# Silapericyclyne, $(Ph_2SiC{\equiv}C)_6$: Spontaneous Conformational Resolution of Boat- and Chair-'Exploded' Cyclohexane

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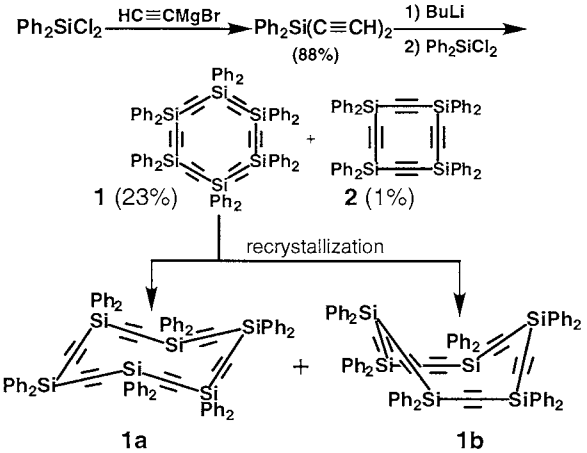
The silapericyclyne, $(Ph_2SiC{\equiv}C)_6$ was found to undergo spontaneous conformational resolution into the chair and boat conformations by crystallization from THF-MeOH. In solution, these two isomers rapidly interconvert, and could not be separately detected even at low temperature by $^1H$ NMR.

Cyclic compounds comprised of silicon atoms and alkyne units have aroused interest because of their interesting electronic properties and structures. The lower ionization energy of the silicon atom compared with carbon has been expected to enhance the through-bond interaction of ethynyl units, and several reports have appeared.[1] In addition, the structures of these compounds have also been of interest, as this system can be seen as an 'exploded' cycloalkane.[2] As an extension of our study on cyclic polysilanes and related compounds,[3] we have synthesized phenyl-substituted cyclic ethynylsilanes ("silapericyclynes") (**1**). Here we report our finding of **1** crystallized in the chair and boat conformations. This is the first case, to the best of our knowledge, in which silapericyclyne undergoes spontaneous separation of two conformers by crystallization.

Silapericyclyne **1** was prepared from $Ph_2Si(C{\equiv}CH)_2$ and $Ph_2SiCl_2$ using the method of Bortolin et al.[4] (Scheme 1) Work-up including crystallization from THF-MeOH gave **1** in 23% yield. From the filtrate, $(Ph_2SiC{\equiv}C)_4$ (**2**) was obtained by recrystallization from THF-$Et_2O$.[5]




Scheme 1.

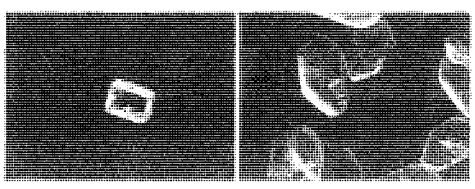


**Figure 1.** Crystal shape of isomers: chair **1a** (left) and boat **1b** (right).

The crystallization of **1** from THF-MeOH (4:1) by slow evaporation at room temperature gave two kinds of crystals: rectangular- and hexagonal-like shapes (Figure 1), and the ratio of the two crystals was about 10/1. The ratio of the two crystals varied by the solvent; hexagonal one generates predominantly from THF-ether-hexane (2/2/1). The X-ray crystallography revealed that the rectangular crystal contained only the chair-form isomer (**1a**)[6] while the hexagonal crystal was the boat-form isomer (**1b**).[7] The ORTEP drawings are shown in Figures 2 and 3. In 1989, Bortlin et al. reported the X-ray structure of $(Me_2SiC{\equiv}C)_6$[8] with the chair conformation. Thus, isomer **1b** is the first example of the boat-form hexasilapericyclynes.

As shown in the crystal structures, these molecules can be seen as an 'exploded' cyclohexane. It is noteworthy that both the boat and chair conformations can exist in the solid state. This can be

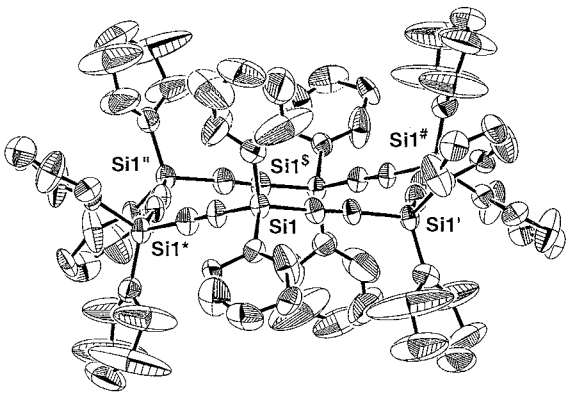



**Figure 2.** Molecular structure of **1a**. Thermal ellipsoids are drawn at the 30% probability level.[9]

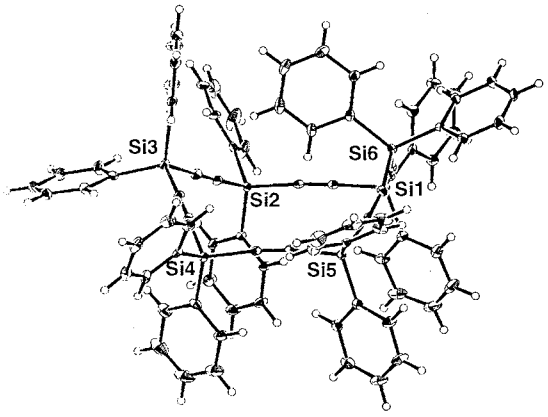



**Figure 3.** Molecular structure of **1b**. Thermal ellipsoids are drawn at the 30% probability level.

clearly explained by the following consideration. Due to the long Si–C ≡ C–Si distance, steric hindrance of the substituents is reduced, which makes the energy level of the chair and boat conformations comparable.

Compound **1a** crystallized in *R*32 space group, and the $C_6$ axis passes through the center of the molecule. There was no symmetric element for **1b**. The average bond lengths and angles for **1a** and **1b** are summarized in Table 1. The difference between **1a** and **1b** is minimal, and all these values are also similar to those of $(Me_2SiC{\equiv}C)_6$.[8] However, the dihedral angle of the skeleton made each compound distinguishable. The dihedral angle of **1a** (Si1$^{\$}$–Si1$^{\#}$–Si1' and Si1–Si1'–Si1$^{\$}$–Si1" mean planes) was 32.5°, and this means that **1a** is much closer to the plane than $(Me_2SiC \equiv C)_6$ (53.5°). The average Si–Si–Si–Si torsion angle was 37.1° for **1a**. For **1b**, the dihedral angles are 67.4° for the Si1–Si2–Si4–Si5 mean plane and the Si1–Si5–Si6 plane, and 47.4° for the Si1–Si2–Si4–Si5 mean plane and the Si2–Si3–Si4 plane. This is intriguing from the viewpoint of homoconjugation that **1a** is near planar.

Table. 1 Average bond lengths and angles of **1a**, **1b**, **2**

| | 1a | 1b | 2 |
|---|---|---|---|
| Si–C(≡C) (Å) | 1.83(2) | 1.836(3) | 1.837(5) |
| C≡C (Å) | 1.205(3) | 1.215(4) | 1.191(6) |
| Si–C≡C (°) | 175(2) | 174.0(3) | 172.7(4) |
| (C≡)C–Si–C(≡C) (°) | 109.8(9) | 107.6(2) | 104.3(2) |

When each crystal of **1a** and **1b** was dissolved in $CDCl_3$, the NMR spectra were identical. Even at -80 °C, no change in the peaks was observed, thus **1a** and **1b** were interchangeable on the NMR time scale. As expected, when a crystal of **1a** or **1b** was added to the recrystallization solution, only crystals of one isomer were formed. This result also supports the fact that there is a rapid interconversion of the two isomers in solution.

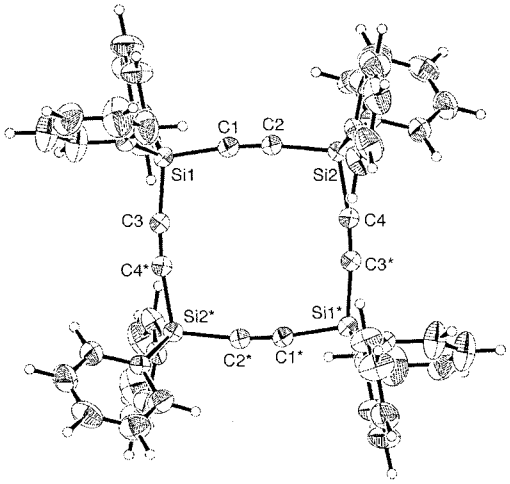



**Figure 4.** Molecular structure of **2**. Thermal ellipsoids are drawn at the 30% probability level.

The structure of the 12-membered cyclic compound **2** is shown in Figure 4.[9] This compound has a symmetric center at the middle of the molecule, and the skeleton was planar. The average bond lengths and angles are shown in Table 1, and bond angles are smaller than those of the other molecules due to smaller ring size; the other values are all normal. The bond lengths and angles are similar to those of $(Me_2SiC \equiv C)_4$ as reported by Hengge et al.[10]

In summary, we synthesized the tetra- and hexasilapericyclynes and determined their structures. For the hexasilapericyclynes, we could separate the chair and boat conformers in the solid state.

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## References and Notes

1 For example, R. Gleiter, W. Schäfer, and H. Sakurai, *J. Am. Chem. Soc.*, **107**, 3046 (1985), and references cited therein.

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4 R. Bortolin, B. Parbhoo, and S.D. Brown, *J. Chem. Soc., Chem. Commun.*, **1988**, 1079.

5 Procedure: To a three-necked flask, $Ph_2Si(C{\equiv}CH)_2$ (2.101 g, 9.04 mmol) and THF (150 ml) was added. The mixture was cooled to -78 °C, and 11.6 ml (1.56 M hexane solution, 18.1 mmol) of BuLi was added in 20 min and stirred for 3 h. This $Ph_2Si(C{\equiv}CLi)_2$ solution was transferred with cannula to the solution of $Ph_2SiCl_2$ (2.408 g, 8.51 mmol) in THF (150 ml) for 2 h at -78 °C. After the transfer, the mixture was warmed to room temperature and stirred for 1 d. After workup, fractional crystallization from THF and $Et_2O$ gave colorless crystals of $(Ph_2SiC{\equiv}C)_6$ **1** in 23% yield (866 mg). The filtrate was concentrated and further recrystallized from THF and $Et_2O$ to give colorless needles of $(Ph_2SiC{\equiv}C)_4$ **2** (35 mg, 1% yield). **1**: colorless crystals, mp 283-287 °C. $^1$H NMR ($CDCl_3$) δ 7.32 (t, 36H, *J*=7.2 Hz), 7.39 (t, 18H, *J*=7.2 Hz), 7.72 (d, 18H, *J*=7.2 Hz) ppm; $^{13}$C NMR ($CDCl_3$) δ 110.9, 128.1, 130.4, 131.5, 135.0 ppm; $^{29}$Si NMR ($CDCl_3$) δ -49.87 ppm; MS (70 eV) *m/z* (%) 1236 ($M^+$, 19), 1158 (7), 1079 (4), 976 (2), 77 (100); IR (KBr) ν 3060, 3040, 1590, 1490, 1425, 1100 cm$^{-1}$. **2**: colorless needles, mp 306-310 °C. $^1$H NMR ($CDCl_3$) δ 7.37 (t, 16H, *J*=7.2 Hz), 7.43 (t, 8H, *J*=7.2 Hz), 7.75 (d, 16H, *J*=7.2 Hz) ppm; $^{13}$C NMR ($CDCl_3$) δ 114.0, 128.1, 130.8, 135.1 ppm; $^{29}$Si NMR ($CDCl_3$) δ -50.04 ppm; MS (70 eV) *m/z* (%) 824 ($M^+$, 100), 746 (24), 667 (13); IR (KBr) ν 3060, 3040, 1590, 1490, 1425, 1110 cm$^{-1}$.

6 Crystal data for **1a**: trigonal, *R*32, $a$ = 18.719(2) Å, $c$ = 19.287(3) Å, $V$ = 5853(1) Å$^3$, $Z$ = 3, $R_1$ = 0.097, $wR_2$ = 0.274 (for all data) based on 1560 observed reflections ($I > 2\sigma$) and 179 variable parameters.

7 Crystal data for **1b**: triclinic, *P* 1, $a$ = 20.0542(4) Å, $b$ = 23.5660(5) Å, $c$ = 16.4534(4) Å, $\alpha$ = 99.825(1)°, $\beta$ = 98.949(1)°, $\gamma$ = 75.919(1)°, $V$ = 7370.3901 Å$^3$, $Z$ = 4, $R$ = 0.065, $Rw$ = 0.074 based on 23610 observed reflections ($I > 3\sigma$) and 1694 variable parameters.

8 R. Bortolin, S.S.D. Brown, and B. Parbhoo, *Inorg. Chim. Acta*, **158**, 137 (1989).

9 The temperature factors of **1a** could not be diminished because of these two reasons. (1) Severe disorder was observed for the phenyl substituents. (2) Reflection pattern changed below -20 °C and gave no lattice parameter, which prohibited the low-temperature measurement.

10 Crystal data for **2**: triclinic, *P* 1, $a$ = 11.975(4) Å, $b$ = 12.234(4) Å, $c$ = 9.073(4) Å, $\alpha$ = 110.27(3)°, $\beta$ = 102.27(3)°, $\gamma$ = 78.70(2)°, $V$ = 1207.6(7) Å$^3$, $Z$ = 1, $R$ = 0.049, $Rw$ = 0.037 based on 2717 observed reflections ($I > 3\sigma$) and 272 variable parameters.

11 E. Hengge and A. Baumegger, *Monatsh. Chem.*, **122**, 661 (1991).