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7-Amino-2-*tert*-butyl-5-methylpyrazolo[1,5-*a*]pyrimidine: a three-dimensional framework structure built from two N—H···N hydrogen bonds

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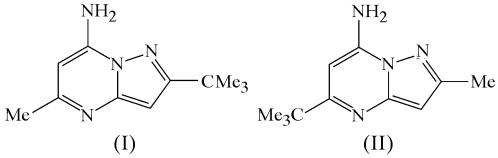
The bond distances in the title compound, $C_{11}H_{16}N_4$, provide evidence for peripheral delocalization of π electrons. The molecules are linked by two independent N—H···N hydrogen bonds into a three-dimensional framework structure.

Comment

We are interested in the synthesis of fused pyrazole systems, in particular pyrazolo[1,5-*a*]pyrimidine, because of their potential biological activity. We report here the structure of 7-amino-2-*tert*-butyl-5-methylpyrazolo[1,5-*a*]pyrimidine, (I) (Fig. 1), and we compare this with the structure of the isomeric compound 7-amino-5-*tert*-butyl-2-methylpyrazolo[1,5-*a*]pyrimidine, (II) (Portilla, Quiroga, de la Torre *et al.*, 2006) and with that of the simpler analogue 7-amino-2,5-dimethylpyrazolo[1,5-*a*]pyrimidine, which crystallizes as a hemihydrate, (III) (Portilla, Quiroga, Cobo *et al.*, 2006).



The bond distances within the fused heterocyclic system (Table 1) show evidence for electronic delocalization. Thus, within the periphery of the classically localized form (I), the N1═C2 and N4═C5 bonds are both formally double bonds, while C3*A*—N4 and C7—N7*A* are both single bonds; however, N1═C2 is not significantly shorter than C3*A*—N4. Similarly, the C3═C3*A* and C6═C7 bonds are both formally double bonds, while C2—C3 and C5—C6 are both formally single bonds; however, the C—C distances in the periphery span an overall range of less than 0.02 Å, with no clear distinction between those which are formally single bonds and those which are formally double bonds. These observations, taken all together, point to a significant contribution to the overall molecular–electronic structure from a peripherally delocalized ten-π-electron form.

The molecules of compound (I) are linked by two independent N—H···N hydrogen bonds (Table 2) into a three-dimensional framework structure, whose formation is rather easily analysed in terms of two simple substructures, one of which is one-dimensional and the other of which is finite and zero-dimensional.

In the one-dimensional substructure, amino atom N7 in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* H7*A*, to the pyrimidine ring atom N4 in the molecule at ($-y+\frac{1}{2}$, $x-\frac{1}{2}+x$, $z+\frac{1}{4}$), while atom N7 at ($-y+\frac{1}{2}$, $x-\frac{1}{2}$, $z+\frac{1}{4}$) in turn

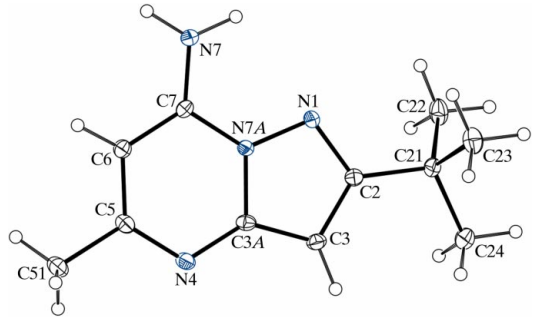


Figure 1
A molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

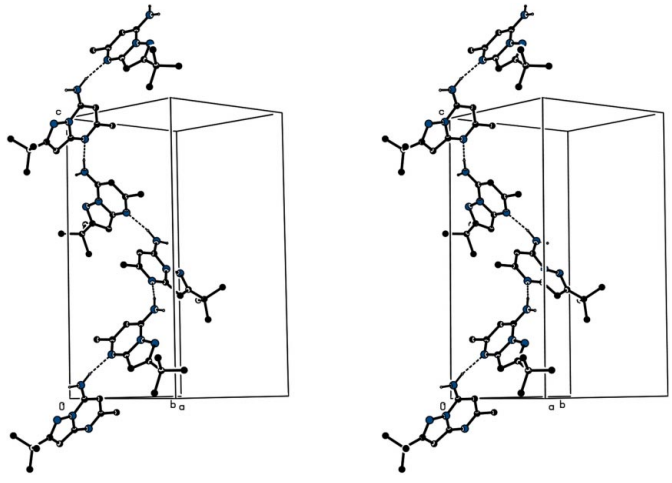


Figure 2
A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded $C(6)$ helical chain generated by the 4_1 screw axis along ($\frac{1}{2}$, 0, z). For the sake of clarity, H atoms bonded to C atoms have been omitted.

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acts as a donor to atom N4 at $(-x+1, -y, z+\frac{1}{2})$, so forming a $C(6)$ (Bernstein *et al.*, 1995) helical chain running along the [001] direction and generated by the 4_1 screw axis along $(\frac{1}{2}, 0, z)$ (Fig. 2). The finite substructure serves to link the $C(6)$ chains; atom N7 in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* H7*B*, to the pyrazole ring atom N1 in the molecule at $(y, x, -z+1)$, so forming an $R_2^2(10)$ motif generated by the twofold rotation axis along $x = y$ at $z = \frac{1}{2}$ (Fig. 3). This motif directly links the $C(6)$ chain along $(\frac{1}{2}, 0, z)$ with the four similar chains along $(0, \frac{1}{2}, z)$, $(0, -\frac{1}{2}, z)$, $(1, -\frac{1}{2}, z)$ and $(1, \frac{1}{2}, z)$, and by propagation of this interaction, all of the $C(6)$ chains, and hence all of the molecules, are linked into a single three-dimensional framework structure, built from only two hydrogen bonds.

In the isomeric compound (II), which crystallizes with $Z' = 2$ in the space group $P\overline{1}$ (Portilla, Quiroga, de la Torre *et al.*, 2006), the supramolecular structure is only one-dimensional, in contrast to the three-dimensional structure of (I); four independent N—H···N hydrogen bonds link the molecules of (II) into chains containing three different types of centrosymmetric ring, one of $R_2^2(10)$ type and two of $R_4^4(14)$ type. In the hemihydrate (III), which crystallizes in the space group $C2$ (Portilla, Quiroga, Cobo *et al.*, 2006), the components are linked by a combination of O—H···N, N—H···N and N—H···O hydrogen bonds into a complex three-dimensional framework. Hence, minor changes in the simple hydrocarbyl substituents in compounds (I)–(III) provoke significant changes both in crystallization behaviour, as manifested in the space groups and Z' values, and in the supramolecular structures.

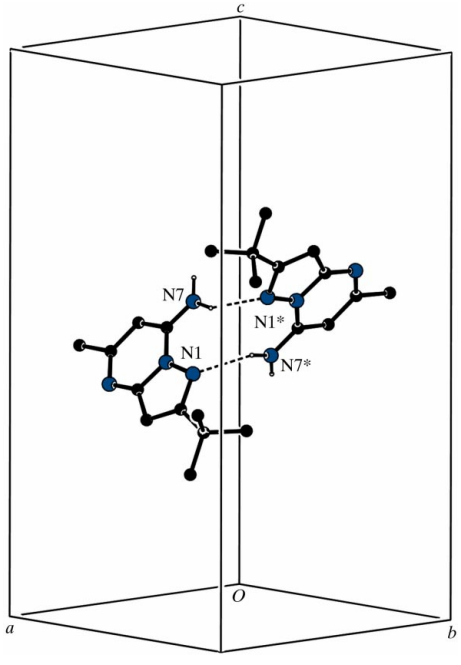

Figure 3
Part of the crystal structure of (I), showing the formation of the $R_2^2(10)$ motif which links the $C(6)$ helical chains. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(y, x, -z+1)$.

Experimental

An intimate mixture of 5-amino-3-*tert*-butyl-1*H*-pyrazole (139 mg, 1 mmol) and 3-aminocrotononitrile (82 mg, 1 mmol) was 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 then extracted with ethanol and, after removal of the solvent, the product was crystallized from ethanol, providing colourless crystals of (I) suitable for single-crystal X-ray diffraction (yield 92%; m.p. 489–490 K). MS *m*/*z* (%): 204 (100, M^+), 189 (18).

Crystal data

$C_{11}H_{16}N_4$
$M_r = 204.28$
Tetragonal, $P4_12_12$
$a = 10.8271$ (2) Å
$c = 19.9208$ (3) Å
$V = 2335.24$ (7) Å^3
$Z = 8$
$D_x = 1.162$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.07$ mm^{-1}
$T = 120$ (2) K
Block, colourless
0.50 × 0.50 × 0.20 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.941$, $T_{max} = 0.985$
16594 measured reflections
1605 independent reflections
1418 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.091$
$S = 1.05$
1605 reflections
140 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0594P)^2 + 0.2575P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.14$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}

Table 1
Selected bond lengths (Å).

N1—C2	1.3491 (19)	C5—C6	1.398 (2)
C2—C3	1.401 (2)	C6—C7	1.389 (2)
C3—C3*A*	1.384 (2)	C7—N7*A*	1.3705 (19)
C3*A*—N4	1.353 (2)	N7*A*—N1	1.3683 (17)
N4—C5	1.332 (2)	C3*A*—N7*A*	1.3906 (18)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N7—H7*A*···N4^{i}	0.95	1.97	2.9034 (18)	168
N7—H7*B*···N1^{ii}	0.95	2.27	3.1202 (19)	149

Symmetry codes: (i) $-y+\frac{1}{2}, x-\frac{1}{2}, z+\frac{1}{4}$; (ii) $y, x, -z+1$.

The systematic absences permitted $P4_12_12$ and $P4_32_12$ as possible space groups, but in the absence of significant resonant scattering, it was not possible to distinguish between these enantiomeric space groups. $P4_12_12$ was selected, although this choice has no chemical significance, and the Friedel-equivalent reflections were merged. All H atoms were located in difference maps and then treated as riding atoms, with C—H distances of 0.95 (CH) or 0.98 Å (CH_3) and N—H distances of 0.95 Å, and with U_{iso}(H) values of kU_{eq}(C,N), where k = 1.5 for the methyl groups and 1.2 otherwise.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve

structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* 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: SK3071). Services for accessing these data are described at the back of the journal.

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