



N,N-Bis(Silylmethyl)anilines: Synthesis and structure

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ABSTRACT

The novel N,N-bis(silylmethyl)anilines $\text{PhN}(\text{CH}_2\text{SiX}_3)_2$ were obtained by the reaction of N-(silylmethyl)anilines $\text{PhNHCH}_2\text{SiX}_3$ with chloromethylsilanes $\text{ClCH}_2\text{SiX}_3$ ($\text{SiX}_3 = \text{SiMe}_3, \text{Si}(\text{OMe})_3$). Their ammonium salts were prepared by the alkylation of N,N-bis(silylmethyl)anilines with MeI. The transesterification of N,N-bis(trimethoxysilyl)methyl)aniline with triethanolamine led to the formation of N,N-bis(silatranymethyl)aniline $\text{Ph}[\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}]_2$. Its molecular structure was determined by single crystal X-ray diffraction. It has been found that two solvates having slightly different molecular structures $\text{Ph}[\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}]_2 \cdot \text{MeCN}$ and $3\text{Ph}[\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}]_2 \cdot 3.24 \text{ MeCN}$ were formed as result of the recrystallization of N,N-bis(silatranymethyl)aniline from MeCN. The geometrical parameters of silatranyl groups $\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$ in these solvates are closely and the lengths of dative bonds $\text{N} \rightarrow \text{Si}$ lie between 2.164(3) Å and 2.168(3) Å in the typical range for silatranyl groups. In crystals of these solvates there are a big voids which vary in size and shape.

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1. Introduction

N-(Silylmethyl)amines $\text{RR}'\text{NCH}_2\text{SiX}_3$ are a fascinating class of organosilicon compounds. Since the first synthesis of such amines by Noll [1] and Sommer [2] in 1951 their unusual structure, reactivity and biological activity have attracted the attention of researchers engaged in the study of the organosilicon compounds [3–6 and lit. therein]. In particular, the silyl groups are an effective electro-auxiliary groups for the oxidation of the compounds containing Si–C–N fragment [7,8]. The introduction of the silyl group in α -position to nitrogen atom leads to lower ionization potential of amine [9–11]. So, for example, the vertical first ionization potentials for $\text{N}(\text{CH}_2\text{SiMe}_3)_3$ and Me_3N were determined as 7.66 eV and 8.44 eV, respectively [11]. Therefore an oxidation of N-(silylmethyl)amines runs very easy and gives rise to the formation of the corresponding radical cations [12–17]. Recently, we have studied the reactivity of some N-(silylmethyl)amines including N-(silatranymethyl)amines $\text{RR}'\text{NCH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$ ($\text{R} = \text{H}, \text{Me}, \text{Ph}, \text{PhCH}_2, \text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$) [18–24]. The N-(silatranymethyl)amines as well as other N-(silylmethyl)amines are involved in the single-electron transfer reactions. So, the irradiation of the mixture of such amines and CCl_4 by daylight led to the

formation of the corresponding N-(silylmethyl)amine hydrochlorides. We showed that the N-methyl-N,N-bis(silylmethyl)amines $\text{MeN}(\text{CH}_2\text{SiX}_3)_2$ exhibit a higher reactivity than amines containing only one CH_2SiX_3 group at nitrogen atom. These results are in good agreement with the experimental observation of the decrease of the ionization potential of amines with the increase of number of CH_2SiMe_3 groups at nitrogen atom [11].

Aromatic amines are an important class of compounds because their derivatives are part of dyes, materials with conductive and nonlinear optical properties, ligands for metal complex catalysts, common pharmaceuticals and biologically active natural products [25–33 and ref. therein]. N-(Silylmethyl)anilines $\text{ArNRCH}_2\text{SiX}_3$ ($\text{R} = \text{H}, \text{Alk}, \text{Ar}$) have attracted considerable attention judging by recent publications. The presence of the geminal fragment N–C–Si in these compounds promotes the single-electron-transfer reactions [34,35] and, as a consequence, the nucleophile-assisted cleavage reactions of the C–Si bonds in their radical cations [36]. This phenomenon presents opportunities for use of such anilines in the synthetic organic chemistry [37–43]. N-(Silylmethyl)anilines are useful synthons for the preparation of a new hybrid materials showing unique properties [44–46]. A derivatives of N-(silylmethyl)anilines $\text{ArNRCH}_2\text{SiArMe}_2$ were synthesized and identified as potent inhibitors of human low-density lipoprotein oxidation mediated by copper(II) [47]. Based on analysis of previous investigations of N-(silylmethyl)amines we can expect enhancement of the reactivity

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of *N,N*-bis(silylmethyl)anilines $\text{ArN}(\text{CH}_2\text{SiX}_3)_2$ in comparison with *N*-(silylmethyl)anilines $\text{ArRNCH}_2\text{SiX}_3$. Herein we report the synthesis of previously unknown *N,N*-bis(silylmethyl)anilines and study of the structure of *N,N*-bis(silatranylmethyl)aniline.

2. Experimental section

2.1. General

The ^1H , ^{13}C , ^{29}Si and ^{15}N NMR spectra of 10-20% solutions of compounds in CDCl_3 , CD_3CN or PhCN were registered on a Bruker DPX 400 and a Bruker AV-400 spectrometers (400.1, 100.6, 79.5 and 40.6 MHz respectively) with tetramethylsilane as an internal standard. The elemental analysis was performed on the Thermo Scientific Flash 2000 Automatic CHNS Analyzer. The melting points of compounds were determined in vacuumed capillaries.

The used solvents were purified according to standard procedures [48]. THF and Et_2O were continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen and stored over molecular sieves 4 Å. The vast majority of reactions were performed in the evacuated Schlenk vessels. It must be noted that the evacuation of the Schlenk vessel allows reactions to be carried out in solution even at high temperature (for MeCN ~ at 160 °C).

2.2. Synthesis of compounds 1-9

2.2.1. *N*-[(Trimethoxysilyl)methyl]aniline 1

The mixture of (chloromethyl)trimethoxysilane (14.07 g, 82.4 mmol) and aniline (19.90 g, 206.1 mmol) was heated at 110 °C for 3 hours. After cooling 50 ml of dry ether was added and the solution was decanted. The precipitate was washed with dry diethyl ether (30 ml) and the solution was decanted. The combined solution was evaporated under reduced pressure and the residue was distilled under reduced pressure. Yield of compound **1** is 16.30 g (71.7 mmol, 87 %), as colorless liquid. B. p. 86-89 °C (0.1 mm Hg), $n_{\text{D}}^{25} = 1.5058$. NMR ^1H (CD_3CN , δ , ppm): 2.56 s (2H, CH_2N), 2.25 br. s (1H, NH), 3.59 s (9H, OMe), 6.60-6.67 m (3H, H_m , 2H_o), 7.10-7.14 m (2H, H_m). NMR ^{13}C (CD_3CN , δ , ppm): 27.29 (CH_2N), 51.24 (OCH₃), 113.33 (C_o), 117.70 (C_n), 129.33 (C_m), 151.46 (C_i). NMR ^{29}Si (CD_3CN , δ , ppm): -47.71. NMR ^{15}N (CD_3CN , δ , ppm): -330.3. Anal. Calcd. for $\text{C}_{10}\text{H}_{17}\text{NO}_3\text{Si}$: C 52.83; H 7.54; N 6.16; Si 12.35. Found: C 52.78; H 7.49; N 6.20; Si 12.46.

2.2.2. *N,N*-Bis[(trimethoxysilyl)methyl]aniline 2

The mixture of (chloromethyl)trimethoxysilane (16.55 g, 97 mmol, excess), compound **1** (19.55 g, 86 mmol) and *N,N*-diisopropylethylamine (12.54 g, 97 mmol) was heated at 110 °C for 34 hours. After cooling 50 ml of dry hexane was added and this mixture thoroughly mixed than the solution decanted. The precipitate was washed with dry hexane (50 ml) and the solution was decanted. The combined solution was evaporated under reduced pressure and the residue was distilled under reduced pressure. Yield of compound **2** is 19.55 g (54 mmol, 54%) as yellow liquid. B. p. 120-122 °C (0.1 mm Hg), $n_{\text{D}}^{20} = 1.5142$. NMR ^1H (CD_3CN , δ , ppm): 2.92 s (2H, CH_2N), 3.49 s (18H, 6CH₃O), 6.56 t (1H, H_p), $^3J = 3.1$ Hz), 6.73 d (2H, H_o , $^3J = 8.2$ Hz), 6.16-6.17 m (2H, H_m). NMR ^{13}C (CD_3CN , δ , ppm): 37.68 (CH_2N), 51.00 (H_3CO), 113.25 (C_o), 116.08 (C_p), 129.68 (C_m), 151.29 (C_i). NMR ^{29}Si (CD_3CN , δ , ppm): -50.01. NMR ^{15}N (CD_3CN , δ , ppm): -341.5. Anal. Calcd. for $\text{C}_{14}\text{H}_{27}\text{NO}_6\text{Si}_2$: C 46.51; H 7.53; N 3.87; Si 15.54. Found: C 46.31; H 7.86; N 3.74; Si 15.63.

2.2.3. Iodmethylate *N,N*-bis[(trimethoxysilyl)methyl]aniline 3

The mixture of compound **2** (1.00 g, 2.8 mmol) and MeI (0.76 g, 5.4 mmol, excess) stood at room temperature for 24 hours in

the evacuated glass ampoule at 0.1 mm Hg. The volatiles were removed under reduced pressure, the solid residue was washed with Et_2O (2 × 20 ml) and finally dried in vacuum. Yield 1.21 g (87 %, 2.4 mmol). M. p. 121 °C (evacuated capillary). NMR ^1H (CD_3CN , δ , ppm): 3.39 s (18H, 6 OCH₃), 3.85 s (3H, $^+\text{NCH}_3$), 3.88 AB d (2H_A , $^+\text{NCH}_2$, $^2J = 15.6$ Hz), 4.10 AB d (2H_B , $^+\text{NCH}_2$, $^2J = 15.6$ Hz), 7.54-7.64 m (3H, 2H_m , 1H_p), 8.02 d (2H, H_o , $^2J = 7.7$ Hz). NMR ^{13}C (CD_3CN , δ , ppm): 51.75 (OCH₃), 55.33 ($^+\text{NCH}_3$), 61.72 ($^+\text{NCH}_2$), 121.93 (C_o), 130.81 (C_m), 131.16 (C_p), 148.55 (C_i). NMR ^{29}Si (CD_3CN , δ , ppm): -58.85. NMR ^{15}N (CD_3CN , δ , ppm): -319.6. Anal. Calcd. for $\text{C}_{15}\text{H}_{30}\text{INO}_6\text{Si}_2$: C 35.78; H 6.01; N 2.78; Si 11.16. Found: C 35.73; H 6.13; N 2.54; Si 11.28.

2.2.4. *N,N*-Bis(silatranylmethyl)aniline 4

The mixture of compound **2** (1.79 g, 4.95 mmol), triethanolamine (1.48 g, 9.92 mmol) and dry THF (10 ml) stirred in the evacuated Schlenk flask at room temperature for 90 hours. The volatiles were removed under reduced pressure, the solid residue was washed with dry THF (2 × 20 ml) and finally dried in vacuum (0.1 mm Hg). Yield 2.12 g (92 %, 4.53 mmol). M. p. 288 - 290 °C (evacuated capillary). NMR (PhCN , δ , ppm): 1.93 s (4H, 2 SiCH₂), 2.69 t (12H, 6 NCH₂, $^3J = 6.0$ Hz), 3.64 t (12H 6 OCH₂, $^3J = 6.0$ Hz), 7.19 m (2H, H_m), 7.21-7.73 m (1H, H_p), 7.75-7.78 m (2H, H_o). NMR ^{13}C (PhCN , δ , ppm): 50.98 (NCH₂), 57.61 (OCH₂), 60.27 (SiCH₂). Anal. Calcd. for $\text{C}_{20}\text{H}_{33}\text{N}_3\text{O}_6\text{Si}_2$: C 51.37; H 7.11; N 8.99; Si 12.01. Found: C 51.46; H 7.28; N 8.79; Si 12.31. A single crystal for X-ray diffraction analysis was obtained from MeCN.

2.2.5. Iodmethylate *N,N*-bis(silatranylmethyl)aniline 5

Method A. The mixture of compound **4** (0.50 g, 1.07 mmol), MeI (0.20 g, 1.41 mmol, excess) and dry MeCN (10 ml) stirred in a glass evacuated ampoule at 110 °C, for 2 hours. The volatiles were removed under reduced pressure, the solid residue was washed with dry Et_2O (3 × 10 ml) and finally dried in vacuum (0.1 mm Hg). Yield 0.64g (98%, 1.05 mmol) as white powder. M. p. 203-204 °C (evacuated capillary). NMR ^1H (CD_3CN , δ , ppm): 2.82 t (12H, 6NCH₂, $^3J = 5.87$ Hz), 3.09 AB d (2H_A , N^+CH_2 , $^2J = 14.8$ Hz), 3.19 AB d (2H_B , $^+\text{NCH}_2$, $^2J = 14.8$ Hz), 3.56 t (12H, 6OCH₂, $^3J = 5.87$ Hz), 3.66 s (3H, CH₃), 7.34 m (1H, H_p), 7.41 m (2H, H_m), 7.60 m (1H, H_o). NMR ^{13}C (CD_3CN , δ , ppm): 51.45 (NCH₂), 53.65 (N^+CH_3), 57.93 (OCH₂), 69.54 (SiCH₂N⁺), 122.06 (C_o), 128.68 (C_p), 129.04 (C_m), 151.72 (C_i). NMR ^{29}Si (CD_3CN , δ , ppm): -85.15. NMR ^{15}N (CD_3CN , δ , ppm): -352.4 (silatrane), -318.5 (ammonium). Anal. Calcd. for $\text{C}_{21}\text{H}_{36}\text{IN}_3\text{O}_6\text{Si}_2$: C 41.38; H 5.95; N 6.89; Si 9.21. Found: C 40.99; H 6.06; N 6.76; Si 9.63.

Method B. The mixture of compound **3** (0.32 g, 0.64 mmol), triethanolamine (0.19 g, 1.27 mmol) and dry MeCN (5 ml) stirred at room temperature for 48 hours. The volatiles were removed under reduced pressure, the solid residue was washed with dry THF (3 × 10 ml) and finally dried in vacuum (0.1 mm Hg, 3 hours). Yield 0.34 g (88%, 0.56 mmol) as white powder.

2.2.6. *N*-[(Trimethylsilyl)methyl]aniline 6

The mixture aniline (30.37 g, 326.12 mmol) and (chloromethyl)trimethylsilane (20.00 g, 163.04 mmol) stirred at 130 °C for 6 hours in the evacuated Schlenk flask. After cooling 40 ml dry Et_2O was added and stirred. The solution was decanted and the solid residue was washed with dry Et_2O (30 ml). The combined solution was evaporated under reduced pressure and the residue distilled in vacuum. Yield compound **6** as colorless liquid 16.06 g (55 %, 89.55 mmol). B. p. 80 °C (2 mm Hg), $n_{\text{D}}^{20} = 1.5250$. NMR ^1H (CDCl_3 , δ , ppm): 0.12 s (9H, SiMe₃), 2.48 s (2H, CH₂), 3.44 br s (1H, NH), 6.64-6.69 m (4H, H_o , 2H_p), 7.15-7.17 m (2H, H_m). NMR ^{13}C (CDCl_3 , δ , ppm): -2.69 (SiCH₃), 33.52 (SiCH₂), 112.42 (C_o), 117.00 (C_p), 129.11 (C_m), 150.52 (C_i). NMR ^{29}Si (CDCl_3 , δ , ppm): 1.05. NMR ^{15}N (CDCl_3 , δ , ppm): -322.8. Anal. Calcd. for

$C_{10}H_{17}NSi$: C 66.97; H 9.55; N 7.81; Si 15.66. Found: C 66.83; H 9.58; N 7.75; Si 15.84.

2.2.7. *N,N*-Bis[(trimethylsilyl)methyl]aniline 7

The mixture of compound **6** (5.00 g (27.88 mmol), (chloromethyl)trimethylsilane (3.42 g, 27.88 mmol), *N,N*-diisopropylethylamine (3.60 g, 27.88 mmol) and dry MeCN (10 ml) stirred at 160 °C for 20 hours in the evacuated Schlenk flask. The volatiles were removed under reduced pressure and added dry hexane (40 ml). The solution was decanted and the solid residue was washed with dry hexane (2 x 20 ml). The combined solution was evaporated under reduced pressure and the residue distilled in vacuum. Yield compound **7** as colorless liquid 5.63 g (76 %, 21.20 mmol). B. p. 73–75 °C (0.3 mm Hg), n_D^{20} 1.5224. NMR 1H (CDCl₃, δ , ppm): 0.06 s (18H, 2SiMe₃), 2.84 s (4H, 2CH₂), 6.48–6.54 m (3H, 2H_o, H_p), 7.11–7.15 m (2H, H_m). NMR ^{13}C (CDCl₃, δ , ppm): -0.57 (SiCH₃), 44.03 (CH₂), 111.79 (C_o), 113.84 (C_p), 128.83 (C_m), 149.33 (C_i). NMR ^{29}Si (CDCl₃, δ , ppm): 1.26. NMR ^{15}N (CDCl₃, δ , ppm): -327.2. Anal. Calcd. for C₁₄H₂₇NSi₂: C 63.32; H 10.25; N 5.27; Si 21.15. Found: C 63.23; H 10.28; N 5.14; Si 21.38.

2.2.8. *N*-(Trimethoxysilyl)methyl-*N*-(trimethylsilyl)methyl)aniline 8

The mixture of compound **6** (9.00 g, 50.20 mmol), (chloromethyl)trimethoxysilane (8.57 g, 50.20 mmol) and *N,N*-diisopropylethylamine (4.69 g, 50.20 mmol) stirred at 170 °C for 15 hours in an evacuated Schlenk flask. After cooling dry Et₂O (30 ml) was added. The solution was decanted and the solid residue was washed with dry Et₂O (2 x 30 ml). The combined solution was evaporated under reduced pressure and the residue distilled in vacuum. Yield of compound **8** as colorless liquid is 8.97 g (57 %, 28.61 mmol). B. p. 92–94 °C (0.3 mm Hg), n_D^{20} 1.5095. NMR 1H (CDCl₃, δ , ppm): 0.06 s (9H, SiMe₃), 2.90 s (2H, CH₂Si(OMe)₃), 2.91 s (2H, CH₂SiMe₃), 3.52 s (9H, 3OCH₃), 6.54–6.58 m (1H, H_p), 6.64–6.66 m (2H, H_o), 7.14–7.23 m (2H, H_m). NMR ^{13}C (CDCl₃, δ , ppm): -0.87 (SiCH₃), 38.05 (NCH₂Si(OMe)₃), 43.53 (NCH₂SiMe₃), 112.06 (C_o), 114.62 (C_p), 128.78 (C_m), 150.12 (C_i). NMR ^{29}Si (CDCl₃, δ , ppm): -50.54 (SiOMe), 1.08 (SiMe). NMR ^{15}N (CDCl₃, δ , ppm): -333.7. Anal. Calcd. for C₁₄H₂₇NO₃Si₂: C 53.63; H 8.68; N 4.47; Si 17.92. Found: C 53.68; H 8.63; N 4.39; Si 17.99.

2.2.9. *N*-(Trimethylsilyl)methyl-*N*-sila-tranylmethyl)aniline 9

The mixture of compound **8** (1.61 g, 5.13 mmol), triethanolamine (0.75 g, 5.13 mmol) and dry THF (10 ml) stirred at room temperature for 36 hours in an evacuated Schlenk flask. The formation of a white precipitate was observed after 24 hours. The volatiles were removed under reduced pressure and the solid residue was washed with dry Et₂O (3 x 20 ml) and dried in vacuum (0.1 mm Hg). Yield of compound **9** as white powder is 1.09 g (58 %, 2.98 mmol). M. p. 176 °C (evacuated capillary). NMR 1H (CD₃CN, δ , ppm): 0.01 s (9H, SiMe₃), 2.48 s (2H, NCH₂Si), 2.83 t (6H, 3NCH₂, $^3J = 5.9$ Hz), 2.97 s (2H, CH₂SiMe₃), 3.68 t (6H, 3OCH₂, $^3J = 5.9$ Hz), 6.31m (1H, H_p), 6.56–6.58 m (2H, H_o), 6.99–7.03 m (2H, H_m). NMR ^{13}C (CD₃CN, δ , ppm): -0.27 (SiCH₃), 42.47 (NCH₂Si), 44.54 (NCH₂SiMe), 51.56 (CH₂N), 58.03 (CH₂O), 112.14 (C_o), 112.82 (C_p), 129.19 (C_m), 151.64 (C_i). NMR ^{29}Si (CD₃CN, δ , ppm): -76.10 (sila-trane), 1.39 (SiMe). NMR ^{15}N (CD₃CN, δ , ppm): -322.0 (N-Ph), -353.6 (sila-trane). Anal. Calcd. for C₁₇H₃₀N₂O₃Si₂: C 55.70; H 8.25; N 7.64; Si 15.32. Found: C 55.76; H 8.31; N 7.66; Si 15.32.

2.3. X-ray diffraction analysis

N,N-Bis(sila-tranylmethyl)aniline **4** forms two types of solvates **4a** and **4b** and their molecular structures were determined by single crystal X-ray diffraction. The structure **4a** was determined at

297 K using the diffractometer Bruker D8 Venture with MoK α radiation source, solved and refined using the Bruker SHELXTL Software Package [49] and refined using the OLEX2 [50]. The H atoms were determined by mixed method. The intensities from single crystal of solvate **4b** were collected at 296 K using the SMART APEX II single crystal diffractometer with a CCD-detector, graphite monochromator and Mo K α radiation source. The absorption corrections were applied using the SADABS program [51]. The structure was solved by the direct methods using package SHELXS and refined in the anisotropic approach for non-hydrogen atoms using SHELXL program [52]. All the hydrogen atoms were positioned geometrically as riding on their parent atoms with d(C–H) = 0.93–0.97 Å for the C–H bonds and U_{iso}(H) = 1.2U_{eq}(C). The main crystal data are shown in Table 1. The crystallographic data are deposited in Cambridge Crystallographic Data Centre (CCDC 2141744, 2111011). The data can be downloaded from the site (www.ccdc.cam.ac.uk/data_request/cif). The coordinates of atoms are in Table 1S and main bond lengths are shown in Table 2S. The Mercury program [53] is used for the visualization of crystal structures.

3. Results and discussion

3.1. Synthesis and NMR study

An earlier study indicated that the interaction of methylamine with (chloromethyl)trimethoxysilane led to the formation of the mixture of mono- and dialkylated products (*N*-methyl-*N*-(trimethoxysilylmethyl)amine and *N*-methyl-*N,N*-bis(trimethoxysilylmethyl)amine, respectively) and their yields depended on the ratio of amine/silane and the reaction conditions (Scheme 1) [54].

However, *N*-[(trimethoxysilyl)methyl]aniline **1** was obtained as single product in 87% yield from the alkylation of aniline by (chloromethyl)trimethoxysilane. *N,N*-Bis(trimethoxysilyl)methyl)aniline **2** was prepared by the interaction of (chloromethyl)trimethoxysilane with compound **1** in the presence of *N,N*-diisopropylethylamine as strong non-nucleophilic base (Scheme 2).

Compound **2** did not interact with (iodomethyl)trimethoxysilane even upon prolonged heating (150 °C, MeCN, previously evacuated Schlenk vessel), whereas it easily formed an adduct with methyl iodide - iodmethylate *N,N*-bis[(trimethoxysilyl)methyl]aniline **3** (Scheme 3).

N,N-Bis(sila-tranylmethyl)aniline **4** was obtained by the interaction of the compound **2** with triethanolamine (Scheme 4).

N,N-Bis(sila-tranylmethyl)aniline **4**, unlike *N*-methyl-*N,N*-bis(sila-tranylmethyl)amine, did not interact with (iodomethyl)trimethoxysilane (140 °C, MeCN, previously evacuated Schlenk vessel), Me₃SiCl (120 °C, 6 h, previously evacuated Schlenk vessel), CCl₄ (MeCN, 25 °C, 80 h, exposure to daylight, previously evacuated Schlenk vessel). However, aniline **4** reacted with excess MeI to form the corresponding iodmethylate *N,N*-bis(sila-tranylmethyl)aniline **5** (Scheme 5, method A). An alternative way of synthesis of compound **5** was based on the transesterification of the compound **3** by triethanolamine (Scheme 5, method B) and its yield was somewhat lower (98% and 88%, respectively for A and B methods).

(Chloromethyl)trimethylsilane reacted with excess of aniline to form *N*-(trimethylsilyl)methyl)aniline **6** as single product. Our results showed that *N,N*-bis[(trimethylsilyl)methyl]aniline **7** can be obtained only by heating of (chloromethyl)trimethylsilane and compound **6** in the presence of *N,N*-diisopropylethylamine as strong non-nucleophilic base (Scheme 6).

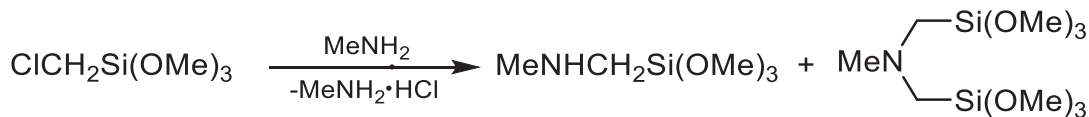
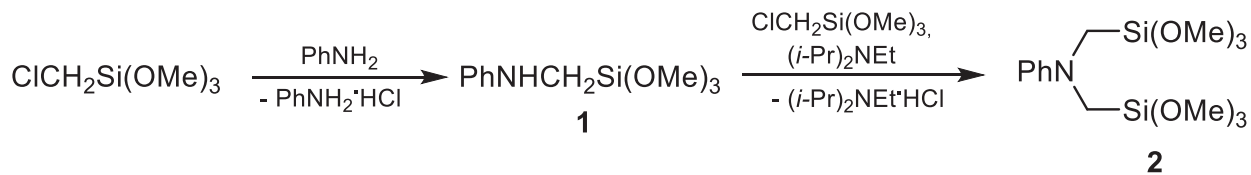
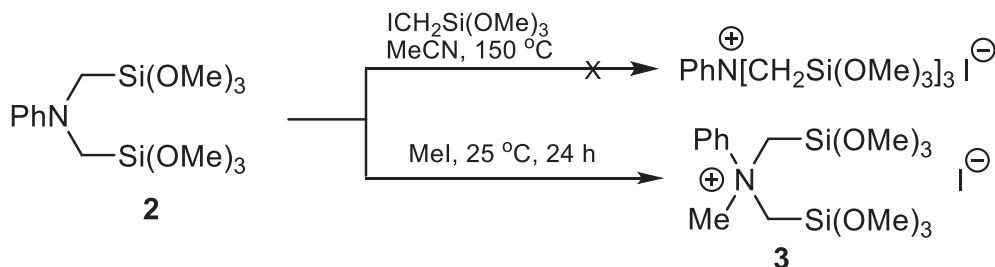
The alkylation of compound **6** by (chloromethyl)trimethoxysilane in the presence of *N,N*-diisopropylethylamine as strong non-nucleophilic base led to the formation of *N*-(trimethoxysilyl)methyl-*N*-[(trimethylsilyl)methyl]aniline **8** (Scheme 7). This reaction took place under drastic conditions (MeCN, 170 °C, 15 h, pre-

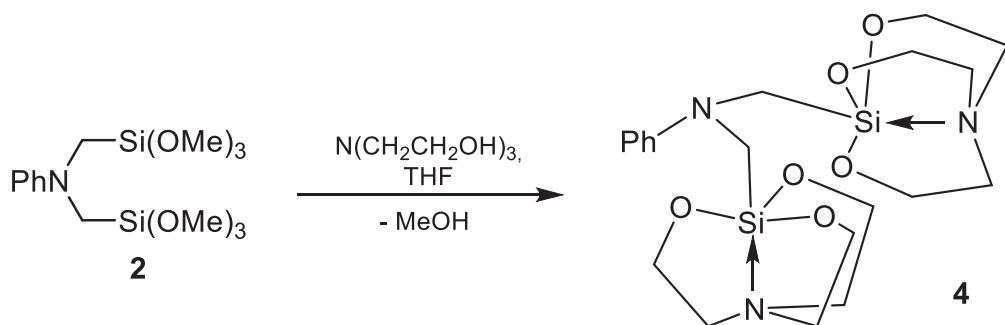
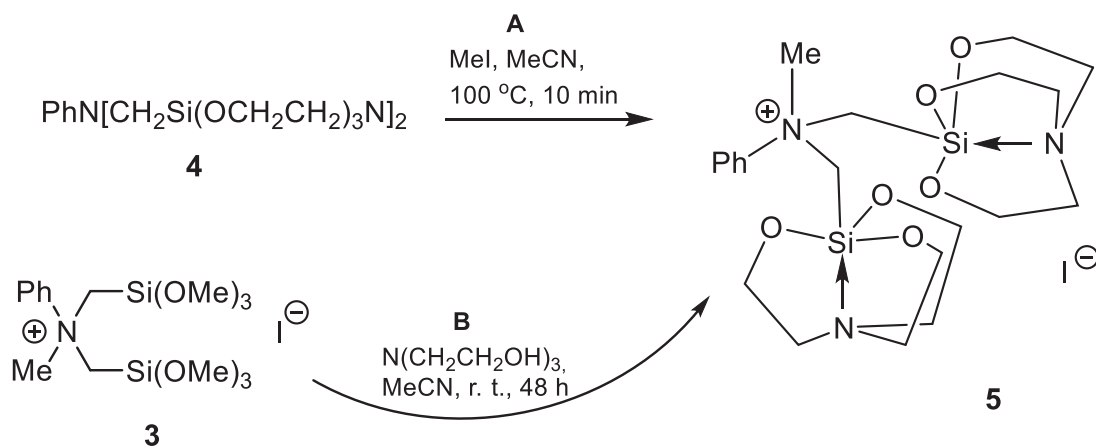
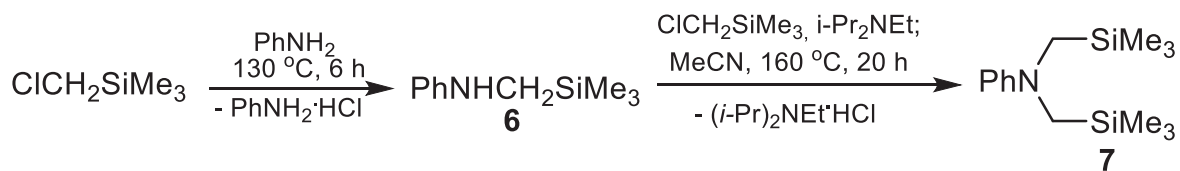
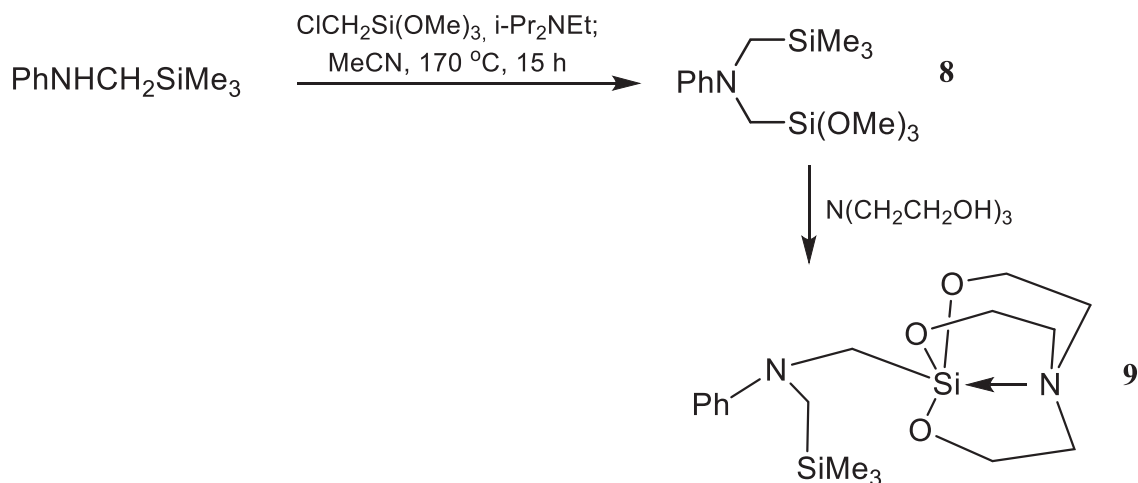
Table 1The crystal structure parameters of solvates compound **4a** and **4b**.

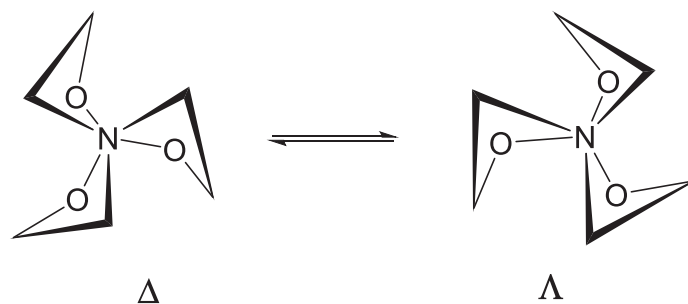
N ^o	4a	4b
CCDC ref. N ^o	2111011	2141744
Chemical formula	C ₂₀ H ₃₃ N ₃ O ₆ Si ₂ ·MeCN	(C ₂₀ H ₃₃ N ₃ O ₆ Si ₂) ₃ × 3.24MeCN
Diffractometer	Bruker D8 Venture	Bruker AXS
Molecular weight	508.73	1535.99
Temperature (K)	297	296
Space group	R-3	R-3
a (Å)	29.696(11)	29.701 (11)
c (Å)	15.964(11)	16.006 (6)
V (Å ³)	12192(19)	12228(11)
Z	18	18
ρ _{calc} (g/cm ³)	1.247	1.259
μ (mm ⁻¹)	0.170	0.173
Reflections measured	60008	42590
Reflections independent	4763	5556
Reflections with F > 4σ(F)	3310	4121
2θ _{max} (°)	52.0	52.93
h, k, l - limits	-36 ≤ h ≤ 36; -36 ≤ k ≤ 35; -19 ≤ l ≤ 19	-37 ≤ h ≤ 37; -37 ≤ k ≤ 36; -19 ≤ l ≤ 19
R _{int}	0.107	0.0988
<i>Refinement results</i>		
The weighed refinement of F ²	w=1/[σ ² (F _o ²)+(0.0974P) ²] where P=max(F _o ² +2F _c ²)/3	w=1/[σ ² (F _o ²)+(0.1215P) ² +25.8878P] where P=max(F _o ² +2F _c ²)/3
Number of refinement parameters	316	314
R1 [F _o > 4σ(F _o)]	0.0497	0.0754
wR2	0.1558	0.2050
Goof	1.037	1.061
Δρ _{max} (e/Å ³)	1.156	0.845
Δρ _{min} (e/Å ³)	-0.277	-0.976
(Δ/σ) _{max}		<0.002
Extinction coefficient (SHELXL 2014/7)	none	none

Table 2The selected geometrical parameters of solvates **4a** and **4b**.

N ^e	conformer	l, Å N→Si	Si-CH ₂	CH ₂ -N	φ, ° N-Si-CH ₂	η _e , %	l _{Ph-N} , Å	Σφ _N , °
4a _{N3Si2}	Δ	2.167(2)	1.907(3)	1.479(4)	176.4(1)	86.9	1.372(3)	359.99
4a _{N1Si1}	Δ	2.168(3)	1.911(3)	1.480(4)	176.0(1)	86.7		
4b _{N1ASi1}	Δ	2.164(3)	1.905(3)	1.465(6)	176.5(2)	87.0	1.367(4)	359.98
4b _{N1BSi2}	Δ	2.164(3)	1.914(3)	1.474(6)	175.8(2)	86.4		

**Scheme 1.** The interaction of methylamine with (chloromethyl)trimethoxysilane [54].**Scheme 2.** Synthesis of *N*-phenyl-*N,N*-bis(trimethoxysilylmethyl)amine **2**.**Scheme 3.** Alkylation *N*-phenyl-*N,N*-bis(trimethoxysilylmethyl)amine.

Scheme 4. Synthesis of *N,N*-bis(silatranyl)methyl)aniline **4**.Scheme 5. Synthesis of iodomethylate *N,N*-bis(silatranyl)methyl)aniline **5**.Scheme 6. Synthesis of *N,N*-bis(trimethylsilyl)methyl)aniline **7**.Scheme 7. Synthesis of *N*-silatranyl-methyl-*N*-[(trimethylsilyl)methyl)aniline.



Scheme 8. Δ - and Λ - forms silatrane (viewed down the N-Si bond).

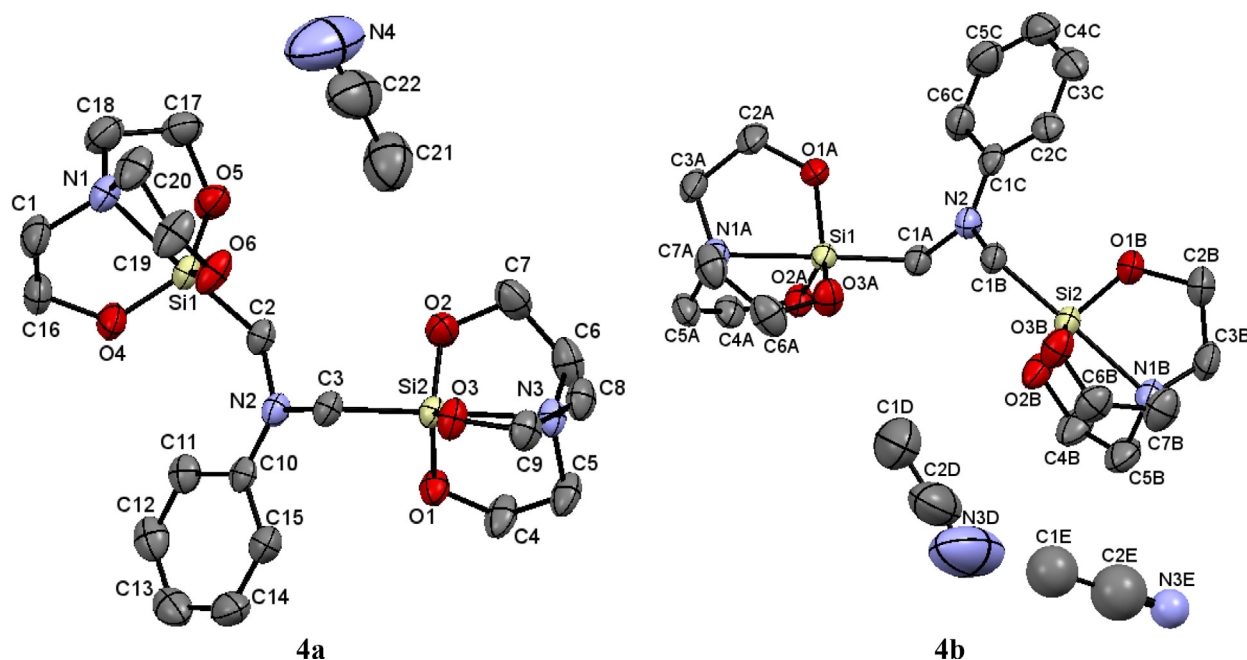


Fig. 1. Crystal structure of solvates **4a** and **4b**, hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level.

viously evacuated Schlenk vessel). The transesterification of the compound **8** by triethanolamine gave rise to *N*-silatranylmethyl-*N*-[(trimethylsilyl)methyl]aniline **9** (Scheme 7).

The structure of compounds **1-3** and **5-9** was confirmed by ^1H , ^{13}C , ^{29}Si and ^{15}N NMR spectroscopy. The compound **4**, in contrast to the $\text{MeN}[\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}]_2$ analogue [24], is practically insoluble in most organic solvents for NMR spectroscopy. This compound is only slightly soluble in benzonitrile and therefore only ^1H and ^{13}C NMR spectra were recorded. The values of the chemical shifts in ^{29}Si NMR spectra of anilines **1-3** and **5-9** lie in the range of the values which are typical for the compounds containing SiMe_3 , $\text{Si}(\text{OMe})_3$ or $\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$ groups [55 and Table 1S in Suppl. Inf.]. It should be noted that the alkylation or protonation of the nitrogen atom of amines produces a significant change of their properties. In particular, the quaternary ammonium cation shows the electron withdrawing effect (σ^* are 0.09 and 4.38 for $-\text{CH}_2\text{NMe}_2$ and $-\text{N}^+\text{Me}_3$ groups, respectively) [56]. This effect is the cause of the downfield shifts of signals NCH_2Si groups in the NMR spectra of compounds **3** and **5** as compared to starting amines **2** and **4**. Similar changes in NMR spectra were detected for the *N*-(silylmethyl)ammonium salts [19,21].

3.2. X-ray study of *N,N*-Bis(silatranylmethyl)aniline **4**

Despite the poor solubility of compound **4**, its crystals were obtained by the dissolving of aniline **4** (0.1 g) in dry acetonitrile (10

ml) in the evacuated glass ampoule at 150–160 °C and the subsequent cooling to room temperature with the temperature gradient of 20 °C/hour. *N,N*-Bis(silatranylmethyl)aniline **4** forms two types of solvates **4a**, **4b** and their molecular structures were determined by single crystal X-ray diffraction (Fig. 1). The asymmetric part of the unit cell of the solvate **4a** $\text{PhN}[\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}]_2 \times \text{MeCN}$ contains one molecule of silatrane **4** and one molecule of MeCN. The asymmetric part of the unit cell of the solvate **4b** $3\text{PhN}[\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}]_2 \times 3.24\text{MeCN}$ contains one molecule of silatrane **4** and one molecule of MeCN in general Wyckoff site (18f) with 100% occupation and one molecule of MeCN in special Wyckoff site (6c) with fractional occupation (~24%). The molecules of silatrane **4** in unit cell are isolated from each other and from solvents, forming 0D blocks (Fig. 27S in Suppl. Inf.).

The selected bond lengths and angles for **4a** and **4b** are presented in Tables 4S and 5S, (Suppl. Inf.). The coordination polyhedron of the silicon atom in compound **4** (Fig. 1) represents a distorted trigonal bipyramid with N atom and C atom in the axial positions and three oxygen atoms occupying the equatorial positions and this geometry is typical for the silatranes [57,58]. All five-membered rings of silatrane skeleton in molecule of compound **4** adopt an 'envelope'-like conformation. Molecule of both solvates of compound **4** contains two silatrane groups which have different spinning of "propeller blades": one such group is Δ -form and other group is Λ -form (Table 2). Yuzo Yoshikawa with co-authors have proposed that the Δ or Λ stereochemistry of silatranes may be

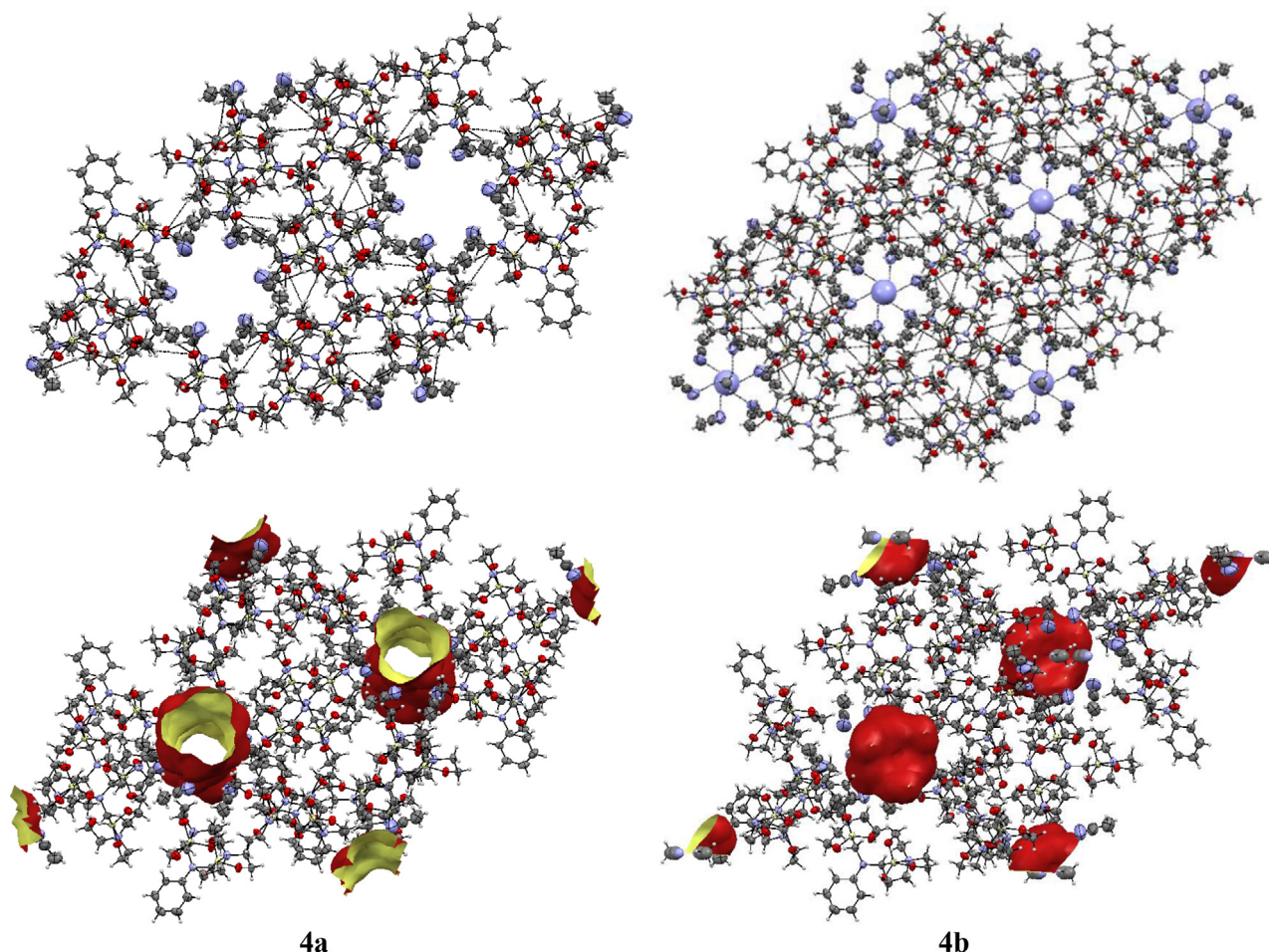


Fig. 2. The supramolecular structure of solvates 4a and 4b with short contacts (top); voids in the structure of solvates 4a and 4b (bottom) (labels of atoms are omitted).

categorized according for absolute configurations of silatrane [59]. The Δ - and Λ -forms have a left- and right-handed propeller (anti-clockwise and clockwise orientation [60]), respectively (Scheme 8).

Authors of this work pointed out that the conformation of each N-Si chelate ring in non-substituted silatrane $\text{RSi}(\text{OCH}_2\text{CH}_2)_3\text{N}$ is interchange and therefore the absolute configurations are not fixed. The similar phenomenon has been found at the investigation of structure of *N*-methyl-*N*-bis(silatranyl)methylamine [24] which also has two silatranyl groups in the different conformations. There is little difference between the geometrical parameters of the solvates **4a** and **4b** (Table 2). The displaces of the silicon atoms relative to the equatorial planes defined by the three oxygen atoms towards the apical substituent in conformers Λ and Δ of the solvates **4a** and **4b** lie between 0.196 Å and 0.200 Å. In these molecules the deviations of the endocyclic nitrogen atoms from the plane of the neighboring carbon atoms are in the interval 0.363–0.372 Å. These values lie within the typical range for silatranyl groups (0.09–0.24 Å for Si atom and 0.34–0.40 Å for N atom) [57,58]. The trigonal bipyramidal (TBP) character η_e of the silicon atom of the silatranyl groups of solvates **4a** and **4b** calculated with the formula 1 [61] varies between 86.4 and 87.0% (Table 2).

$$\eta_e = \left\{ 1/3 \left(\sum_{n=1}^3 \varphi_n \right) \right\} - 109.5 / (120 - 109.5) \times 100$$

where φ is average of angles $\text{O}_{\text{eq}}\text{-Si-O}_{\text{eq}}$ (1)

According to the Cambridge Structural Database [58], the geometrical parameters of compound **4** are typical for silatranes

$\text{RSi}(\text{OCH}_2\text{CH}_2)_3\text{N}$ that clearly establishes the existence of $\text{N} \rightarrow \text{Si}$ dative bond in compound **4**.

It should be noted that the values of the geometric parameters of the axial fragment of aniline **4** and $\text{PhNHCH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$ are closer together than the geometric parameters of the axial fragment of aniline **4** and $\text{MeN}[\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}]_2$ [24] (Table 3). So the length of dative bond $\text{N} \rightarrow \text{Si}$ in compound **4** is significantly shorter than for $\text{MeN}[\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}]_2$ (2.164–2.168 Å and 2.212–2.291 Å, respectively). Curiously, the comparison of the geometric parameters of $\text{MeNHCH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$ [21] and $\text{PhNHCH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$ [23] shows a similar shortening the length of dative bond $\text{N} \rightarrow \text{Si}$ (0.029–0.035 Å) in the aniline derivative (Table 3). This effect is due to the electron-withdrawing properties of the aromatic substituent (σ^* is 0.00 for Me group and 0.60 for Ph group [62]) leading to increased dative binding $\text{N} \rightarrow \text{Si}$. The sum of angles at the exocyclic nitrogen atom (Σ_N) of the compound **4** is $\sim 360^\circ$ as for $\text{PhNHCH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$ [23]. We found in Cambridge Structural Database [58] the several derivatives of aniline ArNAlk_2 with the planar nitrogen atom [63–65].

The supramolecular structure of solvates **4a** and **4b** (Fig. 2) due to intermolecular contacts $\text{C} \cdots \text{H} \cdots \text{O}$ between the hydrogen atoms of molecules of solvent, OCH_2 , NCH_2 silatranyl groups and the equatorial oxygen atoms of the silatranyl groups (Supp. Inf. Fig 28S and 29S). The lengths of these contacts fall in the range between 2.560 Å – 2.898 Å and 2.538 Å – 2.793 Å for solvates **4a** and **4b**, respectively. In these crystals there are conglomerates forming by molecules of compound **4** and MeCN there are voids with approximate volumes 1206.33 Å³ (ca 9.8% of unite cell volume) and

Table 3
The selected geometrical parameters of (*N*-silatranyl)methylamines.

Compound		l, Å		CH ₂ -N	R-N	φ, ° N-Si-CH ₂	Σφ, °N	η _e , %	Ref.
		N→Si	Si-CH ₂						
MeN[CH ₂ Si(OCH ₂ CH ₂) ₃ N] ₂ (1)	Δ	2.212	1.917	1.485	1.464	176.23	333.58	83.14	24
	Δ	2.274	1.893	1.493		175.31		79.84	
MeN[CH ₂ Si(OCH ₂ CH ₂) ₃ N] ₂ (2)	Δ	2.252	1.911	1.469	1.455	176.83	331.29	81.02	
	Δ	2.272	1.911	1.473		178.13		79.02	
MeN[CH ₂ Si(OCH ₂ CH ₂) ₃ N] ₂ (3)	Δ	2.273	1.897	1.468	1.473	177.20	331.46	79.52	
	Δ	2.291	1.906	1.471		175.04		78.06	
MeNHCH ₂ Si(OCH ₂ CH ₂) ₃ N	Δ	2.159	2.188	1.473	1.455	176.59	329.73	87.81	21
(Ph ₃ C)MeNCH ₂ Si(OCH ₂ CH ₂) ₃ N	Δ	2.179	1.902	1.482	1.461	176.09	337.32	85.81	22
PhNHCH ₂ Si(OCH ₂ CH ₂) ₃ N	Δ	2.124	1.897	1.459	1.376	177.59	360.00	90.19	23
	Δ	2.130	1.895	1.466	1.386	178.41	346.83	89.90	

438.78 Å³ (ca 3.6% of unit cell volume) in the solvates **4a** and **4b**, respectively (Fig. 2). The volume of the voids in the crystal lattice has been calculated using the Mercury software [53]. In the unit cell of these solvates there are two full and four quarters voids. The voids of solvate **4a** are a hollow tubes however the voids of solvate **4b** are irregular shape ellipsoid (form of "dried fig"). The volumes of voids of solvates **4a** and **4b** vary almost three times. The reason is that the solvate **4b** contains molecule MeCN which is disordered and bonded by the short contacts C-H...N with three other molecules of MeCN. The lengths of these contacts are equal and constitute 2.538 Å.

4. Conclusion

In order to investigate the structure and reactivity *N*-(silylmethyl)amines closely resembling those already described *N,N*-bis(silylmethyl)amines, the previously unknown *N,N*-bis(silylmethyl)anilines PhN(CH₂SiX₃)₂ (SiX₃ = SiMe₃, Si(OMe)₃, Si(OCH₂CH₂)₃N) and PhN(CH₂SiMe₃)(CH₂SiX₃) (SiX₃ = Si(OMe)₃, Si(OCH₂CH₂)₃N) were obtained. Iodmethylenes of *N,N*-bis(trimetoxysilyl)methyl- and *N,N*-bis(silatranyl)methyl)anilines were prepared. The structure of these compounds was confirmed by ¹H, ¹³C, ²⁹Si and ¹⁵N NMR spectroscopy. The molecular structure of *N,N*-bis(silatranyl)methyl)aniline was determined by single crystal X-ray diffraction. The geometrical parameters of its silatranyl groups are typical for the silatranes. The intermolecular short contacts C-H...O between the hydrogen atoms of molecules of MeCN, groups OCH₂, NCH₂ of silatranyl backbone and the equatorial oxygen atoms of silatranyl groups lead to the formation of two types of solvates: Ph[CH₂Si(OCH₂CH₂)₃N]₂•MeCN and 3Ph[CH₂Si(OCH₂CH₂)₃N]₂•3.24MeCN with close geometrical parameters. The big voids exist in the crystals of solvates and their size and form depend on the number molecules MeCN in the solvate structure.

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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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2022.122438.

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