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Synthesis and Crystal Structures of Silapericyclynes

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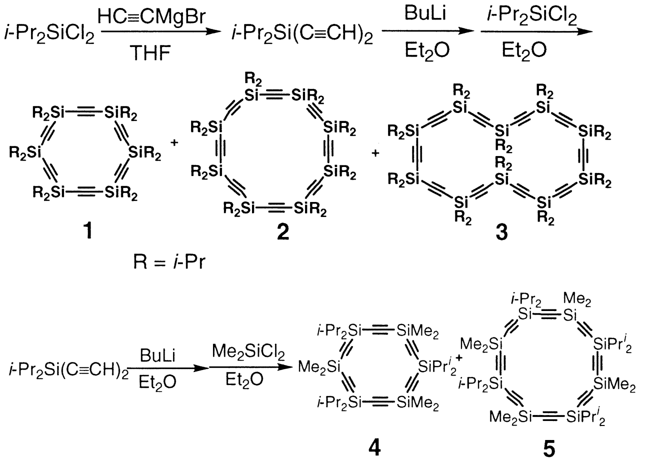
Five new silapericyclynes, $(i\text{-Pr}_2\text{SiC}{\equiv}\text{C})_n$ (n = 6, 8, 10) and $(i\text{-Pr}_2\text{SiC}{\equiv}\text{CMe}_2\text{SiC}{\equiv}\text{C})_n$ (n = 3, 4) were prepared, and their structures were determined by X-ray crystallography. For sila[6]pericyclynes, the ring structures depend upon the steric demand of the substituents on silicon atoms; $(i\text{-Pr}_2\text{SiC}{\equiv}\text{C})_6$ crystallized in nearly planar structure, and $(i\text{-Pr}_2\text{SiC}{\equiv}\text{CMe}_2\text{SiC}{\equiv}\text{C})_3$ formed a chair structure with small dihedral angles (109.6° and 121.7°), while $(\text{Ph}_2\text{SiC}{\equiv}\text{C})_6$ crystallized in boat and chair forms. The crystal structures of larger pericyclynes $(i\text{-Pr}_2\text{SiC}{\equiv}\text{C})_8$, $(i\text{-Pr}_2\text{SiC}{\equiv}\text{C})_{10}$, and $(i\text{-Pr}_2\text{SiC}{\equiv}\text{CMe}_2\text{SiC}{\equiv}\text{C})_4$ showed that the substituents, isopropyl groups, were included inside the rings. These compounds show absorption maxima in the range of 203–221 nm.

As an extension of the study on silicon compounds with unusual structures and electronic properties,[1] we have been interested in the construction of new cyclic compounds which alternate silicon and alkyne units ("silapericyclynes").[2] To date, the molecular structures of several silapericyclynes: $(\text{Ph}_2\text{SiC}{\equiv}\text{C})_6$,[3a] $(\text{Me}_2\text{SiC}{\equiv}\text{C})_4$,[3b] $(\text{Me}_2\text{SiC}{\equiv}\text{C})_5$,[3b] and $(\text{Me}_2\text{SiC}{\equiv}\text{C})_6$,[3c] have been reported. The electronic properties of $(\text{Me}_2\text{SiC}{\equiv}\text{C})_3$ and related compounds were discussed in detail by Sakurai and coworkers.[4] In 1998, we reported the spontaneous separation of both boat and chair conformers of phenyl-substituted $(\text{Ph}_2\text{SiC}{\equiv}\text{C})_6$,[3a] unlike other silapericyclynes. This prompted us to compare the structures of phenyl-substituted silapericyclynes with those of alkyl-substituted ones. To allow such a comparison, we have synthesized the silapericyclynes having isopropyl and isopropyl/methyl substituents on silicon atoms. The primary goal of our study is to show the structure and the electronic properties of larger-size silapericyclynes, which provides an opportunity for accessing electronic properties inherent in these molecules. Here we report the synthesis and structures of $(i\text{-Pr}_2\text{SiC}{\equiv}\text{C})_n$ (n = 6, 8, 10) and $(i\text{-Pr}_2\text{SiC}{\equiv}\text{CMe}_2\text{SiC}{\equiv}\text{C})_n$ (n = 3, 4).

Results and Discussion

Synthesis of Silapericyclynes. The preparation of all silapericyclynes is shown in Scheme 1. The compounds $(i\text{-Pr}_2\text{SiC}{\equiv}\text{C})_n$ were synthesized from diethynyldiisopropylsilane, which was prepared from dichlorodiisopropylsilane and ethynylmagnesium bromide. This diethynylsilane was treated with BuLi, then $i\text{-Pr}_2\text{SiCl}_2$ was added. The analysis by HPLC showed that the reaction had produced several products. Separation with recycle-type preparative HPLC led to the isolation of $(i\text{-Pr}_2\text{SiC}{\equiv}\text{C})_6$ (**1**) (19%), $(i\text{-Pr}_2\text{SiC}{\equiv}\text{C})_8$ (**2**) (7%), and $(i\text{-Pr}_2\text{SiC}{\equiv}\text{C})_{10}$ (**3**) (2%). In a similar manner, isopropyl/methylsilapericyclynes were prepared: $(i\text{-Pr}_2\text{SiC}{\equiv}\text{CMe}_2\text{SiC}{\equiv}\text{C})_3$ (**4**) and $(i\text{-Pr}_2\text{SiC}{\equiv}\text{CMe}_2\text{SiC}{\equiv}\text{C})_4$ (**5**) were obtained in 13% and 11% yields, respectively. The structures of compounds **1**–**5** were established by X-ray crystallography as well as by spectroscopic methods.



Scheme 1.

Structure of Sila[6]pericyclynes. Single crystals of compound **1** were obtained by recrystallization from three different solvents: acetone, THF, or benzene. In each case, the solvent molecules (acetone, THF, or benzene) place themselves above and below the Si_6C_{12} ring (Fig. 1). In all the cases, the compound crystallized in $P\bar{1}$ space group and lattice parameters are similar. In the case of acetone, the solvent molecule is disordered; this is imposed by the symmetry. One part is shown in Fig. 1. The ORTEP drawings of sila[6]pericyclynes **1** (from acetone) are shown in Fig. 2; crystallographic data are listed in Table 1. Interestingly, the 18-membered ring is almost planar, which is quite different from those of previously reported hexasilapericyclynes.[3] In **1**, the dihedral angle between the Si1*–Si3–Si2 and the Si1–Si2–Si1*–Si2* mean planes is 168.4°.[5] By comparison, the corresponding angle in $(\text{Me}_2\text{SiC}{\equiv}\text{C})_6$ was reported to be 126.5°,[3c] and $(\text{Ph}_2\text{SiC}{\equiv}\text{C})_6$ indicates that the angle in chair-form was 148.3°, and that in boat-form was 131.8° and 115.6°.[3a] This difference is thought to be the result of steric demand by the relatively bulky isopropyl groups.[6] Selected bond lengths and angles of **1** are shown in Table 2. Average bond lengths and angles are summarized in Table 3. For **1**, the

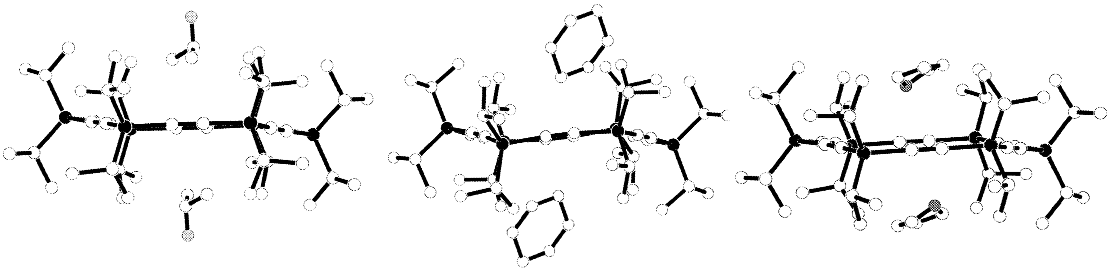


Fig. 1. Molecular structure of **1** recrystallized from acetone (left), benzene (middle), and THF (right).

Table 1. Crystallographic Data for **1**, **2**, and **3**

	1	**2**	**3**
	Crystal data		
Formula	$C_{54}H_{96}O_2Si_6$	$C_{64}H_{112}Si_8$	$C_{80}H_{140}Si_{10}$
Mol wt	945.86	1106.27	1382.84
Cryst descript	colorless prism	colorless prism	colorless prism
Cryst size, mm	0.30×0.30 ×0.15	0.40×0.40 ×0.15	0.50×0.50 × 0.20
Cryst syst	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	12.067(4)	14.191(3)	14.762(6)
b/Å	12.041(4)	15.263(4)	20.214(7)
c/Å	12.057(5)	8.514(2)	8.663(3)
α/deg	101.24(2)	92.608(9)	96.95(3)
β/deg	101.22(1)	99.40(2)	95.88(3)
γ/deg	78.55(3)	78.37(1)	106.33(3)
V/Å^3	1661(1)	1787.4(7)	2436(1)
Z	1	1	1
	Data collection		
Diffractometer	Rigaku RAXIS-IV	Rigaku RAXIS-IV	Rigaku RAXIS-IV
Radiation (λ/Å)	Mo $K\alpha$ (0.71070)	Mo $K\alpha$ (0.71070)	Mo $K\alpha$ (0.71070)
Monochromator	graphite	graphite	graphite
Temperature/°C	−100	20	20
μ/cm^{-1}	1.57	1.84	1.68
No. of rflns measd	4706	6651	11621
No. of obsd reflns	2905	5891	3018
No. of params	291	325	426
	Refinement		
R	0.084	0.065	0.063
R_w	0.087	0.074	0.059
$(\Delta/\sigma)_{max}$	0.45	0	0.03
$(\Delta/\rho)_{max}$/e Å^{-3}	0.28	0.32	0.23
$(\Delta/\rho)_{min}$/e Å^{-3}	−0.28	−0.52	−0.23

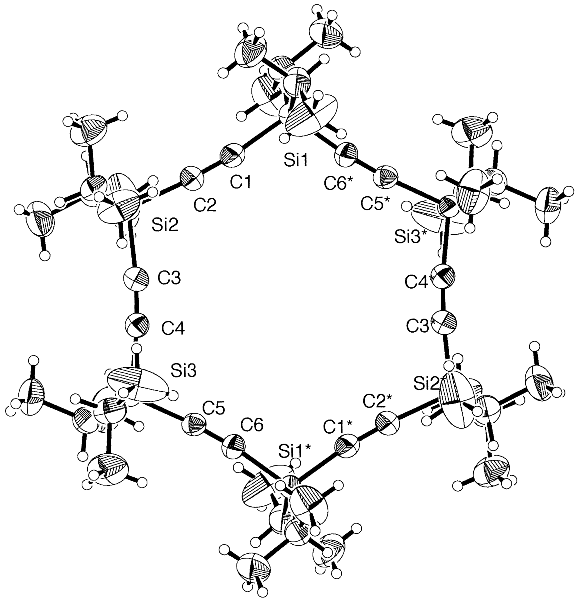


Fig. 2. ORTEP drawing of **1**. Thermal ellipsoids are drawn at the 30% probability level.

Table 2. Selected Bond Lengths and Distances of **1**

	Bond length		
Si(1)–C(1)	1.837(7)	Si(1)–C(6*)	1.839(6)
Si(2)–C(2)	1.835(7)	Si(2)–C(3)	1.846(8)
Si(3)–C(4)	1.839(8)	Si(3)–C(5)	1.832(6)
C(1)–C(2)	1.215(8)	C(3)–C(4)	1.204(8)
C(5)–C(6)	1.198(7)		
	Bond angle		
C(1)–Si(1)–C(6*)	109.0(3)	C(2)–Si(2)–C(3)	109.2(3)
C(4)–Si(3)–C(5)	108.4(3)	Si(1)–C(1)–C(2)	173.8(6)
Si(2)–C(2)–C(1)	175.7(6)	Si(2)–C(3)–C(4)	174.7(6)
Si(3)–C(4)–C(3)	172.9(5)	Si(3)–C(5)–C(6)	175.2(6)
Si(1*)–C(6)–C(5)	174.2(6)		

average Si–C(sp) and C≡C bond lengths are 1.838 Å and 1.204 Å, respectively. The average Si–C≡C and C(sp)–Si–C(sp) bond angles are 174.4° and 108.9°, respectively. These values are similar to those of $(Me_2SiC{\equiv}C)_6$[3c] and $(Ph_2SiC{\equiv}C)_6$.[3a]

With a slight change of substituents, drastic change of the crystal structure was observed. Figure 3 shows the structure of $(i\text{-}Pr_2SiC{\equiv}CMe_2SiC{\equiv}C)_3$ (**4**), and Table 4 shows the crystallographic data of **4**. Compound **4** assumes a chair conformation; the dihedral angles between the Si2–Si3–Si4 or the Si1–Si5–Si6 and the Si1–Si2–Si4–Si5 mean plane are 109.6° and 121.7°, respectively. These dihedral angles are smaller (less planar) than those of **1** (168.4°) and $(Ph_2SiC{\equiv}C)_6$ (131.8° and 148.3°). This result indicates that **4** adopts the most bent structure among sila[6]pericyclynes reported until now. The reason for this structure is the steric effect of substituents.[6] Selected bond lengths and angles of **4** are shown in Table 5.

Structure of Sila[8]pericyclynes. Until now, no structural reports for silapericyclynes containing more than six silicon

Table 3. Average Bond Lengths and Angles of **1**–**5**

Compound	Si–C(sp) (Å)	C≡C (Å)	Si–C≡C(°)	C(sp)–Si–C(sp) (°)
$(Me_2SiC\equiv C)_4$[3b]	1.84	1.207	173.09	103.37
$(Me_2SiC\equiv C)_5$[3b]	1.832	1.21	177.2	106.1
$(Me_2SiC\equiv C)_6$[3c]	1.817	1.220	177.2	106.1
$(Ph_2SiC\equiv C)_4$	1.837	1.191	172.7	104.3
chair-$(Ph_2SiC\equiv C)_6$	1.83	1.205	175	109.8
boat-$(Ph_2SiC\equiv C)_6$	1.836	1.215	174	107.6
$[i\text{-}Pr_2SiC\equiv C]_6$, **1**	1.838	1.204	174.4	108.9
$[i\text{-}Pr_2SiC\equiv C]_8$, **2**	1.839	1.218	172.7	104.3
$[i\text{-}Pr_2SiC\equiv C]_{10}$, **3**	1.836	1.20	172.0	108.8
$[i\text{-}Pr_2SiC\equiv CMe_2SiC\equiv C]_3$, **4**	1.839	1.211	175.3	106.9
$[i\text{-}Pr_2SiC\equiv CMe_2SiC\equiv C]_4$, **5**	1.825	1.203	174.3	107.9

Table 4. Crystallographic Data for **4** and **5**

	4	**5**
	Crystal data	
Formula	$C_{36}H_{60}Si_6$	$C_{48}H_{80}Si_8$
Molecular weight	661.38	881.84
Crystal descript	colorless plate	colorless plate
Crystal size, mm	0.30×0.30 × 0.30	0.40×0.40 × 0.30
Space group	$P\bar{1}$	$C2/c$
a/Å	14.374(1)	22.072(4)
b/Å	14.374(1)	20.613(4)
c/Å	11.911(1)	14.328(4)
α/deg	97.173(6)	
β/deg	107.036(6)	108.50(2)
γ/deg	110.445(6)	
V/Å^3	2231.4(4)	6181(2)
Z	2	4
d_{cal}/g cm^{-3}	0.984	0.947
	Data collection	
Diffractometer	Rigaku RAXIS-IV	Rigaku RAXIS-IV
μ/cm^{-1}	2.07	1.99
2θ, range/deg	55.1	50.0
No. of reflections measured	8052	5356
No. of observed reflections	6818	1248
	Refinement	
R	0.085	0.075
R_w	0.097	0.083
Weighting scheme	$w = 1/\sigma^2 (F_0)$	$w = 1/\sigma^2 (F_0)$
Max shift in final cycle	0.02	0.05
Maximum residual electrons/e$^-$ Å^{-3}	0.75	0.39
Minimum residual electrons/e$^-$ Å^{-3}	−0.90	−0.35
No. of parameters	400	246

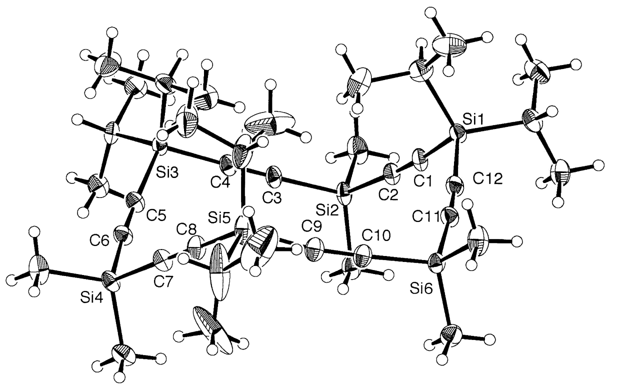


Fig. 3. ORTEP drawing of **4**. Thermal ellipsoids are drawn at the 30% probability level.

Table 5. Selected Bond Lengths and Distances of **4**

	Bond lengths		
Si(1)–C(1)	1.848(6)	Si(1)–C(12)	1.850(6)
Si(2)–C(2)	1.847(6)	Si(2)–C(3)	1.856(5)
Si(3)–C(4)	1.834(5)	Si(3)–C(5)	1.824(5)
Si(4)–C(6)	1.842(5)	Si(4)–C(7)	1.844(5)
Si(5)–C(8)	1.833(6)	Si(5)–C(9)	1.838(5)
Si(6)–C(10)	1.833(5)	Si(6)–C(11)	1.840(6)
C(1)–C(2)	1.213(7)	C(3)–C(4)	1.213(6)
C(5)–C(6)	1.215(7)	C(7)–C(8)	1.214(7)
C(9)–C(10)	1.207(6)	C(11)–C(12)	1.203(7)
	Bond angles		
C(1)–Si(1)–C(12)	108.5(2)	C(2)–Si(2)–C(3)	104.8(2)
C(4)–Si(3)–C(5)	107.9(2)	C(6)–Si(4)–C(7)	105.3(2)
C(8)–Si(5)–C(9)	108.5(2)	C(10)–Si(6)–C(11)	106.5(2)
Si(1)–C(1)–C(2)	174.3(5)	Si(2)–C(2)–C(1)	176.0(4)
Si(2)–C(3)–C(4)	178.2(4)	Si(3)–C(4)–C(3)	178.6(5)
Si(3)–C(5)–C(6)	170.2(4)	Si(4)–C(6)–C(5)	173.0(4)
Si(4)–C(7)–C(8)	178.1(5)	Si(5)–C(8)–C(7)	176.0(4)
Si(5)–C(9)–C(10)	172.1(5)	Si(6)–C(10)–C(9)	177.8(5)
Si(6)–C(11)–C(12)	176.1(5)	Si(1)–C(12)–C(11)	173.5(5)

atoms have appeared.[7] The crystal structures of **2** and **5** are shown in Figs. 4 and 5, respectively. Selected bond lengths and angles are given in Tables 6 and 7. Compound **2** has a symmetric center at the center of the molecule. The 24-membered ring adopts a ladder-like structure (*anti*-tricyclic type, Fig. 6), and the space inside is filled with two isopropyl groups. The average deviation of each silicon atom from the mean plane of the ring is 0.7522(8) Å, and this means that **2** has less planarity than **1** (deviation: 0.165(2) Å).

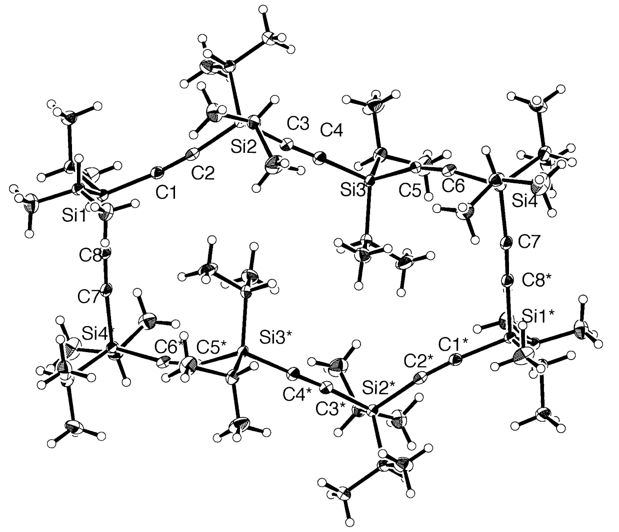


Fig. 4. ORTEP drawing of **2**. Thermal ellipsoids are drawn at the 30% probability level.

Table 6. Selected Bond Lengths and Distances of **2**

Bond length			
Si(1)–C(1)	1.831(3)	Si(1)–C(8)	1.837(4)
Si(2)–C(2)	1.827(4)	Si(2)–C(3)	1.835(4)
Si(3)–C(4)	1.856(4)	Si(3)–C(5)	1.839(3)
Si(4)–C(6)	1.846(3)	Si(4)–C(7)	1.845(4)
C(1)–C(2)	1.241(5)	C(3)–C(4)	1.202(5)
C(5)–C(6)	1.214(4)	C(7)–C(8*)	1.213(5)
Bond angles			
C(1)–Si(1)–C(8)	109.6(2)	C(2)–Si(2)–C(3)	110.1(2)
C(4)–Si(3)–C(5)	109.9(2)	C(6)–Si(4)–C(7)	103.3(2)
Si(1)–C(1)–C(2)	173.0(3)	Si(1)–C(8)–C(7*)	179.0(3)
Si(2)–C(2)–C(1)	172.9(3)	Si(2)–C(3)–C(4)	172.0(3)
Si(3)–C(4)–C(3)	178.5(4)	Si(3)–C(5)–C(6)	161.9(3)
Si(4)–C(6)–C(5)	168.6(3)	Si(4)–C(7)–C(8*)	175.8(3)

Table 7. Selected Bond Lengths and Distances of **5**

Bond length			
Si(1)–C(1)	1.83(1)	Si(2)–C(2)	1.84(1)
Si(2)–C(3)	1.83(1)	Si(3)–C(4)	1.83(1)
Si(3)–C(5)	1.85(1)	Si(4)–C(6)	1.84(1)
Si(4)–C(7)	1.82(1)	Si(5)–C(8)	1.81(1)
C(1)–C(2)	1.21(1)	C(3)–C(4)	1.20(1)
C(5)–C(6)	1.17(1)	C(7)–C(8)	1.23(1)
Bond angles			
C(1)–Si(1)–C(1*)	107.3(8)	C(2)–Si(2)–C(3)	103.1(5)
C(4)–Si(3)–C(5)	110.1(5)	C(6)–Si(4)–C(7)	110.0(6)
Si(1)–C(1)–C(2)	174(1)	Si(2)–C(2)–C(1)	177(1)
Si(2)–C(3)–C(4)	176(1)	Si(3)–C(4)–C(3)	172(1)
Si(3)–C(5)–C(6)	176(1)	Si(4)–C(6)–C(5)	175(1)
Si(4)–C(7)–C(8)	175(1)	Si(5)–C(8)–C(7)	172(1)

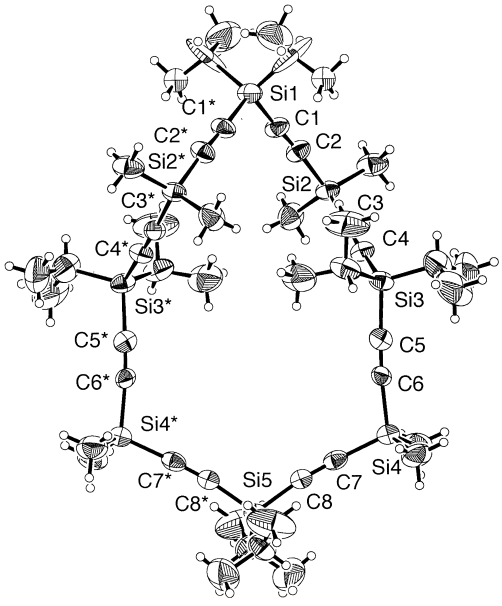


Fig. 5. ORTEP drawing of **5**. Thermal ellipsoids are drawn at the 30% probability level.

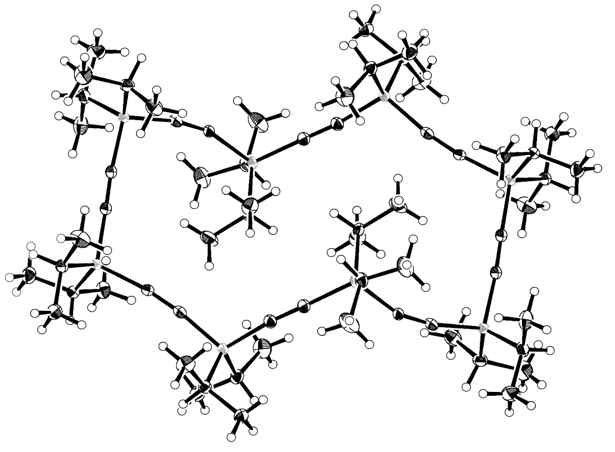


Fig. 6. Side view of **2**.

The 24-membered ring of **5** is twisted, and again the hole inside was filled with the substituents of another molecule (Fig. 7). The large dihedral angle observed for **5** shows a similar tendency to the relationship of sila[6]pericyclynes **1** and **4**.

Structure of Sila[10]pericyclynes. In the case of isopropyl-silapericyclynes, sila[10]pericyclynes **3** was also obtained. The ORTEP drawing is shown in Fig. 8, crystallographic data and selected bond lengths and angles are given in Tables 1 and 8. This compound has a symmetry center at the center of the molecule. The structure kept the twisted-chair–chair–chair form, which is one of the most stable conformations of cyclodecane. The average Si–C(sp) and C≡C bond lengths are 1.836 Å and 1.20 Å, respectively. The average C(sp)–Si–C(sp) and Si–C≡C bond angles are 108.4° and 172.0°, respectively. These values are similar to those of silapericyclynes. But the Si–C≡C bond angle was smaller: the smallest angle of Si–C≡C was 165.0(7)° in Si3–C5–C6 and Si3*–C5*–C6*. This compound also crystallizes with two of isopropyl groups included within the ring.

Electronic Spectra of Silapericyclynes. The UV spectra for silapericyclynes **1**–**5** are shown in Fig. 9, and the absorption maxima of **1**–**5** are summarized in Table 9. Each com-

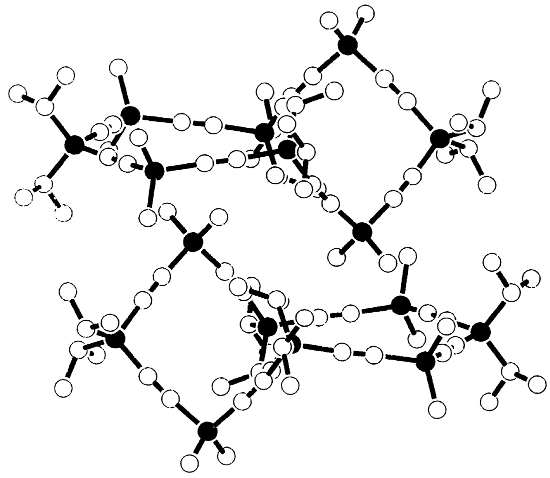


Fig. 7. Packing Diagram of **2**.

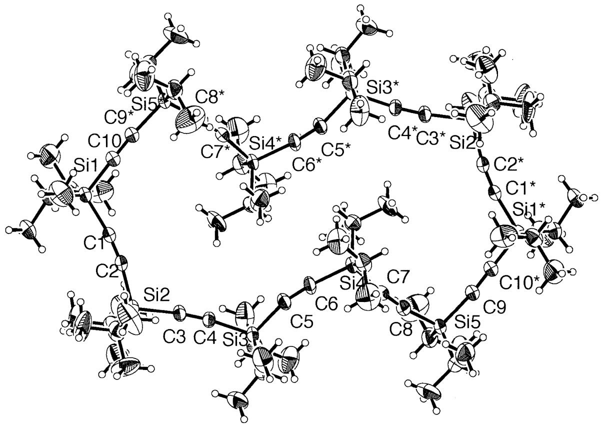


Fig. 8. ORTEP drawing of **3**. Thermal ellipsoids are drawn at the 30% probability level.

Table 8. Selected Bond Lengths and Distances of **3**

Bond lengths			
Si(1)–C(1)	1.842(8)	Si(1)–C(10)	1.825(8)
Si(2)–C(2)	1.823(8)	Si(2)–C(3)	1.843(7)
Si(3)–C(4)	1.845(7)	Si(3)–C(5)	1.836(7)
Si(4)–C(6)	1.838(7)	Si(4)–C(7)	1.828(9)
Si(5)–C(8)	1.831(9)	Si(5)–C(9)	1.846(8)
C(1)–C(2)	1.197(9)	C(3)–C(4)	1.189(8)
C(5)–C(6)	1.199(8)	C(7)–C(8)	1.195(9)
C(9)–C(10*)	1.198(9)		
Bond angles			
C(1)–Si(1)–C(10)	110.4(3)	C(2)–Si(2)–C(3)	110.6(3)
C(4)–Si(3)–C(5)	111.5(4)	C(6)–Si(4)–C(7)	106.1(3)
C(8)–Si(5)–C(9)	103.3(4)	Si(1)–C(1)–C(2)	170.9(7)
Si(2)–C(2)–C(1)	171.0(7)	Si(2)–C(3)–C(4)	173.7(8)
Si(3)–C(4)–C(3)	172.4(8)	Si(3)–C(5)–C(6)	165.0(8)
Si(4)–C(6)–C(5)	173.7(8)	Si(4)–C(7)–C(8)	173.1(8)
Si(5)–C(8)–C(7)	173.0(8)	Si(5)–C(9)–C(10)	172.8(8)
Si(1)–C(10)–C(9*)	174.1(8)		

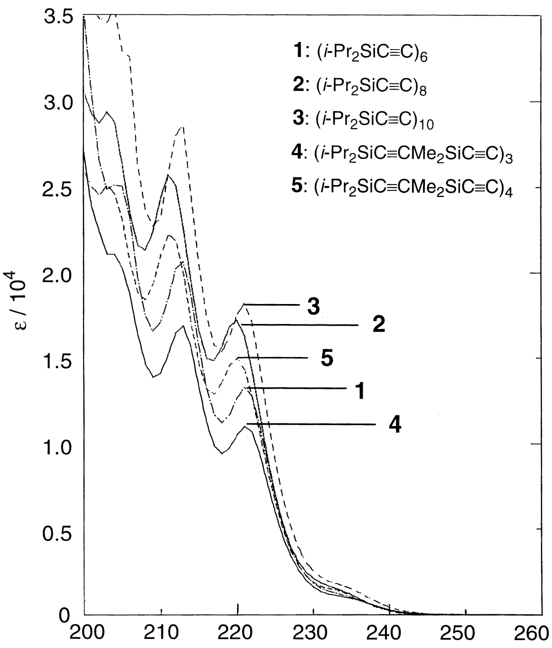


Fig. 9. UV spectra of **1**–**5** in hexane.

pound showed virtually the same transition energies; all-isopropyl compounds **1**–**3** showed only 1 to 2-nm bathochromic shifts compared to isopropyl/methyl compounds **4**–**5**. Recently, Tykwinski et al. thoroughly examined the enyne macrocycles, showing that ring strain has a surprisingly small effect on the electronic transition energies.[8] Our result also showed a similar tendency.

Molar absorption coefficient ε values were not proportional to the number of silicon atoms and acetylene units. Thus, ε values per number of Si-acetylene units for $(i\text{-Pr}_2\text{SiC}{\equiv}\text{C})_6$ (**1**), $(i\text{-Pr}_2\text{SiC}{\equiv}\text{C})_8$ (**2**), and $(i\text{-Pr}_2\text{SiC}{\equiv}\text{C})_{10}$ (**3**) at the 221-nm absorption were 1830, 1660, and 1820, respectively. It is noteworthy that this order (**1** > **3** > **2**) is the same as that of planarity.[9]

For isopropyl/methyl silapericyclynes, again the absorption maxima were observed at similar wavelengths; however, the ε values were quite different from those of **1** and **2**. For sila[6]pericyclynes, ε values at the 221-nm absorption was 11000 for $(i\text{-Pr}_2\text{SiC}{\equiv}\text{C})_6$ **1**, while that for $(i\text{-Pr}_2\text{SiC}{\equiv}\text{CMe}_2\text{SiC}{\equiv}\text{C})_3$ **4** was only 8600. A similar tendency was observed of sila[8]pericyclynes: thus, $(i\text{-Pr}_2\text{SiC}{\equiv}\text{C})_8$ **2** showed absorption maximum at 221 nm (13300), while $(i\text{-Pr}_2\text{SiC}{\equiv}\text{CMe}_2\text{SiC}{\equiv}\text{C})_4$ **5** showed 220 nm (9900). These results clearly demonstrate that the acetylene units can interact through Si atoms, thus enhancement of oscillator strength is observed. A semiempirical MO calculation (PM3) of **1**–**3** indicated that the π (C≡C) orbital interacts with the σ (Si–C(isopropyl)) orbital. We also observed this inverse σ–π conjugation in the extended silapericyclynes.[10] The detailed explanation of the relationship of planarity and molecular orbital is still under investigation; however, it is quite plausible that the planar structure enhances the σ–π interaction.

Experimental

All solvents used in the reactions were purified and dried by the reported methods. Tetrahydrofuran (THF) was purified by distillation from benzophenone ketyl prior to use. All reactions were carried out under an argon atmosphere. All NMR spectra were re-

Table 9. Summary of UV Spectra of **1–5**

Compounds	$\lambda_{\max}$/nm (ε)
(i-$Pr_2SiC{\equiv}C)_6$: **1**	204 (21100), 213 (16900), 221 (11000)
(i-$Pr_2SiC{\equiv}C)_8$: **2**	204 (25100), 213 (20600), 221 (13300)
(i-$Pr_2SiC{\equiv}C)_{10}$: **3**	205 (32900), 213 (28600), 221 (18200)
(i-$Pr_2SiC{\equiv}CMe_2SiC{\equiv}C)_3$: **4**	203 (14300), 211 (12700), 220 (8500)
(i-$Pr_2SiC{\equiv}CMe_2SiC{\equiv}C)_4$: **5**	203 (16800), 211 (14700), 220 (9900)

corded on a JEOL model α-500 (^{1}H, 500.0 MHz; ^{13}C, 125.7 MHz; ^{29}Si, 99.3 MHz). Chemical shifts are reported as δ units relative to $SiMe_4$ as an internal standard. For ^{29}Si NMR, $SiMe_4$ was used as an external standard. Mass spectrometry was performed on a JEOL JMS-D300 instrument. Infrared spectra were measured with a JASCO A-102 spectrometer. UV spectra were recorded with a JASCO Ubest-50 spectrometer. GLC analysis was carried out by a Shimadzu GC-8A instrument using a glass-packed column (ϕ 3.5 × 1000 mm) with 10% silicon KF-96 on Celite 545sk. Preparative HPLC was performed on a LC-09 instrument with JAI gel 1H + 2H columns and chloroform was used as eluent.

Preparation of Diethynyldiisopropylsilane: Ethylmagnesium bromide (1.8 M, THF solution, 260 mL, 2.5 equiv) was added to the acetylene-saturated THF solution (600 mL). Acetylene was bubbled until the completion of the addition. Then the mixture was cooled to −78 °C, and dichlorodiisopropylsilane (33.4 g, 0.18 mol) was added for 1 h. The solution was gradually warmed to room temperature and stirred for 6 h. The reaction mixture was washed with aqueous NH_4Cl, the aqueous layer was extracted with hexane, and the combined organic phase was dried over anhydrous $MgSO_4$. After filtration, evaporation and vacuum distillation gave 24.1 g (81%) of diethynyldiisopropylsilane as colorless liquid. Spectral data: bp 50 °C / 25 mmHg. ^{1}H NMR ($CDCl_3$) δ 1.04 (sep, 2H, J = 6.1 Hz), 1.09 (d, 12H, J = 6.1 Hz), 2.24 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 11.75, 17.28, 83.18, 95.43; ^{29}Si NMR ($CDCl_3$) δ −22.86; IR (neat) 3290, 2947, 2895, 2868, 2039, 1463, 1385, 1367, 1340, 1242, 997, 883, 683 cm^{-1}.

Synthesis of Perisopropylsilapericyclynes: To a solution of i-$Pr_2Si(C{\equiv}CH)_2$ (776 mg, 4.7 mmol) in 60 mL of THF, 6.0 mL of BuLi (1.57 M, hexane solution, 2.0 equiv) was added at −78 °C. After 2 h, the solution of dichlorodiisopropylsilane (874 mg, 1.0 equiv) in ether (2 mL) was added dropwise and the solution was warmed to room temperature. After stirring for 2 h, the mixture was washed with aqueous NH_4Cl, and the aqueous layer was extracted with ether, and the combined organic phase was dried over anhydrous $MgSO_4$. After filtration and evaporation, the crude mixture was passed through a short silica-gel column with hexane as eluent. Crystallization of the mixture from THF and MeOH gave (i-$Pr_2SiC{\equiv}C)_6$ **1** as colorless solid. The filtrate was separated by recycle-type GPC (JAIgel 2H + 2H, $CHCl_3$) and HPLC (5-ODS-H, MeOH/THF = 9/1), and **1**, (i-$Pr_2SiC{\equiv}C)_8$ **2**, and (i-$Pr_2SiC{\equiv}C)_{10}$ **3**. The yield was 19%, 7%, and 2%, respectively. Spectral data of **1**: colorless plate, mp 81–82 °C; ^{1}H NMR ($CDCl_3$) δ 1.00 (sep, 12H, J = 6.7 Hz), 1.07 (d, 72H, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$) δ 12.31, 17.59, 109.23; ^{29}Si NMR ($CDCl_3$) δ −25.56; IR (KBr) 2945, 2929, 2866, 1461, 1385, 1366, 1240, 997, 881, 783 cm^{-1}; MS (70 eV) m/z (%) 828 (M^+, 8), 785 (100), 743 (91), 701 (27), 659 (10), 617 (6), 575 (4), 533 (4), 491 (3). Anal. Found: C, 68.54; H, 10.26%, and ash. Calcd for $C_{48}H_{84}Si_6$: C, 69.49; H, 10.20%. Spectral data of **2**, colorless plate, mp 59–60 °C; ^{1}H NMR ($CDCl_3$) δ 0.99 (sep, 16H, J = 7.1 Hz), 1.07 (d, 96H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 12.17, 17.53, 109.34; ^{29}Si NMR ($CDCl_3$) δ −25.26; IR (KBr) 2945, 2928, 2866, 1464, 1381, 1364, 1238, 995, 883, 781 cm^{-1}; MS (70 eV) m/z (%) 1104 (M^+, 11), 1061 (100), 1020 (28), 977 (8), 906 (5), 843 (20), 509 (31). Anal. Found: C, 67.75; H, 10.19%, and ash. Calcd for $C_{48}H_{84}Si_6$: C, 69.49; H, 10.20%. Spectral data of **3**, colorless plate, mp 51–52 °C; ^{1}H NMR ($CDCl_3$) δ 1.00 (sep, 20H, J = 6.8 Hz), 1.07 (d, 120H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 12.16, 17.50, 109.40; ^{29}Si NMR ($CDCl_3$) δ −25.08; IR (KBr) 2945, 2928, 2864, 1462, 1383, 1364, 1238, 991, 881, 783 cm^{-1}. Anal. Found: C, 68.84; H, 10.23%, and ash. Calcd for $C_{48}H_{84}Si_6$: C, 69.49; H, 10.20%.

Synthesis of *i*-Pr/Me-silapericyclynes: A solution of BuLi in hexane (1.57 M, 6.0 mL) was added dropwise to a solution of diethynyldiisopropylsilane (771 mg, 4.7 mmol) in THF (60 mL) at −78 °C. Dichlorodimethylsilane (607 mg, 4.7 mmol) was added to the solution, and the solution was warmed to room temperature. After 5 h, the reaction mixture was washed with saturated NH_4Cl aq. The aqueous layer was extracted with diethyl ether, and then dried over anhydrous magnesium sulfate. After workup, methanol was added to reaction mixture for the removal of the polymeric by-product. Separation by recycle-type HPLC (ODS, MeOH/THF = 7/3) gave (i-$Pr_2SiC{\equiv}CMe_2SiC{\equiv}C)_3$ (**4**) and [(i-Pr_2-$SiC{\equiv}CMe_2SiC{\equiv}C)_4$ (**5**) as colorless crystals. (**4**: 134 mg, 13%, **5**: 112 mg, 11%). Spectral data of **4**, colorless plate, mp 119–120 °C; ^{1}H NMR ($CDCl_3$) δ 0.31 (s, 18H), 0.95–1.02 (overlap, m, 6H), 1.06 (d, 36H, J = 6.4 Hz). ^{13}C NMR ($CDCl_3$) δ 0.12, 12.12, 17.53, 108.00, 112.38; ^{29}Si NMR ($CDCl_3$) δ −41.47, −25.14. IR (KBr) 2949, 2895, 2866, 1466, 1406, 1385, 1366, 1250, 921, 831 cm^{-1}; MS (70eV) m/z (%) 660 (M^+, 20), 645 (1), 617 (100), 603 (1), 575 (46); Anal. Found: C, 65.25; H, 9.10%. Calcd for $C_{36}H_{60}Si_6$: C, 65.38; H, 9.14%. Spectral data of **5**, colorless plate, mp 118–119 °C; ^{1}H NMR ($CDCl_3$) δ 0.32 (s, 24H), 0.95–1.02 (overlap, m, 8H), 1.06 (d, 48H, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 0.04, 12.12, 17.54, 108.01, 112.38; ^{29}Si NMR ($CDCl_3$) δ −41.72, −25.07; IR (KBr) 2947, 2895, 2866, 1466, 1406, 1385, 1367, 1254, 924, 827 cm^{-1}; MS (70eV) m/z (%) 880 (M^+, 20), 837 (100), 795 (33), 753 (13), 711 (6), 669 (4). Anal. Found: C, 65.20; H, 8.87%. Calcd for $C_{48}H_{80}Si_8$: C, 65.38; H, 9.14%.

X-ray Crystallography of 1 (General Procedure): A colorless plate crystal was mounted on a capillary, and measured by a Rigaku RAXIS-IV imaging plate diffractometer with Mo-$K\alpha$ radiation (λ = 0.71070 Å) at −100 ± 1 °C. The data were corrected for Lorenz and polarization effects. A correction for secondary extinction was applied. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on reflections ($I > 3\sigma(I)$) and converged.

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5 Dihedral angles are defined as the mean angles between two planes. In the case of planar, the dihedral angle is 180°. Compound **1** recrystallized from the other solvent also shows high planarity; the dihedral angle of **1**/benzene was 160.2°, and that of **1**/THF was 168.5°.

6 The result of semiempirical calculation (AM1) indicated that the favorable structure for **1** was planar, and bent structure for **4**.

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9 Estimation of the planarity can be made by the average deviation of each (silicon) atom from the mean plane of all silicon atoms. The values were **1**: 0.165(2) Å, **2**: 0.7522(8) Å, **3**: 0.436(2) Å, **4**: 0.965(1) Å, and **5**: 1.108(4) Å.

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