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The crystal structure of 3,5-difluoroisonicotinic acid, C₆H₃F₂NO₂

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.25 × 0.20 × 0.15 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.18 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	26.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	10438, 1158, 0.062
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 881
$N(\text{param})_{\text{refined}}$:	104
Programs:	Bruker [1], SHELX [2], Olex2 [3, 4]

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Abstract

C₆H₃F₂NO₂, monoclinic, $P2_1/n$ (no. 14), $a = 6.8050(10)$ Å, $b = 6.8443(9)$ Å, $c = 12.7196(14)$ Å, $\beta = 94.562(4)^\circ$, $V = 590.54(13)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0395$, $wR_{\text{ref}}(F^2) = 0.1038$, $T = 150(2)$ K.

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The molecular structure is shown in the figure. Hydrogen bonds are shown as dashed lines. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All of the starting materials were used as received. 1.59 g (0.01 mol) 3,5-difluoroisonicotinic acid was added to a solution mixed by 10 mL THF and 1 mL double-distilled water under room temperature. After stirring for 10 min, the solution was filtered and let evaporate automatically. Many colorless block crystals were harvested, which are suitable for single-XRD measurement, yield 67.3% (based on 3,5-difluoroisonicotinic acid).

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.7052(3)	0.2517(3)	0.19376(14)	0.0182(4)
C2	0.5748(3)	0.2754(3)	0.28316(13)	0.0165(4)
C3	0.3854(3)	0.3507(3)	0.27058(13)	0.0176(4)
C4	0.2684(3)	0.3694(3)	0.35407(14)	0.0188(4)
H4	0.138722	0.420521	0.342231	0.023*
C5	0.5192(3)	0.2450(3)	0.46777(13)	0.0195(4)
H5	0.567202	0.206882	0.536910	0.023*
C6	0.6397(3)	0.2259(3)	0.38566(14)	0.0181(4)
F1	0.82217(16)	0.15257(17)	0.40713(8)	0.0279(3)
F2	0.31187(15)	0.41032(17)	0.17503(8)	0.0257(3)
N1	0.3367(2)	0.3161(2)	0.45141(11)	0.0188(4)
O1	0.61250(19)	0.1734(2)	0.10957(9)	0.0232(4)
H1	0.697(4)	0.168(4)	0.050(2)	0.082(10)*
O2	0.8764(2)	0.3024(2)	0.20209(10)	0.0273(4)

Experimental details

The structure was solved by direct methods with the SHELXS program. All H-atoms from C atoms were positioned with idealized geometry and refined isotropically ($U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$) using a riding model with C–H = 0.950 Å. The hydrogen atom of the carboxyl group was positioned on the basis of a Q peak and refined freely.

Comment

It's known that fluorine-substituted isonicotinic acid derivatives have been used as ligands to construct metal-organic frameworks combined with transition metal and lanthanide, including 2-fluoroisonicotinic acid [5, 6] and 3-fluoroisonicotinic acid [7–10]. The same is true for

3,5-dichloroisonicotinate containing complexes [11, 12]. However crystal structures of mono- or multi-fluorine-substituted have not been reported.

As shown in the figure, the title compound crystallizes with the whole organic molecule as its asymmetric unit. All atoms are nearly co-planar except the two O atoms and one H atom from the carboxyl group. The distances of N1...H1 and O1...H1 are 1.636 and 0.99 Å, respectively, and the bond length of C1—O1 is much longer (1.313 Å) than the bond length of C1=O2 (1.212 Å), which indicates that the carboxyl group is protonated. There is an one-dimesional supramolecular structure generated by the O—H...N hydrogen bond through a head-to-tail mode (see the figure).

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