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Cyclic Silylhydrazines and Their Borane Adducts

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A series of five-, six-, and seven-membered cyclic silylhydrazines have been prepared from the reactions of 1,2-bis(bromosilyl)ethane and 1,3-bis(bromosilyl)propane with 1,1-dimethylhydrazine [leading to 1-(dimethylamino)-1-aza-2,5-disilacyclopentane (**3**) and 1-(dimethylamino)-1-aza-2,6-disilacyclohexane (**4**)] and 1,2-dimethylhydrazine [leading to 1,2-dimethyl-1,2-diaza-3,6-disilacyclohexane (**7**) and 1,2-dimethyl-1,2-diaza-2,7-disilacycloheptane (**8**)] in the presence of triethylamine, respectively. The compounds with endocyclic Si−N−Si units (**3**, **4**) are found to be stable for long periods of time, while those with Si−N−N−Si units (**7**, **8**) decompose within a few days at ambient temperature. Compounds **3** and **4** have been reacted with the Lewis acid BH_3 to give the dimethylamine−borane adducts **5** and **6**. All compounds have been fully characterized by spectroscopic data [IR, MS, NMR (^{1}H, ^{13}C, ^{15}N, ^{29}Si)]. Single crystals of **5** [**6**] grown from the melt and studied by low-temperature X-ray diffraction analyses are orthorhombic, space group *Pbca* (No. 61), with $a = 11.385(1)$ [13.300 (1)] Å, $b = 9.938(1)$ [9.837(1)] Å, $c = 17.156(1)$ [16.364(1)] Å, $d_{calc} = 1.096$ (1.081) g cm^{-3}, and $Z = 8$ [8]. In both compounds, the BH_3 unit is bound to the nonsilylated nitrogen atom, indicating the reduction of the basicity of nitrogen by Si substitution. The silylated nitrogen atoms show planar coordination, while the borylated amine unit is tetrahedrally coordinated. From a comparison of the ring geometries of **5** and **6** with known open-chain structures, it appears that the C_2Si_2N ring system of **5** is clearly more strained than that of **6** (C_3Si_2N). This argument also offers an explanation for the preferred formation of the compounds 1,6-diaza-2,5,7,10-tetrasila-[4.4.0]bicyclodecane (**1**) and bi(1-aza-2,6-disilacyclohexyl) (**2**) as compared to their isomers with different ring sizes. The relative stabilities of these isomers in question have been quantified by *ab initio* (MP2(fc)/6-31G*) calculations of geometries and energies of the systems $[(CH_2)_n(SiH_2)]N{-}N[(SiH_2)(CH_2)_n]$ *versus* the annelated molecules $(CH_2)_n(SiH_2)N_2(CH_2)_n(SiH_2)$ with $n = 1{-}3$. These results show the annelated isomers (ring enlarged) to be lower in energy for $n = 1$ and 2, while for $n = 3$ the N−N bridged nonannelated isomer is preferred.

Introduction

There is presently a renaissance in the chemistry of low-mass silicon compounds, which are considered useful feedstock for advanced materials in modern technologies. Si/N compounds have found applications in the generation of silicon nitride either as bulk material for high-performance ceramics and antiabrasive coatings[1] or as thin films in microelectronic devices.[2] New single-source precursors are developed not only to simplify the deposition process but also to improve safety by employing nonpyrophoric compounds.[3]

During the last few decades a great variety of Si/N compounds have been prepared, but species with highly hydrogenated silicon units are a minority. Hydrogen-rich compounds are among the most promising single-source precursors for Si_3N_4 films as they are volatile and contain a minimum amount of heteroatoms which cause problems through doping of the Si_3N_4 layers. In this context, we recently prepared and investigated a number of silylamines,[4] silylhydrazines,[5] and silylhydroxylamines[6] with highly hydrogenated silyl substituents. In continuation of this work, we report here on cyclic silylhydrazines derived from α,ω-disilaalkanediyl units $-H_2Si-(CH_2)_n-SiH_2-$ with $n = 2, 3$.

In an earlier contribution, we described the formation of the silylhydrazines **1** and **2** from the reactions of anhydrous hydrazine with α,ω-bis(bromosilyl)ethane and -propane, respectively, featuring six-membered rings in both cases.[7] The isomers **1a** and **2a** could not be detected in the reaction mixtures, probably because the formation of five- and seven-membered azasila heterocycles like **1a** and **2a** is disfavored owing to ring strain. Other cyclic silylhydrazines mentioned in the literature[8] (some of them with molecular structures determined[9]) contain fully alkyl-, aryl-, or halogen-substituted silicon atoms with significant steric effects on structure and conformation as compared with the Si/H compounds. Conformational studies of other prototypes in Si/N chemistry with structural elements

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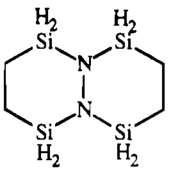
related to those in compounds **1a** and **2a** were expected to shed further light on the ground state properties of this family of compounds.



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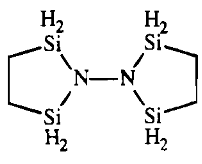
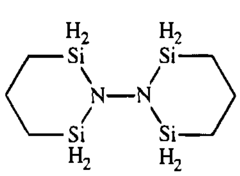


1a



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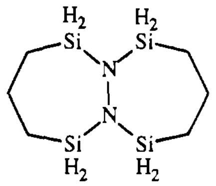

2a

Experimental Section

General Methods and Equipment. All reactions were carried out under an atmosphere of dry nitrogen. The solvents and the triethylamine were dried over CaH_2 and distilled prior to use. All glassware was heated to 160 °C and evacuated and filled with dry nitrogen several times. NMR: JEOL JNM GX-400, spectra taken from solutions in C_6D_6 at 25 °C with internal TMS (^1H, ^{13}C, ^{29}Si) and external CH_3NO_2 (^{15}N) as standards, respectively. IR: Perkin Elmer 1650 FT-IR. GC-MS: Hewlett Packard HP 5890 with mass selective detector 5971A. For the preparation of starting materials 1,2-bis(bromosilyl)ethane and 1,3-bis(bromosilyl)propane, ref 10.

1-(Dimethylamino)-1-aza-2,5-disilacyclopentane (3). Two solutions [23.8 g of 1,2-bis(bromosilyl)ethane (95.9 mmol) in 100 mL of hexane and 7.28 g of *N,N*-dimethylhydrazine (95.9 mmol) in 100 mL of hexane] are added dropwise and at the same rate to 26.6 mL of triethylamine (0.192 mol) dissolved in 500 mL of hexane. The resulting suspension is heated to reflux for 3 h and then cooled to ambient temperature and filtered. The solvent is removed from the filtrate by distillation over a 20 cm Vigreux column, and newly precipitated ammonium salts are filtered off quickly to avoid hydrogen evolution. The filtrate is fractionally distilled (Vigreux column, 15 cm) to yield 5.37 g (38%) of **1**: bp 59 °C (60 mbar); purity >99.9% according to GC analysis. Anal. Calcd (found) for $C_4H_{14}N_2Si_2$ (M_r = 146.34); C, 32.83 (32.61); H, 9.64 (9.51); N, 19.14 (18.92).

^1H-NMR (399.78 MHz, C_6D_6, TMS, 25 °C): $\delta = 1.03$ [m, 4H, H_2C], 2.52 [s, 6H, $(H_3C)_2N$], 4.48 [m, 4H, H_2Si]. ^{13}C-NMR (100.54 MHz, C_6D_6, TMS, 25 °C): $\delta = 1.9$ [t m, $^1J(CH) = 125.2$ Hz, CH_2], 49.2 [q q, $^1J(CH) = 134.4$ Hz, $^3J(CNCH) = 5.2$ Hz, CH_3]. $^{15}N\{^1H\}$-NMR (DEPT, 40.51 MHz, C_6D_6, CH_3NO_2 external, 25 °C): $\delta = -329.9$ [s, NC_2], -312.8 [s, $^1J(NSi) = 14.9$ Hz, NSi_2]. ^{29}Si-NMR (INEPT, 79.43 MHz, C_6D_6, TMS, 25 °C): $\delta = -32.7$ [t m, $^1J(SiH) = 207.4$ Hz]. IR (film): 2125 vs (νSiH). MS (GC-coupled): m/z = 146 [M^+, 100%], 131 [$M^+ - CH_3$], 117, 102 [$C_2H_8NSi_2$], 74.

1-(Dimethylamino)-1-aza-2,6-disilacyclohexane (4). Two solutions [45.7 g of 1,3-bis(bromosilyl)propane (170 mmol) in 50 mL of hexane and 14.0 mL of *N,N*-dimethylhydrazine (170 mmol) in 50 mL of hexane] are added dropwise and at the same rate to 47.1 mL of triethylamine (0.34 mol) dissolved in 500 mL of hexane. The resulting suspension is heated to reflux for 2 h and then slowly cooled to ambient temperature and filtered. The solvent is distilled off, and the residue is fractionally distilled to yield 16.7 g (61%) of **2**: bp 68 °C (22 mbar); mp −4 to −3 °C; purity >99.8% according to GC analysis. Anal. Calcd (found) for $C_5H_{16}N_2Si_2$ (M_r = 160.37): C, 37.45 (36.84); H, 10.06 (10.02); N, 17.47 (17.36).

^1H-NMR (399.78 MHz, C_6D_6, TMS, 25 °C): $\delta = 0.69$ [m, 4H, H_2CSi], 1.68 [m, 2H, H_2CC_2], 2.51 [s, 6H, H_3C], 4.69 [t, $^3J(HSiCH) = 2.6$ Hz, H_2Si]. ^{13}C-NMR (100.54 MHz, C_6D_6, TMS, 25 °C): $\delta = 11.2$ [t m, $^1J(CH) = 120.0$ Hz, CSi], 19.2 [t m, $^1J(CH) = 129.1$ Hz, CC_2], 47.0 [q q, $^1J(CH) = 133.8$ Hz, $^3J(CNCH) = 5.1$ Hz, CH_3]. $^{15}N\{^1H\}$-NMR (DEPT, 40.51 MHz, C_6D_6, CH_3NO_2 external, 25 °C): $\delta = -323.9$ [s, NC_2], -323.0 [s, $^1J(NSi) = 12.7$ Hz, NSi_2]. ^{29}Si-NMR (INEPT, 79.43 MHz, C_6D_6, TMS, 25 °C): $\delta = -37.1$ [t m, $^1J(SiH) = 205.1$ Hz]. IR (film): 2121 s (νSiH). MS (GC-coupled): m/z = 160 [100%, M^+], 145 [$M^+ - CH_3$], 116 [$M^+ - N(CH_3)_2$], 103, 88, 74, 70.

(1-Aza-2,5-disila-1-cyclopentyl)dimethylamine−Borane (5). A 2.09 g sample of **3** (14.3 mmol) is dissolved in 7 mL of THF. The solution is cooled to −78 °C, and 14.0 mL of a 1 M solution of BH_3·THF (14.0 mmol) in THF is added. The mixture is allowed to warm to ambient temperature and is stirred for 10 min, and the solvent is removed in vacuo. The residue consists of ca. 95% **5** and is crystallized by slowly cooling to −20 °C to yield 2.15 g of pure **5** (91%); mp −6 to −4 °C. Anal. Calcd (found) for $C_4H_{17}BN_2Si_2$ (M_r = 160.17): C, 29.99 (29.56); H, 10.70 (10.89); N, 17.49 (17.40); Si, 35.07 (34.61).

^1H-NMR (399.78 MHz, C_6D_6, 20 °C): $\delta = 0.79$ [m, 4H, H_2C], 2.24 [q, broad, 3H, H_3B], 2.74 [s, 6H, H_3C], 4.58 [m, 4H, H_2Si]. ^{11}B-NMR (128.27 MHz, C_6D_6, $B(OMe)_3$ = 18.2 ppm external, 20 °C): $\delta = -6.2$ [q, $^1J(BH) = 97$ Hz]. ^{13}C-NMR (100.54 MHz, C_6D_6, 20 °C): $\delta = 3.3$ [t m, $^1J(CH) = 125.7$ Hz, CH_2], 56.5 [q m, $^1J(CH) = 140.5$ Hz, CH_3]. $^{15}N\{^1H\}$-NMR (DEPT, 40.51 MHz, C_6D_6, CH_3NO_2 external, 20 °C): $\delta = -293.9$ [s, $^1J(NSi) = 12.4$ Hz, NSi_2], no second signal detectable. ^{29}Si-NMR (DEPT, 79.43 MHz, C_6D_6, TMS external, 20 °C): $\delta = -31.3$ [t m, $^1J(SiH) = 218.2$ Hz]. IR (film): 2390 s (ν_{as}BH), 2319 and 2281 m (ν_{sym}BH), 2138 s (νSiH).

(1-Aza-2,5-disila-1-cyclopentyl)dimethylamine−Trichloroalane (5a). A 0.91 g sample of **3** (6.2 mmol) is dissolved in 5 mL of toluene, and 0.83 g of anhydrous $AlCl_3$ (6.2 mmol) is added. The mixture is stirred at 25 °C for 2 h. After filtration and removal of the volatiles under reduced pressure, the liquid residue is crystallized by cooling it to −20 °C. Noncrystalline products are removed, and the residue is recrystallized. The crystals obtained in this way decompose within a few hours.

^1H-NMR (399.78 MHz, C_6D_6, TMS, 10 °C): $\delta = 0.85$ [m, 4H, H_2C], 2.85 [s, 6H, H_3C], 4.63 [m, 4H, H_2Si].

(1-Aza-2,6-disila-1-cyclohexyl)dimethylamine−Borane (6). The procedure is the same as that described for compound **5**: yield 1.83 g (94%); mp 0−1 °C. Anal. Calcd (found) for $C_5H_{19}BN_2Si_2$ (M_r = 174.20): C, 34.47 (34.08); H, 10.99 (11.20); N, 16.08 (16.32); Si, 32.25 (31.85).

^1H-NMR (399.78 MHz, C_6D_6, TMS, 20 °C): $\delta = 0.69$ [m, 4H, H_2CSi], 1.49 [m, 2H, H_2CC_2], 2.38 [q, 3H, H_3B], 2.74 [s, 6H, H_3C], 4.68 [t, $^3J(HSiCH) = 5.2$ Hz, 4H, H_2Si]. ^{11}B-NMR (128.27 MHz, C_6D_6, $B(OMe)_3$ = 18.2 ppm external, 20 °C): $\delta = -7.2$ [q, $^1J(BH) = 99$ Hz]. ^{13}C-NMR (100.54 MHz, C_6D_6, TMS, 20 °C): $\delta = 13.5$ [t m, $^1J(CH) = 120.4$ Hz, CSi], 17.6 [t m, $^1J(CH) = 129.8$ Hz, CC_2], 54.7 [q q q, $^1J(CH) = 140.5$ Hz, $^3J(CNCH) = 7.8$ Hz, $^3J(CNBH) = 3.9$ Hz, CH_3]. $^{15}N\{^1H\}$-NMR (DEPT, 40.51 MHz, C_6D_6, CH_3NO_2 external, 25 °C): $\delta = -301.0$ [s, $^1J(NSi) = 8.5$ Hz, NSi_2], no second signal detectable. ^{29}Si-NMR (DEPT, 79.43 MHz, C_6D_6, TMS, 25 °C): $\delta = -34.0$ [t m, $^1J(SiH) = 215.5$ Hz]. IR (film): 2396 s (νBH), 2138 s (νSiH).

1,2-Dimethyl-1,2-diaza-3,6-disilacyclohexane (7). The procedure is the same as that described for compound **4**. Compounds employed: 45.5 mL of triethylamine (0.33 mol) dissolved in 1 L of hexane, 41.0 g of 1,2-bis(bromosilyl)ethane (165 mmol dissolved in 100 mL of hexane), 14.0 mL of *N,N'*-dimethylhydrazine (165 mmol dissolved in 100 mL of hexane). Many fractions containing traces of the solvent are obtained. A solvent-free product (3.20 g, 13%) is collected finally at bp 33 °C (10 mbar); purity >98% according to GC analysis

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performed immediately after distillation. Anal. Calcd (found) for $C_4H_{14}N_2Si_2$ (M_r = 146.34): C, 32.83 (32.56); H, 9.64 (9.73); N, 19.14 (19.26).

^{1}H-NMR (399.78 MHz, C_6D_6, TMS, 25 °C): $\delta = 0.76$ [m, 4H, H_2C], 2.60 [s, 6H, H_3C], 4.58 [m, 4H, H_2Si]. ^{13}C-NMR (100.54 MHz, C_6D_6, TMS, 25 °C): $\delta = 4.9$ [t m, ^1J(CH) = 123.6 Hz, CH_2], 36.0 [q, ^1J(CH) = 134.2 Hz, CH_3]. ^{15}N{^{1}H}-NMR (DEPT, 40.51 MHz, C_6D_6, CH_3NO_2 external, 25 °C): $\delta = -331.6$ [s, ^1J(NSi) = 20.8 Hz]. ^{29}Si−NMR (DEPT, 79.43 MHz, C_6D_6, TMS, 25 °C): $\delta = -27.6$ [t m, ^1J(SiH) = 200.8 Hz]. IR (film): 2136 s (νSiH). MS (GC-coupled): *m/z* = 146 [100%, M^+], 131 [$M^+ - CH_3$], 116 [$M^+ - 2CH_3$], 102, 88, 76, 58.

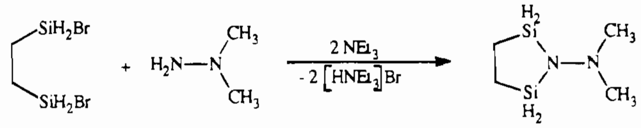
1,2-Dimethyl-3,7-disila-1,2-diazacycloheptane (8). The procedure is the same as that described for compound **4**. Compounds employed: 41.2 mL of triethylamine (0.297 mol) dissolved in 500 mL of hexane, 25.4 mL of 1,3-bis(bromosilyl)propane (0.148 mol) dissolved in 100 mL of hexane, 10.8 mL of *N,N*-dimethylhydrazine (0.148 mol) dissolved in 100 mL of hexane. Fractional distillation yields 4.01 g (17%) of **8** at bp 57 °C (4 mbar); purity >98% according to GC analysis performed immediately after distillation. Anal. Calcd (found) for $C_5H_{16}N_2Si_2$ (M_r = 160.37): C, 37.45 (37.09); H, 10.06 (10.26); N, 17.47 (17.61).

^{1}H-NMR (399.78 MHz, C_6D_6, TMS, 25 °C): $\delta = 0.74$ [m, 4H, H_2-CSi], 1.86 [m, 2H, H_2CC_2], 2.62 [s, 6H, H_3C], 4.49 [t, ^3J(HCSiH) = 2.9 Hz, 4H, H_2Si]. ^{13}C{^{1}H}-NMR (100.54 MHz, C_6D_6, TMS, 25 °C): $\delta = 15.9$ [s, CH_2Si_2], 19.2 [s, CH_2C_2], 34.8 [s, CH_3]. ^{15}N−NMR (INEPT, 40.51 MHz, C_6D_6, CH_3NO_2 external, 25 °C): $\delta = -330.0$ [s, ^1J(NSi) = 21.0 Hz, ^2J(NNSi) = 1.9 Hz]. ^{29}Si−NMR (DEPT, 79.43 MHz, C_6D_6, TMS, 25 °C): $\delta = -26.3$ [t m, ^1J(SiH) = 196.7 Hz]. MS (GC-coupled): *m/z* = 160 [M^+, 100%], 145 [$M^+ - CH_3$], 130, 116, 102, 88.

Crystal Structure Determinations. Suitable crystals of compounds **5** and **6** were sealed under argon at dry ice temperature into glass capillaries and examined directly on the diffractometer. Data were corrected for Lorentz and polarization but not for absorption effects. Structures were solved by direct methods and refined by full-matrix least-squares calculations. The thermal motion was treated anisotropically for all non-hydrogen atoms. All hydrogen atoms were treated isotropically. More detailed information on solution and refinement procedures is given in the Supporting Information, as are the atomic coordinates.

Results and Discussion

The reaction of 1,2-bis(bromosilyl)ethane and 1,3-bis(bromosilyl)propane with 1,1-dimethylhydrazine in the presence of triethylamine affords 1-(dimethylamino)-1-aza-2,5-disilacyclopentane (**3**) and 1-(dimethylamino)-1-aza-2,6-disilacyclohexane (**4**), respectively. In order to obtain acceptable yields, the reactions have to be carried out by applying the Ziegler principle of dilution[11] in order to suppress polymerization.



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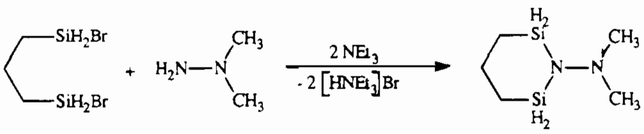
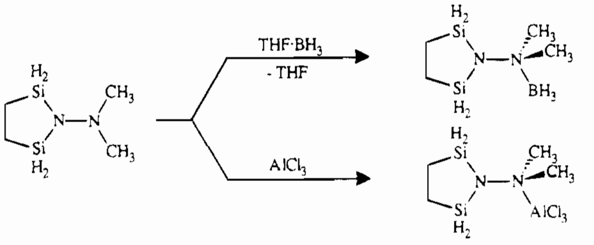


4

Compounds **3** and **4** are liquids at ambient temperature and are highly volatile [bp: **3**, 59 °C (60 mbar); **4**, 68 °C (22 mbar)]. They can be stored at ambient temperature for long periods of time without decomposition but are sensitive to moisture. Oxidation by atmospheric oxygen was not observed, but contacting the hypergolic compounds **3** and **4** with strong oxidants like HNO_3 leads to explosions. The odor of both compounds is intense and aromatic, different from that of similar Si/C analogous compounds.

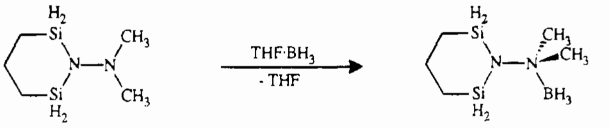
Reacting **3** and **4** with Lewis acids like BH_3 or $AlCl_3$ leads to the formation of 1:1 adducts. The constitution of compounds **5** and **6** was confirmed by spectroscopic methods and by single-crystal X-ray diffraction structure analyses (discussed below). The results clearly show the difference in the basicity of silylated and alkylated nitrogen atoms. Compound **5a** is unstable. Rapidly grown crystals decompose with melting within a few hours.



5

5a

The reactions of symmetric dimethylhydrazine with the difunctional bromosilanes (above) lead to 1,2-dimethyl-1,2-diaza-3,6-disilacyclohexane (**7**) and 1,2-dimethyl-1,2-diaza-3,7-disilacycloheptane (**8**), respectively. The products are obtained only in poor yields (13% and 17%, respectively) even with application of Ziegler's principle. The formation of soluble but nonvolatile polymers is preferred in the reactions. Upon heating during the distillation process, these polymers do not redistribute to form the monomeric **7** and **8**, respectively.



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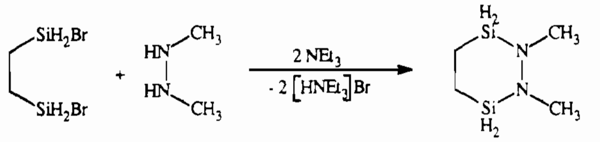

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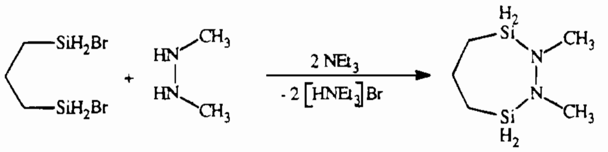

8

Compounds **7** and **8** are unstable in pure form, as well as in solution, but the stability is sufficient to confirm their identity by GC/MS, IR, and NMR spectra. Both compounds decompose at ambient temperature within a few days to give a complex mixture of products. GC/MS analyses indicated the formation of small amounts of **3** (**4**) and **1** (**2**) besides other compounds, respectively, but the main products of the decomposition are nonvolatile polymers. These observations suggest methyl- and silyl-shift reactions as postulated by Ebsworth for the decomposition of dimethylsilylamine [$2Me_2NSiH_3 \rightarrow MeN(SiH_3)_2 + Me_3N$].[12] The low stability of **7** cannot be attributed simply to the endocyclic Si−N−N−Si unit, as **1** also bearing this structural element is a perfectly stable compound.

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[11] Rossa, L.; Vögtle, F. *Top. Curr. Chem.* **1993**, *113*, 1−86.

[12] Ebsworth, E. A. V. *Volatile Silicon Compounds*; Pergamon Press: Oxford, U.K., 1963, p 109.

Table 1. Selected NMR Data for Compounds **1**–**8**

no.	ring size	$\delta(^1H)$ H_2Si	$\delta(^1H)$ H_2CSi	$\delta(^{13}C)$ CSi	$\delta(^{15}N)$ NSi	$^1J(^{29}Si^{15}N)$, Hz	$\delta(^{29}Si)$	$^1J(^{29}Si^1H)$, Hz
1	6	4.58	0.75	5.5	−337.7	13.7	−27.6	205.1
3	5	4.48	1.03	1.9	−312.8	14.9	−32.7	207.4
5	5	4.58	0.79	3.3	−293.9	12.4	−31.3	218.2
7	6	4.58	0.76	4.9	−331.6	20.8	−26.7	200.8
2	6	4.85	0.64	11.7	−342.3	11.8	−27.5	207.1
4	6	4.69	0.69	11.2	−323.0	12.7	−37.1	205.1
6	6	4.68	0.69	13.5	−301.0	8.5	−34.0	215.5
8	7	4.49	0.74	15.9	−330.0	21.0	−26.3	196.7

Table 2. Selected Bond Distances and Angles of **5** and **6**

bond distances, pm			bond angles, deg		
	5	**6**		**5**	**6**
B−N1	162.0(3)	161.7(3)	B−N1−N2	110.0(2)	111.9(2)
C1−N1	148.5(3)	149.0(3)	B−N1−C1	109.2(2)	107.4(2)
C2−N2	149.3(3)	148.8(3)	B−N1−C2	110.9(2)	109.9(2)
Si1−N2	174.2(2)	174.8(2)	C1−N1−N2	109.7(2)	109.0(2)
Si2−N2	175.0(2)	175.6(2)	N1−N2−Si1	124.6(1)	117.2(1)
N1−N2	146.8(2)	148.6(2)	N1−N2−Si2	120.0(1)	118.0(1)
Si1−C3	186.4(2)	186.0(2)	Si1−N2−Si2	115.2(1)	123.7(1)
C3−C5		151.7(3)	N2−Si1−C3	97.6(1)	106.8(1)
C3−C4	154.7(4)		Si1−C3−C5		115.0(2)
			C3−C5−C4		109.6(2)
			Si1−C3−C4	108.5(2)	
			sum of angles at N2	359.8	358.9

Solution NMR Studies. In an attempt to obtain more detailed information about the configuration and conformation of the cyclic silylhydrazines, NMR data for four nuclei (^1H, ^{13}C, ^{15}N, ^{29}Si) were collected. Selected data are listed in Table 1, which is divided in two parts according to the different carbosilanediyl units contained in the compounds.

The only parameter markedly depending on the ring size of the molecules is $\delta(^{13}C)$, which increases with growing ring size. The silyl protons within one group of carbosilanediyl derivatives are not affected by the different bonding situations (Table 1).

The ^{15}N chemical shifts of the pairs **1**/**2** and **7**/**8** are very close together owing to the similar chemical environment of the nitrogen atoms. Compounds **2** and **4** which both contain the 1-aza-2,6-disilacyclohexane skeleton differ as much as 19.3 ppm in $\delta(^{15}N)$ of the tricoordinate atom because of the different hybridization state of the neighboring nitrogen atom (**2**, sp^2; **4**, sp^3). A similar effect is observed for $\delta(^{15}N)$ of the pairs **3**/**5** and **4**/**6**: BH_3 adduct formation is accompanied by a nitrogen deshielding of as much as 20 ppm.

The most informative NMR parameter regarding the Si/N skeleton of the compounds is the $^1J(^{29}Si^{15}N)$ coupling constant. The major contribution to $^1J(^{29}Si^{15}N)$ is the number of silicon atoms attached directly to the nitrogen atom. Furthermore, the $^1J(^{29}Si^{15}N)$ coupling constant depends on the s character of the orbitals employed for the Si−N bond. It is therefore sensitive to changes of the Si−N distance[13] provided the nitrogen atom has the same state of hybridization. The singly silylated compounds **7** and **8** show $^1J(^{29}Si^{15}N)$ values of typically more than 20 Hz. The $^1J(^{29}Si^{15}N)$ values of the pairs **1**/**3** and **2**/**4** are in the range established for Si_2N units. Adduct formation of **3** and **4** with BH_3 decreases the $^1J(^{29}Si^{15}N)$ values of **5** and **6**. These values are comparable to those realized for triply silylated N atoms.

The chemical shifts $\delta(^{29}Si)$ are clearly dependent on the nature of the β-nitrogen atom. For compounds containing two planar sp^2-N atoms (**1**, **2**, **7**, **8**), $\delta(^{29}Si)$ is about 27 ppm; for the compounds **3**–**6** with an sp^3-N atom, the resonance is shifted to higher field. The ^{29}Si resonances of the borylated compounds **5** and **6** appear downfield as compared to those of the free bases **3** and **4**, respectively, owing to the β effect of the positively charged nitrogen atom. The same effect is responsible for the change of the $^1J(^{29}Si^1H)$ coupling constants which are as much as 10 Hz larger for **5** and **6** as compared to **3** and **4**, respectively.

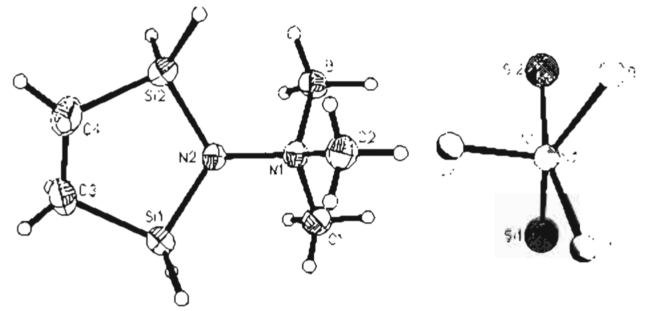

Figure 1. Molecular structure of **5** and view along the N−N bond (ring C atoms omitted).

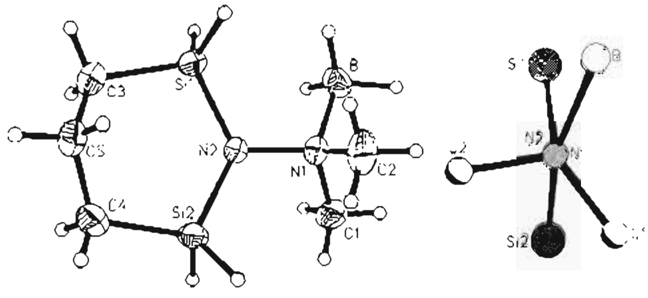

Figure 2. Molecular structure of **6** and view along the N−N bond (ring C atoms omitted).

Crystal Structures of 5 and 6. Solvent-free crystals of **5** and **6** could be grown by slowly cooling melts of the compounds containing some seed crystals to −20 °C. The crystals both belong to the orthorhombic system, space group *Pbca* (No. 61). Selected structural parameters are listed in Table 2; the molecular geometries are presented in Figures 1 and 2. Both compounds are monomeric in the crystal lattices. The result for **5** represents the first structure determination of a 1-aza-2,5-disilacyclopentane ring system with unsubstituted Si atoms.

The configuration of the silylated nitrogen atoms in **5** and **6** is planar, as indicated by the sums of angles (Table 2). By contrast, the amine−borane units exhibit a nearly ideal tetrahedral coordination geometry. The Si−N bond distances of **6** are lenghtened by about 2.2 pm as compared to those of **2**,[7] as also indicated by the smaller $^1J(^{15}N^{29}Si)$ coupling constant of **6**. The N−N bond lengths of **5** and **6** are in the same range as those of **2** and the hydrazine−borane adduct $N_2H_4{\cdot}BH_3$ (147.5 pm).[14] The N−N distance of **6** is only a little longer than that of **5**. This is attributed to the wider Si−N2−Si angle of **6** as compared to **5** causing more steric repulsion between SiH_2 units and the dimethylamine−borane group. The Si−N2−Si angle of **6** is comparable to the values of the noncyclic systems $(H_3Si)_2NN(SiH_3)_2$ [129.5(7)°][15] and $(PhH_2Si)_2NN(SiH_2Ph)_2$ [130.3°],[5] indicating very little ring strain. The corresponding angle in **5** is compressed to 115.2 (1)°, indicating that this ring is more strained than that of **6**. Similar Si−N−Si values have been reported for some 1-aza-2,5-disilacyclopentane ring sys-

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[13] (a) Mitzel, N. W.; Schier, A.; Paul, M.; Schmidbaur, H. *Chem. Ber.* **1993**, *126*, 2027−2032. (b) Kupce, E.; Lukevics, E. *J. Organomet. Chem.* **1988**, *358*, 67−75. (c) Kupce, E.; Lukevics, E. *J. Magn. Reson.* **1988**, *76*, 63−73. (d) Kupce, E.; Lukevics, E. *Organometallics* **1988**, *7*, 1649−1652.

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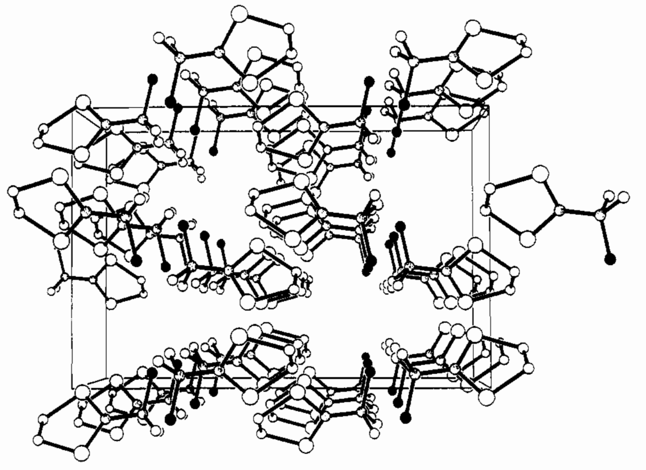


Figure 3. Packing of the molecules of **5** in the crystal lattice. The box represents the unit cell: nitrogen atoms, dotted circles; boron atoms, filled circles.

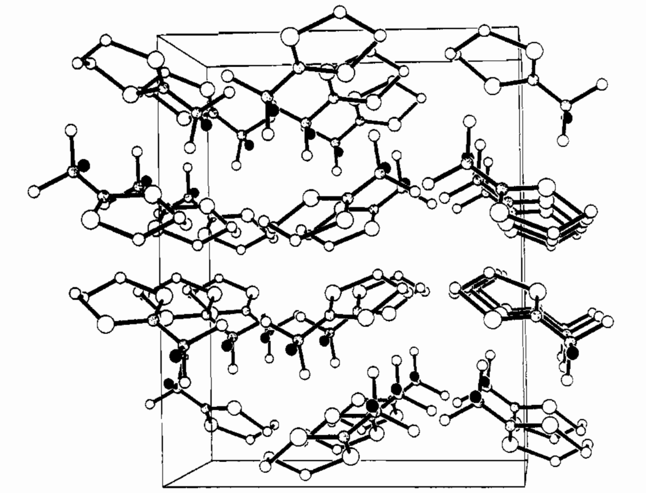


Figure 4. Packing of the molecules of **6** in the crystal lattice. The box represents the unit cell: nitrogen atoms, dotted circles; boron atoms, filled circles.

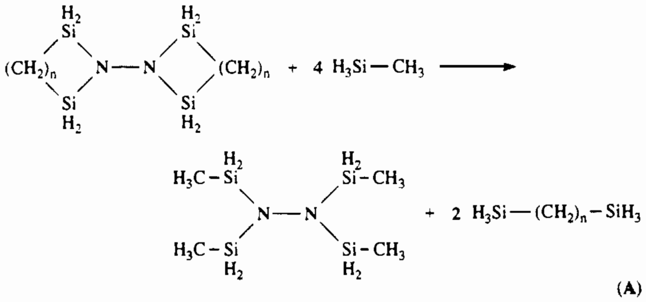
tems with permethylated Si atoms[16] (107.9–114.5°). It is to be expected that the 1-aza-2,5-disilacyclopentane ring in **1a** would show a similar strained geometry which is also shown by *ab initio* computations (see below). By contrast, the differences between the Si–N–N angles of the open-chain compound $(PhH_2Si)_2NN(SiH_2Ph)_2$ and the heterocycle **1** are only marginal, showing the 1,2-diaza-3,6-disilacyclohexane ring to be nearly strain free. This is probably why the formation of **1** is favored over that of the isomeric molecule **1a** (see also next paragraph).

The B–N1 bond distances of **5** and **6** are more than 5 pm longer than that of $N_2H_4{\cdot}BH_3$, but the B–N1–N2 angles of all three compounds are nearly equal. The conformations of **5** and **6** correspond to those expected for the unborylated molecules **3** and **4**.

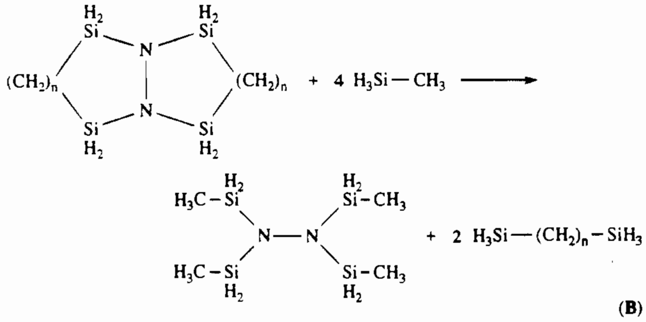
The dimethylamine–borane group is placed in such a position that no eclipsed conformation of the five nitrogen substituents occurs. The orientations of the N1–B vector including the negatively charged B atom are similar in both compounds (see Figures 1 and 2), avoiding parallel orientation to the lone pair of the tricoordinate N atom. The small differences are attributed to N^+-B^- dipole–dipole forces in the crystal lattices.

Plots of the packing of **5** and **6** in the crystals are presented in Figures 3 and 4. In the crystal lattice, the dipolar dimethylamine–borane groups of **5** form layers which alternate with those of the nonpolar carbosilane parts of the molecules. As shown in Figure 3, molecules belonging to different carbosilane layers have their N^+-B^- dipoles oriented in antiparallel directions for maximum interlayer Coulomb attraction. The lattice of compound **6** (Figure 4) also shows the clustering of the dimethylamine–borane groups in layers, but the dipoles are aligned in the same direction in these layers and opposite in neighboring layers, leading to dipole cancellations.

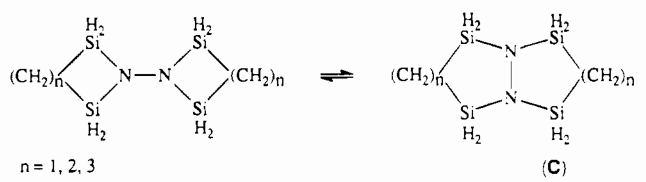
Evaluation of Ring Strain by Computational Methods. The effect of ring strain in compounds **1**, **1a**, **2**, and **2a** is best delineated by computational methods, and it is possible to include also compounds **1a** and **2a**, which are not available experimentally. Attempts to compute relative stabilities by both force field and semiempirical methods (AM1[17]) have shown that these methods are not sufficient to account for the details of the systems. Consequently, we turned to *ab initio* methods to evaluate the ring strain by the following homodesmotic equations



(A)



(B)



(C)

All computations were performed with the GAUSSIAN 92/DFT[18] program package.

Geometries were optimized without any symmetry contraints at the HF/3-21G* level of theory. They were refined at the HF/6-31G* and the MP2(fc)/6-31G* level within the resulting point groups. The nature of the stationary points was determined by analytical frequency calculations at HF/6-31G*. Additional single point computations were performed by employing density functional theory (DFT) at the Becke3LYP/6-311G* level.[19]

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[16] (a) Bao-Shen, Z.; Xiu-Zhong, Z.; Fang-Ming, M.; Xiao-Lan, L. *Acta Chim. Sin. (Engl. Transl.)* **1987**, *45*, 456. (b) van den Steen, F. H.; Kleijn, H.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1990**, 503. (c) Oshita, H.; Mizobe, Y.; Hidai, M. *Chem. Lett.* **1990**, 1303. (d) Byers, J. J.; Pennington, W. T.; Robinson, G. H.; Hrncir, C. *Polyhedron* **1990**, *9*, 2205. (e) Sockwell, S. C.; Hanusa, T. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 3393.

[17] Hyper Chem. Autodesk Inc., 1993.

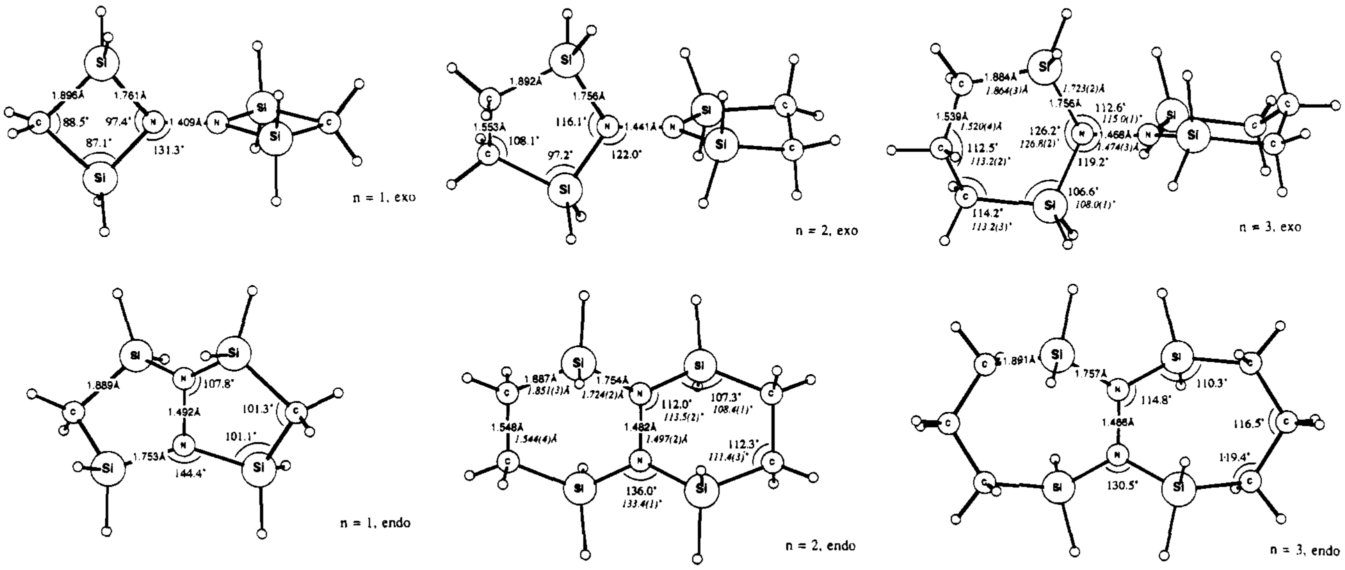

Figure 5. Calculated MP2(fc)/6-31G* geometries of the series $[(CH_2)_n(SiH_2)_2]N-N[(SiH_2)_2(CH_2)_n]$ with $n = 1$, 2, and 3 and their ring size isomers. Calculated bond lengths (Å) and angles (deg) are given as well as those determined by X-ray diffraction if available (in italics).

Table 3. Calculated Strain Energies (kcal mol^{-1})[a]

n	N−N bond	ring size	symm	HF	MP2	Becke3LYP
1	exo	4	D_{2h}	−24.8	−29.9	−22.7
1	endo	5	D_2	−2.9	−8.3	−2.2
exo to endo isomerization energy				−21.9	−21.6	−20.5
2	exo	5	S_4	−2.4	−8.3	−3.5
2	endo	6	D_2	3.4	4.8	2.1
exo to endo isomerization energy				−5.8	−13.1	−5.6
3	exo	6	C_2	2.6	−1.7	1.2
3	endo	7	D_2	−6.5	−9.4	−6.3
exo to endo isomerization energy				9.1	7.7	7.5

[a] See eqs A−C.

The results obtained at various levels of theory are listed in Table 3. These vary somewhat with the methods employed, where DFT (Becke3LYP) generally gives values closer to HF than to MP2. Some conclusions can be drawn unequivocally:

The computed reaction energies according to eq **A** are small but positive for molecules with six-membered rings ($n = 2$, endo; $n = 3$, exo). Hence, silylated hydrazines are best accommodated in six-membered rings rather than in chain configurations. Other ring sizes investigated (4, 5, and 7) are less favorable energetically. Clearly, the smallest ring ($n = 1$, exo) is the most strained. The molecules with five-membered rings ($n = 1$, endo; $n = 2$, exo) are strained only a little, no matter whether the N−N bond is exo- or endocyclic. An even larger ring strain was calculated for the seven-membered ring system.

Exo to endo isomerizations to give larger rings are exothermic for $n = 1$ and 2 but endothermic for $n = 3$. Thus, larger rings are more favorable for $n = 1$ and 2 but less favorable for $n = 3$. The experimentally known compounds $n = 2$, endo (**1**) and $n = 3$, exo (**2**) correspond to the thermodynamically more stable isomers, respectively.

As expected for nitrogen atoms carrying two silyl groups, the sum of bond angles is 360°, denoting planar tricoordination. The N coordination planes are perpendicular if free rotation about the N−N bond is possible, i.e. in the molecules with exocyclic N−N bonds. Such conformations minimize in the nitrogen lone pair repulsion. This is not possible if the N−N bond is endocyclic: the twist about the N−N bond is 49.7, 67.5, and 67.5° for $n = 1$, 2, and 3, respectively.

Only the N−N bond length varies significantly among the various optimized geometries (see Figure 5). With $n = 1-3$ it increases for the exo and decreases for the endo series. This can be rationalized in the following way: for molecules containing exo N−N bonds, the Si−N−Si angle increases with ring size. The larger this angle becomes, the smaller is the nitrogen p orbital contribution to the hybrid orbitals comprising the N−Si bonds. According to NBO analyses,[20] the nitrogen NBO (natural bond orbital) hybrids are $sp^{1.79}$, $sp^{2.95}$, and $sp^{3.40}$ for $n = 1, 2$, and 3, respectively. As a consequence, the p orbital contribution to the N−N bond hybrids increases (an NBO analysis gives $sp^{2.48}$, $sp^{2.95}$, and $sp^{3.40}$ for $n = 1$, 2, and 3) and the N−N distance becomes longer. The Si−N−Si angle decreases in the case of the endocyclic N−N bond containing molecules from $n = 1$ to $n = 3$, and the N−N distances decrease as a consequence.

It should be noted in this context that attempts to prepare the bicyclus with $n = 1$ from bis(bromosilyl)methane and hydrazine led to complex mixtures, the target molecule being detected only in traces by GC/MS analysis.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates and thermal parameters, hydrogen atom parameters, bond distances and angles, and hydrogen atom bond distances and angles (18 pages). Ordering information is given on any current masthead page.

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