

The unusual UV absorption behavior of chloro functionalized oligosilane dendrimers

C. Krempner*, H. Reinke

Institut für Chemie der Universität Rostock, Fachbereich Chemie, A.-Einstein-Str. 3a, D-18059 Rostock, Germany

Received 23 October 2005; accepted 13 November 2005

Available online 27 December 2005

Abstract

The unusual UV spectroscopic behavior of the chloro functionalized oligosilane dendrimers $[\text{R}(\text{Me}_3\text{Si})_2\text{Si}-\text{Me}_2\text{Si}]_3\text{Si}-\text{Cl}$ (**3a,b**) derived from reactions of $\text{R}(\text{Me}_3\text{Si})_2\text{Si}-\text{K}$ (**2a,b**) with $\text{Cl}-\text{Si}(\text{SiMe}_2\text{Cl})_3$ (**1**) is reported (**a**; $\text{R} = \text{SiMe}_3$ and **b**; $\text{R} = \text{Me}$). The dendritic silanol $[\text{Me}(\text{Me}_3\text{Si})_2\text{Si}][\text{Me}(\text{Me}_3\text{Si})_2\text{Si}-\text{Me}_2\text{Si}]_2\text{Si}-\text{SiMe}_2\text{OH}$ (**6**) has been isolated as a side product and was characterized by X-ray structure analysis. © 2005 Elsevier B.V. All rights reserved.

Keywords: Silicon; Silanes; Dendrimers; Silanols; Chlorosilanes

It is largely accepted that the unique electronic and photophysical properties of poly- and oligosilanes are derived from the extensive delocalization of σ -electrons along the silicon backbone and are extremely sensitive to the conformation of the silicon chain as well as the steric and electronic nature of the substituents [1]. Even though the conformation dependence of the absorption and emission spectra of polysilanes is relatively well understood and documented [2], there are, however, very few data concerning the effect of introduction donor groups such as oxygen or halides on the silicon main chain [3,4]. Herein, we report the synthesis, structure and UV absorption behavior of dendritic oligosilanes of first generation bearing hydroxyl- or chloro functionalities in the molecule.

Our strategy for preparing functionalized oligosilane dendrimers involved the use of $\text{ClSi}(\text{SiMe}_2\text{Cl})_3$ (**1**) that can be prepared by reacting $\text{PhSi}(\text{SiMe}_2\text{Ph})_3$ with 4 equiv. of acetyl chloride and AlCl_3 [5]. Addition of **1** at low temperatures to potassium silanides **2a,b**, respectively, and subsequent hydrolysis of the reaction mixture for three days unexpectedly afforded the chlorosilanes **3a,b** as moisture- and air stable crystalline materials (Scheme 1) [6]. The

formation of the initially expected silanols **5a,b** could not be observed under the condition applied, clearly reflecting the effective steric protection of Si–Cl functionality by the neighboring bulky silyl substituents. The structures proposed for **3a,b** could be unequivocally identified by means of NMR, MS, IR data and are in agreement with the results of an elemental analysis.

However, the main product that was isolated in a yield of 41% from the reaction of **1** with the sterically less encumbered potassium silanide **2b** is silanol **6**. The formation of **6** obviously arises from a competitive nucleophilic attack of **2a** towards the tertiary Si–Cl functionality in **1** giving the corresponding chlorosilane **4** intermediately. Whereas the less protected Si–Cl functionality in **4** readily hydrolyze to give silanol **6** selectively, Si–Cl moiety in **3b** is fully embedded by silyl groups and thereby remains unchanged. In addition, the solid-state structure of **6** has been determined by X-ray crystallography [7], suitable single crystals were grown from acetone solutions (Fig. 1). The results reveal compound **6** to be monomeric in the solid state with an OH group fully enclosed by the bulky silyl groups. Structural parameters indicate a slight strain in the molecule; the Si–Si bond lengths lie unremarkably within the range of 2.355–2.385 Å and the Si–Si–Si bond angles are variable but generally within the range 105–120°.

* Corresponding author. Tel.: +49 381 498 6385; fax: +49 381 498 6382.
E-mail address: clemens.krempner@uni-rostock.de (C. Krempner).

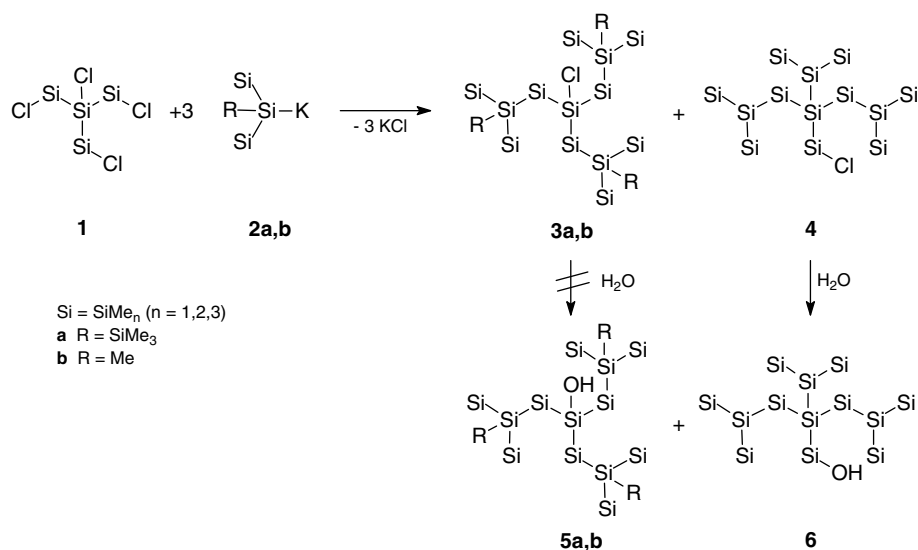
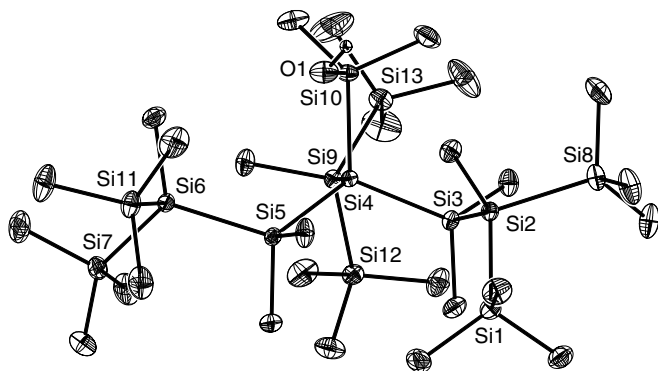
Scheme 1. Synthesis of **3a,b** and **6** (a, R = SiMe₃; b, R = Me).

Fig. 1. Molecular structure of **6** in the crystal (ORTEP, 50% probability level, all H-atoms omitted for clarity). Selected bond lengths (Å) and bond angles (°): Si10–O1 1.6626(14), Si3–Si4 2.3845(6), Si4–Si10 2.3660(6), Si4–Si5 2.3828(6), Si4–Si9 2.3865(6) and Si4–Si3–Si2 120.03(2), Si10–Si4–Si5 107.82(2), Si10–Si4–Si3 107.07(2), Si5–Si4–Si3 107.55(2), Si10–Si4–Si9 108.80(2), Si5–Si4–Si9 114.19(2), Si3–Si4–Si9 111.13(2), Si6–Si5–Si4 120.50(3), Si12–Si9–Si4 117.14(3), Si13–Si9–Si4 119.71(3), Si8–Si2–Si3–Si4 134.14(3), Si1–Si2–Si3–Si4 108.12(3), Si2–Si3–Si4–Si5 64.47(3), Si2–Si3–Si4–Si9 169.87(3), Si3–Si4–Si5–Si6 170.26(3), Si9–Si4–Si5–Si6 65.93(4), Si4–Si5–Si6–Si7 108.65(3), Si4–Si5–Si6–Si11 132.45(3), Si4–Si5–Si6–Si11 132.45(3).

Remarkable is the UV absorption behavior of **3a,b** compared to that of the permethylated analogues **7a,b** first reported by Lambert and Sekiguchi [8]. For comparison, the UV spectra of **3a,b** and **7a,b** have been measured in *n*-heptane solutions ($c = 10^{-5}$ M) at room temperature. As can be seen in Fig. 2, by incorporation a chlorine atom into the central position the absorption maxima of both **3a** ($\lambda_{\text{max}} = 278$ nm, $\epsilon = 2.8 \times 10^4$) and **3b** ($\lambda_{\text{max}} = 282$ nm, $\epsilon = 2.7 \times 10^4$) are significantly shifted to longer wavelength relative to the those of the permethylated analogues **7a** ($\lambda_{\text{max}} = 265$ nm, $\epsilon = 5.2 \times 10^4$) [9] and **7b** ($\lambda_{\text{max}} = 269$ nm, $\epsilon = 5.0 \times 10^4$). In addition, a second very intense absorption appears for **3a** at around 240 nm ($\epsilon = 5.9 \times 10^4$) and

for **3b** at 246 nm ($\epsilon = 4.0 \times 10^4$) being similar to the absorption maximum of Tamao's tethered tetrasilane with an *anti* conformation that was found to be at 243 nm [2a]. The observed bathochromic shift of the absorption maxima with a value of about 13 nm is in striking contrast to the almost negligible differences reported for the trisilanes Me₃Si–Me₂Si–SiMe₂Cl ($\lambda_{\text{max}} = 216$ nm), Me₃Si–MeClSi–SiMe₃ ($\lambda_{\text{max}} = 217$ nm) and Me₃Si–Me₂Si–SiMe₃ ($\lambda_{\text{max}} = 216$ nm) [3a]. To our knowledge, the chloro functionalized oligosilanes **3a,b** are the first examples that exhibit a red shift in the absorption maxima compared to their permethylated analogues. These findings can be understood as an optical band gap reduction resulting from effective interactions between silicon (σ) and chlorine lone pair (n) orbitals similar to silicon oxygen interactions in OH- and OR functionalized poly/oligosilanes [3,4,10]. This is consistent with ground state interactions, which increase because the greater inductive effect associated with the central tertiary silicon compared to secondary or primary silicon atoms in the trisilane series will more effectively equalize the energies of the oxygen p_z and silicon levels. However, since a Cl_p → Si* transition is locally forbidden, the observed bathochromic shift is coupled with reduction in intensity.

Interestingly, the absorption maximum of silanol **6** with 260 nm ($\epsilon = 4.6 \times 10^4$) was found to be significantly at shorter wavelength than those of dendrimers **3a,b** and **7a,b**, though the number of silicon atoms in the longest chain is the same. Therefore, the conformation of the longest oligosilane chains in the solid state has been analyzed on the basis of the X-ray data. Thus, compound **6** adopts an *E-A-G-E* conformation (*A*, *anti*; *E*, *eclipsed*; *G*, *gauche*) [11] in the Si8–Si2–Si3–Si4–Si5–Si6–Si11 chain being obviously less effective for σ -conjugation, compared to **7b** in which *A-O-A-A* conformers were found with significantly larger dihedral angles [8c]. Although the conformation in the solid state might be different from that in solution, it

Download English Version:

<https://daneshyari.com/en/article/1302961>

Download Persian Version:

<https://daneshyari.com/article/1302961>

[Daneshyari.com](https://daneshyari.com)