

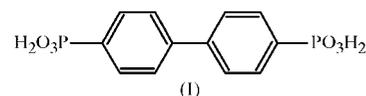
Hydrogen-bonded network in  
biphenyl-4,4'-diphosphonic acidG. Próchniak,<sup>a</sup> J. Zoń,<sup>a</sup> M. Daszkiewicz,<sup>b</sup> A. Pietraszko<sup>b</sup>  
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The crystal structure of the title compound, C<sub>12</sub>H<sub>12</sub>O<sub>6</sub>P<sub>2</sub>, displays two different regions alternating along the *a* axis: a hydrogen-bonded region encompassing the end-positioned phosphonic acid groups and a hydrophobic region formed by the aromatic spacers. The asymmetric unit contains only half of the biphenyl-4,4'-diphosphonic acid (4,4'-bpdp) molecule, which is symmetric with an inversion centre imposed at the mid-point between the two aromatic rings. The periodic organization of the molecules is controlled by two strong O—H...O interactions between the phosphonic acid sites. Weak C—H...π interactions are established in the aromatic regions.

## Comment

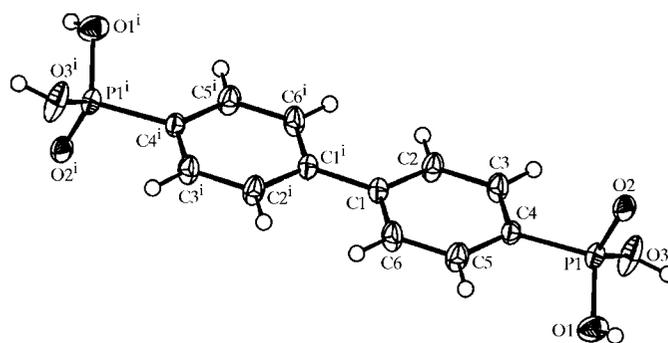
Studies aimed at building predictable structures span from hydrogen-bonded supramolecular networks to hybrid metal-organic frameworks (MOF). The establishment of porosity in coordination polymer structures has been a challenging but central goal in solid-state chemistry, since by analogy with zeolites, it opens up possibilities for chemical separation, gas sorption, ion exchange, sensing and catalysis. The most important factors determining MOFs are the chemical and geometrical preferences of the metal ion and the specificity of the bridging polydentate ligand. Therefore, variable metal-organic phosphonates have been studied with respect to their potential applications in many of the above areas (Kong *et al.*, 2006; Sharma *et al.*, 2000; Cabeza *et al.*, 2002). Bisphosphonates can bind with different coordination modes (from  $\eta^1\mu_1$  up to  $\eta^6\mu_6$ ) depending upon the level of deprotonation and the stereo-accessibility of the donating lone pairs from one side, and the geometry of the metal ion 'vacant' sites from the other side. This allows for the formation of variable coordination arrays (Matczak-Jon & Videnova-Adrabińska, 2005). The use of a rigid spacer between the end-functional sites in diphosphonates reduces the orientational freedom of the ligand and makes the frameworks more predictable (Cao *et al.*, 2004). A distance of 10.665 Å between the two

phosphonate groups in biphenyl-4,4'-diphosphonic acid, (I), allows for porosity of organic-inorganic hybrid networks (Zhang *et al.*, 1998; Poojary *et al.*, 1996). Despite the usefulness of arenediphosphonate molecules as ligands, the crystal structures of the corresponding acids are not known. We present here the crystal organization and the supramolecular network of (I).



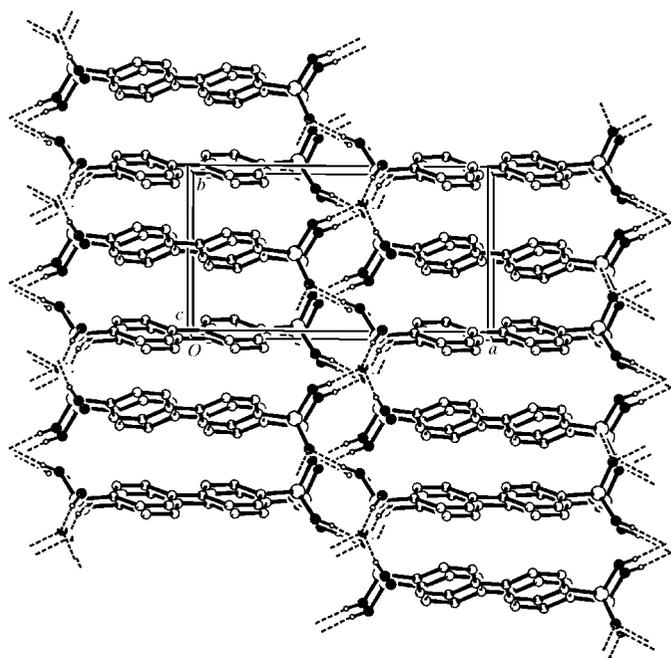
The acid molecule is symmetric with an inversion centre imposed at the mid-point between the two benzene rings (Fig. 1) and, thus, the asymmetric unit of the crystal comprises only one-half of the molecule. The two benzene rings are coplanar and slightly deformed. The P—O bonds of the phosphonic acid group are bisectonal and the P=O bond is axial with respect to the mean molecular plane. Therefore, the spatial orientations of the hydrogen-bond donor and acceptor sites in (I) are not appropriate for the formation of the  $R_2^2(8)$  motifs (Bernstein *et al.*, 1995) observed in the ribbon extensions of dicarboxylic acids, and the studied compound displays a three-dimensional supramolecular network.

A search of the Cambridge Structural Database (CSD, Version 5.27; Allen, 2002) revealed only a single diphosphonic acid structure, the triclinic polymorph of butane-1,4-diphosphonic acid, which forms ribbons *via*  $R_2^2(8)$  (Mahmoudkhani & Langer, 2002). Two different hydrogen-bond interactions control the organization of the molecules in the crystal structure. One of them, assigned as O1—HO1...O2 [2.546 (2) Å], is used to connect the reflection-related molecules in order to form thick molecular monolayers (*bc*). The second hydrogen bond, O3—HO3...O2 [2.568 (2) Å], is established between rotation-related molecules belonging to neighbouring layers and, therefore, joins the monolayers. The overall crystal structure displays two different regions alternating along the *a* axis: the hydrophilic regions where the phosphonic acid groups are arranged and the hydrophobic regions, where the aromatic spacers reside. The biphenyl rings in the latter



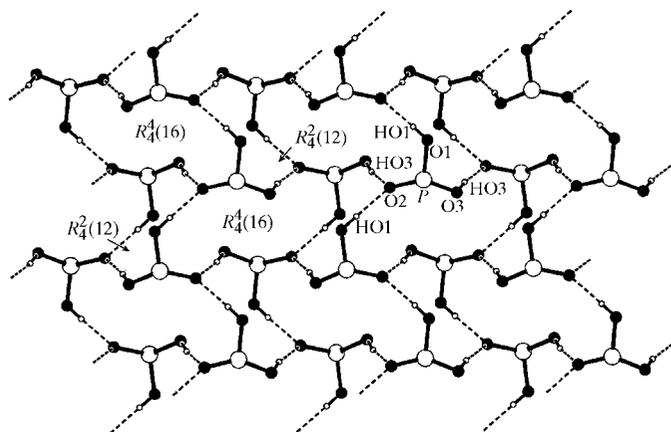
**Figure 1**  
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i)  $-x, 1 - y, 1 - z$ .]

region are arranged with a  $c$ -translation distance in order to form two differently oriented stacks alternating along the  $b$  axis. C—H $\cdots\pi$  interactions are established between adjacent (reflection-related) stacks in the monolayer (Fig. 2). However, with regard to the basic forces responsible for the solid-state organization of the compound and the observed supramolecular network, it is reasonable to describe the structure in terms of pillared hydrogen-bonded monolayers. Thus, each phosphonic acid group serves to bridge four neighbouring phosphonic acid groups in order to form a two-dimensional hydrogen-bonded network parallel to the  $bc$  crystallographic plane (Fig. 3). The (P1)—O3—HO3 $\cdots$ O2(=P1) bond



**Figure 2**

A view of the pillared crystal structure demonstrating the relationships between the differently oriented aromatic stacks. Hydrogen bonds are shown as dashed lines.



**Figure 3**

Presentation of the two-dimensional hydrogen-bonded network and the ring motifs generated. Hydrogen bonds are shown as dashed lines.

extends the screw-related sites into formal chains along the  $b$  axis and (P1)—O1—HO1 $\cdots$ O2(=P1) links the chains into a puckered two-dimensional network. Two centrosymmetric motifs  $R_4^2(12)$  and  $R_4^1(16)$  are generated between the  $c$ -glide chains and propagate along the  $b$  axis. The biphenyl rings, aligned from both sides of the monolayers, act as linkers (pillars) between them and follow the symmetry demands of the hydrogen-bond network.

Only four structures of unsubstituted diphosphonic acids with functional sites not located on the same C atom were found in the CSD and they all belong to the  $\alpha,\omega$  aliphatic family with between 2 and 4 C atoms. The crystal packing of the even-numbered diacids displays some similarity to that of (I). The phosphonic acid sites are also arranged in hydrogen-bonded monolayers, but the connection patterns and symmetry relations, both inside the monolayers and between them, are different. Due to the shortness and flexibility of the aliphatic linker, the pillaring effect is not well expressed. The triclinic polymorph of butanediphosphonic acid demonstrates a two-dimensional interpenetration of two symmetry-independent hydrogen-bonded [via  $R_2^2(8)$ ] ribbons. Numerous hydrogen bonds crosslink two symmetry-independent molecular units of propanediphosphonic acid extending them into a three-dimensional network.

## Experimental

The synthesis of the title compound was carried out in two steps starting from 4,4'-dibromobiphenyl (6.27 g, 0.020 mol) and following a known procedure (Wang *et al.*, 2003). However, the method of isolation of tetraethyl biphenyl-4,4'-diphosphonate was modified and 1,3-diisopropylbenzene and other volatile components of the reaction mixture were removed under reduced pressure. The black residue obtained was extracted with cyclohexane ( $3 \times 50$  ml), filtered, and left for crystallization. The crystals were filtered off and dried in air in order to obtain the crude product (yield: 7.08 g, 83%), which was recrystallized from cyclohexane (30 ml) to obtain pure tetraethyl biphenyl-4,4'-diphosphonate (yielded: 5.73 g, 67%, m.p. 354–356 K).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.29 (*t*,  $J = 7.1$  Hz, 12H,  $\text{CH}_3$ ), 3.96–4.18 (*m*, 8H,  $\text{OCH}_2$ ), 7.58–7.65 (*m*, 4H,  $\text{C}_6\text{H}_4$ ), 7.78–7.88 (*m*, 4H,  $\text{C}_6\text{H}_4$ ).  $^{31}\text{P}\{\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ ):  $\delta$  20.05 (*s*). IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 2986, 2904, 1134, 1249, 1055, 1025, 960, 795, 768, 563, 536. Biphenyl-4,4'-diphosphonic acid was obtained by refluxing tetraethyl biphenyl-4,4'-diphosphonate (4.09 g, 0.0959 mol) in concentrated HCl (40 ml) and water (40 ml) and stirring for 12 h. The resulting solid was filtered off, washed with water (5 ml) and dried in air to yield the final product, (I) (yield: 2.08 g, 93%).  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O-NaOD}$ ):  $\delta$  7.65–7.85 (*m*,  $\text{C}_6\text{H}_4$ ).  $^{31}\text{P}\{\text{H}\}$  NMR (121 MHz,  $\text{D}_2\text{O-NaOD}$ ):  $\delta$  12.83 (*s*). IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 2929, 2710, 2269, 2203, 1601, 1140, 1047, 1001, 547, 525. Crystals suitable for X-ray measurements were obtained from a water–methanol mixture (3:1 *v/v*). The solution was heated and stirred for 2 h. The resulting clear solution was sealed in small glass containers and heated at 348 K for 2 d. Small plate-shaped crystals were obtained upon slow cooling (at a rate of 1 K  $\text{h}^{-1}$ ). The melting point was measured on an Electrothermal Engineering Ltd Melting Point Apparatus IA9100. Five independent measurements show that the crystals melt in the temperature range 632–637 K.

Crystal data

C<sub>12</sub>H<sub>12</sub>O<sub>6</sub>P<sub>2</sub> V = 616.07 (17) Å<sup>3</sup>  
 M<sub>r</sub> = 314.16 Z = 2  
 Monoclinic, P2<sub>1</sub>/c Mo Kα radiation  
 a = 13.0552 (18) Å μ = 0.38 mm<sup>-1</sup>  
 b = 7.0852 (10) Å T = 293 K  
 c = 6.7287 (13) Å 0.53 × 0.35 × 0.02 mm  
 β = 98.176 (14)°

Data collection

Kuma KM-4 diffractometer with a 6361 measured reflections  
 CCD area detector 1246 independent reflections  
 Absorption correction: numerical 879 reflections with I > 2σ(I)  
 (X-SHAPE; Stoe & Cie, 1998) R<sub>int</sub> = 0.044  
 T<sub>min</sub> = 0.873, T<sub>max</sub> = 0.988

Refinement

R[F<sup>2</sup> > 2σ(F<sup>2</sup>)] = 0.036 109 parameters  
 wR(F<sup>2</sup>) = 0.088 Only H-atom coordinates refined  
 S = 0.98 Δρ<sub>max</sub> = 0.32 e Å<sup>-3</sup>  
 1246 reflections Δρ<sub>min</sub> = -0.49 e Å<sup>-3</sup>

Table 1

Selected geometric parameters (Å, °).

P1—O2	1.4920 (15)	C1—C1 <sup>i</sup>	1.496 (4)
P1—O3	1.5287 (17)	C2—C3	1.383 (3)
P1—O1	1.5329 (17)	C3—C4	1.380 (3)
P1—C4	1.777 (2)	C4—C5	1.388 (3)
C1—C6	1.382 (3)	C5—C6	1.379 (3)
C1—C2	1.386 (3)		
O2—P1—O3	114.83 (10)	C6—C1—C1 <sup>i</sup>	121.3 (2)
O2—P1—O1	111.38 (9)	C2—C1—C1 <sup>i</sup>	121.4 (2)
O3—P1—O1	109.12 (10)		
C1 <sup>i</sup> —C1—C2—C3	178.7 (2)	O3—P1—C4—C5	148.30 (19)
O2—P1—C4—C3	89.1 (2)	O1—P1—C4—C5	33.4 (2)
O3—P1—C4—C3	-34.0 (2)	C2—C1—C1 <sup>i</sup> —C6 <sup>i</sup>	0.1 (3)
O1—P1—C4—C3	-148.96 (19)	C2—C1—C1 <sup>i</sup> —C2 <sup>i</sup>	180.0 (2)
O2—P1—C4—C5	-88.6 (2)		

Symmetry code: (i) -x, -y + 1, -z + 1.

The H atoms were visible in the difference maps and were refined with isotropic displacement parameters correlated with the anisotropic displacement parameters of the atoms to which they were bonded [C—H = 0.93 (2)–0.96 (2) Å and U<sub>iso</sub>(H) = 1.2U<sub>eq</sub>(C) or 1.5U<sub>eq</sub>(O)].

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford

Table 2

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O1—HO1...O2 <sup>ii</sup>	0.83 (3)	1.72 (3)	2.546 (2)	171 (3)
O3—HO3...O2 <sup>iii</sup>	0.83 (3)	1.74 (3)	2.567 (2)	170 (3)

Symmetry codes: (ii) x, -y + ½, z - ½; (iii) -x + 1, y + ½, -z + ½.

Diffraction, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *publCIF* (Westrip, 2007).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3089). Services for accessing these data are described at the back of the journal.

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