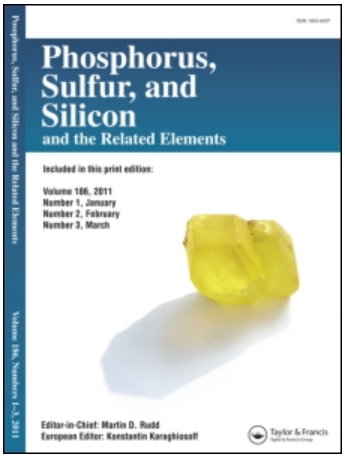

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Self-Assemblies of Extended Hydrogen-Bonded Arrays Using 1,4-Butanebisphosphonic Acid as a Versatile Building Block

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SELF-ASSEMBLIES OF EXTENDED HYDROGEN-BONDED ARRAYS USING 1,4-BUTANEBISPHOSPHONIC ACID AS A VERSATILE BUILDING BLOCK

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*Two organic salts of 1,4-butanebisphosphonic acid, bis(ethylenediammonium) butanebisphosphonate hydrate (**1**) and bis(hexamethylenediammonium) butanebisphosphonate hydrate (**2**), have been structurally characterized using single-crystal x-ray diffraction analyses. Compound **1** exhibits a H-bonded pillared bilayered structure, in which etheylenediammonium cation acts as a spacer between the anions resulting in the formation of two types of cavities. The larger cavity is filled by four water molecules though having hydrophobic character. Thus, the material behaves as a nanoporous organic solid. Compound **2** shows a multidimensional hydrogen bonding networks: one-dimensional arrays parallel to the* b *axis and two-dimensional sheets parallel to the* ab *plane. The N–H···O–P hydrogen bonds, forming H-bonded supramolecular networks, are regarded to be strong and directional hydrogen bonds.*

Keywords: Bisphosphonates; crystal structure; hydrogen bonding; nanoporous solids; supramolecular array

INTRODUCTION

The use of phosphonic acid in the context of supramolecular chemistry and crystal engineering has been limited mainly to metal phosphonates.[1–3] Multifunctional phosphonic acids, such as bisphosphonic acids, aminophosphonic acids, and carboxyphosphonic acid, have

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proven to be good candidates for the preparation of pillared layered metal phosphonates and formation of microporous solids.[3] The idea of using bisphosphonic acids, $H_2O_3P{-}R{-}PO_3H_2$, first has been introduced for the preparation of organized multilayered assemblies of metal bisphosphonates in the form of thin solid films.[1–3]

It has been shown that another interesting property of organic phosphorus acids, namely potential to form extended hydrogen bonded assemblies, could be utilized for preparation of one-, two-, and three-dimensional structures.[4–13] They exhibit similar structural features to their inorganic counterparts (metal phosphonates). This property is related to the three-dentate character and the tetrahedral geometry of the phosphonate moieties. Structure correlations between organic and inorganic salts of phosphonic acid are fascinating and give an insight into the structural possibilities, which facilitates the design of new solid materials.[11–13] Indeed, structural elucidation of metal phosphonates often suffers from the lack of crystalline material suitable for single crystal or powder diffraction studies. Therefore, results from the structural studies of soluble organic or inorganic salts of phosphonic acids are of principle value in the field.[9–13] We recently have reported the crystal structures of butanebisphosphonic acid and its two organic ammonium salts with aniline and *p*-phenylazoaniline.[13]

Here we report the structures of two organic ammonium salts of 1,4-butanebisphosphonic acid with ethylenediamine (**1**) and 1,6-hexamethylenediamine (**2**). These materials are showing complex hydrogen bonded networks. We will demonstrate that bisphosphonic acids are remarkably versatile building blocks for assembling extended structures of both organic and inorganic types.

EXPERIMENTAL

1,4-Butanebisphosphonic acid was purchased from ACROS. ORGANICS. 1,6-Hexamethylenediamine was donated by DuPont. Other chemicals were obtained from Aldrich and Fluka and were used without any further purification. Bis(ethylenediammonium) butanebisphosphonate hydrate (**1**) and bis(hexamethylenediammonium) butanebisphosphonate hydrate (**2**) have been obtained in quantitative yields by mixing the acid (0.1 mmol) and organic amine (0.2 mmol) dissolved separately in the ethanol (5 mL). Then distilled water (~3 mL) was added to the resulting white suspension to obtain a clear solution. After heating to the boiling point of the solvent, the solutions were set aside to crystallize and exposed to air. Slow evaporation of the solvents after few days gave crystals suitable for diffraction studies. 1,4-Butanebisphosphonic

TABLE I Crystallographic and Refinement Data

	1	**2**
Empirical formula	$C_{16}H_{64}N_4O_{16}P_2$	$C_{16}H_{46.66}N_4O_{8.33}P_2$
Crystal system	Triclinic	Monoclinic
Space group	P-1 (No. 2)	C2/c (No. 15)
a [Å]	10.7689(2)	20.4352(7)
b [Å]	12.5685(2)	6.0550(2)
c [Å]	13.9898(1)	42.2056(12)
α [°]	90.024(1)	90
β [°]	108.930(1)	92.720(1)
γ [°]	97.150(1)	90
V [Å^3]	1775.49(5)	5216.4(3)
Z, ρ (calc.) [g· cm^{-3}]	2, 1.180	8, 1.254
T [K]	183(2)	183(2)
μ [mm^{-1}]	0.185	0.212
Refl. collec./unique	11180/6107	11271/3643
R (int.)	0.028	0.051
Data/restrain/parameter	6107/0/405	3643/4/296
R1/wR2 (I>2σ(I))	0.056/0.170	0.065/0.153
R1/wR2 for all data	0.069/0.188	0.093/0.168
Goodness-of-fit on F^2	1.035	1.092
Largest diff. peak/hole [e. Å^{-3}]	1.056/−0.440	0.368/−0.438

[*] $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$.

acid. ^{1}H NMR (200 MHz, D_2O): δ 1.72 (*s*, *br*). ^{31}P NMR (81 MHz, D_2O): δ +35.15.

Bis(ethylenediammonium) butanebisphosphonate hydrate (**1**). m.p. 294°C (decomp.). ^{1}H NMR (200 MHz, D_2O): δ 1.67 (*s*, *br*), 3.23 (*s*, *br*). ^{31}P NMR (81 MHz, D_2O): δ +26.28. Bis(hexamethylene-diammonium) butanebisphosphonate hydrate (**2**). m.p. 298°C (decomp.). ^{1}H NMR (200 MHz, D_2O): δ 1.54 (*m*), 1.77 (*t*), 3.08 (*t*). ^{31}P NMR (81 MHz, D_2O): δ +26.28.

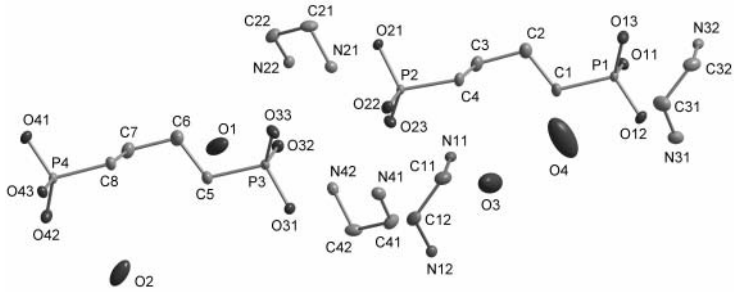

FIGURE 1 The molecular structure of **1** including atom-numbering scheme.

TABLE II The Geometry* of Hydrogen Bonds [Å,°]

Notation	D—H···A	d(D—H)	d(H···A)	d(D···A)	<(DHA)
	1				
{a}	N11—H11A···O41^{i}	0.91	1.86	2.761(3)	168
{b}	N11—H11B···O21^{ii}	0.91	1.87	2.768(3)	168
{c}	N11—H11C···O42^{iii}	0.91	1.81	2.720(3)	173
{d}	N12—H12A···O41^{iii}	0.91	1.79	2.694(3)	174
{e}	N12—H12B···O11^{iv}	0.91	1.83	2.721(3)	167
{f}	N12—H12C···O43^{i}	0.91	1.92	2.821(3)	172
{g}	N21—H21A···O33	0.91	1.82	2.725(3)	173
{h}	N21—H21B···O11^{v}	0.91	1.87	2.767(3)	167
{i}	N21—H21C···O22	0.91	1.85	2.751(3)	170
{j}	N22—H22A···O21	0.91	1.95	2.857(3)	173
{k}	N22—H22B···O21^{vi}	0.91	1.84	2.734(3)	165
{l}	N22—H22C···O32	0.91	1.78	2.684(3)	172
{m}	N31—H31A···O12	0.91	1.81	2.715(3)	178
{n}	N31—H31B···O43^{vii}	0.91	1.93	2.803(3)	159
{o}	N31—H31C···O11^{viii}	0.91	2.00	2.909(3)	178
{p}	N32—H32A···O12^{viii}	0.91	1.85	2.750(3)	172
{q}	N32—H32B···O31^{ix}	0.91	1.88	2.767(3)	165
{r}	N32—H32C···O13	0.91	1.86	2.758(3)	171
{s}	N41—H41A···O22	0.91	1.82	2.724(3)	179
{t}	N41—H41B···O31^{vii}	0.91	1.91	2.785(3)	161
{u}	N41—H41C···O31	0.91	1.94	2.853(3)	177
{v}	N42—H42A···O32	0.91	1.86	2.759(3)	170
{x}	N42—H42B···O43^{x}	0.91	1.87	2.762(3)	165
{y}	N42—H42C···O23	0.91	1.85	2.754(3)	169
	2				
{a}	N21—H21A···O11	0.91	1.97	2.882(5)	175
{b}	N21—H21B···O1^{i}	0.91	1.93	2.782(5)	156
{c}	N21—H21C···O2^{ii}	0.91	1.88	2.763(5)	163
{d}	N22—H22A···O22^{ii}	0.91	1.81	2.699(4)	164
{e}	N22—H22B···O23^{iii}	0.91	1.80	2.711(4)	178
{f}	N22—H22C···O21	0.91	1.83	2.731(5)	169
{g}	N31—H31A···O13^{ii}	0.91	2.20	3.056(6)	156
{h}	N31—H31B···O13^{iv}	0.91	1.87	2.774(5)	176
{i}	N31—H31C···O11	0.91	1.91	2.814(5)	175
{j}	N32—H32A···O23	0.91	1.86	2.745(5)	164
{k}	N32—H32B···O21^{iv}	0.91	1.90	2.811(4)	176
{l}	N32—H32C···O22^{ii}	0.91	1.80	2.707(5)	171
{m}	O1—H1A···O11^{v}	0.81(2)	2.06(3)	2.799(5)	152(6)
{n}	O1—H1B···O12	0.81(2)	1.87(2)	2.673(5)	173(6)
{o}	O2—H2A···O12^{i}	0.81(2)	1.99(3)	2.756(4)	159(5)
{p}	O2—H2B···O12	0.82(2)	1.86(2)	2.674(5)	170(5)
	C21—H21E···O2	0.99	2.57	3.360(6)	137
	C34—H34A···O22^{ii}	0.99	2.49	3.327(6)	142

*Symmetry transformations used to generate equivalent atoms: **1**: (i) x + 2, y, z; (ii) −x + 1, −y + 1, −z; (iii) −x, −y, −z; (iv) x, y−1, z; (v) x−1, y, z; (vi) −x, −y + 1, −z; (vii) −x, −y + 1, −z + 1; (vii) −x + 2, −y + 2, −z + 1; (ix) x + 1, y + 1, z; (x) x + 1, y, z **2**: (i) −x, −y + 2, −z; (ii) x, y−1, z; (iii) −x + 1/2, y−1/2, −z + 1/2; (iv) −x + 1/2, y + 3/2, −z; (v) x, y + 1, z.

Crystal Structure Determination

All data were collected using a Siemens SMART CCD three-cycle diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å, graphite monochromator). Full sphere of reciprocal lattices were scanned by 0.3° steps in ω with a crystal-to-detector distance of 5.97 cm. Preliminary orientation matrices were obtained from the first frames using SMART.[14] The collected frames were integrated using the preliminary orientation matrices that were updated every 100 frames. Final cell parameters were obtained by refinement on the positions of reflections with $I > 10\delta(I)$ after integration of all the frames using SAINT.[14] The data were empirically corrected for absorption and other effects using SADABS.[15] The structures were solved by direct methods and refined by full-matrix least squares on all F^2 data using SHELXTL.[16] The non-H atoms were refined anisotropically, while the H atoms were refined isotropically. The hydrogen atoms on water molecules of **1** have not be located, while for two water molecules of **2**, were located from difference Fourier map and refined with a restrained bond distance of 0.8 Å. Molecular graphics were obtained using Diamond.[17] Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Center as supplementary publication no. CCDC-171902 (**1**) and CCDC-171903 (**2**). (Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

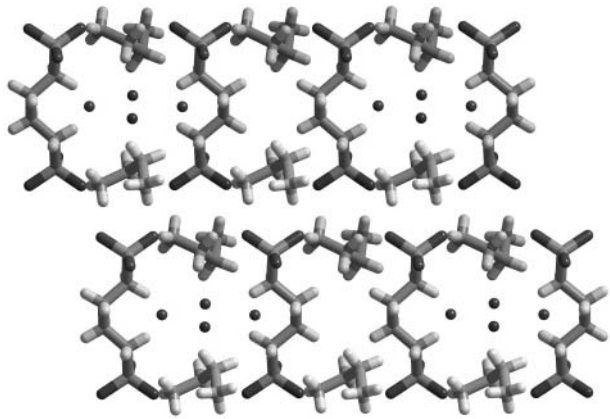

FIGURE 2 Representation of a pillared bilayered unit for **1** including water molecules. The (C–)H atoms are not shown for clarity.

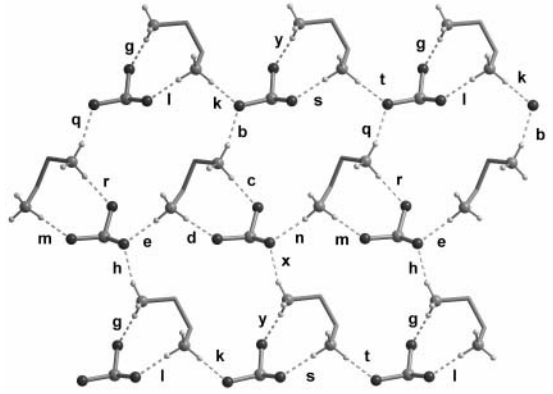

FIGURE 3 The H-bonding network making layers in the structure of **1**. Notations for H-bonds are given according to Table II.

RESULTS AND DISCUSSION

The crystallographic and refinement data for compounds **1** and **2** are summarized in Table I. The geometry of hydrogen bonds is given in Table II.

Bis(ethylenediammonium) butanebisphosphonate hydrate (**1**) crystallizes in the triclinic system with space group P-1 (No. 2). The asymmetric unit contains two bisphosphonate dianions, four ethylenediammonium dications, and four water molecules (see Figure 1). The compound exhibits a pillared bilayered structure, in which the

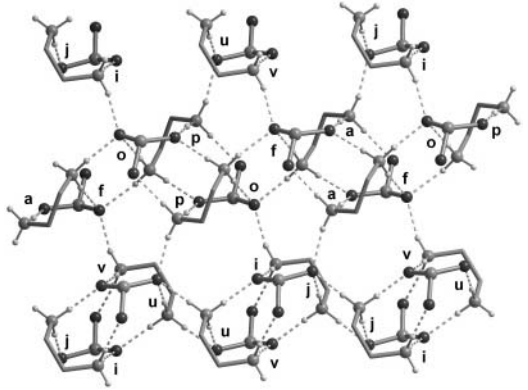

FIGURE 4 Adjacent layers in **1** are linked together via the N–H···O–P H-bonds. Notations for H-bonds are given according to Table II.

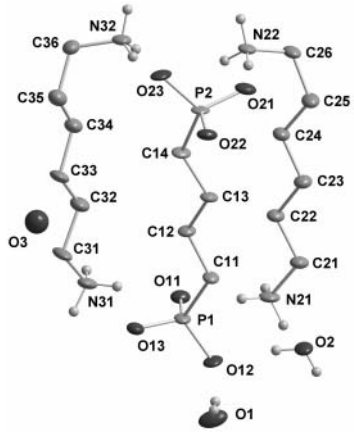

FIGURE 5 The molecular structure of **2** including atom-numbering scheme.

H-bonded sheets are linked together via the alkyl chains of bisphosphonates dianions. Ethylenediammonium dication acts as a spacer between the pillars and thus forming two types of channels (see Figure 2). The channels are interconnected making a two-dimensional net parallel to the H-bonded sheets (the *ab* plane). Larger channels with diameter ~5.7 Å are hosting solvent water molecules. Due to hydrophobic character of these channels, water molecules are not tightly bonded and thus can be removed. Therefore, compound **1** behaves as a nanoporous (also referred to as microporous) organic solid material.[18,19] These materials are related closely to metal bisphosphonates with porous structure. There are two reports on the metal bisphosphonates using butanebisphosphonic acid.[20,21] The supramolecular architecture of three-dimensional H-bonded network of **1** can be described as pillared bilayers linked together via the H-bonds. Architecture of a layer, as a subnetwork, is shown in Figure 3. The [g and l], [y and s], [r and m], or [c and d] hydrogen bonds are forming R2,2(9*) ring motifs. R5,6(19) supramolecular ring motifs are built up from [l, q, r, c, b, and k], [t, s, b, c, n, and q], [d, e, h, k, y, and x] or [m, n, x, t, g, and h] hydrogen bonds. Adjacent layers are linked together by the N—H···O—P hydrogen bonds as shown in Figure 4.

The asymmetric unit of bis(hexamethyelendiammonium) butanebisphosphonate hydrate (**2**) contains two diammonium cations, one

*Assignment of the H-bond descriptors are based on the graph-set theory and previously described.[22] For convenience, the notation Xa,d(n) also has been adopted in this article, in which (X) is the pattern descriptor, (a) is number of acceptors, (d) is number of donors, and (n) is the number of atoms comprising the pattern.

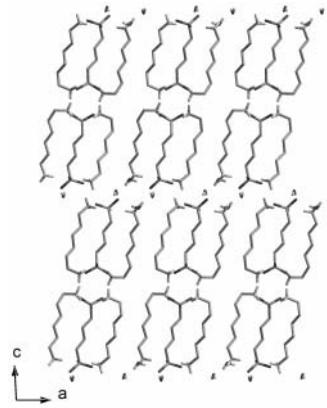

FIGURE 6 Representation of the bilayered structure of **2**. The (C–)H atoms are not shown for clarity.

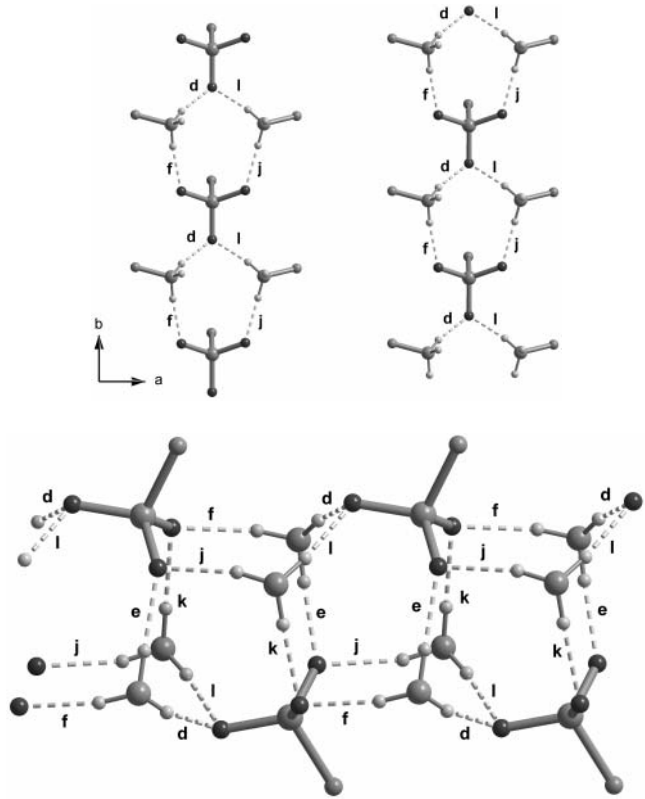

FIGURE 7 One-dimensional H-bonded arrays in the structure of **2**. Notations for H-bonds are given according to Table II.

bisphosphonate dianion, and three water molecules: one of them (O3) has a site occupancy factor of 0.33 (see Figure 5). The structure is composed of interpenetrating pillared H-bonded ribbons each comprising dimeric tapes. Water molecules are contributing in H-bonding network and linking bilayers together (see Figure 6). Material shows no porosity as seen for **1**, but can be regarded as an inclusion compound since water molecules are present between the bilayers.

Supramolecular architecture can be described by its subnetworks: ribbons (along *b* axis) and layers (parallel to *ab* plane). Each ribbon is formed by linking two chains. The hydrogen bonding subnetwork is shown in Figure 7. Two phosphonate dianion and two ammonium cations are linked together via [d, f, j, and l] H-bonds forming chains

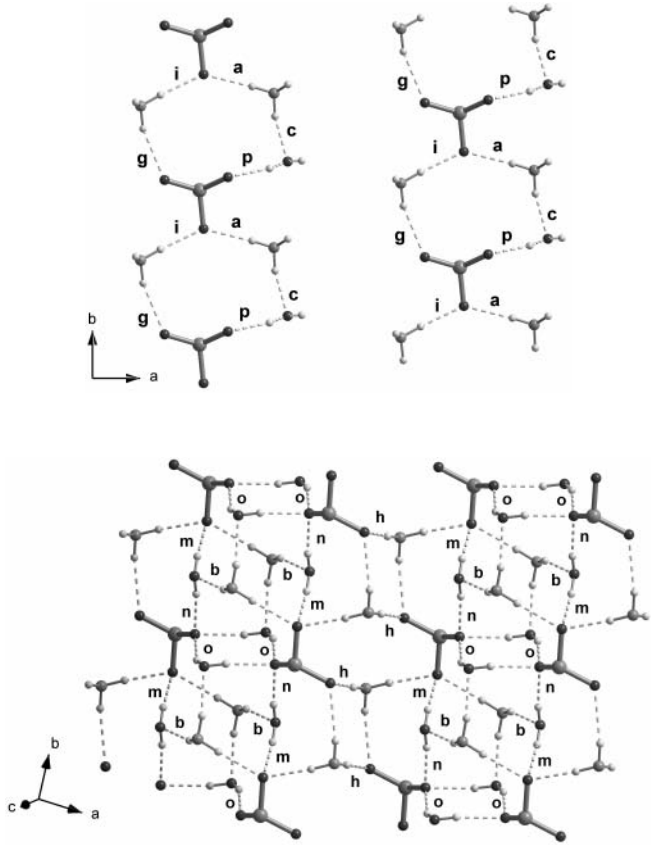

FIGURE 8 The H-bonded chains (top) are linked together to form a two-dimensional network (bottom) in the crystal structure of **2**. See Table II for H-bond notations.

of R3,4(10) ring motifs along *b* axis. These chains are then connected to each other by [e and k] hydrogen bonds (making new R3,4(10) ring motifs) to form ribbons (see Figure 7). On both sides of ribbons along alkyl pillars two phosphonate groups, two ammonium groups, and one water molecule are bonded together via [a, i, g, p, and c] H-bonds forming chains of R4,5(12) ring motifs. Chains are then zipped together by [o and h] hydrogen bonds making a two-dimensional H-bonded network (see Figure 8). Water molecules (O1) are linking chains together via [b, m, and n] H-bonds.

CONCLUSION

Crystal structures of two organic salts of 1,4-butanebisphosphonic acid are reported in this study. Butanebisphosphonate anions are capable of forming extended hydrogen bonds and they are acting as H-bond acceptor from diammonium moieties. Analysis of the N—H···O—P hydrogen bonds, with the N···O distances ranging from 2.68 to 3.05 Å and the N—H···O angles of 156–179°, indicates the strength and directionality of these type of interactions for the compounds in this study as we have also seen for organic ammonium salts of phenylphosphonic acid[12] and butanediphosphonic acid.[13] Compound **1** with a nanoporous structure could be used a model to design a new class of organic nanoporous materials based on bisphosphonic acids. Further experiments are being performed to investigate the host-guest properties of compound **1**.

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