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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

Jin-Ling Wang,[a]* Yun Yang,[b] Xin Zhang[a] and Fang-Ming Miao[a]

[a]College of Chemical and Life Science, Tianjin Normal University, Tianjin 300074, People's Republic of China, and [b]College of Tianjin Commerce, Tianjin 300134, People's Republic of China

Correspondence e-mail: wangjinling43@eyou.com

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.053
wR factor = 0.151
Data-to-parameter ratio = 13.2

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

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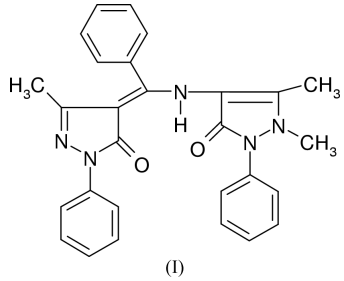
In the title compound, $C_{28}H_{25}N_5O_2$, the carbonyl group of the 5-methyl-2-phenylpyrazol-3-one moiety, the adjacent double bond and the amine N atom of antipyrine are essentially coplanar, the largest deviation from the mean plane being 0.049 (2) Å. The compound is a neutral tridentate ligand in an enamine–keto tautomeric form, due to a strong intramolecular N—H···O hydrogen bond. The dihedral angle between the two pyrazolone rings is 86.2 (3)°, reducing steric hindrance.

Comment

4–Acyl-5-pyrazolones, a family of flexible β-diketonates, are widely used and well known for their applications as analgesics, antipyretics, anti-inflammatory agents and insecticides (Hodnett & Paul, 1972). Therefore, the study of derivatives of 4-acyl-5-pyrazolones is the focus of many research groups working in the fields of coordination chemistry, biomedicine and pharmaceutical chemistry.



(I)

The title compound, (I), prepared by condensation of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) and antipyrine (ATP), is a neutral tridentate ligand in which two O atoms of pyrazolone moieties and the N atom of antipyrine are possible coordinating atoms.

A view of the molecule of (I) is shown in Fig. 1. Atoms O1, C1, C2 and C5 of the PMBP moiety and atom N3 of ATP form a plane, the largest deviation being 0.049 (2) Å for atom C5. The dihedral angle between this mean plane and the pyrazoline ring of PMBP is 3.56 (3)°, close to the value of 5.05 (3)° in 4-[(2-hydroxyphenylamino)phenylmethylene]-5-methyl-2-phenyl-2*H*-pyrazol-3(4*H*)-one (Wang, Zhang & Miao, 2002). The bond lengths within this part of the molecule (Table 1) lie between the classical single- and double-bond lengths, indicating extensive conjugation.

Atoms O2, C6, C7 and N3 of ATP also are coplanar, the largest deviation from the mean plane being 0.010 (2) Å for C7. The dihedral angle between this plane and the adjacent pyrazolone ring of ATP is 6.64 (3)°. The bond lengths in

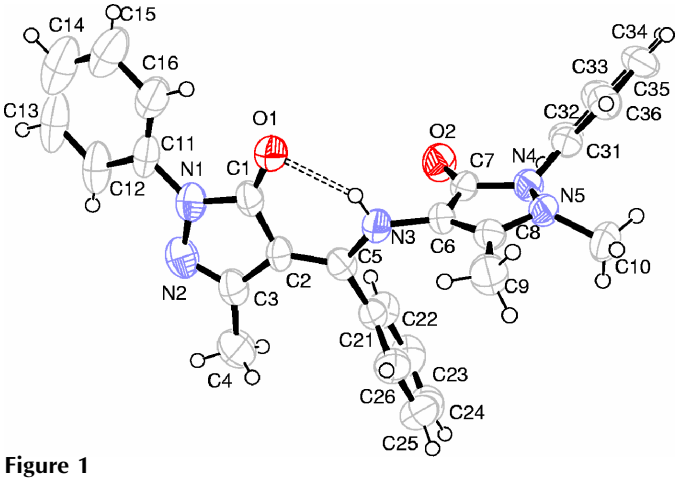


Figure 1
The molecular structure of (I), with 50% probability displacement ellipsoids. Hydrogen bonding is shown as dashed lines.

this part of the molecule (Table 1) also indicate delocalization for the ATP group. The dihedral angle between the two pyrazolone rings is 86.2 (3)°, reducing their steric hindrance.

A strong intramolecular N3—H3···O1 hydrogen bond (Table 2) is observed, leading to an enamine–keto tautomerism. This case is similar to that in 1,5-dimethyl-4-{[*E*-3-oxo-3-(2-thienyl)-1-(trifluoromethyl)-1-propenyl]amino}-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one [N···O = 2.702 (4) Å and the angle at *H* = 139°; Yu *et al.*, 2002]. Intermolecular C—H···O hydrogen bonds are also found.

The displacements of atoms C10 and C31 from the pyrazolone ring of ATP are 0.625 (6) and −0.419 (6) Å, respectively, showing that the methyl group bonded to N5 and the phenyl group bonded to N4 are on opposite sides of the ring. The same result was observed in 3-(2,3-dihydro-1,5-dimethyl-3-oxo-2-phenylpyrazol-4-ylimino)-4,4,4-trifluoro-1-(2-thienyl)-butane-1,2-dione (Wang, Yu *et al.*, 2002). The torsion angle C10—N5—N4—C31 is 57.4 (4)°, close to the value of 55.6 (3)° in 4-(salicylideneamino)-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (Chumakov *et al.*, 2002) and different from the value of 7.75 (2)° in 4-(antipyrin-4-yliminomethyl)benzoic acid (Zhang *et al.*, 2002). Small torsion angles for O1—C1—C2—C5 [−7.5 (6)°] and O2—C7—C6—N3 [2.7 (6)°] show that atoms O1, N3 and O2 could act as the coordinating atoms in this tridentate ligand.

Experimental

0.1 mol of PMBP in 20 ml ethanol solution and 0.1 mol of ATP in 20 ml ethanol solution were refluxed together for 3–4 h over a steam bath. Excess solvent was removed by evaporation and the solution was cooled in an ice bath with stirring. The product separated out as a cream-colored powder, which was collected and dried in air. After washing with cold anhydrous ethanol several times, the compound was dried in a vacuum over $CaCl_2$. Yellow–green single crystals suitable for X-ray analysis were obtained by slow cooling of a warmed ethanol solution. Elemental analysis for $C_{28}H_{25}N_5O_2$: calculated C 72.6, H 5.44, N 15.1%; found: C 71.2, H 5.32, N 15.3%.

Crystal data

$C_{28}H_{25}N_5O_2$	D_x = 1.272 Mg m^{-3}
M_r = 463.53	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 890 reflections
a = 6.986 (3) Å	θ = 2.3–21.9°
b = 27.904 (11) Å	μ = 0.08 mm^{-1}
c = 12.804 (5) Å	T = 293 (2) K
β = 104.127 (8)°	Block, yellow–green
V = 2420.4 (16) Å^3	0.25 × 0.22 × 0.20 mm
Z = 4	

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	1677 reflections with $I > 2\sigma(I)$
	R_{int} = 0.097
φ and ω scans	θ_{max} = 25.0°
Absorption correction: none	$h = -8 \rightarrow 8$
10034 measured reflections	$k = -33 \rightarrow 33$
4285 independent reflections	$l = -15 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0577P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.053	$(\Delta/\sigma)_{max}$ = 0.007
$wR(F^2)$ = 0.151	$\Delta\rho_{max}$ = 0.16 e Å^{-3}
S = 0.85	$\Delta\rho_{min}$ = −0.16 e Å^{-3}
4285 reflections	Extinction correction: *SHELXL*97
324 parameters	Extinction coefficient: 0.0098 (10)
H atoms: see below	

Table 1
Selected geometric parameters (Å).

N1—C1	1.380 (4)	O1—C1	1.249 (4)
N1—N2	1.401 (4)	O2—C7	1.221 (4)
N2—C3	1.316 (4)	C1—C2	1.430 (5)
N3—C5	1.346 (4)	C2—C5	1.375 (4)
N3—C6	1.421 (4)	C2—C3	1.432 (5)
N4—N5	1.402 (3)	C6—C8	1.348 (4)
N4—C7	1.409 (4)	C6—C7	1.423 (5)
N5—C8	1.356 (4)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C10—H10C···O2^{i}	0.96	2.67	3.302 (5)	123
C23—H23···O2^{ii}	0.93	2.53	3.428 (5)	161
N3—H3···O1	0.84 (4)	2.01 (4)	2.745 (4)	146 (4)

Symmetry codes: (i) $x-1, y, z$; (ii) $1-x, 1-y, 2-z$.

The high value of R_{int} is due to the relatively poor crystal quality, compounded by the room-temperature data collection. All aryl and methyl H atoms were positioned geometrically (C—H = 0.93 and 0.96 Å, respectively) and refined as riding atoms. The amine H atom was located from a difference map and refined with an isotropic displacement parameter; N—H = 0.84 (4) Å.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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