

Isomeric Cyclic Disilanediyil Dimethylhydrazines

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Introduction

Current interest in small silicon–nitrogen molecules stems from the role of these compounds as precursors for chemical vapor deposition of silicon nitride¹ or as components for thermal² or sol–gel preparations of silazane frameworks.³ In this context, hydrogen-rich silyl hydrazines are particularly promising candidates owing to their high nitrogen content and surmised low decomposition temperatures.⁴ After our initial studies of simple silylamines⁵ and -hydrazines,^{4,6} we have now also considered the homologous disilanyl compounds with fully hydrogenated SiH₂–SiH₂ units.^{7,8}

The Si–Si–N linkage in compounds of this type is also an intriguing UV chromophore often leading to photoluminescence, which is relevant for photophysical applications of such silicon and silicon nitride based materials.^{9,10}

In the present report, we present the results of our studies of two disilanyl hydrazines generated from *N,N*- and *N,N'*-dimethylhydrazine and a new disilanediyil precursor X–SiH₂–SiH₂–X [X = OSO₂CF₃ (“Tf”)], which was successfully applied already for the synthesis of quite a number of other hydrogen-rich disilane derivatives.^{8,11,12}

Synthesis, Analysis, and Spectroscopic Data of the Compounds. Solutions of the disilanediyilbis(triflate) reagent are readily prepared by treatment of 1,2-di(*p*-tolyl)disilane with 2 equiv of triflic acid in toluene at –10 °C. Addition of equimolar quantities of *N,N*-dimethylhydrazine and two equivalents of triethylamine (as an auxiliary base to trap the triflic acid produced in the reaction) to the solution of Tf–SiH₂SiH₂–Tf

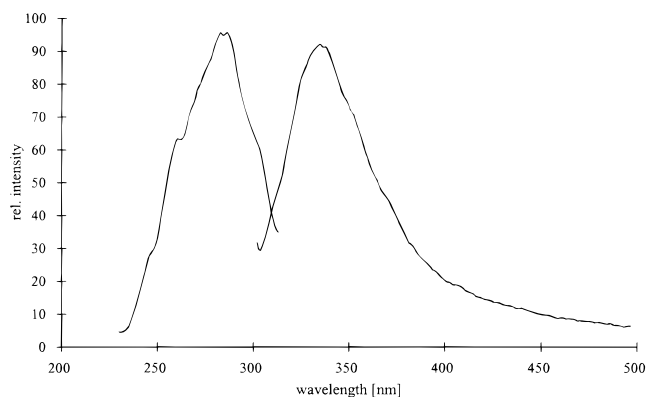


Figure 1. Emission and excitation spectrum of **1** (4×10^{-4} M in chloroform; excitation slit and emission slit, 10 nm).

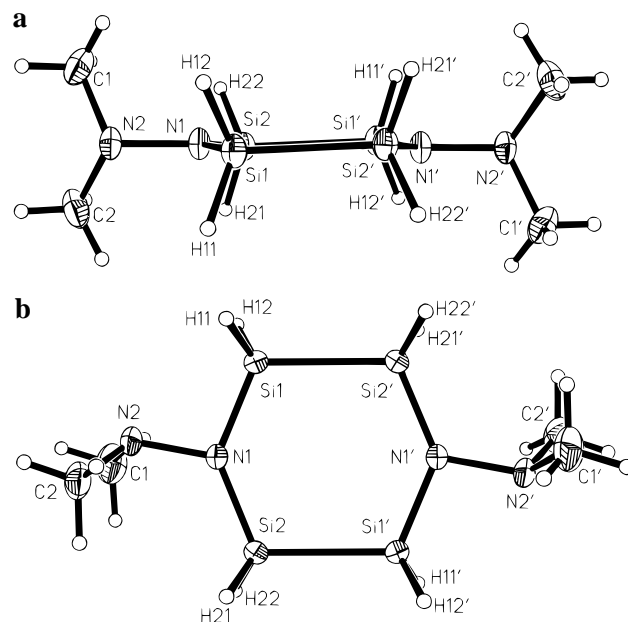


Figure 2. Molecular structure of compound **1** with atomic numbering (ORTEP; 50% probability ellipsoids). (a) Projected parallel to the plane of the silicon atoms; (b) projected perpendicular to the plane of silicon atoms. Selected bond lengths (Å) and angles (deg) are as follows: Si1–N1, 1.7201(9); N1–Si2, 1.7348(9); Si2–Si1', 2.3515(5); N1–N2, 1.4691(11); N2–C1, 1.454(2); N2–C2, 1.456(2); Si2–N1–Si1, 134.40(5); N1–Si1–Si2', 112.70(3); Si1–Si2'–N1', 122.22(3); Si2–N1–N2, 122.90(6); Si1–N1–N2, 102.38(6); N1–N2–C1, 110.58(9); N1–N2–C2, 111.67(8); C1–N2–C2, 111.86(10).

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at –50 °C leads to the formation of the cyclic disilanyl hydrazine **1** in 70% isolated yield (Scheme 1). The triethylammonium triflate separates as a heavy oil and is thus easy to remove from the reaction mixture after warming to ambient temperature. The small amounts of salt impurities remaining in the mother liquor can be precipitated by addition of hexane. The product (**1**) is purified by sublimation in a vacuum and obtained as a colorless, crystalline solid [mp 98 °C], readily soluble in most standard nonprotic solvents, and only moderately sensitive to air and moisture both as a solid and in solution.

The compound was identified by its elemental analysis and by mass spectrometry (Figure 3). The IR (KBr) and Raman spectrum (crystals) show the characteristic bands and lines, respectively, for the disilanediyil unit. Solutions in hexane have UV absorptions at 211 and 258 nm. UV excitation of

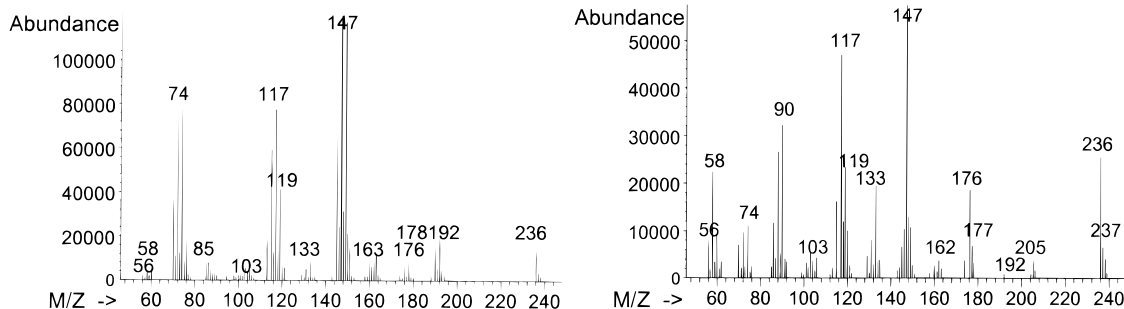
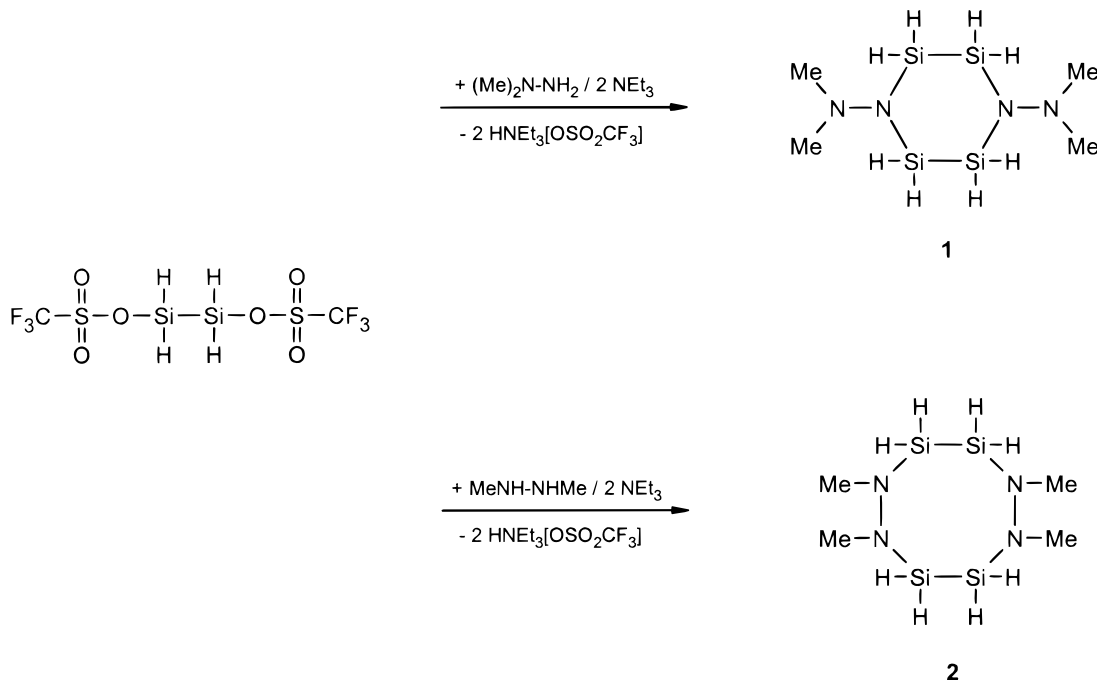


Figure 3. Mass spectra of the isomeric disilanyl hydrazines **1** (left) and **2** (right).

Scheme 1



chloroform solutions at 283 nm leads to an emission with a maximum at 335 nm (Figure 1).

The NMR spectra (in benzene at 25 °C) are in full agreement with the proposed connectivity pattern. The inequivalent nitrogen atoms give rise to two well-separated ^{15}N signals at δ -331.6 and -315.8 ppm (DEPT). The four silicon and the four carbon atoms are found equivalent on the NMR time scale with only one resonance each at δ -57.8 (^{29}Si , DEPT) and δ 45.5 ppm (^{13}C), respectively, which are subject to first- and second-order splittings. All these data suggest a fully symmetrical structure in solution.

In the analogous reaction of $\text{Tf}-\text{SiH}_2\text{SiH}_2-\text{Tf}$ with *N,N'*-dimethylhydrazine, a product **2** is found in the organic phase after removal of the triethylammonium triflate salt, but this disilanyl hydrazine is of much lower stability than compound **1** (Scheme 1). It can be identified by GLC-coupled mass spectrometry (Figure 3) and ^1H NMR spectroscopy, but attempts to purify the product by distillation or crystallization were not successful. According to the GLC analysis, compound **2** is more volatile than its isomer **1**, but obviously it polymerizes rapidly as judged from the viscous residues obtained after heating or after standing at room temperature only for a few hours. These observations suggest methyl- and silyl-shift reactions as postulated for the decomposition of dimethyl(silyl)amine.¹³ The compound and its polymerization product therefore were not investigated any further.

Structural Studies. Crystals of compound **1** are triclinic, space group $P\bar{1}$, with one molecule in the unit cell. The structure could be solved with high precision from a very good data set collected at 199 K.

The molecule has a center of inversion coinciding with the center of a six-membered ring comprising the two disilanediy units and the two nonmethylated nitrogen atoms of the hydrazine moieties (Figure 2a,b).

Surprisingly, the six-membered ring is in a nearly planar conformation, with the two ring nitrogen atoms only slightly above and below the plane of the silicon atoms, respectively, indicating at best a very flat chair form. The two endocyclic nitrogen atoms, N1 and N1', have a planar configuration with the sum of the angles at 359.68°. By contrast, the configuration of N2 (N2'), the nitrogen atoms of the exocyclic -NMe₂ groups, is steeply pyramidal with the sum of angles at 334.11°, only 5° from the value for the ideal tetrahedron (328.44°).

It is immediately obvious from Figure 2b that the two dimethylamino groups are tilted in opposite directions, each of them toward one of the two neighboring silicon atoms (Si1, Si1'). In quantitative terms, the angles N2-N1-Si1 [102.38-(6)°] and N2-N1-Si2 [122.90(6)°] differ by no less than 20°, clearly revealing a sub-van der Waals interaction between N2

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and Si1 [2.49 Å]. This indicates a (4+1) coordination of Si1 in the solid state. It is quite probable that this secondary interaction is also co-determining the flat structure of the six-membered ring on one hand and the orientation of the lone pair of electrons at N2 (i.e. the rotational position of the $-NMe_2$ groups about the N2–N1 bond) on the other. This idea is supported by the structural features of related silazanes with isopropyl groups, which are isoelectronic with dimethylamino groups: in these reference compounds no comparable distortions are detected.¹⁴ Preliminary results of ab initio calculations of compound **1** are also in agreement with the experimental findings.¹⁵

The structural results for the crystalline state require a reconsideration of the spectroscopic data for the solution. In benzene as a solvent, the four silicon atoms and the eight Si-bound hydrogen atoms of the molecule are equivalent on the NMR time scale at room temperature (below). This suggests either a complete decoupling of the N2–Si1 contact by solvation and concomitant free rotation of the $-NMe_2$ groups in solution or a rapid site exchange of the donor atom N2 at Si1 and Si2. In low-temperature experiments (CD_2Cl_2 , $-90^\circ C$) no splitting of the Si–H resonance can be observed (Experimental Section). This indicates that the activation energy for the rotation of the $-NMe_2$ unit is rather small which renders the molecule fluxional in solution on the NMR time scale.

Experimental Section

General Information. All experiments were routinely carried out under an atmosphere of dry, pure nitrogen. Solvents were appropriately dried and saturated with nitrogen, 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. The ^{15}N NMR spectrum was referenced externally to aniline at $\delta -333.6$ ppm. 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). Luminescence measurements were performed on a Perkin-Elmer LS 50 B luminescence spectrometer. Standard equipment was used for all other measurements. Reagents were commercially available or prepared following standard procedures.

***N,N'*-Bis(dimethylamino)-2,3,5,6-tetrasilapiperazine (1).** A freshly prepared solution of 1,2-bis[[(trifluoromethyl)sulfonyl]oxy]disilane^{8,11} [from 1.5 g (6.2 mmol) of 1,2-di(*p*-tolyl)disilane] in toluene (50 mL) is treated with a mixture of 0.37 g (6.2 mmol) of *N,N*-dimethylhydrazine and 1.25 g (12.4 mmol) of triethylamine at $-50^\circ C$ with stirring. The reaction mixture is allowed to warm to $20^\circ C$, the oily triethylammonium triflate is separated, and the solvent is removed in a vacuum. Hexane is added to precipitate all remaining salts. The filtrate is evaporated, and the colorless solid product (**1**, yield 0.51 g, 70%) is purified by sublimation at $80^\circ C/0.05$ Torr and crystallized from hexane, mp $98^\circ C$. MS (EI, 70 eV): m/z 236 (M^+), 192 ($M^+ - C_2H_6N$), 147 (100%, $M^+ - C_4H_{13}N_2$), 117 ($H_5N_2Si_3$), 74 (H_4NSi_2). UV (hexane,

$25^\circ C$): $\lambda_{max} = 211$ nm ($\epsilon_{max} = 3.41 \times 10^3$ L mol $^{-1}$ cm $^{-1}$); $\lambda = 258$ nm (broad). IR (KBr, $25^\circ C$): 2121.6 cm $^{-1}$ (vs, νSiH_2). Raman (crystal, $25^\circ C$): 2129, 2112, 2088 cm $^{-1}$ (νSiH_2), 375 cm $^{-1}$ ($\nu SiSi$). 1H NMR (CD_2Cl_2 , $-90^\circ C$): δ 2.46 (s, 12H, Me), 4.45 (s, $J(Si,H) = 205.1$ Hz, 8H, SiH_2). 1H NMR (C_6D_6 , $25^\circ C$): δ 2.33 (s, 12H, Me), 4.83 (s, $J(Si,H) = 205.1$ Hz, 8H, SiH_2). $^{13}C\{^1H\}$ NMR (vs): δ 45.5 (s, Me). ^{13}C NMR (vs): δ 45.5 (qq, $J(C,H) = 134.2$ and 4.6 Hz, respectively, Me). ^{29}Si NMR (DEPT, vs): $\delta -57.8$ (ttm, $J(Si,H) = 205.1$ and 11.5 Hz, respectively, SiH_2). $^{15}N\{^1H\}$ NMR (DEPT, vs): $\delta -331.6$ (s, NC), -315.8 (s, NSi). Anal. Found: C, 20.66; H, 8.43; N, 22.20. $C_4H_{20}N_4Si_4$ (236.60 g/mol) calcd: C, 20.31; H, 8.52; N, 23.68.

1,2,5,6-Tetramethyl-1,2,5,6-tetraaza-2,3,7,8-tetrasilacyclo-octane (2). As described for **1**, a solution of 1,2-bis[[(trifluoromethyl)sulfonyl]oxy]disilane^{8,11} [from 1.5 g (6.2 mmol) of 1,2-di(*p*-tolyl)disilane] in toluene (50 mL) is treated with a mixture of 0.37 g (6.2 mmol) of *N,N'*-dimethylhydrazine and 1.25 g (12.4 mmol) of triethylamine at $-50^\circ C$ with stirring. The triethylammonium triflate precipitate is separated, and the solvent is removed from the filtrate. Hexane is added to precipitate all remaining ammonium salts. In the filtrate, compound **2** is detected as the sole product by GLC–MS. Attempts to isolate **2** by fractional distillation failed owing to decomposition/polymerization reactions. MS (EI, 70 eV, GC-coupled): m/z 236 (M^+), 205, 176 ($C_4H_{16}N_4Si_2$), 147 (100%, $M^+ - CH_3NSi_2$), 133 ($C_3H_{13}N_2Si_2$), 117 ($H_5N_2Si_3$), 90, 58 ($C_2H_6N_2$). 1H NMR (C_6D_6 , $25^\circ C$): δ 2.54 (s, 12H, Me), 4.60 (s, 8H, SiH_2).

X-ray Crystallography. The sample was mounted in a glass capillary on an Enraf Nonius CAD4 diffractometer and used for measurements of precise cell constants and intensity data collection. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. Graphite-monochromated Mo $K\alpha$ radiation was used. The structure was solved by direct methods and refined by full-matrix least-squares calculations on F^2 . Crystal data for $C_4H_{20}N_4Si_4$. $M_r = 236.60$, colorless crystals, triclinic, $a = 6.095(1)$ Å, $b = 6.902(1)$ Å, $c = 8.343(1)$ Å, $\alpha = 74.78(1)^\circ$, $\beta = 81.60(1)^\circ$, $\gamma = 74.54(1)^\circ$, space group $P1$, $Z = 1$, $V = 325.31(8)$ Å 3 , $\rho_{calc} = 1.208$ g cm $^{-3}$, $F(000) = 128$; $T = -74^\circ C$. Data were corrected for Lorentz and polarization but not for absorption effects [$\mu(Mo K\alpha) = 4.23$ cm $^{-1}$]. From 1384 measured reflections [$(\sin \theta/\lambda)_{max} = 0.64$ Å $^{-1}$], 1373 were used for refinement of 96 parameters; $wR2 = 0.0564$, $R1 = 0.0197$. Residual electron densities: $+0.251/-0.265$. The function minimized was $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/\sum [w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0349$, $b = 0.06$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located on a difference Fourier map and subsequently included in the refinement with isotropic contributions. Selected bond lengths and distances are given in the figure caption.

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Supporting Information Available: Tables of crystallographic parameters, atomic positional and thermal parameters, and bond lengths and angles for compound **1** (3 pages). Ordering information is given on any current masthead page.

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