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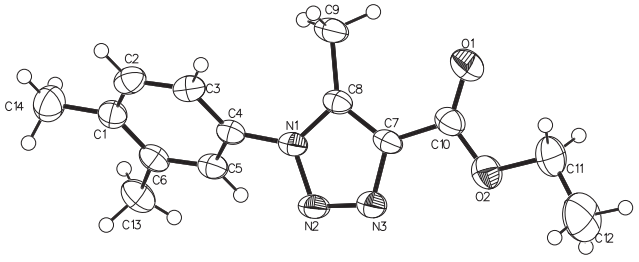
Crystal structure of ethyl 1-(3,4-dimethylphenyl)-5-methyl-1*H*-1,2,3-triazole-4-carboxylate, $C_{14}H_{17}N_3O_2$



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Abstract

$C_{14}H_{17}N_3O_2$, monoclinic, $P2_1/c$ (no. 14), $a = 14.9289(7)$ Å, $b = 7.8070(4)$ Å, $c = 12.4664(7)$ Å, $\beta = 106.821(4)°$, $V = 1390.79(13)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0646$, $wR_{ref}(F^2) = 0.1682$, $T = 293(2)$ K.

CCDC no.: 1572566

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

Table 1: Data collection and handling.

Crystal:	Colourless, parallelepiped
Size:	0.17 × 0.10 × 0.04 nm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
μ:	0.69 cm^{-1}
Diffractometer, scan mode:	Bruker AXS D8-Venture, φ and ω-scans
$2\theta_{max}$, completeness:	59.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13155, 2000, 0.166
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1105
$N(param)_{refined}$:	177
Programs:	Bruker programs [1], SHELX [2], OLEX2 [3], PLATON [4]

Source of material

The title compound was obtained using the synthetic method described earlier [5, 6]. A mixture of dimethylaniline (7.24 mmol) in 4.5 mL of HCl/water (1:1) was cooled at 0–5 °C and added dropwise a solution of sodium nitrite 525 mg (7.60 mmol) in 30 mL of water. The resulting mixture was stirred for 10 min, 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 (3 × 6 mL). The organic phase was dried over anhydrous sodium sulfate and concentrated in vacuum at 30 °C affording the phenylazide. The phenylazide 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, washed with cold water and vacuum dried, obtaining 1.98 g (yield 78%) of the title compound. Finally, crystallization from ethanol gave colourless crystals, mp. 118–120 °C. **IR** (KBr) cm^{-1}: 3085 and 3055 (CAr–H), 1710 (C=O), 1564 (N=N), 1248 (CO–O), 985 (N–N=N). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 7.26 (d, J = 7.8 Hz, 1H), 7.18 (s, 1H), 7.10 (d, J = 7.8 Hz, 1H), 4.42 (q, J = 7.1 Hz, 2H), 2.53 (s, 3H), 2.31 (s, 3H), 2.30 (s, 3H), 1.41 (t, J = 7.1 Hz, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$) δ: 161.9 (C=O), 139.0 (C), 138.9 (C), 138.4 (C), 136.5 (C), 133.1 (C), 130.6 (CH), 126.4 (CH), 122.6 (CH), 61.1 (CH_2), 19.9 (CH_3), 19.6 (CH_3), 14.4 (CH_3), 10.1 (CH_3). **HRESIMS**: m/z 260.1357 for $C_{14}H_18N_3O_2$ $[M + H]^+$, calculated: m/z 260.1399.

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).

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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}
N1	0.44005(17)	0.6373(3)	0.6840(2)	0.0536(7)
N2	0.43402(19)	0.6877(4)	0.5768(2)	0.0661(9)
N3	0.3455(2)	0.6816(4)	0.5197(2)	0.0662(9)
O1	0.14994(19)	0.5468(4)	0.6089(2)	0.0997(10)
O2	0.15645(16)	0.6605(3)	0.4469(2)	0.0822(9)
C1	0.7050(2)	0.6403(4)	0.9202(3)	0.0620(10)
C2	0.6281(3)	0.7028(4)	0.9470(3)	0.0668(10)
H2	0.6356	0.7470	1.0183	0.080*
C3	0.5403(2)	0.7021(4)	0.8714(3)	0.0590(10)
H3	0.4892	0.7459	0.8910	0.071*
C4	0.5295(2)	0.6354(4)	0.7664(3)	0.0518(9)
C5	0.6056(2)	0.5739(4)	0.7373(3)	0.0582(10)
H5	0.5972	0.5306	0.6656	0.070*
C6	0.6948(2)	0.5748(4)	0.8129(3)	0.0593(10)
C7	0.2955(2)	0.6273(4)	0.5882(3)	0.0551(9)
C8	0.3547(2)	0.5970(4)	0.6935(3)	0.0513(9)
C9	0.3374(3)	0.5280(4)	0.7968(3)	0.0721(11)
H9A	0.3924	0.4697	0.8408	0.108*
H9C	0.2859	0.4492	0.7767	0.108*
H9B	0.3228	0.6206	0.8396	0.108*
C10	0.1943(3)	0.6067(5)	0.5511(4)	0.0670(10)
C11	0.0544(3)	0.6479(7)	0.4043(4)	0.1106(16)
H11A	0.0355	0.5286	0.3984	0.133*
H11B	0.0258	0.7047	0.4553	0.133*
C12	0.0245(3)	0.7281(7)	0.2956(5)	0.145(2)
H12A	0.0543	0.6729	0.2462	0.217*
H12C	0.0414	0.8471	0.3026	0.217*
H12B	−0.0422	0.7176	0.2657	0.217*
C13	0.7755(2)	0.5078(5)	0.7764(3)	0.0833(12)
H13C	0.7524	0.4547	0.7042	0.125*
H13A	0.8094	0.4250	0.8298	0.125*
H13B	0.8163	0.6008	0.7719	0.125*
C14	0.7999(3)	0.6437(5)	1.0061(3)	0.0936(13)
H14B	0.8200	0.5286	1.0275	0.140*
H14C	0.7960	0.7063	1.0709	0.140*
H14A	0.8441	0.6984	0.9747	0.140*

[a]Occupancy: 0.854(7)

Comment

1,2,3-Triazoles are an important class of heterocyclic compounds due to their wide range of applications as pharmaceutical agents [7, 8]. The diversity of chemical structures of the 1,2,3-triazole family and their useful biological activities made these compounds attractive targets in organic chemistry and many studies have been reported on the synthesis of these compounds [9–11].

The title compound is isomorphous with the ethyl 1-(4-bromophenyl)-5-methyl-1H-1,2,3-triazole-4 carboxylate analogue [12]. The triazole ring make angles of 7.1(2)° with the lateral chain and 42.41(17)° with the phenyl ring. The crystal packing is stabilized only by van der Waals interactions. All distances and angles are in the normal ranges.

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