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1,2-Dithiolate derivatives of monosilanes and disilanes

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Abstract

The reactions of the chlorosilanes Me_3SiCl, Me_2SiCl_2, $MeSiCl_3$, $SiCl_4$, $SiClMe_2–SiClMe_2$ and $SiCl_2Me–SiCl_2Me$ with ethane-1,2-dithiol and benzene-1,2-dithiol have been investigated. All silicon dithiolates formed have been characterized by ^{1}H-, ^{13}C- and ^{29}Si-NMR. The formation of five-membered rings SiS_2C_2 is accompanied by a strong downfield shift of the ^{29}Si-NMR signals. The molecular structures of $Me_2SiS_2(o\text{-}C_6H_4)$ (**6**), $Si[S_2(o\text{-}C_6H_4)]_2$ (**7**) and $[MeSiS_2(o\text{-}C_6H_4)]_2$ (**11**) are reported. The found geometries are compared with the results of DFT calculations at the B3LYP/6-31G* level, and the observed partial planarizations of the SiS_4 tetrahedrons in the spiro compounds $Si[(SCH_2)_2]_2$ (**1**) and **7** are discussed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Monosilanes; Disilanes

1. Introduction

Since the questionable conclusion of Mayer et al. [1] about a planar tetracoordinated silicon atom in bis(*o*-phenylenedioxy)silane, some interest has arisen in the coordination geometry of silicon in orthothiosilicic acid esters and spiro-bis(ethane-1,2-dithio)silane, $Si[(SCH_2)_2]_2$ (**1**). Wojnowski et al. [2] reported the X-ray structure of **1** showing some deviation of the geometry at silicon from a tetrahedron. The angles S–Si–S which are part of five-membered rings are decreased to 100.1° and 100.5° respectively. Furthermore, the spiro angle between the two S–Si–S′ planes is reduced to 74.4°. This strong distortion was assigned as a result of an intramolecular anomeric effect of interactions between 3p lone pair orbitals of sulfur with σ*(Si–S) antibonding orbitals [3]. Besides this spiro compound, which is also remarkable because of its ^{29}Si-NMR shift of + 57.47 ppm [4], only a few silicon derivatives of dithiols have been synthesized. If the ^{29}Si-NMR shift of $Me_2Si(SCH_2)_2$ (**2**, 41.67 ppm [4]) is compared to that of the acyclic mercapto derivatives $Me_2Si(SMe)_2$ (28.14 ppm [5]) or $Me_2Si(SBu)_2$ (24.8 ppm [6]) containing the same first coordination sphere at silicon, the cyclic compounds exhibit a strong downfield shift. If the ring is expanded to a six-membered ring in $Me_2Si(SCH_2)_2CH_2$ the ^{29}Si-NMR shift decreases to 22.53 ppm [4]. This exceptional low field shift in five-membered rings is also found in cyclic and polycyclic silthianes [7] and can also be used as an indication of the formation of this ring size. A compilation of structural details (bond lengths and angles) as well as ^{29}Si-NMR shifts of silicon sulfur compounds can be found in [8].

In this work we will report on the synthesis and properties of several ethane-1,2-dithiol and benzene-1,2-dithiol derivatives of mono- and disilanes in order to obtain a better understanding of the unusual NMR parameters and structures.

2. Results and discussion

2.1. Ethane-1,2-dithiolate derivatives of methylchloromonosilanes

The reaction of Me_3SiCl with ethane-1,2-dithiol and triethylamine yields the acyclic 1,2-bis(trimethylsilyl-

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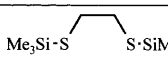
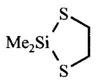
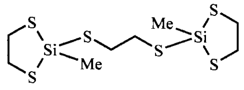
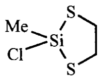
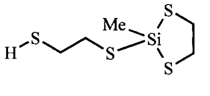
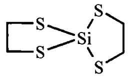
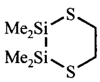
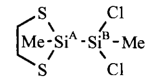
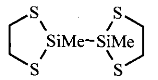
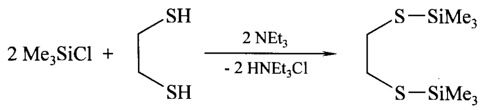
Table 1
^{29}Si, ^{13}C and ^{1}H-NMR chemical shifts (ppm) and coupling constants (Hz) of ethane-1,2-dithiolate derivatives of monosilanes and disilanes

	compound	δ_{Si}	$^{1}J_{SiC}$	δ_C	δ_H
3		15.9	53.3	CH_2: 28.8 CH_3: 1.0	2.60 0.29
2		41.7	56.2	CH_2: 36.8 CH_3: 4.7	3.08 0.62
4a		45.8	63.1	cyclo-CH_2: 37.6 CH_2: 30.1 CH_3: 5.38	3.17 2.98 0.88
4b		47.5		CH_2: 37.3 CH_3: 7.05	3.27 1.07
4c		45.9		cyclo-CH_2: 37.6 CH_2: 32.4, 26.6 CH_3: 5.46	3.17 2.91, 2.82 0.88 SH: 1.70 ($^{3}J_{HH}$: 8.3)
1		57.3	-	CH_2: 37.6	3.18 ($^{3}J_{SiH}$: 6.8)
8		-9.1	45.6	CH_2: 30.1 CH_3: -1.8	2.92 0.44
10		A: 23.2 B: 22.3	49.7 54.6	CH_2: 37.4 CH_3: A: 1.06 B: 5.86	3.15 0.81 0.92
9a		23.8	46.5	CH_2: 37.5 CH_3: 2.4, $^{1}J_{CH}$: 124.1	3.13 0.74

thio)ethane (**3**) whereas treatment of Me_2SiCl_2 with ethane-1,2-dithiol and triethylamine resulted in the formation of cyclic **2** with no indication of any acyclic by-products:



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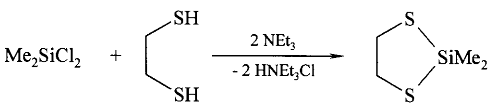


2

The NMR data of **2** and **3** are summarized in Table 1. Whereas δ_{Si} of **3** is only 1.2 ppm low field from the thiobutyl derivative Me_3SiSBu [6], **2** which possess a five-membered ring SiS_2C_2, exhibits a δ_{Si} 16.9 ppm downfield from the comparable thiobutyl derivative $Me_2Si(SBu)_2$. Furthermore the δ_C and δ_H of the ethylene unit are shifted significantly from the values found in ethane-1,2-dithiol (δ_C 28.6 ppm, δ_H (CH_2) 2.75 ppm) and **3**.

More complicated is the reaction of $MeSiCl_3$ with $HS(CH_2)_2SH$ and NEt_3. If the reaction is carried out in a 1:1:2 molar ratio three products can be observed. Besides the bridged dimer $(CH_2S)_2SiMe$–$S(CH_2)_2S$–$MeSi(SCH_2)_2$ (**4a**) the partial substitution product $(CH_2S)_2SiClMe$ (**4b**) and $(CH_2S)_2SiMe$–$S(CH_2)_2SH$ (**4c**) can be observed. The ^{29}Si-NMR shifts of **4a**–**4c** are similar and are, in accordance with the formation of a five-membered ring SiS_2C_2, 16.3 ppm (**4a**), 17.3 ppm (**4b**) and 16.4 ppm (**4c**) downfield from the acyclic analogously thiobutyl substituted silanes $MeSi(SBu)_3$ and $MeSiCl(SBu)_2$ [6], respectively. Also the ethylene units, which are part of the rings, exhibit δ_C and δ_H values at relatively low field, see Table 1. If the reaction of $MeSiCl_3$ with $HS(CH_2)_2SH$ and NEt_3 is repeated in a 1:1.5:3 molar ratio, only **4a** and **4c** are formed in a 4:1 ratio.

The analogous reaction of $SiCl_4$ yields the known spiro compound **1**; no further products, like a semispiro compound $(CH_2S)_2SiCl_2$, could be detected by NMR if the starting molar ratio was changed to 1:1:2. DFT calculations of **1** at the B3LYP/6-31G* level yielded an optimized structure which reflects well the observed deviations from the tetrahedral geometry at silicon, see Table 2 and Fig. 1. The calculated spiro angle of 77.2° is close to the reported value of 74.4°. If this angle is

Table 2
Comparison of the crystal structure geometry of **1** with the results of the DFT calculation at the B3LYP/6-31G* level

Parameter	Crystal structure [2]	DFT calculation	
		Optimized geometry	Geometry with fixed spiro angle
d(SiS) (Å)	2.115(1) and 2.117(1)	2.157	2.161
d(SC) (Å)	1.815(3) and 1.817(3)	1.852	1.853
d(CC) (Å)	1.520(9) and 1.523(6)	1.525	1.525
Spiro angle (°)	74.4	77.2	90
∠SSiS (within the ring) (°)	100.1(1) and 100.5 (1)	100.5	100.6
∠SSiS (between the rings) (°)	104.6(1) and 124.7(1)	106.6 and 122.7	114.1
∠CSSi (°)	96.8(1) and 97.2(1)	96.2	96.2
∠CCS (°)	111.1(2) and 111.2(2)	111.3	111.6
Total energy (H)		−2039.62241	−2039.61975
Total energy with zero point correction (H)		−2039.49984	−2039.49736

fixed to 90°, the calculation results in a structure 6.5 kJ mol^{-1} higher in energy. This is in contrast to earlier EHT calculations which yielded an optimized structure with a spiro angle of 87° [3].

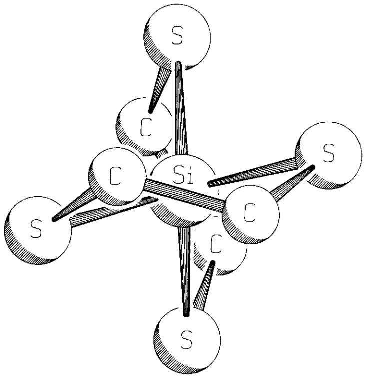
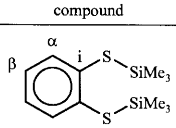
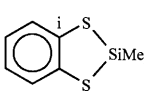
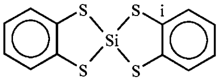
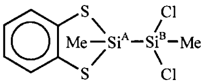
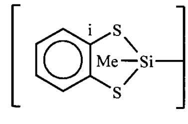


Fig. 1. SCHAKAL plot of the calculated structure of **1** (B3LYP/6-31G*), hydrogen atoms omitted for clarity, showing the partial planarization of the SiS_4 tetrahedron.

Table 3
NMR data of benzene-1,2-dithiolates of monosilanes

compound	δ_{Si}	$^1J_{SiC}$	δ_C	δ_H
5 	18.01	54.6	Me: 1.2 ($^1J_{CH}$: 120.7) i: 137.1 α: 135.7 ($^1J_{CH}$: 161.0) β: 126.7 ($^1J_{CH}$: 160.6)	Me: 0.31 7.48 (2 H), 7.09 (2 H)
6 	40.63	56.9	Me: 4.7 ($^1J_{CH}$: 122.8) i: 137.0 125.1 ($^1J_{CH}$: 161.4) 127.9 ($^1J_{CH}$: 162.1)	Me: 0.75 7.33 (2 H), 6.95 (2 H)
7 	45.4	-	i: 134.8 126.3, 127.0	7.36 (2 H), 7.08 (2 H)
12 	A: 21.2 B: 20.1		Me: A: 1.0 , B: 5.8	Me: A: 0.89 B: 0.97
11 	20.8	47.6	Me: 2.6 i: 137.1 125.5, 128.1	Me: 0.87 7.34 (2 H), 6.97 (2 H)

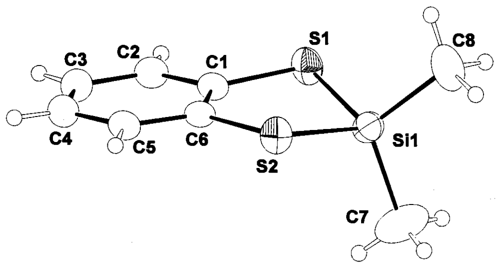


Fig. 2. Molecular structure of **6**.

2.2. Benzene-1,2-dithiolate derivatives of methylchloromonosilanes

The reactions of Me_3SiCl and Me_2SiCl_2 with benzene-1,2-dithiol and triethylamine yielded 1,2-bis(trimethylsilylthio)benzene (**5**) and 2,2-dimethyl-2-sila-1,3-dithiaindane (**6**) respectively, Table 3. Whereas in **5** the δ_{Si} of the $SiMe_3$ units are only 1.0 ppm downfield from the value found in the similar phenylthiotrimethylsilane [9], the $SiMe_2$ unit in **6** is shifted 15.4 ppm downfield from bis(phenylthio)dimethylsilane [9], in agreement with the formation of a five-membered ring SiS_2C_2. Despite the high solubility of **6** even in hexane and its low melting point, single crystals suitable for X-ray analysis could be obtained and Fig. 2 shows the molecular structure of **6**.

If $SiCl_4$ is reacted with benzene-1,2-dithiol and triethylamine the spiro compound bis(*o*-phenylenedithio)silane (**7**) is formed. The ^{29}Si-NMR shift of **7** appears at relatively low field although 17 ppm high field from **1**, whereas the Si-NMR shifts of the monocyclic compounds **2** and **6** differ only by 1.1 ppm. Single crystals of **7** suitable for X-ray analysis could be obtained; Fig. 3 shows the molecular structure of **7**.

Compared to the molecular structure of **6** important differences can be seen: both SiS_2C_2 rings in **7** are planar whereas the SiS_2C_2 ring in **6** adopts an envelope conformation with an angle of 20° between the C_2S_2 and the S_2Si planes. While the spiro angle between the planes C(7)C(8)Si and SiS_2 is 90° in **6** (like in an ideal tetrahedron) this spiro angle between the two five-membered rings in **7** is reduced to 83.39(0.01)° but this is still much closer to 90° than the 74.4° found in **1**. Furthermore the angles CSSi and SSiS within the five-membered rings are enlarged by 1 and 2°, respectively, in **7** in comparison with **6**. The shorter bond distances SiS in **7** than in **6** confirm the general trend also found in silthianes that the SiS bond lengths decrease with the number of sulfur substituents at silicon. Important bond lengths and angles of **6** and **7** are summarized and compared with the results of the DFT calculations in Table 4.

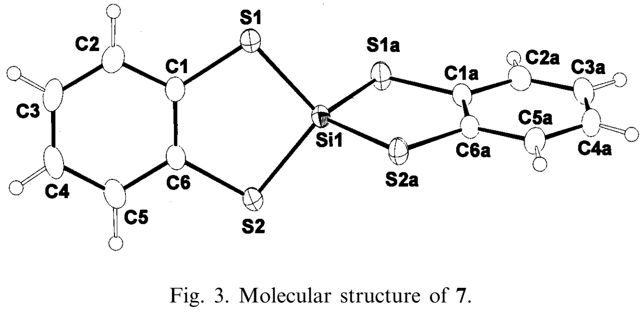


Fig. 3. Molecular structure of **7**.

Table 4
Comparison of bond lengths and angles of the molecular structures of **6**, **7**, and **11** with the results of DFT calculations (B3LYP/6-31G*)

Parameter	**6**		**7**		**11**	
	Observed	Calculated	Observed	Calculated	Observed	Calculated
d(SiSi) (Å)					2.336(3) [a] 2.337(3) [b]	2.363
d(SiS) (Å)	2.1529(6) 2.1541(7)	2.171	2.1299(6) 2.1381(6)	2.153	2.150(2) [a] 2.151(2) [a] 2.153(2) [b] 2.154(2) [b]	2.177
d(SiC) (Å)	1.836(2) 1.853(2)	1.881 1.883			1.852(5) [a] 1.851(6) [b]	1.882
d(SC) (Å)	1.773(2) 1.776(2)	1.793	1.778(2) 1.779(2)	1.788	1.781(5) [a] 1.783(5) [a] 1.776(5) [b] 1.779(5) [b]	1.794
spiro ∠(Si) (°)	90	90	83.39(0.01)	90 [c]	89.2(1) [a] 89.2(2) [b]	90
Envelope ∠ in C_2S_2Si rings (°)	20.0(1)	15.3	0	0	35.3(1) [a] 33.5(1) [b]	13.1
∠(SSiS) (°)	98.18(2)	98.9	100.08(2)	99.6	97.94(7) [a] 98.08(7) [b]	98.7
∠(CSSi) (°)	97.44(5) 97.58(5)	97.6	98.40(6) 98.46(6)	98.5	93.4(2) [a] 93.9(2) [a] 93.9(2) [b] 94.1(2) [b]	97.9

[a] Two independent molecules, molecule a.
[b] Two independent molecules, molecule b.
[c] Fixed at 83.4°: total energy +0.8 kJ mol^{-1}.

In contrast to the DFT calculations of **1** the optimized structure of **7** at the B3LYP/6-31G* level of theory shows a spiro angle of 90°. But if this angle is fixed to the value found in the crystal structure the total energy increases only by 0.8 kJ mol^{-1}. This suggests that the observed partial planarization in this case may also be a result of crystal packing forces.

On the other hand the calculated structures of **6** and **7** parallel the observation that the C_2S_2Si ring in **6** adopts an envelope conformation while the C_2S_2Si rings in **7** are planar. It can be argued that this planarization of the five-membered rings in **7** is a result of the non-bonding interaction of the two orthogonal siladithiaindane ring systems. An envelope conformation would lead to an increase in energy by repulsion of the two indane systems. To sum up, the crystal structures as well as the results of the DFT calculations of **1** and **7** show important differences, especially concerning the spiro angles. These differences are likely to cause the the very different ^{29}Si-NMR chemical shifts of **1** and **7**, whereas in all other cases the ethane-1,2-dithiol and the benzene-*o*-dithiol derivatives show very similar δ_{Si} values.

2.3. 1,2-dithiolate derivatives of methylchlorodisilanes

The reaction of 1,2-dichlorotetramethyldisilane with ethane-1,2-dithiol in the presence of triethylamine yields the six-membered ring compound **8** which has also been prepared earlier [10]. In contrast to the five-membered ring compounds the formation of a six-membered ring results in a significant high field shift of the ^{29}Si-NMR signal (see Table 1) of 7.5 ppm in comparison with the acyclic disilane thiolate $BuS(SiMe_2)_2SBu$ [6]. Differences from five-membered ring compounds are also evident in the ^{13}C and ^{1}H chemical shifts of the methylene units in **8** which appear at approximately 7 ppm (^{13}C) and 0.3 ppm (^{1}H) higher field in comparison with **1**, **2** and **4a**–**4c**. No similar six-membered ring compound is formed in the reaction of 1,2-dichlorotetramethyldisilane with benzene-1,2-dithiol, the NMR spectra of the reaction products rather suggest the formation of open chain oligomers $[-(SiMe_2)_2-S(o\text{-}C_6H_4)S-]_x$.

If 1,1,2,2-tetrachlorodimethyldisilane is reacted with ethane-1,2-dithiol the formation of either a five-membered ring compound or six-membered ring compounds is possible:

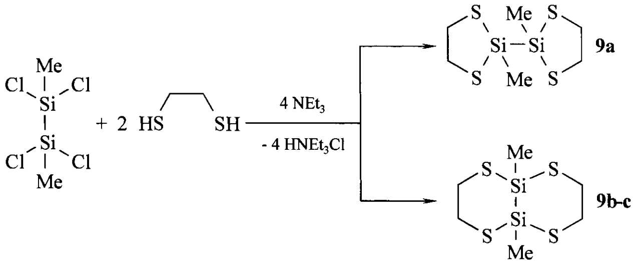


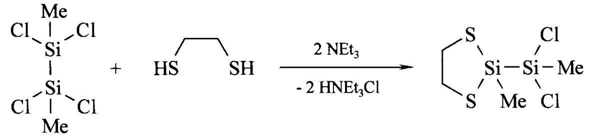
Table 5
Calculated total energies and geometries of **9a**–**9c** (B3LYP/6-31G*)

Parameter	**9a**	**9b**	**9c**
Total energy (H)	−2408.97290	−2408.94512	−2408.95120
Total energy with zero point correction (H)	−2408.77482	−2408.74697	−2408.75302
d(SiSi) (Å)	2.363	2.319	2.348
d(SiS) (Å)	2.183	2.177	2.169/2.175
∠(SSiS) (°)	99.7	113.0	105.0
∠(CSSi) (°)	96.2	102.0	102.1/105.8

DFT calculations at the B3LYP/6-31G* level of the possible isomers of $Si_2Me_2(SCH_2CH_2S)_2$ (see Table 5 and Fig. 4a–c) predict the isomer **9a** with a bis(cyclopentyl) structure to be the most stable, see Scheme 1.

The NMR spectra of the resulting product are in agreement with the formation of five-membered rings (**9a**, Table 1). The ^{29}Si-NMR chemical shift is shifted by 14.7 ppm to lower field in comparison with the acyclic thiolate $(BuS)_2SiMe–SiMe(SBu)_2$ and the ^{1}H- and ^{13}C-shifts of the methylene units are in the range found in the five-membered rings **1**, **2** and **4a**–**4c**.

If only one equivalent of ethane-1,2-dithiol is added to 1,1,2,2-tetrachlorodimethyldisilane in the presence of triethylamine, a partially substituted **10** can be detected in 56% amount besides residual 1,1,2,2-tetrachlorodimethyldisilane and **9a**:



10

The NMR data are in agreement with one C_2S_2Si five-membered ring and one unchanged $SiCl_2Me$ unit. No other partially substituted products can be detected in significant amounts (> 1%). This is in strong contrast to the stepwise reaction of $SiCl_2Me–SiCl_2Me$ with a monodentate thiol like BuSH and shows again the strong stabilization of five membered rings C_2S_2Si.

The results of the reaction of 1,1,2,2-tetrachlorodimethyldisilane with benzene-1,2-dithiol are similar. The formed **11** with a bis(cyclopentyl) structure has a ^{29}Si-NMR chemical shift (Table 3) very close to the value found in **9a**. If only one equivalent of benzene-1,2-dithiol is applied, a partially substituted product **12** analogous to **10** is formed, but in 67% yield as detected by NMR spectroscopy. The ^{29}Si-NMR shifts of **10** and **12** are again similar. Crystals of **11** suitable for X-ray analysis could be obtained from toluene solution. **11** crystallizes in the triclinic space group $P\bar{1}$ with two independent molecules per unit cell, one of them is depicted in Fig. 5. The bond lengths and angles of the two independent molecules are almost identical. Both molecules possess a centre of symmetry between the two silicon atoms.

The molecular structure proves the formation of five-membered rings which adopt an envelope conformation like in **6** with angles between the two planes C_2S_2 and S_2Si of 33.5 and 35.3°. With an angle between

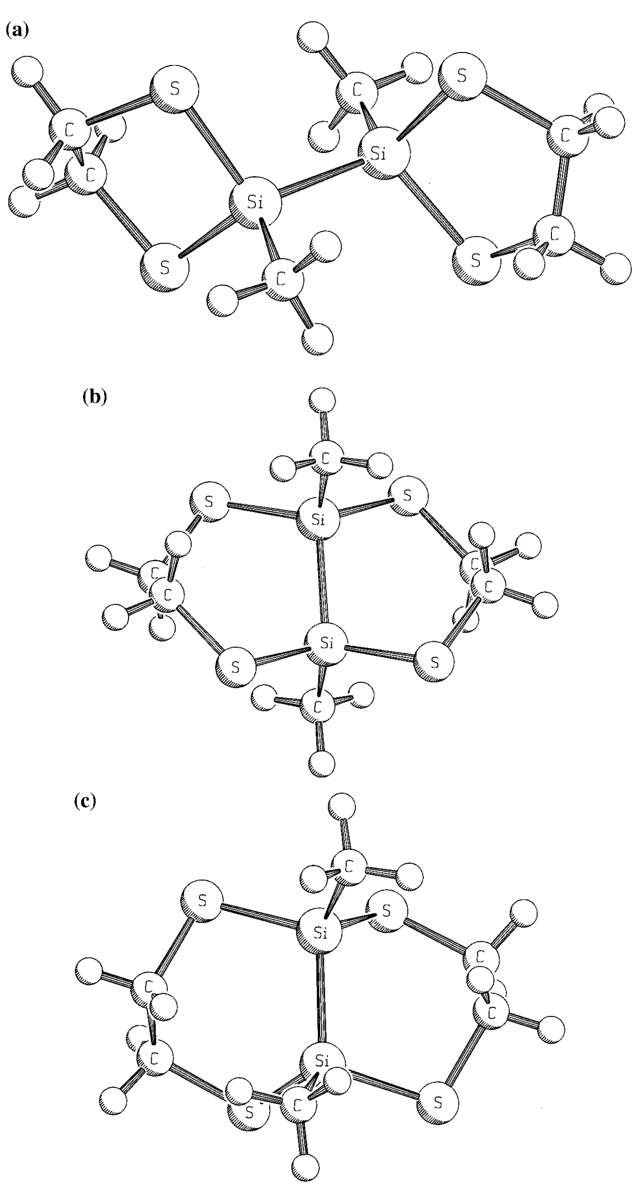
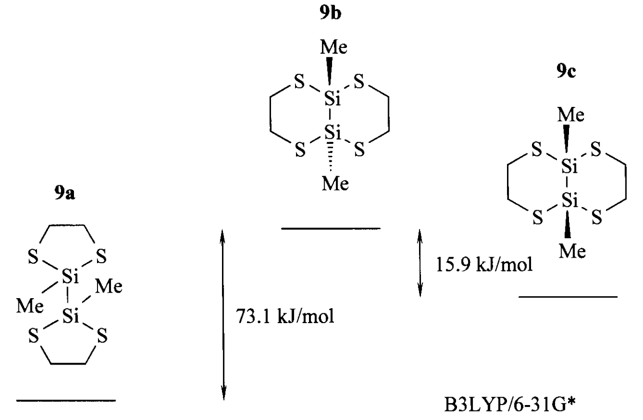


Fig. 4. (a) SCHAKAL plot of the optimized structure of **9a**; (b) SCHAKAL plot of the optimized structure of **9b**; (c) SCHAKAL plot of the optimized structure of **9c**.



Scheme 1. Differences of the calculated total energies (with zero point correction) of the three possible isomers of $Si_2Me_2(SCH_2CH_2S)_2$ (**9a**–**c**).

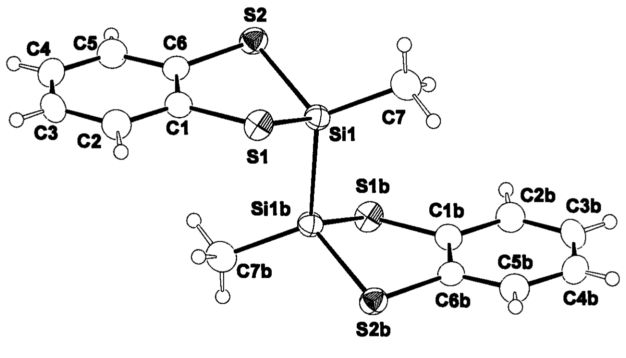


Fig. 5. Molecular structure of one of the two independent molecules of **11**.

the two planes S_2Si and SiCSi* of 89.2° there is virtually no planarization of the silicon tetrahedrons in **11**. Some important bond lengths and angles of **11** are summarized and compared with the results of the DFT calculations in Table 4. The calculations yield the same conformation of **11** as global minimum, however the calculated angles CSSi are some 4° larger resulting in smaller envelope angles in the C_2S_2Si rings.

3. Experimental

3.1. NMR and GC/MS measurments

All NMR spectra were recorded on a Bruker DPX 400 in $CDCl_3$ solution and TMS as internal standard for ^1H, ^{13}C and ^{29}Si. In order to obtain a sufficient signal/noise ratio of ^{29}Si-NMR spectra for obtaining $^1J_{SiC}$ satellites, ^{29}Si INEPT spectra were also recorded. The assignment of ipso carbon atoms in benzene-1,2-dithiolates was simplified by recording ^{13}C APT spectra.

MS spectra were measured on a Hewlett Packard 5971 (ionization energy 70 eV, column 30 m × 0.25 mm × 0.25 μm, phenylmethylpolysiloxane, column temperature 80°C (3 min)/20 K min^{-1}, flow He 0.5 ml min^{-1}).

3.2. Crystal structure analysis

X-ray structure analysis measurements were performed on a Bruker Smart CCD. Crystal data of **6**, **7** and **11** as well as data collection and refinement details are given in Table 6.

All data were corrected for absorption using SADABS [11]. The structures were solved using direct methods (SHELX-97 [12]), refined using least-squares methods (SHELX-97) and drawn using ZORTEP [13].

3.3. Theoretical methods

The ab initio molecular orbital calculations were carried out using the GAUSSIAN 98 series of programs [14]. Geometries were fully optimized at the density functional theory level (DFT), using Becke's three-parameter hybrid exchange functional and the correlation functional of Lee, Yang and Parr (B3LYP) [15]. Geometry optimizations, harmonic frequencies, and zero-point vibrational energies were calculated with the polarized 6-31G* basis set [16]. All structures were identified as true local minima by their Hessian matrices.

The SCHAKAL program [17] has been used for drawings of the optimized structures.

3.4. Starting materials

Ethane-1,2-dithiol, benzene-1,2-dithiol, triethylamine and all used monosilanes Me_xSiCl_{4-x} were commerically available. The disilanes $SiClMe_2$–$SiClMe_2$ [18] and $SiCl_2Me$–$SiCl_2Me$ [19] were prepared as described previously.

3.5. Ethane-1,2-dithiolate derivatives

1.085 g (10 mmol) Me_3SiCl was dissolved in 40 ml dried hexane and 0.376 g (4 mmol) ethane-1,2-dithiol and 0.81 g (1.1 ml, 8mmol) triethylamine were added under stirring. After stirring overnight the mixture was filtered from precipitated triethylammonium chloride and the solvent was removed in vacuo yielding 0.68 g (2.9 mmol) 1,2-bis(trimethylsilylthio)ethane **3** as an oily residue.

3, GC/MS: *m/e* (rel. int.): 238 (M^+, 13), 223 (M − Me, 18), 135 ($MeSiSCH_2CH_2S$, 14), 133 (Me_3SiSCH_2-CH_2, 13), 73 (Me_3Si, 100).

2 was produced applying the same procedure from 0.516 g (4 mmol) Me_2SiCl_2, 0.376 g (4 mmol) $HSCH_2CH_2SH$ and 0.81 g (1.1 ml, 8 mmol) NEt_3.

2, GC/MS: *m*/*e* (rel. int.): 150 (M^+, 52), 135 (M − Me, 100), 109 (17), 107 ($MeSiS_2$, 20), 101 (12), 75 (SSiMe, 29).

Solid **1** was obtained from 0.34 g (2 mmol) $SiCl_4$, 0.376 g (4 mmol) $HSCH_2CH_2SH$ and 0.81 g (1.1 ml, 8 mmol) NEt_3. Starting from a molar ratio $SiCl_4$:$HSCH_2CH_2SH$:NEt_3 = 1:1:2 again pure **1** was produced without the formation of any partially substituted products.

The reaction of 0.30 g (2 mmol) $MeSiCl_3$ with 0.188 g (2 mmol) $HSCH_2CH_2SH$ and 0.405 g (0.55 ml, 4 mmol) NEt_3 (molar ratio: 1:1:2) yielded an oily mixture consisting of 64% **4a** besides 18% **4b** and 18% **4c**. Repetition of the same reaction with 0.30 g (2 mmol) $MeSiCl_3$, 0.282 g (3 mmol) $HSCH_2CH_2SH$ and 0.61 g (0.83 ml, 6 mmol) NEt_3 (molar ratio 1:1.5:3) resulted in the formation of a mixture of 80% **4a** plus 20% **4c**.

4b, GC/MS: *m*/*e* (rel. int.): 170 (M^+, 75), 155 (M − Me, 100), 142 ($S_2SiClMe$, 10), 129 (13), 111 (HSSiClMe, 30), 63 (SiCl, 39) (isotope patterns are in accordance with one $^{35/37}Cl$).

8 was produced by addition of 0.188 g (2 mmol) $HSCH_2CH_2SH$ and 0.405 g (0.55 ml, 4 mmol) NEt_3 to a solution of 0.374 g (2 mmol) $SiClMe_2$–$SiClMe_2$ in 40 ml hexane after filtration from precipitated $HNEt_3Cl$ and removal of the solvent in vacuo, m.p. 23–24°C [10].

8, GC/MS: *m*/*e* (rel. int.): 208 (M^+, 7), 180 ($S_2Si_2Me_4$, 5), 165 ($Me_3SiSCH_2CH_2S$, 100), 135 ($MeSiSCH_2CH_2S$, 5), 90 (Me_2SiS, 7), 75 (MeSiS, 22), 73 (Me_3Si, 42)

9a resulted from the analogous reaction of 0.228 g (1 mmol) $SiCl_2Me$–$SiCl_2Me$ with 0.188 g (2 mmol) $HSCH_2CH_2SH$ and 0.405 g (0.55 ml, 4 mmol) NEt_3 in hexane solution, m.p. 99°C, elemental analysis ($C_6H_{14}S_4Si_2$, calc., found): C: 26.63, 26.27; H: 5.22, 4.91; S: 47.39, 48.01%.

10 was obtained in mixture with **9a** and starting $SiCl_2Me$–$SiCl_2Me$ by treatment of a solution of 0.228 g

Table 6
Crystal data of **6**, **7** and **11** as well as data collection and refinement details

	6	7	11
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	$Pna2_1$	$C2/c$	$P\bar{1}$
Unit cell dimensions			
a (Å)	10.1583(1)	14.7059(3)	8.1987(3)
b (Å)	9.8387(2)	11.0980(3)	10.6739(3)
c (Å)	9.9861(1)	8.0920(3)	10.9473(3)
α (°)	90	90	112.606(1)
β (°)	90	102.322(1)	106.157(2)
γ (°)	90	90	91.006(1)
Volume (Å^3); Z	998.06(2); 4	1290.24(6); 4	841.07(5); 2
Density (calculated) (g cm^{-3})	1.320	1.588	1.448
linear absorption coefficient (mm^{-1})	0.590	0.800	0.694
Radiation used	Mo–K_α		
Temperature (K)	173(2)		
Scan method	ω scans		
Absorption correction	Empirical		
Maximum/minimum transmission	0.70882/0.55396	0.78637/0.48172	0.91826/0.63945
Measured reflections	7417	4345	6490
Independent reflections	2592	1708	4318
Observed reflections	2430	1380	2126
R_{int}	0.0306	0.0535	0.0573
θ range for collection (°)	2.88–30.54	2.32–30.13	2.09–30.14
Completeness to θ_{max} (%)	94.0	89.2	86.9
Refinement method	Full-matrix least-squares on F^2		
final R ($I > 2\sigma(I)$)	R_1: 0.0242	R_1: 0.0305	R_1: 0.0617
R (all data)	R_1: 0.0271	R_1: 0.0466	R_1: 0.1588
H locating and refining	difmap/refall		
Goodness-of-fit on F^2	1.036	1.084	0.959
Maximum/minimum e-density (e Å^{-3})	0.266/−0.185	0.706/−0.653	0.613/−0.469
Data collection program	SMART		
Cell refinement program	SAINT		
Data reduction program	XPREP		
Absorption correction	SADABS		
Structure solving program	SHELXS-97		
Structure refining program	SHELXL-97		
Structure drawing	ZORTEP		

(1 mmol) $SiCl_2Me-SiCl_2Me$ in 40 ml hexane with 0.094 g (1 mmol) $HSCH_2CH_2SH$ and 0.20 g (0.28 ml, 2 mmol) NEt_3. An attempt was made to separate **10** from **9a** by fractional distillation: the product of the reaction of 12.5 g (55 mmol) $SiCl_2Me-SiCl_2Me$ with 4.7 g (50 mmol) $HSCH_2CH_2SH$ and 10.1 g (13.8 ml, 100 mmol) NEt_3 in 150 ml hexane yielded after filtration and removal of the solvent 2.6 g of a fraction at 120–130°C/0.6 kPa. The ^{29}Si-NMR spectrum (obtained after 2 days) revealed that the product was again equilibrated to a mixture of 63% **10**, 18% **9a** and 13% $SiCl_2Me-SiCl_2Me$. Besides these disilanes also 5% **4b** and 1% **1** were observed as decomposition products formed during the distillation.

3.6. Benzene-1,2-dithiolate derivatives

0.22 g (2 mmol) Me_3SiCl was dissolved in 40 ml hexane and 0.12 g (0.85 mmol) o-$C_6H_4(SH)_2$ and 0.20 g (0.28 ml, 2 mmol) NEt_3 were added under stirring. After reacting overnight, the mixture was filtered and the solvent removed in vacuo yielding 0.49 g (1.7 mmol) pure **5** as oily residue.

Similar reaction of 0.129 g (1 mmol) Me_2SiCl_2 with 0.12 g (0.85 mmol) o-$C_6H_4(SH)_2$ and 0.20 g (0.28 ml, 2 mmol) NEt_3 yielded 0.17 g (0.86 mmol) solid **6** (m.p. 55°C).

0.30 g (0.97 mmol) **7** (m.p. > 190°C, dec.) were obtained by the reaction of 0.191 g (1.125 mmol) $SiCl_4$ with 0.32 g (2.25 mmol) o-$C_6H_4(SH)_2$ and 0.45 g (0.63 ml, 4.5 mmol) NEt_3 in 20 ml toluene after filtration and removal of the solvent.

The reaction of 0.281 g (1.5 mmol) $SiClMe_2-SiClMe_2$ with 0.213 g (1.5 mmol) o-$C_6H_4(SH)_2$ and 0.30 g (0.42 ml, 3 mmol) NEt_3 in 20 ml toluene resulted after filtration and removal of the solvent in an oily product whose NMR spectra suggested the formation of $HS(o\text{-}C_6H_4)S(SiMe_2)_2S(o\text{-}C_6H_4)SH$ (δ_{Si}: 3.9 ppm) as main product rather than the expected six-membered ring compound o-$C_6H_4(SSiMe_2)_2$.

Finally the addition of 0.213 g (1.5 mmol) o-$C_6H_4(SH)_2$ and 0.30 g (0.42 ml, 3 mmol) NEt_3 to a solution of 0.171 g (0.75 mmol) $SiCl_2Me-SiCl_2Me$ in 20 ml toluene resulted in the formation of 0.24 g (0.67 mmol) **11** (m.p. 115°C).

12 was obtained in mixture with $SiCl_2Me-SiCl_2Me$ and **11** by a repetition of this reaction with twice the amount of $SiCl_2Me-SiCl_2Me$.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 145927 for **6**, CCDC 145928 for **7**, CCDC: 145929 for **11**. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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