

Two anilinium salts: anilinium hydrogenphosphite and anilinium hydrogenoxalate hemihydrate

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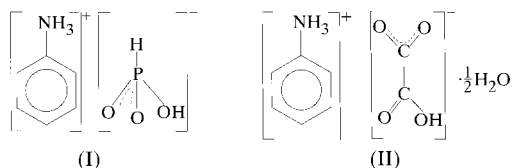
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In the title compounds, $C_6H_5NH_3^+ \cdot H_2PO_3^-$ and $C_6H_5NH_3^+ \cdot C_2HO_4^- \cdot 0.5H_2O$, the NH_3^+ groups of the anilinium ion are ordered at room temperature. The rotation of these groups along the N—C_{aryl} bond, which is often observed at room temperature in other anilinium compounds, is prevented by hydrogen bonds between the NH_3^+ group and the anions. In both compounds, the geometry of the cation is significantly distorted from D_{6h} to a symmetry close to C_{2v} . The angle *ipso* to the substituent is significantly larger than 120° , as expected from the σ -electron-withdrawing character of the NH_3^+ group.

Comment

A number of anilinium compounds exhibit structural phase transformations induced by order/disorder transitions of the NH_3^+ groups. The potential energy barrier for rotation of the NH_3^+ group is small provided the H atoms interact weakly with neighbouring molecules. In this case, the NH_3^+ group behaves as a molecular rotor at room temperature, but the



rotation is eventually inhibited at a lower temperature. Phase transitions have been observed most notably on anilinium halides and in a number of *ortho*- and *para*-substituted anilinium compounds (Hartmann & Weiss, 1991; Krishnan & Weiss, 1983). Anilinium bromide is probably the most thoroughly studied of these compounds, for which X-ray, neutron and several spectroscopic studies have been reported (Schweiss *et al.*, 1983*a*; Kanesaka & Fujii, 1996; Fecher *et al.*, 1981). The structure is orthorhombic above $T_c = 296.7$ K and becomes monoclinic below this temperature. X-ray, neutron and NMR studies have shown that in the high-temperature phase the NH_3^+ group is disordered over two alternate posi-

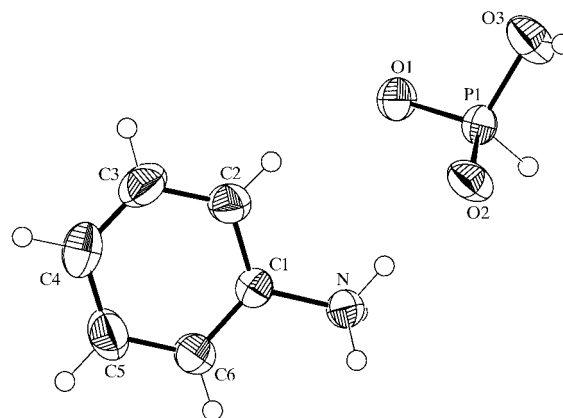


Figure 1
ORTEPII (Johnson, 1976) plot of compound (I). Displacement ellipsoids are drawn at the 50% probability level.

tions and that it becomes ordered in the low-temperature phase. The structural phase transition appears to be explained in terms of the coupling between the shear strain and ordering of the NH_3^+ group *via* an acoustic soft phonon mode. Quasielastic neutron scattering data (Brierley *et al.*, 1982; Schweiss *et al.*, 1983*a,b*) confirm that in the high-temperature phase the NH_3^+ group has a hindered rotation by jumps of 60° around the C_{aryl}—N axis, a model which had been previously suggested based on indirect evidence of NMR and NQR data.

We have decided to investigate other anilinium compounds searching for possible occurrence of low-temperature phase transitions associated with a quenching of the molecular rotation of the NH_3^+ group. We have so far found one new compound, anilinium perchlorate, which possibly falls into this category. The low-temperature behaviour of this compound has been studied recently in our laboratory, and an anomalous behaviour of the dilatation parameters was observed at *ca* 200 K. This anomaly is probably related to a quenching of the rotation of the NH_3^+ group which was shown to be disordered and possibly rotating at room temperature (Paixão *et al.*, 1999).

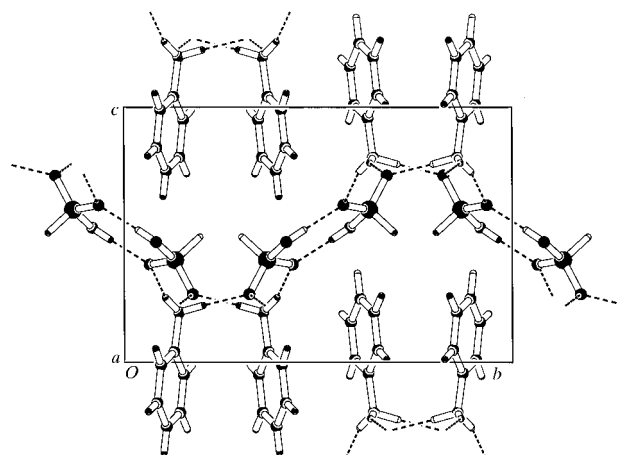


Figure 2
The packing diagram of compound (I) projected along the *a* axis showing the hydrogen-bonding scheme as dashed lines.

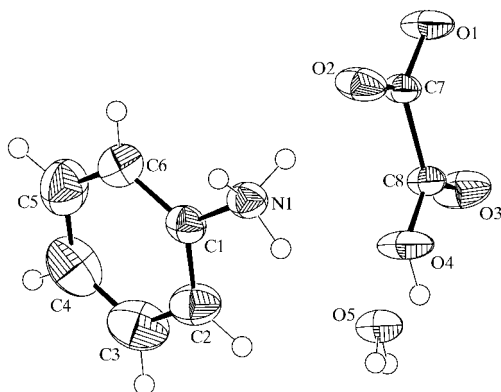


Figure 3
ORTEP (Johnson, 1976) plot of compound (II). Displacement ellipsoids are drawn at the 50% probability level.

Pursuing these studies, we have synthesized and determined the crystal structure at room temperature of two new anilinium salts, anilinium hydrogenphosphite, (I), and anilinium hydrogenoxalate hemihydrate, (II). The X-ray study reported here shows that the NH_3^+ group is well ordered at room temperature in both compounds. Also, powder X-ray diffraction data collected in our laboratory between 100 K and room temperature did not show evidence for any phase transition occurring in this temperature range.

Similar to other anilinium compounds, the symmetry of the benzene ring is closer to C_{2v} (mm) than to D_{6h} ($6/mmm$) (Colapietro *et al.*, 1981). The distortion of the ring is highly significant in the two compounds, involving bond distances as well as angles. The endocyclic angle *ipso* to the substituent is larger than 120° , as expected from the σ -electron withdrawing character of the NH_3^+ group (Domenicano & Murray-Rust, 1979). In both compounds, the two aromatic C—C bonds involving the C atom *ipso* to the substituent, C1—C2 and C1—C6, are somewhat shorter than the central C—C bonds of the ring, C2—C3 and C5—C6. The C1—N distance is close to the lower band of the range reported for anilinium salts [average bond distance: 1.465 (7) Å; Allen *et al.*, 1987].

In both compounds, the N1 atom deviates from the least-squares plane of the ring [(I) 0.032 (3); (II) 0.053 (2) Å]. These deviations correspond to a small out-of-plane bending of the NH_3^+ group by 1.31 (11) and 1.75 (9)°, respectively, for compounds (I) and (II). In compound (I), the substituent is also slightly bent in the plane of the ring towards the atom C6.

No sign was found of static or dynamic disorder of the NH_3^+ groups in both compounds, in contrast with other anilinium salts where the ammonium group is disordered at room temperature (Paixão *et al.*, 1999). In compound (I), the NH_3^+ group is staggered with respect to the ring while in (II), the conformation of the NH_3^+ group is such that one of the H atoms is almost eclipsed with the ring. This eclipsed conformation was found in a number of anilinium salts and it appears to be preferred over the staggered conformation.

The geometry of the anions is unexceptional. Inspection of the P—O bond of the hydrogenphosphite ion clearly shows that the acidic H atom is bonded to O3 as there is a significant lengthening of the P—O3 bond compared with the other two.

The O—P—O bond angles are in the range 107.4 (9)– 115.70 (8)°, which are typical values for this ion. The refined P—H bond length [1.29 (2) Å] is in good agreement with other X-ray studies of phosphite and hydrogenphosphite salts (Pecaut & Bagieu-Beucher, 1993; Averbuch-Pouchot, 1993).

The main remarkable feature of the hydrogenoxalate ion is the twist by 5.15 (3)° around the central C7—C8 bond. Each of the two carboxy groups is planar within 0.004 (1) Å and the H atom is also practically planar with the carboxylic group. The longer than usual Csp^2 — Csp^2 bond [1.5457 (15) Å] is characteristic of the hydrogenoxalate ion [average value 1.549 (9) Å; Allen *et al.*, 1987]. There is a clear asymmetry between the C—O bond lengths of the unionized carboxylic group, which shows that the H atom is not disordered. The C1—O1 and C1—O2 bonds are intermediate between the values of a C=O and a C—O bond and are typical of a delocalized C—O bond of a carboxylate group. Most likely, the small difference between these two bond lengths is due to a distinct participation of atoms O1 and O2 in hydrogen bonding. Compound (II) contains a solvent water molecule sitting on a twofold axis at the special position $4e$.

In each salt, full capability for hydrogen bonding of the anions and amino group is achieved. In compound (I), the strongest hydrogen bond links directly the hydrogenphosphite ions along the 2_1 screw axis [O3...O2 2.550 (7) Å], forming zigzag chains running along **b**. Atom O1 is an acceptor of two protons from the NH_3^+ group [N—H7B...O1 2.804 (2); N—H7C...O1 2.693 (2) Å], the third proton being donated to the O2 atom [N...O2 2.799 (2) Å]. In compound (II), the carboxylic H atom links two hydrogenoxalate ions head-to-tail forming chains parallel to the *b* axis. The carboxy O1 and O2 atoms are acceptors from two distinct H atoms of the NH_3^+ group [N1...O1 2.7955 (15); N1...O2 2.8067 (14) Å], the third H atom being donated to a water molecule [N1...O5 2.8163 (15) Å], forming an infinite two-dimensional network of hydrogen bonds extending in the (100) plane. Atom O3 does not appear to be involved in hydrogen bonding.

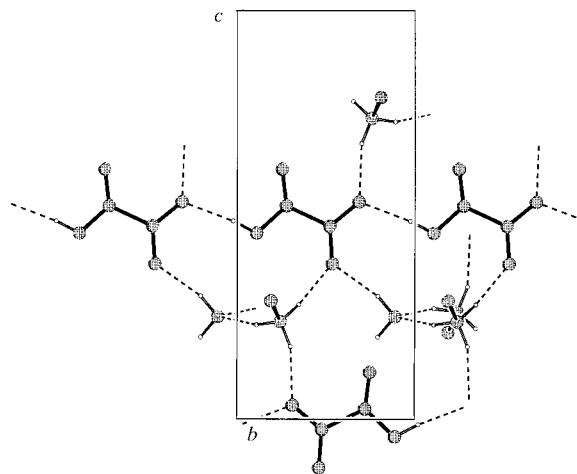


Figure 4
The packing diagram of compound (II) projected along the *a* axis showing the hydrogen-bonding scheme as dashed lines. Benzene rings have been omitted for clarity.

Experimental

Compounds (I) and (II) were synthesized by reacting an aqueous solution of diphenylformamidine (Aldrich, 99%) with phosphoric acid (Aldrich, 85%) and oxalic acid, respectively. Single crystals of prismatic form grew from the solution, by slow evaporation, over a period of a few months from which one small specimen was selected and used for X-ray analysis.

Compound (I)

Crystal data

$C_6H_8N^+ \cdot H_2PO_3^-$ $D_x = 1.409 \text{ Mg m}^{-3}$
 $M_r = 175.12$ Mo $K\alpha$ radiation
 Monoclinic, $P2_1/a$ Cell parameters from 25 reflections
 $a = 6.216(2) \text{ \AA}$ $\theta = 9.74\text{--}15.21^\circ$
 $b = 14.219(6) \text{ \AA}$ $\mu = 0.292 \text{ mm}^{-1}$
 $c = 9.342(3) \text{ \AA}$ $T = 293(2) \text{ K}$
 $\beta = 90.91(3)^\circ$ Prism, colourless
 $V = 825.6(5) \text{ \AA}^3$
 $Z = 4$ $0.34 \times 0.34 \times 0.34 \text{ mm}$

Data collection

Enraf–Nonius CAD-4 diffractometer $\theta_{\max} = 25.98^\circ$
 Profile data from ω -2 θ scans $h = -7 \rightarrow 7$
 3607 measured reflections $k = 0 \rightarrow 17$
 1612 independent reflections $l = -11 \rightarrow 11$
 1221 reflections with $I > 2\sigma(I)$ 3 standard reflections
 $R_{\text{int}} = 0.023$ frequency: 180 min
 intensity decay: 1%

Refinement

Refinement on F^2 $(\Delta/\sigma)_{\max} < 0.001$
 $R[F^2 > 2\sigma(F^2)] = 0.028$ $\Delta\rho_{\max} = 0.25 \text{ e \AA}^{-3}$
 $wR(F^2) = 0.084$ $\Delta\rho_{\min} = -0.25 \text{ e \AA}^{-3}$
 $S = 1.048$ Extinction correction: *SHELXL97*
 1612 reflections (Sheldrick, 1997)
 140 parameters Extinction coefficient: 0.015 (2)
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0380P)^2 + 0.3216P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Table 1

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

P1—O1	1.4919 (14)	P1—O3	1.5538 (16)
P1—O2	1.4954 (15)	P1—H1	1.29 (2)
O1—P1—O2	115.70 (8)	O2—P1—O3	111.75 (9)
O1—P1—O3	107.40 (9)		
N—C1—C2—C3	−178.7 (2)	N—C1—C6—C5	178.3 (2)

Table 2

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O3—H8 \cdots O2 ⁱ	0.82 (3)	1.74 (3)	2.550 (2)	173 (3)
N—H7A \cdots O2 ⁱⁱ	0.94 (3)	1.88 (3)	2.799 (2)	165 (2)
N—H7B \cdots O1 ⁱⁱⁱ	0.87 (3)	2.00 (3)	2.804 (2)	154 (2)
N—H7C \cdots O1	0.93 (3)	1.77 (3)	2.693 (2)	174 (2)

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

Table 3

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

O1—C7	1.2453 (14)	O4—C8	1.3057 (14)
O2—C7	1.2365 (14)	C7—C8	1.5475 (15)
O3—C8	1.1963 (14)		
N1—C1—C2—C3	−178.38 (13)	O2—C7—C8—O4	−5.16 (15)
O1—C7—C8—O3	−5.00 (17)		

Table 4

Hydrogen-bonding geometry (\AA , $^\circ$) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1A \cdots O5 ⁱ	0.939 (19)	1.915 (19)	2.8163 (15)	160.1 (16)
N1—H1B \cdots O1 ⁱⁱ	0.886 (17)	1.949 (17)	2.7955 (15)	159.3 (15)
N1—H1C \cdots O2	0.926 (19)	1.89 (2)	2.8067 (14)	171.2 (17)
O4—H4A \cdots O1 ⁱ	0.85 (2)	1.77 (2)	2.6177 (14)	173 (2)
O5—H5A \cdots O2	0.877 (18)	1.898 (19)	2.7516 (13)	163.8 (17)

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

Compound (II)

Crystal data

$C_6H_8N^+ \cdot C_2HO_4^- \cdot 0.5H_2O$ $D_x = 1.418 \text{ Mg m}^{-3}$
 $M_r = 192.17$ Mo $K\alpha$ radiation
 Monoclinic, $C2/c$ Cell parameters from 25 reflections
 $a = 23.9825(19) \text{ \AA}$ $\theta = 11.43\text{--}16.26^\circ$
 $b = 5.7253(14) \text{ \AA}$ $\mu = 0.117 \text{ mm}^{-1}$
 $c = 13.891(2) \text{ \AA}$ $T = 293(2) \text{ K}$
 $\beta = 109.340(11)^\circ$ Prism, white
 $V = 1799.7(5) \text{ \AA}^3$
 $Z = 8$ $0.49 \times 0.48 \times 0.29 \text{ mm}$

Data collection

Enraf–Nonius CAD-4 diffractometer $\theta_{\max} = 27.47^\circ$
 Profile data from ω -2 θ scans $h = 0 \rightarrow 30$
 2189 measured reflections $k = 0 \rightarrow 7$
 2062 independent reflections $l = -18 \rightarrow 17$
 1735 reflections with $I > 2\sigma(I)$ 3 standard reflections
 $R_{\text{int}} = 0.005$ frequency: 180 min
 intensity decay: 1.7%

Refinement

Refinement on F^2 $(\Delta/\sigma)_{\max} < 0.001$
 $R[F^2 > 2\sigma(F^2)] = 0.034$ $\Delta\rho_{\max} = 0.31 \text{ e \AA}^{-3}$
 $wR(F^2) = 0.101$ $\Delta\rho_{\min} = -0.16 \text{ e \AA}^{-3}$
 $S = 1.054$ Extinction correction: *SHELXL97*
 2062 reflections (Sheldrick, 1997)
 164 parameters Extinction coefficient: 0.0211 (14)
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0529P)^2 + 0.8427P]$
 where $P = (F_o^2 + 2F_c^2)/3$

All H atoms could be clearly located in a difference Fourier synthesis and have been refined isotropically. Examination of the crystal structures with *PLATON* (Spek, 1995) showed that there are no solvent-accessible voids in the crystal lattice for compound (I) and that no further solvent molecules could be accommodated in compound (II). All calculations were performed on a Pentium-II 350 MHz PC running LINUX.

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *HELINA* (Spek, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII*

(Johnson, 1976); 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: SK1377). Services for accessing these data are described at the back of the journal.

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