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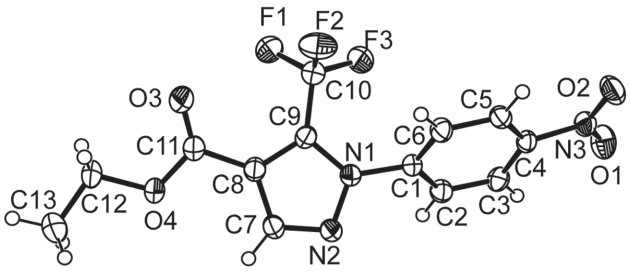
The crystal structure of ethyl 1-(4-nitrophenyl)-5-(trifluoromethyl)-1*H*-pyrazole-4-carboxylate, $C_{13}H_{10}F_3N_3O_4$



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Abstract

$C_{13}H_{10}F_3N_3O_4$, triclinic, $P\bar{1}$ (no. 2), $a = 7.0524(14)$ Å, $b = 7.8044(16)$ Å, $c = 12.954(3)$ Å, $\alpha = 97.93(3)°$, $\beta = 96.29(3)°$, $\gamma = 100.11(3)°$, $V = 688.6(3)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0478$, $wR_{ref}(F^2) = 0.1140$, $T = 200$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.25 × 0.20 × 0.15 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	1.4 cm^{-1}
Diffractometer, scan mode:	Nonius KappCCD, φ and ω
$2\theta_{max}$, completeness:	61°, 98.4%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7772, 4105, 0.031
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2579
$N(param)_{refined}$:	210
Programs:	Nonius programs [1], SHELX [2]

Source of material

Ethyl 1-(4-nitrophenyl)-5-(trifluoromethyl)-1*H*-pyrazole-4-carboxylate was purchased from Sigma-Aldrich. Crystals suitable for the X-ray diffraction experiments were obtained by recrystallization from methanol.

Experimental details

The hydrogen atoms were placed at geometrically idealized positions with C—H distances set to 0.93, 0.97 and 0.96 Å from phenyl, methylene and methyl C atoms, respectively. The isotropic displacement parameters were set equal to $1.2U_{eq}$ and $1.5U_{eq}$ of the parent C atoms.

Comment

Pyrazole derivatives have broad applications in medicinal [3, 4] and agricultural chemistry [5, 6]. The pharmacological activity of these compounds is very diverse. A number of substituted pyrazoles are reported as anti-inflammatory, analgesic, anti-bacterial and anti-cancer agents [3, 4]. It has been found that the presence of a fluoroalkyl substituent on the pyrazole core can significantly increase the lipophilicity and solubility of the compounds and thus improve their biological activity [7–9]. The fluoroalkylated pyrazoles are therefore promising drug and herbicide candidates, while some of them already find practical use, as is the case with the non-steroidal antirheumatic drug celecoxib [10], or a broad-use insecticide

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
F1	0.23950(16)	0.24478(14)	0.13371(8)	0.0545(3)
F2	0.11903(14)	−0.01258(15)	0.16293(9)	0.0621(3)
F3	0.30087(16)	0.01796(16)	0.04237(8)	0.0595(3)
O1	0.27285(19)	0.94909(14)	0.42622(10)	0.0487(3)
O2	0.00370(17)	0.77231(15)	0.43368(10)	0.0476(3)
O3	0.41696(18)	−0.27728(16)	0.09840(11)	0.0572(4)
O4	0.72997(15)	−0.25769(13)	0.16326(8)	0.0358(3)
N1	0.52381(16)	0.22554(15)	0.29754(9)	0.0272(3)
N2	0.69502(17)	0.20633(16)	0.34964(10)	0.0313(3)
N3	0.17602(19)	0.80098(16)	0.42229(10)	0.0331(3)
C1	0.4379(2)	0.37065(17)	0.33726(11)	0.0261(3)
C2	0.5517(2)	0.53877(19)	0.35806(11)	0.0301(3)
H2	0.6829	0.5562	0.3503	0.036*
C3	0.4665(2)	0.68038(18)	0.39055(11)	0.0306(3)
H3	0.5397	0.7944	0.4055	0.037*
C4	0.2712(2)	0.64932(18)	0.40030(11)	0.0267(3)
C5	0.1603(2)	0.48161(18)	0.38674(11)	0.0280(3)
H5	0.0308	0.4640	0.3981	0.034*
C6	0.2464(2)	0.34017(18)	0.35583(11)	0.0293(3)
H6	0.1760	0.2255	0.3476	0.035*
C7	0.7300(2)	0.05689(19)	0.30129(12)	0.0311(3)
H7	0.8388	0.0102	0.3205	0.037*
C8	0.5840(2)	−0.02324(18)	0.21749(11)	0.0295(3)
C9	0.4537(2)	0.08995(18)	0.21664(11)	0.0285(3)
C10	0.2778(2)	0.0844(2)	0.13885(12)	0.0389(4)
C11	0.5641(2)	−0.1974(2)	0.15184(12)	0.0342(3)
C12	0.7245(3)	−0.4309(2)	0.10223(13)	0.0405(4)
H12A	0.7097	−0.4243	0.0276	0.049*
H12B	0.6152	−0.5151	0.1158	0.049*
C13	0.9094(3)	−0.4879(3)	0.13379(16)	0.0586(5)
H13A	1.0166	−0.4045	0.1194	0.088*
H13B	0.9084	−0.6019	0.0947	0.088*
H13C	0.9228	−0.4940	0.2077	0.088*

fipronil [11], both belonging to *N*-phenylpyrazoles. As a part of our ongoing interest on the synthesis, physico-chemical and structural properties of the pyrazole based coordination compounds [12, 13] we examined the crystal structure of the title pyrazole ligand.

The bond lengths and angles within the *N*-phenylpyrazole core are comparable with those reported for the similar pyrazole ligands [14–18]. The C1—N1 bond [1.436(2) Å] allows a rotation of the phenyl relative to the pyrazole ring, thus the dihedral angle between the corresponding ring planes is 49.26(6)°. In similar *N*-phenylpyrazole derivatives this dihedral angle varies in a broad range from 44.8 to 88.9° [15]. The torsion angle C5—C4—N3—O1 of 4.1(2)°, indicates only a slight twisting of the attached nitro group with respect to the phenyl ring. The carbon atom of the pyrazole CF_3 substituent (C10) slightly deviates from the plane of the pyrazole ring [0.14(1) Å]. Inspection of the deviation of F atoms in different fluoromethyl pyrazoles [14, 15] indicates that the CF_3 group can rotate with respect to the pyrazole ring. Thus the displacement of the F1 (chosen as the least deviating from the pyrazole plane) can vary from 0.01 in [15, 16] to 0.7 Å in the present case. The ethyl carboxylate group of the title compound is essentially planar (r.m.s deviation of non-H atoms is 0.05), with the maximum deviation of the terminal C13 atom [0.061(1) Å]. The dihedral angle between the best planes of the pyrazolyl fragment and ethyl carboxylate groups is 13.7(1)°. In the crystal packing, the inversion-related molecules form C–H···O hydrogen-bonded dimers, using the pairs of donors and acceptors from the ethyl carboxylate group [C12—H12a···O3^{i}: C—H 0.97 Å, C···O 3.152(2) Å, H···O 2.60 Å, C—H···O 116°, (i) $-x+1, -y-1, -z$]. The structure is further stabilized by weak C—H···O interactions [C2—H2···O2^{ii}: C—H 0.93 Å, C···O 3.350(2) Å, H···O 2.60 Å, C—H···O 138° (ii) $x+1, +y, +z$], and weak π···π interactions between the neighboring phenyl rings [C*g*···C*g*^{iii} 3.746 Å (iii) $-x+1, -y+1, -z+1$].

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