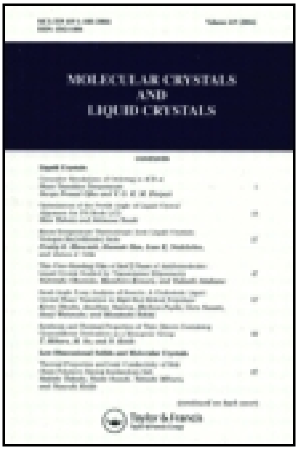

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Self-Association Of Benzene-1,3,5-Tris-(Methylenephosphonic Acid): Evidence of Charge-Assisted Hydrogen Bonds

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SELF-ASSOCIATION OF BENZENE-1,3,5-TRIS-(METHYLENEPHOSPHONIC ACID): EVIDENCE OF CHARGE-ASSISTED HYDROGEN BONDS.

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The synthesis and the solid-state structure of benzene-tris-(methylene-phosphonic acid) is reported in the following article. Surprisingly the three methylenephosphonic acid groups are located on the same side of the benzene ring leading to the formation of an octopus shaped molecule. Furthermore the number of proton per phosphonic acid function is different from the expected value of two per phosphophonic acid function. The single crystal X-ray diffraction reveals that this interesting behaviour arises from the formation of a dimer in the solid-state. Interestingly both charge-assisted hydrogen bonds and hydrogen bonds are observed in this dimer.

We thank Sébastien Martina and Michaël Davi for helping us in the synthesis of compound **1**, Guillaume Lê for his DSC analysis and Margareth Lemarié for her microanalysis. C.F. and V.M. are grateful to the CNRS, FEDER and Région Basse-Normandie for funding.

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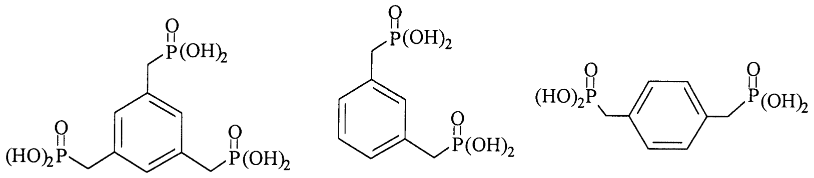
Keywords: supramolecular assembly; phosphonic acid; hydrogen bond

INTRODUCTION

The design of new materials based on supramolecular assemblies has received considerable interest due to their potential application as NLO materials [1], magnetic materials [2] or as sensors [3]. Supramolecular assemblies can be the result of weak links (hydrogen bonds, π-π interaction, electrostatic interactions . . .). Phosphonates and phosphonic acids that are close to phosphate functions present in biological systems, constitute many attractive building blocks that may be useful to design materials based on hydrogen bonding. These substrates have been widely used to form coordination materials based on the interaction with a metal to produce metal-phosphonate hybrid materials [4]. The structure of the phosphonic acid is a key factor in determining the shape of these hybrid materials. For instance, phenylphosphonic acid [5], in the presence of a zirconium salt, yields a two-dimensional layered material while the use of 1,4-phenylbis(phosphonic)acid yields a three-dimensional pillared framework [6]. A second possibility to design materials formed by phosphonic acids as building blocks consists to engage these substrates into a hydrogen bond network. This approach which is as yet less well developed than the metal-phosphonate approach, may be achieved by the generation of hydrogen bonds between two phosphonic acid functions or between phosphonic acids and another partnerships. According to the first strategy, Clearfield *et al.* synthesised a macrocyclic leaflet [7] based on hydrogen bonding between phosphonic acid functions. The second strategy was employed by Schrader et al. to design spheroidal molecular assemblies [8]. Finally Clearfield et al. [9] have recently reported the synthesis of three dimensional materials based on hydrogen bonds between a tris(phosphonic acid) and different amine or pyridine derivatives.

One strategy to produce two and three-dimensional supramolecular assemblies is to use symmetric functionalised organic molecules. As an illustration, Trimesic acid [10], or adamantane-1,3,5,7-tetracarboxylic acids [11] are able to produce *via* hydrogen bonds respectively a two or a three dimensional structure. Ward *et al.* reported supramolecular synthesis of layered materials based on two-dimensional hydrogen bonded networks comprising the symmetric guanidinium ion and alkane or arylsulfonate [12]. Recently Pigge *et al.* observed in the solid state the inclusion of dichloromethane or dimethylsulfoxide with a symmetrically substituted 1,3,5-triaroylbenzene acting as a receptor. [13] The geometry of this triaroylbenzene is a key factor leading to crystalline inclusion complexes.



1 **2** **3**

SCHEME 1 Structure of the target molecules.

Our attention was focused on the synthesis of benzene bis and tris-(methylenephosphonic acids) **1–3** (Scheme 1) in order to design new multi-dimensional supramolecular assemblies based on its self-assembly or on its assembly with a partnership. In this communication, we aim to report the solid-state structure of compound **1** that presents a noteworthy supramolecular feature.

RESULTS AND DISCUSSION

Tris-phosphonic acids **1** was synthesised by hydrolysis of the corresponding diethylphosphonates [14]. The location of the phosphonic functions on the benzylic position allows these chains to adopt different conformations. Usually 1,3,5-tris-substituted benzene with flexible chains, as in compound **1**, crystallises with one chain on one side of the benzene ring while the two other are pointing towards the other side. Nevertheless, one strategy, based on the substitution of a benzene ring with six alternating bulky groups, has been reported to locate three functionalised chains on the same side of the benzene ring. [15] The crystal structure of compound **1**, on the contrary of our predictions, reveals the presence of the three phosphonic acid groups on the same side of the benzene ring (Fig. 1).

Furthermore, in disagreement with the prediction of two hydrogen atoms per phosphonic acid function, a different number of hydrogen on each phosphonic acid group is observed: the first contains three hydrogen atoms, the second two and the third one. Nevertheless this hydrogen distribution is in agreement with the neutrality of the compound **1**. The crystal packing of compound **1** which is a dimer (Fig. 2) contributes to explain this unexpected hydrogen distribution.

The two molecules of the dimer are oriented face to face by the phosphonic acid groups, in such a way that one phosphonic acid function of one molecule (the one which borne one hydrogen) is situated in the centre of the three phosphonic acid groups of the second molecule (Fig. 2). This phosphonic acid group interacts with the three phosphonic acid functions

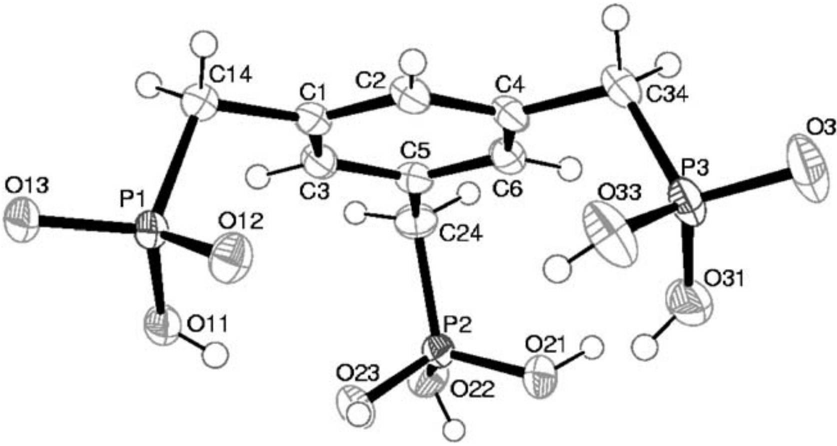


FIGURE 1 The asymmetric unit of compound **1**.

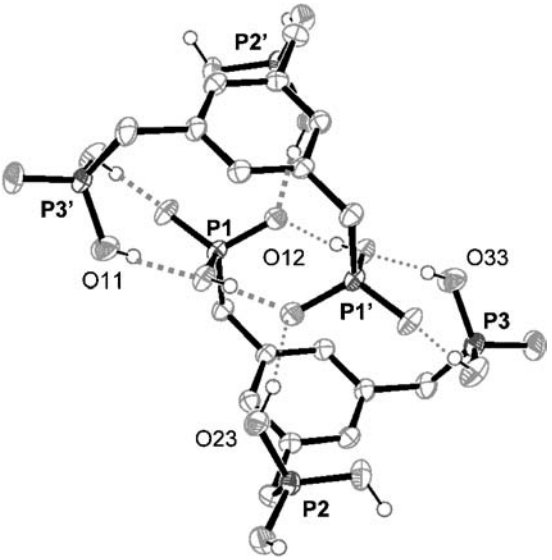


FIGURE 2 Hydrogen-bonded dimer of compound **1**. Only the H atoms of phosphonic groups are present for clarity (Two complementary sets of 4 hydrogen bonds are present by dashed lines of different thickness.).

TABLE 1 Relevant Intermolecular Hydrogen Bonding Parameters in Crystalline Compounds **1** (distances in Å, angles in °).

D-H···A	D-H	H···A	D···A	D-H···A
Dimer H-bonding in unit cell				
O11-H11···O12^{i}	0.734	1.782	2.513	174.34
O23-H23···O12^{i}	0.869	1.694	2.554	170.25
O31-H31···O13^{i}	0.760	1.835	2.594	176.94
O33-H33···O11^{i}	0.720	1.912	2.631	178.22
Other H-bonds				
O21-H21···O32^{ii}	0.925	1.520	2.442	174.34
O22-H22···O13^{iii}	0.869	1.622	2.484	170.97

$^{i}-x+1, -y+1, -z+1,$ $^{ii}-x+2, -y+2, -z,$ $^{iii}\, x+1, y, z-1.$

of the second molecule by a hydrogen bond network. A total of two complementary sets of 4 hydrogen bonds are observed between the molecules in the dimer (O...O contacts are in the range of 2.513–2.631 Å, Table 1).

The location of the hydrogen reveals by the packing of compound **1**, leads to the proximity of phosphonic functions bearing opposite charges (e.g. P_2 and $P_{1'}$; P_1 and $P_{2'}$) thus increasing the strength of the interaction of the two molecules in this dimer due to attractive coulombic interactions. This type of proton exchange, which is commonly observed in the solid state when a base and an acid are co-crystallised [15], is much less observed for acids in the solid state. To the best of our knowledge this is the first observation of charge-assisted hydrogen bonds between two phosphonic acid functions. Finally, two others hydrogen bonds (see Table 1) link these dimers together to define the (101) planes. From this structure the following conclusions can be stated: the oxygen of the phosphonic acid can be donor (e.g. O_{23}), donor and acceptor (O_{11}) or double acceptor (O_{12}); the phosphonic acid functions are able to exchanged proton to form charge-assisted hydrogen bonds that increase the stability of the assembly arising from strong coulombic interactions. The cavity, located between the three arms defined by the methylenephosphonic functions borne by the benzene ring in compound **1,** seems to form a good receptor for a phosphonic acid function. Indeed, a phosphonic acid from another molecule is placed in this cavity and interacts with them by both hydrogen bonds and coulombic interactions.

^{31}P MAS NMR CHARACTERISATION

The best technique used, but only suitable with good shaped crystals, to investigate the structure of supramolecular materials is the single crystal

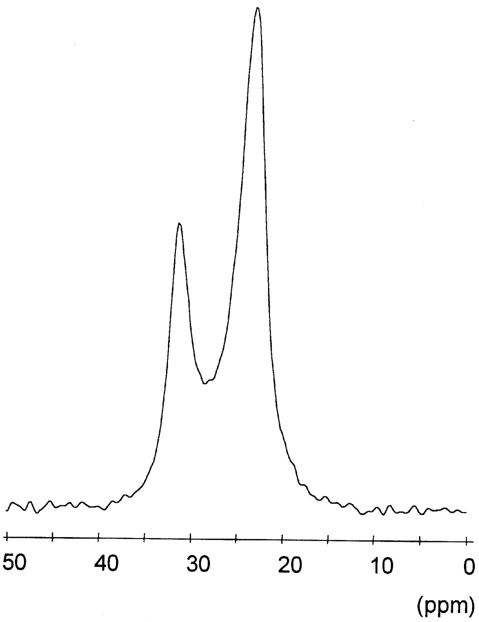


FIGURE 3 ^{31}P MAS NMR (26 KHz, NS = 180): of compound **1**.

X-ray diffraction. In our case the phosphonic acids function allows the use of NMR techniques to get information on the less crystalline samples. The solid-state ^{31}P MAS NMR spectrum of compound **1** presents two signals at 31.3 and 23.6 ppm (Fig. 3). The relative intensity of these two signals, obtained by spectrum deconvolution [16], is 1 to 2. Despite the high spinning frequency (26 KHz) the resolution for the peak at 23.6 ppm was not improved indicating that two phosphorus atoms of compound **1** have a close chemical shift. This result is consistent with the X-ray diffraction study that indicates the presence of three different phosphorus atoms in the asymetric unit. This dimer is broken up in water solution (basic media) since liquid-state ^{31}P NMR reveals only one signal at 24.3 ppm.

CONCLUSION

The tris-phosphonic acid **1** forms in the solid-state a compact dimer *via* hydrogen bonds and charge-assisted hydrogen bonds. The crystal structure of compound **1** illustrates the ability of phosphonic acid functions to exchange proton to form strong attractive electrostatic interaction. From the crystal structure of compound **1**, it can be state that the cavity formed by the methylenephosphonic acid functions placed in the 1,3,5 positions on a benzene ring design a good receptor for one phosphonic acid function.

Single crystal X-ray diffraction and solide-state NMR studies at higher temperature will be enterprise for compound **1** to establish the influence of the temperature on the location of the proton engaged in the charge-assisted hydrogen bonds in the dimer.

In view of these first results, that demonstrate the interest to use phosphonic acid functions for their supramolecular behaviour, the co-crystallisation of benzene bis or tris (methylene phosphonic acid) with guanidinium chloride or other poly-amine will be endeavour. Finally, the structure of compound **1** which possess the three phosphonic acid functions on the same side of the benzene ring, allows us to predict that compound **1** might have cationic chelating properties. Further experiments are in progress to determine the chelating properties of compound **1**.

EXPERIMENTAL

^{1}H, ^{13}C and ^{31}P NMR spectra (liquid-state) were recorded on a Bruker AC 250 spectrometer. Solid-state ^{31}P NMR spectra were recorded in a 2.5 mm MAS probe at 25°C on a Bruker Avance 400 spectrometer operating at a resonance frequency of $\nu_0 = 162$ MHz with a recycling time of 10 s. H_3PO_3 was taken as a reference. Elemental analyse was recorded on a CE Instrument NA 2500.

Synthesis

Benzene-1,3,5-tris(methylenephosphonic acid) **1**: benzene-1,3,5-tris-(diethoxyphosphoryl-methyl) [14] (5.71 g; 10.8 mmol) and 37% aqueous HCl (150 ml) was heated at reflux for 24 h. The excess of HCl and water was removed *in vacuo* to afford compound **1** as a white powder (3.58 g, 92%). Single crystals were isolated by recrystallisation in methanol/water (7/1) with a slow diffusion of diethylether. m.p.(DSC, 40°C/min) = 294°C; $^{1}H(D_2O + K_2CO_3)$: 2.90 (d, $^{2}J = 21.4$ Hz, CH_2-P), 6.89 (m, $^{4}J = 1.67$ Hz, C-H_{Ar}); $^{31}P(D_2O + K_2CO_3)$: 24.3 (s); ^{13}C $(D_2O + K_2CO_3)$: 34.72 (d, $^{1}J_{CP} = 129.9$ Hz, CH_2), 129.36 (m, CH_{Ar}), 133.97 (m, C_{Ar}); ^{31}P MAS NMR (see Fig. 3): 31.3 and 23.6 ppm.

Crystallography

Intensity data for compound **1** was collected on an Enraf-Nonius - CAD4 diffractometer with Mo K_α radiation ($\lambda = 0.71073$ Å) at room temperature. The crystal structures were solved by direct methods using SHELX97 package [18]. All non-hydrogen atoms were refined anisotropically. The all

TABLE 2 Crystal Data and Details of Measurements for Compound **1**

	1
Formula	$C_9H_{15}O_9P_3$
Molecular weight ($g{\cdot}mol^{-1}$)	360.12
T (K)	293(2)
Crystal size (mm)	0.5 × 0.2 × 0.1
System	Triclinic
Space group	P-1
a (Å)	9.1775(8)
b (Å)	9.3240(6)
c (Å)	9.5800(1)
α (°)	67.910(7)
β (°)	67.509(8)
γ (°)	84.237(6)
Cell volume ($Å^3$)	700.92(11)
D_x ($mg\ m^{-3}$)	1.706
θ range (°)	2 to 30
No of reflections used for cell refinement	25
μ (mm^{-1})	0.467
Measured reflections	4289
Unique reflections	4061
Unique reflections with $I > 2\sigma(I)$	3586
R_{int}[a]	0.0244
R (all data)[b]	0.0376
$wR2$ (on F^2, all data)[b]	0.0961 ($A = 0.0619$, $B = 0.1369$)
Goodness of fit on F^2[c]	1.128
Number of refined parameters	250

[a] $R_{int} = \sum |F_o^2 - F_o^2\ (mean)| / \sum [F_o^2]_|$.

[b] $R = \sum \||F_O| - |F_C\|| / \sum [F_O]$

$$wR2 = \left\{\sum\left[w(F_O^2 - F_C^2)^2\right] / \sum\left[w(F_O^2)^2\right]\right\}^{1/2}, \qquad where\ w = 1/\left[\sigma^2(F_O^2) + (AP)^2 + BP\right]$$

$$P = (F_O^2 + 2F_C^2)/3.$$

[c] $S = \left\{\sum\left[w(F_O^2 - F_C^2)^2\right] / (no.\ reflections\ -\ total\ no.\ of\ parameters\ refined)\right\}^{1/2}$.

H atoms were determined *via* difference Fourier maps and refined with isotropic atomic displacement parameters. Crystal data and data collection parameters are summarised in Table 2. CCDC reference number for compound **1** : 151631.

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