

A new polymorph of tetraphenyl-
diboroxaneLinda Kaufmann, Hans-Wolfram Lerner and Michael
Bolte*Institut für Anorganische Chemie, J. W. Goethe-Universität Frankfurt, Max-von-Laue-
Strasse 7, 60438 Frankfurt/Main, Germany

Correspondence e-mail: bolte@chemie.uni-frankfurt.de

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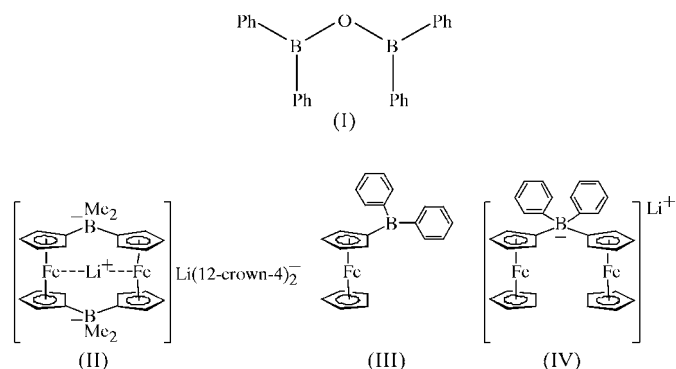
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A new polymorph of tetraphenyldiboroxane [or oxybis-(diphenylborane)], $C_{24}H_{20}B_2O$, (*Ia*), has been found. It is monoclinic, like the already known form, (*Ib*), and can be refined in the same space group, namely $P2_1/c$, or in the equivalent setting $P2_1/n$. The molecular conformations of the two polymorphs differ in the rotations of two of the phenyl rings about the B–C bonds, leading to markedly different packing patterns and cell dimensions.

Comment

Recently, we have synthesized the anionic [1,1]diborata-ferrocenophane, (II), which represents a highly efficient Li^+ scavenger (see scheme below) (Scheibitz *et al.*, 2003), and anionic ferrocene derivatives such as the ferrocenyl borate, (IV) (Kaufmann *et al.*, 2007). The ferrocene derivative, (III), represents a versatile starting material for the synthesis of a broad range of ferrocenyl-substituted polyborates. In an attempt to synthesize the borane, (III), from $FcHgCl$ ($Fc = C_5H_4FeC_5H_5$) and Ph_2BBr , we obtained the title compound, tetraphenyldiboroxane, $Ph_2B-O-BPh_2$, (I), as a side-product in a new polymorph, (*Ia*).



Both B atoms in polymorph (*Ia*) are in trigonal-planar environments (Fig. 1). The sums of the bond angles are

$360.0(2)$ and $359.8(2)^\circ$ for atoms B1 and B2, respectively. Another monoclinic polymorph of the title compound, (*Ib*), has been described at 190 K in the $P2_1/c$ space group, with cell parameters $a = 12.378(5)$ Å, $b = 8.019(2)$ Å, $c = 19.180(7)$ Å, $\beta = 100.89(3)^\circ$ and $V = 1869.51$ Å³ (Lange *et al.*, 2002). The only similarity between the cell parameters of the two polymorphs is that the c axis of (*Ia*) and the b axis of (*Ib*) differ by just 0.1 Å. Since the cell parameters are otherwise completely different, the setting in $P2_1/n$ has been selected for polymorph (*Ia*). A least-squares fit of the two polymorphs shows that the orientations of the phenyl rings attached to atom B2 are almost identical in (*Ia*) and (*Ib*), while the orientations of the phenyl rings attached to atom B1 differ significantly (Fig. 2). This difference can also be illustrated by a comparison of the corresponding torsion angles (Table 1); only the torsion angles about the B1–C1 and B1–C7 bonds differ significantly.

An analysis of short intramolecular distances for both polymorphs reveals two somewhat shorter $X \cdots H$ distances in polymorph (*Ib*), which might be the reason for the different orientations of the phenyl rings [$B2 \cdots H10 = 2.63$ Å in (*Ib*) versus 2.74 Å in (*Ia*), and $C2 \cdots H6 = 2.71$ Å in (*Ib*) versus 2.79 Å in (*Ia*); all C–H distances are 0.93 Å in both polymorphs]. A molecular mechanics calculation with the molecular modelling program *MOMO* (Beck *et al.*, 1991) shows that the conformation of polymorph (*Ia*) is more stable than that of polymorph (*Ib*) by 4.2 kcal mol⁻¹ [1 kcal mol⁻¹ = 4.184 kJ mol⁻¹].

The packing motifs of the two polymorphs are quite different, presumably due to the different orientations of two of the four aromatic rings. The orientations of the packing diagrams (Figs. 3 and 4) have been chosen so that one molecule (shown with dashed bonds) has approximately the same orientation in both figures. Comparison of the diagrams shows that the orientation of the remaining molecules differs markedly.

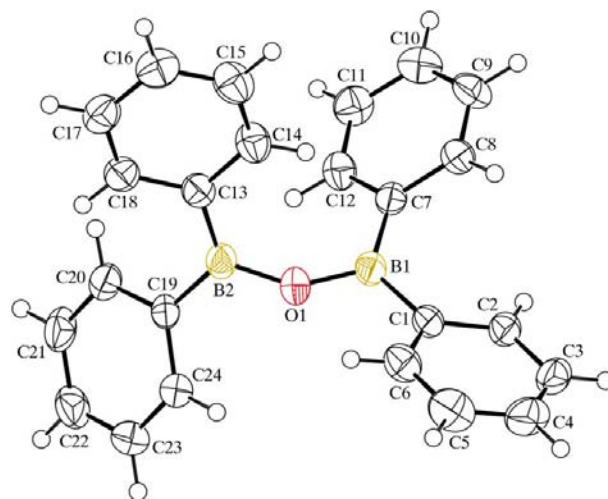


Figure 1

A perspective view of the title polymorph, showing the atom-numbering scheme [identical to that used for (*Ib*)]. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

An analysis of short intermolecular distances in the crystal packing of both polymorphs shows only two notable short distances in (*Ib*) [$C14 \cdots H8^i = 2.96 \text{ \AA}$ and $C21 \cdots H2^{ii} = 2.93 \text{ \AA}$; symmetry codes: (i) $x, y - 1, z$; (ii) $x + 1, y, z$], whereas there

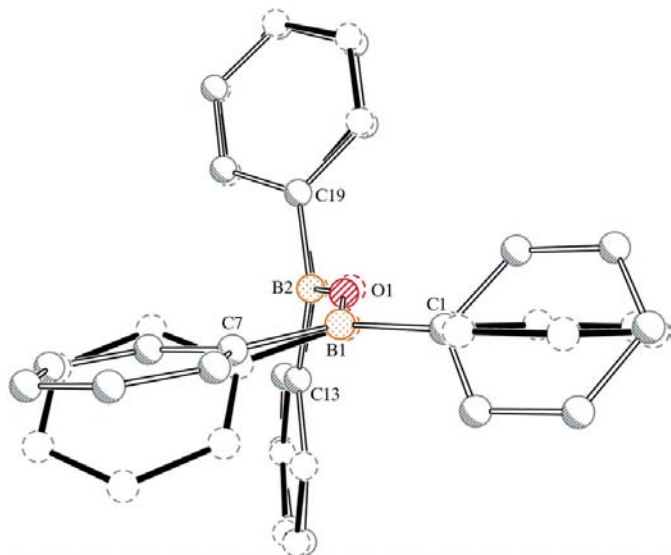


Figure 2

A least-squares fit (fitting the B—O—B fragment and C13—C18 and C19—C24 phenyl rings) of (*Ia*) (full bonds) with (*Ib*) (open bonds); r.m.s. deviation for fitted atoms = 0.103 Å.

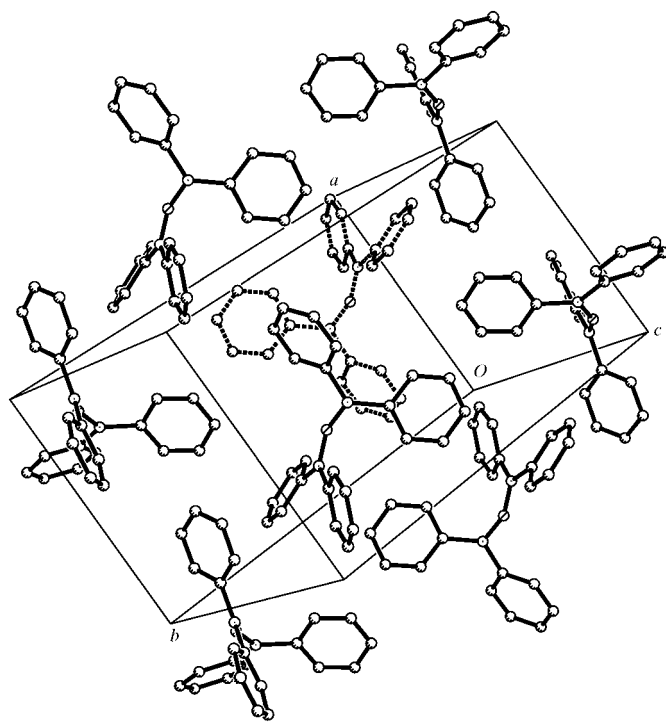


Figure 3

A packing diagram for (*Ia*), viewed approximately on to the (011) plane. H atoms have been omitted for clarity. The molecule drawn with dashed bonds has the same orientation as the molecule drawn with dashed bonds in Fig. 4.

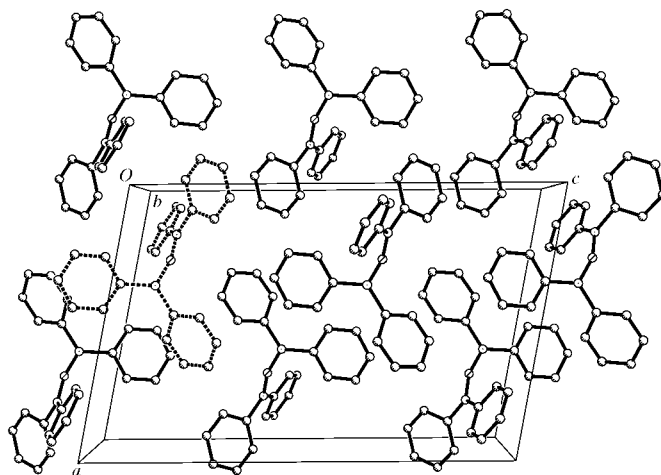


Figure 4

A packing diagram for (*Ib*), viewed on to the (101) plane. H atoms have been omitted for clarity. The molecule drawn with dashed bonds has the same orientation as the molecule drawn with dashed bonds in Fig. 3.

are five intermolecular C \cdots H distances of less than 3 Å in (*Ia*): $C6 \cdots H15^i = 2.99 \text{ \AA}$, $C3 \cdots H9^{ii} = 2.91 \text{ \AA}$, $C10 \cdots H17^{iii} = 2.95 \text{ \AA}$, $C17 \cdots H5^{iv} = 2.90 \text{ \AA}$ and $C20 \cdots H2^v = 2.99 \text{ \AA}$ [symmetry codes: (i) $2 - x, 1 - y, 1 - z$; (ii) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (iv) $x, -1 + y, -1 + z$; (v) $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$]. In addition, there is one very short intermolecular H \cdots H distance in polymorph (*Ia*) [$H4 \cdots H22^{vi} = 2.40 \text{ \AA}$; symmetry code: (vi) $1 + x, y, 1 + z$], for which there is no equivalent in polymorph (*Ib*). The differences in all these intermolecular contacts show that a single molecule is in a different environment in both structures.

A search of the Cambridge Structural Database (Version 5.28, November 2006, updated May 2007; Allen, 2002) for the fragment $(C_{ar})_2B-O-B(C_{ar})_2$ shows just four entries, namely BUBXEB (Cardin *et al.*, 1983), BZBPER (Cynkier & Furmanova, 1980), DTBOPE (Aurivillius, 1974) and UCITEF, which is polymorph (*Ib*) (Lange *et al.*, 2002). It is worth noting that in all of these structures the B—O—B angle is wider than in polymorph (*Ia*) and the B—O bond lengths are shorter (Table 2), although the measurement temperatures of 173 K for (*Ia*) and 190 K for (*Ib*) are almost equal.

Experimental

In an attempt to synthesize the borane (III) from $FcHgCl$ (Fc is ferrocenyl; 0.88 g, 2.09 mmol) with Ph_2BBr (0.51 g, 2.09 mmol) in hexane (45 ml) at 195 K, we obtained $Ph_2B-O-BPh_2$, (*Ia*), as a side product. X-ray quality crystals of the title compound were grown from hexane at 248 K.

Crystal data

$C_{24}H_{20}B_2O$	$V = 1957.7 (3) \text{ \AA}^3$
$M_r = 346.02$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 10.1489 (11) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$b = 19.2851 (16) \text{ \AA}$	$T = 173 (2) \text{ K}$
$c = 10.1658 (11) \text{ \AA}$	$0.19 \times 0.17 \times 0.17 \text{ mm}$
$\beta = 100.286 (8)^\circ$	

Data collection

Stoe IPDSII two-circle diffractometer
19779 measured reflections

3682 independent reflections
2205 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.062$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.111$
 $S = 0.95$
3682 reflections

244 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.29 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.13 \text{ e } \text{\AA}^{-3}$

Table 1

Comparison of the torsion angles ($^\circ$) in the two polymorphs.

	(Ia)	(Ib)
O1–B1–C1–C2	158.3 (2)	–140.9
O1–B1–C7–C8	152.9 (2)	–167.5
B2–O1–B1–C1	155.6 (3)	156.9
B2–O1–B1–C7	–24.0 (5)	–26.4
B1–O1–B2–C13	–54.2 (4)	–59.1
B1–O1–B2–C19	130.2 (3)	126.3
O1–B2–C19–C20	–142.9 (2)	–135.3
O1–B2–C13–C18	–163.2 (2)	–167.1

Table 2

Comparison of the B–O–B angles ($^\circ$) and B–O bond lengths (\AA) for structures containing the fragment $(\text{C}_{\text{ar}})_2\text{B–O–B}(\text{C}_{\text{ar}})_2$.

The B–O bonds of each structure are in order, with the first column containing the shorter of the two B–O bonds.

Compound	B–O–B	B–O	B–O
BUBXEB	165.46	1.359	1.370
BZBPER	159.39	1.340	1.347
DTBOPE	152.63	1.358	1.358
UCITEF	152.69 (2)	1.345 (4)	1.349 (4)
(Ia)	147.34 (19)	1.367 (3)	1.372 (3)

H atoms were located in a difference map, but were positioned geometrically and refined using a riding model, with fixed bond lengths and individual displacement parameters [$\text{C–H} = 0.95 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *PLATON* and *SHELXL97* (Sheldrick, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3095). Services for accessing these data are described at the back of the journal.

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