Novel double-cored oligosilane dendrimers—conformational dependence of the UV absorption spectra†

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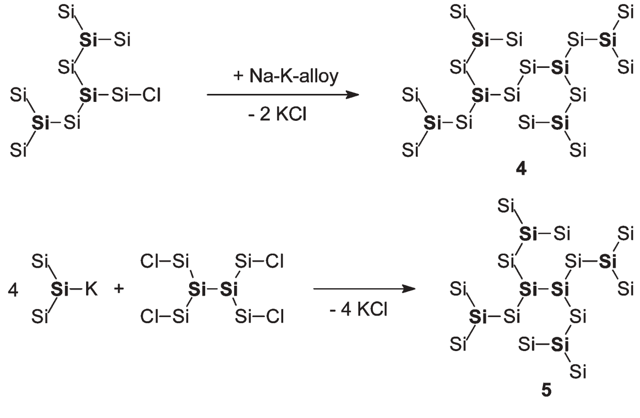
The novel double-cored oligosilane dendrimers {[Me(Me$_3$Si)$_2$-Si–Me$_2$Si]$_2$SiMe–SiMe$_2$}$_2$ (4) and {[Me(Me$_3$Si)$_2$Si–Me$_2$Si]$_2$SiMe}$_2$ (5) have been shown to display unusual UV absorption behaviour as a function of conformation and steric interaction in the longest oligosilane chains.

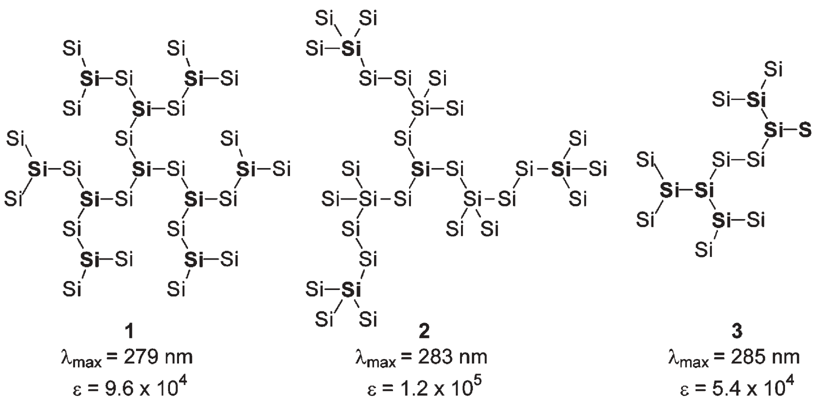
One of the most important properties of oligo and polysilanes is their intense electronic absorption in the near UV that provides a representative example of σ-conjugated systems.[1] Their absorption maxima were found to be red-shifted upon increasing the number of silicon atoms in the chain and strongly dependent on the conformation of the silicon backbone.

Although linear oligo and polysilanes possess unique optical, photoelectric, and other excited state dependent properties,[1] commercial applications have been limited to some extent by the chemical and photochemical sensitivity of the Si–Si bond. It is, however, suggested that branched and dendritic structures are more promising, since these materials should be superior in terms of their increased chemical and photochemical stability,[2] provided that they show improved or at least identical electronic properties as their linear counterparts. There are now a few permethylated dendritic oligosilanes known, among these are the structurally well defined dendrimers **1** and **2** of first and second generation developed by Lambert[3a,e] and Sekiguchi[3b] and **3** a double-cored dendrimer of first generation developed in this laboratory (Scheme 1).[3f]

Unexpectedly, compound **3**, with a longest chain of only 8 Si atoms, exhibits a narrow absorption maximum in the near UV at 285 nm which is significantly shifted to a lower energy than that of n-Si$_8$Me$_{18}$ ($\lambda_{\max}$ = 276 nm)[4] and even than those of Sekiguchi's and Lambert's single-cored dendrimers with longest chains of 11 and 13 Si atoms. This is in sharp contrast to the fact that normally the UV absorption maximum moves to longer wavelengths as the number of Si atoms in the chain increases.[1] Puzzled by these findings, we have synthesized the double-cored dendrimers **4** and **5**† with longest chains of 10 and 8 Si atoms, respectively (Scheme 2). Note that in **5** the dendrimer cores are directly connected to each other, whereas in **4** a disilylene spacer group separates. The structures proposed for **4** and **5** were unambiguously evidenced by means of elemental analysis, MS and NMR data. Both dendrimers are thermally fairly stable; even at 492 K under vacuum no substantial decomposition occurs and they do



Scheme 2 Synthesis of **4** and **5** (Si = SiMe$_n$; n = 1, 2, 3).



Scheme 1 Dendrimers **1–3** (Si = SiMe$_n$; n = 1, 2, 3).

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† Electronic supplementary information (ESI) available: Experimental data for **4** and **5**. See DOI: 10.1039/b515562b

not show any UV spectroscopic changes upon heating heptane solutions to 347 K.

However, at room temperature **4** exhibits an intense signal at 270 nm ($\varepsilon = 7.2 \times 10^4$) and, moreover, an absorption maximum at 292 nm ($\varepsilon = 5.5 \times 10^4$) (Fig. 1, left), a value that is significantly higher than that of n-$Si_{10}Me_{22}$ (λ_{max} = 284 nm)[4] and is the highest observed for dendrimers so far. Apart from the absorption maximum being slightly red-shifted to 294 nm, the absorption behaviour in thin films made from 10^{-2} M hexane solutions on quartz plates is almost identical and even to that in the solid state with a broad maximum ~296 nm.[9]

Completely different is the UV curve of dendrimer **5**, as shown in Fig. 1 (right). Although **5** has the same number of Si atoms in the longest chain as **3**, the absorption maxima in solution (λ_{max} = 271 nm; $\varepsilon = 8.2 \times 10^4$) and in thin films ($\lambda_{max}$ ~272 nm) were found at significantly shorter wavelength than those of **3** and **4**. In striking contrast, the solid state UV spectrum of **5** shows two distinct absorptions with values of approximately 255 and 286 nm.

With respect to the steric situation in **5** compared to that of **4** with a disilylene spacer group, it is suggested that conformational effects, being of significant influence on the absorption maximum according to Michl[5] and Tamao,[6] might be responsible for the different absorption behaviours. Therefore, we have determined the solid-state structure of **5** by single X-ray crystallography; suitable crystals were obtained from acetone solutions.‡ Structural parameters indicate considerable strain in the molecule; the central Si1–Si1 bond length [2.4048 (13) Å] is significantly elongated and the central Si–Si–Si bond angles are widened within the range of 114–116°. A view along the central Si1–Si1 axis of **5** reveals the conformation to be predominantly determined by the steric repulsion of the dendrimer wings (Fig. 2).

The steric strain in the molecule is relieved by increasing the Si6–Si1–Si1–Si2 dihedral angle to a value of 83.55(4)° and decreasing the Si2–Si1–Si1–Si2 angle to 40.17(8)°. Thus, the conformational arrangement in **5** is best described as syn-clinal, whereas that of **3** corresponds to an anti-periplanar arrangement with dihedral angles of approximately 180°. Furthermore, the conformational analysis reveals most of the octasilane chains defined by five dihedral angles to be D–D–O–O–D (Si4–Si3–Si2–Si1–Si1–Si6–Si7–Si8), D–O–D–O–D (Si8–Si7–Si6–Si1–Si1–Si6–Si7–Si8), and D–D–G–D–D (Si4–Si3–Si2–Si1–Si1–Si2–Si3–Si4), indicating a predominance of deviant and ortho segments in the molecule (D, deviant; O, ortho; G, gauche).[7]

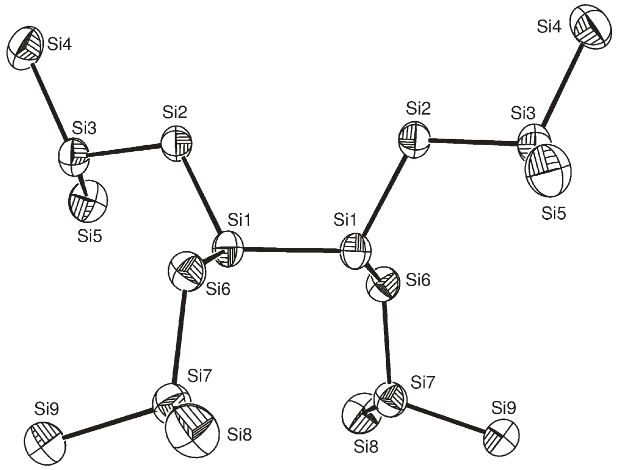

Fig. 2 Molecular structure of **5**. The thermal ellipsoids correspond to 50% probability. Methyl groups omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–Si6, 2.3857(10), Si1–Si2, 2.3942(11), Si1–Si1, 2.4048(13), Si5–Si3–Si2, 116.28(4), Si2–Si1–Si1, 114.54(3), Si3–Si2–Si1, 116.84(4), Si1–Si1–Si2–Si3, 144.84(5), Si1–Si2–Si3–Si5, 76.28(6), Si1–Si2–Si3–Si4, 164.21(4), Si1–Si1–Si6–Si7, 86.90(4), Si1–Si6–Si7–Si9, 91.96(5), Si1–Si6–Si7–Si8, 150.79(4), Si6–Si1–Si1–Si6, 152.72(6), Si2–Si1–Si1–Si2, 40.17(8), Si2–Si1–Si1–Si6, 83.55(4).

The absorption behaviour of **5** in the solid state can be best understood by assuming that dendritic molecules, which have conformers mainly consisting of all-anti or even deviant segments, exhibit a noticeably lower singlet excitation energy than those having gauche and ortho defects in the longest chain. Thus, the absorption maximum of 286 nm most likely corresponds to the D–D–O–O–D and D–O–D–O–D conformers with very similar dihedral angles, whereas the 255 nm absorption, close to that of an

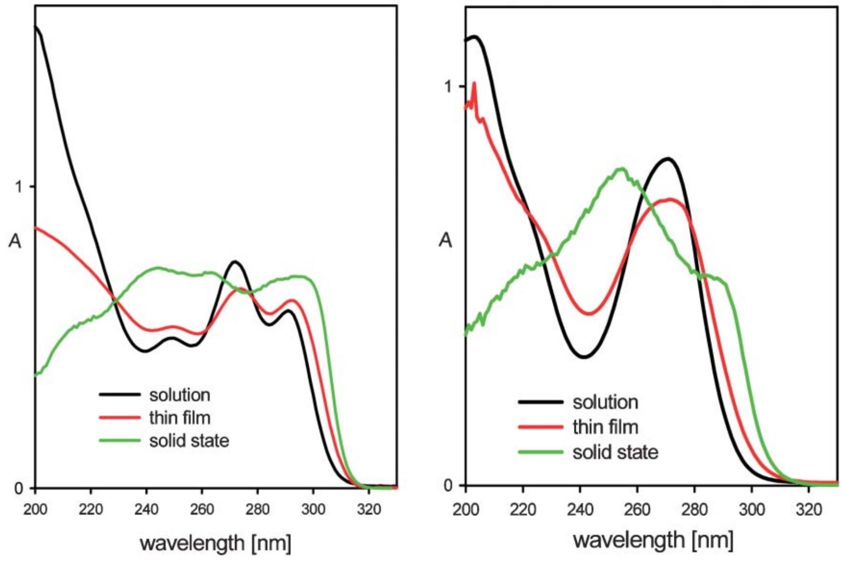

Fig. 1 UV Spectra of **4** (left) and **5** (right).[9]

all-anti pentasilane (253 nm) recently reported,[8] arises from the D–D–G–D–D conformer. These findings are in full agreement with those of Michl[5] and Tamao[6] who demonstrated that the absorption maximum arises mainly from all-anti conformers in linear oligosilanes. Additional syn or gauche fragments do not contribute significantly to the elongation of σ-conjugation. Moreover, σ-conjugation will be interrupted when syn or gauche links are located in the centre of the chains as in the case of the D–D–G–D–D conformer. However, in solution and even in thin films where a conformational flexibility is given, a statistical distribution of various conformers is observed, causing a broadened first intense peak, which is blue shifted with respect to that in the solid state. The fact that the absorption maximum of the decasilane dendrimer **4** is the highest so far observed for permethylated oligosilanes in solution and in the solid state and is very close to that of n-$Si_{10}Me_{22}$ (λ_{max} = 294 nm)[4] at 77 K might be an indication for the existence of conformers which are similar to all-anti ones that are believed to be optimal for σ-conjugation.

From these results it seems evident that double-cored oligosilane dendrimers are superior to single-cored ones with respect to their red-shifted UV absorption maxima in solution and in the solid state. As it was clearly shown for **4** and **5**, the incorporation of a disilylene spacer group that separates both dendrimer wings from each other seems to be crucial to reduce steric repulsion and, more importantly, to realize conformations being optimal for the delocalization of σ-electrons.

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Notes and references

‡ *Crystal data*: 1,1,1,2,3,3,4,5,6,6,7,8,8,8-Tetradecamethyl-2,7-bis(trimethylsilyl)-4,5-bis[1′,1′,2′,3′,3′,3′-hexamethyl-2′-trimethylsilyl-trisilanyl]octasilane (**4**): $C_{38}H_{114}Si_{18}$, M = 1076.86: monoclinic, *C*2/*c* (no. 15), a = 23.2800(7) Å, b = 17.9532(6) Å, c = 17.7010(5) Å, β = 94.237(1)°, V = 7377.9(4) $Å^3$, Z = 4, Dc = 0.970 g cm^{-3}, μ(Mo Kα) = 3.3 cm^{-1}, total reflections 46850, independent reflections 8127 (R_{int} = 0.080), refinements on F^2, $R1$ = 0.0473, $wR2$ = 0.1090. CCDC 275783. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b515562b.

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9 For clarity, the numeric values of the absorbance (A) in the curves for thin films and the solid state are reduced. The UV spectra with the exact values are given in the supporting information.