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4-(1*H*-1,2,4-Triazol-3-yl)-4*H*-1,2,4-triazole monohydrate

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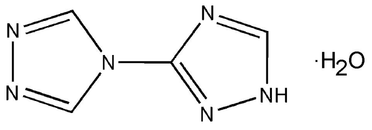
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(N–C) = 0.003 Å; R factor = 0.034; wR factor = 0.089; data-to-parameter ratio = 6.6.

In the title molecule, $C_4H_6N_6O$, the dihedral angle between the two triazole rings is 2.97 (1)°. The crystal structure is stabilized by one N—H···O, two O—H···N and three C—H···N(or O) hydrogen bonds, forming a three-dimensional network.

Related literature

There has been recent interest in substituted 1,2,4-triazoles (Fujigaya *et al.*, 2003; Garcia *et al.*, 1997; Kahn & Martinez, 1998).



Experimental

Crystal data

$C_4H_4N_6 \cdot H_2O$
M_r = 154.15
Monoclinic, *Cc*
a = 3.8716 (3) Å
b = 15.8019 (14) Å
c = 10.8874 (9) Å
β = 91.7850 (10)°
V = 665.75 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 296 (2) K
0.20 × 0.10 × 0.04 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.976, T_{max} = 0.988
2254 measured reflections
727 independent reflections
709 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.089
S = 1.06
727 reflections
110 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···N5^{i}	0.835 (18)	2.15 (2)	2.962 (3)	163 (4)
O1—H1B···N6^{ii}	0.840 (19)	2.10 (2)	2.930 (3)	169 (4)
C2—H2···O1^{iii}	0.93	2.49	3.392 (3)	163
C3—H3···N3^{iv}	0.93	2.50	3.334 (3)	149
C4—H4···N1^{v}	0.93	2.35	3.226 (3)	157
N2—H2A···O1	0.895 (18)	1.879 (19)	2.770 (3)	173 (3)

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2370).

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supplementary materials

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4-(1*H*-1,2,4-Triazol-3-yl)-4*H*-1,2,4-triazole monohydrate

L.-H. Jia, Z.-L. Liu and W. Liu

Comment

Recent interest in substituted 1,2,4-triazoles has arisen in part from their transition metal complexes with intriguing structures and specific magnetic properties (Garcia *et al.*,1997; Kahn & Martinez,1998; Fujigaya *et al.*,2003). However bitriazole ligands have not been extensively exploited up to now, and herein we reported the crystal structure of (I).

In (I) (Fig.2), the two triazole ring are almost coplanar with a dihedral angle of 2.97 (1)° between them. The bond lengths and angles are unremarkable.

The crystal structure is stablized by one N–H···O, two O–H···N and three C–H···N(or O) hydrogen bonds. In detail, the water O atom O1 acts as a hydrogen bond donor, *via*. H1A and H1B, to the atom N5 at (-3/2 + *x*, 1/2 - *y*, -1/2 + *z*) and atom N6 (*x*, 1/2+ *y*, *z*), respectively, forming a one-dimensional chain along the [001] direction. In addition, the atom N2 at (*x*,*y*,*z*) acts as hydrogen bond donor, *via*. H2A, to the water O atom O1 in the same symmetric unit, linking adjacent chains into a three dimensional framework (Fig.3). Analysis using *PLATON* (Spek, 2003) shows that there are other three C–H···N(or O)(Table 2) hydrogen bonds which further stabilize the crystal structure. In addtion, π–π interactions are observed between the triazole ring N1—N3/C1/C2 at (*x*, *y*, *z*) and the other five-numbered ring N4—N6/C3/C4 at (-1+*x*, y, z). The dihedral angle between the two triazole rings is only 2.97 (1)°, with an interplanar spacing of 3.273 (1) Å, a ring centroid separation of 3.635 (1) Å.

Experimental

The title compound (I) was prepared by reacting diformylhydrazine (0.046 mol, 4.0 g) and 3-amino-1,2,4-triazole 0.046 mol,3.9 g). The reactant mixture was heated slowly to 433 K for an hour. The cooled reaction mixture was dissolved in 25 ml of boiling water and filtered. On cooling, 4.4 g of the product separated. Recrystallization from hot water gave large white crystals. Elemental analysis(%) for $C_4H_6N_6O$, found (calculated): C 31.12 (31.13), H 3.80 (3.89), N 54.60 (54.49). IR(cm^{-1},KBr):3352.21, 3119.57,2881.59, 2733.65,1789.84,1657.08,1575.38,1505.81,1371.08,1303.73, 1290.26,1142.12, 1051.33,986.29, 958.04,897.31,877.09,738.58, 629.96,563.66.

Refinement

When the structure of (I) is solved and refined in the centrosymmtric space group C2/c with half a molecule in the asymmetric unit, the structure is disordered with R values that are significantly higher (R1=15 and wR2=34%) and the anistropic displacement parameters have unusual values. In the absence of significant anomalous dispersion effects Friedel pairs were merged. H atoms bonded to O1 and N1 were located from the difference maps with and refined with constraints of O–H = 0.86 (2) Å, H–H =1.35 (2) Å, N–H = 0.86 (2) Å; U_{iso}(H) = 1.5U_{eq}(O) and U_{iso}(H) = 1.2U_{eq}(N). H2, H3 and H4 were placed in calculated positions with C—H = 0.93 Å and U_{iso}(H) =1.2U_{eq}(C).

Figures

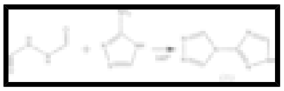

Fig. 1. Reaction scheme.

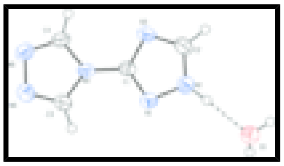

Fig. 2. Molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The dashed line indicates an intermolecular hydrogen bond.

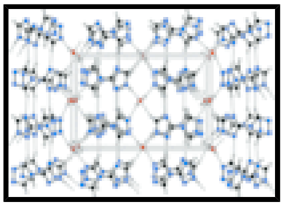

Fig. 3. Part of the crystal structure of (I), showing the formation of a three-dimensional network from hydrogen bonding (dashed lines).

4-(1*H*-1,2,4-Triazol-3-yl)-4*H*-1,2,4-triazole monohydrate

Crystal data

$C_4H_4N_6 \cdot H_2O$	$F_{000} = 320$
$M_r = 154.15$	$D_x = 1.538$ Mg m^{-3}
Monoclinic, *Cc*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: C -2yc	Cell parameters from 1837 reflections
$a = 3.8716$ (3) Å	θ = 2.6–28.1°
$b = 15.8019$ (14) Å	μ = 0.12 mm^{-1}
$c = 10.8874$ (9) Å	$T = 296$ (2) K
β = 91.7850 (10)°	Plate, colorless
$V = 665.75$ (10) Å^3	0.20 × 0.10 × 0.04 mm
$Z = 4$	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	727 independent reflections
Radiation source: fine focus sealed Siemens Mo tube	709 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\rm int} = 0.027$
$T = 298(2)$ K	$\theta_{\rm max} = 27.0°$
0.3° wide ω exposures scans	$\theta_{\rm min} = 2.6°$
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	$h = -4 \rightarrow 4$
$T_{\rm min} = 0.976$, $T_{\rm max} = 0.988$	$k = -18 \rightarrow 20$
2254 measured reflections	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.034$	$w = 1/[\sigma^2(F_o^2) + (0.0579P)^2 + 0.1815P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.089$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.06$	$\Delta\rho_{max} = 0.17$ e Å^{-3}
727 reflections	$\Delta\rho_{min} = -0.21$ e Å^{-3}
110 parameters	Extinction correction: none
6 restraints	
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	

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.

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 $F^2 > 2\text{sigma}(F^2)$ 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}
C1	0.1950 (6)	0.28332 (13)	0.7395 (2)	0.0286 (5)
C2	−0.0527 (8)	0.39041 (17)	0.7999 (2)	0.0403 (6)
H2	−0.1431	0.4331	0.8481	0.048*
C3	0.4923 (7)	0.16139 (17)	0.6439 (2)	0.0383 (6)
H3	0.4433	0.1745	0.5619	0.046*
C4	0.5157 (8)	0.16590 (16)	0.8413 (2)	0.0363 (6)
H4	0.4867	0.1829	0.9222	0.044*
N1	0.0761 (6)	0.31653 (13)	0.63646 (19)	0.0363 (5)
N2	−0.0840 (6)	0.38719 (14)	0.67866 (19)	0.0378 (5)
H2A	−0.187 (8)	0.4237 (18)	0.627 (3)	0.052 (9)*
N3	0.1248 (7)	0.32463 (13)	0.84350 (19)	0.0385 (6)
N4	0.3879 (5)	0.20801 (11)	0.74086 (18)	0.0293 (4)
N5	0.6829 (6)	0.09913 (14)	0.80910 (18)	0.0406 (6)
N6	0.6694 (7)	0.09619 (14)	0.6813 (2)	0.0412 (5)
O1	−0.4451 (6)	0.48966 (11)	0.5130 (2)	0.0423 (5)

H1A	−0.584 (9)	0.465 (2)	0.466 (3)	0.064*
H1B	−0.561 (9)	0.5245 (19)	0.553 (3)	0.064*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0330 (12)	0.0295 (9)	0.0236 (9)	−0.0055 (8)	0.0036 (8)	0.0001 (8)
C2	0.0498 (16)	0.0358 (12)	0.0356 (13)	0.0012 (10)	0.0075 (11)	−0.0059 (10)
C3	0.0481 (16)	0.0390 (12)	0.0278 (11)	0.0028 (10)	0.0025 (11)	−0.0035 (9)
C4	0.0460 (14)	0.0405 (12)	0.0224 (10)	−0.0007 (10)	−0.0013 (10)	0.0025 (9)
N1	0.0455 (13)	0.0365 (11)	0.0268 (9)	0.0037 (8)	0.0011 (8)	0.0003 (7)
N2	0.0440 (13)	0.0332 (10)	0.0363 (10)	0.0019 (8)	0.0039 (9)	0.0028 (8)
N3	0.0513 (14)	0.0393 (11)	0.0251 (9)	0.0028 (9)	0.0041 (9)	−0.0040 (7)
N4	0.0346 (11)	0.0325 (9)	0.0208 (7)	−0.0021 (7)	0.0011 (7)	−0.0002 (7)
N5	0.0477 (15)	0.0401 (12)	0.0336 (11)	0.0011 (9)	−0.0034 (9)	0.0049 (8)
N6	0.0472 (14)	0.0390 (12)	0.0373 (11)	0.0036 (10)	0.0030 (10)	−0.0022 (9)
O1	0.0460 (10)	0.0415 (10)	0.0393 (11)	0.0033 (9)	−0.0030 (8)	−0.0040 (7)

Geometric parameters (Å, °)

C1—N1	1.309 (3)	C4—N5	1.292 (4)
C1—N3	1.342 (3)	C4—N4	1.360 (3)
C1—N4	1.405 (3)	C4—H4	0.9300
C2—N2	1.323 (3)	N1—N2	1.364 (3)
C2—N3	1.326 (4)	N2—O1	2.770 (3)
C2—H2	0.9300	N2—H2A	0.895 (18)
C3—N6	1.296 (4)	N5—N6	1.392 (3)
C3—N4	1.359 (3)	O1—H1A	0.835 (18)
C3—H3	0.9300	O1—H1B	0.840 (19)
N1—C1—N3	116.9 (2)	C2—N2—O1	131.0 (2)
N1—C1—N4	121.40 (19)	N1—N2—O1	119.00 (16)
N3—C1—N4	121.67 (19)	C2—N2—H2A	129 (2)
N2—C2—N3	111.0 (3)	N1—N2—H2A	121 (2)
N2—C2—H2	124.5	C2—N3—C1	101.3 (2)
N3—C2—H2	124.5	C3—N4—C4	104.5 (2)
N6—C3—N4	110.7 (2)	C3—N4—C1	128.46 (19)
N6—C3—H3	124.6	C4—N4—C1	127.06 (19)
N4—C3—H3	124.6	C4—N5—N6	107.2 (2)
N5—C4—N4	110.7 (2)	C3—N6—N5	106.9 (2)
N5—C4—H4	124.6	N2—O1—H1A	115 (3)
N4—C4—H4	124.6	N2—O1—H1B	108 (3)
C1—N1—N2	101.0 (2)	H1A—O1—H1B	107 (3)
C2—N2—N1	109.8 (2)		
N3—C1—N1—N2	0.8 (3)	N6—C3—N4—C1	179.3 (2)
N4—C1—N1—N2	−179.09 (19)	N5—C4—N4—C3	−0.2 (3)
N3—C2—N2—N1	0.3 (3)	N5—C4—N4—C1	−179.5 (2)
N3—C2—N2—O1	175.2 (2)	N1—C1—N4—C3	3.1 (3)
C1—N1—N2—C2	−0.6 (3)	N3—C1—N4—C3	−176.8 (3)

C1—N1—N2—O1	−176.24 (17)	N1—C1—N4—C4	−177.7 (3)
N2—C2—N3—C1	0.2 (3)	N3—C1—N4—C4	2.4 (3)
N1—C1—N3—C2	−0.6 (3)	N4—C4—N5—N6	0.3 (3)
N4—C1—N3—C2	179.2 (2)	N4—C3—N6—N5	0.2 (3)
N6—C3—N4—C4	0.0 (3)	C4—N5—N6—C3	−0.4 (3)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1A···N5^{i}	0.835 (18)	2.15 (2)	2.962 (3)	163 (4)
O1—H1B···N6^{ii}	0.840 (19)	2.10 (2)	2.930 (3)	169 (4)
C2—H2···O1^{iii}	0.93	2.49	3.392 (3)	163
C3—H3···N3^{iv}	0.93	2.50	3.334 (3)	149
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Symmetry codes: (i) $x-3/2$, $-y+1/2$, $z-1/2$; (ii) $x-3/2$, $y+1/2$, z; (iii) x, $-y+1$, $z+1/2$; (iv) $x+1/2$, $-y+1/2$, $z-1/2$; (v) $x+1/2$, $-y+1/2$, $z+1/2$.

Fig. 1

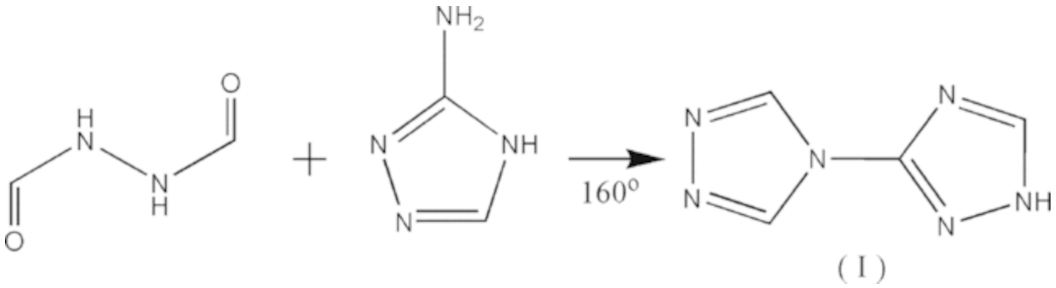

Fig. 2

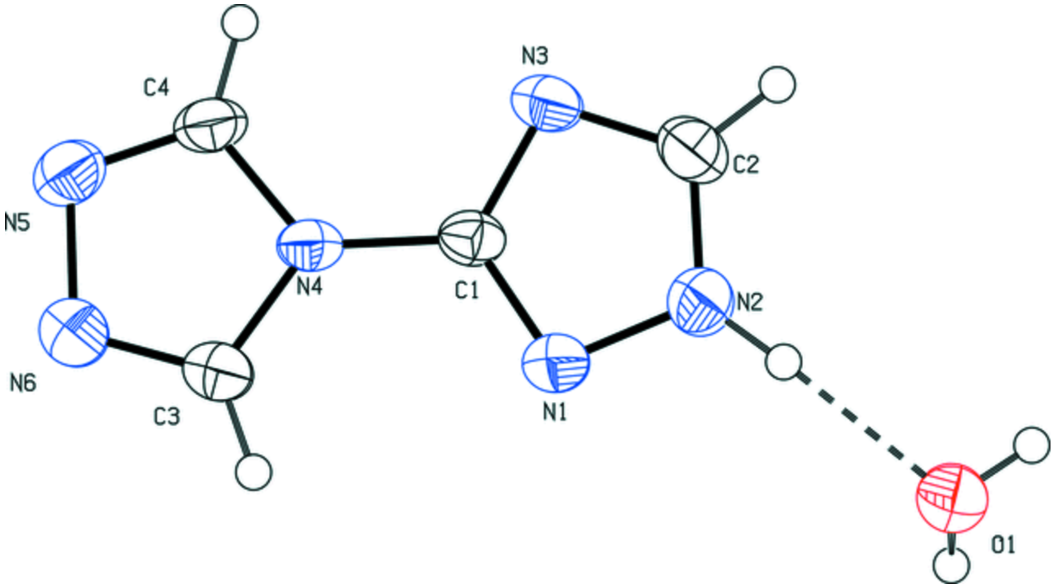

Fig. 3