

Two new polymorphs of 2,6-diamino-
pyrimidin-4(3*H*)-one monohydrateNura Suleiman Gwaram,^a Hamid Khaledi,^{a*} Hapipah
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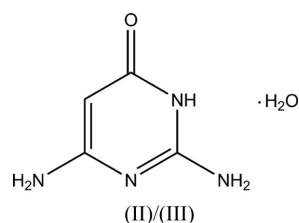
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The title compound, C₄H₆N₄O·H₂O, crystallized simultaneously as a triclinic and a monoclinic polymorph from an aqueous solution of 2,4-diaminopyrimidin-6-ol. Previously, an orthorhombic polymorph was isolated under the same experimental conditions. The molecular geometric parameters in the two present polymorphs and the previously reported orthorhombic polymorph are similar, but the structures differ in the details of their crystal packing. In the triclinic system, the diaminopyrimidinone molecules are connected to one another *via* N—H···O and N—H···N hydrogen bonding to form infinite chains in the [011] direction. The chains are further hydrogen bonded to the water molecules, resulting in a three-dimensional network. In the monoclinic system, the diaminopyrimidinone molecules are hydrogen bonded together into two-dimensional networks parallel to the *bc* plane. The water molecules link the planes to form a three-dimensional polymeric structure.

Comment

Diaminopyrimidines are a class of organic compounds with interesting biological properties (Desharnais *et al.*, 2003) and applications in supramolecular chemistry (Yagai, 2006). Some years ago, Skoweranda *et al.* (1990) reported the crystal structure of 2,6-diaminopyrimidin-4(3*H*)-one, cocrystallized with one molecule of water, in an orthorhombic crystal system, (I). During our studies on the crystallization behavior of 2,4-diaminopyrimidin-6-ol, we obtained two new polymorphs of the reported compound in triclinic, (II), and monoclinic, (III), systems. Our subsequent efforts to obtain the orthorhombic form all failed, and therefore it can be regarded as a disappearing polymorph. In fact, recrystallization of 2,4-diaminopyrimidin-6-ol from an aqueous solution, the conditions used by Skoweranda *et al.*, led to concomitant formation of the triclinic and monoclinic crystals.



The displacement ellipsoid drawing of the three polymorphs is given in Fig. 1. In the three polymorphs, the molecules form three-dimensional hydrogen-bonded networks, albeit with different hydrogen-bond systems. In contrast to the orthorhombic polymorph, (I), in which the water molecules are hydrogen bonded together into infinite chains along the *a* axis, there is no interaction between the water molecules in the two new polymorphs. Moreover, polymorph (I) shows intermolecular N4—H4B···N4ⁱⁱ hydrogen bonding [symmetry code: (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, z$; Fig. 2] which was not observed in polymorphs (II) and (III). In polymorph (II), the adjacent diaminopyrimidinone molecules are connected to one another *via* N—H···O and N—H···N hydrogen bonding around

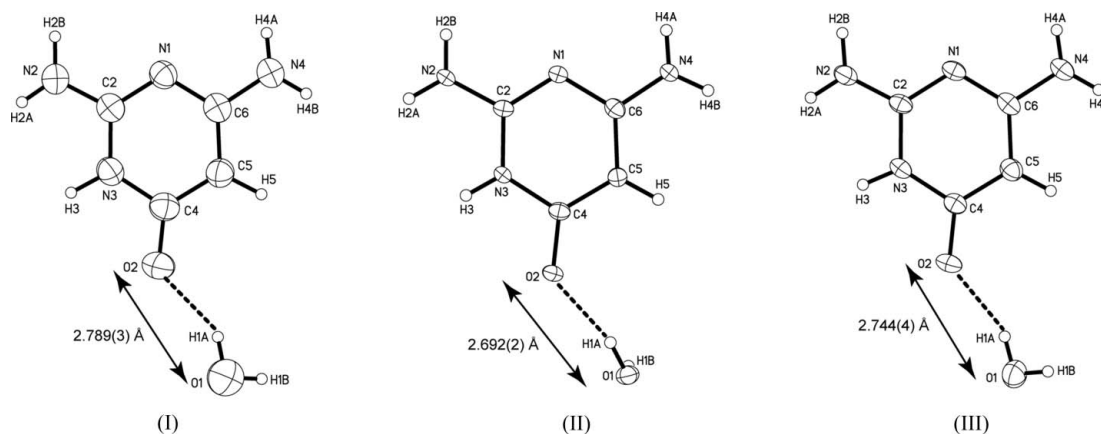


Figure 1

The asymmetric units of the three polymorphs of the title compound, showing the atom-numbering scheme selected to conform to polymorph (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The position of the water molecule has been selected in order to show the shortest hydrogen-bonding interaction between the water molecule and atom O2. The O1···O2 distances are displayed. The structure of polymorph (I) was determined at 293 K (Skoweranda *et al.*, 1990), whereas the data of polymorphs (II) and (III) were collected at 100 K.

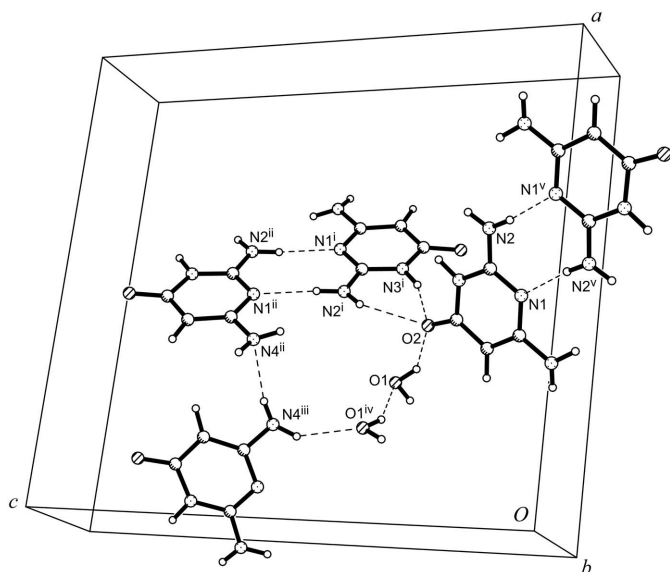


Figure 2

A view of the hydrogen-bonding interactions in polymorph (I) (Skoweranda *et al.*, 1990). [Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x, -y - \frac{1}{2}, z + \frac{1}{2}$; (iii) $-x + \frac{1}{2}, -y, z + \frac{1}{2}$; (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, z$; (v) $-x + 1, -y - 1, -z$.]

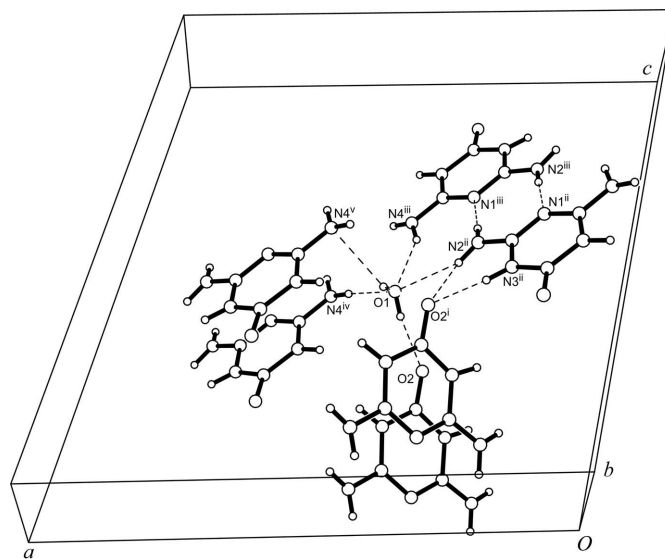


Figure 4

A view of the hydrogen-bonding interactions in polymorph (III). [Symmetry codes: (i) $x, y + 1, z$; (ii) $-x + \frac{1}{2}, y + \frac{3}{2}, -z + \frac{1}{2}$; (iii) $x, -y + 1, z + \frac{1}{2}$; (iv) $-x + 1, y, -z + \frac{1}{2}$; (v) $-x + 1, y + 1, -z + \frac{1}{2}$.]

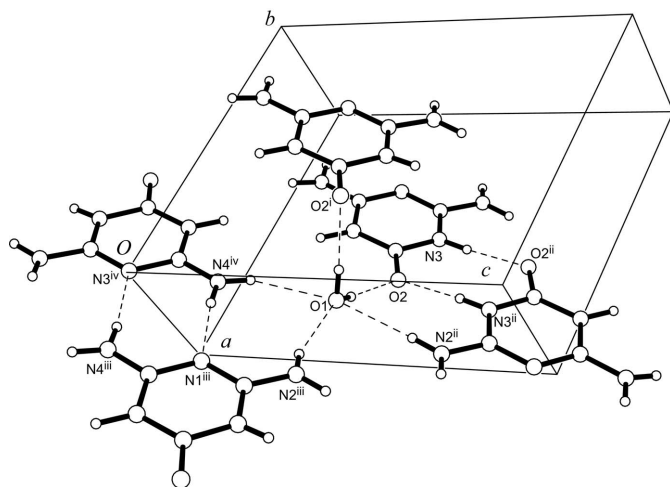


Figure 3

A view of the hydrogen-bonding interactions in polymorph (II). [Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + 2, -y + 1, -z + 1$; (iii) $x - 1, y - 1, z$; (iv) $-x + 1, -y + 1, -z$.]

centers of inversion to form parallel infinite chains in the [011] direction. The water molecule has five hydrogen-bonding interactions that involve five different neighboring pyrimidinone molecules (Fig. 3). As a result, the pyrimidinone chains are linked into a three-dimensional network.

In polymorph (III), pairs of diaminopyrimidinone molecules are N—H...N hydrogen bonded together around centers of inversion. The resulting dimers are further connected together around twofold screw axes along *b* via N2—H2...O2ⁱ and N3—H3...O2ⁱ hydrogen bonding [symmetry code: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$] in a bifurcated system to form two-dimensional networks parallel to the *bc* plane. The water molecule is engaged in five hydrogen-bonding interactions with five neighboring pyrimidinone

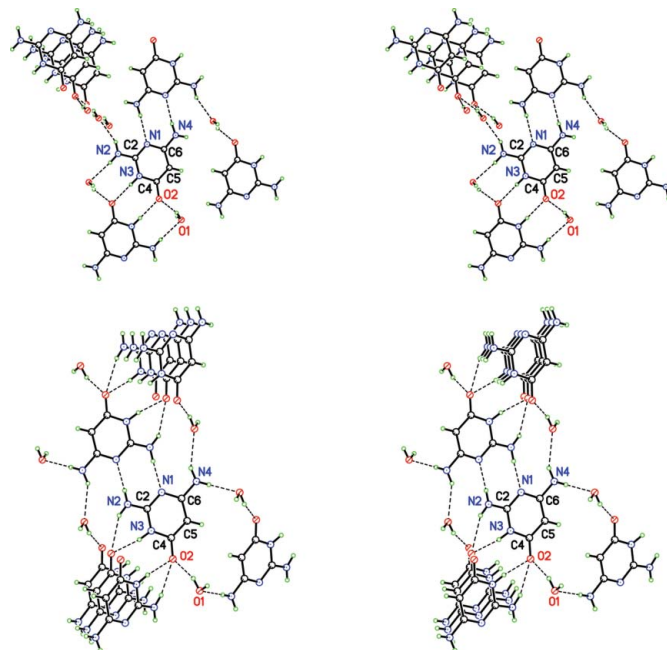


Figure 5

Stereoviews of polymorphs (II) (top) and (III) (bottom). The stacking of the planar molecules is only shown at the periphery of the figure in order to focus on the hydrogen-bonding patterns in the immediate vicinity of the title molecule. The view is selected such that the title molecules are placed in the same orientation. The stacking motif is in the direction of the shortest axial length, namely the *a* axis in (II) and the *b* axis in (III).

molecules (Fig. 4), resulting in a three-dimensional hydrogen-bonded network. Fig. 5 represents the stereoviews of polymorphs (II) and (III).

In both polymorphs, weak π - π stacking occurs between the planar molecules in the direction of the shortest crystallographic axis. The diaminopyrimidinone molecule, including all

H atoms, in the three polymorphs is almost planar [r.m.s. deviation: (I) 0.049 Å, (II) 0.031 Å, (III) 0.053 Å] and the bond lengths and angles are similar (Tables 1 and 3). The amino groups do not appear to be pyramidalized to within the uncertainty of the structure determinations. For (II), the sums of the angles at nitrogen are 359.3 (14) and 359.4 (15)° for N2 and N4, respectively, whereas for (III) the corresponding values are 359 (2) and 356 (2)°. Polymorph (III) does exhibit slightly greater deviations than (II) of the NH₂ groups from the least-squares planes of the pyrimidinone molecule. These displacements are of opposite sign for the N2 and N4 groups in both polymorphs. The density of the monoclinic polymorph (1.538 Mg m⁻³) is greater than that of the triclinic structure (1.492 Mg m⁻³) which might be indicative of higher thermodynamic stability of the monoclinic system (Burger & Ramberger, 1979). The density of polymorph (I) was reported to be 1.476 Mg m⁻³; however the data were collected at 293 K.

Experimental

A portion of commercially available 2,4-diaminopyrimidin-6-ol (0.6 g) was dissolved in distilled water (10 ml) by heating and stirring. The resulting solution was then left at room temperature. In less than an hour, crystals of polymorphs (II) and (III) were obtained simultaneously.

Polymorph (II)

Crystal data

C ₄ H ₆ N ₄ O·H ₂ O	$\gamma = 81.479 (6)^\circ$
$M_r = 144.14$	$V = 320.88 (4) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 3.9293 (3) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 8.6611 (7) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$c = 9.6044 (8) \text{ \AA}$	$T = 100 \text{ K}$
$\alpha = 83.111 (5)^\circ$	$0.45 \times 0.35 \times 0.13 \text{ mm}$
$\beta = 88.090 (6)^\circ$	

Data collection

Bruker APEXII CCD diffractometer	2138 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	1113 independent reflections
$T_{\min} = 0.948, T_{\max} = 0.984$	996 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.017$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.112$	$\Delta\rho_{\text{max}} = 0.20 \text{ e \AA}^{-3}$
$S = 1.04$	$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$
1113 reflections	
112 parameters	
7 restraints	

Polymorph (III)

Crystal data

C ₄ H ₆ N ₄ O·H ₂ O	$V = 1245.4 (14) \text{ \AA}^3$
$M_r = 144.14$	$Z = 8$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 17.236 (11) \text{ \AA}$	$\mu = 0.13 \text{ mm}^{-1}$
$b = 3.987 (3) \text{ \AA}$	$T = 100 \text{ K}$
$c = 18.717 (12) \text{ \AA}$	$0.30 \times 0.07 \times 0.04 \text{ mm}$
$\beta = 104.450 (9)^\circ$	

Table 1

Selected geometric parameters (Å, °) for (II).

O2—C4	1.2815 (18)	N3—C4	1.383 (2)
N1—C2	1.322 (2)	N4—C6	1.335 (2)
N1—C6	1.359 (2)	C4—C5	1.379 (2)
N2—C2	1.336 (2)	C5—C6	1.406 (2)
N3—C2	1.360 (2)		
N1—C2—N2	119.89 (14)	O2—C4—N3	116.60 (13)
N2—C2—N3	117.60 (14)	N4—C6—N1	115.37 (14)
O2—C4—C5	126.64 (14)	N4—C6—C5	121.59 (15)

Table 2

Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1A \cdots O2	0.84 (2)	1.88 (2)	2.6935 (15)	163 (2)
O1—H1B \cdots O2 ⁱ	0.84 (2)	1.92 (2)	2.7485 (16)	170 (2)
N4—H4B \cdots O1 ⁱⁱ	0.87 (2)	2.34 (2)	3.0501 (18)	139 (2)
N4—H4A \cdots N1 ⁱⁱⁱ	0.88 (2)	2.13 (2)	3.0004 (19)	173 (2)
N2—H2B \cdots O1 ^{iv}	0.89 (2)	2.12 (2)	2.9527 (17)	158 (2)
N2—H2A \cdots O1 ^v	0.87 (2)	2.19 (2)	3.0605 (18)	174 (2)
N3—H3 \cdots O2 ^v	0.86 (2)	1.95 (2)	2.8035 (17)	173 (2)

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

Table 3

Selected geometric parameters (Å, °) for (III).

O2—C4	1.274 (4)	N3—C4	1.375 (4)
N1—C2	1.328 (4)	N4—C6	1.354 (4)
N1—C6	1.358 (4)	C4—C5	1.393 (4)
N2—C2	1.323 (4)	C5—C6	1.400 (4)
N3—C2	1.371 (4)		
N2—C2—N1	120.6 (3)	O2—C4—C5	127.1 (3)
N2—C2—N3	117.2 (3)	N4—C6—N1	116.1 (3)
O2—C4—N3	116.8 (3)	N4—C6—C5	120.4 (3)

Data collection

Bruker APEXII CCD diffractometer	2752 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	1131 independent reflections
$T_{\min} = 0.964, T_{\max} = 0.995$	757 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.055$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.148$	$\Delta\rho_{\text{max}} = 0.28 \text{ e \AA}^{-3}$
$S = 1.00$	$\Delta\rho_{\text{min}} = -0.37 \text{ e \AA}^{-3}$
1131 reflections	
112 parameters	
7 restraints	

The C-bound H atoms were placed in idealized locations (C—H = 0.95 Å) and refined as riding on their parent C atoms. The N- and O-bound H atoms were located in a difference Fourier map and were refined with distance restraints of N—H = 0.88 (2) Å and O—H = 0.84 (2) Å. $U_{\text{iso}}(\text{H})$ values were set at $1.2U_{\text{eq}}(\text{parent atom})$.

For both compounds, data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008);

Table 4
Hydrogen-bond geometry (Å, °) for (III).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2 <i>A</i> ...O2 ⁱ	0.89 (2)	2.39 (3)	3.115 (4)	138 (3)
N2—H2 <i>A</i> ...O1 ⁱⁱ	0.89 (2)	2.52 (2)	3.245 (4)	139 (3)
N2—H2 <i>B</i> ...N1 ⁱⁱⁱ	0.90 (2)	2.05 (2)	2.947 (4)	177 (3)
N3—H3...O2 ⁱ	0.88 (2)	1.93 (2)	2.800 (3)	168 (3)
N4—H4 <i>A</i> ...O1 ^{iv}	0.85 (2)	2.34 (2)	3.124 (4)	154 (3)
N4—H4 <i>B</i> ...O1 ^v	0.90 (2)	2.08 (2)	2.975 (4)	174 (3)
O1—H1 <i>A</i> ...O2	0.83 (2)	1.95 (2)	2.742 (3)	160 (4)
O1—H1 <i>B</i> ...N4 ^{vi}	0.84 (2)	2.48 (3)	3.105 (4)	133 (3)

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

program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Bruker, 2007); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3068). Services for accessing these data are described at the back of the journal.

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