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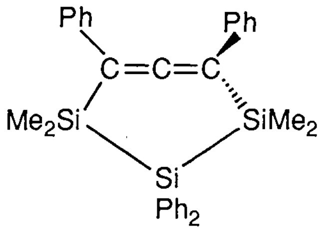
# Synthesis and Structure of Polysilabridged Bisallenes

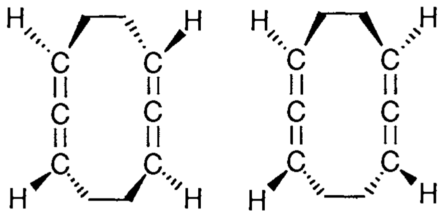
Fusao HOJO, Toshio SHIMIZU, and Wataru ANDO*
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305

Tetrasilacyclodeca-1,2,6,7-tetraenes (**3a**:dl) and (**3b**:meso) are synthesized by the reaction of the $Ph_2C_3$ dianion with tetramethyldichlorodisilane. X-Ray crystallographic analyses of **3a** and **3b** show allenic *sp* carbons to be bent by 4°(average). The optimized structures of disilacycloocta-1,2,5,6-tetraenes estimated by semiempirical PM3 calculations are also reported.

Recently, the chemistry of highly strained unsaturated cyclic compounds has received considerable attention from both theoretical and experimental points of view.[1] Cyclic allenes have attracted interest as one of the strained unsaturated cyclic compounds.[2] Cycloocta-1,2-diene derivatives were known as the smallest isolable cyclic allenes.[3] Recently, we succeeded in isolating trisilacyclohexa-1,2-diene (**1**) and it was found by X-ray analysis that the long Si-Si bonds release the ring strain .[4] There have been attempts to synthesize dimeric allenes and cyclic bisallenes too.[5] Cyclodeca-1,2,6,7-tetraene (**2**) was synthesized by Skattebol for the first time.[5a] However only the meso structure has been characterized. We now report the synthesis and X-ray structure of dl- and meso-tetrasilacyclodeca-1,2,6,7-tetraenes. We also estimated the optimized structures of their smaller ring analogs calculated by PM3 method.



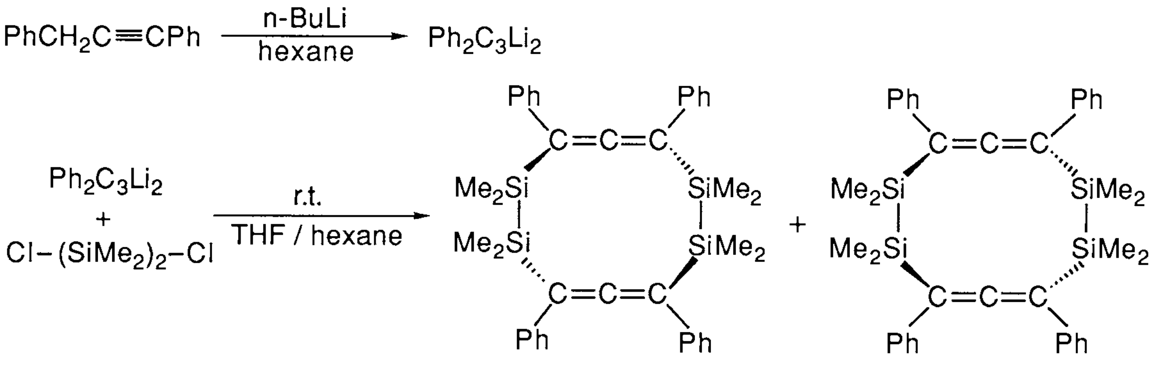
**1**



*dl* *meso*

**2**

The $Ph_2C_3$ dianion[6] prepared from 1,3-diphenylpropyne and 2 equiv of n-butyllithium reacted easily with tetramethyl-1,2-dichlorodisilane to give the two isomers of 4,5,9,10-tetrasilacyclodeca-1,2,6,7-tetraenes **3a** and **3b** in yields of 2% and 6%, respectively. The spectral data of **3a** and **3b** are almost similar.[7-8] Therefore, the stereochemistry could not be determined by the spectral data. Finally, the molecular structures of **3a** and **3b** were determined by X-ray crystallographic analyses[9-10] and are shown in Fig. 1 along with the dihedral geometries around the allenic structure. These dihedral geometries are viewed through C1-C3 and C4-C6, respectively. Selected bond distances and angles are listed in Table 1.



**3a** (dl) **3b** (meso)

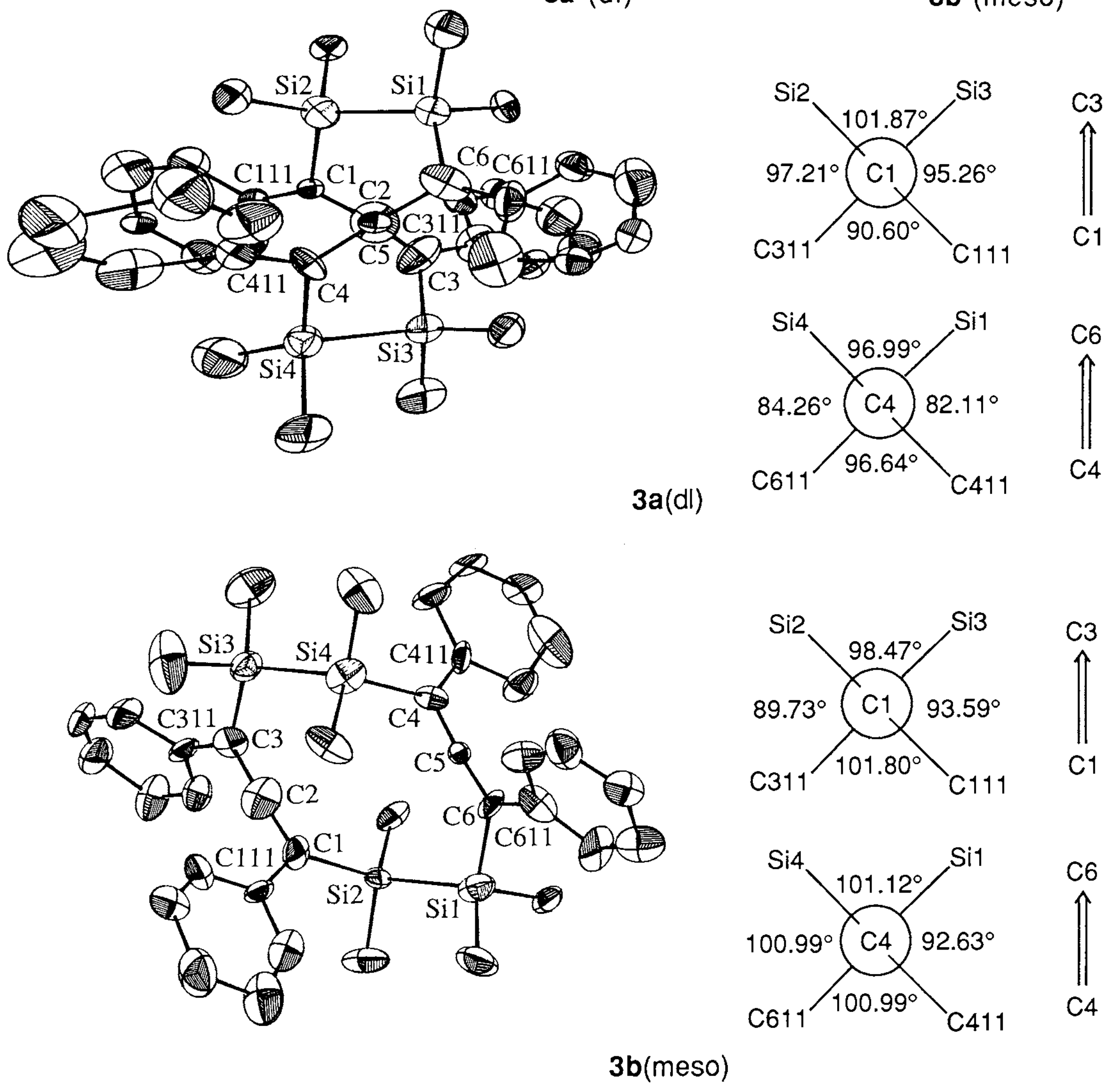
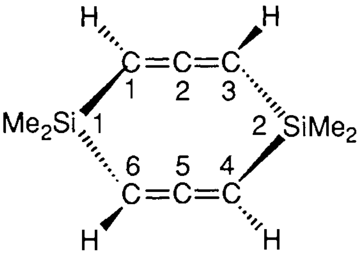


Fig. 1. Molecular structures and dihedral geometries of **3a** and **3b**.

Table 1. The average bond lengths (Å) and bond angles (°) of the tetrasilacyclodeca-1,2,6,7-tetraenes **3a** and **3b**, determinated by X-ray crystallographic analyses

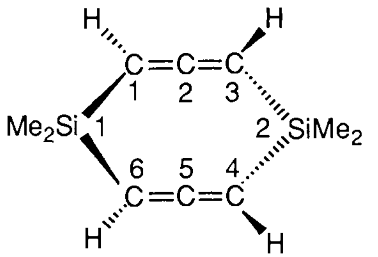
| | 3a | 3b | | 3a | 3b |
|---|---|---|---|---|---|
| C-C | 1.33 | 1.32 | C-C-C | 176 | 176 |
| C-Si | 1.88 | 1.89 | C-C-Si | 117 | 116 |
| Si-Si | 2.32 | 2.36 | C-Si-Si | 111 | 114 |

In **3a** and **3b** the average bent angle on the *sp* carbons of C2 and C5 is found to be 4°, respectively. The dihedral angles, Si1-C6-C4-Si4, and Si2-C1-C3-Si3 of **3a** and **3b** are slightly spread (97°-102°) from normal vertical geometry of allene while that of **2** is contracted.[4)]



*dl*

**4a**



*meso*

**4b**

Table 2. Selected bond lengths (Å), bond angles (°), and torsional angles (°) for the disilacycloocta-1,2,5,6-tetraenes **4a** and **4b**

| | 4a | 4b | | 4a | 4b |
|---|---|---|---|---|---|
| C-C | 1.30 | 1.30 | C-C-C | 174 | 173 |
| C-Si | 1.86 | 1.85 | Si-C-C | 117 | 117 |
| | | | C-Si-C | 107 | 104 |
| Si1-C1-C3-Si2 | 65 | 59 | Si2-C4-C6-Si1 | 69 | 61 |

Semiempirical PM3 calculations[11)] for the smaller ring analogs, 4,8-disilacycloocta-1,2,5,6-tetraenes **4a** and **4b** were carried out. The optimized bond angles, bond lengths, and dihedral angles are summarized in Table 2. Semiempirical PM3 calculations indicate that the cycloocta-1,2,5,6-tetraenes **4a** and **4b** have highly strained cyclic systems than the cyclodeca-1,2,6,7-tetraenes **3a** and **3b**. The bond angles on the allenic *sp* carbons of **4a** and **4b**, C2 and C5 are estimated to be strained by 5°-7° from linear geometry. The differences of the bent angles on the *sp* carbons of **3** and **4** are not large, while the torsional angles of **4a** and **4b** are highly distorted. The torsional angles Si1-C6-C4-Si2 and Si1-C1-C3-Si2 of **4a** are contracted and estimated to be 65° and 69°, respectively. Those of **4b** are also contracted and estimated to be 59° and 61°, respectively. The difference of the dihedral angles around the allenic moiety of **3** and **4** seems to be caused by different force. The tensile force distinctly serves in the cyclic system of **4**. Furthermore, strain of meso isomer **4b** seems to be larger than that of the dl isomer **4a** based on the dihedral angles.

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References

1) For examples: Special issue on strained organic compounds, *Chem. Rev.*, **89**, 973 (1989); A. Greenberg and J. F. Liebman, "Strained Organic Compounds," Academic Press, New York (1978).
2) Reviews: R. P. Johnson, *Chem. Rev.*, **89**, 1111 (1989); M. Jones, Jr., and R. A. Moss, "Reactive Intermediates," Wiley, New York (1985), Vol. 3; D. J. Pasto, *Tetrahedron*, **40**, 2805 (1984); W. Smadja, *Chem. Rev.*, **83**, 263 (1983).
3) J. P. Price and R. P. Johnson, *Tetrahedron Lett.*, **27**, 4679 (1986).
4) T. Shimizu, F. Hojo, and W. Ando, *J. Am. Chem. Soc.*, **115**, 3111 (1993).
5) L. Skattebol, *Tetrahedron Lett.*, **1961**, 167; L. Skattbol and S. Solomon, *Org. Synth.*, **49**, 35 (1969); P. J. Garratt, K. C. Nicolau, and F. Sondheimer, *J. Am. Chem. Soc.*, **94**, 4582 (1973); H. Irngartinger and H-U. Jager, *Tetrahedron Lett.*, **1976**, 3595; S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *J. Am. Chem. Soc.*, **89**, 4840 (1967); M. S. Baird and C. B. Reese, *Tetrahedron*, **32**, 2153 (1976).
6) J. Klein and J. Y. Backer, *J. Chem. Soc., Chem. Commun.*, **1973**, 576.
7) **3a**: Yield 2%. Colorless rods, mp 239-241 °C; $^1$H NMR(400 MHz, $C_6D_6$) δ 0.45 (s, 12H), 0.51 (s,12H), 7.09 (t, *J*=7.4, 4H), 7.21 (dd, *J* =7.4,7.3, 8H), 7.59 (d, *J* =7.3, 8H); $^{13}$C NMR (100 MHz, $C_6D_6$) -1.2 (q), -0.9 (q), 94.5 (s), 127.0 (d), 128.6 (d), 129.4 (d), 137.5 (s), 211.6 (s); $^{29}$Si NMR (79 MHz; $C_6D_6$) -19.9; IR (KBr) $\nu_{max}$ 1889 cm$^{-1}$ (C=C=C); LRMS (EI, 70 eV) m/e 612 (M$^+$), 463, 135, 73 (100%); HRMS (EI, 20 eV) m/e Found: 612.2510. Calcd for $C_{23}H_{34}Si_4$: 612.2520.
8) **3b**: Yield 6%. Colorless rods, mp 195-197 °C; $^1$H NMR(400 MHz, $C_6D_6$) 0.46 (s, 12H), 0.54 (s, 12H), 7.11 (t, *J*=7.4, 4H), 7.25 (dd, *J* =7.4,7.3, 8H), 7.60 (d, *J* =7.3, 8H); $^{13}$C NMR (100 MHz, $C_6D_6$) -0.7 (q), -0.5 (q), 94.8 (s), 127.0 (d), 128.6 (d), 129.3 (d), 138.1 (s), 211.0 (s); $^{29}$Si NMR (79 MHz, $C_6D_6$) -21.2; IR (KBr) $\nu_{max}$ 1887 cm$^{-1}$ (C=C=C); LRMS (EI, 70 eV) m/e 612 (M$^+$), 463, 135, 73 (100%); HRMS (EI, 20 eV) m/e Found: 612.2554. Calcd for $C_{23}H_{34}Si_4$: 612.2520.
9) Crystallographic data **1a**: Fw=613.12, monoclinic, $P2_1$, a=10.538(2), b=18.777(11), c=18.448(3) Å, V=3639.2 Å$^3$, Z=4, Dc=1.12 g cm$^{-3}$, T=23 °C, R=0.057, Rw=0.062 for 2050 reflections (I>3.00σ(I)) with monochromated Mo-Kα radiation.
10) Crystallographic data **1b**: Fw=613.12, monoclinic, $P2_1$, a=12.392(4), b=8.914(2), c=16.258(4) Å, V=1793.5 Å$^3$, Z=2, Dc=1.14 g cm$^{-3}$, T=23 °C, R=0.042, Rw=0.044 for 1677 reflections (I>3.00σ(I)) with monochromated Mo-Kα radiation.
11) MOPAC Version 6.01: J. J. P. Stewart and J. Frank, Seiler Research Labortory, U.S. Air Force Academy, Colorado Springs, CO 80840. Unix version by Teijin Systems Technology Ltd.

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