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Chains, layers, channels and more – supramolecular chemistry of potent diphosphonic tectons with tuned flexibility. The generation of pseudopolymorphs, polymorphs, and adducts

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ABSTRACT

Naphthalene-1,5-diphosphonic acid $[C_{10}H_6(PO_3H_2)_2, H_4NDP(1,5), 1]$ and its more flexible counterpart – naphthalene-1,5-bis(methylphosphonic) acid $[C_{10}H_6(CH_2PO_3H_2)_2, H_4NDP(1C,5C),$ 2] – have been synthesized, characterized and used as building blocks in supramolecular assemblies with 4-(*N*,*N*-dimethylamino)pyridine (DMAP) and morpholine. The two acids generate two distinct solvatomorphs each, which all contain dimethyl sulfoxide (DMSO) molecules. The two adducts of H₄NDP(1,5) with DMAP (**3A** and **3B**) reveal conformational polymorphism caused by the rotation of phosphonic groups. The two adducts of H₄NDP(1C,5C) show unexpected structural diversity, generating a symmetric hydrogen bond and creating a layered structure **4A** or a channel structure **4B**. The adducts of both acids with morpholine (**5A** and **5B**) allow for observing the influence of the conformational flexibility of the acids on the dimensionality of a final hydrogen bond network, which is in general higher for H₄NDP(1C,5C). The structural motifs and trends are analyzed in terms of the geometric criteria of these interactions. For the first time, Hirshfeld surface analysis has also been applied for the investigation of supramolecular interactions of phosphonic acids in different protonation states.



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Naphthalene-1,5-diphosphonic acid $[C_{10}H_6(PO_3H_2)_2$, $H_4NDP(1,5)$, 1] and its more flexible counterpart – naphthalene-1,5-bis(methylphosphonic) acid $[C_{10}H_6(CH_2PO_3H_2)_2$, $H_4NDP(1C,5C)$, 2] – have been synthesized, characterized and used as building blocks in supramolecular assemblies with 4-(*N*,*N*-dimethylamino)pyridine (DMAP) and morpholine. The two acids generate two distinct solvatomorphs each, which all contain dimethyl sulfoxide (DMSO) molecules. The two adducts of $H_4NDP(1,5)$ with DMAP (**3A** and **3B**) reveal conformational polymorphism caused by the rotation of phosphonic groups. The two adducts of $H_4NDP(1C,5C)$ show unexpected structural diversity, generating a symmetric hydrogen bond and creating a layered structure **4A** or a channel structure **4B**. The adducts of both acids with morpholine (**5A** and **5B**) allow for observing the influence of the conformational flexibility of the acids on the dimensionality of a final hydrogen bond network, which is in general higher for $H_4NDP(1C,5C)$. The structural motifs and trends are analyzed in terms of the geometric criteria of these interactions. For the first time, Hirshfeld surface analysis has also been applied for the investigation of supramolecular interactions of phosphonic acids in different protonation states.

INTRODUCTION

Crystal engineering is an already well-established but continuously developing branch of material science.^{1,2} Nevertheless, the accurate prediction of a structure and the properties of a product from the structures of basic substrates, which can be considered a designing process, remains the ultimate goal.^{2,3} The exploration of new crystal structures and interactions responsible for such an arrangement brings a lot of useful information concerning factors important in structure formation, which enables drawing more general conclusions, helpful in the

design process.^{4,5} Geometrical criteria are usually used in the analysis of intermolecular interactions. Recently, Hirshfeld surface (HS) analysis has also become a potent tool for structural investigations.^{6,7}

It should, however, be noted that supramolecular assemblies are vulnerable to environmental changes. From the same building blocks, one can obtain different supramolecular products, depending on the kind of interactions that prevail in the applied conditions. Such supramolecular isomers, with the same chemical composition but different structural arrangements, constitute a group of polymorphs.^{8,9} If the composition is variable only due to the presence of solvent molecules, one is dealing with the pseudopolymorphism (also known as solvatomorphism) phenomenon.¹⁰⁻¹² Both polymorphism and pseudopolymorphism are significant in terms of the modulation of the physicochemical properties of materials, which manifests itself, for example, in pharmacy.¹¹⁻¹⁶

Nonetheless, an important step in crystal structure design is the careful selection of building blocks that will constitute the final solid. Selected units need to contain functional groups that are able to create intermolecular bonding with prefixed directionality. When organic solids are considered, hydrogen bonding is the most important and the most widely studied interaction,¹⁷ which can be supported, for example, by less directional but still influential π - π aromatic interactions.^{18,19} Due to this fact, organic acids containing aromatics in their scaffold are frequently utilized in the synthesis of new materials. Such versatile molecules provide a great opportunity for the introduction of a design factor to the final product structure.

A naphthalene ring is one of the most important aromatic platforms for organic functional ligands. It is usually divergently substituted with functional groups accessible for intermolecular interactions, *i.e.* coordination or hydrogen bonding. This platform is successfully applied in a

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number of novel structures. If a functional group is considered, the most widely explored one, especially in the context of Metal-Organic Frameworks, is the carboxylic group. 1,4- and 2,6- disubstituted naphthalenes perform an important role as linear, rigid linkers between metal centres.^{20,21} In this context, naphthalene-1,5-dicarboxylic acid is prevalent in patent literature.²²⁻²⁵

It is quite the opposite case when the sulfonic function (-SO₃H) is applied.^{26,27} Naphthalene-1,5-disulfonic acid [H₂NDS(1,5)] is frequently used as an organic building unit for supramolecular assemblies,²⁸⁻³³ and in coordination chemistry – as a counter ion^{34,35} or coordination polymer linker.³⁶⁻⁴³ The CSD search⁴⁴ provided 194 structures into which NDS(1,5) moiety is incorporated. In general, sulfonic acids have quite different properties from carboxylic acids. They are much more acidic, thus remain ionized in a wide pH range and are more soluble. The sulfonic group is tetrahedral due to an additional oxygen atom bonded to a central sulfur atom, which introduces some additional conformational flexibility in comparison to the carboxylic group.

Following this approach, substitution of the sulfonic group by a geometrically similar phosphonic one, *i.e.* -PO₃H₂, should give new potent phosphonic tectons,^{45,46} also with some advantages over sulfonated molecules: 1) phosphonic acids are more stable in a free state, whereas sulfonic acids are usually handled as sodium salts; 2) coordination structures of phosphonic acids are less labile and often have high thermal stability; 3) phosphonic acids are also a little less acidic and have two deprotonation states. Especially this last fact enriches the supramolecular chemistry of the phosphonic function in terms of hydrogen bond network generation, as well as providing a better control of accessibility to lone electron pairs due to gradual deprotonation of the group. Such a tecton opens new paths to obtaining novel organic

solids and metal phosphonates, which have already grown into a potent family of hybrid materials.^{27,47-50}

Scheme 1. Representation of potent organic tectons based on a 1,5-naphthalene scaffold: dicarboxylic (NDC), disulfonic (NDS), and diphosphonic (NDP) acids.



In view of the fact that naphthalene-1,5-disulfonic acid is an important tecton, we have obtained its phosphonic analogue, namely naphthalene-1,5-diphosphonic acid, $[H_4NDP(1,5)]$, which had previously remained a missing link in the series of 1,5-disubstituted naphthalenes (Scheme 1). To enable the study of the conformational flexibility issue, we have also obtained its flexible counterpart – naphthalene-1,5-bis(methylphosphonic) acid, $[H_4NDP(1C,5C)]$, with methylene groups introduced between the ring and each group. This facilitates the accommodation of the groups to the requirements of engineered networks, especially coordination ones. We have discussed this behavior in our recent paper concerning the first diphosphonic acids based on a naphthalene ring.¹⁰ There, two 1,4-disubstituted acids proved to be useful in the synthesis of crystalline lanthanum phosphonates with the evident influence of pH and the flexibility of the ligand on the final hybrid structures. Herein, we present two easily obtainable 1,5-diacids (**1** and **2**) as potent supramolecular building units, exploring their abilities

to generate pseudopolymorphs (1A-2B), polymorphs and adducts with 4-(N,N-dimethylamino)pyridine (3A-4B), and morpholine (5A, 5B) (see Scheme 2). We also apply geometrical criteria for interaction analysis assisted by Hirshfeld surface analysis of phosphonic tectons in such diverse environments.

Scheme 2. The building units used in this article and the symbols of the structures.



EXPERIMENTAL SECTION

Synthesis of phosphonic acids. Both compounds (1 and 2) were obtained in accordance with well-known methods^{51,52} with high yield and simple workup (see Electronic Supporting Information (ESI) for detailed description and characterization). During the phosphonylation step of the process (the transformation of compound *b* to *c* in Scheme 3), nickel-catalyzed cross-coupling^{53,54} was applied for 1 and the Arbuzov reaction⁵⁵ for 2. Scheme 3 summarizes the synthetic route for both diphosphonic acids. Their DMSO solvatomorphs were obtained through the slow cooling of saturated DMSO/water solutions (see ESI for details).

Scheme 3. Synthesis of phosphonic acids: a) naphthalene-1,5-diphosphonic acid [1, $H_4NDP(1,5)$]; and b) naphthalene-1,5-bis(methylphosphonic) acid [2, $H_4NDP(1C,5C)$].



Synthesis of acid-base adducts. The general procedure is as follows:

0.10 mmol of acid [0.0288g of H₄NDP(1,5) or 0.0316 g of H₄NDP(1C,5C)] were mixed with a few cm³ of solvent and one equivalent [for $4\mathbf{A} - C_{10}H_6(CH_2PO_3H)_2(C_7H_{11}N_2)_2 \cdot 2H_2O$ and for $4\mathbf{B} - C_{10}H_6(CH_2PO_3H)(CH_2PO_3H_2)(C_7H_{11}N_2) \cdot H_2O$] or two equivalents [for $3\mathbf{A}$ and $3\mathbf{B} - C_{10}H_6(PO_3H)_2(C_7H_{11}N_2)_2$] of $4 \cdot (N,N \cdot dimethylamino)$ pyridine (DMAP). The mixtures were filtered (and also refluxed for $3\mathbf{A}$ and $3\mathbf{B}$) and left for slow evaporation at room temperature. After a few weeks, colorless crystals were obtained with yields ranging from 20 to 60 %. The adducts of both acids with morpholine [$5\mathbf{A} - C_{10}H_6(PO_3H)_2(C_4H_8ONH_2)_2$ and $5\mathbf{B} - C_{10}H_6(CH_2PO_3H)_2(C_4H_8ONH_2)_2$] were obtained from appropriate mixtures with an excess of amine (detailed description in ESI).

X-ray crystallography. All the obtained single crystals were used for data collection on a four-circle KUMA KM4 diffractometer equipped with a two-dimensional CCD area detector. Graphite monochromatized MoK α radiation ($\lambda = 0.71073$ Å) and the ω -scan technique ($\Delta \omega = 1^{\circ}$) were also used for data collection, while additional data collection and reduction, along with absorption correction, were performed using the *CrysAlis* software package.⁵⁶ The structures were solved by direct methods using *SHELXS-97*,⁵⁷ revealing the positions of almost all non-hydrogen atoms. The remaining atoms were located as a result of subsequent difference Fourier syntheses. The structures were refined using *SHELXL-97*⁵⁷ with anisotropic displacement

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parameters. Details of the data collection parameters, crystallographic data and final agreement parameters are listed in Table S1, while selected geometrical parameters can be found in Table S2. The geometry of the hydrogen bonds is listed in Table S3. Visualisation of the structures was conducted using the *Diamond* program,⁵⁸ while a topological simplification of HB networks was performed with the *Topos* package.⁵⁹ Some geometrical features of intermolecular interactions were determined with the help of *Platon* software,⁶⁰ while the Hirshfeld surface and 2D fingerprint calculations⁶¹ were performed using the *Crystal Explorer* package.⁶²

Hirshfeld surface analysis. Hirshfeld surface analysis is a method with a different philosophy than traditional structure viewing: it treats molecular interactions as being a whole.⁶³ Such an analysis provides information about all existing interactions in the structure, not only about those that arbitrarily seem to be important for a crystal engineer. Information about interactions is conveyed by the use of color-coding the surface properties (*i.e.* d_{norm} , shape index, and curvedness functions) onto the surface,⁶⁴ thus the localization of contacts of interest is achieved using color differentiation. HS analysis is almost always connected with considerations of 2D Fingerprint Plots (FP).^{65,66} In such plots, relative areas of points, which can be attributed to certain close contacts, are identified and their percentage share is provided. This quantification of molecular interactions enables an objective comparison of crystal structures. The visual breakdown of the HS and FP into selected contacts (decomposed HSs and FPs) allows for selective viewing and analyzing of a particular type of interactions. HS analysis is also a helpful tool in the comparison of very similar polymorph structures.^{8,67}

RESULTS AND DISCUSSION

The synthesis of phosphonic acids. The synthesis of acids (1 and 2) from commercially available substrates proceeds in three steps, with good to excellent yields. The main step is a

phosphonylation reaction of appropriate dihalides [catalyzed with NiBr₂ for H₄NDP(1,5)]. The dihalides can be dibromide as well as diiodide, but variants of the reactions presented in Scheme 3 appear to be the easiest to access. The molecular structures of obtained esters have been confirmed by spectroscopic examinations as well as single crystal X-ray diffraction studies (**6A** and **6B**) (Fig. S7). Although ester **2c** is mentioned in the available literature, no detailed synthetic and physicochemical descriptions are provided.^{68,69} After a simple workup, the obtained tetraesters can be subjected to an acidic hydrolysis reaction in order to obtain final acids as white solids. Free phosphonic acids are usually utilized as organic building blocks, especially in coordination polymer synthesis. Nonetheless, esters can be hydrolyzed *in situ* in appropriate conditions, providing interesting metal phosphonate structures.^{70,71}

Pseudopolymorphism observed for the structures of acids

Despite the enormous interest in metal phosphonate chemistry, less pronounced investigations of the structures of free phosphonic acids in their solid state have been conducted thus far. However, the examination of such structures can provide valuable information about a given organic building unit and its preferences concerning supramolecular network generation.^{10,72-80}

In the case of both acids, 1 and 2, we describe such structures together with their solvatomorphs (unsolvated – 1A and 2A; and solvated – 1B and 2B). The majority of organic molecular crystal structures do not contain incorporated organic solvents, but if such solvent molecules are present, DMSO is one of the most frequently occurring,⁸¹ and this is also the case here, which allows for an exploration of the solvent's effects on these systems.

Naphthalene-1,5-diphopshonic acid, NDP(1,5) (1A) and its DMSO solvate (1B). The pseudopolymorphs of $H_4NDP(1,5)$ show to what extent the presence of solvent molecules can affect a final superstructure. The free acid crystallizes in the *Pbca* space group. Due to the

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internal C_i symmetry, the molecule lies at the inversion centre, thus the asymmetric unit is comprised of half of the molecule (Fig. S1). All molecules in **1A** are arranged in a well-known motif in phosphonate chemistry, where phosphonic groups constitute hydrogen-bonded layers and are interconnected in the third dimension by organic linkers, in this case – 1,5-disubstituted naphthalenes (Fig. 1). The separation of HB layers is *ca*. 0.5 Å higher for such a linker than for the analogous 1,4-disubstituted naphthalene (6.95 Å vs. 6.40 Å from one terminal phosphorous atom to the other).¹⁰

The predominant force responsible for the arrangement of the molecules is hydrogen bonding. A hydrogen bond network is two dimensional (Fig. 2), parallel to the *ab* plane and is built from two crystallographically independent O-H···O hydrogen bonds (Table S3). Hydroxyl oxygen atoms are single donors, while a phosphoryl oxygen atom is a double acceptor of HBs. This leads to a motif that can be described, according to the graph set theory,⁸² as a second-order R_4^3 (14) ring motif. The complete network is constructed by the multiplication of the motif using a- and b-glide planes. From another point of view, this network can be rebuilt from two first-order chains C(4) constituted by each hydrogen bond. The first one, O1-P1-O3-H3O, is propagated along [100] (light blue), and the second, O1-P1-O2-H2O, runs along [010] (dark blue). The connection of HB layers in the third direction by naphthalene linkers results in the generation of a 3D network.



Figure 1. Projections of the crystal structures of solvatomorphs a) **1A** and b) **1B** together with their topological simplifications.

Acceptor sites are visible on the shape index surface (Fig. S8) as slightly elongated red depressions of the HS above the naphthalene fused ring. Complementary donor sites of these interactions are marked blue around the aromatic hydrogen atoms.

The supramolecular structure of the second pseudopolymorph, **1B**, is drastically different from **1A**: the typical layered structure is broken (Fig. 1). The crystal's symmetry is reduced to the $P\overline{1}$ space group. The asymmetric unit (Fig. S1) consists of half of the acid molecule and one DMSO molecule. Thus, there are two DMSO molecules per one H₄NDP(1,5) moiety. Each solvent molecule is therefore connected *via* an O5····H3-O3 hydrogen bond to the one phosphonic group.

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Another intermolecular hydrogen bonding, (O2-H2···O1), connects adjacent phosphonic groups providing a strong $R_2^2(8)$ motif. This synthon holds together the acid molecules, generating a supramolecular chain which runs along the *c* axis (Fig. 2).



Figure 2. Isolated hydrogen-bonded networks for a) **1A** and b) **1B**. Dashed lines symbolize hydrogen bonds.

DMSO molecules act as pendants in these chains. They also participate in the interactions that hold the whole crystal together in the two other directions. In Figure S8, DMSO molecule interactions with the acid molecule are presented using the shape index surface of **1B**. Along the *a* and *c* axes, mainly van der Waals and H₂C-H···O interactions can be observed. The latter ones appear as red spots around the phosphonic group, as well as being present in the 2D fingerprint plot (Table S4) with $d_e = 1.12$ Å and $d_i = 1.42$ Å. Along the *b* axis, one can distinguish C-H···Cg interactions between one methyl group and the naphthalene ring.

Naphthalene-1,5-bis(methylphosphonic) acid, NDP(1C,5C) (2A) and its DMSO solvate, 2B. H₄NDP(1C,5C) molecules undergo a self-assembly process providing a layered structure, similarly to 1A. Crystal 2A belongs to the monoclinic crystal system with the $P2_1/c$ space group. The asymmetric unit of 2A is, analogically to 1A, comprised of half of the acid molecule (Fig. S1). The organization of the molecules in the crystal is shown in Figure 3. Layers are arranged in an ABAB fashion and are parallel to the *bc* plane. The HB layers are connected by 1,5-





Figure 3. Projections of the crystal structures of solvatomorphs a) **2A** and b) **2B** together with their topological simplifications.

An isolated hydrogen-bonded layer is presented in Figure 4. Another similarity to the **1A** structure can be seen due to the presence of two independent hydrogen bonds (Table S3). Nonetheless, they contribute to the generation of two second-order supramolecular motifs: $R_4^2(12)$ and $R_4^4(16)$. The inversion centre lies at the centre of both motifs. The network can also be considered an assemblage of two first-order graph set motifs. Each hydrogen bond creates one

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C(4) motif, developing the network along the *b* and *c* axis (O1-P1-O3-H3 – dark blue, and O1-P1-O2-H2 – light blue, respectively).



Figure 4. Isolated hydrogen-bonded networks for a) **2A** and b) **2B**. Dashed lines symbolize hydrogen bonds.

The solvent molecules interact with H₄NDP(1C,5C) molecules in a different manner than with H₄NDP(1,5). It may be due to the higher conformational flexibility of the acid molecule, which enables better accommodation of the supramolecular system to external stimuli (DMSO molecules). In the solvated structure **2B**, one deals with the insertion of solvent molecules into the HB layer (Fig. 3). This results in the reduction of the overall dimensionality from 3D to 2D, as well as in the more pronounced separation of the layers, and in the increase of the cell constant *a* from 9.613 to 13.345 Å (*b* and *c* remain almost untouched). Also the β angle is much closer to 90°, but the overall crystal symmetry remains unaffected (Table S1). When analyzing only strong HBs, one can see a chain parallel to [001], composed of O1-P1-O2-H2 atoms. Such chains are joined by organic links along [010] creating a wavy 2D layer. However, DMSO molecules have a substantial influence on the intermolecular interactions present in the crystal. In turn, if the weak C-H···O bonds donated by DMSO are also explored, one can notice that 4 independent hydrogen bonds create 2 HB motifs much the same as in the case of **2A** (Fig. 4).

The HB motifs thus constructed are $R_4^2(10)$ and $R_4^4(16)$, which provides a topology of the HB layers very similar to **2A**. The most pronounced difference is that both these motifs are fourth-order, thus they include all 4 HBs, two of which are donated by the methyl group from the DMSO molecules. The second CH₃ group is directed beyond the layer plane and interacts with the inversion-related second layer through van der Waals and weak C-H…O interactions between the DMSO molecules (the unique C…O distances amount to: 3.34, 3.36, and 3.73 Å). H…H contacts (the main contributors of vdW) constitute 33.3 % of the acid's HS (Fig. 13).

Supramolecular adducts with 4-(N,N-dimethylamino)pyridine (DMAP)

Phosphonic acids are used in the synthesis of engineered organic solids with substantial success.^{73,76,83-89} The reactions of acids with a substituted pyridine base (DMAP) allow for an exploration of the rich supramolecular chemistry of such systems, where interactions can occur due to the presence of a protonated pyridine nitrogen atom, an aromatic ring or a bulky -N(CH₃)₂ substituent.^{86,90} The naphthalene-1,5-diphosphonic acid provides two polymorphic structures, **3A** and **3B**, where subtle conformational changes of the phosphonic group relative to the naphthalene ring introduce a different arrangement of the molecules. These differences can be derived from nucleation processes, in which slightly different crystallization systems are applied. This fact shows the significance of the solvent system on the supramolecular level.⁹¹ The second acid, H₄NDP(1C,5C), gives two kinds of adducts, one of which contains acid and base molecules in a 1:2 ratio (**4A**), similarly to polymorphs **3A** and **3B**, while the second – in a 1:1 ratio (**4B**). These different compositions introduce large structural changes to the final superstructures.

Polymorphs 3A and 3B. The polymorphic adducts of naphthalene-1,5-diphosphonic acid crystallize in the $P\overline{1}$ space group (acid as a dianion with two base molecules per one acid molecule). The asymmetric unit consists of half of the acid molecule and one base molecule (Fig.

S3). The pyridine nitrogen atom in a DMAP molecule is protonated, which is also confirmed by an almost 120° C-N-C angle. When analyzing distances for the P-O bond that (nearly) lies in a naphthalene plane, one can clearly observe that for **3A** there is a bond with the protonated oxygen atom P-OH (1.53 Å), and the electron density of the two remaining bonds is delocalized (1.50 and 1.51 Å). For **3B**, the bond in the plane is ascribed to P-O⁻ (1.51 Å), and the electron density is localized (1.58 Å for P-OH and 1.48 Å for P=O). Both these conformations can be seen in Figure S3. The foregoing observation has clear consequences on the geometrical features of both structures, despite the similar (or even the same – in the case of a low level of detail) topology of supramolecular units.



Figure 5. Projections of crystal structures of polymorphs a) **3A** and b) **3B** together with topological simplifications of the HB networks.

When analyzing only phosphonic acid molecules, hydrogen-bonded chains run along [111] for **3A** and [010] for **3B** (Fig. 5). Monodeprotonated phosphonic groups tend to generate dimeric $R_2^2(8)$ ring motifs, and this is the case in **3A** and **3B**. Strong hydrogen bonds are readily visible on the d_{norm} surface as red spots; while engagement of the phosphonic group of both adducts into a ring motif is visible as a set of two red spots that lie in a coplanar relation to each other. Base molecules serve as important supramolecular tectons in these networks. They are connected through a pyridinium nitrogen atom with the oxygen atom that is (for **3B**) or is not (for **3A**) involved in the $R_2^2(8)$ ring motif, providing N-H…O bonds (Table S3). The different acceptor sites of N-H…O hydrogen bonding are one of the most distinctive differences while viewing d_{norm} polymorph surfaces. In both structures, there is also one significantly stronger interaction, C10-H10…O1, donated by a carbon atom connected directly to the N⁺ pyridinium atom (which results in the activation of the C-H donor).⁹² Thus, other centrosymmetric motifs are generated: $R_4^2(10)$ for **3A** and $R_4^4(14)$ for **3B** (Fig. 6). The resulting 2D hydrogen-bonded layers are parallel to ($\overline{110}$) and (100), respectively.

The pyridine ring plays an important role in the stabilization of the structure, also due to extensive $\pi \cdots \pi$ and C-H $\cdots \pi$ interactions (Fig. S4 and Fig. 7 for the HS). A pair of inversion-related Py rings is arranged in an offset face-to-face manner. This pair is offset to the others and stacked along the *a* axis. The Py rings interact with the naphthalene ones as a result of an edge-to-face arrangement, which is confirmed by the inclination angle of ring planes and also the apparent C-H $\cdots \pi$ interaction (Table 1). Besides the interactions between the rings, the base molecules contribute to the structure's stabilization through C-H \cdots O hydrogen bonds and van der Waals forces, mainly from the *N*,*N*-dimethylamino group. Such an edge-to-face arrangement of the base molecules in both structures (**3A** and **3B**) finds its reflection in the shape index surfaces

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as a set of red spots above the acid's naphthalene ring. (Fig. 7). Additionally, the structures vary in the number of intramolecular C-H···O-P interactions within the H₄NDP(1,5) molecule, which stabilize the conformation of the phosphonic group (Fig. S3). In **3B**, one can find weaker C-H···O bonds donated by the naphthalene ring (C5) and a methyl group (C11) (Table S3 and Fig. S4). The higher number of C-H···O interactions in structure **3B** is reflected on the d_{norm} surface as lighter red spots in the phosphonic group's surroundings.



Figure 6. Isolated hydrogen-bonded networks for polymorphs a) **3A** and b) **3B**. Dashed lines symbolize hydrogen bonds. DMAP fragments are partially transparent for clarity.



Figure 7. Hirshfeld surfaces and 2D fingerprint plots for polymorphs a) **3A** and b) **3B**. Phosphonic tectons are mapped with their shape index (left) and d_{norm} (centre) functions. Specific short contacts are labeled.

The application of the geometrical criterion, *i.e.* a comparison of D-A distances and D-H-A angles, for HB strength leads to the conclusion that structure **3A** has a more optimized geometry with a slightly stronger hydrogen bond network. Additionally, an edge-to-face ring arrangement is closer to the optimal one for **3A** (~90°) than for **3B** (about 78°).

Table 1. A comparison of geometrical parameters for aromatic interactions in polymorphs **3A**and **3B**. Py – pyridinium ring, Naph – naphthalene ring.

Interacting Py rings	Py to Py distance	Py to Py inclination angle	Py to Py slippage (offset shift angle)	
3A				
pair	3.5364(8)	0	2.173 (31.57)	
between	3.5748(8)	0	2.634 (36.39)	

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3B				
pair	3.5350(8)	0	1.431 (22.04)	
between	3.5604(8)	0	1.813 (26.99)	
Py to Naph inclination angle	C-H…Cg distance	C…Cg distance	C-H…Cg angle	
		3A		
89.71(9)	C9-H9 2.99	3.833(2)	151	
3B				
77.73(8)	C7-H7 2.86	3.589(2)	137	

Adducts 4A and 4B. The structures of salts with H₄NDP(1C,5C) provide an opportunity to examine the impact of an acid to base molecules ratio on a final supramolecular arrangement. Adduct 4A, which has a 1:2 acid to base ratio, crystallizes in the triclinic $P\bar{1}$ space group. It presents a structure converging in many ways to structures **3A** and **3B**. The asymmetric unit is composed of half a molecule of acid, one protonated DMAP molecule and, additionally, one water molecule (Fig. S3). The arrangement of molecules (Fig. 8) is primarily governed by a set of HB motifs known from naphthalene-1,5-diphosphonic acid salts. The monodeprotonated phosphonic groups mounted on flexible -CH₂- links create the expected $R_2^2(8)$ motifs. The described synthon connects the acid molecules into supramolecular chains running along the $[1\overline{1}0]$ direction. Due to the presence of water molecules (the O4 atom), these chains are bridged by relatively weak HBs along the *a* axis (Fig. 9). This results in the generation of a hydrogenbonded layer parallel to the (001) plane, a topological simplification of which is depicted in Figure 8. When one introduces the DMAP molecules under consideration, it should be noted that they donate a hydrogen bond from the protonated nitrogen atom to an oxygen atom that is not involved in the $R_2^2(8)$ motif (analogy to polymorph **3A**). Deeper exploration shows additional C11-H11...O4 bonding provided by the *orto*-carbon atom from the pyridine ring donated to the water oxygen atom. On the other side of the NH⁺ group, there is another weakly donating carbon atom which generates C7-H7...O3 interaction with the protonated oxygen atom. These

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interactions are weaker than the corresponding C-H···O interaction in polymorphs (Table S3). Nevertheless, the former interaction creates centrosymmetric $R_6^4(14)$ motif with the N-H···O bond. The latter gives $[R_2^2(7)]$ and contributes to the stabilization of the crystal in the [001] direction, as well as to C-H··· π interactions between the pyridine and naphthalene rings.



Figure 8. Projections of crystal structures of adducts a) **4A** and b) **4B** together with topological simplifications of the HB networks.



Figure 9. Isolated hydrogen-bonded networks for adducts a) **4A** and b) **4B**. Dashed lines symbolize hydrogen bonds. The DMAP fragments and water molecules are partially transparent for clarity.

The reduction of the number of base (and water) molecules per acid molecule to a 1:1 ratio in **4B** leads to a structure with a monoclinic symmetry and has enormous structural consequences. The asymmetric unit consists of halves of acid, base and water molecules (Fig. S3). One DMAP molecule can accept only one proton; therefore, the second group should have two hydrogen atoms unaffected. However, due to the internal C_i symmetry of the acid molecule, both groups have to be the same, thus one hydroxyl group remains intact and the second proton lies at the inversion centre and is shared by two inversion-related phosphonic groups, constituting a strong symmetric hydrogen bond with the O…O distance of 2.468(3) Å (Table S3). In general, the formation of the symmetric HB, even ten times stronger than the typical ones, is rare. The phosphonic group, as a strong donor and acceptor, sometimes allows for the observation of such

a type of bonding.^{74,93} The second HB is generated by a free hydroxyl group with *c*-glide related groups. Together, four phosphonic groups create a strong $R_4^4(16)$ motif (Fig. 9). The supramolecular chain formed from this motif is oriented along the *c* axis. This chain is also connected with four other such chains through naphthalene linkers, which provides a 3D hydrogen-bonded anionic network. As one can see in Figure 8, this network contains 9 x 13 Å supramolecular channels running along the *c* axis. The channels are filled with DMAP and water molecules. These two species interact through a linear N-H…O hydrogen bond, but they only interact weakly with the phosphonic acid framework through uncommonly weak interactions donated by the water molecule. The C7-H7…Cg and C10-H10B…Cg interactions between pyridine and naphthalene rings also help in stabilizing the guests inside the channels. Aromatic interactions are rather scarce due to the strong directionality of the HB network. Interestingly enough, the significant differences in composition and bonding between structures **4A** and **4B** lead to a quite similar participation of all interactions in the Hirshfeld surface.⁹⁴

Adducts with morpholine: 5A and 5B. The two last structures provide an opportunity for the direct comparison of the different influences of phosphonic tectons with varying conformational flexibility on the final supramolecular adduct structure. In addition to the structures with 4-(*N*,*N*-dimethylamino)pyridine, we have obtained, for both phosphonic acids, adducts with morpholine in a 1:2 ratio. They crystallize in the $P2_1/c$ space group. Asymmetric units for 5A and 5B consisting of half an acid and one base molecules can be seen in Figure S5. Crystal packing, shown in Figure 10, is represented by layered structures in both cases. Nonetheless, for H₄NDP(1,5) in 5A, there is a regular arrangement of the acid molecules in layers separated by protonated morpholine molecules along the *a* axis.



Figure 10. Crystal structure projections of a) **5A** and b) **5B** along the *b* axis together with topological simplifications of the HB networks.

The morpholine molecules are more than pendants. Both protons from the NH₂⁺ group force the generation of a $R_3^3(10)$ motif with deprotonated oxygen atoms, which, however, remains in close resemblance to the typical $R_2^2(8)$ motif. The glide-related hydrogen-bonded rings produce a supramolecular chain along the *c* axis (Fig. 11). These chains are connected by naphthalene linkers to give wavy 2D layers, similarly as in the case of structure **2B**. The C-H···O bonds again play an important role in crystal packing in the two remaining directions. The HB chains are interconnected mainly by a C9-H9B···O1 interaction and along the *a* axis by a C6-H6A···O4

bonding (Table S3). The C-H···O bonds are constituted not only by an aliphatic C-H, but also by an aromatic hydrogen atom (C5-H5···O1). This is the shortest C-H···O contact in this structure with $d_e = 1.10$ Å and $d_i = 1.43$ Å.



Figure 11. Isolated hydrogen-bonded networks for adducts a) **5A** and b) **5B**. Dashed lines symbolize hydrogen bonds. The morpholine molecules are partially transparent for clarity.

The morpholine adduct of H₄NDP(1C,5C) (**5B**) also shows a layered structure, where the hydrogen-bonded 2D network parallel to the (100) plane is linked in the [100] direction by naphthalene joints spaced by the base molecules (Fig. 10). This less regular arrangement is clearly a result of the higher flexibility of the phosphonic tecton and is connected with a higher amount of more optimized interactions. An isolated HB layer is shown in Figure 11. The monodeprotonated phosphonic groups generate a dimeric $R_2^2(8)$ synthon, whereas the protonated morpholine nitrogen atom bridges two screw-related phosphonic acid molecules. An additional ring motif $[R_2^2(7)]$ is provided by the C10-H10B···O2 bond. Also here, a carbon donor is activated by the proximity to N⁺.

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2D fingerprints of phosphonic acids, their adducts and quantitative remarks

Strong hydrogen bonds, *e.g.* O-H···O contacts, are readily visible in a 2D fingerprint plot and are referred to in the available literature (mainly in the context of carboxylic acids) as two long narrow spikes pointing toward the bottom left of the plot.⁶ This kind of interaction is also present for herein described systems, but as can be seen from their 2D fingerprint plots, the spikes are not as narrow. In fact, beginning from the tip, they significantly broaden with increasing d_i and d_e values. This is the result of the presence of a tetrahedral phosphonic group having three oxygen atoms; each of them with a different local environment which provides a larger library of possible HBs. So far, only one other phosphonic system, *i.e.* polyphosphonylated calixarene, was investigated using HS and FP analysis, showing similar patterns to what has been described above.^{95,96}

For the herein reported compounds, the shortest O···H contact, described by its $d_i + d_e$ value, is in a range between 1.50 and 1.65 Å (for **3A** and **2A**, respectively). Other hydrogen bond acceptors are engaged in more distant contacts, which results in the wider distribution of points in the 2D fingerprint plots. This is apparent on the upper spike, corresponding to the hydrogen bond donor sites. The lower spike, corresponding to the acceptor sites of the HBs, represents not only strong hydrogen bonding, but also, at higher d_i and d_e values, shows a contribution from weak C-H···O bonding.

It is interesting how the fingerprint plot of a protonated acid differs from the fingerprint plot of a monodeprotonated moiety. To examine this, we compared O···H decomposed 2D fingerprint plots of acid structures with respective adducts, along with their d_{norm} surfaces. For selected examples (1A and 5A), see Figure 12, and for all O···H decomposed 2D fingerprint plots, see Table S4. Generally, FPs of adducts reflect changes in the protonation state of the acid molecule.

A special feature of their plots is a slightly narrowed upper spike while the lower spike is broadened. This observation is explained by the fact that when phosphonic acid forms salt, then the transfer of the proton from the acid to the base molecules occurs. Such a transferred proton is no longer inside the Hirshfeld surface, which results in a decrease in the donor contacts of acid moiety and in an increase of the acceptor ones. The d_{norm} surfaces of acids and monodeprotonated molecules (Fig. 12) are similar, with 4 red spots which are located around the phosphonic group. However, the ratio of acceptor and donor sites differentiates two protonation forms of the phosphonic group. For structure **1A**, one can observe 2 accepting sites and 2 donor sites of O-H···O interactions around the PO₃H₂ group. When an adduct structure is considered (**5A**), for the PO₃H⁻ group there are 3 accepting sites (two deriving from the N-H···O interaction and one from the O-H···O) and one donor site, which remains in agreement with the presented fingerprint plots.



Figure 12. Hirshfeld surfaces and 2D fingerprint plots for a) 1A and b) 5A. Phosphonic tectons are mapped with d_{norm} functions. The features of the diagrams coming from accepting and donating interactions are labeled.

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In all structures (1A-5B), the biggest part of the HS is covered by O···H contacts (44 % on average). The total percentage share of O···H contacts is not dependent on the protonation state of the phosphonic group, and also there is no correlation with the acid structure. This cannot be said about the C···H interactions that, according to Figure 13, cover less of the Hirshfeld surface for structures containing flexible tectons. Here, the exception is structure 2B that has a greater participation of these contacts than its analogue 1B (22.2 % and 16.6 %, respectively). H···H dispersion forces are the second most abundant type of interactions in structures 1A-5B. The structures based on H₄NDP(1C,5C) have a systematically bigger contribution from H···H contacts. For characteristic arrays of points in C···H and H···H decomposed fingerprint plots, please see Table S5 and Table S6, respectively.



Figure 13. The percentage contribution of specific close contacts to the Hirshfeld surfaces for all structures. For **1A**, **2A**, **2B**, **5A**, and **5B**, C···C contributions amount to 2.4, 0.9, 0.4, 2.4, and 1.9 %, respectively. Other contacts are as follows: C···O, S···H, S···O.

Potentiometric studies

Potentiometric measurements reveal that $H_4NDP(1C,5C)$ is slightly less acidic than $H_4NDP(1,5)$. This is manifested by the absence of the monodeprotonated form $H_3NDP(1,5)^-$ in

the water solution for pH 2 and higher (details in ESI). The doubly deprotonated form H_2L^{2-} dominates in lower pHs and is present until pH = 7.8 (more than 10 % of all forms), whereas for $H_4NDP(1C,5C)$ the H_3L^- form is present until pH = 4.6 and the H_2L^{2-} form as far as pH = 9.2. Nevertheless, it has fewer consequences in described adducts with comparatively strong bases than it would probably have in metal phosphonate chemistry (the pK_a for (DMAP)H⁺ is 9.2 and for (Morpholine)H⁺ it is equal to 8.36).⁹⁷ The determination of dissociation constants was difficult due to the presence of dimers in the water solution. Nonetheless, this indicates that the molecules are bound to each other through intermolecular interactions even in a solution.

Sulfonic vs. phosphonic moieties

Both presented phosphonic acids show ease in the creation of crystalline supramolecular adducts with amines. The sulfonic analogue H₂NDS(1,5) also proved to be a versatile supramolecular tecton. Nevertheless, there are clear differences between these species; they arise from a different number of accessible protons. The lack of a protonated oxygen atom in H₂NDS(1,5) prevents it from generating a strong $R_2^2(8)$ synthon in adducts with amines, while such a motif is often present in monodeprotonated phosphonic systems and carboxylic acids. Also, for both H₂NDC(1,5) and H₄NDP(1,5), there can be no charge-assisted HBs, whereas naphthalene-1,5-disulfonic acid remains deprotonated even in its hydrate.²⁹ Full deprotonation of NDS(1,5) manifests itself clearly in the fingerprint plots, where there is only one O…H broad spike representing accepting interactions, which remains in contrast with the herein presented systems that have a monodeprotonated phosphonic group.

CONCLUSIONS

Our present research shows the huge potential resulting from newly obtained diphosphonic tectons. Hirshfeld surface analysis proved to be a useful tool in the exploration and comparison

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of phosphonic supramolecular systems. The analysis of created hydrogen-bonded networks clearly indicates some regularities and common motifs. i) The statistics show that the $R_2^2(8)$ and $R_4^4(16)$ motifs (in 4 and 3 structures, respectively; see Table 2) prevail despite a number of possibilities. These are strong synthons effectively holding phosphonic acid molecules together. Therefore, their presence is expected, especially for a monodeprotonated group. Also an activation of C-H donors by the N⁺ proximity visibly contributes to the stabilization of all adduct structures through C-H···O(Cg) interactions. ii) Both acids have been doubly deprotonated in all adducts (except the unique structure **4B**). iii) Differences caused by the varying conformational flexibility of the presented acids are also apparent, despite the fact that weaker interactions are less demanding and directional than coordination bonds. At any rate, the more flexible building block – naphthalene-1,5-bis(methylphosphonic) acid – usually shows better accommodation in the demonstrated systems due to the possibility of rotation along bonds with the sp^3 carbon atom, which is especially important from the perspective of coordination applications. This provides, in each case, comparatively higher dimensionalities of the HB networks determined by strong HBs (Table 2).

Table 2. A structural summary for all supramolecular networks (**1A** to **5B**). The dimensionality of the HB network was determined taking into account only strong O-H···O and N-H···O hydrogen bonds. Bolded HB motifs do not contain C-H···O bonds.

Compound	1A	1B	3A	3B	5A
Tecton	naphthalene-1,5-diphosphonic acid				
Dimensionality of HB network	3D	1D	1D	1D	2D
Synthon	$R_4^3(14)$	$R_2^2(8)$	$R_2^2(8)$ $R_4^2(10)$	$R_2^2(8)$ $R_4^4(14)$	$R_3^3(10)$
Compound	2A	2B	4A	4B	5B
Tecton	naphth	alene-1,5-	bis(methyl _l	phosphonic	e) acid
Dimensionality of HB network	3D	2D	2D	3D	3D
Synthon	$R_4^2(12)$	$R_4^2(10)$ $R_4^4(16)$	$R_6^4(16)$ $R_6^4(14)$	$R_4^4(16)$	$R_2^2(8)$

 $\begin{array}{|c|c|c|c|c|c|} \hline R_4^4(16) & R_6^6(18) \\ \hline R_6^4(16) & R_6^6(18) \\ \hline R_6^4(16) & R_6^6(18) \\ \hline R_6^4(16) & R_6^6(18) \\ \hline R_6^6(18) & R_6^6(18) \\$

SUPPORTING INFORMATION

Crystallographic date files in CIF format, Detailed synthetic procedures for acids and adducts with spectroscopic characterization, The description of obtainment of single crystals for all structures, Crystal and structure refinement data, Selected distances [Å] and angles [°] and the geometry of potential hydrogen bonds for all the structures, Decomposed 2D fingerprint plots of O…H, C…H, and H…H contacts for all the structures, Figures of asymmetric units and isolated hydrophobic regions for all the structures, Shape index surfaces of tectons molecules for all the structures, The discussion of aromatic interactions, The description of pH-potentiometry experiments for both acids, Spectroscopic discussions are included as Electronic Supplementary Materials. This information is available free of charge via the Internet at http://pubs.acs.org.

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63. The HS analysis takes into account interplay of electron densities of a given molecule (promolecule) and surrounding of this molecule (procrystal).

64. The Hirshfeld surface definition is based on stockholder partitioning concept: in every point inside the space limited by the HS the contribution of an analyzed molecule to the electron density of procrystal is bigger than 50%.

65. The FP are histogram representations of the HS, summarizing all intermolecular interactions as d_e , d_i function and their frequency, where d_e is the distance from the Hirshfeld surface to the nearest nucleus outside the surface and d_i is the distance from the surface to the nearest atom in the molecule itself.

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Two, easily obtainable diphosphonic tectons, based on a 1,5-disubstituted naphthalene platform, have been incorporated into a number of supramolecular systems. They show their great potential in the generation of solvatomorphs, polymorphs and adducts giving variable structures and connectivity. Synthesis, structural and spectroscopic characterization, and analysis of geometrical and topological features as well as Hirshfeld surfaces for all structures are presented.