Incompletely Condensed Silsesquioxanes: Formation and Reactivity

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ABSTRACT: Hydrolysis reaction products from aryltrialkoxysilanes were studied in various solvents with alkali and alkaline earth metal hydroxides. Definite products could be isolated when sodium hydroxide was used. Reaction of trimethoxy- or triethoxyphenylsilane with equimolar amounts of sodium hydroxide to the silicon compound in re-fluxing water-*i*-propanol gave cyclic *sym-cis* tetraphenylsilsesquioxanetetraol tetrasodium salt as the principal product. When a little excess of sodium hydroxide than half molar amounts to the silicon compound was used, only small amounts of the cyclic tetramer was noticed among the initial products together with cubic octaphenylsilsesquioxane, evidenced by mass spectroscopy. Heptaphenylsilsesquioxanetriol trisodium salt was formed after refluxing for 4 h and following stirring for 15 h at room temperature. With longer reaction time, a double-decker octaphenyl silsesquiox-anetetraol tetrasodium salt was obtained in high yield with the consumption of heptaphenylsilsesquioxanetriol. While the silanols of double-decker octaphenyl silsesquioxanetetraol were thermally stable against condensation up to 230 °C, the sodium salt smoothly reacted with dimethyldichlorosilane to give completely condensed cage, 7,7,17,17-tetrameth-yl-1,3,5,9,11,13,15,19-octaphenylhexacyclo[9.13.1^{1,9}.1^{3,15}.1^{5,13}.1^{11,19}]decasiloxane.
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     KEY WORDS   Phenyltri(m)ethoxysilane / *sym-cis* Cyclic Tetrasilsesquioxanetetraol / Heptaphen-ylsilsesquioxanetriol / Double-Decker Octaphenylsilsesquioxanetetraol / POSS / Single-Crystal X-Ray Diffraction /

The development of new materials with specially designed chemical, mechanical or physical properties becomes increasingly important in order to meet the various practical requirements in many fields of application.[1–3]

Over the past decade, completely and incompletely condensed polyhedral oligomeric silsesquioxanes (POSS), obtained by hydrolysis and condensation of trifunctional alkyl- or arylsilane, have attracted considerable interest due to their unique properties such as high thermal stability to enhance the glass transition temperature (T_g),[4–7] low dielectric constant, and oxidative resistance of POSS-based polymeric materials.

Scott[8] initially discovered completely condensed methyl-substituted oligomeric silsesquioxanes in 1946. Barry[9] first showed the cubic or hexagonal prismatic shape of the completely condensed molecules. Brown and Vogt made major contributions to the synthesis of phenyl-substituted silsesquioxane cages.[10] Feher synthesized three new incompletely condensed POSS, namely trisilanols [(c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OH)$_3$, [(c-C$_7$H$_{13}$)$_7$Si$_7$O$_9$(OH)$_3$], and tetrasilanol [(c-C$_7$H$_{13}$)$_6$-Si$_6$O$_7$(OH)$_4$], in 29%, 26% and 7% yield, respectively.[11]

It has been well-recognized that structure of the products, such as cubic and other cages of completely or incompletely condensed form, branched polymers and double-chain polymers, depends on the reaction conditions such as molar ratio of reactants, catalyst, solvent, temperature, concentration, and organic group on silicon atom, which seem to have been generated from multi-step processes *via* many different intermediates.[12]

We reported the tendency of loop formation,[13] and the effect of substitutents on aryl group in the formation of completely-condensed octaarylsilsesquioxane as the benzene insoluble fraction from (substituted phenyl)trimethoxysilane. The firstly formed linear or low branched structures containing 6–9 silicon atoms by intermolecular condensation seem to further condense to form loop and cage structures.[14]

In this report, we deal with the products under strongly basic condition. Special interest was given to the formation of the *sym-cis* cyclic tetramer, tetra-phenylsilsesquioxanetetraol (T4OH), heptaphenylsil-sesquioxanetriol (T7OH) and double-decker octaphen-ylsilsesquioxanetetraol (DDT8OH) structures. Since the T7 and DDT8 are very interesting starting materials for the synthesis of siloxane polymers with unique structure, general synthetic conditions, unambiguous determination of the structure, and stability and reactivity were studied in detail.

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EXPERIMENTAL

General

Fourier transform-infrared (FT-IR) spectra were obtained as KBr disc on a JASCO VALOR-III (resolution of $4\,cm^{-1}$, $400–4000\,cm^{-1}$) with TGS detector at room temperature. High resolution NMR spectra ($500\,MHz$ ^1H, $\delta_{CHCl_3} = 7.26\,ppm$; δ acetone-d_5 = $2.05\,ppm$, $99\,MHz$ ^{29}Si, $\delta_{TMS} = 0.00\,ppm$) were obtained on a Varian NMR spectrometer model Unity INOVA. Spin-lattice relaxation times (T_1) were obtained at spinning rate of $4\,kHz$ with solid state ^{29}Si NMR ($79\,MHz$) of Varian NMR INOVA 400 using an inversion-recovery pulse sequence. GC-MS spectra were measured by a SHIMADZU GC-17A and QP-5000 (quadrupole). For MALDI-TOF MS (Shimadzu-Kratos Kompact MALDI III) analysis, the matrix 2,5-dihydroxybenzoic acid 98% (DHBA) was dissolved in THF ($50\,mg/mL$), and mixed with the sample solution ($0.1\,mg/mL$ in THF) in 1:1 v/v ratio. The samples were dried in air at least for 30 min, and the measurement was done in linear mode, with UV laser ($337\,nm$). The spectra were calibrated by the use of bradykinin. All data were collected by laser power more than $100\,W$, above the threshold in positive ion mode with accumulation of 50–100 shots. Size exclusion chromatography (SEC) was performed on a JASCO high speed liquid chromatograph, model Gulliver 900 with the combination of Shodex KF-801 (exclusion limit: polystyrene, 1.5×10^3 dalton) and KF-802 (exclusion limit: polystyrene, 5.0×10^3 dalton) using THF ($1\,mL/min$) as an eluent. Thermogravimetric analyses (TGA) were performed on a Seiko SSC/5200H instrument at a heating rate of $10\,°C/min$ under nitrogen atmosphere ($50\,mL/min$). In single crystal X-ray analysis, all measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromatic Mo-Kα radiation ($\lambda = 0.71075\,Å$) at $50\,kV$ and $40\,mA$. The structure was solved by direct method (SIR92) and expanded using Fourier techniques (DIRDIF99) for all crystal.

Materials

Phenyltrimethoxysilane (>99.0%), phenyltriethoxysilane (>99.0%), trimethylchlorosilane (>99.0%) and dimethyldichlorosilane (>99.0%) were purchased from Shin-Etsu Chemical and used without further purification. Phenyltri(2-methoxyethoxy)silane was prepared according to the method by Burkhards[15] and purified by distillation [bp $142\,°C/0.2\,Torr$]. Acetic acid (>99.5%) was purchased from Wako Pure Chemical. Tetrahydrofuran (THF) and other solvents were purchased from Wako Pure Chemical and distilled from calcium hydride. (Substituted-phenyl)trimethoxysil-

anes used in this study are (4-methylphenyl)trimethoxysilane [bp = $59\,°C/0.41\,Torr$], (4-methoxyphenyl)trimethoxy silane [bp = $80–81\,°C/0.30\,Torr$], and (4-dimethylaminophenyl)trimethoxysilane [bp = $127–131\,°C/0.53\,Torr$].

The reagents were prepared by typical Grignard reaction. For example, (4-methylphenyl)trimethoxysilane was prepared from 30 mmol of 4-bromotoluene and 33 mmol of dried magnesium turning in 100 mL 2-mouth round bottom flask with 24 mL dry THF. After the reaction occurred, the reaction system was further kept under stirring for 2 h. Grignard reagent obtained was transferred to another 100 mL flask with a dropping funnel, and added dropwise into 45 mmol tetramethoxysilane in 24 mL dry THF in an ice bath. The product (4-methylphenyl)trimethoxysilane was directly distilled from the reaction mixture. The purity was checked by GC-MS. All compounds gave reasonable NMR chemical shifts. (4-methylphenyl) trimethoxysilane, δ: 7.57–7.54 (d, 2H), 7.23–7.21 (d, 2H), 3.62 (s, 9H), 2.37 (s, 3H); (4-methoxyphenyl)trimethoxysilane, δ: 7.57–7.60 (d, 2H), 6.92–6.95 (d, 2H), 3.82 (s, 3H), 3.61 (s, 9H); (4-dimethylaminophenyl)-trimethoxysilane, δ: 7.53–7.50 (d, 2H), 6.75–6.72 (d, 2H), 3.60 (s, 9H), 2.98 (s, 6H).

Hydrolysis of Trialkoxyphenylsilane

Reactions were carried out basically by modifying the previous report.[16] Trialkoxyarylsilane (0.24 mol) was added dropwise to a solution of alkali metal hydroxide (molar ratio of Si:alkali metal = 1:1 or 2:1 mol/mol), solvent (240 mL) and deionized water (0.24–0.28 mol) at a room temperature in about 15 min. The reaction mixture was heated to reflux for 4 h under nitrogen. The solution was cooled to ambient temperature to produce precipitates. After filtration, the precipitate was dried at $70\,°C$ for 5 h in a vacuum oven.

Silylation with Trimethylchlorosilane

Trimethylchlorosilane (42.4 mmol) was added dropwise to the alkali salt precursor (1.3 or 2.4 g) obtained above by molar ratio (Si:Na = 1:1 or 2:1) and triethylamine (35.6 mmol) in THF (20 g) for one minute while stirring by a magnetic stirrer under nitrogen. Stirring was further continued at room temperature for 3 h. Deionized water (10 g) was added to dissolve produced sodium chloride and to hydrolyze unreacted trimethylchlorosilane. The organic layer was separated by means of a separating funnel.

In the case treated with precursor of 1:1, the organic layer was repeatedly washed with deionized water until the aqueous layer became neutral, dried with MgSO_4 and filtered.

In the case of 2:1, n-hexane (10 mL) was added, and

the organic layer was repeatedly washed with deionized water. *n*-Hexane (50 mL) was added to this solution, and the solution was left standing at $-30\,°C$ in a refrigerator for a night. The precipitated solid was filtered and dried at reduced pressure. The products were characterized by FT-IR, ^{1}H, ^{29}Si NMR, MALDI-TOF MS measurements. When product was pure in spectral analyses, fine crystals suitable for X-ray crystallography were obtained by slow evaporation of a 10 wt % THF/*i*-propanol (1:1) solution of the compound. From these procedures, trimethylsilylated T4OTMS (78.3% yield); "cyclic *sym-cis* 1,3,5,7-tetrakis(trimethylsilyl)-tetraphenyltetrasilsesquioxane", T7OTMS (54.1%); "3,7,14-tris(trimethylsilyl)heptaphenyltricyclo[7.3.-3.1^{5,11}]heptasilsesquioxane", DDT8OTMS (68.2%); "5,11,14,17-tetrakis(trimethylsilyl)octaphenyltetracyclo[7.3.3.3^{3,7}] octasilsesquioxane" were obtained.
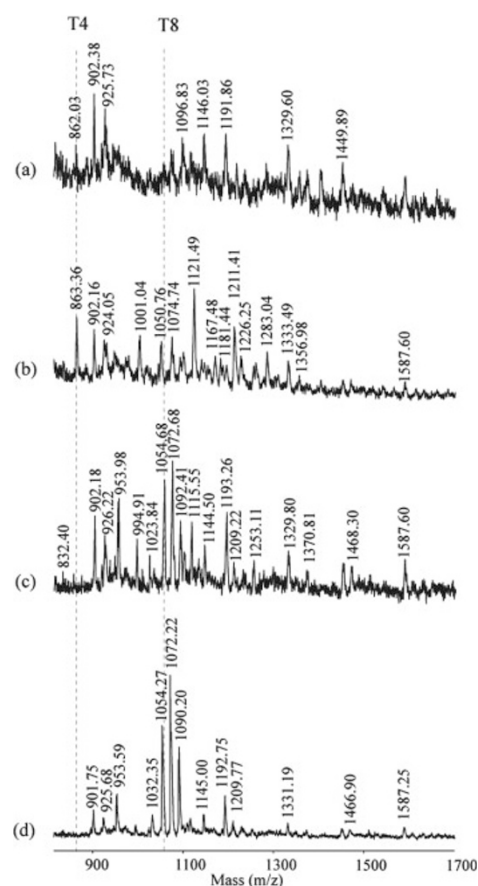
Additional crystallographic data of T7OTMS (CCDC299793) and DDT8OTMS (CCDC299794) can be obtained free of charge *via* www.ccdc.cam.au.uk/data-request/cif, by emailing data-request@ccdc.cam.ac.uk.

5,11,14,17-Tetra(hydro)octaphenyltetracyclo[7.3.3.-3^{3,7}]octasilsesquioxane (DDT8OH)

Acetic acid (0.6 g, 10 mmol) was added dropwise to THF (30 mL) dispersion of double decker tetrasodium salt, 5,11,14,17-tetra(sodio)octaphenyltetracyclo[7.3.-3.3^{3,7}] octasilsesquioxanolate (DDT8ONa, 2.9 g, 2.5 mmol), obtained by refluxing for 4 h, and further stirring for 15 h at room temperature under the standard reaction conditions (phenyltrimethoxysilane, *i*-propanol and NaOH as monomer, solvent and catalyst; monomer/H$_2$O/catalyst = 1.00/1.15/0.66 in molar ratio). Stirring was continued at room temperature for 1 h, and the solution was neutralized with a saturated aqueous sodium hydrogen carbonate (10 mL), and washed with deionized water (10 g). The organic layer was dried over anhydrous magnesium sulfate, filtered and evaporated. The solid was again washed with acetonitrile to obtain a colorless product in 50.3% yield. The compound is soluble in THF, acetone and insoluble in *n*-hexane, methanol, acetonitrile, benzene, toluene, cyclohexane, carbon tetrachloride, dichloromethane, and diethyl ether. Mp 230.7 °C, Single crystals suitable for X-ray crystallography were obtained by slow evaporation of a 10 wt % THF/*i*-propanol (1:1) solution.

^{1}H NMR (500 MHz, CDCl$_3$) δ 2.82 (4H, s, -O*H*), 2.79 (4H, s, -O*H*), 7.23 (8H, t, $J = 7.5$ Hz, *m*-Ph-*H*), 7.28 (8H, t, $J = 7.5$ Hz, *m*-Ph-*H*), 7.38 (4H, t, $J = 7.5$ Hzz, *p*-Ph-*H*), 7.43 (4H, t, $J = 7.5$ Hz, *p*-Ph-*H*), 7.47 (8H, d, *o*-Ph-*H*), 7.63 (8H, d, *o*-Ph-*H*). ^{29}Si{^{1}H} NMR (THF and CDCl$_3$, TMS) δ −69.45 (O*Si*PhOH); −79.62 (O$_3$*Si*Ph). IR(KBr): 1431, 1595 (Si-Ph),

1200–950 (Si-O-Si), 3280 (br, Si-OH) cm^{-1}. MALDI-TOF (*m/z*): 1092.32 ([M + Na]$^+$, calc'd: 1091.08). SEC: M_n 872, M_w 874 M_w/M_n 1.00209. TGA (ceramic yield 82% in N$_2$).

7,7,17,17-Tetramethyl-1,3,5,9,11,13,15,1-octaphenylhexacyclo[9.13.1^{1,9}.1^{3,15}.1^{5,13}.1^{11,19}]decasiloxane (DDT8ODMS)

Dichlorodimethylsilane (0.97 g, 7.5 mmol) was added dropwise to a solution of the tetrasodium salt precursor (DDT8ONa, 2.9 g, 2.5 mmol), triethylamine (0.75 g, 7.5 mmol) in toluene (25 g) for one minute while stirring by a magnetic stirrer under nitrogen. Stirring was further continued at a room temperature for 3 h. Deionized water (10 g) was added to remove the formed salt, and the reaction product was separated as an organic solution by a separating funnel. The organic layer was repeatedly washed with deionized water until the aqueous layer became neutral, dried with anhydrous magnesium sulfate, filtered and evaporated to obtain 1.4 g of a white solid. Product is soluble in THF, benzene, dichloromethane, pyridine, acetone, ethyl ether and insoluble in cyclohexane, methanol, *n*-hexane, acetonitrile. mp 272.9 °C, 47.8% yield.

^{1}H NMR (500 MHz, CDCl$_3$) δ 0.311 (36H, s, C*H*$_3$), 7.19 (8H, t, $J = 7.5$ Hz, *m*-Ph-*H*), 7.26 (8H, t, $J = 7.5$ Hz, *m*-Ph-*H*), 7.34 (4H, t, $J = 7.5$ Hz, *p*-Ph-*H*), 7.39 (4H, t, $J = 7.5$ Hz, *p*-Ph-*H*), 7.43 (8H, d, $J = 7.5$ Hz, *o*-Ph-*H*), 7.54 (8H, d, $J = 7.5$ Hz, *o*-Ph-*H*). ^{29}Si{^{1}H} NMR (CDCl$_3$, TMS) δ −16.56 (O*Si*Me$_3$); −78.60, −79.59 (O$_3$*Si*Ph). IR (KBr): 1431, 1594 (Si-Ph), 1200–950 (Si-O-Si), 1263 (Si-CH$_3$) cm^{-1}. MALDI-TOF (*m/z*): 1203.29 ([M + Na]$^+$, calc'd: 1203.09). SEC: M_n 879, M_w 880, M_w/M_n 1.00.

RESULTS AND DISCUSSION

The synthetic scheme is shown in Scheme 1.

When tri(methoxy)phenylsilane was reacted with water in the presence of sodium hydroxide (Si:Na:H$_2$O = 1.0:1.0:1.0) in alcohol (*i*-propanol or *i*-butanol), a distinct product was formed. The product was capped with trimethylchlorosilane, and the solvent was removed with a rotary evaporator. This compound was identified as tetrakis(trimethylsilylated)

Scheme 1. Reaction of tri(alkoxy)phenylsilane.

Figure 1. MALDI-TOF MS and ^{29}Si NMR spectra of products obtained under reaction condition; monomer/H_2O/NaOH = 1.00/1.00/1.00 mol/mol/mol, refluxing for 4 h and stirring for 15 h at r.t. from trimethoxyphenylsilane.

Figure 2. MALDI-TOF MS spectra of products obtained under reaction condition; Si:Na = 1:1 (a,b) or 2:1 (c,d) mol/mol, refluxing for 1 or 2 h.

cyclic *sym-cis* tetraphenylsilsesquioxane (T4OTMS) as shown in Figure 1. This is an interesting finding similar to Shchegolikhina.[17]

Small amounts of *trans* and *trans-cis* isomers were also formed at higher concentration, or under acidic condition at higher reaction temperature. The isomers exist as equilibrium mixture. The reason why only *sym-cis* isomer was isolated in this report is because of high crystallinity and low solubility of the *sym-cis* isomer. The use of other ordinary organic solvents than alcohol did not give any specific product. Substitution of the para position of phenyl group also gave complex product mixture.

To study the reaction process, products obtained in the reactions with Si:Na = 2.0:1.0 and 1.0:1.0 by refluxing for 1 or 2 h were analyzed.

MALDI-TOF MS spectra shown in Figure 2 indicated a complex product mixture. We could recognize the formation of cubic T8 in the initial stage of the reaction (1 h, 2 h) when the Si and Na was 2:1. Although

T4OTMS was also noticed as a weak peak in 30 min reaction, it was not possible to conclude the formation of T4OTMS without doubt owing to low signal noise ratio. Contrary, when the ratio was 1:1, cubic T8 was not observed even in the initial stage of the reaction. T4OTMS was clearly identified, and its amounts increased with reaction time (final yield, 78.3%).

More interesting products were identified with longer reaction time in the case of the ratio being 2:1.

$$\text{PhSi(OMe)}_3 + H_2O \xrightarrow{\text{NaOH, } i\text{-Butanol}} \text{refluxing 4 h and stirring for 15 h or 40 h at room temperature}$$
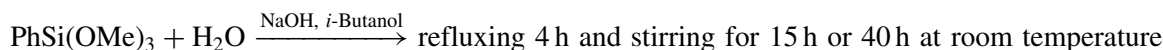
The product formed after 15 h of stirring was isolated as trimethylsilyl(TMS)-capped compound and purified. The change in TOF-MS and ^{29}Si NMR spectra with stirring time at room temperature are shown in Figure 3.

All spectral data suggested the 3,7,14-tris(trimethylsilyl)heptaphenyltricyclo[7.3.3.1^{5,11}] heptasilsesquioxane (T7OTMS). Molecular mass of Na$^+$-ionized products (1170.75) was close to the calculated value (1169.18 m/z) for T7OTMS. ^{29}Si NMR showed three peaks indicating a T^3 structure having a phenyl group.

The X-ray single crystal analysis is shown in Figure 4(a) and Tables I, II.

This product was identified as 3,7,14-tris(trimethylsilyl)heptaphenyltricyclo[7.3.3.1^{5,11}] heptasilsesquioxane (54.1% yield).

After 40 h stirring, another product with 1379.47 m/z (calculated 1379.24) and two ^{29}Si signals at -76.12 and -78.94 (O$_3$SiPh) was obtained after trimethylsilylation. The structure of the purified product was also characterized unambiguously by single crystal XRD after recrystallization by slow evaporation of
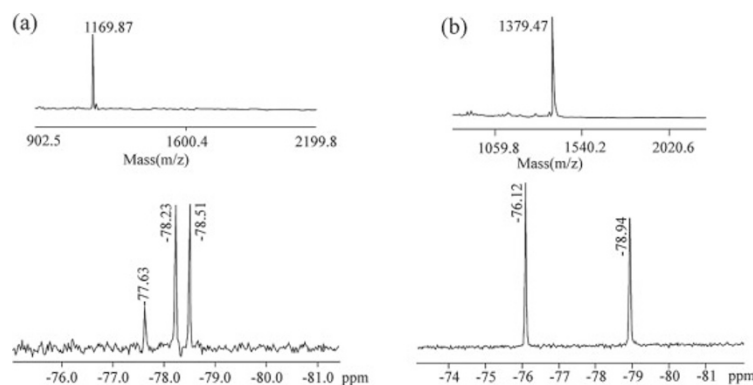
Figure 3. MALDI-TOF MS and ^{29}Si NMR spectra of products obtained from trimethoxyphenylsilane by refluxing for 4 h and stirring for (a) 15 h, (b) 40 h at r.t. in *i*-butanol.
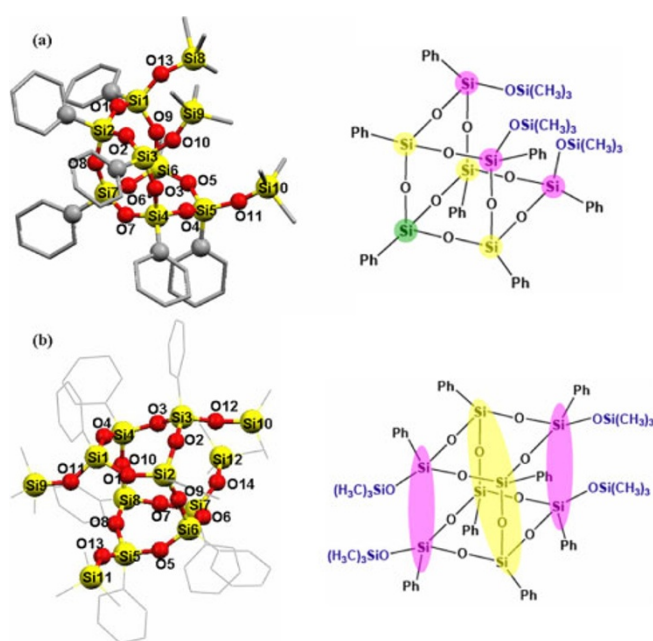
Figure 4. ORTEP plots determined by single-crystal X-ray diffraction for products (a) and (b) in Figure 3.

a 10 wt % THF/*i*-propanol (1:1) solution.

ORTEP plots proved the compound as tetrakis(tri-methylsilylated) "double-decker" octaphenylsilsesquioxane, 5,11,14,17-tetrakis(trimethylsilyl)tetracyclo-[7.3.3.3^{3,7}] octasilsesquioxane (DDT8OTMS, 68.2% yield), (Figure 4b).

The bond distances and angles are also collected in Tables I and II together with cubic octaphenylsilsesquioxane (cubic T8).[18] Silicon-oxygen bond distances [1.61–1.62 Å except for Si(6)-O(5)] and silicon-oxygen-silicon bond angles (~150°) for the cyclic tetra-siloxane structure in upper and lower decks of DDT8OTMS are quite similar with those in cubic Ph$_8$Si$_8$O$_8$ (1.61 Å, 149°). The distances of outer Si-O bond were a little shorter (~1.60 Å). It should be not-ed that the bond distances between silicon-oxygen bonds in the bridge to connect two decks are also a lit-

Table I. Selected bond distances (Å) on product from *i*-butanol

Bond distances (Å)			
15 h		40 h	
Si1-O1	1.619[16]	Si1-O1	1.625[1]
Si1-O9	1.583[18]	Si1-O4	1.617[1]
Si1-O13	1.614[16]	Si1-O11	1.596[2]
Si2-O1	1.608[17]	Si2-O1	1.607[2]
Si2-O2	1.608[18]	Si2-O2	1.611[1]
Si2-O8	1.615[16]	Si2-O9	1.595[1]
Si3-O2	1.621[17]	Si3-O2	1.608[1]
Si3-O3	1.607[16]	Si3-O3	1.618[1]
Si3-O10	1.587[19]	Si3-O12	1.598[2]
Si4-O3	1.609[17]	Si4-O3	1.608[2]
Si4-O4	1.615[18]	Si4-O4	1.609[1]
Si4-O7	1.613[17]	Si4-O10	1.599[1]
Si5-O4	1.607[19]	Si5-O5	1.613[2]
Si5-O5	1.604[17]	Si5-O8	1.618[1]
Si5-O11	1.590[2]	Si5-O13	1.592[1]
Si6-O5	1.599[16]	Si6-O5	1.595[2]
Si6-O6	1.625[16]	Si6-O6	1.604[1]
Si6-O13	1.605[16]	Si6-O9	1.597[1]
Si7-O6	1.619[16]	Si7-O6	1.621[1]
Si7-O7	1.609[16]	Si7-O7	1.617[2]
Si7-O8	1.617[16]	Si7-O14	1.601[2]
		Si8-O7	1.597[2]
		Si8-O8	1.608[1]
		Si8-O10	1.594[1]
Ph$_8$Si$_8$O$_{12}$[18]			
Si O	1.614		

Values in the square bracket indicating the range of error. [1] indicates ±0.001 Å.

tle shorter than those in the decks (~1.60 Å). Inter-stingly, the bond angles (168.8 and 172.5°) of the bridge (Si$_2$-O$_9$-Si$_6$ and Si$_4$-O$_{10}$-Si$_8$) were considerably expended, and bigger than those in the deck or cubic structure.

Yoshida's product was not completely consistent with the proposed double decker structure. It was con-firmed that their error in NMR spectra was generated

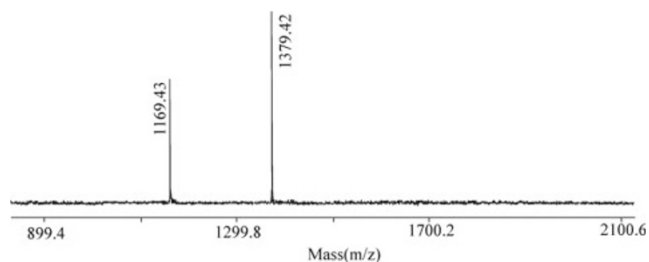**Table II.** Selected bond angles (°) on product from *i*-butanol

Bond angles (°)				
15 h		**40 h**		
O-Si-O		O-Si-O		
O1-Si1-O9	108.44[10]	O4-Si1-O1	109.58[8]	
O1-Si1-O13	108.40[8]	O11-Si1-O4	110.79[8]	
O9-Si1-O13	109.83[9]	O11-Si1-O1	107.38[7]	
O1-Si2-O2	108.81[9]	O2-Si2-O1	108.63[8]	
O1-Si2-O8	108.31[8]	O9-Si2-O2	107.68[8]	
O2-Si2-O8	109.59[8]	O9-Si2-O1	110.60[8]	
O2-Si3-O3	109.42[8]	O3-Si3-O2	109.33[8]	
O2-Si3-O10	108.24[9]	O12-Si3-O3	106.77[7]	
O3-Si3-O10	109.20[10]	O12-Si3-O2	110.92[8]	
O3-Si4-O4	109.02[9]	O4-Si4-O3	109.63[7]	
O3-Si4-O7	110.07[9]	O10-Si4-O3	110.22[8]	
O4-Si4-O7	109.32[8]	O10-Si4-O4	108.35[8]	
O4-Si5-O5	109.58[9]	O8-Si5-O5	109.05[8]	
O4-Si5-O11	108.57[10]	O13-Si5-O8	107.98[7]	
O5-Si5-O11	108.46[9]	O13-Si5-O5	110.39[7]	
O5-Si6-O6	108.81[8]	O6-Si6-O5	109.96[8]	
O5-Si6-O13	108.43[8]	O9-Si6-O5	108.87[9]	
O6-Si6-O13	110.01[8]	O9-Si6-O6	108.47[8]	
O6-Si7-O7	109.75[8]	O7-Si7-O6	109.07[8]	
O6-Si7-O8	108.01[8]	O14-Si7-O6	107.78[8]	
O7-Si7-O8	110.61[8]	O14-Si7-O7	111.20[8]	
Si-O-Si		O8-Si8-O7	109.43[7]	
Si1-O1-Si2	147.89[11]	O10-Si8-O8	108.93[7]	
Si2-O2-Si3	149.54[12]	O10-Si8-O7	109.43[8]	
Si3-O3-Si4	148.81[11]	Si-O-Si		
Si4-O4-Si5	151.65[11]	Si1-O1-Si2	145.3[1]	
Si5-O5-Si6	160.11[11]	Si2-O2-Si3	148.67[9]	
Si6-O6-Si7	142.59[10]	Si3-O3-Si4	143.71[9]	
Si4-O7-Si7	152.15[10]	Si1-O4-Si4	147.43[9]	
Si2-O8-Si7	148.47[10]	Si5-O5-Si6	148.9[1]	
Si1-O9-Si6	159.52[12]	Si6-O6-Si7	146.3[1]	
		Si7-O7-Si8	156.14[8]	
		Si5-O8-Si8	148.8[1]	
		Si2-O9-Si6	168.8[1]	
		Si4-O10-Si8	172.5[1]	
$Ph_8Si_8O_{12}$[18]				
O-Si-O		Si-O-Si		
O Si O	109.0	Si O Si	149.2	

Values in the square bracket indicating the range of error. [8] indicates ±0.08°.

Figure 5. MALDI-TOF MS spectrum of DDT8OTMS synthesized by reported method.[16]

Figure 6. MALDI-TOF MS and ^{29}Si NMR spectra of products obtained from triethoxyphenylsilane in *i*-propanol by refluxing for 4 h and stirring for 15, 40, and 70 h at r.t.
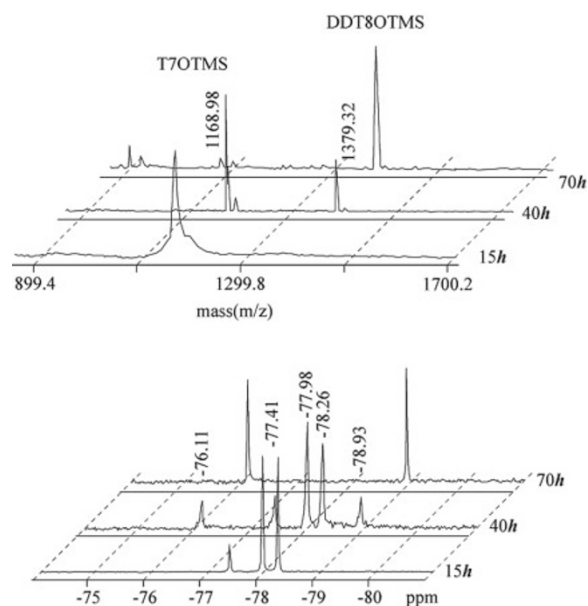
by the existence of T7 as a by-product as evidenced by MALDI-TOF MS spectroscopy (Figure 5).

Conversion of T7 to double decker structure was more clearly seen when phenyltriethoxysilane was used instead of phenyltrimethoxysilane (Figure 6).

The only product after 15 h was the T7, which was slowly converted into the DDT8 after 70 h. Both compounds were present as the major products after 40 h standing. These results strongly supported that the DDT8 was produced with the consumption of T7, different from the case of cubic T8 formation. The possibility for *sym-cis* cyclic tetramer being an intermediate to T7 and DDT8 or cubic T8 will be clarified in future report.

To find effective reaction conditions for the formation of substituted DDT8 structures, the standard reaction conditions were modified. The effects of substituent at para position [hydrogen(∗), methyl(a), methoxy(b), dimethylamino(c)], alkoxy group [methoxy(∗), ethoxy(d), 2-methoxyethoxy(e)], solvent [*i*-propanol(∗), methanol(f), ethanol(g), *n*-butanol(h), *i*-butanol(i)] and catalyst [NaOH(∗), LiOH(j), KOH(k), Ca(OH)$_2$(l)] were studied. Products could not be isolated because of the solubility problems of the crude products in a, f, g, h, k (products were soluble in *i*-propanol), nor in e, j (products could not be recrystallized). Reaction conditions b, c, d, and i gave some products. The products obtained from b,c were a mixture compound, which could not be characterized. Pure T7 was obtained in reaction condition (d, i) like above results.
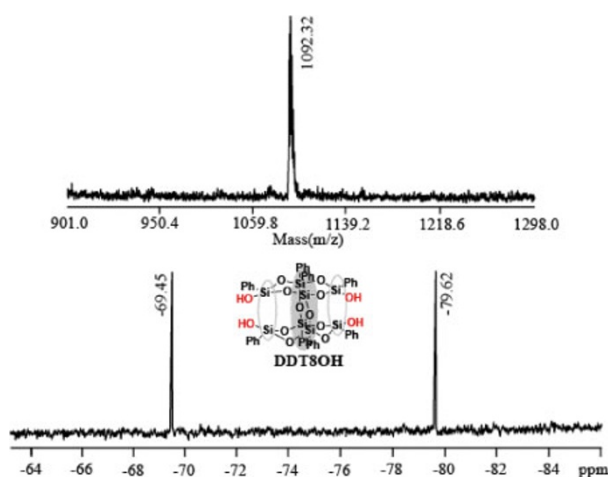
Double-decker 5,11,14,17-tetra(hydro)octaphenyltetracyclo[7.3.3.3^{3,7}] octasilsesquioxane (DDT8OH)

was obtained from DDT8ONa by neutralization with acetic acid, which was also characterized by MALDI-TOF MS, NMR and single crystal XRD analyses after re-precipitation and washing with acetonitrile. MALDI-TOF ($[M + Na]^+$, 1092.32 m/z; calculated 1091.08) and ^{29}Si NMR (-69.45, -79.62) (Figure 7) supported the double decker structure.
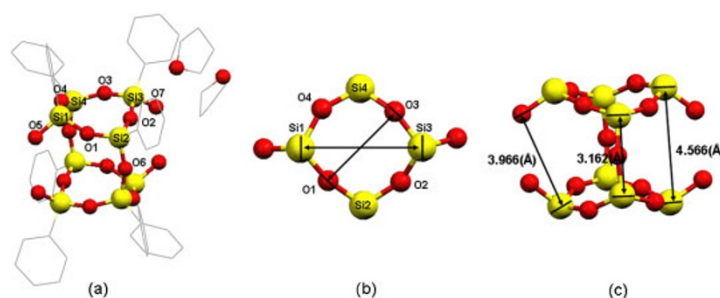
ORTEP plots of DDT8OH determined by XRD analysis are shown in Figure 8(a). Crystal of DDT8OH included two THF molecules in the crystal.

In Figure 8(b), it was shown that the oxygen-oxygen distances in a deck of DDT8OH were averagely 3.62 and 3.71 Å (O_1-O_3 and O_2-O_4), and silicon-silicon distances were 4.16 and 4.29 Å (Si_1-Si_3 and Si_2-Si_4), respectively. The distance between terminal oxygen to facing terminal silane (3.966 and 4.566 Å) was much longer than ordinary Si-O bond (1.609 Å). Selected bond distances and angles were collected in Table III. XRD results of DDT8OH were almost the same to those of DDT8OTMS.

The tetrasiloxane rings in T7 and DDT8 structures have *sym-cis* stereochemistry without trans. One possible mechanism is that T7 was formed by condensation of all cis T4 with lower linear siloxane or three molecules of phenyltrialkoxysilane itself, and then transformed into double decker T8 by the condensation with a phenyltrialkoxysilane, but the mechanism is not clear at present.

^{29}Si NMR of DDT8OH clearly showed that T_1 of silicon atom in the bridge ($O_3$$Si$Ph) is longer than those of silicon atoms in cubic T8, or silicon atoms of silanol of DDT8OH ($O$$Si$PhOH) (Table IV). The silanol silicon stoms showed the shortest T_1. By considering the expanded Si-O-Si bonds of the bridge connecting the two tetrasiloxane decks, it may be reasonable to assume that silicon atoms in the bridge have the lowest mobility among the silicon atoms in the double decker, or the cubic structures.
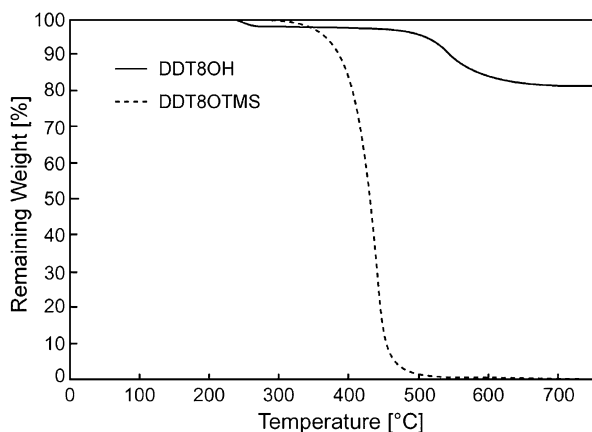
Thermal properties of DDT8OH were compared with DDT8OTMS under nitrogen atmosphere to ex-

Table III. Selected bond distances (Å) and bond angles (°) for DDT8OH

Bond distances (Å)			
Si1-O1	1.616(2)	Si3-O2	1.613(1)
Si1-O4	1.617(1)	Si3-O3	1.617(2)
Si1-O5	1.609(2)	Si3-O7	1.584(2)
Si2-O1	1.600(2)	Si4-O3	1.602(2)
Si2-O2	1.600(1)	Si4-O4	1.603(2)
Si2-O6	1.594(2)		

Bond angles (°)			
O-Si-O			
O4-Si1-O1	110.64(9)	O7-Si3-O3	111.1(1)
O5-Si1-O1	105.2(1)	O4-Si4-O3	110.9(1)
O5-Si1-O4	110.3(1)		
O2-Si2-O1	109.18(8)	Si-O-Si	
O6-Si2-O1	108.58(9)	Si1-O1-Si2	150.36(9)
O6-Si2-O2	109.2(1)	Si2-O2-Si3	165.6(1)
O3-Si3-O2	108.4(1)	Si3-O3-Si4	145.4(2)
O7-Si3-O2	109.4(1)	Si1-O4-Si4	148.3(1)

Table IV. ^{29}Si spin-lattice relaxation times in the laboratory frame T_1 (Si) (ms), chemical shifts δ (ppm)

Silicon atom	^{29}Si spin-lattice relaxation time (T_1, ms)	
	DDT8OH	Cubic type
OSiPhOH	94.5(-70.39)	
O$_3$$Si$Ph	119(-78.74)	112(-77.99)

Figure 7. MALDI-TOF MS and ^{29}Si NMR spectra of and DDT8OH.

Figure 8. ORTEP plot(a) of DDT8OH determined by XRD, (a) all view, (b) top view (c) side view.

Figure 9. TGA curves for DDT8OH and DDT8OTMS.

Table V. Decomposition temperature (T_{dec}) and ceramic yield (%) of DDT8OTMS and DDT8OH obtained by TGA

| Products	Decomposition temperature T_{dec} (°C) [onset]	Ceramic yield (%)
DDT8OTMS	400[a]	0.9
DDT8OH	505	81.5

a: sublimed.

amine the reactivity of the compounds (Figure 9).

The samples (about 11 mg) were heated from 50 °C to 800 °C at the heating rate of 10 °C/min. DDT8OTMS completely lost its weight between 397–495 °C. Sublimation of the compound was likely. On the other hand, DDT8OH lost less than 2.6 wt % between 240–500 °C, presumably due to the desorption of adsorbed or condensed water. Decomposition onset began at 505 °C, and the residue yield was 81.5%. Apparently, reactivity of silanol groups in thermal condensation was very low at low temperature. The results are summarized in Table V.

Thermal condensation of DDT8OH was traced by checking the products from 50 to 300 °C at a heating rate of 10 °C/min under N_2 by SEC. The SEC showed broad distribution (M_n 4700, M_w 25400, M_w/M_n 5.0, polystyrene standard) for the products produced at 300 °C. Tetrafunctional silanols in the double decker DDT8OH seem to condense intermolecularly at higher temperature to give polymeric materials. This may be understood by the long distance between terminal silanol oxygen and facing terminal silicon atom of the counter silanol and long spin-lattice relaxation time of the silicon atoms of the bridge. It seems difficult for the terminal silanol oxygen to attack the facing terminal silicon atom to cause intramolecular condensation due to long distance in molecular structure and low mobility in the solid state.

Intramolecular bridging reactivity of DDT8ONa *via* dimethyl silylation is quite interesting.
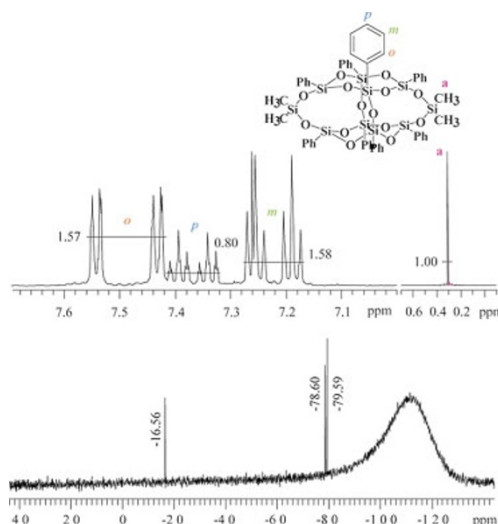
Figure 10. ^{1}H and ^{29}Si NMR of DDT8ODMS obtained by bridging of DDT8ONa with dimethyldichlorosilane.

Reaction of DDT8ONa with dimethyldichlorosilane gave completely condensed cage, 7,7,17,17-tetramethyl-1,3,5,9,11,13,15,19-octaphenylhexacyclo[9.13.1^{1,9}.-1^{3,15}.1^{5,13}.1^{11,19}]decasiloxane (DDT8ODMS) in almost quantitative yield, whose spectra were given in Figure 10. Such high and selective reactivity of facing silanols in the double decker structure will open the possibility to selectively synthesize unique structures of new polysiloxanes.

CONCLUSION

Tetraphenylsilsesquioxanetetraol (T4), heptaphenylsilsesquioxanetriol (T7) and double-decker octaphenylsilsesquioxanetetraol (DDT8) were obtained from phenyl(m)ethoxysilane in alkaline equilibration reactions. The double-decker T8 seems to be produced with the consumption of T7 and T4 in the same condition.

Fine single crystals of trimethylsilylated heptaphenylsilsesquioxane (T7OTMS) and double-decker octaphenylsilsesquioxane (DDT8OTMS) were obtained by slow evaporation of a THF/i-propanol (1:1). Their unambiguous 3D structures were established by single crystal X-ray diffraction analysis.

Pure double decker tetra(hydro)octapheylsilsesquioxane (DDT8OH) was prepared by neutralization of double decker octaphenylsilsesquioxanetetraol tetrasodium salt (DDT8ONa). The tetrasilanol was reluctant to inter or intra molecular condensation till ～230 °C, but was effectively bridged by dimethyldichlorosilane.

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