Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

2-Hydroxyphenyl 2-methylpyrazolo-[1,5-*a*]pyrimidin-6-yl ketone

Jairo Quiroga,[a] Braulio Insuasty,[a] Rodrigo Abonia,[a] Diana Mejía,[a] Manuel Nogueras,[b] Adolfo Sánchez,[b] Justo Cobo[b] and John Nicolson Low[c]*†

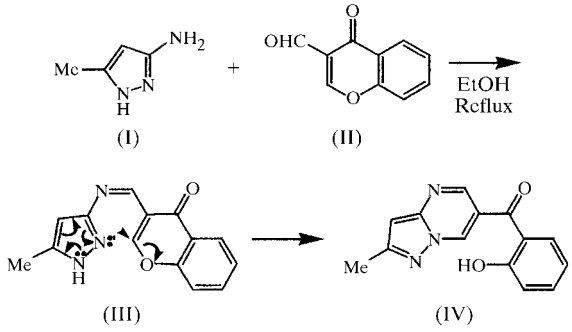
[a]Grupo de Investigación de Compuestos Heterocíclicos, Departamento de Química, Universidad de Valle, AA 25360, Cali, Colombia, [b]Departamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, and [c]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland
Correspondence e-mail: j.n.low@dundee.ac.uk

Received 26 July 2000
Accepted 7 September 2000

The molecules of the title compound, $C_{14}H_{11}N_3O_2$, form a three-dimensional soft hydrogen-bonded network involving C—H···N hydrogen bonds.

Comment

The investigation of the structure of the title compound, (IV), continues our research into the reactions of 3-aminopyrazoles as intermediates in the preparation of fused pyrazole systems with the potential for diverse medical and biological applications. Reactions between such compounds and α- and β-unsaturated carbonyl derivatives were carried out by Earl *et al.* (1975) and Shaw & Hildick (1971). Pyrazolo[1,5-*a*]pyrimidines are very interesting due to their biological activities, which include antileukaemia, antitumour (Quiroga *et al.*, 1998, 1999), antipyretic (Auzzi *et al.*, 1979, and references therein)



and antiparasitic properties (Senga *et al.*, 1975). The title compound, (IV), results from the reaction of 3-amino-5-methylpyrazole, (I), with 4-oxo-4*H*-chromene-3-carbaldehyde, (II), in which condensation takes place between the amino group of the pyrazole ring and the aldehyde of the chromene, in conjunction with nucleophilic displacement of the oxygen of the chromene ring by the attack of N2 of the pyrazole ring on C2 of the chromene (see Scheme).

Compound (IV) can be divided into two isolated moieties: the pyrazolopyrimidine ring and the 2-hydroxyphenylcarbonyl residue. The bond lengths associated with the pyrazolo-[1,5-*a*]pyrimidine ring confirm the configuration depicted in the Scheme. The N8—C3a bond [1.400 (2) Å] is a typical single bond between two trigonal atoms (typical $N_{trig}—C_{trig}$ 1.40 Å; Ladd & Palmer, 1994), because there is no delocalization associated with these atoms. This ring and its substituents are planar within experimental error.

The other moiety of the structure, the 2-hydroxyphenylcarbonyl attached to C6 of the pyrazolopyrimidine ring, is also planar, with a strong intramolecular hydrogen bond in which the hydroxyl O16 atom acts as a donor to the carbonyl O9 atom, giving an *S*(6) primary motif. The phenolic ring is not

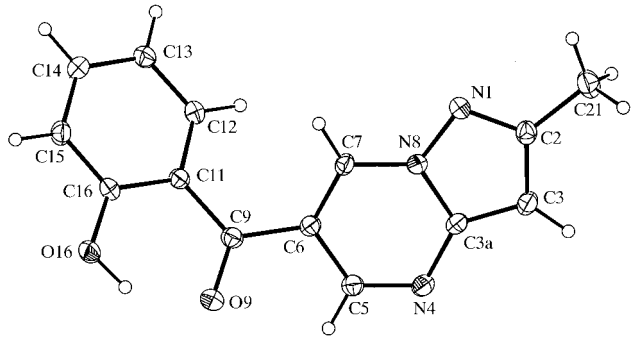


Figure 1
A molecular view of (IV) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

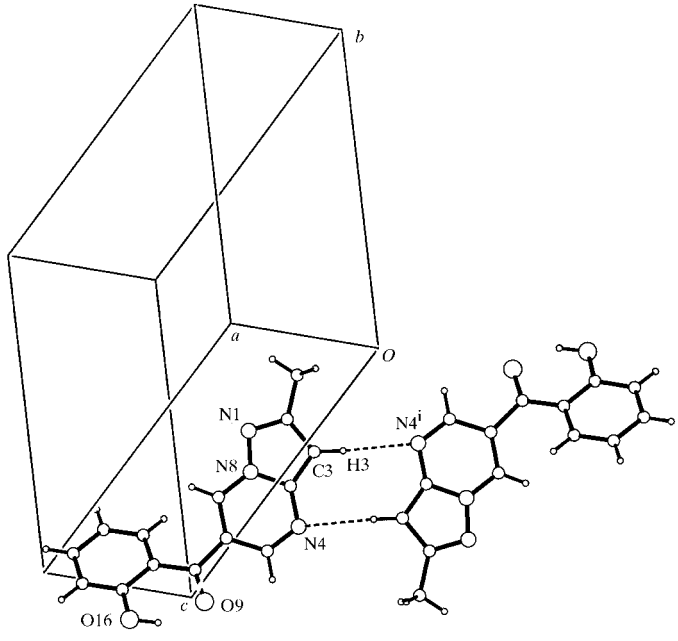


Figure 2
A view of the crystal structure of (IV) showing the dimer formed by the $R_2^2(8)$ ring [symmetry code: (i) $-1-x, -y, 1-z$].

† Postal address: Department of Electronic Engineering & Physics, University of Dundee, Nethergate, Dundee DD1 4HN, Scotland.

constrained by this bond to lie in the same plane as the keto group and its connected atoms, as shown by the O9—C9—C11—C16 torsion angle of 17.2 (3)°. This intramolecular bond between the carbonyl and hydroxy groups confirms the existence of the quinone–hydroxy tautomeric form. The angle between the mean planes of the two rings is 42.53°. Selected bond lengths are given in Table 1.

The two molecules of (IV) are linked to form a dimer by means of C—H···N bonds. Atom C3 acts as a donor to atom N4 at $(-1-x, -y, 1-z)$, with a $D\cdots A$ distance of 3.528 (2) Å. The action of the centre of symmetry at $(-\frac{1}{2}, 0, \frac{1}{2})$ repeats this bond, forming an $R_2^2(8)$ ring (Fig. 2). In addition, atom C15 acts as a donor to atom N1 at $(\frac{3}{2}-x, -\frac{1}{2}+y, \frac{3}{2}-z)$, with a $D\cdots A$ distance of 3.337 (3) Å. This forms a spiral chain around the screw axis at $(\frac{3}{4}, y, \frac{3}{4})$, which in turn forms a $C(7)$ infinite chain along [010]. Both these sets of interactions combine to form a complex three-dimensional continuum of further chains. Full details of the hydrogen bonding are given in Table 2.

Examination of the structure with *PLATON* (Spek, 2000) showed that there were no solvent-accessible voids in the crystal lattice.

Table 1
Selected geometric parameters (Å).

N1—C2	1.338 (2)	N4—C5	1.310 (2)
N1—N8	1.358 (2)	C9—O9	1.241 (2)
C3a—N4	1.363 (2)	C16—O16	1.349 (2)
C3a—N8	1.400 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O16—H16···O9	0.95	1.74	2.562 (2)	144
C3—H3···N4^{i}	0.95	2.61	3.528 (2)	162
C15—H15···N1^{ii}	0.95	2.39	3.337 (3)	172

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

Experimental

A solution of 3-amino-5-methylpyrazole (2.0 mmol) and 4-oxo-4*H*-chromene-3-carbaldehyde (2.0 mmol) in ethanol (10 ml) was heated to reflux for 45 min. Cooling the solution to room temperature afforded bright yellow crystals of (IV) which were filtered off, washed with fresh ethanol and dried. Crystals suitable for X-ray diffraction were obtained after recrystallization from dimethylformamide (yield 80%, m.p. 442–445 K). Analysis calculated for $C_{14}H_{11}N_3O_2$: C 66.40, H 4.38, N 16.59%; found: C 66.32, H 4.25, N 16.45%.

Crystal data

$C_{14}H_{11}N_3O_2$
$M_r = 253.26$
Monoclinic, $P2_1/n$
$a = 5.6004$ (2) Å
$b = 11.8172$ (5) Å
$c = 17.865$ (7) Å
$\beta = 98.71$ (16)°
$V = 1168.67$ (8) Å^3
$Z = 4$
$D_x = 1.439$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2591 reflections
$\theta = 3.64$–27.48°
$\mu = 0.100$ mm^{-1}
$T = 150$ (2) K
Plate, yellow
0.20 × 0.15 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{min} = 0.980$, $T_{max} = 0.993$
8919 measured reflections
2591 independent reflections
1681 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 27.48°$
$h = -7 \rightarrow 7$
$k = -11 \rightarrow 15$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.144$
$S = 1.014$
2591 reflections
173 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0749P)^2 + 0.0357P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.012$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}

H atoms were treated as riding, with C—H = 0.95–0.98 Å and O—H = 0.95 Å. The position of the hydroxyl H atom was based on its position as found on a difference map.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

The X-ray data were collected by the EPSRC X-ray Crystallographic Service at the University of Southampton. The authors thank the staff for all their help and advice.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1109). Services for accessing these data are described at the back of the journal.

References

Auzzi, G., Cecchi, L., Costanzo, A., Pecori Vettori, L., Bruni, F., Piridino, R. & Ciottoli, G. B. (1979). *Farmaco*, **24**, 478–485.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
Earl, R. A., Pugmire, R. J., Revamker, G. R. & Townsend, L. B. (1975). *J. Org. Chem.* **40**, 1822–1828.
Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
Ladd, M. F. C. & Palmer, R. A. (1994). *Structure Determination by X-ray Crystallography*, 3rd ed., pp. 434–435. New York: Plenum Press.
Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
Quiroga, J., Hormaza, A. & Insuasty, B. (1998). *J. Heterocycl. Chem.* **35**, 409–412.
Quiroga, J., Insuasty, B. & Hormaza, A. (1999). *J. Heterocycl. Chem.* **36**, 11–13.
Senga, K., Novinson, T., Springer, R. H., Rao, R. P., O'Brien, D. K., Robins, R. K. & Wilson, H. R. (1975). *J. Med. Chem.* **18**, 312–314.
Shaw, G. & Hildick, B. G. (1971). *J. Chem. Soc. C*, pp. 1610–1613.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (2000). *PLATON*. Version of May 2000. University of Utrecht, The Netherlands.