# The Cyclo[(disilanylene)(butadiyne)]s $[(i\text{-Pr})_2Si(i\text{-Pr})_2SiC{\equiv}CC{\equiv}C]_n$ ($n$ = 2–4)

Keisuke Negishi,[†] Masafumi Unno,[†] and Hideyuki Matsumoto*[†,††]

[†]*Department of Nano-Material Systems, Graduate School of Engineering, Gunma University, Kiryu 376-8515*

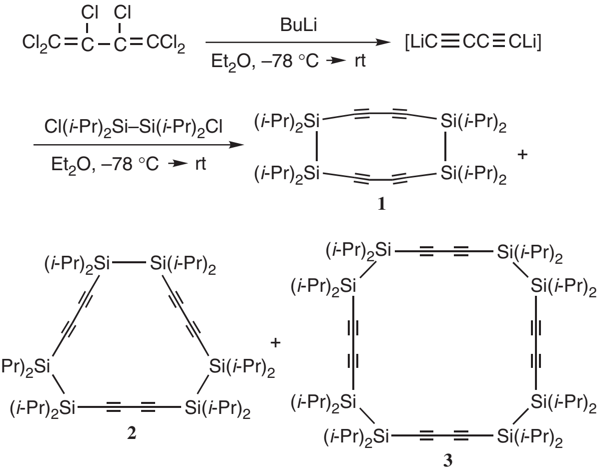
[††]*Core Research for Evolutional Science and Technology, Japan Science and Technology Corporation, Kawaguchi 332-0012*

(Received January 8, 2004; CL-040035)

The new type of the twelve- to twenty-four-membered rings $[(i\text{-Pr})_2Si(i\text{-Pr})_2SiC{\equiv}CC{\equiv}C]_n$ (**1**, $n = 2$; **2**, $n = 3$; **3**, $n = 4$) were synthesized and the molecular structures of **1** and **2** were analyzed by X-ray crystallography. The compounds show unusual electronic properties due to the interaction of the C≡C $\pi$ orbitals with the Si–Si $\sigma$ bonds.

---

In the course of our study on the synthesis and properties of cyclic compounds composed of silicon and carbon–carbon triple bond,[1] we found that the silicon–butadiyne cyclic molecules (extended silapericyclynes), $(i\text{-Pr}_2SiC{\equiv}CC{\equiv}C)_n$ ($n$ = 4–7) exhibit an intriguing electronic properties.[2] Comparison of their UV spectra with those of the corresponding carbon molecules disclosed that the substitution of the silylene unit for the methylene unit shifts the absorption bands to longer wavelengths (10–20 nm). This finding prompted us to synthesize the new rings with the alternate arrangement of a disilanylene unit and a diyne group. We now report the synthesis of the alternating disilanylene–butadiyne cyclooligomers $[(i\text{-Pr})_2Si(i\text{-Pr})_2SiC{\equiv}CC{\equiv}C]_n$ (**1**, $n = 2$; **2**, $n = 3$; **3**, $n = 4$). Prior to our study, several reports have appeared in the literature concerning linear polymers incorporating disilane–butadiyne untis such as $(R_1R_2SiR_1R_2SiC{\equiv}CC{\equiv}C)_n$ ($R_1 = R_2 = Me$; $R_1 = Me$, $R_2 = Et$; $R_1 = Me$, $R_2 = Ph$).[3] However, to our knowledge, no example of the alternating disilanylene–butadiyne rings has been reported to date.[4]



Compounds **1–3** could be obtained by the reaction of the 1,2-dichloro-1,1,2,2-tetraisopropyldisilane (**4**) and 1,4-dilithiobutadiyne (**5**). Typically, a solution of **4** (6.2 mmol) in $Et_2O$ was added dropwise to a stirred solution of **5**, which was generated in-situ from hexachloro-1,3-butadiyne (6.0 mmol) and butyllithium (25 mmol) in $Et_2O$ at −78 °C under argon. The reddish orange mixture was stirred for an additional 16 h. Workup involving the separation with recycle-type HPLC resulted in the isolation of **1** (11% yield), **2** (1.4% yield), and **3** (trace amount). It is noted that the course of the reaction strongly depended upon the substituents on the silicon atom. For example, the production of the cyclic oligomers could not be achieved with a combination of 1,2-dichloro-1,1,2,2-tetramethyldisilane and the dilithiobutadiyne; the combination gave only polymeric products, but their structures were not further examined. The structures of **1** and **2** were determined by X-ray crystallography as well as spectroscopic methods.[5–9]

The X-ray analyses of **1** and **2** reveal several interesting structural features (Figures 1 and 2). As expected, the ring in **1** is strained with the average C(sp)–Si–Si, Si–C≡C, and C≡C–C(sp) bond angles of 103.0°, 168.4°, and 174.7°, respectively. The Si–Si bonds (av 2.388 Å) and the C≡C bonds (av 1.22 Å), however, are not elongated.

In eighteen-membered ring **2**, the average C(sp)–Si–Si, Si–C≡C, and C≡C–C(sp) bond angles are 104.6°, 176.2°, and 178.1°, respectively; slightly distorted but virtually strain free. Also, the average Si–Si and C≡C bond lengths are normal val-

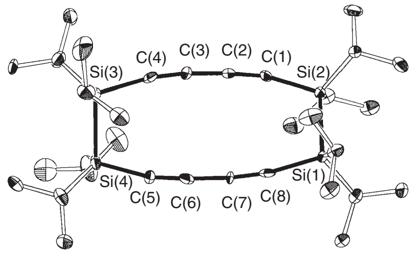


**Figure 1.** Moleculer structure of **1**. Hydrogen atoms are omitted for clearity. Thermal ellipsoids are drawn at the 30% probability level.

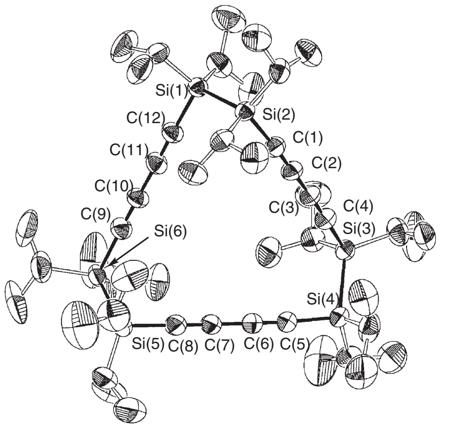


**Figure 2.** Moleculer structure of **2**. Hydrogen atoms are omitted for clearity. Thermal ellipsoids are drawn at the 30% probability level.

ues (2.371 Å and 1.21 Å, respectively).

By comparison of the structural parameters between **1** and the carbon analogue $(Me_2CMe_2CC{\equiv}CC{\equiv}C)_2$ (**6**),[11] our compound does not show significant distortion in the bond angles. The bending at the acetylenic linkage in **1** is smaller than that in the carbon analogue $(Me_2CMe_2CC{\equiv}CC{\equiv}C)_2$ (**6**). The bending angle of 168.4° in the Si–C≡C bond and that in the C≡C–C(sp) bond are 174.7°, while the corresponding angle in the C($sp^3$)–C≡C and C≡C–C(sp) bond angles are 166.6° and 166.4°, respectively. The separation between the diyne units of 3.31 Å between C1 and C8 and that of 3.51 Å between C2 and C7 are longer than the corresponding distance observed in **6** (2.70 Å and 3.24 Å, respectively). The observed trend is attributed to the large difference in the bond length between the Si–Si bond (2.388 Å in **1**) and the C–C bond (1.602 Å in **6**).

Another interesting feature worth mentioning is the electronic properties of compounds **1–3**. These compounds show absorption bands in the region 260–320 nm (Figure 3). The UV spectra for **1–3** look similar in the long-wavelength region, but the small differences in positions between these compounds are observed, presumably arising from the ring strain and conformational changes. However, it is noted that the transition energies of the absorption bands in **1–3** are much lower than those in the carbon systems. For example, **1** shows the intense absorption at 267 ($\varepsilon$ 8710), 282 ($\varepsilon$ 6570), and 300 nm ($\varepsilon$ 3810) and the weak absorption at 319 nm ($\varepsilon$ 320). By comparison, although **6** is more stained than **1** as mentioned above, it shows absorption maxima at 237 ($\varepsilon$ 687), 248 ($\varepsilon$ 750), 264 ($\varepsilon$ 494), 288 nm (sh) ($\varepsilon$ 30).

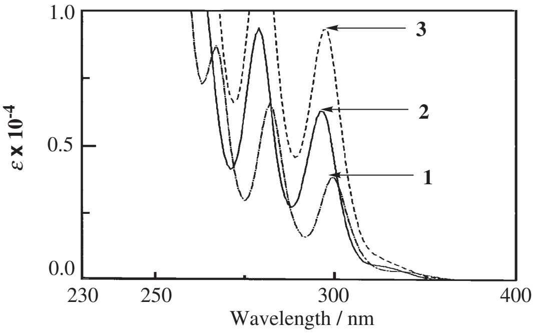


**Figure 3.** UV absorption spetcra of **1–3** in THF.

Previously, Sakurai and co-workers reported that the UV spectrum of 3,3,4,4,7,7,8,8-octamethyl-3,4,7,8-tetrasilacycloocta-1,5-diyne had shown an enhanced bathochromic shift, which should primarily be caused by the destabilization of the HOMO arising from the extensive $\sigma$(Si–Si)–$\pi$(C≡C) conjugation.[14] In light of this precedent, we feel that the large bathochromic shift observed for **1** relative to **6** may be attributable to electronic perturbation of the $\pi$(C≡C) orbitals by conjugation with the $\sigma$(Si–Si) orbitals. A MO calculation (B3LYP/6-31G*) indicates that the lobes of the HOMO of **1** are mainly delocalized in both the Si–Si $\sigma$-bond and C≡C $\pi$-bonds. The result shows that $\pi$-orbitals of the butadiyne units interact with the Si–Si $\sigma$-orbitals and the $\sigma$–$\pi$ conjugation may be the origin of the low electronic transition energies.

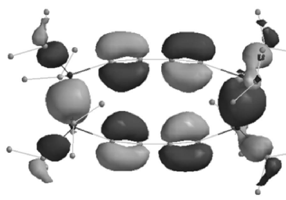


**Figure 4.** HOMO of **1**.

This work was supported in part by Grants-in-Aid for Scientific Research from the Japan Society for the Promotion of Science.

## References and Notes

1 a) M. Unno, T. Saito, and H. Matsumoto, *Chem. Lett.*, **1999**, 1235. b) M. Unno, T. Saito, and H. Matsumoto, *Bull. Chem. Soc. Jpn.*, **24**, 2407 (2001).

2 M. Unno, K. Negishi, and H. Matsumoto, *Chem. Lett.*, **2001**, 340.

3 a) R. J. P. Corriu, C. Guerin, B. Henner, T. Kuhlmann, and A. Jean, *Chem. Mater.*, **2**, 351 (1990). b) M. Ishikawa, Y. Hasegawa, and A. Kunai, *J. Organomet. Chem.*, **381**, C57 (1990). c) R. J. P. Corriu, P. Gerbier, C. Guerin, B. Henner, and P. H. Mutin, *Organometallics*, **11**, 2507 (1992). d) R. J. P. Corriu, P. Gerbier, C. Guerin, and B. Henner, *Chem. Mater.*, **10**, 2137 (2000).

4 Sakurai et al. described $(Me_2SiMe_2SiC{\equiv}CC{\equiv}C)_2$ as a precursor of the octamethyltetrasila[2.2]paracyclophane, but no spectral and X-ray data were given in their literature: H. Sakurai, S. Hoshi, A. Kamiya, A. Hosomi, and C. Kabuto, *Chem. Lett.*, **1986**, 1781.

5 **1**: mp 163–164 °C; $^1$H NMR ($CDCl_3$) $\delta$ 0.97–1.74 (m, 8 H), 1.11 (d, $J = 6.7$ Hz, 24 H), 1.15 (d, $J = 6.4$ Hz, 24 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 12.9, 19.2, 19.6, 85.4, 95.7; $^{29}$Si NMR ($CDCl_3$) $\delta$ −13.1; IR (KBr, $cm^{-1}$) 2943. 2925, 2887, 2864, 2056, 1460, 1385, 1364, 1231, 1070, 1005, 993, 918, 880, 650; MS $m/z$ (%) 552 ($M^+$, 100), 509 (75), 167 (50), 425 (30), 384 (15). **2**: mp 147–149 °C; $^1$H NMR ($CDCl_3$) $\delta$ 1.02–1.26 (m, 12 H), 1.13 (m, 72 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 13.5, 19.3, 19.6, 82.0, 93.2; $^{29}$Si NMR ($CDCl_3$) $\delta$ −18.9; IR (KBr, $cm^{-1}$) 2923, 2889, 2866, 2060, 1460, 1231, 1093, 1067, 995, 992, 881, 652; MS $m/z$ (%) 827 ($M^+$-1, 7), 785 (100), 742 (8). **3**: mp 262–264 °C; $^1$H NMR ($CDCl_3$) $\delta$ 1.12–1.26 (m, 112 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 13.2, 19.0, 19.4, 82.4, 93.2; $^{29}$Si NMR ($CDCl_3$) $\delta$ −20.0; IR (KBr, $cm^{-1}$) 2945, 2887, 2866, 2058, 1462, 1385, 1366, 1229, 1067, 993, 920, 880, 648.

6 Crystal data for **1**: $C_{32}H_{56}Si_4$, $F_w = 553.14$, tetragonal, space group $P4\text{-}2_1c$, $a = 21.620(1)$, $c = 30.584(4)$ Å, $V = 14296(1)$ Å$^3$, $T = 90$ K, $Z = 16$, $D_c = 1.028$ g cm$^{-3}$, $R = 0.074$, $R_w = 0.062$ ($I > 3.0\sigma(I)$) for 5585 observed reflections.

7 The compound crystallized in three independent molecules in the unit cell. However, there are no significant difference in their structural parameters.

8 Crystal data for **2**: $C_{48}H_{86}Si_6$, $F_w = 829.69$, tetragonal, space group $P2_12_12_1$, $a = 13.883(1)$, $b = 16.593(1)$, $c = 25.260(2)$ Å, $V = 5818.9(6)$ Å$^3$, $T = 273$ K, $Z = 4$, $D_c = 0.949$ g cm$^{-3}$, $R = 0.079$, $R_w = 0.099$ ($I > 2.0\sigma(I)$) for 5100 observed reflections.

9 Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-227459 (**1**) and CCDC-227460 (**2**).

10 Unfortunately, single crystals of **3** suitable for X-ray crystallography were not obtained, however, spectroscopic analysis supported this cyclic compounds.

11 C. Santiago, K. N. Houk, G. J. DeCicco, and L. T. Scott, *J. Am. Chem. Soc.*, **100**, 692 (1978).

12 Oxidation half-wave potential and first oxidation potential of **1** are +0.89 V and +1.33 V, respectively (measured by cyclic voltammetry (vs SCE, $CH_2Cl_2$)). The oxidation half-wave potential for **1** is considerably lower than that observed for MeC≡CMe (+2.34 V, vs Ag/Ag$^+$, MeCN).[13]

13 J. H. P. Utley and R. Lines, in "The Chemistry of Carbon–Carbon Triple Bond," ed. by S. Patai, Wiley-Intersceience, New York (1978), Vol. 2, pp 739–752.

14 H. Sakurai, Y. Nakadaira, A. Hosomi, Y. Eriyama, and C. Kabuto, *J. Am. Chem. Soc.*, **105**, 3359 (1983).