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6-Benzyl-7-hydroxy-1-(2-methoxyphenyl)-2,3-dihydro-1*H*,7*H*-imidazo[1,2-*a*]pyrimidin-5-one

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In the crystal structure of the title compound, $C_{20}H_{19}N_3O_3$, only one of the two possible O-enol/O-keto tautomers (7-hydroxy-5-oxo) exists. In the guanidine part of the molecule, partial π-electron delocalization between two N—C bonds is observed, while the third C—N bond has some double-bond character. The conformation of the molecule is influenced by intramolecular C—H$\cdots$O hydrogen bonds and the steric effect of adjacent carbonyl, benzyl and hydroxyl groups. The molecular packing is influenced by strong intermolecular O—H$\cdots$O hydrogen bonds and C—H$\cdots\pi$ interactions.

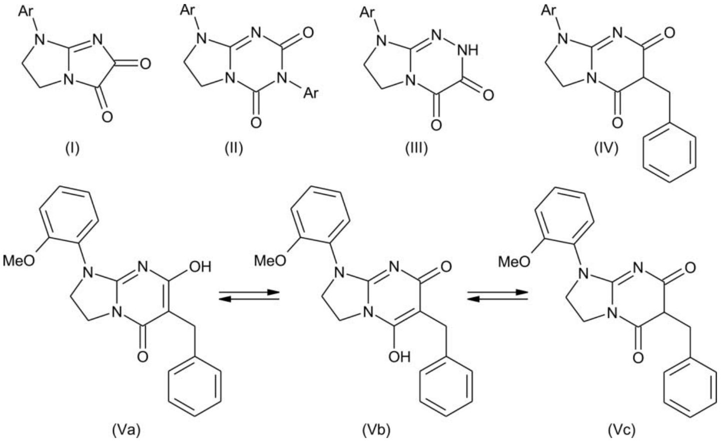
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.005 Å
R factor = 0.050
wR factor = 0.156
Data-to-parameter ratio = 12.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Dioxo derivatives of fused imidazoline ring systems, *e.g.* imidazo[1,2-*a*]imidazoles, (I), imidazo[1,2-*a*][1,3,5]triazines, (II), and imidazo[2,1-*c*][1,2,4]triazines, (III), have been found to have significant analgesic opioid-like action but without the typical narcotic analgesic side-effects (Matosiuk *et al.*, 2002). Modification of their structure led us to the synthesis of 1-aryl-6-benzyl-5,7-dioxo-imidazo[1,2-*a*]pyrimidines, (IV). The tauthomerism of the oxo groups would be responsible for the selectivity of action, as we have already confirmed for imidazo[2,1-*c*][1,2,4]triazines, (III) (Sztanke *et al.*, 2005).



We report here the results of the X-ray crystal structure determination of 1-(2-methoxyphenyl)-6-benzyl-5,7(1*H*)-dioxo-2,3-dihydroimidazo[1,2-*a*]pyrimidine, (V*a*), to help dteremine the keto–enol [(V*a*) and (V*b*)] and keto–keto [(V*c*)] tautomerism type of imidazo[1,2-*a*]pyrimidines, (IV). The complete crystal structure analysis of this compound was expected to yield information concerning the tautomeric equilibrium of heterocycles (IV) in the crystalline state.

A difference electron-density map for compound (V*a*) revealed the position of the H atom in the vicinity of atom O10 and the bond lengths for C7—O10 [1.335 (3) Å] and C9—O11 [1.258 (3) Å] are comparable with those for hydroxyl and carbonyl groups, respectively, found in related structures, *e.g.* 7-methoxy-1-methylimidazo[1,2-*a*]pyrimidin-5(1*H*)-one (Bueno *et al.*, 2003). These two facts indicate unequivocally that the O10-enol/O11-keto tautomeric form, (V*a*), is the only one existing in the crystalline state, with the hydroxyl and carbonyl groups involved in a strong intermolecular O10—H10···O11 (Table 2) resonance-assisted hydrogen bond (RAHB; Gilli *et al.*, 1989).

In the guanidine part of the bicyclic ring system, the N6—C2 bond has some double-bond character and its bond length [1.307 (3) Å] is significantly shorter than the two other N—C bonds [1.350 (3) Å for N1—C2 and 1.364 (3) Å for N3—C2]. It is noteworthy that in the protonated guanidine unit of the non-fused 2-aminoimidazoline ring all N—C bonds have practically the same bond lengths in the range 1.325 (5)–1.330 (6) Å, with full delocalization of the π-electrons over three N—C bonds (Karczmarzyk *et al.*, 2004). The conformation of the molecule, as described by the torsion angles C2—N1—C21—C22, C7—C8—C12—C31 and C8—C12—C31—C32 (Table 1), is influenced by the intramolecular C5—H51···O27 hydrogen bond (Table 2) and the steric effect of the adjacent carbonyl, benzyl and hydroxyl groups.

The molecular packing in the crystal structure of (V*a*) is influenced by an intermolecular O—H···O hydrogen bond linking molecules related by *c*-glide planes into molecular chains along the [001] direction. The chains are held together *via* C—H···π interactions involving benzene rings C31–C36 and C21–C26 (Table 2).

Experimental

The title compound was obtained by the one-step cyclocondensation of 1-(2-methoxyphenyl)-2-aminoimidazoline-2 (Rządkowska *et al.*, 2004) with diethyl benzylmalonate under basic (sodium methoxide) conditions. Crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a solution in propan-2-ol.

Crystal data

$C_{20}H_{19}N_3O_3$
$M_r = 349.38$
Monoclinic, $P2_1/c$
$a = 12.1771$ (6) Å
$b = 13.2172$ (7) Å
$c = 11.0141$ (8) Å
$\beta = 90.785$ (5)°
$V = 1772.52$ (18) Å^3

$Z = 4$
$D_x = 1.309$ Mg m^{-3}
Cu *Kα* radiation
$\mu = 0.73$ mm^{-1}
$T = 298$ (2) K
Prism, colourless
0.59 × 0.42 × 0.35 mm

Data collection

Enraf–Nonius TurboCAD4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.917$, $T_{\max} = 0.996$ (expected range = 0.713–0.774)
3758 measured reflections

3565 independent reflections
1998 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.026$
$\theta_{\max} = 74.2°$
3 standard reflections every 100 reflections intensity decay: none

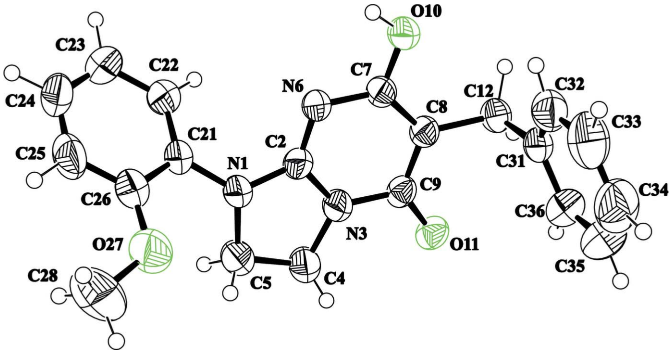


Figure 1
The molecular structure of (V*a*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented as small spheres of arbitrary radii.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.157$
$S = 1.02$
3565 reflections
286 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0729P)^2 + 0.2545P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0110 (7)

Table 1
Selected geometric parameters (Å, °).

O10—C7	1.335 (3)	N3—C4	1.463 (4)
O11—C9	1.258 (3)	N6—C2	1.307 (3)
N1—C2	1.350 (3)	N6—C7	1.357 (3)
N1—C5	1.470 (4)	C4—C5	1.525 (4)
N3—C2	1.364 (3)	C7—C8	1.381 (3)
N3—C9	1.384 (3)	C8—C9	1.408 (3)
C2—N1—C21	124.9 (2)	N3—C4—C5	102.4 (2)
C2—N1—C5	111.2 (2)	N1—C5—C4	104.5 (2)
C21—N1—C5	123.1 (2)	O10—C7—N6	115.7 (2)
C2—N3—C9	122.2 (2)	O10—C7—C8	118.5 (2)
C2—N3—C4	112.6 (2)	N6—C7—C8	125.7 (2)
C9—N3—C4	125.1 (2)	C7—C8—C9	118.0 (2)
C2—N6—C7	114.7 (2)	O11—C9—N3	117.4 (2)
N6—C2—N1	126.7 (2)	O11—C9—C8	127.5 (2)
N6—C2—N3	124.2 (2)	N3—C9—C8	115.1 (2)
N1—C2—N3	109.0 (2)		
C7—C8—C12—C31	89.5 (3)	C8—C12—C31—C32	−86.2 (3)
C2—N1—C21—C22	45.6 (4)		

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

CgA and *CgB* are the centroids of the benzene rings C31–C36 and C21–C26, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H51···O27	1.09 (4)	2.31 (3)	2.871 (4)	110 (3)
O10—H101···O11$^{\rm i}$	0.90 (3)	1.72 (3)	2.617 (2)	169 (2)
C24—H241···*CgA*$^{\rm ii}$	0.98 (4)	2.63 (3)	3.584 (4)	165 (3)
C28—H283···*CgA*$^{\rm iii}$	0.96	2.98	3.562 (5)	120
C33—H331···*CgB*$^{\rm iv}$	0.99 (4)	2.94 (5)	3.747 (4)	139 (3)

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

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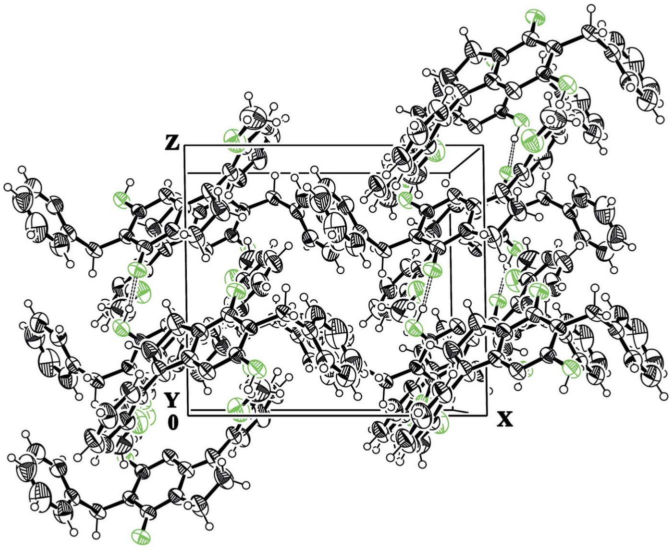

Figure 2
The molecular packing of (V*a*), viewed along the *b* axis. Dashed lines indicate intermolecular O10—H···O11 hydrogen bonds.

Methyl H atoms were placed in idealized positions and included in the refinement in the riding-model approximation [C—H = 0.96 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C)]. The other H atoms were located in a difference Fourier map and their coordinates were refined isotropically [C—H = 0.90 (5)–1.09 (4) Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C,O)].

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*, *PLATON* (Spek, 2003) and *WinGX* (Farrugia, 1999).

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