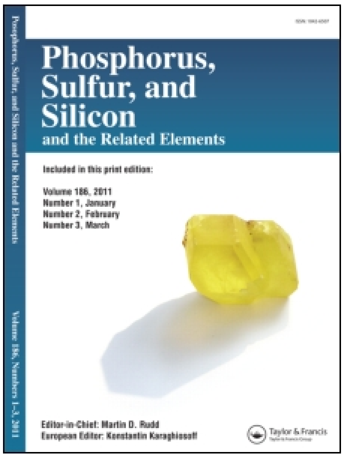

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Synthesis and Crystal Structure of a New Adduct 4-Benzyl Piperidinium Dihydrogenphosphate Phosphoric Acid $[C_{12}H_{16}NH_2]_2\,(H_2PO_4)_2\,H_3PO_4$

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Synthesis and Crystal Structure of a New Adduct 4-Benzyl Piperidinium Dihydrogenphosphate Phosphoric Acid $[C_{12}H_{16}NH_2]_2$ $(H_2PO_4)_2$ H_3PO_4

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A new adduct 4-benzyl piperidinium dihydrogenphosphate monophosphoric acid $[C_{12}H_{16}NH_2]_2(H_2PO_4)_2H_3PO_4$, *has been prepared and analyzed by X-ray diffraction. This adduct compound cristallizes in the monoclinic system, with the acentric space group* $P2_1$ *and the following unit-cell parameters:* $a = 13.103(3)$, $b = 8.737(4)$, $c = 13.620(3)$ *Å,* $\beta = 92.38(2)°$, $Z = 2$, *and* $V = 1557.8(7)$ $Å^3$. *The crystal structure has been solved and refined to* $R = 0.059$ *and* $R_{(w)} = 0.069$ *using 3306 independent reflections. Its structure can be described as inorganic layers of* H_3PO_4 *and* H_2 PO_4^- *entities separated by organic molecules. In this atomic arrangement, H-bonds between the different species play an important role in the tridimensionnel network cohesion. Solid-state*^{13}C *and* ^{31} *P MAS NMR spectroscopies are in agreement with the X-ray structure.* Ab initio *calculations allow the attribution of phosphorus and carbon signals to the independent crystallographic sites and to the various atoms of the organic groups.*

Keywords Hydrogen bonds; IR spectroscopy; layered compounds; NMR spectroscopy; X-ray diffraction

INTRODUCTION

A new class of noncentrosymmetric crystals for quadratic nonlinear optics has recently been developed through a crystal engineering route,

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Address correspondence to Mohamed Rzaigui, Laboratoire de Chimie des Matériaux, Faculté des Sciences de Bizerte, Zarzouna, Bizerte Tunisie, 7021, France. E-mail: Mohamed.Rzaigui@fsb.rnu.tn which combines the high cohesion of inorganic host-matrices with the enhanced polarizablity of organic guest-chromophores.[1] In these compounds, the organic cations are anchored onto the host-matrices through hydrogen bonds, inducing a higher packing cohesion than that observed in NLO organic crystals.

In this work, we report the synthesis, crystal structure, and NMR investigation of a new hybrid organic–inorganic adduct compound, 4-benzyl piperidinium dihydrogenomonophosphate monophosphoric acid, $[C_{12}H_{16}NH_2]_2(H_2PO_4)_2H_3PO_4$. In the phosphate area, adduct compounds are very rare[2,3] and they are in most cases accidentally prepared.

RESULTS AND DISCUSSION

Crystal Structure

Table I lists the experimental parameters used for data collection and determination of the structure. The final atomic coordinates of all non-hydrogen atoms of the title compound and their equivalent temperature

TABLE I Crystal Data and Experimental Parameters Used for the Intensity Data Collection. Procedure and Final Results of the Structure Determination

Empirical Formula	$C_{24}H_{43}N_2O_{12}P_3$
Formula weight	644.53
Crystal system	Monoclinic
Space group	$P2_1$
a	13.1035(3) (Å)
b	8.737(4) (Å)
c	13.620(3) (Å)
β	92.38(2)°
Z	2
V	1557.8(7) (Å^3)
$\rho_{cal.}$	1.372 (g. cm^{-3})
F(000)	682
$\mu(AgK_\alpha)$	0.137 (cm^{-1})
Crystal size (mm)	0.7 × 0.4 × 0.3
Index ranges: ± h, k, l	$h_{max.} = 19$, $k_{max.} = 13$, $l_{max.} = 20$
Reflexions collected	6089
Independent reflexions	5922
R_{int}	0.0223
Refined parameters	369
R [$I > 1.75\ \sigma(I)$]	0.059
$R_{(w)}$	0.069
Goodness of fit	1.240

factors are given in Tables II and III. Those of hydrogen atoms were also determined too but not given to shorten the table.

Structural determination shows that the title compound crystallizes in the monoclinic system with the noncentrosymmetric space group $P2_1$, which is confirmed by a positive second harmonic-generation powder test observed on a sample illuminated by a YAG Nd^{3+} laser radiation at 1.06 μm.

In this structure, there are three crystallographically independent PO_4 tetrahedra. The aggregation of two $H_2PO_4^-$ dihydrogenomonophosphate anions with one H_3 PO_4 molecule gives a repetitive $(H_7P_3O_{12})^{2-}$ unit. This latter is connected to its four $(H_7P_3O_{12})^{2-}$ neighbors through strong hydrogen bonds (O—H···O) (see Table IV), as to build an inorganic layer parallel to the (a,b) planes at z = ½, between which the organic molecules are located (Figure 1).

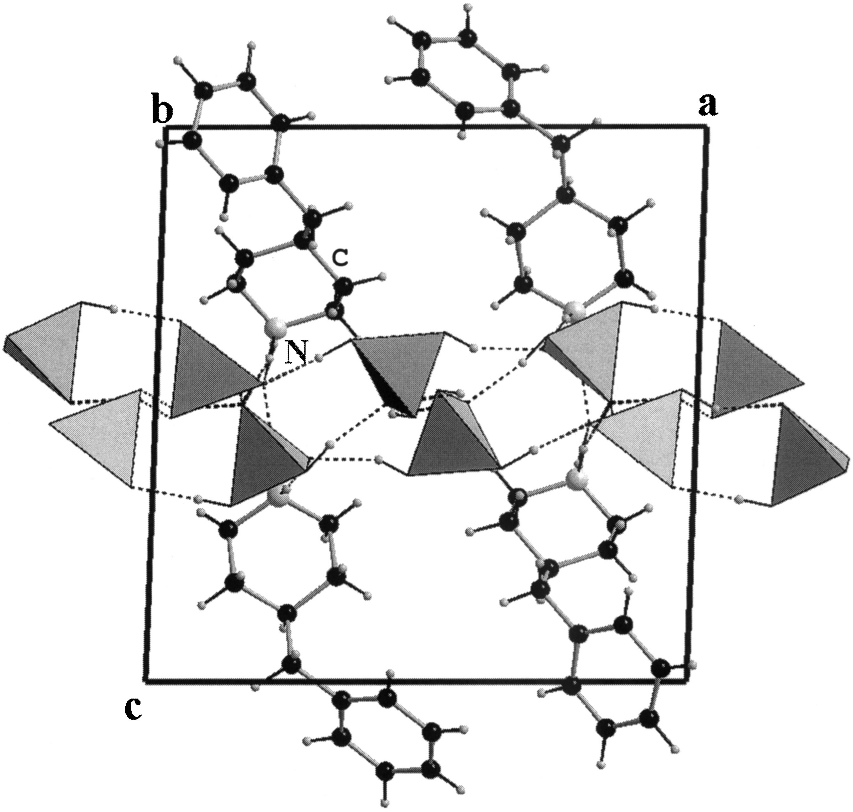


FIGURE 1 Projection of the structure of $[C_{12}H_{16}NH_2]_2(H_2PO_4)_2H_3PO_4$ along the *b* axis. A polyhedral representation is used for PO_4.

TABLE II Final Atomic Coordinates and $B_{eq.}$ ($Å^2$) for the Nonhydrogen Atoms. Estimated Standard Deviations are Given in Parentheses

Atoms	x(σ)	y(σ)	z(σ)	Beq.
P(1)	−0.55298(8)	0.20	0.44725(9)	2.69(2)
P(2)	0.09317(8)	0.2704(2)	0.43215(9)	2.96(2)
P(3)	−0.21710(8)	0.3509(2)	0.40122(9)	3.09(3)
O(1)	−0.4703(2)	0.1769(5)	0.3715(2)	4.00(8)
O(2)	−0.5200(4)	0.3129(5)	0.5250(3)	6.27(12)
O(3)	−0.6438(3)	0.2529(6)	0.3840(3)	6.15(11)
O(4)	−0.5756(3)	0.0538(4)	0.5010(3)	4.64(9)
O(5)	0.0289(2)	0.2664(5)	0.5260(2)	4.58(8)
O(6)	0.1024(3)	0.1023(5)	0.3964(3)	4.95(9)
O(7)	0.1962(2)	0.3351(5)	0.4644(3)	4.25(8)
O(8)	0.0404(2)	0.3582(5)	0.3507(2)	3.80(7)
O(9)	−0.1451(2)	0.3384(6)	0.3163(2)	5.30(10)
O(10)	−0.2802(3)	0.4993(5)	0.3781(3)	4.60(9)
O(11)	−0.1584(2)	0.3647(4)	0.4985(2)	3.16(7)
O(12)	−0.2857(2)	0.2132(5)	0.4017(3)	4.63(9)
N(1)	0.2313(4)	−0.5790(6)	−0.3349(3)	4.55(11)
N(2)	0.2152(4)	−0.3692(5)	0.3642(3)	4.11(10)
C(1)	0.1419(4)	−0.5970(8)	−0.2740(4)	5.05(14)
C(2)	0.1568(4)	−0.5102(8)	−0.1791(4)	4.77(14)
C(3)	0.2556(4)	−0.5531(6)	−0.1231(3)	3.36(10)
C(4)	0.3443(4)	−0.5396(6)	−0.1900(4)	3.81(11)
C(5)	0.3273(4)	−0.6303(8)	−0.2838(3)	4.35(12)
C(6)	0.2674(5)	−0.4521(7)	−0.0314(4)	4.73(14)
C(7)	0.3626(4)	−0.4825(6)	0.0330(3)	3.50(11)
C(8)	0.3645(4)	−0.6022(7)	0.0988(4)	4.16(12)
C(9)	0.4483(5)	−0.6295(8)	0.1605(4)	5.14(14)
C(10)	0.5330(5)	−0.5383(10)	0.1566(5)	5.92(18)
C(11)	0.5324(5)	−0.4206(10)	0.0905(6)	6.44(19)
C(12)	0.4473(5)	−0.3913(7)	0.0292(4)	4.97(15)
C(13)	0.3232(5)	−0.3533(8)	0.3318(4)	5.08(15)
C(14)	0.3381(4)	−0.1958(8)	0.2881(4)	5.20(15)
C(15)	0.2603(4)	−0.1627(7)	0.2041(3)	3.78(11)
C(16)	0.1533(4)	−0.1873(6)	0.2374(4)	3.72(11)
C(17)	0.1393(4)	−0.3433(7)	0.2824(4)	4.46(13)
C(18)	0.2755(4)	0.0003(7)	0.1664(4)	4.86(13)
C(19)	0.2016(4)	0.0470(6)	0.0859(4)	4.07(12)
C(20)	0.1199(6)	0.1418(8)	0.1020(6)	6.53(19)
C(21)	0.0487(6)	0.1776(13)	0.0235(10)	9.1(3)
C(22)	0.0664(8)	0.1126(14)	−0.0659(9)	8.8(3)
C(23)	0.1446(9)	0.0212(11)	−0.0830(6)	8.9(3)
C(24)	0.2108(5)	−0.0104(8)	−0.0071(5)	5.71(17)

TABLE III Main Interatomic Distances (Å) and Bond Angles (°) in $[C_{12}H_{16}NH_2]_2(H_2PO_4)_2H_3PO_4$. Estimated Standard Deviations Are Given in Parentheses

Tetrahedron P(1)O_4				
P(1)	O(1)	O(2)	O(3)	O(4)
O(1)	1.535(4)	110.5(2)	102.2(2)	113.9(3)
O(2)	2.513(6)	1.522(5)	111.4(3)	106.1(3)
O(3)	2.381(5)	2.516(7)	1.524(4)	112.8(3)
O(4)	2.524(6)	2.482(6)	2.498(7)	1.476(4)
Tetrahedron P(2)O_4				
P(2)	O(5)	O(6)	O(7)	O(8)
O(5)	1.560(4)	106.7(3)	106.1(2)	111.8(2)
O(6)	2.498(6)	1.554(4)	111.4(3)	107.0(2)
O(7)	2.455(5)	2.533(6)	1.512(4)	113.8(2)
O(8)	2.530(5)	2.450(6)	2.518(5)	1.494(4)
Tetrahedron P(3)O_4				
P(3)	O(9)	O(10)	O(11)	O(12)
O(9)	1.527(4)	104.2(3)	111.27(1)	109.5(3)
O(10)	2.438(6)	1.563(6)	110.9(3)	110.7(2)
O(11)	2.506(5)	2.530(5)	1.509(3)	110.1(2)
O(12)	2.474(6)	2.521(6)	2.467(5)	1.501(4)
O(1)-H(1)	0.80	H(1)-O(1P(1)	108.9	
O(2)-H(2)	0.85	H(2)-O(2)-P(1)	105.4	
O(3)-H(3)	0.92	H(3)-O(3)-P(1)	109.4	
O(5)-H(4)	0.95	H(4)-O(5)-P(2)	94.3	
O(6)-H(5)	1.00	H(5)-O(6)-P(2)	117.7	
O(9)-H(6)	0.81	H(6)-O(9)-P(3)	118.5	
O(10)-H(7)	0.91	H(7)-O(10)-P(3)	111.6	
$(C_{12}H_{18}N(1))^+$group				
N(1)-C(1)	1.474(8)	N(1)-C(1)-C(2)	112.6(2)	
N(1)-C(5)	1.486(8)	C(1)-C(2)-C(3)	112.7(5)	
C(1)-C(2)	1.497(9)	C(2)-C(3)-C(4)	109.8(4)	
C(2)-C(3)	1.525(8)	C(3)-C(4)-C(5)	112.3(5)	
C(3)-C(4)	1.511(8)	C(4)-C(5)-N(1)	109.4(5)	
C(4)-C(5)	1.514(8)	C(5)-N(1)-C(1)	112.5(4)	
C(3)-C(6)	1.528(8)	C(2)-C(3)-C(6)	108.8(5)	
C(6)-C(7)	1.518(8)	C(4)-C(3)-C(6)	113.1(5)	
C(7)-C(12)	1.372(8)	C(3)-C(6)-C(7)	115.0(5)	
C(7)-C(8)	1.375(8)	C(6)-C(7)-C(12)	121.6(6)	
C(8)-C(9)	1.379(8)	C(6)-C(7)-C(8)	120.1(5)	
C(9)-C(10)	1.374(11)	C(7)-C(8)-C(9)	121.5(6)	
C(10)-C(11)	1.367(12)	C(8)-C(9)-C(10)	120.2(7)	
C(11)-C(12)	1.386(10)	C(9)-C(10)-C(11)	118.7(7)	
		C(11)-C(12)-C(7)	120.2(7)	
		C(10)-C(11)-C(12)	121.1(7)	
$(C_{12}H_{18}N(2))^+$group				
N(2)-C(13)	1.506(8)	N(2)-C(13)-C(14)	109.7(5)	
N(2)-C(17)	1.477(7)	C(13)-C(14)-C(15)	111.9(6)	

(Continued on next page)

TABLE III Main Interatomic Distances (Å) and Bond Angles (°) in $[C_{12}H_{16}NH_2]_2(H_2PO_4)_2H_3PO_4$. Estimated Standard Deviations Are Given in Parentheses*(Continued)*

C(13)-C(14)	1.519(10)	C(14)-C(15)-C(18)	109.6(5)
C(14)-C(15)	1.529(8)	C(14)-C(15)-C(16)	110.4(5)
C(15)-C(16)	1.509(8)	C(15)-C(16)-C(17)	112.4(5)
C(16)-C(17)	1.508(8)	C(16)-C(17)-N(2)	110.8(5)
C(18)-C(19)	1.496(9)	C(17)-N(2)-C(13)	112.1(5)
C(19)-C(24)	1.375(9)	C(15)-C(18)-C(19)	114.4(5)
C(19)-C(20)	1.372(10)	C(18)-C(19)-C(24)	120.0(6)
C(20)-C(21)	1.417(14)	C(18)-C(19)-C(20)	122.2(7)
C(21)-C(22)	1.384(16)	C(19)-C(20)-C(21)	120.1(9)
C(22)-C(23)	1.323(15)	C(20)-C(21)-C(22)	116.5(9)
C(23)-C(24)	1.344(12)	C(21)-C(22)-C(23)	124.3(10)
		C(22)-C(23)-C(24)	117.7(10)
		C(23)-C(24)-C(19)	123.7(9)
		C(24)-C(19)-C(20)	117.7(7)

In this layered organization of mixed phosphate entities of P(1)O_4, P(2)O_4, and P(3)O_4 (Figure 2), it is noteworthy that the O. . . O distances involved in hydrogen bonds [2.458(5) to 2.612(5) Å] have the same order of magnitude as the O$\cdots$O distances in the $H_2PO_4^-$or H_3PO_4 tetrahedra [2.381(5) to 2.533(6) Å], so one could consider the $(H_7P_3O_{12}{}^{2-})_n$ subnetwork as a polyanion. The detailed geometry of the H_2P(1)O_4^-, H_2P(2)O_4^-, and H_3P(3)O_4 entities show that the P—O distances significantly are shorter [1.476(4) to 1.512(4) Å] than the P—OH distances [1.522(5) to 1.563(6) Å] (Table IV), which is in accordance with the data relative to the protonated oxoanions.[4]

TABLE IV Hydrogen-Bond Scheme in $[C_{12}H_{16}NH_2]_2(H_2PO_4)_2H_3PO_4$

D—H···A	D—H(Å)	H···A(Å)	D···A(Å)	D—H···A(°)
O(1)-H(1)···O(12)	0.80	1.72	2.458(5)	151.2
O(2)-H(2)···O(4)	1.01	1.52	2.499(6)	160.3
O(3)-H(3)···O(7)	0.92	1.72	2.509(6)	141.1
O(5)-H(4)···O(11)	0.95	1.87	2.613(5)	132.4
O(6)-H(5)···O(11)	1.00	1.70	2.605(6)	148.3
O(9)-H(6)···O(8)	0.81	1.65	2.462(5)	176.5
O(10)-H(7)···O(4)	0.91	1.70	2.598(6)	168.7
N(1)-H(8)···O(7)	0.86	2.02	2.849(6)	162.5
N(1)-H(9)···O(12)	0.88	1.95	2.813(7)	167.3
N(2)-H(26)···O(7)	0.95	2.00	2.939(7)	171.6
N(2)-H(27)···O(11)	1.00	1.91	2.890(6)	165.4

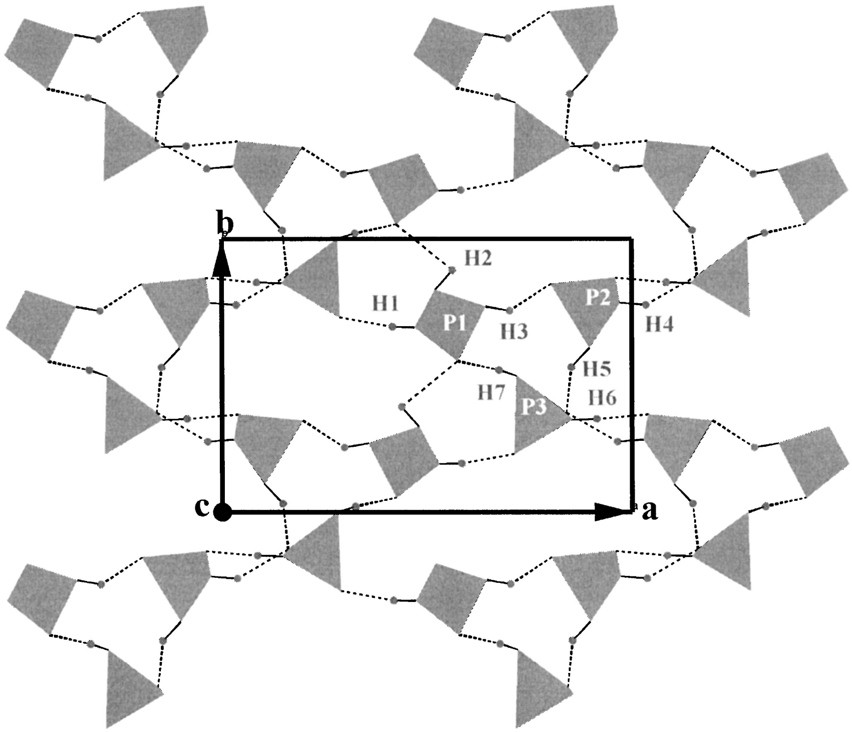


FIGURE 2 Projection along the *c* axis of the inorganic layer structure. Organic radicals are omitted for figure clarity.

In this atomic arrangement, there are two crystallographically independent 4-benzylpiperidinium cations per two dihydrogenomonophosphate $H_2PO_4^-$ anions to perform the electric neutrality of the total complex. These organic groups are anchored onto successive inorganic layers through a hydrogen bond involving the hydrogen atoms of the NH_2 groups with N(H)···O distances varying between 1.91 and 2.02 Å. The $C_{12}H_{16}NH_2$ organic molecule, which contains relocated and asymmetric π-bonds, is a highly polarizable entity in which transparency can be controlled. This property favors the formation of noncentrosymmetric materials as found with benzylamine $C_6H_5CH_2NH_2$, paraphenolamine1.4-$HOC_6H_4NH_2$ and 2,5-$(CH_3)_2C_6H_3NH_2$, which react with H_3PO_4 to form $(C_6H_5CH_2NH_3)H_2PO_4$,[5] [1.4-HOC_6H_4 NH_3]H_2PO_4,[6] and [2,5-$(CH_3)_2C_6H_3NH_3$]H_2PO_4 [7] salts for a second harmonic generation.

The atoms C_7, C_8, C_9, C_{10}, C $_{11}$, and C_{12} of the phenyl ring of the title compound have a good coplanarity and they form a conjugated plane.

The bond lengths of C_7–C_8, C_7–C_{12}, C_8–C_9, C_9–C_{10}, C_{10}–C_{11}, and C_{11}–C_{12} are 1.377(8), 1.369(8), 1.375(8), 1.370(10), 1.367(12), and 1.390(10), respectively, which are between a single bond and a double bond and agree with that in benzene.[6] Furthermore, the distances C_1–C_2, C_2–C_3, C_3–C_4, C_4–C_5, C_3–C_6, and C_6–C_7 are 1.503(4), 1.522(8), 1.511(8), 1.512(8), 1.531(8), and 1.518(4), respectively, clearly indicating six single bonds.

NMR Results

Figure 3 shows the proton-decoupled ^{31}P MAS NMR spectrum of crystalline monophosphate $[C_{12}H_{16}NH_2]_2$ $(H_2PO_4)_2H_3PO_4$. This spectrum is in good agreement with the X-ray structure. Indeed, it exhibits three resonances at −1.8, 1.1, and 2.6 ppm, corresponding to three crystallographically independent phosphorus atoms. These chemical-shift values agree well with those of monophosphates (between −10

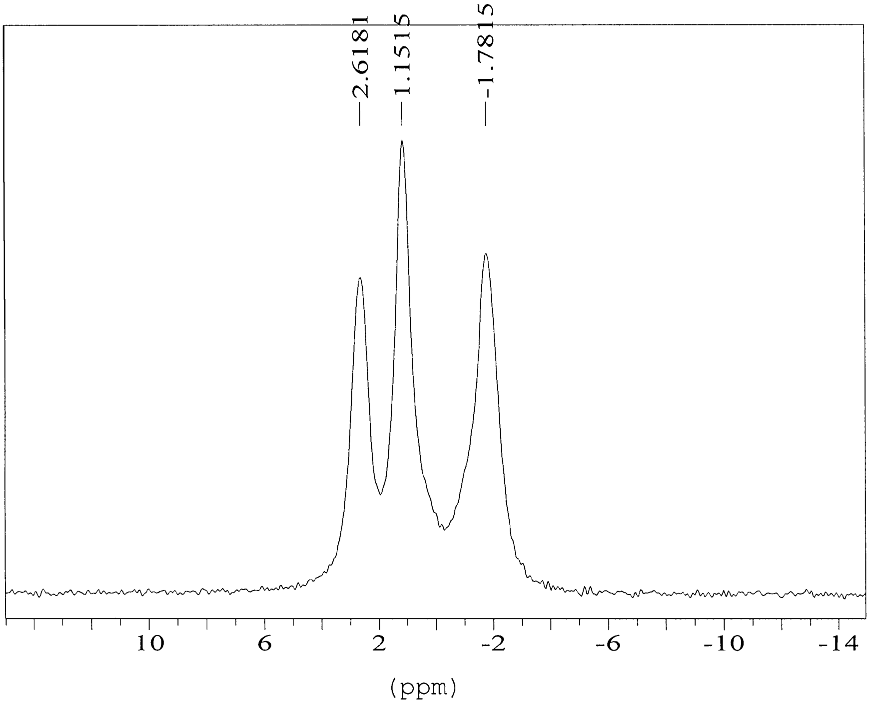


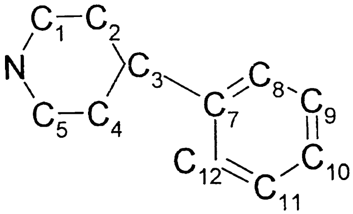
FIGURE 3 ^{31}P MAS-NMR spectrum of crystalline $[C_{12}H_{16}NH_2]_2(H_2PO_4)_2$ H_3PO_4.

and +5 ppm, depending on the compound.[8–15] The attribution of the NMR components to the phosphorus atoms P(1), P(2), and P(3) was done by using *ab initio* calculations. For this purpose, the isotropic chemical shifts of the three phosphorus atoms P(1), P(2), and P(3) in the three PO_4 tetrahedra were calculated. These δ_{iso} values are absolute chemical shifts while the experimental ones correspond to the difference $\delta_{exp} = \delta_{ref} - \delta_{iso}$, where δ_{ref} is the isotropic chemical shift of the reference, typically H_3PO_4 at 85%. We took as a reference the $[PO_4]^{3-}$ tetrahedra after the optimization at the HF/6-31+G* level and calculated, the chemical shifts of the three phosphorous atoms in the structure at the same level of theory. The results are given in Equation (1):

$$\delta_{iso}(P_1) = -20.5\ \text{ppm},\ \delta_{iso}(P_2) = -16.1\ \text{ppm},\ \delta_{iso}(P_3) = -17.5\ \text{ppm}. \qquad (1)$$

It can be seen that these values are relatively different from the experimental ones but this can be due to a bad choice of the reference. If we attribute the signals at −1.8, 2.6, and 1.1 ppm to P_1, P_2, and P_3 respectively, a proof of this explanation is clearly seen, as the difference between the experimental and theoretical chemical shifts is the same in the three cases.

Figure 4 shows the aromatic region of the ^{13}C CP-MAS NMR spectrum of the title compound. The carbon atoms of the organic moiety are labelled as depicted below (Scheme 1):



SCHEME 1

The deconvolution of this spectrum shows that it corresponds to the sum of eight peaks. Even if the attribution of most of these peaks is difficult, the two peaks at ca. 140 ppm can be attributed unambiguously to the C_7 carbon atom, as shown by the theoretical calculations. The presence of two peaks for this carbon atom proves the existence of two independent organic molecules in the asymmetric unit cell as found by X-ray study. A tentative attribution of the other resonances (based on theoretical calculations) is given in Table V.

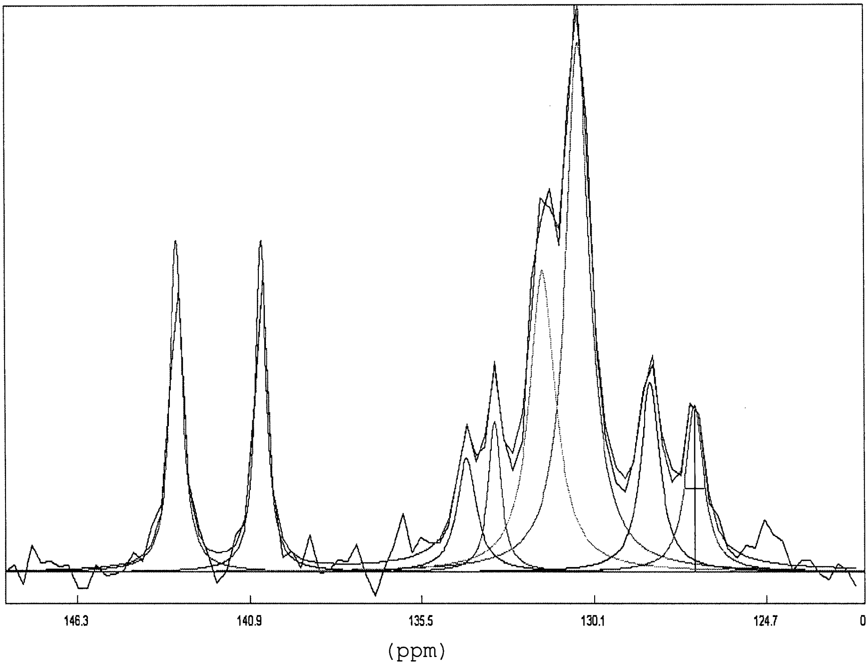


FIGURE 4 ^{13}C CP-MAS-NMR spectrum of crystalline $[C_{12}H_{16}NH_2]_2(H_2PO_4)_2H_3PO_4$.

IR Spectroscopy

The infrared absorption spectrum of the title compound is shown in Figure 5. It exhibits the following:

- broad bands between 3450 and 2300 cm^{-1} and 1650 and 1400 cm^{-1} corresponding to stretching vibrations of 4-benzylpiperidinium (ν NH_2^+, ν C—H) and ν(O—H) of P—OH groups.[16] The absorption band at 1247 cm^{-1} corresponds to the stretching vibration of the C—N bond.
- various valence and bending vibration bands whose number and positions, between 1200 and 350 cm^{-1}, are both characteristic of a monophosphate.[17] The PO_4 tetrahedra gives in IR two stretching

TABLE V

Carbone	C_7	C_8	C_9	C_{10}
δ (ppm)	143.2 and 140.6	128.3 and 133.2	134.1 and 133.2	131.7 and 130.6

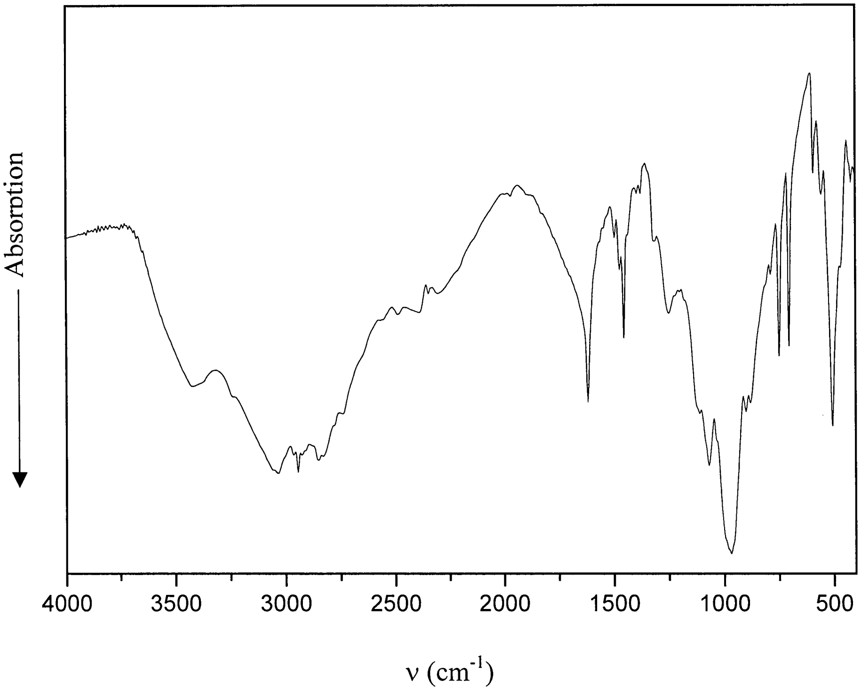


FIGURE 5 IR spectrum of $[C_{12}H_{16}NH_2]_2(H_2PO_4)_2H_3PO_4$ in a KBr pellet.

vibrations, ν_s and ν_{as}, respectively symmetric and asymmetric bands, which are observed in the 1200–1000 cm^{-1} and 1000–800 cm^{-1} ranges. The two bending vibrations δ_s and δ_{as} of the PO_4 tetrahedra are located in the 750–500 cm^{-1} and 500–350 cm^{-1} ranges.

EXPERIMENTAL PART

Synthesis of $[C_{12}H_{16}NH_2]_2(H_2\ PO_4)_2H_3\ PO_4$

Colorless, parallelipedic crystals of 4-benzylpiperidinuim dihydrogenphosphate phosphoric acid were prepared from an aqueous solution containing a stoiechiometric mixture of 4-benzylpiperidine (98%, d = 0.99) and monophosphoric acid H_3PO_4 (85%, d = 1.7) in the molar ratio of 2:3. This mixture is stirred for 10 min and then it slowly evaporated at room temperature. Crystals with suitable dimensions appear after some days.

Schematically the accomplished reaction is:

$$3\,(H_3PO_4) + 2\,(C_{12}H_{16}NH) \longrightarrow (C_{12}H_{16}NH_2)_2(H_2PO_4)_2H_3PO_4. \qquad (2)$$

These crystals are stable, for a long time, in normal conditions of temperature and humidity.

Investigation Techniques

X- Ray Diffraction

A single crystal was used for X-ray measurements, with a MACH 3 Enraf Nonius diffractometer working at 296 K and the wavelength at $K\alpha(Ag) = 0.5608$ Å. The structure was solved by direct methods using the SIR92[19] program and refined by full matrix least-squares techniques based on F using teXsan.[18] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms positions were located by difference-Fourier synthesis and not refined. The details of data collection, refinement, and crystallographic data are summarized in Table I.

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data center as supplementary publication No. 260052. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB12EZ, UK. E-mail: deposit@ccdc.cam.ac.uk

Physical Measurements

All NMR spectra were recorded on a Bruker DSX-500 spectrometer operating at 95.81 MHz for ^{13}C and 202.51 MHz for ^{31}P, with a classical 4 mm probe head allowing spinning rates up to 10 kHz. ^{13}C NMR chemical shifts are given relative to tetramethylsilane and ^{31}P ones are given relative to 85% H_3PO_4 (external references, precision 0.5 ppm). Phosphorus spectra were recorded under classical conditions, while the carbone spectra were recorded by use of cross-polarization from protons (contact time 5 ms).

The IR spectrum was recorded in the range 4000–400 cm^{-1} with a Perkin-Elmer Spectrum 1000 spectrophotometer using samples dispersed in spectroscopically pure KBr pellets.

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