

Structure and UV spectroscopic properties of a novel dendritic oligosilane

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Abstract

The reaction of $(R_2MeSi)_2MeSi-Li$ (**2**) [$R = SiMe_3$] with $[ClMe_2Si]_2$ yields the double-cored dendritic oligosilane $[(RMe_2Si)_2MeSi-SiMe_2]_2$ (**4**). The structure of **4** was obtained from X-ray diffraction data, which verify a total of 16 silicon atoms in the molecule and a longest chain of 8 silicon atoms. **4** exhibits an absorption maximum in the near UV at 285 nm ($\epsilon = 5.6 \times 10^4$), a wavelength that is significantly longer than that of the linear octasilane Si_8Me_{18} and is the longest observed for structurally well-defined oligosilane dendrimers so far.

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1. Introduction

One of the most important properties of oligosilane compounds is their electronic absorption in the near UV that provides a representative example of the σ -conjugation systems [1]. Their absorption maxima were found to be red-shifted upon increasing the number of silicon atoms in the chain and strongly depend on the conformation of the silicon backbone. Although, oligosilanes exhibit thermochromic, conductive, photoconductive, photoresistive and nonlinear optical properties, commercial applications have been limited to some extent by the chemical sensitivity of the Si–Si bond, which is reactive in the presence of electrophiles and nucleophiles. In contrast, dendrimer structures containing silicon atoms connected to three or four other silicon atoms are quite interesting in relation to linear oligosilanes, since these materials should be superior in terms of their thermal and chemical stability [2]. Thus, this paper describes the synthesis, crystal structure and UV spectroscopic properties of a novel double-cored den-

dritic oligosilane having a total of 16 silicon atoms and a longest chain of 8 silicon atoms.

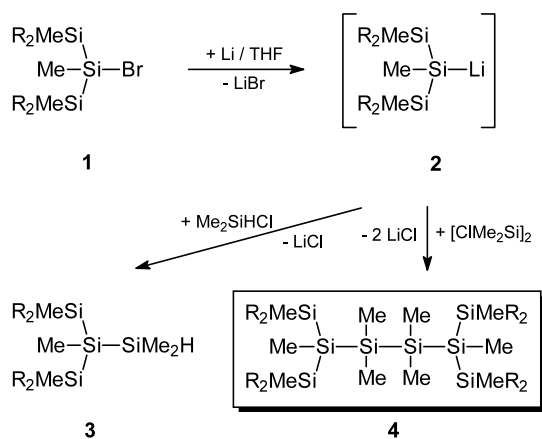
2. Results and discussion

As outlined in Scheme 1, treatment of bromosilane **1** [3] with lithium in THF at 0 °C afforded after 3 h a reddish-brown solution of $(R_2MeSi)_2MeSi-Li$ (**2**). Unfortunately, we did not succeed in crystallizing **2**, and in all cases complete separation of side products from the red oily residue failed. However, the existence of **2** as the main product in solution could be proved by quenching with Me_2SiHCl giving the silane $(R_2MeSi)_2MeSi-SiMe_2H$ (**3**) as colourless liquid in a yield of 81%.

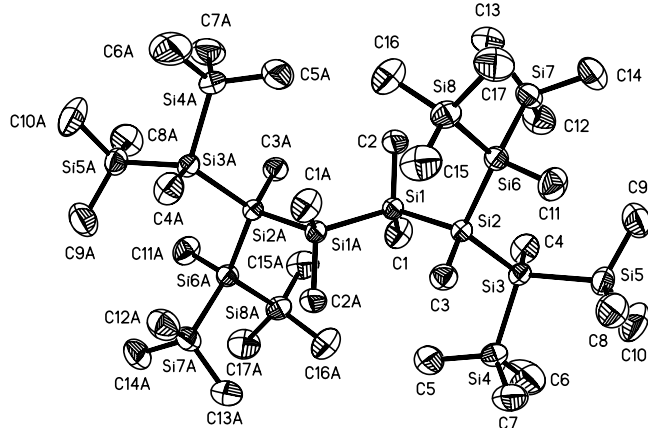
In order to produce dendrimer structures through nucleophilic displacement by anion **2** on two electrophilic silicon atoms possessing good leaving groups, we used $[ClMe_2Si]_2$. In fact, the reaction of two equivalents of **2** with $[ClMe_2Si]_2$ at -78 °C led to a crystalline colourless compound of formula $[(RMe_2Si)_2MeSi-SiMe_2]_2$ (**4**). The structure of **4** was elucidated by means of NMR and MS data and is in full agreement with the results of an X-ray crystal structure analysis. The ^{29}Si -NMR spectrum is particularly useful, because it permits sorting silicon atoms to the number of methyl groups (see Section 3).

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Scheme 1. Synthesis of **3** and **4** (R = SiMe₃).

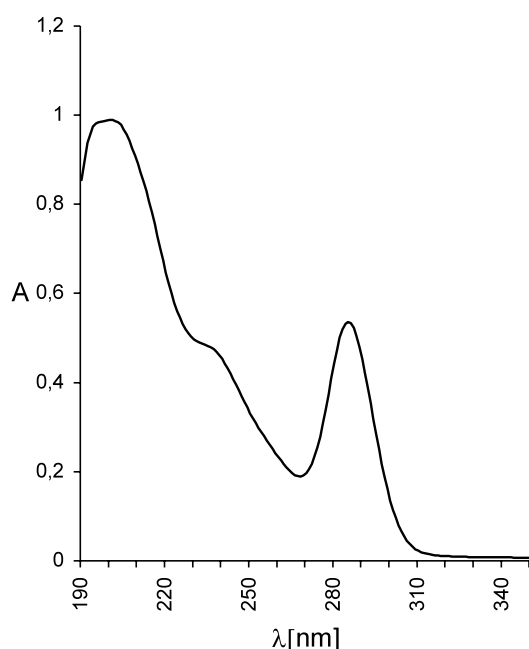
Crystals of **4** suitable for a X-ray crystallography were obtained by recrystallization from acetone. As seen in Fig. 1, the compound has a total of 16 silicon atoms and a longest chain of 8 silicon atoms. Octasilane **4** is described best as a double-cored dendrimer, that have two central silicon cores Si2 and Si2A connected by a Me₂Si–SiMe₂ spacer group. Structural parameters indicate only a slight strain in the molecule. Thus, most of the Si–Si bond lengths lie unremarkably within the range of 2.360–2.370 Å. Only the three bonds emanating from the central core (Si2) are slightly elongated: Si1–Si2 2.393 Å, Si2–Si6 2.386 Å, Si2–Si3 2.392 Å. The Si–Si–Si bond angles are variable but generally within the range 104–118°. However, at the positions where the trimethylsilyl groups of the two (Me₃Si)₂MeSi substituents contact each other, the angles Si5–Si3–Si2 (117.82°) and Si8–Si6–Si2 (118.56°) are widened, reducing the steric interactions. Furthermore, the intramolecular distance C5–C16A (3.753 Å) between the next neighbouring Me₃Si carbon atoms is significantly smaller than the sum of the van der Waals radii [4] of two methyl groups amounting to about 4.0 Å.

Fig. 1. Molecular structure of **4** in the crystal (ORTEP, 50% probability level, H-atoms omitted for clarity).

Selected bond lengths (Å) and angles (°): Si1–Si1A 2.3723(13), Si1–Si2 2.3937(10), Si2–Si6 2.3863(9), Si2–Si3 2.3926(9), Si1A–Si1–Si2 113.38(4), Si6–Si2–Si3 113.86(3), Si6–Si2–Si1 111.00(3), Si3–Si2–Si1 111.31(3), Si5–Si3–Si4 104.15(4), Si5–Si3–Si2 117.82(4), Si4–Si3–Si2 109.15(3), Si8–Si6–Si7 106.80(4), Si8–Si6–Si2 118.56(4), Si7–Si6–Si2 117.64(4), Si2–Si1–Si1A–Si2A 180.0, Si1A–Si1–Si2–Si6 103.91(5), Si1A–Si1–Si2–Si3 128.14(4), Si1–Si2–Si3–Si5 162.04(4), Si6–Si2–Si3–Si4 154.07(4), Si3–Si2–Si6–Si8 166.97(4).

The UV spectrum of **4** measured at room temperature in heptane as solvent is shown in Fig. 2. As can be seen, the branched octasilane **4** exhibit a relatively sharp absorption maximum at 285 nm ($\epsilon = 5.6 \times 10^4$) which is strongly shifted at longer wavelength than that of the linear permethylated octasilane of formula Si₈Me₁₈ ($\lambda_{\text{max}} = 276$ nm) [5]. Surprisingly, even the absorptions maxima of the largest structurally well-defined oligosilane dendrimers having longest chains of 11 and 13 silicon atoms [6] are significantly blue-shifted compared to that of **4** having only octasilane chains in the molecule. These findings are in sharp contrast to the fact that normally the UV absorption maximum moves to longer wavelengths as the number of silicon atoms in the chain increases.

Although the conformation of **4** in solution might be different from that in the solid, the conformational analysis on the basis of the available X-ray data is very instructive. The results reveal that most of the octasilane chains defined by five dihedral angles are C–T–T–T–C and C–T–T–T–T conformers (C, *cis*; T, *trans*) [7], indicating a predominance of *trans* segments in the

Fig. 2. UV absorption spectrum of **4** (1×10^5 M) in heptane.

molecule. Moreover, the Si5–Si3–Si2–Si1–Si1A–Si2A–Si3A–Si5A chain approximately adopts an all-*trans* conformation (T–T–T–T–T), that is believed to be optimal for σ -conjugation [1a]. In comparison to that, the conformation analysis of the dendrimers described by Lambert and Sekiguchi revealed that all-*trans* segments exist only in several hexasilane subunits (T–T–T) and that in most of the longest chains the all-*trans* segments are interrupted by additional *cis* conformers.

In this context, our unexpected results for an octasilane chain can be understood best by assuming that dendritic molecules which have conformers mainly consisting of all-*trans* segments exhibit a noticeably lower singlet excitation energy, than those having *cis* defects in the longest chain. These findings are in full agreement with those of Michl and coworkers [8] and Tamao et al. [9] who elegantly demonstrated by incorporation of tetrasilane and hexasilane moieties into rigid cyclic carbosilane compounds that the absorption maximum arises mainly from the all-*anti* conformers in the oligosilane chains and that additional *cis* fragments do not contribute to the elongation of σ -conjugation. Further studies concerning the structure and optical properties of oligosilane dendrimers with longer silicon chains are in progress.

3. Experimental

3.1. General procedures and materials

All reactions involving organometallic reagents were carried out under an atmosphere of argon using standard Schlenk techniques. ^1H - and ^{13}C -NMR (Bruker AC 250), ^{29}Si -NMR (Bruker ARX 300), measured in [D_6]benzene; tetramethylsilane as internal standard. IR: Nicolet 205 FT-IR. MS: Intectra AMD 402. UV–Vis: Perkin–Elmer Lambda 2, quartz cells of 1.0 cm path length and spectral grade heptane. $(\text{R}_2\text{MeSi})_2\text{MeSiBr}$ (1) [$\text{R} = \text{SiMe}_3$] was prepared as previously described [3].

3.2. 2,4-Bis(trimethylsilyl)-3-dimethylsilyl-1,1,1,2,3,4,5,5,5-nonamethylpentasilane (3)

A suspension of 200 mg (30 mmol) lithium, 1.5 g (3 mmol) **1** and 20 ml THF was stirred at 0 °C for 3 h. After that 0.38 g (4 mmol) of Me_2SiHCl were added and stirring was continued for 30 min. After removal of the solvent, the residue was dissolved in pentane, the solid materials were filtered off. The volatile products were removed under vacuum and the residue was purified by distillation (140 °C, 0.01 mbar). Yield 1.27 g (81%). IR (nujol) $\tilde{\nu} = 2102.7 \text{ cm}^{-1}$ (SiH). ^1H -NMR: $\delta = 4.26$ (sept, $^3J = 4.3 \text{ Hz}$, SiH, 1H), 0.33 (d, $^3J = 4.3 \text{ Hz}$, SiMe_2 , 6H), 0.44 (s, SiMe, 3H), 0.34 (s, SiMe, 6H), 0.27, 0.29 (2s,

SiMe_3 , $2 \times 18\text{H}$) ppm. ^{13}C -NMR: $\delta = -3.4$ (SiMe_2H), 5.7 (SiMe), -8.7 (SiMe), 1.4, 1.3 (SiMe_3) ppm. ^{29}Si -NMR: $\delta = -10.8$, -11.7 (SiMe_3), -33.6 (d, $^1J = 163.1 \text{ Hz}$, SiMe_2H), -65.1 (SiMe), -77.6 (SiMe) ppm. MS: m/z (%): 480 (43) [M^+]; 408 (33) [$\text{M}^+ - \text{SiMe}_3$]. Elemental analysis: Anal. Found: C, 42.38; H, 10.78. Calc. for $\text{C}_{17}\text{H}_{52}\text{Si}_8$ (481.28): C, 42.43; H, 10.89%.

3.3. 3,6-Bis[methyl-bis(trimethylsilyl)silyl]-2,7-bis(trimethylsilyl)-1,1,1,2,3,4,4,5,5,6,7,8,8,8-tetradecamethyloctasilane (4)

A suspension of 200 mg (30 mmol) lithium, 1.5 g (3 mmol) **1** and 20 ml THF was stirred at 0 °C for 3 h. After that 0.28 g (1.5 mmol) $\text{ClMe}_2\text{Si}-\text{SiMe}_2\text{Cl}$ were added at $-78 \text{ }^\circ\text{C}$ and stirring was continued for 30 min. After removal of the solvent, the residue was dissolved in pentane, the solid materials were filtered off. The volatile products were removed under vacuum and the residue was recrystallized from acetone to give 0.29 g **4** in a yield of 21%. m.p.: 173 °C. ^1H -NMR: $\delta = 0.65$ (s, SiMe_2 , 12H), 0.43 (s, SiMe, 12H), 0.68 (s, SiMe, 6H), 0.34, 0.32 (2s, SiMe_3 , $2 \times 36\text{H}$) ppm. ^{13}C -NMR: $\delta = 2.0$, 1.7 (SiMe_3), 1.3 (SiMe_2), -1.7 (SiMe), -6.9 (SiMe) ppm. ^{29}Si -NMR: $\delta = -11.3$, -11.4 (SiMe_3), -31.4 (SiMe_2), -54.4 (SiMe), -76.8 (SiMe) ppm. MS: m/z (%): 959 (15) [M^+]; 886 (56) [$\text{M}^+ - \text{SiMe}_3$]. Elemental analysis: Anal. Found: C, 42.23; H, 10.58. Calc. for $\text{C}_{34}\text{H}_{102}\text{Si}_{16}$ (960.55): C, 42.51; H, 10.70%.

3.4. Crystal structure determination of 4

The data collection was done on a Bruker P4 four-circle diffractometer with Mo- K_α radiation and graphite monochromator in routine ω -scan. The structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically. The hydrogen atoms were put into theoretical positions and refined using the riding model. Further details: crystal size $0.8 \times 0.75 \times 0.46 \text{ mm}^3$, empirical formula $\text{C}_{34}\text{H}_{102}\text{Si}_{16}$, formula weight 960.60, triclinic, $P\bar{1}$, $a = 8.454(2) \text{ \AA}$, $b = 13.1080(10) \text{ \AA}$, $c = 15.919(2) \text{ \AA}$, $\alpha = 66.72(1)^\circ$, $\beta = 88.87(1)^\circ$, $\gamma = 82.67(1)^\circ$, $Z = 1$, temperature 298 K, $\mu = 0.337 \text{ mm}^{-1}$, Θ range $2.43\text{--}22.00^\circ$, largest difference peak/hole $0.237/-0.145 \text{ e \AA}^{-3}$, measured reflections 4802, independent reflections 3851, observed reflections 3583, $R_{\text{int}} = 0.0177$, number of parameters 226, $R_1 = 0.0357$ [$I > 2\sigma(I)$], wR_2 (all data) 0.0990. The structure was refined by the full-matrix least-squares methods on F^2 (SHELXL-97) [10]. The Bruker SHELXTL [11] software package was used for the structure representations.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 201932 for compound **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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