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ISSN: 2056-9890
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Acta Cryst. (2015). E**71**, 1151–1154

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Acta Cryst E
CRYSTALLOGRAPHIC COMMUNICATIONS

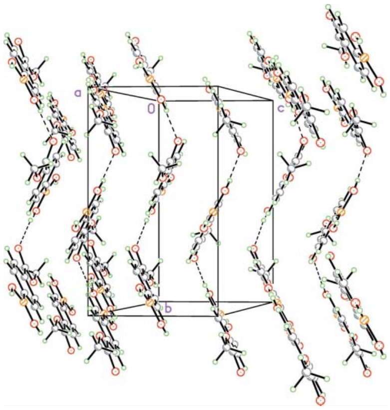
ISSN 2056-9890

Received 6 August 2015
Accepted 25 August 2015

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

Keywords: crystal structure; boronic acid; methoxycarbonyl; ester; protecting groups; Suzuki coupling; hydrogen bonding; inversion dimers; π–π interactions.

CCDC reference: 1416885
Supporting information: this article has supporting information at journals.iucr.org/e



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Crystal structure of 4-(methoxycarbonyl)phenylboronic acid

Keith J. Flanagan* and Mathias O. Senge

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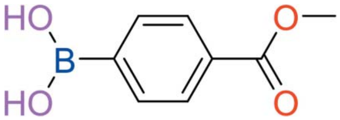
In the title compound, $C_8H_9BO_4$, the methoxycarbonyl group is rotated out of the plane of the benzene ring by 7.70 (6)°. In the crystal, molecules are linked *via* pairs of O—H⋯O hydrogen bonds, involving the boronic acid OH groups, forming inversion dimers. The dimers are linked *via* O—H⋯O hydrogen bonds, involving a boronic acid OH group and the carbonyl O atom, forming undulating sheets parallel to $(10\overline{2})$. Within the sheets there are also C—H⋯O hydrogen bonds present, also involving the carbonyl O atom. The sheets are linked *via* C—H⋯π and offset face-to-face π-interactions between inversion-related molecules [inter-centroid distance = 3.7843 (16) Å, interplanar distance = 3.3427 (4) Å and offset = 1.744 Å], forming a three-dimensional structure.

1. Chemical context

Boronic acids have been widely studied, mainly due to their roles in coupling reactions such as Suzuki (Suzuki, 2011), Chan–Lam (Lam *et al.*, 2000) and Liebeskind–Srogl (Liebeskind & Srogl, 2000). Complexes of boronic acids are well known, and many examples have been structurally characterized (*e.g.*, Roşca *et al.*, 2012; Filthaus *et al.*, 2008; Cyrański *et al.*, 2008; Rettig & Trotter, 1977). Many examples exist of similar compounds such as 2-methylimidazolium (4-carboxybenzene)(2-methylimidazolyl)boronate monohydrate (Aakeröy *et al.*, 2005) and 4-carboxyphenylboronic acid (SeethaLekshmi & Pedireddi, 2007). However, no examples of methoxy-protected derivatives have been published to date. We report herein on the crystal structure of the title compound, the 4-(methoxycarbonyl) derivative of phenylboronic acid.



2. Structural commentary

The title molecule, Fig. 1, is almost completely planar with the methoxycarbonyl group inclined to the benzene ring by 7.70 (6)°. The angle around atom B1, O1—B1—O2 is 118.16 (9)°, very close to the ideal value of 120°. The bond lengths and angles are similar to those reported for 4-carboxyphenylboronic acid derivatives (SeethaLekshmi & Pedireddi, 2007) in which the carboxylic group is rotated from the plane of the benzene ring by *ca* 13.83–26.44°, and the O—B—O bond angles are in the range of ca 118.1–122.5°. Aakeröy *et al.* (2005) reported the structures of 4-acetylpyridine oxime

doi:10.1107/S2056989015015923

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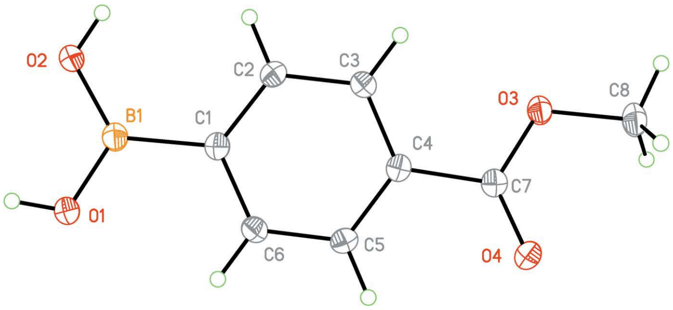

Figure 1
The molecular structure of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

4-carboxybenzeneboronate dihydrate and 4-acetylpyridine oxime 4-carboxybenzeneboronate dihydrate in which the 4-carboxy groups are inclined to the benzene ring by *ca* 10.45–14.08°, close to the value observed for the methoxycarbonyl group in the title compound.

3. Supramolecular features

In the crystal of the title compound, there are hydrogen bonds between the carbonyl atom O4 and the hydroxy group O2–H2*A* of the boronic acid and atom O2 of the boronic acid with a *D*···*A* distance of 2.753 (1) Å (Fig. 2 and Table 1). The hydroxy group O1–-H1*A* of the boronic acid is in an inversion-related hydrogen-bonded network with the oxygen O2 of the boronic acid at a distance of 2.762 (1) Å (Fig. 2 and Table 1).

The presence of the methoxy group on the carbonyl removes hydrogen-bond donation of the carboxylic acid seen in related structures. Atom C8 creates a shield around atom O3, removing its ability to participate in hydrogen bonding due to steric effects. It is noteworthy that the methoxy protecting group is small compared to other protecting groups and therefore exhibits no steric effects on the hydrogen-bonding capabilities to atom O4 in this structure, as seen in other examples. As exemplified by the work of Lemmerer (2012), most literature examples exhibit an almost exclusive head-to-tail hydrogen-bonding network between the boronic and carboxylic acids whereas the title compound exhibits exclusively head-to-head hydrogen-bonding interactions with the boronic acid subunit. This is due to the steric effects and removal of hydrogen-donating abilities in the methoxycarbonyl subunit (Fig. 2). The group can still act as a hydrogen acceptor, as shown in the packing diagram (Fig. 2). Atom O4 can accept H atoms from the hydroxy group O2—H2*A* to create an offset face-to-face overlap in the packing unit. Yang *et al.* (2005) published a structure of the boronic ester derivative of the title compound. This structure showed similar effects, however no hydrogen bonds were visible in the reported structure.

Table 1
Hydrogen-bond geometry (Å, °).

Cg is the centroid of ring C1–C6.

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
$O1—H1A\cdots O2^{i}$	0.86 (2)	1.90 (2)	2.762 (1)	178.4 (18)
$O2—H2A\cdots O4^{ii}$	0.84 (2)	1.94 (2)	2.753 (1)	162.2 (16)
$C2—H2\cdots O4^{ii}$	0.95	2.59	3.500 (1)	160
$C5—H5\cdots Cg^{iii}$	0.95	2.75	3.534 (1)	141

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

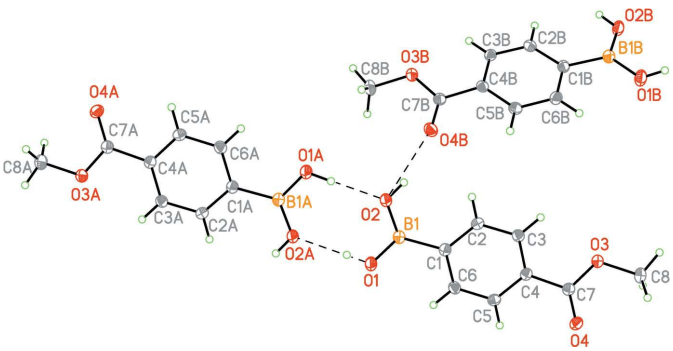

Figure 2
Hydrogen bonding (dashed lines) in the crystal of the title compound [see Table 1 for details; symmetry codes: (A) $-x+2, -y+1, -z+2$; (B) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$]. Displacement ellipsoids are drawn at the 50% probability level.

Hydrogen bonding and π-stacking within the unit cell forms a strong set of dimeric pairs. This can be easily observed in Fig. 3. These dimeric pairs line up to form a zigzag stacking pattern with a consistent spacing throughout the unit cell. This is aided by the hydrogen bond between O4 and O2—H2*A* [2.753 (1) Å] and a close contact between atom O4 and the hydrogen on atom C2 at a distance of 2.59 Å. The unit cell

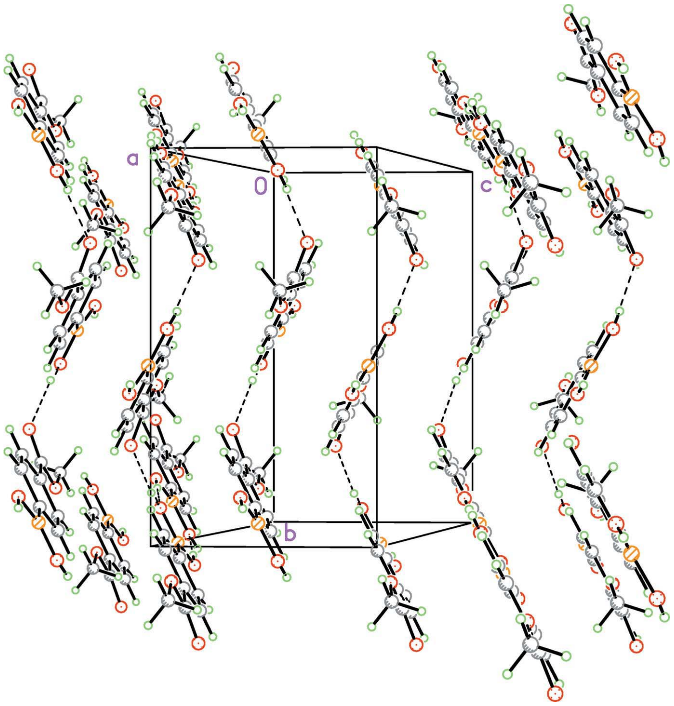

Figure 3
View of the π-aggregated structure as viewed approximately along the *a* axis.

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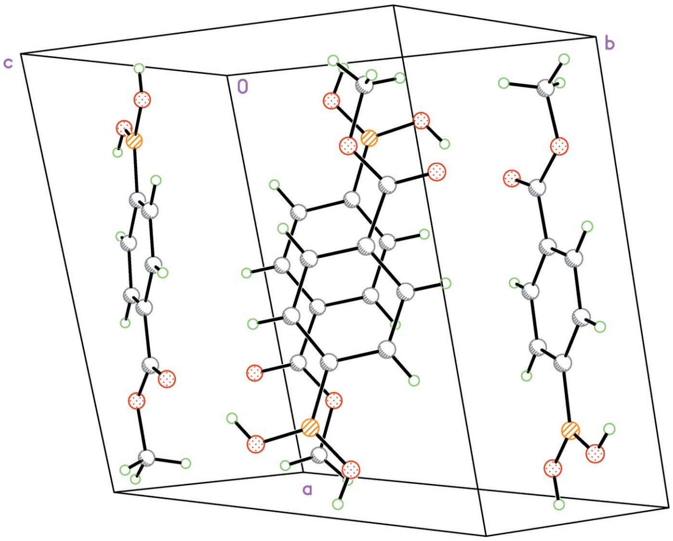

Figure 4
A view approximately along the *b* axis, showing the offset face-to-face π-interactions involving inversion-related molecules.

consists of four molecular units which form π-aggregated pairs in a head-to-tail fashion and are stabilized through offset face-to-face π-interactions [inter-centroid distance = 3.7843 (16) Å; inter-planar distance = 3.3427 (4) Å, offset = 1.744 Å]; see Fig. 4. The hydroxy group O1—H1*A* of the boronic acid is in an inversion-related hydrogen-bonded network with the oxygen O2 of the boronic acid at a distance of 2.762 (1) Å, forming a head-to-head hydrogen-bonded network with adjacent molecules (Fig. 5). There are also C—H$\cdots\pi$ interactions (Table 1) present between the undulating sheets parallel to $(10\overline{2})$. The sum of all of these intermolecular interactions leads to the formation of a three-dimensional structure.

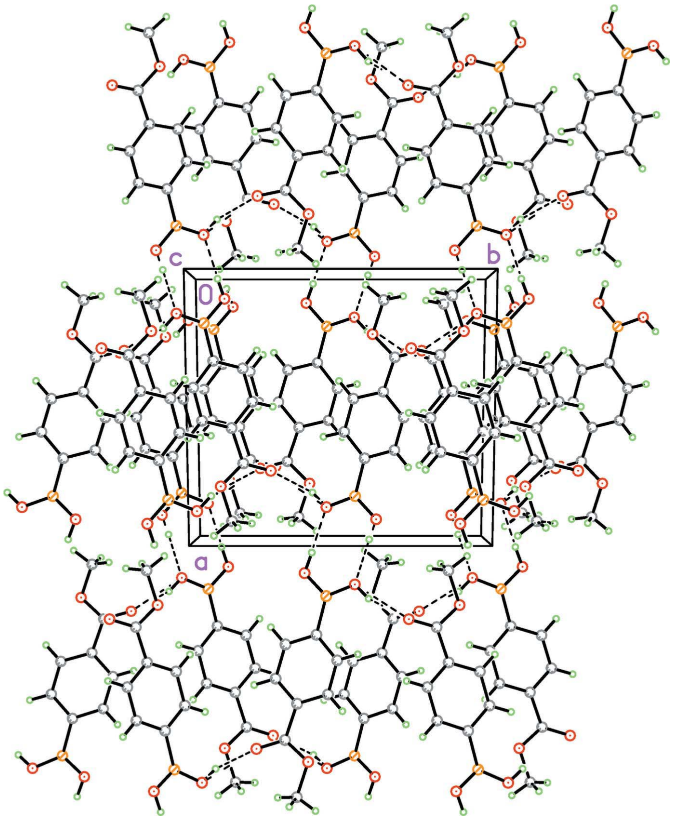

Figure 5
Crystal packing diagram of the title compound viewed along the *c* axis, showing the offset face-to-face π-interactions involving inversion-related molecules (dashed lines; see Table 1 for details).

4. Database survey

A search of the Cambridge Structural Database (Version 5.36, update Nov. 2014; Groom & Allen, 2014) gave fourteen hits for free carboxylic acid derivatives of the title compound and one for the boronic ester. Soundararajan *et al.* (1993) published a structure of 4-carboxy-2-nitrobenzeneboronic acid. The carboxylic group deviated from the mean plane with an angle of *ca* 5.84° and the O—B—O bond angle was *ca* 119.88°. Aakeröy *et al.* (2004) reported the structure of a 4-carboxybenzeneboronic acid 4,4′-bipyridine derivative with the carboxylic group being rotated from the plane by *ca* 4.20° and an O—B—O bond angle of *ca* 118.09°. They also reported the structures of 2-methylimidazolium(4-carboxybenzene)(2-methylimidazolyl)boronate monohydrate, tris(4-(dimethylamino)pyridinium) bis(4-(dimethylamino)pyridine) tris(4-carboxybenzeneboronate) trihydrate and 4-acetylpyridine oxime 4-carboxybenzeneboronate dihydrate which presented out-of-plane tilt angles of *ca* 10.45–27.74° and O—B—O bond angles of *ca* 114.23–124.94° (Aakeröy *et al.*, 2005).

SeethaLekshmi & Pedireddi (2006) reported on a selection of carboxylatophenylboronic acid derivatives, hexaaqua-*M*(II) bis(4-carboxylatophenylboronic acid) tetrahydrate, where *M* is nickel, manganese or cobalt. These structures where similar to the title compound and exhibited similar characteristics for the O—B—O bond angle and the out-of-plane tilt of the carboxyl acid group compared to the title compound. The carboxylic group deviated from the plane with an angle of *ca* 3.40–4.53° and the O—B—O bond angles were in the range of *ca* 121.43–122.18° (SeethaLekshmi & Pedireddi, 2006). They also published a selection of 4-carboxyphenylboronic acids including the monohydrate and the hydrate derivatives of this compound. The carboxylic group deviated from the mean plane with an angle of *ca* 13.83–26.44° and the O—B—O bond angles were in the range of *ca* 118.08–122.50° (SeethaLekshmi & Pedireddi, 2007).

The structure of bis(8-chloro-1-methyl-6-phenyl-4*H*-[1,2,4]triazolo[4,3-a][1,4]benzodiazepine) 4-(dihydroxyboryl)benzoic acid monohydrate exhibited a tilt angle of *ca* 2.14° for the carboxylic group and an O—B—O bond angle of *ca* 126.53° (Varughese *et al.*, 2011). Likewise, the relevant values in the structure of a cyclopentanaminium 4-(dihydroxyboryl)benzoate trihydrate were *ca* 29.67 and 126.53°, respectively (Lemmerer, 2012). Finally, methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate showed similar features to the title compound with a methoxycarbonyl deviation from the ring plane of *ca* 4.97° (Yang *et al.*, 2005).

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5. Synthesis and crystallization

The compound was purchased from Alfa Aesar and was purified with silica gel column chromatography using CH_2Cl_2:MeOH (19:1). The compound was then crystallized from a solution of 1% MeOH in CH_2Cl_2 layered with hexane to give a single crystal suitable for X-ray diffraction.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The donor OH H atoms were located in a difference Fourier map and freely refined. The C-bound H atoms were placed in their expected calculated positions and refined as riding: C—H = 0.95–0.98 Å with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms and $1.2U_{iso}(C)$ for other H atoms.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_8H_9BO_4$
M_r	179.96
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	11.2449 (6), 12.0672 (6), 6.8598 (3)
β (°)	105.121 (1)
V (Å^3)	898.61 (8)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.35 × 0.10 × 0.10
Data collection	
Diffractometer	Bruker *SMART* APEXII area detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.706, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	31992, 2056, 1872
R_{int}	0.021
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.094, 1.10
No. of reflections	2056
No. of parameters	126
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.39, −0.22

Computer programs: *APEX2* and *SAINT-Plus* (Bruker, 2014), *SHELXT* (Sheldrick, 2015*a*), *XP* in *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015*b*) and *publCIF* (Westrip, 2010).

Acknowledgements

This work was supported by a grant from the Science Foundation Ireland (SFI IvP 13/IA/1894).

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supporting information

Acta Cryst. (2015). E**71**, 1151-1154   [doi:10.1107/S2056989015015923]

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Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT-Plus* (Bruker, 2014); data reduction: *SAINT-Plus* (Bruker, 2014); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015b) and *publCIF* (Westrip, 2010).

4-(Methoxycarbonyl)benzeneboronic acid

Crystal data

$C_8H_9BO_4$
$M_r = 179.96$
Monoclinic, $P2_1/c$
$a = 11.2449$ (6) Å
$b = 12.0672$ (6) Å
$c = 6.8598$ (3) Å
$\beta = 105.121$ (1)°
$V = 898.61$ (8) Å^3
$Z = 4$
$F(000) = 376$
$D_x = 1.330$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9864 reflections
$\theta = 2.5$–31.1°
$\mu = 0.10$ mm^{-1}
$T = 100$ K
Block, white
0.35 × 0.10 × 0.10 mm

Data collection

Bruker SMART APEXII area-detector diffractometer
Radiation source: sealed tube
Detector resolution: 8.258 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2014)
$T_{\min} = 0.706$, $T_{\max} = 0.746$
31992 measured reflections
2056 independent reflections
1872 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.021$
$\theta_{\max} = 27.5°$, $\theta_{\min} = 1.9°$
$h = -14 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -8 \rightarrow 8$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.094$
$S = 1.10$
2056 reflections
126 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 0.2551P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.39$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}

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Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.90580 (7)	0.61792 (6)	0.84477 (13)	0.0258 (2)
H1A	0.9797 (19)	0.5946 (15)	0.897 (3)	0.054 (5)*
C1	0.67921 (8)	0.57954 (8)	0.78322 (14)	0.0163 (2)
B1	0.81840 (10)	0.54762 (9)	0.87529 (16)	0.0185 (2)
O2	0.85621 (7)	0.45309 (6)	0.98510 (12)	0.02287 (19)
H2A	0.8020 (17)	0.4076 (14)	0.997 (3)	0.046 (4)*
C2	0.58139 (9)	0.51156 (8)	0.80135 (14)	0.0166 (2)
H2	0.5989	0.4434	0.8724	0.020*
O3	0.21983 (6)	0.60624 (6)	0.54273 (12)	0.02136 (18)
C3	0.45926 (9)	0.54182 (8)	0.71743 (14)	0.0161 (2)
H3	0.3942	0.4945	0.7303	0.019*
O4	0.27900 (6)	0.77238 (6)	0.45341 (11)	0.02041 (18)
C4	0.43313 (8)	0.64218 (8)	0.61442 (13)	0.0153 (2)
C5	0.52908 (9)	0.71113 (8)	0.59350 (14)	0.0169 (2)
H5	0.5112	0.7793	0.5227	0.020*
C6	0.65052 (9)	0.67947 (8)	0.67660 (15)	0.0177 (2)
H6	0.7153	0.7263	0.6610	0.021*
C7	0.30450 (8)	0.68109 (8)	0.52886 (14)	0.0163 (2)
C8	0.09288 (9)	0.64329 (9)	0.47857 (19)	0.0271 (2)
H8A	0.0381	0.5827	0.4945	0.041*
H8B	0.0813	0.7065	0.5614	0.041*
H8C	0.0735	0.6657	0.3364	0.041*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0150 (4)	0.0242 (4)	0.0365 (4)	−0.0005 (3)	0.0034 (3)	0.0100 (3)
C1	0.0156 (4)	0.0176 (5)	0.0155 (4)	0.0006 (3)	0.0036 (3)	−0.0014 (4)
B1	0.0160 (5)	0.0190 (5)	0.0199 (5)	0.0002 (4)	0.0035 (4)	0.0001 (4)
O2	0.0144 (3)	0.0211 (4)	0.0314 (4)	−0.0013 (3)	0.0029 (3)	0.0073 (3)
C2	0.0180 (5)	0.0156 (4)	0.0162 (4)	0.0017 (3)	0.0045 (3)	0.0007 (3)
O3	0.0147 (3)	0.0180 (4)	0.0306 (4)	0.0001 (3)	0.0046 (3)	0.0004 (3)
C3	0.0162 (4)	0.0160 (4)	0.0165 (4)	−0.0010 (3)	0.0051 (3)	−0.0017 (3)
O4	0.0190 (3)	0.0188 (4)	0.0232 (4)	0.0034 (3)	0.0051 (3)	0.0029 (3)
C4	0.0159 (4)	0.0162 (4)	0.0136 (4)	0.0014 (3)	0.0036 (3)	−0.0025 (3)
C5	0.0195 (5)	0.0156 (4)	0.0158 (4)	0.0011 (3)	0.0050 (3)	0.0010 (3)
C6	0.0166 (4)	0.0182 (5)	0.0188 (4)	−0.0015 (3)	0.0054 (3)	0.0007 (3)
C7	0.0172 (4)	0.0170 (4)	0.0148 (4)	0.0004 (3)	0.0045 (3)	−0.0031 (3)
C8	0.0147 (5)	0.0260 (5)	0.0396 (6)	0.0013 (4)	0.0053 (4)	0.0015 (5)

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Geometric parameters (Å, º)

O1—B1	1.3552 (13)	C3—C4	1.3942 (13)
O1—H1A	0.86 (2)	C3—H3	0.9500
C1—C2	1.4034 (13)	O4—C7	1.2191 (12)
C1—C6	1.4035 (13)	C4—C5	1.3992 (13)
C1—B1	1.5752 (14)	C4—C7	1.4880 (13)
B1—O2	1.3720 (13)	C5—C6	1.3891 (13)
O2—H2A	0.841 (18)	C5—H5	0.9500
C2—C3	1.3923 (13)	C6—H6	0.9500
C2—H2	0.9500	C8—H8A	0.9800
O3—C7	1.3336 (12)	C8—H8B	0.9800
O3—C8	1.4503 (12)	C8—H8C	0.9800
B1—O1—H1A	113.1 (12)	C5—C4—C7	117.91 (8)
C2—C1—C6	118.00 (8)	C6—C5—C4	119.75 (9)
C2—C1—B1	122.77 (8)	C6—C5—H5	120.1
C6—C1—B1	119.23 (8)	C4—C5—H5	120.1
O1—B1—O2	118.16 (9)	C5—C6—C1	121.19 (9)
O1—B1—C1	118.02 (9)	C5—C6—H6	119.4
O2—B1—C1	123.82 (9)	C1—C6—H6	119.4
B1—O2—H2A	118.0 (12)	O4—C7—O3	123.30 (9)
C3—C2—C1	121.43 (9)	O4—C7—C4	123.32 (9)
C3—C2—H2	119.3	O3—C7—C4	113.37 (8)
C1—C2—H2	119.3	O3—C8—H8A	109.5
C7—O3—C8	115.73 (8)	O3—C8—H8B	109.5
C2—C3—C4	119.48 (9)	H8A—C8—H8B	109.5
C2—C3—H3	120.3	O3—C8—H8C	109.5
C4—C3—H3	120.3	H8A—C8—H8C	109.5
C3—C4—C5	120.15 (9)	H8B—C8—H8C	109.5
C3—C4—C7	121.91 (8)		
C2—C1—B1—O1	178.38 (9)	C7—C4—C5—C6	178.03 (8)
C6—C1—B1—O1	−1.02 (14)	C4—C5—C6—C1	−0.52 (14)
C2—C1—B1—O2	−1.88 (15)	C2—C1—C6—C5	0.81 (14)
C6—C1—B1—O2	178.73 (9)	B1—C1—C6—C5	−179.77 (9)
C6—C1—C2—C3	−0.29 (14)	C8—O3—C7—O4	−5.45 (14)
B1—C1—C2—C3	−179.69 (9)	C8—O3—C7—C4	174.59 (8)
C1—C2—C3—C4	−0.52 (14)	C3—C4—C7—O4	173.53 (9)
C2—C3—C4—C5	0.82 (14)	C5—C4—C7—O4	−4.78 (14)
C2—C3—C4—C7	−177.45 (8)	C3—C4—C7—O3	−6.51 (13)
C3—C4—C5—C6	−0.31 (14)	C5—C4—C7—O3	175.18 (8)

Hydrogen-bond geometry (Å, º)

Cg is the centroid of ring C1–C6.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···O2^{i}	0.86 (2)	1.90 (2)	2.762 (1)	178.4 (18)

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O2—H2*A*···O4$^{\mathrm{ii}}$	0.84 (2)	1.94 (2)	2.753 (1)	162.2 (16)
C2—H2···O4$^{\mathrm{ii}}$	0.95	2.59	3.500 (1)	160
C5—H5···*Cg*$^{\mathrm{iii}}$	0.95	2.75	3.534 (1)	141

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

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