Crystal structure and Hirshfeld surface analysis of (E)-3-benzylidene-4-oxopentanoic acid

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The asymmetric unit of the title molecule, C_{12}H_{12}O_{3}, contains two independent molecules having opposite conformations and each forming self-dimers through complementary O—H⋯C1/C1/C1/H14 interactions and C—H⋯O hydrogen bonds. These dimers are linked by weak C—H⋯π interactions and C—H⋯O hydrogen bonds into a three-dimensional structure in which one can discern layers parallel to the bc plane. A Hirshfeld surface analysis of the intermolecular interactions is included.

1. Chemical context

Levulinic acid has various derivatives, some of which have a wide range of pharmacological activities. Photodynamic therapy in gastroenterology (Mordon et al., 2005) and cancer treatment for the detection of tumor tissue (Manzo, 2012) are some of the pharmacological applications. These derivatives are also the main compounds used in the synthesis of some pyridazinone derivatives (Boukharsa et al., 2016a,b; Zaoui et al., 2019, 2021). In our research, great attention has been given to the development of diversely functionalized heterocycles (Guerrab et al., 2020, 2021; Abad et al. 2021; Missiou et al., 2021, 2022a,b). Given the wide range of therapeutic applications for such compounds, and in continuation of our research efforts, we report the synthesis, molecular and crystal structure and a Hirshfeld surface analysis of the title compound (see Scheme).

2. Structural commentary

The asymmetric unit consists of two independent molecules (Fig. 1) having opposite configurations, as shown in Fig. 2, where inverting the molecule containing atom O4 allows almost complete overlap between the two independent portions of the asymmetric unit [r.m.s. deviations = 1.204 (no inversion) and 0.163 Å (inversion)]. They also differ in the dihedral angle between their planar parts. Thus, the C2—C1—C7—C8 torsion angle is −143.15 (14)°, while the C14—C13—C19—C20 torsion angle is 139.55 (15)°. The dihedral angle
between the mean plane of the C1–C6 phenyl ring and that defined by atoms C7–C9/C11 is 36.54 (5) in one molecule, while that between the C13–C18 ring and the plane defined by atoms C19–C21/C23 in the other molecule is 41.67 (6). In the first molecule, the dihedral angle between the best planes through C7–C9/C11 and C9/C10/O1/O2 is 81.96 (5), while that between the C19–C21/C23 and C21/C22/O4/O5 planes in the second molecule is 75.53 (6). Finally, the dihedral angle between the mean C8/C11/C12/O3 and C7–C9/C11 planes in the first molecule is 2.88 (12), while that between the mean C20/C23/C24/O6 and C19–C21/C23 planes in the second molecule is 5.22 (3). All bond lengths and angles are as expected.

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

| D—H—A | D—H | H—A | D···A | D—H—A |
|--------|------|------|-------|-------|
| O2—H2A—O1’ | 0.84 (1) | 1.78 (1) | 2.6226 (13) | 178 (2) |
| O5—H5A—O4ii | 0.86 (1) | 1.74 (1) | 2.6000 (13) | 176 (2) |
| C19—H19—O6iii | 0.95 | 2.60 | 3.447 (1) | 148 |

Symmetry codes: (i) −x, −y + 1, −z; (ii) x + 1, y, z + 1; (iii) x, −y + 1, z + 1.

3. Supramolecular features

In the crystal, each independent molecule forms a centrosymmetric self-dimer with the dimers connected by a C—H—...π interaction between C21—H21A and the C7=C8 olefinic bond [H21A—Cg = 2.60 Å, C21—Cg = 3.547 (2) Å] and C21—H21A—Cg = 161°; Cg is the centroid of C7=C8;
The Hirshfeld surface analysis was performed with Crystal-Explorer (Version 21.5; Spackman et al., 2021); the details of the pictorial output are described in a recent publication (Tan et al., 2019). Fig. 5 shows two views of the $d_{\text{norm}}$ surfaces for the two components of the asymmetric unit plotted over the limits from $-0.1211$ to $1.4747$ a.u. The O—H···O hydrogen bonds with which each molecule forms its self-dimer are indicated by the bright red spots in Figs. 5(a) and 5(b), respectively. The weak intermolecular C—H···π interaction with the olefinic double bond appears in Fig. 5(c) as the lighter red spot in the centre of the left side of the drawing, showing the acceptor hydrogen-bond interactions which are connected by the C—H···π interactions. These layers are parallel to the $bc$ plane.
Table 2
Experimental details.

| Crystal data                | C12H12O3 |
|-----------------------------|----------|
| Chemical formula            | C12H12O3 |
| M, g/mol                    | 204.22   |
| Crystal system, space group | Monoclinic, P21/c |
| Temperature (K)             | 125      |
| a, b, c (Å)                 | 15.5987 (3), 13.0782 (3), 11.0396 (2) |
| β (°)                       | 109.063 (1) |
| V (Å³)                      | 2128.60 (8) |
| Z                           | 8        |
| Radiation type              | Cu Kα    |
| μ (mm⁻¹)                    | 0.75     |
| Crystal size (mm)           | 0.35 × 0.18 × 0.07 |

Data collection
Diffractometer
Bruker D8 VENTURE PHOTON (Bruker, 2021). SHELXTL (Sheldrick, 2015a), SHELXL2018 (Sheldrick, 2015b), DIAMOND (Brandenburg & Putz, 2012) and SHELXTL (Bruker, 2021).

Absorption correction
Multi-scan (SADABS; Krause et al., 2015)

Tmin, Tmax
0.85, 0.95

No. of measured, independent and observed [I > 2σ(I)] reflections
36991, 3894, 3477

Rint
0.042

wR2
0.603

| Refinement | R[F² > 2σ(F²)], wR(F²), S |
|------------|---------------------------|
| No. of reflections | 3894                        |
| No. of parameters   | 281                         |
| No. of restraints   | 2                           |
| H-atom treatment   | H atoms treated by a mixture of independent and constrained refinement |

Δρmax, Δρmin (e Å⁻³)
0.26, -0.16

Computer programs: APEX4 and SAINT (Bruker, 2021), SHELXTL (Sheldrick, 2015a), SHELXL2018 (Sheldrick, 2015b), DIAMOND (Brandenburg & Putz, 2012) and SHELXTL (Bruker, 2021).

site, and in a similar location in Fig. 5(d), showing the donor site. Fig. 6 presents the two-dimensional fingerprint plots involving all intermolecular interactions [Fig. 6(a)] and delineated into O···H/H···O [Fig. 6(b)] and C···H···C [Fig. 6(c)] interactions. Figs. 6(d) and 6(e) show the fractions of the overall surface corresponding, respectively, to the two above interactions (28.8% for the former and 18.2% for the latter). For completeness, the H···H interactions constitute 48.4% of the surface.

6. Synthesis and crystallization
A mixture of benzaldehyde (0.01 mol) and levulinic acid (0.02 mol) in a solution of acetic acid (50 ml) was saturated with dry hydrogen chloride gas for 2 h. The mixture was stirred at room temperature for 24 h. The resulting product was extracted and washed with chloroform. The crude compound was recrystallized from acetone to give small colourless crystals (yield: 59%; m.p 398–400 K). IR (KBr, v (cm⁻¹)): 1692 (C=O ketone), 1755 (C=O ester); 1H NMR [300 MHz DMSO-d6, δ (ppm)]: δ 2.42 (s, 3H, CH3), 3.74 (s, 2H, CH2), 7.27–7.75 (m, 5H, phenyl), 7.98 (s, 1H, CH=CH2), 12.11 (s, 1H, OH); 13C NMR [300 MHz DMSO-d6, δ (ppm)]: δ 26.10, 32.83, 128.01, 131.09, 131.52, 133.79, 137.32, 137.43, 171.78, 192.72; MS (ESI+): m/z = 205.88 [M + H]+

7. Refinement
Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms attached to carbon were placed in idealized positions and included as riding contributions with isotropic displacement parameters 1.2–1.5 times those of the attached atoms. H atoms attached to oxygen were placed in locations derived from a difference map and refined with a DFIX 0.84 0.01 instruction.

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Computing details

Data collection: APEX4 (Bruker, 2021); cell refinement: SAINT (Bruker, 2021); data reduction: SAINT (Bruker, 2021); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018 (Sheldrick, 2015b); molecular graphics: DIAMOND (Brandenburg & Putz, 2012); software used to prepare material for publication: SHELXTL (Bruker, 2021).

(E)-3-Benzylidene-4-oxopentanoic acid

Crystal data

C₁₂H₁₂O₃  
Mr = 204.22

Monoclinic, P2₁/c

F(000) = 864  
Dₘ = 1.274 Mg m⁻³

Cu Kα radiation, λ = 1.54178 Å

Cell parameters from 9897 reflections
θ = 3.0–68.3°  
µ = 0.75 mm⁻¹
T = 125 K
Plate, colourless

0.35 × 0.18 × 0.07 mm

Data collection

Bruker D8 VENTURE PHOTON 3 CPAD diffractometer

Radiation source: INCOATEC μS micro-focus source

Mirror monochromator

Detector resolution: 7.3910 pixels mm⁻¹

ω and φ scans

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

36991 measured reflections
3894 independent reflections
3477 reflections with I > 2σ(I)

Refinement

Refinement on F²  
Primary atom site location: dual

Least-squares matrix: full  
Secondary atom site location: difference Fourier map

R[F² > 2σ(F²)] = 0.037  
Hydrogen site location: mixed

wR(F²) = 0.098  
H atoms treated by a mixture of independent

S = 1.04  
and constrained refinement

3894 reflections

w = 1/[σ²(F²) + (0.0449P)² + 0.7261P]  
where P = (F² + 2F₂)/3

281 parameters

2 restraints

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\[(\Delta/\sigma)_{\text{max}} < 0.001\]
\[\Delta \rho_{\text{max}} = 0.26 \text{ e } \text{Å}^{-3}\]

**Special details**

**Experimental.** The diffraction data were obtained from 13 sets of frames, each of width 0.5° in \(\omega\) or \(\phi\), collected with scan parameters determined by the "strategy" routine in APEX3. The scan time varied between 4 and 10 sec/frame, increasing with increasing \(\theta\).

**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. H-atoms attached to carbon were placed in calculated positions (C—H = 0.95 - 0.99 Å) and included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms. Those attached to oxygen were placed in locations derived from a difference map and refined with a DFIX 0.84 0.01 instruction.

**Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)**

|    | x    | y    | z    | \(U_{\text{iso}}\) or \(U_{\text{eq}}\) |
|----|------|------|------|------------------|
| O1 | 0.01466 (6) | 0.43636 (7) | 0.13158 (8) | 0.0335 (2) |
| O2 | 0.11775 (6) | 0.53207 (7) | 0.08370 (9) | 0.0330 (2) |
| H2A| 0.0747 (10)  | 0.5405 (15) | 0.0145 (12) | 0.059 (6)* |
| O3 | 0.15617 (8) | 0.23912 (8) | 0.24312 (9) | 0.0428 (3) |
| C1 | 0.11190 (8) | 0.51281 (10) | 0.51675 (12) | 0.0287 (3) |
| C2 | 0.13778 (9) | 0.52531 (10) | 0.64944 (13) | 0.0319 (3) |
| H2 | 0.149625 | 0.466767 | 0.703342 | 0.038* |
| C3 | 0.14645 (10) | 0.62214 (11) | 0.70370 (14) | 0.0381 (3) |
| H3 | 0.165783 | 0.629690 | 0.794220 | 0.046* |
| C4 | 0.12690 (10) | 0.70747 (11) | 0.62572 (16) | 0.0425 (4) |
| H4 | 0.134096 | 0.773842 | 0.662664 | 0.051* |
| C5 | 0.09682 (11) | 0.69635 (11) | 0.49382 (16) | 0.0425 (4) |
| H5 | 0.081391 | 0.755016 | 0.440322 | 0.051* |
| C6 | 0.08917 (9) | 0.59974 (11) | 0.43962 (14) | 0.0352 (3) |
| H6 | 0.068235 | 0.592658 | 0.349008 | 0.042* |
| C7 | 0.11215 (9) | 0.40800 (10) | 0.46866 (12) | 0.0283 (3) |
| H7 | 0.093428 | 0.356028 | 0.514695 | 0.034* |
| C8 | 0.13551 (8) | 0.37633 (10) | 0.36773 (11) | 0.0277 (3) |
| C9 | 0.16595 (9) | 0.44565 (10) | 0.28089 (12) | 0.0296 (3) |
| H9A| 0.189225 | 0.510133 | 0.326857 | 0.036* |
| H9B| 0.216439 | 0.412547 | 0.259955 | 0.036* |
| C10| 0.09137 (9) | 0.47015 (9) | 0.15870 (11) | 0.0263 (3) |
| C11| 0.13621 (9) | 0.26565 (10) | 0.33666 (12) | 0.0308 (3) |
| C12| 0.11327 (11) | 0.18699 (11) | 0.42061 (14) | 0.0390 (3) |
| H12A| 0.051375 | 0.198520 | 0.421374 | 0.059* |
| H12B| 0.155908 | 0.192707 | 0.508058 | 0.059* |
| H12C| 0.117594 | 0.118474 | 0.387117 | 0.059* |
| O4 | 0.49089 (6) | 0.43991 (8) | 0.62632 (9) | 0.0363 (2) |
Atomic displacement parameters (Å²)

|      | U¹¹ | U²² | U³³ | U¹² | U¹³ | U²³ |
|------|-----|-----|-----|-----|-----|-----|
| O1   | 0.0347 (5) | 0.0383 (5) | 0.0257 (5) | -0.0049 (4) | 0.0075 (4) | 0.0069 (4) |
| O2   | 0.0388 (5) | 0.0329 (5) | 0.0257 (5) | -0.0063 (4) | 0.0082 (4) | 0.0062 (4) |
| O3   | 0.0669 (7) | 0.0353 (5) | 0.0304 (5) | -0.0014 (5) | 0.0219 (5) | -0.0038 (4) |
| C1   | 0.0276 (6) | 0.0284 (7) | 0.0310 (6) | 0.0001 (5) | 0.0108 (5) | 0.0006 (5) |
| C2   | 0.0347 (7) | 0.0313 (7) | 0.0319 (7) | 0.0028 (5) | 0.0139 (5) | 0.0011 (5) |
| C3   | 0.0397 (8) | 0.0382 (8) | 0.0382 (7) | 0.0013 (6) | 0.0154 (6) | -0.0083 (6) |
| C4   | 0.0470 (8) | 0.0284 (7) | 0.0564 (9) | -0.0016 (6) | 0.0229 (7) | -0.0088 (7) |
| C5   | 0.0514 (9) | 0.0283 (7) | 0.0521 (9) | 0.0054 (6) | 0.0226 (7) | 0.0065 (7) |
| C6   | 0.0395 (7) | 0.0314 (7) | 0.0348 (7) | 0.0039 (6) | 0.0123 (6) | 0.0036 (6) |
| C7   | 0.0311 (6) | 0.0269 (6) | 0.0253 (6) | -0.0004 (5) | 0.0070 (5) | 0.0034 (5) |
| C8   | 0.0299 (6) | 0.0280 (6) | 0.0220 (6) | -0.0003 (5) | 0.0040 (5) | 0.0031 (5) |
| C9   | 0.0328 (7) | 0.0298 (7) | 0.0257 (6) | -0.0010 (5) | 0.0088 (5) | 0.0023 (5) |
| C10  | 0.0359 (7) | 0.0216 (6) | 0.0231 (6) | 0.0003 (5) | 0.0120 (5) | -0.0004 (5) |
| C11  | 0.0375 (7) | 0.0303 (7) | 0.0224 (6) | 0.0000 (5) | 0.0067 (5) | -0.0002 (5) |
| C12  | 0.0595 (9) | 0.0266 (7) | 0.0334 (7) | -0.0015 (6) | 0.0185 (7) | -0.0001 (6) |
| O4   | 0.0337 (5) | 0.0428 (6) | 0.0339 (5) | 0.0038 (4) | 0.0131 (4) | 0.0084 (4) |
| O5   | 0.0373 (5) | 0.0402 (6) | 0.0340 (5) | 0.0066 (4) | 0.0155 (4) | 0.0103 (4) |
| O6   | 0.0692 (7) | 0.0404 (6) | 0.0334 (5) | -0.0001 (5) | 0.0218 (5) | -0.0070 (5) |
|   | C13  | C14  | C15  | C16  | C17  | C18  | C19  | C20  | C21  | C22  | C23  | C24  |
|---|------|------|------|------|------|------|------|------|------|------|------|------|
|   | 0.0336 (7) | 0.0330 (7) | 0.0278 (6) | −0.0023 (5) | 0.0074 (5) | −0.0018 (5) | 0.0483 (8) | 0.0373 (8) | 0.0347 (7) | −0.0060 (6) | 0.0183 (6) | −0.0047 (6) |
|   | 0.0520 (9) | 0.0456 (9) | 0.0470 (9) | −0.0059 (7) | 0.0232 (7) | −0.0146 (7) | 0.0508 (9) | 0.0358 (8) | 0.0566 (10) | −0.0040 (7) | 0.0149 (8) | −0.0151 (7) |
|   | 0.0501 (9) | 0.0326 (8) | 0.0489 (9) | −0.0104 (6) | 0.0133 (7) | −0.0038 (7) | 0.0409 (8) | 0.0372 (8) | 0.0359 (7) | −0.0069 (6) | 0.0141 (6) | −0.0040 (6) |
|   | 0.0346 (7) | 0.0309 (7) | 0.0301 (7) | −0.0015 (5) | 0.0128 (5) | 0.0023 (5) | 0.0313 (7) | 0.0310 (7) | 0.0312 (7) | −0.0024 (5) | 0.0141 (5) | 0.0003 (5) |
|   | 0.0320 (7) | 0.0342 (7) | 0.0285 (6) | 0.0003 (5) | 0.0104 (5) | −0.0010 (5) | 0.0363 (7) | 0.0249 (6) | 0.0248 (6) | −0.0014 (5) | 0.0098 (5) | −0.0016 (5) |
|   | 0.0377 (7) | 0.0345 (7) | 0.0334 (7) | −0.0033 (6) | 0.0168 (6) | −0.0026 (6) | 0.0533 (9) | 0.0314 (7) | 0.0414 (8) | −0.0001 (6) | 0.0164 (7) | 0.0000 (6) |

**Geometric parameters (Å, °)**

|   | O1—C10 | 1.2177 (15) | O1—C10 | 1.2177 (15) | O2—H2A | 0.843 (9) | O3—C11 | 1.2221 (16) | O4—C22 | 1.2207 (16) | O5—C22 | 1.3180 (16) |
|---|---------|-------------|---------|-------------|---------|-----------|---------|------------|---------|-------------|---------|-------------|
|   | O2—H2A | 0.843 (9)   | O2—H2A | 0.843 (9)   | O3—C11 | 1.2221 (16)| O3—C11 | 1.2221 (16)| O4—C22 | 1.2207 (16)| O5—C22 | 1.3180 (16) |
|   | O1—C10 | 1.2177 (15) | O1—C10 | 1.2177 (15) | O2—H2A | 0.843 (9) | O3—C11 | 1.2221 (16) | O4—C22 | 1.2207 (16) | O5—C22 | 1.3180 (16) |
|   | O2—H2A | 0.843 (9)   | O2—H2A | 0.843 (9)   | O3—C11 | 1.2221 (16)| O3—C11 | 1.2221 (16) | O4—C22 | 1.2207 (16) | O5—C22 | 1.3180 (16) |
|   | O1—C10 | 1.2177 (15) | O1—C10 | 1.2177 (15) | O2—H2A | 0.843 (9) | O3—C11 | 1.2221 (16) | O4—C22 | 1.2207 (16) | O5—C22 | 1.3180 (16) |

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| Bond                  | Angle (°)   | Bond                  | Angle (°)   |
|----------------------|-------------|----------------------|-------------|
| C3—C2—H2            | 119.6       | C15—C14—H14          | 119.7       |
| C1—C2—H2            | 119.6       | C13—C14—H14          | 119.7       |
| C4—C3—C2            | 119.83 (13) | C16—C15—C14          | 120.35 (14) |
| C4—C3—H3            | 120.1       | C16—C15—H15          | 119.8       |
| C2—C3—H3            | 120.1       | C14—C15—H15          | 119.8       |
| C3—C4—C5            | 120.05 (13) | C15—C16—C17          | 119.83 (14) |
| C3—C4—H4            | 120.0       | C15—C16—H16          | 120.1       |
| C5—C4—H4            | 120.0       | C17—C16—H16          | 120.1       |
| C4—C5—C6            | 120.11 (14) | C18—C17—C16          | 120.04 (14) |
| C4—C5—H5            | 119.9       | C18—C17—H17          | 120.0       |
| C6—C5—H5            | 119.9       | C16—C17—H17          | 120.0       |
| C5—C6—C1            | 120.69 (13) | C17—C18—C13          | 120.83 (13) |
| C5—C6—H6            | 119.7       | C17—C18—H18          | 119.6       |
| C1—C6—H6            | 119.7       | C13—C18—H18          | 119.6       |
| C8—C7—C1            | 128.26 (12) | C20—C19—C13          | 127.13 (13) |
| C8—C7—H7            | 115.9       | C20—C19—H19          | 116.4       |
| C1—C7—H7            | 115.9       | C13—C19—H19          | 116.4       |
| C7—C8—C11           | 120.96 (12) | C19—C20—C23          | 121.25 (12) |
| C7—C8—C9            | 124.70 (12) | C19—C20—C21          | 124.47 (12) |
| C11—C8—C9           | 114.30 (11) | C23—C20—C21          | 114.03 (11) |
| C10—C9—C8           | 112.85 (10) | C22—C21—C20          | 114.69 (11) |
| C10—C9—H9A          | 109.0       | C22—C21—H21A         | 108.6       |
| C8—C9—H9B           | 109.0       | C20—C21—H21B         | 108.6       |
| H9A—C9—H9B          | 107.8       | H21A—C21—H21B        | 107.6       |
| O1—C10—O2           | 123.54 (11) | O4—C22—O5            | 123.84 (12) |
| O1—C10—C9           | 123.69 (11) | O4—C22—C21           | 124.00 (12) |
| O2—C10—C9           | 112.77 (11) | O5—C22—C21           | 112.16 (11) |
| O3—C11—C8           | 119.59 (12) | O6—C23—C20           | 119.67 (13) |
| O3—C11—C12          | 120.27 (12) | O6—C23—C24           | 120.19 (13) |
| C8—C11—C12          | 120.14 (11) | C20—C23—C24          | 120.14 (12) |
| C11—C12—H12A        | 109.5       | C23—C24—H24A         | 109.5       |
| C11—C12—H12B        | 109.5       | C23—C24—H24B         | 109.5       |
| H12A—C12—H12B       | 109.5       | H24A—C24—H24B        | 109.5       |
| C11—C12—H12C        | 109.5       | C23—C24—H24C         | 109.5       |
| H12A—C12—H12C       | 109.5       | H24A—C24—H24C        | 109.5       |
| H12B—C12—H12C       | 109.5       | H24B—C24—H24C        | 109.5       |
| C6—C1—C2—C3         | −4.16 (19)  | C18—C13—C14—C15     | 3.5 (2)     |
| C7—C1—C2—C3         | 174.86 (12) | C19—C13—C14—C15     | −176.45 (14) |
| C1—C2—C3—C4         | 1.8 (2)     | C13—C14—C15—C16     | −0.9 (2)    |
| C2—C3—C4—C5         | 1.4 (2)     | C14—C15—C16—C17     | −1.6 (3)    |
| C3—C4—C5—C6         | −2.2 (2)    | C15—C16—C17—C18     | 1.5 (2)     |
| C4—C5—C6—C1         | −0.3 (2)    | C16—C17—C18—C13     | 1.2 (2)     |
| C2—C1—C6—C5         | 3.4 (2)     | C14—C13—C18—C17     | −3.6 (2)    |
| C7—C1—C6—C5         | −175.55 (13)| C19—C13—C18—C17     | 176.32 (14) |
| C6—C1—C7—C8         | 35.8 (2)    | C18—C13—C19—C20     | −40.4 (2)   |
C2—C1—C7—C8  
C1—C7—C8—C11  
C1—C7—C8—C9  
C7—C8—C9—C10  
C11—C8—C9—C10  
C8—C9—C10—O1  
C8—C9—C10—O2  
C7—C8—C11—O3  
C9—C8—C11—O3  
C7—C8—C11—C12  
C9—C8—C11—C12  

Hydrogen-bond geometry (Å, °)

| D—H···A     | D—H | H···A | D···A  | D—H···A |
|-------------|------|-------|--------|---------|
| O2—H2A···O1i | 0.84 (1) | 1.78 (1) | 2.6226 (13) | 178 (2) |
| O5—H5A···O4ii | 0.86 (1) | 1.74 (1) | 2.6000 (13) | 176 (2) |
| C19—H19···O6iii | 0.95 | 2.60 | 3.447 (1) | 148 |

Symmetry codes: (i) −x, −y+1, −z; (ii) −x+1, −y+1, −z+1; (iii) x, −y+1/2, z+1/2.