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Pseudopolymorphs of 2,6-diaminopyrimidin-4-one and 2-amino-6-methylpyrimidin-4-one: one or two tautomers present in the same crystal

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The derivatives of pyrimidin-4-one can adopt either a 1*H*- or a 3*H*-tautomeric form, which affects the hydrogen-bonding interactions in cocrystals with compounds containing complementary functional groups. In order to study their tautomeric preferences, we crystallized 2,6-diaminopyrimidin-4-one and 2-amino-6-methylpyrimidin-4-one. During various crystallization attempts, four structures of 2,6-diaminopyrimidin-4-one were obtained, namely solvent-free 2,6-diaminopyrimidin-4-one, $C_4H_6N_4O$, (I), 2,6-diaminopyrimidin-4-one–dimethylformamide–water (3/4/1), $C_4H_6N_4O{\cdot}1.33C_3H_7NO{\cdot}0.33H_2O$, (I*a*), 2,6-diaminopyrimidin-4-one dimethylacetamide monosolvate, $C_4H_6N_4O{\cdot}C_4H_9NO$, (I*b*), and 2,6-diaminopyrimidin-4-one–*N*-methylpyrrolidin-2-one (3/2), $C_4H_6N_4O{\cdot}1.5C_5H_9NO$, (I*c*). The 2,6-diaminopyrimidin-4-one molecules exist only as 3*H*-tautomers. They form ribbons characterized by $R_2^2(8)$ hydrogen-bonding interactions, which are further connected to form three-dimensional networks. An intermolecular N—H···N interaction between amine groups is observed only in (I). This might be the reason for the pyramidalization of the amine group. Crystallization experiments on 2-amino-6-methylpyrimidin-4-one yielded two isostructural pseudopolymorphs, namely 2-amino-6-methylpyrimidin-4(3*H*)-one–2-amino-6-methylpyrimidin-4(1*H*)-one–dimethylacetamide (1/1/1), $C_5H_7N_3O{\cdot}C_5H_7N_3O{\cdot}C_4H_9NO$, (II*a*), and 2-amino-6-methylpyrimidin-4(3*H*)-one–2-amino-6-methylpyrimidin-4(1*H*)-one–*N*-methylpyrrolidin-2-one (1/1/1), $C_5H_7N_3O{\cdot}C_5H_7N_3O{\cdot}C_5H_9NO$, (II*b*). In both structures, a 1:1 mixture of 1*H*- and 3*H*-tautomers is present, which are linked by three hydrogen bonds similar to a Watson–Crick C–G base pair.

Comment

Pyrimidin-4-one derivatives are of particular interest in pharmacology and molecular biology. They include nucleobases and many important pharmaceutical drugs, *e.g.* anti-inflammatory (Kawade *et al.*, 2011), anticancer (Lu *et al.*, 2007), antihistaminic and bronchorelaxant agents (Youssouf *et al.*, 2008). Pyrimidin-4-one can exist in three tautomeric forms: as a 1*H*- or 3*H*-tautomer or as a hydroxypyrimidine. An NMR study revealed that the preference of each tautomeric form depends on its state, although no hydroxypyrimidine form has ever been observed. In the solid state, only the 3*H*-tautomer has been found, while in polar solvents, a mixture of 1*H*-and 3*H*-tautomers is observed (López *et al.*, 2000). These results agree with the two crystal structures containing pyrimidin-4-one in the Cambridge Structural Database (CSD, Version 5.31 of November 2009, plus four updates; Allen, 2002), which confirmed that the 3*H*-tautomer is preferred [CSD refcodes BAGQUV (Vaillancourt *et al.*, 1998) and XOLHOW (Bhogala *et al.*, 2008)].

We are interested in the hydrogen-bonding interaction between pyrimidin-4-one derivatives and compounds containing complementary functional groups. Since the occurrence of tautomers results in different synthon combinations (Bhogala *et al.*, 2008), we crystallized 2,6-diaminopyrimidin-4-one and 2-amino-6-methylpyrimidin-4-one to study their tautomeric preferences. Four structures of 2,6-diaminopyrimidin-4-one were obtained during various crystallization experiments, namely solvent-free 2,6-diaminopyrimidin-4-one, (I), a dimethylformamide–water solvate (3/4/1), (I*a*), a dimethylacetamide monosolvate, (I*b*), and an *N*-methylpyrrolidin-2-one (3/2) solvate, (I*c*). Another *N*-methylpyrrolidin-2-one solvate of minor crystal quality was also obtained (Gerhardt *et al.*, 2011). All 2,6-diaminopyrimidin-4-one molecules exist as 3*H*-tautomers. Crystallization attempts on 2-amino-6-methylpyrimidin-4-one yielded two pseudopolymorphs, namely dimethylacetamide monosolvate, (II*a*), and *N*-methylpyrrolidin-2-one monosolvate, (II*b*). In both structures, a 1:1 mixture of 1*H*- and 3*H*-tautomers is present.

2,6-Diaminopyrimidin-4-one, (I), crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit (Fig. 1). One amine group is planar and twisted slightly out of the plane of the ring, while the other is pyramidalized and shows a longer C—NH_2 bond [sums of the C—N—H and H—N—H angles at the N atoms = 359.1 (at N21) and 347.3°

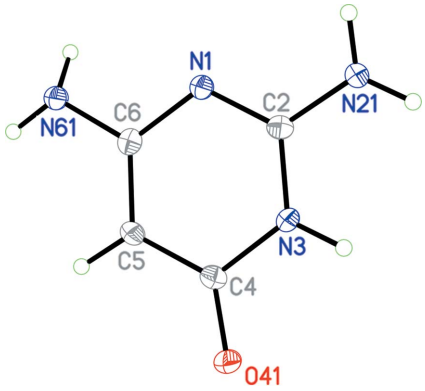
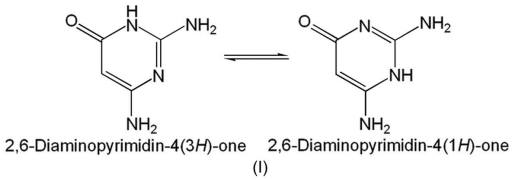
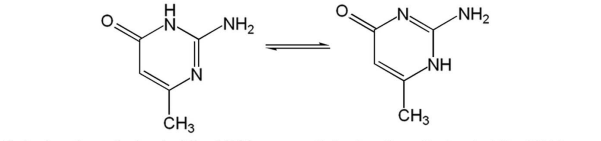


Figure 1
A perspective view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

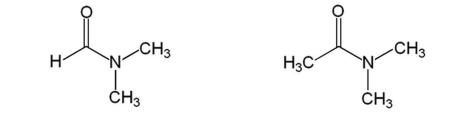
(at N61); C—NH_2 = 1.337 (2) (at N21) and 1.365 (2) Å (at N61)]. The 2,6-diaminopyrimidin-4-one molecules form ribbons characterized by three hydrogen bonds, consisting of one $R_2^2(8)$ interaction (Bernstein *et al.*, 1995) with N—H···O and N—H···N hydrogen bonds, and another $R_2^2(8)$ interaction

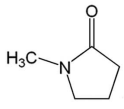


(I)



(II)





(I) 2,6-Diaminopyrimidin-4(3*H*)-one
(I*a*) 2,6-Diaminopyrimidin-4(3*H*)-one · 4/3 DMF · 1/3 H_2O
(I*b*) 2,6-Diaminopyrimidin-4(3*H*)-one · DMAC
(I*c*) 2,6-Diaminopyrimidin-4(3*H*)-one · 3/2 NMP

(II*a*) 2-Amino-6-methylpyrimidin-4(3*H*)-one · 2-Amino-6-methylpyrimidin-4(1*H*)-one · DMAC
(II*b*) 2-Amino-6-methylpyrimidin-4(3*H*)-one · 2-Amino-6-methylpyrimidin-4(1*H*)-one · NMP

with two N—H···N hydrogen bonds (Fig. 2). This arrangement is similar to that in the cytosine–guanine base pair. The ribbons are rippled and further connected into layers by $R_4^3(12)$ interactions. Other N—H···O hydrogen bonds stabilize the layers to form a three-dimensional network.

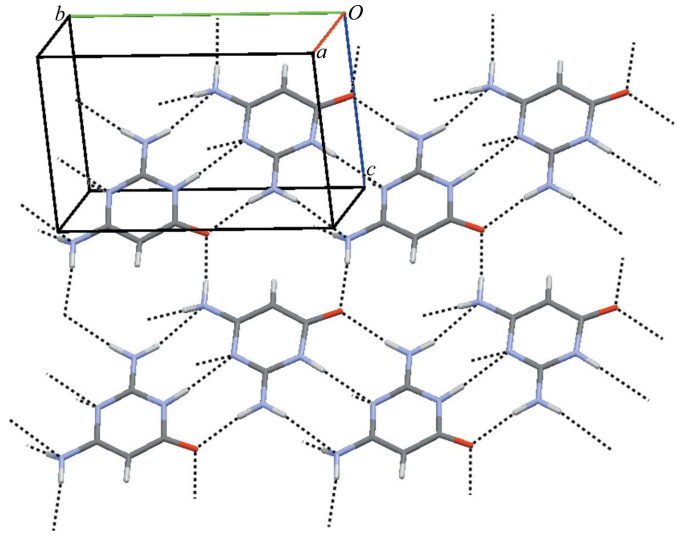


Figure 2
A partial packing diagram for (I). Hydrogen bonds are shown as dashed lines.

Compound (I*a*) formed during crystallization attempts from dimethylformamide (DMF). It crystallizes in the monoclinic space group $P2_1$ with three planar 2,6-diaminopyrimidin-4-one molecules (r.m.s deviations = 0.008, 0.012 and 0.013 Å for all non-H atoms) and four DMF molecules. Since we used non-water-free solvent, one water molecule is also present in the asymmetric unit (Fig. 3). The three 2,6-diaminopyrimidin-4-one molecules show different hydrogen-bond arrangements. Molecules *A* and *B* are connected by either $R_2^2(8)$ N—H···O or $R_2^2(8)$ N—H···N bonds to form planar ribbons running parallel to $(\bar{1}01)$ (Fig. 4). The ribbons are further stabilized by hydrogen bonds to the solvent molecules. One DMF molecule is N—H···O hydrogen bonded only to molecule *A*, while another DMF molecule links molecules *A* and *B* by two N—H···O hydrogen bonds. Furthermore, chains running along the *a* axis consisting of N—H···O hydrogen-bonded molecules *C* are observed (Fig. 5). The chain is stabilized by N—H···O hydrogen bonds with the participation of solvent molecules. One of the two DMF molecules linked to molecule

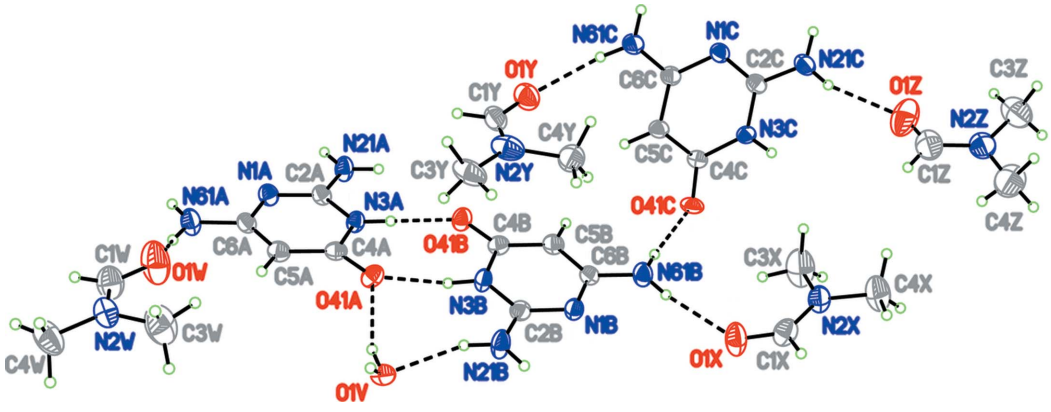


Figure 3
A perspective view of (I*a*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen bonds. One of the dimethylformamide molecules (molecule *Y*) is disordered and only the major occupied site is shown.

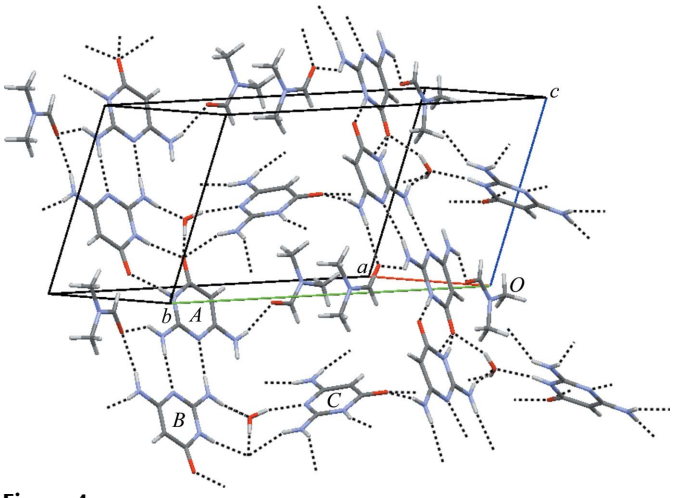


Figure 4
A partial packing diagram for (I*a*). Hydrogen bonds are shown as dashed lines. Only DMF molecules linked to molecules *A* and *B* are shown.

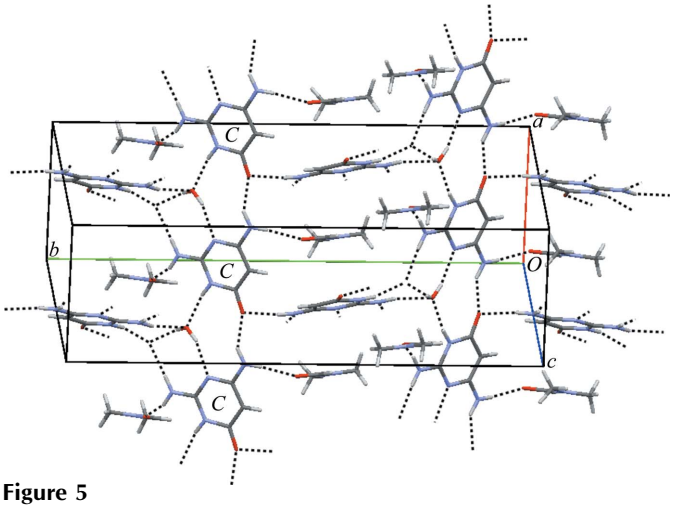


Figure 5
A partial packing diagram for (I*a*). Dashed lines indicate hydrogen bonds. Only DMF molecules linked to molecules *C* are shown. One of the solvent molecules is disordered and its minor occupied site has been omitted.

C is disordered over two sites with a planar arrangement (r.m.s deviation = 0.011 Å). The packing of (I*a*) shows ribbons and chains, which are connected by N—H···O hydrogen bonds to form a three-dimensional network. The water molecule forms hydrogen bonds bridging the three 2,6-diaminopyrimidin-4-one molecules and thus additionally stabilizes the structure.

The dimethylacetamide (DMAC) monosolvate, (I*b*), crystallizes in the monoclinic space group *Cc* with two 2,6-diaminopyrimidin-4-one (r.m.s deviations = 0.013 and 0.025 Å for all non-H atoms) and two DMAC molecules in the asymmetric unit (Fig. 6). In the packing of (I*b*), ribbons consisting of 2,6-diaminopyrimidin-4-one molecules run in two different directions [parallel to $(\bar{1}11)$ and $(\bar{1}\bar{1}1)$]. Similar to (I*a*), the molecules are stabilized either by N—H···O or by N—H···N hydrogen bonds with an $R_2^2(8)$ pattern (Fig. 7). These ribbons are further N—H···O hydrogen bonded to form channels, in which solvent molecules are located (Fig. 8). One DMAC molecule is coplanar with the 2,6-diaminopyrimidin-4-one molecules and shows only van der Waals interactions, while the O atom of the other DMAC molecule is threefold N—H···O hydrogen bonded to 2,6-diaminopyrimidin-4-one molecules.

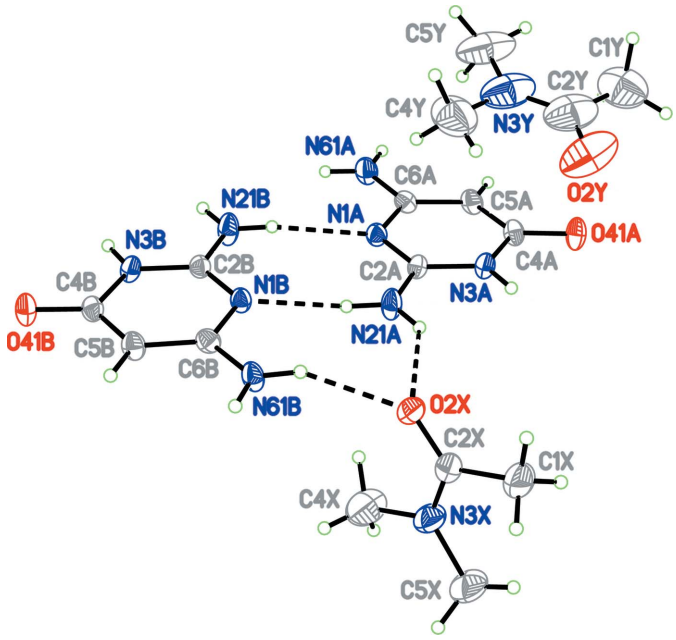


Figure 6
A perspective view of (I*b*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen bonds.

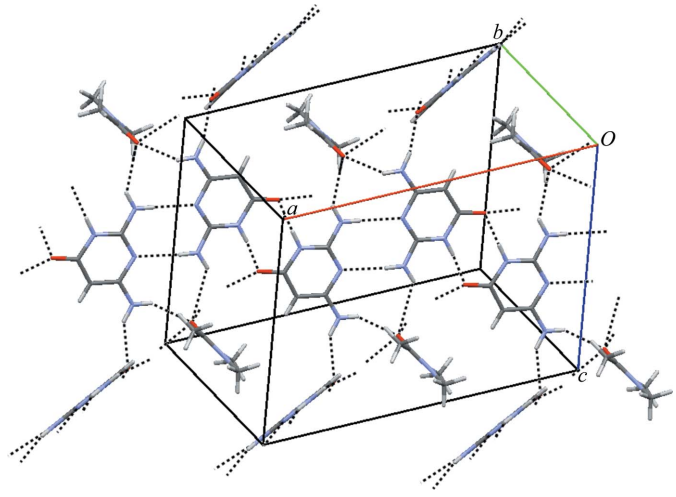


Figure 7
A partial packing diagram for (I*b*). Hydrogen bonds are shown as dashed lines. The solvent molecules, which are only stabilized by van der Waals interactions, have been omitted.

Compound (I*c*) crystallizes as an *N*-methylpyrrolidin-2-one (NMP) solvate with two 2,6-diaminopyrimidin-4-one and three solvent molecules in the asymmetric unit (Fig. 9). The 2,6-diaminopyrimidin-4-one molecules are planar (r.m.s deviations = 0.005 and 0.012 Å for all non-H atoms). $R_2^2(8)$ interactions involving either two N—H···O or two N—H···N hydrogen bonds are again present. Both interactions connect molecules *A* to form ribbons running parallel to (111), which

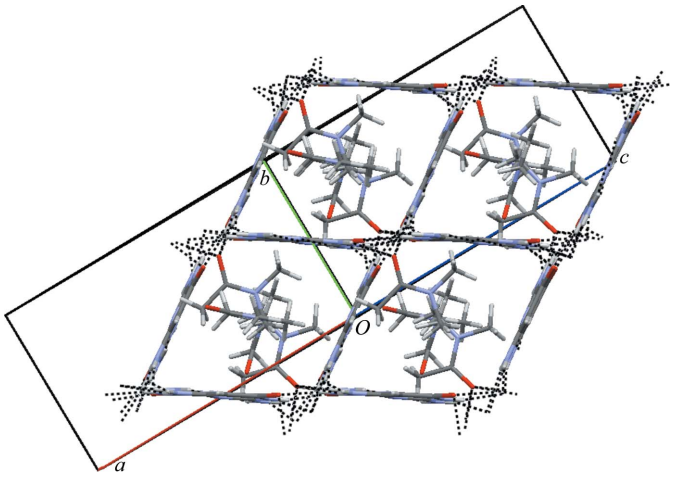


Figure 8
A partial packing diagram for (I*b*). Hydrogen bonds are shown as dashed lines.

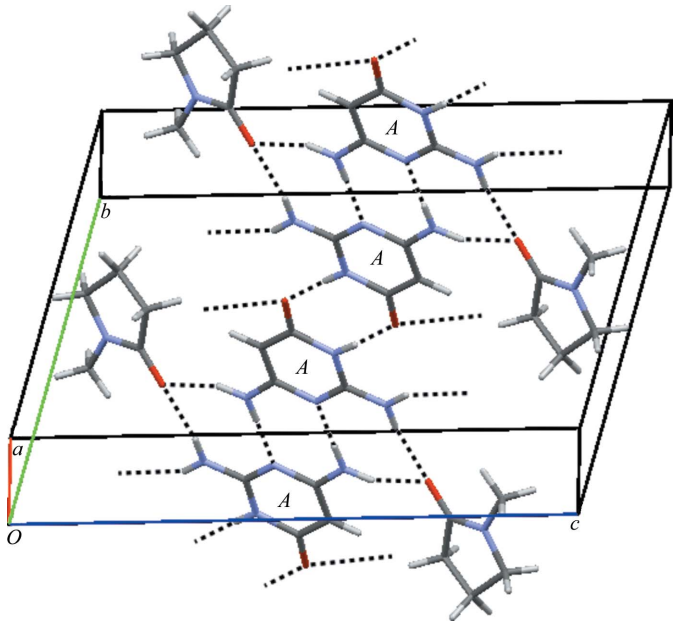


Figure 10
A partial packing diagram for (I*c*). Hydrogen bonds are shown as dashed lines. Only molecules *A* and solvent molecules connected to them are shown.

are additionally stabilized by N—H···O bonds between molecule *A* and one NMP molecule (Fig. 10). In contrast, molecules *B* form dimers stabilized by $R_2^2(8)$ N—H···N hydrogen bonds. Two NMP molecules are N—H···O hydrogen bonded to each molecule *B*, and thus inversion-symmetric arrangements of two molecules *B* and two NMP molecules are formed (Fig. 11). These link the ribbons to form a three-dimensional network.

The two isostructural 2-amino-6-methylpyrimidin-4-one solvates, (II*a*) and (II*b*), crystallize in the triclinic space group $P\overline{1}$ with similar lattice parameters. A 1:1 ratio of 1*H*- and 3*H*-tautomers is present in both crystal structures. The asymmetric unit of (II*a*) consists of the two tautomers and one DMAC molecule (Fig. 12), while (II*b*) crystallizes with the two tautomers and one disordered NMP molecule (Fig. 13). In both structures, the molecules are coplanar with each other, and both the hydrogen-bonding interactions and the crystal packings are similar (Figs. 14 and 15). The two tautomers are linked by two $R_2^2(8)$ interactions involving N—H···O and N—H···N bonds, forming a dimer related to the cytosine–guanine base pair. Two symmetry-equivalent dimers are further connected by two N—H···N interactions with an $R_2^2(8)$

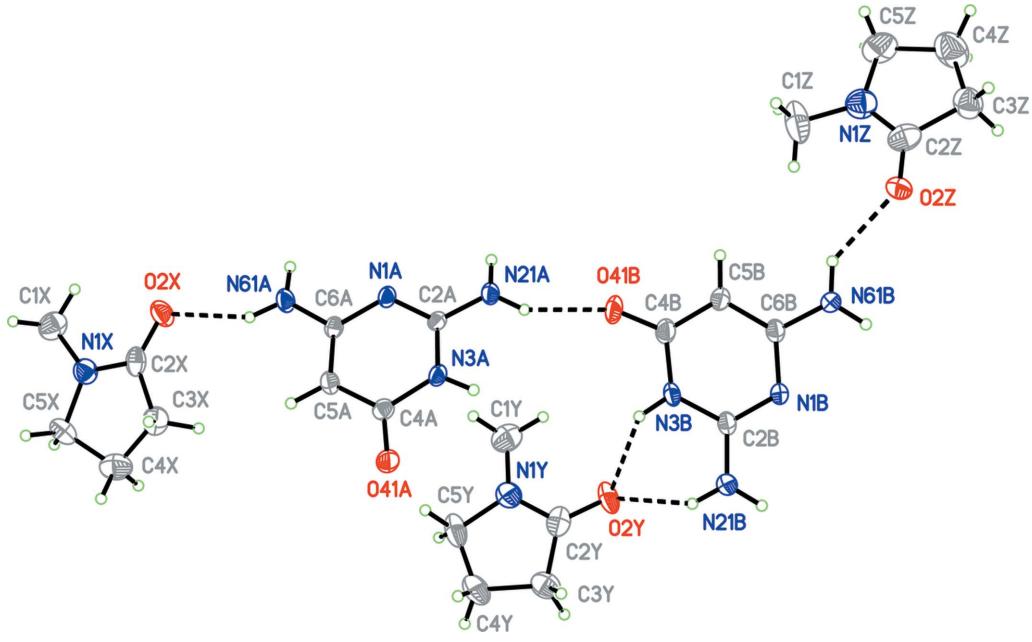


Figure 9
A perspective view of (I*c*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen bonds.

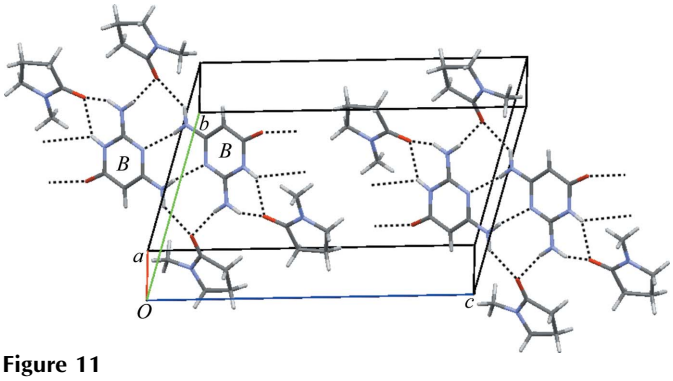


Figure 11
A partial packing diagram for (I*c*). Hydrogen bonds are shown as dashed lines. Only molecules *B* and solvent molecules connected to them are shown.

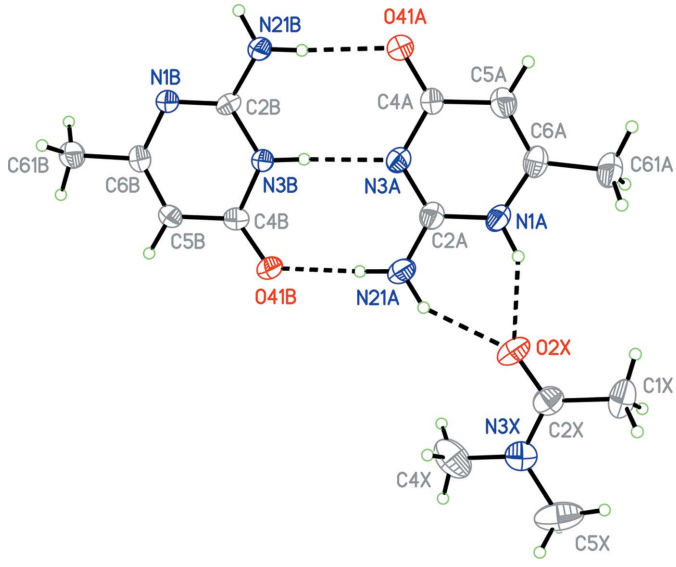


Figure 12
A perspective view of (II*a*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen bonds.

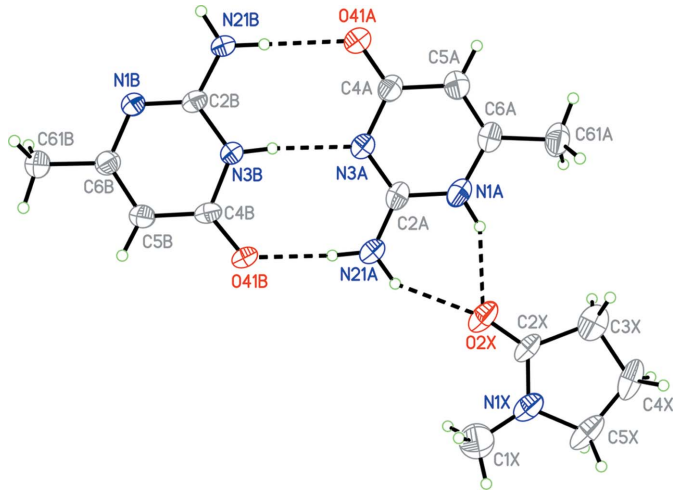


Figure 13
A perspective view of (II*b*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen bonds. The solvent molecule is disordered and only the major occupied site is shown.

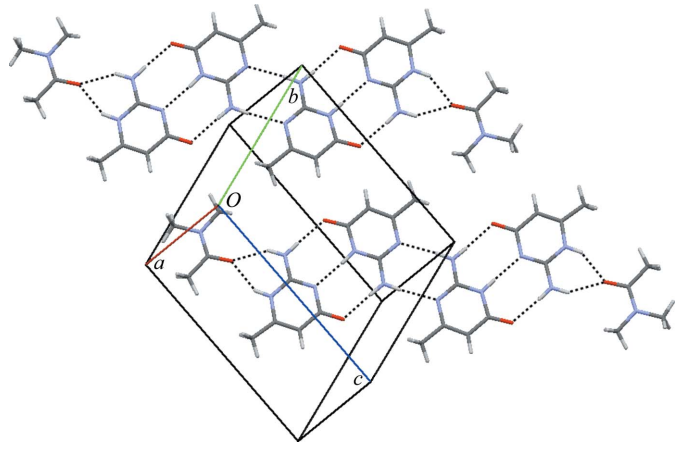


Figure 14
A partial packing diagram for (II*a*). Hydrogen bonds are shown as dashed lines.

pattern to give a tetramer. The O atoms of the solvent molecules, either DMAC in (II*a*) or NMP in (II*b*), adopt identical postions and are $R_2^1(6)$ N—H···O hydrogen bonded to the 3*H*-tautomer. The crystal structures show layers parallel to the (210) plane containing discrete arrangements of the tetramers.

In order to study the preference of the 1*H*- and 3*H*-tautomeric forms, a CSD substructure search for pyrimidin-4-one derivatives was undertaken. 15 entries for the 1*H* form, 39 entries for the 3*H* form and five entries with both tautomeric forms were found [refcodes ICYTIN (Sharma & McConnell, 1965), ICYTIN01 (Portalone & Colapietro, 2007), LEJLAN and LEJLOB (Bannister *et al.*, 1994), and ZERMIS (Toledo *et al.*, 1995)]. Examining only entries containing 2,6-diaminopyrimidin-4-one, no 1*H*-tautomer has been reported [refcodes SEYDIJ (Skoweranda *et al.*, 1990) and GIMZUY (Subashini *et al.*, 2007)]. The preference for the 3*H*-tautomeric form is also shown in two recently reported polymorphs of the monohydrate (Suleiman Gwaram *et al.*, 2011), in the NMP solvate with minor crystal quality (Gerhardt *et al.*, 2011) and in the four crystal structures above, *viz.* (I) and (I*a*)–(I*c*). A possible explanation for the absence of the 1*H*-tautomeric form might be the repulsion of the H atoms from the three amino groups presenting an adjacent donor–donor–donor hydrogen-bonding site. In contrast, 2-amino-6-methylpyrimidin-4-one exists in both 1*H*- and 3*H*-tautomeric forms. In the solvent-free $P2_1/n$ structure it exists as a 1*H*-tautomer (refcode FETSEC; Lowe *et al.*, 1987), while in the solvent-free *C*2/*c* polymorph, both 1*H*- and 3*H*-tautomers are shown as a result of disordered H atoms (refcode ZERMIS; Toledo *et al.*, 1995). The 3*H*-tautomeric form is observed in its cocrystals with glutaric acid and adipic acid (refcodes ZUKXAE and ZUKXEI; Liao *et al.*, 1996). Interestingly, only in the solvates (II*a*) and (II*b*) do both tautomers exist in a 1:1 ratio.

Almost all 2,6-diaminopyrimidin-4-one and 2-amino-6-methylpyrimidin-4-one molecules are planar. The pyramidalization of one amine group in (I) is also observed in the

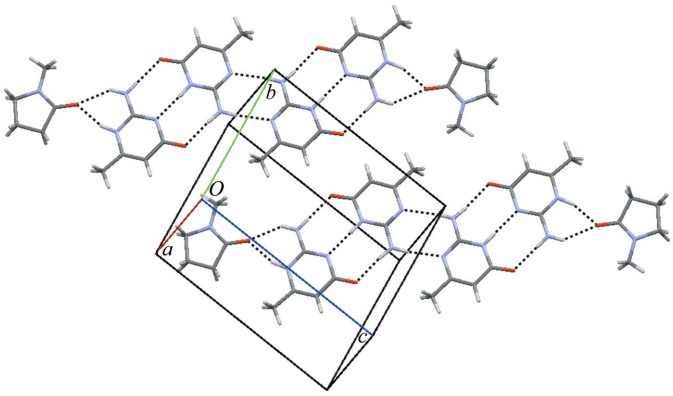


Figure 15
A partial packing diagram for (II*b*). Hydrogen bonds are shown as dashed lines. The minor occupied sites of the solvent molecules have been omitted.

orthorhombic polymorph of 2,6-diaminopyrimidin-4-one monohydrate [refcode SEYDIJ (Skoweranda *et al.*, 1990), form I according to Suleiman Gwaram *et al.* (2011)]. Similar to (I), one C—NH_2 bond is longer than the other [1.334 (2) and 1.359 (2) Å], and the sums of the bond angles at the N atoms are 360 and 354°. Different C—NH_2 bond lengths are also observed in the monoclinic polymorph [form III according to Suleiman Gwaram *et al.* (2011); C—NH_2 = 1.323 (4) and 1.354 (4) Å], but both amine groups are planar [sums of the bond angles at the N atoms = 359 (2) and 356 (2)°, respectively].

Comparing the hydrogen-bond arrangements formed by the 2,6-diaminopyrimidin-4-one molecules, ribbons characterized by $R_2^2(8)$ interactions involving either two N—H···O or two N—H···N bonds are observed in all structures. However, an intermolecular N—H···N interaction between the amine groups is only observed in (I) and in the orthorhombic polymorph (form I), which may explain the pyramidalization of one amine group in these two structures. The crystal packings in the various structures show three-dimensional networks additionally stabilized by solvent molecules. The 1*H*- and 3*H*-tautomers of 2-amino-6-methylpyrimidin-4-one are linked by three hydrogen bonds, similar to what is observed in the Watson–Crick C–G base pair. Identical arrangements are observed in the five CSD entries for pyrimidin-4-one derivatives containing both tautomeric forms. Altogether, (I) and (I*a*)–(I*c*) confirm the 3*H*-tautomer preference of 2,6-diaminopyrimidin-4-one, while there is no preference for 2-amino-6-methylpyrimidin-4-one. It can exist as a 1*H*- or 3*H*-tautomer, or as a 1:1 mixture of both tautomers, as shown in the crystal structures of (II*a*) and (II*b*).

Experimental

Solvent evaporation experiments with commercially available 2,6-diaminopyrimidin-4-one under different conditions yielded (I) and (I*a*)–(I*c*) (Table 7). Single crystals of (II*a*) and (II*b*) were obtained by crystallization of commercially available 2-amino-6-methylpyrimidin-4-one (Table 8). None of the solvents used in the experiments was water-free.

Compound (I)

Crystal data

$C_4H_6N_4O$
M_r = 126.13
Monoclinic, $P2_1/c$
a = 7.7150 (9) Å
b = 9.7229 (7) Å
c = 7.4514 (8) Å
β = 114.453 (8)°
V = 508.81 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.13 mm^{-1}
T = 173 K
0.45 × 0.35 × 0.30 mm

Data collection

Stoe IPDS II two-circle diffractometer
7117 measured reflections
953 independent reflections
737 reflections with $I > 2\sigma(I)$
R_{int} = 0.128

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.092
S = 0.97
953 reflections
103 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Compound (I*a*)

Crystal data

$C_4H_6N_4O{\cdot}4/3C_3H_7NO{\cdot}1/3H_2O$
M_r = 229.59
Monoclinic, $P2_1$
a = 7.4417 (6) Å
b = 25.3217 (18) Å
c = 9.8578 (7) Å
β = 108.476 (6)°
V = 1761.8 (2) Å^3
Z = 6
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 173 K
0.50 × 0.30 × 0.20 mm

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

D—H···A	D—H	H···A	D···A	D—H···A
N21—H21A···O41^{i}	0.90 (2)	1.98 (2)	2.8678 (17)	165.9 (19)
N21—H21B···N61^{ii}	0.89 (2)	2.34 (2)	3.1304 (19)	147.9 (18)
N3—H3···N1^{ii}	0.92 (2)	2.15 (2)	3.0370 (17)	163.2 (17)
N61—H61B···N1^{iii}	0.89 (2)	2.34 (2)	3.2131 (18)	166.8 (16)
N61—H61A···O41^{iv}	0.89 (2)	2.05 (2)	2.9296 (18)	172.5 (17)

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

Table 2
Hydrogen-bond geometry (Å, °) for (I*a*).

D—H···A	D—H	H···A	D···A	D—H···A
N21A—H21A···N1B^{i}	0.88	2.11	2.985 (4)	170
N21A—H21B···O1X^{i}	0.88	2.12	2.820 (4)	136
N3A—H3A···O41B	0.88	1.86	2.734 (3)	175
N61A—H61B···O1W	0.88	2.05	2.872 (4)	155
N21B—H21C···N1A^{ii}	0.88	2.05	2.931 (4)	175
N21B—H21D···O1V	0.88	2.07	2.920 (4)	161
N3B—H3B···O41A	0.88	1.95	2.812 (3)	167
N61B—H61C···O1X	0.88	2.16	3.028 (4)	168
N61B—H61D···O41C	0.88	2.02	2.886 (4)	169
N21C—H21E···O41A^{iii}	0.88	2.11	2.945 (4)	158
N21C—H21F···O1Z	0.88	2.10	2.874 (4)	146
N3C—H3C···O1V^{iv}	0.88	2.03	2.890 (3)	166
N61C—H61E···O41C^{v}	0.88	1.97	2.744 (3)	147
N61C—H61F···O1Y	0.88	2.07	2.949 (4)	173
O1V—H1V···N1C^{vi}	0.84 (1)	2.06 (2)	2.856 (3)	157 (3)
O1V—H2V···O41A	0.84 (1)	1.96 (2)	2.751 (3)	156 (4)

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

Table 3
Hydrogen-bond geometry (Å, °) for (I*b*).

D—H···A	D—H	H···A	D···A	D—H···A
N21A—H21A···N1B	0.88	2.07	2.946 (4)	171
N21A—H21B···O2X	0.88	2.46	3.176 (4)	139
N3A—H3A···O41B^{i}	0.88	1.89	2.765 (3)	174
N61A—H61A···O2X^{ii}	0.88	2.15	2.939 (4)	150
N61A—H61B···O41B^{iii}	0.88	2.22	2.975 (4)	144
N21B—H21C···N1A	0.88	2.16	3.029 (4)	172
N3B—H3B···O41A^{iv}	0.88	1.84	2.700 (4)	166
N61B—H61C···O2X	0.88	2.17	2.960 (4)	149
N61B—H61D···O41A^{v}	0.88	1.95	2.813 (4)	165

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

Table 4
Hydrogen-bond geometry (Å, °) for (I*c*).

D—H···A	D—H	H···A	D···A	D—H···A
N21A—H21A···O2X^{i}	0.88	2.22	3.092 (3)	169
N21A—H21B···O41B	0.88	2.00	2.756 (3)	143
N3A—H3A···O41A^{ii}	0.88	1.87	2.750 (3)	177
N61A—H61A···N1A^{i}	0.88	2.15	3.023 (3)	169
N61A—H61B···O2X	0.88	2.14	2.891 (3)	142
N21B—H21C···O2Z^{iii}	0.88	2.12	2.989 (3)	170
N21B—H21D···O2Y	0.88	2.06	2.832 (3)	146
N3B—H3B···O2Y	0.88	2.15	2.904 (3)	143
N61B—H61C···N1B^{iii}	0.88	2.13	3.001 (3)	170
N61B—H61D···O2Z	0.88	2.11	2.840 (3)	139

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

Data collection

Stoe IPDS II two-circle diffractometer
28505 measured reflections
3380 independent reflections
2636 reflections with $I > 2\sigma(I)$
$R_{int} = 0.170$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.085$
$S = 0.91$
3380 reflections
459 parameters
4 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}

Compound (I*b*)

Crystal data

$C_4H_6N_4O\cdot C_4H_9NO$
$M_r = 213.25$
Monoclinic, Cc
$a = 19.1494$ (13) Å
$b = 7.8704$ (4) Å
$c = 14.9104$ (11) Å
$\beta = 104.868$ (6)°
$V = 2172.0$ (2) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 173$ K
0.50 × 0.35 × 0.30 mm

Data collection

Stoe IPDS II two-circle diffractometer
12494 measured reflections
2054 independent reflections
1922 reflections with $I > 2\sigma(I)$
$R_{int} = 0.096$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.126$
$S = 1.04$
2054 reflections
277 parameters
22 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}

Table 5
Hydrogen-bond geometry (Å, °) for (II*a*).

D—H···A	D—H	H···A	D···A	D—H···A
N21A—H21A···O41B	0.88	1.92	2.803 (4)	178
N21A—H21B···O2X	0.88	2.06	2.843 (4)	147
N1A—H1A···O2X	0.88	2.02	2.807 (4)	149
N3B—H3B···N3A	0.88	1.97	2.844 (4)	177
N21B—H21C···N1B^{i}	0.88	2.10	2.969 (4)	172
N21B—H21D···O41A	0.88	2.00	2.877 (4)	173

Symmetry code: (i) $-x+1, -y, -z$.

Table 6
Hydrogen-bond geometry (Å, °) for (II*b*).

D—H···A	D—H	H···A	D···A	D—H···A
N1A—H1A···O2X	0.88	2.00	2.800 (3)	151
N21A—H21A···O41B	0.88	1.92	2.794 (3)	173
N21A—H21B···O2X	0.88	2.09	2.869 (3)	146
N3B—H3B···N3A	0.88	1.97	2.838 (3)	171
N21B—H21D···O41A	0.88	2.01	2.888 (3)	179
N21B—H21C···N1B^{i}	0.88	2.09	2.962 (3)	172

Symmetry code: (i) $-x+1, -y+2, -z+2$.

Compound (I*c*)

Crystal data

$C_4H_6N_4O\cdot 3/2C_5H_9NO$
$M_r = 274.83$
Triclinic, $P\overline{1}$
$a = 8.4550$ (9) Å
$b = 10.0803$ (9) Å
$c = 17.0735$ (15) Å
$\alpha = 75.558$ (7)°
$\beta = 78.222$ (8)°
$\gamma = 81.363$ (8)°
$V = 1371.9$ (2) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 173$ K
0.25 × 0.20 × 0.20 mm

Data collection

Stoe IPDS II two-circle diffractometer
18821 measured reflections
5116 independent reflections
2940 reflections with $I > 2\sigma(I)$
$R_{int} = 0.091$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.127$
$S = 0.91$
5116 reflections
355 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}

Compound (II*a*)

Crystal data

$C_5H_7N_3O\cdot C_5H_7N_3O\cdot C_4H_9NO$
$M_r = 337.39$
Triclinic, $P\overline{1}$
$a = 7.8763$ (13) Å
$b = 9.6078$ (17) Å
$c = 12.3115$ (19) Å
$\alpha = 108.780$ (13)°
$\beta = 95.194$ (13)°
$\gamma = 99.959$ (13)°
$V = 858.0$ (2) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 173$ K
0.40 × 0.25 × 0.10 mm

Data collection

Stoe IPDS II two-circle diffractometer
7199 measured reflections
3208 independent reflections
1427 reflections with $I > 2\sigma(I)$
$R_{int} = 0.131$

Table 7
Crystallization of 2,6-diaminopyrimidin-4-one.

Crystal	2,6-Diaminopyrimidin-4-one (mg, mmol)	Solvent	Temperature
(I)	4.2, 0.033	Methanol (500 µl)	323 K
(I*a*)	1.9, 0.015	DMF (100 µl)	Room temperature
(I*b*)	2.1, 0.017	DMAC (200 µl)	323 K
(I*c*)	3.0, 0.024	NMP (50 µl)	Room temperature

Table 8
Crystallization of 2-amino-6-methylpyrimidin-4-one.

Crystal	2-Amino-6-methylpyrimidin-4-one (mg, mmol)	Solvent	Temperature
(II*a*)	2.3, 0.018	DMAC (150 µl)	277 K
(II*b*)	1.9, 0.015	NMP (50 µl)	323 K

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.068$	223 parameters
$wR(F^2) = 0.204$	H-atom parameters constrained
$S = 0.82$	$\Delta\rho_{max} = 0.45$ e Å^{-3}
3208 reflections	$\Delta\rho_{min} = -0.47$ e Å^{-3}

Compound (II*b*)

Crystal data

$C_5H_7N_3O{\cdot}C_5H_7N_3O{\cdot}C_5H_9NO$	$\gamma = 91.555\ (8)^\circ$
$M_r = 349.40$	$V = 876.70\ (14)$ Å^3
Triclinic, $P\overline{1}$	$Z = 2$
$a = 7.3321\ (7)$ Å	Mo $K\alpha$ radiation
$b = 9.8805\ (9)$ Å	$\mu = 0.10$ mm^{-1}
$c = 12.5860\ (12)$ Å	$T = 173$ K
$\alpha = 102.835\ (7)^\circ$	0.45 × 0.35 × 0.25 mm
$\beta = 98.830\ (8)^\circ$	

Data collection

Stoe IPDS II two-circle diffractometer	3267 independent reflections
	1883 reflections with $I > 2\sigma(I)$
13229 measured reflections	$R_{int} = 0.149$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.068$	16 restraints
$wR(F^2) = 0.176$	H-atom parameters constrained
$S = 0.82$	$\Delta\rho_{max} = 0.34$ e Å^{-3}
3267 reflections	$\Delta\rho_{min} = -0.35$ e Å^{-3}
242 parameters	

The H atoms, except those bonded to disordered solvent atoms and to solvent water, were initially located by difference Fourier synthesis. Subsequently, H atoms bonded to C atoms were refined using a riding model, with methyl C—H = 0.98 Å, secondary C—H = 0.99 Å and aromatic C—H = 0.95 Å, and with U_{iso}(H) = 1.5U_{eq}(C) for methyl or 1.2U_{eq}(C) for secondary and aromatic H atoms. In (I), H atoms bonded to N atoms were refined isotropically, while in the other structures, they were refined using a riding model, with amide and terminal N—H = 0.88 Å and with U_{iso}(H) = 1.2U_{eq}(N). For the water molecule in (I*a*), the following restraints were applied during refinement: O—H = 0.84 (1) Å and H···H = 1.40 (1) Å, with U_{iso}(H) = 1.2U_{eq}(O). Similarity restraints were applied for the 1,2 and 1,3 distances of both DMAC molecules in (I*b*), and for the minor occupied orientation of the NMP molecule in (II*b*).

In (I*a*), all C atoms of one DMF molecule are disordered over two positions, with a site-occupation factor of 0.67 (1) for the major occupied orientation. In (II*b*), the NMP molecule is disordered over a pseudo-mirror plane along atoms O2*X* and C5*Y*. The site-occupation factor for the major occupied orientation is 0.78 (1). The disordered atoms in (I*a*) and (II*b*) were refined isotropically.

The *E*-value distribution of (I*b*) could not be used as a hint for or against a centrosymmetric space group (mean value of $|E^2 - 1|$ = 0.874). A refinement attempt for (I*b*) in the centrosymmetric space group *C*2/*c* showed difference electron densities higher than 0.50 e Å^{-3} within the nonsolvent molecule, and both solvent molecules are highly disordered. In spite of a possible higher symmetry, tested by *ADDSYM* (Le Page, 1987, 1988; Spek, 2009), (I*b*) was refined in the noncentrosymmetric space group *Cc*, which led to ordered solvent molecules. For (I*a*) and (I*b*), Friedel pairs were merged prior to refinement, due to the absence of anomalous scatterers. The absolute structure was arbitrarily assigned.

For all compounds, data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Version 2.2; Macrae *et al.*, 2008) and *XP* (Sheldrick, 2008); 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: SK3407). Services for accessing these data are described at the back of the journal.

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