Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

2-(2-Pyridylamino)pyridinium chloride phosphorous acid: one-dimensional hydrogen-bonded and π–π stacked supramolecular chains

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Received 14 March 2006
Accepted 27 April 2006

Key indicators

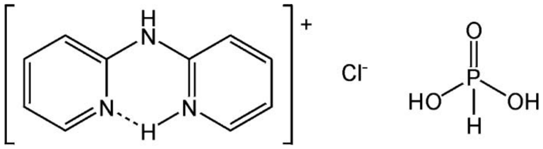
Single-crystal X-ray study
T = 173 K
Mean σ(P–O) = 0.001 Å
Disorder in main residue
R factor = 0.039
wR factor = 0.110
Data-to-parameter ratio = 12.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the crystal structure of the title compound, $C_{10}H_{10}N_3^{+}\cdot Cl^{-}\cdot[P(O)(OH)_2H]$, the chloride ion and phosphorous acid form a one-dimensional hydrogen-bonded chain, while the 2-(2-pyridylamino)pyridinium cations form a second chain through π–π stacking. The two parallel chains are connected *via* a PO···H—N hydrogen bond and a weak pyridinium-to-chloride interaction.

Comment

The title compound, (I), was obtained from an attempted Moedritzer Irani reaction of phosphorous acid, formaldehyde and di-2-pyridylamine in aqueous hydrogen chloride (Moedritzer & Irani, 1966).



(I)

The chloride anion in (I) acts as a double hydrogen-bond acceptor for the two hydroxy groups of phosphorous acid (hydrogen-bond details are listed in Table 2). In doing so, a one-dimensional chain, assigned $C_2^1(6)$ using graph-set theory (Bernstein *et al.*, 1995), is formed along the crystallographic *a* axis. The remaining phosphorous acid O atom acts as a hydrogen-bond acceptor for the amine group of the planar 2-

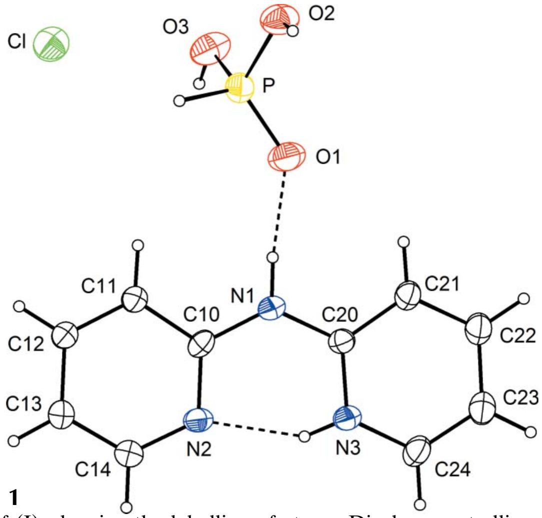


Figure 1
View of (I), showing the labelling of atoms. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen bonds.

(2-pyridylamino)pyridinium cation. Two of these supramolecular strands combine in a zipper-type formation that is stabilized by weak π–π stacking interactions. The stacked 2-(2-pyridylamino)pyridinium cations are tilted by 24.85 (5)° from perpendicular relative to the anion chain, with an interplanar separation of *ca* 3.368 Å [centroid-to-centroid separation = 3.748 (4) Å]. Further stabilization may arise from the pyridinium H4···Cl interactions [3.03 (3) Å].

Experimental

A mixture of phosphorous acid (11.4 g, 4.78 mmol) and di-2-pyridylamine (5.12 g, 29.9 mmol) in water (80 ml) was treated with hydrochloric acid (25%, 140 ml) and heated under reflux until a clear solution resulted. A solution of formaldehyde (35%) in methanol (5.21 g, 60.7 mmol) was added over a period of 20 min and the solution was heated under reflux for 1.5 h. The water was removed *in vacuo* and the solid residue obtained was recrystallized from ethanol to furnish colourless crystals of (I) (yield 76%).

Crystal data

$C_{10}H_{10}N_3^+\cdot Cl^-\cdot H_3O_3P$
$M_r = 289.65$
Triclinic, $P\overline{1}$
$a = 7.504$ (1) Å
$b = 8.840$ (1) Å
$c = 10.710$ (1) Å
$\alpha = 76.288$ (3)°
$\beta = 74.840$ (3)°
$\gamma = 70.054$ (3)°
$V = 635.9$ (1) Å^3
$Z = 2$
$D_x = 1.513$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.43$ mm^{-1}
$T = 173$ (2) K
Prism, colourless
0.50 × 0.24 × 0.19 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: none
7690 measured reflections
3650 independent reflections
3277 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.045$
$\theta_{\rm max} = 30.0$°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.110$
$S = 1.05$
3650 reflections
293 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0633P)^2 + 0.1848P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.50$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.56$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—P	1.473 (1)	O3—P	1.556 (1)
O2—P	1.552 (1)		
P—O2—H2	111.1 (16)	N2—C10—N1	119.0 (4)
P—O3—H3	110.3 (17)	N1—C10—C11	119.1 (4)
O1—P—O2	115.68 (7)	N3—C20—N1	120.1 (2)
O1—P—O3	115.50 (7)	N1—C20—C21	119.5 (3)
O2—P—O3	101.06 (7)	C20—N1—C10	127.4 (2)

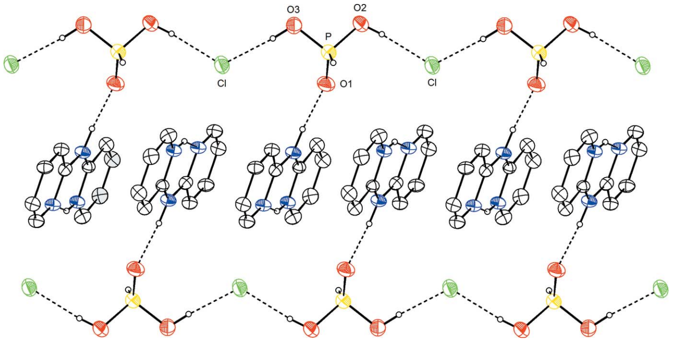


Figure 2
View of the supramolecular one-dimensional chains in (I) that are formed along the crystallographic *a* axis *via* hydrogen-bonding and π–π stacking interactions (dashed lines).

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.91 (3)	1.82 (3)	2.720 (2)	173 (2)
N3—H4···N2	0.81 (4)	1.89 (4)	2.610 (4)	147 (3)
O2—H2···Cl$^{\rm i}$	0.84 (3)	2.13 (3)	2.964 (1)	173 (2)
O3—H3···Cl$^{\rm ii}$	0.89 (3)	2.07 (3)	2.954 (1)	176 (2)

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

The 2-(2-pyridylamino)pyridinium cation is orientationally disordered about its long axis and was modelled over two sites with occupancy factors of 0.849 (4) and 0.151 (4). All non-H atoms, except two C atoms (C20′ and C23′) belonging to the minor orientation of the 2-(2-pyridylamino)pyridinium cation, were refined anisotropically. H atoms bound to carbon were positioned geometrically and treated as riding atoms, with C—H = 0.95Å. All other H atoms were located in a difference Fourier map and were refined isotropically.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff *et al.*, 1996); software used to prepare material for publication: *SHELXL97*.

Mrs Irene Brüdgam (Freie Universität Berlin) is gratefully acknowledged for the X-ray data collection.

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o2152 Beckmann *et al.* • $C_{10}H_{10}N_3^+\cdot Cl^-\cdot H_3O_3P$ *Acta Cryst.* (2006). E**62**, o2151–o2152