

2,6-Bis(2-methylphenyl)-1-nitroso-3,5-diphenyl-
piperidin-4-oneJ. Suresh,^a V. P. Alex Raja,^b R. V. Krishnakumar,^c S. Natarajan,^{d*} S. Perumal^b and A. Mostad^e^aDepartment of Physics, The Madura College, Madurai 625 011, India, ^bSchool of Chemistry, Madurai Kamaraj University, Madurai 625 021, India, ^cDepartment of Physics, Thiagarajar College, Madurai 625 009, India, ^dDepartment of Physics, Madurai Kamaraj University, Madurai 625 021, India, and ^eDepartment of Chemistry, University of Oslo, PO Box 1033, Blindern, N-0315 Oslo 3, NorwayCorrespondence e-mail:
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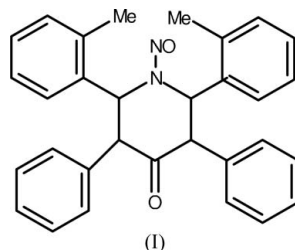
Key indicators

Single-crystal X-ray study
 $T = 105$ K
Mean $\sigma(\text{C}-\text{C}) = 0.001$ Å
 R factor = 0.038
 wR factor = 0.101
Data-to-parameter ratio = 19.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $\text{C}_{31}\text{H}_{28}\text{N}_2\text{O}_2$ the piperidinone ring adopts a twist-boat conformation. A $\text{C}-\text{H}\cdots\text{O}$ hydrogen bond between molecules related through a centre of inversion leads to the formation of dimers. These centrosymmetric dimers have no hydrogen-bond interactions between them and form columns running along the b axis through van der Waals interactions. In addition, a weak $\text{C}-\text{H}\cdots\pi$ interaction involving the 2-methylphenyl ring, with $\text{H}\cdots\pi = 2.64$ Å and an angle of 170° , is observed.

Comment

Precise X-ray crystallographic investigations of the structures of symmetrically shaped molecules are expected to provide insights into the nature and strength of the competition between inter- and intramolecular forces and their role in effecting symmetry carry-over from the free state to the solid. The observed symmetry of a molecule in the solid state is often found to be reduced from that observed in the free state as molecules tend to pack as closely as possible upon crystallization (Kitaigorodskii, 1973). As a consequence, a variety of intermolecular interactions are observed among molecules within the crystal structure. Assuming a direct relationship between the complexity of these interactions and the ratio of the number of acceptors to donors (including weak $\text{C}-\text{H}$ donors, π systems and other types of intermolecular interactions), presumably the mechanism of symmetry carry-over from the free state to the solid might be well understood. In this context, we have undertaken single-crystal X-ray investigations of a series of piperidinone derivatives, and this paper presents a precise description of one such derivative, the title compound, (I). Interestingly, piperidinones belong to an important class of heterocycles, which are found to possess a variety of biological activities including cytotoxic and anti-cancer properties (Dimmock *et al.*, 1990, 2001). Derivatives of piperidinones have also attracted wide attention from chemists and biologists due to their predicted mode of interaction with cellular thiols, with little or no affinity for the hydroxy and amine groups found in nucleic acids (Baluja *et al.*, 1964; Mutus *et al.*, 1989).



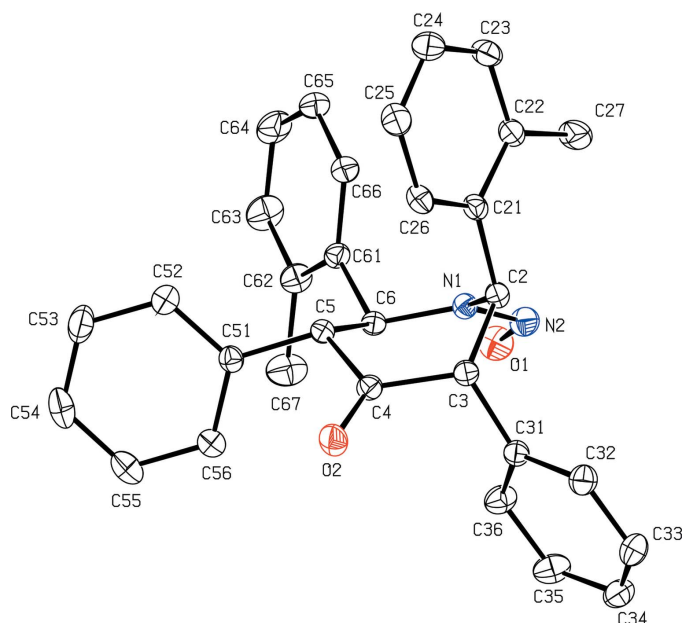


Figure 1

The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

The piperidinone ring (Fig. 1) adopts a twist-boat conformation with atoms C2 and C5 deviating by 0.627 (1) and 0.560 (1) Å, respectively, from the least-squares plane defined by the other atoms (N1, C3, C4 and C6). These values are slightly higher than those observed in the 4-methoxy analogue of (I) (Natarajan *et al.*, 2005) *viz.* 0.592 (2) and 0.492 (2) Å. The twist-boat conformation is also evident from the values observed for the torsion angles of the piperidinone ring (Table 1). The configuration of the aryl rings at the 2- and 3-positions [axial, C21–C2–C3–C31 = 159.65 (8)°] and those at the 5- and 6-positions [equatorial, C51–C5–C6–C61 = –62.28 (10)°] are similar to those observed in the 4-methoxy analogue [67.15 (15) and –155.26 (13)°, respectively]. Least-squares-plane calculations through all of the aryl rings reveal that the dihedral angle between the axially oriented rings at the 2- and 3-positions is 81.9 (1)°, and that between equatorially oriented rings at the 5- and 6-positions is 55.3 (1)°. These values are not far from those observed in the 4-methoxy analogue [78.9 (1) and 50.0 (1)°, respectively]. This result is in accord with the results of ¹H NMR studies of (I) in solution (Alex Raja & Perumal, 2004) and establishes that it adopts the same conformation in both solution and solid state. The nitroso O atom is *syn* to the neighbouring equatorial methylphenyl group at C6 [C6–N1–N2–O1 = –5.77 (12)°] and is comparable to the value of 5.3 (2)° in the 4-methoxy analogue.

Since the ratio of the number of acceptors (carbonyl and nitroso O atoms) to donors (weak aryl C–H) is very small, there is only a C–H···O hydrogen bond between molecules related through a centre of inversion [C26–H26···O2(–x + 2, –y + 1, –z) = 126°], leading to the formation of centrosymmetric dimers (Fig. 2). These centrosymmetric dimers have no hydrogen-bond interactions between them but do form

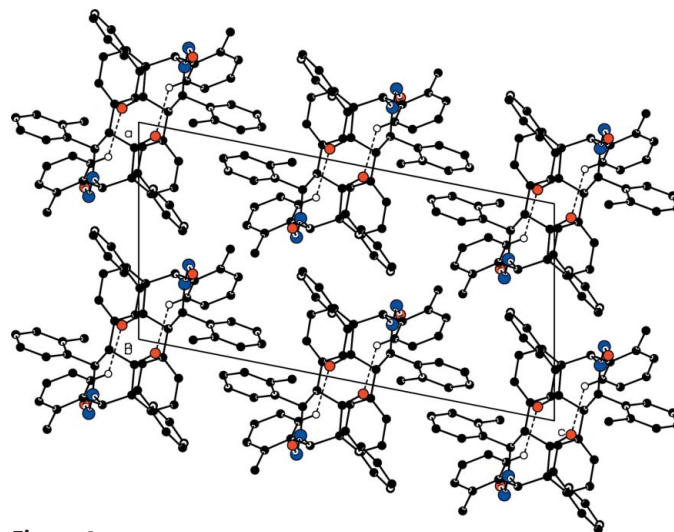


Figure 2

Packing of the molecules of (I) within the unit cell, viewed down the *b* axis. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted.

columns running along the *b* axis through van der Waals interactions. An intramolecular hydrogen bond involving the nitroso O atom as acceptor is observed, in which the 2-substituted methyl C atom is the donor [C67–H67B···O1 = 130.6°; Table 2]. In addition, a weak C33–H33···π interaction involving the 2-methylphenyl ring, with H···π = 2.64 Å and an angle of 170°, is observed. No significant aryl–aryl interactions were observed. Though the unit-cell parameters and the overall geometry of the molecule remain comparable to those observed in the 4-methoxy analogue, the specific interaction pattern and, as a consequence, the molecular aggregation within the crystal structure is different.

Experimental

A mixture of 2,6-bis(2-methylphenyl)-3,5-diphenylpiperidin-4-one (0.75 g, 0.0017 mol) and concentrated HCl (0.4 ml) was dissolved in a 1:1 ethanol–water mixture (20 ml). The temperature of the solution was kept at 338–343 K, and while stirring, a solution of NaNO₂ (0.24 g, 0.003 mol) in a 1:1 ethanol–water mixture (15 ml) was added dropwise over a period of 1 h. The heating and stirring were continued for another 2 h. The reaction mixture was extracted four times with diethyl ether (100 ml) and the extracts were washed with water several times. The combined ether layer was dried over anhydrous sodium bisulfate. After removal of ether, the crude product was recrystallized twice from ethyl acetate to give colourless crystals. Yield 72%, m.p. 495 K.

Crystal data

C₃₁H₂₈N₂O₂
M_r = 460.55
 Monoclinic, *P*2₁/*c*
a = 10.7715 (4) Å
b = 11.0565 (4) Å
c = 20.9841 (7) Å
 β = 101.121 (2)°
V = 2452.17 (15) Å³
Z = 4

D_x = 1.247 Mg m^{–3}
 Mo *K*α radiation
 Cell parameters from 2445 reflections
 θ = 2–20°
 μ = 0.08 mm^{–1}
T = 105 (2) K
 Block, colourless
 0.30 × 0.18 × 0.15 mm

Data collection

Bruker SMART APEX CCD diffractometer	6098 independent reflections
ω scans	5570 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 1998)	$R_{\text{int}} = 0.023$
$T_{\text{min}} = 0.98$, $T_{\text{max}} = 0.99$	$\theta_{\text{max}} = 28.3^\circ$
38278 measured reflections	$h = -14 \rightarrow 14$
	$k = -14 \rightarrow 14$
	$l = -27 \rightarrow 27$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0498P)^2 + 0.9491P]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.101$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.41 \text{ e } \text{\AA}^{-3}$
6098 reflections	$\Delta\rho_{\text{min}} = -0.22 \text{ e } \text{\AA}^{-3}$
318 parameters	
H-atom parameters constrained	

Table 1

Selected torsion angles ($^\circ$).

C2–N1–N2–O1	–169.81 (8)	C2–C3–C4–C5	–6.11 (11)
C6–N1–N2–O1	–5.77 (12)	C3–C4–C5–C6	–43.99 (10)
C6–N1–C2–C3	–51.91 (10)	C2–N1–C6–C5	2.60 (11)
C21–C2–C3–C31	159.65 (8)	C4–C5–C6–N1	45.32 (9)
N1–C2–C3–C4	50.78 (9)	C51–C5–C6–C61	–62.28 (10)

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C67–H67B \cdots O1	0.98	2.70	3.4127 (15)	130
C26–H26 \cdots O2 ⁱ	0.95	2.53	3.1837 (12)	126

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

H atoms were placed at calculated positions and allowed to ride on their carrier atoms with $C-H = 0.95-1.00 \text{ \AA}$ and $U_{\text{iso}} = 1.2U_{\text{eq}}(C)$ for CH_2 and CH groups, and $1.5U_{\text{eq}}$ for CH_3 groups.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97.

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