Two- and Three-Dimensional Hydrogen-Bonded Networks Built from 1,3,5-$[(HO)_2(O)P]_3C_6H_3$ and 4-(Dimethylamino)pyridine

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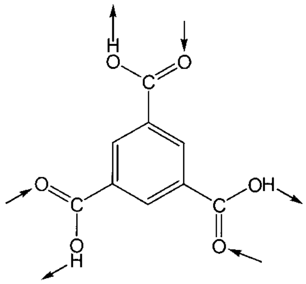
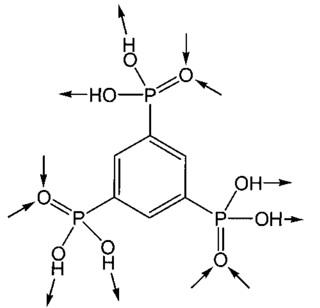
Crystallisation of 3,5-bis(phosphonophenyl)phosphonic acid, 1,3,5-$[(HO)_2(O)P]_3C_6H_3$, from $MeOH/H_2O$ in the presence of 4-(dimethylamino)pyridine, 4-$(Me_2N)C_5H_4N$, gave $[1\text{-}\{(HO)_2(O)P\}\text{-}3,5\text{-}\{(HO)(O)_2P\}_2C_6H_3]^{2-}[\{4\text{-}(Me_2N)C_5H_4NH\}^+]_2$ (**2**) and $[1,3\text{-}\{(HO)_2(O)P\}_2\text{-}5\text{-}\{(HO)(O)_2P\}C_6H_3]^-[4\text{-}(Me_2N)C_5H_4NH]^+$ (**3**). Single-crystal X-ray diffraction analyses revealed a two- and a three-dimensional hydrogen-bonded network for compounds **2** and **3**, respectively. Compound **2** is composed of layers which are formed by hydrogen-bonded motifs of the type R2,2(8) and R4,4(16). These motifs are connected within the layer by additional hydrogen bonds and the benzene spacer. The cation $[4\text{-}(Me_2N)C_5H_4NH]^+$ is located between the layers and determines the interlayer separation of approximately 6.5 Å. In compound **3** a layered network of the hydrogen-bonded building units R2,3(10) was observed. These units are interconnected by four additional hydrogen bonds within the network. The benzene spacer links the adjacent layers to give a three-dimensional structure. Within this network, channels with internal dimensions of ca. 8.5 × 11.3 $Å^2$ which are occupied by the $[4\text{-}(Me_2N)C_5H_4NH]^+$ cations were observed.

Introduction

In the last three decades there has been a tremendous interest in the development of new metal phosphonates due to their great potential for applications based on ion exchangers, catalysts, selective adsorbents, sensors, photochemically active materials, proton conductors and materials for non-linear optics.[1,2] Most of the metal phosphonates based on non-functionalised mono(phosphonic acids), RPO_3H_2, and bis(phosphonic acids), $H_2O_3P{-}R{-}PO_3H_2$, adopt layered and pillared-layered structures. Recently, a growing interest in metal phosphonate clusters has emerged as well.[3−13] In contrast to the intensive studies of metal phosphonates, little attention was drawn to the structure and properties of simple phosphonic acids. Their crystal structures are characterised by the formation of hydrogen bonds of the type $P{-}O{-}H\cdots O{=}P$ which results in a diverse structural chemistry ranging from hydrogen-bonded clusters[14] to two- and three-dimensional polymers.[15−24] However, the prediction of structures even in the case of non-functionalised mono(phosphonic acids) is far from simple because each phosphonic acid moiety might serve as a hydrogen bond acceptor for one or even two hydrogen bond donors through its $P{=}O$ group and as a double hydrogen bond donor through its two $P{-}O{-}H$ groups. In contrast to crystal engineering approaches to organic solids using phosphonic acids, much effort has been made in the development of organic hydrogen-bonded materials using the carboxylic acid dimer motif. One of the most popular organic acids in this context is trimesic acid, 1,3,5-$(HO_2C)_3C_6H_3$, and a large number of studies based on this carboxylic acid have been reported.[25] Surprisingly, its phosphorus-containing counterpart, the triphosphonic acid 1,3,5-$[(HO)_2(O)P]_3C_6H_3$, has not been the subject of crystal engineering studies. This triphosphonic acid might function as a robust synthon for the construction of two- and three-dimensional networks through the formation of strong hydrogen bonds. The only report on 1,3,5-$[(HO)_2(O)P]_3C_6H_3$ stems from 2002 and deals solely with its synthesis.[26]





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A drawback of functional organic solids is often their low thermal stability but it was shown recently that the cocrystallisation of nitrilotri(methylphosphonic acid) with various amines produces aggregates showing thermal stability similar to that obtained for metal phosphonates.[27,28]

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Studies of the crystallisation of phosphonic acids in the presence of amines have shown that a proton is transferred from the phosphonic acid to the amine to give anions of the type $[RP(O)_2OH]^-$.[29–35] As result of their self-assembly through strong hydrogen bonds of the type P−O−H···⁻O−P and the cooperative effect operating within the hydrogen-bonded network, very robust crystalline solids are produced. In a combined theoretical and experimental work on *tert*-butylphosphonic acid we have shown previously that by removal of a proton the hydrogen bond strength in the dimer is increased from ca. $43\ kJ\cdot mol^{-1}$ calculated for $[tBuP(O)(OH)_2]_2$ to ca. $83\ kJ\cdot mol^{-1}$ calculated for $[\{tBuP(O)_2(OH)\}\{tBuP(O)(OH)_2\}]^-$.[14]

Here we report on the synthesis and characterisation of hydrogen-bonded aggregates of the triphosphonic acid 1,3,5-[$(HO)_2(O)P]_3C_6H_3$ (**1**) with 4-(dimethylamino)pyridine. The phosphonic acid was crystallised in the presence of the amine to give $[1\text{-}\{(HO)_2(O)P\}\text{-}3,5\text{-}\{(HO)(O)_2P\}_2C_6H_3]^{2-}[\{4\text{-}(Me_2N)C_5H_4NH\}^+]_2$ (**2**) and $[1,3\text{-}\{(HO)_2(O)P\}_2\text{-}5\text{-}\{(HO)(O)_2P\}C_6H_3]^-[4\text{-}(Me_2N)C_5H_4NH]^+$ (**3**). The single-crystal X-ray structure analyses of both compounds as well as their thermal stability are discussed.

Results and Discussion

The triphosphonic acid 1,3,5-[$(HO)_2(O)P]_3C_6H_3$ (**1**) was prepared from the corresponding arylphosphonic ester 1,3,5-[$(i\text{PrO})_2(O)P]_3C_6H_3$[36] by reaction with Me_3SiBr and subsequent reaction with methanol. The ester was prepared by an Ni-mediated variant of the Arbuzov reaction starting from 1,3,5-tribromobenzene in 80% yield. The recently described synthesis of 1,3,5-[$(MeO)_2(O)P]_3C_6H_3$ starting from 1,3,5-trichlorobenzene and trimethyl phosphite under UV irradiation for three weeks was reported to give a mixture of products from which 1,3,5-[$(MeO)_2(O)P]_3C_6H_3$ was isolated in moderate yield and subsequently hydrolysed to give the corresponding triphosphonic acid.[26]

So far, all of our attempts to crystallise the phosphonic acid **1** without the aid of a template have been unsuccessful. However, co-crystallisation of **1** with 4-(dimethylamino)pyridine from water/methanol gave the 1:2 adduct $[1\text{-}\{(HO)_2(O)P\}\text{-}3,5\text{-}\{(HO)(O)_2P\}_2C_6H_3]^{2-}[\{4\text{-}(Me_2N)C_5H_4NH\}^+]_2$ (**2**) and the 1:1 adduct $[1,3\text{-}\{(HO)_2(O)P\}_2\text{-}5\text{-}\{(HO)(O)_2P\}C_6H_3]^-[4\text{-}(Me_2N)C_5H_4NH]^+$ (**3**). Both salts are soluble in water, but poorly soluble in solvents such as $CHCl_3$, acetone and DMSO. A proton transfer from the phosphonic acid moieties to 4-(dimethylamino)pyridine is observed and thus, in addition to neutral O−H···O hydrogen bonds, ionic hydrogen bonds of the type O−H···O⁻ and O···H−N⁺ are formed. Selected bond lengths and angles are given in Table 1. The asymmetric unit of **2** is shown in Figure 1.

Table 1. Hydrogen bond parameters [Å, °] of compounds **2** and **3**

	D−H	H···A	D···A	D−H···A
2				
O(1)−H···O(8A)	0.85(3)	1.70(3)	2.541(2)	172(3)
N(2)−H···O(8A)	0.84(3)	1.99(3)	2.782(3)	158(3)
O(4)−H···O(6A)	0.83(3)	1.72(3)	2.546(3)	174(3)
N(4)−H···O(3A)	0.96(3)	1.71(3)	2.653(3)	167(3)
O(5)−H···O(9A)	1.05(3)	1.39(3)	2.431(2)	170(3)
O(7)−H···O(2A)	0.90(3)	1.55(3)	2.448(2)	179(4)
3				
N(1)−H···O(5)	0.89(2)	1.90(2)	2.778(2)	172(2)
O(2)−H···O(4A)	0.80(2)	1.76(2)	2.568(2)	175(3)
O(3)−H···O(7A)	0.94(3)	1.56(3)	2.495(2)	172(2)
O(5)−H···O(8A)	0.89(3)	1.64(3)	2.523(2)	176(3)
O(6)−H···O(1A)	0.93(2)	1.57(2)	2.496(2)	171(2)
O(9)−H···O(4A)	0.99(3)	1.55(3)	2.536(2)	175(2)

Both amines act as proton acceptors through their pyridine nitrogen atoms to give the cation $[4\text{-}(Me_2N)C_5H_4NH]^+$. It is noteworthy that the oxygen atom O(8) is involved in hydrogen bonds to N(2) and O(1A) with X···O (X = N, O) bond lengths of 2.782(3) and 2.541(2) Å, respectively, thus acting as a double hydrogen bond acceptor. In contrast, the oxygen atom O(3) exclusively forms an O···H−N⁺ hydrogen bond of 2.653(3) Å with its neighbouring cation $[4\text{-}(Me_2N)C_5H_4NH]^+$. The remaining oxygen atoms form single hydrogen bonds resulting in a total number of eight O−H···O/O−H···O⁻ hydrogen bonds for each triphosphonic acid molecule. Four of the latter are related by symmetry and the O···O distances range from 2.431(2) to 2.546(3) Å. The dianion $[1\text{-}\{(HO)_2(O)P\}\text{-}3,5\text{-}\{(HO)(O)_2P\}_2C_6H_3]^{2-}$ self-assembles through these hydrogen bonds to give a layered structure with the cations [4-

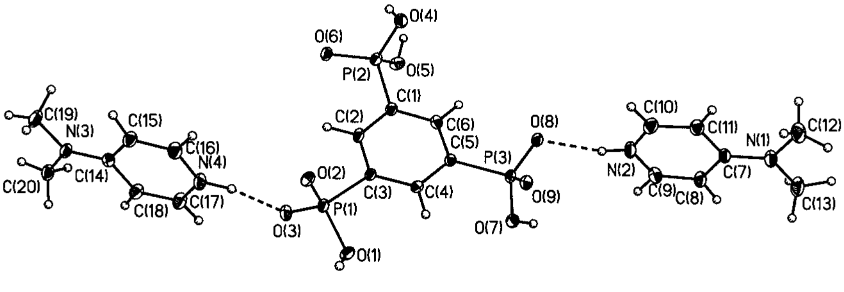

Figure 1. Molecular structure of $[1\text{-}\{(HO)_2(O)P\}\text{-}3,5\text{-}\{(HO)(O)_2P\}_2C_6H_3]^{2-}[\{4\text{-}(Me_2N)C_5H_4NH\}^+]_2$ (**2**): view of the building unit of **2** showing the labeling scheme and the thermal ellipsoids drawn at 30% of probability level; selected bond lengths: P(1)−O(1) 1.570(2) Å, P(1)−O(2) 1.519(2) Å, P(1)−O(3) 1.495(2) Å, P(2)−O(4) 1.552(2) Å, P(2)−O(5) 1.522(2) Å, P(2)−O(6) 1.500(2) Å, P(3)−O(7) 1.538(2) Å, P(3)−O(8) 1.508(2) Å, P(3)−O(9) 1.524(2) Å

$(Me_2N)C_5H_4NH]^+$ sandwiched between the layers, giving rise to an interlayer distance of ca. 6.5 Å (see Figure 2).

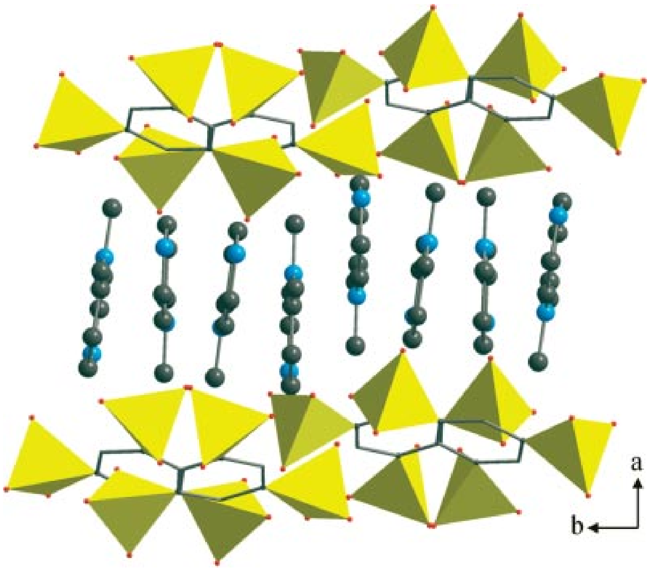

Figure 2. View of the crystal packing diagram of **2** down the *c* axis showing the layered structure; the cations $[4-(Me_2N)C_5H_4NH]^+$ are intercalated between hydrogen-bonded layers (tetrahedron: PO_3C; phosphorus: yellow; carbon: dark grey; nitrogen: blue; oxygen: red)

The layer shown in Figure 3 is best described as being composed of two hydrogen-bonded ring motifs which are assigned to R2,2(8) and R4,4(16) using the graphset theory (see general remarks).[37] Connecting both ring types with the benzene spacer and an additional hydrogen bond results in the two-dimensional network with the amines stacked above and below the *b*,*c* plane.

The asymmetric unit of compound **3** is shown in Figure 4. Similar to **2**, the cation $[4-(Me_2N)C_5H_4NH]^+$ is observed as a result of a proton transfer from **1** to the pyridine nitrogen atom of 4-(dimethylamino)pyridine; the N(1)···O(5) distance amounts to 2.778(2) Å. In addition, O(5) is linked to O(8A) showing an intermolecular distance of 2.523(2) Å. The oxygen atom O(4) is involved in two hydrogen bonds to O(2A) and O(9A) with distances of 2.568(2) and 2.536(2) Å, respectively. The remaining oxygen atoms show single O−H···O hydrogen bonds of 2.495(2) Å [O(3)−O(7A)] and 2.496(2) Å [O(6)−O(1A)]. A total of ten O−H···O/O−H···O⁻ hydrogen bonds for each triphosphonic acid molecule are observed, of which five are related by symmetry. In contrast to the layered structure of **2**, the monoanionic moieties $[1,3-\{(HO)_2(O)P\}_2-5-\{(HO)(O)_2P\}-C_6H_3]^-$ self-assemble to give a three-dimensional hydrogen-bonded network. This network is composed of layers which are formed by extensive hydrogen bonding (see Figure 5) and which are connected through benzene spacers along the *a* axis.

The main structural feature of the layers is the R2,3(10) ring motif shown in Figure 5. Of note is that this motif was also observed as a structure-directing motif in neutral and anionic clusters of *tert*-butylphosphonic acid.[14] The outer sphere of the R2,3(10) unit is composed of two hydrogen

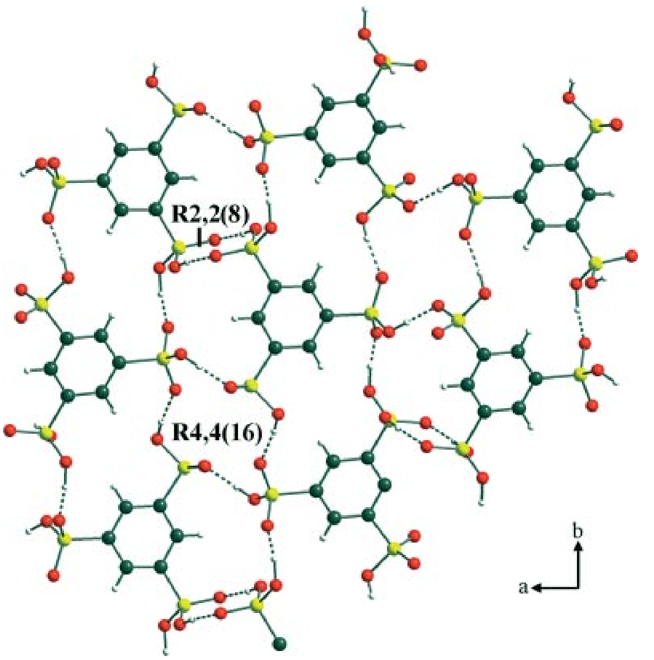

Figure 3. View of the hydrogen-bonded 2-D network in the *b*,*c* plane of **2**; the main structural motifs are dimers having the R2,2(8) notation and tetramers having the R4,4(16) notation; these motifs are linked through an additional hydrogen bond and the benzene spacers within the layer (carbon: dark grey; phosphorus: yellow; oxygen: red; hydrogen: light grey)

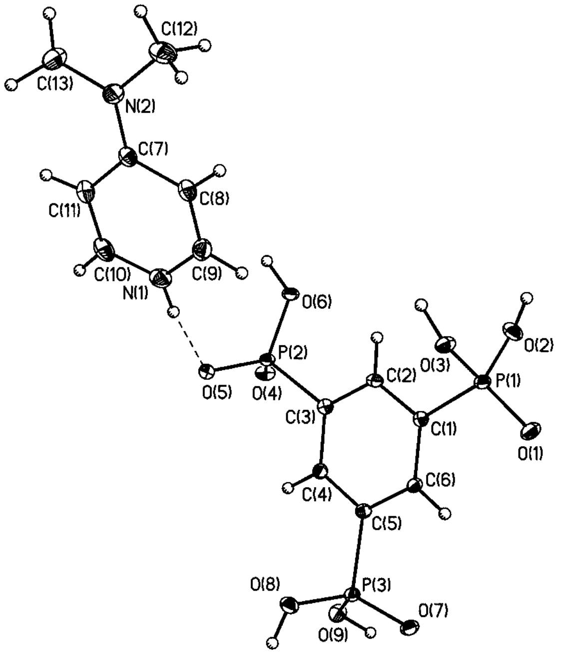

Figure 4. Molecular structure of $[1,3-\{(HO)_2(O)P\}_2-5-\{(HO)(O)_2P\}C_6H_3]^-[4-(Me_2N)C_5H_4NH]^+$ (**3**): view of the building unit of **3** showing the labeling scheme and the thermal ellipsoids drawn at 30% of probability level; selected bond lengths: P(1)−O(1) 1.481(1) Å, P(1)−O(2) 1.552(2) Å, P(1)−O(3) 1.551(1) Å, P(2)−O(4) 1.514(1) Å, P(2)−O(5) 1.512(1) Å, P(2)−O(6) 1.553(1) Å, P(3)−O(7) 1.495(1) Å, P(3)−O(8) 1.542(1) Å, P(3)−O(9) 1.549(1) Å

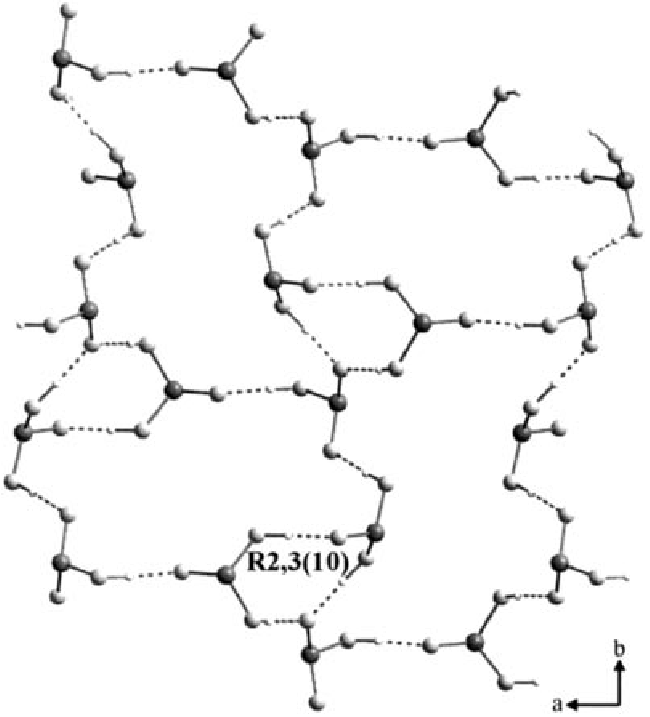

Figure 5. The hydrogen bonded 2-D network of **3**; view of the *a*,*b* plane; the benzene spacer and 4-(dimethylamino)pyridine molecules are omitted for clarity; the main structural motif is a 10-membered ring having the R2,3(10) notation; additional hydrogen bonds link these motifs within the layer; the layers are connected through the benzene spacer along the *c* axis; (phosphorus: grey; oxygen and hydrogen: light grey)

bond acceptors and two hydrogen bond donors. Thus, the R2,3(10) motifs are linked by symmetry-related hydrogen bonds to give the network shown in Figure 5.

The three-dimensional network of compound **3** is illustrated in Figure 6. Large channels with internal dimensions of ca. 8.5 × 11.3 Å^2 run along the *a* axis. These channels are occupied by the $[4\text{-}(Me_2N)C_5H_4NH]^+$ cations which are bonded to the triphosphonic acid framework through hydrogen bonds. Interestingly, supramolecular aggregates prepared from nitrilotri(methylphosphonic acid) with various amines were recently reported to give three-dimensional hexagonal structures with channel dimensions close to the values found for compound **3**.[27] A closer look at the structures of compounds **2** and **3** reveals an interesting relationship. Both are composed of similar staircase-type layers as a result of the planar stacking of the benzene rings (Figure 6). In compound **3** hydrogen bonds connect these layers to give the 3-D structure whereas in compound **2** the additional cations prevent the interconnection, resulting in the 2-D structure.

As a result of the proton transfer from the phosphonic acid to 4-(dimethylamino)pyridine, negative charge is introduced into the hydrogen-bonded network resulting in a very robust framework. The hydrogen bond energy of anionic O−H···O$^-$ bonds in phosphonic acids is significantly increased compared with that of the corresponding O−H···O bond and consequently the O−H···O$^-$ bonds are markedly shorter.[14] In agreement with this observation, the average O(H)···O distances in compounds **2** and **3** are 2.492 and 2.523 Å, respectively. Both distances are significantly shorter than the average O(H)···O distance of 2.607 Å calculated for the most stable gas-phase monoanion of *tert*-butylphosphonic acid, $[\{t\mathrm{BuP(O)_2(OH)}\}\{t\mathrm{BuP(O)(OH)_2}\}_2]^-$.[14] In the solid state typical P−O(H)···O−P distances in the range 2.45−2.60 Å were reported for organic ammonium salts of phosphonic acids. To the best of our knowledge the lower limit is determined by a distance of 2.413 Å reported for an aggregate of nitrilotri(methylphosphonic acid) with phenanthroline.[27,28] The shortest O(H)···O distance in compound **2** amounts to 2.431(2) Å.

The IR spectrum of the triphosphonic acid **1** shows a broad absorption band centred at 3360 cm^{-1}. In contrast, distinct absorption bands at 3240, 3110, 3107 and 2977 cm^{-1} are observed in compound **3** which are red-shifted to

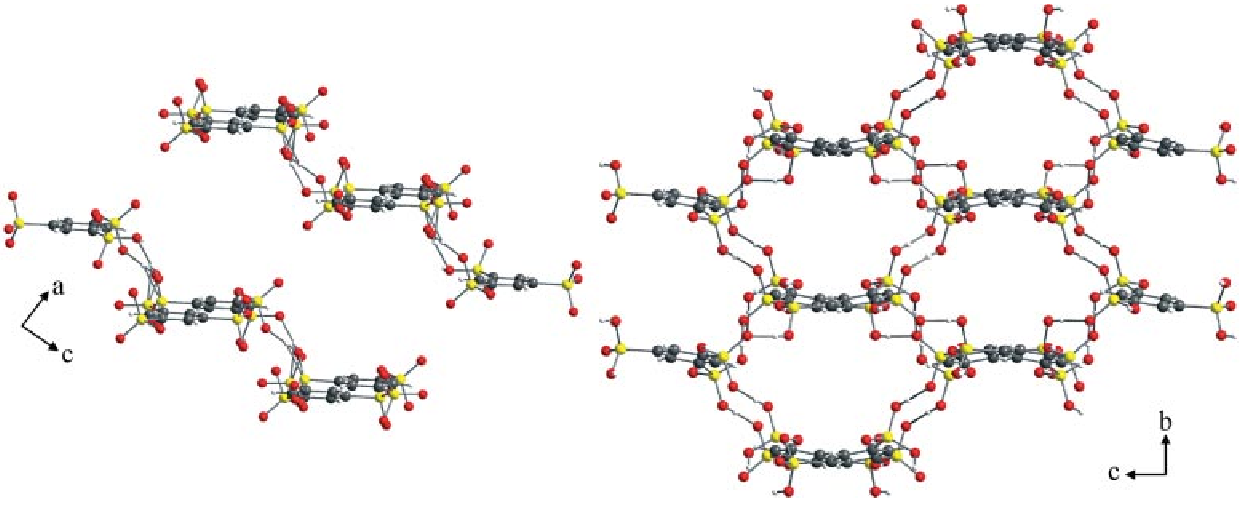

Figure 6. View of the 2-D structure of **2** (left) and the 3-D structure of **3** (right); the cations $[4\text{-}(Me_2N)C_5H_4NH]^+$ are omitted for clarity (carbon: dark grey; phosphorus: yellow; oxygen: red; hydrogen: light grey)

3213, 3100, 3065 and 2938 cm^{-1} in compound **2**. The bands at 3240 cm^{-1} (**3**) and 3213 cm^{-1} (**2**) are assigned to the O−H stretching of a phosphonic acid moiety. No assignment is made for the bands in the region 2938−3110 cm^{-1} which are associated with the O−H vibration as well as with the C−H vibration of 4-(dimethylamino)pyridine.

The thermal stability of compounds **2** and **3** is increased compared to that of the triphosphonic acid **1**. The latter decomposes at 248 °C. The DTA-TG measurements show that **3** starts to melt at 265 °C; an exothermic peak at 365 °C is indicative of its decomposition. The 1:2 adduct **2** starts to decompose at 319 °C without prior melting at lower temperatures.

Conclusion

The co-crystallisation of 1,3,5-$[(HO)_2(O)P]_3C_6H_3$ and 4-(dimethylamino)pyridine gives a two-dimensional structure for the 1:2 adduct **2** and a three-dimensional network for the 1:1 adduct **3**. Although both compounds **2** and **3** are composed of a large number of different hydrogen bond patterns, their structures are best described by the assembly of simple hydrogen-bonded motifs using the graphset theory. In adduct **2** the motifs R2,2(8) and R4,4(16) are interconnected to give a one-dimensional ribbon and the benzene spacer connects these ribbons to give a layered structure. In adduct **3** the R2,3(10) motif is observed solely. Hydrogen bonding connects the motif into a layer and the benzene spacer connects the layers to give a three-dimensional network. This network contains hexagonal channels which are occupied by 4-(dimethylamino)pyridinium cations, $[4\text{-}(Me_2N)C_5H_4NH]^+$. Our results demonstrate that the phosphorus counterpart of 1,3,5-$(HO_2C)_3C_6H_3$ (H_3TMA), the triphosphonic acid 1,3,5-$[(HO)_2(O)P]_3C_6H_3$ (**1**), is a promising building unit in the growing field of supramolecular chemistry and crystal engineering. In contrast to H_3TMA, it allows the design of 3-D networks. The extension of the reported work to other amines will add to the fundamental understanding of the self-assembly process of phosphonic acids and represents a step towards the rational design of 3-D hydrogen-bonded frameworks. Furthermore, the triphosphonic acid **1** holds potential for the preparation of novel three-dimensional metal phosphonates.

Experimental Section

General Remarks: Solvents were distilled from appropriate drying agents prior to use. Elemental analyses were performed with an instrument from Carlo Erba Strumentzione (model 1106). Thermal analyses were recorded using a vacuum thermoanalyser TA1 from Mettler Instrumente AG. The DTA-TG measurements were performed at a heating rate of 6 °C min^{-1} to a maximum temperature of 700 °C in flowing nitrogen using Al_2O_3 as the reference material. ^1H and ^{31}P NMR spectra were recorded at 200.13 MHz (^1H) and 80.02 MHz (^{31}P) at room temperature. Chemical shifts δ are given in ppm and were referenced against Me_4Si (^1H) and 85% H_3PO_4 (^{31}P). IR spectra were obtained with a Bruker FTIR IFS 113v spectrometer and run as KBr discs. Electrospray ionisation mass spectrometric analyses (ESI-MS) were recorded in the positive and the negative mode with a Thermoquest-Finnigan instrument using $MeOH/H_2O$ (1:1) as the mobile phase. The compounds were dissolved in $MeOH/H_2O$ and then diluted with the mobile phase to give solutions of approximate concentration 0.1 mM. The samples were introduced with a syringe pump operating at 10 µL/min. The capillary voltage was kept at 4.5 kV, while the cone-skimmer voltage was varied in the positive mode between 50 and 110 V, and in the negative mode between −70 and −80 V. The ion source temperature was kept at 280 °C. The *m*/*z* values reported correspond to those of the most intense peaks in the corresponding isotope pattern. Similar ESI-MS spectra of compounds **1**−**3** were obtained in the negative mode. In the positive mode the ESI-MS spectra of compounds **2** and **3** are dominated by the 4-(dimethylamino)pyridinium cation $[4\text{-}(Me_2N)C_5H_4NH]^+$ (*m*/*z* = 122.6), but show a similar peak pattern in the range *m*/*z* = 200−1000 as observed for compound **1**.

Graphset Theory:[37] Graphset descriptors indicate the hydrogen bond motif by the general form *Ga*,*d*(*n*). *G* describes the structural unit: C for a chain, D for a finite dimeric system, R for a cyclic system, S for intramolecular hydrogen bonds. The symbols *d* and *a* define the numbers of hydrogen bond donors and acceptors, respectively. The symbol *n* defines the total number of atoms in a motif.

1,3,5-$[(HO)_2(O)P]_3C_6H_3$ (1): Bromotrimethylsilane (27.9 g, 182.03 mmol) was added with a syringe to a solution of 1,3,5-$[(i\text{Pr-}O)_2(O)P]_3C_6H_3$ [36] (10.0 g, 18.20 mmol) in 150 mL of CH_2Cl_2 at 0 °C. The solution was stirred at room temperature for 12 h and after the addition of 250 mL of MeOH, the solution was heated at reflux for 4 h. The solvent was removed in vacuo to give a brownish solid. Addition of 100 mL of acetonitrile gave a suspension. The solid material was filtered off and crystallised from water to give **1** (3.5 g, 61%) as a colourless solid which decomposes at 248 °C. $C_6H_9O_9P_3$ (318.1): calcd. C 22.7, H 2.9; found C 22.3, H 2.8. ^1H NMR (200.13 MHz, [D$_4$]MeOH): δ = 8.25−8.47 (m) ppm. ^{31}P NMR (81.02 MHz, [D$_4$]MeOH): δ = 14.1 ppm. ESI-MS (positive mode, 101 V): *m*/*z* (%) = 318.9 (13) $[1,3,5\text{-}\{(HO)_2(O)P\}_3C_6H_3 + H]^+$, 336.6 (8) $[1,3,5\text{-}\{(HO)_2(O)P\}_3C_6H_3 + H_2O + H]^+$, 350.8 (24) $[1,3,5\text{-}\{(HO)_2(O)P\}_3C_6H_3 + CH_3OH + H]^+$, 636.8 (100) $[2 \times 1,3,5\text{-}\{(HO)_2(O)P\}_3C_6H_3 + H]^+$, 954.8 (14) $[3 \times 1,3,5\text{-}\{(HO)_2(O)P\}_3C_6H_3 + H]^+$, 1272.9 (6) $[4 \times 1,3,5\text{-}\{(HO)_2(O)P\}_3C_6H_3 + H]^+$. ESI-MS (negative mode, −71 V): *m*/*z* (%) = 280.7 (3) $[1,3,5\text{-}\{(HO)_2(O)P\}_3C_6H_3 - 2\ H_2O - H]^-$, 289.9 (12) $[2 \times 1,3,5\text{-}\{(HO)_2(O)P\}_3C_6H_3 - 3\ H_2O - 2\ H]^{2-}$, 298.7 (22) $[1,3,5\text{-}\{(HO)_2(O)P\}_3C_6H_3 - H_2O - H]^-$, 316.8 (100) $[1,3,5\text{-}\{(HO)_2(O)P\}_3C_6H_3 - H]^-$, 330.8 (17) $[1,3,5\text{-}\{(HO)_2(O)P\}_3C_6H_3 - H_2O + CH_3CN - H]^-$, 348.8 (8) $[1,3,5\text{-}\{(HO)_2(O)P\}_3C_6H_3 + CH_3CN - H]^-$, 616.8 (4) $[2 \times 1,3,5\text{-}\{(HO)_2(O)P\}_3C_6H_3 - H_2O - H]^-$, 634.9 (46) $[2 \times 1,3,5\text{-}\{(HO)_2(O)P\}_3C_6H_3 - H]^-$. IR (KBr): ṽ = 278 (w), 303 (w), 360 (w), 470 (m), 537 (m), 580 (w), 606 (w), 693 (m), 740 (w), 805 (w), 890 (m), 916 (m), 947 (m), 995 (s), 1166 (s, br.), 1400 (w), 1655 (s, br.), 2325 (s, br.), 3360 (vs, br.) cm^{-1}.

$[1\text{-}\{(HO)_2(O)P\}\text{-}3,5\text{-}\{(HO)(O)_2P\}_2C_6H_3]^{2-}[\{4\text{-}(Me_2N)C_5H_4NH\}^+]_2$ (2): A solution of 4-(dimethylamino)pyridine (385 mg, 3.15 mmol) in 1 mL of MeOH was added to a solution of 1,3,5-$[(HO)_2(O)P]_3C_6H_3$ (500 mg, 1.57 mmol) in 25 mL of MeOH. A colourless suspension formed and a mixture of 60 mL of MeOH and 50 mL of H_2O was added. The suspension was heated at reflux for 10 min and filtered. Colourless crystals of **2** (410 mg, 46%), which start to decompose at 319 °C, were formed upon slow evap-

Table 2. Crystallographic data for compounds **2** and **3**

	2	**3**
Empirical formula	$C_{20}H_{29}N_4O_9P_3$	$C_{13}H_{19}N_2O_9P_3$
Formula mass	526.38	440.22
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	*Pbca*
Cell constants		
a [Å]	10.271(2)	14.681(3)
b [Å]	14.582(3)	14.891(3)
c [Å]	17.041(3)	16.546(3)
β [°]	105.65(3)	
Volume [Å^3]	2457.7(9)	3617.3(12)
Z	4	8
Density(calculated) [Mg·m^{-3}]	1.520	1.617
Absorption coefficient [mm^{-1}]	0.301	0.381
Crystal size [mm]	0.10 × 0.12 × 0.12	0.12 × 0.10 × 0.12
Theta range for data collection	3.02 to 25.35	3.14 to 27.47
Reflections collected	11338	28062
Independent reflections	4583 [R_{int} = 0.035]	4408 [R_{int} = 0.055]
Goodness-of-fit on F^2	0.871	0.917
R indices [$I > 2\sigma(I)$]	$R1$ = 0.0369, $wR2$ = 0.0783	$R1$ = 0.0311, $wR2$ = 0.0634
R indices (all data)	$R1$ = 0.0688, $wR2$ = 0.0634	$R1$ = 0.0783, $wR2$ = 0.0688
Largest diff. peak/hole [e·Å^{-3}]	0.223/−0.384	0.298/−0.376

oration of the solvent. $C_{20}H_{29}N_4O_9P_3$ (562.4): calcd. C 42.7, H 5.2, N 10.0; found C 43.0, H 5.3, N 10.1. ^{1}H NMR (200.13 MHz, D_2O): δ = 3.03 (s, 12 H, NMe_2), 6.70 (d, 4 H, H_{py}), 7.82 (d, 4 H, H_{py}), 7.94−8.07 (m, 3 H, H_{ar}) ppm. ^{31}P NMR (81.02 MHz, D_2O): δ = 13.2 ppm. IR (KBr): ṽ = 530 (m, br.), 704 (m), 740 (w), 808 (m), 936 (m), 1065 (m), 1130 (m), 1218 (m), 1401 (w), 1442 (w), 1563 (s), 1648 (s), 1873 (w), 1951 (m), 2051 (m), 2938 (s), 3065 (s), 3100 (s), 3213 (s) cm^{-1}.

[1,3-$\{(HO)_2(O)P\}_2$-5-$\{(HO)(O)_2P\}C_6H_3]^-[4-(Me_2N)C_5H_4NH]^+$ (3): A solution of 4-(dimethylamino)pyridine (150 mg, 1.23 mmol) in 1 mL of MeOH was added to a solution of 1,3,5-[$(HO)_2(O)P]_3C_6H_3$ (318 mg, 1.23 mmol) in 10 mL of MeOH. A colourless suspension formed which was dissolved in a mixture of 40 mL of MeOH and 10 mL of H_2O by warming to 50 °C. Colourless crystals of **3** (240 mg, 44%) with a melting point of 265 °C formed upon slow evaporation of the solvent. $C_{13}H_{19}N_2O_9P_3$ (440.2): calcd. C 35.5, H 4.4, N 6.4; found C 35.5, H 4.5, N 6.5. ^{1}H NMR (200.13 MHz, D_2O): δ = 3.00 (s, 6 H, NMe_2), 6.67 (d, 2 H, H_{py}), 7.79 (d, 2 H, H_{py}), 7.96−8.10 (m, 3 H, H_{ar}) ppm. ^{31}P NMR (81.02 MHz, D_2O): δ = 13.6 ppm. IR (KBr): ṽ = 405 (w), 446 (w), 487 (w), 540 (m), 696 (m) 811 (w), 948 (m), 998 (s), 1220 (m), 1384 (w), 1401 (w), 1443 (w), 1564 (m), 1599 (w), 1649 (m), 2281 (s, br.), 2977 (s), 3107 (s), 3110 (s), 3240 (s) cm^{-1}.

X-ray Crystallographic Study: Intensity data for the colourless crystals were collected with a Nonius KappaCCD diffractometer with graphite-monochromated Mo-K_α radiation at 173 K. The data collection covered almost the whole sphere of reciprocal space with two (**2**) and four sets (**3**) at different κ angles and 79 (**2**) and 248 (**3**) frames by ω-rotation (Δ/ω = 1°) at two times 110 (**2**) and 30 s (**3**) per frame. The crystal−detector distance was 3.4 cm. Crystal decay was monitored by repeating the initial frames at the end of data collection. Analysis of the duplicate reflections gave no indication of any decay. The structure was solved by direct methods SHELXS-97[38] and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods (SHELXL-97).[39] The H atoms were located in the difference Fourier map and refined isotropically. Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from *International Tables for X-ray Crystallography.* The figures were created by SHELXTL.[40] Crystallographic data are given in Table 2. CCDC-223048 and -223049 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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