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r-2,*c*-6-Bis(2-chlorophenyl)-*t*-3,*t*-5-dimethyl-1-nitrosopiperidin-4-one oxime

R. Hema,[a] V. Parthasarathi,[a]* K. Ravikumar,[b] B. Sridhar,[b] K. Pandiarajan[c] and G. Muthukumaran[c]

[a]School of Physics, Bharathidasan University, Tiruchirappalli 620024, India, [b]Laboratory of X-ray Crystallography, Indian Institute of Chemical Technology, Hyderabad 500007, India, and [c]Department of Chemistry, Annamalai University, Annamalai Nagar 608002, India

Correspondence e-mail: vpsarati@yahoo.com

Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.003 Å
R factor = 0.038
wR factor = 0.101
Data-to-parameter ratio = 13.9

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

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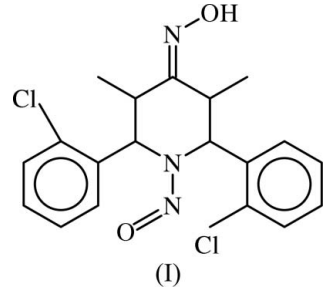
In the title compound, $C_{19}H_{19}Cl_2N_3O_2$, the piperidine ring adopts a distorted boat conformation. In the solid state, the molecules exist as O—H···N-hydrogen-bonded centrosymmetric dimers.

Comment

Many piperidine derivatives are found to possess pharmacological activities and form an essential part of the molecular structures of important drugs. Several 2,6-disubstituted piperidines are useful as tranquillizers (Bockringer & Soenhe, 1961), and possess hypotensive activity (Severs *et al.*, 1965), a combination of stimulant and depressant effects on the central nervous system (Ganelline & Spickett, 1965), as well as bacterial, fungicidal and herbicidal activities (Mobio *et al.*, 1990). Though the piperidine derivatives are pharmacologically important, the *N*-nitroso derivatives are carcinogens in nature (Ferguson, 1975). These *N*-nitroso compounds are often found in a variety of environmental samples. Even though the unsubstituted *N*-nitroso piperidines are potential carcinogens, when an alkyl group is substituted at the α position C2, it reduces the carcinogenicity. If α-positions of C2 and C6 are substituted by methyl groups, it becomes non-carcinogenic. It appears that the blocking of the α positions to the N atom by methyl groups in cyclic nitrosomines reduces the carcinogenic activity (Lijinsky & Taylor, 1975). Most of the piperidine precursors are known to exist in chair conformations (Sekar & Parthasarathy, 1993). The properties of the piperidine derivatives depend on the nature of the side groups and their orientations. The X-ray structure determination of the title compound, (I), aims to find the influence of the nitroso and oximino groups on the conformation of the piperidine ring and as well as 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 (DMNOH) (Sukumar *et al.*,1994), except for the substitution of Cl atoms at the *ortho* positions of the two

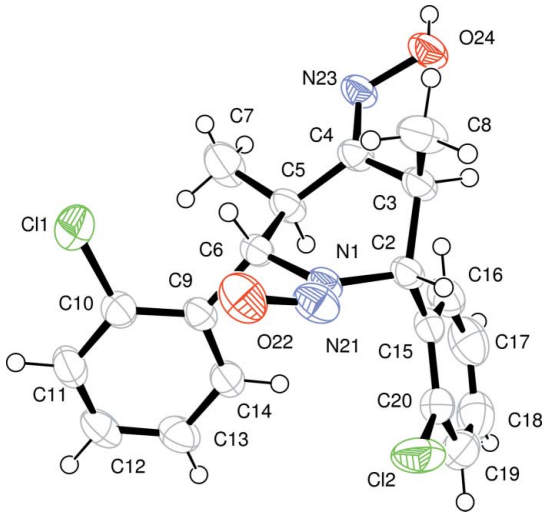


Figure 1
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

benzene rings. The space group of both structures is the same. Superposition of non-H atoms common to the structure of (I) and DMNOH (Sukumar *et al.*, 1994) gives an r.m.s. deviation of 0.200 Å. As observed in DMNOH, the piperidine ring in (I) adopts a distorted boat conformation [Cremer & Pople (1975) puckering parameters are Q = 0.677 (2) Å, θ = 93.44 (15)° and φ = 248.16 (15)°] with the methyl group at C3 in the axial orientation and that at C5 in the equatorial orientation.

From detailed studies of the stereochemistry of various piperidine derivatives, it has been reported that the nitroso group can adopt two possible orientations, namely, roughly in and perpendicular to the mean plane of the piperidine ring, irrespective of the substituents at the 2- and 6-positions of the piperidine ring (Sukumar *et al.*, 1994, and references therein). The dihedral angle between the N1/C3/C4/C6 and nitroso (N1/N21/O22) planes is 44.3 (1)° (39.8° for DMNOH). The dihedral angle between the N1/C3/C4/C6 plane and the oximino group (C4/N23/O24) is 15.9 (2)° (13.8° for DMNOH). The dihedral angle between the nitroso and the oximino groups is 59.8 (2)° [52.8 (2)° for DMNOH].

A survey of the conformations of 2,6-dialkyl-*N*-nitroso piperidine and related compounds suggests two possible orientations for the phenyl rings; when the nitroso group is approximately in the mean plane of the piperidine ring, the phenyl ring would have to adopt a perpendicular orientation, and *vice versa* (Ravindran *et al.*, 1991). As observed in DMNOH, the benzene ring at C2 has a roughly perpendicular orientation, with a C4—C3—C2—C15 torsion angle of 76.14 (19)° [68.6 (3)° for DMNOH], and the benzene ring at C6 has an in-plane orientation, with a C4—C5—C6—C9 torsion angle of −167.79 (15)° [−171.7 (3)° for DMNOH]. The C9—C14 and C15—C20 planes form dihedral angles of 69.70 (6) and 85.16 (6)°, respectively, with respect to the N1/C3/C4/C6 plane. The dihedral angle between the C9—C14 and C15—C20 benzene rings is 69.57 (6)° for (I) and 59.2 (1)° for DMNOH. The variation may be due to the substitution of Cl atoms at the *ortho* positions of the benzene rings.

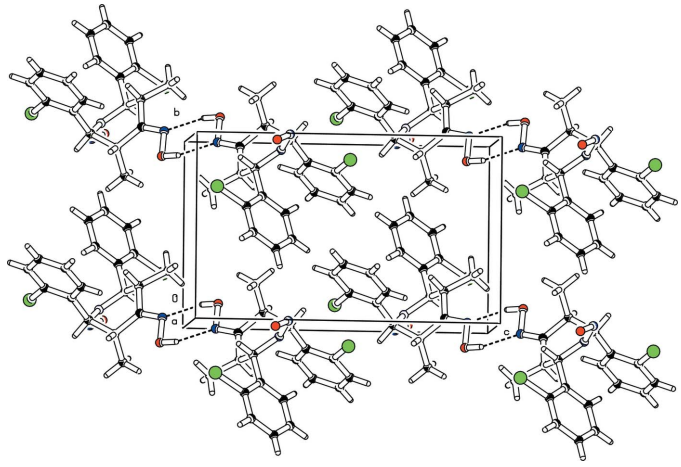


Figure 2
Packing diagram, viewed approximately down the *a* axis, showing the O—H···N hydrogen-bonded (dashed lines) dimers.

In (I), the crystal packing is stabilized by O—H···N hydrogen-bonding interactions (Table 1). The O24—H24···N23($1-x, 2-y, -z$) interactions link pairs of molecules across centres of inversion to form dimers with ring motif $R_2^2(6)$ (Bernstein *et al.*, 1995).

Experimental

t-3,*t*-5-Dimethyl-*r*-2,*c*-6-bis(*o*-chlorophenyl)piperidin-4-one (50 mmol) and sodium acetate trihydrate (150 mmol) were dissolved in boiling ethanol, 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 70%, m.p. 475–477 K).

Crystal data

$C_{19}H_{19}Cl_2N_3O_2$
M_r = 392.27
Triclinic, $P\overline{1}$
a = 7.9168 (7) Å
b = 8.5941 (8) Å
c = 14.1572 (13) Å
α = 90.225 (2)°
β = 101.459 (2)°
γ = 94.810 (2)°
V = 940.49 (15) Å^3
Z = 2
D_x = 1.385 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6230 reflections
θ = 2.4–28.0°
μ = 0.36 mm^{-1}
T = 273 (2) K
Block, colourless
0.20 × 0.18 × 0.18 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scan
Absorption correction: none
9029 measured reflections
3313 independent reflections
3062 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
θ_{max} = 25.0°
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.101
S = 1.04
3313 reflections
238 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 0.427P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O24—H24···N23^{i}	0.82	2.09	2.8052 (19)	146

Symmetry code: (i) $-x+1, -y+2, -z$.

H atoms were placed in idealized positions (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) values of $1.5U_{eq}$(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.

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); software used to prepare material for publication: *SHELXL97*.

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