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5-Chloro-8-hydroxy-6-methyl-1,4-naphthoquinone

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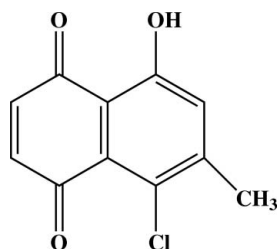
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.001$ Å; R factor = 0.038; wR factor = 0.109; data-to-parameter ratio = 29.3.

The molecule of the title compound, $\text{C}_{11}\text{H}_7\text{ClO}_3$, is planar, with a maximum deviation of 0.0383 (10) Å from the naphthoquinone plane. An intramolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond generates an $S(6)$ ring motif. The crystal packing is stabilized by intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds. Short intramolecular $\text{Cl}\cdots\text{O}$ [2.8234 (8) Å] and $\text{O}\cdots\text{O}$ [2.5530 (11) Å], and intermolecular $\text{Cl}\cdots\text{Cl}$ [3.2777 (3) Å] contacts further stabilize the crystal structure.

Related literature

For the biological activity of the related compound 7-methyljuglone, see: Mahapatra *et al.* (2007); Van der Kooy & Meyer (2006). For the synthesis of 7-methyljuglone from the title compound, see: Musgrave & Skoyles (2001); Mahapatra *et al.* (2007). For bond-length data, see: Allen *et al.* (1987). For graph-set analysis of hydrogen bonding, see: Bernstein *et al.* (1995). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).



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Experimental

Crystal data

$\text{C}_{11}\text{H}_7\text{ClO}_3$
 $M_r = 222.62$
 Monoclinic, $C2/c$
 $a = 10.7546$ (1) Å
 $b = 10.3104$ (1) Å
 $c = 16.8370$ (2) Å
 $\beta = 100.285$ (1)°
 $V = 1836.96$ (3) Å³
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 0.40$ mm⁻¹
 $T = 100$ K
 $0.30 \times 0.21 \times 0.14$ mm

Data collection

Bruker SMART APEXII CCD
 area-detector diffractometer
 Absorption correction: multi-scan
 (SADABS; Bruker, 2005)
 $T_{\min} = 0.891$, $T_{\max} = 0.945$
 17328 measured reflections
 4015 independent reflections
 3356 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.109$
 $S = 1.07$
 4015 reflections
 137 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.61$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.35$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O3}-\text{H1O3}\cdots\text{O2}$	0.86	1.73	2.5530 (11)	161
$\text{C2}-\text{H2A}\cdots\text{O1}^{\text{i}}$	0.93	2.51	3.4124 (12)	163
$\text{C3}-\text{H3A}\cdots\text{O2}^{\text{ii}}$	0.93	2.57	3.3000 (12)	136

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

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2597).

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
 Bernstein, J., Davis, R. E., Shimon, L. & Chang, N. L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
 Bruker (2005). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
 Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.

- Mahapatra, A., Mativandela, S. P. N., Binneman, B., Fourie, P. B., Hamilton, C. J., Meyer, J. J. M., Van der Kooy, F., Houghton, P. & Lall, N. (2007). *Bioorg. Med. Chem.* **15**, 7638–7646.
- Musgrave, O. C. & Skoyles, D. (2001). *J. Chem. Soc. Perkin Trans. 1*, pp. 1318–1320.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Van der Kooy, F. & Meyer, J. J. M. (2006). *S. Afr. J. Chem.* **59**, 60–61.

supporting information

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5-Chloro-8-hydroxy-6-methyl-1,4-naphthoquinone

Daniel Teoh-Chuan Tan, Hasnah Osman, Azlina Harun Kamaruddin, Samuel Robinson Jebas and Hoong-Kun Fun

S1. Comment

5-Hydroxy-7-methyl-1,4-naphthoquinone (7-methyljuglone) has recently been reported to exhibit activity against *Mycobacterium tuberculosis* (Van der Kooy & Meyer, 2006; Mahapatra *et al.*, 2007). Naturally occurring 7-methyljuglone is synthesised from 8-chloro-5-hydroxy-7-methyl-1,4-naphthoquinone in high yield (Musgrave & Skoyles, 2001; Mahapatra *et al.*, 2007). This paper reports the molecular structure of 8-chloro-5-hydroxy-7-methyl-1,4-naphthoquinone; the precursor to synthetic 7-methyljuglone.

The asymmetric unit of (I) consists of one molecule of 8-Chloro-5-hydroxy-7-methyl-1,4-naphthoquinone. The naphthoquinone ring is essentially planar with the maximum deviation from planarity being 0.0383 (10) Å for atom C8. The bond lengths in (I) have normal values (Allen *et al.*, 1987).

An intramolecular O–H \cdots O hydrogen bond generates an S(6) ring motif (Bernstein *et al.*, 1995). The crystal packing is stabilized by intermolecular C–H \cdots O hydrogen bonds (Table 2) (Fig 2). Short intramolecular Cl \cdots O = 2.8234 (8) Å; O \cdots O = 2.5530 (11) Å and intermolecular Cl \cdots Clⁱ = 3.2777 (3) Å [symmetry code: (i) 1 - x, y, 3/2 - z] contacts further stabilize the crystal packing.

S2. Experimental

The title compound was prepared from the Friedel-Crafts acylation of 4-chloro-3-methylphenol with maleic anhydride (Musgrave & Skoyles, 2001). Repeated Soxhlet extraction of the crude Friedel-Crafts product with n-hexane, and silica gel column chromatography purification [chloroform and n-hexane (1:9)] of the n-hexane extract afforded the title compound. Finally, slow evaporation of a n-hexane solution at 305 K gave single crystals of the title compound.

S3. Refinement

H atoms were positioned geometrically [C–H = 0.93 (aromatic) or 0.96 Å (methyl)] and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{aromatic C})$ and $1.5U_{\text{eq}}(\text{methyl C})$. A rotating-group model was used for the methyl groups. The O bound hydrogen atom was located from the Fourier map and refined isotropically with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$.

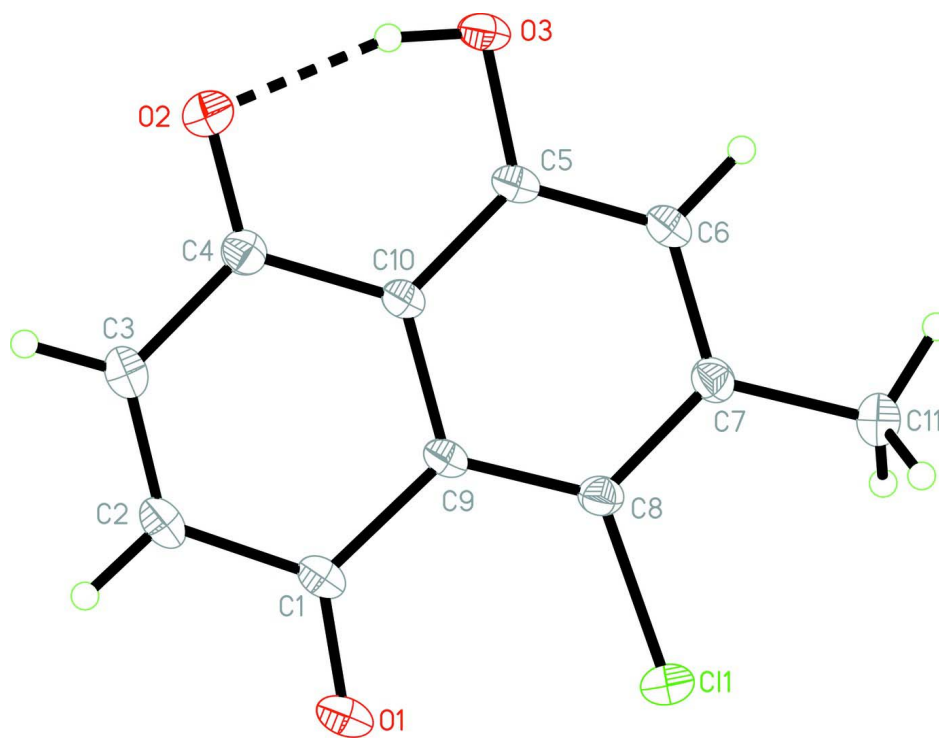


Figure 1

The molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atom numbering scheme. The intramolecular H bond is drawn as a dashed line.

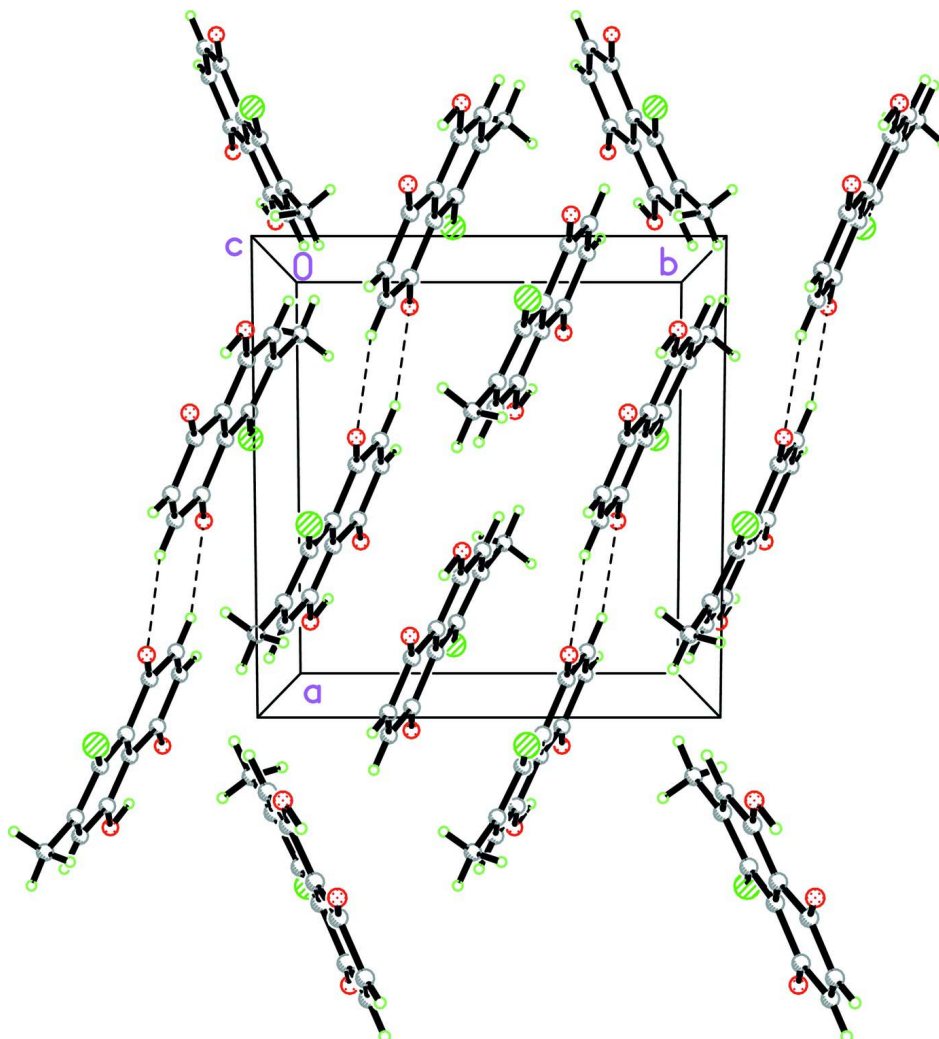


Figure 2

The crystal packing of the title compound, viewed along the *c* axis, showing dimer formation. Dashed lines indicate the hydrogen bonding.

5-Chloro-8-hydroxy-6-methyl-1,4-naphthoquinone

Crystal data

$C_{11}H_7ClO_3$

$M_r = 222.62$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 10.7546 (1) \text{ \AA}$

$b = 10.3104 (1) \text{ \AA}$

$c = 16.8370 (2) \text{ \AA}$

$\beta = 100.285 (1)^\circ$

$V = 1836.96 (3) \text{ \AA}^3$

$Z = 8$

$F(000) = 912$

$D_x = 1.610 \text{ Mg m}^{-3}$

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

Cell parameters from 6307 reflections

$\theta = 2.8\text{--}30.1^\circ$

$\mu = 0.40 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Block, red

$0.30 \times 0.21 \times 0.14 \text{ mm}$

Data collection

Bruker SMART APEXII CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2005)

$T_{\min} = 0.891$, $T_{\max} = 0.945$

17328 measured reflections

4015 independent reflections

3356 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\max} = 35.1^\circ$, $\theta_{\min} = 2.8^\circ$

$h = -12 \rightarrow 17$

$k = -16 \rightarrow 16$

$l = -27 \rightarrow 27$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.109$

$S = 1.07$

4015 reflections

137 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

$w = 1/[\sigma^2(F_o^2) + (0.0595P)^2 + 0.6106P]$

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

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

$\Delta\rho_{\max} = 0.61 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.35 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cyrosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.60008 (2)	0.08776 (3)	0.687132 (14)	0.02314 (8)
O1	0.40351 (7)	0.18970 (8)	0.57005 (5)	0.02395 (16)
O2	0.64859 (7)	0.18264 (8)	0.31989 (4)	0.02085 (15)
O3	0.83772 (7)	0.06289 (8)	0.40048 (4)	0.02028 (14)
H1O3	0.7847	0.1042	0.3653	0.030*
C1	0.46492 (8)	0.18621 (9)	0.51561 (6)	0.01565 (16)
C2	0.40771 (9)	0.23850 (9)	0.43571 (6)	0.01789 (17)
H2A	0.3271	0.2743	0.4292	0.021*
C3	0.46720 (9)	0.23648 (9)	0.37229 (6)	0.01852 (17)
H3A	0.4275	0.2710	0.3232	0.022*
C4	0.59410 (9)	0.18056 (9)	0.37912 (5)	0.01556 (16)
C5	0.77541 (8)	0.06817 (8)	0.46273 (6)	0.01477 (15)
C6	0.83488 (8)	0.01527 (9)	0.53621 (6)	0.01568 (16)
H6A	0.9135	-0.0238	0.5394	0.019*

C7	0.77959 (8)	0.01969 (9)	0.60416 (5)	0.01563 (15)
C8	0.65972 (8)	0.07923 (9)	0.59849 (5)	0.01508 (15)
C9	0.59512 (8)	0.12905 (8)	0.52543 (5)	0.01356 (15)
C10	0.65466 (8)	0.12451 (8)	0.45647 (5)	0.01354 (15)
C11	0.84754 (10)	-0.03753 (11)	0.68182 (6)	0.02193 (19)
H11A	0.9265	-0.0738	0.6736	0.033*
H11B	0.7964	-0.1044	0.6993	0.033*
H11C	0.8632	0.0290	0.7222	0.033*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.02101 (12)	0.03306 (14)	0.01720 (11)	0.00279 (9)	0.00841 (8)	0.00089 (8)
O1	0.0164 (3)	0.0311 (4)	0.0264 (4)	0.0055 (3)	0.0096 (3)	-0.0001 (3)
O2	0.0206 (3)	0.0258 (3)	0.0170 (3)	0.0004 (3)	0.0055 (3)	0.0009 (3)
O3	0.0172 (3)	0.0258 (3)	0.0200 (3)	0.0053 (3)	0.0093 (3)	0.0014 (3)
C1	0.0117 (3)	0.0146 (3)	0.0210 (4)	0.0004 (3)	0.0040 (3)	-0.0023 (3)
C2	0.0123 (4)	0.0162 (4)	0.0243 (4)	0.0018 (3)	0.0009 (3)	-0.0017 (3)
C3	0.0150 (4)	0.0188 (4)	0.0206 (4)	0.0015 (3)	0.0000 (3)	0.0006 (3)
C4	0.0146 (4)	0.0150 (3)	0.0170 (4)	-0.0012 (3)	0.0027 (3)	-0.0009 (3)
C5	0.0122 (3)	0.0152 (3)	0.0181 (4)	-0.0003 (3)	0.0058 (3)	-0.0017 (3)
C6	0.0115 (3)	0.0164 (4)	0.0193 (4)	0.0008 (3)	0.0034 (3)	-0.0012 (3)
C7	0.0126 (3)	0.0168 (4)	0.0171 (4)	-0.0006 (3)	0.0017 (3)	-0.0010 (3)
C8	0.0130 (3)	0.0174 (4)	0.0154 (4)	-0.0011 (3)	0.0043 (3)	-0.0013 (3)
C9	0.0103 (3)	0.0137 (3)	0.0172 (4)	-0.0002 (3)	0.0040 (3)	-0.0017 (3)
C10	0.0113 (3)	0.0141 (3)	0.0156 (3)	0.0001 (3)	0.0033 (3)	-0.0014 (3)
C11	0.0189 (4)	0.0279 (5)	0.0177 (4)	0.0024 (4)	-0.0001 (3)	0.0016 (3)

Geometric parameters (Å, °)

C11—C8	1.7287 (9)	C5—C6	1.3980 (13)
O1—C1	1.2222 (12)	C5—C10	1.4092 (12)
O2—C4	1.2438 (11)	C6—C7	1.3812 (13)
O3—C5	1.3423 (11)	C6—H6A	0.9300
O3—H1O3	0.8581	C7—C8	1.4156 (13)
C1—C2	1.4777 (14)	C7—C11	1.5002 (13)
C1—C9	1.5008 (12)	C8—C9	1.3980 (13)
C2—C3	1.3393 (14)	C9—C10	1.4234 (12)
C2—H2A	0.9300	C11—H11A	0.9600
C3—C4	1.4670 (13)	C11—H11B	0.9600
C3—H3A	0.9300	C11—H11C	0.9600
C4—C10	1.4667 (13)		
C5—O3—H1O3	99.0	C6—C7—C8	118.69 (8)
O1—C1—C2	118.62 (8)	C6—C7—C11	119.62 (8)
O1—C1—C9	123.19 (9)	C8—C7—C11	121.69 (8)
C2—C1—C9	118.18 (8)	C9—C8—C7	121.48 (8)
C3—C2—C1	122.65 (8)	C9—C8—C11	122.56 (7)

C3—C2—H2A	118.7	C7—C8—C11	115.95 (7)
C1—C2—H2A	118.7	C8—C9—C10	118.71 (8)
C2—C3—C4	120.92 (9)	C8—C9—C1	123.27 (8)
C2—C3—H3A	119.5	C10—C9—C1	118.02 (8)
C4—C3—H3A	119.5	C5—C10—C9	119.69 (8)
O2—C4—C10	121.37 (8)	C5—C10—C4	119.08 (8)
O2—C4—C3	119.69 (8)	C9—C10—C4	121.21 (8)
C10—C4—C3	118.94 (8)	C7—C11—H11A	109.5
O3—C5—C6	117.51 (8)	C7—C11—H11B	109.5
O3—C5—C10	122.69 (8)	H11A—C11—H11B	109.5
C6—C5—C10	119.80 (8)	C7—C11—H11C	109.5
C7—C6—C5	121.57 (8)	H11A—C11—H11C	109.5
C7—C6—H6A	119.2	H11B—C11—H11C	109.5
C5—C6—H6A	119.2		
O1—C1—C2—C3	-178.75 (9)	O1—C1—C9—C8	-2.55 (14)
C9—C1—C2—C3	0.15 (13)	C2—C1—C9—C8	178.61 (8)
C1—C2—C3—C4	0.34 (14)	O1—C1—C9—C10	176.82 (9)
C2—C3—C4—O2	-178.28 (9)	C2—C1—C9—C10	-2.03 (12)
C2—C3—C4—C10	1.01 (14)	O3—C5—C10—C9	-178.76 (8)
O3—C5—C6—C7	178.08 (8)	C6—C5—C10—C9	1.06 (13)
C10—C5—C6—C7	-1.75 (13)	O3—C5—C10—C4	-0.34 (13)
C5—C6—C7—C8	0.12 (13)	C6—C5—C10—C4	179.48 (8)
C5—C6—C7—C11	-179.54 (9)	C8—C9—C10—C5	1.20 (13)
C6—C7—C8—C9	2.23 (13)	C1—C9—C10—C5	-178.19 (8)
C11—C7—C8—C9	-178.11 (9)	C8—C9—C10—C4	-177.18 (8)
C6—C7—C8—C11	-177.07 (7)	C1—C9—C10—C4	3.43 (12)
C11—C7—C8—C11	2.59 (12)	O2—C4—C10—C5	-2.09 (13)
C7—C8—C9—C10	-2.87 (13)	C3—C4—C10—C5	178.63 (8)
C11—C8—C9—C10	176.38 (7)	O2—C4—C10—C9	176.30 (8)
C7—C8—C9—C1	176.48 (8)	C3—C4—C10—C9	-2.98 (13)
C11—C8—C9—C1	-4.26 (12)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H1O3 \cdots O2	0.86	1.73	2.5530 (11)	161
C2—H2A \cdots O1 ⁱ	0.93	2.51	3.4124 (12)	163
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