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Selective synthesis of eight-membered siloxane rings with different substituents on the silicon atoms

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Abstract

The selective synthesis of eight-membered silicon-oxygen rings of the general formula $(R_2Si)_2(R'_2Si)_2O_4$ can be achieved using the auxiliary reagent hexabutyldistannoxane. In a first step, the cycles $[CH_2-N(R)]_2SiCl_2$ [$R = tBu$ (**1**), Ph (**2**)] are reacted with the double molar amount of hexabutyldistannoxane to form $[CH_2-N(R)]_2Si(OSnBu_3)_2$ **3** ($R = tBu$) and **4** ($R = Ph$). The syntheses are carried out without any solvent. The distannoxosilanes **3** and **4** are transformed to the eight-membered siloxane rings $(R_2Si)_2(R'_2Si)_2O_4$ $\{R_2 = [CH_2-N(tBu)]_2, R' = Cl$ (**5a**), $R_2 = [CH_2-N(tBu)]_2, R' = Br$ (**5b**), $R_2 = [CH_2-N(Ph)]_2, R' = Me$ (**6**) $\}$ using either $SiCl_4$, $SiBr_4$ or Cl_2SiMe_2 as reactants at ambient temperature. The selective cleavage of the silicon–nitrogen bonds in **6** by addition of a solution of HCl in tetrahydrofuran leads to the chloro- and methyl-substituted cyclotetrasiloxane $(Me_2Si)_2(Cl_2Si)_2O_4$ (**7**). The new cyclotetrasiloxanes **5–7** have been characterised by spectroscopic methods as well as by single crystal X-ray analyses, revealing Si_4O_4 eight-membered cycles with different substituents on the silicon atoms. Depending on the substitution pattern at silicon atoms, varying Si–O bonds and angle are found. *To cite this article: M. Veith et al., C. R. Chimie 6 (2003) 117–124.*

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Résumé

Des cycles à huit chaînons Si_4O_4 , de formule générale $(R_2Si)_2(R'_2Si)_2O_4$, sont obtenus par un processus qui utilise comme réactif l'hexabutyldistannoxane. Dans une première étape, les cycles $[CH_2-N(R)]_2SiCl_2$ [$R = tBu$ (**1**), Ph (**2**)] sont transformés en $[CH_2-N(R)]_2Si(OSnBu_3)_2$ **3** ($R = tBu$) et **4** ($R = Ph$). Les synthèses ont lieu en l'absence de solvant. Les distannoxosilanes **3** et **4** servent de produits de départ pour les cycles $(R_2Si)_2(R'_2Si)_2O_4$ $\{R_2 = [CH_2-N(tBu)]_2, R' = Cl$ (**5a**), $R_2 = [CH_2-N(tBu)]_2, R' = Br$ (**5b**), $R_2 = [CH_2-N(Ph)]_2, R' = Me$ (**6**) $\}$ en les faisant réagir avec $SiCl_4$, $SiBr_4$ ou Cl_2SiMe_2 , à température ambiante. L'ouverture de la liaison Si–N dans le composé **6** se fait par réaction avec une solution de HCl dans le tétrahydrofurane ; le produit obtenu est le cyclotétrasiloxane $(Me_2Si)_2(Cl_2Si)_2O_4$ (**7**), un composé qui contient des atomes de silicium substitués par différents groupes. Les nouveaux cyclotétrasiloxanes **5–7** sont caractérisés par spectrométrie et les structures sont déterminées par diffraction des rayons X. Ils présentent tous des cycles Si_4O_4 à huit chaînons, avec différents substituants sur les atomes de silicium. Les structures des cycles varient fortement selon les substituants. *Pour citer cet article : M. Veith et al., C. R. Chimie 6 (2003) 117–124.*

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Keywords: cyclosiloxanes; siloxanes; methyl(amino)cyclosiloxanes; chloro(amino)cyclosiloxanes; bromo(amino)cyclosiloxanes; methyl(chloro)cyclosiloxanes; X-ray structure analyses

Mots clés : cyclosiloxanes ; siloxanes ; méthyl(amino)cyclosiloxanes ; chloro(amino)cyclosiloxanes ; bromo(amino)cyclosiloxanes ; méthyl(chloro)cyclosiloxanes ; structures aux rayons X

1. Introduction

Cyclosiloxanes with organic groups attached to the silicon atoms may serve as starting materials for linear polysiloxanes using an opening reaction of the Si_nO_n rings [1]. These materials, known as silicones, have a wide range of applications in industry. The substituents at silicon besides the chain lengths determine the physical and chemical properties of silicones [2]. We were interested to synthesise by a versatile step-by-step route Si_nO_n cycles with inorganic substituents at silicon presenting different centres of reactivity to facilitate an exchange with other chemical groups. In contrast to a considerable number of reports on cyclosiloxanes with organic groups, such inorganic representatives are rare [3–5].

We have recently described the selective syntheses of amino- and chloro-substituted cyclotrisiloxanes [6–8]. These six-membered ring compounds are obtained either by salt elimination reactions [6] or by ClSnR_3 elimination between dichlorodiaminosilanes and hexaorganostannoxane [7, 8]. The transfer of this approach to eight-membered Si_4O_4 rings with different substituents on the silicon atoms is discussed in this paper.

2. Experimental

2.1. Methods and materials

Preparation and handling of the compounds described below was performed under exclusion of air and moisture in a nitrogen atmosphere. All solvents were dried with the appropriate drying agents and distilled prior to use. Elemental analyses (C, H, N) were performed on a LECO CHN 900 Elemental Analyzer. The NMR (^1H , ^{13}C , and ^{29}Si) spectra were recorded on Bruker AC-200 and AM-400 spectrometers and referenced relative to TMS. Samples were run at room temperatures using C_6D_6 as lock solvent. The educts **1** [9], **2** [9] and hexabutyldistannoxane [10] were prepared according to published procedures.

2.2. Syntheses

2.2.1. $[(\text{CH}_2)_2\text{N}_2(\text{tBu})_2]\text{Si}(\text{OSnBu}_3)_2$ (**3**)

To 3.5 g (13.0 mmol) $[\text{CH}_2\text{-N}(\text{tBu})]_2\text{SiCl}_2$ (**1**) 13.24 ml (26.0 mmol) hexabutyldistannoxane was added in pure form. The liquid reaction mixture was stirred and heated up to 180 °C for 12 h. Even longer heating does not alter the equilibrium between the educts and products that is reached at this stage. The unreacted starting compounds as well as chlorotributylstannane formed as a by-product are removed by distillation at 10^{-3} atm. The product **3** is found in the residue and can be used without further purification, or can be distilled at 220 °C/ 10^{-3} atm using a column. Yield 9.01 g (60%) as viscous colourless liquid. (Found: C, 50.65; H, 9.24; N, 3.20. Calc. for $\text{C}_{34}\text{H}_{76}\text{N}_2\text{O}_2\text{SiSn}_2$: C, 50.39; H, 9.45; N, 3.46%). ^1H NMR (benzene): δ (ppm) 0.88–1.65 (m, 54 H, SnBu_3), 1.31 (s, 18 H, N^tBu) and 5.62 (s, 4 H, $(\text{CH}_2)_2$). ^{13}C NMR (benzene): δ (ppm) 14.0 (s, 6 C, $\text{Sn}(\text{CH}_2)_3\text{C H}_3$), 16.0 (s, 6 C, $\text{Sn}(\text{C H}_2)_3\text{CH}_3$), 27.8 (s, 6 C, $\text{Sn}(\text{C H}_2)_3\text{CH}_3$), 28.6 (s, 6 C, $\text{Sn}(\text{C H}_2)_3\text{CH}_3$), 31.2 (s, 6 C, $\text{C}(\text{C H}_3)_3$), 42.3 (s, 4 C, $(\text{CH}_2)_2$) and 50.8 (s, 2 C, $\text{C}(\text{CH}_3)_3$). ^{29}Si NMR (benzene): δ (ppm) – 56.6.

2.2.2. $[(\text{CH}_2)_2\text{N}_2(\text{Ph})_2]\text{Si}(\text{OSnBu}_3)_2$ (**4**)

To 3.5 g (11.32 mmol) $[\text{CH}_2\text{-N}(\text{Ph})]_2\text{SiCl}_2$ (**2**) 11.53 ml (22.64 mmol) hexabutyldistannoxane was added under strong stirring, the resulting liquid showing an increase in temperature. Stirring was continued for 60 min, followed by distillation at 80 °C of the formed chlorotributylstannane under reduced pressure (10^{-3} atm). The residue is pure compound **4**, which is obtained as an oily clear liquid (yield 9.61 g (99%)). (Found: C, 53.60; H, 8.48; N, 3.05. Calc. for $\text{C}_{38}\text{H}_{68}\text{N}_2\text{O}_2\text{SiSn}_2$: C, 53.67; H, 8.06; N, 3.29%). ^1H NMR (benzene): δ (ppm) 0.81–1.48 (m, 54 H, SnBu_3), 3.30 (s, 4 H, $(\text{CH}_2)_2$) and 6.78–7.34 (m, 20H, H_{aromat}). ^{13}C NMR (benzene): δ (ppm) 13.9 (s, 6 C, $\text{Sn}(\text{CH}_2)_3\text{C H}_3$), 16.1 (s, 6 C, $\text{Sn}(\text{C H}_2)_3\text{CH}_3$), 27.6 (s, 6 C, $\text{Sn}(\text{C H}_2)_3\text{CH}_3$), 27.9 (s, 6 C, $\text{Sn}(\text{C H}_2)_3\text{CH}_3$), 42.7 (s, 2 C,

(CH₂)₂), 114.9 (s, 4C, C_{ortho}), 117.5 (s, 2C, C_{para}), 129.2 (s, 4C, C_{meta}) and 148.6 (s, 2C, C_{ipso}). ²⁹Si NMR (benzene): δ (ppm) – 62.3.

2.2.3. Syntheses of **5a**, **5b** and **6**

To a solution of 8.95 g (11.02 mmol) **3** or 7.24 g (11.02 mmol) **4** in 25 ml diethylether, the equimolar amount of the respective SiX₄ [X = Cl (1.26 ml), Br (1.37 ml), see below] or dimethyldichlorsilane (1.33 ml) is added dropwise. After a few minutes, the white solids **5a** or **5b** begin to precipitate. Stirring is continued for 5 h. In the case of compound **6**, the solution is stirred for 12 h. The precipitate is separated from the solution by filtration, is washed with small amounts of cold diethylether and finally dried under reduced pressure to give a white powder.

2.2.3.1. $\{[(CH_2)_2N_2(tBu)_2]SiO(Cl)_2SiO\}_2$ (**5a**); $\{[(CH_2)_2N_2(tBu)_2]SiO(Br)_2SiO\}_2$ (**5b**). **5a**: Yield 1.63 g (45%) white powder, m.p. 215 °C (dec.). (Found: C, 36.29; H, 6.45; N, 8.10. Calc. for C₂₀H₄₄Cl₄N₄O₄Si₄: C, 36.47; H, 6.73; N, 8.51%). ¹H NMR (benzene): δ (ppm) 1.09 (s, 36 H, C(C H₃)₃) and 2.84 (s, 8 H, (C H₂)₂). ¹³C NMR (benzene): δ (ppm) 29.1 (s, 12 C, C(C H₃)₃), 41.1 (s, 4 C, (C H₂)₂) and 50.9 (s, 4 C, C(CH₃)₃). **5b**: Yield 1.84 g (40%) white powder of m.p. 240 °C (dec.) (Found: C, 25.81; H, 5.35; N, 6.03%. Calc. for C₂₀H₄₄Br₄N₄O₄Si₄: C, 28.72; H, 5.30; N, 6.69%). ¹H NMR (benzene): δ (ppm) 1.11 (s, 36 H, C(CH₃)₃) and 2.86 (s, 8 H, (CH₂)₂). ¹³C NMR (benzene): δ (ppm) 29.3 (s, 12 C, C(CH₃)₃), 41.2 (s, 4 C, (C H₂)₂) and 51.1 (s, 4 C, C(CH₃)₃). The poor solubility of **5a** and **5b** hampered the registration of the ²⁹Si-NMR spectra.

2.2.3.2. $\{[(CH_2)_2N_2Ph_2]SiO(Me)_2SiO\}_2$ (**6**). Yield 3.04 g (42%) white powder of m.p. > 280 °C. (Found: C, 58.28; H, 6.00; N, 8.33. Calc. for C₃₂H₄₀N₄O₄Si₄: C, 58.49; H, 6.14; N, 8.53%). ¹H NMR (THF): δ (ppm) –0.51 (s, 12 H, Si(CH₃)₂), 2.91 (s, 8 H, (CH₂)₂) and 6.40–6.97 (m, 20 H, H_{aromat}); ¹³C NMR (benzene): δ (ppm) 0.04 (s, 4 C, Si(CH₃)₂), 42.4 (s, 4 C (CH₂)₂); 115.1 (s, 4C, C_{ortho}), 118.5 (s, 2C, C_{para}), 129.2 (s, 4C, C_{meta}) and 146.7 (s, 2C, C_{ipso}). Because of its poor solubility, the ²⁹Si-NMR spectrum of **6** could not be obtained.

2.2.4. $[(Me)_2SiO(Cl)_2SiO]_2$ (**7**)

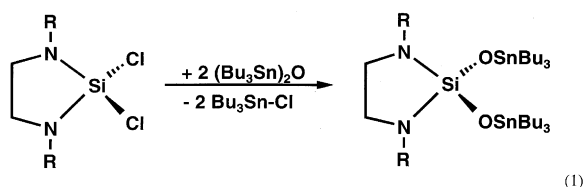
To a solution of 0.845 g (1.29 mmol) **6** in 30 ml THF 14.0 ml of a solution of HCl in THF (0.654 molar) is slowly added dropwise. The hydrochloride precipitate is separated from the solution by filtration. After removing all volatiles under reduced pressure, **7** can be sublimed from the brown oily residue. Yield 0.09 g (18%) colourless crystals of m.p. 35 °C. (Found: C, 12.56; H, 3.05%. Calc. for C₄H₁₂Cl₄O₄Si₄: C, 12.70; H, 3.20%) ¹H NMR (benzene): δ (ppm) 0.05 (s, 12 H, C H₃). ¹³C NMR (benzene): δ (ppm) –0.62 (s, 4 C, C H₃). ²⁹Si NMR (benzene): δ (ppm) –9.5 (2, Si (CH₃)₂) and –70.0 (2, Si Cl₂).

3. Results

3.1. Syntheses

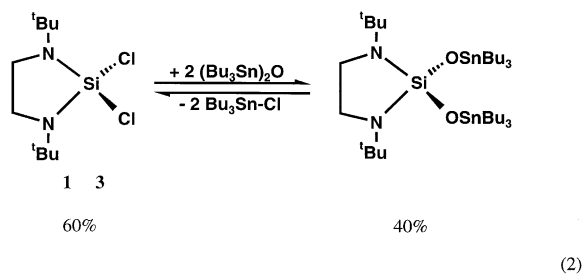
The treatment of the cyclic dichlorodiaminosilanes **1** and **2** with 2 equiv of hexaorganodistannoxane leads to the corresponding distannoxodiaminosilanes **3** and **4**, with elimination of tributylchlorostannane (equation (1)).

The reactions are run without any solvent, so that the by-product tributylchlorostannane can be removed easily by distillation. There seems to exist an influence of the steric demand of the organic substituent on the



Comp.	R
1	^t Bu
2	Ph

Comp.	R
3	^t Bu
4	Ph



nitrogen atoms on the reaction, as the chlorine substitution already occurs at room temperature with phenyl (**2**), whereas heating to 160 °C is necessary with *tert*-butyl (**1**). Also the reaction of **2** with hexabutyldistannoxane is almost quantitative, while the treatment of **1** with hexabutyldistannoxane leads to an equilibrium between **1** and the product **3** in a 60:40 ratio (equation (2)), which can be deduced from the ¹H-NMR spectrum of the solution.

The tin compounds **3** and **4** [11–14] are waxy, very viscous and colourless, and can be purified by Kugelrohr distillation at around 220 °C/10⁻³ atm. The ¹H-, ¹³C- and ²⁹Si-NMR spectra are in accord with cyclic molecules of C₂ symmetry.

The use of the functionalised molecules **3** and **4** for the synthesis of eight-membered siloxane rings is summarised in equation (3). In these reactions, the polar O–Sn bonds as well as the facile halogen transfer from silicon to tin are the driving forces for the cyclisations. The tin compounds **3** or **4** are added to the equimolar amounts of the silanes R₂SiX₂ (X = R = Cl; X = R = Br; R = CH₃, X = Cl) in diethylether. Whereas the cyclotetrasiloxanes **5a** and **5b** precipitate after few minutes from the solution, the formation of compound **6** is only completed after stirring for 12 h (equation (3)).

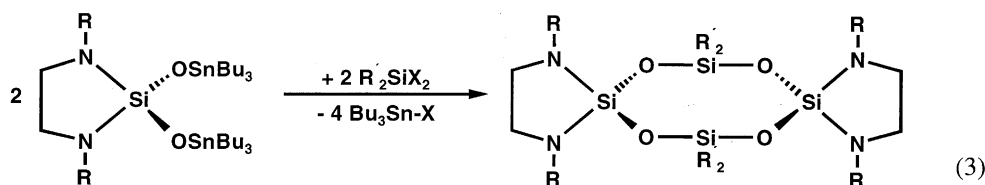
The solvent-free eight-membered siloxane rings are obtained in 40 to 45% yields as white powders, which are almost insoluble in non-polar solvents like toluene, benzene or *n*-hexane, and slightly soluble in tetrahydrofuran.

The ethylene-di-amino substituents attached to the spirocyclic silicon atom have bulky organic groups at the nitrogen atoms that seem to favour the formation of rings. Nevertheless they do not prevent from substitution reactions at the aza-silicon atoms as may be seen from equation (4). By this route the mixed chloro/methyl substituted siloxane ring **7** is prepared in tetrahydrofuran with Ph–N(H)–CH₂–CH₂–N(H)–Ph·2 HCl as by-product.

After filtration of the insoluble amino hydrochloride and removing of all volatile components under reduced pressure, the eight-membered siloxane ring **7** can be sublimed without decomposition as a colourless solid from the oily residue.

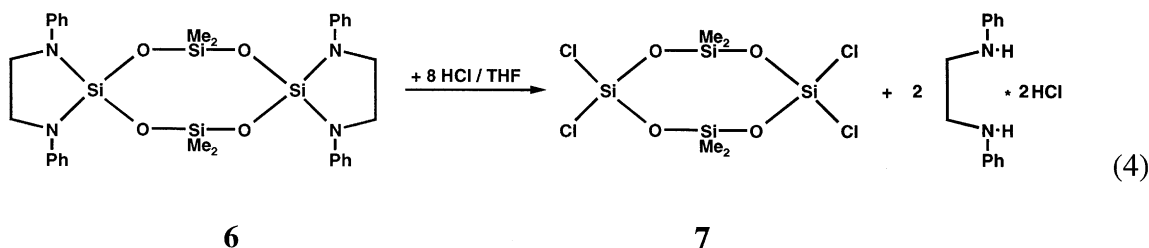
3.2. X-ray crystallography

Colourless crystals of **5a**, **5b** and **6**, suitable for X-ray diffraction studies, were obtained by recrystallisation from hot toluene, or by sublimation (**7**). All



Comp.	R
3	^t Bu
4	Ph

Comp.	R	R'
5a, 5b	^t Bu	Cl, Br
6	Ph	Me



measurements were performed either on a Stoe Image Plate (IPDS) or a four-circle single crystal diffractometer (Siemens) at 293 K. A hemisphere of data was collected using ω -scans and graphite monochromatised radiation. Crystallographic data for compounds **5–6** are summarised in the following section 3.3. The structures were solved by direct methods and refined by the full-matrix least-squares method on F . All non-hydrogen atoms were refined anisotropically and hydrogen atoms were kept fixed in calculated positions with C–H = 0.95 Å. Programs used were SHELX-93 and SHELX-97 [15]. The most important parameters for the crystal and the structure determinations have been assembled in Tables 1–3, whereas the molecular structures of **5–7** are illustrated in Figs. 1–3. The re-

finement of the X-ray structure of compound **7** could not be performed satisfactorily, because only tiny crystals were obtained from **7**; here we only give a graphic representation of **7** ($R = 12.0\%$, Fig. 3).

3.3. Discussion of the structures

Whereas in the eight-membered siloxane rings **6** and **7** the variation of the dihedral angles Si–O–Si–O and O–Si–O–Si is remarkable (**6**: 3.6–34.6°, **7**: 2.5–18.4°) and follow the trend that eight-membered siloxane rings differ from the planarity in contrast to planar six-membered siloxane rings [3], the bis(amino)-chloro derivative **5a** (variation of dihedral angles: 4.4–8.5°) and the bis(amino)-bromo deriva-

Table 1

Crystallographic data and data for structure refinements for $\{[(\text{CH}_2)_2(\text{NtBu})_2]\text{SiO}(\text{Cl})_2\text{SiO}\}_2$ (**5a**), $\{[(\text{CH}_2)_2(\text{NtBu})_2]\text{SiO}(\text{Br})_2\text{SiO}\}_2$ (**5b**), $\{[(\text{CH}_2)_2(\text{NPh})_2]\text{SiO}(\text{Me})_2\text{SiO}\}_2$ (**6**) and $[(\text{Me})_2\text{SiO}(\text{Cl})_2\text{SiO}]_2$ (**7**).

Compound	5a	5b	6	7
Empirical formula	$\text{C}_{20}\text{H}_{44}\text{Cl}_4\text{N}_4\text{O}_4\text{Si}_4$	$\text{C}_{20}\text{H}_{44}\text{Br}_4\text{N}_4\text{O}_4\text{Si}_4$	$\text{C}_{32}\text{H}_{40}\text{N}_4\text{O}_4\text{Si}_4$	$\text{C}_4\text{H}_{12}\text{Cl}_4\text{O}_4\text{Si}_4$
M	658.75	836.55	657.04	378.29
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P\bar{1}$
Unit cell dimensions				
a (Å)	9.708(2)	9.917(2)	9.944(2)	6.454(1)
b (Å)	10.062(2)	10.165(2)	16.663(3)	8.456(9)
c (Å)	10.464(2)	10.571(2)	20.490(4)	8.470(6)
α (°)	97.08(3)	97.82	90	80.55(2)
β (°)	116.58(3)	117.89	101.28(3)	71.04(2)
γ (°)	108.98(3)	106.81	90	82.26(2)
v (Å ³)	819.6(3)	854.0(3)	3329.5(1)	429.6(2)
Z	1	1	4	1
D_{calc} (g cm ⁻³)	1.335	1.599	0.221	1.462
Absorption coefficient	0.539	4.883	1392	0.963
$F(000)$	348	406	1392	192
Crystal size (mm)	$0.2 \times 0.3 \times 0.2$	$0.2 \times 0.3 \times 0.1$	$0.2 \times 0.3 \times 0.2$	$0.1 \times 0.3 \times 0.4$
θ range	2.61–23.93	2.21–25.00	2.42–24.13	3.31–24.03
Reflections collected	5027	3014	10 309	2584
Independent reflections	2332 [$R(\text{int}) = 0.0601$]	3014	2611 [$R(\text{int}) = 0.0519$]	2584
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2332/0/163	3014/0/163	2611/0/199	1211/0/73
Goodness-of-fit on F^2	1.111	1.121	1.032	1.148
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0449$ $wR_2 = 0.1158$	$R_1 = 0.0622$ $wR_2 = 0.1432$	$R_1 = 0.0371$ $wR_2 = 0.0898$	$R_1 = 0.1201$ $wR_2 = 0.2964$
R indices (all data)	$R_1 = 0.0478$ $wR_2 = 0.1181$	$R_1 = 0.0909$ $wR_2 = 0.1635$	$R_1 = 0.0509$ $wR_2 = 0.0948$	$R_1 = 0.1361$ $wR_2 = 0.3322$
Largest diffraction peak and hole (e Å ⁻³)	0.527/–0.364	1.706/–0.503	0.205/–0.218	0.563/–0.767

Table 2

Selected bond lengths (Å) and angles (deg) (e.s.d.s. in parentheses) for $\{[(\text{CH}_2)_2(\text{N}t\text{Bu})_2]\text{SiO}(\text{Cl})_2\text{SiO}\}_2$ (**5a**) and $\{[(\text{CH}_2)_2(\text{N}t\text{Bu})_2]\text{SiO}(\text{Br})_2\text{SiO}\}_2$ (**5b**).

	5a (X = Cl)	5b (X = Br)
Bond lengths		
Si(1)–O(1)	1.6461(2)	1.638(5)
Si(1)–O(2)	1.6368(2)	1.632(5)
Si(2)–O(1)	1.5928(2)	1.579(5)
Si(2)–O(2) [#]	1.5791(2)	1.576(5)
Si(1)–N(1)	1.700(2)	1.692(5)
Si(1)–N(2)	1.692(2)	1.724(6)
Si(2)–X(1)	2.0362(1)	2.199(2)
Si(2)–X(2)	2.0265(2)	2.195(3)
N(1)–C(1)	1.482(3)	1.433(9)
N(1)–C(3)	1.466(4)	1.502(9)
N(2)–C(2)	1.480(4)	1.466(1)
N(2)–C(7)	1.471(4)	1.451(9)
C(1)–C(2)	1.494(4)	1.464(2)
Bond angles		
O(1)–Si(1)–O(2)	102.29(2)	102.0(3)
O(1)–Si(2)–O(2) [#]	114.21(1)	113.5(3)
Si(1)–O(1)–Si(2)	159.94(1)	158.0(4)
Si(1)–O(2)–Si(2) [#]	163.36(2)	166.5(4)
N(1)–Si(1)–N(2)	97.02(2)	96.5(3)
X(1)–Si(2)–X(2)	106.69(5)	106.34(9)
C(1)–N(1)–Si(1)	117.8(2)	110.7(5)
C(2)–N(2)–Si(1)	107.66(2)	106.1(5)
N(1)–C(1)–C(2)	107.1(2)	109.0(7)
N(2)–C(2)–C(1)	107.3(2)	111.4(7)

[#] designs atoms related by symmetry operations.

Table 3

Selected bond distances (Å) and angles (deg) (e.s.d.s. in parentheses) for $\{[(\text{CH}_2)_2\text{N}_2\text{Ph}_2]\text{Si}(\text{Me}_2\text{SiO}_2)\}_2$ (**6**).

Bond lengths		Bond angles	
Si(1)–O(1)	1.602(2)	O(1)–Si(1)–O(2)	106.42(8)
Si(1)–O(2)	1.6107(2)	O(1)–Si(2)–O(2) [#]	109.57(8)
Si(2)–O(1)	1.6235(2)	Si(1)–O(1)–Si(2)	156.53(1)
Si(2)–O(2) [#]	1.6135(2)	Si(1)–O(2)–Si(2) [#]	164.93(1)
Si(1)–N(1)	1.7149(2)	N(1)–Si(1)–N(2)	95.21(8)
Si(1)–N(2)	1.7142(2)	C(15)–Si(2)–C(16)	112.50(2)
Si(2)–C(15)	1.838(3)	C(1)–N(1)–Si(1)	112.32(2)
Si(2)–C(16)	1.836(3)	C(2)–N(2)–Si(1)	112.30(2)
N(1)–C(1)	1.468	N(1)–C(1)–C(2)	110.02(2)
N(1)–C(3)	1.402	N(2)–C(2)–C(1)	110.03(2)
N(2)–C(2)	1.468		
N(2)–C(7)	1.402(3)		
C(1)–C(2)	1.397(3)		

[#] designs atoms related by symmetry operations.

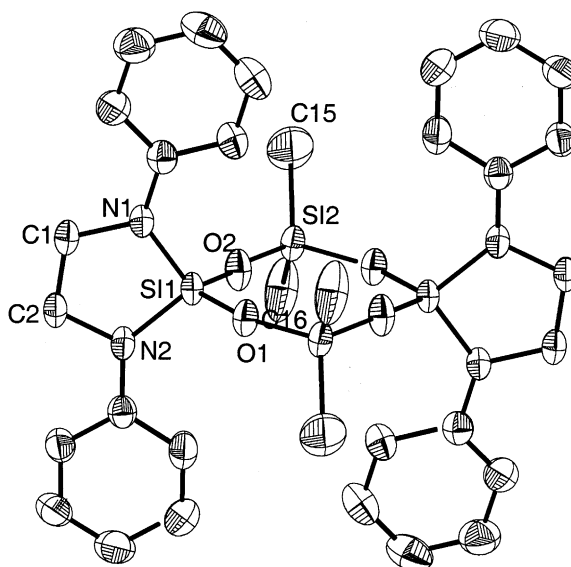


Fig. 1. Molecular structure of $\{[(\text{CH}_2)_2\text{N}_2(\text{Ph})_2]\text{SiO}(\text{Me})_2\text{SiO}\}_2$ (**6**). Thermal ellipsoids are plotted at the 50% probability level; the molecule is centrosymmetric.

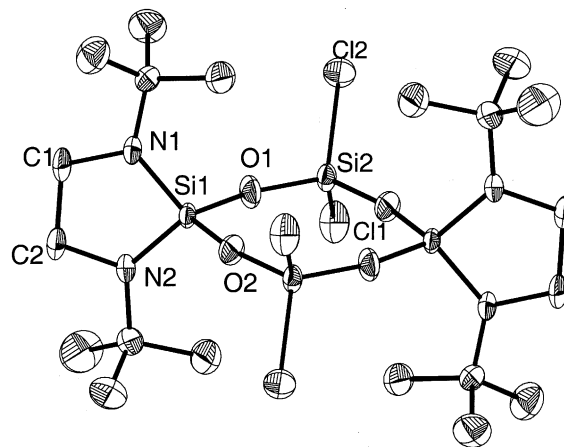


Fig. 2. Molecular structure of centrosymmetric $\{[(\text{CH}_2)_2(\text{N}t\text{Bu})_2]\text{SiO}(\text{Cl})_2\text{SiO}\}_2$ (**5a**) with thermal ellipsoids at the 50% level. The corresponding bromo derivative $\{[(\text{CH}_2)_2(\text{N}t\text{Bu})_2]\text{SiO}(\text{Br})_2\text{SiO}\}_2$ (**5b**) is isostructural and isotypic.

tives **5b** (variation of dihedral angles: 0.4–4.3°) can be considered as almost planar. All molecules **5a**, **5b**, **6** and **7** have crystallographic C_i symmetry and deviate in the case of **5a** and **5b** (not considering the tert-butyl groups) only negligibly from D_{2h} , while in **6** and **7** the twist within the eight-membered rings is more remarkable.

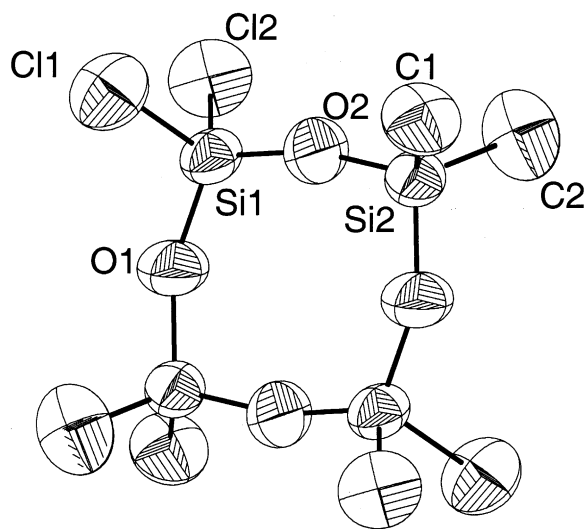


Fig. 3. Molecular structure of centrosymmetric $[(\text{Me})_2\text{SiO}(\text{Cl})_2\text{SiO}]_2(\mathbf{7})$. Thermal ellipsoids are plotted at the 50% level.

As we have found earlier, a gain in electronegativity of substituents bonded to the silicon atoms leads to a shortening of the Si–O bonds and an expansion of the O–Si–O angles [7]. Whereas the evolution of Si–O bonds and Si–O–Si angles in cyclotrisiloxanes is limited by the ring size and consequently ring strain (maximal angles $\sim 133^\circ$), in cyclotetrasiloxanes the Si–O–Si bonding angles are larger ($\sim 145^\circ$) and the Si–O bonding distances usually shorter.

The electronegative chlorine or bromine ligands in **5a** and **5b** result in an electron withdrawal from the silicon atoms, leading to a strong shortening of the adjacent Si–O–bonds. In **5a**, the Si–O bond lengths of the chlorine substituted silicon atoms (mean: $1.586(7)$ Å) are in average similar to those found in octachlorotetrasiloxane $(\text{Cl}_2\text{SiO})_4$ (mean: $1.584(9)$ Å) [3]. Although we expected longer Si–O distances in the bromine derivative **5b** due to lower electronegativity of the bromine atom in comparison to chlorine (E.N. (Pauling): Cl 3.1, Br 2.9 [16]), we found slightly shorter silicon oxygen bonds of $1.578(8)$ Å (mean value). At the spirocyclicly and amino bonded silicon atoms the Si–O bonds are longer in the two derivatives: in **5a** the average length is $1.642(9)$ Å, in **5b** $1.635(8)$ Å, longer as in comparable compounds [17–19]. Interestingly, the Si–O distances of nitrogen-bonded Si(1) (mean: $1.609(1)$ Å) in compound **6** are shorter than those of methyl-bonded Si(2) (mean: $1.619(5)$ Å). Apparently, in this compound the amino substituted sili-

con atom Si(1) has an electron lack compared to Si(2), which has the more electropositive ligands.

Generally, the Si–O–Si angles in cyclotetrasiloxanes show a large variation according to the flexibility of Si–O–Si–O chains and may differ by more than 10° [20–24]. For example, in octachlorocyclotetrasiloxane, the values range from 154.5° to 165.2° [3]; this effect is normally attributed to the packing of the molecules in the solid state. In the present chlorine and bromine derivative **5a** and **5b**, the angle differences are relatively small (**5a**: $159.94(2)^\circ$ to $163.36(3)^\circ$, **5b**: $158.0(4)^\circ$ to $166.5(4)^\circ$). In the mixed methyl and chloro derivate **7**, the Si–O–Si angles range from 153.7° to 164.8° .

The Si–Cl distances in **5a** ($2.065(6)$ and $2.0362(2)$ Å) are longer than in the octachloroderivative $(\text{Cl}_2\text{SiO})_4$ (mean: $2.000(7)$ Å) [3] and in hexachlorodisiloxane $(\text{Cl}_3\text{Si})_2\text{O}$ (by electron diffraction: $2.011(3)$ Å) [25]. The silicon–bromine bonds in **5b** are in the common range [26, 27]. The SiN_2C_2 five-membered rings in **5a** and **5b** are twisted as may be deduced from the sum of the angles within the cycles (**5a**: 527.26° ; **5b**: 533.7°), whereas in **6** the corresponding sum is 539.88° , compatible with an almost planar cycle (theoretical value: 540°). According to the deviation from planarity of the five-membered rings in **5a** and **5b**, the average angle sums at the nitrogen atoms differ from 360° (356.28° and 358.35°), whereas in **6** the nitrogen atoms have a planar coordination sphere. The Si–N bonds in **5a**, **b** and **6** range from $1.692(5)$ Å to $1.724(6)$ Å and are comparable to literature values [9, 28–31].

3.4. Spectroscopy

In ^{29}Si -NMR spectra chlorosiloxanes can usually easily be recognised due to their specific range of chemical displacements and this even holds when dichlorosiloxy groups are combined with other siloxy groups [32–34]. The substitution of chloro atoms in the cyclic bis(amino)dichlorosilanes **1** and **2** by the oxygen atoms of the OSnBu_3 groups is accompanied by a significant low field shift from -33.3 (**1**) and -34.6 ppm (**2**) to -56.2 (**3**) and -62.3 ppm (**4**).

In acyclic $(\text{Cl}_2\text{SiO})_n$ units, the ^{29}Si resonance signal occurs around -71 ppm [35, 36], whereas for the chloro substituted cyclotrisiloxanes $(\text{Cl}_2\text{SiO})_3$, the ^{29}Si NMR signal is found at -58.2 ppm [32, 36]. This shift between the cyclic and acyclic compound can be ex-

plained by the ring tension of the six-membered ring [32]. For the cyclic chloro- and methyl-substituted eight-membered ring **7** (of crystallographic C_i symmetry), two ^{29}Si NMR signals are observed at -9.5 and -70.0 ppm. The NMR resonance for the dimethylsilyl group at -9.5 ppm in **7** appears in the expected range [33, 36]. The second ^{29}Si signal in the NMR spectrum at -70.0 ppm (SiCl_2) however is closer to an open chain $(\text{Cl}_2\text{SiO})_n$ structure than to the six-membered ring, in accord of less strain in the eight-membered Si_4O_4 ring. On the same line, the ^{29}Si NMR signal for the octachlorocyclotetrasiloxane $(\text{Cl}_2\text{SiO})_4$ is found at -69.2 ppm [32, 36].

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC 198174 (**5a**), 198175 (**5b**), 198176 (**6**).

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References

- [1] J. Ackermann, V. Damrath, *Chem. unserer Zeit* 23 (86) (1989).
- [2] W. Noll, *Chemie und Technologie der Silicone*, Verlag Chemie GmbH, Weinheim/Bergstr., 1960.
- [3] U. Wannagat, G. Bogedain, A. Schervan, H.C. Marsmann, D.J. Brauer, H. Bürger, F. Dörrenbach, G. Pawelke, C. Krüger, K.-H. Claus, *Z. Naturforsch.* 46b (1991) 931.
- [4] D.W.S. Chambers, C.J. Wilkins, *J. Chem. Soc.* 5088 (1960).
- [5] J. Haiduc, *The Chemistry of Inorganic Ring Systems*, Part 1, Wiley-Interscience, London, 1970.
- [6] M. Veith, A. Rammo, *Phosphorus, Sulfur, and Silicon* 123 (1997) 75.
- [7] M. Veith, A. Rammo, M. Gießelmann, *Z. anorg. allg. Chem.* 624 (1998) 419.
- [8] M. Veith, A. Rammo, M. Jarczyk, V. Huch, *Mh. Chemie* 130 (1999) 130.
- [9] T. Schlosser, A. Sladek, W. Hiller, H. Schmidbaur, *Z. Naturforsch.* 49b (1994) 1247.
- [10] K.C. Pande, *J. Organomet. Chem.* 13 (1968) 187.
- [11] J. Beckmann, B. Mathieu, W. Nigge, D. Schollmeyer, M. Schürmann, K. Jurkschat, *Organometallics* 17 (1998) 5697.
- [12] B. Morosin, L.A. Harrah, *Acta Crystallogr., Sect. B* 37 (1981) 579.
- [13] B.J. Bridson, M.F. Mahou, K.C. Molloy, P.J. Schofield, *J. Organomet. Chem.* 465 (1994) 145.
- [14] J. Beckmann, K. Jurkschat, D. Schollmeyer, M. Schürmann, *J. Organomet. Chem.* 543 (1997) 229.
- [15] G.M. Sheldrick, *Programme for Structure Determination*, Vers. SHELX-93 and SHELX-97, Göttingen, Germany.
- [16] L. Pauling, *Die Natur der chemischen Bindung*, 3. Aufl. Verlag Chemie, Weinheim, 1962.
- [17] E. Egert, M. Haase, U. Klingebiel, C. Lensch, D. Schmidt, G.M. Sheldrick, *J. Organomet. Chem.* 315 (19) (1986).
- [18] M. Söderholm, D. Carlström, *Acta Chem. Scand., Ser. B* 31 (1977) 193.
- [19] Y.E. Ovchinnikov, V.E. Shklover, Y.T. Struchkov, A.A. Remizova, B.D. Lavrukhin, T.V. Astapova, A.A. Zhdanov, *Z. anorg. allg. Chem.* 524 (1985) 75.
- [20] H.R. Allcock, D.J. Brennan, J.M. Graaskamp, M. Pavez, *Organometallics* 5 (1986) 2434.
- [21] V.E. Shklover, Y.T. Struchkov, A.B. Zachernyk, A.A. Zhdanov, *Cryst. Struct. Commun.* 11 (1982) 1771.
- [22] I.E. Grey, M.J. Hardie, T.J. Ness, C.L. Raston, *Chem. Commun.* 1139 (1999).
- [23] G.K. Henry, D.R. Dowd, R. Bau, G. Manuel, W.P. Weber, *Organometallics* 5 (1986) 1818.
- [24] F.J. Feher, J.J. Schwab, D. Soulivong, J.W. Ziller, *Main Group Chem.* 2 (1997) 123.
- [25] W. Airey, C. Glidewell, A.G. Robiette, G.M. Sheldrick, *J. Mol. Struct.* 8 (1971) 413.
- [26] N. Wiberg, H. Auer, S. Wagner, K. Polborn, G. Kramer, *J. Organomet. Chem.* 619 (2001) 110.
- [27] N.W. Mitzel, J. Riede, H. Schmidbaur, *Acta Crystallogr., Sect. C.* 52 (1996) 980.
- [28] M. Veith, K. Woll, *Chem. Ber.* 126 (1993) 2383.
- [29] D.J. Brauer, H. Bürger, G.R. Liewald, *J. Organomet. Chem.* 308 (1986) 119.
- [30] V.A. Igonin, V.E. Shklover, Y.T. Struchkov, A.B. Zachernyk, V.B. Isayer, *Z. anorg. allg. Chem.* 574 (1989) 119.
- [31] M. Denk, R. Lennon, R. Hayashi, R. West, A.V. Belyakov, H.P. Verne, A. Haaland, M. Wagner, N. Metzler, *J. Am. Chem. Soc.* 116 (1994) 2691.
- [32] H.C. Marsmann, E. Meyer, *Z. anorg. allg. Chem.* 548 (1987) 193.
- [33] G. Engelhardt, H. Jancke, M. Mägi, T. Pehk, E. Lippmaa, *J. Organomet. Chem.* 28 (1971) 293.
- [34] H. Jancke, J. Schulz, E. Popowski, H. Kelling, *J. Organomet. Chem.* 354 (1988) 23.
- [35] E. Rikowsky, H.C. Marsmann, *Polyhedron* 16 (1997) 3357.
- [36] H.C. Marsmann, E. Meyer, M. Vongehr, E.F. Weber, *Makromol. Chem.* 184 (1983) 1817.