

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

## 8-Iodoquinolinium chloride dihydrate

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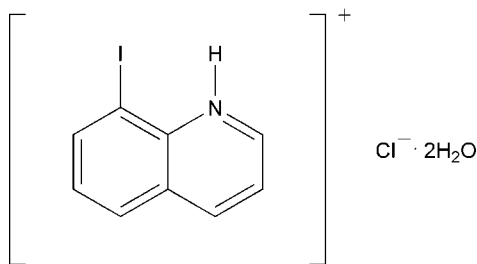
Received 4 August 2008; accepted 29 September 2008

Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  $R$  factor = 0.019;  $wR$  factor = 0.046; data-to-parameter ratio = 14.3.

The title compound,  $\text{C}_9\text{H}_7\text{IN}^+\cdot\text{Cl}^-\cdot 2\text{H}_2\text{O}$ , was obtained during the synthesis of 8-iodoquinoline from 8-aminoquinoline using the Sandmeyer reaction. The 8-iodoquinolinium ion is almost planar. Solvent water molecules and chloride ions form a hydrogen-bonded chain along the  $c$  axis via  $\text{O}-\text{H}\cdots\text{Cl}$  links. The 8-iodoquinolinium ions, which are packed along the  $c$  axis with cationic aromatic  $\pi-\pi$  stacking (centroid-centroid distance = 3.624 Å), are linked to the chain via  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds.

## Related literature

For the synthesis, see: Lucas & Kennedy (1943); Sandmeyer (1884). For a related structure, see: Son & Hoefelmeyer (2008). For related literature, see: Janiak (2000).



## Experimental

## Crystal data

 $\text{C}_9\text{H}_7\text{IN}^+\cdot\text{Cl}^-\cdot 2\text{H}_2\text{O}$  $M_r = 327.54$ Monoclinic,  $P2_1/c$  $a = 8.9600$  (18) Å $b = 17.580$  (4) Å $c = 7.1700$  (14) Å $\beta = 97.13$  (3)° $V = 1120.7$  (4) Å<sup>3</sup> $Z = 4$ Mo  $K\alpha$  radiation $\mu = 3.07$  mm<sup>-1</sup> $T = 100$  (2) K $0.71 \times 0.67 \times 0.54$  mm

## Data collection

Bruker SMART APEXII diffractometer

Absorption correction: multi-scan (SADABS; Bruker, 2006)

 $T_{\min} = 0.219$ ,  $T_{\max} = 0.288$ 

(expected range = 0.145–0.190)

10655 measured reflections

2045 independent reflections

2040 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.020$ 

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.019$  $wR(F^2) = 0.046$  $S = 1.25$ 

2045 reflections

143 parameters

6 restraints

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.79$  e Å<sup>-3</sup> $\Delta\rho_{\text{min}} = -0.65$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1}\cdots\text{O1}$	0.82 (4)	2.03 (4)	2.755 (3)	147 (3)
$\text{N1}-\text{H1}\cdots\text{I1}$	0.82 (4)	2.85 (4)	3.320 (2)	119 (3)
$\text{O1}-\text{H1A}\cdots\text{O2}$	0.84 (1)	1.975 (12)	2.807 (3)	173 (5)
$\text{O1}-\text{H1B}\cdots\text{Cl1}^{\text{i}}$	0.83 (1)	2.75 (3)	3.382 (3)	134 (4)
$\text{O2}-\text{H2A}\cdots\text{Cl1}$	0.84 (1)	2.435 (16)	3.237 (2)	160 (3)
$\text{O2}-\text{H2B}\cdots\text{Cl1}^{\text{ii}}$	0.84 (1)	2.379 (12)	3.211 (2)	170 (3)

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

Data collection: APEX2 (Bruker, 2006); cell refinement: SAINT (Bruker, 2006); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: ORTEP-3 (Farrugia, 1997) and Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: SHELXTL.

This work was supported by funding from the South Dakota 2010 Initiative, Center for Research and Development of Light-Activated Materials. Purchase of the X-ray diffractometer was made possible with funds from the National Science Foundation (EPS-0554609).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2652).

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## supporting information

*Acta Cryst.* (2008). E64, o2076 [doi:10.1107/S1600536808031528]

## 8-Iodoquinolinium chloride dihydrate

Jung-Ho Son and James D. Hoefelmeyer

### S1. Comment

8-Iodoquinoline is a starting material for the synthesis of 8-substituted quinoline derivatives. In this work, 8-iodoquinoline was synthesized starting from 8-aminoquinoline using the Sandmeyer reaction (Sandmeyer, 1884), following the synthesis of iodobenzene (Lucas & Kennedy, 1943). During its synthesis, two 8-iodoquinolinium salt crystals, 8-iodoquinolinium chloride dihydrate and 8-iodoquinolinium triiodide.THF (Son & Hoefelmeyer, 2008) were isolated. The synthesis, characterization and crystal structure of 8-iodoquinolinium chloride dihydrate (Fig. 1) are reported here.

The 8-iodoquinolinium ion is planar, with a maximum deviation of 0.069 (1) Å for the I1 atom. The C8—I1 bond length is 2.110 (3) Å and C9—C8—I1 angle is 121.09 (19) °. A short contact of 3.2083 (10) Å is observed between I1 and C11 ion at (1-x, 1-y, 1-z) that is likely due to ion-dipole interaction. The C8—I1...C11 angle is almost linear (177.13 (8)°).

Lattice water molecules and chloride ions form an extended hydrogen bonding chain network along the *c* axis (Table 1). Hydrogen bonding four-membered rings comprising O2 and C11 are alternately sharing edges with six-membered rings (in chair form) comprising O2, C11 and O1 along the *c* axis (Fig. 2). Atom O1 of the six-membered ring is hydrogen-bonded to atom N1 of the quinolinium ion. The 8-iodoquinolinium ions are parallel to each other and form a  $\pi$ -stack that is propagated along the *c* axis. The  $\pi$ - $\pi$  stacking distance between the 8-iodoquinolinium rings is 3.624 Å (centroid-centroid distance between the 8-iodoquinolinium rings); there may be weak cationic repulsion between the rings (Janiak, 2000).

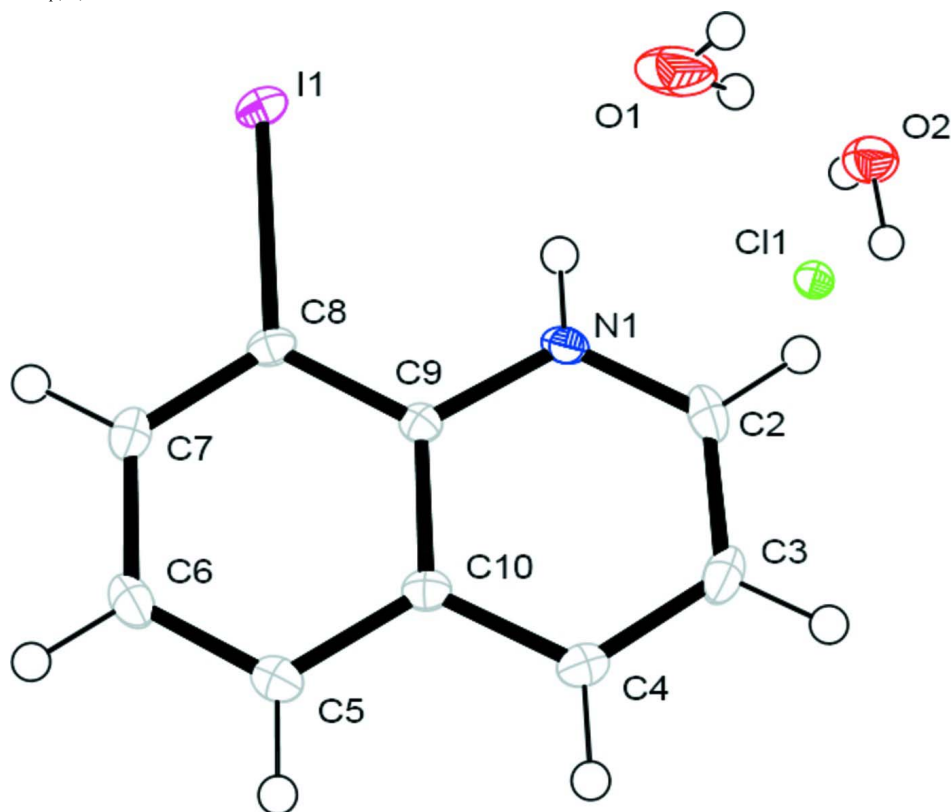
### S2. Experimental

A mixture of 8-aminoquinoline (10 g, 0.069 mol) and water (50 ml) was heated with stirring. The mixture was cooled in an ice bath and concentrated HCl (50 ml) was added to form a red solution. An ice-cooled NaNO<sub>2</sub> (7.8 g, 0.113 mol) solution in water (50 ml) was slowly transferred to the 8-aminoquinoline solution. A light brown precipitate was formed during the addition step but eventually it disappeared to form a reddish transparent solution. KI (17.9 g, 0.108 mol) dissolved in water (25 ml) was then added to the reaction mixture. Bubbles and brownish vapour evolved during the addition. The solution turned to dark brown with a black precipitate. The solution was then refluxed with a watch glass on top of the beaker, and it turned reddish brown with formation of a heavy organic layer; the black precipitate remained. After cooling and standing overnight, golden brown crystals of 8-iodoquinolinium chloride dihydrate had formed spontaneously in the solution. The mixture was neutralized upon addition of NaOH solution, which led to dissolution of the golden brown crystals and retention of the black precipitate. The liquid portion was separated from the black precipitate. 8-iodoquinoline was recovered from the liquid portion upon extraction with toluene. Yield: 10.71 g of 8-iodoquinoline (61%). Physical data for 8-iodoquinolinium chloride dihydrate: m.p. 388-390 K (431-433 K after dehydration). <sup>1</sup>H NMR (methanol-*d*<sub>4</sub>): 7.638–7.716 (dd, 1H, quin *CH*), 8.144–8.214 (dd, 1H, quin *CH*), 8.313–8.360 (dd, 1H, quin *CH*), 8.605–8.647 (dd, 1H, quin *CH*), 9.179–9.228 (dd, 1H, quin *CH*), 9.253–9.288 (dd, 1H, quin *CH*). <sup>13</sup>C NMR (methanol-*d*<sub>4</sub>): 90.253 (quin C8), 124.038 (quin CH), 131.224(quin CH), 131.475 (quin C9/10), 132.070 (quin CH),

139.889 (quin C9/10), 147.113(quin CH), 148.440 (quin CH), 149.608 (quin CH). Analysis calculated for C<sub>9</sub>H<sub>7</sub>ClIN (dehydrated): C 37.08, H 2.42, N 4.80%; found: C 36.76, H 2.40, N 4.85%.

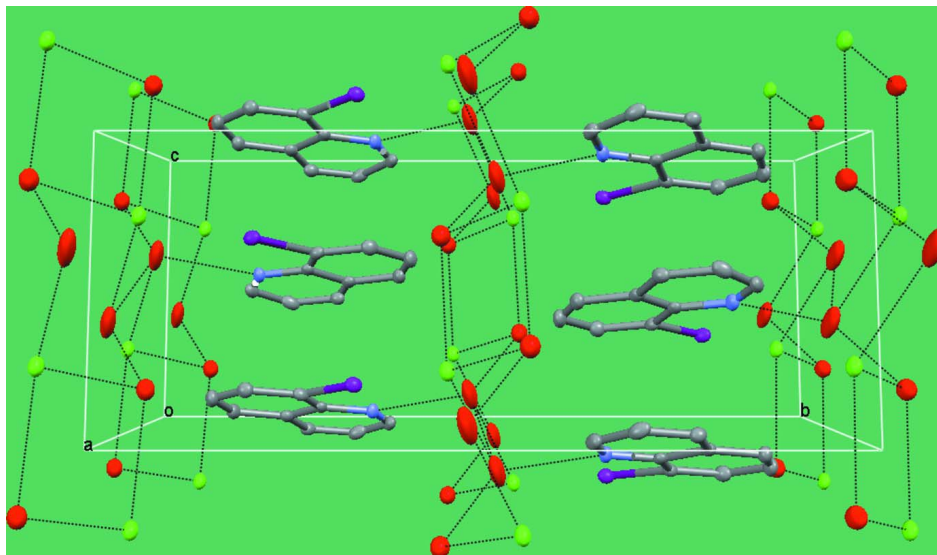
### S3. Refinement

The water H atoms were located in a difference map and refined with O-H and H···H distance restraints of 0.84 (1) Å and 1.37 (2) Å, respectively, and with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . The N-bound H atom was also located in a difference map and refined freely. C-bound H atoms were positioned geometrically (C-H = 0.93 Å) and allowed to ride on the parent atoms with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .



**Figure 1**

Asymmetric unit of 8-iodoquinolinium chloride dihydrate. Displacement ellipsoids are drawn at the 50% probability level.

**Figure 2**

The crystal structure of 8-iodoquinolinium chloride dihydrate, viewed approximately along the *a* axis. Dotted lines represent hydrogen bonds. H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

### 8-Iodoquinolinium chloride dihydrate

#### Crystal data

$C_9H_7IN^+ \cdot Cl^- \cdot 2H_2O$

$M_r = 327.54$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P\ 2ybc$

$a = 8.9600\ (18)\ \text{\AA}$

$b = 17.580\ (4)\ \text{\AA}$

$c = 7.1700\ (14)\ \text{\AA}$

$\beta = 97.13\ (3)^\circ$

$V = 1120.7\ (4)\ \text{\AA}^3$

$Z = 4$

$F(000) = 632$

$D_x = 1.941\ \text{Mg m}^{-3}$

Melting point: 388 K

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

Cell parameters from 9991 reflections

$\theta = 2.3\text{--}28.6^\circ$

$\mu = 3.07\ \text{mm}^{-1}$

$T = 100\ \text{K}$

Block, brown

$0.71 \times 0.67 \times 0.54\ \text{mm}$

#### Data collection

Bruker SMART APEXII  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Bruker, 2003)

$T_{\min} = 0.219$ ,  $T_{\max} = 0.288$

10655 measured reflections

2045 independent reflections

2040 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.020$

$\theta_{\max} = 25.4^\circ$ ,  $\theta_{\min} = 2.3^\circ$

$h = -10 \rightarrow 10$

$k = -21 \rightarrow 21$

$l = -8 \rightarrow 8$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.019$

$wR(F^2) = 0.046$

$S = 1.26$

2045 reflections

143 parameters

6 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

$$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2 + 2.836P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.79 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.65 \text{ e } \text{\AA}^{-3}$

*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.

**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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C2	0.1207 (3)	0.35738 (15)	-0.0118 (4)	0.0175 (6)
H2	0.0968	0.4100	-0.0215	0.021*
C3	0.0078 (3)	0.30408 (17)	-0.0595 (4)	0.0187 (6)
H3	-0.0918	0.3199	-0.1035	0.022*
C4	0.0429 (3)	0.22795 (15)	-0.0418 (4)	0.0155 (5)
H4	-0.0333	0.1909	-0.0724	0.019*
C5	0.2333 (3)	0.12642 (15)	0.0433 (4)	0.0170 (5)
H5	0.1591	0.0881	0.0155	0.020*
C6	0.3795 (3)	0.10627 (15)	0.1040 (4)	0.0190 (6)
H6	0.4053	0.0541	0.1199	0.023*
C7	0.4923 (3)	0.16273 (16)	0.1430 (4)	0.0169 (5)
H7	0.5932	0.1477	0.1821	0.020*
C8	0.4574 (3)	0.23944 (15)	0.1248 (4)	0.0134 (5)
C9	0.3060 (3)	0.26110 (14)	0.0660 (3)	0.0115 (5)
C10	0.1928 (3)	0.20430 (15)	0.0220 (4)	0.0132 (5)
N1	0.2614 (3)	0.33639 (13)	0.0471 (3)	0.0143 (5)
H1	0.326 (4)	0.369 (2)	0.080 (5)	0.029 (10)*
Cl1	0.12024 (7)	0.54723 (4)	0.76556 (9)	0.01743 (14)
I1	0.629687 (18)	0.321563 (10)	0.17166 (2)	0.01562 (7)
O1	0.3734 (3)	0.48091 (13)	0.1171 (4)	0.0404 (6)
H1A	0.320 (4)	0.506 (2)	0.183 (5)	0.061*
H1B	0.363 (5)	0.498 (2)	0.008 (3)	0.061*
O2	0.1749 (2)	0.55620 (12)	0.3282 (3)	0.0240 (4)
H2A	0.183 (4)	0.559 (2)	0.4461 (15)	0.036*
H2B	0.104 (3)	0.5262 (17)	0.294 (4)	0.036*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C2	0.0231 (14)	0.0138 (13)	0.0161 (13)	0.0066 (11)	0.0044 (11)	0.0019 (10)

C3	0.0122 (13)	0.0270 (15)	0.0173 (14)	0.0054 (11)	0.0034 (11)	0.0065 (11)
C4	0.0139 (13)	0.0186 (13)	0.0138 (12)	-0.0033 (10)	0.0014 (10)	-0.0002 (10)
C5	0.0197 (14)	0.0140 (13)	0.0177 (13)	-0.0021 (11)	0.0034 (11)	-0.0005 (10)
C6	0.0231 (15)	0.0126 (13)	0.0217 (14)	0.0031 (11)	0.0041 (11)	0.0006 (11)
C7	0.0141 (13)	0.0192 (13)	0.0174 (13)	0.0039 (11)	0.0024 (10)	0.0004 (11)
C8	0.0121 (12)	0.0158 (13)	0.0124 (12)	-0.0034 (10)	0.0016 (10)	-0.0024 (10)
C9	0.0130 (12)	0.0124 (12)	0.0099 (11)	-0.0005 (10)	0.0041 (9)	0.0003 (9)
C10	0.0143 (13)	0.0149 (12)	0.0111 (12)	-0.0022 (10)	0.0041 (10)	-0.0005 (10)
N1	0.0153 (12)	0.0110 (11)	0.0172 (12)	-0.0028 (9)	0.0043 (9)	0.0004 (9)
C11	0.0163 (3)	0.0132 (3)	0.0221 (3)	-0.0013 (2)	0.0002 (2)	-0.0013 (2)
I1	0.01147 (10)	0.01954 (11)	0.01569 (11)	-0.00378 (6)	0.00106 (7)	-0.00135 (6)
O1	0.0416 (15)	0.0188 (12)	0.0660 (18)	-0.0115 (10)	0.0268 (14)	-0.0137 (11)
O2	0.0235 (11)	0.0214 (11)	0.0267 (11)	-0.0048 (8)	0.0017 (9)	-0.0003 (9)

*Geometric parameters (Å, °)*

C2—N1	1.331 (4)	C7—C8	1.387 (4)
C2—C3	1.390 (4)	C7—H7	0.95
C2—H2	0.95	C8—C9	1.421 (4)
C3—C4	1.377 (4)	C8—I1	2.110 (3)
C3—H3	0.95	C9—N1	1.384 (3)
C4—C10	1.426 (4)	C9—C10	1.430 (4)
C4—H4	0.95	N1—H1	0.82 (4)
C5—C6	1.374 (4)	O1—H1A	0.836 (10)
C5—C10	1.420 (4)	O1—H1B	0.834 (10)
C5—H5	0.95	O2—H2A	0.840 (10)
C6—C7	1.419 (4)	O2—H2B	0.841 (10)
C6—H6	0.95		
N1—C2—C3	121.5 (2)	C8—C7—H7	119.5
N1—C2—H2	119.2	C6—C7—H7	119.5
C3—C2—H2	119.2	C7—C8—C9	119.0 (2)
C4—C3—C2	118.8 (2)	C7—C8—I1	119.89 (19)
C4—C3—H3	120.6	C9—C8—I1	121.09 (19)
C2—C3—H3	120.6	N1—C9—C8	122.6 (2)
C3—C4—C10	120.6 (2)	N1—C9—C10	117.2 (2)
C3—C4—H4	119.7	C8—C9—C10	120.2 (2)
C10—C4—H4	119.7	C5—C10—C4	122.3 (2)
C6—C5—C10	120.2 (2)	C5—C10—C9	119.0 (2)
C6—C5—H5	119.9	C4—C10—C9	118.8 (2)
C10—C5—H5	119.9	C2—N1—C9	123.1 (2)
C5—C6—C7	120.6 (3)	C2—N1—H1	120 (3)
C5—C6—H6	119.7	C9—N1—H1	117 (3)
C7—C6—H6	119.7	H1A—O1—H1B	110 (2)
C8—C7—C6	121.0 (2)	H2A—O2—H2B	107 (2)
N1—C2—C3—C4	1.1 (4)	C6—C5—C10—C9	-0.5 (4)
C2—C3—C4—C10	-0.8 (4)	C3—C4—C10—C5	179.6 (3)

C10—C5—C6—C7	-1.1 (4)	C3—C4—C10—C9	-0.4 (4)
C5—C6—C7—C8	1.4 (4)	N1—C9—C10—C5	-178.7 (2)
C6—C7—C8—C9	0.0 (4)	C8—C9—C10—C5	1.8 (4)
C6—C7—C8—I1	-177.1 (2)	N1—C9—C10—C4	1.3 (3)
C7—C8—C9—N1	179.0 (2)	C8—C9—C10—C4	-178.2 (2)
I1—C8—C9—N1	-3.9 (3)	C3—C2—N1—C9	-0.2 (4)
C7—C8—C9—C10	-1.6 (4)	C8—C9—N1—C2	178.4 (2)
I1—C8—C9—C10	175.50 (18)	C10—C9—N1—C2	-1.0 (4)
C6—C5—C10—C4	179.5 (2)		

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

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H1 $\cdots$ O1	0.82 (4)	2.03 (4)	2.755 (3)	147 (3)
N1—H1 $\cdots$ I1	0.82 (4)	2.85 (4)	3.320 (2)	119 (3)
O1—H1 <i>A</i> $\cdots$ O2	0.84 (1)	1.98 (1)	2.807 (3)	173 (5)
O1—H1 <i>B</i> $\cdots$ C11 <sup>i</sup>	0.83 (1)	2.75 (3)	3.382 (3)	134 (4)
O2—H2 <i>A</i> $\cdots$ C11	0.84 (1)	2.44 (2)	3.237 (2)	160 (3)
O2—H2 <i>B</i> $\cdots$ C11 <sup>ii</sup>	0.84 (1)	2.38 (1)	3.211 (2)	170 (3)

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