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anti-1,2,5,6-Tetra-*tert*-butyl-3,3,4,4,7,7,8,8-octaisopropyltricyclo[4.2.0.0^{2,5}]octasilane

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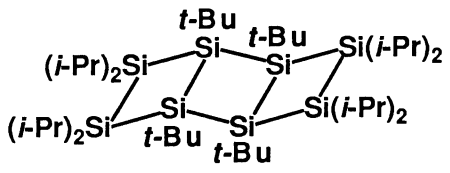
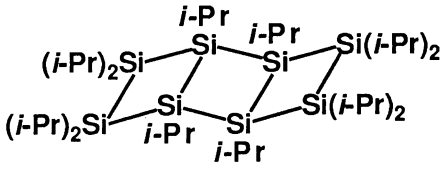
The title ladder polysilane was synthesized by the cross-coupling of *all-trans*-[(*t*-Bu)ClSi]$_4$ and Cl(*i*-Pr)$_2$SiSi(*i*-Pr)$_2$Cl with lithium in 40% yield. X-ray crystallographic analysis of the ladder polysilane shows a highly strained silicon skeleton; the Si-Si bond lengths vary from 2.412(3) to 2.481(2) Å and the Si-Si-Si bond angles of the Si$_4$ rings range from 87.9(1) to 90.5(1)°. By comparison of the structure and UV-visible spectra of this compound with those of the perisopropyl analog, we found that the structures and properties of ladder polysilanes are strongly affected by the substituents.

In recent years, strained polycyclopolysilanes have attracted considerable attention both as synthetic targets and as subjects for investigations on structures and physicochemical properties.[1] In continuation of our study on the chemistry of polycyclopolysilanes consisting of fused cyclotetrasilane rings,[2] we commenced a study of the construction of a ladder polysilane bearing bulky substituents (*e.g.*, *tert*-butyl) since it may show unusual properties due to the steric perturbation of the silicon framework by bulky substituents. In this context, our method for the facile synthesis of *all-trans*-1,2,3,4-tetra-*tert*-butyl-1,2,3,4-tetrachlorocyclotetrasilane[3] has greatly facilitated an attempt to prepare such a molecule. We have thus found that *anti*-1,2,5,6-tetra-*tert*-butyl-3,3,4,4,7,7,8,8-octaisopropyltricyclo[4.2.0.0^{2,5}]octasilane (**1**) could be synthesized by the cross-coupling of the tetrachlorocyclotetrasilane and 1,2-dichloro-1,1,2,2-tetraisopropyldisilane with lithium. Herein, we report the synthesis, structure, and properties of **1** and reveal how the substituents affect the ring geometry and electronic transitions by comparison with the perisopropyl analog (**2**).[4-6]



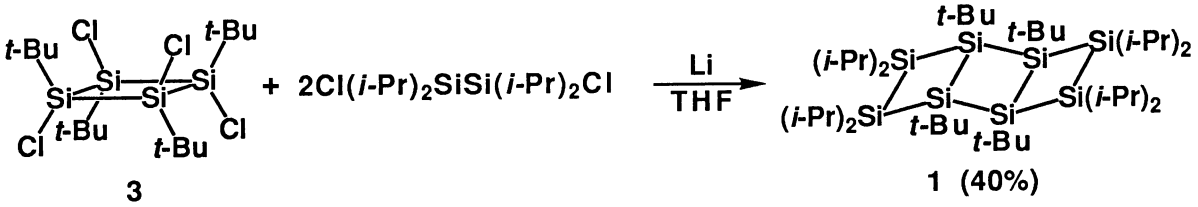
1



2

Compound **1** was synthesized by the coupling reaction of *all-trans*-[(*t*-Bu)ClSi]$_4$ (**3**) and Cl(*i*-Pr)$_2$SiSi(*i*-Pr)$_2$Cl with lithium in 40% yield.[7,8] The reaction proceeded selectively and the *syn*-isomer was not formed under these conditions. It is noted that the all-trans structure of **3** was converted to the anti (*i.e.*, cis-trans-cis) structure of **1**, indicating that inversion of configuration around the silicon atoms occurred during the course of

the reaction. Another route to **1** was also explored. Thus, by the cross-coupling of Br_2(*t*-Bu)SiSi(*t*-Bu)Br_2 and Cl(*i*-Pr)$_2$SiSi(*i*-Pr)$_2$Cl with lithium, **1** could also be obtained, but the yield was very poor (1%). These results indicate that **3** can be used as a superior precursor for the synthesis of **1**.



The structure of **1** was determined by X-ray crystallography.[9] The ORTEPII drawing of **1** is shown in Fig. 1. The Si_8 framework has a twisted anti structure. The Si-Si bond lengths range from 2.412(3) to 2.481(2) Å with an average of 2.439 Å. These values are fairly long compared with those of **2**, which range from 2.346(3) to 2.405(4) Å with an average of 2.388 Å, probably due to the steric hindrance of the bulky *tert*-butyl groups. The cyclotetrasilane rings are not exactly square but have distorted structures with alternating long and short Si-Si bonds, in which the Si(1)-Si(8), Si(2)-Si(3), and Si(5)-Si(6) bonds are especially long while the other Si-Si bonds are relatively short. The Si-Si-Si bond angles of the Si_4 rings range from 87.9(1) to 90.5(1)° with an average of 88.9°. Each cyclotetrasilane ring has a folded structure and the dihedral angles of the Si(2)-Si(3)-Si(4)-Si(5), Si(1)-Si(2)-Si(5)-Si(6), and Si(1)-Si(6)-Si(7)-Si(8) planes are 25.2, 18.6 (18.7), and 22.1 (22.2)°, respectively.[10] These values of the Si-Si-Si bond angles and the dihedral angles of the Si_4 rings are close to those of **2** (Si-Si-Si bond angles: 86.7(1)-90.9(1)°, average 88.8°; dihedral angles of the Si_4 rings: 22.6 (23.4), 23.6 (23.8), and 24.6 (25.2)°).[10] However, three Si_4 rings of **1** array in a more planar manner than those of **2**.

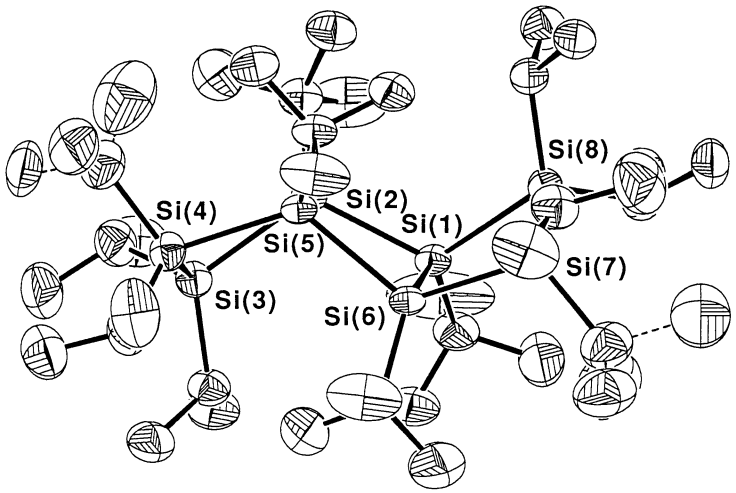


Fig. 1. Molecular structure of **1**. Selected bond distances (Å): Si(1)-Si(2) 2.417(2), Si(1)-Si(6) 2.429(2), Si(1)-Si(8) 2.479(2), Si(2)-Si(3) 2.481(2), Si(2)-Si(5) 2.416(2), Si(3)-Si(4) 2.412(3), Si(4)-Si(5) 2.426(2), Si(5)-Si(6) 2.464(2), Si(6)-Si(7) 2.435(3), Si(7)-Si(8) 2.427(3). The carbon atoms of the isopropyl groups attached to Si(4) and Si(7) are disordered and combined with dashed lines.

The dihedral angles between two Si_4 rings are 117.0-121.4° in **1**, while they are 111.4-112.8° in **2**. The steric repulsion of the *tert*-butyl groups may cause the planar arrangement of the Si_4 rings of the tricyclo[4.2.0.$0^{2,5}$]-octasilane. The Si-C(*i*-Pr) bond lengths (1.908(11)-1.937(12) Å, average 1.924 Å) and Si-C(*t*-Bu) bond lengths (1.951(7)-1.963(8) Å, average 1.957 Å) are normal compared with those so far reported.[2,3]

The highly strained structure of **1** was also revealed by the MM2 calculations.[11] The MM2 optimized structure of **1** very satisfactorily reproduces the X-ray crystal structure. The strain energy of **1** (311 kJ mol^{-1}) is far greater than that of **2** (196 kJ mol^{-1}). The large strain energy of **1** is mainly attributable to the compression energy due to elongation of the Si-Si bonds and increasing van der Waals repulsion of the *tert*-butyl groups.

In Fig. 2, UV-visible spectra of **1** and **2** are shown. The absorption band extends to *ca.* 420 nm in **1** and *ca.* 380 nm in **2**. In the case of **1**, the broad band at 335 nm (ε 4500) has a shoulder at 369 nm (ε 2100), while **2** has the absorption maxima at 308 nm (ε 3200) and 345 nm (ε 1300).[12] The bathochromic shift observed for **1** relative to **2** may be explained in terms of the degree of the steric distortion of the Si skeletons since the increasing strain of the polysilane framework causes the destabilization of the energy level of the HOMO.

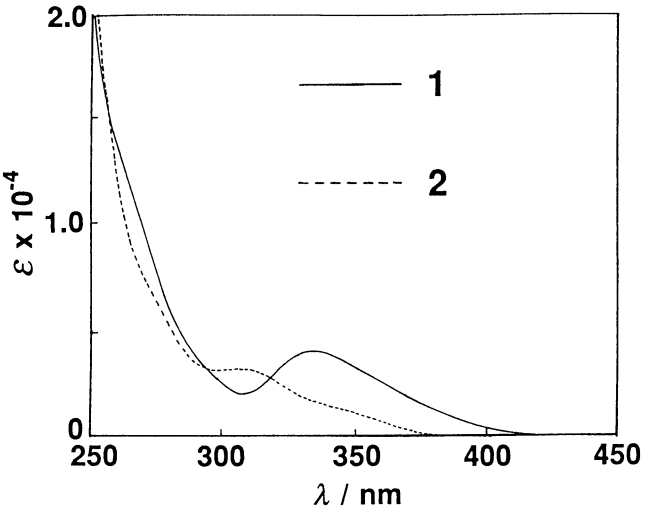


Fig. 2. UV-visible spectra of **1** and **2** in hexane at room temperature.

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4) Co-condensation of $Cl(i\text{-}Pr)_2SiSi(i\text{-}Pr)_2Cl$ (2.93 g, 9.79 mmol) and $Cl_2(i\text{-}Pr)SiSi(i\text{-}Pr)Cl_2$ (4.15 g, 14.6 mmol) with lithium (0.54 g, 78 mmol) in THF (250 ml) at room temperature followed by separation with HPLC (ODS, MeOH/THF = 7/3) gave **2** (0.254 g, 5.6%) as colorless crystals.

5) **2**: ^{1}HNMR (C_6D_6) δ 1.43 (d, 12H, J = 7.5 Hz), 1.45 (d, 12H, J = 7.5 Hz), 1.47 (d, 24H, J = 7.5 Hz), 1.49 (d, 12H, J = 7.5 Hz), 1.52 (d, 12H, J = 7.5 Hz), 1.81 (sep, 4H, J = 7.5 Hz), 1.87 (sep, 4H, J = 7.5 Hz), 1.90 (sep, 4H, J = 7.5 Hz); ^{13}CNMR (C_6D_6) δ 16.7, 16.8, 19.1, 22.0, 22.5, 23.0, 23.4, 23.6, 24.0; IR (KBr, cm^{-1}) 2950, 2850, 1450, 1380, 1360, 1015, 985, 870; MS *m/z* (%) 740 (M^+, 31), 697 (100), 655 (14), 327 (17); UV (λ_{max} in hexane) 308 nm (ε 3200), 345 nm (sh, ε 1300).

6) For X-ray crystallographic data for **2**, see: M. Goto, *Kagakugijutsu Kenkyusho Hokoku*, **86**, 127 (1991).

7) To finely-cut lithium wire (0.069 g, 10 mmol) in THF (10 ml) cooled at -5 °C, a solution of **3** (0.400 g, 0.829 mmol) and $Cl(i\text{-}Pr)_2SiSi(i\text{-}Pr)_2Cl$ (1.00 g, 3.34 mmol) in THF (8 ml) was added dropwise for 10 min. The mixture was stirred for 50 h at -5 °C. After removal of the solvent, a small amount of hexane was added to the residue and the mixture was passed through a short column of silica gel. The eluent was condensed by evaporation and the residue was separated by HPLC (ODS, MeOH/THF = 6/4). The resulting solid was recrystallized from 2-butanone to give **1** (0.27 g, 40%) as yellow crystals.

8) **1**: Sublimed at 180 °C; ^{1}HNMR (C_6D_6) δ 1.41 (d, 12H, J = 7.5 Hz), 1.43 (d, 12H, J = 7.5 Hz), 1.47 (d, 12H, J = 7.5 Hz), 1.47 (s, 36H), 1.49 (d, 12H, J = 7.5 Hz), 2.15 (sep, 4H, J = 7.5 Hz), 2.18 (sep, 4H, J = 7.5 Hz); ^{13}CNMR (C_6D_6) δ 18.0, 19.3, 22.2, 23.4, 23.8, 24.3, 24.6, 34.6; IR (KBr, cm^{-1}) 2950, 2850, 1455, 1385, 1360, 1020, 870, 815; MS *m/z* (%) 796 (M^+, 1), 753 (4), 739 (32), 568 (88), 398 (100); UV (λ_{max} in hexane) 335 nm (ε 4500), 369 nm (sh, ε 2100).

9) Diffraction data were collected using an Enraf-Nonius CAD-4 diffractometer. The structure was solved by the MULTAN78 program[13] and refined by the UNICSIII program.[14] Crystal data for **1**: $C_{40}H_{92}Si_8$, F_w = 797.86, monoclinic, space group $P2_1/n$, a = 10.264(1), b = 50.310(14), c = 10.960(1) Å, β = 113.06(1)°, V = 5207(1) Å^3, Z = 4, D_o = 1.023, D_c = 1.018 g cm^{-3}, R = 0.072, R_w = 0.077 ($w = (0.00472|F_o|^2\text{-}0.1099|F_o|+5.324)^{-1}$) for 5705 observed reflections.

10) When two dihedral angles of the Si_4 ring defined by triangle planes are different, the larger value is written in parentheses.

11) The MM2 calculations[15] were carried out using the X-ray structures of **1** and **2** as initial structures. The force field parameters used were developed in our laboratory for the calculation of the cyclotetrasilanes.[16]

12) The UV absorption bands were simulated by using the Gaussian curve-fitting.

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