Cyclic Diynes with Silicon in the Bridges: Structural and Photoelectron Spectroscopic Investigations

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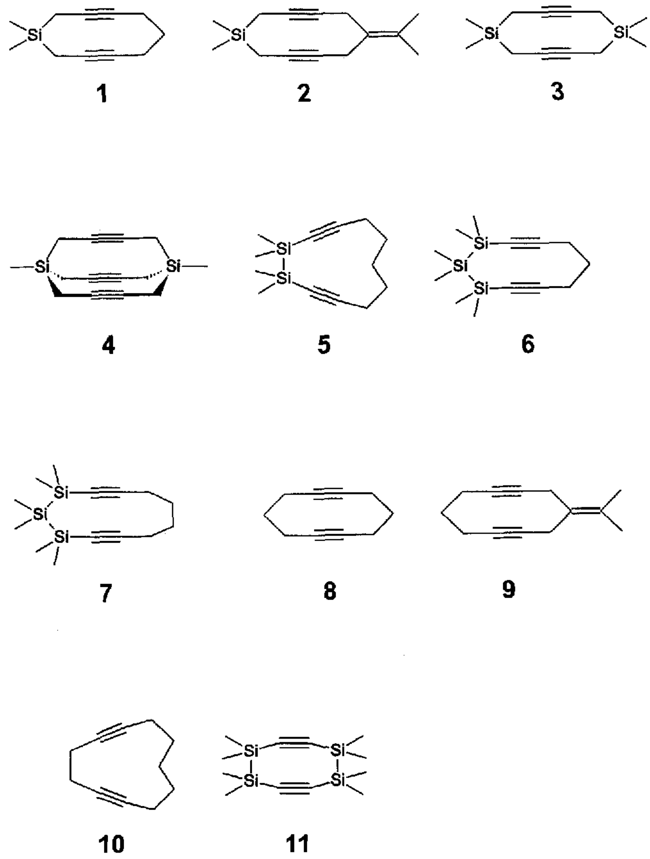
The structures of 6-isopropylidene-1,1-dimethyl-1-silacyclodeca-3,8-diyne (**2**), 1,6-dimethyl-1,6-disilabicyclo[4.4.4]tetradeca-3,8,12-triyne (**4**), and 1,1,2,2,3,3-hexamethyl-1,2,3-trisilacyclodeca-4,9-diyne (**6**) have been investigated by means of X-ray crystallography. In **2** and **6** a chair conformation is adopted in the solid state. In **4** the three butyne groups are twisted around the Si−Si axis against one another. The torsion along the triple bond axis ($Si-CH_2\cdots CH_2Si$) amounts to 29.0(1)°. The He(I) photoelectron (PE) spectra of **2** and **6** together with those of 1,1-dimethyl-1-silacyclodeca-3,8-diyne (**1**), 1,1,6,6-tetramethyl-1,6-disilacyclodeca-3,8-diyne (**3**), 1,1,2,2-tetramethyl-1,2-disilacycloundeca-3,10-diyne (**5**), and 1,1,2,2,3,3-hexamethyl-1,2,3-trisilacycloundeca-4,10-diyne (**7**) have also been recorded. The PE spectra were interpreted on the basis of results from SCF MO calculations (3-21G*). They reveal a smaller splitting of the π-bands in **1**−**3** as compared to cyclodeca-1,6-diyne. In the PE spectra of **5**−**7** we encountered a strong interaction between the silicon chain and the in-plane π-orbitals.

Cyclic diynes and bicyclic triynes are ideal models for the study of the effects of the close proximity of two or three triple bonds on structure,[1] spectroscopic properties, and reactivity.[1][2] Our studies on cyclic diynes in which the triple bonds are connected by methylene bridges have revealed that the interaction between both triple bonds depends on the length of both the triple bonds and the methylene bridge.[3] In order to continue these studies we recently synthesized cyclic diynes containing dimethylsilyl groups as building elements[4] and studied their reactions with organometallic fragments derived from $CpCoL_2$ (L = CO, C_2H_2) or $Fe(CO)_5$.[5] In this paper we describe our studies of the structures and photoelectron spectra of several cyclic and bicyclic alkynes with silicon atoms in the bridges. The structural studies were carried out on 6-isopropylidene-1,1-dimethyl-1-silacyclo-deca-3,8-diyne (**2**), 1,6-dimethyl-1,6-disilabicyclo[4.4.4]tetradeca-3,8,12-triyne (**4**),[6] and 1,1,2,2,3,3-hexamethyl-1,2,3-trisilacyclodeca-4,9-diyne (**6**).[5] He(I) photoelectron spectroscopy was used to investigate **2** and **6**, together with 1,1-dimethyl-1-silacyclodeca-3,8-diyne (**1**),[6] 1,1,6,6-tetramethyl-1,6-disilacyclodeca-3,8-diyne (**3**),[6] 1,1,2,2-tetramethyl-1,2-disilacycloundeca-3,10-diyne (**5**)[4] and 1,1,2,2,3,3-hexamethyl-1,2,3-trisilacycloundeca-4,10-diyne (**7**)[5] (Scheme 1).

For comparison we include in our discussion the data obtained for cyclodeca-1,6-diyne (**8**),[7] 1-isopropylidenecyclodeca-3,8-diyne (**9**),[8] cycloundeca-1,5-diyne (**10**),[3] and 1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diyne (**11**).[9]

Scheme 1

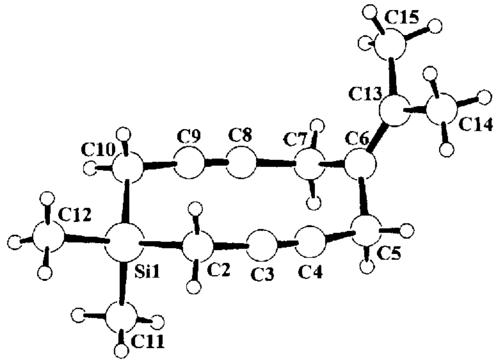


X-ray Structure Determination of 2 and 4−6

Studies on a number of cyclic diynes with dimethylsilyl[4][11] or tetramethyldisilyl fragments in the bridges[4][12] have been reported in the literature. These diynes show less strain than the corresponding hydrocarbons with the same number of bridging units and this was anticipated as being due to the longer C−Si and Si−Si distances as compared to the C−C distance.

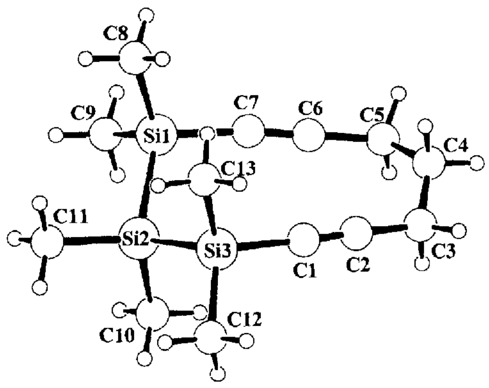
Single crystals of **2** and **6** were obtained by a slow Kugelrohr distillation of both samples in vacuum. The structures of **2** and **6** in the crystal as determined by X-ray crystallography are represented in Figures 1 and 2. Both compounds show a chair conformation as reported for **8**[7] and other 1,6-diheterocyclodeca-3,8-diynes.[2][10] Due to the different bond lengths in the chains connecting both triple bonds, the alkyne units are not parallel to each other as in **8**. This was anticipated, since the Si−C bonds (1.85 Å) and the Si−Si bond (2.34 Å) are considerably longer than a C−C bond (1.54 Å). As a result, the transannular distances between the C(sp) atoms in **2** (3.23 Å and 3.07 Å) and **6** (3.59 Å and 3.13 Å) are considerably longer than in **8** (2.99 Å). In **2**, the average bond angle at the sp-carbon centers amounts to 173.5° and is slightly larger than in **8** (171.7°). The corresponding averaged angles for **6** are: C−C−C = 179.3° and Si−C−C = 172.3°. The stronger cisoid deformation at the Si−C−C angle can be rationalized by a higher flexibility of the Si−C σ-bond as compared to the C−C σ-bond. The C5−C6−C7 bond angle at the sp^2-carbon atom in **2** is rather small [113.8(2)°]. This result correlates with the findings in 4,9-dimethylenecyclodeca-1,6-diyne[8] where the angle at the sp^2-carbon atom in the ring was found to be 117.9(5)°. The reduction of the angle at the sp^2-carbon atom center reduces the repulsive interaction between the CH_3 groups at the exomethylene carbon center and the propargylic CH_2 groups in **2**. It is interesting to note that the bond angle at the CH_2 groups at the 4 and 9 positions of **8** amounts to 115.9°; this value is close to that found at C6 of compound **2** (113.8°).

Figure 1. Molecular Structure of **2**[a]



[a] Selected distances [Å] and angles [°]: Si1−C2 1.871(3), Si1−C10 1.877(3), C2−C3 1.464(3), C3−C4 1.185(3), C4−C5 1.461(3), C5−C6 1.519(3), C6−C13 1.330(3), C6−C7 1.515(3), C7−C8 1.473(3), C8−C9 1.182(3), C4···C8 3.065(3), C3···C9 3.229(3); C2−C3−C4 173.4(3), C3−C4−C5 173.2(2), C4−C5−C6 111.7(2), C5−C6−C7 113.8(2), C6−C7−C8 111.4(2), C7−C8−C9 173.5(2), C8−C9−C10 173.9(3), C2−Si1−C10 112.0(1).

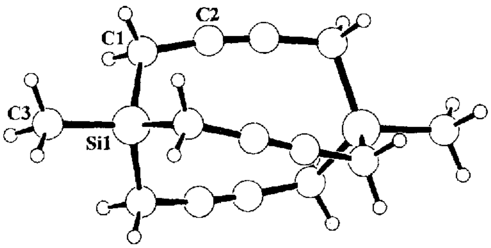
Figure 2. Molecular Structure of **6**[a]



[a] Selected distances [Å] and angles [°]: Si1−Si2 2.3412(7), Si2−Si3 2.3469(8), Si3−C1 1.823(2), Si1−C7 1.833(2), C1−C2 1.195(3), C2−C3 1.469(4), C6−C7 1.195(3), C5−C6 1.470(3), C1···C7 3.591(3), C2···C6 3.133(3); Si1−Si2−Si3 111.23(3), Si2−Si3−C1 107.3(1), Si2−Si1−C7 107.3(1), Si3−C1−C2 171.5(2), Si1−C7−C6 173.1(2), C1−C2−C3 179.3(3), C5−C6−C7 179.2(2).

In the solid state the pentamethylene bridge of the 11-membered ring in **5** shows a zig-zag arrangement with a staggered conformation of the five CH_2 groups.[4] In the disilatetramethyl bridge the methyl groups have a small torsional angle C−Si−Si−C of 19.7(1)°. The transannular distances between the C(sp) centers are 3.523(3) Å and 4.035(3) Å. The angle at the C(sp) centers is, on average, 172.7°. The bond length of the Si(1)−Si(2) bond is nearly the same [2.361(1) Å] in **5** as in **6**. Molecule **4** shows D_3 symmetry (Figure 3). The conformation of the triyne is propeller-like, with an angle of 19(1)° between the triple bonds. The torsion between both $Si(CH_2)_3$ groups is 29.0(1)° (Si1−C1···C1′−Si1′). The bond angle C1−C2−C2′ [172.9(1)°] shows a cisoid deformation of the triple bonds, similar to **8** (171.7°). The bond angle C1−Si1−C1″ amounts to 110.7(1)° and is close to the anticipated tetrahedral angle. In the bicyclic system of **4** the transannular distance between the centers of the triple bonds is found to be 3.361(2) Å. This is greater than the analogous distance in **2** (3.147 Å).

Figure 3. Molecular Structure of **4**[a]

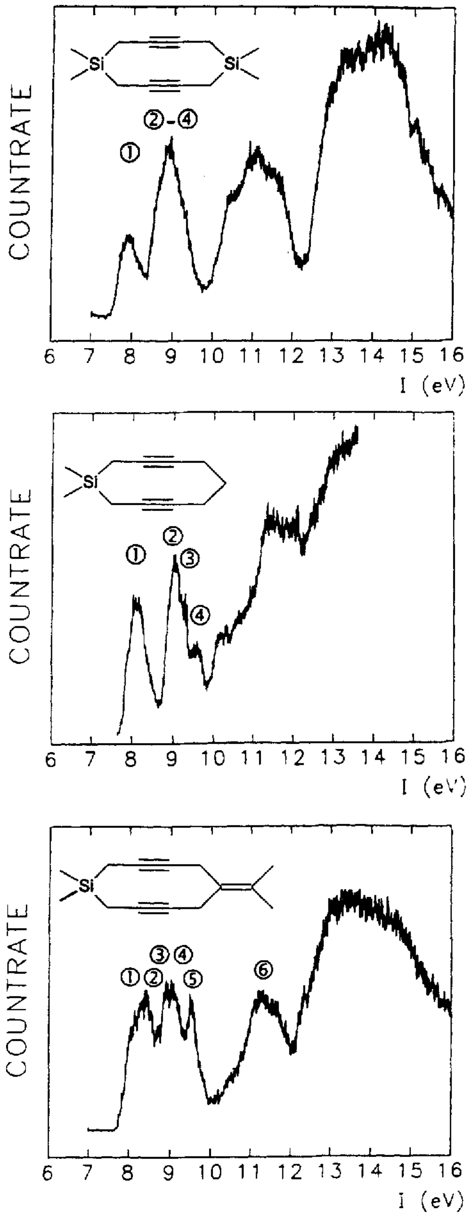


[a] Intramolecular distances [Å] and angles [°]: Si1−C1 1.890(1), C1−C2 1.467(2), C2−C2′ 1.192(3), C2···C2″ 3.361(2), C3−Si1 1.879(3); C3−Si1−C1 108.23(4), C1−Si1−C1″ 110.68(4), C2−C1−Si1 112.87(9), C2′−C2−C1 172.86(7)

Photoelectron-Spectroscopic Investigations of 1−3 and 5−7

The He(I) photoelectron (PE) spectra of **1**−**3** are illustrated in Figure 4. Common to all of them is a group of two or three peaks below 10 eV which are clearly separated from the broad peaks at higher energy. By measuring the areas of the envelopes beneath each of these different peaks we are able to assign these lower energy features to four or five ionization events. The assignments are indicated in the spectra where we have numbered the band positions to which we assign an ionic state. The first bands of **1**−**3** correlate with those of **8** and **9** whose PE spectra have already been the object of a detailed investigation.[7][8] We assume in our interpretation that we can correlate the recorded vertical ionization energies, $I_{v,j}$, directly with calculated orbital energies, ε_j (Koopmans' quotation mark, right theorem[13]), at least for the first ionic states. These calculations were performed using the ab initio HF-SCF method[14] and for all compounds the structures were fully optimized using a 3-21G* basis.[15]

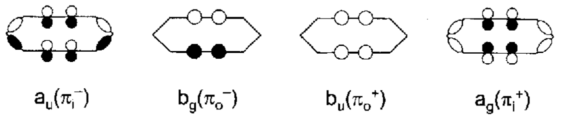
Figure 4. He(I) PE spectra of **1**–**3**



In the PE spectra of compound **3** (Figure 4), as well as those of **1** and **8**, we expect four bands at low ionization energies due to ionization from the π-MOs of the triple bonds. In **3**, which has C_{2h} symmetry, the four linear combinations belong to the irreducible representations A_u, B_g, B_u, and A_g. These are due to the bonding and antibonding linear combinations of the in-plane π-orbitals π_i^+, π_i^- and the out-of-plane π-orbitals π_o^+ and π_o^-, as shown in Scheme 2.

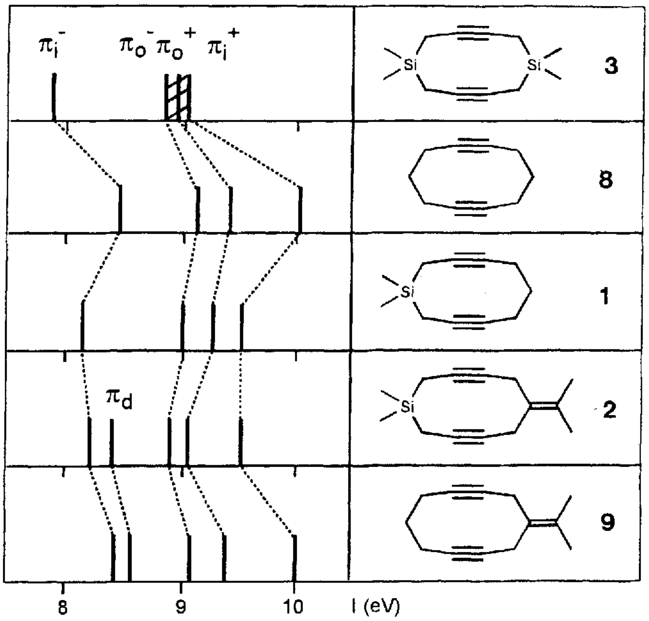
From the areas below the first and second bands in the PE spectrum of **3** we assign the first band to one transition and the second band to three strongly overlapping transitions.

Scheme 2



Based on the same argument (area below peaks) we assign the three peaks in the PE spectrum of **1** to four transitions and in the PE spectrum of **2** to five transitions. In Figure 5 we correlate the bands of the PE spectra of **1**–**3** with those of **8** and **9**. This correlation suggests the central peak (bands 2 and 3 in the case of **1** and bands 3 and 4 in the case of **2**) should be assigned to ionization from the π_o^+ and π_o^- orbitals.

Figure 5. Correlation between the first PE bands of **1**–**3** with those of **8** and **9**



The band at highest energy (band 4 in the case of **1** and band 5 in the case of **2**) results from ionization from the π_i^+ orbital. Due to the strong overlap of bands in the PE spectrum of **3**, bands 2–4 cannot be distinguished. In the PE spectrum of **2** ionization from the isopropylidene π orbital is assumed to result in band 2.

In Table 1 the ionization energies of **1**–**3** are listed and the calculated orbital energies are compared with the empirical assignments. There is a good correlation for both the sequence of the bands and the measured splittings.

The PE spectra of **5** and **6** are shown in Figure 6. In the case of **5** we observe three peaks below 11 eV for which the central one at 9.4 eV has a very high intensity as compared to the other two. The areas below the peaks relate as 1:3:1 suggesting that the second peak is due to three transitions.

This assignment is consistent with the results of SCF calculations (Table 1). These calculations predict three close-lying orbitals with energies between 9.91 and 10.07 eV that

Table 1. Comparison between the recorded vertical ionization energies, $I_{v,j}$, and the calculated orbital energies, ε_j, of **1**–**3** and **5**–**7**; all values in eV

Compound	Band	$I_{v,j}$	Assignment	$-\varepsilon_j$ (3-21G*)
1	1	8.1	18a'' (π_i^-)	8.60
	2	9.0	17a'' (π_o^-)	9.58
	3	9.3	30a' (π_o^+)	9.64
	4	9.5	29a' (π_i^+)	10.15
2	1	8.2	23a'' (π_i^-)	8.61
	2	8.4	36a' (π_d)	9.06
	3	8.9	22a'' (π_o^-)	9.51
	4	9.1	35a' (π_o^+)	9.64
	5	9.5	34a' (π_i^+)	10.28
3	1	7.9	11a$_u$ (π_i^-)	8.52
	2	8.8	10a$_g$ (π_o^-)	9.41
	3	to	19b$_u$ (π_o^+)	9.56
	4	9.1	20a$_g$ (π_i^+)	9.66
5	1	8.5	34a' ($\pi_i^+ - \sigma$)	9.05
	2	9.3	30a'' (π_o^-)	9.91
	3	to	29a'' (π_o^+)	9.98
	4	9.6	33a' (π_i^-)	10.07
	5	10.3	32a' ($\pi_i + \sigma$)	11.20
6	1	8.0	30a'' ($\pi_i^- - \sigma$)	8.59
	2	9.0	42a' ($\pi_i^+ - \sigma^+$)	9.69
	3	to	29a'' (π_o^-)	9.79
	4		41a' (π_o^+)	10.13
	5	9.5	28a'' ($\pi_i^- + \sigma^-$)	10.27
	6	9.2	40a' ($\pi^+ + \sigma^+$)	11.13
7	1	8.0	33a' ($\pi_i^- - \sigma^-$)	8.61
	2	8.8	43a' ($\pi_i^+ - \sigma^+$)	9.63
	3	9.1	32a'' (π_o^-)	9.70
	4	9.2	42a' (π_o^+)	10.11
	5	9.5	31a' ($\pi_i^- - \sigma^-$)	10.28
	6	9.9	41a' ($\pi_i^+ + \sigma^+$)	10.99
	6	9.9	41a' ($\pi_i^+ + \sigma^+$)	10.99

Figure 6. He(I) PE spectra of **5** and **6**

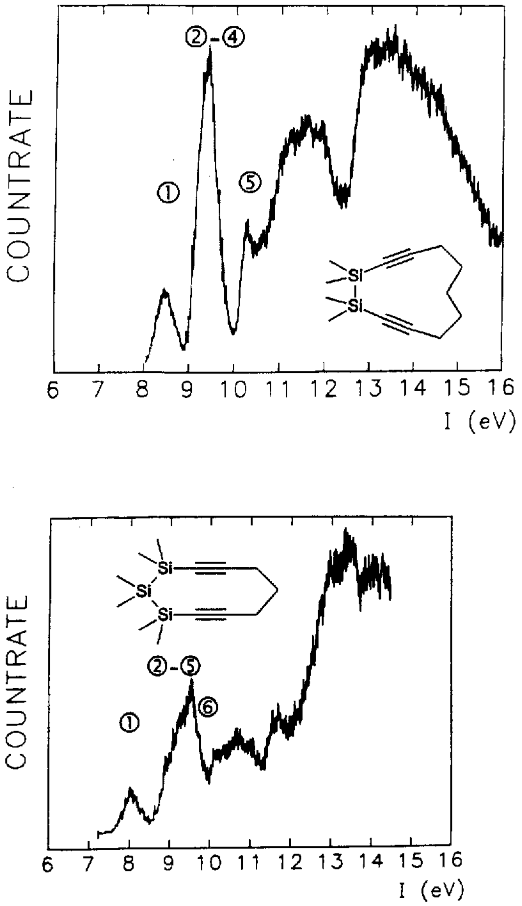
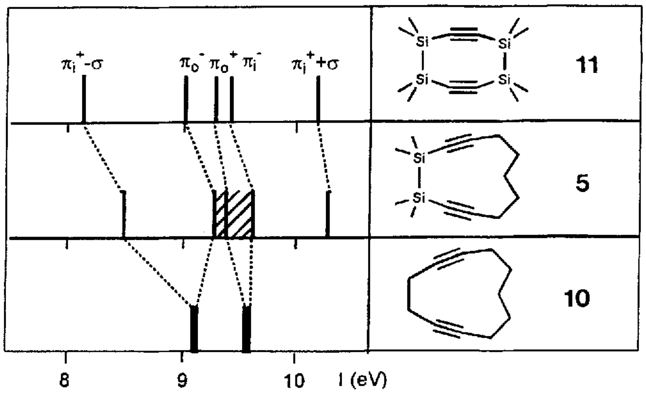
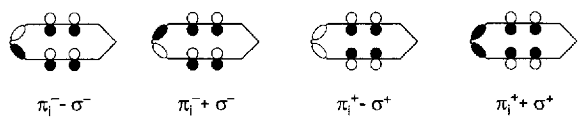


Figure 7. Correlation between the first PE bands of **5** with those of **10** and **11**



Scheme 3



belong to the out-of-plane linear combinations π_o^-, π_o^+, and the antisymmetric in-plane linear combination π_i^-. The calculations predict that the first and fifth transitions arise from ionisation from the molecular orbitals arising from the two $\pi_i^+ - \sigma$(Si–Si) and $\pi_i^+ + \sigma$(Si–Si) linear combinations. This assignment is supported by the correlation between the first PE bands in the PE-spectrum of **5** with those of **10** and **11** (Figure 7).

The PE spectra of **6** and **7** (Figure 6 and Table 1) show one peak at 8 eV which stands out from a broad peak at around 9.3 eV. We assign the fine structure observed for this latter peak as being due to five close-lying bands which arise from the out-of-plane π-MOs (π_o^+, π_o^-) and linear combinations between π^- and σ^- and π_i^+ and σ^+ orbitals. The σ orbitals σ^- and σ^+ are mainly localized on the Si_3 unit. The four in-plane linear combinations $\pi_i^- - \sigma$, $\pi_i^- + \sigma$, $\pi_i^+ - \sigma$, $\pi_i^+ + \sigma$ are shown schematically in Scheme 3.

The main difference between the PE spectra of **5** and those of **6** and **7** is that in **5** the $Me_2Si-SiMe_2$ bridge interacts only with the π_i^+ MO for reasons of symmetry, but leaves π_i^-, π_o^-, and π_o^+ unchanged. In **6** and **7**, however, the $Me_2Si-SiMe_2-SiMe_2$ bridge can interact with π_i^- and π_i^+. Note that the calculations predict different symmetries for the highest occupied MOs of **5** ($\pi_i^+ - \sigma$) as compared to **6** and **7** ($\pi_i^- - \sigma$). This result resembles that obtained for cycloocta-1,5-diyne and **8**.[7]

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Experimental Section

X-ray Structural Analysis of **2**, **4** *and* **6**: Crystals suitable for X-ray diffraction studies were selected. The X-ray data (Table 2) were collected with a Nonius-CAD4 diffractometer (Mo-K_α radiation, graphite monochromator, ω-2Θ scan). Intensities were corrected for Lorentz and polarisation effects. Numerical absorption corrections were applied at the compounds **4** and **6**. All structures were solved by direct methods (**2**: MULTAN[16]; **4** and **6**: SHELXS-86[17]). The structural parameters of the non-hydrogen atoms were refined anisotropically (F^2) according to a full-matrix least-squares technique (**2** and **6**: MolEN[18]; **4**: SHELXL-93[19]). Hydrogen atoms were refined isotropically in **2**, **4**, and calculated in **6**. Disorder effects occured at the atom C4 in compound **6**. This atom was located at two positions with 60 and 40% probability. The crystallographic data for the molecules **2**, **4**, and **6** are given in Table 2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)1223/336-033, e-mail: deposit@chemcrys.cam.ac.uk], on quoting the deposition number CCDC-100602, the names of the authors, and the journal citation.

Table 2. Crystallographic data

Compound	**2**	**4**	**6**
Empirical formula	$C_{14}H_{20}Si$	$C_{14}H_{18}Si_2$	$C_{13}H_{24}Si_3$
Molecular mass [g/mol]	216.4	242.5	264.6
Crystal size [mm]	0.5 × 0.5 × 0.25	0.45 × 0.45 × 0.27	0.5 × 0.5 × 0.45
Crystal color	colorless	colorless	colorless
Space group	$P2_1/n$	$R\bar{3}c$	$P2_1/c$
a [Å]	6.388(2)	9.674(1)	10.296(1)
b [Å]	23.878(6)	9.674(1)	12.132(1)
c [Å]	9.498(2)	24.679(2)	13.867(2)
α [°]	90	90	90
β [°]	108.59(2)	90	100.34(1)
γ [°]	90	120	90
V [Å^3]	1373(1)	2000.0(3)	1703.9(6)
$D_{\text{calcd.}}$ [Mg/m^3]	1.05	1.21	1.03
Z	4	6	4
F(000)	472	780	576
Temperature [K]	293	293	163
$h_{\text{min}}/h_{\text{max}}$	0/8	0/11	0/13
$k_{\text{min}}/k_{\text{max}}$	0/31	0/11	0/16
$l_{\text{min}}/l_{\text{max}}$	−12/12	0/32	−18/18
$(\sin \Theta/\lambda)_{\text{max}}$ [Å^{-1}]	0.66	0.66	0.66
μ [mm^{-1}]	0.14	0.24	0.25
Refl. collected	3569	532	4291
Refl. unique	3294	521	4076
Refl. observed	1815	482	3361
Variables	216	38	154
$(\Delta/\sigma)_{\text{max}}$	<0.01	0.003	<0.01
R	0.041	0.038	0.039
R_w	0.094	0.149	0.118
S (Gof)	1.74	1.42	2.80
$(\Delta\rho)_{\text{max}}$ [e Å^{-3}]	0.20	0.26	0.50
$(\Delta\rho)_{\text{min}}$ [e Å^{-3}]	−0.10	−0.55	−0.10

He(I) PE Spectra of **1**–**3**, **5**–**7**: The He(I) PE spectra were recorded with a Perkin PS18 spectrometer and calibrated using Ar and Xe. A resolution of 20 meV was obtained for the $^2P_{3/2}$ line of Ar.

Preparation of **2**: To a solution of 6.8 g (0.05 mol) of bis(2-propinyl)dimethylsilane[20] in 500 ml of dry THF was added dropwise at −78°C, 62.5 ml (0.1 mol) of a 1.6 M solution of *n*-butyllithium in *n*-hexane. After the addition was completed, 12.1 g (0.05 mol) of 1-bromo-2-bromomethyl-3-methyl-2-butene[21] was added at once and the mixture heated under reflux for 18 h. An aqueous solution of NH_4Cl was added after cooling. The organic phase was separated and the solvent removed under vacuum. The raw material was purified by column chromatography (silica gel/CCl_4) and subsequent Kugelrohr distillation (50°C/0.01 Torr) to yield 100 mg of **2** (0.9%) as colorless crystals, m.p. 88°C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.92 (s, 4 H), 1.73 (s, 6 H), 1.56 (t, 4 H), 0.16 (s, 6 H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 127.3 (s), 124.4 (s), 79.9 (s), 78.6 (s), 23.7 (t), 20.6 (q), 6.9 (t), -3.5 (q). – $C_{14}SiH_{20}$ (216.13): calcd C 77.54, H 9.41; found C 77.70; H 9.39.

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