Synthesis and Crystal Structure of a Nanometer-Scale Dendritic Polysilane

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Received April 13, 1998

A triply convergent synthesis has produced a dendritic polysilane with 13 silicons in the longest chain: $[(Me_3Si)_3SiSiMe_2SiMe_2Si(SiMe_3)_2SiMe_2]_3SiMe$. The structure was proved by assignment of each ^1H, ^{13}C, and ^{29}Si resonance and by solution of the X-ray structure. The molecule represents a polysilane dendrimer that has achieved an approximately spherical shape. The roughly perpendicular distances between antipodal terminal methyls are 1.74, 1.70, and 1.65 nm, describing an approximate sphere with nanometer dimensions. The Si−Si−Si−Si dihedral angles indicate mixtures of gauche, orthogonal, and anti conformations. The longest all-anti segment is AAA, a hexasilane moiety. Despite the presence of numerous twists from gauche and orthogonal conformations, the molecule exhibits two ultraviolet maxima at 260 and 283 nm, with extinction coefficients respectively of 1.80×10^5 and 1.16×10^5. The wavelengths are comparable to that exhibited by linear polysilanes of similar length, but the extinction coefficients of the dendrimer are an order of magnitude higher. Thus electronic effects in dendrimers parallel those in linear polysilanes but possess greater intensity.

Polysilanes are organosilicon structural analogues of polymethylenes and electronic analogues of polyacetylenes. They are composed of linear chains of Si−Si bonds, attached to alkyl or aryl side chains.[1] Cross-linked and hyperbranched polysilanes also are known.[2] Polysilanes exhibit thermochromic, photoresistive, conductive, photoconductive, and nonlinear optical properties.[3] They absorb in the ultraviolet, reaching a λ_{max} close to 300 nm when more than 18 dialkylsilyl units are present in a linear array. Because these transitions are in the ultraviolet rather than the visible, polysilanes offer potential applications that require visual transparency. Exploitation of these favorable properties has been limited to some extent by the chemical sensitivity of the Si−Si bond, which is reactive with both electrophiles and nucleophiles.

We[4,5] and other groups[6−8] have endeavored to construct polysilanes with a dendritic architecture, which should convey several advantages. (1) Surface crowding can exclude electrophilic and nucleophilic reagents from the interior Si−Si bonds, the surface ideally being an array of methyl groups for the permethyl case that we have emphasized. (2) The process of multiple branching that is inherent in the dendritic concept creates numerous redundant pathways, so that molecular properties may survive the loss of portions of the molecule through Si−Si cleavage. (3) A dendrimer has an exact molecular weight, whereas synthetic linear polymers are collections of *n*-mers. Thus X-ray crystallography becomes applicable, and accurate structures can be obtained. (4) Solubility is determined largely by the properties of the surface methyl groups, as solvent molecules tend not to penetrate into the core. Hence these large molecules can have good solubility despite their size.

Previously, we have prepared dendritic polysilanes with a longest chain length of seven silicons.[4,5] The group of Sekiguchi and Sakurai[6] has reported a dendritic polysilane with a chain of 11 silicons. As optical properties appear to approach an optimum with a linear chain of about 18 silicons or more, it has been our goal to synthesize dendritic polysilanes with longer chains to explore the effect of chain length on optical properties. We report herein the synthesis and crystal structure of a dendritic polysilane with a longest chain of 13 silicons. We also report an alternative synthetic approach to large dendritic polysilanes that has yielded an interesting branched polysilane.

Results and Discussion

Our initial strategy for preparing dendritic polysilanes involved a divergent approach in which the Si−

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[1] For a review, see: Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359−1410.

[2] Bianconi, P. A.; Weidman, T. W. *J. Am. Chem. Soc.* **1988**, *110*, 2342−2344. Matyjaszewski, K.; Chrusciel, J.; Maxka, J.; Sasaki, M. *J. Inorg. Organomet. Polym*. **1995**, *5*, 261−279.

[3] For examples, see: Miller, R. D.; Hofer, D.; Sooriyakumaran, R.; Willson, C. G.; Fiskes, G. N.; Guiller, J. E.; Moore, J. *Polym. Mater. Sci. Eng.* **1986**, *55*, 599−603. West, R.; David, L. D.; Djurovich, P. I., Stearley, K. L.; Srinavasan, K. S. V.; Yu, H. *J. Am. Chem. Soc.* **1981**, *103*, 7352−7354.

[4] Lambert, J. B.; Pflug, J. L.; Stern, C. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 98−99.

[5] Lambert, J. B.; Pflug, J. L.; Denari, J. M. *Organometallics* **1996**, *15*, 615−625.

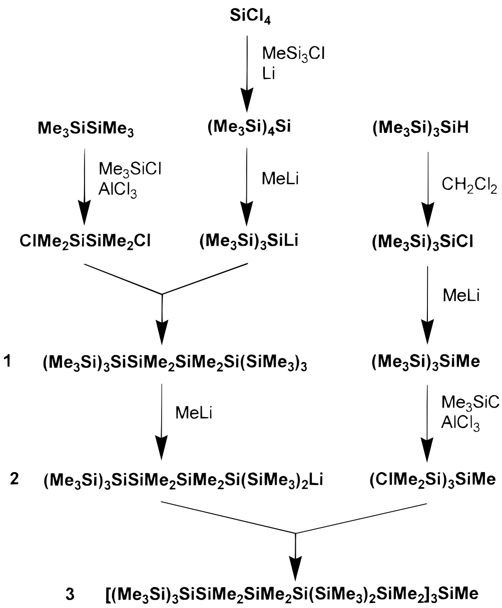
[6] Sekiguchi, A.; Nanjo, M.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* 1995, *117*, 4195−4196. Nanjo, M.; Sekiguchi, A.; Sakurai, H. *Bull. Chem. Soc. Jpn*. **1998**, *71*, 741−747. Nanjo, M.; Sekiguchi, A. *Organometallics* **1998**, *17*, 492−494.

[7] Suzuki, H.; Kimata, Y.; Satoh, S.; Kuriyama, A. *Chem. Lett.* **1995**, 293−294.

[8] Marschner, C.; Hengge, E. Poster PA86, XIth Organosilicon. Symposium, Montpelier, France, September, 1996. Bravo-Zhivotovskii, D.; Yuzafovich, M.; Bendikov, M.; Apeloig, Y.; Klinkhammer, K.; Boese, R. Poster PA54, XIth Organosilicon Symposium, Montpelier, France, September, 1996.

10.1021/om980280f CCC: $15.00
Publication on Web 10/08/1998

Scheme 1



Si bonds were constructed one at a time.[4,5] This type of synthesis is very cumbersome for the preparation of larger polysilanes. Moreover, an inherent part of the synthesis involves the reaction of polychloropolysilanes with polysilyllithium reagents, as in eq 1. The possibility

$$MeSi(SiMe_2Cl)_3 + 3(Me_3Si)_3SiLi \rightarrow MeSi[SiMe_2Si(Me_3Si)_3]_3 \quad (1)$$

of radical reactions and of Si–Si cleavage in both starting material and product by the lithium reagent reduces applicability to larger systems. The method was successful in our laboratory in preparing four dendrimers, three structures of which were proved by X-ray crystallography[4,5] and one by 2D ^{29}Si INADEQUATE.[9] These materials contained longest chains of five or seven silicons. To synthesize dendritic polysilanes with much longer silicon chains, we have explored various convergent approaches.

In 1995, we[10] reported the crystal structure of 2,2,5,5-tetrakis(trimethylsilyl)-1,1,1,3,3,4,4,6,6,6-decamethylhexasilane (**1**), which was obtained in a straightforward manner by the method of eq 2. This molecule, also

$$ClMe_2Si{-}SiMe_2Cl + (Me_3Si)_3Si{-}Li \rightarrow \underset{\mathbf{1}}{(Me_3Si)_3Si{-}Me_2Si{-}Me_2Si{-}Si(SiMe_3)_3} \quad (2)$$

reported by Pannell and co-workers,[11] provides a large polysilane unit that may be converted to a silyllithium reagent. This species in turn may be reacted with a polychloropolysilane in the manner of eq 1 to create large dendrimers.

The complete approach is depicted in Scheme 1. The commercially available starting materials were hexamethyldisilane, tetrachlorosilane, and tris(trimethylsilyl)silane. The last molecule was converted to tris(chlorodimethylsilyl)methylsilane,[12] and tetrachlorosilane was converted to tris(trimethylsilyl)silyllithium.[13] Hexamethyldisilane was dichlorinated and reacted as in eq 1 with tris(trimethylsilyl)silyllithium to form 2,2,5,5-tetrakis(trimethylsilyl)decamethylhexasilane (**1**).[5,10] Reaction of **1** with methyllithium provided the silyllithium reagent 1,1,4,4-tetrakis(trimethylsilyl)-2,2,3,3,5,5,5-heptamethylpentasilyllithium (**2**). This reaction involved cleavage of a bond between one of the entirely Si-substituted silicon atoms and an attached trimethylsilyl group. Pannell[11] reported cleavage of the central bond, but our result is the same as that of Apeloig et al.,[14] who reported the crystal structure of **2**. Reaction of the large silyllithium reagent **2** with tris(chlorodimethylsilyl)methylsilane produced the desired product, **3**, tris[2,2,5,5-tetrakis(trimethylsilyl)hexasilyl]methylsilane.

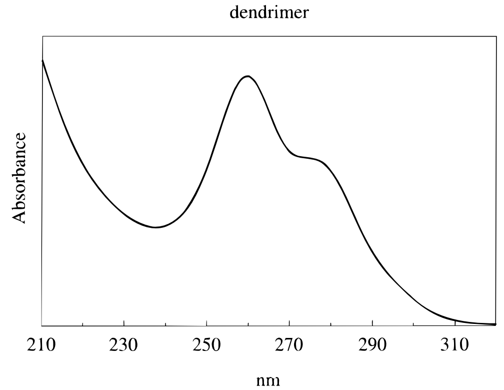
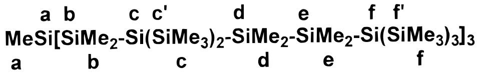


Figure 1. Ultraviolet spectrum of **3**.

The structure was elucidated by NMR spectroscopy, mass spectrometry, ultraviolet spectroscopy, and X-ray diffraction. There are six types of carbons, six types of hydrogens, and eight types of silicons (see structure **3′**).



$$\underset{a}{Me}\overset{a}{Si}[\overset{b}{Si}\underset{b}{Me_2}\text{-}\overset{c}{Si}(\overset{c'}{Si}\underset{c}{Me_3})_2\text{-}\overset{d}{Si}\underset{d}{Me_2}\text{-}\overset{e}{Si}\underset{e}{Me_2}\text{-}\overset{f}{Si}(\overset{f'}{Si}\underset{f}{Me_3})_3]_3$$

3'

The complete NMR assignments may be found in the Experimental Section. The ^{29}Si spectrum is particularly useful, because it permits sorting silicon atoms according to the number of attached methyl groups. The nominal molecular weight of **3** is 1833 (based on a formula of $Si_{31}C_{64}H_{192}$). The highest large cluster in the mass spectrum is centered around 1310, corresponding to loss of part of one of the three large wings [cleavage between silicons b and c in **3′** with loss of $-Si(SiMe_3)_2$-$SiMe_2SiMe_2Si(SiMe_3)_3$ and retention of one methyl group].

The ultraviolet spectrum (Figure 1) contains large maxima at 260 mm with an ϵ of 1.80×10^5 and at 283 nm with an ϵ of 1.16×10^5. The spectrum was invariant to temperature over the range 25–45 °C. A comparable

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(9) Lambert, J. B.; Basso, E.; Ning, Q.; Lim, S. H.; Pflug, J. L. *J. Organomet. Chem.* **1998**, *554*, 113–116.

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(12) Ishikawa, M.; Kumada, M.; Sakurai, H. *J. Organomet. Chem.* **1970**, *23*, 63–69.

(13) Gutekunst, G.; Brook, A. G. *J. Organomet. Chem.* **1982**, *225*, 1–3. Beno, M. A.; Hope, H.; Olmstead, M. M.; Power, P. P. *Organometallics* **1985**, *4*, 2117–2121.

(14) Apeloig, Y.; Yuzefovich, M.; Bendikov, M.; Bravo-Zhivotovskii, D.; Klinkhammer, K. *Organometallics* **1997**, *16*, 1265–1269.

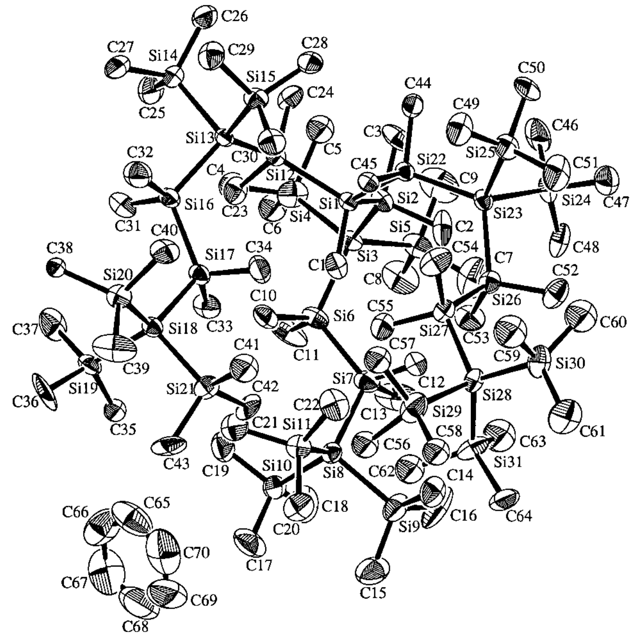

Figure 2. Carbon/silicon skeleton of **3** from X-ray crystallography.

linear polysilane[15] (an array of 12 silicons, as one with 13 appears not to have been characterized) has maxima at 264 nm with an ϵ of 4.3×10^4 and at 285 with an ϵ of 4.35×10^4. Thus the two maxima are at very similar wavelengths for the linear and dendritic materials, but the intensities are about an order of magnitude more intense for the dendrimer, presumably because of the presence of multiple structural pathways. Our largest previous dendrimer, $MeSi[SiMe_2Si(SiMe_3)_3]$ ("**1313**"), with a longest chain of seven silicons,[4,5] had a single absorption maximum at 272 nm and an ϵ of 3.4×10^5. Thus the new dendrimer has gained about 10 nm in the longest absorption over the smaller dendrimers and has comparable intensity. We do not expect the asymptotic absorption of 296 nm[15] until a polysilane chain length of >18 is attained. Further comment about the wavelength position is made below, following analysis of the conformations of the polysilane chains made possible by solution of the X-ray crystal structure.

Crystals suitable for crystallography were obtained by recrystallization from benzene. The solved crystal structure contained one molecule of the solvent benzene and corroborated the spectroscopic conclusions. Figure 2 illustrates the carbon/silicon skeleton in which disorder has been deleted. It indicates that the benzene molecule is outside of the dendrimer. Figures 3 and 4 concentrate on the silicon skeleton. Disorder was present in three parts of the molecule, as shown in Figure 3, in which primes refer to redundant, disordered atoms. Three terminal silicons (Si19, Si20, and Si21) attached to Si18 are disordered (as are the attached but not illustrated methyl carbons C35 on Si19, C38 on Si20, and C41 on Si21). Disorder around Si28 is seen for other terminal silicons Si30 and Si31, as well as for the associated methyl carbons C59−C60 on Si30 and C62−C63 on Si31. The methyl carbons (not shown) on one of the internal bis(trimethylsilyl)silyl groups (C4−C6 on Si4) also are disordered.

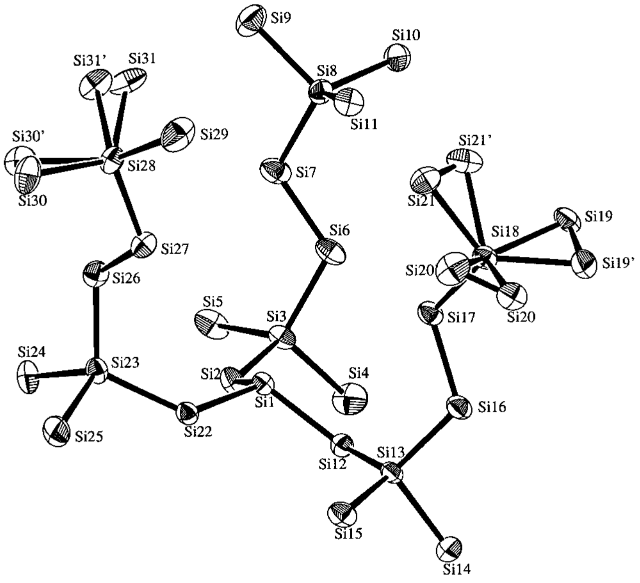

Figure 3. Silicon skeleton of **3** highlighting crystallographic disorders.

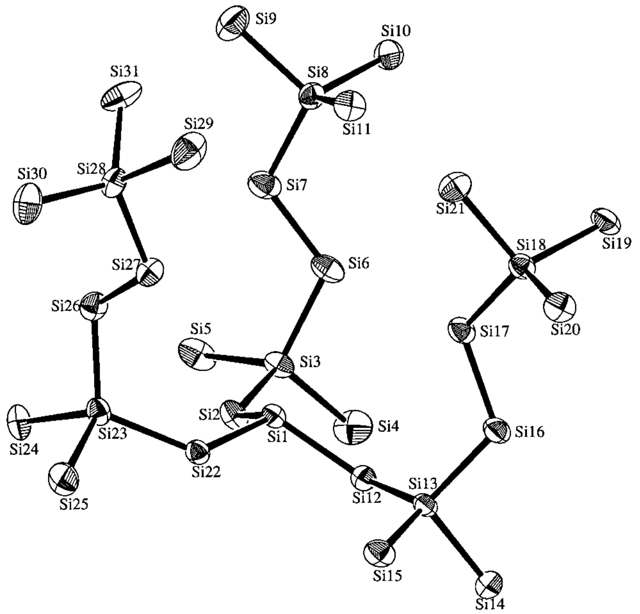

Figure 4. Silicon skeleton of **3** emphasizing its nearly spherical shape.

As seen in Figures 2 and 4, the molecule assumes an approximately spherical shape, with the core silicon not at the center of the sphere but toward one surface. The three wings all point in approximately the same direction (up in Figure 4), giving the impression of a spherical vase or fish bowl with the core silicon close to the base and the wings forming the body. The view of Figure 4 is from the side of the vase. Measurement of the distance between antipodal methyl carbons confirms the spherical shape: 17.4 Å from C6 to C58, 17.0 Å from C36 to C47, and 16.5 Å from C15 to C29. These approximately mutually perpendicular axes have very similar lengths, indicating a spherical structure, in contrast to our earlier dendrimers,[4,5] which were oblate ellipsoids (disk shaped). Thus dendritic polysilanes of this size have achieved the expected large-molecule extreme. The spherical diameter of ca. 1.7 nm indicates a nanoscale structure.

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(15) Boberski, W. G.; Allred, A. L. *J. Organomet. Chem.* **1975**, *88*, 65−72.

Our previous X-ray structures[5] indicated a mix of three conformations for tetrasilane fragments: gauche, orthogonal, and anti. The gauche and anti forms are traditional conformations with Si−Si−Si−Si dihedral angles respectively of ca. 60° and 180°. As predicted by Michl and co-workers,[16] tetrasilanes offer a third conformational family whose dihedral angles cluster around 90° and which hence was called the orthogonal form. We found that our previous dendritic polysilanes[5] exist as a mixture of gauche (G), orthogonal (O), and anti (A) conformations. Molecule **3** has a similar mix, as detailed in the Supporting Information. We classified dihedral angles as gauche for the range 29−73°, orthogonal for the range 80−106°, and anti for the range 156−179°. Quite a few values fall in the range 60−73°, and it is not clear whether these are more properly termed gauche (ca. 60°) or orthogonal (>60° but <110°). They were arbitrarily classified as gauche, but refinement of theory in the future may require their reclassification as orthogonal. Actual values of dihedral angles also are included in the Supporting Information.

The longest all-anti segments are found in several hexasilane fragments (AAA). There are numerous all-gauche hexasilane fragments (GGG). It has frequently been noted[1] that all-anti fragments are optimal for electronic delocalization or σ conjugation. Nonetheless, dendrimer **3** has essentially the same wavelengths of absorption as the linear dodecasilane,[15] in which it is presumed that anti conformers dominate. X-ray structures are not available for linear polysilanes, so it must be assumed that they have a predominantly all-anti conformation. Either anti forms do not in fact dominate in the linear polysilanes, or σ conjugation does not have the anti preference indicated by theory. Whatever the reasons, dendritic polysilanes now appear to have essentially the same wavelengths for electronic absorptions as linear polysilanes, despite the architectural constraints that prohibit long segments of anti conformations. It is remarkable that every orthogonal tetrasilane fragment in **3** is adjacent to an anti fragment (OA or AO, see Supporting Information). Our smaller dendritic polysilanes, however, also contain OO and OG fragments.[5]

The Si−Si bond lengths in **3** lie unremarkably within the range 2.34−2.40 Å. The Si−Si−Si bond angles are variable but generally within the range 102−120°. Low Si−Si−Si bending force constants permit a much larger range than for C−C−C angles. The exceptions to this range, other than apparent anomalies associated with disorder, are the angles around the core silicon.[5] The Si1−Si2−Si3, Si1−Si12−Si13, and Si1−Si22−Si23 angles respectively are 126.0°, 130.6°, and 129.9°. These wider angles around the core silicon reduce strain in the wings. The phenomenon was observed previously in the smaller dendrimer **1313**, whose angles average 130.4° around the core silicon.[5] The bond lengths and angles for **3** are listed fully in the Supporting Information.

We also have been trying to adapt the mercury approach, used by Sekiguchi et al.,[6] for the production of very large dendrimers, but with limited success to date. A Si−H bond is allowed to react with di(*tert*-butyl)mercury to form a disilylmercury reagent, as illustrated in eq 3. In this case, the silylmercury reagent failed to react with lithium in the dark at room temperature.[6]

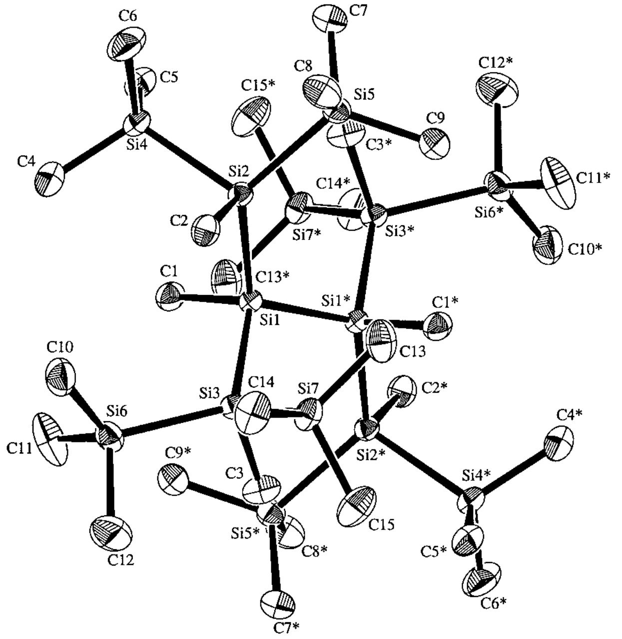

Figure 5. Crystal structure of **4**.

$$[(Me_3Si)_2MeSi]_2MeSi{-}H \rightarrow$$

$$[(Me_3Si)_2MeSi]_2MeSi{-}Hg{-}SiMe[SiMe(SiMe_3)]_2 \xrightarrow{\Delta}$$

$$\underset{\mathbf{4}}{[(Me_3Si)_2MeSi]_2MeSi{-}SiMe[SiMe(SiMe_3)_2]_2} \quad (3)$$

When heated without protection from light, it decomposed without reaction with lithium to form the dimer **4**, 2,5-(trimethylsilyl)-3,4-[methylbis(trimethylsilyl)silyl]-1,1,1,2,3,4,5,6,6,6-decamethylhexasilane, which is a double-cored dendritic polysilane with the longest chain containing only six silicons. The structure was solved by X-ray crystallography and is illustrated in Figure 5. Structural details are given in the Supporting Information.

Conclusions

We have synthesized a dendritic polysilane containing 13 silicons in the longest chain (**3**). Its structure was proved by spectroscopy and crystallography. Its ultraviolet absorption (Figure 1) parallels that of a linear polysilane with a similar length. Despite the presence of numerous gauche and orthogonal structural portions and all-anti structures over no more than six silicons (AAA), the molecule shows longer wavelength absorption than smaller dendrimers. This result supports the expectation that dendrimers of ca. 18 silicons in the longest chain will reach the asymptote for electronic properties observed for linear polysilanes. With their expected more robust properties, these dendritic polysilanes should be superior to linear polysilanes for conductive and nonlinear optical properties. We shall continue to explore synthetic methods to extend dendritic chains from the current maximum reported herein of 13 silicons in the longest chain to the vicinity of 18.

Experimental Section

Tetrahydrofuran (THF) was distilled from sodium/benzophenone immediately prior to use. Chlorotrimethylsilane,

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[16] Teramae, H.; Michl, J. *Mol. Cryst. Liq. Cryst.* **1994**, *256*, 149−159.

hexamethyldisilane, and tris(trimethylsilyl)silane were obtained from Aldrich and used as received. Methyltris(trimethylsilyl)silane was obtained by the method of Baines et al.,[17] tris(chlorodimethylsilyl)methylsilane by the method of Ishikawa et al.,[12] tris(trimethylsilyl)silyllithium by the method of Gutekunst and Brook,[13] and 2,2,5,5-tetrakis(trimethylsilyl)-1,1,1,3,3,4,4,6,6,6-decamethylhexasilane (**1**) by our earlier method.[10]

1,1,4,4-Tetrakis(trimethylsilyl)-2,2,3,3,5,5,5-heptamethylpentasilyllithium (2). A 100 mL, three-necked flask was charged with 5 g (0.0082 mol) of 2,2,5,5-tetrakis(trimethylsilyl)decamethylhexasilane (**1**) and 100 mL of THF. Methyllithium (1.4 M in 7 mL of diethyl ether was added over a 10 min period, and the reaction was allowed to stir at room temperature overnight. The reagent was used without further purification: ^{1}H NMR (toluene-d_8) δ 0.43 (s, 27), 0.54 (s, 18), 0.61 (s, 6), 0.73 (s, 6); ^{13}C NMR (toluene-d_8) δ 1.18, 3.66, 4.08, 7.34; ^{29}Si (toluene-d_8) δ −183.5, −130.5, −33.0, −22.2, −9.6, −5.5.

Tris[2,2,5,5-tetra(trimethylsilyl)hexasilyl]methylsilane (3). A 250 mL, round-bottomed flask was charged with 2,2,5,5-tetrakis(trimethylsilyl)heptamethylpentasilyllithium (**2**) from the previous step in 100 mL of pentane. Tris(chlorodimethylsilyl)methylsilane (8.0 g, 0.025 mol) in 50 mL was added over a 10 min period, and the reaction was allowed to stir overnight at room temperature. The reaction was quenched with 50 mL of H_2O, and the aqueous layer was washed with 3 × 50 mL of diethyl ether. The solution was concentrated and the resulting solid recrystallized to give 4.3 g (0.0033 mol, 13.3%) of the product (see structure **3′** for structural designations): ^{1}H (CDCl$_3$) δ 0.105 (s, 3, a), 0.213 (s, 81, f), 0.263 (s, 54, c), 0.384 (s, 18, e), 0.401 (s, 18, d), 0.543 (s, 18, b); ^{13}C (CDCl$_3$) δ 1.56 (6, e), 2.85 (6, d), 3.61 (27, f), 4.15 or 4.47 (1, a), 4.93 (18, c), 6.51 (6, b); ^{29}Si (CDCl$_3$) δ −127.3 (3, f), −112.5 (3, c), −66.1 (1, a), −29.1 (3, e), −27.7 (3, d), −25.5 (3, b), −9.3 (6, c′), −9.1 (9, f′); UV 260 (1.80 × 10^5), 283 (1.16 × 10^5) nm; MS 1310 (33), 1235 (21), 1020 (34), 931 (9), 857 (5), 786 (100). Anal. Calcd for $C_{64}H_{192}Si_{31}$: C, 41.97; H, 10.48; Si, 47.55. Found: C, 40.85; H, 10.53; Si, 47.25.

1,1,1,2,3,4,5,5,5-Nonamethyl-2,4-bis(trimethylsilyl)pentasilane [$Me_3SiMeSi(SiMe_3)MeHSiMeSi(SiMe_3)SiMe_3$]. A 250 mL Schlenk-valved flask was charged with 12.6 mmol of methylbis(trimethylsilyl)silyllithium and 100 mL of pentane. Methyldichlorosilane (0.65 mL, 0.0063 mol) in 50 mL of pentane was added in portions. A white precipitate formed directly after the addition of methyldichlorosilane. The solution was allowed to stir overnight at room temperature, and the reaction was quenched with water. The aqueous layer was extracted with diethyl ether (3 × 50 mL). The combined organic layer was concentrated to give a colorless oil, which was vacuum distilled. The fraction distilling at 120−125 °C (0.8 mmHg) was collected as the final product: 2.13 g (82%); ^{1}H (C_6D_6) NMR δ 3.50 (m, 1H), 0.25 (d, 3H), 0.13 (s, 3H), 0.14 (s, 3H), 0.15 (s, 18H) 0.16 (s, 18H); ^{13}C NMR δ 0.77, 0.07, −6.31, −10.69; ^{29}Si NMR δ −11.62, −66.93, −83.13; MS (EI) m/z 422 (M$^+$), 407 (M − 15), 348 (M − 73) (100%), 333, 275, 259, 232, 215.

Bis[1,1,1,2,3,4,5,5,5-nonamethyl-2,4-bis(trimethylsilyl)pentasil-3-yl]mercury. The above compound (1.1 g, 0.0026 mol) and 0.41 g (0.0013 mol) of di(*tert*-butyl)mercury were placed in a Schlenk-valved tube, which was covered with aluminum foil. The mixture was subjected to vacuum (ca. 0.8 mmHg) for 1 h and then was heated to 85 °C in an oil bath for 2 days. A yellow oil was formed, and isobutane was removed by vacuum. No further purification was carried out, and the reaction product was used directly in the next step.

2,5-(Trimethylsilyl)-3,4-[methylbis(trimethylsilyl)silyl]-1,1,1,2,3,4,5,6,6,6-decamethylhexasilane (4). To obtain the dimer, the mercury reagent was exposed to light and heated at 100 °C for 3 days. About 10 mL of hexane was added. Mercury and solid material were filtered off, and the solution was concentrated to give a white powder. After sublimation, 0.15 g (13.7%) of pure white crystals were obtained: ^{1}H (CDCl$_3$) NMR δ 0.54 (s, 6H), 0.26 (s, 12H), 0.18 (d, 72H); ^{13}C NMR δ 2.12, 2.08, 1.96, −4.47; ^{29}Si NMR δ −10.26, −43.79, −74.80. Anal. Calcd for $C_{30}H_{90}Si_{14}$: H, 10.67. Found: H, 10.50 (production of silicon carbide during combustion rendered analysis for C and Si impossible).

Crystal Structure of Tris[2,2,5,5-tetrakis(trimethylsilyl)hexasilyl]methylsilane (3). Crystals were obtained by solvent diffusion in mixed benzene and methanol. A colorless, transparent, nearly cubic crystal of $C_{64}H_{192}Si_{31}(C_6H_6)$, having approximate dimensions of 0.12 × 0.11 × 0.42 mm, was mounted on a glass fiber using Paratone oil. All measurements were made on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully selected reflections in the range 14.24° < 2θ < 26.70°. The compound has a formula weight (including the molecule of solvent benzene) of 1910.98, belongs to the space group $P\bar{1}$ (No. 2), and has an atriclinic cell with dimensions $a = 15.704(6)$ Å, $b = 15.865(9)$ Å, $c = 29.067(9)$ Å, $\alpha = 87.30(3)°$, $\beta = 79.69(3)°$, $\gamma = 60.85(4)°$, $V = 6216(5)$ Å^3, $Z = 2$, and a calculated density of 1.02 g cm^{-3}. Diffraction intensities were collected at −120 °C using the $\omega-\theta$ scan technique to a maximum 2θ value of 45.9°. Of the 17 996 reflections that were collected, 17 257 were unique ($R_{\mathrm{int}} = 0.075$). The linear absorption coefficient for Mo Kα was 3.3 cm^{-1}. Azimuthal scans of several reflections indicated no need for absorption correction, but the data were corrected for Lorentz and polarization effects. The structure was solved by direct methods[18] and expanded using Fourier techniques.[19] Some of the non-hydrogen atoms were refined anisotropically, whereas the rest were refined isotropically. Hydrogen atoms were included in fixed positions but were not refined. The final cycle of full-matrix, least-squares refinement[20] was based on 7610 observed reflections ($I > 3.00\sigma(I)$) and 937 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.070$ and $R_w = 0.067$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.53 and −0.34 e Å^{-3}, respectively. All calculations were performed with the teXsan crystallographic software package of Molecular Structure Corporation. Additional crystallographic details are included in the Supporting Information.

Crystal Structure of 2,5-(Trimethylsilyl)-3,4-[methylbis(trimethylsilyl)silyl]-1,1,1,2,3,4,5,6,6,6-decamethylhexasilane (4). Crystals were obtained by solvent diffusion (benzene/methanol). A colorless, nearly cubic crystal of $C_{30}H_{90}Si_{14}$, having approximate dimensions of 0.12 × 0.12 × 0.45 mm, was mounted on a glass fiber. All measurements were made on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully selected reflections in the range 16.90° < 2θ < 23.30°. The compound has a formula weight of 844.24, belongs to the space group $P\bar{1}$ (No. 2), and has an atriclinic cell with dimensions $a = 9.807(3)$ Å, $b = 12.510(4)$ Å, $c = 12.961(3)$ Å, $\alpha = 73.077(2)°$, $\beta = 72.193(2)°$, $\gamma = 67.567(2)°$, $V = 1371.624$ Å^3, $Z = 1$, and a calculated density of 1.02 g cm^{-3}. Diffraction

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intensities were collected at −120 °C using the $\omega-\theta$ scan technique to a maximum 2θ value of 46.9°. Of the 5243 reflections that were collected, 4025 were unique ($R_{\mathrm{int}} = 0.056$). The linear absorption coefficient for Mo Kα was 3.5 cm^{-1}. An analytical absorption correction was applied that resulted in transmission factors ranging from 0.956 to 0.965. The data were corrected for Lorentz and polarization effects, and a correction for secondary extinction was applied (coefficient 4.73843×10^{-7}). The structure was solved by direct methods[18] and expanded using Fourier techniques.[19] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in fixed positions but were not refined. The final cycle of full-matrix, least-squares refinement[20] was based on 2767 observed reflections ($I > 3.00\sigma(I)$) and 200 variable parameters and converged with unweighted and weighted agreements factors of $R = 0.037$ and $R_w = 0.033$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.34 and −0.30 e Å^{-3}, respectively. All calculations were performed with the teXsan crystallographic software package of Molecular Structure Corporation. Additional crystallographic details are included in the Supporting Information.

Acknowledgment. This work was supported by the National Science Foundation (Grant Nos. CHE-9302747 and CHE-9725652).

Supporting Information Available: Tables containing lists of dihedral geometries (A, G, O), crystallographic parameters, atomic coordinates, anisotropic displacement parameters, bond lengths, bond angles, and dihedral angles (62 pages). Ordering information is given on any current masthead page.

OM980280F