1,3-Di-*tert*-butyl-2,2,4,4-tetrahalocyclodisilazanes – Synthesis, X-ray Crystal and Gas-Phase Structures

Christiane Brönneke[a][+], **Regine Herbst-Irmer**[a][+], **Uwe Klingebiel***[a], **Peter Neugebauer**[a], **Martina Schäfer**[a][+], and **Heinz Oberhammer***[b]

Institut für Anorganische Chemie, Universität Göttingen[a],
Tammannstr. 4, D-37077 Göttingen, Germany

Institut für Physikalische und Theoretische Chemie, Universität Tübingen[b],
Auf der Morgenstelle 8, D-72076 Tübingen, Germany

Received February 11, 1997

Keywords: Cyclodisilazanes / 1,3-Di-*tert*-butyl-2,2,4,4-tetrafluorocyclodisilazane / 1,3-Di-*tert*-butyl-2,2,4,4-tetrachlorocyclodisilazane / Structure elucidation / Electron diffraction

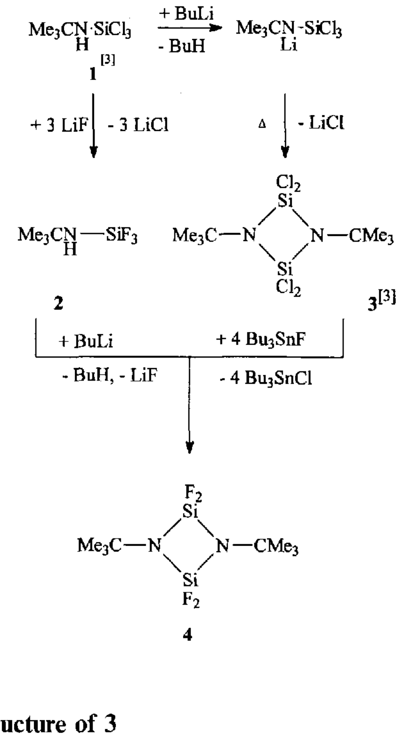
The syntheses of 1,3-di-*tert*-butyl-2,2,4,4-tetrachlorocyclodisilazane (**3**) and of di-*tert*-butyl-2,2,4,4-tetrafluorocyclodisilazane (**4**) are reported. The X-ray crystal structure of **3** and the electron-diffraction gas-phase structure of **4** have been determined. Both cyclodisilazanes possess planar four-membered rings and nearly planar configurations at the nitrogen atoms. The Si–N bond lengths are 171.1(1) pm and 170.6(3) pm and the Si···Si transannular distances 245.0(1) and 241.3(13) pm in **3** and **4**, respectively.

Compared to cyclosilazanes bearing organic substituents, only very few Si–N ring systems in which some or all of the substituents are inorganic are known[1–5]. The former compounds have the following common structural properties: (1) The endocyclic Si–N–Si angles are larger while the N–Si–N angles are smaller than 90°; (2) the endocyclic Si–N bonds are longer than exocyclic Si–N bonds as a result of ring strain. Recently, we reported the first examples of cyclosilazanes bearing silyl groups at the nitrogen and fluorine substituents at the silicon atoms[5]. These compounds display the opposite structural features to their organic-substituted counterparts, i.e., the Si–N–Si angles are smaller while the N–Si–N angles are larger than 90°, and the observed endocyclic Si–N bonds are shorter than the exocyclic bonds. Theoretical calculations for model compounds[5] demonstrate that fluorination of the parent compound, i.e. $(H_2Si{-}NH)_2 \rightarrow (F_2Si{-}NH)_2$, leads to shortening of the endocyclic Si–N bonds from 173 to 170 pm and, thus, to stabilization of the ring system. Furthermore, silylation at the nitrogen atoms, i.e. $(F_2Si{-}NH)_2 \rightarrow (F_2Si{-}NSiH_3)_2$, leads to a decrease in the endocyclic Si–N–Si angles from 92 to 88°. The combined effect of four fluorine atoms at the silicon and of two silyl groups at the nitrogen atoms, leads to an overall shortening of the transannular Si···Si distance. The shortest Si···Si contact (242 pm) has been predicted for $(F_2Si{-}NSiH_3)_2$.

In the present paper we report the synthesis and gas-phase structure of the first cyclodisilazane that is fluorinated at the silicon and alkylated at the nitrogen atoms. Furthermore, we present the crystal structure of the analogous chlorine derivative.

The two routes shown in Scheme 1 lead to the isolation of **4**. Whereas **1**[3] can be fluorinated with LiF in diethyl ether, fluorination of **3** requires the use of the trialkyltin fluorides. 1,3-Di-*tert*-butyl-2,2,4,4-tetrachlorocyclodisilazane (**3**) is a crystalline solid at room temperature and a single-crystal structure analysis was performed.

Scheme 1



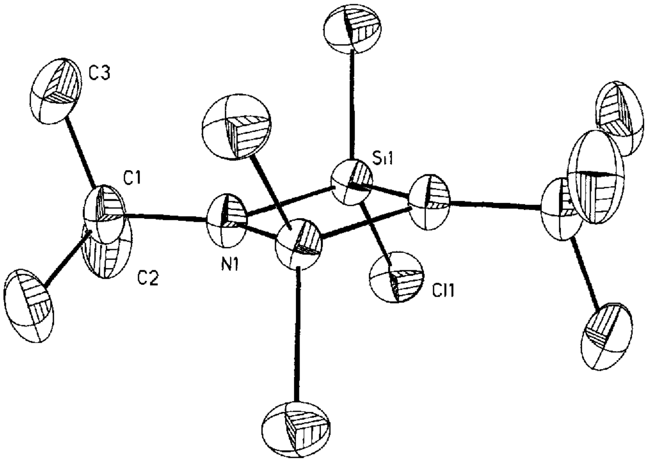
Crystal Structure of 3

Compound **3** crystallizes in the space group *Cmca* with a quarter of a molecule in the asymmetric unit. Hence, the molecule fulfils C_{2h} symmetry. The Si–N–Si ring angle in **3** is larger than 90° while the N–Si–N ring angle is smaller. The transannular Si···Si distance measures 245.0

[+] Crystal structure.

pm. As a result of an inversion centre, **3** has an exactly planar (SiNSiN) four-membered ring (Figure 1). The sum of the angles around the N atom is 358.8°, indicating an essentially planar environment; the bulky *t*Bu groups deviate slightly from the plane in a *trans* fashion.

Figure 1. Crystal structure of **3**[a]

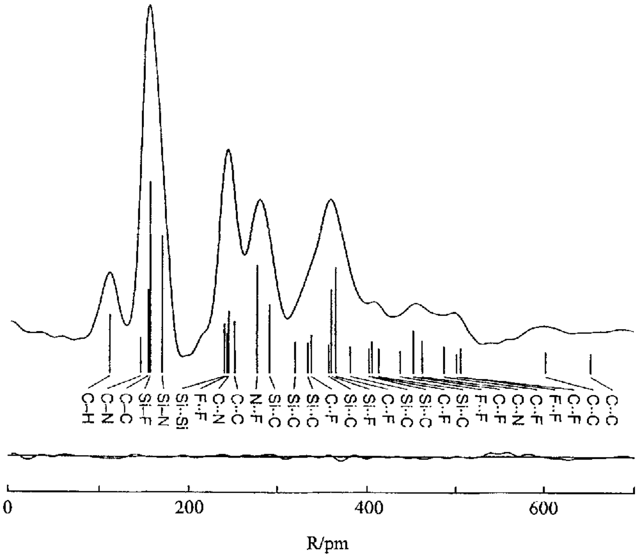


[a] Selected lengths [pm] and angles [°]: Si(1)−Cl(1) 203.2(1), Si(1)−Si(1A) 245.0, Si(1)−N(1A) 171.1(1); N(1A)−Si(1)−N(1) 88.6(1), C(1)−N(1)−Si(1) 133.7(1), Si(1)−N(1)−Si(1A) 91.5(1).

Gas-Phase Structure of 4

The fluorinated derivative **4** is a liquid at room temperature with a b.p. of 85°C. Its high volatility allows a structure determination by gas-electron diffraction. The radial distribution function (RDF) was calculated by Fourier transformation of the molecular intensities and is shown in Figure 2. The experimental RDF is reproduced very well by a structure with planar configuration at the nitrogen atoms. The preliminary geometric parameters derived from the RDF were refined by least-squares fitting of the molecular intensities. The intensities were modified with a diagonal weighting matrix and complex scattering factors were used[6]. Local C_{3v} symmetry was assumed for the methyl and *tert*-butyl groups and the overall symmetry was constrained to C_i. The geometric parameters obtained from this analysis are listed in Table 1 and the molecular structure is shown in Figure 3. The *tert*-butyl groups are rotated by about 15° from an orientation with one C−C bond perpendicular to the ring [ϕ(SiNCC) = 90°]. This "effective" torsional angle is considered to be due to large amplitude torsional vibrations of the *tert*-butyl groups, since the barrier to internal rotation about the N−C bond is expected to be very low. Possible deviations from the exactly planar configuration at the nitrogen atoms were studied in additional least-squares analyses. Puckering of the four-membered ring and out-of-plane bending of the *tert*-butyl groups were considered. In both cases the deviations from planarity were very small [5.6(21)° and 4.2(18)°, respectively] and could be attributed to low-frequency out-of-plane vibrations. Thus, we expect the equilibrium structure of **4** to possess C_{2h} symmetry.

Figure 2. Experimental radial distribution function for **4** and difference curve; the positions of important interatomic distances are indicated by vertical bars



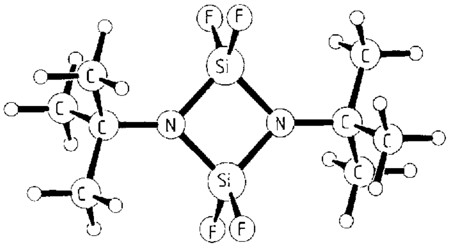
Although the Si−N bonds in **3** and **4** [171.1(1) and 170.6(3) pm] are shorter than such bonds in unstrained silylamines [e.g. 173.4(3) pm in $N(SiH_3)_3$[7], 172.3(1) pm in $CH_3N(SiH_3)_2$[8]], they are considerably longer than those in trichloro- and trifluorosilyldimethylamine [165.7(12)[9] and 165.4(15) pm[10], respectively]. Thus, the considerable shortening of Si−N bonds due to chlorination or fluorination at the silicon atoms is in part counterbalanced by the effects of angle strain in the four-membered rings.

Table 1. Gas-phase structure of **4**[a]

C–H	111.6(6)	N···N	241.2(13)
N–C	145.7(10)	N–Si–N	90.0(6)
C–C	154.6(11)	F–Si–F	102.5(12)
Si–F	156.7(5)	C–C–C	109.4(9)
Si–N	170.6(3)	H–C–H	109.7(14)
Si···Si	241.3(13)	ϕ(SiNCC)[b]	75.3(15)

[a] r_a values in pm and °; uncertainties are 3σ values. − [b] Torsional angle for *tert*-butyl groups.

Figure 3. Gas-phase structure of **4**



The most interesting aspect of $[R_2SiX]_2$ four-membered rings with X = CR'_2, NR′ or O are the extremely short transannular Si···Si contacts. Values of 259.2 pm in 1,3-disilacyclobutane[11], 237.8−263.1 pm in cyclodisilazanes[5,12] and 239.0 pm in tetramesitylcyclodisiloxane[13] have been reported (Table 2). These contacts are equal to or only slightly longer than Si−Si bonds in disilanes (e.g. 231.7 pm in Si_2F_6[15] or 269.7 pm in Si_2tBu_2[16]). Because of the larger spatial requirement of Si compared to C, N or O, a distortion of the four-membered ring to a rhombus with an *increased* Si···Si distance might be anticipated. However, in two cases the experimental structures show a distortion where the Si···Si contacts are *decreased* relative to the X···X distances. The four-membered ring in **4** possesses an exactly quadratic structure. The bonding properties of such four-membered rings, containing two opposite silicon atoms, have been investigated by various theoretical methods[9,17–20]. The presence of a transannular σ bond has been excluded, in agreement with the very small Si···Si coupling constant[21]. Grev and Schäfer[19] explain the short Si···Si contacts in terms of an "unsupported π bond", which lies in the planc of the ring.

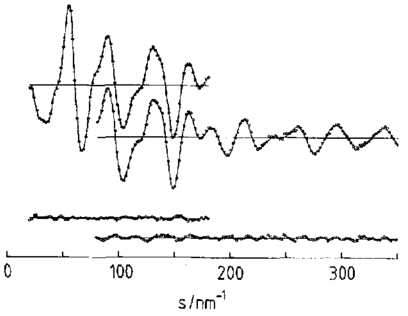
Table 2. Geometric parameters of $[R_2SiX]_2$ four-membered rings; X = CR'_2, NR′ and O

	Si–X	Si···Si	X···X
$[H_2SiCH_2]_2$[a]	188.8	259.2	268.4
$[F_2SiNSiMe(CMe_3)_2]_2$[b]	170.7	237.8	245.0
$[Pr_2SiNC_6H_2(CMe_3)_3]_2$[c]	177.3–180.1	263.1	241.8
$[F_2SiNtBu]_2$[d]	170.6	241.3	241.3
$[Cl_2SiNtBu]_2$[e]	171.1	245.0	238.9
$[Mes_2SiO]_2$[f]	167.0; 167.3	239.0	234.4
$tBu_2SiOSitBu_2NSiMe_3$[g]	177.3; 168.2	247.9	240.5

[a] Gas-phase structure[11]. – [b] Crystal structure[4]. – [c] Crystal structure[12]. – [d] Gas-phase structure, this work. – [e] Crystal structure, this work. – [f] Crystal structure[13]. – [g] Crystal structure[15], first value corresponds to Si–N, second value to Si–O distance.

This work was supported by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie.*

Figure 4. Electron-diffraction intensities for long (top) and short (bottom) nozzle-to-plate distances and differences



Experimental Section

Preparation of N-tert-butyltrifluorosilylamine (**2**): To a solution of 0.3 mol (7.78 g) of LiF in 50 ml of THF, 0.1 mol (20.66 g) of $(CH_3)_3CNHSiCl_3$[3] was added. The mixture was stirred for 10 h at room temperature. A conversion of 100% was achieved. After separation from LiCl, **2** was purified by distillation at 20°C/200 mbar.

Preparation of 1,3-Di-tert-butyl-2,2,4,4-tetrafluorocyclodisilazane (**4**): To a suspension of 0.4 mol (123.61 g) of tri-*n*-butyltin fluoride in 200 ml of diethyl ether, 0.1 mol (34.02 g) of 1,3-di-*tert*-butyl-2,2,4,4-tetrachlorocyclodisilazane[3] was added. The reaction mixture was refluxed for 4 h. After separation from LiCl, **4** was purified by distillation at 85°C.

Crystal Data of **3**[22–24]: $C_8H_{18}Cl_4N_2Si_2$, space group *Cmca*, orthorhombic, a = 1310.1(1), b = 1203.5(2), c = 1002.2(2) pm, V = 1.5802(4) nm^3, Z = 4, $\rho_{calcd.}$ = 1.430 Mg/m^3, crystal size 0.5 × 0.5 × 0.2 mm, λ = 71.073 pm, 2486 reflections at 2Θ = 8–55° measured, of which 948 (R_{int} = 0.0498) were used for refinement on F^2. Refinement with 43 parameters to $wR2$ = 0.0801 (all data) and $R1[I = > 2\sigma(I)]$ = 0.0290. Maximal and minimal residual density: 275 and –291 e nm^{-3} respectively; $wR2 = \sqrt{w(F_o^2 - F_c^2)^2/w(F_o^2)^2}$, $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. Further details of the crystal-structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-406758, the names of the authors, and the journal citation.

Gas-Phase Structure Data of **4**: The gas-electron diffraction intensities were recorded with a Gasdiffraktograph KD-G2[25] at nozzle-to-plate distances of 25 and 50 cm with an accelerating voltage of ca. 60 kV. The sample reservoir was warmed to 25°C and the gas nozzle to 35°C. The electron wavelength was calibrated with ZnO powder diffraction patterns. The photographic plates (Kodak Electron Image plates 18 × 13 cm) were analyzed by the usual methods[26]. Averaged molecular intensities in the s ranges 20–180 and 80–350 nm^{-1} [$s = 4\pi/\lambda \sin(\Theta/2)$, λ = electron wavelength, Θ = scattering angle] are presented in Figure 4.

---

[1] J. Haiduc, D. B. Sowerby, *The Chemistry of Inorganic Homo- and Heterocycles*, Academic Press Inc. (London) Ltd., **1987**, p. 221.
[2] H. Bürger, M. Schulze, U. Wannagat, *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 43.
[3] S. Bartholmei, U. Klingebiel, G. M. Sheldrick, D. Stalke, *Z. Anorg. Allg. Chem.* **1988**, *556*, 129.
[4] B. Tecklenburg, U. Klingebiel, M. Noltemeyer, D. Schmidt-Bäse, *Z. Naturforsch., B: Chem. Sci.* **1992**, *47*, 855.
[5] T. Müller, Y. Apeloig, I. Hemme, U. Klingebiel, M. Noltemeyer, *J. Organomet. Chem.* **1995**, *494*, 133.
[6] J. Haase, *Z. Naturforsch. A: Astrophys. Phys. Chem.* **1970**, *25*, 936.
[7] B. Beagley, A. R. Conrad, *Trans. Faraday Soc.* **1970**, *66*, 2740.
[8] D. G. Anderson, D. W. H. Rankin, *J. Mol. Struct.* **1989**, *195*, 216.
[9] W. Airey, C. Glidewell, A. G. Robiette, G. M. Sheldrick, J. M. Freeman, *J. Mol. Struct.* **1971**, *8*, 423.
[10] W. Airey, C. Glidewell, A. G. Robiette, G. M. Sheldrick, J. M. Freeman, *J. Mol. Struct.* **1978**, *8*, 423.
[11] B. Rempfer, G. Pfafferott, H. Oberhammer, N. Auner, J. E. Boggs, *Acta Chem. Scand.* **1988**, *42A*, 352.
[12] D. Stalke, N. Keweloh, U. Klingebiel, M. Noltemeyer, G. M. Sheldrick, *Z. Naturforsch., B: Chem. Sci.* **1987**, *42*, 1237.
[13] M. J. Fink, K. J. Haller, R. West, J. Michl, *J. Am. Chem. Soc.* **1984**, *106*, 822.
[14] D. Schmidt-Bäse, U. Klingebiel, *J. Organomet. Chem.* **1989**, *364*, 313.
[15] H. Oberhammer, *J. Mol. Struct.* **1976**, *31*, 237.
[16] A. Simon, *Angew. Chem.* **1986**, *98*, 100; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 79.
[17] Y. Appeloig in: S. Patai and Z. Rappoport (Eds.) *The Chemistry of Organic Silicon Compounds*, Part 1, Wiley, Chichester, **1989**, p. 1213.
[18] M. O'Keefe, G. V. Gibbs, *J. Phys. Chem.* **1985**, *89*, 4574.
[19] R. S. Grev, H. F. Schäfer III, *J. Am. Chem. Soc.* **1987**, *109*, 6577.
[20] A. Savin, H. J. Flad, H. W. Preuss, H. G. von Schnering, *Angew. Chem.* **1992**, *104*, 185; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 185.
[21] R. West, *Angew. Chem.* **1987**, *99*, 1231; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1201.
[22] T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615.
[23] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
[24] G. M. Sheldrick, *SHELXL-96*, Universität Göttingen, **1996**.
[25] H. Oberhammer in: *Molecular Structures by Diffraction Methods*, The Chemical Society, London, **1976**, vol. 4, p. 24.
[26] H. Oberhammer, W. Gombler, H. Willner, *J. Mol. Struct.* **1981**, *70*, 273.

[97028]