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5-Amino-8-(1-aminoethylidene)-8*H*-tetrazolo[1,5-*a*]pyridin-7-one dihydrate

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Key indicators

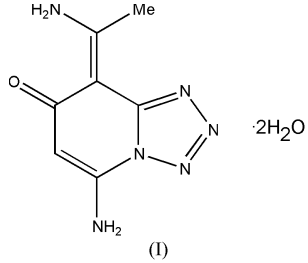
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.051
wR factor = 0.124
Data-to-parameter ratio = 9.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_7H_8N_6O\cdot 2H_2O$, contains a tetrazole ring fused to a substituted pyridone ring. Bond lengths correspond to delocalized π electrons in the tetrazole moiety and a push–pull effect in the pyridone ring. An extended network of hydrogen bonds connects the molecules in planes parallel to the *bc* plane, while the water molecules form chains parallel to the *a* axis.

Comment

The tetrazole ring is present in many molecules displaying different pharmacological activities. A series of tetrazoles show anticonvulsive effects, being able to interact with the benzodiazepine receptors (Rehavi *et al.*, 1982). Further studies on structure–activity relationships have demonstrated that the tetrazole moiety may be considered a group bio-isosteric with a carboxylic acid (Jason, 2002). Many tetrazoles, synthesized on this basis, result in strong non-peptide antagonists of the angiotensin II (Kohara *et al.*, 1995). For these reasons, some find application in pharmaceutical preparations (*e.g.* Irbesartan and Cilostazol).



(I)

The title compound, (I), was synthesized in high yield and crystallized with two water molecules in the asymmetric unit. The molecule is roughly planar; the aminoethyl group (C1/C12/C13/N14) and the tetrazole ring make angles of 0.98 (16) and 0.92 (15)° with the pyridinone ring plane (C1/C6/O11/C5/C4/N3/C2).

No other structures of tetrazolo[1,5-*a*]pyridinones have been reported so far. Bond distances in the tetrazole ring differ notably from those of a reported tetrazolo[1,5-*a*]-pyridine (Patel *et al.*, 2002), the sequence N9—N8—N7—N3 being in the order 1.404 (4), 1.267 (4) and 1.435 (5) Å *versus* 1.359 (3), 1.289 (3) and 1.357 (3) Å; the present structure is characterized by an extensive delocalization of the tetrazole ring electrons. Bond distances and angles compare well with tetrazolopyridazine (Golič *et al.*, 1978) and very well with tetrazolo[1,5-*f*]furazano[4,5-*b*]pyridine 1-oxide (Lowe-Ma *et al.*, 1990). A push–pull effect is evident from the C6—O11 bond length of 1.271 (3) Å.

Compound (I) crystallizes with two water molecules in the asymmetric unit, one of which, O1, lies in the least-squares plane passing through all non-H atoms; it is 0.010 (5) Å from this plane, while the other water, O2, is significantly out of the plane [0.720 (4) Å]. An extensive hydrogen-bond network assembles the molecules in layers parallel to the crystallographic *bc* plane, at distances of 3.387 Å from each other. Besides the O1—H···O2 bridges connecting four molecules of (I), the intramolecular N14—H···O11 and intermolecular N10—H10···N8^{iii} hydrogen bonds also lie in this plane (symmetry code as in Table 2). The O2 water molecule is further engaged as a hydrogen bond donor to the O1 water molecule at ($x+\frac{1}{2}$, $y-\frac{1}{2}$, $-z+2$), so that the water molecules form chains parallel to the *a* axis. The parallel stacking of the planes creates a tubular cavity hosting the water chain. The hydrogen-bond network, reported in Table 2, is shown in Fig. 2, viewed normal to (100).

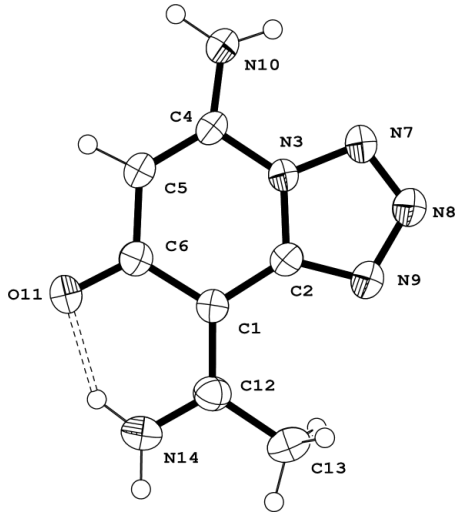


Figure 1
View of (I) (50% probability displacement ellipsoids).

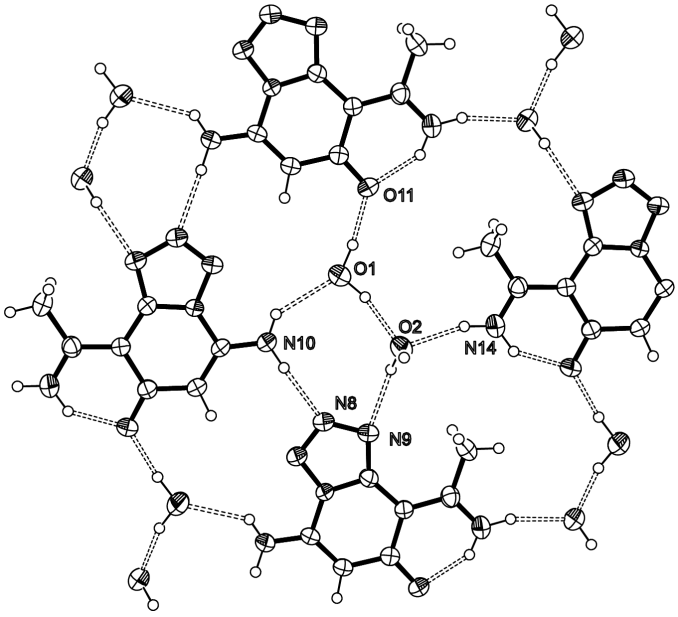


Figure 2
View, normal to (100), of the hydrogen-bond network.

Experimental

To a solution of 4,6-diazido-3-methylisoxazolo[4,5-*c*]pyridine (216 mg, 1 mmol; Donati *et al.*, 1997) in methanol (40 ml), $Mo(CO)_6$ (264 mg, 1 mmol) was added and the mixture refluxed for 4 h. The solvent was evaporated and the residue column-chromatographed on silica gel with chloroform/methanol (95/5 *v*/*v*) as eluant, to give the title compound as a white solid (yield 98 mg, 50%). Slow evaporation of a chloroform solution of this compound gave crystals suitable for X-ray analysis; m.p.: partial modification around 363 K, decomposition in a brown mass at 568 K, without melting.

Crystal data

$C_7H_8N_6O\cdot 2H_2O$
$M_r = 228.23$
Orthorhombic, $P2_12_12_1$
$a = 6.751$ (1) Å
$b = 11.990$ (1) Å
$c = 13.061$ (1) Å
$V = 1057.2$ (2) Å^3
$Z = 4$
$D_x = 1.434$ Mg m^{-3}
Mo Kα radiation
Cell parameters from 42 reflections
$\theta = 4$–38°
$\mu = 0.12$ mm^{-1}
$T = 293$ (2) K
Plate, colourless
0.3 × 0.2 × 0.1 mm

Data collection

Siemens *P*4 diffractometer
ω scans
3578 measured reflections
1789 independent reflections
1049 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 30.0^\circ$
$h = -9 \rightarrow 9$
$k = -16 \rightarrow 16$
$l = -18 \rightarrow 18$
3 standard reflections every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.124$
$S = 0.99$
1789 reflections
182 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0036 (12)

Table 1
Selected geometric parameters (Å, °).

C1—C12	1.415 (4)	C5—C6	1.430 (4)
C1—C2	1.421 (4)	C6—O11	1.270 (3)
C1—C6	1.461 (4)	C12—N14	1.311 (4)
C2—N9	1.345 (3)	C12—C13	1.494 (4)
C2—N3	1.363 (3)	N3—N7	1.357 (3)
C4—N10	1.342 (4)	N7—N8	1.289 (3)
C4—C5	1.353 (4)	N8—N9	1.359 (3)
C4—N3	1.393 (3)		
C12—C1—C2	122.4 (2)	O11—C6—C1	121.1 (2)
C12—C1—C6	121.6 (2)	C5—C6—C1	119.3 (2)
C2—C1—C6	116.0 (2)	N14—C12—C1	119.4 (3)
N9—C2—N3	106.6 (2)	N14—C12—C13	117.0 (3)
N9—C2—C1	133.4 (3)	C1—C12—C13	123.6 (2)
N3—C2—C1	120.0 (2)	N7—N3—C2	109.8 (2)
N10—C4—C5	128.1 (2)	N7—N3—C4	124.7 (2)
N10—C4—N3	115.8 (2)	C2—N3—C4	125.5 (2)
C5—C4—N3	116.1 (2)	N8—N7—N3	105.2 (2)
C4—C5—C6	123.0 (2)	N7—N8—N9	112.8 (2)
O11—C6—C5	119.6 (2)	C2—N9—N8	105.7 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···N9^{i}	0.98 (3)	2.04 (5)	2.896 (4)	146 (5)
O2—H2′···O1^{ii}	0.98 (3)	1.80 (4)	2.753 (6)	164 (5)
O1—H1···O11	0.98 (3)	1.73 (4)	2.703 (3)	169 (6)
O1—H1′···O2	0.98 (3)	1.82 (3)	2.786 (4)	166 (5)
N10—H10···N8^{iii}	0.92 (3)	2.09 (4)	2.998 (3)	174 (4)
N10—H10′···O1^{iv}	0.86 (3)	2.19 (3)	2.886 (4)	139 (3)
N14—H14···O2^{v}	0.91 (4)	1.96 (4)	2.845 (4)	162 (3)
N14—H14′···O11	0.92 (4)	1.78 (4)	2.560 (4)	141 (4)

Symmetry codes: (i) $x, y-1, z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, 2-z$; (iii) $2-x, y-\frac{1}{2}, \frac{5}{2}-z$; (iv) $2-x, \frac{1}{2}+y, \frac{5}{2}-z$; (v) $2-x, \frac{1}{2}+y, \frac{3}{2}-z$.

Friedel pairs were merged before the refinement. A riding model was used for the methyl group H atoms, with U_{iso}(H) freely refined. Equal-distance restraints and a refined common U_{iso} value were used for the H atoms of the water molecules. All other H atoms were located in Fourier maps and freely refined [C—H = 0.94 (3) Å and N—H = 0.86 (3)–0.92 (4) Å].

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 1998).

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