

2,6-Dimethoxy-9,10-anthraquinone

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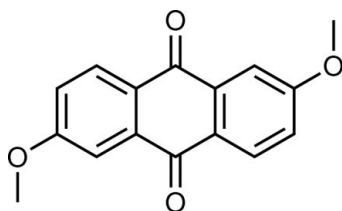
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Key indicators: single-crystal X-ray study; $T = 223$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.057; wR factor = 0.178; data-to-parameter ratio = 15.0.

The title compound, $\text{C}_{16}\text{H}_{12}\text{O}_4$, crystallizes with two half-molecules in the asymmetric unit, each of which is completed by a crystallographic inversion center. The two crystallographically independent molecules have almost the same geometry and are almost planar [maximum deviations = 0.018 (3) and 0.049 (3) Å]. They adopt a conformation in which the $\text{C}_{\text{methyl}}-\text{O}$ bonds are directed along the molecular short axis [C–C–O–C torsion angles of 179.6 (2) and 178.0 (2)°]. In the crystal, the molecular packing is characterized by a combination of a columnar stacking and a herringbone-like arrangement. The molecules form slipped π -stacks along the b axis, in which there are two kinds of columns differing from each other in their slippage. The interplanar distances between neighboring molecules are 3.493 (3) for one column and 3.451 (2) Å for the other.

Related literature

For a study of the effects of alkoxy substituents on the structures and solid-state photophysics of anthraquinones, see: Ohta, Hattori, Kusumoto, *et al.* (2012). For the synthesis, see: Keller & Rüdhardt (1998). For a related structure, see: Ohta, Hattori, Kawase, *et al.* (2012).



Experimental

Crystal data

$\text{C}_{16}\text{H}_{12}\text{O}_4$	$V = 1204.2$ (2) Å ³
$M_r = 268.26$	$Z = 4$
Monoclinic, $P2_1/a$	Mo $K\alpha$ radiation
$a = 16.2689$ (19) Å	$\mu = 0.11$ mm ⁻¹
$b = 3.9357$ (4) Å	$T = 223$ K
$c = 19.9510$ (19) Å	$0.58 \times 0.08 \times 0.06$ mm
$\beta = 109.499$ (3)°	

Data collection

Rigaku R-AXIS RAPID diffractometer	2743 independent reflections
10392 measured reflections	1501 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.066$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.057$	183 parameters
$wR(F^2) = 0.178$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.26$ e Å ⁻³
2743 reflections	$\Delta\rho_{\text{min}} = -0.28$ e Å ⁻³

Data collection: *RAPID-AUTO* (Rigaku, 1999); cell refinement: *PROCESS-AUTO* (Rigaku, 1998); data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KJ2210).

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supporting information

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2,6-Dimethoxy-9,10-anthraquinone

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S1. Comment

9,10-Anthraquinone is an important building block of many dyes and pigments. Recently, we have investigated the effects of alkoxy substituents on the optical properties of anthraquinones both in solution and in the solid state (Ohta, Hattori, Kusumoto, *et al.*, 2012). We have revealed the crystal structure of 2,3,6,7-tetramethoxy-9,10-anthraquinone (Ohta, Hattori, Kawase, *et al.*, 2012). In order to elucidate the substitution effects of the methoxy groups on the crystal packing, the X-ray analysis of the title compound was performed.

The molecular structure of the title compound is shown in Fig. 1. The title compound crystallizes with two halves of the molecule in the asymmetric unit of the unit cell. The complete molecules are located on crystallographic inversion centers. The molecules are almost planar with the maximum deviation of 0.018 (3) Å for C8 in one molecule and 0.049 (3) Å for C16 in another molecule. The molecules prefer the conformations in which the C_{methyl}—O bonds are directed along the short molecular axis. Thus, the torsion angles of C3—C2—O2—C8 and C11—C10—O4—C16 are 179.6 (2) and 178.0 (2)°, respectively. These conformations are similar to the corresponding moiety in 2,3,6,7-tetramethoxy-9,10-anthraquinone (Ohta, Hattori, Kawase, *et al.*, 2012). However, there is a large difference in crystal packing between the title compound and 2,3,6,7-tetramethoxy-9,10-anthraquinone. As shown in Fig. 2, the crystal structure is characterized by a columnar stacking and a herrinbone-like arrangement, although 2,3,6,7-tetramethoxy-9,10-anthraquinone molecules took a slipped-parallel arrangement. Along the *b* axis, there are two columns in which molecules form slipped π -stacks. The interplanar distances between neighboring molecules are 3.493 (3) Å for one column and 3.451 (2) Å for another column. Furthermore, the translational shifts of neighboring molecules in the stacks are as follows: For molecule 1 (C1—C8, O1, and O2), the slip distance between neighboring molecules is 3.94 Å, and the anthraquinone rings in the column slipped relative to each other along the long molecular axis by 0.59 Å and along the short molecular axis by 1.72 Å. In contrast, for molecules 2 (C9—C16, O3, and O4), the slip distance between neighboring molecules is 3.94 Å, and the anthraquinone rings in the column slipped relative to each other along the long molecular axis by 1.89 Å and along the short molecular axis by 0.05 Å.

To examine the influence of crystal packing on the solid-state fluorescence, the fluorescence spectrum and the absolute quantum yield of the title compound were measured with a Hamamatsu Photonics PMA11 calibrated optical multichannel analyzer with a solid-state blue laser ($\lambda_{\text{ex}} = 377$ nm) and a Labsphere IS IS-040-SF integrating sphere, respectively. The crystals showed negligible fluorescence ($\Phi < 0.001$). The fluorescence quenching may result from the π -stacked structure.

S2. Experimental

The title compound was prepared according to the literature procedure (Keller & Rüdhardt, 1998). Single crystals suitable for X-ray analysis were obtained by recrystallization from toluene.

S3. Refinement

All the H atoms were positioned geometrically and refined using a riding model with C—H = 0.94 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic C—H, and C—H = 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for CH₃. The positions of methyl H atoms were optimized rotationally.

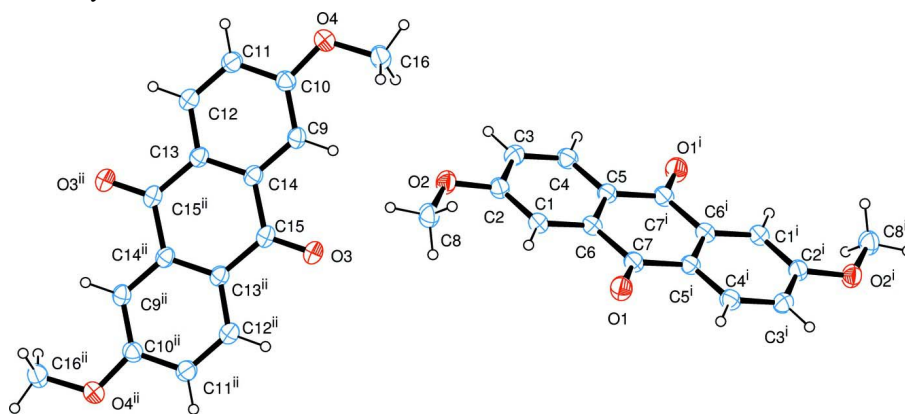


Figure 1

The molecular structure of the title compound, showing the atomic numbering and 50% probability displacement ellipsoids. Symmetry code: (i) $-x, -y + 1, -z$. (ii) $-x + 1, -y + 1, -z + 1$.

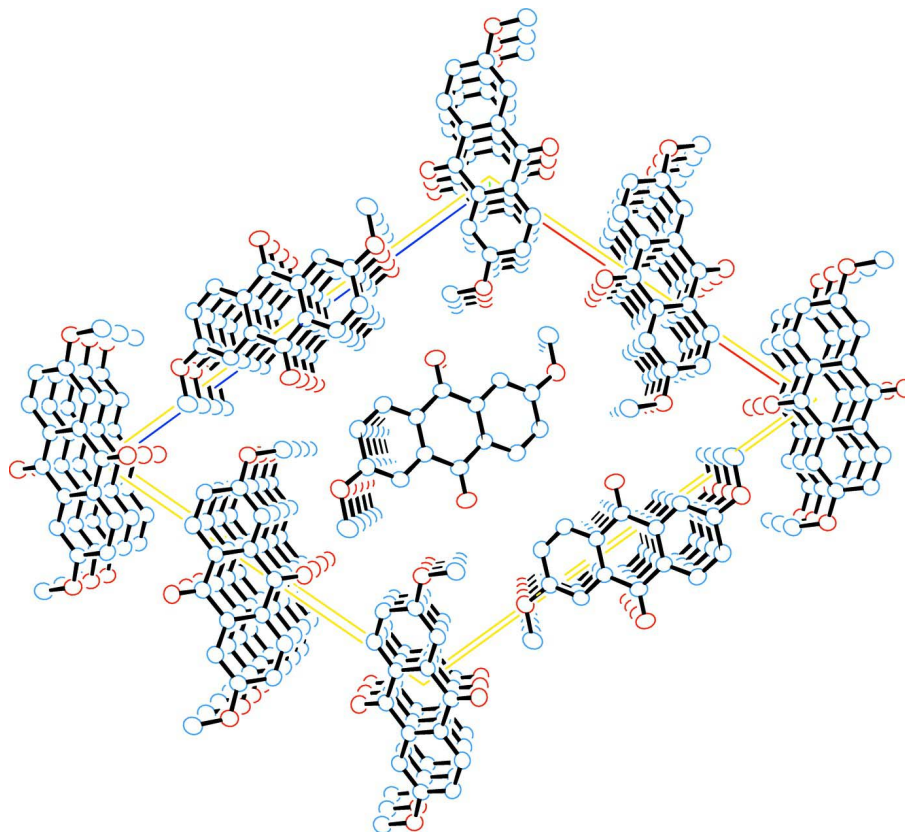


Figure 2

The packing diagram of the title compound, viewed down the b axis. Hydrogen atoms are omitted for clarity.

2,6-dimethoxyanthracene-9,10-dione

Crystal data

$C_{16}H_{12}O_4$

$M_r = 268.26$

Monoclinic, $P2_1/a$

Hall symbol: $-P\ 2yab$

$a = 16.2689$ (19) Å

$b = 3.9357$ (4) Å

$c = 19.9510$ (19) Å

$\beta = 109.499$ (3)°

$V = 1204.2$ (2) Å³

$Z = 4$

$F(000) = 560$

$D_x = 1.48$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 5015 reflections

$\theta = 3.2$ – 27.5 °

$\mu = 0.11$ mm⁻¹

$T = 223$ K

Prism, yellow

$0.58 \times 0.08 \times 0.06$ mm

Data collection

Rigaku R-AXIS RAPID
diffractometer

Radiation source: fine-focus sealed x-ray tube
Graphite monochromator

Detector resolution: 10 pixels mm⁻¹

ω scans

10392 measured reflections

2743 independent reflections

1501 reflections with $I > 2\sigma(I)$

$R_{int} = 0.066$

$\theta_{max} = 27.5$ °, $\theta_{min} = 3.2$ °

$h = -21 \rightarrow 21$

$k = -4 \rightarrow 5$

$l = -22 \rightarrow 25$

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.057$ $wR(F^2) = 0.178$ $S = 1.00$

2743 reflections

183 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0915P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.26 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$ *Special details*

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.10535 (16)	0.2528 (6)	0.13534 (12)	0.0412 (6)
H1	0.0785	0.1497	0.1652	0.049*
C2	0.19519 (17)	0.2826 (6)	0.15742 (12)	0.0424 (6)
C3	0.23494 (17)	0.4388 (6)	0.11278 (12)	0.0452 (6)
H3	0.296	0.4582	0.1275	0.054*
C4	0.18464 (17)	0.5631 (6)	0.04772 (12)	0.0444 (6)
H4	0.2117	0.6696	0.0184	0.053*
C5	0.09401 (16)	0.5337 (6)	0.02449 (11)	0.0387 (6)
C6	0.05487 (16)	0.3753 (6)	0.06904 (11)	0.0389 (6)
C7	-0.04125 (16)	0.3291 (6)	0.04555 (11)	0.0416 (6)
C8	0.21230 (19)	0.0119 (7)	0.26849 (13)	0.0522 (7)
H8A	0.179	-0.1854	0.2455	0.078*
H8B	0.1741	0.1718	0.2805	0.078*
H8C	0.2581	-0.0583	0.3115	0.078*
O1	-0.07545 (12)	0.1767 (5)	0.08334 (8)	0.0541 (5)
O2	0.25054 (12)	0.1718 (5)	0.22088 (8)	0.0506 (5)
C9	0.47309 (16)	0.1926 (6)	0.36503 (12)	0.0401 (6)
H9	0.4168	0.1898	0.331	0.048*
C10	0.54271 (17)	0.0488 (6)	0.34963 (12)	0.0424 (6)
C11	0.62617 (17)	0.0536 (6)	0.39982 (12)	0.0444 (6)
H11	0.6731	-0.0422	0.3888	0.053*
C12	0.64007 (17)	0.1983 (6)	0.46545 (12)	0.0430 (6)
H12	0.6965	0.1982	0.4993	0.052*
C13	0.57121 (15)	0.3458 (6)	0.48250 (11)	0.0380 (6)
C14	0.48757 (15)	0.3411 (6)	0.43153 (11)	0.0377 (5)

C15	0.41234 (15)	0.4966 (6)	0.44723 (12)	0.0409 (6)
C16	0.45117 (19)	-0.1244 (8)	0.23357 (13)	0.0556 (7)
H16A	0.4122	-0.2454	0.2529	0.083*
H16B	0.4552	-0.2453	0.1924	0.083*
H16C	0.4287	0.1026	0.2196	0.083*
O3	0.33925 (12)	0.4938 (5)	0.40245 (8)	0.0542 (5)
O4	0.53622 (12)	-0.1021 (5)	0.28663 (8)	0.0520 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0444 (15)	0.0426 (13)	0.0369 (11)	-0.0015 (11)	0.0141 (10)	-0.0030 (10)
C2	0.0446 (15)	0.0446 (13)	0.0363 (11)	0.0018 (11)	0.0110 (10)	-0.0005 (10)
C3	0.0375 (14)	0.0536 (15)	0.0446 (13)	0.0014 (11)	0.0137 (11)	0.0008 (12)
C4	0.0445 (15)	0.0486 (14)	0.0421 (13)	-0.0036 (11)	0.0172 (11)	-0.0037 (11)
C5	0.0400 (14)	0.0402 (12)	0.0369 (11)	-0.0008 (10)	0.0144 (10)	-0.0015 (10)
C6	0.0425 (14)	0.0399 (12)	0.0361 (11)	-0.0016 (10)	0.0154 (10)	-0.0019 (10)
C7	0.0439 (15)	0.0441 (14)	0.0374 (12)	-0.0019 (11)	0.0145 (11)	-0.0030 (11)
C8	0.0523 (17)	0.0594 (16)	0.0422 (13)	0.0005 (13)	0.0122 (12)	0.0069 (12)
O1	0.0466 (11)	0.0721 (12)	0.0454 (9)	-0.0061 (9)	0.0177 (8)	0.0096 (9)
O2	0.0437 (11)	0.0645 (12)	0.0410 (9)	0.0022 (8)	0.0106 (8)	0.0088 (8)
C9	0.0391 (14)	0.0429 (13)	0.0351 (11)	0.0013 (10)	0.0081 (9)	0.0056 (10)
C10	0.0459 (15)	0.0433 (13)	0.0386 (12)	0.0012 (11)	0.0149 (11)	0.0013 (11)
C11	0.0416 (15)	0.0480 (14)	0.0446 (13)	0.0034 (11)	0.0158 (11)	0.0052 (11)
C12	0.0367 (14)	0.0455 (13)	0.0448 (13)	0.0014 (10)	0.0109 (10)	0.0042 (11)
C13	0.0346 (13)	0.0396 (12)	0.0388 (12)	0.0009 (10)	0.0110 (10)	0.0053 (10)
C14	0.0354 (13)	0.0376 (12)	0.0389 (11)	0.0014 (10)	0.0108 (10)	0.0075 (10)
C15	0.0354 (14)	0.0425 (13)	0.0405 (12)	0.0011 (10)	0.0068 (10)	0.0066 (11)
C16	0.0592 (19)	0.0597 (17)	0.0421 (13)	0.0018 (13)	0.0094 (12)	-0.0066 (13)
O3	0.0367 (11)	0.0701 (12)	0.0484 (10)	0.0058 (9)	0.0042 (8)	-0.0043 (9)
O4	0.0524 (12)	0.0620 (11)	0.0413 (9)	0.0031 (9)	0.0153 (8)	-0.0049 (8)

Geometric parameters (Å, °)

C1—C2	1.384 (4)	C9—C10	1.389 (3)
C1—C6	1.390 (3)	C9—C14	1.396 (3)
C1—H1	0.94	C9—H9	0.94
C2—O2	1.357 (3)	C10—O4	1.362 (3)
C2—C3	1.405 (3)	C10—C11	1.392 (3)
C3—C4	1.373 (3)	C11—C12	1.376 (3)
C3—H3	0.94	C11—H11	0.94
C4—C5	1.395 (4)	C12—C13	1.401 (3)
C4—H4	0.94	C12—H12	0.94
C5—C6	1.401 (3)	C13—C14	1.401 (3)
C5—C7 ⁱ	1.477 (3)	C13—C15 ⁱⁱ	1.474 (3)
C6—C7	1.486 (3)	C14—C15	1.492 (3)
C7—O1	1.232 (3)	C15—O3	1.226 (3)
C7—C5 ⁱ	1.477 (3)	C15—C13 ⁱⁱ	1.474 (3)

C8—O2	1.442 (3)	C16—O4	1.437 (3)
C8—H8A	0.97	C16—H16A	0.97
C8—H8B	0.97	C16—H16B	0.97
C8—H8C	0.97	C16—H16C	0.97
C2—C1—C6	120.0 (2)	C10—C9—C14	119.3 (2)
C2—C1—H1	120	C10—C9—H9	120.3
C6—C1—H1	120	C14—C9—H9	120.3
O2—C2—C1	124.8 (2)	O4—C10—C9	124.3 (2)
O2—C2—C3	115.4 (2)	O4—C10—C11	115.2 (2)
C1—C2—C3	119.7 (2)	C9—C10—C11	120.4 (2)
C4—C3—C2	120.0 (2)	C12—C11—C10	120.1 (2)
C4—C3—H3	120	C12—C11—H11	120
C2—C3—H3	120	C10—C11—H11	120
C3—C4—C5	121.0 (2)	C11—C12—C13	120.8 (2)
C3—C4—H4	119.5	C11—C12—H12	119.6
C5—C4—H4	119.5	C13—C12—H12	119.6
C4—C5—C6	118.7 (2)	C12—C13—C14	118.7 (2)
C4—C5—C7 ⁱ	120.0 (2)	C12—C13—C15 ⁱⁱ	120.0 (2)
C6—C5—C7 ⁱ	121.3 (2)	C14—C13—C15 ⁱⁱ	121.3 (2)
C1—C6—C5	120.6 (2)	C9—C14—C13	120.7 (2)
C1—C6—C7	118.9 (2)	C9—C14—C15	118.8 (2)
C5—C6—C7	120.5 (2)	C13—C14—C15	120.6 (2)
O1—C7—C5 ⁱ	121.2 (2)	O3—C15—C13 ⁱⁱ	121.4 (2)
O1—C7—C6	120.6 (2)	O3—C15—C14	120.5 (2)
C5 ⁱ —C7—C6	118.2 (2)	C13 ⁱⁱ —C15—C14	118.1 (2)
O2—C8—H8A	109.5	O4—C16—H16A	109.5
O2—C8—H8B	109.5	O4—C16—H16B	109.5
H8A—C8—H8B	109.5	H16A—C16—H16B	109.5
O2—C8—H8C	109.5	O4—C16—H16C	109.5
H8A—C8—H8C	109.5	H16A—C16—H16C	109.5
H8B—C8—H8C	109.5	H16B—C16—H16C	109.5
C2—O2—C8	117.2 (2)	C10—O4—C16	117.7 (2)
C6—C1—C2—O2	-179.9 (2)	C14—C9—C10—O4	-179.9 (2)
C6—C1—C2—C3	0.4 (4)	C14—C9—C10—C11	-0.2 (4)
O2—C2—C3—C4	-179.3 (2)	O4—C10—C11—C12	-179.7 (2)
C1—C2—C3—C4	0.4 (4)	C9—C10—C11—C12	0.6 (4)
C2—C3—C4—C5	-0.7 (4)	C10—C11—C12—C13	-0.7 (4)
C3—C4—C5—C6	0.2 (3)	C11—C12—C13—C14	0.4 (4)
C3—C4—C5—C7 ⁱ	179.7 (2)	C11—C12—C13—C15 ⁱⁱ	-179.2 (2)
C2—C1—C6—C5	-0.9 (4)	C10—C9—C14—C13	-0.1 (3)
C2—C1—C6—C7	177.9 (2)	C10—C9—C14—C15	179.6 (2)
C4—C5—C6—C1	0.6 (3)	C12—C13—C14—C9	0.0 (3)
C7 ⁱ —C5—C6—C1	-178.9 (2)	C15 ⁱⁱ —C13—C14—C9	179.6 (2)
C4—C5—C6—C7	-178.1 (2)	C12—C13—C14—C15	-179.7 (2)
C7 ⁱ —C5—C6—C7	2.4 (4)	C15 ⁱⁱ —C13—C14—C15	-0.1 (4)
C1—C6—C7—O1	-1.9 (3)	C9—C14—C15—O3	-0.1 (3)

C5—C6—C7—O1	176.8 (2)	C13—C14—C15—O3	179.6 (2)
C1—C6—C7—C5 ⁱ	178.9 (2)	C9—C14—C15—C13 ⁱⁱ	-179.6 (2)
C5—C6—C7—C5 ⁱ	-2.3 (4)	C13—C14—C15—C13 ⁱⁱ	0.1 (4)
C1—C2—O2—C8	-0.1 (3)	C9—C10—O4—C16	-2.3 (3)
C3—C2—O2—C8	179.6 (2)	C11—C10—O4—C16	178.0 (2)

Symmetry codes: (i) $-x, -y+1, -z$; (ii) $-x+1, -y+1, -z+1$.