σσ* Transition in *anti,cisoid* Alternating Oligosilanes: Clear-Cut Evidence for Suppression of Conjugation Effect by a *cisoid* Turn

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Polysilanes comprising catenated silicon−silicon bonds in their backbones are representative σ-conjugated compounds and are attractive in view of their unique optical properties, such as UV absorption.[1] The absorption maxima λ_{max} of oligo- and polysilanes were found to red-shift as the silicon chain becomes longer, similar to those of the π-conjugated compounds such as polyacetylenes and polyphenylenes. The UV absorption spectra of some polysilanes are found to be thermochromic,[2] which is explained in terms of the silicon backbone conformation change. A recently introduced explanation[3] for the conformational dependence of the spectra of tetrasilanes invoked an avoided crossing of the two lowest-energy valence excited states of B symmetry, and this has been experimentally confirmed by utilizing conformationally constrained tetrasilanes.[4] The UV absorption spectra of conformationally constrained hexasilanes[4b] demonstrated that an *anti* turn effectively extends the σ-conjugated system, while a *syn* turn at the termini does not. For a better understanding of the electronic states in polysilanes, it is highly desirable to extend the investigation to longer silicon chain compounds. In the present paper, we will report the preparation and UV absorption of *anti(A),cisoid(C)*[5] alternating hexa- to decasilanes to discuss the effect on the photophysical properties when an incorporated *syn* turns into an *anti* segment.

The bicyclic disilane **1** with two tetramethylene tethers was used as a monomer unit; the C(Ph)−Si−Si−C(Ph) dihedral angle was found to be 30.7° (*cisoid*) by X-ray crystallography. Reductive condensation of **2** was carried out with lithium metal in the presence of chlorotrimethylsilane as the terminator (Scheme 1).[6] This reaction

Scheme 1

$n = 1 ;$ **3** (15%)
$n = 2 ;$ **4** (13%)
$n = 3 ;$ **5** (8%)
$n = 4 ;$ **6** (5%)
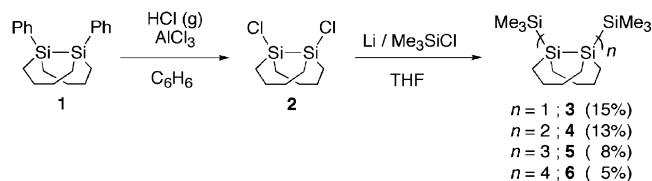
afforded the bis-silylated monomer to the tetramer (**3**−**6**) of the disilane unit, which corresponds to a linear tetrasilane to decasilane. These oligomers were separated by recycling preparative GPC and identified by ¹H, ¹³C, and ²⁹Si NMR as well as mass spectra. The hexasilane **4** was found to have a *CAC* conformation by X-ray crystallography, which demonstrated that the *cisoid* configuration of the disilane units has been retained during the oligo-condensation, and therefore, it is quite reasonable to assume that the octasilane **5** and the decasilane **6** have the *CACAC* and the *CACACAC* conformations, respectively.

The UV absorption spectra of **3**−**6** are shown in Figure 1A. Several significant features are noted: (1) The *C* tetrasilane **3** shows a spectrum reminiscent of that of the pentamethylene analogue.[4b] It contains a shoulder-like absorption without any peak around 240
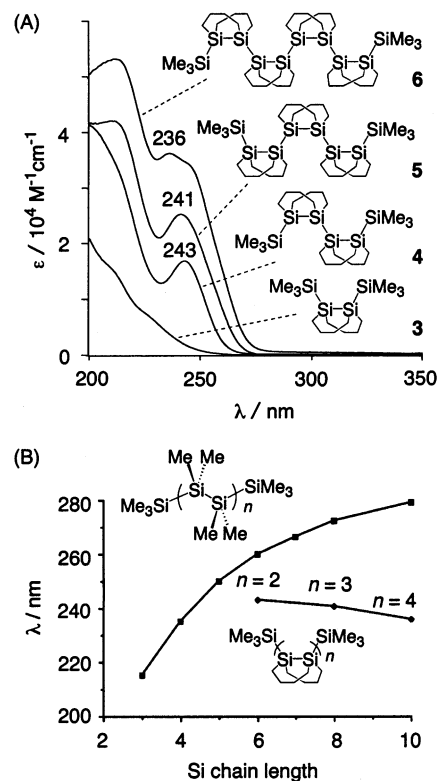

Figure 1. UV absorption spectra of *anti,cisoid*-alternating oligosilanes **3**−**6** (A) and absorption maximum wavelength of constrained and unconstrained oligosilanes (B).

nm, unlike all the other presently studied oligosilanes. This is the only member of the series that contains no *anti* tetrasilane subunit. (2) The *CAC* hexasilane **4** has an absorption maximum at 243 nm derived from the σσ* transition at the central *anti* turn, as observed before for the pentamethylene analogue.[4b] (3) In the series **4**−**6**, the absorption maximum wavelengths λ_{max} remain constant near 240 nm, regardless of the silicon chain length. (4) The absorption maximum of the decasilane **6** at 236 nm is accompanied by a shoulder around 245 nm. (5) The absorption around 210 nm, for which the *cisoid* fragments are responsible, also intensifies as the silicon chain becomes longer.

In Figure 1B, the primary absorption maximum wavelengths of the permethylated oligosilanes,[1a,7] and the *A,C* alternating oligosilanes are plotted against the number of silicon atoms. The absorption maximum of the permethylated oligosilanes steadily shifts toward longer wavelengths as the silicon chain becomes longer because of the elongation of the successive *anti* (or *transoid*) segment length. In contrast, that of the *A,C* alternating oligosilanes remains almost constant around 240 nm, corresponding to absorption derived from the *anti* fragment, irrespective of the increase in the number of silicon atoms.

Table 1. CIS Calculations for Oligosilanes **3**−**6**

oligosilanes	state	$\lambda_{max}^{a,b}$	f^c	oligosilanes	state	$\lambda_{max}^{a,b}$	f^c
3	1B	236	0.0444	**6**	2A	248	0.0244
	2A	225	0.0496		1B	247	0.2006
	3A	211	0.0121		3A	243	0.0079
	2B	**208**	**0.5921**		**2B**	**242**	**1.1346**
4	2A	244	0.0045		3B	236	0.2491
	1B	**242**	**0.3751**				
5	1B	247	0.1225				
	2A	244	0.0844				
	2B	**241**	**0.6389**				

a Transitions appearing at longer than 230 nm are listed except for **3**. *b* The excitation energies were scaled by 0.76. *c* Oscillator strength. Transitions with large oscillator strengths are shown in bold.
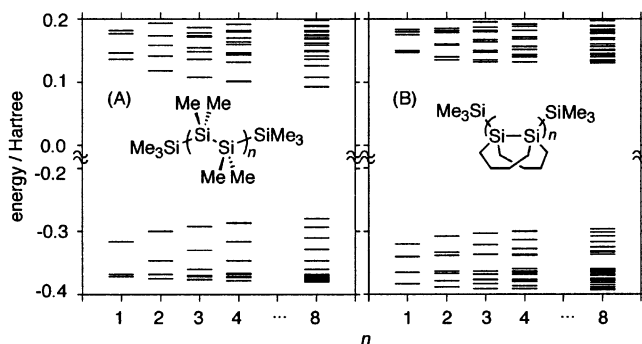
Figure 2. Calculated high-energy occupied and low-energy unoccupied orbital energies of all-*transoid* (A) and *anti,cisoid* alternating oligosilanes (B).

CIS calculations (CIS/6-31G*) for **3**−**6** were carried out and are summarized in Table 1. These results reproduce the absorption spectra quite well although calculations were carried out on one of the possible conformers of each oligosilane, which indicates that their conformations are rigidly controlled by the tetramethylene tethers that leaves little possibility to have the other conformers. The peak of the *CAC* hexasilane **4** that appears at 243 nm is assigned to the $\sigma\sigma^*$ excitation localized at the central Si3−Si4 bond. Its excitation energy is essentially the same as that of a peralkylated tetrasilane of the *anti* conformation.[4b] Obviously, the additional *cisoid* turns at the termini provide no elongation of the σ-conjugated system. For longer-chain homologues, the excitation energy of the most intense transition stays constant, and the corresponding peaks appear around 240 nm regardless of the chain length. For **6**, the observed absorption maximum at 236 nm accompanied with a shoulder at longer wavelengths were also quite well reproduced. Even the absorption maximum of octadecasilane **7**, a virtual octamer built on a computer with an *A,C* alternating conformation, was found to stay around 245 nm (see Supporting Information), while that of the *n*-permethylated octadecasilane appears at 291 nm.[1a]

Figure 2 shows the calculated molecular orbital energies of the permethylated oligosilanes of the all-*transoid* conformation (A) and those of the *A,C* alternating oligosilanes **3**−**7** (B). Clearly, as the silicon chain becomes longer, the HOMO−LUMO gap of the latter decreases much more slowly than that of the all-*transoid* oligomer. For example, the HOMO−LUMO gap difference between hexasilane and octadecasilane is 1.27 eV in (A) and 0.42 eV in (B).

In summary, on the basis of the UV absorption spectra of the *A,C* alternating oligosilanes, we have obtained the first clear-cut

experimental evidence for the generally accepted idea that the σ-conjugation in polysilanes does not effectively extend through a tetrasilane fragment with a small dihedral angle such as a *cisoid* turn,[8−10] as suggested by the simple ladder C model[10] of the σ backbone structure. This result demonstrates that the UV absorption spectral behavior of the all-*transoid* permethylated oligosilanes and the present *A,C* alternating oligosilanes is similar to that of the π-conjugated poly(*p*-phenylene)s and poly(*m*-phenylene)s,[11,12] respectively. Therefore, it can be concluded that the effect of the conformation isomerism on the photophysical properties in the σ-conjugation system corresponds to that of the position isomerism in the π-conjugated system, which has been experimentally clarified more than 60 years after the UV absorption measurements of poly-(*p*-phenylene)s and poly(*m*-phenylene)s.[11a]

Supporting Information Available: Experimental details, X-ray crystallography of **1** and **3**, and computational details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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