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2-Nitroso-1,3-diphenyl-1,2,3,4-tetrahydrobenzo[*b*][1,6]naphthyridine

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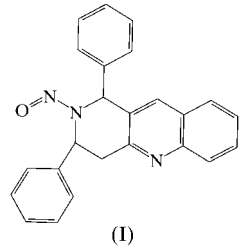
The title compound, $C_{24}H_{19}N_3O$, crystallizes in the centrosymmetric space group $P2_1/a$ with one molecule in the asymmetric unit. The tetrahydropyridine ring has a boat conformation. The dihedral angle between the fused pyridine rings is 16.2 (1)°. The equatorial and axial orientations of the two phenyl groups with respect to the tetrahydropyridine ring are confirmed. The nitroso group is coplanar with the attached C—N—C group. The interplanar angle formed between the fused tetrahydropyridine and benzene planes is 13.4 (1)°. The crystal packing is stabilized by an intermolecular C—H···O hydrogen bond, which forms a *C*(9) graph-set chain running along the [001] direction.

Comment

Nitrosamines are known to have carcinogenic properties (Magee *et al.*, 1976; Ferguson, 1975). Ever since the first demonstration of carcinogenicity in *N*-nitroso compounds (Magee & Barnes, 1956), there have been extensive biochemical and physicochemical studies on their structure–activity relationships (Lijinsky, 1984; Magee *et al.*, 1976). However, there is little information on the detailed geometries of *N*-nitroso compounds, although several solution NMR spectroscopic investigations have been carried out (Fraser & Grindley, 1975; Forrest *et al.*, 1974; Ellis *et al.*, 1974; Priya *et al.*, 1992). Certain *N*-nitrosoureas are used as antitumour agents and antibiotics (Sapse *et al.*, 1988).

1,6-Naphthyridines have extensive pharmacological properties. These derivatives have anti-inflammatory (Di Braccio *et al.*, 1997), antibacterial (Hong *et al.*, 1997), antitumour (Chen *et al.*, 1997), cardiotonic (Mohan & Mishra, 1997), and anticonvulsant and insecticidal (Damon & Nadelson, 1981) properties. They exhibit unique photophysical, photochemical and optical properties due to the charge-transfer interaction between the donor and acceptor substituents. They can behave as non-linear optical materials, which have various applications in the field of telecommunications (Murugan, 1997). In addition, 1,6-naphthyridine derivatives are also used as novel potent adenosine 3′,5′-cyclic phosphate phosphodiesterase III inhibitors (Singh *et al.*, 1995).

We have undertaken the synthesis and structural analysis of a series of cyclic nitrosamines (Senthilkumar *et al.*, 1992, 1995; Ravinderan *et al.*, 1992; Priya *et al.*, 1992). The 1,6-naphthyridine system is known (Reed *et al.*, 1988; Vinick, 1989), but only limited structural data have been reported to date (Balogh *et al.*, 1986; Goméz de Andérez *et al.*, 1992; Govindasamy *et al.*, 2000). Against this background, and in order to obtain detailed information about stereochemical and conformational changes induced by the substituents on the title compound, (I), in the solid state, its X-ray structure determination has been carried out and the results are presented here.



(I)

Fig. 1 shows a view of (I) with the atom-numbering scheme. The N2—N3 and N3═O bond lengths and N2—N3—O bond angle are comparable with the previously reported values of 1.331 (2) Å, 1.231 (2) Å and 115.3 (1)°, respectively (Priya *et al.*, 1992). The N2—N3 bond exhibits partial double-bond character, which leads to restricted rotation about the bond, as was also found from solution NMR studies (Cooney & Brownstein, 1974). The N—C distances in (I) agree well with the literature values (Allen *et al.*, 1987).

The nitroso group of (I) has a coplanar orientation with respect to atoms C2 and C3, as is evident from the C3—N2—N3—O and C2—N2—N3—O torsion angles, respectively. The C11—C1—C2—C19 torsion angle shows that the phenyl ring

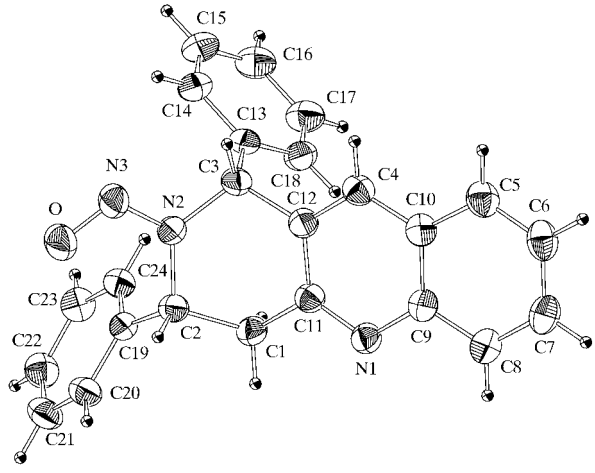


Figure 1
The molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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attached at C2 is equatorially disposed relative to the naphthyridine system, while the C11—C12—C3—C13 torsion angle shows that the phenyl group attached at C3 is axially oriented relative to the naphthyridine system. A similar effect has also been observed by Laavanya *et al.* (2001). The dihedral angle between the fused pyridine rings is 16.2 (1)°. The interplanar angle formed between the fused tetrahydropyridine and benzene planes is 13.4 (1)°. The angle between the planes of the C13–C18 and C19–C24 phenyl rings is 88.9 (1)°.

The substitution of a methyl or nitroso group at the N2 position has been shown to exert a significant influence on the conformation of the ring and the orientation of the ring substituents (Vierhapper, 1980; Baliah & Natarajan, 1989). The tetrahydropyridine ring of (I) has a boat conformation, with a total puckering amplitude (Cremer & Pople, 1975) of Q_T = 0.520 (2) Å and values for the lowest displacement asymmetry parameters (Nardelli, 1983) of Δ_S(C1) = 0.015 (1) and Δ_S(N2—C2) = 0.019 (1).

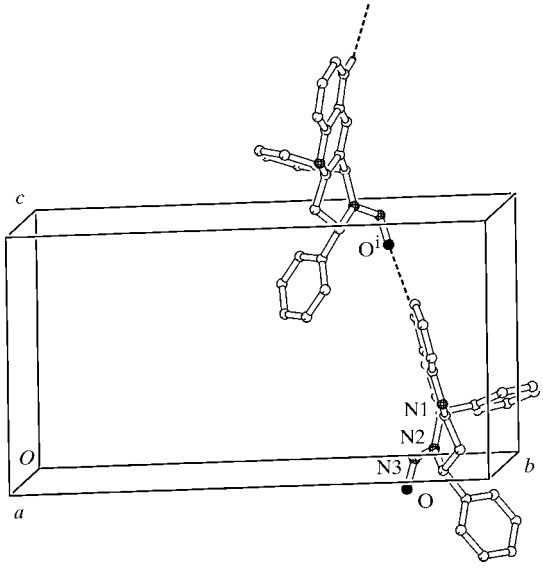

Figure 2
Part of the crystal structure of (I), with the dashed line indicating a hydrogen bond. [Symmetry code: (i) $x+\frac{1}{2}, \frac{3}{2}-y, 1+z$.]

In addition to van der Waals interactions, the crystal packing of (I) is stabilized by a C—H···O intermolecular hydrogen bond, with C5—H5 = 0.93, H5—O^{i} = 2.47 and C5···O^{i} = 3.179 (3) Å, and C5—H5···O^{i} = 133° [symmetry code: (i) $x+\frac{1}{2}, \frac{3}{2}-y, 1+z$]. This intermolecular hydrogen bond forms a $C(9)$ (Bernstein *et al.*, 1995) graph-set chain, *viz.* O—N3—N2—C3—C12—C4—C10—C5—H5, running along the [001] direction (Fig. 2).

Experimental

The title compound was obtained by the nitrosation of the corresponding amine with $NaNO_2$/HCl in ethanol. Diffraction quality crystals of (I) were obtained by recrystallization from ethanol. The parent amine, 1,3-diphenyl-1,2,3,4-tetrahydrobenzo[*b*][1,6]naphthyridine, was obtained as a non-crystalline product by the action of NaN_3/H_2SO_4 on 2,4,6,8-tetraphenyl-3,7-diazabicyclo[3.3.1]nonan-9-one (Sivakumar, 2000).

Compound (I)

Crystal data

$C_{24}H_{19}N_3O$
M_r = 365.42
Monoclinic, $P2_1/a$
a = 9.713 (6) Å
b = 19.265 (8) Å
c = 10.450 (2) Å
β = 105.74 (3)°
V = 1882.1 (14) Å^3
Z = 4
D_x = 1.290 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 4.4–68.0°
μ = 0.64 mm^{-1}
T = 293 (2) K
Plate, pale yellow
0.20 × 0.20 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
3876 measured reflections
3435 independent reflections
2660 reflections with $I > 2\sigma(I)$
R_{int} = 0.052
θ_{max} = 68°
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 23$
$l = -12 \rightarrow 12$
3 standard reflections
every 100 reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.172
S = 1.07
3435 reflections
253 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1135P)^2 + 0.1670P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

O—N3	1.233 (2)	N2—C3	1.484 (2)
N1—C11	1.315 (3)	C1—C11	1.497 (3)
N1—C9	1.373 (2)	C2—C19	1.512 (3)
N2—N3	1.321 (2)	C3—C13	1.524 (3)
N2—C2	1.479 (2)		
N3—N2—C2	121.6 (2)	N2—C3—C12	110.1 (2)
N3—N2—C3	113.4 (2)	N2—C3—C13	111.6 (2)
O—N3—N2	114.4 (2)		
C2—N2—N3—O	−5.0 (3)	C1—C11—C12—C3	4.1 (3)
C3—N2—N3—O	−176.1 (2)	C13—C3—C12—C11	−93.8 (2)
C11—C1—C2—C19	163.6 (2)	C1—C2—C19—C24	−78.4 (2)
N1—C11—C12—C4	1.1 (3)		

All H atoms were fixed geometrically and allowed to ride on their parent atoms, with C—H distances in the range 0.86–0.96 Å, and U_{iso}(H) values of 1.5$_{eq}$(C) for methyl H atoms and 1.2U_{eq}(C) for the other H atoms.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1997) and *PLATON* (Spek, 2000); software used to prepare material for publication: *SHELX*97 and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1587). Services for accessing these data are described at the back of the journal.

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