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1-(2-Pyridyl)-8*H*-pyrrolo[2,1-*c*]-*s*-triazolo[4,3-*a*]-[1,4]benzodiazepinium chloride

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.048
wR factor = 0.113
Data-to-parameter ratio = 12.3

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

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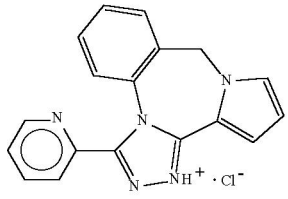
The conformation of the seven-membered ring in the title compound, $C_{18}H_{14}N_5^+\cdot Cl^-$, is close to a boat, and this fragment has an approximate mirror plane of symmetry. The protonation takes place at an N atom of the triazole ring. One strong N—H···Cl and two weak C—H···Cl hydrogen bonds determine the crystal packing.

Comment

In the course of studies on benzodiazepine derivatives, potential new neurodrugs, we solved the crystal structure of the title compound, (I). Similar compounds with the *s*-triazole ring fused to the benzodiazepine skeleton are used clinically as anxiolytics and hypnotics (for example, alprazolam, marketed as Xanax, and triazolam, marketed as Halcion).



(I)

The protonation takes place at one of the N atoms of the triazole ring, and the resulting N—H group acts as a donor in a strong linear hydrogen bond with the chloride anion.

The overall shape of the cation (see Fig. 1) is mainly determined by the conformation of the seven-membered ring, which is close to the cycloheptatriene-like boat (also the bond-length pattern within this ring indicates a similarity to the cycloheptatriene ring). There is an approximate mirror plane that passes through C16 and the midpoint of the C5—N9 bond; the appropriate asymmetry parameter (Duax & Norton, 1975) $\Delta_s = 6.10$. The conformation of the diazepine ring can be also described by the dihedral angles between the central plane of the boat (C4/C10/C15/N17) and the planes of its 'bow' (C15/C16/N17) and 'stern' (C4/C5/N9/C10). The values of the bow and stern angles, of 52.3 (2) and 36.00 (7)°, respectively, compare well with the angles found in similar benzodiazepine derivatives [for example, 55.5 (8) and 36.2 (8)° in 1-methyl-6-phenyl-8-(trifluoromethyl)-4*H*-*s*-triazolo[4,3-*a*][1,4]benzo-Hamor, 1988), and 53.4 (7) and 34.3 (7)° in 8-chloro-6-(2-chlorophenyl)-1-(4-pyridyl)-1,2,4-triazolo[4,3-*a*][1,4]benzo-Hamor, 1989)].

The three rings fused to the central seven-membered ring are planar within experimental error [maximum deviations from the least-squares planes are 0.006 (1) Å for the triazine, 0.012 (2) Å for the benzo and 0.002 (1) Å for the pyrrolo ring].

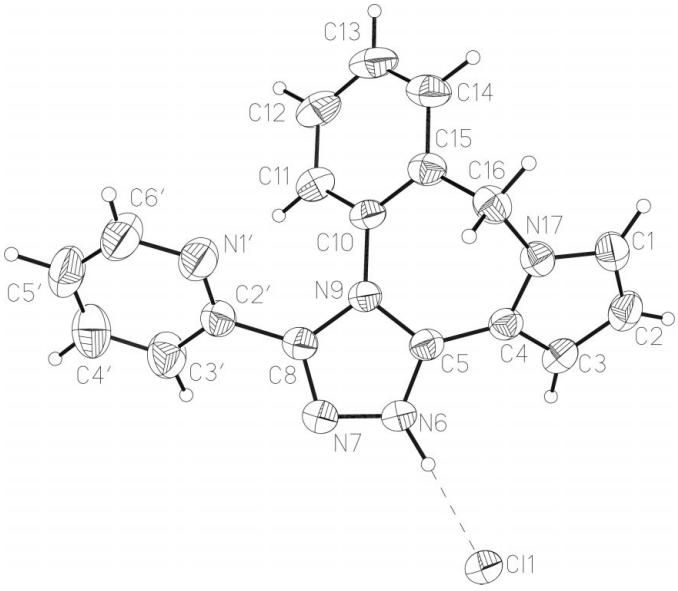


Figure 1
A view of the salt (Siemens, 1989) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level, the H atoms are depicted as spheres of arbitrary radii, and the strong N—H···Cl hydrogen bond is drawn as a dashed line.

The mutual disposition of these rings is obviously enforced by the conformation of the diazepine ring. Relatively free rotation is possible only around the C8—C2′ bond; the dihedral angle between the triazinium and pyridine planes is 43.31 (6)°. The crystal packing is determined mainly by van der Waals interactions and hydrogen bonds accepted by the chloride anion; one strong N—H···Cl and two weaker, but structurally important, C—H···Cl bonds. These bonds connect the cations and anions into layers approximately perpendicular to the [010] direction (Fig. 2).

Experimental

The title compound was provided by Ciba–Geigy. Colourless crystals were grown from an ethanol solution by slow evaporation.

Crystal data

$C_{18}H_{14}N_5^+\cdot Cl^-$
M_r = 335.79
Monoclinic, $P2_1/c$
a = 8.7856 (5) Å
b = 8.2058 (5) Å
c = 22.990 (2) Å
β = 95.513 (6)°
V = 1649.8 (2) Å^3
Z = 4
D_x = 1.352 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 5–35°
μ = 2.12 mm^{-1}
T = 293 (2) K
Block, colourless
0.20 × 0.20 × 0.15 mm

Data collection

CAD-4F four-circle diffractometer
$\omega/2\theta$ scans
3604 measured reflections
3380 independent reflections
3315 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
θ_{max} = 74.8°
$h = 0 \rightarrow 10$
$k = -10 \rightarrow 0$
$l = -28 \rightarrow 28$
2 standard reflections
frequency: 33 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.113
S = 1.26
3380 reflections
274 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.01P)^2 + 0.70P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.55 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0098 (6)

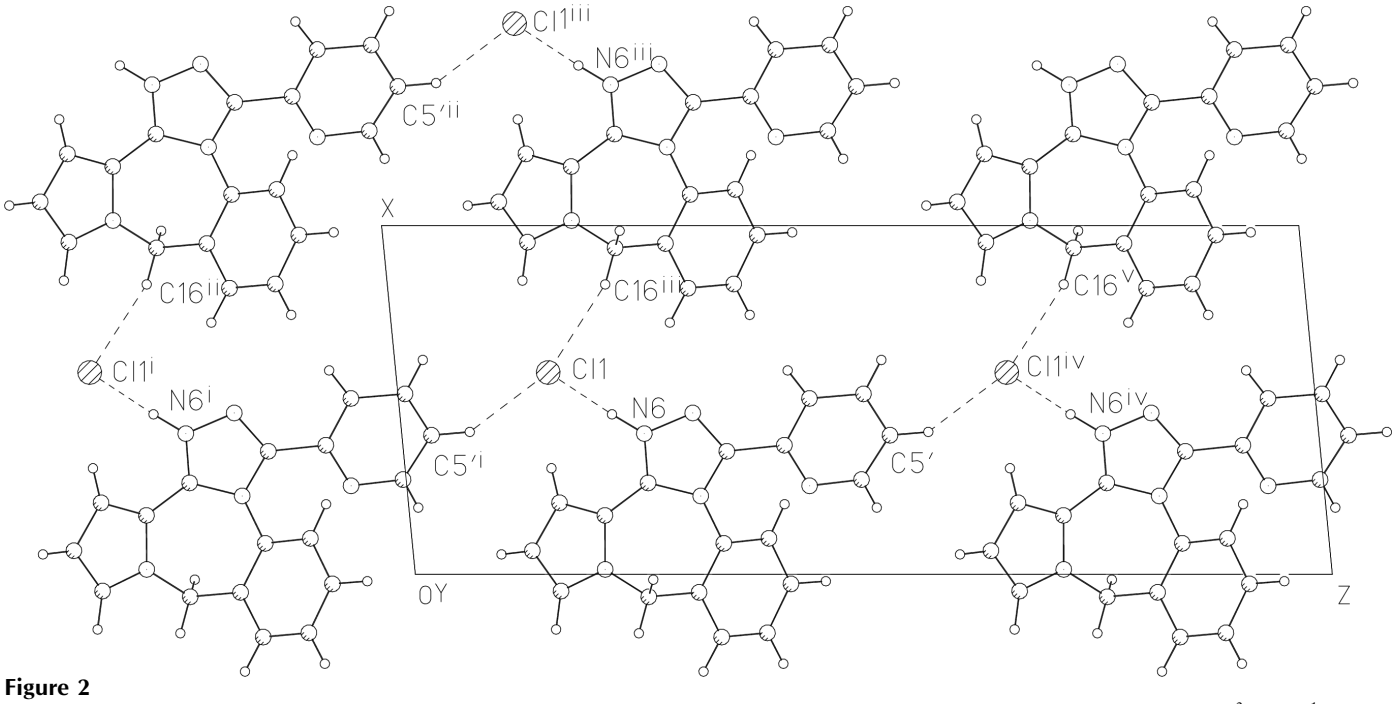


Figure 2
The crystal packing as seen along the y direction (Siemens, 1989). Hydrogen bonds are drawn as dashed lines. [Symmetry codes: (i) $x, \frac{3}{2} - y, -\frac{1}{2} + z$; (ii) $1 + x, \frac{3}{2} - y, -\frac{1}{2} + z$; (iii) $1 + x, y, z$; (iv) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (v) $1 + x, \frac{3}{2} - y, \frac{1}{2} + z$.]

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

D—H···A	D—H	H···A	D···A	D—H···A
N6—H6···Cl1	0.97 (2)	1.98 (2)	2.953 (2)	177 (2)
C16—H16B···Cl1^{i}	0.95 (2)	2.71 (2)	3.624 (2)	161 (2)
C5′—H5′···Cl1^{ii}	0.98 (3)	2.82 (3)	3.531 (2)	130 (2)

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

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *ENPROC* (Rettig, 1978); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation* (Siemens, 1989).

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