Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

An O-bridged BONBON ring system (phenol adduct)

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Received 15 February 2002
Accepted 1 March 2002
Online 8 March 2002

1,4-Diphenyl-3,3:6,6-bis(tetramethylene)-2,5,7-trioxa-3,6-diazonia-1,4-diboratabicyclo[2.2.1]heptane–phenol (1/1), $C_{20}H_{26}B_2N_2O_3\cdot C_6H_5OH$, contains a six-membered boat-shaped BONBON ring, with an O bridge forming a bicyclic system. The phenol molecule shows some disorder, and is linked to the heterocycle by an O—H···O hydrogen bond. The molecular dimensions of the heterocycle differ slightly from those of the parent (phenol-free) crystal, presumably as a result of the hydrogen bonding.

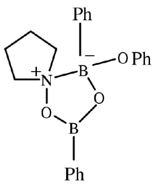
Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.005 Å
H-atom completeness 97%
Disorder in main residue
R factor = 0.046
wR factor = 0.059
Data-to-parameter ratio = 11.1

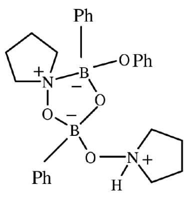
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

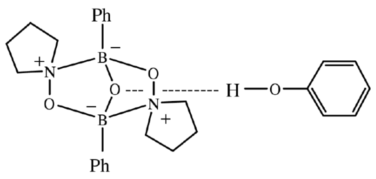
In the course of our investigations of five-membered BOBON heterocycles (substituted 1,3-dioxa-4-azonia-2-bora-5-boratacyclopentanes) (Kliegel *et al.*, 1983, 1984), the synthesis of (I) has been attempted by condensation of *N*-hydroxypyrrolidine with phenylboronic acid (2 mol equivalents) and phenol. The reaction resulted, however, in a crystalline compound containing an additional molecule of *N*-hydroxypyrrolidine. The structure analysis shows that the compound is not the adduct (II), but rather an O—H···O hydrogen bond associate of phenol and an O-bridged BONBON heterocycle (III).



(I)



(II)



(III)

The crystal structure of (III) consists of a boron-containing heterocycle and a phenol molecule. The structure of the heterocycle has already been determined in crystals of the parent compound (without the phenol) (Kliegel *et al.*, 1991). In the parent crystal, the molecule lies on a crystallographic C_2 axis; in the phenol adduct crystal the heterocycle is in a general position, but still has approximate C_2 symmetry (Fig. 1).

In the phenol adduct, the heterocycle contains a six-membered BONBON ring with a boat conformation, bridged

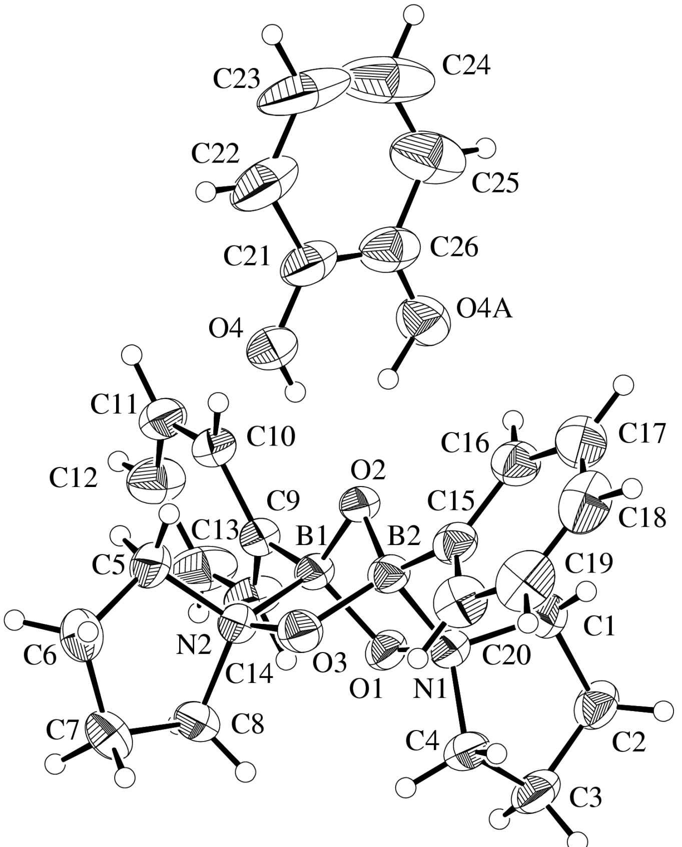


Figure 1
View of the title molecule (33% probability ellipsoids). The low-occupancy C6*A* and C7*A* atoms, and the high-occupancy H atom bonded to C26, have been omitted for clarity; the low-occupancy O4*A* atom is shown.

by an additional O atom to form a bicyclo[2.2.1]heptane-type structure; the BONBO five-membered rings have envelope conformations, with the bridging O atom at the flaps, these conformations being a natural consequence of the presence of the bicyclic ring system. The N atoms are each linked to tetramethylene chains to form exocyclic five-membered rings, one of which shows slight disorder (87:13) (in the parent crystal both tetramethylene rings show disorder, since they are symmetry-related). The non-disordered ring has a half-chair conformation, with N1 and C4 displaced on opposite sides of the C1—C2—C3 plane [dihedral angle magnitudes in the range 10.1–39.5 (2)°]; the major component of the disordered ring has an N2-envelope conformation [dihedral angle magnitudes 2.5–30.9 (3)°], and the minor component a C6*A* envelope conformation [dihedral angle magnitudes 1–20 (2)°].

The phenol molecule also exhibits some disorder (75:25), and is linked to the heterocycle by an O—H···O hydrogen bond (Fig. 1); O···O = 2.659 (2), H···O = 1.91 (4) Å and O—H···O = 177 (4)° for the major component [2.702 (7), 1.77 Å and 155° for the minor component].

The molecular dimensions of the heterocycle in the phenol adduct show some differences from those in the parent crystal, presumably as a consequence of changes in electron density resulting from the donation of one of the lone pairs of the bridging oxygen to the hydrogen bond. This lengthens the B—O(bridge) bonds, mean 1.441 (2) Å, in comparison with the bond in the parent, 1.423 (3) Å, and shortens the B—N [mean 1.676 (2) *versus* 1.703 (3) Å] and perhaps the B—O(N) [mean 1.490 (2) *versus* 1.497 (3) Å] bonds. The B—C(phenyl) bonds are essentially equal in the two crystals, 1.582 (3) *versus* 1.577 (4) Å. The bond angles at the B atom differ from the exact tetrahedral value by about the same in both crystals, with the N—B—O(bridge) angle being the smallest, mean 97.7 (1)° in the adduct and 97.8 (2)° in the parent, and the O(bridge)—B—C(phenyl) being the largest, mean 122.9 (1)° *versus* 122.5 (2)°.

Experimental

For the preparation of (III), *N*-hydroxypyrrolidine (0.44 g, 5 mmol), phenylboronic acid (1.22 g, 10 mmol), and phenol (0.47 g, 5 mmol) were dissolved in 20 ml of ethanol, and the mixture was refluxed for 15 min. After evaporation of the solvent *in vacuo*, the remaining residue was brought to crystallization by the addition of ether. Recrystallization from ethanol yielded 1.46 g (64%) of colorless crystals. M.p. 400 K (from EtOH); IR (KBr): 3500–2500 (broad 'curtain', O—H), 1610, 1600 cm^{-1} (C—C of phenol and phenylboron); ^{1}H NMR (90 MHz, CDCl$_3$-TMS): δ (p.p.m.) 1.0–2.3 (*m*, 2C—CH$_2$CH$_2$—C), 3.10 (*m*, 2NCH$_2$), 3.55 (*m*, 2NCH$_2$), 6.6–7.7 (*m*, 15 aromatic H), 8.10 (*s*, broad, exchangeable, OH); ^{1}H NMR (90 MHz, D_6-DMSO-TMS): δ (p.p.m.) 1.0–2.2 (*m*, 2C—CH$_2$CH$_2$—C), 2.80 (*m*, 2NCH$_2$), 3.33 (*m*, 2NCH$_2$), 6.6–7.9 (*m*, 15 aromatic H), 9.15 (*s*, broad, exchangeable, OH); ^{11}B NMR (64 MHz, CDCl$_3$-Et$_2$OBF$_3$): δ (p.p.m.) 8.8 ($w_{1/2}$ = 300 Hz). Analysis calculated for $C_{26}H_{32}B_2N_2O_4$: C 68.16, H 7.04, N 6.11%; found: C 68.25. H 7.03, N 6.11%. Crystals suitable for X-ray crystallography were obtained by slow crystallization from ethanol.

Crystal data

$C_{20}H_{26}B_2N_2O_3 \cdot C_6H_6O$
$M_r = 458.17$
Monoclinic, $P2_1/n$
$a = 10.448$ (1) Å
$b = 17.276$ (2) Å
$c = 14.525$ (1) Å
$\beta = 109.81$ (1)°
$V = 2466.6$ (4) Å^3
$Z = 4$

$D_x = 1.234$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 41.9$–50.3°
$\mu = 0.65$ mm^{-1}
$T = 294$ K
Block, colorless
0.50 × 0.40 × 0.30 mm

Data collection

Rigaku AFC-6*S* diffractometer
ω–2θ scans
Absorption correction: ψ scan (*AFC*-6 *Software*; Molecular Structure Corporation, 1989)
$T_{\min} = 0.70$, $T_{\max} = 0.83$
5565 measured reflections
5081 independent reflections
3637 reflections with $I > 3\sigma(I)$

$R_{\rm int} = 0.025$
$\theta_{\max} = 77.6$°
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 21$
$l = -18 \rightarrow 17$
3 standard reflections every 300 reflections intensity decay: 15.0%

Refinement

Refinement on F
$R = 0.046$
$wR = 0.059$
$S = 0.95$
3637 reflections
329 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/10[\sigma^2(F_o) + 0.015F_o^2]$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}
Extinction correction: *TEXSAN* (Molecular Structure Corporation, 1989)
Extinction coefficient: 6.5 (4) × 10^{-6}

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Table 1
Selected geometric parameters (Å, °).

O1—N1	1.454 (2)	C7*A*—C8	1.16 (3)
O1—B1	1.485 (2)	C9—C10	1.390 (3)
O2—B1	1.441 (3)	C9—C14	1.388 (3)
O2—B2	1.438 (3)	C9—B1	1.581 (4)
O3—N2	1.460 (2)	C10—C11	1.382 (4)
O3—B2	1.494 (2)	C11—C12	1.369 (3)
O4—C21	1.275 (4)	C12—C13	1.372 (4)
O4*A*—C26	1.189 (8)	C13—C14	1.381 (4)
N1—C1	1.494 (2)	C15—C16	1.378 (2)
N1—C4	1.484 (2)	C15—C20	1.403 (3)
N1—B2	1.675 (2)	C15—B2	1.584 (3)
N2—C5	1.495 (2)	C16—C17	1.387 (4)
N2—C8	1.494 (2)	C17—C18	1.383 (5)
N2—B1	1.676 (2)	C18—C19	1.365 (5)
C1—C2	1.519 (3)	C19—C20	1.380 (4)
C2—C3	1.524 (2)	C21—C22	1.398 (3)
C3—C4	1.511 (3)	C21—C26	1.359 (5)
C5—C6	1.499 (2)	C22—C23	1.391 (9)
C5—C6*A*	1.25 (2)	C23—C24	1.35 (1)
C6—C7	1.507 (4)	C24—C25	1.355 (7)
C6*A*—C7*A*	1.55 (4)	C25—C26	1.386 (5)
C7—C8	1.513 (3)		
N1—O1—B1	104.6 (1)	C12—C13—C14	120.0 (2)
B1—O2—B2	97.5 (1)	C9—C14—C13	121.9 (2)
N2—O3—B2	104.7 (2)	C16—C15—C20	117.1 (2)
O1—N1—C1	107.3 (2)	C16—C15—B2	122.0 (2)
O1—N1—C4	108.1 (1)	C20—C15—B2	120.7 (2)
O1—N1—B2	100.7 (1)	C15—C16—C17	122.0 (2)
C1—N1—C4	103.7 (1)	C16—C17—C18	119.3 (3)
C1—N1—B2	117.0 (1)	C17—C18—C19	120.2 (3)
C4—N1—B2	119.4 (1)	C18—C19—C20	120.1 (3)
O3—N2—C5	107.3 (1)	C15—C20—C19	121.3 (2)
O3—N2—C8	109.4 (2)	O4—C21—C22	119.1 (3)
O3—N2—B1	100.4 (1)	O4—C21—C26	121.6 (2)
C5—N2—C8	104.1 (1)	C22—C21—C26	119.3 (3)
C5—N2—B1	116.7 (1)	C21—C22—C23	118.6 (4)
C8—N2—B1	118.5 (1)	C22—C23—C24	121.1 (4)
N1—C1—C2	105.9 (1)	C23—C24—C25	120.2 (5)
C1—C2—C3	105.8 (1)	C24—C25—C26	119.9 (4)
C2—C3—C4	105.0 (1)	O4*A*—C26—C21	115.7 (4)
N1—C4—C3	104.6 (2)	O4*A*—C26—C25	123.3 (5)
N2—C5—C6	106.0 (2)	C21—C26—C25	120.9 (3)
N2—C5—C6*A*	108.1 (9)	O1—B1—O2	107.2 (2)
C5—C6—C7	106.9 (2)	O1—B1—N2	102.9 (1)
C5—C6*A*—C7*A*	104 (2)	O1—B1—C9	112.6 (2)
C6—C7—C8	105.9 (2)	O2—B1—N2	97.8 (1)
C6*A*—C7*A*—C8	114 (2)	O2—B1—C9	122.5 (2)
N2—C8—C7	106.4 (2)	N2—B1—C9	111.4 (2)
N2—C8—C7*A*	106 (1)	O2—B2—O3	106.7 (2)
C10—C9—C14	116.4 (2)	O2—B2—N1	97.6 (1)
C10—C9—B1	122.0 (1)	O2—B2—C15	121.2 (1)
C14—C9—B1	121.5 (2)	O3—B2—N1	103.2 (1)
C9—C10—C11	122.0 (1)	O3—B2—C15	115.3 (2)
C10—C11—C12	119.9 (2)	N1—B2—C15	110.1 (2)
C11—C12—C13	119.7 (3)		

Disorder is exhibited by one of the five-membered exocyclic substituents in the heterocycle (87:13), and by the OH group of the phenol (75:25); the phenol molecule generally exhibits rather high displacement parameters, which may indicate some further disorder. The low-occupancy C atoms and the high-occupancy OH H atom were refined isotropically; the low-occupancy OH H atom was fixed in a difference map position, and all other H atoms were fixed in calculated sites. Seven low-occupancy H atoms (six at 0.13 and one at 0.25 occupancies) were omitted from the structural model.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structure: *MITHRIL* (Gilmore, 1984); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

We thank the Natural Sciences and Engineering Research Council of Canada and the Fonds der Chemische Industrie, Frankfurt am Main, for financial support.

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