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

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Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.003 Å
R factor = 0.042
wR factor = 0.117
Data-to-parameter ratio = 14.3

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

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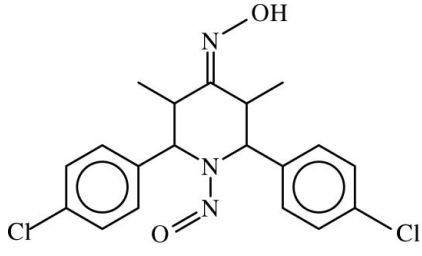
In the title compound, $C_{19}H_{19}Cl_2N_3O_2$, the piperidine ring adopts a distorted boat conformation. In the solid state, the molecules exist as O—H···N hydrogen-bonded centrosymmetric dimers.

Comment

Piperidine derivatives are used clinically to prevent post-operative vomiting, to speed up gastric emptying before anaesthesia or to facilitate radiological evaluation, and to correct a variety of disturbances of gastro-intestinal function (Robinson, 1973). Although 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*-nitrosopiperidines are potential carcinogens, when an alkyl group is substituted at the α position C2, it reduces the carcinogenicity (Hema *et al.*, 2005). Most of the piperidine precursors are known to exist in chair conformations (Sekar & Parthasarathy, 1993). The properties of the piperidine derivatives depend upon the nature of the side groups and their orientations. 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 as well as on the orientation of the substituents.



(I)

Compound (I) is analogous to a related structure, *r*-2,*c*-6-bis(2-chlorophenyl)-*t*-3,*t*-5-dimethyl-1-nitrosopiperidin-4-one oxime, (II) (Hema *et al.*, 2005), except for the substitution of Cl atoms at the *para*-positions of the two benzene rings in (I) instead of the *ortho*-positions in (II). Superposition of non-H atoms common to the structures of (I) and (II) gives an r.m.s. deviation of 0.209 Å (Fig. 2). As observed in (II), the piperidine ring in (I) adopts a distorted boat conformation [Cremer & Pople (1975) puckering parameters are Q = 0.700 (2) Å, θ = 93.40 (16)° and φ = 252.58 (15)°], with the methyl group at C3 in the axial orientation and that at C5 in the equatorial orientation.

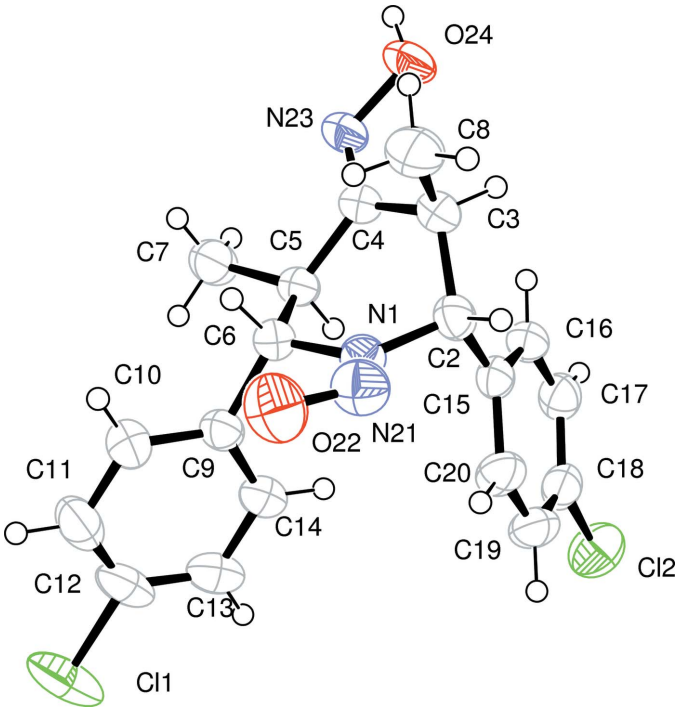


Figure 1
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

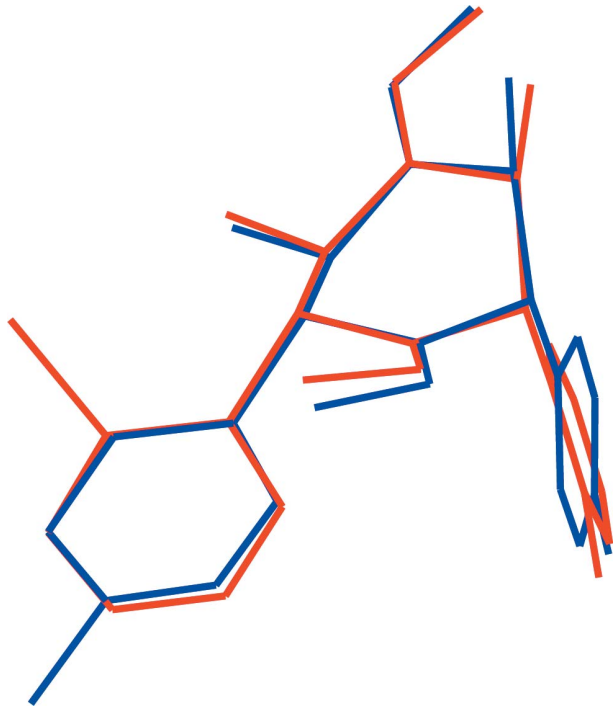


Figure 2
A view of the superposition of the molecules of (I) (blue) and (II) (red).

The dihedral angle between the N1/C3/C4/C6 and the nitroso (N1/N21/O22) planes is 37.92 (15)° [44.3 (1)° for (II)]. The dihedral angle between the N1/C3/C4/C6 plane and the oximino group (C4/N23/O24) is 15.97 (22)° [15.9 (2)°) for (II)]. The dihedral angle between the nitroso and the oximino groups is 53.53 (17)° [59.8 (2)° for (II)].

As observed in (II), the benzene ring at C2 has a roughly perpendicular orientation, with a C4—C3—C2—C15 torsion angle of 69.8 (2)° [76.14 (19)° for (II)], and the benzene ring at C6 has a coplanar orientation, with a C4—C5—C6—C9 torsion angle of −172.80 (14)° [−167.79 (15)° for (II)]. The C9–C14 and C15–C20 planes form dihedral angles of 80.95 (6) and 87.85 (6)°, respectively, with respect to the N1/C3/C4/C6 plane [69.70 (6) and 85.16 (6)°, respectively, for (II)]. The dihedral angles between the C9–C14 and C15–C20 benzene rings are 50.92 (7) for (I) and 69.57 (6)° for (II).

Even though the conformation of the piperidine ring remains the same as in (II), the substitution of Cl atoms at the *para*-position of the benzene rings brings about the following changes. The space group has been changed to $P2_1/n$ in (I) from $P\overline{1}$ in (II). The crystal packing is different in (I) compared with that in (II). The decrease in the dihedral angle between the planes of the two benzene rings from 69.57 (6) to 50.92 (7)° has obviously reduced the strain on the molecule to some extent. This may be attributed to the substitution of the Cl atoms at the *para*-positions instead of at the *ortho*-positions of the benzene rings.

In (I), the molecular packing in the crystal is stabilized by O—H···N interactions (Table 1 and Fig. 3). The O24—H24···N23($1-x, 1-y, 1-z$) 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(*p*-chlorophenyl)piperidin-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 62%, m.p. 459–461 K).

Crystal data

$C_{19}H_{19}Cl_2N_3O_2$
M_r = 392.27
Monoclinic, $P2_1/n$
a = 12.3909 (9) Å
b = 11.1670 (8) Å
c = 14.1980 (10) Å
β = 100.991 (1)°
V = 1928.5 (2) Å^3
Z = 4
D_x = 1.351 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8354 reflections
θ = 2.3–27.3°
μ = 0.36 mm^{-1}
T = 273 (2) K
Needle, colourless
0.24 × 0.11 × 0.09 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: none
17957 measured reflections
3401 independent reflections
2966 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 25.0°
$h = -14 \rightarrow 14$
$k = -13 \rightarrow 13$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.117$
$S = 1.02$
3401 reflections
238 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0609P)^2 + 0.7529P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.35$ 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	2.12	2.850 (2)	148

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

H atoms were placed in idealized positions, with O—H = 0.82 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, or 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: *WinGX* (Farrugia, 1999).

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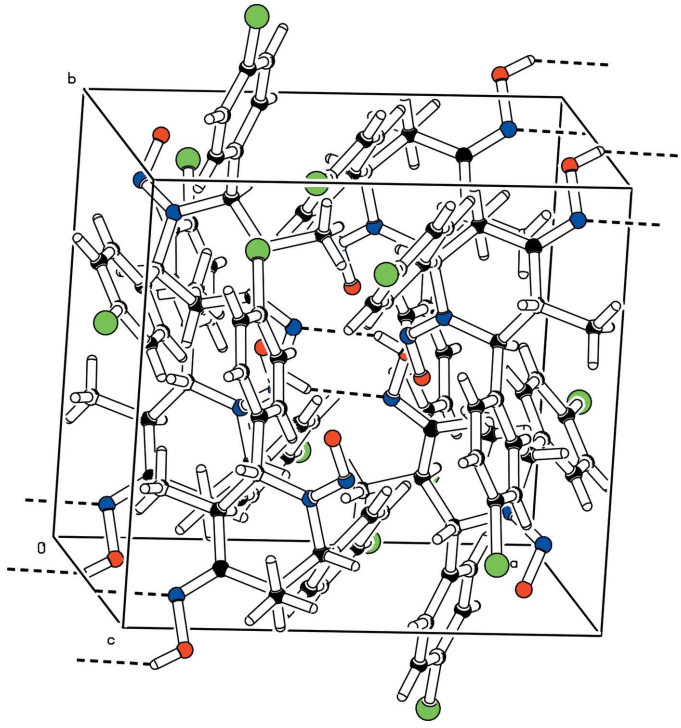

Figure 3
A packing diagram, viewed approximately down the *c* axis, showing the O—H···N hydrogen-bonded (dashed lines) dimers.

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