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Crystal structure of 6,9-dimethyl-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazepin-8(9*H*)-one 0.40-hydrate

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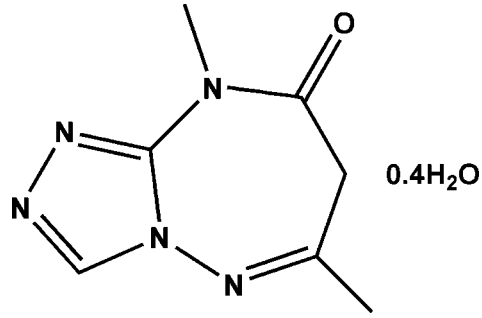
In the molecule of the title compound, $C_7H_9N_5O\cdot0.40H_2O$, the seven-membered heterocyclic ring exhibits a boat conformation, whereas the five-membered triazole ring is almost planar (r.m.s. deviation = 0.005 Å). In the crystal, centrosymmetric dimers are linked by pairs of C—H···O hydrogen bonds into dimers, which are further connected *via* O—H···N and C—H···N hydrogen bonds, forming a three-dimensional network. The structure contains a partially occupied water molecule lying on a twofold axis with an occupancy factor of 0.4.

Keywords: crystal structure; 1,2,4-triazepin-8(9*H*)-one; pharmacological and biological activities; hydrogen bonding.

CCDC reference: 1035668

1. Related literature

For pharmacological and biological activities of 1,2,4-triazole and 1,2,4-triazepine derivatives, see: Gupta *et al.* (2011); Mathew *et al.* (2006); Reed *et al.* (2010). For related structures, see: Essassi *et al.* (1977); Doubia *et al.* (2007); Zemama *et al.* (2009).



2. Experimental

2.1. Crystal data

$C_7H_9N_5O\cdot0.4H_2O$
M_r = 186.44
Monoclinic, $C2/c$
a = 11.4970 (18) Å
b = 11.4527 (18) Å
c = 14.867 (2) Å
β = 109.615 (4)°
V = 1843.9 (5) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 296 K
0.40 × 0.34 × 0.30 mm

2.2. Data collection

Bruker X8 APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.637, T_{max} = 0.746
14175 measured reflections
2039 independent reflections
1600 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.125
S = 1.04
2039 reflections
123 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2A···N3^{i}	0.97	2.58	3.449 (3)	149
C5—H5···O1^{ii}	0.93	2.29	3.211 (2)	173
O2—H1···N3^{iii}	0.87	2.08	2.939 (2)	167

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT-Plus* (Bruker, 2009); data reduction: *SAINT-Plus*; 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, 2012); software used to prepare material for publication: *PLATON* (Spek, 2009) and *publCIF* (Westrip,2010).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: RZ5141).

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supporting information

Acta Cryst. (2015). E**71**, o1–o2 [https://doi.org/10.1107/S2056989014025687]

Crystal structure of 6,9-dimethyl-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazepin-8(9*H*)-one 0.40-hydrate

Abdellah Harmaoui, Rachid Bouhfid, El Mokhtar Essassi, Mohamed Saadi and Lahcen El Ammari

S1. Comment

1,2,4-Triazole derivatives are known to possess wide biological significance and diverse pharmacological activities (Mathew *et al.*, 2006; Reed *et al.*, 2010). 1,2,4-Triazepine derivatives were also reported to possess antibacterial, antiviral and psychotropic activities (Gupta *et al.*, 2011). They are also the reactants for the synthesis of other heterocyclic compounds (Essassi *et al.*, 1977; Doubia *et al.*, 2007; Zemama *et al.*, 2009). The aim of the present paper is to report the crystal structure of the title compound.

The molecule of the title compound is build up from two fused five- and seven-membered rings linked to two methyl groups and crystallizing with a partial water molecule as shown in Fig. 1. The triazepine ring adopts a boat conformation as indicated by the puckering amplitude Q = 0.7865 (17) Å and spherical polar angle θ = 88.80 (12)°, with φ = 60.07 (13)°. The triazole ring is close to be planar, with a maximum deviation of 0.007 (2) Å for atom C5. In the crystal, centrosymmetrically-related molecules are linked by pairs of weak C—H···O hydrogen bonds into dimeric units, which are further connected into a three-dimensional network by O—H···N and C—H···O hydrogen bonds (Fig. 2, Table 1).

S2. Experimental

To a solution of 1 g (0,06 mol) of6-methyl-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazepin-8(9*H*)-one in 30 ml of sodium methoxide (prepared from 30 ml of methanol and 0.15 g of sodium) was added 1 g (0.007 mol) of methyl iodide and the mixture was heated for 5 h. The solution was then concentrated to dryness under reduced pressure and the residue was extracted with chloroform. The precipitate obtained was chromatographed on a silica column (eluent: chloroform/ethanol 95:5 *v*/*v*). The purified product was crystallized from ethanol to give colourless crystals with a yield of 50%.

S3. Refinement

All H atoms were located in a difference Fourier map and refineded as riding, with C—H = 0.93-0.97 Å, O–H = 0.90 Å, and with U_{iso}(H) = 1.2 U_{eq}(C) or 1.5 U_{eq}(C, O) for methyl and water H atoms. The oxygen atom of the water molecule lies on a two-fold axis with an occupancy factor of 0.4.

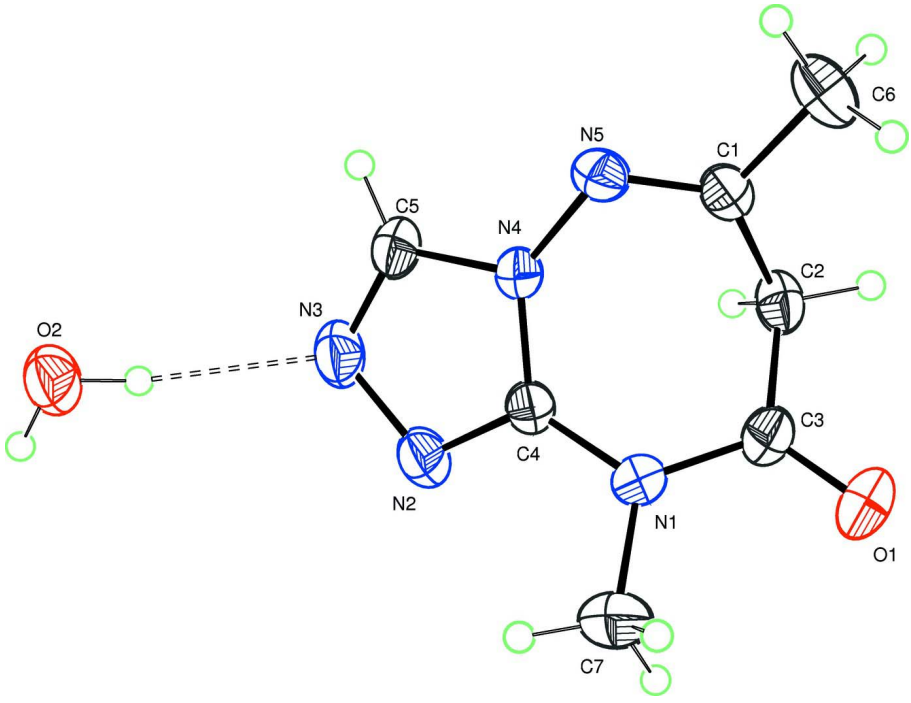

Figure 1

The asymmetric unit of the title compound with displacement ellipsoids drawn at the 50% probability level, showing the intermolecular O—H···N hydrogen bond (dashed line).

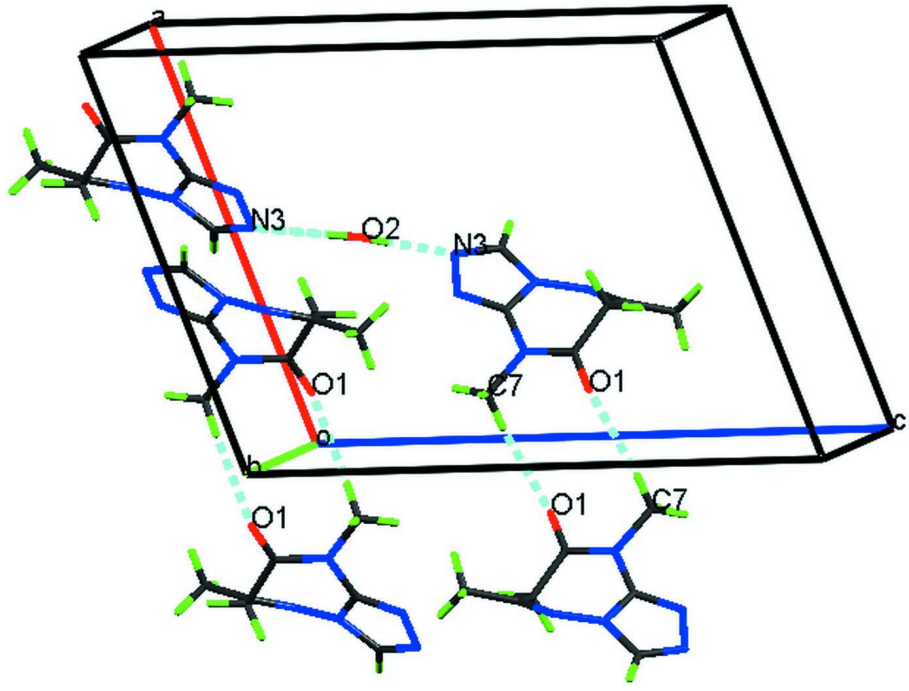

Figure 2

Partiel crystal packing of the title compound, showing molecules linked through C—H···O and O—H···N hydrogen bonds (dashed lines).

6,9-Dimethyl-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazepin-8(9*H*)-one 0.40-hydrate

Crystal data

$C_7H_9N_5O·0.4H_2O$
M_r = 186.44
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
a = 11.4970 (18) Å
b = 11.4527 (18) Å
c = 14.867 (2) Å
β = 109.615 (4)°
V = 1843.9 (5) Å^3
Z = 8
F(000) = 784
D_x = 1.343 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 2039 reflections
θ = 2.6–27.1°
μ = 0.10 mm^{-1}
T = 296 K
Block, colourless
0.40 × 0.34 × 0.30 mm

Data collection

Bruker X8 APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and *ω* scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.637, T_{max} = 0.746
14175 measured reflections
2039 independent reflections
1600 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 27.1°, θ_{min} = 2.6°
h = −14→14
k = −14→14
l = −19→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.125
S = 1.04
2039 reflections
123 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
$w = 1/[\sigma^2(F_o^2) + (0.0565P)^2 + 1.2827P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.33958 (13)	0.65257 (14)	0.16698 (10)	0.0369 (3)	
C2	0.34033 (16)	0.52181 (14)	0.16066 (11)	0.0433 (4)	
H2A	0.4176	0.4962	0.1544	0.052*	
H2B	0.3344	0.4885	0.2190	0.052*	

C3	0.23480 (17)	0.47878 (14)	0.07690 (12)	0.0476 (4)	
C4	0.33342 (14)	0.57338 (13)	−0.02393 (10)	0.0362 (3)	
C5	0.46928 (15)	0.70820 (15)	−0.00967 (12)	0.0453 (4)	
H5	0.5204	0.7725	0.0124	0.054*	
C6	0.30729 (19)	0.70739 (19)	0.24624 (12)	0.0571 (5)	
H6A	0.3102	0.7908	0.2412	0.086*	
H6B	0.3652	0.6828	0.3063	0.086*	
H6C	0.2256	0.6839	0.2424	0.086*	
C7	0.1424 (2)	0.4639 (2)	−0.09733 (15)	0.0758 (7)	
H7A	0.1563	0.4934	−0.1533	0.114*	
H7B	0.0623	0.4881	−0.0976	0.114*	
H7C	0.1464	0.3802	−0.0970	0.114*	
N1	0.23754 (13)	0.50997 (12)	−0.01151 (9)	0.0445 (4)	
N2	0.37481 (14)	0.56109 (13)	−0.09512 (10)	0.0478 (4)	
N3	0.46286 (14)	0.64862 (14)	−0.08511 (10)	0.0508 (4)	
N4	0.39103 (11)	0.66406 (11)	0.03305 (8)	0.0346 (3)	
N5	0.36603 (12)	0.72045 (11)	0.10833 (9)	0.0388 (3)	
O1	0.15060 (15)	0.42096 (14)	0.08579 (11)	0.0790 (5)	
O2	0.5000	0.7639 (2)	−0.2500	0.0618 (6)	0.80
H1	0.5068	0.7196	−0.2959	0.093*	0.80

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0326 (7)	0.0460 (8)	0.0320 (7)	0.0009 (6)	0.0109 (6)	−0.0009 (6)
C2	0.0514 (9)	0.0455 (9)	0.0367 (8)	0.0024 (7)	0.0195 (7)	0.0089 (7)
C3	0.0595 (10)	0.0394 (9)	0.0497 (9)	−0.0114 (7)	0.0260 (8)	0.0005 (7)
C4	0.0434 (8)	0.0345 (7)	0.0327 (7)	−0.0018 (6)	0.0153 (6)	0.0007 (6)
C5	0.0470 (9)	0.0483 (9)	0.0455 (9)	−0.0091 (7)	0.0221 (7)	0.0049 (7)
C6	0.0644 (11)	0.0709 (12)	0.0426 (9)	0.0104 (10)	0.0265 (9)	−0.0051 (9)
C7	0.0784 (15)	0.0916 (16)	0.0559 (12)	−0.0408 (13)	0.0204 (11)	−0.0244 (11)
N1	0.0507 (8)	0.0441 (7)	0.0390 (7)	−0.0160 (6)	0.0157 (6)	−0.0057 (6)
N2	0.0624 (9)	0.0490 (8)	0.0380 (7)	−0.0019 (7)	0.0247 (7)	−0.0020 (6)
N3	0.0572 (9)	0.0588 (9)	0.0451 (8)	−0.0025 (7)	0.0287 (7)	0.0055 (7)
N4	0.0393 (7)	0.0348 (6)	0.0332 (6)	−0.0042 (5)	0.0166 (5)	−0.0007 (5)
N5	0.0427 (7)	0.0383 (7)	0.0369 (6)	−0.0023 (5)	0.0154 (5)	−0.0066 (5)
O1	0.0913 (11)	0.0827 (11)	0.0718 (10)	−0.0466 (9)	0.0389 (9)	−0.0012 (8)
O2	0.0912 (18)	0.0554 (13)	0.0507 (13)	0.000	0.0395 (13)	0.000

Geometric parameters (Å, º)

C1—N5	1.2788 (19)	C5—N4	1.3610 (19)
C1—C6	1.488 (2)	C5—H5	0.9300
C1—C2	1.501 (2)	C6—H6A	0.9600
C2—C3	1.500 (2)	C6—H6B	0.9600
C2—H2A	0.9700	C6—H6C	0.9600
C2—H2B	0.9700	C7—N1	1.472 (2)
C3—O1	1.216 (2)	C7—H7A	0.9600

C3—N1	1.373 (2)	C7—H7B	0.9600
C4—N2	1.306 (2)	C7—H7C	0.9600
C4—N4	1.3632 (19)	N2—N3	1.397 (2)
C4—N1	1.383 (2)	N4—N5	1.4029 (17)
C5—N3	1.294 (2)	O2—H1	0.8745
N5—C1—C6	117.59 (15)	H6A—C6—H6B	109.5
N5—C1—C2	123.80 (14)	C1—C6—H6C	109.5
C6—C1—C2	118.61 (14)	H6A—C6—H6C	109.5
C3—C2—C1	111.08 (13)	H6B—C6—H6C	109.5
C3—C2—H2A	109.4	N1—C7—H7A	109.5
C1—C2—H2A	109.4	N1—C7—H7B	109.5
C3—C2—H2B	109.4	H7A—C7—H7B	109.5
C1—C2—H2B	109.4	N1—C7—H7C	109.5
H2A—C2—H2B	108.0	H7A—C7—H7C	109.5
O1—C3—N1	121.38 (17)	H7B—C7—H7C	109.5
O1—C3—C2	122.69 (16)	C3—N1—C4	122.68 (14)
N1—C3—C2	115.92 (14)	C3—N1—C7	119.17 (15)
N2—C4—N4	110.65 (13)	C4—N1—C7	117.80 (14)
N2—C4—N1	125.12 (14)	C4—N2—N3	106.54 (13)
N4—C4—N1	124.04 (13)	C5—N3—N2	107.42 (13)
N3—C5—N4	110.76 (15)	C5—N4—C4	104.61 (13)
N3—C5—H5	124.6	C5—N4—N5	123.08 (13)
N4—C5—H5	124.6	C4—N4—N5	131.27 (12)
C1—C6—H6A	109.5	C1—N5—N4	115.05 (13)
C1—C6—H6B	109.5		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*A*···N3^{i}	0.97	2.58	3.449 (3)	149
C5—H5···O1^{ii}	0.93	2.29	3.211 (2)	173
O2—H1···N3^{iii}	0.87	2.08	2.939 (2)	167

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