Binary Si/N-[4.4]-Spirocycles with Two SiH_2SiH_2 Loops

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Tetra(alkylamino)silanes $Si(NHR)_4$ with R = Me, *n*-Pr, *n*-Bu, and *i*-Pr (**1a−d)** have been prepared via improved methods and characterized by complementary analytical and spectroscopic data. The reaction of **1a−c** with 2 equiv of Tf-SiH_2SiH_2-Tf (Tf = trifluoromethylsulfonyloxy, "triflate") and triethylamine in toluene gives good yields of the spirocyclic compounds $[(SiH_2NR)_2]_2Si$ (**2a−c**). **2a** is obtained as a crystalline, but highly volatile, product (mp 35 °C, $bp_{0.05}$ 46−47 °C), the crystal and molecular structure of which has been determined by single-crystal X-ray diffraction methods (monoclinic, space group $P2_1/n$, $Z = 8$). The lattice contains two independent molecules in the asymmetric unit, which have very similar dimensions. The two five-membered rings are almost planar and close to perpendicular to each other. Owing to sterical hindrance, the analogous reaction of **1d** gives only low yields of the corresponding spirocycle $\{[SiH_2N(i\text{-Pr})]_2\}_2Si$, **2d**. A silylammonium salt $\{[SiH_2N(i\text{-Pr})]_2Si-[NH(i\text{-Pr})]-[NH_2(i\text{-Pr})]\}^+Tf^-$ (**3**) is produced as a major product. Compound **3** is one of the very few silylammonium salts as confirmed by a full structural analysis (monoclinic, space group $P2_1/c$, $Z = 4$). In the crystal, 2 equiv are grouped together as a centrosymmetrical cluster of two cations and two anions with hydrogen bonds between the amino/ammonio and the sulfonate groups. Equimolar quantities of **1d** and the 1,2-disilanediylbis(triflate) in the presence of NEt_3 give good yields of the monocyclic compound $[SiH_2N(i\text{-Pr})]_2$-$Si[NH(i\text{-Pr})]_2$, **4**. Compounds **1a−d** and **2a−c** are hydrogen- and silicon-rich precursor molecules for the production of silicon nitride in pyrolytic, plasma- or laser-induced (thermal) decomposition and for the preparation of silazane networks and gels by controlled aminolysis or by metathesis of the Si−Si bonds.

Introduction

Tetra(alkoxy)silanes $Si(OR)_4$ are important precursor compounds for the chemical vapor deposition of silica and silicate thin films (e.g. from tetra(ethoxy)silane, TEOS) and for sol-gel processes to generate siloxane and heterosiloxane networks.[1] The related tetra(alkylamino)silanes $Si(NHR)_4$ are far less well represented in the current research and development activities for the analogous deposition of silicon nitride[2] or for the preparation of polysilazane networks.[3]

In our own pertinent studies of small, hydrogen- and silicon-rich silicon−nitrogen species, we have recently been engaged in systematic investigations of various classes of Si/N compounds, including disilazanes (Si−N−Si),[4] disilanylamines (Si−Si−N),[5] silylhydrazines (Si−N−N),[6] silylhydroxylamines (Si−N−O),[7] and finally poly(amino)silanes (Si−N).[8] In the individual papers published as an account, the literature on the corresponding area of Si−N chemistry has been briefly summarized. A more comprehensive treatment is available in the latest volume of the Gmelin series.[9]

Continuing this work, we then turned to bicyclic compounds comprising both disilazane and disilanylamine units at fully aminated silicon spiro centers (**2a−d**). Owing to their compact and symmetrical structure, these compounds were expected to be quite volatile despite a relatively high molecular mass, allowing further processing from the vapor phase, and to be highly soluble in a large variety of low-polarity solvents, making them amenable to controlled solvolysis. The presence of reactive SiH_2-SiH_2 loops provides sites for dehydrogenative[10] or desilanative coupling reactions,[11] as well as for photochemical activation,[12] which could lead to crosslinking or further derivatization prior to solvolysis.

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Experimental Section

General. All experiments were routinely carried out under an atmosphere of dry, pure nitrogen. Solvents were appropriately dried, distilled, and saturated with nitrogen prior to use, and glassware was oven-dried and filled with nitrogen. NMR spectra were obtained on a Jeol JNM-GX 400 spectrometer using dry degassed C_6D_6 as the solvent. ^{15}N-NMR spectra were referenced externally to aniline at δ −333.6 ppm. Infrared spectra were recorded on a Perkin-Elmer FT-IR 577 spectrometer. GLC-MS analyses were performed on an HP 5890/II gas−liquid chromatography system with a mass-selective detector HP 5971 A (EI, 70 eV). UV spectra were recorded on a Perkin-Elmer UV/vis Lambda 2 spectrometer. Elemental analyses were performed at the Microanalytical Laboratory of the Technische Universität München. In general carbon and nitrogen contents were found too low due to formation of silicon carbide and silicon nitride, respectively. 1,2-Di(*p*-tolyl)disilane and 1,2-bis(trifluoromethylsulfonyloxy)disilane were prepared according to literature procedures.[13] Other reagents were commercially available and appropriately dried prior to use.

Tetra(methylamino)silane (1a). The synthesis followed a modified literature procedure.[14,15] Methylamine is bubbled through a solution of 10.0 g (59 mmol) of tetrachlorosilane in 50 mL of diethyl ether at −30 °C with stirring. After the usual workup, the product is purified by distillation at 45 °C/0.05 Torr. It solidifies in the receiver as a colorless solid (**1a**, yield 4.4 g, 50%), mp 37 °C. MS (EI, 70 eV): *m/z* 148 (M^+). ^1H NMR (C_6D_6, 25 °C): δ 0.34 (s, 4H, NH), 2.48 (s, 12H, Me). $^{13}C\{^1H\}$ NMR (vs): δ 27.8 (s, Me). $^{29}Si\{^1H\}$ NMR (vs): δ −36.0 (s, SiN_4).

Tetra(*n*-propylamino)silane (1b). A 10.0 g (59 mmol) amount of tetrachlorosilane is slowly added to a solution of 43.0 g (0.73 mol) of *n*-propylamine in 50 mL of diethyl ether at −10 °C with stirring. During the addition of the tetrachlorosilane, another 50 mL of diethyl ether is added to allow continuous stirring. The reaction mixture is allowed to warm to 20 °C and stirring is continued for ca. 1 h (reaction progress controlled by GLC−MS analysis). The ammonium salts are separated, and the solvent and the unreacted *n*-propylamine are removed from the filtrate in a vacuum. Hexane is added to precipitate all remaining salts. The filtrate is fractionally distilled in a vacuum to give a colorless liquid (**1b**, yield 9.1 g, 59%), bp 75 °C/0.05 Torr. MS (EI, 70 eV): *m/z* 260 (M^+). ^1H NMR (C_6D_6, 25 °C): δ 0.45 (s, 4H, NH), 0.82 (t, J(H,H) = 7.3 Hz, 12H, Me), 1.33 (sex, J(H,H) = 7.3 Hz, 8H, CH_2Me), 2.68 (m, 8H, CH_2N). $^{13}C\{^1H\}$ NMR (vs): δ 11.7 (s, Me), 28.4 (s, CH_2Me), 43.9 (s, CH_2N). $^{29}Si\{^1H\}$ NMR (vs): δ −40.5 (s, SiN_4).

Tetra(*n*-butylamino)silane (1c). The synthesis followed a modified literature procedure, as described for **1b**.[14] Published analytical and spectroscopic data were confirmed and complemented. A 10.0 g (59 mmol) amount of tetrachlorosilane is slowly added to a solution of 44.0 g (0.60 mol) of *n*-butylamine in 50 mL of diethyl ether at −10 °C with stirring. As described for **1b** above, the product is obtained as a colorless liquid (**1c**, yield 11.8 g, 63%), bp 108 °C/0.05 Torr. MS (EI, 70 eV): *m/z* = 316 (M^+). ^1H NMR (C_6D_6, 25 °C): δ 0.43 (s, 4H, NH), 0.87 (t, J(H,H) = 7.3 Hz, 12H, Me), 1.31 (m, 16H, 2 × CH_2), 2.76 (t, J(H,H) = 6.6 Hz, 8H, CH_2N). $^{13}C\{^1H\}$ NMR (vs): δ 14.3 (s, Me), 20.5 (s, CH_2Me), 37.7 (s, CH_2), 41.6 (s, CH_2N). $^{29}Si\{^1H\}$ NMR (vs): δ −40.5 (s, SiN_4).

Tetra(isopropylamino)silane (1d). A 11.9 g (70 mmol) amount of tetrachlorosilane is slowly added to a solution of 27.5 g (0.47 mol) of isopropylamine in 50 mL of diethyl ether at −30 °C with stirring. After completion of the reaction and workup (above), the product is purified by sublimation at 60 °C/0.05 Torr to give a colorless solid (**1d**, yield 11.0 g, 60%), mp 65 °C. MS (EI, 70 eV): *m/z* = 260 (M^+). ^1H NMR (C_6D_6, 25 °C): δ 0.35 (s, 4H, NH), 1.10 (d, J(H,H) = 6.7 Hz, 24H, Me), 3.21 (sept, J(H,H) = 6.7 Hz, 4H, CH). $^{13}C\{^1H\}$ NMR (vs): δ 28.3 (s, Me), 42.6 (s, CH). $^{29}Si\{^1H\}$ NMR (vs): δ −45.9 (s, SiN_4).

1,4,6,9-Tetramethyl-1,4,6,9-tetraaza-2,3,5,7,8-pentasilaspiro[4.4]nonane (2a). A freshly prepared solution of 1,2-bis(trifluoromethylsulfonyloxy)disilane [from 2.0 g (8.2 mmol) of 1,2-di(*p*-tolyl)disilane] in toluene (50 mL) is treated with a solution of 0.61 g (4.1 mmol) of **1a** and 1.67 g (16.5 mmol) of triethylamine in toluene (10 mL) at −50 °C with stirring. The reaction mixture is allowed to warm to 20 °C, the oily triethylammonium triflate is separated, and the solvent removed from the filtrate. Hexane is added to precipitate all remaining ammonium salts. The filtrate is fractionally distilled in a vacuum to give a colorless liquid (**2a**, yield 0.69 g, 63%), bp 46−47 °C/0.05 Torr. It solidifies in the receiver. Crystals are obtained by slow cooling of the melt, mp 35 °C. MS (EI, 70 eV): *m/z* = 264 (M^+). UV (hexane, 25 °C): λ_{max} = 207 nm; λ = 260 nm (broad). IR (KBr, 25 °C): 2102.5 cm^{-1} (vs, νSiH_2). ^1H NMR (C_6D_6, 25 °C): δ 2.31 (s, 12H, Me), 4.62 (s, J(Si,H) = 203.6 Hz, 8H, SiH_2). $^{13}C\{^1H\}$ NMR (vs): δ 31.7 (s, Me). ^{29}Si NMR (DEPT, vs): δ −45.5 (tm, J(Si,H) = 203.6 Hz, respectively, SiH_2). $^{29}Si\{^1H\}$ NMR (vs): δ −45.5 (s, SiH_2), −27.3 (s, SiN_4). ^{15}N NMR (DEPT, vs): δ −392.5 (s, NSi). Anal. Found: H, 7.47. $C_4H_{20}N_4Si_5$ (264.69 g/mol) calcd: H, 7.62.

1,4,6,9-Tetra-*n*-propyl-1,4,6,9-tetraaza-2,3,5,7,8-pentasilaspiro[4.4]nonane (2b). A freshly prepared solution of 1,2-bis(trifluoromethylsulfonyloxy)disilane [from 1.5 g (6.2 mmol) of 1,2-di(*p*-tolyl)disilane] in toluene (50 mL) is treated with a mixture of 0.80 g (3.1 mmol) of **1b** and 1.25 g (12.4 mmol) of triethylamine at −50 °C with stirring. Workup as described for **2a** (above) gives a colorless liquid (**2b**, yield 0.70 g, 60%), bp 113−115 °C/0.05 Torr. MS (EI, 70 eV): *m/z* = 376 (M^+). IR (liquid, 25 °C): 2105.2 cm^{-1} (vs, νSiH_2). ^1H NMR (C_6D_6, 25 °C): δ 0.78 (t, J(H,H) = 7.3 Hz, 12H, Me), 1.51 (sex, J(H,H) = 7.3 Hz, 8H, CH_2Me), 2.64 (m, 8H, CH_2N), 4.58 (s, J(Si,H) = 202.9 Hz, 8H, SiH_2). $^{13}C\{^1H\}$ NMR (vs): δ 12.0 (s, Me), 25.2 (s, CH_2Me), 48.5 (s, CH_2N). ^{29}Si NMR (DEPT, vs): δ −50.7 (tm, J(Si,H) = 202.9 Hz, SiH_2). $^{29}Si\{^1H\}$ NMR (vs): δ −50.7 (s, SiH_2), −24.6 (s, SiN_4). ^{15}N NMR (DEPT, vs): δ −373.3 (s, NSi). Anal. Found: C, 37.64; H, 9.41; N, 14.11. $C_{12}H_{36}N_4Si_5$ (376.88 g/mol) calcd: C, 38.33; H, 9.57; N, 14.89.

1,4,6,9-Tetra-*n*-butyl-1,4,6,9-tetraaza-2,3,5,7,8-pentasilaspiro[4.4]nonane (2c). A freshly prepared solution of 1,2-bis(trifluoromethylsulfonyloxy)disilane [from 1.5 g (6.2 mmol) of 1,2-di(*p*-tolyl)disilane] in toluene (50 mL) is treated with a mixture of 0.98 g (3.1 mmol) of **1c** and 1.25 g (12.4 mmol) of triethylamine at −50 °C with stirring. Workup as described for **2a** gives a colorless liquid (**2c**, yield 0.73 g, 55%), bp 129 °C/0.05 Torr. MS (EI, 70 eV): *m/z* 432 (M^+). IR (liquid, 25 °C): 2106.1 cm^{-1} (vs, νSiH_2). ^1H NMR (C_6D_6, 25 °C): δ 0.88 (t, J(H,H) = 7.7 Hz, 12H, Me), 1.23 (sex, J(H,H) = 7.7 Hz, 8H, CH_2Me), 1.58 (m, 8H, CH_2), 2.79 (m, 8H, CH_2N), 4.70 (s, J(Si,H) = 202.9 Hz, 8H, SiH_2). $^{13}C\{^1H\}$ NMR (vs): δ 14.2 (s, Me), 20.9 (s, CH_2Me), 34.3 (s, CH_2), 46.2 (s, CH_2N). ^{29}Si NMR (DEPT, vs): δ −50.7 (tm, J(Si,H) = 202.9 Hz, SiH_2). $^{29}Si\{^1H\}$ NMR (vs): δ −50.7 (s, SiH_2), −24.4 (s, SiN_4). ^{15}N NMR (DEPT, vs): δ −373.5 (s, NSi). Anal. Found: C, 43.92; H, 10.03; N, 12.28. $C_{16}H_{44}N_4Si_5$ (432.98 g/mol) calcd: C, 44.38; H, 10.24; N, 12.94.

1,4,6,9-Tetraisopropyl-1,4,6,9-tetraaza-2,3,5,7,8-pentasilaspiro[4.4]nonane (2d), 2,2-Diisopropylamino-1,3-diisopropyl-2,4,5-trisilaimidazolidine (4), and the Silylammonium Triflate 3. A freshly prepared solution of 1,2-bis(trifluoromethylsulfonyloxy)disilane [from 1.5 g (6.2 mmol) of 1,2-di(*p*-tolyl)disilane] in toluene (50 mL) is treated with a solution of 0.80 g (3.1 mmol) of **1d** and 1.25 g (12.4 mmol) of triethylamine in toluene (10 mL) at −50 °C with stirring. The reaction is continued for 24 h at −20 °C. The mixture is allowed to warm to 20 °C, and the oily triethylammonium triflate is separated. **4** (ca. 97%) and **2d** (ca. 3%, derived from GLC−MS analysis) are detected as volatile components. The solvent is removed, and hexane is added to the reaction mixture. Insoluble products are filtered, and the filtrate is concentrated. Colorless crystals of **3** (yield 0.31 g, 11%) are obtained at −30 °C, mp >200 °C (decomposition). Hexane is evaporated from

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Table 1. Crystal Data, Data Collection, and Structure Refinement for Compounds **2a** and **3**

	2a	**3**
crystal data		
empirical formula	$C_4H_{20}N_4Si_5$	$C_{13}H_{35}F_3N_4O_3SSi_3$
M_r	264.69	468.78
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a (Å)	12.782(1)	9.326(1)
b (Å)	16.007(1)	18.263(2)
c (Å)	15.631(1)	15.089(1)
α (deg)	90	90
β (deg)	109.04(1)	105.37(1)
γ (deg)	90	90
V (Å^3)	3023.2(4)	2478.0(4)
ρ_{calc} (g cm^{-3})	1.163	1.257
Z	8	4
F(000)	1136	1000
μ(Mo Kα) (cm^{-1})	4.46	3.17
data collection		
T (°C)	−96	−80
scan mode	$\omega-\theta$	$\omega-\theta$
hkl range	$0 \rightarrow 15, 0 \rightarrow 19, -19 \rightarrow 18$	$-11 \rightarrow 10, 0 \rightarrow 21, 0 \rightarrow 17$
sin(θ/λ)$_{max}$ (Å^{-1})	0.62	0.60
no. of measd reflcns	6215	3496
no. of unique reflcns	5916 [$R_{int} = 0.0149$]	3377 [$R_{int} = 0.0265$]
no. of reflcns used for refinement	5844	3372
abs corr	none	none
refinement		
refined parameters	299	272
H atoms (found/calcd)	16/24	7/28
final R values [$I > 2\sigma(I)$]		
$R1^a$	0.0348	0.0653
$wR2^b$	0.0924	0.1435
(shift/error)$_{max}$	<0.001	<0.001
ρ_{fin}(max/min) (e Å^{-3})	0.294/−0.286	0.459/−0.330

[a] $R = \Sigma(||F_o - F_c|)/\Sigma|F_o|$. [b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$, $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0474$ (**2a**), 0.0675 (**3**); $b = 1.55$ (**2a**), 3.74 (**3).**

the filtrate, and careful fractional distillation at 90−100 °C/0.05 Torr gives a mixture of **4** (ca. 70%) and **2d** (ca. 30%). For **2d**. MS (EI, 70 eV): m/z 376 (M^+). ^{1}H NMR (C_6D_6, 25 °C): δ 1.23 (d, J(H,H) = 6.7 Hz, 24H, Me), 3.41 (sept, J(H,H) = 6.7 Hz, 4H, CH), 4.61 (s, J(Si,H) = 203.2 Hz, 8H, SiH_2). ^{13}C{^{1}H} NMR (vs): δ 24.6 (s, Me), 44.6 (s, CH). ^{29}Si NMR (DEPT, vs): δ −64.5 (tm, J(Si,H) = 203.2 Hz, SiH_2). ^{29}Si{^{1}H} NMR (vs): δ −64.5 (s, SiH_2), −27.6 (s, SiN_4).

For **3**. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 1.08 (d, J(H,H) = 6.1 Hz, 12H, *Me*CNH), 1.22 (d, J(H,H) = 6.1 Hz, 12H, *Me*CN), 2.41 (s, 1H, NH), 3.08 (sept, J(H,H) = 6.1 Hz, 2H, *CH*NH), 3.43 (sept, J(H,H) = 6.1 Hz, 2H, CHN), 4.46 (s, J(Si,H) = 199.0 Hz, 4H, SiH_2), NH_2 not detected. ^{13}C{^{1}H} NMR (vs): δ 24.6 (s, *Me*CNH), 28.1 (s, *Me*CN), 42.9 (s, CHNH), 44.6 (s, CHN), CF_3 not detected due to low solubility. ^{29}Si NMR (DEPT, vs): δ −65.5 (ttd, J(Si,H) = 199.0, 9.8, and 7.9 Hz, respectively, SiH_2). ^{29}Si{^{1}H} NMR (vs): δ −65.5 (s, SiH_2), SiN_4 not detected. Anal. Found: C, 33.40; H, 7.71; N, 11.78. $C_{13}H_{35}F_3N_4O_3SSi_3$ (468.78 g/mol) calcd: C, 33.31; H, 7.53; N, 11.95.

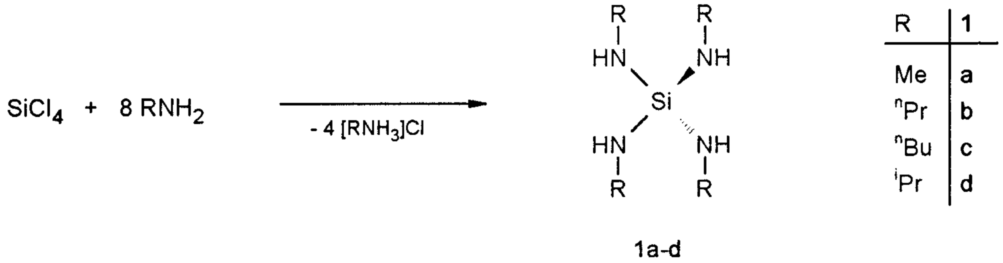
2,2-Di(*N,N'*-isopropylamino)-1,3-diisopropyl-2,4,5-trisilaimidazolidine (4). A freshly prepared solution of 1,2-bis(trifluoromethylsulfonyloxy)disilane [from 1.0 g (4.1 mmol) of 1,2-di(*p*-tolyl)disilane] in toluene (30 mL) is treated with a solution of 1.07 g (4.1 mmol) of **1d** and 0.83 g (8.2 mmol) of triethylamine in toluene (10 mL) at −50 °C with stirring. The reaction mixture is allowed to warm to 20 °C, the oily triethylammonium triflate is separated and the solvent removed from the filtrate. Hexane is added to precipitate all remaining ammonium salts. The filtrate is fractionally distilled in a vacuum to give a colorless liquid (**4**, yield 0.72 g, 55%), bp 90 °C/0.05 Torr. MS (EI, 70 eV): $m/z = 318$ (M^+). IR (liquid, 25 °C): 3399.5 cm^{-1} (s, νNH), 2110.4 cm^{-1} (vs, νSiH_2). ^{1}H NMR (C_6D_6, 25 °C): δ 0.21 (d, J(H,H) = 10.4 Hz, 2H, NH), 0.97 (d, J(H,H) = 6.1 Hz, 12H, *Me*CNH), 1.21 (d, J(H,H) = 6.1 Hz, 12H, MeCN), 3.01 (dsept, J(H,H) = 10.4 and 6.1 Hz, respectively, 2H, *CH*NH), 3.37 (sept, J(H,H) = 6.1 Hz, 2H, CHN), 4.67 (s, J(Si,H) = 199.7 Hz, 4H, SiH_2). ^{13}C{^{1}H} NMR (vs): δ 24.7 (s, *Me*CNH), 28.1 (s, *Me*CN), 42.7 (s, CHNH), 44.5 (s, CHN). ^{29}Si NMR (DEPT, vs): δ −65.3 (ttd, J(Si,H) = 199.7, 9.9, and 7.8 Hz, respectively, SiH_2). ^{29}Si{^{1}H} NMR (vs): δ −65.3 (s, SiH_2), −37.3 (s, SiN_4). ^{15}N NMR (DEPT, vs): δ −354.3 (s, NSi), −341.9 (s, NHSi). Anal. Found: C, 44.89; H, 10.64; N, 17.03. $C_{12}H_{34}N_4Si_3$ (318.69 g/mol) calcd: C, 45.23; H, 10.75; N, 17.58.

Crystal Structure Determinations. Specimens of suitable quality and size of compounds **2a** and **3** were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection on an Enraf Nonius CAD4 diffractometer (Mo *K*a radiation, λ(Mo K_a) = 0.710 73 Å). During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for either compound. Lp correction was applied, but intensity data were not corrected for absorption effects. The structures were solved by direct methods (SHELXS-86) and completed by full-matrix least-squares techniques against F^2 (SHELXL-93). The thermal motion of all non-hydrogen atoms was treated anisotropically. All Si-*H* and N-*H* atoms were located and refined with isotropic contributions, whereas all C-*H* atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions ($U_{iso(fix)} = 1.5U_{eq}$ of the attached C atom). Further information on crystal data, data collection, and structure refinement is summarized in Table 1. Important interatomic distances and angles are shown in the corresponding figure captions. Anisotropic thermal parameters, tables of distances and angles, and atomic coordinates have been deposited with Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request on quoting CSD Nos. 407611 (**2a**) and 407612 (**3**).

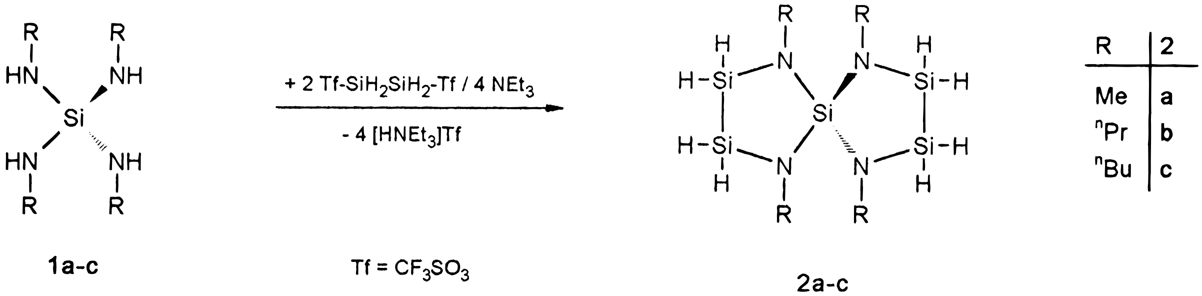
Results

Tetra(alkylamino)silanes $Si(NHR)_4$ were included in this study because these compounds are the most convenient starting

Scheme 1



Scheme 2



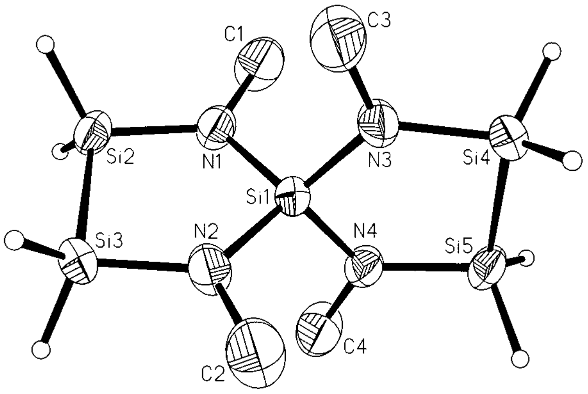


Figure 1. Molecular structure of compound **2a** (ORTEP drawing with 50% probability ellipsoids, C-*H* atoms omitted for clarity). Selected bond lengths (Å) and angles (deg) (bond lengths and angles of the second independent molecule in parentheses): Si2−Si3 2.3126(9) [2.3182(10)], Si4−Si5 2.3094(9) [2.3129(9)]; Si−N (av) 1.719(2), Si−H (av.) 1.39(3); N1−Si1−N2 103.56(9) [103.80(9)], N3−Si1−N4 103.43 (9) [103.39(8)], N1−Si1−N3 112.06(10) [111.49 (9)], N2−Si1−N4 111.72(10) [112.29(9)], Si1−N1−Si2 121.69(11) [121.61(11)], Si1−N2−Si3 121.54(11) [121.16(11)], Si1−N3−Si4 122.04(11) [121.14(10)], Si1−N4−Si5 121.33(11) [120.97(10)], N1−Si2−Si3 96.40(7) [96.40(7)], N2−Si3−Si2 96.48(7) [96.44(7)], N3−Si4−Si5 96.04(7) [96.68(7)], N4−Si5−Si4 96.62(7) [96.40(6)].

materials for cyclization reactions. Four members of the homologous series were prepared with R = Me, *n*-Pr, *n*-Bu, i-Pr (**1a**−**d**) (Scheme 1). With slight modifications of the experimental conditions given in the literature good yields of pure compounds could be obtained (Experimental Section). The analytical and spectroscopic data given in some of the earlier work were naturally incomplete and complementary data have now been provided where necessary.[14,15] It should be noted that a crystal structure with important reference data is available on compound **1a**.[15] General features of the molecular structures and dynamics of tetrakis(dialkylamino)silanes $\mathrm{Si(NR_2)_4}$ have been presented and discussed in a very recent publication from this laboratory.[8b]

Spirocyclization of compounds **1a**−**c** was accomplished by treatment of these precursors with 2 equiv of 1,2-disilanediylbis(triflate) and triethylamine as an auxiliary base to trap the triflic acid produced as a byproduct (Scheme 2).

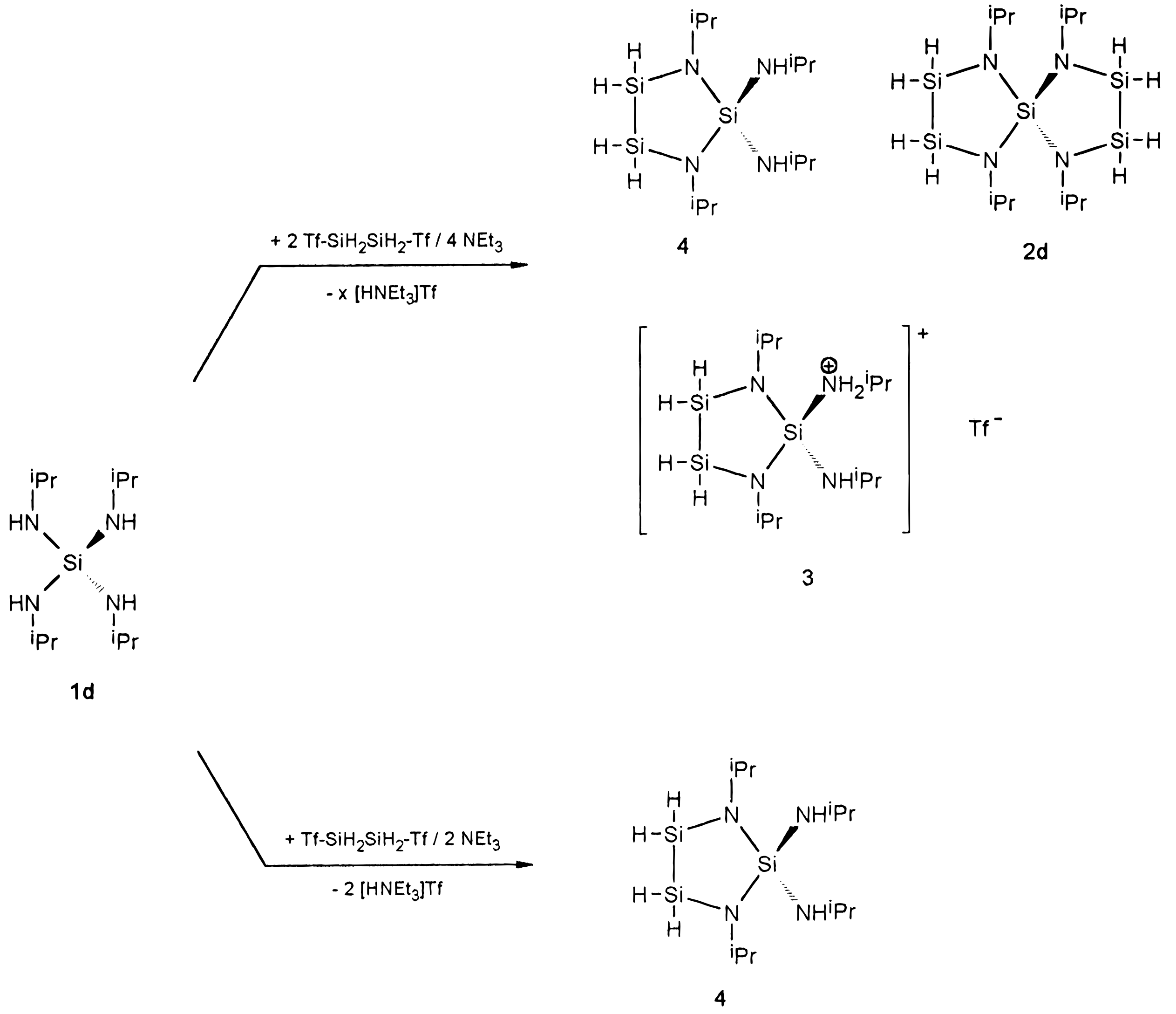
Following a standard workup procedure already employed in the preparation of disilanylamines,[13] the product **2a** was obtained in 63% yield as a readily distillable liquid (bp 46−47 °C/0.05 Torr), which crystallized in the receiver (mp 35 °C). The set of physical data collected by mass, IR, UV, and NMR spectroscopy is in full agreement with the proposed formula. The compound is not photoluminescent in solution (UV/vis excitation in chloroform) or in the solid state. The colorless, distillable liquids **2b**,**c** are also accessible in high yield via this cyclization route. The structure of compounds **2b**,**c** is easily confirmed by analytical and spectroscopic data providing evidence for the incorporation of two $\mathrm{SiH_2{-}SiH_2}$ loops into the spirobicyclic system.

The analogous cyclization reaction with the *i*-Pr compound **1d** gives only very low yields of the corresponding spirocyclic silazane **2d** (Scheme 3). This is probably due to steric congestion which leads to very low reaction rates. Very surprisingly the reaction stops at the stage of a novel monocyclic silylammonium triflate (**3**), which was identified by its analytical, spectroscopic, and crystal data (below). This result suggests that a monocyclic tetraaminosilane (**4**, below) is able to compete successfully with triethylamine as a base for triflic acid.

Monocyclization of **1d** with only 1 equiv of the bistriflate gives high yields of the neutral compound **4** with two *i*-propylamino groups dangling free (Scheme 3). In this first cyclization, steric hindrance is still less stringent.

Molecular Structures. Crystals of the spirocyclic silazane **2a** (obtained by slow cooling of the melt) are monoclinic, space group $P2_1/n$, with $Z = 8$ formula units in the unit cell. The asymmetric unit contains two crystallographically independent molecules with very similar structures (Figure 1), such that no separate discussion of the parameters is necessary. The five-membered rings of the molecules are almost planar and the methyl carbon atoms are also in or close to these planes. With an interplanar angle of 86.1° (89.6°) there is a slight deviation from the perpendicular arrangement of the two planes at each of the two spiro centers, and thus the maximum symmetry (point group D_{2d}) is destroyed, and none of the possible symmetry elements is retained.

Scheme 3



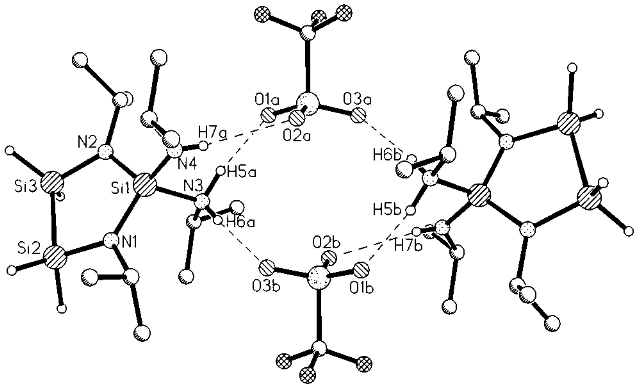


Figure 2. Molecular structure of compound **3** showing the interactions between two silylammonium cations and two triflate counterions (ball-and-stick diagram, C-*H* atoms omitted for clarity). Selected distances (Å): H5−O1 1.679, H6−O3 1.693, H7−O2 1.704.

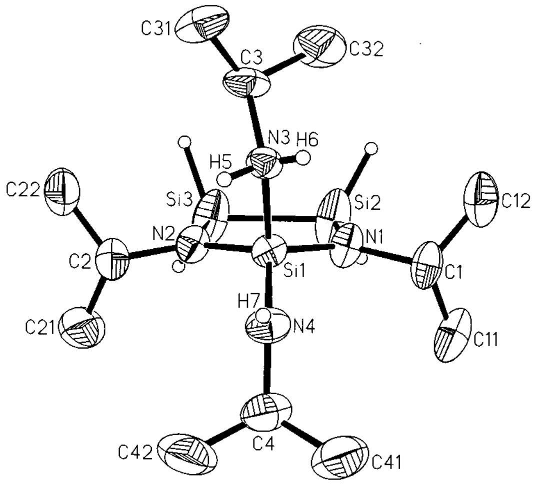


Figure 3. Molecular structure of the silylammonium cation (**3**) (ORTEP drawing with 50% probability ellipsoids, C-*H* atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Si2−Si3 2.315(3), Si1−N1 1.698 (5), Si1−N2 1.707 (4), Si1−N3 1.825(5), Si1−N4 1.666(5), Si2−N1 1.736(5), Si3−N2 1.737(5), Si−H (av.) 1.46(7); N1−Si1−N2 106.9(2), N3−Si1−N4 99.3(3), Si1−N1−Si2 119.2(3), Si1−N2−Si3 118.5(3), N1−Si2−Si3 96.7(2), N2−Si3−Si2 97.2(2).

The endocyclic angles N−Si−N at the spiro center are all smaller than the tetrahedral angle [e.g. N1−Si1−N2 103.56(9)°, average 103.55(9)°], complemented by exocyclic angles correspondingly larger [e.g. N1−Si1−N3 112.06(10)°, average 111.89(10)°]. The sums of the angles at the eight crystallographically independent nitrogen atoms are very close to 360°, attesting to the planar configuration of these atoms. Interestingly enough, the analogous spirobicylic compound with two CH_2-CH_2 units shows twisted five-membered rings with nonplanar nitrogen atoms and an endocyclic angle N−Si−N at the spiro center of 92.8(1)°.[16]

The Si−Si bonds [average 2.3133(9) Å] are in the range documented for strain-free standard single-bond distances. The large endocyclic Si−N−Si angles [e.g. Si1−N1−Si2 121.69(11)°, average 121.44(11)°] are compensated by small endocyclic N−Si−Si angles [e.g. N1−Si2−Si3 96.40(7)°, average 96.43(7)]. This internal relation of bond angles of a ring system is a good example for the very general rule that abnormal bending of angles is energetically least costly at larger atoms with strongly polar bonds (like Si−N). This is immediately obvious from a comparison of the carbon and silicon analogs which reveals, e.g., a substantially larger endocyclic N−C−C angle of 106.1(2)°.[16]

The planarity of the five-membered rings and of the configuration of the nitrogen atoms leads to a fully staggered orientation of the methyl groups relative to the two hydrogen atoms of the neighboring SiH_2 groups but to an eclipsed conformation of the two neighboring SiH_2 groups. Again, because of the larger atomic radius of silicon, this is the energetically best tolerable solution to the conformational dilemma.

There are no unusual contacts between the molecules with their compact structures.

Crystals of the silylammonium salt **3** (from toluene/hexane) are monoclinic, space group $P2_1/c$, with $Z = 4$ formula units in the unit cell. The lattice contains ion quadruples with an inversion center as the crystallographically imposed element of symmetry relating two triflate anions and two silylammonium cations (Figure 2).

The cation has a virtually planar five-membered ring (Figure 3) with an isopropylamino and an isopropylammonio ligand attached to the unique silicon atom (Si1). The ring nitrogen atoms are in a planar configuration placing the $CHMe_2$ carbon atoms in the ring plane. The overall configuration of the heterocycle in **3** closely resembles that of the prototype **2a**.

The nitrogen atom of the dangling *i*-PrNH− group is also planarized with an angle Si1−N4−C4 as large as 128.0(5)° (sums of angles at N4 360.0°). By contrast, the nitrogen atom in the *i*-Pr-$NH_2^{(+)}$- group is tetrahedral with an angle Si1−N3−C3 = 119.8(4)°, about 10° smaller than in the reference group. The two hydrogen atoms of the ammonium group have been located in the Fourier map and refined.

Even more convincing evidence of the ammonium nature of the *i*-$PrNH_2Si$ group is the significant lengthening of the bond Si1−N3 [1.825(5)Å] as compared to both Si1−N4 [1.666(5) Å] and Si1−N1/Si1−N2 [1.6985(5)/1.707(4) Å]. The new data should be considered benchmark values for the structural parameters of the few existing silylammonium cations.

The parameters of the hydrogen bonds between cations and anions are listed in Figure 2. Both hydrogen atoms of the NH_2 group and the hydrogen atom of the NH group are engaged in contacts with the oxygen atoms of the triflate counterions, rendering each hydrogen atom N−H---O coordinated with an average distance NH---O of 1.69 Å.

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Supporting Information Available: Tables of crystal data, structure refinement details, all atomic fractional coordinates, thermal parameters, and interatomic distances and angles (8 pages). Ordering information is given on any current masthead page.

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