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Crystal structure of 2-hydroxy-3-(prop-2-yn-1-yl)naphthalene-1,4-dione

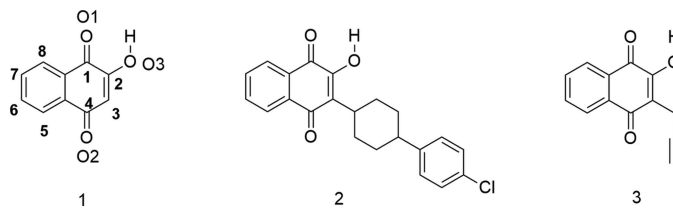
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The naphthoquinone unit of the title compound, C₁₃H₈O₃, is essentially planar, with an r.m.s. deviation of 0.013 Å for the non-H atoms. The essentially linear propargyl group is tilted by *ca* 113° relative to the naphthoquinone plane. In the crystal, molecules are linked *via* a pair of O—H...O hydrogen bonds, forming an inversion dimer. The dimers are further linked *via* pairs of C—H...O hydrogen bonds into a tape structure along [20 $\bar{1}$]. No π – π stacking is observed in the present case as it could be expected for naphthoquinone derivatives.

1. Chemical context

Lawsone (2-hydroxynaphthalene-1,4-dione), **1**, shows promising in the synthesis of analogues of atovaquone, **2**, an anti-malarial drug (Nixon *et al.*, 2013) also used in immunosuppressed patients affected by pneumonia caused by *Pneumocystis carinii* (Cirioni *et al.*, 1995; Comley *et al.*, 1995). Recent studies have shown that it can be also useful in the fight against cancer (Fiorillo *et al.*, 2016; Ashton *et al.*, 2016). Thus far unknown, 2-hydroxy-3-(prop-2-yn-1-yl)naphthalene-1,4-dione (**3**) was obtained in a two steps one-pot procedure by reacting **1** with propargyl iodide, prepared *in situ* from propargyl bromide and potassium iodide. It opens the possibility for the synthesis of triazoles at the C3 position of **1** by [2 + 3] alkyne–azide 1,3-dipolar cycloaddition enabling the preparation of 3-substituted lawsone derivatives with potential pharmacological activity, including atovaquone (**2**) analogues.



Treatment of **1** with a base leads to the formation of the corresponding enolate that can be *O*- or *C*-alkylated depending on the nature of the counter-ion, reaction conditions and nature of the alkyl electrophile (Jordão *et al.*, 2015). When **1** was reacted with propargyl bromide and sodium carbonate in DMF the 2-*O*-propargyl derivative was obtained in 20% yield (Valença *et al.*, 2017). The 3-*C*-propargyl derivative had not been described thus far. In view of the importance of acetylenic compounds for [2 + 3] alkyne–azide 1,3-

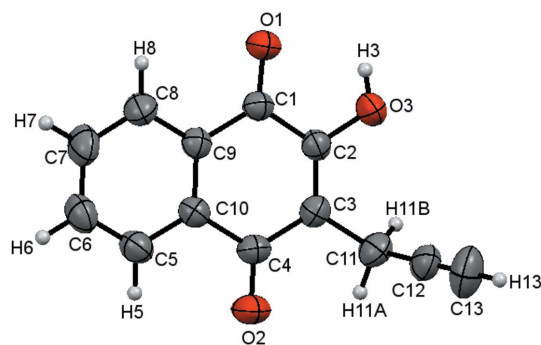


Figure 1
The molecular structure of the title compound **3**. Displacement ellipsoids are drawn at the 50% probability level.

dipolar cycloaddition reactions, known as the *click* reaction, we decided to investigate the 2-*O*- versus 3-*C*-propargylation of **1**. The 3-*C*-propargyl derivative is considered to be an interesting intermediate for the synthesis of 3-triazolo analogues of atovaquone, **2**, and other bioactive 1,4-naphthoquinones. After evaluating the influence of organic and inorganic bases, protic and aprotic solvents, alkylating agents, temperature and reaction time, we obtained **3** in 28% yield. No product of *O*-alkylation was observed in the reaction mixture.

2. Structural commentary

The molecular structure of the title compound, **3**, is shown in Fig. 1. The naphthoquinone unit is essentially planar, with an r.m.s. deviation of 0.013 Å for the non-H atoms. The C–O bond lengths [C1–O1 = 1.2217 (18) Å, C2–O3 = 1.3412 (18) Å and C4–O2 = 1.2488 (19) Å] confirm the presence of 2-hydroxynaphthalene-1,4-dione in the crystalline state and are in agreement with the lengths found by Dekkers *et al.* (1996). The ¹H and ¹³C NMR spectra and HMBC experiments confirm atoms C1 and C4 as carbonyls, as well as a hydroxy group at C2. The propargyl group adopts a nearly perpendicular position [C3–C11–C12 = 112.70 (14)°] regarding the naphthalene ring system to avoid hindrance with the O2 and O3 atoms. The naphthoquinone ring system is characterized by the torsion angles C4–C3–C11–C12 = –100.96 (19)° and C2–C3–C11–C12 = 79.9 (2)°.

3. Supramolecular features

In the crystal, O–H···O and C–H···O hydrogen bonds (O3–H3···O1ⁱ and C5–H5···O2ⁱⁱ; symmetry codes as in Table 1) are responsible for an infinite tape structure running along [20 $\bar{1}$]. All the naphthoquinone units are arranged in a parallel manner with respect to each other, as shown in Fig. 2. π – π stacking interactions are expected for naphthoquinone derivatives (Meyer *et al.*, 2003). However, this type of interaction is not observed here, probably because of the C3 propargyl substituent.

Table 1
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>
O3–H3···O1 ⁱ	0.89 (3)	2.06 (3)	2.8118 (19)	142 (3)
C5–H5···O2 ⁱⁱ	0.93	2.49	3.231 (2)	137

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

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.39, last update May 2018; Groom *et al.*, 2016) for 2-hydroxy-naphthalene-1,4-dione revealed 40 structures and approximately 787 structures which possess the naphthalene-1,4-dione moiety. 2-Hydroxy-3-(3-oxobutyl)naphthalene-1,4-dione (Nasiri *et al.*, 2006) and 2-hydroxy-3-(methyl-prop-1-en-1-yl)naphthalene-1,4-dione (Alcantara Emiliano *et al.*, 2016), compounds with structural similarity to the title compound, were also found. These compounds present a group linked to C3 with an angle nearly perpendicular to the naphthoquinone ring.

5. Synthesis and crystallization

The synthetic scheme is shown in Fig. 3. A mixture of propargyl bromide (0.75 ml, 4.47 mmol) and sodium iodide (1.30 g, 5.33 mmol) in dry acetone (3.5 ml) was stirred for 30 min at room temperature in a closed system. Then, a solution of lawsone (0.1 g, 2.4 mmol) and diisopropylethylamine (0.51 ml, 2.93 mmol) in a 2:1 (*v/v*) mixture of water/*tert*-butanol (24 ml) was added and the reaction mixture was stirred for a further 24 h at 353 K. The reaction was quenched with dichloromethane (*ca* 40 ml) and the heterogeneous mixture was transferred to a separatory funnel. The aqueous

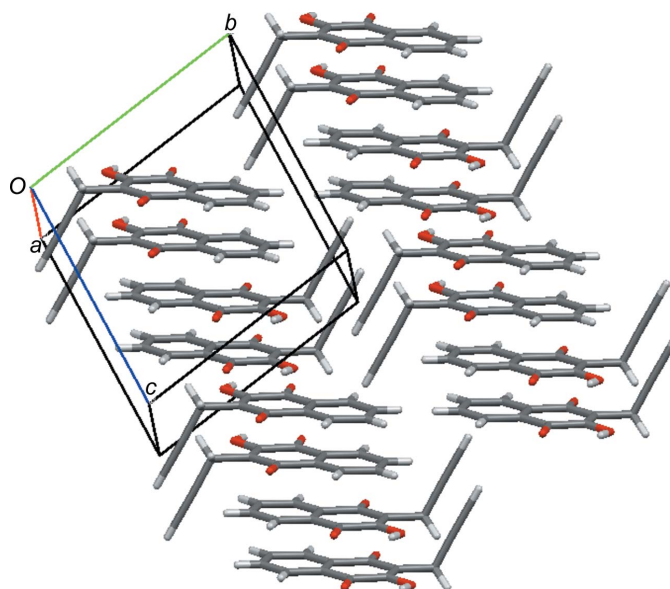


Figure 2
A packing diagram of the title compound.

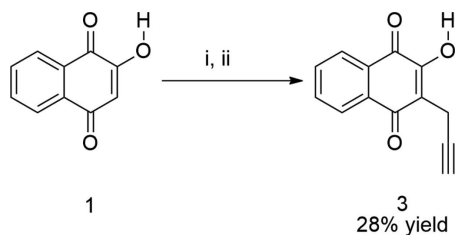


Figure 3

The synthetic scheme of the title compound, **3**; (i) propargyl bromide, sodium iodide and dry acetone, 0.5 h; (ii) diisopropylethylamine and *t*-BuOH/H₂O, 353 K, 24 h.

phase was separated and the organic layer was extracted with 1 mol l⁻¹ hydrochloric acid (3 × 40 ml) and water (3 × 40 ml). The organic layer was dried over anhydrous sodium sulfate and concentrated to dryness. The crude red solid product (0.45 g) was purified by column chromatography (silica) using a 99.5:0.5 (v/v) mixture of hexane/*tert*-butanol containing 0.1% of acetic acid as eluent. Pure title compound was obtained in 28% yield (0.143 g, m.p. 396.7–397.2 K). Single crystals suitable for X-ray analysis were obtained by slow evaporation of a hexane/*tert*-butanol solution (ca 0.5 mg ml⁻¹) at room temperature. The infrared and NMR spectral data and corresponding spectra of **3** are available in the supporting information.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. C-bound H atoms were placed geometrically (C–H = 0.93–0.97 Å) and were refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The O-bound H atom was located in a difference Fourier map and freely refined [O–H = 0.89 (3) Å].

Funding information

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References

- Alcantara Emiliano, S., Welma Duarte Silva, S., Alves Pereira, M., R. dos Santos Malta, V. & Luciano Balliano, T. (2016). *Acta Cryst. E* **72**, 188–190.
- Ashton, T. M., Fokas, E., Kunz-Schughart, L. A., Folkes, L. K., Anbalagan, S., Huether, M., Kelly, C. J., Pirovano, G., Buffa, F. M., Hammond, E. M., Stratford, M., Muschel, R. J., Higgins, G. S. & Mckenna, W. G. (2016). *Nat. Commun.* **7**, 12308.
- Cirioni, O., Giacometti, A., Balducci, M., Burzacchini, F. & Scalise, G. (1995). *J. Antimicrob. Chemother.* **36**, 740–741.
- Comley, J. C. W., Yeates, C. L. & Friend, T. J. (1995). *J. Antimicrob. Chemother.* **39**, 806–809.

Table 2

Experimental details.

Crystal data	
Chemical formula	C ₁₃ H ₈ O ₃
<i>M</i> _r	212.19
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.3695 (4), 9.5278 (8), 10.2972 (9)
α , β , γ (°)	96.814 (7), 93.432 (7), 102.977 (7)
<i>V</i> (Å ³)	507.68 (8)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.10
Crystal size (mm)	0.4 × 0.2 × 0.05
Data collection	
Diffractometer	Rigaku Xcalibur Atlas Gemini ultra
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.720, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	7946, 2508, 1563
<i>R</i> _{int}	0.033
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.695
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.051, 0.147, 1.05
No. of reflections	2508
No. of parameters	149
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.21, -0.5

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b) and *OLEX2* (Dolomanov et al., 2009).

- Dekkers, J., Kooijman, H., Kroon, J. & Grech, E. (1996). *Acta Cryst. C* **52**, 2896–2899.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Fiorillo, M., Lamb, R., Tanowitz, H. B., Mutti, L., Krstic-Demonacos, M., Cappello, A. R., Martinez-Outschoorn, U. E., Sotgia, F. & Lisanti, M. F. (2016). *Oncotarget*, **7**, 34084–34099.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst. B* **72**, 171–179.
- Jordão, A. K., Vargas, M. D., Pinto, A. C., da Silva, F. de C. & Ferreira, V. F. (2015). *RSC Adv.* **5**, 67909–67943.
- Meyer, E. A., Castellano, R. K. & Diederich, F. (2003). *Angew. Chem.* **42**, 1210–1250.
- Nasiri, H. R., Madej, M. G., Lancaster, C. R. D., Schwalbe, H. & Bolte, M. (2006). *Acta Cryst. C* **62**, o671–o673.
- Nixon, G. L., Moss, D. M., Shone, A. E., Lalloo, D. G., Fisher, N., O'Neill, P. M., Ward, S. A. & Biagini, G. A. (2013). *J. Antimicrob. Chemother.* **68**, 977–985.
- Rigaku OD (2015). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, Oxfordshire, England.
- Sheldrick, G. M. (2015a). *Acta Cryst. A* **71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst. C* **71**, 3–8.
- Valença, W. O., Baiju, T. V., Brito, F. G., Araujo, M. H., Pessoa, C., Cavalcanti, B. C., Simore, C. A., Jacob, C., Namboothiri, I. N. N. & da Silva Júnior, E. N. (2017). *ChemistrySelect*, **2**, 4301–4308.

supporting information

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Crystal structure of 2-hydroxy-3-(prop-2-yn-1-yl)naphthalene-1,4-dione

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OD, 2015); data reduction: *CrysAlis PRO* (Rigaku OD, 2015); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

2-Hydroxy-3-(prop-2-yn-1-yl)naphthalene-1,4-dione

Crystal data

$C_{13}H_8O_3$
 $M_r = 212.19$
 Triclinic, $P\bar{1}$
 $a = 5.3695$ (4) Å
 $b = 9.5278$ (8) Å
 $c = 10.2972$ (9) Å
 $\alpha = 96.814$ (7)°
 $\beta = 93.432$ (7)°
 $\gamma = 102.977$ (7)°
 $V = 507.68$ (8) Å³
 $Z = 2$

$F(000) = 220$
 $D_x = 1.388$ Mg m⁻³
 Melting point = 396.8–397.5 K
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 1721 reflections
 $\theta = 3.2$ – 28.7 °
 $\mu = 0.10$ mm⁻¹
 $T = 293$ K
 Prism, colourless
 $0.4 \times 0.2 \times 0.05$ mm

Data collection

Rigaku Xcalibur Atlas Gemini ultra
 diffractometer
 Radiation source: fine-focus sealed X-ray tube,
 Enhance (Mo) X-ray Source
 Graphite monochromator
 Detector resolution: 10.4186 pixels mm⁻¹
 ω scans
 Absorption correction: multi-scan
 (CrysAlis PRO; Rigaku OD, 2015)

$T_{\min} = 0.720$, $T_{\max} = 1.000$
 7946 measured reflections
 2508 independent reflections
 1563 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$
 $\theta_{\max} = 29.6$ °, $\theta_{\min} = 2.8$ °
 $h = -7 \rightarrow 7$
 $k = -12 \rightarrow 12$
 $l = -13 \rightarrow 14$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.147$
 $S = 1.05$
 2508 reflections
 149 parameters
 0 restraints
 Primary atom site location: dual

Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0639P)^2 + 0.058P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.21$ e Å⁻³
 $\Delta\rho_{\min} = -0.5$ e Å⁻³

Special details

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O3	0.6461 (3)	0.33269 (14)	0.01419 (12)	0.0536 (4)
H3	0.796 (5)	0.389 (3)	0.002 (3)	0.104 (10)*
O1	0.9195 (2)	0.59305 (13)	0.12532 (12)	0.0518 (3)
O2	0.0447 (3)	0.36386 (14)	0.31887 (13)	0.0647 (4)
C1	0.7232 (3)	0.54469 (17)	0.17533 (15)	0.0388 (4)
C2	0.5615 (3)	0.39989 (17)	0.11881 (15)	0.0403 (4)
C3	0.3415 (3)	0.33844 (17)	0.16560 (15)	0.0419 (4)
C4	0.2483 (3)	0.41556 (18)	0.27733 (16)	0.0431 (4)
C5	0.3230 (4)	0.6358 (2)	0.44404 (17)	0.0511 (4)
H5	0.1693	0.5951	0.4767	0.061*
C6	0.4664 (4)	0.7695 (2)	0.50175 (19)	0.0586 (5)
H6	0.4109	0.8182	0.5740	0.070*
C7	0.6917 (4)	0.8311 (2)	0.4525 (2)	0.0642 (6)
H7	0.7871	0.9218	0.4915	0.077*
C8	0.7782 (3)	0.7597 (2)	0.34557 (18)	0.0530 (5)
H8	0.9302	0.8021	0.3123	0.064*
C9	0.6345 (3)	0.62361 (16)	0.28851 (15)	0.0389 (4)
C10	0.4061 (3)	0.56178 (17)	0.33796 (15)	0.0397 (4)
C11	0.1798 (4)	0.19019 (18)	0.10516 (18)	0.0536 (5)
H11A	0.0054	0.1811	0.1290	0.064*
H11B	0.1751	0.1833	0.0103	0.064*
C12	0.2779 (4)	0.07067 (19)	0.14761 (17)	0.0552 (5)
C13	0.3566 (5)	-0.0258 (2)	0.1781 (2)	0.0829 (7)
H13	0.4196	-0.1030	0.2026	0.099*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O3	0.0570 (8)	0.0492 (7)	0.0513 (7)	0.0084 (6)	0.0167 (6)	-0.0053 (5)
O1	0.0456 (7)	0.0531 (7)	0.0548 (7)	0.0048 (6)	0.0176 (6)	0.0060 (5)
O2	0.0540 (8)	0.0635 (9)	0.0699 (9)	-0.0031 (6)	0.0256 (7)	0.0043 (7)
C1	0.0372 (9)	0.0400 (8)	0.0405 (8)	0.0091 (7)	0.0057 (7)	0.0094 (6)
C2	0.0433 (9)	0.0397 (9)	0.0391 (9)	0.0119 (7)	0.0057 (7)	0.0047 (6)
C3	0.0437 (9)	0.0374 (8)	0.0430 (9)	0.0075 (7)	0.0018 (7)	0.0040 (7)
C4	0.0395 (9)	0.0443 (9)	0.0453 (9)	0.0061 (7)	0.0073 (7)	0.0110 (7)
C5	0.0499 (10)	0.0575 (11)	0.0468 (10)	0.0140 (8)	0.0121 (8)	0.0047 (8)
C6	0.0615 (12)	0.0620 (12)	0.0503 (10)	0.0185 (10)	0.0071 (9)	-0.0096 (8)
C7	0.0615 (13)	0.0533 (11)	0.0678 (13)	0.0076 (10)	0.0001 (10)	-0.0172 (9)
C8	0.0441 (10)	0.0488 (10)	0.0611 (11)	0.0041 (8)	0.0066 (8)	-0.0004 (8)

C9	0.0377 (9)	0.0390 (8)	0.0402 (8)	0.0101 (7)	0.0019 (7)	0.0046 (6)
C10	0.0389 (9)	0.0430 (9)	0.0380 (8)	0.0106 (7)	0.0049 (7)	0.0055 (7)
C11	0.0497 (10)	0.0458 (10)	0.0582 (11)	0.0004 (8)	0.0023 (9)	0.0006 (8)
C12	0.0671 (12)	0.0395 (10)	0.0515 (10)	0.0016 (9)	0.0070 (9)	-0.0039 (8)
C13	0.113 (2)	0.0483 (12)	0.0862 (16)	0.0257 (13)	-0.0048 (14)	0.0002 (11)

Geometric parameters (Å, °)

O3—H3	0.88 (3)	C6—H6	0.9300
O3—C2	1.3426 (19)	C6—C7	1.375 (3)
O1—C1	1.2217 (18)	C7—H7	0.9300
O2—C4	1.2189 (19)	C7—C8	1.384 (3)
C1—C2	1.485 (2)	C8—H8	0.9300
C1—C9	1.473 (2)	C8—C9	1.392 (2)
C2—C3	1.340 (2)	C9—C10	1.390 (2)
C3—C4	1.465 (2)	C11—H11A	0.9700
C3—C11	1.521 (2)	C11—H11B	0.9700
C4—C10	1.499 (2)	C11—C12	1.458 (3)
C5—H5	0.9300	C12—C13	1.161 (3)
C5—C6	1.376 (3)	C13—H13	0.9300
C5—C10	1.381 (2)		
C2—O3—H3	106.5 (17)	C6—C7—C8	120.80 (18)
O1—C1—C2	118.90 (14)	C8—C7—H7	119.6
O1—C1—C9	123.40 (15)	C7—C8—H8	120.5
C9—C1—C2	117.69 (14)	C7—C8—C9	119.08 (17)
O3—C2—C1	115.90 (14)	C9—C8—H8	120.5
C3—C2—O3	120.71 (15)	C8—C9—C1	120.23 (15)
C3—C2—C1	123.38 (14)	C10—C9—C1	119.71 (14)
C2—C3—C4	119.88 (15)	C10—C9—C8	120.07 (15)
C2—C3—C11	122.10 (15)	C5—C10—C4	119.53 (15)
C4—C3—C11	118.01 (15)	C5—C10—C9	119.69 (15)
O2—C4—C3	121.03 (16)	C9—C10—C4	120.78 (14)
O2—C4—C10	120.40 (15)	C3—C11—H11A	109.1
C3—C4—C10	118.56 (14)	C3—C11—H11B	109.1
C6—C5—H5	119.8	H11A—C11—H11B	107.8
C6—C5—C10	120.37 (17)	C12—C11—C3	112.70 (14)
C10—C5—H5	119.8	C12—C11—H11A	109.1
C5—C6—H6	120.0	C12—C11—H11B	109.1
C7—C6—C5	119.98 (17)	C13—C12—C11	178.3 (2)
C7—C6—H6	120.0	C12—C13—H13	180.0
C6—C7—H7	119.6		
O1—C1—C2—O3	-0.4 (2)	C4—C3—C11—C12	-100.96 (19)
O1—C1—C2—C3	-179.15 (16)	O2—C4—C10—C5	2.0 (3)
C9—C1—C2—O3	178.72 (14)	O2—C4—C10—C9	-177.93 (16)
C9—C1—C2—C3	-0.1 (2)	C3—C4—C10—C5	-179.45 (16)
O1—C1—C9—C8	-1.0 (2)	C3—C4—C10—C9	0.7 (2)

O1—C1—C9—C10	178.81 (15)	C10—C5—C6—C7	1.0 (3)
C2—C1—C9—C8	179.98 (14)	C6—C5—C10—C4	179.40 (17)
C2—C1—C9—C10	-0.2 (2)	C6—C5—C10—C9	-0.7 (3)
O3—C2—C3—C4	-178.09 (15)	C5—C6—C7—C8	-0.5 (3)
O3—C2—C3—C11	1.0 (2)	C6—C7—C8—C9	-0.4 (3)
C1—C2—C3—C4	0.7 (2)	C7—C8—C9—C1	-179.48 (16)
C1—C2—C3—C11	179.77 (15)	C7—C8—C9—C10	0.7 (3)
C2—C3—C4—O2	177.64 (16)	C1—C9—C10—C4	-0.1 (2)
C2—C3—C4—C10	-0.9 (2)	C1—C9—C10—C5	-180.00 (16)
C11—C3—C4—O2	-1.5 (2)	C8—C9—C10—C4	179.73 (15)
C11—C3—C4—C10	179.92 (15)	C8—C9—C10—C5	-0.2 (2)
C2—C3—C11—C12	79.9 (2)		

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>
O3—H3...O1 ⁱ	0.89 (3)	2.06 (3)	2.8118 (19)	142 (3)
C5—H5...O2 ⁱⁱ	0.93	2.49	3.231 (2)	137

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