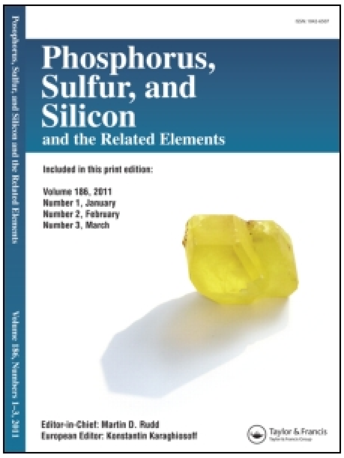

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Crystal Structure and Spectroscopic Studies of [2,6-$(C_2H_5)_2C_6H_3NH_3]_2H_3P_3O_{10}$

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Crystal Structure and Spectroscopic Studies of $[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2H_3P_3O_{10}$

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Crystal growth of a new organic cation trihydrogeno-triphosphate, $[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2H_3P_3O_{10}$*, is given. This material was prepared at r. t. conditions by the reaction of organic amine and triphosphoric acid. The obtained compound is monoclinic* $P2_1/c$ *with the following unit-cell parameters:* $a = 14.006(2)$, $b = 10.042(2)$, $c = 19.207(9)$ *Å,* $\beta = 97.86(3)^\circ$, $Z = 4$, *and* $V = 2676(1)$ *Å*^{3}*. Determination, by X-ray diffraction, and refinement to* $R = 0.044$ *and* $R_w = 0.057$*, of its crystal structure, show that the three dimensional network is built up of inorganic layers between which the organic cations are stacked. The cohesion is assured by different interaction types. Solid-state* ^{13}C *and* ^{31}P *MAS NMR spectroscopies are in agreement with the X-ray structure.*

Keywords Crystal structure; NMR spectroscopy; triphosphate; X-ray diffraction

INTRODUCTION

The interaction between triphosphate acid $H_5P_3O_{10}$ and organic molecules, such as amines, can lead to the formation of hybrid materials. With similar reagents, only some compounds have been described, $[3,5\text{-}(CH_3O)_2C_6H_3NH_3]_3H_2P_3O_{10}$[1], $[2\text{-}C_2H_5C_6H_4NH_3]_3H_2P_3O_{10}$,[2] $[4\text{-}(CH_3O)C_6H_4CH_2NH_3]_4H_2P_3O_{10}H_4P_3O_{10}$,[3] and $[C_4N_2H_{12}]_2HP_3O_{10}.H_2O$.[4] Acidic anions of these phosphates, are observed to have a strong tendency to assemble via strong hydrogen bonds and build infinite network such as chains, ribbons, layers, and three dimensional network. The present work reports synthesis, crystal structure, IR, and NMR data of a new hybrid organic–inorganic compound, $[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2H_3P_3O_{10}$.

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RESULTS AND DISCUSSION

Crystal Structure

The final atomic coordinates of all non hydrogen atoms of the title compound and their B equivalent temperature factors are given in the Table I. Those of hydrogen atoms have been determined too but not given to shorten the table.

TABLE I Final Atomic Coordinates and $B_{eq.}$ ($Å^2$) of the Non-Hydrogen Atoms in $[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2H_3P_3O_{10}$ Structure. Estimated Standard Deviations are Given in Parentheses.

Atoms	x (σ)	y (σ)	z (σ)	Beq.
P(1)	0.49841(4)	0.48148(6)	0.86915(3)	2.409(12)
P(2)	0.49881(4)	0.22900(6)	0.93966(3)	2.426(12)
P(3)	0.44674(5)	−0.00701(6)	0.85829(3)	2.774(13)
O(1)	0.55939(12)	0.4443(2)	0.81330(8)	3.37(4)
O(2)	0.56689(11)	0.5222(2)	0.93600(8)	3.22(4)
O(3)	0.41945(11)	0.5771(2)	0.84870(8)	2.86(4)
O(4)	0.45007(11)	0.3453(2)	0.89106(8)	2.89(4)
O(5)	0.4809(1)	0.2564(2)	1.01292(8)	3.54(4)
O(6)	0.59961(11)	0.2081(2)	0.92798(9)	3.28(4)
O(7)	0.43086(11)	0.1071(2)	0.91387(8)	2.87(4)
O(8)	0.4740(1)	0.0663(2)	0.79506(8)	3.85(4)
O(9)	0.35841(13)	−0.0873(2)	0.84696(9)	3.87(4)
O(10)	0.53715(13)	−0.0846(2)	0.89052(10)	3.94(5)
N(1)	0.7013(1)	0.2741(2)	1.06704(10)	2.88(4)
N(2)	0.66053(13)	0.3096(2)	1.28277(11)	3.05(5)
C(1)	0.8051(2)	0.2972(3)	1.07128(12)	2.84(5)
C(2)	0.8645(2)	0.1869(3)	1.0667(2)	3.92(6)
C(3)	0.9641(2)	0.2126(4)	1.0716(2)	5.86(9)
C(4)	0.9983(2)	0.3392(4)	1.0783(2)	6.16(10)
C(5)	0.9388(2)	0.4469(3)	1.0811(2)	5.11(8)
C(6)	0.8388(2)	0.4269(3)	1.0777(1)	3.49(6)
C(7)	0.7708(2)	0.5433(3)	1.0781(2)	4.63(7)
C(8)	0.8117(3)	0.6789(4)	1.0803(3)	9.3(1)
C(9)	0.8280(2)	0.0457(3)	1.0552(2)	5.11(8)
C(10)	0.8017(3)	0.0124(4)	0.9789(2)	7.96(12)
C(11)	0.7630(2)	0.3446(3)	1.28676(12)	2.91(5)
C(12)	0.7871(2)	0.4791(3)	1.28410(13)	3.58(6)
C(13)	0.8844(2)	0.5090(3)	1.2852(2)	5.18(8)
C(14)	0.9526(2)	0.4080(4)	1.2883(2)	6.26(10)
C(15)	0.9268(2)	0.2781(4)	1.2928(2)	5.39(9)
C(16)	0.8302(2)	0.2417(3)	1.2929(1)	3.66(6)
C(17)	0.7122(2)	0.5865(3)	1.2828(2)	4.52(7)
C(18)	0.7464(4)	0.7248(4)	1.2946(3)	10.1(2)
C(19)	0.8050(2)	0.0982(3)	1.3062(2)	4.06(7)
C(20)	0.7930(2)	0.0765(3)	1.3815(2)	4.58(7)

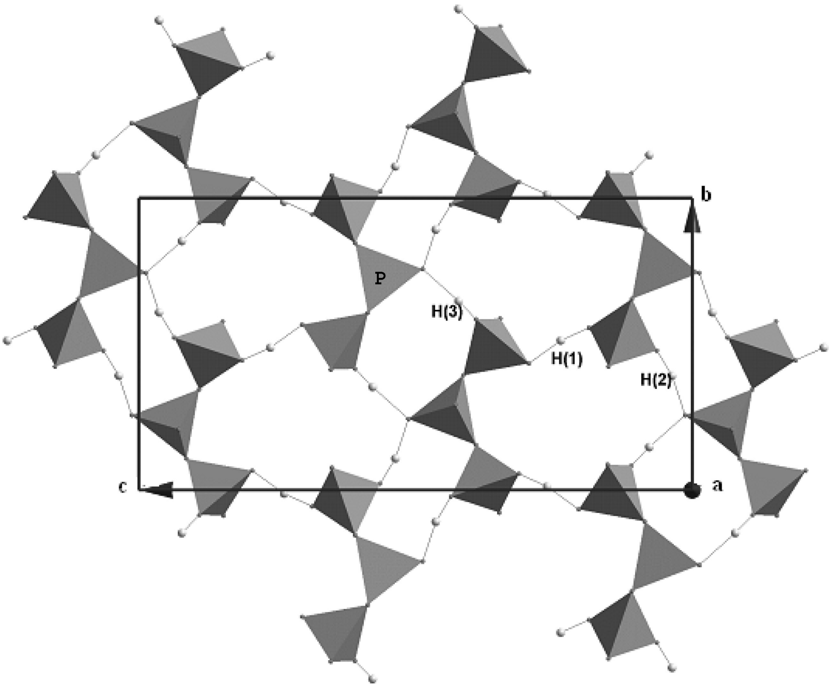

FIGURE 1 Layer organisation of $H_3P_3O_{10}$ groups in the [2,6-$(C_2H_5)_2$-$C_6H_3NH_3]_2H_3P_3O_{10}$ structure viewed in the a direction. The phosphoric anion is given in a tetrahedral representation. Other atoms are indicated by their symbols. Hydrogen bonds are indicated by dotted lines. Organic groups are not represented for figure clarity.

The main feature of the atomic arrangement in [2,6-$(C_2H_5)_2C_6H_3NH_3]_2H_3P_3O_{10}$is the existence of infinite layers built of $H_3P_3O_{10}^{2-}$ inorganic groups and located at x = ½ in a plan parallel to bc plan (Figure 1). In such layers, each $H_3P_3O_{10}^{2-}$ group is connected to its adjacent neighbors by strong hydrogen bonds ($d_{O\cdots O} < 2.73$).[5] Between these inorganic layers, the organic cations are located (Figure 2) to form a stable three dimensional network through different interactions (electrostatic, H-bonds, Van der wall, etc.). The $P_3O_{10}^{-5}$ group involved in the mineral layer has no internal symmetry and so is built by three independent tetrahedra: $P(1)O_4$, $P(2)O_4$, and $P(3)O_4$. The detailed geometry of the triphosphate group [H_2PO_3—O—PO_2—O—HPO_3] (Table II), shows that the P-O distances (ranging from 1.588(2) to 1.607(2) Å) for P-O-P bridging oxygen are apparently larger than the terminal P-O distances (ranging from

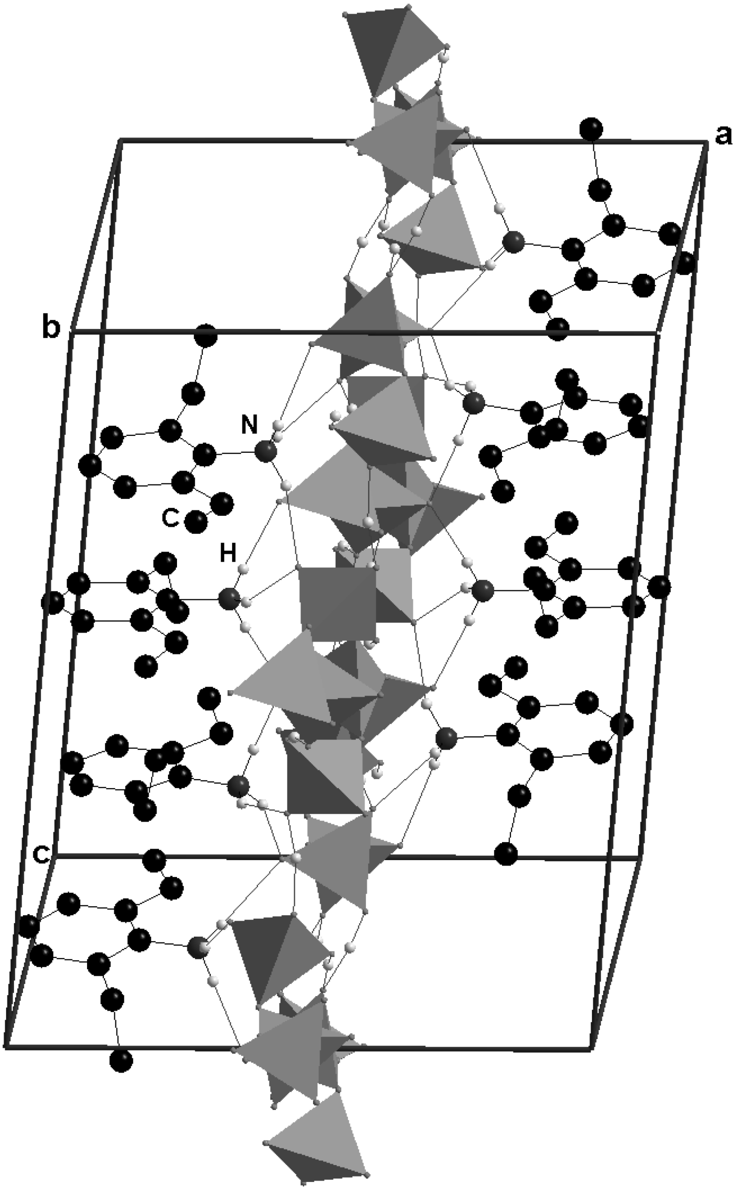

FIGURE 2 Structure projection of $[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2H_3P_3O_{10}$, along the b axis. The phosphoric anion is given in a tetrahedral representation. Other atoms are indicated by their symbols. Hydrogen bonds are indicated by dotted lines.

TABLE II Main Interatomic Distances (Å) and Bond Angles (°) in $H_3P_3O_{10}^{2-}$ Anion of $[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2H_3P_3O_{10}$. Estimated Standard Deviations are Given in Parentheses

Tetrahedron $P(1)O_4$				
P(1)	O(1)	O(2)	O(3)	O(4)
O(1)	1.517(2)	107.96(12)	116.75(12)	105.97(12)
O(2)	2.472(3)	1.549(2)	113.82(12)	104.10(12)
O(3)	2.539(3)	2.536(3)	1.477(2)	107.21(11)
O(4)	2.488(3)	2.489(3)	2.484(3)	1.607(2)
Tetrahedron $P(2)O_4$				
P(2)	O(4)	O(5)	O(6)	O(7)
O(4)	1.590(2)	107.79(12)	111.02(12)	101.01(11)
O(5)	2.487(3)	1.487(2)	117.3(1)	105.48(12)
O(6)	2.526(3)	2.530(3)	1.475(2)	112.85(12)
O(7)	2.453(3)	2.448(3)	2.552(3)	1.588(2)
Tetrahedron $P(3)O_4$				
P(3)	O(7)	O(8)	O(9)	O(10)
O(7)	1.601(2)	105.06(12)	107.44(13)	106.12(13)
O(8)	2.473(3)	1.513(2)	116.64(13)	106.5(1)
O(9)	2.477(3)	2.537 (3)	1.467(2)	114.3(1)
O(10)	2.511(3)	2.449(4)	2.529(4)	1.541(3)

P(1)-P(2) = 2.874(1) P(2)-P(3) = 2.877(1) P(1)-P(2)-P(3) = 119.12(4)
O(1)-H(1) = 1.08 O(2)-H(2) = 1.05 O(10)-H(3) = 0.89

1.467(2) to 1.549(2) Å). The P-P distances in this triphosphate group have usual values [$P_1P_2 = 2.874(1)$ and $P_2P_3 = 2.877(1)$ Å] as in other organic cation triphosphates such as $[2\text{-}C_2H_5C_6H_4NH_3]_3H_2P_3O_{10}$,[2] [$P_1P_2 = 2.936(3)$ and $P_2P_3 = 2.914(4)$ Å].

The two independent organic groups $[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]^+$establish with inorganic layers hydrogen bonds involving the NH_3 groups. Geometrical characteristics of these H-bonds are described in Table III. The two arene rings (A_1: $C_1 \cdots C_6$ and A_2:

TABLE III Hydrogen–Bond Scheme in $[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2H_3P_3O_{10}$ Structure

D–H···O	D–H(Å)	H···A(Å)	D···A(Å)	D–H···A(°)
O(1)–H(1)···O(8)	1.08	1.35	2.405(3)	164.0
O(2)–H(2)···O(5)	1.05	1.52	2.556(3)	167.3
O(10)–H(3)···O(5)	0.89	1.68	2.570(3)	175.5
N(1)–H(4)···O(6)	0.89	2.04	2.926(4)	173.7
N(1)–H(5)···O(9)	0.91	1.84	2.706(3)	158.5
N(1)–H(6)···O(3)	0.89	2.11	2.908(3)	149.5
N(2)–H(7)···O(6)	0.96	2.17	3.031(3)	149.2
N(2)-H(8)···O(8)	0.88	1.90	2.799(3)	150.3
N(2)–H(9)···O(3)	0.95	1.96	2.855(3)	155.7

$C_{11}\cdots C_{16}$) of these molecules are planar (r.m.s. deviation of fitted atoms equal to 0.0072 Å for A_1 and 0.0121 Å for A_2), but they do not have a similar orientation, since they form dihedral angle of 8.66° between them.

NMR Results

The^{31}P MAS NMR spectrum of the crystalline 2,6-diethylanilinium triphosphate is shown in Figure 3 and is in good agreement with the X-ray structure. Indeed, it exhibits three resonance peaks at –10.3, -14.7, et-20.6 ppm with their corresponding spinning side bands. These chemical shift values, which agrees with those of other triphosphates,[2]are higher than those related to monophosphates, between 10 and -5 ppm depending on the compound,[6–12] indicating that these values are mainly defined by tetrahedral condensation of phosphates. The existence of these three signals indicates the presence of three independent phosphoric sites in the unit cell of this compound which agrees perfectly with the X-ray results.

The ^{13}C CP-MAS-NMR spectrum of the title compound is given in Figure 4. In this spectrum, the presence of a resonance peak number greater than four (six in the approximately intensity ratio 1:1:2:1:1:2) in

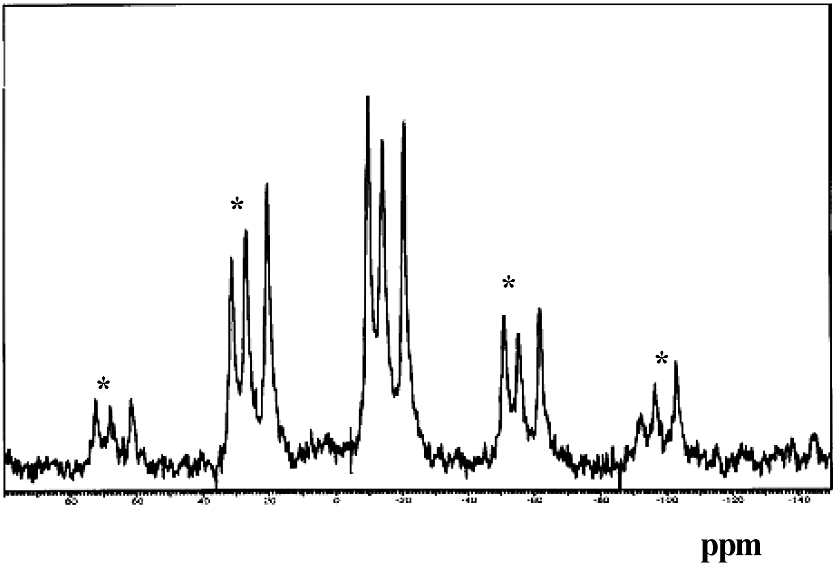

FIGURE 3 ^{31}P MAS-NMR spectrum of $[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2H_3P_3O_{10}$. *Spinning side bands.

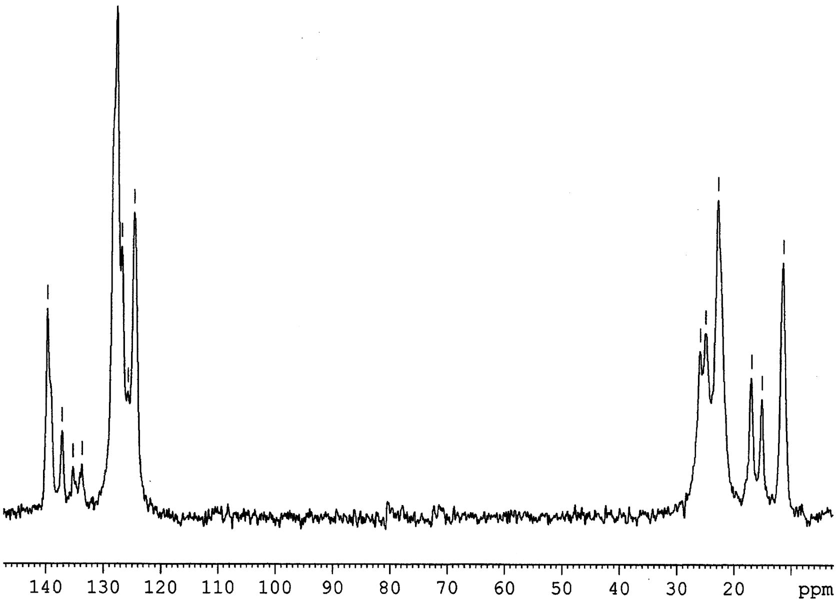

FIGURE 4 ^{13}C CP-MAS-NMR spectrum of $[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2H_3P_3O_{10}$.

the resonance range of the aliphatic carbons, between 10 and 30 ppm, proves the existence of two crystallographically independent organic moieties in the asymmetric unit of the compound structure. In fact, each organic cation gives four resonances peaks related to its two ethyl groups. This result is also in good agreement with the X-ray data. The other resonance signals at higher chemical shifts, between 120 and 140 ppm, are related to the aromatic carbon atoms.

IR Spectroscopy

The IR spectrum of crystalline 2,6-diethylanilinium triphosphate is shown in Figure 5. The most representative and characteristic vibrational modes of this compound are compared with those of the representative bands of similar triphosphates,[2] which can be written ($O_3P\text{-}O\text{-}PO_2\text{-}O\text{-}PO_3$). The performed assignments could be briefly commented, as follows.

- The high-frequency region, between 3200–1800 cm^{-1}, is relatively complicated because of the superposition of broad bands in the region correspond to the valence vibrations of C-H, N-H and O-H groups interconnected by a system of hydrogen bonds in the crystal.[13]

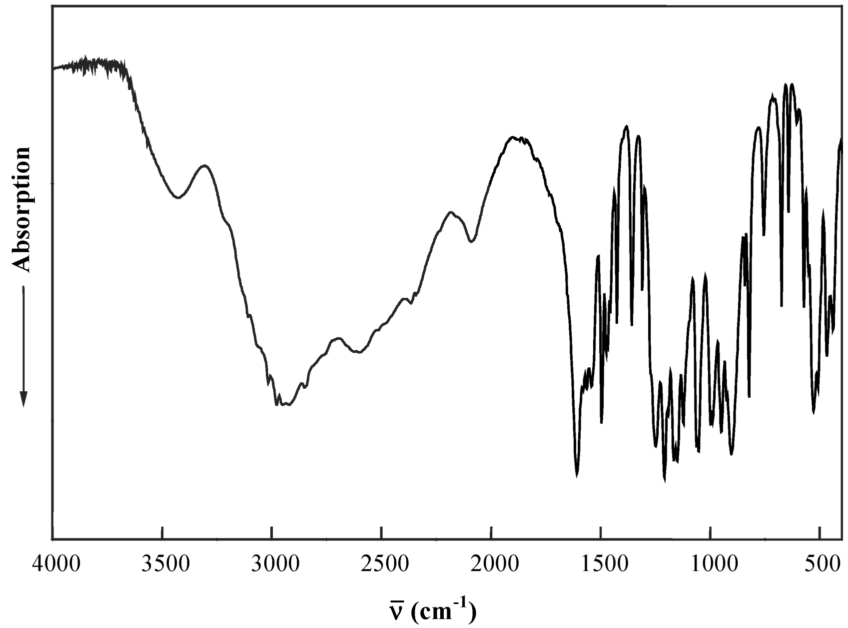

FIGURE 5 IR spectrum of $[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2H_3P_3O_{10}$in KBr pellet.

- The observed bands at 1300 and 1100 cm^{-1} can be attributed to the stretching vibrations, asymmetric and symmetric, of PO_2 central atomic group, while those at 1200 and 950 cm^{-1} correspond to the PO_3terminal atomic groups.[14,15]
- Bands ranging from 975 to 650 cm^{-1} are related to stretching POP modes,[16] and those below, situated in the interval 600–400 correspond to the bending vibrations of the PO_3terminal atomic groups.[2]
- Frequencies in the range 1630–1570 cm^{-1}are assigned to C=C stretching as well as the NH_3 bending.[17]
- The bands in the 810–680 cm^{-1} range can be attributed to $\gamma(C_{aryl}\text{–}H)$ and $\gamma(C_{aryl}\text{–}C_{aryl})$.[18]

EXPERIMENTAL

Synthesis of $[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2H_3P_3O_{10}$

The title compound, $[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2H_3P_3O_{10}$, was prepared by an acid-base reaction. An aqueous solution of triphosphoric acid $H_5P_3O_{10}$ was first obtained by passing a solution of pentasodium triphosphate, $Na_5P_3O_{10}$ (6.7 g, 25 mmol), through an ion exchange resin (Amberlite IR 120) in its H-state. The $Na_5P_3O_{10}$ salt was prepared according to the process described by Combridge.[19] Distilled $(C_2H_5)_2C_6H_3NH_2$ (V = 4 mL, 50 mmol) was added drop by drop to the $H_5P_3O_{10}$ solution, under continuous stirring. When the resulting cloudy solution becomes transparent, it is slowly evaporated at room temperature until the formation of colorless and transparent crystals of $[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2H_3P_3O_{10}$.

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 wave-length $K\alpha(Ag) = 0.5608$ Å. The structure was solved by direct methods using SIR92 program[20] and refined by full matrix least-squares techniques based on F using teXsan software.[21] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms position were located by difference-Fourier synthesis and not refined. The details of data collection, refinement and crystallographic data are summarized in Table IV.

TABLE IV Crystal Data and Experimental Parameters Used for the Intensity Data Collection

Empirical formula	$C_{20}H_{35}N_2O_{10}P_3$
Formula weight	556.43
Crystal system	Monoclinic
Space group	$P2_1/c$
a	14.006(2) (Å)
b	10.042(2) (Å)
c	19.207(9) (Å)
β	97.86(3)°
Z	4
V	2676(1) (Å^3)
$\rho_{cal.}$	1.381 (g·cm^{-3})
F(000)	1176
$\mu(AgK_\alpha)$	2.760 (cm^{-1})
Crystal size [mm]	0.55 × 0.40 × 0.18
Index ranges: ±h, k, l	$h_{max.} = 16$, $k_{max.} = 11$, $l_{max.} = 22$
Observed reflexions	8166
Independent reflexions	3506
R_{int}	0.050
Refined parameters	319
R [I > 2 σ(I)]	0.044
$R_{(w)}$	0.057
Goodness-of-fit	1.68

Crystallographic data (CIF) for the structure reported in this paper have been deposited in the Cambridge Crystallographic Data center as supplementary publication No CCDC 625912 Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB12EZ, UK (Fax: +44(1223)336-033 ; e-mail: deposit@ccdc.cam.ac.uk).

Physical Measurements

NMR spectroscopy. ^{31}P MAS-NMR spectrum were obtained with a solid state high-resolution Bruker DSC-300 spectrometer operating at 121.51 MHz. The spinning rate was 10 kHz. The $\pi/2$ pulse was 4 μs and the time interval between successive scans 10 s. All measurements were carried out at room temperature, with H_3PO_4 (85%) as an external standard reference.

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

CONCLUSION

The number of organic cation triphosphates remains limited in bibliography. These triphosphates are difficult to crystallize in aqueous media because $H_3P_3O_{10}^{2-}$ anion includes P-O-P bonds which are sensitive to the hydrolysis phenomena. The use of organic molecule stabilize the triphosphate anion and leads to a new material of chemical formula $[2,6\text{-}(C_2H_5)_2C_6H_3NH_3]_2H_3P_3O_{10}$. The atomic arrangement of the title compound can be described by inorganic layers anchoring the organic cations through hydrogen bonds. Solid-state ^{13}C and ^{31}P MAS NMR spectroscopies are in agreement with the X-ray structure.

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