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Crystal structure of 2-bromo-1,4-dihydroxy-9,10-anthraquinone

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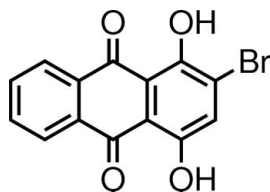
In an attempt to brominate 1,4-dipropoxy-9,10-anthraquinone, a mixture of products, including the title compound, $C_{14}H_7BrO_4$, was obtained. The molecule is essentially planar (r.m.s. deviation = 0.029 Å) and two intramolecular O—H...O hydrogen bonds occur. In the crystal, the molecules are linked by weak C—H...O hydrogen bonds, Br...O contacts [3.240 (5) Å], and π – π stacking interactions [shortest centroid–centroid separation = 3.562 (4) Å], generating a three-dimensional network.

Keywords: crystal structure; 1,4-dihydroxy-9,10-anthraquinone; hydrogen bonds.

CCDC reference: 1025364

1. Related literature

For the original synthesis of the title compound, see: Peters & Tenny (1977). For related crystal structures of 1,4-dihydroxy-9,10-anthraquinone derivatives, see: Nigam & Deppisch (1980); Hall *et al.* (1988). For 1,4-dipropoxy-9,10-anthraquinone, see: Kitamura *et al.* (2004).



2. Experimental

2.1. Crystal data

$C_{14}H_7BrO_4$
 $M_r = 319.11$

Orthorhombic, $Pca2_1$
 $a = 18.977$ (3) Å

$b = 3.7811$ (4) Å
 $c = 15.5047$ (18) Å
 $V = 1112.5$ (2) Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 3.70$ mm⁻¹
 $T = 200$ K
 $0.5 \times 0.4 \times 0.05$ mm

2.2. Data collection

Rigaku R-Axis RAPID diffractometer
Absorption correction: numerical (NUMABS; Higashi, 1999)
 $T_{\min} = 0.322$, $T_{\max} = 0.912$

15045 measured reflections
2476 independent reflections
2103 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.091$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.057$
 $wR(F^2) = 0.099$
 $S = 1.11$
2476 reflections
179 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\max} = 0.85$ e Å⁻³
 $\Delta\rho_{\min} = -1.36$ e Å⁻³
Absolute structure: Flack x determined using 846 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons & Flack, 2004)
Absolute structure parameter: 0.000 (11)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H1...O4	0.80 (9)	1.82 (9)	2.536 (8)	148 (9)
O2–H2...O3	0.99 (10)	1.65 (10)	2.568 (9)	152 (8)
C3–H3...O4 ⁱ	0.95	2.46	3.396 (9)	169
C9–H9...O1 ⁱⁱ	0.95	2.59	3.308 (10)	133
C9–H9...O2 ⁱⁱⁱ	0.95	2.69	3.394 (10)	132

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

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7282).

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supporting information

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Crystal structure of 2-bromo-1,4-dihydroxy-9,10-anthraquinone

Wataru Furukawa, Munenori Takehara, Yoshinori Inoue and Chitoshi Kitamura

S1. Comment

Anthraquinone and its derivatives are important dyestuff molecules. In this work, we attempted to brominate 1,4-dipropoxy-9,10-anthraquinone (Kitamura *et al.*, 2004) with elementary bromine in acetic acid to obtain 2-bromo-1,4-dipropoxy-9,10-anthraquinone. As a result, the reaction afforded a complex mixture of products containing 2-bromo-1,4-dihydroxy-9,10-anthraquinone, C₁₄H₇BrO₄ (I). Synthesis of the title compound, (I), was already reported by Peters & Tenny (1977) using a different method. However, the X-ray structure of (I) was not reported so far. We report here the crystal structure of the title compound, (I).

The title compound crystallizes in the orthorhombic space group *Pca*2₁ with a Flack parameter of 0.000 (11). The molecular structure of (I) is shown in Figure 1. The molecule is nearly planar with the maximum deviation of 0.053 (7) Å for O2. The bond length of C6—O3 and C13—O4 is 1.246 (9) Å and 1.238 (9) Å, respectively. The length of the single C—O bond of C1—O1 and C4—O2 is 1.340 (9) Å and 1.348 (10) Å, respectively. There are two intramolecular hydrogen bonds, O1—H1···O4 and O2—H2···O3. The distance of O1—O4 and O2—O3 is 2.536 (8) Å and 2.568 (9) Å, respectively. These values are in good agreement with those observed for 1,4-dihydroxy-9,10-anthraquinone (Nigam & Deppisch, 1980) and 2,3-dichloro-1,4-dihydroxy-9,10-anthraquinone (Hall *et al.*, 1988).

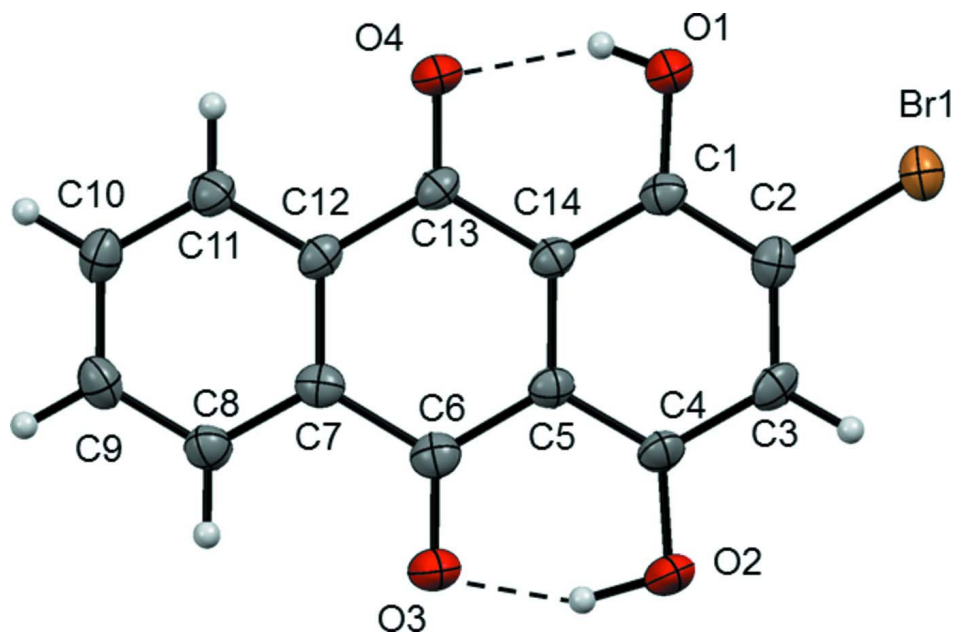
As shown in Figure 2, in the crystal, molecules are linked by C—H···O hydrogen bonds (Table 1) and Br···O contacts [Br1···O3ⁱ = 3.240 (5) Å; symmetry code: (i) *x* - 1/2, -*y* + 1, *z*], whose value is shorter than the sum of van der Waals radii of bromine and oxygen atoms. The molecules are π -stacked along the *a* axis with an interplanar distance of 3.450 Å.

S2. Experimental

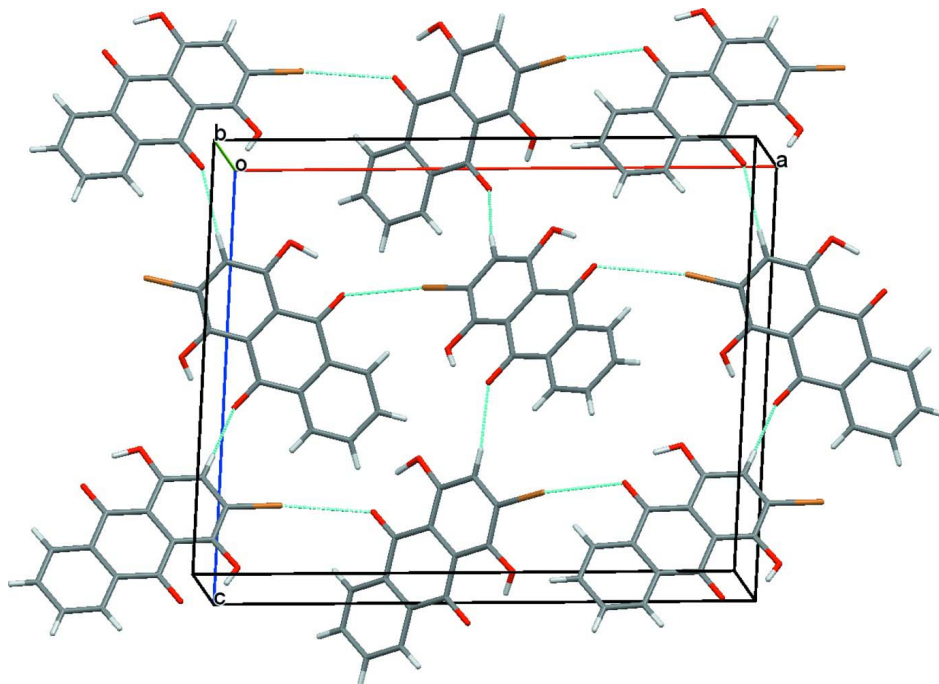
A mixture of 1,4-dipropoxy-9,10-anthraquinone (653 mg, 2.01 mmol), iron powder (50 mg, 0.89 mmol), bromine (0.40 g, 2.5 mmol) in acetic acid (20 ml) was stirred at 80 °C under air. The reaction was quenched with an aqueous solution of Na₂SO₃. Then the reaction products were precipitated. After filtration, the residue was subjected to column chromatography on silica gel using CH₂Cl₂-hexane as the eluent to afford the title compound (18 mg, 2.8% yield) as a red solid. Red platelets were obtained by slow evaporation of a CH₂Cl₂ solution.

S3. Refinement

All the aromatic H atoms were positioned geometrically and refined using a riding model with C—H = 0.95 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The H atoms of the OH groups were located in a difference Fourier map and freely refined [O1—H1 = 0.80 (9) Å and O2—H2 = 0.99 (10) Å].

**Figure 1**

The molecular structure of (I), showing 50% probability displacement ellipsoids. The intramolecular hydrogen bonds are drawn by dashed lines.

**Figure 2**

The crystal packing of (I), showing short contacts of selected C–H...O and Br...O interactions by blue lines.

2-Bromo-1,4-dihydroxy-9,10-anthraquinone*Crystal data*C₁₄H₇BrO₄ $M_r = 319.11$ Orthorhombic, *Pca*2₁

Hall symbol: P 2c -2ac

 $a = 18.977$ (3) Å $b = 3.7811$ (4) Å $c = 15.5047$ (18) Å $V = 1112.5$ (2) Å³ $Z = 4$ $F(000) = 632$ $D_x = 1.905$ Mg m⁻³

Melting point: 485 K

Mo *K*α radiation, $\lambda = 0.71073$ Å

Cell parameters from 12445 reflections

 $\theta = 3.4$ – 27.5° $\mu = 3.70$ mm⁻¹ $T = 200$ K

Platelet, red

 $0.5 \times 0.4 \times 0.05$ 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

Absorption correction: numerical

(NUMABS; Higashi, 1999)

 $T_{\min} = 0.322$, $T_{\max} = 0.912$

15045 measured reflections

2476 independent reflections

2103 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.091$ $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.4^\circ$ $h = -24 \rightarrow 24$ $k = -4 \rightarrow 4$ $l = -20 \rightarrow 20$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.057$ $wR(F^2) = 0.099$ $S = 1.11$

2476 reflections

179 parameters

1 restraint

0 constraints

Primary atom site location: structure-invariant

direct methods

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

 $w = 1/[\sigma^2(F_o^2) + (0.0171P)^2 + 1.2737P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.85$ e Å⁻³ $\Delta\rho_{\min} = -1.36$ e Å⁻³Extinction correction: *SHELXL*, $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.017 (2)

Absolute structure: Flack x determined using846 quotients $[(I^-) - (I)] / [(I^+) + (I)]$ (Parsons &

Flack, 2004)

Absolute structure parameter: 0.000 (11)

Special details

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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	-0.12607 (3)	0.68820 (18)	0.29479 (9)	0.0301 (2)
O1	-0.0661 (3)	0.3974 (18)	0.4573 (4)	0.0354 (15)
O2	0.1215 (3)	0.3132 (19)	0.1883 (4)	0.0381 (15)
O3	0.2118 (2)	0.0436 (14)	0.2927 (4)	0.0350 (11)

O4	0.0247 (3)	0.1085 (17)	0.5543 (3)	0.0361 (15)
C1	-0.0179 (4)	0.373 (2)	0.3944 (5)	0.0242 (16)
C2	-0.0352 (4)	0.4934 (18)	0.3106 (5)	0.0258 (17)
C3	0.0105 (4)	0.476 (2)	0.2437 (5)	0.0259 (17)
H3	-0.0024	0.5634	0.1885	0.031*
C4	0.0786 (5)	0.325 (2)	0.2576 (5)	0.0262 (18)
C5	0.0979 (4)	0.209 (2)	0.3392 (5)	0.0222 (17)
C6	0.1685 (4)	0.061 (2)	0.3529 (5)	0.0271 (17)
C7	0.1876 (4)	-0.062 (2)	0.4400 (5)	0.0236 (15)
C8	0.2550 (4)	-0.196 (2)	0.4556 (5)	0.0280 (17)
H8	0.2885	-0.2062	0.4101	0.034*
C9	0.2731 (4)	-0.312 (2)	0.5369 (6)	0.0304 (18)
H9	0.319	-0.4027	0.5471	0.037*
C10	0.2248 (5)	-0.299 (2)	0.6038 (6)	0.0310 (19)
H10	0.2378	-0.3771	0.6598	0.037*
C11	0.1572 (4)	-0.171 (2)	0.5885 (5)	0.0282 (17)
H11	0.1239	-0.1641	0.6342	0.034*
C12	0.1385 (4)	-0.054 (2)	0.5078 (5)	0.0228 (16)
C13	0.0675 (4)	0.0989 (19)	0.4941 (5)	0.0234 (15)
C14	0.0487 (4)	0.2263 (19)	0.4077 (5)	0.0226 (15)
H1	-0.051 (5)	0.30 (2)	0.499 (6)	0.034*
H2	0.164 (5)	0.20 (2)	0.212 (6)	0.034*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0287 (4)	0.0284 (4)	0.0332 (4)	0.0024 (3)	-0.0052 (4)	0.0010 (8)
O1	0.030 (3)	0.052 (4)	0.024 (3)	0.008 (3)	0.002 (2)	0.003 (3)
O2	0.033 (3)	0.061 (4)	0.021 (3)	0.002 (3)	0.006 (2)	0.007 (3)
O3	0.031 (3)	0.048 (3)	0.025 (2)	0.003 (2)	0.006 (3)	0.000 (5)
O4	0.032 (4)	0.055 (5)	0.022 (3)	0.007 (3)	0.006 (2)	0.003 (3)
C1	0.025 (4)	0.026 (5)	0.021 (3)	-0.004 (3)	0.000 (3)	-0.003 (4)
C2	0.029 (4)	0.021 (4)	0.028 (5)	-0.002 (2)	-0.004 (3)	0.001 (4)
C3	0.038 (5)	0.017 (4)	0.023 (4)	-0.002 (3)	0.001 (3)	0.007 (3)
C4	0.027 (5)	0.028 (5)	0.023 (4)	-0.003 (3)	0.003 (3)	0.007 (4)
C5	0.025 (4)	0.018 (4)	0.023 (4)	-0.002 (3)	0.003 (3)	0.002 (4)
C6	0.030 (4)	0.025 (4)	0.026 (4)	-0.002 (3)	0.001 (3)	-0.003 (4)
C7	0.025 (4)	0.021 (4)	0.025 (4)	-0.003 (3)	0.002 (3)	-0.005 (3)
C8	0.025 (4)	0.028 (4)	0.031 (4)	0.000 (3)	0.003 (3)	0.004 (4)
C9	0.022 (4)	0.031 (4)	0.039 (5)	0.001 (3)	-0.003 (4)	0.002 (5)
C10	0.034 (5)	0.030 (5)	0.029 (4)	-0.001 (3)	-0.005 (4)	0.006 (5)
C11	0.029 (4)	0.031 (4)	0.024 (4)	0.000 (3)	0.000 (3)	-0.002 (4)
C12	0.030 (4)	0.017 (4)	0.022 (4)	-0.002 (3)	0.001 (3)	0.002 (3)
C13	0.030 (4)	0.022 (4)	0.019 (3)	-0.002 (3)	0.000 (3)	-0.001 (3)
C14	0.026 (4)	0.021 (4)	0.020 (3)	-0.001 (3)	0.001 (3)	-0.002 (3)

Geometric parameters (Å, °)

Br1—C2	1.890 (7)	C5—C6	1.467 (12)
O1—C1	1.340 (9)	C6—C7	1.474 (11)
O1—H1	0.80 (9)	C7—C8	1.396 (11)
O2—C4	1.348 (10)	C7—C12	1.405 (10)
O2—H2	0.99 (10)	C8—C9	1.379 (12)
O3—C6	1.246 (9)	C8—H8	0.95
O4—C13	1.238 (9)	C9—C10	1.384 (13)
C1—C14	1.397 (10)	C9—H9	0.95
C1—C2	1.414 (10)	C10—C11	1.391 (12)
C2—C3	1.354 (10)	C10—H10	0.95
C3—C4	1.431 (12)	C11—C12	1.375 (11)
C3—H3	0.95	C11—H11	0.95
C4—C5	1.387 (10)	C12—C13	1.481 (10)
C5—C14	1.416 (10)	C13—C14	1.467 (10)
C1—O1—H1	108 (7)	C12—C7—C6	120.9 (7)
C4—O2—H2	102 (5)	C9—C8—C7	120.0 (7)
O1—C1—C14	122.5 (7)	C9—C8—H8	120
O1—C1—C2	119.2 (7)	C7—C8—H8	120
C14—C1—C2	118.3 (7)	C8—C9—C10	120.6 (8)
C3—C2—C1	122.6 (7)	C8—C9—H9	119.7
C3—C2—Br1	120.2 (6)	C10—C9—H9	119.7
C1—C2—Br1	117.1 (5)	C9—C10—C11	119.7 (8)
C2—C3—C4	118.8 (7)	C9—C10—H10	120.2
C2—C3—H3	120.6	C11—C10—H10	120.2
C4—C3—H3	120.6	C12—C11—C10	120.4 (7)
O2—C4—C5	123.9 (8)	C12—C11—H11	119.8
O2—C4—C3	116.0 (7)	C10—C11—H11	119.8
C5—C4—C3	120.2 (7)	C11—C12—C7	120.1 (7)
C4—C5—C14	119.7 (7)	C11—C12—C13	119.4 (7)
C4—C5—C6	119.6 (7)	C7—C12—C13	120.4 (7)
C14—C5—C6	120.7 (7)	O4—C13—C14	121.3 (7)
O3—C6—C5	120.9 (8)	O4—C13—C12	120.0 (7)
O3—C6—C7	120.5 (7)	C14—C13—C12	118.6 (6)
C5—C6—C7	118.6 (7)	C1—C14—C5	120.3 (7)
C8—C7—C12	119.2 (7)	C1—C14—C13	119.1 (7)
C8—C7—C6	119.9 (7)	C5—C14—C13	120.6 (7)
O1—C1—C2—C3	−179.7 (7)	C9—C10—C11—C12	−0.7 (14)
C14—C1—C2—C3	−1.1 (11)	C10—C11—C12—C7	−0.1 (13)
O1—C1—C2—Br1	1.0 (9)	C10—C11—C12—C13	−176.8 (7)
C14—C1—C2—Br1	179.6 (5)	C8—C7—C12—C11	1.0 (12)
C1—C2—C3—C4	1.2 (12)	C6—C7—C12—C11	179.8 (8)
Br1—C2—C3—C4	−179.5 (6)	C8—C7—C12—C13	177.6 (7)
C2—C3—C4—O2	179.5 (7)	C6—C7—C12—C13	−3.6 (11)
C2—C3—C4—C5	−2.2 (13)	C11—C12—C13—O4	−2.7 (12)

O2—C4—C5—C14	-178.8 (7)	C7—C12—C13—O4	-179.3 (8)
C3—C4—C5—C14	3.0 (14)	C11—C12—C13—C14	179.3 (7)
O2—C4—C5—C6	-0.7 (15)	C7—C12—C13—C14	2.6 (11)
C3—C4—C5—C6	-178.8 (7)	O1—C1—C14—C5	-179.6 (7)
C4—C5—C6—O3	1.6 (13)	C2—C1—C14—C5	1.9 (11)
C14—C5—C6—O3	179.6 (7)	O1—C1—C14—C13	-1.2 (11)
C4—C5—C6—C7	-179.6 (8)	C2—C1—C14—C13	-179.8 (6)
C14—C5—C6—C7	-1.5 (11)	C4—C5—C14—C1	-2.9 (12)
O3—C6—C7—C8	0.7 (12)	C6—C5—C14—C1	179.0 (7)
C5—C6—C7—C8	-178.2 (8)	C4—C5—C14—C13	178.7 (8)
O3—C6—C7—C12	-178.2 (7)	C6—C5—C14—C13	0.7 (11)
C5—C6—C7—C12	3.0 (11)	O4—C13—C14—C1	2.5 (11)
C12—C7—C8—C9	-0.9 (13)	C12—C13—C14—C1	-179.5 (7)
C6—C7—C8—C9	-179.8 (8)	O4—C13—C14—C5	-179.2 (7)
C7—C8—C9—C10	0.1 (14)	C12—C13—C14—C5	-1.1 (11)
C8—C9—C10—C11	0.8 (14)		

Hydrogen-bond geometry (Å, °)

<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>
O1—H1...O4	0.80 (9)	1.82 (9)	2.536 (8)	148 (9)
O2—H2...O3	0.99 (10)	1.65 (10)	2.568 (9)	152 (8)
C3—H3...O4 ⁱ	0.95	2.46	3.396 (9)	169
C9—H9...O1 ⁱⁱ	0.95	2.59	3.308 (10)	133
C9—H9...O2 ⁱⁱⁱ	0.95	2.69	3.394 (10)	132

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