Crystal structures of three
N-(pyridine-2-carbonyl)pyridine-2-carboxamides as potential ligands for supramolecular chemistry

Xiaowen Xu, Richard Hoogenboom and Kristof Van Hecke

Acta Cryst. (2021). E77, 958–964

This open-access article is distributed under the terms of the Creative Commons Attribution Licence
https://creativecommons.org/licenses/by/4.0/legalcode, which permits unrestricted use, distribution, and
reproduction in any medium, provided the original authors and source are cited.
Crystal structures of three $N$-(pyridine-2-carbonyl)pyridine-2-carboxamides as potential ligands for supramolecular chemistry

Xiaowen Xu,a Richard Hoogenbooma and Kristof Van Heckeab*

aSupramolecular Chemistry Group, Centre of Macromolecular Chemistry (CMaC), Department of Organic and Macromolecular Chemistry, Ghent University, Krijgslaan 281-S4, B-9000 Ghent, Belgium, and bXStruct, Department of Chemistry, Ghent University, Krijgslaan 281-S3, B-9000 Ghent, Belgium. *Correspondence e-mail: Kristof.VanHecke@UGent.be

The synthesis and single-crystal X-ray structures of three $N$-(pyridine-2-carbonyl)pyridine-2-carboxamide imides, with or without F atoms on the 3-position of the pyridine rings are reported, namely, $N$-(pyridine-2-carbonyl)pyridine-2-carboxamide, $C_{12}H_{9}N_{3}O_{2}$ (1), $N$-(3-fluoropyridine-2-carbonyl)pyridine-2-carboxamide, $C_{12}H_{8}FN_{3}O_{2}$ (2), and 3-fluoro-$N$-(3-fluoropyridine-2-carbonyl)pyridine-2-carboxamide, $C_{12}H_{7}F_{2}N_{3}O_{2}$ (3). The above-mentioned compounds were synthesized by a mild, general procedure with an excellent yield, providing straightforward access to symmetrical and/or asymmetrical heterocyclic ureas. The crystal structures of 1 and 2 are isomorphous, showing similar packing arrangements, i.e. double layers of parallel (face-to-face) molecules alternating with analogous, but perpendicularly oriented, double layers. In contrast, the crystal structure of 3, containing a fluoro- group at the 3-position of both pyridine rings, shows molecular arrangements in a longitudinal, tubular manner along the c axis, with the aromatic pyridine and carbonyl/flourine moieties facing towards each other.

1. Chemical context

$N$-(Pyridine-2-carbonyl)pyridine-2-carboxamide systems and their derivatives have been shown to be very useful intermediates for the construction of molecular building blocks, able to self-assemble into a wide range of super-architectures taking advantage of acceptor–donor–donor–acceptor (ADDA) arrays of hydrogen-bonding sites (Corbin et al., 2001). Further interest in this family of compounds has involved the investigation of their metal coordination complexes, which possess strong luminescence characteristics (Das et al., 2018), as well as their electrochemical (Gasser et al., 2012), magnetic (Kajiwara et al., 2010) and catalytic properties (Chowdhury et al., 2007). Consequently, the synthesis of $N$-(pyridine-2-carbonyl)pyridine-2-carboxamide, containing different functional groups, at a large scale and in a high yield is of great importance in the field of supramolecular chemistry. Previously reported studies have shown the conversion of 2-aminopyridine to 1 in a single step (Gerchuk & Taits, 1950; Corbin et al., 2001). However, the utilized reaction conditions were, to some extent, harsh and the reported yield of the compound was rather low (< 32%), presumably because of the inferior nucleophilicity of the –NH$_2$ groups at the 2-position of the pyridine rings. Moreover, the use of this procedure is limited to the synthesis of symmetrical imides. The synthesis of high-yield asymmetrical imides, bearing different functional groups on the pyridine rings, is still challenging.
Herein, we report the single-crystal X-ray structural analysis of the imides N-(pyridine-2-carbonyl)pyridine-2-carboxamide (1) (R₁ = H, R₂ = H), N-(3-fluoropyridine-2-carbonyl)pyridine-2-carboxamide (2) (R₁ = F, R₂ = H) and 3-fluoro-N-(3-fluoropyridine-2-carbonyl)pyridine-2-carboxamide (3) (R₁ = F, R₂ = F), prepared via a simple, straightforward synthesis method that does not involve high pressure nor harsh conditions and can be carried out on a large scale.

2. Structural commentary

The structure of 1, although determined at a different temperature of 200 K, has previously been deposited in the CSD (refcode COJNAT; Castaneda & Gabidullin, 2019). Compound 1 crystallizes in the non-centrosymmetric orthorhombic space group Pna2₁, with the asymmetric unit consisting of one N-(pyridine-2-carbonyl)pyridine-2-carboxamide molecule. The molecular structure of 1 is found almost completely planar, with a dihedral angle of 6.1 (2)° between the best planes through the two pyridine rings (Fig. 1a).

The structure of 2 is isomorphous with 1, although the 3-fluoro-N-(pyridine-2-carbonyl)pyridine-2-carboxamide molecules are rotated 90° with respect to 1 (Fig. 2). Similarly to 1, the asymmetric unit contains one planar 3-fluoro-N-(pyridine-2-carbonyl)pyridine-2-carboxamide molecule, which shows a dihedral angle of 5.2 (2)° between the best planes through the two pyridine rings. Here, the fluoro group is found disordered over both pyridine rings, i.e. a transverse disorder by 180° rotation along the axis through the imide N—H function occurs, showing refined occupancy factors of 0.563 (8) and 0.437 (8) for the first (F₁A) and second fluoro (F₁B) site, respectively (Fig. 1b).
Compound 3 crystallizes in the centrosymmetric monoclinic space group \(P2_1/a\), with the asymmetric unit consisting of only half of a total 3-fluoro-N-(3-fluoro-pyridine-2-carbonyl)-pyridine-2-carboxamide molecule. The second half is generated by symmetry, i.e. a twofold axis runs through the N—H imide atoms. In contrast to the previous structures of 1 and 2, the molecular structure of 3 is not planar, with a dihedral angle of 29.73 (11)° between the best planes through the two pyridine rings (Fig. 1c).

### 3. Supramolecular features

Despite the presence of two pyridine rings in the molecular structure of 1, only weak \(\pi-\pi\) interactions are present in the crystal packing, with rather large centroid–centroid distances ranging from 4.969 (2) to 5.497 (2) \(\text{Å}\). However, clear \(\text{C}=\text{O} \cdots \pi\) contacts are observed in the crystal packing \([\text{C6} \cdots \text{O1} \cdots \text{Cg1}(x, y, -1 + z) = 3.861 (3) \text{Å}; \text{Cg1 is the centroid of the C1–C5/N1 ring}]\). Intramolecular potential hydrogen bonds are found between the imide N2—H2 hydrogen atom and both pyridine nitrogen atoms \([\text{N2} \cdots \text{H2} \cdots \text{N1} = 2.15 (6) \text{Å}; \text{N2} \cdots \text{H2} \cdots \text{N3} = 2.15 (5) \text{Å}]\), while non-classical intermolecular hydrogen bonds can be observed between the first pyridine rings and carbonyl O2 atoms of symmetry-equivalent molecules \([\text{C3} \cdots \text{H3} \cdots \text{O2}^i = 2.48 \text{Å}; \text{symmetry code: (i) } \frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} + z, \text{ while these first pyridine rings are further connected to each other via similar hydrogen bonds with the pyridine N1 atoms } [\text{C5} \cdots \text{H5} \cdots \text{N1}^i = 2.51 \text{Å}; \text{symmetry code: (ii) } -x, 1 - y, -\frac{1}{2} + z] \) (Table 1). As such, in the packing, double layers of parallel (face-to-face) molecules of 1 are observed, parallel with the (100) plane, alternating with analogous double layers, oriented perpendicular to the former layers (Fig. 3). For the structure of 2, analogous to 1, only weak \(\pi-\pi\) interactions are present in the crystal packing between the 3-fluoro-pyridine rings, with centroid–centroid distances in the range 4.915 (3) to 5.473 (3) \(\text{Å}\), while \(\text{C}=\text{O} \cdots \pi\) contacts are also observed in the crystal packing \([\text{C6} \cdots \text{O1} \cdots \text{Cg1}(x, y, -1 + z) = 3.865 (4) \text{Å}; \text{Cg1 is the centroid of the C1–C5/N1 ring}]\). Analogous to 1, intramolecular potential hydrogen bonds

| \(D\) | \(H\) | \(A\) | \(D\) | \(H\) | \(A\) |
|------|------|------|------|------|------|
| N2   | H2   | N1   | 0.90 (5) | 2.15 (6) | 2.614 (5) |
| N2   | H2   | N3   | 0.90 (5) | 2.15 (5) | 2.637 (4) |
| C3   | H3   | O2   | 0.95   | 2.48   | 3.343 (5) |
| C5   | H5   | N1   | 0.95   | 2.51   | 3.393 (5) |

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

![Figure 3](image-url-1)

**Figure 3**

Packing in the structure of 1, showing (a) the perpendicularly oriented molecules, viewed down the \(a\) axis and (b) the double layers of parallel-oriented (face-to-face) molecules, interchanged with analogous double layers, perpendicular to the former layers.

![Figure 4](image-url-2)

**Figure 4**

Packing in the structure of 2, showing (a) the perpendicularly oriented molecules, viewed down the \(a\) axis and (b) the double layers of parallel-oriented (face-to-face) molecules, interchanged with analogous double layers, perpendicular to the former layers. C10—H10 \(C_F\) hydrogen bonds are indicated. Hydrogen atoms and disorder of the fluorine atoms are omitted for clarity.

---

*Acta Cryst. (2021). E77*

Xu et al. • C\(_{12}\)H\(_{15}\)N\(_3\)O\(_2\), C\(_{15}\)H\(_{16}\)F\(_{12}\)N\(_3\)O\(_2\) and C\(_{15}\)H\(_{15}\)F\(_2\)N\(_3\)O\(_2\) 3 of 7
between the imide N2—H2 hydrogen atom and both pyridine nitrogen atoms are observed [N2—H2···N1 = 2.16 (6) Å; N2—H2···N3 = 2.11 (6) Å], while non-classical intermolecular hydrogen bonds occur between the first pyridine rings and carbonyl O2 atoms of symmetry-equivalent molecules [C3—H3···O2 = 2.43 Å; symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y, z$]. Additionally, C—H···F hydrogen bonds are observed with the two disordered fluorine moieties [C3—H3···F1ii = 2.40 Å; C10—H10···F1iii = 2.45 Å; symmetry code: (iii) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} - z$] (Table 2). However, in the packing, analogous to 1, alternating double layers of parallel (face-to-face) molecules of 2 are observed, parallel with the (100) plane (Fig. 4). Hence, the extra C—H···F bonds do not alter the overall architecture.

For 3, besides weak π–π interactions between the pyridine rings [centroid–centroid distances in the range 4.3776 (13)–5.9437 (13) Å], one strong π–π contact is observed between the pyridine ring and its symmetry-equivalent [Cg···Cg(1/2 - x, 1/2 - y, 1/2 - z) = 3.6334 (13) Å; Cg is the centroid of the C1–C5/ N1 ring]. Analogous to 1 and 2, intramolecular potential hydrogen bonds are observed between the imide N2—H2 hydrogen atom and the pyridine nitrogen atom [N2—H2···N1 = 2.265 (15) Å], while non-classical intermolecular hydrogen bonds between the pyridine rings and carbonyl O1 atoms of symmetry-equivalent molecules are found [C4—H4···O1i = 2.49 Å; symmetry code: (ii) $-x, -\frac{1}{2} + y, \frac{3}{2} - z$] (Table 3). Additionally, although significantly longer, other hydrogen bonds are formed between the pyridine ring and the carbonyl O1 atom [C5—H5···O1i = 2.61 Å] and C—H···F hydrogen bonds are observed with the fluorine moieties [C5—H5···F1ii = 2.66 Å; C3—H3···F1iii = 2.58 Å; symmetry codes: (iii) $-x, 1 - y, -z$]. This gives rise to a different packing assembly, i.e. the molecules are arranged in a longitudinal, tubular manner along the c-axis direction, while the aromatic pyridine and the carbonyl/fluorine moieties, face towards each other (Fig. 5).

**Table 2**

| Hydrogen-bond geometry (Å, °) for 2. |
|-------------------------------------|
| D—H···A | D—H | H···A | D···A | D—H···A |
|-------------------------------------|
| N2—H2···N1 | 0.92 (5) | 2.16 (6) | 2.614 (6) | 109 (4) |
| N2—H2···N3 | 0.92 (5) | 2.11 (6) | 2.622 (5) | 114 (5) |
| C3—H3···O1i | 0.95 | 2.43 | 3.320 (6) | 156 |
| C3—H3···F1ii | 0.95 | 2.40 | 3.049 (8) | 125 |
| C5—H5···N1i | 0.95 | 2.53 | 3.420 (6) | 156 |
| C10—H10···F1iii | 0.95 | 2.45 | 3.969 (7) | 152 |

**Table 3**

| Hydrogen-bond geometry (Å, °) for 3. |
|-------------------------------------|
| D—H···A | D—H | H···A | D···A | D—H···A |
|-------------------------------------|
| N2—H2···N1 | 0.84 (4) | 2.27 (2) | 2.671 (2) | 110 (1) |
| N2—H2···N1i | 0.84 (4) | 2.27 (2) | 2.671 (2) | 110 (1) |
| C4—H4···O1i | 0.95 | 2.49 | 3.135 (3) | 125 |
| C5—H5···O1i | 0.95 | 2.61 | 3.207 (3) | 122 |
| C3—H3···F1ii | 0.95 | 2.58 | 3.398 (5) | 145 |
| C5—H5···F1i | 0.95 | 2.66 | 3.604 (5) | 176 |

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

4. Database survey

A survey of compounds related to 1, 2 and 3, deposited with the Cambridge Structural Database (CSD 2021.1, version 5.42 updates May 2021; Groom et al., 2016) resulted in three other compounds with refcodes COJNAT, WUXQOW and ZAVVAV.

As previously mentioned, COJNAT (Castaneda & Gable, 2019) represents the same structure as 1, although determined at 200 K. When fitting the molecular structures of COJNAT and 1, an r.m.s.d. of 0.0107 Å is obtained.
The structure with refcode WUXQOW (Sahu et al., 2010) represents an analogous structure to 1, but featuring quinoline moieties instead of pyridine rings, i.e. N,N-bis(quinolin-2-ylcarbonyl)amine. Similarly to 1, the molecular structure is also found to be almost completely planar, with a dihedral angle of 1.34 (4)° between the best planes through the two quinoline moieties.

The structure with refcode ZAVVAV (Zebret et al., 2012) represents another N-(pyridine-2-carbonyl)pyridine-2-carboxamide system, in this case featuring two methoxy substituents, one on each pyridine ring, i.e. methyl 6-[[6-(methoxy carbonyl)pyridin-2-yl][carbonyl]carbamoyl]pyridine-2-carboxylate. Here, because of steric hindrance of the substituents, the planes defined by the two pyridine rings are distorted by 14.52 (11)°.

5. Synthesis and crystallization

The known compound 1 was prepared in excellent yield by the reaction between 2-pyridinecarboxyl chloride and 2-pyridinecarboxamide under mild conditions. By introducing a fluoro group at the 3-position of 2-pyridinecarboxyl chloride and/or 2-pyridinecarboxamide, the new compounds 2 and 3 could be obtained, also in excellent yield. Details for the synthesis of the precursors and the products are given below. Unless otherwise stated, all reagents were used as received.

2-Pyridinecarboxyl chloride

The preparation of 2-pyridinecarboxyl chloride was performed according to a previously reported procedure (Eller et al., 2006). Commercially available lithium 3-fluoropicolinate (1.47 g, 10 mmol) was recrystallized from a mixture of EtOH–H₂O (9:1), which was acidified with several drops of concentrated HCl (36.5%) to afford 3-fluoropropionic acid. Yield: 91%. ¹H NMR (300 MHz, DMSO-d₆) δ 8.49 (dt, J = 4.4 Hz, 1H), 7.94–7.81 (m, 1H), 7.64–7.70 (m, 1H). ¹³C NMR (101 MHz, DMSO-d₆) δ 164.35, 159.27, 145.26, 126.36, 126.16.

2-Pyridinecarboxylic acid

The preparation of 3-fluoropropionic acid was performed according to a previously reported procedure (Eller et al., 2006). Commercially available lithium 3-fluoropicolinate (1.47 g, 10 mmol) was recrystallized from a mixture of EtOH–H₂O (9:1), which was acidified with several drops of concentrated HCl (36.5%) to afford 3-fluoropropionic acid. Yield: 91%. ¹H NMR (300 MHz, DMSO-d₆) δ 8.49 (dt, J = 4.4 Hz, 1H), 7.94–7.81 (m, 1H), 7.64–7.70 (m, 1H). ¹³C NMR (101 MHz, DMSO-d₆) δ 164.35, 159.27, 145.26, 138.65, 138.27, 125.59.

3-Fluoropropionic acid (1)

2-Pyridinecarboxyl chloride (212.32 mg, 1.5 mmol) and 2-pyridinecarboxamide (170.98 mg, 1.4 mmol) were dissolved in toluene (20 ml). The resulting reaction mixture was refluxed at 383 K overnight. The solvent was removed under reduced pressure and the residue was purified by a silica column with an eluent of hexane/ethyl acetate (5/1) to afford the product. Yield: 88%. ¹H NMR (300 MHz, DMSO-d₆) δ 8.63 (d, J = 4.7 Hz, 1H), 8.11 (s, 1H), 8.06–7.94 (m, 2H), 7.64 (s, 1H), 7.63–7.55 (m, 1H).

3-Fluoropropionic acid (2)

20 ml of NH₃/methanol (NH₃ ca 7 N in methanol solution) was added slowly to 2-pyridinecarboxyl chloride at 273 K under stirring. The resulting reaction mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed under reduced pressure and the residue was purified by a silica column with an eluent of hexane/ethyl acetate (5/1) to afford the product. Yield: 85%. ¹H NMR (300 MHz, DMSO-d₆) δ 8.34 (dt, J = 4.2, 1.4 Hz, 1H), 7.63 (s, 1H), 7.54–7.40 (m, 2H), 6.30 (s, 1H). ¹³C NMR (101 MHz, DMSO-d₆) δ 164.96, 164.91, 158.20, 144.12, 144.07, 137.26, 128.42, 128.37, 126.36, 126.16.

N-(Pyridine-2-carbonyl)pyridine-2-carboxamide (3)

2-Pyridinecarboxyl chloride (212.32 mg, 1.5 mmol) and 2-pyridinecarboxamide (170.98 mg, 1.4 mmol) were dissolved in toluene (20 ml). The resulting reaction mixture was refluxed at 383 K overnight. The solvent was removed under reduced pressure and the residue was purified by a silica column with an eluent of hexane/ethyl acetate (5/1) to afford the product. Yield: 91%. ¹H NMR (300 MHz, DMSO-d₆) δ 13.03 (s, 1H), 8.75 (dd, J = 4.8, 1.7, 0.9 Hz, 2H), 8.35 (dt, J = 7.9, 1.1 Hz, 2H), 7.94 (td, J = 7.7, 1.7 Hz, 2H), 7.56 (dddd, J = 7.6, 4.8, 1.2 Hz, 2H). ¹³C NMR (101 MHz, DMSO-d₆) δ 162.65, 149.15, 148.67, 137.73, 127.50, 123.49.

N-(Pyridine-2-carbonyl)pyridine-2-carboxamide (4)

2-Pyridinecarboxyl chloride (212.32 mg, 1.5 mmol) and 2-pyridinecarboxamide (170.98 mg, 1.4 mmol) were dissolved in toluene (20 ml). The resulting reaction mixture was refluxed at 383 K overnight. The solvent was removed under reduced pressure and the residue was purified by a silica column with an eluent of hexane/ethyl acetate (5/1) to afford the product. Yield: 89%. ¹H NMR (300 MHz, DMSO-d₆) δ 12.72 (s, 1H), 8.81 (dddd, J = 4.8, 1.6, 0.9 Hz, 1H), 8.66 (dt, J = 4.5, 1.4 Hz, 1H), 8.22 (dt, J = 7.8, 1.1 Hz, 1H), 8.13 (td, J = 7.7, 1.7 Hz, 1H), 8.02 (dddd, J = 11.3, 8.5, 1.2 Hz, 1H), 7.92–7.85 (m, 1H), 7.78 (dddd, J = 7.5, 4.8, 1.3 Hz, 1H). ¹³C NMR (101 MHz, DMSO-d₆) δ 161.88, 160.91, 159.53, 159.47, 158.21, 148.97, 148.16, 144.99, 144.93, 138.66, 135.97, 135.92, 130.72, 130.67, 128.35, 127.45, 127.26, 122.94.
## Crystal data

| 1 | 2 | 3 |
|---|---|---|
| Chemical formula | C$_3$H$_7$N$_2$O$_2$ | C$_3$H$_7$FN$_2$O$_2$ | C$_3$H$_7$F$_2$N$_2$O$_2$ |
| $M_r$ | 227.22 | 245.21 | 263.21 |
| Crystal system, space group | Orthorhombic, $Pna2_1$ | Orthorhombic, $Pna2_1$ | Monoclinic, $E2/a$ |
| Temperature (K) | 100 | 100 | 100 |
| $a$, $b$, $c$ (Å) | 16.2689 (6), 12.8086 (7), 4.9983 (2) | 16.6058 (10), 12.9096 (7), 4.9153 (3) | 6.7062 (3), 14.1190 (5), 11.2074 (5) |
| $\alpha$, $\beta$, $\gamma$ (°) | 90, 90, 90 | 90, 90, 90 | 90, 97.140 (4), 90 |
| $V$ (Å$^3$) | 1041.56 (8) | 1053.71 (11) | 1052.94 (8) |
| $Z$ | 4 | 4 | 4 |
| Radiation type | Cu $K\alpha$ | Cu $K\alpha$ | Cu $K\alpha$ |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement | H atoms treated by a mixture of independent and constrained refinement | H atoms treated by a mixture of independent and constrained refinement |
| No. of reflections | 2028 | 1798 | 1083 |
| $R_{	ext{int}}$, $R_{	ext{free}}$ maximum | 0.076, 0.627 | 0.32, 0.28 | 0.32, 0.28 |
| $\Delta F_{	ext{max}}$, $\Delta F_{	ext{min}}$ (e Å$^{-3}$) | 0.060, 0.170, 1.07 | 0.055, 0.152, 1.03 | 0.055, 0.161, 1.04 |
| No. of parameters | 157 | 176 | 88 |
| No. of restrained parameters | 1 | 1 | 0 |
| Absolute structure | Flack $x$ determined using 673 | Flack $x$ determined using 450 | Flack $x$ determined using 673 |
| Absolute structure parameter | 0.32 (3) | 0.28, 0.28 | 0.28, 0.28 |

Data collection

| 1 | 2 | 3 |
|---|---|---|
| Diffractometer | SuperNova, Dual, Cu at zero, Atlas OD, 2015 | SuperNova, Dual, Cu at zero, Atlas OD, 2015 | SuperNova, Dual, Cu at zero, Atlas OD, 2015 |
| Absorption correction | Gaussian (CrysAlis PRO; Rigaku OD, 2015) | Gaussian (CrysAlis PRO; Rigaku OD, 2015) | Gaussian (CrysAlis PRO; Rigaku OD, 2015) |
| $T_{	ext{min}}$, $T_{	ext{max}}$ | 0.187, 0.563 | 0.098, 0.995 | 0.093, 0.996 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 8626, 2028, 1831 | 5774, 1798, 1567 | 5200, 1083, 856 |
| $R_{	ext{int}}$, $R_{	ext{free}}$ maximum | 0.076, 0.627 | 0.32, 0.28 | 0.32, 0.28 |

## Refinement

| 1 | 2 | 3 |
|---|---|---|
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.060, 0.170, 1.07 | 0.055, 0.152, 1.03 | 0.055, 0.161, 1.04 |
| No. of reflections | 2028 | 1798 | 1083 |
| No. of parameters | 157 | 176 | 88 |
| No. of restrained parameters | 1 | 1 | 0 |
| $\Delta F_{	ext{max}}$, $\Delta F_{	ext{min}}$ (e Å$^{-3}$) | 0.32, 0.30 | 0.28, 0.28 | 0.29, 0.32 |
| Absolute structure | Flack $x$ determined using 673 | Flack $x$ determined using 450 | Flack $x$ determined using 673 |
| Absolute structure parameter | 0.060, 0.170, 1.07 | 0.055, 0.152, 1.03 | 0.055, 0.161, 1.04 |

Computer programs: CrysAlis PRO (Rigaku OD, 2015), SHELXS (Sheldrick, 2008), SHELXL (Sheldrick, 2015) and OLEX2 (Dolomanov et al., 2009).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. For all structures, the imide N−H hydrogen atoms could be located from a difference electron-density Fourier map, and were further refined with isotropic temperature factors fixed at 1.2 times $U_{eq}$ of the parent atoms.

For the structure of 2, the 3-fluoropyridine atom is disordered at both pyridine sites, showing final occupancy factors of 0.563 (8) and 0.437 (8), for the first and second site, respectively.

### Funding information

Funding for this research was provided by: Fonds Wetenschappelijk Onderzoek (grant No. AUGE/11/029); Bijzonder Onderzoeksfonds UGent (grant No. 01N03217); China Scholarship Council (scholarship No. 201506780014).

### References

Aluri, B. R., Niaz, B., Kindermann, M. K., Jones, P. G. & Heinicke, J. (2011). *Dalton Trans.* **40**, 211–224.

Cai, S., Chen, C., Shao, P. & Xi, C. (2014). *Org. Lett.* **16**, 3142–3145.

Castaneda, R. & Gabidullin, B. (2019). CSD Communication (CCDC 1945074). CCDC, Cambridge, England.

Chowdhury, H., Rahman, S. H., Ghosh, R., Sarkar, S. K., Fun, H.-K. & Ghosh, B. K. (2007). *J. Mol. Struct.* **826**, 170–176.

Corbin, P. S., Zimmerman, S. C., Thiessen, P. A., Hawryluk, N. A. & Murray, T. J. (2001). *J. Am. Chem. Soc.* **123**, 10475–10488.

Das, K., Dolai, S., Voitkeich, P. & Manna, S. C. (2018). *Polyhedron*. **149**, 7–16.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Eller, G. A., Wimmer, V., Haring, A. W. & Holzer, W. (2006). *Synthesis*, pp. 4219–4229.

Gasser, G., Mari, C., Burkart, M., Green, S. J., Ribas, J., Stoeckli-Evans, H. & Tucker, J. H. R. (2012). *New J. Chem.* **36**, 1819–1827.

Gerchuk, M. & Taits, S. (1950). *Zh. Obshch. Khim.* **20**, 910–916.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.

Kajiwara, T., Tanaka, H., Nakano, M., Takaishi, S., Nakazawa, Y. & Yamashita, M. (2010). *Inorg. Chem.* **49**, 8358–8370.

Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* **B69**, 249–259.

Rigaku OD (2015). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.

Sahu, R., Padhi, S. K., Jena, H. S. & Manivannan, V. (2010). *Inorg. Chim. Acta*, **363**, 1448–1454.

Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.

Zebret, S., Dupont, N., Besnard, C., Bernardinelli, G. & Hamacek, J. (2012). *Dalton Trans.* **41**, 4817–4823.
Crystal structures of three \(N\)-(pyridine-2-carbonyl)pyridine-2-carboxamides as potential ligands for supramolecular chemistry

Xiaowen Xu, Richard Hoogenboom and Kristof Van Hecke

Computing details
For all structures, data collection: CrysAlis PRO (Rigaku OD, 2015); cell refinement: CrysAlis PRO (Rigaku OD, 2015); data reduction: CrysAlis PRO (Rigaku OD, 2015); program(s) used to solve structure: SHELXS (Sheldrick, 2008); program(s) used to refine structure: SHELXL (Sheldrick, 2015); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

\(N\)-(Pyridine-2-carbonyl)pyridine-2-carboxamide (1)

Crystal data

\begin{align*}
\text{C}_{12}\text{H}_{9}\text{N}_{3}\text{O}_{2} & \quad D_x = 1.449 \text{Mg m}^{-3} \\
M_r = 227.22 & \quad \text{Cu K\textalpha radiation, } \lambda = 1.54184 \text{ Å} \\
\text{Orthorhombic, } Pna2_1 & \quad \text{Cell parameters from 4719 reflections} \\
a = 16.2689 (6) \text{ Å} & \quad \theta = 4.2–74.0^\circ \\
b = 12.8086 (7) \text{ Å} & \quad \mu = 0.85 \text{ mm}^{-1} \\
c = 4.9983 (2) \text{ Å} & \quad T = 100 \text{ K} \\
V = 1041.56 (8) \text{ Å}^3 & \quad \text{Block, clear colourless} \\
Z = 4 & \quad 0.20 \times 0.12 \times 0.06 \text{ mm} \\
F(000) = 472 & \quad \text{Data collection}
\end{align*}

| SuperNova, Dual, Cu at zero, Atlas diffractometer | \(T_{\text{min}} = 0.187, T_{\text{max}} = 0.563\) |
| Radiation source: micro-focus sealed X-ray tube, SuperNova (Cu) X-ray Source | 8626 measured reflections |
| Mirror monochromator | 2028 independent reflections |
| Detector resolution: 10.4839 pixels mm\(^{-1}\) | 1831 reflections with \(I > 2\sigma(I)\) |
| \(\omega\) scans | \(R_{\text{int}} = 0.076\) |
| (CrysAlisPro; Rigaku OD, 2015) | \(\theta_{\text{max}} = 75.3^\circ, \theta_{\text{min}} = 4.4^\circ\) |
|  | \(h = -14\rightarrow 20\) |
|  | \(k = -15\rightarrow 15\) |
|  | \(l = -5\rightarrow 6\) |

Refinement

Refinement on \(F^2\)

| Least-squares matrix: full | Primary atom site location: structure-invariant direct methods |
| \(R[F^2 > 2\sigma(F^2)] = 0.060\) | Hydrogen site location: mixed |
| \(wR(F^2) = 0.170\) | \(H\) atoms treated by a mixture of independent and constrained refinement |
| \(S = 1.07\) | \(w = 1/[\sigma^2(F^2) + (0.1236P)^2 + 0.0215P]\) |
| 2028 reflections | where \(P = (F^2 + 2F^2)/3\) |
| 157 parameters | \((\Delta/d)_{\text{max}} < 0.001\) |
| 1 restraint | \(\Delta \rho_{\text{max}} = 0.32 \text{ e Å}^{-3}\) |
Δρ_{min} = −0.30 e Å^{-3}  

Absolute structure: Flack x determined using 673 quotients \(|I'|-|I'\|)/(|I'|+|I'|)\) (Parsons et al., 2013)  

Absolute structure parameter: 0.0 (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  | 0.29400 (14)  | 0.3937 (2)    | 0.2999 (6)    | 0.0362  | 0.0362 |
| O2  | 0.22855 (16)  | 0.2512 (2)    | 0.7000 (6)    | 0.0343  | 0.0343 |
| N1  | 0.10762 (18)  | 0.4562 (3)    | −0.0277 (7)   | 0.0301  | 0.0301 |
| N2  | 0.16131 (17)  | 0.3339 (2)    | 0.3528 (7)    | 0.0299  | 0.0299 |
| N3  | 0.01890 (19)  | 0.2587 (3)    | 0.5153 (7)    | 0.0335  | 0.0335 |
| C1  | 0.1883 (2)    | 0.4642 (3)    | 0.0217 (8)    | 0.0288  | 0.0288 |
| C2  | 0.2393 (2)    | 0.5328 (3)    | −0.1112 (8)   | 0.0322  | 0.0322 |
| H2A | 0.296091      | 0.536900      | −0.068626     | 0.039*  |        |
| C3  | 0.2060 (2)    | 0.5956 (3)    | −0.3071 (9)   | 0.0372  | 0.0372 |
| H3  | 0.239464      | 0.643907      | −0.401515     | 0.045*  |        |
| C4  | 0.1232 (2)    | 0.5872 (3)    | −0.3640 (9)   | 0.0372  | 0.0372 |
| H4  | 0.098806      | 0.628601      | −0.500275     | 0.045*  |        |
| C5  | 0.0767 (2)    | 0.5170 (3)    | −0.2176 (8)   | 0.0344  | 0.0344 |
| H5  | 0.019566      | 0.512061      | −0.255151     | 0.041*  |        |
| C6  | 0.2213 (2)    | 0.3943 (3)    | 0.2372 (8)    | 0.0279  | 0.0279 |
| C7  | 0.1662 (2)    | 0.2696 (3)    | 0.5753 (8)    | 0.0284  | 0.0284 |
| C8  | 0.0840 (2)    | 0.2245 (3)    | 0.6517 (8)    | 0.0290  | 0.0290 |
| C9  | −0.0551 (2)   | 0.2220 (3)    | 0.5853 (10)   | 0.0361  | 0.0361 |
| H9  | −0.101987     | 0.245492      | 0.489110      | 0.043*  |        |
| C10 | −0.0664 (2)   | 0.1513 (3)    | 0.7923 (9)    | 0.0371  | 0.0371 |
| H10 | −0.119977     | 0.127904      | 0.838484      | 0.045*  |        |
| C11 | 0.0010 (3)    | 0.1157 (4)    | 0.9290 (9)    | 0.0410  | 0.0410 |
| H11 | −0.004963     | 0.066767      | 1.070577      | 0.049*  |        |
| C12 | 0.0785 (2)    | 0.1526 (3)    | 0.8565 (9)    | 0.0368  | 0.0368 |
| H12 | 0.126414      | 0.128826      | 0.946242      | 0.044*  |        |
| H2  | 0.110 (3)     | 0.341 (4)     | 0.286 (12)    | 0.044*  |        |

Atomic displacement parameters (Å²)

|     | U^11          | U^22          | U^33          | U^12          | U^13          | U^23          |
|-----|---------------|---------------|---------------|---------------|---------------|---------------|
| O1  | 0.0224 (11)   | 0.0457 (15)   | 0.0404 (17)   | 0.0004 (11)   | −0.0002 (11)  | 0.0017 (13)   |
| O2  | 0.0291 (12)   | 0.0387 (14)   | 0.0352 (15)   | 0.0032 (10)   | −0.0065 (10)  | 0.0041 (12)   |
| N1  | 0.0235 (13)   | 0.0340 (15)   | 0.0328 (17)   | 0.0006 (11)   | −0.0019 (12)  | −0.0011 (13)  |
| N2  | 0.0235 (13)   | 0.0350 (15)   | 0.0312 (17)   | 0.0004 (11)   | −0.0032 (12)  | 0.0022 (13)   |
| N3  | 0.0286 (14)   | 0.0353 (16)   | 0.0365 (19)   | −0.0011 (11)  | 0.0011 (13)   | 0.0023 (15)   |

Acta Cryst. (2021). E77, 958-964
|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| C1 | 0.0270 (15) | 0.0290 (16) | 0.0302 (19) | 0.0025 (13) | 0.0024 (14) | −0.0040 (14) |
| C2 | 0.0270 (16) | 0.0333 (18) | 0.036 (2) | −0.0007 (13) | 0.0064 (15) | −0.0024 (16) |
| C3 | 0.0379 (19) | 0.0334 (18) | 0.040 (2) | 0.0007 (15) | 0.0100 (17) | 0.0029 (17) |
| C4 | 0.0424 (19) | 0.0361 (18) | 0.033 (2) | 0.0081 (17) | 0.0016 (17) | −0.0015 (16) |
| C5 | 0.0308 (16) | 0.0393 (18) | 0.033 (2) | 0.0036 (15) | 0.0007 (16) | −0.0005 (17) |
| C6 | 0.0214 (15) | 0.0318 (17) | 0.0304 (19) | 0.0016 (12) | −0.0011 (13) | −0.0024 (15) |
| C7 | 0.0303 (16) | 0.0281 (16) | 0.0269 (18) | 0.0034 (13) | −0.0011 (14) | 0.0002 (14) |
| C8 | 0.0283 (16) | 0.0296 (17) | 0.0292 (19) | 0.0010 (13) | −0.0011 (13) | −0.0032 (15) |
| C9 | 0.0262 (16) | 0.0390 (19) | 0.043 (2) | −0.0019 (15) | 0.0023 (16) | 0.0022 (16) |
| C10 | 0.0350 (17) | 0.0367 (18) | 0.040 (2) | −0.0063 (15) | 0.0072 (16) | −0.0006 (17) |
| C11 | 0.043 (2) | 0.041 (2) | 0.038 (3) | −0.0062 (16) | 0.0010 (18) | 0.0060 (18) |
| C12 | 0.0346 (17) | 0.041 (2) | 0.035 (2) | −0.0004 (15) | −0.0030 (15) | 0.0069 (17) |

**Geometric parameters (Å, °)**

| Bond | Length (Å) | Bond | Length (Å) | Bond | Length (Å) | Bond | Length (Å) |
|---|---|---|---|---|---|---|---|
| O1—C6 | 1.224 (4) | C3—C4 | 1.380 (6) | O1—C6—C1 | 122.3 (3) |
| O2—C7 | 1.214 (4) | C4—H4 | 0.9500 | O2—C7—C8 | 122.5 (3) |
| N1—C1 | 1.339 (4) | C4—C5 | 1.385 (6) | N2—C7 | 1.385 (6) |
| N1—C5 | 1.327 (5) | C5—H5 | 0.9500 | N3—C8 | 1.387 (6) |
| N2—C6 | 1.373 (5) | C7—C8 | 1.506 (5) | N4—C9 | 1.370 (6) |
| N2—C7 | 1.385 (5) | C8—C12 | 1.380 (6) | N5—C10 | 0.9500 |
| N2—H2 | 0.90 (5) | C9—C10 | 1.387 (6) | N6—C11 | 0.9500 |
| N3—C8 | 1.333 (5) | C10—H10 | 0.9500 | N7—C12 | 1.394 (6) |
| N3—C9 | 1.339 (5) | C10—C11 | 1.370 (6) | N8—C12 | 0.9500 |
| C1—C2 | 1.379 (5) | C11—C12 | 1.394 (6) |  |
| C1—C6 | 1.499 (5) |  |  |  |
| C2—H2A | 0.9500 |  |  |  |
| C2—C3 | 1.378 (6) |  |  |  |
| C3—H3 | 0.9500 |  |  |  |
|  |  |  |  |  |  |  |
| C5—N1—C1 | 117.3 (3) | O1—C6—C1 | 122.3 (3) |  |
| C6—N2—C7 | 129.2 (3) | N2—C6—C1 | 112.6 (3) |  |
| C6—N2—H2 | 116.3 (3) | O2—C7—N2 | 125.1 (3) |  |
| C7—N2—H2 | 114 (3) | O2—C7—C8 | 122.5 (3) |  |
| C8—N3—C9 | 117.8 (4) | N2—C7—C8 | 112.4 (3) |  |
| N1—C1—C2 | 123.3 (4) | N3—C8—C7 | 116.7 (3) |  |
| N1—C1—C6 | 115.9 (3) | N3—C8—C12 | 123.1 (4) |  |
| C2—C1—C6 | 120.7 (3) | C12—C8—C7 | 120.1 (3) |  |
| C1—C2—H2A | 120.7 | N3—C9—H9 | 118.6 |  |
| C3—C2—C1 | 118.6 (3) | N3—C9—C10 | 122.9 (4) |  |
| C3—C2—H2A | 120.7 | C10—C9—H9 | 118.6 |  |
| C2—C3—H3 | 120.5 | C9—C10—H10 | 120.5 |  |
| C2—C3—C4 | 119.0 (4) | C11—C10—C9 | 118.9 (4) |  |
| C4—C3—H3 | 120.5 | C11—C10—H10 | 120.5 |  |
| C3—C4—H4 | 120.8 | C10—C11—H11 | 120.6 |  |
| C3—C4—C5 | 118.3 (4) | C10—C11—C12 | 118.7 (4) |  |
| C5—C4—H4 | 120.8 | C12—C11—H11 | 120.6 |  |
| N1—C5—C4 | 123.5 (4) | C8—C12—C11 | 118.6 (4) |  |
N1—C5—H5 118.3  C8—C12—H12 120.7
C4—C5—H5 118.3  C11—C12—H12 120.7
O1—C6—N2 125.1 (3)

O2—C7—C8—N3 173.6 (4)  C3—C4—C5—N1 −1.0 (6)
O2—C7—C8—C12 −5.5 (5)  C5—N1—C1—C2 1.0 (6)
N1—C1—C2—C3 −0.8 (6)  C5—N1—C1—C6 −179.9 (3)
N1—C1—C2—C3 179.4 (4)  C6—N2—C7—O2 −4.7 (6)
N1—C1—C6—N2 −1.1 (5)  C6—N2—C7—C8 174.7 (3)
N1—C1—C6—N2 175.2 (4)  C7—N2—C6—O1 7.6 (6)
N1—C1—C6—O1 −5.8 (5)  C7—N2—C6—C1 −171.9 (3)
N3—C9—C10—C11 −1.1 (7)  C7—C8—C12—C11 177.4 (4)
N3—C9—C10—C11 −1.1 (7)  C8—N3—C9—C10 0.3 (6)
C1—N1—C5—C4 −0.1 (6)  C9—N3—C8—C7 −178.0 (3)
C1—N1—C5—C4 178.0 (3)  C9—N3—C8—C12 1.0 (6)
C2—C1—C6—O1 −1.5 (5)  C9—C10—C11—C12 0.5 (7)
C2—C1—C6—N2 178.0 (3)  C10—C11—C12—C8 0.7 (7)
C2—C3—C4—C5 1.1 (6)  C10—C11—C12—C8 0.7 (7)

Hydrogen-bond geometry (Å, °)

| D—H···A          | D—H   | H···A  | D···A | D—H···A |
|------------------|--------|--------|-------|---------|
| N2—H2···N1       | 0.90 (5) | 2.15 (6) | 2.614 (5) | 111 (4) |
| N2—H2···N3       | 0.90 (5) | 2.15 (5) | 2.637 (4) | 113 (5) |
| C3—H3···O2i      | 0.95   | 2.48   | 3.343 (5) | 152     |
| C5—H5···N1ii     | 0.95   | 2.51   | 3.393 (5) | 154     |

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

N-(3-Fluoropyridine-2-carbonyl)pyridine-2-carboxamide (2)

Crystal data

C12H8FN3O2  
Mr = 245.21
Ortorthombic, Pnai21  
Cell parameters from 2360 reflections
a = 16.6058 (10) Å  
b = 12.9096 (7) Å  
c = 4.9153 (3) Å  
V = 1053.71 (11) Å³  
Z = 4
F(000) = 504

Data collection

SuperNova, Dual, Cu at zero, Atlas diffractometer
Cu Kα radiation, λ = 1.54184 Å
θ = 3.4–74.8°  
µ = 1.03 mm⁻¹  
T = 100 K
Block, clear colourless
0.26 × 0.10 × 0.05 mm

5774 measured reflections
1798 independent reflections
1567 reflections with I > 2σ(I)

θmax = 75.9°, θmin = 5.3°  
l = −19→20  
k = −15→16  
l = −6→5
Refinement

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.055$

$wR(F^2) = 0.152$

$S = 1.03$

1798 reflections

176 parameters

1 restraint

Primary atom site location: structure-invariant direct methods

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0898P)^2 + 0.4172P]$ where $P = (F_o^2 + 2F_c^2)/3$

$\Delta/\sigma_{\text{max}} < 0.001$

$\Delta \rho_{\text{max}} = 0.28$ e Å$^{-3}$

$\Delta \rho_{\text{min}} = -0.28$ e Å$^{-3}$

Absolute structure: Flack $x$ determined using 450 quotients $[(I)+(I)]/[(I)-(I)]$ (Parsons et al., 2013)

Absolute structure parameter: 0.2 (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 ($\AA^2$)

|          | x          | y          | z          | $U_{eq}/U_{eq}$ | Occ. (<1) |
|----------|------------|------------|------------|----------------|-----------|
| O2       | 0.27904 (19) | 0.7427 (2) | 0.1952 (8) | 0.0338 (8)     |           |
| O1       | 0.21184 (17) | 0.8809 (3) | 0.5995 (8) | 0.0359 (8)     |           |
| N3       | 0.4847 (2)   | 0.7588 (3) | 0.3876 (9) | 0.0309 (9)     |           |
| N2       | 0.3438 (2)   | 0.8296 (3) | 0.5407 (9) | 0.0271 (8)     |           |
| N1       | 0.3932 (2)   | 0.9540 (3) | 0.9257 (8) | 0.0269 (8)     |           |
| C12      | 0.4327 (3)   | 0.6517 (4) | 0.0372 (11)| 0.0407 (12)    |           |
| H12      | 0.387317     | 0.626086   | −0.059309  | 0.049*         | 0.563 (8) |
| C8       | 0.4221 (3)   | 0.7223 (3) | 0.2426 (10)| 0.0267 (9)     |           |
| C9       | 0.5586 (3)   | 0.7247 (3) | 0.3242 (12)| 0.0358 (11)    |           |
| H9       | 0.603043     | 0.749297   | 0.427390   | 0.043*         |           |
| C10      | 0.5730 (3)   | 0.6555 (4) | 0.1156 (11)| 0.0393 (11)    |           |
| H10      | 0.626396     | 0.634525   | 0.073279   | 0.047*         |           |
| C11      | 0.5087 (3)   | 0.6176 (4) | −0.0299 (12)| 0.0433 (13)    |           |
| H11      | 0.516473     | 0.569153   | −0.172922  | 0.052*         |           |
| C7       | 0.3403 (2)   | 0.7643 (3) | 0.3213 (10)| 0.0270 (9)     |           |
| C6       | 0.2827 (2)   | 0.8864 (3) | 0.6609 (9) | 0.0257 (9)     |           |
| C1       | 0.3139 (2)   | 0.9587 (3) | 0.8767 (10)| 0.0247 (9)     |           |
| C2       | 0.2642 (3)   | 1.0262 (3) | 1.0150 (10)| 0.0300 (10)    |           |
| H2A      | 0.208315     | 1.028822   | 0.973723   | 0.036*         | 0.437 (8) |
| C3       | 0.2959 (3)   | 1.0902 (3) | 1.2140 (12)| 0.0351 (11)    |           |
| H3       | 0.262391     | 1.137086   | 1.310847   | 0.042*         |           |
| C4       | 0.3766 (3)   | 1.0842 (3) | 1.2677 (11)| 0.0341 (10)    |           |
| H4       | 0.400053     | 1.126025   | 1.405499   | 0.041*         |           |
| C5       | 0.4234 (3)   | 1.0164 (3) | 1.1188 (10)| 0.0302 (9)     |           |
| H5       | 0.476909     | 1.013741   | 1.154679   | 0.036*         |           |
| F1B      | 0.3801 (4)   | 0.6170 (5) | −0.1240 (16)| 0.046 (2)      | 0.437 (8) |
| F1A      | 0.1855 (3)   | 1.0352 (3) | 0.9733 (12)| 0.0368 (16)    | 0.563 (8) |
| H2       | 0.395 (3)    | 0.837 (4)  | 0.611 (14) | 0.044*         |           |
### Atomic displacement parameters (Å²)

|   | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$    | $U^{13}$    | $U^{23}$    |
|---|-------------|-------------|-------------|-------------|-------------|-------------|
| O2 | 0.0306 (15) | 0.0302 (14) | 0.0407 (19) | −0.0041 (12)| −0.0077 (16)| −0.0028 (15) |
| O1 | 0.0223 (15) | 0.0426 (17) | 0.043 (2)   | −0.0018 (12)| −0.0037 (15)| 0.0012 (16)  |
| N3 | 0.0279 (18) | 0.0288 (17) | 0.036 (2)   | −0.0004 (13)| −0.0008 (17)| −0.0003 (17)|
| N2 | 0.0239 (17) | 0.0283 (17) | 0.029 (2)   | −0.0004 (13)| −0.0022 (15)| −0.0039 (15) |
| N1 | 0.0249 (17) | 0.0281 (16) | 0.028 (2)   | −0.0030 (13)| −0.0019 (15)| −0.0021 (15)|
| C12| 0.055 (3)   | 0.034 (2)   | 0.033 (3)   | 0.006 (2)   | −0.009 (3)  | −0.003 (2)   |
| C8 | 0.029 (2)   | 0.0221 (16) | 0.029 (2)   | −0.0005 (14)| −0.0027 (18)| 0.0019 (17)  |
| C9 | 0.033 (2)   | 0.028 (2)   | 0.047 (3)   | 0.0006 (17)| 0.003 (2)   | −0.001 (2)   |
| C10| 0.045 (2)   | 0.030 (2)   | 0.043 (3)   | 0.0102 (19)| 0.012 (2)   | 0.005 (2)    |
| C11| 0.061 (3)   | 0.036 (2)   | 0.033 (3)   | 0.010 (2)   | 0.004 (3)   | −0.004 (2)   |
| C7 | 0.031 (2)   | 0.0227 (18) | 0.027 (2)   | −0.0036 (15)| −0.003 (2)  | 0.0033 (17)  |
| C6 | 0.0198 (18) | 0.0282 (18) | 0.029 (3)   | −0.0029 (15)| −0.0016 (17)| 0.0038 (19)  |
| C1 | 0.0218 (18) | 0.0222 (16) | 0.030 (2)   | −0.0014 (14)| −0.0005 (19)| 0.0011 (16)  |
| C2 | 0.028 (2)   | 0.0232 (18) | 0.039 (3)   | 0.0010 (15)| 0.006 (2)   | 0.0045 (19)  |
| C3 | 0.043 (3)   | 0.0250 (19) | 0.037 (3)   | −0.0003 (17)| 0.009 (2)   | −0.003 (2)   |
| C4 | 0.044 (3)   | 0.0276 (19) | 0.030 (2)   | −0.0053 (18)| 0.005 (2)   | −0.002 (2)   |
| C5 | 0.030 (2)   | 0.0301 (19) | 0.031 (2)   | −0.0040 (16)| −0.001 (2)  | −0.002 (2)   |
| F1B| 0.036 (4)   | 0.053 (4)   | 0.050 (5)   | −0.002 (3)  | −0.012 (3)  | −0.025 (4)   |
| F1A| 0.020 (2)   | 0.028 (2)   | 0.062 (4)   | 0.0007 (16)| 0.002 (2)   | 0.001 (2)    |

### Geometric parameters (Å, °)

|   | C9—C10  | C10—H10  | C10—C11  | C11—H11  | C11—C6   | C6—C1    | C6—C1   | C1—C2   | C2—C3   | C3—C4   | C4—C5   | C5—H5   | C1—C5   | C5—H5   | C1—C5   | C5—H5   | C1—C5   | C5—H5   |
|---|---------|----------|----------|----------|----------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| C2—C12 | 1.224 (5) | 1.217 (5) | 1.346 (6) | 1.340 (6) | 1.370 (6) | 1.384 (6) | 0.92 (6) | 1.342 (6) | 1.342 (6) | 1.372 (7) | 1.376 (7) | 1.262 (8) | 1.511 (6) | 0.9500  | 1.381 (7) | 1.384 (7) | 1.380 (6) | 1.272 (6) | 0.9500  |
| C8—C7  | 1.118 (4) | 0.829 (4) | 0.829 (2) | 0.090 (2) | 0.080 (2) | 0.110 (2) | 0.120 (2) | 0.110 (2) | 0.120 (2) | 0.110 (2) | 0.120 (2) | 0.110 (2) | 0.120 (2) | 0.110 (2) | 0.120 (2) | 0.110 (2) | 0.120 (2) | 0.110 (2) | 0.120 (2) |

Acta Cryst. (2021). E77, 958-964

sup-6
C11—C12—H12 119.8  C2—C1—C6  122.2 (4)
F1B—C12—C8  127.5 (6)  C1—C2—H2A  120.1
F1B—C12—C11 111.7 (6)  C1—C2—C3  119.8 (4)
N3—C8—C12  121.5 (4)  C3—C2—H2A  120.1
N3—C8—C7  115.7 (4)  F1A—C2—C1  124.6 (5)
C12—C8—C7  122.8 (4)  F1A—C2—C3  115.6 (4)
N3—C9—H9  118.5  C1—C2—H2A  120.1
N3—C9—C10  122.9 (5)  C4—C3—C2  118.4 (4)
C10—C9—H9  118.5  C4—C3—H3  120.8
C9—C10—H10 120.6  C3—C4—H4  120.5
C11—C10—H10 120.6  C5—C4—H4  120.5
C12—C11—H11 120.9  C3—C4—C5  119.0 (4)
C10—C11—C12 118.3 (5)  N1—C5—C4  123.0 (4)
C10—C11—H11 120.9  N1—C5—H5  118.5
C12—C7—N2  125.0 (4)  C4—C5—H5  118.5
O2—C7—N2  125.0 (4)  C11—C12—C8—C7 178.6 (4)
O1—C6—C1—C2 127.5 (6)  C7—N2—C6—O1  6.0 (7)
O1—C6—C1—C2 127.5 (6)  C7—N2—C6—C1  −172.9 (4)
N2—C6—C1—C2 127.5 (6)  C6—N2—C7—O2  −2.1 (7)
N3—C8—C7—O2  175.2 (4)  C6—N2—C7—C8  176.3 (4)
N3—C8—C7—N2 175.2 (4)  C6—N2—C7—O2  176.3 (4)
N3—C9—C10—C11 175.2 (4)  C6—C1—C2—C3  179.2 (4)
N2—C6—C1—C2 175.2 (4)  C6—C1—C2—F1A  −0.4 (7)
N2—C6—C1—C2 175.2 (4)  C6—C1—C2—F1A  −0.4 (7)
N1—C1—C2—C3 −1.2 (7)  C1—N1—C5—C4  0.2 (6)
N1—C1—C2—F1A 179.2 (4)  C1—N1—C5—C4  0.2 (6)
C12—C8—C7—O2 179.2 (4)  C1—N1—C5—C4  0.2 (6)
C12—C8—C7—N2 −1.2 (7)  C2—C3—C4—C5  1.2 (7)
C8—N3—C9—C10 −1.2 (7)  C3—C4—C5—N1 −1.3 (7)
C8—C12—C11—C10 −1.2 (7)  C5—N1—C1—C6 −179.3 (4)
C9—N3—C8—C12 −1.2 (7)  C5—N1—C1—C6 −179.3 (4)
C9—N3—C8—C12 −1.2 (7)  C5—N1—C1—C6 −179.3 (4)
C9—C10—C11—C12 −1.2 (7)  C1—N1—C5—C4  0.2 (6)
C11—C12—C8—N3 −1.2 (7)  C1—N1—C5—C4  0.2 (6)

### Hydrogen-bond geometry (Å, °)

| D—H···A       | D—H   | H···A | D···A  | D—H···A |
|---------------|--------|-------|--------|---------|
| N2—H2···N1    | 0.92 (5)| 2.16 (6)| 2.614 (6)| 109 (4) |
| N2—H2···N3    | 0.92 (5)| 2.11 (6)| 2.622 (5)| 114 (5) |
| C3—H3···O2²   | 0.95   | 2.43  | 3.320 (6)| 156     |
| C3—H3···F1B³  | 0.95   | 2.40  | 3.049 (8)| 125     |
| C5—H5···N1⁴   | 0.95   | 2.53  | 3.420 (6)| 156     |
| C10—H10···F1A⁵| 0.95   | 2.45  | 3.169 (7)| 132     |

Symmetry codes: (i) −x+1/2, y+1/2, z+3/2; (ii) −x+1, −y+2, z+1/2; (iii)x+1/2, −y+3/2, z−1.
3-Fluoro-N-(3-fluoropyridine-2-carbonyl)pyridine-2-carboxamide (3)

Crystal data

C_{12}H_{7}F_{2}N_{3}O_{2}  

\( F(000) = 536 \)

\( M_r = 263.21 \)

Monoclinic, \( \text{I}\2/a \)

\( a = 6.7062 (3) \) Å

\( b = 14.1190 (5) \) Å

\( c = 11.2074 (5) \) Å

\( \beta = 97.140 (4)^\circ \)

\( V = 1052.94 (8) \) Å\(^3\)

\( Z = 4 \)

\( F(000) = 536 \)

\( D_r = 1.660 \text{ Mg m}^{-3} \)

Cell parameters from 1899 reflections

\( \theta = 5.0\text{–}74.9^\circ \)

\( \mu = 1.22 \text{ mm}^{-1} \)

\( T = 100 \text{ K} \)

Block, clear colourless

\( 0.11 \times 0.09 \times 0.06 \) mm

Data collection

SuperNova, Dual, Cu at zero, Atlas diffractometer

Radiation source: micro-focus sealed X-ray tube, SuperNova (Cu) X-ray Source

Mirror monochromator

Detector resolution: 10.4839 pixels mm\(^{-1}\)

\( \omega \) scans

Absorption correction: gaussian

(CrysAlisPro; Rigaku OD, 2015)

\( T_{\text{min}} = 0.993, T_{\text{max}} = 0.996 \)

5200 measured reflections

856 reflections with \( I > 2\sigma(I) \)

Refinement

Refinement on \( F^2 \)

Least-squares matrix: full

\( R[F^2 > 2\sigma(F^2)] = 0.055 \)

\( wR(F^2) = 0.161 \)

\( S = 1.04 \)

1083 reflections

88 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Hydrogen site location: mixed

\( H \) atoms treated by a mixture of independent and constrained refinement

\( w = 1/[\sigma^2(F_o^2) + (0.0954P)^2 + 0.7955P] \)

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

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

\( \Delta \rho_{\text{max}} = 0.29 \text{ e Å}^{-3} \)

\( \Delta \rho_{\text{min}} = -0.32 \text{ e Å}^{-3} \)

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.

Fractions atom coordinates and isotropic or equivalent isotropic displacement parameters (Å\(^2\))

|   | \( x \)   | \( y \)   | \( z \)   | \( U_{\text{eq}}\) |
|---|----------|----------|----------|----------------|
| F1| 0.1012 (3) | 0.49942 (9) | 0.14190 (14) | 0.0349 (5) |
| O1| 0.1649 (3) | 0.53996 (11) | 0.37977 (16) | 0.0296 (5) |
| N1| 0.0596 (3) | 0.29674 (13) | 0.33292 (17) | 0.0204 (5) |
| N2| 0.250000 | 0.41071 (19) | 0.500000 | 0.0218 (6) |
| C2| 0.0612 (4) | 0.41086 (16) | 0.1771 (2) | 0.0245 (6) |
| C1| 0.0945 (3) | 0.38567 (15) | 0.2979 (2) | 0.0217 (5) |
| C5| -0.0104 (3) | 0.23375 (15) | 0.2494 (2) | 0.0208 (5) |
| H5| -0.037842 | 0.171355 | 0.274533 | 0.025* |
|        | x     | y     | z     | vx    | vy    | vz    | ic    | pm   | F1   | O1   | N1   | N2   | C2   | O1   | N1   | N2   | C5   | C4   | C3   | C6   | C6   | C2   | N1   | N5   | C6   | C6   | C2   | C1   | C5   | C4   | C3   | C2   | C1   | C5   | C4   | C3   | C2   | C1   | C5   | C4   | C3   | C2   | C1   | C5   | C4   | C3   | C2   | C1   |
|--------|-------|-------|-------|-------|-------|-------|-------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| C4     | −0.0453 (3) | 0.25475 (16) | 0.1273 (2) | 0.0233 (5) |
| H4     | −0.094044  | 0.207588  | 0.070604  | 0.028* |
| C3     | −0.0075 (4)  | 0.34557 (16) | 0.0902 (2) | 0.0247 (6) |
| H3     | −0.028177  | 0.362470  | 0.007558  | 0.030* |
| C6     | 0.1711 (3)   | 0.45473 (15) | 0.3944 (2) | 0.0213 (5) |
| H2     | 0.250000  | 0.351 (3)   | 0.500000  | 0.026* |

**Atomic displacement parameters (Å²)**

|        | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|--------|------|------|------|------|------|------|
| F1     | 0.0551 (11) | 0.0191 (7) | 0.0292 (9) | −0.0062 (6) | −0.0002 (7) | 0.0071 (6) |
| O1     | 0.0404 (10) | 0.0157 (8) | 0.0316 (10) | 0.0016 (7) | 0.0006 (8) | 0.0023 (7) |
| N1     | 0.0190 (9)  | 0.0171 (9) | 0.0254 (10) | 0.0017 (7) | 0.0038 (7) | 0.0014 (7) |
| N2     | 0.0254 (13) | 0.0141 (12) | 0.0262 (15) | 0.0000  | 0.0042 (11) | 0.0000  |
| C2     | 0.0262 (11) | 0.0165 (10) | 0.0309 (13) | 0.00012 (9) | 0.0042 (10) | 0.0048 (9) |
| C1     | 0.0203 (11) | 0.0167 (11) | 0.0278 (12) | 0.00022 (8) | 0.0023 (9) | 0.0021 (9) |
| C5     | 0.0188 (10) | 0.0174 (10) | 0.0270 (12) | 0.00007 (8) | 0.0058 (9) | 0.0008 (8) |
| C4     | 0.0213 (11) | 0.0223 (11) | 0.0258 (12) | 0.0025 (8) | 0.0014 (9) | −0.0022 (9) |
| C3     | 0.0276 (11) | 0.0239 (12) | 0.0222 (12) | 0.0039 (9) | 0.0014 (10) | 0.0028 (9) |
| C6     | 0.0222 (11) | 0.0162 (10) | 0.0259 (12) | 0.0014 (8) | 0.0051 (9) | 0.0009 (9) |

**Geometric parameters (Å, °)**

|        |       |       |       |       |       |       |
|--------|-------|-------|-------|-------|-------|-------|
| F1—C2  | 1.348 (2) | C2—C3 | 1.378 (3) |
| O1—C6  | 1.214 (3) | C1—C6 | 1.498 (3) |
| N1—C1  | 1.344 (3) | C5—H5 | 0.9500 |
| N1—C5  | 1.334 (3) | C5—C4 | 1.391 (3) |
| N2—C6i | 1.383 (3) | C4—H4 | 0.9500 |
| N2—C6  | 1.383 (3) | C4—C3 | 1.381 (3) |
| N2—H2  | 0.85 (4)  | C3—H3 | 0.9500 |
| C2—C1  | 1.391 (3) |       |       |       |       |       |
| C5—N1—C1 | 118.5 (2) | N1—C5—C4 | 123.4 (2) |
| C6—N2—C6 | 126.6 (3) | C4—C5—H5 | 118.3 |
| C6—N2—H2 | 116.71 (13) | C5—C4—H4 | 120.7 |
| C6—N2—H2 | 116.71 (13) | C3—C4—C5 | 118.6 (2) |
| F1—C2—C1 | 120.5 (2) | C3—C4—H4 | 120.7 |
| F1—C2—C3 | 118.4 (2) | C2—C3—C4 | 117.8 (2) |
| C3—C2—C1 | 121.1 (2) | C2—C3—H3 | 121.1 |
| N1—C1—C2 | 120.7 (2) | C4—C3—H3 | 121.1 |
| N1—C1—C6 | 117.0 (2) | O1—C6—N2 | 124.3 (2) |
| C2—C1—C6 | 122.3 (2) | O1—C6—C1 | 123.0 (2) |
| N1—C5—H5 | 118.3 | N2—C6—C1 | 112.68 (19) |

|        |       |       |       |       |       |       |
|--------|-------|-------|-------|-------|-------|-------|
| F1—C2—C1—N1 | −178.3 (2) | C1—C2—C3—C4 | 1.0 (4) |
| F1—C2—C1—C6 | 1.3 (4)  | C5—N1—C1—C2 | −1.0 (3) |
| F1—C2—C3—C4 | 179.1 (2) | C5—N1—C1—C6 | 179.41 (19) |
| N1—C1—C6—O1 | −162.6 (2) | C5—C4—C3—C2 | −0.6 (3) |
### Hydrogen-bond geometry (Å, °)

|          | D—H   | H···A  | D···A  | D—H···A |
|----------|-------|-------|-------|---------|
| N2—H2···N1 | 0.84 (4)| 2.27 (2)| 2.671 (2)| 110 (1) |
| N2—H2···N1' | 0.84 (4)| 2.27 (2)| 2.671 (2)| 110 (1) |
| C4—H4···O1" | 0.95 | 2.49 | 3.135 (3) | 125 |
| C5—H5···O1" | 0.95 | 2.61 | 3.207 (3) | 122 |
| C3—H3···F1" | 0.95 | 2.58 | 3.398 (3) | 145 |
| C5—H5···F1" | 0.95 | 2.66 | 3.604 (3) | 176 |

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