organic compounds

Methyl 1-methyl-1H-1,2,3-triazole-4-carboxylate

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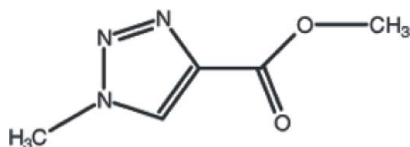Correspondence e-mail: akkurt@erciyes.edu.tr

The title molecule, $C_5H_7N_3O_2$, has an almost planar conformation, with a maximum deviation of 0.043 (3) Å, except for the methyl H atoms. In the crystal structure, intermolecular C—H···O hydrogen bonds link the molecules into layers parallel to the bc plane. Intermolecular π–π stacking interactions [centroid–centroid distances = 3.685 (2) and 3.697 (2) Å] are observed between the parallel triazole rings.

Related literature

For related structures, see: Prabakaran *et al.* (2009*a,b*); Beitelman *et al.* (2007); Jabli *et al.* (2010). For the properties and applications of related compounds, see: Dehne (1994); Fan & Katritzky (1996); Genin *et al.* (2000); Velazquez *et al.* (1998).

Experimental

Crystal data

$C_5H_7N_3O_2$	$\gamma = 76.528$ (14)°
$M_r = 141.14$	$V = 324.37$ (10) Å³
Triclinic, $P\bar{1}$	$Z = 2$
$a = 5.697$ (1) Å	Mo $K\alpha$ radiation
$b = 7.1314$ (11) Å	$\mu = 0.11$ mm^{-1}
$c = 8.6825$ (16) Å	$T = 293$ K
$\alpha = 71.053$ (16)°	$0.15 \times 0.10 \times 0.05$ mm
$\beta = 86.865$ (15)°	

Data collection

Oxford Diffraction Xcalibur Eos (Nova) CCD detector diffractometer	1108 independent reflections
	800 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.049$
6915 measured reflections	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.064$	93 parameters
$wR(F^2) = 0.173$	H-atom parameters constrained
$S = 1.13$	$\Delta\rho_{max} = 0.26$ e Å^{-3}
1108 reflections	$\Delta\rho_{min} = -0.23$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1A···O1^i	0.96	2.59	3.509 (5)	160
C5—H5B···O1^{ii}	0.96	2.39	3.277 (5)	153

Symmetry codes: (i) $x, y, z + 1$; (ii) $x - 1, y, z$.

Data collection: *CrysAlis PRO CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO CCD*; data reduction: *CrysAlis PRO RED* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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supporting information

Methyl 1-methyl-1*H*-1,2,3-triazole-4-carboxylate

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S1. Comment

1,2,3-Triazoles are useful synthetic targets in organic synthesis and are associated with biological properties such as antiviral, antibacterial, antiepileptic and antiallergic (Velazquez *et al.*, 1998; Genin *et al.*, 2000). They have also found applications as agrochemicals, dyes, hotographic materials, and in corrosion inhibition (Fan & Katritzky, 1996; Dehne, 1994). In continuous of our earlier reports (Prabakaran *et al.*, 2009a,b), here the crystal structure of the title compound is presented.

As shown in Fig. 1, the conformation of the title molecule is almost planar, with a maximum deviation of -0.043 (3) Å for O1, except the H atoms of two methyl groups.

In the crystal structure, molecules connect to each other, via the intermolecular C—H···O hydrogen bonds (Table 1, Fig. 2), into two-dimensional layers parallel to the *bc* plane, and intermolecular π–π stacking interactions [$Cg1···Cg1(1 - x, -y, 2 - z)$ = 3.685 (2) Å and $Cg1···Cg1(1 - x, 1 - y, 2 - z)$ = 3.697 (2) Å, where Cg1 is a centroid of the triazole ring] between the parallel triazole rings contribute to the stabilization of the structure.

S2. Experimental

To methyl 1*H*-1,2,3-triazole-4-carboxylate (2 g) in dry DMF (15 ml) maintained at 273 K in nitrogen atmosphere, was added K_2CO_3 (1.3 g), methyliodide (0.98 ml), the mixture was then stirred at 273 K for 1 h, allowed to warm to room temperature and stirred till completion of reaction, monitored by TLC. The reaction mixture on LCMS analysis showed three isomers well separated with their significant retention time and high purity. Three fractions were identified by mass spectroscopy. The solvent was evaporated under vacuo and the residue was isolated into individual isomers by column chromatography. The single crystals of the title compound for X-ray structure analysis were obtained from ether solution by slow evaporation.
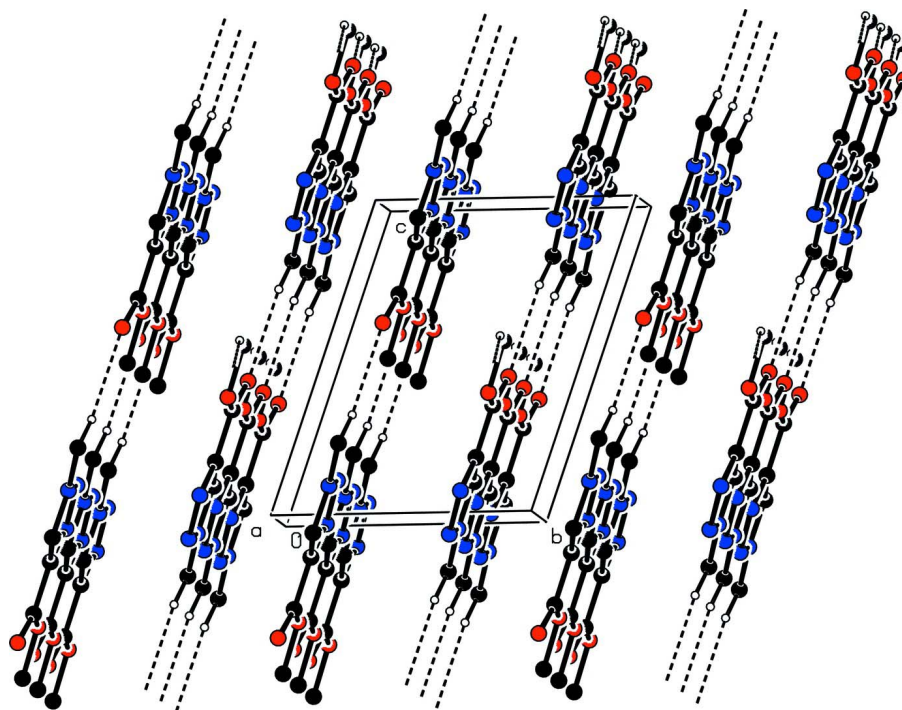
S3. Refinement

H atoms were positioned geometrically with C—H = 0.93-0.96 Å, and were refined in riding mode with $U_{iso}(H)$ = 1.2 or $1.5U_{eq}(C)$. In the final refinement cycles, the inconsistent 33 reflections were omitted.
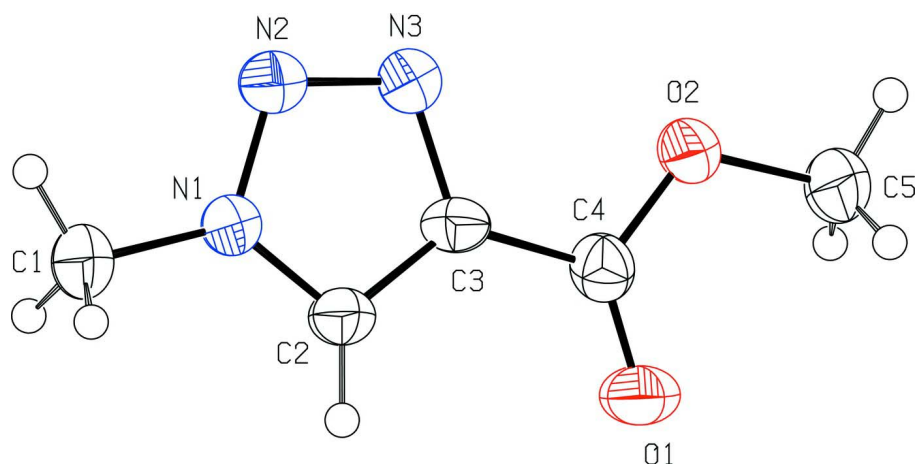
Figure 1

The title molecule showing the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

Figure 2

View of the crystal packing of (I), viewed down the a axis. The H atoms not involved in the hydrogen bonding pattern have been omitted for clarity.

Methyl 1-methyl-1H-1,2,3-triazole-4-carboxylate

Crystal data

$C_5H_7N_3O_2$	$a = 5.697$ (1) Å
$M_r = 141.14$	$b = 7.1314$ (11) Å
Triclinic, $P\overline{1}$	$c = 8.6825$ (16) Å
Hall symbol: -P 1	$\alpha = 71.053$ (16)°

$\beta = 86.865\ (15)°$
$\gamma = 76.528\ (14)°$
$V = 324.37\ (10)$ Å³
$Z = 2$
$F(000) = 148$
$D_x = 1.445$ Mg m⁻³
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1326 reflections
$\theta = 2.0–20.7°$
$\mu = 0.11$ mm⁻¹
$T = 293$ K
Block, colourless
$0.15 \times 0.10 \times 0.05$ mm

Data collection

Oxford Xcalibur Eos (Nova) CCD detector
   diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
ω scans
6915 measured reflections
1108 independent reflections

800 reflections with $I > 2\sigma(I)$
$R_{int} = 0.049$
$\theta_{max} = 25.0°$, $\theta_{min} = 3.1°$
$h = -6\rightarrow6$
$k = -8\rightarrow8$
$l = -10\rightarrow10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.173$
$S = 1.13$
1108 reflections
93 parameters
0 restraints
Primary atom site location: structure-invariant
   direct methods

Secondary atom site location: difference Fourier
   map
Hydrogen site location: inferred from
   neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0741P)^2 + 0.2349P]$
   where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.26$ e Å⁻³
$\Delta\rho_{min} = -0.23$ e Å⁻³

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted R-factors wR and all goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -R-factor-obs etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
O1	0.6694 (5)	0.2352 (5)	0.5832 (3)	0.0591 (13)
O2	0.2797 (4)	0.2639 (4)	0.6475 (3)	0.0440 (9)
N1	0.7108 (5)	0.2390 (4)	1.0644 (3)	0.0361 (10)
N2	0.4740 (5)	0.2478 (5)	1.0897 (4)	0.0430 (11)
N3	0.3757 (5)	0.2534 (5)	0.9553 (4)	0.0417 (10)
C1	0.8687 (7)	0.2325 (6)	1.1941 (5)	0.0471 (14)
C2	0.7651 (6)	0.2415 (5)	0.9131 (4)	0.0369 (11)
C3	0.5521 (6)	0.2492 (5)	0.8434 (4)	0.0342 (11)
C4	0.5106 (6)	0.2486 (5)	0.6793 (4)	0.0373 (12)
C5	0.2257 (7)	0.2676 (7)	0.4852 (5)	0.0532 (14)
H1A	0.77460	0.24230	1.28750	0.0700*

H1B	0.94680	0.34440	1.15670	0.0700*
H1C	0.98850	0.10660	1.22340	0.0700*
H2	0.91520	0.23860	0.86500	0.0440*
H5A	0.26750	0.38410	0.40620	0.0790*
H5B	0.05650	0.27540	0.47490	0.0790*
H5C	0.31730	0.14580	0.46690	0.0790*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0354 (15)	0.103 (3)	0.0513 (18)	−0.0203 (15)	0.0119 (13)	−0.0399 (17)
O2	0.0336 (14)	0.0667 (18)	0.0370 (15)	−0.0139 (12)	−0.0013 (11)	−0.0216 (13)
N1	0.0315 (16)	0.0468 (19)	0.0314 (17)	−0.0104 (13)	0.0007 (13)	−0.0133 (13)
N2	0.0346 (17)	0.057 (2)	0.0386 (18)	−0.0098 (14)	0.0038 (14)	−0.0178 (15)
N3	0.0348 (16)	0.055 (2)	0.0354 (18)	−0.0108 (14)	0.0002 (14)	−0.0140 (14)
C1	0.045 (2)	0.062 (3)	0.036 (2)	−0.0133 (19)	−0.0046 (17)	−0.0165 (19)
C2	0.0306 (18)	0.047 (2)	0.036 (2)	−0.0126 (16)	0.0054 (15)	−0.0155 (17)
C3	0.0286 (18)	0.038 (2)	0.039 (2)	−0.0116 (15)	0.0068 (15)	−0.0144 (16)
C4	0.038 (2)	0.039 (2)	0.038 (2)	−0.0120 (16)	−0.0022 (18)	−0.0137 (17)
C5	0.046 (2)	0.082 (3)	0.040 (2)	−0.025 (2)	−0.0030 (18)	−0.023 (2)

Geometric parameters (Å, º)

O1—C4	1.205 (4)	C3—C4	1.459 (5)
O2—C4	1.331 (4)	C1—H1A	0.9600
O2—C5	1.449 (5)	C1—H1B	0.9600
N1—N2	1.345 (4)	C1—H1C	0.9600
N1—C1	1.462 (5)	C2—H2	0.9300
N1—C2	1.328 (4)	C5—H5A	0.9600
N2—N3	1.307 (5)	C5—H5B	0.9600
N3—C3	1.361 (5)	C5—H5C	0.9600
C2—C3	1.367 (5)		
O1···C5^i	3.277 (5)	C4···N2^{vii}	3.439 (5)
O2···N3	2.731 (4)	C5···C1^x	3.435 (6)
O1···H1A^{ii}	2.5900	C5···O1^{vi}	3.277 (5)
O1···H5A	2.6300	C1···H5B^{ix}	2.8500
O1···H5B^i	2.3900	C4···H5A^{iv}	3.0300
O1···H5C	2.5900	H1A···O1^{xi}	2.5900
O1···H1C^{iii}	2.8400	H1A···H5B^{ix}	2.4500
O1···H5A^{iv}	2.8500	H1B···N3^{viii}	2.9100
O1···H5C^v	2.8700	H1C···O1^{iii}	2.8400
O1···H2	2.8900	H2···O1	2.8900
O2···H2^{vi}	2.7300	H2···O2^i	2.7300
N2···C3^{vii}	3.438 (5)	H2···N3^i	2.8100
N2···C4^{vii}	3.439 (5)	H5A···O1	2.6300
N3···O2	2.731 (4)	H5A···O1^{iv}	2.8500
N3···C1^{viii}	3.434 (6)	H5A···C4^{iv}	3.0300

N3⋯C3vii	3.376 (5)	H5B⋯O1vi	2.3900
N3⋯H2vi	2.8100	H5B⋯C1x	2.8500
N3⋯H1Bviii	2.9100	H5B⋯H1Ax	2.4500
C1⋯C5ix	3.435 (6)	H5C⋯O1	2.5900
C1⋯N3viii	3.434 (6)	H5C⋯O1v	2.8700
C3⋯N3vii	3.376 (5)	H5C⋯H5Cv	2.5200
C3⋯N2vii	3.438 (5)		
C4—O2—C5	115.6 (3)	N1—C1—H1B	109.00
N2—N1—C1	120.4 (3)	N1—C1—H1C	110.00
N2—N1—C2	110.7 (3)	H1A—C1—H1B	109.00
C1—N1—C2	129.0 (3)	H1A—C1—H1C	109.00
N1—N2—N3	107.9 (3)	H1B—C1—H1C	109.00
N2—N3—C3	107.9 (3)	N1—C2—H2	128.00
N1—C2—C3	105.0 (3)	C3—C2—H2	127.00
N3—C3—C2	108.6 (3)	O2—C5—H5A	109.00
N3—C3—C4	123.5 (3)	O2—C5—H5B	109.00
C2—C3—C4	127.9 (3)	O2—C5—H5C	110.00
O1—C4—O2	123.8 (3)	H5A—C5—H5B	109.00
O1—C4—C3	123.3 (3)	H5A—C5—H5C	109.00
O2—C4—C3	112.9 (3)	H5B—C5—H5C	109.00
N1—C1—H1A	109.00		
C5—O2—C4—O1	−1.1 (6)	N2—N3—C3—C4	178.5 (3)
C5—O2—C4—C3	179.0 (3)	N1—C2—C3—N3	0.7 (4)
C1—N1—N2—N3	179.6 (3)	N1—C2—C3—C4	−178.0 (3)
C2—N1—N2—N3	0.8 (4)	N3—C3—C4—O1	−176.4 (4)
N2—N1—C2—C3	−0.9 (4)	N3—C3—C4—O2	3.5 (5)
C1—N1—C2—C3	−179.6 (4)	C2—C3—C4—O1	2.1 (6)
N1—N2—N3—C3	−0.3 (4)	C2—C3—C4—O2	−178.0 (4)
N2—N3—C3—C2	−0.2 (4)		

Symmetry codes: (i) $x+1$, y, z; (ii) x, y, $z−1$; (iii) $−x+2$, $−y$, $−z+2$; (iv) $−x+1$, $−y+1$, $−z+1$; (v) $−x+1$, $−y$, $−z+1$; (vi) $x−1$, y, z; (vii) $−x+1$, $−y$, $−z+2$; (viii) $−x+1$, $−y+1$, $−z+2$; (ix) $x+1$, y, $z+1$; (x) $x−1$, y, $z−1$; (xi) x, y, $z+1$.

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C1—H1A⋯O1xi	0.96	2.59	3.509 (5)	160
C5—H5B⋯O1vi	0.96	2.39	3.277 (5)	153

Symmetry codes: (vi) $x−1$, y, z; (xi) x, y, $z+1$.