Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS
ISSN 2056-9890

Crystal structures of (*E*)-*N*′-(2-hydroxy-5-methylbenzylidene)isonicotinohydrazide and (*E*)-*N*′-(5-fluoro-2-hydroxybenzylidene)isonicotinohydrazide

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Received 20 May 2016
Accepted 15 June 2016

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

Keywords: crystal structure; iron chelator; isonicotinohydrazide; hydrogen bonds.

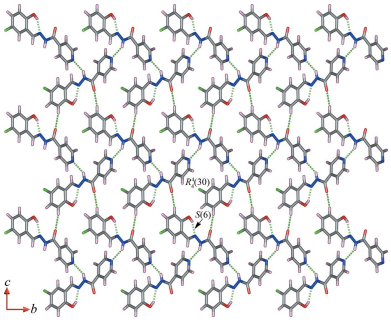
CCDC references: 1485834; 1485833

Supporting information: this article has supporting information at journals.iucr.org/e

Two derivatives of the well-known iron chelator, (*E*)-*N*′-(2-hydroxybenzylidene)isonicotinohydrazide (SIH), substituted in the 5-position of the 2-hydroxybenzene ring by a methyl and a fluorine group *viz.* (*E*)-*N*′-(2-hydroxy-5-methylbenzylidene)isonicotinohydrazide, $C_{14}H_{13}N_3O_2$, (I), and (*E*)-*N*′-(5-fluoro-2-hydroxybenzylidene)isonicotinohydrazide, $C_{13}H_{10}FN_3O_2$, (II), have been prepared and characterized by single-crystal X-ray diffraction, ^{1}H NMR and mass spectrometry. The molecules of both compounds deviate slightly from planarity [r.m.s. deviations are 0.145 and 0.110 Å for (I) and (II), respectively] and adopt an *E* conformation with respect to the double bond of the hydrazone bridge. In each molecule, there is an intramolecular O—H···N hydrogen bond forming an *S*(6) ring motif. The dihedral angles between the mean planes of the isonicotinoyl ring and the cresol ring in (I) or the fluorophenol ring in (II) are 10.49 (6) and 9.43 (6)°, respectively. In the crystals of both compounds, zigzag chains are formed *via* N—H···N hydrogen bonds, in the [10$\bar{1}$] direction for (I) and [010] for (II). In (I), the chains are linked by weak C—H···π and π–π stacking interactions [centroid-to-centroid distances = 3.6783 (8) Å; inter-planar angle = 10.94 (5)°], leading to the formation of a three-dimensional supramolecular architecture. In (II), adjacent chains are connected through C—H···O hydrogen bonds to form sheets parallel to (100), which enclose $R_4^4(30)$ ring motifs. The sheets are linked by weak C—H···π and π–π [centroid-to-centroid distance = 3.7147 (8) Å; inter-planar angle = 10.94 (5)°] interactions, forming a three-dimensional supramolecular architecture.

1. Chemical context

Hydrazone-based chelators for metal ions have received a significant amount of attention (Bendova *et al.*, 2010; Hrušková *et al.*, 2016). Compounds from this class, such as salicyl aldehyde isonicotinoyl hydrazide (SIH), have been studied as potential metal chelators in biological systems (Hrušková *et al.*, 2011). These compounds have also been shown to be effective in protecting against metal-based oxidative stress (Jansová *et al.*, 2014). In our research we are interested in developing probes for metal ions (Carter *et al.*, 2014). We have therefore synthesized the title compounds, which are derivatives of the chelator SIH containing a signalling unit.



2. Structural commentary

The molecular structures of the title compounds, (I) and (II), are illustrated in Figs. 1 and 2, respectively. They consist of an

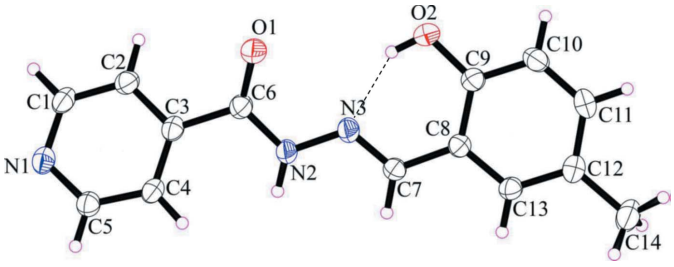


Figure 1
The molecular structure of compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. The intramolecular O—H···N hydrogen bond is shown as a dashed line (see Table 1).

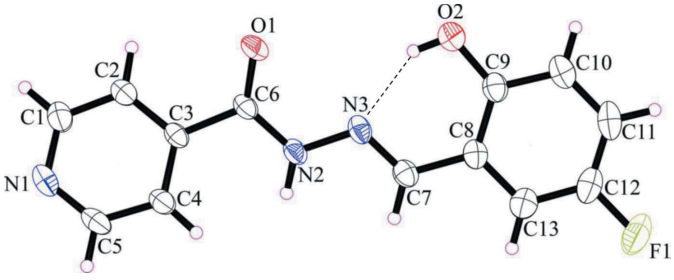
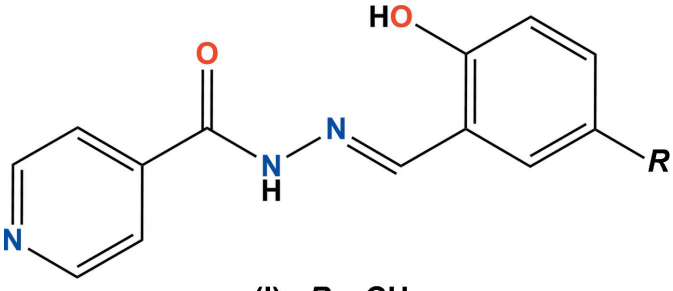


Figure 2
The molecular structure of compound (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. The intramolecular O—H···N hydrogen bond is shown as a dashed line (see Table 2).

isonicotinoyl moiety linked by a –C7═N3–N2– linkage to a cresol unit in (I) and a fluorophenol ring in (II). The molecules deviate slightly from planarity with the r.m.s deviations for the fitted atoms being 0.145 for (I) and 0.110 Å for (II). In each molecule, there is an intramolecular O—H···N hydrogen bond forming an *S*(6) ring motif. Both compounds have an *E* conformation with respect to the double bond of the hydrazone bridge (C7═N3) with the C8—C7═N3—N2 torsion angles being −179.03 (12) and −177.61 (11)° for (I) and (II), respectively. The dihedral angles between the mean planes of the isonicotinoyl moiety and the cresol moiety in (I), or the fluorophenol moiety in (II) are 10.49 (6) and 9.43 (6)°, respectively. The bond lengths and angles in the title molecules agree reasonably well with those found in closely related structures (Chumakov *et al.*, 2001; Yang, 2006*a*,*b*; Kargar *et al.*, 2010; Sedaghat *et al.*, 2014)



(I) $R = CH_3$
(II) $R = F$

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

*Cg*1 is the centroid of the N1/C1–C5 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*O*···N3	0.82	1.87	2.5857 (16)	145
N2—H2*N*···N1^{i}	0.86	2.19	3.0232 (17)	164
C10—H10···*Cg*1^{ii}	0.93	2.85	3.5259 (17)	130

Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (ii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$.

Table 2
Hydrogen-bond geometry (Å, °) for (II).

*Cg*1 is the centroid of the N1/C1–C5 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···N3	0.82	1.92	2.6329 (15)	145
N2—H2*A*···N1^{i}	0.86	2.19	2.8889 (15)	138
C10—H10···O1^{ii}	0.93	2.51	3.2573 (18)	138
C11—H11···*Cg*1^{iii}	0.93	2.98	3.8917 (18)	168

Symmetry codes: (i) $-x+2, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x-1, -y+\frac{1}{2}, z-\frac{1}{2}$.

3. Supramolecular features

In the crystals of both compounds, zigzag chains are formed *via* N—H···N hydrogen bonds (Tables 1 and 2), in direction [10$\bar{1}$] for (I) and [010] for (II). In (I), the chains are linked by weak C—H···π and π–π stacking interactions [centroid-to-centroid distances = 3.6783 (8) Å; inter-planar angle = 10.94 (5)°], leading to the formation of a three-dimensional supramolecular architecture (Fig. 3). In (II), adjacent chains are connected through C—H···O hydrogen bonds to form sheets parallel to (100), which enclose $R_4^4(30)$ ring motifs. Weak C—H···π and π—π [centroid-to-centroid distance = 3.7147 (8) Å, inter-planar angle = 10.94 (5)°] interactions link

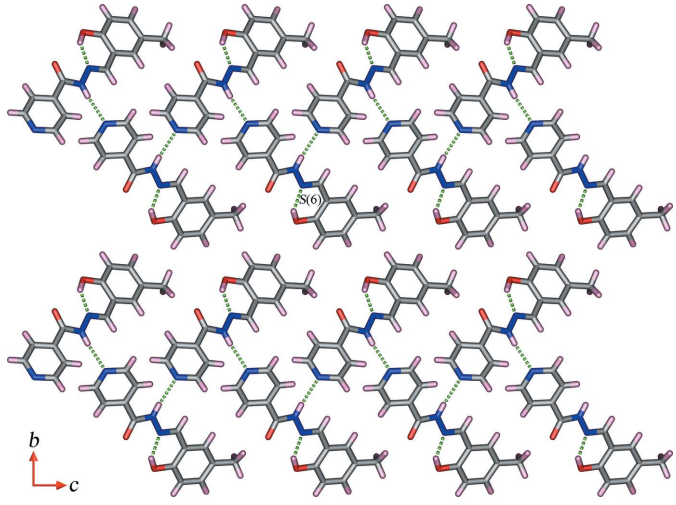


Figure 3
Partial view along the *a* axis of the crystal packing of compound (I), showing the hydrogen-bonded (dashed lines; see Table 1) zigzag chains parallel to [10$\bar{1}$].

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_{14}H_{13}N_3O_2$	$C_{13}H_{10}FN_3O_2$
M_r	255.27	259.24
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$
Temperature (K)	296	296
a, b, c (Å)	8.5318 (4), 15.9973 (8), 9.4637 (5)	8.9195 (3), 10.1128 (3), 13.6254 (4)
β (°)	102.738 (2)	103.481 (1)
V (Å^3)	1259.87 (11)	1195.16 (6)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.09	0.11
Crystal size (mm)	0.30 × 0.22 × 0.22	0.32 × 0.26 × 0.26
Data collection		
Diffractometer	Bruker D8 QUEST CMOS	Bruker APEX2 D8 QUEST CMOS
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.685, 0.746	0.685, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26052, 2996, 2111	31833, 2848, 2128
R_{int}	0.045	0.039
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.659	0.658
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.126, 1.01	0.042, 0.124, 1.03
No. of reflections	2996	2848
No. of parameters	174	174
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.20, −0.22	0.26, −0.29

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009), *ORTEP-3 for Windows* (Farrugia, 2012), *DIAMOND* (Brandenburg, 2006), *publCIF* (Westrip, 2010) and *enCIFer* (Allen *et al.*, 2004).

the sheets, forming a three-dimensional supramolecular architecture (Fig. 4).

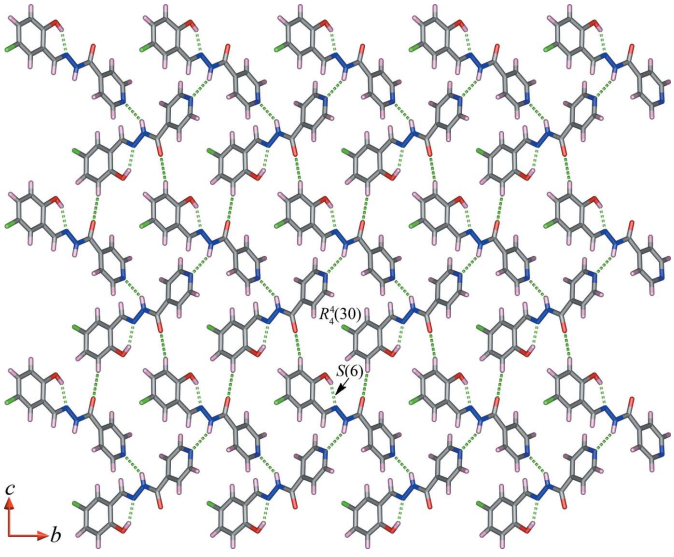


Figure 4
Partial view along the *a* axis of the crystal packing of compound (II), showing the N—H···N and C—H···O hydrogen-bonded (dashed lines; see Table 2) sheet propagating in the *bc* plane.

4. Database survey

A search of the Cambridge Structural Database (Version 5.37, last update November 2015; Groom *et al.*, 2016) indicated the presence of 40 structures containing the (*E*)-*N*-(2-hydroxybezylydene)isonicotinohydrazide substructure. They include the isotypic crystal structures with chloride (UCAREV, Chumakov *et al.*, 2001; UCAREV01, Yang, 2006*a*), bromide (XENDOK, Yang, 2006*b*; XENDOK01, Sedaghat *et al.*, 2014) and methoxy (VACHAK, Kargar *et al.*, 2010) groups substituted at the 5-position of the phenyl ring. In the crystals of all three compounds, the N—H···N hydrogen bond involving the hydrazone hydrogen and the pyridine nitrogen atoms organize the molecules into a herringbone motif, while in the crystal of the methoxy compound there are also weak N—H···O and C—H···O hydrogen bonds present forming $R_1^2(6)$ ring motifs.

5. Synthesis and crystallization

A solution of isonicotinic acid hydrazide (0.184 g, 1.34 mmol) and the appropriately substituted salicyl aldehyde (1.47 mmol) in a mixture of ethanol (3 ml) and water (1 ml) containing a catalytic amount of acetic acid was heated to reflux for 5 h. The reaction mixture was allowed to cool to room temperature, resulting in the formation of a white precipitate. The reaction mixture was filtered and the isolated solid was washed with diethyl ether and dried *in vacuo*. The compounds were isolated as white crystalline solids in 73% and 66% yield for

the methyl (I) and fluoro (II) derivatives, respectively. Single crystals suitable for X-ray diffraction were grown by slow evaporation of methanolic solutions of the title compounds.

Spectroscopic data for (I): ^{1}H NMR (400 MHz, DMSO-d_6) d 2.25 (1H, s, CH_3), 6.84 (1H, d, J = 8.4, CH—Ph), 7.12 (1H, dd, J = 2.0, J = 8.4, CH—Ph), 7.40 (1H, d, J = 1.6, CH—Ph), 7.84 (2H, d, J = 6.0, CH—Py), 8.63 (1H, s, CH═N), 8.79 (2H, d, J = 6.0, CH—Py), 10.82 (1H, s, NH), 12.26 (1H, s, OH). HR–MS (ES$^+$) $C_{14}H_{14}N_3O_2$ requires 256.1086 $[M+H]^+$; found 256.1051.

Spectroscopic data for (II): ^{1}H NMR (400 MHz, DMSO-d_6) d 6.94 (1H, dd, J = 4.4, J = 8.8, CH—Ph), 7.16 (1H, td, J = 3.2, J = 8.8, CH—Ph), 7.46 (1H, dd, J = 3.2, J = 9.6, CH—Ph), 7.84 (2H, d, J = 6.0, CH—Py), 8.67 (1H, s, CH═N), 8.80 (2H, d, J = 6.0, CH—Py), 10.84 (1H, s, NH), 12.35 (1H, s, OH). HR–MS (ES$^+$) $C_{13}H_{11}FN_3O_2$ requires 260.0835 $[M+H]^+$; found 260.0831.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms bonded to C, N, and O atoms were placed at calculated positions and refined using a riding-model approximation: N—H = 0.86 Å, O—H = 0.82 Å, and C—H = 0.93–0.96 Å with U_{iso}(H) = 1.5U_{eq}(C-methyl,O) and 1.2U_{eq}(N,C) for other H atoms.

Acknowledgements

This work was supported by a National Research Councils of Thailand grant provided by the Naresuan University Division of Research Administration (R2558B106). The authors thank the Faculty of Science and Technology, Thammasat University, for funds to purchase the X-ray diffractometer.

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supporting information

Acta Cryst. (2016). E**72**, 980-983 [doi:10.1107/S2056989016009762]

Crystal structures of (*E*)-*N*′-(2-hydroxy-5-methylbenzylidene)isonicotinohydrazide and (*E*)-*N*′-(5-fluoro-2-hydroxybenzylidene)isonicotinohydrazide

Kittipong Chainok, Sureerat Makmuang and Filip Kielar

Computing details

For both compounds, data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009), *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010) and *enCIFer* (Allen *et al.*, 2004).

(I) (*E*)-*N*′-(2-Hydroxy-5-methylbenzylidene)isonicotinohydrazide

Crystal data

$C_{14}H_{13}N_3O_2$
M_r = 255.27
Monoclinic, $P2_1/n$
a = 8.5318 (4) Å
b = 15.9973 (8) Å
c = 9.4637 (5) Å
β = 102.738 (2)°
V = 1259.87 (11) Å^3
Z = 4
$F(000)$ = 536
D_x = 1.346 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6456 reflections
θ = 2.9–27.3°
μ = 0.09 mm^{-1}
T = 296 K
Block, colourless
0.30 × 0.22 × 0.22 mm

Data collection

Bruker D8 QUEST CMOS diffractometer
Radiation source: microfocus sealed x-ray tube, Incoatec Iμus
GraphiteDouble Bounce Multilayer Mirror monochromator
Detector resolution: 10.5 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
T_{min} = 0.685, T_{max} = 0.746
26052 measured reflections
2996 independent reflections
2111 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 27.9°, θ_{min} = 2.9°
h = −11→11
k = −21→21
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.126
S = 1.01
2996 reflections
174 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0596P)^2 + 0.2954P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.55036 (17)	0.49610 (7)	0.82618 (13)	0.0710 (4)
O2	0.21987 (15)	0.36743 (7)	0.62695 (11)	0.0575 (3)
H2O	0.2779	0.4085	0.6481	0.086*
N1	0.84669 (14)	0.76238 (8)	0.96854 (13)	0.0422 (3)
N2	0.43283 (14)	0.57825 (7)	0.63975 (12)	0.0390 (3)
H2N	0.4281	0.6255	0.5957	0.047*
N3	0.33377 (14)	0.51301 (7)	0.58586 (13)	0.0392 (3)
C1	0.81205 (18)	0.69573 (9)	1.04127 (15)	0.0430 (4)
H1	0.8580	0.6923	1.1398	0.052*
C2	0.71232 (18)	0.63196 (9)	0.97872 (15)	0.0418 (4)
H2	0.6922	0.5868	1.0340	0.050*
C3	0.64217 (16)	0.63598 (8)	0.83192 (15)	0.0362 (3)
C4	0.67688 (16)	0.70444 (9)	0.75506 (15)	0.0377 (3)
H4	0.6321	0.7096	0.6565	0.045*
C5	0.77918 (17)	0.76509 (9)	0.82720 (15)	0.0406 (3)
H5	0.8025	0.8106	0.7741	0.049*
C6	0.53873 (18)	0.56378 (9)	0.76673 (16)	0.0415 (3)
C7	0.23407 (16)	0.51994 (8)	0.46483 (14)	0.0365 (3)
H7	0.2291	0.5691	0.4116	0.044*
C8	0.12838 (16)	0.45084 (8)	0.41038 (14)	0.0336 (3)
C9	0.12462 (17)	0.37797 (9)	0.49306 (15)	0.0393 (3)
C10	0.02068 (19)	0.31395 (9)	0.43625 (17)	0.0463 (4)
H10	0.0153	0.2664	0.4914	0.056*
C11	−0.07485 (18)	0.31991 (10)	0.29884 (17)	0.0453 (4)
H11	−0.1419	0.2755	0.2622	0.054*
C12	−0.07365 (16)	0.39037 (10)	0.21364 (15)	0.0409 (4)
C13	0.02749 (17)	0.45510 (9)	0.27258 (15)	0.0378 (3)
H13	0.0283	0.5034	0.2182	0.045*
C14	−0.1769 (2)	0.39481 (12)	0.06279 (18)	0.0601 (5)
H14A	−0.1905	0.3397	0.0218	0.090*
H14B	−0.1260	0.4299	0.0039	0.090*
H14C	−0.2800	0.4176	0.0664	0.090*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0903 (10)	0.0412 (7)	0.0624 (8)	−0.0114 (6)	−0.0244 (7)	0.0126 (6)
O2	0.0751 (8)	0.0487 (7)	0.0403 (6)	−0.0108 (6)	−0.0055 (5)	0.0119 (5)
N1	0.0409 (7)	0.0425 (7)	0.0401 (7)	0.0010 (5)	0.0022 (5)	−0.0074 (5)
N2	0.0408 (7)	0.0309 (6)	0.0400 (7)	−0.0020 (5)	−0.0022 (5)	−0.0019 (5)
N3	0.0409 (7)	0.0332 (6)	0.0404 (7)	−0.0023 (5)	0.0021 (5)	−0.0041 (5)
C1	0.0457 (8)	0.0465 (9)	0.0320 (7)	0.0056 (7)	−0.0018 (6)	−0.0044 (6)
C2	0.0475 (8)	0.0376 (8)	0.0368 (8)	0.0037 (6)	0.0019 (6)	0.0009 (6)
C3	0.0341 (7)	0.0348 (7)	0.0368 (7)	0.0065 (6)	0.0018 (6)	−0.0044 (6)
C4	0.0371 (8)	0.0406 (8)	0.0323 (7)	0.0043 (6)	0.0011 (6)	−0.0025 (6)
C5	0.0419 (8)	0.0392 (8)	0.0391 (8)	0.0003 (6)	0.0057 (6)	−0.0022 (6)
C6	0.0446 (8)	0.0357 (8)	0.0395 (8)	0.0018 (6)	−0.0007 (6)	−0.0010 (6)
C7	0.0411 (8)	0.0301 (7)	0.0368 (7)	0.0008 (6)	0.0053 (6)	0.0005 (6)
C8	0.0354 (7)	0.0314 (7)	0.0339 (7)	0.0027 (6)	0.0076 (5)	−0.0027 (5)
C9	0.0439 (8)	0.0386 (8)	0.0350 (7)	−0.0010 (6)	0.0076 (6)	0.0011 (6)
C10	0.0547 (9)	0.0361 (8)	0.0491 (9)	−0.0080 (7)	0.0136 (7)	0.0034 (6)
C11	0.0411 (8)	0.0418 (8)	0.0531 (9)	−0.0100 (7)	0.0107 (7)	−0.0105 (7)
C12	0.0348 (7)	0.0454 (8)	0.0406 (8)	0.0022 (6)	0.0046 (6)	−0.0080 (6)
C13	0.0408 (8)	0.0344 (7)	0.0362 (7)	0.0032 (6)	0.0041 (6)	0.0012 (6)
C14	0.0527 (10)	0.0672 (11)	0.0513 (10)	−0.0003 (9)	−0.0081 (8)	−0.0085 (8)

Geometric parameters (Å, º)

O1—C6	1.2140 (17)	C5—H5	0.9300
O2—H2O	0.8200	C7—H7	0.9300
O2—C9	1.3566 (17)	C7—C8	1.4476 (19)
N1—C1	1.3371 (19)	C8—C9	1.4083 (19)
N1—C5	1.3353 (18)	C8—C13	1.3969 (18)
N2—H2N	0.8600	C9—C10	1.383 (2)
N2—N3	1.3687 (16)	C10—H10	0.9300
N2—C6	1.3547 (17)	C10—C11	1.377 (2)
N3—C7	1.2720 (17)	C11—H11	0.9300
C1—H1	0.9300	C11—C12	1.387 (2)
C1—C2	1.376 (2)	C12—C13	1.384 (2)
C2—H2	0.9300	C12—C14	1.505 (2)
C2—C3	1.3878 (19)	C13—H13	0.9300
C3—C4	1.382 (2)	C14—H14A	0.9600
C3—C6	1.5011 (19)	C14—H14B	0.9600
C4—H4	0.9300	C14—H14C	0.9600
C4—C5	1.3808 (19)		
C9—O2—H2O	109.5	C8—C7—H7	120.2
C5—N1—C1	116.49 (12)	C9—C8—C7	121.54 (12)
N3—N2—H2N	122.1	C13—C8—C7	120.15 (12)
C6—N2—H2N	122.1	C13—C8—C9	118.31 (12)
C6—N2—N3	115.88 (12)	O2—C9—C8	122.64 (13)

C7—N3—N2	120.30 (12)	O2—C9—C10	118.14 (13)
N1—C1—H1	118.1	C10—C9—C8	119.21 (13)
N1—C1—C2	123.76 (13)	C9—C10—H10	119.6
C2—C1—H1	118.1	C11—C10—C9	120.72 (14)
C1—C2—H2	120.5	C11—C10—H10	119.6
C1—C2—C3	119.05 (14)	C10—C11—H11	119.1
C3—C2—H2	120.5	C10—C11—C12	121.76 (13)
C2—C3—C6	117.42 (13)	C12—C11—H11	119.1
C4—C3—C2	117.92 (13)	C11—C12—C14	120.79 (14)
C4—C3—C6	124.62 (12)	C13—C12—C11	117.23 (13)
C3—C4—H4	120.6	C13—C12—C14	121.98 (15)
C5—C4—C3	118.81 (13)	C8—C13—H13	118.6
C5—C4—H4	120.6	C12—C13—C8	122.74 (13)
N1—C5—C4	123.95 (14)	C12—C13—H13	118.6
N1—C5—H5	118.0	C12—C14—H14A	109.5
C4—C5—H5	118.0	C12—C14—H14B	109.5
O1—C6—N2	122.27 (13)	C12—C14—H14C	109.5
O1—C6—C3	121.01 (13)	H14A—C14—H14B	109.5
N2—C6—C3	116.73 (12)	H14A—C14—H14C	109.5
N3—C7—H7	120.2	H14B—C14—H14C	109.5
N3—C7—C8	119.63 (13)		

O2—C9—C10—C11	−177.73 (14)	C5—N1—C1—C2	−0.3 (2)
N1—C1—C2—C3	−0.2 (2)	C6—N2—N3—C7	−177.70 (13)
N2—N3—C7—C8	−179.03 (12)	C6—C3—C4—C5	−177.39 (13)
N3—N2—C6—O1	3.1 (2)	C7—C8—C9—O2	−0.7 (2)
N3—N2—C6—C3	−176.69 (12)	C7—C8—C9—C10	179.63 (13)
N3—C7—C8—C9	4.8 (2)	C7—C8—C13—C12	178.65 (13)
N3—C7—C8—C13	−174.87 (13)	C8—C7—N3—N2	−179.03 (12)
C1—N1—C5—C4	0.7 (2)	C8—C9—C10—C11	1.9 (2)
C1—C2—C3—C4	0.2 (2)	C9—C8—C13—C12	−1.0 (2)
C1—C2—C3—C6	177.94 (13)	C9—C10—C11—C12	−1.5 (2)
C2—C3—C4—C5	0.1 (2)	C10—C11—C12—C13	−0.2 (2)
C2—C3—C6—O1	−19.9 (2)	C10—C11—C12—C14	178.89 (15)
C2—C3—C6—N2	159.99 (13)	C11—C12—C13—C8	1.5 (2)
C3—C4—C5—N1	−0.6 (2)	C13—C8—C9—O2	178.91 (14)
C4—C3—C6—O1	157.69 (16)	C13—C8—C9—C10	−0.7 (2)
C4—C3—C6—N2	−22.5 (2)	C14—C12—C13—C8	−177.64 (14)

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the N1/C1–C5 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*O*···N3	0.82	1.87	2.5857 (16)	145
N2—H2*N*···N1^{i}	0.86	2.19	3.0232 (17)	164
C10—H10···*Cg*1^{ii}	0.93	2.85	3.5259 (17)	130

Symmetry codes: (i) *x*−1/2, −*y*+3/2, *z*−1/2; (ii) −*x*+1/2, *y*−1/2, −*z*+3/2.

(II) (*E*)-*N*′-(5-Fluoro-2-hydroxybenzylidene)isonicotinohydrazide

Crystal data

$C_{13}H_{10}FN_3O_2$
$M_r = 259.24$
Monoclinic, $P2_1/c$
$a = 8.9195$ (3) Å
$b = 10.1128$ (3) Å
$c = 13.6254$ (4) Å
$\beta = 103.481$ (1)°
$V = 1195.16$ (6) Å^3
$Z = 4$
$F(000) = 536$
$D_x = 1.441$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9934 reflections
$\theta = 3.1$–28.5°
$\mu = 0.11$ mm^{-1}
$T = 296$ K
Block, colourless
0.32 × 0.26 × 0.26 mm

Data collection

Bruker APEX2 D8 QUEST CMOS diffractometer
Radiation source: microfocus sealed x-ray tube, Incoatec Iμus
GraphiteDouble Bounce Multilayer Mirror monochromator
Detector resolution: 10.5 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
$T_{min} = 0.685$, $T_{max} = 0.746$
31833 measured reflections
2848 independent reflections
2128 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 27.9°$, $\theta_{min} = 3.1°$
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.124$
$S = 1.03$
2848 reflections
174 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0595P)^2 + 0.282P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}
Extinction correction: SHELXL2014 (Sheldrick, 2015b), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.020 (3)

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
F1	0.20524 (13)	−0.04313 (11)	0.46463 (10)	0.0868 (4)
O1	0.82356 (13)	0.59703 (11)	0.44402 (7)	0.0572 (3)
O2	0.53778 (15)	0.31773 (13)	0.30688 (8)	0.0650 (3)
H2	0.5959	0.3608	0.3508	0.097*
N1	1.11088 (14)	0.82083 (13)	0.75798 (9)	0.0497 (3)
N2	0.75299 (13)	0.47336 (11)	0.56431 (8)	0.0404 (3)

H2A	0.7633	0.4582	0.6276	0.048*
N3	0.65442 (13)	0.39828 (11)	0.49277 (8)	0.0410 (3)
C1	1.12858 (18)	0.81537 (17)	0.66408 (12)	0.0553 (4)
H1	1.2031	0.8689	0.6466	0.066*
C2	1.04204 (17)	0.73427 (16)	0.59110 (11)	0.0497 (4)
H2B	1.0577	0.7346	0.5260	0.060*
C3	0.93237 (14)	0.65288 (12)	0.61510 (9)	0.0355 (3)
C4	0.91374 (17)	0.65656 (14)	0.71277 (10)	0.0429 (3)
H4	0.8417	0.6026	0.7327	0.052*
C5	1.00507 (19)	0.74261 (15)	0.78056 (10)	0.0502 (4)
H5	0.9910	0.7455	0.8460	0.060*
C6	0.83297 (15)	0.57142 (13)	0.53241 (9)	0.0376 (3)
C7	0.57486 (15)	0.31041 (13)	0.52504 (10)	0.0413 (3)
H7	0.5825	0.3020	0.5940	0.050*
C8	0.47255 (15)	0.22351 (13)	0.45483 (10)	0.0408 (3)
C9	0.46263 (16)	0.22688 (15)	0.35051 (11)	0.0457 (3)
C10	0.37199 (18)	0.13466 (17)	0.28799 (13)	0.0569 (4)
H10	0.3694	0.1346	0.2194	0.068*
C11	0.28665 (18)	0.04408 (16)	0.32564 (14)	0.0597 (4)
H11	0.2260	−0.0174	0.2834	0.072*
C12	0.29224 (18)	0.04568 (15)	0.42667 (15)	0.0567 (4)
C13	0.38397 (17)	0.13144 (15)	0.49236 (12)	0.0499 (4)
H13	0.3870	0.1282	0.5610	0.060*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0769 (7)	0.0678 (7)	0.1118 (9)	−0.0293 (6)	0.0143 (7)	0.0139 (6)
O1	0.0767 (7)	0.0616 (7)	0.0271 (5)	−0.0163 (6)	−0.0006 (5)	−0.0004 (4)
O2	0.0697 (8)	0.0754 (8)	0.0453 (6)	−0.0252 (6)	0.0041 (5)	−0.0007 (6)
N1	0.0495 (7)	0.0494 (7)	0.0426 (7)	0.0033 (6)	−0.0048 (5)	−0.0125 (5)
N2	0.0452 (6)	0.0399 (6)	0.0297 (5)	−0.0020 (5)	−0.0040 (4)	−0.0007 (4)
N3	0.0404 (6)	0.0380 (6)	0.0379 (6)	0.0007 (5)	−0.0044 (5)	−0.0031 (5)
C1	0.0519 (9)	0.0616 (10)	0.0502 (9)	−0.0136 (8)	0.0077 (7)	−0.0123 (7)
C2	0.0530 (8)	0.0598 (9)	0.0356 (7)	−0.0099 (7)	0.0092 (6)	−0.0088 (6)
C3	0.0382 (7)	0.0351 (6)	0.0291 (6)	0.0058 (5)	−0.0007 (5)	−0.0021 (5)
C4	0.0532 (8)	0.0409 (7)	0.0324 (6)	0.0015 (6)	0.0051 (6)	−0.0022 (5)
C5	0.0662 (9)	0.0509 (8)	0.0294 (6)	0.0075 (8)	0.0026 (6)	−0.0066 (6)
C6	0.0418 (7)	0.0377 (7)	0.0285 (6)	0.0027 (6)	−0.0011 (5)	−0.0016 (5)
C7	0.0413 (7)	0.0394 (7)	0.0393 (7)	0.0042 (6)	0.0013 (6)	−0.0011 (6)
C8	0.0348 (7)	0.0358 (7)	0.0475 (7)	0.0039 (5)	0.0008 (5)	−0.0004 (6)
C9	0.0396 (7)	0.0462 (8)	0.0469 (8)	−0.0005 (6)	0.0016 (6)	−0.0020 (6)
C10	0.0514 (9)	0.0605 (10)	0.0525 (9)	−0.0037 (8)	−0.0006 (7)	−0.0119 (7)
C11	0.0464 (8)	0.0472 (9)	0.0759 (12)	−0.0042 (7)	−0.0051 (8)	−0.0132 (8)
C12	0.0435 (8)	0.0398 (8)	0.0824 (12)	−0.0038 (6)	0.0060 (8)	0.0060 (7)
C13	0.0452 (8)	0.0445 (8)	0.0572 (9)	0.0022 (6)	0.0060 (7)	0.0051 (7)

Geometric parameters (Å, º)

F1—C12	1.3651 (19)	C3—C6	1.5061 (17)
O1—C6	1.2154 (15)	C4—H4	0.9300
O2—H2	0.8200	C4—C5	1.387 (2)
O2—C9	1.3537 (18)	C5—H5	0.9300
N1—C1	1.3263 (19)	C7—H7	0.9300
N1—C5	1.322 (2)	C7—C8	1.4537 (18)
N2—H2A	0.8600	C8—C9	1.404 (2)
N2—N3	1.3783 (15)	C8—C13	1.393 (2)
N2—C6	1.3513 (17)	C9—C10	1.388 (2)
N3—C7	1.2775 (18)	C10—H10	0.9300
C1—H1	0.9300	C10—C11	1.365 (2)
C1—C2	1.378 (2)	C11—H11	0.9300
C2—H2B	0.9300	C11—C12	1.366 (2)
C2—C3	1.375 (2)	C12—C13	1.372 (2)
C3—C4	1.3796 (18)	C13—H13	0.9300
C9—O2—H2	109.5	N2—C6—C3	115.07 (11)
C5—N1—C1	116.85 (12)	N3—C7—H7	119.7
N3—N2—H2A	120.8	N3—C7—C8	120.53 (13)
C6—N2—H2A	120.8	C8—C7—H7	119.7
C6—N2—N3	118.31 (11)	C9—C8—C7	122.23 (13)
C7—N3—N2	116.98 (11)	C13—C8—C7	119.03 (13)
N1—C1—H1	118.4	C13—C8—C9	118.72 (13)
N1—C1—C2	123.25 (15)	O2—C9—C8	122.70 (13)
C2—C1—H1	118.4	O2—C9—C10	117.61 (14)
C1—C2—H2B	120.2	C10—C9—C8	119.68 (14)
C3—C2—C1	119.64 (13)	C9—C10—H10	119.5
C3—C2—H2B	120.2	C11—C10—C9	121.06 (15)
C2—C3—C4	117.76 (12)	C11—C10—H10	119.5
C2—C3—C6	118.48 (11)	C10—C11—H11	120.7
C4—C3—C6	123.65 (12)	C10—C11—C12	118.57 (14)
C3—C4—H4	120.8	C12—C11—H11	120.7
C3—C4—C5	118.37 (14)	F1—C12—C11	118.92 (15)
C5—C4—H4	120.8	F1—C12—C13	118.30 (16)
N1—C5—C4	124.13 (13)	C11—C12—C13	122.77 (15)
N1—C5—H5	117.9	C8—C13—H13	120.5
C4—C5—H5	117.9	C12—C13—C8	119.09 (15)
O1—C6—N2	123.74 (12)	C12—C13—H13	120.5
O1—C6—C3	121.15 (12)		
F1—C12—C13—C8	−179.45 (13)	C4—C3—C6—N2	−18.13 (18)
O2—C9—C10—C11	−176.72 (15)	C5—N1—C1—C2	0.6 (2)
N1—C1—C2—C3	−0.8 (3)	C6—N2—N3—C7	−176.78 (12)
N2—N3—C7—C8	−177.61 (11)	C6—C3—C4—C5	−175.40 (12)
N3—N2—C6—O1	−0.3 (2)	C7—C8—C9—O2	−5.4 (2)
N3—N2—C6—C3	177.26 (10)	C7—C8—C9—C10	174.98 (13)

N3—C7—C8—C9	3.5 (2)	C7—C8—C13—C12	−177.30 (13)
N3—C7—C8—C13	−178.08 (12)	C8—C7—N3—N2	−177.61 (11)
C1—N1—C5—C4	0.2 (2)	C8—C9—C10—C11	2.9 (2)
C1—C2—C3—C4	0.1 (2)	C9—C8—C13—C12	1.1 (2)
C1—C2—C3—C6	176.36 (13)	C9—C10—C11—C12	−0.1 (2)
C2—C3—C4—C5	0.6 (2)	C10—C11—C12—F1	178.91 (14)
C2—C3—C6—O1	−16.5 (2)	C10—C11—C12—C13	−2.3 (2)
C2—C3—C6—N2	165.85 (12)	C11—C12—C13—C8	1.7 (2)
C3—C4—C5—N1	−0.8 (2)	C13—C8—C9—O2	176.21 (13)
C4—C3—C6—O1	159.53 (14)	C13—C8—C9—C10	−3.4 (2)

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the N1/C1–C5 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···N3	0.82	1.92	2.6329 (15)	145
N2—H2*A*···N1^{i}	0.86	2.19	2.8889 (15)	138
C10—H10···O1^{ii}	0.93	2.51	3.2573 (18)	138
C11—H11···*Cg*1^{iii}	0.93	2.98	3.8917 (18)	168

Symmetry codes: (i) −*x*+2, *y*−1/2, −*z*+3/2; (ii) −*x*+1, *y*−1/2, −*z*+1/2; (iii) *x*−1, −*y*+1/2, *z*−1/2.