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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1299). Services for accessing these data are described at the back of the journal.

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Intramolecular N—H···π(phenyl) and intermolecular C—H···π(phenyl) interactions in 5-amino-4-(4-methoxyphenyl)-2-phenyl-7-piperidino-1,6-naphthyridine-8-carbonitrile–benzene (2/1)

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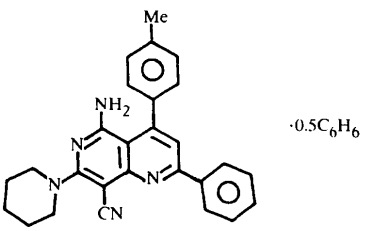
Abstract

The structure of the title compound, $C_{27}H_{25}N_5O\cdot 0.5C_6H_6$, has been determined from X-ray diffraction data. The compound crystallizes from benzene in the triclinic system, space group $P\bar{1}$, with two molecules in the asymmetric unit. The naphthyridine ring system is almost planar and the six-membered piperidine ring adopts a chair conformation. Intramolecular N—H···π interactions are observed in the system with an N···π(phenyl centroid) distance of 3.619 (3) Å, and C—H···π interactions between the naphthyridine molecule and the solvent are also observed.

Comment

A number of 1,6-naphthyridine derivatives have been found to possess anti-inflammatory, anticonvulsant and insecticidal activities, and their physiological activity has been studied (Damon & Nadelson, 1981, 1982; Takeuchi & Hamada, 1976). 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). The piperidine ring substituted at the seventh position of the 1,6-naphthyridine ring leads to pharmacological activity and is essential in the molecular structure of some important drugs (Lu *et al.*, 1991). However, few structural data have been reported for these compounds (Balogh *et al.*, 1986). For these reasons, the title compound, (I), was synthesized and its structure has been determined.



(I)

All the aromatic rings are planar with normal geometry and the piperidine ring, *C*, adopts a chair conformation. In molecule *A*, rings *C*, *D* and *E* make dihedral angles of 52.3 (1), 10.3 (1) and 63.8 (1)°, respectively, with the naphthyridine system (rings *A* and *B*), whereas in molecule *B*, these angles are 29.2 (5), 22.5 (6) and 80.0 (5)°, respectively. A *ZORTEP* (Zsolnai, 1997) plot of the two molecules in the asymmetric unit is shown in Fig. 1; the benzene solvent molecule, which is essentially planar and possesses usual geometry, has been omitted for clarity.

Amino N—H···π(phenyl) interactions have recently been theoretically postulated in model systems and experimentally described in globular proteins. It has also been suggested that such interactions may provide stability, contribute to the folding process and/or have a functional role in proteins (Levitt & Perutz, 1988). In

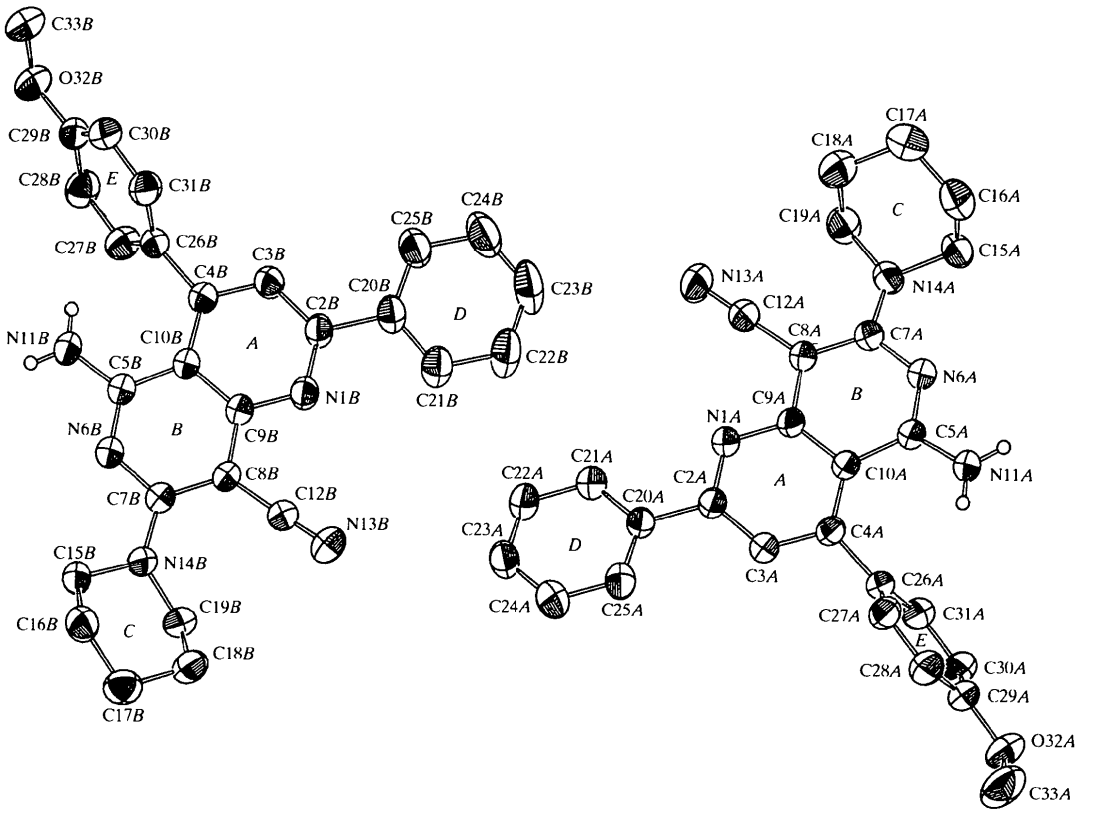


Fig. 1. The molecular structure of the title compound (Zsolnai, 1997), with 30% probability displacement ellipsoids. H atoms and the benzene solvent molecule have been omitted for clarity.

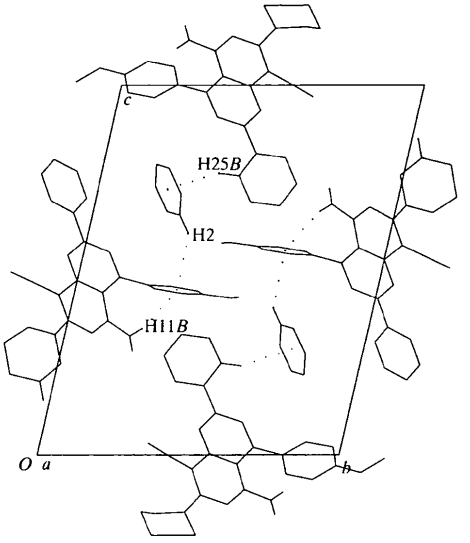


Fig. 2. Packing of the *A* molecules and solvent viewed down the *a* axis and showing selected N—H···π intramolecular and C—H···π intermolecular interactions. The cell is completed by a set of *B* molecules at $(1-x, 1-y, 1-z)$. H atoms involved in these interactions are shown, but other H atoms have been omitted for clarity.

addition, the preferred geometry is one in which the N—H (N11*A*—H11*B*) bond is perpendicular to the phenyl ring (C26*A*–C31*A*, centroid *Cg*1) plane, with the NH proton and the CH (C2—H2) proton of the solvent (C1–C6, centroid *Cg*3) directed towards the centroid of ring *E* (*Cg*1) of molecule *A* and the proton at C25*B* (C25*B*—H25*B*) directed towards the centroid (*Cg*3) of the solvent (see Fig. 2 and Table 2). The interesting nature of such cooperative N—H···π and C—H···π contacts and their possible utility as design elements in molecular recognition have been extensively discussed in several recent publications (Steiner *et al.*, 1995). The details of the intramolecular and intermolecular hydrogen-bond interactions (N—H···π, C—H···π, C—H···N, N—H···N and C—H···O) are comparable with the literature values (Steiner, 1998; Dastidar & Goldberg, 1996) and are given in Table 2. These interactions stabilize the crystal packing.

Experimental

A mixture of *p*-methoxybenzylacetophenone (1 g, 4.2 mmol), malononitrile (0.55 g, 8.4 mmol) and piperidine (0.71 g,

8.4 mmol) in ethanol (25 ml) was heated to reflux for 10 h. The reaction mixture was concentrated under reduced pressure and purified by column chromatography over silica gel (100–200 mesh). Elution with petroleum ether/benzene (1:1) gave the product as a pale-brown solid (m.p. 483–485 K), which was recrystallized from benzene.

Crystal data

$C_{27}H_{25}N_5O{\cdot}0.5C_6H_6$
M_r = 474.57
Triclinic
$P\overline{1}$
a = 9.6477 (1) Å
b = 14.9004 (2) Å
c = 18.0803 (3) Å
α = 75.920 (1)°
β = 84.206 (1)°
γ = 75.546 (1)°
V = 2439.01 (6) Å^3
Z = 4
D_x = 1.292 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 8192 reflections
θ = 1.45–33.18°
μ = 0.081 mm^{-1}
T = 293 (2) K
Slab
0.54 × 0.40 × 0.18 mm
Yellow

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: none
18 579 measured reflections
13 284 independent reflections

8940 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 30°
$h = -13 \rightarrow 13$
$k = -20 \rightarrow 20$
$l = -25 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.183
S = 1.073
13284 reflections
649 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0570P)^2 + 1.2585P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.341 e Å^{-3}
$\Delta\rho_{min}$ = −0.229 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*	1.329 (2)	N1*B*—C2*B*	1.323 (3)
N1*A*—C9*A*	1.359 (2)	N1*B*—C9*B*	1.360 (2)
C2*A*—C3*A*	1.404 (3)	C2*B*—C3*B*	1.405 (3)
C2*A*—C20*A*	1.490 (3)	C2*B*—C20*B*	1.492 (3)
C4*A*—C26*A*	1.496 (2)	C4*B*—C26*B*	1.499 (3)
C12*A*—N13*A*	1.143 (3)	C12*B*—N13*B*	1.145 (3)
C3*A*—C2*A*—C20*A*	121.35 (18)	C3*B*—C2*B*—C20*B*	122.01 (18)
C3*A*—C4*A*—C26*A*	116.30 (17)	C3*B*—C4*B*—C26*B*	116.03 (17)
N14*A*—C7*A*—C8*A*	125.76 (18)	N14*B*—C7*B*—C8*B*	123.69 (17)
N13*A*—C12*A*—C8*A*	177.3 (3)	N13*B*—C12*B*—C8*B*	178.1 (3)
N14*A*—C7*A*—C8*A*—C12*A*	−12.3 (4)		
C8*A*—C7*A*—N14*A*—C15*A*	160.2 (2)		
C3*A*—C2*A*—C20*A*—C21*A*	−167.2 (2)		
C3*A*—C4*A*—C26*A*—C27*A*	−60.5 (3)		
N14*B*—C7*B*—C8*B*—C12*B*	−13.5 (3)		
C8*B*—C7*B*—N14*B*—C15*B*	164.4 (2)		
C3*B*—C2*B*—C20*B*—C21*B*	−160.1 (2)		
C3*B*—C4*B*—C26*B*—C27*B*	97.7 (2)		

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

*Cg*1, *Cg*2 and *Cg*3 are the centroids of ring *E* of molecule *A*, ring *E* of molecule *B* and the benzene solvent molecule, respectively.

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
N11*A*—H11*B*···*Cg*1	2.80	3.619 (3)	159
C19*A*—H19*A*···N13*A*	2.53	3.326 (3)	139
C16*A*—H16*A*···*Cg*2^{i}	2.87	3.777 (3)	155
C25*B*—H25*B*···*Cg*3^{ii}	2.93	3.733 (5)	145
C2—H2···*Cg*1^{iii}	2.79	3.579 (4)	143
C15*A*—H15*B*···N11*B*^{i}	2.68	3.461 (3)	138
N11*A*—H11*A*···N6*B*^{i}	2.61	3.441 (2)	161
C17*B*—H17*C*···O32*A*^{iv}	2.76	3.633 (3)	149

Symmetry codes: (i) $x, 1+y, z-1$; (ii) $2-x, 1-y, -z$; (iii) $1-x, 2-y, -z$; (iv) $x, y-1, 1+z$.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). 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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