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6-(4-Chlorophenyl)-4-[4-(dimethylamino)-phenyl]-2-(pyrrolidin-1-yl)nicotinonitrile

S. Thinagar,[a]* D. Velmurugan,[a] S. Shanmuga Sundara Raj,[b] Hoong-Kun Fun[b] and V. Raghukumar[c]

[a]Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Chennai 600 025, India, [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [c]Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, India

Correspondence e-mail: d velu@yahoo.com

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.054
wR factor = 0.160
Data-to-parameter ratio = 18.2

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

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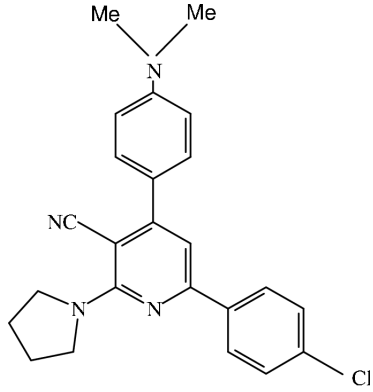
The title compound, $C_{24}H_{23}ClN_4$, crystallizes in space group $P\overline{1}$, with two crystallographically independent molecules in the asymmetric unit. In both molecules, the pyrrolidine ring adopts a half-chair conformation. The molecular packing in the crystal is stabilized by intermolecular C—H···N hydrogen bonds, through the formation of hydrogen-bonded molecular chains.

Comment

Nicotine-containing compounds show interesting biological properties. The nicotinic acid derivative *N,N*-diethylnicotinamide, which is commonly known as DENA, has a respiratory stimulating property (Hökelek & Necefouglu, 1996). 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 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). The X-ray investigation of the title compound, (I), was taken up as a part of our study of the structures of nicotine derivatives.



(I)

The asymmetric unit of the title compound, (I), contains two molecules; the corresponding bond lengths and angles of these two molecules agree with each other, except for some differences in $Csp^3—Csp^3$ distances in the pyrrolidine ring. A molecular fit for these two molecules shows a weighted r.m.s. deviation of 0.52 Å. The geometry of the two molecules differ slightly in the orientations of the dimethylaminophenyl ring and the nitrile group with respect to the pyridine ring. The N2—C2—C3 angles [124.2 (2) and 124.6 (2)°] are wider than the N1—C2—N2 angles [114.8 (1) and 114.7 (2)°], as a result of the repulsive force exerted by the nitrile group on the

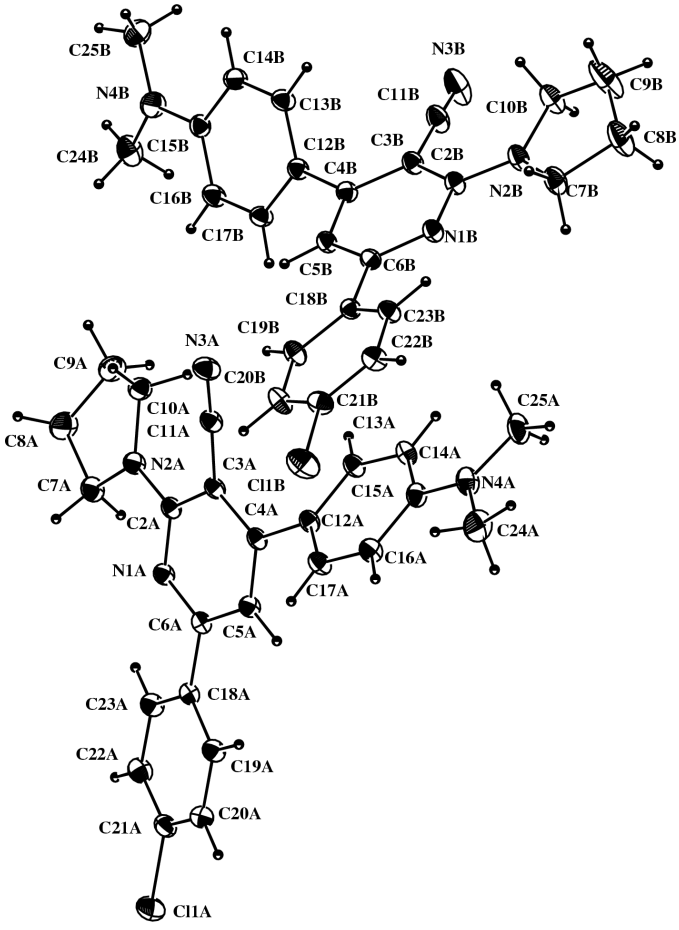


Figure 1
View of the two independent molecules of the title compound, showing 30% probability displacement ellipsoids and the atom-numbering scheme for the non-H atoms.

pyrrolidine ring. Also, as a result of steric repulsion between atoms H5 and H19 (H5···H19 = 2.18 Å each), the exocyclic angles C5—C6—C18 [122.9 (2) and 122.4 (2)°] are wider compared with N1—C6—C18 [115.0 (1) and 115.0 (1)°]. Similar distortions in the bond angles have been reported previously for a related structure (Thinagar *et al.*, 2002). The pyrrolidine rings of both molecules adopt half-chair conformations, with ΔC^2(N2) values of 0.012 (1) and 0.002 (1) (Nardelli, 1983), and the mean planes through them form dihedral angles of 18.4 (1) and 13.1 (1)° with the respective pyridine rings. The twisting of the chlorophenyl ring from the pyridine ring is less [12.83 (9) and 14.36 (9)°] compared to that of the other phenyl ring [43.14 (9) and 49.36 (9)°].

In the asymmetric unit, the two crystallographically independent molecules are linked by C19*B*—H19*B*···N3*A* hydrogen bonds. These pairs, translated one unit along the *b* axis, are linked by C19*A*—H19*A*···N3*B* hydrogen bonds, to form an infinite one-dimensional molecular chain (Table 2). The molecules of these chains are interlinked to those in the adjacent inversion-related chain by C24*B*—H24*F*···N3*A*($1-x$, $1-y$, $1-z$) hydrogen bonds, to form double-chain structures.

Experimental

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

Crystal data

$C_{24}H_{23}ClN_4$	$Z = 4$
$M_r = 402.91$	$D_x = 1.276$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 11.1490$ (1) Å	Cell parameters from 7711 reflections
$b = 13.7330$ (1) Å	$\theta = 1.4$–$28.3°$
$c = 14.6666$ (1) Å	$\mu = 0.20$ mm^{-1}
$\alpha = 100.487$ (1)°	$T = 293$ (2) K
$\beta = 93.240$ (1)°	Block, yellow
$\gamma = 107.014$ (1)°	0.48 × 0.44 × 0.26 mm
$V = 2096.93$ (2) Å^3	

Data collection

Siemens SMART CCD area-detector diffractometer	6307 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.048$
ω scans	$\theta_{max} = 28.3°$
Absorption correction: none	$h = -13 \rightarrow 14$
14581 measured reflections	$k = -17 \rightarrow 14$
9579 independent reflections	$l = -12 \rightarrow 19$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.054$	$w = 1/[\sigma^2(F_o^2) + (0.0793P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.160$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.97$	$\Delta\rho_{max} = 0.35$ e Å^{-3}
9579 reflections	$\Delta\rho_{min} = -0.32$ e Å^{-3}
527 parameters	

Table 1
Selected geometric parameters (Å, °).

N2*A*—C2*A*	1.355 (2)	N2*B*—C7*B*	1.476 (2)
N2*A*—C10*A*	1.454 (2)	N4*B*—C15*B*	1.386 (2)
N2*A*—C7*A*	1.470 (2)	N4*B*—C25*B*	1.436 (3)
N4*A*—C15*A*	1.375 (2)	N4*B*—C24*B*	1.439 (3)
N4*A*—C24*A*	1.445 (3)	C7*B*—C8*B*	1.511 (3)
N4*A*—C25*A*	1.447 (3)	C8*B*—C9*B*	1.416 (4)
N2*B*—C2*B*	1.354 (2)	C9*B*—C10*B*	1.516 (3)
N2*B*—C10*B*	1.455 (2)		
N1*A*—C2*A*—N2*A*	114.81 (14)	N1*B*—C2*B*—N2*B*	114.66 (15)
N2*A*—C2*A*—C3*A*	124.19 (16)	N2*B*—C2*B*—C3*B*	124.62 (16)
N1*A*—C6*A*—C18*A*	114.99 (14)	N1*B*—C6*B*—C18*B*	115.00 (14)
C5*A*—C6*A*—C18*A*	122.89 (15)	C5*B*—C6*B*—C18*B*	122.37 (15)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C19*B*—H19*B*···N3*A*	0.93	2.55	3.461 (3)	167
C19*A*—H19*A*···N3*B*^{i}	0.93	2.47	3.378 (3)	164
C24*B*—H24*F*···N3*A*^{ii}	0.96	2.59	3.457 (3)	150
C23*A*—H23*A*···N1*A*	0.93	2.42	2.755 (2)	101
C23*B*—H23*B*···N1*B*	0.93	2.41	2.745 (3)	101

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

All the H atoms were fixed geometrically and allowed to ride on the corresponding non-H atoms, with C—H distances of 0.93–0.97 Å, and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms and $1.2U_{eq}(C)$ for all other H atoms. Rotating-group refinement was used for the methyl H atoms. Large displacement parameters for atom C9*B* indicate the possibility of conformational disorder for the pyrrolidine ring. This resulted in a shortening of the C8*B*—C9*B* [1.416 (4) Å] bond. Attempts to refine the structure using a disorder model for the pyrrolidine ring resulted in unrealistic Csp^3—Csp^3 distances and hence the original model was retained.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; 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); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1983, 1995).

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