Kurzmitteilungen / Short Communications

Solid-State Structure of Tris(phenylsilyl)amine

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The solid-state structure of tris(phenylsilyl)amine (**1**) has been determined by single-crystal X-ray diffraction analysis. The compound crystallizes in the trigonal space group *R*3 with three formula units in the unit cell. The molecules, which display crystallographic C_3 symmetry, contain almost completely planar NSi_3 units with a propeller-like arrangement of the phenyl rings attached to them. By contrast, the carbon analogue tribenzylamine is strongly pyramidal at nitrogen, which – in the absence of steric effects – clearly demonstrates the planarization effect of silicon as a substituent to nitrogen in tertiary amines.

The most intriguing structural feature of tri*silyl*amines is the planarity of the substituents at the nitrogen atom, as deduced from *gas phase electron diffraction* data of small molecules like $(H_3Si)_3N$[1], $(MeSiH_2)_3N$[2], and $(Me_3Si)_3N$[3], or corroborated by results from vibrational spectroscopy and by dipole moment and other studies of colligative properties. Owing to low melting points and/or waxy consistency of the compounds, *solid state* structure determinations of simple trisilylamines without electronegative substituents (F, O, or another N) by *X-ray diffraction* analysis have been restricted to only one example, however, i.e. (phenylsilyl)bis(trimethylsilyl)amine[4] with two very bulky substituents. Since bulky substituents like isopropyl groups may induce N-planarity even in trialkylamines[5], the result may not really be representative for strainfree trisilylamines. We now report on the solid state structure of a symmetrically substituted trisilylamine with a constitutionally non-forced structure, tris(phenylsilyl)amine (**1**), which was prepared[4] in the course of our search for new single-source feedstock precursors for plasma-enhanced chemical vapor deposition (PECVD)[6] of Si_3N_4 films. Since **1** is the Si analogue of tri*benzyl*amine, which has been shown to have a strongly pyramidal nitrogen atom by X-ray diffraction analysis already twenty years ago[7], the comparison of both structures should directly demonstrate the influence of the element directly bound to nitrogen on the configuration of nitrogen in tertiary amines.

$[(C_6H_5)H_2Si]_3N$ **1**

Crystalline samples of **1** are obtained by diluting the molten material (m.p. 14°C) with a minimum amount of pentane and cooling the resulting solution to −22°C. The compound crystallizes in the acentric trigonal space group *R*3 with three formula units in the unit cell. The molecular structure of **1** is shown in Figure 1, selected bond lengths and angles are given in the figure caption.

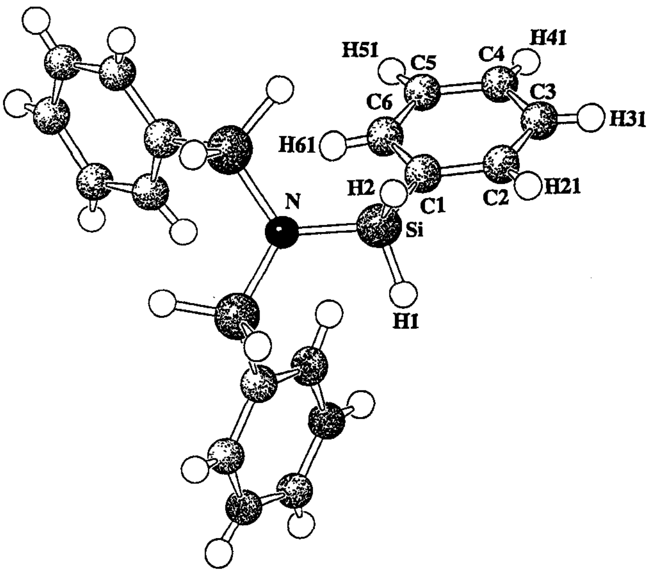

Figure 1. Molecular structure of compound **1** with atomic numbering. Distances [Å] and angles [°]: Si–N 1.735(1), Si–C1 1.868(1), Si–H1 1.36(2), Si–H2 1.35(2); N–Si–C1 113.0(1), N–Si–H1 107(1), N–Si–H2 106.1(8), H1–Si–H2 106(1), C1–Si–H1 112.2(9), C1–Si–H2 111.9(8), Si–N–Si′ 119.5(1)

The three $SiH_2(C_6H_5)$ groups of the individual molecules are related by a crystallographic threefold axis passing through the nitrogen atom perpendicularly to the Si_3 triangle. Like in the other trisilylamines studied in the gas phase[1–3] and in the solid state[4], but in contrast to the pyramidal geometry of the NC_3 group in tribenzylamine, the NSi_3 skeleton in **1** is almost completely planar, as indicated by three Si–N–Si angles of 119.5(1)°. The N atom deviates by 0.123(3) Å from the Si_3 plane. The Si–N bond lengths of 1.735(1) Å are in good agreement with Si–N distances found for other trisilylamines and are indicative of a partial multiple-bond character. By symmetry, the phenyl rings are arranged as a three-blade propeller. Though not enforced by crystallographic symmetry, the situation is similar in this regard to the tribenzylamine analogue. The angles between normals to the Si_3-plane and the planes of the phenyl rings in **1** are 55°, with the planes of the phenyl rings almost vertical to one another (89°). The orientation of the phenyl rings relative to the $N(SiH_2)_3$ moiety can be referred to as axial, and this again is similar in the tribenzylamine analogue. The only striking difference between both structures is thus the planarity of the nitrogen atom in **1**, induced by silicon substitution (Figure 2). Nitrogen planarization is thus clearly an inherent phenomenon even in completely strain-free and sterically non-crowded silylamine molecules.

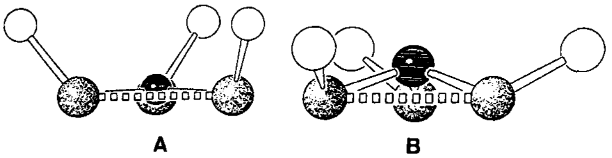

Figure 2. Side view A of **1** and B of tribenzylamine. Hydrogen atoms omitted, empty circles represent C1 atoms of the phenyl rings

Experimental

Compound **1** was prepared by the published procedure[4]. High quality crystals of **1** were grown by cooling the molten material (m.p. 14°C), which was diluted with a minimum amount of pentane, to −22°C. The structure of **1** was solved by direct methods (SHELXS-86), completed by Fourier synthesis and refined anisotropically by full matrix methods (SHELX-76). All hydrogen atoms were located in the final difference Fourier maps and refined isotropically. Further information on crystal data, structure solution and refinement is given in Tables 1–3, and further details are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldhafen 2, on quoting the depository number CSD-56485, the names of the authors, and the journal citation.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters for compound **1** [$U_{eq} = (U_1 \cdot U_2 \cdot U_3)^{1/3}$, where U_1, U_2, and U_3 are the eigenvalues of the U_{ij} matrix; e.s.d. values in parentheses]

Atom	X/A	Y/B	Z/C	U(eq.)
Si	0.53336(3)	0.18909(3)	0.06887	0.024
N	0.66667	0.33333	0.0571(2)	0.026
C1	0.5150(1)	0.0838(1)	-0.0677(1)	0.023
C2	0.4101(1)	-0.0354(1)	-0.0649(1)	0.028
C3	0.3926(1)	-0.1224(1)	-0.1576(2)	0.034
C4	0.4798(1)	-0.0931(1)	-0.2539(1)	0.031
C5	0.5838(1)	0.0242(1)	-0.2583(1)	0.031
C6	0.6003(1)	0.1119(1)	-0.1662(1)	0.027

Table 2. Hydrogen atom parameters for compound **1**

Atom	X/A	Y/B	Z/C	U(iso)
H21	0.356(1)	-0.058(1)	0.003(1)	0.026(3)
H31	0.322(2)	-0.197(2)	-0.150(2)	0.054(5)
H41	0.461(1)	-0.151(2)	-0.316(2)	0.036(4)
H51	0.646(2)	0.051(2)	-0.323(2)	0.042(4)
H61	0.667(1)	0.193(1)	-0.171(2)	0.036(4)
H1	0.436(2)	0.210(2)	0.078(2)	0.052(5)
H2	0.540(1)	0.142(2)	0.183(2)	0.040(4)

Table 3. Crystal data, structure solution, and refinement for compound **1**

$C_{18}H_{21}NSi_3$, $M_r = 335.63$, crystal system trigonal, space group $R3$, $a = 12.445(1)$, $b = 12.445(1)$, $c = 10.403(1)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 120°$, $V = 1395.34$ Å^3, $\varrho_{calcd.} = 1.199$ g cm^{-3}, $Z = 3$, $F(000) = 534$ e, $\mu(\text{Mo-}K_\alpha) = 2.100$ cm^{-1}, $T = -60$°C, radiation Mo-K_α, scan ω, scan width [in ω] 0.8°, hkl range ±14, +14, ±12, $\sin(\Theta/\lambda)_{max} = 0.61$ Å^{-1}, measured reflections 1811, unique reflections 578, $R_{int} = 0.015$, observed reflections 574, $F_o \geqslant 2\sigma(F_o)$, refined parameters 94, R (R_w) = 0.0221 (0.0268)[a], (shift/error)$_{max}$ 0.001, ϱ(max/min) +0.44, −0.31 eÅ^{-3}

[a] R (R_w) = 0.0228 (0.0271) for the model with the inverse configuration.

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CAS Registry Number

1: 139494-18-1