organic papers

(E)-N²-{3-[(6-Chloropyridin-3-yl)methyl]-5-cyano-3H-1,2,3-triazol-4-yl}-N¹,N¹-bis(2-hydroxyethyl)-formamidine

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Key indicators

Single-crystal X-ray study
$T = 298$ K
Mean σ(C–C) = 0.003 Å
R factor = 0.055
wR factor = 0.142
Data-to-parameter ratio = 16.0

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

In the title compound, $C_{14}H_{16}ClN_7O_2$, the triazole ring carries cyano and formamidine substituents and is bound *via* a methylene bridge to a chloropyridine unit. There is evidence of significant electron delocalization in the triazolyl system. Intramolecular O—H···O and intermolecular C—H···N, C—H···O and O—H···N hydrogen bonds, together with strong π–π stacking interactions, stabilize the structure.

Comment

Neonicotinoid insecticides act as nicotinic acetylcholine receptor inhibitors and have attracted increasing attention because of their safety, low toxicity, wide range of activities and high potency (Shiokawa *et al.*, 1986). It has been found that most biologically active nicotinic compounds contain the 3-aminomethylpyridine group (Yamamoto *et al.*, 1994). 1,2,3-Triazoles have also been widely used in pharmaceuticals, agrochemicals, dyes, photographic materials, and in corrosion inhibition (Fan & Katrisky, 1996; Dehne, 1994; Abu-Orabi *et al.*, 1989). As structure–activity relationships are very useful in the rational design of pharmaceuticals and agrochemicals, we report here the crystal structure of the title triazole derviative, (I) (Fig. 1 and Table 1), which was synthesized by introducing a pyridine ring into a 1,2,3-triazole molecular framework. In (I), the C7—N4, C10—N7, C9—N2 and C9—N6 bonds are significantly shorter than a normal single C—N bond (1.47 Å; Sasada, 1984) and close to the value for a C=N bond (1.28 Å; Wang *et al.*, 1998). This indicates significant electron delocalization in the triazolyl system. An intramolecular O—H···O hydrogen bond links the OH groups of the bis-hydroxyethyl system.

(I)
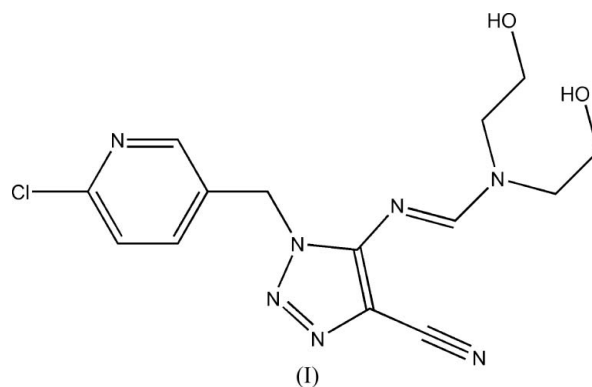
Intermolecular O—H···N, C—H···N and C—H···O hydrogen bonds contribute strongly to the stability of the crystal structure (Fig. 2 and Table 2). Strong π–π stacking interactions are also found between adjacent N1/C1–C5 rings with centroid–centroid distances of 3.819 (1) Å, dihedral
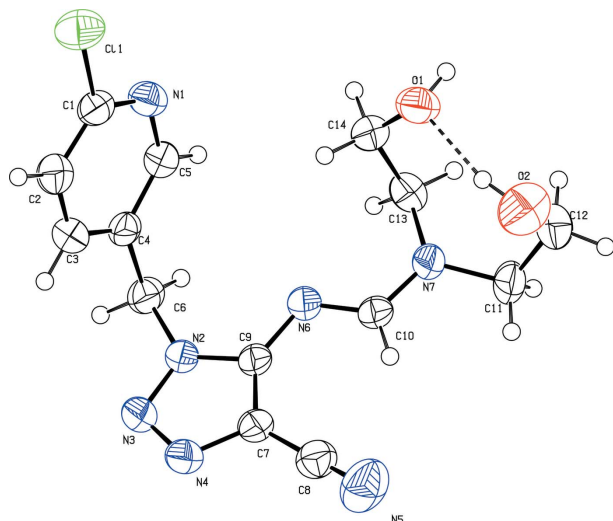
Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. The intramolecular hydrogen bond is drawn as a dashed line.

angles of 0.03 (1)° and a shortest interplanar distance of 3.627 Å.

Experimental

Diethanolamine (2 mmol) in anhydrous acetonitrile (2 ml) was added dropwise to a solution of (E)-ethyl-N-3-[(6-chloropyridin-3-yl)-methyl]-5-cyano-3H-1,2,3-triazol-4-ylformimidate (1 mmol) in anhydrous acetonitrile (8 ml) at room temperature. The mixture was stirred until the reaction was complete (monitored by thin-layer chromatography) and the solution was concentrated under vacuum. The residue was recrystallized from anhydrous ethanol to give the title compound (yield 80%). Colourless crystals of (I) suitable for X-ray structure analysis were grown from anhydrous ethanol.

Crystal data

$C_{14}H_{16}ClN_7O_2$	$Z = 4$
$M_r = 349.79$	$D_x = 1.411$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 7.6293$ (9) Å	$\mu = 0.26$ mm^{-1}
$b = 8.1921$ (9) Å	$T = 298$ (2) K
$c = 26.351$ (3) Å	Block, colourless
$\beta = 90.438$ (2)°	$0.30 \times 0.20 \times 0.20$ mm
$V = 1646.9$ (3) Å^3	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	9222 measured reflections
φ and ω scans	3558 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)	2902 reflections with $I > 2\sigma(I)$
$T_{min} = 0.927$, $T_{max} = 0.951$	$R_{int} = 0.025$
	$\theta_{max} = 27.0°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0579P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.055$	$+ 0.7964P]$
$wR(F^2) = 0.142$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} = 0.004$
3558 reflections	$\Delta\rho_{max} = 0.33$ e Å^{-3}
223 parameters	$\Delta\rho_{min} = -0.27$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	
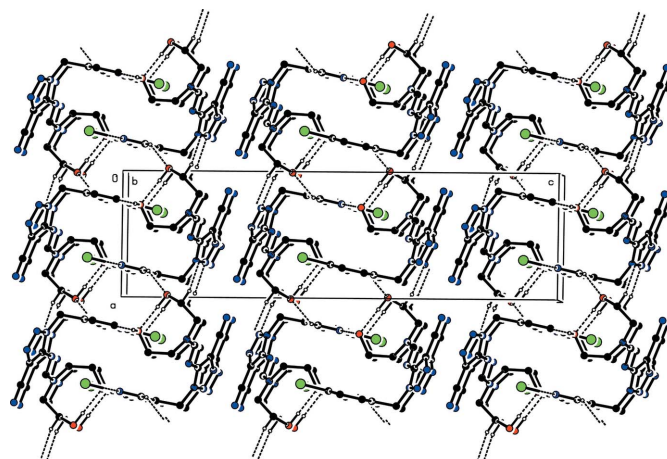
Figure 2
The packing of (I). Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted.

Table 1
Selected bond lengths (Å).

C7—N4	1.365 (3)	C10—N7	1.316 (3)
C7—C9	1.391 (3)	N2—C9	1.345 (3)
C7—C8	1.422 (4)	N2—N3	1.357 (3)
C8—N5	1.139 (4)	N3—N4	1.295 (3)
C10—N6	1.294 (3)	C9—N6	1.364 (3)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2A$\cdots$O1	0.92 (5)	1.91 (5)	2.802 (3)	164 (4)
C12—H12A$\cdots$N3^i	0.97	2.61	3.533 (3)	158
C5—H5$\cdots$O2^{ii}	0.93	2.54	3.356 (3)	146
O1—H1$\cdots$N1^{iii}	0.83 (4)	2.05 (4)	2.873 (3)	168 (3)

Symmetry codes: (i) $x + 1, y + 1, z$; (ii) $x - 1, y, z$; (iii) $-x + 1, -y + 1, -z + 2$.

The H atoms of the OH groups were located in a difference Fourier map and were refined freely. All other H atoms were placed in calculated positions, with C—H distances in the range 0.93–0.98 Å. They were included in the final cycles of refinement using a riding-model approximation, with $U_{iso}(H) = 1.2$–$1.5U_{eq}$(carrier atom). A rotating group model was used for the methyl groups.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); 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, 1997); software used to prepare material for publication: *SHELXTL*.

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