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Synthesis, Structures, and Reactions of 1,2,3-Tris(diethylamino)-1,2,3,4-tetrakis(1,1,2-trimethylpropyl)cyclotetrasilanes

Masafumi Unno, Ryoji Tanaka, Toshie Kuribara, Mina Saito, and Hideyuki Matsumoto*

Department of Applied Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376

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The reaction of dichloro(diethylamino)thexylsilane (thexyl = 1,1,2-trimethylpropyl) with lithium gave 1,2,3-tris(diethylamino)-1,2,3,4-tetrathexylcyclotetrasilane (**2**) as a mixture of four diastereomers (*r*-1,*t*-2,*c*-3,*t*-4-**2**, *r*-1,*t*-2,*t*-3,*t*-4-**2**, *r*-1,*t*-2,*c*-3,*c*-4-**2**, and *r*-1,*c*-2,*t*-3,*t*-4-**2**). The isomers were separated and identified by ^{1}H, ^{13}C, and ^{29}Si NMR, IR, Mass, and UV spectroscopy. The structures of *r*-1,*t*-2,*c*-3,*t*-4-**2**, *r*-1,*t*-2,*t*-3,*t*-4-**2**, and *r*-1,*t*-2,*c*-3,*c*-4-**2** were confirmed by X-ray crystallography. The Si–Si bond lengths are 2.391(1)—2.499(2) Å for *r*-1,*t*-2,*c*-3,*t*-4-**2**, 2.389(2)—2.478(1) Å for *r*-1,*t*-2,*t*-3,*t*-4-**2**, and 2.397(2)—2.485(2) Å for *r*-1,*t*-2,*c*-3,*t*-4-**2**. In these molecules, there is a significant change in the structures of the Si_4 frameworks; the dihedral angles were 18° for *r*-1,*t*-2,*c*-3,*t*-4-**2**, 34° for *r*-1,*t*-2,*t*-3,*t*-4-**2**, and 3° for *r*-1,*t*-2,*c*-3,*t*-4-**2**. The chlorodeamination or bromodeamination of **2** with HCl or HBr afforded 1,2,3-trichloro-1,2,3,4-tetrathexylcyclotetrasilane or 1,2,3-tribromo-1,2,3,4-tetrathexylcyclotetrasilane, respectively. Also, a tetrachlorocyclotetrasilane, 1,2,3,4-tetrachloro-1,2,3,4-tetrathexylcyclotetrasilane was obtained via cyclotetrasilanyllithium.

As a part of our investigation on the chemistry of octasilacubanes,[1] we have attempted to develop a route to the sila-functional cyclotetrasilanes which would serve as building blocks in the preparation of polyhedral polysilanes. Quite recently, Tamao and co-workers have reported the syntheses of a variety of polyfunctionalized alkyldi-, tri-, and tetrasilanes via reductive cross-coupling reactions of the corresponding aminochlorosilanes with lithium.[2] Also in 1995, we reported the synthesis of aminodisilanes bearing bulky alkyl substituents, 1,1,2,2-tetrakis(diethylamino)-1,2-dithexyldisilane (thexyl or Thex denotes 1,1,2-trimethylpropyl hereafter) and 1,2-di-*t*-butyl-1,1,2,2-tetrakis(diethylamino)disilane which could be converted to the corresponding 1,1,2,2-tetrachlorodisilanes by the chlorodeamination with HCl.[3] These results have prompted us to study the syntheses of alkyl-substituted polyaminocyclotetrasilanes. Prior to our work, many reports have appeared in the literature concerning syntheses and properties of cyclotetrasilanes.[4] However, no work has been reported on the synthesis of cyclotetrasilanes bearing amino groups. In this paper, we report the following new information: (1) The dechlorinative coupling of dichloro(diethylamino)thexylsilane (**1**) with lithium led unexpectedly to a heptasubstituted cyclotetrasilane, 1,2,3-tris(diethylamino)-1,2,3,4-tetrathexylcyclotetrasilane (**2**); (2) the X-ray structures of three isomers of *r*-1,*t*-2,*c*-3,*t*-4-**2**, *r*-1,*t*-2,*t*-3,*t*-4-**2**, and *r*-1,*t*-2,*c*-3,*c*-4-**2**;[5] (3) conversion of **2** into 1,2,3-trichloro-1,2,3,4-tetrathexylcyclotetrasilane (**3**) or 1,2,3-tribromo-1,2,3,4-tetrathexylcyclotetrasilane (**4**) by chlorodeamination with HCl or bromodeamination with HBr. Also, we report the preparation of 1,2,3,4-tetrachloro-1,2,3,4-tetrathexylcyclotetrasilane (**5**).

Results and Discussion

Preparation of Triaminocyclotetrasilanes. When dichloro(diethylamino)thexylsilane ($Thex(NEt)_2SiCl_2$, **1**) was allowed to react with 10% excess of lithium metal in tetrahydrofuran (THF) at 0 °C, heptasubstituted cyclotetrasilane **2** was formed in 46% yield as a stereoisomeric mixture. The reaction was also accompanied by several other minor products, of which the structures were not further examined, but 1,2,3,4-tetrakis(diethylamino)-1,2,3,4-tetrathexylcyclotetrasilane was not detected in the reaction mixture. Although the coupling reaction resulted in the concurrent occurrence of deamination, resulting in the formation of monohydride **2**, the formation of the cyclotetrasilane is remarkable, as compound **2** is subject to chloro- or bromodeamination (vide infra).

The generation of monohydride **2** is explained by the cleavage of the Si–N bond with lithium. We thought that at the stage of the construction of Si_4 ring, one of the Et_2N groups was displaced by lithium to decrease the steric hindrance caused by the interaction between the bulky thexyl and Et_2N groups, and that the resulting cyclotetrasilanyllithium ($Thex_4(NEt_2)_3Si_4Li$, **6**) decomposed into **2** during workup. It is noted that, in the reductive coupling reactions of hindered chlorosilanes, removal of a substituents was observed in some cases.[6] The formation of **6** is supported by the following results: (1) the addition of MeOD to the reaction mixture resulted in the isolation of deuteriocyclotetrasilane, $Thex_4(NEt_2)_3Si_4D$ (*d*-content > 97% from NMR); (2) the result of ^{7}Li NMR of the reaction mixture showed signals at 1.63 and 1.73 ppm, and after treatment with EtOH, only the signal due to EtOLi was observed.[7]

Four of six possible diastereomers were isolated by recycle-type preparative HPLC (chromatogram shown in Fig. 1; ODS, THF/MeOH = 8/2); the yields were 6% (Fr-1: *r*-1,*t*-2,*c*-3,*t*-4-**2**) 23% (Fr-2: *r*-1,*t*-2,*t*-3,*t*-4- and *r*-1,*c*-2,*t*-3,*c*-4-**2**), 7% (Fr-3: *r*-1,*t*-2,*c*-3,*c*-4-**2**), and 2% (Fr-4: *r*-1,*c*-2,*t*-3,*t*-4- and *r*-1,*t*-2,*t*-3,*c*-4-**2**) and total yield was 38%. The structures of these compounds were defined by the procedure described in the following section (Fig. 1, Scheme 1).

Structure Identification. The structures of *r*-1,*t*-2,*c*-3,*t*-4-**2**, *r*-1,*t*-2,*t*-3,*t*-4-**2**, and *r*-1,*t*-2,*c*-3,*c*-4-**2** were confirmed by X-ray crystallography. For the fourth isomer, we could not obtain crystals suitable for X-ray analysis, but we can determine its structure based on its spectral data. The number of possible isomers is eight, including two enantiomer pairs. From X-ray analysis, four isomers were already defined and there are four possibilities left. Scheme 2 depicts the structures of these isomers. From ^{29}Si NMR, the fourth isomer showed four peaks, and three kinds of diethylamino groups were observed in ^{13}C NMR. As in the case of *r*-1,*t*-2,*t*-3,*t*-4-**2**, this fact indicates that the molecule has no symmetrical plane. As a consequence, *r*-1,*c*-2,*c*-3,*c*-4- and *r*-1,*c*-2,*c*-3,*t*-4-forms can be excluded. The remained two isomers are enantiomers of each other, and as in the case of *r*-1,*t*-2,*t*-3,*t*-4-**2**, both are thought to be included with the same amount. They are *r*-1,*c*-2,*t*-3,*t*-4- and *r*-1,*t*-2,*t*-3,*c*-4-forms.

The ORTEP drawings of *r*-1,*t*-2,*c*-3,*t*-4-**2**, *r*-1,*t*-2,*t*-3,*t*-4-**2**, and *r*-1,*t*-2,*c*-3,*c*-4-**2** were shown in Fig. 2. Crystallographic data and selected bond lengths and angles are given in Tables 1, 2, 3, and 4. One of the isomers was racemic and an enantiomer pair (*r*-1,*t*-2,*t*-3,*t*-4-, and *r*-1,*c*-2,*t*-3,*c*-4-**2**) is included in the same lattice. The first isomer, *r*-1,*t*-2,*c*-3,*t*-4-**2**, crystallizes in the *P*2$_1$/*c* space group with four molecules per unit cell. The Si(1)–Si(2) and Si(2)–Si(3) bond lengths are both 2.499(2) Å and this is the second longest distance for cyclotetrasilanes reported so far, next to *t*-Bu$_7$Si$_4$H.[6] The other two bonds connected to the Si–H silicon are within

Table 1. Summary of Crystal Data, Data Collection, and Refinement

	r-1,*t*-2,*c*-3,*t*-4-**2**	*r*-1,*t*-2,*t*-3,*t*-4- and *r*-1,*c*-2,*t*-3,*c*-4-**2**	*r*-1,*t*-2,*c*-3,*c*-4-**2**
		Crystal data	
Formula	$C_{36}H_{83}N_3Si_4$	$C_{36}H_{83}N_3Si_4$	$C_{36}H_{83}N_3Si_4$
Mol wt	670.41	670.41	670.41
Cryst descript	Colorless prisms	Colorless prisms	Colorless prisms
Cryst size/mm	0.3 × 0.2 × 0.1	0.5 × 0.5 × 0.1	0.2 × 0.2 × 0.3
Cryst syst	Monoclinic	Triclinic	Monoclinic
Space group	*P*2$_1$/*c*	$P\bar{1}$	*P*2$_1$/*c*
a/Å	11.328(3)	11.865(1)	11.292(3)
b/Å	33.776(3)	17.381(2)	33.674(6)
c/Å	12.163(3)	11.0779(9)	11.997(3)
α/deg		95.958(8)	
β/deg	111.19(2)	104.758(7)	110.45(2)
γ/deg		101.029(8)	
V/Å^3	4338(1)	2140.1(4)	4274(1)
Z	4	2	4
		Data collection	
Diffractometer	Rigaku AFC5R	Rigaku AFC7S	Rigaku AFC7S
Radiation (λ/Å)	Cu $K\alpha$ (1.5418)	Cu $K\alpha$ (1.5418)	Cu $K\alpha$ (1.5418)
Monochromator	Graphite	Graphite	Graphite
Temerature/°C	20.0	20.0	20.0
μ/mm^{-1}	1.447	1.467	1.469
2θrange/deg	5—120.1	5—120.1	5—120.1
Range of *h*,*k*,*l*	0—12,0—36,−14—14	0—13,−20—20,−12—12	0—13,0—38,−13—13
Scan type	ω–2θ	ω–2θ	ω–2θ
Scan width/deg	1.63+0.30tan θ	1.05+0.30tan θ	0.63+0.30tan θ
No. of reflns measd	6944	6737	6869
No. of find reflns	6579	6371	6507
No. of obsd reflns ($\lvert F_o \rvert \geq 3\sigma(F_o)$)	2966	4350	3091
		Refinement	
R	0.060	0.048	0.063
R_w	0.079	0.052	0.072
Weighting scheme	$w=1/\sigma^2(F_o)$	$w=1/\sigma^2(F_o)$	$w=1/\sigma^2(F_o)$
No. of params	407	701	393

Table 2. Selected Bond Lengths (Å) and Angles (deg) for *r*-1,*t*-2,*c*-3,*t*-4-**2**

Bond lengths			
Si(1)–Si(2)	2.499(2)	Si(1)–Si(4)	2.395(2)
Si(1)–N(1)	1.754(5)	Si(1)–C(5)	1.957(6)
Si(2)–Si(3)	2.499(2)	Si(2)–N(2)	1.748(5)
Si(2)–C(15)	1.954(6)	Si(3)–Si(4)	2.391(3)
Si(3)–N(3)	1.753(5)	Si(3)–C(25)	1.956(6)
Si(4)–C(31)	1.942(6)	N(1)–C(1)	1.49(1)
N(1)–C(1′)	1.62(2)	N(1)–C(3)	1.442(8)
N(2)–C(11)	1.461(7)	N(2)–C(13)	1.447(8)
N(3)–C(21)	1.476(8)	N(3)–C(23)	1.432(9)
Bond angles			
Si(2)–Si(1)–Si(4)	85.57(8)	Si(2)–Si(1)–N(1)	116.9(2)
Si(2)–Si(1)–C(5)	116.3(2)	Si(4)–Si(1)–N(1)	110.7(2)
Si(4)–Si(1)–C(5)	115.7(2)	N(1)–Si(1)–C(5)	109.9(3)
Si(1)–Si(2)–Si(3)	90.48(7)	Si(1)–Si(2)–N(2)	111.6(2)
Si(1)–Si(2)–C(15)	110.2(2)	Si(3)–Si(2)–N(2)	119.5(2)
Si(3)–Si(2)–C(15)	111.0(2)	N(2)–Si(2)–C(15)	112.0(2)
Si(2)–Si(3)–Si(4)	85.66(8)	Si(2)–Si(3)–N(3)	114.2(2)
Si(2)–Si(3)–C(25)	116.9(2)	Si(4)–Si(3)–N(3)	107.7(2)
Si(4)–Si(3)–C(25)	117.9(2)	N(3)–Si(3)–C(25)	111.8(3)
Si(1)–Si(4)–Si(3)	95.71(8)	Si(1)–Si(4)–C(31)	127.7(2)
Si(3)–Si(4)–C(31)	125.2(2)	Si(1)–N(1)–C(1)	125.3(6)
Si(1)–N(1)–C(1′)	122.1(9)	Si(1)–N(1)–C(3)	120.2(4)
C(1)–N(1)–C(3)	114.1(7)	C(1′)–N(1)–C(3)	111(1)
Si(2)–N(2)–C(11)	120.3(4)	Si(2)–N(2)–C(13)	127.0(4)
C(11)–N(2)–C(13)	112.2(5)	Si(3)–N(3)–C(21)	122.2(4)
Si(3)–N(3)–C(23)	122.2(5)	C(21)–N(3)–C(23)	114.6(5)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for *r*-1,*t*-2,*t*-3,*t*-4-**2**

Bond lengths			
Si(1)–Si(2)	2.478(1)	Si(1)–Si(4)	2.405(1)
Si(1)–N(1)	1.751(3)	Si(1)–C(5)	1.949(4)
Si(2)–Si(3)	2.486(1)	Si(2)–N(2)	1.746(3)
Si(2)–C(15)	1.969(4)	Si(3)–Si(4)	2.389(2)
Si(3)–N(3)	1.753(3)	Si(3)–C(25)	1.970(4)
Si(4)–C(31)	1.966(4)	N(1)–C(1)	1.461(5)
N(1)–C(3)	1.461(5)	N(2)–C(11)	1.455(5)
N(2)–C(13)	1.447(5)	N(3)–C(21)	1.472(6)
N(3)–C(23)	1.452(6)		
Bond angles			
Si(2)–Si(1)–Si(4)	85.50(4)	Si(2)–Si(1)–N(1)	115.6(1)
Si(2)–Si(1)–C(5)	115.3(1)	Si(4)–Si(1)–N(1)	111.1(1)
Si(4)–Si(1)–C(5)	114.2(1)	N(1)–Si(1)–C(5)	112.4(2)
Si(1)–Si(2)–Si(3)	87.66(5)	Si(1)–Si(2)–N(2)	119.3(1)
Si(1)–Si(2)–C(15)	109.6(1)	Si(3)–Si(2)–N(2)	114.4(1)
Si(3)–Si(2)–C(15)	114.3(1)	N(2)–Si(2)–C(15)	110.1(2)
Si(2)–Si(3)–Si(4)	85.63(5)	Si(2)–Si(3)–N(3)	109.9(1)
Si(2)–Si(3)–C(25)	124.6(2)	Si(4)–Si(3)–N(3)	109.4(1)
Si(4)–Si(3)–C(25)	113.2(2)	N(3)–Si(3)–C(25)	111.1(2)
Si(1)–Si(4)–Si(3)	91.62(5)	Si(1)–Si(4)–C(31)	128.6(1)
Si(3)–Si(4)–C(31)	129.7(2)	Si(1)–N(1)–C(1)	123.8(3)
Si(1)–N(1)–C(3)	122.4(3)	C(1)–N(1)–C(3)	113.7(3)
Si(2)–N(2)–C(11)	125.0(3)	Si(2)–N(2)–C(13)	120.5(3)
C(11)–N(2)–C(13)	114.0(4)	Si(3)–N(3)–C(21)	120.8(3)
Si(3)–N(3)–C(23)	124.1(3)	C(21)–N(3)–C(23)	114.4(4)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for *r*-1,*t*-2,*c*-3,*c*-4-**2**

Bond lengths			
Si(1)–Si(2)	2.485(3)	Si(1)–Si(4)	2.397(2)
Si(1)–N(1)	1.751(5)	Si(1)–C(5)	1.948(7)
Si(2)–Si(3)	2.485(2)	Si(2)–N(2)	1.752(5)
Si(2)–C(15)	1.951(7)	Si(3)–Si(4)	2.401(3)
Si(3)–N(3)	1.748(6)	Si(3)–C(25)	1.952(6)
Si(4)–C(31)	1.951(7)	N(1)–C(1)	1.63(2)
N(1)–C(3)	1.447(8)	N(2)–C(11)	1.447(8)
N(2)–C(13)	1.457(8)	N(3)–C(21)	1.463(9)
N(3)–C(23)	1.451(9)		
Bond angles			
Si(2)–Si(1)–Si(4)	86.62(8)	Si(2)–Si(1)–N(1)	117.0(2)
Si(2)–Si(1)–C(5)	115.7(2)	Si(4)–Si(1)–N(1)	118.0(2)
Si(4)–Si(1)–C(5)	109.0(2)	N(1)–Si(1)–C(5)	109.0(3)
Si(1)–Si(2)–Si(3)	91.24(8)	Si(1)–Si(2)–N(2)	113.6(2)
Si(1)–Si(2)–C(15)	109.1(2)	Si(3)–Si(2)–N(2)	120.6(2)
Si(3)–Si(2)–C(15)	108.4(2)	N(2)–Si(2)–C(15)	111.9(3)
Si(2)–Si(3)–Si(4)	86.54(8)	Si(2)–Si(3)–N(3)	114.4(2)
Si(2)–Si(3)–C(25)	116.2(2)	Si(4)–Si(3)–N(3)	117.1(2)
Si(4)–Si(3)–C(25)	107.7(2)	N(3)–Si(3)–C(25)	112.5(3)
Si(1)–Si(4)–Si(3)	95.52(8)	Si(1)–Si(4)–N(31)	129.6(2)
Si(3)–Si(4)–C(31)	127.4(2)	Si(1)–N(1)–C(1)	125.1(5)
Si(1)–N(1)–C(3)	121.9(5)	C(1)–N(1)–C(3)	107.7(6)
Si(2)–N(2)–C(11)	126.8(4)	Si(2)–N(2)–C(13)	119.3(4)
C(11)–N(2)–C(13)	113.4(5)	Si(3)–N(3)–C(21)	123.1(5)
Si(3)–N(3)–C(23)	122.3(5)	C(21)–N(3)–C(23)	113.2(6)

the normal range. The cyclotetrasilane ring is folded and dihedral angles are 17.8° and 16.6°. These values are relatively small compared with those of [*t*-BuMeSi]$_4$, [*t*-Bu(*c*-C$_6$H$_{11}$)Si]$_4$, or [*t*-BuPhSi]$_4$.[8] The Si(1)–Si(4)–C(31) and Si(3)–Si(4)–C(31) bond angles are quite large (127.7(2)° and 125.2(2)°, respectively), and thexyl group on Si(4) occupies the pseudoequatrial position to release the steric congestion. These structural features resemble those of *t*-Bu$_7$Si$_4$H.[6] The structural parameters of isomer *r*-1,*t*-2,*t*-3,*t*-4-**2** are significantly different from those of *r*-1,*t*-2,*c*-3,*t*-4-**2** and *r*-1,*t*-2,*c*-3,*c*-4-**2**.

The average Si–Si bond length (2.440 Å) is slightly shorter than those of *r*-1,*t*-2,*c*-3,*t*-4-**2** (2.446 Å) and *r*-1,*t*-2,*c*-3,*c*-4-**2** (2.442 Å). The most different feature of *r*-1,*t*-2,*t*-3,*t*-4-**2** from other isomers is the very large dihedral angles. They are 33.5° for Si(1)–Si(2)–Si(3) and Si(1)–Si(3)–Si(4) planes and 32.3° for Si(1)–Si(2)–Si(4) and Si(2)–Si(3)–Si(4) planes. The third isomer, *r*-1,*t*-2,*c*-3,*c*-4-**2**, crystallizes in the $P2_1/c$ space group with four molecules per unit cell and the lattice parameters are very close to those of *r*-1,*t*-2,*c*-3,*t*-4-**2**. In this isomer, the cyclotetrasilane ring is almost planer and dihedral angles are 3.1 and 3.0°.

The reason why different dihedral angles are observed in each isomer can be explained as follows. Generally, in cyclotetrasilane, vicinal *cis*-substituents occupy an eclipsed conformation when the ring is planer. On the other hand, when the dihedral angles increase, the substituents in the 1, 3-positions come closer and that results in the increase of the steric hindrance. In the case of *r*-1,*t*-2,*t*-3,*t*-4-**2**, there are two couples of vicinal *cis*-thexyl groups and no 1,3-*cis*-thexyl groups. This allows *r*-1,*t*-2,*t*-3,*t*-4-**2** to possess large dihedral angles to release 1,2-repulsion. In *r*-1,*t*-2,*c*-3,*c*-4-**2**, no vicinal *cis*-thexyl groups and two couples of 1,3-*cis*-thexyl groups exist. This is the reason of the almost planar structure of *r*-1,*t*-2,*c*-3,*c*-4-**2**. The situation of *r*-1,*t*-2,*c*-3,*t*-4-**2** locates between *r*-1,*t*-2,*t*-3,*t*-4-**2** and *r*-1,*t*-2,*c*-3,*c*-4-**2**, with two couples of vicinal *cis*-thexyl groups and a couple of 1,3-*cis*-thexyl groups. As a result, dihedral angles of *r*-1,*t*-2, *c*-3,*t*-4-**2** are between those of *r*-1,*t*-2,*t*-3,*t*-4-**2** and *r*-1,*t*-2, *c*-3,*c*-4-**2**.

Halogenation Reactions. Aminosilanes can be easily transformed into halosilane with the reaction with HCl, HBr, and acetyl chloride.[2,10] The isomeric mixture of **2** was dissolved in benzene and HCl or HBr gas was bubbled at room temperature. Removal of salt and solvent, followed by recrystallization, gave trichlorotetrathexylcyclotetrasilane ($Thex_4Si_4Cl_3H$, **3**) and tribromotetrathexylcyclotetrasilane ($Thex_4Si_4Br_3H$, **4**), respectively (Scheme 3). Yields were 62% for **3** and 46% for **4**. Both compounds were moderately stable and can be handled in the air; however, they slowly decomposed over a prolonged period. The spectra of **3** and **4** clearly show that the obtained trihalosilanes were single isomers.[11] NMR spectra shows similar features for **3** and **4**; a single Si–H peak was observed in ^1H NMR, three peaks were seen in ^{29}Si NMR. In the case of dephenylchlorination of cyclotetrasilane, only all-*trans* isomer was reported to be obtained from an isomeric mixture of starting compounds.[9c] So far, the reaction mechanism is not known; a similar reaction pathway can be proposed also in our case.

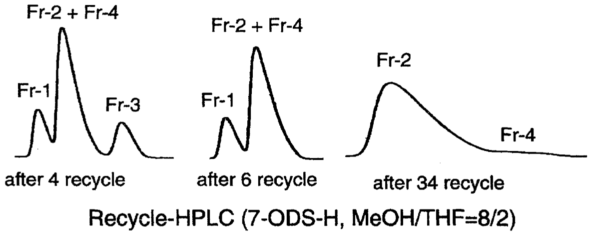
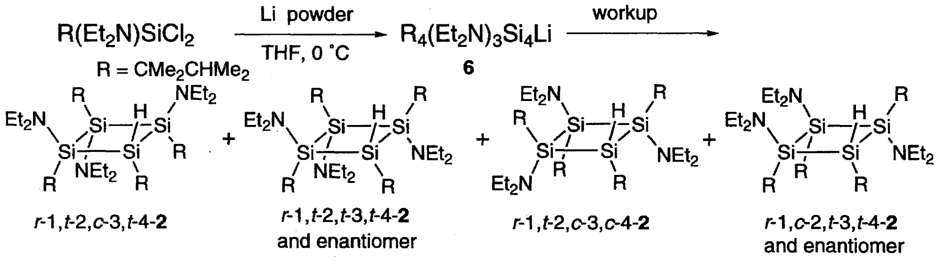


Fig. 1. HPLC chromatogram of **2** (7-ODS-H, MeOH/THF=8/2).

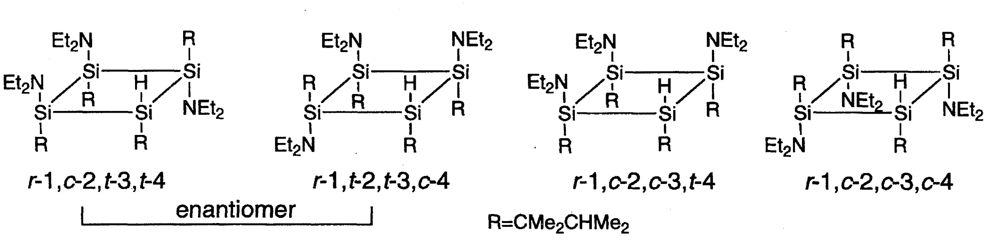
Synthesis of Tetrachlorotetrathexylcyclotetrasilane. The transformation of trihalocyclotetrasilane **3** or **4** to tetrahalocyclotetrasilane could not be done by the known methods. As mentioned before, we observed that lithium compound of cyclotetrasilane generated in the coupling reaction and abstracted hydrogen at workup stage. Then we tried direct halogenation of this lithium compound. The reaction pathway is shown in Scheme 4. Thus Cl_2 gas was bubbled carefully to the mixture at the end of coupling reaction; then the mixture was worked up as usual. The obtained product was $Thex_4(NEt_2)_3Si_4Cl$ (isomeric mixture), and halogenation reaction was performed without isolation. Tetrachlorotetrathexylcyclotetrasilane **5** was obtained in 13% yield from **1**. From spectral data, this compound was single isomer. Compound **5** is the first tetrahalocyclotetrasilane bearing thexyl groups. Coupling reaction of dichloro(phenyl)thexylsilane exclusively gave cyclotrisilane, and halogenation of this compound was impossible because cleavage of the ring was predominant in all reaction conditions.[12]

Spectral Properties. For isomers of **2**, three or four peaks were obtained in ^{29}Si NMR. Silicon atoms attached to hydrogen showed peaks in −41.91 to −48.43 ppm. Other peaks were observed in the region of 15.93 to 34.51 ppm. For **3** and **4**, three peaks are observed in ^{29}Si NMR, indicating that the molecules have symmetry planes. For tetrachlorotetrathexylcyclotetrasilane **5**, reflecting high symmetry, peaks of only one thexyl group were observed in ^1H and ^{13}C NMR spectra, and a single peak was observed in ^{29}Si NMR.

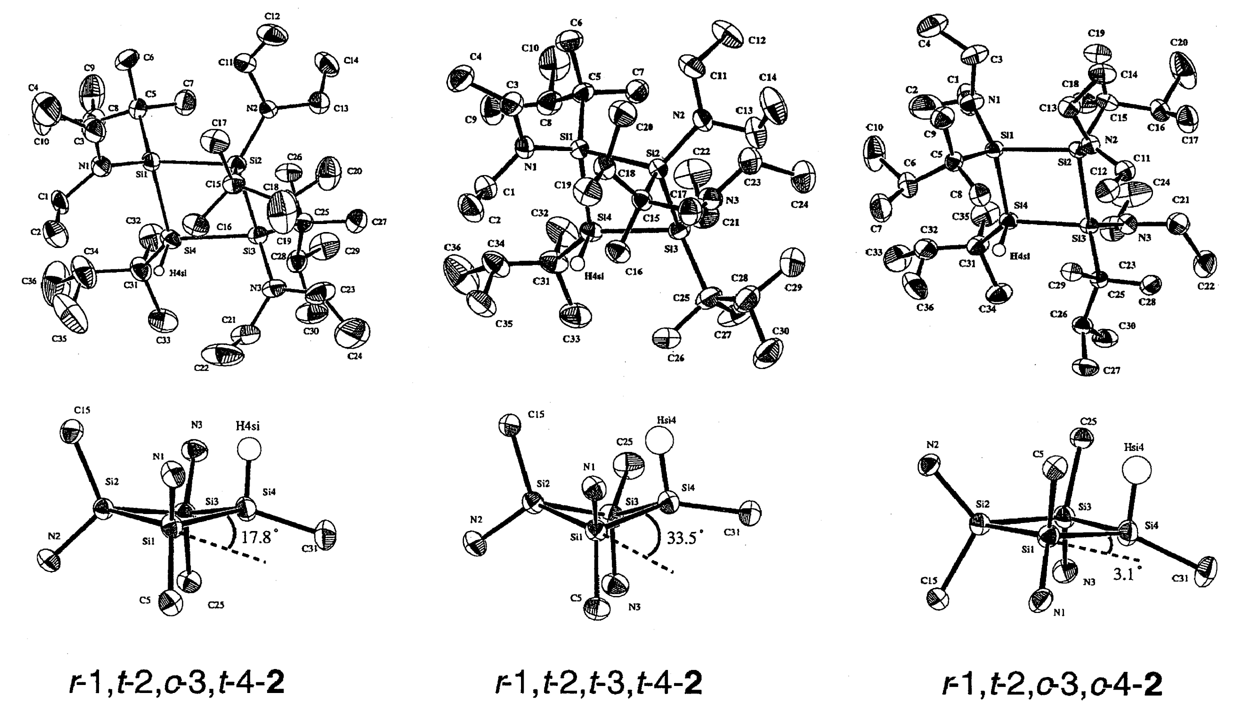
In Fig. 3, UV spectra of **2**, **3**, and **4** are shown. For **2**, the spectra resemble each other; λ_{max} was 310 nm (ε 1600) for *r*-1,*t*-2,*c*-3,*t*-4-**2**, 300 nm (ε 2000) for *r*-1,*t*-2,*t*-3,*t*-4-**2**, and 331 nm (ε 640) and 280 nm (ε 4400) for *r*-1,*t*-2,*c*-3,*c*-4-**2**. As in the case of other chlorinated cyclopolysilanes,[9c,13]



Scheme 1.



Scheme 2.



r-1,*t*-2,*c*-3,*t*-4-**2** *r*-1,*t*-2,*t*-3,*t*-4-**2** *r*-1,*t*-2,*c*-3,*c*-4-**2**

Fig. 2. ORTEP drawings and sideview of the frameworks of *r*-1,*t*-2,*c*-3,*t*-4-**2**, *r*-1,*t*-2,*t*-3,*t*-4-**2**, and *r*-1,*t*-2,*c*-3,*c*-4-**2**. Thermal ellipsoids are drawn at the 30% probability level.

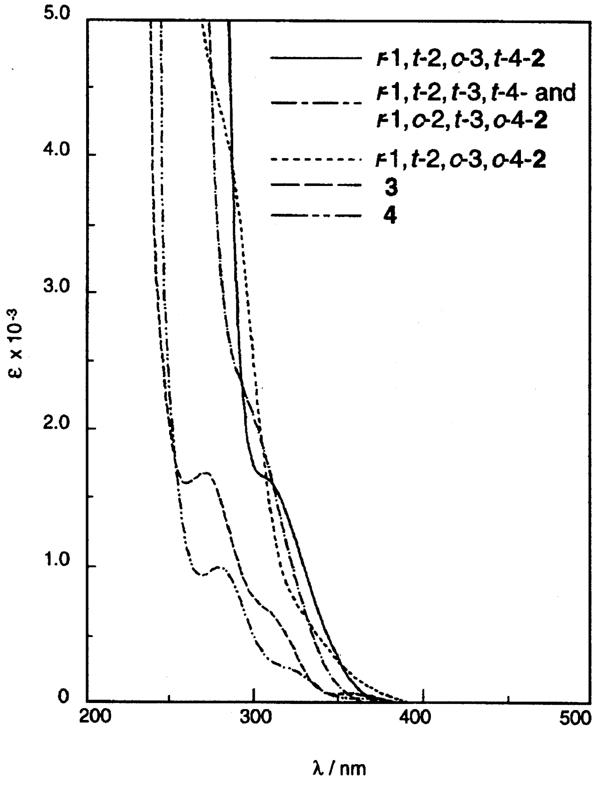
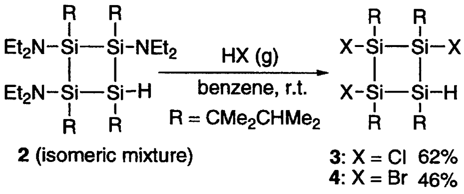


Fig. 3. UV spectra of **2**, **3**, and **4** in hexane.



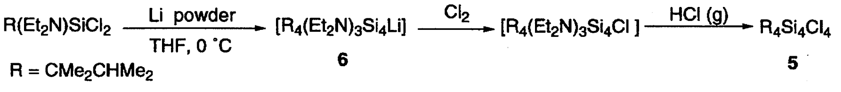
Scheme 3.

halogenation of **2** leads to a bathochromic shift of the lowest energy transition. For trichloride **3**, three absorption maxima were observed (360 nm, ε 80; 315 nm (shoulder), ε 590; 272 nm, ε 1690); as for tribromide **4** (362 nm, ε 40; 322 nm (shoulder), ε 260; 280 nm, ε 1000).

In summary, the reductive coupling reaction of aminodichloro(thexyl)silane gave an isomeric mixture of triaminotetrathexylcyclotetrasilane **2**. The structures of **2** were determined by X-ray crystallography. A halogenation reaction of isomeric mixture of **2** gave single isomers of trihalotetrathexylcyclotetrasilanes **3** and **4** selectively. Also, direct chlorination of lithium compound **6** followed by deaminochlorination with HCl gave tetrachlorotetrathexylcyclotetrasilane **5** as a single isomer.

Experimental

NMR spectra were recorded on a JEOL Model α-500 (^{1}H, 500.0 MHz; ^{7}Li, 194.3 MHz; ^{13}C, 125.7 MHz; ^{29}Si, 99.3 MHz). Mass spectrometry was performed by JEOL JMS-D300. Infrared spectra



Scheme 4.

were measured with a JASCO A-102 spectrometer. Analytical HPLC was done by JASCO 875UV/880PU and UV-970/880PU with Chemco 4.6 mm×250 mm 5-ODS-H column. All reactions were carried out under an atmosphere of argon or nitrogen. Trichloro(thexyl)silane was prepared using the method of Ogino et al.[14)]

Preparation of Dichloro(diethylamino)-1,1,2-trimethylpropylsilane (1): Diethylamine (6.4 ml, 60 mmol) and THF (10 ml) were added dropwise to a mixture of thexyltrichlorosilane (13.2 g, 60 mmol), triethylamine (9.2 ml, 66 mmol) and THF (60 ml) at 0 °C over 1 h. The reaction mixture was then stirred for 20 h at room temperature. Hexane (160 ml) was added to the mixture and the resulting triethylamine hydrochloride was removed by filtration. The filtrate was concentrated and the residue was distilled under reduced pressure to give **1** (yield 12.5 g, 82%).

1: Colorless liquid, bp 58 °C/1 mmHg (1 mmHg = 133.322 Pa). ^{1}H NMR (CDCl$_3$) $\delta = 0.94$ (d, $J = 6.9$ Hz, 6H), 1.04 (s, 6H), 1.07 (t, $J = 7.0$ Hz, 6H), 1.88 (sept, $J = 6.8$ Hz, 1H), 3.02 (q, $J = 7.0$ Hz, 4H); ^{13}C NMR (CDCl$_3$) $\delta = 14.0$, 18.4, 20.3, 31.7, 33.1, 39.6; ^{29}Si NMR (CDCl$_3$) $\delta = 3.2$; IR (NaCl) ν 2970, 1463, 1380, 1202, 1157, 1030, 939 cm^{-1}; MS (30 eV) m/z 255 (M$^+$; 14), 156 (100). HRMS Calcd for $C_{10}H_{23}Cl_2NSi$: M, 255.0977. Found: m/z 255.0976.

4-Deuterio-1,2,3-tris(diethylamino)-1,2,3,4-tetrakis(1,1,2-trimethylpropyl)cyclotetrasilane: To a suspension of lithium (0.13 g, 19 mmol) and THF (30 ml) was added a solution of **1** (2.04 g, 8.0 mmol) in THF (14 ml) at −20 °C. After 16 h, the starting material disappeared. An aliquot of the reaction mixture was taken and ^{7}Li NMR was measured; two peaks at 1.63 and 1.75 ppm were observed. Ethanol was added to this mixture; the generated salt was removed and then ^{7}Li NMR was measured. One peak at 3.40 ppm was observed and this was identified as EtOLi. MeOD (0.63 g) was added to the rest of the mixture, then hexane (100 ml) was added and salt was removed with a short column (neutral alumina). The solvent was removed and separation with column chromatography (silica/hexane) followed by fractional crystallization from acetone gave Thex$_4$(NEt$_2$)$_3$Si$_4$D as a white solid as a mixture of isomers (0.47 g, 35% yield). ^{1}H NMR (C$_6$D$_6$) $\delta = 0.96$—1.20 (m, 42H), 1.21—1.40 (m, 24H), 2.28—2.50 (m, 4H), 3.10—3.40 (m, 12H, CH$_2$), no Si-H peaks were observed; IR (KBr) ν 3000, 2100, 1540 (Si–D), 1470, 1380, 1175, 1020, 920 cm^{-1}; MS (70 eV) m/z 585 (M$^+$ − Thex; 25), 399 (100); relative intensity (%): 589 (4), 588 (8), 587 (25), 586 (55), 585 (100), 584 (15).

Synthesis of 1,2,3-Tris(diethylamino)-1,2,3,4-tetrakis(1,1,2-trimethylpropyl)cyclotetrasilane (2): To a suspension of lithium (0.12 g, 18 mmol) and THF (30 ml) was added a solution of **1** (2.06 g, 8.0 mmol) in THF (25 ml) over 15 min at 0 °C. The reaction mixture was then warmed to room temperature and stirred for 54 h. Methanol (2 ml) was added to the mixture and the solvent was removed. Distilled hexane was added to the mixture and the salt was filtered by a neutral alumina column. The solvent was removed and acetone was added to the residue to give 6.43 g (46% yield) of crude mixture as a white solid. A part of the mixture (100 mg) was subjected to recycle-type HPLC (column: 7-ODS-H, eluent: MeOH/THF = 8/2) and four fractions were obtained. The yields of *r*-1,*t*-2,*c*-3,*t*-4-**2**, *r*-1,*t*-2,*t*-3,*t*-4- and *r*-1,*c*-2,*t*-3,*c*-4-**2**, *r*-1,*t*-2,*c*-3,*c*-4-**2**, and *r*-1,*c*-2,*t*-3,*t*-4- and *r*-1,*t*-2,*t*-3,*c*-4-**2** were 14 mg (6%), 50 mg (23%), 15 mg (7%), and 5 mg (2%), respectively. Separated fractions were recrystallized from acetone to give crystals.

r-1,*t*-2,*c*-3-Tris(diethylamino)-1,2,3,*t*-4-tetrakis(1,1,2-trimethylpropyl)cyclotetrasilane (*r*-1,*t*-2,*c*-3,*t*-4-**2**): Colorless crystals, mp 196—199 °C; ^{1}H NMR (C$_6$D$_6$) $\delta = 0.96$ (d, $J = 6.7$ Hz, 6H), 1.03 (d, $J = 6.7$ Hz, 6H), 1.07 (t, $J = 7.0$ Hz, 6H), 1.08 (d, $J = 6.7$ Hz, 6H), 1.13 (t, $J = 7.0$ Hz, 12H), 1.18 (d, $J = 7.0$ Hz, 6H), 1.27 (s, 6H), 1.29 (s, 6H), 1.32 (s, 6H), 1.35 (s, 6H), 2.28 (sept, $J = 6.8$ Hz, 1H), 2.33 (sept, $J = 6.7$ Hz, 1H), 2.44 (sept, $J = 6.8$ Hz, 2H), 3.20—3.27 (m, 12H, CH$_2$), 4.51 (s, 1H); ^{13}C NMR (C$_6$D$_6$) $\delta = 13.01$, 13.96, 17.32, 18.47, 19.69, 20.15, 20.89, 22.48, 24.67, 26.05, 28.82, 33.37, 35.50, 38.01, 44.91, 45.62; ^{29}Si NMR (C$_6$D$_6$) $\delta = -41.91$, 25.06, 25.48; IR (KBr) ν 3000, 2100, 1470, 1380, 1175, 1020, 920 cm^{-1}; MS (70 eV) m/z 584 (M$^+$ − Thex; 25), 399 (100). HRMS Calcd for $C_{30}H_{70}Si_4N_3$: M, 584.4646. Found: m/z 584.4637.[15)]

r-1,*t*-2,*t*-3-Tris(diethylamino)-1,2,3,*t*-4-tetrakis(1,1,2-trimethylpropyl)cyclotetrasilane and *r*-1,*c*-2,*t*-3-tris(diethylamino)-1,2,3,*c*-4-tetrakis(1,1,2-trimethylpropyl)cyclotetrasilane (*r*-1,*t*-2,*t*-3,*t*-4- and *r*-1,*c*-2,*t*-3,*c*-4-**2**): Colorless crystals, mp 189.7—190.6 °C; ^{1}H NMR (C$_6$D$_6$) $\delta = 1.00$ (d, $J = 6.8$ Hz, 6H), 1.04 (d, $J = 6.8$ Hz, 6H), 1.08 (t, $J = 7.0$ Hz, 12H), 1.12 (t, $J = 7.0$ Hz, 6H), 1.24 (d, $J = 6.8$ Hz, 6H), 1.27 (s, 6H), 1.29 (s, 6H), 1.31 (d, $J = 6.8$ Hz, 12H), 1.33 (s, 6H), 1.34 (s, 6H), 2.24 (sept, $J = 6.8$ Hz, 1H), 2.35—2.38 (m, 3H, CH), 3.19—3.30 (m, 12H, CH$_2$), 4.32 (s, 1H); ^{13}C NMR (C$_6$D$_6$) $\delta = 13.47$, 14.03, 14.04, 17.04, 18.68, 18.74, 19.45, 19.55, 19.80, 20.02, 20.12, 21.51, 23.87, 23.95, 24.80 (overlap), 25.10, 25.66, 26.32, 29.89, 32.15, 32.88, 33.73, 34.40, 35.65, 38.67, 45.28, 45.60, 45.98; ^{29}Si NMR (C$_6$D$_6$) $\delta = -42.36$, 23.79, 25.58, 30.55; IR (KBr) ν 3000, 2140, 1465, 1380, 1170, 1020, 920 cm^{-1}; MS (70 eV) m/z 584 (M$^+$ − Thex; 25), 399 (100). HRMS Calcd for $C_{30}H_{70}Si_4N_3$: M, 584.4646. Found: m/z 584.4639.

r-1,*t*-2,*c*-3-Tris(diethylamino)-1,2,3,*c*-4-tetrakis(1,1,2-trimethylpropyl)cyclotetrasilane (*r*-1,*t*-2,*c*-3,*c*-4-**2**): Colorless crystals, mp 189.7—190.6 °C; ^{1}H NMR (C$_6$D$_6$) $\delta = 1.07$ (d, $J = 6.8$ Hz, 6H), 1.08 (t, $J = 7.0$ Hz, 6H), 1.11 (t, $J = 7.0$ Hz, 12H), 1.12 (d, $J = 6.8$ Hz, 6H), 1.13 (d, $J = 6.8$ Hz, 12H), 1.30 (s, 6H), 1.39 (s, 6H), 2.24—2.34 (m, 4H, CH), 3.15—3.31 (m, 12H, CH$_2$), 4.17 (s, 1H); ^{13}C NMR $\delta = 13.43$, 14.30, 18.42, 19.73 (overlap), 19.83, 23.86, 24.88, 25.30, 25.44, 29.68, 33.78, 33.96, 35.08, 35.40, 36.05, 44.13, 46.39; ^{29}Si NMR $\delta = -48.43$, 22.52, 34.51; IR (KBr) ν 2980, 2080, 1460, 1375, 1165, 1020, 915 cm^{-1}; MS (70 eV) m/z 584 (M$^+$ − Thex; 10), 369 (100). HRMS Calcd for $C_{36}H_{83}Si_4N_3$: M, 669.5664. Found: m/z 669.5636.

r-1,*c*-2,*t*-3-Tris(diethylamino)-1,2,3,*t*-4-tetrakis(1,1,2-trimethylpropyl)cyclotetrasilane and *r*-1,*t*-2,*t*-3-Tris(diethylamino)-1,2,3,*c*-4-tetrakis(1,1,2-trimethylpropyl)cyclotetrasilane (*r*-1,*c*-2,*t*-3,*t*-4- and *r*-1,*t*-2,*t*-3,*c*-4-**2**): White solid, mp 197.5—198.9 °C; ^{1}H NMR (C$_6$D$_6$) $\delta = 1.04$—1.42 (m, 66H), 2.28—2.46 (m, 4H, CH), 3.13—3.28 (m, 8H, CH$_2$), 3.34—3.43 (m, 4H, CH$_2$), 4.39 (s, 1H); ^{13}C NMR (C$_6$D$_6$) $\delta = 13.15$, 13.43, 13.85, 18.34, 18.71, 19.26, 19.74, 20.09, 21.17, 23.69, 24.04, 24.46, 25.56, 25.81, 26.00, 28.94, 29.56, 33.87, 35.30, 35.94, 36.24, 42.75, 44.66, 45.58; ^{29}Si NMR (C$_6$D$_6$) $\delta = -46.43$, 15.93, 25.85, 29.36; MS (70 eV) m/z 584 (M$^+$ − Thex; 7), 197 (100). HRMS Calcd for $C_{30}H_{70}Si_4N_3$: M, 584.4646. Found: m/z 584.4648.

X-Ray Crystallography of *r*-1,*t*-2,*c*-3,*t*-4-2: Colorless crystals of *r*-1,*t*-2,*c*-3-tris(diethylamino)-1,2,3,*t*-4-tetrakis(1,1,2-trimethylpropyl)cyclotetrasilane (*r*-1,*t*-2,*c*-3,*t*-4-**2**) were obtained from acetone by slow evaporation. Cell parameters were refined by the least-squares method using 25 reflections ($55.51 < 2\theta < 56.85°$). The space group $P2_1/c$ was uniquely determined from systematic absences ($h0l: l \neq 2n$; $0k0: k \neq 2n$). The intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standards decreased by −1.5%. A polynomial correction factor was applied to the data to account for this phenomenon. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.86 to 1.10. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 1.74155e − 8). The structure was solved by SHELXS86[16] and expanded using Fourier techniques. A disorder was observed in one of the diethylamino groups (C(1) and C(2)) in 0.606 and 0.394 ratio. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were carried out using the teXsan crystallographic software package.[17] Details of crystal data, data collection and refinement are listed in Table 1.

X-Ray Crystallography of *r*-1,*t*-2,*t*-3,*t*-4- and *r*-1,*c*-2,*t*-3,*c*-4-2: Colorless crystals of *r*-1,*t*-2,*t*-3-tris(diethylamino)-1,2,3,*t*-4-tetrakis(1,1,2-trimethylpropyl)cyclotetrasilane and *r*-1,*c*-2,*t*-3-tris(diethylamino)-1,2,3,*c*-4-tetrakis(1,1,2-trimethylpropyl)cyclotetrasilane (*r*-1,*t*-2,*t*-3,*t*-4- and *r*-1,*c*-2,*t*-3,*c*-4-**2**) were obtained from acetone by slow evaporation. Cell parameters were refined by the least-squares method using 25 reflections ($56.16 < 2\theta < 56.90°$). The space group $P\overline{1}$ was uniquely determined based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure. The intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standards decreased by −9.6%. A polynomial correction factor was applied to the data to account for this phenomenon. An empirical absorption correction was applied, which resulted in transmission factors ranging from 0.73 to 1.43. The data were corrected for Lorentz and polarization effects. The structure was solved by SHELXS86[16] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atom on silicon was refined isotropically. Other hydrogen atoms were included but not refined. All calculations were carried out using the teXsan crystallographic software package.[17] Details of crystal data, data collection and refinement are listed in Table 1.

X-Ray Crystallography of *r*-1,*t*-2,*c*-3,*c*-4-2: Colorless crystals of *r*-1,*t*-2,*c*-3-tris(diethylamino)-1,2,3,*c*-4-tetrakis(1,1,2-trimethylpropyl)cyclotetrasilane (*r*-1,*t*-2,*c*-3,*c*-4-**2**) were obtained from acetone by slow evaporation. Cell parameters were refined by the least-squares method using 25 reflections ($32.83 < 2\theta < 48.29°$).The space group $P2_1/c$ was uniquely determined from systematic absences ($h0l : l \neq 2n$; $0k0 : k \neq 2n$). The intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standards decreased by −2.8%. A polynomial correction factor was applied to the data to account for this phenomenon. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.69 to 1.76. The data were corrected for Lorentz and polarization effects. The structure was solved by SHELXS86[16] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atom on silicon was refined isotropically. Other hydrogen atoms were included but not refined. Details of crystal data, data collection and refinement are listed in Table 1.

Synthesis of 1,2,3-Trichloro-1,2,3,4-tetrakis(1,1,2-trimethylpropyl)cyclotetrasilane (3): Through a solution of an isomeric mixture of **2** (1.00 g, 1.49 mmol) in benzene (10 ml) was passed hydrogen chloride for 1 h at room temperature. Hexane (30 ml) was added to the solution and diethylamine hydrobromide was removed with a glass fiber filter. The filtrate was evaporated and the residue was recrystallized from acetone to give **3** (yield 0.51 g, 62%).

3: Colorless crystals, mp 126.8—127.5 °C; ^{1}H NMR (C_6D_6) $\delta = 0.98$ (d, $J = 6.8$ Hz, 6H), 1.00 (d, $J = 6.8$ Hz, 6H), 1.02 (d, $J = 6.8$ Hz, 6H), 1.03 (d, $J = 6.8$ Hz, 6H), 1.24 (s, 6H), 1.29 (s, 6H), 1.34 (s, 6H), 1.36 (s, 6H), 1.92 (sept, 1H), 2.15—2.20 (m, 3H, CH), 4.54 (s, 1H); ^{13}C NMR (C_6D_6) $\delta = 18.86$, 18.92, 19.08, 19.57, 21.77, 22.05, 22.79, 25.26, 32.12, 33.52, 34.87, 34.97, 35.98, 37.41; ^{29}Si NMR (C_6D_6) $\delta = -41.97$, 26.02, 27.19; IR (KBr) ν 2950, 2090, 1460, 1380, 1130, 750; MS (70 eV) *m*/*z* 558 (M^+; 7), 308 (100). HRMS Calcd for $C_{24}H_{53}Si_4Cl_3$: M, 558.2290. Found: *m*/*z* 558.2283.

Synthesis of 1,2,3-Tribromo-1,2,3,4-tetrakis(1,1,2-trimethylpropyl)cyclotetrasilane (4): To a solution of isomeric mixture of **2** (1.00 g, 1.49 mmol) in benzene (8 ml) was passed hydrogen bromide for 30 min at room temperature. Hexane (30 ml) was added to the solution and diethylamine hydrobromide was removed with a glass fiber filter. The filtrate was evaporated and the residue was recrystallized from acetone to give **4** (yield 0.48 g, 46%).

4: Pale yellow crystals, mp 132.5—136.5 °C; ^{1}H NMR (C_6D_6) $\delta = 0.97$ (d, $J = 6.8$ Hz, 6H), 1.00 (d, $J = 6.8$ Hz, 6H), 1.01 (d, $J = 6.8$ Hz, 6H), 1.05 (d, $J = 6.8$ Hz, 6H), 1.29 (s, 6H), 1.36 (s, 6H), 1.37 (s, 6H), 1.42 (s, 6H), 1.96 (sept, $J = 6.8$ Hz, 1H), 2.23—2.33 (m, 3H, CH), 4.84 (s, 1H); ^{13}C NMR (C_6D_6) $\delta = 18.82$, 18.87, 19.29, 19.90, 22.51, 23.04, 23.72, 25.38, 32.16, 33.28, 35.00, 35.16, 35.88, 37.26; ^{29}Si NMR (C_6D_6) $\delta = -43.69$, 10.48, 16.54; IR (KBr) ν 3000, 2100, 1470, 1380, 1135, 745; MS (70 eV) *m*/*z* 690 (M^+; 3), 442 (100). HRMS Calcd for $C_{24}H_{53}Si_4Br_3$: M, 690.0774. Found: *m*/*z* 690.0752.

Synthesis of 1,2,3,4-Tetrachloro-1,2,3,4-tetrakis(1,1,2-trimethylpropyl)cyclotetrasilane (5): Lithium (244 mg, 35 mmol) and THF (40 ml) was placed in a two-necked flask and Thex(NEt_2)-$SiCl_2$ (**1**, 3.00 g, 11.7 mmol) was added at 0 °C. After 40 min of stirring, excess lithium was removed by filtration through glass wool, and Cl_2 diluted in Ar was bubbled into the solution carefully until the yellow brown color became colorless. Then the HCl gas was introduced for 30 min. The mixture was passed through a glass filter and the solvent was removed. Recrystallization from pentane gave **5** as pale yellow plates (232 mg, 13%).

5: mp 170.3—173.0 °C; ^{1}H NMR ($CDCl_3$) $\delta = 1.00$ (d, $J = 6.7$ Hz, 24H), 1.27 (s, 24H), 2.13 (sept, $J = 6.7$ Hz, 4H); ^{13}C NMR ($CDCl_3$) $\delta = 18.92$, 22.03, 34.79, 35.64; ^{29}Si NMR ($CDCl_3$) $\delta = 19.84$; IR (KBr) ν 2950, 2875, 1460, 1375, 1365, 1030, 750; MS (30 eV) *m*/*z* 592 (M^+; 11), 426 (100), 340 (61), 241 (37), 113 (36), 84 (52). HRMS Calcd for $C_{24}H_{52}Si_4Cl_4$: M, 592.1901. Found: *m*/*z* 592.1931.

We thank Dr. Motoo Shiro at Rigaku Corporation for his measurements of X-ray crystallography of *r*-1,*t*-2,*c*-3,*t*-4-**2**. This work was supported by Grants-in-aid from the Ministry of Education, Science, Sports and Culture. We wish to thank Shin-Etsu Chemical Co., Ltd., and Toshiba Silicon Co., Ltd. for financial support. This paper is dedicated to Dr. Edwin Hengge in memory of his stay in Kiryu with us.

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4) For recent review, see: a) E. Hengge and R. Janoschek, *Chem. Rev.*, **95**, 1495 (1995); b) A. Sekiguchi and H. Sakurai, in "Advance in Organometallic Chemistry," ed by F.G.A. Stone and

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5) Stereoisomers were termed basicly following IUPAC rule E-2.3.4. Four-membered rings are placed with hydrogen atom upside, then silicon atom next to Si–H is chosen as a reference and named clockwise. The authors appreciate one of the refrees' kind suggestion of the nomenclature in detail.

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8) For example, 36.8° for all-*trans*-[*t*-BuMeSi]$_4$,[9a)] 34° for *r*-1,*c*-2,*c*-3,*t*-4-[*t*-Bu(*c*-C_6H_{11})Si]$_4$,[9b)] 32.8° for *r*-1,*c*-2,*t*-3,*t*-4-[*t*-BuPhSi]$_4$.[9c)]

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11) Preliminary result of X-ray crystallography of **3** showed that this was all-*trans* isomer. Due to the severe disorder, the position of thexyl groups could not be determined.

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15) Several attempts to obtain good elemental analyses met with failure due to the formation of silicon carbide. For example, a micro combustion of *r*-1,*t*-2,*c*-3,*t*-4-**2** afforded the values of C, 63.75; H, 12.61; N, 5.89% (Calcd for $C_{36}H_{83}Si_4N_3$: C, 64.58; H, 12.49; N, 6.28%) and left ashes.

16) G. M. Sheldrick, "SHELXS86," "Crystallographic Computing 3," Oxford University Press, Oxford (1985).

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