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Hepta-tert-butylcyclotetrasilane: a highly crowded cyclotetrasilane ☆

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Abstract

The reaction of di-tert-butyldichlorosilane with lithium produced hepta-tert-butylcyclotetrasilane (**1**) and *trans*-1,1,2,3,3,4-hexa-tert-butylcyclotetrasilane (**2**). The structures of **1** and **2** were determined by X-ray crystallography. Crystal data for **1**: orthorhombic, *Cmcm*, $a = 12.071(1)$ Å, $b = 17.964(2)$ Å, $c = 15.431(4)$ Å, $V = 3346.0(8)$ Å^3, $Z = 4$, $R = 0.067$, $R_w = 0.051$ for 1160 reflections. Crystal data for **2**: tetragonal, $P4_2/m$, $a = 9.159(1)$ Å, $c = 18.292(1)$ Å, $V = 1534.6(2)$ Å^3, $Z = 2$, $R = 0.047$, $R_w = 0.056$ for 768 reflections. Compound **1** is a highly crowded molecule which contains unusually long Si–Si bonds (2.542(2) Å) and a folded cyclotetrasilane ring with relatively small dihedral angles of 15.2° and 16.1°. In the UV spectrum of **1**, absorption extends to the longer wavelength region than **2** and other alkyl-substituted cyclotetrasilanes so far reported. The oxidation potential of **1** (1.02 V vs. SCE) is significantly low compared with those of **2** and other less crowded cyclotetrasilanes.

Keywords: Silicon; Cyclotetrasilane; Crystal structure

1. Introduction

The chemistry of cyclotetrasilanes has been investigated extensively [1]. Cyclotetrasilanes with various substituents have been synthesized and their structures reported [2,3]. As a part of our study on cyclotetrasilanes [3], we have attempted to construct highly crowded cyclotetrasilanes and perturb electronic properties of cyclotetrasilanes by steric hindrance. We have been interested in the condensation of di-tert-butyldichlorosilane with lithium as a route to poly-tert-butyl-substituted cyclotetrasilanes. To date, two reports have appeared on such condensation. In 1984, Watanabe et al. reported that the condensation of di-tert-butyldichlorosilane with lithium (or sodium) resulted in the formation of 1,1,2,2-tetra-tert-butyldisilane, but no cyclic products such as cyclotetra- and cyclotrisilanes could be obtained in the reaction [4]. Also, in 1988 Boudjouk et al. reported that the reaction of di-tert-butyldichlorosilane with lithium under ultrasonic irradiation gave *trans*-1,1,2,3,3,4-hexa-tert-butylcyclotetrasilane in 15% yield along with 65% of 1,1,2,2-tetra-tert-butyldisilane; the X-ray structure of the cyclotetrasilane was not mentioned [5]. However, in our study, hepta-tert-butylcyclotetrasilane was obtained together with tetra-tert-butyldisilane and hexa-tert-butylcyclotetrasilane in the reaction of di-tert-butyldichlorosilane with lithium. We report here the syntheses, structures and properties of hepta-tert-butylcyclotetrasilane and *trans*-1,1,2,3,3,4-hexa-tert-butylcyclotetrasilane.

2. Results and discussion

By condensation of di-tert-butyldichlorosilane with lithium in THF, hepta-tert-butylcyclotetrasilane (**1**) and *trans*-1,1,2,3,3,4-hexa-tert-butylcyclotetrasilane (**2**) were synthesized in 5 and 18% yields, respectively, along with 1,1,2,2-tetra-*tert*-butyldisilane (19%). Compounds **1** and **2** were obtained as colorless crystals which are stable in the air. Hexa-tert-butylcyclotrisilane was not detected in the reaction mixture, while the formation of the cyclotrisilane has been reported in the coupling reactions of di-tert-butyldibromosilane with lithium [5] and di-tert-butyldiiodosilane with lithium naphthalenide [6].

The structures of **1** and **2** were determined by X-ray crystallography (Figs. 1 and 2). Crystallographic data, positional parameters and selected bond distances and angles are given in Tables 1–5.

☆ Dedicated to Professor Hideki Sakurai on the occasion of his retirement from Tohoku University.

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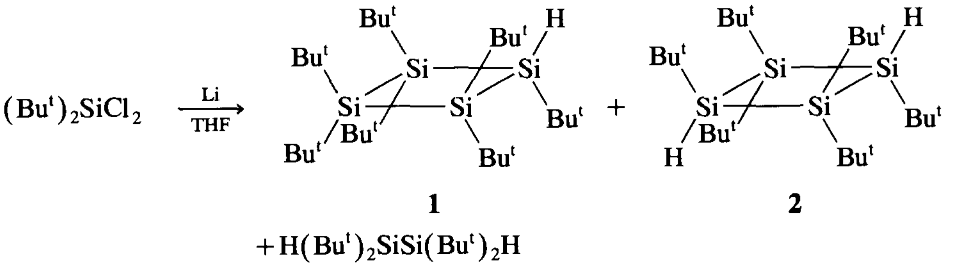

Compound **1** has the highly strained cyclotetrasilane ring. The Si(1)–Si(2) bond distance (2.542(2) Å) is the longest of cyclotetrasilanes reported so far (cf. *cis-cis-trans*-$[{}^tBu(c\text{-}C_6H_{11})Si]_4$: 2.460(3) Å [2r]; $[({}^tBuCH_2)_2Si]_4$: 2.433(19) Å [3b]), while the Si(2)–Si(3) bond distance is typical (2.398(2) Å). The Si(2)–Si(1)–

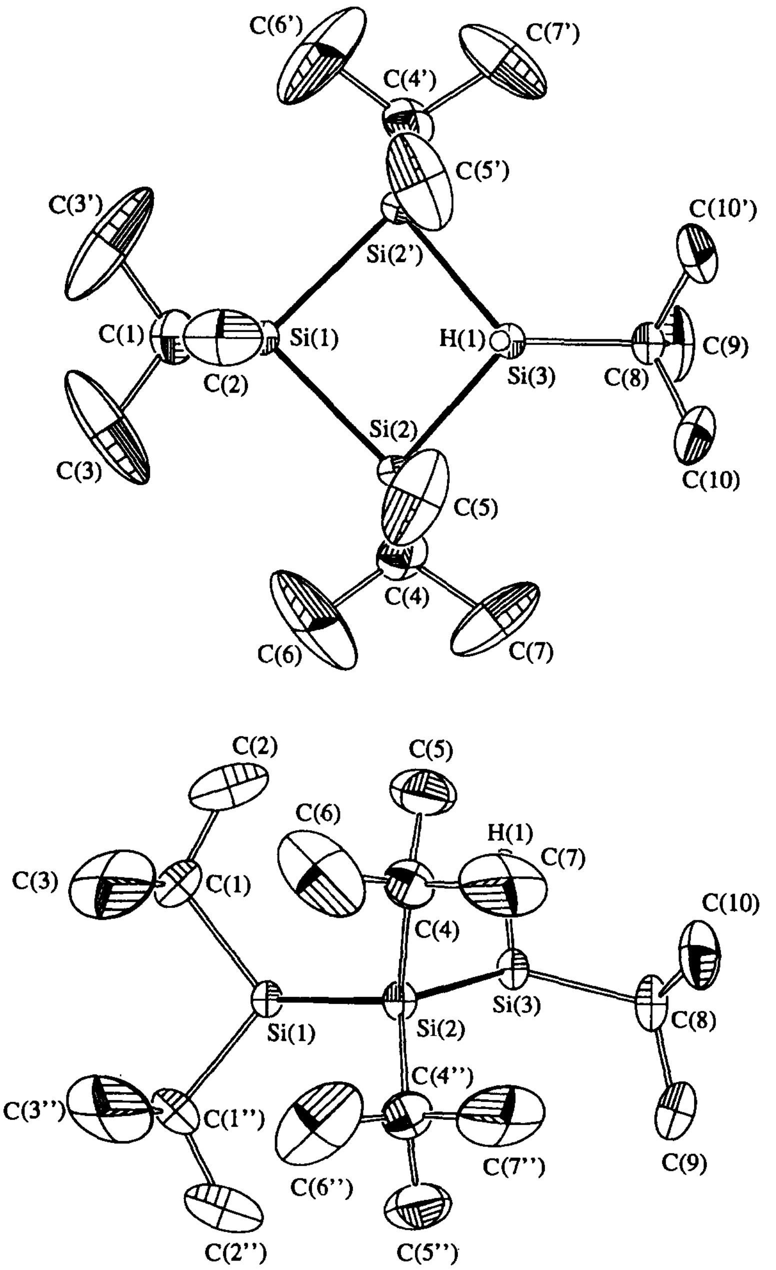

Fig. 1. ORTEPII drawing of **1** viewed along the *c* axis (top) and viewed along the *a* axis (bottom). Thermal ellipsoids are drawn at the 30% probability level.

Si(2′) and Si(1)–Si(2)–Si(3) bond angles are typical, but the Si(2)–Si(3)–Si(2′) bond angle (96.0(1)°) is significantly larger. The cyclotetrasilane ring has a folded structure and the dihedral angles between the Si(1)–Si(2)–Si(3) and Si(1)–Si(2′)–Si(3) planes and between the Si(1)–Si(2)–Si(2′) and Si(2)–Si(3)–Si(2′) planes are 15.2 and 16.1°, respectively. The fold angles are relatively small compared with those of other tert-butyl-substituted cyclotetrasilanes (cf. all-*trans*-$[(Bu^{t})MeSi]_4$: 36.8° [2e]; *cis-cis-trans*-$[(Bu^{t})(c\text{-}C_6H_{11})Si]_4$: 34° [2r]; all-*trans*-$[(Bu^{t})ClSi]_4$: 26.6° [3f]; *cis-cis-trans*-$[(Bu^{t})PhSi]_4$: 27.7° [3f]; *cis-trans-cis*-$[(Bu^{t})PhSi]_4$: 32.8° [3f]). The Si(3) atom has highly distorted configuration. The Si(2)–Si(3)–C(8) bond angle is considerably large (125.7(1)°) and the Si(2)–Si(3)–H(1) bond angle is small (97.4°). Therefore, the tert-butyl group on the Si(3) atom occupies the pseudo-equatorial position which is located at the side of the cyclotetrasilane plane. These structural features seem favorable for reducing the steric repulsion among the tert-butyl groups.

The X-ray analysis of **2** shows the rather different cyclotetrasilane structure. The cyclotetrasilane ring has $2/m$ symmetry and is completely planar. The four Si–Si bond lengths are equal, and having the same typical value (2.387(1) Å). The Si(1)–Si(2)–Si(1″) bond angle (93.7(1)°) is larger than the Si(2)–Si(1)–Si(2′) bond angle (86.4(1)°). This implies that the cyclotetrasilane ring has the somewhat rhombic structure. The result is compared with other planar cyclotetrasilanes with methyl [2k] and trialkylsilyl [1a, 2j] substituents, in which the Si–Si–Si bonds are nearly right angles and the cyclotetrasilane rings are regular squares. The Si(2) atom has a highly distorted configuration, as indicated by the Si(3) atom of **1**. The Si(1)–Si(2)–C(5) bond angles are large (128.3(1)°) while the Si(1)–Si(2)–H(1) bond angles are small (97.3°).

In UV spectra of **1** and **2** (Fig. 3) the lowest energy transition occurs at 315 and 275 nm, respectively. It is noted that the absorption maximum of **1** occurs in the longer wavelength region than that of **2** or any other alkyl-substituted cyclotetrasilane [2,3,7,8]. The bathochromic shift observed for **1** is ascribed to the highly strained cyclotetrasilane framework and the destabilized HOMO.

Oxidation potentials (E_{p}^{ox}) of **1** and **2** measured by cyclic voltammetry are 1.02 and 1.29 V vs. SCE in dichloromethane, respectively. The oxidation potentials of other cyclotetrasilanes have been reported to range from 1.1 to 1.3 V vs. SCE in dichloromethane [8], indicating **1** has a relatively strong electron-donating property. This result is in good agreement with that observed in the UV spectrum of **1**.

3. Experimental details

All operations were carried out under a nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from

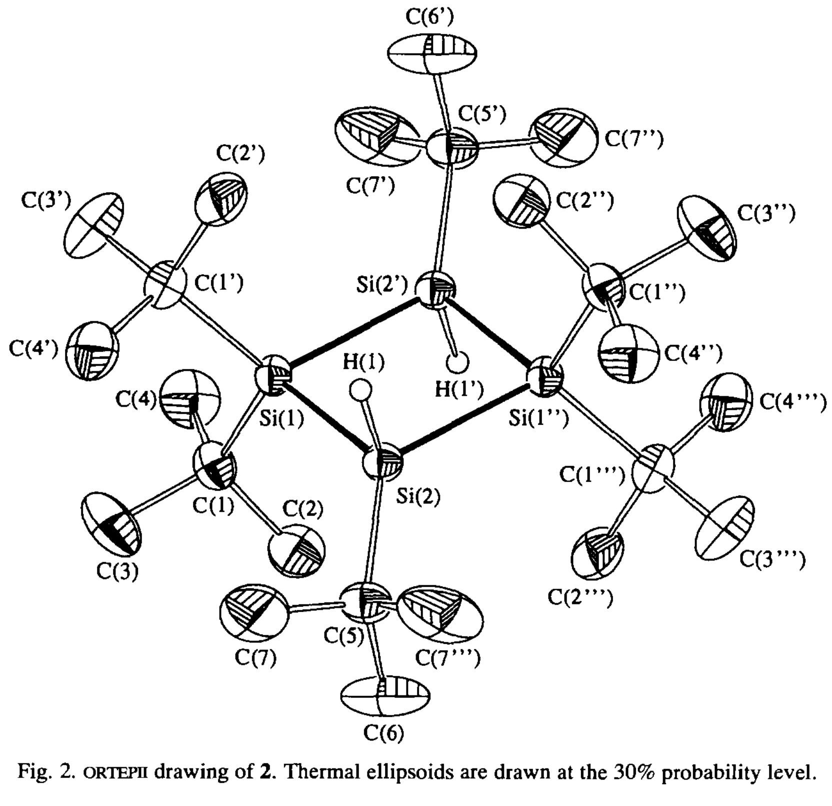

Fig. 2. ORTEPII drawing of **2**. Thermal ellipsoids are drawn at the 30% probability level.

Table 1
Summary of crystal data, data collection and refinement for **1** and **2**

	1	**2**
Crystal data		
Formula	$C_{28}H_{64}Si_4$	$C_{24}H_{56}Si_4$
Molecular weight	513.16	457.05
Crystal description	colorless prisms	colorless prisms
Crystal size (mm)	0.4 × 0.5 × 0.5	0.25 × 0.25 × 0.1
Crystal system	orthorhombic	tetragonal
Space group	*Cmcm*	$P4_2/m$
a (Å)	12.071(1)	9.159(1)
b (Å)	17.964(2)	
c (Å)	15.431(4)	18.292(1)
V (Å^3)	3346.0(8)	1534.6(2)
Z	4	2
$D_{\text{meas.}}$ (g cm^{-3})	1.021	0.983
$D_{\text{calc.}}$ (g cm^{-3})	1.019	0.989
Data collection		
Diffractometer	Rigaku AFC-7S	Rigaku AFC-6S
Radiation (λ (Å))	Mo-Kα (0.7107)	Cu-Kα (1.5418)
μ (cm^{-1})	1.86	18.56
Absorption correction	none	empirical
T_{min}		0.854
T_{max}		1.205
Variation of standards	< 1%	< 1%
$2\theta_{\text{max}}$ (°)	55.0	120.2
Scan type	$\omega - 2\theta$	$\omega - 2\theta$
Scan width (°)	$1.31 + 0.35 \tan\theta$	$1.47 + 0.30 \tan\theta$
No. of reflections measured	2149	1337
No. of independent reflections	2149	1185
No. of observed reflections ($I > 3\sigma(I)$)	1160	768
Refinement		
R	0.067	0.047
R_w	0.051	0.056
Weighting scheme	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$
S	2.68	1.52
$(\Delta/\sigma)_{\text{max}}$	0.001	< 0.001
$(\Delta\rho)_{\text{max}}$ (e Å^{-3})	0.40	0.27
$(\Delta\rho)_{\text{min}}$ (e Å^{-3})	−0.36	−0.21
Extinction correction	secondary	secondary
Extinction coefficient	3.19×10^{-7}	2.60×10^{-6}
No. of parameters	94	70

sodium benzophenone ketyl. Di-tert-butyldichlorosilane (Petrarch Systems) and lithium powder (Fluka, 50–200 μm) were used as received. IR spectra were recorded on a JASCO A-102 spectrometer. ^{1}H, ^{13}C and ^{29}Si NMR spectra were obtained with a JEOL JNM-A500 spectrometer. Mass spectra were recorded on a JEOL JMS-DX302 mass spectrometer. UV spectra were obtained with a JASCO Ubest-50 spectrophotometer.

3.1. Synthesis of hepta-tert-butylcyclotetrasilane (1) and trans-1,1,2,3,3,4-hexa-tert-butylcyclotetrasilane (2)

A mixture of di-tert-butyldichlorosilane (1.00 g, 4.69 mmol) and lithium powder (0.100 g, 14.4 mmol) in

Table 2
Fractional atomic coordinates and equivalent isotropic thermal parameters for **1**

Atom	x	y	z	B_{eq} [a] (Å^2)
Si(1)	0	0.2164(1)	0.25	2.88(5)
Si(2)	0.1476(1)	0.1155(1)	0.25	3.14(4)
Si(3)	0	0.0296(2)	0.2213(2)	3.22(8)
C(1)	0	0.2843(4)	0.1492(5)	6.1(2)
C(2)	0	0.2471(6)	0.0627(5)	9.8(3)
C(3)	0.1029(7)	0.3336(4)	0.1505(5)	21.0(4)
C(4)	0.2427(4)	0.1087(3)	0.1477(3)	6.2(1)
C(5)	0.1770(7)	0.0992(4)	0.0659(4)	13.6(3)
C(6)	0.3159(7)	0.1755(5)	0.1391(6)	20.7(4)
C(7)	0.3123(5)	0.0376(4)	0.1478(4)	14.4(3)
C(8)	0	−0.0751(5)	0.25	5.0(3)
C(9)	0	−0.0945(9)	0.3457(13)	9.2(7)
C(10)	0.1017(9)	−0.1110(5)	0.2066(7)	8.2(4)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $B_{\text{eq}} = (8\pi^2/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \boldsymbol{a}_j$.

Table 3
Bond distances (Å) and angles (°) for **1** [a]

Bond distances			
Si(1)–Si(2)	2.542(2)	C(1)–C(3)	1.526(7)
Si(1)–C(1)	1.976(7)	C(4)–C(5)	1.500(8)
Si(2)–Si(3)	2.398(2)	C(4)–C(6)	1.496(7)
Si(2)–C(4)	1.955(5)	C(4)–C(7)	1.528(7)
Si(3)–C(8)	1.934(9)	C(8)–C(9)	1.52(2)
C(1)–C(2)	1.49(1)	C(8)–C(10)	1.54(1)
Bond angles			
Si(2)–Si(1)–Si(2′)	89.0(1)	C(2)–C(1)–C(3)	105.7(5)
Si(2)–Si(1)–C(1)	116.1(1)	C(3)–C(1)–C(3′)	109.0(9)
C(1)–Si(1)–C(1″)	103.8(5)	Si(2)–C(4)–C(5)	112.1(4)
Si(1)–Si(2)–Si(3)	86.4(1)	Si(2)–C(4)–C(6)	111.6(4)
Si(1)–Si(2)–C(4)	117.1(2)	Si(2)–C(4)–C(7)	112.0(4)
Si(3)–Si(2)–C(4)	104.3(2)	C(5)–C(4)–C(6)	109.2(6)
Si(3)–Si(2)–C(4″)	123.0(2)	C(5)–C(4)–C(7)	101.4(5)
C(4)–Si(2)–C(4″)	107.7(3)	C(6)–C(4)–C(7)	110.1(6)
Si(2)–Si(3)–Si(2′)	96.0(1)	Si(3)–C(8)–C(9)	116.5(8)
Si(2)–Si(3)–C(8)	125.7(1)	Si(3)–C(8)–C(10)	107.9(5)
Si(1)–C(1)–C(2)	115.3(6)	C(9)–C(8)–C(10)	109.1(6)
Si(1)–C(1)–C(3)	110.3(5)	C(10)–C(8)–C(10′)	105.8(9)

[a] Single- and double-primed atoms are generated by the crystallographic symmetry operators $(-x, y, z)$ and $(x, y, 1/2 - z)$, respectively.

Table 4
Fractional atomic coordinates and equivalent isotropic thermal parameters for **2**

Atom	x	y	z	B_{eq} [a] (Å^2)
Si(1)	0.5	0	0.0952(1)	3.14(3)
Si(2)	0.3416(2)	0.0819(2)	0	3.22(4)
C(1)	0.5993(5)	0.1457(5)	0.1533(2)	4.3(1)
C(2)	0.6425(6)	0.2731(5)	0.1054(3)	6.1(1)
C(3)	0.5019(6)	0.2053(6)	0.2135(3)	7.5(2)
C(4)	0.7388(5)	0.0862(6)	0.1872(3)	6.4(1)
C(5)	0.2136(6)	0.2475(6)	0	4.5(2)
C(6)	0.2890(10)	0.3937(8)	0	9.8(3)
C(7)	0.1175(8)	0.2412(7)	0.0650(4)	11.1(2)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $B_{\text{eq}} = (8\pi^2/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \boldsymbol{a}_j$.

Table 5
Bond distances (Å) and angles (°) for **2** [a]

Bond distances			
Si(1)–Si(2)	2.387(1)	C(1)–C(3)	1.520(7)
Si(1)–C(1)	1.933(4)	C(1)–C(4)	1.521(7)
Si(2)–C(5)	1.918(6)	C(5)–C(6)	1.507(10)
C(1)–C(2)	1.511(6)	C(5)–C(7)	1.480(8)
Bond angles			
Si(2)–Si(1)–Si(2′)	86.4(1)	Si(1)–C(1)–C(4)	111.8(3)
Si(2)–Si(1)–C(1)	118.0(1)	C(2)–C(1)–C(3)	107.2(4)
Si(2)–Si(1)–C(1′)	109.4(1)	C(2)–C(1)–C(4)	107.1(4)
C(1)–Si(1)–C(1′)	113.3(2)	C(3)–C(1)–C(4)	109.0(4)
Si(1)–Si(2)–Si(1″)	93.7(1)	Si(2)–C(5)–C(6)	115.0(5)
Si(1)–Si(2)–C(5)	128.3(1)	Si(2)–C(5)–C(7)	109.4(4)
Si(1)–C(1)–C(2)	109.8(3)	C(6)–C(5)–C(7)	107.9(4)
Si(1)–C(1)–C(3)	111.7(3)	C(7)–C(5)–C(7‴)	106.9(6)

[a] Single-, double- and triple-primed atoms are generated by the crystallographic symmetry operators $(1-x, -y, z)$, $(1-x, -y, -z)$ and $(x, y, -z)$, respectively.

THF (5 ml) was stirred for 20 h at room temperature. A large amount of hexane was added to the reaction mixture, and insoluble materials were removed by filtration. The solvent was removed by evaporation, and the residue was passed through a short column of silica gel with hexane as an eluent. The resulting mixture was subjected to recycle-type HPLC on ODS with methanol/THF (7:3) as an eluent to give **1** (31 mg, 5%) and **2** (94 mg, 18%) as colorless crystals.

1: m.p. 178.5–180°C. ^{1}H NMR (C_6D_6): δ 1.32 (s, 9H), 1.41 (s, 18H), 1.44 (s, 9H), 1.46 (s, 9H), 1.47 (s, 18H), 4.12 (s, 1H). ^{13}C NMR (C_6D_6): δ 22.5 (1C, $C(CH_3)_3$), 24.1 (1C, $C(CH_3)_3$), 25.3 (2C, $C(CH_3)_3$), 25.5 (2C, $C(CH_3)_3$), 28.2 (1C, $C(CH_3)_3$), 33.4 (3C, $C(CH_3)_3$), 34.6 (6C, $C(CH_3)_3$), 34.7 (3C, $C(CH_3)_3$), 34.9 (6C, $C(CH_3)_3$), 36.2 (3C, $C(CH_3)_3$). ^{29}Si NMR (C_6D_6): δ − 36.2 (Si(3)), 31.7 (Si(2) and Si(2′)), 41.8 (Si(1)). IR (KBr, cm^{-1}): 2950, 2860, 2060, 1460, 1385, 1360, 1170, 1010, 805, 745, 705. MS: m/z 512 (3, M$^+$), 456 (1), 399 (5), 343 (14), 73 (100). UV (λ_{max} in hexane) 274 (ε 3060), 315 nm (550). HRMS. Found: 512.4070. $C_{28}H_{64}Si_4$ calc.: 512.4085.

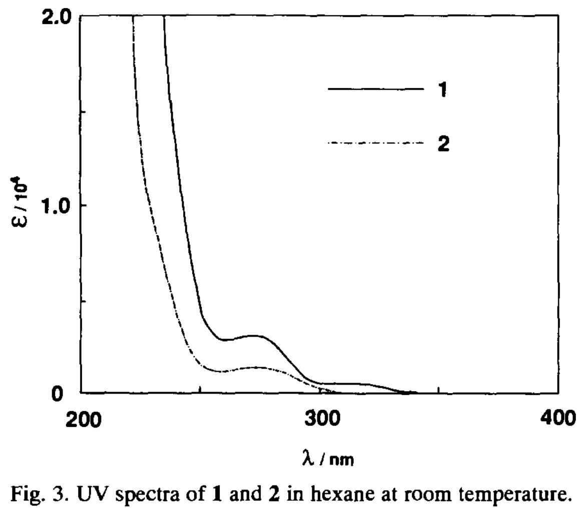

Fig. 3. UV spectra of **1** and **2** in hexane at room temperature.

2: m.p. 221–224°C. ^{1}H NMR (C_6D_6): δ 1.26 (s, 18H), 1.32 (s, 36H), 4.20 (s, 2H). ^{13}C NMR (C_6D_6): δ 21.3 (2C, $C(CH_3)_3$), 23.5 (4C, $C(CH_3)_3$), 32.3 (12C, $C(CH_3)_3$), 33.0 (6C, $C(CH_3)_3$). ^{29}Si NMR (C_6D_6): δ −35.1 (Si(2) and Si(2′)), 32.0 (Si(1) and Si(1″)). IR (KBr, cm^{-1}): 2920, 2850, 2060, 1455, 1385, 1360, 1180, 1010, 815, 770, 675. MS: m/z 456 (6, M$^+$), 399 (29), 343 (16), 287 (10), 73 (100). UV (λ_{max} in hexane) 275 nm (ε 1370).

3.2. *X-ray crystallographic analysis of 1 and 2*

Colorless crystals of **1** and **2** were obtained from an acetone solution by slow evaporation. A crystal specimen of **1** was sealed in a glass capillary and used for data collection on a Rigaku AFC-7S diffractometer using graphite-monochromated Mo-Kα radiation. In the case of **2**, a crystal specimen was mounted on a glass fiber and used for data collection on a Rigaku AFC-6S diffractometer using graphite-monochromated Cu-Kα radiation. Cell parameters were refined by the least-squares method using 25 reflections with $33.3 < 2\theta < 37.9°$ (**1**) and $51.9 < 2\theta < 56.8°$ (**2**). Intensity data were collected in the range of $2\theta < 55.0°$ (**1**) and $2\theta < 120.2°$ (**2**) by the $\omega - 2\theta$ scan technique at room temperature. Three standard reflections were measured after every 150 reflections; they showed no decay. The data were corrected for Lorentz and polarization effects. In the case of **2**, an empirical absorption correction based on a ψ scan was also applied. The structure was solved by direct methods using SHELXS86 [9] for **1** and SIR88 [10] for **2**. In the case of **1**, the orientation of the molecules was found to be disordered, with the cyclotetrasilane rings upside-down in the equal probability. Non-hydrogen atoms were refined by the full-matrix least-squares method with anisotropic thermal parameters using teXsan [11]. A secondary extinction correction was applied in the least-squares method. Hydrogen atoms bound to silicon atoms were located by difference Fourier synthesis. The remaining hydrogen atoms were located at calculated positions. All hydrogen atoms were not refined. Atomic scattering factors were taken from Ref. [12]. All calculations were carried out on a Silicon Graphics INDY computer. Details of crystal data, data collection and refinement are listed in Table 1.

Acknowledgments

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