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Supramolecular patterns in benzyladeninium *p*-toluenesulfonate

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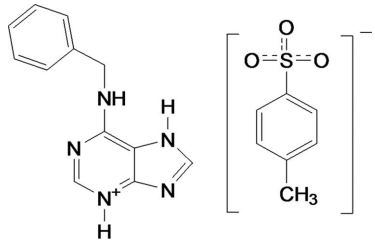
In the title compound (systematic name: 6-benzylamino-7*H*-purin-3-ium *p*-toluenesulfonate), $C_{12}H_{12}N_5^+\cdot C_7H_7O_3S^-$, the adenine moiety exists as the N^3-protonated N^7—H tautomer. The dihedral angle between the adenine ring system and the phenyl ring is 82.76 (11)°. Two of the sulfonate O atoms form C—H···O and N—H···O hydrogen bonds with the H atoms on the N and C atoms in the 3- and 8-positions, respectively, of the adenine moiety, leading to a zigzag chain. Two antiparallel zigzag chains are linked by the remaining sulfonate O atom through Hoogsteen-site H atoms (*i.e.* those on the N atoms in the 6- and 7-positions) of the adenine moiety, leading to a double chain. An annulus formed by a pair of inversion-related anions and cations has been identified. An intramolecular toluenesulfonate–phenyl C—H···π interaction is also present.

Comment

N^6-Substituted aminopurine compounds such as N^6-furfuryladenine (FA), N^6-benzyladenine (BA) and *trans*-zeatin are plant hormones classified under the name cytokinins. They are responsible for proliferation, growth regulation, antioxidance, mutation, enzyme inhibition, *etc.*, in plant cells (Francis & Sorrell, 2001). The cyclin-dependent kinases (CDK) are important functional enzymes controlled by cytokinins during apoptosis, neuronal stimulations and transcription. These kinases are influenced particularly by 2,9-disubstituted cytokinins (Trávníček & Kryštof, 2004). BA enhances the apical dominance, flowering and sometimes causes heterogeneity and inhibition of rooting and growth (Trávníček *et al.*, 2004). BA derivatives are used in neurological, antitumour and parasitic treatments (Bressi *et al.*, 2000; Haung *et al.*, 2007). Some of the bimetallic BA compounds mimic superoxide dismutase (SOD) and have antidiabetic activity (Dvorák *et al.*, 2010).

The asymmetric unit of the title compound, (I), consists of one benzyladeninium cation (BAH^+) and one toluenesulfonate anion (Fig. 1 and Table 1). BAH^+ exists as the N3-protonated N7—H tautomer, as reported earlier (Umadevi *et al.*, 2001; Nirmalram *et al.*, 2011; Balasubramanian *et al.*, 1996), in contrast to adenine systems where the N9—H tautomer predominates and the protonation site is N1 (Ślósarek *et al.*, 2006). The N3 protonation of the base is confirmed from the C2—N3—C4 bond angle of 116.9 (2)°, which is wider than the value of 110.7 (2)° in neutral BA (Raghunathan *et al.*, 1983). The dihedral angle between the benzyl substituent and the adenine ring system is 82.76 (11)°. The free N1 position, the dihedral angle of *ca* 80° and the distal orientation of the N6 substituent with respect to N7 are important requisites for cytokinin activity, and these features also occur in the title crystal structure.



(I)

The crystal structure of (I) comprises a three-dimensional network of N—H···O, C—H···O, C—H···π and π–π interactions which gives rise to the following supramolecular patterns. In the toluenesulfonate anion, all sulfonate O atoms act as hydrogen-bond acceptors: one (O3) forms an N—H···O hydrogen bond with the protonated N3 hydrogen of a BAH^+ cation; O2 forms a C—H···O hydrogen bond with the acidic C8 hydrogen of adjacent BAH^+, leading to a zigzag supramolecular chain of graph-set notation $C_2^2(9)$ (Fig. 2). This chain is crosslinked with an antiparallel chain: the remaining sulfonate O atom (O1) forms N—H···O hydrogen bonds to the Hoogsteen-site H atoms of adenine (N6—H and N7—H), forming a double chain (Fig. 3) and an $R_2^1(7)$ motif. This motif has been recently identified in cobalt complexes of the N^6-furfuryladenine cation and N^6-benzyladenine cation (Tamilselvi & Muthiah, 2010).

Because of the interplay of double chains, two inversion-related BAH^+ cations and two inversion-related sulfonate anions, a supramolecular annulus (Fig. 4) is formed. In this

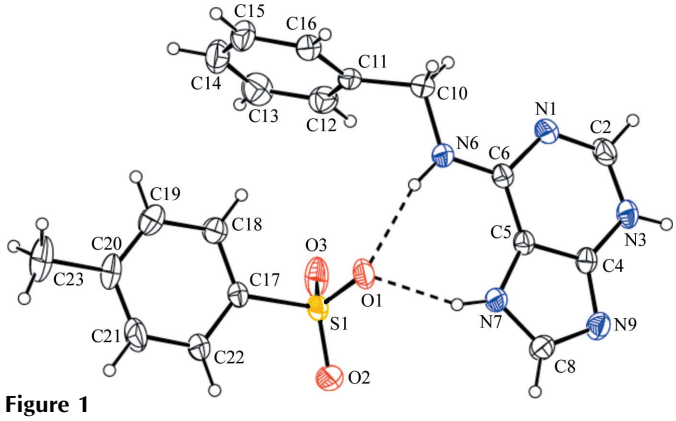


Figure 1
A view of the components of (I), with displacement ellipsoids drawn at the 50% probability level.

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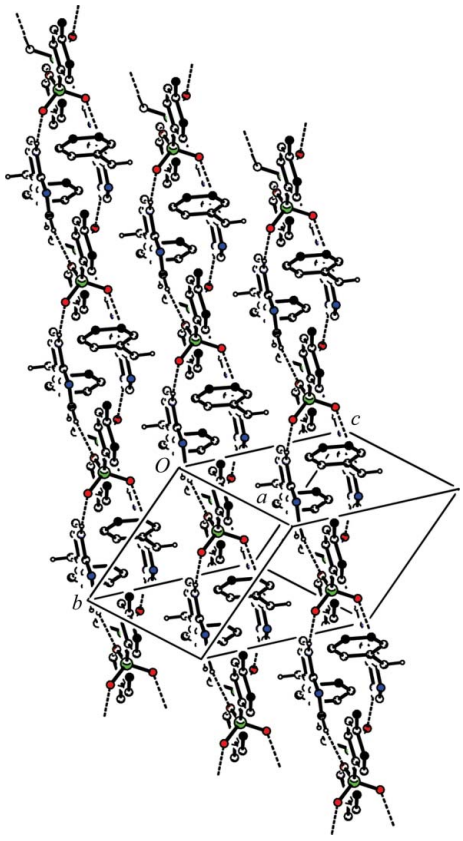

Figure 2
A view of the structure of (I), showing the double chains formed by two $C_2^2(9)$ chains. H atoms not involved in hydrogen bonding have been omitted for clarity.

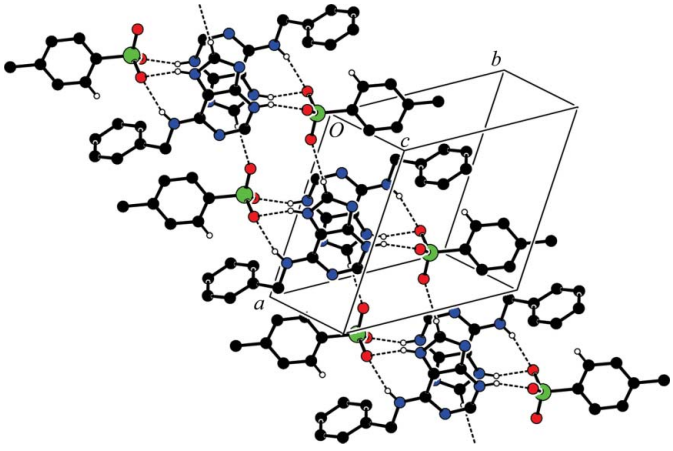

Figure 3
A view of a double chain illustrating the $R_4^4(14)$ motif and C—H$\cdots\pi$ interactions. H atoms not involved in hydrogen bonding have been omitted for clarity.

annulus, the inversion-related purine rings (N1, C2, N3, C4, C5, C6, N7, C8 and N9) and [N1^{i}–N9^{i}; symmetry code: (i) $-x+1, -y, -z+1$] adopt an antiparallel stacking arrangement through face-to-face (π–π) interaction with a corresponding centroid–centroid distance of 3.377 (3) Å (the centroid is defined with respect to the nine-atom purine system); the interplanar distance between stacked purine rings

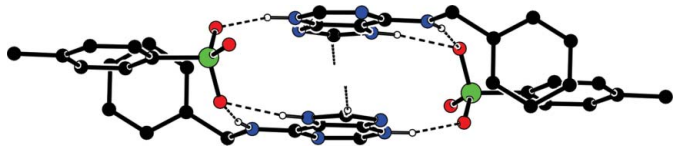

Figure 4
A view of one annulus showing the antiparallel stacking of purine moieties. H atoms not involved in hydrogen bonding have been omitted for clarity.

is 3.330 (3) Å. These values are well within the range reported earlier (Garcia-Teran *et al.*, 2004; Verma *et al.*, 2010). Two annuli are connected by an $R_4^4(14)$ motif. An edge-to-face (C—H$\cdots\pi$) interaction is observed between the C18—H18 group of toluenesulfonate and the C11–C16 phenyl ring (centroid *Cg*) of BAH$^+$, with a H18$\cdots$*Cg* distance of 2.86 Å and a C18—H18$\cdots$*Cg* angle of 162° (Wang *et al.*, 2007). The double chains are linked by a π–π stacking interaction between the toluenesulfonate and pyrimidine rings, with a centroid–centroid distance of 3.6127 (15) Å (Verma *et al.*, 2010).

Experimental

N^6-Benzyladenine (56.3 mg, 0.25 mmol) was dissolved in methanol (20 ml). *p*-Toluenesulfonic acid (47.4 mg, 0.25 mmol) was dissolved in ethanol (20 ml). The solutions were mixed and heated for 30 min over a water bath. Colourless needle-shaped crystals of (I) appeared after a few days of evaporation at room temperature.

Crystal data

$C_{12}H_{12}N_5^+\cdot C_7H_7O_3S^-$
M_r = 397.46
Triclinic, $P\overline{1}$
a = 9.5741 (10) Å
b = 9.9089 (11) Å
c = 11.3324 (12) Å
α = 99.957 (6)°
β = 90.886 (7)°
γ = 116.562 (6)°
V = 941.87 (18) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.20 mm^{-1}
T = 296 K
0.12 × 0.10 × 0.08 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.976, T_{max} = 0.984
17454 measured reflections
6129 independent reflections
3345 reflections with $I > 2\sigma(I)$
R_{int} = 0.063

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.210
S = 0.97
6129 reflections
254 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.65 e Å^{-3}
$\Delta\rho_{min}$ = −0.65 e Å^{-3}

Methyl H atoms were located in a difference Fourier synthesis and subsequently idealized and refined as a rigid rotating group, with C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C). Other C-bonded H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H = 0.93 (aromatic) or 0.97 Å (methylene), and with U_{iso}(H) = 1.2U_{eq}(C). All N-bonded H atoms were placed in idealized positions and constrained to ride 0.86 Å from their parent atoms, with U_{iso}(H) = 1.2U_{eq}(N).

Table 1
Selected geometric parameters (Å, °).

S1—O1	1.4636 (18)	N6—C10	1.459 (3)
S1—O2	1.435 (2)	N6—C6	1.324 (3)
S1—O3	1.4500 (19)	N7—C8	1.349 (3)
N1—C2	1.304 (3)	N7—C5	1.372 (3)
N3—C2	1.340 (4)		
O1—S1—C17	105.96 (10)	C6—N6—C10	123.38 (19)
O1—S1—O2	111.84 (11)	C5—N7—C8	106.15 (19)
O1—S1—O3	111.22 (12)	C4—N9—C8	103.0 (2)
C2—N1—C6	119.3 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O3^{i}	0.86	1.95	2.712 (3)	147
N6—H6···O1	0.86	2.12	2.959 (3)	165
N7—H7···O1	0.86	1.99	2.770 (2)	150
C8—H8···O2^{ii}	0.93	2.31	3.225 (4)	168

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

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON* and *Mercury* (Macrae *et al.*, 2008).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM3103). Services for accessing these data are described at the back of the journal.

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