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N^6-Furfuryladenine (kinetin) hydrochloride

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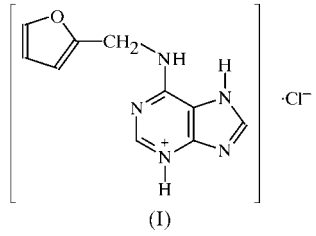
In the title compound, N^6-furfuryladenin-3-ium chloride, $C_{10}H_{10}N_5O^+\cdot Cl^-$, the adenine moiety exists as the N3-protonated N7–H tautomer. The orientation of the N6 substituent (furfuryl moiety) is distal to the imidazole ring of the adenine base. The dihedral angle between the adenine plane and the furfuryl ring plane is 76.1 (2)°. Three N—H···Cl hydrogen bonds are responsible for the formation of a supramolecular chain-like pattern. These supramolecular chains are interconnected by C—H···Cl hydrogen bonds to form a hydrogen-bonded sheet and a three-dimensional hydrogen-bonded network.

Comment

Kinetin (N^6-furfuryladenine) is a highly potent growth factor or cytokinin (Skoog & Armstrong, 1970). Many N6-substituted adenine derivatives function as plant-growth stimulants (Hall, 1973). Cytokinin is the generic name used to designate plant-growth substances, and cytokinins occur in a wide range of plant tissues, being found abundantly in root tips, xylum sap, developing fruits, tumour tissues and germinating seeds. Kinetin was isolated from an autoclaved sample of herring sperm DNA (Miller *et al.*, 1955). It was found to be very active in promoting mitosis and cell division in tobacco callus tissue *in vitro* and it is the reference compound for comparing the cytokinin activity of other cytokinins. Some synthetic N6-substituted adenines also show cytokinin activity, depending upon their conformation (Pattabhi, 1990), for example, N^6-benzyladenine is a synthetic cytokinin. The crystal structures of N^6-benzyladenine hydrochloride (Umadevi, 1997), N^6-benzyladenine hydrobromide (Umadevi *et al.*, 2001), a cupric chloride complex of the benzyl adeninium ligand (Balasubramanian *et al.*, 1996) and a cupric chloride complex of the N^6-furfuryladeninium moiety (Umadevi *et al.*, 2002) have already been reported from our laboratory.

Weak hydrogen bonds play an important role in stabilizing crystal structures (Desiraju & Steiner, 1999). Recently, Thallapally & Nangia (2001) have analysed C—H···Cl hydrogen bonds using the Cambridge Structural Database (CSD, Version 5.22; Allen, 2002). They suggested that C—H···Cl^- and C—H···Cl—*M* often behave as hydrogen bonds, but C—H···Cl—C is generally a van der Waals interaction.



(I)

The aim of the present study was to understand the conformation and hydrogen-bonding patterns of N^6-furfuryladenine hydrochloride (FUCL), (I).

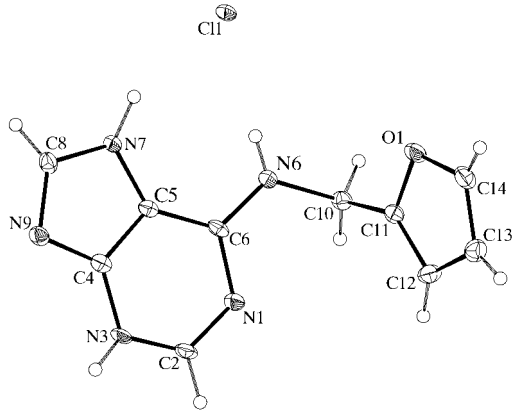


Figure 1
A view of the molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

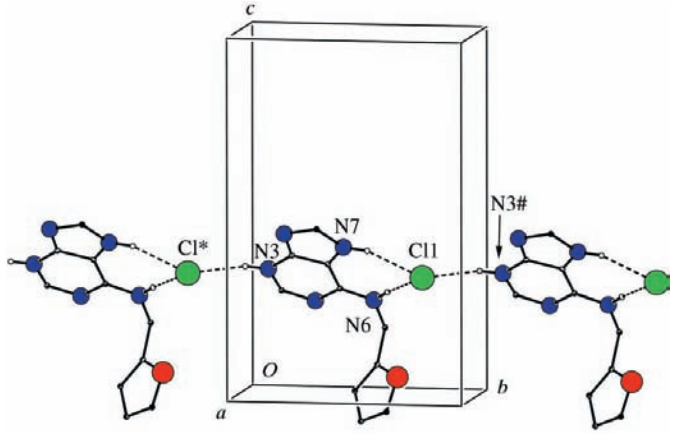


Figure 2
A view of the hydrogen-bonded supramolecular chains in (I). Atoms marked with an asterisk (*) or hash (#) are at the equivalent positions (x, $y-1$, z) and (x, $y+1$, z), respectively.

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A view of the molecule of (I) is shown in Fig. 1. The compound crystallizes in space group $P2_1$ and the absolute crystal structure has not yet been determined. The asymmetric unit contains an N^6-furfuryladeninium moiety and a Cl^- anion.

In the crystal structure of neutral N^6-furfuryladenine (Soriano-Garcia & Parthasarathy, 1977), an H atom resides at the N9 position (N9–H tautomer). In monoprotonated adenine systems, N1 is the protonation site (Voet & Rich, 1970). However, in the present crystal structure, interestingly, the adenine moiety exists as the N7–H tautomer with the H atom at N3; N9 carries no H atom. Further evidence for the presence of the H atoms on these sites comes from the enhancement of the corresponding internal angles; the internal angles at N3 and N7 are 118.4 (3) and 106.4 (3)°, respectively, while the corresponding angles in neutral N^6-furfuryladenine are 110.9 (3) and 102.8 (3)°, respectively (Soriano-Garcia & Parthasarathy, 1977).

In the crystal structure of neutral N^6-furfuryladenine, where the molecule exists as the N9–H tautomer, the internal angle at N9 (C4—N9—C8) is 106.9 (3)°, whereas in the present structure, the corresponding angle is significantly less, at 102.6 (3)°. This suggests that in (I), N9 carries no H atom. In both these compounds, the angles at N1 do not differ significantly [119.5 (3)° in (I) and 118.8 (3)° in the neutral compound], suggesting that, in both crystal structures, there is no H atom at N1. Thus, it can be concluded that in (I), the base exists as the N3-protonated N7–H tautomer.

The enhancement of internal bond angles on protonation sites is already well established (Taylor & Kennard, 1982). It is very interesting to note that the N1 position remains unprotonated, even under acidic conditions, in (I), and also in a copper complex of N^6-benzyladenine (Balasubramanian *et al.*, 1996), a copper complex of N^6-furfuryladenine (Umadevi *et al.*, 2002) and a copper complex of an N^6-benzyladenine derivative (Trávníček *et al.*, 2001). The above copper complexes of adenine derivatives were also prepared under slightly acidic conditions; the adenine moieties exist as the N7–H tautomer, with protonation at N3 and coordination at N9.

The orientation of the N6 substituent in (I) is distal to the imidazole ring of the adenine base. The dihedral angle between the adenine plane and the furfuryl ring plane is 76.1 (2)°. This is in agreement with the range of values (63–108°) proposed for cytokinin activity (Raghunathan & Pattabhi, 1981; Raghunathan *et al.*, 1983; Soriano-Garcia & Parthasarathy, 1977; Balasubramanian *et al.*, 1996; Umadevi *et al.*, 2002). The N6 substituent is also distal to the imidazole ring, as in other cytokinins (Soriano-Garcia & Parthasarathy, 1977; Raghunathan & Pattabhi, 1981; Bugg & Thewalt, 1972; McMullan & Sundaralingam, 1971; Walker & Tollin, 1982). Selected bond lengths and angles are listed in Table 1.

The N7 and N6 H atoms of the same adeninium moiety in (I) are hydrogen bonded to a Cl^- anion *via* N—H···Cl hydrogen bonds, forming a seven-membered ring with graph-set $R_2^1(7)$ (Bernstein *et al.*, 1995). The N3 H atom of the neighbouring adeninium moiety is also hydrogen bonded to this Cl^- anion, leading to a hydrogen-bonded supramolecular chain, made up of Cl^- anions and furfuryladeninium cations arranged in an alternating manner, running parallel to the *b* axis. A view of this supramolecular chain is shown in Fig. 2.

Two such chains are further interconnected by C—H···Cl hydrogen bonds involving the C8 H atom of the adeninium moieties, generating a hydrogen-bonded sheet-like pattern. Two such sheets are further crosslinked by C—H···Cl hydrogen bonds involving a methylene H atom of the furfuryladeninium moiety, forming a three-dimensional network. In the crystal structure of N^6-benzyladenine hydrobromide (Umadevi *et al.*, 2001), a base pair is formed *via* N3—H···N9 hydrogen bonds. In the structure of (I), there is no base pairing and the crystal structure is dominated by N—H···Cl and C—H···Cl hydrogen bonds and π–π stacking. The centroid-to-centroid distance between the overlapping phenyl and imidazole planes is 3.494 (3) Å. Details of the hydrogen bonds are given in Table 2.

Experimental

N^6-Furfuryladenine (Loba Chemie, India) was dissolved in the minimum amount of dilute hydrochloric acid and then recrystallized from methanol to yield crystals of (I).

Crystal data

$C_{10}H_{10}N_5O^+\cdot Cl^-$
M_r = 251.68
Monoclinic, $P2_1$
a = 4.5610 (8) Å
b = 8.8980 (17) Å
c = 13.562 (3) Å
β = 92.138 (5)°
V = 550.02 (19) Å^3
Z = 2
D_x = 1.520 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1010 reflections
θ = 2.7–30.0°
μ = 0.34 mm^{-1}
T = 100 (2) K
Plate, colourless
0.26 × 0.24 × 0.04 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
2063 measured reflections
1957 independent reflections
1704 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 30.7°
$h = -4 \rightarrow 4$
$k = -12 \rightarrow 11$
$l = -8 \rightarrow 18$

Table 1
Selected geometric parameters (Å, °).

O1—C11	1.383 (5)	N6—C6	1.330 (5)
O1—C14	1.373 (5)	N6—C10	1.465 (6)
N1—C2	1.319 (5)	N7—C5	1.368 (5)
N1—C6	1.364 (5)	N7—C8	1.353 (6)
N3—C2	1.333 (6)	N9—C4	1.346 (6)
N3—C4	1.370 (5)	N9—C8	1.341 (6)
C11—O1—C14	106.4 (3)	N7—C5—C6	135.7 (3)
C2—N1—C6	119.5 (3)	C4—C5—C6	119.8 (3)
C2—N3—C4	118.4 (3)	N6—C6—C5	123.2 (4)
C6—N6—C10	122.3 (3)	N1—C6—C5	117.8 (3)
C5—N7—C8	106.4 (3)	N1—C6—N6	119.0 (4)
C4—N9—C8	102.6 (3)	N7—C8—N9	113.7 (4)
N1—C2—N3	125.3 (4)	N6—C10—C11	112.6 (4)
N3—C4—C5	119.1 (4)	O1—C11—C12	109.0 (4)
N3—C4—N9	127.9 (3)	O1—C11—C10	116.5 (3)
N9—C4—C5	113.0 (3)	O1—C14—C13	110.6 (4)
N7—C5—C4	104.4 (3)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···Cl1^{i}	0.88 (7)	2.17 (7)	3.031 (3)	167 (4)
N6—H6···Cl1	0.82 (5)	2.41 (4)	3.218 (4)	170 (4)
N7—H7···Cl1	0.94 (5)	2.28 (5)	3.165 (3)	157 (4)
C8—H8···Cl1^{ii}	0.94 (4)	2.69 (4)	3.428 (5)	135 (3)
C10—H10*B*···Cl1^{iii}	1.01 (5)	2.75 (5)	3.504 (4)	132 (3)

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

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0782P)^2 + 0.0320P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R(F) = 0.048$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.125$	$\Delta\rho_{max} = 0.59$ e Å^{-3}
$S = 1.03$	$\Delta\rho_{min} = -0.37$ e Å^{-3}
1957 reflections	Absolute structure: Flack (1983), 141 Friedel pairs
194 parameters	Flack parameter = 0.60 (10)
All H-atom parameters refined	

All H atoms were located from a difference Fourier map and were refined isotropically [C—H = 0.81 (6)–1.01 (5) Å].

Data collection and cell refinement: *SMART* (Bruker, 1999); data reduction: *SAINT* (Bruker, 1999); structure solution: *SHELXS*97 (Sheldrick, 1997); structure refinement: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *PLATON* (Spek, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1200). Services for accessing these data are described at the back of the journal.

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