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## Structure Reports

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## 5,6-Dimethyl-1,2,9,10-tetrahydropyrano-[3,2-f]chromene-3,8-dione

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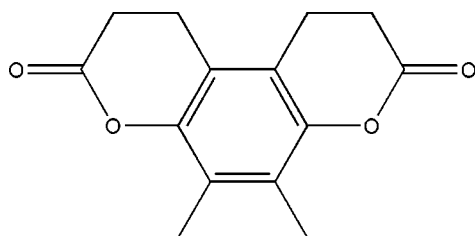
Received 18 June 2012; accepted 18 June 2012

Key indicators: single-crystal X-ray study;  $T = 92$  K; mean  $\sigma(\text{C}-\text{C}) = 0.001$  Å;  $R$  factor = 0.050;  $wR$  factor = 0.148; data-to-parameter ratio = 36.0.

The title molecule,  $\text{C}_{14}\text{H}_{14}\text{O}_4$ , lies on a twofold rotation axis that bisects the central benzene ring, with only one half-molecule in the asymmetric unit. The pyranone systems adopt distorted twist-boat conformations, with the two methylene C atoms displaced by 0.537 (1) and 0.163 (2) Å from the best-fit plane through the remaining five C and O atoms (r.m.s. deviation = 0.073 Å). In the crystal, bifurcated  $\text{C}-\text{H}\cdots(\text{O},\text{O})$  hydrogen bonds link pairs of adjacent molecules in an obverse fashion, stacking molecules along  $c$ . These contacts are further stabilized by very weak  $\pi-\pi$  interactions between adjacent benzene rings with centroid-centroid distances of 4.1951 (4) Å. Additional  $\text{C}-\text{H}\cdots\text{O}$  contacts link these stacks, giving a three-dimensional network.

## Related literature

For the synthesis, see: Lecea *et al.* (2010). For details of the Cambridge Structural Database, see: Allen (2002) and for related structures, see: Cameron *et al.* (2011); Goswami *et al.* (2011). For standard bond lengths, see: Allen *et al.* (1987).



## Experimental

## Crystal data

$\text{C}_{14}\text{H}_{14}\text{O}_4$   
 $M_r = 246.25$   
 Monoclinic,  $C2/c$   
 $a = 16.0726$  (2) Å  
 $b = 8.7982$  (1) Å  
 $c = 8.0555$  (1) Å  
 $\beta = 96.1134$  (7)°

$V = 1132.65$  (2) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.11$  mm<sup>-1</sup>  
 $T = 92$  K  
 $0.53 \times 0.50 \times 0.22$  mm

## Data collection

Bruker APEXII CCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Bruker, 2011)  
 $T_{\min} = 0.570$ ,  $T_{\max} = 0.748$   
 9744 measured reflections  
 2989 independent reflections  
 2358 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.038$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$   
 $wR(F^2) = 0.148$   
 $S = 1.08$   
 2989 reflections  
 83 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.47$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.38$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C61}-\text{H61A}\cdots\text{O1}^{\text{i}}$	0.98	2.54	3.3907 (11)	145
$\text{C2}-\text{H2A}\cdots\text{O1}^{\text{ii}}$	0.99	2.60	3.4301 (12)	142
$\text{C2}-\text{H2A}\cdots\text{O2}^{\text{ii}}$	0.99	2.64	3.4813 (10)	143
$\text{C2}-\text{H2B}\cdots\text{O1}^{\text{iii}}$	0.99	2.44	3.3528 (11)	154

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

Data collection: APEX2 (Bruker, 2011); cell refinement: APEX2 (Bruker, 2011) and SAINT (Bruker, 2011); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008) and TITAN2000 (Hunter & Simpson, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008) and TITAN2000; molecular graphics: SHELXTL (Sheldrick, 2008) and Mercury (Macrae *et al.*, 2008); software used to prepare material for publication: SHELXL97, enCIFer (Allen *et al.*, 2004), PLATON (Spek, 2009) and publCIF (Westrip 2010).

We thank the New Economy Research Fund (grant No. UOO-X0808) for support of this work and the University of Otago for the purchase of the diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5941).

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## supporting information

*Acta Cryst.* (2012). E68, o2216 [https://doi.org/10.1107/S1600536812027699]

**5,6-Dimethyl-1,2,9,10-tetrahydropyrano[3,2-*f*]chromene-3,8-dione****Shailesh K. Goswami, Lyall R. Hanton, C. John McAdam, Stephen C. Moratti and Jim Simpson****S1. Comment**

Our current research interests involve the preparation of redox monomers for the synthesis of electroactive gels. The title compound (I), a chromene-dione was obtained as a by-product of the synthesis of the desired 6-hydroxy-7,8-dimethylchroman-2-one as previously reported by Lecea *et al.* (2010). The chromene-dione (I) provides access to an exciting new redox-active cross-linker in three steps through ring opening, oxidation and condensation reactions.

The asymmetric unit of the title compound contains only one half of the molecule, which lies on a twofold rotation axis that bisects the central benzene ring (Fig 1) The pyranone ring systems adopt distorted twist boat conformations, with the C2 and C3 methylene carbon atoms displaced by 0.537 (1) and 0.163 (2) Å respectively from the best fit plane through C1/(O1)/O2/C5/C4 which has an r.m.s. deviation 0.073 Å. A search of the Cambridge Database (Allen, 2002) revealed no comparable compounds, with or without substitution on the benzene ring. However we have previously reported closely related chroman-2-one derivatives without a second pyranone ring system (Goswami *et al.*, 2011, Cameron *et al.*, 2011). Bond lengths in the structure are not unusual (Allen *et al.*, 1987) and are comparable to those in the chroman-2-one compounds mentioned previously.

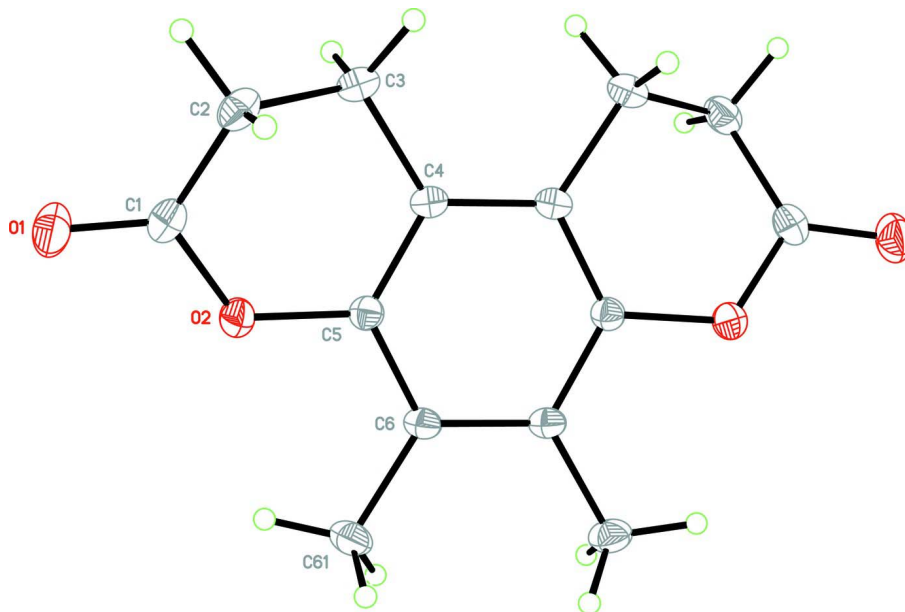
In the crystal structure, bifurcated C2–H2A···O1 hydrogen bonds link pairs of adjacent molecules in an obverse fashion stacking molecules along *c*. Very weak  $\pi$ – $\pi$  interactions,  $Cg\cdots Cg = 4.1951$  (4) Å, between adjacent benzene rings bolster these contacts further, Fig. 2. Additional C–H···O contacts, Table 1, generate layers of molecules in planes parallel to (1,0,1), Fig 3 while the overall result of this series of contacts is an extended three dimensional network, Fig. 4.

**S2. Experimental**

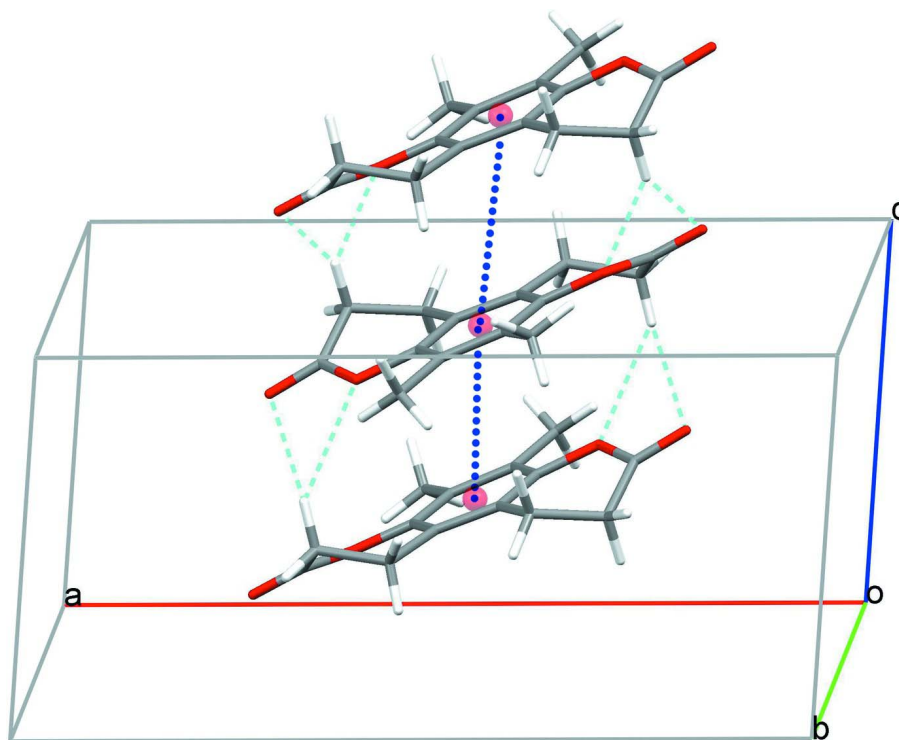
The title compound was obtained as a by-product from a Friedel-Crafts type addition reaction of 2,3-dimethylhydroquinone with acrylic acid during the synthesis of 6-hydroxy-7,8-dimethylchroman-2-one (Lecea *et al.*, 2010). Following work-up according to the literature, X-ray quality crystals of (I) were obtained from dichloromethane solution.

**S3. Refinement**

All H-atoms bound to carbon were refined using a riding model with  $d(C-H) = 0.99$  Å,  $U_{iso} = 1.2U_{eq}(C)$  for methylene and 0.98 Å,  $U_{iso} = 1.5U_{eq}(C)$  for CH<sub>3</sub> H atoms.



**Figure 1**  
The structure of (I) with ellipsoids drawn at the 50% probability level.



**Figure 2**  
Bifurcated C–H...O hydrogen bonds (dashed lines), augmented by  $\pi$ – $\pi$  stacking interactions (dotted lines) stacking molecules along *c*.

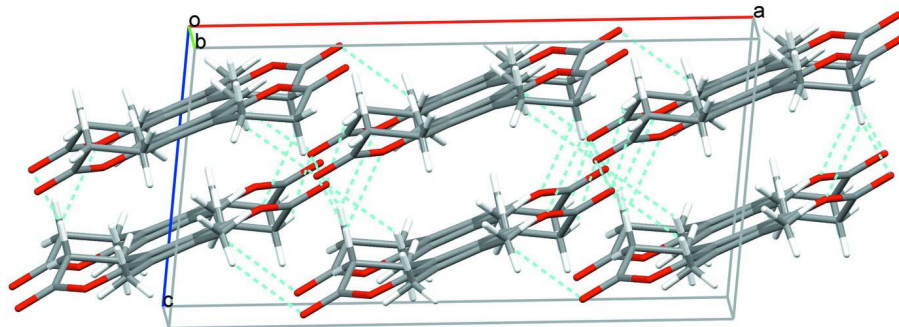


Figure 3

Layers of molecules in planes parallel to (101). Hydrogen bonds are drawn as dashed lines.

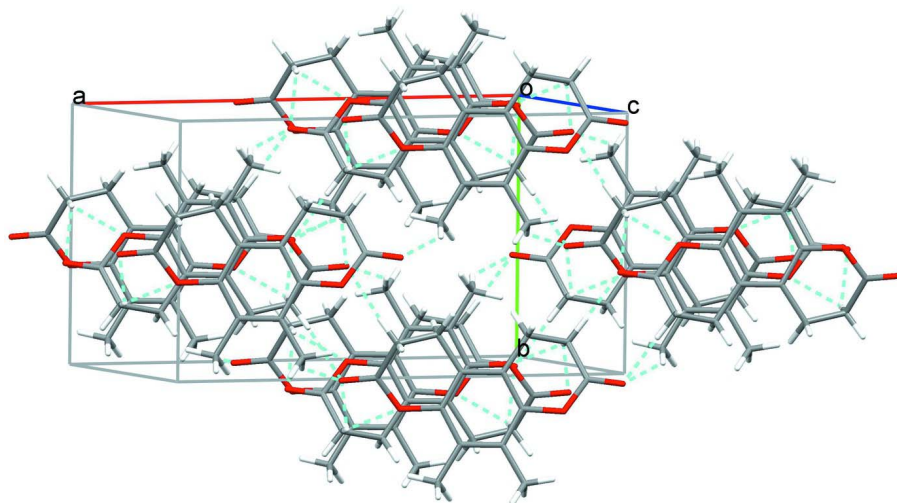


Figure 4

Overall packing of (I) with hydrogen bonds drawn as dashed lines.

### 5,6-dimethyl-1,2,9,10-tetrahydropyrano[3,2-*f*]chromene-3,8-dione

#### Crystal data

$C_{14}H_{14}O_4$

$M_r = 246.25$

Monoclinic,  $C2/c$

Hall symbol:  $-C\ 2yc$

$a = 16.0726\ (2)\ \text{\AA}$

$b = 8.7982\ (1)\ \text{\AA}$

$c = 8.0555\ (1)\ \text{\AA}$

$\beta = 96.1134\ (7)^\circ$

$V = 1132.65\ (2)\ \text{\AA}^3$

$Z = 4$

$F(000) = 520$

$D_x = 1.444\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3955 reflections

$\theta = 2.6\text{--}38.3^\circ$

$\mu = 0.11\ \text{mm}^{-1}$

$T = 92\ \text{K}$

Rectangular block, yellow

$0.53 \times 0.50 \times 0.22\ \text{mm}$

#### Data collection

Bruker APEXII CCD area-detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\varphi$  &  $\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Bruker, 2011)

$T_{\min} = 0.570$ ,  $T_{\max} = 0.748$

9744 measured reflections

2989 independent reflections

2358 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.038$   
 $\theta_{\text{max}} = 39.3^\circ$ ,  $\theta_{\text{min}} = 3.6^\circ$

$h = -27 \rightarrow 26$   
 $k = -14 \rightarrow 7$   
 $l = -13 \rightarrow 14$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.050$   
 $wR(F^2) = 0.148$   
 $S = 1.08$   
 2989 reflections  
 83 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  
 $w = 1/[\sigma^2(F_o^2) + (0.0702P)^2 + 0.4368P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.47 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.38 \text{ e } \text{\AA}^{-3}$

*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.

**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 ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.76307 (4)	-0.03359 (9)	0.53742 (9)	0.02826 (17)
C1	0.70230 (5)	-0.04789 (10)	0.61199 (10)	0.01983 (16)
O2	0.64973 (4)	0.07377 (7)	0.61147 (8)	0.01902 (14)
C2	0.68037 (5)	-0.18492 (10)	0.70770 (10)	0.02081 (16)
H2A	0.6997	-0.1700	0.8274	0.025*
H2B	0.7099	-0.2745	0.6682	0.025*
C3	0.58596 (5)	-0.21578 (9)	0.68795 (10)	0.01919 (15)
H3A	0.5684	-0.2533	0.5737	0.023*
H3B	0.5728	-0.2952	0.7681	0.023*
C4	0.53894 (4)	-0.07275 (8)	0.71898 (9)	0.01485 (14)
C5	0.57500 (4)	0.06647 (8)	0.68637 (9)	0.01470 (14)
C6	0.53839 (4)	0.20612 (8)	0.71558 (9)	0.01519 (14)
C61	0.57956 (5)	0.35308 (10)	0.67541 (12)	0.02167 (17)
H61A	0.6030	0.4022	0.7792	0.033*
H61B	0.5380	0.4204	0.6156	0.033*
H61C	0.6245	0.3325	0.6053	0.033*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0216 (3)	0.0340 (4)	0.0307 (3)	0.0048 (2)	0.0097 (2)	0.0013 (3)
C1	0.0175 (3)	0.0226 (4)	0.0194 (3)	0.0039 (2)	0.0021 (2)	-0.0023 (3)

O2	0.0158 (2)	0.0186 (3)	0.0232 (3)	0.00139 (18)	0.0047 (2)	0.0013 (2)
C2	0.0214 (3)	0.0204 (4)	0.0207 (3)	0.0070 (3)	0.0026 (3)	0.0000 (3)
C3	0.0220 (3)	0.0143 (3)	0.0212 (3)	0.0028 (2)	0.0018 (2)	-0.0018 (2)
C4	0.0165 (3)	0.0124 (3)	0.0152 (3)	0.0007 (2)	-0.0003 (2)	-0.0005 (2)
C5	0.0140 (3)	0.0145 (3)	0.0154 (3)	0.0003 (2)	0.0009 (2)	0.0001 (2)
C6	0.0150 (3)	0.0122 (3)	0.0178 (3)	-0.0004 (2)	-0.0007 (2)	0.0006 (2)
C61	0.0196 (3)	0.0149 (3)	0.0302 (4)	-0.0028 (2)	0.0012 (3)	0.0024 (3)

*Geometric parameters (Å, °)*

O1—C1	1.2065 (10)	C3—H3B	0.9900
C1—O2	1.3634 (10)	C4—C5	1.3920 (10)
C1—C2	1.4934 (13)	C4—C4 <sup>i</sup>	1.3962 (14)
O2—C5	1.4018 (9)	C5—C6	1.3931 (10)
C2—C3	1.5329 (11)	C6—C6 <sup>i</sup>	1.4058 (14)
C2—H2A	0.9900	C6—C61	1.5033 (11)
C2—H2B	0.9900	C61—H61A	0.9800
C3—C4	1.5025 (11)	C61—H61B	0.9800
C3—H3A	0.9900	C61—H61C	0.9800
O1—C1—O2	116.80 (8)	C5—C4—C4 <sup>i</sup>	118.34 (4)
O1—C1—C2	126.11 (8)	C5—C4—C3	118.59 (7)
O2—C1—C2	117.07 (7)	C4 <sup>i</sup> —C4—C3	123.06 (4)
C1—O2—C5	121.45 (6)	C4—C5—C6	123.53 (7)
C1—C2—C3	112.01 (7)	C4—C5—O2	120.97 (6)
C1—C2—H2A	109.2	C6—C5—O2	115.40 (6)
C3—C2—H2A	109.2	C5—C6—C6 <sup>i</sup>	118.10 (4)
C1—C2—H2B	109.2	C5—C6—C61	121.25 (7)
C3—C2—H2B	109.2	C6 <sup>i</sup> —C6—C61	120.66 (4)
H2A—C2—H2B	107.9	C6—C61—H61A	109.5
C4—C3—C2	110.14 (7)	C6—C61—H61B	109.5
C4—C3—H3A	109.6	H61A—C61—H61B	109.5
C2—C3—H3A	109.6	C6—C61—H61C	109.5
C4—C3—H3B	109.6	H61A—C61—H61C	109.5
C2—C3—H3B	109.6	H61B—C61—H61C	109.5
H3A—C3—H3B	108.1		
O1—C1—O2—C5	176.44 (7)	C4 <sup>i</sup> —C4—C5—O2	-174.81 (8)
C2—C1—O2—C5	-4.87 (11)	C3—C4—C5—O2	5.95 (11)
O1—C1—C2—C3	-142.07 (9)	C1—O2—C5—C4	-19.48 (11)
O2—C1—C2—C3	39.38 (10)	C1—O2—C5—C6	164.02 (7)
C1—C2—C3—C4	-49.20 (9)	C4—C5—C6—C6 <sup>i</sup>	1.15 (14)
C2—C3—C4—C5	27.91 (10)	O2—C5—C6—C6 <sup>i</sup>	177.55 (8)
C2—C3—C4—C4 <sup>i</sup>	-151.29 (9)	C4—C5—C6—C61	-179.02 (7)
C4 <sup>i</sup> —C4—C5—C6	1.40 (14)	O2—C5—C6—C61	-2.62 (11)
C3—C4—C5—C6	-177.84 (7)		

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

*Hydrogen-bond geometry (Å, °)*

<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>
C61—H61A···O1 <sup>ii</sup>	0.98	2.54	3.3907 (11)	145
C2—H2A···O1 <sup>iii</sup>	0.99	2.60	3.4301 (12)	142
C2—H2A···O2 <sup>iii</sup>	0.99	2.64	3.4813 (10)	143
C2—H2B···O1 <sup>iv</sup>	0.99	2.44	3.3528 (11)	154

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