

Synthesis of Volatile Cyclic Silylamines and the Molecular Structures of Two 1-Aza-2,5-disilacyclopentane Derivatives

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Received March 18, 1997[⊗]

An optimized synthetic procedure for α,ω -bis(bromosilyl)alkanes, $\text{BrH}_2\text{Si}(\text{CH}_2)_n\text{SiH}_2\text{Br}$ (with $n = 2$ and 3), is proposed. 1,2-Bis(bromosilyl)ethane reacts with ammonia to give 1,4-bis(1-aza-2,5-disilacyclopentane-1-yl)-1,4-disilabutane, traces of 1,6-diaza-2,5,7,10,11,14-hexasilabicyclo[4.4.4]tetradecane and nonvolatile products. The primary reaction products undergo slow redistribution reactions whereby (1-aza-2,5-disilacyclopentane-1-yl)-1,4-disilabutane is formed as the major product. Reactions of α,ω -bis(bromosilyl)alkanes, $\text{BrH}_2\text{Si}(\text{CH}_2)_n\text{SiH}_2\text{Br}$ (with $n = 2$ and 3), with isopropylamine afford the heterocycles 1-isopropyl-1-aza-2,5-disilacyclopentane and 1-isopropyl-1-aza-2,6-disilacyclohexane, whereas the analogous reaction with bis(bromosilyl)methane gives 1,5-diisopropyl-1,5-diaza-2,4,6,8-tetrasilacyclooctane rather than a four-membered ring compound. All compounds have been characterized by elemental analysis, mass spectrometry, and IR and NMR spectroscopy [^1H , ^{13}C , ^{15}N and ^{29}Si including the measurement of $^1J(^{29}\text{Si}^{15}\text{N})$ coupling constants]. The molecular structure of 1-isopropyl-1-aza-2,5-disilacyclopentane, determined by analysis of gas-phase electron-diffraction data augmented by restraints derived from *ab initio* calculations, is compared with the molecular structure of the isoelectronic 1-(dimethylamino)-1-aza-2,5-disilacyclopentane. The latter also was determined by gas-phase electron-diffraction (supported by *ab initio* calculations) and by low-temperature crystallography. The presence of a β -donor $\text{Si}\cdots\text{N}$ interaction in the latter compound, leading to a narrow $\text{Si}-\text{N}-\text{N}$ angle, is apparent from a significant distortion of the molecular structure as compared with the isoelectronic reference compound.

Introduction

There have been many synthesis and structure investigations of cyclic silylamines,¹ but most of the reported examples contain silicon atoms completely substituted with aryl, alkyl, or other substituents. The basic aza-sila heterocycles bearing only hydrogen substituents besides the ring atoms are unknown in most cases. However, such organosilylamine molecules are promising precursors for the chemical vapor deposition (CVD)² of silicon nitride for applications in microelectronic devices and solar cells.³ Advantages can be seen in the low molecular weights, high volatilities, and the reduced contents of carbon, which is always incorporated to some extent in the deposited layers during the CVD process if contained in the source

molecules. In this context we have recently reported studies on open chain silylamines^{4–6} as well as open chain⁷ and cyclic^{8,9} silylhydrazines. Furthermore, we have started investigations on hydridosilylated hydroxylamines^{10–12} for the CVD of silicon oxynitride.^{13,14}

We have described the formation of cyclic silylhydrazines and their borane adducts^{8,9} from bifunctional α,ω -bis(bromosilyl)alkanes, $\text{BrH}_2\text{Si}(\text{CH}_2)_n\text{SiH}_2\text{Br}$ (with $n = 2$ and 3), with NH-functional hydrazines. In this paper we present a series of new cyclic silylamines derived from α,ω -disilylalkanediyl units, $-\text{H}_2\text{Si}(\text{CH}_2)_n\text{SiH}_2-$, with $n = 1, 2$, and 3 . Compounds containing these units with $n = 2$ and 3 tend to eliminate the C_2 and C_3 backbones as the corresponding alkenes, as has been shown in CVD experiments using $\text{BrH}_2\text{Si}(\text{CH}_2)_n\text{SiH}_2\text{Br}$ as precursors, which lead to almost carbon-free layers of silicon in the low temperature regime.¹⁵ Mass spectrometric studies showed similar extrusions of ethene to take place for the bicyclic hydrazine system 1,6-diaza-2,5,7,10-tetrasilabicyclo[4.4.0]decane.¹⁶

We wished to investigate the structural chemistry of cyclic Si/N compounds more fully in order to establish a basis for the chemical behavior (including the chemistry in CVD processes)

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[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1997.

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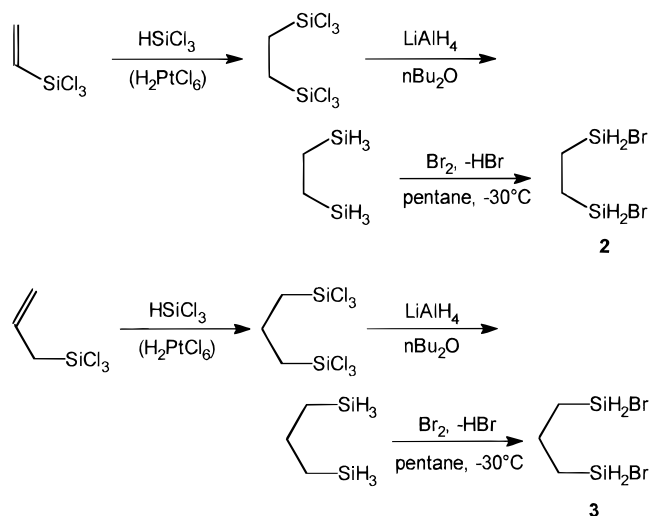
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Scheme 1



of this class of compounds. Our recent progress in restrained analysis of gas electron-diffraction data^{17,18} now enables us to cope with structure elucidation of systems with comparatively high molecular complexity, as will be demonstrated by two examples.

Preparation of α,ω -Bis(bromosilyl)alkanes. α,ω -Bis(bromosilyl)alkanes $\text{BrH}_2\text{Si}(\text{CH}_2)_n\text{SiH}_2\text{Br}$ [with $n = 1$ (**1**),⁹ **2** (**2**), and **3** (**3**)¹⁰] are known from the literature. Our interest in compounds containing the $\text{SiH}_2(\text{CH}_2)_n\text{SiH}_2$ linkage as well as recent chemical vapor deposition (CVD) experiments using **2** and **3** as molecular sources for the epitaxial growth of β - SiC ¹⁵ made it necessary to develop optimized routes to the brominated carbosilanes **2** and **3**.

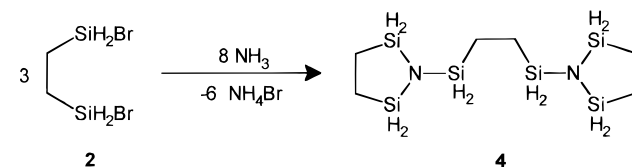
In contrast to earlier reports,¹⁰ the hydrosilylation reactions of trichlorosilane with either vinyl- or allylsilane does not require high pressure. In the presence of Speier's catalyst, trichlorosilane adds smoothly to the neat (trichlorosilyl)alkenes under reflux. Scaling up to kilogram quantities is achieved easily. Various alkali metal hydrides have been tested for the reduction of the bis(trichlorosilyl)alkanes, but we have been unable to find any suitable replacement for the expensive LiAlH_4 .

The major problem in the synthesis of **2** and **3** was the selectivity of the α,ω -dibromination. Among the many systems tested, the inert solvent pentane turned out to give the best selectivity and yield. The choice of the temperature is crucial, and -30 to -40°C was found to be the optimum range. Under these conditions more than 2-fold bromination can almost be avoided completely (Scheme 1).

Preparation of the Silylamines. A mixture of silylamines is formed by admitting a stream of dry ammonia into a solution of **2**. The composition depends on the reaction conditions and can be monitored by GC/MS and NMR. The dominant species is the bicyclic compound **4** [1,4-bis(disilapyrrolidin-1-yl)-1,4-disilabutane] comprising two five-membered $\text{C}_2\text{Si}_2\text{N}$ rings linked by a four-membered Si_2C_2 unit. Compound **4** can be purified by distillation (Scheme 2).

The formation of the isomer **5** is not observed under these reaction conditions, but it is obtained in small amounts, in

Scheme 2



addition to **4**, by dropping **2** into a liquid ammonia/pentane emulsion. In contrast to the reaction conditions described first, the large excess of ammonia favors the double amination of **2** and therefore disfavors to some extent the closure to five-membered rings so that the formation of **5** becomes a possible side reaction. Compound **5** could not be obtained in pure form but was enriched to a 70% solution in **4** by careful distillation.

The mass spectra (GC coupled) of the isomers **4** and **5** are substantially different, as is shown in Figure 1. The spectra are not characteristic enough to determine the constitutions of the compounds. The higher symmetry of **5** (Chart 1) can be deduced from the ^1H NMR spectrum, and allows the assignment of the mass spectra. The small quantities of **5** obtained limited the number of applications of spectroscopic methods for the purpose of identification.

Spectroscopic observation of the composition of the reaction mixture over a period of many weeks showed that rearrangements were taking place, including transsilylation reactions. Even initially formed nonvolatile (presumably polymeric) raw products undergo redistribution products to give **6** as the major product, which can be isolated by distillation after 5 months of storage at ambient temperature. However, if **4** is present in pure form, no such redistribution reactions can be observed, which indicates that the rearrangements occur only in the presence of ammonium salts, which are formed during the primary reactions.

1-Aza-2,5-disilacyclopentane (**7**) (Chart 2) is the basic ring structure of the sila-aza heterocycles present in compounds **4** and **5**. However, all attempts to isolate **7** from mixtures of the reactions of **2** with liquid NH_3 failed, although it was detected by its mass spectrum in the GC coupling ($<0.1\%$ content).

The organobromosilane **2** reacts with isopropylamine to give 1-isopropyl-1-aza-2,5-disilacyclopentane (**8**). An analogous reaction using **3** instead of **2** as silylating agent affords 1-isopropyl-1-aza-2,6-disilacyclohexane (**9**) as the product (Scheme 3).

An alternative synthetic pathway to these compounds has been tested, *i.e.* the reaction of bis(trichlorosilyl)ethane with isopropylamine, which was expected to lead to the corresponding Si-chlorinated heterocycles and finally give access to the Si-hydrido heterocycles. However, because the composition of the reaction products was so complex, this method was not investigated any further.

In contrast to the preparation procedures for **8** and **9** the reaction of **1** with isopropylamine leads to the formation of an eight-membered ring (**10**) containing two Si_2N units. The formation of the four-membered heterocycle **11** was not observed, probably because of high ring strain in such a system (Scheme 4).

All the silylamines described in this paper are moisture-sensitive compounds, but are stable if stored at ambient temperature in pure form. Compounds **4**, **6**, and **8–10** have been characterized by elemental analysis, mass spectrometry, and IR and NMR spectroscopy (see Experimental Section).

NMR Studies on Cyclic Silylamines. The resonances of four nuclei (^1H , ^{13}C , ^{15}N , ^{29}Si) have been studied by heteronuclear NMR spectroscopy. The complete data set is given in the Experimental Section. ^1H and ^{13}C NMR parameters are in

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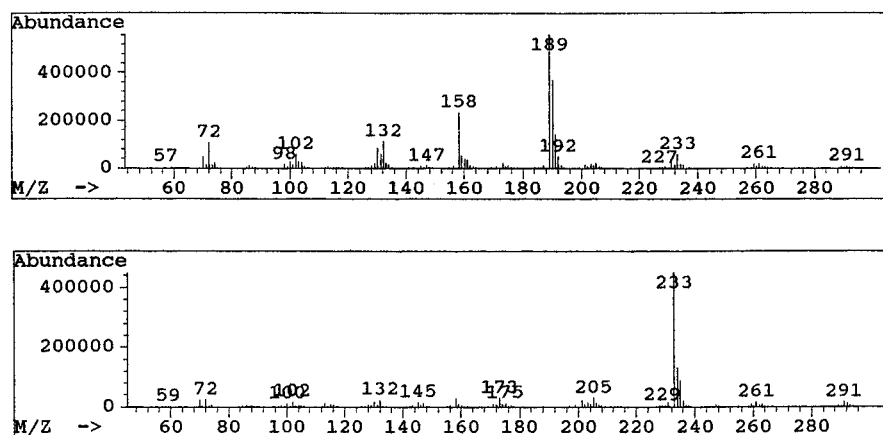
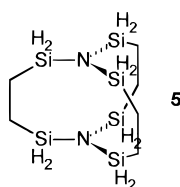
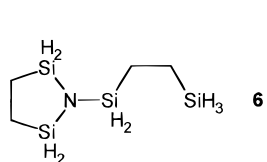


Figure 1. Mass spectra (GC coupled) of two isomers of $C_6H_{24}N_2Si_6$: **4** (top); **5** (bottom).

Chart 1



Scheme 4

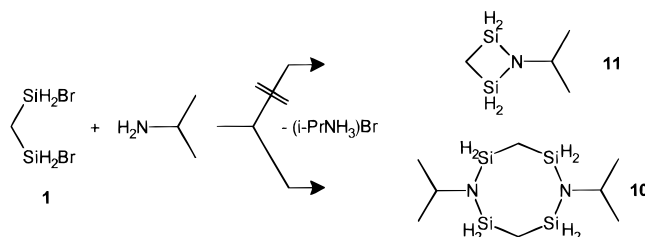
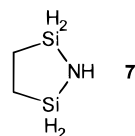


Chart 2



Scheme 3

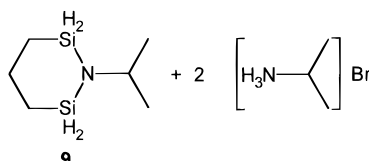
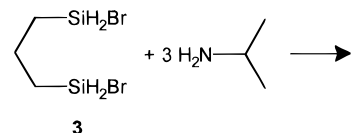
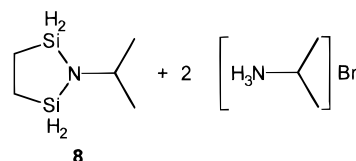
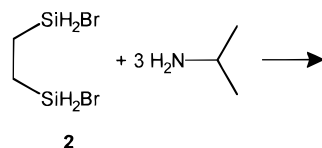


Table 1. Selected ^{15}N and ^{29}Si NMR Data (Chemical Shifts in ppm; Coupling Constants in Hz)

	$\delta(^{15}N)$	$\delta(^{29}Si_{endo})$	$\delta(^{29}Si_{exo})$	$^1J(^{29}Si^{15}N_{endo})$	$^1J(^{29}Si^{15}N_{endo})$
4	-383.0	-13.2	-21.9	8.6	8.6
6	-393.0	-13.3	-22.7	8.6	9.7
8	-352.8	-24.1		14.5	
9	-362.7	-30.9		12.4	
10	-360.6	-22.5		16.5	

constants $^1J(^{29}Si^{15}N)$ depend on the extent of silylation of the N atom, as we have found earlier for open-chain silylamines.⁶ The assignment of these coupling constants is based on the different natural abundance of each ^{29}Si – ^{15}N bond resulting in different intensities of the satellite peaks. The triply silylated amines **4** and **6** show values which are clearly smaller than those of the doubly silylated compounds **8**–**10**. Correlation of $^1J(^{29}Si^{15}N)$ with the Si–N bond lengths is not possible for all these compounds, because of the lack of structural data; however, the value of $^1J(^{29}Si^{15}N)$ for **8** is 14.5 Hz, while that for the isoelectronic 1-(dimethylamino)-1-aza-2,5-disilacyclopentane (**12**)⁹ is 12.7 Hz, consistent with the slightly shorter Si–N bonds in **8**, as shown by gas electron-diffraction (see below; **8**, 1.721, and **12**, 1.728 Å, both averaged over the two nonequivalent Si–N bonds in the molecules).

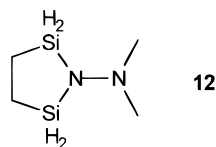
The chemical shifts $\delta(^{29}Si)$ of **4** and **6** reflect the influence of ring closure. The resonances of the endocyclic Si atoms are shifted about 9 ppm to low frequencies as compared to those of the exocyclic ones. Further spectroscopic data can be obtained from the Experimental Section and deserve no detailed comments.

Structural Studies on Five-Membered Aza–Sila Heterocycles. As most of the compounds described above are liquids at ambient temperature, it is difficult to obtain structural information using standard crystallographic methods. However, we determined the molecular structure of **8** by means of electron diffraction in the gas phase and compared it with the structure of the isoelectronic 1-(dimethylamino)-1-aza-2,5-disilacyclopentane (**12**), the synthesis of which we reported earlier.⁹ We have recently introduced the method of augmenting the structural

the range established for this class of compounds. Selected chemical shifts and coupling constants deduced from ^{15}N and ^{29}Si NMR spectra are listed in Table 1.

The chemical shifts $\delta(^{15}N)$ for the compounds described in this paper cover a large range (353–393 ppm). The triply silylated ^{15}N atoms of **4** and **6** are more shielded than the doubly silylated atoms in **8**–**10**, but even **4** and **6**, which are compounds with very similar environments at the nitrogen atoms, differ in their $\delta(^{15}N)$ values by about 10 ppm. The one-bond coupling

Chart 3



information from experimental gas-phase data with flexible restraints derived from *ab initio* calculations with assigned uncertainties, which are based on the estimated reliability of the calculated parameters. As compared to the rigid constraints of unknown reliability which have been used so far, this approach combines the advantages of electron diffraction and spectroscopic and computational methods and in doing so the best possible structures presently attainable for free molecules are obtained. For a detailed description of the procedure, called the SARACEN method, we refer to our recent papers.^{17,18} The structures of **8** and **12** (Chart 3) have the largest numbers of parameters refined by this procedure so far but do not represent the upper limit of molecular complexity for which this method can be applied.

Numerous models have been tested to fit the experimental molecular scattering intensities including those with local C_2 symmetry for the ring systems and various conformations of the isopropyl and dimethylamino groups in **8** and **12**, respectively. In both cases the best fit to the diffraction data was achieved with geometries which are very close to those predicted by *ab initio* calculations, which is also, in the case of **12**, that determined by low-temperature crystallography (see below). The final refined parameter values are given in Table 2 together with the theoretical data for comparison.

Despite the progress we have achieved with our refinement procedure, the large number of geometric parameters necessary for the definition of these systems required the adoption of some assumptions (mainly concerning hydrogen atom positions) to simplify the problem. Those include equal H–C–H angles in the methyl groups as well as equal lengths for all C–H and for all Si–H distances in each molecule. Only one of the angles H–C–Si and H–Si–N and one of the torsion angles H–C–Si–N and H–Si–N–Si in each molecule was refined, while the remaining three of each parameter set were tied to the refining ones by fixed differences derived from the *ab initio* calculations. The model of **8** was then defined by 28 geometrical parameters and that of **12** by 27 parameters, which are described in Table 2 and discussed in the following text.

Table 2 also contains a description of the flexible restraints and their uncertainties, which were applied to most of the differences between parameters which are similar in nature and for which theoretical predictions are generally reliable. The values for the restraints were adopted from the highest level *ab initio* calculations (MP2/6-31G*). The uncertainties were chosen to be 0.005 Å for differences between closely related distances (*i.e.* distances between the same sort of atoms; p_2 , p_4 , p_5) and 0.01 for differences between less closely related distances (p_7 and the difference between the independent parameter p_6 and the dependent parameter p_{30}). The uncertainties for restraints on the parameters p_{13} and p_{17} describing differences in angles were set to 1.0°. A restraint on p_{11} was assigned an uncertainty of 1.0° for **8** but 2.0° as used for **12**, because, according to our experience, computed values for Si–N–N angles^{21,22} may be improved significantly at levels of

theory higher than MP2/6-31G*. The uncertainties for the differences between torsional angles were set to 2.0° for p_{15} , which relates the torsional angles in the five-membered ring. Angle parameters describing the position of hydrogen atoms have been included in the refinement, and all these parameters are subject to flexible restraints. Uncertainties were set at 1.5° for bond angles, 2.0° for torsional angles and 5° for the twist angle of the methyl groups. The uncertainties of more complex parameters, namely the tilt angle of the CH₃ groups p_{26} and the deviation of the NC (**8**) and NN vectors (**12**) from the Si₂N planes, were set to 1.0°.

The Si–H bond lengths for both compounds were determined by gas-phase vibrational spectroscopy using known relationships between the stretching frequencies and the bond lengths,^{23,24} while assuming that the H–Si stretching modes do not couple with one another. The values $r_0(\text{SiH})$ came finally out to be 1.493 Å (**8**) and 1.490 Å (**12**) and were converted to r_α values by calculated corrections and included in the refinement as restraints with estimated uncertainties of 0.003 Å. This decreased markedly the correlation with other distances close to 1.5 Å.

The amplitudes of vibration were calculated from a force field obtained at the RHF/6-31G* level of theory by using the ASYM40 program.²⁵ Unless they could be refined, these amplitudes were used in the refinements. The amplitudes for all distances between two non-hydrogen atoms and many non-hydrogen to hydrogen distances were refined either freely, tied in groups with fixed calculated ratios for amplitudes of very similar nature, or tied by flexible restraints for related distances. Some of the absolute values of refining amplitudes were also subject to restraints. Detailed information about tying schemes and applied restraints is listed in the supplementary material.

The structures were then refined taking perpendicular amplitude corrections into account (shrinkage effect); these were obtained from the same force field calculations which provided the amplitudes of vibration. The radial distribution curves of both compounds are presented in Figures 2 and 3, each showing more than eight resolved peaks. The overall experimental and calculated geometries are in good agreement.

A crystal of **12** could be grown by *in situ* techniques on the diffractometer. The solid-state structure consists of essentially non-interacting molecules: the closest intermolecular Si···N distance is 3.65 Å, which is beyond the sum of Si and N van der Waals radii (3.54 Å).¹⁸ There are no other important intermolecular forces which could lead to a serious distortion with respect to the geometry of the free molecule (see packing diagram in Figure 4). Accordingly, good agreement between the crystal and gas phase structure is observed (compare Tables 3 and 2).

The five-membered ring systems in both compounds, **8** and **12**, deviate significantly from C_2 symmetry. In each compound the two Si–N distances are similar, as are the two Si–C distances, with differences of less than 0.01 Å. The five-membered rings show twisted geometries with the asymmetry becoming evident from the differences between the two torsion angles Si–N–Si–C [GED, **8**, 1.1(21), and **12**, 6.3(20)°; XRD, **12**, 6.0(2)°; CALC, **8**, 2.9, and **12**, 5.8°], the differences between the ring angles N–Si–C [GED, **8**, 2.7(8), and **12**, 1.7(9)°; XRD, **12**, 0.6(1)°; CALC, **8**, 0.3, and **12**, 1.1°], and the differences between the ring angles Si–C–C [GED, **8**, 5.8(16), and **12**, 2.0-

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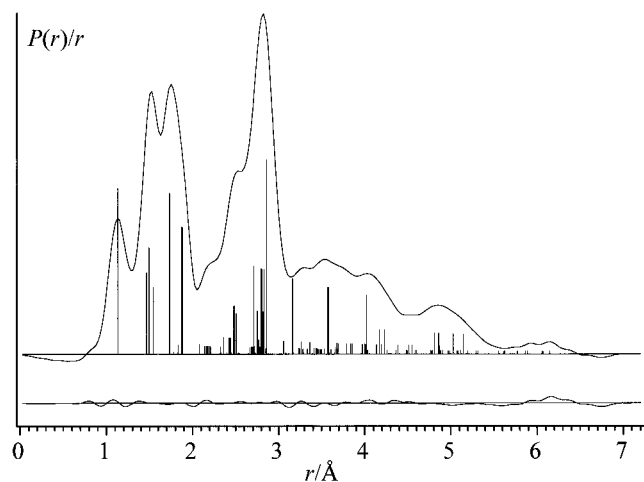
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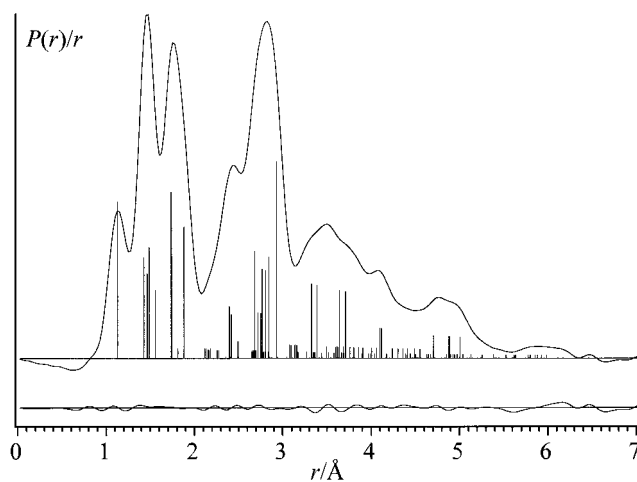
Table 2. Parameter Definitions and Values As Determined by Gas Electron Diffraction of **8** and **12** and *ab Initio* Calculated Geometries (MP2/6-31G*) for Comparison (Distances in Å; Angles in deg; Esd's in Parentheses)

parameter	8			12		
	GED		$r_e, <_e$	GED		<i>ab initio</i> $r_e, <_e$
	$r_{\alpha}, <_{\alpha}$	restraint		$r_{\alpha}, <_{\alpha}$	restraint	
	Independent					
p_1 Si(2)–N(1)	1.721(3)		1.751	1.724(3)		1.753
p_2 Δ (Si–N)	–0.001(5)	–0.002(5)	0.001	0.008(5)	0.009(5)	0.009
p_3 Si(2)–C(3)	1.868(4)		1.889	1.867(3)		1.893
p_4 Δ (Si–C)	–0.010(5)	–0.008(5)	–0.008	–0.002(5)	–0.001(5)	0.001
p_5 [C/N(6)–C(8)]–[N(1)–C/N(6)]	0.043(9)	0.049(10)	0.049	0.0214(9)	0.020(10)	0.020
p_6 C/N(6)–C(8)			1.525	1.443(4)		1.459
p_7 Δ [(C/N(6)–C(8/7))]	0.002(5)	0.003(5)	0.003	0.000(5)	0.001(5)	0.001
p_8 Si–H	1.460(3)	1.462(3)	1.494	1.459(3)	1.460(3)	1.491
p_9 C–H	1.078(2)		1.096	1.089(2)		1.096
p_{10} \angle C/N(6)–N(1)–Si(2)	122.6(6)		121.6	116.4(6)		115.6
p_{11} Δ (\angle C/N–N–Si)	3.0(10)	3.7(10)	3.7	11.7(11)	14.5(20)	14.5
p_{12} \angle N(1)–Si(2)–C(3)	102.8(5)		99.5	99.4(6)		97.9
p_{13} Δ (\angle N–Si–C)	–2.7(8)	–0.3(10)	–0.3	–1.7(9)	–1.3(10)	–1.3
p_{14} τ [Si(5)–N(1)–Si(2)–C(3)]	8.9(13)		11.5	5.1(13)		6.7
p_{15} Δ (Si–N–Si–C)	–1.1(21)	–2.9(20)	–2.9	6.3(20)	5.8(20)	5.8
p_{16} \angle N(1)–C/N(6)–C(8)	112.7(8)		111.1	112.1(8)		109.9
p_{17} Δ (\angle N–C/N–C)	–0.5(8)	0.1(10)	0.1	0.6(10)	0.3(10)	0.3
p_{18} τ [Si(2)–N(1)–C/N(6)–C(8)]	93.3(32)		95.3	120.6(45)		119.5
p_{19} τ [C(7)–C/N(6)–N(1)–C(8)]	122.5(15)		124.8	126.5(12)		123.2
p_{20} \angle N(1)–Si(2)–H(21)	112.7(15)	111.2(15)	111.2	112.3(15)	112.4(15)	112.4
p_{21} τ [Si(5)–N(1)–Si(2)–H(22)]	133.6(18)	132.3(20)	132.3	127.1(19)	125.7(20)	125.7
p_{22} \angle Si(2)–C(3)–H(32)	106.7(13)	108.3(15)	108.3	105.2(11)	108.0(15)	108.0
p_{23} τ [N(1)–Si(2)–C(3)–H(32)]	89.2(18)	92.5(20)	92.5	90.5(18)	90.3(20)	90.3
p_{24} \angle C/N(6)–C(8)–H(81)	110.0(10)	110.5(15)	110.5	111.7(8)	110.0(15)	110.0
p_{25} torsion(CH ₃)	–124.1(37)	–120.3(50)	–120.3	–117.7(29)	–120.5(5)	–120.5
p_{26} tilt(CH ₃)	–0.8(11)	0.0(10)	0.0	3.0(10)	2.7(1.0)	2.7
p_{27} Δ {[Si ₂ N]/[N(1)–C/N(6)]}	3.7(9)	3.6(10)	3.6	–1.1(9)	–1.5(10)	–1.5
p_{28} \angle N(1)–C(6)–H(21)	107.3(16)	107.4(15)	107.4			
	Dependent					
p_{29} \angle C(7)–C/N(6)–C(8)	108.7(12)	111.5(15)	111.5	111.3(10)	111.4(15)	111.4
p_{30} [C/N(6)–C(8)]–[C(3)–C(4)]	0.026(9)	0.025(10)	0.022	0.101(9)	0.092(10)	0.092

**Figure 2.** Observed and final weighted difference radial distribution curves for **8**. Before Fourier inversion the data were multiplied by $s \exp[(-0.002s^2)/(Z_{\text{Si}}-f_{\text{Si}})/(Z_{\text{N}}-f_{\text{N}})]$. The vertical sticks represent the individual contributions of interatomic distances with the important ones being listed in Table 4.

(16)°; XRD, **12**, 0.4(1)°; CALC, **8**, 0.8, and **12**, 0.6°. The Si–C distances in both compounds are very similar to that in H₃SiCH₂CH₂SiH₃ [r_{α} : 1.880(1) Å by GED],¹⁷ indicating that the effects of electronegative substitution and the inclusion in a ring system of the SiH₂CH₂CH₂SiH₂ unit probably cancel out.

All experiments (GED, XRD) and *ab initio* calculations for **8** and **12** agree that the ring nitrogen atoms have completely planar coordination geometries. However, the Si–N–Si angles in the two compounds are significantly different [GED, **8**, 111.8–(4), and **12**, 115.5(2)°; XRD, **12**, 115.9(1)°; CALC, **8**, 112.9,

**Figure 3.** Observed and final weighted difference radial distribution curves for **12**. Before Fourier inversion the data were multiplied by $s \exp[(-0.002s^2)/(Z_{\text{Si}}-f_{\text{Si}})/(Z_{\text{N}}-f_{\text{N}})]$. The vertical sticks represent the individual contributions of interatomic distances with the important ones being listed in Table 4.

and **12**, 115.6°. These angles are much narrower than in compounds with noncyclic Si₂N–*i*Pr systems (*ca.* 128°).²⁶

Most intriguingly, the exocyclic Si–N–C angles in **8** are close [122.6(6) and 125.5(6)°; CALC, 121.6 and 125.3°], whereas the corresponding Si–N–N angles in the isoelectronic **12** differ by no less than 11.7(11)° (GED) [GED, 116.4(6) and

(26) Hedberg, L.; Mills, I. M. *ASYM20, ASYM40, Programs for Force Constants and Normal Coordinate Analysis*, Version 3.0, June 1994. See also: Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc.* **1993**, *160*, 117.

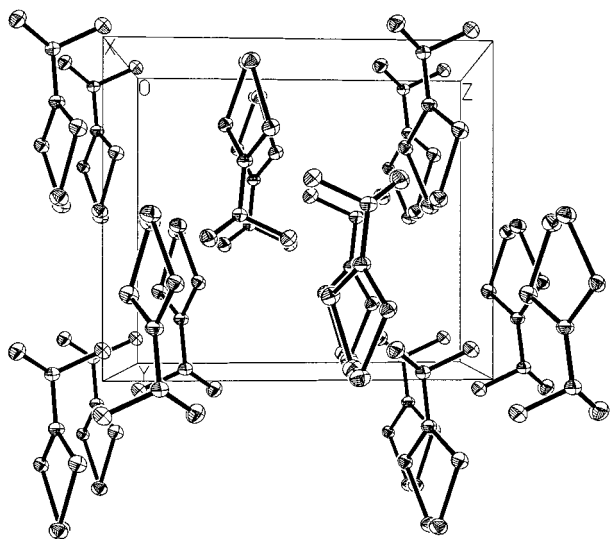


Figure 4. Packing of molecules of **12** in the crystal showing the absence of any structure-distorting intermolecular interactions. Non-hydrogen atoms are shown as thermal ellipsoids at the 50% probability level, and hydrogen atoms, as circles of arbitrary size.

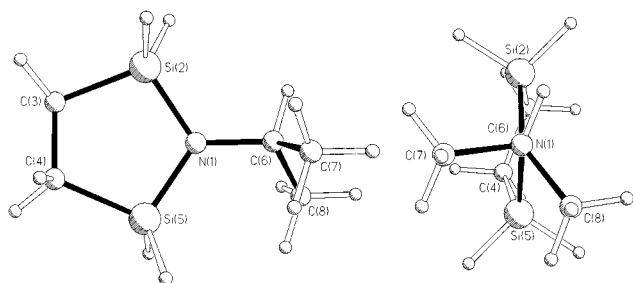


Figure 5. Molecular structure of **8** as determined by gas electron diffraction showing the applied atom-numbering scheme. The inset shows the conformation of the isopropyl group relative to the ring by a view along the NC bond.

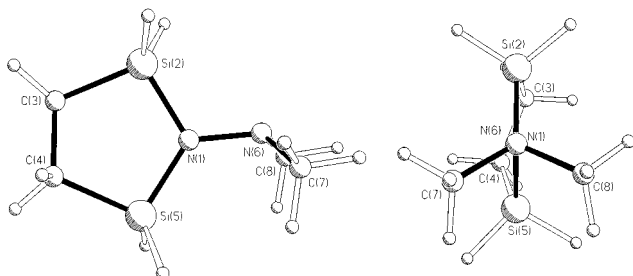


Figure 6. Molecular structure of **12** as determined by gas electron diffraction showing the applied atom-numbering scheme. The inset shows the conformation of the dimethylamino group relative to the ring by a view along the NC bond.

128.1(6)°; XRD, 115.0(1) and 129.1(1)°; CALC, 114.3 and 130.1°]. As the steric effects in both compounds, **8** and **12**, are rather similar, the observed deviations can only be due to electronic effects. As we have reported earlier, Si–N–N fragments often show rather acute Si–N–N angles, due to weak β -donor Si \cdots N interactions: The angle Si–N–N in (Me₂NNMe)₂SiCl₂ is as narrow as 107.7(3)° (expected ca. 120°).²¹ This effect is even more pronounced in Si–O–N systems: *Ab initio* calculations (MP2/6-311G**) predict angles as small as 90.0° for FH₂SiONMe₂.²² The β -donor Si \cdots N interaction in **12** leads to a bending of the N–N vector toward one silicon atom Si(2); however, as the lone pair of electrons at nitrogen is oriented to one side, the interaction appears not to be purely electrostatic in nature. This interaction probably also is

responsible for the slight differences in the Si–N bond lengths and the smaller Si–N–Si angle in **12** as compared to **8**.

Both the β -donor Si \cdots N interaction and the repulsion between the p-type lone pair of electrons at N(1) and the lone pair at the exocyclic nitrogen atom N(6) result in an almost perfectly orthogonal orientation. In contrast, the isopropyl group of the isoelectronic compound **8** is twisted about the N–C axis to some extent, since these effects are absent. The barrier to rotation in **12** has been computed to be 70 kJ mol⁻¹ by *ab initio* methods (single point calculations at HF/6-31G* with fixed geometry while rotating the Me₂N group in steps of 15°), approximately in the same range as established experimentally (NMR) for open-chain silylhydrazines.¹⁶

The β -donor Si \cdots N interaction in **12** can be suppressed by complexing the β -nitrogen lone pair of electrons with the Lewis acid BH₃. This was shown earlier by the determination of the solid-state structure of the adduct **12**·BH₃.⁹ The Si–N–N angles of 124.6(1) and 120.0(1)° in **12**·BH₃ are much smaller than the corresponding ones in **12**.

Conclusion. The major conclusions to be gleaned from this work are as follows:

1. We have developed an optimized route for the preparation of α,ω -bis(bromosilyl)alkanes.

2. α,ω -Bis(bromosilyl)alkanes turned out to be excellent bifunctional reagents for ring closure reactions with primary amines or ammonia to give a broad range of Si/N/C heterocycles. With BrH₂Si(CH₂)_nSiH₂Br (*n* = 2, 3), five- and six-membered rings are readily formed, whereas bis(bromosilyl)methane gives an eight-membered ring system with two H₂SiCH₂SiH₂ units rather than a four-membered CSi₂N ring product.

3. The molecular structure in the gas-phase of 1-isopropyl-1-aza-2,5-disilacyclopentane (**8**) has been determined by using a recently developed method of data analysis which makes use of restraints derived from theoretical calculations. The present work demonstrates the good performance of this method for comparatively complex molecular structures. A comparison of this geometry with the molecular geometry of the isoelectronic 1-(dimethylamino)-1-aza-2,5-disilacyclopentane (**12**) showed the latter to have a Si–N– β -donor interaction between the exocyclic nitrogen atom and one of the endocyclic silicon atoms. While this interaction is predictably weak, the molecular structure is completely independent of the phase and is thus very similar in the solid state. The molecular structures could also be confirmed by *ab initio* calculations.

Clearly the ring structure in 1-(dimethylamino)-1-aza-2,5-disilacyclopentane (**12**) prevents the Si–N–N unit from adopting its preferred geometry, which probably includes a much smaller Si–N–N angle. Studies on such open-chain systems are subject of our present investigations, which aim at the understanding of the various electronic and steric effects responsible for the strength of Si–N– β -donor interactions.

Experimental Section

Standard inert-gas techniques were applied. ¹H, ¹⁵N, and ²⁹Si NMR: Jeol JNM-GX 400 spectrometer. GC/MS: Hewlett Packard 5890 Series II. IR: Perkin-Elmer FTIR 1650.

1,2-Bis(bromosilyl)ethane (2). 1,2-Bis(trichlorosilyl)ethane: 3.5 mL of Speier's catalyst (0.1 M solution of H₂PtCl₆ in 2-propanol) were mixed with 50 mL of trichlorosilane. One half of this was mixed with 1000 mL of vinyltrichlorosilane (7.86 mol) in a 4 L vessel equipped with a high capacity reflux condenser, and the remaining catalyst mixture is added to 800 mL of trichlorosilane and placed in a dropping funnel. The vessels contents were heated to reflux (sudden exothermic

Table 3. Selected Geometrical Data for **12** As Determined by Low-Temperature Crystallography

	8		12		
	GED	MP2/6-31G*	GED	MP2/6-31G*	XRD
		Bond Lengths (Å)			
N(1)-Si(2)	1.721(3)	1.751	1.724(3)	1.753	1.730(2)
Si(2)-C(3)	1.868(4)	1.889	1.867(3)	1.893	1.872(2)
C(3)-C(4)	1.528(9)	1.550	1.544(7)	1.551	1.551(3)
C(4)-Si(5)	1.858(4)	1.891	1.865(3)	1.892	1.876(2)
Si(5)-N(1)	1.720(3)	1.753	1.732(3)	1.744	1.733(2)
N(1)-C/N(6)	1.458(4)	1.476	1.422(4)	1.439	1.452(2)
C/N(6)-C(7)	1.504(6)	1.528	1.443(5)	1.460	1.455(2)
C/N(6)-C(8)	1.502(4)	1.525	1.443(4)	1.459	1.455(2)
		Bond Angles (deg)			
Si(2)-N(1)-Si(5)	111.8(4)	112.9	115.5(2)	114.3	115.9(1)
Si(2)-N(1)-C/N(6)	122.6(6)	121.6	116.4(6)	115.6	115.0(1)
Si(5)-N(1)-C/N(6)	125.5(6)	125.3	128.1(6)	130.1	129.1(1)
N(1)-Si(2)-C(3)	102.8(5)	99.5	99.4(6)	97.9	98.5(1)
Si(2)-C(3)-C(4)	105.0(10)	106.5	107.8(10)	107.7	108.6(1)
C(3)-C(4)-Si(5)	110.8(11)	107.4	109.8(12)	108.3	108.3(1)
N(1)-Si(5)-C(4)	100.0(8)	99.2	97.7(6)	96.6	97.9(1)
N(1)-C/N(6)-C(7)	112.3(8)	111.2	112.7(6)	111.4	109.5(1)
N(1)-C/N(6)-C(8)	112.7(8)	111.1	112.1(8)	109.9	110.0(1)
C(7)-C/N(6)-C(8)	108.7(12)	111.5	111.3(10)	111.4	110.6(2)
		Torsion Angles (deg)			
C(3)Si(2)N(1)Si(5)	8.9(13)	11.5	5.1(13)	6.7	5.7(1)
C(4)Si(5)N(1)Si(2)	7.8(13)	8.6	11.4(13)	12.5	11.7(1)
Si(2)N(1)C/N(6)C(7)	93.3(32)	95.3	120.6(45)	119.5	115.3(1)
Si(2)N(1)C/N(6)C(8)	122.5(15)	124.8	126.5(12)	123.2	121.7(1)

reaction!) and kept at this temperature for 15 min. The contents of the dropping funnel were then added dropwise to the refluxing mixture and the heating reduced so that mild reflux was maintained. After addition of 1 equiv of trichlorosilane the temperature inside the vessel reached *ca.* 190 °C. The remaining trichlorosilane was slowly added, which reduced the boiling temperature. After 2 h of further refluxing, the reaction mixture was distilled under reduced pressure, whereby the excess of trichlorosilane was condensed in a trap (−196 °C). Yield: 2242 g of 1,2-bis(trichlorosilyl)ethane (96%), bp 72 °C (6 mbar). **1,2-Disilylethane**: 207.5 g of lithium aluminium hydride (5.47 mol) was placed into a 4 L vessel equipped with a mechanical stirrer. The apparatus was cooled to −78 °C, and 1 L of cold (*ca.* −30 °C) di-*n*-butyl ether was slowly added (Caution: Efficient cooling is crucial to avoid the dangerous, spontaneous decomposition of LiAlH₄ by heat of solvation!). The mixture was allowed to warm to −10 °C while stirring, and 1083 g of 1,2-bis(trichlorosilyl)ethane (3.65 mol) was added dropwise, while not allowing the mixture to get warmer than 20 °C (Caution: Cooling below *ca.* −10 °C must be avoided, because too slow a reaction leading to accumulation of a large surplus of 1,2-bis(trichlorosilyl)ethane might give a mixture which reacts very exothermically upon a small increase in the temperature!). After complete addition the mixture was heated to *ca.* 60–70 °C for 2 h. The volatile 1,2-disilylethane was condensed into a trap (−196 °C) with occasional pumping and stirring and heating the mixture to not more than 30 °C. The trap's contents were fractionally distilled using a 20 cm Vigreux column. Yield: 251 g of 1,2-disilylethane (76%), bp 44–46 °C. **-1,2-Bis(bromosilyl)ethane (2)**: 200 g of 1,2-disilylethane (2.21 mol) is dissolved in 700 mL of pentane and cooled to −78 °C. A 227 mL volume of dry bromine (4.42 mol) is placed into a dropping funnel (Caution: If cooling is not efficient, vapors of 1,2-disilylethane and bromine react explosively!). After the solution was allowed to warm −40 to −30 °C and the temperature was kept constant, the bromine was added at such a rate that only a slight brownish color appeared in the solution. Hydrogen bromide gas left the apparatus after passing a dry ice cooled condenser and a paraffin filled valve and was dissolved in water in a falling-film absorber. After complete addition of bromine, the mixture was stirred for 14 h, while the evolving HBr atmosphere was occasionally replaced by nitrogen. The solvent was removed by distillation and the residue fractionally distilled under reduced pressure (20 cm Vigreux column). Yield: 488 g (89%) of 1,2-bis(bromosilyl)ethane, bp 65–66 °C (13 mbar).

1,3-Bis(bromosilyl)propane (3). The procedure is the same as described for **2**. 1,3-Bis(trichlorosilyl)propane was prepared from 310.4

g of allyltrichlorosilane (1.76 mol), which must be free of triethylammonium chloride (to be removed by cryofiltration), 200 mL of trichlorosilane (1.98 mol), and 1.0 mL of Speier's catalyst; yield 495.6 g (91%), bp 77–78 °C (4 mbar). 1,3-Disilylpropane was prepared from 914 g of 1,3-bis(trichlorosilyl)propane (2.94 mol) and 167 g of LiAlH₄ (4.40 mol) in 1 L of di-*n*-butyl ether; yield 228.6 g (75%), bp 80 °C. 1,3-Bis(bromosilyl)propane (**3**) was prepared from 121.7 g of 1,3-disilylpropane (1.17 mol) and 119.5 mL of bromine (2.33 mol) in 400 mL of pentane; yield 253.9 g (83%), bp 69 °C (2 mbar).

1,4-Bis(1-aza-2,5-disilacyclopentane-1-yl)-1,4-disilabutane (4) and 1,6-Diaza-2,5,7,10,11,14-hexasilabicyclo[4.4.4]tetradecane (5). A 300 mL volume of pentane and the same amount of dry liquid ammonia were placed in a two-necked flask fitted with dropping funnel (without pressure compensation) and dry ice condenser. The mixture was kept at −50 °C and emulsified by vigorous stirring. A 142.4 g amount of 1,2-bis(bromosilyl)ethane (0.57 mol) was placed in the dropping funnel and added dropwise by applying a slight nitrogen pressure. The reaction proceeded very exothermically (Caution: Care must be taken to avoid sudden rise in pressure by rapid vaporization of liquid ammonia!). The resulting suspension was stirred for 1 h. Then cooling was stopped and the excess of ammonia allowed to distill off. The mixture was filtered and the pentane removed by distillation. The liquid residue was distilled under reduced pressure, and the raw product was purified by another distillation using a Spaltrrohr column to yield 17.32 g (31%) of **4**, bp 92 °C (0.1 mbar). Anal. Calcd (found) for C₆H₂₄N₂Si₆ (*M_r* = 292.78): H, 8.26 (8.23); C, 24.61 (24.39); N, 9.57 (9.72).

¹H-NMR (399.78 MHz, C₆D₆): δ = 0.83–0.85 [m, 12H, H₂C], 4.57 [m, 8H, H₂Si-cycl.], 4.62 [m, 4H, H₂Si-exocycl.]. ¹³C{¹H} NMR (100.54 MHz, C₆D₆): δ = 4.9 [s, C-endocycl.], 6.3 [s, C-exocycl.]. ¹⁵N-NMR (DEPT, 40.51 MHz, C₆D₆): δ = −383.0 [s, ¹J(NSi) = 8.6 Hz (for both Si)]. ²⁹Si-NMR (INEPT, 79.43 MHz, C₆D₆): δ = −21.9 [t m, ¹J(HSi) = 202.2 Hz, SiH₂-exocycl.], −13.2 [t m, ¹(HSi) = 211.0 Hz, SiH₂-endocycl.]. IR (film): 2128 s (ν_{SiH}). MS (GC-coupled): *m/z* = 291 [M⁺], 289 [M⁺ − 2H], 261 [M⁺ − SiH₂], 259, 233 [M⁺ − SiH₂ − C₂H₄], 189 [100%, M⁺ − H − C₂H₈NSi₂-ring], 158 [M⁺ − 2H − C₂H₁₀NSi₃], 145, 132, 102 [C₂H₈NSi₂-ring].

By repeated distillation of the lower boiling fractions (*ca.* 63 °C) using a Spaltrrohr column, the small amounts of **5** (<50 mg) can be enriched to *ca.* 79% (GC), the remainder being **4**. The spectra can be assigned as follows. ¹H NMR (399.78 MHz, C₆D₆): δ = 0.81 [m, 12H, CH₂], 4.67 [m, 12H, SiH₂]. MS (GC-coupled): *m/z* = 291 [M⁺], 261 [M⁺ − SiH₂], 233 [100%, M⁺ − SiH₂CH₂CH₂], 205 [233 − C₂H₄], 158, 145, 132, 102.

(1-Aza-2,5-disilacyclopentan-1-yl)-1,4-disilabutane (6). The procedure is the same as described for **4** using 40.64 g of 1,2-bis-(bromosilyl)ethane (0.164 mol), 100 mL of liquid ammonia, and 150 mL of pentane. As described before, the reaction mixture was filtered and the pentane removed by distillation. The resulting slightly yellow liquid was then kept at ambient temperature for 5 months, while observing the composition by occasional GC/MS analysis. After conversion of 80% of the volatile (GC) contents, the mixture was distilled using a 10 cm Vigreux column to yield 7.93 g (25%) of **6**, bp 42 °C (1 mbar). Anal. Calcd (found) for $C_6H_{24}N_2Si_6$ ($M_r = 191.53$): H, 8.95 (9.07); C, 25.08 (24.69); N, 7.31 (7.39).

1H NMR (399.78 MHz, C_6D_6): $\delta = 0.64$ [m, 2H, H_2CSiH_3], 0.75 [m, 2H, H_2CSiH_2 (endocycl.)], 0.87 [m, 2H, H_2CSiH_2 (endocycl.)], 3.61 [t, $^3J(HSiCH) = 3.6$ Hz, 3H, H_3Si], 4.53 [m, 4H, H_2Si (endocycl.)], 4.55 [t, $^3J(HSiCH) = 3.1$ Hz, 2H, H_2Si (exocycl.)]. $^{13}C\{^1H\}$ NMR (100.54 MHz, C_6D_6): $\delta = -0.7$ [s, $^1J(CSi) = 53.3$ Hz, $CSiH_3$], 5.1 [s, $^1J(CSi) = 56.1$ Hz, C(endocycl.)], 9.8 [s, $^1J(CSi) = 57.5$ Hz, $CSiH_2$ (exocycl.)]. $^{15}N\{^1H\}$ NMR (DEPT, 40.51 MHz, C_6D_6): $\delta = -393.0$ [s, $^1(NSi$ (endocycl.)) = 8.6 Hz, $^1(NSi$ (exocycl.)) = 9.7 Hz]. ^{29}Si -NMR (DEPT, 79.43 MHz, C_6D_6): $\delta = -54.8$ [q t, $^1J(SiH) = 183.5$ Hz, $^2J(SiCH) = 6.4$ Hz, $^3J(SiCCH) = 6.4$ Hz, SiH_3], -22.7 [t t t, $^1J(SiH) = 202.2$ Hz, $^2J(SiCH) = 6.3$ Hz, $^3J(SiCCH) = 6.3$ Hz, Si(exocycl.)], -13.3 [t m, $^1J(SiH) = 206.5$ Hz, Si(endocycl.)]. MS (GC-coupled): $m/z = 191$ [M^+], 190 [$M^+ - H$], 160 [$M^+ - SiH_3$], 132 [100%, $M^+ - SiH_3 - C_2H_4$], 102 [$C_2H_8NSi_2$], 72.

1-Isopropyl-1-aza-2,5-disilacyclopentane (8). A 50 mL volume of a hexane solution of 17.74 g of 1,2-bis(bromosilyl)ethane (71.4 mmol) and 50 mL of a hexane solution of 4.22 g of isopropylamine (71.4 mmol) were each placed in a dropping funnel and added simultaneously at the same rate to a triethylamine solution (14.43 g, 0.143 mol in 500 mL of hexane) with intense stirring. The resulting suspension was heated to reflux for 3 h, cooled to 0 °C, and filtered. The solvent was removed by distillation and the residue fractionally distilled (20 cm Vigreux column) to yield 7.89 g (76%) of **8**, bp 59 °C (40 mbar). Anal. Calcd (found) for $C_5H_{15}NSi_2$ ($M_r = 145.35$): H, 10.40 (10.26); C, 41.32 (40.97); N, 9.64 (9.75).

1H NMR (399.78 MHz, C_6D_6): $\delta = 0.91$ [t t, $^3J(HCSiH) = 2.6$ Hz, $^4J(HCCSiH) = 1.3$ Hz, 4H, CH_2], 1.16 [d, $^3J(HCCH) = 6.5$ Hz, 6H, CH_3], 3.28 [sept, $^3J(HCCH) = 6.5$ Hz, 1, CH], 4.57 [t t, $^3J(HSiCH) = 2.6$ Hz, $^4J(HSiCCH) = 1.3$ Hz, 4H, SiH_2]. ^{13}C NMR (100.54 MHz, C_6D_6): $\delta = 3.2$ [t t t, $^1J(CH) = 125.5$ Hz, CH_2], 25.3 [q d, $^1J(CH) = 125.5$ Hz, CH], 46.2 [d sept, $^1J(CH) = 134.7$ Hz, $^2J(CCH) = 4.3$ Hz]. $^{15}N\{^1H\}$ NMR (INEPT, 40.51 MHz, C_6D_6): $\delta = -352.8$ [s, $^1(NSi) = 14.5$ Hz]. ^{29}Si NMR (INEPT, 79.43 MHz, C_6D_6): $\delta = -24.1$ [t m, $^1J(SiH) = 201.7$ Hz]. IR (film): 2108 ss (ν_{SiH}). IR (gas): 2112 ss. MS (GC-coupled): $m/z = 145$ [M^+], 130 [$M^+ - CH_3$], 117 [$C_3H_{11}NSi_2^+$], 114, 103 [$M^+ - C_3H_6$], 102, 100, 86, 76, 72, 65, 57.

1-Isopropyl-1-aza-2,6-disilacyclohexane (9). The procedure was the same as described for **8** using 14.4 g of triethylamine (0.143 mol), 500 mL of hexane, and 50 mL of solutions of 17.74 g of bis-(bromosilyl)ethane (71.4 mmol) and 4.22 g of isopropylamine (71.4 mmol). Yield: 16.2 g of **9** (69%), bp 63 °C (22 mbar). Anal. Calcd (found) for $C_6H_{17}NSi_2$ ($M_r = 159.38$): H, 10.75 (10.86); C, 45.22 (44.89); N, 8.79 (8.64).

1H NMR (270.17 MHz, C_6D_6): $\delta = 0.71$ [m, 4H, H_2CSi], 1.14 [d, $^3J(HCCH) = 6.6$ Hz, 6H, H_3C], 1.72 [m, 2H, H_2CC_2], 3.08 [sept, $^3J(HCCH) = 6.6$ Hz, 1H, HC], 4.60 [t, $^3J(HSiCH) = 2.7$ Hz, 4H, H_2Si]. ^{13}C -NMR (100.54 MHz, C_6D_6): 11.6 [t m, $^1J(CH) = 120.2$ Hz, $^1J(CSi) = 56.1$ Hz, CH_2Si], 19.2 [t m, $^1J(CH) = 129.4$ Hz, CH_2C_2], 23.6 [q q d, $^1J(CH) = 117.2$ Hz, $^3J(CCCH) = 5.1$ Hz, $^2J(CCH) = 3.2$ Hz, CH_3], 49.7 [d sept, $^1J(CH) = 134.2$ Hz, $^2J(CCH) = 4.3$ Hz, CH]. $^{15}N\{^1H\}$ NMR (DEPT, 40.51 MHz, C_6D_6): $\delta = -362.7$ [s, $^1(NSi) = 12.4$ Hz]. ^{29}Si NMR (DEPT, 79.43 MHz, C_6D_6): $\delta = -30.9$ [t m, $^1J(SiH) = 199.6$ Hz]. MS (GC-coupled): $m/z = 159$ [M^+], 144 [100%, $M^+ - CH_3$], 130, 116 [$M^+ - H - C_3H_6$], 86, 72.

1,5-Diisopropyl-1,5-diaza-2,4,6,8-tetrasilacyclooctane (10). Two hexane solutions each 50 mL in volume, one containing 21.7 g of bis-(bromosilyl)methane (122 mmol) and the other 10.4 mL of isopropylamine (122 mmol), were dropped simultaneously into a vigorously stirred solution of 33.8 mL of triethylamine (0.24 mol) in 500 mL of hexane. The resulting suspension was heated for 3 h to reflux, slowly cooled to ambient temperature, and then filtered. A 34.2 g amount of

Table 4. Experimental Parameters for the Electron-Diffraction Measurements and Refinements

	compd 8		compd 12	
	data set 1	data set 2	data set 1	data set 2
no. of plates	3	3	4	4
camera dist (mm)	257.32	93.41	258.08	93.23
s range (\AA^{-1})				
s_{min}	2.0	12.0	2.0	12.0
s_{max}	16.4	32.8	16.4	32.8
weight points (\AA^{-1})				
s_1	4.0	14.4	4.0	14.4
s_2	14.0	30.4	14.0	30.4
s interval (\AA^{-1}): Δs	0.2	0.4	0.2	0.4
corr param	0.226	0.267	0.154	0.083
scale factor	0.834(14)	0.601(23)	0.810(5)	0.630(18)
wavelength (\AA)	0.05684	0.05687	0.05667	0.05670

triethylammonium bromide (78%) was obtained. The solvent was removed from the filtrate by a careful distillation using a 20 cm Vigreux column. The liquid residue was fractionally distilled to yield 4.2 g of **12** (26%), bp 36 °C (0.1 mbar). Anal. Calcd (found) for $C_8H_{26}N_2Si_4$ ($M_r = 262.65$): H, 9.98 (10.13); C, 36.58 (36.41); N, 10.67 (10.43).

1H NMR (399.78 MHz, $CDCl_3$): $\delta = 0.22$ [m, 4H, H_2CSi_2], 1.20 [t, $^3J(HCCH) = 6.7$ Hz, 12H, H_3C], 3.27 [sept, $^3J(HCCH) = 6.7$ Hz, 2H, HC], 4.50 [t m, $^3J(HSiCH) = 3.7$ Hz, 8H, H_2Si]. $^{13}C\{^1H\}$ NMR (100.54 MHz, $CDCl_3$): $\delta = 0.9$ [s, CSi], 25.2 [s, CH_3], 49.4 [s, CH]. $^{15}N\{^1H\}$ NMR (DEPT, 40.51 MHz, $CDCl_3$): $\delta = -360.6$ [s, $^1(NSi) = 16.5$ Hz]. ^{29}Si NMR (DEPT, 79.43 MHz, $CDCl_3$): $\delta = -22.5$ [t m, $^1J(SiH) = 204.0$ Hz].

Electron Diffraction. Electron scattering intensity data for **8** and **12** were recorded on Kodak electron image plates using the Edinburgh gas diffraction apparatus.²⁷ The samples of **8** and **12** were held at 22 and 48 °C and the inlet nozzle at 86 and 88 °C, respectively, during the experiments. Scattering data for benzene were recorded concurrently and used to calibrate the camera distance and electron wavelength, which are given in Table 1. Data were obtained in digital form using the Joyce Loebel MDM6 microdensitometer²⁸ at the EPSRC Daresbury Laboratory. The data analysis followed standard procedures, using established data reduction²⁸ and least-squares refinement programs²⁹ and the scattering factors established by Fink and co-workers.³⁰ Further parameters are listed in Table 4; the correlation matrices are given in the Supporting Information.

Crystal Data for 12. $C_8H_{14}N_2Si_2$: $M = 146.35$, monoclinic, space group $P2_1/c$, $a = 10.050(3)$ Å, $b = 8.547(4)$ Å, $c = 9.878(3)$ Å, $\beta = 95.20(3)^\circ$, $V = 845.0(5)$ Å³ [from 44 reflections, $28 \leq 2\theta \leq 32^\circ$, $\lambda = 0.71073$ Å, $T = 110.0(2)$ K], $Z = 4$, $D_{calcd} = 1.115$ Mg m⁻³, $\mu(Mo K\alpha) = 0.338$ mm⁻¹. A colorless crystal cylinder was grown by cooling the sample sealed in a glass capillary from 160.5 to 158.5 K at a rate of 10 K h⁻¹ (after growing a suitable seed crystal) on a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems open-flow cryostat³¹ and graphite-monochromated Mo $K\alpha$ X-radiation. Empirical absorption correction by ψ -scans was applied ($T_{min,max}$: 0.711 and 0.846). A total of 2693 reflections of which 2467 were independent ($R_{int} = 0.0277$) were collected to $2\theta_{max} = 60^\circ$ as ω - θ scans. Of these 1888 had $F_o \geq 4\sigma(F_o)$. The structure was solved by direct methods using SHELXTL/PC³² and refined on F_o^2 using SHELXL93³³ with non-H atoms allowed anisotropic thermal motion. After their location in a Fourier difference synthesis the H atoms could be refined

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isotropically without geometrical restraints. With the weighting scheme $w^{-1} = \sigma^2(F_o^2) + (0.0564P)^2$, $P = 1/3[\text{MAX}(F_o^2, 0) + 2F_c^2]$ final convergence gave conventional $R_1[F_o \geq 4\sigma(F_o)] = 0.0390$ and $wR_2[F_o^2, \text{all data}] = 0.0987$ for 130 refined parameters, with $S[F^2] = 1.029$. A secondary extinction correction³³ refined to 0.1401(75), and the final Fourier difference synthesis had no feature outside the range $+0.45 \rightarrow -0.45 \text{ e } \text{\AA}^{-3}$.

Ab Initio Calculations. *Ab initio* molecular orbital calculations were carried out on the systems **8** and **12** using the Gaussian 92 program.³⁴ Geometries were optimized at the SCF level using the standard 3-21G*³⁵⁻³⁷ and 6-31G*^{38,39} basis sets. The larger basis set was also applied for final optimizations at the MP2 level of theory, and the "frozen core" approximation was used; *i.e.* only valence electrons were considered in the electron correlation treatment.⁴⁰ Harmonic vibrational frequencies calculations were obtained from analytical first and second

derivatives at the SCF level of theory. Molecular geometries and absolute energies are reported in the tables and the Supporting Information.

Acknowledgment. This work has been supported by the EPSRC (Research Grant GR/K04194) and the European Union (Marie Curie fellowship for N.W.M.). We are grateful to Drs. A. J. Blake, P. T. Brain, and H. E. Robertson for establishing the crystallographic and electron diffraction data sets and to the EPSRC Daresbury Laboratory for microdensitometer facilities.

Supporting Information Available: A total of Cartesian coordinates of the calculated structures of **8** and **12** at the MP2/6-31G* level of theory, graphs of the observed and final weighted difference combined molecular intensity curves for the GED studies of **8** and **12**, a table of selected interatomic distances and amplitudes, and full correlation matrix tables for the GED refinement of **8** and **12** (6 pages). An X-ray crystallographic file, in CIF format, is available on the Internet only. Ordering and access information is given on any current masthead page.

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