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Ethyl 4-oxo-1,4-dihydropyridine-3-carboxylate

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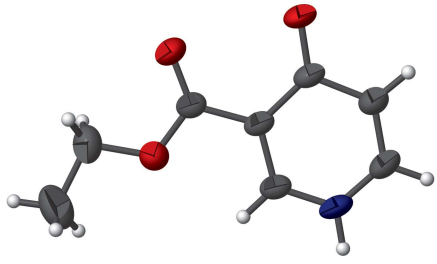
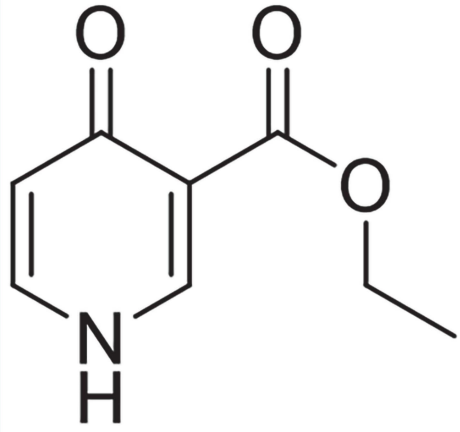
The title compound, $C_8H_9NO_3$, likely generated through hydrolysis and esterification of 3′-carboxy-3-methyl-(1,4′-bipyridin)-1-ium chloride by ethanol, which contained water, has a nearly planar conformation. The crystal structure is sustained by one-dimensional chains along the *a*-axis direction based on bifurcated N—H···(O,O) hydrogen bonds between the NH group of the 4-oxo-1,4-dihydropyridine ring and the two carbonyl O atoms.

3D view



Chemical scheme



Structure description

The title compound (Fig. 1) was first synthesized by Ross (1966). It may be a potential inhibitor of the glycolytic process by which many cancer cells derive an appreciable proportion of their energy requirement (Ross, 1966). Balogh *et al.* (1980) demonstrated that the compound exhibited antimicrobial activity. In our study, the compound was obtained serendipitously during an attempt to grow single crystals of 3′-carboxy-3-methyl-(1,4′-bipyridin)-1-ium chloride in ethanol. The compound has a nearly planar conformation, as evidenced by the dihedral angle between the 4-oxo-1,4-dihydropyridine ring and the ester moiety [2.3 (2)°]. In the crystal, the molecules form chains propagating parallel to the *a*-axis through bifurcated hydrogen bonds between the NH group and the two carbonyl oxygen atoms. The hydrogen bond parameters for NH···O=C (ring) are: 1.96 (2) Å for bond length, and 134.9 (17)° for the bond angle. The corresponding parameters for NH···O=C (ester) are 2.15 (2) Å and 139.6 (17)° (Fig. 2, Table 1).

Synthesis and crystallization

The title compound was obtained during an attempt to grow single crystals of 3′-carboxy-3-methyl-(1,4′-bipyridin)-1-ium chloride by slow evaporation of an ethanolic solution. 3′-Carboxy-3-methyl-(1,4′-bipyridin)-1-ium chloride was dissolved in bulk ethanol at 343 K, and then the resulting solution was left in a refrigerator. Colorless plate-shaped

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	0.90 (2)	1.96 (2)	2.6771 (15)	134.9 (17)
N1—H1···O2^{i}	0.90 (2)	2.15 (2)	2.9002 (17)	139.6 (17)

Symmetry code: (i) $x-1, y, z$.

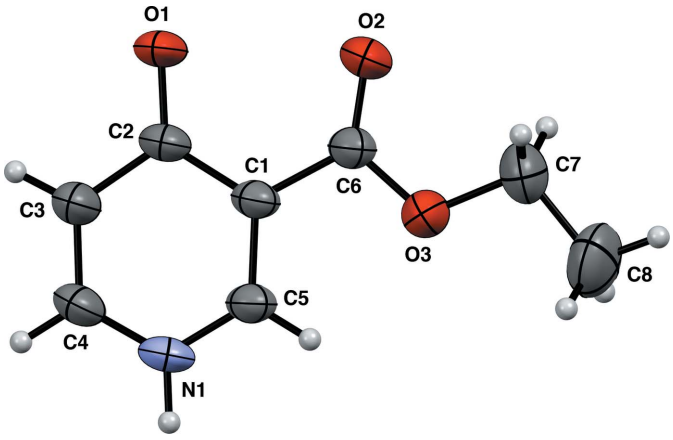


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

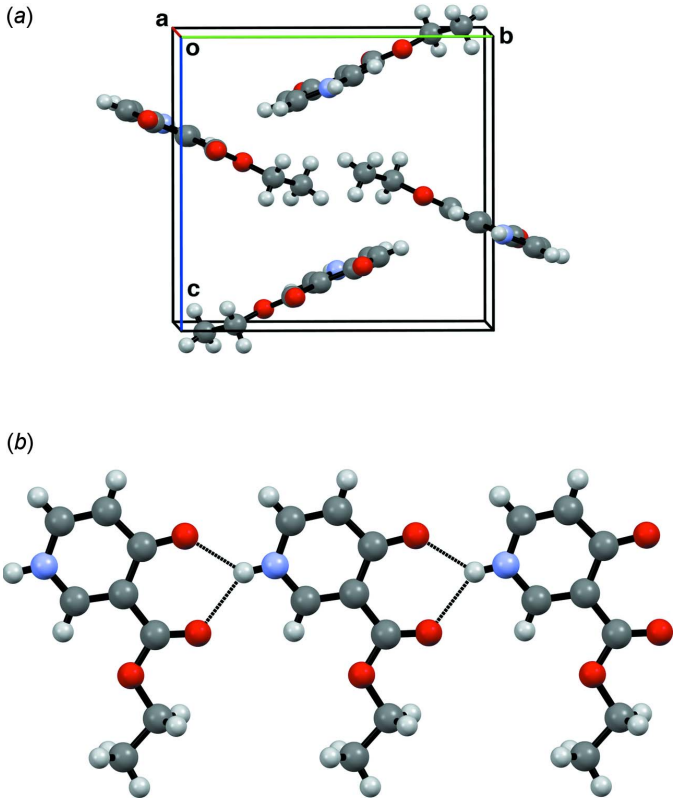


Figure 2
(*a*) Packing of the molecules in the title compound viewed along the *a* axis; (*b*) Chain sustained by bifurcated hydrogen bonds between the NH group and two carbonyl O atoms (blue dashed lines).

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_8H_9NO_3$
M_r	167.16
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	6.4973 (2), 11.5323 (5), 11.2908 (5)
β (°)	91.500 (4)
V (Å^3)	845.72 (6)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.86
Crystal size (mm)	0.07 × 0.03 × 0.02
Data collection	
Diffractometer	Rigaku Oxford Diffraction, Synergy Custom system, HyPix
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2020)
T_{min}, T_{max}	0.311, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5379, 1693, 1456
R_{int}	0.022
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.633
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.129, 1.11
No. of reflections	1693
No. of parameters	114
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.21, −0.22

Computer programs: *CrysAlis PRO* (Rigaku OD, 2020), *SHELXS* (Sheldrick, 2008), *SHELXL* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2020) and *OLEX2* (Dolomanov *et al.*, 2009).

crystals (Fig. 3) were harvested after several days. Structure determination by single-crystal X-ray diffraction revealed the identity of the crystals to be ethyl 4-oxo-1,4-dihydropyridine-3-carboxylate. Hydrolysis and esterification of 3′-carboxy-3-methyl-[1,4′-bipyridin]-1-ium chloride may have led to the title compound (Fig. 4).

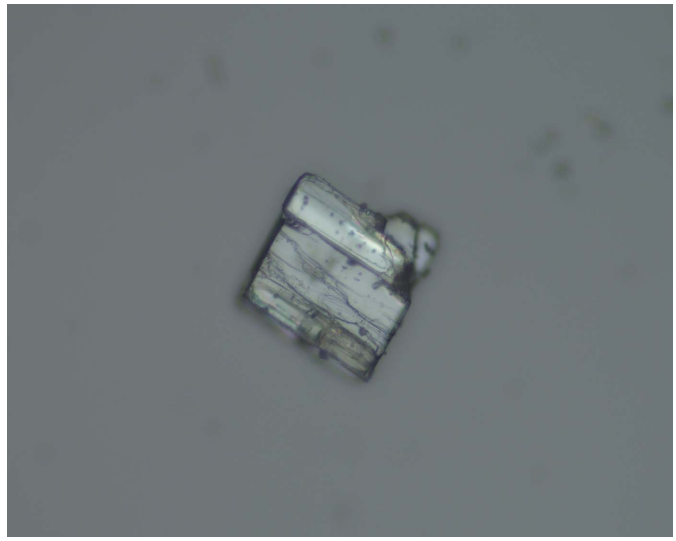


Figure 3
A representative crystal of I.

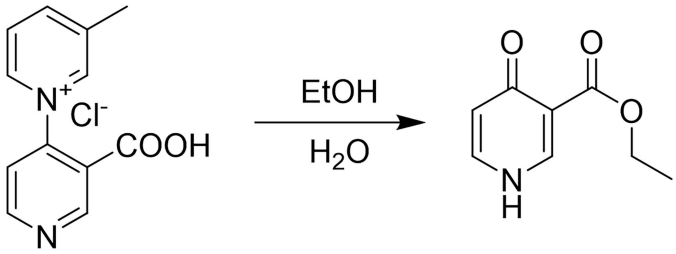


Figure 4
Reaction scheme.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Funding information

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full crystallographic data

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Crystal data

$C_8H_9NO_3$
M_r = 167.16
Monoclinic, $P2_1/c$
a = 6.4973 (2) Å
b = 11.5323 (5) Å
c = 11.2908 (5) Å
β = 91.500 (4)°
V = 845.72 (6) Å^3
Z = 4
$F(000)$ = 352
D_x = 1.313 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 3630 reflections
θ = 6.8–76.4°
μ = 0.86 mm^{-1}
T = 293 K
Needle, clear light colourless
0.07 × 0.03 × 0.02 mm

Data collection

Rigaku Oxford Diffraction, Synergy Custom system, HyPix diffractometer
Radiation source: Rotating-anode X-ray tube, Rigaku (Cu) X-ray Source
Mirror monochromator
Detector resolution: 10.0000 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2020)
T_{min} = 0.311, T_{max} = 1.000
5379 measured reflections
1693 independent reflections
1456 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 77.4°, θ_{min} = 6.8°
h = −8→7
k = −14→5
l = −13→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.129
S = 1.11
1693 reflections
114 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0674P)^2 + 0.1472P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.52166 (14)	0.40585 (10)	0.20366 (11)	0.0600 (4)
O2	0.57531 (15)	0.62403 (10)	0.09977 (11)	0.0584 (4)
O3	0.28325 (16)	0.71651 (9)	0.05152 (11)	0.0555 (3)
N1	−0.08871 (17)	0.47182 (12)	0.17157 (11)	0.0471 (3)
C1	0.25305 (18)	0.53513 (12)	0.14051 (12)	0.0388 (3)
C2	0.33512 (19)	0.42840 (13)	0.19022 (13)	0.0436 (4)
C3	0.1821 (2)	0.34638 (14)	0.22568 (15)	0.0538 (4)
H3	0.224295	0.274979	0.255937	0.065*
C4	−0.0203 (2)	0.36993 (15)	0.21635 (15)	0.0517 (4)
H4	−0.114786	0.315080	0.241186	0.062*
C5	0.04315 (19)	0.55121 (13)	0.13385 (13)	0.0421 (3)
H5	−0.008399	0.619967	0.101877	0.051*
C6	0.3901 (2)	0.62675 (12)	0.09660 (13)	0.0421 (3)
C7	0.3996 (3)	0.81144 (16)	0.00264 (19)	0.0663 (5)
H7A	0.470155	0.786241	−0.067519	0.080*
H7B	0.501453	0.839160	0.060290	0.080*
C8	0.2495 (4)	0.90531 (19)	−0.0281 (2)	0.0899 (7)
H8A	0.317924	0.965688	−0.070384	0.135*
H8B	0.194250	0.936516	0.043203	0.135*
H8C	0.139659	0.874119	−0.076909	0.135*
H1	−0.224 (3)	0.4880 (17)	0.1645 (17)	0.071 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0234 (5)	0.0609 (7)	0.0956 (9)	0.0027 (4)	0.0007 (5)	0.0191 (6)
O2	0.0296 (5)	0.0541 (7)	0.0918 (9)	−0.0041 (4)	0.0038 (5)	0.0110 (6)
O3	0.0411 (6)	0.0456 (6)	0.0799 (8)	0.0017 (4)	0.0029 (5)	0.0130 (5)
N1	0.0211 (5)	0.0596 (8)	0.0608 (7)	−0.0002 (5)	0.0018 (5)	0.0002 (6)
C1	0.0255 (6)	0.0448 (8)	0.0460 (7)	0.0000 (5)	0.0022 (5)	−0.0028 (6)
C2	0.0241 (6)	0.0512 (8)	0.0555 (8)	−0.0001 (5)	0.0018 (5)	0.0018 (6)
C3	0.0321 (7)	0.0519 (9)	0.0774 (11)	−0.0012 (6)	0.0020 (7)	0.0147 (8)
C4	0.0288 (7)	0.0588 (9)	0.0678 (10)	−0.0075 (6)	0.0045 (6)	0.0075 (7)
C5	0.0279 (6)	0.0467 (8)	0.0517 (8)	0.0028 (5)	0.0006 (5)	−0.0024 (6)
C6	0.0307 (6)	0.0423 (7)	0.0532 (8)	0.0010 (5)	0.0016 (5)	−0.0022 (6)
C7	0.0674 (11)	0.0478 (9)	0.0842 (12)	−0.0088 (8)	0.0079 (9)	0.0110 (8)
C8	0.1063 (19)	0.0616 (13)	0.1014 (17)	0.0040 (11)	−0.0053 (14)	0.0288 (11)

Geometric parameters (Å, º)

O1—C2	1.2450 (16)	C1—C2	1.449 (2)
O2—C6	1.2032 (16)	C1—C5	1.3765 (17)
O3—C6	1.3395 (17)	C1—C6	1.4760 (19)
O3—C7	1.448 (2)	C2—C3	1.437 (2)
N1—C4	1.350 (2)	C3—C4	1.344 (2)

N1—C5	1.3314 (19)	C7—C8	1.492 (3)
C6—O3—C7	117.28 (12)	C4—C3—C2	121.85 (15)
C5—N1—C4	120.66 (12)	C3—C4—N1	121.15 (14)
C2—C1—C6	121.28 (11)	N1—C5—C1	122.33 (13)
C5—C1—C2	119.33 (12)	O2—C6—O3	122.66 (13)
C5—C1—C6	119.40 (12)	O2—C6—C1	125.66 (13)
O1—C2—C1	124.89 (13)	O3—C6—C1	111.68 (11)
O1—C2—C3	120.46 (14)	O3—C7—C8	107.00 (16)
C3—C2—C1	114.65 (12)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.90 (2)	1.96 (2)	2.6771 (15)	134.9 (17)
N1—H1···O2^{i}	0.90 (2)	2.15 (2)	2.9002 (17)	139.6 (17)

Symmetry code: (i) $x-1$, y, z.