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New polyhedral oligosilsesquioxanes via the catalytic hydrogenation of aryl-containing silsesquioxanes

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Abstract

The hydrolytic condensation of $RSiCl_3$ (R = benzyl, *m*-tolyl, 3,5-dimethylphenyl) gives good yields of the corresponding octameric aryl silsesquioxanes (**1**). A single-crystal X-ray diffraction study of highly soluble **1** (R = benzyl) reveals that highly efficient crystal packing can be accomplished without the inclusion of solvent or the strong intermolecular π-stacking arrangements that normally lead to poor solubility properties. The catalytic hydrogenation of aryl polyhedral oligosilsesquioxanes (POSS) affords high yields of the corresponding aliphatic silsesquioxanes. These new silsesquioxanes display thermal and physical properties comparable to the corresponding aryl-containing POSS but generally have much greater solubilities in common organic solvents. The catalytic hydrogenation of $[Ph_{12}Si_{12}O_{20}]$ affords iso-$[Cy_{12}Si_{12}O_{20}]$, which possesses local C_{2v} rather than D_{6h} symmetry.

Introduction

Polyhedral oligosilsesquioxanes (i.e., $[RSiO_{3/2}]_n$) are an interesting class of three-dimensional silsesquioxanes derived from the hydrolytic condensation of trifunctional organosilicon monomers (i.e., $RSiX_3$) [1]. Since their discovery [2] in 1946, most of the practical interest in polyhedral oligosilsesquioxanes (POSS) has focussed on phenyl oligosilsesquioxanes, which exhibit remarkable thermal stabilities and, in many instances, can be prepared in high yields from readily available phenyl trichlorosilane [3,6]. Recently hydridosilsesquioxanes [4] (i.e., $[HSiO_{3/2}]_n$) have also attracted interest as photo-resists [5] and precursors to spherosilicates [7], but the lack of an efficient, high-yield synthetic route to hydridosilsesquioxanes has impeded the development of these and other practical applications. The susceptibility of many benzylic carbon-heteroatom bonds toward hydrogenolysis prompted us

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to examine the reactivity of **1** toward H_2/Pd. We report here that under standard hydrogenolysis conditions, the only product from the reaction of **1** with H_2/Pd results from quantitative hydrogenation of other aryl-containing POSS proceeds with similar facility and provides ready access to a wide variety of potentially useful silsesquioxanes.

Experimental

Phenyltrichlorosilane (Aldrich), benzyltrichlorosilane (Petrarch), and *p*-tolyltrichlorosilane (Petrarch) were obtained commercially and used without further purification. 10% Pd/C was obtained from Aldrich Chemical Company. *m*-Tolyltrichlorosilane, 3,5-dimethylphenyltrichlorosilane, and benzyltrichlorosilane were prepared from the appropriate Grignard reagent and $SiCl_4$ [8]. Silsesquioxanes $[PhSiO_{3/2}]_8$ (**5**) [3a], $[PhSiO_{3/2}]_{12}$ (**6**) [3a], and $[p\text{-tolSiO}_{3/2}]_8$ (**4**) [6], were prepared from the corresponding aryltrichlorosilanes. Reagent grade solvents were used without further purification.

All hydrogenation reactions were performed in a 300 ml Parr 4561 Mini-Reactor with Pyrex liners. NMR spectra were recorded on Bruker WM-250 (^1H, 250.1 MHz; ^{13}C, 62.5 MHz; ^{29}Si, 49.7 MHz), General Electric QE-300 (^1H 300.15 MHz; ^{13}C 75.04 MHz) or GN-500 (^1H, 500.1 MHz; ^{13}C, 125.03 MHz; ^{29}Si, 99.36 MHz) NMR Spectrometers. All chemical shifts are reported in units of δ (ppm downfield from tetramethylsilane), but were most often measured relative to (residual) ^1H or ^{13}C resonances in the deuterated solvents: $CDCl_3$ (δ 7.260 for ^1H, δ 77.000 for ^{13}C), C_6D_6 (δ 7.150 for ^1H, σ 128.000 for ^{13}C). CH_x assignments in ^{13}C NMR spectra were based on standard DEPT experiments at 125 MHz. Infrared spectra were recorded in pressed KBr pellets on a Perkin–Elmer PE-281 IR Spectrophotometer. Electron impact mass spectral analysis were conducted on a VG 7070e High Resolution Mass Spectrometer. Melting points were measured using a Mel-Temp melting point apparatus and are uncorrected.

The X-ray crystal structure of **1** was determined on a Syntex $P2_1$ automated four-circle diffractometer at −60 °C. All crystallographic calculations were performed using either our locally modified version of the UCLA Crystallographic Computing Package or the SHELXTL PLUS program set. A summary of pertinent experimental details are summarized in Table 1. Fractional coordinates and equivalent isotropic temperature factors of non-H atoms are given in Table 2. A complete description of the experimental details, tabulations of bond distances and angles, thermal parameters, and structure factors are available from the authors.

Preparation of $[PhCH_2SiO_{3/2}]_8$ *(1)*

Benzyltrichlorosilane (2.5 g, 11.1 m*M*) was carefully added with vigorous stirring to 40 ml of 95% ethanol. The homogeneous solution was refluxed for 2 days, then concentrated (78 °C) to 15 ml and decanted to give a sticky white solid. Trituration with 1/1 acetone/methanol (30 ml) and recyrstallization from CH_2Cl_2/acetone/methanol (1/2/2 v/v/v) afforded white needles of **1**. Yield: 485 mg (31%). m.p. 162–165 °C. ^1H NMR (500.1 MHz, $CDCl_3$, 25 °C) δ 7.190 (dd, *J* 7.2, 7.0 Hz, 2H), 7.130 (t, *J* 7.2 Hz, 1H), 6.907 (d, *J* 7.0 Hz, 2H), 2.00 (s, 2H). ^{13}C NMR (125.76 MHz, $CDCl_3$, 25 °C) δ 136.55, 128.77, 128.18, 124.70, 21.10. ^{29}Si NMR (49.7 MHz, $CDCl_3$, 25 °C) δ −71.28. IR (KBr) 3085 (m), 3070 (w), 3030 (m), 2935 (w), 1945

Table 1

Structure determination summary for $[(C_6H_5CH_2)_8Si_8O_{12}]$ (1)

Crystal data	
Empirical formula	$C_{56}H_{56}O_{12}Si_8$
Color	Colorless prisms
Crystal size (mm^3)	0.4×0.4×0.6
Space group	Triclinic, P1 bar
Unit cell dimensions	a 10.9733(18) Å
	b 14.3699(23) Å
	c 17.9436(45) Å
	α 87.344(17)°
	β 89.496(17)°
	γ 87.480(13)°
Volume	2823.59(97) $Å^3$
Formula units per cell	2
Formula weight	1145.7 AMU
Density (calc.)	1.346 g/cm^3
Absorption coefficient	2.43 cm^{-1}
F(000)	4864 e^-
Data collection	
Diffractometer	Syntex P21
Radiation	Mo-K_α (λ 0.71073 Å)
Temperature	−70 °C
Monochromator	Highly oriented graphite crystal
2θ range	4.0 to 40.0°
Scan type	2θ
Scan speed	Fixed; 6.00°/min (in 2θ)
Scan range	2.00° plus K_α separation
Standard reflections	3 measured every 97 reflections
Index ranges	$0 \leq h \leq 26$, $0 \leq k \leq 14$, $-30 \leq l \leq 28$
Reflections collected	10481
Unique reflections	7475 ($I > 0$)
Observed reflections	4476 ($F > 3.0\sigma(F)$)
Solution and refinement	
System used	Nicolet SHELXTL PLUS (MicroVAX II)
Solution	Direct methods
Refinement method	Full-matrix least-squares
Quantity minimized	Sum of $s(F_0 - F_c)^2$
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0005F^2$
Final residuals (obs. data)	R_F 8.2%, R_{wF} 14.5 %
Residuals (unique data)	R_F 8.2%, R_{wF} 14.5%
Goodness-of-fit	4.28
Number of variables	685
Data-to-parameter ratio	6.5/1
Largest and mean Δ/σ	0.00, 0.00

(w), 1870 (w), 1805 (w), 1605 (m), 1495 (s), 1455 (s), 1410 (m), 910 (m), 840 (s), 830 (s), 805 (m), 770 (s), 620 (w) cm^{-1}. Mass spectrum (65 eV, 200 °C), m/e (relative intensity), 1144 (M^+, 19%), 1053 ($M^+ - C_7H_7$, 58%), 962 ($M^+ - 2(C_7H_7)$, 60%)), 871 ($M^+ - 3(C_7H_7)$, 12%), 780 ($M^+ - 4(C_7H_7)$, 5%), 91 ($C_7H_7^+$, 100%). Anal. Found: C, 58.46; H, 4.97. $C_{56}H_{56}O_{12}Si_8$ calcd.: C, 58.71; H, 4.93%.

Table 2

Atomic coordinates and equivalent isotropic temperature factors

Atom	x	y	z	$U \times 10^4$
C(01)	0.9833(8)	0.1908(5)	0.4593(4)	367(47)
C(02)	1.0972(8)	0.1270(5)	0.4595(4)	343(45)
C(03)	1.1733(9)	0.1267(6)	0.3992(5)	485(56)
C(04)	1.2762(10)	0.0662(7)	0.3962(6)	641(72)
C(05)	1.2984(10)	0.0041(7)	0.4549(7)	653(74)
C(06)	1.2236(11)	0.0026(6)	0.5168(6)	633(72)
C(07)	1.1207(9)	0.0635(6)	0.5189(5)	499(58)
C(08)	0.6434(8)	0.4275(5)	0.3976(4)	350(45)
C(09)	0.5796(8)	0.3490(5)	0.4384(4)	355(46)
C(10)	0.5126(8)	0.3654(5)	0.5012(4)	368(46)
C(11)	0.4472(9)	0.2933(6)	0.5360(5)	479(56)
C(12)	0.4515(10)	0.2057(6)	0.5097(5)	528(61)
C(13)	0.5236(10)	0.1890(6)	0.4485(5)	547(62)
C(14)	0.5867(8)	0.2583(5)	0.4127(5)	427(51)
C(15)	0.6939(7)	0.5758(5)	0.6616(4)	328(43)
C(16)	0.7343(7)	0.6204(5)	0.7319(4)	315(43)
C(17)	0.8101(9)	0.5723(6)	0.7838(4)	442(53)
C(18)	0.8438(9)	0.6141(6)	0.8478(5)	505(58)
C(19)	0.8068(9)	0.7031(7)	0.8622(4)	490(57)
C(20)	0.7306(9)	0.7512(6)	0.8113(5)	516(59)
C(21)	0.6955(8)	0.7100(6)	0.7463(5)	439(52)
C(22)	1.0531(8)	0.3355(5)	0.7197(4)	389(48)
C(23)	1.1757(8)	0.2819(5)	0.7239(4)	335(44)
C(24)	1.1934(9)	0.1995(5)	0.6875(4)	430(51)
C(25)	1.3079(10)	0.1525(6)	0.6894(5)	530(60)
C(26)	1.4028(10)	0.1854(8)	0.7273(6)	629(70)
C(27)	1.3840(9)	0.2672(8)	0.7639(5)	599(67)
C(28)	1.2706(9)	0.3156(6)	0.7615(4)	462(55)
C(29)	0.1453(8)	0.1286(5)	0.9097(4)	350(45)
C(30)	0.0589(7)	0.1887(5)	0.9553(4)	302(42)
C(31)	−0.0108(8)	0.1511(6)	1.0131(4)	414(50)
C(32)	−0.0942(8)	0.2030(7)	1.0521(5)	474(56)
C(33)	−0.1088(8)	0.2992(7)	1.0342(5)	513(60)
C(34)	−0.0387(10)	0.3377(6)	0.9774(6)	594(66)
C(35)	0.0438(8)	0.2842(5)	0.9387(4)	412(50)
C(36)	0.4204(7)	−0.0900(5)	0.7670(4)	317(43)
C(37)	0.2971(7)	−0.1316(5)	0.7637(4)	301(42)
C(38)	0.2884(8)	−0.2289(5)	0.7722(4)	390(49)
C(39)	0.1746(10)	−0.2684(6)	0.7650(5)	496(58)
C(40)	0.0713(10)	−0.2118(8)	0.7516(5)	568(65)
C(41)	0.0783(8)	−0.1169(7)	0.7455(5)	497(59)
C(42)	0.1904(9)	−0.0779(6)	0.7502(5)	458(55)
C(43)	0.8146(7)	0.0907(5)	0.8500(4)	336(44)
C(44)	0.7812(7)	0.1587(5)	0.7873(4)	328(44)
C(45)	0.7447(8)	0.2501(5)	0.8002(5)	430(52)
C(46)	0.7136(10)	0.3130(6)	0.7427(5)	559(63)
C(47)	0.7152(10)	0.2866(7)	0.6706(5)	590(66)
C(48)	0.7516(10)	0.1973(7)	0.6551(5)	565(64)
C(49)	0.7844(9)	0.1334(6)	0.7132(5)	447(53)
C(50)	0.5340(9)	0.3122(5)	1.0088(5)	485(56)
C(51)	0.4764(8)	0.3851(5)	0.9538(4)	375(47)
C(52)	0.3520(9)	0.4045(5)	0.9561(5)	433(53)
C(53)	0.2986(11)	0.4727(6)	0.9088(6)	601(66)

Table 2 (continued)

Atom	x	y	z	$U \times 10^4$
C(54)	0.3727(14)	0.5201(6)	0.8582(6)	710(79)
C(55)	0.4928(13)	0.5013(7)	0.8550(5)	683(78)
C(56)	0.5462(10)	0.4329(6)	0.9039(5)	549(61)
O(01)	0.8753(5)	0.3696(3)	0.4532(3)	337(31)
O(02)	0.7592(5)	0.5058(3)	0.5215(3)	354(31)
O(03)	0.9138(5)	0.4706(3)	0.6316(3)	324(30)
O(04)	1.0233(5)	0.3285(3)	0.5648(3)	340(30)
O(05)	1.1105(5)	0.3587(3)	0.4284(3)	352(31)
O(06)	0.8486(5)	0.5364(4)	0.3860(3)	404(33)
O(07)	0.6043(5)	0.1404(3)	0.9406(3)	314(29)
O(08)	0.3732(5)	0.1673(3)	0.9743(3)	295(28)
O(09)	0.3598(5)	0.0245(3)	0.8886(3)	353(31)
O(10)	0.5917(5)	−0.0052(4)	0.8573(3)	363(32)
O(11)	0.2670(5)	0.0164(3)	1.0242(3)	368(32)
O(12)	0.4640(5)	−0.1391(3)	0.9193(3)	362(31)
Si(01)	1.0007(2)	0.3150(1)	0.4768(1)	286(11)
Si(02)	0.7853(2)	0.4609(1)	0.4415(1)	288(12)
Si(03)	0.8177(2)	0.5474(1)	0.5946(1)	274(11)
Si(04)	1.0339(2)	0.4009(1)	0.6299(1)	280(11)
Si(05)	0.2889(2)	0.0841(1)	0.9512(1)	279(11)
Si(06)	0.6818(2)	0.0524(1)	0.9077(1)	289(11)
Si(08)	0.5110(2)	0.1875(1)	0.9989(1)	292(11)

[a] $U_{eq} = [1(6\pi^2) \times \Sigma\beta(a_{ij} \cdot a_i \cdot a_j)]$.

Preparation of [m-tolSiO$_{3/2}$]$_8$ (2)

m-Tolyltrichlorosilane (2.8 g, 12.5 m*M*) was carefully added with vigorous stirring to 35 ml of 95% ethanol. The mixture was refluxed for 3 days, then decanted to give a gummy solid, which was triturated with acetone. Recrystallization from CH_2Cl_2/acetone afforded colorless crystals, which rapidly desolvated upon isolation. Yield: 438 mg (25%). m.p. 406–409 °C. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C) δ 7.607 (s, 1H), 7.570 (t, J 4.2 Hz, 1H), 7.255 (d, J 3.7 Hz, 1H), 7.255 (d, J 4.6 Hz, 1), 2.316 (s, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$, 25 °C) δ 137.07, 134.98, 131.44, 131.33, 130.18, 127.72. 21.39. ^{29}Si NMR (49.7 MHz, $CDCl_3$, 25 °C) δ −78.1. IR (KBr) 3030 (w), 2920 (w), 2860 (w), 1600 (w), 1580 (w), 1480 (w), 1450 (w), 1230 (s), 1120(s), 1000 (m), 870 (m), 780 (s), 710 (w), 700 (s), 620 (w) cm^{-1}. Mass spectrum (65 eV, 200 °C), M/e (relative intensity), 1144 (M^-, 35%), 1053 ($M^+ - C_7H_7$, 100%), 962 ($M^+ - 2(C_7H_7)$, 65%), 871 ($M^+ - 3(C_7H_7)$, 9%).

Preparation of [3,5-Me$_2$C$_6$H$_3$SiO$_{3/2}$]$_8$ (3)

3,5-Dimethylphenyltrichlorosilane (2.8 g, 11.8 m*M*) was carefully added with vigorous stirring to 35 ml of 95% ethanol. The mixture was refluxed for 3 days, then decanted to give a gummy solid, which was triturated with 1/1 acetone/methanol. Recrystallization from CH_2Cl_2/acetone afforded colorless crystals. Yield: 408 mg (22%). mp 310–312 °C. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C) δ 7.429 (s, 2H), 7.074 (s, 1H), 2.285 (s, 6H). ^{13}C NMR (125.76 MHz, $CDCl_3$, 25 °C) δ 136.97, 132.26, 132.14, 130.26, 21.24. ^{29}Si NMR (49.7 MHz, $CDCl_3$, 25 °C) δ −78.1. IR (KBr) 3020 (m), 2920 (m), 1595 (m), 1475 (w), 1450 (w), 1410 (m), 1380 (m), 1280 (m), 1090 (s), 880 (vs), 850 (vs), 695 (vs) cm^{-1}. Mass spectrum (65 eV, 200 °C), *m/e* (relative intensity), 1257 (M^+, 84%), 1151 ($M^+ - C_8H_9$, 100%), 1047 ($M^+ - 2(C_8H_9)$, 20%), 943 ($M^+ - 3(C_8H_9)$, 20%).

Hydrogenation of 1–6

In a typical reaction, the aryl silsesquioxane (~ 100 mg), catalyst (~ 40 mg of 10% Pd/C), and solvent (20 ml of 88/12 ethyl acetate/acetic acid) were placed in the Pyrex liner of the Parr mini-reactor. After purging three times with H_2 (pressurizing to 500 psig and venting), the reactor was charged with H_2 (1–35 atm) and heated with stirring at 150–200 °C. Upon cooling, the catalyst was removed by vacuum filtration and washed with chloroform. Rotary evaporation of the filtrate to ~ 2 ml (mostly acetic acid) and the addition of acetone quantitatively precipitated the product, which was recrystallized from CH_2Cl_2/acetone. Specific reaction conditions, product yields and melting point data are collected in Table 3.

For **7**: ^1H NMR (250.1 MHz) δ 1.718 (m, 5H), 1.486 (m, 1H), 1.196 (m, 3H), 0.947 (m, 2H), 0.568 (d, J 7 Hz, 2H). ^{13}C NMR (125.76 MHz) δ 36.236 (CH_2), 33.086 (CH), 26.577 (CH_2), 26.259 (CH_2), 21.020 (CH_2). IR 2920 (s), 2855 (m), 1450 (m), 1315 (w), 1260 (w), 1235 (w), 1185 (m), 1110 (s), 1060 (m), 890 (w), 850 (w), 805 (w), 790 (w), 750 (w), 735 (w) cm^{-1}. Mass spectrum (65 eV, 200 °C) 1192 (M^+, 4%), 1095 ($M^+ - C_7H_{13}$, 100%)), 999 ($M^+ - 2(C_7H_{13})$, 13%), 903 ($M^+ - 3(C_7H_{13})$, 4%).

For **8**: Mass spectrum (65 eV, 200 °C) 1192 (M^+, 0.5%), 1095 ($M^+ - C_7H_{13}$, 100%)), 999 ($M^+ - 2(C_7H_{13})$, 45%), 903 ($M^+ - 3(C_7H_{13})$, 15%). IR 2930 (s), 2855 (m), 1460 (m), 1450 (m), 1245 (m), 1195(m), 1110 (s), 900 (w), 850 (w), 700 (w) cm^{-1}.

Table 3

Summary of hydrogenation reactions

Starting material	Product(s)	Cond. [a]	Yield [b]	M.p. (°C)
$(C_6H_5CH_2)_8(Si_8O_{12})$ (**1**)	$(c\text{-}C_6H_{11}CH_2)_8(Si_8O_{12})$ (**7**)	i	100 (92)	253–254
$(3\text{-}MeC_6H_4)_8(Si_8O_{12})$ (**2**)	$(3\text{-}MeC_6H_{10})_8(Si_8O_{12})$ (70/30 *cis/trans*) [c] (**8**)	ii	100 (95)	340–360
$(3,5\text{-}Me_2C_6H_3)_8(Si_8O_{12})$ (**3**)	$(3,5\text{-}Me_2C_6H_9)_8(Si_8O_{12})$ (3 isomers) [c] (**9**)	ii	100 (88)	240–260
$(4\text{-}MeC_6H_4)_8(Si_8O_{12})$ (**4**)	$(4\text{-}MeC_6H_{10})_8(Si_8O_{12})$ (74:26 *cis/trans*) [c] (**10**)	ii	100 (93)	355–380
$(C_6H_5)_8(Si_8O_{12})$ (**5**)	$(c\text{-}C_6H_{11})_8(Si_8O_{12})$ [d] (**11**)	ii	100 (93)	> 400
$(C_6H_5)_{12}(Si_{12}O_{18})$ (**6**)	$(c\text{-}C_6H_{11})_{12}(Si_{12}O_{18})$ (**12**)	ii	100 (93)	> 400

[a] Conditions: (i) 1 atm, 150 °C; (ii) 34 atm, 200 °C. [b] Yields: The crude yield is virtually quantitative by ^1H NMR spectroscopy. The isolated yield of recrystallized product is given in parentheses. [c] Isomers: *cis* and *trans* refer to configurations of methyl substituents relative to the Si–O framework on the cyclohexyl rings. Based on normal selectivity patterns for catalytic hydrogenation reactions of this type, the major isomer is assumed to be the *cis*-isomer. [d] Identical in all respects to **11** prepared by the hydrolytic condensation of $c\text{-}C_6H_{11}SiCl_3$ [3b].

Major isomer (*cis*, 70%): partial ^{1}H NMR (500.1 MHz) δ 0.874 (dd, *J* 6.7, 1.5 Hz, CH_3). ^{13}C NMR (125.76 MHz) δ 35.54, 35.18, 27.63, 26.11 (CH_2); 33.62, 23.17 (CH); 23.24 (CH_3). ^{29}Si NMR (49.7 MHz) δ −68.8.

Minor isomer (*trans*. 30%): partial ^{1}H NMR (500.1 MHz) δ 0.912 (d, *J* 6.7 Hz, CH_3). ^{13}C NMR (125.76 MHz) δ 33.76, 33.62, 26.40, 22.82, 20.34 (CH_2); 28.44, 18.70 (CH); 20.34 (CH_3). ^{29}Si NMR (49.7 MHz) δ −67.7.

For **9**: Mass spectrum (65 eV, 200 °C) 1304 (M^+, 1%), 1193 ($M^+ - C_8H_{15}$, 100%), 1082 ($M^+ - 2(C_8H_{15})$, 32%), 972 ($M^+ - 3(C_8H_{15})$, 20%). IR 2950 (s), 2900 (s), 2840 (m), 1455 (s), 1440 (w), 1380 (m), 1360 (w), 1310 (m), 1280 (w), 1210 (s), 1110(vs), 990 (m), 940 (w), 890 (m), 855(m), 845 (m), 805 (m) cm^{-1}. ^{1}H NMR (500.1 MHz) δ 1.75, 1.74, 1.65, 1.36, 0.98, 0.83 (broad multiplets), 0.53 (pseudo quartet), 0.88 (*d*, *J* 7 Hz, CH_3, ~ 25% of total integral). ^{13}C NMR (125.76 MHz) δ 44.24, 34.73, 34.71, 34.66, 34.48 (CH_2); 33.47, 22.75 (CH); 22.87 (CH_3). ^{29}Si NMR (49.7 MHz) δ −67.6 (v br s, ~ 17%), −68.6 (br s, ~ 58%), −68.8 (br s, ~ 25%).

For **10**: Mass spectrum (65 eV, 200 °C) 1192 (M^+, 1%), 1095 ($M^+ - C_7H_{13}$, 100%)), 999 ($M^+ - 2(C_7H_{13})$, 38%), 903 ($M^+ - 3(C_7H_{13})$, 13%. IR 2920 (s), 2860 (s), 1450 (m), 1380 (m), 1330 (w), 280 (m), 1200 (m), 1115 (s), 880 (m) cm^{-1}. ^{29}Si NMR (49.7 MHz) δ −68.3 (broad singlet for both isomers).

Major isomer (*cis*. 74%): partial ^{1}H NMR (500.1 MHz) δ 0.914 (dd, *J* 4.7, 1.3 Hz, CH_3). ^{13}C NMR (125. 76 MHz) δ 32.86 (s, CH_2), 23.18 (br s, CH_2), 30 (br s, CH), 22 (br s, CH), 19.79 (br s, CH_3).

Major isomer (*trans*. 26%): partial ^{1}H NMR (500.1 mHz) δ 0.856 (d, *J* 5.1 Hz, CH_3). ^{13}C NMR (125.76 MHz) δ 32.26 (s, CH_2), 26.58 (br s, CH_2), 32.77 (br s, CH), 22.76 (br s, CH), 23.19 (br s, CH_3).

For **11**: ^{1}H NMR (500.1 MHz) δ 1.731 (br m, 5H), 1.233 (br m, 5H), 0.755 (br m, 1H). ^{13}C NMR (125.76 MHz) δ 27.054 (s, CH_2), 26.903 (s, CH_2), 26.641 (s, CH_2), 23.165 (s, CH). IR 2930 (s), 2860 (s), 1450 (m), 1272 (m), 1280 (m), 1200 (m), 1110 (vs), 1045 (m), 1030 (m), 900 (m), 852 (m), 830 (w), 750 (w) cm^{-1}. 29Si NMR (48.7 MHz) δ −69.80.

For **12**: ^{1}H NMR (500.1 MHz) δ 1.75 (m, 5H), 1.22 (br m, 5H), 0.68 (br m, 1H). ^{13}C NMR (125.76 MHz) δ 27.72, 27.70, 27.67, 27.02, 26.97, 26.82 (s, CH_2); 24.62, 24.01 (2/1 for CH). IR 2930 (s), 2860 (s), 1450 (m), 1280 (m), 1270 (m), 1200 (s), 1110 (s), 1040 (m), 1030 (m), 900 (m), 850 (m), 830 (w), 750 (w) cm^{-1}. Mass spectrum (65 eV, 200 °C) 1537 ($M^+ - C_6H_{11}$, 100%), 1454 ($M^+ - 2(C_6H_{11})$, 18%), 1371 ($M^+ - 3(C_6H_{11})$, 7%). ^{29}Si NMR (49.7 MHz) δ −71.29 (s, 1 Si), −74.29 (s, 2Si).

Results and discussion

Silsesquioxane **1** was synthesized by the hydrolytic condensation of benzyl trichlorosilane in 95% ethanol (0.3 *M*, 78 °C, 2 d). Unlike most POSS syntheses based on dilute hydrolytic condensation reactions [1], the product does not spontaneously precipitate from the reaction mixtures. Concentration of the condensate solution (7 °C, 1 atm) and trituration of the resulting resin with 1/1 acetone/methanol does, however, produce a fine white powder, which affords large colorless crystals of **1** (24% yield) upon recrystallization from CH_2Cl_2/acetone.

The extremely high solubility of **1** in many organic solvents (vide intra) was puzzling in light of the apparent absence of solvent molecules in the highly

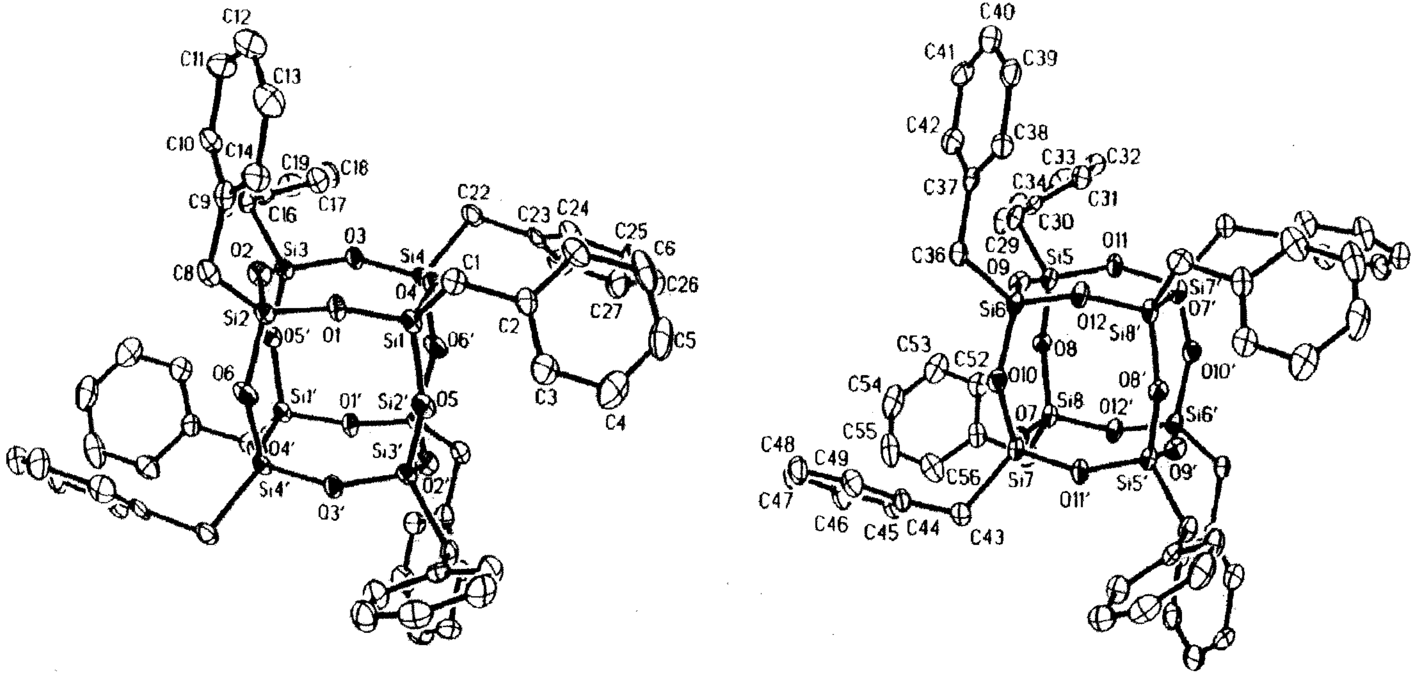


Fig. 1. Perspective ORTEP Plot of **1**. Two crystallographically independent "molecular halves" are present in the asymmetric unit. Whole molecules derived from each half are plotted with 20% thermal ellipsoids. The ranges for Si–O and Si–C bond distances are 1.600(5)–1.627(5) and 1.826(8)–1.868(8) Å, respectively. The ranges for Si–O–Si and O–Si–O bond angles are 141.0(4)–154.5(4) and 105.3(4)–113.2(4) degrees, respectively. The spatial orientation of the two molecules in the unit cell is not shown.

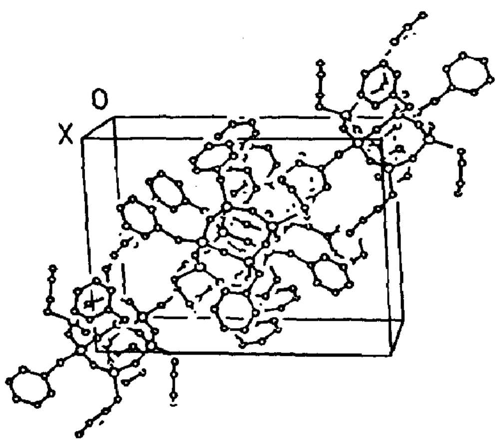


Fig. 2. Packing diagram of **1** showing the spatial orientation of molecules in the unit cell which are derived from the two crystallographically independent "molecular halves" present in the asymmetric unit.

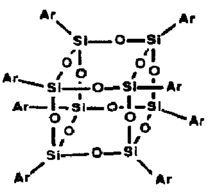
crystalline lattice of **1**. Since efficient crystal packing in POSS frequently leads to poor solubility properties, which in turn can be used to drive high-yield, base-catalyzed equilibrative syntheses of POSS, a single-crystal X-ray diffraction study of **1** was performed to examine the nature of the crystal packing in **1**. A perspective plot of **1** is shown in Fig. 1.

The molecules crystallize in the space group *P*1 bar with two crystallographically independent "molecular halves". Crystallographic inversion generates the second half of each molecule in the unit cell. The average Si–O and Si–C bond distances (1.616 ± .007 and 1.845 ± .012 Å, respectively) and Si–O–Si and O–Si–O bond angles (148.9 ± 4.8 ° and 109.4 ± 1.5 °, respectively) exhibit no peculiarities and are well within their accepted ranges [1,7b,10,11]. As might be expected based on solubility properties, there is a complete lack of both intra and inter-molecular π-stacking interactions in the crystal lattice of **1**. Quite remarkably, though, very efficient crystal packing (Fig. 2) can still occur without either solvent inclusion, a very common occurrence with POSS, or π-stacking interactions, which generally provide sufficient lattice energy in other POSS to drastically reduce solubilities (vide infra).

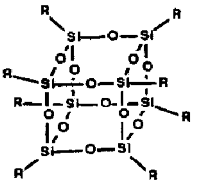
The hydrogenation of **1** over 10% Pd/C proceeds smoothly in ethyl acetate/acetic acid at 1 atm and 150 ° C to afford virtually quantitative yields of the corresponding cyclohexylmethylsilsesquioxane (**7**). The ^{1}H and ^{13}C NMR spectra of the crude product show no evidence for either C–Si hydrogenolysis or Si–O cleavage.

Other aryl silsesquioxanes can also be cleanly hydrogenated, although somewhat higher temperatures and greater pressures of H_2 must be used. The results from the catalytic hydrogenation reactions of a number of aryl silsesquioxanes, including two new aryl-T_8's (**2** and **3**), are shown in Table 3. In all cases the yield of hydrogenation products is virtually quantitative. As expected, hydrogenation of **2**, **3** and **4** is relatively nonselective and affords mixtures of *cis* and *trans* hydrogenation products.

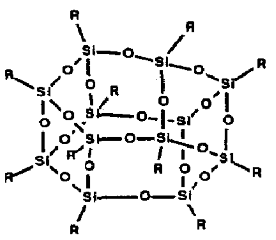
It is interesting to note that the hydrogenation of **6** to **12** finally provides unambiguous evidence that the structure of **6** has local C_{2v} symmetry, rather than



1 Ar = $PhCH_2$
2 3-MePh
3 3,5-Me_2Ph
4 4-MePh
5 Ph



7 R = $CyCH_2$
8 3-MeCy
9 3,5-Me_2Cy
10 4-MeCy
11 Cy



6 R = Ph
12 Cy

D_{6h} symmetry. Both the ^{29}Si NMR spectrum and the methine region of the ^{13}C NMR spectrum of **12** exhibit two resonances in a 1/2 ratio, clearly indicating that **12** (and therefore **6**) has an "iso-T_{12}" structure. This structure, first proposed for **6** by Brown [3a], was never confirmed, although a crystal structure of iso-$Ph_{12}T_{12}$ prepared by an entirely different route has been reported by Clegg, Sheldrick, and Vater [9].

The physical properties of **7**–**12** exhibit many similarities to the aryl-POSS from which they were derived, such as high air and thermal stability. (**11** and **12** do not melt below 400 °C!). There are, however, several differences which may have practical importance, such as improved solubility properties. In general removal of intermolecular arene stacking interactions and/or the formation of many isomeric hydrogenation products (e.g., **8**, **9**, and **10**) leads to increased solubility. For example, the solubility of **10** in chloroform is > 1.1 g/ml, compared to 0.22 g/ml for **4**. Similarly, the solubilities of **11** (43 mg/ml ($CHCl_3$) and **12** (27 mg/ml $CHCl_3$) in most organic solvents are much higher than **5** and **6**, which are virtually insoluble. Curiously, this trend does not hold for **1** (0.475 g/ml $CHCl_3$) and **7** (0.003 g/ml $CHCl_3$). The surprisingly low solubility of **7** in most organic solvents graphically illustrates both the cumulative effects of efficient crystal packing in this predominantly aliphatic molecule and the difficulties associated with predicting the solubility properties of POSS.

In summary, the catalytic hydrogenation of aryl-containing POSS provides a convenient new source for potentially useful silsesquioxanes. The hydrogenation of **5** and **6** is particularly notable because the requisite phenyl silsesquioxanes can be prepared in nearly quantitative yields from readily available phenyl trichlorosilane [3a,6]. Since these new silsesquioxanes display thermal and physical properties comparable to the corresponding aryl-containing POSS, but frequently have much greater solubilities in common organic solvents, they may offer advantages for a number of applications utilizing POSS.

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