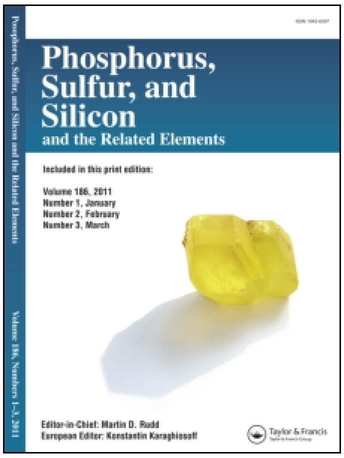

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Synthesis, Crystal Structure, and NMR Spectroscopy of a New *P*-Phenylenediamonium Diphosphate [*p*-$NH_3C_6H_4NH_3$]$H_2P_2O_7$

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Synthesis, Crystal Structure, and NMR Spectroscopy of a New *P*-Phenylenediamonium Diphosphate [*p*-$NH_3C_6H_4NH_3$]$H_2P_2O_7$

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Crystal growth and characterization by X-ray diffraction and NMR spectroscopy of a new p-phenylenediamonium diphosphate [p-$NH_3C_6H_4NH_3$]$H_2P_2O_7$ are reported. This compound crystallizes in a triclinic unit cell ***P1*** *with the parameters* $a = 7.130(3)$, $b = 9.047(3)$, $c = 9.350(2)\,\text{Å}$, $\alpha = 133.44(2)^\circ$, $\beta = 95.02(2)^\circ$, $\gamma = 107.11(4)^\circ$, $Z = 2$, $V = 514.3(15)\,\text{Å}^3$, *and* $D_x = 1.848\ \text{g.cm}^{-3}$. *The crystal structure has been solved and refined to* $R = 0.0273$, *using 3678 independent reflections. The atomic arrangement is build up by infinite ribbons of* $[H_2P_2O_7]^{2-}$ *anions, extending along the a-direction at* $y = 1/2$. *Between these ribbons are located the p-phenylenediammonium entities, which form hydrogen bonds N—H···O with some external oxygen atoms of phosphoric groups. Crystallographic results are correlated with that of the solid state* ^{13}C *and* ^{31}P *MAS NMR spectroscopy.*

Keywords Hydrogen bonds; NMR spectroscopy; ribbons; X-ray diffraction

INTRODUCTION

In organic-cation diphosphates, the acidic diphosphate anions $[HP_2O_7]^{3-}$, $[H_2P_2O_7]^{2-}$, and $[H_3P_2O_7]^{-}$ exhibit a characteristic geometry so as to built infinite networks via hydrogen bonds with various geometries: ribbons, chains, layers, and a three-dimensional network. In

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the present investigation, we report the synthesis and crystal structure of a new organic-cation acidic diphosphate $[p\text{-}NH_3C_6H_4NH_3]H_2P_2O_7$. The characterization of this latter by ^{31}P and ^{13}C NMR spectroscopy is also reported.

RESULTS AND DISCUSSION

Crystal Structure

All data concerning the experimental parameters used for the structure determination as well as their final results are gathered in Table I. The final atomic coordinates of $[p\text{-}NH_3C_6H_4NH_3]H_2P_2O_7$ and their B_{eq} are reported in Table II. The asymmetric unit of the crystal structure, depicted in an Oak Ridge Thermal Ellipsoid Plot Program (ORTEP)[15] drawing (Figure 1), consists of two PO_4 tetrahedra and two halves of

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

Empirical Formula	$C_6H_{12}N_2P_2O_7$
Formula weight	286.12
Crystal system	triclinic
Space group	$P\bar{1}$
a	7.130(3) (Å)
b	9.047(3) (Å)
c	9.350(2) (Å)
α	133.44(2)
β	95.02(2)
γ	107.11 (4)
Z	2
V	514.3 (15) $Å^3$
ρcal.	1.848 (g. cm^{-3})
F(000)	296
μ (AgK_α)	0.239 (mm^{-1})
Crystal size [mm]	0.55 × 0.5 × 0.2
Index ranges: ± h, k, 1	$h_{max.} = 10$, $k_{max.} = 12$, $1_{max.} = 14$
Reflexions collected	3875
Independent reflexions	3678
R_{int}	0.0186
Refined parameters	154
R [$I > 3\sigma(I)$]	0.0273
$R_{(w)}$	0.038
Goodness of fit	1.390
Determination	direct method SIR 92[12]
Program used	teXsan[13]
Drawing made with	Diamond[14]

TABLE II The Final Atomic Coordinates and $B_{eq.}$ ($Å^2$) in $[p\text{-}NH_3C_6H_4NH_3]H_2P_2O_7$

Atoms	x(σ)	y(σ)	z(σ)	Beq.($Å^2$)
P(1)	0.55448(3)	0.17357(3)	0.85868(3)	1.087(4)
P(2)	0.15573(3)	0.20885(3)	0.87382(3)	1.138(4)
O(E11)	0.65841(12)	0.33527(10)	0.84441(10)	1.90(1)
O(E12)	0.50192(12)	0.01130(10)	0.70747(9)	2.047(13)
O(E13)	0.67700(11)	0.16410(11)	0.99963(9)	1.96(1)
O(L12)	0.35985(10)	0.18428(10)	0.92791(9)	1.619(13)
O(E21)	0.2217(1)	0.39291(10)	0.88367(10)	2.14(1)
O(E22)	0.05232(12)	0.08091(10)	0.70431(9)	1.995(13)
O(E23)	0.04584(10)	0.19583(10)	1.00095(9)	1.714(13)
N(1)	0.25709(13)	0.17208(10)	0.25294(10)	1.67(1)
N(2)	−0.19467(12)	0.21581(10)	0.55966(10)	1.465(13)
C(1)	0.38059(13)	0.34171(11)	0.38069(11)	1.35(1)
C(2)	0.3942(2)	0.36994(12)	0.53820(12)	1.64(2)
C(3)	0.5147(2)	0.53105(13)	0.65981(12)	1.71(2)
C(4)	−0.09416(13)	0.36227(11)	0.52853(10)	1.21(1)
C(5)	0.0095(2)	0.52231(12)	0.65727(11)	1.54(2)
C(6)	0.1062(2)	0.66211(12)	0.62806(11)	1.51(2)
H(1)	0.8091	0.1860	0.9972	2.911
H(2)	0.2691	0.4775	0.9813	3.800
H(3)	0.2033	0.1803	0.1686	2.909
H(4)	0.1649	0.1091	0.2876	2.073
H(5)	0.3271	0.1185	0.2243	3.372
H(6)	0.3285	0.2823	0.5647	2.186
H(7)	0.5229	0.5543	0.7704	2.976
H(8)	−0.2830	0.1322	0.4773	1.357
H(9)	−0.2499	0.2512	0.6358	3.278
H(10)	−0.1106	0.1722	0.5856	2.157
H(11)	0.0225	0.5336	0.7641	2.745
H(12)	0.1734	0.7757	0.7091	2.145

Estimated standard deviations are given in parentheses. $B_{eq} = 4/3\Sigma_i\Sigma_j \mathbf{a_i} \cdot \mathbf{a_j}\beta ij$.

organic cations. Atoms that formed these entities occupy the general positions in the unit cell.

The aggregation of two dihydrogenodiphosphates $[H_2P_2O_7]^{2-}$ anions gives a repetitive $[H_4P_4O_{14}]^{4-}$ unit. The latter is connected to its two neighbors through the strong hydrogen bonds O(E)-H(OE)···O(E) $d(O—O)_{moy}$ 2.569 Å and the weak hydrogen bonds N(1,2)-H(N)···O(E) $d(N—O)_{moy}$ 2.836 Å, to form infinite ribbons built by the $[H_2P_2O_7]^{2-}$ groups in the a direction at y = 1/2 (Figure 2). These rows are interconnected in a three-dimensional way through hydrogen bonds between the NH_3 groups of the p-phenylenediamonium cations and some oxygen atoms of the $[H_2P_2O_7]^{2-}$ groups (Figure 3). This row crosses the center

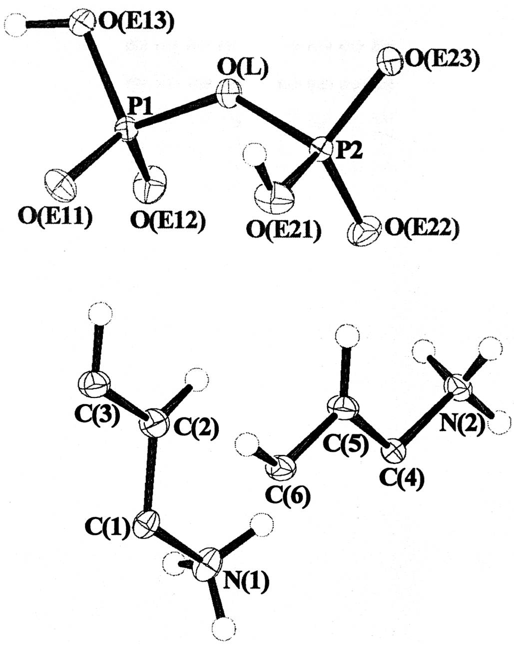


FIGURE 1 An ORTEP drawing of the asymmetric unit of the title compound, representing heaving atoms as 30% probability ellipsoids and H atoms as spheres of arbitrary radius.

of the unit cell parallel to the a direction with a period of two $[H_2P_2O_7]^{2-}$ units (Figure 2). The same kind of ribbon has previously been observed in $K_2H_2P_2O_7$,[1] $[NH_4]_2H_2P_2O_7$,[2] and $[NH_3\text{-}C_2H_4\text{-}OH]_2H_2P_2O_7$.[3]

In this structure, the $[H_2P_2O_7]^{2-}$ group has no internal symmetry, so it is built by two independent PO_4 tetrahedra, $P(1)O_4$ and $P(2)O_4$, while a majority of the known P_2O_7 in the bibliography have a twofold symmetry, such as $Cs_2H_2P_2O_7$,[4] $Ag_2H_2P_2O_7$,[5] $[NH_3(CH_2)_2NH_3]_2$ P_2O_7,[6] $[C_3H_{12}N_2]_2P_2O_7$,[7] $4H_2O$, $[m\text{-}CH_3C_6H_4NH_3]H_2P_2O_7$,[8] and $[2\text{-}C_2H_5C_6H_4NH_3]_2H_2P_2O_7$.[9]

The detailed geometry of $[H_2P_2O_7]^{2-}$ anion Table III shows three different types of P-O distances; the longest ones, 1.594(6) Å and 1.604(6) Å, correspond to the briding oxygen atom. The intermediate ones, 1.562(2) Å and 1.553(11) Å, correspond to the P—O bonding. The shortest ones spread between 1.490(3) Å and 1.504(2) Å, which correspond to the external oxygen atoms. The average values for the P—O distances and O—P—O angles are 1.536 Å and 109.27° for the $P(1)O_4$ tetrahedron and 1.537 Å and 109.35° for the $P(2)O_4$ tetrahedron. The P-P distance is 2.96(1) Å, and the P—O—P angle 135.7(2)°.

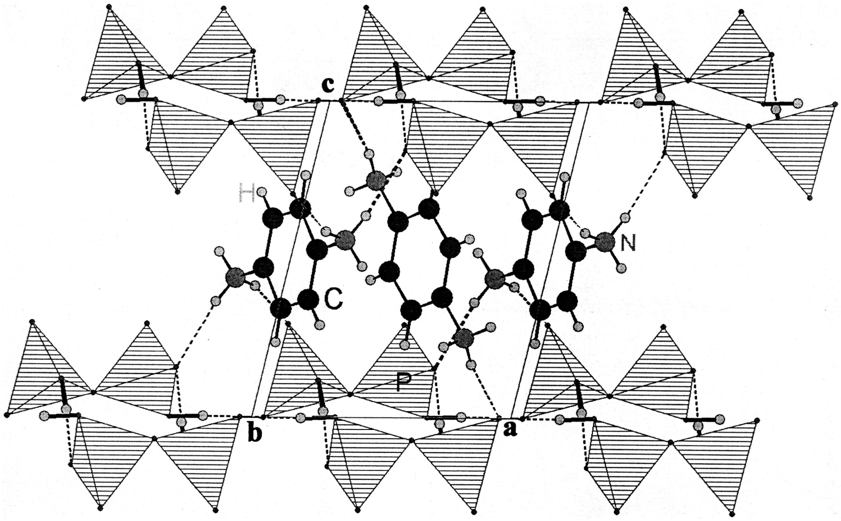


FIGURE 2 An atomic arrangement of [p-$NH_3C_6H_4NH_3$]$H_2P_2O_7$ in projection along the b-direction. The phosphoric anion is given in a polyhedral representation.

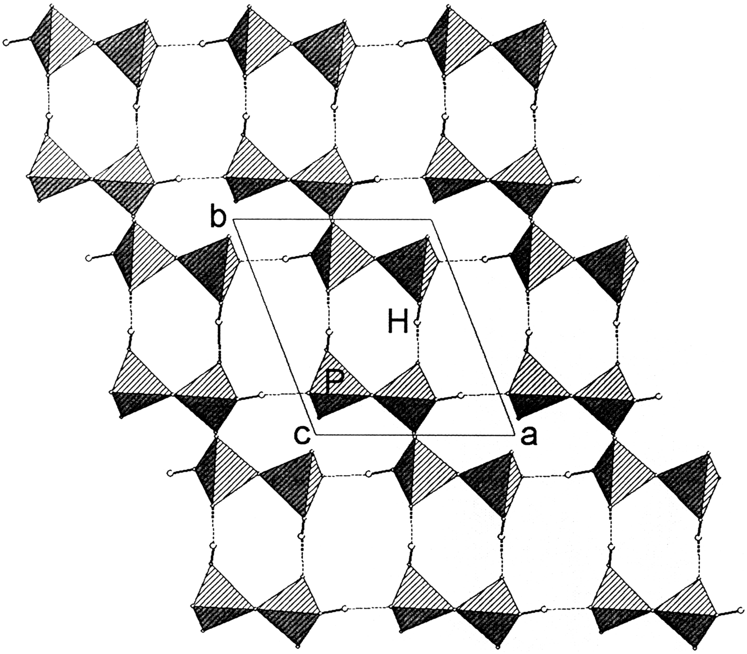


FIGURE 3 An atomic arrangement of [p-$NH_3C_6H_4NH_3$]$H_2P_2O_7$ in projection along the c-direction. The phosphoric anion is given in a polyhedral representation. Organic groups are not represented for figure clarity.

TABLE III The Main Interatomic Distances (Å) and Bond Angles (°) in the [p-$HN_3C_6H_4NH_3$]$H_2P_2O_7$ anion. Estimated Standard Deviations Are Given in Parentheses

		The P(1)O_4 Tetrahedron		
P(1)	O(E11)	O(E12)	O(E13)	O(L)
O(E11)	1,497(13)	2,513(2)	2,529(1)	2,537(7)
O(E12)	114,40(b)	1,492(11)	2,513(2)	2,541(4)
O(E13)	111,5(2)	110,71(6)	1,562(2)	2,381(10)
O(L)	110,27(11)	110,78(13)	98,0(2)	1,594(6)
		The P(2)O_4 Tetrahedron		
P(2)	O(E21)	O(E22)	O(E23)	O(L)
O(E21)	1,553(11)	2,472(2)	2,537(2)	2,519(3)
O(E22)	108,49(6)	1,490(3)	2,555(9)	2,547(7)
O(E23)	112,16(6)	117,1(2)	1,504(2)	2,416(10)
O(L)	105,8(2)	110,60(10)	102,0(2)	1,604(6)
P(1)-P(2)	2,96(1)	P(1)-O(L)-P(2)	135,7(2)	
		P(1)-O(E13)-H(1)	112,3	
		P(2)-O(E21)-H(2)	114,9	
		The ($C_3H_6N(1)$)$^+$ Group		
N(1)-C(1)	1,456(2)	N(1)-C(1)-C(2)	119,27(11)	
C(1)-C(2)	1,380(2)	C(1)-C(2)-C(3)	119,16(11)	
C(2)-C(3)	1,389(2)	H(3)-N(1)-H(5)	106,7	
N(1)-H(3)	0,89	H(3)-N(1)-H(4)	113,3	
N(1)-H(4)	0,91	H(4)-N(1)-H(5)	104,3	
N(1)-H(5)	0,79			
		The ($C_3H_6N(2)$)$^+$ Group		
N(2)-C(4)	1,462(2)	N(2)-C(4)-C(5)	118,95(10)	
C(4)-C(5)	1,385(2)	C(4)-C(5)-C(6)	119,12(10)	
C(5)-C(6)	1,394(2)	H(8)-N(2)-H(9)	110,0	
N(2)-H(8)	0,86	H(8)-N(2)-H(10)	105,5	
N(2)-H(9)	0,84	H(9)-N(2)-H(10)	109,1	
N(2)-H(10)	0,87			

In this atomic arrangement, there are two crystallographically independent p-phenylenediamonium per $[H_2P_2O_7]^{2-}$ anion to ensure the electric neutrality of the total complex. The (p-$NH_3C_6H_4NH_3$)$^{2+}$ groups are anchored onto successive layers, which establishes hydrogen bonds involving the hydrogen atoms of the N(1)H_3 and N(2)H_3 groups and some external oxygen atoms of the $[H_2P_2O_7]^{2-}$ anion (Table IV). This type of hydrogen bond, with H(N)···O distances varying between 1.92Å and 2.14Å, participate in the cohesion of the three-dimensional network (Figure 2).

The dihedral angles between the first ring (C(1), C(2), and C(3)) and the second one (C(4), C(5), and C(6)) of the two independent p-phenylenediamonium is 4.99°. In these rings, the bond lengths of C(1)-C(2), C(2)-C(3), C(4)-C(5), and C(5)-C(6) are 1.380(2), 1.389(2),

TABLE IV The Hydrogen-Bond Scheme in the [p-NH$_3$C$_6$H$_4$NH$_3$]H$_2$P$_2$O$_7$ Structure

D—H···A	D—H (Å)	H···A (Å)	D—H···A (Å)	D···A (Å)
O(E13)-H(OE13)···O(E23)	0.91	1.66	169.5	2.559(13)
O(E21)-H(OE23)···O(E11)	0.88	1.71	168.4	2.579(2)
N(1)-H(N11)···O(E23)	0.89	1.92	170.0	2.800(4)
N(1)-H(N12)···O(E22)	0.91	1.98	162.7	2.859(6)
N(1)-H(N13)···O(E12)	0.79	2.14	143.5	2.810(7)
N(2)-H(N21)···O(E12)	0.86	1.91	166.1	2.751(6)
N(2)-H(N22)···O(E11)	0.84	2.04	169.7	2.867(3)
N(2)-H(N23)···O(E22)	0.87	2.08	163.4	2.929(6)

1.385(2), and 1.394(2) Å, respectively, which are between a single bond and a double bond and agree with that in benzene.[10] Furthermore, the distances N(1)–C(1) and N(2)–C(4) [1.456(2) and 1.462(2) Å] clearly indicate two single bonds.

NMR Results

The proton-decoupled ^{31}P MAS NMR spectrum of crystalline p-phenylenediammonium diphosphate [p-NH$_3$C$_6$H$_4$NH$_3$]H$_2$P$_2$O$_7$, reported in

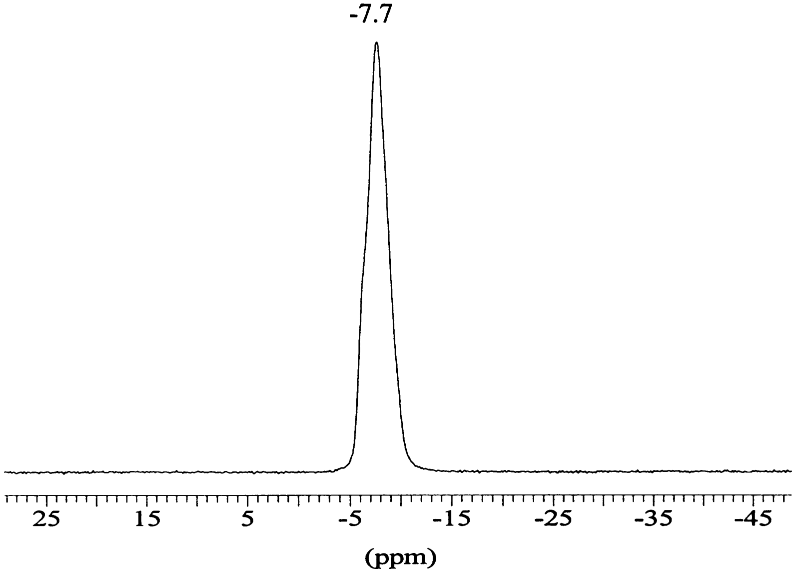


FIGURE 4 ^{31}P MAS-NMR spectrum of crystalline [p-NH$_3$C$_6$H$_4$NH$_3$]H$_2$P$_2$O$_7$.

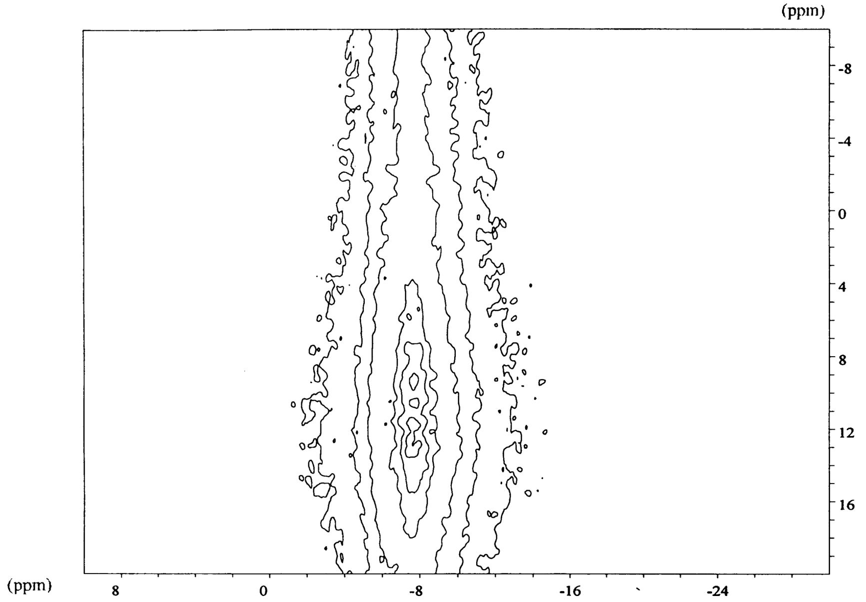
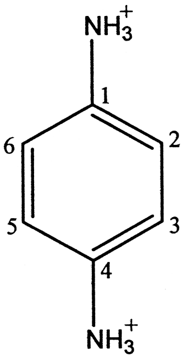


FIGURE 5 A two-dimensional spectrum ^{31}P-H of $[p\text{-}NH_3C_6H_4NH_3]H_2P_2O_7$.

Figure 4 displays only one sharp peak at −7.7 ppm ($\Delta\nu_{1/2} = 243$ Hz); such a chemical shift value agrees with those of the dihydrogenodiphosphate $[(CH_3)_2C(NH_3)CH_2OH]H_2P_2O_7$.[11] Thus, the two crystallographic sites cannot be distinguished by ^{31}P NMR because their electronic environment is very similar. The presence of a resonance signal in the two-dimensional ^{31}P-H spectrum for a short contact time of 100 μs (Figure 5) proves that phosphorus atoms are close to acidic protons ($\delta = 10$–12 ppm) and confirms the presence of a $H_2P_2O_7{}^{2-}$ entity in the structure compound as found by an X-ray diffraction study. The obtention of the same spectrum at a longer contact time of 10 ms proves that, in this case, only the proton of the P-OH group transfers its polarization to the phosphorus atom.

The ^{13}C CP MAS NMR spectrum of the so-synthesized diphosphate is given in Figure 6. The carbon atoms of the organic group are labelled as depicted in Scheme 1:

The first resonance peak corresponding to the chemical value of 123.0 ppm is assigned to the two carbon atoms in the α position of $NH_3{}^+$ (C1 and C4). The other signals are attributed to the C2, C3, C5, and C6 carbons.



SCHEME 1

EXPERIMENTAL

The Synthesis of $[p\text{-}NH_3C_6H_4NH_3]H_2P_2O_7$

The diphosphoric acid, freshly prepared from an aqueous solution of $Na_4P_2O_7$ (6.62 g, 25 mmol), was passed through an ion-exchange resin (Amberlite IR 120) and was immediately neutralized with an alcoholic solution of p-phenylendiamine (2.7 g, 25 mmol) until obtaining a final

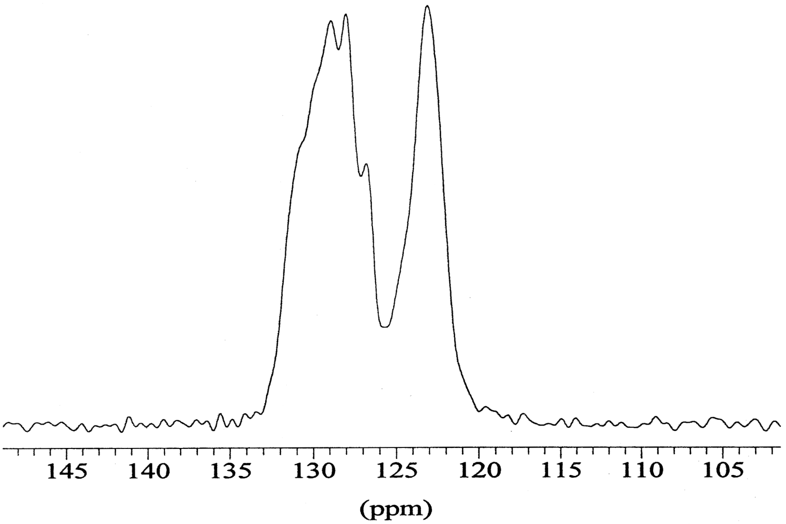


FIGURE 6 ^{13}C CP-MAS-NMR spectra of $[p\text{-}NH_3C_6H_4NH_3]H_2P_2O_7$.

solution of pH = 3. The processed chemical reaction corresponds to the following equation:

$$[\text{p-NH}_2\text{C}_6\text{H}_4\text{NH}_2] + \text{H}_4\text{P}_2\text{O}_7 \longrightarrow [\text{p-NH}_3\text{C}_6\text{H}_4\text{NH}_3]\text{H}_2\text{P}_2\text{O}_7 \qquad (1)$$

After five days of slow evaporation at r.t. crystals with suitable dimensions appeared. The yield was 3.50 g (49%). The compound chemical formula was determined by resolving its crystal structure by X-ray diffraction.

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 was $K\alpha(\text{Ag}) = 0.5608$ Å. The structure was solved by direct methods using the SIR92[12] program and refined by a full matrix least-squares techniques based on F using teXsan.[13] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms positions were located by difference-Fourier synthesis and were not refined. The details of data collection, refinement, and crystallographic data are summarized in Table I.

Crystallographic data (CIF) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data center as supplementary publication No. 267290. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, 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 121.51 MHz for ^{31}P, with a classical 4-mm probehead 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). Phosphorous spectra were recorded under classical MAS conditions both with or without cross polarization, while the carbon ones were recorded only by the use of cross-polarization from protons (contact time 5 ms). 2D HETCOR ^{31}P-^{1}H NMR spectra were obtained with the classical sequence. Two contact times (100 μs and 10 ms) were used in order to determine what kind of protons transferred polarization to the phosphorus atoms.

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