organic compounds

4-(4-Fluoro-3-phenoxyphenyl)-6-(4-fluorophenyl)-2-oxo-1,2-dihydro-pyridine-3-carbonitrile and the 6-(4-methylphenyl)- analogue

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The crystal structures of the title compounds, *viz.* $C_{24}H_{14}F_2N_2O_2$, (I), and $C_{25}H_{17}FN_2O_2$, (II), respectively, have been determined in order to unravel the role of an ordered F atom in generating stable supramolecular assemblies. On changing the substitution from fluorine to a methyl group, C—H···F interactions are replaced by C—H···π interactions, revealing the importance of such weak interactions when present alongside N—H···O and C—H···O hydrogen bonds. The dihedral angle between the planes of the 4-fluorophenyl ring and the pyridine ring is 26.8 (1)° in (I), while that between the planes of the 4-methylphenyl and pyridine rings is 29.5 (1)° in (II).

Comment

Crystal engineering *via* manipulation of hydrogen bonding has attracted a lot of interest in recent literature (Aakeröy, 1997; Guru Row, 1999; Desiraju, 2000, 2002; Hunter *et al.*, 2001). Weak C—H···π interactions (Nishio *et al.*, 1995; Umezawa *et al.*, 1999; Takahashi *et al.*, 2000), π stacking (Hunter, 1993, 1994) and C—H···O (Steiner, 2002) interactions have been found to generate different crystalline motifs. Organo-halo compounds have been found also to generate motifs *via* C—H···*X*, *X*···*X* and C—*X*···π interactions (Thalladi *et al.*, 1998). It has been shown that fluorine does not readily accept hydrogen bonding and hence behaves differently than Cl and Br (Shimoni & Glusker, 1994; Howard *et al.*, 1996; Dunitz & Taylor, 1997; Desiraju & Parthasarathi, 1989). Recently, it has been recognized that disordered fluorine alongside a perfectly ordered F atom plays an important role in stabilizing the crystalline lattice formed on cryocooling of liquid fluorinated amines (Chopra *et al.*, 2006). We have been interested in the role that organic fluorine plays in the packing of molecules that exhibit biological activity. Against this background, we report here the molecular and crystal structures of 4-(4-fluoro-

3-phenoxyphenyl)-6-(4-fluorophenyl)-2-oxo-1,2-dihydro-pyridine-3-carbonitrile, (I), and 4-(4-fluoro-3-phenoxyphen-yl)-6-(4-methylphenyl)-2-oxo-1,2-dihydropyridine-3-carbo-nitrile, (II), in order to evaluate the importance of fluorine in


(I) *X*=F
(II) *X*=Me
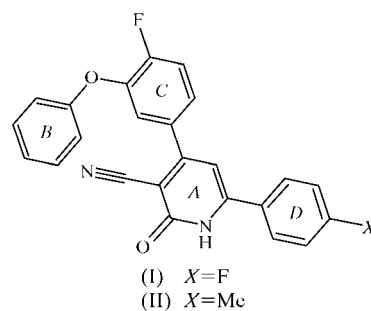
the context of crystal engineering and also to study the influence of substituents of different sizes on the structural parameters of the molecule. Compounds (I) and (II) have important applications in the agrochemical industry, and their biological activity has been studied (Mohan, 2006).

Figs. 1 and 2 are *ORTEP-3* (Farrugia, 1997) views of the molecules of (I) and (II). Relevant bond lengths, bond angles and torsion angles are given in Tables 1 and 3. The two compounds are isomorphous and apart from the additional C—H···F interaction in (I) [which is not present in (II)] are *ipso facto* isostructural. The structures of (I) and (II) have the same molecular dimensions. The bond distances in the
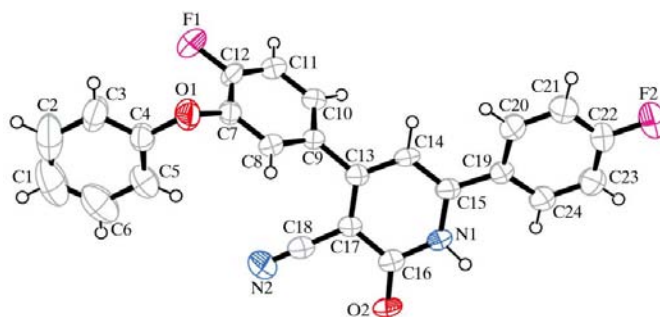
Figure 1
*ORTEP-3* (Farrugia, 1997) view of (I), drawn with 50% probability displacement ellipsoids.
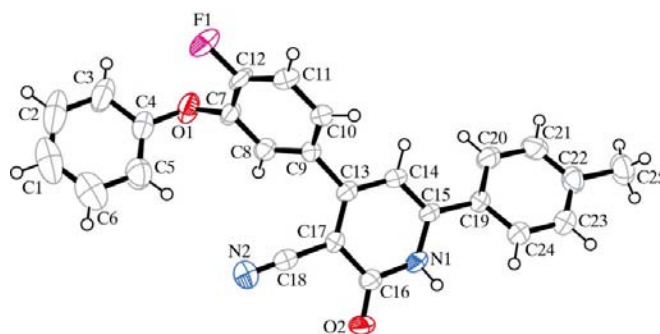
Figure 2
ORTEP-3 (Farrugia, 1997) view of (II), drawn with 50% probability displacement ellipsoids.
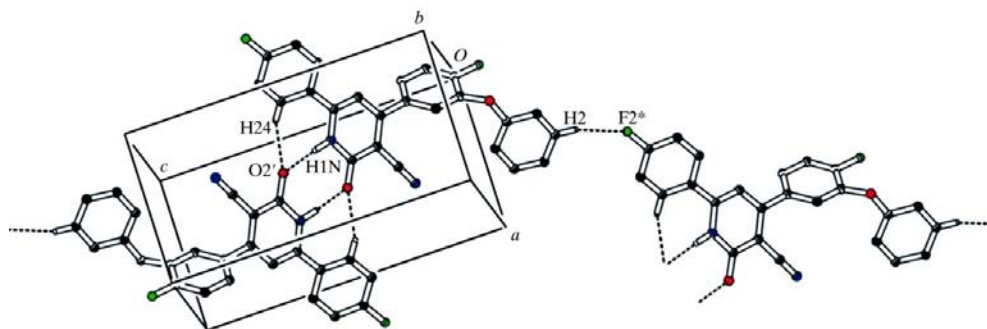
Figure 3
The packing of (I), highlighting N—H···O/C—H···O hydrogen-bonded dimers and C—H···F interactions (hydrogen bonds are shown as dashed lines). Other H atoms have been omitted for clarity. Primes (′) and asterisks (*) on atom labels indicate symmetry-related positions at $(1 - x, 1 - y, 1 - z)$ and $(x + 1, y - 1, z - 1)$, respectively.
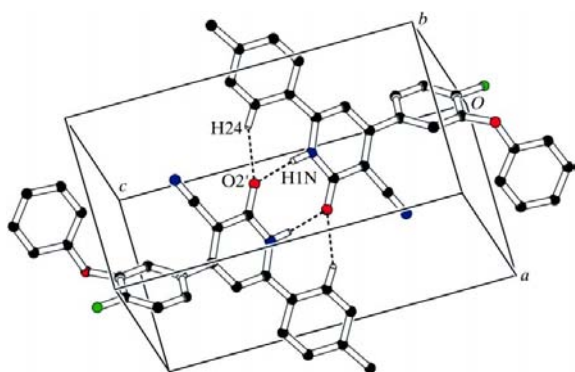
Figure 4
The packing of (II), highlighting N—H···O/C—H···O hydrogen-bonded dimers (hydrogen bonds are shown as dashed lines). Other H atoms have been omitted for clarity. The prime (′) indicates the symmetry-related position at $(1 - x, 1 - y, 1 - z)$.

dihydropyridine ring A (C16/C17/C13/C14/C15/N1) are 1.360 (3)–1.434 (5) Å in (I) and (II), suggesting possible resonance delocalization of the π electrons over the ring (Allen *et al.*, 1987). Ring A is almost planar, with atoms C14 and C15 deviating by 0.011 (4) and −0.011 (3) Å from the plane passing through C13, N1 and C17. The corresponding deviations in (II) are −0.009 (4) and 0.009 (4) Å, respectively. Steric interactions force the benzene rings out of the plane of ring A by 56.1 (1) and 26.8 (1)° for the fluorophenoxy (ring C) and fluorophenyl (ring D) groups in (I). Similar dihedral twists are observed for (II), the values being 55.4 (1) and 29.5 (1)°, respectively. The triple-bond character of the C18≡N2 bond [1.147 (3) and 1.144 (4) Å] and the C17—C18≡N2 bond angle of ∼179° defining the linearity of the cyano group are typical of this group of 2-oxopyridine-3-carbonitrile compounds (Black *et al.*, 1992; Hussain *et al.*, 1996).

The supramolecular assembly in (I) is built up by a network of strong N—H···O hydrogen bonds (involving H1N and O2; Table 2), forming molecular dimers (Fig. 3); these are further stabilized by C—H···O interactions (involving H24) to O2, leading to the formation of bifurcated hydrogen bonds (Jeffrey *et al.*, 1985) that form motifs that can be described as

$R_2^2(8)$ and $R_2^2(14)$ using the graph-set formalism (Bernstein *et al.*, 1995). Weak intermolecular C—H···F interactions involving atom F2 link the molecular dimers, forming chains described by the graph-set descriptor $C(18)$. Furthermore, π–π aromatic interactions, with a $Cg3···Cg3$ distance of 3.605 (3) Å ($Cg3$ is the centroid of ring C), provide additional stability.

In (II), replacement of a fluoro group by a methyl group leads to an identical supramolecular assembly (Fig. 4 and Table 4), except that the C—H···F interaction is now replaced by a C—H···π weak interaction involving atom H25C and the electron-rich 4-methylphenyl group (ring D, with centroid $Cg4$) acting as an electron donor, leading to formation of dimers. These C—H···π interactions further link the molecules that are linked by N—H···O and C—H···O hydrogen bonds similar to those observed in (I), forming alternating dimers built up by a co-operative interplay of strong hydrogen bonds, weak intermolecular interactions and isotropic van der Waals interactions. The $Cg3···Cg3$ stacking distance between C rings is 3.680 (3) Å, which is similar to the value observed in (I). In conclusion, ordered organic fluorine plays an important role in generating a stable packing motif in the crystalline lattice.

Experimental

The general procedure for the syntheses of compounds (I) and (II) is in accordance with literature methods (Dandia *et al.*, 1996; Bhatt *et al.*, 2001). Equimolar (0.02 mol) quantities of 4-fluoro-3-(phenoxyphenyl)benzaldehyde (in MeOH) were added to a mixture of 4-substituted acetophenones (X = F and methyl) in the presence of 40% NaOH (5 ml), and the mixture was stirred at 298 K for 24 h. The contents were poured into crushed ice and purified by recrystallization from ethanol to obtain the pure chalcone. To a mixture of this chalcone, cyanoacetamide was added in an equal amount in absolute ethanol and in the presence of pyridine as catalyst. The reaction mixture was refluxed for 4 h, cooled and ice-cold water added. Pale-yellow crystals were obtained in both cases, and were purified by recrystallization from isopropyl alcohol. Crystals of (I) and (II) suitable for X-ray diffraction were grown from acetone solutions by slow evaporation at 275–277 K.

organic compounds

Compound (I)

Crystal data

$C_{24}H_{14}F_2N_2O_2$
$M_r = 400.37$
Triclinic, $P\bar{1}$
$a = 7.572 (4)$ Å
$b = 9.337 (5)$ Å
$c = 14.027 (8)$ Å
$\alpha = 80.546 (10)°$
$\beta = 86.710 (12)°$
$\gamma = 81.598 (10)°$

$V = 967.2 (9)$ Å^3
$Z = 2$
$D_x = 1.375$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 290 (2)$ K
Block, colorless
$0.09 \times 0.03 \times 0.02$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
$T_{min} = 0.948$, $T_{max} = 0.998$

10089 measured reflections
3843 independent reflections
3260 reflections with $I > 2\sigma(I)$
$R_{int} = 0.073$
$\theta_{max} = 26.4°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.074$
$wR(F^2) = 0.121$
$S = 0.98$
3843 reflections
275 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0358P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.14$ e Å^{-3}
$\Delta\rho_{min} = -0.15$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

F1—C12	1.361 (3)	C13—C17	1.378 (4)
O1—C7	1.387 (3)	C13—C14	1.401 (4)
N1—C15	1.371 (3)	F2—C22	1.354 (3)
N1—C16	1.390 (4)	C15—C14	1.364 (4)
O2—C16	1.244 (3)	C18—N2	1.147 (3)
C15—N1—C16	124.1 (3)	N2—C18—C17	179.6 (4)
C14—C15—N1	118.3 (3)		
C24—C19—C15—C14	153.2 (3)	C4—O1—C7—C8	103.8 (3)
C14—C13—C9—C8	125.1 (3)	C7—O1—C4—C3	140.3 (3)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1N$\cdots$O2^i	0.94 (4)	1.85 (4)	2.786 (4)	175 (3)
C24—H24$\cdots$O2^i	0.93	2.42	3.191 (4)	140
C2—H2$\cdots$F2^{ii}	0.93	2.51	3.399 (6)	159

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x + 1, y - 1, z - 1$.

Compound (II)

Crystal data

$C_{25}H_{17}FN_2O_2$
$M_r = 396.41$
Triclinic, $P\bar{1}$
$a = 7.828 (5)$ Å
$b = 9.523 (7)$ Å
$c = 13.952 (10)$ Å
$\alpha = 76.460 (13)°$
$\beta = 87.250 (14)°$
$\gamma = 83.705 (15)°$

$V = 1004.9 (12)$ Å^3
$Z = 2$
$D_x = 1.310$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 290 (2)$ K
Plate, colorless
$0.15 \times 0.14 \times 0.05$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
$T_{min} = 0.946$, $T_{max} = 0.996$

10474 measured reflections
3976 independent reflections
1997 reflections with $I > 2\sigma(I)$
$R_{int} = 0.067$
$\theta_{max} = 26.4°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.096$
$wR(F^2) = 0.159$
$S = 1.14$
3976 reflections
276 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

F1—C12	1.360 (4)	C14—C15	1.362 (5)
O1—C7	1.386 (4)	C14—C13	1.399 (4)
O2—C16	1.239 (4)	C16—C17	1.434 (5)
N1—C15	1.370 (4)	C13—C17	1.386 (4)
N1—C16	1.383 (4)	C18—N2	1.144 (4)
C15—N1—C16	125.7 (3)	N2—C18—C17	179.2 (4)
C14—C15—N1	117.8 (3)		
C14—C13—C9—C8	127.0 (4)	C14—C15—C19—C24	150.1 (4)
C4—O1—C7—C8	104.1 (4)	C7—O1—C4—C3	134.9 (4)

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1N$\cdots$O2^i	0.86 (4)	1.97 (4)	2.828 (5)	174 (3)
C24—H24$\cdots$O2^i	0.93	2.49	3.173 (5)	130
C25—H25$C\cdots Cg4^{ii}$	0.96	2.85	3.535 (5)	130

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x, -y + 2, -z + 1$.

For both (I) and (II), the amine H atom was located from a difference Fourier map and refined isotropically. The other H atoms were placed in idealized positions (C—H = 0.93 and 0.96 Å) and constrained to ride on the parent atom, with $U_{iso}(H)$ values of $1.2U_{eq}(C)$ for aromatic or $1.5U_{eq}(C)$ for methyl H atoms.

For both compounds, data collection: SMART (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SIR92 (Altomare et al., 1993); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997) and CAMERON (Watkin et al., 1993); software used to prepare material for publication: PLATON (Spek, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB3010). Services for accessing these data are described at the back of the journal.

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