Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Ethyl 2-{1,3-bis[(6-chloro-3-pyridyl)methyl]-imidazolidin-2-ylidene}-2-cyanoacetate ethanol solvate

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Key indicators

Single-crystal X-ray study
T = 292 K
Mean σ(C–C) = 0.002 Å
Disorder in solvent or counterion
R factor = 0.055
wR factor = 0.167
Data-to-parameter ratio = 17.2

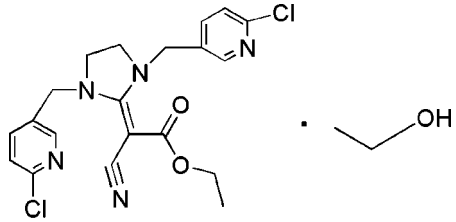
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 3 April 2006
Accepted 8 April 2006

In the title compound, $C_{20}H_{19}Cl_2N_5O_2\cdot C_2H_5OH$, all atoms of the ethanol solvent molecule are disordered over two positions. Intermolecular O—H···O and C—H···O hydrogen bonds and O—H···π interactions contribute to the stability of the crystal structure.

Comment

Imidacloprid is an example of a highly effective low-toxicity neonicotinoid insecticide, marketed by the Bayer company since 1984 (Tang, 2002; Chao *et al.*, 2002). Subsequently, many neonicotinoid analogues have been developed (Shiokawa *et al.*, 1986). The 3-(aminomethyl)pyridine group proved to be an active moiety in these insecticides (Yamamoto *et al.*, 1994), with the two N atoms of the active group interacting with the nicotine acetylcholine receptor (nAchR) of the insects with fatal effects. Here, we report the crystal structure of a related chloromethylpyridine derivative, the title compound, (I), which was synthesized by the reaction of ethyl 2-cyano-2-(imidazolidin-2-ylidene)acetate with 2-chloro-5-(chloromethyl)pyridine.



(I)

Atoms C7, C8, N2, N3, C15 of the five-membered imidazolidine ring of (I) are almost coplanar, with an r.m.s. deviation of 0.0180 Å. The dihedral angles between the imidazolidine and N1- and N4-pyridine rings are 113.42 (14) and 114.01 (15)°, respectively.

In the crystal structure, O3—H3*A*···O1 hydrogen bonds between the ethanol solvent molecule and the acetate group and C19—H19*B*···O1 hydrogen bonds between adjacent molecules of (I) stabilize the structure (Table 1). Furthermore, there is evidence for an O—H···π interaction involving the minor component of the disordered ethanol solvate molecule, with O3′—H3′···*Cg*1 = 3.392 (9) Å, where *Cg*1 is the centroid of the N2/C7/C8/N3/C15 ring.

Experimental

A solution of 2-chloro-5-chloromethylpyridine (10 mmol) in anhydrous dimethylformamide (10 ml) was added dropwise to a mixture

of ethyl 2-cyano-2-(imidazolidin-2-ylidene)acetate (5 mmol) and sodium hydride (10 mmol) in anhydrous dimethylformamide (20 ml) in an ice-bath. The mixture was then stirred at room temperature until thin-layer chromatography indicated that the reaction was complete. The solvent was removed, water added and the product mixture extracted into chloroform. The product was purified by flash column chromatography on silica gel using petroleum ether–ethyl acetate (1:2 *v*/*v*) as eluent, to give a white solid (yield 62%, m.p. 429 K). Crystals of compound (I) were obtained from a solution in absolute ethanol.

Crystal data

$C_{20}H_{19}Cl_2N_5O_2\cdot C_2H_6O$
M_r = 478.37
Monoclinic, $P2_1/n$
a = 11.6424 (10) Å
b = 18.1817 (15) Å
c = 11.9659 (10) Å
β = 113.573 (1)°
V = 2321.6 (3) Å^3
Z = 4
D_x = 1.369 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.31 mm^{-1}
T = 292 (2) K
Block, colourless
0.30 × 0.30 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: none
26922 measured reflections
5526 independent reflections
4039 reflections with $I > 2\sigma(I)$
R_{int} = 0.060
θ_{max} = 28.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.167
S = 1.10
5526 reflections
321 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.098P)^2 + 0.0282P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0100 (15)

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

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9A···O1	0.97	2.46	2.944 (2)	111
C19—H19B···O1^{i}	0.97	2.57	3.448 (2)	150
O3—H3A···O1^{ii}	0.82	2.30	3.086 (4)	160

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

All H atoms bound to C and O were refined using a riding model, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic H atoms, C—H = 0.97 Å and U_{iso}(H) = 1.2U_{eq}(C) for CH_2 and C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for CH_3 atoms, and with O—H = 0.82 Å and U_{iso}(H) = 1.5U_{eq}(O) for the OH groups. All atoms in the ethanol molecule are disordered over two positions. The occupancy factors refined to 0.613 (5)/0.387 (5).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001; data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PLATON*.

The authors are grateful to the Natural Science Foundation of China for financial support (grant No. 20302002).

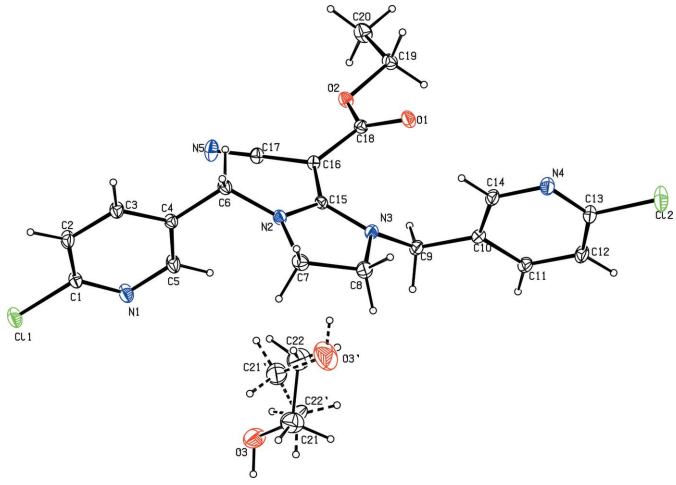


Figure 1
The structure of (I), showing the atom-labelling scheme and with displacement ellipsoids drawn at the 30% probability level. The minor disorder component of the ethanol solvent molecule is shown with bonds represented by dashed lines.

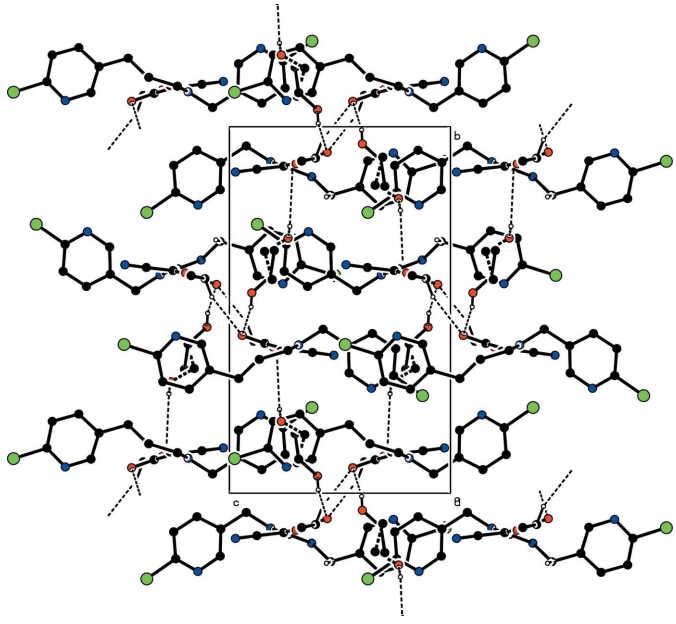


Figure 2
A packing diagram for (I). Hydrogen bonds and O—H···π interactions are shown as dashed lines. H atoms not involved in these interactions have been omitted.

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