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5-Hydroxy-8-nitro-1,4-naphthoquinone

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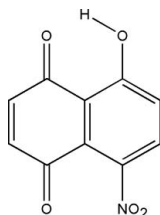
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.001$ Å; R factor = 0.041; wR factor = 0.120; data-to-parameter ratio = 18.4.

The title compound, $\text{C}_{10}\text{H}_5\text{NO}_5$, features an intramolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond, forming a six-membered ring with an $S(6)$ ring motif. The nitro group makes a dihedral angle of $71.66(5)^\circ$ with the plane of the benzene ring to which it is bound. The two rings are almost coplanar, with a dihedral angle of $4.44(5)^\circ$. Short intermolecular distances between the centroids of the six-membered rings [3.7188(6)–3.8299(6) Å] indicate the existence of $\pi-\pi$ interactions. The interesting features of the crystal structure are the short intermolecular $\text{O}\cdots\text{O}$ and $\text{O}\cdots\text{N}$ interactions. The crystal packing is stabilized by intramolecular $\text{O}-\text{H}\cdots\text{O}$ and intermolecular $\text{C}-\text{H}\cdots\text{O}$ ($\times 3$) hydrogen bonds, and $\text{C}-\text{H}\cdots\pi$ interactions.

Related literature

For related literature on hydrogen-bond motifs, see Bernstein *et al.* (1995). For values of bond lengths, see Allen *et al.* (1987). For related literature, see, for example: Guingant & Barreto (1987); Larsen *et al.* (1996); Krohn *et al.* (2004); Krohn *et al.* (2004); Cui *et al.* (2006); Anuradha *et al.* (2006).



Experimental

Crystal data

$\text{C}_{10}\text{H}_5\text{NO}_5$
 $M_r = 219.15$

Monoclinic, $P2_1/n$
 $a = 8.6809(2)$ Å

[‡] Additional correspondence author, e-mail: ohasnah@usm.my.

$b = 8.4250(2)$ Å
 $c = 12.1845(3)$ Å
 $\beta = 93.946(1)^\circ$
 $V = 889.02(4)$ Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 0.14$ mm⁻¹
 $T = 100.0(1)$ K
 $0.35 \times 0.14 \times 0.13$ mm

Data collection

Bruker SMART APEXII CCD
area-detector diffractometer
Absorption correction: multi-scan
(SADABS; Bruker, 2005)
 $T_{\min} = 0.900$, $T_{\max} = 0.982$

22792 measured reflections
3028 independent reflections
2493 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.041$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.119$
 $S = 1.11$
3028 reflections
165 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.50$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.23$ e Å⁻³

Table 1

Selected interatomic and centroid-centroid distances (Å).

$\text{Cg}1$ and $\text{Cg}2$ are the centroids of the $\text{C}1-\text{C}5/\text{C}10$ and $\text{C}5-\text{C}10$ rings, respectively.

$\text{Cg}1\cdots\text{Cg}2^{\text{i}}$	3.7188 (6)	$\text{O}5\cdots\text{O}5^{\text{ii}}$	3.0367 (11)
$\text{Cg}1\cdots\text{Cg}2^{\text{i}}$	3.8299 (6)	$\text{O}5\cdots\text{N}1^{\text{ii}}$	3.0608 (11)
$\text{O}2\cdots\text{O}5^{\text{i}}$	2.9940 (11)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$\text{Cg}1$ is the centroid of the $\text{C}1-\text{C}5/\text{C}10$ ring.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O}1-\text{H}1\text{O}1\cdots\text{O}2$	0.889 (18)	1.769 (19)	2.5695 (10)	148.5 (16)
$\text{C}2-\text{H}2\cdots\text{O}3^{\text{iii}}$	0.969 (15)	2.547 (16)	3.1853 (12)	123.4 (12)
$\text{C}3-\text{H}3\cdots\text{O}5^{\text{ii}}$	0.970 (15)	2.577 (15)	3.3827 (13)	140.6 (11)
$\text{C}7-\text{H}7\cdots\text{O}1^{\text{iv}}$	0.982 (16)	2.561 (16)	3.1851 (13)	121.4 (12)
$\text{C}8-\text{H}8\cdots\text{Cg}1^{\text{v}}$	0.950 (15)	2.976 (14)	3.6548 (11)	129.5 (11)

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

Data collection: APEX2 (Bruker, 2005); cell refinement: APEX2; data reduction: SAINT (Bruker, 2005); 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, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2591).

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supporting information

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5-Hydroxy-8-nitro-1,4-naphthoquinone

Daniel Teoh-Chuan Tan, Hasnah Osman, Azlina Harun Kamaruddin, Reza Kia and Hoong-Kun Fun

S1. Comment

5-Hydroxy-1,4-naphthoquinone (juglone) and its 5-acetoxy-2-bromo analogue is the essential dienophile in the highly convergent and regioselective Diels-Alder synthesis of ochromycinone (Guingant & Barreto, 1987; Larsen *et al.*, 1996; Krohn *et al.*, 2004) a type of natural anthraquinone which exhibits remarkable antibiotic and antitumour activities (Krohn *et al.*, 2004; Cui *et al.*, 2006). Our aim is to prepare aromatic ring substituted juglone analogues for the purpose of synthesizing new ochromycinone analogues. The title compound was prepared by the direct nitration of juglone with nickel(II) nitrate. The method outlined previously (Anuradha *et al.*, 2006) predicted a *ortho*-nitro product. However the product that we obtained is a *para*-nitro product.

Compound (I), (Fig. 1), features an intramolecular O—H \cdots O hydrogen bond to form a six-membered ring, producing a *S*(6) ring motif (Bernstein *et al.*, 1995). The bond lengths and angles are within the normal ranges (Allen *et al.*, 1987). The two phenyl rings are almost coplanar with the dihedral angle of 4.44 (5) $^\circ$. The nitro group is not coplanar with the benzene ring and its orientation is indicated by the dihedral angle of 71.66 (5) $^\circ$ with the plane of the benzene ring to which it is bound. The short intermolecular distances between the centroids of six-membered rings [3.7188 (6) - 3.8299 (6) Å] prove existence of π - π interactions (Table 1). The interesting feature of the crystal structure is the short intermolecular O \cdots O and O \cdots N interactions (Table 1). The crystal packing, (Fig. 2), of the compound shows one-dimensional infinite chains along the *b* axis. The crystal packing is stabilized by the intramolecular O—H \cdots O, intermolecular C—H \cdots O hydrogen bonds, π - π , and C—H \cdots π interactions.

S2. Experimental

8-Nitro-5-hydroxy-1,4-naphthoquinone was prepared from 5-hydroxy-1,4-naphthoquinone by the protocol outlined by (Anuradha *et al.*, 2006). Single crystals of 8-nitro-5-hydroxy-1,4-naphthoquinone was obtained by slow evaporation of a chloroform solution at 286 K $^\circ$ C.

S3. Refinement

All of the H-atoms were located from the difference Fourier map and refined freely.

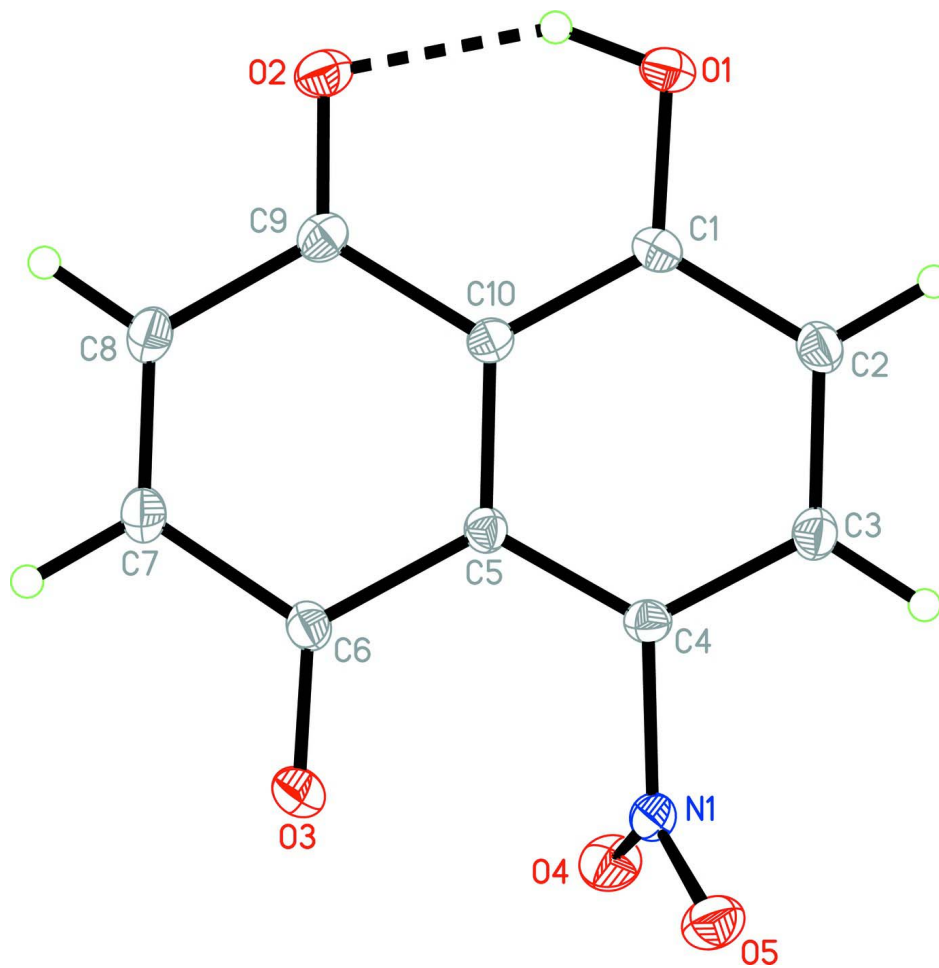


Figure 1

The molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atomic numbering. Intramolecular hydrogen bond is drawn as a dashed line.

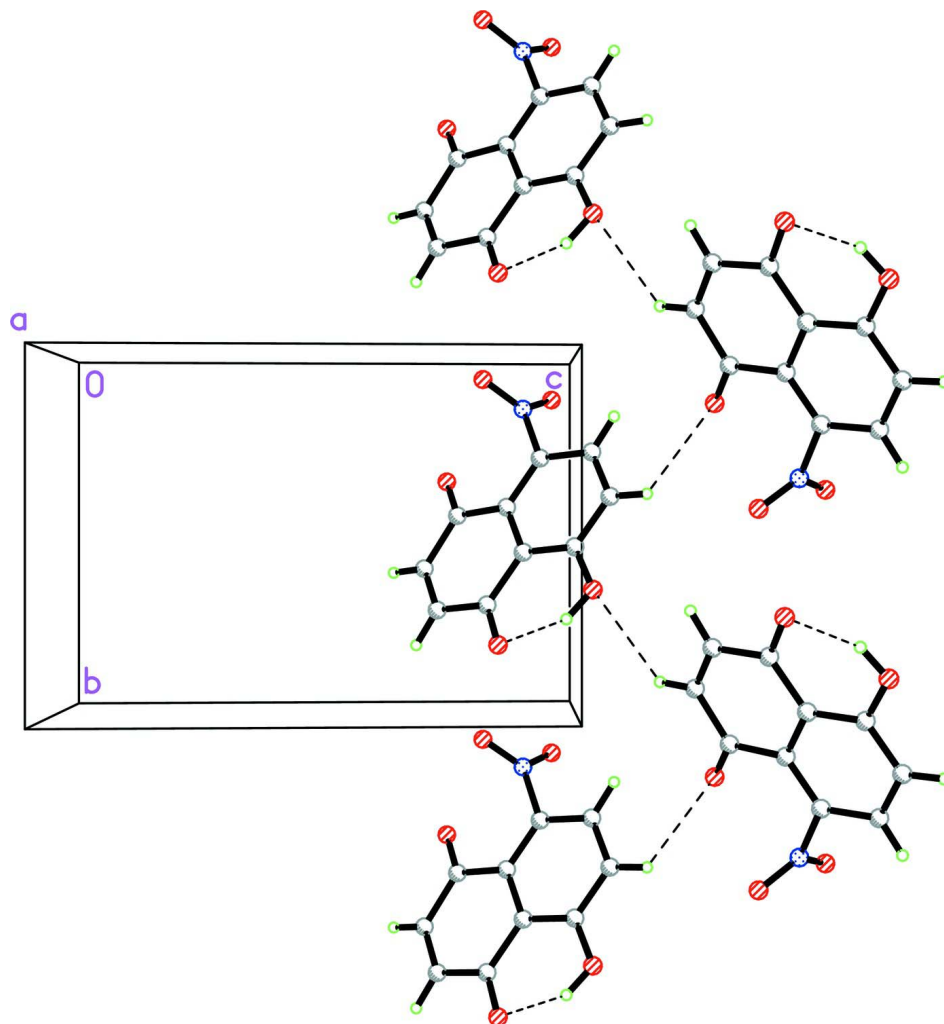


Figure 2

The crystal packing of (I) shows a one-dimensional infinite chain along the [010] direction when viewed down the *a*-axis. Intramolecular and intermolecular interactions are drawn as dashed lines.

5-Hydroxy-8-nitro-1,4-naphthoquinone

Crystal data

$C_{10}H_5NO_5$

$M_r = 219.15$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 8.6809 (2) \text{ \AA}$

$b = 8.4250 (2) \text{ \AA}$

$c = 12.1845 (3) \text{ \AA}$

$\beta = 93.946 (1)^\circ$

$V = 889.02 (4) \text{ \AA}^3$

$Z = 4$

$F(000) = 448$

$D_x = 1.637 \text{ Mg m}^{-3}$

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

Cell parameters from 5257 reflections

$\theta = 2.8\text{--}31.8^\circ$

$\mu = 0.14 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Block, brown

$0.35 \times 0.14 \times 0.13 \text{ mm}$

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)
 $T_{\min} = 0.901$, $T_{\max} = 0.982$

22792 measured reflections
3028 independent reflections
2493 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.041$
 $\theta_{\max} = 31.8^\circ$, $\theta_{\min} = 2.8^\circ$
 $h = -12 \rightarrow 12$
 $k = -12 \rightarrow 12$
 $l = -18 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.119$
 $S = 1.11$
3028 reflections
165 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 atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0671P)^2 + 0.1177P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.50 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. The low-temperature data was collected with the Oxford Cyrosystem Cobra low-temperature attachment.

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.60929 (9)	0.14448 (9)	0.47684 (6)	0.01684 (17)
O2	0.70729 (9)	0.29533 (9)	0.65117 (6)	0.01718 (17)
O3	1.13635 (9)	-0.14728 (9)	0.74975 (6)	0.01826 (17)
O4	0.97394 (10)	-0.42986 (9)	0.67891 (6)	0.02146 (19)
O5	1.11804 (9)	-0.37894 (9)	0.54429 (6)	0.01912 (18)
N1	1.01058 (10)	-0.34927 (10)	0.60140 (7)	0.01427 (18)
C1	0.71200 (11)	0.03181 (12)	0.50785 (8)	0.01280 (18)
C2	0.71889 (11)	-0.10405 (12)	0.44177 (8)	0.01457 (19)
C3	0.81830 (11)	-0.22605 (12)	0.47321 (8)	0.01431 (19)
C4	0.91370 (11)	-0.21081 (11)	0.56968 (8)	0.01219 (18)
C5	0.91680 (11)	-0.07504 (11)	0.63367 (7)	0.01156 (18)
C6	1.03288 (11)	-0.05166 (12)	0.72840 (8)	0.01326 (19)
C7	1.02414 (12)	0.09636 (13)	0.79222 (8)	0.0172 (2)
C8	0.91880 (12)	0.20847 (12)	0.76649 (8)	0.0168 (2)

C9	0.80517 (11)	0.19086 (12)	0.67159 (8)	0.01387 (19)
C10	0.81225 (11)	0.04769 (11)	0.60319 (8)	0.01189 (18)
H8	0.9139 (16)	0.3051 (18)	0.8063 (12)	0.022 (4)*
H2	0.6513 (17)	-0.1106 (19)	0.3752 (12)	0.025 (4)*
H3	0.8222 (16)	-0.3231 (18)	0.4307 (12)	0.020 (3)*
H7	1.1034 (18)	0.1097 (19)	0.8530 (13)	0.029 (4)*
H1O1	0.620 (2)	0.223 (2)	0.5255 (16)	0.049 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0161 (3)	0.0151 (4)	0.0187 (4)	0.0031 (3)	-0.0031 (3)	0.0017 (3)
O2	0.0197 (4)	0.0144 (4)	0.0176 (3)	0.0040 (3)	0.0029 (3)	0.0005 (3)
O3	0.0190 (4)	0.0170 (4)	0.0179 (3)	0.0025 (3)	-0.0051 (3)	0.0005 (3)
O4	0.0285 (4)	0.0150 (4)	0.0210 (4)	0.0010 (3)	0.0023 (3)	0.0054 (3)
O5	0.0161 (3)	0.0181 (4)	0.0234 (4)	0.0026 (3)	0.0032 (3)	-0.0025 (3)
N1	0.0159 (4)	0.0110 (4)	0.0155 (4)	-0.0001 (3)	-0.0015 (3)	-0.0010 (3)
C1	0.0114 (4)	0.0132 (4)	0.0136 (4)	0.0000 (3)	-0.0003 (3)	0.0021 (3)
C2	0.0142 (4)	0.0156 (5)	0.0135 (4)	-0.0011 (3)	-0.0018 (3)	-0.0004 (3)
C3	0.0152 (4)	0.0138 (4)	0.0138 (4)	-0.0011 (3)	0.0000 (3)	-0.0021 (3)
C4	0.0122 (4)	0.0110 (4)	0.0133 (4)	0.0007 (3)	0.0005 (3)	0.0008 (3)
C5	0.0120 (4)	0.0112 (4)	0.0114 (4)	-0.0010 (3)	0.0002 (3)	-0.0001 (3)
C6	0.0143 (4)	0.0130 (4)	0.0122 (4)	-0.0011 (3)	-0.0012 (3)	0.0005 (3)
C7	0.0203 (5)	0.0157 (5)	0.0150 (4)	-0.0008 (4)	-0.0030 (3)	-0.0026 (4)
C8	0.0204 (5)	0.0144 (5)	0.0153 (4)	-0.0006 (4)	-0.0005 (3)	-0.0035 (3)
C9	0.0155 (4)	0.0123 (4)	0.0141 (4)	-0.0002 (3)	0.0031 (3)	0.0002 (3)
C10	0.0123 (4)	0.0110 (4)	0.0124 (4)	0.0001 (3)	0.0011 (3)	0.0004 (3)

Geometric parameters (Å, °)

O1—C1	1.3388 (11)	C3—C4	1.3964 (13)
O1—H1O1	0.89 (2)	C3—H3	0.970 (15)
O2—C9	1.2367 (12)	C4—C5	1.3836 (13)
O3—C6	1.2211 (12)	C5—C10	1.4087 (13)
O4—N1	1.2229 (11)	C5—C6	1.4921 (13)
O5—N1	1.2274 (11)	C6—C7	1.4744 (14)
N1—C4	1.4741 (12)	C7—C8	1.3369 (15)
C1—C2	1.4031 (14)	C7—H7	0.982 (16)
C1—C10	1.4091 (13)	C8—C9	1.4748 (14)
C2—C3	1.3793 (14)	C8—H8	0.950 (15)
C2—H2	0.969 (15)	C9—C10	1.4699 (13)
Cg1...Cg2 ⁱ	3.7188 (6)	O5...O5 ⁱⁱ	3.0367 (11)
Cg1...Cg2 ⁱ	3.8299 (6)	O5...N1 ⁱⁱ	3.0608 (11)
O2...O5 ⁱ	2.9940 (11)		
C1—O1—H1O1	107.7 (12)	C4—C5—C6	122.07 (8)
O4—N1—O5	124.96 (9)	C10—C5—C6	119.72 (8)

O4—N1—C4	117.90 (8)	O3—C6—C7	120.63 (9)
O5—N1—C4	117.04 (8)	O3—C6—C5	121.69 (9)
O1—C1—C2	118.06 (8)	C7—C6—C5	117.58 (8)
O1—C1—C10	121.79 (9)	C8—C7—C6	122.22 (9)
C2—C1—C10	120.15 (9)	C8—C7—H7	121.9 (10)
C3—C2—C1	119.94 (9)	C6—C7—H7	115.8 (9)
C3—C2—H2	121.4 (9)	C7—C8—C9	121.51 (9)
C1—C2—H2	118.6 (9)	C7—C8—H8	122.7 (9)
C2—C3—C4	119.26 (9)	C9—C8—H8	115.8 (9)
C2—C3—H3	121.6 (9)	O2—C9—C10	121.66 (9)
C4—C3—H3	119.1 (9)	O2—C9—C8	119.96 (9)
C5—C4—C3	122.53 (9)	C10—C9—C8	118.38 (9)
C5—C4—N1	121.19 (8)	C5—C10—C1	119.86 (9)
C3—C4—N1	116.27 (8)	C5—C10—C9	120.27 (8)
C4—C5—C10	118.10 (8)	C1—C10—C9	119.86 (9)
O1—C1—C2—C3	-177.19 (9)	O3—C6—C7—C8	175.40 (10)
C10—C1—C2—C3	3.41 (15)	C5—C6—C7—C8	-1.17 (15)
C1—C2—C3—C4	-1.45 (15)	C6—C7—C8—C9	-0.45 (16)
C2—C3—C4—C5	-2.37 (15)	C7—C8—C9—O2	178.62 (10)
C2—C3—C4—N1	176.71 (9)	C7—C8—C9—C10	-1.51 (15)
O4—N1—C4—C5	72.88 (12)	C4—C5—C10—C1	-2.00 (14)
O5—N1—C4—C5	-110.47 (10)	C6—C5—C10—C1	174.21 (8)
O4—N1—C4—C3	-106.21 (10)	C4—C5—C10—C9	176.79 (8)
O5—N1—C4—C3	70.44 (11)	C6—C5—C10—C9	-7.00 (14)
C3—C4—C5—C10	4.07 (14)	O1—C1—C10—C5	178.97 (9)
N1—C4—C5—C10	-174.97 (8)	C2—C1—C10—C5	-1.65 (14)
C3—C4—C5—C6	-172.05 (9)	O1—C1—C10—C9	0.17 (14)
N1—C4—C5—C6	8.92 (14)	C2—C1—C10—C9	179.56 (9)
C4—C5—C6—O3	4.45 (15)	O2—C9—C10—C5	-174.82 (9)
C10—C5—C6—O3	-171.60 (9)	C8—C9—C10—C5	5.31 (14)
C4—C5—C6—C7	-179.01 (9)	O2—C9—C10—C1	3.97 (15)
C10—C5—C6—C7	4.94 (13)	C8—C9—C10—C1	-175.90 (9)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1O1 \cdots O2	0.889 (18)	1.769 (19)	2.5695 (10)	148.5 (16)
C2—H2 \cdots O3 ⁱⁱⁱ	0.969 (15)	2.547 (16)	3.1853 (12)	123.4 (12)
C3—H3 \cdots O5 ⁱⁱ	0.970 (15)	2.577 (15)	3.3827 (13)	140.6 (11)
C7—H7 \cdots O1 ^{iv}	0.982 (16)	2.561 (16)	3.1851 (13)	121.4 (12)
C8—H8 \cdots Cg1 ^v	0.950 (15)	2.976 (14)	3.6548 (11)	129.5 (11)

Symmetry codes: (ii) $-x+2, -y-1, -z+1$; (iii) $x-1/2, -y-1/2, z-1/2$; (iv) $x+1/2, -y+1/2, z+1/2$; (v) $-x+3/2, y+1/2, -z+3/2$.