Synthesis, Structure, and Reaction of the Tetrahydroxycyclotetrasiloxane, $[(i\text{-Pr})(OH)SiO]_4$

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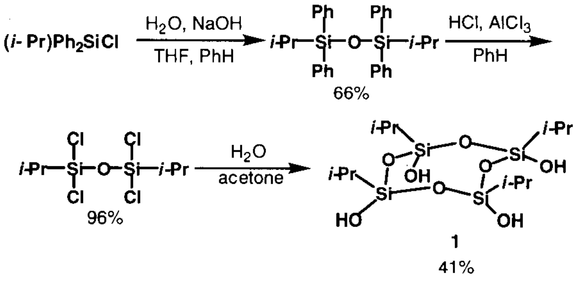
cis,cis,cis-1,3,5,7-Tetrahydroxy-1,3,5,7-tetraisopropylcyclotetrasiloxane (**1**) was synthesized. The X-ray crystallography of **1** revealed that four molecules of **1** and four molecules of water compose a cluster in the lattice. Dehydration of **1** with *N,N'*-dicyclohexylcarbodiimide (DCC) gave octa(isopropylsilsesquioxane) in good yield.

Recently, silsesquioxanes have been attracting growing interest, especially as cage compounds. Previously, we reported the synthesis of cage and ladder silsesquioxanes from silanetriols or 1,1,3,3-disiloxanetetraols using DCC as the dehydrating reagent.[1] We have thus commenced to study the synthesis of polyhydroxycyclopolysiloxane of the type $[R(HO)SiO]_n$ with the objective that they can serve as the starting materials for the cage and ladder polysiloxanes. For tetrahydroxycyclotetrasiloxane, $(c\text{-}C_6H_{11})_4Si_4O_4(OH)_4$[2] and $Ph_4Si_4O_4(OH)_4$[3] were reported in 1965, however, no crystal structure has been reported. In the latter case, they showed that the reaction from $Ph_4Si_4O_4(OH)_4$ gave ladder-type siloxanes, but no transformation to the cage siloxanes has been reported until now. Rebrov et al. indicated the generation of cyclic siloxane as an intermediate of the cage siloxanes, but it was not isolated.[4] We herein report the synthesis, X-ray structure, and the reaction of the novel tetrahydroxycyclotetrasiloxane, *cis,cis,cis*-1,3,5,7-tetrahydroxy-1,3,5,7-tetraisopropylcyclotetrasiloxane (**1**).

The preparation of compound **1** was performed as shown in Scheme 1.[5] The treatment of (isopropyl)diphenylchlorosilane with aqueous NaOH solution in THF/benzene (1/1.3) afforded 1,3-diisopropyl-1,1,3,3-tetraphenyldisiloxane in 66% yield. The obtained disiloxane was allowed to react with gaseous HCl in the presence of $AlCl_3$ in benzene to produce 1,1,3,3-tetrachloro-1,3-diisopropyldisiloxane in 96% yield. Tetrahydroxycyclotetrasiloxane **1** was synthesized by dropwise adding the tetrachlorodisiloxane in acetone to water at 0 °C for 15 min. The mixture was stirred at 0 °C for 12 h, then warmed to room temperature and stirred for 4 d. The generated solid was filtered and recrystallization from benzene/hexane/water gave **1** in 41% yield.[6] The NMR (^{1}H, ^{13}C{^{1}H}, and ^{29}Si{^{1}H}) spectra of **1** disclosed that all the isopropyl groups and four silicon atoms were equivalent; the results indicate that **1** exists as a single isomer.



Scheme 1.

The structure was established by X-ray crystallography. The crystal obtained from the recrystallization from benzene/hexane/water (2/1/1) was subjected to X-ray analysis in the presence of water in a sealed capillary.[7] The molecular structure is shown in Figure 1, and all isopropyl groups occupy *cis,cis,cis* positions. In the Si_4O_4 framework, the average Si–O bond length was 1.593(9) Å and average Si–O–Si and O–Si–O bond angles were 152.7(6)° and 110.4(5)°, respectively. For the hydroxyl groups, the average Si–O bond length was 1.60(1) Å and average O–Si–O bond angle was 109.3(5)°. The molecule has a folded structure.

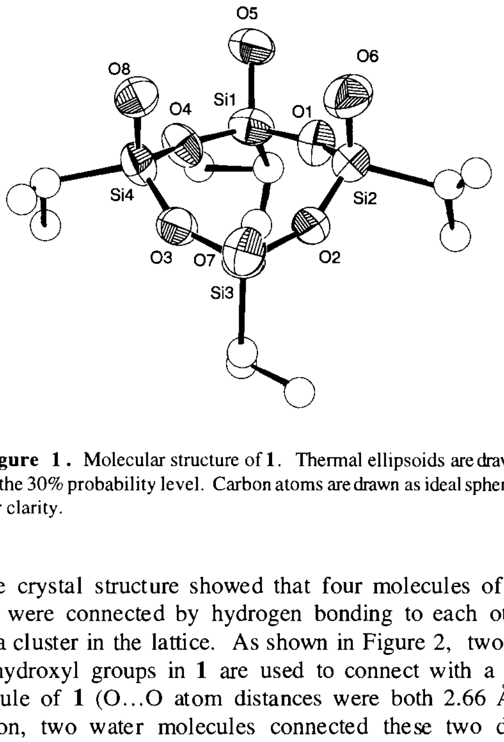


Figure 1. Molecular structure of **1**. Thermal ellipsoids are drawn in the 30% probability level. Carbon atoms are drawn as ideal spheres for clarity.

The crystal structure showed that four molecules of **1** and water were connected by hydrogen bonding to each other to form a cluster in the lattice. As shown in Figure 2, two of the four hydroxyl groups in **1** are used to connect with a second molecule of **1** (O...O atom distances were both 2.66 Å). In addition, two water molecules connected these two dimeric species **1** to form a cluster (O...O atom distances were 2.63, 2.77, 2.78, and 2.96 Å). The distances of the O...O atoms indicate hydrogen bonding (shown by the dotted lines in Figure 2). The molecular packing of **1** showed that the hydrophilic part is surrounded by the hydrophobic part consisting of isopropyl groups, and these clusters are located in the lattice like molecules. The intermolecular hydrogen bonding was observed in several silanols,[8] however, **1** is the first example having the crystal structure of the cyclic tetrasiloxane, and also the first observation of the silanol clusters connected to water.

So far as we know, there are no examples of the preparation of silsesquioxanes from cyclic silanols. Taking advantage of the observed all-*cis* configuration of **1**, we attempted to convert **1** to the octasilsesquioxane with the previously described method.[1] Thus, **1** was treated with DCC in DMSO at 180 °C for 3 d to give octasilsesquioxane **2** as a colorless solid. The yield was

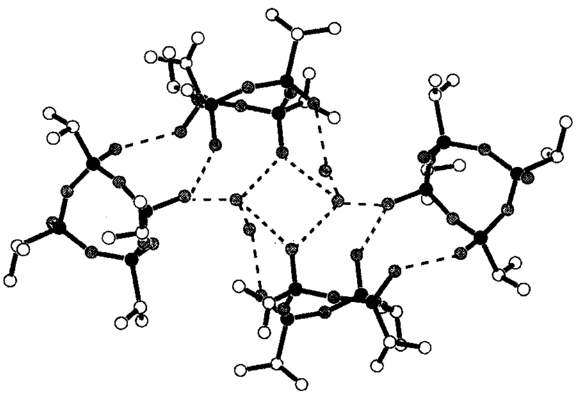
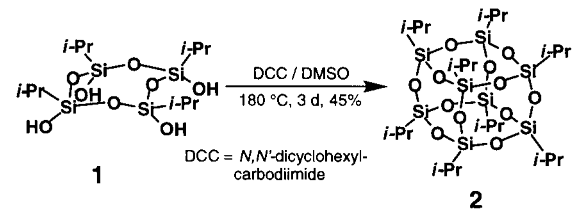


Figure 2. Molecular Packing of **1**. Dotted lines indicate possible hydrogen bonding. Black: silicon, gray: oxygen, white: carbon.

45%.[9] The other portion of the reaction was collected and analyzed by GPC, and found to be polymeric compounds (39%).



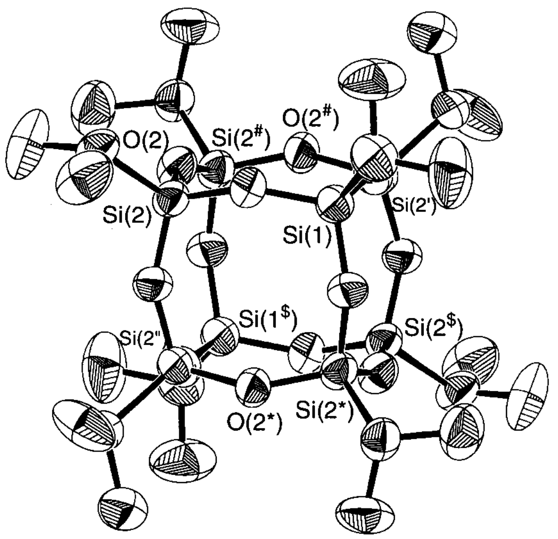


Figure 3. ORTEP drawing of **2**. Thermal ellipsoids are drawn in the 30% probability level.

The crystal structure of **2** was established by X-ray crystallography.[10] The ORTEP drawing is shown in Figure 3. The molecule has a C_3 symmetry axis which goes through Si (1) and Si ($1^{\$}$), and a C_2 symmetry axis which goes through O (2^{*}) and O ($2^{\#}$). As a result, the isopropyl group on the Si (1) atom showed disorder. The average Si-O bond lengths was 1.610 Å, and average Si–O–Si bond angles was 149.5°; the average O–Si–O bond angles was 108.9°. These values are all within the normal range.

In summary, we synthesized tetrahydroxycyclotetrasiloxane **1** in good yield, and determined its crystal structure. In the lattice, four molecules of **1** and water formed a cluster. The dehydrative coupling of **1** gave octasilsesquioxane **2** in relatively good yield.

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References and notes

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5 We first tried the direct synthesis from isopropyltrichlorosilane, however, we could not optimize the reaction conditions of hydrolysis in our hands, and **1** was not obtained.
6 **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) ppm; ^{13}C NMR (DMSO-d_6) δ 12.46, 17.38 ppm; ^{29}Si NMR (DMSO-d_6) δ -59.66 ppm; MS (70 eV) *m/z* (%) 373 (M$^+$-*i*-Pr, 4), 355 (100); IR (KBr) ν 3250, 2950, 2880, 1465, 1385, 1255, 1105, 1065, 1005, 885 cm^{-1}; Anal Found: C, 34.65; H, 7.83%. Calcd for $C_{12}H_{32}Si_4O_8$: C, 34.59, H, 7.74%.
7 Crystal data for **1**: monoclinic, *C2/c*, *a* = 16.349(3) Å, *b* = 32.885(3) Å, *c* = 11.135(3) Å, β = 124.74(1)°, *V* = 4919(1) Å^3, *Z* = 8, *R* = 0.096, *Rw* = 0.081 for 1011 reflections. Due to several unsuccessful attempts of recrystallization and measurement, a good refinement of the substituents was not possible. However, this phenomenon is generally observed in the crystallography of silanols and related compounds.[8]
8 For example: N. Winkhofer, H. Roesky, M. Noltemeyer, and W. T. Robinson, *Angew. Chem., Int. Ed. Engl.*, **31**, 599 (1992), and references cited therein.
9 **2**: colorless crystals, mp 193 °C (sublimed), 243–246 °C (sealed). ^{1}H NMR (CDCl$_3$) δ 0.87 (sep, 8H, *J* = 7.3 Hz), 1.01 (d, 48H, *J* = 7.3 Hz) ppm; ^{13}C NMR (CDCl$_3$) δ 11.50, 16.76 ppm; ^{29}Si NMR (CDCl$_3$) δ -66.26 ppm; MS (70 eV) *m/z* (%) 717 (M$^+$-*i*-Pr, 100), 675 (9); IR (KBr) v 2960, 2880, 1465, 1385, 1360, 1255, 1100, 1065, 995 cm^{-1}; Anal Found: C, 37.86; H, 7.49%. Calcd for $C_{24}H_{56}Si_8O_{12}$: C, 37.86; H, 7.41%.
10 Crystal data for **2**: trigonal, $R\bar{3}$, *a* = 15.392(3) Å, *c* = 15.233(4) Å, *V* = 3117(1) Å^3, *Z* = 3, *R* = 0.061, *Rw* = 0.063 for 802 reflections.