

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

5-Methyl-1-phenyl-1*H*-1,2,3-triazole-4-carboxylic acid

Jin Rui Lin, Ji Yuan Yao and Hong Zhao*

Ordered Matter Science Research Center, College of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096, People's Republic of China
Correspondence e-mail: zhaohong@seu.edu.cn

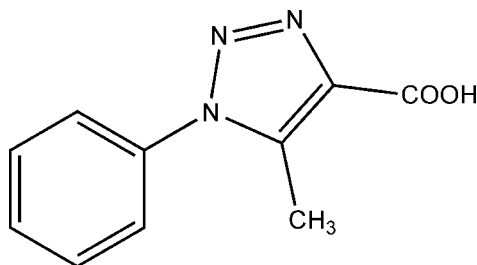
Received 25 July 2008; accepted 25 August 2008

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å;
R factor = 0.063; wR factor = 0.149; data-to-parameter ratio = 17.0.

The title compound, $\text{C}_{10}\text{H}_9\text{N}_3\text{O}_2$, was synthesized from azidobenzene and ethyl acetylacetate. A pair of hydrogen bonds [2.617 (2) Å] interconnects a pair of the carboxyl groups, forming an $R_2^2(8)$ inversion dimer, a frequent motif in carboxylic acids. In the title structure, the bonding H atom in the aforementioned O—H...O hydrogen bond is significantly shifted towards the acceptor O atom [the donor and acceptor O—H distances are 1.25 (4) and 1.38 (4) Å, respectively]. A plot of the O...O versus O—H distances in compounds with paired carboxyl groups shows that the title structure belongs to the group of structures with abnormally long O—H distances with regard to the O...O contacts. The displacement of the bonding H atom towards the centre of the hydrogen bond is concomitant with more equal C—O bonding distances in the carboxyl group.

Related literature

For related literature, see: El Khadem *et al.* (1968); Olesen *et al.* (2003); Tian *et al.* (2005); Allen (2002); Etter *et al.* (1990); Radl *et al.* (2000).



Experimental

Crystal data

$\text{C}_{10}\text{H}_9\text{N}_3\text{O}_2$
 $M_r = 203.20$
Monoclinic, $C2/c$
 $a = 23.616$ (3) Å
 $b = 7.7189$ (15) Å
 $c = 12.606$ (2) Å
 $\beta = 113.18$ (3)°

$V = 2112.5$ (8) Å³
 $Z = 8$
Mo $K\alpha$ radiation
 $\mu = 0.09$ mm⁻¹
 $T = 293$ (2) K
 $0.20 \times 0.18 \times 0.15$ mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan
(*CrystalClear*; Rigaku, 2005)
 $T_{\min} = 0.965$, $T_{\max} = 0.977$

10370 measured reflections
2400 independent reflections
1583 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.053$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.062$
 $wR(F^2) = 0.148$
 $S = 1.08$
2400 reflections
141 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.14$ e Å⁻³
 $\Delta\rho_{\min} = -0.18$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O2}-\text{H2}\cdots\text{O1}^{\dagger}$	1.25 (4)	1.38 (4)	2.617 (2)	173 (3)

Symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL/PC* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL/PC*.

This work was supported by a start-up grant from Southeast University to HZ.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FB2106).

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
El Khadem, H., Mansour, H. A. R. & Meshreki, M. H. (1968). *J. Chem. Soc. C*, pp. 1329–1331.
Etter, M. C., MacDonald, J. & Bernstein, J. (1990). *Acta Cryst.* **B46**, 256–262.
Olesen, P. H., Sorensen, A. R., Urso, B., Kurtzhals, P., Bowler, A. N., Ehrbar, U. & Hansen, B. F. (2003). *J. Med. Chem.* **46**, 3333–3341.
Radl, S., Hezky, P., Konvicka, P. & Krejci, J. (2000). *Collect. Czech. Chem. Commun.* **65**, 1093–1108.
Rigaku (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
Tian, L., Sun, Y., Li, H., Zheng, X., Cheng, Y., Liu, X. & Qian, B. (2005). *J. Inorg. Biochem.* **99**, 1646–1652.

supplementary materials

Acta Cryst. (2008). E64, o1843 [doi:10.1107/S1600536808027311]

5-Methyl-1-phenyl-1*H*-1,2,3-triazole-4-carboxylic acid

J. R. Lin, J. Y. Yao and H. Zhao

Comment

Many triazole-related molecules have received much attention because of their biological activities (Olesen *et al.*, 2003; Tian *et al.*, 2005). We report herein the crystal structure of the title compound (Fig. 1).

The molecules are arranged into inversion dimers *via* carboxyl groups that are interconnected by pairs of the O-H \cdots O hydrogen bonds (Fig. 2). The graph-set motif is $R^2_2(8)$ (Etter *et al.*, 1990). The peculiarity of the title structure consists in the displacement of the bonding hydrogen towards the centre of the hydrogen bond (Tab. 1). Though not unprecedented, Fig. 3 shows that the title structure belongs among rather rare examples where in a relatively long O \cdots O hydrogen bond the involved hydrogen is shifted towards the centre. The displacement of the bonding hydrogen towards the centre of the hydrogen bond is concomitant to more equal C-O bonding distances in the carboxyl group.

The dihedral angle between the triazole and phenyl ring planes is 41.85 (1) $^\circ$.

Experimental

The title compound was prepared from azidobenzene according to the reported method (El Khadem *et al.*, 1968). The colourless prisms (average size: 0.5 \times 0.8 \times 1.0 mm) were obtained by slow evaporation from 95% ethanol/water solution at room temperature.

Refinement

All the hydrogen atoms could have been discerned in the difference electron density map, nevertheless, all the H atoms attached to the carbon atoms were constrained in a riding motion approximation. $C_{\text{aryl}}\text{---H}=0.93$ Å, with $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})$. $C_{\text{methyl}}\text{---H}=0.96$ Å, with $U_{\text{iso}}(\text{H})=1.5U_{\text{eq}}(\text{C})$. The hydroxyl hydrogen was refined freely.

Figures

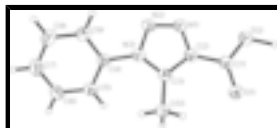


Fig. 1. The title molecule, showing the atomic numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.



Fig. 2. Packing diagram of the title molecules, showing the structure along the *b* axis.

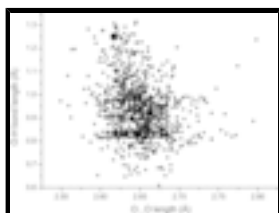


Fig. 3. The O-H vs. O...O distances (Å) for the structural motif of the pairs of the carboxyl groups that are interconnected by the hydrogen bonds. The structures were found in the Cambridge Structural Database (Allen, 2002; CSD version 5.29 including the updates from January 25, 2008). The query has been limited for the structures with the R factor <0.05; with no errors, no disorder. The polymers and the powder samples were excluded as well. 1028 hits were found. The title structure is symbolized by the large circle in the left upper corner of the plot.

5-Methyl-1-phenyl-1*H*-1,2,3-triazole-4-carboxylic acid

Crystal data

$C_{10}H_9N_3O_2$

$M_r = 203.20$

Monoclinic, *C2/c*

Hall symbol: -C 2yc

$a = 23.616 (3) \text{ \AA}$

$b = 7.7189 (15) \text{ \AA}$

$c = 12.606 (2) \text{ \AA}$

$\beta = 113.18 (3)^\circ$

$V = 2112.5 (8) \text{ \AA}^3$

$Z = 8$

$F_{000} = 848$

$D_x = 1.278 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 2025 reflections

$\theta = 2.8\text{--}27.5^\circ$

$\mu = 0.09 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Prism, colourless

$0.20 \times 0.18 \times 0.15 \text{ mm}$

Data collection

Rigaku SCXmini
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293(2) \text{ K}$

ω scans

Absorption correction: multi-scan
(CrystalClear; Rigaku, 2005)

$T_{\min} = 0.965$, $T_{\max} = 0.977$

10370 measured reflections

2400 independent reflections

1583 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.053$

$\theta_{\text{max}} = 27.5^\circ$

$\theta_{\text{min}} = 2.8^\circ$

$h = -30 \rightarrow 30$

$k = -9 \rightarrow 10$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Secondary atom site location: difference Fourier map

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.062$$

$$wR(F^2) = 0.148$$

$$S = 1.08$$

2400 reflections

141 parameters

31 constraints

Primary atom site location: structure-invariant direct methods

Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2 + 0.4952P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.14 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and 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 threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.41473 (10)	0.1278 (3)	0.72134 (18)	0.0555 (5)
C2	0.34886 (9)	0.1172 (3)	0.69727 (16)	0.0491 (5)
C3	0.31868 (9)	0.1493 (2)	0.76949 (15)	0.0461 (5)
C4	0.20319 (9)	0.1379 (2)	0.72119 (16)	0.0466 (5)
C5	0.20037 (10)	0.0713 (3)	0.82132 (17)	0.0538 (5)
H5	0.2350	0.0218	0.8780	0.065*
C6	0.14517 (11)	0.0799 (3)	0.8352 (2)	0.0655 (6)
H6	0.1426	0.0364	0.9020	0.079*
C7	0.09414 (11)	0.1525 (3)	0.7506 (2)	0.0761 (7)
H7	0.0571	0.1574	0.7603	0.091*
C8	0.09745 (10)	0.2184 (3)	0.6509 (2)	0.0734 (7)
H8	0.0626	0.2666	0.5940	0.088*
C9	0.15210 (9)	0.2129 (3)	0.63569 (18)	0.0578 (5)
H9	0.1547	0.2585	0.5695	0.069*
C10	0.34155 (10)	0.2068 (3)	0.89199 (16)	0.0579 (6)
H10A	0.3099	0.2716	0.9041	0.087*
H10B	0.3773	0.2786	0.9091	0.087*
H10C	0.3522	0.1073	0.9417	0.087*
N1	0.30730 (8)	0.0743 (2)	0.58988 (14)	0.0577 (5)
N2	0.25230 (8)	0.0763 (2)	0.59058 (13)	0.0571 (5)
N3	0.25867 (7)	0.1228 (2)	0.70044 (13)	0.0475 (4)

supplementary materials

O1	0.45271 (7)	0.1465 (2)	0.82345 (13)	0.0733 (5)
O2	0.43008 (7)	0.1161 (3)	0.63484 (13)	0.0799 (6)
H2	0.4867 (19)	0.125 (5)	0.661 (3)	0.193 (17)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0557 (12)	0.0670 (14)	0.0444 (12)	0.0033 (10)	0.0201 (10)	0.0024 (10)
C2	0.0508 (11)	0.0572 (12)	0.0404 (11)	0.0029 (9)	0.0190 (9)	0.0016 (8)
C3	0.0505 (11)	0.0472 (11)	0.0407 (10)	0.0013 (8)	0.0182 (9)	0.0020 (8)
C4	0.0488 (10)	0.0506 (11)	0.0416 (11)	-0.0023 (9)	0.0190 (9)	-0.0050 (8)
C5	0.0562 (12)	0.0617 (13)	0.0443 (11)	-0.0008 (9)	0.0206 (10)	-0.0031 (9)
C6	0.0660 (14)	0.0826 (16)	0.0573 (14)	-0.0081 (12)	0.0343 (12)	-0.0071 (11)
C7	0.0548 (14)	0.102 (2)	0.0797 (17)	-0.0006 (13)	0.0350 (14)	-0.0096 (15)
C8	0.0528 (13)	0.0884 (18)	0.0717 (16)	0.0117 (12)	0.0165 (12)	0.0013 (13)
C9	0.0566 (13)	0.0654 (14)	0.0481 (12)	0.0046 (10)	0.0169 (10)	0.0026 (10)
C10	0.0580 (12)	0.0714 (15)	0.0429 (11)	-0.0024 (10)	0.0184 (10)	-0.0071 (10)
N1	0.0544 (10)	0.0770 (12)	0.0430 (10)	0.0019 (9)	0.0208 (8)	-0.0018 (8)
N2	0.0567 (11)	0.0774 (13)	0.0381 (9)	-0.0015 (8)	0.0196 (8)	-0.0064 (8)
N3	0.0505 (9)	0.0554 (10)	0.0372 (8)	0.0005 (7)	0.0178 (7)	-0.0002 (7)
O1	0.0532 (9)	0.1133 (14)	0.0506 (9)	-0.0020 (8)	0.0176 (8)	-0.0084 (8)
O2	0.0585 (10)	0.1372 (16)	0.0504 (9)	0.0041 (9)	0.0282 (8)	0.0032 (9)

Geometric parameters (\AA , $^\circ$)

C1—O1	1.254 (2)	C6—H6	0.9300
C1—O2	1.281 (2)	C7—C8	1.386 (3)
C1—C2	1.465 (3)	C7—H7	0.9300
C2—N1	1.364 (3)	C8—C9	1.378 (3)
C2—C3	1.382 (3)	C8—H8	0.9300
C3—N3	1.356 (2)	C9—H9	0.9300
C3—C10	1.489 (3)	C10—H10A	0.9600
C4—C5	1.389 (3)	C10—H10B	0.9600
C4—C9	1.389 (3)	C10—H10C	0.9600
C4—N3	1.438 (2)	N1—N2	1.302 (2)
C5—C6	1.384 (3)	N2—N3	1.380 (2)
C5—H5	0.9300	O2—H2	1.25 (4)
C6—C7	1.376 (3)		
O1—C1—O2	123.66 (19)	C8—C7—H7	119.7
O1—C1—C2	119.41 (19)	C9—C8—C7	120.3 (2)
O2—C1—C2	116.94 (19)	C9—C8—H8	119.8
N1—C2—C3	109.96 (17)	C7—C8—H8	119.8
N1—C2—C1	120.64 (17)	C8—C9—C4	118.7 (2)
C3—C2—C1	129.38 (19)	C8—C9—H9	120.7
N3—C3—C2	103.29 (16)	C4—C9—H9	120.7
N3—C3—C10	124.88 (17)	C3—C10—H10A	109.5
C2—C3—C10	131.79 (18)	C3—C10—H10B	109.5
C5—C4—C9	121.47 (19)	H10A—C10—H10B	109.5

C5—C4—N3	120.56 (18)	C3—C10—H10C	109.5
C9—C4—N3	117.90 (17)	H10A—C10—H10C	109.5
C6—C5—C4	118.8 (2)	H10B—C10—H10C	109.5
C6—C5—H5	120.6	N2—N1—C2	108.68 (15)
C4—C5—H5	120.6	N1—N2—N3	107.15 (15)
C7—C6—C5	120.2 (2)	C3—N3—N2	110.92 (15)
C7—C6—H6	119.9	C3—N3—C4	131.92 (16)
C5—C6—H6	119.9	N2—N3—C4	117.15 (15)
C6—C7—C8	120.5 (2)	C1—O2—H2	113.8 (15)
C6—C7—H7	119.7		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2 \cdots O1 ⁱ	1.25 (4)	1.38 (4)	2.617 (2)	173 (3)

Symmetry codes: (i) $-x+1, y, -z+3/2$.

Fig. 1

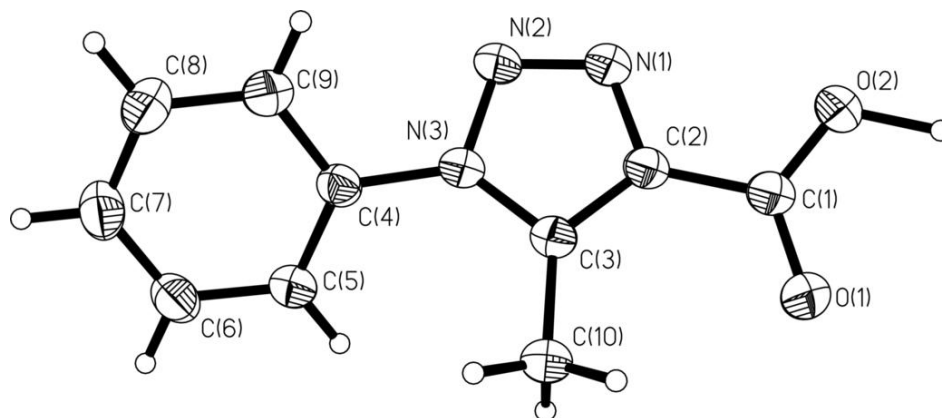


Fig. 2

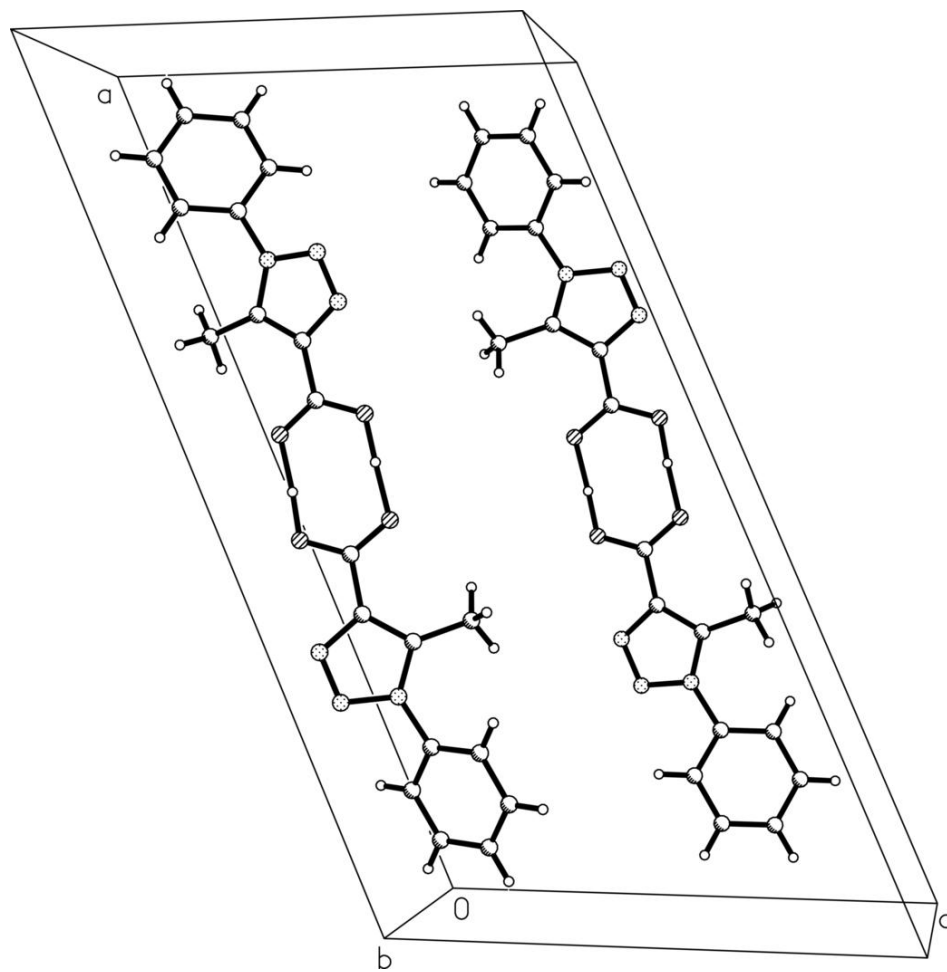


Fig. 3

