Extended Silapericyclynes

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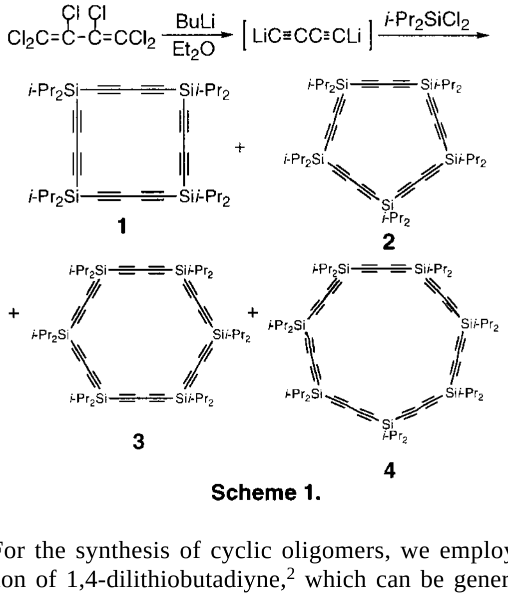
The synthesis of medium to large-membered cyclic silicon-butadiyne compounds ('extended silapericyclynes') was accomplished by the reaction of dilithiobutadiyne with dichlorodiisopropylsilane. The cyclic tetramer, pentamer, hexamer, and heptamer were obtained in 8%, 5%, 4%, and 2% yields, respectively. The structure of the tetramer was determined, and column-like packing was observed. The UV spectra of all compounds are also shown.

We have been recently interested in the synthesis, structures and properties of the cyclic compounds comprised of silicon and acetylene units ('silapericyclynes'). In 1999, we reported the spontaneous separation of the boat and chair conformers of the hexasilapericyclyne $(Ph_2SiC{\equiv}C)_6$.[1] We now report the synthesis of silicon-butadiyne cyclic molecules, $(i\text{-}Pr_2SiC{\equiv}CC{\equiv}C)_n$ ($n = 4$–7). Prior to our study, several reports have appeared in the literature concerning the silicon-butadiyne polymers $(R^1R^2SiC{\equiv}CC{\equiv}C)_n$ ($R^1{=}R^2{=}$Me, Et, Ph, Me_3Si; $R^1{=}$Me, $R^2{=}$Ph; $R^1{=}$Me, $R^2{=}$H; $R^1{=}$Ph, $R^2{=}$H).[2] However, to the best of our knowledge, no example of the cyclic oligomers of the silicon-butadiyne has been reported to date.



Scheme 1.

For the synthesis of cyclic oligomers, we employed the reaction of 1,4-dilithiobutadiyne,[2] which can be generated in situ from hexachlorobutadiene and butyllithium, with dichlorodiisopropylsilane. We found that the course of the reaction is highly sensitive to the experimental conditions,[3,4] and indeed, the production of the oligomers could be achieved with a combination of the dilithiobutadiyne and $i\text{-}Pr_2SiCl_2$ (Scheme 1). The separation with recycle-type HPLC gave four fractions, which were identified as the cyclic tetramer **1**, pentamer **2**, hexamer **3**, and heptamer **4**. The yields of 8% (**1**), 5% (**2**), 4% (**3**), 2% (**4**) were obtained.[5]

Compound **1** was characterized by X-ray crystallography as well as by spectroscopic methods.[6] However, unfortunately, single crystals suitable for X-ray analysis were not obtained for the higher oligomers **2**–**4**. The identification of these oligomers was made by mass, IR, and NMR spectroscopies. The crystal structure of **1** is shown in Figure 1.[7] The asymmetric unit contains two independent molecules, and the molecule A (contains Si1, Si2, Si1', Si2' atoms) has a symmetry center at the center of the molecule, while molecule B (contains Si3, Si4, Si5, Si4' atoms) has the symmetry axis passing through the Si5 and Si3 atoms. As a result of these symmetric elements, both molecules are planar. The average bond lengths (Si–C(sp): 1.827 Å, C≡C: 1.200 Å) fall within the usual range. The average Si–C≡C and C(sp)–Si–C(sp) angles were 174.9° and 104.0°, respectively; slightly distorted but virtually strain free. The space inside the molecules (ca. 6.2 Å diagonally) is occupied by the isopropyl groups of the other molecules. Two molecules (A and B) are nearly parallel; the dihedral angle of each plane is 12.0°. In addition, the molecules occupy a column-like packing, and the mean distance of the planes of the molecules is 4.3 Å.

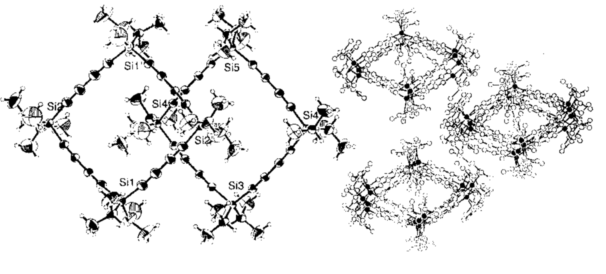


Figure 1. ORTEP drawing (left) and packing diagram (right) of **1**. Thermal ellipsoids are drawn at the 30% probability level.

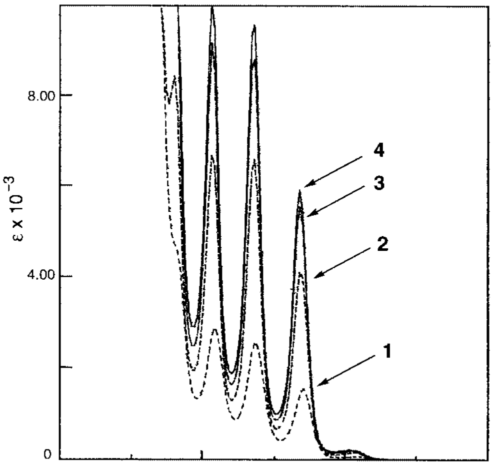
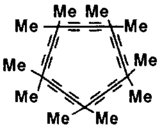


Figure 2. UV spectra of **1**–**4** and $(Pr_3SiC{\equiv}C)_2$ in hexane

Table 1. Results of UV spectra (hexane)

Compound	Absorption maxima / nm (ε)
1	254 (2900), 268 (2590), 285 (1560), 303 (70)
2	253 (6690), 268 (6600), 284 (4120), 303 (150)
3	253 (9100), 268 (8710), 284 (5500), 302 (210)
4	253 (10200), 268 (9750), 284 (5930), 302 (220)
5	232 (5510), 245 (6210), 259 (4660)[a]
6	243 (9000), 256 (8000), 272 (4000)[b]

[a]ref 8, in cyclohexane. [b]ref 9, in *t*-butyl ether.



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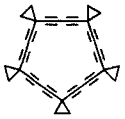

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The UV spectra of compounds **1**–**4** are shown in Figure 2, and the absorption maxima of **1**–**4** and carbon analogues, $(Me_2CC{\equiv}CC{\equiv}C)_5$ (**5**),[8] and $(C_2H_4CC{\equiv}CC{\equiv}C)_5$ (**6**),[9] are listed in Table 1. The following futures are worthy of note regarding the electronic spectra of **1**–**4**. The absorptions of the silapericyclynes show little variation in the electronic transition energies; no bathochromic shift for all four absorption maxima virtually occurs upon going from **1** to **4**. Although the structural parameters were not available except for **1**, the result indicates that conformational and strain effects on the transition energies are not important in the medium-ring region (**1**–**4**). Interestingly, quite recently, Tykwinski et al. thoroughly examined the extent and effects of ring strain in the enyne macrocycles, concluding that ring strain has a surprisingly small effect on the electronic transition energies of the macrocycles.[10]

Comparison of the spectra with those of carbon systems **5** and **6** discloses that the substitution of silicon atoms for the carbon atoms significantly lowers the electronic transition energies for the three absorption maxima. For example, the absorption maxima of the 25-membered rings **5** and **6** at 259 and 272 nm, respectively, shift to 285 nm in **2**. Furthermore, a smaller HOMO–LUMO energy difference in **1**–**4** is clearly shown by the fact that they exhibit absorptions at 302–303 nm; the corresponding absorption is not observed in both **5** and **6**. Details of these absorptions have not been clarified yet, but we think they might be attributed to the result of σ–π conjugation, as the ε values of these absorptions are small. A semiempirical MO calculation (PM3) of **1** indicates that the π-orbitals of the butadiyne unit interact with eight Si–C(isopropyl) σ-orbitals, and the energy level of the orbital is raised. This type of inverse σ–π conjugation is reminiscent of the unusual electronic properties of benzo[1,2:4,5]bis(1,1,2,2-tetraisopropyldisilacyclobutene).[11]

In summary, the synthesis of extended silapericyclynes proved their unique features; i.e., UV properties, column-like packing with the interior space filled with substituents of another molecule, and the electronic delocalization as indicated by the calculation. We are currently investigating the chemical and thermal properties of these silapericyclynes.

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References and Notes

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3 Oxidative coupling of *i*-$Pr_2Si(C{\equiv}CH)_2$ with copper reagents including Hay catalyst[4] failed in spite of multiple trials.

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5 Procedure: To a three-necked flask, 1.57 g (6.0 mmol) of hexachloro-1,3-butadiene was added dropwise to a stirred –78 °C solution of BuLi (1.50 M in hexane, 16.5 mL, 24.8 mmol) and Et_2O (300 mL). After the addition, the mixture was warmed to room temperature and stirred for 2 h. The reaction mixture was cooled to –78 °C, *i*-Pr_2SiCl_2 (1.22 g, 6.6 mmol) was added, and after it was warmed to room temperature, the mixture was stirred for 18 h. After workup, solvent was removed under reduced pressure, and the crude products was purified by dry column chromatography (silica, hexane/Et_2O = 99/1) and recycle-type GPC (JAIgel 2H+2H, $CHCl_3$) to afford tetramer ([*i*-$Pr_2SiC{\equiv}CC{\equiv}C]_4$) **1** (8%), pentamer ([*i*-$Pr_2SiC{\equiv}CC{\equiv}C]_5$) **2** (5%), hexamer ([*i*-$Pr_2SiC{\equiv}CC{\equiv}C]_6$) **3** (4%), heptamer ([*i*-$Pr_2SiC{\equiv}CC{\equiv}C]_7$) **4** (2%), and polymeric compound (49%) whose structure was not determined.

6 **1**: colorless crystals, ^1H NMR ($CDCl_3$) δ 0.99–1.04 (overlap, m, 8H), 1.08 (d, *J* = 6.4 Hz, 48H) ppm; ^{13}C NMR ($CDCl_3$) δ 11.9, 17.5, 80.4, 90.8 ppm; ^{29}Si NMR ($CDCl_3$) δ –21.4 ppm; MS (70 eV) *m/z* (%) 648 (M^+, 84), 605 (100), 563 (47), 521 (32), 479 (11); IR (KBr) *ν* 2947, 2929, 2893, 2071, 1462, 1240 cm^{-1}; Anal Calcd for $C_{40}H_{56}Si_4$: C, 74.00; H, 8.69%. Found: C, 73.96; H, 8.64%. **2**: colorless needles, ^1H NMR ($CDCl_3$) δ 1.01–1.06 (overlap, m, 10H), 1.09 (d, *J* = 5.8 Hz, 60H) ppm; ^{13}C NMR ($CDCl_3$) δ 12.2, 17.5, 79.1, 90.3 ppm; ^{29}Si NMR ($CDCl_3$) δ –21.9 ppm; MS (70 eV) *m/z* (%) 810 (M^+, 100), 767 (54), 725 (57), 683 (31), 641 (13), 599 (10); IR (KBr) *ν* 2947, 2868, 2071, 1460, 1236 cm^{-1}; Anal Calcd for $C_{50}H_{70}Si_5$: C, 74.00; H, 8.69%. Found: C, 73.86; H, 8.45%. **3**: colorless needles, ^1H NMR ($CDCl_3$) δ 1.01–1.06 (overlap, m, 12H), 1.09 (d, *J* = 5.8 Hz, 72H) ppm; ^{13}C NMR ($CDCl_3$) δ 12.3, 17.5, 79.0, 90.3 ppm; ^{29}Si NMR ($CDCl_3$) δ –21.8 ppm; MS (70eV) *m/z* (%) 972 (M^+, 100), 930 (74), 884 (73), 846 (78), 804 (23), 761 (13); IR (KBr) *ν* 2947, 2868, 2070, 1462, 1236 cm^{-1}; Anal Calcd for $C_{60}H_{84}Si_6$: C, 74.00; H, 8.69%. Found: C, 73.86; H, 8.55%. **4**: colorless needles, ^1H NMR ($CDCl_3$) δ 1.01–1.07 (overlap, m, 14H), 1.08 (d, *J* = 5.5 Hz, 84H) ppm; ^{13}C NMR ($CDCl_3$) δ 12.3, 17.5, 79.0, 90.2 ppm; ^{29}Si NMR ($CDCl_3$) δ –21.7 ppm; IR (KBr) *ν* 2947, 2868, 2070, 1462, 1238 cm^{-1}; MS (70eV) *m/z* (%) 1134 (M^+, 92), 1092 (58), 1050 (40), 966 (20), 882 (9); Anal Calcd for $C_{70}H_{98}Si_7$: C, 74.00; H, 8.69%. Found: C, 73.63; H, 8.51%. Polymeric compounds: ^1H NMR ($CDCl_3$) δ 1.01–1.07 (overlap, m), 1.09 (d, *J* = 5.6 Hz), 3.56 (s) ppm; ^{13}C NMR ($CDCl_3$) δ 12.4, 17.5, 79.0, 90.2 ppm; ^{29}Si NMR ($CDCl_3$) δ –21.8 ppm; IR (KBr) *ν* 2947, 2868, 2070, 1462, 1261 cm^{-1}.

7 Crystallographic data of **1**: monoclinic, *C*2/*c*, a = 22.099(1)Å, b = 22.0481(9) Å, c = 18.373(1) Å, β= 93.230(2)°, V = 8938.1(7) Å^3, Z = 8, D_{calcd} = 0.965 g/cm^3, R = 0.082, R_w = 0.091 for 384 parameters.

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