

Ethyl 2-ethoxy-1,6-dihydropyrimidine-5-carboxylate

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Key indicators

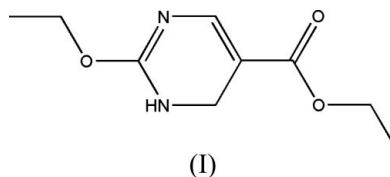
Single-crystal X-ray study
 $T = 294$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.045
 wR factor = 0.141
Data-to-parameter ratio = 15.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $\text{C}_9\text{H}_{14}\text{N}_2\text{O}_3$, the non-H atoms are approximately coplanar. The molecules are linked through intermolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds, forming chains that run along the b axis.

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Comment

In an attempt to reduce 2-ethoxypyrimidine-5-carboxylic acid ethyl ester by LiAlH_4 to (2-ethoxypyrimidine-5-yl)methanol, a key intermediate to a new potent herbicide, we obtained the title compound, (I) (Fig. 1).



In the pyrimidine ring of compound (I), the $\text{C}-\text{N}$ and $\text{C}-\text{C}$ bond lengths are intermediate between single and double bonds (Table 1). This is due to a strong electron delocalization throughout the ring that extends to the carboxylic group. The longer bonds within the ring, $\text{N1}-\text{C4}$ and $\text{C4}-\text{C3}$, approximate the reported values for single $\text{N}-\text{C}$ and $\text{C}-\text{C}$ bonds, respectively (Allen *et al.*, 1987), giving evidence of the reduction of the pyridine ring during the synthetic procedure. The non-H atoms are approximately coplanar, with an average deviation of 0.03 (2) Å. The molecules are linked through intermolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds, forming chains that run along the b axis (Fig. 2 and Table 2). The chains are further assembled in sheets, but there is no evidence of further hydrogen-bonding interactions.

Experimental

To a suspension of LiAlH_4 (1.27 g, 30.0 mmol) in 120 ml anhydrous tetrahydrofuran was added ethyl 2-ethoxypyrimidine-5-carboxylic acid ethyl ester (2.4 g, 12.4 mmol) at room temperature. The reaction mixture was stirred at room temperature for 5 h. To the mixture, cooled with an ice-bath, were successively added water (1.4 ml), 15% potassium hydroxide (1.3 ml) and water (4 ml); the mixture was then filtrated and concentrated in vacuum. The residue was purified by column chromatography on silica gel to give ethyl 2-ethoxy-1,6-dihydropyrimidine-5-carboxylic acid ethyl ester. Recrystallization from ethyl acetate gave single crystals suitable for X-ray diffraction. Analysis, calculated for $\text{C}_9\text{H}_{14}\text{N}_2\text{O}_3$: C 54.53, H 7.12, N 14.13%; found: C 54.27, H 6.99, N 14.18%. Ethyl 2-ethoxypyrimidine-5-carboxylic acid ethyl ester was previously prepared from ethyl 2-methylthiopyrimidine-5-carboxylic acid ethyl ester (Arukwe & Undheim, 1986) with sodium ethoxide.

Crystal data

C₉H₁₄N₂O₃
M_r = 198.22
 Monoclinic, *P*2₁/*c*
a = 13.131 (8) Å
b = 10.194 (7) Å
c = 7.940 (5) Å
 β = 102.290 (11)°
V = 1038.5 (11) Å³

Z = 4
D_x = 1.268 Mg m⁻³
 Mo *K*α radiation
 μ = 0.10 mm⁻¹
T = 294 (2) K
 Prism, colourless
 0.40 × 0.18 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.960, *T_{max}* = 0.985

5607 measured reflections
 2089 independent reflections
 1155 reflections with *I* > 2σ(*I*)
R_{int} = 0.033
 θ_{max} = 26.3°

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.045
wR(*F*²) = 0.141
S = 0.99
 2089 reflections
 133 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0671P)^2 + 0.1799P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.19 e Å⁻³
 Δρ_{min} = -0.20 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

N1—C1	1.353 (3)	O1—C1	1.343 (2)
N1—C4	1.439 (3)	O1—C8	1.452 (3)
N2—C1	1.300 (3)	C3—C4	1.465 (3)
N2—C2	1.416 (3)	C3—C5	1.471 (3)
C4—N1—C1—N2	-2.9 (3)	C1—N1—C4—C3	4.5 (3)
C4—N1—C1—O1	177.11 (18)	C2—C3—C4—N1	-2.5 (3)
C1—N2—C2—C3	3.2 (3)	C5—C3—C4—N1	176.90 (17)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1A...N2 ⁱ	0.89 (2)	2.21 (2)	3.094 (3)	178.2 (19)

Symmetry code: (i) -*x* + 1, *y* + ½, -*z* + ½.

All H atoms were initially located in a difference Fourier map. The H1A coordinates and isotropic displacement parameter were freely refined. The remaining H atoms were treated as riding atoms with C—H distances ranging from 0.93 to 0.97 Å and with *U*_{iso}(H) = 1.2*U*_{eq}(C) or *U*_{iso}(H) = 1.5*U*_{eq}(C) for the methyl groups.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1999); 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, 1999); software used to prepare material for publication: MERCURY (Bruno *et al.*, 2002).

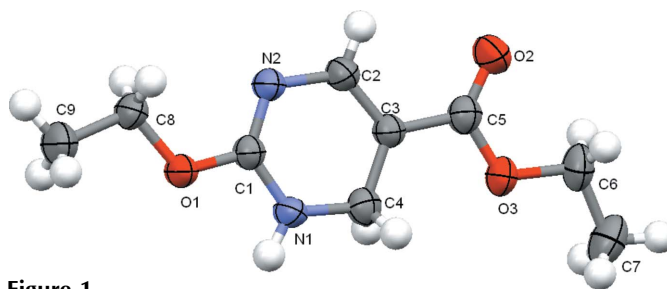


Figure 1

View of (I), with displacement ellipsoids drawn at the 30% probability level.

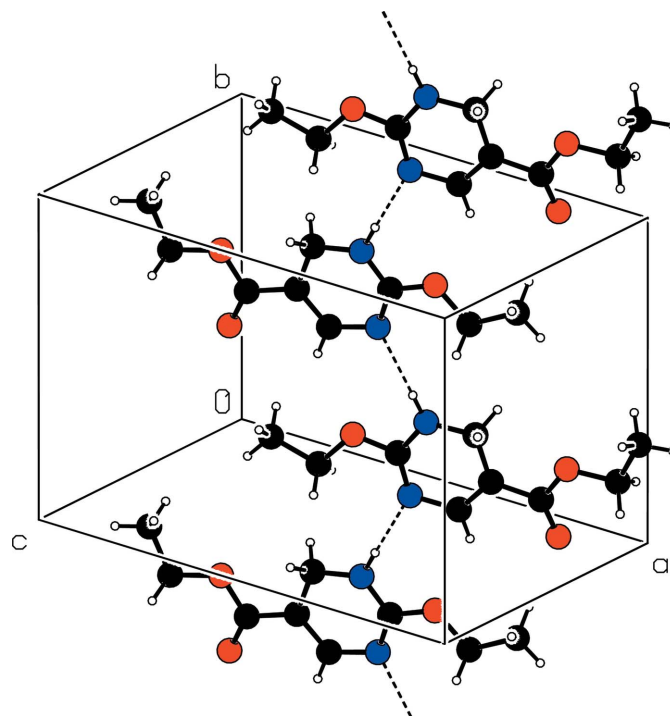


Figure 2

Part of the crystal structure of (I), showing the formation of chains. Hydrogen bonds are shown as dashed lines.

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