

Crystal Structure of a New Organic Dihydrogenmonophosphate Monohydrate [4-NH₂-6-OCH₃-C₄H₃N₂]₂(H₂PO₄)₂·H₂O

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Abstract: The atomic arrangement of the title compound, [4-NH₂-6-OCH₃-C₄H₃N₂]₂(H₂PO₄)₂·H₂O, can be described by inorganic layers of H₂PO₄⁻ anions and water molecules parallel to *ab*-plane at *z* = ¼ and *z* = ¾, between which organic cations [4-NH₂-6-OCH₃-C₄H₃N₂]⁺ are located. The crystal packing is influenced by O-H...O, N-H...O, N-H...N and C-H...O hydrogen bonds. All ring atoms of the organic entity are coplanar. The exocyclic N atoms are electron receiving centers, which is consistent with features of imino resonance evidenced by bond lengths.

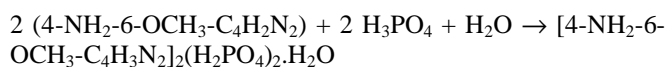
Keywords: Single-crystal X-ray diffraction, 4-Amino-6-methoxypyrimidine, dihydrogenmonophosphate.

INTRODUCTION

The combination of organic molecules and inorganic materials was the starting point for the development of new hybrid compounds having many practical and potential applications in various fields, such as biomolecular sciences, catalysis, fuel cell, liquid crystal-material development and quadratic nonlinear optics [1-3]. In these hybrid compounds, organic phosphates are particularly interesting. They are interconnected by strong hydrogen bonds so as to build infinite networks with various geometries such as ribbons [4], chains [5] or layers [6, 7]. In order to investigate the influence of hydrogen bonds on the chemical and structural features, we report here the synthesis and the crystal structure investigation of a new hybrid organic-inorganic compound [4-NH₂-6-OCH₃-C₄H₃N₂]₂(H₂PO₄)₂·H₂O.

MATERIALS AND METHODOLOGY

The [4-NH₂-6-OCH₃-C₄H₃N₂]₂(H₂PO₄)₂·H₂O compound (Fig. 1) was prepared in a Petri dish according to the following chemical reaction:



by mixing in equimolecular proportions (1:1) two reagents 4-Amino-6-methoxypyrimidine (Across 98) and monophosphoric acid (80.5 weight % from Fluka) in aqueous medium at room temperature. The resulting solution has been slowly evaporated at room temperature until the formation of single crystals suitable for X-ray structure analysis and remained stable under normal conditions of temperature and humidity.

Intensity data were collected on an Enraf-Nonius MACH3 automated four-circle diffractometer using graphite monochromated MoK_α radiation, λ = 0.7107 Å. The structure was solved by direct methods using the SIR92 [8] program and refined by full matrix least-squares techniques based on

F using SHELX-L [9]. The drawings were made with Diamond [10]. All nonhydrogen atoms were refined anisotropically. All H atoms were located from the difference Fourier map and freely refined to prove their real existence. However in the final refinement, those hydrogen atoms attached to the carbon atoms were repositioned geometrically. The H atoms were then initially refined with soft restraints on the bond lengths and angles to regularise their geometry (C---H in the range 0.93--0.98, N---H in the range 0.86--0.89 and O---H = 0.82 Å) and U~iso~(H) (in the range 1.2-1.5 times U~eq~ of the parent atom), after which the positions were refined with riding constraints. Crystal data and experimental parameters used for the intensity data collection are summarised in Table 1.

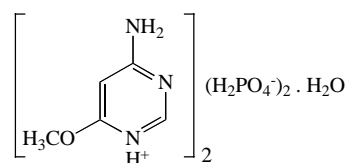


Fig. (1). Chemical diagram of the [4-NH₂-6-OCH₃-C₄H₃N₂]₂(H₂PO₄)₂·H₂O compound.

RESULTS AND DISCUSSION

The main geometrical features of the different entities of [4-NH₂-6-OCH₃-C₄H₃N₂]₂(H₂PO₄)₂·H₂O are reported in Tables 2 and 3.

A perspective view of the asymmetric unit of the structure drawing with 35% probability thermal ellipsoids is depicted in Fig. (2), while the complete atomic arrangement is shown in Fig. (4).

Fig. (2) shows that the asymmetric unit of the [4-NH₂-6-OCH₃-C₄H₃N₂]₂(H₂PO₄)₂·H₂O consists of two crystallographically independent 4-Amino-6-methoxypyrimidinium cations, two crystallographically independent dihydrogenmonophosphate H₂PO₄⁻ anions and a water molecule. The atomic arrangement of [4-NH₂-6-OCH₃-C₄H₃N₂]₂(H₂PO₄)₂·

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Table 1. Crystal and Experimental Data

<i>Crystal data</i>	
2(C ₅ H ₈ N ₃ O).2(H ₂ O ₄ P).H ₂ O	Z = 4
$M_r = 464.28$	$D_x = 1.626 \text{ Mg m}^{-3}$
Monoclinic, $P12_1/n1$	Mo $K\alpha$ radiation
$a = 15.012 (2) \text{ \AA}$	Cell parameters from 0 reflections
$b = 6.663 (2) \text{ \AA}$	$\theta = 0-0^\circ$
$c = 19.258 (3) \text{ \AA}$	$\mu = 0.3 \text{ mm}^{-1}$
$\beta = 100.05 (2)^\circ$	$T = 293 \text{ K}$
$V = 1896.9 (7) \text{ \AA}^3$	Prism, colorless
<i>Data collection</i>	
Serial diffractometer	$R_{\text{int}} = 0.026$
$\omega/2\theta$ scan	$\theta_{\text{max}} = 28.0^\circ$
Absorption correction: gaussian	$h = -19 \rightarrow 19$
$T_{\text{min}} = 0.886, T_{\text{max}} = 0.907$	$k = 0 \rightarrow 8$
7823 measured reflections	$l = -10 \rightarrow 25$
4568 independent reflections	0 standard reflections
3100 reflections with $I > 2.0\sigma(I)$	every . reflections
<i>Refinement</i>	
Refinement on F	H atoms constrained to parent site
$R[F^2 > 2\sigma(F^2)] = 0.050$	Calculated weights Method, part 1, Chebychev polynomial, [weight] = $1.0/[A_0 * T_0(x) + A_1 * T_1(x) \dots + A_{n-1} * T_{n-1}(x)]$ where A_i are the Chebychev coefficients listed below and $x = F / F_{\text{max}}$ Method = Robust Weighting $W = [\text{weight}] * [1 - (\Delta F / 6 * \sigma(F)^2)^2]$ A_i are: 1.68 1.48 1.12
$wR(F^2) = 0.055$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.73 \text{ e \AA}^{-1}$
2832 reflections	$\Delta\rho_{\text{min}} = -0.47 \text{ e \AA}^{-1}$
263 parameters	

Table 2. Geometric Parameters ($\text{\AA}, ^\circ$) of [4-NH₂-6-OCH₃-C₄H₃N₂]₂(H₂PO₄)₂.H₂O

P1—O1	1.568 (2)	N1—C4	1.337 (3)
P1—O2	1.567 (2)	N2—C1	1.364 (3)
P1—O3	1.510 (2)	N2—C4	1.302 (3)
P1—O4	1.5029 (2)	N3—C1	1.327 (3)
P2—O5	1.481 (2)	N4—C6	1.355 (4)
P2—O6	1.511 (2)	N4—C9	1.342 (4)
P2—O7	1.572 (2)	N5—C8	1.362 (4)
P2—O8	1.536 (3)	N5—C9	1.304 (3)
O10—C3	1.328 (3)	N6—C8	1.331 (3)
O10—C5	1.443 (3)	C1—C2	1.415 (4)
O11—C6	1.330 (3)	C2—C3	1.365 (3)
O11—C10	1.437 (4)	C6—C7	1.368 (4)
N1—C3	1.360 (3)	C7—C8	1.406 (4)
O1—P1—O2	107.37 (12)	C8—N5—C9	116.4 (2)

(Table 2). Contd.....

O1—P1—O3	104.98 (11)	N2—C1—N3	116.2 (2)
O2—P1—O3	111.24 (11)	N2—C1—C2	121.6 (2)
O1—P1—O4	111.99 (11)	N3—C1—C2	122.3 (2)
O2—P1—O4	106.91 (11)	C1—C2—C3	117.1 (2)
O3—P1—O4	114.21 (11)	C2—C3—N1	119.9 (2)
O5—P2—O6	117.28 (15)	C2—C3—O10	127.8 (2)
O5—P2—O7	111.37 (13)	N1—C3—O10	112.4 (2)
O6—P2—O7	102.19 (13)	N1—C4—N2	124.6 (2)
O5—P2—O8	112.91 (15)	N4—C6—O11	112.8 (2)
O6—P2—O8	106.78 (17)	N4—C6—C7	120.4 (2)
O7—P2—O8	105.12 (19)	O11—C6—C7	126.8 (3)
C3—O10—C5	117.2 (2)	C6—C7—C8	116.6 (2)
C6—O11—C10	117.4 (2)	C7—C8—N5	122.4 (2)
C3—N1—C4	119.6 (2)	C7—C8—N6	120.8 (3)
C1—N2—C4	117.2 (2)	N5—C8—N6	116.7 (3)
C6—N4—C9	118.9 (2)	N4—C9—N5	125.2 (3)

Table 3. Hydrogen-Bond Parameters (Å, °) for [4-NH₂-6-OCH₃-C₄H₃N₂]₂(H₂PO₄)₂·H₂O

D-H...A	D...A	D...H	H...A	D-H...A
O1—H1...O9 ⁱ	2.595 (4)	0.82	1.80	162
O2—H2...O6 ⁱⁱ	2.609 (4)	0.80	1.81	174
O8—H3...O6 ⁱⁱ	2.556 (4)	0.83	1.76	160
O7—H4...O3 ⁱⁱ	2.605 (4)	0.83	1.81	161
O9—H5...O4 ⁱⁱⁱ	2.729 (4)	0.82	1.93	166
O9—H6...O4 ^{iv}	2.870 (4)	0.81	2.06	172
N1—H7...O3 ^v	2.629 (4)	0.86	1.78	166
C4—H8...O8 ^v	3.270 (4)	0.92	2.47	146
N3—H10...N5	3.083 (4)	0.85	2.23	178
N3—H11...O4	2.825 (4)	0.86	1.98	168
C5—H13...O1 ^{vi}	3.270 (4)	0.96	2.43	145
C5—H14...O5 ^{vii}	3.316 (4)	0.96	2.58	134
C5—H14...O11 ^{vii}	3.435 (4)	0.96	2.59	147
N4—H15...O5	2.575 (4)	0.85	1.73	176
C9—H16...O2	3.326 (4)	0.92	2.54	143
N6—H17...N2	2.987 (4)	0.86	2.13	174
N6—H18...O7 ^v	3.131(4)	0.85	2.28	177

Symmetry codes: ⁱ1-x, 1-y, 1-z; ⁱⁱ3/2-x, -1/2+y, 3/2-z; ⁱⁱⁱ1/2+x, 3/2-y, -1/2+z; ^{iv}1-x, 2-y, 1-z; ^v-1/2+x, 3/2-y, -1/2+z; ^{vi}1/2-x, 1/2+y, 3/2-z; ^{vii}-1+x, y, z.

H₂O can be described by inorganic layers of H₂PO₄⁻ anions and water molecules parallel to *ab*-planes (Fig. 3). In such layers, each P(2)O₄ tetrahedron is associated to four neighboring phosphate anions (two P(1)O₄²⁻ and two P(2)O₄²⁻)

through O-H...O hydrogen bonds. However, the P(1)O₄²⁻ is bonded to two P(2)O₄²⁻ anions (via O-H...O hydrogen bonds), on the one hand, and to three water molecules (through O(w)-H...O and O-H...O(w) hydrogen bonding

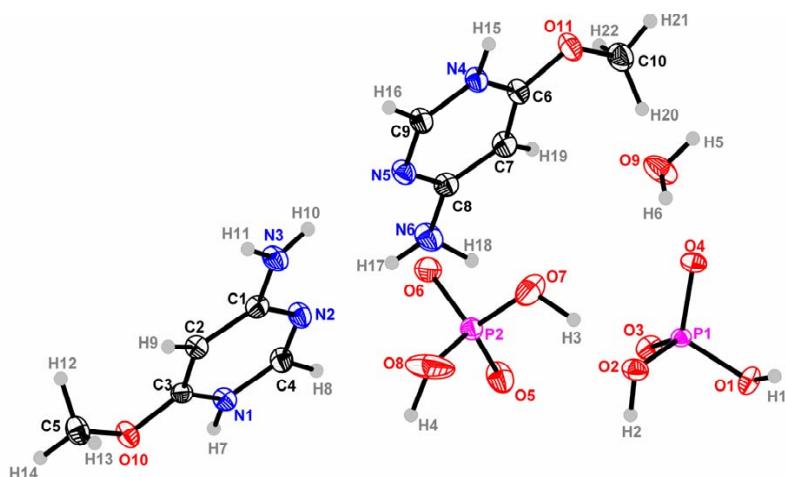


Fig. (2). Perspective view of the asymmetric unit of $[4\text{-NH}_2\text{-6-OCH}_3\text{-C}_4\text{H}_3\text{N}_2]_2(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ with the atom numbering scheme and thermal ellipsoids at 35 % of probability and arbitrary sphere for the H atoms.

interactions), on the other hand. These intermolecular hydrogen bonds generate edge-fused $[\text{R}_2^4(14)$ and $\text{R}_2^4(10)$ motif [11, 12]. Between these inorganic layers, located at $z = 1/4$ and $z = 3/4$, are anchored the organic cations through N-H...O, N-H...N and C-H...O hydrogen bonds (Fig. 4, Table 3).

cordance with that observed in $[3,5\text{-(CH}_3\text{-O)}_2\text{C}_6\text{H}_3\text{NH}_3]_2(\text{H}_2\text{PO}_4)_2$ where the P-P distance is 4.705(3) Å [14] and in $(\text{C}_6\text{H}_8\text{N}_3\text{O})_2(\text{H}_2\text{PO}_4)_2$ where the P-P distances between successive phosphoric atoms in each layer vary from 4.354(2) to 4.890(2) Å [15].

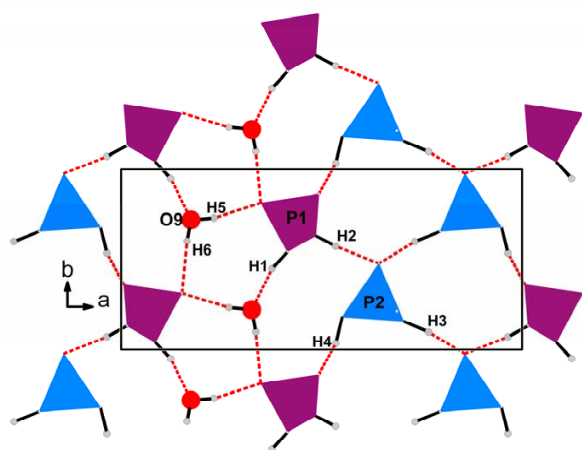


Fig. (3). Projection of the structure of $[4\text{-NH}_2\text{-6-OCH}_3\text{-C}_4\text{H}_3\text{N}_2]_2(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ along the c axis. A polyhedral representation is used for the H_2PO_4^- tetrahedron.

Examination of the H_2PO_4^- geometrical feature (Table 2) shows two kinds of P-O distances. The largest ones in the range [1.569(3) and 1.571(3) Å] can be attributed to P-OH distances, the shortest ones ranging from 1.476(3) to 1.510(3) Å correspond to the phosphorous atom doubly bonded to oxygen atom (P = O). The average values of the P-O distances and the O-P-O angles are respectively 1.534(3) Å and 109.37(2)°. These values are in full agreement with those observed in such anions in other dihydrogenomonophosphates [13]. The short P-P distances, varying from 4.459(4) to 4.819(4) Å, between neighboring phosphoric atoms in the layer, are in favor of the general formation of $[\text{H}_2\text{PO}_4]_n^{n-}$ polyanions in the crystal structure, but not the individualization of the H_2PO_4^- groups. This polymeric structure is in ac-

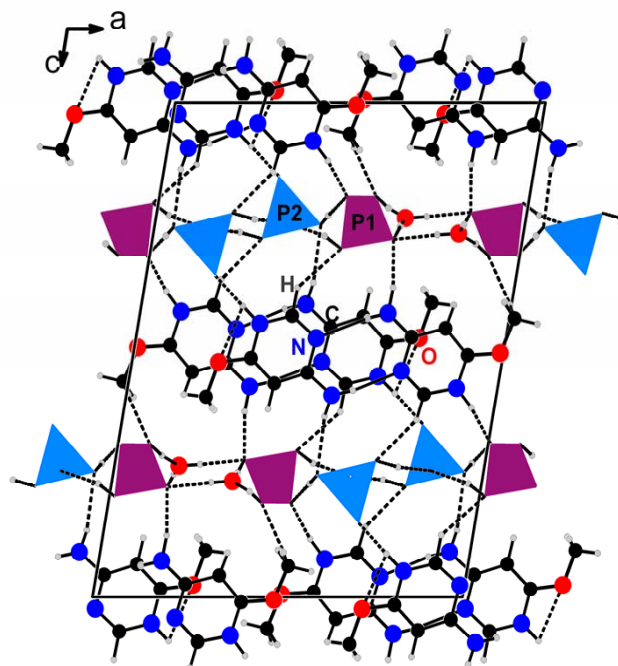


Fig. (4). Projection of the structure of $[4\text{-NH}_2\text{-6-OCH}_3\text{-C}_4\text{H}_3\text{N}_2]_2(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ along the b axis. A polyhedral representation is used for the H_2PO_4^- tetrahedron. The hydrogen bonds are indicated by dashed lines.

Examination of the two organic entity geometries shows that the atoms C1, C2, C3, N1, C4 and N2 of the first pyridiminy ring and the atoms C6, C7, C8, N5, C9 and N4 of the second one have a good coplanarity. They form conjugated planes with respective maximum deviations of 0.0054 and 0.0040 Å. The mean values of C-C and C-N bond lengths are 1.358 Å and 1.357 Å (Table 2), which are between those of a single bond and a double bond, agreeable

with those in literature. These two pyridiminy rings display an almost coplanar configuration, with a dihedral angle of 5.51° . The C-N-C angle for protonated atoms N1 [$119.5(3)^\circ$] and N4 [$118.6(3)^\circ$] are, respectively, 2.1° and 2.5° larger than that at the unprotonated atoms N2 [$117.4(3)^\circ$] and N5 [$116.1(3)^\circ$]. Protonation of the nitrogen atoms N1 and N4 decreases their electronegativity; hence the corresponding C-N-C angles become larger [16]. Furthermore, the 4-Amino-6-methoxypyrimidine is protonated in acidic solution. The bonding of the H atom to the ring N atom of 4-Amino-6-methoxypyrimidine, but not to the amino N atom, gives a great stability to the structure by imino resonance. This is well supported by the bond lengths N3-C1 [$1.319(4) \text{ \AA}$] and N6-C6 [$1.334(5) \text{ \AA}$], which are approximately equal to C=N double bond length, indicating that atoms N3 and N6 of the imino groups must be sp^2 hybridized. This is also confirmed by the fact that atoms C1, N3, H10 and H11 lie almost in the plane of the first pyrimidiny ring, with a maximum deviation of 0.039 \AA for atom H10. Similarly, the C8, N6, H17 and H18 lie almost in the plane of the second pyrimidiny ring, with a maximum deviation of 0.111 \AA for H18.

ACKNOWLEDGEMENTS

We would like to thank the Ministry of Scientific Research Technology and Competing Development of Tunisia for its financial support.

SUPPLEMENTARY MATERIAL

Supplementary material can be viewed at www.bentham.org/open/tocryj

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Received: June 25, 2008

Revised: September 23, 2008

Accepted: September 23, 2008

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