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Ethyl 4-amino-5-cyano-6-[(2-hydroxyethyl)amino]-2-methylnicotinate

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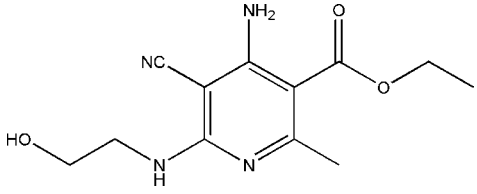
Key indicators: single-crystal X-ray study; T = 302 K; mean σ(C–C) = 0.003 Å; R factor = 0.058; wR factor = 0.172; data-to-parameter ratio = 14.9.

In the title compound, $C_{12}H_{16}N_4O_3$, all bond lengths and angles are within normal ranges. An O—H···N and an N—H···O intramolecular hydrogen bond contribute to the approximately planar molecular conformation. In the crystal structure, intermolecular N—H···O and N—H···N hydrogen bonds link the molecules into ribbons parallel to the [1$\bar{1}$0] direction.

Related literature

For biological functions of nicotine, see: Yildiz (2004). For normal ranges of molecular bond lengths in organic compounds, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{12}H_{16}N_4O_3$
M_r = 264.29
Triclinic, $P\bar{1}$
a = 7.8350 (7) Å
b = 9.1368 (9) Å
c = 10.3272 (10) Å
α = 79.720 (2)°
β = 77.381 (2)°
γ = 64.657 (2)°
V = 648.97 (11) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 302 (2) K
0.35 × 0.20 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.966, T_{max} = 0.990
4521 measured reflections
2767 independent reflections
1991 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.172
S = 1.06
2767 reflections
186 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3A···N1	0.861 (17)	2.25 (3)	2.780 (2)	120 (3)
N2—H2B···O1	0.895 (15)	1.832 (17)	2.613 (2)	144.6 (19)
N4—H4A···N3^{i}	0.84 (2)	2.45 (2)	3.105 (2)	136.1 (19)
N2—H2A···O3^{ii}	0.859 (15)	2.175 (18)	2.887 (2)	140 (2)

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2296).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bruker (2000). *SMART* (Version 5.625), *SAINT* (Version 6.01), *SHELXTL* (Version 6.10) and *SADABS* (Version 2.03). Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Yildiz, D. (2004). *Toxicon*, **43**, 619–632.

supplementary materials

Acta Cryst. (2007). E**63**, o4015 [**doi:10.1107/S1600536807043383**]

Ethyl 4-amino-5-cyano-6-[(2-hydroxyethyl)amino]-2-methylnicotinate

Q.-Y. Ren, H.-W. He, C.-F. Jin and Y.-C. Gu

Comment

Pyridine derivatives are important compounds because of their presence in numerous natural products. For example, nicotine is found in a wide variety of plants, playing an important role in metabolism and possessing a wide spectrum of biological activities (Yildiz, 2004). We report here the crystal structure of the title compound, (I).

In (I), all bond lengths and angles are within normal ranges (Allen *et al.*, 1987). Two intramolecular hydrogen bonds - O—H···N and N—H···O (Table 1), respectively, contribute to the approximately planar molecular conformation. In the crystal, intermolecular N—H···O and N—H···N hydrogen bonds (Table 1) link the molecules into ribbons parallel to direction [1–10] (Fig. 2).

Experimental

2-[Amino-(2-hydroxy-ethylamino)-methylene]-malononitrile (1.52 g, 10 mmol) and ethyl acetoacetate (1.6 g, 12 mmol) were added to a solution of Zinc nitrate (3.56 g, 20 mmol) in ethanol (15 ml) at room temperature while stirring. The mixture was then refluxed for 12 h. The precipitate was filtered and washed with water, recrystallized from ethanol to give the title compound (yield 39%). Crystals of (I) suitable for X-ray structure analysis were grown from ethanol.

Refinement

C-bound H atoms were placed in calculated positions, with C—H distances in the range 0.93–0.97 Å, and included in the final cycles of refinement using a riding-model approximation, with U_{iso}(H) = 1.2–1.5U_{eq}(C). The rest H atoms were located on a difference map, and refined with bond restraints O—H = 0.85 (2) Å, N—H = 0.85 (2) Å (for H4A) or 0.88 (2) Å (for H2A and H2B), with U_{iso}(H)=1.2Ueq(N) or 1.5Ueq(O).

Figures

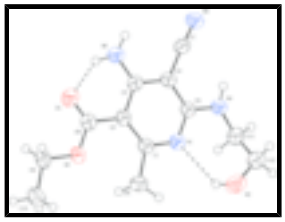

Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

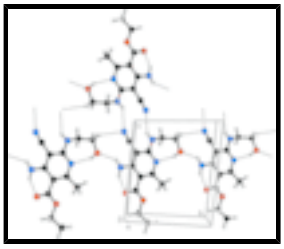

Fig. 2. A portion of the crystal packing showing hydrogen bonds as dashed lines.

Ethyl 4-amino-5-cyano-6-[(2-hydroxyethyl)amino]-2-methylnicotinate

Crystal data

$C_{12}H_{16}N_4O_3$	$Z = 2$
$M_r = 264.29$	$F_{000} = 280$
Triclinic, $P\overline{1}$	$D_x = 1.352$ Mg m^{-3}
Hall symbol: -p 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 7.8350$ (7) Å	Cell parameters from 1450 reflections
$b = 9.1368$ (9) Å	$\theta = 3.2$–20.8º
$c = 10.3272$ (10) Å	$\mu = 0.10$ mm^{-1}
$\alpha = 79.720$ (2)º	$T = 302$ (2) K
$\beta = 77.381$ (2)º	Block, colourless
$\gamma = 64.657$ (2)º	0.35 × 0.20 × 0.10 mm
$V = 648.97$ (11) Å^3	

Data collection

Bruker SMART CCD area detector diffractometer	2767 independent reflections
Radiation source: fine-focus sealed tube	1991 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.033$
$T = 302$(2) K	$\theta_{max} = 27.0$º
phi and ω scans	$\theta_{min} = 2.0$º
Absorption correction: multi-scan (SADABS; Bruker, 2000)	$h = -10 \rightarrow 10$
$T_{min} = 0.966$, $T_{max} = 0.990$	$k = -11 \rightarrow 11$
4521 measured reflections	$l = -11 \rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.058$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.172$	$w = 1/[\sigma^2(F_o^2) + (0.0955P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$

2767 reflections	$\Delta\rho_{max} = 0.27$ e Å^{-3}
186 parameters	$\Delta\rho_{min} = -0.29$ e Å^{-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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.4786 (3)	0.2753 (2)	0.45970 (17)	0.0404 (4)
C2	0.6483 (2)	0.1345 (2)	0.43570 (17)	0.0372 (4)
C3	0.7156 (2)	0.0230 (2)	0.54871 (17)	0.0359 (4)
C4	0.6070 (2)	0.0620 (2)	0.67547 (17)	0.0377 (4)
C5	0.4355 (2)	0.2018 (2)	0.68772 (17)	0.0362 (4)
C6	0.3927 (3)	0.4091 (3)	0.3547 (2)	0.0642 (7)
H6A	0.3536	0.3671	0.2930	0.096*
H6B	0.4861	0.4498	0.3080	0.096*
H6C	0.2837	0.4956	0.3963	0.096*
C7	0.6634 (3)	−0.0413 (2)	0.79306 (18)	0.0416 (5)
C8	0.7589 (3)	0.0936 (2)	0.30234 (18)	0.0419 (5)
C9	0.7834 (3)	0.1527 (2)	0.06883 (18)	0.0508 (5)
H9A	0.7946	0.0472	0.0532	0.061*
H9B	0.9111	0.1486	0.0606	0.061*
C10	0.6766 (3)	0.2811 (3)	−0.0303 (2)	0.0607 (6)
H10A	0.5483	0.2884	−0.0181	0.091*
H10B	0.7395	0.2536	−0.1188	0.091*
H10C	0.6734	0.3839	−0.0176	0.091*
C11	0.1222 (3)	0.3504 (2)	0.8233 (2)	0.0510 (5)
H11A	0.0591	0.3219	0.9096	0.061*
H11B	0.0634	0.3361	0.7558	0.061*
C12	0.0869 (4)	0.5254 (3)	0.8139 (2)	0.0636 (6)
H12A	−0.0431	0.5853	0.8561	0.076*
H12B	0.1725	0.5358	0.8634	0.076*
N1	0.3761 (2)	0.30703 (18)	0.58156 (14)	0.0422 (4)
N2	0.8725 (2)	−0.11440 (19)	0.53691 (17)	0.0473 (4)
H2B	0.928 (3)	−0.122 (2)	0.4515 (16)	0.057*
H2A	0.900 (3)	−0.174 (2)	0.6103 (17)	0.057*

N3	0.7004 (3)	−0.1181 (2)	0.89125 (17)	0.0560 (5)
N4	0.3234 (2)	0.23730 (19)	0.80702 (16)	0.0461 (4)
H4A	0.372 (3)	0.164 (3)	0.866 (2)	0.055*
O1	0.9108 (2)	−0.02184 (18)	0.28168 (15)	0.0628 (5)
O2	0.67814 (19)	0.19305 (16)	0.20107 (12)	0.0496 (4)
O3	0.1129 (3)	0.59692 (18)	0.68257 (16)	0.0728 (5)
H3A	0.111 (5)	0.532 (3)	0.633 (3)	0.109*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0431 (10)	0.0397 (9)	0.0313 (10)	−0.0113 (8)	−0.0064 (8)	0.0004 (7)
C2	0.0384 (10)	0.0388 (9)	0.0303 (9)	−0.0129 (8)	−0.0036 (7)	−0.0026 (7)
C3	0.0368 (9)	0.0315 (8)	0.0367 (10)	−0.0112 (7)	−0.0068 (7)	−0.0023 (7)
C4	0.0415 (10)	0.0340 (9)	0.0330 (10)	−0.0117 (8)	−0.0089 (8)	0.0019 (7)
C5	0.0379 (9)	0.0355 (9)	0.0310 (9)	−0.0115 (7)	−0.0052 (7)	−0.0018 (7)
C6	0.0650 (14)	0.0540 (12)	0.0347 (11)	0.0083 (11)	−0.0050 (10)	0.0024 (9)
C7	0.0395 (10)	0.0347 (9)	0.0383 (10)	−0.0056 (8)	−0.0027 (8)	−0.0018 (8)
C8	0.0452 (11)	0.0421 (10)	0.0360 (10)	−0.0155 (9)	−0.0056 (8)	−0.0050 (8)
C9	0.0582 (13)	0.0539 (12)	0.0309 (10)	−0.0174 (10)	0.0040 (9)	−0.0084 (9)
C10	0.0656 (15)	0.0747 (15)	0.0353 (11)	−0.0241 (12)	−0.0067 (10)	−0.0024 (10)
C11	0.0446 (11)	0.0516 (11)	0.0409 (11)	−0.0098 (9)	0.0026 (8)	−0.0024 (9)
C12	0.0740 (15)	0.0466 (11)	0.0450 (13)	−0.0019 (10)	−0.0076 (11)	−0.0041 (9)
N1	0.0429 (9)	0.0391 (8)	0.0318 (8)	−0.0065 (7)	−0.0040 (7)	−0.0007 (6)
N2	0.0499 (10)	0.0387 (8)	0.0378 (9)	−0.0058 (7)	−0.0049 (8)	0.0002 (7)
N3	0.0602 (11)	0.0499 (10)	0.0359 (9)	−0.0054 (8)	−0.0073 (8)	0.0056 (8)
N4	0.0455 (10)	0.0412 (9)	0.0321 (9)	−0.0025 (7)	−0.0042 (7)	0.0027 (7)
O1	0.0578 (9)	0.0564 (9)	0.0436 (8)	0.0027 (7)	0.0005 (7)	−0.0081 (7)
O2	0.0509 (8)	0.0531 (8)	0.0286 (7)	−0.0074 (6)	−0.0020 (6)	−0.0051 (6)
O3	0.0843 (12)	0.0443 (8)	0.0532 (10)	−0.0013 (8)	0.0004 (8)	0.0061 (7)

Geometric parameters (Å, °)

C1—N1	1.342 (2)	C9—C10	1.493 (3)
C1—C2	1.410 (2)	C9—H9A	0.9700
C1—C6	1.504 (2)	C9—H9B	0.9700
C2—C3	1.436 (2)	C10—H10A	0.9600
C2—C8	1.474 (2)	C10—H10B	0.9600
C3—N2	1.330 (2)	C10—H10C	0.9600
C3—C4	1.409 (2)	C11—N4	1.461 (2)
C4—C5	1.403 (2)	C11—C12	1.490 (3)
C4—C7	1.424 (2)	C11—H11A	0.9700
C5—N1	1.344 (2)	C11—H11B	0.9700
C5—N4	1.349 (2)	C12—O3	1.409 (3)
C6—H6A	0.9600	C12—H12A	0.9700
C6—H6B	0.9600	C12—H12B	0.9700
C6—H6C	0.9600	N2—H2B	0.895 (15)
C7—N3	1.142 (2)	N2—H2A	0.859 (15)
C8—O1	1.212 (2)	N4—H4A	0.84 (2)

C8—O2	1.333 (2)	O3—H3A	0.861 (17)
C9—O2	1.452 (2)		
N1—C1—C2	123.25 (16)	C10—C9—H9B	110.1
N1—C1—C6	111.78 (16)	H9A—C9—H9B	108.4
C2—C1—C6	124.95 (16)	C9—C10—H10A	109.5
C1—C2—C3	117.65 (15)	C9—C10—H10B	109.5
C1—C2—C8	124.27 (16)	H10A—C10—H10B	109.5
C3—C2—C8	118.08 (16)	C9—C10—H10C	109.5
N2—C3—C4	119.91 (16)	H10A—C10—H10C	109.5
N2—C3—C2	122.47 (16)	H10B—C10—H10C	109.5
C4—C3—C2	117.61 (15)	N4—C11—C12	115.13 (18)
C5—C4—C3	120.14 (15)	N4—C11—H11A	108.5
C5—C4—C7	118.39 (15)	C12—C11—H11A	108.5
C3—C4—C7	121.43 (15)	N4—C11—H11B	108.5
N1—C5—N4	117.00 (15)	C12—C11—H11B	108.5
N1—C5—C4	121.62 (15)	H11A—C11—H11B	107.5
N4—C5—C4	121.38 (16)	O3—C12—C11	114.25 (18)
C1—C6—H6A	109.5	O3—C12—H12A	108.7
C1—C6—H6B	109.5	C11—C12—H12A	108.7
H6A—C6—H6B	109.5	O3—C12—H12B	108.7
C1—C6—H6C	109.5	C11—C12—H12B	108.7
H6A—C6—H6C	109.5	H12A—C12—H12B	107.6
H6B—C6—H6C	109.5	C1—N1—C5	119.62 (15)
N3—C7—C4	176.31 (18)	C3—N2—H2B	110.1 (13)
O1—C8—O2	120.50 (17)	C3—N2—H2A	115.4 (15)
O1—C8—C2	124.55 (18)	H2B—N2—H2A	134 (2)
O2—C8—C2	114.94 (16)	C5—N4—C11	123.93 (15)
O2—C9—C10	107.96 (16)	C5—N4—H4A	109.6 (16)
O2—C9—H9A	110.1	C11—N4—H4A	123.3 (16)
C10—C9—H9A	110.1	C8—O2—C9	115.70 (15)
O2—C9—H9B	110.1	C12—O3—H3A	105 (2)
N1—C1—C2—C3	−1.8 (3)	C1—C2—C8—O1	175.22 (19)
C6—C1—C2—C3	176.79 (18)	C3—C2—C8—O1	−5.7 (3)
N1—C1—C2—C8	177.27 (16)	C1—C2—C8—O2	−5.8 (3)
C6—C1—C2—C8	−4.2 (3)	C3—C2—C8—O2	173.23 (14)
C1—C2—C3—N2	179.06 (17)	N4—C11—C12—O3	78.5 (3)
C8—C2—C3—N2	−0.1 (3)	C2—C1—N1—C5	0.4 (3)
C1—C2—C3—C4	0.2 (2)	C6—C1—N1—C5	−178.30 (17)
C8—C2—C3—C4	−178.96 (15)	N4—C5—N1—C1	−177.88 (16)
N2—C3—C4—C5	−176.27 (17)	C4—C5—N1—C1	2.6 (3)
C2—C3—C4—C5	2.7 (2)	N1—C5—N4—C11	18.9 (3)
N2—C3—C4—C7	1.3 (3)	C4—C5—N4—C11	−161.55 (17)
C2—C3—C4—C7	−179.74 (15)	C12—C11—N4—C5	−83.0 (2)
C3—C4—C5—N1	−4.2 (3)	O1—C8—O2—C9	0.1 (3)
C7—C4—C5—N1	178.16 (15)	C2—C8—O2—C9	−178.88 (15)
C3—C4—C5—N4	176.30 (16)	C10—C9—O2—C8	−177.24 (15)
C7—C4—C5—N4	−1.4 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3A···N1	0.861 (17)	2.25 (3)	2.780 (2)	120 (3)
N2—H2B···O1	0.895 (15)	1.832 (17)	2.613 (2)	144.6 (19)
N4—H4A···N3^{i}	0.84 (2)	2.45 (2)	3.105 (2)	136.1 (19)
N2—H2A···O3^{ii}	0.859 (15)	2.175 (18)	2.887 (2)	140 (2)
C12—H12A···N3^{iii}	0.97	2.62	3.442 (3)	142

Symmetry codes: (i) −*x*+1, −*y*, −*z*+2; (ii) *x*+1, *y*−1, *z*; (iii) *x*−1, *y*+1, *z*.

Fig. 1

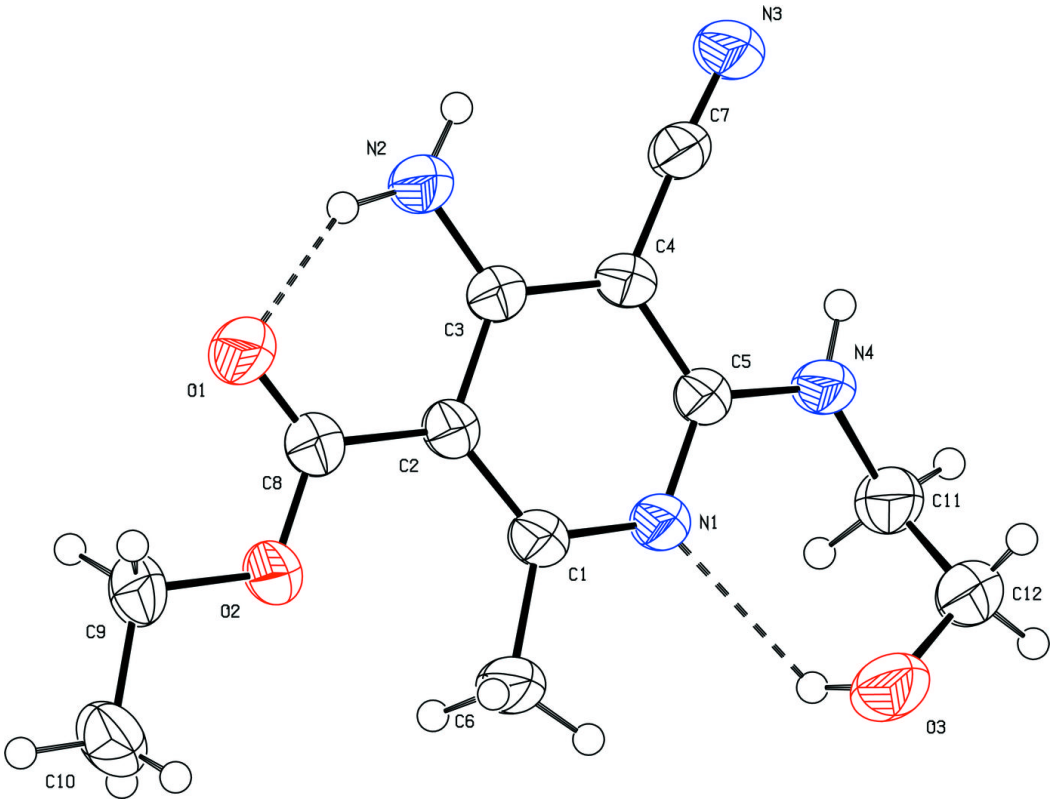

Fig. 2