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## Two forms of (naphthalen-1-yl)boronic acid

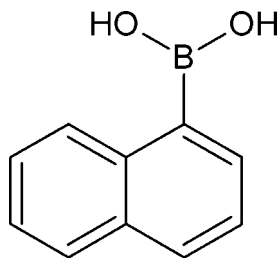
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Two polymorphs of the title compound,  $C_{10}H_9BO_2$ , were prepared by recrystallization from different solvents at room temperature. Both forms demonstrate nearly identical molecular structures with all naphthalene group atoms located in one plane and all boronic acid atoms in another: the dihedral angles between these planes are  $39.88(5)$  and  $40.15(5)^\circ$  for the two asymmetric molecules of the orthorhombic form and  $40.60(3)^\circ$  for the single asymmetric molecule in the monoclinic form. In each extended structure, molecules form dimers, connected *via* two  $O-H\cdots O$  hydrogen bonds. The dimers are connected by further  $O-H\cdots O$  hydrogen bonds, forming layered networks in the (001) plane and the (100) plane in the orthorhombic and monoclinic forms, respectively. The resulting layers are practically identical in both forms. However, these layers are shifted along the [010] axis in the two forms, resulting in a slightly more effective packing for monoclinic structure (packing index = 0.692) compared to the orthorhombic form (0.688).

### 1. Chemical context

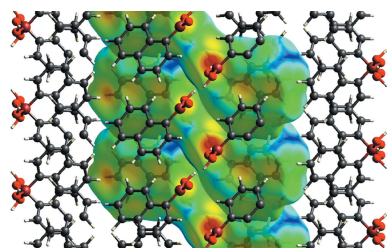
Naphthalene boronic acids ( $\alpha$ - and  $\beta$ -) were first synthesized by Michaelis (1894) along with other arylboronic acid by reaction of diarylmercury with boron trichloride with subsequent hydrolysis. A more practical procedure (König & Scharrnbeck, 1930) included the reaction of naphthylmagnesium bromide with tri-(isobutyl)borate. In both cases, the existence of two different forms of title compound was suggested, one forming plate-like crystals and another one forming needles.



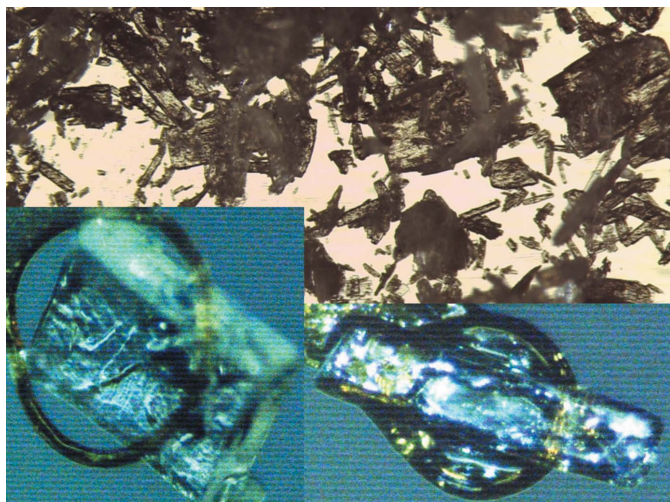
These compounds were originally investigated because of their potential in biochemistry (König & Scharrnbeck, 1930; Gao *et al.*, 2003; Hall, 2011) and later as reactants in the Suzuki reaction (Hall, 2011). 1-Naphthalene boronic acid is now commercially available and was the source for this study.

### 2. Synthesis and crystallization

A sample of 1-naphthalene boronic acid was purchased from Aldrich. Its FTIR spectrum coincided with that reported by



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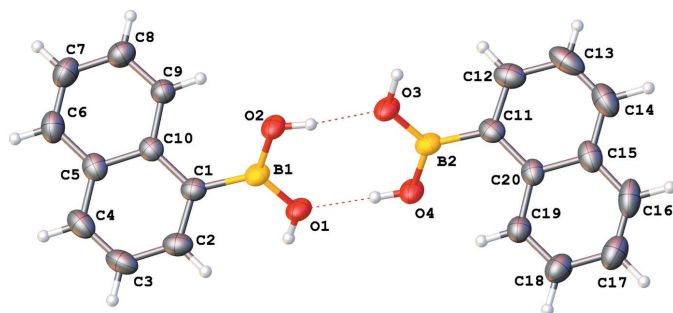


**Figure 1**  
Crystals of the different polymorphs in starting material (view area  $1 \times 2$  mm). Plate (left): orthorhombic. Needle (right): monoclinic.

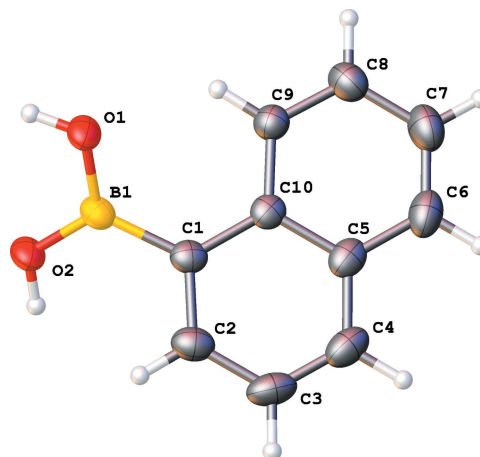
the manufacturer. Under the microscope, a number of relatively large (up to 0.5 mm) crystals were visible, some of them suitable for single crystal X-ray data collection (Fig. 1). Experimental data revealed an orthorhombic structure for the plate-shaped crystals. Recrystallization from hot water yielded very thin plates. This polycrystalline sample showed a powder diffractogram that was slightly different from the raw material and the calculated pattern of the orthorhombic form. Attempts at slow crystallization from ethanol and toluene solution resulted in larger and better shaped crystals, some of which were orthorhombic plates and other were visibly non-orthorhombic needles (Fig. 1). Several such crystals were tested: here we report the best data for both the orthorhombic and monoclinic forms.

### 3. Structural commentary

The molecules of naphthalene boronic acid in both crystal structures (Figs. 2 and 3) have the usual bond distances and angles. There is one molecule in the asymmetric unit of the monoclinic structure. In the non-centrosymmetric orthorhombic structure, the two molecules in the asymmetric unit



**Figure 2**  
Numbering scheme of the title compound with 50% probability displacement ellipsoids (orthorhombic polymorph).

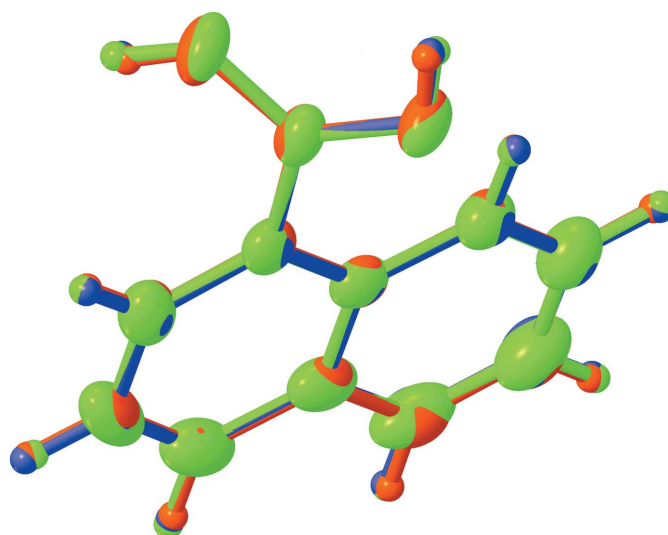


**Figure 3**  
Numbering scheme of the title compound with 50% probability displacement ellipsoids (monoclinic polymorph).

have very similar structures: they almost coincide (after inversion for one of them) with each other as well, as with the unique molecule from the monoclinic structure (Fig. 4).

In the monoclinic structure, the mean plane of the naphthalene fragment is tilted from plane of boron and two oxygen atoms with an angle of  $40.60(3)^\circ$ . The boron atom deviates by  $0.0449(16)$  Å from the mean plane of the naphthalene ring system.

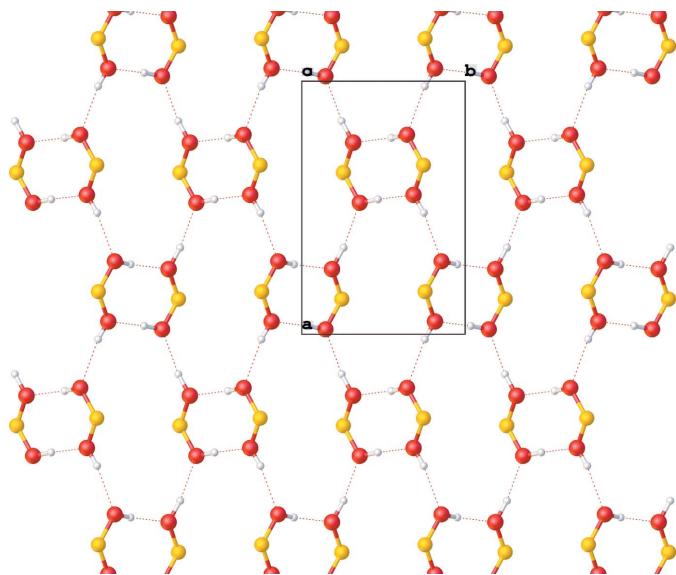
In the orthorhombic structure, there are two independent molecules. When superimposed, the angle between the mean planes of the naphthalene ring systems is only  $0.88(6)^\circ$ . Two boron atoms and four oxygen atoms are located at another plane together with adjacent hydrogen atoms. These planes are tilted to a similar extent to the monoclinic structure, with dihedral angles to the mean plane of each naphthalene group of  $39.88(5)$  and  $40.15(5)^\circ$  [mean tilt =  $39.83(5)^\circ$ ]. These numbers differ from those for the monoclinic form by less than  $1^\circ$ .



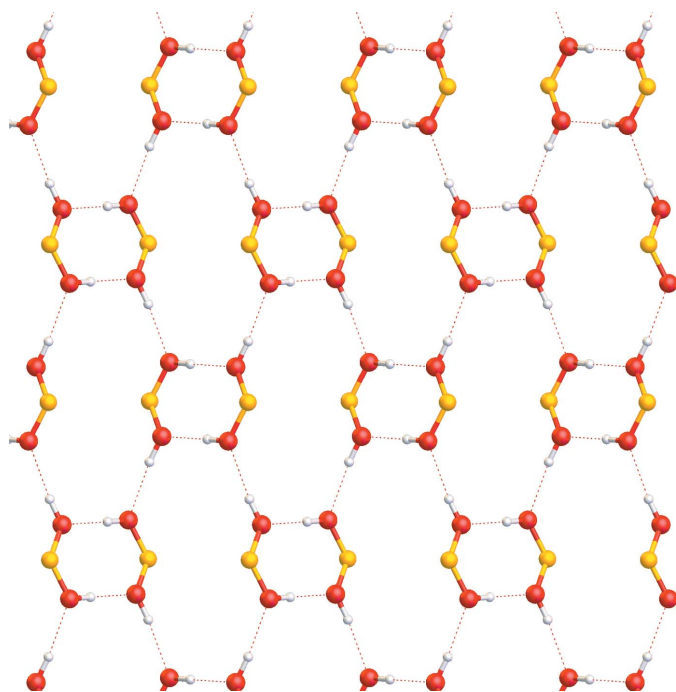
**Figure 4**  
Overlay of the two polymorph molecules (red & green – orthorhombic, blue – monoclinic) with appropriate inversion.

#### 4. Supramolecular features

In both forms, pairs of molecules are connected through a pair of O—H...O hydrogen bonds (Tables 1 and 2) into dimers. There is also an intramolecular C—H...O contact. The dimers are further connected *via* O—H...O hydrogen bonds, forming a layered network in plane (001) and in plane (100) in the orthorhombic and monoclinic forms, respectively (Figs. 5 and 6). The resulting layers are practically identical in both forms (compare Figs. 7 and 8, Figs. 9 and 10).



**Figure 5**  
Layered network of hydrogen bonds in the orthorhombic form. View is along the [001] axis, only boronic acid groups are shown.



**Figure 6**  
Layered network of hydrogen bonds in the monoclinic form. View is along the [001] axis, only boronic acid groups are shown.

**Table 1**  
Hydrogen-bond geometry (Å, °) for the orthorhombic polymorph.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1...O2 <sup>i</sup>	0.81 (4)	1.98 (4)	2.766 (2)	165 (4)
O2—H2...O3	0.90 (3)	1.86 (3)	2.750 (3)	171 (3)
O3—H3...O4 <sup>ii</sup>	0.96 (4)	1.82 (4)	2.761 (2)	167 (3)
O4—H4...O1	0.89 (4)	1.85 (4)	2.739 (3)	175 (3)
C9—H9...O2	0.95	2.45	3.092 (3)	124
C19—H19...O4	0.95	2.42	3.063 (3)	125

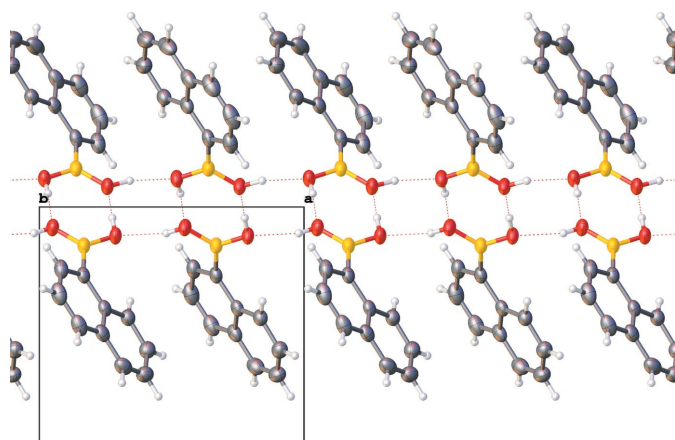
Symmetry codes: (i)  $x + \frac{1}{2}, -y + \frac{3}{2}, z$ ; (ii)  $x - \frac{1}{2}, -y + \frac{1}{2}, z$ .

**Table 2**  
Hydrogen-bond geometry (Å, °) for the monoclinic polymorph.

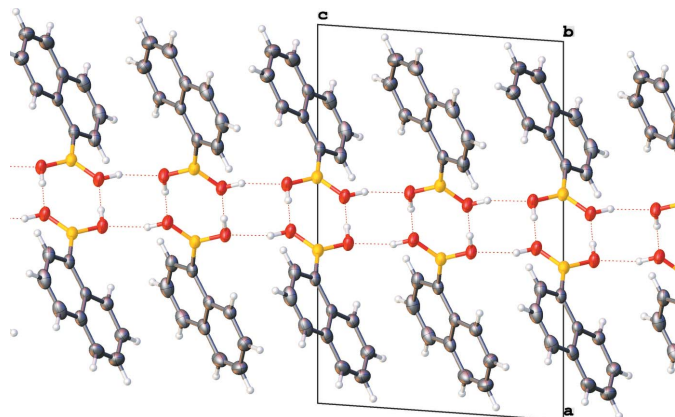
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1...O2 <sup>i</sup>	0.897 (18)	1.846 (18)	2.7411 (13)	176.3 (17)
O2—H2...O1 <sup>ii</sup>	0.888 (19)	1.891 (19)	2.7607 (11)	166.0 (17)
C9—H9...O1	0.98 (1)	2.43 (1)	3.0911 (15)	124 (1)

Symmetry codes: (i)  $-x + 1, -y, -z + 1$ ; (ii)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ .

There are no directional intermolecular interactions between adjacent layers and, therefore, no strong interactions between them. However, these layers are shifted with respect to the [010] axis (compare Figs. 9 and 10), resulting in a slightly



**Figure 7**  
Packing of the orthorhombic form. View is along the [010] axis.



**Figure 8**  
Packing of the monoclinic form. View is along the [010] axis.



**Table 3**  
Experimental details.

	Orthorhombic polymorph	Monoclinic polymorph
Crystal data		
Chemical formula	$C_{10}H_9BO_2$	$C_{10}H_9BO_2$
$M_r$	171.98	171.98
Crystal system, space group	Orthorhombic, $Pna2_1$	Monoclinic, $P2_1/c$
Temperature (K)	173	173
$a, b, c$ (Å)	9.6655 (4), 6.2286 (3), 29.1778 (13)	14.8469 (11), 6.1023 (4), 9.6797 (7)
$\alpha, \beta, \gamma$ (°)	90, 90, 90	90, 93.978 (3), 90
$V$ (Å <sup>3</sup> )	1756.58 (14)	874.87 (11)
$Z$	8	4
Radiation type	Cu $K\alpha$	Cu $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.71	0.71
Crystal size (mm)	0.59 × 0.44 × 0.14	0.66 × 0.18 × 0.16
Data collection		
Diffractometer	Bruker PHOTON-100 CMOS	Bruker PHOTON-100 CMOS
Absorption correction	Multi-scan (SADABS; Bruker, 2015)	Multi-scan (SADABS; Bruker, 2015)
$T_{min}, T_{max}$	0.671, 0.972	0.759, 0.951
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	52115, 3764, 3447	25253, 1857, 1576
$R_{int}$	0.040	0.038
$(\sin \theta/\lambda)_{max}$ (Å <sup>-1</sup> )	0.636	0.633
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.035, 0.094, 1.02	0.035, 0.091, 1.04
No. of reflections	3764	1857
No. of parameters	253	133
No. of restraints	1	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.22, -0.15	0.23, -0.15
Absolute structure	Flack $x$ determined using 1548 quotients [[ $I^+$ )-( $I^-$ )]/[( $I^+$ )+( $I^-$ )] (Parsons et al., 2013)	-
Absolute structure parameter	0.07 (6)	-

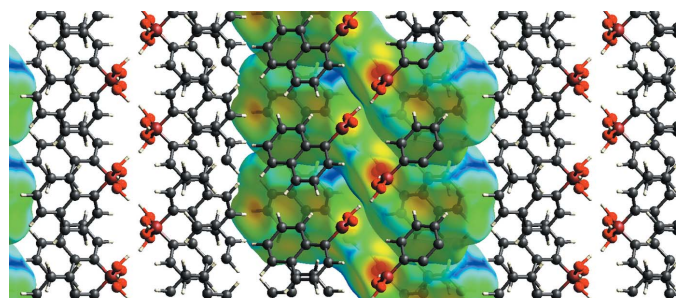
Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *OLEX2* (Dolomanov *et al.*, 2009), *CrystalExplorer* (Spackman & Jayatilaka, 2009) and *PLATON* (Spek, 2009).

more effective packing of the monoclinic structure (packing index = 0.692) (Kitaigorodskii, 1961; Spek, 2009) compared to the orthorhombic structure (packing index = 0.688). This layer-shift is the only visible difference between the two forms.

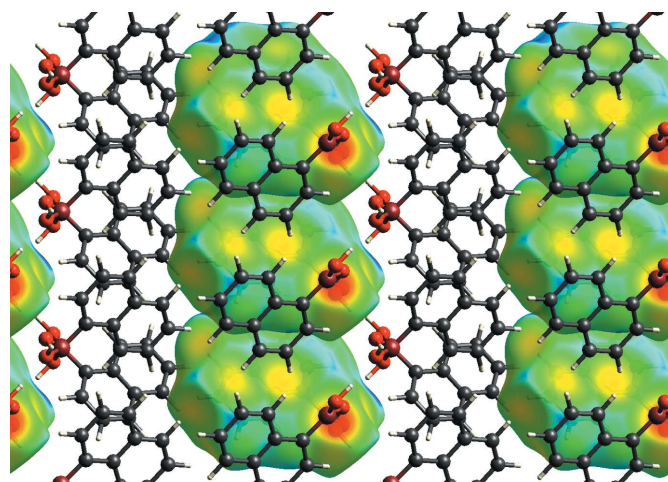
### 5. Database survey

There are no naphthalene boronic acid structures deposited in the Cambridge Structural Database (CSD Version 5.37; Groom *et al.*, 2016). The simplest arylboronic acid, phenylboronic acid, crystallizes in a non-centrosymmetric ortho-

rhombic space group (refcodes PHBORA and PHBORA01). Instead of a layered network, its molecules form an infinite chain in the crystal (Cyránski *et al.*, 2008; Rettig & Trotter, 1977).



**Figure 9**  
Packing diagram of the orthorhombic form. View is along the [100] axis. Hirshfeld surface shown for some molecules.



**Figure 10**  
Packing diagram of the monoclinic form. View is along the [001] axis. Hirshfeld surface shown for some molecules.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All hydrogen atoms of hydroxyl groups were refined in an isotropic approximation. Aromatic hydrogen atoms were refined with riding coordinates and  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{iso}}(\text{C})$ .

## Acknowledgements

Financial support from the State University of New York for acquisition and maintenance of the X-ray diffractometer is gratefully acknowledged.

## References

- Bruker (2013). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2015). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cyrański, M. K., Jezierska, A., Klimentowska, P., Panek, J. J. & Sporzyński, A. (2008). *J. Phys. Org. Chem.* **21**, 472–482.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Gao, X., Zhang, Y. & Wang, B. (2003). *Org. Lett.* **5**, 4615–4618.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Hall, D. G. (2011). Editor. *Boronic Acids: Preparation and Applications in Organic Synthesis, Medicine and Materials*. New York: Wiley–VCH.
- Kitaigorodskii, A. I. (1961). In *Organic Chemical Crystallography*. New York: Consultants Bureau.
- König, W. & Scharrnbeck, W. (1930). *J. Prakt. Chem.* **128**, 153–170.
- Michaelis, A. (1894). *Ber. Dtsch. Chem. Ges.* **27**, 244–262.
- Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* **B69**, 249–259.
- Rettig, S. J. & Trotter, J. (1977). *Can. J. Chem.* **55**, 3071–3075.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.

## supporting information

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## Two forms of (naphthalen-1-yl)boronic acid

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## Computing details

For both compounds, data collection: *APEX2* (Bruker, 2013); cell refinement: *S SAINT* (Bruker, 2013); data reduction: *S SAINT* (Bruker, 2013); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b). Molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009) and *CrystalExplorer* (Spackman & Jayatilaka, 2009) for (1); *OLEX2* (Dolomanov *et al.*, 2009) for (2). Software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009) and *PLATON* (Spek, 2009) for (1); *OLEX2* (Dolomanov *et al.*, 2009) for (2).

## (1) (Naphthalen-1-yl)boronic acid

## Crystal data

$C_{10}H_9BO_2$

$M_r = 171.98$

Orthorhombic, *Pna2<sub>1</sub>*

$a = 9.6655$  (4) Å

$b = 6.2286$  (3) Å

$c = 29.1778$  (13) Å

$V = 1756.58$  (14) Å<sup>3</sup>

$Z = 8$

$F(000) = 720$

$D_x = 1.301$  Mg m<sup>-3</sup>

Cu  $K\alpha$  radiation,  $\lambda = 1.54178$  Å

Cell parameters from 9127 reflections

$\theta = 3.0\text{--}78.2^\circ$

$\mu = 0.71$  mm<sup>-1</sup>

$T = 173$  K

Plate, colourless

$0.59 \times 0.44 \times 0.14$  mm

## Data collection

Bruker PHOTON-100 CMOS  
diffractometer

Radiation source: sealedtube

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2015)

$T_{\min} = 0.671$ ,  $T_{\max} = 0.972$

52115 measured reflections

3764 independent reflections

3447 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.040$

$\theta_{\max} = 78.7^\circ$ ,  $\theta_{\min} = 3.0^\circ$

$h = -12 \rightarrow 12$

$k = -7 \rightarrow 7$

$l = -36 \rightarrow 36$

## Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.094$

$S = 1.02$

3764 reflections

253 parameters

1 restraint

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0563P)^2 + 0.2507P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.22$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.15$  e Å<sup>-3</sup>

Absolute structure: Flack  $x$  determined using  
 1548 quotients  $[(F^+)-(F^-)]/[(F^+)+(F^-)]$  (Parsons et  
 al., 2013)  
 Absolute structure parameter: 0.07 (6)

### Special details

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
O3	0.24283 (16)	0.3150 (3)	0.47433 (6)	0.0415 (4)
H3	0.158 (4)	0.244 (6)	0.4672 (11)	0.062*
O4	0.48065 (16)	0.3548 (3)	0.46451 (6)	0.0398 (4)
H4	0.467 (4)	0.466 (6)	0.4831 (12)	0.060*
C11	0.3612 (2)	0.0750 (4)	0.41412 (9)	0.0367 (5)
C12	0.2783 (3)	-0.1033 (4)	0.42012 (11)	0.0472 (6)
H12	0.222 (2)	-0.1146 (6)	0.4475 (10)	0.057*
C13	0.2731 (3)	-0.2707 (5)	0.38704 (13)	0.0581 (8)
H13	0.220 (2)	-0.383 (5)	0.3918 (2)	0.070*
C14	0.3497 (3)	-0.2587 (5)	0.34829 (12)	0.0549 (8)
H14	0.3444 (4)	-0.387 (4)	0.3237 (8)	0.066*
C15	0.4357 (3)	-0.0818 (4)	0.33976 (10)	0.0451 (6)
C16	0.5152 (3)	-0.0637 (6)	0.29893 (10)	0.0566 (8)
H16	0.5105 (4)	-0.182 (4)	0.2757 (9)	0.068*
C17	0.5970 (3)	0.1086 (6)	0.29054 (10)	0.0555 (8)
H17	0.653 (2)	0.1169 (6)	0.2611 (11)	0.067*
C18	0.6038 (3)	0.2752 (5)	0.32268 (9)	0.0485 (7)
H18	0.666 (2)	0.407 (5)	0.3163 (2)	0.058*
C19	0.5287 (2)	0.2649 (4)	0.36254 (8)	0.0389 (5)
H19	0.5350	0.3799	0.3838	0.047*
C20	0.4422 (2)	0.0882 (4)	0.37291 (8)	0.0358 (5)
B2	0.3611 (3)	0.2548 (5)	0.45182 (10)	0.0352 (6)
O1	0.44946 (17)	0.6845 (3)	0.52575 (6)	0.0410 (4)
H1	0.520 (4)	0.747 (6)	0.5329 (13)	0.061*
O2	0.21178 (16)	0.6447 (3)	0.53618 (6)	0.0393 (4)
H2	0.224 (4)	0.548 (5)	0.5138 (12)	0.059*
C1	0.3326 (2)	0.9282 (4)	0.58539 (8)	0.0337 (5)
C2	0.4169 (2)	1.1032 (4)	0.57782 (10)	0.0417 (6)
H2A	0.4712	1.1076	0.5507	0.050*
C3	0.4253 (3)	1.2758 (4)	0.60894 (11)	0.0484 (7)
H3A	0.4842	1.3941	0.6025	0.058*
C4	0.3491 (3)	1.2734 (4)	0.64824 (11)	0.0460 (6)
H4A	0.3552	1.3901	0.6691	0.055*
C5	0.2613 (2)	1.0981 (4)	0.65810 (9)	0.0386 (5)
C6	0.1826 (3)	1.0920 (5)	0.69941 (9)	0.0462 (6)

H6	0.1876	1.2092	0.7202	0.055*
C7	0.1010 (3)	0.9220 (5)	0.70950 (9)	0.0482 (6)
H7	0.0499	0.9201	0.7373	0.058*
C8	0.0916 (3)	0.7484 (5)	0.67893 (9)	0.0437 (6)
H8	0.0343	0.6294	0.6862	0.052*
C9	0.1647 (2)	0.7492 (4)	0.63858 (8)	0.0361 (5)
H9	0.1567	0.6308	0.6182	0.043*
C10	0.2520 (2)	0.9235 (4)	0.62674 (8)	0.0328 (5)
B1	0.3317 (3)	0.7451 (5)	0.54832 (9)	0.0347 (5)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O3	0.0220 (7)	0.0608 (11)	0.0418 (9)	−0.0033 (8)	0.0009 (6)	−0.0085 (8)
O4	0.0227 (7)	0.0537 (10)	0.0430 (10)	−0.0004 (8)	−0.0010 (6)	−0.0104 (8)
C11	0.0239 (10)	0.0383 (12)	0.0479 (13)	0.0028 (9)	−0.0073 (9)	−0.0001 (11)
C12	0.0329 (11)	0.0453 (14)	0.0633 (17)	−0.0010 (11)	−0.0080 (12)	0.0086 (12)
C13	0.0457 (15)	0.0360 (13)	0.093 (3)	−0.0063 (12)	−0.0258 (16)	0.0035 (14)
C14	0.0487 (16)	0.0426 (14)	0.073 (2)	0.0077 (12)	−0.0200 (14)	−0.0160 (14)
C15	0.0370 (12)	0.0442 (14)	0.0541 (16)	0.0115 (10)	−0.0158 (11)	−0.0128 (12)
C16	0.0511 (16)	0.0719 (19)	0.0469 (16)	0.0244 (15)	−0.0136 (12)	−0.0248 (15)
C17	0.0450 (15)	0.079 (2)	0.0421 (15)	0.0145 (15)	−0.0012 (11)	−0.0093 (14)
C18	0.0381 (14)	0.0660 (18)	0.0414 (14)	0.0042 (13)	−0.0002 (10)	−0.0029 (12)
C19	0.0309 (12)	0.0461 (13)	0.0396 (12)	0.0038 (10)	−0.0037 (10)	−0.0061 (10)
C20	0.0270 (9)	0.0387 (12)	0.0417 (13)	0.0079 (9)	−0.0074 (9)	−0.0064 (10)
B2	0.0231 (12)	0.0454 (14)	0.0371 (13)	0.0006 (11)	−0.0011 (10)	0.0038 (11)
O1	0.0234 (7)	0.0568 (11)	0.0427 (10)	−0.0046 (8)	0.0025 (6)	−0.0069 (8)
O2	0.0212 (7)	0.0542 (10)	0.0424 (9)	0.0002 (7)	0.0011 (6)	−0.0093 (8)
C1	0.0242 (9)	0.0371 (11)	0.0399 (12)	0.0030 (9)	−0.0045 (8)	0.0034 (10)
C2	0.0284 (11)	0.0433 (13)	0.0533 (15)	−0.0009 (10)	−0.0037 (10)	0.0086 (11)
C3	0.0369 (14)	0.0342 (12)	0.0741 (19)	−0.0046 (11)	−0.0109 (13)	0.0058 (12)
C4	0.0382 (14)	0.0351 (12)	0.0647 (18)	0.0031 (11)	−0.0148 (11)	−0.0056 (12)
C5	0.0313 (11)	0.0391 (12)	0.0453 (14)	0.0080 (10)	−0.0107 (9)	−0.0030 (10)
C6	0.0454 (14)	0.0501 (14)	0.0430 (14)	0.0113 (12)	−0.0084 (11)	−0.0114 (11)
C7	0.0440 (14)	0.0630 (16)	0.0377 (13)	0.0078 (13)	0.0009 (10)	−0.0025 (12)
C8	0.0379 (13)	0.0500 (14)	0.0433 (13)	0.0023 (12)	0.0010 (10)	0.0045 (10)
C9	0.0303 (11)	0.0386 (11)	0.0395 (12)	0.0016 (9)	−0.0025 (9)	−0.0011 (9)
C10	0.0248 (9)	0.0345 (11)	0.0392 (12)	0.0050 (9)	−0.0070 (8)	0.0009 (9)
B1	0.0228 (12)	0.0439 (13)	0.0374 (13)	0.0014 (10)	−0.0004 (9)	0.0007 (11)

*Geometric parameters (Å, °)*

O3—H3	0.95 (4)	O1—H1	0.81 (4)
O3—B2	1.371 (3)	O1—B1	1.368 (3)
O4—H4	0.89 (4)	O2—H2	0.90 (3)
O4—B2	1.363 (3)	O2—B1	1.364 (3)
C11—C12	1.381 (4)	C1—C2	1.379 (4)
C11—C20	1.438 (3)	C1—C10	1.436 (3)



C11—B2	1.570 (4)	C1—B1	1.572 (4)
C12—H12	0.97 (3)	C2—H2A	0.9500
C12—C13	1.422 (5)	C2—C3	1.410 (4)
C13—H13	0.88 (4)	C3—H3A	0.9500
C13—C14	1.353 (5)	C3—C4	1.363 (4)
C14—H14	1.07 (4)	C4—H4A	0.9500
C14—C15	1.403 (4)	C4—C5	1.413 (4)
C15—C16	1.422 (4)	C5—C6	1.426 (4)
C15—C20	1.435 (3)	C5—C10	1.424 (3)
C16—H16	1.00 (4)	C6—H6	0.9500
C16—C17	1.355 (5)	C6—C7	1.353 (4)
C17—H17	1.02 (4)	C7—H7	0.9500
C17—C18	1.400 (4)	C7—C8	1.405 (4)
C18—H18	1.03 (4)	C8—H8	0.9500
C18—C19	1.373 (3)	C8—C9	1.373 (4)
C19—H19	0.9500	C9—H9	0.9500
C19—C20	1.415 (3)	C9—C10	1.417 (3)
B2—O3—H3	119 (2)	B1—O1—H1	116 (3)
B2—O4—H4	113 (2)	B1—O2—H2	113 (2)
C12—C11—C20	117.9 (2)	C2—C1—C10	118.1 (2)
C12—C11—B2	119.0 (2)	C2—C1—B1	117.8 (2)
C20—C11—B2	123.1 (2)	C10—C1—B1	124.1 (2)
C11—C12—H12	119.2	C1—C2—H2A	118.9
C11—C12—C13	121.6 (3)	C1—C2—C3	122.3 (3)
C13—C12—H12	119.2	C3—C2—H2A	118.9
C12—C13—H13	119.7	C2—C3—H3A	119.9
C14—C13—C12	120.5 (3)	C4—C3—C2	120.1 (2)
C14—C13—H13	119.7	C4—C3—H3A	119.9
C13—C14—H14	119.5	C3—C4—H4A	119.9
C13—C14—C15	121.0 (3)	C3—C4—C5	120.3 (3)
C15—C14—H14	119.5	C5—C4—H4A	119.9
C14—C15—C16	122.1 (3)	C4—C5—C6	120.9 (2)
C14—C15—C20	119.1 (3)	C4—C5—C10	119.8 (2)
C16—C15—C20	118.8 (3)	C10—C5—C6	119.3 (2)
C15—C16—H16	119.0	C5—C6—H6	119.5
C17—C16—C15	122.0 (3)	C7—C6—C5	121.1 (2)
C17—C16—H16	119.0	C7—C6—H6	119.5
C16—C17—H17	120.2	C6—C7—H7	119.9
C16—C17—C18	119.6 (3)	C6—C7—C8	120.1 (3)
C18—C17—H17	120.2	C8—C7—H7	119.9
C17—C18—H18	119.7	C7—C8—H8	119.7
C19—C18—C17	120.5 (3)	C9—C8—C7	120.6 (3)
C19—C18—H18	119.7	C9—C8—H8	119.7
C18—C19—H19	119.0	C8—C9—H9	119.4
C18—C19—C20	122.0 (2)	C8—C9—C10	121.2 (2)
C20—C19—H19	119.0	C10—C9—H9	119.4
C15—C20—C11	119.8 (2)	C5—C10—C1	119.3 (2)

C19—C20—C11	123.0 (2)	C9—C10—C1	122.9 (2)
C19—C20—C15	117.1 (2)	C9—C10—C5	117.8 (2)
O3—B2—C11	122.1 (2)	O1—B1—C1	121.8 (2)
O4—B2—O3	116.9 (2)	O2—B1—O1	117.1 (2)
O4—B2—C11	121.1 (2)	O2—B1—C1	121.0 (2)
C11—C12—C13—C14	-0.4 (4)	C1—C2—C3—C4	0.3 (4)
C12—C11—C20—C15	-0.3 (3)	C2—C1—C10—C5	0.2 (3)
C12—C11—C20—C19	178.6 (2)	C2—C1—C10—C9	-178.3 (2)
C12—C11—B2—O3	-38.2 (3)	C2—C1—B1—O1	37.5 (3)
C12—C11—B2—O4	140.1 (2)	C2—C1—B1—O2	-140.3 (2)
C12—C13—C14—C15	0.0 (4)	C2—C3—C4—C5	0.0 (4)
C13—C14—C15—C16	-178.8 (3)	C3—C4—C5—C6	179.0 (2)
C13—C14—C15—C20	0.2 (4)	C3—C4—C5—C10	-0.2 (3)
C14—C15—C16—C17	179.2 (3)	C4—C5—C6—C7	-178.4 (2)
C14—C15—C20—C11	0.0 (3)	C4—C5—C10—C1	0.1 (3)
C14—C15—C20—C19	-179.1 (2)	C4—C5—C10—C9	178.7 (2)
C15—C16—C17—C18	-0.3 (4)	C5—C6—C7—C8	-0.5 (4)
C16—C15—C20—C11	179.0 (2)	C6—C5—C10—C1	-179.2 (2)
C16—C15—C20—C19	0.0 (3)	C6—C5—C10—C9	-0.6 (3)
C16—C17—C18—C19	0.2 (4)	C6—C7—C8—C9	-0.1 (4)
C17—C18—C19—C20	0.0 (4)	C7—C8—C9—C10	0.4 (4)
C18—C19—C20—C11	-179.1 (2)	C8—C9—C10—C1	178.5 (2)
C18—C19—C20—C15	-0.1 (3)	C8—C9—C10—C5	0.0 (3)
C20—C11—C12—C13	0.5 (3)	C10—C1—C2—C3	-0.4 (3)
C20—C11—B2—O3	140.8 (2)	C10—C1—B1—O1	-142.0 (2)
C20—C11—B2—O4	-41.0 (3)	C10—C1—B1—O2	40.3 (3)
C20—C15—C16—C17	0.2 (4)	C10—C5—C6—C7	0.9 (3)
B2—C11—C12—C13	179.6 (2)	B1—C1—C2—C3	-179.9 (2)
B2—C11—C20—C15	-179.3 (2)	B1—C1—C10—C5	179.7 (2)
B2—C11—C20—C19	-0.3 (3)	B1—C1—C10—C9	1.2 (3)

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 $\cdots$ O2 <sup>i</sup>	0.81 (4)	1.98 (4)	2.766 (2)	165 (4)
O2—H2 $\cdots$ O3	0.90 (3)	1.86 (3)	2.750 (3)	171 (3)
O3—H3 $\cdots$ O4 <sup>ii</sup>	0.96 (4)	1.82 (4)	2.761 (2)	167 (3)
O4—H4 $\cdots$ O1	0.89 (4)	1.85 (4)	2.739 (3)	175 (3)
C9—H9 $\cdots$ O2	0.95	2.45	3.092 (3)	124
C19—H19 $\cdots$ O4	0.95	2.42	3.063 (3)	125

Symmetry codes: (i)  $x+1/2, -y+3/2, z$ ; (ii)  $x-1/2, -y+1/2, z$ .

## (2) (Naphthalen-1-yl)boronic acid

## Crystal data

$C_{10}H_9BO_2$   
 $M_r = 171.98$   
 Monoclinic,  $P2_1/c$   
 $a = 14.8469$  (11) Å  
 $b = 6.1023$  (4) Å  
 $c = 9.6797$  (7) Å  
 $\beta = 93.978$  (3)°  
 $V = 874.87$  (11) Å<sup>3</sup>  
 $Z = 4$

$F(000) = 360$   
 $D_x = 1.306$  Mg m<sup>-3</sup>  
 Cu  $K\alpha$  radiation,  $\lambda = 1.54178$  Å  
 Cell parameters from 9898 reflections  
 $\theta = 3.0$ – $77.0$ °  
 $\mu = 0.71$  mm<sup>-1</sup>  
 $T = 173$  K  
 Prism, colourless  
 $0.66 \times 0.18 \times 0.16$  mm

## Data collection

Bruker PHOTON-100 CMOS  
 diffractometer  
 Radiation source: sealedtube  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (SADABS; Bruker, 2015)  
 $T_{\min} = 0.759$ ,  $T_{\max} = 0.951$   
 25253 measured reflections

1857 independent reflections  
 1576 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.038$   
 $\theta_{\max} = 77.4$ °,  $\theta_{\min} = 3.0$ °  
 $h = -18 \rightarrow 18$   
 $k = -7 \rightarrow 7$   
 $l = -12 \rightarrow 11$

## Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.035$   
 $wR(F^2) = 0.091$   
 $S = 1.04$   
 1857 reflections  
 133 parameters  
 0 restraints

Hydrogen site location: mixed  
 H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0435P)^2 + 0.2015P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.23$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.15$  e Å<sup>-3</sup>

## Special details

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.42757 (6)	0.14734 (15)	0.62491 (7)	0.0348 (2)
H1	0.4697 (12)	0.043 (3)	0.6194 (17)	0.058 (5)*
O2	0.44930 (6)	0.18505 (15)	0.39004 (8)	0.0361 (2)
H2	0.4335 (12)	0.247 (3)	0.309 (2)	0.067 (5)*
C1	0.32826 (8)	0.42799 (19)	0.49000 (11)	0.0301 (3)
C2	0.34171 (9)	0.6083 (2)	0.40723 (12)	0.0374 (3)
H2A	0.3975 (9)	0.6190 (3)	0.3608 (7)	0.045*
C3	0.27729 (10)	0.7770 (2)	0.38806 (13)	0.0441 (3)
H3	0.2893 (2)	0.903 (2)	0.3287 (10)	0.053*
C4	0.19841 (10)	0.7660 (2)	0.45170 (13)	0.0431 (3)

H4	0.1527 (8)	0.887 (2)	0.4375 (3)	0.052*
C5	0.18023 (8)	0.5861 (2)	0.53761 (12)	0.0356 (3)
C6	0.09731 (9)	0.5709 (2)	0.60194 (14)	0.0445 (3)
H6	0.0525 (8)	0.688 (2)	0.5877 (3)	0.053*
C7	0.07934 (9)	0.3962 (3)	0.68300 (14)	0.0477 (3)
H7	0.0219 (10)	0.3879 (3)	0.7264 (8)	0.057*
C8	0.14332 (9)	0.2281 (2)	0.70431 (13)	0.0411 (3)
H8	0.1299 (2)	0.100 (2)	0.7651 (10)	0.049*
C9	0.22382 (8)	0.2367 (2)	0.64330 (11)	0.0327 (3)
H9	0.2672 (6)	0.1175 (18)	0.6589 (3)	0.039*
C10	0.24527 (8)	0.41549 (18)	0.55791 (11)	0.0296 (3)
B1	0.40328 (9)	0.2462 (2)	0.50178 (12)	0.0300 (3)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0376 (5)	0.0461 (5)	0.0209 (4)	0.0093 (4)	0.0038 (3)	0.0008 (3)
O2	0.0375 (5)	0.0500 (5)	0.0212 (4)	0.0078 (4)	0.0055 (3)	0.0041 (4)
C1	0.0372 (6)	0.0315 (6)	0.0212 (5)	-0.0021 (5)	-0.0008 (4)	-0.0028 (4)
C2	0.0476 (7)	0.0370 (6)	0.0274 (6)	-0.0065 (5)	0.0009 (5)	0.0002 (5)
C3	0.0669 (9)	0.0306 (6)	0.0333 (6)	-0.0033 (6)	-0.0060 (6)	0.0046 (5)
C4	0.0575 (8)	0.0333 (6)	0.0367 (7)	0.0098 (6)	-0.0093 (6)	-0.0037 (5)
C5	0.0429 (7)	0.0357 (6)	0.0271 (6)	0.0062 (5)	-0.0058 (5)	-0.0069 (5)
C6	0.0384 (7)	0.0532 (8)	0.0413 (7)	0.0139 (6)	-0.0034 (5)	-0.0098 (6)
C7	0.0334 (7)	0.0664 (9)	0.0434 (7)	0.0036 (6)	0.0047 (5)	-0.0042 (7)
C8	0.0368 (6)	0.0500 (7)	0.0366 (7)	-0.0038 (6)	0.0036 (5)	0.0016 (6)
C9	0.0335 (6)	0.0348 (6)	0.0293 (6)	0.0010 (5)	-0.0007 (4)	-0.0010 (5)
C10	0.0349 (6)	0.0311 (6)	0.0221 (5)	0.0009 (5)	-0.0022 (4)	-0.0051 (4)
B1	0.0308 (6)	0.0366 (7)	0.0226 (6)	-0.0031 (5)	0.0024 (4)	-0.0013 (5)

*Geometric parameters (Å, °)*

O1—H1	0.899 (19)	C4—C5	1.4146 (18)
O1—B1	1.3620 (15)	C5—C6	1.4206 (19)
O2—H2	0.886 (19)	C5—C10	1.4243 (16)
O2—B1	1.3706 (14)	C6—H6	0.979 (16)
C1—C2	1.3839 (16)	C6—C7	1.361 (2)
C1—C10	1.4382 (16)	C7—H7	0.977 (16)
C1—B1	1.5705 (18)	C7—C8	1.4036 (19)
C2—H2A	0.971 (15)	C8—H8	1.008 (16)
C2—C3	1.4085 (19)	C8—C9	1.3703 (17)
C3—H3	0.983 (16)	C9—H9	0.977 (14)
C3—C4	1.362 (2)	C9—C10	1.4180 (16)
C4—H4	1.004 (16)		
B1—O1—H1	114.0 (10)	C7—C6—C5	120.98 (12)
B1—O2—H2	117.8 (11)	C7—C6—H6	119.5
C2—C1—C10	118.00 (11)	C6—C7—H7	120.0

C2—C1—B1	118.27 (11)	C6—C7—C8	119.95 (12)
C10—C1—B1	123.72 (10)	C8—C7—H7	120.0
C1—C2—H2A	118.9	C7—C8—H8	119.7
C1—C2—C3	122.23 (12)	C9—C8—C7	120.68 (13)
C3—C2—H2A	118.9	C9—C8—H8	119.7
C2—C3—H3	119.9	C8—C9—H9	119.4
C4—C3—C2	120.12 (12)	C8—C9—C10	121.23 (11)
C4—C3—H3	119.9	C10—C9—H9	119.4
C3—C4—H4	119.7	C5—C10—C1	119.49 (11)
C3—C4—C5	120.60 (12)	C9—C10—C1	122.78 (10)
C5—C4—H4	119.7	C9—C10—C5	117.72 (11)
C4—C5—C6	121.00 (12)	O1—B1—O2	116.98 (11)
C4—C5—C10	119.56 (12)	O1—B1—C1	121.32 (10)
C6—C5—C10	119.43 (12)	O2—B1—C1	121.66 (10)
C5—C6—H6	119.5		
C1—C2—C3—C4	-0.16 (19)	C6—C5—C10—C9	-0.34 (16)
C2—C1—C10—C5	0.31 (15)	C6—C7—C8—C9	-0.5 (2)
C2—C1—C10—C9	179.01 (10)	C7—C8—C9—C10	0.45 (18)
C2—C1—B1—O1	139.56 (12)	C8—C9—C10—C1	-178.73 (11)
C2—C1—B1—O2	-38.24 (16)	C8—C9—C10—C5	-0.01 (16)
C2—C3—C4—C5	0.06 (19)	C10—C1—C2—C3	-0.04 (17)
C3—C4—C5—C6	-178.59 (12)	C10—C1—B1—O1	-41.91 (16)
C3—C4—C5—C10	0.22 (18)	C10—C1—B1—O2	140.30 (11)
C4—C5—C6—C7	179.08 (12)	C10—C5—C6—C7	0.27 (18)
C4—C5—C10—C1	-0.41 (16)	B1—C1—C2—C3	178.58 (11)
C4—C5—C10—C9	-179.17 (10)	B1—C1—C10—C5	-178.22 (10)
C5—C6—C7—C8	0.2 (2)	B1—C1—C10—C9	0.47 (16)
C6—C5—C10—C1	178.42 (10)		

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*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...O2 <sup>i</sup>	0.897 (18)	1.846 (18)	2.7411 (13)	176.3 (17)
O2—H2...O1 <sup>ii</sup>	0.888 (19)	1.891 (19)	2.7607 (11)	166.0 (17)
C9—H9...O1	0.98 (1)	2.43 (1)	3.0911 (15)	124 (1)

Symmetry codes: (i)  $-x+1, -y, -z+1$ ; (ii)  $x, -y+1/2, z-1/2$ .