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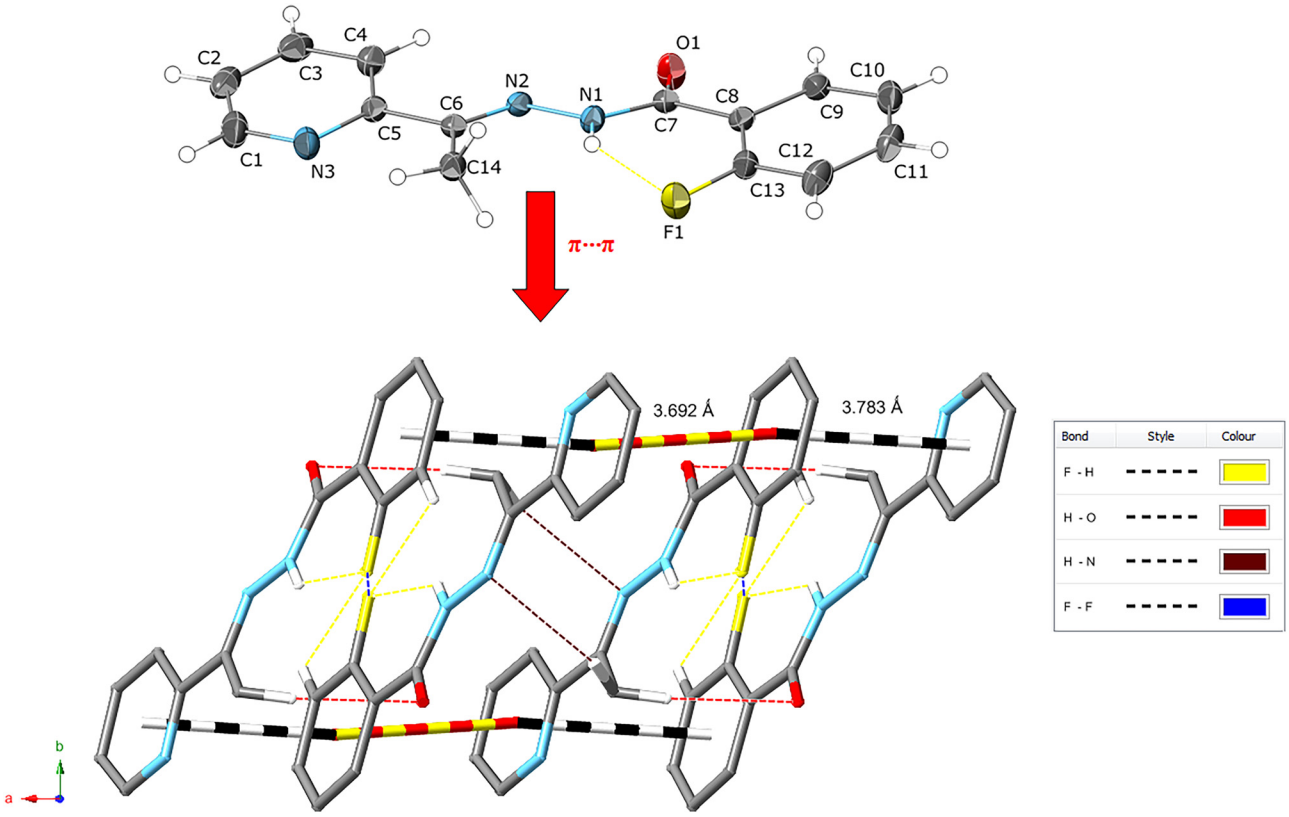
The crystal structure of 2-acetylpyridine-ortho-fluoro-phenylhydrazone, $C_{14}H_{12}FN_3O$



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Abstract

$C_{14}H_{12}FN_3O$, monoclinic, $P2_1/n$ (no. 14), a = 7.4339(2) Å, b = 19.1864(5) Å, c = 8.6861(3) Å, β = 105.705(1)°, V = 1192.65(6) Å^3, Z = 4, $R_{gt}(F)$ = 0.0367, $wR_{ref}(F^2)$ = 0.0486, T = 133(2) K.

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The molecular structure is shown in the figure. Table 1 contains the crystallographic data. The list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.13 × 0.12 × 0.10 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	0.10 mm^{-1}
Diffractometer, scan mode:	Bruker APEX2, φ and ω scans
θ_{max}, completeness:	27.1°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	8338, 2626, 0.049
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2,283
$N(param)_{refined}$:	220
Programs:	Bruker,[1–3] SHELX[4,5]

1 Source of materials

The Schiff base was prepared by mixing equimolar amounts of 2-acetyl-pyridine (10 mmol, 1.21 g) with 2-fluoro-carboxylic acid hydrazide (10 mmol, 1.54 g) in ethanol. The mixed solution was refluxed for 3 h and then was cooled to ambient temperature. The solvent was evaporated under reduced pressure to produce the final compound which was crystallized from ethanol-chloroform (1:4 V/V) as colorless prism-shaped crystals. 1H NMR (DMSO-d_6): δ (ppm) 1.9 (3H, CH3), 7.28–7.32 (4H, m, Ph), 7.56–7.62 (4H, m, PY), 9.97, 10.1 (1H, d, NH (N–H···F)); 13C NMR (DMSO-d_6): δ (ppm) 21.1, 116.63, 116.84, 122.74, 122.89, 125.05, 125.27, 130.62, 133.39, 133.48, 158.49, 160.97, 163.52, 168.68. Anal. Calc. for I: C_{14} $H_{12}FN_3O$ (%) (Mr = 257.27): C, 65.36; H, 4.70; N, 16.33. Found: C, 65.34; H, 4.68; N, 16.32.

2 Experimental details

All chemicals and solvents were used as purchased without further purifications. The high resolution NMR spectra were recorded at room temperature in DMSO-d_6 solution by a Bruker DRX 400 NMR spectrometer (1H 400 MHz; 13C 100 MHz, using TMS as external standard). The intensity data for the compound were collected on a Bruker–Nonius Kappa–CCD diffractometer equipped with a Mo*Kα* IμS microfocus source and an Apex2 CCD detector. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans.[1–3] The structure was solved by Direct Methods (SHELX[4]) and refined against F_o^2 (SHELX-2018).[5] All hydrogen were located by difference Fourier synthesis and refined isotropically. All non-hydrogen atoms were refined anisotropically.[5] MERCURY[6] was used for structure representations.

3 Comment

Acylhydrazones, (–C(O)–NH–N=CH–), and their metal complexes have been proved to possess biological activity, antioxidant activity, luminescent properties and catalytic properties, which makes the study of this class of compounds receive considerable attention.[7–12] Non-covalent interactions such as hydrogen bonding, $\pi\cdots\pi$ stacking and C–H$\cdots\pi$ interactions could be employed to assemble interesting supramolecular networks of some hydrazone ligands and their metal complexes.[8,12–14] Therefore, in continuation to our interest in acylhydrazones and supramolecular chemistry, we have explored the involvement of H-bonds, halogen bonds (e.g. X···X and C–H···X (X = halogen) and $\pi\cdots\pi$) interactions between aromatic systems in the formation of supramolecular assemblies of new fluorinated phenylhydrazone compounds. We believed that the existence of F atom would increase the acidity of the C–H aromatic ring, promoting its role in H-bonds and the formation of $\pi\cdots\pi$ stacking interactions assisted by halogen bonds (X···X), which are not observed in similar compounds.[15–20] From this perspective, the crystal structure (see top part of the figure, 50 % probability ellipsoids) of a new fluorinated acylhydrazone compound, derived from the condensation reaction of 2-acetyl-pyridine with 2-fluoro-carboxylic acid hydrazide is reported, was explored to understand the role of halogen-based bonds in building new mixed "phenyl pyridyl" embraces in its supramolecular architecture.

The bond distances and angles of the Schiff base molecule of the compound fall in normal ranges.[8,15–20] The crystal structure exhibits intramolecular hydrogen bond between the hydrazone N–H group and the F atom, N1–H1···F1 [1.982(1) Å, 134.97(3)°], and forms the six-membered ring motif (see top part of the figure). The molecule is twisted with dihedral angle between the pyridine and the fluorinated phenyl rings of 2.93(5)°.The molecule has a trans configuration with respect to the methylidene unit with torsion angle C6–N2–N1–C7 of 177.73(1)°. The double C6–N2 bond [1.290(2) Å] is within the normal range of similar compounds,[8,16–20]. The N1–C7 bond [1.366(2) Å] is significantly longer than the double C6–N2 bond, which is expected for sp^2-hybridized C–N bonds, indicating conjugation over the hydrazone moiety. The carbonyl oxygen atom is deviated [0.410(1) Å] out of the mean plane passing through the fluorinated phenyl, pyridine rings and the acylhydrazone group, as a result of weak intermolecular hydrogen bond interactions as discussed later on.

The supramolecular self-assembled structure formed through C–H···N intermolecular hydrogen bond between the azomethine –C=N–N– and the methyl groups, resulting in symmetrical $R_2^2(8)$ rings. $\pi\cdots\pi$ stacking interactions are observed between the fluorinated phenyl…pyridine rings connected the centrosymmetric molecules into dimers with centroid-to-centroid distance being 3.692(2) Å and with an inter-plane angle of 2.934(3)°. Each centrosymmetric dimer is further connected via longer stacked interactions [3.783(1) Å; $-x$, $1-y$, $1-z$] leading to chains of stacked molecules along a-axis. All the aryl…aryl interactions are in the offset-face-to-face motif, see bottom part of the figure. These interactions between each two centrosymmetric dimers are further supported by weak hydrogen bonds of the type C14–H14B···O1 [2.679(1) Å, 152.37(1)°, $-x$, $1-y$, $1-z$]. Due to the high polarity of the C–F

bond, the dimeric supramolecules are also involved in other interactions via two types of F···F [2.914(3) Å; C13–F1–F1 106.15(1)°; $-x$, $1-y$, $-z$] and C_{phenyl}–H···F [C12–H12···F1; 2.562(6) Å; 132.59(1)°; $-x$, $1-y$, $-z$] intermolecular interactions, and therefore, the dimeric supramolecules, "aryl embraces", are largely controlled by fluorine interaction effects, in the c-direction (see bottom part of the figure), forming layers in ac plane. The formed layers (in the ac plane) are interconnected (in the b direction) in a zigzag assembly through C=O···H–C_{phenyl} interactions. Considering these non-classical intermolecular hydrogen bonding and stacking interactions, the molecules are arranged in a 3D extended structure.

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