

## Crystal structure of 4,5-dimethyl-1,3-dioxol-2-one

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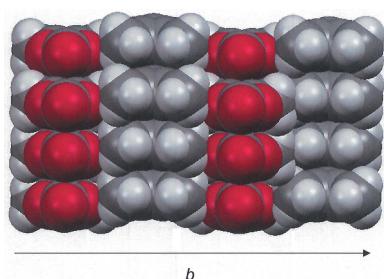
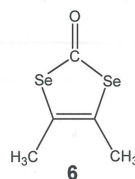
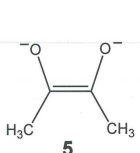
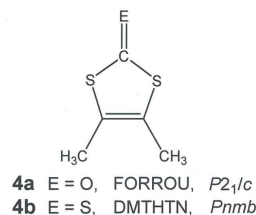
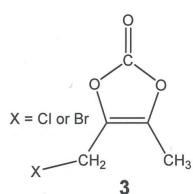
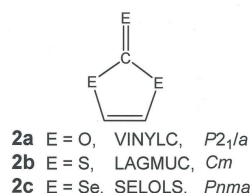
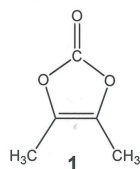
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The planar title compound 4,5-dimethyl-1,3-dioxol-2-one, C<sub>5</sub>H<sub>6</sub>O<sub>3</sub>, **1**, crystallizes with its molecular C<sub>2</sub> axis coincident with a crystallographic mirror plane in space group P2<sub>1</sub>/m. In the plane defined by the *b* axis and an *ac* face diagonal, antiparallel linear strands of **1**, formed by simple translation, associate to form sheets with close H···H and O···O intermolecular contacts. Between the sheets, parallel strands of **1** place the carbonyl O atom near the five-membered ring centroid of a neighboring molecule with close O···O and O···C contacts.

## 1. Chemical context

4,5-Dimethyl-1,3-dioxol-2-one, **1** (Fig. 1 and scheme), is a simple derivative of vinylene carbonate, **2a**, that has attracted recent attention as a key component of non-aqueous electrolyte blends for advanced Li ion batteries (Park *et al.*, 2021; Liu *et al.*, 2017; Kotani & Kadota, 2016; Xu *et al.*, 2010). Its 4-chloromethyl and 4-bromomethyl derivatives, **3**, have significance in the pharmaceutical industry as building elements in the preparation of antibiotics such as prulifloxacin (Cao *et al.*, 2013), cefuroxime variants (Webber, 1987), and ampicillin (Sakamoto *et al.*, 1984; Xiao, 2004). In principle, by analogy to the usefulness that the related 4,5-dimethyl-1,3-dithiol-2-one, **4a**, enjoys as a masked form of the dimethyldithiolene ligand (Chandrasekaran *et al.*, 2009), **1** could function as a protected form of the dimethyldioxolene(2-) ligand, **5**, that is liberated by straightforward base hydrolysis.



Although a few coordination complexes with the dimethyldioxolene ligand are known, they have been prepared by oxidative addition of the corresponding  $\alpha$ -diketone to a low-valent metal precursor (Chisholm *et al.*, 1983) or by an obscure route involving the reductive coupling of CO(g) with methyl ligands (Hofmann *et al.*, 1985). This context of demonstrated usefulness and unrealized, but plausible, possibility for **1** persuaded us to undertake a study of its utility as a dioxolene ligand precursor. In an early research stage, serendipitously obtained diffraction-quality crystals of **1** provided an opportunity for characterization by X-ray diffraction, details of which are reported herein.

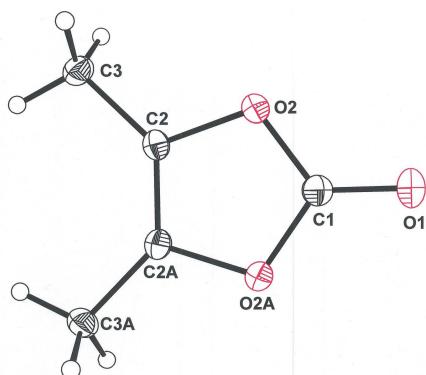
## 2. Structural commentary

Compound **1** crystallizes in the monoclinic space group  $P2_1/m$  upon a crystallographic mirror plane that coincides with the carbonyl bond (Fig. 1).

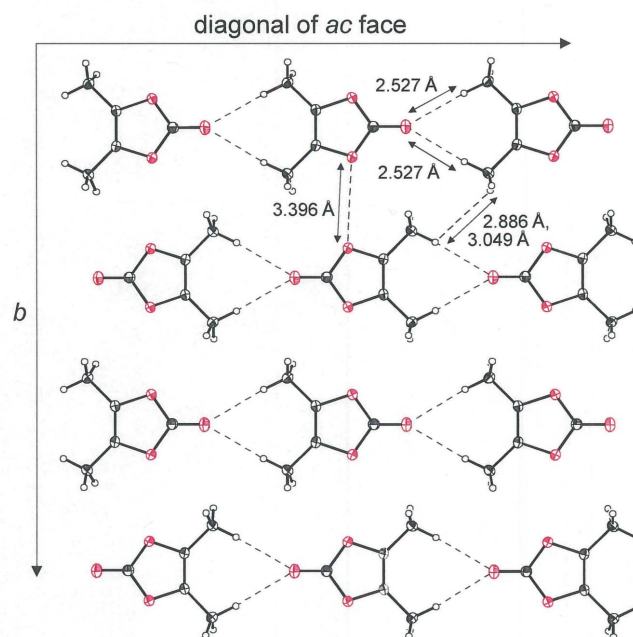
## 3. Supramolecular features

Molecules of **1** are aligned as one-dimensional strands by simple translation along one of the diagonals of the  $ac$  face of the unit cell (Fig. 2). The C=O oxygen atom of **1** forms close contacts of 2.53 Å with the hydrogen atoms from each of the methyl groups of the molecule aligned before or behind (Table 1), at a distance that approaches the sum of the van der Waals radii of the elements (Batsanov, 2001). These strands are further organized into two-dimensional sheets through side-by-side placement but with an alternating orientation of the polarized, carbonyl end of the molecules (Fig. 2). The  $b$  axis defines the 2nd dimension of these sheets. Between strands within these sheets, interatomic H...H separations are 2.89 and 3.05 Å, while nearest O...O distances between rings are 3.3962 (13) Å. Fig. 3 presents a perspective of these sheets that is approximately along the  $b$  axis of the cell such that the close stacking between them is visible.

An alternative description of the third dimension of the packing is that the one-dimensional strands noted above translate as a whole along the  $a$  axis of the cell with an offset

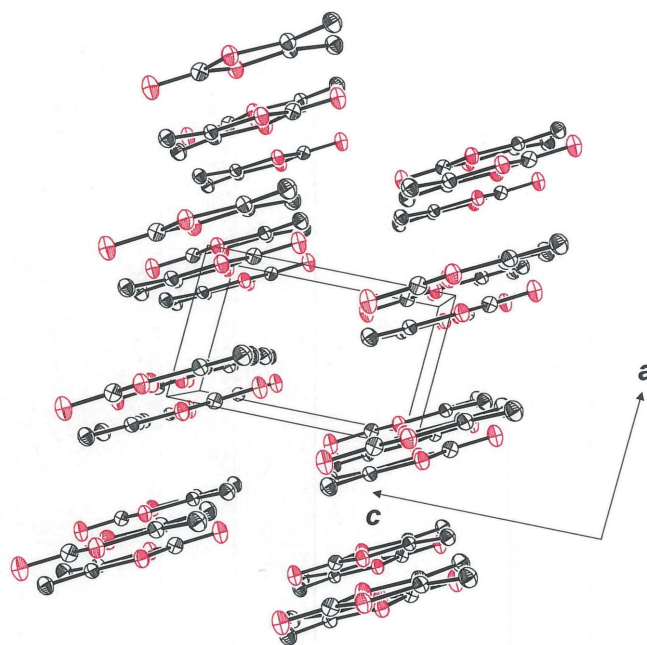


**Figure 1**  
Displacement ellipsoid plot (50% probability) of 4,5-dimethyl-1,3-dioxol-2-one (**1**) with non-H atom labeling.



**Figure 2**  
Packing diagram for 4,5-dimethyl-1,3-dioxol-2-one (**1**) illustrating the sheetlike arrangement in the plane defined by the  $b$  axis and an  $ac$  face diagonal. Displacement ellipsoids are at the 50% level, and closest intermolecular contacts are indicated.

that places the carbonyl oxygen atom of one molecule of one strand near the five-membered ring centroid of a neighboring molecule (Fig. 4). In contrast to the *intrasheet* strands depicted in Fig. 2, which are antiparallel, the neighboring *intersheet* strands are all oriented in the same direction. The closest



**Figure 3**  
Cell packing diagram of **1** with a view along the  $b$  axis of the cell. Displacement ellipsoids are drawn at the 50% level, and all H atoms are omitted for clarity.

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

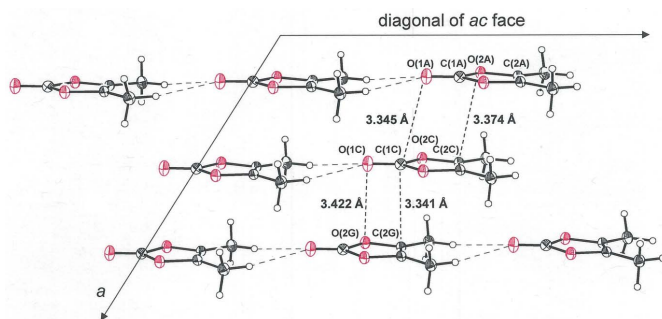
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C3-H3A\cdots O1^i$	0.98	2.53	3.4976 (13)	171

Symmetry code: (i)  $x - 1, y, z + 1$ .

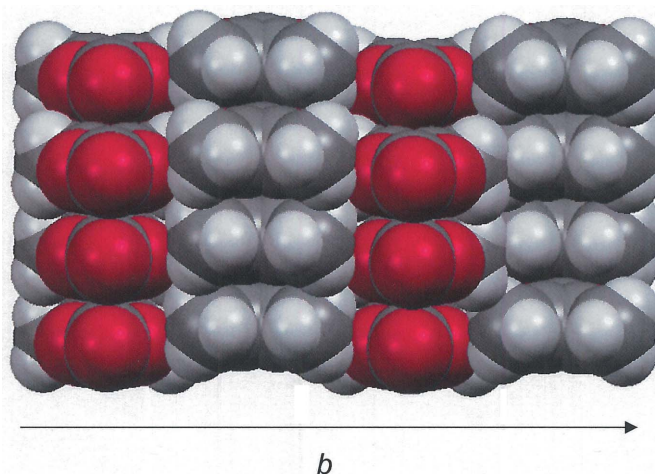
intermolecular  $C\cdots C$  and  $C\cdots O$  contacts between these parallel strands are the  $C_c\cdots C_o$  separation of 3.3413 (16) Å, the  $O_c\cdots C_c$  spacing of 3.3452 (18) Å, and the  $O_r\cdots C_o$  distance of 3.3742 (13) Å ( $c$  = carbonyl,  $o$  = olefin,  $r$  = ring). It is likely that the electrostatic interactions of polarized bonds, *e.g.*, placement of the negative end of the  $\delta^{(-)}O=C^{\delta(+)}$  carbonyl dipole above the positive end of the same bond in the sheet below, exert a decisive role in guiding the organization and spacing of one molecular plane over another. An end-on view of these sheets in space-filling presentation mode emphasizes the packing efficiency imposed by these cumulative intermolecular interactions (Fig. 5).

#### 4. Database survey

Of the relatively few vinylenecarbonates that have been structurally characterized, only **1** and the parent compound **2a** (Cser, 1974) are simple, symmetrically substituted variants. All other structurally identified compounds bearing this moiety are more complex organic molecules that have been prepared and studied as angiotensin II receptor blockers (Yanagisawa *et al.*, 1996; Dams *et al.*, 2015; Zhang *et al.*, 2017). Despite its ostensible similarity to **1**, compound **2a** crystallizes in a rather different fashion. Although arranged into extended sheets, which also contain the  $b$  axis, molecules of **2a** are not organized into discernible linear strands but instead are twisted relative to their neighbors so as to accommodate multiple  $C-H\cdots O$  hydrogen-bonding interactions (Fig. 6). A glide plane, rather than simple translation, relates one molecule of **2a** to another in the horizontal direction (Fig. 6). As their different space groups would necessitate, the packing arrangements for vinylenetri-thiocarbonate (**2b**, CSD refcode LAGMUC; Mereiter & Rosenau, 2005) and vinylenetri-selenolate (**2c**, SELOLS; Lyubovskaya *et al.*, 1976) contrast greatly with **2a**.



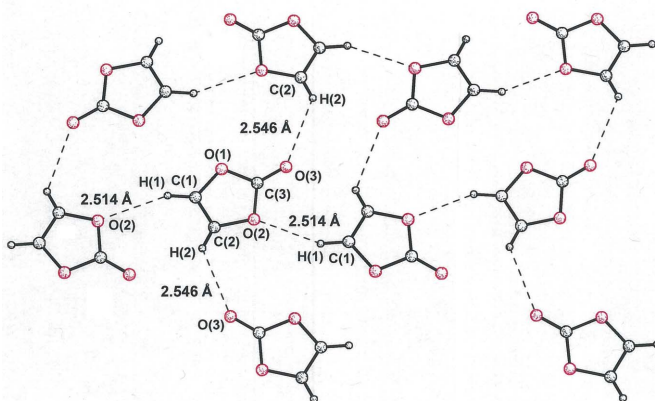
**Figure 4**  
View of the cell packing arrangement in **1** depicting the closest intermolecular contacts between linear strands extending in the direction of a diagonal to the  $ac$  face. Displacement ellipsoids are at the 50% level.



**Figure 5**  
Space-filling plot of the unit-cell packing in **1** as viewed along the length of the linear strands, which are orthogonal to the paper plane.

The former reveals linear strands of molecules arranged in sheets with a parallel orientation of all strands. Intermolecular  $\pi$ - $\pi$  stacking interactions appear to be the decisive packing force between sheets. The latter, when viewed along the  $b$  axis of the cell, reveals a herringbone-like pattern in the arrangement of molecules.

Compounds similar to **1** with methyl substituents at the 4 and 5 positions of the ring include **4a**, already noted, and the all-sulfur form, **4b** (DMTHTN; Smith & Luss, 1980). Compound **4b** occurs in the same space group (No. 62,  $Pnma$ ) as **2c** with a qualitatively similar packing arrangement that differs in having the herringbone pattern visible when viewed along the cell's  $a$  axis. Compound **4a** crystallizes in  $P2_1/c$  on a general position with similar generalities of description pertinent to its packing pattern as found for **2a**. However, adjacent strands of **4b** that are generated by the glide plane operation are slightly out of plane relative to one another. The selenium analogue (**6**) of **1** and **4a** has not been characterized crystallographically but is a target of current study in our laboratory.



**Figure 6**  
Ball and stick representation of the sheetlike arrangement in **2a**, where molecules (left-to-right) are related by a glide-plane operation rather than simple translation. Closest intermolecular contacts are illustrated.

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	C <sub>5</sub> H <sub>6</sub> O <sub>3</sub>
<i>M<sub>r</sub></i>	114.10
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>m</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	3.8283 (10), 10.972 (2), 6.1096 (10)
$\beta$ (°)	93.523 (2)
<i>V</i> (Å <sup>3</sup> )	256.15 (10)
<i>Z</i>	2
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.12
Crystal size (mm)	0.27 × 0.21 × 0.16
Data collection	
Diffractometer	Bruker SMART APEX
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>	0.967, 0.980
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	2310, 636, 617
<i>R<sub>int</sub></i>	0.027
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.667
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>	0.030, 0.077, 1.10
No. of reflections	636
No. of parameters	42
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.30, -0.21

Computer programs: *SMART* (Bruker, 2000), *SAINTE-Plus* (Bruker, 2004), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), and *SHELXTL* (Sheldrick, 2008).

## 5. Synthesis and crystallization

The sample of 4,5-dimethyl-1,3-dioxol-2-one used in this study was purchased from AK Scientific, Inc. and recrystallized by evaporation of a MeOH solution from a test tube at room temperature.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms are added in calculated positions and refined with isotropic displacement parameters that are approximately 1.5 times those of the carbon atom to which they are attached. The C–H distances are fixed at 0.98 Å.

## Acknowledgements

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ongoing support with operational costs for the diffraction facility.

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## supporting information

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## Computing details

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART* (Bruker, 2000); data reduction: *SAINTE-Plus* (Bruker, 2004); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

## 4,5-Dimethyl-1,3-dioxol-2-one

## Crystal data

$C_5H_6O_3$

$M_r = 114.10$

Monoclinic,  $P2_1/m$

$a = 3.8283$  (10) Å

$b = 10.972$  (2) Å

$c = 6.1096$  (10) Å

$\beta = 93.523$  (2)°

$V = 256.15$  (10) Å<sup>3</sup>

$Z = 2$

$F(000) = 120$

$D_x = 1.479$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 2113 reflections

$\theta = 3.2$ – $28.3$ °

$\mu = 0.12$  mm<sup>-1</sup>

$T = 100$  K

Block, white

$0.27 \times 0.21 \times 0.16$  mm

## Data collection

Bruker SMART APEX  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\pi$  and  $o$  scans

Absorption correction: multi-scan  
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.967$ ,  $T_{\max} = 0.980$

2310 measured reflections

636 independent reflections

617 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\max} = 28.3$ °,  $\theta_{\min} = 3.3$ °

$h = -4 \rightarrow 4$

$k = -14 \rightarrow 14$

$l = -8 \rightarrow 8$

## Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.077$

$S = 1.10$

636 reflections

42 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

$w = 1/[\sigma^2(F_o^2) + (0.0345P)^2 + 0.0767P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.30$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.21$  e Å<sup>-3</sup>

Extinction correction: SHELXL,

$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.22 (2)

*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  $F^2 > 2\sigma(F^2)$  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.

Hydrogen atoms were added in calculated positions and refined with isotropic displacement parameters that are approximately 1.5 times those of the carbon atom to which they are attached. The C–H distances assumed were 0.98 Å.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.1654 (3)	0.250000	0.67266 (16)	0.0247 (3)
O2	−0.08340 (16)	0.35049 (6)	0.94742 (10)	0.0174 (2)
C1	0.0147 (3)	0.250000	0.8382 (2)	0.0177 (3)
C2	−0.2444 (2)	0.31041 (8)	1.13620 (13)	0.0156 (2)
C3	−0.3662 (2)	0.40519 (8)	1.28542 (15)	0.0190 (2)
H3A	−0.479500	0.366409	1.407001	0.028*
H3B	−0.534168	0.458611	1.204840	0.028*
H3C	−0.165882	0.453408	1.343402	0.028*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0293 (6)	0.0271 (5)	0.0186 (5)	0.000	0.0091 (4)	0.000
O2	0.0204 (4)	0.0160 (4)	0.0162 (4)	−0.0002 (2)	0.0045 (2)	0.0011 (2)
C1	0.0185 (6)	0.0176 (6)	0.0169 (6)	0.000	0.0008 (4)	0.000
C2	0.0145 (4)	0.0180 (5)	0.0145 (4)	−0.0006 (3)	0.0020 (3)	0.0009 (3)
C3	0.0206 (5)	0.0168 (4)	0.0199 (4)	0.0004 (3)	0.0044 (3)	−0.0027 (3)

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

O1—C1	1.1949 (16)	C2—C3	1.4773 (12)
O2—C1	1.3537 (10)	C3—H3A	0.9800
O2—C2	1.4110 (10)	C3—H3B	0.9800
C2—C2 <sup>i</sup>	1.3257 (18)	C3—H3C	0.9800
C1—O2—C2	107.30 (7)	C2—C3—H3A	109.5
O1—C1—O2 <sup>i</sup>	125.46 (5)	C2—C3—H3B	109.5
O1—C1—O2	125.46 (5)	H3A—C3—H3B	109.5
O2 <sup>i</sup> —C1—O2	109.07 (10)	C2—C3—H3C	109.5
C2 <sup>i</sup> —C2—O2	108.16 (4)	H3A—C3—H3C	109.5
C2 <sup>i</sup> —C2—C3	134.74 (5)	H3B—C3—H3C	109.5
O2—C2—C3	117.09 (7)		

C2—O2—C1—O1	-178.43 (12)	C1—O2—C2—C2 <sup>i</sup>	-0.72 (8)
C2—O2—C1—O2 <sup>i</sup>	1.19 (12)	C1—O2—C2—C3	178.50 (8)

Symmetry code: (i)  $x, -y+1/2, z$ .

*Hydrogen-bond geometry (Å, °)*

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
C3—H3A...O1 <sup>ii</sup>	0.98	2.53	3.4976 (13)	171

Symmetry code: (ii)  $x-1, y, z+1$ .