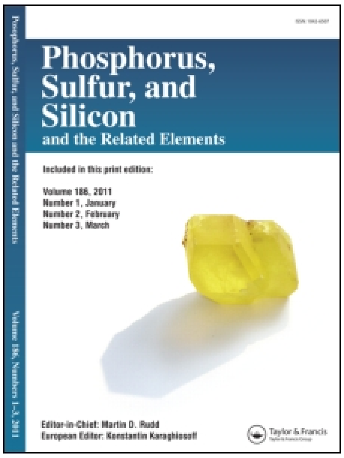

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Crystal Structure and Spectroscopic Studies of a New Organic Dihydrogenmonophosphate $[1\text{-}(2,3\text{-}(CH_3)_2\text{-}C_6H_3)C_4H_{10}N_2]H_2PO_4$

A. Oueslati[a]; K. Brahim[b]; C. Ben Nasr[a]; M. Rzaigui[a]
[a] Laboratoire de Chimie des Matériaux, Faculté des Sciences de Bizerte, Zarzouna, Tunisie [b] Laboratoire de Thermodynamique Appliquée, Faculté des Sciences de Tunis, El Manar, Tunisie

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Crystal Structure and Spectroscopic Studies of a New Organic Dihydrogenmonophosphate $[1\text{-}(2,3\text{-}(CH_3)_2\text{-}C_6H_3)C_4H_{10}N_2]H_2PO_4$

A. Oueslati
Laboratoire de Chimie des Matériaux, Faculté des Sciences de Bizerte, Zarzouna, Tunisie

K. Brahim
Laboratoire de Thermodynamique Appliquée, Faculté des Sciences de Tunis, El Manar, Tunisie

C. Ben Nasr
M. Rzaigui
Laboratoire de Chimie des Matériaux, Faculté des Sciences de Bizerte, Zarzouna, Tunisie

The crystal synthesis and structure of a new organic dihydrogenmophosphate $[1\text{-}(2,3\text{-}(CH_3)_2\text{-}C_6H_3)C_4H_{10}N_2]H_2PO_4$ *are reported. This compound crystallizes in the monoclinic* $P2_1/n$ *with* $a = 7.545(2)$ Å, $b = 26.315(4)$ Å, $c = 7.798(6)$ Å, $\beta = 115.01(4)^\circ$, $V = 1403.0(1)$ Å^3, *and* $Z = 4$. *Crystal structure was solved and refined to* $R = 0.046$, *using 1981 independent reflections. It can be described by inorganic layers including the* $H_2PO_4^-$ *anions and the* NH_2^+ *ammonium groups parallel to (a, c) planes and situated at* $y =^1/_4$ *and* $y =^3/_4$. *The interlayer spacing is occupied by the organic molecules which perform different interactions around the 3D network cohesion. A characterization of this compound by solid-state* ^{13}C *and* ^{31}P *MAS NMR and ATG is also reported.*

Keywords ATG; IR spectroscopy; NMR spectroscopy; X-ray diffraction

INTRODUCTION

Organic phosphate complexes have been widely studied due to their numerous practical and potential uses in various fields such as bimolecular sciences, catalysts, fuel cell, liquid crystal-material developers, and quadratic non linear optic.$^{1-6}$ In these materials, the anions

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Address correspondence to C. Ben Nasr, Laboratoire de Chimie des Matériaux, Faculté des Sciences de Bizerte, Zarzouna 7021, Tunisie. E-mail: cherif.bennasr@fsb.rnu.tn

are observed to have a strong tendency to assemble via strong hydrogen bonds and build an infinite network such as ribbons[7] chains,[8,9] layers.[10,11] This depends on the nature and the shape of the organic molecule. As a contribution to the study of this phosphate family, we report in this article, the chemical preparation and the structural investigation of a new 1-(2,3-dimethylphenyl)piperazinium dihydrogenmonophosphate, $[1\text{-}(2,3\text{-}(CH_3)_2\text{-}C_6H_3)C_4H_{10}N_2]H_2PO_4$. The solid-state ^{13}C and ^{31}P MAS NMR spectroscopies are also reported.

RESULTS AND DISCUSSION

Structure Description

Structural determination shows that the title compound crystallizes in the monoclinic space group $P2_1/n$. The final atomic coordinates and thermal parameters of all atoms are given in Table I. Those of hydrogen atoms were also determined but not given in order to shorten the Table. Interatomic distances, bond angles, and hydrogen bonding schemes are given in Table II and Table III, respectively.

TABLE I Final Atomic Coordinates and Thermal Parameters in $[1\text{-}(2,3\text{-}CH_3\text{-}C_6H_3)C_4H_{10}N_2]H_2PO_4$

Atom	x (σ)	y (σ)	z (σ)	B_{eq}(Å^2)
P(0)	0.19839(6)	0.73796(2)	0.23402(6)	0.02489(13)
O(1)	0.0254(2)	0.69939(5)	0.1426(2)	0.0359(4)
O(2)	0.3834(2)	0.70470(5)	0.2675(2)	0.0373(4)
O(3)	0.1811(2)	0.77979(5)	0.0959(2)	0.0310(4)
O(4)	0.2092(2)	0.75534(5)	0.4227(2)	0.0312(4)
N(1)	0.0182(2)	0.68821(6)	0.5753(2)	0.0311(4)
N(2)	0.2977(2)	0.60708(6)	0.7158(2)	0.0283(4)
C(1)	−0.0229(3)	0.63675(7)	0.4857(3)	0.0322(5)
C(2)	0.1642(3)	0.68503(8)	0.7780(3)	0.0362(6)
C(3)	0.3458(3)	0.65833(7)	0.7940(3)	0.0355(5)
C(4)	0.1662(3)	0.61081(7)	0.5143(3)	0.0305(5)
C(5)	0.4632(3)	0.57444(7)	0.7512(3)	0.0296(5)
C(6)	0.4354(3)	0.52159(7)	0.7470(3)	0.0286(5)
C(7)	0.5925(3)	0.48935(7)	0.7733(3)	0.0327(5)
C(8)	0.7746(3)	0.50982(8)	0.8088(3)	0.0402(6)
C(9)	0.8031(3)	0.56192(9)	0.8209(3)	0.0448(6)
C(10)	0.6468(3)	0.59441(8)	0.7918(3)	0.0393(6)
C(11)	0.2408(3)	0.49938(8)	0.7168(3)	0.0374(6)
C(12)	0.5699(3)	0.43266(8)	0.7717(3)	0.0466(7)

Estimated SD are given in parentheses.

TABLE II Main Interatomic Distances (Å) and Angles (°) in $[1\text{-}(2,3\text{-}CH_3\text{-}C_6H_3)C_4H_{10}N_2]\ H_2PO_4$ Atomic Arrangement

		PO$_4$ tetrahedron		
P	O(1)	O(2)	O(3)	O(4)
O (1)	1.567 (2)	2.457 (3)	2.520 (2)	2.510 (3)
O (2)	103.00 (11)	1.573 (2)	2.510 (3)	2.513 (3)
O (3)	110.14 (10)	109.14 (11)	1.507 (2)	2.549 (3)
O (4)	109.32 (11)	109.18 (10)	115.34 (11)	1.510 (2)
O(1)-H(1) = 1.00 Å			P-O(1)-H(1) = 105.6°	
O(2)-H(2) = 1.00 Å			P-O(2)-H(2) = 113.5°	

	$[1\text{-}(2,3\text{-}CH_3\text{-}C_6H_3)C_4H_{10}N_2]^+$ group		
N(1)-C(1)	1.495(3)	C(2)-N(1)-C(1)	110.9(2)
N(1)-C(2)	1.499(4)	N(1)-C(2)-C(3)	110.6(2)
C(2)-C(3)	1.497(4)	C(2)-C(3)-N(2)	110.0(2)
C(3)-N(2)	1.461(3)	C(3)-N(2)-C(4)	108.8(2)
N(2)-C(4)	1.464(3)	C(4)-N(2)-C(5)	112.6(2)
C(4)-C(1)	1.511(4)	C(5)-N(2)-C(3)	115.3(2)
N(2)-C(5)	1.442(3)	N(2)-C(4)-C(1)	111.0(2)
C(5)-C(6)	1.405(4)	C(4)-C(1)-N(1)	110.1(2)
C(6)-C(11)	1.504(4)	N(2)-C(5)-C(6)	118.5(2)
C(6)-C(7)	1.400(4)	C(6)-C(5)-C(10)	120.3(2)
C(7)-C(12)	1.501(4)	C(10)-C(5)-N(2)	121.2(2)
C(7)-C(8)	1.391(4)	C(5)-C(6)-C(11)	120.9(2)
C(8)-C(9)	1.385(4)	C(11)-C(6)-C(7)	119.8(2)
C(9)-C(10)	1.395(4)	C(7)-C(6)-C(5)	119.2(2)
C(10)-C(5)	1.388(4)	C(6)-C(7)-C(12)	121.0(3)
		C(12)-C(7)-C(8)	119.1(2)
		C(8)-C(7)-C(6)	119.9(2)
		C(7)-C(8)-C(9)	120.6(2)
		C(8)-C(9)-C(10)	120.0(3)
		C(9)-C(10)-C(5)	119.9(3)

Estimated SD are given in parentheses.

TABLE III Bond lengths (Å) and angles (°) in Hydrogen bonding scheme of $[1\text{-}(2,3\text{-}CH_3\text{-}C_6H_3)C_4H_{10}N_2]H_2PO_4$

O(N)—H···O	O(N)···O	O(N)—H	H···O	O(N)—H···O
O(1)—H(1)···O4	2.568(3)	1.00	1.59	165.0
O(2)—H(2)···O3	2.628(3)	1.00	1.64	169.4
N(1)—H(3)···O3	2.748(3)	1.04	1.74	160.8
N(1)—H(4)···O4	2.839(3)	0.95	1.90	171.0

Estimated SD are given in parentheses.

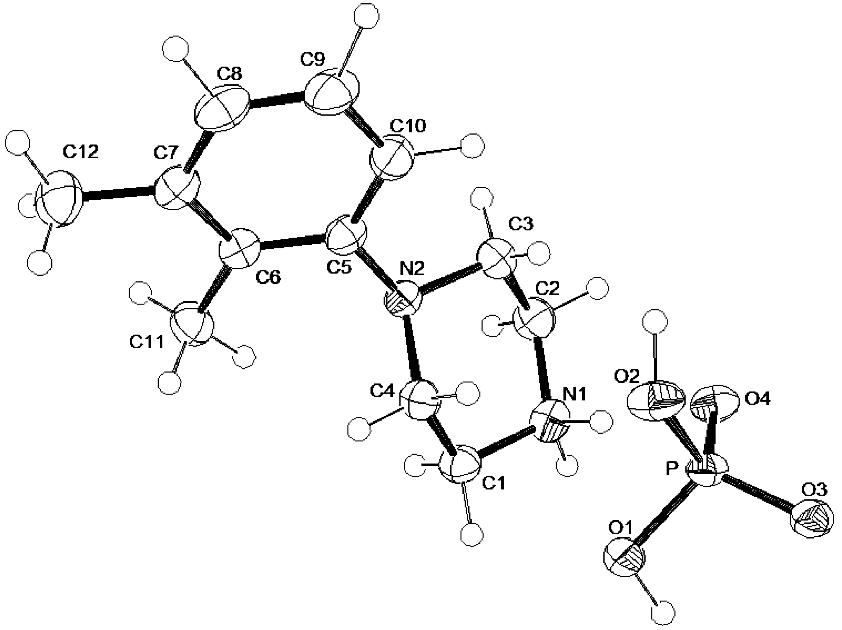

FIGURE 1 Asymmetric unit of $[1(2,3\text{-}(CH_3)_2\text{-}C_6H_3)C_4H_{10}N_2]H_2PO_4$. Thermal ellipsoids are shown at 40% probability.

The molecular configuration of this compound is shown in the ORTEP drawing (Figure 1). Charge neutrality is achieved by the presence of one organic cation for one $H_2PO_4^-$anion. The atomic arrangement contains inorganic layers including the $H_2PO_4^-$ anions and the NH_2^+ammonium groups (Figure 2). In these layers, the $H_2PO_4^-$ groups are connected by strong O—H· · ·O hydrogen bonds to form infinite chains in the direction [1 0 1]. These chains are interconnected by means N-H. . . O hydrogen bonds, generated by the organic entity, so as to build the inorganic layers parallel to (a, c) planes, located at $y = {}^1/_4$ and $y = {}^3/_3$ (Figure 3). The organic entities, trapped in the interlayer spacing, perform the 3D network cohesion through hydrogen bonds.

The detailed geometry of $H_2PO_4^-$ groups, gathered in Table II, shows that the P—O bonds are significantly shorter [1.507(2) Å, 1.510(2) Å] than the P—OH bonds [1.567(2) Å, 1.573(2) Å]. This is in agreement with the data relative to the protonated oxoanions.[12] Relatively short distances, ranging from 1.59 Å to 1.90 Å, characterize all H· · ·O bonds, which maintain the cohesion of this arrangement. It is worth noticing that the O· · ·O distance involved in the hydrogen bonding network [2.568(3) Å] is of the same order of magnitude as the O—O distance in

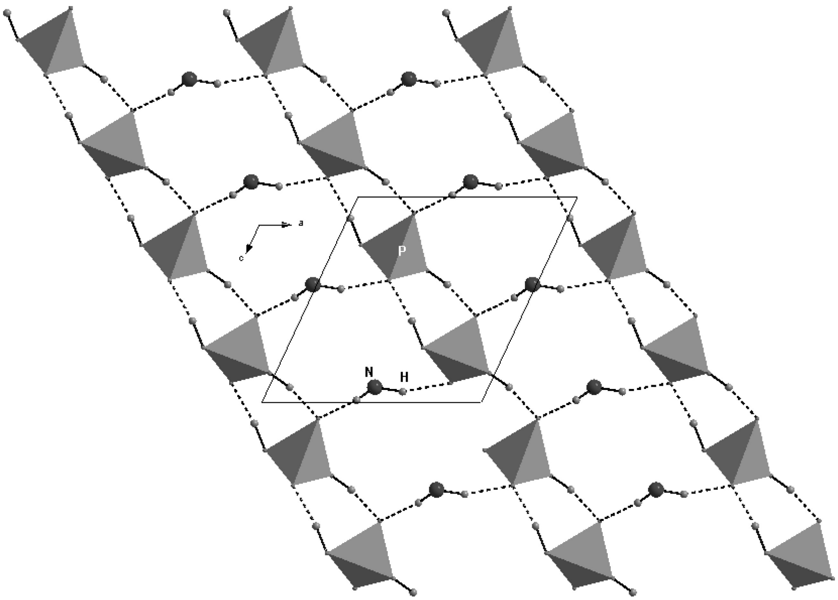

FIGURE 2 Projection of the structure of [1(2,3-$(CH_3)_2$-C_6H_3)$C_4H_{10}N_2$] H_2PO_4 along the b axis. A polyhedral representation is used for the PO_4 tetrahedron. The other atoms are labeled on the figure. The hydrogen bonds are denoted by dotted lines.

the PO_4 tetrahedron (2.457(3) Å to 2.549(3) Å). This is in favor of the general formation of $[H_2PO_4]_n^{n-}$ polyanions in the crystal structure, but not the individualization of the $H_2PO_4^-$ groups.

The calculated average values of distortion indices corresponding to the different angles and distances in the PO_4 tetrahedra [DI(PO) = 0.019, DI(OPO) = 0.020 and DI(OO) = 0.007], exhibit a pronounced distortion of the PO distances and OPO angles if compared to OO distances; so the phosphate group can be considered as a rigid regular arrangement of oxygen atoms, with the P atom displaced from their centroid.[13] As expected, O—P—O angle (115.34°) is significantly bigger than O—P—OH ones (mean angle of 109.73°) and the HO—P—OH angles are again significantly smaller (103.00°). Such geometrical features have also been observed in other crystal structures.[14,15]

Examination of the organic moiety geometrical features shows that the atoms C5, C6, C7, C8, C9 and C10 of the phenyl ring of the title compound have a good coplanarity, and they form a conjugated plane with average deviation of 0.0042 Å. The mean value of C—C bond lengths [1.394 Å] which is between single bond and double bond agrees with

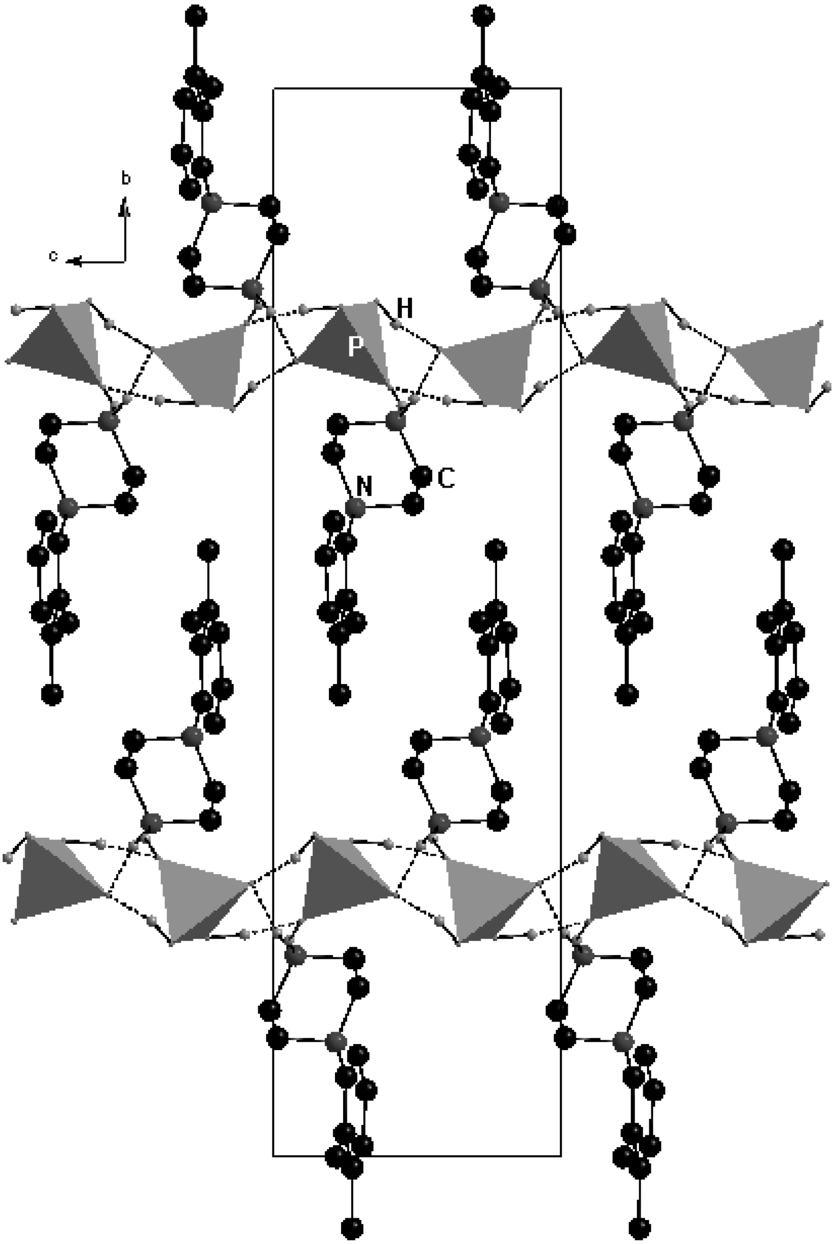

FIGURE 3 Projection of the structure of [1-(2,3-CH_3-C_6H_3)$C_4H_{10}N_2$]H_2PO_4 along the a axis. The phosphoric anions are given in the tetrahedra representation. The other atoms are labeled on the figure. The hydrogen bonds are denoted by dotted lines.

that in paraphenolammonium dihydrogenophosphate [1.383 Å].[16] The C—C distances and C—C—C— angles spreads from 1.385(4) to 1.405(4) Å and 118.5(2) to 120.6(2)°, respectively. These values show clearly that in 1-(2,3-dimethylphenyl)piperazinium the carbon ring of the phenyl group is regular. Furthermore, in the piperazinium cation the C1-N1-C2 angle [110.9(2)°] is larger than C3-N2-C4 [108.8(2)°]. This is due to the increasing of the N1 nitrogen atom electronegativity after receiving the proton.[17]

NMR Results

The proton decoupled ^{31}P MAS NMR spectrum of the crystalline dihydrogenmonophosphate $[1\text{-}(2,3\text{-}(CH_3)_2\text{-}C_6H_3)C_4H_{10}N_2]H_2PO_4$ is shown in Figure 4. It exhibits a single resonance peak with two spinning side bands. The signal chemical shift value (6.8 ppm) agrees with those corresponding to monophosphates.[18–24] The existence of a single peak in

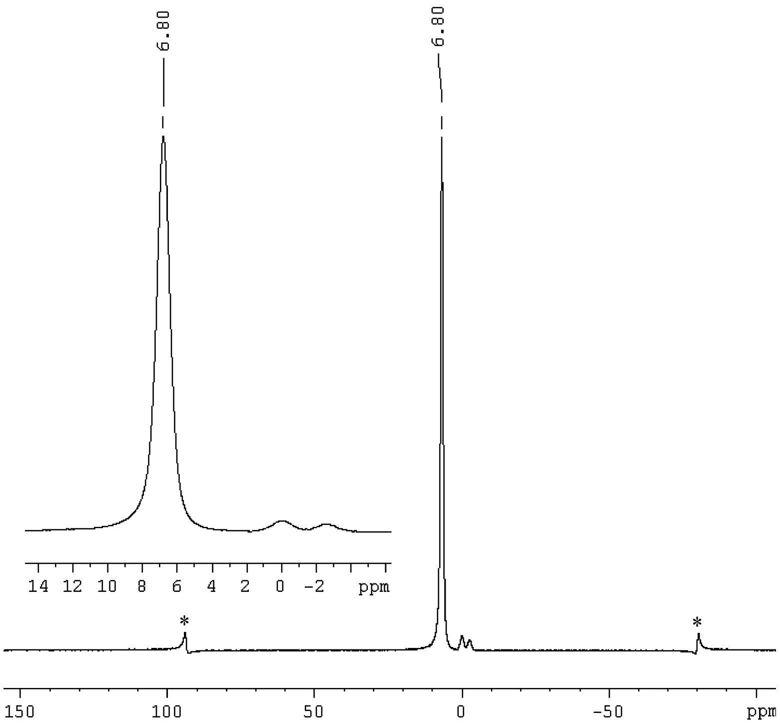

FIGURE 4 ^{31}P MAS-NMR spectrum of $[1\text{-}(2,3\text{-}(CH_3)_2\text{-}C_6H_3)C_4H_{10}N_2]H_2PO_4$. * spinning sidebands.

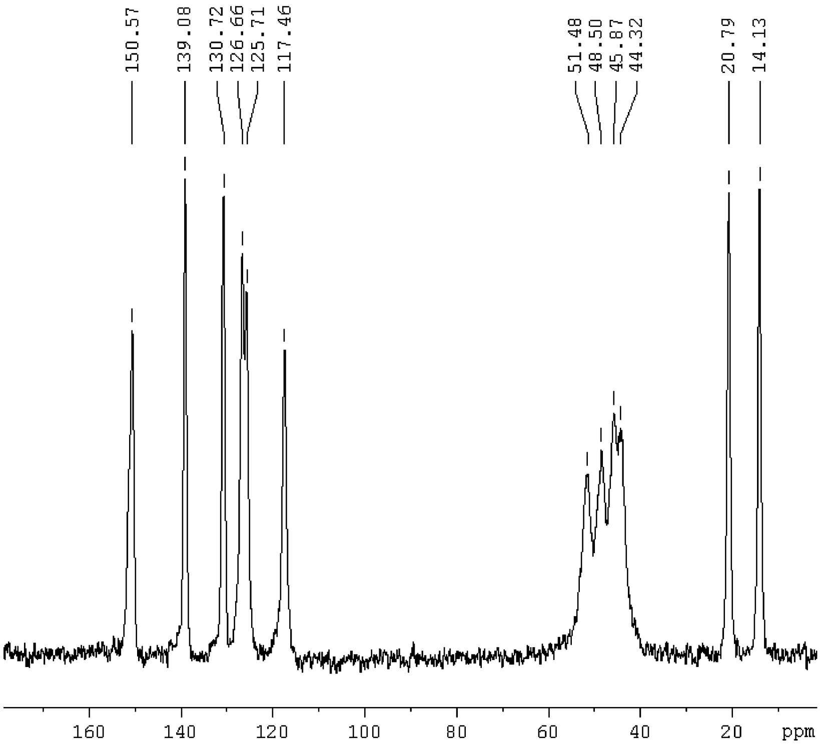

FIGURE 5 ^{13}C CP-MAS NMR spectrum of $[1\text{-}(2,3\text{-}(CH_3)_2\text{-}C_6H_3)C_4H_{10}N_2]$ H_2PO_4.

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 spectrum of the as-synthesized hydrogenmonophosphate displays twelve different signals (Figure 5). This spectrum exhibits three resonance regions. The first one, whose chemical shift peaks are 14.1 and 20.8 ppm, is related to the methyl groups substituted to the phenyl ring. Peaks ranging from 44.3 to 51.5 ppm correspond to the carbon atom of the piperazinium cation. The most shifted NMR lines, whose chemical shifts ranging from 117.6 to 150.6 ppm, are attributed to the aromatic carbon atoms. To assign NMR components to different carbon atoms, we have calculated the chemical shifts by means the ChemDraw Ultra 10.0 software. The carbon atoms are labeled as depicted in Figure 1. The obtained results are regrouped in Table IV. 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 (Figure 1).

TABLE IV Calculated (δ_{iso}) and Experimental (δ_{exp}) Chemical Shifts of the Organic Group Carbon Atoms in [1-[2,3-CH_3-C_6H_3]$C_4H_{10}N_2$]H_2PO_4

Carbon atoms	C1 and C2	C3 and C4	C5	C6	C7
δ_{iso} (ppm)	48.4	49.5	147.2	120.7	137.7
δ Corrected*	49.2	50.3	148.0	121.5	138.5
δ_{exp} (ppm)	44.3 and 45.9	48.5 and 51.5	150.6	126.7	139.1
Carbon atoms	C8	C9	C10	C11	C12
δ_{iso} (ppm)	119.8	126.5	107.0	13.3	18.8
δ Corrected*	120.6	127.3	107.8	14.1	19.6
δ_{exp} (ppm)	125.7	130.7	117.5	14.1	20.8

*Theoretical chemical shift determined by calibrating the peak of the C11 methyl carbon atom.

IR Spectroscopy Investigation

The IR spectrum of crystalline [1(2,3-$(CH_3)_2$-C_6H_3)$C_4H_{10}N_2$]H_2PO_4 is shown in Figure 6. The most representative and characteristic vibrational modes of this compound can be compared to those of similar monophosphates.[25] Some aspects of the performed assignments are briefly commented, as follows.

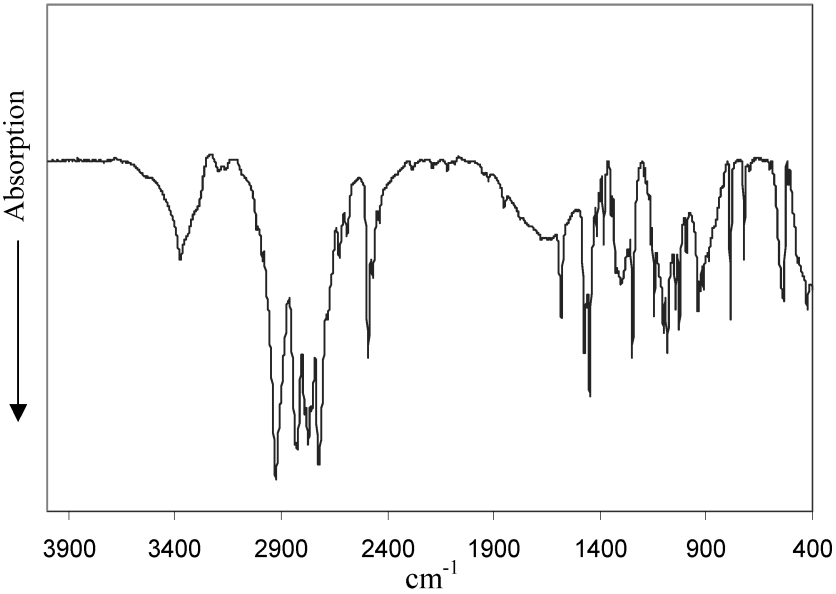

FIGURE 6 IR absorption spectrum of [1-(2,3-$(CH_3)_2$-C_6H_3)$C_4H_{10}N_2$]H_2PO_4.

- The high-frequency region, between 3500–2800 cm^{-1} corresponds to the valence vibrations of C—H, N—H and O—H groups interconnected by a system of hydrogen bonds in the crystal.[26]
- Bands in the 1600–1200 cm^{-1} region correspond to the bending vibrations of N—H and O—H groups and to the valence vibrations of C=C and C—N groups.
- The observed bands at 1145 and 1099 cm^{-1} can be attributed to the stretching vibrations, asymmetric and symmetric, of the PO_2 atomic group, while those at 995 and 939 cm^{-1} correspond to the $P(OH)_2$ atomic group of $H_2PO_4^-$ anion.[27]
- The band at 1247 cm^{-1} corresponds to the in-plane bending vibration δ(P—O—H), while the out-of-plane bending vibration is observed at 786 cm^{-1}.[27]
- Bands at 543 and 426 cm^{-1} are attributed to out-of-plane bending vibrations $\gamma_{as}$and γ_s.[28,29]
- Supplementary frequencies in $\nu_s(PO_4)$ domain are attributed to out-of-plane bending vibration modes γ (C_{aryl}–H) and γ (C_{aryl}–C).[30]

Thermal Analysis

The curve corresponding to TGA analysis in open air is given in Figure 7. This curve shows a continuous weight loss in the range

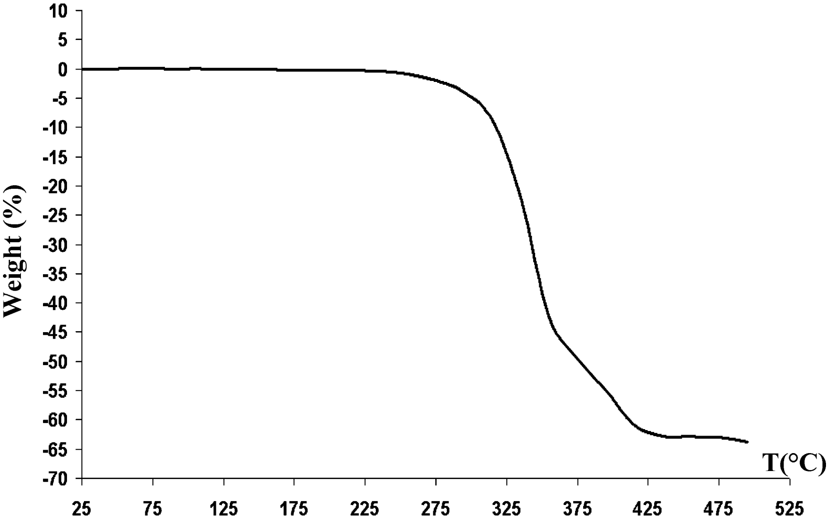

FIGURE 7 TGA curves of $[1\text{-}(2,3\text{-}(CH_3)_2\text{-}C_6H_3)C_4H_{10}N_2]H_2PO_4$ at rising temperature.

[225–500°C] characterized by an important weight loss. The corresponding phenomena could be interpreted by acomplete degradation of the organic molecule (weight loss: calculated 63.3%, experimental 63.8%). A viscous matter of polyphosphoric acids with a carbon black residue was obtained at the end of the TGA analysis.

EXPERIMENTAL

Chemical Preparation

The title compound was prepared according to the following chemical reaction:

$$[1-(2,3-(CH_3)2-C_6H_3)C_4H_9N_2]+H_3PO_4$$
$$\rightarrow [1-(2,3-(CH_3)2-C_6H_3)C_4H_{10}N_2]H_2PO_4$$

by mixing 1,7 mL (25 mmol) of concentrated phosphoric acid (Fluka, 85% wt, d = 1,7) to a solution of acetone and distilled water (V/V) containing 7.207 g (25 mmol) of 1-(2,3-dimethylphenyl)piperazine (Acros). The resulting solution was slowly evaporated at room temperature for several days until the formation of single crystals of $[1\text{-}(2,3\text{-}(CH_3)_2\text{-}C_6H_3)C_4H_{10}N_2]H_2PO_4$(m = 4.7 g, yield = 65%). The crystals obtained are stable for months under normal conditions of temperature and humidity. The compound chemical formula was determined from X-ray diffraction data.

Investigation Techniques

The title compound has been studied by various physico-chemical methods: X-ray diffraction, solid state NMR spectroscopy, infrared spectroscopy, thermal analysis, and electrical conductivity.

X-ray Diffraction

A single crystal was carefully selected under polarizing microscope in order to perform its structural analysis by X-ray diffraction. Intensity data were collected on an Enraf-Nonius MACH3 automated four-circle diffractometer using graphite monochromated Mo$K\overline{\alpha}$ radiation, $\lambda = 0.7107$ Å. The structure was solved by direct methods using SIR92 program[31] and refined by full matrix least-squares techniques based on F using teXsan.[32] The drawings were made with Diamond.[33] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms position were located by difference-Fourier synthesis and not refined. Crystal data and experimental parameters used for the intensity data collection are summarised in Table V.

TABLE V Crystal Data, Experimental Parameters Used for the Intensity Data Collection, Strategy, and Final Results of the Structure Determination.

I -Crystal data	
Empirical formula	$[1\text{-}(2,3\text{-}CH_3\text{-}C_6H_3)C_4H_{10}N_2]H_2PO_4$
Formula weight	288.28
Crystal system	monoclinic
Space group	$P2_1/n$
a	7.545(2) Å
b	26.315(4) Å
c	7.798(6) Å
β	115.01(4)°
Z	4
V	1403.0(1) Å^3
$\rho_{cal.}$	1.365 g cm^{-3}
F (000)	616
μ(Mo Kα)	2.081 cm^{-1}
Crystal sizes (mm)	0.40 × 0.35 × 0.25
Index ranges: ±h , k , l	($h_{max} = 8$, $k_{max} = 31$, $l_{max} = 9$)
Collected reflections	4498
Independent reflections	2537
Unique reflections included	1981($I > 3\sigma(I)$)
R_{int}	0.01
Refined parameters	172
R($I > 3\sigma(I)$)	0.046
R_w	0.063
Goodness of fit	1.860

Crystallographic Data (CIF) for the structure reported in this article have been deposited in to the Cambridge Crystallographic Data Center as supplementary publication No 632649. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB 12EZ, UK (Fax: +44(1223)336-033; e-mail: deposit@ccdc.cam.ac. uk).

Physical Measurements

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 probehead 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.

Infrared spectroscopy. Spectra were recorded in the range 4000–400 cm^{-1} with a "Perkin-Elmer FTIR-1000" spectrophotometer using a sample dispersed in a spectroscopically pure KBr pellet.

Thermal behavior. Thermal analysis was performed using the "multimodule 92 Setaram" analyzer operating from room temperature up to 500°C at an average heating rate of 5°C/min.

CONCLUSION

$[1(2,3\text{-}(CH_3)_2\text{-}C_6H_3)C_4H_{10}N_2]H_2PO_4$ was prepared as single crystals at r.t. and characterized by various physico-chemical methods. On the structural level, the atomic arrangement of the title compound can be described by inorganic layers including the $H_2PO_4^-$ anchoring the organic entities. The number of Solid-state ^{13}C and ^{31}P MAS NMR components is in agreement with the one of crystallographically independent sites. Upon heating, this monophosphate was stable until 225°C. After heating at 500°C, a viscous matter of polyphosphoric acids with a carbon black residue was obtained.

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