

## 2-Amino-6-ethoxy-4-methylpyridine-3,5-dicarbonitrile

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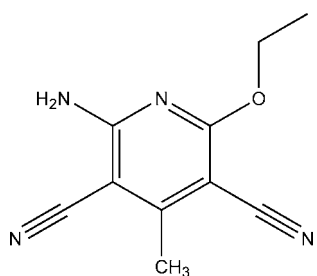
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Key indicators: single-crystal X-ray study;  $T = 173$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.035;  $wR$  factor = 0.101; data-to-parameter ratio = 15.3.

In the title compound,  $\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}$ , the crystal packing is stabilized by intermolecular  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bonds between adjacent pyridine rings, resulting in a two-dimensional layer structure. The H atoms of the 4-methyl group are disordered [site occupation factors 0.643 (14) and 0.357 (14)].

### Related literature

For an alternative preparation of the title compound, see: Uray & Kriessmann (1984); Alberola *et al.* (1967). For a review describing the preparation, reactions and applications of substituted pyridine derivatives, see: Spitzner (2005).



### Experimental

#### Crystal data

$\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}$   
 $M_r = 202.22$

Triclinic,  $P\bar{1}$   
 $a = 5.5050$  (11) Å

$b = 7.3500$  (15) Å  
 $c = 12.385$  (3) Å  
 $\alpha = 86.27$  (3)°  
 $\beta = 81.33$  (3)°  
 $\gamma = 84.19$  (3)°  
 $V = 492.22$  (18) Å<sup>3</sup>

$Z = 2$   
Mo  $K\alpha$  radiation  
 $\mu = 0.09$  mm<sup>-1</sup>  
 $T = 173$  (2) K  
 $0.71 \times 0.08 \times 0.06$  mm

#### Data collection

Bruker–Nonius X8 APEXII  
diffractometer  
Absorption correction: multi-scan  
(SADABS; Sheldrick, 2004)  
 $T_{\min} = 0.936$ ,  $T_{\max} = 0.994$

9312 measured reflections  
2247 independent reflections  
1809 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.026$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$   
 $wR(F^2) = 0.101$   
 $S = 1.05$   
2247 reflections  
147 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.27$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.24$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N2}-\text{H2}\cdots\text{N3}^i$	0.883 (15)	2.230 (15)	3.1040 (17)	170.1 (13)
$\text{N2}-\text{H1}\cdots\text{N4}^{ii}$	0.865 (16)	2.308 (16)	3.1676 (17)	172.8 (13)

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

Data collection: APEX2 (Bruker, 2003); cell refinement: APEX2; data reduction: SAINT (Bruker, 2003); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997) and DIAMOND (Brandenburg, 2005); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2070).

### References

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**supplementary materials**

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## 2-Amino-6-ethoxy-4-methylpyridine-3,5-dicarbonitrile

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### Comment

In the title compound the pyridine ring is essentially planar and the ethoxy group lies within the molecule plane (C9—O1—C5—N1 2.04 (14), C5—O1—C9—C10 - 170.90 (9)°) with the methylene protons in staggered geometry with respect to the pyridine N atom (N1). The amino group is almost planar with the protons in eclipsed geometry with respect to the pyridine ring, indicating conjugation of the *p*-type lone-pair of N2 with the aromatic ring. The methyl group of I was found to be disordered. The H atoms were split over two positions with occupancy factors refined to 0.643 (14) and 0.357 (14) (Fig. 1).

In the crystal structure, the molecules of I are held together by the formation of four intermolecular N—H···N hydrogen bonds per molecule within the pyridine-ring plane, leading to a two-dimensional layered network. Only weak van der Waals interactions can be assumed between the adjacent layers (Fig.2).

### Experimental

The title compound is described in the literature (Uray & Kriessmann 1984; Alberola *et al.*, 1967) and was unintentionally obtained as a by-product of an attempted reaction of malonitrile with cyanur chloride in an ethanol/sodium ethanolate solution in 12% yield. Crystallization from a n-heptane/ethyl acetate solution at ambient temperature gave colourless X-ray quality crystals. <sup>1</sup>H-NMR (Acetone-d<sub>6</sub>, 25°C): δ = 1.34 (t, 3H, OCH<sub>2</sub>CH<sub>3</sub>), 2.48 (s, 3H, CH<sub>3</sub>), (q, 2H, OCH<sub>2</sub>CH<sub>3</sub>).

### Refinement

H atoms bonded to N2 were located in a difference map and refined freely. Other H atoms were positioned geometrically and refined using a riding model, with C—H = 0.98 (C8, C10) or 0.99 Å (C9) and with  $U_{\text{iso}}(\text{H}) = 1.5$  times  $U_{\text{eq}}(\text{C})$  (methyl groups) or with  $U_{\text{iso}}(\text{H}) = 1.2$  times  $U_{\text{eq}}(\text{C})$  (methylene group). Torsion angles of all methyl groups were allowed to refine. For the methyl group at C8 ideal disorder was assumed, with two positions rotated from each other by 60°. The occupancy factors of each part were refined freely (0.643 (14)/0.357 (14)).

### Figures

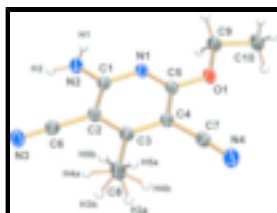


Fig. 1. Molecular structure of (I), showing the atomic numbering scheme and displacement ellipsoids drawn at the 50% probability level. Both components of the disordered methyl group are shown.

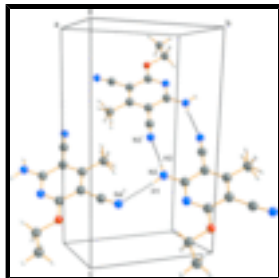


Fig. 2. Part of the packing diagram of (I). Unique N—H...N interactions represented by dashed lines are shown for one molecule of (I). Symmetry code: (i)  $-x + 2, -y + 2, -z + 1$ ; (ii)  $x + 1, y - 1, z$ .

## 2-Amino-6-ethoxy-4-methylpyridine-3,5-dicarbonitrile

### Crystal data

$C_{10}H_{10}N_4O$	$Z = 2$
$M_r = 202.22$	$F_{000} = 212$
Triclinic, $P\bar{1}$	$D_x = 1.364 \text{ Mg m}^{-3}$
Hall symbol: $-P 1$	Mo $K\alpha$ radiation
$a = 5.5050 (11) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$b = 7.3500 (15) \text{ \AA}$	Cell parameters from 4290 reflections
$c = 12.385 (3) \text{ \AA}$	$\theta = 5.6\text{--}60.3^\circ$
$\alpha = 86.27 (3)^\circ$	$\mu = 0.09 \text{ mm}^{-1}$
$\beta = 81.33 (3)^\circ$	$T = 173 (2) \text{ K}$
$\gamma = 84.19 (3)^\circ$	Needle, colourless
$V = 492.22 (18) \text{ \AA}^3$	$0.71 \times 0.08 \times 0.06 \text{ mm}$

### Data collection

Bruker-Nonius Apex X8 CCD diffractometer	2247 independent reflections
Radiation source: sealed tube	1809 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.026$
$T = 173(2) \text{ K}$	$\theta_{\text{max}} = 27.5^\circ$
$\omega$ scans	$\theta_{\text{min}} = 2.8^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	$h = -7 \rightarrow 7$
$T_{\text{min}} = 0.936, T_{\text{max}} = 0.994$	$k = -9 \rightarrow 9$
9312 measured reflections	$l = -15 \rightarrow 16$

### Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.035$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.101$	$w = 1/[\sigma^2(F_o^2) + (0.0579P)^2 + 0.0638P]$
	where $P = (F_o^2 + 2F_c^2)/3$

$S = 1.05$   $(\Delta/\sigma)_{\max} < 0.001$   
 2247 reflections  $\Delta\rho_{\max} = 0.27 \text{ e } \text{\AA}^{-3}$   
 147 parameters  $\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$   
 Primary atom site location: structure-invariant direct methods Extinction correction: none

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\text{sigma}(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	-0.07335 (13)	0.94702 (10)	0.87234 (6)	0.0251 (2)	
C2	0.48464 (18)	1.09638 (14)	0.64233 (8)	0.0219 (2)	
C4	0.09244 (18)	1.17003 (14)	0.74881 (9)	0.0220 (2)	
N1	0.30361 (15)	0.86890 (12)	0.77104 (7)	0.0224 (2)	
N2	0.67687 (17)	0.78992 (13)	0.66985 (8)	0.0271 (2)	
H2	0.811 (3)	0.8114 (19)	0.6238 (12)	0.035 (4)*	
H1	0.674 (3)	0.686 (2)	0.7068 (12)	0.037 (4)*	
N3	0.84730 (17)	1.18521 (13)	0.49830 (8)	0.0305 (2)	
N4	-0.28058 (18)	1.40401 (14)	0.79863 (8)	0.0325 (2)	
C1	0.48938 (18)	0.91833 (14)	0.69423 (8)	0.0214 (2)	
C3	0.28386 (19)	1.22428 (14)	0.67055 (9)	0.0227 (2)	
C5	0.11391 (18)	0.99004 (14)	0.79666 (8)	0.0211 (2)	
C6	0.68578 (19)	1.14525 (14)	0.56238 (9)	0.0240 (2)	
C7	-0.11812 (19)	1.29557 (15)	0.77955 (9)	0.0243 (2)	
C8	0.2722 (2)	1.41415 (15)	0.61911 (10)	0.0311 (3)	
H3A	0.1455	1.4285	0.5707	0.047*	0.643 (14)
H4A	0.4328	1.4356	0.5766	0.047*	0.643 (14)
H5A	0.2307	1.5028	0.6763	0.047*	0.643 (14)
H5B	0.3938	1.4828	0.6451	0.047*	0.357 (14)
H4B	0.1066	1.4756	0.6391	0.047*	0.357 (14)
H3B	0.3086	1.4084	0.5394	0.047*	0.357 (14)
C9	-0.0559 (2)	0.76583 (15)	0.92725 (9)	0.0273 (3)	
H9	0.0733	0.7559	0.9755	0.033*	
H10	-0.0137	0.6704	0.8729	0.033*	
C10	-0.3038 (2)	0.74272 (17)	0.99326 (10)	0.0324 (3)	
H11	-0.3475	0.8424	1.0435	0.049*	
H12	-0.2976	0.6250	1.0352	0.049*	

# supplementary materials

H13                    −0.4281                    0.7456                    0.9441                    0.049\*

## Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0256 (4)	0.0216 (4)	0.0255 (4)	−0.0024 (3)	0.0028 (3)	0.0048 (3)
C2	0.0232 (5)	0.0204 (5)	0.0219 (5)	−0.0042 (4)	−0.0022 (4)	0.0016 (4)
C4	0.0235 (5)	0.0195 (5)	0.0225 (5)	−0.0018 (4)	−0.0031 (4)	0.0009 (4)
N1	0.0244 (4)	0.0196 (4)	0.0224 (5)	−0.0025 (3)	−0.0019 (4)	0.0027 (3)
N2	0.0252 (5)	0.0208 (5)	0.0317 (5)	0.0012 (4)	0.0022 (4)	0.0048 (4)
N3	0.0280 (5)	0.0267 (5)	0.0331 (6)	−0.0010 (4)	0.0031 (4)	0.0055 (4)
N4	0.0318 (5)	0.0253 (5)	0.0365 (6)	0.0014 (4)	0.0028 (4)	0.0027 (4)
C1	0.0227 (5)	0.0210 (5)	0.0210 (5)	−0.0029 (4)	−0.0042 (4)	−0.0007 (4)
C3	0.0257 (5)	0.0200 (5)	0.0225 (5)	−0.0030 (4)	−0.0037 (4)	0.0013 (4)
C5	0.0222 (5)	0.0217 (5)	0.0197 (5)	−0.0043 (4)	−0.0031 (4)	0.0006 (4)
C6	0.0258 (5)	0.0199 (5)	0.0259 (6)	−0.0008 (4)	−0.0042 (4)	0.0010 (4)
C7	0.0277 (5)	0.0218 (5)	0.0229 (5)	−0.0054 (4)	−0.0014 (4)	0.0028 (4)
C8	0.0311 (5)	0.0217 (5)	0.0363 (7)	−0.0005 (4)	0.0037 (5)	0.0082 (5)
C9	0.0296 (5)	0.0225 (5)	0.0281 (6)	−0.0038 (4)	−0.0014 (4)	0.0077 (4)
C10	0.0313 (6)	0.0339 (6)	0.0302 (6)	−0.0085 (5)	0.0017 (5)	0.0071 (5)

## Geometric parameters ( $\text{\AA}$ , $^\circ$ )

O1—C5	1.3332 (13)	N4—C7	1.1435 (15)
O1—C9	1.4564 (13)	C3—C8	1.4954 (15)
C2—C3	1.3941 (15)	C8—H3A	0.9800
C2—C1	1.4195 (15)	C8—H4A	0.9800
C2—C6	1.4280 (15)	C8—H5A	0.9800
C4—C3	1.3913 (15)	C8—H5B	0.9800
C4—C5	1.4152 (15)	C8—H4B	0.9800
C4—C7	1.4269 (15)	C8—H3B	0.9800
N1—C5	1.3163 (14)	C9—C10	1.5008 (15)
N1—C1	1.3490 (14)	C9—H9	0.9900
N2—C1	1.3391 (14)	C9—H10	0.9900
N2—H2	0.883 (15)	C10—H11	0.9800
N2—H1	0.865 (16)	C10—H12	0.9800
N3—C6	1.1474 (14)	C10—H13	0.9800
C5—O1—C9	117.88 (8)	C3—C8—H3A	109.5
C3—C2—C1	119.74 (10)	C3—C8—H4A	109.5
C3—C2—C6	120.02 (10)	C3—C8—H5A	109.5
C1—C2—C6	120.23 (10)	C3—C8—H5B	109.5
C3—C4—C5	118.45 (10)	C3—C8—H4B	109.5
C3—C4—C7	119.89 (10)	H5B—C8—H4B	109.5
C5—C4—C7	121.66 (10)	C3—C8—H3B	109.5
C5—N1—C1	118.29 (9)	H5B—C8—H3B	109.5
C1—N2—H2	122.8 (9)	H4B—C8—H3B	109.5
C1—N2—H1	118.2 (10)	O1—C9—C10	106.66 (9)
H2—N2—H1	118.5 (14)	O1—C9—H9	110.4

N2—C1—N1	116.17 (10)	C10—C9—H9	110.4
N2—C1—C2	122.23 (10)	O1—C9—H10	110.4
N1—C1—C2	121.59 (10)	C10—C9—H10	110.4
C4—C3—C2	117.85 (10)	H9—C9—H10	108.6
C4—C3—C8	120.51 (10)	C9—C10—H11	109.5
C2—C3—C8	121.64 (10)	C9—C10—H12	109.5
N1—C5—O1	120.24 (10)	H11—C10—H12	109.5
N1—C5—C4	124.07 (10)	C9—C10—H13	109.5
O1—C5—C4	115.69 (9)	H11—C10—H13	109.5
N3—C6—C2	179.73 (12)	H12—C10—H13	109.5
N4—C7—C4	175.40 (11)		
C5—N1—C1—N2	-179.18 (9)	C1—C2—C3—C8	179.22 (10)
C5—N1—C1—C2	0.63 (15)	C6—C2—C3—C8	-0.09 (16)
C3—C2—C1—N2	179.63 (10)	C1—N1—C5—O1	-179.82 (9)
C6—C2—C1—N2	-1.06 (16)	C1—N1—C5—C4	-0.20 (16)
C3—C2—C1—N1	-0.16 (16)	C9—O1—C5—N1	2.04 (14)
C6—C2—C1—N1	179.15 (9)	C9—O1—C5—C4	-177.61 (9)
C5—C4—C3—C2	1.12 (15)	C3—C4—C5—N1	-0.69 (16)
C7—C4—C3—C2	-179.37 (10)	C7—C4—C5—N1	179.80 (10)
C5—C4—C3—C8	-178.83 (10)	C3—C4—C5—O1	178.95 (9)
C7—C4—C3—C8	0.68 (16)	C7—C4—C5—O1	-0.56 (15)
C1—C2—C3—C4	-0.73 (16)	C5—O1—C9—C10	-170.90 (9)
C6—C2—C3—C4	179.96 (9)		

*Hydrogen-bond geometry* ( $\text{\AA}$ ,  $^\circ$ )

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N2—H2 $\cdots$ N3 <sup>i</sup>	0.883 (15)	2.230 (15)	3.1040 (17)	170.1 (13)
N2—H1 $\cdots$ N4 <sup>ii</sup>	0.865 (16)	2.308 (16)	3.1676 (17)	172.8 (13)

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

Fig. 1

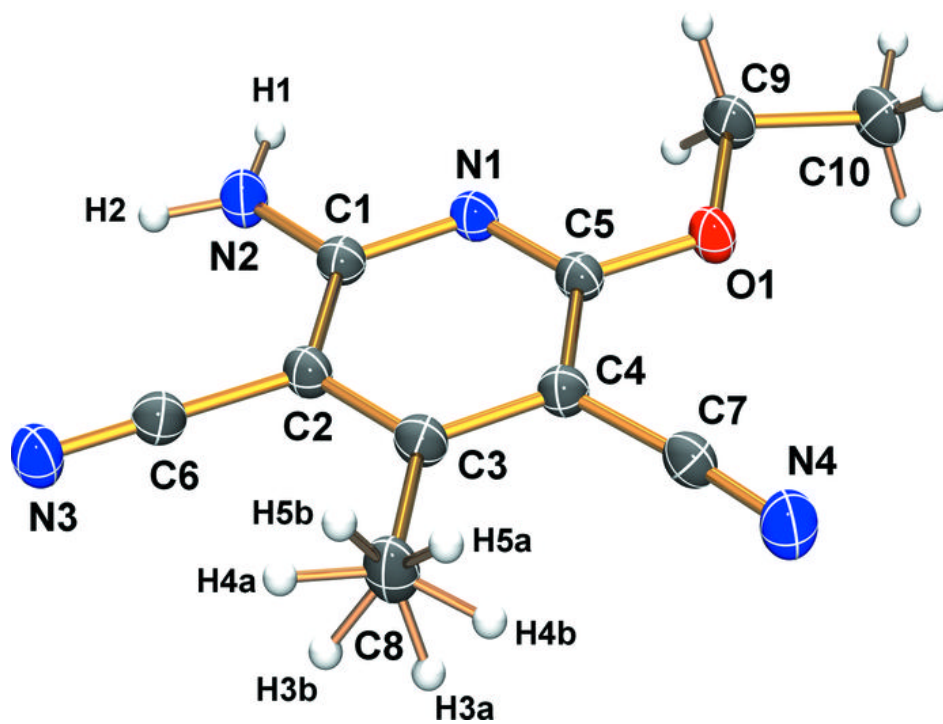




Fig. 2

