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Methyl 3-(2-chloro-5-ethyl-3-pyridyl)-3-hydroxy-2-methylenepropanoate

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Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.002 Å
R factor = 0.038
wR factor = 0.110
Data-to-parameter ratio = 18.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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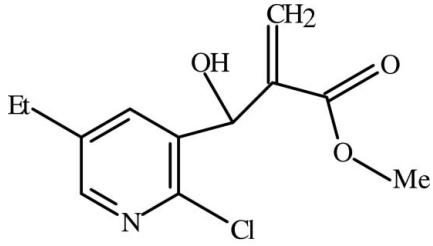
The molecule of title compound, $C_{12}H_{14}ClNO_3$, has an L-shaped conformation, with the methyl propanoate unit at the base. The molecules are linked *via* O—H···N hydrogen bonds into infinite chains of graph-set motif *C*(6) running along the *b* axis. In addition, the structure is further stabilized by C—H···O, C—H···Cl and C—H···π interactions.

Comment

The Baylis–Hillman (Baylis & Hillman, 1972) (BH) reaction and related processes have become increasingly important for synthetic organic chemists, because the resulting adducts with a variety of functional groups and stereochemistry may be subjected to numerous transformations (Basavaiah *et al.*, 2003). However, there are numerous problems commonly associated with this process, most notably the slow reaction. In our efforts directed towards studying the chemical transformations of substituted 2-chloropyridine-3-carboxaldehydes (Narender *et al.*, 2005), we have observed that these molecules undergo extremely fast BH reactions under normal conditions. These adducts have been evaluated for *in vitro* anti-malarial activity (Narender *et al.*, 2005). In a continuation of our studies on these important BH adducts (Swamy *et al.*, 2005), we report here the crystal structure of the title compound (I).



(I)

Compound (I) posesses a stereogenic centre, C6, with a relative configuration (*S*) (Fig.1); it belongs to a centrosymmetric space group and is thus a recemate. The dihedral angle between the mean plane through the pyridine ring (atoms N1/C1–C5) and that of the propanoate unit (atoms O3/O4/C6—C8) is 88.4 (1)°. The hydroxyl group is tilted towards the pyridine ring, as seen from the relevant bond angles (Table 1). The C6—H6···Cl intramolecular interaction closes the five-membered pseudo-ring Cl1—C5—C4—C6—H6 according to an *S*(5) pattern (Bernstein *et al.*, 1995). Similar interactions have been reported in the literature (Pálinkó, 1999). In the crystal structure of (I), molecules are connected by O—H···N hydrogen bonds (Table 2) into infinite *C*(6) chains along the *b*

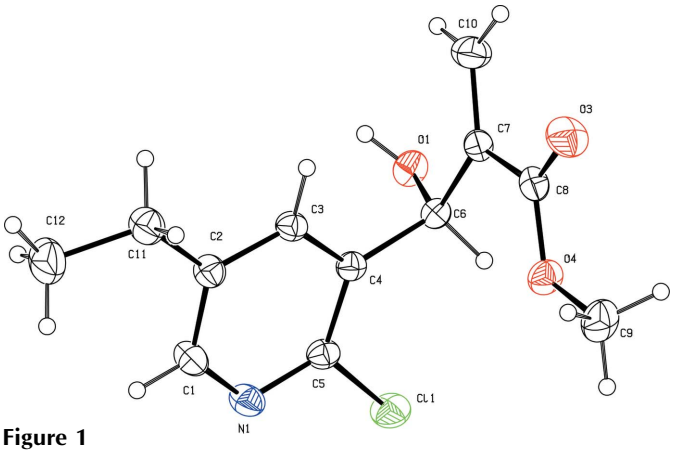


Figure 1
The molecular structure of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

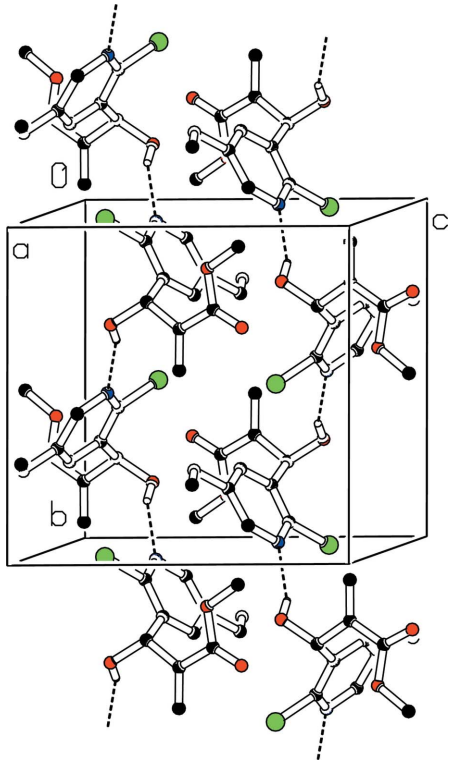


Figure 2
Packing diagram of (I), showing the molecular chains formed through O—H···N hydrogen bonding (dashed lines) along the *b* axis. H atoms have been omitted unless involved in hydrogen bonding.

axis (Fig. 2). In addition, the structure is further stabilized by C—H···O and C—H···π interactions (Table 2).

Experimental

Compound (I) was prepared by the coupling of 2-chloro-5-ethylpyridine-3-carbaldehyde (5 mmol) and methyl acrylate (5 mmol) in methanol (5 ml), the reaction mixture being stirred at room temperature in the presence of 1,4-diaza-bicyclo[2.2.2]octane (5 mmol) for 15 min. The mixture was washed with water. Compound (I) was extracted with chloroform (yield 96%). Crystals were grown by slow evaporation of a chloroform solution.

Crystal data

$C_{12}H_{14}ClNO_3$
M_r = 255.69
Monoclinic, $P2_1/c$
a = 10.5383 (15) Å
b = 10.9564 (16) Å
c = 11.0465 (16) Å
β = 107.534 (2)°
V = 1216.2 (3) Å^3
Z = 4
D_x = 1.396 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8559 reflections
θ = 2.7–27.9°
μ = 0.31 mm^{-1}
T = 273 (2) K
Block, colourless
0.22 × 0.18 × 0.16 mm

Data collection

Bruker SMART Apex CCD diffractometer
ω scans
Absorption correction: none
13476 measured reflections
2858 independent reflections
2601 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 28.0°
$h = -13 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.110
S = 1.04
2858 reflections
157 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0659P)^2 + 0.2604P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.3490 (18)	C8—O3	1.2004 (16)
C2—C11	1.5129 (18)	C8—O4	1.3380 (17)
C5—N1	1.3175 (17)	C9—O4	1.4470 (16)
C6—O1	1.4184 (14)		
O1—C6—C7	112.42 (10)	O1—C6—C4	109.37 (9)
C4—C6—C7—C8	73.49 (13)	C6—C7—C8—O4	5.58 (15)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···N1^{i}	0.82	2.11	2.8627 (15)	153
C9—H9B···O3^{ii}	0.96	2.65	3.256 (2)	121
C6—H6···Cl1	0.98	2.68	3.0942 (13)	106
C10—H10B···O1	0.93	2.50	2.8164 (18)	100
C11—H11A···$Cg1^{iii}$	0.97	3.08	3.836	136

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+2, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x, -y-\frac{1}{2}, z-\frac{1}{2}$. $Cg1$ is the centroid of the pyridine ring

All H atoms were placed in geometrically idealized positions and allowed to ride on their parent atoms, with C—H distances in the range 0.93–0.98 Å, and with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C) for other H atoms. The O—H distance was fixed at 0.82 Å, with U_{iso}(H) = 1.5U_{eq}(O).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; 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 *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

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