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all-anti-Pentasilane: Conformation Control of Oligosilanes Based on the Bis(tetramethylene)-Tethered Trisilane Unit

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Summary: A bicyclic trisilane unit affords all-anti peralkylated pentasilane with dihedral angles $\omega > 178°$. *Its UV and MCD spectra as well as the X-ray crystallography of a related compound demonstrate the highly* σ*-conjugated system due to the rigidity of the silicon chain conformation.*

Since the first reports of the UV absorption of oligosilanes in 1964,[1] the unique photophysical and electronic properties of oligo- and polysilanes have drawn attention due to the σ delocalization within the silicon framework.[2] The thermochromic behavior of their UV absorption spectra demonstrated the fact that the σ conjugation system is sensitive to the silicon backbone conformation.[3] Recent studies of oligosilanes with a discrete conformation have unveiled the conformation dependence of the oligosilane σ conjugation: an anti conformation (SiSiSiSi dihedral angle $\omega = 180°$) effectively extends the conjugation, while conformations with a small dihedral angle such as syn, cisoid, and gauche ($\omega \approx 0-60°$) do not.[4,5] For a highly conjugated system, it is desirable to precisely control the silicon backbone to be anti. However, the peralkylated poly- and oligosilanes possess a transoid ($\omega \approx 165°$) or deviant ($\omega \approx 150°$) conformation[6] as an energy minimum, while the anti conformation corresponds to a local maximum on the energy surface. The low rotation barrier around Si−Si produces a large number of conformers, resulting in a short effective conjugation length along the silicon backbone.[7,8] Thus, many attempts have been examined to control the silicon backbone in a discrete conformation, in which the conformation is controlled in a manner such as matrix isolation,[9] utilization of cyclic[10] or bicyclic[11] structures, introduction of bulky[12] or chiral[13,14] substituents, incorporation of pentacoordinate silicon atoms,[15] or inclusion into cyclodextrins.[16,17]

We have prepared several conformationally controlled tetra- and hexasilanes using an oligomethylene-tethered bicyclic disilane unit (Chart 1) and found them to significantly elucidate the conformation dependence of the photophysical properties in oligosilanes.[11] However, during the studies attempting preparation of longer oligosilanes using the disilane unit, the following intrinsic problems in this methodology have been found. (1) The bicyclic disilane unit possesses syn and anti configurational isomers. Due to the thermodynamic stability of the former,[11a] oligosilanes comprising more syn units are preferably formed. (2) Poor solubility due to the rigid bicyclic structure prevents the formation of longer silicon chain oligosilanes.[11a] (3) The interunit Si−Si bond preferably forms the gauche to eclipsed ($\omega = 60-120°$) conformation rather than anti.[11a,18] To overcome these shortcomings of the bicyclic disilane unit, we have designed a bicyclic trisilane unit suitable for all-anti oligo- and polysilanes, as shown in Chart 1. The advantages of this unit are as follows. (1) Only the anti conformation is possible within the unit. (2) Introduction of substituents such as long alkyl groups on the central silicon atom renders a good solubility to the oligo- and

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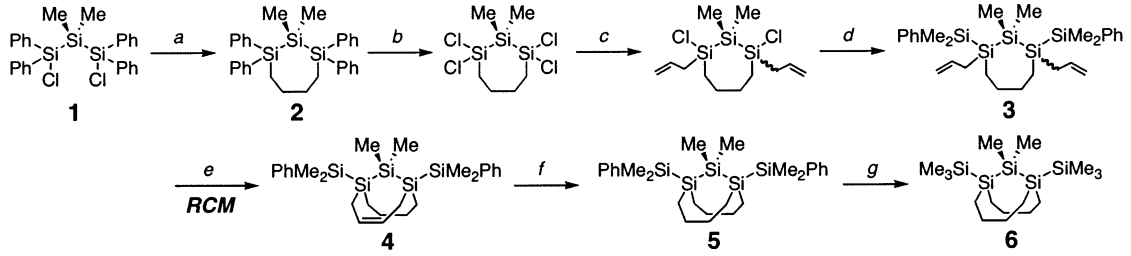
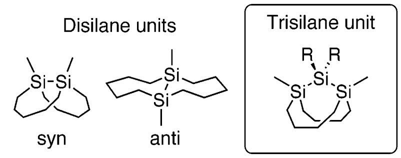
10.1021/om049695t CCC: $27.50

Scheme 1[a]



[a] Conditions: (a) ClMg(CH$_2$)$_4$MgCl, 83%; (b) HCl(g), AlCl$_3$, 93%; (c) (1) Et$_2$NH, Et$_3$N, (2) allylmagnesium bromide, (3) HCl(g), 70% (three steps); (d) PhMe$_2$SiLi, 48%; (e) IMesRuCl$_2$(PCy$_3$)(=CHPh), 74% based on cis isomer; (f) H$_2$, RhCl(PPh$_3$)$_3$, 95%; (g) (1) TfOH, (2) MeMgBr, 79% (two steps).

Chart 1



polysilanes comprising the trisilane unit. (3) The most stable conformation about the interunit Si−Si bond is expected to be anti (ω = 180°), as estimated by calculations. Details will be reported elsewhere. In a preliminary study, we prepared a pentasilane composed of the bis(tetramethylene)-tethered bicyclic trisilane unit and obtained its photophysical properties to confirm the effectiveness of the unit for conformation control in the silicon backbone.

The synthetic route to the pentasilane **6** is outlined in Scheme 1. Starting from the 1,3-dichlorotrisilane **1**, the monocyclic structure was constructed by the reaction with a di-Grignard reagent. After successive introduction of allyl and dimethylphenylsilyl groups at the 1,3-positions of **2** via exhaustive dephenylchlorination and partial amination, ring-closing metathesis (RCM) of **3** catalyzed by the benzylidene ruthenium complex (a so-called second-generation Grubbs catalyst)[19] afforded the bicyclic structure in moderate yield.[20] Hydrogenation at the unsaturated bond in the "tether," followed by replacement of the phenyl groups in the termini by methyl groups, afforded the target pentasilane **6**.

X-ray crystallography was performed on the diphenyl-substituted pentasilane **5**. There were two crystallographically independent molecules in a unit cell, and one of the structures is shown in Figure 1. The Si−Si bond lengths are in the normal range (2.34−2.35 Å). The Si(2)−Si(3)−Si(4) bond angle is quite small (104.19(6)°) for an sp^3 silicon because of the ring strain originating from the bicyclic structure. Most significantly, the dihedral angles in the silicon backbone are 179.00(5) and 179.11(5)°.[21] To the best of our knowledge, the conformation of the pentasilane **5** is the closest to the ideal all-anti structure among the already synthesized peralkylated oligosilanes. Due to the robust bicyclic structure, the conformation of the methylated pentasilane **6** should also be all-anti.

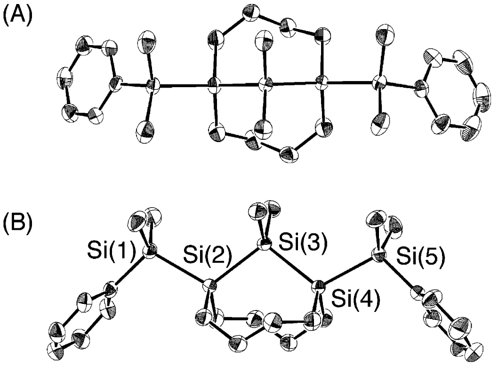


Figure 1. X-ray structure of **5** (ORTEP plot, 50% probability for thermal ellipsoids): (A) top view; (B) side view. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): Si(1)−Si(2) = 2.3495(15), Si(2)−Si(3) = 2.3413(15), Si(3)−Si(4) = 2.3422(15), Si(4)−Si(5) = 2.3396(16); Si(1)−Si(2)−Si(3) = 112.77(6), Si(2)−Si(3)−Si(4) = 104.19(6), Si(3)−Si(4)−Si(5) = 113.47(6); Si(1)−Si(2)−Si(3)−Si(4) = −179.00(5), Si(2)−Si(3)−Si(4)−Si(5) = −179.11(5).

Table 1. Summary of UV and MCD Spectra of 6 and *n*-Si$_5$Me$_{12}$[a]

	UV		MCD	
compd	λ_{max}/nm	$\epsilon/10^4$	λ_{MCD}/nm	$[\Theta]_M$
6	253	4.08	n.d.[b]	−
n-Si$_5$Me$_{12}$	250	2.09	251	0.17
	−	−	232	0.18

[a] All spectra were measured in 3-methylpentane at room temperature. [b] Not detected.

The results of the spectroscopic studies on **6** and *n*-Si$_5$Me$_{12}$ are summarized in Table 1 and shown in Figure 2. As plotted in Figure 2A, the UV absorption band of **6** corresponding to the lowest energy $\sigma\sigma^*$ transition is much narrower even at room temperature as compared with *n*-Si$_5$Me$_{12}$. The small Si(2)−Si(3)−Si(4) bond angle might affect the excitation energy of the $\sigma\sigma^*$ transition, but it should be very small on the basis of the literature data.[22] The MCD spectra of these pentasilanes are shown in Figure 2B. No MCD signal corresponding to the lowest energy $\sigma\sigma^*$ transition is observed for **6**, while two negative B terms are found for *n*-Si$_5$Me$_{12}$ in the same and slightly higher energy regions. The present results of the UV and MCD spectroscopy imply that the silicon backbone of **6** is rigidly constrained to be all-anti even in solution at room temperature, while that in *n*-Si$_5$Me$_{12}$ possesses several conformations other than the predominant all-transoid. These results are also

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[19] IMes = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene: (a) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953. (b) Tranka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18.

[20] All attempts to introduce the second tetramethylene tether using the 1,4-di-Grignard or dilithio reagents failed.

[21] The dihedral angles of the other molecule are 173.22(5) and 175.41(5)°.

[22] Obata, K.; Kira, M. *Organometallics* **1999**, *18*, 2216.

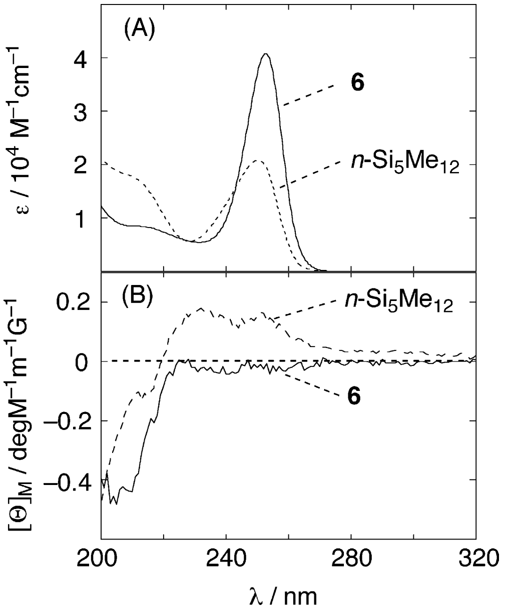

Figure 2. UV (A) and MCD (B) spectra of **6** (solid line) and n-Si$_5$Me$_{12}$ (broken line).

consistent with the conformation analysis of n-Si$_5$Me$_{12}$ and the empirical rule derived from Michl's and our previous observations that the silicon backbone conformation with a larger dihedral angle ω exhibits a weaker MCD signal corresponding to the lowest energy $\sigma\sigma^*$ transition.[23] The latter endows the MCD spectroscopy with the utility to detect an conformation other than anti in the silicon framework of oligosilanes together with UV absorption spectroscopy.

In summary, we have synthesized the pentasilane **6** with its conformation rigidly constrained to all-anti on the basis of the bis(tetramethylene)-tethered bicyclic trisilane unit. Its narrow and intense UV absorption band demonstrates a definite difference from the band for n-Si$_5$Me$_{12}$ and affirms the significance of the precise conformation control in the silicon main chain. More detailed photophysical analyses of **5** and **6** as well as the preparation of longer oligosilanes and polysilanes on the basis of the trisilane unit are now in progress.

Note Added after ASAP: A typo occurred in the caption of Scheme 1 posted on June 10, 2004. The corrected version was posted later that day.

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Supporting Information Available: Text, tables, and figures giving details of the synthesis and characterization of all the new compounds discussed in this paper and a CIF file giving X-ray crystallographic data for **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049695T

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