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A hydrogen-bonded chain of rings in 7-amino-5-*tert*-butyl-2-methylpyrazolo[1,5-*a*]pyrimidine, and a hydrogen-bonded framework structure in 3,7-diamino-2,5-dimethylpyrazolo[1,5-*a*]pyrimidine monohydrate

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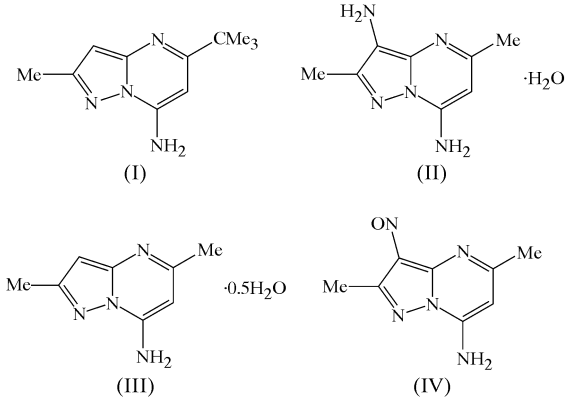
In 7-amino-5-*tert*-butyl-2-methylpyrazolo[1,5-*a*]pyrimidine, $C_{11}H_{16}N_4$, which crystallizes with $Z' = 2$ in the space group $P\overline{1}$, the independent molecules are linked by four N—H···N hydrogen bonds into chains containing three types of ring. In 3,7-diamino-2,5-dimethylpyrazolo[1,5-*a*]pyrimidine monohydrate, $C_8H_{11}N_5{\cdot}H_2O$, the molecular components are linked into a three-dimensional framework structure by a combination of O—H···N, N—H···N and N—H···O hydrogen bonds.

Comment

We report here the structures of 7-amino-5-*tert*-butyl-2-methylpyrazolo[1,5-*a*]pyrimidine, (I) (Fig. 1), and 3,7-diamino-2,5-dimethylpyrazolo[1,5-*a*]pyrimidine monohydrate, (II) (Fig. 2), which we compare with the structure of 7-amino-2,5-dimethylpyrazolo[1,5-*a*]pyrimidine hemihydrate, (III). The structure of (III) was determined many years ago using diffraction data collected at ambient temperature (Mornon *et al.*, 1975) and it was recently redetermined using diffraction data collected at 120 K (Portilla *et al.*, 2006). The heterocyclic system in (I) differs from that in (III) only in the replacement of the methyl substituent on the pyrimidine ring by a *tert*-butyl substituent, while the heterocyclic system in (II) differs from that in (III) only by the incorporation of a second amino group, and this provides an opportunity to observe the effects of simple changes of substituent upon the supramolecular aggregation. Compound (I) was prepared in a similar fashion to compound (III) (Portilla *et al.*, 2006), here using a solvent-free cyclocondensation between 5-amino-3-methyl-1*H*-pyrazole and 4,4-dimethyl-3-oxopentanenitrile induced by microwave irradiation. Compound (II) was prepared by nitrosation of (III) to yield (IV), followed by palladium-catalyzed reduction with hydrazine.



The pattern of the bond lengths in both (I) and (II) closely mimics the pattern found for (III), and it is not necessary to discuss this in detail again. Following the earlier discussion (Portilla *et al.*, 2006), it can be concluded that in all three of these compounds there is a considerable degree of aromatic 10-π-electron delocalization around the periphery of the heterocyclic components.

Compound (I) crystallizes with $Z' = 2$, and within the selected asymmetric unit (Fig. 1) the two independent molecules are linked by two N—H···N hydrogen bonds (Table 1), forming an $R_2^2(10)$ (Bernstein *et al.*, 1995) dimer. Dimers of this type are then linked by two further N—H···N hydrogen bonds to form a complex chain of rings. Atoms N17 and N27 in the dimeric unit at (x, y, z) act as hydrogen-bond donors *via* atoms H17*B* and H27*B*, respectively, to the ring atoms N24 at ($-x$, $1 - y$, $2 - z$) and N14 at ($1 - x$, $1 - y$, $1 - z$), so generating by inversion two distinct $R_4^4(14)$ motifs centred at (0, $\frac{1}{2}$, 1) and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), respectively. Propagation by inversion of these two interactions then generates a chain of edge-fused rings running parallel to the [10$\overline{1}$] direction, with $R_4^4(14)$ rings containing pairs of N17 atoms centred at (n, $\frac{1}{2}$, $1 - n$) (n = zero

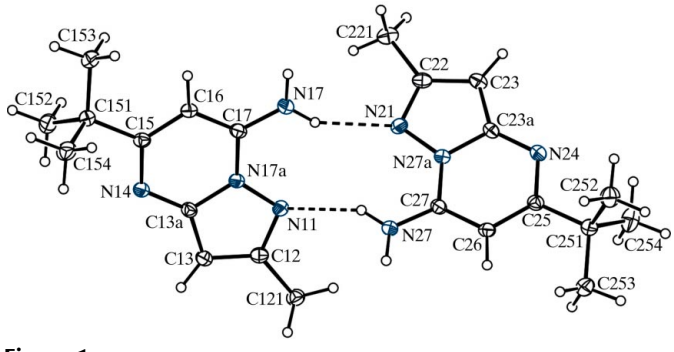


Figure 1
The two independent molecules of compound (I), showing the atom-labelling scheme and the N—H···N hydrogen bonds (dashed lines) within the selected asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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or integer), $R_4^4(14)$ rings containing pairs of N27 atoms centred at $(\frac{1}{2}+n, \frac{1}{2}, \frac{1}{2}-n)$ (n = zero or integer) and $R_2^2(10)$ rings occupying the intermediate locations in the chain (Fig. 3).

Within the selected asymmetric unit of compound (II) (Fig. 2), the components are linked by an N—H···O hydrogen bond (Table 2). The amino group bonded to atom C3 exhibits orientational disorder, and this was modelled in terms of one H-atom site with full occupancy and two H-atom sites each with 0.5 occupancy. While such disorder undoubtedly complicates the analysis and the full description of the overall supramolecular aggregation, it is possible in this case to demonstrate the occurrence of a three-dimensional hydrogen-bonded structure without reference to this disordered amino group. It may be noted here that the only two possible hydrogen-bond acceptors adjacent to atom N3 in the molecule at (x, y, z), *viz*. atoms O1 and N3 in the molecules are $(2-x, \frac{1}{2}+y, \frac{3}{2}-z)$ and $(2-x, 2-y, 1-z)$, respectively, are both distant from the reference N3 atom by more than 3.2 Å (Table 2), and the corresponding $D\cdots A$ and H$\cdots A$ distances are probably too long for significant hydrogen bonding to occur. Hence, without effective tethering *via* hydrogen bonds, the amino group based on N3 is more or less free to rotate about the N3—C3 bond and this possibly accounts for the observed disorder. Therefore, we analyse the supramolecular aggregation of compound (II) without reference to the amino group based on N3.

Two O—H···N hydrogen bonds link the bimolecular aggregates into a sheet, and adjacent sheets are linked by paired N—H···N hydrogen bonds to form a single three-dimensional framework structure. The water molecule at (x, y, z) acts as hydrogen-bond donor, *via* atoms H1*A* and H1*B*, to atoms N1 at $(1-x, -\frac{1}{2}+y, \frac{3}{2}-z)$ and N4 at $(2-x,$

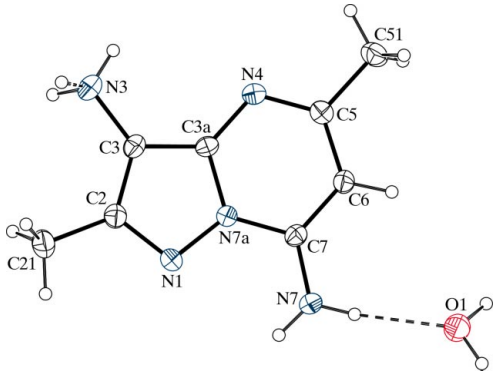

Figure 2
The independent components of compound (II), showing the atom-labelling scheme and the N—H···O hydrogen bond (dashed line) within the selected asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The atoms bonded to atom N3 are disordered; see *Comment* for discussion.

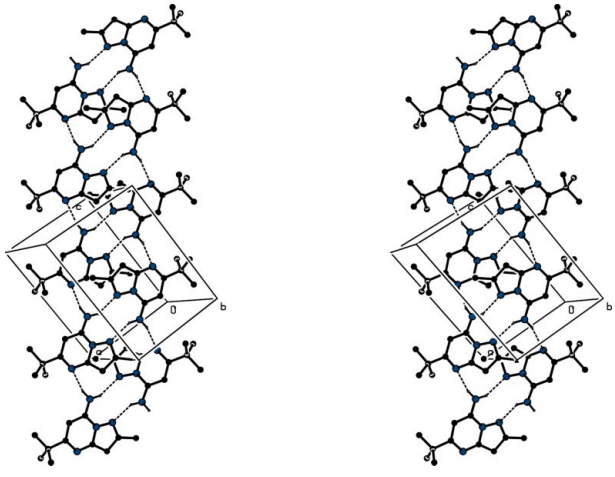

Figure 3
A stereoview of part of the crystal structure of compound (I), showing the formation of a chain along [10$\bar{1}$] built from $R_2^2(10)$ rings and two types of $R_4^4(14)$ ring. For the sake of clarity, H atoms bonded to C or N atoms which are not involved in the motifs shown have been omitted.

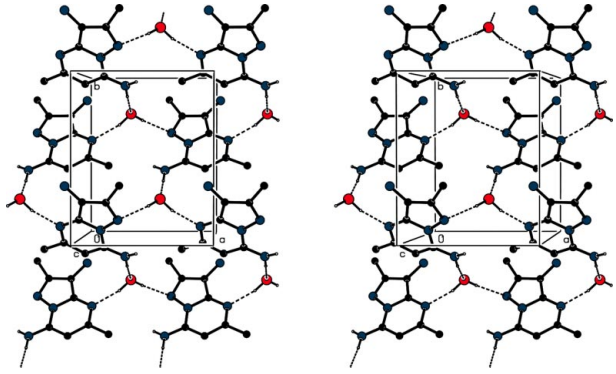

Figure 4
A stereoview of part of the crystal structure of compound (II), showing the formation of a sheet of $R_6^6(22)$ rings parallel to (001). For the sake of clarity, H atoms bonded to C or N atoms which are not involved in the motif shown have been omitted.

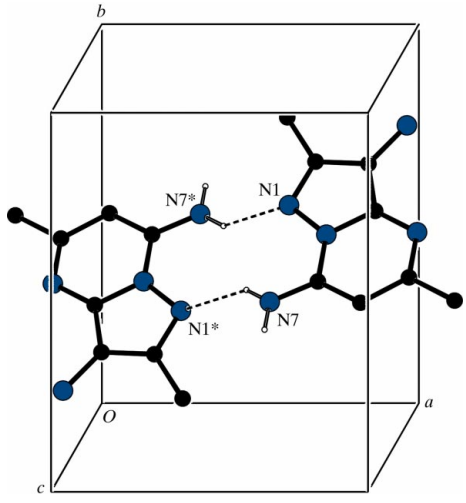

Figure 5
A part of the crystal structure of compound (II), showing the formation of the $R_2^2(10)$ motif linking the (001) sheets. For the sake of clarity, the water molecules and H atoms bonded to C or N atoms which are not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1-x, 1-y, 1-z)$.

$-\frac{1}{2}+y, \frac{3}{2}-z$), so forming a sheet parallel to (001) built from a single type of $R_6^6(22)$ ring (Fig. 4). Two sheets of this type pass through each unit cell, generated by the 2_1 screw axes at $y=\frac{1}{4}$ and $y=\frac{3}{4}$, and lying in the domains $-0.04 < z < 0.54$ and $0.46 < z < 1.04$, respectively. The (001) sheets are linked by a centrosymmetric $R_2^2(10)$ motif, in which paired N—H···N hydrogen bonds link the heterocyclic molecules at (x, y, z) and $(1-x, 1-y, 1-z)$ (Fig. 5). Propagation of this motif links each (001) sheet to the two adjacent sheets, so forming a continuous framework.

In compound (III), where the water molecules lie across twofold rotation axes in the space group $C2$, the molecular components are linked by a combination of O—H···N, N—H···N and N—H···O hydrogen bonds into a three-dimensional framework structure (Portilla *et al.*, 2006). Within that structure, it is possible to identify a centrosymmetric $R_2^2(10)$ motif, precisely similar to that found here in compound (II) (Fig. 5), but there are no further similarities between the supramolecular structures of (I), (II) and (III).

Experimental

For the synthesis of compound (I), equimolar quantities (2 mmol of each component) of 5-amino-3-methyl-1*H*-pyrazole and 4,4-dimethyl-3-oxopentanenitrile were placed in an open Pyrex glass vessel and irradiated in a domestic microwave oven for 2.5 min at 600 W. The reaction mixture was extracted with ethanol. After removal of the solvent, the resulting product, (I), was crystallized from a solution in ethanol to give colourless crystals suitable for single-crystal X-ray diffraction (m.p. 490–491 K, yield 90%). MS (30 eV) *m*/*z* (%): 204 (100, M^+), 189 (12). For the synthesis of compound (II), a solution of sodium nitrite (30 mmol) in water (10 ml) was added to a solution of 7-amino-2,5-dimethylpyrazolo[1,5-*a*]pyrimidine (Portilla *et al.*, 2006) (10 mmol) in ethanol (20 ml). To this solution was then added, dropwise at 273–283 K with magnetic stirring, a mixture of concentrated sulfuric acid (5 ml), water (10 ml) and ethanol (10 ml). The resulting solid was collected by filtration and crystallized from a solution in ethanol to yield 7-amino-2,5-dimethyl-3-nitrosopyrazolo[1,5-*a*]pyrimidine as green crystals (m.p. 501–502 K, yield 95%). MS (30 eV) *m*/*z* (%): 191 (100, M^+), 150 (27), 135 (42). To a solution of this nitroso compound (2 mmol) in methanol (20 ml) was added hydrazine hydrate (6 mmol) and a catalytic amount (50 mg) of palladium on activated carbon. This mixture was then heated under reflux with magnetic stirring for 3 h. After removal of the catalyst from the hot solution by filtration, the filtrate was cooled and the resulting solid product, (II), was collected by filtration and crystallized from a solution in ethanol to yield yellow crystals suitable for single-crystal X-ray diffraction (m.p. 484–486 K, yield 80%). MS (30 eV) *m*/*z* (%): 177 (57, M^+), 136 (31), 109 (100).

Compound (I)

Crystal data

$C_{11}H_{16}N_4$
$M_r = 204.28$
Triclinic, $P\overline{1}$
$a = 9.8216$ (5) Å
$b = 11.3582$ (7) Å
$c = 12.2783$ (8) Å
$\alpha = 70.429$ (3)°
$\beta = 69.895$ (4)°
$\gamma = 66.454$ (4)°
$V = 1147.66$ (12) Å^3
$Z = 4$
$D_x = 1.182$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.08$ mm^{-1}
$T = 120$ (2) K
Plate, colourless
0.15 × 0.10 × 0.04 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.982$, $T_{max} = 0.997$
22882 measured reflections
4863 independent reflections
2931 reflections with $I > 2\sigma(I)$
$R_{int} = 0.066$
$\theta_{max} = 26.8°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.150$
$S = 1.04$
4863 reflections
280 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0716P)^2 + 0.1822P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.015 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
N17—H17A···N21	0.88	2.20	3.017 (3)	155
N17—H17*B*···N24^{i}	0.88	2.20	3.054 (2)	165
N27—H27A···N11	0.88	2.23	3.021 (3)	150
N27—H27*B*···N14^{ii}	0.88	2.10	2.951 (2)	162

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

Compound (II)

Crystal data

$C_8H_{11}N_5\cdot H_2O$
$M_r = 195.23$
Monoclinic, $P2_1/c$
$a = 8.0970$ (2) Å
$b = 9.8881$ (3) Å
$c = 11.9661$ (3) Å
$\beta = 96.230$ (5)°
$V = 952.40$ (5) Å^3
$Z = 4$
$D_x = 1.362$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 120$ (2) K
Plate, yellow
0.50 × 0.36 × 0.10 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.938$, $T_{max} = 0.990$
12664 measured reflections
2188 independent reflections
1631 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.151$
$S = 1.06$
2188 reflections
129 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0821P)^2 + 0.2832P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.034 (7)

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*A*···N1^{i}	0.90	2.17	3.059 (2)	168
O1—H1*B*···N4^{ii}	0.90	1.94	2.817 (2)	166
N3—H3*A*···O1^{iii}	0.86	2.57	3.386 (2)	158
N3—H3*C*···N3^{iv}	0.86	2.43	3.279 (2)	171
N7—H7*A*···O1	0.86	2.10	2.933 (2)	163
N7—H7*B*···N1^{v}	0.86	2.45	3.205 (2)	147

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

Compound (I) crystallized in the triclinic system; space group $P\overline{1}$ was assumed and confirmed by the analysis. For compound (II), the space group $P2_1/c$ was uniquely assigned from the systematic absences. All H atoms were located in difference maps, and then treated as riding atoms. For compound (I), the distances were C—H = 0.95 (aromatic) or 0.98 Å (methyl) and N—H = 0.88 Å, and for compound (II), the distances were C—H = 0.93 (aromatic) or 0.96 Å (methyl), N—H = 0.86–0.87 Å and O—H = 0.90 Å, with U_{iso}(H) = kU_{eq}(C, N,O), where k = 1.5 for O—H or methyl groups and 1.2 for all other H atoms. In compound (II), the amino group containing N3 was modelled using three sites, with one, labelled H3*A*, of unit occupancy and two others, labelled H3*B* and H3*C*, each with 0.5 occupancy.

For both compounds, data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *OSCAIL* (McArdle, 2003) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3040). Services for accessing these data are described at the back of the journal.

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