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ORIGINAL PAPER

Hydrogen Bonded Supramolecular Assembly in *N*^{6}-Benzyladeninium Nitrate and *N*^{6}-Benzyladeninium 3-Hydroxy Picolinate: A Synthetic Cytokinin

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Abstract *N*^{6}-benzyladeninium nitrate, (**1**), $C_{12}H_{12}N_5^+$ NO_3^- crystallizes in $P2_1/c$, with $a = 15.0035(13)$, $b = 5.3788(5), c = 16.8954(13)$ Å, $\beta = 107.331(6)°, Z = 4$ and *N*^{6}-benzyladeninium 3-hydroxy picolinate, (**2**), $C_{12}H_{12}$ N_5^+ $C_6H_4NO_3^-$, crystallizes in $P1$, with $a = 8.3017(4)$, $b = 14.6170(7)$, $c = 14.7909$ (8) Å, $\alpha = 78.801$ (4), $\beta = 81.979$ (4),$\gamma = 88.849$ (4)°, $Z = 4$. In both the salts, the cation exists as N(7)H tautomer with protonation at the N_3 atom. The dihedral angle of 76.64 (16)° for (**1**), 67.91(12)° for (cation A) and 68.27 (13)° for (cation B) in (**2**), between the adenine plane and phenyl ring plane, the distal orientation of the N6 substituent with respect to the imidazole ring and the free N1 position, make these benzyladeninium cations meet all the requirements necessary for cytokinin activity. The crystal structures are stabilized by N–H···N, N–H···O, C–H···O hydrogen bonds and C–H···π stacking interaction between symmetry related benzyladenine molecule.

Keywords *N*^{6}-benzyladenine salts · Crystal structure · Cytokinin activity · Supramolecular architecture

Introduction

Cytokinins are well known plant growth substances [1], which play a vital role in the development process of plants. They occur abundantly in plant tissues, root tips, xylum sap developing fruits, tumour tissues and germinating seeds. Among different classes of cytokinins, adenine type aromatic cytokinins like zeatin, kinetin (*N*^{6}-furfuryladenine) and benzyladenine have been found to markedly influence the biological activity. Zeatin and kinetin are naturally occurring cytokinins, whereas benzyladenine is a synthetic cytokinin.The crystal structures of cytokinins have been investigated in a variety of crystalline environments; *N*^{6}-benzyladenine [2], *N*^{6}-furfuryladenine [3], *N*^{6}-benzyladenine hydrochloride [4], *N*^{6}-benzyladenine hydrobromide [5], *N*^{6}-benzyladenine sulphosalicylate monohydrate [6], *N*^{6}-furfuryladenine hydrochloride [7], copper complex of *N*^{6}-furfuryladenine [8] and a copper complex of *N*^{6}-benzyladenine [9]. The aim of the present study is to understand the conformations and supramolecular architectures of *N*^{6}-benzyladeninium nitrate and *N*^{6}-benzyladeninium 3-hydroxy picolinate.

Experimental

Crystals were prepared by dissolving; *N*^{6}-benzyladenine (Loba Chemie, India) in methanol and addition of 0.5 ml of dilute nitric acid for (**1**) and 3-hydroxy picolinic acid (Aldrich) in 20 ml of water in 1:1 ratio for (**2**). The resultant solution was heated for 15 min over a water bath and kept for slow evaporation. After a few days, colorless crystals were obtained (The quality of the crystals obtained was poor. Our efforts to crystallize these compounds in a variety of solvents were not fruitful).

Data collection: APEX2 [10]; cell refinement: SAINT [10]; data reduction: SAINT [10]; program(s) used to solve structure: SHELXS97 [11]; program(s) used to refine structure: SHELXL97 [11]; molecular graphics: PLATON [12]; software used to prepare material for publication: PLATON [12]. All hydrogen atoms were positioned geometrically and were refined using riding model. The N–H and C–H bond lengths are 0.86 and 0.93–0.97 Å,

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respectively [*U*iso(H) = 1.2Ueq(parent atom)]. Crystallographic details and hydrogen bonding geometries for the compounds are given in Tables 1 and 2, respectively.

Results and Discussion

The probable tautomeric forms assumed by adenines and adenine based cytokinins in normal and acidic conditions have been reviewed [13]. As expected the benzyladenine molecule of the title compounds exist as N(7)H tautomer with protonation at the N3 atom. The evidence for the presence of the H atoms on these sites is further confirmed by the changes in bond angles at N1, N3, N7 and N9. The internal angles at N1 and N9 do not differ largely, whereas N3 and N7 show a significant change. The dihedral angle of 76.4 (2)° for (**1**), 67.91(12)° for (cation A) and 68.27 (13)° for (cation B) in (**2**), between the adenine plane and phenyl ring plane, the distal orientation of the N6 substituent with respect to the imidazole ring and the free N1 position, are the salient features reported as the requirements necessary for cytokinin activity [3, 14–17]. The molecular geometry of these compounds, in terms of bond length and bond angles are in good agreement with the crystal structures of N^6-benzyladenine hydrochloride [4], N^6-benzyladenine hydrobromide [5], and N^6-benzyladenine copper complex [9].

Table 2 Hydrogen bonding geometry (Å, °) for compounds **1** and **2**

D–H···A	D–H	H···A	D···A	D–H···A
Compound **1**				
N3–H3···N9^{i}	0.86	2.00	2.846 (5)	168
N6–H6···O1	0.86	2.00	2.824 (5)	160
N7–H7···O2	0.86	1.90	2.745 (5)	165
C8–H8···O2^{ii}	0.93	2.35	3.235 (6)	160
C8–H8···O3^{ii}	0.93	2.56	3.386 (6)	149
C10–H10A···N1	0.97	2.42	2.869 (5)	108
C12–H12···N6	0.93	2.54	2.867 (6)	101
C15–H15···O1^{iii}	0.93	2.55	3.468 (7)	171
Compound **2**				
O3B–H3B1···O2B	0.82	1.81	2.536 (3)	146
O3A–H3A1···O2A	0.82	1.83	2.548 (3)	146
N3A–H3A···O1B^{iv}	0.86	2.52	2.967 (3)	113
N3A–H3A···N17B^{iv}	0.86	1.97	2.811 (3)	168
N3B–H3B···O1A	0.86	2.52	2.963 (3)	113
N3B–H3B···N17A	0.86	1.92	2.766 (3)	169
N6A–H6A···O2A	0.86	1.96	2.789 (3)	162
N6B–H6B···O2B	0.86	1.97	2.802 (3)	162
N7A–H7A···O1A	0.86	1.79	2.642 (3)	173
N7B–H7B···O1B	0.86	1.79	2.645 (3)	173
C2A–H2A···O1B^{iv}	0.93	2.54	3.017 (4)	113
C2B–H2B···O1A	0.93	2.54	3.012 (4)	112

Symmetry codes: (i) = 2 − *x*, −1/2 + *y*, 3/2 − *z*; (ii) = 2 − *x*, 2 − *y*, 1 − *z*; (iii) = 1 − *x*, −1/2 + *y*, 1/2 − *z*; (iv) = *x*, −1 + *y*, *z*

Table 1 Crystal data and structure refinement for compounds **1** and **2**

Compound reference	**1**	**2**
Chemical formula	$C_{12}H_{12}N_5^+\ NO_3^-$	$C_{12}H_{12}N_5^+\ C_6H_4NO_3^-$
Formula mass	288.28	364.37
Crystal system	Monoclinic	Triclinic
a/Å	15.0035(13)	8.3017(4)
b/Å	5.3788(5)	14.6170(7)
c/Å	16.8954(13)	14.7909(8)
α/°	90.00	78.801(4)
β/°	107.331(6)	81.979(4)
γ/°	90.00	88.849(4)
Unit cell volume/Å^3	1301.57(19)	1743.37(15)
Temperature/K	296	296 (2)
Space group	*P*21/*c*	$P\,\bar{1}$
No. of formula units per unit cell, *Z*	4	4
No. of reflections measured	6478	18163
No. of independent reflections	1130	3575
R_{int}	0.0446	0.0484
Final R_1 values ($I > 2\sigma(I)$)	0.0386	0.0427
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0981	0.1071
Final R_1 values (all data)	0.0572	0.0641
Final $wR(F^2)$ values (all data)	0.1116	0.1242
Goodness of fit on F^2	0.958	1.008

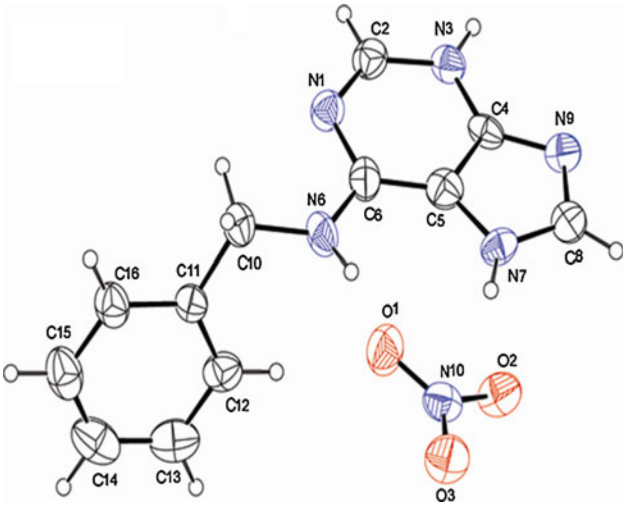

Fig. 1 *ORTEP* view of the compound (**1**) with 30% probability displacement ellipsoids

The asymmetric unit of (**1**) contains one N^6-benzyladenine cation and a nitrate anion (Fig. 1). The 2_1 screw related N^6-benzyladenine cations are linked by N(3)–H···N(9) hydrogen bonds. The nitrate ion forms an interesting network of hydrogen bonds with the benzyl adenine cation. The N6H and N7H of the benzyl adenine cation form a cyclic ring motif with graph set [18] $R_2^2(9)$ with the oxygen atoms (O1 and O2) of the nitrate anion through N–H···O hydrogen bonds. This type of motif is very much similar to the fork like interaction observed in aminopyrimidine carboxylates [19, 20]. Interestingly there exists a C–H···O interaction involving the C8–H8 of the benzyl adenine cation with the O2 and O3 atom of the nitrate anion. The three centered hydrogen bond $R_1^2(4)$ bridges the symmetry related benyladenine nitrate pairs. This arrangement leads to the creation of a new dimeric unit with motif $R_4^2(10)$, facilitated by a bifurcated hydrogen

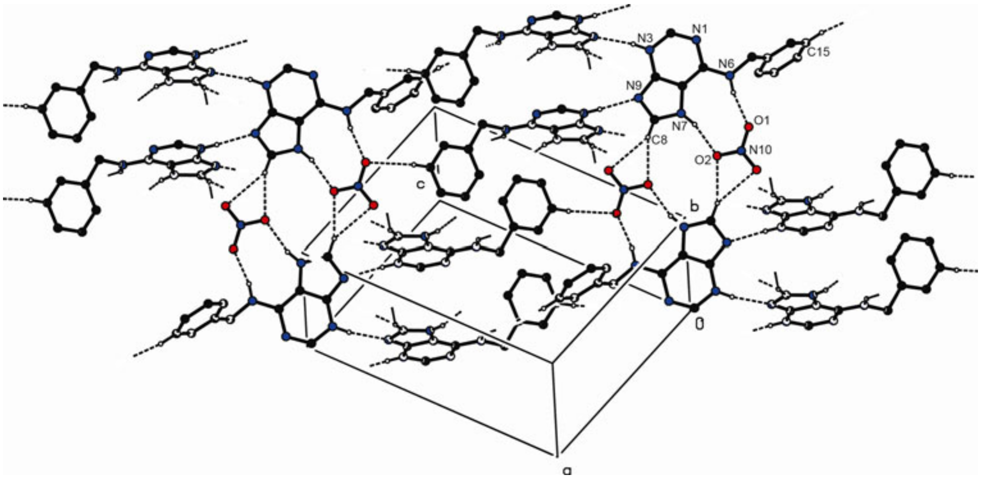

Fig. 2 A view of the supramolecular interactions in compound (**1**). *Dashed lines* indicate hydrogen bonds and H atoms not involved in hydrogen bonding have been omitted for clarity

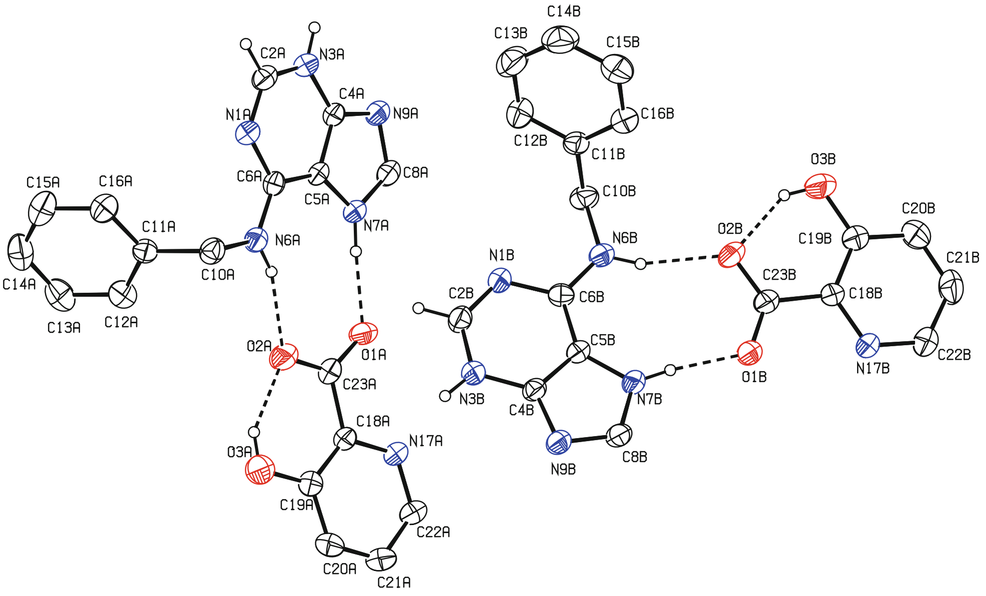

Fig. 3 *ORTEP* view of the compound (**2**) with 30% probability displacement ellipsoids

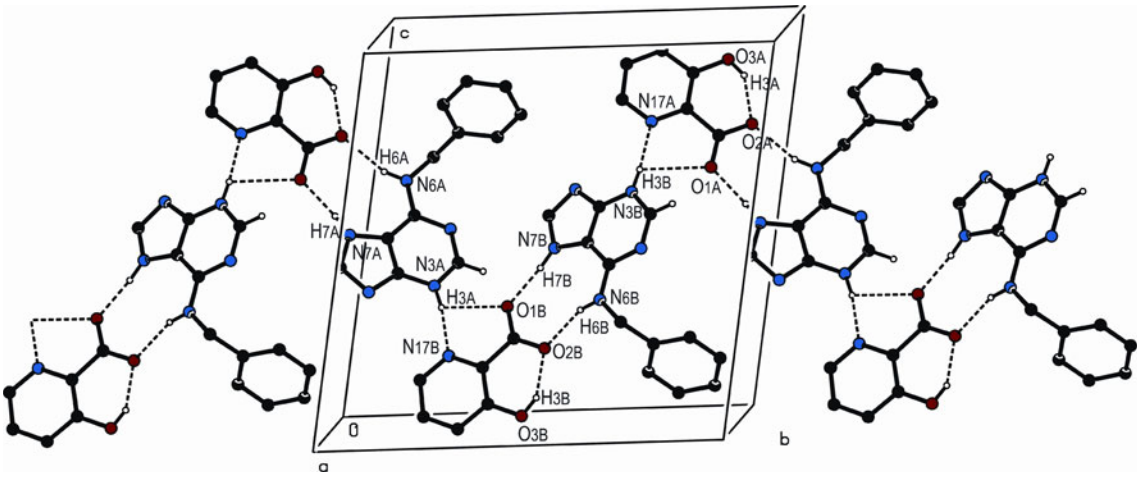

Fig. 4 View of the chain along the b axis for compound (**2**)

bond donor and a bifurcated acceptor (O2). The combination of $R_2^2(9)$ and $R_4^2(10)$ leads to the formation of an array of hydrogen bonds. Two such dimeric units thus formed are linked via C–H···O hydrogen bonds as shown in (Fig. 2). The crystal structure is further stabilized by C–H$\cdots\pi$ interaction between the symmetry related benzyladenine molecule.

The compound (**2**) crystallizes with two independent molecules in the asymmetric unit, (A and B) (Fig. 3). The two molecules adopt similar geometry and supramolecular interaction. In each of the 3-hydroxy picolinate anion (A and B), an intramolecular O–H···O hydrogen bond exists between the hydroxyl and carboxylate group with graph set notation S(6). The protonated N^6-benzyladenine cation (A and B) interacts with the carboxylate group of the 3-hydroxy picolinate anion (A and B) through N–H···O hydrogen bonds with graph set $R_2^2(9)$. This motif is very much similar to that observed in (**1**). The hydrogen atom at N3 of the cation, acts as a bifurcated donor to O1 and N17 of the anion to form a ring motif $R_1^2(5)$ through N–H···N and N–H···O hydrogen bonds. This ring motif, plays a major role in interlinking the two independent molecules to form a zigzag chain of alternate assembly along the b axis (Fig. 4) Such chains running parallel to one another are connected via C–H$\cdots\pi$ interaction between the cations A and B.

Supplementary Material

CCDC-795111 for (**1**) and 795105 for (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge athttp://www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 IEZ, UK; fax: C44 (0) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk].

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