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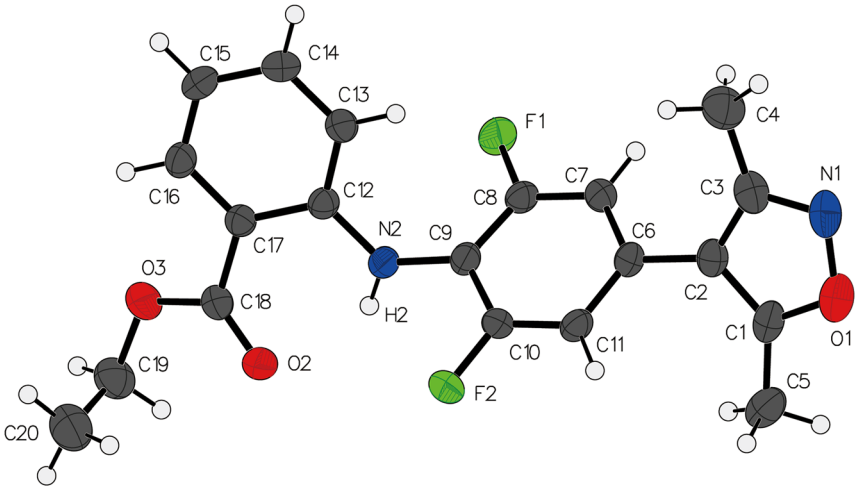
Crystal structure of ethyl 2-((4-(3,5-dimethylisoxazol-4-yl)-2,6-difluorophenyl)amino)benzoate, $C_{20}H_{18}F_2N_2O_3$



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Abstract

$C_{20}H_{18}F_2N_2O_3$, monoclinic, $P2_1/n$ (no. 14), a = 7.5573(10) Å, b = 14.519(2) Å, c = 16.245(2) Å, β = 98.187(3)°, V = 1764.4(4) Å^3, Z = 4, $R_{gt}(F)$ = 0.0420 w$R_{ref}(F^2)$ = 0.1142, T = 205 K.

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The molecular structure is shown in the figure. 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:	Colourless needle
Size:	0.18 × 0.11 × 0.05 mm
Wavelength:	MoKα radiation (0.71073 Å)
μ:	0.11 mm^{-1}
Diffractometer, scan mode:	Bruker Apex-II, φ and ω
θ_{max}, completeness:	27.5°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	15,609, 4025, 0.039
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2974
$N(param)_{refined}$:	298
Programs:	Bruker [1], Shelx [2, 3], Olex2 [4]

1 Source of materials

A mixture of ethyl 2-((4-(2,4-dioxopentan-3-yl)-2,6-difluorophenyl)amino) benzoate (1.88 g, 5 mmol), triethylamine (1.01 g, 10 mmol) and hydroxylamine hydrochloride (0.41 g, 6 mmol) was dissolved in ethanol (10 mL). The mixture was refluxed for 6 h, until the TLC indicated the reaction was completed. The mixture was concentrated. The title compound was separated by silica-gel column chromatography with ethyl acetate-petroleum ether (30 %) gradient solvent system. The target product was obtained as a white solid. Yield: 58.5 %.

2 Experimental details

The crystal structure was solved using the Shelxt program [2] and refined in Shelxl [3]. The Olex2 software package [4] was utilized to visually display the crystal structure.

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.2935 (2)	0.80581 (10)	0.53134 (11)	0.0371 (4)
C2	0.3319 (2)	0.73045 (10)	0.58256 (10)	0.0327 (3)
C3	0.4293 (2)	0.76722 (11)	0.65499 (11)	0.0412 (4)
C4	0.5159 (3)	0.72262 (14)	0.73242 (12)	0.0536 (5)
H4A	0.424941	0.702219	0.764865	0.080*
H4B	0.594336	0.766410	0.764596	0.080*
H4C	0.585005	0.670039	0.718477	0.080*
C5	0.1946 (2)	0.81475 (12)	0.44590 (11)	0.0472 (4)
H5A	0.130192	0.872723	0.440930	0.071*
H5B	0.110604	0.764217	0.435008	0.071*
H5C	0.278543	0.813159	0.405957	0.071*
C6	0.28626 (19)	0.63283 (9)	0.56408 (9)	0.0296 (3)
C7	0.2203 (2)	0.57651 (10)	0.62226 (9)	0.0327 (3)
H7	0.199177	0.600960	0.673540	0.039*
C8	0.1863 (2)	0.48490 (10)	0.60434 (9)	0.0319 (3)
C9	0.22075 (19)	0.44286 (9)	0.53144 (9)	0.0296 (3)
C10	0.2770 (2)	0.50286 (10)	0.47370 (9)	0.0307 (3)
C11	0.3098 (2)	0.59481 (10)	0.48769 (9)	0.0318 (3)
H11	0.347890	0.631852	0.446102	0.038*
C12	0.26996 (19)	0.27538 (9)	0.55691 (9)	0.0280 (3)
C13	0.3653 (2)	0.28517 (10)	0.63687 (9)	0.0325 (3)
H13	0.384196	0.344355	0.659897	0.039*
C14	0.4321 (2)	0.20939 (11)	0.68256 (10)	0.0349 (3)
H14	0.494160	0.217623	0.736437	0.042*
C15	0.4085 (2)	0.12110 (11)	0.64970 (10)	0.0363 (4)
H15	0.452531	0.069626	0.681258	0.044*
C16	0.3193 (2)	0.11017 (10)	0.57005 (10)	0.0339 (3)
H16	0.305434	0.050714	0.547146	0.041*
C17	0.2492 (2)	0.18554 (10)	0.52266 (9)	0.0295 (3)
C18	0.1540 (2)	0.17082 (10)	0.43736 (10)	0.0355 (3)
C19A[a]	0.0050 (3)	0.06043 (14)	0.34238 (12)	0.0415 (5)
H19A[a]	−0.070596	0.112649	0.321602	0.050*
H19B[a]	−0.072768	0.007291	0.347210	0.050*
C19B[b]	0.157 (3)	0.0582 (15)	0.3270 (11)	0.052 (4)
H19C[b]	0.231956	0.007105	0.313141	0.063*
H19D[b]	0.179670	0.110817	0.292292	0.063*
C20A[a]	0.1305 (3)	0.03886 (15)	0.28244 (13)	0.0498 (6)
H20A[a]	0.063474	0.017272	0.230660	0.075*
H20B[a]	0.213250	−0.008657	0.305498	0.075*
H20C[a]	0.196616	0.093895	0.272023	0.075*
C20B[b]	−0.028 (3)	0.0317 (15)	0.3064 (12)	0.053 (4)
H20D[b]	−0.053577	−0.018749	0.341994	0.079*
H20E[b]	−0.050344	0.012334	0.248756	0.079*
H20F[b]	−0.103807	0.083778	0.314671	0.079*
F1	0.11410 (14)	0.43314 (6)	0.66054 (6)	0.0473 (3)
F2	0.30249 (14)	0.46603 (6)	0.39964 (5)	0.0447 (3)
N1A[c]	0.452 (3)	0.8603 (9)	0.6456 (10)	0.0479 (17)
N1B[d]	0.3608 (18)	0.8846 (11)	0.5727 (13)	0.0417 (18)
N2	0.19246 (19)	0.34965 (8)	0.51139 (9)	0.0350 (3)
H2	0.160 (2)	0.3392 (12)	0.4608 (12)	0.042*
O1A[c]	0.3577 (13)	0.8811 (7)	0.5657 (7)	0.0511 (19)
O1B[d]	0.443 (4)	0.8536 (11)	0.6524 (12)	0.052 (3)
O2	0.11793 (17)	0.23072 (8)	0.38560 (7)	0.0451 (3)
O3A[a]	0.1019 (2)	0.08292 (8)	0.42402 (8)	0.0403 (4)
O3B[b]	0.210 (2)	0.0825 (8)	0.4125 (7)	0.039 (3)

[a]Occupancy: 0.911 (4), [b]Occupancy: 0.089 (4), [c]Occupancy: 0.580 (14), [d]Occupancy: 0.420 (14).

3 Comment

Diphenylamine and its derivatives are frequently employed as stabilizers in nitrocellulose-based explosives and propellants, in perfumery, as well as antioxidants in the rubber and elastomer industry. It serves as a foundation for multiple derivatives, employed in the production of dyes, pharmaceuticals, photography chemicals, and other specialized applications, making it a widely produced compound in global chemical industries [5]. In previous studies, the presence of intramolecular hydrogen bonding in the crystals of diphenylamine derivatives has been observed [6, 7]. This article presents a newly discovered diphenylamine derivative and provides a detailed analysis of its crystal structure.

The reported compound exhibits a molecular structure whereby all bond lengths, bond angles, and dihedral angles between atoms fall within the range observed in previously reported similar molecular structures [8–11]. The two substituated phenyl rings exhibit a dihedral angle of 63.8°. Intramolecular hydrogen bonding is observed within the molecule, specifically involving N2–H2···O2, with a bond angle of 130.88(12)° and a bond length of 2.0211(16) Å. Furthermore, weak C–H···[pi] interactions are formed between the phenyl rings and the methyl and ethyl groups.

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