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Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.045
 wR factor = 0.076
Data-to-parameter ratio = 13.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

4-(Antipyrin-4-yliminomethyl)benzoic acid

The title compound, $\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_3$, 4-(1,2-dihydro-1,5-dimethyl-3-oxo-2-phenyl-3*H*-pyrazol-4-yliminomethyl)benzoic acid, has a basal plane containing a benzoic acid moiety and a pyrazole ring. The phenyl ring is twisted out of the plane with a dihedral angle of $70.25(4)^\circ$. Molecules are associated in a one-dimensional zigzag structure through $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonding and weak interactions between the carboxylic acid group and the antipyrine moiety.

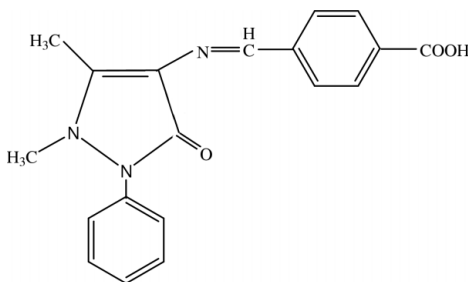
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Comment

In recent years, there has been considerable interest in the chemistry of antipyrine and its derivatives. These compounds have been widely used in spectrophotometric determination of metal ions. Many of these reagents give intense colours with transition-metal ions, providing sensitive probes (Saraswathi *et al.*, 1999) and some of them can also coordinate to rare earth ions to form metal complexes with interesting structures (Singh *et al.*, 1999). Antipyrine Schiff base derivatives may possess antibacterial and anti-inflammatory activities (Alaudeen *et al.*, 1995) and can serve as antiparasitic and analgesic agents (Gursoy *et al.*, 2000). Their complexes with platinum(II) and cobalt(II) ions have been shown to act as antitumor substances (Stupariu *et al.*, 1995).



(I)

We report here the synthesis and structure of the title compound, (I). The X-ray crystallographic study shows that the bond lengths and angles are within normal ranges. The $\text{C}7-\text{O}1$ bond distance is slightly longer than that in the 4-aminoantipyrine derivative 4-[[*(1E)*-(2-hydroxyphenyl)methylidene]amino]-1,5-dimethyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-3-one, in which the $\text{C}-\text{O}$ double-bond distance is $1.230(2)\text{ \AA}$ (Hökelek *et al.*, 2001). The $\text{C}-\text{N}$ bond lengths of $\text{N}1-\text{C}7$ and $\text{N}3-\text{C}8$ are normal for $\text{C}-\text{N}$ single-bond distances. The distance between $\text{N}3$ and $\text{C}10$ is typical for a $\text{C}=\text{N}$ double-bond distance. These bonds are comparable with those in *N*-(1*H*-benzoimidazol-2-ylmethyl)-*N*-(2,6-dichlorophenyl)amine (Eryigit & Kendi, 1998). The $\text{N}1-\text{N}2$

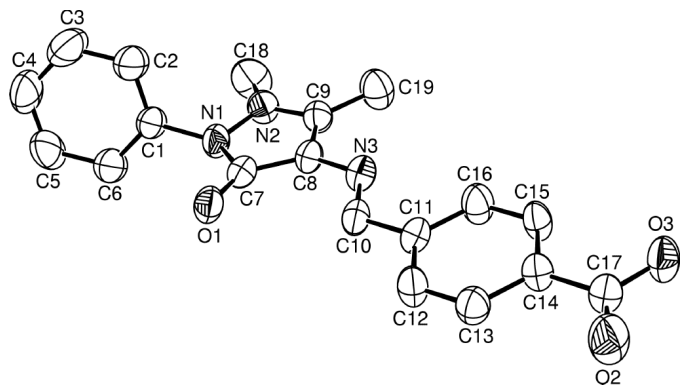


Figure 1

The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme.

single-bond length is comparable with that in 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (Manikandan *et al.*, 2000). The title compound has a basal plane involving the benzoic acid moiety and the pyrazole ring with a mean deviation of 0.05 Å. The phenyl ring is twisted out of the plane, with a dihedral angle of 70.25 (4)°. The orientation of the phenyl ring is defined by the torsion angles N2–N1–C1–C2 of –58.5 (3)° and N2–N1–C1–C6 of 123.9 (2)°. The shortest distance between the carboxylic acid moiety and the phenyl ring is 3.283 (2) Å for C1···O3 ($x, -y+3/2, z-1/2$). Compared with 4-[[1*E*)-(2-hydroxyphenyl)methylidene]amino]-1,5-dimethyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-3-one (Hökelek *et al.*, 2001), due to introducing the carboxylic acid group in the title compound, the molecules in the crystal are arranged in a head-to tail fashion, with intermolecular hydrogen bonds (Table 2) and weak interactions between the carboxylic acid moiety and the phenyl ring, to form a one-dimensional zigzag structure.

Experimental

The title compound was synthesized by condensation of *p*-carboxybenzaldehyde and 4-aminoantipyrine based on the following procedure. A 25 ml ethanol solution of 4-aminoantipyrine (0.20 g, 0.1 mmol) was mixed with 0.15 g (0.1 mmol) *p*-carboxybenzaldehyde in 15 ml ethanol (95%). The reaction mixture was stirred at room temperature overnight, whereupon a yellow precipitate was formed; this was collected by filtration and washed with ethanol and ether several times. Single crystals suitable for crystallographic analysis were obtained by slow evaporation of an acetonitrile solution of the compound.

Crystal data

C₁₉H₁₇N₃O₃
M_r = 335.36
 Orthorhombic, *Pbca*
a = 13.0859 (14) Å
b = 11.4837 (13) Å
c = 22.422 (2) Å
V = 3369.5 (6) Å³
Z = 8
D_x = 1.322 Mg m⁻³

Mo *K*α radiation
 Cell parameters from none reflections
 θ = –28–28°
 μ = 0.09 mm⁻¹
T = 293 (2) K
 Prism, yellow
 0.30 × 0.20 × 0.15 mm

Data collection

SMART APEX CCD diffractometer
 φ and ω scans with κ offsets
 16 332 measured reflections
 2986 independent reflections
 1643 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.086$
 $\theta_{\text{max}} = 25.1^\circ$
 $h = -15 \rightarrow 8$
 $k = -13 \rightarrow 13$
 $l = -26 \rightarrow 26$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.076$
 $S = 1.03$
 2986 reflections
 228 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.015P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.14 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

C1–C6	1.362 (3)	C10–C11	1.461 (2)
C1–N1	1.426 (2)	C11–C12	1.381 (2)
C7–O1	1.248 (2)	C14–C17	1.479 (3)
C7–N1	1.387 (2)	C17–O2	1.203 (2)
C8–N3	1.385 (2)	C17–O3	1.319 (2)
C9–N2	1.332 (2)	C18–N2	1.444 (2)
C10–N3	1.274 (2)	N1–N2	1.391 (2)
C6–C1–C2	120.8 (2)	C9–C8–C7	108.03 (18)
O1–C7–N1	123.57 (18)	O2–C17–O3	123.1 (2)
O1–C7–C8	131.25 (19)	O2–C17–C14	123.9 (2)
N1–C7–C8	105.13 (18)	O3–C17–C14	113.0 (2)
C9–C8–N3	121.32 (19)	C7–N1–N2	108.90 (16)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O3–H33···O1 ¹	0.82	1.80	2.603 (2)	166

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

All H atoms were placed in geometrically calculated positions (C–H = 0.93 Å and N–H = 0.86 Å), with $U_{\text{iso}} = 1.2U_{\text{eq}}$ (parent atom).

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

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