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## Structure Reports

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6-Hydroxy-1,2-dihydro-4*H*-pyrrolo-[3,2,1-*ij*]quinolin-4-oneVictor B. Rybakov,<sup>a\*</sup> Svitlana V. Shishkina,<sup>b</sup> Igor V. Ukrainets,<sup>c</sup> Olga V. Gorokhova<sup>c</sup> and Xeniya V. Andreeva<sup>c</sup>

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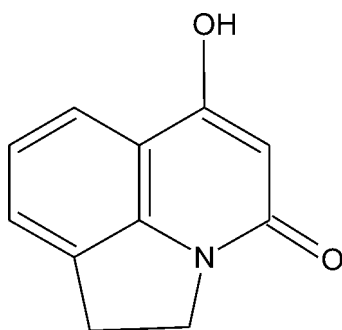
Received 28 January 2013; accepted 29 January 2013

Key indicators: single-crystal X-ray study;  $T = 295$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.044;  $wR$  factor = 0.125; data-to-parameter ratio = 19.1.

The molecule of the title compound,  $\text{C}_{11}\text{H}_9\text{NO}_2$ , is essentially planar [r.m.s. deviation of the non-H atoms = 0.056 (1) Å]. In the crystal, strong  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds form zigzag chains along the  $b$  axis. The molecules form stacks along the  $a$  axis due to  $\pi-\pi$  interactions, the shortest distance between the centroids of the benzene and pyridinone rings being 3.6146 (7) Å.

## Related literature

For condensation of secondary anilines with triethyl methanetricarboxylate, see: Kutyrev & Kappe (1997); Jönsson *et al.* (2004); Ukrainets *et al.* (2006, 2010, 2011). For standard bond lengths, see: Allen *et al.* (1987). For a related structure, see: Baumer *et al.* (2004).



## Experimental

## Crystal data

 $\text{C}_{11}\text{H}_9\text{NO}_2$  $M_r = 187.19$ 

Monoclinic,  $P2_1/c$   
 $a = 7.9987$  (3) Å  
 $b = 7.6297$  (2) Å  
 $c = 14.3500$  (4) Å  
 $\beta = 101.386$  (3)°  
 $V = 858.51$  (5) Å<sup>3</sup>

$Z = 4$   
Mo  $K\alpha$  radiation  
 $\mu = 0.10$  mm<sup>-1</sup>  
 $T = 295$  K  
 $0.20 \times 0.10 \times 0.10$  mm

## Data collection

Agilent Xcalibur Sapphire3 CCD diffractometer  
Absorption correction: multi-scan (*CrysAlis RED*; Agilent, 2011)  
 $T_{\min} = 0.983$ ,  $T_{\max} = 1.000$

7610 measured reflections  
2501 independent reflections  
1806 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.023$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$   
 $wR(F^2) = 0.125$   
 $S = 1.07$   
2501 reflections  
131 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.23$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.15$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O2}-\text{H2}\cdots\text{O1}^i$	1.09 (2)	1.51 (2)	2.5922 (13)	172 (2)

Symmetry code: (i)  $-x, y + \frac{1}{2}, -z + \frac{1}{2}$ 

Data collection: *CrysAlis CCD* (Agilent, 2011); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Agilent, 2011); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: YK2087).

## References

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## supporting information

*Acta Cryst.* (2013). E69, o340 [doi:10.1107/S1600536813003000]

## 6-Hydroxy-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one

Victor B. Rybakov, Svitlana V. Shishkina, Igor V. Ukrainets, Olga V. Gorokhova and Xeniya V. Andreeva

### S1. Comment

By now the most convenient method of obtaining ethyl esters of *N*-substituted 4-hydroxy-2-oxo-1,2-dihydroquinoline-3-carboxylic acids which are widely used in synthesis of the biologically active substances is condensation of the corresponding secondary anilines with triethyl methanetricarboxylate (Kutyrev & Kappe, 1997; Jönsson *et al.*, 2004; Ukrainets *et al.*, 2006; 2010; 2011). The method is efficient and gives higher yields. However, as it turned out, in such reactions specific by-products of the same type are also formed besides the targeted esters - (usually 2%–6% by HPLC). Taking condensation of indoline (**1**) with triethyl methanetricarboxylate (**2**) as an example (Fig. 1), we showed that in this case the by-product is 6-hydroxy-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one (**3**), and its yield is determined by water content in the initial reaction mixture. The source of this impurity can be our main product - ethyl 6-hydroxy-4-oxo-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]-quinoline-5-carboxylate (**4**), which readily undergoes partial hydrolysis and then decarboxylation at high temperature.

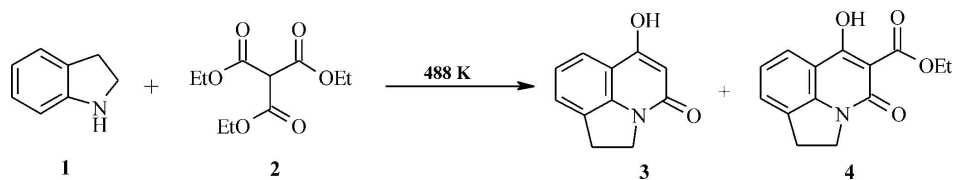
In the title molecule, C<sub>11</sub>H<sub>9</sub>NO<sub>2</sub>, the heterotricycle is essentially planar (Fig. 2). The bond lengths and angles are within the normal ranges (Allen *et al.*, 1987). Strong O2—H2···O1<sup>i</sup> intermolecular hydrogen bonds (Table 1) form folded chains along the *b* axis (Fig. 3). Symmetry code: (i)  $-x, y + 1/2, -z + 1/2$ .

### S2. Experimental

As shown in Fig. 1, Indoline (**1**) (11.2 ml, 0.1 mol) was added dropwise with stirring to triethyl methanetricarboxylate (**2**) (63.3 ml, 0.3 mol) heated to 488 K, at such a rate that the temperature of the reaction mixture was maintained within  $\pm 5$  K of the initial temperature. The ethanol eliminated during the reaction was distilled through a suitable still-head. After adding all the indoline, the reaction mixture was kept at the same temperature for 30 min, after which it was cooled. The excess of triethyl methanetricarboxylate was removed in *vacuo*. To the residue was added 50 ml of xylene. The insoluble solid quinolin-4-one (**3**) was filtered off, washed with hexane, and dried. Yield: 0.77 g (4.1%). *M.p.* 577–579 K (*DMF*).

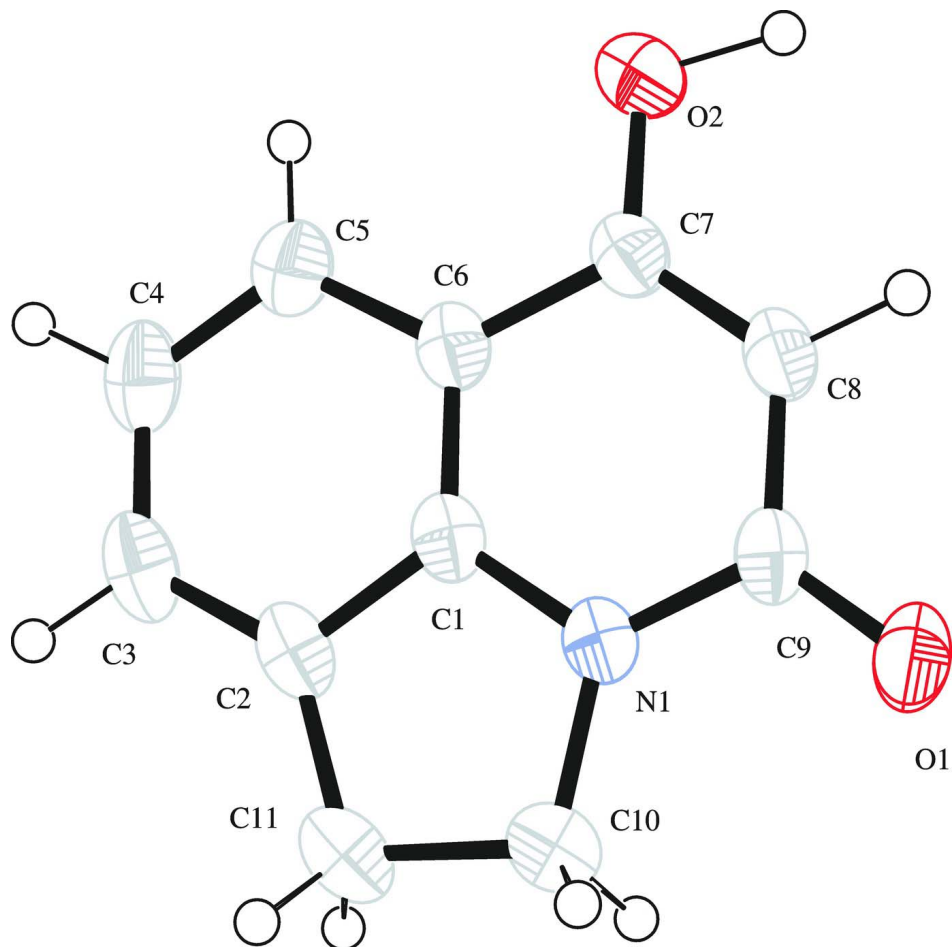
### S3. Refinement

The H atom of hydroxyl group was located from electron density difference map and refined isotropically. The methylene and aromatic H atoms were placed in calculated positions and refined in the riding model approximation with C—H = 0.97 Å for methylene and C—H = 0.93 Å for aryl H atoms with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .



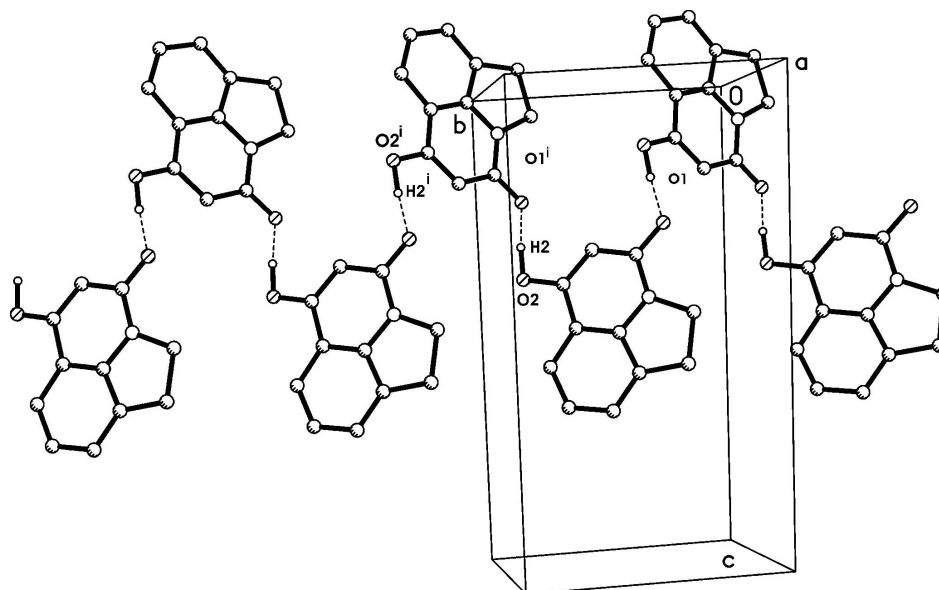
**Figure 1**

Synthesis path to the title compound.



**Figure 2**

View of the title compound with the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. H atoms are presented as a small spheres of arbitrary radius.

**Figure 3**

The O—H...O hydrogen bonds in the crystals of the title compound (shown by dashed lines). Symmetry code: (i)  $-x, y+1/2, -z+1/2$ .

### 6-Hydroxy-1,2-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one

#### Crystal data

$C_{11}H_9NO_2$

$M_r = 187.19$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P\ 2ybc$

$a = 7.9987$  (3) Å

$b = 7.6297$  (2) Å

$c = 14.3500$  (4) Å

$\beta = 101.386$  (3)°

$V = 858.51$  (5) Å<sup>3</sup>

$Z = 4$

$F(000) = 392$

$D_x = 1.448$  Mg m<sup>-3</sup>

Melting point = 577–579 K

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

Cell parameters from 2056 reflections

$\theta = 3.0$ – $30.0$ °

$\mu = 0.10$  mm<sup>-1</sup>

$T = 295$  K

Prism, colourless

$0.20 \times 0.10 \times 0.10$  mm

#### Data collection

Agilent Xcalibur Sapphire3 CCD  
diffractometer

Radiation source: Enhance (Mo) X-ray Source  
Graphite monochromator

Detector resolution: 16.1827 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan  
(*CrysAlis RED*; Agilent, 2011)

$T_{\min} = 0.983$ ,  $T_{\max} = 1.000$

7610 measured reflections

2501 independent reflections

1806 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 30.0$ °,  $\theta_{\min} = 3.0$ °

$h = -10 \rightarrow 11$

$k = -10 \rightarrow 10$

$l = -20 \rightarrow 19$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.125$

$S = 1.07$

2501 reflections

131 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  
 $w = 1/[\sigma^2(F_o^2) + (0.0595P)^2 + 0.0832P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.23 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.15 \text{ e } \text{Å}^{-3}$

*Special details*

**Experimental.** *CrysAlis RED* (Agilent Technologies, 2011). Empirical absorption correction using spherical harmonics, implemented in *SCALE3 ABSPACK* scaling algorithm.

**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 (Å<sup>2</sup>)*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.20058 (12)	0.29009 (13)	0.28449 (6)	0.0523 (3)
O2	-0.01907 (13)	0.82083 (12)	0.38558 (7)	0.0489 (3)
H2	-0.093 (3)	0.819 (3)	0.3132 (16)	0.101 (7)*
N1	0.26368 (13)	0.36896 (13)	0.43936 (7)	0.0369 (2)
C1	0.25940 (14)	0.48889 (16)	0.51022 (8)	0.0345 (3)
C2	0.35421 (15)	0.43260 (18)	0.59709 (8)	0.0407 (3)
C3	0.36190 (17)	0.5414 (2)	0.67396 (9)	0.0507 (4)
H3	0.4236	0.5086	0.7333	0.061*
C4	0.27589 (18)	0.7023 (2)	0.66225 (10)	0.0519 (4)
H4	0.2836	0.7763	0.7144	0.062*
C5	0.18033 (17)	0.75496 (18)	0.57616 (9)	0.0439 (3)
H5	0.1230	0.8617	0.5709	0.053*
C6	0.17035 (15)	0.64553 (16)	0.49625 (8)	0.0354 (3)
C7	0.07582 (15)	0.67526 (15)	0.40090 (8)	0.0362 (3)
C8	0.08626 (15)	0.55614 (16)	0.33158 (8)	0.0391 (3)
H8	0.0262	0.5785	0.2704	0.047*
C9	0.18435 (15)	0.39879 (16)	0.34778 (8)	0.0379 (3)
C10	0.36451 (18)	0.21387 (18)	0.47642 (10)	0.0479 (3)
H10B	0.4609	0.1991	0.4454	0.057*
H10A	0.2951	0.1087	0.4670	0.057*
C11	0.42503 (18)	0.25294 (19)	0.58354 (10)	0.0487 (3)
H11B	0.3808	0.1665	0.6219	0.058*
H11A	0.5486	0.2530	0.6007	0.058*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0555 (6)	0.0572 (6)	0.0394 (5)	0.0028 (5)	-0.0024 (4)	-0.0165 (4)
O2	0.0565 (6)	0.0446 (5)	0.0426 (5)	0.0102 (4)	0.0021 (4)	0.0046 (4)
N1	0.0369 (5)	0.0396 (5)	0.0321 (5)	0.0004 (4)	0.0017 (4)	-0.0005 (4)
C1	0.0318 (5)	0.0421 (6)	0.0288 (5)	-0.0053 (5)	0.0044 (4)	0.0008 (4)
C2	0.0345 (6)	0.0538 (7)	0.0320 (6)	-0.0018 (5)	0.0020 (5)	0.0062 (5)
C3	0.0463 (7)	0.0741 (10)	0.0284 (6)	-0.0025 (7)	-0.0008 (5)	0.0013 (6)
C4	0.0527 (8)	0.0683 (9)	0.0339 (7)	-0.0054 (7)	0.0063 (6)	-0.0129 (6)
C5	0.0445 (7)	0.0480 (7)	0.0394 (7)	-0.0032 (6)	0.0087 (5)	-0.0069 (5)
C6	0.0343 (6)	0.0409 (6)	0.0304 (5)	-0.0046 (5)	0.0050 (4)	-0.0002 (5)
C7	0.0351 (6)	0.0394 (6)	0.0332 (6)	-0.0019 (5)	0.0043 (4)	0.0043 (5)
C8	0.0388 (6)	0.0462 (7)	0.0292 (6)	-0.0026 (5)	-0.0007 (5)	0.0020 (5)
C9	0.0350 (6)	0.0451 (6)	0.0315 (6)	-0.0054 (5)	0.0015 (5)	-0.0041 (5)
C10	0.0469 (7)	0.0455 (7)	0.0485 (8)	0.0067 (6)	0.0029 (6)	0.0036 (6)
C11	0.0417 (7)	0.0592 (8)	0.0429 (7)	0.0056 (6)	0.0025 (6)	0.0124 (6)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O1—C9	1.2555 (14)	C4—H4	0.9300
O2—C7	1.3387 (15)	C5—C6	1.4079 (18)
O2—H2	1.09 (2)	C5—H5	0.9300
N1—C9	1.3610 (15)	C6—C7	1.4445 (16)
N1—C1	1.3733 (15)	C7—C8	1.3622 (17)
N1—C10	1.4711 (16)	C8—C9	1.4279 (17)
C1—C6	1.3855 (17)	C8—H8	0.9300
C1—C2	1.3930 (16)	C10—C11	1.547 (2)
C2—C3	1.3721 (19)	C10—H10B	0.9700
C2—C11	1.5104 (19)	C10—H10A	0.9700
C3—C4	1.401 (2)	C11—H11B	0.9700
C3—H3	0.9300	C11—H11A	0.9700
C4—C5	1.3780 (19)		
C7—O2—H2	109.2 (11)	O2—C7—C8	123.24 (11)
C9—N1—C1	121.90 (10)	O2—C7—C6	117.37 (11)
C9—N1—C10	126.97 (11)	C8—C7—C6	119.40 (11)
C1—N1—C10	111.12 (10)	C7—C8—C9	123.57 (10)
N1—C1—C6	123.70 (10)	C7—C8—H8	118.2
N1—C1—C2	111.62 (11)	C9—C8—H8	118.2
C6—C1—C2	124.68 (11)	O1—C9—N1	119.54 (11)
C3—C2—C1	117.58 (13)	O1—C9—C8	124.72 (11)
C3—C2—C11	133.96 (12)	N1—C9—C8	115.74 (11)
C1—C2—C11	108.44 (11)	N1—C10—C11	104.24 (10)
C2—C3—C4	119.38 (12)	N1—C10—H10B	110.9
C2—C3—H3	120.3	C11—C10—H10B	110.9
C4—C3—H3	120.3	N1—C10—H10A	110.9
C5—C4—C3	122.35 (13)	C11—C10—H10A	110.9

C5—C4—H4	118.8	H10B—C10—H10A	108.9
C3—C4—H4	118.8	C2—C11—C10	104.54 (10)
C4—C5—C6	119.32 (13)	C2—C11—H11B	110.8
C4—C5—H5	120.3	C10—C11—H11B	110.8
C6—C5—H5	120.3	C2—C11—H11A	110.8
C1—C6—C5	116.67 (11)	C10—C11—H11A	110.8
C1—C6—C7	115.50 (10)	H11B—C11—H11A	108.9
C5—C6—C7	127.82 (12)		
C9—N1—C1—C6	2.51 (18)	C1—C6—C7—O2	176.62 (10)
C10—N1—C1—C6	-178.40 (11)	C5—C6—C7—O2	-2.35 (19)
C9—N1—C1—C2	-177.90 (11)	C1—C6—C7—C8	-3.23 (17)
C10—N1—C1—C2	1.20 (15)	C5—C6—C7—C8	177.81 (12)
N1—C1—C2—C3	179.39 (11)	O2—C7—C8—C9	-178.65 (11)
C6—C1—C2—C3	-1.01 (19)	C6—C7—C8—C9	1.18 (19)
N1—C1—C2—C11	-1.98 (14)	C1—N1—C9—O1	175.65 (11)
C6—C1—C2—C11	177.61 (11)	C10—N1—C9—O1	-3.3 (2)
C1—C2—C3—C4	-0.2 (2)	C1—N1—C9—C8	-4.50 (17)
C11—C2—C3—C4	-178.33 (14)	C10—N1—C9—C8	176.56 (11)
C2—C3—C4—C5	1.2 (2)	C7—C8—C9—O1	-177.46 (12)
C3—C4—C5—C6	-1.2 (2)	C7—C8—C9—N1	2.70 (18)
N1—C1—C6—C5	-179.39 (11)	C9—N1—C10—C11	179.12 (11)
C2—C1—C6—C5	1.07 (18)	C1—N1—C10—C11	0.08 (15)
N1—C1—C6—C7	1.52 (17)	C3—C2—C11—C10	-179.78 (15)
C2—C1—C6—C7	-178.02 (11)	C1—C2—C11—C10	1.92 (14)
C4—C5—C6—C1	0.04 (18)	N1—C10—C11—C2	-1.19 (14)
C4—C5—C6—C7	179.00 (12)		

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>
O2—H2...O1 <sup>i</sup>	1.09 (2)	1.51 (2)	2.5922 (13)	172.0 (19)

Symmetry code: (i)  $-x, y+1/2, -z+1/2$ .