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6-(4-Hydroxybenzylamino)purin-3-ium chloride: a protonated form of *para*-topoline

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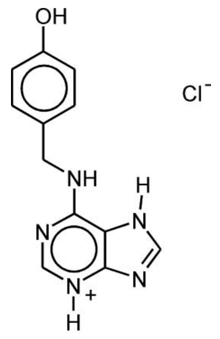
Key indicators: single-crystal X-ray study; T = 110 K; mean σ(C–C) = 0.002 Å; R factor = 0.030; wR factor = 0.082; data-to-parameter ratio = 12.1.

The structure of the title compound, $C_{12}H_{12}N_5O^+\cdot Cl^-$, comprises a 6-(4-hydroxybenzylamino)purinium cation and a chloride anion. The cation exists as the N3-H tautomer. Intermolecular N—H···N hydrogen bonds connect cations into centrosymmetric dimers, with an N···N distance of 2.821 (2) Å. Furthermore, the secondary structure is stabilized by O—H···Cl and N—H···Cl hydrogen bonds, weak nonbonding interatomic contacts of the types C—H···Cl [3.1652 (4) Å] and C—H···C [2.897 (2) Å], and π–π stacking interactions [3.357 (4) Å].

Related literature

For similar structures of the protonated forms of aromatic cytokinins derived from 6-benzylaminopurine, see: Maloň *et al.* (2001, 2002); Trávníček *et al.* (1997, 2004, 2005); Trávníček & Matiková-Maľarová (2006).



Experimental

Crystal data

$C_{12}H_{12}N_5O^+\cdot Cl^-$
M_r = 277.72
Monoclinic, $P2_1/c$
a = 4.2503 (1) Å
b = 25.5022 (7) Å
c = 11.3995 (3) Å
β = 99.457 (3)°
V = 1218.82 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.31 mm^{-1}
T = 110 (2) K
0.40 × 0.35 × 0.25 mm

Data collection

Oxford Diffraction Xcalibur2 CCD diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2002)
T_{min} = 0.931, T_{max} = 1.000 (expected range = 0.861–0.925)
10101 measured reflections
2132 independent reflections
2034 reflections with $I > 2\sigma(I)$
R_{int} = 0.009

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.082
S = 1.16
2132 reflections
176 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N6—H6A···Cl1	0.88	2.36	3.2262 (14)	168
N7—H7A···Cl1	0.88	2.25	3.0709 (13)	156
N3—H3A···N9^{i}	0.88	1.96	2.8209 (18)	166
O1—H1W···Cl1^{ii}	0.83 (3)	2.30 (3)	3.1151 (13)	170 (2)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97* and *DIAMOND*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2186).

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supplementary materials

Acta Cryst. (2007). E**63**, o3859 [**doi:10.1107/S1600536807039979**]

6-(4-Hydroxybenzylamino)purin-3-ium chloride: a protonated form of *para*-topoline

Z. Trávnícek, **K. M. George**, **M. Matiková-Malarová** and **P. Baran**

Comment

The structure of the title compound (I) was determined within the framework of our systematic crystallographic investigations of plant growth hormones, called cytokinins, derived from 6-benzylaminopurine (Trávníček et al., 1997, 2004, 2005; Trávníček & Matiková-Maľarová, 2006; and Maloň et al., 2001, 2002).

The molecular structure of (I) contains a 6-(4-hydroxybenzylamino)purinium cation and a chloride anion (Fig. 1). The cation exists as the N3-protonated N7 tautomer and contains three different aromatic ring systems, i.e. benzene, pyrimidine and imidazole. Each of these deviates slightly from planarity, with maximum deviations from the least-squares planes being 0.005 (2) Å for C12, 0.007 (2) Å for C2 and 0.002 (2) Å for C8 (Brandenburg, 2006). The dihedral angle between benzene ring and purine skeleton is 65.32 (4)°, whilst the pyrimidine and imidazole rings are nearly co-planar with their dihedral angle being only 0.61 (4)A%. The interatomic parameters in (I) are comparable to those found for similar N3-protonated N7 tautomers of 6-benzylaminopurine derivatives (Trávníček et al. 2004). The N—H···N hydrogen bonds connect two cations into centrosymmetric dimers in the bc plane (Fig. 2, Table 1). The cations and chloride anions are connected via hydrogen bonds of the type N—H···Cl and O—H···Cl (Fig. 2 and 3). Moreover, π-π stacking interactions between purine rings of neighbouring molecules [$C5\cdots C8^{iii}$ = 3.357 (4) Å; symmetry code: (iii) −1 + x, y, z] together with the C—H···Cl and C—H···C contacts contribute to the stabilization of the secondary structure (Fig. 3) [$C8\cdots Cl1^{iv}$ = 3.1652 (4) Å, $C9\cdots C6^{v}$ = 2.897 (2) Å; symmetry codes: (iv) 1 − x, 1 − y, 1 − z; (v) 1 + x, y, z].

Experimental

A few colorless crystals of the title compound (I) were obtained from the mother liquor, as a by-product, during the synthesis of a Ru complex under acidic conditions (conc. HCl).

Refinement

All H atoms of were located in difference maps and refined using a riding model, with C–H distances = 0.95–0.99 Å and N–H = 0.88 Å, and with $U_{iso}(H) = 1.2U_{eq}(C,N)$. The O–H atom was refined freely.

Figures

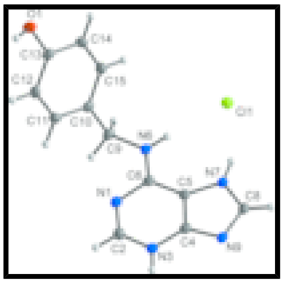

Fig. 1. A view of the molecular structure of (I) showing atom labelling. Non-H atoms are drawn with the 50% probability displacement ellipsoids.

Fig. 2. Part of the crystal structure of (I), viewed along the *a* axis, showing the hydrogen bonding as dashed lines.

Fig. 3. Part of the crystal structure of (I), viewed along the *c* axis, showing non-bonding and π-stacking interactions (dashed lines). Most of the H-atoms have been omitted for clarity.

6-(4-Hydroxybenzylamino)purin-3-ium chloride

Crystal data

$C_{12}H_{12}N_5O^+\cdot Cl^-$

$M_r = 277.72$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 4.2503\ (1)$ Å

$b = 25.5022\ (7)$ Å

$c = 11.3995\ (3)$ Å

$\beta = 99.457\ (3)°$

$V = 1218.82\ (5)$ Å^3

$Z = 4$

$F_{000} = 576$

$D_x = 1.513$ Mg m^{-3}

Mo *K*α radiation
$\lambda = 0.71073$ Å

Cell parameters from 10605 reflections

$\theta = 3.0–31.9°$

$\mu = 0.31$ mm^{-1}

$T = 110\ (2)$ K

Prism, colourless

0.40 × 0.35 × 0.25 mm

Data collection

Oxford Diffraction Xcalibur2 CCD diffractometer

Radiation source: Enhance (Mo) X-ray Source

Monochromator: graphite

Detector resolution: 8.361 pixels mm^{-1}

$T = 110(2)$ K

rotation method, ω scans

Absorption correction: multi-scan
(CrysAlis RED; Oxford Diffraction, 2002)

$T_{min} = 0.931$, $T_{max} = 1.000$

10101 measured reflections

2132 independent reflections

2034 reflections with $I > 2\sigma(I)$

$R_{int} = 0.009$

$\theta_{max} = 25.0°$

$\theta_{min} = 3.0°$

$h = -4\rightarrow 5$

$k = -30\rightarrow 30$

$l = -13\rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.030$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.082$	$w = 1/[\sigma^2(F_o^2) + (0.0385P)^2 + 0.7626P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.16$	$(\Delta/\sigma)_{max} < 0.001$
2132 reflections	$\Delta\rho_{max} = 0.29$ e Å^{-3}
176 parameters	$\Delta\rho_{min} = -0.17$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Experimental. Absorption correction: *CrysAlis RED* (Oxford Diffraction) empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.4740 (3)	0.12382 (4)	0.66975 (11)	0.0232 (3)
Cl1	0.36116 (9)	0.412050 (15)	0.42073 (3)	0.02078 (14)
N1	0.9597 (3)	0.37404 (5)	0.85376 (12)	0.0175 (3)
N3	0.7284 (3)	0.43903 (5)	0.96037 (12)	0.0176 (3)
H3A	0.7130	0.4535	1.0293	0.021*
N6	0.8406 (3)	0.36780 (5)	0.64812 (11)	0.0160 (3)
H6A	0.7363	0.3799	0.5805	0.019*
N7	0.3877 (3)	0.46270 (5)	0.66656 (11)	0.0166 (3)
H7A	0.3524	0.4572	0.5893	0.020*
N9	0.3541 (3)	0.49887 (5)	0.84217 (12)	0.0174 (3)
C2	0.9189 (4)	0.39766 (6)	0.95251 (14)	0.0188 (3)
H2A	1.0344	0.3843	1.0247	0.023*
C4	0.5601 (4)	0.45766 (6)	0.85696 (14)	0.0161 (3)
C5	0.5878 (4)	0.43435 (6)	0.75049 (13)	0.0154 (3)
C6	0.7962 (4)	0.39114 (6)	0.74745 (14)	0.0153 (3)

C8	0.2564 (4)	0.50041 (6)	0.72518 (14)	0.0183 (3)
H8A	0.1091	0.5256	0.6871	0.022*
C9	1.0543 (4)	0.32272 (6)	0.64404 (14)	0.0172 (3)
H9A	1.2364	0.3258	0.7101	0.021*
H9B	1.1404	0.3238	0.5685	0.021*
C10	0.8926 (4)	0.27056 (6)	0.65340 (14)	0.0162 (3)
C11	0.9549 (4)	0.24111 (6)	0.75725 (14)	0.0193 (3)
H11A	1.0938	0.2547	0.8241	0.023*
C12	0.8174 (4)	0.19219 (6)	0.76476 (14)	0.0197 (3)
H12A	0.8646	0.1723	0.8359	0.024*
C13	0.6111 (4)	0.17244 (6)	0.66816 (14)	0.0177 (3)
C14	0.5451 (4)	0.20129 (6)	0.56378 (14)	0.0189 (3)
H14A	0.4039	0.1878	0.4973	0.023*
C15	0.6868 (4)	0.24985 (6)	0.55734 (14)	0.0176 (3)
H15A	0.6422	0.2694	0.4856	0.021*
H1W	0.467 (6)	0.1153 (10)	0.739 (2)	0.044 (7)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0367 (7)	0.0164 (6)	0.0162 (6)	−0.0072 (5)	0.0040 (5)	0.0014 (5)
Cl1	0.0259 (2)	0.0208 (2)	0.0155 (2)	0.00258 (15)	0.00303 (16)	−0.00167 (14)
N1	0.0188 (7)	0.0159 (7)	0.0181 (7)	0.0002 (5)	0.0040 (5)	0.0001 (5)
N3	0.0213 (7)	0.0174 (7)	0.0146 (6)	0.0007 (5)	0.0041 (5)	−0.0017 (5)
N6	0.0183 (7)	0.0141 (6)	0.0158 (6)	0.0002 (5)	0.0031 (5)	−0.0008 (5)
N7	0.0210 (7)	0.0145 (6)	0.0140 (6)	−0.0001 (5)	0.0021 (5)	0.0000 (5)
N9	0.0207 (7)	0.0137 (6)	0.0182 (7)	0.0011 (5)	0.0041 (5)	−0.0010 (5)
C2	0.0199 (8)	0.0186 (8)	0.0179 (8)	0.0001 (6)	0.0032 (6)	0.0013 (6)
C4	0.0172 (8)	0.0143 (8)	0.0174 (8)	−0.0031 (6)	0.0050 (6)	−0.0009 (6)
C5	0.0166 (8)	0.0137 (8)	0.0162 (8)	−0.0033 (6)	0.0032 (6)	−0.0001 (6)
C6	0.0150 (8)	0.0130 (7)	0.0184 (8)	−0.0046 (6)	0.0042 (6)	0.0001 (6)
C8	0.0208 (8)	0.0135 (8)	0.0206 (8)	0.0014 (6)	0.0035 (6)	0.0006 (6)
C9	0.0175 (8)	0.0155 (8)	0.0198 (8)	0.0012 (6)	0.0064 (6)	−0.0023 (6)
C10	0.0158 (8)	0.0153 (8)	0.0187 (8)	0.0027 (6)	0.0068 (6)	−0.0022 (6)
C11	0.0216 (8)	0.0191 (8)	0.0162 (8)	0.0011 (6)	0.0001 (6)	−0.0033 (6)
C12	0.0269 (9)	0.0174 (8)	0.0146 (8)	0.0032 (6)	0.0028 (6)	0.0027 (6)
C13	0.0217 (8)	0.0147 (8)	0.0178 (8)	0.0010 (6)	0.0067 (6)	−0.0009 (6)
C14	0.0221 (8)	0.0194 (8)	0.0146 (7)	−0.0008 (6)	0.0012 (6)	−0.0022 (6)
C15	0.0210 (8)	0.0173 (8)	0.0149 (7)	0.0021 (6)	0.0039 (6)	0.0022 (6)

Geometric parameters (Å, °)

O1—C13	1.371 (2)	C4—C5	1.374 (2)
O1—H1W	0.83 (3)	C5—C6	1.418 (2)
N1—C2	1.313 (2)	C8—H8A	0.9500
N1—C6	1.366 (2)	C9—C10	1.509 (2)
N3—C2	1.342 (2)	C9—H9A	0.9900
N3—C4	1.360 (2)	C9—H9B	0.9900
N3—H3A	0.8800	C10—C15	1.389 (2)

N6—C6	1.320 (2)	C10—C11	1.390 (2)
N6—C9	1.4708 (19)	C11—C12	1.386 (2)
N6—H6A	0.8800	C11—H11A	0.9500
N7—C8	1.343 (2)	C12—C13	1.385 (2)
N7—C5	1.377 (2)	C12—H12A	0.9500
N7—H7A	0.8800	C13—C14	1.388 (2)
N9—C8	1.331 (2)	C14—C15	1.384 (2)
N9—C4	1.360 (2)	C14—H14A	0.9500
C2—H2A	0.9500	C15—H15A	0.9500

C13—O1—H1W	109.3 (17)	N7—C8—H8A	123.5
C2—N1—C6	119.64 (14)	N6—C9—C10	113.33 (12)
C2—N3—C4	117.00 (13)	N6—C9—H9A	108.9
C2—N3—H3A	121.5	C10—C9—H9A	108.9
C4—N3—H3A	121.5	N6—C9—H9B	108.9
C6—N6—C9	123.76 (13)	C10—C9—H9B	108.9
C6—N6—H6A	118.1	H9A—C9—H9B	107.7
C9—N6—H6A	118.1	C15—C10—C11	118.24 (15)
C8—N7—C5	106.86 (13)	C15—C10—C9	120.98 (14)
C8—N7—H7A	126.6	C11—C10—C9	120.74 (14)
C5—N7—H7A	126.6	C12—C11—C10	121.04 (15)
C8—N9—C4	103.62 (13)	C12—C11—H11A	119.5
N1—C2—N3	125.74 (15)	C10—C11—H11A	119.5
N1—C2—H2A	117.1	C13—C12—C11	119.76 (14)
N3—C2—H2A	117.1	C13—C12—H12A	120.1
N9—C4—N3	127.83 (14)	C11—C12—H12A	120.1
N9—C4—C5	111.82 (14)	O1—C13—C12	122.22 (14)
N3—C4—C5	120.35 (14)	O1—C13—C14	117.67 (14)
C4—C5—N7	104.70 (13)	C12—C13—C14	120.08 (15)
C4—C5—C6	120.17 (14)	C15—C14—C13	119.43 (15)
N7—C5—C6	135.12 (14)	C15—C14—H14A	120.3
N6—C6—N1	119.58 (14)	C13—C14—H14A	120.3
N6—C6—C5	123.32 (14)	C14—C15—C10	121.44 (14)
N1—C6—C5	117.09 (14)	C14—C15—H15A	119.3
N9—C8—N7	113.00 (14)	C10—C15—H15A	119.3
N9—C8—H8A	123.5		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H6A···Cl1	0.88	2.36	3.2262 (14)	168
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Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+2; (ii) *x*, −*y*+1/2, *z*+1/2.

Fig. 1

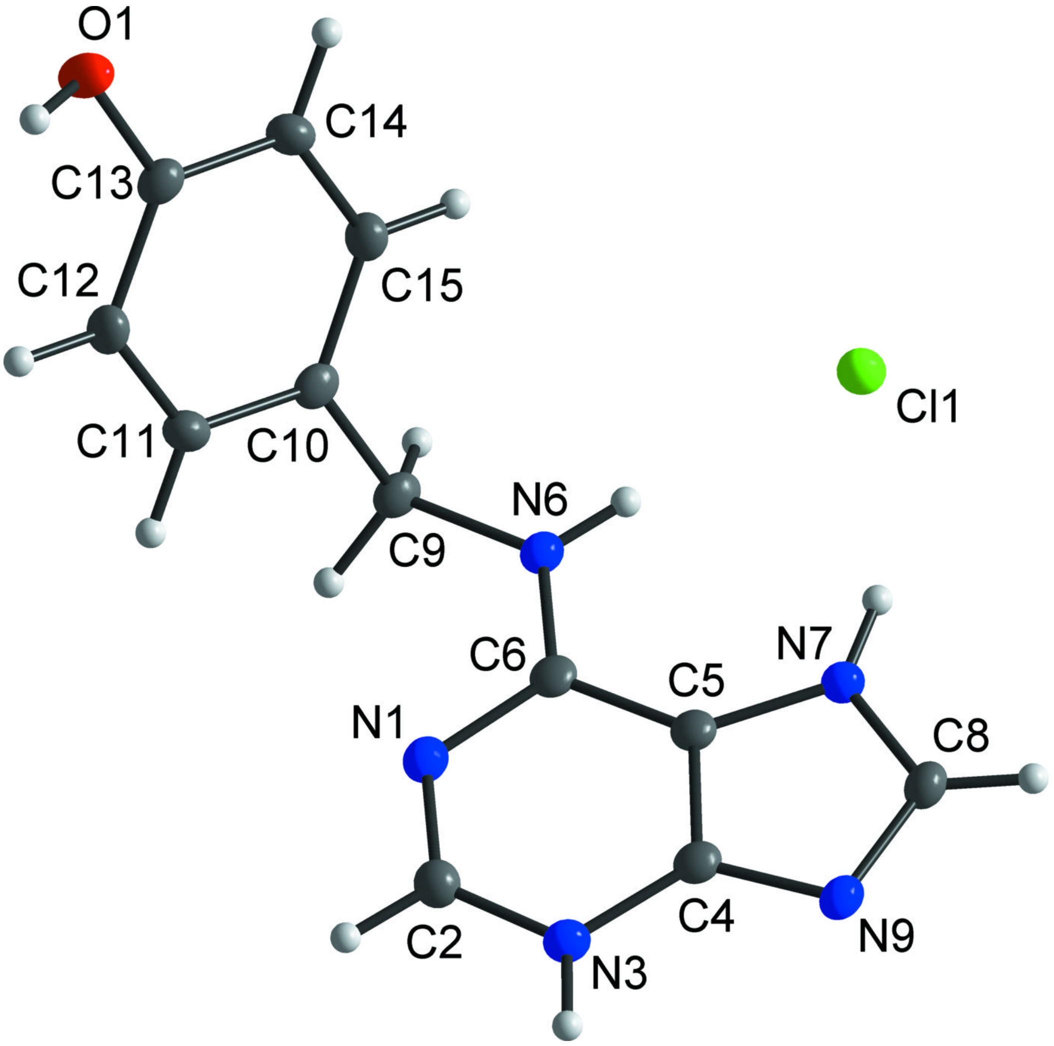

Fig. 2

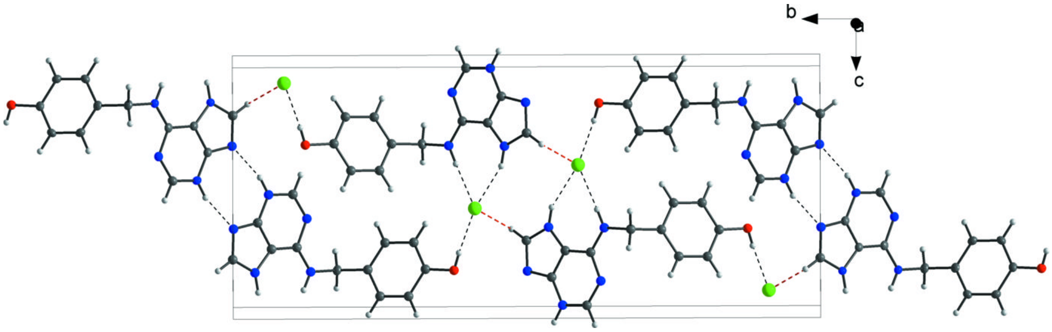

Fig. 3