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4-[*N*,*N*-Bis(2-cyanoethyl)amino]-pyridine

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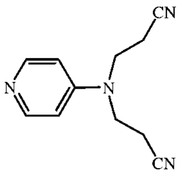
The title compound, 3,3′-(4-pyridylimino)dipropanenitrile, $C_{11}H_{12}N_4$, has a twofold axis and consists of a pyridine ring head and two cyanoethyl tails, the three groups being linked by an N atom. The planar geometry around the amino N atom suggests conjugation with the π-system of the pyridine ring. The molecules are stacked in a layer structure *via* relatively weak to very weak intermolecular $C-H\cdots\pi$ and $C-H\cdots N$ hydrogen-bond interactions.

Comment

Hydrogen bonding is very important in determining the physical properties of materials, the conformation of biopolymers and the molecular packing, and in molecular recognition (Crabtree *et al.*, 1998). Recently, increasing interest has concentrated on a series of new hydrogen-bonding interactions which are different from classical hydrogen bonding. The π-electrons, such as those of an aromatic ring and C—C or C—N multiple bonds, have been shown to be able to act as weak proton acceptors (Atwood *et al.*, 1991; Brammer *et al.*, 1991; Shubina *et al.*, 1997; Yao *et al.*, 1997). It is well known that 4-(*N*,*N*-dimethylamino)pyridine (DMAP) and its derivatives are efficient catalysts in many organic reactions (Höfle *et al.*, 1978; Scriven, 1983; Steglich & Hoefle, 1969). As a derivative of DMAP, the title compound, (I), also has potential catalytic properties in some organic reactions (Huang *et al.*, 1994). In this work, the X-ray crystal structure analysis of (I) has been carried out in order to investigate the weak intermolecular hydrogen-bonding interactions.



(I)

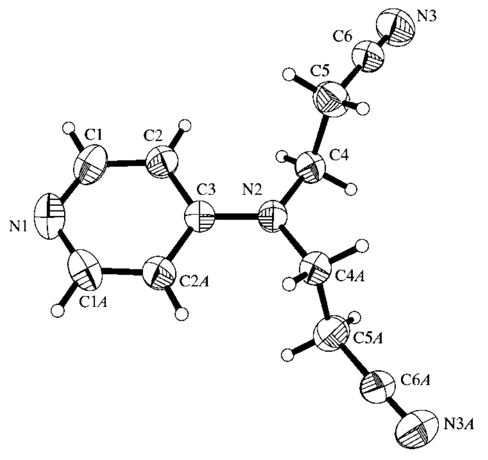


Figure 1
The molecular structure of (I), with ellipsoids drawn at the 30% probability level. [Symmetry code: $(A)\ 2-x, y, \frac{1}{2}-z$.]

The title compound, (I), consists of a pyridine ring head and two cyanoethyl tails (Fig. 1). Atoms N1, C3 and N2 lie on the twofold axis. The head and tails are all bonded to atom N2, which is not only in the plane of the pyridine ring, but also in the plane of the tails. The C1—C2—C3—N2 and N2—C4—C5—C6 torsion angles are 179.3 (1) and 179.0 (2)°, respectively. Similar to aminopyridines and their derivatives (Chao *et al.*, 1977; Ohms & Guth, 1983), the sum of the bond angles around atom N2 is 360° (Table 1). The dihedral angle between the ring plane and the plane defined by atoms N2/C4/C4($2-x$, y, $z-\frac{1}{2}$) is 12.4 (2)°. The N2—C3 bond length [1.374 (3) Å] is about midway between those in 2-aminopyridine [1.351 (2) Å; Chao *et al.*, 1975*a*] and 3-aminopyridine [1.384 (4) Å; Chao *et al.*, 1975*b*]. This geometric conformation reflects the conjugation between the lone pair of N2 and the π-system of the pyridine ring (Chao & Schempp, 1977).

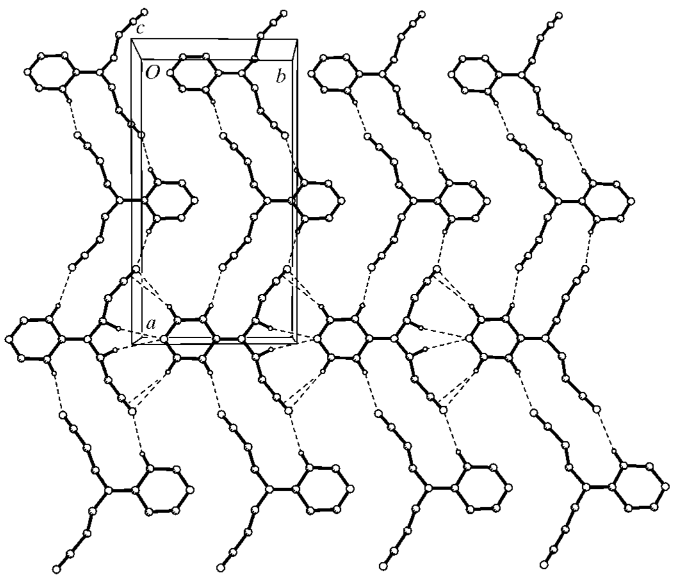


Figure 2
One crystal packing layer of (I). The molecular chains are along the *b* axis. H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: $(A)\ 2-x, y, \frac{1}{2}-z$; $(B)\ \frac{3}{2}-x, \frac{3}{2}-y, -z$; $(')\ x, 1+y, z$.]

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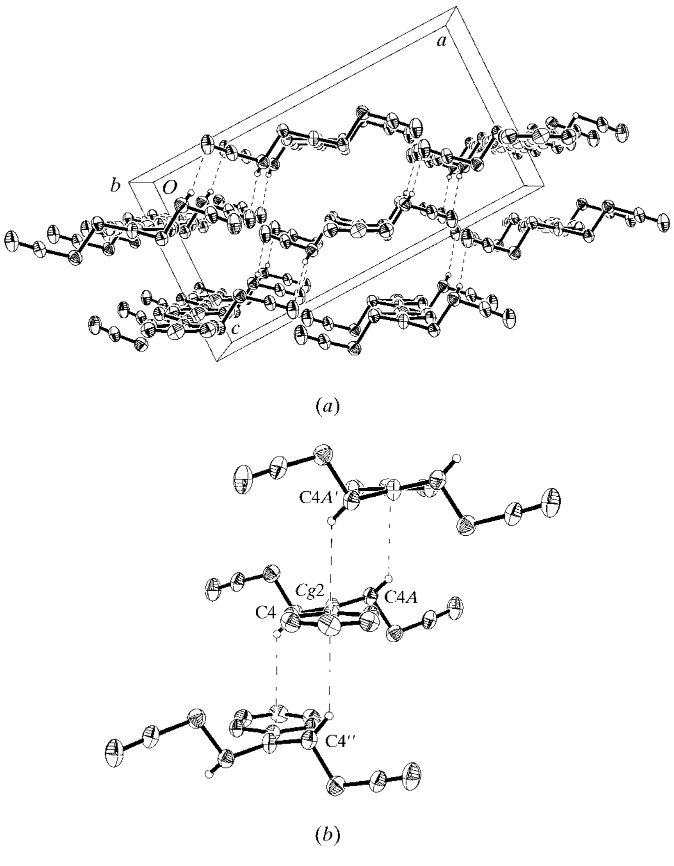
The molecules stack as a layer structure. Neighboring layers slide laterally with respect to one another. Each layer is composed of numerous molecular chains. These parallel molecular chains extend along the *b* axis and all the molecules of a chain have the same head-to-tail orientation (Fig. 2). Adjacent chains have a different molecular orientation and are connected by C2—H2···N3($\frac{3}{2}-x$, $\frac{3}{2}-y$, $-z$) hydrogen bonds (Table 2). In these chains, adjacent molecules are also connected by C4—H4*B*···N1(x, $y+1$, z) and C1—H1···N3(x, $y-1$, z) hydrogen bonds (see Fig. 2). The nitrile groups also act as proton acceptors in C1—H1···*Cg*1(x, $y-1$, z), where *Cg*1 is the centre of the nitrile group. The geometry of this weak C—H···π hydrogen bond is similar to that observed in 2α,4′β-dihydroxy-2β,4′α-diethynylspiro[5.5]undec-2′-ene (Subramanian *et al.*, 1996).

The pyridine-ring planes are parallel to each other and the distance between adjacent layers is 3.687 (5) Å. This is greater than the separations observed for stacking interactions (3.3–3.6 Å; Glówka *et al.*, 1999; Hunter & Sanders, 1990). Neighboring layers are linked by a C5—H5*A*···N3($\frac{3}{2}-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$) hydrogen bond (see Fig. 3), with C···N distances of 3.686 (4) Å. Although this distance is longer than some hydrogen-bond lengths, it can still be considered a reasonable length for weak hydrogen bonding (Komasa *et al.*, 1998; Taylor & Kennard, 1982). There are other types of hydrogen bonding between adjacent layers, as shown in Fig. 3, where pyridine rings act as weak proton acceptors. One molecule in a layer bonds to two neighboring layers through a C4—H4*A*···*Cg*2($2-x$, $1-y$, $-z$) hydrogen bond, where *Cg*2 denotes the centroid of the pyridine ring. The C4···*Cg*2 distance and the angle at H4*A* are 3.550 (5) Å and 131°, respectively. The geometry of this hydrogen bond is similar to that observed in 3-*O*-benzyl-1,2-*O*-isopropylidene-5,6-dideoxy-α-D-ribohex-5-yno-1,4-furanose (Ciunik & Jarosz, 1998), *N*-(2,6-dimethylphenyl)-5-methylisoxazole-3-carboxamide (Lutz *et al.*, 1996) and 4-(4*H*-1,2,4-triazol-4-yl)-2-chlorophenylmethanimine (Ciunik *et al.*, 2002).



(*a*)

(*b*)

Figure 3
(*a*) The C—H···N hydrogen bonding and (*b*) the C—H···π hydrogen bonding between adjacent layers, viewed along the *a* axis. H atoms not participating in the hydrogen bonds have been omitted for clarity. [Symmetry codes: (*A*) $2-x, y, \frac{1}{2}-z$; (*A*′) $x, 1-y, \frac{1}{2}+z$; (″) $2-x$, $1-y$, $-z$.]

Experimental

4-Aminopyridine (8.0 g, 0.085 mol) and hydroquinone (0.02 g, 0.18 mmol) were added to acrylonitrile (50 ml). The reaction mixture was refluxed for 3 h, filtered and the solid product recrystallized from dimethylformamide (DMF). The white powder of (I) was filtered off, washed with methanol and dried in a vacuum desiccator (yield: 14.5 g, 85.2%). Colorless block-shaped single crystals of (I) (m.p. 481.1–482.7 K) were obtained by recrystallization from DMF. Elemental analysis calculated for $C_{11}H_{12}N_4$ (%): C 65.98, H 6.04, N 27.98; found: C 65.79, H 6.30, N 27.84; IR data (cm^{-1}): 2256 (*s*, CN), 1602 (*s*, C=N$_{py}$), 1521 (*s*, C=C$_{py}$); MS (*m*/*z*): 201 (*M* + 1, 100%).

Crystal data

$C_{11}H_{12}N_4$
$M_r = 200.25$
Monoclinic, *C*2/*c*
$a = 15.355$ (4) Å
$b = 8.321$ (2) Å
$c = 8.264$ (2) Å
$\beta = 92.12$ (1)°
$V = 1055.2$ (5) Å^3
$Z = 4$

$D_x = 1.261$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 756 reflections
$\theta = 2.5$–27.1°
$\mu = 0.08$ mm^{-1}
$T = 293$ (2) K
Block, colorless
0.30 × 0.30 × 0.20 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
2589 measured reflections
922 independent reflections
820 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.026$
$\theta_{\max} = 25.0°$
$h = -15 \rightarrow 18$
$k = -8 \rightarrow 9$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.094$
$S = 1.04$
922 reflections
71 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.02P)^2 + 1.20P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.012$
$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.129 (5)

The positions of all H atoms were fixed geometrically (C—H = 0.93 and 0.97 Å).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.328 (2)	C4—N2	1.4462 (19)
C1—C2	1.371 (3)	C4—C5	1.525 (2)
C2—C3	1.394 (2)	C5—C6	1.454 (3)
C3—N2	1.374 (3)	C6—N3	1.132 (2)
N1—C1—C2	125.81 (19)	C3—N2—C4^{i}	121.54 (9)
C2^{i}—C3—C2	115.8 (2)	C3—N2—C4	121.54 (9)
C1^{i}—N1—C1	114.0 (2)	C4^{i}—N2—C4	116.92 (19)

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

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

*Cg*1 is the centre of the nitrile group and *Cg*2 is the centroid of the pyridine ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···*Cg*1^{i}	0.93	2.80	3.667 (5)	140
C1—H1···N3^{i}	0.93	2.86	3.770 (5)	167
C2—H2···N3^{ii}	0.93	2.62	3.524 (3)	165
C4—H4*A*···*Cg*2^{iii}	0.97	2.84	3.550 (5)	131
C4—H4*B*···N1^{iv}	0.97	2.81	3.576 (4)	136
C5—H5*A*···N3^{v}	0.97	2.74	3.686 (4)	164

Symmetry codes: (i) $x, y - 1, z$; (ii) $\frac{3}{2} - x, \frac{3}{2} - y, -z$; (iii) $2 - x, 1 - y, -z$; (iv) $x, 1 + y, z$; (v) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1120). Services for accessing these data are described at the back of the journal.

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