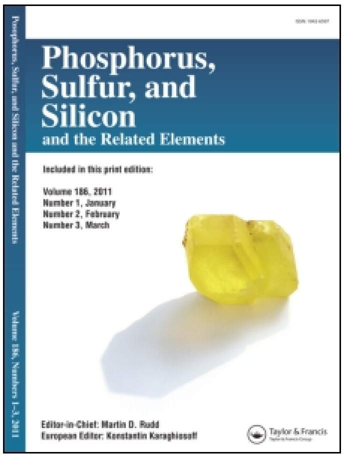

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Crystal Structure and Characterization of a New Noncentrosymmetric Organic Monophosphate: [2-$CH_2NH_3C_5H_4N$]H_2PO_4

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CRYSTAL STRUCTURE AND CHARACTERIZATION OF A NEW NONCENTROSYMMETRIC ORGANIC MONOPHOSPHATE: [2-$CH_2NH_3C_5H_4N$]H_2PO_4

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Chemical preparation, crystal structure, thermal analysis, and spectroscopic investigations are given for a new noncentrosymmetric organic cation dihydrogenmonophosphate [2-$CH_2NH_3C_5H_4N$]H_2PO_4 (abbreviated as 2AMPDP). This compound crystallizes in the orthorhombic space group $Pca2_1$ with the following unit cell parameters: a = 16.308(1), b = 6.967(4), c = 7.905(2) Å, V = 898.1(4) Å^3, and Z = 4. The crystal structure of this compound contains infinite ($H_2PO_4^-$)$_n$ chains extending along the c direction built up from H-bonds occurring between the $H_2PO_4^-$ anions. These chains are interconnected by organic groups via hydrogen bonds so as to build a three-dimensional network. Solid-state ^{31}P and ^{13}C MAS NMR spectroscopies are in good agreement with the X-ray structure results.

Supplemental materials are available for this article. Go to the publisher's online edition of **Phosphorus, Sulfur, and Silicon and the Related Elements** ***to view the free supplemental file.***

Keywords Crystal structure; hydrogen bonds; MAS-NMR spectroscopy; thermal analysis

INTRODUCTION

Chemists and physicists of the solid state have shown an increasing interest in the study of organic, aromatic, conjugated compounds and organic–inorganic polar crystals due to their nonlinear optical coefficients.[1–3] Molecules of these materials possess correlated and highly delocalized π-electron states.[4] The building motif of a cation in such noncentrosymmetric structures depends upon the ability of host anions to aggregate.[5,6] For that purpose, an organic cation monophosphate could be used as an interesting model. Within a systematic investigation of the environment of these anions in new organic materials and of their contribution in the formation of new nonlinear compounds, we report in this article the synthesis, the crystal structure, and the physicochemical studies of a new noncentrosymmetric organic monophosphate.

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RESULTS AND DISCUSSION

Structure Description

Interatomic distances and angles are listed in Table I. The asymmetric unit of the crystal structure (Figure 1) consists of one dihydrogenmonophosphate anion ($H_2PO_4^-$) and one organic cation $(C_6N_2H_{10})^+$. A view of the structure projected along the *b* axis direction shows that the inorganic atomic arrangement has a layered organization around the planes $x = 0$ and $x = 1/2$. The organic cations are located in the interlayer spacing and neutralize the negative charge (see Figure S1, available online in the Supplemental Materials).

In fact, the structure exhibits two kinds of hydrogen bonds (Table I): O—H···O and N—H···O. Within each inorganic layer, the $H_2PO_4^-$ groups are interconnected by O—H···O hydrogen bonds to form infinite corrugated chains extending along the *c* direction. These chains are themselves interconnected by the NH_3^+ groups of the organic cation to form layers parallel to the (*b*, *c*) plane (see Figures S1 and S2, available online in the Supplemental Materials). The strength of the O—H···O hydrogen bond ($d_{H\cdots O} = 1.83$Å) and the short distances P–P = 4.844(2)Å between successive phosphoric atoms in each chain could allow us to consider the $[H_2PO_4]_n^{n-}$ subnetwork as a polymeric species. Similar values in the $[H_2PO_4]_n^{n-}$ arrangement have also been noted in other crystal structures.[10–12] Inside each $H_2PO_4^-$ anion, the P–O bonds [1.494(2)Å and 1.502(2)Å] are shorter than P–OH bonds [1.579(2)Å and 1.569(1)Å] as pointed out by Cruickshank.[13] The average

Table I Main interatomic distances (Å) and bond angles (°) in the $[2\text{-}CH_2NH_3C_5H_4N]H_2PO_4$

P(1)O$_4$ tetrahedron				
P1	O1	O2	O3	O4
O1	**1.579(2)**	106.291(1)	111.471(1)	111.7(9)
O2	2.514(2)	**1.569(1)**	109.70(9)	107.2(9)
O3	2.452(2)	2.511(2)	**1.502(2)**	116.3(1)
O4	2.544(2)	2.466(2)	2.546(3)	**1.494(2)**
$[2\text{-}CH_2NH_3C_5H_4N]^+$ group				
N1—C1	1.482(2)	N1—C1-C2	113.8(2)	
C1—C2	1.505(2)	C1—C2—C3	124.4(2)	
C2—C3	1.383(3)	C1—C2—N2	113.8(2)	
C3—C4	1.389(3)	C3—C2—N2	121.9(2)	
C4—C5	1.380(3)	C2—C3—C4	119.2(2)	
C5—C6	1.372(4)	C3—C4—C5	119.2(2)	
C6—N2	1.339(3)	C4—C5—C6	117.6(2)	
N2—C2	1.337(2)	C5—C6—N2	124.2(2)	
		C6—N2—C2	117.9(2)	
The hydrogen bonds				
D—H···*A*	*D—H(Å)*	H...*A(Å)*	*D...A(Å)*	*D*—H...*A(°)*
O1—H1···O4^{i}	0.82	1.83	2.543 (2)	145
O2—H2···N2^{ii}	0.82	1.89	2.696 (2)	165
N1—H1A···O3	0.89	1.87	2.740 (2)	167
N1—H1B···O4^{iii}	0.89	1.88	2.763 (3)	171
N1—H1C···O3^{iv}	0.89	1.89	2.760 (2)	166

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

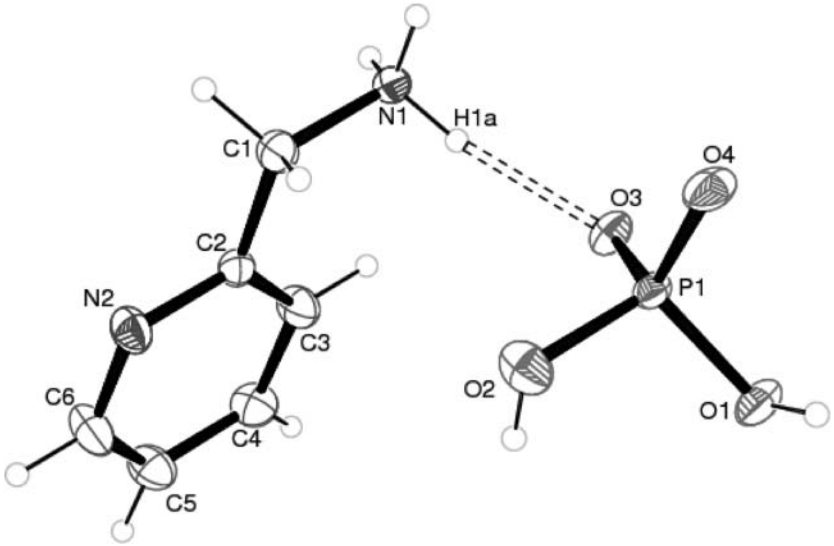

Figure 1 ORTEP drawing of the title compound, with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 35% probability level.

values of P–O distances and OPO angles are 1.535Å and 109.44°, respectively. They are in good agreement with those generally observed in such anions in other phosphates.[12] The organic cations of (2AMPDP) are organized in opposite directions along the *a*-axis and located between the inorganic layers. The interplane distance between the rings of the cations is in the vicinity of 3.905Å.

Regarding the two nitrogen atoms of the organic molecule, the amino group is protonated but not the pyridine nitrogen, because, in this case, the nitrogen of the amino group is slightly more basic than the nitrogen of the pyridinic cycle. The same case of protonation was observed in the compounds of pyridyl-2-methylaminiumnitrate[14] and 3-ammoniummethylpyridine dihydrogen-monophosphate.[11] It is worth noting that distances and angles in the pyridinic cycle of the title compound are quite similar to those observed in isolated organic molecule,[16] and to those observed in other compounds analogs.[11,14]

NMR Results

The proton decoupled ^{31}P MAS NMR spectrum of the crystalline dihydrogen-monophosphate [2-$CH_2NH_3C_5H_4N$]·H_2PO_4 is shown in Figure 2. It exhibits a single resonance peak with two spinning side bands. The signal chemical shift value (–1.1 ppm) agrees with those corresponding to monophosphates.[16–22] The existence of a single peak in the spectrum clearly indicates the presence of only one crystallographic site in the unit-cell of this compound, which agrees with the X-ray results.

The ^{13}C CP/MAS NMR spectrum of the as-synthesized hydrogenmonophosphate displays 6 different signals (see Figure S3, in the Supplemental Materials). The first resonance peak at lower chemical shift, 41.3 ppm, is related to the methylenic C1 carbon atom. The most shifted NMR lines, whose chemical shifts range from 124.00 to 150.00 ppm,

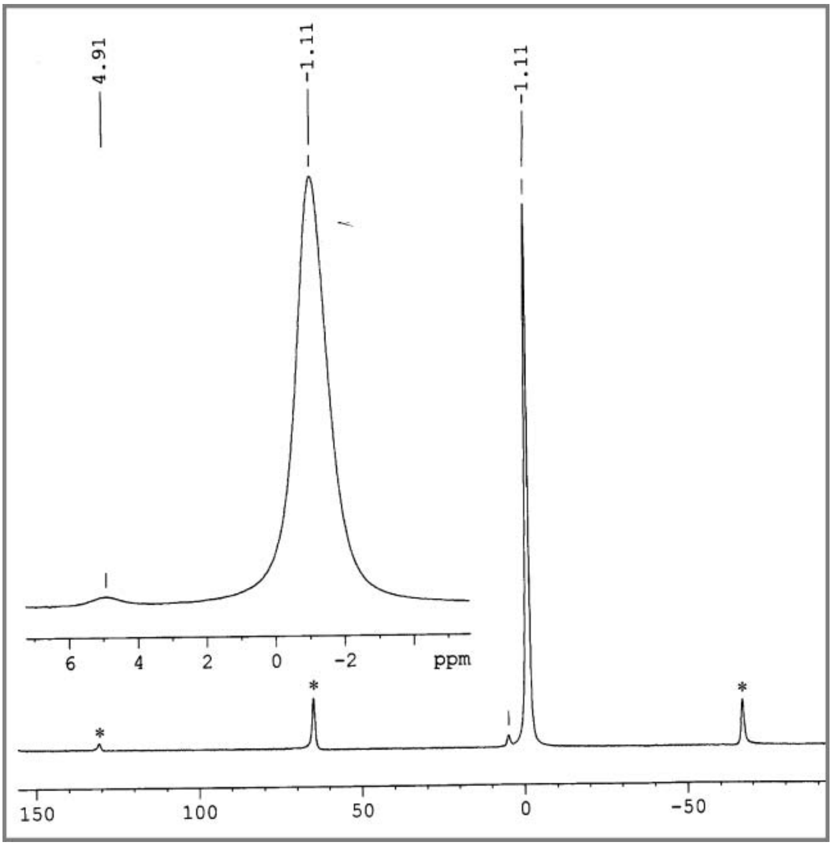

Figure 2 ^{31}P NMR spectra of [2-$CH_2NH_3C_5H_4N$]H_2PO_4. *Spinning side bands.

are attributed to the pyridinic carbon atoms. To assign NMR components to different carbon atoms, we have calculated the chemical shifts by means of the ChemDraw Ultra 10.0 software. The carbon atoms are labeled as depicted in Figure 1. The obtained results are grouped in Table S2 (see the Supplemental Materials). This number of signals is in good agreement with the X-ray results, as only one organic molecule is found in the asymmetric unit cell.

Thermal Analysis

The two curves corresponding to differential thermal analysis (DTA) and thermogravimetric analysis (TGA) in following argon are given in Figure S4 (see the Supplemental Materials). The DTA curve shows that the monophosphate is stable until 465 K, where it undergoes a melting transformation. At the same time, the material undertakes a continuous decomposition of the organic group over a wide temperature range (465–687 K) leading at the end of the experiment to a black deposit of carbon in a viscous matter. This is also confirmed by the significant weight loss observed in the TGA curve.

Table II Crystal data and experimental parameters used for the intensity data collection: Strategy and final results of the structure determination of [2-$CH_2NH_3C_5H_4N$]H_2PO_4

Empirical formula	[2-$CH_2NH_3C_5H_4N$]H_2PO_4
CCDC No	665357
Formula weight	206,14 g.mol^{-1}
Crystal system	orthorhombic
Space group	$Pca2_1$
a	16.308 (2) Å
b	6.967 (5) Å
c	7.905 (4) Å
Z	4
V	898.1 (8) Å^3
ρ_{cal}	1.525 g. cm^{-3}
F(000)	432
μ (MoK$\overline{\alpha}$)	0.292 mm^{-1}
Index ranges : h,k,l	$h_{max} = 0$, $k_{max} = 9$, $l_{max} = 0$ $h_{min} = -22$, $k_{min} = -9$, $l_{min} = -11$
Collected unique reflections ($R_{int} = 0.01$)	2682
Flack's parameter	0.15(10)
Unique reflections included	1393 with $I > 2\sigma(I)$
Refined parameters	121
$R[F^2 > 2\sigma(F^2)]$	0.028
$wR(F^2)$	0.075
$\Delta\rho_{min}$, $\Delta\rho_{max}$	−0.28, 0.33 e Å^3
Goodness-of-fit	1.08
$(\Delta/\sigma)_{max}$	0.001

CONCLUSION

In conclusion, we have prepared and characterized by X-ray diffraction, thermal behavior, and NMR analysis, a novel noncentrosymmetric structure of organic cation monophosphate material with formula [2-$CH_2NH_3C_5H_4N$]H_2PO_4. The present study may be profitable not only because of novel structure features, but also because the new noncentrosymmetric structure may be useful in NLO materials.

EXPERIMENTAL

Chemical Preparation

A solution of 2-aminomethylpyridine (0.035 mol) in ethanol (5 mL) was added dropwise under stirring to a solution (20 mL) of H_3PO_4 (0.05 M) (Fluka, 85% weight). Crystals of the title compound are obtained by slow evaporation at room temperature of this mixture, when the majority of the solution is evaporated. The crystals are stable for a long time under normal conditions of temperature and moisture.

Investigation Techniques

X-Ray diffraction. The intensity data were collected at room temperature using a Enraf-Nonius CAD4 diffractometer with MoKα radiation. The cell parameters were determined from a least-squares refinement of 25 reflections. Two standard reflections were periodically measured every 120 minutes during data collection. Unique reflections (2682) were measured, of which 1393 had $I \geq 2\sigma$ (I) and were used for structure determination and refinement. The structure was solved and refined by full-matrix least squares method using the program SHELX97[7] in the WinGX package.[8] All non-hydrogen atoms were refined isotropically and then anisotropically by full matrix least-squares method. All hydrogen atoms were placed geometrically and treated as riding. An ORTEP drawing[22] of the molecular structure is shown in Figure 1. The parameters used for the X-ray diffraction data collection as well as the strategy used for the crystal structure determination and its final results are reported in Table II. Crystallographic data (CIF) for the structure reported in this article have been deposited in the Cambridge Crystallographic Data centre as supplementary materials No CCDC 665357. Copies of the data can be obtained, free of charge, upon application to the CCDC, 12 Union Road, Cambridge CB12EZ, UK (Fax: +44(1223) 336–033; e-mail: deposit@ccdc.cam.ac.uk).

NMR spectroscopy. All NMR spectra were recorded on a Bruker DSX-300 spectrometer operating at 75.49 MHz for ^{13}C and 121.57 MHz for ^{31}P with a classical 4 mm probe-head, allowing spinning rates up to 10 KHz. ^{13}C and ^{31}P NMR chemical shifts are given relative to tetramethylsilane and 85% H_3PO_4, respectively (external references; precision 0.5 ppm). The ^{13}C spectrum was recorded by use of cross-polarization (CP) from protons (contact time 5 ms) and MAS. In all cases, it was checked that there was a sufficient delay between the scans, allowing a full relaxation of the nuclei.

Thermal behavior. Thermal analysis was performed using the Multimodule 92 Setaram Analyzer operating from room temperature up to 823 K at an average heating of 5°C/min^{-1}.

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