5-Amino-3-methyl-1-phenyl-1H-pyrazole-4-carbaldehyde hemihydrate: a polarized electronic structure within hydrogen-bonded sheets of $R_{10}^{8}(34)$ rings

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In the title compound, $C_{11}H_{11}N_3O \cdot 0.5H_2O$, the water molecule lies across a twofold rotation axis in the space group *Pbcn*. The bond distances in the organic component provide evidence for polarization of the electronic structure. The molecular components are linked into puckered sheets of $R_{10}^{8}(34)$ rings by a combination of O—H···N and N—H···O hydrogen bonds; adjacent sheets are weakly linked by an aromatic π–π stacking interaction. Comparisons are made with some fused-ring analogues.

Comment

The Vilsmeier–Haack formylation reaction allows access to a large variety of heterocyclic carbaldehyde derivatives, all of which permit a wide range of functional elaboration, acting in particular as extremely valuable intermediates for the synthesis of new fused heterocyclic systems. Accordingly, we have now prepared the title compound, (I) (Häufel & Breitmaier, 1974), as a versatile precursor for the synthesis of fused pyrazole derivatives of potential pharmaceutical interest, and we report here its molecular and supramolecular structure, which we briefly compare with those of the fused analogues (II) (Trilleras *et al.*, 2008) and (III) (Low *et al.*, 2006) (see scheme).

Compound (I) is a stoichiometric hemihydrate (Fig. 1) and the asymmetric unit consists of one molecule of the organic component in a general position with a water molecule lying across a twofold rotation axis. Within the selected asymmetric unit, the water molecule lies across the axis along $(\frac{1}{2}, y, \frac{3}{4})$ and the two molecular components are linked by an O—H···N hydrogen bond (Fig. 1 and Table 2).

The formyl group is almost coplanar with the pyrazole ring, as shown by the value of the C5—C4—C41—O41 torsion angle of $-1.5 (5)°$. The displacement of formyl atom O41 from the mean plane of the pyrazole ring is only 0.020 (2) Å. This coplanarity may be a consequence of both the intramolecular N—H···O hydrogen bond (Table 2), which forms an $S(6)$ motif (Bernstein *et al.*, 1995), and the electronic delocalization (see discussion below). However, the two rings are very far from being coplanar and their planes make a dihedral angle of 47.5 (2)°, possibly as a consequence of H···H repulsion between the H atoms bonded to atoms C16 and N51.
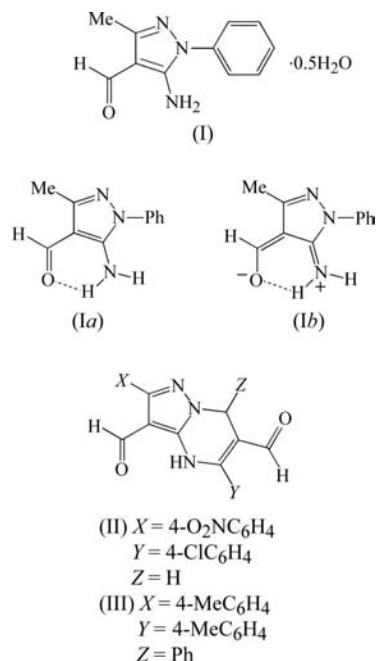
The bond distances (Table 1) within the organic component provide evidence for polarization of the electronic structure. The C5—N51 bond is short for its type [mean value (Allen *et al.*, 1987) = 1.355 Å, lower quartile value = 1.340 Å], as is the
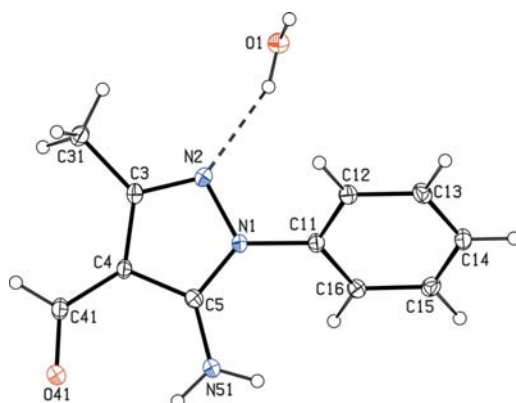

Figure 1
The independent components of compound (I), showing the atom-labelling scheme and the hydrogen bond (dashed line) linking the components within the selected asymmetric unit. Atom O1 lies on a twofold rotation axis. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.
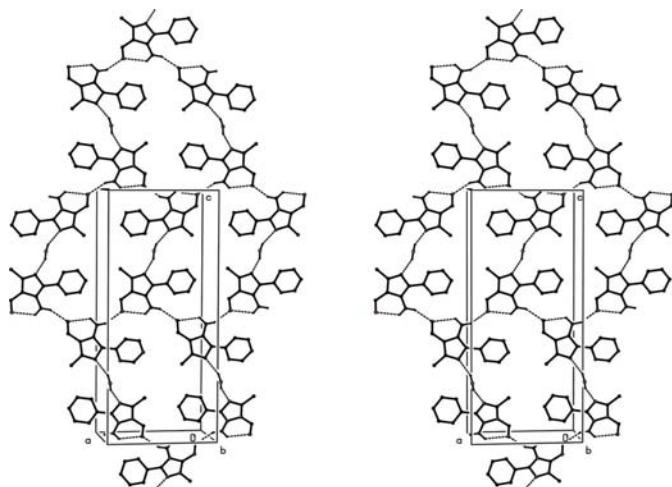
Figure 2
A stereoview of part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded sheet parallel to (010) and containing $S(6)$ and $R_{10}^8(34)$ rings. Hydrogen bonds are shown as dashed lines. For the sake of clarity, H atoms bonded to C atoms have been omitted.

C4—C41 bond (mean value = 1.464 Å, lower quartile value = 1.453 Å). However, the C4—C5 bond is long for its type (mean value = 1.369 Å, upper quartile value = 1.383 Å), as is the C41—O41 bond (mean value = 1.192 Å, upper quartile value = 1.197 Å). These values provide evidence for an important contribution to the electronic structure of the polarized form (Ib), in addition to the unpolarized form (Ia). A significant contribution from form (Ib) effectively precludes any aromatic-type delocalization within the pyrazole ring. Consistent with this deduction, the N2—C3 and N1—C5 bonds are both short for their types (mean values = 1.329 and 1.357 Å, respectively), while the N1—N2 bond is long for its type (mean value = 1.366 Å), indicating significant bond fixation, as opposed to electronic delocalization, within the pyrazole ring. The polarization of the electronic structure deduced (Trilleras *et al.*, 2008) for compounds (II) and (III) is more extensive than that in (I), but one of the canonical forms proposed for compounds (II) and (III) is exactly analogous to form (Ia).

In addition to the intramolecular hydrogen bond formed *via* atom H51B (Table 2), amino atom N51 at (x, y, z) also acts as a hydrogen-bond donor, *via* atom H51A, to atom O41 in a second pyrazole molecule at $(-\frac{1}{2} + x, \frac{3}{2} - y, 1 - z)$. The combination of this N—H$\cdots$O hydrogen bond and the two symmetry-related O—H$\cdots$N hydrogen bonds formed by the water molecule links the molecular components into a deeply puckered sheet lying parallel to (010) and containing only a single type of ring, of $R_{10}^8(34)$ type, in addition to the $S(6)$ rings within the pyrazole component (Fig. 2). Two sheets of this type, related to one another by inversion, pass through each unit cell. The only direction-specific interactions between adjacent sheets are weak aromatic π–π stacking interactions between the phenyl rings at (x, y, z), lying in the reference sheet, and the corresponding rings at $(\frac{1}{2} - x, \frac{1}{2} + y, z)$ and $(\frac{1}{2} - x, -\frac{1}{2} + y, z)$, which lie in the two adjacent sheets. For each

interaction, the ring planes make a dihedral angle of 2.67 (2)° with an interplanar spacing of *ca* 3.457 Å; the ring-centroid separation is 3.847 (2) Å and the ring-centroid offset is *ca* 1.72 Å. By this means, the hydrogen-bonded sheets are weakly linked into a three-dimensional structure.

In contrast with the sheet formation in (I), the crystal structure of (II) is determined by the formation of a chain of rings built from a combination of N—H$\cdots$O and C—H$\cdots$O hydrogen bonds (Trilleras *et al.*, 2008), while in (III) centrosymmetric dimers built from paired N—H$\cdots$O hydrogen bonds are linked into sheets by the combined action of two C—H$\cdots$O hydrogen bonds (Low *et al.*, 2006).

Experimental

A sample of compound (I) was prepared according to the published procedure of Häufel & Breitmaier (1974). Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation, at ambient temperature and in air, from a solution in 2-propanol.

Crystal data

$C_{11}H_{11}N_3O\cdot0.5H_2O$	$V = 1999.4\ (4)$ Å^3
$M_r = 210.24$	$Z = 8$
Orthorhombic, $Pbcn$	Mo $K\alpha$ radiation
$a = 10.8346\ (14)$ Å	$\mu = 0.10$ mm^{-1}
$b = 7.4952\ (9)$ Å	$T = 120$ K
$c = 24.621\ (3)$ Å	$0.28 \times 0.17 \times 0.12$ mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer	16503 measured reflections
	1842 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	1267 reflections with $I > 2\sigma(I)$
$T_{min} = 0.973$, $T_{max} = 0.989$	$R_{int} = 0.091$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.055$	143 parameters
$wR(F^2) = 0.126$	H-atom parameters constrained
$S = 1.16$	$\Delta\rho_{max} = 0.24$ e Å^{-3}
1842 reflections	$\Delta\rho_{min} = -0.29$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—N2	1.396 (3)	N1—C11	1.425 (4)
N2—C3	1.309 (4)	C4—C41	1.406 (4)
C3—C4	1.409 (4)	C41—O41	1.228 (3)
C4—C5	1.403 (4)	C5—N51	1.331 (3)
C5—N1	1.328 (3)		
C5—C4—C41—O41	−1.5 (5)	N2—N1—C11—C12	43.6 (4)

All H atoms were located in difference maps. H atoms bonded to C or N atoms were then treated as riding atoms in geometrically idealized positions, with C—H = 0.95 (aromatic and formyl) or 0.98 Å (methyl) and N—H = 0.88 Å, and with $U_{iso}(H) = kU_{eq}$(carrier), where $k = 1.5$ for the methyl group, which was permitted to rotate but not to tilt, and 1.2 for all other H atoms bonded to C or N atoms. The unique H atom of the water molecule was permitted to ride at the position deduced from a difference map, with $U_{iso}(H) = 1.2U_{eq}(O)$, giving an O—H distance of 0.86 Å and an H—O—H angle of 108°.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1$\cdots$N2	0.86	2.12	2.927 (3)	158
N51—H51A$\cdots$O41^i	0.88	2.07	2.897 (3)	156
N51—H51B$\cdots$O41	0.88	2.30	2.883 (3)	123

Symmetry code: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 1$.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* and *PLATON*.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Duisenberg, A. J. M., Hooft, R. W. W., Schreurs, A. M. M. & Kroon, J. (2000). *J. Appl. Cryst.* **33**, 893–898.
Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.
Häufel, J. & Breitmaier, E. (1974). *Angew. Chem. Int. Ed. Engl.* **13**, 604.
Low, J. N., Cobo, J., Trilleras, J. & Glidewell, C. (2006). *Acta Cryst.* E**62**, o4930–o4932.
Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
Sheldrick, G. M. (2003). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Trilleras, J., Quiroga, J., Low, J. N., Cobo, J. & Glidewell, C. (2008). *Acta Cryst.* C**64**, o341–o343.