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4-[*N*,*N*-Bis(2-hydroxyimino-2-phenylethyl)amino]-1,5-dimethyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-3-one monohydrate

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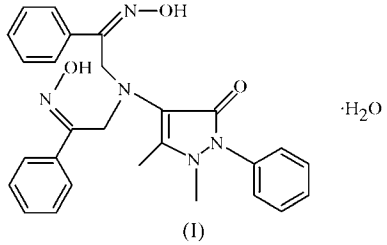
The title compound, $C_{27}H_{27}N_5O_3\cdot H_2O$, is built up from pyrazolinone, phenyl and acetophenone oxime moieties. The 2-phenyl substituent is nearly perpendicular to the pyrazolinone ring, with a dihedral angle of 87.66 (1)°. The acetophenone oxime moieties are twisted out of the pyrazolinone-ring plane by 47.04 (1)°. The molecules in the crystal pack in an antiparallel fashion and are held together by hydrogen-bonded water molecules and intermolecular O—H···O and O—H···N hydrogen bonds.

Comment

In recent years, there has been considerable interest in the chemistry of antipyrine and its derivatives. These compounds exhibit a wide range of biological activities and applications (Ismail, 2000; Abd El Rehim *et al.*, 2001; Yadav *et al.*, 2003; Madhu *et al.*, 2003). X-Ray crystallographic studies of antipyrine Schiff base derivatives have been abundantly reported (You *et al.*, 2003; Yu *et al.*, 2002; Wang *et al.*, 2002; Liang *et al.*, 2002, 2004). However, the comparatively less well known oxime derivatives have not been adequately explored in crystal engineering; a recent survey of the Cambridge Structural Database (Version 5.25; Allen, 2002) found 370 entries



(I)

containing the oxime moiety (Aakeröy *et al.*, 2001, 2002). We describe here the structure of the title compound, (I), which contains both oxime and pyrazolinone functionalities.

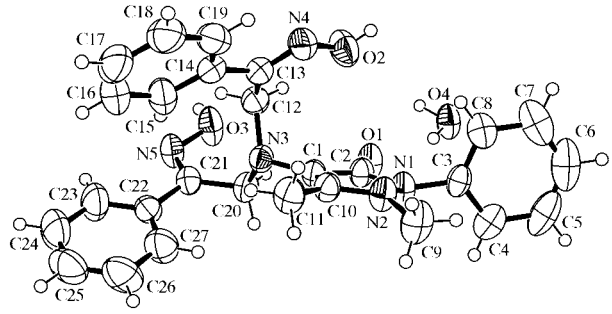


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level.

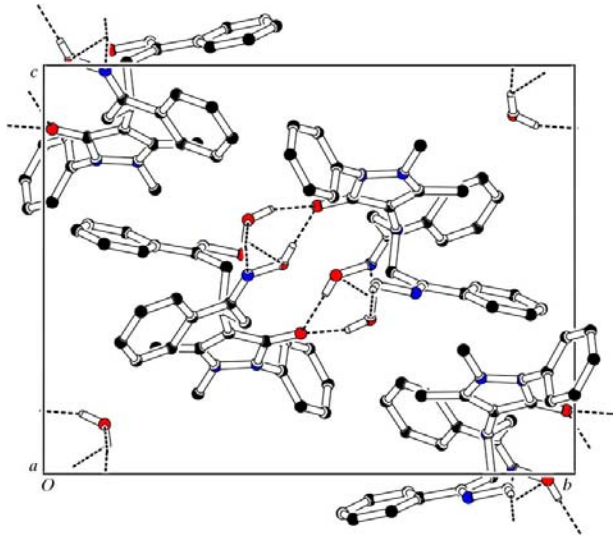


Figure 2
A packing diagram for (I). The dashed lines show the hydrogen bonding.

A view of the molecule of (I) is shown in Fig. 1. The C2—O1 bond distance is slightly longer than that in the 4-amino-antipyrine derivatives 4-{[(1*E*)-(2-hydroxyphenyl)methylidene]amino}-1,5-dimethyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-3-one (Hökelek *et al.*, 2001) and 4-(antipyrin-4-yliminomethyl)benzoic acid (Zhang *et al.*, 2002), in which the C=O double-bond distances are 1.230 (2) and 1.248 (2) Å, respectively. The bond lengths and angles in the acetophenone oxime moieties are in the normal ranges and compare well with the literature values for similar compounds (Aakeröy *et al.*, 2001). The dihedral angle between the pyrazolinone ring and the C3–C8 phenyl ring is 87.66 (1)°, whereas the C14–C19 plane deviates from the pyrazolinone ring by 47.04 (1)°. The angle between the C22–C27 and C14–C19 rings is 69.97 (1)°.

Previous structural studies of molecules containing both oxime and carboxylic acid moieties have demonstrated that there is a pronounced preference for heteromeric (oxime–acid) interactions over homomeric motifs, in the absence of other strong hydrogen-bond donors or acceptors (Aakeröy *et al.*, 2002; Téllez *et al.*, 2002). The supramolecular network of

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(I) is built up of moderate intermolecular hydrogen bonds involving the oxime O—H moiety and the aminoantipyrine carbonyl O atom of adjacent molecules (O3···O1 and O2···O4; Fig. 2). Neighbouring molecules are held together by water molecules of crystallization, which are hydrogen-bonded to the pyrazolinone carbonyl O atom *via* O4—H4*C*···O1 and to the oxime N atom *via* O4—H4*B*···N5^{ii} [symmetry code: (ii) $1-x,\ 1-y,\ 1-z$]. The water molecule on each side further interacts with the oxime O atom to form a three-centre hydrogen bond, to satisfy both the donor and acceptor functionality. The hydrogen bonds between the oxime and pyrazolinone moieties can be considered strong because of the short O—H distances and the O—H···O angles, which are close to 180° (Table 2).

The structure of (I), incorporating antipyrine, acetophenone oxime and water, is a rare example among the reported structures of compounds incorporating mainly aminoantipyrine Schiff base and carboxylic acid derivatives. Such structures have potential applications in catalysis or separation (Aakeröy *et al.*, 2001). Each molecule has eight lone pairs (three on each oxime group and two on the carbonyl group) available for accepting hydrogen bonds. Since water is a hydrogen-bond donor and acceptor, the molecules form many intermolecular hydrogen bonds to assemble the molecules in this specific manner. Of course, the size and shape of the molecule are also of key importance to the resulting structure.

Experimental

4-Aminoantipyrine (4-ATP; 1 mol) and α-bromoacetophenone oxime (2 mol), alternatively called (*E*)-2-bromo-1-phenylethanone oxime, were mixed in ethanol–water (50 ml, 1:1 *v*/*v*) and heated at 343 K for 2 h with vigorous stirring. The resulting beige-coloured precipitate was filtered off, washed three times with EtOH–H_2O (1:1 *v*/*v*) and then with diethyl ether and finally air dried (yield 82.5%). Recrystallization from ethanol (95%) gave colourless block-shaped crystals of (I) suitable for single-crystal X-ray analysis. IR (KBr, *ν*, cm^{-1}): 3280 (O—H), 3153 (Ar CH), 2885 (N—CH_3, CH_2), 1605 and 1612 (C═N, C═O), 1548 (C═C), 964 (N—O), 895, 840, 691, 557; ESI–MS (*m*/*z*): 470.

Crystal data

$C_{27}H_{27}N_5O_3\cdot H_2O$
M_r = 487.55
Monoclinic, $P2_1/c$
a = 10.385 (6) Å
b = 18.024 (4) Å
c = 14.229 (5) Å
β = 102.05 (5)°
V = 2604.6 (19) Å^3
Z = 4
D_x = 1.243 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 1.8–25.0°
μ = 0.09 mm^{-1}
T = 293 (2) K
Block, colourless
0.46 × 0.38 × 0.12 mm

Data collection

Siemens *P*4 diffractometer
ω scans
4862 measured reflections
4592 independent reflections
2956 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 25.0°
$h = -1 \rightarrow 12$
$k = -1 \rightarrow 21$
$l = -16 \rightarrow 16$
3 standard reflections
every 97 reflections
intensity decay: none

Table 1
Selected geometric parameters (Å, °).

O1—C2	1.259 (3)	N2—C9	1.446 (3)
O3—N5	1.393 (3)	N3—C20	1.475 (3)
N1—C2	1.384 (3)	N3—C12	1.480 (3)
N1—N2	1.403 (3)	N4—C13	1.285 (3)
N1—C3	1.428 (3)	N5—C21	1.288 (3)
N1—N2—C9	119.9 (2)	C21—N5—O3	112.8 (2)
C1—N3—C12	111.90 (19)	O1—C2—N1	121.5 (2)
C13—N4—O2	112.4 (2)	N3—C12—C13	110.9 (2)
C1—N3—C12—C13	−64.3 (3)	O3—N5—C21—C22	178.7 (2)
O2—N4—C13—C14	179.0 (2)	N3—C20—C21—N5	105.1 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*A*···O4^{i}	0.82	1.88	2.663 (3)	159
O3—H3*A*···O1^{ii}	0.82	1.88	2.695 (3)	178
O4—H4*C*···O1	0.86 (4)	1.99 (4)	2.779 (3)	152 (4)
O4—H4*B*···N5^{ii}	0.99 (4)	1.87 (4)	2.848 (4)	170 (3)
O4—H4*B*···O3^{ii}	0.99 (4)	2.57 (4)	3.372 (3)	138 (3)

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.155
S = 1.02
4592 reflections
334 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0636P)^2 + 0.8613P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.006
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

The water H atoms were refined isotropically, with U_{iso} values in the range 0.105 (12)–0.110 (14) Å^2. The other H atoms were treated using a riding model, with fixed C—H distances of 0.93–0.97 Å for CH groups, 0.97 Å for CH_2 groups and 0.96 Å for CH_3 groups (HFIX 137, 33), and with an O—H distance of 0.82 Å (HFIX 83). The U_{iso}(H) values for these H atoms were fixed at either 1.2 or 1.5U_{eq}(parent).

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *PLUTON* (Spek, 1997); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1488). Services for accessing these data are described at the back of the journal.

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