Hydrogen phosphate and dihydrogen phosphate salts of 4-aminoazobenzene

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4-Amino-*trans*-azobenzene {or 4-[(*E*)-phenyldiazenyl]aniline} can form isomeric salts depending on the site of protonation. Both orange bis{4-[(*E*)-phenyldiazenyl]anilinium} hydrogen phosphate, $2C_{12}H_{12}N_3^+ \cdot HPO_4^{2-}$, and purple 4-[(*E*)-phenyldiazenyl]anilinium dihydrogen phosphate phosphoric acid solvate, $C_{12}H_{12}N_3^+ \cdot H_2PO_4^- \cdot H_3PO_4$, (II), have layered structures formed through $O—H\cdots O$ and $N—H\cdots O$ hydrogen bonds. Additionally, azobenzene fragments in (I) are assembled through $C—H\cdots\pi$ interactions and in (II) through $\pi–\pi$ interactions. Arguments for the colour difference are tentatively proposed.

Comment

4-Aminoazobenzene has three N atoms, each possessing an unshared electron pair. In addition to the *cis–trans* isomerism, each of the N atoms can be protonated and isomeric cations can thus be formed. This property is potentially applicable in the design of piezochromic materials because two groups of salts, according to colour, can be distinguished. So far, purple and orange salts have been isolated. In our preliminary studies, we have found that the orange hydrogen phosphate salt of 4-amino-*trans*-azobenzene {4-[(*E*)-phenyldiazenyl]-aniline}, when pressed into a KBr pellet, turns purple over a period of a few minutes to a few days (Lukić *et al.*, 2007). We have encountered difficulties in determining the exact reaction taking place in the KBr pellet that causes the colour change. To the best of our knowledge, no work has reported results on colour changes in the solid state of salts of 4-amino-azobenzene. Even though the number of salts of 4-amino-azobenzene characterized in the solid state is still relatively small, an assumption can be made about the cause of the colour change. Tentatively, we propose that the colour of 4-aminoazobenzene salts depends on the site of protonation. In the Cambridge Structural Database (Version 5.27; August 2006; Allen, 2002), three orange salts are reported, all having the amino group protonated, and one purple salt with only the azo group protonated. Undoubtedly, finding an unequivocal answer about the origin of this effect requires a broader study.

In this paper, as a first step in this investigation, we report the crystal structures of the hydrogen phosphate, (I), and dihydrogen phosphate, (II), salts of 4-aminoazobenzene.
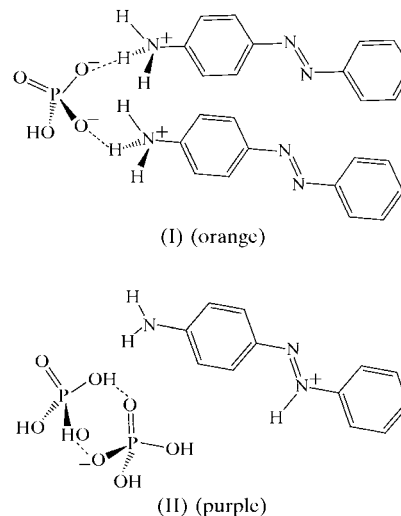
(I) (orange)

(II) (purple)

The formula unit of the orange salt (I) consists of two 4-aminoazobenzene molecules, both in the *trans* configuration and protonated on the amino N atom, along with a hydrogen phosphate anion (Fig. 1). The purple compound (II) consists of one 4-aminoazobenzene molecule, also in the *trans* configuration, protonated on an azo group N atom, a dihydrogenphosphate anion and one solvent molecule of phosphoric acid (Fig. 2). In compound (II), alternatively, the hydrogen-bonded phosphoric acid and dihydrogen phosphate units could be considered as jointly forming the anion. Different sites of protonation of 4-aminoazobenzene result in quite different geometries for the cations. This is probably the cause of the different colours of these salts. In both compounds, the geometry of the cation deviates significantly from planarity, but the deviation is more pronounced in the purple salt (II). The relative twist of the phenyl ring is 18.0 (1)° in compound (II), and 2.2 (3) and 6.8 (2)° in compound (I). This larger value in (II) can be explained by repulsions between H atoms of the phenyl ring and a hydrogen-bond acceptor which approaches the protonated azo group.
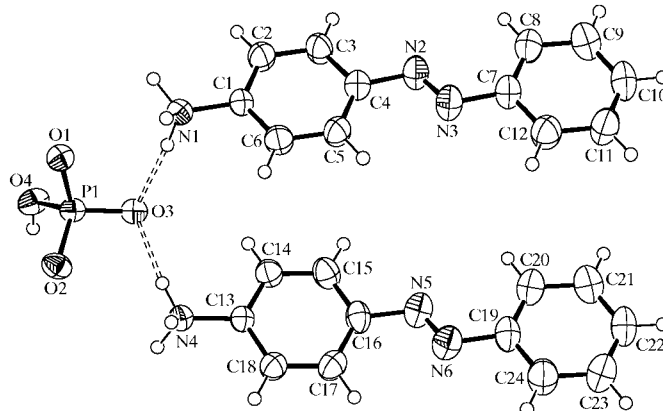

Figure 1
A view of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

organic compounds

Both compounds have many possible hydrogen-bond donor groups of the type NH or OH and they are all, in accord with Etter's first rule (Etter *et al.*, 1990), involved in hydrogen bonds. In (I), the anions are linked through O—H···O hydrogen bonds (Table 1) and form a chain running in the [001] direction (Fig. 3). There are adjacent chains of anions in the (100) plane, which are related by inversion. In this way, layers of anions are formed even though there is no hydrogen bonding between the chains. A layer of anions is surrounded by cations which, through N—H···O hydrogen bonds, connect the chains. This forms a complex hydrogen-bonding network and a sheet structure parallel to the (100) plane (Fig. 4). There are no strong interactions between the sheets. The morphology of the orange crystals also reveals this. Crystals, obtained by evaporation from ethanol, are plate-like with {100} as the two most developed planes. Crystals also show pronounced cleavage parallel to the same planes. The hydroxyl group of the hydrogen phosphate ion is involved in hydrogen bonding only as a donor group so that, with seven remaining hydrogen-bond donor groups in (I), two O atoms are acceptors in two interactions and one in three (Table 1). The relative orientation of the non-polar azobenzene fragments is such that a C—H···π interaction is formed. Atoms H2 and H8 are at distances of 3.304 and 3.090 Å, respectively, from the mean planes of the benzene rings of the azobenzene fragment at $(x, \frac{3}{2} - y, -\frac{1}{2} + z)$, and at distances of 3.322 and 3.140 Å, respectively, from the centroids of these rings. The second independent azobenzene fragment forms C—H···π interactions with two adjacent molecules. Firstly, atoms H14 and H20 lie 2.885 and 3.061 Å, respectively, from the mean planes (2.999 and 3.101 Å, respectively, from the centroids) of the benzene rings of the azobenzene fragment at $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$. The second interaction is towards one benzene ring of the azobenzene fragment at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$. The distance of H23 from the mean plane of the benzene ring is 3.47 Å (2.96 Å from its centroid). This interaction could also account for the deviation from planarity of the azobenzene fragment.

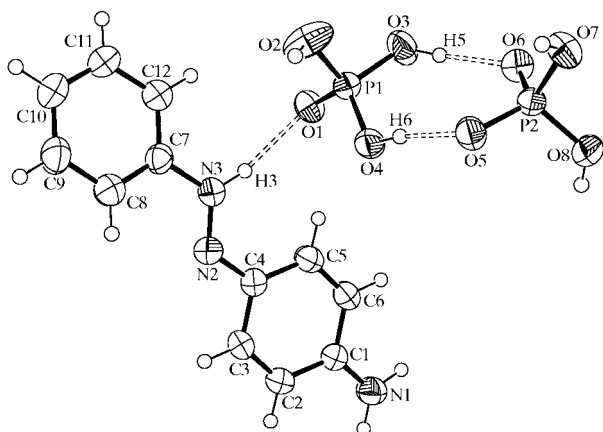Compound (II) is also in accord with Etter's rule as it has eight independent possible hydrogen-bond donor groups and all of them are involved in hydrogen bonds. A network is formed through five O—H···O and three N—H···O hydrogen bonds (Table 2). Dihydrogen phosphate anions and molecules of phosphoric acid are connected through O—H···O hydrogen bonds and form a chain running in the [100] direction. This chain is surrounded by cations, each forming three hydrogen bonds of the N—H···O type and linking anionic chains. A two-dimensional network is thus formed parallel to the (001) plane (Fig. 5). Azobenzene fragments within this layer are related by translation in the [100] direction and are in contact through π–π stacking interactions.

In order to elucidate the chemical reaction taking place in the KBr pellet, we shall try to obtain further structural evidence with other salts of 4-amino-*trans*-azobenzene and to record UV–vis spectra of these salts in KBr pellets.
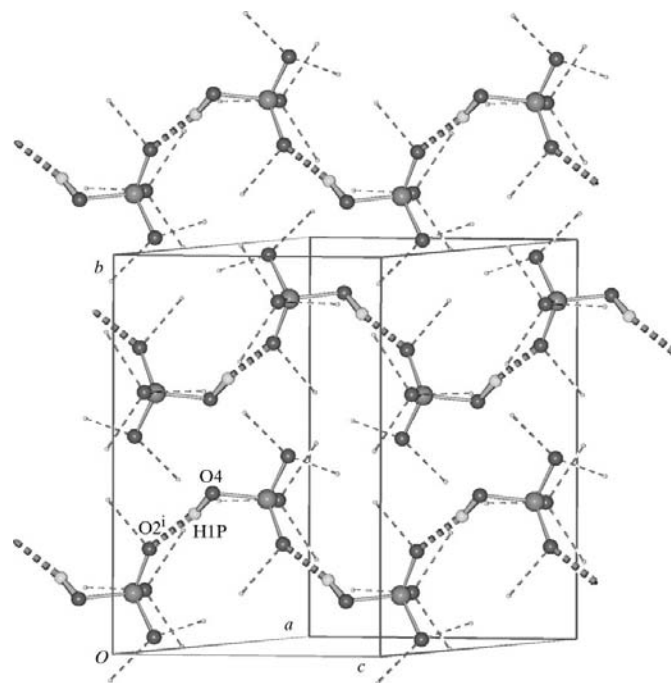

Figure 3
A layer of anions in (I) in the (100) plane. Chains of anions are formed in the [001] direction. Hydrogen bonds connecting hydrogen phosphate ions are shown with thicker dashed lines. [Symmetry code: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.]
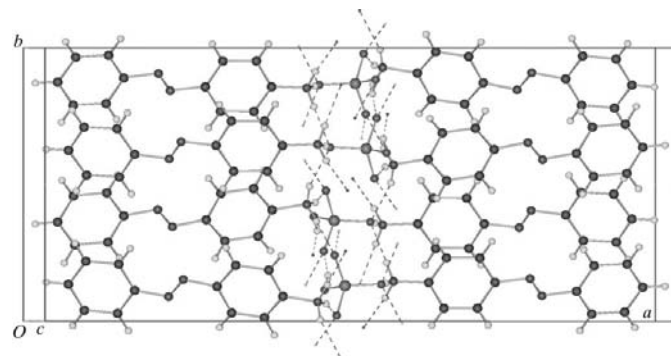

Figure 2
A view of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Figure 4
The two-dimensional network of hydrogen bonds in (I), extending in the (100) plane, perpendicular to the plane of the drawing.

Refinement
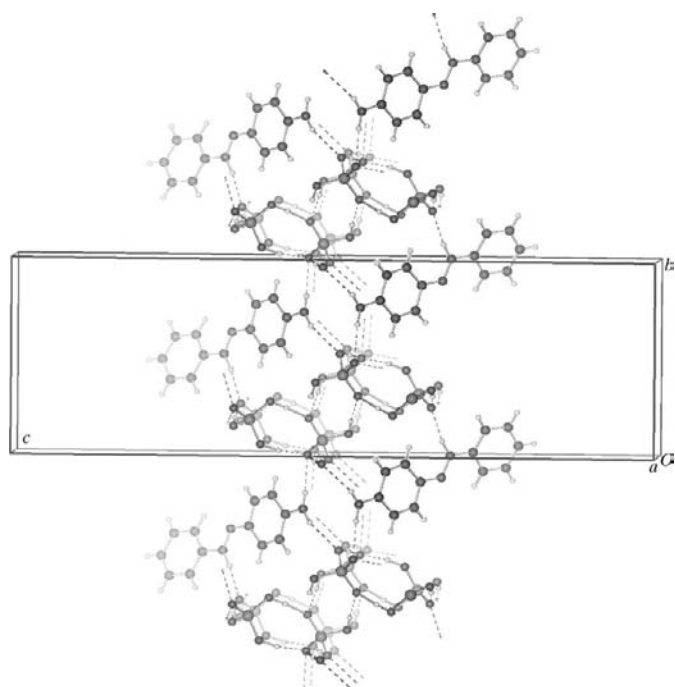
Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.140P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.075$	$+ 1.0658P]$
$wR(F^2) = 0.229$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.003$
4676 reflections	$\Delta\rho_{max} = 0.95$ e Å^{-3}
338 parameters	$\Delta\rho_{min} = -0.55$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H3A⋯O2^{ii}	0.88 (2)	1.84 (3)	2.721 (3)	173 (3)
N4—H4A⋯O3	0.88 (2)	2.02 (3)	2.901 (3)	176 (3)
N1—H2A⋯O1^{iii}	0.89 (2)	1.86 (3)	2.737 (3)	166 (3)
N1—H1A⋯O3	0.87 (2)	1.97 (3)	2.811 (3)	161 (3)
N4—H6A⋯O1^{iv}	0.88 (2)	1.78 (3)	2.663 (3)	173 (3)
N4—H5A⋯O3^{v}	0.88 (2)	1.96 (3)	2.816 (3)	161 (3)
O4—H1P⋯O2^{i}	0.87 (2)	1.68 (3)	2.523 (3)	164 (3)

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

Salt (II)

Crystal data

$C_{12}H_{12}N_3^+ \cdot H_2PO_4^- \cdot H_3PO_4$	$Z = 4$
$M_r = 393.23$	$D_x = 1.560$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 4.5515$ (4) Å	$\mu = 0.31$ mm^{-1}
$b = 10.5973$ (9) Å	$T = 293$ (2) K
$c = 34.705$ (3) Å	Plate, purple
$V = 1673.9$ (3) Å^3	$0.55 \times 0.15 \times 0.02$ mm

Data collection

Oxford Xcalibur-3 CCD area-detector diffractometer	22198 measured reflections
ω scans	4015 independent reflections
Absorption correction: analytical (Alcock, 1970)	3323 reflections with $I > 2\sigma(I)$
$T_{min} = 0.911$, $T_{max} = 0.993$	$R_{int} = 0.041$
	$\theta_{max} = 28.1°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0585P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.101$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.07$	$\Delta\rho_{max} = 0.23$ e Å^{-3}
4015 reflections	$\Delta\rho_{min} = -0.24$ e Å^{-3}
251 parameters	Absolute structure: Flack (1983), 1631 Friedel pairs
H atoms treated by a mixture of independent and constrained refinement	Flack parameter: −0.11 (10)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H5⋯O6	0.86 (3)	1.78 (3)	2.647 (3)	176 (3)
O4—H6⋯O5	0.84 (3)	1.72 (3)	2.554 (3)	169 (3)
N3—H3⋯O1	0.91 (3)	2.03 (3)	2.899 (3)	161 (3)
O2—H4⋯O1^{i}	0.87 (4)	1.71 (4)	2.568 (3)	168 (4)
O7—H7⋯O6^{i}	0.82 (3)	1.72 (3)	2.537 (2)	171 (3)
N1—H2⋯O7^{ii}	0.90 (4)	2.17 (4)	2.994 (3)	149 (3)
O8—H8⋯O5^{iii}	0.85 (4)	1.75 (4)	2.579 (3)	167 (4)
N1—H1⋯O6^{iv}	0.91 (4)	2.12 (4)	3.011 (3)	168 (3)

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

Figure 5
The two-dimensional network of hydrogen bonds in (II), extending in the (001) plane.

Experimental

For the preparation of (I), 4-aminoazobenzene (5 mmol, 0.986 g) and H_3PO_4 (5.5 mmol, 5.5 ml of 1.0 mol dm^{-3} aqueous solution) were dissolved in 96% EtOH (10 ml), with mild heating and stirring over a period of 3 h. This resulted in a dark-purple solution. Orange crystals precipitated after cooling. The crystals were rinsed three times with 96% EtOH and dried in air (yield 1.08 g, 88%). Crystals of (I) suitable for single-crystal X-ray diffraction were obtained after one week by slow evaporation of an EtOH solution [50 mg of (I) in 5 ml of 96% EtOH] at room temperature. For the preparation of (II), a further 10 ml of H_3PO_4 (aqueous, $c = 1.0$ mol dm^{-3}) was added to the mother liquor left from the preparation of (I) and the resulting purple solution was left to evaporate at room temperature. After approximately three weeks, purple plate-shaped crystals of (II) were isolated and used as obtained in the diffraction experiment.

Salt (I)

Crystal data

$2C_{12}H_{12}N_3^+ \cdot HPO_4^{2-}$	$Z = 4$
$M_r = 492.47$	$D_x = 1.363$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 26.757$ (4) Å	$\mu = 0.16$ mm^{-1}
$b = 11.2998$ (15) Å	$T = 293$ (2) K
$c = 7.9943$ (12) Å	Plate, orange
$\beta = 96.709$ (12)°	$0.45 \times 0.40 \times 0.04$ mm
$V = 2400.5$ (6) Å^3	

Data collection

Oxford Xcalibur-3 CCD area-detector diffractometer	3382 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.058$
17388 measured reflections	$\theta_{max} = 26.0°$
4676 independent reflections	

organic compounds

In both structures, the H atoms bonded to N and O atoms were located from a difference Fourier map and then refined isotropically with a common U_{iso} value, and with N—H bond distances restrained to 0.86 Å and O—H bond distances restrained to 0.90 Å. H atoms bonded to C atoms were placed at geometrically calculated positions, with C—H bond distances fixed at 0.93 Å and $U_{iso}(H)$ values of $1.2U_{eq}(C)$. Refinement of the Flack parameter (Flack, 1983; Flack & Bernardinelli, 2000) was attempted for structure (II) using the TWIN and BASF commands in *SHELXL97* (Sheldrick, 1997), but it did not converge (shift/s.u. = 1.06 consecutively in an indefinite number of refinement cycles). Attempted refinement of the inverted structure led to instabilities in *SHELXL97*, but we observed that the value of x had settled at approximately 1.08 (9). If the Flack parameter was refined without refining the other parameters, the value $x = -0.1$ (1) was found. For the inverted structure, also without refinement of the atomic parameters, the result was $x = 1.1$ (1). From these results (high s.u. and lack of convergence) we cannot make a definite decision about the absolute structure of (II). The reported absolute structure was chosen as the more probable one.

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *SCHAKAL99* (Keller, 1999); software used to prepare material for publication: *PARST* (Nardelli, 1995) and *SHELXL97* (Sheldrick, 1997).

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