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Molecular Properties of Some New Cyclic Ethynylsilanes

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Summary. The question about conjugation between $-C\equiv C-$ and $-SiMe_2-$ groups in $[-C\equiv C-SiMe_2-]_n$ with $n=4$ and 5 has been investigated by AM 1 calculations which show strong conjugation. In the structure determination (AM 1, X-ray) and in the Raman spectra no significant differences to normal values are observed. The NMR $Si-C\equiv$ coupling constant and UV spectra are presented.

Keywords. Ethynylsilanes; Conjugation; Structure determination; Raman spectra.

Molekulare Eigenschaften einiger neuer cyclischer Ethinylsilane

Zusammenfassung. Die Frage der Konjugation zwischen $-C\equiv C-$ und $-SiMe_2-$ Gruppen in $[-C\equiv C-SiMe_2-]_n$ mit $n=4$ und 5 wurde mittels AM 1-Rechnungen untersucht, wobei starke Konjugation resultierte. Bei Strukturuntersuchungen (AM 1 und Röntgenbeugung) und in den Raman-Spektren wurden keine signifikanten Unterschiede zu normalen Werten beobachtet. Die NMR $Si-C\equiv$ Kopplungskonstante und UV-Spektren werden angegeben.

Introduction

Ethynylsilanes are a class of compounds which stimulate interest in theoretical as well as technical respects. With regard to technical application these compounds are feasible precursors for the synthesis of silicon carbide ceramics. Theoretical interests concern the possibility of electronic bond interactions between carbon-carbon triple bonds and $SiMe_2$-groups.

Recently we found a new and simple route to prepare cyclic and oligomeric ethynyl silanes [1]. When acetylene is passed into a suspension of alkali metal or a potassium/sodium alloy in *THF* and simultaneously dialkyldichlorosilane is added, ethinylsilanes are formed. With dimethyldichlorosilane we isolated two ring systems with four and five $[-SiMe_2-C\equiv C-]$-units. Beside these two fully characterized compounds $[-SiMe_2-C\equiv C-]_5$(**1**) and $[-SiMe_2-C\equiv C-]_4$(**2**) larger

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* This paper is dedicated to Professor Dr. mult. Victor Gutmann on the occasion of his 70th birthday with warmest personal wishes

ring compounds up to 12 units were detected. Additionally, by reaction of a mixture of $[-\mathrm{Si}Me_2-\mathrm{C}\equiv\mathrm{C}-]_n$ with n = 4, 5, 6 with a catalytic amount of n-butyllithium in *THF* a ring with eight units $[-\mathrm{Si}Me_8-\mathrm{C}\equiv\mathrm{C}-]_8$ (**3**) is formed in high purity and good yield.

To discuss the bonding problems mentioned above, we have investigated the cystal structure and also NMR, IR, Raman, and UV spectra.

Results and Discussion

X-Ray Structures

$[-\mathrm{Si}Me_2-\mathrm{C}\equiv\mathrm{C}-]_5$ (**1**)

Crystal data. $C_{20}H_{30}Si_5$, $M=410.9$, monoclinic, space group $P2_1/c$, $a=22.460(3)$, $b=10.569(1)$, $c=11.833(2)$ Å, $\beta=93.11(1)°$, $U=2805$ Å^3, $Z=4$, $D_c=0.973\ \mathrm{g\,cm^{-3}}$, $\lambda=1.5418$ Å, $F(000)=880$, $\mu(\mathrm{CuK}_\alpha)=24.2\ \mathrm{cm^{-1}}$, crystal size $0.40\times0.40\times0.30$ mm.

Data collection. Unit-cell dimensions were determined and intensity data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated CuK_α radiation and an $\Theta/2\Theta$ scan procedure. A total of 9317 reflections were collected ($1<2\Theta<60°$). The segment of reciprocal space scanned was: (h) $-25\rightarrow25$, (k) $0\rightarrow11$, (l) $0\rightarrow13$. The reflection intensities were corrected empirically for absorption using psi-scans; maximum transmission factor 0.998, minimum value 0.900.

Structure solution and refinement. The structure was solved by the application of routine direct methods (SHELX-86) [2] and refined by full matrix least squares (SHELX-76) [3]. The asymmetric unit contains one independent molecule. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined isotropically.

The final residuals R and R_w were 0.050 and 0.041 for the 347 variables and 4035 data for which $F_0\geqslant0\,\sigma(F_0)$. The functions minimised were $R=\Sigma(|F_0|-|F_c|)/\Sigma|F_0|$ and $R_w=[\Sigma w(|F_0|-|F_c|)^2/\Sigma wF_0{}^2]^{1/2}$ with $w=1/\sigma^2(F_0)$.

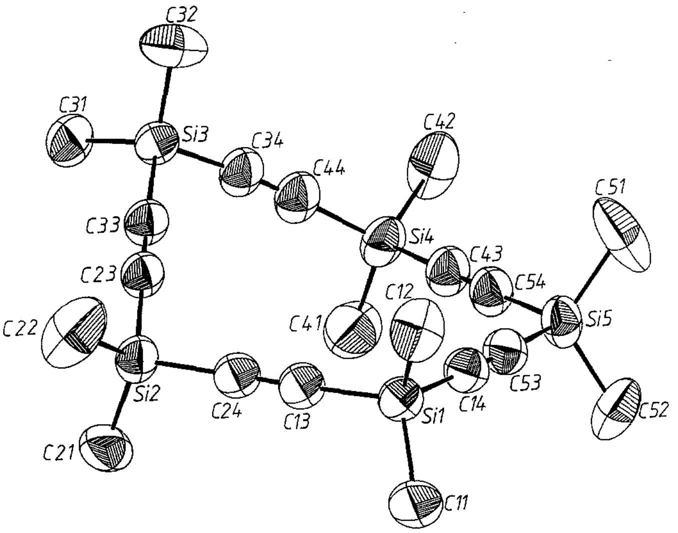

Fig. 1. Molecular structure and numbering scheme for compound **1**

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters for $C_{20}H_{30}Si_5$ (**1**)

Atom	x	y	z	B_{equ}
Si 1	0.07338 (3)	0.10665 (7)	0.36593 (6)	5.18 (2)
Si 2	0.24281 (3)	0.24472 (7)	0.15504 (6)	5.46 (2)
Si 3	0.41963 (3)	0.11643 (7)	0.38413 (5)	5.02 (2)
Si 4	0.35559 (3)	−0.31299 (8)	0.45986 (6)	5.94 (2)
Si 5	0.15062 (3)	−0.26778 (8)	0.56459 (6)	5.78 (2)
C 11	0.0100 (1)	0.0660 (3)	0.2673 (2)	7.95 (8)
C 12	0.0540 (1)	0.2313 (3)	0.4656 (2)	7.45 (7)
C 13	0.13636 (9)	0.1573 (2)	0.2855 (2)	5.50 (6)
C 14	0.09834 (9)	−0.0336 (2)	0.4446 (2)	5.08 (5)
C 21	0.2443 (1)	0.1564 (3)	0.0199 (2)	7.53 (8)
C 22	0.2387 (1)	0.4150 (3)	0.1341 (3)	9.82 (9)
C 23	0.30963 (9)	0.2047 (2)	0.2437 (2)	5.36 (6)
C 24	0.17853 (9)	0.1917 (2)	0.2335 (2)	5.48 (6)
C 31	0.4855 (1)	0.1191 (3)	0.2984 (2)	6.74 (7)
C 32	0.4318 (1)	0.2117 (3)	0.5141 (2)	8.05 (8)
C 33	0.40153 (9)	−0.0467 (3)	0.4203 (2)	5.58 (6)
C 34	0.35426 (9)	0.1731 (2)	0.2999 (2)	5.30 (6)
C 41	0.3563 (1)	−0.4031 (3)	0.3267 (3)	9.82 (9)
C 42	0.3988 (1)	−0.3934 (3)	0.5768 (3)	8.46 (8)
C 43	0.2791 (1)	0.2918 (3)	0.4983 (2)	5.88 (6)
C 44	0.38547 (9)	−0.1545 (2)	0.4379 (2)	5.97 (6)
C 51	0.1516 (1)	−0.2472 (3)	0.7196 (2)	9.14 (9)
C 52	0.1094 (1)	−0.4104 (3)	0.5136 (3)	7.85 (8)
C 53	0.11772 (9)	−0.1268 (2)	0.4932 (2)	5.27 (6)
C 54	0.2277 (1)	−0.2789 (2)	0.5229 (2)	5.84 (6)

The fractional atomic coordinates and equivalent isotropic temperature factors B_{equ} are listed in Table 1. Table 2 lists the bond lengths and angles. The molecular structure and atom numbering are shown in Fig. 1.

The structure of (Me_2SiC ≡ C)$_5$ (Fig. 1) consists of a symmetrical but not planar fifteen-membered ring which adopts an envelope conformation. In its C_s-symmetry ($2 \equiv m$) four of the five silicon atoms are in one common plane with the fifth one lying out of the plane. From Fig. 1 it is apparent that the insertion of C ≡ C units into adjacent Me_2Si groups of the cyclic (Me_2Si)$_5$ retains the overall geometry of the ring [4]. The pentagon is nearly equilateral with a total length of 4.88(1) Å. The atoms Si(2)C(24)C(13)Si(1)C(14)C(53)Si(5)C(54)C(43)Si(4) lie in the same plane with a maximal deviation of 0.022 Å, likewise the atoms Si(2)C(23)C(33)Si(3)C(34)C(44)Si(4) with a deviation of 0.044 Å. The dihedral angle between the planes is 133.7 (1)°. The valence angles at the silicon $Me-\mathrm{Si}-Me$ are larger than tetrahedral [111.4(1)° − 113.5(1)°], but smaller in the $\equiv\mathrm{C}-\mathrm{Si}-\mathrm{C}\equiv$ moieties [104.73(6)° − 106.83(6)°], which is the reason why the acetylene groups within the ring are slightly bent inward, except for the nearly linear group C(13)C(24) (Tab. 2). The endocyclic torsion angles at the Si...Si axes (Tab. 3) show the

Table 2. Bond lengths [Å] and angles [deg] for $C_{20}H_{30}Si_5$ (**1**)

Bond lengths			
Si(1)−C(13)	1.827(1)	Si(1)−C(11)	1.843(2)
Si(1)−C(14)	1.822(1)	Si(1)−C(12)	1.837(2)
Si(2)−C(23)	1.833(1)	Si(2)−C(21)	1.854(2)
Si(2)−C(24)	1.845(1)	Si(2)−C(22)	1.819(2)
Si(3)−C(33)	1.830(1)	Si(3)−C(31)	1.840(2)
Si(3)−C(34)	1.829(1)	Si(3)−C(32)	1.846(2)
Si(4)−C(43)	1.816(1)	Si(4)−C(41)	1.842(2)
Si(4)−C(44)	1.828(2)	Si(4)−C(42)	1.853(2)
Si(5)−C(53)	1.847(2)	Si(5)−C(51)	1.846(2)
Si(5)−C(54)	1.829(1)	Si(5)−C(52)	1.853(2)
C(13)−C(24)	1.213(1)	C(33)−C(44)	1.216(2)
C(14)−C(53)	1.210(2)	C(43)−C(54)	1.213(1)
C(23)−C(34)	1.220(1)		
Bond angles			
C(13)−Si(1)−C(14)	106.22(5)	C(11)−Si(1)−C(12)	111.8(1)
C(23)−Si(2)−C(24)	106.30(5)	C(21)−Si(2)−C(22)	112.6(1)
C(33)−Si(3)−C(34)	104.73(6)	C(31)−Si(3)−C(32)	111.4(1)
C(43)−Si(4)−C(44)	106.40(6)	C(41)−Si(4)−C(42)	112.0(2)
C(53)−Si(5)−C(54)	106.83(6)	C(51)−Si(5)−C(52)	113.5(1)
Average of four angles			
C(11)/(12)−Si(1)−C(13)/(14)	109.6(3)		
C(21)/(22)−Si(2)−C(23)/(24)	109.4(5)		
C(31)/(32)−Si(3)−C(33)/(34)	110.1(4)		
C(41)/(42)−Si(4)−C(43)/(44)	109.6(5)		
C(51)/(52)−Si(5)−C(53)/(54)	109.1(7)		
Si(1)−C(13)−C(24)	179.1(1)	Si(2)−C(24)−C(13)	179.6(1)
Si(1)−C(14)−C(53)	176.3(1)	Si(5)−C(53)−C(14)	177.4(1)
Si(2)−C(23)−C(33)	177.0(1)	Si(3)−C(33)−C(23)	176.8(1)
Si(3)−C(34)−C(44)	174.5(1)	Si(4)−C(44)−C(33)	175.6(1)
Si(4)−C(43)−C(54)	179.1(1)	Si(5)−C(54)−C(43)	176.8(1)

symmetry of the molecule, which consists of one mirror plane (point group C_s). The part Si(2)..Si(1)..Si(5)..Si(3) of the molecule adopts an exactly eclipsed conformation with the torsion angle 0.00°. Similar angular distortions at silicon have been observed in $(Me_2SiC\equiv C)_6$ [5], $(Me_2Si)_5$ and $\alpha-\alpha'$ − silaalkadiynes [6]. The bond lengths in $(Me_2SiC\equiv C)_5$ are in the ranges: Si − *Me* 1.819(2) − 1.854(2) Å; Si − C ≡ 1.816 − 1.847(2)Å; C ≡ C 1.210(2) − 1.220(1) Å. The Si − *Me* bond lengths are within expected values. However, the Si − C ≡ bond distances are partly shorter than in related compounds like $\alpha-\alpha'$-silaalkadiynes [6] with an average bond length of 1.843(1) Å. The C ≡ C bond distances are within the range found in $\alpha-\alpha'$-silaalkadiynes [1.217(1) Å], nevertheless they are longer than in cyclic organic alkynes [1.18–1.19 Å].

Table 3. Endocyclic torsion angles [deg] for **1**

Si(5)...Si(1)...Si(2)...Si(3)	−30.36
Si(1)...Si(5)...Si(4)...Si(3)	29.00
Si(2)...Si(1)...Si(5)...Si(4)	0.00
Si(1)...Si(2)...Si(3)...Si(4)	47.02
Si(5)...Si(4)...Si(3)...Si(2)	−45.76

$[-\mathrm{Si}Me_2-\mathrm{C}\equiv\mathrm{C}-]_4$ (**2**)

Crystal data. $C_{16}H_{24}Si_4$, $M_r = 328.7$, monoclinic, space group $P2_1/c$, $a = 9.853(1)$, $b = 9.672(1)$, $c = 11.808(1)$ Å, $\beta = 112.00(1)°$, $U = 1\,043.34$ Å^3, $Z = 2$, $D_c = 1.046$ g cm^{-3}, $\lambda = 0.71069$ Å, $F(000) = 176$, $\mu(\mathrm{MoK}_\alpha) = 1.18$ cm^{-1}, crystal size $0.35 \times 0.30 \times 0.40$ mm.

Data collection. Unit-cell dimensions were determined by precession methods and intensity data were collected at −50°C on a Syntex $P2_1$ diffractometer using graphite monochromated MoK_α radiation and a ω-scan procedure. A total of 2 069 reflections were collected ($2\Theta < 50°$). The segment of reciprocal space scanned was $(h)\ -11 \rightarrow 11$, $(k)\ 0 \rightarrow 11$, $(l)\ 0 \rightarrow 21$. The reflection intensities were corrected for absorption using empirical methods.

Solution and refinement of the structure were the same as used above for $C_{20}H_{24}Si_5$. The asymmetric unit contains a half molecule of $C_{16}H_{24}Si_4$, the second half is generated through space symmetry conditions. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were refined isotropically. The final residuals R and R_w were 0.0332 and 0.0304 for the 139 variables and 1 557 data for which $F_0 \geqslant 4\sigma(F_0)$.

Table 4 lists the fractional atomic coordinates and the equivalent isotropic temperature factors U_{equ} with $U_{equ} = (U_1 \cdot U_2 \cdot U_3)^{1/3}$ (U_1, U_2, U_3 ... eigenvalues of the U_{ij}-matrix, standard deviations in brackets). Table 5 lists the bond lengths and angles, the molecular structure and atom labelling are shown in Fig. 2.

The structure of $(Me_2\mathrm{SiC}\equiv\mathrm{C})_4$ (Fig. 2) consists of a symmetrical, planar twelve-membered ring with D_{4h} symmetry. The square is nearly equilateral with a total length of 4.86(2) Å and the angles 89.5(2)°. 90.4(2)°. The atoms C(31)C(11)Si(1)C(12)C(21)Si(2) and their symmetry generated counterparts lie in a common plane with a maximum deviation of 0.056 Å. Similarly to the structure

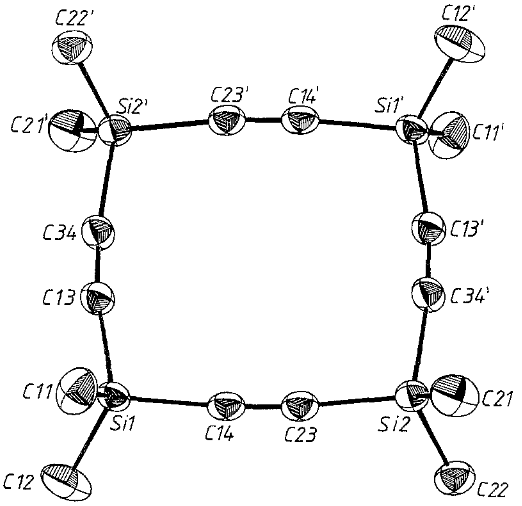

Fig. 2. Molecular structure and numbering scheme for compound **2** (symmetry generated marked)

Table 4. Fractional atomic coordinates and isotropic displacement parameters for $C_{16}H_{24}Si_4$ (**2**)

Atom	X/A	Y/B	Z/C	U_{equ}
Si 1	0.90427 (6)	0.22769 (6)	0.64351 (5)	0.032
Si 2	0.65184 (5)	0.62905 (5)	0.40928 (5)	0.033
C 11	1.0870 (2)	0.2626 (2)	0.6417 (2)	0.039
C 12	0.7960 (2)	0.3770 (2)	0.5607 (2)	0.036
C 13	0.8263 (3)	0.0676 (3)	0.5599 (3)	0.060
C 14	0.9102 (3)	0.2195 (4)	0.8011 (3)	0.058
C 21	0.7332 (2)	0.4755 (2)	0.5017 (2)	0.038
C 23	0.4997 (3)	0.5766 (4)	0.2682 (2)	0.051
C 24	0.5937 (3)	0.7521 (3)	0.5017 (2)	0.049
C 31	1.1973 (2)	0.2985 (2)	0.6278 (2)	0.039

Table 5. Bond lengths [Å] and angles [deg] for $C_{16}H_{24}Si_4$ (**2**)

Bond lengths[a]			
Si (1) − C (13)	1.840 (2)	Si (1) − C (11)	1.842 (3)
Si (1) − C (14)	1.844 (2)	Si (1) − C (12)	1.841 (3)
Si (2) − C (23)	1.839 (2)	Si (2) − C (21)	1.847 (3)
Si (2) − C (34)′	1.839 (2)	Si (2) − C (22)	1.845 (3)
C (13) − C (34)	1.209 (3)	C (14) − C (23)	1.205 (3)
Bond angles[a]			
C (13) − Si (1) − C (14)	102.96 (9)	C (11) − Si (1) − C (12)	110.7 (2)
C (23) − Si (2) − C (34)′	103.77 (9)	C (21) − Si (2) − C (22)	112.6 (1)
Average of four angles			
C (11)/C (12) − Si (1) − C (13)/C (14)	110.6 (1)		
C (21)/C (22) − Si (2) − C (34)/(23)	109.9 (1)		

[a] Symmetry operation relating designated atoms to reference atoms is $(x, y, z) : ()'\ -x, -y, -z$

above the valence angles at silicon *Me* − Si − *Me* are larger than tetrahedral [110.7(2)°, 112.6(1)°], but smaller for ≡C − Si − C ≡ [102.96(9)°, 103.77(9)°] with the acetylene groups bent outwards due to ring strain (Table 5).

The bond lengths in $[Me_2SiC\equiv C]_4$ are in the ranges Si − Me 1.841(3) − 1.847(3) Å; Si − C ≡ 1.839(2) − 1.844(2) Å; C ≡ C 1.205(3) and 1.209(3) Å. Surprisingly the Si − *Me* and Si − C ≡ bond lengths in the molecule $(Me_2SiC\equiv C)_4$ correspond better with each other than in $(Me_2SiC\equiv C)_5$.

Calculated and observed structure factor amplitudes of both molecules together with a complete list of atomic coordinates and thermal parameters have been deposited. Further details of the structure determination are available from Forschungsinformationszentrum Karlsruhe GmbH, D-7514 Eggenstein-Leopoldshafen 2 on quoting the reference number CSD-54935 for the molecule $C_{20}H_{30}Si_5$ and for $C_{16}H_{24}Si_4$, the names of the authors, and the full literature citation.

Semi-Empirical Calculations

The $[-\mathrm{Si}Me_2-\mathrm{C}\equiv\mathrm{C}-]_4$ molecule (**2**) has been investigated by means of the semi-empirical AM 1 method [7]. The structure has been optimized in D_{4h} symmetry of the ring. Calculated bond lengths and angles are $\mathrm{C}\equiv\mathrm{C}$ 120.7 pm, $\equiv\mathrm{C}-\mathrm{Si}$ 176.2 pm, $H_3C-\mathrm{Si}$ 183.3 pm, $< -\mathrm{C}\equiv\mathrm{C}-\mathrm{Si}$ 173.1°, $\geqslant\mathrm{C}-\mathrm{Si}-\mathrm{C}\leqslant$ $<109.9°$. They are in good agreement with well known standard data or are at least not unexpected. In general, they are also in good agreement with the measured data from the X-ray diffraction, only the $\equiv\mathrm{C}-\mathrm{Si}$ distance was found to be longer.

In **2** four $\mathrm{C}\equiv\mathrm{C}$ bonds are separated by four Si*Me*$_2$ groups. The following alternative is of considerable importance for the characterisation of the electronic structure: either the molecular orbital energies of the $\mathrm{C}\equiv\mathrm{C}-$ π-MO's and of the Si π-MO's are essentially different or almost degenerate. For the first case, we have

Table 6. MO Scheme of **2**

	MO energy (eV)
+ − − +	
− −	−10.36 (HOMO)
− −	
+ − − +	
	−10.56 −10.56
+ 0 0 −	
0 0	−11.04 (Siπ)
0 0	
− 0 0 −	
0 − − 0	
+ +	−11.24 (C≡Cπ)
+ +	
0 − − 0	
	−11.80 −11.80
+ + + +	
+ +	−12.08
+ +	
+ + + +	

to expect four almost degenerate $C\equiv C$ π-MO's and four almost degenerate Si π-MO's. In the second case strong conjugation between $-C\equiv C-$π- and Si π-MO's may occur which leads to an eightfold splitting of π-MO's.

The calculation of **2** indicates the latter case to be present with strong conjugation between $C\equiv C$ π- and Si π-MO's which leads to an overall splitting of MO's of 1.72 eV. In a scheme (Table 6) the HOMO is characterized by the maximum antibonding $\equiv C-Si$ interaction, whereas in the lowest π-MO the bonding $\equiv C-Si$ interaction is a maximum. The center of the splitting manifold is 11.24 eV. The corresponding orbital is characterized by four non-interacting $C\equiv C$ π-fragments where the silicon atoms do not contribute for symmetry reasons. For comparison, the π-MO energy of the free C_2H_2 molecule is 11.50 eV. The orbital with four non-interacting Si π-fragments, where the acetylenes do not contribute for symmetry reasons, lies very close to the former, with an energy of 11.04 eV. No unusual charge shifts are observed in compound **2**. The atomic valence charge at carbon in $C\equiv C$ in **2** is calculated to be 4.48 in close agreement with that in $C_2(SiH_3)_2$ of 4.46. The $C\equiv C$ bond length in **2** (120.7 pm) is exactly the same as in $C_2(SiH_3)_2$.

One can expect that the situation in case of the five-membered ring is very close to that of the calculated four-membered ring, therefore the ring with five units was not calculated separately.

Spectroscopic Investigations

The most interesting spectroscopic results are summarised in Table 7. In the $C\equiv C$-stretching vibrional frequencies derived from the Raman spectra, which reflect the bonding strength, one cannot see any significant differences. The small differences to other silicon containing ethyne derivatives or acetylene itself (values included in Table 7) are mainly caused by the different weights of the substituents.

The silicon-carbon coupling constant over one bond exhibits a very high value. However, this may have various causes. Not only special bond interactions, but

Table 7. Spectroscopic data

Compound	$\sphericalangle$ Si−C−C	$\sphericalangle$ C−Si−C	r_{Si-C} (pm)	$r_{C\equiv C}$ (pm)	Ra ν_1 (CC) (cm^{-1})	$^1J(SiC\equiv)$ (Hz)	Ref.
$[-Si(Me)_2-C\equiv C-]_4$	173.09°	103.37°	184	120.7	2 132	–	
$[-Si(Me)_2-C\equiv C-]_5$	177.22°	106.1°	183.2	121	2 134	89	
$[-Si(Me)_2-C\equiv C-]_6$	176.7°	107.5°	181.7	122.0	2 137	89	[9]
$[-Si(Me)_2-C\equiv C-]_8$	–	–	–	–	2 134	–	
$Si(C\equiv C-SiMe_3)_4$	176.6°	–	182.4	118	2 050		[8]
$Si(C\equiv CH)_4$	–	–	–	–	2 053		[10]
$Me_2Si-C\equiv C-SiMe_2$ $\vert \qquad\qquad \vert$ $Me_2Si-C\equiv C-SiMe_2$	166.7°	–	183.9	118.3	2 082.4		[11]
$Et_3Si-C\equiv C-SiEt_3$						74.8	[12]
$HC\equiv CH$	–	–	–	120.7	1 974		

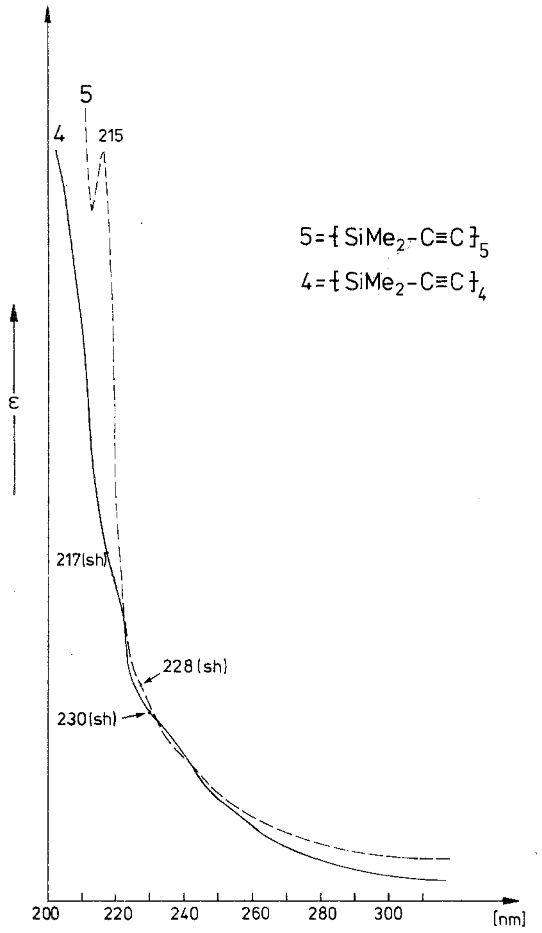

Fig. 3. UV spectra of **1** and **2**

also unusual bond angles and other influences could be the origin of the high value. On the other hand, this high value points towards a stronger p-character of the Si – C bond.

UV spectra were recorded for compounds **1** and **2** (Fig. 3). One can see some bathochromic shifted absorption maxima and some shoulders. This bathochromic shift indicates a possible conjugation.

Conclusion

The observed structures are in agreement with the expected geometries of the molecules. The ring with four units exhibits a planar square-like structure. The bond angles at the Si atom are somewhat smaller than the tetrahedron angle and the Si – C ≡ C-angle with 170 to 175° is close to the linear arrangement. These small deviations seem to be caused mainly by the strained cyclic system and not by electronic effects. This interpretation is supported by the angles of the cycle with five units. This compound shows a non-planar cyclic structure in which the Si – C ≡ C-and the C – Si – C-angle are closer to the normal values, a fact probably due to reduced ring strain.

A similar conclusion can be drawn from a discussion of the estimated bond lengths. Some typical bond distances and angles are shown in Table 7. The table also contains data from the ring with six Si – C ≡ C-units. This cycle with further reduced ring strain, once more, exhibits quite normal angles.

The Si – C distances are nearly equal in all compounds investigated, making a comparison difficult.

More instructive is the C ≡ C-triple bond distance. As one can see, the different compounds do not show significant deviations and also in acetylene itself, the distance is the same. Only a few other structures have been investigated earlier, such as the structure with four ethyne units on one Si atom, investigated by Schmidbaur [8] or a cycle with SiSi bonds from Sakurai et al. [11]. In these examples one also cannot see significant differences in bond distances.

The semi-empirical AM 1 calculations indicate a strong conjugation between the carbon-carbon-triple bond and the silicon π-MO's which leads to an overall splitting of the corresponding MO's of 1.73 eV. The HOMO describes the maximum antibonding interaction between the carbon-carbon-triple bond and silicon, whereas in the lowest π-MO the bonding interaction is maximal. The total energy did not change from usual values. Therefore, significant deviations of bond distances and vibrations upon conjugation cannot be expected; and in view of the results of the AM 1 calculation it is not surprising that we found quite normal values.

The conjugation effects, manifested in the strong splitting of the π-MO's, should show some effects in the PE- and UV spectroscopic results, because these methods are sensitive toward changes in orbital energies. On the other hand, the resolution of these spectra is very low and an interpretation becomes difficult. As one can see from the calculation many molecular orbitals have similar energies and therefore one cannot expect a significant and helpful resolution of the PE spectra. The same situation is encountered in the UV spectra (Fig. 3). One can see some bathochromic shifted absorption maxima and some shoulders but an interpretation is not possible.

So, in conclusion, the calculation shows strong conjugation but we do not have significant experimental data to confirm this. On the other hand, all data do not exclude any interaction and values of the Si – C coupling constant over one bond and the results of the UV spectroscopy point in this direction.

Experimental

Compounds **1** and **2** were prepared by recently published methods [1].

Hexadecamethyl-1,4,7,10,13,16,19,22-octasila-cyclotetracosa-2,5,8,11,14,17,20,23-octain (**3**)

To 0.5 g of a mixture of $-[\mathrm{Si}Me_2-\mathrm{C}\equiv\mathrm{C}]_n-$ ($n=4$, 5, 6) in 100 ml *THF*, 0.14 ml *n*-butyllithium solution (1.6 *m*) were added and stirred. After several hours a white precipitate was formed, six days later about 50% of the starting material had reacted to **3**. After filtration the product was washed with pentane. Yield 0.25 g (about 50%), m.p. 242°C.

MS [*m/e*]: 656 (M^+), 641, 583, 553, 313, 284, 231, 201, 155, 110, 73. IR [cm^{-1}]: 1 254, 1 250, 1 245, 840, 788, 779, 764, 667, 321. Raman [cm^{-1}]: 2 134.

Coupling constants over one and two bonds were measured with a modified INEPT-INADEQUATE method [13], the accuracy is better than ± 0.3 Hz. IR spectra were recorded with a Perkin Elmer 883 grating spectrometer. Raman spectra were measured with a SPEX RAMALOG and mass spectra with a Finnigan MAT212 with electron-ionisation (70 eV). The UV spectra were recorded with a Perkin Elmer 550 SE.

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