

Supramolecular hydrogen-bonded networks in adeninium phenylacetate phenylacetic acid monohydrate and adeninium 3-carboxypropionate monohydrate

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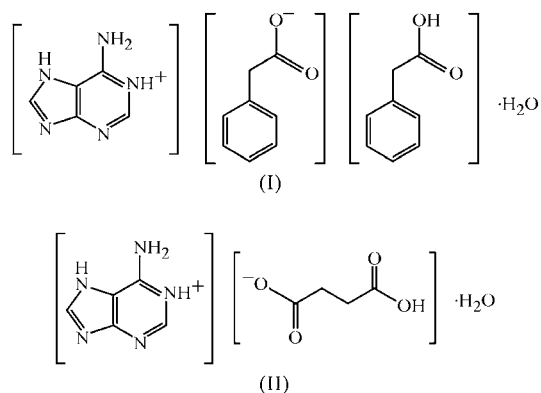
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In the title compounds, $C_5H_6N_5^+ \cdot C_8H_7O_2^- \cdot C_8H_8O_2 \cdot H_2O$, (I), and $C_5H_6N_5^+ \cdot C_4H_3O_4^- \cdot H_2O$, (II), the adeninium cations form N—H...O hydrogen bonds with their anion counterparts and adeninium–adeninium self-association base pairs with the $R_2^2(10)$ motif (Bernstein *et al.*, 1995). A complete hydrogen-bonding motif analysis is presented. Conventional hydrogen bonds lead to layer structures in (I) and to two-dimensional infinite polymeric ribbons in (II). C—H...O interactions are found in both structures, while weak π – π stacking interactions are only observed in (I).

Comment

Protonated nucleobases are present in many biochemical processes, such as enzymatic reactions and the stabilization of triplex structures, and they play a key role in a newly emerging feature of nucleic acid chemistry, namely acid–base catalysis (Lippert, 2005). Among the nucleobases, adenine shows the widest range of binding possibilities (Salam & Aoki, 2000) because it exhibits at least five donor sites and forms a great variety of complexes. Adenine forms hydrogen bonds with other nucleobases that can lead to the formation of supramolecular structures, which can be of chemical and biological interest (Shipman *et al.*, 2000; Bazzicalupi *et al.*, 2001). Phenylacetic acid has been found to be an active auxin (a type of plant hormone) molecule, predominantly found in fruits and also used in penicillin G production (Hillenga *et al.*, 1995). Succinic acid is a dicarboxylic acid which occurs naturally in plant and animal tissues and plays a significant role in intermediary metabolism (Krebs cycle) in the body. Our particular interest lies in the structure of the crystalline complexes of adenine with aromatic and dicarboxylic acids and examining the interactions between the components. Recently, we reported the crystal structure of bis(adeninium) phthalate phthalic acid 1.45-hydrate (Sridhar & Ravikumar, 2007). In

the present study, the crystal structures of adeninium phenylacetate phenylacetic acid hydrate, (I), and adeninium succinate hydrate, (II), are presented.



The asymmetric unit of (I) contains one adeninium cation, one phenylacetate anion, one neutral phenylacetic acid and one water molecule (Fig. 1).

Adeninium cations can be either mono- or diprotonated and the bond lengths and angles are dependent on the degree of protonation (Hingerty *et al.*, 1981; Langer & Huml, 1978). It is well documented that the N9H amine form of adenine is the most stable in the gas phase and in water solution ($pK_a = 9.8$) (Gu & Leszczynski, 1999; Perun *et al.*, 2005). This canonical tautomeric form contains three basic N atoms. The most basic site ($pK_a = 4.2$) is N1, which accepts the first proton; the next protonation occurs at N7, and the next at N3.

In both structures, atom N1 is protonated, which can be seen from the increase in the C2–N1–C6 bond angles (Tables 1 and 3); the corresponding value for neutral adenine is 119.8° (Voet & Rich, 1970). The location of the H atom bonded to atom N1 in the difference Fourier map and the successful refinement of this H atom confirmed the site of protonation in both structures.

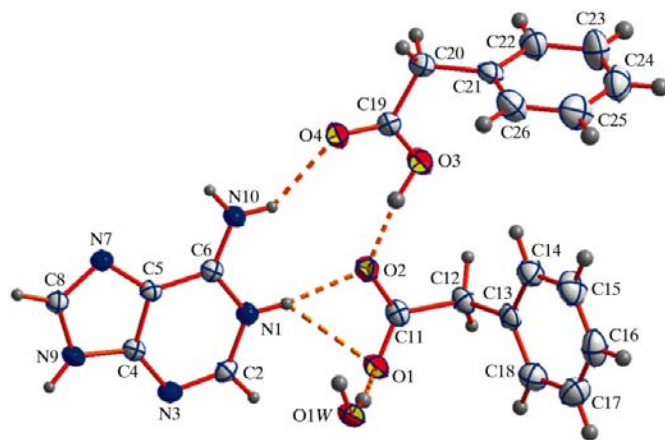


Figure 1

A view of the components of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.

The adeninium base is nearly planar and the dihedral angle between the least-squares planes through the six- and five-membered rings is $0.42(9)^\circ$ for (I) and $0.95(8)^\circ$ for (II).

The molecular geometries of phenylacetic acid in its anionic and neutral forms in (I) are in good agreement with those of a similar structure (Hodgson & Asplund, 1991). The near equality of C—O distances and O—C—C angles (Table 1) clearly shows the existence of the carboxylate group based on C11, whilst differences in the C—O distances and O—C—C angles (Table 1) confirm the carboxyl group (C19). In the phenylacetate anion, the mean plane of the carboxylate group (C11/O1/O2) is rotated from the plane of the benzene ring (C13–C18) by $71.9(1)^\circ$, while in the neutral phenylacetic acid,

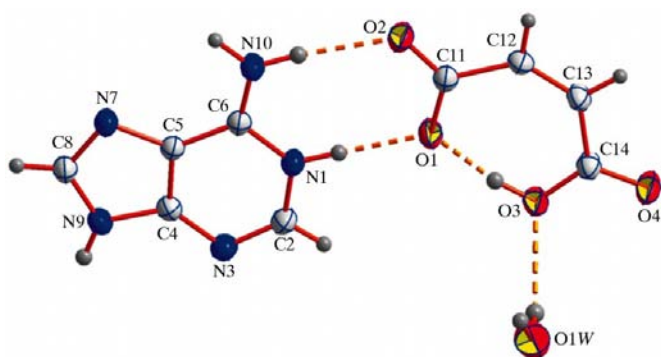


Figure 2
A view of the components of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.

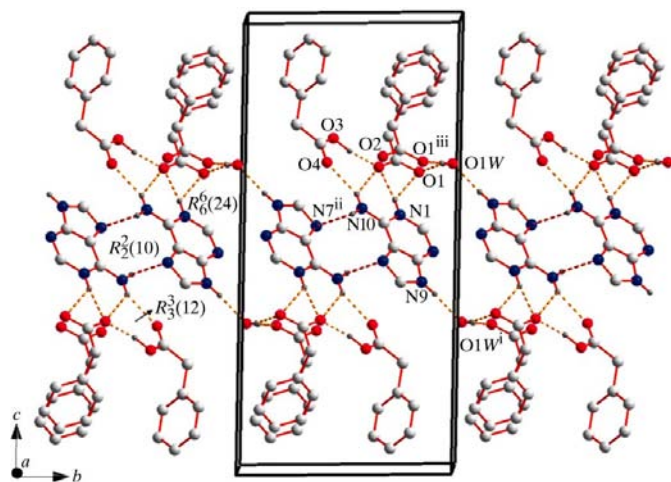


Figure 3
A packing diagram for (I), viewed down the *a* axis. Dashed lines indicate O—H...O and N—H...O hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted for clarity. Only atoms involved in the hydrogen bonding are labelled. [Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $-x + 2, -y + 1, -z + 1$; (iii) $x + 1, y, z$.]

the plane of the carboxyl group (C19/O3/O4) is rotated by $85.7(1)^\circ$ with respect to its attached benzene ring plane (C21–C26).

The asymmetric unit of (II) comprises one adeninium cation, one succinate anion and one water molecule, with one of the carboxyl groups in the succinic acid deprotonated (Fig. 2). The two carboxyl groups are in a *cis* orientation with respect to the central C—C bond (Table 3). The O—H bond of the carboxyl group is in a *trans* conformation with respect to the C=O bond of the carboxylate group, as evidenced from the H3O—O3—C14—O4 torsion angle of $-177(1)^\circ$. This orientation can be attributed to an intramolecular O—H...O hydrogen bond involving the carboxyl and carboxylate groups of the succinate anion, leading to the formation of an *S*(7) motif (Bernstein *et al.*, 1995).

In the crystal structure of (I), there are six different modes of hydrogen-bonding interactions *viz.* cation–cation, cation–anion, cation–neutral, anion–neutral, cation–water and water–anion (Table 2), while in the crystal structure of (II), only four different modes of hydrogen-bonding interactions are observed, *viz.* cation–cation, cation–anion, anion–anion and water–anion (Table 4). The adeninium cation forms N—H...O hydrogen bonds with the phenylacetate anion, the neutral phenylacetic acid and the water molecule in (I) (Table 2), while in (II), it forms N—H...O hydrogen bonds with only the succinate anion (Table 4). In both structures, intermolecular N—H...N hydrogen bonds involving the Hoogsteen faces (atoms N10 and N7) of the adeninium cations form a centrosymmetric dimer generating a characteristic $R_2^2(10)$ motif (Figs. 3 and 4). In (I), the Watson–Crick edges (atoms N1 and N10) of the cation link the anion and the neutral phenylacetic acid molecule through a three-centred hydrogen-bonding pattern (Jeffrey & Saenger, 1991). The anion and neutral phenylacetic acid molecules are interconnected by a strong O—H...O hydrogen bond (entry 6, Table 2). Thus, the combination of these N—H...O and O—H...O hydrogen bonds leads to the formation of an $R_3^3(12)$ motif. In (II), the Watson–Crick edges of the cation link the

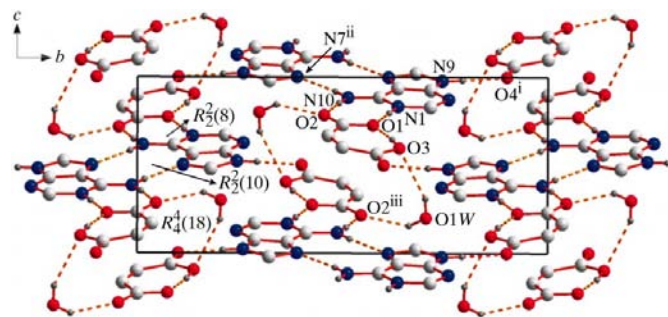


Figure 4
A packing diagram for (II), viewed down the *a* axis. Dashed lines indicate O—H...O and N—H...O hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted for clarity. Only atoms involved in the hydrogen bonding are labelled. [Symmetry codes: (i) $x - 1, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $-x, -y + 1, -z + 2$; (iii) $-x + 1, -y + 1, -z + 1$.]

succinate anion through N—H···O hydrogen bonds, generating an $R_2^2(8)$ motif (Fig. 4).

The water molecule plays a dual role as both donor and acceptor in the hydrogen-bonding interactions in (I) (Table 2). It participates in three hydrogen bonds, acting as donor to an adjacent phenylacetate anion and a symmetry-related anion (symmetry code: $x + 1, y, z$) via O—H···O hydrogen bonds, and as an acceptor to an adeninium cation via an intermolecular N—H···O hydrogen bond. In (II), the water molecule acts only as a donor and links the two succinate anions via O—H···O hydrogen bonding.

In (I), the combination of O—H···O, N—H···O and N—H···N hydrogen bonds involving the adeninium cations, the phenylacetate anions and the neutral phenylacetic acid molecules leads to hydrogen-bonded columns, which extend parallel to the c axis. Each column consists of chains of adeninium cations sandwiched between the hydrophilic chains of phenylacetate anions and the neutral phenylacetic acid molecules. The water molecule in turn produces a hydrogen-bonded network cavity of $R_6^6(24)$ motif (Fig. 3) by cross-linking the columns of adeninium cations, phenylacetate anions and neutral phenylacetic acid molecules to give hydrogen-bonded layers which lie parallel to the (010) plane. There are two short N3···N3' distances in the cavity [$N3···N3(-x + 1, -y + 2, -z + 1) = 3.233(2) \text{ \AA}$ and $N3···N3(-x, -y + 2, -z + 1) = 3.409(2) \text{ \AA}$].

In (II), the $R_2^2(10)$ and $R_2^2(8)$ motifs are arranged alternately and form hydrogen-bonded columns in the crystal packing along the c axis (Fig. 4). Each hydrogen-bonded column is further interlinked to its adjacent glide-related columns by intermolecular N—H···O hydrogen bonds (Table 4). Water molecules connect neighbouring hydrogen-bonded columns and form a rather circular-shaped hydrogen-bonded network cavity (Fig. 4), thereby generating a characteristic $R_4^4(18)$ motif. These hydrogen-bonded columns aggregate as infinite two-dimensional hydrogen-bonded polymeric ribbons.

It is noteworthy that in (I), the water molecule does not have any interactions with the neutral phenylacetic acid, while in (II), it links to the cation only through a weak C—H···O interaction. In both structures, weak C—H···O interactions are observed in the crystal packing. In (I), possible weak π – π stacking interactions exist between the aromatic rings of the adeninium base, with the distance between the centroids of the rings defined by atoms C4/C5/N7/C8/N9 and atoms N1/C2/N3/C4/C5/C6 at $(x + 1, y, z)$ being $3.768(1) \text{ \AA}$, the interplanar spacing being $3.259(1) \text{ \AA}$ and the centroid offset being 1.89 \AA . No such π – π stacking interaction is observed in (II).

Experimental

To obtain crystals of (I) suitable for X-ray study, adenine (0.135 g, 1 mmol) and phenylacetic acid (0.136 g, 2 mmol) were dissolved in water (10 ml) and the solution was allowed to evaporate slowly. Crystals of (II) were obtained by the slow evaporation of an equimolar solution of adenine (0.135 g) and succinic acid (0.118 g) in water (10 ml).

Compound (I)

Crystal data

$C_5H_6N_5^+ \cdot C_8H_7O_2^- \cdot C_8H_8O_2 \cdot H_2O$	$\gamma = 83.239(4)^\circ$
$M_r = 425.44$	$V = 1059.2(4) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 4.7805(10) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.303(2) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$c = 21.678(5) \text{ \AA}$	$T = 294(2) \text{ K}$
$\alpha = 88.886(4)^\circ$	$0.22 \times 0.18 \times 0.12 \text{ mm}$
$\beta = 87.595(3)^\circ$	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	3687 independent reflections
8134 measured reflections	2786 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.131$	
$S = 1.05$	$\Delta\rho_{max} = 0.22 \text{ e \AA}^{-3}$
3687 reflections	$\Delta\rho_{min} = -0.14 \text{ e \AA}^{-3}$
308 parameters	

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I).

C11—O1	1.241(2)	C19—O4	1.196(2)
C11—O2	1.262(2)	C19—O3	1.295(2)
C2—N1—C6	123.41(16)	O4—C19—O3	122.76(18)
O1—C11—O2	121.99(17)	O4—C19—C20	122.11(18)
O1—C11—C12	119.20(17)	O3—C19—C20	115.11(17)
O2—C11—C12	118.77(17)		

Table 2

Hydrogen-bond geometry (\AA , $^\circ$) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N···O2	0.89(2)	1.89(2)	2.773(2)	170(2)
N1—H1N···O1	0.89(2)	2.49(2)	3.156(2)	131.8(17)
N9—H9N···O1W ⁱ	0.85(2)	1.88(2)	2.720(2)	173.4(19)
N10—H10A···O4	0.86(2)	2.09(2)	2.806(2)	140.9(18)
N10—H10B···N7 ⁱⁱ	0.89(2)	2.10(2)	2.946(2)	158.6(17)
O3—H3O···O2	0.99(3)	1.61(3)	2.587(2)	171(3)
O1W—H2W···O1	0.85(3)	2.11(3)	2.945(2)	170(3)
O1W—H1W···O1 ⁱⁱⁱ	0.91(3)	1.83(3)	2.733(2)	172(3)
C8—H8···O4 ⁱⁱ	0.93	2.32	3.168(3)	152

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

Compound (II)

Crystal data

$C_5H_6N_5^+ \cdot C_4H_3O_4^- \cdot H_2O$	$V = 1198.3(7) \text{ \AA}^3$
$M_r = 269.23$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.539(3) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$b = 17.149(6) \text{ \AA}$	$T = 294(2) \text{ K}$
$c = 7.450(3) \text{ \AA}$	$0.25 \times 0.15 \times 0.07 \text{ mm}$
$\beta = 100.503(5)^\circ$	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	10914 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2001)	2112 independent reflections
$T_{min} = 0.97, T_{max} = 0.98$	1934 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.124$	
$S = 1.16$	
2112 reflections	$\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$
197 parameters	$\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$
4 restraints	

Table 3
Selected geometric parameters (\AA , $^\circ$) for (II).

C11—O2	1.2410 (19)	C11—O1	1.279 (2)
C2—N1—C6	124.03 (13)	O4—C14—O3	120.04 (14)
O2—C11—O1	122.79 (14)	O4—C14—C13	118.51 (13)
O2—C11—C12	117.76 (14)	O3—C14—C13	121.45 (13)
O1—C11—C12	119.45 (13)		
C11—C12—C13—C14	-1.2 (3)		

Table 4
Hydrogen-bond geometry (\AA , $^\circ$) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N \cdots O1	0.914 (10)	1.821 (16)	2.734 (2)	179 (2)
N9—H9N \cdots O4 ⁱ	0.87 (3)	1.90 (3)	2.763 (2)	176 (2)
N10—H10A \cdots O2	0.91 (2)	2.01 (2)	2.917 (2)	174 (2)
N10—H10B \cdots N7 ⁱⁱ	0.943 (19)	2.06 (2)	2.964 (2)	161 (2)
O3—H3O \cdots O1	0.883 (10)	1.583 (11)	2.4557 (17)	169 (2)
O1W—H1W \cdots O2 ⁱⁱⁱ	0.89 (3)	2.06 (2)	2.789 (2)	138 (2)
O1W—H2W \cdots O3	0.87	2.42	3.219 (3)	154
C2—H2 \cdots O1W ^{iv}	0.93	2.44	3.365 (3)	177
C13—H13 \cdots O4 ^v	0.93	2.46	3.372 (2)	168

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

All N-bound H atoms, O-bound H atoms and H atoms of the water molecules were located in a difference Fourier map and their positions and isotropic displacement parameters were refined. In compound (II), the N1—H1N and O3—H3O distances were restrained with set values of 0.89 (1) and 0.86 (1) \AA , respectively. Distance restraints were also applied to O1W—H1W and H1W \cdots H2W of the water molecule, with set values of 0.86 (1) and

1.55 (1) \AA , respectively. All other H atoms were located in a difference density map, but were positioned geometrically and included as riding atoms, with C—H distances in the range 0.93–0.98 \AA , and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

For both compounds, data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg & Putz, 2005); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3054). Services for accessing these data are described at the back of the journal.

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