

1,1,2,2-Tetramethyl-1,2-disilacycloocta-3,7-diyne — structure and bonding properties of a highly strained cyclic diyne

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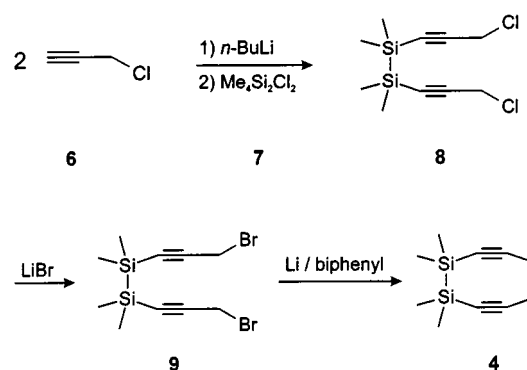
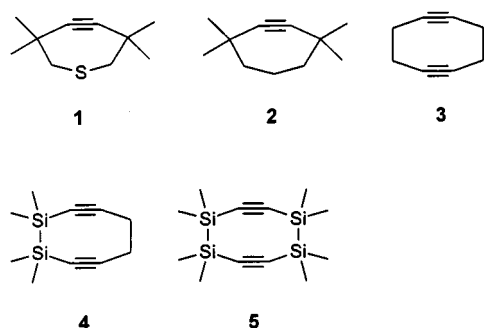
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1,1,2,2-Tetramethyl-1,2-disilacycloocta-3,7-diyne (**4**) could be prepared by reaction of 1,8-dibromo-4,4,5,5-tetramethyl-4,5-disilaocta-2,6-diyne (**9**) with lithium in the presence of catalytic amounts of biphenyl. X-Ray investigations on single crystals of **4** revealed an almost planar structure adopting C_{2v} symmetry. The transannular distances between the pairs of carbon atoms in the triple bonds are 2.672 and 3.153 Å, respectively. The analysis of the He(I) photoelectron spectrum of **4** reveals a strong interaction between the in-plane π -orbitals of the triple bonds and the Si–Si σ -bond.

Highly strained cyclic mono- and diynes such as 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne (**1**),¹ 3,3,7,7-tetramethylcyclo-



Scheme 1

heptyne (**2**),² cycloocta-1,5-diyne (**3**),³ and 1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diyne (**5**)⁴ deserve special interest. Due to the *cis*-deformation of the triple bonds in these species enhanced reactivity has been reported.^{5,6}

The close proximity of the triple bonds in **3** and **5** was made responsible for a strong interaction between both alkyne units as exemplified in PE spectroscopic studies.^{7,8} The missing link between **3** and **5** is 1,1,2,2-tetramethyl-1,2-disilacycloocta-3,7-diyne (**4**). In this paper we report its structure and He(I) photoelectron (PE) spectrum.

For the synthesis of **4** we make use of the observation that ethano bridged medium sized diynes can be prepared from terminal dibromides and lithium in the presence of diphenyl.^{9,10} In the case of the synthesis of **4** the necessary starting material was prepared from the lithium salt of propargyl chloride (**6**) (propargyl = prop-2-ynyl) and 1,2-dichloro-1,1,2,2-tetramethyl-disilane (**7**) (Scheme 1). The resulting 1,8-dichloro-4,4,5,5-tetramethyl-4,5-disilaocta-2,6-diyne (**8**) was isolated in about 70% yield. The exchange of the chlorine atoms by bromine atoms to give **9** was achieved in 85% yield. The ring closure to **4** was accomplished in 10% yield by reacting **9** at -78°C with lithium in the presence of catalytic amounts of biphenyl. The alkyne proved to be a colorless liquid which was solidified by keeping it below room temperature. Single crystals of **4** were grown in pentane at -20°C . The structure of **4** in the crystal as determined by X-ray crystallography is shown in Fig. 1.

The eight-membered ring of **4** is almost planar, the ethano group deviates slightly from the plane avoiding a fully eclipsed conformation of the hydrogen atoms. In contrast, the $\text{Si}_2(\text{CH}_3)_4$ group seems to make no attempt to avoid being completely eclipsed (Fig. 1b). Due to the longer Si–Si bond of the Si_2Me_4

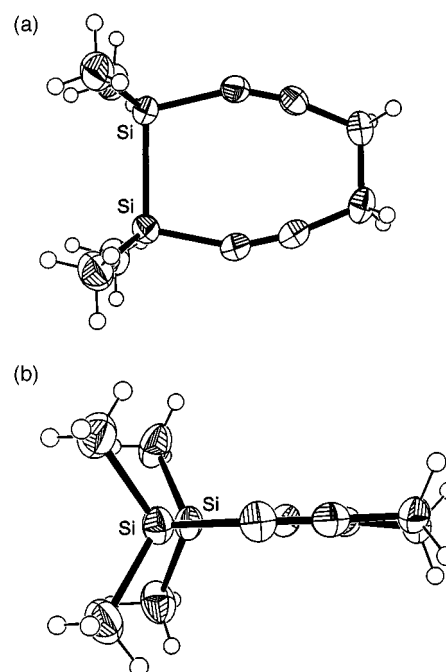
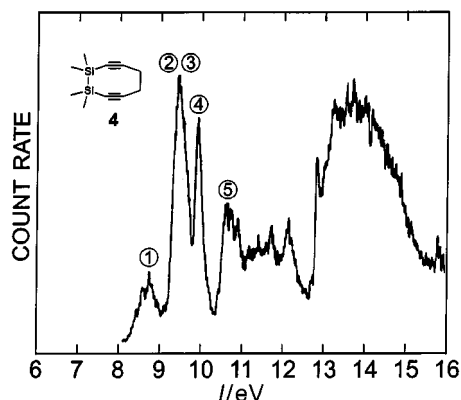
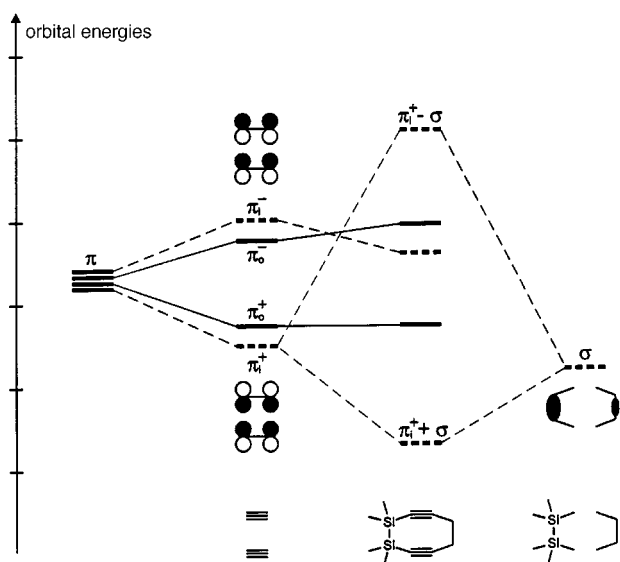


Fig. 1 Molecular structure of **4** a) front view, b) side view.

moiety (2.369 Å) as compared to the C–C σ -bond of the ethano bridge (1.552 Å) the sp centers adopt a rhombic quadrangle (Fig. 1a). The bending of the triple bond is stronger (24°) at the Si_2Me_4 side than at the ethano side ($10\text{--}11^\circ$). In Table 1 we have compared the most relevant bond distances and bond angles of

Table 1 Comparison of selected bond lengths [\AA] and bond angles [$^\circ$] in **3–5**

Compound	Transannular distance	C(sp)–C(sp)	Distance between sp^3 -centers	Bond angles at sp-centers	Bond angles at sp^3 -centers
3 ³	2.597	1.212	1.570	159.3	110.4
4	2.672	1.200(2)	1.552(2)	169.1(2)/168.3(2)	112.0(1)/112.2(1)
5 ⁴	3.155	1.205(2)	2.369(1)	156.3(1)/155.8(1)	102.1(1)/102.5(1)
	3.223	1.183	2.369	168.6	103.4
	3.269	1.182	2.351	164.1	105.8

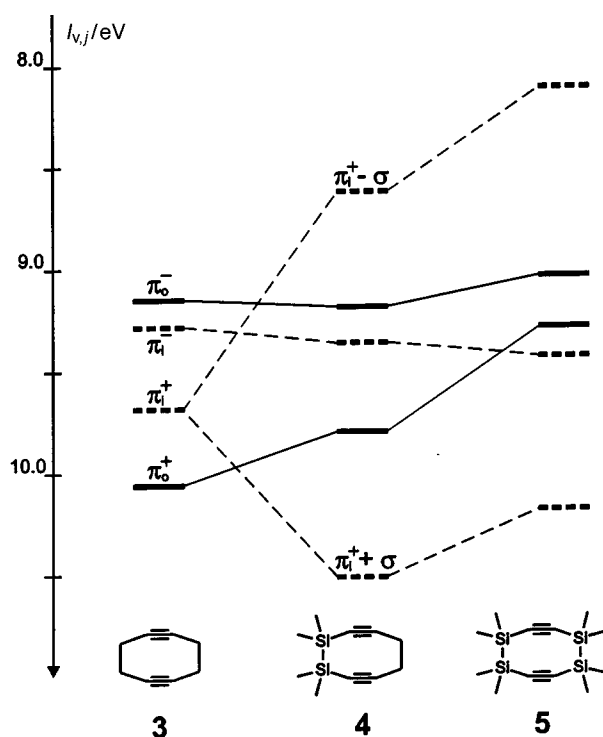
**Fig. 2** He(I) photoelectron spectrum of **4**.**Fig. 3** Qualitative interaction diagram for the four π -MOs of two alkyne units (left) and the highest occupied σ -orbital of the σ -frame of **4** to yield the highest MOs of **4**.

3–5. The most strained diyne is **3**, in which all bonds between the sp and sp^3 centers are bent by almost 21° .³ The successive replacement of the ethano bridges in **3** by the longer Si_2Me_4 bridges relieves strain. This shows up in smaller deviations from linearity of the triple bonds on the side of the ethano bridge as compared to the side of the Si_2Me_4 bridge. The replacement of the short C–C bridge in **3** by the longer Si–Si and Si–C bonds in **4** and **5** leads to an angle contraction on the Si–Si-side of **4** and **5**. Thus, the $\text{SiMe}_2\text{–SiMe}_2\text{–C}$ angles are smaller (102° in **4**, $103\text{–}105.8^\circ$ in **5**) than the $\text{CH}_2\text{–CH}_2\text{–C}$ angles (110.4° in **3** and 112° in **4**). The higher strain in **3** as compared to **4** shows up also in the C–C bond length of the ethano bridge(s). This distance is found to be 1.570 \AA in **3** and 1.552 \AA in **4**.

The photoelectron spectrum of **4** is shown in Fig. 2. It shows four distinct peaks below 11 eV to which we assign five transitions. Due to the larger area below the second peak as compared to the third one we assign to the former two transitions (bands 2 and 3). To relate the observed bands to the molecular

Table 2 Comparison between the recorded vertical ionization energies ($I_{v,j}$) and the calculated orbital energies ($-\varepsilon_j$) of **4**. The orbital energies are based on HF–SCF calculations using a 3-21G* basis set. All values in eV

Band	$I_{v,j}$	Assignment (C_2)	$-\varepsilon_i$
1	8.64	27a $\pi_i^+ - \sigma$	9.10
2	9.20	26a π_o^-	9.80
3	9.38	25b π_i^-	9.85
4	9.81	24b π_o^+	10.39
5	10.45	25a $\pi_i^+ + \sigma$	11.45

**Fig. 4** Correlation between the first bands of the PE spectra of **3–5**.

orbitals of **4** we make use of Koopmans' approximation¹¹ which allows correlation of the vertical ionization energy ($I_{v,j}$) with the calculated orbital energy (ε_j). In Fig. 3 we have derived the sequence of the highest occupied molecular orbitals of **4** from an interaction diagram for the four π MOs resulting from the two triple bonds and the C–C and Si–Si σ -bonds, respectively. Due to the close proximity of the π -systems, both the in plane (π_i) and out of plane (π_o) orbitals split considerably in a bonding (+) and antibonding (–) linear combination. The low ionization energy of the Si–Si σ -bond is responsible for a strong interaction between σ and π_i^+ which gives rise to a strong splitting into $\pi_i^+ + \sigma$ and $\pi_i^+ - \sigma$ as shown in the center of Fig. 3. The simple interaction diagram of Fig. 3 was corrected of the hyperconjugative effect of the Si– CH_3 and the C–H bonds which stabilize π_i^- more than π_o^- . This leads to the orbital sequence predicted by an HF–SCF calculation using a 3-21G* basis set¹² as shown in Table 2.

In Fig. 4 we have correlated the first PE bands of **3–5**. It

demonstrates the strong effect of the Si–Si σ -bond on the orbital sequence. In going from **3** to **4** and **5** we notice a diminution of the gap between π_o^+ and π_o^- . This is anticipated due to the continuous increase of the distance between the triple bonds in **3–5**. For **5** bands 2–4 are very close together and an unequivocal assignment does not seem possible. The one given in Fig. 4 deviates slightly from that predicted by HF/3-21G* calculations.¹³

Conclusion

The results presented for **4** show nicely that this molecule stands in between **3** and **5**, indeed. This shows up in the values for the transannular distances between the sp centers and the deviations from linearity of the bond angles at the sp centers. It is also seen from the splitting between the π_o^+ and π_o^- bands in the PE spectra. There is a considerable difference between **3** on the one hand and **4** and **5** on the other. This can best be seen in Fig. 4. In **3** the HOMO is assigned to π_o^- while in **4** and **5** this is the $\pi_i^+ - \sigma$ orbital. This difference is caused by the strong interaction between the Si–Si bond(s) and the π_i^+ linear combination in **4** and **5** which is of course not possible in **3**.

Experimental

General

All reactions were carried out under argon atmosphere with magnetic stirring. The solvents were purified and dried using standard procedures. The ¹H and ¹³C NMR spectra were recorded at 300 and 75 MHz in CDCl₃ if not otherwise noted. Chemical shifts are given in ppm. Elemental analyses were performed at the Mikroanalytisches Laboratorium der Universität Heidelberg, Germany.

1,8-Dichloro-4,4,5,5-tetramethyl-4,5-disilaocta-2,6-diyne **8**

To a solution of 17.1 g (0.23 mol) of propargyl chloride (**6**) in 140 ml of dry ether was added at -85°C 23 ml (10 M in hexane) of *n*-butyllithium (0.23 mol). Subsequently at -80°C 18.7 g (0.1 mol) of 1,2-dichloro-1,1,2,2-tetramethyldisilane were added. To this solution was added 12 ml of dry DMSO in 25 ml of diethyl ether. The solution was warmed to 10°C within one hour and hydrolyzed with ice–water. The phases were separated and the aqueous phase extracted twice with ether. The ethereal solution was dried with MgSO₄ and the solvent removed. Fractional distillation ($79^\circ\text{C}/0.1\text{ mbar}$) gave 18.1 g (69%) of 1,8-dichloro-4,4,5,5-tetramethyl-4,5-disilaocta-2,6-diyne (**8**) as a colorless liquid. δ_{H} 4.1 (s, 4H), 0.3 (s, 12H); δ_{C} 102.2 (s), 89.5 (s), 30.6 (t), -3.6 (q); $\tilde{\nu}$ (neat)/cm⁻¹ 2959, 2897, 2178, 1407; (HRMS, EI) 250.9889, calc. for C₉H₁₃Si₂³⁷Cl₂ (M – CH₃)⁺: 250.9874. (Found: C 45.64; H 6.31. Calc. for C₁₀H₁₆Si₂Cl₂: C 45.61; H 6.12%).

1,8-Dibromo-4,4,5,5-tetramethyl-4,5-disilaocta-2,6-diyne **9**

A solution of 13.2 g of **8** (0.05 mol) in 300 ml of acetone and 86.9 g (1.0 mol) of LiBr was refluxed for 12 h. After cooling 50 ml of silica gel was added and the solvent removed. The raw material was purified by silica gel chromatography with diethyl ether as solvent to yield 14.9 g (85%) of **9** as a slightly yellow oil. δ_{H} (200 MHz) 3.7 (s, 4H), 0.1 (s, 12H); δ_{C} (50 MHz) 102.7 (s), 90.2 (s), 14.8 (t), -3.4 (q); $\tilde{\nu}$ (neat)/cm⁻¹ 2959, 2896, 2174, 1705, 1406; (HRMS, EI) 338.8881, calc. for C₉H₁₃Si₂⁸¹Br₂ (M – CH₃)⁺: 338.8882.

1,1,2,2-Tetramethyl-1,2-disilacycloocta-3,7-diyne **4**

To 2.4 g (0.35 mol) of lithium powder and 0.3 g (2 mmol) of biphenyl were added at -75°C 350 ml of dry THF in such a way that the solution remained a deep green color. Subsequently a solution of 8.8 g (25 mmol) of **9** in 75 ml of dry

Table 3 Crystal data and structure refinement for **4**

Empirical formula	C ₁₀ H ₁₆ Si ₂
Formula weight	192.41
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i>	4
Unit cell dimensions	<i>a</i> = 7.3605(1) Å <i>a</i> = 90° <i>b</i> = 13.2811(2) Å <i>b</i> = 90.4960 (10)° <i>c</i> = 12.3457(2) Å <i>c</i> = 90°
Volume	1206.82(3) Å ³
Density (calculated)	1.06 Mg m ⁻³
Absorption coefficient	0.25 mm ⁻¹
Crystal size	.34 × .26 × .18 mm ³
Theta range for data collection	2.2 to 25.6°
Index ranges	$-7 \leq h \leq 8$, $-15 \leq k \leq 15$, $-14 \leq l \leq 14$
Reflections collected	8781
Independent reflections	2088 (<i>R</i> (int) = 0.0259)
Observed reflections	1770 (<i>I</i> > 2σ(<i>I</i>))
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.97 and 0.69
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2088/0/173
Goodness-of-fit on <i>F</i> ²	1.04
Final <i>R</i> indices (<i>I</i> > 2σ(<i>I</i>))	<i>R</i> 1 = 0.029, <i>wR</i> 2 = 0.075
Largest diff. peak and hole	0.24 and -0.20 e Å^{-3}

THF was added at -75°C within 20–30 min. This was accompanied by decolorization of the solution. After three hours the lithium was filtered in the presence of air. The progress of the reaction was followed by GC–MS. It was advantageous to interrupt the reaction before it was completed because **4** can be reduced by Li biphenylide. The solvent was removed and the raw product purified by chromatography on Alox III with petroleum ether as solvent. Further purification was achieved by Kugelrohr distillation ($110^\circ\text{C}/1.2\text{ mbar}$) to yield colorless crystals which melted at room temperature. δ_{H} 2.6 (s, 4H), 0.2 (s, 12H); δ_{C} 116.5 (s), 93.2 (s), 19.7 (t), -2.9 (q); $\tilde{\nu}$ (KBr)/cm⁻¹ 2957, 2173, 2150, 1695, 1407 cm⁻¹; (HRMS, EI) 192.0832 calc. 192.0791. (Found: C 62.25; H 8.56. Calc. for C₁₀H₁₆Si₂: C 62.42; H 8.38%).

X-Ray structural analysis of **4**

The measurements were performed at 200 K with a Siemens X-ray diffractometer equipped with a SMART CCD detector system using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073\text{ Å}$) from a sealed-tube X-ray source (50 KV/30 mA). The SMART software package¹⁴ was used for data collection as well as frame integration. Structure solution and refinement were carried out using the SHELXTL-PLUS software package.¹⁵ The structure was solved by direct methods. Full matrix least squares refinement was carried out against *F*². The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically. The crystallographic data are listed in Table 3.†

Photoelectron spectra

The photoelectron spectrum of **4** was recorded with a PS18 spectrometer (Perkin-Elmer) at room temperature. The calibration was performed with Ar and Xe. A resolution of 20 meV on the ²P_{3/2} Ar line was obtained.

† Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, available via the RSC web page (<http://www.rsc.org/authors>). Any request to the CCDC for this material should quote the full literature citation and the reference number 188/161. See <http://www.rsc.org/suppdata/p2/1999/947/> for crystallographic files in .cif format.

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