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N^6-Benzyladenine hydrobromide and the solid-state conformation of cytokinins

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.014 Å
R factor = 0.067
wR factor = 0.173
Data-to-parameter ratio = 7.5

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

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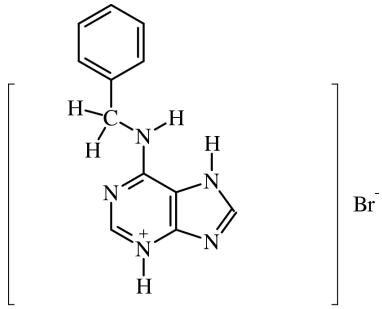
In the title compound, N^6-benzyladenine hydrobromide [N^6-benzyladeninium bromide], $C_{12}H_{12}N_5^+\cdot Br^-$, the adenine moiety exists as the N3-protonated N7-H tautomer. The N6 substituent is distal to N7 and the phenyl ring makes a dihedral angle of 108.43 (12)° with the adenine plane. Thus, protonation of benzyladenine does not affect the conformational requirements for cytokinin activity. The conformation of the title compound has been compared with other cytokinins.

Comment

Many N6-substituted adenine derivatives function as plant growth stimulants (Hall, 1973). Kinetin (N^6-furfurylaminopurine) is one of the naturally occurring cytokinins. Some of the N6-substituted adenines synthesized also show cytokinin activity depending upon their conformation (Pattabhi, 1990). N^6-Benzyladenine hydrobromide (BABR), (I), has been investigated to explore the conformation of this molecule in a variety of crystalline and chemical environments. The *ZORTEP* diagram (Zsolnai, 1997) of the molecule with the atom-labeling scheme is shown in Fig. 1.



(I)

N^6-Benzyladenine exists as the N9-H tautomer in the crystal structure (Raghunathan *et al.*, 1983). In monoprotonated adenine systems, N1 is the protonation site (Voet & Rich, 1970). However, in this crystal structure, very interestingly, the adenine moiety exists as the N7-H tautomer with the proton at N3. The H atoms at N7 and N3 were located in a difference Fourier map. Further evidence for the presence of the H atoms on these sites comes from the enhancement of the corresponding internal bond angles. The enhancement of the internal bond angles on protonation sites has been already well established (Taylor & Kennard, 1982). In the crystal structure of a copper complex of benzyladenine (Balasubramanian *et al.*, 1996) also, which was prepared under slightly acidic conditions, the adenine moieties exist as the N7-H

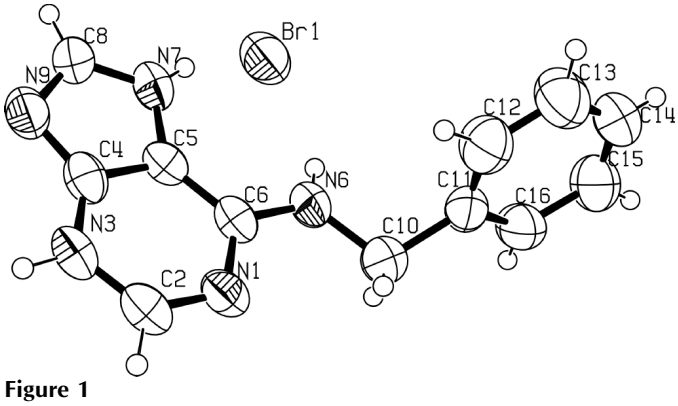


Figure 1
ZORTEP diagram (Zsolnai, 1997) of the title compound showing 50% probability displacement ellipsoids.

tautomer with protonation at N3 and coordination at N9. In BABR, the internal angle at N9 is 103.2 (7)°, which agrees well with that observed in N^6-benzyladenine existing as the N7-H tautomer. In the crystal structure of N^6-benzoyladenine (Raghunathan & Pattabhi, 1981), the adeinine moiety exists as the N7-H tautomer rather than the normal N9-H tautomer for neutral adenines and this is due to intramolecular hydrogen bonding. It is interesting to note that the N1 position is maintained free even under acidic conditions in BABR and in a copper complex of N^6-benzyladenine (Balasubramanian *et al.*, 1996).

There is no significant base stacking. This is in agreement with the packing patterns of other cytokinins previously reported. The molecules are packed by N—H···N and N—H···Br interactions.

The dihedral angle between the adenine plane and the phenyl-ring plane is 108.43 (12)°. This is in agreement with the range of values nearly 90° proposed for cytokinin activity. The N6 substituent is also distal to N7 as in other cytokinins (Sariano-Garcia & Parthasarathi, 1977; Raghunathan & Pattabhi, 1981; Bugg & Thewalt, 1972; McMullan & Sundaralingam, 1971; Walker & Tollin, 1982). Thus, a free N1, distal conformation of the N6 substituent with respect to N7, absence of base stacking and a near 90° value of the dihedral angle (between the adenine ring and the plane of the N6-substituent) seem to be necessary conditions for cytokinin activity.

Experimental

N^6-Benzyladenine (Loba Chemie, India) was dissolved in the minimum amount of dilute hydrobromic acid and recrystallized from a methanol/*n*-pentane mixture.

Crystal data

$C_{12}H_{12}N_5^+\cdot Br^-$
M_r = 306.16
Monoclinic, $P2_1/c$
a = 18.581 (3) Å
b = 5.163 (2) Å
c = 13.344 (3) Å
β = 93.71 (2)°
V = 1277.5 (6) Å^3
Z = 4
D_x = 1.592 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 40 reflections
θ = 6.8–16.3°
μ = 4.31 mm^{-1}
T = 293 K
Needle, colourless
0.33 × 0.18 × 0.15 mm

Data collection

Siemens AED diffractometer
ω–2θ scans
Absorption correction: refdelf (Parkin *et al.*, 1995)
T_{min} = 0.327, T_{max} = 0.488
1608 measured reflections
1556 independent reflections
1556 reflections with $I > 2\sigma(I)$
R_{int} = 0.106
θ_{max} = 69.9°
$h = -22 \rightarrow 22$
$k = 0 \rightarrow 6$
$l = -16 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.067
$wR(F^2)$ = 0.173
S = 1.04
1556 reflections
208 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0956P)^2 + 1.1524P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.94 e Å^{-3}
$\Delta\rho_{min}$ = −1.44 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0025 (5)

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.318 (10)	N6—C10	1.444 (12)
N1—C6	1.352 (9)	N7—C5	1.384 (9)
N3—C2	1.342 (12)	N7—C8	1.321 (10)
N3—C4	1.348 (9)	N9—C4	1.350 (10)
N6—C6	1.318 (10)	N9—C8	1.334 (10)
C2—N1—C6	119.3 (6)	N3—C4—C5	118.9 (7)
C2—N3—C4	118.2 (7)	N7—C5—C4	103.7 (6)
C6—N6—C10	124.7 (8)	N7—C5—C6	135.3 (6)
C5—N7—C8	107.4 (6)	N1—C6—N6	119.5 (7)
C4—N9—C8	103.5 (6)	N6—C6—C5	122.8 (7)
N1—C2—N3	124.9 (7)	N1—C6—C5	117.8 (6)
N9—C4—C5	112.1 (6)	N7—C8—N9	113.4 (7)
N3—C4—N9	129.0 (7)	N6—C10—C11	111.1 (8)

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···N9^{i}	0.86 (7)	2.12 (7)	2.925 (10)	156 (7)
N6—H6···Br1^{ii}	0.85 (7)	2.60 (7)	3.408 (7)	159 (6)
N7—H7···Br1^{ii}	0.77 (7)	2.50 (6)	3.244 (6)	161 (5)
C2—H2···Br1^{iii}	1.00 (8)	2.75 (8)	3.631 (8)	147 (6)
C8—H8···Br1^{iv}	0.89 (9)	2.75 (9)	3.534 (8)	147 (7)
C10—H10*B*···N1	0.86 (9)	2.45 (9)	2.806 (14)	106 (7)

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

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *DIFABS* (Walker & Stuart, 1983); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP*97 (Zsolnai, 1997); software used to prepare material for publication: *PLATON* (Spek, 1990).

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