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# Synthesis, crystal structure and computational studies of 4-nitrobenzylphosphonic acid

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#### Abstract

4-Nitrobenzylphosphonic acid (**1a**) has been synthesized and structurally characterized by vibrational spectroscopy (IR and Raman) and single-crystal X-ray diffraction. Additionally, Hirshfeld surface analysis and computational methods have been used to compare the intermolecular interactions in the crystal structures of **1a** and its carboxylic analogue, 4-nitrobenzylcarboxylic acid (**4-NBCA**). The crystal structure analysis of **1a** has revealed that the acid molecules are extended into helical chains along the *b* axis using one of the hydrogen bonds established between phosphonic groups. The second (P)O–H···O(P) hydrogen bond cross-links the inversion-related chains to form a thick monolayer with phosphonic groups arranged inwards and aromatic rings outwards. The nitro groups serve to link the neighbouring monolayers by weak C–H···O(N) hydrogen bonds. Computations have confirmed the great contribution of electrostatic interactions for the crystal lattice stability. The cohesive energy, computed for the crystal structure of **1a** exceeds 200 kJ·mol<sup>-1</sup> in magnitude and is nearly twice as large as that of **4-NBCA**. The calculated cohesive energy values have been further related to the results of thermal analyses.

#### Keywords

Phosphonic acid; Hydrogen-bonding interaction; Vibrational spectroscopy; Single-crystal X-ray diffraction; Hirshfeld surface; Periodic calculations.

#### 1. Introduction

Over the past few decades, metal phosphonates have attracted a great deal of research interest due to their structural diversity and many potential applications in gas storage [1], heterogeneous catalysis [2], ion exchange [3], proton conductivity [4], corrosion inhibition [5] and sensor devices [6]. In recent years, considerable effort has been put into exploring metal phosphonate cage compounds, as they can exhibit single molecule magnet (SMM) properties [7]. Phosphonate ligands (RPO<sub>3</sub><sup>2-</sup>) appear to be ideal for stabilizing polymetallic complexes as they possess three donor O atoms and are, in principle, capable of binding up to nine metal centers. Recently, 4-nitrobenzylphosphonic acid had been used to coordinate paramagnetic transition metal ions, which has resulted in the formation of two new high nuclearity cage compounds [8], but the crystal structure of the acid itself has not been determined yet.

This paper concerns the results of infrared and Raman spectroscopy studies and singlecrystal X-ray diffraction analysis of 4-nitrobenzylphosphonic acid (**1a**). The crystal structure of **1a** is also compared with its carboxylic analogue, namely 4-nitrobenzylcarboxylic acid (**4-NBCA**, CSD refcode SEMTAF) [9], using Hirshfeld surface analysis and computational approach supported by thermal analysis. Recently, Hirshfeld surface analysis has also been applied for the investigation of intermolecular interactions of naphthalene-based phosphonic acids in different protonation states [10]. However, to the best of our knowledge, no computational studies, aimed at evaluating the strength of intermolecular interactions responsible for the solid state organization of phosphonic acids, have been reported until now.

#### 2. Experimental section

#### 2.1. Materials

4-Nitrobenzyl bromide and triethyl phosphite (98%) were purchased from Arcos Organics. 4-Nitobenzylcarboxylic acid was obtained from Sigma-Aldrich. Hexane and concentrated hydrochloric acid (36-38%) were supplied by POCH S.A. All reagents were used as received without further purification.

#### 2.2. Synthesis

#### 2.2.1. (i) Diethyl 4-nitrobenzylphosphonate (3)

A flask with 4-nitrobenzyl bromide (**2**, 0.997 g, 4.62 mmol) and triethyl phosphite (2.5 mL, 14.08 mmol) was partially immersed in an ultrasonic bath at 25°C, the temperature was gradually raised to 90°C and held at that temperature until the substrate was completely dissolved. Stirring and heating were continued in a metal bath of Wood's alloy at 97°C for 1 h. After cooling, the excess of triethyl phosphite was removed from the reaction mixture by extraction with hexane (4 x 3 mL). The residue was dried under reduced pressure to obtain ester **3** as yellow oil. Yield: 0.626 g (55%). <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>):  $\delta$  8.23 (*d*, <sup>3</sup>*J*<sub>HH</sub> = 8.8 Hz, 2H, arom. H), 7.53 (*dd*, <sup>3</sup>*J*<sub>HH</sub> = 8.8 Hz, <sup>4</sup>*J*<sub>PH</sub> = 2.5 Hz, 2H, arom. H), 3.92 (*dq*, <sup>3</sup>*J*<sub>PH</sub> = 7.0 Hz, <sup>3</sup>*J*<sub>HH</sub> = 7.0 Hz, 4H, O–CH<sub>2</sub>–CH<sub>3</sub>), 3.30 (*d*, <sup>2</sup>*J*<sub>PH</sub> = 22.4 Hz, 2H, CH<sub>2</sub>–P), 1.32 ppm (*t*, <sup>3</sup>*J*<sub>HH</sub> = 7.0 Hz, 6H, O–CH<sub>2</sub>–CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121.50 MHz, CDCl<sub>3</sub>):  $\delta$  25.06 ppm (*s*).

#### 2.2.2. (ii) 4-Nitrobenzylphosphonic acid (1)

Compound **3** (0.626 g, 2.56 mmol) was hydrolyzed by refluxing with concentrated hydrochloric acid (10 mL) for 8 h. After cooling, beige fine crystalline product **1** was collected by vacuum filtration, washed with ice-cold water (2 x 3 mL) and dried under reduced pressure. Yield: 0.348 g (62%). <sup>1</sup>H NMR (300.13 MHz, D<sub>2</sub>O-Na<sub>2</sub>CO<sub>3</sub>):  $\delta$  7.98 (*d*, <sup>3</sup>*J*<sub>HH</sub> = 8.9 Hz, 2H, arom. H), 7.31 (*dd*, <sup>4</sup>*J*<sub>PH</sub> = 2.3 Hz, <sup>3</sup>*J*<sub>HH</sub> = 8.9 Hz, 2H, arom. H), 2.92 ppm (*d*, <sup>2</sup>*J*<sub>PH</sub> = 20.8 Hz, 2H, CH<sub>2</sub>–P). <sup>31</sup>P{<sup>1</sup>H} NMR (121.50 MHz, D<sub>2</sub>O-Na<sub>2</sub>CO<sub>3</sub>):  $\delta$  18.16 ppm (*s*).

#### 2.2.3. Crystallization of 4-nitrobenzylphosphonic acid (1a)

4-Nitrobenzylphosphonic acid (1, 30.0 mg, 0.138 mmol) was dissolved in distilled water (1 mL) and left at room temperature for slow evaporation of the solvent. After five days,

beige needle-shaped crystals of **1a** were obtained. Yield: 12.4 mg (41%). The phase purity of **1a** was confirmed by comparison of simulated and experimental powder XRD patterns (Fig. S1).

#### 2.2.4. Crystallization of 4-nitrobenzylcarboxylic acid (4-NBCA)

4-Nitrobenzylcarboxylic acid (30.0 mg, 0.166 mmol) was dissolved in distilled water (4 mL) and left at room temperature for slow evaporation of the solvent. The next day, white needle-shaped crystals of **4-NBCA** were obtained. Yield: 22.5 mg (75%). The phase purity of **4-NBCA** was confirmed by comparison of simulated and experimental powder XRD patterns (Fig. S2).

#### 2.3. NMR spectroscopy in solution

The <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were acquired at room temperature on a Bruker Avance DRX-300 spectrometer, operating at 300.13 MHz (<sup>1</sup>H) and 121.50 MHz (<sup>31</sup>P). NMR samples were prepared by dissolving 50  $\mu$  of **3** in CDCl<sub>3</sub> (500  $\mu$ ) and 20 mg of **1** and 13 mg of sodium carbonate in D<sub>2</sub>O (500  $\mu$ ).

#### 2.4. Vibrational spectroscopy

The FT-IR spectrum of **1a** was recorded on a Bruker Vertex 70v FT-IR spectrometer in the range of 4000–370 cm<sup>-1</sup> with a resolution of 2 cm<sup>-1</sup> using the KBr pellet technique. The Raman spectrum of **1a** was collected on a Bruker MultiRAM FT-Raman spectrometer in the range of  $3600-50 \text{ cm}^{-1}$  with a resolution of 2 cm<sup>-1</sup> using the Nd:YAG laser line at 1064 nm. Instrument control, spectra analysis and correction for fluorescence effect in the case of Raman measurement were performed using the Bruker OPUS software.

#### 2.5. Single-crystal X-ray data collection and structure determination

Single-crystal X-ray diffraction measurement of **1a** was carried out at 295 K on a fourcircle KUMA KM4 diffractometer equipped with two-dimensional CCD area detector. Graphite monochromatized Mo-Koradiation ( $\lambda$ = 0.71073 Å) and  $\omega$ -scan technique ( $\Delta \omega = 1^{\circ}$ ) were used for data collection. Data collection and reduction along with absorption correction were performed using CrysAlis software package [11]. The structure was solved by direct methods using SHELXS-97 [12], which revealed the positions of almost all non-hydrogen

atoms. The remaining atoms were located from subsequent difference Fourier syntheses. The positions of H atoms attached to benzene C atoms were constrained (C–H = 0.93 Å) with  $U_{iso}(H) = 1.2U_{eq}(C)$ . The positions of H atoms of the methylene group were constrained (C–H = 0.97 Å) with  $U_{iso}(H) = 1.5U_{eq}(C)$ . The positions of H atoms of the phosphonic group were refined with  $U_{iso}(H) = 1.5U_{eq}(O)$ . The structure was refined using SHELXL-97 [12] with the anisotropic thermal displacement parameters. Visualizations of the structure were made with the Diamond 3.1 program [13]. Details of the data collection parameters, crystallographic data and final agreement parameters are collected in Table 1.

Empirical formula	$O_2NC_6H_4CH_2PO_3H_2$
Formula weight (g·mol <sup>-1</sup> )	217.11
Crystal system, space group	Monoclinic, P21/c (No. 14)
<i>a</i> (Å)	12.910(3)
b (Å)	8.627(2)
<i>c</i> (Å)	8.355(2)
ι (°)	90.00
μ(°)	104.090(10)
;(°)	90.00
$V(\text{\AA}^3)$	902.5(4)
Z	4
$D_{\rm calc}/D_{\rm obs}~({\rm g}\cdot{\rm cm}^{-3})$	1.598/1.59
$\mu$ (mm <sup>-1</sup> )	0.300
<i>F</i> (000)	448
Crystal size (mm)	$0.28 \times 0.23 \times 0.19$
Radiation type, wavelength, $\lambda$ (Å)	Mo K <i>q</i> 0.71073
Temperature (K)	295(2)
$\theta$ range (°)	2.87–29.31
Absorption correction	Numerical, CrysAlis Red
$T_{\min}/T_{\max}$	0.9206/0.9451
Reflections collected / unique / observed	11145/2331/1220
R <sub>int</sub>	0.0668

Table 1. Crystal data and details of the structure determination for compound 1a.

Refinement on	$\overline{F^2}$	-
$R[F^2 > 2\epsilon(F^2)]$	0.0555	
$wR(F^2 \text{ all reflections})^{a)}$	0.0885	
Goodness-of-fit, S	1.001	
$4_{\text{max}}, 4_{\text{min}}, (e \cdot \text{\AA}^{-3})$	+0.275, -0.307	

<sup>a)</sup>  $wR = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma w F_o^4\}^{\frac{1}{2}}; w^{-1} = [\partial(F_o^2) + (aP)^2] \text{ where } a = 0.0200 \text{ and } P = (F_o^2 + 2F_c^2)/3.$ 

#### 2.6. Powder X-ray diffraction data collection

The experimental powder XRD patterns of **1a** and **4-NBCA** were acquired on a PANalytical X'Pert diffractometer equipped with a Cu Koradiation source ( $\lambda$ = 1.54182 Å), and operated at 40 kV and 30 mA. The data were collected at room temperature in the range of  $2\theta$ = 5–40°. On the other hand, the corresponding simulated powder XRD patterns were generated using Diamond 3.1 software.

#### 2.7. Simultaneous thermal analysis

The combined TG-DTA-MS analyses were performed using a simultaneous thermal analyzer NETZSCH STA 449 F3 Jupiter coupled with a quadrupole mass spectrometer QMS 403 C Aëolos. The samples (17.3 mg of **1a** and 20.4 mg of **4-NBCA**) were placed inside  $Al_2O_3$  crucibles. The measurements were carried out in the range of 35–600°C with a heating rate of 4°C·min<sup>-1</sup> and under dynamic air atmosphere (N<sub>2</sub>/O<sub>2</sub> 80:20) with a gas flow of 20 mL·min<sup>-1</sup>. The data acquisition and processing were realized using NETZSCH Proteus software.

#### 2.8. Computational details

Two sets of coordinates were used for the purpose of the energetic analysis, i.e. the experimentally determined structure with the X–H bonds (where X stands for any atom different from hydrogen) elongated to neutron-normalized values, and the computationally optimized crystal geometry. Geometry optimization was carried out at the DFT(B3LYP)/pVTZ level of theory [14-16] in CRYSTAL09 [17]. During the optimization procedure atomic coordinates were varied, while cell parameters were kept fixed at the

experimental values. Structure optimization prior to further computational studies is particularly important in the case of low-resolution crystal structures, since it allows to obtain reliable values for the X–H bond distances and for the bond directionality (which cannot be achieved by simple X–H elongation to neutron-normalized values). Indeed, this is visible when we compare the experimental and optimized crystal structures of **1a** (Fig. S3). Both structures are generally very similar with largest discrepancies observed for the positions of the hydrogen atoms, especially for those involved in strong hydrogen bonds. In the case of our study, structure optimization additionally helped to relate the structure of **1a** with the literature structure of **4-NBCA** at the common ground.

Cohesive energy computations were performed using the CRYSTAL09 program package [17] at the DFT(B3LYP) level of theory [14, 15] with the pVTZ molecular all-electron basis set [16]. Both Grimme dispersion correction [18, 19] and correction for basis set superposition error (BSSE) were applied [20]. Ghost atoms were selected up to 5 Å distance from the considered molecule in a crystal lattice, and were used for the BSSE estimation. The evaluation of Coulomb and exchange series was controlled by five thresholds, set arbitrarily to the values of  $10^{-7}$ ,  $10^{-7}$ ,  $10^{-7}$ ,  $10^{-25}$ . Shrinking factor was equal to 8, which refers to 170 **k**-points in the irreducible Brillouin zone and assures the full convergence of the total energy. The cohesive energy ( $E_{coh}$ ) was calculated as described below [21]:

$$E_{\rm coh} = \frac{1}{Z} E_{\rm bulk} - E_{\rm mol}$$

where  $E_{\text{bulk}}$  is the total energy of the system (calculated per unit cell) and  $E_{\text{mol}}$  is the energy of the molecule extracted from the bulk. Z stands for the number of molecules in the unit cell.

Additionally, the optimized geometry was subjected to crystal interlayer interaction computation. All of the calculation parameters were set identical as for the purpose of the cohesive energy estimation. The only difference was introduced to ghost atom definition, where an upper and lower molecular layers were additionally used as ghost function sets in order to obtain BSSE. The interlayer interaction energy ( $E_{intl}$ ) calculation formula is analogous to that for cohesive energy [22]:

$$E_{\rm intl} = \frac{1}{n} E_{\rm bulk} - E_{\rm slab}$$

where  $E_{\text{slab}}$  is the energy of a molecular slab extracted from the bulk, while *n* indicates the slab number per a unit cell. Therefore, the resulting stabilization energy falls on a part of a

slab belonging to the unit cell. CRYSTAL09 automatically assigns the slab group symmetry and cuts out the repeatable fragment.

Finally, dimer interaction energies were evaluated within the supramolecular approach. Alike above, the calculations were carried out at the DFT(B3LYP)/pVTZ level of theory with the BSSE and Grimme corrections applied.

#### 3. Results and discussion

Although 4-nitrobenzylphosphonic acid (1) was first synthesized by Litthauer in 1889 [23], its crystal structure has not been determined to date. In current work 1 has been prepared according to the modified literature procedure of Coogan and Harger [24]. Diethyl 4-nitrobenzylphosphonate (3), obtained via Michaelis-Arbuzov reaction of 4-nitrobenzyl bromide (2) and triethyl phosphite, has been transformed into 1 by means of acidic hydrolysis (Scheme 1). Single crystals of 4-nitrobenzylphosphonic acid (1a) have been achieved by recrystallization of 1 from water.



Scheme 1. Synthetic route to compound 1. Reagents: (i)  $P(OC_2H_5)_3$  and (ii) HCl.

IR and Raman spectroscopy studies have confirmed the presence of nitro and phosphonic functional groups in the structure of **1a**. The nitro group exhibits two very strong bands at 1521 and 1345 cm<sup>-1</sup> arising from the asymmetric and symmetric stretching vibrations. In turn, the phosphonic group gives rise to a series of strong bands in the region 1300–900 cm<sup>-1</sup>. The well resolved band, observed at 1268 cm<sup>-1</sup>, is associated with the P=O stretching vibration, while the two broad bands at 1077 and 950 cm<sup>-1</sup> correspond to the asymmetric and symmetric stretching vibrations of PO<sub>2</sub> group. Additional not well resolved bands, observed in this region, are connected with the deformation vibrations of (P)O–H groups. The presence of two very strong (P)O–H…O(P) hydrogen bonds with the O…O distance lower than 2.6 Å is manifested also by the medium absorption, extended in the whole region 3500–1650 cm<sup>-1</sup>, which is connected with the O–H stretching vibrations. The complementary IR and Raman

spectra of **1a** are shown in Fig. 1. The positions and intensities of all observed vibrational modes together with their tentative assignments are given in Table 2.



Figure 1. Complementary IR (red) and Raman (green) spectra of compound 1a.

IR	Raman	Band assignment <sup>a)</sup>
3111 m		$\downarrow$ $\gamma$ (C-H)
3085 m	3084 vw	
2971 m	2970 vw	vas(CH <sub>2</sub> )
2936 m	2932 vw	\s(CH <sub>2</sub> )
2850 m		
2764 m, br		<b>\</b> (O-H)
2450 m		
2213 m, br		<b>\</b> (O-H)
1941 w		
1808 w		
1698 w		
1610 m		$\int y(C-C)$
1599 m	1599 w	

 Table 2. Positions and assignments of vibrational bands, observed in FTIR and Raman spectra of compound 1a.



<sup>a)</sup>Abbreviations: vs – very strong, s – strong, m – medium, w – weak, vw – very weak, br – broad, v– stretching, as – asymmetric, s – symmetric,  $\delta$ – in-plane deformation vibration,  $\rho$ – rocking.

The single-crystal X-ray diffraction analysis has revealed that **1a** crystallizes in the monoclinic  $P2_1/c$  space group with one molecule in the asymmetric part of the unit cell (Fig. 2). All N–O and P–O bond lengths (Table 3) are typical for the nitro group and the non-dissociated phosphonic group, respectively [25]. The nitro group is coplanar with the benzene ring, as indicated by the dihedral angle of  $1.903(293)^\circ$  formed by the O41/N4/O42 plane with the C1–C6 ring.



**Figure 2.** The asymmetric part of the unit cell of compound **1a**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

C7–P1	1.779(3)	C4-N4	1.481(5)
P1011	1.506(2)	N4041	1.214(4)
P1012	1.541(2)	N4042	1.218(3)
P1013	1.542(2)		
C1C7P1	115.8(2)	O12-P1-O13	109.69(13)
O11-P1-O12	108.50(12)	O41-N4-O42	123.7(4)
O11–P1–O13	115.12(14)		
-			

Table 3. Selected geometric parameters (Å, °) for compound 1a.



**Figure 3.** A side view of two monolayers of compound **1a**, demonstrating the intralayer O– H…O hydrogen-bonding interactions.

The acid molecules are organized into thick molecular monolayers with phosphonic groups located inside and aromatic rings arranged outside from both sides of the layer. The twodimensional hydrogen-bonded network of the monolayer is created merely by phosphonicphosphonic interactions (Fig. 3). Formally it can be disentangled into C(4) helical chains, extended along the *b* axis and formed by O12–H12···O11<sup>i</sup> hydrogen bonds. The neighbouring, opposite running chains are further interlinked by O13–H13···O11<sup>ii</sup> hydrogen bonds. The (P)O–H···O(P) hydrogen-bonded network is characterized by two centrosymmetric ring motifs denoted as  $R_4^2(12)$  and  $R_4^4(16)$  (Fig. 4) [26]. A search in the Cambridge Structural Database (CSD version 5.35 of November 2013) [27] using the Solid Form Module of Mercury 3.3 revealed that a similar two-dimensional hydrogen-bonded pattern is observed in the crystal structures of only six more phosphonic acids (CALGON, FECTOW, NISPAH, OLOPUA, RIGNUR, YOJTAT).



**Figure 4.** The two-dimensional hydrogen-bonded network of compound **1a**, formed between the phosphonic groups. Aromatic rings, nitro and methylene groups are omitted for clarity. [Symmetry codes: (vi) -x+1, -y+1, -z+1; (vii) -x+1,  $y+1/_2$ ,  $-z+1/_2$ ; (viii) -x+1, -y+2, -z+1.]

Two weak C–H···O hydrogen bonds, donated from the methylene group toward the O-atoms of the nitro group and the phosphonic group, additionally stabilize the two-dimensional network. One of them, C7–H71···O41<sup>iv</sup>, established between translation-related molecules along the chain, is responsible for the pitch of the helix, while the other, C7–H72···O12<sup>iii</sup>, connects the chains. The 4-nitrobenzyl groups are arrayed from both sides of the monolayer. The benzene rings are inclined at an angle of  $56.087(61)^{\circ}$  versus *bc* plane. The distal nitro groups are used to interlink the neighbouring monolayers via a weak C5–H5···O42<sup>v</sup> hydrogen bond, donated from an aromatic C–H group to the O-atom of the nitro group (Fig. 5).



**Figure 5.** The three-dimensional packing arrangement of compound **1a**. The hydrogen bonds are drawn as dashed lines (red for O–H···O, green for intralayer C–H···O and pink for interlayer C–H···O).

D–H····A	d(D-H)	d(H····A)	d(D····A)	<d-h…a< th=""></d-h…a<>
O12–H12…O11 <sup>i</sup>	0.90 (3)	1.66 (3)	2.550 (3)	173 (3)
O13-H13…O11 <sup>ii</sup>	0.81 (3)	1.81 (3)	2.581 (3)	159 (3)
С7–Н72…О12 <sup>ііі</sup>	0.97	2.57	3.356 (4)	138
C7–H71····O41 <sup>iv</sup>	0.97	2.58	3.453 (4)	150
С5–Н5…О42 <sup>v</sup>	0.93	2.58	3.255 (4)	130

Table 4. Hydrogen bond geometry (Å, °) for compound 1a.

Symmetry codes: (i) -x+1, y-1/2, -z+1/2; (ii) x, -y+3/2, z+1/2; (iii) -x+1, -y+1, -z; (iv) x, y+1, z; (v) -x, y+1/2, -z+1/2.

In order to profoundly examine the strength and role of the above listed hydrogen bonds and other intermolecular contacts, and to estimate their importance for the crystal lattice stability, Hirshfeld surface analysis and computational study have been conducted. Hirshfeld surface constitutes a useful tool in crystal engineering. It allows for crystal packing investigations and for certain quantification of the contributions coming from different close contacts present in a crystal lattice (Supplementary Materials). The Hirshfeld surface for **1a** 

mapped with  $d_{norm}$  property is visualised in Fig. 6a. It reflects interatomic contact distances in respect to atom van der Waals radii (red colour stands for the close contacts, while blue for the distant ones). On the basis of such a Hirshfeld surface, the related fingerprint plot has been derived (Fig. 6b). The Hirshfeld surface around the phosphonic group is coated with three large red spots of the same size, which means that it participates in strong O-H···O hydrogenbonding interactions. On the other hand, much smaller pale red spots on the  $d_{norm}$  surface are related to almost every H-atom coming from the hydrocarbon fragment and both O-atoms belonging to the nitro group, which indicates that the crystal lattice is rich in weak C-H···O hydrogen bonds. Two long broadening spikes at the sides of the main body of the fingerprint plot correspond not only to the O–H···O hydrogen-bonding interactions but also, at higher  $d_i$ and  $d_e$  values, reveal the contribution from C–H···O hydrogen bonds. Consequently, the total percentage share of H···O contacts constitutes over 50% of the total number of intermolecular contacts, which demonstrates their importance for the structure stability (Fig. 6c). In turn, the second most numerous contacts, H...H, which are very common in the case of crystal structures of organic molecules, contribute to about 20% of the total (Fig. 6d). The Hirshfeld surface analysis shows the existence of other weak intermolecular contacts, for which the percentage participations to the Hirshfeld surface area are presented in Fig. 6e.



**Figure 6.** (a) The Hirshfeld surface for compound **1a** mapped with  $d_{norm}$  function; (b) The corresponding 2D fingerprint plot; (c-d) The fingerprint plots, broken down into contributions from H···O and H···H contacts; (e) The percentage contributions of various close intermolecular contacts to the Hirshfeld surface area. Other contacts constitute H···N, N···O, C···N.

The energy studies have confirmed the importance of the hydrogen-bonded network for the crystal lattice stability. Periodically calculated cohesive energy amounts to  $-226.2 \text{ kJ} \cdot \text{mol}^{-1}$ . In the case of crystal structure of such a small organic molecule, this result indicates a great electrostatic nature of the strongest contacts [22, 28]. Two main hydrogen bonds, namely O12-H12···O11<sup>i</sup> and O13-H13···O11<sup>ii</sup>, involving the neighbouring phosphonic groups, constitute the principal intermolecular interaction in D1 and D2 dimer motifs, respectively (Fig. 7). The estimated interaction energies of these and other dimers are given in Table 5. As it was mentioned previously, the dimeric units are further connected into  $R_4^2(12)$  and  $R_4^4(16)$ ring motifs leading to the formation of a molecular layer parallel to the *bc* plane. Both ring motifs are characterized by significant stabilization energy values reaching from -222.0 to -365.0 kJ·mol<sup>-1</sup>. Another interesting and relatively strong interacting molecular configuration 16

is D3. It is built up from the C7-H72...O12<sup>iii</sup> hydrogen bond and the C2-H2...O11<sup>iii</sup> contact, established between the hydrocarbon fragment and the phosphonic group. These interactions together with the C7-H71···O41<sup>iv</sup> hydrogen bond and the C3<sup>iv</sup>-H3<sup>iv</sup>···O11 contact, constituting the two times weaker D4 dimer, contribute supplementary to the stability of the layered structure. As a consequence, the interactions within the layers are much stronger than those keeping the layers together. It is also clearly seen from the calculated interlayer interaction energy, which is equal to  $-22.2 \text{ kJ} \cdot \text{mol}^{-1}$ . The interlayer interactions are based mainly on the weak C5–H5···O42<sup>v</sup> hydrogen bond, donated from the aromatic C–H group to the O-atom of the nitro group, (D5) and the contact formed between the nitro groups (D7). This may be reflected in the crystal morphology and mechanical properties, as for example, in the tendency of crystal to stratify in a particular crystallographic direction [29, 30]. It is also worth noting that the D6 and D7 dimers are quite well stabilized, however, no regular hydrogen bonds are formed. D6 is created by face-to-face (FF)  $\pi\pi$  interactions between aromatic rings and the C3-H3...O13<sup>ix</sup> contact, whereas D7 is held mainly by the interlayer interaction of the nitro groups located anti-parallel one above another (weak N4---O42 electrostatic contacts).

Structural motif	Interaction energy <sup>a)</sup> (kJ·mol <sup>-1</sup> )	Structural motif	Interaction energy <sup>a)</sup> $(kJ \cdot mol^{-1})$
D1 <sup>i</sup> [C(4)]	-64.6	D6 <sup>ix</sup>	-19.3
D2 <sup>ii</sup> [C(4)]	-70.7	D7 <sup>x</sup>	-21.0
D3 <sup>iii</sup> [ $R_2^2(8)$ ]	-54.3	$R_4^2(12)$	-222.0
$D4^{iv} [R_2^2(9)]$	-25.5	$R_4^4(16)$	-365.0
$D5^{v}$ [D(3)]	-9.3		

Table 5. Interaction energy values calculated for selected structural motifs of compound 1a.

<sup>a)</sup> for optimized geometry with usage of periodic optimization in the CRYSTAL09 package Symmetry codes: (ix) -x,  $y-\frac{1}{2}$ ,  $-z+\frac{1}{2}$ ; (x) -x, -y, -z.



**Figure 7.** Schematic representation of dimer motifs related to interaction energy values given in Table 5.

The comparison of the crystal structures of **1a** and the 4-nitrobenzylcarboxylic acid (**4**-**NBCA**), especially in terms of their hydrogen bond connectivity patterns, constitutes another interesting aspect of the research. The compound **1a** can be considered as an analogue of **4**-**NBCA**, where the flat carboxyl group is replaced by the nonplanar phosphonic group. Both compounds display layered structures in the solid state, but the organization of their layers is different. The functional groups of the compounds are provided with good donors and acceptors capable to form strong hydrogen bonds, which are decisive for the self-recognition and control the self-organization process. However, the compounds differ in number, the

spatial orientation and approachability of the hydrogen bond sides, which has burden consequences for the supramolecular architectures. On the other hand, the weak C-H…O hydrogen bonds are also important for the packing patterns. The hydrogen-bonded network of the monolayer in **1a** is formed via two strong (P)O–H···O(P) hydrogen bonds, one of which extends the molecules into C(4) helical chains, and the other cross-links the chains to form a gird network with 12- and 16-membered ring motifs. The C-H...O hydrogen bonds, donated from the methylene group are only used to stabilize the monolayer. Another C-H. O hydrogen bond, donated toward the nitro group serves to connect the layers in threedimensional network. As far as the 4-NBCA is concerned, the basic molecular extension formed explicitly by the use of  $(C)O-H\cdots O(C)$  hydrogen bonds is the centrosymmetric dimer with  $R_2^2(8)$  ring motif. This structural motif is obviously characterized by the most significant interaction energy of -81.1 kJ·mol<sup>-1</sup>. Two weak C-H···O hydrogen bonds, donated toward the hydroxyl O-atom of the carboxyl group, are utilized to expand the dimers in two dimensions, forming double-stranded zig-zag chains that are further interconnected in the monolayer. The O-atoms of the nitro group due to greater interatomic distances are inaccessible as hydrogen bond acceptors and do not participate in any hydrogen-bonding interactions. Thus, the nitro group is much less involved in the structure stabilization than it is in 1a (Supplementary Materials). The corresponding Hirshfeld surface and fingerprint plot for 4-NBCA are presented in Figs. 8a and 8b. In comparison to 1a, a minor part of the Hirshfeld surface of 4-NBCA is covered with red spots, indicating a lower number of close contacts such as hydrogen-bonding interactions (compare Figs. 6a and 8a). Additionally, two long spikes in the fingerprint plot of 4-NBCA, related to H…O contacts, are narrower, which suggests a smaller contribution from weak C-H···O hydrogen bonds to the total  $d_{norm}$  surface area (compare Figs. 6b and 8b). Generally, the supramolecular network of 4-NBCA is less developed with a greater participation of H···H dispersion forces at the expense of H···O contacts. As a result, the cohesive energy is almost twice less advantageous than that of **1a** and amounts to  $-128.9 \text{ kJ} \cdot \text{mol}^{-1}$ .



**Figure 8.** (a) The Hirshfeld surface for **4-NBCA** mapped with  $d_{norm}$  function; (b) The corresponding 2D fingerprint plot; (c-d) The fingerprint plots, broken down into contributions from H···O and H···H contacts; (e) The percentage contributions of various close intermolecular contacts to the Hirshfeld surface area. Other contacts constitute H···N, N···O, C···N.

The calculated cohesive energy of a crystal should reflect its enthalpy of sublimation. Furthermore, the cohesive energy controls to a great extent also the melting point of a solid. Generally, the higher the cohesive energy of a crystal is, the higher should be its melting point. Metal crystals, are a good illustration to this statement, since there is almost a linear correlation between both parameters in them. In the case of the studied crystals, the calculated values for cohesive energy strongly suggest that **1a** should be characterized by the higher melting point than **4-NBCA**. In order to verify this presumption, the derived cohesive energy values have been further related to the results of thermal analyses. The obtained TG-DTA curves for **1a** and **4-NBCA** are shown in Figs S5 and S6, respectively. The first endothermic peak on the DTA curves is attributed to the melting process. Compound **1a** displays a melting point of 226.2°C, while **4-NBCA** of 155.0°C. These results are in agreement with the

expectations. Obviously the energetically favourable **1a** is characterized with higher melting temperature compared to the carboxylic analogue, **4-NBCA**.

#### 4. Conclusion

4-Nitrobenzylphosphonic acid (1a) has been synthesized and structurally characterized. The solid state organization of 1a demonstrates a layered structure with C-H···O(N) hydrogen-bonding interactions between the layers. The two-dimensional hydrogen-bonded network consists of  $R_4^2(12)$  and  $R_4^4(16)$  ring motifs, which reveal considerable stabilization energy values reaching from -222.0 to -365.0 kJ·mol<sup>-1</sup>. The adjacent monolayers are held together via weak interactions involving the nitro group and this is reflected by the interlayer interaction energy of  $-22.2 \text{ kJ·mol}^{-1}$ . In comparison to 4-nitrobenzylcarboxylic acid (4-NBCA), the supramolecular architecture of 1a is more complicated and richer in stronger intermolecular interactions in large part because of the phosphonic group, which is more productive in hydrogen bond formation than the carboxyl group. As a result, the cohesive energy of 1a is equal to  $-226.2 \text{ kJ·mol}^{-1}$  and is almost twice as big as that of 4-NBCA.

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#### **Appendix A. Supplementary materials**

Details on data collection and refinement, fractional atomic coordinates, anisotropic displacement parameters and full list of bond lengths and angles in CIF format have been deposited at the Cambridge Crystallographic Data Centre, No. CCDC 950613. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Graphical abstract



#### Highlights

- 4-Nitrobenzylphosphonic acid (1a) has been synthesized and characterized.
- 1a displays a layered structure with weak C-H···O(N) hydrogen bonds between layers.
- The layer is composed of  $R_4^2(12)$  and  $R_4^4(16)$  ring motifs, exhibiting large stabilization energies.
- The cohesive energy of **1a** is much more advantageous than that of its carboxylic analogue.