

3-Fluorosalicylaldoxime

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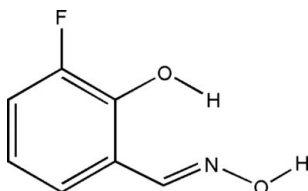
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Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.037; wR factor = 0.095; data-to-parameter ratio = 9.3.

In contrast with many salicylaldoxime derivatives, which form crystal structures based on hydrogen-bonded ring motifs, 3-fluorosalicylaldoxime, $\text{C}_7\text{H}_6\text{FNO}_2$, forms hydrogen-bonded chains. Each chain interacts with two chains above and two chains below *via* π - π stacking contacts [centroid-centroid distance = 3.6353 (1) Å].

Related literature

Chain formation is characteristic of salicylaldoximes bearing large substituents [*e.g.* Cambridge Structural Database (Allen, 2002) refcodes HEPKET10 (Kozioł & Kosturkiewicz, 1984) and HELBOP (Maurin, 1994)]. The structures of 3-fluorosalicylaldoxime (this work), one of the polymorphs of salicylaldoxime [designated phase III by Wood *et al.* (2006)] and 3-hydroxysalicylaldoxime (Wood *et al.*, 2007) are exceptions to this rule.



Experimental

Crystal data

$\text{C}_7\text{H}_6\text{FNO}_2$
 $M_r = 155.13$

Orthorhombic, $Pna2_1$
 $a = 7.0497$ (3) Å

$b = 10.5161$ (4) Å
 $c = 9.1022$ (4) Å
 $V = 674.79$ (5) Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 0.13$ mm⁻¹
 $T = 150$ K
 $0.36 \times 0.34 \times 0.19$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 2006)
 $T_{\min} = 0.50$, $T_{\max} = 0.98$

5425 measured reflections
981 independent reflections
840 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.095$
 $S = 1.00$
981 reflections
106 parameters
3 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.24$ e Å⁻³
 $\Delta\rho_{\min} = -0.22$ e Å⁻³

Data collection: SMART (Siemens, 1993); cell refinement: SAINT; data reduction: SAINT (Siemens, 1995); program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: CRYSTALS (Betteridge *et al.*, 2003); molecular graphics: DIAMOND (Brandenburg, 2004); software used to prepare material for publication: CRYSTALS.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2020).

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supplementary materials

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3-Fluorosalicylaldoxime

P. A. Wood, R. S. Forgan, S. Parsons, E. Pidcock and P. A. Tasker

Comment

3-Fluoro-salicylaldoxime (I) crystallizes with one molecule in the asymmetric unit in the space group $Pna2_1$. The molecule forms an intramolecular phenolic OH \cdots N hydrogen bond [O5 \cdots N2 = 2.586 (3) Å] (Figure 1) and an intermolecular oximic OH \cdots O hydrogen bond [O1 \cdots O5 = 2.815 (2) Å] with a neighbouring molecule related by the 2_1 screw axis. These two interactions taken together form a secondary level C(5) chain running parallel to the crystallographic c axis (Figure 2).

Each chain interacts with two chains above and two chains below *via* π - π stacking contacts in which the C-atoms in one ring lie 3.357 (2) to 3.583 (2) Å from the plane of the other ring. The dihedral angle between the two phenyl planes is 3.91 (7)°. The molecule also forms three close contacts involving the fluoro group C9H9 \cdots F6 [C9 \cdots F6 = 3.304 (3) Å], O5H5 \cdots F6 [O5 \cdots F6 = 3.034 (2) Å] and N2 \cdots F6 [N2 \cdots F6 = 3.011 (2) Å] (Figure 3).

Experimental

All solvents and reagents were used as received from Aldrich and Fisher. ^1H and ^{13}C NMR were obtained using a Bruker AC250 spectrometer at ambient temperature. Chemical shifts (δ) are reported in parts per million (p.p.m.) relative to internal standards. Fast atom bombardment mass spectrometry (FABMS) was carried out using a Kratos MS50TC spectrometer with a thioglycerol matrix. Analytical data was obtained from the University of St Andrews Microanalytical Service.

KOH (0.674 g, 10.20 mmol) and $\text{NH}_2\text{OH}\cdot\text{HCl}$ (0.709 g, 10.20 mmol) were dissolved in EtOH, mixed thoroughly and a white KCl precipitate removed by filtration. 3-Fluorosalicylaldehyde (1.000 g, 7.14 mmol) was added to the filtrate, and the mixture refluxed for 3 hr. The solvent was removed *in vacuo*, and the residue redissolved in CHCl_3 , washed with water 3 times and dried over MgSO_4 . The solvent was removed *in vacuo* to yield the crude product as a white powder (0.980 g, 88.5%). A pale yellow block suitable for x -ray diffraction was grown by slow evaporation of a hexane/chloroform solution. (Anal. Calc. for $\text{C}_7\text{H}_6\text{FNO}_2$: C, 54.2; H, 3.9; N, 9.0. Found: C, 54.3; H, 3.5; N, 9.2%); ^1H NMR (250 MHz, CDCl_3): δ (H) (p.p.m.) 6.78 (dt, 1H, ArH_b), 6.90 (dd, 1H, ArH_a), 7.05 (m, 1H, ArH_c), 8.16 (s, 1H, CHN); ^{13}C NMR (63 MHz, CDCl_3) δ (C) (p.p.m.) 118.0 (1 C, aromatic CH), 118.7 (1 C, aromatic C-CHN), 119.8 (1 C, aromatic CH), 126.0 (1 C, aromatic CH), 145.9 (1 C, aromatic C—F), 152.8 (1 C, ArCHN), 153.6 (1 C, aromatic C—OH); FABMS m/z 156 (MH)⁺, 70%.

Following data collection (see Table 1) an absorption correction was applied using the program *SADABS*. $T_{\text{max}}/T_{\text{min}}$ is larger than calculated on the basis of the crystal dimensions. However, multi-scan procedures (such as *SADABS*) correct for all systematic errors that lead to disparities in the intensities of equivalent data. It is possible that the larger than expected range of transmission is accounted for by crystal decay or absorption by the mounting fibre.

Refinement

The hydrogen atoms were located in a Fourier difference map. The positional and isotropic displacement parameters were then refined subject to restraints [$C-H = 0.93$ (2) Å, $O-H = 0.82$ (2) Å and $U_{iso}(H) = 1.5 U_{eq}(C \text{ or } O)$]. In subsequent cycles of least squares all the $U_{iso}(H)$ values were

fixed and the H-atoms attached to C were constrained to ride on their parent atoms. H1 and H5 were refined subject to distance restraints equal to 0.84 (5) Å.

Figures

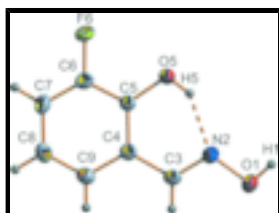


Fig. 1. Molecular structure of I with probability ellipsoids drawn at the 50% level.

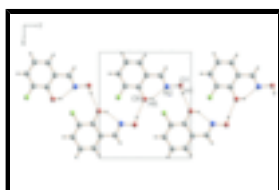


Fig. 2. H-bonded chain formation in the crystal structure of I.

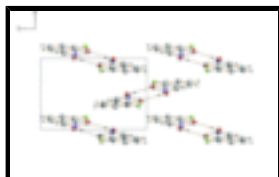


Fig. 3. Packing of C(5) chains in the crystal structure of I showing π - π stacking interactions. This view is along the chains shown in Fig. 2.

3-fluorosalicylaldoxime

Crystal data

$C_7H_6FN_1O_2$

$M_r = 155.13$

Orthorhombic, $Pna2_1$

Hall symbol: P 2c -2n

$a = 7.0497$ (3) Å

$b = 10.5161$ (4) Å

$c = 9.1022$ (4) Å

$V = 674.79$ (5) Å³

$Z = 4$

$F_{000} = 320$

$D_x = 1.527$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 2462 reflections

$\theta = 3-30^\circ$

$\mu = 0.13$ mm⁻¹

$T = 150$ K

Block, pale yellow

$0.36 \times 0.34 \times 0.19$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	840 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.034$
$T = 150$ K	$\theta_{\text{max}} = 30.3^\circ$
ω scans	$\theta_{\text{min}} = 3.0^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 2006)	$h = -9 \rightarrow 9$
$T_{\text{min}} = 0.50$, $T_{\text{max}} = 0.98$	$k = -14 \rightarrow 14$
5425 measured reflections	$l = -11 \rightarrow 12$
981 independent reflections	

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F^2) + (0.05P)^2]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$
$R[F^2 > 2\sigma(F^2)] = 0.037$	$(\Delta/\sigma)_{\text{max}} = 0.0001$
$wR(F^2) = 0.095$	$\Delta\rho_{\text{max}} = 0.24 \text{ e } \text{\AA}^{-3}$
$S = 1.00$	$\Delta\rho_{\text{min}} = -0.22 \text{ e } \text{\AA}^{-3}$
981 reflections	Extinction correction: ?
106 parameters	Extinction coefficient: ?
3 restraints	
Primary atom site location: structure-invariant direct methods	
Hydrogen site location: difference Fourier map	

Special details

Experimental. Used Oxford Cryosystems low temperature device. Data collection strategy optimized with COSMO.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.4921 (3)	0.18525 (14)	0.8860 (2)	0.0413
N2	0.4610 (3)	0.17539 (15)	0.7354 (2)	0.0308
C3	0.4249 (3)	0.28150 (17)	0.6744 (3)	0.0291
C4	0.3910 (3)	0.28594 (19)	0.5162 (2)	0.0269
C5	0.3791 (3)	0.17354 (18)	0.4329 (3)	0.0257
O5	0.3996 (2)	0.05548 (13)	0.4920 (2)	0.0309
C6	0.3441 (3)	0.18391 (19)	0.2834 (3)	0.0300
F6	0.3325 (2)	0.07390 (12)	0.2058 (2)	0.0401
C7	0.3223 (3)	0.2981 (2)	0.2124 (3)	0.0328
C8	0.3356 (3)	0.4092 (2)	0.2956 (3)	0.0327
C9	0.3695 (3)	0.4030 (2)	0.4445 (3)	0.0295

supplementary materials

H1	0.520 (5)	0.111 (3)	0.909 (4)	0.0609*
H3	0.4159	0.3549	0.7269	0.0344*
H5	0.426 (4)	0.063 (3)	0.579 (3)	0.0455*
H7	0.3001	0.2989	0.1116	0.0381*
H8	0.3191	0.4887	0.2494	0.0387*
H9	0.3797	0.4761	0.4983	0.0346*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0687 (12)	0.0326 (8)	0.0228 (7)	0.0036 (8)	-0.0049 (7)	0.0006 (6)
N2	0.0405 (10)	0.0290 (8)	0.0228 (9)	-0.0002 (7)	-0.0001 (7)	-0.0011 (6)
C3	0.0360 (10)	0.0231 (8)	0.0280 (10)	-0.0005 (8)	0.0018 (8)	-0.0042 (7)
C4	0.0282 (10)	0.0256 (9)	0.0268 (10)	-0.0002 (7)	0.0019 (8)	0.0000 (7)
C5	0.0300 (9)	0.0229 (9)	0.0242 (9)	0.0009 (7)	0.0024 (8)	0.0000 (7)
O5	0.0462 (9)	0.0225 (6)	0.0241 (6)	0.0008 (6)	0.0000 (6)	-0.0008 (5)
C6	0.0328 (11)	0.0306 (10)	0.0268 (11)	0.0021 (7)	0.0003 (8)	-0.0045 (8)
F6	0.0606 (9)	0.0332 (6)	0.0266 (6)	0.0058 (5)	-0.0048 (6)	-0.0086 (5)
C7	0.0370 (11)	0.0379 (11)	0.0235 (8)	0.0050 (8)	0.0004 (9)	0.0033 (8)
C8	0.0345 (11)	0.0299 (9)	0.0336 (10)	0.0036 (7)	0.0005 (9)	0.0075 (8)
C9	0.0331 (9)	0.0237 (9)	0.0316 (9)	0.0018 (7)	0.0001 (8)	-0.0012 (7)

Geometric parameters (\AA , $^\circ$)

O1—N2	1.392 (2)	O5—H5	0.82 (3)
O1—H1	0.83 (3)	C6—F6	1.358 (2)
N2—C3	1.272 (2)	C6—C7	1.372 (3)
C3—C4	1.460 (3)	C7—C8	1.395 (3)
C3—H3	0.911	C7—H7	0.931
C4—C5	1.407 (3)	C8—C9	1.378 (3)
C4—C9	1.401 (3)	C8—H8	0.943
C5—O5	1.361 (2)	C9—H9	0.915
C5—C6	1.387 (3)		
N2—O1—H1	102 (3)	C5—C6—F6	116.98 (19)
O1—N2—C3	113.33 (16)	C5—C6—C7	123.4 (2)
N2—C3—C4	119.43 (17)	F6—C6—C7	119.62 (18)
N2—C3—H3	121.9	C6—C7—C8	118.0 (2)
C4—C3—H3	118.6	C6—C7—H7	119.4
C3—C4—C5	120.97 (18)	C8—C7—H7	122.6
C3—C4—C9	120.34 (19)	C7—C8—C9	120.4 (2)
C5—C4—C9	118.70 (18)	C7—C8—H8	119.4
C4—C5—O5	123.17 (17)	C9—C8—H8	120.1
C4—C5—C6	118.26 (19)	C4—C9—C8	121.2 (2)
O5—C5—C6	118.57 (19)	C4—C9—H9	118.8
C5—O5—H5	108.9 (19)	C8—C9—H9	120.0

Fig. 1

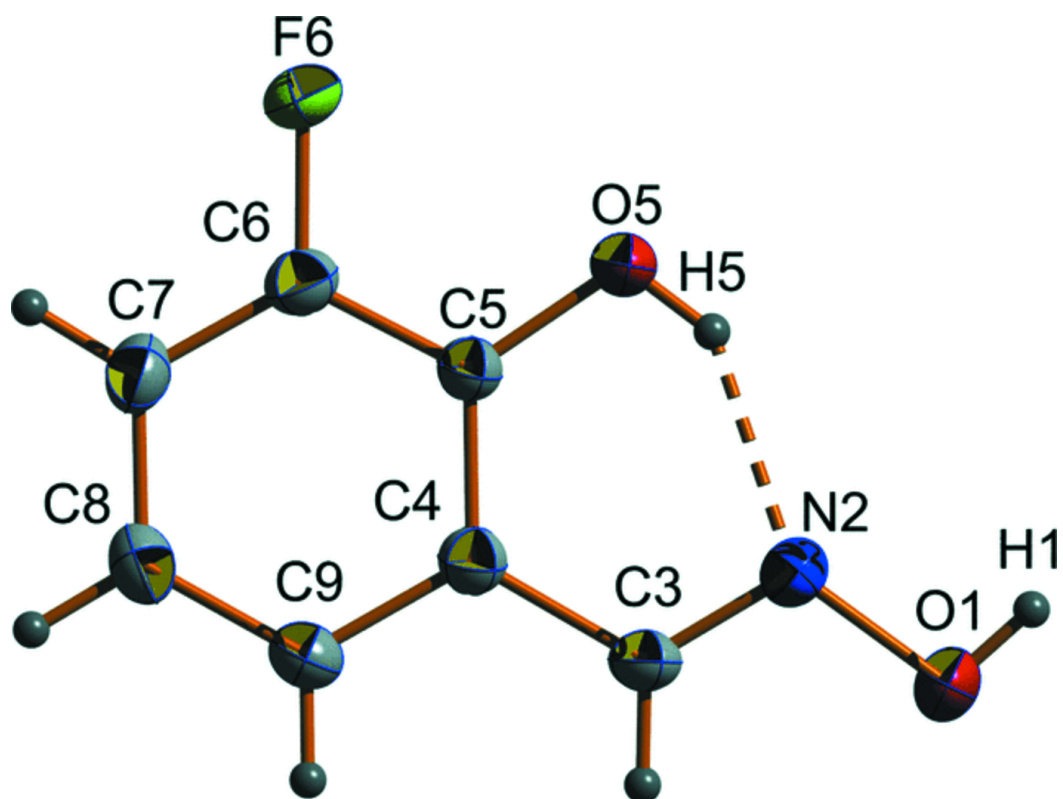


Fig. 2

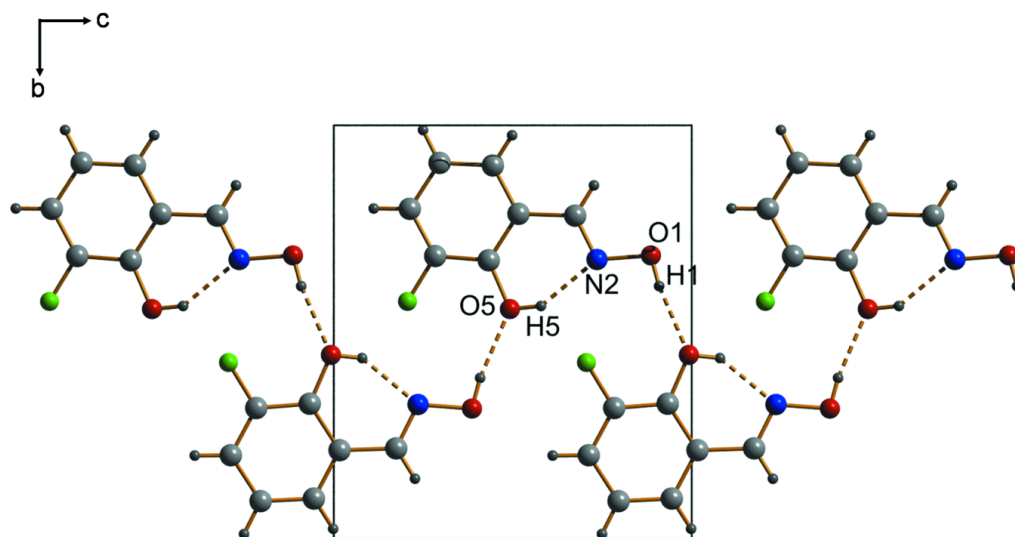


Fig. 3

