SYNTHESIS AND STRUCTURES OF BIS[*N*,*N*'-BIS(TRIMETHYLSILYL)-2-METHYL-1,3,2-DIAZASILACYCLOPENTANE] AND BIS(*N*-TRIMETYL-SILYL-2-METHYL-4,5-BENZO-1,3,2-DIAZASILACYCLOPENTENE)[1]

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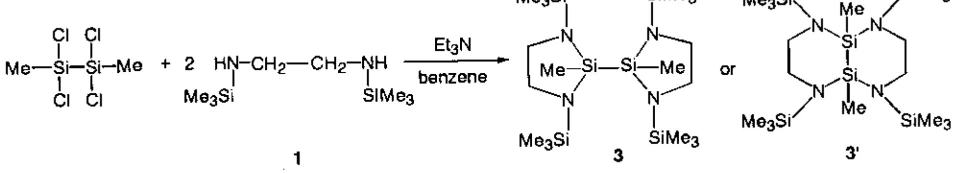
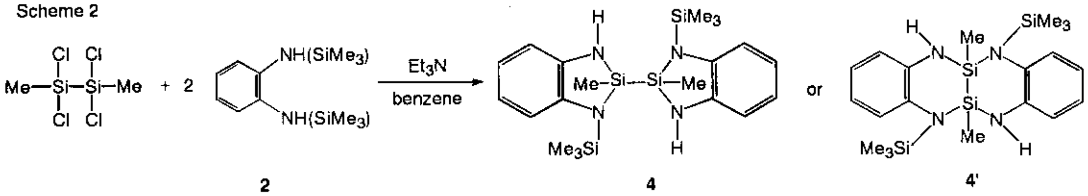
Abstract- The reaction of 1,2-dimethyl-1, 1, 2, 2-tetrachlorodisilane with *N*, *N*'-bis(trimethylsilyl)-ethylenediamine and -*o*-phenylenediamine in the presence of triethylamine yielded bis(2-silaimidazolidine) (**3**) and bis(2-silaimidazoline) (**4**) derivatives in 38 and 61% yields, respectively. The structures of **3** and **4** were determined by the X-ray analyses.

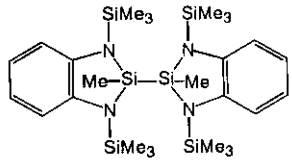
The chemistry of silicon-nitrogen compounds has been extensively investigated, since Si-N polymers (polysilazanes),[2] while several complements to polysiloxanes, are applied in industry.[3] Recently, interest in cyclic silazanes[3a] and polysilazanes[3] has been renewed because of their potential use as precursors to Si_3N_4, Si_3N_4/SiC mixtures, and related ceramic materials.[3c, 4, 5] Though the chemistry of silicon-nitrogen compounds is very active, little work has been done with diamine reagents and polyhalodisilanes. In this paper we report the products and their structural features of the related reactions of *N*, *N*'-bis(trimethylsilyl)-ethylenediamine (**1**) and -*o*-phenylenediamine (**2**) with $(MeSiCl_2)_2$. Bis[*N*, *N*'-bis(trimethylsilyl)-2-methyl-1,3,2-diazasilacyclopentane] (**3**) resulted as a sole product from the base-assisted condensation reaction of **1** with $(MeSiCl_2)_2$. The reaction of **2** with $(MeSiCl_2)_2$ gave bis(*N*-trimethylsilyl-2-methyl-4,5-benzo-1,3,2-diazasilacyclo-4-pentene) (**4**) as white crystals. The two syntheses shown in Scheme 1 and 2 yield one uniform product each, which is not readily distinguished from their possible isomers, compounds **3** (isomeric to **3'**) and **4** (isomeric to **4'**), not to give **5** and **6**. The desilylation process in the formation of **4** is not determined, but one of the explanation is that the highly labile intermediate of type **7** eliminates trimethylsilyl chloride to give **4**.[6] By spectroscopic methods only, it is extremely difficult to determine unambiguously which the isomers are actually produced. In the nmr spectra the spin systems for the equivalent nuclei are similar for both pairs of structural isomers, and there are no data available to determine the ring size from chemical shift values of the ring atoms. The mass spectra should show the mass peaks of the monocycles

Scheme 1



Scheme 2





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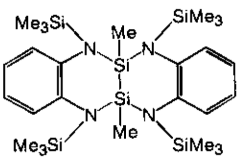

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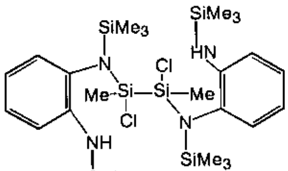

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the equivalent nuclei are similar for both pairs of structural isomers, and there are no data available to determin size from chemical shift values of the ring atoms. The mass spectra should show the mass peaks of the monocycles resulting from cleavage of the Si-Si bond in the isomers (**3**) and (**4**). In fact the mass spectra of **3** and **4** contain indeed peaks at 245 and 221 mass units (equal to half the molecular mass), respectively. But according to literature, such findings do not rigorously exclude the presence of the isomers (**3'**) and (**4'**). Then crystallography was the method of choice to clarify this point for **3** and **4**. The crystal data of **3** and **4** are listed in Table 1. The results of structure determination are shown in Figure 1 for **3** and Figure 2 for **4**. Selected bond lengths and angles are listed in Table 2 for **3** and Tables 3 and 4 for **4**. All nitrogen atoms of **3** are almost trigonal planar environment (angle sums: 360.0 (5)° at N1, 357.8 (5)° at N2, 358.2 (5)° at N3, and 358.3 (5)° at N4), but both 2-silaimidazolidine skeletons have half chair conformation. The small degree of pyramidicity at nitrogen and lack of variation in Si-N distances indicate that the π component (whether it is of a p-σ* or p-d type)[7] in Si-N bonds of silylamines must have an extremely small, even negligible, effect on the structural parameters.[8] The Si-N bond lengths of **3** are 1.733 (7)-1.746 (6) Å, which are similar to those of simple silylamines (e. g. 1.735(1) Å in $N^{t}Bu(SiH_3)_2$[9], 1.725(3) Å in $NH(SiH_3)_2$[10], 1.738(5) Å in $NH(SiMe_3)_2$[12], and 1.755(3) Å in $N(SiMe_3)_3$[12]). The structural parameters of silylamines[13] are very similar, and it seems that the Si-N distances are not significantly affected by the oxidation state of the nitrogen atoms or by effects of sterical crowding. [12]

Table 1 Summary of Crystal Data Collection for **3** and **4**

	3	**4**
formula	$C_{18}H_{50}N_4Si_6$	$C_{20}H_{34}N_4Si_4$
fw	491.14	442.86
cryst syst	monoclinic	triclinic
space group	$P2_1/c$ (#14)	P-1 (#2)
a (Å)	17.633(3)	9.893(2)
b (Å)	10.002(1)	9.891(2)
c (Å)	19.981(3)	29.554(2)
α (deg)		94.24(1)
β (deg)	114.84(1)	95.91(1)
γ (deg)		118.10(2)
V ($Å^3$)	3197.8	2512.5
Z	4	4
d (calcd) (g/cm^3)	1.02	1.17
cryst size (mm^3)	0.70x0.50x0.50	0.30x0.30x0.50
color; habit	white, rod	white, rod
F(000) (e)	1080	952
μ (MoKα) (cm^{-1})	2.7	2.4
radiation (λ=0.71069 Å, graphite monochrometer)	MoKα	MoKα
diffractometer	CAD4	CAD4
scan	$\omega-2\theta$	$\omega-2\theta$
scan range (θ) (deg)	2-50	2-50
hkl range		
no of measd reflns	6141	9369
no of unique reflns	5942	8811
R_{int}		
no of obsd reflns $I \geq 3\sigma(I)$	3103	3321
no of refined params	253	505
R	0.072	0.073
R_w	0.087	0.088
$(\text{shift/error})_{max}$	2.33σ	0.46σ
$\Delta\rho$fin (max/min)(e/$Å^3$)	0.39 (7) / -0.12 (0)	0.44 (9) / -0.11 (0)

Table 2 Selected Bond Lengths (Å) and Angles (degree) of **3**

Bond Length (Å)			
Si1—Si2	2.369 (3)	N1—C1	1.49 (1)
Si1—N1	1.733 (7)	N2—C2	1.51 (1)
Si1—N2	1.738 (6)	N3—Si5	1.716 (8)
Si2—N3	1.746 (6)	N4—Si6	1.705 (7)
Si2—N4	1.739 (8)	N3—C3	1.51 (1)
Si1—C5	1.89 (1)	N4—C4	1.50 (1)
Si2—C6	1.909 (8)	C1—C2	1.44 (1)
N1—Si3	1.717 (5)	C3—C4	1.39 (2)
N2—Si4	1.726 (6)		

Bond Angles (degree)			
Si1—N1—C1	108.2 (4)	Si2—Si1—C5	110.1 (3)
Si1—N2—C2	108.8 (4)	Si2—Si1—N1	111.6 (3)
Si3—N1—C1	117.1 (5)	Si2—Si1—N2	113.8 (2)
Si4—N2—C2	115.6 (5)	N1—Si1—N2	95.6 (3)
N1—C1—C2	110.5 (9)	C5—Si1—N1	112.1 (4)
N2—C2—C1	110.3 (9)	C5—Si1—N2	112.9 (4)
Si2—N3—Si5	133.1 (4)	Si1—Si2—C6	111.9 (3)
Si2—N4—Si6	133.0 (3)	Si1—Si2—N3	111.9 (2)
Si2—N3—C3	108.8 (6)	Si1—SI2—N4	112.7 (3)
Si2—N4—C4	108.6 (6)	N3—Si2—N4	95.4 (3)
Si5—N3—C3	116.3 (5)	C6—Si2—N3	112.1 (4)
Si6—N4—C4	116.7 (6)	C6—Si2—N4	111.8 (4)
N3—C3—C4	111.8 (7)	Si1—N1—Si3	134.7 (5)
N4—C4—C3	114.0 (9)	Si1—N2—Si4	133.4 (5)

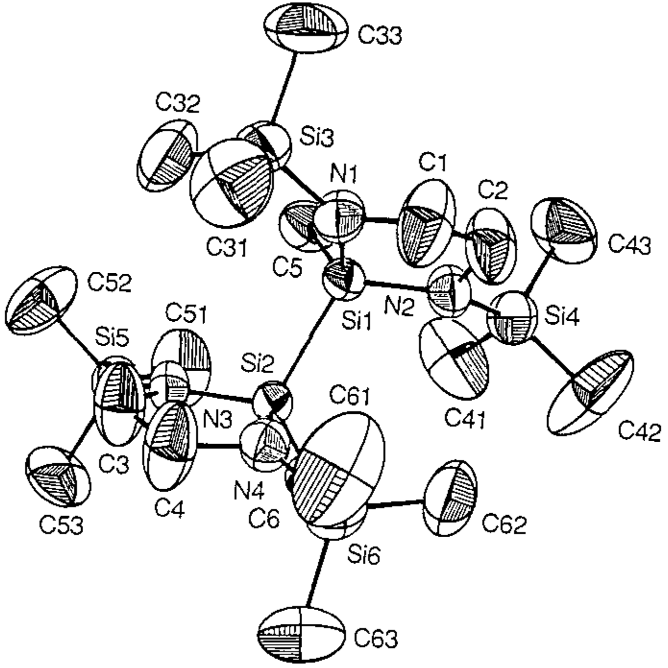

Figure 1 ORTEP Drawing of **3**

Table 3 Selected Bond Lengths (Å) of **4**

molecule (1)		molecule (2)	
Si11—Si12	2.370(5)	Si21—Si22	2.366(4)
Si11—C11	1.89(2)	Si21—C21	1.90(1)
Si12—C12	1.89(1)	Si22—C22	1.90(2)
Si11—N111	1.746(7)	Si21—N211	1.75(1)
Si11—N112	1.76(1)	Si21—N212	1.770(9)
Si12—N121	1.749(9)	Si22—N221	1.741(8)
Si12—N122	1.75(1)	Si22—N222	1.74(1)
Si13—N122	1.74(1)	Si23—N222	1.754(9)
Si14—N112	1.738(8)	Si25—N212	1.72(1)
N111—C101	1.39(2)	N211—C207	1.39(1)
N112—C102	1.43(1)	N212—C208	1.44(1)
N121—C108	1.40(1)	N221—C201	1.39(2)
N122—C107	1.44(1)	N222—C202	1.42(1)
C101—C102	1.41(1)	C201—C202	1.44(2)
C102—C103	1.41(2)	C202—C203	1.41(2)
C103—C104	1.40(1)	C203—C204	1.38(1)
C104—C105	1.41(2)	C204—C205	1.43(2)
C105—C106	1.38(2)	C205—C206	1.38(2)
C106—C101	1.39(1)	C206—C201	1.36(1)
C107—C108	1.43(2)	C207—C208	1.43(2)
C108—C109	1.41(1)	C208—C209	1.40(1)
C109—C110	1.42(2)	C209—C210	1.39(2)
C110—C111	1.39(2)	C210—C211	1.39(2)
C111—C112	1.39(2)	C211—C212	1.44(2)
C112—C107	1.41(2)	C212—C207	1.39(2)

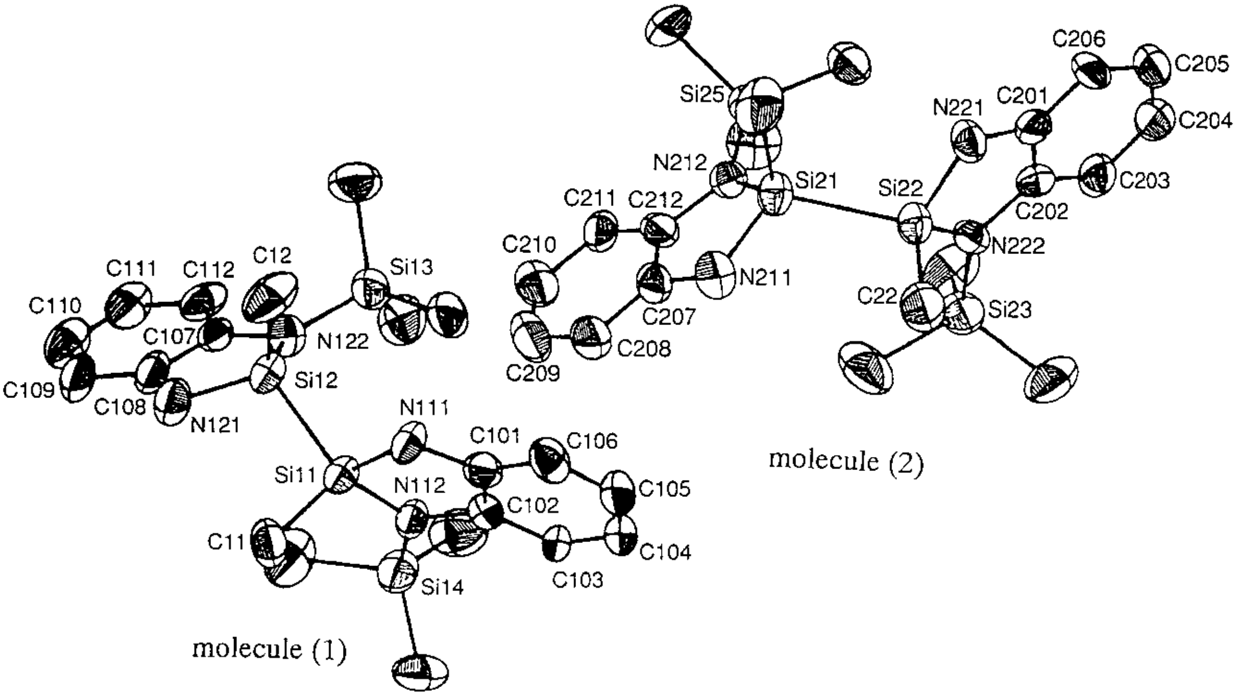

Figure 2 ORTEP Drawing of 4

Table 4 Selected Bond Angles (degree) of **4**

molecule (1)		molecule (2)	
Si12—Si11—N111	111.0(3)	Si22—Si21—N211	112.0(3)
Si12—Si11—N112	120.6(3)	Si22—Si21—N212	120.8(4)
Si12—Si11—C11	106.0(4)	Si22—Si21—C21	104.8(4)
N111—Si11—N112	93.1(4)	N211—Si21—N212	93.6(4)
N111—Si11—C11	111.5(5)	N211—Si21—C21	114.0(6)
N112—Si11—C11	114.0(5)	N212—Si21—C21	111.9(5)
Si11—Si12—N121	111.5(4)	Si21—Si22—N221	111.3(3)
Si11—Si12—N122	121.1(4)	Si21—Si22—N222	120.8(3)
Si11—Si12—C12	105.4(4)	Si21—Si22—C22	105.6(4)
N121—Si12—N122	93.7(4)	N221—Si22—N222	92.6(4)
N121—Si12—C12	112.6(6)	N221—Si22—C22	112.2(5)
N122—Si12—C12	112.5(6)	N222—Si22—C22	114.1(6)
Si11—N111—C101	110.9(6)	Si21—N211—C207	110.1(8)
Si11—N112—Si14	127.4(5)	Si21—N212—Si25	126.6(4)
Si11—N112—C102	108.6(6)	Si21—N212—C208	107.8(8)
Si14—N112—C102	123.8(8)	Si25—N212—C208	124.3(7)
Si12—N121—C108	109.5(8)	Si22—N221—C201	112.1(7)
Si12—N122—Si13	126.5(4)	Si22—N222—Si23	126.8(5)
Si12—N122—C107	108.9(8)	Si22—N222—C202	109.8(7)
Si13—N122—C107	123.4(8)	Si23—N222—C202	123.1(8)
N111—C101—C102	113.3(8)	N221—C201—C202	111.7(8)
N111—C101—C106	126(1)	N221—C201—C206	128.(1)
C102—C101—C106	120.(1)	C202—C201—C206	120.(1)
N112—C102—C101	114.(1)	N222—C202—C201	114.(1)
N112—C102—C103	125.3(8)	N222—C202—C203	127(1)
C101—C102—C103	120.8(8)	C201—C202—C203	119.7(9)
C102—C103—C104	117.(1)	C202—C203—C204	119.(1)
C103—C104—C105	122.(1)	C203—C204—C205	121.(1)
C104—C105—C106	120.0(9)	C204—C205—C206	119(1)
C101—C106—C105	120.(1)	C201—C206—C205	121.(1)
N122—C107—C108	112.4(9)	N211—C207—C208	114.1(9)
N122—C107—C112	127.(1)	N211—C207—C212	125.(1)
C108—C107—C112	120.9(9)	C208—C207—C212	120.6(9)
N121—C108—C107	114.4(9)	N212—C208—C207	113.4(8)
N121—C108—C109	126.(1)	N212—C208—C209	126.(1)
C107—C108—C109	120.(1)	C207—C208—C209	120.1(9)
C108—C109—C110	118.(1)	C208—C209—C210	119.(1)
C109—C110—C111	122.(1)	C209—C210—C211	121.0(9)
C110—C111—C112	121.(1)	C210—C211—C212	121.(1)
C107—C112—C111	119.(1)	C207—C212—C211	118.(1)

The dihedral angle of C5-Si1-Si2-C6 is 79.37°. In addition, the C1-C2 and C3-C4 bonds are too short (1.49(1) and 1.42(1) Å) for a C-C single bond. This feature can be explained by a model in which the disorder is caused by two further twisted conformations.[14] Two independent molecules [molecules (1) and (2) in Tables 3 and 4] of **4** are present in the symmetric unit. Four 2-silaimidazoline skeletons are almost planar [angle sums: 539.9(6)° and 538.9(8) for molecule (1), 540.2(6) and 539.0(8) for molecule (2)]. The dihedral angles of C11-Si11-Si12-C12 and C21-Si21-Si22-C22 are 95.65° and 97.64°, respectively.

EXPERIMENTAL

General Consideration

All manipulations were performed using standard Schlenk technique under an atmosphere of argon. All liquids were transferred using a syringe or cannula. Benzene and hexane were distilled from sodium/benzophenone ketyl under nitrogen. Triethylamine was distilled from KOH prior to use. Ir spectra were recorded on a JASCO FT/IR-5000 using KBr tablet. Uv spectra were carried out on JASCO Ubest-55 spectrophotometer. ^{29}Si Nmr spectra were obtained on a Bruker AM400 spectrometer and were referenced to external tetramethylsilane. ^{1}H Nmr spectra were recorded on a JEOL EX90 spectrometer and were referenced to the residual solvent proton resonances which were calibrated against tetramethylsilane. Mass spectra were recorded on JEOL JMS SX102A mass spectrometer. Elemental analyses were carried out on Perkin Elmer 2400 by the Chemical Analytical Center of the University of Tsukuba. *N*, *N*'-Bis(trimethylsilyl)ethylenediamine,[15] *N*, *N*'-bis(trimethylsilyl)-*o*-phenylenediamine,[16] and $(MeSiCl_2)_2$[17] were prepared as described in the literature.

Reaction of 1,2-Dimethyl-1,1,2,2-tetrachlorodisilane with N,N'-Bis(trimethylsilyl)ethylenediamine

1,2-Dimethyl-1,1,2,2-tetrachlorodisilane (3.4 g, 15 mmol), triethylamine (8.8 ml, 63 mmol) and 48 ml of benzene were placed in a 100 ml three-necked round-bottomed flask equipped with a reflux condenser, a dropping funnel and a rubber septum. *N*, *N*'-Bis(trimethylsilyl)ethylenediamine (6.16 g, 30 mmol) in 20 ml of benzene was added while stirring. After stirring overnight, the precipitate was filtered off and the solvent was removed *in vacuo*. Bis[*N*, *N*'-bis(trimethylsilyl)-2-methyl1-1,3,2-diazasilacyclopentane] (**3**) (2.80 g, 38%) was obtained after recrystallization from hexane as colorless crystals, mp 119-120 °C. ^{1}H Nmr (C_6D_6) δ 0.19 (s, 36H), 0.42 (s, 6H), 2.9 (m, 8H); ^{13}C nmr (C_6D_6) δ 0.8 (q), 6.0 (q), 47.2 (t); ^{29}Si nmr (C_6D_6) δ 1.8 ($SiMe_3$), 3.2 (SiMe); ir (KBr) ν/cm^{-1} 1253 (s) (MeSi), 982 (s), 938 (s) (Si-N); mass, m/z 490 (M^+), 475 (M^+-15), 245; Anal. Calcd for $C_{18}H_{50}N_4Si_6$, C, 44.01; H, 10.26, N, 11.41. Found: C, 43.82; H, 9.91; N, 11.18.

Reaction of 1,2-Dimethyl-1,1,2,2-tetrachlorodisilane with o-$C_6H_4(NHSiMe_3)_2$

1,2-Dimethyl-1,1,2,2-tetrachlorodisilane (1.5 g, 6.6 mmol), triethylamine (4.0 ml, 28 mmol) and 20 ml of benzene were placed in a 100 ml three-necked round-bottomed flask equipped with a reflux condenser, a dropping funnel and a rubber septum. *o*-$C_6H_4(NHSiMe_3)_2$ (3.54 g, 14 ml) in 10 ml of benzene was added while stirring. After stirring 2 h, the precipitate was filtered off, and the solvent was removed *in vacuo*. Bis[*N*, *N*'-bis(trimethylsilyl)-2-methyl-1,3,2-diazasilacyclopentene] (**4**) (1.96 g, 61%) was obtained after while stirring. After stirring 2 h, the precipitate was filtered off, and the solvent was removed *in vacuo*. Bis[*N*, *N'*-bis(trimethylsilyl)-2-methyl-1,3,2-diazasilacyclopentene] (**4**) (1.96 g, 61%) was obtained after recrystallization from hexane as colorless crystals, mp 133 °C (decomp.). ^{1}H Nmr (C_6D_6) δ 0.14 (s, 18H), 0.27 (s, 6H), 2.73 (s, 2H), 6.44-6.62 (m, 8H); ^{13}C nmr (C_6D_6) δ 0.5 (q), 5.5 (q), 111.3 (d), 114.2 (d), 117.7 (d), 119.3 (d), 140.3 (s), 142.4 (s); ^{29}Si nmr (C_6D_6) δ 2.6 ($SiMe_3$), 3.1 (SiMe); ir (KBr) ν/cm^{-1} 3390 (w), 3366 (w) (NH), 1593 (s), 1502 (s), (C_6H_4), 1276 (s) (MeSi), 928 (m) (Si-N); uv (hexane) λmax/ nm 217 (ε 30390), 252 (6590), 305 (6500); mass, m/z 422 (M^+), 427 (M^+-15), 221; Anal. Calcd for $C_{20}H_{34}N_2Si_4$: C, 54.24; H, 7.74; N, 12.65. Found: C, 54.94; H, 7.45; N, 12.25.

X-ray Structure Analysis of 3 and 4

Suitable crystals of **3** and **4** were grown from a concentrated hexane solution. A colorless red shaped crystals of **3** and **4**, whose dimensions were 0.70x0.50x0.50 and 0.30x0.30x0.50, respectively, were mounted on a glass fiber with epoxy resin. X-Ray crystallographic analyses were performed with the use of an Enraf Nonius diffractometer for **3** and **4** equipped with a graphite crystal monochrometor. Orientation matrices and unit cell parameters were determined by the least squares fitting of 25 centered reflections obtained by using the CAD4 automatic search, center, index, and least squares routines. All data processing was performed on a VAX4000 computer by using MolEN structure solving programs. Details on crystal and intensity data collection are given in Table 1. The structures were solved by direct methods using MULTAN 80 program. In the final cycles of refinement, all non-hydrogens were assumed to vibrate. Bond lengths (Å) and angles (degree) for **3** are given in Table 2 and for **4** in Tables 3 and 4.

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