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# Dimethyl 4,5-dichlorophthalate

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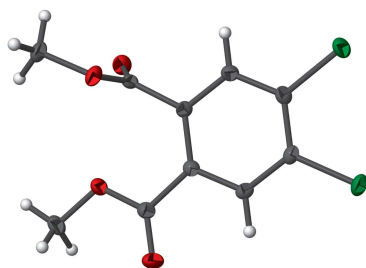
Keywords: crystal structure; carbonyl; ester; metathesis; catalyst.

CCDC reference: 720360

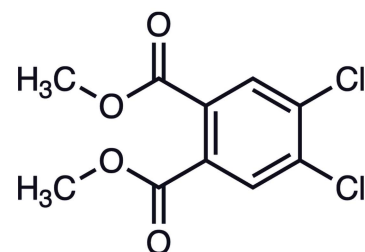
Structural data: full structural data are available from iucrdata.iucr.org

While endeavoring to synthesize new chlorinated ligands for ruthenium-based metathesis catalysts, the title compound dimethyl 4,5-dichlorophthalate,  $C_{10}H_8Cl_2O_4$ , was prepared from commercially available 4,5-dichlorophthalic acid in  $\sim 77\%$  yield. The title molecule, which also finds utility as a precursor molecule for the synthesis of drugs used in the treatment of Alzheimer's disease, shows one carbonyl-containing methyl ester moiety lying nearly co-planar with the chlorine-derivatized aromatic ring while the second methyl ester shows a significant deviation of  $101.05(12)^\circ$  from the least-squares plane of the aromatic ring. Within the crystal, structural integrity is maintained by the concerted effects of electrostatic interactions involving the electron-deficient carbonyl carbon atom and the electron-rich aromatic ring along the  $a$ -axis direction and  $C-H \cdots O$  hydrogen bonds between neighboring molecules parallel to  $b$ .

## 3D view



## Chemical scheme



## Structure description

While endeavoring to synthesize new chlorinated ligands for ruthenium-based metathesis catalysts (Anderson *et al.*, 2006), the title compound, **1**, was prepared from commercially available 4,5-dichlorophthalic acid in  $\sim 77\%$  yield. The title molecule also finds utility as a precursor molecule for the synthesis of drugs used in the treatment of Alzheimer's disease (Hennessy & Buchwald, 2005).

Compound **1** crystallizes in the centrosymmetric triclinic space group  $P\bar{1}$  with a full molecule of the title compound as the contents of asymmetric unit (Fig. 1, Table 1). Within the structure of **1**, one of the carbonyl-containing ester groups is nearly co-planar with the aromatic ring demonstrating a deviation of  $3.41(12)^\circ$  from the least-squares plane of the chlorine-derivatized aromatic ring. The second ester group reveals a much

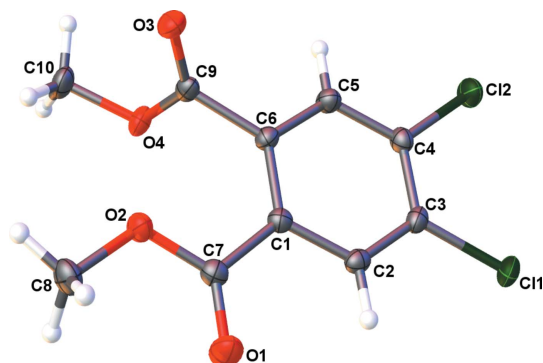


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**Table 1**  
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C5-H5\cdots O1^i$	0.95	2.33	3.2327 (15)	159
$C10-H10B\cdots O3^{ii}$	0.98	2.68	3.5380 (16)	147

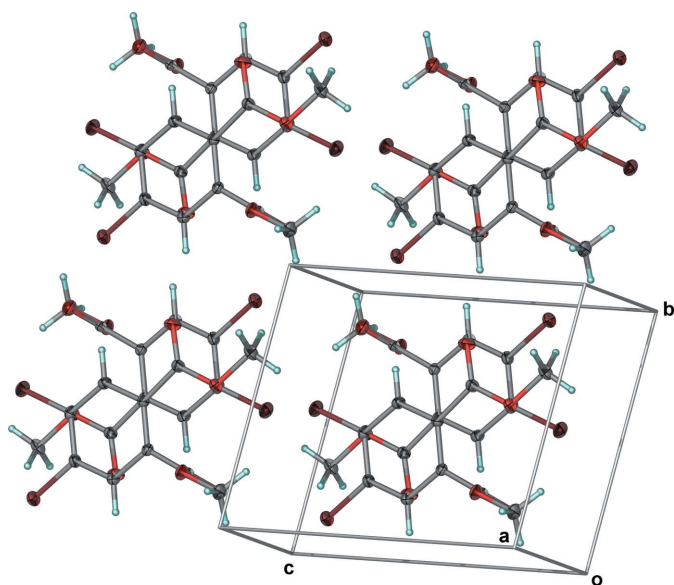
Symmetry codes: (i)  $x, y-1, z$ ; (ii)  $-x+1, -y, -z$ .



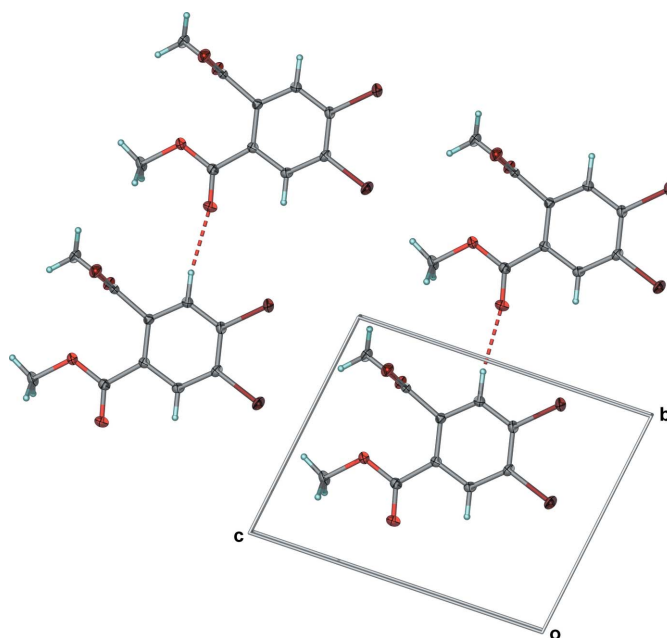
**Figure 1**  
Anisotropic displacement ellipsoid plot of **1** with ellipsoids set to the 50% probability level.

larger deviation from planarity as the dihedral angle involving the second carbonyl group is  $101.05(12)^\circ$ .

Looking down the  $a$ -axis, and involving a second molecule of **1** related by inversion, the centroid of the electron-rich, chlorine-derivatized aromatic ring of the first molecule lies above the electron-deficient carbonyl carbon atom of the second at a distance of  $3.4600(12)$  Å, suggesting the presence of electrostatic interactions (Fig. 2). In addition to the electrostatic interactions, when looking into the  $bc$ -plane, between

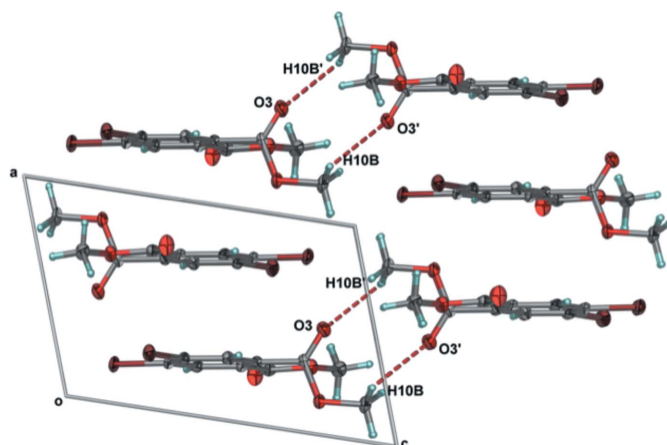


**Figure 2**  
Solid-state expansion of **1** showing the superposition of the electron-rich aromatic ring centroid and the electron-deficient carbonyl carbon atom. Anisotropic displacement ellipsoids have been set to the 50% probability level.



**Figure 3**  
Projection of **1** within the  $bc$ -plane showing the  $C-H\cdots O$  hydrogen bonding between neighboring molecules along  $b$  to form one-dimensional arrays. Anisotropic displacement ellipsoids have been set to the 50% probability level. Dashed lines represent hydrogen bonds.

$H5$  on the aromatic ring and  $O1$  from the carbonyl that is nearly co-planar with the aromatic ring, a  $C-H\cdots O$  [ $d(C5\cdots O1) = 3.23$  Å;  $\Theta(C5-H5-O1) = 159^\circ$ ] hydrogen bond was observed (Fig. 3, Table 2). A one-dimensional array of symmetry-equivalent molecules of **1** linked by  $C-H\cdots O$  hydrogen bonds results along the  $b$ -axis direction when looking into the  $bc$ -plane (Fig. 3). While there are no additional interactions between neighboring, co-planar one-dimensional arrays parallel to one another along  $c$ , weak  $C-H\cdots O$  [ $d(C10\cdots O3) = 3.54$  Å;  $\Theta(C10-H10B-O3) = 147^\circ$ ] interactions with a neighboring layer having the symmetry



**Figure 4**  
Projection of **1** within the  $ac$ -plane showing the formation of the  $R_2^2(10)$  centrosymmetric dimer facilitated by weak  $C-H\cdots O$  interactions between layers. Anisotropic displacement ellipsoids have been set to the 50% probability level. Dashed lines represent the  $C-H\cdots O$  interactions.

Table 2

Experimental details.

Crystal data	
Chemical formula	C <sub>10</sub> H <sub>8</sub> Cl <sub>2</sub> O <sub>4</sub>
<i>M<sub>r</sub></i>	263.06
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.0204 (6), 7.7661 (6), 10.5392 (8)
$\alpha$ , $\beta$ , $\gamma$ (°)	97.733 (1), 109.293 (1), 90.217 (1)
<i>V</i> (Å <sup>3</sup> )	536.69 (7)
<i>Z</i>	2
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.60
Crystal size (mm)	0.35 × 0.29 × 0.28
Data collection	
Diffractometer	Bruker <i>APEX</i> CCD area detector
Absorption correction	Multi-scan ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.838, 0.927
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	5934, 2582, 2417
<i>R<sub>int</sub></i>	0.031
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.668
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.026, 0.073, 1.04
No. of reflections	2582
No. of parameters	147
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.45, -0.21

Computer programs: *APEX2* and *SAINT* (Bruker, 2016), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2014/7* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

code (1 - *x*, -*y*, -*z*) yielded a centrosymmetric dimer (Fig. 4, Table 2) having the *R*<sub>2</sub><sup>2</sup>(10) graph-set notation (Bernstein *et al.*, 1995).

### Synthesis and crystallization

Compound **1** was synthesized by adding 4,5-dichlorophthalic acid (23.68 mmol, 5.566 g) to 70 ml of CH<sub>3</sub>OH in a 200 ml flask. While stirring, 1.0 ml H<sub>2</sub>SO<sub>4</sub> (98%) was added dropwise

and the mixture was allowed to reflux at 70°C overnight. The product was extracted with ethyl acetate, and washed with water, concentrated NaHCO<sub>3</sub>, 10% NaHCO<sub>3</sub>, and then a saturated solution of NaCl. After filtering through Na<sub>2</sub>SO<sub>4</sub> to remove trace moisture, the solvent was removed *in vacuo* to yield a clear oil, which later crystallized into small rods. Recrystallization from the mixed solvents of isopropyl alcohol and dichloromethane produced X-ray quality crystals of **1** up to 2 mm.

### Refinement

Crystal data, data collection and structure refinement details for **1** are summarized in Table 2. The choice of the space group *P* $\bar{1}$  for **1** was unambiguously verified by *PLATON* (Spek, 2003; Spek, 2020).

### Funding information

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## full crystallographic data

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## Dimethyl 4,5-dichlorophthalate

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*Crystal data*

$C_{10}H_8Cl_2O_4$	$Z = 2$
$M_r = 263.06$	$F(000) = 268$
Triclinic, $P\bar{1}$	$D_x = 1.628 \text{ Mg m}^{-3}$
$a = 7.0204 (6) \text{ \AA}$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$b = 7.7661 (6) \text{ \AA}$	Cell parameters from 548 reflections
$c = 10.5392 (8) \text{ \AA}$	$\theta = 2.4\text{--}27.7^\circ$
$\alpha = 97.733 (1)^\circ$	$\mu = 0.60 \text{ mm}^{-1}$
$\beta = 109.293 (1)^\circ$	$T = 173 \text{ K}$
$\gamma = 90.217 (1)^\circ$	Irregular, colorless
$V = 536.69 (7) \text{ \AA}^3$	$0.35 \times 0.29 \times 0.28 \text{ mm}$

*Data collection*

Bruker APEX CCD area detector diffractometer	5934 measured reflections
Radiation source: Fine-focus sealed tube	2582 independent reflections
Graphite monochromator	2417 reflections with $I > 2\sigma(I)$
phi and $\omega$ scans	$R_{\text{int}} = 0.031$
Absorption correction: multi-scan (SADABS; Krause <i>et al.</i> , 2015)	$\theta_{\text{max}} = 28.3^\circ$ , $\theta_{\text{min}} = 2.1^\circ$
$T_{\text{min}} = 0.838$ , $T_{\text{max}} = 0.927$	$h = -9 \rightarrow 9$
	$k = -10 \rightarrow 10$
	$l = -14 \rightarrow 14$

*Refinement*

Refinement on $F^2$	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.026$	$w = 1/[\sigma^2(F_o^2) + (0.0368P)^2 + 0.1955P]$
$wR(F^2) = 0.073$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{\text{max}} = 0.001$
2582 reflections	$\Delta\rho_{\text{max}} = 0.45 \text{ e \AA}^{-3}$
147 parameters	$\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$
0 restraints	
Primary atom site location: dual	

*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.** All non-hydrogen atoms were refined anisotropically. H atoms bound to C atoms were constrained to ride on the atoms onto which they are bonded, where C—H = 0.95 (aromatic) or 0.98 Å (methyl) with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.81953 (5)	0.48342 (4)	0.83259 (3)	0.02349 (9)
C12	0.74478 (5)	0.08068 (4)	0.71750 (3)	0.02487 (9)
O1	0.76916 (17)	0.76700 (12)	0.40055 (10)	0.0310 (2)
O2	0.69277 (14)	0.55617 (11)	0.22210 (9)	0.02121 (18)
O3	0.50933 (14)	0.17388 (12)	0.16137 (9)	0.02470 (19)
O4	0.84744 (13)	0.20884 (11)	0.21752 (8)	0.02113 (18)
C1	0.73795 (16)	0.47447 (14)	0.43804 (11)	0.0158 (2)
C2	0.77075 (17)	0.53010 (15)	0.57530 (12)	0.0170 (2)
H2	0.7904	0.6508	0.6094	0.020*
C3	0.77483 (17)	0.41014 (15)	0.66231 (11)	0.0172 (2)
C4	0.74445 (17)	0.23318 (15)	0.61230 (12)	0.0181 (2)
C5	0.71216 (18)	0.17662 (15)	0.47593 (12)	0.0185 (2)
H5	0.6921	0.0558	0.4423	0.022*
C6	0.70903 (17)	0.29623 (14)	0.38820 (11)	0.0159 (2)
C7	0.73570 (17)	0.61539 (15)	0.35369 (12)	0.0179 (2)
C8	0.6829 (2)	0.68909 (17)	0.13612 (13)	0.0247 (3)
H8A	0.6390	0.6352	0.0408	0.037*
H8B	0.8168	0.7473	0.1603	0.037*
H8C	0.5863	0.7746	0.1491	0.037*
C9	0.67274 (18)	0.22206 (14)	0.24202 (12)	0.0175 (2)
C10	0.8297 (2)	0.14662 (17)	0.07783 (12)	0.0249 (3)
H10A	0.7640	0.2330	0.0200	0.037*
H10B	0.7485	0.0365	0.0474	0.037*
H10C	0.9646	0.1283	0.0717	0.037*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C11	0.02835 (16)	0.02741 (16)	0.01490 (15)	−0.00009 (11)	0.00920 (12)	−0.00131 (11)
C12	0.03392 (18)	0.02289 (16)	0.01804 (15)	−0.00098 (12)	0.00730 (12)	0.00740 (11)
O1	0.0505 (6)	0.0152 (4)	0.0266 (5)	0.0004 (4)	0.0124 (4)	0.0022 (3)
O2	0.0281 (4)	0.0181 (4)	0.0175 (4)	−0.0002 (3)	0.0066 (3)	0.0052 (3)
O3	0.0253 (5)	0.0269 (4)	0.0174 (4)	−0.0058 (3)	0.0021 (3)	0.0010 (3)
O4	0.0235 (4)	0.0248 (4)	0.0136 (4)	0.0029 (3)	0.0056 (3)	−0.0005 (3)
C1	0.0142 (5)	0.0158 (5)	0.0169 (5)	0.0010 (4)	0.0045 (4)	0.0026 (4)
C2	0.0152 (5)	0.0161 (5)	0.0188 (5)	0.0008 (4)	0.0056 (4)	−0.0004 (4)
C3	0.0156 (5)	0.0217 (5)	0.0139 (5)	0.0011 (4)	0.0052 (4)	0.0000 (4)
C4	0.0183 (5)	0.0196 (5)	0.0164 (5)	0.0003 (4)	0.0049 (4)	0.0050 (4)
C5	0.0216 (5)	0.0155 (5)	0.0171 (5)	−0.0003 (4)	0.0048 (4)	0.0019 (4)
C6	0.0155 (5)	0.0165 (5)	0.0143 (5)	0.0002 (4)	0.0034 (4)	0.0011 (4)
C7	0.0168 (5)	0.0167 (5)	0.0204 (5)	0.0019 (4)	0.0059 (4)	0.0036 (4)
C8	0.0292 (6)	0.0237 (6)	0.0243 (6)	0.0038 (5)	0.0098 (5)	0.0115 (5)
C9	0.0242 (6)	0.0125 (5)	0.0150 (5)	0.0009 (4)	0.0049 (4)	0.0030 (4)
C10	0.0342 (7)	0.0261 (6)	0.0147 (5)	0.0029 (5)	0.0097 (5)	−0.0001 (4)

*Geometric parameters (Å, °)*

C11—C3	1.7305 (12)	C2—C3	1.3865 (16)
C12—C4	1.7272 (12)	C3—C4	1.3931 (16)
O1—C7	1.2042 (15)	C4—C5	1.3871 (16)
O2—C7	1.3330 (15)	C5—H5	0.9500
O2—C8	1.4500 (14)	C5—C6	1.3915 (15)
O3—C9	1.2022 (15)	C6—C9	1.5069 (16)
O4—C9	1.3359 (15)	C8—H8A	0.9800
O4—C10	1.4503 (14)	C8—H8B	0.9800
C1—C2	1.3940 (16)	C8—H8C	0.9800
C1—C6	1.4018 (15)	C10—H10A	0.9800
C1—C7	1.4969 (15)	C10—H10B	0.9800
C2—H2	0.9500	C10—H10C	0.9800
C7—O2—C8	115.05 (9)	C5—C6—C9	116.26 (10)
C9—O4—C10	115.31 (10)	O1—C7—O2	123.60 (11)
C2—C1—C6	119.63 (10)	O1—C7—C1	123.11 (11)
C2—C1—C7	115.67 (10)	O2—C7—C1	113.29 (9)
C6—C1—C7	124.70 (10)	O2—C8—H8A	109.5
C1—C2—H2	119.8	O2—C8—H8B	109.5
C3—C2—C1	120.33 (10)	O2—C8—H8C	109.5
C3—C2—H2	119.8	H8A—C8—H8B	109.5
C2—C3—C11	119.14 (9)	H8A—C8—H8C	109.5
C2—C3—C4	119.92 (10)	H8B—C8—H8C	109.5
C4—C3—C11	120.94 (9)	O3—C9—O4	125.21 (11)
C3—C4—C12	121.06 (9)	O3—C9—C6	124.09 (11)
C5—C4—C12	118.80 (9)	O4—C9—C6	110.60 (10)
C5—C4—C3	120.14 (10)	O4—C10—H10A	109.5
C4—C5—H5	119.9	O4—C10—H10B	109.5
C4—C5—C6	120.23 (10)	O4—C10—H10C	109.5
C6—C5—H5	119.9	H10A—C10—H10B	109.5
C1—C6—C9	124.00 (10)	H10A—C10—H10C	109.5
C5—C6—C1	119.74 (10)	H10B—C10—H10C	109.5
C11—C3—C4—C12	1.42 (14)	C4—C5—C6—C1	-0.23 (17)
C11—C3—C4—C5	-178.93 (9)	C4—C5—C6—C9	-179.96 (10)
C12—C4—C5—C6	179.38 (9)	C5—C6—C9—O3	78.67 (15)
C1—C2—C3—C11	179.08 (9)	C5—C6—C9—O4	-97.92 (12)
C1—C2—C3—C4	-0.50 (17)	C6—C1—C2—C3	0.00 (17)
C1—C6—C9—O3	-101.05 (14)	C6—C1—C7—O1	-176.90 (12)
C1—C6—C9—O4	82.36 (13)	C6—C1—C7—O2	3.20 (16)
C2—C1—C6—C5	0.37 (17)	C7—C1—C2—C3	179.72 (10)
C2—C1—C6—C9	-179.92 (10)	C7—C1—C6—C5	-179.33 (10)
C2—C1—C7—O1	3.39 (17)	C7—C1—C6—C9	0.38 (18)
C2—C1—C7—O2	-176.51 (10)	C8—O2—C7—O1	-1.71 (17)
C2—C3—C4—C12	-179.00 (8)	C8—O2—C7—C1	178.18 (9)
C2—C3—C4—C5	0.65 (17)	C10—O4—C9—O3	6.33 (17)

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C3—C4—C5—C6	-0.28 (18)	C10—O4—C9—C6	-177.12 (9)
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*Hydrogen-bond geometry (Å, °)*

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<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>
C5—H5···O1 <sup>i</sup>	0.95	2.33	3.2327 (15)	159
C10—H10B···O3 <sup>ii</sup>	0.98	2.68	3.5380 (16)	147

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