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5-Amino-4-(4-methoxyphenyl)-2-phenyl-7-(pyrrolidin-1-yl)-1,6-naphthyridine-8-carbonitrile

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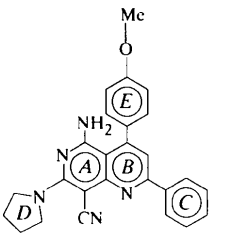
Abstract

In the crystal of the title compound, $C_{26}H_{23}N_5O$, there are two independent molecules in the asymmetric unit. The naphthyridine moiety in both molecules is slightly folded. The dihedral angles between the fused pyridine rings in the molecules are 5.7 (1) and 8.2 (1)°, respectively. The pyrrolidine ring in both molecules adopts a half-chair conformation. The molecular structure is stabilized by a C—H···N-type intramolecular hydrogen bond within the two molecules in the asymmetric unit and the packing is stabilized by intermolecular N—H···O hydrogen bonds.

Comment

As a part of our ongoing X-ray crystal structure analysis of some compounds of biological and photochemical interest and to give the structural basis for a better understanding of the effect of structural and conformational change on biological activity, the structure determination of the title compound, (I), was undertaken. Naphthyridine derivatives have a wide range of biological activities such as anti-inflammatory, anticonvulsant (Balogh *et al.*, 1986), insecticidal (Takeuchi & Hamada, 1975) and antibacterial (Datta *et al.*, 1995). The naphthyridine derivatives also act as a dye (Irikawa & Iijima, 1998). Since naphthyridine derivatives come under the class of heterocyclic compounds, it is expected that they possess laser and non-linear optical properties (Lowe, 1984; Shanmugasundaram *et al.*, 1993; Murugan *et al.*, 1998).



(I)

The bond lengths and bond angles agree with each other in both molecules. The average value of the C—C distances in the phenyl rings of molecules *A* and *B*

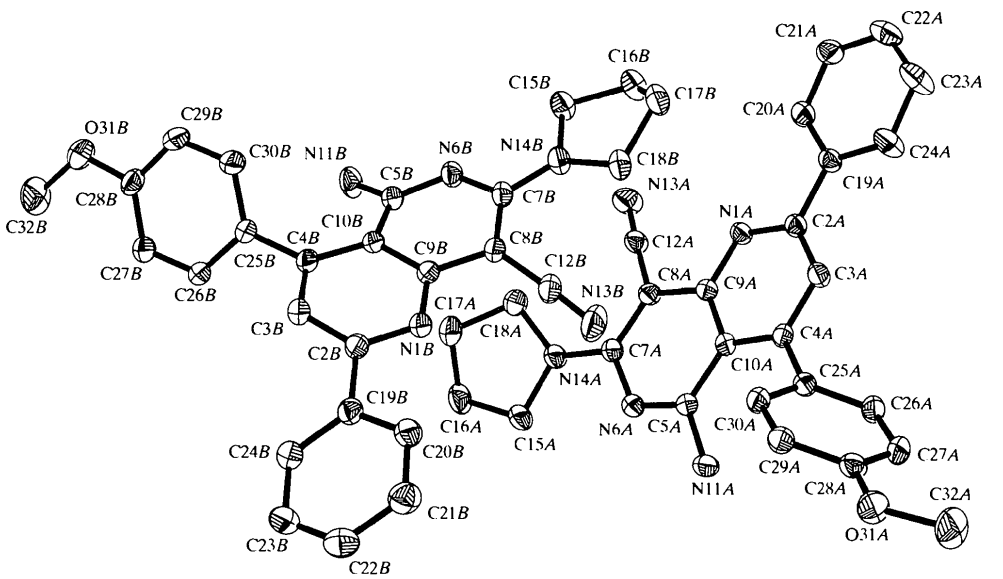


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids (*XP* in *SHELXTL*; Sheldrick, 1997) and the atom-numbering scheme.

are 1.386 (3) and 1.384 (3) Å, respectively, and the N—C distances in both molecules are comparable with the related structures previously studied (Gómez de Andérez *et al.*, 1992). The bond distances C5—N11 in both molecules are shorter than the typical C—N single bond distance (1.47 Å) indicating conjugation of the amino group. Similarly, the bond distance C8—C12 in both molecules is shorter than the typical C—C single bond distance (1.53 Å) as a consequence of conjugation of the C12—N13 nitrile group with the aromatic system of naphthyridine. The naphthyridine ring in both molecules is slightly folded with a dihedral angle between the fused pyridine rings (rings *A* and *B*) of 5.7 (1) for molecule *A* and 8.2 (1)° for molecule *B*.

The least-squares planes through the phenyl rings make dihedral angles of 7.1 (1) (ring *C*) and 59.2 (1)° (ring *E*) with ring *B* in molecule *A*; for molecule *B* the corresponding dihedral angles are 21.7 (1) and 53.8 (1)°, respectively. The total puckering amplitude Q_T (Cremer & Pople, 1975) of the pyrrolidine rings is 0.385 (3) and 0.351 (3) Å in molecules *A* and *B*, respectively, and the asymmetry parameter (Nardelli, 1983) ΔC_2(N14) = 0.013 (1), equal in both rings, reveals a half-chair conformation. The best plane through the pyrrolidine ring makes a dihedral angle with the pyridine ring *A* of 30.1 (1) and 21.1 (1)° in molecule *A* and *B*, respectively. The sums of the bond angles around N14, 357.4 (3) and 358.8 (3)° in molecules *A* and *B* respectively, indicate sp^2 hybridization.

N11 deviates significantly from the least-squares plane through the pyridine ring to which it is attached and its deviation is −0.183 (2) for molecule *A* and −0.381 (2) Å for molecule *B*. The methoxy group in molecule *A* is twisted through 8.2 (3)° but in molecule *B* it is coplanar [C27—C28—O31—C32 = 1.4 (4)°] to the attached phenyl ring.

Apart from the normal van der Waals interactions, the molecular structure is stabilized by an intramolecular C—H···N-type hydrogen bond and molecular packing by an intermolecular N—H···O-type hydrogen bond (Table 2); N11*B*—H11*C*···O31*B*($2-x$, $2-y$, $-z$) = 126°.

Experimental

A solution of 4-methoxybenzalacetophenone (2.4 mmol), malononitrile (4.8 mmol) and pyrrolidine (4.8 mmol) in ethanol (20 ml) was refluxed for 25 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography. The solid thus obtained was recrystallized from a methanol–chloroform (1:1) solution after slow evaporation.

Crystal data

$C_{26}H_{23}N_5O$
M_r = 421.49
Triclinic
$P\bar{1}$
a = 9.6808 (1) Å
b = 11.4468 (2) Å
c = 19.8557 (1) Å
α = 100.047 (1)°
β = 95.804 (1)°
γ = 90.318 (1)°
V = 2154.84 (5) Å^3
Z = 4
D_x = 1.299 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 6064 reflections
θ = 2.75–33.16°
μ = 0.082 mm^{-1}
T = 293 (2) K
Block
0.52 × 0.48 × 0.20 mm
Yellow

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: none
13 995 measured reflections
9533 independent reflections
6085 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 27.5°
$h = -12 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = 0 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.160
S = 1.084
9533 reflections
577 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2 + 0.6740P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.205 e Å^{-3}
$\Delta\rho_{min}$ = −0.262 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1*A*—C2*A*	1.328 (3)	N1*B*—C2*B*	1.326 (3)
N1*A*—C9*A*	1.359 (3)	N1*B*—C9*B*	1.355 (3)
C3*A*—C4*A*	1.385 (3)	C3*B*—C4*B*	1.379 (3)
C5*A*—N6*A*	1.319 (3)	C5*B*—N6*B*	1.327 (3)
C5*A*—N11*A*	1.357 (3)	C5*B*—N11*B*	1.348 (3)
N6*A*—C7*A*	1.359 (3)	N6*B*—C7*B*	1.359 (3)
C7*A*—N14*A*	1.354 (3)	C7*B*—N14*B*	1.349 (3)
N14*A*—C18*A*	1.466 (3)	N14*B*—C18*B*	1.468 (3)
N14*A*—C15*A*	1.475 (3)	N14*B*—C15*B*	1.469 (3)
C2*A*—N1*A*—C9*A*	118.6 (2)	C2*B*—N1*B*—C9*B*	118.6 (2)
C7*A*—N14*A*—C18*A*	124.1 (2)	C7*B*—N14*B*—C18*B*	124.5 (2)
C7*A*—N14*A*—C15*A*	121.8 (2)	C7*B*—N14*B*—C15*B*	122.3 (2)
C18*A*—N14*A*—C15*A*	111.5 (2)	C18*B*—N14*B*—C15*B*	112.0 (2)
C28*A*—O31*A*—C32*A*	117.6 (2)	C28*B*—O31*B*—C32*B*	118.3 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C30*A*—H30*A*···N13*B*	0.93	2.57	3.492 (3)	170
N11*B*—H11*C*···O31*B*^{i}	0.86	2.49	3.076 (3)	126

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

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *XP* in *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1423). Services for accessing these data are described at the back of the journal.

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N-(4-Chloro-2-iodophenyl)-*N*-methylcinnamamide

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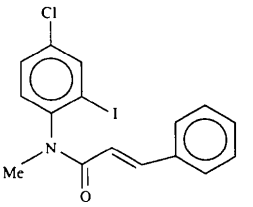
Abstract

In the title compound, $C_{16}H_{13}ClINO$, the cinnamamide group is almost planar. The phenyl rings are almost perpendicular, making an interplanar angle of 83.1 (1)° with one another. The molecules are packed as dimers through C—H···O hydrogen bonds.

Comment

We are interested in the synthetic potential of the title compound, (I), and of other acyclamides, which can react with a wide range of nucleophilic compounds and therefore present new possibilities in the synthesis of heterocyclic compounds (Augustin *et al.*, 1980). We have undertaken the X-ray structure analysis of (I) as an extension of studies on the molecular packing of cinnamamide derivatives.



(I)

The bond lengths and angles of the cinnamamide group in (I) are comparable with reported values (Schmidt, 1964; Iwamoto & Kashino, 1990; Iwamoto *et al.*, 1989). In the cinnamoyl part of the molecule, the C1—C7, C7—C8 and C8—C9 bond distances of 1.461 (5), 1.326 (4) and 1.493 (4) Å, respectively, are comparable with reported values of 1.467 (2), 1.329 (2) and 1.485 (2) Å, respectively, for the analog *N*-methyl-*N*-(2-nitrophenyl)cinnamamide (Subramanian *et al.*, 1999). The widening of the C1—C7—C8 angle [126.8 (3)°] is due to intramolecular repulsion between C2 and C8 [H2*A*···H8*A* = 2.29 and C2···C8 = 3.025 (6) Å]. Structural studies reveal that the N11 atom is sp^2 hybridized, in spite of the lack of coplanarity of ring *B* and the cinnamoyl moiety.

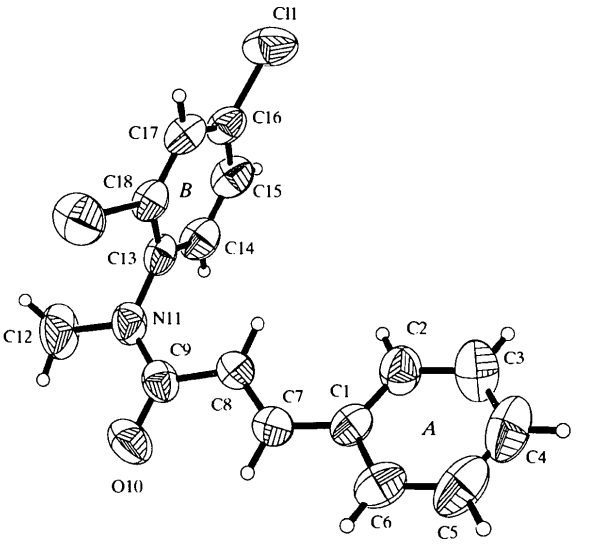


Fig. 1. The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme.