

# Superlattice structure of octa-*tert*-butylpentacyclo[4.2.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]octasilane found by reinvestigation of X-ray structure analysis

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## Abstract

X-ray structure analysis is reinvestigated for octa-*tert*-butylpentacyclo[4.2.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]octasilane (<sup>t</sup>BuSi)<sub>8</sub> (trigonal, *R*32, *a* = *b* = 12.232(3) Å, *c* = 125.186(4) Å,  $\gamma$  = 120°, *V* = 16221(2) Å<sup>3</sup>, *Z* = 15, *R* = 0.049, *R*<sub>w</sub> = 0.052). The crystal symmetry and the molecular structure are the same as those in our previous report. It is, however, found that the molecule forms a superlattice structure, in which the *c* axis of the unit cell is five times as long as that given in the previous report.

**Keywords:** Silicon; Cluster; Octasilacubane; Superlattice structure; Crystal structure

## 1. Introduction

Octasilacubane, a silicon analogue for cubane, is receiving interest in organosilicon chemistry because it contains a highly strained silicon backbone [1]. Although the strained energy of octasilacubane is estimated to be lower than cubane [2], a molecule containing an octasilacubane framework had not been synthesized for a long time.

The first claim of the synthesis of such a molecule was made in 1988 [3]. This octasilacubane was substituted with *tert*-butyldimethylsilyl groups and was characterized by mass and NMR spectra. Crystallographical proof of the framework did not come until 1992, when X-ray analyses for octasilacubanes with various substituents, such as *tert*-butyl [4], 2,6-diethylphenyl [5], and 1,1,2-trimethylpropyl groups [6] were successively reported.

In a previous report, we determined the molecular structure of the octasilacubane with *tert*-butyl substituents (**1**) [4]. The crystal contained a three-fold axis due to the high symmetry of the substituents as well as the silicon backbone. Recently, a polymorphic crystal

form has been reported in **1** [7,8]. The X-ray structure analysis was, however, not acceptable (*R* = 0.0996 for 789 independent reflections). In our previous report, the number of the observed reflections was insufficient to converge the *R* factor to less than 0.068. These results have made us reinvestigate the X-ray structure analysis of the compound.

In this paper, we show the superlattice structure of **1** together with the refined X-ray data.

## 2. Results and discussion

The positional parameters for **1** are given in Table 1. The unit cell is shown in Fig. 1. The crystal belongs to the trigonal space group *R*32 with *a* = *b* = 12.232 (2) Å, *c* = 125.186 (2) Å, and  $\gamma$  = 120°. This space group is the same as the one in the previous report [4]. However, as can be seen in Fig. 1, the refined analysis shows that the crystal forms a superlattice structure along the *c* axis. The lattice constants of *c* is five times as long as the previous one of 25.067 Å.

In the unit cell, there are three types of molecule, molecules 1, 2, and 3 (Fig. 2). They all have similar molecular structures, but their bond lengths and angles are slightly different. Hence they cannot be associated with symmetry operations with each other. All molecules

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lie on a three-fold axis of the crystal. In addition, molecule 1 lies on a two-fold axis of the crystal, while molecules 2 and 3 do not lie on a two-fold axis. The unit cell consists of 15 molecules and contains three of molecule 1, six of molecule 2, and six of molecule 3, as shown in Fig. 1. From the bottom to the top, they are stacked in the order 132231322313223. Formation of a superlattice structure has not yet been reported for octasilacubanes with other types of substituent.

The characteristic feature of **1** that is different from other substituted octasilacubanes is that **1** has highly symmetrical *tert*-butyl groups as its substituents. This is reflected in the crystal structure of **1**: it has a three-fold axis which is not observed in the crystals of other octasilacubanes. It is suggested that formation of a

superlattice structure is caused primarily by the difference in the symmetry of the substituents.

The selected bond lengths and angles of the molecules are listed in Table 2. The Si–Si bond lengths of the three molecules are 2.374–2.400 Å. The Si–Si–Si bond angles are between 89.5 and 90.9°. These refined values are similar to those in the previous report [4]. The structures of molecules 1, 2, and 3 are not very different from each other. They have silicon backbones quite similar in shape to a cube, although the backbones are slightly distorted.

The Si–Si distances are longer than the typical Si–Si bond distance of ca. 2.34 Å [9,10]. The bond extension is also observed for other octasilacubanes [3–5]. One of the reasons could be the strain of the Si–Si bond arising

Table 1  
Atomic positional and equivalent thermal parameters for (<sup>t</sup>BuSi)<sub>8</sub>

Atom	x	y	z	B <sub>eq</sub> (Å <sup>2</sup> )
Si(1)	0.0000	0.0000	0.01665(5)	2.80(8)
Si(2)	0.1828(4)	0.0921(4)	0.00558(4)	3.20(8)
Si(3)	0.6667	0.3333	0.14984(6)	2.77(8)
Si(4)	0.5969(4)	0.4455(4)	0.13871(4)	3.03(9)
Si(5)	0.4839(4)	0.2631(4)	0.12765(4)	3.08(10)
Si(6)	0.6667	0.3333	0.11661(6)	2.90(8)
Si(7)	0.3333	0.6667	0.08288(6)	2.96(9)
Si(8)	0.2230(4)	0.7402(4)	0.07188(3)	2.82(7)
Si(9)	0.1502(4)	0.5569(4)	0.06088(4)	2.88(8)
Si(10)	0.3333	0.6667	0.04985(6)	2.82(8)
C(1)	0.0000	0.0000	0.0320(2)	4.4(4)
C(2)	0.353(1)	0.179(1)	0.0111(1)	5.8(4)
C(3)	0.029(2)	–0.100(2)	0.0362(2)	6.3(5)
C(4)	0.365(2)	0.096(2)	0.0190(2)	11.3(7)
C(5)	0.388(2)	0.310(2)	0.0159(2)	9.4(5)
C(6)	0.445(2)	0.197(2)	0.0011(2)	10.4(6)
C(7)	0.6667	0.3333	0.1645(2)	4.6(4)
C(8)	0.527(2)	0.553(2)	0.1438(1)	4.4(4)
C(9)	0.321(1)	0.204(1)	0.1226(1)	4.3(3)
C(10)	0.6667	0.3333	0.1008(2)	4.0(3)
C(11)	0.696(2)	0.237(2)	0.1694(1)	6.7(5)
C(12)	0.633(2)	0.650(2)	0.1507(2)	8.0(6)
C(13)	0.408(2)	0.471(2)	0.1506(2)	12.1(8)
C(14)	0.504(2)	0.613(2)	0.1337(2)	7.2(5)
C(15)	0.224(2)	0.159(2)	0.1316(2)	9.2(5)
C(16)	0.296(2)	0.300(2)	0.1165(2)	7.4(5)
C(17)	0.276(2)	0.091(2)	0.1157(2)	7.2(5)
C(18)	0.611(2)	0.415(2)	0.0971(20)	11.8(9)
C(19)	0.3333	0.6667	0.0986(2)	3.4(3)
C(20)	0.123(1)	0.805(1)	0.0770(1)	3.6(3)
C(21)	–0.025(1)	0.453(1)	0.0559(1)	3.7(3)
C(22)	0.3333	0.6667	0.0349(2)	4.2(2)
C(23)	0.360(2)	0.798(2)	0.1025(1)	7.1(5)
C(24)	0.025(1)	0.721(1)	0.0855(1)	5.7(3)
C(25)	0.203(1)	0.935(1)	0.0821(1)	5.2(3)
C(26)	0.051(1)	0.825(2)	0.0682(1)	5.3(4)
C(27)	–0.114(2)	0.421(2)	0.0653(2)	6.9(4)
C(28)	–0.029(1)	0.339(2)	0.0509(1)	6.3(4)
C(29)	–0.051(2)	0.530(2)	0.0467(1)	6.6(4)
C(30)	0.262(2)	0.534(2)	0.0302(2)	6.5(5)

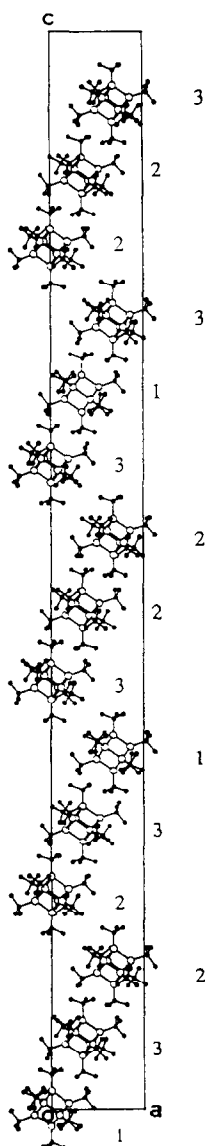
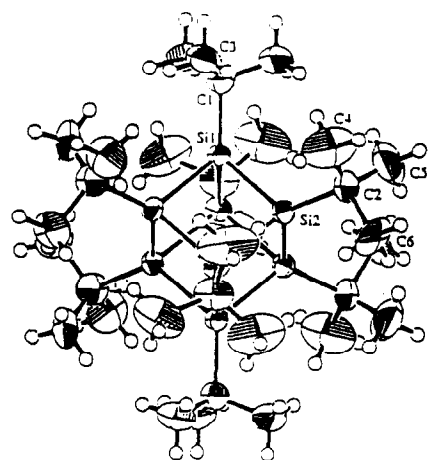


Fig. 1. Trigonal unit cell of **1**. The perspective view perpendicular to the *c* axis. Open and filled circles show silicon and carbon atoms respectively. Molecules appear from the bottom to the top of the unit cell in the order 132231322313223.

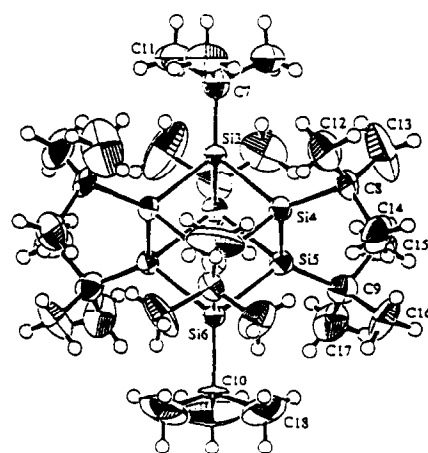
from the cubic backbone structure. This is deduced from the experiments showing that permethyldisilane [9] and permethylcyclohexasilane [10], whose backbones are not strained, have Si–Si distances of ca. 2.34 Å, while permethylcyclotetrasilane has longer distances of ca. 2.36 Å [11].

The bulkiness of the substituents is also considered to affect the structure. It can be seen that the average Si–Si distance is shorter in **1** than in the 1,1,2-trimethylpropyl-substituted octasilacubane (2.398–2.447 Å). This might be due to the lesser bulkiness of the *tert*-butyl groups compared with 1,1,2-trimethylpropyl: the latter has two more methyl groups compared with *tert*-butyl ones.

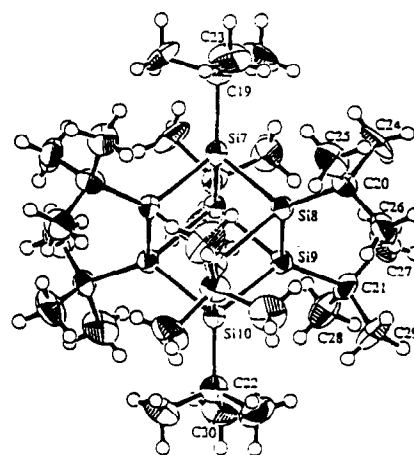
It is observed that some intermolecular C–C distances are less than 4 Å, the sum of the van der Waals radius for methyl carbon of ca. 2 Å (C(11)–C(12) = 4.00(3); C(16)–C(24) = 3.88(3); C(18)–C(24) =



molecule 1



molecule 2



molecule 3

Fig. 2. ORTEP drawing of **1** with 50% anisotropic ellipsoids.

Table 2  
Intramolecular bond distances (Å) and angles (deg)

Molecule 1			
Si(2)–Si(2)	2.381(6)	Si(2)–Si(1)–Si(2)	89.5(2)
Si(2)–Si(2)	2.374(8)	Si(1)–Si(2)–Si(2)	90.9(2)
Si(2)–Si(2)	2.400(8)	Si(1)–Si(2)–Si(2)	90.3(2)
		Si(2)–Si(2)–Si(2)	89.3(3)
Si(1)–C(1)	1.92(3)		
Si(2)–C(2)	1.94(2)	Si(2)–Si(1)–C(1)	125.6(2)
		Si(1)–Si(2)–C(2)	123.4(6)
C(1)–C(3)	1.52(2)	Si(2)–Si(2)–C(2)	125.5(5)
C(2)–C(4)	1.48(2)	Si(2)–Si(2)–C(2)	126.5(5)
C(2)–C(5)	1.56(2)		
C(2)–C(6)	1.62(2)		
Molecule 2			
Si(3)–Si(4)	2.392(6)	Si(4)–Si(3)–Si(4)	89.5(3)
Si(5)–Si(6)	2.393(6)	Si(5)–Si(6)–Si(5)	90.0(3)
Si(4)–Si(5)	2.392(6)	Si(3)–Si(4)–Si(5)	90.4(2)
Si(4)–Si(5)	2.390(6)	Si(3)–Si(4)–Si(5)	90.5(2)
		Si(4)–Si(5)–Si(6)	89.9(3)
Si(3)–C(7)	1.83(3)	Si(4)–Si(5)–Si(6)	90.0(2)
Si(4)–C(8)	2.00(1)	Si(5)–Si(4)–Si(5)	90.1(3)
Si(5)–C(9)	1.85(2)	Si(4)–Si(5)–Si(4)	89.6(3)
Si(6)–C(10)	1.98(2)		
		Si(4)–Si(3)–C(7)	125.6(2)
C(7)–C(11)	1.52(2)	Si(5)–Si(6)–C(10)	125.3(2)
C(8)–C(12)	1.51(2)	Si(3)–Si(4)–C(8)	125.8(6)
C(8)–C(13)	1.55(2)	Si(5)–Si(4)–C(8)	124.2(6)
C(8)–C(14)	1.56(2)	Si(5)–Si(4)–C(8)	125.1(6)
C(9)–C(15)	1.53(2)	Si(6)–Si(5)–C(9)	124.7(6)
C(9)–C(16)	1.55(2)	Si(4)–Si(5)–C(9)	124.6(5)
C(9)–C(17)	1.48(2)	Si(4)–Si(5)–C(9)	126.9(5)
C(10)–C(18)	1.54(2)		
Molecule 3			
Si(7)–Si(8)	2.395(6)	Si(8)–Si(7)–Si(8)	90.2(3)
Si(9)–Si(10)	2.391(6)	Si(9)–Si(10)–Si(9)	90.0(3)
Si(8)–Si(9)	2.392(6)	Si(7)–Si(8)–Si(9)	89.7(2)
Si(8)–Si(9)	2.394(6)	Si(7)–Si(8)–Si(9)	89.7(2)
		Si(8)–Si(9)–Si(10)	90.1(2)
Si(7)–C(19)	1.97(2)	Si(8)–Si(9)–Si(10)	90.0(2)
Si(8)–C(20)	1.87(1)	Si(9)–Si(8)–Si(9)	89.9(3)
Si(9)–C(21)	1.97(1)	Si(8)–Si(9)–Si(8)	90.4(3)
Si(10)–C(22)	1.87(3)		
		Si(8)–Si(7)–C(19)	125.1(2)
C(19)–C(23)	1.55(2)	Si(9)–Si(10)–C(22)	125.3(2)
C(20)–C(24)	1.55(2)	Si(7)–Si(8)–C(20)	124.9(5)
C(20)–C(25)	1.53(2)	Si(9)–Si(8)–C(20)	125.4(5)
C(20)–C(26)	1.50(2)	Si(9)–Si(8)–C(20)	126.0(5)
C(21)–C(27)	1.51(2)	Si(10)–Si(9)–C(21)	126.3(5)
C(21)–C(28)	1.50(2)	Si(8)–Si(9)–C(21)	124.3(5)
C(21)–C(29)	1.61(2)	Si(8)–Si(9)–C(21)	124.8(5)
C(22)–C(30)	1.53(2)		

### 3. Experimental details

#### 3.1. Sample preparation

**1** was prepared according to a previously reported method [4]. *tert*-Butyltrichlorosilane  $t\text{-BuSiCl}_3$  (**2**) is obtained from a commercial source (Petrach) and was purified by sublimation prior to use. All procedures were performed in an argon atmosphere. Typically, **2** (5.0 g, 25.2 mmol) in toluene (10 ml) was added dropwise into the refluxing mixture of toluene (50 ml), 12-crown-4 (0.45 g, 2.5 mmol), and molten sodium (1.71 g, 75 mmol) within 10 min while stirring. After 5 h of refluxing, the precipitates, including the product as well as salt, were separated by filtration, and treated with ethanol–hexane (1/4 in volume) to decompose unreacted sodium, washed with water to remove the salt, replaced by ethanol, and washed with hexane to remove compounds unexpectedly oxidized, and then dried in vacuo. This procedure yielded reddish-purple crystals (hexagonal plate, up to 100  $\mu\text{m}$  in diameter and 30  $\mu\text{m}$  thick) with a 20% yield (450 mg). Crystals suitable for X-ray structure analysis were obtained as follows. 500 mg of **1** was dissolved in refluxing toluene (500 ml), then kept at 40–50°C for 12 h. Reddish-purple crystals were obtained with dimensions of 0.2 to 0.5 mm cubes.

#### 3.2. Spectroscopic data

High resolution mass spectrum (electron impact, 70 eV):  $m/z$  found 680.3780, calc. for  $\text{C}_{32}\text{H}_{72}\text{Si}_8$  680.3788. IR (diffuse reflection, corrected by Kubelka–Munk method): 2962 (vs), 2944 (vs), 2926 (vs), 2884 (vs), 2852 (vs), 1469 (s), 1457 (s), 1386 (m), 1358 (s), 1175 (s), 1008 (m), 934 (m), 816 (s), 609 (m)  $\text{cm}^{-1}$ . Raman ( $\text{Ar}^+$  5145 Å): 324 (m), 436 (s), 462 (m), 591 (s), 608 (s), 805 (s), 929 (m), 997 (w), 1167 (vs), 1454 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (299.95 MHz, *o*-xylene- $d_{10}$ , 88°C):  $\delta$  1.483 ( $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR (75.44 MHz, *o*-xylene- $d_{10}$ , 88°C):  $\delta$  25.983 ( $\text{C}(\text{CH}_3)_3$ ), 32.786 ( $\text{C}(\text{CH}_3)_3$ ).  $^{29}\text{Si}$  NMR (59.60 MHz, DEPT, *o*-xylene- $d_{10}$ , 88°C):  $\delta$  13.042.  $^{13}\text{C}$  NMR (100.58 MHz, solid state, CP/MAS):  $\delta$  26.360, 27.142 ( $\text{C}(\text{CH}_3)_3$ ), 33.392, 33.856 ( $\text{C}(\text{CH}_3)_3$ ).  $^{29}\text{Si}$  NMR (79.46 MHz, solid state, CP/MAS):  $\delta$  6.6, 10.6. The splits in the solid state  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra might be due to the anisotropic structure of crystalline **1**. M.p.: not found, decomposed at ca. 350°C.

#### 3.3. X-ray structure analysis

Cell constants and other pertinent data are listed in Table 3. A purple prismatic crystal of  $\text{Si}_8\text{C}_{32}\text{H}_{72}$  having approximate dimensions of  $0.2 \times 0.2 \times 0.3 \text{ mm}^3$  was mounted on a glass fiber. All measurements were

3.86(3)). The repulsive force between molecules in this overcrowded packing may also lead to the formation of the superlattice structure.

In summary, the superlattice structure was found in **1** by refining the X-ray structure analysis. This structure has never been observed with the other octasilacubanes.

Table 3  
Crystallographic data

Compound	C <sub>32</sub> H <sub>72</sub> Si <sub>8</sub>
Formula weight	681.60
Crystal dimensions, (mm <sup>3</sup> )	0.2 × 0.2 × 0.3
Crystal color	purple
Crystal system	trigonal
a (Å)	12.232(3)
c (Å)	125.186(4)
γ (deg)	120
V (Å <sup>3</sup> )	16221(2)
Space group	R32-D <sub>3</sub> <sup>7</sup>
Z	15
d(calc.) (g cm <sup>-3</sup> )	1.046
Radiation	Cu K α (λ = 1.54178) graphite monochromated
T (K)	298 ± 1
No. of reflections collected	7141
No. of unique reflections	3859
No. of observations (I <sub>0</sub> > 3σ)	2241
No. of variables	301
Data/parameter ratio	7.5
R	0.049
R <sub>w</sub>	0.052

made on a Rigaku AFC7R diffractometer with graphite monochromated Cu K α radiation and a 12 kW rotating anode generator. All calculations were performed using the teXsan [12] crystallographic software package from Molecular Structure Corporation.

Cell constants and an orientation matrix for data collection, obtained from a least squares refinement using the setting angles of 25 carefully centered reflections in the range 86.80 < 2θ < 89.75°, corresponded to a rhombohedral (hexagonal axes) hexagonal cell. Two samples were taken for X-ray diffraction measurements and both of them exhibited the same unit cell parameters supporting the superlattice structure. We thus solved the structure on the basis of the unit cell parameter.

The data were collected at a temperature of 25 ± 1°C using the ω scan technique to a maximum 2θ value of 150.1°. Omega scans of several intense reflections made prior to data collection had an average width at half-height of 0.23° with a take-off angle of 6.0°. Scans of (1.86 + 0.30 tan θ)° were made at a speed of 16.0° min<sup>-1</sup> (in omega). The weak reflections (I < 10.0σ(I)) were rescanned (maximum of four scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm, the crystal to detector distance was 235 mm, and the computer-controlled detector aperture was set to 3.0 × 3.0 mm<sup>2</sup> (horizontal × vertical).

Of the 7147 reflections collected, 3859 were unique

(R<sub>int</sub> = 0.036). The intensities of three representative reflections were measured after every 150 reflections. No data decay correction was applied. The linear absorption coefficient μ for Cu K α radiation is 24.7 cm<sup>-1</sup>. An empirical absorption correction using the program DIFABS [13] was applied which resulted in transmission factors ranging from 0.82 to 1.73. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least squares refinement was based on 2241 observed reflections (I > 3.00σ(I)) and 301 variable parameters and converged with unweighted and weighted agreement factors of R = Σ||F<sub>o</sub>| - |F<sub>c</sub>|| / Σ|F<sub>o</sub>| = 0.049 and R<sub>w</sub> = [Σω(|F<sub>o</sub>| - |F<sub>c</sub>||)<sup>2</sup> / ΣωF<sub>o</sub><sup>2</sup>]<sup>1/2</sup> = 0.052. A molecular drawing of 1 with full atom labeling and tables listing bond distances, bond angles, and anisotropic thermal parameters are available from the authors.

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