1-silatricyclo-[3.3.3.01,5]undecanes) $RSi(OCH_2CH_2)_3N$ are key compounds in the chemistry of organic derivatives of the pentacoordinate silicon atom, which are well studied by various methods [1–4]. The unique structural features, unusual spectral characteristics and reactivity of silatranes are caused by the intramolecular dative bond N→Si [5–7], forming a tricyclic cage with a trigonal bipyramidal silicon atom. The high relevance of the study of these compounds still remains, which is confirmed by recent publications [8–20].

α-Silylamines $RR'NCH_2SiX_3$ are original organosilicon compounds having interesting physico-chemical properties and biological activity [21,22]. In particular, silyl group serves as an effective electroauxiliary for the oxidation of the compounds containing Si—C—N group [23,24]. The introduction of the silyl group in α-position to nitrogen atom allows significantly to decrease the ionization potential of amine. The ionization potentials of a-silylamines are much lower than those of the organic amines [25–27]. So, for example, the values of vertical first ionization potentials of $N(CH_2SiMe_3)_3$ and Me_3N are 7.66 eV and 8.44 eV, respectively [27]. The oxidation of these compounds runs very easy and gives rise to formation of corresponding radical cations [28–33]. Our recent studies have shown that α-(silatranylmethyl)amines $RR'NCH_2Si(OCH_2CH_2)_3N$ are high reactivity [34–39]. These compounds are typical α-silylamines and they are involved in the single electron transfer reactions. The interaction of α-(silatranylmethyl)amines with CCl_4 under the irradiation of daylight lead to the formation of the corresponding 1-(aminomethyl)silatranes hydrochloride in high yields. The intermediates of this reaction are a carbon-centered radicals of α-(silatranylmethyl)amines. Their existence was proved by ESR spectroscopy at the interaction of N-methyl-N,N-bis(silatranylmethyl) amine with tetrachloromethane [35]. According to the assumed mechanism of this reaction the cation radical of amine can be formed on the first stage reaction. However they were not detected under the conditions of these experiments. The formation of cation radical of N-methyl-N,N-bis(silatranylmethyl)amine was proved by ESR spectroscopy at the investigation of the reaction of this silatrane with $AgNO_3$ [36]. The significant donor inductive effect of the silatranylmethyl group $CH_2Si(OCH_2CH_2)_3N$ ($\sigma^* = -2.24$) [40] affords the abnormally high basicity of the exocyclic nitrogen atom of α-(silatranylmethyl)amines [41] and, as a consequence, leads to their high reactivity.

N-Methyl-N,N-bis(silatranylmethyl)amine **1** belongs among the poorly explored type of silatranes $X(CH_2Si(OCH_2CH_2)_3N)_2$ (X = O, S,

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NR) containing two silatranylmethyl groups at heteroatom with lone pair and only a few such compounds are described in the literature [42–44]. Almost 20 years ago we obtained silatrane **1** [42] and for a long time we got failure in the study of its structure by X-ray crystallography. Continuing these investigations we obtained the crystals of compound **1**, and we describe below the results of study of its structure by X-ray analysis and some new data about its reactivity.

2. Experimental section

2.1. General

The ^{1}H, ^{13}C, ^{29}Si and ^{15}N NMR spectra of 10–20% solutions of compounds in CD_3CN, DMSO-d_6 or DMF-d7 were registered on a Bruker DPX 400 and и Bruker AV-400 spectrometers (400.1, 100.6, 79.5 and 40.6 MHz respectively) with tetramethylsilane as internal standard.

The GC-MS analysis was performed on a SHIMADZU-GCMS-QP5050 (chromatography column Ultra 2). Elemental analysis is performed on the Thermo Scientific Flash 2000 Automatic CHNS Analyzer. All reactions were performed in the Schlenk vessels in an argon atmosphere. The used solvents MeCN, Et_2O, THF and MeOH were purified according to standard procedures [45]. THF and Et_2O were continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen and stored over molecular sieves 4A. Me_3SiCl, Me_3SiI were purchased from Alfa Aesar and used as received. Triethanolamine was purified by low-pressure distillation and stored over molecular sieves 4A. N-Methyl-N,N-bis(silatranylmethyl)amine synthesized according to Ref. [42] and its monocrystal for X-ray analysis was obtained by recrystallisation from THF. The melting point of compounds **2**–**6** was determined in vacuumed capillaries. ICH_2SiMe_3 was prepared according to literature procedure [46]. $ICH_2Si(OMe)_3$ and $ICH_2Si(OCH_2CH_2)_3N$ were obtained according to literature procedures [47,48].

2.2. General methodology of the interaction of compound **1** with $X(CH_2)_nSiY_3$ ($X = Cl, I$; $SiY_3 = SiMe_3, Si(OCH_2CH_2)_3 N$, $n = 0, 1$)

The compound **1** was placed in a carefully dried and the argon-filled Schlenk vessel equipped with a magnetic stirrer. The vessel was evacuated and dry MeCN (10 mL) was condensed. Then, the corresponding silane was added in one portion through a glass adapter with a rubber tube. The Teflon high-vacuum valve of Schlenk flask was closed and the reaction mixture was stirred (the reaction time and temperature are indicated below for each compound). Volatile compounds were removed in vacuo. The rest was washed with dry diethyl ether (2 × 30 mL), which was removed by decantation, the product was dried in vacuum.

2.3. N-Methyl-N,N-bis(silatranylmethyl)amine hydrochloride (**2**)

Compound **2** was obtained by interaction of amine **1** (1.44 g, 3.55 mmol) with Me_3SiCl (0.38 g, 3.56 mmol), (4 h, 25 °C). Yield 1.51 g (96%, 3.42 mmol), colorless crystals, M. p. 272–273 °C. ^{1}H NMR (DMSO-d_6, δ, ppm): 2.10 AB dd (2H$_A$, NCH_2Si $^{2}J = 14.2$ Hz, $^{3}J_{NHCH2} = 6.7$ Hz), 2.21 dd (2H$_B$, NCH_2Si, $^{2}J = 14.2$ Hz, $^{3}J_{NHCH2} = 3.2$ Hz), 2.69 d (3H, NMe, $^{3}J = 4.7$ Hz), 2.96 t (12H, $6NCH_2$, $^{3}J = 5.8$ Hz), 3.72 t (12H, $6OCH_2$, $^{3}J = 5.8$ Hz) 6.69 s (1H, NH). ^{13}C NMR (DMSO-d_6, δ, ppm): 46.06 (MeN), 50.04 (NCH_2Si), 53.59 (NCH_2), 56.58 (OCH_2). ^{29}Si NMR (DMSO-d_6, δ, ppm): -84.60.^{15}N NMR (DMSO-d_6, δ, ppm): −351.8 (NCH_2), −340.6 (NHMe). Anal. Calcd. for $C_{15}H_{32}O_6N_3Si_2Cl$: C 40.76; H 7.30; N 9.51; Si 12.71; Cl 8.02. Found: C 40.68; H 7.26; N 9.60; Si 12.82; Cl 8.13.

Volatile compounds and Et_2O have been combined and was evaporated at 30 mm Hg мм. The rest (2 mL, 0.65 g) is yellowish liquid. The analysis data of GC-MS show the presence of a molecular ion $[M]^{+}$ 113 m/z from Me_3SiCH_2CN. ^{1}H ($CDCl_3$ δ ppm): 0.22 c 9H, $SiMe_3$), 1.61 c (2H, CH_2). ^{13}C NMR ($CDCl_3$, δ, ppm): 1.97 (MeSi), 4.77 (CH_2), 119.06 (CN). ^{29}Si NMR ($CDCl_3$, δ, ppm): 4.49.

2.4. N-Methyl-N,N-bis(silatranylmethyl)amine hydroiodide (**3**)

Compound **3** was obtained by interaction of amine **1** (1.59 g, 3.92 mmol) with Me_3SiI (0.79 g, 3.92 mmol), (1 h, 25 °C). Yield 2.08 g (99%, 3.90 mmol), white powder, M. p. 243–244 °C. ^{1}H NMR (DMSO-d_6, δ, ppm): 2.20 AB q (4H, CH_2NCH_2, $^{2}J = 14.2$ Hz), 2.73 s (3H, NMe), 2.97 t (12H, $6NCH_2$, $^{3}J = 5.8$ Hz), 3.47 s (1H, NH), 3.72 t (12H, $6OCH_2$, $^{3}J = 5.8$ Hz). ^{13}C NMR (DMSO-d_6, δ, ppm): 45.80 (NMe), 49.99 (NCH_2Si), 53.43 (NCH_2), 56,53 (OCH_2). ^{29}Si NMR (DMSO-d_6, δ, ppm): -84.81.^{15}N NMR (DMSO-d_6, δ, ppm): -351.9 (NCH_2), −341.6 (NHMe). Anal. Calcd. for $C_{15}H_{32}O_6N_3Si_2I$: C 33.77; H 6.05; N 7.88; Si 10.53; I 23.79. Found: C 33.86; H 6.12; N 7.96; Si 10.59; I 23.71.

Volatile compounds and Et_2O have been combined and was evaporated at 30 mm Hg. Me_3SiCH_2CN was obtaihed by distillation. Yield 0.30 g (2.65 mmol, 68%), B. p. 65–70 °C/20 mm Hg, n_D^{20} 1.4208. The spectral data are identical by the above parameters.

2.5. N-Methyl-N-[(trimethylsilyl)methyl]-N,N-bis(silatranylmethyl) ammonium iodide (**4**)

Compound **4** was obtained by interaction of amine **1** (1.32 g, 3.25 mmol) with ICH_2SiMe_3 (0.71 g, 3.32 mmol), (3 h, 100 °C). Yield 1.98 g (98%, 3.21 mmol), white powder, M. p. 264.3 °C. ^{1}H NMR (CD_3CN, δ, ppm): 0.18 s (9H, $SiMe_3$), 2.66 q (4H, $2NCH_2$, $^{2}J = 14.7$ Hz), 2.93 t (12H, $6NCH_2$, $^{3}J = 5.98$ Hz), 3.11 s (3H, NMe), 3.33 s (2H, CH_2SiMe_3), 3.74 t (12H, $6OCH_2$, $^{3}J = 5.98$ Hz). ^{13}C NMR (CD_3CN, δ, ppm): 0.22 (SiMe), 51.46 (NCH_2), 58.05 (OCH_2), 58.59 (NMe), 62.99 (NCH_2SiMe_3), 65.94 (NCH_2). ^{29}Si NMR (CD_3CN, δ, ppm): −1.76 (CH_2SiMe_3), −84.14 (silatrane). ^{15}N NMR (CD_3CN, δ, ppm): −352.7 (NCH_2), −327.7 (NMe). Anal. Calcd. for $C_{19}H_{42}O_6Si_3N_3I$: C 36.82; H 6.83; N 6.78; Si 13.60; I 20.48. Found: C 36.90; H 6.75; N 6.54; Si 13.81; I 20.43. Crystals for X-ray analysis were obtained by recrystallisation from MeCN.

2.6. N-Methyl-N-[(trimethoxysilyl)methyl]-N,N-bis(silatranylmethyl)ammonium iodide (**5**)

Compound **5** was obtained by interaction of amine **1** (1.61 g, 3.96 mmol) with $ICH_2Si(OMe)_3$ (1.24 g, 4.75 mmol), (3 h, 100 °C). Yield 2.65 g (96%, 3.82 mmol), white powder, M. p. 182–184 °C. ^{1}H NMR (CD_3CN, δ, ppm): 2.74 AB q [4H, $2C\underline{H}_2Si$, $^{2}J_{AB} = 14.5$ Hz], 2.94 t [12H, $2NC\underline{H}_2$, $^{3}J = 5.9$ Hz), 3.11 s (3H, NMe), 3.36 s [2H, $NCH_2Si(OMe)_3$], 3.59 s [9H, $(MeO)_3Si$], 3.75 t [12H, CH_2O, $^{3}J = 5.9$ Hz). ^{13}C NMR (CD_3CN, δ, ppm): 51.52 [$N(\underline{C}H_2CH_2O)_3Si$], 51.56 (SiOMe), 55.73 ($NCH_2Si{-}OMe$), 57.90 (NMe), 58.10 [$N(CH_2\underline{C}H_2O)_3Si$], 6.76 [$N\underline{C}H_2Si(OCH_2CH_2)_3N$]. ^{29}Si NMR ($CD_3CN$, δ, ppm): -54.81 ($Si(OMe)_3$), - 84.16 (silatrane). ^{15}N NMR (CD_3CN, δ, ppm): −352.9 (NCH_2), −330.8 (NMe). Anal. Calcd. for $C_{19}H_{42}O_9Si_3N_3I$: C 34.18; H 6.34; N 6.29; Si 12.62; I 19.00. Found: C 34.10; H 6.42; N 6.11; Si 12.83; I 18.56.

2.7. N-Methyl-N-N,N-tris(silatranylmethyl)ammonium iodide (**6**)

Compound **6** was obtained by interaction of amine **1** (1.54 g, 3.80 mmol) with $ICH_2Si(OCH_2CH_2)_3N$ (1.20 g, 3.80 mmol) in 30 mL dry acetonitrile, (20 h, 120 °C). Yield 1.50 g (55%, 2.09 mmol), white crystals, M. p. 305 °C. ^{1}H NMR (DMF-d7, δ, ppm): 2.84 s (6H,

$3NCH_2$), 2.98 t (18H, NCH_2, $^3J = 5.9$ Hz), 3.21 s (3H, NMe), 3.76 t (18H, OCH_2,$^3J = 5.9$ Hz). ^{13}C NMR (DMF-d7, δ, ppm): 5.14 (CH_2N), 57.83 (NMe), 57.85 (CH_2O), 64.98 (NCH_2). ^{29}Si NMR (DMF-d7, δ, ppm): -82.29. Anal. Calcd. for $C_{22}H_{45}O_9Si_3N_4I$: C 36.66; H 6.29; N 7.77; Si 11.69; I 17.61. Found: C 36.51; H 6.31; N 7.21; Si 10.94; I 17.54. Crystals for X-ray analysis were obtained by recrystallisation from MeOH.

2.8. X-ray analysis

The molecular structures of compounds **1**, **4** and **6** were determined by single-crystal X-ray diffraction. Crystal data were collected on a Bruker D8 Venture diffractometer with detector Photone 100 using the ω - 2θ scans. Reflection intensity was integrated by using Bruker SAINT software [49]. Accounting for the absorption of X-rays by a crystal was introduced from an analysis of the intensities of equivalent reflections. After averaging the intensities of the equivalent reflexes, only independent reflexes were used. The structures were solved and refined by direct methods using the SHELX programs set [50]. Non-hydrogen atoms were refined anisotropically using SHELX [50]. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication **CCDC 1936847**, **CCDC 1936848** and **CCDC 1936849.** These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Details of crystallographic data and experimental conditions are presented in Table 1.

3. Results and discussion

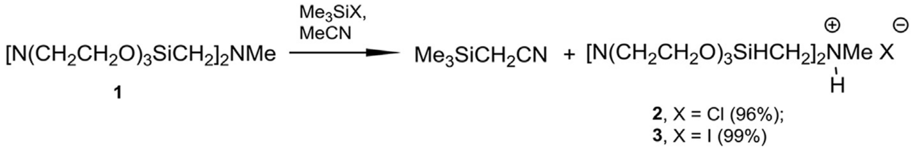
3.1. The interaction of amine 1 with $X(CH_2)_nSiY_3$ ($X = Cl, I; SiY_3 = SiMe_3, Si(OCH_2CH_2)_3 N, n = 0, 1$)

Over many years, a large body of knowledge about neutral intermolecular complexes of the different halosilanes with base has been accumulated. Among them complexes silanes with nitrogen bases have attracted increased attention. The trifluoro(phenylethynyl) silane with pyridine forms a pentacoordinate complex $PhC{\equiv}CSiF_3Py$ through intermolecular interaction N→Si [51]. The first X-ray diffraction study of complex of two pyridine molecules with $SiCl_4$ has shown that this complex has a octahedral configuration with the pyridine molecules in axial positions [52]. Complexes of H_nSiCl_{4-n} ($n = 1, 2$) and $RSiCl_3$ (R = Me, Ph) with pyridine, 3-picoline, 1,10-phenanthroline, 2,2′-bipyridine and N,N,N′,N′-tetramethylethylenediamine were obtained and characterized by spectral and X-ray methods [53–55]. The existence of a specific 1:2 molecular complexes between the free bases *meso*-tetraarylporphyrins and Me_3SiCl or t-$BuSiMe_2Cl$ in chloroform at room temperature was proved by spectrlal methods [56].

In this work we explored the interaction of amine **1** with trimethylhalogenosilanes Me_3SiX (X = Cl, I) in acetonitrile. We expected that these silanes will be able to the formation of intermolecular complexes with compound **1** with the participation of its exocyclic nitrogen atom. However the trimethylsilylacetonitrile and corresponding N-methyl-N,N-bis(silatranylmethyl)amine hydrohalogenide **2a,b** were isolated as a result of this reaction (Scheme 1).

Table 1
Crystallographic data and experimental conditions.

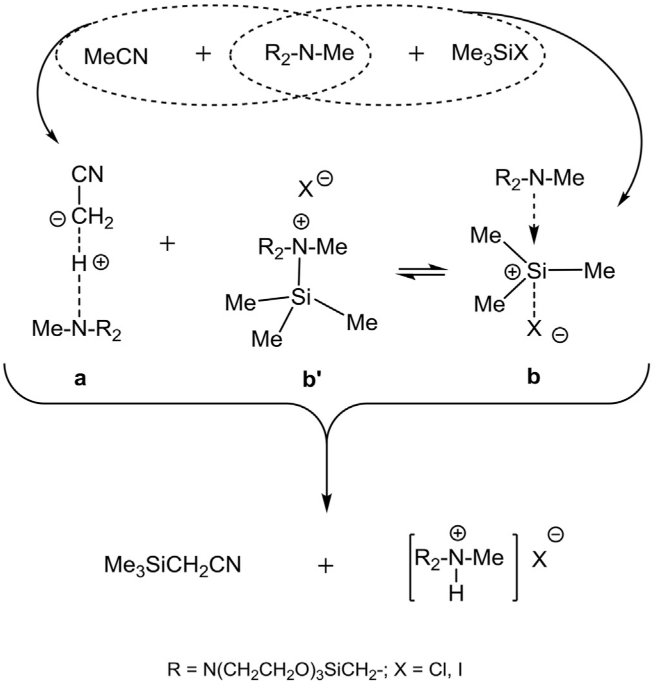
Compound	1	4	6
	1936849	**1936847**	**1936848**
Empirical formula	$3(C_{15}H_{31}N_3O_6Si_2)$	$I{\cdot}C_{19}H_{42}N_3O_6Si_3$	$1(I){\cdot}C_{22}H_{45}N_4O_9Si_3$
Formula weight/g·mol^{-1}	1216.82	619.72	720.79
Crystal system	orthorhombic	monoclinic	trigonal
Space group	*Pca2₁*	*P 2₁/n*	*R-3*
a/Å	42.566(19)	7.024(4)	14.343(6)
b/Å	10.385(4)	27.247(13)	14.343(6)
c/Å	13.320(7)	14.560(8)	24.899(11)
α, β, γ/°	90	90, 100.49(3), 90	90, 90, 120
Volume/Å^3	5888(5)	2740(2)	4436(4)
Z	4	4	6
Density (calculated)/ g·cm^{-3}	1.373	1.502	1.619
Absorptions coefficient/ mm^{-1}	0.22	1.34	1.26
Radiation (λ/Å)	MoKα (0.71073)	MoKα (0.71073)	MoKα (0.71073)
Temperature/K	293(2)	293(2)	100.15(2)
2Θ range/°	4.4–55.8	5.0–51.0	4.8–50.4
Crystal size/mm	0.26 × 0.22 × 0.11	0.50 × 0.29 × 0.13	0.32 × 0.30 × 0.11
Crystal habit	clear, prism, colorless	colorless prism	clear, cube, colorless
F(000)	2616	1280	2232
Index ranges	$-52 \leq h \leq 54, -13 \leq k \leq 13, -17 \leq l \leq 17$	$-8 \leq h \leq 8, -33 \leq k \leq 33, -17 \leq l \leq 18$	$-18 \leq h \leq 18, -18 \leq k \leq 17, -32 \leq l \leq 32$
Reflections collected	53,428	56,123	49,720
Independent reflections	13,348	5430	2267
Number of ref. parameters	707	321	120
R_1/wR_2 [$I > 2\sigma(I)$]	0.0665/0.1263	0.0302/0.0657	0.0226/0.0590
R_1/wR_2 (all data)	0.1547/0.1603	0.0424/0.0701	0.0238/0.0595
Goodness-of-fit on F^2	1.00	1.05	1.11
Largest diff. peak and hole/e·Å^{-3}	0.71/−0.47	0.40/−0.54	2.00/−0.65
Weight scheme	$w = 1/[\sigma^2(F_o^2) + (0.0708\ P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0287\ P)^2\ ]+1.9777P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0423\ P)^2 + 19.4124P]$ where $P = (F_o^2 + 2F_c^2)/3$



Scheme 1. Reaction of amine **1** with silanes Me_3SiX (X = Cl, I) in acetonitrile.

Acetonitrile is used widely as solvent, but it is also an important building block in organic synthesis [57]. The trimethylsilylacetonitrile from acetonitrile can be accessed by several different processes [58–61]. The electrosynthesis with use of an aluminium sacrificial anode, Me_3SiCl, MeCN and tetrabutylammonium chloride leads to the production of mixture Me_3SiCH_2CN and $(Me_3Si)_2CHCN$ (in the ratio 7:3) [58]. The interaction of an excess of (trifluoromethyl)trimethylsilane with tetramethylammonium fluoride in MeCN solution causes the formation of Me_3SiCH_2CN [59]. The direct C-silylation of acetonitrile by system $Me_3SiCl/Li/THF$ give rise to the corresponding α-silylated nitriles in yield 30% [60]. The interaction of 1,1-bis(trimethylsilyl)-2,2-dimethylhydrazine with MeI in acetonitrile proceeds with the cleavage of the Si—N bond and the formation of trimethylsilylacetonitrile and $[Me_3N^+NHSiMe_3]I$ (92% and 81%, respectively) [61].

The absence of the reaction of the compound **1** with MeCN as well as the reaction between Me_3SiX and MeCN is of special note. The possible mechanism of the formation of trimethylsilylacetonitrile at the interaction of amine **1** with trimethylhalogenosilanes Me_3SiX (X = Cl, I) in acetonitrile is presented on Scheme 2. First, a weak hydrogen bond C—H···N (**a**) between amine **1** (as strong base [35–37]) and MeCN (as weak C—H acid) can exists and it lead to an activation of C—H bond of acetonitrile. There is evidence, for example, that the C—H acids are able to form 1:1 complexes with guanidine-like N-bases which are fully dissociated in acetonitrile solution [62,63]. Secondly, the silane Me_3SiX has the ability to form of complexes with amine **1**. Both neutral compound with pentacoordinate silicon atom (**b**) and the intimate (or solvated) ion pair **(b')** of these complexes can occur in solution.



Scheme 2. The possible mechanism of the formation of trimethylsilylacetonitrile.

A white sediment was obtained at the interaction of Me_3SiCl with amine **1** in benzonitrile solution. Unfortunately, we failed to study the structure of this resulting complex. Our difficulty caused by its sparsely distributed in PhCN as well as its high reactivity with the majority solvents. We note that the trialkylsilanes Me_3SiX (X = Hal, OTf) form the complexes with Lewis bases [56,63–66]. The stable at room temperature complex $[Me_3Si(NMI)]^+Cl^-$ was obtained by reaction of Me_3SiCl with N-methylimidazole (NMI) and its ionic structure was proved by the X-ray analysis [66]. Probably the interaction between the intermediates **a** and **b** or/and **b'** generated in amine **1**/Me_3SiX/MeCN (X = Cl, I) ternary system gives rise to Me_3SiCH_2CN and compound **2** or **3**, respectvely. Recently was showed that the combining the Lewis acid $(C_2F_5)_3PF_2$ with triethylamine in acetonitrle solution enables the deprotonation of acetonitrile, affording the salt $[HNEt_3][P(C_2F_5)_3PF_2(CH_2CN)]$ [67].

Compound **1** is typical amine and as nucleophile reacts with (iodomethyl)silanes ICH_2SiX_3 giving the corresponding tetraalkylammonium iodide **4** and **5** with almost quantitative yield (Scheme 3).

The reaction between amine **1** and 1-(iodomethyl)silatrane proceeds slowly and under more rigid conditions (120 °C, 20 h) affording compound **6** with reasonable yield (only 55%) (Scheme 3). The lowering of electrophilicity of 1-(iodomethyl)silatrane compared to (iodomethyl)silanes caused by the significant donor inductive effect of the silatranylmethyl group $CH_2Si(OCH_2CH_2)_3N$ ($\sigma^* = -2.24$) [40]. There are no the alkylation of amine **1** by 1-(chloromethyl)silatrane in similar conditions.

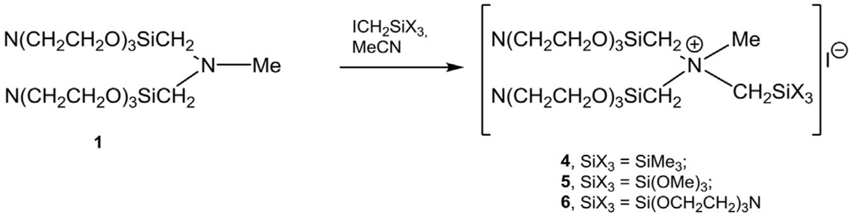
The structure of compounds **2**–**6** was confirmed by NMR spectroscopy and for compounds **1**, **4** and **6** were obtained data X-ray analysis.

3.2. NMR study

As compared to N-methyl-N,N-bis(silatranylmethyl)amine **1** compounds **2**–**6** show a significant low-field shift of signals of the $N\text{-}CH_3$ and $N\text{—}CH_2\text{—}Si$ groups in the ^1H NMR spectra (Table 2). This fact gives evidence of the quaternization of the exocyclic nitrogen atom in compounds **2**–**6**. The alkylation or protonation of the nitrogen atom of amine is followed by significant changing of its properties. In particular, the quaternary ammonium cations exhibit the electron withdrawing effect (σ^* are 0.09 and 4.38 for $-CH_2NMe_2$ and $-N^+Me_3$ groups, respectively) [68]. Early the similar changes in NMR spectra were demonstrated at the formation of the N-(silatranylmethyl)ammonium salts [36].

3.3. X-ray study

Single crystal X-ray diffraction study of compounds **1**, **4** and **6** showed that their molecules crystallize in the orthorhombic $Pca2_1$ space group, monoclinic $P\ 2_1/n$ space group and trigonal R3 space group, respectively. The ORTEP view of compounds **1**, **4** and **6** are shown in Figs. 1–3, the selected bond lengths and bond angles are listed in Table 3. The independent part of the unit cell of compound **1** contains 12 independent conformers **1A**, **1B** and **1C**, there are 4 molecules for every kind. Molecules **1A**, **1B** and **1C** have different spinning of “propeller blades” i.e. three five-membered



Scheme 3. The reaction of amine **1** with (iodomethyl)silanes ICH_2SiX_3.

Table 2
Chemical shifts of the signals of the N-CH_3 and N–CH_2–Si groups in the ^1H NMR spectra.

Compound	δ, ppm		Solvent	Ref.
	R–N	N–CH_2–Si		
1	2.17	1.89	CD_3CN	36
2	2.69	2.10, 2.21	DMSO-d_6	this work
2	2.82	2.15, 2.37	CD_3CN	36
3	2.73	2.20	DMSO-d_6	this work
4	3.11	2.66	CD_3CN	this work
5	3.11	2.74	CD_3CN	this work
6	3.21	2.84	DMF-d7	this work

coordination cycles in α-envelope conformation against their third order pseudo axis. Molecule **1A** contains silatrane groups in Δ- and Λ-forms but silatrane groups in molecules **1B** and **1C** exist in Δ-forms. The definition of Δ or Λ stereochemistry of silatranes was suggested by Yuzo Yoshikawa with co-authors for absolute configurations of silatrane [69]. The Δ- and Λ-forms have a left- and right-handed propeller (anticlockwise and clockwise orientation [70]), respectively (Scheme 4). Authors [69] note that the conformation of each chelate ring in nonsubstituted silatrane $RSi(OCH_2CH_2)_3N$ is exchangeable, and therefore the absolute configurations are not fixed. The independent part of the unit cell of compound **4** contains four independent molecules and their silatrane groups exist in Δ,Δ forms. The independent part of the unit cell of compound **6** contains 12 molecules and their silatrane groups exist in Λ,Λ,Λ forms.

The coordination polyhedron of the silicon atom in silatrane groups of molecules **1A**, **1B, 1C, 4** and **6** is a slightly distorted trigonal bipyramid with N atom and CH_2 in the axial positions and three oxygen atoms occupying the equatorial sites. The N→Si–CH_2 fragment is almost linear (173.9–178.1) in all these compounds. According to the Cambridge Structural Database [71], the values of length N→Si in molecules of compound **1, 4** and **6** lie within the typical range for silatranes (1.964 Å – 2.420 Å) and clearly verify the existence of Si–N dative bond. The lengths of Si–CH_2 bond in compound **1, 4** and **6** lie between 1.893 Å and 1.927 Å. The trigonal bipyramidal (TBP) character η_e of the silicon atom can be calculated according to Tamao's method (Eq. (1) [72]). The values of this

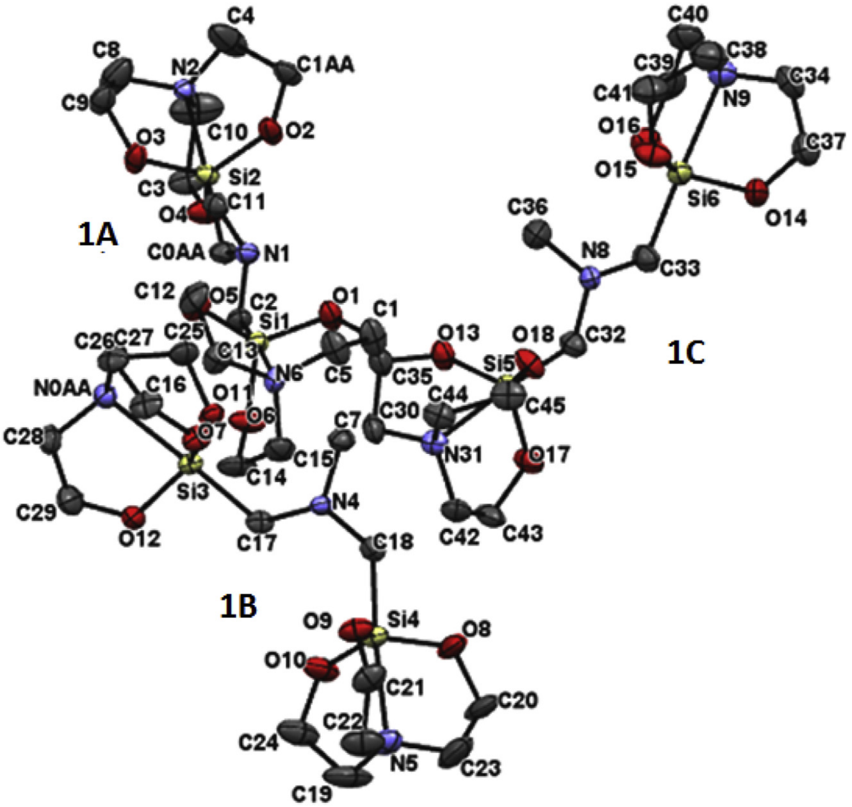


Fig. 1. Three independent molecules **1A**, **1B** and **1C** found in the asymmetric unite of compound **1.** The ORTEP plot is shown in thermal ellipsoids drawn at 50% probability, hydrogen atoms were omitted for cleairity.

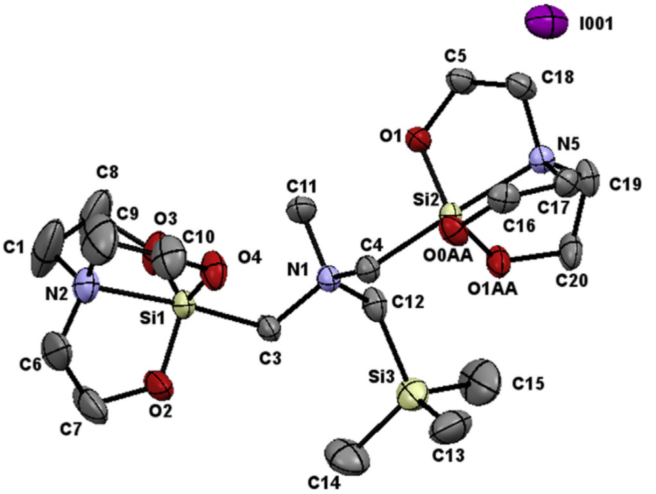


Fig. 2. The molecular structure of compound **4.** The ORTEP plot is shown in thermal ellipsoids drawn at 50% probability, hydrogen atoms were omitted for clearity.

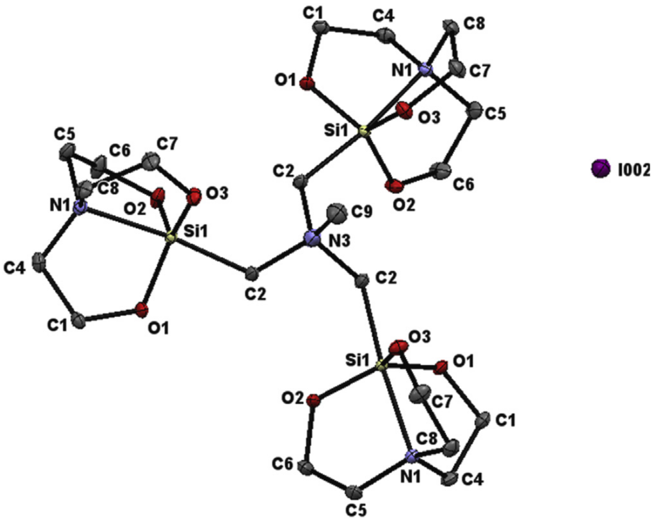
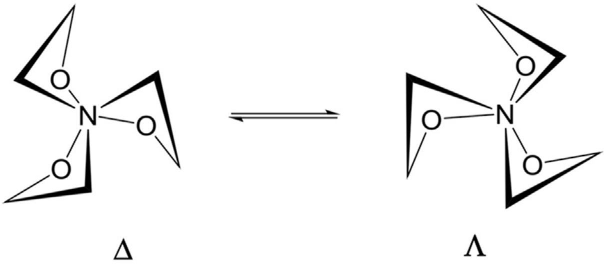


Fig. 3. The molecular structure of compound **6.** The ORTEP plot is shown in thermal ellipsoids drawn at 50% probability, hydrogen atoms were omitted for clearity.

characteristic for compound **1, 4** and **6** vary from 78.06% to 91.90%. It must be emphasized that the values of the geometric parameters of these compounds and previously studied silatranes containing group $-CH_2N$ in axial position are closely (Table 4).



Scheme 4. Δ- and Λ-forms silatrane (viewed down the N–Si bond).

$$\eta_e = \left[1 - \frac{120 - 1\Big/3\sum_{n=1}^{3}\Theta_n}{120 - 109.5}\right] \times 100\% \qquad (1)$$

where θ is average of angles $O_{eq}-Si-O_{eq}$

Note the length of dative bond N→Si of molecules **1A-1C** is longer than in molecules **4** and **6** (Δl lie between 0.105 Å and 0.199 Å), but length of $Si-CH_2$ bond is shorter on 0.001–0.034 Å. The reason of this is high electron withdrawing effect of ammonium groups [68]. The length dative bond N→Si in silatranes $RSi(OCH_2CH_2)_3N$ decreases on increasing the electronwithdrawing properties of the axial substituent R [1]. The conservation of the total order of the axial bonds is one of the fundamental property of compounds with the pentacoordinate silicon atom: an increase in the order of the Si→N bond is followed by reduction in the order R–Si bond [73]. The axial bonds lengths of silatranes **1**, **4** and **6** are subject to this rule.

An unexpected fact is that the geometric parameters of molecule **1A** differs essentially from the geometric parameters of molecules **1B** and **1C**. So the lengths of dative bond N→Si of Λ- and Δ-conformers in molecule **1A** are 2.212 Å and 2.274 Å, respectively. Conformers **1B**, **1C** are practically degenerate states and distinctions between the lengths of coordination bonds N→Si of their Δ-conformers is substantially under (0.02 Å and 0.018 Å for **1B**, **1C**, respectively). As discussed above silatrane groups in molecules **1B** and **1C** exist in Δ-forms the molecule **1A** contains the silatrane groups in Δ- and Λ-topological forms. The reason of the formation of silatrane with right- or left-oriented corner of the envelope is a plane deformation of the CH_2 group during the formation of structure. According to the quantum chemical research conformer **1A** is slightly more stability than the conformers **1B** and **1C** (ΔE = 0.73 kcal/mol). The calculations were carried out within the GAUSSIAN 09 software package [74] using the B3LYP/6-31G (p, d) method. The exocylic nitrogen atom in the conformers **1A**, **1B** and **1C** has the pyramidal configuration (the sum of angles

Table 3
The conformation of siatrane groups and select geometrical parameters of compound **1**, **4** and **6**.

Nº	Conformation of siatrane group	l, Å				φ,° N–Si–CH₂	Φ,° Si–C–N–Me	∑φ,° N	ηe, %
		N→Si	Si–CH₂	CH₂–N	Me–N				
1A	Λ	2.212	1.917	1.485	1.464	176.23	40.85	333.58	83.14
	Δ	2.274	1.893	1.493		175.31	−50.20		79.84
1B	Δ	2.252	1.911	1.469	1.455	176.83	−64.85	331.29	81.02
	Δ	2.272	1.911	1.473		178.13	55.35		79.02
1C	Δ	2.273	1.897	1.468	1.473	177.20	−45.47	331.46	79.52
	Δ	2.291	1.906	1.471		175.04	167.26		78.06
4	Δ	2.101	1.927	1.523	1.499	175.90	−63.10		91.71
	Δ	2.107	1.918	1.523		175.10	−42.66		91.30
6	Λ,Λ,Λ	2.092	1.924	1.503	1.531	173.91	73.63		91.90

Table 4
The select geometrical parameters of (N-silatranylmethyl)amines.

Compound	l, Å				φ,° N–Si–CH$_2$	∑φ,° N	η_e, %	Ref.
	N→Si	Si–CH$_2$	CH$_2$–N	Me–N				
$MeNHCH_2Si(OCH_2CH_2)_3N$	2.159	2.188	1.473	1.455	176.59	329.73	87.81	34
$(Ph_3C)MeNCH_2Si(OCH_2CH_2)_3N$	2.179	1.902	1.482	1.461	176.09	337.32	85.81	38
$PhNHCH_2Si(OCH_2CH_2)_3N$	2.124	1.897	1.459	1.376	177.59	360.00	90.19	39
	2.130	1.895	1.466	1.386	178.41	346.83	89.90	
$[MeNH_2CH_2Si(OCH_2CH_2)_3N]^+Cl^-$	2.078	1.921	1.503	1.482	176.99		93.81	34
$[Me_3NCH_2Si(OCH_2CH_2)_3N]^+I^-$	2.083	1.986	1.538	1.500	175.67		93.91	71
				1.585				
				1.478				

(2Me–N–CH$_2$, CH$_2$–N–CH$_2$) is 333.58°, 331.29° 331.46°, respectively). The pyramidal configuration nitrogen atom is usual for the most part of the non-aromatic amines [71].

Conformers **1A**, **1B** and **1C** are bound together by the short contacts C–H⋯H–C between exocyclic groups NCH$_2$Si, fragments OCH$_2$C and NCH$_2$C of silatrane cage and oxygen atoms. The lenghts of these contacts fall in the range between 2.246 Å - 2.644 Å (For a more detailed discussion of the subject see Supp. Inf.). The availability of these short contacts lead to formation in crystal packing of alternating zigzag molecular layers which stack down the c-axis. It is not improbable that the anomaly of the lenght of dative bond N→Si in molecule **1A** is caused by effect of crystal packing.

4. Conclusion

These results show that the N-methyl-N,N-bis(silatranylmethyl) amine is strong base and good nucleophile. As base this amine gives rise to the deprotonation of acetonitrile, but this reaction runs only in the system amine **1**/MeCN/Me$_3$SiX (X = Cl, I) and leads to the formation of Me$_3$SiCH$_2$CN and N-methyl-N,N-bis(silatranylmethyl) amine hygrohalogenide. The key stage is the formation of the intermolecular complexes between amine **1** and Me$_3$SiX. Amine **1** is good nucleophile and its interaction with ICH$_2$SiX$_3$ (SiX$_3$ = SiMe$_3$, Si(OMe)$_3$ and Si(OCH$_2$CH$_2$)$_3$N gives rise to the formation of the corresponding ammonium salts **4**–**6**. The structure of compounds **2**–**6** was confirmed by NMR spectroscopy and compound **1**,**4** and **6** were investigated by X-Ray method. N-Methyl-N,N-bis(silatranylmethyl)amine is first example amine, containing two groups CH$_2$Si(OCH$_2$CH$_2$)$_3$N at nitrogen atom. The structural parameters of silatranyl groups compound **1** and related N-(silatranylmethyl) amines are closely. The geometry of exocyclic nitrogen atom is typical for tertiary amines. These results allows us to assume that the fundamental reason of the strong basicity of exocyclic nitrogen atom of amine **1** caused by the high donor inductive effect of two silatranylmethyl group CH$_2$Si(OCH$_2$CH$_2$)$_3$N.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2020.121319.

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