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2,6-Bis(4-methylphenyl)-1-nitroso-3,5-diphenyl-2,3,5,6-tetrahydropyridin-4(1*H*)-one

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.049
wR factor = 0.152
Data-to-parameter ratio = 15.3

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

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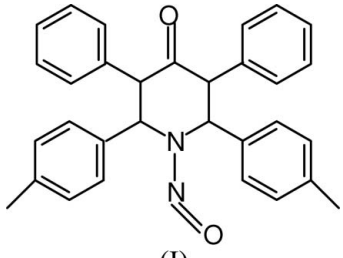
In the title molecule, $C_{31}H_{28}N_2O_2$, the piperidinone ring adopts the usual twist-boat conformation. The aryl rings at positions 2 and 3 are axial and those at positions 5 and 6 are equatorial. In the crystal structure, there are no hydrogen bonds nor are there any significant $\pi\cdots\pi$ stacking interactions and, apart from two weak C—H$\cdots\pi$(arene) interactions, molecules are separated by normal van der Waals distances.

Comment

The piperidine ring is a distinct structural feature of a variety of alkaloid natural products and drug candidates (Watson *et al.*, 2000). Piperidinone derivatives play a variety of biological roles, such as bactericidal, fungicidal and herbicidal (Mobio *et al.*, 1989; Dimmock *et al.*, 1992, 1994; Rameshkumar *et al.*, 2003). Recently, in our laboratory, we have determined the crystal structures of some nitroso-piperidinone derivatives with unsubstituted phenyl rings at the 3 and 5 positions and varying substituents on the phenyl rings at the 2 and 6 positions of the nitroso-piperidinone group, namely 4-methoxy (PIP1; Natarajan *et al.*, 2005), 2-methyl (PIP2; Suresh *et al.*, 2005*a*), 2-methoxy (PIP3; Suresh, Alex Raja, Natarajan *et al.*, 2005) and 2-chloro (PIP4; Suresh *et al.*, 2005*b*). The crystal structure of the title compound, (I), was determined as an extension of our work on the structure–property relationships of nitroso-piperidinone derivatives.



(I)

The molecular structure of (I) is shown in Fig. 1. The piperidinone ring adopts a twist-boat conformation with atoms C2 and C5 deviating by 0.566 (3) and 0.429 (4) Å, respectively, from the least-squares plane defined by N1/C3/C4/C6. The coresponding deviations in PIP2 are 0.627 (1) and 0.560 (1) Å. The twist-boat conformation is also evident from the torsion angles in the piperidinone ring (Table 1). The torsion angle involving atoms C2 and C3 [C21—C2—C3—C31] and atoms C5 and C6 [C51—C5—C6—C61] are similar to those observed in the PIP2 analogue [159.65 (8) and 62.28 (10)°, respectively]. The dihedral angle between the C21–C26 benzene ring and the C31–C36 phenyl ring is

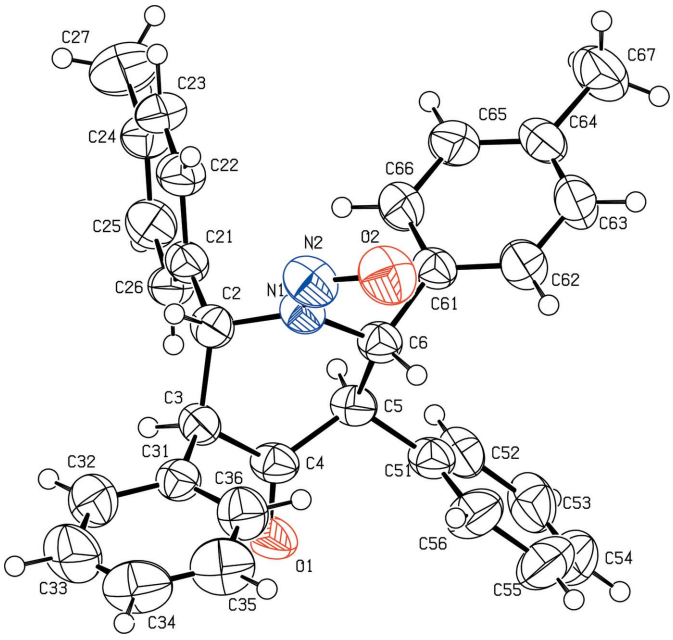


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and H atoms as small spheres.

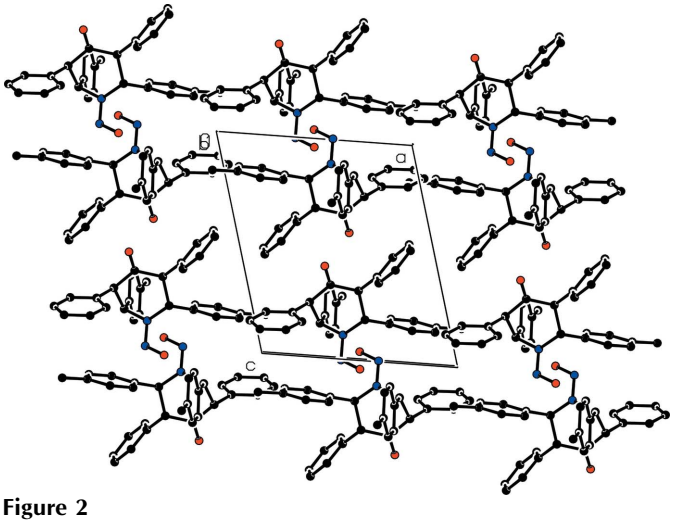


Figure 2
Packing diagram of (I). H atoms have been omitted for clarity.

84.64 (11)°, and that between the C51–C56 and C61–C66 rings is 56.79 (10)°. These values are not dissimilar to those observed in PIP2 [81.9 (1) and 55.3 (1)°, respectively]. The nitroso O atom is *syn* to the neighbouring equatorial methylphenyl group at C6, as evidenced by the O2—N2—N1—C6 torsion angle whose value is comparable to that of 5.77 (12)° in PIP2.

In the crystal structure, except for two weak C—H···π interections (Table 2), there are no hydrogen bonds, nor are there any significant $\pi\cdots\pi$ stacking interactions and molecules are separated by normal van der Waals distances (Fig. 2). In conclusion, changing the position of the methyl group on the phenyl rings compared to PIP2 appears to alter the intermolecular interactions within the crystal structure.

Experimental

A mixture of 2,6-bis(4-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 333–343 K and a solution of $NaNO_2$ (0.24 g, 0.003 mol) in a 1:1 ethanol–water mixture (15 ml) was added dropwise with stirring over a period of 1 h. The heating and stirring were continued for another 2 h. The reaction mixture was extracted 4 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 the ether, the crude product was recrystallized twice from ethyl acetate to give colourless crystals (yield 72%, m.p. 467 K).

Crystal data

$C_{31}H_{28}N_2O_2$
M_r = 460.55
Triclinic, $P\overline{1}$
a = 10.4373 (13) Å
b = 12.0428 (13) Å
c = 12.6808 (14) Å
α = 67.947 (12)°
β = 71.053 (9)°
γ = 78.081 (12)°
V = 1390.7 (3) Å^3
Z = 2
D_x = 1.100 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.07 mm^{-1}
T = 293 (2) K
Block, colourless
0.26 × 0.18 × 0.12 mm

Data collection

Nonius MACH3 four-circle diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.985, T_{max} = 0.992
5778 measured reflections
4893 independent reflections
2525 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 25.0°
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.152
S = 1.00
4893 reflections
319 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0769P)^2 + 0.0251P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ <0.001
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.024 (3)

Table 1
Selected torsion angles (°).

C21—C2—C3—C31	149.3 (2)	C6—C5—C4—C3	−37.0 (3)
N1—C2—C3—C4	44.1 (3)	O2—N2—N1—C2	−175.7 (2)
C61—C6—C5—C51	−71.9 (3)	O2—N2—N1—C6	−5.0 (3)
N1—C6—C5—C4	32.8 (3)	C3—C2—N1—C6	−51.4 (3)
C2—C3—C4—C5	−3.4 (3)	C5—C6—N1—C2	11.9 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
C66—H66···*Cg*	0.93	2.69	3.613 (4)	169
C67—H67*A*···*Cg*^{i}	0.96	2.72	3.608 (4)	153

Symmetry code: (i) $x+1, y, z$. *Cg* is the centroid of the C21–C26 ring.

H atoms were placed in calculated positions, with C—H = 0.93–0.98 Å, and refined using the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$ for CH_2 and CH groups, and $1.5U_{eq}$ for CH_3 groups. During the refinement of the structure, electron density peaks were located, close to inversion centers, that were believed to be highly disordered solvent molecules, possibly ethyl acetate and/or diethyl ether. Attempts to model the solvent molecules were not successful. The SQUEEZE option in *PLATON* (Spek, 2003) indicated there to be a solvent cavity of volume 214.1 Å^3 containing approximately 31 electrons. In the final cycles of refinement, this contribution to the electron density was removed from the observed data. The density, the *F*(000) value, the molecular weight and the formula are given without taking into account the results obtained with SQUEEZE. Similar treatments of disordered solvent molecules have been carried out by Stähler *et al.* (2001), Cox *et al.* (2003), Mohamed *et al.* (2003) and Athimoolam *et al.* (2005).

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius,1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1996); 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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