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Tris(p-tolylsilyl)amine

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(*Received* 14 *June* 1994; *accepted* 26 *October* 1994)

Abstract

The title compound, C₂₁H₂₇NSi₃, shows a virtually planar coordination geometry of the N atom. Unlike in (PhH₂Si)₃N, the three p-tolylsilyl substituents are not related by crystallographic symmetry.

Comment

The planar configuration of the N atom is the most striking structural feature of most of the silylated nitrogen compounds (Lucevics, Pudova & Strukokovich, 1989). Only a few exceptions of this general rule are known: aminosilanes with NH₂ substituents at bulky organosilyl groups (Ruhlandt-Senge, Bartlett, Olmstead & Power, 1993), two silylhydrazine compounds (Dressler, Niecke, Pohl, Saak, Schoeller & Schaefer, 1986; Schrenk & Mattes, 1988), and silylated hydroxylamines (Mitzel, Angermaier & Schmidbaur, 1994). In the latter two cases,

the deviation from a planar N-atom coordination geometry could be related to the electronegative bonding partners N in hydrazines and O in hydroxylamines, and lone-pair repulsion effects, as supported by theoretical calculations (Mitzel, Hofmann, Waterstradt, Schleyer & Schmidbaur, 1994).

All trisilylamines studied until now show a completely flat geometry at the N atoms. (H₃Si)₃N (Hedberg, 1955; Beagley & Conrad, 1970), (Me₂HSi)₃N (Ebsworth, Murray, Rankin & Robertson, 1981) and (Me₃Si)₃N (Anderson, Rankin & Robertson, 1990) were studied by electron diffraction in the gas phase, and the solid-state structures of a few compounds were elucidated by single-crystal X-ray diffraction: (H₃Si)₃N (Barrow & Ebsworth, 1984), (Cl₃Si)₃N and (Cl₃Si)N(SiCl₂)₂N(SiCl₃) (Wannagat, Flindt, Brauer, Büger & Dörrenbach, 1989), (PhH₂Si)₃N (Mitzel, Schier & Schmidbaur, 1992) and some amines with mixed ligands (Mitzel, Schier, Beruda & Schmidbaur, 1992).

(I)
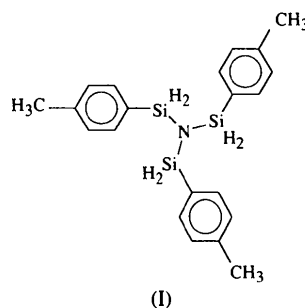
The present investigation of tris(p-tolylsilyl)amine, (I), is part of a more extensive study of the factors contributing to nitrogen planarization in Si–N systems.

A perspective view showing the atomic numbering scheme is given in Fig. 1. Selected bond lengths and angles are listed in Table 2.
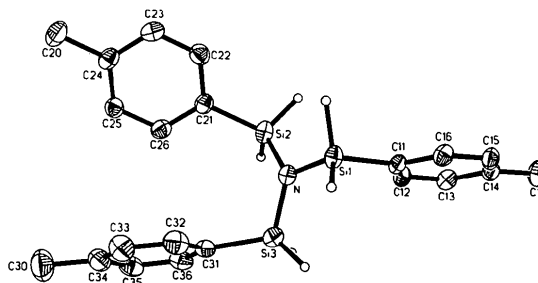

Fig. 1. Plot of tris(p-tolylsilyl)amine. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

Tris(p-tolysilyl)amine (I) was prepared by a known method (Mitzel, Riede, Schier, Paul & Schmidbaur, 1993) and crystallized by slowly cooling the melt diluted with a minimum amount of hexane to 253 K.

Crystal data

$C_{21}H_{27}NSi_3$
$M_r = 377.71$
Monoclinic
$P2_1$
$a = 9.710\,(1)$ Å
$b = 7.386\,(1)$ Å
$c = 15.236\,(1)$ Å
$\beta = 90.67\,(1)^\circ$
$V = 1092.6$ Å^3
$Z = 2$
$D_x = 1.148$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15-19^\circ$
$\mu = 0.22$ mm^{-1}
$T = 193$ K
Needle
$0.45 \times 0.40 \times 0.30$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4776 measured reflections
4698 independent reflections
4530 observed reflections
$[F > 4\sigma(F)]$

$\theta_{max} = 27^\circ$
$h = -12 \rightarrow 12$
$k = -9 \rightarrow 9$
$l = 0 \rightarrow 19$
3 standard reflections monitored every 100 reflections
intensity decay: 1.3%

Refinement

Refinement on F
$R = 0.0280$
$wR = 0.0304$
$S = 0.411$
4530 reflections
249 parameters
Unit weights applied
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Si1	0.78888 (4)	0.00260	0.37506 (3)	0.031 (1)
Si2	0.85867 (5)	−0.3144 (1)	0.26074 (3)	0.033 (1)
Si3	0.82527 (6)	0.0552 (1)	0.18173 (4)	0.046 (1)
N	0.8325 (2)	−0.0834 (2)	0.2736 (1)	0.033 (1)
C11	0.5988 (2)	0.0070 (3)	0.3900 (1)	0.026 (1)
C12	0.5078 (2)	−0.0710 (2)	0.3293 (1)	0.029 (1)
C13	0.3668 (2)	−0.0709 (3)	0.3428 (1)	0.030 (1)
C14	0.3123 (2)	0.0048 (3)	0.4181 (1)	0.029 (1)
C15	0.4018 (2)	0.0827 (3)	0.4789 (1)	0.030 (1)
C16	0.5425 (2)	0.0849 (3)	0.4648 (1)	0.029 (1)
C10	0.1591 (2)	0.0002 (3)	0.4335 (1)	0.042 (1)
C21	1.0409 (2)	−0.3935 (2)	0.2632 (1)	0.029 (1)
C22	1.0970 (2)	−0.4768 (3)	0.3378 (1)	0.033 (1)
C23	1.2322 (2)	−0.5372 (3)	0.3395 (1)	0.033 (1)
C24	1.3164 (2)	−0.5166 (3)	0.2671 (1)	0.031 (1)
C25	1.2612 (2)	−0.4364 (3)	0.1923 (1)	0.031 (1)
C26	1.1257 (2)	−0.3761 (3)	0.1902 (1)	0.031 (1)
C20	1.4646 (2)	−0.5794 (3)	0.2705 (2)	0.043 (1)
C31	0.9893 (2)	0.0474 (3)	0.1202 (1)	0.033 (1)
C32	1.1104 (2)	0.1114 (3)	0.1589 (1)	0.040 (1)
C33	1.2351 (2)	0.0958 (3)	0.1168 (1)	0.043 (1)
C34	1.2433 (2)	0.0184 (3)	0.0341 (1)	0.039 (1)
C35	1.1220 (2)	−0.0430 (3)	−0.0051 (1)	0.037 (1)
C36	0.9974 (2)	−0.0297 (3)	0.0369 (1)	0.036 (1)
C30	1.3798 (2)	−0.0003 (4)	−0.0113 (2)	0.062 (1)

Table 2. *Selected geometric parameters* (Å, °)

N—Si1	1.728 (2)	C23—C24	1.389 (2)
N—Si2	1.736 (2)	C24—C25	1.387 (2)
N—Si3	1.735 (2)	C25—C26	1.390 (2)
Si1—C11	1.862 (2)	C21—C26	1.397 (2)
Si2—C21	1.864 (2)	C31—C32	1.392 (3)
Si3—C31	1.858 (2)	C32—C33	1.382 (3)
C11—C12	1.397 (2)	C33—C34	1.386 (3)
C12—C13	1.387 (2)	C34—C35	1.390 (2)
C13—C14	1.386 (2)	C35—C36	1.385 (3)
C14—C15	1.388 (2)	C31—C36	1.395 (3)
C15—C16	1.385 (2)	C14—C10	1.509 (2)
C11—C16	1.394 (2)	C24—C20	1.513 (2)
C21—C22	1.397 (2)	C34—C30	1.508 (3)
C22—C23	1.386 (2)		
Si1—N—Si2	120.0 (1)	C32—C31—C36	117.9 (2)
Si2—N—Si3	119.5 (1)	C31—C32—C33	121.0 (2)
Si3—N—Si1	119.8 (1)	C32—C33—C34	121.1 (2)
N—Si1—C11	111.7 (1)	C33—C34—C35	117.9 (2)
N—Si2—C21	116.5 (1)	C34—C35—C36	121.4 (2)
N—Si3—C31	111.2 (1)	C35—C36—C31	120.7 (2)
C12—C11—C16	117.4 (1)	C12—C11—Si1	122.1 (1)
C11—C12—C13	121.3 (2)	C16—C11—Si1	120.4 (1)
C12—C13—C14	120.7 (2)	C10—C14—C13	120.4 (2)
C13—C14—C15	118.5 (1)	C10—C14—C15	121.1 (2)
C14—C15—C16	120.8 (2)	C22—C21—Si2	121.0 (1)
C15—C16—C11	121.3 (2)	C26—C21—Si2	121.6 (1)
C22—C21—C26	117.4 (2)	C20—C24—C23	120.6 (2)
C21—C22—C23	121.1 (2)	C20—C24—C25	121.1 (2)
C22—C23—C24	121.0 (2)	C32—C31—Si3	120.0 (1)
C23—C24—C25	118.1 (2)	C36—C31—Si3	122.0 (1)
C24—C25—C26	120.9 (2)	C30—C34—C33	121.0 (2)
C25—C26—C21	121.1 (2)	C30—C34—C35	121.2 (2)

Calculations with the molecule and its inverse yielded the same R factors, and were indistinguishable. Si-H atoms were found and refined isotropically; aryl H atoms were found but not refined; for Me-H atoms one H atom was found for each group, the remainder were calculated. All were allowed to ride on their parent C atom with $U = 0.08$ Å^2.
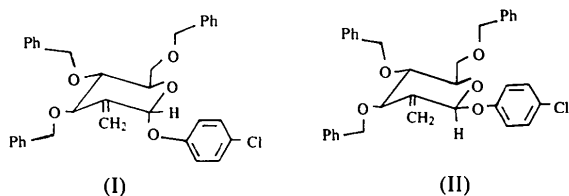
Data collection and cell refinement: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction: local programs. Programs used to solve and refine structure: *SHELXTL-Plus/PC* (Sheldrick, 1989).

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p-Chlorophenyl 3,4,6-Tri-O-benzyl-2-deoxy-2-methylene-β-D-glucopyranoside

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Abstract

The title compound, $C_{34}H_{33}ClO_5$, has a β configuration at the anomeric centre C1. The pyranose ring adopts a chair conformation with all the substituents in equatorial positions. The molecular packing is achieved through van der Waals interactions.

Comment

The title compound was prepared as an intermediate to prove the mechanism of the reaction of a new Ferrier system (Booma & Balasubramanian, 1993*a*) with phenols (Booma & Balasubramanian, 1993*b*). Structure (I) was originally suggested for this compound but NMR NOE experiments indicated structure (II) with a β configuration at the anomeric centre C1 (Fig. 1). The present paper reports the X-ray structure, confirming this configuration in the crystal. A perspective view of the molecule is given in Fig. 1.
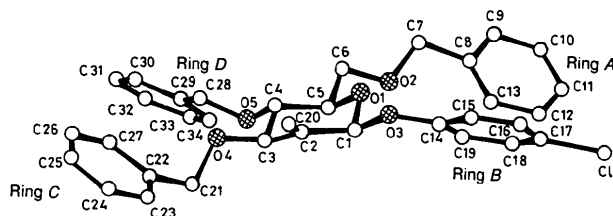
The pyranose ring adopts a chair conformation ($\Delta C_m = 8.2°$, $\Delta C_2 = 10.1°$) (Duax, Weeks & Rohrer, 1976). All the phenyl rings are planar [$\chi^2 = 1.0$, 19.0, 3.6 and 2.8 for rings A (C8–C13), B (C14–C19), C (C22–C27) and D (C29–C34), respectively]; the angles between the planes are A–B 121.0(3)°, B–C 137.0(2)°, C–D 147.1(2)°, A–D 128.9(3)°, A–C 18.5(2)° and B–D 16.4(2)°. The moiety C6—O2—C7—C8 is planar and makes an angle of 27.7(4)° with ring A.

The C28—O5 bond is synplanar with respect to the C29—C34 bond. The substituents at C1, C3, C4 and C5 are all in equatorial positions. The packing in the unit cell is governed only by van der Waals interactions.

Fig. 1. A perspective view of the title compound.

Experimental

Crystal data

$C_{34}H_{33}ClO_5$	Cu $K\alpha$ radiation
$M_r = 558.093$	$\lambda = 1.5418$ Å
Orthorhombic	Cell parameters from 25
$P2_12_12_1$	reflections
$a = 8.236(3)$ Å	$\theta = 15$–$25°$
$b = 14.967(4)$ Å	$\mu = 1.4$ mm^{-1}
$c = 24.032(5)$ Å	$T = 293$ K
$V = 2962(1)$ Å^3	Needle
$Z = 4$	$0.24 \times 0.12 \times 0.10$ mm
$D_x = 1.24$ Mg m^{-3}	Colourless
$D_m = 1.25(2)$ Mg m^{-3}	Crystal source: recrystallized
D_m measured by flotation	from CHCl$_3$–EtOH

Data collection

Enraf–Nonius diffractometer	$\theta_{max} = 60°$
$\omega/2\theta$ scans	$h = 0 \rightarrow 8$
Absorption correction:	$k = 0 \rightarrow 16$
none	$l = 0 \rightarrow 26$
2538 measured reflections	3 standard reflections
2538 independent reflections	monitored every 200
2214 observed reflections	reflections
[$I > 3\sigma(I)$]	intensity decay: <3%