Twisted oxygen-containing oligosilanes—unprecedented examples of σ–n mixed conjugated systems†

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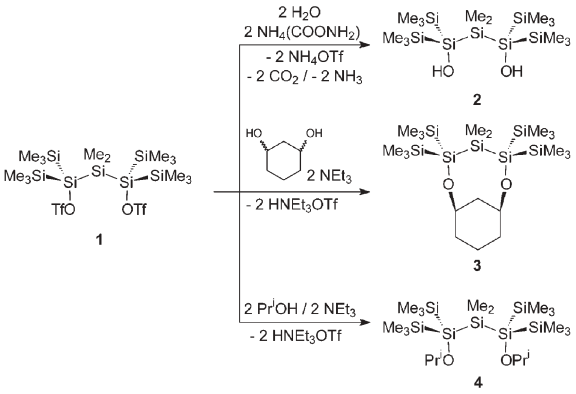
Twisting the silicon backbone conformation in oxygen containing oligosilanes towards dihedral angles of 120–130° either by intramolecular hydrogen bonding or incorporation into a covalently bonded ring system effectively extends the delocalization of electrons in these σ–n mixed conjugated systems.

One of the most characteristic features of oligo and polysilanes is the extensive delocalization of σ-bonded electrons (σ-conjugation) along the silicon main chain, resulting in unique opto-electronic properties such as intense emissions and absorptions in the near UV.[1] These properties are extremely sensitive to the silicon main chain conformation and the electronic nature of the substituents. For peralkylated oligosilanes it has been unequivocally demonstrated that σ-conjugation is effectively extended by an anti conformation (SiSiSiSi dihedral angle $\omega = 180°$) in the tetrasilane subunits of the silicon chain.[2] In addition, strong electronic coupling with the silicon chain is seen, when oxygen-containing donor groups such as OR, OH and $OSiR_3$ are attached, resulting in a substantial decrease of the optical band gaps.[3] However, the origin of this electronic interaction and its correlation with the silicon backbone conformation and the opto-electronic properties is not yet fully understood.[4] Our experimental results supported by DFT calculations on oxygen-containing oligosilanes reported herein reveal the extent of (σ–n)-conjugation to be much stronger in compounds that have twisted silicon backbone conformations ($\omega \sim 120$–130°) than those with larger dihedrals angles of *ca.* 160–180°.

The oxygen-containing oligosilanes **2–4** each with longest chains of five silicon atoms were synthesized as outlined in Scheme 1. The UV absorption curves of **2–4** and of the permethylated analogue $Me(Me_3Si)_2Si–SiMe_2–Si(SiMe_3)_2Me$ (**5**)[5] are shown in Fig. 1. Remarkably, hexane solutions of diol **2** and bicyclic **3** exhibit in the UV spectrum rather similar absorption maxima at around 300 and 299 nm, respectively, being tremendously shifted to longer wavelength relative to permethylated **5** (λ_{max} = 255 nm). It can be argued that these significant differences in energy are largely due to optical band gap reductions resulting from interactions between silicon (σ) and oxygen lone pair (n) orbitals, as has been noted frequently.[3a–c,4a] On the other hand, the absorption maximum of the diisopropoxide **4** (λ_{max} = 272 nm) is significantly shifted to shorter wavelength relative to **2** and **3**, although the same number of oxygen atoms is attached at the same position to the silicon backbone. Similar behavior is seen in the solid state UV spectra (diffuse reflectance). The absorption maximum of **2** (317 nm) is 14 nm bathochromic shifted relative to that of **4** (303 nm),† which suggests that the unusually low energy absorption of **2** and **3** is caused by conformational effects rather than by electronic ones.



Scheme 1 Synthesis of **2–4**.

To determine the silicon backbone conformation of **2** and **3** in the solid state, X-ray measurements have been carried out.‡ The results reveal **2** to be a dimer with OH groups adopting a *cis* orientation (Fig. 2), whereas **3** is a monomeric eight-membered

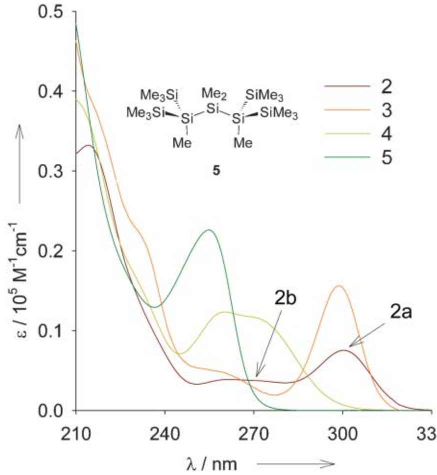


Fig. 1 UV spectra of **2–5** in *n*-hexane at room temperature. Absorption maxima of **2**: λ_{max} = 300 nm $\varepsilon = 0.75 \times 10^4$ M^{-1} cm^{-1}; $\lambda_1 \sim 272$ nm $\varepsilon \sim 0.37 \times 10^4$ M^{-1} cm^{-1} **3**: λ_{max} = 299 nm, $\varepsilon = 1.56 \times 10^5$ M^{-1} cm^{-1}; **4**: λ_{max} = 272 nm, $\varepsilon = 1.15 \times 10^4$ M^{-1} cm^{-1}; **5**: λ_{max} = 255 nm, $\varepsilon = 2.26 \times 10^4$ M^{-1} cm^{-1}.

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† Electronic supplementary information (ESI) available: experimental data of 2–4 and optimized structures of 2, 4 and 5. See DOI: 10.1039/b618438c

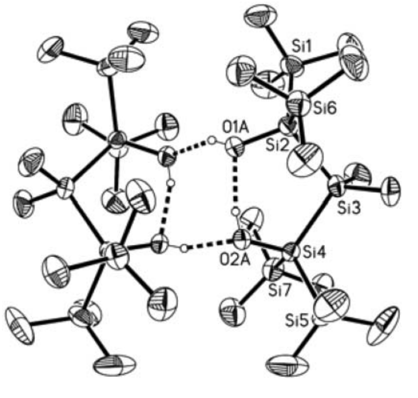

Fig. 2 Molecular structure of **2**. The thermal ellipsoids correspond to 30% probability (hydrogen atoms attached to carbon are omitted). The hydroxyl H atoms are equally disordered over two sites, only one set is shown in this Figure (primed atoms: $2 - x$, y, $\frac{1}{2} - z$). Selected bond lengths [Å] and angles [°]: O1A–Si2 1.674(2), O2A–Si4 1.677(1), average Si–Si 2.3567(9), O1A···O1A′ 2.690(3), O1A···O2A 2.723(2), O2A···O2A′ 2.781(3), Si1–Si2–Si3–Si4 132.18(4), Si6–Si2–Si3–Si4 99.25(4), Si2–Si3–Si4–Si5 127.56(4), Si2–Si3–Si4–Si7 106.38(4).

ring compound, (Fig. 3). The dimer of **2** lies about a twofold axis. The two monomer-units are connected through alternating inter- and intramolecular hydrogen bonds, forming an eight-membered ring structure. The measured O2–O2A, O1–O1A and O2A–O1A distances that determine the hydrogen bond strength in the molecule are 278.1(3), 269.0(3) and 272.3(2) pm, respectively. Interestingly, the O2A–O1A distance is the shortest observed for intramolecularly hydrogen-bonded silanols.[6] Remarkably, in both compounds the conformations of the pentasilane chains, each defined by two dihedral angles, are almost identical (see Table 1). There are three different combinations of conformers for the pentasilane chains; *E–E*, *E–O* and *O–O* (*E*, eclipsed, $\omega \sim 120°$; *O*, ortho, $\omega \sim 90°$).[7] It is worth noting that none of these twisted conformers is close to an all-anti conformer *A–A* (*A*, anti, $\omega \sim 180°$) that is believed to be optimal for σ-conjugation.[1]

The observed twisted conformations in the solid state are the result of ring formation either by strong covalent bonds as in the eight-membered ring system of **3** or by relatively weak hydrogen bonds as shown for **2**. However, due to possible interactions of **2** with solvent molecules which may cause cleavage of hydrogen bonds, the aggregation and consequently the conformational arrangement in solution may differ markedly from that in the solid state. Therefore, temperature dependent IR measurements of **2** in solution (CCl_4; $c = 10^{-3}$ M) were performed. To assign the observed OH stretching frequencies either to associated or non-associated OH groups the OH stretching frequencies have been calculated for the optimized structures **2a** and **2b** (*vide infra*) and compared with the experimental IR data. The results seen in Fig. 4 clearly reveal only monomers to be present in solution.[8] In fact mainly three absorption bands were observed which are ascribed to the OH stretching frequencies of two stable species; the intramolecularly hydrogen bonded conformer **2a** and the non-associated species **2b**. Upon increasing the temperature from 293 to 343 K the intensity of the signal belonging to the non-associated monomer only slightly increases relative to those of the hydrogen bonded monomer **2a**, which indicates the latter to be relatively stable in solution. This is consistent with the variable-temperature UV spectra in n-heptane, which show the energy of the broad absorption maximum of **2** to be almost unchanged upon increasing the temperature.

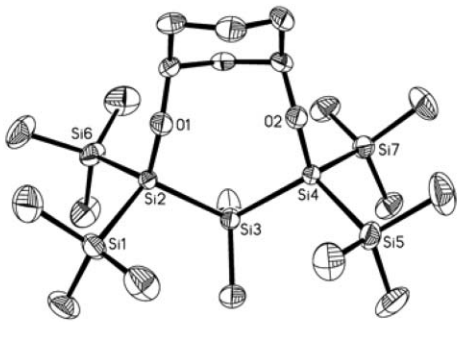

Fig. 3 Molecular structure of **3**. The thermal ellipsoids correspond to 30% probability (hydrogen atoms are omitted). The cyclohexyl group is unequally disordered with two different orientations relative to the oligosilyl part. Only the major orientation is shown. Selected bond lengths [Å] and angles [°]: O1–Si2 1.659(2), O2–Si4 1.659(2), average Si–Si 2.3588(8), Si6–Si2–Si3–Si4 128.48(3), Si1–Si2–Si3–Si4 110.31(4), Si2–Si3–Si4–Si5 107.76(4), Si2–Si3–Si4–Si7 129.50(3).

Table 1 *SiSiSiSi* dihedral angles [°] and $\Delta E_{\text{HOMO-LUMO}}$ [eV]

	2[a]	**3**[a]	**2a**[b]	**2b**[b]	**4a**[b]	**4b**[b]	**5**[b]
ω	132	130	138	173	156	173	167
ω	128	129	136	162	156	167	166
ω	106	110	96	72	83	66	72
ω	99	108	91	46	83	45	43
ΔE	—	—	4.816	5.17	5.197	5.388	5.66

[a] From X-ray data [b] Calculated.

To estimate the impact of oxygen substitution on structural parameters and optical band gaps, we have undertaken molecular orbital calculations employing density functional theory (B3LYP)[9] on **2**, **4** and **5**. To simplify this approach the OH groups in **2** have been constrained into syn (**2a**) and anti (**2b**) position relative to each other and the geometries have been fully optimized, respectively (see Fig. 5 and Table 1). The calculated conformers **2a** and **2b** represent minima, which are similar in energy. The rotational energy barrier for the conversion of the hydrogen-bonded **2a** into **2b** is calculated to be 35 kJ mol^{-1} with a calculated

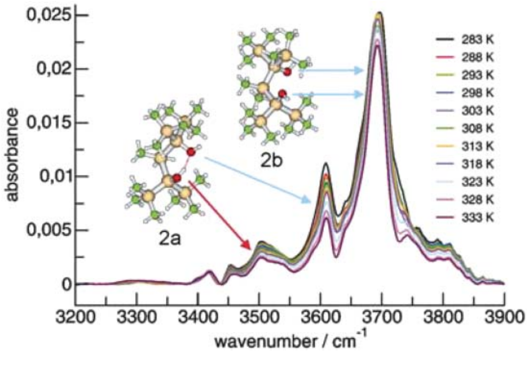

Fig. 4 IR spectra of **2** in CCl_4 ($c = 10^{-3}$ M) as a function of temperature (O–H stretching vibrations region). Values for the observed OH stretching frequencies of the following species: **2a**: 3505 cm^{-1} (intra), 3607 cm^{-1} (non-assoc.); **2b**: 3692 cm^{-1} (non-assoc.).

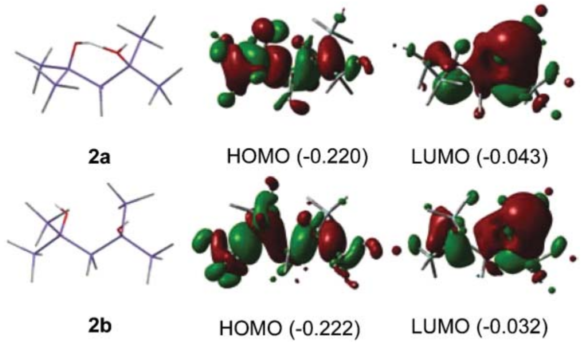

Fig. 5 Optimized geometries (red: oxygen, blue: silicon, gray: carbon, hydrogen atoms except for OH have been omitted for clarity) and energies for **2a** [E(RB + HF − LYP) = −2737.19831452 [intramolecular O···O distance 2.84 Å] and **2b** [E(RB + HF − LYP) = −2737.19195798] and GaussView representations of the frontier molecular orbitals.

counterpoise-corrected binding energy of 16.7 kJ mol^{-1}.[10] The optimized structure **2a** shows a twisted silicon backbone conformation having dihedral angles, which closely resembles that of **2** and **3** in the solid-state. In contrast, conformer **2b** shows large dihedral angles being similar to those calculated for **4**[11] and **5** ($\omega \sim$ 160–180°), which implies that conformers with large dihedral angles are energetically preferred, when intramolecular hydrogen bonding is not involved. Consequently, energetically less favored twisted conformers ($\omega \sim$ 120–130°) need to be stabilized by strong intramolecular hydrogen bonding or ring formation.

From these findings it seems evident that in solution and also in the solid-state the energetically low-lying σ–σ* transitions of **2** and **3** arise from a twisted silicon backbone conformation. According to our DFT calculations this conformation is seen in the intramolecular hydrogen bonded monomer **2a**. With respect to the non-associated conformer **2b**, however, it is worth noting the coexistence of a very broad absorption band in the UV spectrum of **2** with a maximum of *ca* 272 nm (Fig. 1). Despite its low intensity, this broadened band may be ascribed to conformer **2b**.

Returning to the large optical gap between **2/3** and **4**, there is a correlation with the calculated HOMO–LUMO energy gaps of twisted species **2a** and non-twisted **2b**. The HOMO's of **2a** and **2b** mainly involve interactions from the Si–Si σ-orbitals of the pentasilane chain. In addition, **2a** and **2b** have some antibonding interactions with the oxygen p_π-orbitals,[12] which are compensated to some extent by bonding hyperconjugative interactions of the methyl groups with the OH groups.[13] In the LUMO's of **2a** and **2b**, there is a strong σ–n mixing of the oxygen lone pairs with the orbitals of the silicon chain. Due to its bonding character the energy of the LUMO is significantly lower than that of **5**. The extent of this orbital interaction depends on the conformation of the pentasilane chain (Fig. 5). The LUMO of **2a** is largely delocalized along the pentasilane chain, whereas in **2b** the delocalization of the LUMO is reduced to a tetrasilane subunit and therefore higher in energy. Consequently there is an overall decrease in the HOMO–LUMO energy gap in the order **5** > **4b** > **4a** ∼ **2b** > **2a**, which correlates well with the optical trend seen in the UV spectra of **2–5**.

In conclusion, our preliminary findings reported herein reveal that the remarkable red shift of the UV absorption maximum of **2** and **3** arise from twisted silicon backbone conformations. DFT calculations on the constrained conformers **2a** and **2b** clearly show the σ-orbitals of the silicon backbone to be strongly coupled with the oxygen lone pair orbitals in the LUMO reducing the HOMO–LUMO band gap significantly. These orbital interactions may decrease the energy of the LUMO stronger in twisted conformers ($\omega \sim$ 120–130°) than in energetically favored anti-conformers ($\omega \sim$ 160–180°). Our findings are in striking contrast to those found for peralkylated oligosilanes, in which twisted conformations do not significantly contribute to the extent of σ-conjugation.[1,2]

Notes and references

‡ *Crystal data*: **2** (CCDC 618042): $C_{14}H_{44}O_2Si_7$, M = 441.12 g mol^{-1}, colorless needle, 0.65 × 0.32 × 0.31 mm, orthorhombic, *Pbcn*, Z = 8, a = 10.1051(7), b = 23.259(2), c = 25.278(2) Å, V = 5941.2(7) Å^3, ρ_{calc} = 0.986 g cm^{-3}, μ = 0.326 mm^{-1}, 27455 measured reflections, 6118 independent reflections (R_{int} = 0.0277), 208 parameters, $R1(F)$ = 0.0427 for 3973 reflections with $I > 2\sigma(I)$ and $wR2(F^2)$ = 0.1355 for all data. **3** (CCDC 618041): $C_{20}H_{52}O_2Si_7$, M = 521.25 g mol^{-1}, colorless block, 0.80 × 0.80 × 0.52 mm, monoclinic, $P2_1/c$, Z = 4, a = 11.0842(9), b = 30.120(3), c = 10.5929(9) Å, β = 107.816(3)°, V = 3366.9(5) Å^3, ρ_{calc} = 1.028 g cm^{-3}, μ = 0.297 mm^{-1}, 87851 measured reflections, 10829 independent reflections (R_{int} = 0.0339), 317 parameters, $R1(F)$ = 0.0574 for 7773 reflections with $I > 2\sigma(I)$ and $wR2(F^2)$ = 0.1557 for all data. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b618438c

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8 The IR spectrum of **2** in nujol exhibits a very broad band at 3312 cm^{-1}, which corresponds to the dimer in the solid state.
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10 The rotational energy barrier was determined by calculations where one of the SiSiSiSi dihedral angles was varied in 10° increments, with all of the other parameter being fully optimized.
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