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N^4-Methyl-N^4-(2-methylphenyl)-1*H*-pyrazolo[3,4-*d*]pyrimidine-4,6-diamine–ethanol–hydrazine (1/0.865/0.135): hydrogen-bonded ribbons containing four independent ring types

Jorge Trilleras,[a]‡ Jairo Quiroga,[a] Justo Cobo[b] and Christopher Glidewell[c]*

[a]Grupo de Investigación de Compuestos Heterociclícos, Departamento de Química, Universidad de Valle, AA 25360, Colombia, [b]Departamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, and [c]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland
Correspondence e-mail: cg@st-andrews.ac.uk

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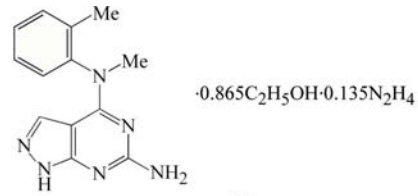
N^4-Methyl-N^4-(2-methylphenyl)-1*H*-pyrazolo[3,4-*d*]pyrimidine-4,6-diamine crystallizes from ethanol as a mixed solvate, $C_{13}H_{14}N_6\cdot0.865C_2H_6O\cdot0.135N_2H_4$, (I), where the hydrazine has been carried through from the initial preparation. Within the heterocyclic component, the 2-methylphenyl substituent is disordered over two sets of sites. There is an intramolecular C—H···π(arene) hydrogen bond, which may control the molecular conformation of the heterocycle. The heterocyclic molecules are linked by two independent N—H···N hydrogen bonds in a chain containing two types of $R_2^2(8)$ ring. The ethanol component is linked to this chain by a combination of O—H···N and N—H···O hydrogen bonds and the hydrazine component by two N—H···N hydrogen bonds, so generating two $R_3^3(9)$ rings and thus forming a ribbon containing four distinct ring types.

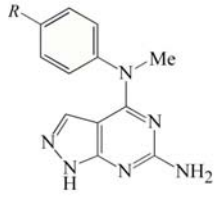
Comment

We recently reported the structures of nine N^4-substituted 1*H*-pyrazolo[3,4-*d*]pyrimidine-4,6-diamines, some of which crystallized in solvent-free form, while others were found to be either stoichiometric monohydrates or stoichiometric hemihydrates; one example only, namely 4-(pyrrolidin-1-yl)-1*H*-pyrazolo[3,4-*d*]pyrimidine-4,6-diamine, crystallized as an ethanol hemisolvate hemihydrate (Trilleras *et al.*, 2008). Where the N^4 substituent was of the *N*-aryl-*N*-ethyl or *N*-aryl-*N*-methyl type, compounds (II)–(VI) (see scheme), the molecular conformations were all very similar and appeared to be controlled by an intramolecular C—H···π(arene) hydrogen bond with the N^4-aryl unit as the acceptor. In those compounds which carried no other potential hydrogen-bonding sites in the N^4 substituent, the molecules were linked into hydrogen-bonded sheets, but in the single example which carried additional hydrogen-bonding capacity in the N^4 substituent, *viz.* 2-[4-(6-amino-1*H*-pyrazolo[3,4-*d*]pyrimidin-4-yl)piperazin-1-yl]ethanol, the hydrogen-bonded structure is three-dimensional.

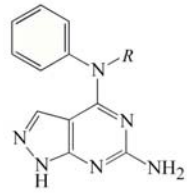


·0.865C_2H_5OH·0.135N_2H_4

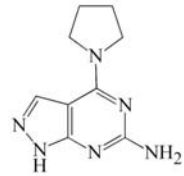
(I)



(II) *R* = H
(III) *R* = Me
(IV) *R* = MeO

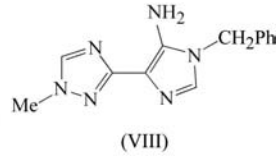


(V) *R* = Et
(VI) *R* = $PhCH_2$



·0.5C_2H_5OH·0.5H_2O

(VII)



(VIII)

As a continuation of the earlier study, we now report the structure of the title compound, (I), as a further example of this class; it crystallizes as a mixed solvate (Fig. 1) and, uniquely in this series, forms only a one-dimensional hydrogen-bonded structure. The heterocyclic compound crystallizes as a mixed solvate containing, in the crystal selected for data collection, 0.865 (11) molecules of ethanol and 0.135 (11) molecules of hydrazine per molecule of heterocycle corresponding overall to one solvent molecule per heterocyclic molecule. The roles of the two solvent components in the hydrogen-bonding scheme are entirely equivalent (see Table 2). A second form of disorder was found for the methyl group in the 2-methylphenyl substituent, corresponding to a 180° rotation about the N14—C11 bond.

The coordination at atom N14 is planar within experimental uncertainty, and the overall conformation is thus definable in terms of just two torsion angles (Table 1); hence, the benzene ring is almost orthogonal to the pyrazole ring, with a dihedral angle between the planes of these two rings of 89.6 (2)°. Associated with this conformation is a rather short C—H···π(arene) hydrogen bond, whose dimensions (Table 2) are

‡ Present address: Departamento de Química, Facultad de Ciencias Básicas, Universidad del Atlántico, Km 7, Antigua Vía a Puerto Colombia, Barranquilla, Atlántico, Colombia.

strikingly similar to those of the corresponding interactions in compounds (II) and (V) (Trilleras *et al.*, 2008).

Two independent N—H···N hydrogen bonds (Table 2) link the pyrazolopyrimidine units into a chain containing two distinct $R_2^2(8)$ (Bernstein *et al.*, 1995) motifs. Ring atom N1 at (x, y, z) acts as donor to atom N7 at $(\frac{1}{2} - x, \frac{3}{2} - y, 1 - z)$, so forming a centrosymmetric $R_2^2(8)$ ring, centred at $(\frac{1}{4}, \frac{3}{4}, \frac{1}{2})$; in addition, amino atom N16 at (x, y, z) acts as donor to atom N5 at $(-x, y, \frac{1}{2} - z)$, so forming a second $R_2^2(8)$ ring lying across the twofold rotation axis along $(0, y, \frac{1}{4})$. The combination of these two interactions then generates a puckered chain of rings running parallel to the [101] direction (Fig. 2). The solvent molecules lie on the edges of the chain of $R_2^2(8)$ rings, but the occupation of a given solvent site by either ethanol or hydrazine does not alter the topology of the resulting hydrogen-bonded ring (Table 2). The major ethanol component is linked to the chain by a combination of O—H···N and N—H···O hydrogen bonds, forming an $R_3^3(9)$ ring, such that a pair of these rings lies on either side of the centrosymmetric $R_2^2(8)$ ring, while the minor hydrazine component is linked to the chain by two N—H···N hydrogen bonds. The resulting arrays of three edge-fused rings have $R_4^4(18)$ peripheries (Fig. 2).

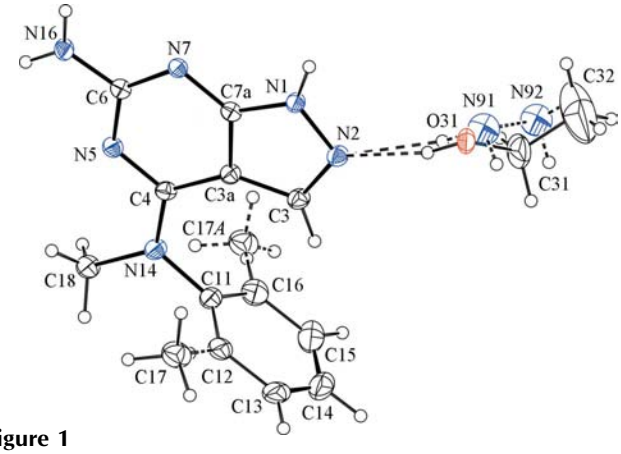


Figure 1
The independent molecular components of compound (I) showing the atom-labelling scheme, with displacement ellipsoids drawn at the 30% probability level. The dashed lines involving atom N2 represent O—H···N and N—H···N hydrogen bonds; all other dashed lines represent covalent bonds within the minor components of the structure.

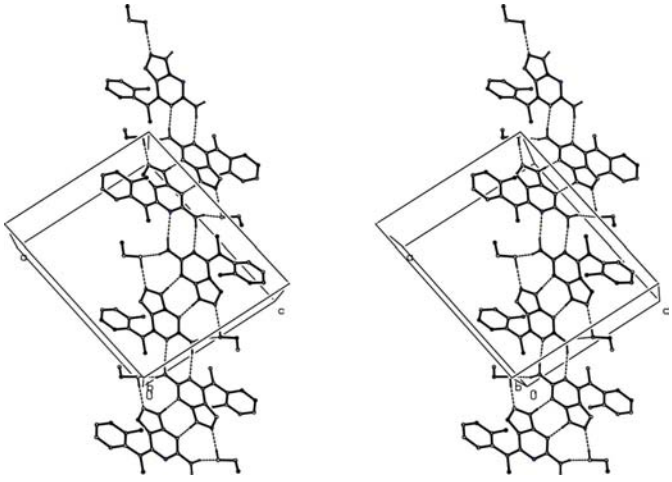


Figure 2
A stereoview of part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded chain of rings parallel to [101]. For the sake of clarity, H atoms bonded to C atoms, the minor orientation of the disordered 2-methylphenyl substituent and the minor-occupancy hydrazine component have all been omitted.

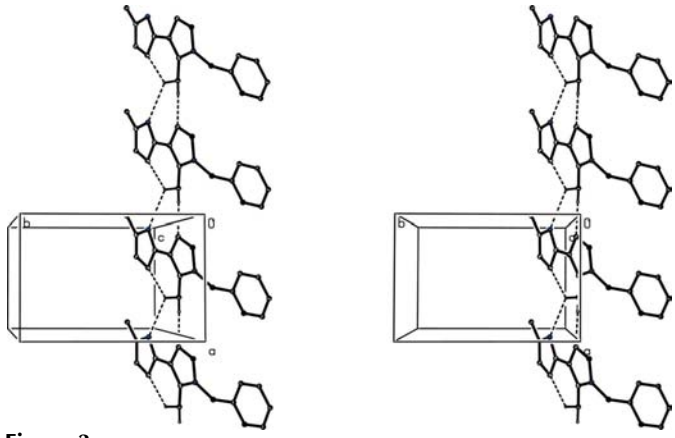


Figure 3
A stereoview of part of the crystal structure of compound (VIII) (FUHHAR; Afshar *et al.*, 1987), showing the formation of a chain of edge-fused $S(6)$ and $R_2^2(7)$ rings. The original atom coordinates have been used. For the sake of clarity, H atoms bonded to C atoms have been omitted.

An entirely similar array of edge-fused rings is found in the stoichiometric monohydrate formed by compound (VI) (Trilleras *et al.*, 2008). In this hydrate, the asymmetric unit contains two molecules of the heterocyclic component and two molecules of water, and these are linked into an array of one $R_2^2(8)$ and two $R_3^3(9)$ rings closely analogous to the corresponding array in compound (I). The principal difference is that in (VI) the array has only approximate noncrystallographic centrosymmetry and, after formation of this aggregate, there still remain two N—H and two O—H bonds per aggregate which are available to link the aggregates further into chains, which are themselves linked into sheets by a C—H···π(arene) hydrogen bond. In the structures of each of (III)–(VI), which all crystallize either as monohydrates [(III) and (VI)] or hemihydrates [(IV) and (V)], it is possible to identify one-dimensional substructures. However, in each such substructure the water component is integral to the chain formation, as it is in the mixed solvate (VII), while in compound (I) the solvent components are pendent from the chain while doubtless reinforcing its formation.

Isomeric with the heterocyclic component of the title compound (I) is the imidazolyl-1,2,4-triazole (VIII) [CSD (Allen, 2002) refcode FUHHAR (Afshar *et al.*, 1987)]. In the structure of (VIII), three independent N—H···N hydrogen bonds, *viz.* one intramolecular and two intermolecular, link the molecules into a chain of continuous edge-fused rings in which $S(6)$ rings alternate with $R_2^2(7)$ rings (Fig. 3).

Experimental

Compound (I) was prepared by reaction of the corresponding 2-amino-6-chloro-5-formyl-N^4-methyl-N^4-(2-methylphenylamino)-

pyrimidine with hydrazine hydrate using methods described previously (Boudet & Knochel, 2006; Trilleras *et al.*, 2008). Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in ethanol.

Crystal data

$C_{13}H_{14}N_6\cdot0.865C_2H_6O\cdot0.135N_2H_4$
M_r = 298.48
Monoclinic, $C2/c$
a = 16.349 (3) Å
b = 14.051 (2) Å
c = 13.625 (3) Å
β = 99.308 (18)°
V = 3088.7 (10) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 120 K
0.35 × 0.28 × 0.22 mm

Data collection

Bruker Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.964, T_{max} = 0.982
22447 measured reflections
3539 independent reflections
2074 reflections with $I > 2\sigma(I)$
R_{int} = 0.067

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.065
$wR(F^2)$ = 0.191
S = 1.03
3539 reflections
217 parameters
5 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Table 1
Selected torsion angles (°).

N5—C4—N14—C11	−179.7 (2)	C4—N14—C11—C12	88.1 (3)

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

Cg represents the centroid of the C11–C16 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···*Cg*	0.95	2.52	3.296 (3)	138
N91—H912···N2	0.91	2.05	2.94 (3)	160
O31—H31···N2	0.84	1.93	2.755 (3)	166
N1—H1···N7^{i}	0.88	1.98	2.859 (3)	177
N16—H16*A*···O31^{i}	0.88	2.09	2.949 (4)	165
N16—H16*A*···N91^{i}	0.88	2.20	3.05 (3)	163
N16—H16*B*···N5^{ii}	0.88	2.24	3.103 (3)	165

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

At an early stage in the refinement it became apparent that the 2-methylphenyl substituent was disordered over two orientations: with restraints applied to the two independent C(aryl)—C(methyl) distances, the final refined site occupancies were 0.763 (5) and 0.237 (5). Similarly, it was apparent that the solvent site was occupied primarily by ethanol, but with a second minor component also present; in the initial structure solution, the solvent component appeared as three distinct maxima, all of different sizes. The minor component was modelled as hydrazine, presumably from the initial preparation and carried through the subsequent purification steps. Independent refinement of the two solvent occupancies gave a sum of 0.993 (11); hence, the total occupancy was thereafter fixed at unity. With restraints applied to the C—O and C—C distances in the ethanol molecule, 1.45 (2) Å in each case, and to the hydrazine N—N distance, 1.46 (2) Å, the final occupancies were 0.865 (11) for ethanol and 0.135 (11) for hydrazine (the hydrazine component was refined only isotropically). An alternative disorder model including methanol as the minor component in place of hydrazine gave marginally higher R values and larger residual densities, but it was rejected (*a*) because of the unsatisfactorily long C—O distance [1.552 (16) Å] which resulted despite a bond-length restraint similar to that imposed on the N—N distance in the hydrazine model and (*b*) because no methanol had been employed either in the preparation or in the crystallization. All H atoms, apart from those in the hydrazine and in the minor-occupancy methyl group containing atom C17*A*, were located in difference maps; the remaining atoms were placed in calculated positions. Thereafter all H atoms were treated as riding atoms in geometrically idealized positions, such that the methyl groups were permitted to rotate but not to tilt, with distances C—H = 0.95 (aromatic), 0.98 (CH_3) or 0.99 Å (CH_2), N—H = 0.88–0.91 Å and O—H = 0.84 Å, and with U_{iso}(H) = kU_{eq}(carrier), where k = 1.5 for the hydrazine, hydroxyl and methyl groups and 1.2 for all other H atoms.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DIRAX*/*LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *OSCAIL* (McArdle, 2003) and *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* and *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3199). Services for accessing these data are described at the back of the journal.

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