undergo a strong upfield shift characteristic of "entwined" compounds, as evidenced long ago.[12] From the data in Table 1, it is evident that dpp is coordinated in both complexes $\mathbf{3}^{2+}$ and $\mathbf{5}^{4+}$. For instance, H_m undergoes an upfield shift with respect to the free ligand of $\Delta\delta = -1.13$ and -0.88 ppm for $\mathbf{3}^{2+}$ and $\mathbf{5}^{4+}$, respectively. For H_o, the shift is even more spectacular in $\mathbf{5}^{4+}$ ($\Delta\delta = -1.59$ ppm) probably because of the strong ring current exerted by the terpyridine (terpy) unit onto this proton.

2) The CH_3 groups borne by the phen chelate included in the filament are also strongly upfield shifted by complexation, owing to a similar "entwining" effect as that observed for H_o and H_m. The chemical shifts are strikingly similar for **4** and $\mathbf{5}^{4+}$, but they are significantly different from those of $\mathbf{3}^{2+}$: $\Delta\delta \sim -0.6$ ppm for $\mathbf{3}^{2+}$ with respect to **4** or $\mathbf{5}^{4+}$; thus, the dmp unit of $\mathbf{5}^{4+}$ is free.
3) H_6, $H_{6''}$, and $H_{4'}$ of the terpy part also undergo substantial chemical shift changes upon complexation. Whereas the corresponding chemical shift values are similar in **2**, $\mathbf{3}^{2+}$, and **4** ($\delta = 8.76 \pm 0.08$ for H_6; $\delta = 8.73 \pm 0.02$ for $H_{6''}$, and $\delta = 7.97 \pm 0.01$ for $H_{4'}$), they are noticeably different in $\mathbf{5}^{4+}$ (strong upfield shift for H_6 and $H_{6''}$; relatively strong downfield shift for $H_{4'}$). These observations are consistent with the "entwining" effect, placing H_6 and $H_{6''}$ in the shielding region of the dpp unit belonging to the ring for a (dpp)(terpy) complex. They also unambiguously demonstrate that both Zn^{2+} centers in $\mathbf{5}^{4+}$ are coordinated to the terpy fragments.

From the ^1H NMR data, it can be concluded that each Zn^{2+} ion of $\mathbf{5}^{4+}$ is coordinated to a dpp chelate and a terpy unit, that is the molecule is in the contracted situation, as represented in Scheme 2.

In conclusion, the present rotaxane dimer is the first unimolecular linear array capable of stretching and contracting at will under the action of a chemical stimulus. From CPK model estimations, the length of the compound changes from 83 Å to 65 Å between both situations, that is roughly by the same relative amount as natural muscles (~27%).

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Conformation Control of Oligosilanes Based on Configurationally Constrained Bicyclic Disilane Units**

Kohei Tamao,* Hayato Tsuji, Masayoshi Terada, Masahiro Asahara, Shigehiro Yamaguchi, and Akio Toshimitsu

One of the most important properties of polysilane compounds is their electronic absorption in the UV region that provides a representative example of the σ-conjugation systems.[1] It is generally accepted that *both* the absorption wavelengths, λ_{max}, and the intensities depend on the chain length of the silicon backbone in the *anti* conformation, while the *gauche* conformations behave as defects in the σ conjugation. This idea has been successfully used to explain the thermochromic behavior of long-chain polysilanes.

However, little is understood about the origin of the conformation-dependency of the electronic absorptions. Recently, a new explanation has been proposed by Michl and coworkers[2] based on their pioneering theoretical and experimental studies on tetrasilane model systems. These systems

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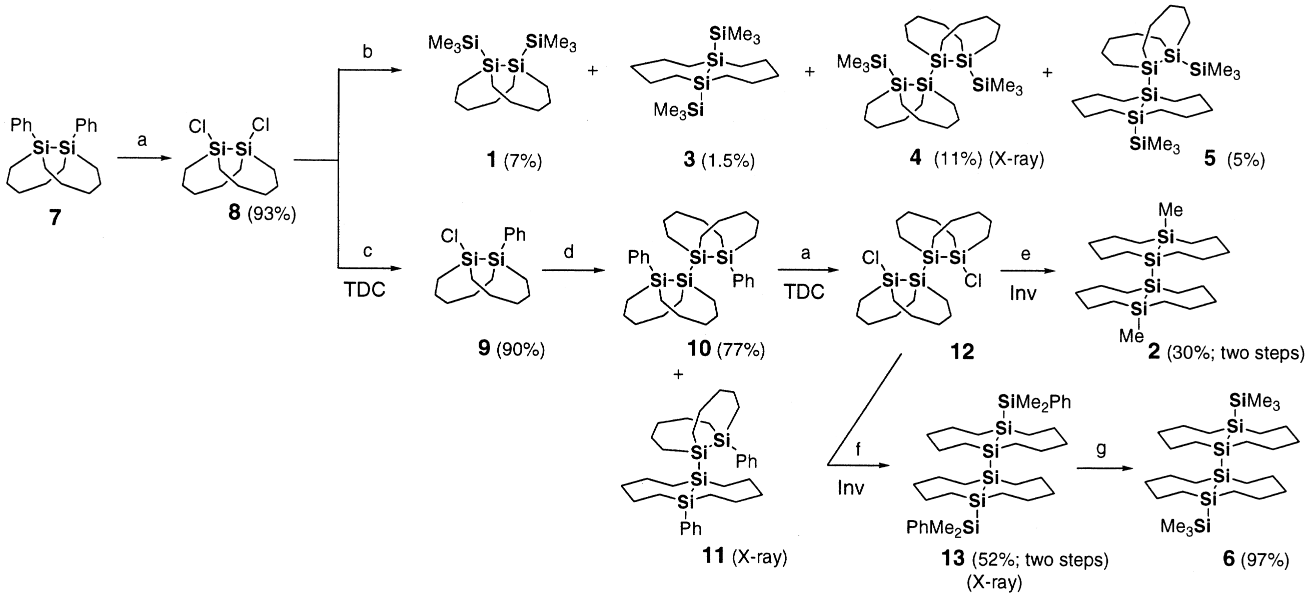
Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

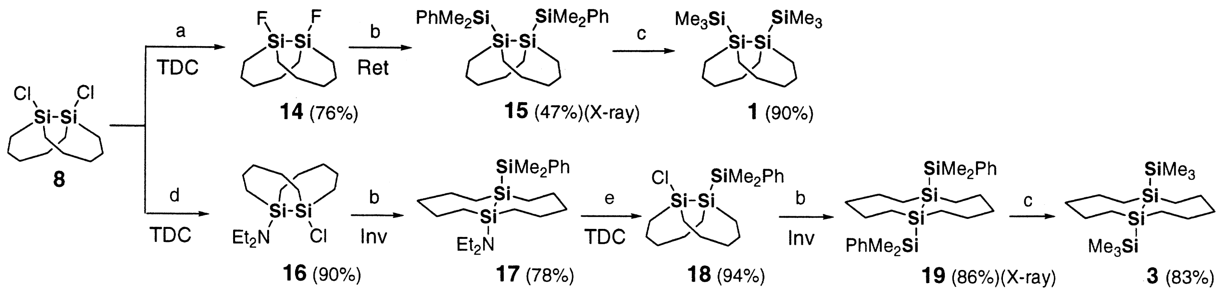


Scheme 1. Synthesis of **1**–**6**. a) HCl(gas)/ AlCl$_3$, C$_6$H$_6$; b) Li/Me$_3$SiCl, THF; c) PhMgCl, THF; d) Li, THF; e) MeLi, Et$_2$O; f) PhMe$_2$SiLi, THF; g) 1) TfOH, C$_6$H$_6$; 2) MeMgI, Et$_2$O. TDC = thermodynamically controlled conditions; Inv = inversion of configuration. Experimental details and workup procedures are available in the Supporting Information.

are the shortest polysilane units to have conformational isomers defined by the dihedral angle (ω) around the central Si–Si bond. According to this new explanation there are two absorptions assigned to the $\sigma-\sigma^*$ and the $\sigma-\pi^*$ transitions in which the σ and σ^* orbitals are of the silicon backbone and the π^* orbitals primarily consist of the σ^* orbitals of the two substituents on each silicon atom; the energies of these two absorptions are not conformation dependent but the intensities are. Thus, in the *anti* conformation ($\omega = 180°$), the low-energy absorption ($\sigma-\sigma^*$) is strong and the high-energy absorption ($\sigma-\pi^*$) is very weak, while in the *syn* conformation ($\omega = 0°$), the high-energy absorption (σ-σ^*) is strong and the low-energy absorption ($\sigma-\pi^*$) is very weak; the intensities of the two absorptions would be medium and comparable to each other in conformers in which $\omega = 90-135°$. Experimental support of this important theory is essential to fully understand the σ conjugation and should best be obtained with conformationally defined oligosilanes. However, it is one of the most difficult tasks in organic chemistry to obtain desired conformational isomers at will. The energy-minimum stable conformers, that is, the *anti*, and the *gauche* ($\omega = 60°$), or similar conformers in the oligosilane case, can be fixed under thermodynamically controlled conditions such as in low-temperature matrices[2] or in crystals.[3, 4] Whereas, to fix the conformers which do not correspond to the local energy minima requires special techniques. For instance, by introducting the tetrasilane skeleton into five- to eight-membered cyclic carbosilane compounds Michl and co-workers have prepared several conformers in which $\omega = 0-80°$.[5]

Herein we report the syntheses and UV absorption spectra of tetrasilane and hexasilane compouds in which the dihedral angles ω are controlled to *syn* (*S*), *anti* (*A*), and "*second-eclipsed*"[6] (*E*) ($\approx 120°$) by the use of disilane units that are configurationally constrained to *syn* or *anti* by two pentamethylene tethers.[7]

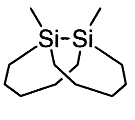
The syntheses of the tetrasilane compounds **1**–**3** and the hexasilane compounds **4**–**6** from the single key compound **7** (which is readily converted into **8**) are summarized in Schemes 1 and 2.[8] The tetrasilane compounds **1** and **3** which contain one disilane unit (*syn* or *anti*) and the hexasilanes **4** and **5** which contain two disilane units (*syn*, *syn* and *anti*, *syn*) were formed by the reductive coupling reaction of the dichlorodisilane **8** with lithium (Scheme 1) and were separated by gel permeation chromatography (GPC). The tetra-



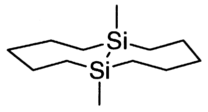
Scheme 2. Selective synthesis of **1** and **3**. a) ZnF$_2$, Et$_2$O; b) PhMe$_2$SiLi, THF; c) 1) TfOH, C$_6$H$_6$; 2) MeMgI, Et$_2$O; d) Et$_2$NH/Et$_3$N, THF; e) HCl(gas), Et$_2$O. TDC = thermodynamically controlled conditions; Inv = inversion of configuration; Ret = retention of configuration. Experimental details and workup procedures are available in the Supporting Information.

silane compound **2** and the hexasilane compound **6** which contain two *anti*-disilane units were prepared by stereodefined transformations including the selective formation of the *syn*-chlorodisilane units under thermodynamically controlled conditions (TDC) and stereospecific substitution reactions with inversion of configuration (Inv)[9] (Scheme 1). By use of a similar methodology we also developed alternative selective synthetic routes to **1** and **3** (Scheme 2).[10]

The UV absorption spectral data of the tetrasilane compounds **1**–**3** and of the hexasilane compounds **4**–**6** are summarized in Tables 1 and 2, respectively, together with the particular dihedral angles determined by X-ray crystallography for the five compounds **4**, **11**, **13**, **15**, and **19**.[11] The dihedral angles of the *syn*-disilane units (ω in **15**, ω_1 and ω_3 in **4**, and ω_3 in **11**) were found to be constrained between 7–30° (*S*) and those of the *anti*-disilane units (ω in **19**, ω_1 and ω_3 in **13**, and ω_1 in **11**) between 170–180° (*A*). In **4** and **11**, the unconstrained dihedral angles (ω_2) around the central Si–Si bond between the two disilane units, *syn*, *syn* and *anti*, *syn*, were found to be 180° (*A*) and 177.5° (*A*), respectively. In **13**, the dihedral angle ω_2 between the two *anti*-disilane units was found to be 117.5° (*E*). PM3 calculations indicate that the most stable conformer of **6** has a dihedral angle ω_2 between the two *anti*-disilane units of 115°, while in the most stable conformer of **4** the dihedral angle ω_2 between the two *syn*-disilane units is 180°.



syn-disilane unit



anti-disilane unit

Table 1. UV absorptions and dihedral angles of Si-Si-Si-Si framework of tetrasilane compouns **1**–**3**.

UV absorption		Dihedral angles determined by X-ray crystallography		
Compound	λ_{max} [nm] (ε)	Compound	ω[°]	Conformation[a]
1	≈210 (sh[b], 1.3×10^4)	**15**	7.1	*S*
2	204 (2.2×10^4) 230 (1.7×10^4)	**13**	117.5	*E*
3	238 (3.0×10^4)	**19**	180	*A*

Table 2. UV absorptions and dihedral angles of Si-Si-Si-Si framework of the hexasilane compounds **4**–**6**.

UV absorption		Dihedral angles determined by X-ray crystallography				
Compound	λ_{max} [nm] (ε)	Compound	ω_1[°]	ω_2[°]	ω_3[°]	Conformation[a]
4	239 (2.2×10^4)	**4**	13.1(30.0)[b]	180(180)[b]	13.1(30.0)[b]	*SAS*
5	255 (3.1×10^4)	**11**	179.2[c]	177.5	8.0[c]	*AAS*
6	≈225 (sh[d],1.2×10^4) 259 (5.3×10^4)	**13**	171.1	117.5	170.2	*AEA*

[a] *S* = *syn*, *A* = *anti*, *E* = second-eclipsed. [b] There are two independent molecules in crystals. [c] The Si-Si-Si-C dihedral angle in **11**. [d] sh = shoulder.

The UV absorption spectra of tetrasilanes **1**–**3** measured at room temperature in 2,2,4-trimethylpentane are shown in Figure 1; the spectrum of decamethyltetrasilane Si_4Me_{10} is included for comparison. The *A*-tetrasilane compound **3** has an absorption maximum at 238 nm with an absorbance of greater intensity than that of Si_4Me_{10}. The *E*-tetrasilane compound **2** with a dihedral angle of ≈120° has "twin" absorption maxima of medium intensity at 204 and 230 nm. The absorption of the *S*-tetrasilane compound **1** appears as a shoulder at around 210 nm. These results seem to be consistent with the theoretical prediction.[2] The strong absorption in the *A*-tetrasilane compound **3** is assigned to the low-energy $\sigma-\sigma^*$ transition, the shoulder-like absorption around 210 nm of the *S*-tetrasilane compound **1** is assigned to the high-energy $\sigma-\sigma^*$ transition, and the $\sigma-\pi^*$ transition of compounds **1** and **3** is expected at around 230–240 nm for **1** and at around 210 nm for **3**; however, this transition is hardly recognizable presumably because of its very low intensity. The "twin" absorption maxima in **2** are assigned to the high- and low-energy transitions of the tetrasilane unit which has a dihedral angle of approximately 120°.

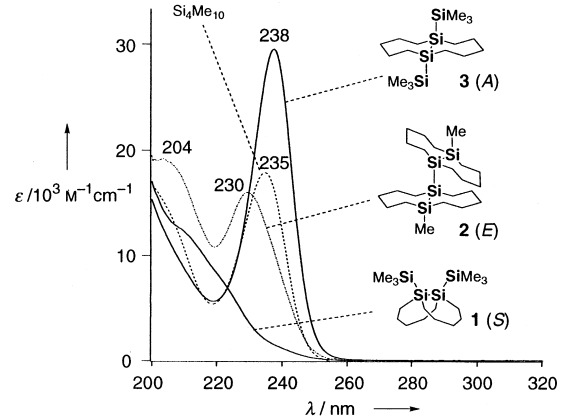


Figure 1. UV absorption spectra of the tetrasilane compounds **1**–**3** and Si_4Me_{10}.

Figure 2 shows the UV absorption spectra of hexasilanes **4**, **5**, and **6**, in the sequence **4**, **5**, **6** the λ_{max} shifts from 239 for **4** to 259 nm for **6** and the intensity almost triples. The absorption spectrum of the *SAS*-hexasilane **4** has a λ_{max} at 239 nm which corresponds to the combined spectra of the *S*-tetrasilane compound **1** and the *A*-tetrasilane compound **3**. This result is best understood by assuming that this absorption maximum arises from the tetrasilane skeleton of the *anti* conformation and that the additional *syn* segments do not contribute to the elongation of the σ conjugation. A comparison of the spectra of the *SAS*-hexasilane compound **4** and *AAS*-hexasilane compound **5** clearly shows the significant contribution of the additional *anti* segment to the elongation of the σ conjugation. The strong but slightly red-shifted absorption observed in the

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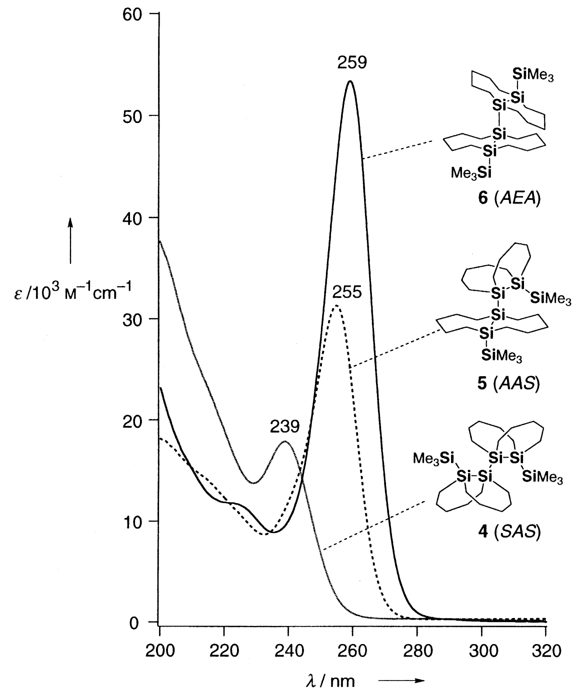

Figure 2. UV absorption spectra of the hexasilane compounds **4**–**6**.

AEA-hexasilane compound **6** indicates that the connection of two constrained *A* conformations with one *E* conformation is the main contribution to the enhancement in the intensity.[12]

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[10] Stereospecific substitution with retention of configuration (Ret) is also part of the preparation of **1**.

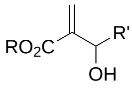
[11] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-141477 (**4**), -141479 (**11**), -141478 (**13**), -141475 (**15**), and -141476 (**19**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[12] The λ_{max} of **6** in the solid state was confirmed to be the same as that in solution, and suggests that the dihedral angle ω_2 around the "non-constrained" Si–Si bond is comparable in both the solution and the solid state.

Asymmetric Synthesis of Baylis–Hillman-Type Allyl Alcohols via a Chiral Acetylenic Ester Titanium Alkoxide Complex[**]

Daisuke Suzuki, Hirokazu Urabe, and Fumie Sato*

Functionalized allyl alcohols such as **1** and **2** are useful intermediates in organic synthesis.[1, 2] Several recent reports have revealed that the asymmetric Baylis–Hillman reaction



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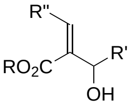
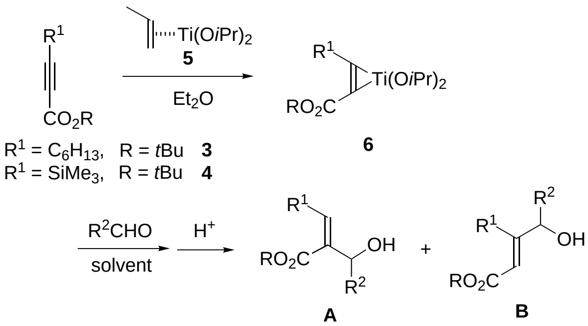


2

afforded alcohols **1** in a highly optically active form.[1, 3] However, asymmetric synthesis of the homologues **2**, which contain a substituent β to the acrylate group, has not been successful by this method.[4] We recently reported the first generation of the acetylenic ester Group 4 transition metal complexes such as **6**[5] from esters **3** or **4** and a low-valent titanium complex, $[(\eta^2\text{-propene})\text{Ti}(\text{O}i\text{Pr})_2]$ (**5**)[6] (Scheme 1).



Scheme 1. Reaction of acetylene complex **6** with aldehydes.

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