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Hydrogen-bonded sheets in 2-(2-aminophenyl)-1*H*-benzimidazol-3-ium dihydrogen phosphate

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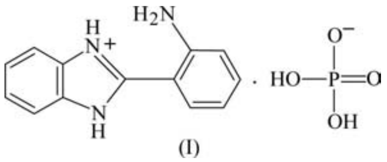
The title salt, $C_{13}H_{12}N_3^+ \cdot H_2PO_4^-$, contains a nonplanar 2-(2-aminophenyl)-1*H*-benzimidazol-3-ium cation and two different dihydrogen phosphate anions, both situated on twofold rotation axes in the space group *C*2. The anions are linked by O—H···O hydrogen bonds into chains of $R_2^2(8)$ rings. The anion chains are linked by the cations, *via* hydrogen-bonding complementarities and electrostatic interactions, giving rise to a sheet structure with alternating rows of organic cations and inorganic anions. Comparison of this structure with that of the pure amine reveals that the two compounds generate characteristically different sheet structures. The anion–anion chain serves as a template for the assembly of the cations, suggesting a possible application in the design of solid-state materials.

Comment

Anions serve as useful building blocks for the formation of self-assembled supramolecular architectures in both organic and inorganic systems (Gale, 2000, 2001). They can assemble in well defined fashions and, by relying on the combined strength of electrostatic and hydrogen-bonding interactions, it is possible to generate reproducible topologies. Partially protonated oxoanions derived from sulfuric and phosphoric acids are two such interesting systems (Braga *et al.*, 2004). We are particularly interested in observing how dihydrogen phosphate would assemble and its role in molecular association. In this context, we report here the preparation and structural characterization of the title salt, 2-(2-aminophenyl)-1*H*-benzimidazol-3-ium dihydrogen phosphate, (I). Benzimidazolylaniline (BIMD) is a derivative of pharmaceutically useful benzimidazole compounds (Velík *et al.*, 2004, and references therein).



(I)

The asymmetric unit of (I) (Fig. 1) comprises one BIMD cation and one-half of two different dihydrogen phosphate (DPH) anions (P1/O1/O2 and P2/O3/O4) lying across twofold rotation axes along $(0, y, \frac{1}{2})$ and $(0, y, 0)$, respectively. BIMD is nonplanar, with the planes of the benzimidazole heterocycle (N1/C2/N3/C3a/C4–C7/C7a) and aniline (N14/C8–C13) making an angle of 38.6 (1)°; the N1—C2—C8—C13 torsion angle is 36.7 (4)°. In DPH, the two P—O distances for the OH groups, as expected, are significantly longer [P1—O2 = 1.561 (2) Å and P2—O4 = 1.563 (2) Å] than the other two [P1—O1 = 1.5015 (17) Å and P2—O3 = 1.4996 (17) Å].

In (I), the $H_2PO_4^-$ anions are linked by two O—H···O hydrogen bonds (Table 1) to form an $R_2^2(8)$ ring (Bernstein *et al.*, 1995). The hydrogen bond involving atom O2 as donor is the more nearly linear of these and has a shorter H···O distance. The $R_2^2(8)$ ring motif, extending on either side, gives rise to a chain (Fig. 2). This hydrogen-bonded anionic framework serves as template for the assembly of the cations, resulting in a sheet structure parallel to the *bc* plane with alternate rows of cations and anions. Due to amine–imine tautomerism, there are two equivalent salt links, N3—H3···O1 and N1—H1···O3^{i} [symmetry code: (i) $x, 1 + y, z$]. The sheet, apart from the salt bridges, is stabilized by N14—H14*A*···O1 hydrogen bonds. Intersheet contact is maintained by C11—H11···O4^{ii} [symmetry code: (ii) $\frac{1}{2} + x, \frac{1}{2} + y, 1 + z$] and van der Waals interactions. Atom H14*B* does not participate in any nonbonded interaction scheme. However, this is not an unusual observation in the case of amino groups. The characteristic sheet structure in the present example is mainly the result of the complementary nature of the molecules, *i.e.* one with an excess of donors and the other deficient in them, in an

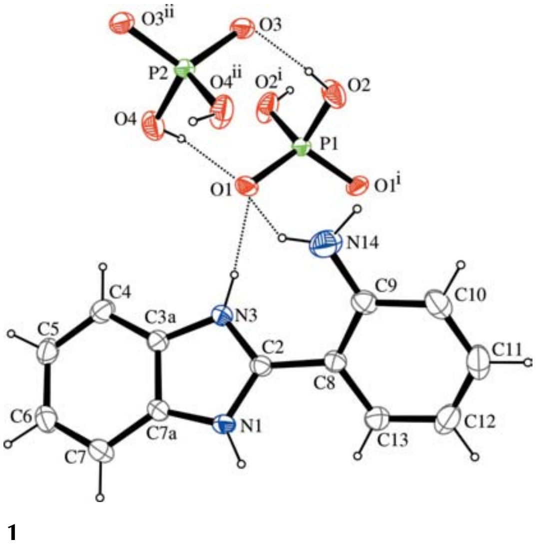


Figure 1
A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines represent hydrogen bonds. [Symmetry codes: (i) $-x, y, 1 - z$; (ii) $-x, y, -z$.]

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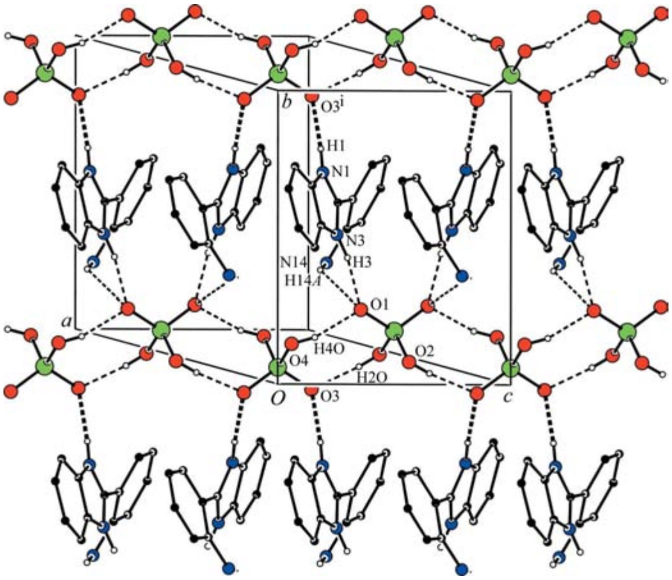

Figure 2
The hydrogen-bonded sheet structure of (I) in the *bc* plane, formed by alternating rows of organic cations and inorganic anions. Only relevant H atoms are shown. [Symmetry code: (i) *x*, 1 + *y*, *z*.]

attempt to make up this numerical imbalance. Using the idea of hydrogen-bond complementarity, which involves both geometric factors and a suitable balance of the number of hydrogen-bond donors and acceptors, several self-assembled supramolecular architectures have been designed (Aakerby & Schultheiss, 2007, and references therein).

The structure of the corresponding neutral imidazole, namely 2-(1*H*-benzimidazol-2-yl)aniline, (II), has been reported previously in the space group *Pbca* (Das *et al.*, 2003; Shylaja *et al.*, 2008). It is interesting to compare the packing of salt (I) with the neutral imidazole, (II), primarily because (II) is deficient in acceptors while (I) has an excess of them. The packing in (II) is characterized by BIMD molecules forming a sheet structure in the *ab* plane. BIMD molecules are arranged into a linear chain *via* intermolecular N—H···N hydrogen bonds along the *b* axis. These chains are linked into sheets by N—H···π and C—H···π interactions (shown in Supplementary Fig. 3). In view of the inadequate number of acceptors, the energetically next-favourable π-acceptors are utilized to fulfil this imbalance and maximize lattice interactions. The hierarchical choice of intermolecular interactions is a phenomenological rule governing supramolecular assembly.

A search of the Cambridge Structural Database (CSD, Version 5.28; Allen, 2002) revealed 27 examples of hydrogen-bonded DPH, forming $R_2^2(8)$ rings and extending into infinite linear chains (CSD refcodes ACUXIG, BIDPEJ, CLQUON01, CPAIMZ, DASNUH, DAYHOB, DUNHID, EDUQUP, EJEGAB, FAXGUH, FEDMIL, FIJHEL, GEXXAI, GOLTOQ, IDAPEI01, ISUZIF, LELXIJ, MATKAT, MPHAZP, NELVUV, PAMRAX, PROCPH, REZNEP, SASBIX, SEGGER, SODCUJ and XAPRUC). FAXGUH and IDAPE101 are examples of metal-coordinated DPH. HAHGED is another example containing extended nonlinear chains of $R_2^2(8)$ type, forming a honeycomb structure (Braga *et al.*, 2004). Some interesting packings have been observed. The oxoanion–oxoanion one-dimensional motif in NELVUV gives rise to a sheath-like structure of cations around it (Light *et al.*, 2001). In LELXIJ, the linear DPH chains form a hydrated layer structure, resulting in alternating cationic and anionic layers (Braga *et al.*, 1999) The oligomeric assembly of DPH observed in (I) serves as an interesting example of a template-assembled supramolecular architecture.

Experimental

Initially, compound (II) was synthesized by standard phosphoric acid cyclization, *i.e.* the Phillips method (Phillips, 1928*a*,*b*), by heating equimolar quantities of technical grade 1,2-phenylenediamine and 2-aminobenzoic acid (anthranilic acid) in polyphosphoric acid for 4 h at about 473 K [yield 60%, m.p. 484 (1) K]. Compound (I) was prepared from (II) by dissolving it in ethanol and adding dropwise an equimolar quantity of 85% syrupy orthophosphoric acid. The resulting grey precipitate was filtered off, washed with water and dried at 323–333 K in an oven [yield 86%, m.p. 545 (1) K]. Compound (I) was crystallized from a mixture of methanol and water (70:30 *v*/*v*) by slow evaporation; colourless crystals appeared within a week.

The second-harmonic generation (SHG) efficiency of (I) was measured relative to potassium dihydrogen phosphate (KDP) by a standard powder technique (Kurtz & Perry, 1968) using an Nd:YAG laser (λ = 1064 nm, 8 ns pulse and 3.4 mJ per pulse). The compound exhibits a weak activity of 0.15 times that of KDP.

As the CSD search was quite time-consuming, it was carried out in stages. Firstly, a sub-database of 132 structures containing dimeric DPH units was created. The final search for infinitely extended chains was then carried out using this sub-database, yielding 27 hits.

Crystal data

$C_{13}H_{12}N_3^+\cdot H_2PO_4^-$
M_r = 307.24
Monoclinic, *C*2
a = 18.3700 (11) Å
b = 10.0050 (13) Å
c = 7.9145 (14) Å
β = 113.575 (2)°
V = 1333.2 (3) Å^3
Z = 4
Mo *K*α radiation
μ = 0.23 mm^{-1}
T = 295 (2) K
0.33 × 0.28 × 0.22 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
T_{min} = 0.91, T_{max} = 0.96
6829 measured reflections
2612 independent reflections
2374 reflections with $I > 2\sigma(I)$
R_{int} = 0.025

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2O···O3	0.81 (3)	1.82 (3)	2.619 (3)	172 (4)
O4—H4O···O1	0.81 (2)	1.85 (2)	2.641 (3)	163 (4)
N1—H1···O3^{i}	0.87 (2)	1.875 (19)	2.736 (3)	169 (3)
N3—H3···O1	0.875 (17)	1.820 (16)	2.686 (3)	170 (2)
N14—H14*A*···O1	0.88 (3)	2.51 (3)	3.128 (4)	128 (3)
C11—H11···O4^{ii}	0.93	2.52	3.444 (4)	172
N14—H14*A*···N3	0.88 (3)	2.44 (3)	3.022 (4)	125 (3)

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.090$
$S = 1.10$
2612 reflections
209 parameters
7 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}
Absolute structure: Flack (1983), with 1224 Friedel pairs
Flack parameter: 0.02 (10)

H atoms attached to N and O atoms were refined isotropically, with N—H and O—H distances restrained in the ranges 0.88 (1)–0.89 (1) and 0.81 (1)–0.82 (1) Å, respectively, and with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(imidazole N) or $1.5U_{\rm eq}$(O, amine N). H atoms attached to aromatic C atoms were positioned geometrically, with C—H distances of 0.93 Å, and refined as riding on their parent atoms, with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C). The correct absolute structure was established by the anomalous dispersion effect of the P atoms (1224 Bijvoet pairs), as described by the Flack parameter value of 0.02 (10) (Flack, 1983; Flack & Bernardinelli, 1999). In the refined structure, compound (I) contains an intramolecular N14—H14*A*···N3 short contact (Table 1), as also observed in (II).

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2003); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3204). Services for accessing these data are described at the back of the journal.

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