organic papers

t-3-Methyl-1-nitroso-*r*-2,*c*-6-diphenylpiperidin-4-one oxime monohydrate

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Key indicators

Single-crystal X-ray study
$T = 273$ K
Mean σ(C–C) = 0.005 Å
R factor = 0.050
wR factor = 0.136
Data-to-parameter ratio = 7.3

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

In the title compound, $C_{18}H_{19}N_3O_2 \cdot H_2O$, the piperidine ring adopts a distorted boat conformation. In the solid state, the molecules are linked by intermolecular O—H···O and O—H···N hydrogen bonds involving water molecules.

Comment

Many piperidine derivatives are found to possess pharmacological activities and form an essential part of the molecular structure of important drugs. The piperidine ring is a feature of oral anaesthetics (McElvain, 1927) and narcotic analgesics (Lu *et al.*, 1991). The X-ray structure determination of the title compound, (I), was carried out with the aim of establishing the influence of the nitroso and oximino groups on the conformation of the piperidine ring and also on the orientation of the substituents.

(I)
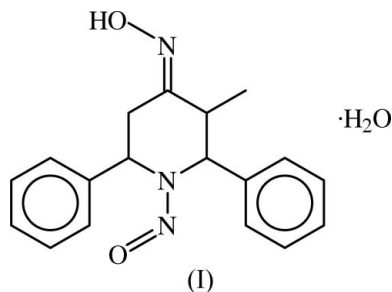
Compound (I) is analogous to a related structure, 3,5-dimethyl-*N*-nitroso-4-oximino-2,6-diphenylpiperidine-4-one oxime, (II) (Sukumar *et al.*, 1994), except for the presence of a methyl group at C5 in (II). As observed in (II), the piperidine ring in (I) adopts a distorted boat conformation [Cremer & Pople (1975) puckering parameters are $Q = 0.657$ (3) Å, $\theta = 94.1$ (3)° and $\varphi = 251.5$ (2)°], with the methyl group at C3 in the axial orientation (Fig. 1). The dihedral angle between the N1/C3/C4/C6 and nitroso (N1/N21/O22) planes is 35.7 (1)° [39.8 (1)° for (II)]. The dihedral angle between the N1/C3/C4/C6 and the oximino (C4/N23/O24) planes is 16.8 (3)° [13.8 (3)° for (II)]. The dihedral angle between the nitroso and oximino groups is 52.0 (2)° [52.8 (2)° for (II)].

As observed in (II), the benzene ring at C2 has a roughly perpendicular orientation, with a C4—C3—C2—C14 torsion angle of 74.3 (3)° [68.6 (3)° for (II)], and the benzene ring at C6 has a coplanar orientation, with a C4—C5—C6—C8 torsion angle of −170.8 (3)° [−171.7 (3)° for (II)]. The C8–C13 and C14–C19 planes form dihedral angles of 75.8 (1) and 87.3 (1)°, respectively, with the N1/C3/C4/C6 plane. The dihedral angle between the C8–C13 and C14–C19 benzene rings is 66.9 (1)° for (I) and 59.2 (1)° for (II).
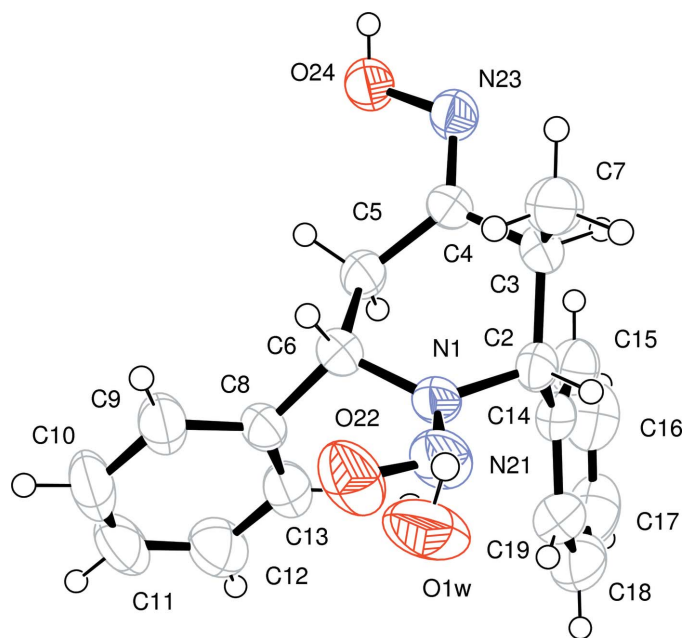
Figure 1
A view of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary radii.

Figure 2
A view of the superposition of the structures of compounds (I) (black), (II) (green), (III) (red) and (IV) (blue).

Superposition of the non-H atoms common to the structures of (I) and (II) gives an r.m.s. deviation of 0.546 Å. For comparison, the matrix of the r.m.s. deviations for the superposition of the non-H atoms common to the structures of (I), (II), r-2,c-6-bis(2-chlorophenyl)-t-3,t-5-dimethyl-1-nitrosopiperidin-4-one oxime, (III) (Hema, Parthasarathi, Ravikumar, Sridhar, Pandiarajan & Muthukumaran, 2005), and r-2,c-6-bis(4-chlorophenyl)-t-3,t-5-dimethyl-1-nitrosopiperidin-4-one oxime, (IV) (Hema, Parthasarathi, Ravikumar, Sridhar & Pandiarajan, 2005) is given in Table 1, with the superposition shown in Fig. 2. The data in Table 1 show that the most profound effect on the conformation of the piperidine derivatives is observed when there is no substituent, such as a methyl group, present at the C5 postion of the piperidine ring. A comparative study on the structures of these molecules shows that the substitution of heavy atoms such as Cl at the *para*- and *ortho*-positions of the phenyl rings does not significantly alter the conformation of the piperidine ring.

In (I), the molecular packing is stabilized by O—H···O and O—H···N intermolecular interactions involving water molecules (Fig. 3). The water molecule links three different piperidine molecules. Atom O24 of the oximino group acts as a donor for an intermolecular O—H···O($-1 + x$, $1 + y$, z) interaction (*via* atom H24), while atom O1W of the water molecule acts as the acceptor, to form a chain described by a graph-set motif of $C(10)$ (Bernstein *et al.*, 1995; Table 2). Atom O1W is similarly involved in another intermolecular O—H···N($1 - x$, $-\frac{1}{2} + y$, $-z$) interaction with the oximino atom N23 (*via* atom H1W) of another adjacent molecule and thereby links the molecules into a continuous chain to form a graph-set motif of $C(5)$. Interestingly, atom O1W acts as a donor for two other intermolecular interactions in the same
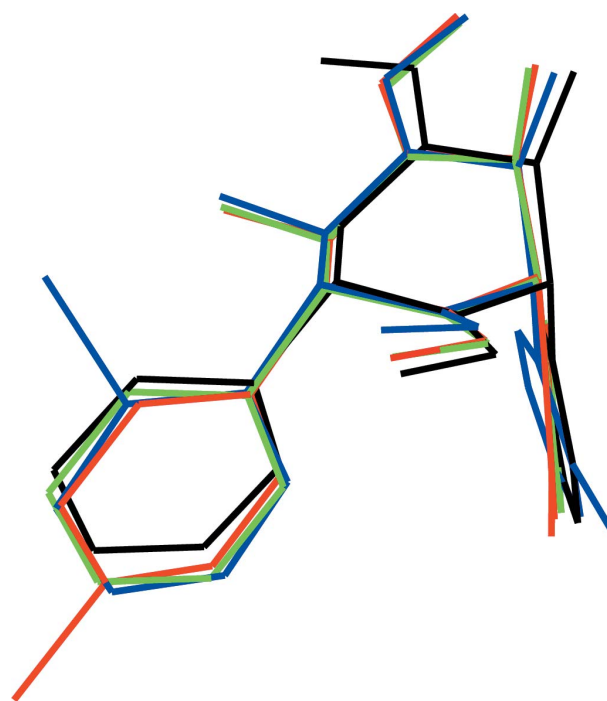
asymmetric unit. Atom O1W acts as donor *via* atom HW2 to atoms O22 and N21 of the nitroso group substituted at N1.

Experimental

t-3-Methyl-*r*-2,*c*-6-diphenylpiperidine-4-one (50 mmol) and sodium acetate trihydrate (150 mmol) were dissolved in boiling ethanol (100 ml), and hydroxylamine hydrochloride (60 mmol) was added. The mixture was heated under reflux for 15 min and poured into water. The separated compound, (I), was filtered off and recrystallized from ethanol (yield 75%, m.p. 445–447 K).
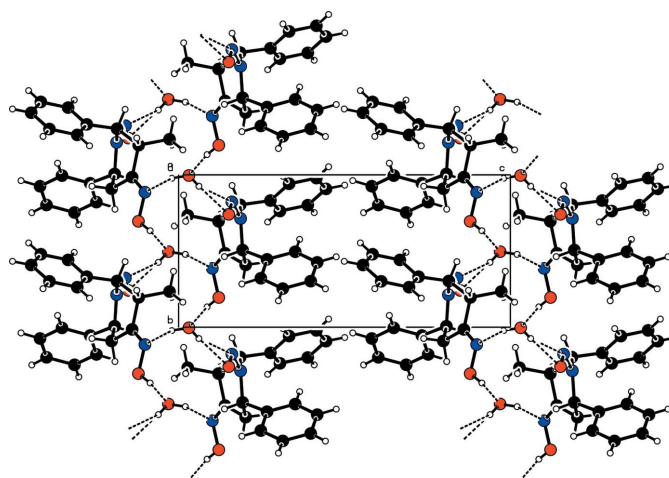

Figure 3
The crystal packing of (I), viewed down the *a* axis. Dashed lines indicate O—H···O and O—H···N hydrogen bonds.

Crystal data

$C_{18}H_{19}N_3O_2 \cdot H_2O$
$M_r = 327.38$
Monoclinic, $P2_1$
$a = 7.9578\ (13)$ Å
$b = 7.0567\ (12)$ Å
$c = 15.642\ (3)$ Å
$\beta = 100.483\ (3)°$
$V = 863.7\ (3)$ Å^3
$Z = 2$

$D_x = 1.259$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3835 reflections
$\theta = 2.6–25.0°$
$\mu = 0.09$ mm^{-1}
$T = 273\ (2)$ K
Block, colourless
$0.24 \times 0.24 \times 0.20$ mm

Data collection

Bruker SMART CCD area detector diffractometer
ω scans
Absorption correction: none
8200 measured reflections
1665 independent reflections

1544 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 25.0°$
$h = -9 \rightarrow 9$
$k = -8 \rightarrow 8$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.136$
$S = 1.08$
1665 reflections
227 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1019P)^2 + 0.0428P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}

Table 1
Matrix of r.m.s. deviations (Å) for the superposition of the non-H atoms common to the structures of (I)–(IV).

Compound	(I)	(II)	(III)
(II)	0.546		
(III)	0.577	0.200	
(IV)	0.536	0.132	0.209

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O24—H24···O1W^i	0.82	1.84	2.636 (4)	164
O1W—H1W···N23^{ii}	0.87 (6)	2.16 (6)	2.947 (4)	150 (5)
O1W—H2W···O22	0.80 (8)	2.03 (9)	2.822 (5)	169 (8)
O1W—H2W···N21	0.80 (8)	2.48 (8)	3.233 (5)	158 (8)

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

H atoms of the water molecule were located in a difference Fourier map and their positions were refined freely along with their isotropic displacement parameters. All other H atoms were placed in idealized positions, with O—H = 0.82 Å and C—H = 0.93–0.98 Å, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.5U_{eq}$(carrier atom) for methyl and hydroxy H atoms, and $1.2U_{eq}(C)$ for the remaining H atoms. The methyl groups were allowed to rotate freely about their C—C bond. In the absence of any significant anomalous scattering effects, Friedel pairs were merged. The absolute configuration was assigned to correspond to that of the known chiral centres in a precursor molecule, which remained unchanged during the synthesis of the title compound.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *QMOL* (Gans & Shalloway, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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