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Triphenylboroxin complex with *N*-cyclohexylhydroxylamine and its isobutyraldehyde nitrone

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Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.007 Å
R factor = 0.047
wR factor = 0.057
Data-to-parameter ratio = 17.0

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

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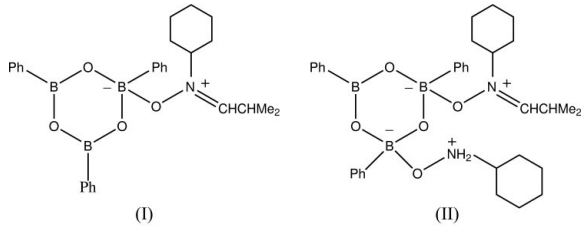
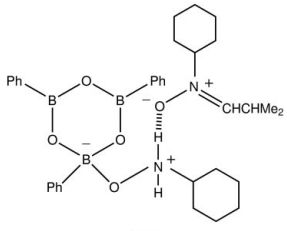
N-Cyclohexylhydroxylamine(O–B)triphenylboroxin *N*-cyclohexyl-*C*-(2-propyl)nitrone hemibenzene hemisolvate, $C_{24}H_{28}B_3NO_4.C_{10}H_{19}NO{\cdot}0.5C_6H_6$, contains one molecule of *N*-cyclohexylhydroxylamine in its *N*-oxide form added to a boroxin heterocycle, with one molecule of *N*-cyclohexyl-*C*-(2-propyl)nitrone linked by an O···H—N hydrogen bond to the protonated hydroxylamine moiety, and a molecule of benzene which is located on a centre of inversion.

Comment

Triphenylboroxin and *N*-cyclohexyl-*C*-(2-propyl)nitrone form the 1:1 B–O–N adduct (I). *B,N*-Betainic complexes of this type, which are readily obtained as crystalline compounds from boroxins and nitrones [a series of various nitrone–triphenylboroxin 1:1 complexes has been synthesized (Lubkowitz, 1992)], correspond with other nitrone adducts of arylboronates (Paetzold *et al.*, 1976; Kliegel, Preu *et al.*, 1985) and diarylborinates (Kliegel, Lauterbach *et al.*, 1987; Kliegel, Metge *et al.*, 1997, 1998*a*,*b*; Kliegel *et al.*, 2000, 2001). Addition of an equimolar amount of *N*-cyclohexylhydroxylamine to (I) was expected to give the complex (II), a double-addition product of the nitrone as well as the hydroxylamine, the latter presumably in its *N*-oxide form, as was established recently for the B–O–N complex from triphenylboroxin and *N,N*-diethylhydroxylamine (Kliegel *et al.*, 2002). An N–B coordination between the hydroxylamine and the boron compound could not be entirely excluded at this point, however.



(I) (II)



(III)

The crystalline reaction product (method *A*), which could also be obtained in a three-component one-pot reaction from 3 mole equivalents (m.e.) of phenylboronic acid, 2 m.e. of *N*-cyclohexylhydroxylamine and 1 m.e. of isobutyraldehyde (method *B*), shows, indeed, the elemental analysis of (II).

Some spectroscopic data, however, might call the adduct structure (II) into question. Comparing the IR spectra of (I) and of the adduct, the nitrone-C═N vibration is shifted from 1660 in (I) to about 1600 cm^{-1} in the adduct, and in the ^1H NMR spectra, the signal of the N═CH methine H atom is displaced from $\delta = 6.97$ in (I) to 6.73 p.p.m. in the adduct. Both the IR and the ^1H NMR data of the nitrone portion of the adduct coincide roughly with those of free *N*-cyclohexylisobutyraldonitrone. The X-ray analysis establishes the molecular structure (III) for the adduct, representing a triphenylboroxin complex with *N*-cyclohexylhydroxylamine in its *N*-oxide form, and the *N*-cyclohexylisobutyraldonitrone linked by an O···H—N^+ hydrogen bond to the hydroxylamine moiety [the crystals contain, additionally, benzene from the solvent mixture used for obtaining single crystals].

Obviously the *N*-alkylhydroxylamine (*N*-oxide form) is the stronger nucleophile and substitutes for the azomethine *N*-oxide (nitrone). It seems that, in this case, a mono-coordination with the boroxin ring system is preferred over a twofold coordination, as depicted in (II). This is in line with the findings regarding the complex formation between triphenylboroxin, *N,N*-diethylhydroxylamine, and *N,N*-dimethylformamide (Kliegel *et al.*, 2002). Multiple coordination had been suggested previously for a nitrone adduct of triphenyboroxin (Paetzold *et al.*, 1975).

The crystal structure of (III) contains three separate fragments: an *N*-cyclohexylhydroxylamine–triphenylboroxin complex, an *N*-cyclohexyl-*C*-(2-propyl)nitrone (Fig. 1), and a benzene molecule which lies on a centre of inversion. The six-membered boroxin ring has an approximate envelope conformation, the O1—B2—O2—B3—O3 ring portion forming a rather distorted plane, with B1 on the 'flap' [a more accurate description is perhaps a boat conformation, with B1, and to a lesser extent O2, displaced from the plane of the other four atoms]. The ring dimensions are very similar to those in related boroxin ring systems containing one tetrahedral sp^3 B atom (Kliegel, Motzkus *et al.*, 1985; Kliegel *et al.*, 2002); in particular, two of the O—B bonds are short [O1—B2 = 1.345 (4) Å and O3—B3 = 1.347 (4) Å], with a high amount of double-bond character by (pp)π back donation. The longest O—B distance [O4—B1 = 1.530 (4) Å] is found in the exocyclic donor–acceptor bond between the *N*-oxide form of *N*-cyclohexylhydroxylamine and the boroxin moiety, very much like in the previously reported *N,N*-diethylhydroxylamine adduct (Kliegel *et al.*, 2002). The geometry of the nitrone molecule, which shows a *Z* configuration with near planarity around the C═N double bond [C31—N2 = 1.304 (5) Å], is typical for aldonitrones (Bedford *et al.*, 1991, and references therein; Kliegel, Preu *et al.*, 1985; Kliegel *et al.*, 1998*a*,*b*; Olszewski & Stadnicka, 1995; Greci & Sgarabotto, 1984; Christensen *et al.*, 1990).

The hydroxylamine–boroxin complex and the nitrone are linked by an N1—H1···O5 hydrogen bond: N···O = 2.751 (3), N—H = 0.98 (calculated H-atom site, assuming tetrahedral angles at N1), H···O = 1.80 Å and N—H···O = 163°. There is also an intra-boroxine contact which might represent a bifurcation of this hydrogen-bond system [N1—H1···O3: N···O = 2.904 (3), H···O = 2.45 Å and N—H···O = 108°]; this arrangement results in fairly short O5···B3 [2.860 (5) Å] and O5···O3 [2.991 (3) Å] distances. Finally, there is an inter-boroxin hydrogen bond [N1—H2···O4: N···O = 2.852 (3), N—H = 0.98, H···O = 2.03 Å and N—H···O = 141°].

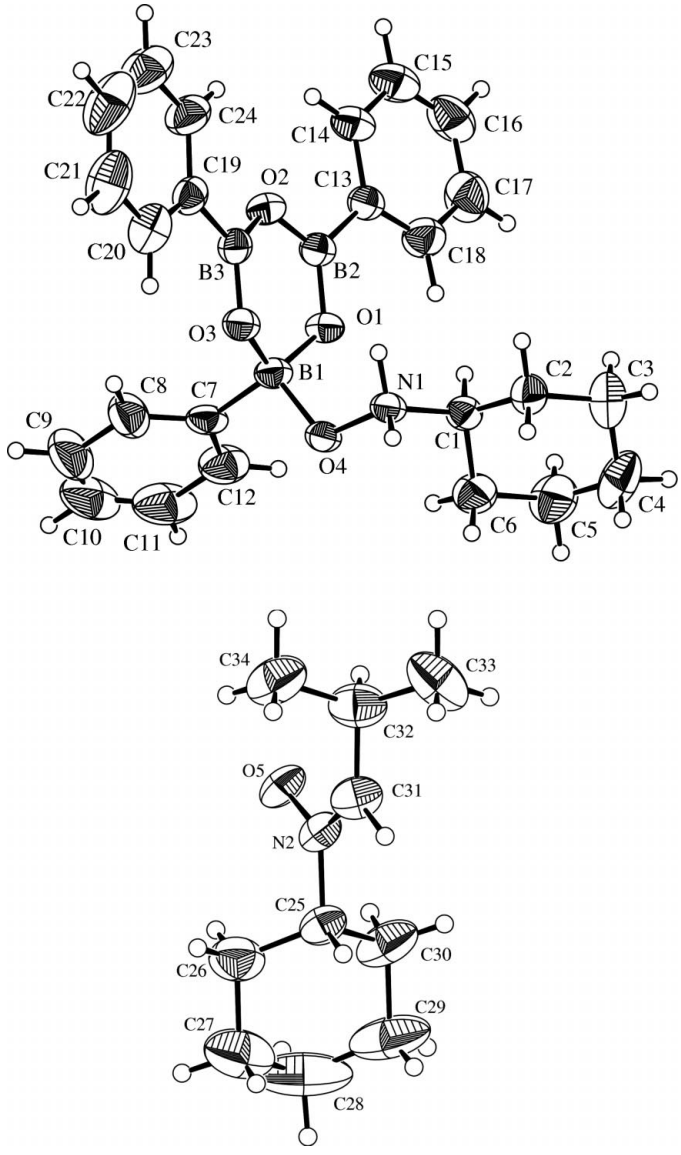


Figure 1
Views of the hydroxylamineboroxin complex and the nitrone components of the structure (ellipsoids drawn at the 33% probability level).

The thermal motion is rather high, as evidenced by the ellipsoids in Fig. 1.

Experimental

N-Cyclohexyl-*C*-(2-propyl)nitrone(O–B)triphenylboroxin, (I): triphenylboroxin (2.50 g, 8 mmol) and *N*-cyclohexyl-*C*-(2-propyl)-nitrone (1.35 g, 8 mmol) [*N*-(2-methylpropylidene)cyclohexanamine *N*-oxide; prepared according to the literature (Coates & Cummings, 1986)] were dissolved in 50 ml of ethanol and refluxed for 30 min. The solvent was distilled off *in vacuo* and the remaining oil mixed with a small amount of toluene. A crystalline substance was obtained after addition of petroleum ether and cooling. Yield: 3.66 g (95%) of

colorless crystals; m.p. 413–415 K (from toluene/petroleum ether). IR (KBr): 1660 (C═N), 1600 cm^{-1} (phenyl—C═C). ^1H NMR (90 MHz, DMSO-d_6/TMS), δ (p.p.m.): 1.00 [d, J = 7 Hz, $(CH_3)_2C$], 1.06–1.90 [m, $(CH_2)_5$], 3.02 (m, J = 7 Hz, N═C—CH), 3.77 (m, N-CH), 6.97 (d, J = 7 Hz, N═CH), 7.15–7.43 (m, 9 aromatic H), 7.68–7.96 (m, 6 aromatic H). Analysis calculated for $C_{28}H_{34}B_3NO_4$: C 69.92, H 7.12, B 6.74, N 2.91%; found: C 69.92, H 7.13, B 6.95, N 3.04%.

N-Cyclohexylhydroxylamine(O–B)triphenylboroxin *N*-cyclohexyl-*C*-(2-propyl)nitrone, (III) [2-(cyclohexylammonio-oxy)-2,4,6-triphenyl-1,3,5-trioxa-4,6-dibora-2-boratacyclohexane *N*-(2-methylpropylidene)cyclohexanamine *N*-oxide]: method *A*: (I) (1.44 g, 3 mmol) and *N*-cyclohexylhydroxylamine (0.35 g, 3 mmol) were suspended in 30 ml of ethanol and refluxed for 30 min. The solution was evaporated to half of the volume and mixed with 200 ml of petroleum ether. Upon cooling, 1.69 g (90%) of colorless crystals were obtained; m.p. 379–380 K (from ethanol/petroleum ether). IR (KBr): 2710, 2560 (N—H), 1600 cm^{-1} (C═N/C═C). ^1H NMR (90 MHz, DMSO-d_6–TMS), δ (p.p.m.): 1.00 [d, J = 7 Hz, $(CH_3)_2$], 1.11–2.24 [m, 2 $(CH_2)_5$], 2.89 (m, J = 7 Hz, N═C-CH), 3.17–3.83 (m and m, 2N-CH), 6.73 (d, J = 7 Hz, N═CH), 7.03–7.49 (m, 9 aromatic H), 7.68–7.81 (m, 6 aromatic H), 7.91 (s, exchangeable, NH), 9.50 (s, very broad, exchangeable, NH). Analysis calculated for $C_{34}H_{47}B_3N_2O_5$: C 68.50, H 7.95, B 5.44, N 4.70%; found: C 68.22, H 7.97, B 5.34, N 4.80%.

Method *B*: phenylboronic acid (1.83 g, 15 mmol) and *N*-cyclohexylhydroxylamine (1.15 g, 10 mmol) were dissolved in 40 ml of ethanol and mixed with 2-methylpropionaldehyde (isobutyraldehyde) (0.36 g, 5 mmol). After 1 h of refluxing, the solution was evaporated to a small volume. Addition of petroleum ether and cooling yielded 2.69 g (90%) of colorless crystals, identical with the product from method *A*.

Single crystals suitable for X-ray analysis were obtained by slow crystallization from a solvent mixture of ethanol, petroleum ether, and a small amount of benzene.

Crystal data

$C_{24}H_{28}B_3NO_4{\cdot}C_{10}H_{19}NO{\cdot}0.5C_6H_6$
M_r = 635.24
Monoclinic, $P2_1/n$
a = 13.660 (1) Å
b = 19.504 (3) Å
c = 14.433 (2) Å
β = 106.626 (8)°
V = 3684.6 (8) Å^3
Z = 4
D_x = 1.145 Mg m^{-3}
Cu Kα radiation
Cell parameters from 25 reflections
θ = 46.5–73.8°
μ = 0.58 mm^{-1}
T = 294 K
Prism, colorless
0.35 × 0.30 × 0.25 mm

Data collection

Rigaku AFC-6*S* diffractometer
ω–2θ scans
Absorption correction: ψ scan (*AFC*-6; Molecular Structure Corporation, 1989)
T_{min} = 0.84, T_{max} = 0.87
7579 measured reflections
7215 independent reflections
3098 reflections with $I > 3\sigma(I)$
R_{int} = 0.038
θ_{max} = 77.5°
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 24$
$l = -18 \rightarrow 17$
3 standard reflections
every 250 reflections
intensity decay: 2.2%

Refinement

Refinement on F
R = 0.047
wR = 0.057
S = 1.89
7215 reflections
425 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o) + 0.0004F_o^2]$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Extinction correction: *teXsan* (Molecular Structure Corporation, 1989)
Extinction coefficient: 1.69 (3) × 10^{-6}

Table 1
Selected geometric parameters (Å, °).

O1—B1	1.463 (5)	C13—C18	1.377 (6)
O1—B2	1.345 (4)	C13—B2	1.557 (6)
O2—B2	1.376 (5)	C14—C15	1.366 (6)
O2—B3	1.384 (5)	C15—C16	1.360 (7)
O3—B1	1.460 (5)	C16—C17	1.374 (8)
O3—B3	1.347 (4)	C17—C18	1.391 (7)
O4—N1	1.422 (3)	C19—C20	1.372 (6)
O4—B1	1.530 (4)	C19—C24	1.383 (5)
O5—N2	1.306 (3)	C19—B3	1.550 (6)
N1—C1	1.491 (4)	C20—C21	1.404 (8)
N2—C25	1.478 (5)	C21—C22	1.36 (1)
N2—C31	1.304 (5)	C22—C23	1.338 (9)
C1—C2	1.509 (4)	C23—C24	1.379 (8)
C1—C6	1.510 (4)	C25—C26	1.483 (6)
C2—C3	1.513 (6)	C25—C30	1.523 (5)
C3—C4	1.514 (8)	C26—C27	1.500 (7)
C4—C5	1.492 (7)	C27—C28	1.506 (9)
C5—C6	1.512 (7)	C28—C29	1.50 (1)
C7—C8	1.383 (6)	C29—C30	1.495 (8)
C7—C12	1.376 (5)	C31—C32	1.465 (6)
C7—B1	1.600 (5)	C32—C33	1.547 (7)
C8—C9	1.388 (6)	C32—C34	1.506 (5)
C9—C10	1.35 (1)	C35—C36	1.34 (1)
C10—C11	1.33 (1)	C35—C37^{i}	1.36 (1)
C11—C12	1.407 (7)	C36—C37	1.34 (1)
C13—C14	1.392 (5)		
B1—O1—B2	121.2 (3)	C24—C19—B3	121.2 (3)
B2—O2—B3	118.4 (3)	C19—C20—C21	121.3 (4)
B1—O3—B3	121.2 (3)	C20—C21—C22	118.8 (5)
N1—O4—B1	114.2 (2)	C21—C22—C23	121.1 (6)
O4—N1—C1	113.6 (2)	C22—C23—C24	120.2 (6)
O5—N2—C25	115.3 (3)	C19—C24—C23	121.5 (4)
O5—N2—C31	123.1 (3)	N2—C25—C26	111.2 (3)
C25—N2—C31	121.6 (3)	N2—C25—C30	109.1 (3)
N1—C1—C2	107.9 (2)	C26—C25—C30	111.1 (3)
N1—C1—C6	110.9 (3)	C25—C26—C27	111.5 (4)
C2—C1—C6	111.3 (3)	C26—C27—C28	110.6 (5)
C1—C2—C3	110.1 (3)	C27—C28—C29	111.8 (5)
C2—C3—C4	111.8 (4)	C28—C29—C30	112.8 (5)
C3—C4—C5	111.2 (4)	C25—C30—C29	109.9 (4)
C4—C5—C6	112.3 (4)	N2—C31—C32	123.9 (3)
C1—C6—C5	110.0 (3)	C31—C32—C33	110.7 (4)
C8—C7—C12	116.2 (3)	C31—C32—C34	109.7 (4)
C8—C7—B1	121.9 (3)	C33—C32—C34	110.6 (4)
C12—C7—B1	121.8 (4)	C36—C35—C37^{i}	119.8 (7)
C7—C8—C9	122.1 (4)	C35—C36—C37	121.6 (6)
C8—C9—C10	119.7 (6)	C35^{i}—C37—C36	118.6 (7)
C9—C10—C11	120.4 (6)	O1—B1—O3	111.2 (3)
C10—C11—C12	120.4 (5)	O1—B1—O4	107.5 (3)
C7—C12—C11	121.0 (5)	O1—B1—C7	113.1 (3)
C14—C13—C18	116.0 (3)	O3—B1—O4	107.4 (3)
C14—C13—B2	122.1 (3)	O3—B1—C7	112.4 (3)
C18—C13—B2	121.9 (4)	O4—B1—C7	104.8 (2)
C13—C14—C15	122.4 (4)	O1—B2—O2	121.0 (4)
C14—C15—C16	120.2 (4)	O1—B2—C13	120.9 (4)
C15—C16—C17	120.0 (5)	O2—B2—C13	118.1 (3)
C16—C17—C18	119.0 (4)	O2—B3—O3	120.7 (3)
C13—C18—C17	122.4 (4)	O2—B3—C19	117.7 (3)
C20—C19—C24	117.1 (4)	O3—B3—C19	121.5 (4)
C20—C19—B3	121.6 (4)		

Symmetry code: (i) $2-x, 1-y, 1-z$.

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*; molecular graphics: *teXsan*; software used to prepare material for publication: *teXsan*.

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