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Crystal structure of 7,8-dichloro-4-oxo-4*H*-chromene-3-carbaldehyde

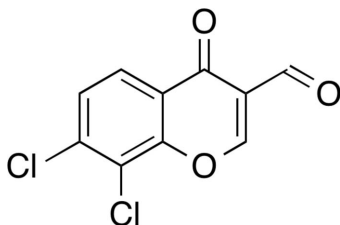
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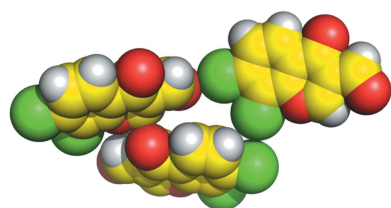
In the title compound, $C_{10}H_4Cl_2O_3$, a dichlorinated 3-formylchromone derivative, the fused-ring system is slightly puckered [dihedral angle between the benzene and pyran rings = 3.66 (10°)]. The dihedral angle between the pyran ring and the formyl plane is 8.64 (7°). In the crystal, molecules are linked through π - π stacking interactions [centroid-centroid distance between the benzene and pyran rings = 3.727 (2) Å], C-H \cdots O hydrogen bonds and short C \cdots O contacts [2.838 (4) Å]. Halogen bonds between the formyl O atoms and the Cl atoms at the 7-position [Cl \cdots O = 2.984 (3) Å, C-Cl \cdots O = 170.83 (12°) and Cl \cdots O-C = 116.05 (19°)] are also formed along the *a* axis, resulting in helical structures constructed by C-H \cdots O hydrogen bonds and Cl \cdots O halogen bonds along the *b* axis. In addition, type II halogen-halogen contacts between the chlorine atoms at the 7- and 8-positions [Cl \cdots Cl = 3.519 (2) Å, C-Cl \cdots Cl = 171.24 (10°) and 88.74 (11°)] are observed.

1. Chemical context

Halogen bonding and halogen-halogen interactions have recently attracted much attention in medicinal chemistry, chemical biology, supramolecular chemistry and crystal engineering (Auffinger *et al.*, 2004; Metrangolo *et al.*, 2005; Wilcken *et al.*, 2013; Sirimulla *et al.*, 2013; Persch *et al.*, 2015). Halogen bonding is defined as a net attractive interaction between an electrophilic region of a halogen atom in a molecule and a nucleophilic region of an atom in a molecule, and is characterized by a short contact between the two atoms. Halogen-halogen interactions are generally classified into two categories, type I ($\theta_1 = \theta_2$) and type II ($\theta_1 = 180$, $\theta_2 = 90$) where θ_1 and θ_2 are the two C-Cl \cdots Cl angles. The type I contact is considered to be van der Waals, and the type II is halogen bonding, *i.e.*, an electrostatic interaction (Mukherjee *et al.*, 2014; Metrangolo *et al.*, 2014).



I have recently reported the crystal structures of chlorinated 3-formylchromone derivatives 7-chloro-4-oxo-4*H*-chromene-3-carbaldehyde (Ishikawa, 2014*b*), 8-chloro-4-oxo-4*H*-chromene-3-carbaldehyde (Ishikawa, 2014*a*) and 6,8-dichloro-4-oxochromene-3-carbaldehyde (Ishikawa & Motohashi, 2013). As for the monochlorinated 3-formylchromones, a type I van der Waals contact is observed in 7-chloro-4-oxo-4*H*-chro-



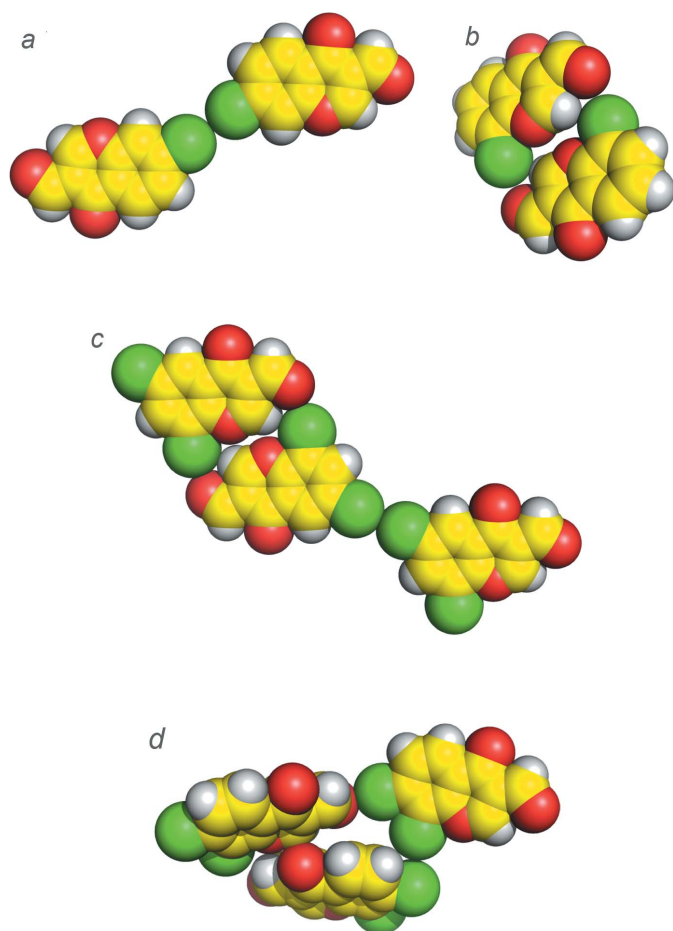


Figure 1
Sphere models of the crystal structures of (a) 7-chloro-4-oxo-4*H*-chromene-3-carbaldehyde (Ishikawa, 2014*b*), (b) 8-chloro-4-oxo-4*H*-chromene-3-carbaldehyde (Ishikawa, 2014*a*), (c) 6,8-dichloro-4-oxochromene-3-carbaldehyde (Ishikawa & Motohashi, 2013) and (d) the title compound.

7-chloro-4-oxo-4*H*-chromene-3-carbaldehyde (Fig. 1*a*), and a van der Waals contact is observed between the formyl oxygen atom and the chlorine atom in 8-chloro-4-oxo-4*H*-chromene-3-carbaldehyde (Fig. 1*b*). On the other hand, as for the dichlorinated 3-formylchromone, halogen bonding between the formyl oxygen atom and the chlorine atom at the 8-position and a type I short halogen–halogen contact between the chlorine atoms at the 6-position are observed in 6,8-dichloro-4-oxochromene-3-carbaldehyde (Fig. 1*c*). As part of our investigation into these types of chemical bonding, I herein report the crystal structure of a dichlorinated 3-formylchromone, 7,8-dichloro-4-oxo-4*H*-chromene-3-carbaldehyde. The main objective of this study is to reveal the interaction modes of the chlorine substituents of the title compound in the solid state.

2. Structure commentary

The molecular structure of the title compound is shown in Fig. 2. The fused-ring system is slightly puckered [dihedral angle between the benzene and pyran rings = 3.66 (10)°]. The

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>
C1–H1···O2 ⁱ	0.95	2.28	3.113 (4)	146 (1)
C4–H2···O3 ⁱⁱ	0.95	2.47	3.398 (4)	167 (1)
C6–Cl1···O3 ⁱⁱⁱ	1.72 (1)	2.98 (1)	4.693 (4)	171 (1)
C10–O3···Cl1 ^{iv}	1.21 (1)	2.98 (1)	3.678 (4)	116 (1)
C6–Cl1···Cl2 ^v	1.72 (1)	3.52 (1)	3.884 (4)	89 (1)
C7–Cl2···Cl1 ^{vi}	1.72 (1)	3.52 (1)	5.229 (4)	171 (1)

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

dihedral angle between the pyran ring and the formyl plane is 8.64 (7)°.

3. Supramolecular features

In the crystal, the molecules are linked through π – π stacking interactions between molecules related by translation-symmetry¹ [centroid–centroid distance between the benzene and pyran rings of the 4*H*-chromene units = 3.727 (2) Å; symmetry code: (i) $x, y + 1, z$], and through C–H···O hydrogen bonds that involve C1/O2 and C4/O3 atoms, as shown in Fig. 3 and listed in Table 1.

Halogen bonds are formed between the chlorine atom at the 7-position and the formyl oxygen atomⁱⁱ along the *a*-axis direction [C11···O3ⁱⁱ = 2.984 (3) Å, C6–Cl1···O3ⁱⁱ = 170.83 (12)°, C11···O3ⁱⁱ–C10ⁱⁱ = 116.05 (19)°; symmetry code (ii) $x - \frac{1}{2}, -y, z$], resulting in helical structures constructed by C–H···O hydrogen bonds and Cl···O halogen bonds along the *b*-axis direction, as shown in Figs. 3 and 4. In addition, type II halogen–halogen contacts are observed between the chlorine atoms at the 7- and 8-positionⁱⁱⁱ [C11···Cl2ⁱⁱⁱ = 3.519 (2) Å, C7ⁱⁱⁱ–Cl2ⁱⁱⁱ···C11 = 171.24 (10)°, C6–Cl1···Cl2ⁱⁱⁱ = 88.74 (11)°; symmetry code (iii) $-x, -y, z + \frac{1}{2}$], as shown in Fig. 1*d*. These electrostatic interactions around the chlorine atoms in the title compound are likely due to the cooperativity of the electron-withdrawing chlorine atoms at the 7- and 8-

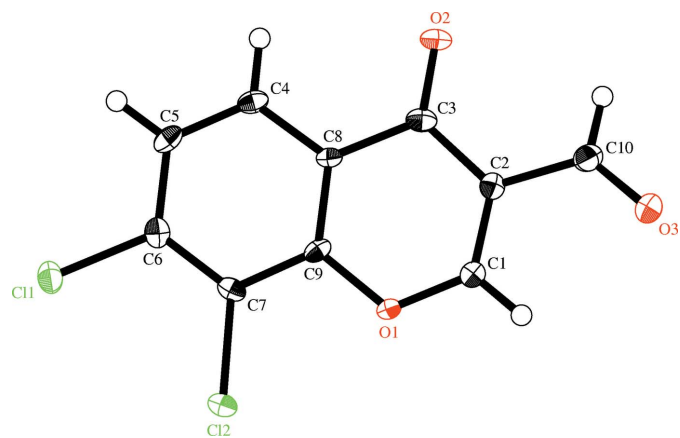


Figure 2
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radius.

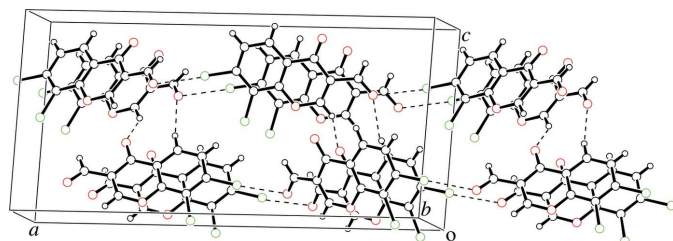


Figure 3
A packing view of the title compound. C—H...O hydrogen bonds and Cl...O halogen bonds are represented as dashed lines.

positions. Thus, it is suggested that the chlorine atoms should make their σ -holes larger, and their electropositive regions contact the electronegative regions of the oxygen and chlorine atoms.

In addition to the C—H...O hydrogen bonds, halogen bonds and type II halogen–halogen contacts, an unusually short contact is revealed between the α,β -unsaturated carbonyl O2 and the C—H group of C1^{iv} [2.838 (4) Å; symmetry code (iv) $-x + \frac{1}{2}, y, z + \frac{1}{2}$; Fig. 1*d*]. This interesting feature is possibly caused by a dipole–dipole interaction between the O atom and the C—H group that is enhanced by the polarizing effect of the two chlorine atoms at the 7- and 8-positions of the chromone ring. These observations should be helpful in understanding interactions of halogenated ligands with proteins, and thus valuable for rational drug design.

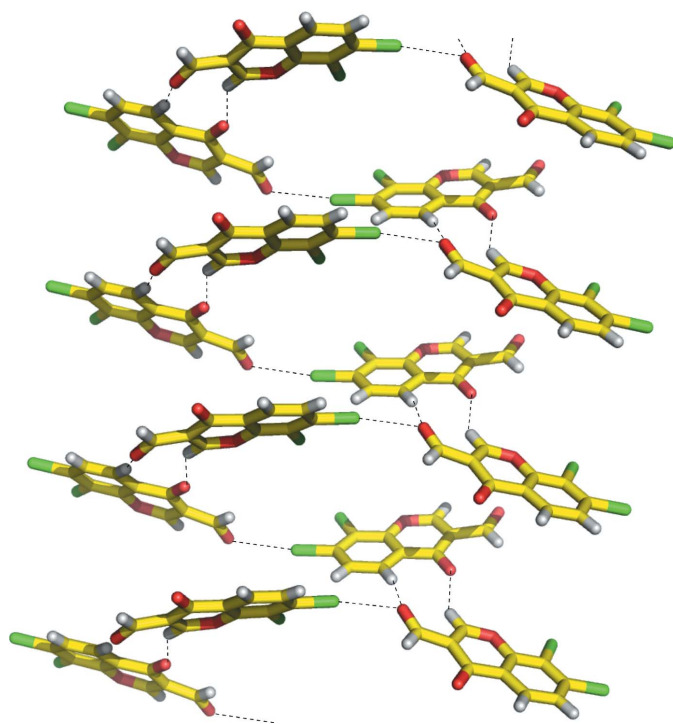


Figure 4
A helical structure constructed by C—H...O hydrogen bonds and Cl...O halogen bonds in the crystal packing.

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₁₀ H ₄ Cl ₂ O ₃
<i>M_r</i>	243.05
Crystal system, space group	Orthorhombic, <i>Pca</i> 2 ₁
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	23.091 (7), 3.7704 (18), 10.729 (5)
<i>V</i> (Å ³)	934.1 (7)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.67
Crystal size (mm)	0.41 × 0.12 × 0.05
Data collection	
Diffractometer	Rigaku AFC-7R
No. of measured, independent and observed [<i>F</i> ² > 2.0σ(<i>F</i> ²)] reflections	1571, 1291, 1155
<i>R</i> _{int}	0.015
(sin θ/λ) _{max} (Å ⁻¹)	0.650
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.025, 0.057, 1.05
No. of reflections	1291
No. of parameters	136
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.24, -0.27
Absolute structure	Flack (1983), 169 Friedel pairs
Absolute structure parameter	0.06 (8)

Computer programs: *WinAFC Diffractometer Control Software* (Rigaku, 1999), *SIR2008* (Burla *et al.*, 2007), *SHELXL97* (Sheldrick, 2008) and *CrystalStructure* (Rigaku, 2010).

4. Synthesis and crystallization

3',4'-Dichloro-2'-hydroxyacetophenone was prepared from 2,3-dichlorophenol by a Fries rearrangement reaction. To a solution of 3',4'-dichloro-2'-hydroxyacetophenone (5.9 mmol) in *N,N*-dimethylformamide (20 ml) was added dropwise POCl₃ (11.7 mmol) at 273 K. After the mixture had been stirred for 14 h at room temperature, water (100 ml) was added. The precipitates were collected, washed with water, and dried *in vacuo* (yield: 64%). ¹H NMR (400 MHz, CDCl₃): δ = 7.82 (*d*, 1H, *J* = 8.8 Hz), 8.08 (*d*, 1H, *J* = 8.8 Hz), 9.05 (*s*, 1H), 10.10 (*s*, 1H). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a tetrahydrofuran solution of the title compound at room temperature.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The C-bound hydrogen atoms were placed in geometrical positions and refined using a riding model [C—H 0.95 Å, *U*_{iso}(H) = 1.2*U*_{eq}(C)].

Acknowledgements

The University of Shizuoka is acknowledged for instrumentation support.

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Crystal structure of 7,8-dichloro-4-oxo-4*H*-chromene-3-carbaldehyde

Yoshinobu Ishikawa

Computing details

Data collection: *WinAFC Diffractometer Control Software* (Rigaku, 1999); cell refinement: *WinAFC Diffractometer Control Software* (Rigaku, 1999); data reduction: *WinAFC Diffractometer Control Software* (Rigaku, 1999); program(s) used to solve structure: *SIR2008* (Burla *et al.*, 2007); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *CrystalStructure* (Rigaku, 2010); software used to prepare material for publication: *CrystalStructure* (Rigaku, 2010).

7,8-Dichloro-4-oxo-4*H*-chromene-3-carbaldehyde

Crystal data

$C_{10}H_4Cl_2O_3$

$M_r = 243.05$

Orthorhombic, *Pca*2₁

Hall symbol: P 2c -2a

$a = 23.091$ (7) Å

$b = 3.7704$ (18) Å

$c = 10.729$ (5) Å

$V = 934.1$ (7) Å³

$Z = 4$

$F(000) = 488.00$

$D_x = 1.728$ Mg m⁻³

Mo *K*α radiation, $\lambda = 0.71069$ Å

Cell parameters from 22 reflections

$\theta = 15.8$ – 17.3°

$\mu = 0.67$ mm⁻¹

$T = 100$ K

Plate, yellow

$0.41 \times 0.12 \times 0.05$ mm

Data collection

Rigaku AFC-7R
diffractometer

ω scans

1571 measured reflections

1291 independent reflections

1155 reflections with $F^2 > 2.0\sigma(F^2)$

$R_{int} = 0.015$

$\theta_{max} = 27.5^\circ$

$h = 0 \rightarrow 29$

$k = -4 \rightarrow 2$

$l = -7 \rightarrow 13$

3 standard reflections every 150 reflections

intensity decay: 1.1%

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.025$

$wR(F^2) = 0.057$

$S = 1.05$

1291 reflections

136 parameters

1 restraint

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0252P)^2 + 0.2201P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.24$ e Å⁻³

$\Delta\rho_{min} = -0.27$ e Å⁻³

Absolute structure: Flack (1983), 169 Friedel
pairs

Absolute structure parameter: 0.06 (8)

Special details

Refinement. Refinement was performed using all reflections. The weighted R -factor (wR) and goodness of fit (S) are based on F^2 . R -factor (gt) are based on F . The threshold expression of $F^2 > 2.0 \sigma(F^2)$ is used only for calculating R -factor (gt).

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	−0.02754 (3)	0.3441 (2)	0.16617 (7)	0.02008 (17)
C12	0.05650 (3)	−0.0003 (3)	−0.03533 (8)	0.01821 (16)
O1	0.17307 (8)	−0.0690 (6)	0.04845 (18)	0.0137 (5)
O2	0.24923 (9)	0.3154 (5)	0.36500 (17)	0.0179 (5)
O3	0.34477 (9)	−0.3040 (6)	0.12579 (19)	0.0254 (6)
C1	0.22935 (12)	−0.1270 (8)	0.0740 (3)	0.0136 (7)
C2	0.25652 (12)	−0.0155 (7)	0.1782 (3)	0.0140 (6)
C3	0.22568 (13)	0.1862 (9)	0.2724 (3)	0.0149 (7)
C4	0.12566 (13)	0.3790 (8)	0.3362 (3)	0.0156 (7)
C5	0.06756 (13)	0.4108 (8)	0.3106 (3)	0.0169 (7)
C6	0.04536 (12)	0.2967 (8)	0.1961 (3)	0.0156 (7)
C7	0.08124 (12)	0.1435 (8)	0.1075 (3)	0.0132 (7)
C8	0.16288 (12)	0.2231 (8)	0.2485 (3)	0.0116 (7)
C9	0.13996 (12)	0.1023 (8)	0.1362 (3)	0.0127 (7)
C10	0.31843 (13)	−0.1099 (9)	0.1950 (3)	0.0195 (7)
H1	0.2515	−0.2554	0.0145	0.0163*
H2	0.1406	0.4626	0.4133	0.0187*
H3	0.0423	0.5109	0.3710	0.0203*
H4	0.3385	−0.0119	0.2642	0.0233*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0144 (3)	0.0234 (4)	0.0224 (4)	0.0021 (3)	0.0007 (4)	0.0024 (4)
C12	0.0181 (3)	0.0216 (4)	0.0149 (3)	−0.0005 (4)	−0.0043 (4)	−0.0019 (4)
O1	0.0147 (10)	0.0162 (12)	0.0102 (10)	0.0015 (9)	−0.0001 (9)	−0.0031 (9)
O2	0.0218 (10)	0.0199 (11)	0.0122 (11)	−0.0014 (10)	−0.0039 (10)	−0.0028 (11)
O3	0.0199 (12)	0.0330 (14)	0.0233 (13)	0.0064 (11)	−0.0001 (9)	−0.0089 (12)
C1	0.0154 (13)	0.0113 (16)	0.0140 (15)	0.0000 (12)	0.0013 (13)	0.0014 (13)
C2	0.0152 (14)	0.0118 (14)	0.0148 (15)	0.0014 (11)	0.0005 (13)	0.0027 (16)
C3	0.0214 (15)	0.0128 (16)	0.0106 (14)	−0.0016 (13)	−0.0019 (13)	0.0040 (14)
C4	0.0224 (15)	0.0113 (16)	0.0130 (16)	−0.0017 (13)	0.0003 (13)	−0.0023 (13)
C5	0.0209 (15)	0.0161 (18)	0.0137 (15)	−0.0012 (14)	0.0064 (13)	−0.0008 (13)
C6	0.0148 (13)	0.0111 (15)	0.0208 (18)	0.0000 (12)	0.0011 (12)	0.0024 (14)
C7	0.0152 (14)	0.0106 (15)	0.0139 (15)	−0.0045 (13)	−0.0033 (12)	0.0026 (13)
C8	0.0149 (14)	0.0112 (16)	0.0087 (14)	−0.0025 (12)	−0.0002 (12)	−0.0002 (12)
C9	0.0193 (14)	0.0093 (14)	0.0095 (14)	0.0016 (12)	0.0030 (12)	0.0016 (12)
C10	0.0209 (15)	0.0208 (17)	0.0166 (16)	0.0003 (14)	0.0012 (13)	−0.0017 (14)

Geometric parameters (Å, °)

C11—C6	1.723 (3)	C4—C5	1.375 (5)
C12—C7	1.723 (3)	C4—C8	1.403 (4)
O1—C1	1.346 (4)	C5—C6	1.399 (5)
O1—C9	1.374 (4)	C6—C7	1.387 (4)
O2—C3	1.233 (4)	C7—C9	1.399 (4)
O3—C10	1.207 (4)	C8—C9	1.393 (4)
C1—C2	1.349 (5)	C1—H1	0.950
C2—C3	1.452 (4)	C4—H2	0.950
C2—C10	1.484 (5)	C5—H3	0.950
C3—C8	1.479 (4)	C10—H4	0.950
C11…C12	3.1821 (13)	C11…H3	2.7981
C12…O1	2.850 (3)	O2…H2	2.6203
O1…C3	2.860 (4)	O2…H4	2.6344
O2…C1	3.570 (4)	O3…H1	2.4697
O2…C4	2.880 (4)	C1…H4	3.2719
O2…C10	2.907 (4)	C3…H1	3.2841
O3…C1	2.803 (4)	C3…H2	2.6882
C1…C7	3.587 (4)	C3…H4	2.7113
C1…C8	2.758 (5)	C6…H2	3.2648
C2…C9	2.765 (4)	C7…H3	3.2742
C4…C7	2.803 (4)	C8…H3	3.2642
C5…C9	2.766 (4)	C9…H1	3.1865
C6…C8	2.785 (4)	C9…H2	3.2686
C11…C12 ⁱ	3.5191 (17)	C10…H1	2.5378
C11…O3 ⁱⁱ	2.984 (3)	H1…H4	3.4723
C12…C11 ⁱⁱⁱ	3.5191 (17)	H2…H3	2.3217
O1…O2 ^{iv}	3.533 (3)	C11…H3 ^{xi}	3.2315
O1…O2 ^v	3.032 (3)	C11…H4 ⁱⁱ	3.4992
O1…C8 ^{vi}	3.434 (4)	C12…H3 ⁱⁱⁱ	3.1499
O1…C9 ^{vi}	3.352 (4)	C12…H3 ^{xi}	3.1018
O2…O1 ^{vii}	3.032 (3)	C12…H4 ^v	3.2415
O2…O1 ^{viii}	3.533 (3)	O1…H1 ^{ix}	3.5807
O2…C1 ^{vii}	2.838 (4)	O1…H4 ^v	3.0689
O2…C1 ^{viii}	3.113 (4)	O2…H1 ^{vii}	2.6840
O2…C2 ^{ix}	3.227 (4)	O2…H1 ^{viii}	2.2789
O2…C2 ^{vii}	3.586 (4)	O2…H4 ^{ix}	3.4425
O2…C3 ^{ix}	3.473 (4)	O3…H2 ^{iv}	2.4674
O2…C10 ^{ix}	3.252 (4)	O3…H4 ^{vi}	3.0577
O3…C11 ^x	2.984 (3)	C1…H1 ^{ix}	3.3865
O3…C2 ^{vi}	3.415 (4)	C2…H1 ^{ix}	3.3630
O3…C4 ^{iv}	3.398 (4)	C3…H1 ^{ix}	3.5280
O3…C10 ^{vi}	3.186 (5)	C3…H1 ^{vii}	3.1298
C1…O2 ^{iv}	3.113 (4)	C3…H1 ^{viii}	3.3849
C1…O2 ^v	2.838 (4)	C4…H2 ^{vi}	3.5694
C1…C2 ^{vi}	3.587 (5)	C5…H3 ^{vi}	3.5033

C1...C3 ^{vi}	3.354 (5)	C6...H3 ^{vi}	3.5082
C1...C3 ^v	3.597 (5)	C8...H2 ^{vi}	3.4070
C1...C8 ^{vi}	3.445 (5)	C10...H2 ^{iv}	3.5538
C2...O2 ^{vi}	3.227 (4)	C10...H4 ^{vi}	3.5117
C2...O2 ^v	3.586 (4)	H1...O1 ^{vi}	3.5807
C2...O3 ^{ix}	3.415 (4)	H1...O2 ^{iv}	2.2789
C2...C1 ^{ix}	3.587 (5)	H1...O2 ^v	2.6840
C2...C3 ^{vi}	3.254 (5)	H1...C1 ^{vi}	3.3865
C3...O2 ^{vi}	3.473 (4)	H1...C2 ^{vi}	3.3630
C3...C1 ^{ix}	3.354 (5)	H1...C3 ^{vi}	3.5280
C3...C1 ^{vii}	3.597 (5)	H1...C3 ^{iv}	3.3849
C3...C2 ^{ix}	3.254 (5)	H1...C3 ^v	3.1298
C3...C10 ^{ix}	3.510 (5)	H1...H2 ^{iv}	2.9187
C4...O3 ^{viii}	3.398 (4)	H1...H4 ^v	3.5172
C4...C8 ^{ix}	3.428 (5)	H2...O3 ^{viii}	2.4674
C4...C9 ^{ix}	3.486 (4)	H2...C4 ^{ix}	3.5694
C5...C6 ^{ix}	3.596 (5)	H2...C8 ^{ix}	3.4070
C5...C7 ^{ix}	3.532 (5)	H2...C10 ^{viii}	3.5538
C6...C5 ^{vi}	3.596 (5)	H2...H1 ^{viii}	2.9187
C6...C7 ^{ix}	3.432 (5)	H3...C11 ^{xii}	3.2315
C7...C5 ^{vi}	3.532 (5)	H3...C12 ⁱ	3.1499
C7...C6 ^{vi}	3.432 (5)	H3...C12 ^{xii}	3.1018
C8...O1 ^{ix}	3.434 (4)	H3...C5 ^{ix}	3.5033
C8...C1 ^{ix}	3.445 (5)	H3...C6 ^{ix}	3.5082
C8...C4 ^{vi}	3.428 (5)	H4...C11 ^x	3.4992
C8...C9 ^{ix}	3.567 (5)	H4...C12 ^{vii}	3.2415
C9...O1 ^{ix}	3.352 (4)	H4...O1 ^{vii}	3.0689
C9...C4 ^{vi}	3.486 (4)	H4...O2 ^{vi}	3.4425
C9...C8 ^{vi}	3.567 (5)	H4...O3 ^{ix}	3.0577
C10...O2 ^{vi}	3.252 (4)	H4...C10 ^{ix}	3.5117
C10...O3 ^{ix}	3.186 (5)	H4...H1 ^{vii}	3.5172
C10...C3 ^{vi}	3.510 (5)		
C1—O1—C9	118.3 (3)	C3—C8—C4	121.6 (3)
O1—C1—C2	124.5 (3)	C3—C8—C9	119.5 (3)
C1—C2—C3	120.8 (3)	C4—C8—C9	119.0 (3)
C1—C2—C10	118.3 (3)	O1—C9—C7	116.2 (3)
C3—C2—C10	120.9 (3)	O1—C9—C8	122.3 (3)
O2—C3—C2	123.5 (3)	C7—C9—C8	121.5 (3)
O2—C3—C8	122.4 (3)	O3—C10—C2	123.8 (3)
C2—C3—C8	114.2 (3)	O1—C1—H1	117.736
C5—C4—C8	120.0 (3)	C2—C1—H1	117.719
C4—C5—C6	120.4 (3)	C5—C4—H2	119.983
C11—C6—C5	119.3 (3)	C8—C4—H2	119.980
C11—C6—C7	120.0 (3)	C4—C5—H3	119.801
C5—C6—C7	120.7 (3)	C6—C5—H3	119.790
C12—C7—C6	122.8 (3)	O3—C10—H4	118.100
C12—C7—C9	118.8 (2)	C2—C10—H4	118.125

C6—C7—C9	118.3 (3)		
C1—O1—C9—C7	-177.5 (3)	C8—C4—C5—C6	-1.6 (5)
C1—O1—C9—C8	1.3 (4)	C8—C4—C5—H3	178.4
C9—O1—C1—C2	-2.9 (4)	H2—C4—C5—C6	178.4
C9—O1—C1—H1	177.1	H2—C4—C5—H3	-1.6
O1—C1—C2—C3	-0.8 (5)	H2—C4—C8—C3	-0.4
O1—C1—C2—C10	178.1 (3)	H2—C4—C8—C9	180.0
H1—C1—C2—C3	179.2	C4—C5—C6—C11	-179.4 (3)
H1—C1—C2—C10	-1.9	C4—C5—C6—C7	1.3 (5)
C1—C2—C3—O2	-174.8 (3)	H3—C5—C6—C11	0.6
C1—C2—C3—C8	5.5 (4)	H3—C5—C6—C7	-178.7
C1—C2—C10—O3	-6.0 (5)	C11—C6—C7—C12	1.0 (4)
C1—C2—C10—H4	173.9	C11—C6—C7—C9	-178.62 (18)
C3—C2—C10—O3	172.8 (3)	C5—C6—C7—C12	-179.7 (3)
C3—C2—C10—H4	-7.2	C5—C6—C7—C9	0.7 (5)
C10—C2—C3—O2	6.3 (5)	C12—C7—C9—O1	-3.2 (4)
C10—C2—C3—C8	-173.4 (3)	C12—C7—C9—C8	178.01 (18)
O2—C3—C8—C4	-6.1 (5)	C6—C7—C9—O1	176.4 (3)
O2—C3—C8—C9	173.5 (3)	C6—C7—C9—C8	-2.4 (4)
C2—C3—C8—C4	173.6 (3)	C3—C8—C9—O1	3.7 (4)
C2—C3—C8—C9	-6.8 (4)	C3—C8—C9—C7	-177.6 (3)
C5—C4—C8—C3	179.6 (3)	C4—C8—C9—O1	-176.7 (3)
C5—C4—C8—C9	-0.0 (4)	C4—C8—C9—C7	2.0 (4)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1—H1 \cdots O2 ^{iv}	0.95	2.28	3.113 (4)	146 (1)
C4—H2 \cdots O3 ^{viii}	0.95	2.47	3.398 (4)	167 (1)
C6—C11 \cdots O3 ⁱⁱ	1.72 (1)	2.98 (1)	4.693 (4)	171 (1)
C10—O3 \cdots C11 ^x	1.21 (1)	2.98 (1)	3.678 (4)	116 (1)
C6—C11 \cdots C12 ⁱ	1.72 (1)	3.52 (1)	3.884 (4)	89 (1)
C7—C12 \cdots C11 ⁱⁱⁱ	1.72 (1)	3.52 (1)	5.229 (4)	171 (1)

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