

Methyl 2-(benzoyloxy)benzoate

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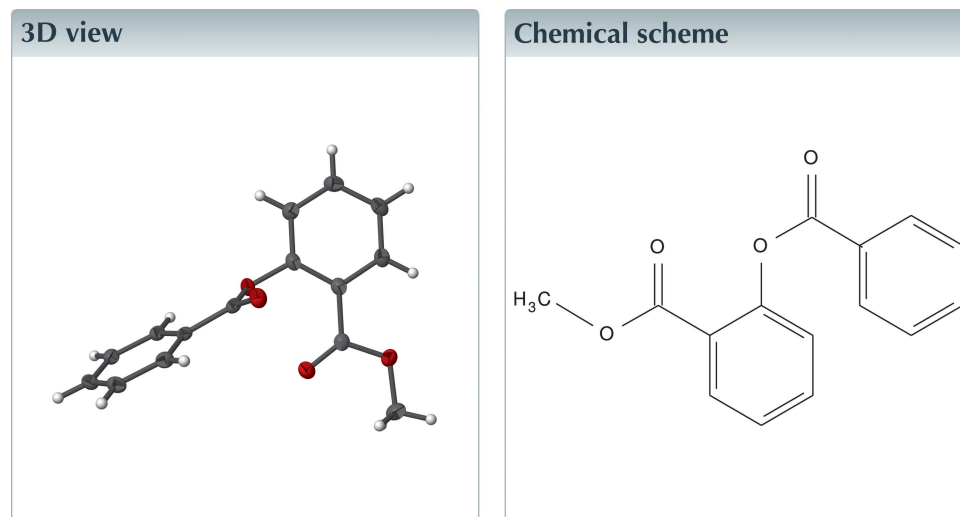
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Keywords: crystal structure; benzoyloxybenzoate; C–H··· π interactions; offset π – π interactions.

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

In the title compound, C₁₅H₁₂O₄, the arene rings are inclined at an angle of 65.97 (6)°. The pendant methyl ester substituent has an extended conformation. In the crystal, molecules are linked by C–H··· π interactions, forming chains propagating along the *b*-axis direction. The chains are linked *via* offset π – π interactions [intercentroid distance = 3.640 (1) Å], forming sheets parallel to (10 $\bar{1}$).



Structure description

Esters are a class of organic compounds which are of synthetic interest. Esters of salicylic acid such as acetyl salicylic acid (phenolic ester), phenyl salicylate and methyl salicylate (carboxylic esters) are widely used as drugs (Khanum *et al.*, 2005). Methyl salicylate is a volatile organic compound which is used for the post-harvest treatment of fruits to protect them from chilling injury by protecting the cell wall of the lipid from oxidative affects. It is also used as an anaesthetic in aquaculture. The non-toxic effect of this ester has extended its utility as a flavoring agent in food and commercial products (Ozaki *et al.*, 2015). The vast significance of such esters has enhanced the interest in exploring their structure–activity relationships and to search for esters as biological lead compounds. With these observations in mind, and as a part of our ongoing research on such molecules (Mohammed *et al.*, 2016), we report here the synthesis and crystal structure of the title ester derivative.

The molecular structure of the title compound is shown in Fig. 1. The molecule is non-planar, the arene rings (C1–C6 and C8–C13) being inclined at a dihedral angle of 65.97 (6)°. The pendant methyl ester chain has an extended conformation, as indicated by

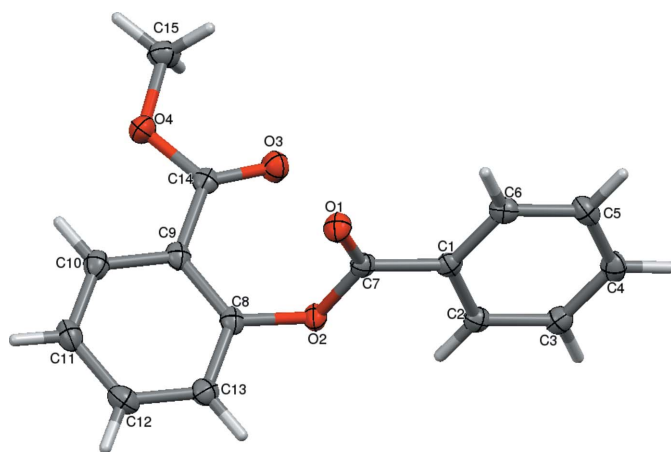


Figure 1
The molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids for the non-H atoms are drawn at the 50% probability level.

the C15—O4—C14—C9 torsion angle of 179.46 (11)°, and lies in the plane of the C18—C13 benzene ring, subtending a dihedral angle of 3.97 (1)°.

In the crystal, molecules are linked by C—H··· π interactions, forming chains propagating along the *b*-axis direction (Table 1 and Fig. 2). The chains are linked *via* offset π – π interactions [$Cg1 \cdots Cg1^{ii} = 3.640$ (1) Å; *Cg1* is the centroid of the C1–C6 ring; interplanar distance = 3.403 (1) Å; slippage =

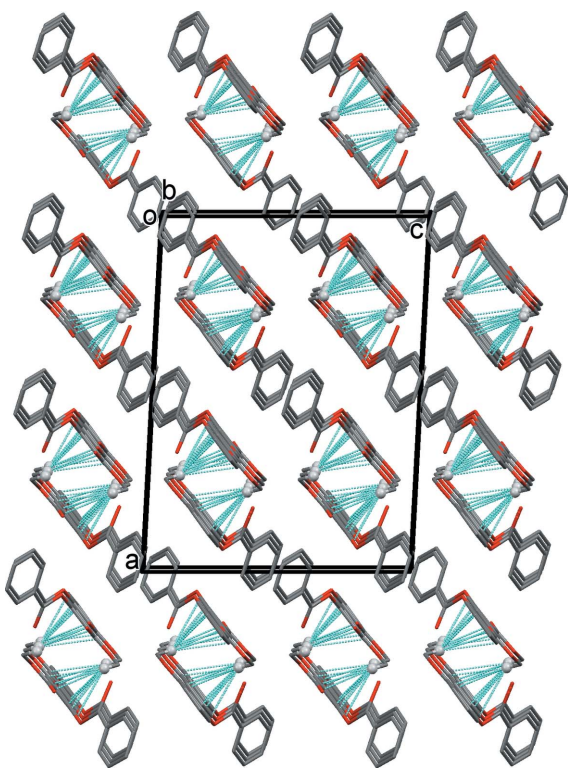


Figure 2
A view along the *b* axis of the crystal packing of the title compound. The C—H··· π interactions are illustrated as dashed lines (see Table 1), and for clarity, only H atom H15A (grey ball) has been included.

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

Cg2 is the centroid of the C8–C13 ring.

<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>
C15—H15A··· <i>Cg2</i> ⁱ	0.96	2.77	3.6021 (17)	137

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

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₁₅ H ₁₂ O ₄
<i>M_r</i>	256.25
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	19.4344 (7), 8.5216 (3), 14.6195 (5)
β (°)	93.075 (2)
<i>V</i> (Å ³)	2417.68 (15)
<i>Z</i>	8
Radiation type	Cu K α
μ (mm ⁻¹)	0.85
Crystal size (mm)	0.29 × 0.27 × 0.25
Data collection	
Diffractometer	Bruker X8 Proteum
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2013)
<i>T_{min}</i> , <i>T_{max}</i>	0.790, 0.815
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	9409, 1986, 1830
<i>R_{int}</i>	0.036
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.584
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.036, 0.094, 1.05
No. of reflections	1986
No. of parameters	173
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.20, -0.25

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXS97* and *SHELXL97* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2008).

1.293 Å; symmetry code: (ii) $-x, -y + 1, -z$], forming sheets parallel to (10 $\bar{1}$); see Table 1.

Synthesis and crystallization

To a stirred solution of methyl 2-hydroxybenzoate (20 mmol) in dry dichloromethane (25 ml), triethylamine (42 mmol) was added at 0°C and stirred for 30 minutes. Benzoyl chloride (28 mmol) was then added dropwise and the resulting mixture stirred at room temperature. After the completion of the reaction, which was monitored by TLC, the organic layer was washed with 5% hydrochloric acid (3 × 15 ml), followed by distilled water (15 ml) and brine solution (10 ml). The solvent was dried over anhydrous sodium sulfate and evaporated under reduced pressure to obtain the title compound. The product obtained was further purified by recrystallization from ethanol. Yield: 87%, m.p 105–107°C.

IR (KBr, cm⁻¹): ν 3580–3660 (OH), 1670 (C=O), 1323 (O—CH₃). ¹H NMR (400 MHz, DMSO-*d*₆): δ 2.8 (*s*, 3H, CH₃), 7.1–8.1 (*m*, 4H, Ar—H), 11.5 (*s*, 1H, OH). LCMS (*M*⁺): (152).

Analysis calculated for: C₈H₈O₃: C, 63.15; H, 5.30; found: C, 63.01; H, 5.26%.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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References

- Bruker (2013). *APEX2, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Khanum, S. A., Shashikanth, S., Umesha, S. & Kavitha, R. (2005). *Eur. J. Med. Chem.* **40**, 1156–1162.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Mohammed, Y. H. I., Naveen, S., Lokanath, N. K., Manjunath, H. R., Al-Ghorbani, M. & Khanum, S. A. (2016). *IUCrData*, **1**, x160415.
- Ozaki, H., Sugihara, K., Tamura, Y., Fujino, C., Watanabe, Y., Uramaru, N., Sone, T., Ohta, S. & Kitamura, S. (2015). *Food Chem. Toxicol.* **86**, 116–123.
- Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.

full crystallographic data

IUCrData (2016). **1**, x161934 [<https://doi.org/10.1107/S2414314616019349>]

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Methyl 2-(benzoyloxy)benzoate

Crystal data

$C_{15}H_{12}O_4$

$M_r = 256.25$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 19.4344\ (7)\ \text{\AA}$

$b = 8.5216\ (3)\ \text{\AA}$

$c = 14.6195\ (5)\ \text{\AA}$

$\beta = 93.075\ (2)^\circ$

$V = 2417.68\ (15)\ \text{\AA}^3$

$Z = 8$

$F(000) = 1072$

$D_x = 1.408\ \text{Mg m}^{-3}$

Cu $K\alpha$ radiation, $\lambda = 1.54178\ \text{\AA}$

Cell parameters from 1830 reflections

$\theta = 4.6\text{--}64.3^\circ$

$\mu = 0.85\ \text{mm}^{-1}$

$T = 296\ \text{K}$

Rectangle, white

$0.29 \times 0.27 \times 0.25\ \text{mm}$

Data collection

Bruker X8 Proteum
diffractometer

Radiation source: Bruker MicroStar microfocus
rotating anode

Helios multilayer optics monochromator

Detector resolution: $18.4\ \text{pixels mm}^{-1}$

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2013)

$T_{\min} = 0.790$, $T_{\max} = 0.815$

9409 measured reflections

1986 independent reflections

1830 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 64.3^\circ$, $\theta_{\min} = 4.6^\circ$

$h = -21 \rightarrow 22$

$k = -9 \rightarrow 9$

$l = -17 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.094$

$S = 1.05$

1986 reflections

173 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

$w = 1/[\sigma^2(F_o^2) + (0.0508P)^2 + 1.6772P]$

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

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

$\Delta\rho_{\max} = 0.20\ \text{e \AA}^{-3}$

$\Delta\rho_{\min} = -0.25\ \text{e \AA}^{-3}$

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors.

Weighted R-factors wR and all goodnesses 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 observed criterion of $F^2 > 2\sigma(F^2)$ is used only for calculating $-R$ -factor-obs 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.16120 (5)	0.39065 (11)	0.10809 (6)	0.0220 (3)
O2	0.07331 (4)	0.34373 (11)	0.19949 (6)	0.0193 (3)
O3	0.16433 (5)	0.52333 (11)	0.30331 (7)	0.0247 (3)
O4	0.24143 (5)	0.39439 (11)	0.39470 (6)	0.0237 (3)
C1	0.06319 (7)	0.55993 (15)	0.09895 (8)	0.0172 (4)
C2	-0.00477 (7)	0.58022 (16)	0.12255 (9)	0.0185 (4)
C3	-0.04390 (7)	0.70056 (16)	0.08286 (9)	0.0204 (4)
C4	-0.01551 (7)	0.80070 (16)	0.02034 (9)	0.0221 (4)
C5	0.05259 (7)	0.78183 (16)	-0.00239 (9)	0.0226 (4)
C6	0.09183 (7)	0.66187 (16)	0.03662 (9)	0.0201 (4)
C7	0.10575 (7)	0.42714 (15)	0.13432 (8)	0.0174 (4)
C8	0.11023 (7)	0.21766 (16)	0.23893 (9)	0.0184 (4)
C9	0.16657 (7)	0.24064 (16)	0.30100 (9)	0.0185 (4)
C10	0.20047 (7)	0.10705 (16)	0.33598 (9)	0.0217 (4)
C11	0.17828 (8)	-0.04234 (17)	0.31165 (10)	0.0243 (4)
C12	0.12089 (7)	-0.06161 (17)	0.25246 (9)	0.0245 (4)
C13	0.08685 (7)	0.06899 (17)	0.21591 (9)	0.0217 (4)
C14	0.18925 (7)	0.40106 (16)	0.33073 (9)	0.0184 (4)
C15	0.26715 (8)	0.54508 (17)	0.42693 (10)	0.0265 (4)
H2	-0.02370	0.51340	0.16470	0.0220*
H3	-0.08930	0.71420	0.09820	0.0240*
H4	-0.04210	0.88080	-0.00650	0.0260*
H5	0.07170	0.84990	-0.04380	0.0270*
H6	0.13730	0.64890	0.02140	0.0240*
H10	0.23870	0.11880	0.37640	0.0260*
H11	0.20190	-0.12970	0.33510	0.0290*
H12	0.10520	-0.16180	0.23720	0.0290*
H13	0.04840	0.05650	0.17600	0.0260*
H15A	0.27720	0.60950	0.37550	0.0400*
H15B	0.30840	0.53000	0.46510	0.0400*
H15C	0.23290	0.59570	0.46160	0.0400*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0188 (5)	0.0254 (5)	0.0221 (5)	0.0031 (4)	0.0042 (4)	0.0022 (4)
O2	0.0170 (5)	0.0214 (5)	0.0195 (5)	0.0020 (4)	0.0019 (4)	0.0052 (4)
O3	0.0258 (5)	0.0213 (5)	0.0268 (5)	0.0038 (4)	-0.0006 (4)	-0.0003 (4)
O4	0.0239 (5)	0.0244 (5)	0.0224 (5)	-0.0029 (4)	-0.0035 (4)	0.0024 (4)

C1	0.0198 (7)	0.0171 (6)	0.0145 (6)	-0.0012 (5)	-0.0006 (5)	-0.0031 (5)
C2	0.0199 (7)	0.0193 (7)	0.0162 (6)	-0.0015 (5)	0.0008 (5)	-0.0012 (5)
C3	0.0189 (7)	0.0207 (7)	0.0215 (7)	0.0017 (5)	0.0001 (5)	-0.0037 (5)
C4	0.0280 (8)	0.0165 (7)	0.0214 (7)	0.0032 (6)	-0.0009 (5)	-0.0015 (5)
C5	0.0309 (8)	0.0172 (7)	0.0200 (7)	-0.0013 (6)	0.0037 (6)	0.0016 (5)
C6	0.0203 (7)	0.0204 (7)	0.0198 (7)	-0.0010 (5)	0.0034 (5)	-0.0027 (5)
C7	0.0182 (7)	0.0202 (7)	0.0136 (6)	-0.0030 (5)	-0.0004 (5)	-0.0008 (5)
C8	0.0180 (7)	0.0211 (7)	0.0166 (6)	0.0032 (5)	0.0050 (5)	0.0039 (5)
C9	0.0186 (7)	0.0215 (7)	0.0159 (6)	0.0013 (5)	0.0054 (5)	0.0030 (5)
C10	0.0197 (7)	0.0258 (7)	0.0197 (7)	0.0023 (6)	0.0024 (5)	0.0039 (5)
C11	0.0267 (8)	0.0211 (7)	0.0255 (7)	0.0037 (6)	0.0051 (6)	0.0058 (6)
C12	0.0297 (8)	0.0203 (7)	0.0239 (7)	-0.0042 (6)	0.0060 (6)	0.0006 (6)
C13	0.0216 (7)	0.0253 (7)	0.0184 (7)	-0.0022 (6)	0.0026 (5)	0.0021 (5)
C14	0.0163 (7)	0.0235 (7)	0.0157 (6)	0.0004 (6)	0.0047 (5)	0.0017 (5)
C15	0.0279 (8)	0.0272 (8)	0.0242 (7)	-0.0063 (6)	0.0001 (6)	-0.0021 (6)

Geometric parameters (Å, °)

O1—C7	1.2039 (16)	C9—C14	1.4938 (19)
O2—C7	1.3693 (15)	C10—C11	1.384 (2)
O2—C8	1.3990 (16)	C11—C12	1.384 (2)
O3—C14	1.2083 (17)	C12—C13	1.387 (2)
O4—C14	1.3433 (16)	C2—H2	0.9300
O4—C15	1.4476 (17)	C3—H3	0.9300
C1—C2	1.3936 (19)	C4—H4	0.9300
C1—C6	1.3961 (18)	C5—H5	0.9300
C1—C7	1.4786 (18)	C6—H6	0.9300
C2—C3	1.3854 (19)	C10—H10	0.9300
C3—C4	1.3864 (19)	C11—H11	0.9300
C4—C5	1.3911 (19)	C12—H12	0.9300
C5—C6	1.3803 (19)	C13—H13	0.9300
C8—C9	1.3979 (19)	C15—H15A	0.9600
C8—C13	1.381 (2)	C15—H15B	0.9600
C9—C10	1.3984 (19)	C15—H15C	0.9600
C7—O2—C8	116.12 (10)	O4—C14—C9	111.33 (11)
C14—O4—C15	115.07 (11)	C1—C2—H2	120.00
C2—C1—C6	120.05 (12)	C3—C2—H2	120.00
C2—C1—C7	121.88 (12)	C2—C3—H3	120.00
C6—C1—C7	117.99 (12)	C4—C3—H3	120.00
C1—C2—C3	119.63 (12)	C3—C4—H4	120.00
C2—C3—C4	120.19 (13)	C5—C4—H4	120.00
C3—C4—C5	120.25 (13)	C4—C5—H5	120.00
C4—C5—C6	119.91 (12)	C6—C5—H5	120.00
C1—C6—C5	119.98 (12)	C1—C6—H6	120.00
O1—C7—O2	122.75 (11)	C5—C6—H6	120.00
O1—C7—C1	125.44 (12)	C9—C10—H10	119.00
O2—C7—C1	111.77 (11)	C11—C10—H10	119.00

O2—C8—C9	121.77 (12)	C10—C11—H11	120.00
O2—C8—C13	116.69 (12)	C12—C11—H11	120.00
C9—C8—C13	121.50 (13)	C11—C12—H12	120.00
C8—C9—C10	117.43 (12)	C13—C12—H12	120.00
C8—C9—C14	121.72 (12)	C8—C13—H13	120.00
C10—C9—C14	120.85 (12)	C12—C13—H13	120.00
C9—C10—C11	121.37 (13)	O4—C15—H15A	109.00
C10—C11—C12	119.94 (13)	O4—C15—H15B	109.00
C11—C12—C13	119.82 (13)	O4—C15—H15C	109.00
C8—C13—C12	119.88 (13)	H15A—C15—H15B	109.00
O3—C14—O4	122.79 (12)	H15A—C15—H15C	109.00
O3—C14—C9	125.86 (12)	H15B—C15—H15C	110.00
C8—O2—C7—O1	3.93 (17)	C4—C5—C6—C1	-0.2 (2)
C8—O2—C7—C1	-178.47 (10)	O2—C8—C9—C10	-179.43 (12)
C7—O2—C8—C9	72.72 (16)	O2—C8—C9—C14	1.8 (2)
C7—O2—C8—C13	-109.40 (13)	C13—C8—C9—C10	2.8 (2)
C15—O4—C14—O3	-1.61 (18)	C13—C8—C9—C14	-175.99 (13)
C15—O4—C14—C9	179.46 (11)	O2—C8—C13—C12	-179.96 (13)
C6—C1—C2—C3	0.90 (19)	C9—C8—C13—C12	-2.1 (2)
C7—C1—C2—C3	-175.76 (12)	C8—C9—C10—C11	-1.3 (2)
C2—C1—C6—C5	-0.68 (19)	C14—C9—C10—C11	177.47 (13)
C7—C1—C6—C5	176.11 (12)	C8—C9—C14—O3	-2.8 (2)
C2—C1—C7—O1	169.87 (13)	C8—C9—C14—O4	176.09 (12)
C2—C1—C7—O2	-7.66 (17)	C10—C9—C14—O3	178.45 (13)
C6—C1—C7—O1	-6.86 (19)	C10—C9—C14—O4	-2.66 (18)
C6—C1—C7—O2	175.62 (11)	C9—C10—C11—C12	-0.9 (2)
C1—C2—C3—C4	-0.3 (2)	C10—C11—C12—C13	1.6 (2)
C2—C3—C4—C5	-0.5 (2)	C11—C12—C13—C8	-0.2 (2)
C3—C4—C5—C6	0.8 (2)		

Hydrogen-bond geometry (Å, °)

Cg2 is the centroid of the C8—C13 ring.

<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>
C15—H15A...Cg2 ⁱ	0.96	2.77	3.6021 (17)	137

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