

Tetrakis(1-naphthylamino)silane and its tetrahydrofuran trisolvate

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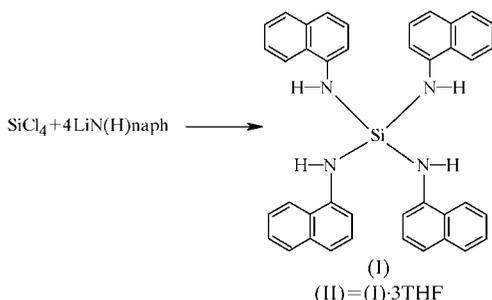
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In both title structures, $C_{40}H_{32}N_4Si$ and $C_{40}H_{32}N_4Si \cdot 3C_4H_8O$, the angles around the Si atom deviate significantly from the tetrahedral value [104.34 (7)–116.63 (7)° in the nonsolvate and 99.91 (15)–116.85 (15)° in the solvate]. The amino H atoms in the solvated structure are involved in hydrogen bonding with two of the tetrahydrofuran solvent molecules.

Comment

The lithiated homoleptic polyimide complexes of main group elements are of great interest due to their versatility in forming a variety of clusters and cages (Brask & Chivers, 2001; Aspinall *et al.*, 2002). The aggregation depends to a large extent on the bulk of the nitrogen substituents. Recently, we reported the crystal structure of a novel tetrakis(imide) tetraanion, $[Si(Nnaph)_4][\{Li \cdot (THF)_2\}_2[Li \cdot OEt_2]_2] \cdot Et_2O$ (Copey *et al.*, 2006) (Nnaph is naphthylimide and THF is tetrahydrofuran). In this paper, we report the structures of $[Si(NHnaph)_4]$, (I), and its tetrahydrofuran trisolvate, $[Si(NHnaph)_4] \cdot 3THF$, (II). Compound (I) was also prepared earlier by interacting *tert*-butylammonium chloride with $[Si(Nnaph)_4][Li \cdot OEt_2]_4$ (Brask *et al.*, 2000).



The structure of (I) (Fig. 1) contains independent molecules wherein the naphthalene rings are individually planar, with maximum deviations of the atoms from the mean planes of 0.0365 (13), 0.0232 (15), 0.0381 (13) and 0.0297 (15) Å for atoms C1, C18, C29 and C33 from the least-squares planes of

naphthalene rings C1–C10, C11–C20, C21–C30 and C31–C40, respectively. Rings C1–C10 and C31–C40 are inclined at 16.11 (5)° with respect to each other, while the other two rings lie approximately at right angles to these planes; the angle between rings C1–C10 and C11–C20 is 83.27 (3)°, while the angle between rings C21–C30 and C31–C40 is 74.13 (4)°. The N atoms deviate significantly from the mean planes of the rings, with atoms N1, N2, N3 and N4 lying 0.083 (2), 0.018 (2), 0.058 (2) and 0.042 (2) Å out of the respective naphthalene rings. Furthermore, the angles around Si1 deviate significantly from the tetrahedral value and lie in a wide range, between 104.34 (7) and 116.63 (7)°; the Si–N–C angles lie in the narrow range 127.99 (11)–130.61 (11)°.

The structure of (II) (Fig. 2), on the other hand, contains independent molecules of (I) hydrogen bonded to two THF molecules (Table 3) and a third THF solvent molecule, which is not involved in any close interactions. The naphthalene rings in (II) are also individually planar, with maximum deviations of the atoms from the mean planes of 0.051 (3), 0.024 (4), 0.048 (3) and 0.020 (4) Å for atoms C3, C13, C21 and C33 from the least-squares planes of naphthalene rings C1–C10, C11–C20, C21–C30 and C31–C40, respectively. The orientation of the naphthalene rings is influenced by the hydrogen-bonded THF molecules. Thus, the mean planes of rings C1–C10 and C31–C40 in (II) form an angle of 40.90 (11)°, compared with 16.11 (5)° in (I). Rings C1–C10 and C11–C20 lie approximately at right angles [85.52 (8)°], while the angle between rings C21–C30 and C31–C40 is 81.29 (9)°.

The N atoms in (II) deviate from the mean planes of the rings even more than the corresponding N atoms in (I), with atoms N1, N2, N3 and N4 lying 0.120 (4), 0.073 (5), 0.173 (4) and 0.048 (5) Å out of the mean planes of the respective naphthalene rings. Furthermore, the tetrahedral angles around Si1 in (II) also lie in a wide range, *viz.* between

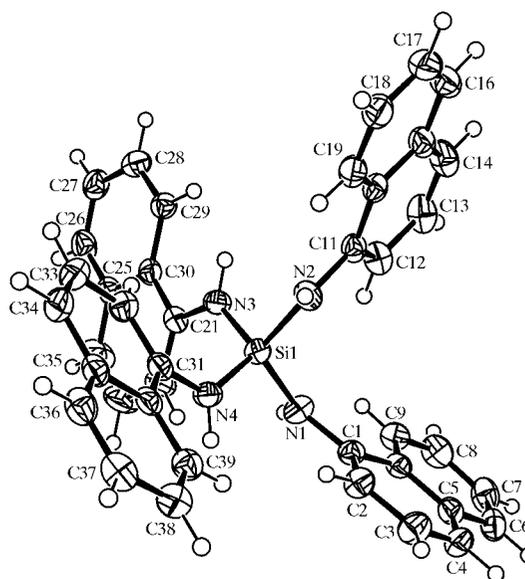


Figure 1

A view of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

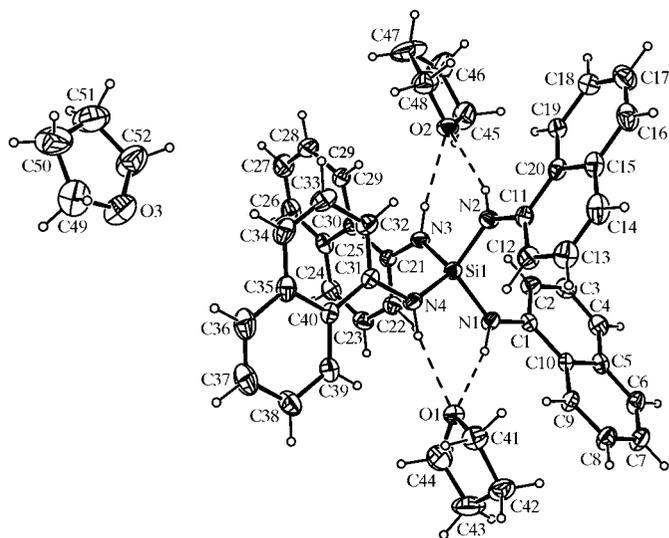


Figure 2

A view of the components of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds.

99.91 (15) and 116.85 (15)°, while the Si–N–C angles lie in the narrow range 127.5 (3)–131.2 (3)°. Similar bond angles around Si and N atoms have been observed in closely related structures, *e.g.* tetrakis(phenylamino)silane (Clade & Jansen, 2005), tetrakis(2-fluorophenylamino)silane (Mokros & Jansen, 1996) and tetrakis(pentafluorophenylamino)silane (Jansen *et al.*, 1992).

The conformational differences between the silane molecules in (I) and (II) are evident from a comparison of the Si–N–C–C torsion angles listed in Tables 1 and 2, and of Figs. 1 and 2. The THF molecules O1/C41–C44 and O2/C45–C48 in (II) adopt C41- and C48-envelope conformations, with atoms C41 and C48 out of the planes of the remaining ring atoms by 0.469 (7) and 0.335 (9) Å, respectively. The third molecule of THF, O3/C49–C52, is apparently planar, with a maximum deviation of 0.036 (3) Å for atom O3, but this component may be subject to some disorder.

Experimental

To a solution of 2-naphthylamine (3.58 g, 25 mmol) in diethyl ether (30 ml), ⁿBuLi (10 ml, 25 mmol, 2.5 M solution in hexanes) was added dropwise at 273 K. The bright-yellow solution obtained was stirred at room temperature for 2 h and cooled to 263 K. A solution of SiCl₄ (1.06 g, 6.25 mmol) in diethyl ether (10 ml) was added dropwise. The solution was allowed to warm to room temperature and stirred for a further period of 12 h. LiCl was removed by filtration and the light-purple solution was subjected to vacuum to give Si(NHnaph)₄ as colourless crystals in 95% yield (3.63 g). Recrystallization from toluene gave X-ray quality crystals of (I). Recrystallization from THF provided crystals of (II) solvated with three molecules of THF. Analytical data: m.p. 448 K (decomposition); analysis calculated for C₄₀H₃₂N₄Si: C 80.50, H 5.40, N 9.38%; found: C 79.84, H 5.76, N 9.10%; ¹H NMR (THF-*d*₈): δ 7.66–7.11 (*m*, 28H, naph), 2.10 (*s*, 4H, NH); ²⁹Si NMR (THF-*d*₈): δ –53.3 (*s*).

Compound (I)

Crystal data

C₄₀H₃₂N₄Si
M_r = 596.79
 Monoclinic, *P*2₁/*n*
a = 10.695 (2) Å
b = 22.718 (4) Å
c = 13.516 (2) Å
 β = 109.50 (1)°

V = 3095.6 (9) Å³
Z = 4
 Mo Kα radiation
 μ = 0.11 mm⁻¹
T = 173 (2) K
 0.30 × 0.28 × 0.22 mm

Data collection

Nonius KappaCCD area-detector diffractometer
 Absorption correction: multi-scan (SORTAV; Blessing, 1997)
T_{min} = 0.967, *T_{max}* = 0.976

12258 measured reflections
 7035 independent reflections
 5131 reflections with *I* > 2σ(*I*)
R_{int} = 0.031

Refinement

R[*F*² > 2σ(*F*²)] = 0.045
wR(*F*²) = 0.122
S = 1.01
 7035 reflections

406 parameters
 H-atom parameters constrained
 Δρ_{max} = 0.27 e Å⁻³
 Δρ_{min} = -0.30 e Å⁻³

Table 1

Selected geometric parameters (Å, °) for (I).

Si1–N2	1.7082 (13)	N1–C1	1.408 (2)
Si1–N4	1.7097 (14)	N2–C11	1.415 (2)
Si1–N1	1.7125 (14)	N3–C21	1.404 (2)
Si1–N3	1.7195 (14)	N4–C31	1.418 (2)
N2–Si1–N4	107.00 (7)	N1–Si1–N3	105.52 (7)
N2–Si1–N1	115.86 (7)	C1–N1–Si1	130.19 (11)
N4–Si1–N1	107.85 (7)	C11–N2–Si1	127.99 (11)
N2–Si1–N3	104.34 (7)	C21–N3–Si1	130.61 (11)
N4–Si1–N3	116.63 (7)	C31–N4–Si1	128.33 (11)
Si1–N1–C1–C2	35.2 (2)	Si1–N3–C21–C22	-0.1 (2)
Si1–N1–C1–C10	-144.35 (13)	Si1–N3–C21–C30	179.84 (12)
Si1–N2–C11–C12	-22.5 (2)	Si1–N4–C31–C32	34.5 (2)
Si1–N2–C11–C20	158.05 (12)	Si1–N4–C31–C40	-144.82 (12)

Compound (II)

Crystal data

C₄₀H₃₂N₄Si·3C₄H₈O
M_r = 813.10
 Monoclinic, *P*2₁/*c*
a = 21.048 (7) Å
b = 14.672 (7) Å
c = 15.160 (9) Å
 β = 104.46 (2)°

V = 4533 (4) Å³
Z = 4
 Mo Kα radiation
 μ = 0.10 mm⁻¹
T = 173 (2) K
 0.10 × 0.08 × 0.06 mm

Data collection

Nonius KappaCCD area-detector diffractometer
 Absorption correction: multi-scan (SORTAV; Blessing, 1997)
T_{min} = 0.990, *T_{max}* = 0.994

17657 measured reflections
 9976 independent reflections
 3609 reflections with *I* > 2σ(*I*)
R_{int} = 0.175

Refinement

R[*F*² > 2σ(*F*²)] = 0.078
wR(*F*²) = 0.230
S = 0.98
 9976 reflections

544 parameters
 H-atom parameters constrained
 Δρ_{max} = 0.33 e Å⁻³
 Δρ_{min} = -0.24 e Å⁻³

Table 2
Selected geometric parameters (Å, °) for (II).

Si1—N4	1.706 (3)	N1—C1	1.415 (4)
Si1—N1	1.709 (3)	N2—C11	1.399 (4)
Si1—N3	1.710 (3)	N3—C21	1.408 (4)
Si1—N2	1.715 (3)	N4—C31	1.416 (4)
N4—Si1—N1	100.39 (15)	N3—Si1—N2	99.91 (15)
N4—Si1—N3	112.71 (15)	C1—N1—Si1	129.9 (3)
N1—Si1—N3	116.85 (15)	C11—N2—Si1	129.9 (3)
N4—Si1—N2	115.52 (15)	C21—N3—Si1	131.2 (3)
N1—Si1—N2	112.27 (15)	C31—N4—Si1	127.5 (3)
Si1—N1—C1—C2	−19.4 (5)	Si1—N3—C21—C22	−27.7 (5)
Si1—N1—C1—C10	159.4 (3)	Si1—N3—C21—C30	154.5 (3)
Si1—N2—C11—C12	−10.3 (5)	Si1—N4—C31—C32	−17.8 (5)
Si1—N2—C11—C20	170.7 (3)	Si1—N4—C31—C40	163.2 (3)

Table 3
Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1N...O1	0.88	2.19	3.051 (4)	164
N4—H4N...O1	0.88	2.18	3.028 (4)	163
N2—H2N...O2	0.88	2.26	3.103 (5)	160
N3—H3N...O2	0.88	2.17	3.033 (4)	168

For both structures, H atoms were included in the refinement in geometrically idealized positions, with N—H = 0.88 Å and C—H = 0.95 or 0.99 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. The final difference maps were free of any chemically significant features. A degree of thermal disorder was apparent in the free THF component in structure (II), as judged by the large displacement parameters and the rather short C—C and C—O bonds.

For both compounds, data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SAPI91* (Fan, 1991); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3147). Services for accessing these data are described at the back of the journal.

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