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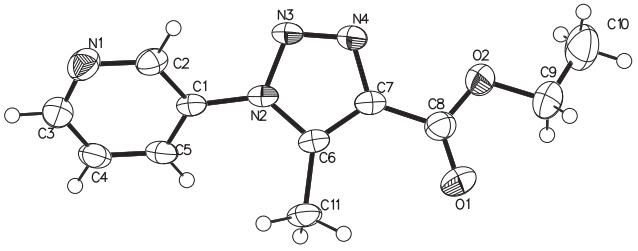
Crystal structure of ethyl 5-methyl-1-(pyridin-3-yl)-1*H*-1,2,3-triazole-4-carboxylate, $C_{11}H_{12}N_4O_2$



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Abstract

$C_{11}H_{12}N_4O_2$, monoclinic, $P2_1/c$ (no. 14), $a = 12.0258(15)$ Å, $b = 8.0563(10)$ Å, $c = 12.4478(13)$ Å, $\beta = 104.157(4)°$, $V = 1169.4(2)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0619$, $wR_{ref}(F^2) = 0.1616$, $T = 293(2)$ 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.

Source of materials

The title compound was obtained using the synthetic method described by Kalmaraj *et al.* [4]. A mixture of 3-aminopyridine (7.24 mmol) in 4.50 mL of HCl/water (1:1) was cooled at 0–5 °C and added dropwise a solution of sodium nitrite 525 mg

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.20 × 0.10 × 0.09 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	1.0 cm^{-1}
Diffractometer, scan mode:	Bruker D8-Venture, φ and ω
$2\theta_{max}$, completeness:	52.8°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	30360, 2387, 0.062
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1697
$N(param)_{refined}$:	156
Programs:	Bruker programs [1], OLEX2 [2], SHELX [3]

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

Atom	x	y	z	U_{iso}*/U_{eq}
O1	0.37425(17)	0.4462(3)	0.25567(18)	0.0956(7)
O2	0.33715(15)	0.3149(3)	0.09306(16)	0.0782(6)
N1	−0.27754(18)	0.4910(3)	0.2075(2)	0.0757(7)
N2	0.01575(16)	0.3800(2)	0.20036(13)	0.0498(5)
N3	0.00426(18)	0.3277(3)	0.09342(14)	0.0598(5)
N4	0.10594(17)	0.3232(3)	0.07596(15)	0.0600(6)
C1	−0.08503(18)	0.3944(3)	0.24116(16)	0.0481(5)
C5	−0.0923(2)	0.3206(3)	0.33902(17)	0.0574(6)
H5	−0.030273	0.263514	0.382722	0.069*
C4	−0.1938(2)	0.3338(3)	0.37000(19)	0.0647(7)
H4	−0.202074	0.285931	0.435574	0.078*
C3	−0.2830(2)	0.4190(4)	0.3025(2)	0.0719(7)
H3	−0.351374	0.426953	0.324400	0.086*
C2	−0.1785(2)	0.4790(3)	0.1786(2)	0.0610(6)
H2	−0.171798	0.529956	0.113455	0.073*
C6	0.12696(19)	0.4092(3)	0.25018(17)	0.0493(5)
C7	0.1834(2)	0.3732(3)	0.16983(17)	0.0526(6)
C8	0.3076(2)	0.3835(3)	0.1790(2)	0.0644(7)
C9	0.4610(3)	0.3085(5)	0.0996(3)	0.1056(12)
H9A	0.492621	0.419888	0.108546	0.127*
H9B	0.499427	0.243363	0.163473	0.127*
C10	0.4798(3)	0.2365(6)	0.0021(4)	0.1204(14)
H10A	0.448907	0.126112	−0.006140	0.181*
H10B	0.560692	0.232254	0.006991	0.181*
H10C	0.442697	0.302312	−0.060733	0.181*
C11	0.1686(2)	0.4705(3)	0.36622(19)	0.0659(7)
H11A	0.110064	0.536834	0.385508	0.099*
H11B	0.236307	0.536367	0.372030	0.099*
H11C	0.186173	0.377557	0.415781	0.099*

(7.60 mmol) in 30 mL of water. The resulting mixture was stirred for 10 minutes, then it was slowly added a solution of sodium azide (612 mg, 9.41 mmol) in 60 mL of cold water. The mixture was stirred for 30 min and extracted with 10 mL of diethyl ether and washed successively with water (three times, 6 mL). The organic phase was dried over anhydrous sodium sulfate and concentrated in vacuum at 30 °C affording pyridine azide. The pyridine azide obtained was dissolved in DMSO and 7.96 mmol (1.1 eq) of ethyl acetoacetate and 1.0 g of K_2CO_3 (1 eq) were added. The mixture was stirred for 3 h and the reaction stopped by adding 30 mL of cold water. The precipitate obtained was filtered under vacuum, washed with cold water and vacuum dryed, obtaining 1.98 g (yield 78%) of the title compound. Finally, crystallization from ethanol gave colourless crystals, m.p. 75–76 °C. **IR** (cm^{-1}) *ν*: 3062, 3036 (C_{Ar}—H); 2981 (C_{sp3}—H); 1630 (C=O$^-$), 1508 (N=N); 1483, 1466, 1447 (C_{Ar}—C_{Ar}); 1446 ($COO^-{}_{as}$). **^{1}H NMR** (500 MHz, DMSO-d_6) *δ* (ppm): 8.72 (s, 1H, H5), 8.71 (d, J = 1.3 Hz, 1H, H3), 8.02 (d, J = 7.2 Hz, 1H, H1), 7.66 (dd, J = 7.9 y 4.6 Hz, 1H, H2), 2.45 (s, 3H, H12). **^{13}C NMR** (500 MHz, DMSO-d_6) *δ* (ppm): 166.20 (C13), 151.13 (C3), 146.15 (C5), 144.32 (C8), 136.67 (C9), 134.12 (C1), 133.65 (C6), 125.64 (C2), 10.20 (C12). **HRESIMS:** m/z 233.1 for $C_{11}H_{13}N_4O_2$ $[M+H]^+$, calculated: m/z 232.2

Experimental details

H atoms were refined with fixed individual displacement parameters, using a riding model with C—H distances of 0.93 Å (for aromatic rings), 0.92 Å; 0.96 Å (for CH_2 and CH_3, respectively), with U(H) values of $1.2U_{eq}$(C) (for CH in aromatic moiety and CH_2), and $1.5U_{eq}$(C) (for CH_3).

Comment

There are numerous papers which report the preparation and characterization of complexes based on 1,2,3-triazole derivatives [5–8]. As a ligand with multiple coordination sites, 1,2,3-triazole-4-carboxylic acid has gained much interest, since it can bridge different metal centers to afford coordination polymers, which show extraordinary structural diversity and luminescent properties [9]. This work forms part of our continuing efforts in the synthesis, structural characterization, and determination of the photophysical properties of metal-organic hybrids based on d^{10} ions and flexible organic ligands [10–14].

In the title compound the triazole fragment makes a dihedral angle of 50.31(13)° and 10.10(18)° with the pyridine and the lateral chain fragments respectively. In the crystal structure weak C_{sp2}—H···N intermolecular interactions are observed. All bond distances and angles are in normal ranges.

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