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1,3-Dimethyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene-1,3-dicarboxylate

Long-tao Yi[a]* and Zhi-qiang Liu[b]

[a]Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310007, People's Republic of China, and [b]State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, People's Republic of China
Correspondence e-mail: cyinyc@163.com

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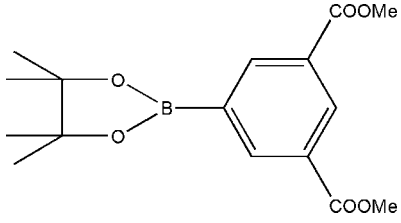
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.046; wR factor = 0.142; data-to-parameter ratio = 18.0.

The title compound, $C_{16}H_{21}BO_6$, has has approximate C_2 symmetry, but no crystallographically imposed molecular symmetry. In the crystal, molecules are packed into parallel columns along the a axis. Short intermolecular C—H···O contacts stabilize the crystal packing.

Related literature

For the synthesis of organoboronic esters, see: Kikuchi *et al.* (2008). For the synthesis of the title compound, see: Coventry *et al.* (2005).



Experimental

Crystal data

$C_{16}H_{21}BO_6$ M_r = 320.14
Orthorhombic, *Pbca*
a = 7.2163 (2) Å
b = 20.9627 (4) Å
c = 22.4624 (4) Å
V = 3397.96 (13) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 296 K
1.00 × 0.40 × 0.20 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.766, T_{max} = 0.982
22413 measured reflections
3864 independent reflections
2177 reflections with $I > 2\sigma(I)$
R_{int} = 0.043

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.142
S = 1.01
3864 reflections
215 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C16—H16*C*···O4^{i}	0.96	2.53	3.381 (3)	148

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5730).

References

Bruker (2005). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Coventry, D. N., Batsanov, A. S., Goeta, A. E. H., Judith, A. K., Marder, T. B. & Perutz, R. N. (2005). *Chem. Commun.* **16**, 2172–2174.
Kikuchi, T., Takagi, J., Isou, H., Ishiyama, T. & Miyaura, N. (2008). *Chem. Asian J.* **3**, 2082–2090.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

Acta Cryst. (2012). E**68**, o275 [doi:10.1107/S1600536811054559]

1,3-Dimethyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene-1,3-dicarboxylate

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S1. Comment

Arylboronic acids and arylborates are the key reagents in Suzuki-Miyaura coupling reaction. Transition metal-catalyzed C—H borylation of arenes is a direct, economical and environmentally kind method to synthesize organoboronic esters and is widely studied (Kikuchi *et al.*, 2008). Recently, we have synthesized the title compound by direct Ir-catalyzed borylation and determined its X-ray structure.

The two *meta*-position methoxycarbonyl are almost co-planar with the benzene ring. The C—B bond is 1.556 (2) Å. Because the borolane ring adopts a somewhat twist conformation and C2, C9 atoms displace to opposite sides of the BO_2 plane, the title molecule has no crystallographic symmetry.

The molecules pack into columns along the *a*- axis uniformly and exhibit paralled patterns. Besides, there are some short intermolecular O···H (for example, O3···H8a, O4···H16c distances are 2.636 Å, 2.530 Å, respectively). We believe that these short intermolecular contacts are helpful for stabilization of the molecular packing in crystals.

S2. Experimental

The title compound was synthesized *via* Ir-catalyzed borylation (Coventry *et al.*, 2005) of diethyl isophthalate. Catalyst precursor $[Ir(COD)]Cl]_2$ (60 mg) and ligand dtbpy (4,4′-di-*tert*-bultyl-2,2′-dipyridyl) (120 mg) with a small amount of B_2pin_2 (pin=$O_2C_2Me_4$) ((160 mg) were loaded in a Schlenk tube and dissolved in 2 ml THF under argon. The mixture was stirred vigorously till the bluish violet solution turned to amaranthine. Then diethyl isophthalate (1.94 g, 10.0 mmol) and B_2pin_2 (2.54 g, 10.0 mmol) in 15 ml THF was added into this tube. The mixture was heated in oil bath at 80°C for 24 h. After cooling to room temperature, the mixture then went through a short silica pad to remove the residual Ir catalyst and the final compound was purified by column chromatography using dichloromethane, giving 2.56 g (80% yield) white crystalline product. Crystals were grown by slow evaporation of a hexane solution.

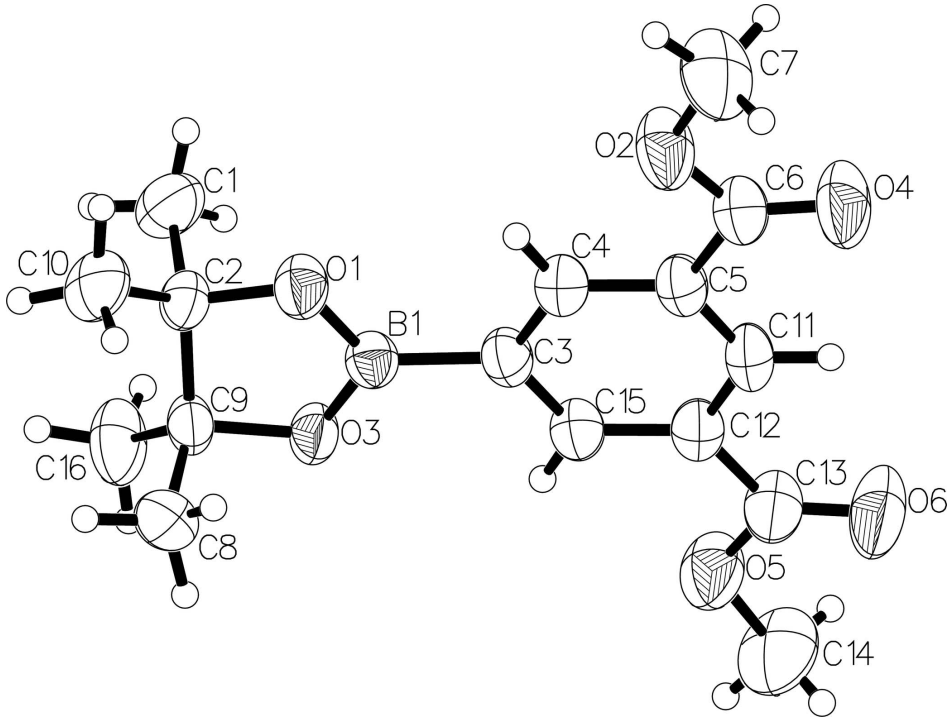

Figure 1

Molecular structure of the title compound. Displacement elliposoid is drawn at 50% probability level.

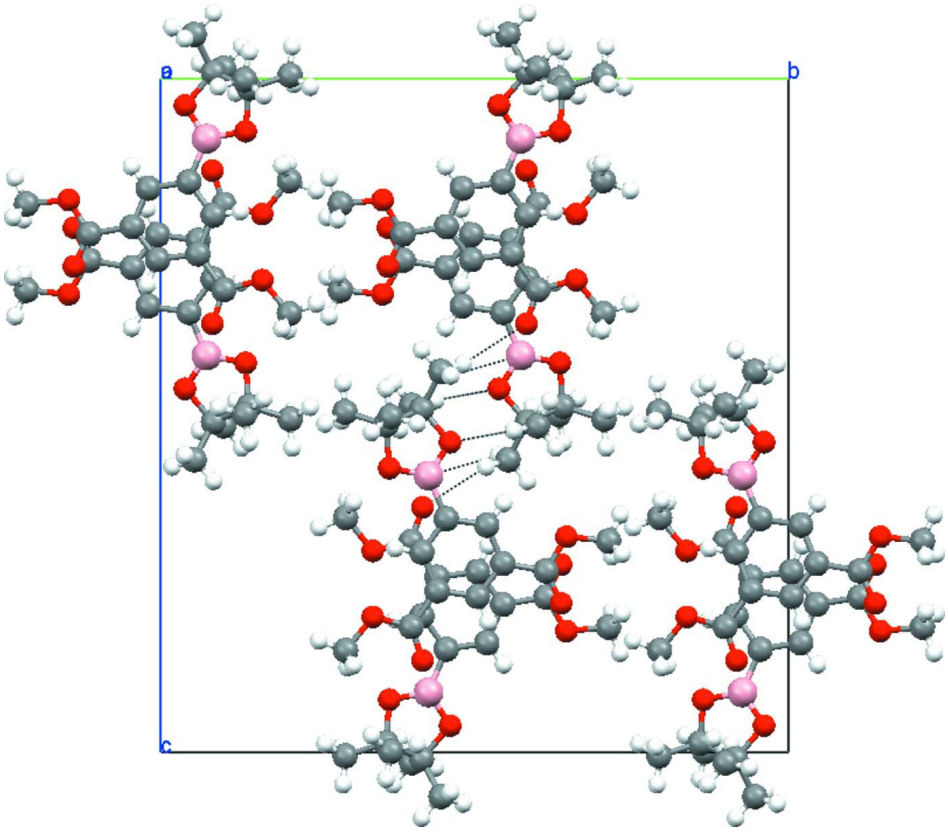

Figure 2

The packing pattern of the title molecules in crystal viewed down the *a*- axis. O···H and B···H intermolecular short contacts are also showed.

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Crystal data

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$M_r = 320.14$
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
$a = 7.2163\ (2)$ Å
$b = 20.9627\ (4)$ Å
$c = 22.4624\ (4)$ Å
$V = 3397.96\ (13)$ Å^3
$Z = 8$
$F(000) = 1360$
$D_x = 1.252$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3703 reflections
$\theta = 2.7–20.6°$
$\mu = 0.09$ mm^{-1}
$T = 296$ K
Pod, colourless
1.00 × 0.40 × 0.20 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min} = 0.766$, $T_{max} = 0.982$
22413 measured reflections
3864 independent reflections
2177 reflections with $I > 2\sigma(I)$
$R_{int} = 0.043$
$\theta_{max} = 27.5°$, $\theta_{min} = 1.8°$
$h = -9\rightarrow9$
$k = -27\rightarrow26$
$l = -27\rightarrow29$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.142$
$S = 1.01$
3864 reflections
215 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0653P)^2 + 0.3179P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.14$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0031 (5)

Special details

Experimental. SADABS (Bruker, 2005) was used for absorption correction. R(int) was 0.0776 before and 0.0475 after correction. The Ratio of minimum to maximum transmission is 0.9190. The $\lambda/2$ correction factor is Not present.

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.67152 (17)	0.13558 (5)	0.42187 (5)	0.0525 (4)
O2	0.6570 (2)	0.16197 (6)	0.20099 (6)	0.0739 (5)
O3	0.74902 (17)	0.03889 (5)	0.46030 (5)	0.0484 (3)
O4	0.6855 (2)	0.08265 (7)	0.13639 (6)	0.0817 (5)
O5	0.8187 (2)	−0.14641 (6)	0.32004 (7)	0.0785 (5)
O6	0.8121 (3)	−0.13786 (7)	0.22123 (7)	0.0903 (6)
C1	0.4427 (3)	0.13373 (9)	0.49842 (10)	0.0679 (6)
H1A	0.3750	0.1642	0.4751	0.102*
H1B	0.4192	0.1411	0.5399	0.102*
H1C	0.4037	0.0914	0.4880	0.102*
C2	0.6479 (2)	0.14086 (7)	0.48620 (8)	0.0439 (4)
C3	0.7180 (2)	0.04498 (8)	0.34685 (7)	0.0452 (4)
C4	0.6938 (2)	0.08372 (9)	0.29731 (8)	0.0474 (4)
H4	0.6698	0.1269	0.3028	0.057*
C5	0.7043 (2)	0.05958 (8)	0.23990 (8)	0.0462 (4)
C6	0.6823 (3)	0.10082 (9)	0.18671 (9)	0.0546 (5)
C7	0.6358 (4)	0.20504 (11)	0.15139 (9)	0.0952 (9)
H7A	0.7436	0.2027	0.1264	0.143*
H7B	0.6216	0.2478	0.1659	0.143*
H7C	0.5282	0.1933	0.1288	0.143*
C8	0.9702 (3)	0.10025 (10)	0.51525 (9)	0.0702 (6)

H8A	1.0391	0.0619	0.5225	0.105*
H8B	0.9880	0.1293	0.5478	0.105*
H8C	1.0128	0.1197	0.4790	0.105*
C9	0.7647 (3)	0.08423 (8)	0.50955 (7)	0.0461 (4)
C10	0.7157 (3)	0.20608 (8)	0.50516 (9)	0.0651 (6)
H10A	0.8413	0.2118	0.4922	0.098*
H10B	0.7102	0.2094	0.5477	0.098*
H10C	0.6386	0.2383	0.4876	0.098*
C11	0.7376 (3)	−0.00497 (9)	0.23160 (8)	0.0515 (5)
H11	0.7437	−0.0216	0.1933	0.062*
C12	0.7619 (2)	−0.04497 (8)	0.28033 (8)	0.0481 (5)
C13	0.7995 (3)	−0.11372 (10)	0.26942 (10)	0.0621 (6)
C14	0.8615 (5)	−0.21352 (10)	0.31398 (12)	0.1040 (9)
H14A	0.7605	−0.2348	0.2945	0.156*
H14B	0.8803	−0.2318	0.3527	0.156*
H14C	0.9721	−0.2184	0.2907	0.156*
C15	0.7531 (2)	−0.01959 (8)	0.33725 (8)	0.0488 (5)
H15	0.7709	−0.0463	0.3698	0.059*
C16	0.6931 (4)	0.05342 (10)	0.56561 (9)	0.0764 (7)
H16A	0.5692	0.0383	0.5591	0.115*
H16B	0.6928	0.0841	0.5973	0.115*
H16C	0.7717	0.0182	0.5761	0.115*
B1	0.7131 (3)	0.07327 (9)	0.41089 (9)	0.0421 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0751 (9)	0.0423 (7)	0.0400 (7)	0.0040 (6)	−0.0016 (6)	−0.0003 (5)
O2	0.1243 (13)	0.0555 (9)	0.0418 (8)	−0.0010 (8)	−0.0037 (8)	0.0037 (6)
O3	0.0700 (9)	0.0377 (6)	0.0375 (7)	0.0065 (5)	−0.0026 (6)	−0.0054 (5)
O4	0.1359 (14)	0.0728 (10)	0.0364 (8)	0.0053 (9)	0.0016 (8)	−0.0029 (7)
O5	0.1204 (13)	0.0542 (9)	0.0610 (10)	0.0147 (8)	0.0004 (9)	−0.0028 (7)
O6	0.1523 (17)	0.0612 (9)	0.0573 (10)	0.0077 (9)	0.0085 (10)	−0.0174 (7)
C1	0.0513 (12)	0.0673 (13)	0.0853 (16)	0.0041 (10)	0.0048 (11)	−0.0188 (11)
C2	0.0520 (11)	0.0382 (9)	0.0417 (10)	0.0004 (7)	0.0012 (8)	−0.0070 (7)
C3	0.0483 (10)	0.0526 (10)	0.0349 (10)	−0.0010 (8)	0.0002 (8)	−0.0016 (8)
C4	0.0514 (11)	0.0490 (10)	0.0419 (10)	−0.0024 (8)	0.0019 (8)	−0.0032 (8)
C5	0.0492 (11)	0.0538 (11)	0.0357 (10)	−0.0045 (8)	0.0019 (8)	−0.0023 (8)
C6	0.0643 (13)	0.0580 (12)	0.0415 (12)	−0.0046 (9)	0.0020 (9)	−0.0024 (9)
C7	0.165 (3)	0.0633 (14)	0.0578 (15)	0.0008 (15)	−0.0084 (15)	0.0172 (12)
C8	0.0604 (14)	0.0768 (14)	0.0736 (15)	0.0113 (10)	−0.0213 (11)	−0.0182 (11)
C9	0.0623 (12)	0.0421 (9)	0.0337 (10)	0.0029 (8)	−0.0058 (8)	−0.0074 (7)
C10	0.0740 (14)	0.0416 (10)	0.0797 (16)	−0.0033 (9)	−0.0017 (11)	−0.0137 (10)
C11	0.0601 (12)	0.0596 (11)	0.0349 (10)	−0.0051 (9)	0.0023 (8)	−0.0088 (9)
C12	0.0517 (11)	0.0502 (10)	0.0424 (11)	−0.0024 (8)	0.0007 (8)	−0.0064 (8)
C13	0.0777 (15)	0.0574 (12)	0.0514 (13)	−0.0001 (10)	0.0035 (11)	−0.0059 (10)
C14	0.163 (3)	0.0530 (14)	0.096 (2)	0.0214 (15)	0.0036 (18)	0.0028 (13)
C15	0.0546 (11)	0.0509 (11)	0.0410 (10)	−0.0012 (8)	0.0001 (8)	−0.0019 (8)

C16	0.128 (2)	0.0618 (13)	0.0393 (12)	0.0006 (12)	0.0063 (12)	0.0024 (10)
B1	0.0470 (11)	0.0404 (10)	0.0390 (12)	−0.0019 (8)	−0.0001 (9)	0.0004 (9)

Geometric parameters (Å, º)

O1—B1	1.363 (2)	C7—H7A	0.9600
O1—C2	1.459 (2)	C7—H7B	0.9600
O2—C6	1.334 (2)	C7—H7C	0.9600
O2—C7	1.442 (2)	C8—C9	1.526 (3)
O3—B1	1.349 (2)	C8—H8A	0.9600
O3—C9	1.4629 (19)	C8—H8B	0.9600
O4—C6	1.193 (2)	C8—H8C	0.9600
O5—C13	1.335 (2)	C9—C16	1.506 (3)
O5—C14	1.447 (2)	C10—H10A	0.9600
O6—C13	1.198 (2)	C10—H10B	0.9600
C1—C2	1.514 (3)	C10—H10C	0.9600
C1—H1A	0.9600	C11—C12	1.390 (2)
C1—H1B	0.9600	C11—H11	0.9300
C1—H1C	0.9600	C12—C15	1.386 (2)
C2—C10	1.513 (2)	C12—C13	1.487 (3)
C2—C9	1.547 (2)	C14—H14A	0.9600
C3—C4	1.389 (2)	C14—H14B	0.9600
C3—C15	1.394 (2)	C14—H14C	0.9600
C3—B1	1.556 (2)	C15—H15	0.9300
C4—C5	1.387 (2)	C16—H16A	0.9600
C4—H4	0.9300	C16—H16B	0.9600
C5—C11	1.387 (3)	C16—H16C	0.9600
C5—C6	1.483 (3)		
B1—O1—C2	106.12 (12)	O3—C9—C16	109.10 (14)
C6—O2—C7	115.49 (16)	O3—C9—C8	106.34 (14)
B1—O3—C9	106.86 (13)	C16—C9—C8	110.94 (17)
C13—O5—C14	116.17 (17)	O3—C9—C2	101.54 (12)
C2—C1—H1A	109.5	C16—C9—C2	115.20 (16)
C2—C1—H1B	109.5	C8—C9—C2	112.88 (15)
H1A—C1—H1B	109.5	C2—C10—H10A	109.5
C2—C1—H1C	109.5	C2—C10—H10B	109.5
H1A—C1—H1C	109.5	H10A—C10—H10B	109.5
H1B—C1—H1C	109.5	C2—C10—H10C	109.5
O1—C2—C10	108.03 (14)	H10A—C10—H10C	109.5
O1—C2—C1	106.63 (14)	H10B—C10—H10C	109.5
C10—C2—C1	110.76 (15)	C5—C11—C12	120.31 (16)
O1—C2—C9	102.36 (12)	C5—C11—H11	119.8
C10—C2—C9	114.95 (15)	C12—C11—H11	119.8
C1—C2—C9	113.30 (15)	C15—C12—C11	119.27 (17)
C4—C3—C15	117.82 (16)	C15—C12—C13	122.17 (17)
C4—C3—B1	121.00 (16)	C11—C12—C13	118.56 (17)
C15—C3—B1	121.15 (16)	O6—C13—O5	123.02 (19)

C5—C4—C3	121.65 (17)	O6—C13—C12	124.89 (19)
C5—C4—H4	119.2	O5—C13—C12	112.09 (17)
C3—C4—H4	119.2	O5—C14—H14A	109.5
C11—C5—C4	119.35 (16)	O5—C14—H14B	109.5
C11—C5—C6	118.62 (16)	H14A—C14—H14B	109.5
C4—C5—C6	122.02 (16)	O5—C14—H14C	109.5
O4—C6—O2	122.50 (18)	H14A—C14—H14C	109.5
O4—C6—C5	125.10 (18)	H14B—C14—H14C	109.5
O2—C6—C5	112.40 (16)	C12—C15—C3	121.59 (17)
O2—C7—H7A	109.5	C12—C15—H15	119.2
O2—C7—H7B	109.5	C3—C15—H15	119.2
H7A—C7—H7B	109.5	C9—C16—H16A	109.5
O2—C7—H7C	109.5	C9—C16—H16B	109.5
H7A—C7—H7C	109.5	H16A—C16—H16B	109.5
H7B—C7—H7C	109.5	C9—C16—H16C	109.5
C9—C8—H8A	109.5	H16A—C16—H16C	109.5
C9—C8—H8B	109.5	H16B—C16—H16C	109.5
H8A—C8—H8B	109.5	O3—B1—O1	113.93 (15)
C9—C8—H8C	109.5	O3—B1—C3	123.55 (16)
H8A—C8—H8C	109.5	O1—B1—C3	122.52 (16)
H8B—C8—H8C	109.5		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C16—H16*C*···O4^{i}	0.96	2.53	3.381 (3)	148

Symmetry code: (i) −*x*+3/2, −*y*, *z*+1/2.