Novel Five- and Six-Membered Diazasilacycloalkanes: Synthesis, Structure and Properties

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

The reactions of N,N'-dimethylethylenediamine 1 and N,N'-diphenylethylenediamine 2 with equimolar amounts of 1,2-dichlorotetramethyldisilane 3 give six-membered heterocycles. Fivemembered rings are formed in the reaction of the diamines \mathbf{I} and $\mathbf{2}$ with 1,1,2,2-tetrachlorodimethyldisilane 4 as well as with hexachlorodisilane 5. Whilst the conversions of the disilanes 3 and 4 with the diamine 2 gave no products of a disproportionation reaction, the treatment of the disilane 4 with the diamine 1 and of the disilane 5 with both diamines resulted in cyclic aminosubstituted monosilanes which originate from the disproportionation of 4 and 5 beside the expected five-membered cyclic disilanes. All compounds have been characterized by multi-nuclear NMR, IR and mass spectroscopy. In case of the N-phenylsubstituted compounds 6, 7 and 9 the crystal structures have been determined by X-ray diffraction analysis. Bis-[N,N'-diphenyl-2-methyl-1,3-diaza-2-silacyclopentane] 6 crystallizes in the chiral orthorhombic space group $P2_12_12_1$ (Z = 4). Both silaimidazolidine rings in **6** show half chair conformation. All nitrogen atoms of this molecule are almost planarized (sum of angles: 356.3° at N1, 359.5° at N2, 356.7° at N3 and 357.5° at N4). Bis-[N,N'-diphenyl-2-chloro-1,3-diaza-2-silacyclopentane] 7, resulting from the reaction of disilane 5 with diamine 2, crystallizes in the orthorhombic space group Pbcn (Z = 4). Its nitrogen atoms are almost planar (sum of angles: 357.9° at N1, 356.7° at N2). N,N'-diphenyl-2,2,3,3-tetramethyl-1,4-diaza-2,3-disilacyclohexane 9 crystallizes in the chiral monoclinic space group $P2_1$ (Z = 2) and shows a twisted conformation. One nitrogen atom has a trigonal planar environment (sum of angles: 359.9° at N1), while the angle sum of the second one indicates a trigonal pyramidal conformation (sum of angles at N2: 350.6°).

Key words: Aminosilane, Disilane, Heterocycle, Diazasilacyclopentane, Diazadisilacyclohexane

Introduction

The chemistry of silicon-nitrogen compounds has been extensively investigated because of their potential use as precursors for silicon nitride ceramics [1]. Simple linear and cyclic aminosilanes are also interesting model compounds to study SiN polymer systems [2]. Thus, it seems useful to characterize such molecular silanes by different methods of structure analysis. Acyclic aminooligosilanes [3] as well as cyclic aminomonosilanes [4–8] have been described, and the first synthesis of cyclic aminosilanes was carried out by Yoder and Zuckerman [4]. The characterization of those molecules was rather scarce before recent investigations of Schmidbaur *et al.* [6] filled this void. However, the chemistry of cyclic aminooligosilanes has hardly been investigated till now [9]. In this paper we report results concerning the syntheses, physical properties and structural features of cyclic aminosubstituted disilanes: 1,3-diaza-2-silacyclopentanes with methyland chlorosubstituted silicon atoms and 2,2,3,3-tetramethyl-1,4-diaza-2,3-disilacyclohexanes (Scheme 1).



Scheme 1.

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Results and Discussion

Preparation of the cyclic aminodisilanes

The desired compounds were synthesized by reacting various chlorodisilanes (3, 4, 5) with equimolar amounts of the appropriate *N*,*N*'-diorganoethylenediamines (1 and 2). The reactions were carried out in *n*-hexane/toluene with an excess of triethylamine (Scheme 2). Competing disproportionation of the disilane (additionally to Si-Cl substitution) was observed in case of the reactions of disilane **4** with diamine **1** and hexachlorodisilane **5** with both diamines **1** and **2**.

The treatment of 1,1,2,2-tetrachlorodimethyldisilane **4** with N,N'-diphenylethylenediamine **2** solely yielded aminosilanes **6** and **8**, respectively, with fivemembered heterocyclic moieties. Hetero[4.4]bicyclohexane molecules were not detected. In contrast, the reaction of the disilane **4** with N,N'-dimethylethylenediamine **1** as well as the reactions of hexachlorodisilane **5** with both diamines **1** and **2** yielded a more complex product mixture. Beside the expected dimeric diazasilacyclopentanes (**7**, **10**, **11**) it additionally consisted of aminosubstituted products (**7a**, **7b**, **10a**, **11a**, **11b**) of the primary disilane disproportionation reaction of **4** and **5** (Scheme 3).

Surprisingly, cyclic aminosilanyl hydrides were detected in the resulting product mixture. The disproportionation reaction of **4** and **5** is the supposed origin of the monosilanes **4a** and **5a** and the silylenes **4b** and **5b**, respectively. From the reaction of disilane **4** with diamine **1** only the monosilane **10a** formed by the reaction of trichloromethylsilane **4a** with the diamine **1** was isolated. Tetrachlorosilane **5a** reacted with the

Lewis-base R = Me (4), Cl (5) Me (4a), Cl (5a) R = Me (4b), Cl (5b) 2 i 7a (R = C)7b (R = Cl, R' 11b (R = Cl, R' R' = Ph) 10a (R = R' = Me) 7 (R = Cl, R' = Ph) 10 (R = R' = Me) 11 (R = Cl, R' = Me) 11a (R' = Me) NEt₃ / - [HNEt₃]C ·ŃН ΗŃ 1 (R' = Me), 2 (R' = Ph) Lewis-base = NEt₃ or diamines 1 or 2

Scheme 3.

diamines 1 and 2 to give the mono- and spirocyclic aminosilanes 7a [6b] and 11a, respectively. Moreover, the dichlorosilylene 5b inserted into the N-H bond of the diamines 1 or 2. The subsequent ring closure under HCl-elimination yielded the monocyclic aminosilanes 7b and 11b. Coupled ²⁹Si NMR spectra were analyzed to obtain an unequivocal structural proof for the formation of these Si-H derivatives.

Scheme 2.



Fig. 1. Molecular structures of the silaimidazolidines a) bis-[N,N'-diphenyl-2-methyl-1,3diaza-2-silacyclopentane] **6** and b) bis-[N,N'-diphenyl-2-chloro-1,3-diaza-2-silacyclopentane] **7** (ORTEP plot, 50% probability ellipsoids), hydrogen atoms are omitted for clarity.

X-ray structure analysis of the five-membered cycles bis-[N,N'-diphenyl-2-methyl-1,3-diaza-2-silacyclopentane] (**6**) and bis-[N,N'-diphenyl-2-chloro-1,3-diaza-2-silacyclopentane] (**7**)

The molecular structures of the N,N'-diphenylethylenediamine substituted disilanes **6** and **7** are shown in Fig. 1. Selected bond lengths and angles are listed in Table 1, crystal data as well as data collection and refinement details are given in Table 5.

Compound **6** crystallizes in the chiral orthorhombic space group $P2_12_12_1$ with 4 molecules in the unit cell. In case of **7** we found a space filling pattern according to the centrosymmetric orthorhombic space group *Pbcn* (Z = 4). The molecules of **7** have a twofold axis of symmetry (Fig. 1b). Both heterocycles exhibit dimeric silaimidazolidine skeletons. Unlike the situation in some of the reported monomeric silaimidazolidines with planar five-membered rings, our novel heterocyclopentanes show a half chair configuration, exhibiting one of the carbon atoms above and one slightly below the N-Si-N plane (Fig. 2).

The torsion angles C1-Si1-Si2-C16 $[-81.8(1)^{\circ}]$ in **6** and C11-Si1-Si1'-C11' $[-103.07(6)^{\circ}]$ in **7** indicate staggered conformation in each case due to the bulky phenyl substituents at the nitrogen



Fig. 2. The twisted ring skeletons of a) bis-[N,N'-diphenyl-2-methyl-1,3-diaza-2-silacyclopentane] **6** and b) bis-[N,N'-diphenyl-2-chloro-1,3-diaza-2-silacyclopentane] **7** (ORTEP plot, 50% probability ellipsoids), H-atoms and phenyl groups are omitted for clarity.

Table 1. Selected bond lengths [Å], angles [°] and dihedral angles [°] of $\mathbf{6}$ and $\mathbf{7}$.

	6	7
Si1-Si2(Si1')	2.373(1)	2.382(2)
Si1-N1	1.746(2)	1.710(3)
Si1-N2	1.740(2)	1.714(3)
Si2(Si1')-N3(N1')	1.745(2)	1.710(3)*
Si2(Si1')-N4(N2')	1.744(2)	1.714(3)*
N1-C2	1.465(3)	1.476(5)
N1-C4	1.402(3)	1.406(5)
N2-C3	1.468(3)	1.463(4)
N2-C10	1.401(3)	1.409(5)
C2-C3	1.526(3)	1.506(6)
C17(C2')-C18(C3')	1.517(4)	1.506(6)*
N1-Si1-N2	92.62(9)	94.9(2)
N1-Si1-C1(Cl1)	114.1(1)	111.9(1)
N1-Si1-Si2(Si1')	108.56(8)	110.5(1)
N1-C2-C3	108.4(2)	108.1(3)
N2-Si1-C1(Cl1)	111.6(1)	111.6(1)
N2-Si1-Si2(Si1')	113.53(7)	119.0(1)
N2-C3-C2	108.7(2)	109.0(3)
N3(N1')-Si2(Si1')-N4(N2')	92.96(9)	94.9(2)*
N3(N1')-Si2(Si1')-C16(Cl1')	112.2(1)	111.9(1)*
N3(N1')-Si2(Si1')-Si1	109.39(8)	110.5(1)*
N3(N1')-C17(C2')-C18(C3')	108.4(2)	108.1(3)*
N4(N2')-Si2(Si1')-C16(Cl1')	112.3(1)	111.6(1)*
N4(N2')-Si2(Si1')-Si1	112.24(8)	119.0(1)*
N4(N2')-C18(C3')-C17(C2')	109.0(2)	109.0(3)*
C1(Cl1)-Si1-Si2(Si1')-C16(Cl1')	-81.8(1)	-103.07(6)
C1(Cl1)-Si1-Si2(Si1')-N3(N1')	150.5(1)	134.0(1)
C1(Cl1)-Si1-Si2(Si1')-N4(N2')	48.8(1)	25.9(1)
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* Symmetry derived by local twofold symmetry.

atoms in the silaimidazolidine skeletons. The nitrogen atoms of the molecules **6** and **7** are almost planarized (sum of angles **6**: 356.3° at N1, 359.5° at N2, 356.7° at N3 and 357.5° at N4; sum of angles **7**: 357.9° at N1, 356.7° at N2). The Si-N bond lengths in **6** [1.740(2)–1.746(2) Å] and **7** [1.710(3)–1.714(3) Å] are in the usual range of silylamines {*e.g.* 1.718(2) Å in MeCl(PhMeN)Si-Si(NMePh)ClMe [3d], 1.733(7)–1.746(6) Å in bis-[*N*,*N*'-bis-(trimethylsil-





Fig. 3. Molecular structure of a) 1,4-diaza-2,3disilacyclohexane **9** with atomic numbering scheme and b) sideview of the cyclohexane ring in **9** (ORTEP plot, 50% probability ellipsoids, H-atoms at arbitrary size).

yl)-2-methyl-1,3-diaza-2-silacyclopentane] [9b], 1.7373(19) - 1.7508(18) Å in bis-[N,N'-di-^tbuty]-1,3-diaza-2-silacyclopentane] [9c]}. The Si-Si bond lengths [2.373(1) Å in 6, 2.382(2) Å in 7] are typical for tetracoordinated organodisilanes. In addition, C-C distances of the ethylene bridges [C-C: 1.526(3) and 1.517(4) Å in 6, 1.506(6) Å in 7] are in the range of typical C-C single bonds and correspond to the results of Schlosser et al. [6b] [the heterocycles are slightly twisted, C-C bond lengths: 1.522(2) Å-1.534(4) Å, Si-N bond lengths: 1.675(2) Å-1.705(2) Å], Diedrich et al. [8] [twisted ring structure, C-C bond length: 1.511(3) Å, Si-N bond lengths: 1.724(2) - 1.739(2) Å] and Haaf et al. [9c] [C-C bond length: 1.5214(17) Å, Si-N bond lengths: 1.738(1)-1.738(1) Å] for silaimidazolidine structures.

X-ray structure analysis of the six-membered cycle N,N'-diphenyl-2,2,3,3-tetramethyl-1,4-diaza-2,3-di-silacyclohexane (9)

The molecular structure of **9** is shown in Fig. 3. Selected structural parameters are listed in Table 2, crystal data as well as data collection and refinement details are given in Table 5.

Compound **9** crystallizes in the chiral monoclinic space group $P2_1$ (Z = 2). The six-membered heterocycle **9** has a twisted configuration (see Fig. 3b). The torsion angles within the 1,4-diaza-2,3-disilacyclohexane ring are 19.95(7)° along N1-Si1-Si2-N2 and 76.5(2)° along N1-C1-C2-N2. The sum of angles at the nitrogen atom N1 indicates a planar conformation (359.9°), but N2 is significantly pyramidalized (sum of angles: 350.6°). Contrary to the expectation, the different configurations at the nitrogen atoms N1 and N2 are not reflected in the Si-N distances [Si1-N1: 1.757(1) Å, Si2-N2: 1.751(2) Å]. A significant pyramidalization of the nitrogen atom N2 should cause a lengthening of the Si2-N2 bond compared with the distance Si1-N1 due

Table 2. Selected bond lengths [Å], angles [°] and dihedral angles [°] of **9**.

0 1 1			
Si1-Si2	2.337(1)	Si1-N1	1.757(1)
Si1-C3	1.877(2)	Si1-C4	1.875(2)
Si2-N2	1.751(2)	Si2-C5	1.875(2)
Si2-C6	1.864(2)	N1-C1	1.476(2)
N1-C7	1.405(2)	N2-C2	1.477(2)
N2-C13	1.427(2)	C1-C2	1.513(3)
N1-Si1-C3	111.66(9)	N1-Si1-C4	112.3(1)
C3-Si1-C4	108.6(1)	N1-Si1-Si2	104.81(5)
C3-Si1-Si2	110.99(8)	C4-Si1-Si2	108.41(9)
N2-Si2-C5	112.4(1)	N2-Si2-C6	110.8(1)
C5-Si2-C6	108.9(2)	N2-Si2-Si1	102.85(5)
C5-Si2-Si1	110.8(1)	C6-Si2-Si1	111.00(9)
C7-N1-C1	114.7(1)	C7-N1-Si1	124.2(1)
C1-N1-Si1	121.0(1)	C13-N2-C2	116.6(1)
C13-N2-Si2	119.2(1)	C2-N2-Si2	114.8(1)
N1-C1-C2	116.8(2)	N2-C2-C1	113.8(2)
N1-Si1-Si2-N2	19.95(7)	N1-C1-C2-N2	76.5(2)
C3-Si1-Si2-C6	17.8(1)	C4-Si1-Si2-C5	19.8(1)
Si1-N1-C7-C8	19.5(2)	Si2-N2-C13-C18	61.2(2)

to the weakened π -donor action of N2. Such effects are not obvious from the molecular structure, but the conformations of the nitrogen atoms remarkably influence the ²⁹Si NMR shifts of Si1 and Si2 in the solid state.

The Si1-Si2 distance [2.337(1) Å] is slightly shorter than in **6** [2.373(1) Å] and **7** [2.382(2) Å]. Both silicon atoms have an almost tetrahedral conformation.

NMR spectra

The ¹H, ¹³C, ¹⁵N and ²⁹Si NMR spectroscopic data of the dimeric heterocycles 6-13 are gathered in Table 3. The dependence of the ¹⁵N chemical shifts on the heterocycles' ring size is demonstrated in Fig. 4a.

The ¹⁵N NMR investigations of cyclic aminosubstituted monosilanes of Schlosser *et al.* [6b] did not reveal any significant effect by replacing the small substituents at the nitrogen atoms by bulky groups. Our results display significant shifts to higher fields upon



Table 3. ¹H, ¹³C, ²⁹Si (δ in ppm relative to TMS) and ¹⁵N NMR shifts (δ in ppm relative to CH₃NO₂).

Compound	$^{1}\mathrm{H}$	¹³ C	²⁹ Si	¹⁵ N
6	0.75 (s)	4.4	-5.0	-313
	2.90 (m)	44.6		
	3.27 (m)	114.8		
	6.65 (m)	117.8		
	6.77 (m)	129.1		
	7.17 (m)	147.2		
7	2.94 (m)	44.2	-26.4	-315
	3.28 (m)	116.0		
	6.90 (m)	120.0		
	7.19 (m)	129.0		
		144.7		
8	0.58 (s)	0.3	-4.9 (Si ^A)	-313
	0.88 (s)	8.3	22.0 (Si ^B)	
	3.64 (m)	45.4	${}^{1}J_{\rm SiSi} = 133 {\rm Hz}$	
	6.90 (m)	115.4	5.51	
	7.26 (m)	119.1		
		129.4		
		146.4		
9	0.39 (s)	0.0	-7.6	-317
	3.67 (s)	52.5		
	6.86 (m)	117.8		
	7.21 (m)	118.8		
		128.7		
		150.9		
10	0.30(s)	-6.2	-14.0	-362
	2.70(s)	33.8		
	2.75/2.77 (m)	51.1		
11	2.70 (s)	33.6	-25.1	-364
	3.21 (s)	51.2		
12	0.69 (s)	0.2	-1.3 (Si ^A)	_
	0.92 (s)	7.0	21.0 (Si ^B)	
	2.66(s)	36.4		
	3.27/3.30 (m)	52.6		
13	0.44 (s)	-2.0	-9.5	-366
	2.79 (s)	37.6	${}^{1}J_{\rm SiC} = 47 {\rm Hz}$	2.50
	3.18 (s)	54.6	- SIC 17 112	
	0.10 (0)	00		

Fig. 4. a) 15 N NMR and b) 29 Si NMR chemical shifts in 1,3-diaza-2-sila-cycloalkanes (6, 7, 10 and 11) and 1,4-diaza-2,3-disilacycloalkanes (9 and 13).

substitution of NPh (-313, -315 and -317 ppm) by NMe (-362, -364 and -366 ppm) in the disilanes (see Fig. 4a). These results are in good agreement with the investigations of Wrackmeyer [10], Martin [11] and Witanowski [12]. However, we did not observe any indication for a dependence of δ (¹⁵N) on the substitution pattern of the silicon atom.

The ²⁹Si chemical shift values of our novel diazasilacycloalkanes are shown in Figure 4b. The ²⁹Si NMR data monitor a great variation depending on the directly Si-bonded substituents, the organic groups at the nitrogen atoms as well as the ring size of the heterocycle. As expected, substitution of the methyl group for chlorine at the silicon atom gives rise to strong $\delta(^{29}\text{Si})$ upfield shift in the investigated 1,3-diaza-2silacyclopentanes. However, the substituents situated further away influence the chemical shift of the silicon atom as well. Upon replacing the NMe group (10, 13) by a NPh group (6, 9) an upfield shift of the 29 Si NMR resonance in both the five- and the six-membered heterocycles is observed. Although the silicon atom causes a significant planarization of Si-linked nitrogen atoms, this effect is additionally supported by bulky groups or substituents with π -electron systems at the nitrogen atom. Therefore a better N \rightarrow Si π -donor interaction is supported with the NPh substituent. The results of ²⁹Si CP MAS NMR investigations of the NPh substituted disilanes 6, 7 and 9 have pointed out the great influence of the geometrical environment around the silicon atoms on their NMR characteristics. The ²⁹Si CP MAS NMR spectrum of compound 9 clearly shows the influence of the two different conformations of the nitrogen atoms on the ²⁹Si chemical shift value.



Fig. 5. Coupled and decoupled (insert) 29 Si NMR spectra of the product mixture obtained by the reaction of the disilane 5 with diamine 2.

The silicon atom substituted by the pyramidalized NPh group is less shielded (-0.5 ppm), but the resonance of the silicon atom at the planarized nitrogen atom shows an upfield shift (-14.2 ppm) compared with the ²⁹Si chemical shift detected for **9** in CDCl₃ solution (-7.6 ppm).

The formation of amino cycles with Si-H moieties was verified by the analysis of coupled 29 Si NMR spectra. The coupled and decoupled 29 Si NMR spectra of the product mixture obtained by the reaction of the disilane **5** and diamine **2** are exhibited in Figure 5 as representative examples.

The ²⁹Si peak of the SiH group centered at –29.3 ppm (see the decoupled ²⁹Si NMR spectrum in Fig. 5, insert) is split into a doublet due to the ¹J(²⁹Si-¹H) coupling. The values of ¹J(²⁹Si-¹H) (**7b**: ¹J_{SiH} = 309 Hz; **11b**: ¹J_{SiH} = 236 Hz) are typical for silicon hydrides with electronegative substituents [13, 14].

The ¹H NMR data of the investigated compounds correlate well with the results of the X-ray structure analyses. The spectra of the ring systems with NPh as well as NMe substituents (of the Si-Me substituted compounds **6**, **8**, **9**, **10**, **12**, **13**) consist of three distinct peaks or groups of peaks (the SiCH₃, the ring CH₂ and the NMe or NPh group). The protons of the ethylene bridge of our five-membered heterocycles appear both as a singulet and a multiplet. The shape of the signal of the ethylene protons depends on the substituents at the



Fig. 6. Bis-[*N*,*N*'-diphenyl-2-methyl-1,3-diaza-2-silacyclopentane] **6** shows a complex ¹H NMR spectrum due to the mutual coupling of the protons of the CH₂ group above and below the ring (ABA'B' system).

ring silicon atom. In case of two different substituents there is no bisecting plane containing the ring. Thus, there are diastereotopic CH_2 protons above and below the ring and a complex spectrum (ABA'B' pattern) due to the mutual coupling of these protons is emerging (see Fig. 6). The NMe substituted six-membered heterocycle **13** was already isolated by Wannagat and Eisele [9a]. Our ¹H chemical shifts of **13** are well in accordance with their results.

The ¹H NMR spectra of compounds **7** and **11** exhibit signals of the ring CH_2 as well as the NPh and the NMe group, respectively.

IR spectra

Selected characteristic vibrations in the IR spectra of the five- and six-membered rings are given in Table 4.

The ring size as well as the substituent at the nitrogen atom influence the values of the typical frequencies in the IR spectra of silylamines. Henglein and Lienhard [15] assigned the absorption in the region between $950-930 \text{ cm}^{-1}$ to the v_{as} (Si-N) bond stretching mode in silaimidazolidine derivatives. They have also noted that the rather sharp absorption at 1350 cm⁻¹ is characteristic in case of the five-membered cycle, but it is absent in acyclic silylamines. The experimental results of Yoder and Zuckerman [4b] revealed a larger range regarding the silicon-nitrogen bond vibrations (970–930 cm⁻¹). Comparison of spectra from acyclic and cyclic silylamines exhibit that both monoand spirocyclic silaimidazolidines contain three bands

Compound	IR	
6	1356	v Ring
	1251	$\delta_{\rm s}$ SiMe
	1116, 1104, 1092	v CN
	943	$v_{\rm as}$ SiN
	749, 727, 689	v SiC
	442	v SiSi
7	1359	v Ring
	1118, 1100, 1093	v CN
	947	$v_{\rm as}$ SiN
	557	v SiCl
	469	v SiSi
8	1352	v Ring
	1252	$\delta_{\rm s}$ SiMe
	1111	v CN
	949	$v_{\rm as}$ SiN
	753, 690	v SiC
	522	v SiCl
	494	v SiSi
9	1326	v Ring
	1269, 1249	δ_{s} SiMe
	1118	v CN
	965, 953	$v_{\rm as}$ SiN
	765, 750, 724, 693	v SiC
	_	v SiSi
10	1323	v Ring
	1253	$\delta_{\rm s}$ SiMe
	1116	v CN
	932	v _{as} SiN
	752, 696	v SiC
	474	v SiSi
11	1348	v Ring
	1124, 1095	v CN
	937	v _{as} SiN
	542	v SiCl
	458	v SiSi
13	1314	v Ring
	1244	δ_{s} SiMe
	1123	v CN
	908	v _{as} SiN
	758, 713, 682	v SiC
	_	v SiSi

Table 4. Selected IR frequencies $[cm^{-1}]$.

in the region 1380-1330 cm⁻¹, but only two bands in the spectra of the acyclic derivatives. Our results are in good agreement with those data. Three bands in the 1360-1310 cm⁻¹ region are observed for the herein presented five-membered heterocycles. Our sixmembered ring systems exhibit similar IR spectroscopic behavior (1380-1310 cm⁻¹), but one of those three bands is significantly shifted to lower wave numbers. In the same way this absorption is shifted to lower frequencies if NPh is exchanged for NMe.

No distinct trend is found regarding the influence of the substitution pattern on the Si-Si and the Si-C stretching vibrations. Most likely, there are various interfering effects. Nevertheless, the v_{SiMe} and v_{CN} frequencies characterize independently vibrating groups, as expected.

Conclusion

N-Phenyl and *N*-methyl substituted cyclic aminosilanes were prepared and characterized by multinuclear NMR and IR spectroscopy. Correlations between ²⁹Si and ¹⁵N NMR shifts as well as IR spectroscopic data and the silaheterocycles' substitution patterns were found.

N,N'-Diphenylethylenediamine is a suitable starting material for preparing well defined crystalline cyclic aminodisilanes. A more detailed insight in the influence of the molecules' geometrical properties on their spectroscopic behavior is offered by the results of Xray structure analyses of three novel cyclic aminodisilanes.

Experimental Section

General remarks

NMR spectra were recorded in CDCl₃ with TMS as internal standard on a Bruker DPX 400 spectrometer at 40.544, 79.495, 100.613 and 400.130 MHz for ¹⁵N, ²⁹Si, ¹³C and ¹H. CH₃NO₂ ($\delta_N = 0$ ppm) in CDCl₃ was used as external standard for ¹⁵N NMR spectra. ²⁹Si CP MAS NMR spectra were recorded on a Bruker AvanceTM 400 MHz WB.

IR spectra $(4000-400 \text{ cm}^{-1})$ were measured with a Nicolet-FT-IR spectrometer using pressed KBr pellets or films on KBr plate techniques.

Mass spectra were recorded on a Hewlett Packard 5971 (ionisation energy: 70 eV, column: 30 m \times 0.25 mm \times 0.25 μ m, phenylmethylpolysiloxane, column temperature: 80 °C (3 min)/20 °C/min, flow: He 0.5 ml/min).

Starting materials: The N,N'-substituted ethylenediamines **1** and **2**, triethylamine (NEt₃) as well as hexachlorodisilane **5** were commercially available. N,N'-Dimethylethylenediamine **1** was distilled from CaH₂ prior to use. N,N'-Diphenylethylenediamine **2** was dried in vacuum. Triethylamine and the solvents (*n*-hexane, toluene) were dried over KOH and distilled from sodium wire. 1,2-Dichlorotetramethyldisilane **3** and 1,1,2,2-tetrachlorodimethyldisilane **4** were prepared as previously described [16]. All reactions were carried out under argon using standard Schlenk techniques.

Bis-[N,N'-diphenyl-2-methyl-1,3-diaza-2-silacyclopentane] (6)

12.7 g (60 mmol) **2** and 22.9 g (226 mmol) NEt₃ were dissolved in toluene and stirred at ambient temperature. 6.45 g (28 mmol) 1,1,2,2-tetrachlorodimethyldisilane **4**, dissolved

in *n*-hexane, were added dropwise. After heating to 70 °C for one hour and stirring at ambient temperature overnight the solvents were removed in vacuum and replaced by *n*-hexane. Filtration from precipitated NEt₃·HCl and removal of the solvent yielded the disilane **6** as colorless crystalline residue (33% yield, 4.7 g). Single crystals of **6** were grown from a solution in *n*-hexane.

¹H NMR: $\delta = 0.79$ (s, 6 H, SiCH₃), 2.93 – 2.97 and 3.30 – 3.34 (m, 4 H, ~N-CH₂-CH₂), 6.68 – 7.24 (m, 20 H, ~N-C₆H₅). – ¹³C NMR: $\delta = 4.4$ (SiCH₃), 44.7 (N-CH₂-CH₂), 114.9 (C_{ortho}), 117.9 (C_{para}), 129.1 (C_{meta}), 147.3 (C_{ipso}). – ²⁹Si: $\delta = -5.0$ (CDCl₃). – ²⁹Si CP MAS: $\delta = -2.9 / -3.8. - ^{15}N$: $\delta = -313. -$ GC/MS: m/z (%) = 506 (27) [M], 491 (2) [M–CH₃], 429 (1) [M–C₆H₅], 388 (12) [M–N(C₆H₅)C₂H₄], 253 (100) [M/2]. – C₃₀H₃₄N₄Si₂ (506.79): calcd. C 71.10, H 6.76, N 11.06; found C 71.90, H 7.08, N 11.23.

Bis-[N,N'-diphenyl-2-chloro-1,3-diaza-2-silacyclopentane] (7)

The amines 2 (7.9 g, 37 mmol) and NEt₃ (9.4 g, 93 mmol) were dissolved in toluene. 5.0 g (19 mmol) hexachlorodisilane 5, dissolved in *n*-hexane, were added dropwise to the stirred mixture of amines. After stirring at ambient temperature overnight the solvents were removed in vacuum and replaced by *n*-hexane. Filtration from precipitated NEt₃·HCl and removal of the solvent yielded the desired product 7 as colorless crystalline solid beside the monomeric by-products 7a and 7b. Recrystallization from *n*-hexane yielded 21% (2.1 g) of 7. Single crystals of 7 were grown from a solution in *n*-hexane.

¹H NMR: $\delta = 2.91 - 2.95$ and 3.28 - 3.30 (m, 4 H, ~N-CH₂-CH₂), 6.86 - 7.21 (m, 20 H, ~N-C₆H₅). – ¹³C NMR: $\delta = 44.2$ (N-CH₂-CH₂), 116.0 (C_{ortho}), 120.0 (C_{para}), 129.0 (C_{meta}), 144.7 (C_{ipso}). – ²⁹Si: $\delta = -26.4$ (CDCl₃). – ²⁹Si CP MAS: $\delta = -24.9$. – ¹⁵N: $\delta = -315$. – C₂₈H₂₈Cl₂N₄Si₂ (546.64): calcd. C 61.41, H 5.15, Cl 12.95, N 10.23; found C 62.40, H 5.48, Cl 13.9, N 10.10.

(2,2-Dichloro-N,N'-diphenyl-1,3-diaza-2-silacyclopentane) (7a)

¹H NMR: δ = 3.33 – 3.41 (m, 4 H, ~N-CH₂-CH₂), 6.96 – 7.24 (m, 20 H, ~N-C₆H₅). – ¹³C NMR: δ = 43.1 (N-CH₂-CH₂), 115.6 (C_{ortho}), 120.6 (C_{para}), 129.3 (C_{meta}), 143.5 (C_{ipso}). – ²⁹Si: δ = –33.5. – GC/MS: m/z (%) = 308 (100) [M], 231 (3) [M-C₂H₅], 204 (20) [M-N(C₆H₅)CH₂], 154 (8) [M-2·C₆H₅].

(2-Chloro-N,N'-diphenyl-1,3-diaza-2-silacyclopentane) (**7b**)

¹H NMR: $\delta = 3.33 - 3.41$ (m, 4 H, ~N-CH₂-CH₂), 5.95 (s, 1 H, Si-H, ¹*J*_{SiH} = 309 Hz), 6.79 - 6.90 (m, 20 H, ~N-

C₆H₅). 13 C NMR: δ = 43.8 (N-CH₂-CH₂), 115.1 (C_{ortho}), 119.8 (C_{para}), 129.3 (C_{meta}), 144.9 (C_{ipso}). 29 Si: δ = $^{-29.3}$ (d, $^{1}J_{SiH}$ = 309 Hz). $^{-1}$ R (KBr): v = 2186 cm⁻¹ (w, Si-H).

2-Dichloromethylsilyl-2-methyl-N,N'-dimethyl-1,3-diaza-2silacyclopentane (**8**)

A solution of 1,1,2,2-tetrachlorodimethyldisilane (12.0 g, 53 mmol) and NEt₃ (15.0 g, 149 mmol) in toluene was cooled to 0 °C. Then 11.0 g (52 mmol) **2**, dissolved in toluene, were added dropwise to the mixture. The suspension was stirred for 1 h at 0 °C before the precipitated NEt₃·HCl was filtered off. The solvent was evaporated in vacuum. Extraction of the solid residue with *n*-hexane yielded 13.3 g (70%) of **8**.

¹H NMR: $\delta = 0.58$ (s, 3 H, SiCH₃), 0.88 (s, 3 H, SiCH₃), 3.64 (m, 4 H, ~N-CH₂-CH₂), 6.81–7.31 (m, 10 H, ~N-C₆H₅). – ¹³C NMR: $\delta = 0.3$ (SiCH₃), 8.3 (SiCH₃), 45.4 (~N-CH₂-CH₂), 115.4 (C_{ortho}), 119.1 (C_{para}), 129.4 (C_{meta}), 146.4 (C_{ipso}). – ²⁹Si NMR: $\delta = -4.9$ (Si^A), 22.0 (Si^B). – ¹⁵N NMR: $\delta = -313$. – C₁₆H₂₀Cl₂N₂Si₂ (367.42): calcd. C 52.30, H 5.49, N 7.62; found C 51.90, H 6.00, N 7.42.

N,N'-Diphenyl-2,2,3,3-tetramethyl-1,4-diaza-2,3-disila-cyclohexane (9)

The same procedure as described for **6** was realized by reaction of 7.48 g (40 mmol) 1,2-dichlorotetramethyldisilane **3** with 9.3 g (44 mmol) **2** and 36.3 g (359 mmol) NEt₃. A colorless crystalline residue (4.6 g, 36% yield) **9** was obtained.

¹H NMR: δ = 0.54 (s, 12 H, SiCH₃), 3.81 (m, 4 H, ~N-CH₂-CH₂), 6.93 – 7.38 (m, 10 H, ~N-C₆H₅). – ¹³C NMR: δ = 0.2 (SiCH₃), 52.6 (N-CH₂-CH₂), 118.1 (C_{ortho}), 119.0 (C_{para}), 128.9 (C_{meta}), 151.1 (C_{ipso}). – ²⁹Si NMR: δ = -7.6 (CDCl₃). – ²⁹Si CP MAS: δ = -0.5/ – 14.2. – ¹⁵N NMR: δ = -317. – GC/MS: m/z (%) = 326 (44) [M], 311 (100) [M–CH₃], 220 (29) [M–N(C₆H₅)CH₃], 206 (67) [M–N(C₆H₅)C₂H₅]. – C₁₈H₂₆N₂Si₂ (326.58): calcd. C 66.20, H 8.02, N 8.58; found C 64.95, H 8.2, N 8.29.

Bis-[*N*,*N*'-*dimethyl*-2-*methyl*-1,3-*diaza*-2-*silacyclopentane*] (10)

5.9 g (68 mmol) **1** and 13.7 g (136 mmol) NEt₃ were dissolved in *n*-hexane and stirred at ambient temperature. 7.6 g (34 mmol) 1,1,2,2-tetrachlorodimethyldisilane **4**, dissolved in *n*-hexane, were added dropwise. After refluxing for one hour and stirring at ambient temperature overnight the solvents were removed in vacuum and replaced by *n*-hexane. The precipitated NEt₃·HCl was filtered off and the solvent evaporated in vacuum. The colorless oily residue was distilled under reduced pressure (B.p. 190–195 °C/10 Torr) and yielded 3.9 g (45%) of **10** as a colorless oil beside the monosilane **10a**.

10: ¹H NMR: $\delta = 0.30$ (s, 6 H, SiCH₃), 2.70 (s, 12 H, ~N-CH₃), 2.75 (m, 4 H, ~N-CH₂-CH₂), 2.77 (m, 4 H, ~N-CH₂-CH₂). – ¹³C NMR: $\delta = 6.2$ (SiCH₃), 33.8 (N-CH₃), 51.1 (N-CH₂-CH₂). – ²⁹Si NMR: $\delta = -14.0. - ^{15}$ N NMR: $\delta = -362. - \text{GC/MS:} m/z$ (%) = 243 (1) [M-CH₃], 172 (82) [M-{N(CH₃)C₂H₄}₂], 129 (100) [M/2]. – C₁₀H₂₆N₄Si₂ (258.51): calcd. C 46.46, H 10.14, N 21.67; found C 45.70, H 9.52, N 20.99.

(*N*,*N*'-Dimethyl-2,2-chloromethyl-1,3-diaza-2-silacyclopentane) (**10a**)

¹H NMR: $\delta = 0.69$ (s, 3 H, SiCH₃), 2.52 (s, 6 H, ~N-CH₃), 2.87 (s, 4 H, ~N-CH₂-CH₂). – ¹³C NMR: $\delta = 3.8$ (SiCH₃, ¹*J*_{SiC} = 86.6 Hz), 33.8 (N-CH₃), 47.7 (N-CH₂-CH₂). – ²⁹Si NMR: $\delta = -0.5$.

Bis-[N,N'-dimethyl-2-chloro-1,3-diaza-2-silacyclopentane] (11)

The amines **1** (11.7 g, 133 mmol) and NEt₃ (22.5 g, 223 mmol) were dissolved in toluene. 6.0 g (23 mmol) hexachlorodisilane **5**, dissolved in *n*-hexane, were added dropwise with stirring. After stirring at ambient temperature overnight, the solvents were removed in vacuum and replaced by *n*-hexane. Filtration from precipitated NEt₃·HCl and removal of the solvent yielded a colorless oily residue. This was distilled under reduced pressure to give 2.1 g of **11a** as a colorless oil (B.p. 94–98 °C/2 Torr) and beside that a mixture of **11**, **11a** and **11b** as colorless oil (1.2 g, B.p. 108– 142 °C/2 Torr).

11: ¹H NMR: δ = 2.70 (s, 12 H, SiCH₃), 3.21 (s, ~N-CH₂-CH₂). – ²⁹Si: δ = -25.1. – ¹⁵N: δ = -364. – GC/MS: m/z (%) = 300 (100) [M], 285 (5) [M–CH₃], 241 (18) [M–4·CH₃], 213 (31) [M–N(CH₃)₂(CH₂CH₂)].

(1,4,6,9-Tetramethyl-1,4,6,9-tetraaza-5-silaspiro-[4,4]nonan) (**11a**)

¹H NMR: $\delta = 2.74$ (s, 12 H, SiCH₃), 3.21 (s, ~N-CH₂-CH₂). – ²⁹Si: $\delta = -29.6$. – ¹⁵N: $\delta = -366$. – GC/MS: m/z(%) = 200 (100) [M], 184 (19) [M–CH₃], 114 (42) [M– N(CH₃)₂CH₂CH₂].

(2-Chloro-N,N'-diphenyl-1,3-diaza-2-silacyclopentane) (11b)

¹H NMR: $\delta = 2.79$ (s, 6 H, SiCH₃), 3.21 (s, ~N-CH₂-CH₂), 4.61 (s, 1 H, SiH, ¹J_{SiH} = 237 Hz). – ²⁹Si: $\delta = -30.8$ (d, ¹J_{SiH} = 236 Hz). – ¹⁵N: $\delta = -343.5$. – IR (KBr): $\nu =$ 2127 cm⁻¹ (s, Si-H). 2-Dichloromethylsilyl-2-methyl-N,N'-dimethyl-1,3-diaza-2silacyclopentane (12)

24.5 g (279 mmol) **1** were added dropwise to a solution of 1,1,2,2-tetrachlorodimethyldisilane (63.5 g, 279 mmol) and NEt₃ (112.5 g, 1114 mmol) in *n*-hexane. After stirring at ambient temperature overnight, the solvents were removed in vacuum and replaced by *n*-hexane. Filtration from precipitated NEt₃·HCl and removal of the solvent yielded a colorless oily residue. It was distilled under reduced pressure to give 17.6 g (26%) of **12** as a colorless oil (B.p. 86 °C/2 Torr) beside the monosilane **10a**.

12: ¹H NMR: δ = 0.69 (s, 3 H, SiCH₃), 0.92 (s, 3 H, SiCH₃), 2.66 (s, 6 H, ~N-CH₃), 3.27 (s, 4 H, ~N-CH₂-CH₂). – ¹³C NMR: δ = 0.2 (SiCH₃), 7.0 (SiCH₃), 36.4 (~N-CH₃), 52.6 (~N-CH₂-CH₂). – ²⁹Si NMR: δ = –1.3 (Si^A), 21.0 (Si^B). – GC/MS: m/z (%) = 243 (1) [M], 227 (33) [M – CH₃], 184 (22) [M –4·CH₃], 129 (100) [M –SiCl₂CH₃]. – C₆H₁₆Cl₂N₂Si₂ (243.28): calcd. C 29.6, H 6.6, N 11.5; found C 28.8, H 6.4, N 12.5.

N,N'-Dimethyl-2,2,3,3-tetramethyl-1,4-diaza-2,3-disila-cyclohexane (13)

The same procedure was used as described to synthesize **6**. 11.4 g (61 mmol) 1,2-dichlorotetramethyldisilane **3** were added to a mixture of 6.2 g (70 mmol) ethylenediamine **1** and 29.0 g (287 mmol) NEt₃ and yielded 5.6 g (45%) **13** as a colorless oil. B.p. 102 - 108 °C/15 Torr.

¹H NMR: $\delta = 0.43$ (s, 12 H, SiCH₃), 2.77 (s, 6 H, ~N-CH₃), 3.17 (s, 4 H, ~N-CH₂-CH₂). – ¹³C NMR: $\delta = -2.1$ (SiCH₃, ¹*J*_{SiC} = 47.5 Hz), 37.6 (N-CH₃), 54.6 (~N-CH₂-CH₂). – ²⁹Si NMR: $\delta = -9.5$. – ¹⁵N NMR: $\delta = -366$. – GC/MS: *m/z* (%) = 202 (3) [M], 187 (100) [M-CH₃], 172 (5) [M-2·CH₃], 159 (15) [M-N(C₂H₅)], 144 (48) [M – N(C₃H₈)]. – C₈H₂₂N₂Si₂ (202.44): calcd. C 47.46, H 10.95, N 13.84; found C 46.13, H 9.05, N 13.21.

X-ray crystallographic study

The X-ray structure analyses of **6**, **7** and **9** were performed on a Rigaku AFC7 diffractometer with a Mercury CCD detector at ambient temperature. For data collection, unit cell refinement and data reduction the program package Crystal Clear [17] was used. The structures were solved using direct methods (SHELXS-97 [18]) and refined with leastsquares-methods (SHELXL-97 [18]). Molecular diagrams were drawn using ORTEP3 [19].

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC-251417 (6), CCDC-251418 (7) and CCDC-251419 (9). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

	6	7	9
Empirical formula	C ₃₀ H ₃₄ N ₄ Si ₂	$C_{28}H_{28}Cl_2N_4Si_2$	C ₁₈ H ₂₆ N ₂ Si ₂
Formula weight [g mol ⁻¹]	506.79	547.62	326.59
Unit cell dimensions			
a [Å]	7.5468(4)	7.4902(5)	9.0081(7)
<i>b</i> [Å]	18.672(1)	19.680(1)	8.4125(8)
<i>c</i> [Å]	19.5591(9)	18.306(2)	12.5693(9)
β[°]	90	90	95.811(4)
Z	4	4	2
$D_{\text{calc}} [\text{g cm}^{-3}]$	1.221	1.348	1.145
Linear absorption coefficient μ [mm ⁻¹]	0.155	0.355	0.186
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	P2 ₁ 2 ₁ 2 ₁ (No. 19)	<i>Pbcn</i> (No. 60)	<i>P</i> 2 ₁ (No. 4)
Type of diffractometer	Rigaku AFC7 (Mercury CCD)	Rigaku AFC7 (Mercury CCD)	Rigaku AFC7 (Mercury CCD)
Radiation $[\lambda, Å]$	Mo-K _{α} (0.71073)	Mo-K _{α} (0.71073)	Mo-K _{α} (0.71073)
Monochromator	graphite	graphite	graphite
Crystal size [mm ³]	$0.51 \times 0.37 \times 0.21$	$0.36 \times 0.20 \times 0.20$	$0.97 \times 0.40 \times 0.32$
Temperature [K]	295(2)	295(2)	295(2)
θ Range for collection [°]	2.18 - 28.00	2.07 - 27.00	2.27 - 29.00
Index ranges	$-9 \le h \le 9$	$-9 \le h \le 9$	$-12 \le h \le 12$
-	$-18 \le k \le 24$	$-22 \le k \le 25$	$-11 \le k \le 8$
	$-25 \le l \le 25$	$-23 \le l \le 21$	$-17 \le l \le 17$
Measured reflections	25965	28874	12990
Independent reflections	6628	2955	4549
Observed reflections	6166	2753	4396
Completeness to θ_{max} [%]	99.8	99.9	99.6
Cut-off criterion	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Number of parameters	328	163	204
Flack parameter	0.00(13)		0.03(10)
Final $R_1/wR_2[I > 2\sigma(I)]$	0.0509 / 0.1310	0.0783 / 0.1730	0.0384 / 0.1037
R_1/wR_2 (all data)	0.0554 / 0.1338	0.0851 / 0.1763	0.0397 / 0.1049
Goodness-of-fit on F^2	1.080	1.371	1.044
Max / min e-density [eÅ ⁻³]	0.327 / -0.227	0.572 / -0.228	0.302 / -0.240

Table 5. Crystallographic parameters and experimental details for the compounds 6, 7, 9.

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