



# Crystallographic and spectroscopic characterization of 3-chloro-5-fluorosalicylaldehyde

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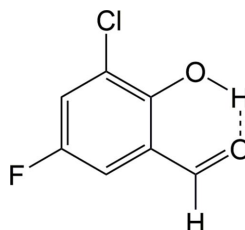
Edited by S. Parkin, University of Kentucky, USA

**Keywords:** crystal structure; hydrogen bonding; halogenated salicylaldehyde derivative.**CCDC reference:** 2041401**Supporting information:** this article has supporting information at journals.iucr.org/e

The title compound (systematic name: 3-chloro-5-fluoro-2-hydroxybenzaldehyde),  $C_7H_4ClFO_2$ , is a dihalogenated salicylaldehyde derivative that has been studied for its antibacterial characteristics. The salicylaldehyde engages in intramolecular hydrogen bonding with an  $O-H\cdots O$  distance of 2.6231 (19) Å while the molecules pack together *via* weak intermolecular  $C-H\cdots O$ ,  $C-H\cdots F$  and  $F\cdots O$  interactions and offset face-to-face  $\pi$ -stacking.

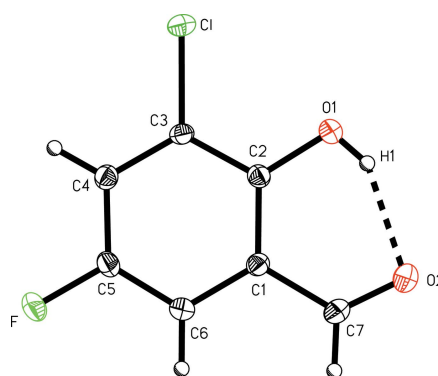
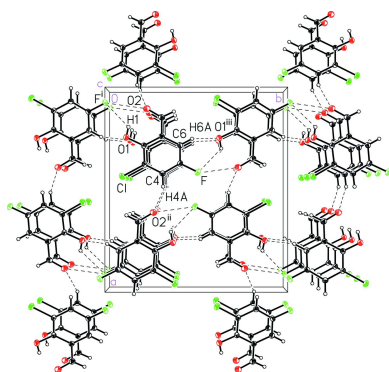
## 1. Chemical context

Salicylaldehyde and its derivatives, including the title compound 3-chloro-5-fluoro-2-hydroxybenzaldehyde, (I), play an important role in the synthesis of novel antimicrobial complexes (Bozkır *et al.*, 2012; Dahlgren *et al.*, 2010; Sari *et al.*, 2013). The title compound, commonly known as 3-chloro-5-fluorosalicylaldehyde, may be synthesized by the formylation of 2-chloro-4-fluorophenol with chloroform through reflux with concentrated NaOH(aq) (Balko *et al.*, 2007).



## 2. Structural commentary

The molecular structure of the title compound (Fig. 1) is planar, with an r.m.s. deviation from the plane of all non-

**Figure 1**

A view of 3-chloro-5-fluorosalicylaldehyde, (I), depicting the intramolecular hydrogen bonding with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level.



**Table 1**  
Hydrogen-bond geometry (Å, °).

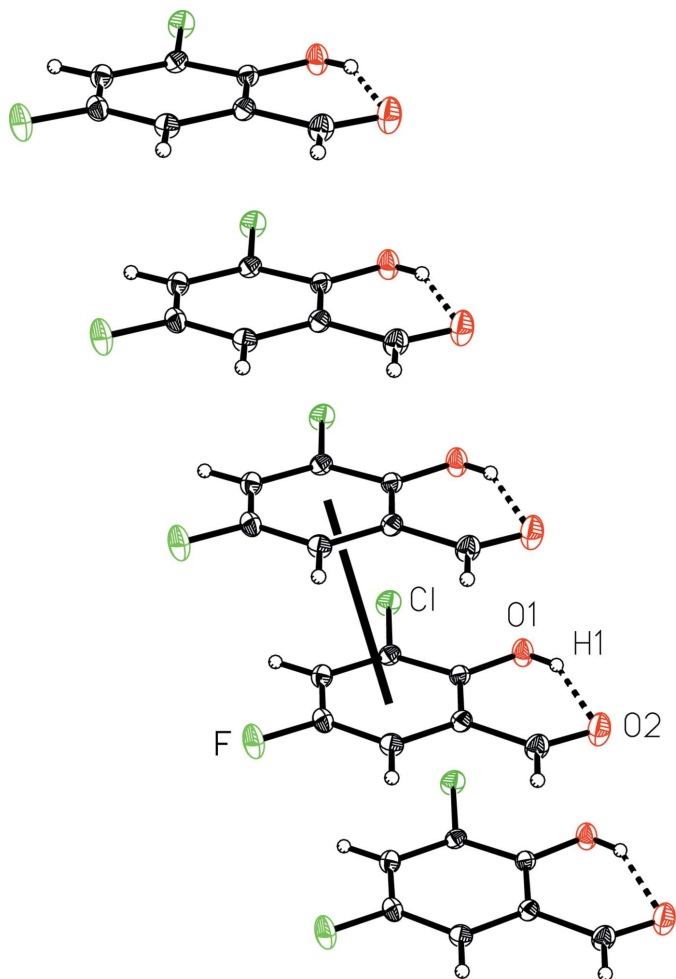
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1-H1\cdots F^i$	0.77 (3)	2.47 (3)	3.0101 (18)	128 (2)
$O1-H1\cdots O2$	0.77 (3)	1.93 (3)	2.6231 (19)	150 (3)
$C4-H4A\cdots O2^{ii}$	0.95	2.37	3.254 (2)	155
$C6-H6A\cdots O1^{iii}$	0.95	2.55	3.377 (2)	145

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

hydrogen atoms of 0.0135 Å. The molecule engages in intramolecular hydrogen bonding between the phenol hydrogen atom and formyl functional group oxygen with an  $O1\cdots O2$  distance of 2.6231 (19) Å characterizing the  $O1-H1\cdots O2$  interaction. The  $C3-Cl$  and  $C5-F$  bond lengths were found to be 1.7334 (16) and 1.3529 (19) Å, respectively.

### 3. Supramolecular features

The molecules pack together in the solid state with weak intermolecular  $C-H\cdots O$ ,  $C-H\cdots F$  and  $F\cdots O$  interactions

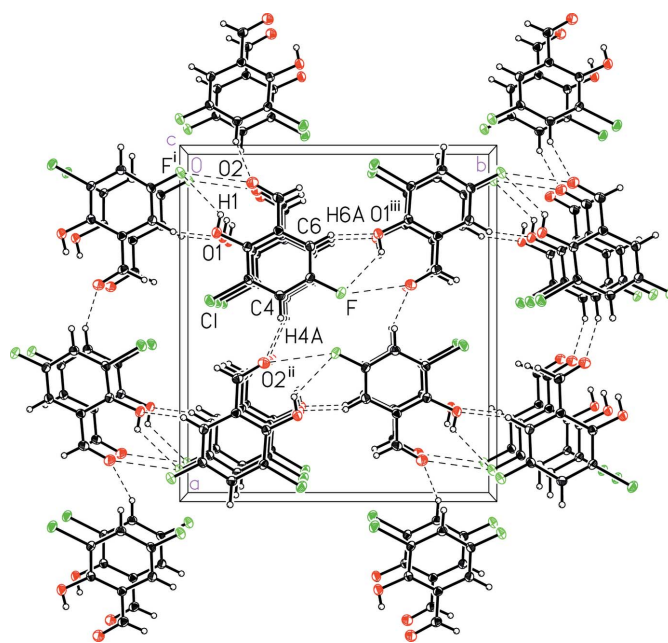


**Figure 2**  
A view of the intermolecular  $\pi$ -stacking in 3-chloro-5-fluorosalicylaldehyde, (I), with the thick line indicating a centroid-to-centroid relationship.

and an offset face-to-face  $\pi$ -stacking geometrical relationship. Molecules of 3-chloro-5-fluorosalicylaldehyde form one-dimensional  $\pi$ -stacking chains (Fig. 2), which are characterized by a ring centroid-to-centroid distance of 3.7154 (3) Å, a centroid-to-plane distance of 3.3989 (8) Å, and a ring-offset slippage of 1.501 (2) Å. These  $\pi$ -stacking chains are linked together to form the three-dimensional structure through weak intermolecular  $C-H\cdots O$  and  $C-H\cdots F$  contacts (Table 1 and Fig. 3). Specifically,  $O1-H1\cdots F^i$ ,  $C4-H4A\cdots O2^{ii}$ , and  $C6-H6A\cdots O1^{iii}$  intermolecular interactions (symmetry codes as defined in Table 1), with donor-acceptor distances of 3.0101 (18), 3.254 (2) and 3.377 (2) Å, respectively. In addition, an  $O2\cdots F^i$  contact with a distance of 2.880 (2) Å is observed. Notably, there are no close halogen-halogen interactions.

### 4. Database survey

The Cambridge Structural Database (Version 5.40, update of March 2020; Groom *et al.*, 2016) contains many halogenated benzene structures and relatively few halogenated salicylaldehyde structures. Literature aryl  $C-Cl$  and  $C-F$  bond lengths, as seen in halogenated benzene crystal structures, are similar to those seen in the title compound. For example, the  $C-Cl$  distances in 1,2- and 1,3-dichlorobenzene range between 1.731 (3) and 1.756 (3) Å (ABUMIT and ABUMOZ; Boese *et al.*, 2001), while the  $C-F$  distances in 1,3-difluorobenzene are found to be between 1.3486 (14) and 1.3553 (13) Å (PUGDAX; Kirchner *et al.*, 2009). Related salicylaldehyde structures that differ in the number of halogen atoms include unsubstituted salicylaldehyde itself (YADJOE;



**Figure 3**  
A view of the packing and weak intermolecular  $C-H\cdots O$ ,  $C-H\cdots F$  and  $F\cdots O$  interactions in 3-chloro-5-fluorosalicylaldehyde, (I). Symmetry codes are defined in Table 1.

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	C <sub>7</sub> H <sub>4</sub> ClFO <sub>2</sub>
<i>M<sub>r</sub></i>	174.55
Crystal system, space group	Orthorhombic, <i>Pna</i> 2 <sub>1</sub>
Temperature (K)	125
<i>a</i> , <i>b</i> , <i>c</i> (Å)	14.2730 (13), 12.7102 (12), 3.7154 (3)
<i>V</i> (Å <sup>3</sup> )	674.02 (10)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
<i>μ</i> (mm <sup>-1</sup> )	0.52
Crystal size (mm)	0.45 × 0.10 × 0.02
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2017)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.87, 0.99
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	16131, 2052, 1985
<i>R<sub>int</sub></i>	0.030
(sin θ/ <i>λ</i> ) <sub>max</sub> (Å <sup>-1</sup> )	0.715
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.023, 0.066, 1.07
No. of reflections	2052
No. of parameters	104
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δ <i>ρ</i> <sub>max</sub> , Δ <i>ρ</i> <sub>min</sub> (e Å <sup>-3</sup> )	0.34, -0.19
Absolute structure	Flack <i>x</i> determined using 837 quotients [( <i>I</i> <sup>+</sup> ) - ( <i>I</i> <sup>-</sup> )] / [( <i>I</i> <sup>+</sup> ) + ( <i>I</i> <sup>-</sup> )] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.07 (2)

Computer programs: *APEX2* and *SAINT* (Bruker, 2017), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2017/1* (Sheldrick, 2015b), *SHELXTL* (Sheldrick, 2008), *OLEX2* (Dolomanov *et al.*, 2009), and *Mercury* (Macrae *et al.*, 2020).

Kirchner *et al.*, 2011), 5-chlorosalicylaldehyde (RAJGOA01; Aitken *et al.*, 2013; RAJGOA, Jin *et al.*, 2011), and 3,5-dichlorosalicylaldehyde (MIXYEEY; Azizul & Ng, 2008). As with the title compound, each of these structures exhibits strong intramolecular hydrogen bonding between the phenol hydrogen atom and formyl oxygen atom.

## 5. Synthesis and crystallization

3-Chloro-5-fluorosalicylaldehyde (I, 97%) was purchased from Aldrich Chemical Company, USA, and was used as received.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon were included in calculated positions and refined using a riding model with C—H = 0.95 and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C) for the aryl H atoms. The position of the phenolic hydrogen atom was found in the difference map and refined freely.

## 7. Analytical Data

<sup>1</sup>H NMR (Bruker Avance III 400 MHz, CDCl<sub>3</sub>): δ 7.23 (*dd*, 1H, C<sub>aryl</sub>H, *J*<sub>meta</sub> = 3.0 Hz, *J*<sub>H-F</sub> = 7.2 Hz), 7.42 (*dd*, 1H, C<sub>aryl</sub>H, *J*<sub>meta</sub> = 3.0 Hz, *J*<sub>H-F</sub> = 7.8 Hz), 9.86 (*s*, 1H, OH), 11.21 (*s*, 1H, C(=O)H). <sup>13</sup>C NMR (<sup>13</sup>C{<sup>1</sup>H}, 100.6 MHz, CDCl<sub>3</sub>): δ 116.90 (*d*, C<sub>aryl</sub>H, *J*<sub>C-F</sub> = 22.6 Hz), 120.24 (*d*, C<sub>aryl</sub>, *J*<sub>C-F</sub> = 6.6 Hz), 123.15 (*d*, C<sub>aryl</sub>, *J*<sub>C-F</sub> = 9.1 Hz), 124.72 (*d*, C<sub>aryl</sub>H, *J*<sub>C-F</sub> = 26.4 Hz), 153.85 (*d*, C<sub>aryl</sub>, *J*<sub>C-F</sub> = 2.2 Hz), 154.85 (*d*, C<sub>aryl</sub>F, *J*<sub>C-F</sub> = 244.0 Hz), 194.97 (C(=O)H). <sup>19</sup>F NMR (<sup>19</sup>F{<sup>1</sup>H}, 376.5 MHz, CDCl<sub>3</sub>): δ -121.50. IR (Thermo Nicolet iS50, ATR, cm<sup>-1</sup>): 3081 (*m br*, O—H & C<sub>aryl</sub>—H *str*), 2859 [*w*, C(=O)—H *fermi doublet str*], 2733 [*w*, C(=O)—H *fermi doublet str*], 1803 (*w*), 1754 (*w*), 1664 (*s*, C=O *str*), 1623 (*m*), 1583 (*w*), 1524 (*w*), 1462 (*m*), 1436 (*s*), 1373 (*m*), 1351 (*w*), 1294 (*s*), 1238 (*s*), 1183 (*s*), 1119 (*s*), 982 (*s*), 902 (*m*), 894 (*m*), 875 (*s*), 802 (*s*), 727 (*s*), 708 (*s*), 578 (*m*), 530 (*s*), 493 (*s*), 458 (*m*). GC/MS (Agilent MS 5975/GC 7890): *M*<sup>+</sup> = 174 (calc. exact mass 173.99).

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## supporting information

*Acta Cryst.* (2020). E76, 1810-1812 [https://doi.org/10.1107/S2056989020014425]

## Crystallographic and spectroscopic characterization of 3-chloro-5-fluorosalicylaldehyde

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### Computing details

Data collection: *APEX2* (Bruker, 2017); cell refinement: *SAINTE* (Bruker, 2017); data reduction: *SAINTE* (Bruker, 2017); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2017/1* (Sheldrick, 2015b); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008), *OLEX2* (Dolomanov *et al.*, 2009), and *Mercury* (Macrae *et al.*, 2020).

### 3-Chloro-5-fluoro-2-hydroxybenzaldehyde

#### Crystal data

$C_7H_4ClFO_2$

$M_r = 174.55$

Orthorhombic, *Pna*2<sub>1</sub>

$a = 14.2730$  (13) Å

$b = 12.7102$  (12) Å

$c = 3.7154$  (3) Å

$V = 674.02$  (10) Å<sup>3</sup>

$Z = 4$

$F(000) = 352$

$D_x = 1.720$  Mg m<sup>-3</sup>

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

Cell parameters from 9931 reflections

$\theta = 2.9$ – $30.5^\circ$

$\mu = 0.52$  mm<sup>-1</sup>

$T = 125$  K

Needle, colourless

$0.45 \times 0.10 \times 0.02$  mm

#### Data collection

Bruker APEXII CCD  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.3333 pixels mm<sup>-1</sup>

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2017)

$T_{\min} = 0.87$ ,  $T_{\max} = 0.99$

16131 measured reflections

2052 independent reflections

1985 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$

$\theta_{\max} = 30.5^\circ$ ,  $\theta_{\min} = 2.2^\circ$

$h = -20 \rightarrow 20$

$k = -18 \rightarrow 17$

$l = -5 \rightarrow 5$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.066$

$S = 1.07$

2052 reflections

104 parameters

1 restraint

Primary atom site location: dual

Secondary atom site location: difference Fourier  
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 0.1224P]$

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

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

$\Delta\rho_{\max} = 0.34$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.19$  e Å<sup>-3</sup>

Absolute structure: Flack  $x$  determined using  
837 quotients  $[(F^-)-(F)]/[(F^+)+(F)]$  (Parsons *et al.*, 2013)  
Absolute structure parameter: 0.07 (2)

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl	0.43892 (3)	0.11149 (3)	0.78847 (17)	0.02049 (11)
F	0.41791 (7)	0.50784 (8)	0.7158 (3)	0.0246 (3)
O1	0.25167 (10)	0.12611 (10)	0.4770 (4)	0.0204 (3)
H1	0.202 (2)	0.137 (2)	0.412 (8)	0.036 (8)*
O2	0.11001 (9)	0.23221 (11)	0.2114 (4)	0.0256 (3)
C1	0.24600 (12)	0.31544 (12)	0.4365 (4)	0.0143 (3)
C2	0.29149 (11)	0.22104 (12)	0.5277 (4)	0.0142 (3)
C3	0.38146 (11)	0.22705 (12)	0.6760 (4)	0.0141 (3)
C4	0.42463 (11)	0.32301 (13)	0.7379 (4)	0.0157 (3)
H4A	0.485639	0.326265	0.8395	0.019*
C5	0.37672 (11)	0.41404 (13)	0.6482 (5)	0.0160 (3)
C6	0.28892 (11)	0.41307 (13)	0.4973 (4)	0.0157 (3)
H6A	0.258084	0.476816	0.435752	0.019*
C7	0.15263 (10)	0.31310 (13)	0.2738 (6)	0.0186 (3)
H7A	0.123791	0.378134	0.213767	0.022*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl	0.02085 (18)	0.01654 (18)	0.02407 (19)	0.00416 (13)	-0.00540 (17)	0.00218 (18)
F	0.0206 (5)	0.0149 (5)	0.0384 (7)	-0.0046 (4)	-0.0032 (5)	-0.0033 (5)
O1	0.0189 (6)	0.0142 (6)	0.0281 (7)	-0.0017 (5)	-0.0059 (5)	0.0005 (5)
O2	0.0192 (5)	0.0225 (6)	0.0350 (9)	-0.0014 (5)	-0.0094 (6)	-0.0006 (5)
C1	0.0138 (7)	0.0147 (7)	0.0145 (6)	0.0007 (5)	-0.0012 (5)	0.0000 (6)
C2	0.0156 (7)	0.0133 (7)	0.0136 (6)	-0.0007 (5)	-0.0007 (6)	0.0000 (6)
C3	0.0153 (7)	0.0133 (7)	0.0139 (6)	0.0024 (5)	-0.0015 (5)	0.0006 (5)
C4	0.0141 (6)	0.0165 (7)	0.0166 (8)	0.0001 (5)	-0.0005 (6)	-0.0012 (6)
C5	0.0160 (7)	0.0135 (7)	0.0185 (7)	-0.0025 (6)	0.0011 (6)	-0.0017 (6)
C6	0.0167 (7)	0.0136 (7)	0.0167 (7)	0.0011 (6)	0.0001 (6)	0.0005 (6)
C7	0.0162 (7)	0.0192 (7)	0.0205 (7)	0.0022 (5)	-0.0031 (7)	0.0008 (8)

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

Cl—C3	1.7334 (16)	C2—C3	1.399 (2)
F—C5	1.3529 (19)	C3—C4	1.386 (2)

O1—C2	1.3470 (19)	C4—C5	1.385 (2)
O1—H1	0.77 (3)	C4—H4A	0.95
O2—C7	1.217 (2)	C5—C6	1.373 (2)
C1—C6	1.402 (2)	C6—H6A	0.95
C1—C2	1.406 (2)	C7—H7A	0.95
C1—C7	1.464 (2)		
C2—O1—H1	106 (2)	C5—C4—H4A	120.8
C6—C1—C2	120.99 (14)	C3—C4—H4A	120.8
C6—C1—C7	118.83 (14)	F—C5—C6	118.71 (15)
C2—C1—C7	120.18 (14)	F—C5—C4	118.49 (14)
O1—C2—C3	119.41 (14)	C6—C5—C4	122.79 (15)
O1—C2—C1	122.42 (14)	C5—C6—C1	118.19 (15)
C3—C2—C1	118.17 (14)	C5—C6—H6A	120.9
C4—C3—C2	121.43 (14)	C1—C6—H6A	120.9
C4—C3—C1	119.70 (12)	O2—C7—C1	123.44 (15)
C2—C3—C1	118.87 (12)	O2—C7—H7A	118.3
C5—C4—C3	118.42 (15)	C1—C7—H7A	118.3

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>
O1—H1...F <sup>i</sup>	0.77 (3)	2.47 (3)	3.0101 (18)	128 (2)
O1—H1...O2	0.77 (3)	1.93 (3)	2.6231 (19)	150 (3)
C4—H4A...O2 <sup>ii</sup>	0.95	2.37	3.254 (2)	155
C6—H6A...O1 <sup>iii</sup>	0.95	2.55	3.377 (2)	145

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