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

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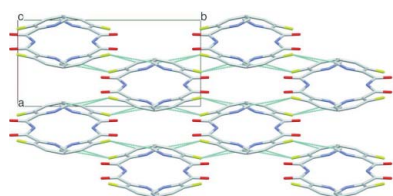
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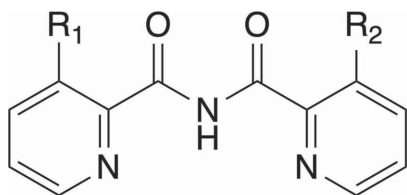
The synthesis and single-crystal X-ray structures of three *N*-(pyridine-2-carbonyl)pyridine-2-carboxamide imides, with or without F atoms on the 3-position of the pyridine rings are reported, namely, *N*-(pyridine-2-carbonyl)pyridine-2-carboxamide, C₁₂H₉N₃O₂ (**1**), *N*-(3-fluoropyridine-2-carbonyl)pyridine-2-carboxamide, C₁₂H₈FN₃O₂ (**2**), and 3-fluoro-*N*-(3-fluoropyridine-2-carbonyl)pyridine-2-carboxamide, C₁₂H₇F₂N₃O₂ (**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/fluorine 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 & Tait, 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 –NH₂ 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.



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- 1:** $R_1 = \text{H}; R_2 = \text{H}$
2: $R_1 = \text{F}; R_2 = \text{H}$
3: $R_1 = \text{F}; R_2 = \text{F}$

Herein, we report the single-crystal X-ray structural analysis of the imides *N*-(pyridine-2-carbonyl)pyridine-2-carboxamide (**1**) ($R_1 = \text{H}$, $R_2 = \text{H}$), *N*-(3-fluoropyridine-2-carbonyl)pyridine-2-carboxamide (**2**) ($R_1 = \text{F}$, $R_2 = \text{H}$) and 3-fluoro-*N*-(3-fluoropyridine-2-carbonyl)pyridine-2-carbox-

amide (**3**) ($R_1 = \text{F}$, $R_2 = \text{F}$), 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 *Pna*2₁, 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. 1*a*).

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 (F1*A*) and second fluoro (F1*B*) site, respectively (Fig. 1*b*).

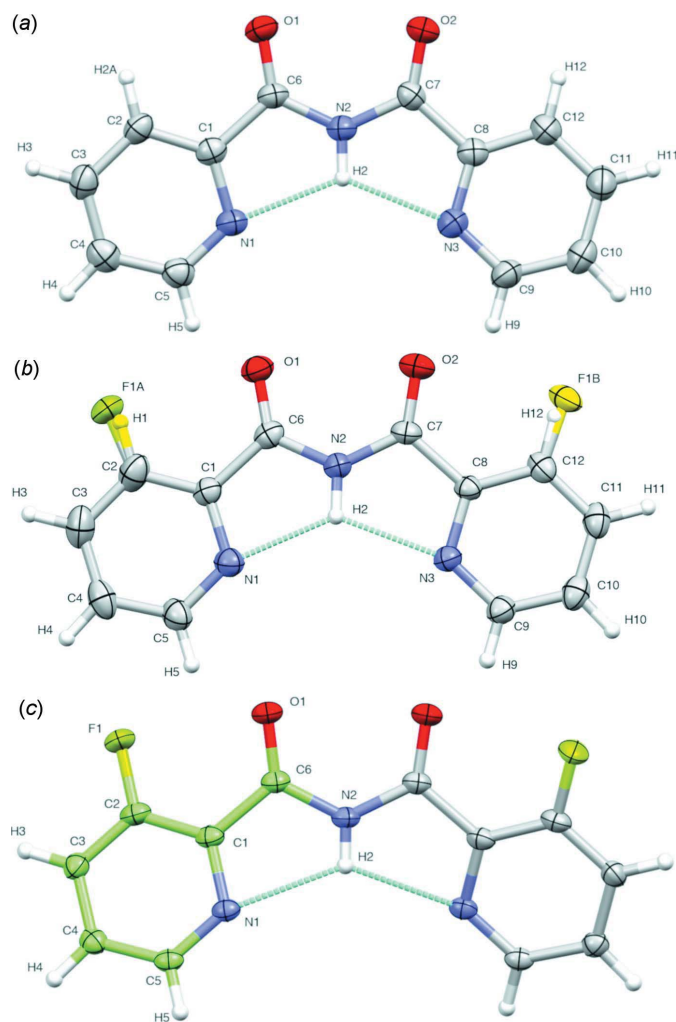


Figure 1
Molecular structures of (a) **1**, (b) **2** and (c) **3**, showing thermal displacement ellipsoids drawn at the 50% probability level and the atom-labelling scheme. The disorder in **2** (b) is shown in yellow. The carbon atoms in the asymmetric unit of **3** (c) are shown in green. Intramolecular hydrogen bonds are indicated.

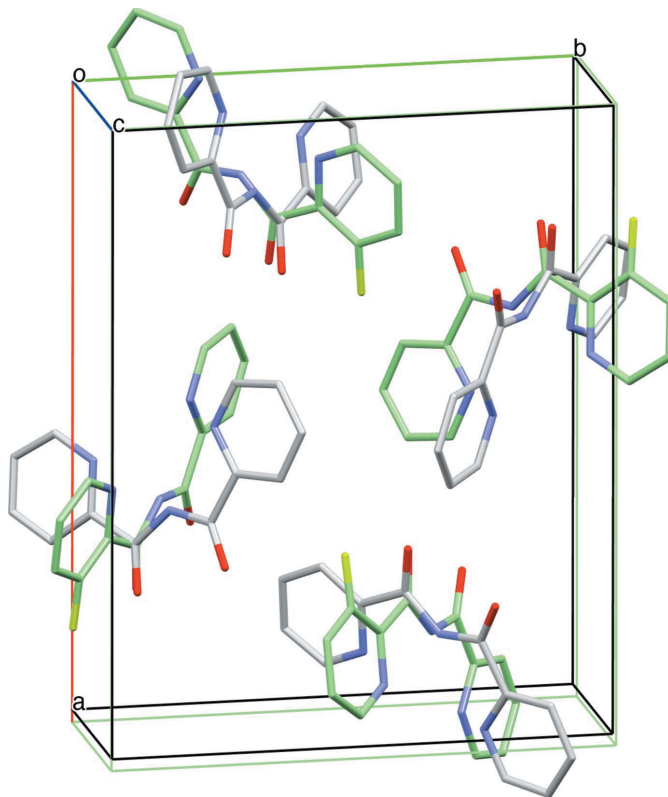


Figure 2
Unit-cell fit of the structures of **1** and **2**, showing a 90° rotation of the molecules of **2** (in green). Hydrogen atoms and disorder of the fluorine atoms are omitted for clarity.

Compound **3** crystallizes in the centrosymmetric monoclinic space group $I2/a$, 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 π – π interactions are present in the crystal packing, with rather large centroid–centroid distances ranging from 4.969 (2) to 5.497 (2) Å. However, clear C=O... π contacts are observed in the crystal packing [C6—O1...Cg1($x, y, -1 + z$) = 3.861 (3) Å; 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 [N2—H2...N1 = 2.15 (6) Å; N2—H2...N3 = 2.15 (5) Å], while non-classical intermolecular hydrogen bonds can be observed between the first pyridine rings and carbonyl O2 atoms of symmetry-equivalent molecules [C3—H3...O2ⁱ = 2.48 Å; symmetry code: (i) $\frac{1}{2} - x,$

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
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...O2 ⁱ	0.95	2.48	3.343 (5)	152
C5—H5...N1 ⁱⁱ	0.95	2.51	3.393 (5)	154

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

$\frac{1}{2} + y, -\frac{3}{2} + z]$, while these first pyridine rings are further connected to each other *via* similar hydrogen bonds with the pyridine N1 atoms [C5—H5...N1ⁱⁱ = 2.51 Å; 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 π – π 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) Å, while C=O... π contacts are also observed in the crystal packing [C6—O1...Cg1($x, y, -1 + z$) = 3.865 (4) Å; Cg1 is the centroid of the C1–C5/N1 ring]. Analogous to **1**, intramolecular potential hydrogen bonds

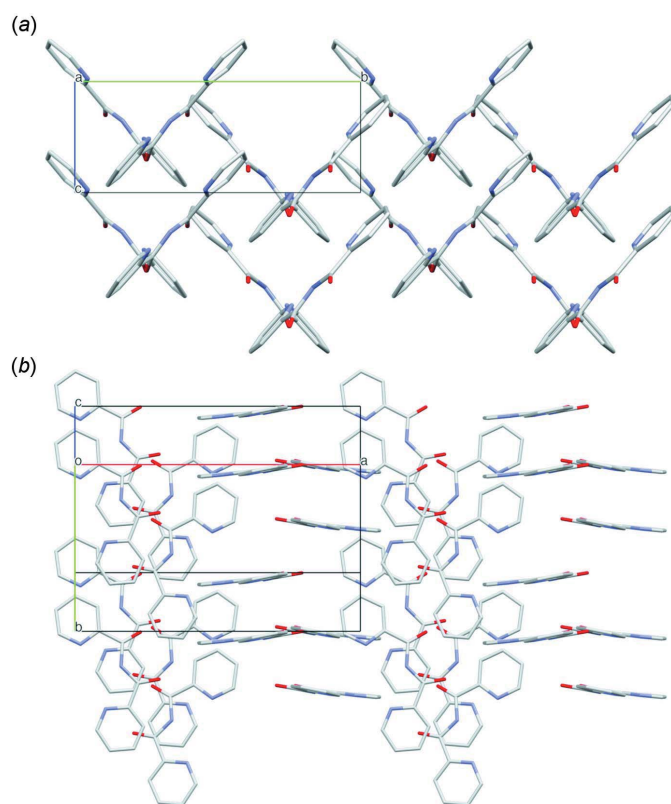


Figure 3

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.

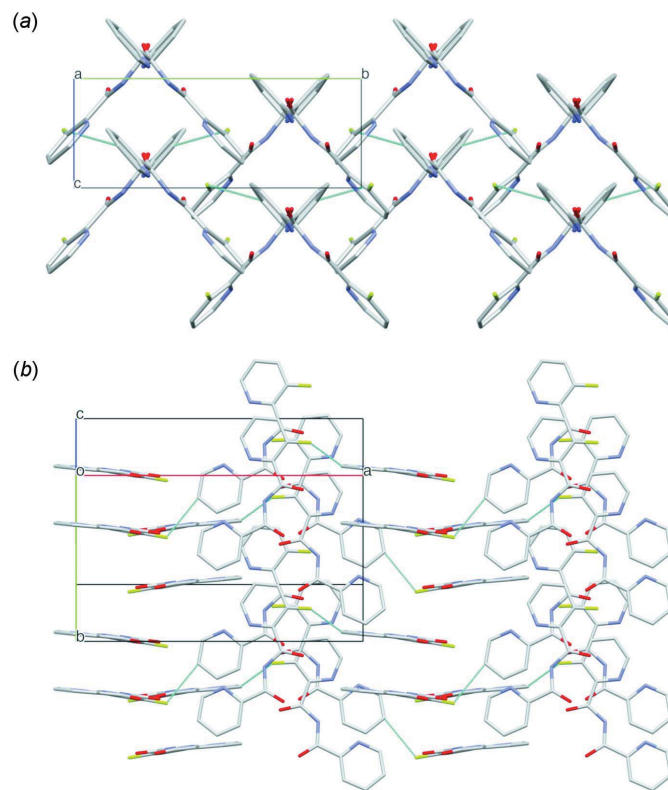


Figure 4

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...F1A hydrogen bonds are indicated. Hydrogen atoms and disorder of the fluorine atoms are omitted for clarity.

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

<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>
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...O2 ⁱ	0.95	2.43	3.320 (6)	156
C3—H3...F1B ⁱ	0.95	2.40	3.049 (8)	125
C5—H5...N1 ⁱⁱ	0.95	2.53	3.420 (6)	156
C10—H10...F1A ⁱⁱⁱ	0.95	2.45	3.169 (7)	132

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

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...O2ⁱ = 2.43 Å; symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y$,

Table 3
Hydrogen-bond geometry (Å, °) for **3**.

<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>
N2—H2...N1	0.84 (4)	2.27 (2)	2.671 (2)	110 (1)
N2—H2...N1 ⁱ	0.84 (4)	2.27 (2)	2.671 (2)	110 (1)
C4—H4...O1 ⁱⁱ	0.95	2.49	3.135 (3)	125
C5—H5...O1 ⁱⁱ	0.95	2.61	3.207 (3)	122
C3—H3...F1 ⁱⁱⁱ	0.95	2.58	3.398 (3)	145
C5—H5...F1 ⁱⁱ	0.95	2.66	3.604 (3)	176

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

$\frac{3}{2} + z]$, while these first pyridine rings are further connected to each other *via* similar hydrogen bonds with the pyridine N1 atoms [C5—H5...N1ⁱⁱ = 2.53 Å; symmetry code: (ii) $1 - x, 2 - y, \frac{1}{2} + z]$. Additionally, C—H...F hydrogen bonds are observed with the two disordered fluorine moieties [C3—H3...F1Bⁱ = 2.40 Å; C10—H10...F1Aⁱⁱⁱ = 2.45 Å; symmetry code: (iii) $\frac{1}{2} + x, \frac{3}{2} - y, -1 + z]$ (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 [$Cg \cdots Cg(\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z) = 3.6334$ (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...O1ⁱⁱ = 2.49 Å; symmetry code: (ii) $-x, -\frac{1}{2} + y, \frac{1}{2} - z]$ (Table 3). Additionally, although significantly longer, other hydrogen bonds are formed between the pyridine ring and the carbonyl O1 atom [C5—H5...O1ⁱⁱ = 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).

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 & Gabi-dullin, 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.

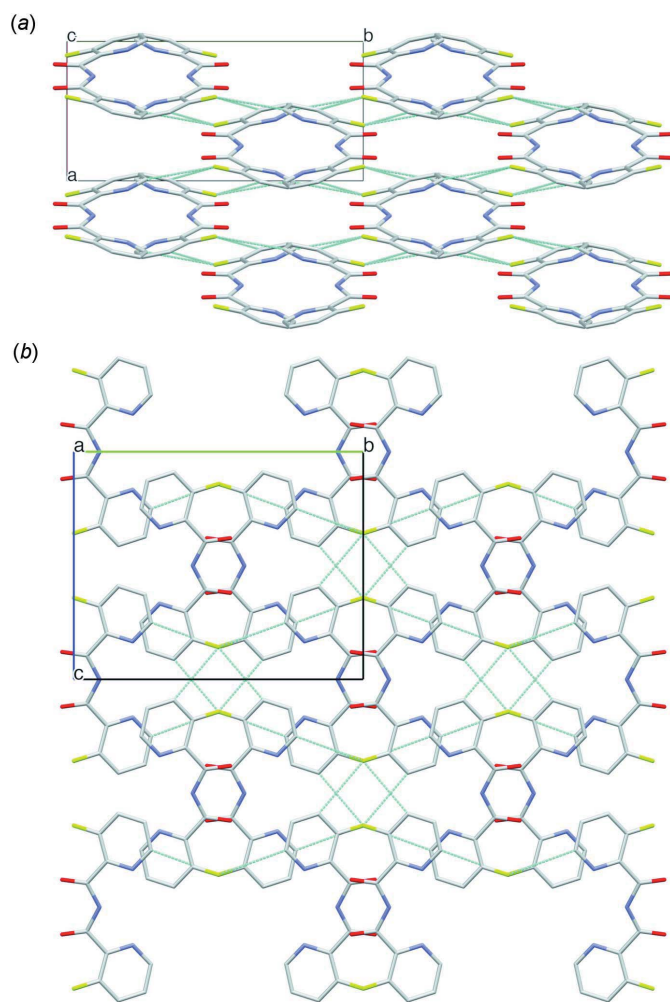


Figure 5
Packing in the structure of **3**, showing (a) the longitudinal tubular arrangement of the molecules along the *c* axis and (b) the aromatic pyridine and the carbonyl/fluorine moieties facing towards each other. C5—H5...F1 and C3—H3...F1 hydrogen bonds are indicated. Hydrogen atoms are omitted for clarity.

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-(methoxycarbonyl)pyridin-2-yl]carbonyl)carbamoylpyridine-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-pyridinecarbonyl chloride and 2-pyridinecarboxamide under mild conditions. By introducing a fluoro group at the 3-position of 2-pyridinecarbonyl 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.

3-Fluoropyridine-2-carboxylic acid

The preparation of 3-fluoropyridine-2-carboxylic 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-fluoropyridine-2-carboxylic acid. Yield: 91%. ¹H NMR (300 MHz, DMSO-*d*₆) δ 8.49 (*d*, *J* = 4.4 Hz, 1H), 7.94–7.81 (*m*, 1H), 7.64–7.70 (*m*, 1H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 164.35, 159.27, 145.26, 138.65, 128.27, 125.59.

2-Pyridinecarbonyl chloride

The preparation of 2-pyridinecarbonyl chloride was performed according to a previously reported procedure (Aluri *et al.*, 2011). 2-Pyridinecarboxylic acid (1.23 g, 10 mmol) and SOCl₂ (11.9 g, 100 mmol) were dissolved in 100 ml of dry toluene with 10 drops of DMF. The reaction mixture was refluxed at 383.15 K for 3 h. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The resulting viscous residue was used directly in the next step without further purification.

3-Fluoropyridine-2-carbonyl chloride

The preparation of 3-fluoropyridine-2-carbonyl chloride was performed according to a previously reported procedure (Aluri *et al.*, 2011). 3-Fluoropyridine-2-carboxylic acid (1.41 g, 10 mmol) and SOCl₂ (11.9 g, 100 mmol) were dissolved in 100 ml of dry toluene with 10 drops of DMF. The reaction mixture was refluxed at 383 K for 3 h. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The resulting viscous residue was used directly in the next step without further purification.

2-Pyridinecarboxamide

The preparation of 2-pyridinecarboxamide was performed according to a previously reported procedure (Cai *et al.*, 2014). 20 ml of NH₃/methanol solution (NH₃ *ca* 7 N in methanol solution) was slowly added to 2-pyridinecarbonyl 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: 88%. ¹H NMR (300 MHz, DMSO-*d*₆) 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-Fluoropyridin-2-carboxamide

20 ml of NH₃/methanol (NH₃ *ca* 7 N in methanol solution) was added slowly to 3-fluoropyridine-2-carbonyl 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 silica column with an eluent of hexane/ethyl acetate (5/1) to afford the product. Yield 85%. ¹H NMR (300 MHz, CDCl₃) 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, CDCl₃) 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 (**1**)

2-Pyridinecarbonyl 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 (3/1) to afford the product. Yield: 91%. ¹H NMR (300 MHz, CDCl₃) δ 13.03 (*s*, 1H), 8.75 (*ddd*, *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 (*ddd*, *J* = 7.6, 4.8, 1.2 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 162.65, 149.15, 148.67, 137.73, 127.50, 123.49.

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

3-Fluoropyridine-2-carboxamide (238.47 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 (3/1) to afford the product. Yield: 89%. ¹H NMR (300 MHz, DMSO-*d*₆) δ 12.72 (*s*, 1H), 8.81 (*ddd*, *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 (*ddd*, *J* = 11.3, 8.5, 1.2 Hz, 1H), 7.92–7.85 (*m*, 1H), 7.78 (*ddd*, *J* = 7.5, 4.8, 1.3 Hz, 1H). ¹³C NMR (101 MHz, DMSO-*d*₆) 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.

3-Fluoro-*N*-(3-fluoropyridine-2-carbonyl)pyridine-2-carboxamide (**3**)

3-Fluoropyridine-2-carboxamide (238.47 mg, 1.5 mmol) and 3-fluoropyridine-2-carbonyl chloride (196.04 mg, 1.4 mmol) were dissolved in toluene (20 ml). The resulting reaction

Table 4
Experimental details.

	1	2	3
Crystal data			
Chemical formula	C ₁₂ H ₉ N ₃ O ₂	C ₁₂ H ₈ FN ₃ O ₂	C ₁₂ H ₇ F ₂ N ₃ O ₂
<i>M_r</i>	227.22	245.21	263.21
Crystal system, space group	Orthorhombic, <i>Pna</i> 2 ₁	Orthorhombic, <i>Pna</i> 2 ₁	Monoclinic, <i>I</i> 2/ <i>a</i>
Temperature (K)	100	100	100
<i>a</i> , <i>b</i> , <i>c</i> (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)
α , β , γ (°)	90, 90, 90	90, 90, 90	90, 97.140 (4), 90
<i>V</i> (Å ³)	1041.56 (8)	1053.71 (11)	1052.94 (8)
<i>Z</i>	4	4	4
Radiation type	Cu <i>K</i> α	Cu <i>K</i> α	Cu <i>K</i> α
μ (mm ^{−1})	0.85	1.03	1.22
Crystal size (mm)	0.20 × 0.12 × 0.06	0.26 × 0.10 × 0.05	0.11 × 0.09 × 0.06
Data collection			
Diffractionmeter	SuperNova, Dual, Cu at zero, Atlas	SuperNova, Dual, Cu at zero, Atlas	SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Gaussian (<i>CrysAlis PRO</i> ; Rigaku OD, 2015)	Gaussian (<i>CrysAlis PRO</i> ; Rigaku OD, 2015)	Gaussian (<i>CrysAlis PRO</i> ; Rigaku OD, 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.187, 0.563	0.983, 0.995	0.993, 0.996
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	8626, 2028, 1831	5774, 1798, 1567	5200, 1083, 856
<i>R</i> _{int}	0.076	0.054	0.069
(sin θ /λ) _{max} (Å ^{−1})	0.627	0.629	0.628
Refinement			
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	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 restraints	1	1	0
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
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ^{−3})	0.32, −0.30	0.28, −0.28	0.29, −0.32
Absolute structure	Flack <i>x</i> determined using 673 quotients [(<i>I</i> ⁺) − (<i>I</i> [−])]/[(<i>I</i> ⁺) + (<i>I</i> [−])] (Parsons <i>et al.</i> , 2013)	Flack <i>x</i> determined using 450 quotients [(<i>I</i> ⁺) − (<i>I</i> [−])]/[(<i>I</i> ⁺) + (<i>I</i> [−])] (Parsons <i>et al.</i> , 2013)	—
Absolute structure parameter	0.0 (3)	0.2 (3)	—

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

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 (3/1) to afford the product. Yield: 80%. ¹H NMR (300 MHz, DMSO-*d*₆) δ 12.53 (*s*, 1H), 8.64 (*dt*, *J* = 4.5, 1.4 Hz, 2H), 8.02 (*ddd*, *J* = 11.3, 8.5, 1.2 Hz, 2H), 7.91–7.80 (*m*, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) 160.75, 159.72, 159.66, 158.05, 156.16, 144.97, 144.92, 136.12, 136.08, 130.62, 130.56, 127.36, 127.17.

Crystals of **1**, **2**, and **3**, suitable for single-crystal X-ray diffraction analysis were prepared by slow evaporation of a 10 mg ml^{−1} acetonitrile solution at room temperature. All crystals appeared as colourless blocks.

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.

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supporting information

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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

$C_{12}H_9N_3O_2$	$D_x = 1.449 \text{ Mg m}^{-3}$
$M_r = 227.22$	Cu $K\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$
Orthorhombic, $Pna2_1$	Cell parameters from 4719 reflections
$a = 16.2689 (6) \text{ \AA}$	$\theta = 4.2\text{--}74.0^\circ$
$b = 12.8086 (7) \text{ \AA}$	$\mu = 0.85 \text{ mm}^{-1}$
$c = 4.9983 (2) \text{ \AA}$	$T = 100 \text{ K}$
$V = 1041.56 (8) \text{ \AA}^3$	Block, clear colourless
$Z = 4$	$0.20 \times 0.12 \times 0.06 \text{ mm}$
$F(000) = 472$	

Data collection

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

Refinement

Refinement on F^2	Primary atom site location: structure-invariant
Least-squares matrix: full	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
$S = 1.07$	and constrained refinement
2028 reflections	$w = 1/[\sigma^2(F_o^2) + (0.1236P)^2 + 0.0215P]$
157 parameters	where $P = (F_o^2 + 2F_c^2)/3$
1 restraint	$(\Delta/\sigma)_{\max} < 0.001$
	$\Delta\rho_{\max} = 0.32 \text{ e \AA}^{-3}$

$$\Delta\rho_{\min} = -0.30 \text{ e } \text{\AA}^{-3}$$

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 ($\text{\AA}^2$)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.29400 (14)	0.3937 (2)	0.2999 (6)	0.0362 (7)
O2	0.22855 (16)	0.2512 (2)	0.7000 (6)	0.0343 (7)
N1	0.10762 (18)	0.4562 (3)	−0.0277 (7)	0.0301 (7)
N2	0.16131 (17)	0.3339 (2)	0.3528 (7)	0.0299 (7)
N3	0.01890 (19)	0.2587 (3)	0.5153 (7)	0.0335 (8)
C1	0.1883 (2)	0.4642 (3)	0.0217 (8)	0.0288 (8)
C2	0.2393 (2)	0.5328 (3)	−0.1112 (8)	0.0322 (8)
H2A	0.296091	0.536690	−0.068626	0.039*
C3	0.2060 (2)	0.5956 (3)	−0.3071 (9)	0.0372 (9)
H3	0.239464	0.643907	−0.401515	0.045*
C4	0.1232 (2)	0.5872 (3)	−0.3640 (9)	0.0372 (9)
H4	0.098806	0.628601	−0.500275	0.045*
C5	0.0767 (2)	0.5170 (3)	−0.2176 (8)	0.0344 (8)
H5	0.019566	0.512061	−0.255151	0.041*
C6	0.2213 (2)	0.3943 (3)	0.2372 (8)	0.0279 (8)
C7	0.1662 (2)	0.2696 (3)	0.5753 (8)	0.0284 (8)
C8	0.0840 (2)	0.2245 (3)	0.6517 (8)	0.0290 (8)
C9	−0.0551 (2)	0.2220 (3)	0.5853 (10)	0.0361 (9)
H9	−0.101987	0.245492	0.489110	0.043*
C10	−0.0664 (2)	0.1513 (3)	0.7923 (9)	0.0371 (9)
H10	−0.119977	0.127904	0.838484	0.045*
C11	0.0010 (3)	0.1157 (4)	0.9290 (9)	0.0410 (10)
H11	−0.004963	0.066767	1.070577	0.049*
C12	0.0785 (2)	0.1526 (3)	0.8565 (9)	0.0368 (9)
H12	0.126414	0.128826	0.946242	0.044*
H2	0.110 (3)	0.341 (4)	0.286 (12)	0.044*

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

	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)

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, °)

O1—C6	1.224 (4)	C3—C4	1.380 (6)
O2—C7	1.214 (4)	C4—H4	0.9500
N1—C1	1.339 (4)	C4—C5	1.385 (6)
N1—C5	1.327 (5)	C5—H5	0.9500
N2—C6	1.373 (5)	C7—C8	1.506 (5)
N2—C7	1.385 (5)	C8—C12	1.380 (6)
N2—H2	0.90 (5)	C9—H9	0.9500
N3—C8	1.333 (5)	C9—C10	1.387 (6)
N3—C9	1.339 (5)	C10—H10	0.9500
C1—C2	1.379 (5)	C10—C11	1.370 (6)
C1—C6	1.499 (5)	C11—H11	0.9500
C2—H2A	0.9500	C11—C12	1.394 (6)
C2—C3	1.378 (6)	C12—H12	0.9500
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)	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—C6—O1	179.4 (4)	C6—N2—C7—O2	−4.7 (6)
N1—C1—C6—N2	−1.1 (5)	C6—N2—C7—C8	174.7 (3)
N2—C7—C8—N3	−5.8 (5)	C6—C1—C2—C3	−179.8 (3)
N2—C7—C8—C12	175.2 (4)	C7—N2—C6—O1	7.6 (6)
N3—C8—C12—C11	−1.6 (6)	C7—N2—C6—C1	−171.9 (3)
N3—C9—C10—C11	−1.1 (7)	C7—C8—C12—C11	177.4 (4)
C1—N1—C5—C4	−0.1 (6)	C8—N3—C9—C10	0.3 (6)
C1—C2—C3—C4	−0.3 (6)	C9—N3—C8—C7	−178.0 (3)
C2—C1—C6—O1	−1.5 (5)	C9—N3—C8—C12	1.0 (6)
C2—C1—C6—N2	178.0 (3)	C9—C10—C11—C12	0.5 (7)
C2—C3—C4—C5	1.1 (6)	C10—C11—C12—C8	0.7 (7)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N2—H2 $\cdots$ N1	0.90 (5)	2.15 (6)	2.614 (5)	111 (4)
N2—H2 $\cdots$ N3	0.90 (5)	2.15 (5)	2.637 (4)	113 (5)
C3—H3 $\cdots$ O2 ⁱ	0.95	2.48	3.343 (5)	152
C5—H5 $\cdots$ N1 ⁱⁱ	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

 $C_{12}H_8FN_3O_2$ $M_r = 245.21$ Orthorhombic, $Pna2_1$ $a = 16.6058$ (10) Å $b = 12.9096$ (7) Å $c = 4.9153$ (3) Å $V = 1053.71$ (11) Å³ $Z = 4$ $F(000) = 504$ $D_x = 1.546$ Mg m^{−3}Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 2360 reflections

 $\theta = 3.4\text{--}74.8^\circ$ $\mu = 1.03$ mm^{−1} $T = 100$ K

Block, clear colourless

 $0.26 \times 0.10 \times 0.05$ mm

Data collection

SuperNova, Dual, Cu at zero, Atlas
diffractometerRadiation source: micro-focus sealed X-ray
tube, SuperNova (Cu) X-ray Source

Mirror monochromator

Detector resolution: 10.4839 pixels mm^{−1} ω scansAbsorption correction: gaussian
(CrysAlisPro; Rigaku OD, 2015) $T_{\min} = 0.983, T_{\max} = 0.995$

5774 measured reflections

1798 independent reflections

1567 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.054$ $\theta_{\max} = 75.9^\circ, \theta_{\min} = 5.3^\circ$ $h = -19 \rightarrow 20$ $k = -15 \rightarrow 16$ $l = -6 \rightarrow 5$

*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 $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.28 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$ 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 ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	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	0.479609	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 ($\text{\AA}^2$)

	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)	0.0026 (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 ($\text{\AA}$, $^\circ$)

O2—C7	1.224 (5)	C9—C10	1.381 (7)
O1—C6	1.217 (5)	C10—H10	0.9500
N3—C8	1.346 (6)	C10—C11	1.376 (8)
N3—C9	1.340 (6)	C11—H11	0.9500
N2—C7	1.370 (6)	C6—C1	1.505 (6)
N2—C6	1.384 (6)	C1—C2	1.380 (6)
N2—H2	0.92 (6)	C2—H2A	0.9500
N1—C1	1.341 (5)	C2—C3	1.384 (7)
N1—C5	1.342 (6)	C2—F1A	1.327 (6)
C12—H12	0.9500	C3—H3	0.9500
C12—C8	1.372 (7)	C3—C4	1.369 (7)
C12—C11	1.376 (7)	C4—H4	0.9500
C12—F1B	1.262 (8)	C4—C5	1.381 (6)
C8—C7	1.511 (6)	C5—H5	0.9500
C9—H9	0.9500		
C9—N3—C8	118.0 (4)	O2—C7—C8	122.4 (4)
C7—N2—C6	129.1 (4)	N2—C7—C8	112.6 (3)
C7—N2—H2	113 (4)	O1—C6—N2	124.9 (4)
C6—N2—H2	118 (4)	O1—C6—C1	122.9 (4)
C1—N1—C5	117.9 (4)	N2—C6—C1	112.2 (3)
C8—C12—H12	119.8	N1—C1—C6	115.9 (3)
C8—C12—C11	120.5 (5)	N1—C1—C2	121.9 (4)

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	C2—C3—H3	120.8
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—C9	118.8 (5)	C3—C4—C5	119.0 (4)
C11—C10—H10	120.6	C5—C4—H4	120.5
C12—C11—H11	120.9	N1—C5—C4	123.0 (4)
C10—C11—C12	118.3 (5)	N1—C5—H5	118.5
C10—C11—H11	120.9	C4—C5—H5	118.5
O2—C7—N2	125.0 (4)		
O1—C6—C1—N1	178.5 (4)	C11—C12—C8—C7	178.6 (4)
O1—C6—C1—C2	−1.9 (7)	C7—N2—C6—O1	6.0 (7)
N3—C8—C7—O2	175.2 (4)	C7—N2—C6—C1	−172.9 (4)
N3—C8—C7—N2	−3.2 (5)	C6—N2—C7—O2	−2.1 (7)
N3—C9—C10—C11	−1.7 (8)	C6—N2—C7—C8	176.3 (4)
N2—C6—C1—N1	−2.6 (5)	C6—C1—C2—C3	179.2 (4)
N2—C6—C1—C2	177.0 (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—C2—C3—C4	0.0 (7)
C12—C8—C7—O2	−4.7 (6)	C2—C3—C4—C5	1.2 (7)
C12—C8—C7—N2	176.8 (4)	C3—C4—C5—N1	−1.3 (7)
C8—N3—C9—C10	1.0 (7)	C5—N1—C1—C6	−179.3 (4)
C8—C12—C11—C10	0.6 (8)	C5—N1—C1—C2	1.1 (6)
C9—N3—C8—C12	0.6 (7)	F1B—C12—C8—N3	−175.0 (6)
C9—N3—C8—C7	−179.4 (4)	F1B—C12—C8—C7	5.0 (9)
C9—C10—C11—C12	0.9 (7)	F1B—C12—C11—C10	175.1 (6)
C11—C12—C8—N3	−1.3 (7)	F1A—C2—C3—C4	179.6 (5)

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

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
N2—H2 $\cdots$ N1	0.92 (5)	2.16 (6)	2.614 (6)	109 (4)
N2—H2 $\cdots$ N3	0.92 (5)	2.11 (6)	2.622 (5)	114 (5)
C3—H3 $\cdots$ O2 ⁱ	0.95	2.43	3.320 (6)	156
C3—H3 $\cdots$ F1B ⁱ	0.95	2.40	3.049 (8)	125
C5—H5 $\cdots$ N1 ⁱⁱ	0.95	2.53	3.420 (6)	156
C10—H10 $\cdots$ F1A ⁱⁱⁱ	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*C₁₂H₇F₂N₃O₂ $M_r = 263.21$ Monoclinic, $I2/a$ $a = 6.7062$ (3) Å $b = 14.1190$ (5) Å $c = 11.2074$ (5) Å $\beta = 97.140$ (4)° $V = 1052.94$ (8) Å³ $Z = 4$ $F(000) = 536$ $D_x = 1.660$ Mg m⁻³Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 1899 reflections

 $\theta = 5.0\text{--}74.9^\circ$ $\mu = 1.22$ mm⁻¹ $T = 100$ K

Block, clear colourless

 $0.11 \times 0.09 \times 0.06$ mm*Data collection*SuperNova, Dual, Cu at zero, Atlas
diffractometerRadiation source: micro-focus sealed X-ray
tube, SuperNova (Cu) X-ray Source

Mirror monochromator

Detector resolution: 10.4839 pixels mm⁻¹ ω scansAbsorption correction: gaussian
(CrysAlisPro; Rigaku OD, 2015) $T_{\min} = 0.993$, $T_{\max} = 0.996$

5200 measured reflections

1083 independent reflections

856 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.069$ $\theta_{\max} = 75.4^\circ$, $\theta_{\min} = 5.1^\circ$ $h = -7 \rightarrow 8$ $k = -17 \rightarrow 17$ $l = -14 \rightarrow 13$ *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 $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.29$ e Å⁻³ $\Delta\rho_{\min} = -0.32$ 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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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*

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)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
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)	0.000	0.0042 (11)	0.000
C2	0.0262 (11)	0.0165 (10)	0.0309 (13)	0.0012 (9)	0.0042 (10)	0.0048 (9)
C1	0.0203 (11)	0.0167 (11)	0.0278 (12)	0.0022 (8)	0.0023 (9)	0.0021 (9)
C5	0.0188 (10)	0.0174 (10)	0.0270 (12)	0.0007 (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—C6 ⁱ	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 ⁱ —N2—C6	126.6 (3)	C4—C5—H5	118.3
C6 ⁱ —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)

N1—C1—C6—N2	17.9 (3)	C3—C2—C1—N1	−0.2 (4)
N1—C5—C4—C3	−0.6 (3)	C3—C2—C1—C6	179.3 (2)
C2—C1—C6—O1	17.8 (4)	C6 ⁱ —N2—C6—O1	1.68 (18)
C2—C1—C6—N2	−161.7 (2)	C6 ⁱ —N2—C6—C1	−178.8 (2)
C1—N1—C5—C4	1.4 (3)		

Symmetry code: (i) $-x+1/2, y, -z+1$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2 $\cdots$ N1	0.84 (4)	2.27 (2)	2.671 (2)	110 (1)
N2—H2 $\cdots$ N1 ⁱ	0.84 (4)	2.27 (2)	2.671 (2)	110 (1)
C4—H4 $\cdots$ O1 ⁱⁱ	0.95	2.49	3.135 (3)	125
C5—H5 $\cdots$ O1 ⁱⁱ	0.95	2.61	3.207 (3)	122
C3—H3 $\cdots$ F1 ⁱⁱⁱ	0.95	2.58	3.398 (3)	145
C5—H5 $\cdots$ F1 ⁱⁱ	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) $-x, -y+1, -z$.