Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

C—H···N and C—H···π interactions in 2-ethoxy-4,6-diphenylpyridine-3-carbonitrile

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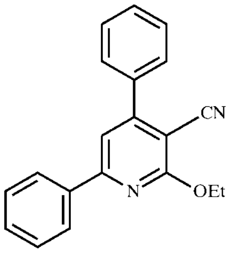
Received 29 July 2002
Accepted 7 October 2002
Online 8 November 2002

The title compound, $C_{20}H_{16}N_2O$, has two molecules in the asymmetric unit and the crystal structure shows that the central pyridine ring of each molecule has a flat boat conformation. The terminal C atom in one of the molecules is disordered over two positions, with relative occupancies of 0.594 (14) and 0.398 (14). Intermolecular C—H···N and C—H···π interactions and π–π stacking, along with intramolecular C—H···N and C—H···π interactions, help to stabilize the structure.

Comment

The title compound, (I), belongs to the 2-pyridine class of compounds, which show a wide spectrum of biological activities (Perez-Medina *et al.*, 1947). The present work continues our structural studies of the 2-pyridine group of compounds (Patel *et al.*, 2002*a*,*b*).



(I)

Compound (I) crystallizes in the monoclinic space group $P2_1/c$ with two molecules in the asymmetric unit, denoted *A* and *B*. A perspective view of the two molecules is shown in Fig. 1 (Johnson, 1965). The pyridine rings of molecules *A* and *B* have quite similar geometries. The shortening of the C—N distances [1.313 (3) and 1.346 (3) Å in molecule *A*, and 1.349 (3) and 1.299 (3) Å in molecule *B*] and the opening of the N1—C1—C2 angle [123.9 (2)° in molecule *A* and 124.6 (3)° in molecule *B*] may be attributed to the size of the substituent at C1, correlating well with the values observed in the *ortho*-substituted derivative 2-(2,3-isopropylidenedioxypropyloxy)-3-cyano-4,6-diphenylpyridine (Patel *et al.*, 2002*c*). However, when the *ortho* substituent is only an O atom, the bond length and angle are normal (Patel *et al.*, 2002*a*,*b*). The bond distances and angles of the phenyl rings of molecules *A* and *B* in (I) are consistent with those observed in other similar structures (Patel *et al.*, 2002*b*; Black *et al.*, 1992; Hussain *et al.*, 1996).

The flat boat conformation of the dihydropyridine ring of molecules *A* and *B* is reported in the literature for other compounds incorporating this moiety (Lokaj *et al.*, 1991; Fonseca *et al.*, 1986). The cyano atoms C18 and N2 of molecule *A* deviate by 0.173 (4) and 0.310 (5) Å, respectively, from the pyridine ring plane, while atoms C18′ [−0.031 (4) Å] and N2′ [−0.058 (6) Å] are coplanar with the pyridine plane in molecule *B*. The phenyl rings of both molecules are planar. Steric hindrances rotate the phenyl rings out of the plane of the central pyridine ring by 35.49 (8) and 24.61 (1)° (molecule *A*), and by 41.0 (1) and 22.3 (1)° (molecule *B*). A similar orientation of the phenyl rings has been observed in other derivatives of 1,4-dihydropyridine reported by our group and by others (Patel *et al.*, 2002*a*; Bolte, 1998).

The significant difference in the conformations of molecules *A* and *B* is in the relative orientations of the ethoxy moiety. The ethoxy group in molecule *B* is orthogonal to the pyridine ring plane [C1′—O1′—C19′—C20′ = 94.1 (6)°], thereby avoiding steric interaction, while in molecule *A* it is coplanar with the heterocyclic ring plane [C1—O1—C19—C20 = 170.1 (2)°].

The terminal ethoxy C atom of molecule *B* is disordered over two positions, resulting in a shortening of the C19′—C20′ [1.350 (6) Å] and C19′—C20*A* [1.392 (9) Å] distances. The torsion angles defining the orientations of various substituents at the central pyridine ring are summarized as follows for molecule *A*, with the values for molecule *B* given in brackets: C3—C2—C18—N2 = 146 (6)° [35 (43)°], C1—C2—C18—N2 = −33 (6)° [−149 (43)], C2—C1—O1—C19 = −172.0 (2)° [179.1 (3)°] and N1—C1—O1—C19 = 8.1 (3)° [−0.6 (4)°]

An intermolecular network of C—H···π and π–π-stacking interactions plays a significant role in the stability of the structure of (I). In addition, there is an intramolecular C—H···N interaction (Fig. 2) involving pyridine atom N1′ and ethoxy atom C19′ [C19′···N1′ = 2.709 (5) Å, H19*D*···N1′ = 2.34 Å and C19′—H19*D*···N1′ = 102°]. Cyano atom N2 of molecule *A* interacts with phenyl atom C15′ of a symmetry-related molecule *B* at (x, $\frac{3}{2} - y$, $z - \frac{1}{2}$) [C15′···N2 = 3.399 (6) Å, H15′···N2 = 2.55 Å and C15′–H15′···N2 = 153°]. The hydrogen bonding in the structure of (I) is supported by π–π stacking between the pyridine ring plane of molecule *A* and that of molecule *B* at (1 + x, y, z), with their centroids separated by 3.926 (2) Å.

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DOI: 10.1107/S0108270102018383

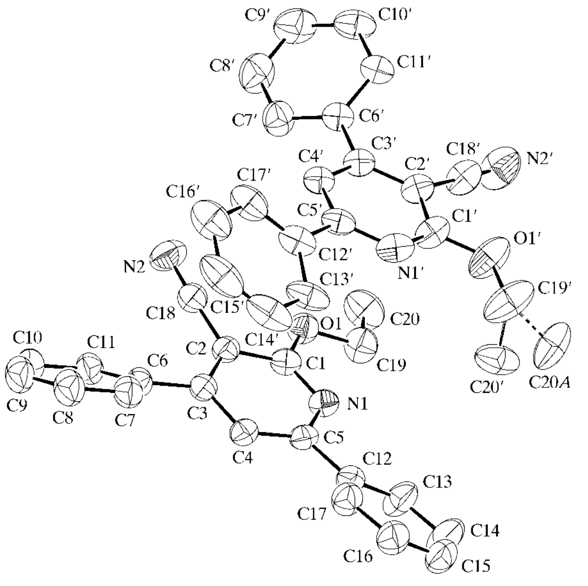

Figure 1
A view of the two independent molecules in (I), showing the atom-numbering scheme; molecule *B* is labelled with primes. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

There are two intramolecular C—H···π interactions in the structure of (I). In the first, phenyl atom C13′ of molecule *B* interacts with the pyridine ring of molecule *A* [C13′···*Cg*1 = 3.392 (3) Å, H13′···*Cg*1 = 3.18 Å and C13′—H13′···*Cg*1 = 95°; *Cg*1 is the centroid of the C1–C5/N1 ring]. In the second interaction, ethoxy atom C19 of molecule *A* interacts with the pyridine ring of molecule *B* [C19···*Cg*2 = 3.868 (3) Å, H19*B*···*Cg*2 = 3.37 Å and C19—H19*B*···*Cg*2 = 114°; *Cg*2 is the centroid of the C1′–C5′/N1′ ring].

There are also two intermolecular C—H···π interactions (Desiraju & Steiner, 1999) linking symmetry-related molecules *A* and *B*, and these are dominant in the structure of (I), providing strong packing. In the first of these interactions, phenyl atom C10 of molecule *A* interacts with the symmetry-related phenyl ring of molecule *B* at $(1 + x, \frac{3}{2} - y, \frac{1}{2} + z)$ [C10···*Cg*3 = 3.498 (4) Å, H10···*Cg*3 = 2.71 Å and C10—H10···*Cg*3 = 143°; *Cg*3 is the centroid of the C1′–C5′/N1′ ring at $(1 + x, \frac{3}{2} - y, \frac{1}{2} + z)$]. In the second interaction, *ortho*-substituted phenyl atom C17′ of molecule *B* interacts with the symmetry-related phenyl ring of molecule *A* at $(x - 1, y, z)$ [C17′···*Cg*4 = 3.653 (4) Å, H17′···*Cg*4 = 2.95 Å and C17′—H17′···*Cg*4 = 134°; *Cg*4 is the centroid of the C1–C5/N1 ring at $(x - 1, y, z)$].

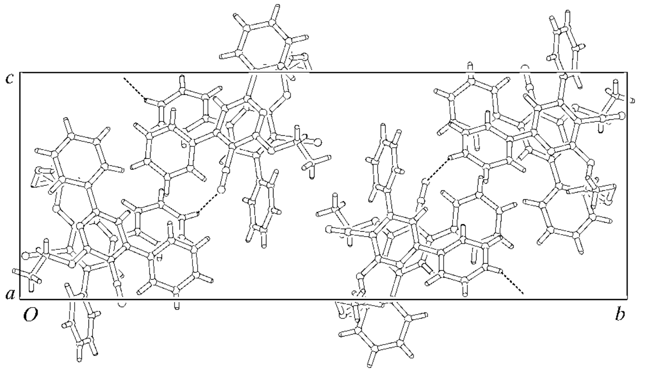

Figure 2
The molecular packing in (I), viewed along the *bc* plane, showing the hydrogen-bonding interactions.

Experimental

The title compound was synthesized according to the method of Shah (2000); full details of the synthesis will be published elsewhere. Thin plate-like crystals of (I) were grown by slow evaporation from a solution in a mixture of chloroform and ethanol (1:1).

Crystal data

$C_{20}H_{16}N_2O$
$M_r = 300.31$
Monoclinic, $P2_1/c$
$a = 8.5542$ (10) Å
$b = 32.027$ (3) Å
$c = 12.3910$ (7) Å
$\beta = 104.493$ (3)°
$V = 3286.6$ (5) Å^3
$Z = 8$
$D_x = 1.214$ Mg m^{-3}
$D_m = 1.204$ Mg m^{-3}
D_m measured by flotation in an aqueous potassium iodide solution
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 25$–35°
$\mu = 0.60$ mm^{-1}
$T = 293$ (2) K
Plate, colourless
0.2 × 0.1 × 0.1 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scan (North *et al.*, 1968)
$T_{\min} = 0.930$, $T_{\max} = 0.940$
6001 measured reflections
5612 independent reflections
3150 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.061$
$\theta_{\max} = 67.9°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 30$
$l = 0 \rightarrow 14$
2 standard reflections frequency: 60 min intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.160$
$S = 1.02$
5612 reflections
426 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0770P)^2 + 0.3042P]$
$(\Delta/\sigma)_{\max} = 0.050$
$\Delta\rho_{\max} = 0.13$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.336 (3)	O1′—C19′	1.431 (4)
O1—C19	1.463 (3)	N1′—C1′	1.299 (3)
N1—C1	1.313 (3)	N2′—C18′	1.133 (4)
N2—C18	1.142 (3)	C2′—C18′	1.444 (4)
C2—C18	1.437 (3)	C19′—C20′	1.337 (6)
C19—C20	1.477 (4)	C19′—C20*A*	1.394 (8)
O1′—C1′	1.350 (3)		
C1—O1—C19	117.81 (19)	C1′—O1′—C19′	119.0 (3)
C1—N1—C5	118.1 (2)	C1′—N1′—C5′	117.6 (2)
N1—C1—C2	123.9 (2)	N1′—C1′—C2′	124.6 (3)
N2—C18—C2	177.2 (3)	N2′—C18′—C2′	179.5 (3)
O1—C19—C20	107.6 (2)	C20′—C19′—O1′	110.3 (4)
N1—C5—C12—C17	154.8 (2)	N1′—C5′—C12′—C17′	156.8 (3)
C4—C3—C6—C11	−142.1 (2)	C2′—C3′—C6′—C11′	−41.7 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C19′—H19*D*···N1′	0.97	2.34	2.709 (5)	102
C15′—H15′···N2^{i}	0.93	2.55	3.399 (4)	153

Symmetry code: (i) $x, \frac{3}{2} - y, z - \frac{1}{2}$.

H atoms were treated as riding, with C—H distances in the range 0.93–0.97 Å.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *MolEN* (Fair, 1990); data reduction: *MolEN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1965) and *PLATON* (Spek, 1997); software used to prepare material for publication: *SHELXL*97.

The authors are grateful to Dr Babu Varghese of the RSIC, Indian Institute of Technology, Madras, India, for the X-ray data collection, and the Department of Physics, Sardar Patel University, for financial support of this work. JMM is grateful to the UGC for a teacher fellowship award.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1195). Services for accessing these data are described at the back of the journal.

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