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Unusual Locking of Silicon Chains into *all-transoid* Conformation by Pentacoordinate Silicon Atoms

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Conformation of flexible linear chains are of fundamental importance in determining the physical properties of organic and inorganic polymers.[1] Over the past decade, a great deal of effort has been made for conformational control of silicon chains[2] because electronic and optical properties of σ-conjugated silicon polymers such as polysilanes and polycarbosilanes are highly sensitive to subtle changes in the backbone conformation.[3] In this regard, conformational locking of the silicon chains into an *all-transoid* form is essential for realizing the useful physical properties of silicon compounds,[4] since *all-transoid* conformation allows effective σ-conjugation along the silicon chain.[2g,3b] However, conformational control of a silicon chain is extremely difficult, since the rotational barriers about Si−Si single bonds are so small that essentially free rotation occurs at room temperature. For example, the energy barrier to the rotation about the Si2−Si3 bond of Si_4Me_{10} is predicted to be only 3.5 kcal/mol, which is significantly smaller than that of the corresponding C3−C4 bond of octamethylhexane (>20 kcal/mol), revealing the greater flexibility of silicon chains compared with carbon chains.[5]

We report herein unusual locking of silicon chains into *all-transoid* conformation by pentacoordinate silicon atoms. Thus, the internal rotation about the Si−Si single bonds of pentacoordinate pentasilane **1** was found to be nearly completely inhibited even in a room-temperature solution, although there are no significant steric interactions between the substituents (Figure 1).

Pentacoordinate pentasilane **1** was prepared by the reaction of *N*-methyl-*N*-trimethylsilylacetamide with $\{Me_3SiSi(CH_2Cl)Cl\}_2SiMe_2$ (1:1 mixture of diastereomers) in hexane at room temperature.[6] The reaction stereoselectively gave the *dl*-isomer of **1**, which was recrystallized from hexane/benzene to give analytically pure **1** in 81% yield as colorless, benzene-containing crystals.

X-ray analysis of **1** revealed that strong intramolecular O → Si coordination in an *N*-[(chlorosilyl)methyl]amide system led to the almost undistorted trigonal bipyramidal (TBP) structure of **1** as indicated by the high %TBP$_a$ and %TBP$_e$ values for the pentacoordinate silicon atoms (89 and 99%, respectively).[7] The most remarkable feature of the crystal structure of **1** is the *all-transoid* conformation of the silicon backbone. Thus, pentacoordinate pentasilane **1** has a stretched silicon chain; the Si−Si bond lengths (2.3353(8), 2.3480(9) Å), Si−Si−Si bond angles (113.50(3), 111.66(4)°), and Si−Si−Si−Si dihedral angle (163.61(3)°) meet expectations for the *all-transoid* conformation.

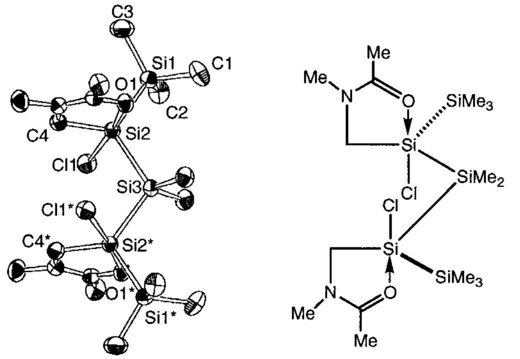

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Figure 1. X-ray structure of **1**. All hydrogen atoms and crystalline solvent are omitted for clarity. Selected bond distances (Å), bond angles (deg), and dihedral angle (deg): Si1−Si2 2.3480(9), Si2−Si3 2.3353(8), Si2−O1 1.990(2), Si2−Cl1 2.3499(7); C4−Si2−Cl1 88.22(7), Si1−Si2−Cl1 97.24(3), Si3−Si2−Cl1 90.96(3), Si1−Si2−C4 122.06(7), Si1−Si2−Si3 113.50(3), Si3−Si2−C4 124.08(7), O1−Si2−Cl1 170.70(5), Si2−Si3−Si2* 111.66(4); Si1−Si2−Si3−Si2* 163.61(3).

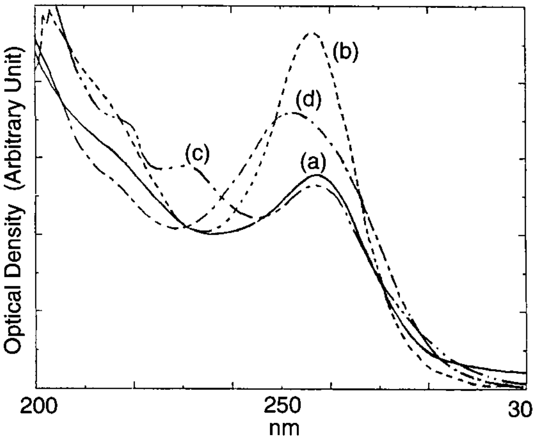

Figure 2. UV spectra of (a) a thin film of **1**, (b) **1** in ether solution, (c) a thin film of **2**, and (d) **1** in acetonitrile solution.

The solid-state UV spectrum of the thin film of **1** exhibited an intense absorption at 257 nm, which is attributed to the $\sigma_{SiSi} \rightarrow \sigma^*_{SiSi}$ excitation of the silicon backbone with the *all-transoid* conformation (Figure 2a).[6b] A weak absorption around 220 nm is assignable to the amide chromophore. To our surprise, the UV spectrum of **1** in ether solution was essentially similar to the solid-state spectrum, showing an intense absorption at 257 nm ($\epsilon = 22\,000\ M^{-1}\ cm^{-1}$) (Figure 2b). The obvious similarity between the solid state and the solution spectra reveals that the most stable conformation of **1** is *all-transoid* even in a room-temperature solution, because UV spectra of oligosilanes are highly sensitive to the conformational change of the silicon backbones.[3a] In sharp contrast, the conformational properties of tetracoordinate oligosi-

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(1) (a) Dehong, H.; Ji, Y.; Kim, W.; Bagchi, B.; Rossky, P. J.; Barbara, P. F. *Nature* **2000**, *405*, 1030−1033. (b) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: New Jersey, 1992.

(2) (a) Obata, K.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **1997**, *119*, 11345−11346. (b) Yuan, C.-H.; West, R. *Macromolecules* **1994**, *27*, 629−630. (c) KariKari, E. K.; Greso, A. J.; Farmer, B. L.; Miller, R. D.; Rabolt, J. F. *Macromolecules* **1993**, *26*, 3937−3945. (d) Schilling, F. C.; Lovinger, A. J.; Davis, D. D.; Bovey, F. A.; Zeigler, J. M. *Macromolecules* **1993**, *26*, 2716−2723. (e) Harrah, L. A.; Zeigler, J. M. *Macromolecules* **1987**, *20*, 601−608. (f) Miller, R. D.; Hofer, D.; Rabolt, J. *J. Am. Chem. Soc.* **1985**, *107*, 2172−2174. (g) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359−1410 and references therein.

(3) a) Imhof, R.; Teramae, H.; Michl, J. *Chem. Phys. Lett.* **1997**, *270*, 500−505. (b) Klingensmith, K. A.; Downing, J. W.; Miller, R. D.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 7438−7439.

(4) The term "*all-transoid*" denotes a backbone conformation whose dihedral angle is close to 165°. In the recent past, this conformation has been confused with "*all-trans* conformation"; however, "*all-trans*" should refer to a dihedral angle of 180°.

(5) Neumann, F.; Teramae, H.; Downing, J. W.; Michl, J. *J. Am. Chem. Soc.* **1998**, *120*, 573−582.

(6) Recently, we have reported that introduction of pentacoordinate silicon atoms into oligosilanes leads to a drastic change in the electron transition energies of the Si−Si bonds: (a) El-Sayed, I.; Hatanaka, Y.; Muguruma, C.; Shimada, S.; Tanaka, M.; Koga, N.; Mikami, M. *J. Am. Chem. Soc.* **1999**, *121*, 5095−5096. (b) Muguruma, C.; Koga, N.; Hatanaka, Y.; El-Sayed, I.; Mikami, M.; Tanaka, M. *J. Phys. Chem. A* **2000**, *104*, 4928−4935.

(7) %TBP values indicate the degree of pentacoordinate character of a silicon atom: Tamao, K.; Hayashi, T.; Ito, Y.; Shiro, M. *Organometallics* **1992**, *11*, 2099−2114.

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lanes are strikingly different from those of **1**. For instance, the UV spectrum of the thin film of analogous tetracoordinate pentasilane $Me_3SiSi(Cl)MeSiMe_2Si(Cl)MeSiMe_3$ **2** (viscous liquid) showed three absorption maxima at 215, 230, and 255 nm, indicating that **2** exists as a mixture of several conformers in liquid state (Figure 2c).[8] These results imply that the pentacoordinate silicon atoms effectively hinder the segmental motion of the silicon chains, stabilizing the *all-transoid* conformation.

^{29}Si NOE (nuclear Overhauser effect) experiments in deuterated benzene solution have provided conclusive evidence for the conformational rigidity of **1** in room-temperature solution. The negative NOE η values of ^{29}Si nucleus are correlated to the segmental motion of the silicon chains in solution.[9] The $-\eta$ value of the central Si3 atom of **1** (-24.89 ppm) comes close to the limit, that is, 2.37 (94% DD relaxation),[10] indicating that the segmental motion of the Si2−Si3−Si2* skeleton is nearly completely hindered. Thus, it is clear that the rotation about the Si2−Si3 bonds is completely inhibited in NMR time scale in ether and benzene solutions. In contrast, ^{29}Si NOE experiment in CD_3CN revealed a marked decrease in the $-\eta$ value of the central Si3 atom (-11.75 ppm; $-\eta = 1.86$; 74% DD relaxation), indicating that the rotation about the Si2−Si3 bond is allowed in polar solvent. Consequently, the UV spectrum of **1** in acetonitrile solution displayed a broadening of the band with a significant decrease of the intensity ($\lambda_{max} = 253$ nm, $\epsilon = 7500$ M^{-1} cm^{-1}) (Figure 2d), apparently due to the conformational lability of **1** in acetonitrile.

The origin of the conformational locking by the pentacoordinate silicon atoms is profoundly interesting. The relatively short Si2−Si3 bond length of **1** (2.3353(8) Å), which is comparable to that of $Me_3Si-SiMe_3$ (2.340(9) Å),[11] suggests that there is no appreciable steric interaction between the Si2 and Si3 atoms. Therefore, the conformational rigidity of **1** cannot be explained by the steric interference alone. To gain an insight into the nature of the rotational barriers about the Si2−Si3 bonds, the potential energy profile for the rotation was calculated by freezing the Si1*−Si2*−Si3−Si2 dihedral angle (ω) at 160° and optimizing all other coordinates (Figure 3).[12] The energy curves calculated by semiempirical PM3 method[13] are essentially consistent with the experimental observations: for example, the presence of the *all-transoid* minimum at 200° [160° as ω(Si1−Si2−Si3−Si2*)] and two energy maxima at 100° and 340°, which are 14.9 and 16.8 kcal/mol higher in energy than the *all-transoid* minimum, respectively.

In Figure 3, the calculated dipole moments of pentasilane **1** as a function of the dihedral angle ω are also shown. It is obvious that the change of the dipole moments of **1** is closely similar to that of the potential energy curve. Moreover, the hypervalent Cl−Si−O bonds should have a large dipole moment as a result of donor−acceptor O → Si interaction involving charge transfer.[14] All of these things make it clear that electrostatic interactions between the strongly polarized Cl−Si−O bonds play a critical role in hindering the rotation about the Si2−Si3 bonds. Thus, the *all-transoid* conformer is effectively stabilized by cancellation of the bond dipole moments, whereas other conformers would be significantly destabilized by unfavorable alignment of the bond dipoles.[15] The conformational lability of **1** in highly polar solvents such as acetonitrile is entirely consistent with this conclusion.[16]

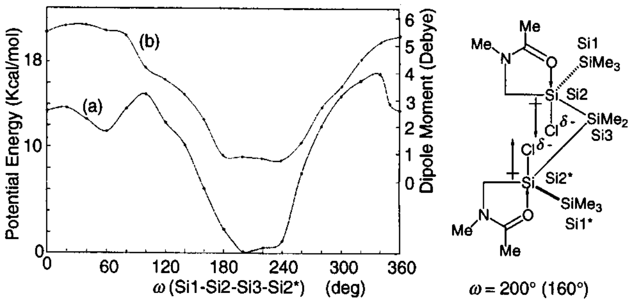

Figure 3. (a) Potential energy of **1** as a function of the dihedral angle ω (Si1−Si2−Si3−Si2*). For the rotation around the Si2−Si3 bond, change of the ω is positive for counterclockwise rotation when viewed from the side of the Si1 atom. (b) Change of dipole moment of **1** as a function of the ω (Si1−Si2−Si3−Si2*).

These results can be sharply contrasted with the situation in tetracoordinate peralkylated silicon chains, where the contribution of electrostatic interactions to the rotational barriers are negligible.[5] Thus, it is concluded that retardation of the free rotation about Si−Si bonds by pentacoordinate silicon atoms is a unique and most practical method for locking the conformations of silicon chains. Although conformational control of oligosilanes by steric interactions between the substituents[17] or conformationally rigid cyclic systems[8a,18] have been recently reported, this is the first example where hypervalent silicon atoms exert a strong influence on the backbone conformation. This strategy will stimulate the development of useful organic materials with unique electronic and optical properties which cannot be realized by tetracoordinate silicon compounds.[19]

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Supporting Information Available: Experimental details and characterization data for all new compounds, including the results of NOE experiments and X-ray experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[8] Silicon chains adopting *all-transoid* conformation usually exhibit a single absorption band: (a) Mazieres, S.; Raymond, M. K.; Raabe, G.; Prodi, A.; Michl, J. *J. Am. Chem. Soc.* **1997**, *119*, 6682−6683. (b) Plitt, H. S.; Balaji, V.; Michl, J. *Chem. Phys. Lett.* **1993**, *213*, 158−162.

[9] The silicon atoms with limited mobility relax predominantly via the dipole−dipole mechanism as shown by the large $-\eta$ values (DD relaxation), while more mobile silicon atoms tend to relax via a spin−rotation mechanism as indicated by smaller $-\eta$ values (SR relaxation): (a) Levy, G. C.; Cargioli, J. D.; Juliano, P. C.; Mitchell, T. D. *J. Am. Chem. Soc.* **1973**, *95*, 3445−3454. (b) Pannell, K. H.; Bassindale, A. R. *J. Organomet. Chem.* **1982**, *229*, 1−9.

[10] NOE η value of -2.52 corresponds to 100% DD relaxation. The contribution of DD relaxation mechanism to spin−lattice (T_1) ralaxation is indicated by % DD relaxation value defined as $-\eta/2.52 \times 100$.[9b]

[11] Beagley, B.; Monaghan, J. J.; Hewitt, T. G. *J. Mol. Struct.* **1971**, *8*, 401−411.

[12] Although this method does not yield all conformational minima of **1**, it is sufficient for quantitative understanding of the nature of the rotational barriers.

[13] Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221−264.

[14] Tandula, S. N.; Voronkov, M. G.; Alekseev, N. V. *Top. Curr. Chem.* **1986**, *131*, 99−189. Ab initio calculations (B3LYP/6-31G**) on model compound, pentacoordinate (*O−Si*) chelate $(H_3Si)_2Si(Cl)CH_2NHCHO$ indicated that the pentacoordinate silicon moiety has a dipole moment of 5.75 D.

[15] The PM3 calculations indicate the charge distributions for Cl (-0.665), Si2 (0.549), and O (-0.310) atoms.

[16] Wong, M. W.; Frisch, M. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 4776−4782.

[17] Tanaka, R.; Unno, M.; Matsumoto, H. *Chem. Lett.* **1999**, 595−596.

[18] Tamao, K.; Tsuji, H.; Terada, M.; Asahara, M.; Yamaguchi, S.; Toshimitsu, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3287−3290.

[19] For example, the emission property of **1** is vastly different from those of tetracoordinate oligosilanes. Thus, **1** exhibited fluorescence emission at 283.4 nm when excited at 260.0 nm in isooctane at room temperature. The observed Stokes shift (3175 cm^{-1}) is markedly small, compared to that of tetracoordinate oligosilanes such as $Me_{12}Si_5$ which shows the emission at 370 nm with a large Stokes shift (13 000 cm^{-1}).[8b]