Structure of 2-(Diphenylmethylsiloxy)-2-phenyl-1,3,2-oxazaborinane

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Abstract. $C_{22}H_{26}BNO_2Si$, $M_r = 375\cdot4$, orthorhombic, $P2_12_12_1$, $a = 10\cdot055$ (3), $b = 11\cdot385$ (3), $c = 18\cdot928$ (4) Å, $V = 2167$ (3) Å^3, $Z = 4$, $D_x = 1\cdot15$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0\cdot71073$ Å, $\mu = 1\cdot2$ cm^{-1}, $F(000) = 800$, $T = 294$ K, $R = 0\cdot0352$ for 2217 observed refections. The tetrahedral —BO$_2$NC and —SiO(Me)Ph$_2$ units are joined through a B—O—Si bridge [B—O 1·439 (4), Si—O 1·585 (2) Å, B—O—Si 152·2 (2)°]. The BOC$_3$N ring has a chair conformation with B—O 1·461 (3) and B—N 1·639 (4) Å. The molecules are linked to form infinite chains extending in the **a** direction by hydrogen bonding between N—H units and the adjacent O(ring) atom of a molecule related by a 2$_1$ screw axis; the N···O distance is 2·971 (3) Å.

Introduction. Reaction between PhB(OSiMePh$_2$)$_2$ and NH$_2$—CH$_2$—CH$_2$—CH$_2$—OH in dichloromethane for 30 min at room temperature afforded the title compound in 26·7% yield. Recrystallization from heptane/dichloromethane (3:2) produced crystals suitable for our X-ray analysis. Although the structure of 2-(triphenylsiloxy)-4,4,6-trimethyl-1,3,2-dioxaborinane, a B—O—Si-containing molecule with a trigonal planar BO$_3$ grouping, is known (Ferguson, Lough, Sheehan & Spalding, 1990), there appear to be no reports of discrete molecules containing tetracoordinate boron and silicon bonded through oxygen. There are several borosilicate mineral structures in the literature [see for example datolite, CaBSiO$_4$OH (Foit, Philips & Gibbs, 1973); homilite, Ca$_{2\cdot00}$(Fe$_{0\cdot90}$Mn$_{0\cdot03}$)B$_{2\cdot00}$Si$_{2\cdot00}$O$_{9\cdot86}$(OH)$_{0\cdot14}$ (Miyawaki, Nakai & Nagashima, 1985)].

Experimental. Accurate cell dimensions and crystal orientation matrix were determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 25 reflections in the range $11 < \theta < 18°$. Crystal dimensions 0·36 × 0·31 × 0·27 mm; intensities of reflections with indices h 0 to 11, k 0 to 13, l −24 to 24 (*i.e.* Friedel reflections with hkl and $hk\bar{l}$) with $2 < 2\theta < 48°$ measured; ω–2θ scans, ω-scan width $(0\cdot6 + 0\cdot35\tan\theta)°$; graphite-monochromated Mo $K\alpha$ radiation; intensities of three reflections measured every 2 h showed no evidence of crystal decay. In all, 3968 reflections were measured, 3427 unique, 2217 with $I > 3\sigma(I)$ labelled observed and used in structure solution and refinement. Data corrected for Lorentz and polarization effects. Space group $P2_12_12_1$ was determined uniquely by the systematic absences ($h00$ absent if $h = 2n + 1$; $0k0$ absent if $k = 2n + 1$; $00l$ absent if $l = 2n + 1$). The structure was solved with the aid of *MULTAN*82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Refinement on F was by full-matrix least-squares calculations, initially with isotropic and then with anisotropic thermal parameters. A difference map showed maxima in positions consistent with the expected locations of the H atoms. In the final rounds of calculations, the H atoms were positioned on geometrical grounds (C—H, N—H 0·95 Å) and included (as riding atoms) in the structure-factor calculations with an overall B_{iso} of 7·0 Å^2. Parallel refinement cycles with the hand of the molecule reversed led to slightly higher final R factors, but no significant differences in molecular dimensions. The final cycle of refinement included 245 variable parameters, $R = 0\cdot0352$, $wR = 0\cdot0398$ (the corresponding values for the enantiomorph were 0·0354 and 0·0402); goodness of fit 1·27, $w = 1/[\sigma^2(F_o) + 0\cdot04(F_o)^2]$. Max. shift/e.s.d. in final refinement cycle $<0\cdot005$; density in final difference map ±0·22 e Å^{-3}; there were no chemically significant features. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed on a PDP11/73 computer using *SDP-Plus* (B. A. Frenz & Associates, Inc., 1983).

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Table 1. *Positional and thermal parameters and their e.s.d.'s*

Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as: $4/3(a^2B_{11} + b^2B_{22} + c^2B_{33} + ab\cos\gamma B_{12} + ac\cos\beta B_{13} + bc\cos\alpha B_{23})$.

|	x	y	z	$B(Å^2)$
Si	0·38078 (7)	0·05916 (7)	0·37052 (4)	4·37 (1)
O1	0·5265 (2)	0·2874 (2)	0·47120 (9)	4·67 (4)
O2	0·3578 (2)	0·1442 (2)	0·43569 (9)	4·59 (4)
N	0·2860 (2)	0·3226 (2)	0·4932 (1)	4·46 (5)
C2	0·2795 (3)	0·3966 (3)	0·4289 (2)	5·80 (7)
C3	0·4152 (3)	0·4510 (3)	0·4153 (2)	6·52 (8)
C4	0·5211 (3)	0·3573 (3)	0·4095 (2)	5·84 (8)
C5	0·3307 (3)	0·1284 (3)	0·2866 (2)	6·40 (8)
C11	0·4198 (2)	0·1686 (2)	0·5661 (1)	4·35 (6)
C12	0·3884 (3)	0·0524 (3)	0·5814 (1)	5·07 (6)
C13	0·3931 (3)	0·0072 (3)	0·6489 (2)	6·53 (8)
C14	0·4316 (3)	0·0771 (4)	0·7031 (2)	7·18 (9)
C15	0·4666 (4)	0·1901 (4)	0·6910 (2)	7·7 (1)
C16	0·4615 (3)	0·2358 (3)	0·6230 (2)	6·13 (7)
C21	0·2762 (3)	−0·0749 (2)	0·3860 (1)	4·59 (6)
C22	0·1779 (3)	−0·0768 (3)	0·4372 (2)	5·57 (7)
C23	0·1037 (3)	−0·1753 (3)	0·4507 (2)	6·81 (8)
C24	0·1243 (3)	−0·2741 (3)	0·4117 (2)	7·10 (8)
C25	0·2173 (4)	−0·2750 (3)	0·3599 (2)	7·7 (1)
C26	0·2942 (4)	−0·1766 (3)	0·3472 (2)	6·64 (9)
C31	0·5569 (3)	0·0071 (2)	0·3635 (1)	4·71 (6)
C32	0·6093 (3)	−0·0694 (4)	0·4111 (2)	7·15 (8)
C33	0·7377 (3)	−0·1119 (4)	0·4064 (2)	7·93 (9)
C34	0·8160 (3)	−0·0796 (4)	0·3534 (2)	8·1 (1)
C35	0·7696 (4)	−0·0019 (5)	0·3068 (2)	12·9 (1)
C36	0·6417 (3)	0·0427 (4)	0·3119 (2)	9·4 (1)
B	0·4047 (3)	0·2241 (3)	0·4890 (2)	4·10 (7)
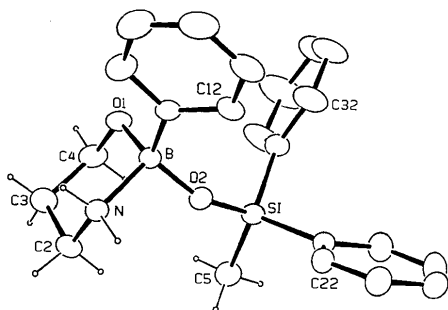
Fig. 1. A view of the molecule with our numbering scheme; phenyl rings are numbered C*i*1–C*i*6 (i = 1–3). For clarity, no phenyl hydrogens are shown. Ellipsoids are at the 20% level except for H atoms which are shown as small spheres.
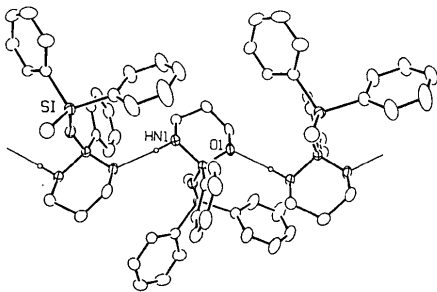

Fig. 2. A diagram showing the hydrogen-bonded chains which are developed along the **a** direction; for clarity hydrogens are omitted except for the one involved in hydrogen bonding. Ellipsoid levels are as in Fig. 1.

Table 2. *Bond lengths (Å), angles (°) and hydrogen-bond geometry (Å, °)*

Si—O2	1·585 (2)	C13—C14	1·356 (5)
Si—C5	1·844 (3)	C14—C15	1·354 (6)
Si—C21	1·876 (3)	C15—C16	1·389 (5)
Si—C31	1·872 (3)	C21—C22	1·386 (4)
O1—C4	1·414 (4)	C21—C26	1·383 (4)
O1—B	1·461 (3)	C22—C23	1·370 (4)
O2—B	1·439 (4)	C23—C24	1·361 (5)
N—C2	1·483 (4)	C24—C25	1·356 (5)
N—B	1·639 (4)	C25—C26	1·383 (5)
C2—C3	1·520 (4)	C31—C32	1·359 (4)
C3—C4	1·511 (4)	C31—C36	1·358 (4)
C11—C12	1·390 (4)	C32—C33	1·382 (5)
C11—C16	1·386 (4)	C33—C34	1·327 (5)
C11—B	1·597 (4)	C34—C35	1·333 (6)
C12—C13	1·378 (4)	C35—C36	1·386 (6)
O2—Si—C5	111·7 (1)	Si—C21—C26	121·7 (2)
O2—Si—C21	107·1 (1)	C22—C21—C26	116·9 (3)
O2—Si—C31	112·7 (1)	C21—C22—C23	122·1 (3)
C5—Si—C21	109·2 (1)	C22—C23—C24	119·5 (3)
C5—Si—C31	109·4 (1)	C23—C24—C25	120·3 (3)
C21—Si—C31	106·5 (1)	C24—C25—C26	120·3 (3)
C4—O1—B	115·8 (2)	C21—C26—C25	120·9 (3)
Si—O2—B	152·2 (2)	Si—C31—C32	121·5 (2)
C2—N—B	112·4 (2)	Si—C31—C36	123·4 (2)
N—C2—C3	109·3 (2)	C32—C31—C36	115·1 (3)
C2—C3—C4	110·9 (3)	C31—C32—C33	122·9 (3)
O1—C4—C3	111·4 (2)	C32—C33—C34	120·4 (3)
C12—C11—C16	115·6 (3)	C33—C34—C35	118·4 (3)
C12—C11—B	123·1 (2)	C34—C35—C36	121·4 (4)
C16—C11—B	121·3 (2)	C31—C36—C35	121·6 (4)
C11—C12—C13	122·7 (3)	O1—B—O2	115·1 (2)
C12—C13—C14	119·5 (3)	O1—B—N	106·5 (2)
C13—C14—C15	120·2 (3)	O1—B—C11	109·0 (2)
C14—C15—C16	120·3 (3)	O2—B—N	103·2 (2)
C11—C16—C15	121·6 (3)	O2—B—C11	115·0 (2)
Si—C21—C22	121·4 (2)	N—B—C11	107·2 (2)
HN2···O1^i	2·03	O1^i···HN2—N	169·6
O1^i···N	2·971 (3)		

Symmetry code: (i) $-0·5 + x, 0·5 - y, 1 - z$.

Atomic coordinates and details of molecular geometry are given in Tables 1 and 2.* Fig. 1 is a view of the molecule and Fig. 2 shows the intermolecular hydrogen bonding; these diagrams were prepared using *ORTEP*II (Johnson, 1976).

Discussion. The title molecule contains two tetrahedrally coordinated units (BO_2CN and $SiOC_3$) linked through an O atom, Fig. 1. The angles at silicon are within 3·2° of 109·5° whereas there is a much larger variation at boron (6·3°). The B—O—Si angle is remarkably large, 152·2 (2)°, suggestive of hybridization at oxygen between sp^2 and sp. It is noteworthy that the B—O—Si angles in both the minerals datolite and homilite are close to 120°

[mean values 124·3 (1) and 121·8 (1)°, respectively] and in 2-(triphenylsiloxy)-4,4,6-trimethyl-1,3,2-dioxaborinane, the angle is 133·1 (2)° (Ferguson *et al.*, 1990). The dihedral angle Si—O2—B—O1 is 26·9 (5)° and the Si atom is 0·334 (1) Å from the plane defined by B, O1 and O2.

The Si—O bond length [1·585 (2) Å] is at the lower end of the known range of Si—O distances (1·55 to 1·80 Å; James & Oldfield, 1986). The B—O distances are slightly different being 1·439 (4) Å for B—O(Si) and 1·461 (3) Å for B—O(ring), respectively.

Typical values of B—O distances for tetrahedrally coordinated boron in complexes which also contain B—N bonds lie within the range 1·43 (1) Å [in N(CH$_2$CH$_2$O)$_3$B (Taira & Osaki, 1971)] to 1·484 (3) Å [in Ph$_2$BOCH$_2$CH$_2$NH$_2$ (Rettig & Trotter, 1973)]. The corresponding Si—O and B—O(Si) distances in 2-(triphenylsiloxy)-4,4,6-trimethyl-1,3,2-dioxaborinane are 1·634 (2) and 1·363 (5) Å.

At first sight it is tempting to ascribe the shorter Si—O distance and the larger B—O—Si angle in the title compound compared with those in 2-(triphenylsiloxy)-4,4,6-trimethyl-1,3,2-dioxaborinane to an increase in the Si—O π-bonding component in the former compound. However, extensive studies of Si—O—Si-bonded compounds have shown that attempted correlations of Si—O distances, Si—O—Si angles, and theoretically calculated σ- and π-bonding components have produced controversial results (James & Oldfield, 1986). Hence we are reluctant to suggest that an increase in Si—O π-bonding is solely responsible for the effects mentioned above and we are continuing our studies of B—O—Si compounds to try to elucidate the structure–bonding relationships.

The BOC$_3$N ring adopts a chair conformation with the 2-phenyl substituent equatorial (Fig. 1), with atoms N, C2, O1 and C4 coplanar; atoms B and C3 are respectively 0·678 and −0·675 Å above and below this plane. The B—N distance is 1·639 (4) Å; in the comparable compound Ph$_2$BO(CH$_2$)$_3$NH$_2$, the BOC$_3$N ring is also in a chair conformation and the B—N distance is 1·643 (3) Å (Rettig & Trotter, 1983). The remaining Si—C, C—C, C—N and C—O bond lengths are all as anticipated.

In the crystal structure the molecules are linked to form infinite chains extending in the **a** direction by hydrogen bonding between one N—H moiety and an adjacent O(ring) atom of a molecule related by a 2$_1$ screw axis; the N···O distance is 2·971 (3) Å (Fig. 2). The other N—H group and the bridging oxygen (O2) do not take part in any hydrogen bonding.

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Structure of Phenoxathiin (Phenothioxin), C$_{12}$H$_8$OS, at 223 K

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Abstract. $M_r = 200·25$, orthorhombic, $P2_12_12_1$, $a = 7·758$ (2), $b = 20·506$ (3), $c = 5·896$ (2) Å, $V = 938·0$ (4) Å^3, $Z = 4$, $D_x = 1·42$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2·88$ cm^{-1}, $F(000) = 416$, $T = 223$ K, $R = 0·044$ for 1414 unique reflections having $I > 3\sigma_I$. The phenoxathiin molecule is constituted of two very

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