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{2-[(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-ylimino)methyl]-phenoxy}acetic acid nitrate

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.006 Å
R factor = 0.065
wR factor = 0.198
Data-to-parameter ratio = 9.4

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

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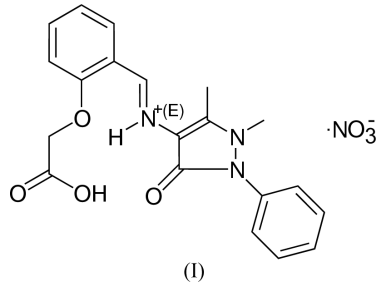
The title compound, $C_{20}H_{20}N_3O_4^+.NO_3^-$, has been synthesized and characterized by elemental analysis and single-crystal X-ray diffraction. The cations and anions form chains parallel to the *a* axis through intermolecular hydrogen bonds.

Comment

Antipyrine (2,3-dimethyl-1-phenyl-5-pyrazolone) and its derivatives exhibit a wide range of biological activities and applications (Ismail, 2000; Abd El Rehim *et al.*, 2001; Yadav *et al.*, 2003). Antipyrine shows minimal protein binding and is rapidly and completely absorbed from the gastrointestinal tract and extensively metabolized by the cytochrome P450 liver enzymes (Poulsen & Loft, 1988). Estimates of half-life and systemic clearance of antipyrine have been used for the *in vivo* assessment of hepatic drug oxidation in different species (Koning & Cantilena, 1994). Owing to its low pK_a value and its small degree of plasma protein binding, antipyrine is distributed in total body water. Schiff bases of salicyladehyde have demonstrated significant biological activity and new examples are being tested for their antitumor, antimicrobial, and antiviral activity (Tarafder *et al.*, 2002; CukurovAli *et al.*, 2002; Ali *et al.*, 2002). A new antipyrine derivative is reported here.



(I)

The title compound, (I), is a nitrate salt (Fig. 1). The bond lengths and angles of the antipyrine moiety are in normal ranges, similar to those observed in a similar antipyrine Schiff base (Liang *et al.*, 2002). The dihedral angle between the pyrazoline and C13–C18 phenyl rings is 52.8 (4)°. The torsion angles N2—N1—C13—C14 and C1—N1—C13—C18 are −141.5 (4) and −114.8 (4)°, respectively. Atom O1 deviates from the pyrazoline mean plane by 0.063 (4) Å, whereas C19 and C20 deviate from it on the opposite side by 0.507 (5) and 0.097 (5) Å, respectively. Because of conjugation through the imino double bond C6═N3, the pyrazoline and C7–C12 substituted phenyl ring are essentially coplanar (mean deviation from the overall plane is 0.0012 Å); the dihedral angle between the two rings is 2.2 (4)°. As expected, the molecular structure adopts a *trans* configuration about the C6═N3 bond.

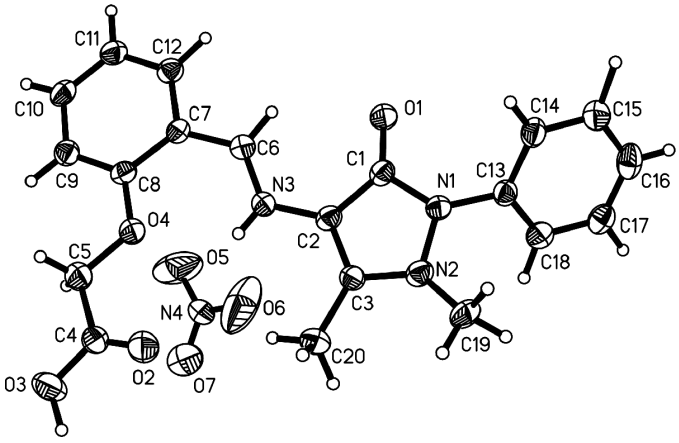


Figure 1
The structure of the title compound, (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme.

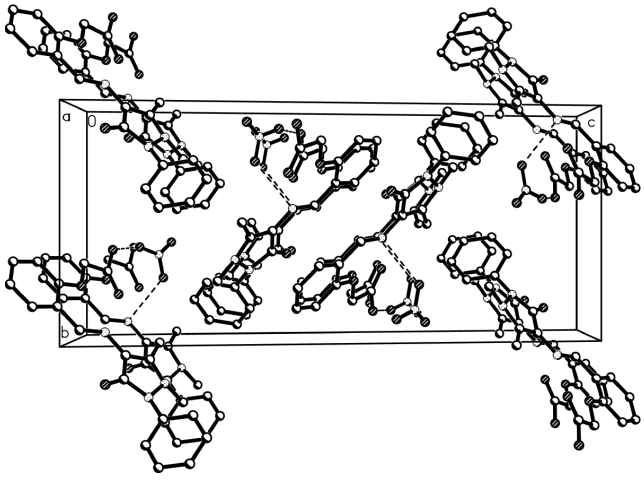


Figure 2
Crystal packing of (I), viewed along the *a* axis.

In the crystal structure, the cations and anions are connected by hydrogen bonds (Table 1), to form chains parallel to the *a* axis (Fig. 2).

Experimental

Salicylaldehyde, chloroacetic acid and 4-aminoantipyrine were available commercially and were used without further purification. A mixture of salicylaldehyde (0.10 mol, 12.2 g), chloroacetic acid (0.10 mol, 9.4 g) and sodium hydroxide (0.21 mol, 8.4 g) in distilled water (50 ml) was heated at 353 K for 1 h, with stirring. The mixture was steam-distilled to remove the excess salicylaldehyde. An appropriate amount of concentrated hydrochloric acid was added to the stirred solution. The resulting yellow solid of (2-formylphenoxy)-acetic acid was filtered off and washed three times with EtOH/H_2O (1:1 by volume), and dried in a vacuum desiccator using P_4O_{10} (yield 82.7%). Analysis found: C 59.98, H 4.49, N 35.54%; calculated for $C_9H_8O_4$: C 60.00, H 4.48, N 35.52%.

This intermediate (1.0 mmol, 180.2 mg) and 4-aminoantipyrine (1.0 mmol, 203.4 mg) were dissolved in methanol (10 ml). The mixture was stirred for 30 min at room temperature to give copious amounts of a brown solid. This was isolated and washed three times with methanol. Recrysallization from methanol afforded well-formed brown crystals of {2-[(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-ylimino)methyl]phenoxy}acetic acid (DMPA). The product was dried in a vacuum desiccator using P_4O_{10} (yield 77.2%). Analysis found: C 65.72, H 5.25, N 11.54, O 17.55%; calculated for $C_{20}H_{19}N_3O_4$: C 65.74, H 5.24, N 11.50, O 17.52%.

DMPA (0.2 mmol, 73.08 mg) was dissolved in methanol (5 ml) and a nitric acid solution (0.2 mmol in 2 ml distilled water) was added to the stirred solution. After keeping the resulting solution in air for 8 d, yellow crystals of (I) were formed at the bottom of the vessel on slow evaporation of the solvent. The crystals were isolated, washed three times with methanol, and dried in a vacuum desiccator using P_4O_{10} (yield 72.8%). Analysis found: C 56.08, H 4.73, N 13.07, O 26.17%; calculated for $C_{20}H_{20}N_4O_7$: C 56.07, H 4.71, N 13.08, O 26.14%.

Crystal data

$C_{20}H_{20}N_3O_4^+\cdot NO_3^-$	D_x = 1.445 Mg m^{-3}
M_r = 428.40	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 1434 reflections
a = 7.102 (3) Å	θ = 3.1–21.5°
b = 11.110 (5) Å	μ = 0.11 mm^{-1}
c = 25.177 (10) Å	T = 298 (2) K
β = 97.608 (7)°	Block, yellow
V = 1969.1 (14) Å^3	0.37 × 0.29 × 0.21 mm
Z = 4	

Data collection

Bruker SMART CCD area-detector diffractometer	3390 independent reflections
φ and ω scans	1737 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	R_{int} = 0.050
T_{min} = 0.960, T_{max} = 0.977	θ_{max} = 25.0°
9917 measured reflections	$h = -8 \rightarrow 8$
	$k = -13 \rightarrow 11$
	$l = -29 \rightarrow 29$

Refinement

Refinement on F^2	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)]$ = 0.065	$w = 1/[\sigma^2(F_o^2) + (0.1199P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.198	$(\Delta/\sigma)_{max} < 0.001$
S = 0.89	$\Delta\rho_{max}$ = 0.57 e Å^{-3}
3390 reflections	$\Delta\rho_{min}$ = −0.32 e Å^{-3}
360 parameters	

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H1···O5^{i}	0.96 (4)	1.75 (4)	2.567 (5)	141 (3)
N3—H4···O4	0.79 (3)	2.16 (3)	2.724 (4)	129 (3)

Symmetry code: (i) $1 + x, y, z$.

All H atoms were refined isotropically, giving C—H distances in the range 0.88 (5)–1.16 (5), N—H = 0.79 (3), and O—H = 0.96 (4) Å.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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