organic papers

3-{[(1Z)-(3-Methyl-5-oxo-1-phenyl-1,5-dihydro-pyrazol-4-ylidene)(phenyl)methyl]amino}propionic acid

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In the title compound, $C_{20}H_{19}N_3O_3$, the pyrazolone moiety and the N atom of the 3-aminopropionic acid group are essentially coplanar. The compound is a ligand in an enamine–keto form and its structure is stabilized by two strong intramolecular N—H⋯O hydrogen bonds. Glide-related molecules form O—H⋯N hydrogen-bonded chains along the c axis.

Comment

1-Phenyl-3-methyl-4-benzoylpyrazolon-5-one (HPMBP) is widely used and well known for its extractive ability. In recent years, both HPMBP and its metal complexes have been found to exhibit good antibacterial activity. The metal complexes also show analgesic activity (Liu *et al.*, 1980; Li *et al.*, 1997; Zhou *et al.*, 1999). In a search for new compounds, we synthesized the title compound, (I), and we report its crystal structure here.

(I)
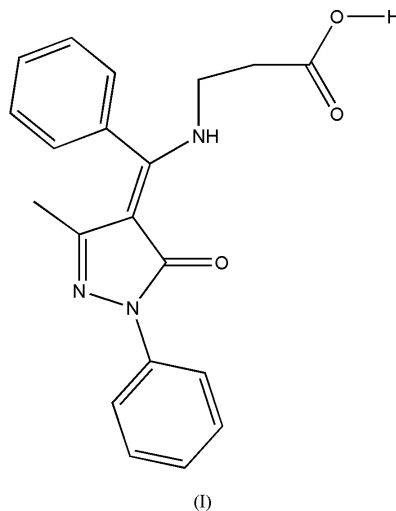
In compound (I), the O atom of the 5-methyl-2-phenyl-pyrazol-3-one moiety and the N atom of the 3-aminopropionic acid group are available for coordination with metals. The pyrazole ring is planar. Atoms O3, C4, C5 and C6 of the HPMBP moiety and atom N1 of the 3-aminopropionic acid are coplanar, with a maximum deviation from the mean plane of 0.040 (1) Å for atom C4. The dihedral angle between this plane (O3/C4/C5/C6/N1) and the pyrazole ring of the HPMBP moiety is 1.8 (2)°, indicating that they are essentially coplanar, as seen in 4-{[3,4-dihydro-5-methyl-3-oxo-2-phenyl-2*H*-pyrazol-4-ylidene](phenyl)methylamino}-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one, (II) [3.56 (3)°; Wang *et al.*, 2003]. The bond lengths in this part of the molecule lie
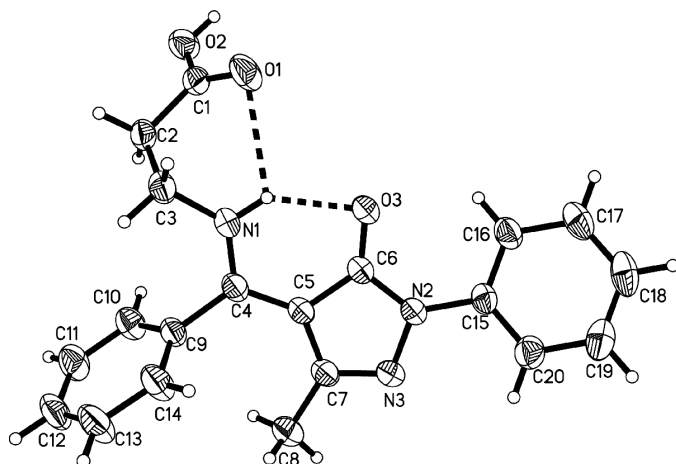
Figure 1
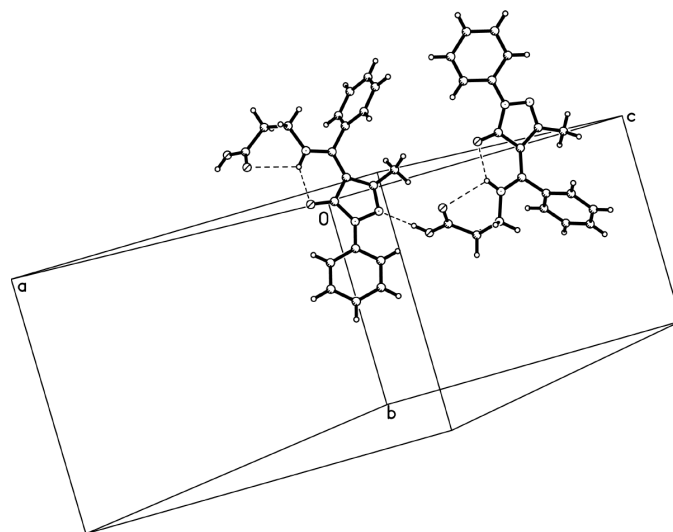A view of (I), showing 30% probability displacement ellipsoids and the atomic numbering scheme. N—H···O hydrogen bonds are shown as dashed lines.

Figure 2
Part of the O—H···N hydrogen-bonded chain in the unit cell of (I). Hydrogen bonds are shown as dashed lines.

between classical single- and double-bond values, indicating extensive delocalization. Atoms O1, O2, C1, C2 and C3 of the 3-aminopropionic acid moiety are coplanar, the largest deviation from this plane being 0.072 (1) Å for atom C2. The dihedral angle between this plane and the O3/C4/C5/C6/N1 plane is 62.5 (1)°.

Strong intramolecular N1—H1···O1 and N1—H1···O3 hydrogen bonds (Table 2) observed in the molecular structure of (I) are indicative of the enamine–keto form. This is similar to the situation in (II) [N···O 2.745 (4) Å and N—H···O 146 (4)°; Wang *et al.*, 2003]. Glide-related molecules are linked *via* O2—H2···N3^i hydrogen bonds to form chains along the *c* axis [symmetry code (i): *x*, 1 − *y*, *z* − $\frac{1}{2}$]. Part of the chain structure is shown in Fig. 2. The crystal packing is further stabilized by C—H···O interactions (Table 2).

Experimental

Compound (I) was synthesized by refluxing a mixture of 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (10 mmol) and 3-aminopropanoic acid (10 mmol) in propan-2-ol (80 ml) over a steam bath for about 16 h. Excess solvent was removed by evaporation and the solution was cooled to room temperature. After 2 d, a yellow block solid was obtained and this was dried in air. The product was recrystallized from propan-2-ol, to afford pale-yellow crystals of (I) suitable for X-ray analysis.

Crystal data

$C_{20}H_{19}N_3O_3$	$D_x = 1.264$ Mg m^{-3}
$M_r = 349.38$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 2719
$a = 22.779$ (3) Å	reflections
$b = 11.7073$ (12) Å	$\theta = 2.5$–22.0°
$c = 16.8032$ (16) Å	$\mu = 0.09$ mm^{-1}
$\beta = 124.978$ (6)°	$T = 293$ (2) K
$V = 3671.7$ (8) Å^3	Block, yellow
$Z = 8$	$0.42 \times 0.38 \times 0.34$ mm

Data collection

Bruker SMART CCD area-detector	$R_{int} = 0.019$
diffractometer	$\theta_{max} = 27.0°$
φ and ω scans	$h = -24 \rightarrow 29$
10864 measured reflections	$k = -14 \rightarrow 13$
3998 independent reflections	$l = -21 \rightarrow 21$
2599 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.052P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$+ 0.9087P]$
$wR(F^2) = 0.118$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
3998 reflections	$\Delta\rho_{max} = 0.15$ e Å^{-3}
243 parameters	$\Delta\rho_{min} = -0.14$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

N1—C4	1.317 (2)	O3—C6	1.2453 (18)
N1—C3	1.458 (2)	C1—C2	1.503 (2)
N2—C6	1.3797 (19)	C2—C3	1.509 (2)
N2—N3	1.4016 (16)	C4—C5	1.406 (2)
N2—C15	1.4175 (19)	C4—C9	1.4929 (19)
N3—C7	1.315 (2)	C5—C7	1.422 (2)
O1—C1	1.1999 (18)	C5—C6	1.4421 (19)
O2—C1	1.317 (2)		
C4—N1—C3	127.81 (13)	C4—C5—C7	132.45 (13)
O1—C1—O2	123.30 (15)	C4—C5—C6	121.36 (14)
O1—C1—C2	123.61 (16)	O3—C6—N2	125.62 (13)
N1—C4—C5	118.43 (13)	O3—C6—C5	129.57 (14)
N1—C4—C9	118.60 (14)		
O1—C1—C2—C3	−8.0 (2)	C3—N1—C4—C5	−173.33 (15)
O2—C1—C2—C3	171.71 (14)	N1—C4—C5—C6	7.5 (2)
C4—N1—C3—C2	−115.01 (18)	C9—C4—C5—C6	−170.06 (14)
C1—C2—C3—N1	−61.02 (18)	C4—C5—C6—O3	−3.6 (3)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1$\cdots$O1	0.91 (2)	2.46 (2)	2.931 (2)	112 (1)
N1—H1$\cdots$O3	0.91 (2)	1.93 (2)	2.693 (2)	140 (2)
O2—H2$\cdots$N3^{i}	0.85 (3)	1.85 (3)	2.696 (2)	177 (3)
C2—H2$A\cdots$O2^{ii}	0.97	2.52	3.414 (3)	153
C3—H3$A\cdots$O1^{iii}	0.97	2.46	3.421 (3)	169
C16—H16$\cdots$O3	0.93	2.40	2.926 (2)	115
C20—H20$\cdots$O2^{iv}	0.93	2.58	3.377 (3)	144

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

The H atoms bonded to atoms N1 and O2 were located in a difference map and refined isotropically. The O2—H2 distance was restrained to 0.85 (1) Å and U_{iso}(H2) was set at $1.5U_{\mathrm{eq}}$(O2). The remaining H atoms were positioned geometrically (C—H = 0.93–0.97 Å) and treated as riding, with U_{iso}(H) = $1.2U_{\mathrm{eq}}$(C).

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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