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Crystal and molecular structures of *Si*-(iodomethyl)silatranes with methyl substituents in β-position relative to the nitrogen atom

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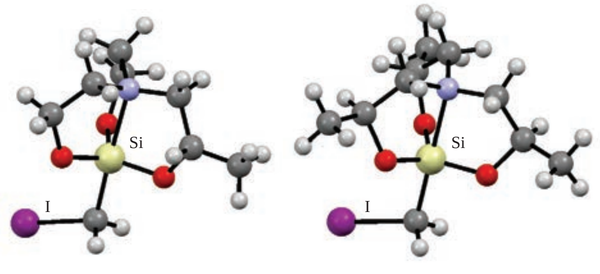
Crystal and molecular structures of two silatranes, 1-iodomethyl-3-methyl- and 1-iodomethyl-3,7,10-trimethyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecanes, were determined by X-ray analysis. Comparison of their structural and geometrical characteristics with those of other silatranes shows that the presence of methyl substituents β-positioned to nitrogen atoms increases the length of the dative Si←N bond, whereas the introduction of iodine into the axial position of the silatrane slightly decreases the length of the Si←N bond.

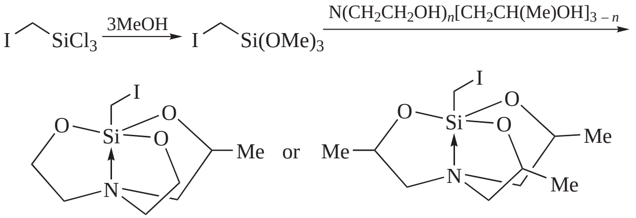


Silatranes, including those halogenated on the silicon atom, possess different types of biological activity.[1,2] 1-(4-Chlorophenyl)silatrane exhibits a high toxicity and can be used as zoocide.[1] 1-(Chloromethyl)silatrane has revealed a stimulating effect on the biosynthesis of collagen,[2] and preparations on its basis are widely used in medicine to solve problems of hair regeneration. Due to their structural features and broad applications, silatranes remain interesting target for researchers.[3–5]

There were no structural data on iodomethyl derivatives of silatranes prior to our previous study.[6] Meantime, the structural features of halogen-substituted silatranes,[7–9] as well as those with methyl substituents at the α- and β-positions of the silatrane core were reported.[10–12] Here, the molecular and crystal structure of 1-iodomethyl-3-methyl-silatrane **1** and 1-iodomethyl-3,7,10-trimethylsilatrane **2** were investigated and the structure-forming role of the iodine atom and methyl group in these compounds in comparison with chlorine-, fluorine-, α-methyl and β-methyl-substituted silatranes was discussed.

Silatranes **1** and **2** were obtained by reacting (iodomethyl)-trimethoxysilane with the corresponding alkanolamines in the presence of a sodium methoxide catalyst in 30 and 34% yields, respectively, according to the previously described procedure[13] (Scheme 1).[†]

The molecular structures of compounds **1** and **2** are shown in Figure 1. All five-membered rings of silatrane skeleton in molecules of **1** and **2** adopt an ‘envelope’-like conformation, the



1 **2**

Scheme 1

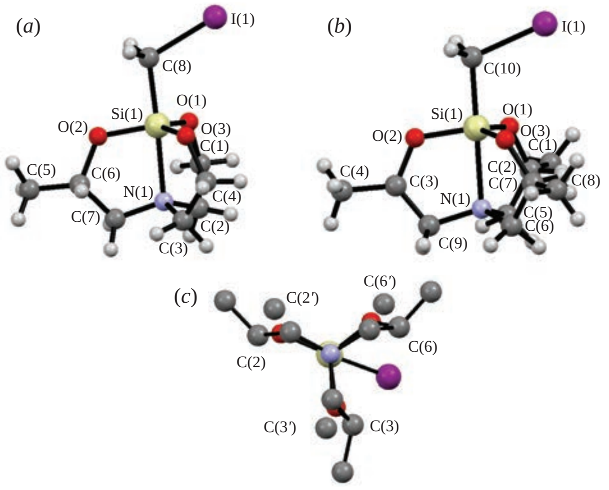
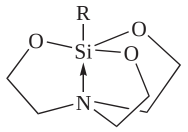


Figure 1 Molecular structures of silatranes (*a*) **1** and (*b*), (*c*) **2**. Selected bond lengths (Å) and angles (º): for **1**: I(1)–C(8) 2.153(4), C(8)–Si(1) 1.903(4), Si(1)–O(2) 1.665(3), O(2)–C(6) 1.431(6), C(6)–C(5) 1.412(7), C(6)–C(7) 1.445(7), C(7)–N(1) 1.448(6), N(1)–Si(1) 2.130(3); I(1)–C(8)–Si(1) 114.7(2), C(8)–Si(1)–O(2) 93.5(2), C(8)–Si(1)–N(1) 177.6(2); for **2**: I(1)–C(10) 2.151(4), C(10)–Si(1) 1.900(4), Si(1)–O(2) 1.647(3), O(2)–C(3) 1.476(8), C(3)–C(4) 1.503(8), C(3)–C(9) 1.490(8), C(9)–N(1) 1.466(5), N(1)–Si(1) 2.163(3); I(1)–C(10)–Si(1) 111.0(2), C(10)–Si(1)–O(2) 96.9(2), C(10)–Si(1)–N(1) 179.2(2).

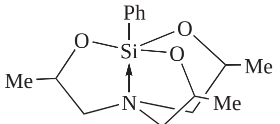
[†] IR spectra were measured on a Varian 3100 spectrometer in KBr. The ^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded in $CDCl_3$ at room temperature on Bruker DPX-400 and AV-400 spectrometers (400.13, 100.61, 79.46 MHz, respectively). Chemical shifts were referred to TMS.

Compound **1** was synthesized by the reaction of (iodomethyl)trimethoxysilane with diethanolisopropanolamine.[13] IR (ν/cm^{-1}): 2972, 2926, 2875, 1458, 1383, 1271, 1095, 1005, 797, 702, 557. ^{1}H NMR δ: 1.22 (d, 3H, Me, ^{3}J 6.1 Hz), 1.88 (s, 2H, ICH_2), 2.31, 2.89 (dd, 1H, NCH_2CH_2, ^{2}J 12.0 Hz, ^{3}J 11.3 and 4.0 Hz), 2.86 (m, 4H, NCH_2CH_2), 3.75–3.87 (m, 4H, carbon atoms α-positioned to the nitrogen atom occupy the 'flap' sites, which is typical of silatranes.[3,4,11] The carbon atoms C^2, C^3 and C^6 in the silatranyl fragment of compound **2** are disordered, the population of the positions is 0.58 : 0.42 [Figure 1(*c*)].‡

To analyze the geometric characteristics of silatranes **1** and **2**, we compared them with those of analogous compounds: 1-(iodomethyl)silatrane **3**,[6] 1-(chloromethyl)silatrane **4**,[7] 1-(dichloromethyl)silatrane **5**,[8] 1-(trifluoromethyl)silatrane **6**,[9] 1-methylsilatrane **7**,[10] 1-phenyl-3,7,10-trimethylsilatrane **8**[11] and tetramethylsilatrane **9**.[12] Characteristic bond lengths and angles of silatranes **1**–**9** are given in Table 1.



3 R = CH_2I
4 R = CH_2Cl
5 R = $CHCl_2$
6 R = CF_3
7 R = Me



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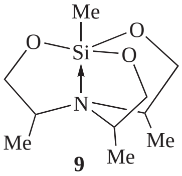

9

The length of the transannular bond Si$\leftarrow$N in the molecule of compound **4** (2.120 Å)[7] is reduced in comparison with compound **7** (2.174 Å),[10] which is due to the electron-withdrawing properties of the chloromethyl group. For dichloromethyl derivative **5**, this distance is even smaller and is 2.063 Å,[8] and for trifluoromethyl derivative **6** is 2.024 Å.[9] In the molecules of 1-(iodomethyl)- and 1-(iodopropyl)silatranes,[6] the lengths of the coordination bond Si$\leftarrow$N are 2.118 and 2.162 Å, respectively. Thus, the introduction of halogen into the axial position of the silatrane decreases the length of the Si$\leftarrow$N bond; the higher the electronegativity of the halogen atom and the larger the number of these atoms the stronger this decrease. The introduction of electron-donor methyl substituents into the equatorial position, on the contrary, causes elongation of this distance. Thus, comparison between silatranes **1**, **2** and **3** indicates that the length of the Si$\leftarrow$N bond in these compounds increases with raising number of β-methyl groups.

Table 1 Geometrical characteristics of silatranes **1**–**9**.

Silatrane	Si–N/Å	Si–C/Å	C–Si–N/deg
1	2.130	1.903	177.6
2	2.163	1.900	179.2
3	2.118	1.897	176.0
4	2.111	1.921	176.2
5	2.063	1.926	176.4
6	2.024	1.946	179.5
7	2.160	1.880	180.0
8	2.164	1.890	178.7
9	2.325	1.872	178.5

It can be seen from Table 1 that the Si–C bond lengths in halogen-substituted silatranes **1**–**6** are 0.007–0.074 Å longer than those in silatranes **7**–**9**.

In silatrane molecules, the C–Si–N angle is almost 180°, the greatest deviation from this angle is observed in structures **3**–**5** (176°). This deviation is due to the presence of substituents that affect the distribution of the electron density in the molecule and, consequently, its structure. The iodomethyl, chloromethyl and dichloromethyl groups distort the symmetry of the molecule, affecting the silatranyl core, while the CF_3 group is similar to the methyl group and almost does not influence the symmetry of the molecule.

We did not find structures similar to silatrane **1** with one substituent in the β-position in CCDC database. For silatrane **2**, such an isostructural analogue was 1-phenyl-3,7,10-trimethylsilatane **8**.[11] Their geometric characteristics are very close (see Table 1), despite of the differences in the substituent at the silicon atom. In contrast to compound **8** which can form two types of diastereomers,[11] silatrane **2** exists in the crystal only in a form of asymmetric diastereomer [see Figure 1(*c*)]. In the substituted five-membered rings of compound **2**, the methyl groups occupy the axial positions.

Comparison between the structures of tetramethylsilatrane **9**[12] with methyl substituents in the α-position and unsubstituted methylsilatrane **7**[10] shows that in these molecules the lengths of all bonds in five-membered heterocycles are close, and coordination bond Si$\leftarrow$N lengths are 2.325 and 2.160 Å, respectively. Therefore, the presence of the Me group in the α-position has a more significant effect on the Si$\leftarrow$N bond length than the Me group in the β-position.

In the crystal packing of silatranes **1** and **2**, the intermolecular distance I···I is 3.832 and 3.687 Å, respectively (Figure 2). These values are approximately 0.2–0.4 Å shorter than the sum of the Van der Waals radii.[15] Such an I···I-contact can be attributed to

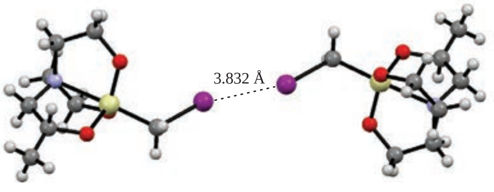

Figure 2 I···I interactions in crystal packing of compound **1**.

OCH_2), 3.99 (m, 1H, OC*H*Me). ^{13}C NMR δ: –12.43 (ICH_2Si), 20.36 (Me), 51.50, 52.06 (NCH_2CH_2), 57.41, 57.47 (OCH_2), 58.01 (NCH_2CH), 63.42 (OCH). ^{29}Si NMR δ: –80.37. Found (%): C, 29.46; H, 5.07; Si, 7.69; I, 38.60. Calc. for $C_8H_{16}INO_3Si$ (%): C, 29.19; H, 4.90; Si, 8.53; I, 38.61.

Compound **2** was synthesized by the reaction of (iodomethyl)trimethoxysilane with triisopropanolamine and MeONa additive as described in ref. 13. IR (ν/cm^{-1}): 2974, 2928, 2880, 1455, 1378, 1332, 1264, 1146, 1109, 1058, 972, 880, 799, 696, 547. ^1H NMR δ: 1.19, 1.20, 1.21, 1.28 (d, Me, ^3J 6.0 and 6.6 Hz), 2.29, 2.89 (dd, CH_2N, ^2J 12.2 Hz, ^3J 12 and 3.9 Hz), 2.35, 2.92 (dd, CH_2N, ^2J 12.4 Hz, ^3J 12 and 3.9 Hz), 2.74, 2.98 (dd, CH_2N, ^2J 13.2 Hz, ^3J 6.7 and 4.7 Hz), 1.89, 1.91 (s, ICH_2Si), 3.95, 4.18 (m, OCH). ^{13}C NMR δ: –11.49, –11.43 (ICH_2Si), 20.27, 20.42, 20.45, 23.38 (Me), 58.87, 60.97, 61.72, 64.82 (NCH_2), 63.19, 64.53, 64.63, 66.21 (OCH). ^{29}Si NMR δ: –79.81, –82.01, –82.04. Found (%): C, 33.70; H, 5.57; Si, 8.02; I, 35.12. Calc. for $C_{10}H_{20}INO_3Si$ (%): C, 33.62; H, 5.64; Si, 7.86; I, 35.52.

‡ Crystals of compounds **1** and **2** suitable for single crystal X-ray structural analysis were grown from 2 : 1 heptane–chloroform mixture (**1**), heptane (**2**). X-ray analysis data were obtained on a Bruker D8 Venture diffractometer with MoKα-radiation (λ = 0.71073) using the φ and ω scans. The structures were solved and refined by direct methods using the SHELX programs set.[14] Data were corrected for absorption effects using the multi-scan method (SADABS). Non-hydrogen atoms were refined anisotropically using SHELX.[14]

Crystal data for **1**: $C_8H_{16}INO_3Si$ (M_r = 329.14), colourless plate (0.17×0.19×0.46 mm), monoclinic. space group $P2_1/n$, a = 8.2895(6), b = 15.4002(11) and c = 9.3646(7) Å, β = 102.892(2)°, V = 1165.3(5) Å^3, Z = 4, T = 296 K, μ(MoKα) = 2.833 mm^{-1}, d_{calc} = 1.876 g cm^{-3}, 35076 reflections collected and 3042 independent reflections, 127 refined parameters, S = 1.079, final R factor is 4.27 (R_{int} = 0.0904).

Crystal data for **2**: $C_{10}H_{20}INO_3Si$ (M_r = 356.25), yellow plate (0.15×0.30×0.50 mm), orthorhombic, space group $Pbca$, a = 17.3133(13), b = 8.4960(5) and c = 19.3028(12) Å, V = 2839.3(3) Å^3, Z = 8, T = 100 K, μ(MoKα) = 2.334 mm^{-1}, d_{calc} = 1.667 g cm^{-3}, 199247 reflections collected and 3029 independent reflections, 176 refined parameters, S = 1.063, final R factor is 4.57 (R_{int} = 0.1048).

CCDC 1438786 and 1438787 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

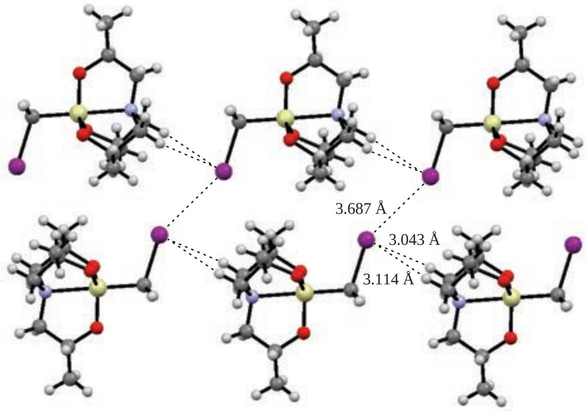

Figure 3 Fragment of crystal packing of compound **2**.

type I of Van der Waals interactions.[16,17] In silatrane **2**, the iodine atoms interact with the hydrogen atoms of the silatranyl fragment of neighboring molecules, the bond lengths I···H are 3.043 and 3.114 Å (Figure 3).

Thus, analysis of X-ray data for compounds **1** and **2** demonstrates that the introduction of iodine atom into the axial position of the silatrane slightly decreases the length of the Si←N bond, whereas the presence of β-methyl substituents increases it. In the crystal, molecules of compound **1** are nearly symmetric, distorted by the methyl substituent, while molecules of compound **2** are asymmetric.

All measurements were performed using the equipment of the Baikal Center for Collective Use of the Siberian Branch of the Russian Academy of Sciences.

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