



## Salts of N-silylmethyl derivatives of DBU: Synthesis and structure

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## ABSTRACT

DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) reacts as a nucleophilic base with  $\text{ClCH}_2\text{Si}(\text{OMe})_3$  forming the 1-[(trimethoxysilyl)methyl]-2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepin-1-ium chloride  $[\text{DBUCH}_2\text{Si}(\text{OMe})_3]^+\text{Cl}^-$ . The interaction of this compound with triethanolamine gives the chloride N-silatranylmethyl derivatives of DBU -  $[\text{DBUCH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}]^+\text{Cl}^-$  which is transformed upon subsequent treatment by  $\text{NaBPh}_4$  to corresponding salt  $[\text{DBU}-\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}]^+\text{BPh}_4^-$ . Their structure was proved by NMR and X-ray analysis.

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## 1. Introduction

The DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) is sterically hindered, tertiary amidine which has often been used as a non-nucleophilic base ( $\text{pK}_a$  is 12 in water) in organic chemistry. Traditionally DBU widely used for carrying out dehydrohalogenation reactions [1–3]. However, sometimes unexpected side-products were obtained from these reactions and there are few reports where DBU has been employed as a nucleophilic base also [3–9].

We found only a few examples of the formation of salts between DBU and haloalkylsilanes. Quaternization of DBU by  $\text{ClCH}_2\text{SiMe}_3$  led to the formation of the corresponding ammonium salt - 1-[(trimethylsilyl)methyl]-2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepin-1-ium chloride (**A**) (Scheme 1) [10,11]. This compound is precursor for the synthesis of the room-temperature ionic liquids with high thermal stability and a greener synthetic profile [11].

The silica-bonded 5-*n*-propyloctahydropyrimido[1,2- $\alpha$ ]azepinium chloride (SB-DBU)Cl from 3-chloropropyl silica (SilprCl) and (DBU) was prepared (Scheme 2) [12]. The interaction of 3-chloropropyltrimethoxysilane with cellulose nanofiber (CNF) was obtained a modified cellulose nanofiber (CNF@Cl) which reacts with DBU gave rise to formation of the nanocatalyst CNF@DBU@Cl) (Scheme 2) [13]. Also in this way the immobilized DBU on silica or nanocomposite  $\text{Fe}_3\text{O}_4@\text{nSiO}_2@\text{mSiO}_2$

were prepared (Scheme 2) [14]. (SB-DBU)Cl, (CNF@Cl) and  $\text{Fe}_3\text{O}_4@\text{nSiO}_2@\text{mSiO}_2\text{DBU@Cl}$  are the effective heterogeneous catalysts in organic chemistry [12–14]. The synthesis and study of the structure of salts of N-silylmethylated derivatives of DBU is the main goal of this work and below we describe our results.

## 2. Experimental

## 2.1. Material and methods

$^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  and  $^{15}\text{N}$  NMR spectra were recorded on a Bruker DPX 400 spectrometer (400.13, 100.61, 79.5 and 40.53 MHz, respectively) with  $\text{Me}_4\text{Si}$  as an internal standard.

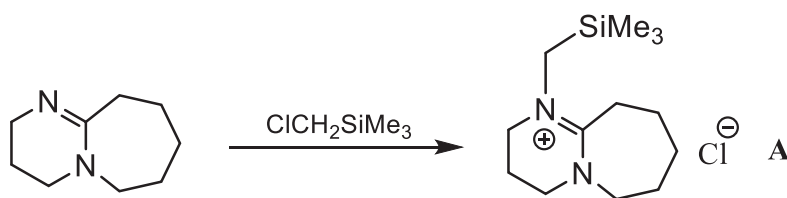
All reactions and other manipulations were carried out in thoroughly dried glassware in argon atmosphere.  $\text{CDCl}_3$  was distilled over  $\text{P}_2\text{O}_5$  prior to use and stored over molecular sieves 4A. Elemental analysis is performed on the thermo scientific flash 2000 automatic CHNS analyzer. Melting points were determined using the boetius block apparatus. The solvents were purified by standard procedures prior to use [15].

## 2.2. X-ray study and refinement

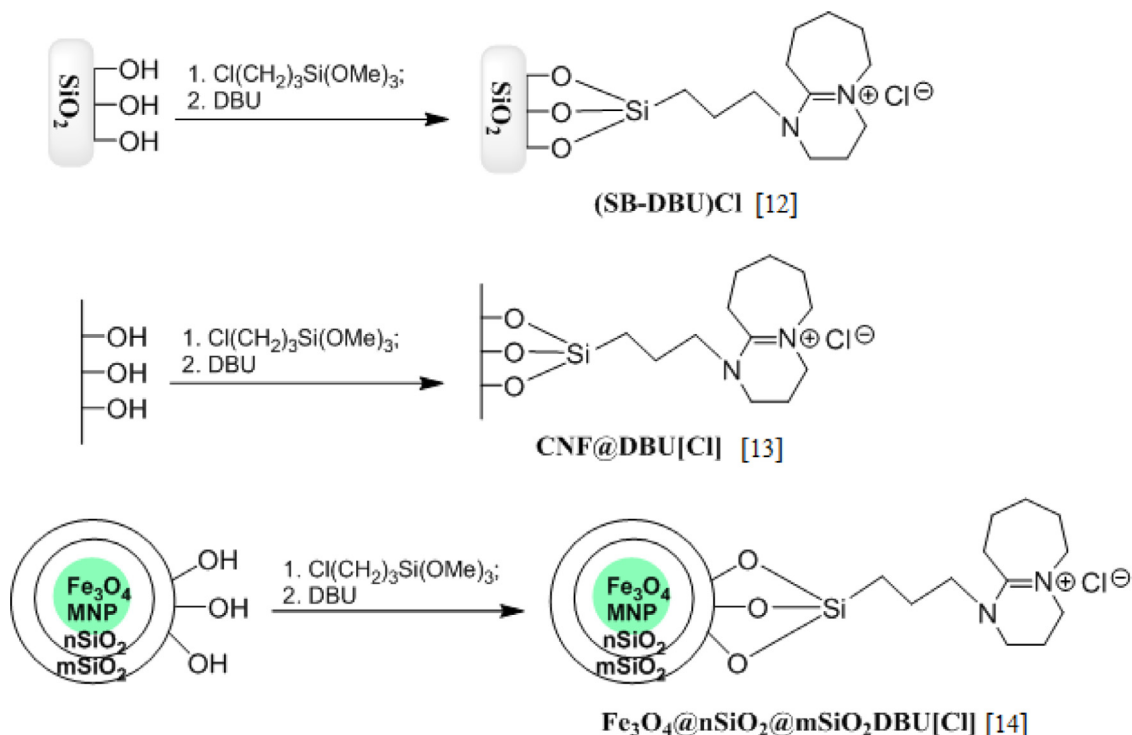
Details of crystallographic data and experimental conditions are presented in Table 1. The determination of the unit cell and the data collection for compounds **1** and **5** was performed on a Bruker D8 Venture Photon 100 CMOS diffractometer with  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073$ ) at 297.0(2) K using the  $\omega$ - $\varphi$  scan technique. The intensities from single crystal of compound **3**

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**Scheme 1.** The quaternization of DBU by  $\text{ClCH}_2\text{SiMe}_3$ .



**Scheme 2.** The immobilization of DBU on silica ( $\text{SiO}_2$ ), cellulose nanofiber (CNF) or nanocomposite  $\text{Fe}_3\text{O}_4@m\text{SiO}_2@m\text{SiO}_2$ .

( $\text{C}_{16}\text{H}_{20}\text{N}_3\text{O}_3\text{Si}$ )( $\text{C}_{24}\text{H}_{30}\text{B}$ )  $\times$  0.5( $\text{C}_4\text{H}_8\text{O}$ ) of  $0.5 \times 0.3 \times 0.3$  mm dimensions were collected at 296 K using the SMART APEX II single crystal diffractometer (Bruker AXS, analytical equipment of Krasnoyarsk center of collective use of SB RAS) equipped with a CCD-detector, graphite monochromator and Mo  $K\alpha$  radiation source. The orientation matrix and cell parameters were defined and refined for the set of 28,865 reflections. The unit cell corresponds to monoclinic symmetry. Space group  $C2/c$  was determined from the statistical analysis of the intensities of all the reflections. Data were corrected for absorption effects using the multi-scan method SADABS [16]. The ratio of minimum to maximum apparent transmission was 0.929. The structure of compound **1** was solved by Bruker SHELXTL Software Package [17] and refined using the OLEX2 [18]. The H atoms were determined by rider method. The structure of compound **3** was solved by the direct methods using package SHELXS and refined in the anisotropic approach for non-hydrogen atoms using SHELXL program [19]. All the hydrogen atoms were positioned geometrically as riding on their parent atoms with  $d(\text{C}-\text{H}) = 0.93\text{--}0.97$  Å for the C–H bonds and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The structural tests for the presence of missing symmetry elements and possible voids were produced using the PLATON program [20]. The main bond lengths are given in Supp. Inf. (Tables 1S–3S). The crystallographic data are deposited in Cambridge Crystallographic data centre CCDC 2,109,601 (1), 2,141,744–2,141,745 (3) and 2,131,006 (5). The data can be downloaded from the site ([www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)).

### 2.3. Synthesis

#### 2.3.1. 1-[(Trimethoxysilyl)methyl]-2,3,4,6,7,8,9,10-octahydropirimido[1,2- $\alpha$ ]azepin-1-ium chloride (1)

(Chloromethyl)trimethoxysilane (8.92 g, 52.30 mmol), DBU (7.96 g, 52.30 mmol) and 50 mL  $\text{Et}_2\text{O}$  was heated at 90 °C for 20 h in the Schlenk apparatus and after cooling solvent was decanted. The residue was washed by dry  $\text{Et}_2\text{O}$  (50 mL  $\times$  3) and dried in a vacuum. Yield of compound **1** as white powder is 16.30 g (97%). M. p. 127–129 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 1.73–1.87 m (6H, 7, 8, 9- $\text{CH}_2$ ), 2.16 quintet (2H, 3- $\text{CH}_2$ ,  $^3J = 6.0$  Hz), 2.92 m (2H, 10- $\text{CH}_2$ ), 3.23 s (2H,  $\text{CH}_2\text{Si}$ ), 3.63 t (2H, 2- $\text{CH}_2$ ,  $^3J = 6.0$  Hz), 3.64 s (9H, 3O $\text{CH}_3$ ), 3.70 t (2H, 4- $\text{CH}_2$ ,  $^3J = 6.0$  Hz), 3.77 m (2H, 6).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ ,  $\delta$ , ppm): 20.01 (10-C), 20.35 (3-C), 22.87 (9-C), 26.34 (8-C), 28.50 (7-C), 40.17 ( $\text{SiCH}_2\text{N}^+$ ), 49.26, 49.25 (2,4-C), 51.40 (O $\text{CH}_3$ ), 55.48 (6-C), 165.80 (N=C).  $^{29}\text{Si}$  NMR ( $\text{CD}_3\text{CN}$ ,  $\delta$ , ppm): -55.41.  $^{15}\text{N}$  NMR ( $\text{CD}_3\text{CN}$ ,  $\delta$ , ppm): -270.2 (1-N). Anal. Found, %: C 48.28; H 8.67; N 8.51; Si 8.92. Calcd for  $\text{C}_{13}\text{H}_{27}\text{ClN}_2\text{O}_3\text{Si}$ , %: C 48.36; H 8.43; N 8.68; Si 8.70.

#### 2.3.2. 1-((2,8,9-Trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)methyl)-2,3,4,6,7,8,9,10-octahydropyrimido[1,2- $\alpha$ ]azepin-1-ium chloride (2)

The mixture of compound **1** (3.68 g (11.40  $\mu\text{mol}$ )), tris(2-hydroxyethyl)amine (1.70 g, 11.40 mmol) and 10 mL dry MeCN was heated at 100 °C for 4 h in the Schlenk apparatus. Then the volatile substances were removed in vacuo (0.1 mm Hg). The residue was

**Table 1**  
The crystal structure parameters of compounds **1**, **3** and **5**.

	1	3	5
CCDC no.	2,109,601	2,141,744–2,141,745	2,131,006
Emp. formula	C <sub>13</sub> H <sub>27</sub> N <sub>2</sub> O <sub>3</sub> Si, Cl	C <sub>84</sub> H <sub>104</sub> B <sub>2</sub> N <sub>6</sub> O <sub>7</sub> Si <sub>2</sub>	C <sub>24</sub> H <sub>20</sub> B • C <sub>10</sub> H <sub>19</sub> N <sub>2</sub>
Form weight	322.90	1387.49	486.48
Collection T, K	297	296	293
Cryst syst	monoclinic	monoclinic	Monoclinic
Space group	P2 <sub>1</sub> /n	C2/c, 4	P2 <sub>1</sub> /n
a, Å	11.887(8)	25.868 (3)	29.906(16)
b, Å	12.569(8)	9.8229 (10)	9.874(6)
c, Å	12.247(7)	32.162 (3)	30.735(19)
α, deg	90.0	90.0	90.0
β, deg	113.42(2)	108.436 (2)	110.23(3)
γ, deg	90.0	90.0	90.0
V, Å <sup>3</sup>	1679.00(18)	7753.2 (14)	8516(9)
Z	4	4	12
P <sub>calc</sub> , Mg/m <sup>3</sup>	1.277	1.185	1.138
μ (mm <sup>-1</sup> )	0.31	0.104	0.07
Reflections with F > 4σ(F)	2231	3618	7593
2θ <sub>max</sub> (°)	52.2	46.54	52.2
h, k, l - limits	-14 ≤ h ≤ 14; -15 ≤ k ≤ 15; -15 ≤ l ≤ 14	-28 ≤ h ≤ 28; -10 ≤ k ≤ 10; -35 ≤ l ≤ 35	-36 ≤ h ≤ 36; -12 ≤ k ≤ 12; -37 ≤ l ≤ 37
no. of coll reflns	42,233	28,865	126,749
no. of indep reflns	3332	5568	16,792
R <sub>int</sub>	0.0305	0.0938	0.1086
no. of params	184	450	1015
Goof	1.03	1.025	1.02
R1 [F <sub>o</sub> > 4σ(F <sub>o</sub> )], wR <sub>2</sub>	R <sub>1</sub> = 0.0465, wR <sub>2</sub> = 0.0987	R <sub>1</sub> = 0.0946, wR <sub>2</sub> = 0.2284	R <sub>1</sub> = 0.0669, wR <sub>2</sub> = 0.1421
Δρ <sub>max</sub> (e/Å <sup>3</sup> )	0.26	0.617	0.55
Δρ <sub>min</sub> (e/Å <sup>3</sup> )	-0.25	-0.380	-0.31
The weighed refinement of F <sup>2</sup>	w = 1/[σ <sup>2</sup> (F <sub>o</sub> <sup>2</sup> ) ± (0.0456P) <sup>2</sup> ± 0.846P] where P = (F <sub>o</sub> <sup>2</sup> ± 2F <sub>c</sub> <sup>2</sup> )/3	w = 1/[σ <sup>2</sup> (F <sub>o</sub> <sup>2</sup> ) + (0.1054P) <sup>2</sup> + 27.2695P] where P = max(F <sub>o</sub> <sup>2</sup> + 2F <sub>c</sub> <sup>2</sup> )/3	w = 1/[σ <sup>2</sup> (F <sub>o</sub> <sup>2</sup> ) ± (0.068P) <sup>2</sup> ± 2.3453P]
Extinction coefficient (SHELXL 2014/7)	none	none	None

washed by dry THF (20 mL x 3) and dried in a vacuum. Yield of compound **2** as colorless viscous mass is 3.98 g (10.58 mmol, 93%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 1.68–1.78 m (6H, 7,8,9-CH<sub>2</sub>), 2.07 quintet (2H, 3-CH<sub>2</sub>, <sup>3</sup>J = 6.1 Hz), 2.72s (2H, SiCH<sub>2</sub>N<sup>+</sup>), 2.88–2.91 m (2H, 10-CH<sub>2</sub>), 3.06 t (6H, 3CH<sub>2</sub>N, <sup>3</sup>J = 6.0 Hz), 3.53 t (2H, 2-CH<sub>2</sub>, <sup>3</sup>J = 6.0 Hz), 3.55 t (2H, 4-CH<sub>2</sub>, <sup>3</sup>J = 6.0 Hz), 3.64 m (2H, 6-CH<sub>2</sub>) 3.80 t (6H, 3OCH<sub>2</sub>, <sup>3</sup>J = 6.0 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm): 20.30 (3-C), 23.16 (9-C), 26.62 (8-C), 28.52 (7-C), 28.62 (10-C), 46.84 (SiCH<sub>2</sub>N<sup>+</sup>), 48.67 (2-C), 48.96 (4-C), 50.78 (NCH<sub>2</sub>-silatrane), 54.57 (6-C), 57.16 (OCH<sub>2</sub>), 164.37 (N=C). <sup>29</sup>Si NMR (CDCl<sub>3</sub>, δ, ppm): -82.9. <sup>15</sup>N NMR (CD<sub>3</sub>CN, δ, ppm): -353.5 (N-silatrane), -265.5 (5-N), -258.5 (1-N=).

### 2.3.3. 1-((2,8,9-Trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)methyl)-2,3,4,6,7,8,9,10-octa-hydro-pyrimido[1,2-α]azepin-1-ium tetraphenylborate (3)

The mixture of compound **2** (4.29 g, 11.40 mmol), NaB(Ph)<sub>4</sub> (4.59 g, 13.40 mmol) and dry MeCN (20 mL) heated at 80 °C for 1 h with stirring. Then MeCN was removed an added dry CHCl<sub>3</sub> (30 mL) and the formed precipitate was separated by centrifugation. As a result of the subsequent evaporation of the solution under reduced pressure, recrystallization of the residue from absolute THF (15 mL), and drying in a vacuum (0.1 mm Hg) was obtained compound **3** (5.04 g (7.6 mmol, 67%) colorless crystalline substance. M. p. = 158 °C (evacuated capillary). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 1.29s (2H, 7-CH<sub>2</sub>), 1.42 m (2H, 9-CH<sub>2</sub>), 1.48 m (4H, 3,8-CH<sub>2</sub>), 2.31 t (6H, 3NCH<sub>2</sub>, <sup>3</sup>J = 6.0 Hz), 2.51 m (2H, 10-CH<sub>2</sub>), 2.52s (2H, SiCH<sub>2</sub>N<sup>+</sup>), 3.63 t (2H, 4-CH<sub>2</sub>, <sup>3</sup>J = 5.7 Hz), 2.83 m (2H, 6-CH<sub>2</sub>), 3.08 t (2H, 2-CH<sub>2</sub>, <sup>3</sup>J = 5.2 Hz), 3.42 t (6H, 3OCH<sub>2</sub>, <sup>3</sup>J = 6.0 Hz), 6.87 t (4H, H-p, <sup>3</sup>J = 7.1 Hz), 7.0 t (8H, H-m, <sup>3</sup>J = 7.1 Hz), 7.35 broad s (8H, H-o). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm): 19.8 (3-C), 22.92 (9-C), 26.62 (7-C), 28.18 (8-C), 28.31 (10-C), 46.59 (SiCH<sub>2</sub>N<sup>+</sup>), 48.17 (2-C), 48.25 (4-C), 50.19 (NCH<sub>2</sub>-silatrane), 53.88 (6-C), 56.87 (OCH<sub>2</sub>), 121.71 (C-p), 125.38 (C-o), 136.00 (C-m), 163.83 q (C-i, <sup>1</sup>J<sub>C-B</sub> = 49.2 Hz), 163.84 (N=C). <sup>29</sup>Si NMR (CDCl<sub>3</sub>, δ, ppm): -82.6. <sup>15</sup>N NMR, (CD<sub>3</sub>CN, δ,

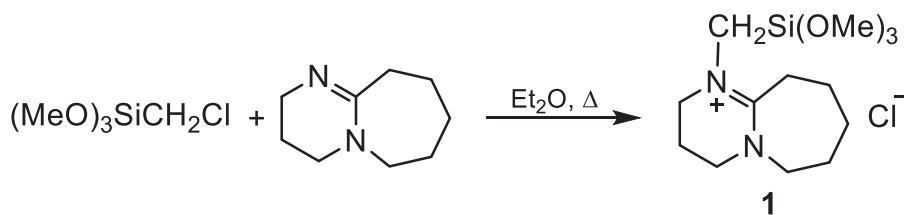
ppm): -352.5 (N-silatrane), -265.7 (5-N), -258.3 (1-N=). Anal. Found, %: C 72.51; H 8.02; N 6.18. Calcd for C<sub>40</sub>H<sub>50</sub>BN<sub>3</sub>O<sub>3</sub>Si, %: C 72.82; H 7.64; N 6.37.

### 2.3.4. 1-Methyl-2,3,4,6,7,8,9,10-octahydropyrimido[1,2-α]azepin-1-ium chloride 4

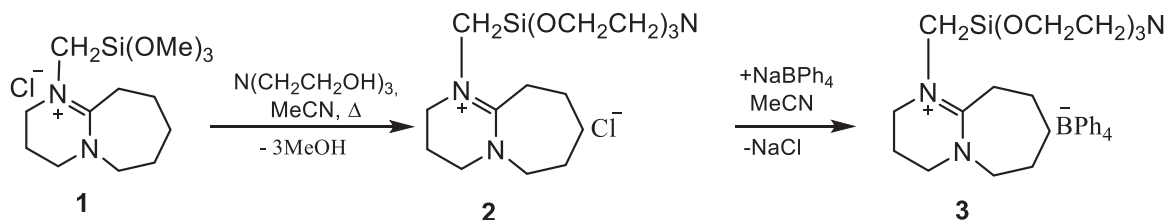
The mixture of DBU 0.76 g (5.00 mmol), 0.26 g (5.15 mmol) MeCl and 10 mL MeCN stirred in an evacuated Schlenk flask at 25 °C for 24 h. Then volatiles were removed under reduced pressure and the residue was washed with diethyl ether (3 × 10 mL). The solid residue was dried in a vacuum to obtain a colorless crystalline compound **4** 1.00 g (99%, 4.93 mmol), M. p. 132 °C (evacuated capillary). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 1.78–1.86 m (6H, 7,8,9-CH<sub>2</sub>), 2.22 quintet (2H, 3-CH<sub>2</sub>, <sup>3</sup>J = 6.1 Hz), 3.01–3.04 m (2H, 10-CH<sub>2</sub>), 3.42 s (3H, NMe), 3.67–3.72 m (4H, 2,4-CH<sub>2</sub>), 3.79–3.81 m (2H, 6-CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm): 20.16 (3-C), 22.42 (7-C), 26.35 (8-C), 28.45 (9-C), 28.98 (10-C), 41.71 (NMe), 49.13, 49.21 (2,4-C), 55.47 (6-C), 166.82 (N=C). Anal. Found, %: C 59.30, H 9.42, N 13.79, Cl 17.53. Calcd for C<sub>10</sub>H<sub>19</sub>ClN<sub>2</sub>, %: C 59.25, H 9.45, N 13.82, Cl 17.19.

### 2.3.5. 1-Methyl-2,3,4,6,7,8,9,10-octa-hydro-pyrimido[1,2-α]azepin-1-ium tetraphenylborate (5)

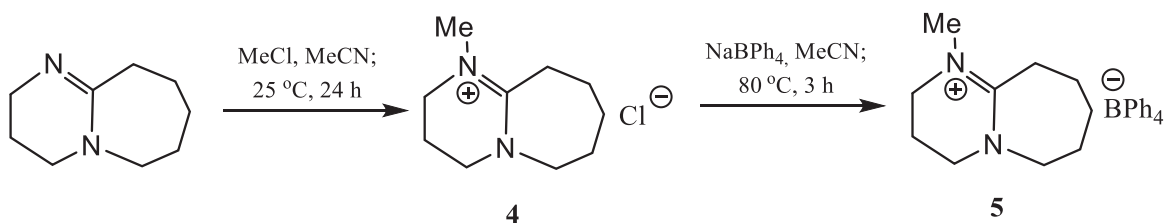
The mixture of compound **4** 1.00 g (4.93 mmol), 1.69 g (4.93 mmol) sodium tetraphenylborate and 50 mL MeCN stirred at 80 °C for 3 h. Then the reaction mixture was filtered and the filtrate was evaporated in vacuo. Colorless crystalline compound **5** was isolated 2.30 g (96%, 4.72 mmol), M. p. 248 – 250 °C (evacuated capillary). A single crystal for X-ray structural analysis was obtained from acetonitrile. <sup>1</sup>H NMR (MeCN, δ, ppm): 1.60–1.67 m (4H, 7,9-CH<sub>2</sub>), 1.69–1.74 m (2H, 8-H), 1.95 quintet (2H, 3-CH<sub>2</sub>, <sup>3</sup>J = 6.1 Hz), 2.68–2.71 m (2H, 10-CH<sub>2</sub>), 3.10 s (3H, NMe), 3.29–3.32 m (2H, 4-CH<sub>2</sub>), 3.34–3.37 m (2H, 2-CH<sub>2</sub>), 3.50–3.52 m (2H, 6-CH<sub>2</sub>), 6.84 t (4H, H<sub>p</sub>, <sup>3</sup>J = 7.1 Hz), 6.99 t (8H, H<sub>m</sub>, <sup>3</sup>J = 7.1 Hz), 7.28 broad s (8H, H<sub>o</sub>). <sup>13</sup>C NMR (MeCN, δ, ppm): 20.52 (3-C), 22.88 (9-C), 26.88 (7-C), 29.09



**Scheme 3.** The interaction of (chloromethyl)trimethoxysilane with DBU.



**Scheme 4.** The synthesis of salts [DBUCH<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]<sup>+</sup>X<sup>-</sup> (X = Cl (2), BPh<sub>4</sub> (3)).



**Scheme 5.** The synthesis of salts [DBUMe]<sup>+</sup>X<sup>-</sup> (X = Cl (4), BPh<sub>4</sub>(5)).

(8,10-C), 41.52 (NMe), 49.50, 49.55 (2,4-C), 55.62 (6-C), 122.77 (C<sub>p</sub>), 126.59 (C<sub>o</sub>), 136.75 (C<sub>m</sub>), 164.82 (C<sub>i</sub>, <sup>1</sup>J<sub>C-B</sub> = 49.2 Hz), 166.04 (N=C). Found, %: C 83.90, H 8.13, N 5.69. Calcd for C<sub>34</sub>H<sub>39</sub>BN<sub>2</sub>: C 83.94, H 8.08, N 5.76.

### 3. Results and discussion

#### 3.1. Synthesis and NMR study

1-((Trimethoxysilyl) methyl)-2,3,4,6,7,8,9,10-octahydropyrimido [1, 2 $\alpha$ ] azepin-1-ium chloride **1** was prepared in almost quantitative yield at the interaction of (chloromethyl)trimethoxysilane with DBU (Scheme 3).

The interaction of equimolar mixture of the compound **1** and tris(2-hydroxyethyl)amine gave rise to the formation of 1-((2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)methyl)-2,3,4,6,7,8,9,10-octahydropyrimido[1,2- $\alpha$ ]azepin-1-ium chloride **2** (Scheme 4). This compound could not be isolated in the solid (crystalline) state, it exist as the hard glassy mass (at 10–15 °C) or the viscous honey-like mass (at 25–30 °C). Therefore compound **2** was converted to the 1-((2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)methyl)-2,3,4,6,7,8,9,10-octahydropyrimido[1,2- $\alpha$ ]azepin-1-ium tetraphenylborate **3** (Scheme 4).

The reaction of DBU with methyl chloride in acetonitrile leads to the formation of the corresponding 1-methyl-2,3,4,6,7,8,9,10-octahydropyrimido[1,2- $\alpha$ ]azepin-1-ium chloride **4** with a quantitative yield (Scheme 5). Compound **4** reacts with NaBPh<sub>4</sub> forming 1-methyl-2,3,4,6,7,8,9,10-octahydropyrimido[1,2- $\alpha$ ]azepin-1-ium tetraphenylborate **5**.

The data of multinuclear NMR spectroscopy are proof the structure of the compounds **1–5** and the elemental analysis confirms their composition. The results of <sup>1</sup>H and <sup>13</sup>C NMR analysis of the compounds **1–5** points to the fact of the quaternization of the nitrogen atom of amidine part of their molecules: the values of the

chemical shifts lie in the expected range of the characteristic values of the N-alkylated or N-protonated derivatives of DBU [9,21,22] (Table 2). A significant low-field shift of the signals of the N-CH<sub>2</sub>-Si groups in the <sup>1</sup>H NMR spectra of compounds **1–3** demonstrated at the formation of the N-(silylmethyl)ammonium salts. Early the similar changes in NMR spectra were demonstrated at the formation of the N-(silatranylmethyl)ammonium salts [23].

#### 3.2. X-Ray investigation of compounds 1, 3 and 5

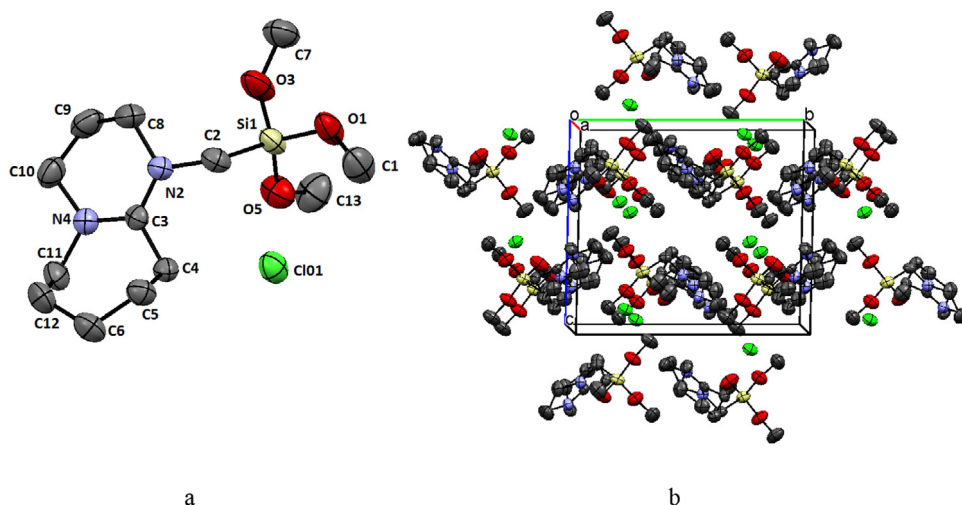
##### 3.2.1. X-Ray of compound 1

The suitable crystals of compound **1** were grown from tetrahydrofuran solution. The asymmetric unit of 1-[(trimethoxysilyl) methyl]-2,3,4,6,7,8,9,10-octahydropyrimido[1,2 $\alpha$ ]azepin-1-ium chloride **1** contains one molecule and unit cell contains four molecules. It should be noted that the compound **1** is a representative of poorly studied trialkoxysilanes containing an ammonium group in the geminal position. We found only one compound **B** whose structure was studied by X-ray diffraction [24]. The molecular structure of compound **1** is presented in Fig. 1a and structural parameters are presented in Table 1S (supporting information). The selected geometrical parameters for compounds **1** and **B** are given in Table 3. The polyhedron of silicon atom of these be described as tetrahedral with all bond lengths and angles within the range of the expected values. A significant difference is observed only in the bond lengths Si-C (1.857(3) Å and 1.878(2) Å for compounds **1** and **B**, respectively).

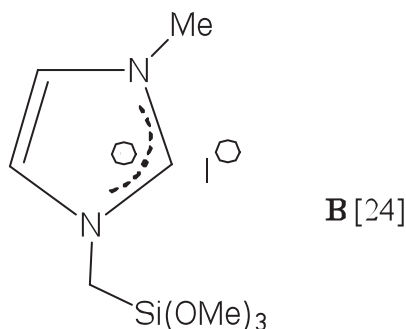
The short contacts of chlorine ions with hydrogen atoms Cl-H(5), Cl-H(2), Cl-H(1C) (2.903 Å, 2.769 Å and 2.730 Å, respectively) and short contact H(1B)-H(7B) 2.319 Å between neighboring molecules (see Supp. Inf. Fig. 14S) provide the supramolecular structure of compound **1** in the crystal. The molecules of compound **1** form zig-like chains which linked contacts Cl-H(4B) and Cl-H(11A) (2.849 Å and 2.846 Å, respectively) (Fig. 2b).

**Table 2**The selected NMR data for compounds **1–5** and related compounds.

Compound	<sup>15</sup> N1	δ, ppm <sup>15</sup> N5	<sup>15</sup> Nsilatrane	<sup>13</sup> C (C=N)	<sup>29</sup> Si	Ref.
<b>1</b>	–270.2 (CD <sub>3</sub> CN)			165.80 (CD <sub>3</sub> CN)	–55.4 (CD <sub>3</sub> CN)	This work
	–258.5	–265.5 (CD <sub>3</sub> CN)	– 353.5	164.37 (CDCl <sub>3</sub> )	–82.9 (CDCl <sub>3</sub> )	This work
<b>3</b>	–258.3 (CD <sub>3</sub> CN)	–265.3 (CD <sub>3</sub> CN)	– 352.5	163.84 (CDCl <sub>3</sub> )	–82.6 (CDCl <sub>3</sub> )	This work
<b>4</b>				166.82		This work
<b>5</b>				155.04		This work
[DBUCH <sub>2</sub> SiMe <sub>3</sub> ] <sup>+</sup> Cl <sup>–</sup>				165.29		11
[DBUCH <sub>2</sub> SiMe <sub>3</sub> ] <sup>+</sup> Tf <sub>2</sub> N <sup>–</sup>				165.17		11
DBU	–290.0	–173.0		161.5		21
[DBUH] <sup>+</sup> CF <sub>3</sub> COO <sup>–</sup>	–263.4	–260.6		166.2		21
[DBUH <sub>2</sub> ] <sup>+</sup> 2CF <sub>3</sub> COO <sup>–</sup>	–259.2	–265.1		167.1		21

**Fig 1.** The short contacts between molecules of compound **1** (a). Crystal structure of compound **1** along axis a (b).**Table 3**Selected geometrical parameters for compounds **1** and **B**.

	l, Å				φ, °				Ref.
	Si–C	N–CSi	Si–O	O–C	N–C–Si	Si–OMe	O–Si–C <sub>2</sub>	O–Si–O	
<b>1</b>	1.857(3)	1.481(3)	1.603(2) 1.604(3) 1.609(2)	1.411(5) 1.375(4) 1.409(5)	115.(2)	127.2(2) 129.4(2) 124.7(2)	110.4(1) 111.6(1) 106.6(1)	106.5(1) 113.6(1) 108.2(1)	this work
<b>B</b>	1.878(2)	1.480(3)	1.612(2) 1.612(2) 1.624(2)	1.430(4) 1.430(3) 1.432(4)	113.4(1)	126.1(2) 127.2(2) 124.0(2)	112.8(1) 105.3(1) 108.0(1)	107.9(1) 107.9(1) 115.1(1)	[24]



### 3.2.2. X-Ray of compound **3**

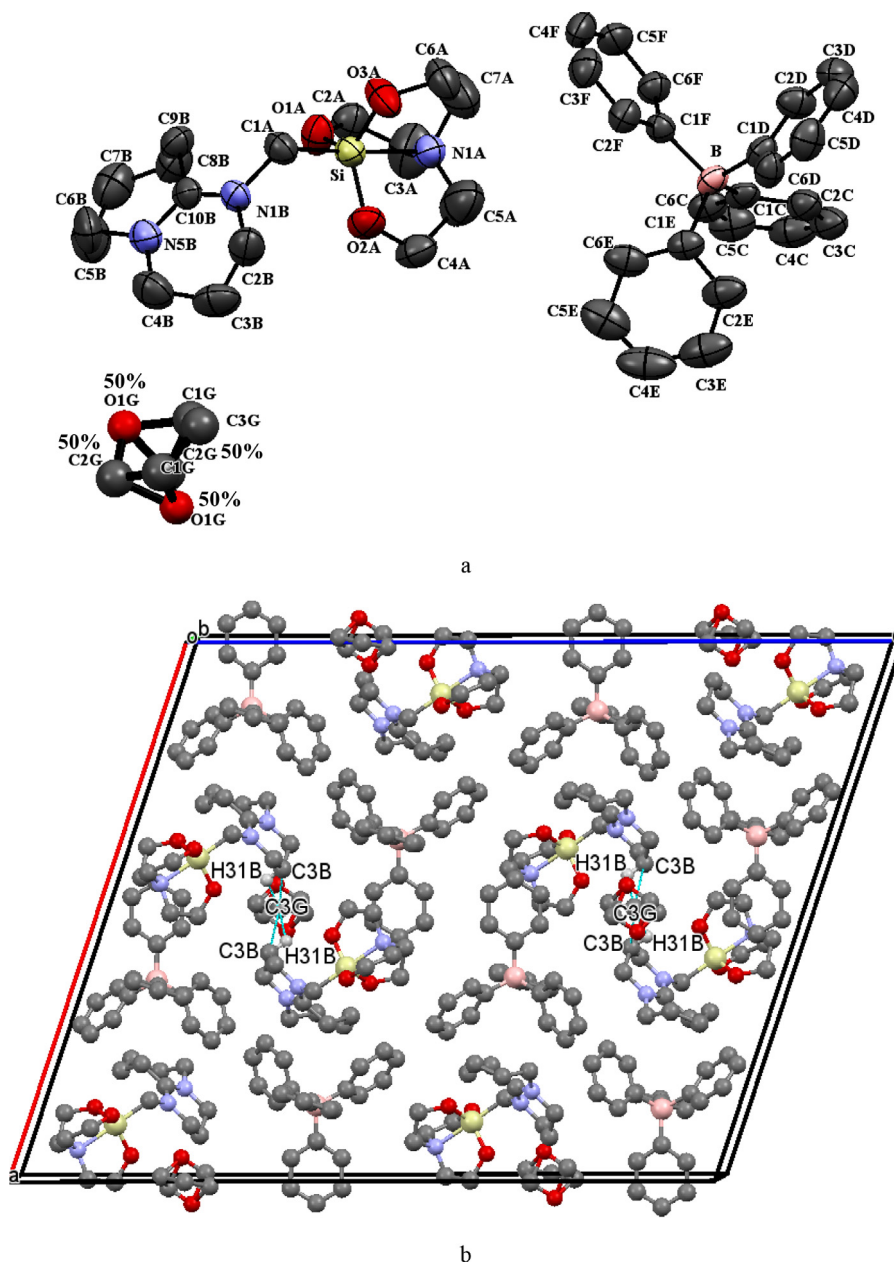
The suitable crystals of compound **3** were grown from THF solution. The asymmetric unit of 1-((2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)methyl)-2,3,4,6,7,8,9,10-octa-hydro-pyrimido[1,2- $\alpha$ ]azepin-1-ium tetraphenylborate (C<sub>16</sub>H<sub>20</sub>N<sub>3</sub>O<sub>3</sub>Si)(C<sub>24</sub>H<sub>30</sub>B)  $\times$  0.5(C<sub>4</sub>H<sub>8</sub>O) contains one molecule of compound **3** and half of molecule THF. The molecular structure

of compound **3** was showed on the Fig. 2a. The coordination polyhedron of the silicon atom in this compound represents a distorted trigonal bipyramid with N atom and C atom in the axial positions and three oxygen atoms occupying the equatorial positions. All five-membered rings of silatrane skeleton in the molecule of compound **3** adopt an ‘envelope’-like conformation. The values of the N–Si bond distance is 2.097 (6) Å and the N–Si–CH<sub>2</sub> fragment is almost linear 176.1 (Table 3). It must be emphasized that the values of the geometric parameters of compound **3** and previously studied silatranes containing an ammonium group in the  $\alpha$ -position to the silicon atom are closely (Table 4 and [25] and ref. therein]). The trigonal bipyramidal (TBP) character  $\eta_e$  of the silicon atom can be calculated according to Tamao's method (Eq. (1), [28,29]). The value of this characteristic for compound **3** is 91.7%.

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

where  $\varphi$  is average of angles O<sub>eq</sub>–Si–O<sub>eq</sub>

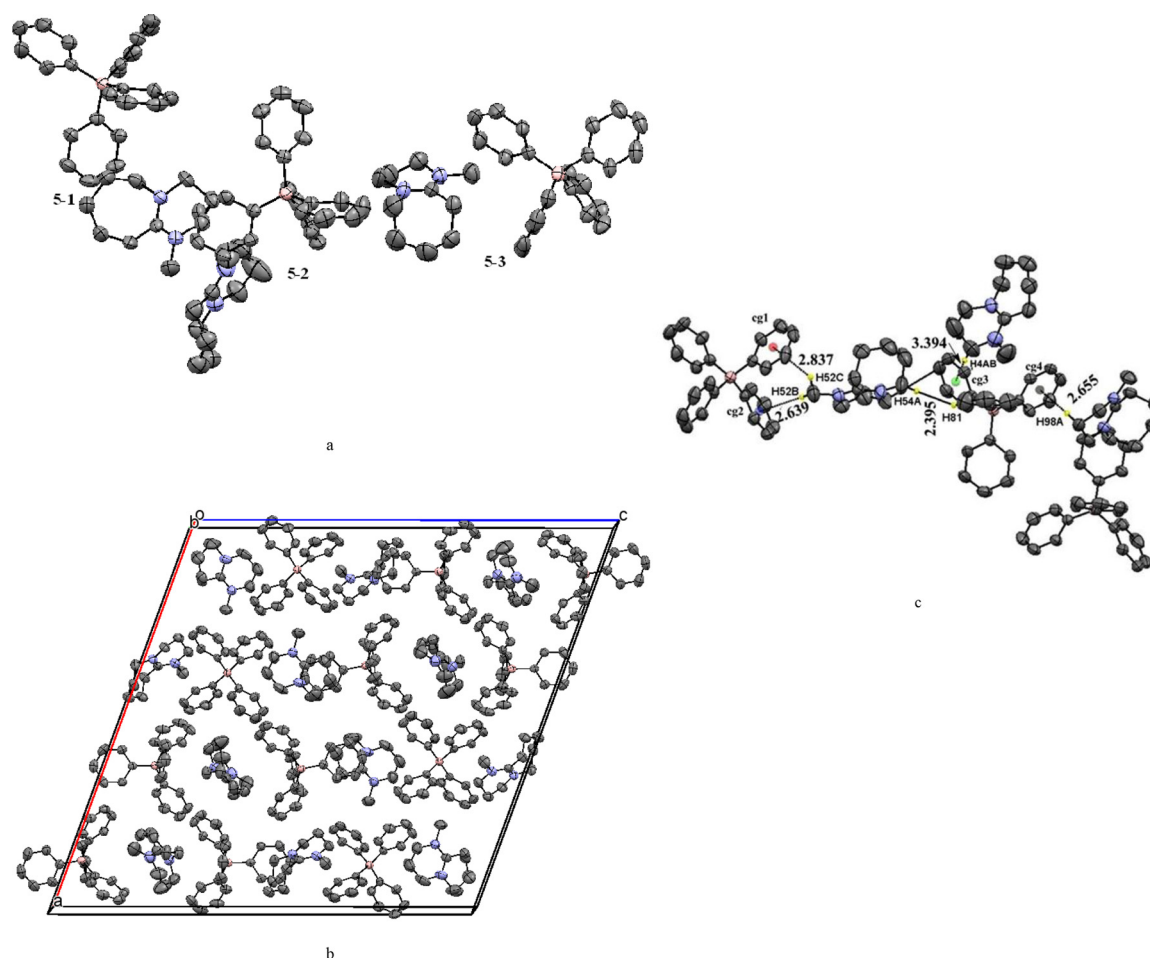




**Fig. 2.** The molecular structure of compound **3** (Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability) (a). Crystal structure of compound **3** along axis *b* (b).

**Table 4**  
The select geometrical parameters of compound **3** and related compounds.

Compound	l, Å			$\varphi$ , ° N-Si-CH <sub>2</sub>	$\Sigma\varphi$ , °	$\eta_e$ , %	Ref.
	N-Si	Si-CH <sub>2</sub>	CH <sub>2</sub> -N				
<b>3</b>	2.097(6)	1.902(7)	1.474(8)	176.1(2)	357.4	91.7	This work
[MeNH <sub>2</sub> CH <sub>2</sub> Si] <sup>+</sup> Cl <sup>-*</sup>	2.078(2)	1.921(3)	1.503(4)	177.0(1)	358.1	93.8	[26]
[Me <sub>3</sub> NCH <sub>2</sub> Si] <sup>+</sup> I <sup>-*</sup>	2.083(2)	1.986(2)	1.538(2)	175.77)	358.1	93.8	[27]
Si = Si(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N							



**Fig. 3.** The asymmetric unit of compound **5** (a). Crystal structure of compound **5** along axis b (b). The short contacts in compound **5** (cg1 – centroid (C2AA C14 C3AA C13 C0AA C1AA), cg2 – centroid (C12 C23 C24 C9 C10 C11), cg3 – centroid (C84 C85 C86 C87 C82 C83), cg4 – centroid (C77 C88 C89 C74 C75 C76)) (c).

In the crystal of compound **3** each cation  $[\text{DBUCH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}]^+$  is surrounded by four anions  $\text{BPh}_4^-$  (Fig. 2b). The short contacts  $\text{H}_{42\text{B}}-\text{H}_{6\text{D}}$ ,  $\text{H}_{52\text{B}}-\text{C}_{4\text{E}}$ ,  $\text{H}_{32\text{A}}-\text{H}_{2\text{D}}$ ,  $\text{H}_{51\text{B}}-\text{C}_{5\text{D}}$ ,  $\text{H}_{52\text{A}}-\text{C}_{3\text{D}}$  (2.335 Å, 2.571 Å, 2.331 Å, 2.837 Å and 2.840 Å, respectively) between hydrogen atoms of cation  $[\text{DBUCH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}]^+$  and hydrogen or carbon atoms of anion  $\text{BPh}_4^-$  as well as

$\text{C}_{6\text{A}}-\text{C}_{4\text{F}}$  (3.360 Å) between carbon atoms of  $\text{OCH}_2$  fragment of silatranyl group and anion  $\text{BPh}_4^-$  are shown in Supp. Inf. The solvent molecule  $\text{C}_4\text{H}_8\text{O}$  is disordered over two orientations by 2-fold axis (Fig. 7S). The non-covalent interactions  $\text{H}_{31\text{B}}(\text{DBU})-\text{C}_{3\text{G}}(\text{THF})$  (2.851 Å) between hydrogen atoms of DBU and carbon atoms of solvent (THF) bind fragments of neighboring molecules. The sum of the above-listed short contacts provide the three-dimensional mesh structure in the crystal of compound **3**.

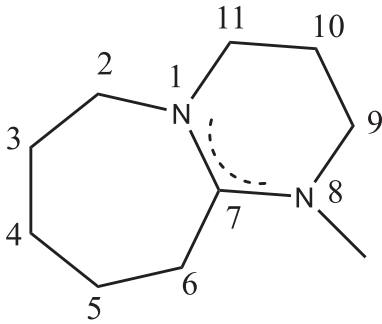
### 3.2.3. X-Ray of compound 5

The suitable crystals of compound **5** were grown from acetonitrile solution. The asymmetric unit of 1-methyl-2,3,4,6,7,8,9,10-octahydropirimido[1,2 $\alpha$ ]azepin-1-ium tetraphenylborate **5** contains three molecules **5-1**, **5-2** and **5-3** (Fig. 3a) and unit cell contains twelve molecules. The molecular structure of each molecule with the numbers and symbols of the atoms are given in Supp. Inf. (Fig.). Note that the compound **5** is a representative of the salts of N-alkylated DBU, which have been little studied by the X-ray method. In the crystal of compound **5** each cation  $[\text{DBU}-\text{MeN}]^+$  is surrounded by four anions  $\text{BPh}_4^-$  just as in compound **3** (Fig. 3b).

Apparently, the existence of such a supramolecular structure of compound **5** is provided by short contacts  $\text{H}_{54}-\text{H}_{81}$ ,  $\text{H}_{52\text{C}}-\pi_{\text{cg1}}$ ,  $\text{H}_{52\text{B}}-\pi_{\text{cg1}}$ ,  $\text{H}_{4\text{AB}}-\pi_{\text{cg3}}$  and  $\text{H}_{98\text{A}}-\pi_{\text{cg4}}$  (2.395, 2.837, 2.639, 3.394 and 2.655 Å) (Fig. 3c).

### 3.2.4. The structure of DBU fragment in compounds 1, 3 and 5

The Cambridge Structural Database contains only three examples of N-alkylated salts of DBU, among them the 1-benzyl-2,3,4,6,7,8,9,10-octahydropirimido[1,2 $\alpha$ ]azepin-1-ium bromide **6** [30], 1-octadecyl-2,3,4,6,7,8,9,10-octahydropirimido[1,2 $\alpha$ ]azepin-1-ium iodide **7** [31] and bis(*m*-1-(5-ethoxycarbonyl-2-oxy-3-(oxymethyl)benzyl)-2,3,4,6,7,8,9,10-octahydropyrimido-(1,2-*a*)azepin-1-ium)-hexacarbonyl-di-rhenium(I) **8** [32]. The select geometrical parameters of DBU fragment of compounds **1**, **3**, **5-8** are shown in the Table 5. In these salts the bond distances between carbon C7 and nitrogen atoms N1 lie in the range from 1.312 to 1.341 Å and the bond distances between carbon C7 and nitrogen atoms N8 lie in the range from 1.311 to 1.345 Å. It is necessary to stress that in the neutral cyclic amidines the experimental values of bond lengths  $\text{N}=\text{C}$  and  $\text{N}-\text{C}$  vary considerably, for example (*S*)-9-hydroxymethyl-1,5-diazabicyclo(4.3.0)non-5-ene these values are 1.279 Å and 1.343 Å, respectively [33]. The bridge atoms N1, N8 and C7 are nearly planar: the sum of their angles lie in the range from 356.83° to 360°. The exception is the sum of angles at atom N8 for compound **7** (356.83°). These structure factors are indicated that the positive charge is delocalized onto both nitrogen atoms of amidinium cations in a similar way to

**Table 5**The select geometrical parameters of N-alkylated DBU fragment in compounds **1**, **3** and **5** related compounds **6–8**.


Compound	l, Å					$\Sigma\varphi$ , °			Ref.
	N8-C7	N1-C7	N8-C9	N1-C2	N1-C11	N1	N8	C7	
<b>1</b>	1.325	1.326	1.468	1.481	1.467	358.65	359.64	359.93	This work
<b>3</b>	<b>1.311</b>	<b>1.341</b>	<b>1.463</b>	<b>1.470</b>	<b>1.442</b>	<b>359.70</b>	<b>359.84</b>	<b>359.96</b>	This work
<b>5-1</b>	1.328	1.312	1.457	1.466	1.475	359.96	359.94	359.93	This work
<b>5-2</b>	1.327	1.329	1.486	1.481	1.463	359.69	359.99	360.00	This work
<b>5-3</b>	1.325	1.322	1.466	1.478	1.458	359.75	359.79	360.00	This work
<b>6</b>	1.334	1.317	1.470	1.484	1.472	359.75	359.96	360.00	[30]
<b>7</b>	<b>1.304</b>	<b>1.332</b>	<b>1.436</b>	<b>1.496</b>	<b>1.412</b>	<b>359.95</b>	<b>356.83</b>	<b>359.96</b>	[31]
<b>8</b>	1.345	1.316	1.490	1.492	1.460	359.99	358.14	359.56	[32]

acyclic amidinium cations [34]. Among compounds **1**, **3** and **5–8** the DBU skeleton in compound **7** is more deformed than in other compound. Probably cause is a significant steric effect of 1-octadecyl group. Note that the equalization of bond lengths of the fragment N1C7N8 in the compound **3** is significantly less than N-silylmethylated derivatives DBU **1** and **5**. The reason of such distinction has to do with the super electron donor effect of silatranymethyl group  $-\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3$  N ( $\sigma^* = -2.24$  [35]).

#### 4. Conclusion

(Chloromethyl)trimethoxysilane reacts with DBU giving the corresponding ammonium salt which upon interaction with triethanolamine forms 1-((2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)methyl)-2,3,4,6,7,8,9,10-octahydropyrimido[1,2- $\alpha$ ]azepin-1-ium chloride as viscous honey-like mass. This compound could not be isolated in the solid state and 1-((2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)methyl)-2,3,4,6,7,8,9,10-octahydropyrimido[1,2- $\alpha$ ]azepin-1-ium tetraphenylborate was synthesized as a result of the exchange reaction with NaBPh<sub>4</sub>. The structure of the last compounds was proved by NMR spectroscopy and X-ray analysis. The values of its geometric parameters and previously studied silatranes containing an ammonium group in the  $\alpha$ -position to the silicon atom are closely. The trigonal bipyramidal (TBP) character  $\eta_e$  of the silicon atom is 91.7%. It is interesting to note that, in the crystal of compounds **3** and **5** each cation ( $[\text{DBUCH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3 \text{N}]^+$  or  $[\text{DBUME}]^+$ , respectively) is surrounded by four anions BPh<sub>4</sub>.

#### 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.

#### CRediT authorship contribution statement

**B.A. Gostevskii:** Investigation, Methodology. **A.I. Albanov:** Investigation, Methodology. **A.V. Vaschenko:** Investigation, Method-

ology. **M.S. Molokeev:** Investigation, Writing – original draft. **N.F. Lazareva:** Conceptualization, Writing – original draft.

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#### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.molstruc.2022.132896](https://doi.org/10.1016/j.molstruc.2022.132896).

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