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8,10-Diiodo-2,6-dioxo-4λ^3-ioda-3,5-dioxatricyclo[5.3.1.0^{4,11}]undeca-1(11),7,9-triene-9-carboxylic acid

Daopeng Sheng, Lu Han, Yi Zhang and Yanzhao Yang*

Key Laboratory for Special Functional Aggregated Materials of the Education Ministry, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, People's Republic of China
Correspondence e-mail: yzhyang@sdu.edu.cn

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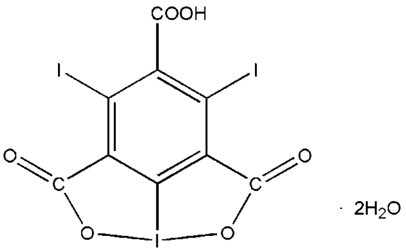
Key indicators: single-crystal X-ray study; T = 130 K; mean σ(C–C) = 0.010 Å; R factor = 0.042; wR factor = 0.097; data-to-parameter ratio = 16.6.

In the title compound, $C_9HI_3O_6\cdot 2H_2O$, the molecule is located on a twofold axis that gives rise to disorder of the carboxyl group. This disorder is correlated with the disorder of one of the H atoms of the water molecule. The carboxyl group is twisted relative to the attached benzene ring by 75.1 (4)°. The intramolecular I$\cdots$O distance is 2.112 (6) Å. Molecules are linked *via* O—H$\cdots$O hydrogen bonding, C—I$\cdots$O halogen bonding, with I$\cdots$O distances in the range 3.156 (5)–3.274 (6) Å, and dipolar C=O$\cdots$C=O interactions between the carboxyl and carboxylate groups, with an O$\cdots$C distance of 2.944 (10) Å.

Related literature

For general background to 1,3,5-triiodobenzene derivatives, see: Morin *et al.* (1987); Yu & Watson (1999). For information on the related compound 1,3,5-triiodo-2,4,6-trimethylbenzene, see: Bosch & Barnes (2002); Boudjada *et al.* (2001); Reddy *et al.* (2006). For the crystal structures of 5-amino-2,4,6-triiodoisophthalic acid monohydrate and 5-amino-2,4,6-triiodoisophthalic acid–4,4′-bipyridine *N*,*N*′-dioxide–water (1/1/1), see: Beck & Sheldrick (2008); Zhang *et al.* (2011).



Experimental

Crystal data

$C_9HI_3O_6\cdot 2H_2O$
M_r = 621.83
Monoclinic, $C2/c$
a = 14.7667 (8) Å
b = 11.9890 (6) Å
c = 9.7419 (5) Å
β = 127.4236 (5)°
V = 1369.68 (12) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 6.88 mm^{-1}
T = 130 K
0.32 × 0.14 × 0.12 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*APEX2*; Bruker, 2007) $T_{\min}$ = 0.217, $T_{\max}$ = 0.492
4078 measured reflections
1547 independent reflections
1515 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.016

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.097
S = 1.23
1547 reflections
93 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 2.36 e Å^{-3}
$\Delta\rho_{\min}$ = −2.23 e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H3$\cdots$O1W	0.82	2.08	2.772 (9)	142
O1W—H1$W\cdots$O3	0.82	1.98	2.772 (9)	163
O1W—H2$W\cdots$O1$W^{\rm i}$	0.82	1.94	2.730 (14)	160
O1W—H3$W\cdots$O1$^{\rm ii}$	0.82	2.24	3.053 (9)	172

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2447).

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Beck, T. & Sheldrick, G. M. (2008). *Acta Cryst.* E**64**, o1286.
Bosch, E. & Barnes, C. L. (2002). *Cryst. Growth Des.* **2**, 299–302.
Boudjada, A., Hernandez, O., Meinnel, J., Mani, M. & Paulus, W. (2001). *Acta Cryst.* C**57**, 1106–1108.
Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Morin, J. P., Boutelet, I., Toutain, H. & Fillastre, J. P. (1987). *Pathol. Biol.* **35**, 1215–1220.
Reddy, C. M., Kirchner, M. T., Gundakaram, R. C., Padmanabhan, K. A. & Desiraju, G. R. (2006). *Chem. Eur. J.* **12**, 2222–2234.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Yu, S. B. & Watson, A. D. (1999). *Chem. Rev.* **99**, 2353–2378.
Zhang, K.-L., Zhang, J.-B. & Ng, S. W. (2011). *Acta Cryst.* E**67**, o793.

supplementary materials

Acta Cryst. (2012). E**68**, o706 [doi:10.1107/S1600536812005351]

8,10-Diiodo-2,6-dioxo-4λ^3-ioda-3,5-dioxatricyclo[5.3.1.0^{4,11}]undeca-1(11),7,9-triene-9-carboxylic acid

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Comment

Iodine-based compounds have always been used as contrast agents for X-ray imaging (Morin *et al.*, 1987). The 1,3,5-tri-iodo-benzene core has been the basis of many contrast agents (Yu & Watson, 1999). In this paper, we present the crystal structure of a new compound based on 1,3,5-triiodobenzene core.

In the title compound the organic molecule is located on a twofold axis what results in disorder of the carboxylic group (Fig. 1). In the crystal structure, there are hydrogen bonds between symmetry related water molecules as well as between the water molecule and the carboxylic group. It indicates that one of the hydrogen atoms of the water molecule has to be disordered and this disorder is evidently correlated with the disorder of the carboxylic group. The hydrogen atom and the oxygen atom forming hydrogen bond between the water molecule and the carboxylic group are either from the water molecule or the carboxylic group. There is also a hydrogen bond between the water molecule and the carboxylate O1 atom. Hydrogen atom involved in this interaction has full occupancy. The dihedral angle between the plane of the carboxyl group and the benzene ring is 75.1 (4)°.

In addition to hydrogen bond, the structure is stabilized by halogen bonding between the I2 atom and the carboxylate group O1 and O2 atoms. There is also a halogen bond between the water molecule and I1 atom (Fig. 2). A dipolar interaction between carboxyl C6—O3 and carboxylate C4 also is observed (C···O 2.95 Å) (Fig. 3).

Experimental

A mixture of 1,3,5-triiodo-2,4,6-trimethylbenzene (5 g) and excess of potassium permanganate (80 g) was dissolved in pyridine (60 ml) and heated under reflux for 24 h to produce the title compound (m.p. 573 K, decompose). Crystallization was carried out from a mixture of water and methanol (*v*/*v* 1:2). Colorless crystals suitable for X-ray single-crystal diffraction were obtained by slow evaporation method.

Refinement

H atom of the carboxylic group was placed in geometrically calculated position and refined using a riding model the the occupantion factor of 0.5. Positions of H atoms from the water molecule were calculated after analysis of possible hydrogen-bond interactions. The occupantion factors of H1W and H2W were assigned as 0.5.

The isotropic displacement parameters of all H atoms were set to 1.5 times the equivalent displacement parameter of their parent O atoms.

Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *APEX2* (Bruker, 2007); data reduction: *APEX2* (Bruker, 2007); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97*

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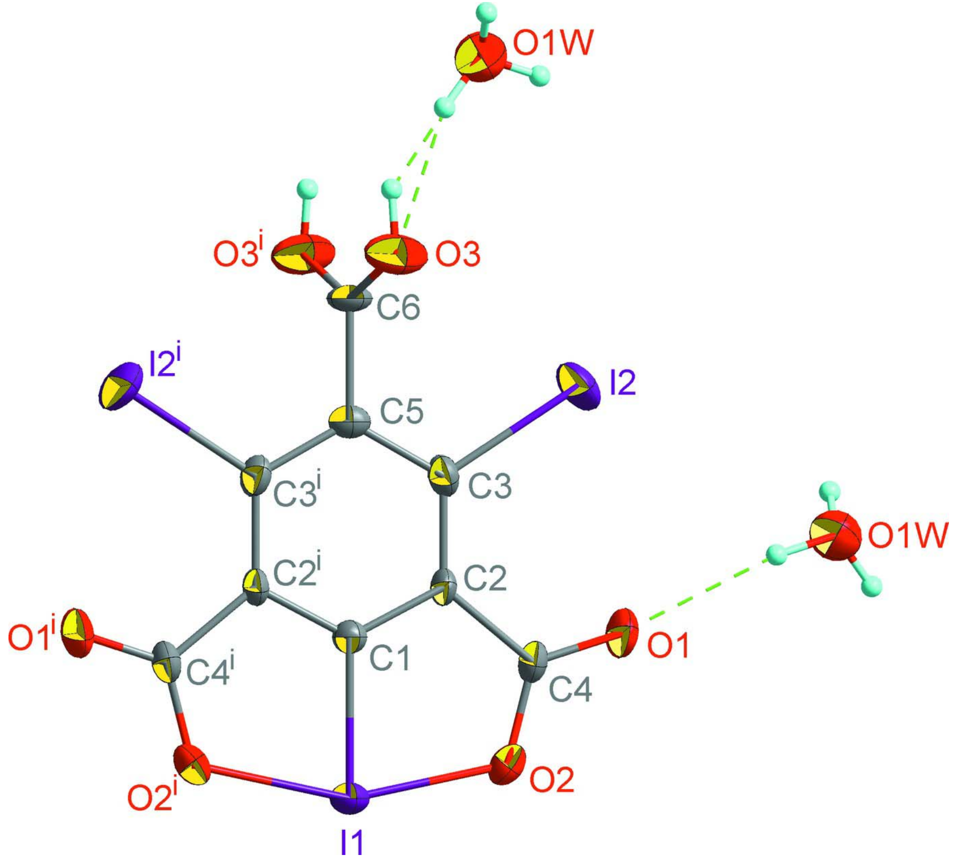

Figure 1

Molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. Symmetry code: (i) 1 - *x*, *y*, 1.5 + *z*.

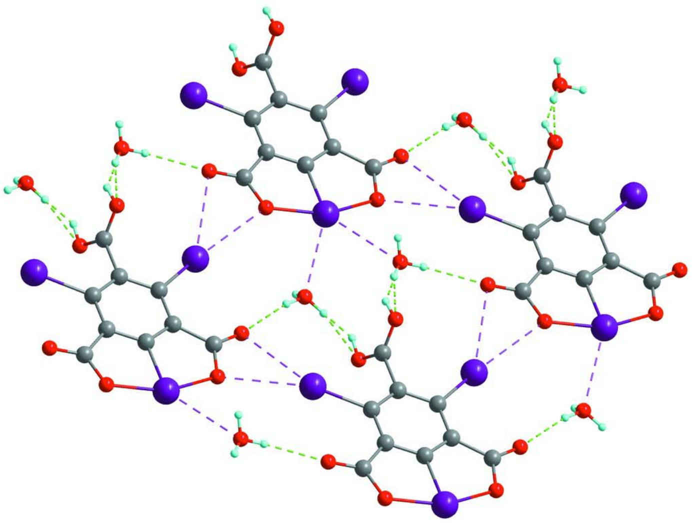

Figure 2

Partial view of the crystal structure. Molecules are linked by O—H···O (green dashed lines) and O—H···I hydrogen bonds (purple dashed lines).

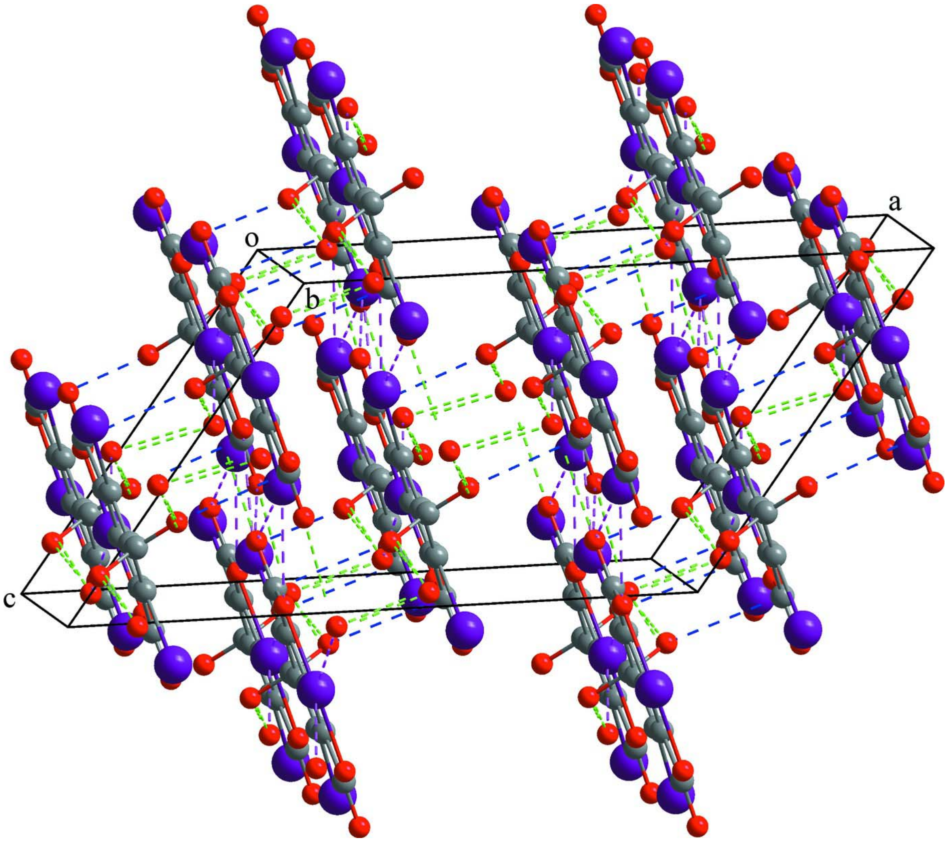

Figure 3

Packing of the title compound, hydrogen atoms are omitted for clarity. Hydrogen bonds (green), halogen bonds (purple) and dipolar interaction (blue) are shown as dashed lines.

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Crystal data

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b = 11.9890 (6) Å
c = 9.7419 (5) Å
β = 127.4236 (5)°
V = 1369.68 (12) Å^3
Z = 4

$F(000)$ = 1128
D_x = 3.016 Mg m^{-3}
Melting point: 573 K
Mo $K\alpha$ radiation, λ = 0.71069 Å
Cell parameters from 3350 reflections
θ = 2.4–27.4°
μ = 6.88 mm^{-1}
T = 130 K
Prism, colourless
0.32 × 0.14 × 0.12 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*APEX2*; Bruker, 2007)
$T_{\min}$ = 0.217, $T_{\max}$ = 0.492

4078 measured reflections
1547 independent reflections
1515 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
$\theta_{\max}$ = 27.4°, $\theta_{\min}$ = 2.4°
$h = -10 \rightarrow 19$
$k = -14 \rightarrow 15$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.097
S = 1.23
1547 reflections
93 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
$w = 1/[\sigma^2(F_o^2) + (0.0157P)^2 + 40.7765P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 2.36 e Å^{-3}
$\Delta\rho_{\min}$ = −2.23 e Å^{-3}

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.

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}	Occ. (<1)
C1	0.5000	0.3381 (8)	0.7500	0.0216 (19)	
C2	0.4147 (5)	0.3903 (6)	0.5979 (8)	0.0207 (13)	
C3	0.4155 (6)	0.5066 (6)	0.5979 (9)	0.0249 (14)	
C4	0.3340 (6)	0.3120 (6)	0.4528 (9)	0.0248 (14)	

C5	0.5000	0.5629 (8)	0.7500	0.0222 (19)	
C6	0.5000	0.6916 (8)	0.7500	0.027 (2)	
I1	0.5000	0.16946 (5)	0.7500	0.02526 (18)	
I2	0.29502 (5)	0.59994 (5)	0.37929 (8)	0.0469 (2)	
O1	0.2532 (5)	0.3419 (5)	0.3093 (7)	0.0386 (14)	
O2	0.3559 (5)	0.2049 (5)	0.4946 (7)	0.0313 (12)	
O3	0.5338 (6)	0.7375 (5)	0.6751 (9)	0.0474 (16)	
H3	0.5308	0.8054	0.6818	0.071*	0.50
O1W	0.4370 (6)	0.9449 (6)	0.5383 (9)	0.0494 (16)	
H1W	0.4763	0.8910	0.5958	0.074*	0.50
H2W	0.4756	0.9896	0.5303	0.074*	0.50
H3W	0.3831	0.9240	0.4416	0.074*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.021 (4)	0.019 (4)	0.021 (5)	0.000	0.011 (4)	0.000
C2	0.017 (3)	0.024 (3)	0.012 (3)	0.000 (2)	0.004 (2)	−0.001 (2)
C3	0.021 (3)	0.030 (4)	0.017 (3)	0.005 (3)	0.008 (3)	0.004 (3)
C4	0.021 (3)	0.031 (4)	0.015 (3)	−0.002 (3)	0.007 (3)	−0.003 (3)
C5	0.026 (5)	0.018 (4)	0.029 (5)	0.000	0.020 (4)	0.000
C6	0.039 (6)	0.012 (4)	0.035 (6)	0.000	0.025 (5)	0.000
I1	0.0282 (3)	0.0169 (3)	0.0269 (3)	0.000	0.0148 (3)	0.000
I2	0.0427 (4)	0.0392 (3)	0.0341 (3)	0.0125 (2)	0.0104 (3)	0.0160 (2)
O1	0.031 (3)	0.042 (3)	0.019 (3)	0.000 (3)	0.003 (2)	−0.004 (2)
O2	0.030 (3)	0.029 (3)	0.024 (3)	−0.008 (2)	0.011 (2)	−0.008 (2)
O3	0.074 (5)	0.028 (3)	0.069 (5)	0.000 (3)	0.058 (4)	0.005 (3)
O1W	0.050 (4)	0.044 (4)	0.048 (4)	−0.008 (3)	0.026 (3)	−0.002 (3)

Geometric parameters (Å, º)

C1—C2$^{\mathrm{i}}$	1.380 (8)	C5—C3$^{\mathrm{i}}$	1.400 (8)
C1—I1	2.022 (9)	C5—C6	1.543 (13)
C2—C3	1.394 (10)	C6—O3	1.237 (7)
C2—C4	1.501 (9)	I1—O2	2.113 (5)
C3—C5	1.400 (8)	O3—H3	0.8200
C3—I2	2.085 (7)	O1W—H1W	0.8201
C4—O1	1.216 (9)	O1W—H2W	0.8200
C4—O2	1.326 (9)	O1W—H3W	0.8201
C4···O3$^{\mathrm{ii}}$	2.944 (10)	I2···O2$^{\mathrm{iv}}$	3.156 (5)
I1···O1W$^{\mathrm{iii}}$	3.173 (7)	I2···O1$^{\mathrm{iv}}$	3.274 (6)
C2$^{\mathrm{i}}$—C1—C2	126.1 (9)	C3—C5—C3$^{\mathrm{i}}$	122.3 (9)
C2$^{\mathrm{i}}$—C1—I1	117.0 (5)	C3—C5—C6	118.8 (5)
C2—C1—I1	117.0 (5)	O3$^{\mathrm{i}}$—C6—O3	127.1 (10)
C1—C2—C3	116.8 (6)	O3—C6—C5	116.5 (5)
C1—C2—C4	114.3 (6)	C1—I1—O2	78.38 (15)
C3—C2—C4	128.9 (6)	O2$^{\mathrm{i}}$—I1—O2	156.8 (3)
C2—C3—C5	119.0 (7)	C4—O2—I1	116.1 (4)

C2—C3—I2	122.3 (5)	C6—O3—H3	109.5
C5—C3—I2	118.7 (6)	H1W—O1W—H2W	109.6
O1—C4—O2	121.6 (7)	H1W—O1W—H3W	109.5
O1—C4—C2	124.1 (7)	H2W—O1W—H3W	109.6
O2—C4—C2	114.2 (6)		

C2^{i}—C1—C2—C3	0.5 (5)	I2—C3—C5—C3^{i}	−179.6 (5)
I1—C1—C2—C3	−179.5 (5)	C2—C3—C5—C6	−179.5 (5)
C2^{i}—C1—C2—C4	179.7 (6)	I2—C3—C5—C6	0.4 (5)
I1—C1—C2—C4	−0.3 (6)	C3—C5—C6—O3^{i}	105.1 (5)
C1—C2—C3—C5	−0.9 (9)	C3—C5—C6—O3	−74.9 (5)
C4—C2—C3—C5	180.0 (6)	C3^{i}—C5—C6—O3	105.1 (5)
C1—C2—C3—I2	179.1 (4)	C2^{i}—C1—I1—O2	179.6 (4)
C4—C2—C3—I2	0.1 (11)	C2—C1—I1—O2	−0.4 (4)
C1—C2—C4—O1	179.7 (7)	O1—C4—O2—I1	180.0 (6)
C3—C2—C4—O1	−1.3 (13)	C2—C4—O2—I1	−1.5 (8)
C1—C2—C4—O2	1.2 (9)	C1—I1—O2—C4	1.1 (5)
C3—C2—C4—O2	−179.7 (7)	O2^{i}—I1—O2—C4	1.1 (5)
C2—C3—C5—C3^{i}	0.5 (5)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O1*W*	0.82	2.08	2.772 (9)	142
O1*W*—H1*W*···O3	0.82	1.98	2.772 (9)	163
O1*W*—H2*W*···O1*W*^{v}	0.82	1.94	2.730 (14)	160
O1*W*—H3*W*···O1^{iv}	0.82	2.24	3.053 (9)	172

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