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Triphenylboroxin *N*,*N*-diethylhydroxylamine adduct (dimethylformamide solvate)

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Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.006 Å
R factor = 0.081
wR factor = 0.264
Data-to-parameter ratio = 14.6

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

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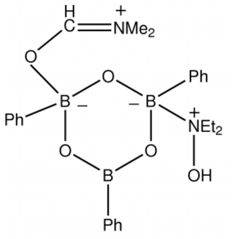
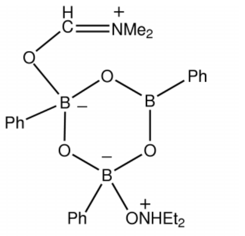
N,*N*-Diethylhydroxylamine(*O*–*B*)triphenylboroxin *N*,*N*-dimethylformamide [2-(diethylammoniooxy)-2,4,6-triphenyl-1,3,5-trioxa-4,6-dibora-2-boratacyclohexane *N*,*N*-dimethylformamide], $C_{22}H_{26}B_3NO_4{\cdot}C_3H_7NO$, contains one molecule of *N*,*N*-diethylhydroxylamine in its *N*-oxide form added to a boroxin heterocycle, with *N*,*N*-dimethylformamide solvent linked by an O$\cdots$H—N hydrogen bond to the protonated hydroxylamine moiety.

Comment

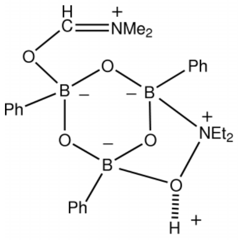
The reaction of triphenylboroxin (or 3 mol of phenylboronic acid) with *N*,*N*-diethylhydroxylamine and *N*,*N*-dimethylformamide results in the formation of a crystalline 1:1:1 adduct, the structure of which could not be established unambiguously by simple spectroscopic methods. [Similar 1:1:1 adducts are obtained from various triarylboroxins with different *N*-alkyl- and *N*,*N*-dialkylhydroxylamines, and several *N*-alkyl- and *N*,*N*-dialkylformamides and -acetamides (Kliegel & Drückler, 2002).] Since amide *O*–*B* adducts to boron compounds are generally known (Kliegel *et al.*, 1989, and references therein) and amine *N*–*B* adducts to boroxins have been reported (Yalpani & Boese, 1983, and references therein; Ferguson *et al.*, 1990), the dual addition product (I) had to be considered a likely structure. Also, an isomeric complex, (II), containing the *O*–*B*-coordinated *N*,*N*-diethylhydroxylamine in its *N*-oxide form, is suggested by already established structures of *O*–*B*-coordinated boron complexes of *N*-mono-



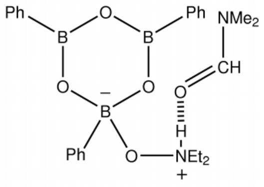
(I)



(II)



(III)



(IV)

alkylhydroxylamines (Kliegel *et al.*, 1992, 1992*a*) and *N*,*N*-dialkylhydroxylamines (Kliegel *et al.*, 1992*b*). The BOBON ring part in the alternative structure, (III), formed by twofold *N–B*/*O–B* coordination of the hydroxylamine to the boroxin ring, is reminiscent of the BOBON heterocyclic ring part in the bicyclic compounds from *N*,*N*-dialkylhydroxylamines and phenylboronic acid (Kliegel *et al.*, 1991, 2002). The X-ray analysis, however, reveals that none of these three molecular constitutions (I)–(III) is realised, but rather the structure (IV), a dimethylformamide solvate of an *N*,*N*-diethylhydroxylamine triphenylboroxin *O–B* adduct. Obviously, the dimethylformamide O atom prefers the interaction with the Brönsted acid ammonium N—H rather than with the Lewis acid boron moiety, forming an $O\cdots H{-}N^+$ hydrogen bond.

The structure of (IV) (Fig. 1) was determined initially with room-temperature data, which indicated considerable thermal motion. Anomalous displacement parameters and bond distances were noted for one *N*-ethyl substituent and, to a lesser extent, for the dimethylformamide solvent. Attempts to refine disordered models for the C21/C22 ethyl group and for the $N2Me_2$ moiety were unsuccessful. Efforts were therefore made to collect data at lower temperature. Rapid cooling to 173 K resulted in break-up of the crystal and loss of the single-crystal diffraction pattern. Slow cooling revealed loss of the diffraction pattern at about 273 K, probably corresponding to a phase change. Data were recollected at 273 K, and the results (reported here), while still not completely satisfactory (high *R* values, poor geometry in the ethyl groups, *etc.*), do establish the molecular structure unambiguously. The 294 K results are very similar, with slightly larger cell edges as expected (13.049, 14.090 and 7.932 Å, and 92.84, 97.18 and 71.88°), and displacement parameters about 30% larger than those at 273 K.

The crystal structure of (IV) contains a six-membered boroxin ring which has a shallow envelope conformation with B1 on the 'flap', caused by one tetrahedral sp^3-hybridized (B1) and two trigonal sp^2-hybridized B atoms, which force a roughly planar O1—B2—O2—B3—O3 ring part and two very short O—B bonds with considerable π-bond character: O1—B2 [1.346 (4) Å] and O3—B3 [1.343 (3) Å]. This resembles the geometry of other boroxin ring systems containing one tetracoordinated B atom (Kliegel *et al.*, 1985). The exocyclic O4—B1 bond length [1.508 (3) Å] is similar to the O—B distances (1.492–1.511 Å) of other *N*-alkylhydroxylamine *O–B* adducts to cyclic phenylboronates (Kliegel *et al.*, 1992, 1992*a*,*b*).

The dimensions of the *N*,*N*-dimethylformamide molecule correspond to those expected, with some double-bond character for the N—C(O) bond [N2—C23 = 1.330 (8) Å]; the π-bond order estimated from a bond length *versus* HMO–π-bond order plot (Häfelinger, 1970) is 0.66, and that calculated (Paolini, 1990) is 0.65. The double-bond character of the amide C═O is retained, however, for the most part [C23—O5 = 1.22 (1) Å], with a π-bond order of 0.80 (estimated) and 0.94 (calculated). The protonated *N*,*N*-diethylhydroxylamine moiety and the *N*,*N*-dimethylformamide molecule are linked by an N1—H30···O5 hydrogen bond; N···O = 2.741 (5), N—H = 0.90 (3) and H···O = 1.92 (3) Å, and N—H···O = 152 (2)°; there is also an intra-boroxine contact which might represent a bifurcation of this hydrogen-bond system; N1—H30···O3, N···O = 2.817 (3) and H···O = 2.38 (3) Å, and N—H···O = 110 (2)°.

Experimental

Preparation of *N*,*N*-diethylhydroxylamine(*O–B*)triphenylboroxin *N*,*N*-dimethylformamide, (IV). Method A: triphenylboroxin (1.56 g, 5 mmol), *N*,*N*-diethylhydroxylamine (0.45 g, 5 mmol), and *N*,*N*-dimethylformamide (0.37 g, 5 mmol) were dissolved in 15 ml of chloroform and slightly warmed. After addition of a small amount of cyclohexane, crystallization commenced. Yield: 1.63 g (69%) of colorless crystals; m.p. 385–386 K (from ether). Method B: to a solution of phenylboronic acid (1.83 g, 15 mmol) in 20 ml ether, *N*,*N*-diethylhydroxylamine (0.45 g, 5 mmol) and *N*,*N*-dimethylformamide (0.37 g, 5 mmol) were added. After 30 min at room temperature, crystallization commenced. The crystals were separated after 1 h. Yield: 1.02 g (43%) of colorless crystals which are analytically pure; m.p. 385–386 K (from ether). The mother liquor was evaporated to obtain additional material. IR (KBr): 1675 (N—C═O), 1600 cm^{-1} (phenyl–C═C). ^1H NMR (90 MHz, $CDCl_3$–TMS), δ (p.p.m.): 1.34 (*t*, *J* = 5 Hz, 2C-CH_3), 2.50 and 2.60 [*s* and *s*, $N(CH_3)_2$], 3.21 (*q*, *J* = 5 Hz, $2CH_2$–C), 7.02–8.19 (*m*, 15 aromatic H), 7.51 (*s*, O═CH), 9.29 (*s*, broad, exchangeable, NH). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3), δ (p.p.m.): 29.3 ($w_{1/2}$ = 600 Hz), 7.3 ($w_{1/2}$ = 300 Hz). Analysis calculated for $C_{25}H_{33}B_3N_2O_5$: C 63.35, H 7.02, N 5.91%; found: C 63.20, H 7.10, N 5.75%. Single crystals suitable for X-ray crystallographic anaylsis were obtained from the ether solution of the reaction product (method B) without recrystallization.

Crystal data

$C_{22}H_{26}B_3NO_4{\cdot}C_3H_7NO$
$M_r = 473.98$
Triclinic, $P\bar{1}$
$a = 13.0046$ (7) Å
$b = 14.071$ (1) Å
$c = 7.9235$ (8) Å
$\alpha = 92.79$ (2)°
$\beta = 96.95$ (2)°
$\gamma = 71.85$ (1)°
$V = 1367.5$ (2) $Å^3$

$Z = 2$
$D_x = 1.151$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5239 reflections
$\theta = 3.0$–25.0°
$\mu = 0.08$ mm^{-1}
$T = 273$ K
Prism, colorless
0.50 × 0.25 × 0.10 mm

Data collection

Rigaku/ADSC CCD diffractometer
CCD scans (both φ and ω scans)
Absorption correction: multi-scan (*d*TREK*; Molecular Structure Corporation, 1997)
$T_{min} = 0.96$, $T_{max} = 0.99$
11 054 measured reflections

4675 independent reflections
2346 reflections with $I > 3\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 25.0°$
$h = -15 \rightarrow 15$
$k = -16 \rightarrow 16$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.081$
$wR(F^2) = 0.264$
$S = 1.40$
4675 reflections
320 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + 0.0025(F_o^2)^2]$
$(\Delta/\sigma)_{max} = 0.05$
$\Delta\rho_{max} = 0.56$ e $Å^{-3}$
$\Delta\rho_{min} = -0.38$ e $Å^{-3}$

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Table 1
Selected geometric parameters (Å, °).

O1—B1	1.477 (4)	C4—C5	1.358 (7)
O1—B2	1.346 (4)	C5—C6	1.393 (6)
O2—B2	1.384 (4)	C7—C8	1.392 (4)
O2—B3	1.390 (3)	C7—C12	1.385 (4)
O3—B1	1.475 (4)	C7—B2	1.563 (4)
O3—B3	1.343 (3)	C8—C9	1.396 (4)
O4—N1	1.411 (4)	C9—C10	1.354 (5)
O4—B1	1.508 (3)	C10—C11	1.359 (5)
O5—C23	1.22 (1)	C11—C12	1.383 (4)
N1—C19	1.454 (4)	C13—C14	1.388 (4)
N1—C21	1.610 (8)	C13—C18	1.393 (4)
N2—C23	1.330 (8)	C13—B3	1.554 (4)
N2—C24	1.44 (1)	C14—C15	1.384 (4)
N2—C25	1.36 (1)	C15—C16	1.367 (5)
C1—C2	1.396 (5)	C16—C17	1.360 (5)
C1—C6	1.383 (4)	C17—C18	1.374 (4)
C1—B1	1.595 (5)	C19—C20	1.416 (7)
C2—C3	1.371 (5)	C21—C22	1.24 (1)
C3—C4	1.368 (6)		
B1—O1—B2	121.9 (2)	C7—C12—C11	121.5 (3)
B2—O2—B3	119.2 (2)	C14—C13—C18	116.7 (3)
B1—O3—B3	122.2 (2)	C14—C13—B3	122.4 (2)
N1—O4—B1	114.3 (2)	C18—C13—B3	120.9 (2)
O4—N1—C19	110.2 (3)	C13—C14—C15	120.7 (3)
O4—N1—C21	111.6 (4)	C14—C15—C16	120.7 (3)
C19—N1—C21	113.9 (4)	C15—C16—C17	119.8 (3)
C23—N2—C24	122.9 (9)	C16—C17—C18	119.8 (3)
C23—N2—C25	115.5 (9)	C13—C18—C17	122.2 (3)
C24—N2—C25	121.4 (7)	N1—C19—C20	111.3 (4)
C2—C1—C6	115.3 (3)	N1—C21—C22	112.8 (9)
C2—C1—B1	122.7 (3)	O5—C23—N2	127.8 (9)
C6—C1—B1	121.9 (3)	O1—B1—O3	109.9 (2)
C1—C2—C3	123.0 (4)	O1—B1—O4	108.3 (2)
C2—C3—C4	119.6 (4)	O1—B1—C1	111.8 (2)
C3—C4—C5	119.8 (4)	O3—B1—O4	108.5 (2)
C4—C5—C6	120.1 (4)	O3—B1—C1	112.4 (3)
C1—C6—C5	122.1 (4)	O4—B1—C1	105.6 (2)
C8—C7—C12	116.9 (3)	O1—B2—O2	120.9 (2)
C8—C7—B2	120.5 (3)	O1—B2—C7	119.9 (3)
C12—C7—B2	122.5 (3)	O2—B2—C7	119.2 (2)
C7—C8—C9	121.1 (3)	O2—B3—O3	120.4 (3)
C8—C9—C10	119.9 (3)	O2—B3—C13	119.2 (2)
C9—C10—C11	120.4 (3)	O3—B3—C13	120.4 (2)
C10—C11—C12	120.2 (3)		

Atom H30 (bonded to N1) was refined and all other H atoms were fixed.

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: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *TEXSAN*; molecular graphics: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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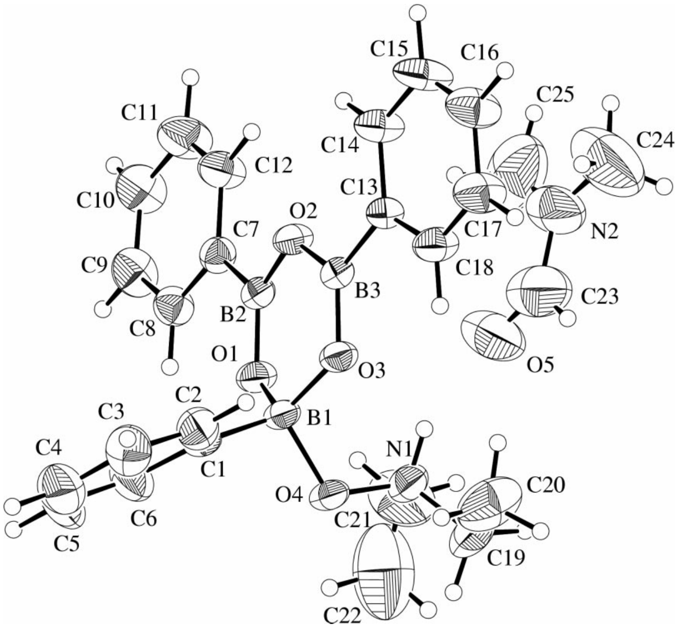

Figure 1
View of the title structure, with ellipsoids at the 30% probability level.

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