organic compounds

2-Methoxy-3-(trimethylsilyl)phenyl-boronic acid

Krzysztof Durka, Sergiusz Luliński* and Janusz Serwatowski

Physical Chemistry Department, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

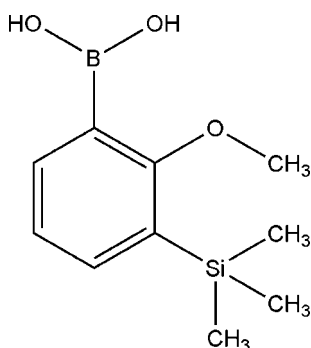Correspondence e-mail: serek@ch.pw.edu.pl

The molecular structure of the title compound, $C_{10}H_{17}BO_3Si$, features an intramolecular O—H⋯O hydrogen bond; the boronic group group has an *exo–endo* conformation. In the crystal, the molecules interact with each other by O—H⋯O hydrogen bonds, producing centrosymmetric dimers that are linked by weak π–π stacking interactions featuring specific short B⋯C contacts [*e.g.* 3.372 (2) Å], forming an infinite columnar structure aligned along the *a*-axis direction.

Related literature

For structures of related *ortho*-alkoxy arylboronic acids, see: Cyrański *et al.* (2012). For binding energies of other boronic acid dimers, see: Cyrański *et al.* (2008); Durka *et al.* (2012). For the *PIXEL* program, see Gavezzotti (2003). For the synthesis, see: Durka *et al.* (2010).

Experimental

Crystal data

$C_{10}H_{17}BO_3Si$	$b = 9.7082$ (10) Å
$M_r = 224.14$	$c = 14.1415$ (16) Å
Monoclinic, $P2_1/n$	$\beta = 104.26$ (1)°
$a = 9.1832$ (11) Å	$V = 1221.9$ (2) Å³
$Z = 4$	$T = 100$ K
Mo $K\alpha$ radiation	$0.16 \times 0.12 \times 0.10$ mm
$\mu = 0.18$ mm^{-1}	

Data collection

Bruker APEXII diffractometer	11175 measured reflections
Absorption correction: multi-scan (Blessing, 1995)	2939 independent reflections
$T_{min} = 0.744$, $T_{max} = 0.780$	2154 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	1 restraint
$wR(F^2) = 0.097$	H-atom parameters constrained
$S = 1.02$	$\Delta\rho_{max} = 0.36$ e Å^{-3}
2939 reflections	$\Delta\rho_{min} = -0.30$ e Å^{-3}
136 parameters	

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O2—H2⋯O1	0.84	2.04	2.7532 (14)	142
O3—H3⋯O2^i	0.84	1.97	2.8051 (14)	175

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

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2010); data reduction: *SAINT* and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *PLATON* (Spek, 2009).

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supplementary materials

2-Methoxy-3-(trimethylsilyl)phenylboronic acid

Krzysztof Durka, Sergiusz Luliński and Janusz Serwatowski

1. Introduction

2. Experimental

2.1. Synthesis and crystallization

The preparation of the title compound (I) was described previously (Durka *et al.*, 2010). Crystals suitable for single-crystal X-ray diffraction analysis were grown by slow evaporation of an acetone solution of (I).

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All hydrogen atoms were placed in calculated positions with C—H distances of 0.95 Å (phenyl) and 0.98 Å (methyl), and an O—H distance of 0.84 Å, and with U_{iso}(phenyl-H) = $1.2U_{eq}$(C), U_{iso}(methyl-H) = $1.5U_{eq}$(C) and U_{iso}(hydroxyl-H)=$1.5U_{eq}$(O).

3. Results and discussion

The ability of arylboronic acids to form supramolecular structures *via* hydrogen-bonding interactions of $B(OH)_2$ groups is well known. The molecular structure of (I) is shown in Fig. 1. The boronic group is only slightly twisted with respect to the benzene ring whereas the methoxy group is twisted almost perpendicularly. The trimethylsilyl group is slightly bent with respect to the aromatic ring. The boronic group has an *exo-endo* conformation. The *endo*-oriented OH group is engaged into the intramolecular O—H⋯O bond with the methoxy O atom to form a six-membered ring typical of structures of related *ortho*-alkoxyarylboronic acids (Cyrański *et al.*, 2012). The molecules of (I) are linked *via* almost linear O—H⋯O bridges to give centrosymmetric dimers. The periodic calculations performed in PIXEL programme (Gavezzotti, 2003) show that the dimer interaction energy is equal to -58.5 kJ/mol, which is comparable to the binding energies of other boronic acids dimers reported in the literature (Cyrański *et al.*, 2008; Durka *et al.*, 2012). The supra-molecular architecture in (I) extends through π—π stacking interactions of aromatic rings in the parallel-displaced fashion. The boron atoms are also engaged in these mutual interactions, which is manifested by a relatively short B1⋯C2 contact of 3.372 (2) Å. Short B1⋯C2 interactions were described in more detail for the structures of fluorinated 1,4-phenylenediboronic acids (Durka *et al.*, 2012). Thus, another centrosymmetric motif can be distinguished. The interaction energy of such dimers amounts to -33.5 kJ/mol. As a result of H-bonding and π—π interactions, a specific columnar network is formed in the *a* axis direction (Figs 2 & 3). The total cohesive energy calculated for asymmetric unit equals to -111.7 kJ/mol. In conclusion, hydrogen-bonding interactions of boronic groups are operative to form centrosymmetric dimeric structure of (I). The extended supramolecular assembly is due to π—π stacking interactions of aromatic rings additionally involving the boron atoms.

Computing details

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2010); data reduction: *SAINT* (Bruker, 2010) and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *PLATON* (Spek, 2009).
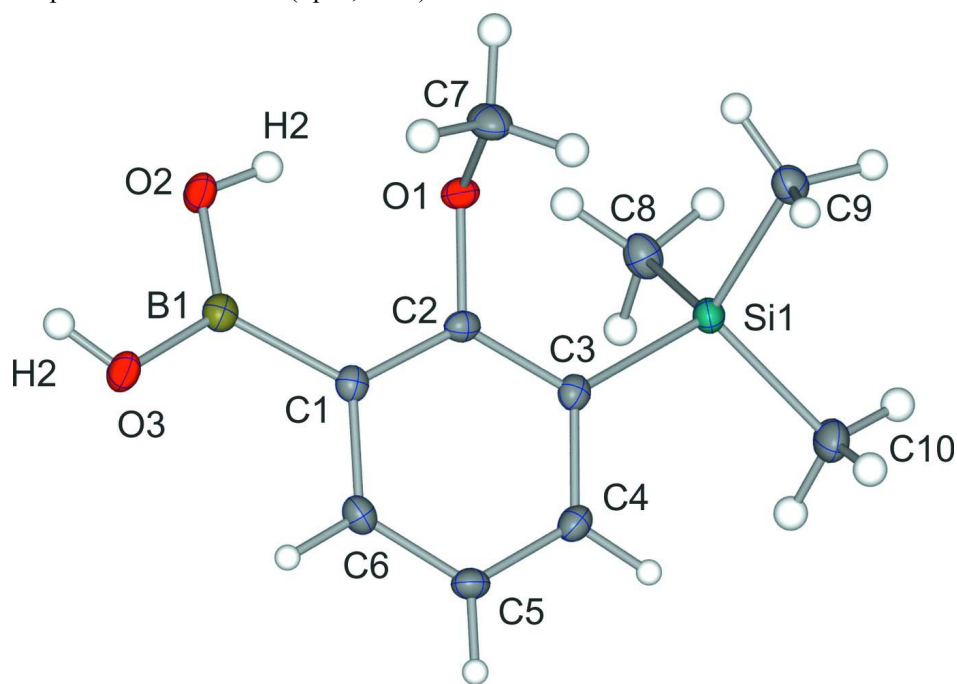

Figure 1

View of the title compound (I) with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.
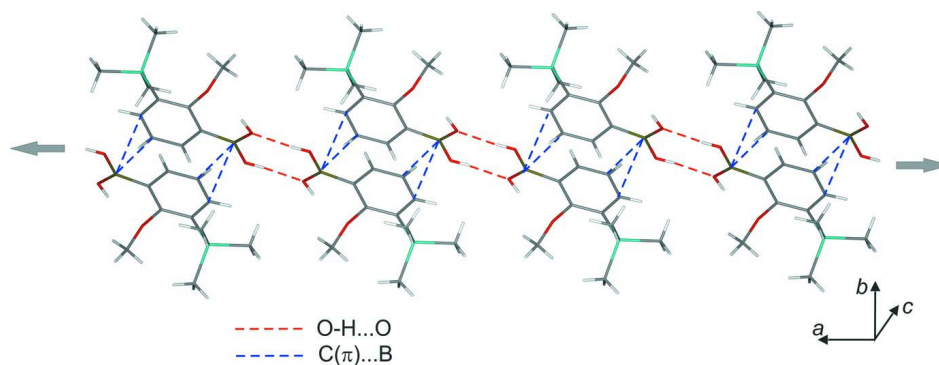
Figure 2

Part of the crystal structure of (I) showing formation of a column along the [100] direction. The O–H⋯O, C–H⋯O and C(π)⋯B interactions are depicted as red and blue dashed lines, respectively.
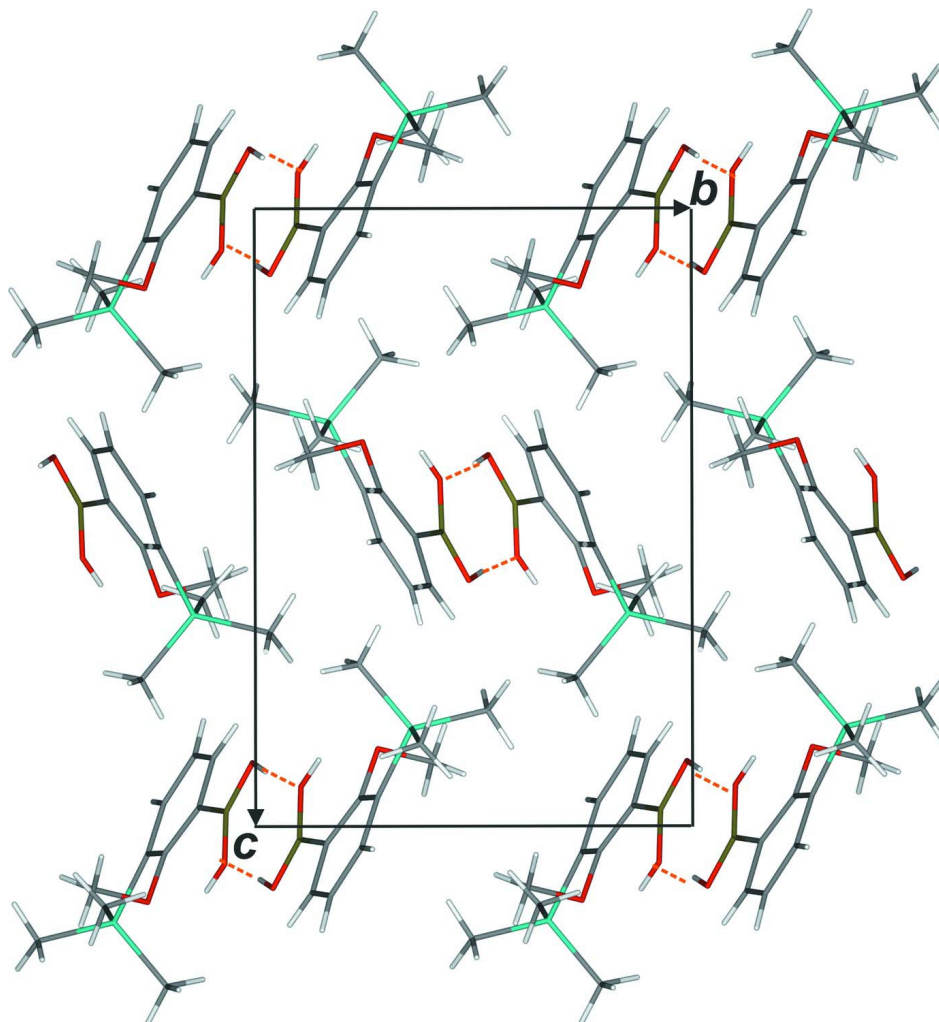
Figure 3

Packing diagram viewed along the *a* axis, indicating the columns of O—H···O and C(*π*)···B interacting molecules of (I).

2-Methoxy-3-(trimethylsilyl)phenylboronic acid

Crystal data

$C_{10}H_{17}BO_3Si$	$D_x = 1.218$ Mg m^{-3}
$M_r = 224.14$	Melting point: 353 K
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 9.1832$ (11) Å	Cell parameters from 1540 reflections
$b = 9.7082$ (10) Å	$\theta = 2.7–28.7°$
$c = 14.1415$ (16) Å	$\mu = 0.18$ mm^{-1}
$\beta = 104.26$ (1)°	$T = 100$ K
$V = 1221.9$ (2) Å^3	Unshaped, colourless
$Z = 4$	$0.16 \times 0.12 \times 0.10$ mm
$F(000) = 480$	

Data collection

Bruker APEXII diffractometer	11175 measured reflections
Radiation source: TXS rotating anode	2939 independent reflections
Multi-layer optics monochromator	2154 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.029$
Absorption correction: multi-scan (Blessing, 1995)	$\theta_{max} = 28.6°$, $\theta_{min} = 3.0°$
$T_{min} = 0.744$, $T_{max} = 0.780$	$h = -11 \rightarrow 10$
	$k = -13 \rightarrow 12$
	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.034$	$w = 1/[\sigma^2(F_o^2) + (0.0567P)^2]$
$wR(F^2) = 0.097$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
2939 reflections	$\Delta\rho_{max} = 0.36$ e Å^{-3}
136 parameters	$\Delta\rho_{min} = -0.30$ e Å^{-3}
1 restraint	

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	$U_{iso}*/U_{eq}$
Si1	0.39406 (5)	0.65611 (4)	0.15682 (3)	0.01408 (12)
O1	0.70378 (11)	0.73383 (10)	0.12400 (7)	0.0157 (2)
O3	0.81381 (12)	0.97690 (11)	−0.10209 (7)	0.0183 (2)
H3	0.9024	1.0067	−0.0879	0.027*
O2	0.89567 (11)	0.91160 (11)	0.06290 (8)	0.0181 (2)
H2	0.8636	0.8703	0.1059	0.027*
C5	0.62375 (16)	0.85346 (14)	−0.02981 (11)	0.0135 (3)
C1	0.44068 (16)	0.73526 (14)	0.04527 (11)	0.0137 (3)
C9	0.47875 (18)	0.48146 (15)	0.18637 (11)	0.0178 (3)
H9A	0.5884	0.4884	0.2002	0.027*
H9B	0.4423	0.4198	0.1307	0.027*
H9C	0.4499	0.4447	0.2437	0.027*
C3	0.35918 (16)	0.84434 (16)	−0.11483 (11)	0.0156 (3)
H3A	0.2810	0.8643	−0.1710	0.019*
C6	0.58695 (16)	0.77454 (15)	0.04402 (11)	0.0129 (3)
C4	0.50551 (17)	0.88657 (15)	−0.11005 (11)	0.0152 (3)
H4	0.5257	0.9389	−0.1622	0.018*
C2	0.32783 (16)	0.77273 (15)	−0.03699 (11)	0.0153 (3)
H2A	0.2267	0.7484	−0.0396	0.018*
C7	0.77696 (18)	0.60998 (17)	0.10250 (12)	0.0212 (4)
H7A	0.8574	0.5845	0.1593	0.032*
H7B	0.8197	0.6265	0.0465	0.032*

H7C	0.7034	0.5350	0.0871	0.032*
C8	0.45625 (19)	0.77761 (16)	0.26146 (12)	0.0201 (3)
H8A	0.4101	0.8680	0.2437	0.030*
H8B	0.5659	0.7866	0.2773	0.030*
H8C	0.4254	0.7419	0.3184	0.030*
C10	0.18585 (17)	0.63586 (17)	0.13142 (13)	0.0212 (4)
H10A	0.1377	0.7259	0.1156	0.032*
H10B	0.1592	0.5980	0.1892	0.032*
H10C	0.1514	0.5731	0.0762	0.032*
B1	0.78433 (19)	0.91554 (17)	−0.02287 (13)	0.0147 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Si1	0.0142 (2)	0.0130 (2)	0.0156 (2)	−0.00051 (17)	0.00465 (16)	0.00139 (17)
O1	0.0130 (5)	0.0178 (5)	0.0149 (5)	0.0014 (4)	0.0006 (4)	0.0013 (4)
O3	0.0152 (5)	0.0225 (6)	0.0175 (6)	−0.0043 (4)	0.0045 (4)	0.0013 (5)
O2	0.0151 (5)	0.0229 (6)	0.0163 (5)	−0.0054 (5)	0.0036 (4)	0.0018 (5)
C5	0.0145 (7)	0.0115 (7)	0.0148 (7)	−0.0002 (6)	0.0044 (6)	−0.0022 (6)
C1	0.0144 (7)	0.0112 (7)	0.0158 (7)	−0.0001 (6)	0.0045 (6)	−0.0018 (6)
C9	0.0205 (8)	0.0158 (7)	0.0172 (8)	−0.0011 (6)	0.0046 (6)	0.0007 (6)
C3	0.0138 (7)	0.0159 (7)	0.0152 (7)	0.0009 (6)	−0.0001 (6)	0.0010 (6)
C6	0.0129 (7)	0.0120 (7)	0.0127 (7)	0.0009 (6)	0.0010 (6)	−0.0019 (6)
C4	0.0189 (8)	0.0134 (7)	0.0137 (7)	−0.0008 (6)	0.0048 (6)	0.0009 (6)
C2	0.0120 (7)	0.0146 (7)	0.0189 (8)	−0.0007 (6)	0.0032 (6)	−0.0018 (6)
C7	0.0189 (8)	0.0213 (8)	0.0235 (9)	0.0057 (6)	0.0054 (7)	0.0040 (7)
C8	0.0259 (9)	0.0175 (8)	0.0182 (8)	−0.0007 (7)	0.0080 (7)	0.0000 (7)
C10	0.0174 (8)	0.0217 (8)	0.0262 (9)	−0.0011 (6)	0.0084 (7)	0.0035 (7)
B1	0.0154 (8)	0.0128 (8)	0.0168 (9)	0.0006 (7)	0.0055 (7)	−0.0025 (7)

Geometric parameters (Å, º)

Si1—C10	1.8668 (16)	C9—H9B	0.9800
Si1—C8	1.8684 (16)	C9—H9C	0.9800
Si1—C9	1.8693 (16)	C3—C2	1.391 (2)
Si1—C1	1.8960 (15)	C3—C4	1.390 (2)
O1—C6	1.4103 (17)	C3—H3A	0.9500
O1—C7	1.4458 (18)	C4—H4	0.9500
O3—B1	1.354 (2)	C2—H2A	0.9500
O3—H3	0.8400	C7—H7A	0.9800
O2—B1	1.381 (2)	C7—H7B	0.9800
O2—H2	0.8400	C7—H7C	0.9800
C5—C6	1.402 (2)	C8—H8A	0.9800
C5—C4	1.401 (2)	C8—H8B	0.9800
C5—B1	1.574 (2)	C8—H8C	0.9800
C1—C2	1.402 (2)	C10—H10A	0.9800
C1—C6	1.401 (2)	C10—H10B	0.9800
C9—H9A	0.9800	C10—H10C	0.9800
C10—Si1—C8	108.52 (8)	C3—C4—C5	121.24 (14)

C10—Si1—C9	107.31 (7)	C3—C4—H4	119.4
C8—Si1—C9	111.49 (7)	C5—C4—H4	119.4
C10—Si1—C1	108.24 (7)	C3—C2—C1	122.12 (14)
C8—Si1—C1	108.39 (7)	C3—C2—H2A	118.9
C9—Si1—C1	112.76 (7)	C1—C2—H2A	118.9
C6—O1—C7	111.44 (11)	O1—C7—H7A	109.5
B1—O3—H3	109.5	O1—C7—H7B	109.5
B1—O2—H2	109.5	H7A—C7—H7B	109.5
C6—C5—C4	116.59 (13)	O1—C7—H7C	109.5
C6—C5—B1	123.85 (13)	H7A—C7—H7C	109.5
C4—C5—B1	119.35 (13)	H7B—C7—H7C	109.5
C2—C1—C6	115.73 (13)	Si1—C8—H8A	109.5
C2—C1—Si1	121.55 (11)	Si1—C8—H8B	109.5
C6—C1—Si1	122.32 (11)	H8A—C8—H8B	109.5
Si1—C9—H9A	109.5	Si1—C8—H8C	109.5
Si1—C9—H9B	109.5	H8A—C8—H8C	109.5
H9A—C9—H9B	109.5	H8B—C8—H8C	109.5
Si1—C9—H9C	109.5	Si1—C10—H10A	109.5
H9A—C9—H9C	109.5	Si1—C10—H10B	109.5
H9B—C9—H9C	109.5	H10A—C10—H10B	109.5
C2—C3—C4	119.67 (14)	Si1—C10—H10C	109.5
C2—C3—H3A	120.2	H10A—C10—H10C	109.5
C4—C3—H3A	120.2	H10B—C10—H10C	109.5
C5—C6—C1	124.48 (14)	O3—B1—O2	118.90 (14)
C5—C6—O1	118.37 (12)	O3—B1—C5	119.49 (14)
C1—C6—O1	117.14 (13)	O2—B1—C5	121.60 (14)
C10—Si1—C1—C2	2.07 (14)	Si1—C1—C6—O1	9.56 (18)
C8—Si1—C1—C2	−115.45 (13)	C7—O1—C6—C5	−83.99 (16)
C9—Si1—C1—C2	120.62 (12)	C7—O1—C6—C1	97.38 (15)
C10—Si1—C1—C6	174.45 (12)	C2—C3—C4—C5	2.7 (2)
C8—Si1—C1—C6	56.93 (14)	C6—C5—C4—C3	0.8 (2)
C9—Si1—C1—C6	−67.00 (14)	B1—C5—C4—C3	−174.09 (14)
C4—C5—C6—C1	−4.2 (2)	C4—C3—C2—C1	−3.1 (2)
B1—C5—C6—C1	170.43 (14)	C6—C1—C2—C3	0.0 (2)
C4—C5—C6—O1	177.24 (12)	Si1—C1—C2—C3	172.85 (11)
B1—C5—C6—O1	−8.1 (2)	C6—C5—B1—O3	172.48 (14)
C2—C1—C6—C5	3.8 (2)	C4—C5—B1—O3	−13.0 (2)
Si1—C1—C6—C5	−168.98 (11)	C6—C5—B1—O2	−8.9 (2)
C2—C1—C6—O1	−177.64 (12)	C4—C5—B1—O2	165.67 (14)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O1	0.84	2.04	2.7532 (14)	142
O3—H3···O2ⁱ	0.84	1.97	2.8051 (14)	175

Symmetry code: (i) −x+2, −y+2, −z.