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# Crystal structure of 3-acetoxy-2-methyl-benzoic acid

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In the title molecule, $C_{10}H_{10}O_4$, the carboxylic acid group is twisted by 11.37 (15)° from the plane of the benzene ring and the acetoxy group is twisted from this plane by 86.60 (17)°. In the crystal, molecules are linked by pairs of O—H⋯O hydrogen bonds, forming inversion dimers with the expected $R_2^2(8)$ graph-set motif.

## 1. Related literature

For related structures, see: Chiari *et al.* (1981); Fronczek *et al.* (1982); Montis & Hursthouse (2012); Shoaib *et al.* (2014); Wheatley (1964).
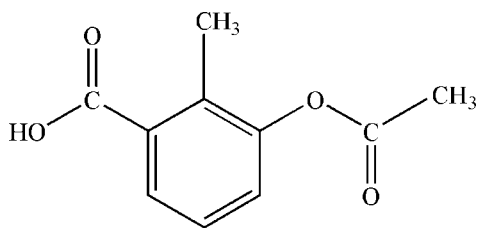


## 2. Experimental

### 2.1. Crystal data

$C_{10}H_{10}O_4$

$M_r = 194.18$

Orthorhombic, $Pbca$
$a = 7.754$ (2) Å
$b = 11.346$ (3) Å
$c = 21.187$ (6) Å
$V = 1864.0$ (9) Å$^3$

$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.11$ mm$^{-1}$
$T = 293$ K
$0.38 \times 0.22 \times 0.06$ mm

### 2.2. Data collection

Bruker SMART APEXII DUO CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min} = 0.960$, $T_{max} = 0.994$

14775 measured reflections
2131 independent reflections
1017 reflections with $I > 2\sigma(I)$
$R_{int} = 0.095$

### 2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.184$
$S = 1.03$
2131 reflections
133 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.22$ e Å$^{-3}$
$\Delta\rho_{min} = -0.18$ e Å$^{-3}$

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

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| O1—H1⋯O2$^i$ | 0.93 (5) | 1.70 (5) | 2.622 (3) | 176 (3) |

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

Supporting information for this paper is available from the IUCr electronic archives (Reference: LH5765).

## References

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# supporting information

## Crystal structure of 3-acetoxy-2-methylbenzoic acid

**Matheswaran Saranya, Annamalai Subashini, Chidambaram Arunagiri and Packianathan Thomas Muthiah**

### S1. Comment

Crystal structures of 2-acetoxy-3-methylbenzoic acid (3-methyl aspirin) (Chiari *et al.*, 1981) and 2-acetoxy-6-methyl-benzoic acid (6-methyl aspirin) have already been reported in the literature (Fronczek *et al.* 1982). Aspirin is a unique drug as it is effective against pain, it has anti-pyretic and anti-inflammatory properties, and it is widely used during heart attacks or strokes. The crystal and molecular structure of aspirin has been reported by Wheatley in 1964. We report herein on the crystal structure of the title molecule.

The molecular structure of the title compound is shown in Fig. 1. There are some very definite angular distortions within the molecule, both in the benzene ring and the carboxyl group, but more particularly, in the acetyl group. The internal angle at C3 (123.6 (3)°) is greater than 120° (the expected value in terms of hybridization principles), and that at C2 is less (116.2 (2)°). The carboxyl group is bent away from the methyl and acetyl group, possibly by repulsion between O1 and O2, so that there is a substantial increase in the angle C2—C1—C7, and a decrease in C6—C1—C7. The angle O1—C7—O2 is greater than 120°, again suggesting repulsion between oxygen atoms. The carboxyl group is twisted by 11.37 (15)° out of the plane of the benzene ring, and the acetoxy group is twisted out of plane by 86.60 (17)°.

Certain torsion angles reveal conformational changes in the carboxyl and acetoxy groups caused by methyl substitution at C2. Atoms C7 and C8 lie in the plane of the benzene ring and O3 is slightly out of plane. The deviations of atoms C7, C8 and O3 from the least-squares plane of the benzene ring are -0.015 (3), 0.010 (3) and 0.111 (2) Å, respectively.

A similar situation is exists in 2-acetoxy-6-methyl benzoic acid (Fronczek *et al.* 1982). Comparison of the C2—C3—O3—C9 angle (94.8 (3)°) reveals that the acetoxy group is skewed slightly away from the methyl group in this structure. There is also a slight but significant twist in the ester backbone, C3—O3—C9—C10 = -178.3 (3)°, present in the title compound, a result quite similar to that in 6-methyl aspirin (Fronczek *et al.* 1982). In the crystal, pairs of O—H···O hydrogen bonds form inversion dimers with the expected $R^2_2(8)$ graph-set motif (Fig. 2). The carboxyl oxygen atom O1 acts as a donor in an intermolecular hydrogen bond to atom O2, producing an $R^2_2(8)$ ring, thus creating a hydrogen-bonded dimer. This type of motif is commonly observed (Shoaib *et al.*, 2014; Montis & Hursthouse *et al.*, 2012).

### S2. Experimental

A hot methanol solution (20 ml) of 3-acetoxy-2-methyl benzoic acid [3 A2MBA] (1 mm 0.194 g, Alfa aesar) was stirred at room temperature for 20 minutes. The resulting solution was kept as such for crystallization. After a few days colourless block-shaped crystals were appeared from the mother liquor.

### S3. Refinement

H atoms bonded to C atoms were positioned geometrically and treated as riding with C—H = 0.93–0.96Å and $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C_{methyl})$. The hydroxyl H atom was refined independently with an isotropic displacement parameter.
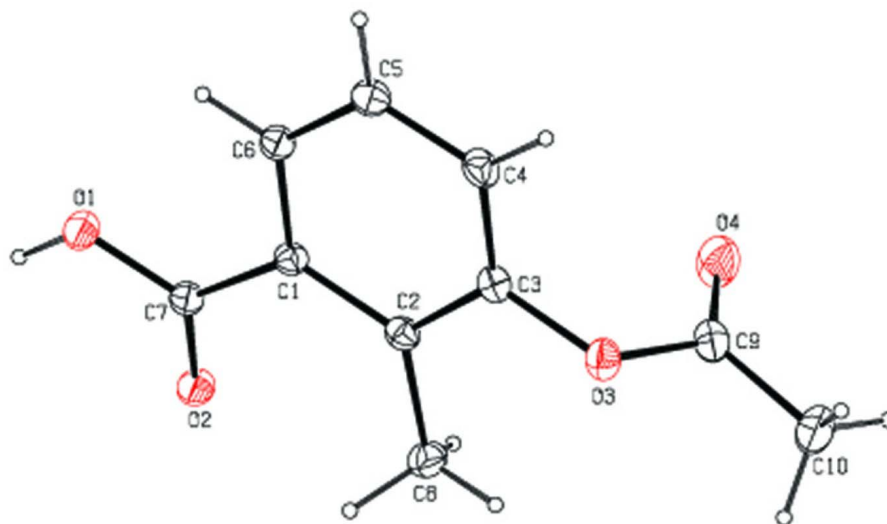
**Figure 1**

The molecular structure of the title compound with displacement ellipsoids drawn at the 30% probability level.
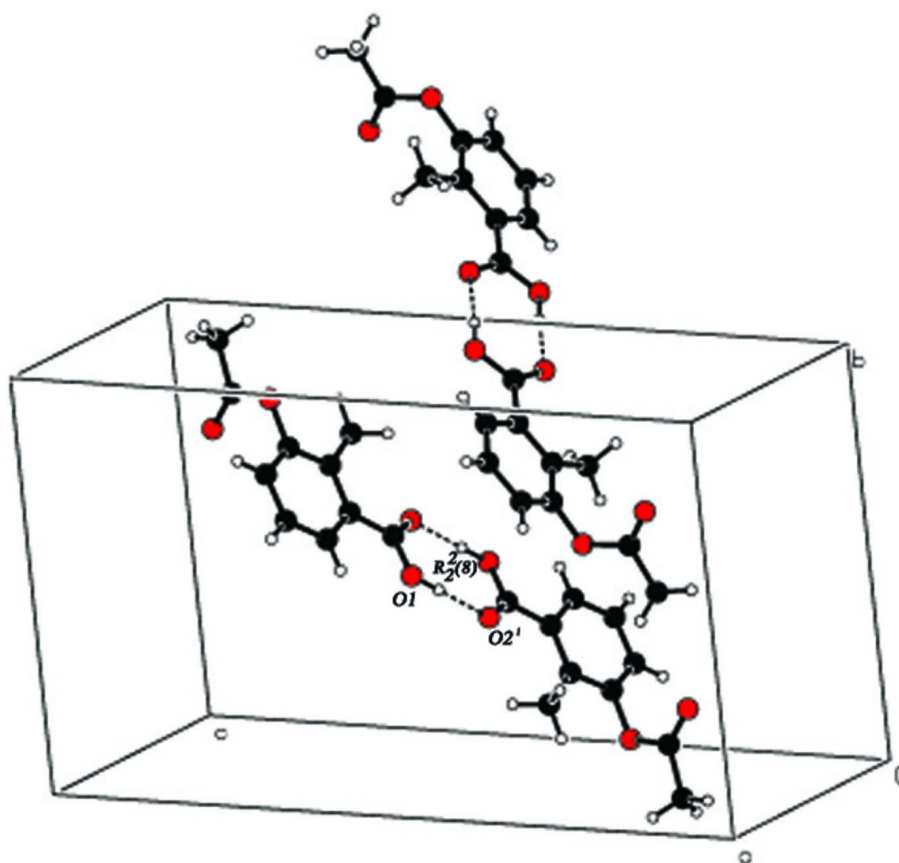


**Figure 2**

Part of the crystal structure with hydrogen bonds shown as dashed lines [symmetry code: (i) -*x*, -*y* + 2, -*z* + 1].

**3-Acetoxy-2-methylbenzoic acid**

*Crystal data*

| | |
|---|---|
| $C_{10}H_{10}O_4$ | $F(000) = 816$ |
| $M_r = 194.18$ | $D_x = 1.384$ Mg m$^{-3}$ |
| Orthorhombic, *Pbca* | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -P 2ac 2ab | $\theta = 1.9$–27.5° |
| $a = 7.754$ (2) Å | $\mu = 0.11$ mm$^{-1}$ |
| $b = 11.346$ (3) Å | $T = 293$ K |
| $c = 21.187$ (6) Å | Block, colourless |
| $V = 1864.0$ (9) Å$^3$ | $0.38 \times 0.22 \times 0.06$ mm |
| $Z = 8$ | |

*Data collection*

| | |
|---|---|
| Bruker SMART APEXII DUO CCD area-detector diffractometer | 14775 measured reflections |
| | 2131 independent reflections |
| | 1017 reflections with $I > 2\sigma(I)$ |
| Radiation source: fine-focus sealed tube | $R_{int} = 0.095$ |
| Graphite monochromator | $\theta_{max} = 27.5°$, $\theta_{min} = 1.9°$ |
| $\varphi$ and $\omega$ scans | $h = -10 \rightarrow 10$ |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2009) | $k = -13 \rightarrow 14$ |
| | $l = -27 \rightarrow 27$ |
| $T_{min} = 0.960$, $T_{max} = 0.994$ | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.063$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.184$ | |
| $S = 1.02$ | H atoms treated by a mixture of independent and constrained refinement |
| 2131 reflections | |
| 133 parameters | $w = 1/[\sigma^2(F_o^2) + (0.0778P)^2 + 0.1948P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 0 restraints | |
| Primary atom site location: structure-invariant direct methods | $(\Delta/\sigma)_{max} < 0.001$ |
| | $\Delta\rho_{max} = 0.22$ e Å$^{-3}$ |
| | $\Delta\rho_{min} = -0.18$ e Å$^{-3}$ |

*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 e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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 (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.2256 (3) | 0.9740 (2) | 0.49706 (10) | 0.0671 (8) |
| O2 | 0.0048 (2) | 0.88776 (19) | 0.45072 (9) | 0.0665 (8) |
| O3 | 0.3342 (3) | 0.54490 (19) | 0.34035 (9) | 0.0677 (8) |

| O4 | 0.3190 (4) | 0.6303 (3) | 0.24740 (11) | 0.1057 (13) |
| C1 | 0.2878 (3) | 0.8175 (3) | 0.42969 (12) | 0.0500 (9) |
| C2 | 0.2399 (3) | 0.7163 (3) | 0.39650 (12) | 0.0523 (10) |
| C3 | 0.3732 (4) | 0.6518 (3) | 0.36983 (12) | 0.0547 (10) |
| C4 | 0.5439 (4) | 0.6833 (3) | 0.37411 (13) | 0.0659 (13) |
| C5 | 0.5868 (4) | 0.7823 (3) | 0.40696 (14) | 0.0658 (11) |
| C6 | 0.4601 (3) | 0.8482 (3) | 0.43437 (13) | 0.0565 (10) |
| C7 | 0.1608 (4) | 0.8942 (3) | 0.45996 (12) | 0.0534 (10) |
| C8 | 0.0586 (4) | 0.6754 (3) | 0.38841 (14) | 0.0688 (11) |
| C9 | 0.3081 (4) | 0.5436 (4) | 0.27810 (16) | 0.0690 (14) |
| C10 | 0.2636 (5) | 0.4254 (3) | 0.25496 (17) | 0.0927 (17) |
| H1 | 0.141 (6) | 1.022 (4) | 0.514 (2) | 0.139 (18)* |
| H4 | 0.62880 | 0.63780 | 0.35490 | 0.0790* |
| H5 | 0.70160 | 0.80480 | 0.41070 | 0.0790* |
| H6 | 0.49030 | 0.91550 | 0.45680 | 0.0680* |
| H8A | 0.00260 | 0.72250 | 0.35680 | 0.1030* |
| H8B | −0.00190 | 0.68300 | 0.42770 | 0.1030* |
| H8C | 0.05830 | 0.59430 | 0.37540 | 0.1030* |
| H10A | 0.23420 | 0.42970 | 0.21100 | 0.1390* |
| H10B | 0.16700 | 0.39560 | 0.27840 | 0.1390* |
| H10C | 0.36050 | 0.37380 | 0.26040 | 0.1390* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0434 (12) | 0.0748 (16) | 0.0830 (14) | 0.0033 (11) | −0.0008 (10) | −0.0255 (12) |
| O2 | 0.0386 (12) | 0.0773 (15) | 0.0836 (14) | 0.0004 (10) | 0.0012 (9) | −0.0192 (12) |
| O3 | 0.0830 (15) | 0.0599 (15) | 0.0602 (13) | 0.0060 (12) | 0.0015 (10) | −0.0054 (10) |
| O4 | 0.151 (3) | 0.102 (2) | 0.0642 (15) | −0.014 (2) | −0.0150 (15) | 0.0037 (16) |
| C1 | 0.0414 (15) | 0.0559 (18) | 0.0527 (15) | 0.0009 (13) | 0.0003 (11) | −0.0004 (13) |
| C2 | 0.0460 (16) | 0.0602 (19) | 0.0507 (15) | 0.0017 (14) | 0.0011 (12) | 0.0033 (14) |
| C3 | 0.0574 (19) | 0.0575 (19) | 0.0492 (15) | 0.0071 (15) | 0.0023 (12) | −0.0001 (14) |
| C4 | 0.0500 (19) | 0.082 (3) | 0.0658 (19) | 0.0084 (17) | 0.0086 (13) | −0.0084 (17) |
| C5 | 0.0405 (16) | 0.079 (2) | 0.078 (2) | 0.0027 (16) | 0.0030 (14) | −0.0089 (18) |
| C6 | 0.0455 (16) | 0.0625 (19) | 0.0615 (17) | 0.0021 (14) | 0.0026 (13) | −0.0065 (15) |
| C7 | 0.0439 (17) | 0.0598 (19) | 0.0565 (16) | 0.0001 (15) | 0.0012 (13) | −0.0051 (14) |
| C8 | 0.0564 (19) | 0.070 (2) | 0.080 (2) | −0.0075 (16) | 0.0007 (14) | −0.0101 (17) |
| C9 | 0.069 (2) | 0.079 (3) | 0.059 (2) | 0.0072 (19) | 0.0002 (15) | −0.0072 (19) |
| C10 | 0.095 (3) | 0.090 (3) | 0.093 (3) | −0.001 (2) | −0.010 (2) | −0.030 (2) |

*Geometric parameters (Å, º)*

| O1—C7 | 1.300 (4) | C4—C5 | 1.363 (5) |
|---|---|---|---|
| O2—C7 | 1.228 (3) | C5—C6 | 1.364 (4) |
| O3—C3 | 1.397 (4) | C9—C10 | 1.469 (6) |
| O3—C9 | 1.334 (4) | C4—H4 | 0.9300 |
| O4—C9 | 1.182 (5) | C5—H5 | 0.9300 |
| O1—H1 | 0.93 (5) | C6—H6 | 0.9300 |

| | | | |
|---|---|---|---|
| C1—C2 | 1.397 (4) | C8—H8A | 0.9600 |
| C1—C6 | 1.384 (3) | C8—H8B | 0.9600 |
| C1—C7 | 1.462 (4) | C8—H8C | 0.9600 |
| C2—C8 | 1.490 (4) | C10—H10A | 0.9600 |
| C2—C3 | 1.387 (4) | C10—H10B | 0.9600 |
| C3—C4 | 1.374 (4) | C10—H10C | 0.9600 |
| | | | |
| O1···O2$^{i}$ | 2.622 (3) | C7···C5$^{ix}$ | 3.506 (4) |
| O2···C7$^{i}$ | 3.369 (4) | C7···O3$^{ii}$ | 3.057 (4) |
| O2···C8 | 2.779 (4) | C8···C9 | 3.383 (5) |
| O2···O1$^{i}$ | 2.622 (3) | C8···O2 | 2.779 (4) |
| O2···O3$^{ii}$ | 3.195 (3) | C9···C8 | 3.383 (5) |
| O3···C7$^{iii}$ | 3.057 (4) | C10···O4$^{iii}$ | 3.413 (5) |
| O3···O2$^{iii}$ | 3.195 (3) | C6···H8C$^{ii}$ | 3.0600 |
| O3···C1$^{iii}$ | 3.337 (4) | C6···H8B$^{viii}$ | 2.9600 |
| O4···C4$^{iv}$ | 3.397 (4) | C7···H8B | 2.7900 |
| O4···C4 | 3.257 (4) | C7···H1$^{i}$ | 2.59 (5) |
| O4···C10$^{ii}$ | 3.413 (5) | C9···H8C | 2.8900 |
| O4···C2 | 3.363 (4) | H1···O1$^{i}$ | 2.85 (5) |
| O1···H6 | 2.3200 | H1···O2$^{i}$ | 1.70 (5) |
| O1···H6$^{v}$ | 2.7200 | H1···C7$^{i}$ | 2.59 (5) |
| O1···H1$^{i}$ | 2.85 (5) | H1···H1$^{i}$ | 2.32 (7) |
| O2···H5$^{vi}$ | 2.6700 | H4···O4$^{vii}$ | 2.6200 |
| O2···H8B | 2.3700 | H5···O2$^{x}$ | 2.6700 |
| O2···H1$^{i}$ | 1.70 (5) | H6···O1 | 2.3200 |
| O2···H8A | 2.7300 | H6···O1$^{v}$ | 2.7200 |
| O3···H8C | 2.3300 | H8A···O2 | 2.7300 |
| O4···H4$^{iv}$ | 2.6200 | H8A···O4$^{iv}$ | 2.8300 |
| O4···H8A$^{vii}$ | 2.8300 | H8B···O2 | 2.3700 |
| C1···O3$^{ii}$ | 3.337 (4) | H8B···C7 | 2.7900 |
| C2···O4 | 3.363 (4) | H8B···C6$^{ix}$ | 2.9600 |
| C3···C7$^{iii}$ | 3.501 (5) | H8C···O3 | 2.3300 |
| C4···O4 | 3.257 (4) | H8C···C9 | 2.8900 |
| C4···O4$^{vii}$ | 3.397 (4) | H8C···C6$^{iii}$ | 3.0600 |
| C5···C7$^{viii}$ | 3.506 (4) | H10B···H10C$^{iv}$ | 2.5300 |
| C7···C3$^{ii}$ | 3.501 (5) | H10C···H10B$^{vii}$ | 2.5300 |
| C7···O2$^{i}$ | 3.369 (4) | | |
| | | | |
| C3—O3—C9 | 119.0 (3) | O3—C9—O4 | 121.6 (4) |
| C7—O1—H1 | 112 (3) | C3—C4—H4 | 121.00 |
| C2—C1—C7 | 122.1 (2) | C5—C4—H4 | 121.00 |
| C6—C1—C7 | 118.0 (3) | C4—C5—H5 | 120.00 |
| C2—C1—C6 | 120.0 (3) | C6—C5—H5 | 120.00 |
| C1—C2—C8 | 124.4 (2) | C1—C6—H6 | 119.00 |
| C3—C2—C8 | 119.5 (3) | C5—C6—H6 | 119.00 |
| C1—C2—C3 | 116.2 (2) | C2—C8—H8A | 109.00 |
| O3—C3—C2 | 118.6 (3) | C2—C8—H8B | 109.00 |
| O3—C3—C4 | 117.6 (3) | C2—C8—H8C | 109.00 |

| | | | |
|---|---|---|---|
| C2—C3—C4 | 123.6 (3) | H8A—C8—H8B | 110.00 |
| C3—C4—C5 | 118.9 (3) | H8A—C8—H8C | 109.00 |
| C4—C5—C6 | 119.6 (3) | H8B—C8—H8C | 110.00 |
| C1—C6—C5 | 121.8 (3) | C9—C10—H10A | 109.00 |
| O1—C7—C1 | 114.8 (3) | C9—C10—H10B | 109.00 |
| O2—C7—C1 | 123.9 (3) | C9—C10—H10C | 109.00 |
| O1—C7—O2 | 121.3 (3) | H10A—C10—H10B | 110.00 |
| O3—C9—C10 | 112.1 (3) | H10A—C10—H10C | 109.00 |
| O4—C9—C10 | 126.4 (3) | H10B—C10—H10C | 110.00 |
| | | | |
| C9—O3—C3—C2 | 94.8 (3) | C2—C1—C7—O2 | −12.0 (5) |
| C9—O3—C3—C4 | −89.2 (3) | C6—C1—C7—O1 | −10.6 (4) |
| C3—O3—C9—O4 | 0.8 (5) | C6—C1—C7—O2 | 167.6 (3) |
| C3—O3—C9—C10 | −178.3 (3) | C1—C2—C3—O3 | 175.0 (2) |
| C6—C1—C2—C3 | 0.1 (4) | C1—C2—C3—C4 | −0.7 (4) |
| C6—C1—C2—C8 | −179.8 (3) | C8—C2—C3—O3 | −5.1 (4) |
| C7—C1—C2—C3 | 179.7 (3) | C8—C2—C3—C4 | 179.2 (3) |
| C7—C1—C2—C8 | −0.2 (4) | O3—C3—C4—C5 | −174.9 (3) |
| C2—C1—C6—C5 | 0.4 (4) | C2—C3—C4—C5 | 0.9 (5) |
| C7—C1—C6—C5 | −179.3 (3) | C3—C4—C5—C6 | −0.5 (5) |
| C2—C1—C7—O1 | 169.8 (3) | C4—C5—C6—C1 | −0.2 (5) |

Symmetry codes: (i) −*x*, −*y*+2, −*z*+1; (ii) −*x*+1/2, *y*+1/2, *z*; (iii) −*x*+1/2, *y*−1/2, *z*; (iv) *x*−1/2, *y*, −*z*+1/2; (v) −*x*+1, −*y*+2, −*z*+1; (vi) *x*−1, *y*, *z*; (vii) *x*+1/2, *y*, −*z*+1/2; (viii) *x*+1/2, −*y*+3/2, −*z*+1; (ix) *x*−1/2, −*y*+3/2, −*z*+1; (x) *x*+1, *y*, *z*.

*Hydrogen-bond geometry (Å, º)*

| *D*—H⋯*A* | *D*—H | H⋯*A* | *D*⋯*A* | *D*—H⋯*A* |
|---|---|---|---|---|
| O1—H1⋯O2<sup>i</sup> | 0.93 (5) | 1.70 (5) | 2.622 (3) | 176 (3) |

Symmetry code: (i) −*x*, −*y*+2, −*z*+1.