

An OBONC five-membered heterocycle

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Key indicators

Single-crystal X-ray study
T = 294 K
Mean $\sigma(\text{C}-\text{C})$ = 0.004 Å
H-atom completeness 95%
Disorder in solvent or counterion
R factor = 0.040
wR factor = 0.038
Data-to-parameter ratio = 10.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.4-[(2-Hydroxy-1-naphthyl)methyl]-2,2,5-triphenyl-1,3-dioxo-4-azonia-2-boratacyclopent-4-ene ethanol solvate, $\text{C}_{30}\text{H}_{24}\text{BNO}_3 \cdot \text{C}_2\text{H}_6\text{O}$, contains a five-membered O—B—O—N=C ring, which is nearly planar (slight *B*-envelope).

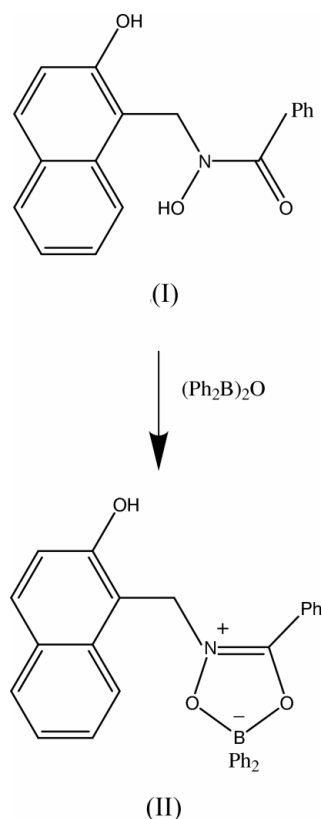
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Comment

The synthesis of the hydroxamic acid (I) by monoacylation of the corresponding hydroxylaminomethylnaphthol (Runti & Collino, 1959; Möhrle *et al.*, 1977; Möhrle & Lappenberg, 1978) has not been reported so far, but is now accomplished by application of 2,4,6-trimethylpyridine (2,4,6-collidine) as a sterically hindered base, a method which has been effectively used for monoacylation of mixed diols (Ishihara *et al.*, 1993). Proof of the *N*-monoacylation of (I) with benzoyl chloride could be furnished by diphenylboron chelate formation of the bidentate hydroxamate ligand moiety. The X-ray analysis establishes the postulated chelate structure (II) and excludes other possible chelate rings involving the phenolic hydroxyl group or formed by one of the possible isomeric *O*-benzoyl derivatives of (I).



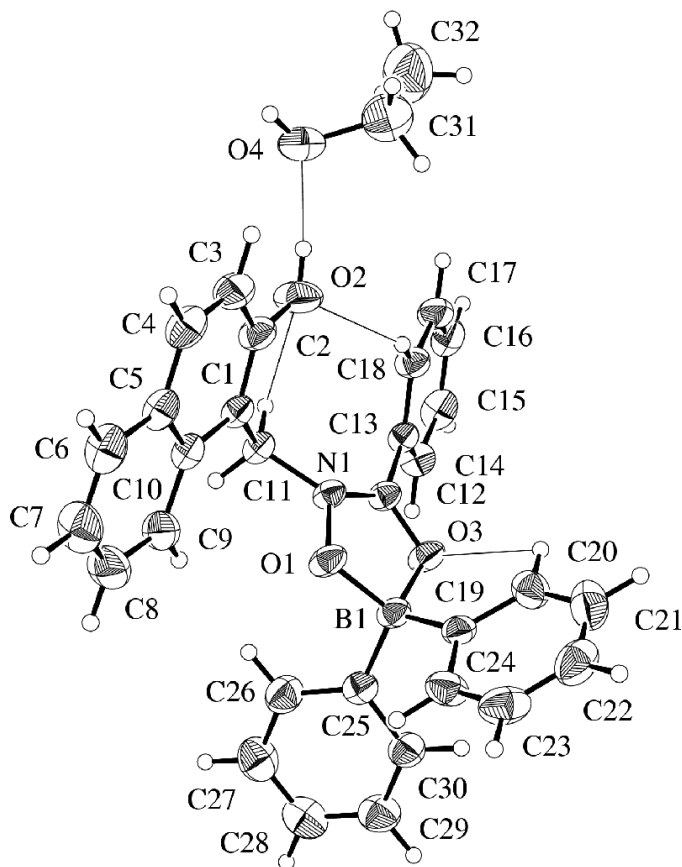


Figure 1
View of the structure of (II)·EtOH with 50% probability ellipsoids.

The molecule of (II)·EtOH contains a five-membered O—B—O—N=C ring, which is nearly planar [slight *B*-envelope, with dihedral angles with magnitudes in the range 0.2 to 3.5 (2)°], similar to the geometry in related substances (Rettig *et al.*, 1977, 1978; Kliegel *et al.*, 1983, 1990, 1996; Kliegel, Schumacher *et al.*, 1991; Kliegel, Tajerbashi *et al.*, 1991). The short C—N bond [1.301 (2) Å] indicates that the most important canonical structure is that shown in the chemical diagram, with a C=N double bond, with perhaps a minor contribution from the resonance structure with a C=O double bond [C—O = 1.294 (2) Å]. The molecule is linked to the disordered ethanol solvent by an O2—H1···O4 (major component) hydrogen bond, O···O = 2.632 (2), H···O = 1.82 (3) Å and O—H···O = 164 (4)°; the ethanol O4—H group does not appear to act as a hydrogen-bond donor. There are also three possibly significant intramolecular C—H···O interactions (Fig. 1), C···O = 2.73–3.10 and H···O = 2.30–2.51 Å.

Experimental

1-[(*N*-Benzoyl-*N*-hydroxyamino)methyl]-2-naphthol (I): 1-[(*N*-hydroxyamino)methyl]-2-naphthol hydrochloride (Möhrle *et al.*, 1977) (2.26 g, 10 mmol) was suspended in 50 ml of dichloromethane. After addition of 2,4,6-trimethylpyridine (3.64 g, 30 mmol), benzoyl

chloride (1.41 g, 10 mmol) was added dropwise with stirring. After 3 h at room temperature, the clear solution was poured into 60 ml of 1 M HCl. At the interface of the solution phases, crystals were formed, which were separated and recrystallized from ethanol/H₂O. Yield: 1.70 g (58%) of colorless needles, m.p. 425 K. IR (KBr): 3305–3052 (O—H), 1599 cm⁻¹ (C=O/C=C). ¹H NMR (90 MHz, DMSO-*d*₆-TMS), δ (p.p.m.): 5.36 (s, CH₂), 7.20–7.93 (*m*, 10 aromatic H), 8.16 (*d*, *J* = 8 Hz, 1 aromatic H), 9.96 (*s*, broad, exchangeable, 2 OH). Analysis calculated for C₁₈H₁₅NO₃: C 73.71, H 5.15, N 4.78%; found C 73.73, H 5.13, N 4.69%. The compound gives a violet color reaction with FeCl₃, indicating the hydroxamic acid function.

4-[(2-Hydroxy-1-naphthyl)methyl]-2,2,5-triphenyl-1,3-dioxo-4-azonia-2-boratacyclopenten-4-ene, (II), ethanol solvate: (I) (0.29 g, 1 mmol) and oxybis(diphenylborane) (0.17 g, 0.5 mmol) were dissolved in 5 ml of ethanol. Cooling yielded 0.37 g (73%) of colorless crystals, m.p. 398 K (from ethanol). IR (KBr): 3528 (O—H), 1632 cm⁻¹ (C=N). ¹H NMR (90 MHz, CDCl₃-TMS), δ (p.p.m.): 1.20 (*t*, *J* = 7 Hz, CH₃), 1.50 (*s*, broad, exchangeable, OH), 3.65 (*q*, *J* = 7 Hz, OCH₂), 5.52 (*s*, NCH₂), 7.00–7.86 (*m*, 21 aromatic H). ¹¹B NMR (64 MHz, CDCl₃-Et₂OBF₃), δ (p.p.m.): 14.1 (*w*_{1/2} = 428 Hz), 45.3 (*w*_{1/2} = 214 Hz): ratio of peak areas 20:1 [the main peak at 14.1 p.p.m. indicates the tetracoordinate boron nucleus in (II), whereas the small signal at 45.3 p.p.m. points to a trigonal Ph₂BO moiety, probably arising from partial solvolysis (Kliegel *et al.*, 2000, and references therein)]. EI mass spectrum (70 eV, 498 K), *m/z*: 457 (63%, *M*⁺ - C₂H₅OH), 380 (22%, *M*⁺ - C₂H₅OH - C₆H₅), 312 (100%, [PhBO]₃). Analysis calculated for C₃₀H₂₄BNO₃·C₂H₅OH: C 76.35, H 6.01, B 2.15, N 2.78%; found: C 75.98, H 5.93, B 2.13, N 2.71%. The compound gives a blue color reaction with diphenylcarbazone in methanolic solution, indicating the presence of a diphenylboron moiety (Neu, 1960; Friese & Umland, 1978). Crystals suitable for X-ray crystallography were obtained by slow crystallization from ethanol.

Crystal data

C₃₀H₂₄BNO₃·C₂H₆O
*M*_r = 503.40
 Triclinic, *P* $\bar{1}$
a = 11.5792 (6) Å
b = 13.0972 (8) Å
c = 9.0779 (5) Å
 α = 96.780 (5)°
 β = 93.245 (4)°
 γ = 82.833 (4)°
V = 1355.18 (13) Å³

Z = 2
*D*_x = 1.234 Mg m⁻³
 Cu K α radiation
 Cell parameters from 25 reflections
 θ = 43.8–54.4°
 μ = 0.64 mm⁻¹
T = 294 K
 Prism, colorless
 0.35 × 0.35 × 0.25 mm

Data collection

Rigaku AFC-6S diffractometer
 ω -2 θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
*T*_{min} = 0.73, *T*_{max} = 0.85
 5819 measured reflections
 5525 independent reflections
 3873 reflections with *I* > 3 σ (*I*)

*R*_{int} = 0.014
 θ _{max} = 77.5°
h = 0 → 14
k = -16 → 16
l = -11 → 11
 3 standard reflections every 200 reflections
 intensity decay: 5.7%

Refinement

Refinement on *F*
R = 0.040
wR = 0.038
S = 0.97
 3873 reflections
 374 parameters
 H atoms treated by a mixture of independent and constrained refinement

w = 1/ σ^2 (*F*_o)
 $(\Delta/\sigma)_{\text{max}}$ = 0.02
 $\Delta\rho_{\text{max}}$ = 0.12 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.14 e Å⁻³
 Extinction correction: Zachariasen (1967)
 Extinction coefficient: 3.12 (3) × 10⁻⁵

Table 1
Selected geometric parameters (Å, °).

O1–N1	1.384 (2)	C13–C14	1.385 (2)
O1–B1	1.537 (2)	C13–C18	1.385 (3)
O2–C2	1.357 (2)	C14–C15	1.379 (3)
O3–C12	1.294 (2)	C15–C16	1.372 (3)
O3–B1	1.564 (2)	C16–C17	1.367 (3)
N1–C11	1.468 (2)	C17–C18	1.381 (3)
N1–C12	1.301 (2)	C19–C20	1.389 (3)
C1–C2	1.374 (3)	C19–C24	1.392 (3)
C1–C10	1.428 (3)	C19–B1	1.590 (3)
C1–C11	1.502 (2)	C20–C21	1.388 (4)
C2–C3	1.407 (3)	C21–C22	1.359 (4)
C3–C4	1.346 (3)	C22–C23	1.368 (4)
C4–C5	1.417 (3)	C23–C24	1.391 (3)
C5–C6	1.411 (3)	C25–C26	1.395 (3)
C5–C10	1.423 (3)	C25–C30	1.386 (3)
C6–C7	1.348 (4)	C25–B1	1.602 (3)
C7–C8	1.392 (4)	C26–C27	1.391 (3)
C8–C9	1.365 (3)	C27–C28	1.360 (4)
C9–C10	1.405 (3)	C28–C29	1.365 (4)
C12–C13	1.468 (2)	C29–C30	1.387 (3)
N1–O1–B1	106.71 (12)	C14–C13–C18	119.4 (2)
C12–O3–B1	108.85 (13)	C13–C14–C15	120.5 (2)
O1–N1–C11	115.01 (13)	C14–C15–C16	119.6 (2)
O1–N1–C12	112.05 (13)	C15–C16–C17	120.3 (2)
C11–N1–C12	130.78 (15)	C16–C17–C18	120.8 (2)
C2–C1–C10	118.8 (2)	C13–C18–C17	119.4 (2)
C2–C1–C11	118.5 (2)	C20–C19–C24	115.8 (2)
C10–C1–C11	122.3 (2)	C20–C19–B1	123.7 (2)
O2–C2–C1	118.1 (2)	C24–C19–B1	120.4 (2)
O2–C2–C3	120.3 (2)	C19–C20–C21	122.4 (2)
C1–C2–C3	121.6 (2)	C20–C21–C22	120.0 (3)
C2–C3–C4	120.1 (2)	C21–C22–C23	119.8 (3)
C3–C4–C5	121.4 (2)	C22–C23–C24	120.0 (2)
C4–C5–C6	121.3 (2)	C19–C24–C23	121.9 (2)
C4–C5–C10	118.6 (2)	C26–C25–C30	115.9 (2)
C6–C5–C10	120.0 (2)	C26–C25–B1	123.0 (2)
C5–C6–C7	121.0 (2)	C30–C25–B1	121.1 (2)
C6–C7–C8	119.5 (2)	C25–C26–C27	121.6 (2)
C7–C8–C9	121.4 (2)	C26–C27–C28	120.6 (2)
C8–C9–C10	121.1 (2)	C27–C28–C29	119.3 (2)
C1–C10–C5	119.5 (2)	C28–C29–C30	120.3 (2)
C1–C10–C9	123.5 (2)	C25–C30–C29	122.3 (2)
C5–C10–C9	117.0 (2)	O1–B1–O3	98.35 (13)
N1–C11–C1	115.26 (15)	O1–B1–C19	111.3 (2)
O3–C12–N1	113.91 (15)	O1–B1–C25	111.5 (2)
O3–C12–C13	119.00 (15)	O3–B1–C19	109.6 (2)
N1–C12–C13	127.1 (2)	O3–B1–C25	110.2 (2)
C12–C13–C14	118.5 (2)	C19–B1–C25	114.7 (2)
C12–C13–C18	121.9 (2)		

The ethanol molecule is disordered; the O and β -C atoms were modelled as twofold disordered and the α -C atom as threefold disordered. The low-occupancy ethanol-C atoms (C31a and C31b)

and the naphthyl hydroxy-H atom (H1) were refined isotropically; other non-H atoms were refined anisotropically and the other H atoms were fixed in idealized sites (minor component H atoms were not included).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1995); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992–1997); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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