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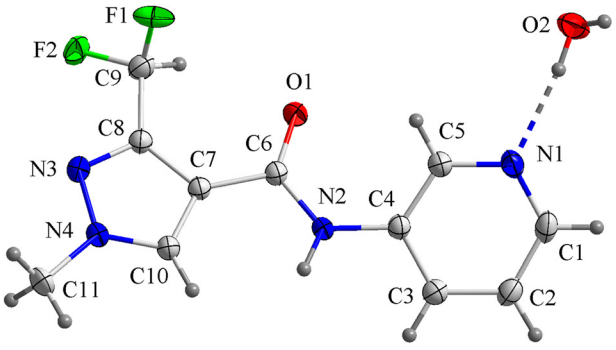
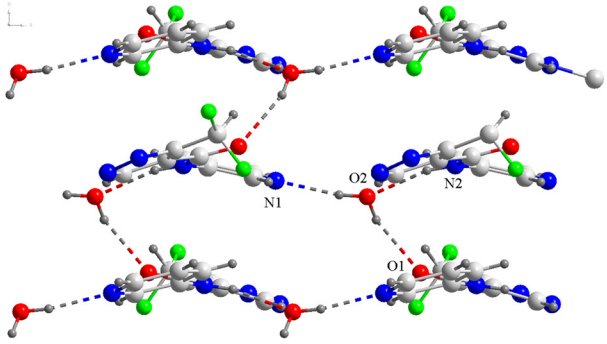
Synthesis and crystal structure of 4-(difluoromethyl)-1-methyl-N-(pyridin-3-yl)-1H-pyrazole-3-carboxamide hydrate, $C_{11}H_{12}F_2N_4O_2$





https://doi.org/10.1515/ncrs-2024-0487
Received December 27, 2024; accepted January 27, 2025;
published online February 7, 2025

CCDC no.: 2419858

$C_{11}H_{12}F_2N_4O_2$, monoclinic, $P2_1/n$, a = 8.2282(16) Å, b = 7.1146(13) Å, c = 21.567(4) Å, β = 100.016(3)°, V = 1243.3(4) Å^3, Z = 4, $R_{gt}(F)$ = 0.0403, $wR_{ref}(F^2)$ = 0.1210, T = 296(2) K.

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.32 × 0.19 × 0.15 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.12 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω scans
θ_{max}, completeness:	25.5°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	8568, 2311, 0.022
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2,070
$N(param)_{refined}$:	182
Programs:	Bruker,[1] SHELX[2,3], Diamond[4]

1 Source of materials

3-Aminopyridine, triethylamine, and dichloromethane were added to a 100 mL one-necked flask, cooled to 0 °C, and a solution of 4-(difluoromethyl)-1-methyl-1*H*-pyrazole-3-carbonyl chloride dissolved in dichloromethane was added slowly under stirring conditions. And they were stirred for 6 h at room temperature. The title compound was obtained by elution and purification using silica gel column chromatography. The crystals of the title compound were obtained after 1 week (Tables 1 and 2).

2 Experimental details

All H atoms were included in calculated positions and refined as riding atoms, with C–H = 0.90–0.97 Å with

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5314 (2)	0.2166 (3)	0.39550 (8)	0.0481 (4)
H1	0.4755	0.2106	0.4294	0.058*
C2	0.6962 (2)	0.2619 (3)	0.40672 (8)	0.0480 (4)
H2	0.7502	0.2872	0.4474	0.058*
C3	0.7806 (2)	0.2693 (2)	0.35673 (8)	0.0416 (4)
H3	0.8922	0.2998	0.3633	0.050*
C4	0.69683 (19)	0.2305 (2)	0.29671 (7)	0.0346 (4)
C5	0.53036 (19)	0.1870 (2)	0.28957 (8)	0.0413 (4)
H5	0.4731	0.1609	0.2494	0.050*
C6	0.72601 (18)	0.2565 (2)	0.18464 (7)	0.0344 (3)
C7	0.84539 (18)	0.2362 (2)	0.14155 (7)	0.0334 (3)
C8	0.81450 (19)	0.2648 (2)	0.07603 (7)	0.0357 (4)
C9	0.6580 (2)	0.3254 (3)	0.03556 (8)	0.0472 (4)
H9	0.5985	0.4116	0.0591	0.057*
C10	1.00780 (18)	0.1787 (2)	0.15396 (7)	0.0378 (4)
H10	1.0683	0.1482	0.1932	0.045*
C11	1.2256 (2)	0.1201 (4)	0.08794 (9)	0.0626 (6)
H11A	1.2835	0.2293	0.0773	0.094*
H11B	1.2144	0.0315	0.0539	0.094*
H11C	1.2864	0.0634	0.1253	0.094*
N1	0.44847 (17)	0.1808 (2)	0.33800 (7)	0.0475 (4)
N2	0.78679 (15)	0.2298 (2)	0.24661 (6)	0.0376 (3)
H2A	0.8913	0.2104	0.2564	0.045*
N3	0.94591 (17)	0.2274 (2)	0.05003 (6)	0.0414 (4)
N4	1.06216 (16)	0.1749 (2)	0.09917 (6)	0.0410 (4)
O1	0.58099 (14)	0.2949 (2)	0.16469 (5)	0.0487 (4)
O2	0.11221 (18)	0.1078 (3)	0.30265 (7)	0.0684 (5)
F1	0.56210 (16)	0.1759 (2)	0.01635 (8)	0.0894 (5)
F2	0.68776 (16)	0.4112 (2)	−0.01736 (6)	0.0845 (5)
H2B	0.215 (4)	0.118 (4)	0.3169 (12)	0.081 (8)*
H2C	0.080 (3)	0.014 (4)	0.3211 (12)	0.080 (8)*

U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C) for all other H atoms.

3 Comments

Succinate dehydrogenase inhibitors (SDHI) are highly active against a wide range of pathogenic fungi and have become the fastest growing new fungicides in recent years.[5] Succinate dehydrogenase inhibitors mainly inhibit the activity of succinate dehydrogenase in pathogenic fungi, block the electron transfer from succinate to ubiquinone, inhibit the tricarboxylic acid (TCA) cycle, reduce adenosine triphosphate (ATP) synthesis, reduce the metabolic level of pathogenic fungi, and ultimately inhibit the growth of mycelium.[6,7] Based on the analysis of commercially available SDHI, it has been found that such fungicides usually consist of three fragments: carboxylic acid, amide bond and amine.[8,9] Most of the newly developed SDHIs undergo group substitution and active substructure splicing while retaining the amide bond backbone.[10] SDHI fungicides have the advantages of novel structure, ease of development, high activity, high selectivity, and good market prospects.[11,12] Although it has been applied as an agricultural fungicide for nearly 70 years, it is still widely concerned by researchers in the field of pesticides and is one of the hotspots for the creation of new pesticides.[13]

In the molecules of the title structure bond lengths and angles are very similar to those given in the literature.[14,15] In the title structure, the dihedral angle between pyridine ring and pyrazole ring is 32.18(6)°. The torsion angles of C8–C7–C6–O1, C8–C7–C6–N2, C7–C6–N2–C5 and C6–N2–C5–C4 are 3.1(2)°, −177.0(1)°, −176.0(1)° and 25.9(2)°, respectively. Intermolecular N–H···O hydrogen bonds and O–H···N hydrogen bonds connect adjacent molecules to form a one-dimensional chain structure. Intermolecular O–H···O hydrogen bonds further connect adjacent one-dimensional chain structures to form two-dimensional network structures.

Acknowledgments: X-ray data were collected at Instrumental Analysis Center Nanchang Hangkong University, Nanchang, 330063, People's Republic of China.
Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: This research was funded by the Special Funding for Major Scientific and Technological Research and Development in Jiangxi Province (20203ABC28W016), Central Finance Forestry Science and Technology Promotion Demonstration Fund Project (JXTG[2024]27), Jiangxi Provincial Forestry Bureau Science and Technology Innovation Project (Innovation Special Project [2024]3) and Ji'an Science and Technology Programme (20222-191725, 20223-127620, 2024H-100185).
Conflict of interest: The authors declare no conflicts of interest regarding this article.

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