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Synthesis of Ladder and Cage Silsesquioxanes from 1,2,3,4-Tetrahydroxycyclotetrasiloxane

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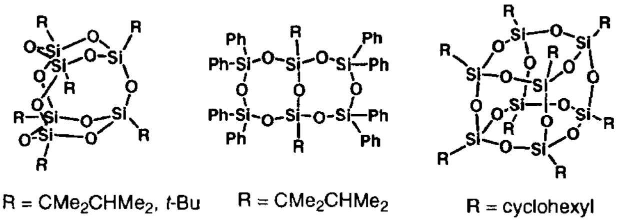
The versatility of *cis,cis,cis*-1,3,5,7-tetrahydroxy-1,3,5,7-tetraisopropylcyclotetrasiloxane (**1**) as a precursor of cage and ladder siloxanes is presented. Compound **1** reacted with 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane in pyridine to give 1,3,5,5,7,7,9,11,13,13,15,15-*cis-cisoid-cis*-dodecaisopropyltricyclo[9.5.1.1^{3,9}]octasiloxane (**2**) in 20% yield. The reaction proceeded with retention of the configuration of the silicon atoms, and only *syn*-type isomer was obtained. The reaction of **1** with 1,1,3,3-tetrachloro-1,3-diisopropyldisiloxane in pyridine produced hexakis(isopropylsilsesquioxane) (T_6) (**3**) in 25% yield. Treatment of **1** with dicyclohexylcarbodiimide (DCC) as dehydrating reagent led to the formation of octakis(isopropylsilsesquioxane) (T_8) (**4**) in 45% yield. The crystal structures of **2**, **3**, and **4** are reported.

In recent years, considerable attention has been directed to the chemistry of silanols and silsesquioxanes.[1] Silsesquioxane is the term for the compounds with formula $(RSiO_{1.5})_n$; they may form cage, ladder, and sheet-like oligomers and polymers. For this property, especially in the field of silicone industry, silsesquioxanes whose structures are well-defined have been highly demanded, for the sake of designing high performance materials. Previously, we reported the synthesis, structures, and properties of hexasilsesquioxanes ($R_6Si_6O_9$, R = 1,1,2-trimethylpropyl, *t*-Bu),[2a] bicyclic ladder siloxanes,[2b] and octasilsesquioxane ($R_8Si_8O_{12}$, R = cyclohexyl) (Scheme 1).[2b] Quite recently, we have also demonstrated the synthesis, X-ray structure, and properties of *cis,cis,cis*-1,3,5,7-tetrahydroxy-1,3,5,7-tetraisopropylcyclotetrasiloxane (**1**), and dehydration of **1** with dicyclohexylcarbodiimide (DCC) leading to octakis(isopropylsilsesquioxane).[3] The choice of substituents is very important for the synthesis of ladder and cage silsesquioxanes; if the substituents are too small, only polymeric compounds are obtained, while using bulky substituents reduces the reactivity and makes the reaction sluggish. We thought that isopropyl groups are adequate for this synthesis, and we are interested in examining the versatility of **1** as precursors of cage and ladder siloxanes. Here we report: 1) synthesis of 1,3,5,5,7,7,9,11,13,13,15,15-*cis-cisoid-cis*-dodecaisopropyltricyclo[9.5.1.1^{3,9}]octasiloxane (**2**) and hexakis(isopropylsilsesquioxane) (**3**) by the reaction of **1** with 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane and 1,1,3,3-tetrachloro-1,3-diisopropyldisiloxane, respectively (Scheme 2); 2) detailed experimental procedures for the synthesis of octakis(isopropylsilsesquioxane) (**4**); 3) structural properties of **2**, **3**, and **4** determined by X-ray crystallography.


R = CMe_2CHMe_2, *t*-Bu   R = CMe_2CHMe_2 R = cyclohexyl

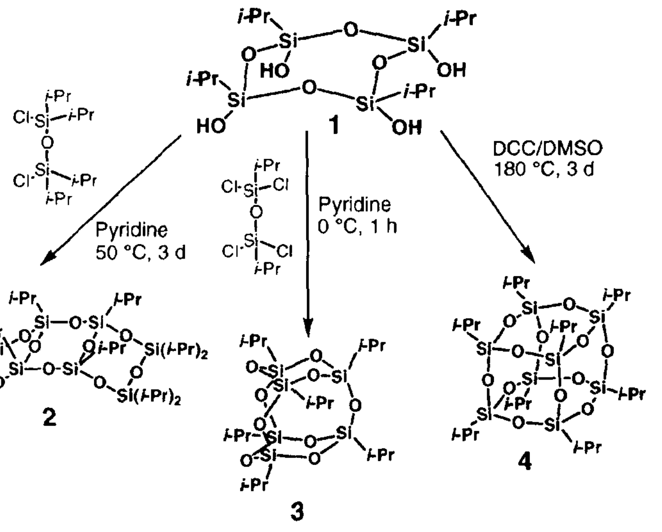
Scheme 1.

Results and Discussion

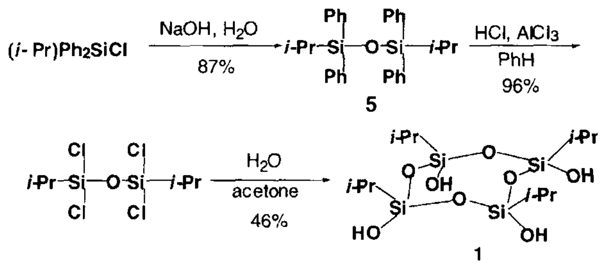
Preparation of *cis,cis,cis*-1,3,5,7-Tetrahydroxy-1,3,5,7-tetraisopropylcyclotetrasiloxane (1). In the previous paper,[3] we reported the three-step synthesis of **1** from chloro(isopropyl)diphenylsilane (Scheme 3), in which diisopropyltetraphenyldisiloxane (**5**) was prepared by hydrolysis of chlorosilane with NaOH in water/THF/benzene. This method, however, needed a very long reaction time (27 d, yield 66%). But we found the reaction in refluxing aqueous NaOH gave **5** in 7 d, and yield was 87%. The next two steps are identical to those previously reported.

In the previous paper, we described that we could not succeed in the one step synthesis of **1** from trichloroisopropylsilane.[3] However, careful control of the reaction conditions has made it possible to prepare **1** in one step (Scheme 4). Thus, an acetone solution of trichloroisopropylsilane was added to water at 0 °C for 30 min; then the solution was stirred at 0 °C for 21 h, and for 5 d at room temperature. Compound **1** was then isolated in 22% yield as a colorless solid.

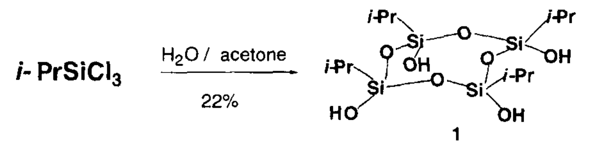
Synthesis of Tricyclic Ladder Siloxane 2 from 1. In 1965, Brown et al. reported the synthesis of *syn*-tricyclic ladder siloxane, $Me_8Ph_4Si_8O_{10}$,[4] and Shklover determined the structure in 1978.[5] For the *anti*-isomer, Shklover reported the structure in 1981.[6b] They prepared these ladder siloxanes by the reactions of 1,3,5,7-tetrahydroxy-1,3,5,7-tetraphenylcyclotetrasiloxane and dichlorodimethylsilane in the presence of stoichiometric amounts of pyridine.[6] We found that **1** is a convenient precursor of ladder siloxanes, and we performed



Scheme 2.



Scheme 3.



Scheme 4.

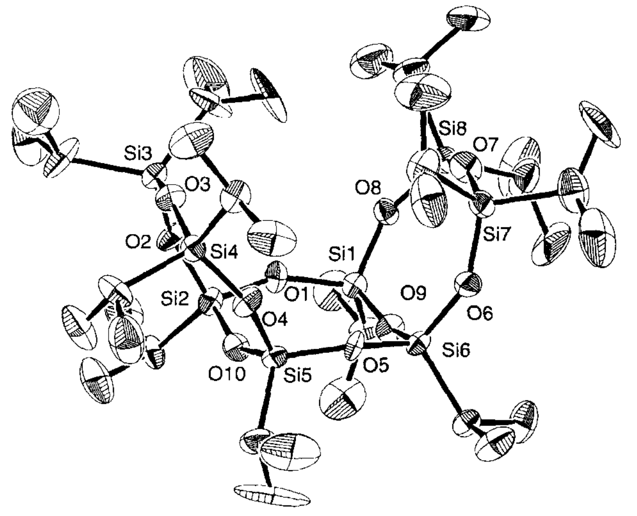


Fig. 1. ORTEP drawing of **2**. Thermal ellipsoids are drawn at the 30% probability level.

the reaction of **1** with 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane in pyridine. Tricyclooctasiloxane **2** was obtained in 20% isolated yield (Scheme 2). Compound **1** is stable enough to survive in pyridine solution. That is in striking contrast to phenyl-substituted cyclic silanols; Feher et al. reported that the tetraphenylcyclotetrasiloxanetetraol had showed a rapid decomposition in the presence of pyridine.[7] Our case is the first result of the ladder siloxane with single substituents.

The structure of **2** was determined unequivocally by X-ray crystallography. The ORTEP drawing is shown in Fig. 1. Crystallographic data, selected bond lengths and angles are given in Tables 1 and 2. This compound crystallized in $P2_1/n$ space group, and no symmetric elements existed. The average Si–O bond length was 1.621 Å, and the average Si–O–Si bond angle was 153.0°; the average O–Si–O angle was 109.2°. All these values are within the normal range, showing that this molecule is strain-free. It is noteworthy that only *syn*-form ladder siloxane was obtained. This fact indicates that the configuration around Si atoms was retained in this reaction condition. The structural parameters of **2** (e.g., Si–O bond lengths, Si–O–Si angles, O–Si–O angles) are similar with those for ladder siloxanes previously reported.

Synthesis of Cage Silsesquioxane from 1. Essentially, the same reaction procedure as that in the previous section was applied. The reaction of **1** with tetrachlorodiisopropyldisiloxane in pyridine gave hexasilsesquioxane (T_6) **3** in 25% yield (Scheme 2). Until now, six hexasilsesquioxanes were reported and their crystal structures have been determined. Mollow et al. reported the structure of hexa(cyclohexylsilsesquioxane).[8] They followed the preparation reported by Brown in 1965.[9] The structures of two hexasilicate ($(Me_4N)_6Si_6O_{15}$ and $([Ni(NH_2C_2H_4NH_2)_3]_3Si_6O_{15})$ was also reported,[10] and Hoebbel reported hexakis(trimethylsilyloxysilsesquioxane) prepared from these silicates.[11] We have synthesized hexakis(1, 1, 2-trimethylpropylsilsesquioxane) and hexakis(*t*-butylsilsesquioxane) by the reaction of silanol with DCC, which shortened the reaction time compared with the previously reported methods.[2c] As shown in these cases, construction of T_6 structure usually needs bulky substituents. The synthesis of **3** shown here is the first example to prepare

Table 1. Crystallographic Data for **2**, **3**, and **4**

	2	**3**	**4**
		Crystal data	
Formula	$C_{36}H_{84}O_{10}Si_8$	$C_{18}H_{42}O_9Si_6$	$C_{24}H_{56}O_{12}Si_8$
Mol wt	901.74	571.04	761.38
Cryst. descript	Colorless prism	Colorless prism	Colorless prism
Cryst. size/mm	0.40 × 0.40 × 0.40	0.40 × 0.40 × 0.40	0.50 × 0.50 × 0.30
Cryst. syst.	Monoclinic	Monoclinic	Trigonal
Space group	$P2_1/n$	$P2_1/m$	$R\bar{3}$
a/Å	11.146(5)	9.772(2)	15.372(3)
b/Å	36.663(8)	14.766(5)	
c/Å	13.526(2)	10.844(2)	15.233(4)
β/deg	100.620(9)	93.14(2)	
V/Å^3	5432.9600	1562.4(6)	3117(1)
Z	4	2	3
		Data collection	
Diffractometer	Rigaku RAXIS-IV	Rigaku AFC7S	Rigaku AFC7S
Radiation (λ/Å)	Mo$K\alpha$ (0.71070)	Mo$K\alpha$ (0.71070)	Cu$K\alpha$ (1.54178)
Monochromator	Graphite	Graphite	Graphite
Temperature/°C	−100	20	20
μ/cm^{-1}	2.40	3.05	28.51
No. of rflns measd	7458	3941	1144
No. of ind reflns	7458	3733	1034
No. of obsd reflns	3806	1719	802
	$I > 3\sigma(I)$	$I > 2\sigma(I)$	$I > 3\sigma(I)$
No. of params	491	166	82
		Refinement	
R	0.081	0.060	0.061
R_w	0.058	0.055	0.063
$(\Delta/\sigma)_{max}$	0.33	0.00	0.02
$(\Delta/\rho)_{max}$/e Å^{-3}	0.49	0.25	0.21
$(\Delta/\rho)_{min}$/e Å^{-3}	−0.46	−0.28	−0.21

the cage silsesquioxane from two different starting materials, which enabled us to construct the T_6 skeleton exclusively. In addition, it is also possible to prepare the T_6 with different substituents. The structure was confirmed by X-ray crystallography; the ORTEP drawing is shown in Fig. 2; crystallographic data, selected bond lengths and angles are given in Tables 1 and 3. This compound crystallized in $P2_1/m$ space group, and the symmetry plane passed through Si(1), O(1), Si(2), O(5), O(6) atoms. The average Si–O bond length was 1.631(5) Å; this value is similar to that of $(CySiO_{1.5})_6$ (1.634(8) Å, Cy = cyclohexyl).[8]

When **1** was treated with dicyclohexylcarbodiimide (DCC), octasilsesquioxane (T_8) **4** was obtained in 45% yield, as previously reported (Scheme 2).[3] The relatively good yield for **4** can be explained by the fact that the starting material (**1**) is all-*cis* form and suitable for the construction of cage silsesquioxane. Here we show the detailed structural data. The ORTEP drawing is shown in Fig. 3. Crystallographic data, selected bond lengths and angles are given in Tables 1 and 4. As T_8 is a common structure for cage silsesquioxanes, many structural reports have appeared so far.[1b] However, no results dealing T_6 and T_8 with same substituents have appeared to our best knowledge. Here we can compare the difference of the structure of the skeleton, excluding the effects due to substituents. The average Si–O bond length of T_8 was 1.610(9) Å, and slightly shorter than that of T_6 (1.631(5) Å). This is the result of greater steric repulsion of substituents in T_6. Thus, the average Si–O length for six-membered ring in T_6 was 1.634(5) Å, or even longer. The average Si–O–Si bond angles for T_8 were 149.5(6)°, and for T_6, they were 130.3(3)° for six-membered ring and 139.1(3)° for eight-membered ring. On the other hand, average O–Si–O bond angles were 108.1(2)° for T_6 and 108.9(10)° for T_8, and they are similar to each other. These results show that the different ring size mostly affected Si–O–Si bond angles, and other values are basically similar.

In summary, here we showed the new synthetic methods for ladder and cage silsesquioxanes from tetrahydroxytetraisopropylcyclotetrasiloxane (**1**). This method is suitable for the preparation with variable-size compounds (e.g., T_6, T_8, and tricyclic ladder siloxane) starting from the same starting material.

Experimental

Preparation of 1,3-Diisopropyl-1,1,3,3-tetraphenyldisiloxane (5): Chloroisopropyldiphenylsilane (100 g, 0.38 mol) was added to aqueous NaOH (20%, 200 ml) in a plastic Erlenmeyer flask equipped with a condenser. The mixture was heated to reflux.

Table 2. Selected Bond Lengths and Distances of **2**

Bond lengths			
Si(1)–O(1)	1.612(6)	Si(1)–O(8)	1.618(7)
Si(1)–O(9)	1.610(6)	Si(1)–C(1)	1.81(1)
Si(2)–O(1)	1.636(6)	Si(2)–O(2)	1.602(7)
Si(2)–O(10)	1.624(6)	Si(2)–C(4)	1.825(9)
Si(3)–O(2)	1.616(6)	Si(3)–O(3)	1.608(6)
Si(3)–C(7)	1.88(1)	Si(3)–C(10)	1.87(1)
Si(4)–O(3)	1.648(6)	Si(4)–O(4)	1.615(7)
Si(4)–C(13)	1.85(1)	Si(4)–C(16)	1.85(1)
Si(5)–O(4)	1.615(6)	Si(5)–O(5)	1.613(6)
Si(5)–O(10)	1.628(6)	Si(5)–C(19)	1.84(1)
Si(6)–O(5)	1.622(6)	Si(6)–O(6)	1.607(6)
Si(6)–O(9)	1.626(6)	Si(6)–C(22)	1.86(1)
Si(7)–O(6)	1.643(6)	Si(7)–O(7)	1.617(6)
Si(7)–C(25)	1.86(1)	Si(7)–C(28)	1.86(1)
Si(8)–O(7)	1.636(6)	Si(8)–O(8)	1.616(6)
Si(8)–C(31)	1.89(1)	Si(8)–C(34)	1.90(1)
Bond angles			
O(1)–Si(1)–O(8)	107.4(4)	O(1)–Si(1)–O(9)	109.2(3)
O(1)–Si(1)–C(1)	110.2(4)	O(8)–Si(1)–O(9)	109.6(3)
O(8)–Si(1)–C(1)	110.8(4)	O(9)–Si(1)–C(1)	109.5(4)
O(1)–Si(2)–O(2)	108.5(3)	O(1)–Si(2)–O(10)	109.3(3)
O(1)–Si(2)–C(4)	111.4(4)	O(2)–Si(2)–O(10)	110.6(3)
O(2)–Si(2)–C(4)	109.4(5)	O(10)–Si(2)–C(4)	107.6(4)
O(2)–Si(3)–O(3)	109.5(4)	O(2)–Si(3)–C(7)	107.4(4)
O(2)–Si(3)–C(10)	109.3(6)	O(3)–Si(3)–C(7)	108.2(5)
O(3)–Si(3)–C(10)	106.9(4)	C(7)–Si(3)–C(10)	115.4(7)
O(3)–Si(4)–O(4)	109.9(3)	O(3)–Si(4)–C(13)	106.7(5)
O(3)–Si(4)–C(16)	106.2(4)	O(4)–Si(4)–C(13)	110.6(5)
O(4)–Si(4)–C(16)	107.9(4)	C(13)–Si(4)–C(16)	115.3(5)
O(5)–Si(5)–O(10)	109.7(3)	O(5)–Si(5)–C(19)	110.9(5)
O(10)–Si(5)–C(19)	110.4(5)	O(4)–Si(5)–O(5)	108.0(3)
O(4)–Si(5)–O(10)	108.7(4)	O(4)–Si(5)–C(19)	109.1(5)
O(5)–Si(6)–O(6)	109.0(4)	O(5)–Si(6)–O(9)	107.8(4)
O(5)–Si(6)–C(22)	112.2(4)	O(6)–Si(6)–C(22)	108.6(4)
O(9)–Si(6)–C(22)	109.2(4)	O(6)–Si(6)–O(9)	110.1(3)
O(6)–Si(7)–O(7)	109.3(3)	O(6)–Si(7)–C(25)	109.6(5)
O(6)–Si(7)–C(28)	109.6(6)	O(7)–Si(7)–C(25)	106.7(5)
C(25)–Si(7)–C(28)	114.9(6)	O(7)–Si(7)–C(28)	106.6(5)
O(7)–Si(8)–O(8)	109.8(3)	O(7)–Si(8)–C(31)	107.5(5)
O(7)–Si(8)–C(34)	106.5(5)	O(8)–Si(8)–C(31)	111.2(5)
O(8)–Si(8)–C(34)	107.9(5)	C(31)–Si(8)–C(34)	113.8(6)
Si(1)–O(1)–Si(2)	147.9(4)	Si(2)–O(2)–Si(3)	157.0(4)
Si(3)–O(3)–Si(4)	156.4(5)	Si(4)–O(4)–Si(5)	154.1(5)
Si(5)–O(5)–Si(6)	148.0(4)	Si(6)–O(6)–Si(7)	148.9(5)
Si(7)–O(7)–Si(8)	157.9(5)	Si(1)–O(8)–Si(8)	150.6(4)
Si(1)–O(9)–Si(6)	157.0(5)	Si(2)–O(10)–Si(5)	152.5(4)

Additional NaOH (5 g×5 times) was added, and the starting material disappeared after 7 d. Benzene (150 ml) was added to the reaction mixture and the organic layer was washed with water (150 ml). The aqueous phase was extracted three times with benzene. The combined organic phase was dried over anhydrous magnesium sulfate and evaporated. The residue was recrystallized from ethanol to give **5** (77.4 g, 87%). **5**: Colorless crystals, mp 93—95 °C; ^{1}HNMR (CDCl$_3$) $\delta = 0.97$ (d, 12 H, $J = 7.4$ Hz), 1.40 (sep, 2H, $J = 7.4$ Hz), 7.28 (t, 8H), 7.37 (t, 4H), 7.49 (d, 8H); ^{13}C NMR (CDCl$_3$) $\delta = 13.69$, 17.13, 127.51, 129.45, 134.97, 135.27; ^{29}Si NMR (CDCl$_3$) $\delta = -14.20$; MS (70 eV) *m/z* (%) 423 (M$^+$–*i*-Pr; 100); IR (KBr) 3067, 2997, 2959, 2941, 2922, 2887, 2862, 2851, 2000—1650, 1485, 1460, 1427, 1383, 1364, 1111, 1084, 1069, 1028, 991, 918, 881, 739, 71 4, 700, 635 cm^{-1}. Anal. Found: C, 77.18; H, 7.35%. Calcd for C$_{12}$H$_{32}$O$_8$Si$_4$: C, 77.20, H, 7.34%.

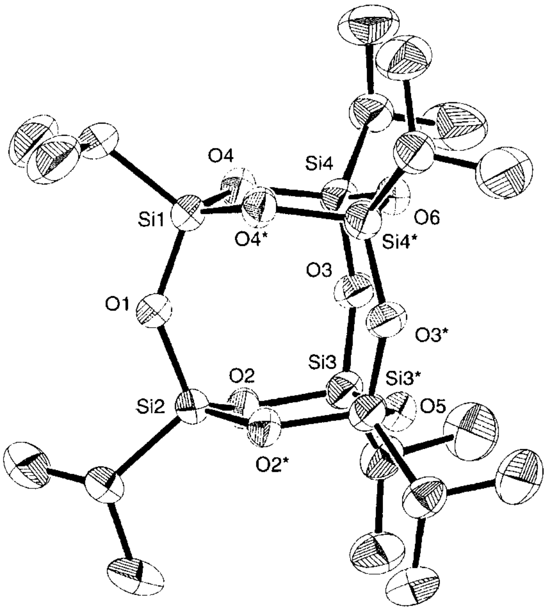


Fig. 2. ORTEP drawing of **3**. Thermal ellipsoids are drawn at the 30% probability level.

Table 3. Selected Bond Lengths and Distances of **3**

Bond lengths			
Si(1)–O(1)	1.618(5)	Si(1)–O(4)	1.637(4)
Si(1)–C(1)	1.824(9)	Si(2)–O(1)	1.641(5)
Si(2)–O(2)	1.633(4)	Si(2)–C(3)	1.826(9)
Si(3)–O(2)	1.631(4)	Si(3)–O(3)	1.617(4)
Si(3)–O(5)	1.633(3)	Si(3)–C(6)	1.840(6)
Si(4)–O(3)	1.628(4)	Si(4)–O(4)	1.628(4)
Si(4)–O(6)	1.640(3)	Si(4)–C(9)	1.810(7)
Bond angle			
O(1)–Si(1)–O(4)	109.0(2)	O(1)–Si(1)–C(1)	110.1(3)
O(4)–Si(1)–O(4*)	106.5(2)	O(4)–Si(1)–C(1)	111.1(2)
O(1)–Si(2)–O(2)	108.8(2)	O(2)–Si(2)–O(2*)	106.2(2)
O(1)–Si(2)–C(3)	110.0(4)	O(2)–Si(2)–C(3)	111.5(2)
O(2)–Si(3)–O(3)	108.5(2)	O(2)–Si(3)–O(5)	106.4(2)
O(3)–Si(3)–O(5)	109.0(2)	O(2)–Si(3)–C(6)	111.7(2)
O(3)–Si(3)–O(6)	108.5(2)	O(5)–Si(3)–C(6)	110.6(3)
O(3)–Si(4)–O(4)	109.0(2)	O(3)–Si(4)–O(6)	108.5(2)
O(3)–Si(4)–C(9)	110.3(3)	O(4)–Si(4)–O(6)	106.3(2)
O(4)–Si(4)–C(9)	110.7(3)	O(6)–Si(4)–C(9)	111.9(3)
Si(1)–O(1)–Si(2)	139.4(3)	Si(1)–O(2)–Si(3)	130.5(2)
Si(3)–O(3)–Si(4)	138.9(2)	Si(1)–O(4)–Si(4)	130.1(2)
Si(3)–O(5)–Si(3*)	130.5(3)	Si(4)–O(6)–Si(4*)	130.6(3)

Preparation of 1,1,3,3-Tetrachloro-1,3-diisopropyldisiloxane. To a solution of **5** (28.5 g, 61 mmol) and anhydrous aluminum chloride (1.12 g, 8.4 mmol) in benzene (150 ml) was passed hydrogen chloride for 1 h at room temperature. Acetone (2 ml) was added to the reaction mixture to quench aluminum chloride, and argon gas was bubbled. After filtration of the solid, the filtrate was concentrated and distilled under reduced pressure to give tetrachlorodiisopropyldisiloxane (17.6 g, 96%). (*i*-PrSiCl$_2$)$_2$ O: Colorless

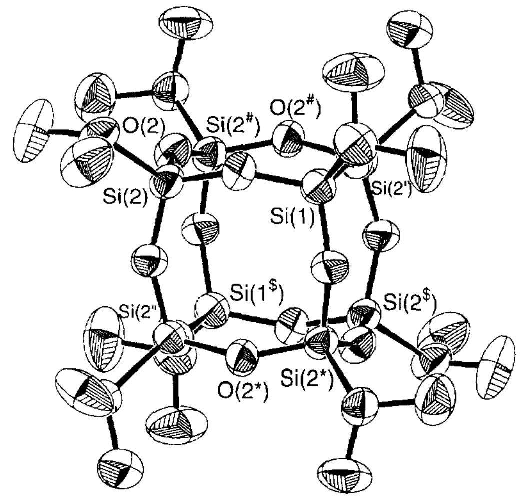


Fig. 3. ORTEP drawing of **4**. Thermal ellipsoids are drawn at the 30% probability level.

Table 4. Selected Bond Lengths and Distances of **4**

Bond lengths			
Si(1)–O(1)	1.613(4)	Si(1)–C(1)	1.85(1)
Si(2)–O(1)	1.607(4)	Si(2)–O(2)	1.612(4)
Si(2)–O(2″)	1.609(4)	Si(2)–C(3)	1.826(7)
Bond angles			
O(1)–Si(1)–O(1*)	108.9(2)	O(1)–Si(1)–C(1)	110.0(1)
Si(2)–O(2)–Si(2#)	149.4(2)	O(1)–Si(2)–O(2)	108.7(2)
O(1)–Si(2)–O(2″)	108.9(2)	O(2)–Si(2)–O(2″)	109.1(2)
O(1)–Si(2)–C(3)	110.4(3)	O(2)–Si(2)–C(3)	109.8(2)
O(2″)–Si(2)–C(3)	109.9(3)	Si(1)–O(1)–Si(2)	149.6(3)

liquid, bp 98 °C/19 mmHg (1 mmHg = 133.322 Pa); ^{1}H NMR ($CDCl_3$) δ = 1.14 (d, 12H, J = 7.3 Hz), 1.37 (sept, 2H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ = 15.71, 19.27; ^{29}Si NMR ($CDCl_3$) δ = – 13.77; MS (70 eV) m/z (%) 300 (M^+; 2), 257 (78), 229 (100); IR (NaCl) 2968, 2959, 2936, 2899, 2876, 1466, 1391, 1371, 1252, 1165, 1107, 1069, 1003, 926, 883, 681, 656, 586 cm^{-1}. HRMS (30 eV) Found: m/z 297.9331. Calcd for $C_6H_{14}Si_2OCl_4$: M, 297.9337.

Synthesis of *cis,cis,cis*-1,3,5,7-Tetrahydroxy-1,3,5,7-tetraisopropylcyclotetrasiloxane (1) from 1,1,3,3-Tetrachloro-1,3-diisopropyldisiloxane: Tetrachlorodiisopropyldisiloxane (10.0 g, 33 mmol) in acetone (24 ml) was added dropwise to water (277 ml) at 0 °C for 105 min. The mixture was stirred at 0 °C for 16 h, then warmed to room temperature and stirred for 4 d. The generated solid was filtered, washed with benzene, and dried under reduced pressure to give **1** (3.14 g, 46%). **1**: Colorless crystals, mp 165—169 °C; ^{1}H NMR (DMSO-d_6) δ = 0.70 (sept, 4H, J = 7.3 Hz), 0.95 (d, 24H, J = 7.3 Hz), 6.26 (s, 4H); ^{13}C NMR (DMSO-d_6) δ = 12.46, 17.38; ^{29}Si NMR (DMSO-d_6) δ = – 59.66; MS (70 eV) m/z (%) 373 (M^+–i-Pr; 4), 355 (100); IR (NaCl) 3225, 2959, 2945, 2897, 2868, 1464, 1385, 1366, 1258, 1165, 1113, 1067, 1003, 910, 897, 887, 876, 864, 723, 654, 586 cm^{-1}. Anal. Found: C, 34.65; H, 7.83%. Calcd for $C_{12}H_{32}O_8Si_4$: C, 34.59, H, 7.74%.

Synthesis of *cis,cis,cis*-1,3,5,7-Tetrahydroxy-1,3,5,7-tetraisopropylcyclotetrasiloxane (1) from Trichloroisopropylsilane: Trichloroisopropylsilane (7.07 g, 40 mmol) in acetone (33 ml) was added dropwise to water (400 ml) at 0 °C for 30 min. The mixture was stirred at 0 °C for 21 h, then warmed to room temperature and stirred for 5 d. The generated solid was filtered, washed with benzene, and dried under reduced pressure to give **1** (0.931 g, 22%).

Synthesis of Tricyclic Ladder Siloxane 2. 1,3-Dichloro-1,1,3,3-tetraisopropyldisiloxane was prepared by the reported methods.[12] This compound (1.26 g, 4.0 mmol) was added dropwise to a solution of **1** (0.42 g, 1.0 mmol) in pyridine (10 ml) at room temperature over 5 min. The mixture was stirred for 35 min, then warmed to 50 °C and stirred for 3 d. Hexane (30 ml) was added to the reaction mixture and the organic layer was washed with water (30 ml). The aqueous phase was extracted three times with hexane. The combined organic phase was dried over anhydrous magnesium sulfate and evaporated. The residue was recrystallized from methanol to give tricyclic ladder siloxane **2** (0.18 g, 20%). 1,3,5,5,7,7,9,11,13,13,15,15-*cis-cisoid-cis*-Dodecaisopropyltricyclo[9.5.1.1^{3,9}]-octasiloxane (**2**): Colorless crystals, mp 196—197 °C. ^{1}H NMR ($CDCl_3$) δ = 0.83—0.95 (overlap, m, 12H), 1.01—1.04 (overlap, m, 72H); ^{13}C NMR ($CDCl_3$) δ = 12.76, 14.08, 14.72, 16.99, 17.15, 17.26, 17.41, 17.41, 17.45;[13] ^{29}Si NMR ($CDCl_3$) δ = – 67.09, –23.64; MS (70 eV) m/z (%) 857 (M^+–i-Pr; 41); IR (KBr) 2959, 2945, 2893, 2868, 1466, 1387, 1364, 1258, 1163, 1099, 1065, 1013, 1001, 993, 885, 727, 706, 692, 559 cm^{-1}. Anal. Found: C, 47.04; H, 9.34%. Calcd for $C_{24}H_{56}O_{12}Si_8$: C, 47.95, H, 9.39%.

Synthesis of Hexakis(isopropylsilsesquioxane) (3): Under a nitrogen atmosphere, **1** (0.42 g, 1.0 mmol) was dissolved in 10 ml of pyridine. Tetrachlorodiisopropyldisiloxane (0.30 g, 1.0 mmol) was added dropwise at 0 °C. The mixture was stirred for 1 h and water and hexane was added to the mixture. The organic phase was separated and an aqueous phase was extracted three times with hexane. The combined organic phase was dried over anhydrous magnesium sulfate and concentrated. The residue was triturated from methanol to give 0.14 g (25%) of **3**. 1,3,5,7,9,11-hexaisopropyltetracyclo[5.5.1.1^{3,11}.1^{5,9}]hexasiloxane (**3**): Colorless crystals, mp 140—141 °C; ^{1}H NMR ($CDCl_3$) δ = 0.98 (sept, 6H, J = 6.8 Hz), 1.04 (d, 36H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ = 11.15, 16.37; ^{29}Si NMR ($CDCl_3$) δ = – 54.16; MS (70 eV) m/z (%) 527 (M^+–i-Pr; 100); IR (NaCl) 2959, 2868, 1466, 1385, 1366, 1259, 1165, 1084, 1051, 1003, 922, 889, 789, 745, 611, 560 cm^{-1}. Anal. Found: C, 37.62; H, 7.49%. Calcd for $C_{18}H_{42}O_9Si_6$: C, 37.86, H, 7.41%.

Synthesis of Octakis(isopropylsilsesquioxane) (4): In a two-necked flask were placed **1** (1.25 g 3.00 mmol), DCC (2.04 g, 9.90 mmol), and DMSO (15 ml), and the solution was heated to 180 °C for 3 d. Benzene (15 ml) was added to the mixture, and the resulting dicyclohexylurea was removed by filtration. The filtrate was washed with water (60 ml), and the aqueous phase was extracted three times with hexane. The combined organic phase was dried over anhydrous magnesium sulfate and evaporated. The resulting semisolid was triturated with acetone to give octakis(isopropylsilsesquioxane) (**4**) (0.52 g, 45%). The other portion of reaction was collected and analyzed by GPC, and found to be polymeric compounds (39%). 1,3,5,7,9,11,13,15-octaisopropylpentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (**4**): Colorless crystals, mp 193 °C (sublimed), 243—246 °C (sealed); ^{1}H NMR ($CDCl_3$) δ = 0.87 (sept, 8H, J = 7.3 Hz), 1.01 (d, 48H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ = 11.50, 16.76; ^{29}Si NMR ($CDCl_3$) δ = – 66.26; MS (70 eV) m/z (%) 717 (M^+–i-Pr, 100), 675 (9); IR (KBr) 2959, 2947, 2932, 2895, 2868, 1466, 1385, 1364, 1258, 1165, 1105, 1070, 1005, 922, 889, 716, 557 cm^{-1}. Anal. Found: C, 37.86; H, 7.49%. Calcd for $C_{24}H_{56}O_{12}Si_8$: C, 37.86, H, 7.41%.

X-Ray Crystallography of 2: Colorless crystals of **2** were obtained from ethanol/hexane by slow evaporation. A colorless plate crystal having approximate dimensions of 0.4×0.4×0.4 mm was mounted on a capillary and measured by a Rigaku RAXIS-IV imaging plate diffractometer with Mo$K\alpha$ radiation (λ = 0.71069 Å) at -100 ± 1 °C. The structure was solved by SHELXS86.[14] The data were corrected for Lorenz and polarization effects. A correction for secondary extinction was applied. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 3806 observed reflections ($I > 3\sigma(I)$) and 491 variable parameters and converged (largest parameter shift was 0.33 times its esd) with weighted agreement factors of R = 0.081, and R_w = 0.058.

X-Ray Crystallography of 3: Colorless crystals of **3** were obtained from pentane/acetone by slow evaporation. A colorless plate crystal having approximate dimensions of 0.4×0.4×0.4 mm was mounted on a capillary and measured by a Rigaku AFC-7S diffractometer with Mo$K\alpha$ radiation (λ = 0.71069 Å) at 20 ± 1 °C using ω–2θ scan technique to a maximum 2θ value of 55.0°. The structure was solved by SIR92.[15] An empirical absorption correction using the program DIFABS[16] was applied, which resulted in transmission factors ranging from 0.44 to 1.00. The data were corrected for Lorenz and polarization effects. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1719 observed reflections ($I > 2\sigma(I)$) and 166 variable parameters and converged (largest parameter shift was 0.002 times its esd) with weighted agreement factors of R = 0.060, and R_w = 0.055.

X-Ray Crystallography of 4: Colorless crystals of **4** were obtained from hexane by slow evaporation. A colorless plate crystal having approximate dimensions of 0.5×0.5×0.3 mm was mounted on a capillary and measured by a Rigaku AFC-7S diffractometer with Cu$K\alpha$ radiation (λ = 1.54178 Å) at 15 ± 1 °C using ω–2θ scan technique to a maximum 2θ value of 55.0°. The structure was solved by SHELXS86.[14] The data were corrected for Lorenz and Polarization effects. An empirical absorption correction using the program DIFABS[16] was applied, which resulted in transmission factors ranging from 0.29 to 1.00. A correction for secondary extinction was applied. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 802 observed reflections ($I > 3\sigma(I)$) and 82 variable parameters and converged (largest parameter shift was 0.02 times its esd) with weighted agreement factors of R = 0.061, and R_w = 0.063.

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