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1-Anilino-5-methyl-1*H*-1,2,3-triazole-4-carbaldehyde

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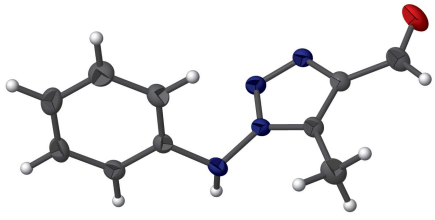
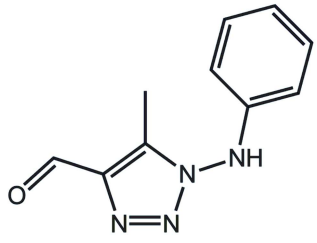
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{10}H_{10}N_4O$, is twisted about the N_{ring}—N_{amine} bond with the dihedral angle between the 1,2,3-triazolyl and N-bound phenyl rings being 79.14 (9)°. The C-bound aldehyde group is coplanar with the triazolyl ring, with the N—C—C—O torsion angle being 3.5 (3)°. While coplanar, the aldehyde O atom is orientated in the opposite direction to the triazolyl-bound methyl group. The most prominent feature of the molecular packing is the formation of zigzag chains (glide symmetry) along the *b* axis and mediated by amine-N—H···N(triazolyl) hydrogen bonds. The chains are connected into supramolecular layers by phenyl- and methyl-C—H···O(aldehyde) interactions, with phenyl groups projecting to either side. Layers stack along the *c* axis with no directional interactions between them.

3D view



Chemical scheme



Structure description

Interest in 1,2,3-triazoles relates, in part, to their biological activity (Dehaen & Bakulev, 2014). For example, compounds related to the title compound have been evaluated previously for activity against Cantagalo virus (Jordão *et al.*, 2009) and for anti-tubercular activity (Jordão *et al.*, 2011).

The title compound, Fig. 1, comprises two effectively co-planar regions. Thus, the aldehyde group connected at C1 is co-planar with the 1,2,3-triazolyl ring (r.m.s. deviation = 0.007 Å), forming a N4—C1—C10—O1 torsion angle of 3.5 (3)°. Indeed, the r.m.s.

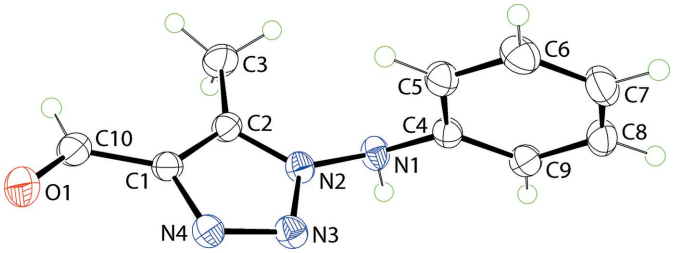


Figure 1
The molecular structure of the title compound showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level.

deviation of the least-squares plane through all non-hydrogen atoms in the molecule excluding those of the phenyl ring is 0.019 Å. The latter sits almost prime to the remainder of the molecule, forming a dihedral angle of 79.14 (9)° with the triazolyl ring. The aldehyde-O1 atom occupies a position *anti* with respect to the triazolyl-bound methyl group.

Amine-N—H···N(triazoyl) hydrogen bonds feature in the crystal structure, Table 1, and lead to supramolecular zigzag chains along the *b* axis. The chains thus formed are linked into a layer in the *ab* plane, Fig. 2, by phenyl-C—H···O(aldehyde) and methyl-C—H···O(aldehyde) interactions, indicating the aldehyde-O atom accepts two interactions. The phenyl groups lie to either side of the supramolecular layers that stack along the *c* axis. However, there are no directional interactions between successive layers.

1,2,3-Triazole derivatives generated in the biological studies (*e.g.* Jordão *et al.*, 2009) have provided crystals enabling delineation of the dependency of molecular packing patterns upon the electronegativity of the substituents, *i.e.* *N*-aryl-amino-1,2,3-triazole esters (Cunha *et al.*, 2013) and *N*-(aryl-amino)-1,2,3-triazole-4-carbohydrazides (Seth *et al.*, 2015).

Synthesis and crystallization

To a solution of oxalyl chloride (3.00 mmol) in anhydrous CH_2Cl_2 (3.7 mL), maintained under nitrogen at −78°C, was added dropwise DMSO (0.42 mL, 6.0 mmol). After stirring for 15 mins, a solution of the precursor alcohol (Cunha *et al.*, 2016; 1.00 mmol) in DMSO (2 mL), followed by anhydrous CH_2Cl_2 (6.0 mL), were added dropwise. The reaction mixture was maintained at −78°C for 90 mins and Me_3N (1.05 mL, 1.0 mmol) was then added dropwise. After stirring for 20 mins, aqueous NaCl was added, and the organic layer was extracted and concentrated under reduced pressure. The resulting residue was column chromatographed using silica gel and ethyl acetate:hexane (3:7) as eluent to give the pure triazole in 80% yield, as a yellow solid; m.p. 118–120°C. IR (KBr) ν_{max} (cm^{-1}) 3282 (N—H); 1689 (C═O). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.57 (*s*, 3H, CH_3), 6.52 (dd, 2H, *J* = 0.9 and 8.5 Hz, H5 & H9), 7.04 (*tt*, 1H, *J* = 0.9 and 7.3 Hz, H7), 7.24–7.30 (*m*, 2H, H6 and H8), 7.66 (*bs*, 1H, N–H), 10.2 (*s*, 1H, CHO). ^{13}C

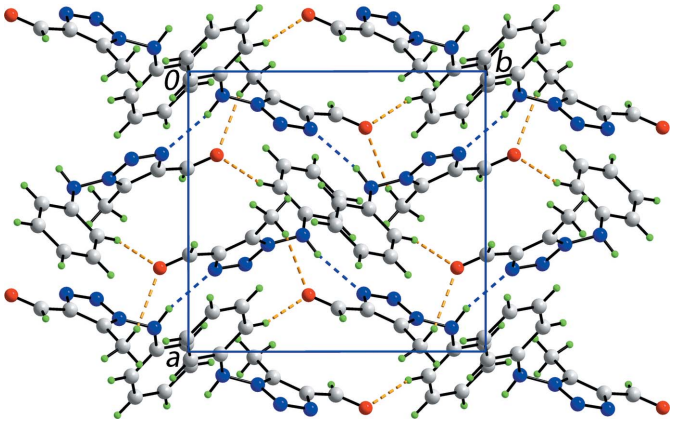


Figure 2
A view of the supramolecular layer in the title compound shown in projection down the *c* axis. The N—H···N and C—H···O interactions are shown as blue and orange dashed lines, respectively.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···N4^{i}	0.89 (2)	2.23 (2)	3.101 (2)	168 (1)
C3—H3*C*···O1^{i}	0.98	2.56	3.181 (2)	121
C5—H5···O1^{ii}	0.95	2.42	3.345 (2)	163

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{10}H_{10}N_4O$
M_r	202.22
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	120
a, *b*, *c* (Å)	10.2208 (5), 10.8693 (6), 18.1059 (6)
V (Å^3)	2011.44 (16)
Z	8
Radiation type	Mo *Kα*
μ (mm^{-1})	0.09
Crystal size (mm)	0.42 × 0.36 × 0.14
Data collection	
Diffractometer	Bruker–Nonius 95mm CCD camera on κ-goniostat diffractometer
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2003)
T_{min}, T_{max}	0.713, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15215, 2310, 1639
R_{int}	0.056
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.651
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.047, 0.138, 1.05
No. of reflections	2310
No. of parameters	141
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.26, −0.25

Computer programs: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *DIAMOND* (Brandenburg, 2006), *publCIF* (Westrip, 2010).

NMR (75 MHz, $CDCl_3$): δ 8.3 (CH_3), 113.7 (C5 & C9), 123.1 (C7), 129.5 (C6 & C8), 139.2 (C1 or C2), 142.2 (C1 or C2), 144.7 (C4), 186.0 (CHO). Anal. calcd. for $C_{10}H_{10}N_4O$: C, 59.40; H, 4.98; N, 27.71. Found: C, 59.38; H, 4.95; N, 27.88.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Owing to poor agreement, a reflection, *i.e.* (2 1 2), was removed from the final cycles of refinement.

Acknowledgements

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full crystallographic data

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Crystal data

$C_{10}H_{10}N_4O$
M_r = 202.22
Orthorhombic, *Pbca*
a = 10.2208 (5) Å
b = 10.8693 (6) Å
c = 18.1059 (6) Å
V = 2011.44 (16) Å^3
Z = 8
F(000) = 848
D_x = 1.336 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71069 Å
Cell parameters from 2601 reflections
θ = 2.9–27.5°
μ = 0.09 mm^{-1}
T = 120 K
Block, colourless
0.42 × 0.36 × 0.14 mm

Data collection

Bruker–Nonius 95mm CCD camera on κ-goniostat diffractometer
Radiation source: Bruker-Nonius FR591 rotating anode
Graphite monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ & ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.713, T_{max} = 1.000
15215 measured reflections
2310 independent reflections
1639 reflections with $I > 2\sigma(I)$
R_{int} = 0.056
θ_{max} = 27.5°, θ_{min} = 3.0°
h = −13→13
k = −14→12
l = −16→23

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.138
S = 1.05
2310 reflections
141 parameters
1 restraint
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0767P)^2 + 0.2474P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Extinction correction: *SHELXL2014* (Sheldrick, 2014), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.008 (2)

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.79842 (12)	0.40421 (12)	0.54426 (7)	0.0402 (4)
N1	0.91541 (13)	0.88492 (13)	0.41939 (7)	0.0247 (3)
H1N	0.8472 (13)	0.9349 (14)	0.4211 (10)	0.030*
N2	0.88217 (12)	0.76712 (12)	0.44112 (7)	0.0219 (3)
N3	0.81206 (12)	0.69078 (13)	0.39631 (7)	0.0248 (3)
N4	0.79436 (12)	0.58967 (13)	0.43324 (7)	0.0238 (3)
C1	0.85041 (15)	0.60189 (15)	0.50173 (8)	0.0229 (4)
C2	0.90728 (15)	0.71584 (15)	0.50683 (8)	0.0233 (4)
C3	0.98009 (17)	0.77895 (18)	0.56623 (9)	0.0348 (5)
H3A	1.0446	0.8348	0.5444	0.052*
H3B	1.0250	0.7178	0.5969	0.052*
H3C	0.9189	0.8261	0.5968	0.052*
C4	0.99103 (15)	0.89324 (15)	0.35369 (8)	0.0227 (4)
C5	1.08721 (16)	0.80734 (16)	0.33814 (9)	0.0287 (4)
H5	1.1020	0.7401	0.3706	0.034*
C6	1.16142 (17)	0.82057 (18)	0.27480 (10)	0.0344 (5)
H6	1.2264	0.7611	0.2633	0.041*
C7	1.14220 (17)	0.91920 (18)	0.22815 (10)	0.0347 (5)
H7	1.1929	0.9271	0.1844	0.042*
C8	1.04906 (16)	1.00614 (17)	0.24536 (9)	0.0311 (4)
H8	1.0377	1.0756	0.2142	0.037*
C9	0.97184 (15)	0.99312 (15)	0.30771 (9)	0.0259 (4)
H9	0.9063	1.0523	0.3188	0.031*
C10	0.84565 (17)	0.50441 (17)	0.55572 (10)	0.0315 (4)
H10	0.8818	0.5199	0.6032	0.038*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0422 (8)	0.0268 (8)	0.0518 (9)	−0.0059 (6)	−0.0096 (6)	0.0107 (6)
N1	0.0283 (7)	0.0169 (7)	0.0289 (7)	0.0013 (6)	0.0038 (6)	0.0016 (6)
N2	0.0249 (7)	0.0178 (7)	0.0231 (7)	−0.0021 (6)	0.0009 (5)	−0.0018 (5)
N3	0.0271 (7)	0.0229 (8)	0.0246 (7)	−0.0037 (6)	−0.0002 (5)	−0.0033 (6)
N4	0.0253 (7)	0.0211 (8)	0.0250 (7)	−0.0009 (6)	0.0003 (5)	−0.0014 (6)
C1	0.0209 (8)	0.0225 (9)	0.0251 (9)	0.0000 (6)	−0.0016 (6)	0.0001 (6)
C2	0.0230 (8)	0.0226 (9)	0.0242 (8)	0.0014 (7)	−0.0019 (6)	0.0013 (6)
C3	0.0390 (10)	0.0330 (11)	0.0325 (10)	−0.0082 (8)	−0.0130 (7)	0.0001 (8)
C4	0.0246 (8)	0.0210 (9)	0.0224 (8)	−0.0042 (7)	−0.0014 (6)	−0.0011 (6)
C5	0.0274 (8)	0.0259 (10)	0.0328 (9)	0.0004 (7)	0.0014 (7)	0.0034 (7)

C6	0.0273 (9)	0.0358 (12)	0.0401 (11)	0.0027 (8)	0.0073 (7)	−0.0010 (8)
C7	0.0325 (10)	0.0409 (12)	0.0306 (10)	−0.0068 (8)	0.0076 (7)	0.0025 (8)
C8	0.0351 (9)	0.0292 (10)	0.0289 (9)	−0.0075 (7)	−0.0009 (7)	0.0061 (7)
C9	0.0274 (8)	0.0223 (9)	0.0282 (9)	−0.0019 (7)	−0.0018 (7)	−0.0009 (7)
C10	0.0310 (9)	0.0273 (10)	0.0363 (10)	−0.0017 (8)	−0.0078 (7)	0.0044 (8)

Geometric parameters (Å, º)

O1—C10	1.209 (2)	C3—H3C	0.9800
N1—N2	1.3818 (18)	C4—C9	1.382 (2)
N1—C4	1.421 (2)	C4—C5	1.385 (2)
N1—H1N	0.885 (9)	C5—C6	1.383 (2)
N2—C2	1.3387 (19)	C5—H5	0.9500
N2—N3	1.3639 (17)	C6—C7	1.379 (3)
N3—N4	1.2990 (18)	C6—H6	0.9500
N4—C1	1.372 (2)	C7—C8	1.377 (3)
C1—C2	1.371 (2)	C7—H7	0.9500
C1—C10	1.442 (2)	C8—C9	1.385 (2)
C2—C3	1.477 (2)	C8—H8	0.9500
C3—H3A	0.9800	C9—H9	0.9500
C3—H3B	0.9800	C10—H10	0.9500
N2—N1—C4	115.52 (13)	C9—C4—N1	118.49 (14)
N2—N1—H1N	111.4 (12)	C5—C4—N1	120.88 (14)
C4—N1—H1N	114.8 (12)	C6—C5—C4	119.21 (16)
C2—N2—N3	112.09 (13)	C6—C5—H5	120.4
C2—N2—N1	126.28 (13)	C4—C5—H5	120.4
N3—N2—N1	121.57 (12)	C7—C6—C5	120.72 (17)
N4—N3—N2	106.36 (12)	C7—C6—H6	119.6
N3—N4—C1	108.97 (13)	C5—C6—H6	119.6
C2—C1—N4	108.98 (14)	C8—C7—C6	119.56 (16)
C2—C1—C10	129.21 (15)	C8—C7—H7	120.2
N4—C1—C10	121.81 (15)	C6—C7—H7	120.2
N2—C2—C1	103.59 (13)	C7—C8—C9	120.55 (16)
N2—C2—C3	123.40 (15)	C7—C8—H8	119.7
C1—C2—C3	133.01 (15)	C9—C8—H8	119.7
C2—C3—H3A	109.5	C4—C9—C8	119.38 (16)
C2—C3—H3B	109.5	C4—C9—H9	120.3
H3A—C3—H3B	109.5	C8—C9—H9	120.3
C2—C3—H3C	109.5	O1—C10—C1	123.98 (16)
H3A—C3—H3C	109.5	O1—C10—H10	118.0
H3B—C3—H3C	109.5	C1—C10—H10	118.0
C9—C4—C5	120.52 (15)		
C4—N1—N2—C2	124.41 (16)	C10—C1—C2—C3	−0.6 (3)
C4—N1—N2—N3	−58.74 (18)	N2—N1—C4—C9	146.17 (14)
C2—N2—N3—N4	−1.04 (17)	N2—N1—C4—C5	−37.6 (2)
N1—N2—N3—N4	−178.30 (12)	C9—C4—C5—C6	−1.9 (2)

N2—N3—N4—C1	1.16 (16)	N1—C4—C5—C6	−178.06 (15)
N3—N4—C1—C2	−0.93 (17)	C4—C5—C6—C7	1.3 (3)
N3—N4—C1—C10	179.48 (15)	C5—C6—C7—C8	0.8 (3)
N3—N2—C2—C1	0.45 (17)	C6—C7—C8—C9	−2.1 (3)
N1—N2—C2—C1	177.56 (14)	C5—C4—C9—C8	0.6 (2)
N3—N2—C2—C3	−179.19 (15)	N1—C4—C9—C8	176.79 (14)
N1—N2—C2—C3	−2.1 (2)	C7—C8—C9—C4	1.5 (3)
N4—C1—C2—N2	0.27 (17)	C2—C1—C10—O1	−176.00 (18)
C10—C1—C2—N2	179.83 (16)	N4—C1—C10—O1	3.5 (3)
N4—C1—C2—C3	179.87 (17)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···N4^{i}	0.89 (2)	2.23 (2)	3.101 (2)	168 (1)
C3—H3*C*···O1^{i}	0.98	2.56	3.181 (2)	121
C5—H5···O1^{ii}	0.95	2.42	3.345 (2)	163

Symmetry codes: (i) −*x*+3/2, *y*+1/2, *z*; (ii) −*x*+2, −*y*+1, −*z*+1.