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Ethyl 4-hydroxymethyl-2-methylpyridine-5-carboxylate

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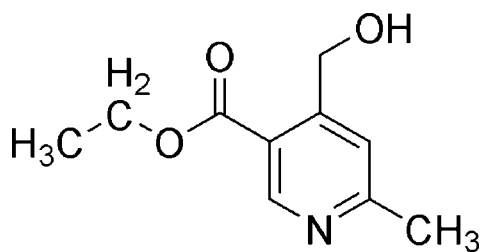
Received 14 April 2008; accepted 14 April 2008

 Key indicators: single-crystal X-ray study; $T = 87$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.050; wR factor = 0.134; data-to-parameter ratio = 15.3.

The title compound, $\text{C}_{10}\text{H}_{13}\text{NO}_3$, was obtained as a by-product of the aldolization reaction of furo[3,4-*c*]pyridin-3(1*H*)-one with thiophene-2-carboxaldehyde. The substituents on the pyridine ring are nearly coplanar, with an 8.1 (2°) rotation of the hydroxymethyl group from this plane. The molecules assemble in the crystal structure as chains *via* $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonding between the pyridine N atom and a neighbouring hydroxymethyl OH group.

Related literature

For related literature, see: Goswami *et al.* (2006), Wu *et al.* (2006). For bond-length data, see: Allen *et al.*, (1987).



Experimental

Crystal data

 $\text{C}_{10}\text{H}_{13}\text{NO}_3$
 $M_r = 195.21$
 Monoclinic, $P2_1/n$
 $a = 4.4998$ (2) Å
 $b = 15.4499$ (8) Å
 $c = 14.2036$ (7) Å

 $\beta = 96.417$ (1) $^\circ$
 $V = 981.27$ (8) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

 $\mu = 0.10$ mm⁻¹
 $T = 87$ (2) K
 $0.32 \times 0.18 \times 0.12$ mm

Data collection

 Siemens SMART CCD diffractometer
 Absorption correction: none
 5759 measured reflections

 1987 independent reflections
 1786 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.081$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.134$
 $S = 1.02$
 1987 reflections

 130 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.30$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.28$ e Å⁻³
Table 1

 Hydrogen-bond geometry (Å, $^\circ$).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O3}-\text{H3}\cdots\text{N1}^{\dagger}$	0.82	2.01	2.8227 (17)	170

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

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2697).

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supplementary materials

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Comment

The molecular structure of the title compound is shown in Fig. 1. The bond lengths and angles are normal (Allen *et al.*, 1987). The ethyl ester group is nearly coplanar with the pyridine ring (C1-C5,N1 rmsd 0.0064 Å; C2,C8,C9,C10,O1,O2 rmsd 0.0064 Å, interplanar angle 2.17 (9)°). The hydroxymethyl group is rotated slightly out of the plane (O3—C7—C3—C4 8.1 (2)°).

The molecules in the crystal are connected *via* hydrogen bonding between the pyridine N atom and an adjacent OH group (Table 1) to give chains along the *c* axis (Figure 2a). These chains are stacked along the *a* axis (Figure 2 b). Similar hydrogen bonding interactions are observed in other hydroxymethyl substituted pyridines (Goswami *et al.*, 2006, Wu *et al.*, 2006).

Experimental

The title compound was obtained as a by-product of the aldolization reaction of furo[3,4-*c*]pyridin-3(1*H*)-one with thiophene-2-carboxaldehyde. The desired product was not isolated, only the starting material and the title compound were characterized after the reaction.

Ethyl 4-(hydroxymethyl)-6-methylnicotinate (I): Furo[3,4-*c*]pyridin-3(1*H*)-one (II) (110 mg, 0.74 mmol, 1 eq.) was suspended in EtOH (15 ml) at 65°C. Thiophene-2-carboxaldehyde (III) (99 mg, 0.88 mmol) and triethylamine (18 mg, 0.18 mmol) were then added and the reaction mixture stirred at 80°C for 6 days. After cooling to room temperature the reaction was quenched with 1*M* HCl and extracted with EtOAc. The organic layer was rinsed with water and dried over MgSO₄. Removal of MgSO₄ by filtration and evaporation of solvent under reduced pressure gave the crude product. This product was dissolved in dichloromethane and stored at 4°C to yield colorless crystals (25 mg, 17% yield) which were isolated by filtration and identified as the title compound. ¹H NMR (400 MHz, CD₃)₂SO, 298 K) δ 8.83 (s, 1 H), 7.03 (s, 1 H), 5.43 (s, 1 H), 4.83 (br s, 2 H), 4.30 (q, *J* = 7.1 Hz, 2 H), 2.54 (s, 3 H), 1.32 (t, *J* = 7.1 Hz, 3 H). LCMS (APCI⁺) calcd for C₁₀H₁₃NO₃ 195 (MH⁺), found 196.

Refinement

Hydrogen atoms were placed in calculated positions and refined using the riding model [O—H 0.82 Å, C—H 0.93–0.97 Å], with $U_{\text{iso}}(\text{H}) = 1.5$ times $U_{\text{eq}}(\text{O})$ and $U_{\text{iso}}(\text{H}) = 1.2$ or 1.5 times $U_{\text{eq}}(\text{C})$.

Figures

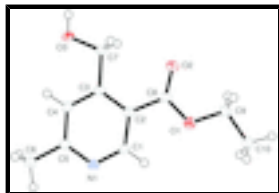


Fig. 1. Structure of (I) showing 50% probability displacement ellipsoids for non-hydrogen atoms and hydrogen atoms as arbitrary spheres.

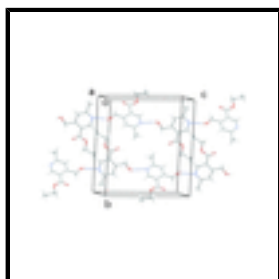


Fig. 2. Illustration of the arrangement of the complex (I) in the crystal along the *a* axis showing pyridine N...H—O hydrogen bonding arrangement.

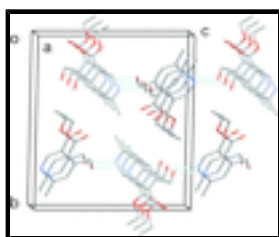


Fig. 3. Illustration of the arrangement of the complex (I) in the crystal along the *a* axis showing stacking of hydrogen bonded chains.

Ethyl 4-hydroxymethyl-2-methylpyridine-5-carboxylate

Crystal data

$C_{10}H_{13}NO_3$

$M_r = 195.21$

Monoclinic, $P2_1/n$

$a = 4.4998$ (2) Å

$b = 15.4499$ (8) Å

$c = 14.2036$ (7) Å

$\beta = 96.417$ (1)°

$V = 981.27$ (8) Å³

$Z = 4$

$F(000) = 416$

$D_x = 1.321$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4149 reflections

$\theta = 2.0$ – 26.3 °

$\mu = 0.10$ mm⁻¹

$T = 87$ K

Needle, colourless

$0.32 \times 0.18 \times 0.12$ mm

Data collection

Siemens SMART CCD
diffractometer

Radiation source: fine-focus sealed tube
graphite

Area-detector ω scans

5759 measured reflections

1987 independent reflections

1786 reflections with $I > 2\sigma(I)$

$R_{int} = 0.081$

$\theta_{max} = 26.3$ °, $\theta_{min} = 2.0$ °

$h = -5 \rightarrow 5$

$k = -19 \rightarrow 17$

$l = -17 \rightarrow 12$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.049$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.134$	H-atom parameters constrained
$S = 1.02$	$w = 1/[\sigma^2(F_o^2) + (0.0608P)^2 + 0.7105P]$
1987 reflections	where $P = (F_o^2 + 2F_c^2)/3$
130 parameters	$(\Delta/\sigma)_{\max} < 0.001$
0 restraints	$\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.4226 (3)	0.73560 (9)	0.54034 (9)	0.0197 (3)
O1	0.7485 (3)	0.96228 (7)	0.64708 (8)	0.0207 (3)
O2	0.5468 (3)	0.95300 (8)	0.78490 (8)	0.0255 (3)
O3	-0.0290 (3)	0.75164 (8)	0.84444 (8)	0.0215 (3)
H3	-0.0566	0.7606	0.8997	0.032*
C1	0.5219 (4)	0.81023 (11)	0.58079 (11)	0.0184 (4)
H1	0.6416	0.8453	0.5474	0.022*
C2	0.4576 (3)	0.83885 (10)	0.66979 (11)	0.0167 (3)
C3	0.2720 (3)	0.78652 (11)	0.72042 (10)	0.0167 (3)
C4	0.1707 (4)	0.70920 (11)	0.67810 (11)	0.0189 (4)
H4	0.0480	0.6732	0.7092	0.023*
C5	0.2507 (4)	0.68475 (11)	0.58930 (11)	0.0191 (4)
C6	0.1465 (5)	0.60006 (12)	0.54492 (12)	0.0290 (4)
H6A	-0.0682	0.5987	0.5366	0.044*
H6B	0.2204	0.5532	0.5854	0.044*
H6C	0.2206	0.5942	0.4844	0.044*
C7	0.1868 (4)	0.81091 (11)	0.81720 (11)	0.0184 (4)
H7A	0.3629	0.8099	0.8633	0.022*

supplementary materials

H7B	0.1053	0.8691	0.8152	0.022*
C8	0.5846 (3)	0.92273 (11)	0.70790 (11)	0.0184 (4)
C9	0.8760 (4)	1.04629 (11)	0.67761 (12)	0.0218 (4)
H9A	1.0137	1.0397	0.7348	0.026*
H9B	0.7187	1.0860	0.6906	0.026*
C10	1.0378 (4)	1.08024 (12)	0.59824 (12)	0.0242 (4)
H10A	1.1936	1.0406	0.5864	0.036*
H10B	1.1235	1.1357	0.6156	0.036*
H10C	0.8994	1.0861	0.5421	0.036*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0253 (7)	0.0210 (7)	0.0131 (6)	0.0006 (5)	0.0027 (5)	0.0001 (5)
O1	0.0250 (6)	0.0200 (6)	0.0180 (6)	-0.0041 (5)	0.0057 (5)	-0.0031 (5)
O2	0.0332 (7)	0.0261 (7)	0.0180 (6)	-0.0048 (5)	0.0073 (5)	-0.0061 (5)
O3	0.0263 (6)	0.0275 (6)	0.0115 (5)	-0.0033 (5)	0.0060 (5)	-0.0002 (5)
C1	0.0216 (8)	0.0205 (8)	0.0137 (7)	-0.0002 (6)	0.0043 (6)	0.0020 (6)
C2	0.0169 (7)	0.0200 (8)	0.0127 (7)	0.0034 (6)	0.0001 (6)	0.0000 (6)
C3	0.0174 (7)	0.0216 (8)	0.0108 (7)	0.0038 (6)	0.0005 (6)	0.0028 (6)
C4	0.0223 (8)	0.0220 (8)	0.0123 (7)	-0.0013 (6)	0.0022 (6)	0.0032 (6)
C5	0.0237 (8)	0.0206 (8)	0.0127 (7)	0.0007 (6)	0.0005 (6)	0.0001 (6)
C6	0.0450 (11)	0.0257 (9)	0.0170 (8)	-0.0089 (8)	0.0062 (7)	-0.0030 (7)
C7	0.0215 (8)	0.0218 (8)	0.0123 (7)	-0.0003 (6)	0.0032 (6)	0.0003 (6)
C8	0.0191 (7)	0.0210 (8)	0.0151 (7)	0.0024 (6)	0.0021 (6)	0.0006 (6)
C9	0.0255 (8)	0.0184 (8)	0.0217 (8)	-0.0018 (6)	0.0026 (7)	-0.0035 (6)
C10	0.0270 (8)	0.0234 (9)	0.0219 (8)	-0.0051 (7)	0.0015 (7)	-0.0014 (7)

Geometric parameters (\AA , $^\circ$)

N1—C1	1.342 (2)	C4—H4	0.9300
N1—C5	1.349 (2)	C5—C6	1.504 (2)
O1—C8	1.344 (2)	C6—H6A	0.9600
O1—C9	1.4649 (19)	C6—H6B	0.9600
O2—C8	1.219 (2)	C6—H6C	0.9600
O3—C7	1.420 (2)	C7—H7A	0.9700
O3—H3	0.8200	C7—H7B	0.9700
C1—C2	1.400 (2)	C9—C10	1.503 (2)
C1—H1	0.9300	C9—H9A	0.9700
C2—C3	1.415 (2)	C9—H9B	0.9700
C2—C8	1.493 (2)	C10—H10A	0.9600
C3—C4	1.391 (2)	C10—H10B	0.9600
C3—C7	1.515 (2)	C10—H10C	0.9600
C4—C5	1.402 (2)		
C1—N1—C5	117.54 (14)	H6B—C6—H6C	109.5
C8—O1—C9	115.95 (13)	O3—C7—C3	109.70 (13)
C7—O3—H3	109.5	O3—C7—H7A	109.7
N1—C1—C2	124.43 (15)	C3—C7—H7A	109.7

N1—C1—H1	117.8	O3—C7—H7B	109.7
C2—C1—H1	117.8	C3—C7—H7B	109.7
C1—C2—C3	118.16 (15)	H7A—C7—H7B	108.2
C1—C2—C8	119.48 (14)	O2—C8—O1	122.94 (15)
C3—C2—C8	122.36 (14)	O2—C8—C2	124.91 (15)
C4—C3—C2	117.04 (14)	O1—C8—C2	112.14 (13)
C4—C3—C7	120.10 (14)	O1—C9—C10	107.08 (13)
C2—C3—C7	122.86 (14)	O1—C9—H9A	110.3
C3—C4—C5	121.03 (15)	C10—C9—H9A	110.3
C3—C4—H4	119.5	O1—C9—H9B	110.3
C5—C4—H4	119.5	C10—C9—H9B	110.3
N1—C5—C4	121.78 (15)	H9A—C9—H9B	108.6
N1—C5—C6	117.43 (14)	C9—C10—H10A	109.5
C4—C5—C6	120.79 (15)	C9—C10—H10B	109.5
C5—C6—H6A	109.5	H10A—C10—H10B	109.5
C5—C6—H6B	109.5	C9—C10—H10C	109.5
H6A—C6—H6B	109.5	H10A—C10—H10C	109.5
C5—C6—H6C	109.5	H10B—C10—H10C	109.5
H6A—C6—H6C	109.5		
C5—N1—C1—C2	-0.4 (2)	C3—C4—C5—N1	-1.5 (2)
N1—C1—C2—C3	-0.9 (2)	C3—C4—C5—C6	178.53 (15)
N1—C1—C2—C8	179.21 (14)	C4—C3—C7—O3	-8.1 (2)
C1—C2—C3—C4	1.0 (2)	C2—C3—C7—O3	172.83 (13)
C8—C2—C3—C4	-179.12 (14)	C9—O1—C8—O2	-1.5 (2)
C1—C2—C3—C7	-179.91 (14)	C9—O1—C8—C2	178.51 (12)
C8—C2—C3—C7	0.0 (2)	C1—C2—C8—O2	-178.81 (16)
C2—C3—C4—C5	0.1 (2)	C3—C2—C8—O2	1.3 (2)
C7—C3—C4—C5	-178.98 (14)	C1—C2—C8—O1	1.2 (2)
C1—N1—C5—C4	1.6 (2)	C3—C2—C8—O1	-178.66 (13)
C1—N1—C5—C6	-178.42 (15)	C8—O1—C9—C10	-177.70 (13)

Hydrogen-bond geometry (Å, °)

<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>
O3—H3 \cdots N1 ⁱ	0.82	2.01	2.8227 (17)	170.

Symmetry codes: (i) $x-1/2, -y+3/2, z+1/2$.

Fig. 1

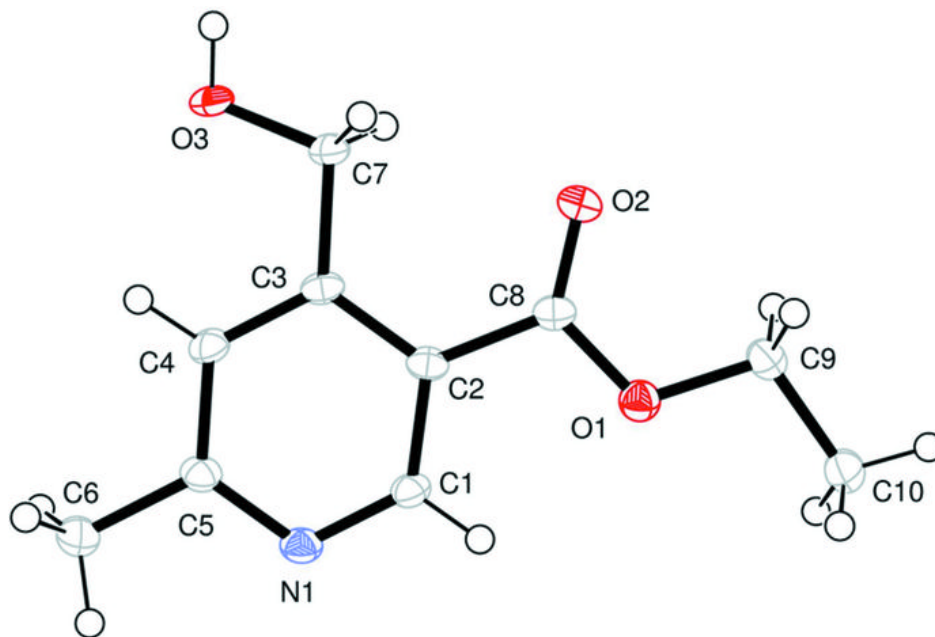


Fig. 2

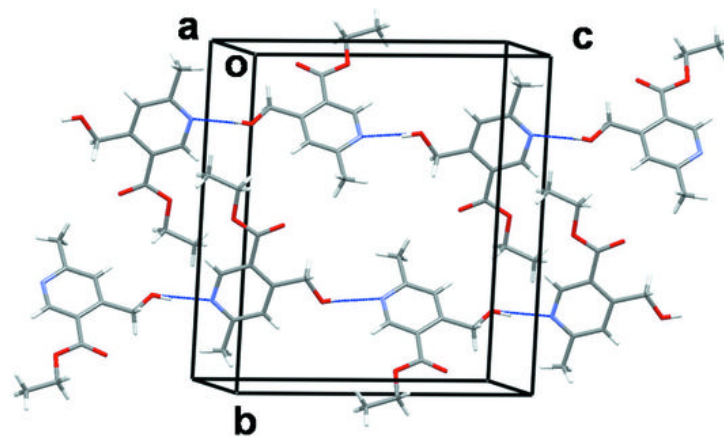


Fig. 3

