Synthesis and structure of a difunctional siloxane dendron

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A difunctional dendron composed of three spiro-linked cyclosiloxane fragments was synthesized by a convergent way. This is of interest for the preparation of cylindrical and spherical dendritic molecules with the inorganic siloxane core and peripheral organic layer. The structures of the dendron synthesized and intermediates containing the Si-Cl, Si-H, Si-OH groups were confirmed by data from mass-spectrometry and X-ray diffraction.

Key words: organospirocyclosiloxanes, polysiloxane dendrimer, difunctional dendron, convergent scheme, bis(2-chloro-4,4,6,6-tetraphenylcyclosiloxan-2-yl) oxide, bis(2-hydroxy-4,4,6,6-tetraphenylcyclotrisiloxan-2-yl) oxide.

Organocardocyclosiloxane compounds^{1,2} contain cyclotri- (Q_3) or cyclotetrasiloxane (Q_4) cores devoid of organic margins and connected by spiro-bonds with other QD₂ fragments bearing organic substituents at the silicon atoms ($Q = SiX_{4/2}$, D = RR'SiX, where X = O or NH; the nomenclature of the structure fragments of the siloxane molecules is given in Ref. 3). The inorganic part of such compounds are presented by cyclosiloxane backbone, which accounts for their thermostability and acid resistance. Due to the presence of hydrocarbon marginal groups, organospirocyclosiloxanes have molecular structures and are soluble in many organic solvents. They are crystalline substances with increased heat resistance and thermal stability compared to the linear organosiloxanes. These structures can be regarded as the first-generation organosilicon dendrimeric molecules built of self-similar cyclic structural fragments of silicon dioxide containing organic substituents at the periphery.⁴

The framework for the formation of the next-generation polysiloxane dendritic molecules is a difunctional dendron built of spiro-linked siloxane rings and incorporating the D- and Q-siloxane fragments.

Such type of structure with the hard molecular backbone and space-separated organic (polyorganosiloxane) and inorganic functional parts contains all the prerequisites for the synthesis of the well-ordered hybrid organic-inorganic systems.



The aim of the present work is the preparation of a difunctional siloxane dendron as a functional structural unit capable of self-organization according to a convergent scheme that have been suggested by us previously⁵ from a difunctional organocyclosiloxane as a starting building block. This route implies stepwise formation of a dispirosiloxane structure (Scheme 1).

Scheme 1



In studies of compounds of such a structure, it should be taken into account that the flexibility inherent in organocyclosiloxanes was also characteristic of the molecules of the compounds-precursors and manifested itself in the violation of their ideal symmetry and deformation of the rings. The crystal lattices of cardocyclosiloxanes with diphenyl margins possessed holes (up to 150 Å^3 in volume) filled with disordered solvent molecules that has not been removed by evacuation.⁶ which distorts the results of the elemental analysis. The IR spectra provided only a tool for qualitative establishing the presence of the cyclotrisiloxane fragments in the products and the NMR spectra were poorly informative (except for the specially synthesized trimethylsilyl derivatives). Since the inorganic constituent of such siloxane decreases their volatility, the conventional electron-impact ionization mass-spectrometry does not offer adequate information on the molecular weights and chemical structures of these derivatives.⁷ The molecular weights and compositions of the target products were confirmed by the MALDI-TOF mass spectra where the peaks of single-charged ions related to clusters of the

Published in Russian in Izvestiva Akademii Nauk. Seriya Khimicheskaya, No. 2, pp. 367-374, February, 2010. 1066-5285/10/5902-0374 © 2010 Springer Science+Business Media, Inc. molecules containing the alkali metal cations, as well as to the protonated and solvated species, were observed. The measured isotopic distributions and the m/z values are in good agreement with the theoretical ones.

Results and Discussion

The synthesis of a dendron by a convergent scheme implied dimerization of the cyclosiloxane fragments followed by condensation of the resulting difunctional bis-(cyclotrisiloxanyl) oxide with tetrachlorosilane.⁵ The difunctional organocyclotrisiloxanes with the phenyl substituents at the silicon atoms, *viz.*, 2,2-dichloro-4,4,6,6-tetraphenylcyclotrisiloxane (1) and 2-chloro-4,4,6,6-tetraphenylcyclotrisiloxane (2), were used as the starting compounds for the preparation of bis(cyclotrisiloxanyl) oxides.

We expected that the synthesis of the hydroxyl-containing bis(cyclotrisiloxanyl) oxide would be carried out by hydrolytic condensation (Scheme 2) of dichlorotrisiloxane 1. According to the GPC data, at the ratio of 1 and H_2O of 1:3, hydrolysis results in the formation of oligomers containing from 3 to 5 rings in the chain.



n = 1—5

The IR spectrum of the reaction product, besides a doublet in the region of 1025 and 1040 cm⁻¹ typical of the starting cyclosiloxane **1**, contains a band at 1080–1090 cm⁻¹ indicating the presence of unstrained siloxane bonds between the cyclic fragments.⁸ Blocking the hydroxy groups with chlorotrimethylsilane (Scheme 3) allowed determination of the intensity ratio of the H_{Me} : H_{Ph} signals in the ¹H NMR spectrum of the reaction products of 2 : 7, which corresponds on average to three siloxane fragments in the molecule.

The formation of a set of the condensation products is apparently due to the lability of the intermediates, which can be explained by the presence of functional groups in the "inorganic" part of the molecule, as well as by the features of the hydrolytic condensation, which is mainly a heterofunctional process in the neutral medium.⁹ Synthesis of monocyclic diol **3** was carried out by hydrolysis of compound **1** in the presence of ammonium carbonate; virtually no formation of oligomeric products was observed. Performing the hydrolysis of dichloride **1** in a such man-



ner that would provide the preferential formation of bis(hydroxycyclotrisiloxanyl) oxide **4** was unsuccessful.



According to the X-ray diffraction data, compound **3** crystallizes in the form of solvate with THF. There are four independent molecules of **3** and four THF molecules in the unit cell. The principal geometric parameters of the independent molecules in the crystal, except for turn of the phenyl rings, do not differ (Table 1).

The six-membered rings are characterized by the flattened conformation with maximum deviation of the silicon atoms from 0.07 to 0.24 Å. The Si–O bond lengths in the ring are in the range from 1.614(3) to 1.655(3) Å and the Si(1) - O(H) bond lengths are in the range from 1.578(3) to 1.622(3) Å. The analysis of the crystal packing in 3 showed that one of the hydroxyl groups in each of the independent molecules forms strong H-bond with the hydroxyl group of the other molecule assembling the molecules into dimers (Fig. 1). The distances O...O characterizing the H-bond strengths are in the range of 2.672(5)-2.719(4) Å. In turn, the other OH group in the molecule forms an H-bond with the solvate molecule of THF (the distances O...O are in the range of 2.582(4) - 2.665(4) Å). It should be noted that although the formation of the H-bonds with THF molecules is generally not characteristic (the analysis of the Cambridge Structural Database revealed only 39 such structures), but, if present, such H-bonds are always strong (the average distance O...O is 2.683 Å). Thus, the major structural unit in the crystal of 3 is the H-bonded dimer with two solvate molecules of THF, which probably results in the sufficiently high stability of **3**.

The formation of dicyclic compound **4** by homofunctional condensation of monocyclic diol **3** was do-

Table 1. Selected bolid lengths (a) and bolid angles (b) in the structure of	Table 1.	. Selected bond	lengths (d)	and bond angles	(ω) i	in the structure	of	3
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Parameter	Value	Parameter	Value	Parameter	Value
Bond	d∕Å	Bond	d∕Å	Angle	ω/deg
Si(1A) - O(5A)	1.614(3)	Si(3D) - O(3D)	1.644(2)	Si(2B) - O(2B) - Si(3B)	130.82(16)
Si(1A) - O(4A)	1.605(3)	Si(3D) - C(19D)	1.855(4)	Si(1B) - O(3B) - Si(3B)	133.81(17)
Si(1A) - O(1A)	1.624(3)	Si(3D) - C(13D)	1.860(3)	O(4C) - Si(1C) - O(5C)	110.13(15)
Si(1A) - O(3A)	1.641(3)			O(4C) - Si(1C) - O(1C)	111.45(17)
Si(2A) - O(1A)	1.632(3)	Angle	ω/deg	O(5C) - Si(1C) - O(1C)	109.06(17)
Si(2A) - O(2A)	1.650(3)	O(5A)-Si(1A)-O(4A)	110.76(15)	O(4C) - Si(1C) - O(3C)	109.94(16)
Si(2A) - C(1A)	1.807(5)	O(5A)-Si(1A)-O(1A)	108.88(17)	O(5C) - Si(1C) - O(3C)	109.56(15)
Si(2A) - C(7A)	1.860(4)	O(4A)-Si(1A)-O(1A)	110.98(16)	O(1C) - Si(1C) - O(3C)	106.63(15)
Si(3A) - O(3A)	1.622(3)	O(5A) - Si(1A) - O(3A)	109.91(16)	O(1C) - Si(2C) - O(2C)	106.95(16)
Si(3A) - O(2A)	1.648(3)	O(4A) - Si(1A) - O(3A)	109.43(15)	O(1C) - Si(2C) - C(1C)	109.80(16)
Si(3A) - C(13A)	1.803(5)	O(1A) - Si(1A) - O(3A)	106.81(15)	O(2C) - Si(2C) - C(1C)	108.83(16)
Si(3A) - C(19A)	1.856(4)	O(1A) - Si(2A) - O(2A)	108.22(16)	O(1C) - Si(2C) - C(7C)	110.20(18)
Si(1B) - O(5B)	1.586(3)	O(1A) - Si(2A) - C(1A)	109.48(17)	O(2C) - Si(2C) - C(7C)	108.57(15)
Si(1B) - O(3B)	1.614(3)	O(2A) - Si(2A) - C(1A)	109.06(17)	C(1C) - Si(2C) - C(7C)	112.3(2)
Si(1B) = O(1B)	1 621(3)	O(1A) - Si(2A) - C(7A)	109 35(16)	O(3C) - Si(3C) - O(2C)	108 14(14)
Si(1B) - O(4B)	1.622(2)	O(2A) - Si(2A) - C(7A)	108.81(16)	O(3C) - Si(3C) - C(14C)	108.96(18)
Si(2B) - O(2B)	1.625(3)	C(1A) - Si(2A) - C(7A)	111.8(2)	O(2C) - Si(3C) - C(14C)	109.2(2)
Si(2B) - O(1B)	1.645(2)	O(3A) - Si(3A) - O(2A)	108.08(15)	O(3C) - Si(3C) - C(20C)	109.2(2) 109.40(17)
Si(2B) - C(7B)	1.857(3)	O(3A) - Si(3A) - C(13A)	108 85(19)	O(2C) - Si(3C) - C(20C)	110 10(18)
Si(2B) - C(1B)	1.876(3)	O(2A) - Si(3A) - C(13A)	110.2(2)	C(14C) - Si(3C) - C(20C)	110.99(18)
Si(3B) - O(3B)	1.637(3)	O(3A) - Si(3A) - C(19A)	109.38(18)	Si(2C) = O(1C) = Si(1C)	133 32(17)
Si(3B) - O(2B)	1.645(3)	O(2A) - Si(3A) - C(19A)	109.9(2)	Si(2C) = O(2C) = Si(3C)	130.11(16)
Si(3B) - C(19B)	1.853(4)	C(13A) - Si(3A) - C(19A)	110.4(2)	Si(3C) = O(3C) = Si(1C)	132.9(2)
Si(3B) - C(13B)	1.864(4)	Si(1A) - O(1A) - Si(2A)	132.24(17)	O(5D) - Si(1D) - O(1D)	108.93(15)
Si(1C) - O(4C)	1.602(3)	Si(2A) - O(2A) - Si(3A)	130.28(17)	O(5D) - Si(1D) - O(4D)	108.45(13)
Si(1C) = O(5C)	1.605(3)	Si(3A) = O(3A) = Si(1A)	133.0(2)	O(1D) - Si(1D) - O(4D)	111.14(14)
Si(1C) - O(1C)	1.627(3)	O(5B) - Si(1B) - O(3B)	108.25(16)	O(5D) - Si(1D) - O(3D)	111.07(14)
Si(1C) - O(3C)	1.635(3)	O(5B) - Si(1B) - O(1B)	111.28(15)	O(1D) - Si(1D) - O(3D)	106.66(14)
Si(2C) - O(1C)	1.622(3)	O(3B) - Si(1B) - O(1B)	106.39(14)	O(4D) - Si(1D) - O(3D)	110.59(14)
Si(2C) - O(2C)	1.649(3)	O(5B) - Si(1B) - O(4B)	108.61(13)	O(2D) - Si(2D) - O(1D)	107.11(15)
Si(2C) - C(1C)	1.819(4)	O(3B) - Si(1B) - O(4B)	111.68(14)	O(2D) - Si(2D) - C(7D)	109.37(14)
Si(2C) - C(7C)	1.860(4)	O(1B) - Si(1B) - O(4B)	110.62(14)	O(1D) - Si(2D) - C(7D)	108.88(15)
Si(3C) - O(3C)	1.616(3)	O(2B) - Si(2B) - O(1B)	108.16(14)	O(2D) - Si(2D) - C(1D)	110.46(14)
Si(3C) - O(2C)	1.655(3)	O(2B) - Si(2B) - C(7B)	110.11(16)	O(1D) - Si(2D) - C(1D)	109.87(14)
Si(3C) - C(14C)	1.831(4)	O(1B) - Si(2B) - C(7B)	108.19(16)	C(7D) - Si(2D) - C(1D)	111.05(18)
Si(3C) - C(20C)	1.878(4)	O(2B) - Si(2B) - C(1B)	108.70(17)	O(2D) - Si(3D) - O(3D)	107.93(14)
Si(1D) - O(5D)	1.578(3)	O(1B) - Si(2B) - C(1B)	110.23(14)	O(2D) - Si(3D) - C(19D)	108.16(18)
Si(1D) - O(1D)	1.614(3)	C(7B) - Si(2B) - C(1B)	111.41(16)	O(3D) - Si(3D) - C(19D)	111.34(17)
Si(1D) - O(4D)	1.619(2)	O(3B) - Si(3B) - O(2B)	107.48(15)	O(2D) - Si(3D) - C(13D)	109.36(16)
Si(1D) - O(3D)	1.621(2)	O(3B) - Si(3B) - C(19B)	107.14(17)	O(3D) - Si(3D) - C(13D)	107.63(14)
Si(2D) - O(2D)	1.650(3)	O(2B) - Si(3B) - C(19B)	109.48(14)	C(19D) - Si(3D) - C(13D)	112.32(16)
Si(2D) - O(1D)	1.652(3)	O(3B) - Si(3B) - C(13B)	108.96(15)	Si(1D) - O(1D) - Si(2D)	131.04(16)
Si(2D) - C(7D)	1.849(4)	O(2B) - Si(3B) - C(13B)	111.53(14)	Si(1D) - O(3D) - Si(3D)	133.1(2)
Si(2D) - C(1D)	1.858(4)	C(19B) - Si(3B) - C(13B)	112.1(2)	Si(3D) - O(2D) - Si(2D)	130.47(16)
Si(3D)-O(2D)	1.618(3)	Si(1B) - O(1B) - Si(2B)	132.7(2)		

cumented.¹⁰ However, no evidence for its structure was presented. The attempts to carry out condensation of monocycle **3** were undertaken, *viz.*, heating in bulk to 250 °C, in a solvent (THF), and in trifluoroacetic acid. In all cases, mixtures of oligometric products with a higher degree of polymerization (according to the GPC data) were produced, no cardocyclic compounds were isolated. Thus, we did not succeed in terminating

the condensation process at the step of the formation of dimer 4. For the preparation of 4 as an individual compound, we developed another synthetic approach including two steps.

In the first step (Scheme 4), bis(2-chloro-4,4,6,6-tetraphenylcyclotrisiloxan-2-yl) oxide (5) was synthesized by partial hydrolysis of dichloride 1 at a ratio 1 : H₂O of 2 : 1. In this case, hydrolysis was also accompanied by



Fig. 1. General view of H-bonded dimer 3.

condensation, but dichloride **5** was readily isolated from the reaction mixture by recrystallization.

Scheme 4



In the second step (Scheme 5), hydrolysis of dichloride 5 was carried out in neutral medium. The yield of diol 4 was 75–82%. The data from elemental analysis, IR spectroscopy, and mass spectrometry confirm the composition and structure of compound 4.

The IR-spectra of 4 and 5 display the intense absorption band consisting of two maxima at 1025 and 1040 cm⁻¹, the former corresponding to the asymmetric stretching vibrations of the Si–O bond in the strained siloxane rings and the latter being typical of the rings containing functional groups.⁸ In addition, there is an absorption band of

Scheme 5



the siloxane bond that links the cyclic fragments (a maximum at 1080 cm^{-1}). Its position corresponds to the asymmetric stretching vibrations of the group Si-O-Si in linear siloxanes. The IR spectral data confirm that cyclosiloxane fragments are not split during condensation. Diol 4 undergoes spontaneous self-dimerization, which is confirmed by mass spectral data, the IR spectrum being virtually unchanged.

For additional confirmation of the structure of diol **4**, we prepared its bis(trimethylsilyl) derivative **6** (Scheme 6).

Scheme 6



In the IR spectrum of compound 6, the position of the absorption band of the newly formed bond Si-O-Si co-

incides with that of the siloxane bond between the cyclic fragments, which is in agreement with the data in Ref. 8. The ratio of the integral intensities of the signals for the protons H_{Me} : H_{Ph} in the ¹H NMR spectrum is 1:2.2, which corresponds to two cyclosiloxane fragments in the molecule.

As an alternative route for the preparation of diol **4**, we considered oxidation of the hydride groups in bis(4,4,6,6-tetraphenylcyclotrisiloxan-2-yl) oxide (**7**), which was synthesized by hydrolytic condensation of 2-chloro-4,4,6,6-tetraphenylcyclotrisiloxane (**2**) (Scheme 7).

Scheme 7



The ratio of the integral intensities of the signals for the protons at the silicon atoms and for the phenyl protons in the 1 H NMR spectrum is equal to 1 : 20, which confirms its structure.

The attempt to oxidize compound 7 in the presence of Pd/C according to a known procedure¹¹ was not successful. Thus, only the method for preparation of diol 4 by hydrolysis of its dichloride precursor 5 makes it possible to synthesize compound 4 on a preparative scale.

Using heterofunctional condensation of diol **4** with tetrachlorosilane (Scheme 8) in THF or diethyl ether both in the presence of acceptor of HCl, *viz.*, aniline or *m*-nitro-aniline, and in the absence of an acceptor, 15,15-dichloro-2,2,4,4,10,10,12,12-octaphenyldispiro[5.1.5.3]heptasiloxane (dendron) (**8**) was prepared (Table 2).

Scheme 8



The synthesis of 8 in THF without an acceptor was

analogous to that of cyclosiloxanes 1 and 2. The yield of

the dendron in this case was lower (43%) than those of the

 Table 2. Dependence of the yield of dendron 8 on the reaction conditions

Solvent	HCl acceptor	<i>t</i> */h	The yield of 8 (%)
THF	_	170	43
THF	Aniline	5	12
THF	<i>m</i> -Nitroaniline	5	61
Diethyl ether	The same	5	14

* Reaction time.

corresponding monocycles, which is probably explained by greater lability of compound **4** compared to the linear siloxanes and by the easiness of its condensation in the acidic medium.

The maximum yield of the dendron (61%) was obtained in the reaction in THF using *m*-nitroaniline as the acceptor of HCl.

The structure of dendron **8** studied by the X-ray diffraction analysis is shown in Fig. 2. Compound **8** crystallizes in the form of a solvate with one molecule of CCl₄. Compound **8** occupies special position in the crystal, the symmetry plane passes through the atoms Cl(1), Cl(2), Si(1), and O(2). The principal geometric parameters of **8** are close to those of compound **3**. For example, the silicon-containing rings in the molecule are planar with the maximal deviation of the spiro atom Si(2) from the plane of the tetraphenylcyclotrisiloxane fragment equal to 0.07 Å. The Si–O bond lengths vary in the range of 1.604(2)–1.647(4) Å. The analysis of crystal packing showed that all intermolecular contacts in **8** correspond to the usual van der Waals interactions. The geometric parameters of **8** are presented in Table 3.

With the aim of preparing a hydroxyl-containing analog of dendron **8**, we carried out its hydrolysis under the conditions similar to those used for the hydrolysis of ring **1**, *i.e.*, in excess of water in the presence of $(NH_4)_2CO_3$ to keep the medium neutral (Scheme 9).

Scheme 9



n = 1 (**9**), 2 (**10**), 3 (**11**), 4 (**12**)

However, in this case, a mixture of hydroxyl-containing dendron coupling products is produced. The presence of four oligomeric products with the terminal hydroxyl



Fig. 2. General view of dendron 8. The second positions of the chlorine atoms are not shown.

Bond	$d/\text{\AA}$	Angle	ω/deg	Angle	ω/deg
Si(1)-O(1)	1.611(2)	O(1) - Si(1) - O(1A)	109.0(1)	O(4) - Si(3) - O(3)	106.59(9)
Si(1)-Cl(2)	2.016(2)	O(1) - Si(1) - Cl(2')	113.12(8)	O(4) - Si(3) - C(1)	108.2(1)
Si(1)-Cl(1)	2.016(2)	O(1) - Si(1) - Cl(2')	113.12(8)	O(3) - Si(3) - C(1)	111.3(1)
Si(1)-Cl(1')*	2.018(2)	O(1) - Si(1) - Cl(2)	103.51(9)	O(4) - Si(3) - C(7)	109.9(1)
$Si(1) - Cl(2')^*$	2.012(2)	O(1A) - Si(1) - Cl(2)	103.51(9)	O(3) - Si(3) - C(7)	107.3(1)
Si(2)-O(3)	1.604(2)	O(1) - Si(1) - Cl(1)	113.86(9)	C(1) - Si(3) - C(7)	113.35(12)
Si(2)-O(5)	1.609(2)	O(1A) - Si(1) - Cl(1)	113.86(9)	O(4) - Si(4) - O(5)	106.22(9)
Si(2)-O(2)	1.619(2)	Cl(2) - Si(1) - Cl(1)	112.1(1)	O(4) - Si(4) - C(13)	110.56(11)
Si(2)-O(1)	1.632(2)	O(1) - Si(1) - Cl(1')	106.96(9)	O(5) - Si(4) - C(13)	108.65(11)
Si(3)-O(4)	1.633(2)	O(1A) - Si(1) - Cl(1')	106.96(9)	O(4) - Si(4) - C(19)	108.91(10)
Si(3)-O(3)	1.647(2)	Cl(2') - Si(1) - Cl(1')	107.28(11)	O(5) - Si(4) - C(19)	110.94(11)
Si(3) - C(1)	1.847(3)	O(3) - Si(2) - O(5)	108.83(9)	C(13) - Si(4) - C(19)	111.44(12)
Si(3) - C(7)	1.850(3)	O(3) - Si(2) - O(2)	110.9(1)	Si(1) - O(1) - Si(2)	131.49(12)
Si(4)-O(4)	1.628(2)	O(5) - Si(2) - O(2)	110.2(1)	Si(2)-O(2)-Si(2A)	133.17(18)
Si(4)-O(5)	1.643(2)	O(3) - Si(2) - O(1)	109.6(1)	Si(2) - O(3) - Si(3)	131.93(11)
Si(4)-C(13)	1.848(3)	O(5) - Si(2) - O(1)	110.0(1)	Si(4) - O(4) - Si(3)	133.72(11)
Si(4)-C(19)	1.851(3)	O(2)—Si(2)—O(1)	107.3(1)	Si(2)—O(5)—Si(4)	132.41(12)

Table 3. Selected bond lengths (*d*) and bond angles (ω) in the structure of **8**

* The Cl(1') and Cl(2') atoms relate to the second position of the disordered SiCl₂ group.

groups was established by mass spectrometry. The isolation of 15,15-dihydroxy-2,2,4,4,10,10,12,12-octaphenyl-dispiro[5.1.5.3]-heptasiloxane (9, n = 1) from the reaction mixture by reprecipitation or recrystallization failed.

Experimental

The starting silicon tetrachloride, trichlorosilane, dichlorodiphenylsilane, pyridine, and trimethylchlorosilane were freshly distilled in an inert atmosphere prior to use. The solvents used were THF (successively dried and distilled over CaH_2 and LiAlH₄), CCl₄, diethyl ether, and hexane (dried and distilled over CaH₂).

Difunctional tetraphenylcyclotrisiloxanes 1 and 2 were synthesized according to a known procedure⁸ by the reactions of 1,3-dihydroxytetraphenyldisiloxane with tetrachloro- and trichlorosilane in the presence and in the absence of an HCl acceptor. THF was used as a solvent. Ammonium carbonate (analytically pure grade) as the hydrogen chloride acceptor was used without additional purification.

The ¹H NMR spectra were recorded on a Bruker WP-200 SY (200.13 MHz) instrument. $CDCl_3$ was used as the solvent and the internal standard.

Gas chromatographic analysis was carried out on a Model 3700 (Russia) chromatograph (catharometer as the detector; helium as the carrier gas; columns $2 \text{ m} \times 3 \text{ mm}$ with SE-30 (5%) on Chromaton-N-AW). Integration of chromatograms was carried out with an Interchrom integrator (Bulgaria).

Gel permeation chromatography was carried out on Waters μ -Styragel columns (the pore sizes were 10⁵, 10⁴, 10³, and 10⁶ Å) and Silasorb 600 silylated with hexamethyldisilazane (the particle size was 7.5 μ m) using toluene as the eluent and a Waters 410 or RIDK 102 differential refractometer as the detector.

The IR spectra were registered on a UR-10 instrument in KBr pellets.

The X-ray diffraction studies for compounds **3** and **8** were performed on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (λ (Mo- $K\alpha$) = 0.71073 Å, graphite monochromator, ω -scanning technique). The processing and averaging of experimental data were performed using a SAINT Plus¹² software with the semiempirical allowance for absorption.¹³

The structures of compound **3** and **8** were solved by direct methods and refined by the full-matrix least-squares method in the isotropic appoximation based on F_{hkl}^2 with the successive syntheses of electron density. The analysis of the differential Fourier syntheses showed that the phenyl rings, the carbon atoms of THF in **3** and chlorine atoms of the SiCl₂ and CCl₄ groups in **8** are disordered with the equal values of populations. The positions of the hydrogen atoms, except for the atoms of the hydroxyl groups, were calculated from the geometry, whereas the latter was localized from the Fourier syntheses. The structure refinements were performed using the SHELX TL 5.10 program package (see Ref. 14). Principal crystallographic and structure refinement parameters for compounds **3** and **8** are summarized in Table 4.

The MALDI-TOF mass spectra were recorded on a Bruker Reflex IY instrument in the linear mode. 2,5-Dihydroxybenzoic acid was used as a matrix. The m/z measurement accuracy was <35 ppm.

Hydrolytic condensation of 2,2-dichloro-4,4,6,6-tetraphenylcyclotrisiloxane (1). A solution of 1 (12.4 g, 24.2 mmol) in THF (25 mL) was added with stirring to a cooled (0–1 °C) solution of water (1.31 g, 72.6 mmol) in THF (125 mL) for 2.5 h and 60% of THF was distilled off. Then hexane (20 mL) was added, the precipitate that formed was filtered off and dried *in vacuo*. According to GPC data, the crystals (6.8 g) obtained were a mixture of oligomers. IR (CCl₄), v/cm⁻¹: 1025, 1040 (SiOSi cyclic); 1080–1090 (SiOSi linear); 704, 726, 1128, 1595 (SiC_{Ph}). After treatment of the obtained crystals with Me₃SiCl and Py (a 1% solution in THF), a mixture of trimethylsilyl derivatives was obtained. ¹H NMR (CDCl₃), &: 0.18 (s, 18 H_{Me}); 7.05–7.77 (m, 63 H_{Ph}).

2,2-Dihydroxy-4,4,6,6-tetraphenylcyclotrisiloxane (3). To a cooled $(-3 \,^{\circ}\text{C})$ solution of water (0.4 g, 22 mmol) and $(\text{NH}_4)_2\text{CO}_3$ (1 g, 10.4 mmol) in THF (20 mL), a solution of **1** (5.32 g, 10.4 mmol) in THF (16 mL) was added for 0.5 h. The mixture was stirred for additional 1 h at room temperature. The precipitate that formed was filtered off, 70% of the solvent was removed and hexane (10 mL) was then added. White crystal flakes of **3** (4.68 g, 95%) were isolated by recrystallization. M.p. 62 °C. Found (%): C, 60.98; H, 4.66; Si, 17.79. C₂₄H₂₂O₅Si₃. Calculated (%): C, 60.93; H, 4.52; Si. 17.76. IR (KBr), v/cm⁻¹: 1028–1041 (SiOSi cyclic); 1080 (SiOSi linear); 704, 726, 1128, 1600 (SiC_{Ph}); 3383, 3568, 3619 (SiOH).

Bis(2-chloro-4,4,6,6-tetraphenylcyclotrisiloxan-2-yl) oxide (5). A solution of water (0.1 g, 5.55 mmol) in THF (6 mL) was

 Table 4. Crystallographic data and main details of structure re

 finement for compounds 3 and 8

Parameter	Compound			
	3	8		
Molecular formula	C ₂₈ H ₃₀ O ₆ Si ₃	C49H40Cl6O9Si7		
Molecular weight	546.79	1182.24		
Crystal system	Triclinic	Orthorhombic		
Space group	$P\overline{1}$	Pnma		
T/K	120	120		
Z(Z')	8(4)	4(0.5)		
a/Å	18.182(5)	18.337(3)		
b/Å	18.403(5)	28.187(4)		
c/Å	20.760(5)	10.952(2)		
α/deg	64.379(6)	90.00		
β/deg	64.432(5)			
γ/deg	73.872(5)	90.00		
$V/Å^3$	5615(2)	5660.9(14)		
$d_{\rm calc}/{\rm g}{\rm cm}^{-3}$	1.294	1.347		
Absorption	2.09	4.55		
coefficient μ/mm^{-1}				
F(000)	2304	2360		
$2\theta_{\rm max}/{\rm deg}$	52	54.0		
Number of reflections measured	33501 (0.0456)	37980 (0.0798)		

added with stirring to a solution of **1** (6.2 g, 12.1 mmol) in THF (10 mL) for 1.3 h. The reaction mixture was stirred for additional 3 h. Then THF was completely removed, the product was recrystallized from dry CCl₄. Needle-like crystals of **5** (4.9 g, 84%) were obtained. M.p. 132–134 °C. Found (%): C, 59.27; H, 4.18; Si, 16.82; Cl, 7.21. C₄₈H₄₀Cl₂O₇Si₆. Calculated (%): C, 59.51; H, 4.13; Si, 17.37; Cl, 7.23. MALDI-TOF MS, found: *m/z* 989.08 [M + Na]⁺. C₄₈H₄₀Cl₂O₇Si₆Na; calculated: *m/z* 989.05. Found: *m/z* 1005.05 [M + K]⁺. C₄₈H₄₀Cl₂O₇Si₆K; calculated: *m/z* 1005.03. IR (CCl₄), v/cm⁻¹: 1025, 1040 (SiOSi cyclic); 1080 (SiOSi linear); 704, 726, 1128, 1602 (SiC_{Ph}).

Bis(2-hydroxy-4,4,6,6-tetraphenylcyclotrisiloxan-2-yl) oxide (4). To a cooled ($-3 \,^{\circ}$ C) solution of water (0.4 g, 22 mmol) and (NH₄)₂CO₃ (1 g, 10.4 mmol) in dry THF (20 mL), a solution of **5** (1.09 g, 1.12 mmol) in THF (16 mL) was added for 1.5 h. The mixture was stirred for additional 1 h at room temperature. The precipitate that formed was filtered off, 70% of the solvent was removed and hexane (10 mL) was added. Colorless crystals of **4** (0.85 g, 82%) were obtained by recrystallization. M.p. 93–95 °C. Found (%): C, 61.48; H, 4.64; Si, 17.63. C₄₈H₄₂O₉Si₆. Calculated (%): C, 61.93; H, 4.52; Si, 18.06. MALDI-TOF MS, found: *m/z* 953.14 [M + Na]⁺. C₄₈H₄₂O₉Si₆Na; calculated: *m/z* 953.13. Found: *m/z* 969.12 [M + K]⁺. C₄₈H₄₂O₉Si₆K; calculated: *m/z* 969.10. IR (CCl₄), v/cm⁻¹: 1025, 1040 (SiOSi cyclic); 1080 (SiOSi linear); 704, 726, 1128, 1602 (SiC_{Ph}); 3383, 3568, 3619 (SiOH).

Dimer of compound 4. The dimer formed when a dilute solution of **4** (0.2 mol L⁻¹) in THF was left for 4 days at 25 °C. MS MALDI-TOF, found: m/z 1865.28 [M + Na]⁺. C₉₆H₈₂O₁₇Si₁₂Na; calculated: m/z 1865.26. Found: m/z 1881.25 [M + K]⁺. C₉₆H₈₂O₁₇Si₁₂K; calculated: m/z 1881.23. IR (KBr), v/cm⁻¹: 1028–1041 (SiOSi cyclic); 1080 (SiOSi linear); 704, 726, 1128, 1600 (SiC_{Ph}); 3383, 3568, 3619 (SiOH).

Bis(2-trimethylsiloxy-4,4,6,6-tetraphenylcyclotrisiloxan-2-yl)oxide (6). A solution of **4** (0.05 g, 0.054 mmol) in dry THF (2 mL) was quickly added to a solution of Me₃SiCl (0.06 mL, 0.27 mmol) and pyridine (0.01 mL, 0.0108 mmol) in dry THF (2 mL). The mixture was stirred for 10 h. The precipitate that formed was filtered off, the solvent and excess of Me₃SiCl were removed *in vacuo* at 35 °C for 2 h. White crystalline compound **6** (0.056 g, 97%) was obtained. M.p. 86–87 °C. Found (%): C, 60.76; H, 5.6; Si, 20,14. C₅₄H₅₈O₉Si₈. Calculated (%): C, 60.23; H, 5.4; Si, 20.85. MALDI-TOF MS, found: *m/z* 1097.23 [M + Na]⁺ C₅₄H₅₈O₉Si₈Na; calculated: *m/z* 1097.21. Found: *m/z* 1113.20 [M + K]⁺. C₅₄H₅₈O₉Si₈K; calculated: *m/z*: 1113.18. ¹H NMR (CDCl₃), &: 0.18 (s, 18 H, SiMe₃); 7.05–7.77 (m, 40 H, Ph). IR (CCl₄), v/cm⁻¹: 1029–1040 (SiOSi cyclic); 1090 (SiOSi linear); 704, 726, 1129, 1595 (SiC_{Ph}), 855, 1260 (SiC_{Me}).

Bis(4,4,6,6-tetraphenylcyclotrisiloxan-2-yl) oxide (7). A solution of **2** (3.36 g, 7.05 mmol) in THF (3 mL) was added to a cooled (0 °C) mixture of H₂O (0.063 g, 3.5 mmol) and $(NH_4)_2CO_3$ (0.336 g, 3.5 mmol) in THF (3 mL) for 20 min. The mixture was stirred at room temperature for 9.5 h and the precipitate that formed was filtered off. The product was isolated by recrystallization from a mixture of THF and hexane. Colorless needle-like crystals of **7** (2.3 g, 73%) were obtained. M.p. 156–158 °C. Found (%) C, 64.20; H, 4.72; Si, 18.74. C₄₈H₄₂O₇Si₆. Calculated (%): C, 64.07; H, 4.67; Si, 18.74. MALDI-TOF MS, found: *m/z*: 921.16 [M + Na]⁺. C₄₈H₄₂O₇Si₆Na; calculated: *m/z* 937.11. ¹H NMR (CDCl₃), & 4.59 (s, 2 H, SiH); 7.00–7.77 (m, 40 H, Ph). IR (KBr), v/cm⁻¹: 1030, 1040 (SiOSi cyclic); 1090 (SiOSi linear); 702, 727, 1127, 1599 (SiC_{Ph}); 2249 (SiH).

15,15-Dichloro-2,2,4,4,10,10,12,12-octaphenyldispiro-[5.1.5.3]heptasiloxane (8). To a solution of **4** (0.48 g, 0.516 mmol) and *m*-nitroaniline (0.142 g, 1 mmol) in dry THF (2.5 mL) that was cooled to $-5 \,^{\circ}$ C, a solution of SiCl₄ (0.06 mL, 0.516 mmol) in dry THF (1 mL) was added with stirring. The reaction mixture was stirred for 3 h at room temperature. The precipitate that formed was filtered off and THF was completely removed. The product was isolated by crystallization from dry CCl₄. White crystals of **8** (0.32 g, 61%) were collected. M.p. 145–148 °C. MALDI-TOF MS, found: *m/z* 1029.08 [M + 3H]⁺. C₄₈H₄₃Cl₂O₉Si₇, calculated: *m/z* 1029.06. Found: *m/z* 1047.09 [M + 3 H + H₂O]⁺. C₄₈H₄₅Cl₂O₁₀Si₇, calculated: *m/z* 1047.07. Found: *m/z* 1065.08. IR (CCl₄), v/cm⁻¹: 1022, 1042 (SiOSi cyclic); 1129, 1486, 1599 (SiC_{Ph}).

Hydrolysis of dendron 8. To a cooled $(-3 \,^{\circ}\text{C})$ solution of water (0.4 g, 22 mmol) and $(\text{NH}_4)_2\text{CO}_3$ (1 g, 10.4 mmol) in THF (20 mL), a solution of **8** (1.15 g, 1.12 mmol) in dry THF (16 mL) was added for 2 h. The precipitate that formed was filtered off and the solvent was removed. A noncrystallizable mixture (1.04 g) of oligomers (in a ratio of 14.4 : 8.4 : 1 : 1.8, according to the GPC data) was obtained. According to the mass-spectral data, hydroxyl-containing condensation products are present, n = 1-4 (see Scheme 9).

15,15-Dihydroxy-2,2,4,4,10,10,12,12-octaphenyldispiro-[5.1.5.3]heptasiloxane (9, n = 1, 56.3%). MALDI-TOF MS, found: m/z 1013.12 [M + Na]⁺. C₄₈H₄₂O₁₁Si₇Na; calculated: m/z 1013.10. Found: m/z 1029.09 [M + K]⁺. C₄₈H₄₂O₁₁Si₇K; calculated: m/z 1029.07.

Compound 10 (n = 2, 32.7%**).** MALDI-TOF MS, found: m/z 1985.21 [M + Na]⁺. C₉₆H₈₂O₂₁Si₁₄Na; calculated: m/z 1985.19. Found: m/z 2001.19 [M + K]⁺. C₉₆H₈₂O₂₁S₁₄K; calculated: m/z 2001.17. Found: m/z 2003.22 [M + Na + H₂O]⁺. C₉₆H₈₄O₂₂Si₁₄Na; calculated: m/z 2003.20. Found: m/z 2021.24 [M + Na + 2 H₂O]⁺. C₉₆H₈₆O₂₃Si₁₄Na; calculated: m/z 2021.22.

Compound 11 (n = 3, 3.9%). MALDI-TOF MS, found: m/z: 2975.32 [M + Na + H₂O]⁺. C₁₄₄H₁₂₄O₃₂Si₂₁Na; calculated: m/z 2975.30. Found: m/z 2993.33 [M + Na + 2H₂O]⁺. C₁₄₄H₁₂₆O₃₃Si₂₁Na; calculated: m/z 2993.31.

Compound 12 (n = 4, 7.1%). MALDI-TOF MS, found: m/z: 3947.42 [M + Na + H₂O]⁺. C₁₉₂H₁₆₄O₄₂Si₂₈Na; calculated: m/z 3947.40. Found: m/z: 3965.44 [M + Na + 2 H₂O]⁺. C₁₉₂H₁₆₆O₄₃Si₂₈Na; calculated: m/z 3965.41.

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