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Supramolecular hydrogen-bonding networks in bis(adeninium) phthalate phthalic acid 1.45-hydrate

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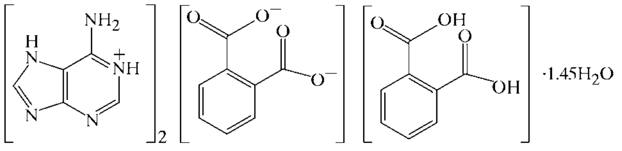
In the title compound, $2C_5H_6N_5^+\cdot C_8H_4O_4^{2-}\cdot C_8H_6O_4\cdot 1.45H_2O$, the asymmetric unit comprises two adeninium cations, two half phthalate anions with crystallographic C_2 symmetry, one neutral phthalic acid molecule, and one fully occupied and one partially occupied site (0.45) for water molecules. The adeninium cations form N—H···O hydrogen bonds with the phthalate anions. The cations also form infinite one-dimensional polymeric ribbons *via* N—H···N interactions. In the crystal packing, hydrogen-bonded columns of cations, anions and phthalate anions extend parallel to the *c* axis. The water molecules crosslink adjacent columns into hydrogen-bonded layers.

Comment

Adenine is one of the two purine nucleobases used in forming nucleotides of the nucleic acids DNA and RNA. It occurs in the free form in tea, and in the combined form in nucleic acids, ATP, vitamin B12 and several coenzymes. The adenine nucleobase provides interesting building blocks for the formation of extended structures, due not only to the multiple possibilities in which bases may interact *via* hydrogen bonds, but also to the possible π–π stacking between them (Houlton, 2001). Adenine and guanine form 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). Phthalic acid is a small carboxylic acid that has special relevance to environmental chemists and geochemists. It represents common functional groups found in natural organic matter (Salzjimenez, 1994). Our particular interest lies in the structure of the title crystalline complex, (I), of adenine with phthalic acid, and the interactions between the components.



(I)

The asymmetric unit of (I) contains two adeninium cations (denoted 1 and 2), two half-phthalate dianions having crystallographic C_2 symmetry, one neutral phthalic acid molecule, and one fully occupied and one partially occupied site (0.45) for water molecules. The structure of (I), with the atom numbering, is shown in Fig. 1. The crystal structure of adenine–phthalic acid–water (3:1:6) has already been reported (Takenaka & Sasada, 1982).

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). In (I), atoms N21 and N31 of the independent cations are protonated, which is reflected in an increase in the C22—N21—C26 [123.5 (15)°] and C32—N31—C36 [122.81 (14)°] bond angles. The corresponding value for neutral adenine (Voet & Rich, 1970) is 119.8°. The site of protonation is further confirmed by the location in a difference Fourier map of the H atoms bonded to atoms N21 and N31, and the

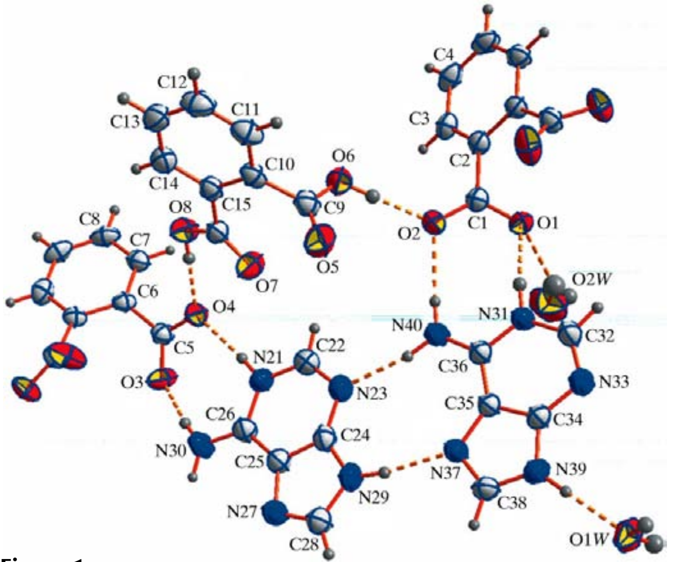


Figure 1
A view of the components of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines. The two symmetry-independent anions have crystallographic C_2 symmetry.

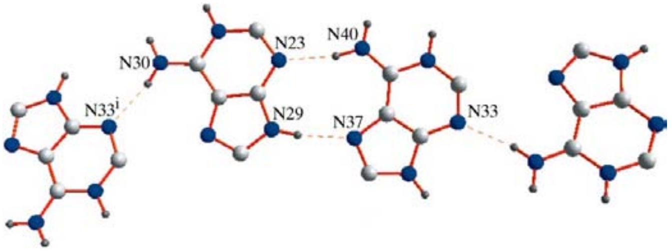


Figure 2
A view of the one-dimensional polymeric chain of adeninium–adeninium pairs mimicking the Watson–Crick pattern. Dashed lines indicate N—H···N hydrogen bonds. For the sake of clarity, H atoms attached to C atoms have been omitted. [Symmetry code: (i) $x, 1 - y, z - \frac{1}{2}$.]

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successful refinement of the H-atom positions. The molecular geometries of the two independent cations in (I) are very similar.

The structural features of the neutral and dianionic phthalic acid entities of (I) are similar to those of phthalic acid (Langkilde *et al.*, 2004). In the neutral phthalic acid molecule, the C9/O5/O6 carboxylic acid group is almost perpendicular [87.4 (1)°] to the plane of the benzene ring (C10–C15), while the other carboxylic acid group, C16/O7/O8, is inclined at an angle of 19.5 (1)°. In the C_2-symmetric phthalate anions, the planes of both carboxylate groups are equally rotated from the plane of the benzene rings [44.0 (1) and 46.6 (2)° for the planes defined by atoms C1/O1/O2 and C5/O3/O4, respectively].

Within the asymmetric unit of (I), atoms N29 and N40 act as hydrogen-bond donors, *via* atoms H29 and H402, respectively, to atoms N37 and N23 (Table 1), thereby forming a characteristic $R_2^2(9)$-type motif (Bernstein *et al.*, 1995) which mimics the Watson–Crick pattern. This pair of cations is further linked by intermolecular N—H⋯N hydrogen bonds involving atoms N30 and N33, to form an infinite zigzag one-dimensional polymeric ribbon which runs parallel to the *c* axis (Fig. 2).

In the crystal structure of (I), π–π interactions are observed between the cations. The fusing bond (C24—C25) of cation 1 lies over the centre of the five-membered ring of cation 2 at $(1 - x, 1 - y, 1 - z)$, with an interplanar spacing of 3.491 (2) Å. The distance between the centroid of the N21/C22/N23/C24–C26 ring and the centroid of the C34/C35/N37/C38/N39 ring at $(1 - x, 1 - y, 1 - z)$ is 3.535 (1) Å and the offset distance is 0.56 Å. Similarly, the centre of the five-membered ring of cation 1 is over the fusing bond (C34—C35) in cation 2 at $(1 - x, 1 - y, 1 - z)$, with an interplanar spacing of 3.445 (1) Å. The corresponding distance between the centroid of the N31/C32/N33/C34–C36 ring and the centroid of the C24/C25/N27/C28/N29 ring at $(1 - x, 1 - y, 1 - z)$ is 3.772 (1) Å with an offset distance of 1.53 Å.

The neutral phthalic acid molecule links the two independent phthalate anions through O—H⋯O hydrogen bonds and their aggregation yields an infinite chain which runs parallel to the *c* axis. Each of the two symmetry-independent phthalate anions, in turn, links to one of the two independent adeninium cations *via* N—H⋯O hydrogen bonds, which results in an $R_2^2(8)$ motif. Thus, the combination of all O—H⋯O, N—H⋯O and N—H⋯N hydrogen bonds involving the adeninium cations, the phthalate anions and the phthalic acid molecules leads to hydrogen-bonded columns, which extend parallel to the *c* axis. Each column consists of chains of adeninium cations sandwiched between two outer chains of phthalate anions and phthalic acid molecules (Fig. 3).

The water molecules (O1*W* and O2*W*) play an active role in the hydrogen bonding (Table 1). They participate in five hydrogen bonds, acting as donors to two phthalate anions and as an acceptor of an interaction from one adeninium cation. While one water molecule (O1*W*) plays a dual role of donor and acceptor, the other (O2*W*) acts only as a donor. The water

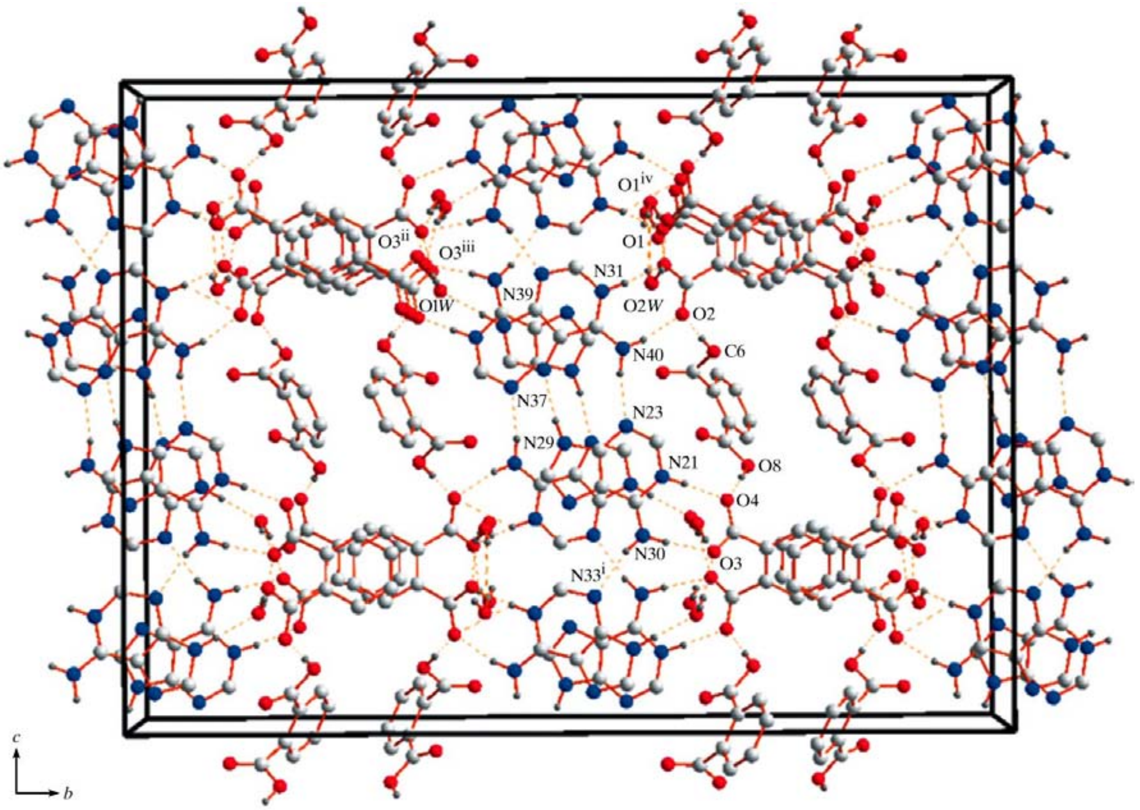

Figure 3
A packing diagram for (I), viewed down the *a* axis. Dashed lines indicate hydrogen bonds and H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (i) $x, 1 - y, z - \frac{1}{2}$; (ii) $x, 1 - y, z + \frac{1}{2}$; (iii) $2 - x, 1 - y, 1 - z$; (iv) $2 - x,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

molecules serve to crosslink the columns of adeninium cations, phthalate anions and phthalic acid molecules to give hydrogen-bonded layers which lie parallel to the (010) plane.

A possible π–π interaction is observed between the independent phthalate anions of (I), with the distance between the centroids of the rings defined by atoms C2/C3/C4 and atoms C6/C7/C8 at ($\frac{1}{2} - x, \frac{3}{2} - y, \frac{1}{2} + z$) being 3.600 (1) Å, the interplanar spacing being 3.266 (1) Å and the centroid offset being 1.51 Å. These π–π interactions interconnect the hydrogen-bonded layers to complete the three-dimensional lattice. A short interatomic contact is observed between atom C22 of adeninium cation 1 and carbonyl atom O7 of the phthalic acid molecule [C22$\cdots$O7 = 2.991 (2) Å and H22$\cdots$O7 = 2.52 Å], which is a consequence of the dense packing of the components induced by the complex hydrogen bonding.

Experimental

Adenine and phthalic acid (both purchased from Sisco Research Laboratories PVT Ltd, Mumbai, India) were mixed in a 1:1 stoichiometric ratio and dissolved in water. Crystals were obtained by slow evaporation.

Crystal data

$2C_5H_6N_5^+\cdot C_8H_4O_4^{2-}\cdot C_8H_6O_4\cdot$-$1.45H_2O$
$M_r = 628.65$
Orthorhombic, *Pbcn*
$a = 7.0100$ (5) Å
$b = 33.052$ (2) Å
$c = 24.2496$ (17) Å
$V = 5618.4$ (7) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.12$ mm^{-1}
$T = 293$ (2) K
0.19 × 0.17 × 0.09 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
50712 measured reflections
4961 independent reflections
4499 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.104$
$S = 1.06$
4961 reflections
472 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max} = 0.27$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.20$ e Å^{-3}

One water molecule (O2*W*) lies close to one of its symmetry-related counterparts. Hence, the site-occupation factor of this water molecule cannot exceed 0.5 and indeed refined to 0.454 (6). All N-bound H atoms of the adeninium cations and the O-bound H atoms of the neutral phthalic acid molecule, plus the H atoms of the water molecules, were located in a difference Fourier map and their positions and isotropic displacement parameters were refined. The N31—H31 distance was restrained with a set value of 0.89 (1) Å. Distance restraints were also applied to the H atoms of one water molecule (O2*W*). All other H atoms were positioned geometrically and treated as riding on their parent C atoms, with C—H = 0.93 Å and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C).

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N21—H21$\cdots$O4	0.91 (2)	1.84 (2)	2.7408 (18)	171 (2)
N29—H29$\cdots$N37	0.92 (2)	1.97 (2)	2.888 (2)	171 (2)
N30—H301$\cdots$O3	0.90 (2)	1.86 (2)	2.757 (2)	172 (2)
N30—H302$\cdots$N33$^{\rm i}$	0.88 (2)	2.11 (2)	2.971 (2)	169 (2)
N31—H31$\cdots$O1	0.93 (2)	1.67 (2)	2.5930 (19)	174 (2)
N39—H39$\cdots$O1*W*	0.91 (2)	1.86 (2)	2.766 (2)	174 (2)
N40—H401$\cdots$O2	0.87 (2)	2.01 (2)	2.851 (2)	164 (2)
N40—H402$\cdots$N23	0.95 (2)	2.00 (2)	2.935 (2)	168 (2)
O6—H6$\cdots$O2	0.93 (3)	1.70 (3)	2.6356 (18)	177 (3)
O8—H8$\cdots$O4	0.88 (3)	1.74 (3)	2.6207 (18)	175 (2)
O1*W*—H1*W*$\cdots$O3$^{\rm ii}$	0.86 (3)	1.94 (3)	2.769 (2)	162 (3)
O1*W*—H2*W*$\cdots$O3$^{\rm iii}$	0.83 (4)	2.24 (4)	3.060 (2)	172 (4)
O2*W*—H3*W*$\cdots$O1$^{\rm iv}$	0.894 (11)	2.00 (5)	2.786 (4)	146 (7)
O2*W*—H4*W*$\cdots$O1	0.896 (10)	2.30 (7)	3.074 (6)	145 (10)

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

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: *SHELXTL/PC* (Sheldrick, 1990) and *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: LN3036). Services for accessing these data are described at the back of the journal.

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