

6-(4-Methoxyphenyl)-4-phenyl-2-(pyrrolidin-1-yl)-nicotinonitrile

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$

R factor = 0.064

wR factor = 0.177

Data-to-parameter ratio = 17.7

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

The pyrrolidine ring in the title molecule, $\text{C}_{23}\text{H}_{21}\text{N}_3\text{O}$, adopts a half-chair conformation. In the solid state, $\text{C}-\text{H}\cdots\text{N}$ intermolecular hydrogen bonds link inversion-related molecules, forming cyclic dimers. The structure is further stabilized by weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds and van der Waals forces.

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Comment

Nicotine derivatives have a wide range of biological applications. Niacin is a vitamin that contains nicotinamide, deficiency of which makes the body lose copper, thereby giving rise to the pellagra disease (Hökelek & Necefouglu, 1999). The nicotinic acid derivative *N,N*-diethylnicotinamide, which is commonly known as DENA, has a respiratory stimulating property (Hökelek & Necefouglu, 1996). The redox pair NAD^+ (nicotinamide adenine dinucleotide) molecule, which is the oxidized form of the coenzyme NADH, plays a key role in energy-producing processes (Stryer, 1988) and in the redox processes catalysed by various protein families, the dehydrogenases being the largest group (Guillot *et al.*, 2000). Against this background and in order to obtain detailed information on the molecular conformation in the solid state, the X-ray study of the title compound, (I), was carried out and the results are presented here.

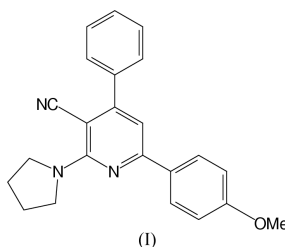


Fig. 1 shows the molecular structure of (I), with 30% probability displacement ellipsoids and the atom-numbering scheme. The values of the $\text{N}sp^2-\text{C}sp^2$ bond distances, $\text{N1}-\text{C6}$ [1.342 (2) Å] and $\text{N1}-\text{C2}$ [1.345 (2) Å], agree well with reported values (Leban *et al.*, 1996; Hökelek & Necefouglu, 1996). The $\text{C3}-\text{C2}-\text{N2}$ angle [122.6 (2)°] is wider than the $\text{N1}-\text{C2}-\text{N2}$ angle [116.6 (2)°], as a result of the repulsive force exerted by the nitrile group on the pyrrolidine ring. The widening of the exocyclic angle $\text{C5}-\text{C6}-\text{C18}$ [122.2 (2)°] compared with $\text{N1}-\text{C6}-\text{C18}$ [115.7 (2)°] might be a consequence of steric repulsion between atoms H5 and H19 ($\text{H5}\cdots\text{H19} = 2.22\text{ \AA}$). The sum of the angles around N2 [356.5 (2)°] indicates an sp^2 hybridization for this atom. The pyrrolidine ring adopts a half-chair conformation, with asymmetry parameter $\Delta\text{C}_2(\text{N2}) = 0.005$ (1) (Nardelli, 1983).

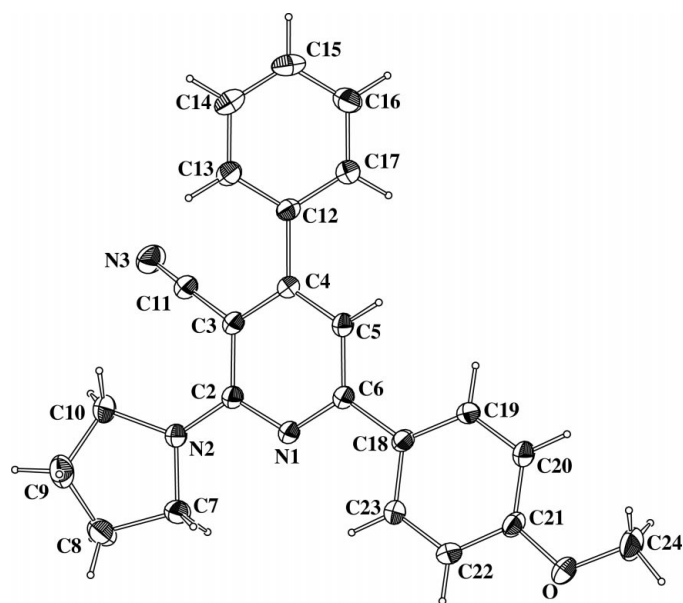


Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids.

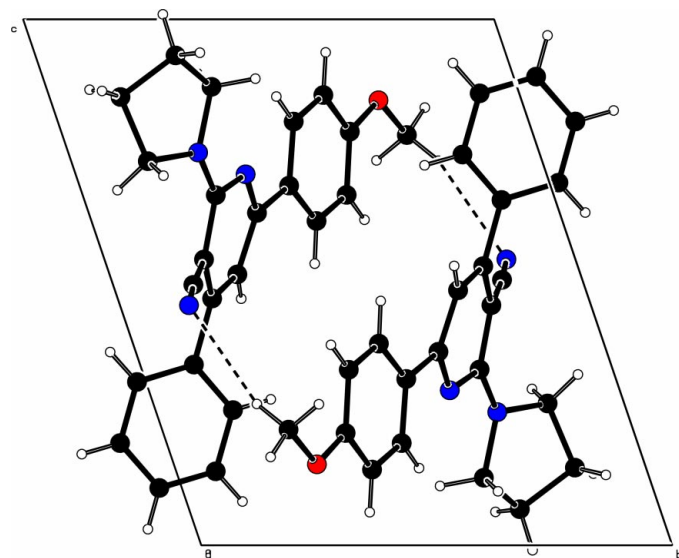


Figure 2
A view of the C—H...N hydrogen-bonded dimer of (I).

The pyridine ring is planar, with a maximum deviation of 0.070 (2) Å for C2, and it forms a dihedral angle of 31.20 (7)° with the mean plane through the pyrrolidine ring. The dihedral angle between the pyridine and phenyl ring planes is 43.41 (6)°. The dihedral angle between the planes passing through the pyridine and methoxyphenyl rings [14.7 (1)°] is slightly larger than that reported [9.04 (6)°] for a related structure (Fun *et al.*, 1996). The methoxy group is coplanar with the attached phenyl ring. In the crystal, inversion-related molecules exist as C—H...N hydrogen-bonded dimers, *i.e.* the molecules form a cyclic dimer (Table 2) with graph-set descriptor $R_2^2(26)$ (Bernstein *et al.*, 1995). The ring for $R_2^2(26)$ is N3ⁱ—C11ⁱ—C3ⁱ—C4ⁱ—C5ⁱ—C6ⁱ—C18ⁱ—C19ⁱ—C20ⁱ—

C21ⁱ—Oⁱ—C24ⁱ—H24Cⁱ—N3—C11—C3—C4—C5—C6—C18—C19—C20—C21—O—C24—H24C [symmetry code: (i) $-x, 1-y, 1-z$] (Fig. 2). The dimers are linked by weak C15—H15...Oⁱⁱ [symmetry code: (ii) $x, y-1, z-1$] hydrogen bonds, to form infinite one-dimensional chains. The crystal structure is further stabilized by van der Waals forces.

Experimental

To a refluxing solution of 4-methoxybenzoylacetophenone (1.8 mmol) in ethanol (10 ml), malononitrile (1.8 mmol) and pyrrolidine (1.8 mmol) were added, and the resulting solution was refluxed for 9 h. The solvent was distilled off under reduced pressure and the resulting residue was purified by column chromatography using silica-gel eluent (100–200 mesh). Single crystals were obtained by slow evaporation using a petroleum ether–ethyl acetate (1:3) solvent system.

Crystal data

C₂₃H₂₁N₃O
M_r = 355.43
 Triclinic, *P* $\bar{1}$
a = 7.9336 (5) Å
b = 10.3841 (6) Å
c = 12.4407 (7) Å
 α = 105.158 (1)°
 β = 104.077 (1)°
 γ = 100.400 (1)°
V = 926.35 (9) Å³

Z = 2
D_x = 1.274 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 3290 reflections
 θ = 1.8–28.3°
 μ = 0.08 mm⁻¹
T = 293 (2) K
 Plate, pale yellow
 0.42 × 0.20 × 0.16 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 6584 measured reflections
 4310 independent reflections
 2663 reflections with $I > 2\sigma(I)$

*R*_{int} = 0.047
 θ_{\max} = 28.3°
 h = -9 → 10
 k = -13 → 11
 l = -16 → 15

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.064$
 $wR(F^2) = 0.177$
 $S = 0.94$
 4310 reflections

244 parameters
 H-atom parameters constrained
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.28 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.30 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

N1—C6	1.342 (2)	N1—C2	1.345 (2)
C2—N2—C10	124.31 (16)	N2—C2—C3	122.59 (17)
C2—N2—C7	120.85 (16)	N1—C6—C18	115.73 (16)
C10—N2—C7	111.43 (15)	C5—C6—C18	122.21 (17)
N1—C2—N2	116.61 (16)		

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C23—H23...N1	0.93	2.46	2.780 (3)	100
C24—H24C...N3 ⁱ	0.96	2.61	3.511 (4)	156
C15—H15...O ⁱⁱ	0.93	2.64	3.498 (2)	153

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $x, y-1, z-1$.

The H atoms were fixed geometrically and allowed to ride on the attached non-H atoms, with C–H distances of 0.93, 0.96 or 0.97 Å, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2U_{\text{eq}}(\text{C})$ for all other atoms. The data coverage was only 94% complete, owing to the poor diffraction quality of the crystal.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1997); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

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