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**Crystal Structure
Communications**
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2,3,5,6-Tetrakis[3,5-bis(trifluoromethyl)phenoxy]-2,5-bis(dimethylamino)2,3,5,6-tetrabora-1,4-dioxane diethyl ether 0.667-solvate

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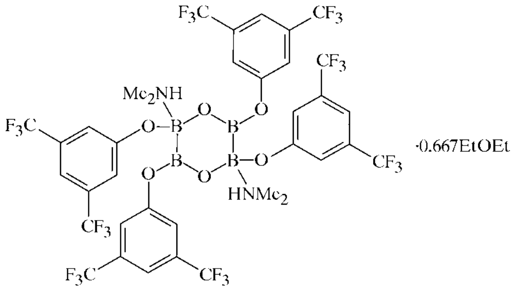
The title compound, $C_{36}H_{26}B_4F_{24}N_2O_6\cdot0.667C_4H_{10}O$, has centrosymmetric tetraboradioxane molecules, half each of three of these comprising the asymmetric unit together with a molecule of diethyl ether. Disorder affects most of the CF_3 groups and one ethyl group of the solvent molecule. The B_4O_2 rings are approximately planar and contain two B atoms with trigonal geometry and two with distorted tetrahedral geometry, the B—O bonds for the four-coordinate B atoms being longer than those for the three-coordinate B atoms. N—H···O hydrogen bonds link two of the crystallographically independent molecules together in chains, while the third molecule forms discrete trimolecular clusters with two solvent molecules *via* N—H···O hydrogen bonds. This is the first crystallographically characterized example of a tetraboradioxane molecule containing both four- and three-coordinate B atoms.

Comment

The title compound, (I), was an unexpected hydrolysis product obtained in a study of diboron compounds with amine and alkoxide/aryloxide substituents. It crystallizes with three independent half-molecules in the asymmetric unit, together with one molecule of diethyl ether, which is retained in the structure during subsequent recrystallization from toluene and pentane (Fig. 1). The identity of the solvent molecule as diethyl ether rather than pentane is shown by more satisfactory displacement parameters for the central atom when assigned as O rather than C, and by its participation as acceptor in an N—H···O intermolecular hydrogen bond (see below). The three crystallographically independent borinane molecules are centrosymmetric and have approximately planar B_4O_2 rings [r.m.s. deviations = 0.008, 0.029 and 0.047 Å; endocyclic torsion angles are in the range 2.1 (6)–13.4 (7)°]. Their centroids lie at $(0, 0, \frac{1}{2})$ (for the molecule containing atoms B1 and B2), $(\frac{1}{2}, \frac{1}{2}, 0)$ (atoms B3 and B4) and $(\frac{1}{2}, 0, \frac{1}{2})$ (atoms B5 and B6).



(I)

Only three structures have been reported previously with B_4O_2 rings that are not part of a polycyclic system; two are cocrystals of $B_4O_2(OH)_4$ in which each B atom has a hydroxy substituent (Carmalt *et al.*, 1997; Baber *et al.*, 2006), and the third is $B_4O_2(N^iPr)_4$, in which each B atom has a diisopropylamide substituent (Maringgele *et al.*, 1997). The title structure is unprecedented in this series in having one substituent on each of two B atoms and two on each of the other two, giving two B atoms with trigonal geometry and two with distorted tetrahedral geometry. It resembles the previously reported hydroxy-substituted compounds in having an almost planar ring, while the amido-substituted ring is markedly folded into a boat conformation because of steric interaction of the bulky substituents.

The four-coordinate B atoms of (I) have longer B—O bonds than the three-coordinate B atoms, as expected (Table 1); the shorter endocyclic B—O bonds are similar in length to those of the previously reported B_4O_2 rings. The B—B bond lengths are in the range normally associated with Lewis base adducts

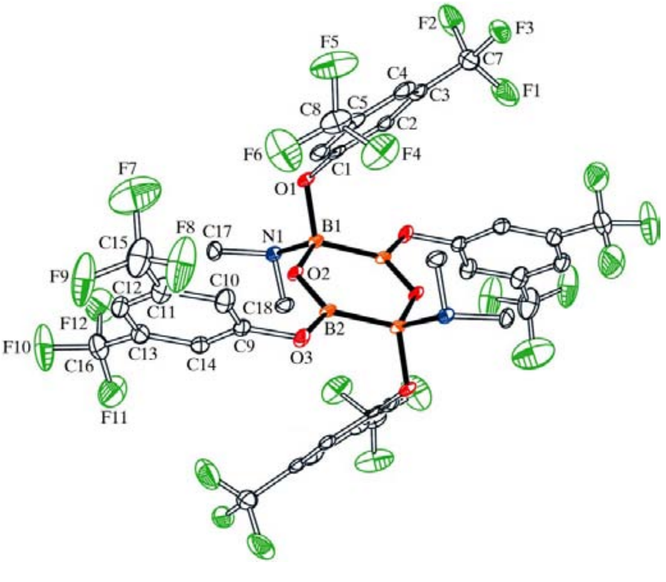


Figure 1
The structure of one independent molecule of (I), showing the atom-labelling scheme for the asymmetric unit and 25% probability displacement ellipsoids. H atoms and the minor disorder components of the CF_3 groups have been omitted.

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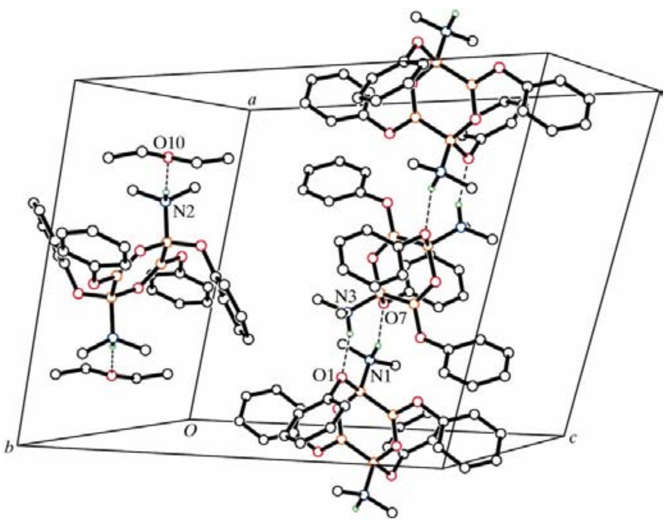

Figure 2
Hydrogen bonds (dashed lines) linking two of the molecules into chains, and forming trimolecular clusters from the third molecule and two solvent molecules. Atoms of the asymmetric unit involved in hydrogen bonds are labelled. CF_3 groups, H atoms not involved in hydrogen bonding and the second disorder component of the diethyl ether molecules have been omitted.

of diboron(4) compounds (Nguyen *et al.*, 1995; Clegg *et al.*, 1997) and are, as expected from the increased coordination numbers at boron, longer than those in the corresponding parent diboron compounds themselves (Clegg *et al.*, 1998).

Two of the three B_4O_6 rings in the unit cell of (I) are approximately parallel, with a dihedral angle of 11.26 (16)°, while the third is approximately perpendicular to these, with dihedral angles of 85.05 (18) and 85.35 (18)°. The molecules with almost parallel rings have centroids at $(0, 0, \frac{1}{2})$ and $(\frac{1}{2}, 0, \frac{1}{2})$ and are linked by pairs of N—H···O hydrogen bonds in which aryloxy O atoms serve as acceptors (Table 2); these molecules thus form chains along the *a* axis. The third molecule, with its centroid at $(\frac{1}{2}, \frac{1}{2}, 0)$, is linked to two solvent molecules by N—H···O hydrogen bonds, forming discrete trimolecular clusters (Fig. 2). These clusters are arranged along the *a* axis but have no significant interactions with each other, the shortest distance between them being an H···H distance of 2.56 Å. It is possible that essentially the same structure could be formed for other solvates with solvent molecules having a size similar to that of diethyl ether and capable of accepting hydrogen bonds in the same way. Presumably, the hydrogen bonding between the borinane and ether molecules is maintained during recrystallization from nonpolar hydrocarbon solvents, so that the diethyl ether molecules are incorporated into the resulting crystal structure.

Experimental

In a nitrogen-filled glove-box, a solution of 3,5-bis(trifluoromethyl)phenol (2.32 g, 10.1 mmol) in diethyl ether (30 ml) was added to a stirred solution of $B_2(NMe_2)_4$ (0.50 g, 2.5 mmol) in diethyl ether (20 ml). The resulting mixture was stirred at room temperature for 1 h. The white solid precipitate was collected by filtration, washed with pentane (3 × 20 ml), dissolved in a mixture of toluene and pentane (3:1 *v*/*v*), and cooled to 243 K. The product, (I), was obtained as colourless crystals in 80% yield (4.4 g). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.40 (*s*, *br*, 2H, $HNMe_2$), 2.66 (*s*, 12H, $HNMe_2$), 7.45 [*s*, 4H, 3,5-$(CF_3)_2C_6H_3$], 7.26 [*s*, 8H, 3,5-$(CF_3)_2C_6H_3$]; ^{11}B{^{1}H} NMR (64 MHz, $CDCl_3$): δ 33.4 (*s*, *br*, 2B), 2.4 (*s*, 2B). The compound apparently results from hydrolysis due to adventitious water being present, most likely in the starting phenol.

Crystal data

$C_{36}H_{26}B_4F_{24}N_2O_6\cdot0.667C_4H_{10}O$
$M_r = 1131.24$
Triclinic, $P\overline{1}$
$a = 14.8006$ (10) Å
$b = 15.1969$ (10) Å
$c = 18.1644$ (12) Å
$\alpha = 79.708$ (2)°
$\beta = 67.589$ (2)°
$\gamma = 71.879$ (2)°
$V = 3581.3$ (4) Å^3
$Z = 3$
Mo $K\alpha$ radiation
$\mu = 0.17$ mm^{-1}
$T = 160$ (2) K
0.54 × 0.46 × 0.35 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
21840 measured reflections
12279 independent reflections
6698 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.204$
$S = 0.93$
12279 reflections
1295 parameters
2645 restraints
H-atom parameters constrained
$\Delta\rho_{\rm max} = 0.73$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.54$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

B1—O1	1.507 (5)	B3—N2	1.616 (5)
B1—O2	1.459 (5)	B4—O5	1.343 (5)
B1—B2^{i}	1.737 (6)	B4—O6	1.404 (6)
B1—N1	1.592 (6)	B5—O7	1.503 (6)
B2—O2	1.356 (5)	B5—O8	1.470 (5)
B2—O3	1.390 (5)	B5—B6^{iii}	1.724 (7)
B3—O4	1.483 (6)	B5—N3	1.601 (6)
B3—O5	1.474 (6)	B6—O8	1.343 (5)
B3—B4^{ii}	1.741 (7)	B6—O9	1.409 (5)
O1—B1—O2	109.7 (3)	B3—O4—C19	122.7 (3)
O1—B1—B2^{i}	113.1 (3)	B3—O5—B4	124.4 (4)
O1—B1—N1	100.8 (3)	B3^{ii}—B4—O5	123.8 (4)
O2—B1—B2^{i}	112.9 (3)	B3^{ii}—B4—O6	119.4 (4)
O2—B1—N1	106.6 (3)	O5—B4—O6	116.7 (4)
B2^{i}—B1—N1	113.0 (3)	O7—B5—O8	108.3 (3)
B1—O2—B2	124.3 (3)	O7—B5—B6^{iii}	113.5 (3)
B1^{i}—B2—O2	122.8 (4)	O7—B5—N3	101.3 (3)
B1^{i}—B2—O3	120.5 (3)	O8—B5—B6^{iii}	112.8 (3)
O2—B2—O3	116.7 (3)	O8—B5—N3	106.7 (3)
O4—B3—O5	107.8 (4)	B6^{iii}—B5—N3	113.4 (4)
O4—B3—B4^{ii}	117.5 (3)	B5—O8—B6	121.6 (3)
O4—B3—N2	99.4 (3)	B5^{iii}—B6—O8	124.4 (4)
O5—B3—B4^{ii}	111.4 (3)	B5^{iii}—B6—O9	118.4 (4)
O5—B3—N2	105.2 (3)	O8—B6—O9	117.2 (4)
B4^{ii}—B3—N2	114.4 (3)		

Symmetry codes: (i) $-x, -y, -z + 1$; (ii) $-x + 1, -y + 1, -z$; (iii) $-x + 1, -y, -z + 1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O7	0.93	1.96	2.833 (4)	155
N2—H2···O10	0.93	2.06	2.961 (6)	163
N3—H3···O1	0.93	2.10	2.988 (4)	160

H atoms were positioned geometrically, with C—H = 0.95–0.99 Å and N—H = 0.93 Å, and refined as riding, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N) [1.5$U_{\rm eq}$(C) for methyl groups]. Most of the CF_3 groups are disordered over two orientations, with occupancy factors in the range 0.53 (3)–0.74 (5) for the major components; one ethyl group of the solvent molecule is disordered, with occupancy factors 0.505 (19):0.495 (19). Restraints were applied to the geometry and displacement parameters of the disordered atoms.

Data collection: *SMART* (Bruker, 1997); cell refinement: local programs; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2005); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3048). Services for accessing these data are described at the back of the journal.

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