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Key indicators

Single-crystal X-ray study
T = 173 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
Disorder in solvent or counterion
R factor = 0.043
wR factor = 0.102
Data-to-parameter ratio = 16.1

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

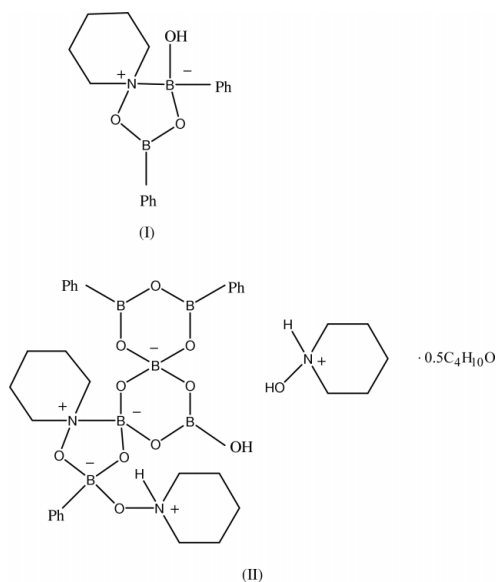
A polycyclic condensate of phenylboronic and boric acids with *N*-hydroxypiperidine

1-Hydroxypiperidinium 16-hydroxy-6,6-pentamethylene-11-, 13,19-triphenyl-19-(1-piperidiniumoxy)-8,10,12,14,15,17,18-, 20-octaoxa-6-azonia-11,13,16-tribora-7,9,19-triboratatrispiro-[5.0.1.5.3.3]icosane diethyl ether hemisolvate, $\text{C}_{33}\text{H}_{49}\text{B}_6\text{N}_3\text{O}_{11} \cdot 0.5\text{C}_4\text{H}_{10}\text{O}$, contains a tetracyclic ring system, with two boroxine, a BOBON, and a piperidinium ring spiro-fused; the diethyl ether solvent molecule is disordered over an inversion centre.

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Comment

In an attempt to synthesize the BOBON heterocycle, (I), by reacting 2 mol of phenylboronic acid and 1 mol of *N*-hydroxypiperidine, a crystalline compound was isolated. The elemental analysis showed, as expected, a B:N ratio of 2:1, but deviated in the contents of the other elements. In addition, in the ^1H NMR spectrum, the ratio of peak areas of the phenyl and piperidine signals was 1:1 instead of 2:1. Thus, a structure like (I) had to be excluded. Additionally, the distinct ^1H NMR signal of an ethyl group pointed to the participation of the



solvent (diethyl ether) in the crystal. The X-ray crystallographic analysis revealed the polycyclic molecular structure (II), containing, in fact, six B atoms in proportion to the three N atoms of the *N*-hydroxypiperidine moieties. Three molecules each of phenylboronic and of boric acid are incorporated by anhydride bonds into the tetracyclic condensate, which contains two boroxine ring systems and a BOBON five-membered heterocycle. Thus, half of the applied quantity of phenylboronic acid has been dephenylated by hydrolytic or oxidative B—C fission during the reaction, being transformed

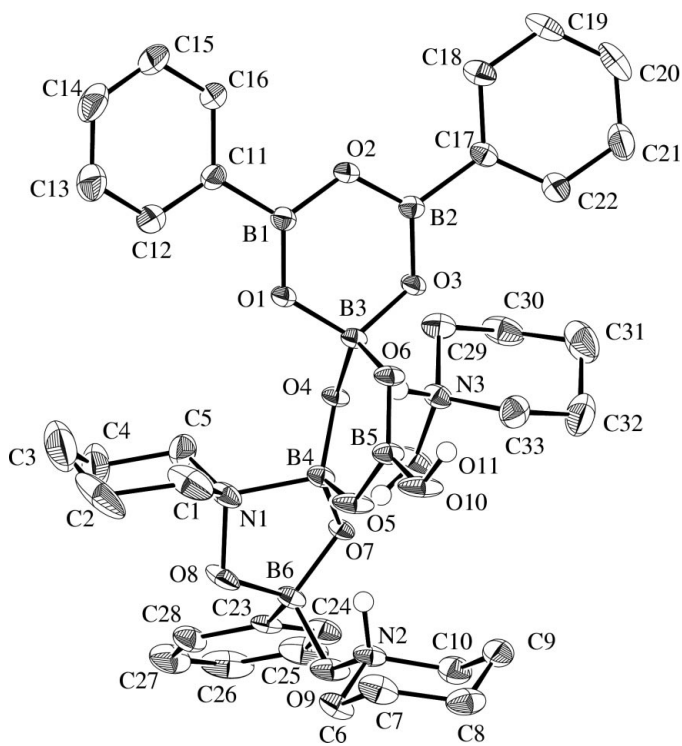


Figure 1
A view of the structure of (II) (50% probability ellipsoids). H atoms bonded to C atoms have been omitted.

into boric acid. Of the three *N*-hydroxypiperidine molecules, one is a spiro-connected part of the BOBON ring, and the other two participate, one as an O—B coordinated Lewis-base ligand and the other as a protonated Brønsted base.

The crystal structure of (II) contains a tetracyclic anion, an *N*-hydroxypiperidinium cation, and a molecule of diethyl ether solvent, which is disordered over a centre of inversion. In the anion, the diphenylboroxine ring B1/O2/B2/O3/B3/O1 (Fig. 1), a boroxine ring with one tetrahedral sp^3 -hybridized and two trigonal sp^2 -hybridized B atoms, has two very short O—B bonds with considerable π -bond character, O1—B1 [1.345 (2) Å] and O3—B2 [1.347 (2) Å]. This ring-system geometry resembles closely that of the tetraphenylboroxine ring previously described and discussed in comparison with the literature data (Kliegel *et al.*, 1985). The structure of pure triphenylboroxine with three sp^2 boron ring members was published somewhat later (Brock *et al.*, 1988). The second boroxine ring system within (II), B3/O4/B4/O5/B5/O6, containing one sp^2 - and two sp^3 -hybridized B atoms, is nearly perpendicular to the ring plane of the first (above-mentioned) boroxine ring. It shows planarity around the boric acid moiety at B5, including O5, O6, and O10, caused by O—B pp (π) back donation; thus, the B5—O5, B5—O6, and B5—O10 bonds possess considerable double-bond character [bond lengths: 1.376 (2), 1.352 (2), and 1.355 (2) Å, respectively]. The BOBON ring system is characterized by two sp^3 boron ring members, with O—B distances in the single-bond range, *viz.* 1.443 (2), 1.451 (2), and 1.512 (2) Å. The N1—B4 bond of 1.656 (2) Å is long, but quite normal for an N—B coordinative bond to a borate ester moiety.

The anion contains one intra-anion hydrogen bond, *i.e.* N2—H···O5, with N···O = 2.682 (2), N—H = 0.96 (2), H···O = 1.72 (2) Å and N—H···O = 176 (2)°; there may be some bifurcation in this system, with a weaker N2—H···O7 component, with N···O = 2.838 (2), H···O = 2.40 (2) Å and N2—H···O7 = 107 (2)°. The anion and cation are linked by strong O—H···O and N—H···O hydrogen bonds: O11—H···O7, with O···O = 2.592 (2), O—H = 1.12 (3), H···O = 1.48 (3) Å and O—H···O = 168 (2)°; N3—H···O4, with N···O = 2.621 (2), N—H = 0.98 (2), H···O = 1.65 (2) Å and N—H···O = 168 (1)°. Finally, there is an inter-anion hydrogen bond, O10—H···O6, with O···O = 2.662 (2), O—H = 0.87 (2), H···O = 1.80 (2) Å, and O—H···O = 175 (2)°.

The structure was initially determined at room temperature (294 K). The results are similar to those presented here for a crystal at 173 K, but some comparisons are interesting. The bond distances measured at 294 K are generally slightly shorter than those at 173 K, by up to about 0.01 Å, indicating the need for thermal libration corrections at the higher temperature. The displacement parameters are, as expected, smaller at the lower temperature, except for those in the three outer atoms of each piperidine ring, where the values are rather similar at both temperatures; this suggests some possible minor disorder in these regions.

Experimental

Phenylboronic acid (1.22 g, 10 mmol) and *N*-hydroxypiperidine (0.51 g, 5 mmol) were dissolved in 40 ml of diethyl ether with slight warming. After storing for some hours at room temperature, crystallization commenced. Yield: 0.61 g (48%) of colorless crystals; m.p. above 383 K (decomposition between 383 and 443 K). IR (KBr): 3500–2500 (broad ‘curtain’, N—H, O—H), 1600 cm^{-1} (phenyl—C=C). ^1H NMR (90 MHz, D_6 -DMSO—TMS), δ (p.p.m.): 1.08 (*t*, J = 6 Hz, CH_3), 1.3–3.4 (*m*, 3 (CH_2)₅N), 3.35 (*q*, J = 6 Hz, CH_2O), 7.0–8.0 (*m*, 15 aromatic H), 6–10 (*m*, very broad, exchangeable, 2NH, 2 OH). Analysis calculated for $\text{C}_{33}\text{H}_{49}\text{B}_6\text{N}_3\text{O}_{11} \cdot 1/2(\text{C}_2\text{H}_5)_2\text{O}$: C 54.90, H 7.11, B 8.47, N 5.49%; found: C 54.92, H 7.32, B 8.56, N 5.49%. Single crystals suitable for X-ray crystallography were obtained from the ether solution of the reaction products without recrystallization.

Crystal data

$\text{C}_5\text{H}_{12}\text{NO}^+ \cdot \text{C}_{28}\text{H}_{37}\text{B}_6\text{N}_2\text{O}_{10}^- \cdot$	$Z = 2$
$0.5\text{C}_4\text{H}_{10}\text{O}$	$D_x = 1.226 \text{ Mg m}^{-3}$
$M_r = 765.68$	Mo $K\alpha$ radiation
Triclinic, $P\bar{1}$	Cell parameters from 9653 reflections
$a = 10.636 (2) \text{ \AA}$	$\theta = 2.3\text{--}27.9^\circ$
$b = 15.340 (2) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$c = 15.545 (2) \text{ \AA}$	$T = 173 \text{ K}$
$\alpha = 105.467 (2)^\circ$	Chip, colorless
$\beta = 107.949 (4)^\circ$	$0.40 \times 0.30 \times 0.20 \text{ mm}$
$\gamma = 109.453 (2)^\circ$	
$V = 2073.3 (5) \text{ \AA}^3$	

Data collection

Quantum CCD diffractometer	8500 independent reflections
CCD scans	5491 reflections with $I > 3\sigma(I)$
Absorption correction: multi-scan	$R_{\text{int}} = 0.038$
(<i>d</i> *T _{REK} ; Molecular Structure Corporation, 1997)	$\theta_{\text{max}} = 27.9^\circ$
$T_{\text{min}} = 0.96$, $T_{\text{max}} = 0.98$	$h = -12 \rightarrow 13$
19307 measured reflections	$k = -19 \rightarrow 17$
	$l = -20 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.102$
 $S = 1.41$
 8500 reflections
 527 parameters

H atoms were treated by a mixture
 of constrained and independent
 refinement
 $w = 1/[\sigma^2(F_o^2)]$
 $(\Delta/\sigma)_{\max} = 0.036$
 $\Delta\rho_{\max} = 0.49 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.49 \text{ e } \text{\AA}^{-3}$

N- and O-bound H atoms were refined, while the other H atoms were refined as riding on their parent atoms.

Data collection: *d*TREK* (Molecular Structure Corporation, 1997); cell refinement: *d*TREK*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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Table 1

Selected geometric parameters (\AA , $^\circ$).

O1—B1	1.345 (2)	C4—C5	1.508 (3)
O1—B3	1.464 (2)	C6—C7	1.517 (2)
O2—B1	1.394 (2)	C7—C8	1.512 (3)
O2—B2	1.385 (2)	C8—C9	1.518 (3)
O3—B2	1.347 (2)	C9—C10	1.519 (2)
O3—B3	1.480 (2)	C11—C12	1.397 (2)
O4—B3	1.468 (2)	C11—C16	1.399 (2)
O4—B4	1.418 (2)	C11—B1	1.567 (2)
O5—B4	1.452 (2)	C12—C13	1.385 (2)
O5—B5	1.376 (2)	C13—C14	1.380 (3)
O6—B3	1.479 (2)	C14—C15	1.370 (3)
O6—B5	1.352 (2)	C15—C16	1.388 (3)
O7—B4	1.443 (2)	C17—C18	1.397 (2)
O7—B6	1.451 (2)	C17—C22	1.393 (2)
O8—N1	1.443 (2)	C17—B2	1.571 (2)
O8—B6	1.512 (2)	C18—C19	1.394 (2)
O9—N2	1.428 (2)	C19—C20	1.372 (3)
O9—B6	1.514 (2)	C20—C21	1.379 (3)
O10—B5	1.355 (2)	C21—C22	1.391 (3)
O11—N3	1.428 (2)	C23—C24	1.397 (2)
O12—C34	1.636 (8)	C23—C28	1.391 (2)
O12—C36	1.16 (1)	C23—B6	1.611 (2)
N1—C1	1.488 (2)	C24—C25	1.392 (2)
N1—C5	1.494 (2)	C25—C26	1.372 (3)
N1—B4	1.656 (2)	C26—C27	1.373 (3)
N2—C6	1.484 (2)	C27—C28	1.395 (2)
N2—C10	1.486 (2)	C29—C30	1.506 (3)
N3—C29	1.484 (2)	C30—C31	1.513 (3)
N3—C33	1.490 (2)	C31—C32	1.521 (3)
C1—C2	1.558 (4)	C32—C33	1.507 (3)
C2—C3	1.524 (4)	C34—C35	1.267 (8)
C3—C4	1.487 (4)	C35—C36 ¹	1.56 (1)

B1—O1—B3	122.1 (1)	C19—C20—C21	119.9 (2)
B1—O2—B2	119.4 (1)	C20—C21—C22	119.8 (2)
B2—O3—B3	121.8 (1)	C17—C22—C21	121.8 (2)
B3—O4—B4	123.9 (1)	C24—C23—C28	116.5 (1)
B4—O5—B5	122.4 (1)	C24—C23—B6	120.3 (2)
B3—O6—B5	124.0 (1)	C28—C23—B6	123.2 (2)
B4—O7—B6	112.2 (1)	C23—C24—C25	121.8 (2)
N1—O8—B6	108.3 (1)	C24—C25—C26	120.3 (2)
N2—O9—B6	113.5 (1)	C25—C26—C27	119.3 (2)
C34—O12—C36	119.9 (5)	C26—C27—C28	120.4 (2)
O8—N1—C1	107.8 (1)	C23—C28—C27	121.7 (2)
O8—N1—C5	109.7 (1)	N3—C29—C30	111.3 (1)
O8—N1—B4	102.4 (1)	C29—C30—C31	110.4 (2)
C1—N1—C5	111.1 (2)	C30—C31—C32	110.2 (2)
C1—N1—B4	114.7 (1)	C31—C32—C33	111.2 (2)
C5—N1—B4	110.8 (1)	N3—C33—C32	111.8 (1)
O9—N2—C6	109.9 (1)	O12—C34—C35	113.0 (4)
O9—N2—C10	109.0 (1)	O12—C36—C35 ¹	125.5 (8)
C6—N2—C10	111.7 (1)	O1—B1—O2	121.1 (2)
O11—N3—C29	108.3 (1)	O1—B1—C11	121.8 (2)
O11—N3—C33	110.5 (1)	O2—B1—C11	117.1 (1)
C29—N3—C33	113.1 (1)	O2—B2—O3	121.0 (2)
N1—C1—C2	111.6 (2)	O2—B2—C17	118.4 (1)
C1—C2—C3	112.0 (2)	O3—B2—C17	120.6 (2)
C2—C3—C4	108.3 (2)	O1—B3—O3	111.7 (1)
C3—C4—C5	110.2 (2)	O1—B3—O4	111.1 (1)
N1—C5—C4	114.1 (2)	O1—B3—O6	108.6 (1)
N2—C6—C7	109.2 (1)	O3—B3—O4	107.8 (1)
C6—C7—C8	111.4 (1)	O3—B3—O6	107.1 (1)
C7—C8—C9	110.5 (1)	O4—B3—O6	110.5 (1)
C8—C9—C10	110.8 (1)	O4—B4—O5	114.3 (1)
N2—C10—C9	109.6 (1)	O4—B4—O7	114.5 (1)
C12—C11—C16	117.0 (2)	O4—B4—N1	111.5 (1)
C12—C11—B1	121.5 (1)	O5—B4—O7	110.7 (1)
C16—C11—B1	121.4 (2)	O5—B4—N1	105.4 (1)
C11—C12—C13	121.7 (2)	O7—B4—N1	99.0 (1)
C12—C13—C14	119.8 (2)	O5—B5—O6	120.4 (1)
C13—C14—C15	120.1 (2)	O5—B5—O10	116.4 (1)
C14—C15—C16	120.2 (2)	O6—B5—O10	123.1 (1)
C11—C16—C15	121.3 (2)	O7—B6—O8	105.1 (1)
C18—C17—C22	117.0 (2)	O7—B6—O9	112.8 (1)
C18—C17—B2	122.2 (2)	O7—B6—C23	113.8 (1)
C22—C17—B2	120.8 (1)	O8—B6—O9	107.6 (1)
C17—C18—C19	121.3 (2)	O8—B6—C23	114.1 (1)
C18—C19—C20	120.2 (2)	O9—B6—C23	103.5 (1)

Symmetry code: (i) $2 - x, 2 - y, 2 - z$.

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