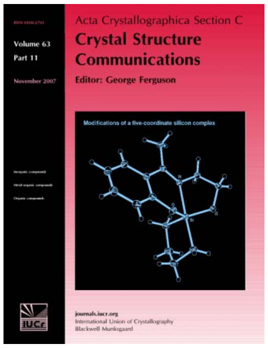
Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701
Editor: **George Ferguson**

A structural systematic study of three isomers of difluoro-*N*-(4-pyridyl)benzamide

Joyce McMahon, Frankie P. Anderson, John F. Gallagher and Alan J. Lough

Acta Cryst. (2008). C**64**, o493–o497



Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A structural systematic study of three isomers of difluoro-*N*-(4-pyridyl)-benzamide

Joyce McMahon,[a] Frankie P. Anderson,[b] John F. Gallagher[a]* and Alan J. Lough[c]

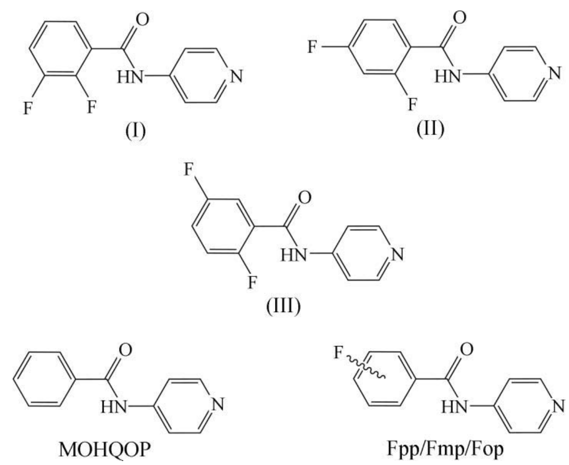
[a]School of Chemical Sciences, Dublin City University, Dublin 9, Ireland, [b]School of Chemical Sciences, National Institute for Cellular Biotechnology, Dublin City University, Dublin 9, Ireland, and [c]Department of Chemistry, 80 St George Street, University of Toronto, Ontario, Canada M5S 3H6
Correspondence e-mail: john.gallagher@dcu.ie

Received 18 June 2008
Accepted 18 July 2008
Online 9 August 2008

The isomers 2,3-, (I), 2,4-, (II), and 2,5-difluoro-*N*-(4-pyridyl)-benzamide, (III), all with formula $C_{12}H_8F_2N_2O$, all exhibit intramolecular C—H···O=C and N—H···F contacts [both with *S*(6) motifs]. In (I), intermolecular N—H···O=C interactions form one-dimensional chains along [010] [N···O = 3.0181 (16) Å], with weaker C—H···N interactions linking the chains into sheets parallel to the [001] plane, further linked into pairs *via* C—H···F contacts about inversion centres; a three-dimensional herring-bone network forms *via* C—H···π(py) (py is pyridyl) interactions. In (II), weak aromatic C—H···N(py) interactions form one-dimensional zigzag chains along [001]; no other interactions with H···N/O/F < 2.50 Å are present, apart from long N/C—H···O=C and C—H···F contacts. In (III), N—H···N(py) interactions form one-dimensional zigzag chains [as *C*(6) chains] along [010] augmented by a myriad of weak C—H···π(arene) and O=C···O=C interactions and C—H···O/N/F contacts. Compound (III) is isomorphous with the parent *N*-(4-pyridyl)benzamide [Noveron, Lah, Del Sesto, Arif, Miller & Stang (2002). *J. Am. Chem. Soc.* **124**, 6613–6625] and the three 2/3/4-fluoro-*N*-(4-pyridyl)benzamides [Donnelly, Gallagher & Lough (2008). *Acta Cryst.* C**64**, o335–o340]. The study expands our series of fluoro(pyridyl)benzamides and augments our understanding of the competition between strong hydrogen-bond formation and weaker influences on crystal packing.

Comment

Our group has initiated a structural systematic study of fluoro-*N*-(pyridyl)benzamide isomers (Donnelly *et al.*, 2008) and are augmenting this research with the closely related difluoro-*N*-(pyridyl)benzamide series (see scheme) of which a total of 18 isomers are possible through condensation of the 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-difluorobenzoyl chlorides with the 4-/3-/2-aminopyridines. In contrast to the abundance of mono-substituted fluorobenzene (FC_6H_4–*X*) and pentafluorobenzene (F_5C_6–*Y*) derivatives in structural chemistry, there is a paucity of structural information on all six possible difluorobenzene derivatives ($F_2C_6H_3$–*Z*) (*X*,*Y*,*Z* = remainder of molecule) from analysis of structural data in the Cambridge Structural Database (CSD, Version 5.29; Allen, 2002) (Fig. 1).



In contrast to the 3531 (8) structures containing the pentafluorobenzene (C_6F_5–*Y*) group, the cumulative reported total of the six $C_6F_2H_3Z$ difluorobenzene groups in compounds (at 438) is only < 13% of the C_6F_5 reported systems (see Fig. 1).

Disorder in the orientation of the aromatic ring can arise and can influence the choice of a particular difluorobenzene fragment in crystal structures in order to minimize solid-state disorder effects. The potential for twofold rotational disorder is at a minimum in the more symmetrical 2,6-F_2 and 3,5-F_2 (no change on twofold rotation about the C_{ipso}—C_{para} axis) and at a maximum in the 2,3-F_2 and 2,5-F_2 systems (two F atoms have to occupy different H-atom sites); the potential for disorder also exists for 2,4-F_2 and 3,4-F_2 substitution (where only one F atom has to swop sites with a H atom after twofold rotation). No disorder is present in any of the title 2,3-difluoro-*N*-(4-pyridyl)benzamide, (I), 2,4-difluoro-*N*-(4-pyridyl)benzamide, (II), and 2,5-difluoro-*N*-(4-pyridyl)benzamide, (III), systems.

Many structural studies have been reported to date on a variety of organic molecular classes and often with a particular

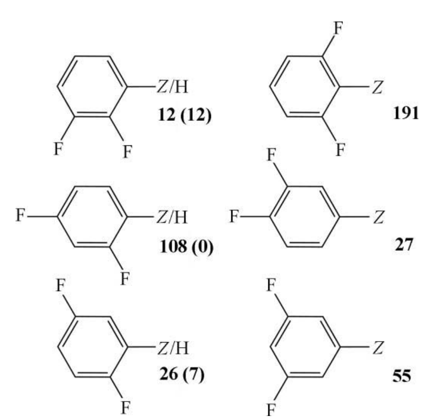


Figure 1
Relative abundance of difluorobenzene fragments in the CSD (Version 5.29, January 2008 updates). *X* = any element and *Z* = any element but H.

emphasis on polymorphism, pseudopolymorphism and isomers (Gelbrich *et al.*, 2007; Wardell *et al.*, 2007, 2008; Chopra & Row, 2008). Augmenting our initial communication (Donnelly *et al.*, 2008), we report here the molecular and crystal structures of isomers (I)–(III).

The three isomers (I)–(III) are depicted in Figs. 2–4 and in the packing diagrams (Figs. 5–8). The geometric data (bond lengths and angles) are normal and are not discussed except for comparisons with related systems and their hydrogen bonding/packing (interactions in Tables 1–3 and torsion angles in Table 4). The defining feature of the molecular conformation is the benzene–pyridine dihedral angle, which is mutually oriented at 10.02 (8)° in (I), 7.02 (13)° in (II) and 42.39 (6)° in (III). In all three systems, the *ortho*-F atom is positioned *cisoid* to the carbonyl O atom and as such there are two intramolecular contacts present involving C22···O1 and N1···F12 [both with *S*(6) motifs]. The C22···O1 distances vary from 2.868 (2) to 2.8807 (18) Å (C—H···O = 114–120°); however, N1···F1 varies from 2.720 (3) [in (II)] to 2.7803 (14) Å [in (I)], with angles ranging from 109.7 (15) [in (III)] to 131 (3)° [in (I)] (as torsion angle C1—N1—C21—C26 increases; Table 4). The intramolecular contact data for (III) are similar to data for 2-fluoro-*N*-(4-pyridyl)benzamide (Fop) (Donnelly *et al.*, 2008). Moreover, (III) is isomorphous with all three 4-/3-/2-fluoro-*N*-(4-pyridyl)benzamide isomers (Fpp/Fmp/Fop) and differs in composition with an extra F atom replacing a H atom on the benzene ring (see scheme) (Donnelly *et al.*, 2008). For comparison, the unit-cell similarity indices Π of (III) with Fmp and Fop are 0.003 and 0.002, respectively (Kálmán *et al.*, 1993).

In (I), standard amide N—H···O=C hydrogen bonds (Table 1) form chains along [010], further linked by C14—H14···N24(py)^{ii} interactions [py is pyridyl; symmetry code: (ii) *x* + 1, *y*, *z*; Table 1] to form sheets of $R_4^4(28)$ rings parallel to (001) (Fig. 5). Pairs of inversion-related sheets form short C—H···F contacts and these pairs of sheets form a three-dimensional network *via* C—H···π(py) interactions.

In (II), a C—H···N(py) hydrogen bond (Table 2) forms a zigzag *C*(10) chain along [001] (Fig. 6); there are no other interactions with a H···O/N/F distance < 2.5 Å. Conventional amide N—H···O=C interactions [as *C*(4) chains or $R_2^2(8)$ rings] are absent and the closest amide–amide contact is N1···O1^{i} of 3.460 (3) Å [symmetry code: (i) *x*, *y* + 1, *z*]; this is 0.45 Å longer than for (I). The three closest intermolecular contacts with the carbonyl O1 atom range from 2.69 to 2.76 Å, with corresponding C—H···O1 angles in the range 126–141°. There are also two weak C15/23—H15/23···F14 contacts, with C···F distances of 3.322 (3) and 3.339 (3) Å. Though the interaction distances differ between (I) and (II), there is a broad similarity in overall packing.

In (III), the primary interaction is an N—H···N(py) hydrogen bond (Table 3), which forms a zigzag *C*(6) chain along the [010] direction (Fig. 7). This interaction is augmented by longer C—H···π(arene) hydrogen bonds (Table 3), dipolar C=O···O=C interactions (Fig. 8) and weaker C—H···N/O/F contacts, forming a three-dimensional network. The C=O···(O=C)^{i} interactions link molecules about inversion centres in an antiparallel arrangement, with C1···O1^{i} distances of 3.150 (2) Å [symmetry code: (i) −*x* + 2, −*y*, −*z* + 1] (Fig. 8). The internal angles within the C=O···(O=C)^{i} motif are 85.00 (10)° (for C1=O1···C1^{i}) and 95.00 (10)° (for O1=C1···O1^{i}), and close to the idealized antiparallel arrangement [90° angles – motif (II)] (Allen *et al.*, 1998).

The data for (III) are similar to Fop (Donnelly *et al.*, 2008), where the C1···O1^{i} distance is 3.1919 (16) Å. The closest intermolecular amide–amide distance is N1···O1^{ii} of 4.005 (2) Å [with H1···O1^{ii} = 3.37 (2) Å; symmetry code: (ii) *x* − 1, *y*, *z*] along the [100] axis, highlighting the lack of

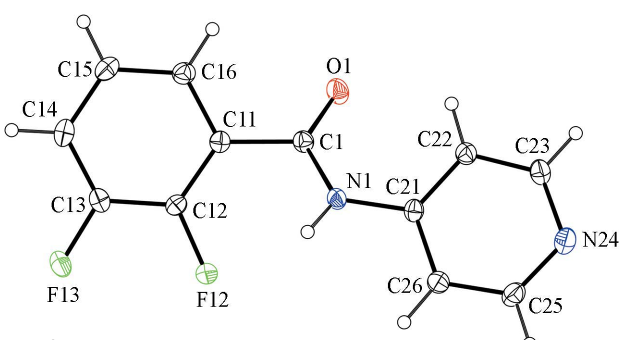


Figure 2
A view of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

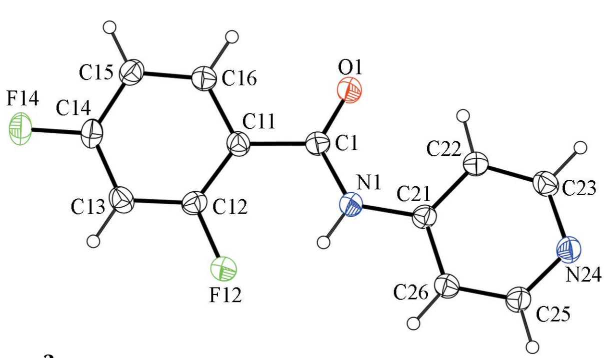


Figure 3
A view of (II), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

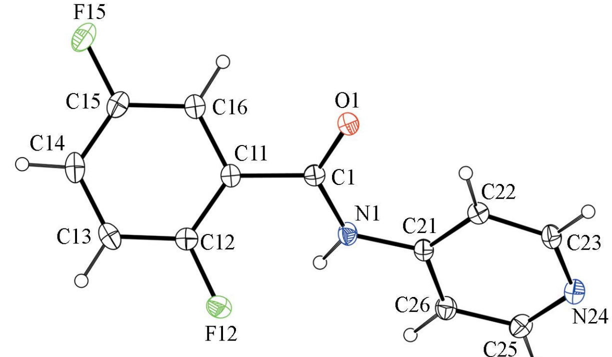


Figure 4
A view of (III), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

conventional intermolecular amide–amide hydrogen bonding in (III). This N1···O1[ii] distance is longer than the corresponding N···O distances in the Fpp, Fmp and Fop isomers [3.438 (2)–3.7854 (16) Å] (Table 5) (these isomers have N—H···N(py) as their primary interaction) (Donnelly *et al.*, 2008). The trend of increasing amide–carbonyl N···O distance correlates well with the increasing unit-cell '*a*' dimension (amide–amide distance along [100]) and decreasing benzene–pyridine dihedral angle (preventing closer intermolecular N···O approach).

The primary interactions in (I)–(III) differ, although (I) and (II) are more closely matched in comparison to the hydrogen bonding in (III) [where N—H···N(py) hydrogen bonding dominates] and they also differ in intermolecular N—H···O distance. The influence of π–π stacking interactions is small for (I)–(III) and with no substantial aromatic ring overlap; there are no parallel and overlapping aromatic planes within 3.5 Å of each other.

It is of interest that (III) crystallizes in the same space group, *viz.* $P2_1/c$ (No. 14), and with a similar unit cell as the Fpp/Fmp/Fop series (Donnelly *et al.*, 2008) and also the parent *N*-(4-pyridyl)benzamide, (IV) (CSD refcode MOHQOP; Noveron *et al.*, 2002) (Table 5). This isomorphous series of five

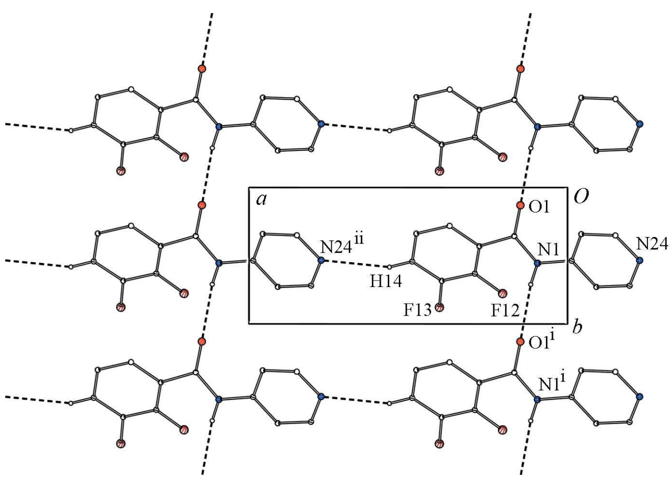


Figure 5
The primary N—H···O═C interactions in (I), forming *C*(4) chains along [010] and linked by C—H···N interactions to form sheets. H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (i) $x, y+1, z$; (ii) $x+1, y, z$.]

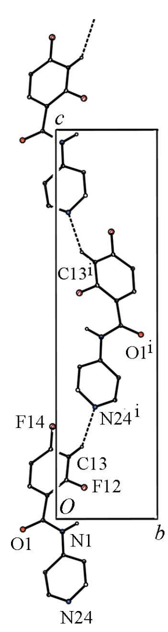


Figure 6
A view of the C—H···N interaction propagating in the [001] direction and forming a chain in (II). H atoms attached to C atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry code: (i) $x, y-\frac{1}{2}, z+\frac{1}{2}$.]

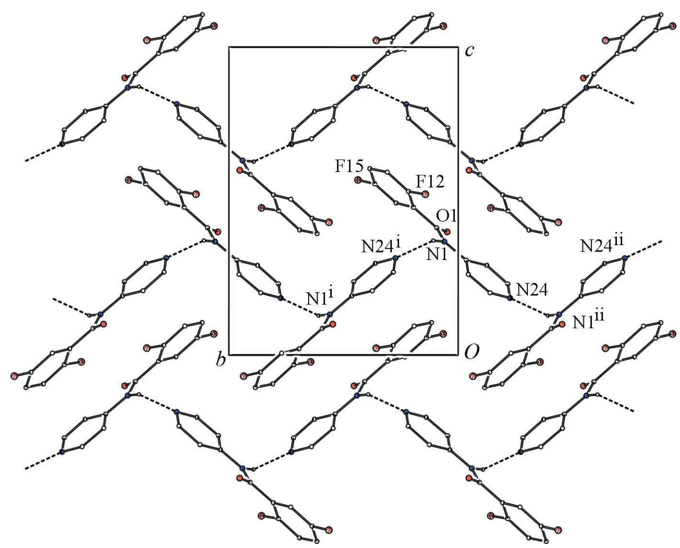


Figure 7
A view of the intermolecular N—H···N interactions in (III), forming zigzag chains along [010] and similar to the isomorphous series (Donnelly *et al.*, 2008). [Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$.]

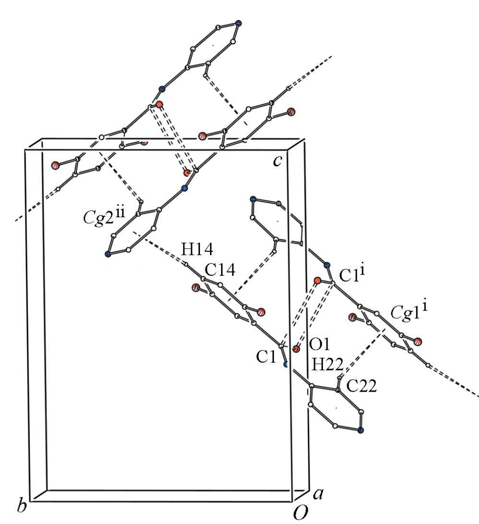


Figure 8
A view of the C—H···π(arene) (linking chains into sheets) and antiparallel C═O···O═C interactions (linking sheets into a three-dimensional network) in (III). H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (i) $-x+2, -y, -z+1$; (ii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.]

compounds facilitates comparisons (where H is replaced by F) on progressing from the parent (IV) to the isomorphous Fpp/Fmp/Fop series to (III). The molecular conformations of (III) and the Fpp/Fmp/Fop series are similar as the spatial orientation of the 2,5-F_2 atoms on the benzene ring in (III) compares favourably with the *ortho*-substituted F atom in Fop and the *meta*-substituted F atom in Fmp (Table 5). The dominance and influence of the amide–pyridine N—H···N hydrogen bonding in the packing for all five compounds is notable as it competes with potential N—H···O═C interactions and other weaker types of hydrogen bonding; there is a negligible influence of the isosteric replacement of H atoms by F atoms on packing. The molecular similarity in combination with the dominance of N—H···N hydrogen bonding influences the observed isomorphism in the five structures (IV), Fpp/Fmp/Fop and (III).

In expanding our structural systematic study of fluoro(pyridyl)benzamides, incorporating isomers, polymorphs and pseudopolymorphs, we are striving to group together examples with similar properties and behaviour as well as making comparisons with related published work so as 'not to impose a discontinuity on Nature's continuum' (Threlfall & Gelbrich, 2007). Work is in progress to expand this fluoro(pyridyl)benzamide series.

Experimental

For the preparation of (I)–(III) (Fink & Kurys, 1996), typically, the 2,3-, 2,4- and 2,5-difluorobenzoyl chlorides in dry CH_2Cl_2 (20–30 ml) were added dropwise (over a period of 2–3 min) to a cold (273 K) 20–30 ml solution of 4-aminopyridine containing Et_3N (1.5 ml) and the reaction was stirred overnight at room temperature. Typical organic work-up and washing furnished the products in reasonable yields of 40–90%. Crystals suitable for diffraction were grown from $CHCl_3$ as colourless blocks over a period of 1–2 weeks. The three compounds gave clean ^{1}H and ^{13}C NMR spectra in δ_6-DMSO and the IR spectra (in $CHCl_3$ solution, KBr disks) are as expected.

For (I), m.p. 385–387 K (uncorrected); IR ($\nu_{C=O}$ cm^{-1}): 1684 (*s*), 1674 (*m*) ($CHCl_3$); 1667 (*s*) (KBr); ^{1}H NMR (400 MHz, DMSO): δ 10.98 (*s*, 1H, N—H), 8.51 (*d*, 2H, 4-py), 7.70 (*d*, 2H, 4-py), 7.67 (*m* [2 *td*], 1H, 2,3-Fbenz), 7.53 (*m* [*tt*], 1H, 2,3-Fbenz), 7.38 (*m* [2 *td*], 1H, 2,3-Fbenz). For (II), m.p. 391–393 K (uncorrected); IR ($\nu_{C=O}$ cm^{-1}): 1662 (*s*) ($CHCl_3$); 1685 (*s*), 1674 (*s*) (KBr); ^{1}H NMR (400 MHz, DMSO): δ 10.85 (*s*, 1H, N—H), 8.50 (*d*, 2H, 4-py), 7.69 (*d*, 2H, 4-py), 7.80 (*m*, 1H, 2,4-Fbenz), 7.47 (*m* [*td*], 1H, 2,4-Fbenz), 7.26 (*m* [*td*], 1H, 2,4-Fbenz). For (III), m.p. 433–435 K (uncorrected); IR ($\nu_{C=O}$ cm^{-1}): 1684 (*s*) ($CHCl_3$); 1685 (*s*) (KBr); ^{1}H NMR (400 MHz, DMSO): δ 10.93 (*s*, 1H, N—H), 8.51 (*d*, 2H, 4-py), 7.70 (*d*, 2H, 4-py), 7.61 (*m*, 1H, 2,5-Fbenz), 7.48 (*m*, 2H, 2,5-Fbenz).

Compound (I)

Crystal data

$C_{12}H_8F_2N_2O$
M_r = 234.20
Monoclinic, $P2_1/n$
a = 12.5700 (6) Å
b = 5.1257 (2) Å
c = 16.5178 (8) Å
β = 107.847 (2)°
V = 1013.03 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.13 mm^{-1}
T = 150 (1) K
0.38 × 0.36 × 0.30 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.889, T_{max} = 0.965
5827 measured reflections
2292 independent reflections
1872 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.107
S = 1.05
2292 reflections
158 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

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

*Cg*1 is the centroid of the pyridine ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.88 (2)	2.21 (2)	3.0181 (16)	152.3 (16)
N1—H1···F12	0.88 (2)	2.212 (18)	2.7803 (14)	122.2 (15)
C22—H22···O1	0.95	2.36	2.8807 (18)	114
C14—H14···N24^{ii}	0.95	2.59	3.4273 (19)	147
C15—H15···*Cg*1^{iii}	0.95	2.86	3.5941 (16)	135
C25—H25···F13^{iv}	0.95	2.49	3.4240 (18)	166

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

Compound (II)

Crystal data

$C_{12}H_8F_2N_2O$
M_r = 234.20
Monoclinic, $P2_1/c$
a = 8.3187 (6) Å
b = 5.5868 (6) Å
c = 21.715 (2) Å
β = 98.517 (6)°
V = 998.07 (16) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.13 mm^{-1}
T = 150 (2) K
0.24 × 0.16 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.969, T_{max} = 0.996
6812 measured reflections
2248 independent reflections
1197 reflections with $I > 2\sigma(I)$
R_{int} = 0.083

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···F12	0.92 (4)	2.03 (3)	2.720 (3)	131 (3)
C22—H22···O1	0.95	2.29	2.868 (3)	118
C13—H13···N24^{i}	0.95	2.60	3.430 (3)	146

Symmetry code: (i) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.

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

*Cg*1 and *Cg*2 are the centroids of the benzene and pyridine rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···N24^{i}	0.89 (2)	2.24 (2)	3.010 (2)	145.3 (17)
N1—H1···F12	0.89 (2)	2.32 (2)	2.7465 (17)	109.7 (15)
C22—H22···O1	0.95	2.29	2.873 (2)	119
C22—H22···*Cg*1^{ii}	0.95	2.86	3.4966 (18)	126
C14—H14···*Cg*2^{iii}	0.95	2.95	3.8012 (19)	149

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.157$
$S = 1.01$
2248 reflections
158 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Compound (III)

Crystal data

$C_{12}H_8F_2N_2O$
$M_r = 234.20$
Monoclinic, $P2_1/c$
$a = 6.2088$ (4) Å
$b = 11.0182$ (5) Å
$c = 14.8139$ (9) Å
$\beta = 93.018$ (3)°
$V = 1012.01$ (10) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.13$ mm^{-1}
$T = 150$ (2) K
0.22 × 0.16 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.932$, $T_{max} = 0.988$
6136 measured reflections
2295 independent reflections
1555 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.120$
$S = 1.04$
2295 reflections
159 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Table 4
Comparison of selected torsion/dihedral angles (°) in (I)–(III) and Fop.

	(I)	(II)	(III)	Fop†
O1—C1—N1—C21	−0.6 (2)	1.7 (4)	7.0 (3)	6.1 (2)
O1—C1—C11—C12	149.52 (15)	161.5 (2)	−148.88 (16)	−147.55 (14)
C11—C1—N1—C21	−179.45 (12)	−177.7 (2)	−175.26 (14)	−176.77 (12)
C1—N1—C21—C26	−156.89 (14)	−169.8 (2)	−172.89 (16)	11.2 (2)
Benzene–pyridine	10.02 (8)	7.02 (8)	42.39 (6)	46.34 (5)

† Fop is 2-fluoro-*N*-(4-pyridyl)benzamide (Donnelly *et al.*, 2008).

H atoms attached to C atoms were treated as riding using *SHELXL97* (Sheldrick, 2008) defaults at 150 (1) K, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. N-bound H atoms were refined freely with isotropic displacement parameters to bond lengths of 0.88 (2) Å in (I), 0.92 (4) Å in (II) and 0.89 (2) Å in (III).

For all compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) and *SORTX* (McArdle, 1995); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PREP8* (Ferguson, 1998).

Table 5
Comparison of unit-cell, volume and selected geometric parameters in five isomorphous (4-pyridyl)benzamides.

Space group $P2_1/c$ (No. 14) with $Z = 4$.

X	MOHQOP†	Fpp‡	Fmp‡	Fop‡	(III)§
Formula	$C_{12}H_{10}N_2O$	$C_{12}H_9FN_2O$	$C_{12}H_9FN_2O$	$C_{12}H_9FN_2O$	$C_{12}H_8F_2N_2O$
a	5.6830 (2)	5.6506 (3)	5.7537 (3)	5.9832 (3)	6.2088 (3)
b	11.1380 (3)	11.3882 (8)	11.2421 (4)	11.1508 (5)	11.0182 (5)
c	15.2124 (16)	15.4314 (8)	15.1672 (7)	14.8921 (7)	14.8139 (9)
β	95.0784 (13)	95.602 (3)	94.188 (2)	94.986 (3)	93.018 (3)
V (Å^3)	959.12 (6)	988.27 (10)	978.45 (8)	989.80 (8)	1012.01 (10)
N···N (Å)	3.01412 (16)	3.022 (2)	3.049 (2)	3.0213 (17)	3.010 (2)
N···O (Å)	3.4388 (13)	3.438 (2)	3.562 (2)	3.7854 (16)	4.005 (2)
C_6/C_5N (°)	45.95 (6)	51.95 (6)	48.75 (6)	46.34 (5)	42.39 (6)

† MOHQOP is *N*-(4-pyridyl)benzamide (Noveron *et al.*, 2002). ‡ Fpp/Fmp/Fop are 4-/3-/2-fluoro-*N*-(4-pyridyl)benzamides (Donnelly *et al.*, 2008). § This work.

JFG thanks Dublin City University for the grants in aid for undergraduate research; special thanks go to Mr Damien McGuirk for providing excellent technical assistance in the undergraduate research laboratories.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3225). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Allen, F. H., Baalham, C. A., Lommerse, J. P. M. & Raithby, P. R. (1998). *Acta Cryst.* B**54**, 320–329.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Chopra, D. & Row, T. N. G. (2008). *CrystEngComm*, **10**, 54–67.
Donnelly, K., Gallagher, J. F. & Lough, A. J. (2008). *Acta Cryst.* C**64**, o335–o340.
Ferguson, G. (1998). *PREP8*. University of Guelph, Canada.
Fink, D. M. & Kurys, B. E. (1996). *Tetrahedron Lett.* **37**, 995–998.
Gelbrich, T., Hursthouse, M. B. & Threlfall, T. L. (2007). *Acta Cryst.* B**63**, 621–632.
Kálmán, A., Párkányi, L. & Argay, G. (1993). *Acta Cryst.* B**49**, 1039–1049.
McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.
Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
Noveron, J. C., Lah, M. S., Del Sesto, R. E., Arif, A. M., Miller, J. S. & Stang, P. J. (2002). *J. Am. Chem. Soc.* **124**, 6613–6625.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Threlfall, T. L. & Gelbrich, T. (2007). *Cryst. Growth Des.* **7**, 2297.
Wardell, S. M. S. V., de Souza, M. V. N., Vasconcelos, T. R. A., Ferreira, M. L., Wardell, J. L., Low, J. N. & Glidewell, C. (2008). *Acta Cryst.* B**64**, 84–100.