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2-Carboxypyridinium hydrogen chloranilate

Kazuma Gotoh, Hirokazu Nagoshi and Hiroyuki Ishida*

Department of Chemistry, Faculty of Science, Okayama University, Okayama 700-8530, Japan

Correspondence e-mail: ishidah@cc.okayama-u.ac.jp

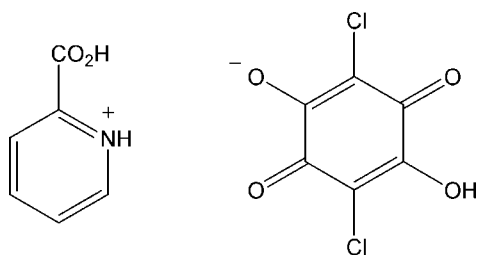
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Key indicators: single-crystal X-ray study; $T = 103$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.045; wR factor = 0.144; data-to-parameter ratio = 17.0.

In the crystal structure of the title salt, $\text{C}_6\text{H}_6\text{NO}_2^+ \cdot \text{C}_6\text{H}_3\text{Cl}_2\text{O}_4^-$, the pyridine ring and the mean plane of the hydrogen chloranilate anion form a dihedral angle of 77.40 (8)°. The ionic components are held together by $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds, forming a supramolecular ladder. $\text{C}-\text{H} \cdots \text{O}$ interactions are also present.

Related literature

For the structures of related carboxypyridinium hydrogen chloranilates, see: Gotoh *et al.* (2006); Tabuchi *et al.* (2005); Ishida (2009).



Experimental

Crystal data

$\text{C}_6\text{H}_6\text{NO}_2^+ \cdot \text{C}_6\text{H}_3\text{Cl}_2\text{O}_4^-$
 $M_r = 332.10$
 Monoclinic, $P2_1/c$
 $a = 9.4166$ (8) Å
 $b = 19.6900$ (16) Å
 $c = 6.7089$ (6) Å
 $\beta = 99.043$ (3)°

$V = 1228.45$ (18) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.56$ mm⁻¹
 $T = 103$ K
 $0.30 \times 0.30 \times 0.23$ mm

Data collection

Rigaku R-AXIS RAPID-II
 diffractometer
 Absorption correction: multi-scan
 (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.847$, $T_{\max} = 0.880$

9710 measured reflections
 3433 independent reflections
 2228 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.047$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.144$
 $S = 1.10$
 3433 reflections
 202 parameters

H atoms treated by a mixture of
 independent and constrained
 refinement
 $\Delta\rho_{\max} = 0.47$ e Å⁻³
 $\Delta\rho_{\min} = -0.92$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N1}-\text{H1} \cdots \text{O1}$	0.92 (4)	2.11 (3)	2.932 (2)	147 (3)
$\text{O2}-\text{H2} \cdots \text{O5}^{\text{i}}$	0.79 (3)	2.05 (3)	2.746 (2)	148 (3)
$\text{O6}-\text{H6} \cdots \text{O4}^{\text{ii}}$	0.90 (3)	1.63 (3)	2.528 (2)	177.1 (15)
$\text{C8}-\text{H8} \cdots \text{O4}^{\text{iii}}$	0.95	2.50	3.338 (3)	147
$\text{C9}-\text{H9} \cdots \text{O3}^{\text{iv}}$	0.95	2.33	3.227 (3)	156
$\text{C11}-\text{H11} \cdots \text{O1}^{\text{v}}$	0.95	2.46	3.374 (3)	162

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

Data collection: *PROCESS-AUTO* (Rigaku/MSC, 2004); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2376).

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supporting information

Acta Cryst. (2009). E65, o614 [doi:10.1107/S1600536809006412]

2-Carboxypyridinium hydrogen chloranilate

Kazuma Gotoh, Hirokazu Nagoshi and Hiroyuki Ishida

S1. Comment

The title salt, (I), was prepared in order to extend our study on D—H···A hydrogen bonding (D = N, O or C; A = N, O or Cl) in chloranilic acid – substituted-pyridine systems (Gotoh *et al.*, 2006; Tabuchi *et al.*, 2005).

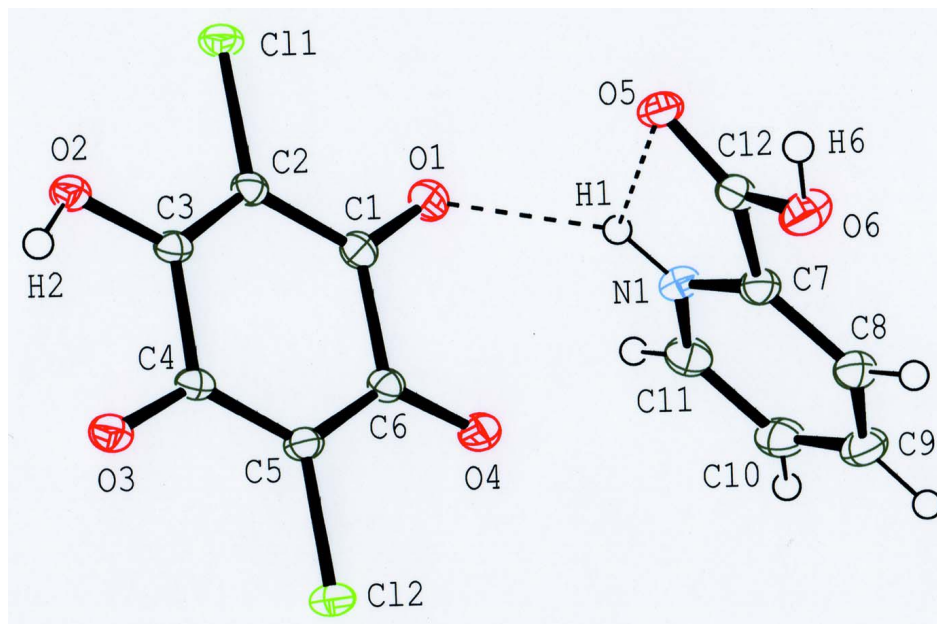
Compound (I) comprises 2-carboxypyridinium cations and hydrogen chloranilate anions in the ratio 1:1. Ions directly connected by an N—H···O hydrogen bond, Fig. 1, form a dihedral angle between their respective mean planes of 77.40 (8)°. In the cation, the carboxy O5/O6/C12 plane forms a dihedral angle of 11.44 (6)° with the pyridine ring, which is similar to those of 2.74 (6) and 10.01 (3)° observed in 3-carboxypyridinium hydrogen chloranilate and 4-carboxypyridinium hydrogen chloranilate monohydrate, respectively (Ishida, 2009). The ions are further connected by O—H···O hydrogen bonds (Table 1) to afford a supramolecular ladder running along the *c* axis (Fig. 2). The ladders are linked by weaker N—H···O hydrogen bonds and C—H···O contacts to form a 3-D network (Table 1).

S2. Experimental

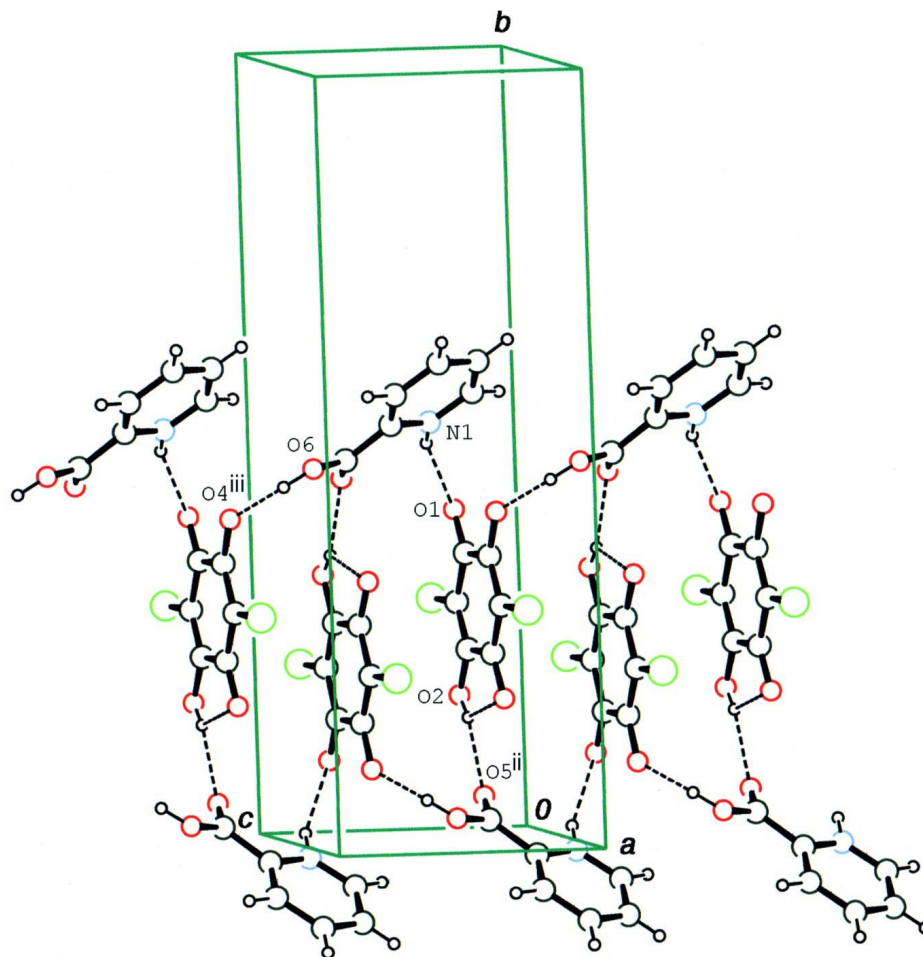
Crystals were obtained by slow evaporation from a methanol solution (*ca* 30 ml) containing a 1:1 molar ratio of chloranilic acid (0.302 g) and picolinic acid (0.179 g).

S3. Refinement

The H atoms attached to O and N were located from a difference Fourier map and refined isotropically to O—H = 0.79 (3) & 0.90 (3) Å and N—H = 0.92 (4) Å. The remaining H atoms were included in the riding approximation with C—H = 0.95 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

**Figure 1**

Molecular components of (I) showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Intra- and inter-molecular N—H···O hydrogen bonds are indicated by dashed lines.

**Figure 2**

A partial packing diagram, viewed approximately along the *a* axis, showing the hydrogen-bonded supramolecular ladder. Dashed lines show N—H...O and O—H...O hydrogen bonds (symmetry codes as given in Table 1).

2-Carboxypyridinium hydrogen chloranilate

Crystal data

$C_6H_6NO_2^+ \cdot C_6HCl_2O_4^-$
 $M_r = 332.10$
 Monoclinic, $P2_1/c$
 Hall symbol: -P 2ybc
 $a = 9.4166$ (8) Å
 $b = 19.6900$ (16) Å
 $c = 6.7089$ (6) Å
 $\beta = 99.043$ (3)°
 $V = 1228.45$ (18) Å³
 $Z = 4$

$F(000) = 672.00$
 $D_x = 1.795$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å
 Cell parameters from 7392 reflections
 $\theta = 3.0$ – 30.0 °
 $\mu = 0.56$ mm⁻¹
 $T = 103$ K
 Platelet, dark purple
 $0.30 \times 0.30 \times 0.23$ mm

Data collection

Rigaku R-AXIS RAPID-II
 diffractometer
 Detector resolution: 10.00 pixels mm⁻¹

ω scans
 Absorption correction: multi-scan
 (ABSCOR; Higashi, 1995)

$T_{\min} = 0.847$, $T_{\max} = 0.880$
 9710 measured reflections
 3433 independent reflections
 2228 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.047$

$\theta_{\max} = 30.0^\circ$
 $h = -13 \rightarrow 13$
 $k = -27 \rightarrow 27$
 $l = -8 \rightarrow 9$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.144$
 $S = 1.10$
 3433 reflections
 202 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
 $w = 1/[\sigma^2(F_o^2) + (0.0659P)^2 + 0.8975P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.47 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.92 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	-0.17894 (6)	0.28996 (3)	0.27912 (9)	0.02060 (16)
C12	0.46528 (6)	0.29140 (3)	0.10812 (9)	0.02077 (16)
O1	0.00723 (19)	0.40867 (8)	0.2367 (3)	0.0218 (4)
O2	0.01147 (19)	0.17042 (9)	0.2397 (3)	0.0184 (3)
O3	0.27117 (18)	0.17271 (8)	0.1488 (3)	0.0196 (4)
O4	0.27772 (19)	0.41277 (8)	0.1577 (3)	0.0209 (4)
O5	0.12383 (18)	0.45615 (9)	0.6917 (3)	0.0215 (4)
O6	0.3466 (2)	0.47658 (10)	0.8601 (3)	0.0265 (4)
N1	0.1860 (2)	0.52690 (11)	0.3720 (3)	0.0199 (4)
C1	0.0667 (2)	0.35416 (11)	0.2174 (3)	0.0164 (4)
C2	-0.0036 (2)	0.28950 (11)	0.2347 (3)	0.0160 (4)
C3	0.0678 (2)	0.23079 (11)	0.2188 (3)	0.0154 (4)
C4	0.2206 (2)	0.22965 (11)	0.1715 (3)	0.0155 (4)
C5	0.2899 (2)	0.29272 (11)	0.1544 (4)	0.0170 (4)
C6	0.2232 (2)	0.35480 (12)	0.1732 (3)	0.0165 (4)
C7	0.2794 (3)	0.52837 (12)	0.5464 (4)	0.0198 (5)
C8	0.3984 (3)	0.56970 (13)	0.5626 (4)	0.0229 (5)
H8	0.4656	0.5708	0.6840	0.027*
C9	0.4194 (3)	0.60996 (13)	0.3987 (4)	0.0262 (5)
H9	0.5010	0.6388	0.4077	0.031*

C10	0.3206 (3)	0.60759 (13)	0.2230 (4)	0.0268 (5)
H10	0.3332	0.6352	0.1109	0.032*
C11	0.2035 (3)	0.56488 (13)	0.2118 (4)	0.0239 (5)
H11	0.1357	0.5624	0.0913	0.029*
C12	0.2418 (3)	0.48289 (12)	0.7090 (4)	0.0195 (5)
H1	0.109 (5)	0.498 (2)	0.363 (6)	0.053 (11)*
H2	0.071 (4)	0.1437 (17)	0.227 (5)	0.032 (9)*
H6	0.319 (4)	0.4534 (18)	0.964 (6)	0.043 (10)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0146 (3)	0.0253 (3)	0.0233 (3)	0.0013 (2)	0.0076 (2)	-0.0006 (2)
C12	0.0151 (3)	0.0258 (3)	0.0230 (3)	-0.0018 (2)	0.0080 (2)	-0.0011 (2)
O1	0.0207 (8)	0.0196 (8)	0.0256 (9)	0.0020 (7)	0.0051 (7)	-0.0022 (7)
O2	0.0163 (8)	0.0164 (7)	0.0238 (9)	0.0013 (7)	0.0074 (7)	-0.0008 (7)
O3	0.0176 (8)	0.0201 (8)	0.0220 (8)	0.0016 (7)	0.0063 (7)	-0.0008 (7)
O4	0.0232 (9)	0.0200 (8)	0.0210 (9)	-0.0027 (7)	0.0083 (7)	0.0019 (6)
O5	0.0177 (8)	0.0212 (8)	0.0274 (9)	-0.0017 (7)	0.0094 (7)	0.0018 (7)
O6	0.0221 (9)	0.0336 (10)	0.0235 (9)	-0.0063 (8)	0.0024 (7)	0.0050 (8)
N1	0.0145 (9)	0.0229 (10)	0.0229 (10)	-0.0018 (8)	0.0050 (8)	0.0000 (8)
C1	0.0182 (10)	0.0180 (10)	0.0130 (10)	0.0007 (9)	0.0020 (8)	0.0001 (8)
C2	0.0130 (10)	0.0197 (10)	0.0152 (10)	0.0009 (8)	0.0023 (8)	-0.0019 (8)
C3	0.0154 (10)	0.0183 (10)	0.0132 (10)	-0.0002 (8)	0.0048 (8)	0.0005 (8)
C4	0.0149 (10)	0.0193 (10)	0.0132 (10)	0.0009 (8)	0.0048 (8)	0.0003 (8)
C5	0.0132 (10)	0.0207 (10)	0.0176 (10)	-0.0013 (9)	0.0041 (8)	-0.0006 (9)
C6	0.0165 (10)	0.0204 (10)	0.0133 (10)	-0.0014 (9)	0.0039 (8)	-0.0011 (8)
C7	0.0179 (11)	0.0184 (11)	0.0241 (12)	0.0001 (9)	0.0067 (9)	-0.0006 (9)
C8	0.0188 (11)	0.0236 (12)	0.0272 (13)	0.0000 (10)	0.0066 (10)	-0.0018 (10)
C9	0.0223 (12)	0.0231 (12)	0.0355 (14)	-0.0031 (10)	0.0118 (11)	0.0023 (11)
C10	0.0292 (13)	0.0248 (12)	0.0291 (13)	0.0006 (11)	0.0129 (11)	0.0049 (10)
C11	0.0229 (12)	0.0270 (12)	0.0221 (12)	0.0049 (10)	0.0051 (10)	0.0028 (10)
C12	0.0210 (11)	0.0193 (10)	0.0197 (11)	-0.0002 (9)	0.0076 (9)	-0.0021 (9)

Geometric parameters (Å, °)

C11—C2	1.723 (2)	C1—C6	1.548 (3)
C12—C5	1.727 (2)	C2—C3	1.350 (3)
O1—C1	1.227 (3)	C3—C4	1.521 (3)
O2—C3	1.318 (3)	C4—C5	1.416 (3)
O2—H2	0.79 (3)	C5—C6	1.389 (3)
O3—C4	1.237 (3)	C7—C8	1.375 (3)
O4—C6	1.263 (3)	C7—C12	1.497 (3)
O5—C12	1.218 (3)	C8—C9	1.394 (4)
O6—C12	1.305 (3)	C8—H8	0.9500
O6—H6	0.90 (4)	C9—C10	1.383 (4)
N1—C11	1.340 (3)	C9—H9	0.9500
N1—C7	1.349 (3)	C10—C11	1.379 (4)

N1—H1	0.92 (4)	C10—H10	0.9500
C1—C2	1.448 (3)	C11—H11	0.9500
C3—O2—H2	107 (3)	O4—C6—C1	115.8 (2)
C12—O6—H6	112 (2)	C5—C6—C1	117.90 (19)
C11—N1—C7	122.5 (2)	N1—C7—C8	119.6 (2)
C11—N1—H1	119 (2)	N1—C7—C12	115.0 (2)
C7—N1—H1	118 (2)	C8—C7—C12	125.4 (2)
O1—C1—C2	122.6 (2)	C7—C8—C9	119.3 (2)
O1—C1—C6	118.5 (2)	C7—C8—H8	120.4
C2—C1—C6	118.91 (19)	C9—C8—H8	120.4
C3—C2—C1	120.4 (2)	C10—C9—C8	119.5 (2)
C3—C2—C11	121.40 (18)	C10—C9—H9	120.2
C1—C2—C11	118.15 (17)	C8—C9—H9	120.2
O2—C3—C2	123.3 (2)	C11—C10—C9	119.5 (2)
O2—C3—C4	114.75 (19)	C11—C10—H10	120.3
C2—C3—C4	121.9 (2)	C9—C10—H10	120.3
O3—C4—C5	126.4 (2)	N1—C11—C10	119.7 (2)
O3—C4—C3	115.7 (2)	N1—C11—H11	120.2
C5—C4—C3	117.85 (19)	C10—C11—H11	120.2
C6—C5—C4	122.9 (2)	O5—C12—O6	126.9 (2)
C6—C5—C12	119.23 (17)	O5—C12—C7	120.4 (2)
C4—C5—C12	117.86 (17)	O6—C12—C7	112.7 (2)
O4—C6—C5	126.3 (2)		
O1—C1—C2—C3	-177.9 (2)	C4—C5—C6—C1	0.7 (3)
C6—C1—C2—C3	2.1 (3)	C12—C5—C6—C1	-179.21 (16)
O1—C1—C2—C11	1.3 (3)	O1—C1—C6—O4	-0.9 (3)
C6—C1—C2—C11	-178.77 (16)	C2—C1—C6—O4	179.2 (2)
C1—C2—C3—O2	177.7 (2)	O1—C1—C6—C5	179.2 (2)
C11—C2—C3—O2	-1.4 (3)	C2—C1—C6—C5	-0.7 (3)
C1—C2—C3—C4	-3.3 (3)	C11—N1—C7—C8	-0.6 (4)
C11—C2—C3—C4	177.58 (16)	C11—N1—C7—C12	179.6 (2)
O2—C3—C4—O3	3.3 (3)	N1—C7—C8—C9	0.7 (4)
C2—C3—C4—O3	-175.8 (2)	C12—C7—C8—C9	-179.5 (2)
O2—C3—C4—C5	-177.73 (19)	C7—C8—C9—C10	-0.1 (4)
C2—C3—C4—C5	3.2 (3)	C8—C9—C10—C11	-0.7 (4)
O3—C4—C5—C6	177.0 (2)	C7—N1—C11—C10	-0.2 (4)
C3—C4—C5—C6	-1.8 (3)	C9—C10—C11—N1	0.8 (4)
O3—C4—C5—C12	-3.0 (3)	N1—C7—C12—O5	-11.4 (3)
C3—C4—C5—C12	178.11 (16)	C8—C7—C12—O5	168.8 (2)
C4—C5—C6—O4	-179.2 (2)	N1—C7—C12—O6	168.4 (2)
C12—C5—C6—O4	0.8 (3)	C8—C7—C12—O6	-11.4 (3)

Hydrogen-bond geometry (\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	0.92 (4)	2.11 (3)	2.932 (2)	147 (3)

N1—H1...O5	0.92 (4)	2.33 (4)	2.698 (2)	103 (2)
N1—H1...O5 ⁱ	0.92 (4)	2.34 (4)	2.900 (2)	119 (3)
O2—H2...O3	0.79 (3)	2.11 (3)	2.612 (2)	122 (3)
O2—H2...O5 ⁱⁱ	0.79 (3)	2.05 (3)	2.746 (2)	148 (3)
O6—H6...O4 ⁱⁱⁱ	0.90 (3)	1.63 (3)	2.528 (2)	177.1 (15)
C8—H8...O4 ^{iv}	0.95	2.50	3.338 (3)	147
C9—H9...O3 ^v	0.95	2.33	3.227 (3)	156
C11—H11...O1 ^{vi}	0.95	2.46	3.374 (3)	162

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