Bull. Chem. Soc. Jpn., ***78***, *393–404 (2005)*

Award Accounts

The Chemical Society of Japan Award for Young Chemists for 2003

Novel Stable Silicon-Based π-Electron Systems: Synthesis, Unique Structure, and Properties of Cyclic, Spiroconjugated, and Cumulative Silicon–Silicon Doubly-Bonded Compounds

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In this account, the synthesis, structure, and reactions of cyclic, spiro-conjugated, and cumulative silicon–silicon doubly-bonded compounds are described. Photochemical and thermal interconversion among Si_4R_6 isomers including cyclotetrasilene **1**, cyclotrisilene **2**, and bicyclo[1.1.0]tetrasilane **7** occur without apparent participation of the corresponding tetrasila-1,3-diene, in contrast to the related interconversion among C_4H_6 isomers. Whereas parent spiropentadiene, the simplest spiroconjugation system, is known to survive only below -100 °C, spiropentasiladiene **3** is thermally very stable and shows remarkable spiroconjugation between the two ring π systems. The skeleton of isolable trisilaallene **4**, the first stable silicon compound with tetracoordinate divalent (formally sp-hybridized) silicon atom, is not linear but remarkably bent. The considerable conjugation between two cumulative Si=Si double bonds was observed. The structural feature of **4** is quite different from that of carbon-based allenes having linear structure without conjugation between two π-bonds.

Organic π-electron systems have been extensively studied for a long time. They have recently been used for functional organic materials such as organic magnets, semi- and superconductors, chemical sensors, and non-linear optical devices. The fascinating properties of the organic π-electron systems would be attributed in part to their structural diversity. Therefore, the syntheses of organic π-electron systems with new structures, analyses of their properties, and their applications to functional materials have been continuously studied.

In contrast to the organic π-electron systems, the number and structural diversity of the silicon–silicon doubly-bonded compounds (disilenes) as well as silicon–carbon doubly-bonded compounds (silenes) are quite limited.[1] These multiply-bonded silicon compounds are generally known as reactive intermediates with an inherent tendency to readily undergo oligomerization or reactions with other molecules such as oxygen and water under ambient conditions, primarily due to the poor π overlap of more diffused 3p orbitals compared to the 2pπ–2pπ overlap of ethylene. Therefore, they were not obtained as isolable compounds until about 25 years ago.[2,3] Since the first isolations of a stable disilene by West[4] and of a silene by Brook[5] (Chart 1) using bulky substituents as steric protecting groups (so-called "kinetic stabilization") in 1981, the chemistry of the stable unsaturated (or low-coordinate) silicon compounds has been rapidly explored. However, until the mid 1990s, the types of isolated disilenes were still confined to acyclic disilenes including only one silicon–silicon double bond, with limited kinds of substituents such as bulky aryl and alkyl groups.

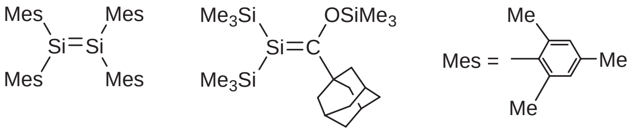
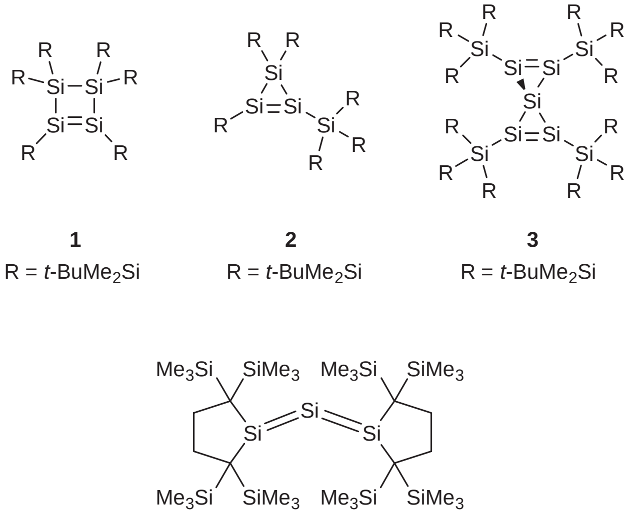


Chart 1.

In 1994, stable tetrakis(trialkylsilyl)disilenes and their germanium analogues were synthesized as the first persilyl-substituted Si=Si and Ge=Ge doubly-bonded compounds.[6,7] These materials conveyed the unique steric and electronic substituent effects of trialkylsilyl groups on the structure, properties, and reactivities of the Si=Si and Ge=Ge double bonds.[8] During the course of our study on the stable disilenes, we successfully synthesized a silicon analog of cyclobutene, cyclotetrasilene **1**[9] as the first stable cyclic disilene,[10,11] and then, cyclotrisilene **2**[12] as the first silicon analog of cyclopropene (Chart 2). A unique interconversion between Si_4R_6 isomers, which was quite different from that between C_4H_6 systems, was revealed. The synthesis of stable spiropentasiladiene **3**[13] was achieved as the first isolable spiropentadiene derivative of group-14 elements and the spiroconjugation of spiropentadiene systems was disclosed. Furthermore, we synthesized trisilaallene **4**[14]

Published on the web March 11, 2005; DOI 10.1246/bcsj.78.393



1 R = *t*-BuMe$_2$Si

2 R = *t*-BuMe$_2$Si

3 R = *t*-BuMe$_2$Si

4

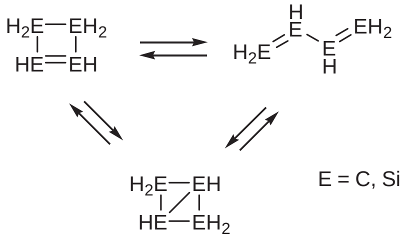
Chart 2.

as the first cumulative silicon–silicon doubly-bonded compound and the first stable compound with a tetravalent dicoordinate silicon atom (formally sp-hybridized silicon atom). Trisilaallene **4** showed quite different structure and electronic properties from those of carbon-based allenes. In this account I summarize our recent results on the chemistry of these silicon–silicon doubly-bonded compounds **1**–**4** as novel silicon-based π-electron systems.

1. Cyclic Disilenes

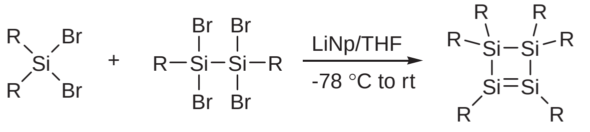
Cyclotetrasilene is one of the most interesting compounds among cyclic disilenes, because the thermal and photochemical interconversions among the Si_4R_6 derivatives including cyclotetrasilene, bicyclo[1.1.0]tetrasilane, and tetrasila-1,3-butadiene (Scheme 1, E = Si) are expected to constitute an interesting chemistry as the silicon version of the well-studied chemistry of C_4H_6 derivatives (cyclobutene, bicyclobutane, and butadiene, E = C).[15] In this section, the synthesis, structure, and reactions of a stable cyclotetrasilene, cyclotrisilene, and of related compounds are discussed.

1.1 Synthesis. The first cyclic disilene, hexakis(*tert*-butyldimethylsilyl)cyclotetrasilene **1**, was synthesized in 14% yield by the reductive condensation of the corresponding dibromosilane **5** and tetrabromodisilane **6** having bulky *tert*-butyldimethylsilyl substituents with lithium naphthalenide (Scheme 2).[9] Compound **1** is air-sensitive but has thermally very stable bright orange crystals (mp 263–265 °C). Interestingly, the mixture of **5** and **6** reduced by lithium naphthalenide at −78 °C was hydrolyzed at 0 °C to afford mainly *cis*-hydroxycyclotetrasilane **8**, that is a hydrolysis product of bicyclo[1.1.0]tetrasilane **7** (a valence isomer of **1**) (Scheme 3). The results indicate that the initial product of the reductive condensation was not **1** but **7** that converts to **1** at room temperature. Details of the thermal conversion from **7** to **1** will be mentioned in section 1.4.



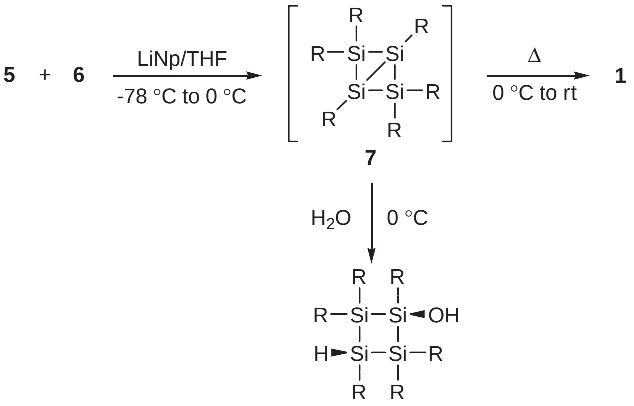
E = C, Si

Scheme 1.



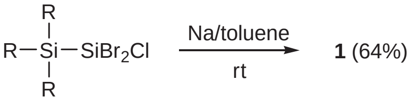
5 **6** **1** (14%) R = *t*-BuMe$_2$Si

Scheme 2.



7 **8**

Scheme 3.

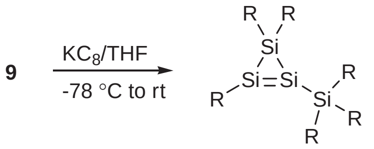


9 R = *t*-BuMe$_2$Si

Scheme 4.

To improve the yield of cyclic disilene **1**, we developed tris(*tert*-butyldimethylsilyl)silyl-substituted dibromochlorosilane **9** as a new precursor for **1**. Reductive dehalogenation of **9** using sodium dispersion in toluene at room temperature provided **1** in 64% yield (Scheme 4).[12] Interestingly when **9** was reduced by potassium graphite (KC_8), the major product was not **1** but cyclotrisilene **2**, which was isolated as air-sensitive dark red crystals in 67% yield (Scheme 5). Compound **2** was the first example of a three-membered disilene.

1.2 Molecular Structure. Bright orange prisms of cyclotetrasilene **1** suitable for a single-crystal X-ray diffraction study were obtained by recrystallization from heptane. The molecular structure of cyclotetrasilene **1** is shown in Fig. 1. The silicon–silicon double-bond length is 2.174(4) Å, which is shorter than those of tetrakis(trialkylsilyl)disilenes (2.202–2.251 Å)[6] and diiodotetrakis(tri-*tert*-butylsilyl)cyclotetrasilene (2.257(2) Å) reported by Wiberg.[16] The Si3–Si4 single bond opposite to Si=Si double bond (2.450 Å) is unusually longer



2 (67%)
R = t-BuMe$_2$Si

Scheme 5.

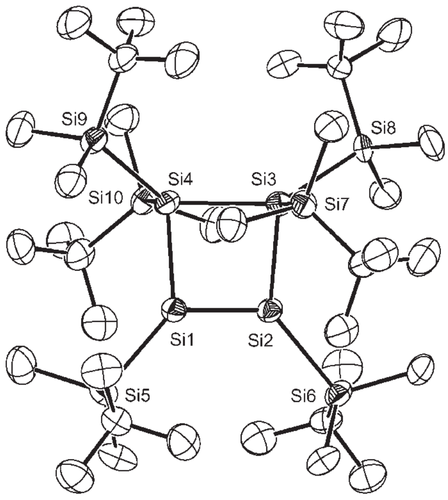
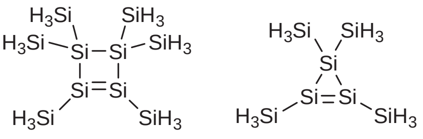


Fig. 1. Molecular structure of cyclotetrasilene **1**.



10 **13**

Chart 3.

than the typical Si–Si single bond length of cyclic oligosilanes (av. 2.372 Å).[17] The four-membered ring is not planar but is folded with out-of-plane angles of about 37°. The silicon–silicon double bond adopts a slight twist arrangement. The twist angle θ defined by the dihedral angle between two Si(sp^3)–Si(sp^2)–Si(sp^3) planes is 12.3°. A model compound hexakis(trihydrosilyl)cyclotetrasilene (**10**, Chart 3) optimized at the B3LYP/6-31G(d) level has a C_{2v} symmetry and its four-membered ring and Si=Si double bond are planar. Steric repulsion between vicinal *tert*-BuMe$_2$Si groups on Si3 and Si4 would be the major reason for the folding of the four-membered ring, the long Si3–Si4 bond, and also for the deformation of the Si=Si double bond.

Recrystallization of cyclotrisilene **2** from hexane at room temperature afforded dark red prisms suitable for a single-crystal X-ray diffraction study (Fig. 2).[18] Data collection was carried out at 230 K because the single crystal of **2** cracked below 230 K. The Si=Si double-bond distance in **2** is 2.132(2) Å, which is similar to the bond distances of the known three-membered disilenes, tetrakis(di-*tert*-butylmethylsilyl)cyclotrisilene (**11**) (2.138(4) Å)[19] and tetrakis(di-*tert*-butylmethylsilyl)-1-disilagermirene **12** (2.146(1) Å),[20] reported by Sekiguchi et al. Two unsaturated silicon atoms in **2** adopt different geometries. The unsaturated silicon atom Si1 bound to a *tert*-BuMe$_2$Si group is slightly pyramidalized, whereas the silicon atom Si2 bound to (*tert*-BuMe$_2$Si)$_3$Si group is planar. The sums of angles around the unsaturated silicon atoms are 356.7° for Si1 and 360.0° for Si2, and the dihedral angle Si6–Si2–Si1–Si10 was 21.4(2)°. Since the optimized structure of a model tetrakis(trihydrosilyl)cyclotrisilene (**13**, Chart 3) calculated at the B3LYP/6-31G(d) level has C_{2v} symmetry with a planar Si=Si double bond,[13] pyramidalization at Si1 atoms in **2** would be mainly due to steric repulsion among substituents. In accord with the steric hindrance between substituents on Si2 and Si3 being heavier than that between substituents on Si1 and Si3, the Si2–Si3 bond (2.339(2) Å) is a little longer than the Si1–Si3 bond (2.327(2) Å).

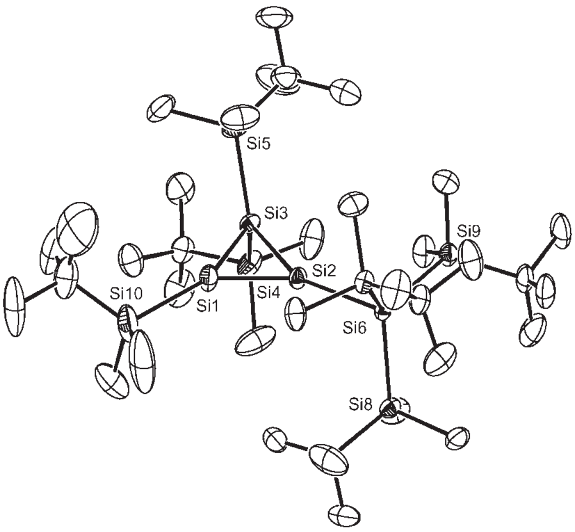


Fig. 2. Molecular structure of cyclotrisilene **2**.

1.3 ^{29}Si NMR and UV–Vis Spectra. The ^{29}Si resonance of the unsaturated silicon atoms (δ(Si$_u$)) in cyclotetrasilene **1** (160.4 ppm) is a little lower than that in the acyclic tetrakis(*tert*-butyldimethylsilyl)disilene (142.1 ppm),[6] whereas the δ(Si$_u$) of cyclotrisilene **2** (+81.9 and +99.8 ppm) as well as **11** (+97.7 ppm) are significantly higher than those for the acyclic disilenes. The tendency of the δ(Si$_u$) values among **2**, tetrasilyldisilene, and **1** is quite parallel to that of the chemical shifts of the unsaturated carbons (δ(C$_u$)) among cyclopropene (108.7), ethylene (123.5), and cyclobutene (137.2).[21] The δ(Si$_u$) of cyclooligosilenes and δ(C$_u$) of the corresponding cycloalkenes would have the same origin.

Cyclotetrasilene **1** and cyclotrisilene **2** showed characteristic π–π^* transition bands ($\lambda_{\max}$/nm (ε) 465 (6800) for **1** and 482 (2600) for **2**). Although both maxima are red-shifted compared with that of the corresponding tetrakis(*tert*-butyldimethylsilyl)disilene ($\lambda_{\max}$ 424 nm),[6] the extent of the red-shift is larger in **2** due to the greater ring strain. The π–π^* absorption band maximum of cyclotrisilene **2** appeared at much longer wavelength with larger absorption coefficient than **11** ($\lambda_{\max}$/nm (ε) 466 (440))[19] suggesting significant conjugation between π-orbital of the Si=Si double bond and the σ(Si–Si)-orbitals in a tris(*tert*-butyldimethylsilyl)silyl substituent in **2**.

1.4 Interconversion among Si$_4$R$_6$ Isomers. Cyclotetrasilene **1** showed an interesting photochromic behavior. Upon irradiation of cyclotetrasilene **1** in 3-methylpentane with a high-

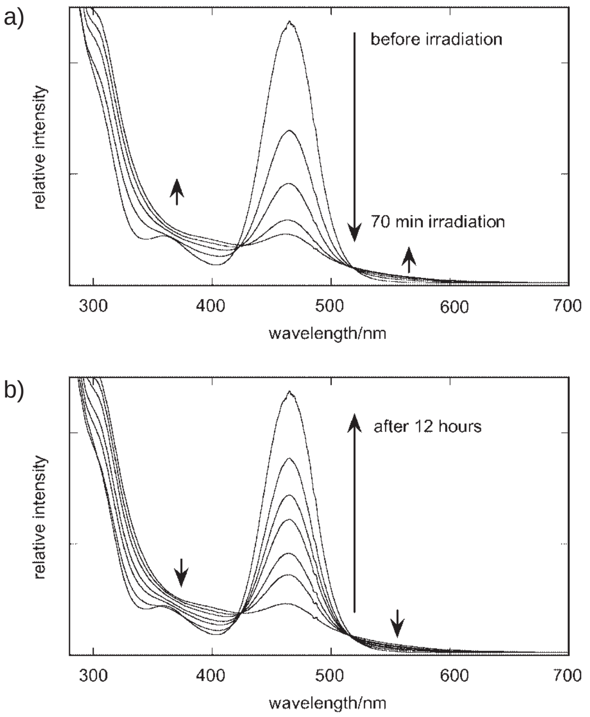
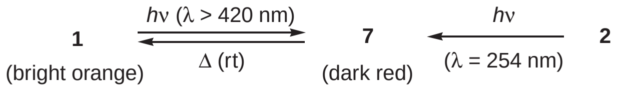
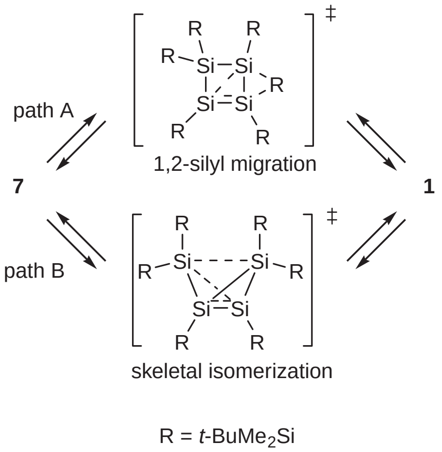


Fig. 3. Photochemical and thermal conversion between cyclotetrasilene **1** and bicyclotetrasilane **7** monitored by UV–vis spectroscopy: (a) photolysis of **1**, (b) thermal conversion from **7** to **1**.

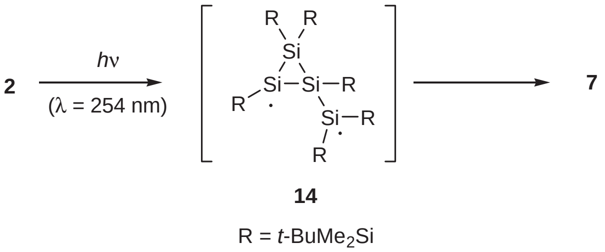


Scheme 6.

pressure Hg arc lamp (λ > 420 nm) at 288 K, the color of the solution turned from the original bright orange to dark red. The photolysis of **1** gave a 1:9 mixture of **1** and bicyclo[1.1.0]tetrasilane **7** at the photostationary state as determined by UV–vis spectroscopy (Fig. 3). When the mixture was left for 12 h in the dark at room temperature, the color of the mixture turned again to bright orange and **1** was reproduced quantitatively (Scheme 6). The photochemical conversion of **1** to **7** and the thermal reversion were able to be repeated more than ten times without any appreciable side reactions. The first-order rate and the activation parameters for the thermal isomerization of **7** to **1** were determined: $k = 5.67 \times 10^5$ s^{-1} at 288 K, $\Delta H^{\ddagger} = 16.5$ kcal•mol^{-1}, $\Delta S^{\ddagger} = -20.8$ cal•mol^{-1}•K^{-1}. The large negative $\Delta S^{\ddagger}$ value suggests that the transition-state structure of the thermal isomerization would be significantly restricted. There are two possible pathways for the isomerization of **7** to **1**, as shown in Scheme 7: a concerted or a step-wise isomerization involving 1,2-silyl migration accompanied by cleavage of the central bridge Si–Si bond of **7** (path A) and a concerted skeletal isomerization (path B). By labeling the two R groups (R = *tert*-BuMe$_2$Si) on bridgehead silicon atoms of **7** by two R* groups (R* = *tert*-Bu(CD$_3$)$_2$Si), the thermal isomerization from **7** to **1** was confirmed to proceed via 1,2-silyl migration (path A).[9b] Müller revealed by DFT calculations that the 1,2-hydrogen migration from parent bicyclo[1.1.0]tetrasilane to cyclotetrasilene is a more favorable process than the multi-step mechanism including tetrasila-1,3-diene.[22] By similar labeling experiments, the photochemical isomerization of **1** to **7** was also found to proceed via 1,2-silyl migration.



Scheme 7.

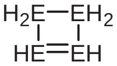
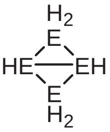
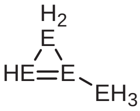
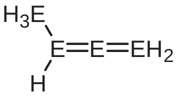


Scheme 8.

Cyclotrisilene **2**, which is also one of the isomers of **1** and **7**, shows interesting photochemical isomerization. When a dark red toluene-d_8 solution of **2** was irradiated using a low-pressure mercury-arc lamp ($\lambda = 254$ nm) at 243 K, the solution turned gradually dark brown. After 70 min irradiation, the ^{1}H NMR spectrum of the mixture showed the complete consumption of cyclotrisilene **2** together with the formation of the corresponding bicyclo[1.1.0]tetrasilane **7** (ca. 90% yield) (Scheme 6). The photochemical isomerization of cyclotrisilene **2** is rationalized by a mechanism including 1,2-silyl migration as proposed for the isomerization of cyclotetrasilene **1**[9] and disilagermirene **12**.[20] The formation of an intermediate 1,3-silyl biradical **14** via 1,2-migration of a trialkylsilyl group, followed by intramolecular radical recombination, affords **7**. In contrast to the clean photolysis of **2**, thermolysis of **2** at 423 K gave a mixture of unidentified products (Scheme 8).

In these isomerizations of Si$_4$R$_6$ systems, we found no evidence for the participation of the corresponding tetrasila-1,3-diene and tetrasila-1,2-diene. Alkylcyclopropenes are known to give the ring opening products such as allenes and/or butadienes during photolysis,[23] whereas thermolysis of bicyclo[1.1.0]butane gives 1,3-butadiene rather than cyclobutene.[24] The absence of the corresponding 1,3- and 1,2-dienes in the Si$_4$R$_6$ interconversion would result from their high thermal instability. At the B3LYP/6-311+G(d,p) level with ZPE correction, transoid- and cisoid-tetrasila-1,3-dienes and tetrasila-1,2-diene were calculated to be 33.3, 34.2, and 21.7 kcal/mol

Table 1. Relative Energy among Si_4H_6 Isomers (kcal/mol)[a,b]

E					
C	14.8	31.1	32.4	0.0 (transoid) 3.5 (cisoid)	9.4[c)]
Si	3.0	0.0	21.6	33.3 (transoid) 34.2 (cisoid)	21.7[c)]

a) Ref. 25. b) At the B3LYP/6-311+G(d,p) level with ZPE correction. c) Ref. 22.

higher in energy, respectively, than parent bicyclo[1.1.0]tetrasilane (Table 1).[22,25] Interestingly, the relative energy for 1-silylcyclotrisilene (21.6 kcal/mol) is rather high and the value is comparable to that for tetrasila-1,2-diene at the same level. In sharp contrast, buta-1,3-diene is the most stable isomer among C_4H_6 isomers; 1-methylpropa-1,2-diene, 1-methylcyclopropene, and bicyclo[1.1.0]butane are 9.4, 32.4, and 31.1 kcal/mol lower in energy, respectively, than buta-1,3-diene at the same level. The relative stabilities among Si_4H_6 isomers are remarkably different from those among C_4H_6 isomers. The difference in relative energy should be responsible in part for the apparent differences in the interconversion mode between two sets of M_4R_6 isomers (M = C and Si).

2. Spiropentasiladiene

Conjugation between π-bonds (π-conjugation) plays very important roles in developing the useful properties and functionality in organic materials. In contrast, very few investigations on conjugations between silicon–silicon double bonds have been reported. An isolable tetrasilabutadiene prepared by Weidenbruch et al. has *s*-cis butadiene structure with two Si=Si double bonds that adopt a twist conformation.[26–28] Absorption bands of the compound were significantly red-shifted compared to the related disilenes, suggesting conjugation between the two Si=Si double bonds. We were able to isolate a silicon version of spiropentadiene as the first spiroconjugated disilene and to evaluate the conjugation between their two Si=Si double bonds.

2.1 Synthesis. When we investigated the reactivity of cyclotrisilene **2** toward alcohols, a very small amount of a dark red compound remained together with the ethanol adduct of **2** in the reaction mixture. Detailed analysis of the product as well as the preparation reaction of **2** shown in Scheme 5 revealed that tetrakis[tris(*tert*-butyldimethylsilyl)silyl]spiropentasiladiene **3** formed in 3.5% yield together with cyclotrisilene **2** in the reduction of **9** with KC_8.[13] The quite low solubility of **3** toward usual organic solvents made it possible for us to isolate **3** by careful recrystallization. The parent spiropentadiene **15a** and its chloro derivative **15b** (Chart 4) were not able to be isolated because of their thermal instability.[29] Compound **3** is the first example of isolable spiropentadiene comprising group-14 elements.

2.2 Molecular Structure. X-ray single-crystal analysis reveals that spiropentasiladiene **3** is a nano-sized molecule with twenty-one silicon atoms and has a long axis of more than 1.5 nm (Fig. 4a). In the solid state, the silicon skeleton of **3** has nearly D_2 symmetry (Figs. 4b and 4c); the two three-membered rings in **3** are not perpendicular to each other but are slightly twisted with a dihedral angle of 78.26° (Fig. 4c). The Si=Si double bond did not adopt a planar geometry, but was slightly twisted. The dihedral angle of Si2–Si1–Si6–Si7 was 30.0(5)° and the sums of bond angles around unsaturated atoms were 358.9° for Si1 and 358.0° for Si6, respectively. Optimized structure of a model tetrakis(trihydrosilyl)spiropentasiladiene **16a** has a D_{2d} symmetry with two three-membered ring perpendicular to each other and planar Si=Si double bonds. Deformation from the ideal D_{2d} to D_2 symmetry observed in the structure of spiropentasiladiene **3** would result from heavy steric repulsion between extremely bulky (*tert*-$BuMe_2Si)_3Si$ substituents.

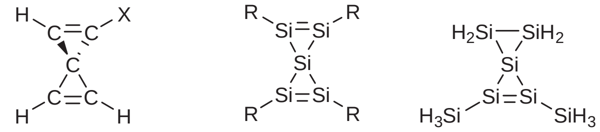

X = H (**15a**), Cl (**15b**)
R = SiH_3 (**16a**)
H (**16b**)
17

Chart 4.

The Si=Si double bonds (2.186(3) Å) and the single Si–Si bonds (2.320(2)–2.323(2) Å) in the three-membered ring of **3** are 0.05 Å longer and 0.03–0.04 Å shorter, respectively, than the corresponding bonds in cyclotrisilenes **2**[12] and **11**.[19] Since similar bond elongation and shortening were found in the model compound **16a** (D_{2d} symmetry, 2.168 Å for Si=Si double bond and 2.324 Å for endocyclic Si–Si bond) compared to **13** (C_{2v} symmetry, 2.136 Å for Si=Si double bond and 2.339 Å for endocyclic Si–Si bond), we can conclude that the modifications of the bond lengths in **3** as well as **16a** may result from effective interactions between the bonding π-orbital of a Si=Si bond and the low-lying Walsh-type σ* orbitals of Si–Si bonds in the other three-membered ring.[30]

2.3 Spiroconjugation in Spiropentasiladiene. Spiroconjugation is through-space interaction between two perpendicular π-type orbitals and has been theoretically well understood.[31] In spiropentadiene **15a**, the smallest spiroconjugation system, whereas interactions between bonding π-orbitals are symmetrically forbidden, those between antibonding π*-orbitals are allowed, resulting in two possible π–π* transitions (Fig. 5). By using isolable spiropentasiladiene **3**, we revealed the intrinsic spiroconjugation between two π* orbitals of the Si=Si double bond and the additional conjugation between two π-orbitals caused by the deformation of the silicon

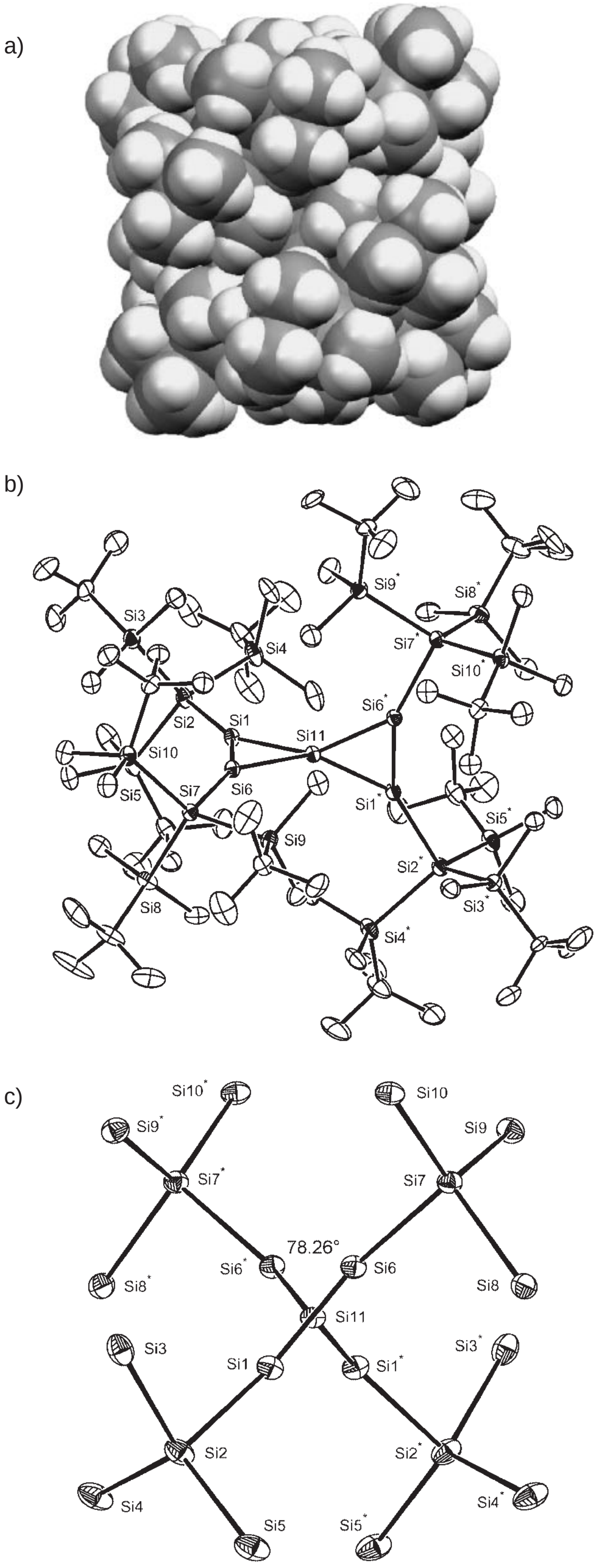


Fig. 4. Molecular structure of spiropentasiladiene **3**: (a) space-filling model, (b) whole molecules, and (c) a view along the axis through the centers of the Si=Si double bond. In (b) and (c), carbon and hydrogen atoms are omitted for clarity.

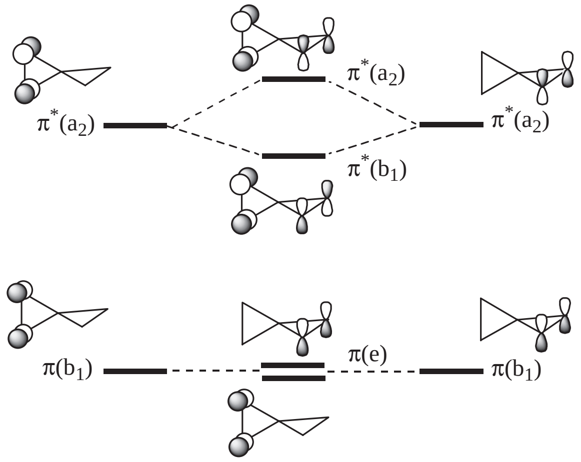


Fig. 5. Spiroconjugation of parent spiropentadiene **15a**.

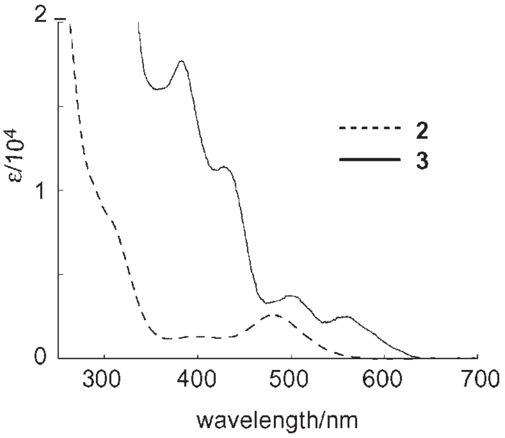


Fig. 6. UV–vis spectra of cyclotrisilene **2** and spiropentasiladiene **3** in 3-methylpentane.

skeleton.

The UV-spectrum of spiropentasiladiene **3** in 3-methylpentane was considerably different from that of cyclotrisilenes, **2** and **11** (Fig. 6). Spiropentasiladiene **3** showed four distinct absorption bands in the visible region ($\lambda_{\max}$/nm ($\varepsilon/10^4$) = 560 (0.253), 500 (0.364), 428 (1.17), 383 (1.81)). The longest absorption maximum at 560 nm was remarkably red-shifted compared to the π–π^* transition bands for **2** (482 nm)[12] and **11** (466 nm).[19] Although this red-shift indicated the existence of significant spiroconjugation between two perpendicular Si=Si double bonds, the number of absorption bands was not explained by the qualitative spiroconjugation model, where only the interaction between two π^*-orbitals is allowed (Fig. 5). The spectral pattern was qualitatively rationalized by the theoretical calculations for model compounds: spiropentasiladiene with D_{2d} symmetry **16b** (D_{2d}), and that with D_2 symmetry similar to those observed for **3** in the solid state **16b** (D_2). Molecular orbitals and their orbital energies at the B3LYP/6-311++G(3df,2p) level are shown in Fig. 7. As expected for spiropentadiene, compound **16b** (D_{2d}) was calculated to have two split π^* orbitals (b_1 and a_2) and two degenerate π orbitals (Fig. 7, left). Large separation between two π^* orbital levels indicates the existence of considerable through-space interaction between the two π^* orbitals. Interestingly,

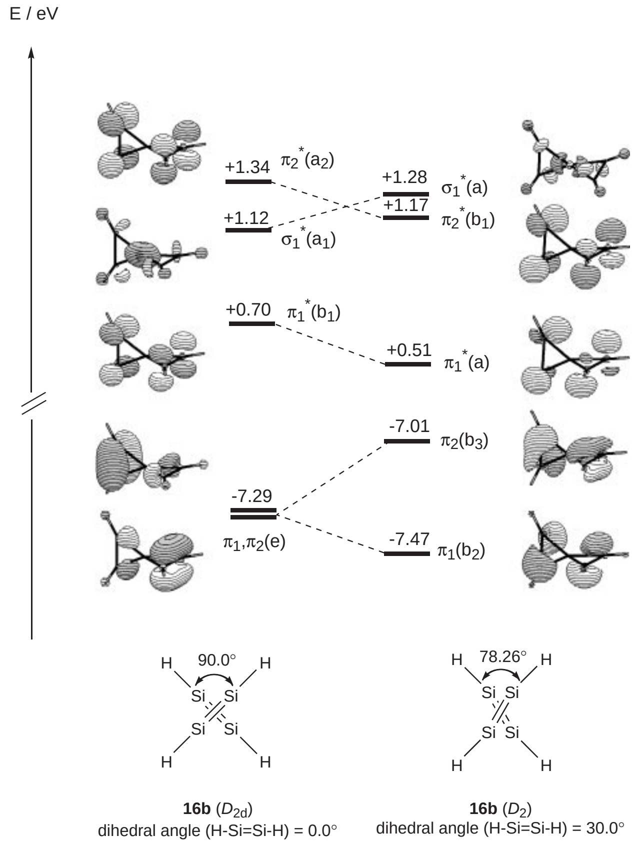


Fig. 7. Schematic molecular orbital diagram for parent spiropentasiladiene **16b** (D_{2d}) and distorted **16b** (D_2) at the HF/6-311++G(3df,2p)//B3LYP/6-31G(d) level.

when the distortion of silicon skeleton observed in **3** was introduced to the model compound **16b**, the degeneracy of bonding π orbitals was removed by through-space interaction between the two π-orbitals, as shown in distorted spiropentasiladiene **16b** (D_2) (Fig. 7, right). The through-space interactions between π^* orbitals as well as between π orbitals found in distorted spiropentadiene **16b** (D_2) may cause the splitting of the low-energy absorption bands and the red-shift of the longest wavelength band, as observed experimentally in spiropentasiladiene **3**. Interestingly, model compound **16b** (D_2) is only 1.8 kcal/mol less stable than **16b** (D_{2d}), indicating that spiropentasiladiene has a shallow potential surface concerning the deformation of the silicon skeleton, as mentioned above.

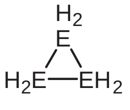
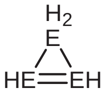
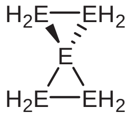
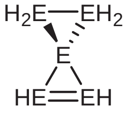
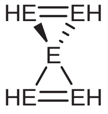
The ^{29}Si resonance of the unsaturated silicon atoms (δ(Si$_u$)) in spiropentasiladiene **3** appeared at +154.0 ppm, shifted to a lower field by +60 ppm compared with those in cyclotrisilenes **2** (+81.9 and +99.8 ppm) and **11** (+97.7 ppm). The δ(Si$_u$) values were also well reproduced in the pertinent model compounds by DFT calculations; the resonances were +178.3, +105.3, and +110.1 ppm for **16a** (D_{2d}), spiropentasilene **17** (C_{2v}, Chart 4), and cyclotrisilene **13** (C_{2v}), respectively, at the GIAO/B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d) level. Because the δ(Si$_u$) in various disilenes are related to the reciprocal of the energy differences between σ and π^* orbitals of the Si=Si bond,[32] the remarkable lower-field shift of δ(Si$_u$) in **3** may be the evidence for the through-space interaction between π^* orbitals. Unfortunately, the resonance due to the central ^{29}Si nucleus in **3** was not experimentally observed. The corresponding resonance in **16a** (D_{2d}) was evaluated at −45.9 ppm by the GIAO calculations.

2.4 Strain Energy of Cyclic Disilenes. In sharp contrast to the thermal instability of spiropentasiene, spiropentasiladiene **3** is very stable with a melting point of 216–218 °C, probably in part due to steric protection by four extremely bulky tris(*tert*-butyldimethylsilyl)silyl groups. Theoretical calculations showed that one of the major factors of the thermal stability of **3** is the small strain energy (SE) of the ring system.

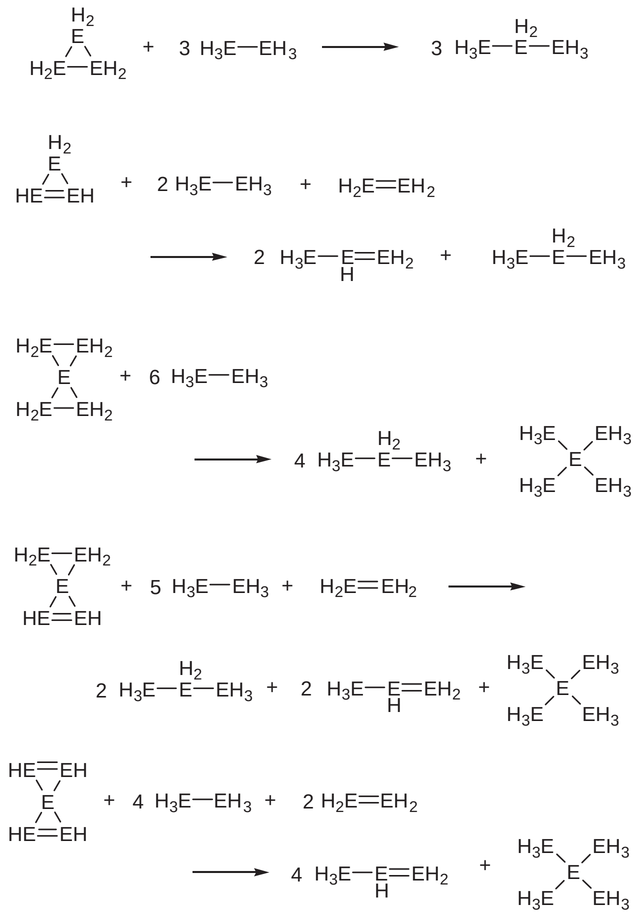
The SE values of parent cyclopropane, cyclopropene, spiropentane, spiropentene and spiropentadiene, and their silicon analogues were calculated as the heats of the homodesmotic reactions[33] as shown in Table 2 and Scheme 9 (B3LYP/6-311++G(3df,2p)//B3LYP/6-31G(d) level). The strain energy calculated for parent spiropentasiladiene Si_5H_4 with D_{2d} symmetry was 61.1 kcal/mol. This SE value is much smaller than that of the corresponding carbon-based spiropentadiene (D_{2d}, 114.2 kcal/mol).

Interestingly, the SE value of cyclopropene (55.5 kcal/mol) is more than twice as large as that of cyclopropane (25.8 kcal/mol), whereas the SE value of cyclotrisilene (34.6 kcal/mol) is comparable to that of cyclotrisilane (35.4 kcal/mol). In other words, introduction of the C=C double bond into the carbon-based three-membered ring increases remarkably the SE value, while introduction of the Si=Si double bond into the silicon-based three-membered ring causes no considerable change of the SE value. Recently, Inagaki et al. carried out the detailed theoretical studies of the ring strains of cycloalkenes and their silicon analogs. They found that the ring strain is relaxed by the cyclic orbital interaction between a π-orbital and a σ^*-orbital on the saturated atoms in the rings. While the three-, four-, and five-membered silicon rings are considerably stabilized by the cyclic interaction, the stabilization is less significant for the hydrocarbons.[34]

Table 2. Strain Energies (SE) of Cyclic Disilenes (kcal/mol)[a,b)]

E					
C	25.8	55.5	55.4	85.7	114.2
Si	35.4	34.6	63.9	68.3	61.1

a) All strain energies were obtained using homodesmic reactions. b) SE were estimated at the B3LYP/6-311++G(3df,2p)//B3LYP/6-31G(d) level.



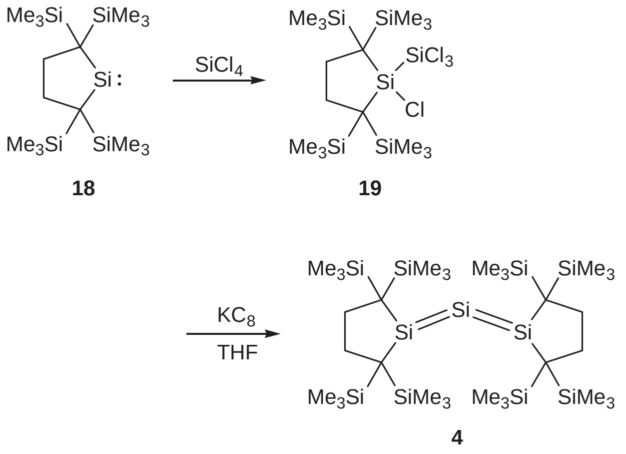
E = C, Si

Scheme 9.

3. Trisilaallene

Tetravalent dicoordinate carbon atoms (sp-hybridized carbon atoms) are often found in triply-bonded compounds such as acetylenes and nitriles and cumulative doubly-bonded compounds like carbon dioxide, ketenes, and allenes. Although the germanium,[35] tin,[36] and lead[37] analogs of acetylene and a tristannaallene[38] have recently been isolated, their silicon analogs have seldom been reported. Trapping of transient X=Si=X species[39] and evidence of the existence of silicon analogues of acetylene in solution[40] have been reported.[41] We successfully synthesized an isolable trisilaallene **4** as the first compound with tetravalent dicoordinate (formally sp-hybridized) silicon atom and the first cumulative silicon–silicon doubly-bonded compound.[42]

3.1 Synthesis. Isolable trisilaallene **4**[14] was prepared using isolable dialkylsilylene **18** as a starting material.[43] 1,1,1,2-Tetrachlorodisilane **19**, which was prepared by the insertion of silylene **18** into the Si–Cl bond in $SiCl_4$,[44] was reduced by potassium graphite to give **4** in good yield (Scheme 10). Trisilaallene **4** is air-sensitive but thermally very stable dark green crystals (mp 198–200 °C).



Scheme 10.

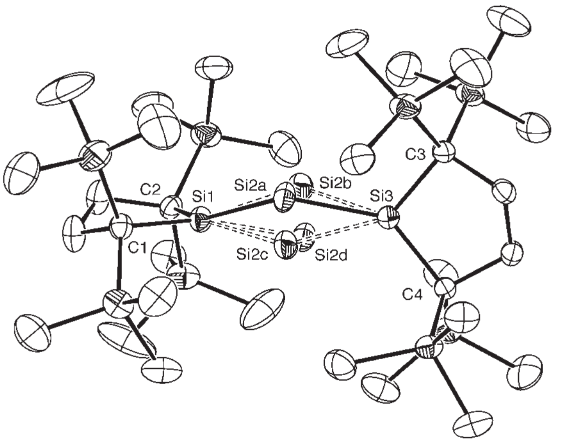


Fig. 8. Molecular structure of trisilaallene **4**.

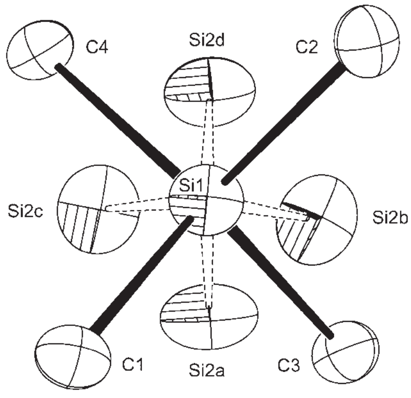
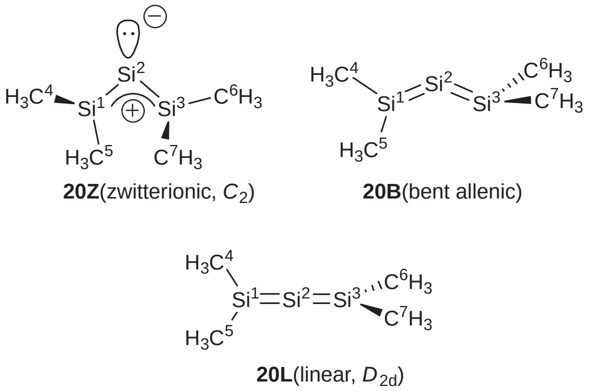


Fig. 9. A view along the axis through terminal Si1 and Si3 atoms of trisilaallene **4**.

3.2 Molecular Struture of Trisilaallene. X-ray single crystal analysis revealed quite unusual structural characteristics of trisilaallene **4** (Figs. 8 and 9). In contrast to carbon allenes, the trisilaallene skeleton does not adopt a linear structure but rather a bent structure. The central tetravalent dicoordinate silicon atom (Si2) in the crystal was found at four positions labelled Si2a to Si2d in Fig. 8 with different occupancy factors at 223 K. As shown in Fig. 9, Si2a–Si2d are in four quadrants divided by two perpendicular planes of C1–Si1–C2 and C3–Si3–C4, respectively. The environments of the four quadrants are slightly different owing to the non-planarity of the terminal silicon atoms Si1 and Si3 (vide infra), resulting

Table 3. Temperature-Dependent Site Occupancy Factor of Si2a–Si2d in **4**

Crystal	Tempeature/K	Site occupancy factor			
		Si2a	Si2b	Si2c	Si2d
1	123.0	0.755(2)	0.175(2)	0.070(2)	0.0
2	127.1	0.716(3)	0.185(3)	0.099(2)	0.0
2	173.0	0.606(3)	0.208(3)	0.150(3)	0.036(3)
1	223.0	0.528(3)	0.220(3)	0.186(3)	0.065(2)
2	223.0	0.517(3)	0.222(3)	0.194(3)	0.067(2)
2	273.0	0.460(3)	0.228(3)	0.217(3)	0.095(3)



20Z(zwitterionic, C_2)

20B(bent allenic)

20L(linear, D_{2d})

Chart 5.

Table 4. Selected Structural Parameters of Si_3Me_4 Derivatives **20**[a)]

Compound	Distance/Å	Angles/deg	Dihedral angle/deg		$\delta(^{29}Si)$[b)]		Relative energy /kcal mol^{-1}
	Si^1–Si^2, Si^2–Si^3	Si^1–Si^2–Si^3	C^4–Si^1–Si^3–C^6	C^5–Si^1–Si^3–C^7	Si^1 (Si^3)	Si^2	
20Z (C_2)	2.246, 2.246	92.44	−50.7	−35.7	354.8	38.7	0.0
20B	2.187, 2.177	136.45	−79.1	−94.0	212.1, 220.6	143.8	+8.8
20L (D_{2d})	2.128, 2.128	180.0	−90.0	−90.0	98.3	210.4	+16.3

a) Geometry was optimized at the B3LYP/6-31+G(d,p) level. b) GIAO/B3LYP/6-311+G(2df,p) level. c) HF/6-311+G(d,p)//B3LYP/6-31+G(d,p) level.

in slightly different occupancies of Si2a–Si2d. Interestingly, temperature-dependent X-ray analysis for two different single crystals of **1** showed that the populations for Sia to Sid are almost independent of crystals, but are significantly dependent on temperature: the populations are 46, 23, 22, and 10% at 273 K, but 76, 18, 7, and 0% at 123 K, respectively (Table 3). The energy differences between four positions are estimated to be within 1 kcal/mol. These phenomena would be explained by a dynamic disorder mediated by a rotation of the Si2 atom around the Si1–Si3 axis, as observed in single crystals such as azobenzene and stilbene.[45]

The structure including Si2a with the highest occupancy factor obtained at −150 °C should represent the most stable geometry of trisilaallene **4**. The Si1–Si2a–Si3 skeleton at −150 °C is remarkably bent, with the bent angle of 136.49(6)°, indicating that the central silicon atom Si2 is not sp-hybridized silicon. Distances between Si1–Si2a and Si2a–Si3 of 2.177(1) and 2.188(1) Å, respectively, are in the range of the typical Si=Si double bond distances (2.138–2.261 Å).[17] Terminal silacyclopentane rings are almost perpendicular to each other, with the dihedral angle between C1–Si1–C2 and C3–Si3–C4 planes of 92.4°. Terminal unsaturated silicons adopt pyramidalized geometry. The sums of bond angles are 354.1° for Si1 and 354.9° for Si3. These structural parameters indicate that trisilaallene **4** is the first cumulative disilene with the two Si=Si double bond sharing one unsaturated silicon atom.

Interestingly, the molecular structure of trisilaallene **4** obtained by X-ray analysis was incompatible with the optimized structure of the model compound obtained by DFT calculation. The structure of Si_3Me_4 optimized at the B3LYP/6-31+G(d,p) (**20Z**) is not linear or bent allenic, but is zwitterionic (Chart 5, Table 4). In **20Z**, the Si–Si–Si angle is quite acute (92.4°) and the deviation of methyl carbon atom from the Si–Si–Si plane is small (the dihedral angle of C5–Si1–Si2–Si3 was 26.6°). The HOMO and LUMO of **20Z** were symmetric and antisymmetric π orbitals delocalizing at three skeletal silicon atoms, respectively (Fig. 10) and the HOMO−1 was a non-bonding orbital localizing at the central silicon atoms. Then we calclulated a model compound **20B** with structural parameters around skeletal silicon atoms and carbon atoms bound to terminal silicon atoms similar to those experimentally observed for **4**. The HOMO and HOMO−1 of **20B** were twisted bonding π-orbitals delocalized on three silicon atoms with different orbital energies; LUMO and LUMO+1 were the corresponding anti-bonding orbitals, showing significant conjugation between the two Si=Si π-orbitals. Thus, **20B** can be better described as a bent allene rather than a zwitterion. Compound **20B** is calculated to be 8.8 kcal/mol less stable than **20Z**. This small energy difference would cause easy deformation from the most stable zwitterionic structure **20Z** to the bent allenic structure **20B**. Terminal bulky substituents of trisilaallene **4** not only kinetically protect the Si=Si double bond, but also modify its electronic structure. Differences in structure between **20Z** and **4** would result from severe steric repulsion caused when a structure similar to **20Z** was applied to **4**. In contrast to carbon-based allenes, the linear structure of Me_4Si_3 (**20L**) optimized as a saddle point with two imaginary frequencies is +16.3 kcal·mol^{-1} higher in energy than the most stable **20Z**.

The bent structure of trisilaallene **4** observed in the solid state is also evidenced in solution by the highly symmetric ^{1}H, ^{13}C, and ^{29}Si NMR spectra and the ^{29}Si resonances of the unsaturated silicon nuclei. All trimethylsilyl groups in **4** are equivalent even at −80 °C. The ^{29}Si NMR resonances found at 157 and 197 ppm in benzene-d_6 are assigned to Si2 and Si1 (Si3) nuclei, respectively. These resonances are in

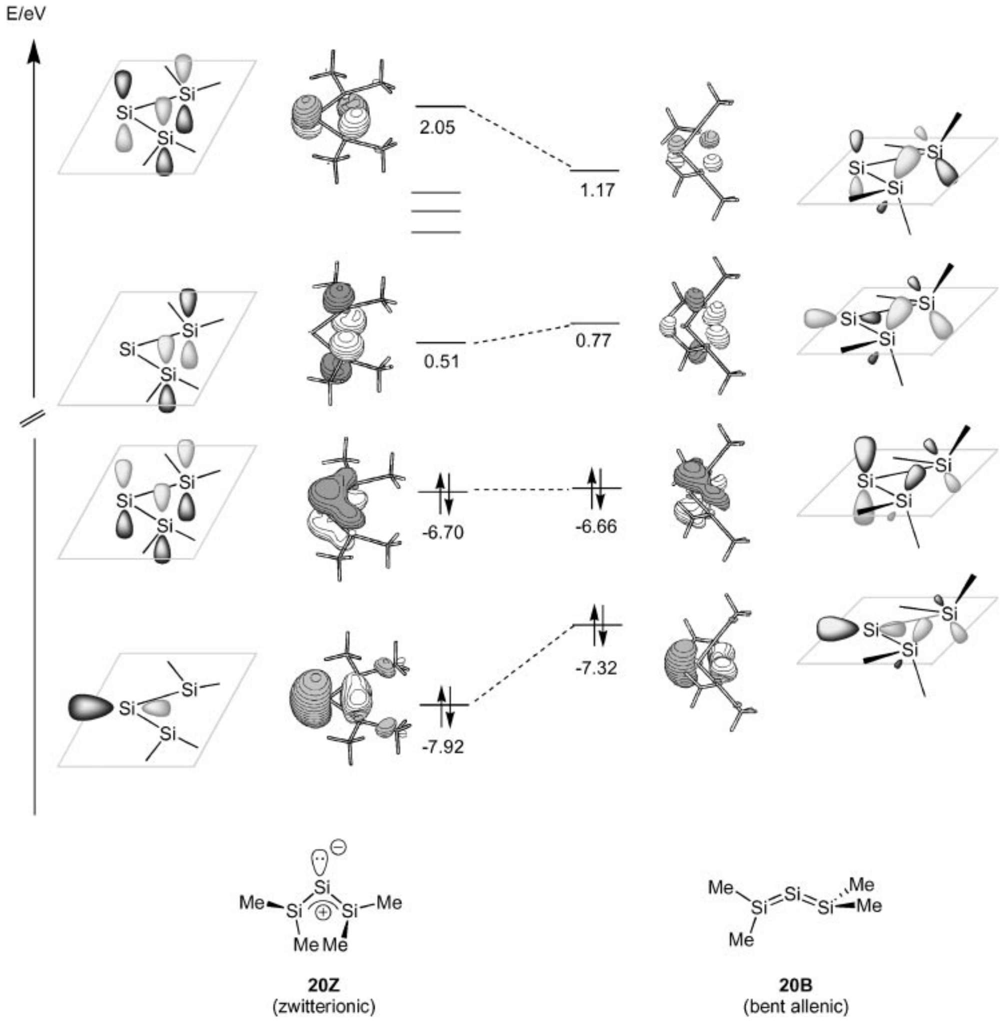


Fig. 10. Schematic molecular orbital diagram for Me_4Si_3 derivatives **20Z** and **20B** optimized at the HF/6-311+G(d,p)//B3LYP/6-31G+(d,p) level.

good accord with the theoretical values calculated at the GIAO/6-311+G(2df,p)//B3LYP/6-31+G(d,p) level for the model Me_4Si_3 with the bent allenic structure (**20B**). The calculated ^{29}Si resonances for central Si2 and terminal Si1 (Si3) nuclei for **20B** are 144 and 221 (212) ppm, respectively, whereas they are 39 and 355 ppm for **20Z** and 210 and 98 ppm for **20L** (Table 4).

3.4 Conjugation between Two Cumulative Silicon–Silicon Double Bonds. Because a carbon-based allene has two perpendicular π-bonds in the linear skeleton, no conjugation exists between the two π bonds, and the π–π^* transition band appears in the same region as the π–π^* transition band maximum of ethylene. We found the remarkable conjugation between two Si=Si double bonds in trisilaallene **4** due its bent structure.

The UV–vis absorption maxima of **4** were found at 390 nm (ε 21300) and 584 nm (ε 700) in hexane (Fig. 11). The two-splitting-band feature as well as the remarkable red shift of the longest absorption band of **4** compared with π–π^* transition band for tetramethyldisilene ($\lambda_{\max} = 350$ nm)[46] is consistent with significant conjugation between the two Si=Si double bonds, as suggested by the molecular orbital calculations of **20B**. Conjugation between the two Si=Si double bonds in **4** would be stronger than spiroconjugation observed in spiropentasiladiene **3** and stronger than those in tetrasilabutadienes.[26,28]

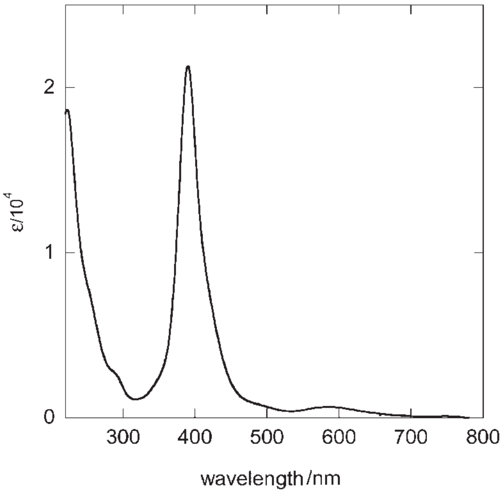


Fig. 11. UV–vis spectrum of trisilaallene **4** in 3-methylpentane.

Conclusion

I successfully synthesized cyclic, spiroconjugated, and cumulative silicon–silicon doubly bonded compounds as novel silicon-based π-electron systems and disclosed their unusual properties that can be compared with those of the corresponding their carbon-systems. During the course of our study, various types of heavy group 14 elements-based π-electron systems, such as heavy ketones,[47] heavy aromatic compounds,[48] heavy cyclic and conjugated alkenes,[1m,26,28] and heteronuclear heavy alkenes[1n] have been synthesized and their structures, bonding nature, properties, and reactivity have been well elucidated.[1h–1n] These extensive studies may provide unique and useful materials with heavy element-based π-electron systems owing to their intrinsic properties of silicon and related heavy elements.

The following collaborators achieved the study described in this article. First of all, I would like to express my sincere appreciation to Professor Mitsuo Kira (Tohoku University) for his daily valuable discussions, advice, and encouragement throughout the course of this research. I wish to express my thanks to Dr. Chizuko Kabuto for her helpful discussions and technical advice of X-ray crystallography. I am also grateful to Dr. Shintaro Ishida (trisilaallene) and Mr. Makoto Tamura (cyclotrisilene and spiropentasiladiene) for their invaluable contributions and other members of Professor Kira's laboratory in Tohoku University for their helpful discussions.

This work was partially supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology.

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