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all-anti-Octasilane: Conformation Control of Silicon Chains Using the Bicyclic Trisilane as a Building Block

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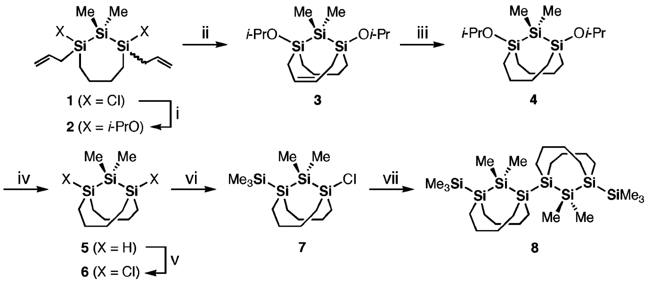
Structure control of flexible linear chains is of fundamental importance for optimizing the physical properties of organic and organometallic polymers. Linear polysilanes are the most typical one-dimensional polymers and show remarkable photophysical and electronic properties due to the σ-electron delocalization over the silicon framework (σ-conjugation), which is highly sensitive to the conformation of the silicon backbone.[1] Since the polysilane main chain has a random-coil structure without any constraint due to the low rotational barrier around the Si−Si single bond,[2] the relationship between the structure and the photophysical properties has not been elucidated until recently. The latest studies on a discrete conformer of oligosilanes revealed that the anti conformation, with a SiSiSiSi dihedral angle ω of 180°, is the most effective for the extension of the σ-conjugation. Thus, much effort has been made, including utilization of a cyclic[3] or bicyclic[4] structure, introduction of bulky[5] or chiral[6,7] substituents, incorporation of pentacoordinate silicon atoms,[8] or inclusion into cyclodextrins,[9,10] in order to control the silicon backbone conformation. Some of these approaches have indeed attained a close "all-anti" [11] conformation up to hexasilanes, but the development of a general method is still on the horizon.

As one of the potential building blocks for the ideal all-anti polysilane, we have designed a bis(tetramethylene)-tethered trisilane. Our preliminary study demonstrated that the *intra*-unit conformation is rigidly constrained to all-anti using the pentasilane comprising the bicyclic trisilane.[12] Herein we report the synthesis, structure, and UV absorption of the octasilane **8**, a trimethylsilyl-capped dimer of the trisilane unit. The *inter*-unit conformation of **8** has been successfully controlled to predominantly all-anti, even in solution at room temperature.

The synthetic route to the octasilane **8** is outlined in Scheme 1. The 1,3-diallyl-1,3-dichlorotrisilane **1**[12] was transformed into the isopropoxy-substituted trisilane **2**. The bicyclic structure was constructed by ring-closing metathesis (RCM) using a 0.2 molar amount (m.a.) of the second-generation Grubbs catalyst (IMesRuCl$_2$(PCy$_3$)(=CHPh)),[13] and subsequent hydrogenation of the internal olefin afforded the 1,3-diisopropoxy-substituted bicyclic trisilane **4**. Compound **4** was transformed into the 1,3-dichlorotrisilane **6** by reaction with diisobutylaluminum hydride (DIBAH), followed by radical-induced chlorination on the terminal silicon atoms using carbon tetrachloride. The reductive condensation of **6** was attempted with lithium naphthalenide (LiNaph) in the presence of chlorotrimethylsilane, but this reaction afforded only the mono-trimethylsilyl-capped chlorotetrasilane **7** as the main product, together with a trace amount of the bis-trimethylsilyl-capped monomer (pentasilane) and dimer **8** (octasilane). The resulting chlorotetrasilane **7** was subjected to the reductive homo-coupling reaction using LiNaph to produce the target octasilane **8**.

Scheme 1. Preparation of Octasilane **8**[a]



[a] Reagents and conditions: (i) *i*-PrOH, imidazole, room temperature, 94% (cis/trans = 1/1); (ii) IMesRuCl$_2$(PCy$_3$)(=CHPh) (0.2 m.a.), CH$_2$Cl$_2$ (0.01 M), reflux, 93% based on *cis*-**2**; (iii) H$_2$ (1 atm), RhCl(PPh$_3$)$_3$ (0.05 m.a.), toluene, 50 °C, 76%; (iv) DIBAH (6.0 m.a.), toluene, 0 °C; (v) CCl$_4$, room temperature, 96% (two steps); (vi) LiNaph (2 m.a.), Me$_3$SiCl, THF, −78 °C to room temperature, 74%; (vii) LiNaph (1.3 m.a.), THF, 0 °C to room temperature, 30%.

The crystal structure of compound **8** was determined by an X-ray crystallographic analysis. The disordered structure was observed for the tetramethylene tethers. One of the structures with a higher occupancy is shown in Figure 1. As expected, eight silicon atoms form the all-anti framework with the dihedral angles $\omega > 179.3°$: not only the *intra*-unit but also the *inter*-unit conformations are successfully controlled exactly to anti in the crystal state. To the best of our knowledge, this is the longest all-anti oligosilane to date among the structurally defined ones.

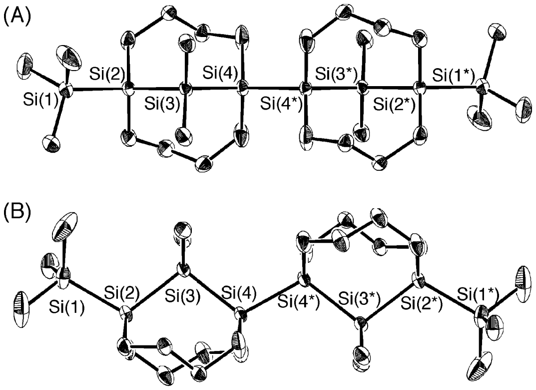


Figure 1. X-ray crystal structure of **8** (ORTEP drawing, 50% probability for thermal ellipsoids): (A) top view and (B) side view. Selected bond lengths (Å), bond angles (°), and torsion angles (°): Si(1)−Si(2) = 2.3562(9), Si(2)−Si(3) = 2.3419(8), Si(3)−Si(4) = 2.3534(8), Si(4)−Si(4*) = 2.3409(1), Si(1)−Si(2)−Si(3) = 112.43(3), Si(2)−Si(3)−Si(4) = 104.39(3), Si(3)−Si(4)−Si(4*) = 112.76(4), Si(1)−Si(2)−Si(3)−Si(4) = 179.85(3), Si(2)−Si(3)−Si(4)−Si(4*) = −179.30(4), Si(3)−Si(4)−Si(4*)−Si(3*) = 180.

The UV absorption spectra of octasilane **8** at 293 and 77 K are shown in Figure 2, and the data are summarized in Table 1, together

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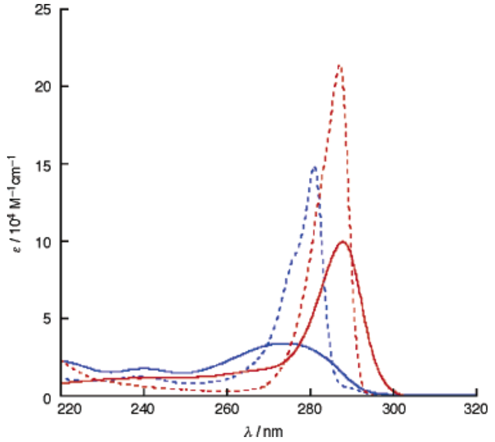

Figure 2. UV absorption spectra of **8** (red) and n-Si_8Me_{18} (blue) in 3-methylpentane at 293 (solid line) and 77 K (dashed line).

Table 1. Summary of UV Absorption Spectra of **8** and n-Si_8Me_{18}[a]

	293 K		77 K	
compound	λ_{max}/nm	$\epsilon/10^4$	λ_{max}/nm	$\epsilon/10^4$
8	288	10	287	21
n-Si_8Me_{18}	274	3.4	281	15

[a] All spectra were measured in 3-methylpentane.

with the data of n-Si_8Me_{18}[14] for comparison. At 293 K, the absorption maximum of **8** corresponding to the lowest-energy $\sigma\sigma^*$ transition significantly shifts to a longer wavelength, and the extinction coefficient ϵ is 3 times greater than that of n-Si_8Me_{18}. These results demonstrate the effective extension of σ-conjugation in **8** and little deviation from the all-anti conformation due to the rigid trisilane unit even in a room-temperature solution, whereas the n-Si_8Me_{18} has significant amount of rotational isomers at this temperature. Upon cooling of the sample to 77 K, the λ_{max} of n-Si_8Me_{18} red shifts by 7 nm, with a remarkable enhancement of the molar absorption coefficient, indicating that the thermodynamically most stable all-transoid[11] conformation becomes predominant at the lower temperature.[15] In sharp contrast, the primary band of the octasilane **8** showed only a slight blue shift, as seen in the oligosilanes with a rigid conformation.[14] The small shift in λ_{max} of **8** indicates that the all-anti conformation is predominant for **8**, even at room temperature.

Calculations have been performed to analyze the conformation, and the ground-state potential energy of **8** was drawn as a function of the inter-unit SiSiSiSi dihedral angle ω (Supporting Information). It was found that the point at $\omega = 180°$ corresponds to the global minimum, and a shallow potential valley centered around $\omega \approx \pm 50°$ lies ca. 3 kcal/mol higher in energy. This result is not discouraging, because even a pentasilane, n-Si_5Me_{12}, is reported to have nine stable conformers other than all-transoid within 3 kcal/mol (at HF/3-21G* level),[16a] and thus n-Si_8Me_{18} should have much more. In contrast, the silicon chain of the octasilane **8** is predominantly controlled to all-anti, and only one conformational isomer exists since there is only one Si−Si bond that allows twisting about it.

Another outstanding point of this molecular design is that the energy minimum appears at the anti limit with exactly $\omega = 180°$, not transoid with $\omega \approx \pm 165°$, as seen in the permethylated oligosilanes n-Si_nMe_{2n+2}. The origin of the transoid conformer of n-Si_nMe_{2n+2} is the 1,3-steric repulsion between the methyl groups.[16b] Between our bicyclic trisilane units, such a repulsion is reduced due to tethering of the tetramethylenes, thus keeping the rotational barrier almost unchanged, which produces the two-isomer system similar to n-Si_4H_{10}. These results clearly demonstrate the practical significance of the bicyclic trisilane unit as a powerful building block to attain the longer all-anti polysilane, an ideal σ-conjugated system.

In summary, we have synthesized the octasilane **8** composed of two bicyclic trisilane units with trimethylsilyl groups at the termini. Its X-ray crystal structure and the spectroscopic data demonstrate the effective σ-delocalization over the silicon framework, which is a definitive difference from the unconstrained n-Si_8Me_{18}. More detailed spectroscopic studies, such as photoluminescence, as well as the preparation of longer oligo- and polysilanes having bicyclic trisilane units are now under investigation.

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Supporting Information Available: Experimental details, spectral data, crystallographic data, and results of theoretical calculations for the ground-state potential energy of **8** (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Kumada, M.; Tamao, K. *Adv. Organomet. Chem.* **1968**, *6*, 19. (b) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359. (c) West, R. In *The Chemistry of Organic Silicon Compounds*; Rappoport, R. Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 2001; Vol. 3, pp 541−563.
(2) Tsuji, H.; Michl, J.; Tamao, K. *J. Organomet Chem.* **2003**, *685*, 9 and references therein.
(3) (a) Imhof, R.; Teramae, H.; Michl, J. *Chem. Phys. Lett.* **1997**, *270*, 500. (b) Mazières, S.; Raymond, M. K.; Raabe, G.; Prodi, A.; Michl, J. *J. Am. Chem. Soc.* **1997**, *119*, 6682. (c) Fogarty, H. A.; Tsuji, H.; David, D. E.; Ottosson, C. H.; Ehara, M.; Nakatsuji, H.; Tamao, K.; Michl, J. *J. Phys. Chem. A* **2002**, *106*, 2369.
(4) (a) Tamao, K.; Tsuji, H.; Terada, M.; Asahara, M.; Yamaguchi, S.; Toshimitsu, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3287. (b) Tsuji, H.; Terada, M.; Toshimitsu, A.; Tamao, K. *J. Am. Chem. Soc.* **2003**, *125*, 7686.
(5) Tanaka, R.; Unno, M.; Matsumoto, H. *Chem. Lett.* **1999**, 595.
(6) (a) Fujiki, M. *J. Am. Chem. Soc.* **1994**, *116*, 11976. (b) Koe, J. R.; Fujiki, M.; Nakashima, H. *J. Am. Chem. Soc.* **1999**, *121*, 9734. (c) Fujiki, M. *J. Am. Chem. Soc.* **2000**, *122*, 3336.
(7) Obata, K.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **1997**, *119*, 11345.
(8) (a) El-Sayed, I.; Hatanaka, Y.; Muguruma, C.; Shimada, S.; Tanaka, M.; Koga, N.; Mikami, M. *J. Am. Chem. Soc.* **1999**, *121*, 5095. (b) El-Sayed, I.; Hatanaka, Y.; Onozawa, S.; Tanaka, M. *J. Am. Chem. Soc.* **2001**, *123*, 3597. (c) Hatanaka, Y. *J. Organomet. Chem.* **2003**, *685*, 207.
(9) Okumura, H.; Kawaguchi, A.; Harada, A. *Macromol. Rapid Commun.* **2002**, *23*, 781.
(10) (a) Sakamoto, K.; Naruoka, T.; Kira, M. *Chem. Lett.* **2003**, *32*, 380. (b) Sanji, T.; Yoshiwara, A.; Sakurai, H.; Tanaka, M. *Chem. Commun.* **2003**, 1506.
(11) For the notation of the conformation: Michl, J.; West, R. *Acc. Chem. Res.* **2000**, *33*, 821.
(12) Tsuji, H.; Fukazawa, A.; Yamaguchi, S.; Toshimitsu, A.; Tamao, K. *Organometallics* **2004**, *23*, 3375.
(13) 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.
(14) Obata, K.; Kira, M. *Organometallics* **1999**, *18*, 2216.
(15) Rooklin, D. W.; Schepers, T.; Raymond-Johansson, M. K.; Michl, J. *Photochem. Photobiol. Sci.* **2003**, *2*, 511.
(16) (a) Albinsson, B.; Antic, D.; Neumann, F.; Michl, J. *J. Phys. Chem. A* **1999**, *103*, 2184. (b) Neumann, F.; Teramae, H.; Downing, J. W.; Michl, J. *J. Am. Chem. Soc.* **1998**, *120*, 573.

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