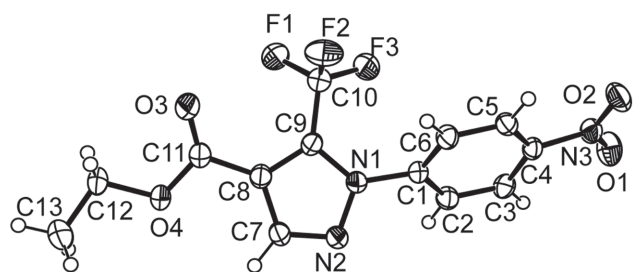


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The crystal structure of ethyl 1-(4-nitrophenyl)-5-(trifluoromethyl)-1*H*-pyrazole-4-carboxylate, $C_{13}H_{10}F_3N_3O_4$



DOI 10.1515/ncrs-2016-0393

Received December 9, 2016; accepted April 5, 2017; available online May 8, 2017

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, $\alpha = 97.93(3)^\circ$, $\beta = 96.29(3)^\circ$, $\gamma = 100.11(3)^\circ$, $V = 688.6(3)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0478$, $wR_{ref}(F^2) = 0.1140$, $T = 200$ K.

CCDC no.: 1542451

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 (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{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 CF₃ 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 CF₃ 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···O3ⁱ: 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···O2ⁱⁱ: 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 $\pi\cdots\pi$ interactions between the neighboring phenyl rings [Cg···Cgⁱⁱⁱ 3.746 Å (iii) $-x+1, -y+1, -z+1$].

Acknowledgements: G. A. B. and S. B. N. thank to the Ministry of Education, Science and Technological Development of the Republic of Serbia for financial support (Project No. 172014 and 172035). Ž. K. J. and M. K. thank the Ministry of Science of the Republic of Montenegro for financial support - National project.

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