

Synthesis and structure of 1,6-diaza-2,2-dimethoxy-2-silacyclooctane¹

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Abstract

1,4-Diaza-8,8,8-trimethoxy-8-silaoctane (**1**) loses methanol upon heating and gives an eight-membered silatrane-like silaheterocycle, 1,6-diaza-2,2-dimethoxy-2-silacyclooctane (**2**).

Keywords: Silicon; Silatrane; Hypercoordination

1. Introduction

High coordination numbers (larger than four) are nowadays a well established and thoroughly investigated feature in silicon chemistry. From the multitude of reviews, just one from a major contributor to this field of research, R.J.P. Corriu, need be cited [1]. Silatrane as a special class of higher coordinated silicon compounds have also been reviewed [2]. In this connection we were interested in cyclic silicon compounds with intramolecular pendant nitrogen donors [3]. Speier et al. [4] had described the synthesis of 1-aza-1-(2'-aminoethyl)-2-silacyclopentanes, and they appeared to be likely candidates for our aims. Our reinvestigation showed the structure assignment in Ref. [4] to be erroneous.

2. Synthesis and analysis

The synthesis of the "2/3-silatrane" **2** was carried out by the procedure described in Ref. [4] (Scheme 1).

The open-chain compound **1** was isolated by vacuum distillation as a colourless, slightly viscous liquid. When

1 was heated to reflux, methanol formed and ring-closure took place. **2** was distilled in vacuo, and solidified to a colourless, quite moisture sensitive solid. It was still contaminated by **1**, but could be purified by several recrystallizations from ether.

The composition of **1** and **2** was confirmed by mass spectrometry, elemental analysis (**1**) and NMR spectroscopy. While ¹H and ¹³C NMR spectroscopy showed no remarkable features, the ²⁹Si and ¹⁵N NMR spectra gave more information. The prominent feature in the ⁵⁰Si NMR spectra was the upfield shift of the resonances, from $\delta -41.7$ to -67.8 ppm, on going from **1** to **2**; this is due to the donor coordination of the "free" nitrogen centre to the silicon atom. Further confirmation was provided by the additional shift, to -75.8 ppm, when the sample was cooled to -80°C . The changes in the ¹⁵N NMR shifts (from $-248.2/-265.5$ to $-239.9/-258.3$ ppm) were not so marked, but the $\Delta\delta$ value remained the same (18.3 vs. 17.3 ppm), i.e. both nitrogen atoms were affected in the same way regardless of whether they were covalently bound or simply acting as donors to silicon. The data overall could be regarded as consistent with the structure assignment of Speier et al. [4], a 1-aza-2(2'-aminoethyl)-2-silacyclopentane.

3. Structure

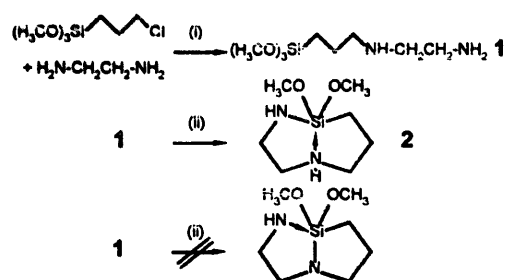
Compound **2** crystallizes as a colourless single crystalline prism from diethyl ether solution provided it is free of **1**. The unambiguous determination of its structure was made by a single-crystal X-ray diffraction

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¹ Dedicated to Professor Robert Corriu in recognition of his outstanding contributions to organosilicon chemistry.

² Crystal structure determination.

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Scheme 1. Reaction conditions: (i) reflux, five-fold excess $(\text{H}_2\text{N}-\text{CH}_2\text{CH}_2)_2$, $(\text{H}_2\text{N}-\text{CH}_2)_2\text{HCl}$, 90% yield; (ii) reflux, $-\text{MeOH}$.

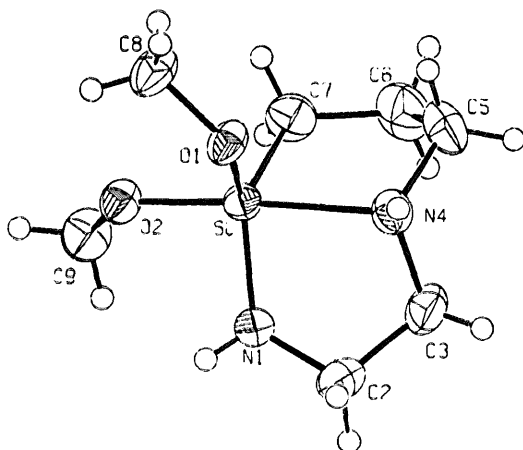


Fig. 1. PLATON drawing with ellipsoids at 50% probability level and numbering scheme of the silaheterocycle 2.

study, which showed that 2 is a 1,6-diaza-2-silacyclooctane and not that proposed by Speier et al. [4] (Fig. 1, Tables 1 and 2).

In 2 the silicon atom is pentacoordinate; the distance between the donor nitrogen and silicon (2.13 \AA) is within the normal range for such interactions [5]. The coordination geometry is not quite trigonal bipyramidal.

Table 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) of the silaheterocycle *cyclo*-($\text{NH}-\text{CH}_2\text{CH}_2-\text{NH}-\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_2$) (2)

Atom	x	y	z	U_{eq}
C(2)	849(2)	7860(2)	3837(1)	43(1)
C(3)	-81(2)	6403(2)	3579(1)	46(1)
C(5)	-542(2)	4771(2)	2185(2)	51(1)
C(6)	-1923(3)	5684(3)	1602(2)	59(1)
C(7)	-1113(2)	7029(2)	1191(1)	45(1)
C(8)	3321(3)	7114(2)	855(1)	47(1)
C(9)	-52(3)	10558(2)	1197(1)	47(1)
N(1)	903(2)	8643(2)	2976(1)	36(1)
N(4)	585(2)	5840(1)	2756(1)	35(1)
O(1)	2620(1)	6902(1)	1681(1)	35(1)
O(2)	1169(1)	9386(1)	1325(1)	35(1)
Si	871(1)	7769(1)	1927(1)	28(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2

Selected bond lengths (\AA) and angles ($^\circ$) for 2

C(7)–Si	1.891(2)	C(5)–N(4)–H(4)	108.4(13)
N(1)–Si	1.7146(13)	Si–N(4)–H(4)	111.3(13)
N(4)–Si	2.1261(13)	O(1)–Si–N(1)	119.62(6)
O(1)–Si	1.6715(10)	O(1)–Si–O(2)	95.34(5)
O(2)–Si	1.7154(11)	N(1)–Si–O(2)	95.48(6)
		O(1)–Si–C(7)	111.64(8)
C(2)–N(1)–Si	124.33(11)	N(1)–Si–C(7)	124.62(8)
C(2)–N(1)–H(1)	116(2)	O(2)–Si–C(7)	99.43(7)
Si–N(1)–H(1)	118(2)	O(1)–Si–N(4)	85.04(5)
C(3)–N(4)–C(5)	114.80(14)	N(1)–Si–N(4)	80.94(6)
C(3)–N(4)–Si	105.89(10)	O(2)–Si–N(4)	176.04(5)
C(5)–N(4)–Si	107.43(11)	C(7)–Si–N(4)	84.06(7)
C(3)–N(4)–H(4)	109.0(13)		

The angles from N4 to the equatorial atoms (N1, O1, C7) are less than 90° , while those from the "O2-side" are larger. The angles in the equatorial plane range from 111.6 to 124.6° and reflect the restrictions imposed by the eight-membered ring. The coordinated N4 has a distorted tetrahedral geometry, whereas N1 is nearly planar ($\Sigma \angle = 358^\circ$), as is expected for a silicon-bound nitrogen atom. The donor coordination makes the trans Si–O slightly longer than the equatorial Si–O bond

Table 3

Crystal data and structure refinement for 2

Empirical formula	$\text{C}_7\text{H}_{18}\text{N}_2\text{O}_2\text{Si}$
Formula weight	190.36
Temperature (K)	230
Wavelength (\AA)	0.71069
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 7.944(2) \text{ \AA}$ $\alpha = 90^\circ$ $b = 8.8600(8) \text{ \AA}$ $\beta = 98.336(10)^\circ$ $c = 14.6054(12) \text{ \AA}$ $\gamma = 90^\circ$
Volume (\AA^3)	1017.1(2)
Z	4
Density (calc.) (Mg m^{-3})	1.243
Absorption coefficient	0.158 mm^{-1}
$F(000)$	416
Crystal size (mm^3)	$1.33 \times 0.95 \times 0.57$
θ range for data collection	2.70 to 27.51°
Index ranges	$-10 \leq h \leq 10$, $0 \leq k \leq 11$, $-18 \leq l \leq 18$
Reflections collected	4847
Independent reflections	2342 [$R_i = 0.0209$]
Absorption correction	Semi-empirical from ψ -scans
Max. and min. transmission	0.98 and 0.85
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2342/0/182
Goodness-of-fit on F^2	1.048
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0365$, $wR_2 = 0.1065$ (2077 reflections)
R indices (all data)	$R_1 = 0.0415$, $wR_2 = 0.1102$
Extinction coefficient	0.006(3)
Largest difference peak and hole $e \text{ \AA}^{-3}$	0.331 and -0.263

(Si–O1 1.67, Si–O2 1.72 Å). There are no intermolecular interactions.

4. Conclusion

The ring-closure of 1,6-diaza-2,2-dimethoxy-2-silaoctane (**1**) with loss of methanol led exclusively to an eight-membered ring system with a silatrane-like structure (**2**), and not, as previously concluded in Ref. [4], to a five-membered ring species. Obviously the larger degree of flexibility in the pseudo-bicyclic system **2** is responsible for this behaviour. Alternative ways of making compounds of the five-membered ring type must be sought.

5. Experimental section

Compounds **1** and **2** were prepared analogously as previously described [4]. Since **2** is moisture sensitive its manipulation must be carried out under dry nitrogen, using standard Schlenk procedures. Solvents were pre-dried and freshly distilled from Na/K. **1** gave a correct elemental analysis, **2** proved to be too moisture sensitive. Mass spectra were obtained on a HP5995B spectrometer (EI) or a GC/MS couple (Chrompack CP 9000, 10m CP-Sil-5CB-MS; Finnigan ITD 800, CI). NMR spectra were performed on Bruker AM300 and DPX300 spectrometers.

5.1. 1,4-Diaza-8,8,8-trimethoxy-8-silaoctane (**1**)

^1H NMR (300 MHz, CDCl_3 , 20°C): δ (ppm) 0.37–0.43 (m, 2H; Si– CH_2), 0.88 (s, br, 3H; NH), 1.30–1.36 (m, 2H; CH_2), 2.33–2.41 (m, 2H; CH_2), 2.50–2.55 (m, 2H; CH_2), 3.30 (s, 9H; OCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3 , 20°C): δ (ppm) 6.22 (s; Si– CH_2), 22.75, 41.45, 49.96 (s; CH_2), 52.02 (s, O– CH_3). $^{29}\text{Si}\{^1\text{H}\}$ NMR (59.6 MHz, CDCl_3 , 20°C): δ (ppm) –41.65. $^{15}\text{N}\{^1\text{H}\}$ NMR (30.4 MHz, CDCl_3 , 20°C): δ (ppm) –248.2, –265.5. MS (CI): m/z (%) 223 (100) [$\text{M}^+ + 1$], 153 (29), 137 (26), 121 (68).

5.2. 1,6-Diaza-2,2-dimethoxy-2-silacyclooctane (**2**)

^1H NMR (300 MHz, CDCl_3 , 20°C): δ (ppm) 0.42 (t, 2H; $J(\text{H,H}) = 7.3$ Hz; Si– CH_2), 0.99 (s, br, 1H; NH), 1.40 ('quin', 2H; $J(\text{H,H}) = 6.5$ Hz; Si– CH_2 – CH_2), 2.06 (s, br, 1H; NH), 2.31 ('q', 2H; $J(\text{H,H}) = 6.2$ Hz;

Si– CH_2 – CH_2 – CH_2), 2.53 ('q', 2H; $J(\text{H,H}) = 5.7$ Hz; N– CH_2), 2.76 ('q', 2H; $J(\text{H,H}) = 5.9$ Hz; N– CH_2), 3.20 (s, 6H; CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3 , 20°C): δ (ppm) 8.31 (s, Si– CH_2 ; $^1J(\text{Si,C}) = 99.3$ Hz), 22.58, 38.79, 44.99, 45.06 (s, CH_2), 49.77 $^{29}\text{Si}\{^1\text{H}\}$ NMR (59.6 MHz, CDCl_3 , 20°C): δ (ppm) –67.8 (20°C), –75.8 (–80°C). $^{15}\text{N}\{^1\text{H}\}$ NMR (30.4 MHz, CDCl_3 , 20°C): δ (ppm) –239.98, –258.26. MS (EI): m/z (%) 192 (21) [$\text{M}^+ + 2$], 160 (100), 130 (44), 121 (18), 91 (19), 44 (30).

5.3. Crystal structure determination of **2**

A colourless, prismatic crystal of **2** was selected and mounted on an automatic four circle diffractometer (STADI-4, Stoe). Data was collected using the ω – θ scan method, and were corrected for Lorentz, polarization and absorption. The structure was solved by direct methods [6] and refined by full-matrix least-squares. All hydrogen atoms were located in difference Fourier maps and refined isotropically [7]. 25 reflections from the θ range 14 to 18° were chosen for the least-squares unit cell refinement. For further details see Table 3.

6. Supplementary material available

A complete list of bond distances and angles, and tables of anisotropic displacement and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

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