

Formation and characterization of cyclic and polycyclic silthianes containing Si–Si bonds

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Abstract

The reactions of several organochlorosilanes and -oligosilanes with H₂S and NEt₃ have been investigated. Different bicyclic silthianes with bis-cyclopentyl, bicyclo-[3,3,0]-octane, bicyclo-[2,2,1]-heptane (norbornane), bicyclo-[3,2,1]-octane, bicyclo-[2,2,2]-octane and bicyclo-[3,2,1]-nonane skeletons were formed and have been characterized by MS and ¹H-, ¹³C- and ²⁹Si-NMR. The reaction of 1,1,2-tetrachlorodimethyldisilane with H₂S and NEt₃ yields 1,3,5,7,9,11-hexamethyl-1,3,5,7,9,11-hexasila-2,4,6,8,10,12-hexathiatetracyclo-[5,5,0^{3,11},0^{5,9}]-dodecane (**4c**) containing three disilane units. Density functional theory calculations proved the general observation that compounds with Si₃S₂ five-membered rings are preferred. The crystal structures of **4c**, 1,3,3,5,7,7-hexamethyl-1,3,5,7-tetrasilane-2,4,6,8-tetrathiabicyclo-[3,3,0]-octane (**6**) and 1,2,2,4,4,5,6,6,8,8-decamethyl-1,2,4,5,6,8-hexasila-3,7-dithiabicyclo-[3,3,0]-octane (**9**) have been determined. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Silane; Oligosilane; Silthiane; ²⁹Si-NMR; X-ray structure

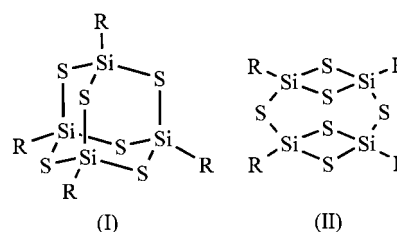
1. Introduction

Cyclic and polycyclic silthianes have been investigated for some time but most research has been concentrated on silthianes derived from monosilanes R_{4-n}SiCl_n. Starting from dichlorosilanes the four- and six-membered ring compounds (R₂SiS)_{2,3} can be synthesized, and trichlorosilanes yield silsesquithianes (RSiS_{3/2})₄ which usually possess an adamantane-like structure (I) [1], but in cases of sterically more demanding substituents (R = 1,1,2-trimethylpropyl) a double-decker-like structure (II) has also been observed [2] (Scheme 1).

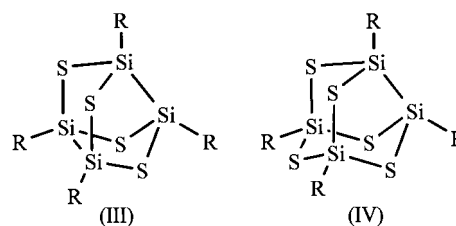
Attempts to build a bis-noradamantane-like structure (III) by reacting ^tBuSiCl₂-^tBuSiCl₂ with Li₂S in THF resulted in extensive insertion of sulfur into Si–Si bonds and formation of (^tBuSi)₄S₅ with a noradamantane structure (IV) in 20% yield [3] (Scheme 2).

Only a few reports deal with cyclic silthianes containing Si–Si bonds. Cyclo-(SiMe₂)_xS (x = 4, 5, 6) have been prepared by reaction of α,ω-dichlorooligosilanes

Cl(SiMe₂)_xCl with Li₂S in THF [4]. 1,2-Dichlorotetramethyldisilane reacts with H₂S in the presence of pyridine to form the six-membered ring compound S(Si₂Me₄)₂S (**1**) [5]. If **1** is heated with (Me₂SiS)₃ (**2a**)



Scheme 1.

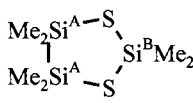
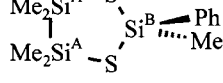
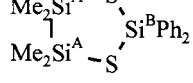
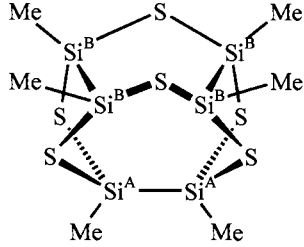
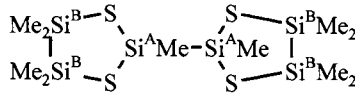


Scheme 2.

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Table 1
NMR chemical shifts (ppm) and $^1J_{\text{SiC}}$ (Hz) data of silthianes **3a–c**, **4c** and **5a**

compound	δ_{Si}	$^1J_{\text{SiC}}$	δ_{C} (SiMe)	δ_{H} (SiMe)
3a 	A: 11.0	46.5	1.09	0.48
	B: 34.1	58.3	8.46	0.62
3b 	A: 11.4	46.7	0.84 / 1.05	0.35 / 0.51
	B: 25.5	60.3 (Me)	1.91 ^a	0.84 ^a
		76.8 (Ph)		
3c 	A: 11.1	46.7	0.88 ^b	0.40 ^b
	B: 17.8			
4c 	A: 28.5 ^{c)}		4.14 ^{c)}	0.71 ^{c)}
	B: 14.1 ^{c)}		4.88 ^{c)}	0.78 ^{c)}
5a 	A: 20.25	48.6	7.17	0.73
	B: 12.55	46.2	1.41 / 0.90	0.49 / 0.50

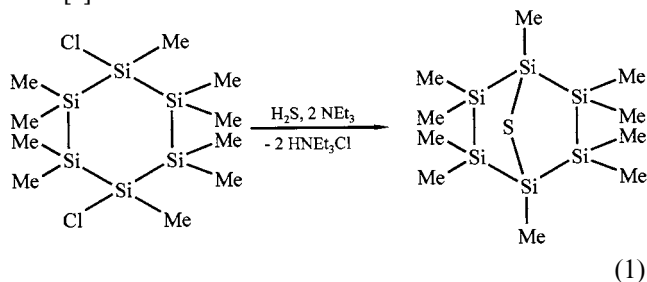
^{a)} Ph: ^{13}C : i: 138.5, o: 133.6, m: 127.7, p: 129.9, ^1H : 7.36 (3 H), 7.73 (2 H)

^{b)} Ph: ^{13}C : i: 136.6, o: 134.7, m: 127.7, p: 130.1, ^1H : 7.35 (3 H), 7.72 (2 H)

^{c)}: in C_6D_6

for 3 days (70°C) in the presence of pyridine, the five-membered ring compound $\text{Si}_2\text{Me}_4(\text{S})_2\text{SiMe}_2$ (**3a**) is formed in 75% yield [6], which suggests that a five-membered Si_3S_2 ring is the most stable ring size in this system.

1,4-Dichlorodecamethylcyclohexasilane forms on treatment with H_2S in the presence of NEt_3 decamethylhexasila-7-thianorbornane in a surprisingly clean reaction [7]:



The crystal structure of the norbornane has an SiS bond length of 2.169(3) Å and a relatively small SiSSI

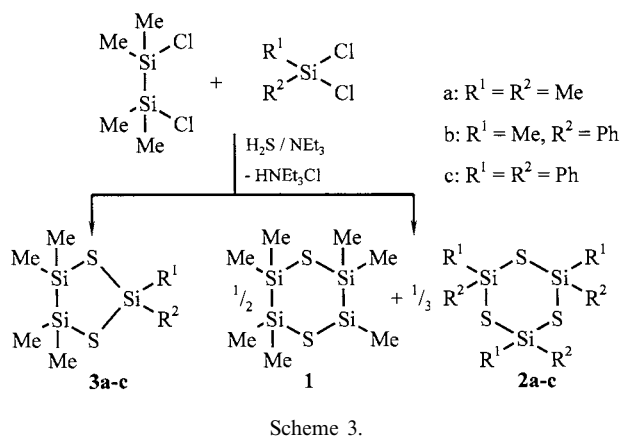
angle of 94.9° as a result of the topology of this bicyclic skeleton.

2. Results and discussion

In this work we report on the formation of cyclic, bicyclic and tetracyclic silthianes from methylchlorooligosilanes by treatment with hydrogen sulfide and triethylamine.

2.1. 1,2,4-Trisila-3,5-dithiacyclopentanes

Based on the observation made in Ref. [6] that five-membered rings Si_3S_2 appear to be the most stable ring size, we tried to synthesize such compounds directly by mixing a dichloromonosilane with 1,2-dichlorotetramethyldisilane in a 1:1 molar ratio and subsequently treating this mixture with H_2S and NEt_3 in hexane solution. NMR investigations showed that indeed the five-membered ring compounds **3a–c** are



Scheme 3.

formed in a 55 mol% amount, but the six-membered ring compounds **1** and **2a-c** are also present. The NMR data of **3a-c** are summarized in Table 1 (Scheme 3).

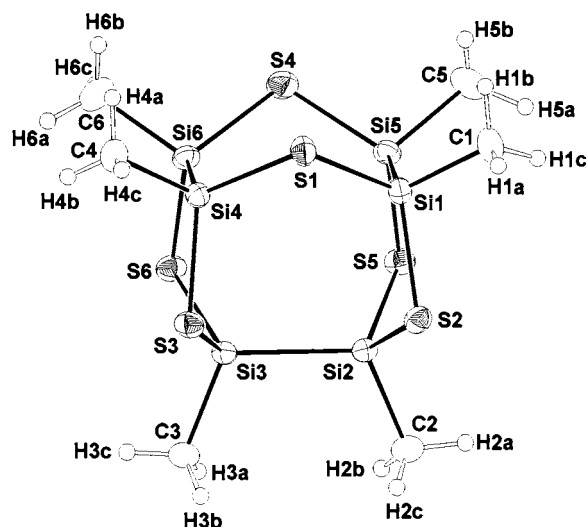
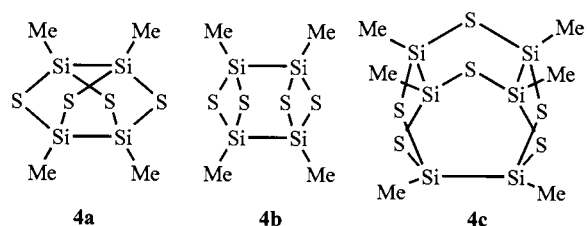
Compared with the acyclic thiobutyl substituted compounds $\text{Me}_2\text{Si}(\text{SBU})_2$ and $\text{BuS}(\text{SiMe}_2)_2\text{SBU}$ [8] containing the same silyl units, the six-membered rings **1** and **2a** show a ^{29}Si -NMR shift to higher field (**1**: -3.2 ppm relative to $\text{BuS}(\text{SiMe}_2)_2\text{SBU}$ and **2a**: -3.7 ppm relative to $\text{Me}_2\text{Si}(\text{SBU})_2$), whereas the resonances of the same silyl groups in the five-membered ring **3a** are shifted significantly to lower field, the S_2SiMe_2 unit by 9.3 ppm and the Si_2Me_4 unit by 12.6 ppm. The five-membered ring compounds **3b** and **3c** behave similarly in comparison with the acyclic silanes $\text{PhMeSi}(\text{SBU})_2$ and $\text{Ph}_2\text{Si}(\text{SBU})_2$ [8] and the six-membered rings $(\text{PhMeSiS})_3$ and $(\text{Ph}_2\text{SiS})_3$ [9].

Density functional theory (DFT) calculations on compounds **1**, **2a** and **3a** (see Table 2) indicate that six molecules of **3a** are 36.0 kJ mol^{-1} lower in energy than three molecules of **1** and two molecules of **2a** according to the redistribution (Eq. (2)):



2.2. 1,3,5,7,9,11-Hexamethyl-1,3,5,7,9,11-hexasila-2,4,6,8,10,12-hexathiatetracyclo-[5,5,0,0^{3,11},0^{5,9}]-dodecane (**4c**)

The treatment of 1,1,2,2-tetrachlorodimethyldisilane with H_2S and NEt_3 yielded no hexane soluble products,

Fig. 1. The molecular structure of **4c**.

Scheme 4.

and therefore the reaction was carried out in toluene. Colorless crystals were obtained after filtration from precipitated HNEt_3Cl and evaporation of the solvent. Initially we expected the formation of a bis-noradaman-tan structure (**4a**) or a bis-nordoubledecker structure (**4b**), but ^1H -, ^{13}C - and ^{29}Si -NMR spectroscopy revealed two signals in a 2:1 ratio, which can only be explained by a structure with at least three disilane units. A crystal structure analysis of the product confirmed that three disilane units are indeed present, forming a tetracyclo-[5,5,0,0^{3,11},0^{5,9}]-dodecane cage, **4c** (Fig. 1, Scheme 4).

The observed SiS as well as SiSi bond lengths in **4c** (Table 3) are in the usual range of $2.11\text{--}2.18 \text{ \AA}$ [10] for SiS single bonds and $2.33\text{--}2.38 \text{ \AA}$ [11] for Si-Si single bonds. The SiSSi bond angles at S(1) and S(4), which

Table 2
Calculated geometry parameters and total energies (B3LYP/6-31G*) of the compounds **1**, **2a** and **3a**

Compound	$d(\text{SiSi})$ (Å)	$d(\text{SiS})$ (Å)	$\angle \text{SiSiSi}$ (°)	$\angle \text{SiSiS}$ (°)	$\angle \text{SSiS}$ (°)	Total energy (H)	Total energy with zero point corr. (H)
1	2.365	2.187	109.2	110.5	–	–2273.89799	–2273.59077
2a	–	2.172	109.0	–	113.4	–2302.80119	–2302.56720
3a	2.358	2.179 ^a / 2.185 ^b	103.8	102.2	111.6	–1904.55117	–1904.32007

^a $\text{S-Me}_2\text{Si-S}$.

^b $\text{Si-Me}_2\text{Si-S}$.

Table 3
Selected bond lengths and angles of **4c**

Atoms	Bond lengths (Å)	Atoms	Bond angles (°)
S(1)–Si(1)	2.1404(10)	Si(1)–S(1)–Si(4)	105.06(4)
S(1)–Si(4)	2.1499(10)	Si(1)–S(2)–Si(2)	100.14(4)
S(2)–Si(1)	2.1469(10)	Si(3)–S(3)–Si(4)	100.27(4)
S(2)–Si(2)	2.1515(10)	Si(5)–S(4)–Si(6)	104.95(4)
S(3)–Si(3)	2.1438(10)	Si(5)–S(5)–Si(2)	100.59(4)
S(3)–Si(4)	2.1444(10)	Si(6)–S(6)–Si(3)	100.47(4)
S(4)–Si(5)	2.1286(10)	S(1)–Si(1)–S(2)	114.49(4)
S(4)–Si(6)	2.1340(11)	S(1)–Si(1)–Si(5)	113.58(4)
S(5)–Si(5)	2.1386(10)	S(2)–Si(1)–Si(5)	105.96(4)
S(5)–Si(2)	2.1498(10)	S(5)–Si(2)–S(2)	109.31(4)
S(6)–Si(6)	2.1387(10)	S(5)–Si(2)–Si(3)	110.32(4)
S(6)–Si(3)	2.1448(9)	S(2)–Si(2)–Si(3)	110.20(4)
Si(1)–Si(5)	2.3481(11)	S(3)–Si(3)–Si(6)	110.33(4)
Si(2)–Si(3)	2.3642(11)	S(3)–Si(3)–Si(2)	110.40(4)
Si(4)–Si(6)	2.3578(10)	S(6)–Si(3)–Si(2)	110.12(4)
Si(1)–C(1)	1.863(3)	S(3)–Si(4)–Si(1)	112.95(4)
Si(2)–C(2)	1.857(3)	S(3)–Si(4)–Si(6)	105.87(4)
Si(3)–C(3)	1.859(3)	S(1)–Si(4)–Si(6)	114.13(4)
Si(4)–C(4)	1.850(3)	S(4)–Si(5)–Si(5)	114.27(5)
Si(5)–C(5)	1.862(3)	S(4)–Si(5)–Si(1)	114.86(4)
Si(6)–C(6)	1.862(3)	S(5)–Si(5)–Si(1)	105.46(4)
		S(4)–Si(6)–Si(6)	114.14(5)
		S(4)–Si(6)–Si(4)	113.84(4)
		S(6)–Si(6)–Si(4)	105.61(4)

are part of six-membered rings, are 4–5° larger than the SiSSi bond angles at the other four sulfur atoms, which are part of five-membered rings. Ab initio calculations of **4a–c** (Table 4) reveal that **4a** is lower in energy than **4b** and that the structure of **4c** is energetically even more preferred (Scheme 5).

The lower energy of **4a** with respect to **4b** correlates with the fact that **4a** contains four of the preferred five-membered rings Si₃S₂, whereas in **4b** only the less favorable four-membered rings Si₂S₂ and six-membered rings Si₄S₂ can be found. The high overall ring strain of such small tricyclic systems (calculated SiSSi bond angles in **4a** and **4b** are smaller than 90°) forces the system to form the larger tetracyclic cage **4c**. The optimized geometry of **4c** calculated by ab-initio methods is in complete agreement with the X-ray structure analysis, however the calculated Si–Si as well as SiS bond lengths

Table 4
Calculated geometry parameters and total energies (B3LYP/6-31G*) of the compounds **4a**, **4b** and **4c**

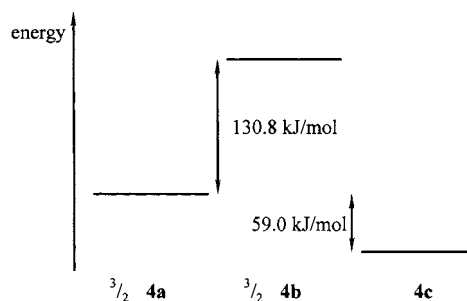
Compound	<i>d</i> (SiSi) (Å)	<i>d</i> (SiS) (Å)	∠ SiSSi (°)	∠ SSiS (°)	Total energy (H)	Total energy with zero point corr. (H)
4a	2.440	2.180	86.7	103.5	–2910.69797	–2910.53392
4b	2.422	2.190	76.4	94.8	–2910.66369	–2910.50071
4c	2.384/2.394 ^a	2.174/2.177 ^b	99.9/107.3 ^c	114.1/109.2 ^d	–4366.07013	–4365.82337

^a Si(2)–Si(3).

^b Si(2)–S and Si(3)–S.

^c Si(1)–S(1)–Si(4) and Si(5)–S(4)–Si(6).

^d S(2)–Si(2)–S(5) and S(3)–Si(3)–S(6).



Scheme 5.

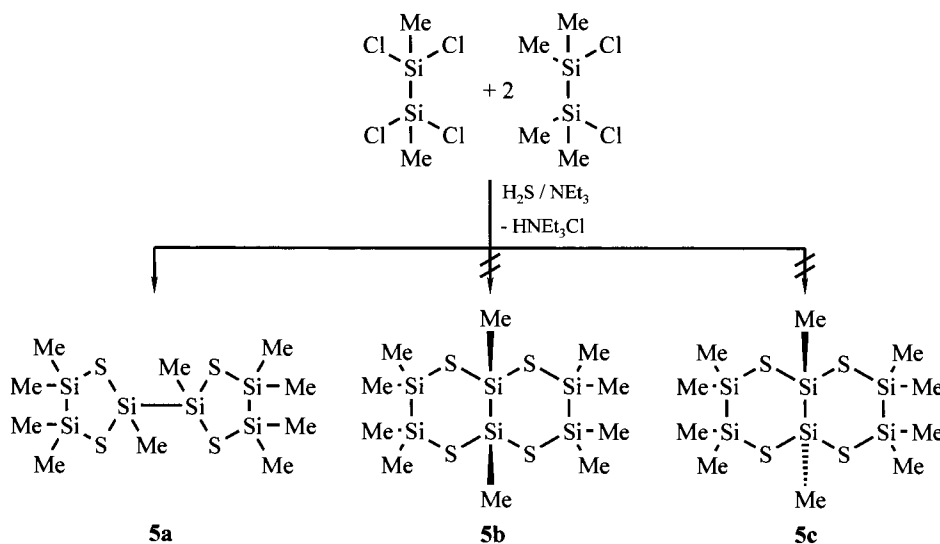
are 0.02–0.03 Å larger and the SiSSi bond angles at S(1) and S(4) are 2–3° larger than the observed data.

Compared with the acyclic compound (BuS)₂SiMe–SiMe(SBu)₂, which exhibits a ²⁹Si-NMR shift of 9.1 ppm [8], the ²⁹Si-NMR chemical shifts in **4c** are shifted to lower field. The four equivalent silicon atoms, which take part in both a Si₃S₂ five-membered ring and in a Si₄S₂ six-membered ring are shifted by 5.0 ppm, while the two other silicon atoms (part of five-membered rings) are shifted to a lower field by 19.4 ppm. These effects parallel the trends in monocyclic silthianes, where the formation of a five-membered ring is accompanied by a low-field shift of 10–14 ppm, and a six-membered ring results in a high-field shift of 3–5 ppm in comparison with acyclic thiobutyl substituted compounds containing the same silyl unit.

2.3. Bis-(1,3,3,4,4-pentamethyl-1,3,4-trisila-2,5-dithiacyclopent-1-yl) (**5a**)

The treatment of a 2:1 mixture of SiClMe₂–SiClMe₂ and SiCl₂Me–SiCl₂Me with H₂S and NEt₃ yielded, besides some **1**, the new bicyclic silthiane **5a**. No further products with the possible decaline like structures **5b** or **5c** could be observed by NMR spectroscopy (Scheme 6).

The assignment of **5a** as the five-membered ring isomer is supported by the ²⁹Si-NMR chemical shift of the SiMe₂ units, which is very close to the shift observed for the five-membered ring compounds **3a–c**, and also the Si-NMR shift at a relatively low field for the SiMe units. Furthermore, the splitting of the ¹H-



Scheme 6.

and ^{13}C -NMR signals of the diastereotopic SiMe_2 units support the bicyclic structure **5a**.

2.4. Bicyclo-[3,3,0]-octanes

If a 1:2 mixture of $\text{SiCl}_2\text{Me}-\text{SiCl}_2\text{Me}$ and Me_2SiCl_2 is treated with H_2S and NEt_3 , the work-up results in an oily residue of 1,3,3,5,7,7-hexamethyl-1,3,5,7-tetrasil-2,4,6,8-tetrathiabicyclo-[3,3,0]-octane (**6**) together with some **2a**. Compound **4c**, which is probably also formed, is insoluble in hexane and was therefore removed together with the precipitated ammonium salt. In order to get **6** free of **2a**, the ratio of the chlorosilanes was changed to 1:1. This time **6** was found as the only hexane soluble product. Single crystals suitable for X-ray analysis were obtained from hexane solution, Fig. 2. Selected bond lengths and angles of **6** are summarized in Table 7.

The crystal structure analysis of **6** reveals the expected bicyclo-[3,3,0]-octane skeleton with SiSSi angles of 99° (Table 7), which is close to the SiSSi angles of the five-membered rings in **4c** (100 – 100.5°) and approximately 6° smaller than the SiSSi angles in the six-membered rings of **4c** (105°) and published data for the six-membered ring compounds $(\text{PhMeSiS})_3$: 106.2° [12] and $(\text{MeSiS}_{3/2})_4$: 104.5° [13]. Both five-membered rings adopt an envelope conformation with angles between the two planes of 50.39 (0.05°) in the ring $\text{Si}(1)-\text{Si}(1a)-\text{S}(1a)-\text{Si}(2)-\text{S}(1)$ and 48.24 (0.05°) in the ring $\text{Si}(1)-\text{Si}(1a)-\text{S}(2a)-\text{Si}(3)-\text{S}(2)$.

It is known from different SiO_2 modifications that the SiOSi angle has a major influence on the ^{29}Si -NMR shift [14,15] ranging from -107 ppm in α -quartz [16] (mean SiOSi angle: 143.6° [17]) to -128.2 ppm in zunyite [18] (SiOSi angle: 180° [19]). The bond polarization theory has been applied to fit the ^{29}Si -NMR shifts

with the molecular geometry of SiO_2 networks [20]. From these results it seems likely that the SiSSi bond angle in cyclic silthianes also has an important influence on the ^{29}Si -NMR shifts if silicon atoms with the same first coordination sphere are compared.

Because of the formation of five-membered rings, the ^{29}Si -NMR signals in **6** (Table 8) show again the expected downfield shifts of 20.75 ppm (SiMe , part of two five-membered rings) and 10.5 ppm (SiMe_2) compared with the same silyl units in the acyclic thiobutyl substituted compounds $(\text{BuS})_2\text{SiMe}-\text{SiMe}(\text{SBu})_2$ and $\text{Me}_2\text{Si}(\text{SBu})_2$ [8].

In comparison with the compounds **2a** and **4c** (the reaction products if $\text{SiCl}_2\text{Me}-\text{SiCl}_2\text{Me}$ or Me_2SiCl_2 , respectively, are treated separately with $\text{H}_2\text{S}/\text{NEt}_3$) the formation of **6** is energetically preferred. According to Eq. (3):



three molecules of **6** are 29.9 kJ mol^{-1} lower in energy than **4c** and two molecules of **2a** (calculated energies,

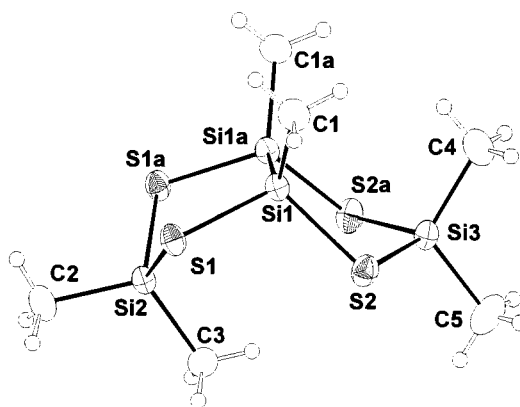
Fig. 2. The molecular structure of **6**.

Table 5
Calculated geometry parameters and total energies (B3LYP/6-31G*) of the compounds **6**, **10a–b** and **11**; for assignment of Si and S see Fig. 2, Scheme 8, and Eq. (4)

Compound	$d(\text{SiSi})$ and $d(\text{SiS})$ (Å)	Bond angles (°)	Total energy (H)	Total energy with zero point corr. (H)
6	Si(1)–Si(1a): 2.381	Si(1)–S(1)–Si(2): 100.4	–2990.56098	–2990.32305
	Si(1)–S(1): 2.165	Si(1)–S(2)–Si(3): 101.0		
	Si(2)–S(1): 2.184	Si(1a)–Si(1)–S(1): 105.8		
	Si(1)–S(2): 2.178	Si(1a)–Si(1)–S(2): 105.9		
	Si(3)–S(2): 2.178	S(1)–Si(2)–S(1a): 110.3		
		S(2)–Si(3)–S(2a): 109.1		
10a	Si(1)–Si(2): 2.370	Si(1)–S(1)–Si(1): 89.1	–2592.30580	–2592.07037
	Si(1)–S(1): 2.183	Si(1)–S(2)–Si(2): 99.5		
	Si(1)–S(2): 2.182	Si(1)–Si(2)–S(2): 102.1		
	Si(2)–S(2): 2.200	Si(2)–Si(1)–S(2): 108.9		
		Si(2)–Si(1)–S(1): 101.2		
		S(1)–Si(1)–S(2): 109.2		
10b	Si(1)–Si(2): 2.366	Si(2)–S(1)–Si(2): 113.1	–2592.29259	–2592.05752
	Si(1)–S(2): 2.186	Si(1)–S(2)–Si(1): 78.8/79.1		
	Si(1)–S(2'): 2.192	Si(1)–Si(2)–S(1): 109.5		
	Si(2)–S(1): 2.187	Si(2)–Si(1)–S(2): 106.5/109.4		
		S(2)–Si(1)–S(2): 96.6		
11	Si(1)–Si(2): 2.372	Si(1)–S(1)–Si(3): 89.3	–2592.30320	–2592.06758
	Si(1)–S(2): 2.201	Si(2)–S(2)–Si(3): 100.0		
	Si(2)–S(2): 2.195	Si(1)–Si(2)–S(2): 101.9		
	Si(3)–S(1): 2.170	Si(2)–Si(1)–S(1): 99.4		
	Si(3)–S(2): 2.176	S(1)–Si(3)–S(2): 108.2		
		S(2)–Si(3)–S(2): 111.5		

Table 6
Calculated geometry parameters and total energies (B3LYP/6-31G*) of the compounds **12a–b** and **14**; for assignment of Si and S see Scheme 9 and Eq. (5)

Compound	$d(\text{SiSi})$ and $d(\text{SiS})$ (Å)	Bond angles (°)	Total energy (H)	Total energy with zero point corr. (H)
12a	Si(1)–Si(2): 2.378	Si(1)–S(1)–Si(4): 96.4	–2961.65838	–2961.34679
	Si(1)–Si(3): 2.366	Si(2)–S(2)–Si(4): 102.0		
	Si(4)–Si(5): 2.368	Si(3)–S(3)–Si(5): 109.8		
	Si(1)–S(1): 2.197	S(1)–Si(4)–S(2): 109.8		
	Si(2)–S(2): 2.192	Si(2)–Si(1)–Si(3): 113.2		
	Si(3)–S(3): 2.186			
	Si(4)–S(1): 2.181			
	Si(4)–S(2): 2.180			
	Si(5)–S(3): 2.188			
12b	Si(1)–Si(2): 2.369	Si(1)–S(1)–Si(4): 104.8	–2961.65709	–2961.34571
	Si(3)–Si(4): 2.368	Si(2)–S(2)–Si(3): 106.3		
	Si(1)–S(1): 2.188	S(2)–Si(3)–S(2): 114.7		
	Si(2)–S(2): 2.194	Si(2)–Si(1)–Si(2): 110.7		
	Si(3)–S(2): 2.177			
	Si(4)–S(1): 2.192			
14	Si(1)–Si(2): 2.370	Si(2)–S(1)–Si(3): 105.6	–2961.65849	–2961.34649
	Si(2)–S(1): 2.195	Si(1)–Si(2)–S(1): 107.0		
	Si(3)–S(1): 2.172	S(1)–Si(3)–S(1): 112.4		
		Si(2)–Si(1)–Si(2): 105.7		

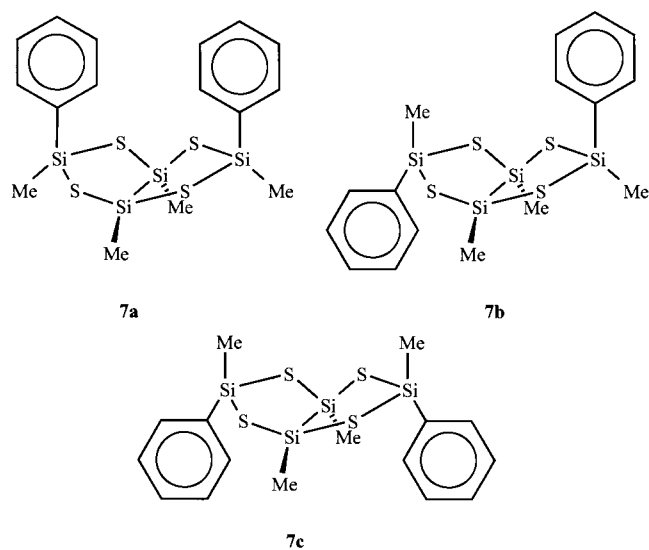
see Tables 4 and 5). The calculated geometry of **6** is in complete agreement with the result of the crystal structure analysis with envelope conformations of both five-membered rings and one SiMe_2 unit in *exo*

and one in *endo* position. However, as for **4c** the calculated d_{SiSi} and d_{SiS} are 0.02–0.03 Å longer and the angles SiSSi are 1–2° larger than the observed data.

Three isomers of 3,7-diphenyl-1,3,5,7-tetramethyl-1,3,5,7-tetrasilolane-2,4,6,8-tetrathiabicyclo-[3,3,0]-octane (**7a–c**) were obtained by a similar reaction of a mixture of $\text{SiCl}_2\text{Me–SiCl}_2\text{Me}$ and two equivalents of PhMeSiCl_2 . The three isomers differ in the spatial orientation of the two phenyl groups (Scheme 7):

Compound **7b** is formed with 49% yield and can be assigned unambiguously because it contains two different ^{29}Si -NMR signals in this region. The isomer which is formed with a yield of only 9%, very likely corresponds to the structure of **7a**, because in **7a** the two phenyl rings hinder each other and make this isomer less favorable. Consequently the third isomer, which is formed with a yield of 42%, possesses the structure **7c**. Finally, the reaction of a mixture of $\text{SiCl}_2\text{Me–SiCl}_2\text{Me}$ and two equivalents of Ph_2SiCl_2 with H_2S and NEt_3 resulted in the formation of 3,3,7,7-tetraphenyl-1,5-dimethyl-1,3,5,7-tetrasilolane-2,4,6,8-tetrathiabicyclo-[3,3,0]-octane (**8**).

The ^{29}Si -NMR shifts of the central Si_2Me_2 units in **7a–c** and **8** are almost the same as those found for **6a** supporting



Scheme 7.

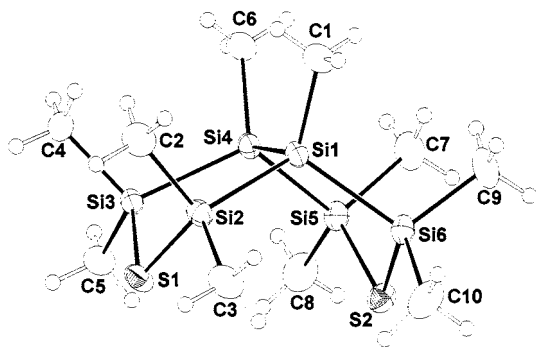


Fig. 3. The molecular structure of **9**.

Table 7
Selected bond lengths and angles of **6**

Atoms	Bond lengths (Å)	Atoms	Bond angles (°)
S(1)–Si(1)	2.1343(7)	Si(1)–S(1)–Si(2)	99.28(3)
S(1)–Si(2)	2.1563(7)	Si(1)–S(2)–Si(3)	98.96(3)
S(2)–Si(1)	2.1460(7)	S(1)–Si(1)–S(2)	109.76(3)
S(2)–Si(3)	2.1475(7)	S(1)–Si(1)–Si(1a)	104.92(2)
Si(1)–C(1)	1.855(2)	S(2)–Si(1)–Si(1a)	105.40(2)
Si(1)–Si(1a)	2.3600(12)	S(1)–Si(2)–S(1a)	106.67(4)
Si(2)–C(2)	1.851(3)	S(2a)–Si(3)–S(2)	109.15(4)
Si(2)–C(3)	1.852(3)	C(2)–Si(2)–C(3)	112.42(16)
Si(3)–C(4)	1.846(3)	C(4)–Si(3)–C(5)	112.86(19)
Si(3)–C(5)	1.846(4)		

the bicyclo-[3,3,0]-octane structures of these compounds. Furthermore, the ^{29}Si -NMR signals of the SiPhMe and SiPh_2 units are very close to those of **3b** and **3c** and shifted by 7.4–8.6 ppm (SiPhMe) and 5.4 ppm (SiPh_2) downfield as compared with $\text{PhMeSi}(\text{SBU})_2$ and $\text{Ph}_2\text{Si}(\text{SBU})_2$ [8] as a result of the formation of five-membered rings.

Another silthiane with a bicyclo-[3,3,0]-octane skeleton was prepared by the reaction of 1,1,2,2-tetrakis(chlorodimethylsilyl)-1,2-dimethyldisilane with H_2S and NEt_3 . The only observed silicon containing reaction product was the expected 1,2,2,4,4,5,6,6,8,8-decamethyl-1,2,4,5,6,8-hexasila-3,7-dithiabicyclo-[3,3,0]octane (**9**). After sublimation, crystals of **9** suitable for crystal structure analysis could be obtained, Fig. 3.

The crystal structure analysis of **9** shows the expected bicyclo-[3,3,0]-octane skeleton with SiSSi angles of 101–102° (Table 9), which is again in the range of the SiSSi angles of the five-membered rings in **4c** and **6**. All Si–Si as well as Si–S bond lengths are in the usual ranges of 2.33–2.35 and 2.15–2.16 Å, respectively. The SiSiSi angles in the five-membered rings Si_4S are in the range 102–103°, whereas the angles $\text{Si}(6)–\text{Si}(1)–\text{Si}(4)$ and $\text{Si}(5)–\text{Si}(4)–\text{Si}(3)$ between the two rings are expanded to 114–115°. Both five-membered rings adopt an envelope conformation with angles of 42.34 (0.04)° in the ring $\text{Si}(1)–\text{Si}(2)–\text{S}(1)–\text{Si}(3)–\text{Si}(4)$ and 44.35 (0.03)° in the ring $\text{Si}(1)–\text{Si}(6)–\text{S}(2)–\text{Si}(5)–\text{Si}(4)$. The angle between the planes $\text{Si}(1)–\text{Si}(2)–\text{Si}(3)–\text{Si}(4)$ and $\text{Si}(1)–\text{Si}(4)–\text{Si}(5)–\text{Si}(6)$ is 119.06(0.02)°. Compared with the ^{29}Si -NMR shifts of the same hexasilane skeleton in the acyclic compound $(\text{BuSM}_2\text{Si})_2\text{SiMe–SiMe–}(\text{SiMe}_2\text{SBU})$ of –74.7 ppm (SiMe) and 5.7 ppm (SiMe_2), the signals are shifted by 3.4 (SiMe) and 10.7 ppm (SiMe_2) to lower field in accordance with the formation of five-membered rings, although in this case Si_4S rings are present. The ^{13}C - and ^1H -NMR shifts of the SiMe groups also differ significantly, see Section 3.10 and Table 8, but the $^1J_{\text{SiC}}$ coupling constants remain almost unchanged.

Table 8
NMR chemical shifts (ppm) and $^1J_{\text{SiC}}$ (Hz) data of silthianes **6**, **7a–c**, **8** and **9** with a bicyclo-[3,3,0]-octane skeleton

compound	δ_{Si}	$^1J_{\text{SiC}}$	δ_{C} (SiMe)	δ_{H} (SiMe)
6 	A: 29.85 B: 35.29	52.2 58.7	5.24 8.19 / 7.48	0.91 0.66 / 0.73
7a 	A: 30.6 B: 26.1		5.6 7.5	
7b 	A: 30.3 B: 26.8 / 26.0		5.1 7.7 / 6.1	
7c 	A: 29.2 B: 25.6		4.5 6.4 ^{a)}	0.98 0.67
8 	A: 28.7 B: 17.3		4.7	0.69
9 	A: -71.3 B: 16.4	45.2 $^1J_{\text{SiSi}}: 64.1$	-12.05 3.78 / 4.36	0.28 0.49 / 0.54

^{a)}: Ph, ^{13}C : i: 133.15, o: 133.8, m: 128.0, p: 130.5

2.5. Bicyclo-[2,2,1]-heptanes (norbornanes)

The reaction of 1,1,2-trichlorotrimethyldisilane with H_2S and NEt_3 yielded 1,2,2,4,5,5-hexamethyl-1,2,4,5-tetrasil-3,6,7-trithianorbornane (**10a**) as the only product. The proposed structure is in agreement with the mass spectrum and with the presence of two ^{29}Si -NMR and three ^{13}C - and ^1H -NMR signals (Table 10) due to the splitting of the diastereotopic methyl groups in the SiMe_2 units. The theoretically also possible structure **10b** bears only two different methyl groups which

would result in only two ^{13}C - and ^1H -NMR signals (Scheme 8).

Furthermore, the Si-NMR shifts for **10a** are found 11.0 ppm (SiMe) and 11.3 ppm (SiMe₂) downfield from the values for the acyclic thiobutyl substituted compound $(\text{BuS})_2\text{SiMe-SiMe}_2(\text{SBu})$ [8], strongly supporting a structure with five-membered rings.

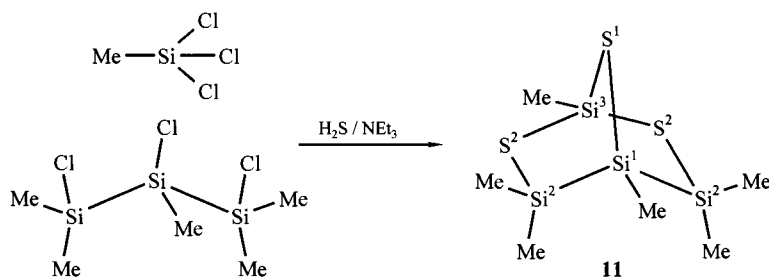
The calculated structure of **10a** (see Fig. 4) reveals a SiSSi angle at S(2) in the usual range for five-membered rings as well as a relatively small angle at S(1) of only 89.1°, which is even 5° smaller than the SiSSi angle

Table 9
Selected bond lengths and angles of **9**

Atoms	Bond lengths (Å)	Atoms	Bond angles (°)
Si(1)–Si(3)	2.1541(8)	Si(3)–Si(1)–Si(2)	102.11(3)
Si(1)–Si(2)	2.1573(8)	Si(5)–Si(2)–Si(6)	101.31(3)
Si(2)–Si(5)	2.1509(8)	Si(2)–Si(1)–Si(6)	114.36(3)
Si(2)–Si(6)	2.1515(8)	Si(2)–Si(1)–Si(4)	102.45(3)
Si(1)–Si(2)	2.3443(8)	Si(6)–Si(1)–Si(4)	102.02(3)
Si(1)–Si(6)	2.3471(8)	Si(1)–Si(2)–Si(1)	106.56(3)
Si(1)–Si(4)	2.3512(8)	Si(1)–Si(3)–Si(4)	106.87(3)
Si(3)–Si(4)	2.3417(7)	Si(5)–Si(4)–Si(3)	115.26(3)
Si(4)–Si(5)	2.3371(8)	Si(5)–Si(4)–Si(1)	102.02(3)
Si(1)–C(1)	1.890(2)	Si(3)–Si(4)–Si(1)	102.24(3)
Si(4)–C(6)	1.888(2)	S(2)–Si(5)–Si(4)	106.38(3)
		S(2)–Si(6)–Si(1)	106.41(3)

found in decamethylhexasila-7-thianorborene [7]. The calculations showed that the experimentally observed isomer **10a** is 33.7 kJ mol⁻¹ lower in energy than **10b** with a strained four-membered ring.

An isomeric compound, 1,2,2,4,6,6-hexamethyl-1,2,4,6-tetrasil-3,5,7-trithianorborene (**11**), has been prepared by reacting a 1:1 molar mixture of 1,2,3-trichloropentamethyltrisilane and methyltrichlorosilane with H₂S and NEt₃. The mass spectrum and the three ²⁹Si-NMR signals detected at a relatively low field are in agreement with the norbornane structure **11**. The GC-MS spectra of **10a** and **11** differ only in the retention times and in the relative intensities of the parent peak and fragment peaks.



The ²⁹Si-NMR signals of the trisilane unit in **11** are shifted by 15.7 (Si^A) and 6.4 ppm (Si^B) to lower field compared with the acyclic derivative BuSSiMe₂–SiMe(SBu)–SiMe₂(SBu) [8]. The chemical shift of Si^A is only 1.3 ppm upfield from value found for the bridgehead silicon atoms in decamethylhexasila-7-thianorborene [7] with the same first coordination sphere. The calculated structure of **11** (Table 5) shows similar bond parameters as the isomeric compound **10a**. For instance, the bond angles SiSSi at S(1) and S(2) are almost identical. A comparison of the calculated total energies (with zero point correction) reveals that the norbornane **10a** is 7.3 kJ mol⁻¹ lower in energy than the isomer **11**.

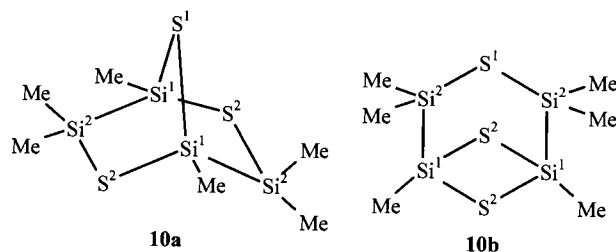
2.6. Bicyclo-[3,2,1]-octane and bicyclo-[3,3,1]-nonane

The treatment of a 1:1 mixture of 1,1,2-trichlorotrimethyldisilane and 1,2,3-trichloropentamethyltrisilane with H₂S and NEt₃ resulted in the formation of 1,2,2,4,4,5,5,6,6-octamethyl-1,2,4,5,6-pentasila-3,7,8-trithiabicyclo-[3,2,1]-octane (**12a**). The structure is in agreement with the observed mass spectrum and the five ²⁹Si-NMR signals including two different ¹J_{SiSi} coupling constants in the trisilane unit. As expected, eight different signals for the eight methyl groups are found by ¹H- and ¹³C-NMR spectroscopy. In the alternative structure **12b** (Scheme 9) with a bicyclo-[2,2,2]-octane skeleton the two SiMe₂ groups of the trisilane unit are equal, what should result in only four Si- and five C- and H-NMR signals.

The formation of **12a** containing a five-membered ring shows again that isomers with this ring size are preferred.

The calculated energies of the two isomers (Table 6) differ by only 2.8 kJ mol⁻¹, the experimentally observed isomer **12a** being lower in energy than **12b**.

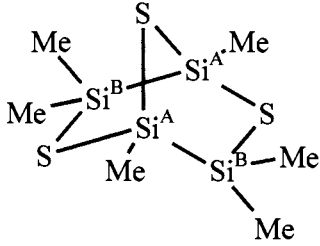
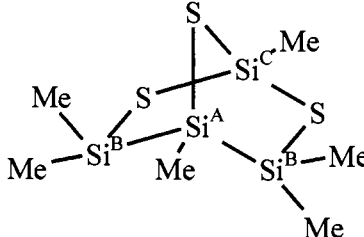
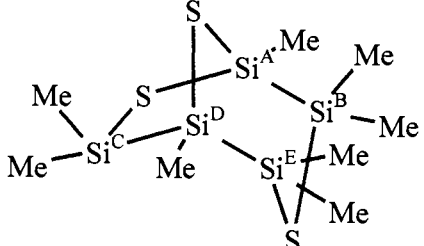
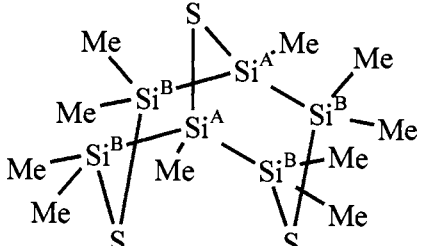
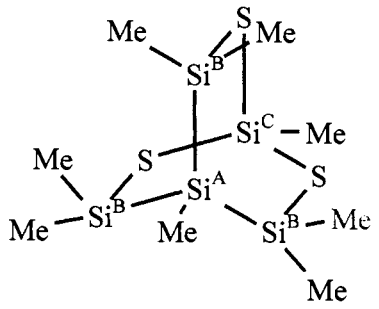
The DFT calculation of **12a** reveal that the six-membered ring adopts a chair conformation, while the five-membered ring has an envelope conformation. Due to the increased ring size of one cyclus, the angles SiSSi are larger than the calculated values for **10a** and **11**. The angle at S(2) is comparable with the angle in **3a**, and the angle at S(3) is similar to the angle in **1**, also containing a Si₄S₂ six-membered ring. The geometry of



Scheme 8.

Table 10

NMR chemical shifts (ppm) and coupling constants $^1J_{\text{SiC}}$ and $^1J_{\text{SiSi}}$ (Hz) of the bicyclic silthianes **10a**, **11**, **12a**, **13a** and **14**

compound	δ_{Si}	$^1J_{\text{SiC}}$	δ_{C} (SiMe)	δ_{H} (SiMe)
10a 	A: 21.3	47.6	2.4	0.91
	B: 10.5	46.6	0.1 / 0.3	0.40 / 0.58
		$^1J_{\text{SiSi}}$: 100.6		
11 	A: -8.9	$^1J_{\text{SiSi}}$: 72.9	-7.8	0.81
	B: 7.7		1.16 / 1.28	0.45 / 0.64
	C: 28.1		7.2	1.03
12a 	A: 22.1	44.7	C: -3.7	A-E: 0.378,
	B: -2.6	$^1J_{\text{SiSi}}$: 105.9	A, B, D-E: 0.415, 0.465,	
	C: 12.9		0.87, 1.74,	0.527, 0.559,
	D: -12.9		a) 1.85, 1.92,	0.609, 0.724,
	E: -2.1		46.6	2.27 (2 C), 0.740
			4.00	
13a 	A: -27.5		-2.1	
	B: -3.3		2.35 / 2.82	0.46 / 0.58
14 	A: -89.0	36.9	-15.6	0.04
		$^1J_{\text{SiSi}}$: 66.6		
	B: -1.0		46.2	3.4
C: 12.0	66.0		10.7	0.83

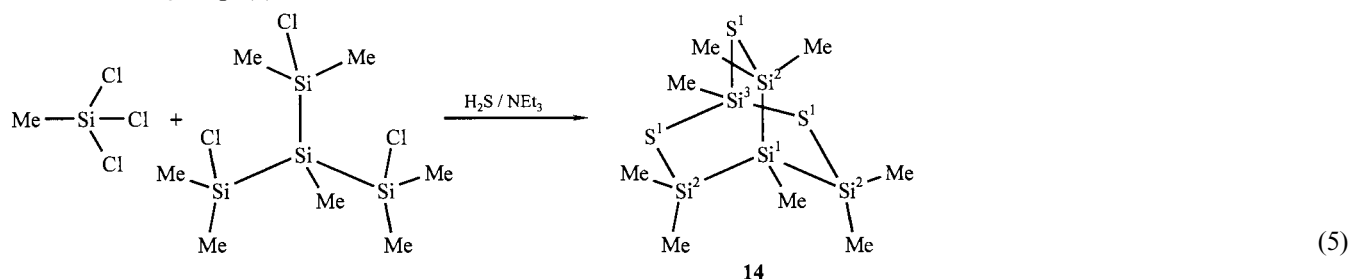
a) $^1J_{\text{SiC SiD}}$: 72.4, $^1J_{\text{SiD SiE}}$: 79.2

12b is very similar to the isomeric compound **14**. The calculated SiSSi angles of 104.8 and 106.3° are almost identical to the value of 105.6° in **14**.

If 1,2,3-trichloropentamethyltrisilane alone is reacted with H₂S and NEt₃, 1,2,2,4,4,5,6,6,8,8-decamethyl-1,2,4,5,6,8-hexasila-3,7,9-trithiabicyclo-[3,3,1]-nonane (**13a**) is formed. This bicyclus contains two six-membered rings Si₄S₂ and can also be regarded as an adamantane structure with one missing corner. The only possible alternative structure **13b** is built up of only one six-membered ring and two seven-membered rings. **13b** should show three different ²⁹Si-NMR signals, but only two signals with a 2:1 ratio are observed, which is in agreement with structure **13a** (Scheme 10).

2.7. 1,2,2,4,6,6,7,7-Octamethyl-1,2,4,6,7-pentasila-3,5,8-trithiabicyclo-[2,2,2]-octane (**14**)

Compound **14** is formed by the reaction of a 1:1 molar mixture of MeSi(SiMe₂Cl)₃ and MeSiCl₃ with H₂S and NEt₃, Eq. (5):



Since this compound is built of six-membered rings, the ²⁹Si-NMR signals of all silyl groups are shifted to higher field (SiMe: -9.6 ppm, SiMe₂: -5.8 ppm, SiMe₃: -17.5 ppm) compared with the acyclic compounds MeSi(SiMe₂SBu)₃ and MeSi(SBu)₃ [8].

The DFT calculation of **14** (Table 6, Fig. 5) reveals SiSSi angles of 105.6° which are typical for six-membered rings. A comparison of the total energies (with zero point correction) of **14** with the isomeric com-

ound **12b** indicates a difference of only 2.0 kJ mol⁻¹, **14** being the energetically preferred isomer.

3. Experimental

3.1. NMR and GC-MS measurements

All NMR spectra were recorded on a Bruker DPX 400 in CDCl₃ solution and TMS as internal standard for ¹H-, ¹³C- and ²⁹Si-NMR. In order to get a sufficient signal/noise ratio of ²⁹Si-NMR spectra for obtaining ¹J_{SiC} or ¹J_{SiSi} satellites, ²⁹Si INEPT spectra were also recorded. The assignment of *ipso* carbon atoms in phenyl substituents was simplified by recording ¹³C APT spectra.

Mass 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 **4c**, **6** and **9** as well as data collection and refinement details are given in Table 11.

All data were corrected for absorption using SADABS [21]. The structures were solved using direct methods (SHELX-97 [22]), refined using least-squares methods (SHELX-97) and drawn using ZORTEP [23].

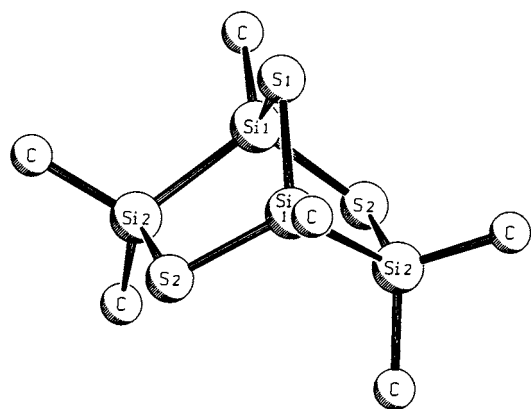
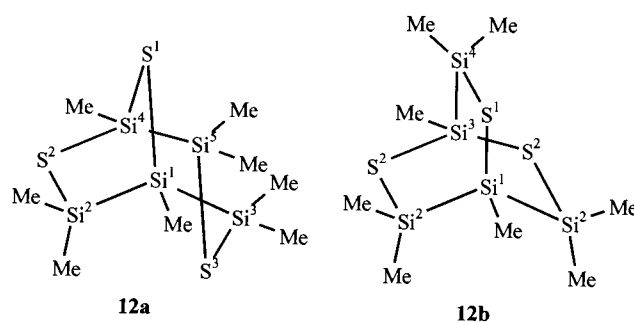
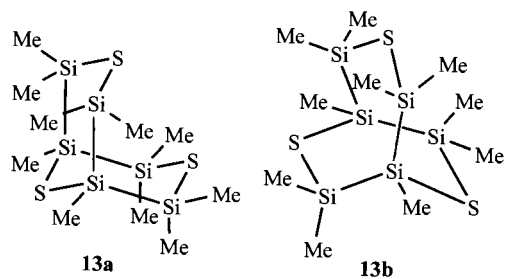


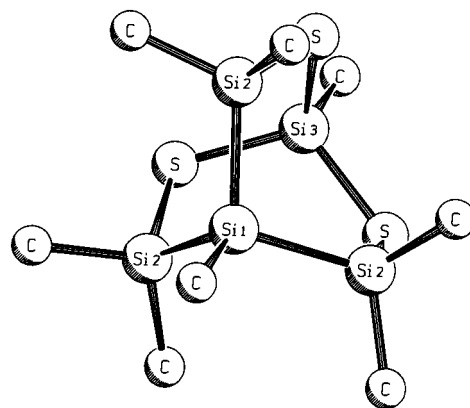
Fig. 4. Schakal plot of the optimized structure of **10a**, hydrogen atoms are omitted.



Scheme 9.



Scheme 10.

Fig. 5. Schakal plot of the optimized structure of **14**, hydrogen atoms are omitted.

3.3. Theoretical methods

The ab initio molecular orbital calculations were carried out using the Gaussian 98 series of programs [24]. Geometries were fully optimized at the DFT level, using Becke's three-parameter hybrid exchange func-

tional and the correlation functional of Lee, Yang and Parr (B3LYP) [25]. Geometry optimizations, harmonic

Table 11
Crystal data of **4c**, **6** and **9** as well as data collection and refinement details

	4c	6	9
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$Pnma$	$P2_1/n$
Unit cell dimensions			
a (Å)	10.3954(4)	12.1879(4)	9.9221(2)
b (Å)	8.1079(3)	10.1585(4)	12.5947(1)
c (Å)	24.2696(9)	13.5404(5)	18.0410(3)
α (°)	90	90	90
β (°)	100.973(1)	90	104.747(1)
γ (°)	90	90	90
Volume (Å ³)	2008.16(13)	1676.45(11)	2180.24(6)
Z	4	4	4
D_{calc} (g cm ⁻³)	1.492	1.311	1.167
Linear absorption coefficient (mm ⁻¹)	1.022	0.823	0.561
Radiation used	Mo-K α	Mo-K α	Mo-K α
Temperature (K)	173(2)	173(2)	173(2)
Scan method	ω scans	ω scans	ω scans
Absorption correction	Empirical	Empirical	Empirical
Max./min. transmission	0.812213/0.580765	0.867692/0.737513	0.765533/0.376927
Measured reflections	8945	7891	10 008
Independent reflections	5386	2369	5408
Observed reflections	3747	1748	4073
R_{int}	0.0336	0.0435	0.0339
θ Range for collection (°)	1.71–30.29	2.25–30.43	1.99–30.35
Completeness to θ_{max} (%)	89.3	88.6	82.5
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Final R ($I > 2\sigma(I)$)	R_1 : 0.0392	R_1 : 0.0347	R_1 : 0.0393
R (all data)	R_1 : 0.0712	R_1 : 0.0610	R_1 : 0.0610
H-locating and refining	difmap/refall	difmap/refall	difmap/refall
Goodness-of-fit on F^2	0.977	1.025	0.988
Max./min. e-density (e Å ⁻³)	0.613/–0.557	0.345/–0.359	0.368/–0.718
Data collection program	SMART	SMART	SMART
Cell refinement program	SAINT	SAINT	SAINT
Data reduction program	XPREP	XPREP	XPREP
Absorption correction	SADABS	SADABS	SADABS
Structure solving program	SHELXS-97	SHELXS-97	SHELXS-97
Structure refining program	SHELXL-97	SHELXL-97	SHELXL-97
Structure drawing	ZORTEP	ZORTEP	ZORTEP

frequencies, and zero-point vibrational energies were calculated with the polarized 6-31G* basis set [26]. All structures were identified as true local minima by their Hessian matrices.

3.4. Starting materials

H₂S (N25, Air Liquide), triethylamine, BuSH, BuLi and all monosilanes Me_xPh_ySiCl_z are commercially available. The oligosilanes SiClMe₂–SiClMe₂ [27], SiCl₂Me–SiClMe₂ [28], SiCl₂Me–SiCl₂Me [29], SiClMe₂–SiClMe–SiClMe₂ [30], SiMe(SiClMe₂)₃ and [MeSi(SiClMe₂)₂]₂ [31] were prepared as described previously.

3.5. 1,2,4-Trisila-3,5-dithiacyclopentanes

SiClMe₂–SiClMe₂ (0.374 g, 2 mmol) and Me₂SiCl₂ (0.258 g, 2 mmol) were dissolved in 20 ml *n*-hexane. H₂S was bubbled through the stirred solution and at the same time triethylamine (1.11 ml, 8 mmol) were slowly added by a syringe. After 20 min the reaction mixture was filtered from precipitated triethylammonium chloride and the solvent was removed in vacuo yielding an oily residue which consisted of 55% **3a** as well as **1** and **2a** (determined by NMR).

1, GC–MS: *m/e* [relative intensity]: 296 [M⁺, 23], 281 [M – Me, 13], 237 [M – SiMe₂H, 11], 116 [Si₂Me₄, 100], 73 [SiMe₃, 92].

2a, GC–MS: 270 [M⁺, 21], 255 [M – Me, 100], 165 [Si₂S₂Me₃, 73], 73 [SiMe₃, 35].

3a, GC–MS: 238 [M⁺, 50], 223 [M – Me, 65], 165 [Si₂S₂Me₃, 34], 163 [Si₂Me₅S, 30], 73 [SiMe₃, 100].

The same reaction was repeated with PhMeSiCl₂ (0.382 g, 2 mmol) instead of Me₂SiCl₂ and yielded a solid mixture of 55% **3b** as well as **1** and the two isomers of (PhMeSiS)₃.

3b, GC–MS: 300 [M⁺, 36], 285 [M – Me, 22], 227 [Si₂S₂Me₂Ph, 9], 209 (9), 195 [Si₂SMe₂Ph, 5], 165 [Si₂S₂Me₃, 12], 135 [SiMe₂Ph, 100], 105 [SiPh, 6], 73 [SiMe₃, 20].

(PhMeSiS)₃: ²⁹Si-NMR, δ/ppm: 13.1 (2 Si), 12.95 (1 Si) [*cis,cis,trans*-isomer [12] (85%)] and 12.8 [all-*trans*-isomer (15%)].

Repetition of the same reaction with Ph₂SiCl₂ (0.506 g, 2 mmol) instead of Me₂SiCl₂ yielded a mixture of 55% **3c** as well as **1** and (Ph₂SiS)₃ as solid residue.

3c, GC–MS: 362 [M⁺, 53], 347 [M – Me, 9], 289 [Si₂S₂MePh₂, 5], 284 (15), 271 (12), 269 (7), 227 [Si₂S₂Me₂Ph, 73], 209 (7), 197 [Si₂S₂Ph, 38], 135 [SiMe₂Ph, 100], 105 [SiPh, 13], 77 [Ph, 8], 73 [SiMe₃, 14].

3.6. Synthesis of 1,3,5,7,9,11-hexamethyl-1,3,5,7,9,11-hexasila-2,4,6,8,10,12-hexathiatetra-cyclo-[5,5,0,0^{3,11},0^{5,9}]-dodecane (**4c**)

SiCl₂Me–SiCl₂Me (0.684 g, 3 mmol) was dissolved in 40 ml toluene and a stream of H₂S was passed through the solution while NEt₃ (1.77 ml, 12.8 mmol) was added by syringe. The product was filtered from precipitated triethylammonium chloride and concentrated to a volume of 1 ml. Colorless crystals of **4c** (0.23 g, 51%, *F* > 190°C) crystallized from the solution. Since **4c** is almost insoluble in CDCl₃, NMR spectra were taken in C₆D₆. Single crystals of **4c** suitable for X-ray analysis were obtained by slow cooling of a hot saturated solution in C₆D₆.

3.7. Synthesis of bis-(1,3,3,4,4-pentamethyl-1,3,4-trisila-2,5-dithiacyclopent-1-yl) (**5a**)

SiCl₂Me–SiCl₂Me (0.228 g, 1 mmol) and SiClMe₂–SiClMe₂ (0.374 g, 2 mmol) were dissolved in 40 ml hexane 1.15 ml (8 mmol) NEt₃ were slowly added while H₂S was bubbled through the solution. After filtration from the precipitated ammonium salt and removal of the solvent in vacuo a solid mixture of **5a** (60%) and **1** (40%) remained. Also formed **4c** is insoluble in hexane and was therefore removed by filtration.

3.8. Synthesis of 1,3,5,7-tetrasila-2,4,6,8-tetrathiabicyclo-[3,3,0]-octanes (**6**, **7a–c**, **8**)

SiCl₂Me–SiCl₂Me (0.342 g, 1.5 mmol) and Me₂SiCl₂ (0.387 g, 3 mmol) were dissolved in 40 ml *n*-hexane. H₂S was bubbled through the stirred solution while 1.66 ml (12 mmol) triethylamine were slowly added by a syringe. After 40 min the reaction mixture was filtered from precipitated triethylammonium chloride and the solvent was removed in vacuo yielding an oily residue which consisted of 78% **6** and 22% **2a** (determined by NMR). In order to get **6** free from **2a**, the molar ratio SiCl₂Me–SiCl₂Me:Me₂SiCl₂ was changed from 1:2 to 1:1. The reaction was repeated with SiCl₂Me–SiCl₂Me (1.14 g, 5 mmol) and Me₂SiCl₂ (0.65 g, 5 mmol) dissolved in 100 ml hexane and NEt₃ (4.15 ml, 30 mmol) was added while H₂S passed through the solution. After filtration the solution was concentrated to 2 ml when colorless needles of **6** crystallized from the solution, *F* 75–77°C.

6, GC–MS: 330 [M⁺, 36], 315 [M – Me, 26], 165 [Si₂S₂Me₃, 100], 73 [SiMe₃, 20].

Analog reaction of a mixture of SiCl₂Me–SiCl₂Me (0.456 g, 2 mmol) and PhMeSiCl₂ (0.764 g, 4 mmol) dissolved in 50 ml hexane with H₂S and NEt₃ (2.3 ml, 16 mmol) yielded, after work-up, a semicrystalline mixture of the three isomers **7a–c** as well as 15% of

the two isomers of $(\text{PhMeSiS})_3$ (see Section 3.5). Repetition of this reaction with Ph_2SiCl_2 (1.01 g, 4 mmol) instead of PhMeSiCl_2 yielded a solid product which consisted of 45% **8** as well as 30% $(\text{Ph}_2\text{SiS})_3$ (δ_{Si} : 4.5 ppm, [9]) and 25% $(\text{Ph}_2\text{SiS})_2$ (δ_{Si} : -3.5 ppm, [9]).

3.9. Synthesis of 1,2,2,4,4,5,6,6,8,8-decamethyl-1,2,4,5,6,8-hexasila-3,7-dithiabicyclo-[3,3,0]-octane (**9**)

Through a solution of $[\text{SiMe}(\text{SiClMe}_2)_2]_2$ (0.35 g, 0.76 mmol) in 25 ml hexane was bubbled H_2S while NEt_3 (0.43 ml, 3.1 mmol) was added. After filtration and evaporation of the solvent, a viscous oil remained. Sublimation at $120^\circ\text{C}/0.03$ Torr yielded 0.2 g (69%) pure **9** as a crystalline product, F 75°C .

9, GC-MS: 382 [M^+ , 73], 367 [$\text{M} - \text{Me}$, 38], 323 [$\text{M} - \text{SiMe}_2\text{H}$, 32], 309 [$\text{M} - \text{SiMe}_3$, 61], 277 [Si_5SMe_7 , 13], 249 [Si_4SMe_7 , 19], 131 [Si_2Me_5 , 16], 73 [SiMe_3 , 100], 59 [SiMe_2H , 15].

3.10. Synthesis of 1,1,2,2-tetrakis-(butylthiodimethylsilyl)-1,2-dimethyldisilane

$[\text{SiMe}(\text{SiClMe}_2)_2]_2$ (0.23 g, 0.5 mmol) was added to a BuSLi solution made from BuSH (0.18 g, 2 mmol) and BuLi (1.25 ml, 1.6 M, 2 mmol) in 10 ml dry THF. After stirring for 2 h and filtration from precipitated LiCl the solvent was removed in vacuo yielding $[\text{SiMe}(\text{SiMe}_2(\text{SBu}))_2]_2$ (0.25 g, 0.37 mmol) as a colorless oily residue. NMR, δ/ppm : ^{29}Si : 5.7 (SiMe_2 , $^1J_{\text{SiC}}$: 44.7, $^1J_{\text{SiSi}}$: 64.6 Hz), -74.7 (SiMe); ^{13}C : 2.21 (SiMe_2), -8.5 (SiMe), 26.85 (SCH_2), 35.2 (SCH_2CH_2), 22.0 ($\text{SCH}_2\text{CH}_2\text{CH}_2$), 13.7 ($\text{S} \sim \text{CH}_3$); ^1H : 0.545 (SiMe_2), 0.400 (SiMe), 2.53 (SCH_2), 1.59 (SCH_2CH_2), 1.42 ($\text{SCH}_2\text{CH}_2\text{CH}_2$), 0.91 ($\text{S} \sim \text{CH}_3$).

3.11. Synthesis of tetrasilatritianorbornanes (**10a**, **11**)

1,2,2,4,5,5-Hexamethyl-1,2,4,5-tetrasila-3,6,7-trithianorbornane (**10a**) resulted from the reaction of a solution of $\text{SiCl}_2\text{Me}-\text{SiClMe}_2$ (0.52 g, 2.5 mmol) in 20 ml hexane with H_2S and 1.04 ml (7.5 ml) NEt_3 after filtration from the precipitated ammonium salt and evaporation of the solvent in vacuo as viscous oil, Kp $80^\circ\text{C}/0.03$ Torr.

10a, GC-MS: 298 [M^+ , 47], 283 [$\text{M} - \text{Me}$, 40], 239 [$\text{M} - \text{SiMe}_2\text{H}$, 24], 223 [$\text{Si}_3\text{S}_2\text{Me}_5$, 22], 165 [$\text{Si}_2\text{S}_2\text{Me}_3$, 27], 73 [SiMe_3 , 100].

The treatment of a mixture of 0.266 g (1 mmol) $\text{SiClMe}(\text{SiClMe}_2)_2$ and 0.150 g (1 mmol) MeSiCl_3 dissolved in 20 ml hexane with H_2S and 0.83 ml (6 mmol) NEt_3 resulted after filtration and evaporation of the solvent in 0.25 g of an oily residue of 1,2,2,4,6,6-hexamethyl-1,2,4,6-tetrasila-3,5,7-trithianorbornane (**11**, 82%) besides 10% $(\text{MeSiS}_{3/2})_4$ (δ_{Si} : 17.2%, [9]) and 8% **13a**.

11, GC-MS: 298 [M^+ , 38], 283 [$\text{M} - \text{Me}$, 34], 239 [$\text{M} - \text{SiMe}_2\text{H}$, 21], 223 [$\text{Si}_3\text{S}_2\text{Me}_5$, 19], 165 [$\text{Si}_2\text{S}_2\text{Me}_3$, 21], 73 [SiMe_3 , 100].

3.12. Synthesis of 1,2,2,4,4,5,6,6-octamethyl-1,2,4,5,6-pentasila-3,7,8-trithiabicyclo-[3,2,1]-octane (**12a**)

$\text{SiClMe}(\text{SiClMe}_2)_2$ (0.266 g, 1 mmol) and $\text{SiCl}_2\text{Me}-\text{SiClMe}_2$ (0.208 g, 1 mmol) were dissolved in 25 ml hexane and 0.83 ml (6 mmol) NEt_3 were slowly added while H_2S was bubbled through the solution. After filtration from the ammonium salt and evaporation of the solvent 0.28 g of an oily residue remained which consisted of 65% **12a** besides 25% **10a** and 10% **13a**.

12a, GC-MS: 356 [M^+ , 26], 341 [$\text{M} - \text{Me}$, 21], 297 [$\text{M} - \text{SiMe}_2\text{H}$, 13], 283 [$\text{M} - \text{SiMe}_3$, 13], 191 [Si_3SMe_5 , 18], 176 [Si_3SMe_4 , 18], 116 [Si_2Me_4 , 21], 73 [SiMe_3 , 100], 59 [SiMe_2H , 11].

3.13. Synthesis of 1,2,2,4,4,5,6,6,8,8-decamethyl-1,2,4,5,6,8-hexasila-3,7,9-trithiabicyclo-[3,3,1]-nonane (**13a**)

$\text{SiClMe}(\text{SiClMe}_2)_2$ (0.398 g, 1.5 mmol) was dissolved in 20 ml hexane and while H_2S passed through the solution NEt_3 (0.63 ml, 4.5 mmol) was slowly added. After filtration and removal of the solvent an oily residue of **13a** remained. **13a** was also a by-product in the synthesis of **11** and **12a**.

13a, GC-MS: 414 [M^+ , 7], 399 [$\text{M} - \text{Me}$, 4], 249 [Si_4SMe_7 , 19], 234 [Si_4SMe_6 , 27], 191 [Si_3SMe_5 , 11], 131 [Si_2Me_5 , 21], 116 [Si_2Me_4 , 17], 73 [SiMe_3 , 100], 59 [SiMe_2H , 12].

3.14. Synthesis of 1,2,2,4,6,6,7,7-octamethyl-1,2,4,6,7-pentasila-3,5,8-trithiabicyclo-[2,2,2]-octane (**14**)

A solution of $\text{SiMe}(\text{SiClMe}_2)_3$ (0.34 g, 1.05 mmol) and MeSiCl_3 (0.157 g, 1.5 mmol) in 25 ml hexane were reacted with NEt_3 (0.87 ml, 6.3 mmol), while H_2S bubbled through the solution. After filtration and evaporation of the solvent 0.3 g of a semisolid residue of **14** remained.

14, GC-MS: 356 [M^+ , 31], 341 [$\text{M} - \text{Me}$, 20], 297 [$\text{M} - \text{SiMe}_2\text{H}$, 12], 283 [$\text{Si}_4\text{S}_3\text{Me}_5$, 11], 191 [Si_3SMe_5 , 14], 176 [Si_3SMe_4 , 13], 131 [Si_2Me_5 , 17], 116 [Si_2Me_4 , 16], 73 [SiMe_3 , 100], 59 [SiMe_2H , 13].

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. **4c**: CCDC 141105, **6**:

CCDC 141106 and 9: CCDC 141107. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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