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Design, synthesis and noncentrosymmetric solid state organization of three novel pyridylphosphonic acids[†]

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Three pyridylphosphonic acids, 3-pyridylphosphonic acid 1, 5-(dihydroxyphosphoryl)nicotinic acid 2, and 3,5-pyridinediyldiphosphonic acid 3, were synthesized and structurally investigated by solid state FT-IR and single crystal X-ray diffraction methods. All compounds appear in zwitterionic forms in the solid state with a proton transferred from the phosphonic group toward the pyridine N-atom. Strong hydrogen-bond interactions O–H···O and N–H···O organize the molecules of the compounds into polar three-dimensional networks. The crystal structures are additionally stabilized *via* weaker C–H··· O hydrogen bonds and π ··· π or C=O··· π interactions. Powder second harmonic generation and solution NMR spectra were measured as well. The NMR spectra revealed that the double bonds of the functional groups (P=O and C=O), although differently oriented *versus* the N_{py} atom, are coplanar with the aromatic rings in all stable, low energy conformers of compounds 1–3 in solution. In crystals, however, the P=O bonds are tilted toward the ring by 10.77(7)° in 1, 70.42(8)° in 2 and by 43.97(7)° and 6.56(8)° in 3. All three compounds exhibit moderate powder SHG efficiencies compared to that of urea.

Introduction

The rapid development of metallosupramolecular chemistry is derived from the enhanced need for novel functional materials. To a great extent it is oriented toward synthesis and characterization of hybrid coordination compounds, since the unique characteristics of the organic and inorganic components in them are combined in a complementary fashion, which leads to unusual solid state structures with novel properties. A variety of crystalline architectures with different dimensionalities, pore sizes and geometries, and versatile properties have been obtained by changing the compositional range, and varying the metal and the coordination sites, which gives an access to a vast area of complex multifunctional materials useful for selective adsorption and separation,1-5 gas storage,6-8 ion exchange9-14 and catalysis.15-18 Prototypes of this class of solids are the metalcarboxylates and phosphonates, which have been extensively investigated for a long time.

However, the properties of the metal-organic framework (MOF), and therefore the physicochemical and optical characteristics of the material, are determined by the network connectivity, which requires a selection and preparation of the modulus (building unit), as well as a selection and structural modification of the organic linker by changing the topology and the juxtaposition of the functional groups. Very recently, pyridylphosphonic acids were applied as ligands. Search in the Cambridge Structural Database (CSD, Version 5.31)¹⁹ has retrieved thirty five structures of 2-pyridylphosphonates and seven of 4-pyridylphosphonates with d- and f-block metal ions. Three metal complexes (Cd^{II}, Co^{II} and Sn^{IV}) with 3-pyridylphosphonic acid are known, but the crystal structure of the acid itself has not been determined yet. Pyridylphosphonic acids may appear also as important agents in design of Bio-MOFs,²⁰ since many phosphonates containing a pyridine fragment display biological activity and are used as agrochemicals or drugs. Therefore, synthesis and characterization of novel phosphonic acids with nitrogen containing aromatic systems and the phosphonic/ate group(s) attached as a ring substituent are highly desired. A recent review²¹ summarizes different synthetic methods for a direct phosphonylation of azaheterocyclic aromatics.

In this paper we describe the synthesis and discuss the solid state organization of three pyridylphosphonic acids, namely 3-pyridylphosphonic acid 1, 5-(dihydroxyphosphoryl)nicotinic acid 2 and 3,5-pyridinediyldiphosphonic acid 3. Two of them (2 and 3) are novel compounds, previously not reported in the literature. All three compounds are phosphonic analogous of the

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nicotinic 4 and dinicotinic 5 acids, which have a broad use as ligands. In solid state the molecules of 4 and 5 self-recognize via O-H...N interactions forming helices which are further arranged into polar monolayers.^{22,23} However, the layers are packed into centrosymmetric crystal structures by electrostatic and offset face-to-face (OFF) interactions. Our aim was to design organic ligands predisposed for: (a) hydrogen-bond controlled self-recognition and self-assembly into acentric structures: (b) polytopic coordination in order to form multidimensional coordination polymers. Therefore, we postulated that the replacement of the planar carboxylic group(s) with the tetrahedral phosphonic group(s) will lead to non-centrosymmetric structures. There were some arguments for this presumption. The way the molecules of 1-3 self-recognize should not be very different from that in 4 and 5 and the meta-position of the functional groups versus the N_{py} atom may support helical arrangements via N-H···O and/or O-H···O interactions. However, the additional hydrogen-bond donor and acceptor sites and the non-planarity of the phosphonic group may allow for hydrogen-bond controlled interactions in three dimensions.

Experimental section

Syntheses

Synthesis of diethyl pyridylphosphonates 1", 2"(A) and 3"(A) (Scheme 1) by general procedure²⁴. The corresponding bromoderivative of pyridine (20.0 mmol 3-bromopyridine 1', methyl 5bromonicotinate²⁵ 2' or 10.0 mmol 3,5-dibromopyridine 3'), diethyl phosphite (24.0 mmol, 3.1 mL), triethylamine (24.0 mmol, 3.3 mL), toluene (10 mL) and tetrakis-(triphenylphosphine)palladium (0.80 mmol, 0.9244 g) were heated at 85 °C while continuously stirred under argon atmosphere for 12 h. A precipitate of triethylamine hydrobromide, which was formed during the reaction, was filtered under reduced pressure and the by-product was washed with toluene (5 mL). The combined toluene filtrates were evaporated under reduced pressure to dryness. The residue was subjected to column chromatography on silica gel using ethyl acetate or CHCl₃-ethyl acetate as an eluent to obtain pure esters as oils. The eluates were monitored by TLC ($R_{\rm f}$ data are given in the experimental part below) and ¹H, as well as, ³¹P NMR in CDCl₃. The structures of final products were additionally confirmed by ¹H, ¹³C{¹H} NMR in CDCl₃ (esters 1", 2"(A) and 3"(A)), D₂O (acids 1 and 3), D₂O/ DCl (acid 2). The ${}^{31}P{}^{1}H$ NMR data are given in the experimental section below.

Diethyl 3-pyridylphosphonate 1". 3.486 g, 81%, $R_{\rm f} = 0.17$ (silica gel on PET foils with fluorescent indicator 254 nm, ethyl acetate, UV lamp for visualization). ³¹P{¹H} NMR (121 MHz, CDCl₃): δ 14.5 (s). IR (neat, film): $\nu_{\rm max}$ 2985m, 1582m, 1408m, 1255s, 1145m, 1053s, 1023s, 971s, 793m, 711m, 569m cm⁻¹.

Methyl 5-(diethoxyphosphoryl)nicotinate 2"(A). 2.186 g, 40%, $R_f = 0.08$ (silica gel on PET foils with fluorescent indicator 254 nm, CHCl₃ : ethyl acetate = 5 : 1 v/v, UV lamp for visualization). ³¹P{¹H} NMR (121 MHz, CDCl₃): δ 24.4 (s). IR (neat, film): ν_{max} 2986m, 1733s, 1591m, 1444m, 1415m, 1318m, 1292s,



A: PhMe, H(O)P(OEt)₂, Et₃N, Pd(PPh₃)₄, Ar, 12h, 85°C
B: MeCN, H(O)P(O*i*-Pr)₂, (*i*-Pr)₂NEt, Pd(AcO)₂, 1,1'bis(diphenylphosphino)ferrocene (dppf), Ar, 24h, reflux
C: HCl - H₂O, 20h, reflux

1': R	$^{1}=H$	1": R	² =Et	R ³ =H	1: R	$^{4}=H$
2':	COOMe	2"(A):	Et	COOMe	2:	COOH
2':	COOMe	2"(B):	<i>i</i> -Pr	COOMe	2:	COOH
3':	Br	3"(A):	Et	$P(O)(OEt)_2$	3:	PO_3H_2
3':	Br	3"(B) :	<i>i</i> -Pr	$P(O)(OEt)_2$	3:	PO_3H_2

Scheme 1 Synthetic route to compounds 1–3.

1257s, 1200m, 1174m, 1111m, 1052s, 1023s, 972m, 764m, 703m, 657m, 570m cm⁻¹.

Tetraethyl 3,5-pyridinediyldiphosphonate 3"(A). 2.015 g, 43%, $R_f = 0.06$ (silica gel on PET foils with fluorescent indicator 254 nm, ethyl acetate, UV lamp for visualization). ³¹P{¹H} NMR (121 MHz, CDCl₃): δ 12.8 (s). IR (neat, film): ν_{max} 2985m, 1579m, 1562m, 1411m, 1394m, 1260s, 1201m, 1124m, 1264m, 1098m, 1043s, 1023s, 972s, 853m, 795m, 711m, 565s cm⁻¹.

An alternative synthesis (B) of the esters 2'' and 3'' is described in the ESI[†].

General procedure for synthesis of pyridylphosphonic acids 1–3 (Scheme 1). Pyridylphosphonic acids 1–3 were obtained from their esters 1''-3'' (10 mmol) by refluxing for 12 h with a mixture of concentrated hydrochloric acid (10 mL) and water (10 mL). After that the reaction mixture was evaporated to dryness under water aspirator pressure, then water (5 mL) was added and the mixture was evaporated again to dryness. The residue was treated with methanol (5 mL), evaporated under reduced pressure to obtain a solid crude product which was crystallized from water–ethanol or water (as indicated in the Experimental section) to give pure pyridylphosphonic acids 1–3.

3-Pyridylphosphonic acid 1. 1.0340 g, 65%, mp 249–253 °C (H₂O–EtOH). ³¹P{¹H} NMR (121 MHz, D₂O): δ 2.1 (s). Elemental analysis calc. for C₅H₆NO₃P: C, 37.75; H, 3.80; N, 8.81; P, 19.47%. Found: C, 37.44; H, 3.53; N, 8.68; P, 19.38%.

5-(Dihydroxyphosphoryl)nicotinic acid 2. 1.1374 g, 56%, mp $305-310 \ ^{\circ}C \ (H_2O)$. ${}^{31}P{}^{1}H} NMR \ (121 \ MHz, D_2O-DCl)$: $\delta \ 14.2$ (s). Elemental analysis calc. for $C_6H_6NO_5P$: C, 35.48; H, 2.98; N, 6.90; P, 15.25%. Found: C, 35.38; H, 2.82; N, 6.74; P, 15.18%.

3,5-Pyridinediyldiphosphonic acid 3. 1.1714 g, 49%, mp 285–292 °C (H₂O). ³¹P{¹H} NMR (121 MHz, D₂O): δ 13.9 (s). Elemental analysis calc. for C₅H₇NO₆P₂: C, 25.12; H, 2.95; N, 5.86; P, 25.91%. Found: C, 25.30; H, 2.82; N, 5.82; P, 25.83%.

X-Ray single crystal analysis

Suitable single crystals of 1, 2 and 3 were used for data collection on a four-circle κ -geometry KUMA KM4 diffractometer

equipped with a two-dimensional area CCD detector. The graphite monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å) and the ω -scan technique ($\Delta \omega = 1^{\circ}$) were used for data collection. The 960 images, covering over 99% of the Ewald sphere, were performed for six different runs. One image was used as a standard after every 40 images for monitoring the stability of the crystals, as well as for monitoring the data collection. No correction on the relative intensity variation was necessary. Data collection and reduction along with absorption correction were performed using CrysAlis software package.27 The minimum and maximum transmission factors are 0.952 and 0.975 for 1, 0.922 and 0.985 for 2 and 0.966 and 0.997 for 3. The structures, solved by direct methods using SHELXS-97, gave the positions of almost all non-hydrogen atoms. The remaining atoms were located from subsequent difference Fourier syntheses. The structures were refined using SHELXL-97 with the anisotropic thermal displacement parameters.²⁸ The hydrogen atoms of the aromatic ring were located from the difference Fourier maps, but in the final refinement their positions were constrained to thermal parameters and distances. Details of the data collection parameters, crystallographic data and final agreement parameters are collected in Table 1. Selected geometrical parameters are listed in Table 2.

Powder second harmonic measurements and their computations

Powdered samples of the investigated compounds and of urea, which was used as the standard, were mounted between glass microscope slides. The powders were ungraded, but with similar grain sizes for all samples.

	Compounds		
	1	2	3
Formula	C ₅ H ₆ NO ₃ P	C ₆ H ₆ NO ₅ P	C ₅ H ₇ NO ₆ P ₂
Molecular weight	159.08	203.09	239.06
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>Pna</i> 2 ₁ (No. 33)	Fdd2 (No. 43)	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (No. 19)
alÅ	7.5460(15)	19.948(3)	7.0495(14)
b/Å	10.948(2)	28.534(4)	10.490(2)
c/Å	7.8040(16)	5.304(1)	10.813(2)
$V/Å^3$	644.7(2)	3019.0(8)	799.6(3)
Ζ	4	16	4
$D_{\rm calcd}/{\rm g}~{\rm cm}^{-3}$	1.639	1.787	1.986
$D_{\rm obs}/{\rm g}~{\rm cm}^{-3}$	1.630	1.790	1.980
μ/mm^{-1}	0.365	0.352	0.548
Crystal size/mm ³	$0.26 \times 0.24 \times$	0.27 imes 0.16 imes	$0.26 \times 0.21 \times$
	0.22	0.14	0.16
T/K	295	295	295
λ/Å	0.71073	0.71073	0.71073
Total/unique/ observed	8140/1643/1466	9629/1680/1525	10503/2077/1814
Reflections (R_{int})	(0.018)	(0.026)	(0.024)
$R \left[F^2 > 2\sigma(F^2) \right]^a$	0.0209	0.0249	0.0220
wR [F^2 all refls]	0.0531	0.0592	0.0548
Flack parameter	0.12(7)	-0.02(8)	0.04(8)
S	0.955	1.001	1.002
$\Delta \rho_{\rm max}, \Delta \rho_{\rm min}/e \ {\rm \AA}^{-3}$	+0.162, -0.174	+0.248, -0.192	+0.235, -0.256
$a w = 1/[\sigma^2(F_0^2) + (0^2)]$	$(0.0380P)^2$ for 1, w	$r = 1/[\sigma^2(F_o^2) + (0, \sigma^2)]$	$(0.0367P)^2$ for 2 and

 $w = 1/[\sigma^2(F_o^2) + (0.0372P)^2]$ for **3**, where $P = (F_o^2 + 2F_c^2)/3$.

Table 2 Selected bond lengths (Å) and bond angles (°) for compounds 1-3

1			
C3–P3	1.8215(14)	C3–P3–O31	107.81(6)
P3-O31	1.4954(12)	C3–P3–O32	107.77(7)
P3-O32	1.5031(10)	C3–P3–O33	103.83(6)
P3-O33	1.5633(11)	O31-P3-O32	117.68(6)
N1-C6	1.3325(18)	O31–P3–O33	111.61(6)
N1-C2	1.3373(17)	O32–P3–O33	107.22(5)
		C2-N1-C6	121.59(12)
		O31–P3–C3–C2	-13.35(13)
2			
C3-C31	1.510(3)	C3–C31–O31	122.64(17)
C31–O31	1.198(2)	C3-C31-O32	112.30(15)
C31–O32	1.303(2)	O31-C31-O32	125.06(19)
C5–P5	1.8159(16)	C5-P5-O51	108.66(8)
P5051	1.4948(14)	C5-P5-O52	105.72(7)
P5052	1.5165(13)	C5-P5-O53	104.71(9)
P5053	1.5658(17)	O51-P5-O52	114.83(8)
N1-C6	1.341(2)	O51-P5-O53	114.10(8)
N1-C2	1.337(3)	O52–P5–O53	108.01(8)
		C2-N1-C6	122.87(16)
		O31-C31-C3-C2	-1.4(3)
		O51-P5-C5-C6	95.24(17)
3			
C3–P3	1.8013(17)	C3–P3–O31	108.39(7)
P3-O31	1.4880(12)	C3–P3–O32	105.62(7)
P3–O32	1.5212(12)	C3–P3–O33	105.59(7)
P3–O33	1.5375(14)	O31–P3–O32	116.85(7)
C5–P5	1.8062(16)	O31–P3–O33	112.38(7)
P5–O51	1.4916(13)	O32–P3–O33	107.25(7)
P5–O52	1.5229(13)	C5–P5–O51	108.66(7)
P5–O53	1.5456(13)	C5–P5–O52	105.72(7)
N1-C6	1.331(3)	C5–P5–O53	106.76(7)
N1-C2	1.341(2)	O51–P5–O52	115.63(7)
		O51–P5–O53	110.28(7)
		O52–P5–O53	109.34(7)
		C2-N1-C6	123.36(16)
		O31–P3–C3–C2	-132.38(14)
		O51–P5–C5–C6	-173.78(13)

The laser system used for the investigation was previously described.^{29,30} Briefly, a beam from a SESAM mode-locked Nd-YLF oscillator is amplified in a flashlamp-pumped Nd-YLF amplifier resulting in approx. 6 ps pulses at 1054 nm with the repetition rate of 20 Hz and the energies in mJ range. The amplifier beam is attenuated and used without focussing. The measurements were performed in transmission geometry, the second harmonic being detected, after filtering off the fundamental, with a photomultiplier whose output was monitored with a digital oscilloscope. The relative powder second harmonic efficiencies (Table 4) were calculated as an average from the ratios of the reading obtained for the investigated sample and that of urea at several different laser pulse energies (in the range ~10 μ J per pulse).

Second-order nonlinear optical properties of the investigated molecules were also evaluated using the AM1 method^{31,32} as implemented in the MOPAC-7 quantum chemical program. The second-order hyperpolarizabilities were computed for AM1-optimized molecular geometries taken in two forms: that of a neutral molecule and that of a zwitterion built by transferring one of the protons from the phosphonic group to the pyridine nitrogen atom (Table 5).

Table 3	Geometry of	the hydrogen	bonds for compound	ds 1–3 (Å, °)	
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$D-H\cdots A$	D–H	H····A	D····A	D–H…A
1				
1. O33–H33…O31 ⁱ	1.006(16)	1.522(16)	2.5181(15)	170.1(15)
2. N1–H1…O32 ⁱⁱ	1.049(14)	1.519(15)	2.5559(16)	169.0(15)
Symmetry codes: (i) $-\frac{1}{2} + x$, ³ 2	$y_2 - y, z;$ (ii) $\frac{3}{2} - x, \frac{1}{2} + y, -\frac{1}{2}$	+ <i>z</i>		
1. O53–H53…O51 ⁱ	0.87(3)	1.72(3)	2.5195(19)	153(3)
2. O32–H32····O52 ⁱⁱ	0.87(3)	1.72(3)	2.589(2)	175(2)
3. N1–H1…O52 ⁱⁱⁱ	1.00(3)	1.64(3)	2.632(2)	175(2)
Symmetry codes: (i) $-x$, $\frac{1}{2} - y$	$y, -\frac{1}{2} + z;$ (ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1$	+ z; (iii) $\frac{1}{4} - x$, $-\frac{1}{4} + y$, $-\frac{1}{4} + z$	z	
3				
1. O32−H32···O52 ⁱ	1.199(14)	1.286(15)	2.4711(17)	168.1(17)
2. O53–H53···O31 ⁱⁱ	0.986(14)	1.543(16)	2.5248(14)	173.5(14)
3. O33–H33…O51 ⁱⁱⁱ	0.918(16)	1.634(17)	2.5458(18)	171.5(19)
4. N1–H1…O51 ⁱⁱ	0.88(2)	2.34(2)	2.999(2)	131.8(16)
5. N1–H1···O53 ^{iv}	0.88(2)	2.50(2)	2.959(2)	112.7(15)
6. N1–H1…O52 ^v	0.88(2)	2.454(19)	3.050(2)	125.3(16)
7. C2–H2····O32	0.9300	2.5400	2.936(2)	106.00
8. C6–H6…O31 ⁱⁱ	0.9300	2.3200	3,158(2)	149.00
9. C4–H4…O52 ⁱⁱⁱ	0.9300	2.4400	3.348(2)	166.00
10. C2–H2····O33 ^{vi}	0.9300	2.5800	3.382(2)	145.00
Symmetry codes: (i) $1 - x$, $\frac{1}{2}$ +	$-y, \frac{1}{2} - z;$ (ii) $\frac{1}{2} - x, -y, -\frac{1}{2} + \frac{1}{2}$	z ; (iii) $-x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$; (iv) 1 +	$-x, y, z; (v) \frac{1}{2} + x, -\frac{1}{2} - y, -z; (v) \frac{1}{2} + x, -\frac{1}{2} - y, -z; (v) \frac{1}{2} + x, -\frac{1}{2} + y, -\frac{1}{2} + y, -z; (v) \frac{1}{2} + x, -\frac{1}{2} + y, -z; (v) \frac{1}{2} + y, -\frac{1}{2} + y, -\frac{1}{2}$	vi) $\frac{1}{2} + x$, $\frac{1}{2} - y$, $-z$

Compound	1	2	3	Urea
Relative powder SHG efficiency	0.37 ± 0.06	0.58 ± 0.04	0.13 ± 0.03	1

Table 5 Computed vector parts of the second-order hyperpolarizabilities for compounds 1-3

Molecule form	Hyperpolarizability component	Value at $0 \text{ eV} (at.u.)^a$	Value at 0.5 eV (at.u.)
1 zwitterion	Brsha	322.25	336.73
	Busha	48.54	47.45
	B _z sho	59.93	62.83
	β _{vect} SHG	331.35	345.81
1 neutral	β _x shg	28.74	28.06
	β _v shg	117.38	129.78
	β _z shg	-244.26	-269.36
	β _{vect} SHG	272.52	300.30
2 zwitterion	β _x shG	241.70	255.43
	β _{v.shg}	178.58	184.07
	βz.shg	-77.17	-81.37
	β _{vect.SHG}	310.27	325.19
2 neutral	βx.shg	-53.08	-55.18
	β _{v.shg}	-100.81	-107.88
	β _{z.SHG}	9.22	11.40
	$\beta_{\text{vect.SHG}}$	114.30	121.71
3 zwitterion	β _{x.shg}	-224.64	-239.78
	β _{v.SHG}	327.52	340.56
	β _{z.SHG}	-46.87	-50.79
	$\beta_{\text{vect.SHG}}$	399.92	419.59
3 neutral	β _{x.shg}	-60.76	-65.39
	β _{v.SHG}	-19.99	-22.49
	β _{z.SHG}	-10.16	-6.45
	$\beta_{vect,SHG}$	64.77	69.45
^{<i>a</i>} The factor to	convert atomic units to e	esu units is 8.657	1×10^{-33} .

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Infrared spectroscopy

The FT-IR spectra of the compounds were measured in KBr pellets and nujol mulls ($4000-400 \text{ cm}^{-1}$) using a Bruker IFS-88 spectrometer with a resolution of 2 cm⁻¹. In addition the spectra of the partly deuterated 3-pyridylphosphonic acid were measured. Dideutero-3-pyridylphosphonic acid was obtained by dissolving the compound **1** (0.020 g) in deuterium oxide (2 mL), followed by evaporation to dryness under reduced pressure. This procedure was repeated one more time and the residual crystal-line compound was air dried. The frequencies of all observed bands and their tentative assignments are collected in Table S1 (ESI†).

NMR spectroscopy in solution

The ¹³C, ¹H{³¹P}, ¹H, ³¹P{¹H}, ¹³C{¹H} NMR spectra were recorded at room temperature on a Bruker Avance DRX300 instrument, operating at 300.13 MHz (¹H), 121.50 (³¹P) and 75.46 MHz (¹³C). Proton and phosphorus decoupling was achieved by power gated decoupling using Waltz 16 sequence. Reference for ¹³C and ¹H NMR was solvent-chloroform lines (singlet $\delta_{\rm H} = 7.26$ ppm, triplet $\delta_{\rm C} = 77.00$ ppm). NMR spectra were analyzed using MestreC program.³³

Theoretical NMR data calculations

A conformational search was performed using molecular mechanic (MM+) and semiempirical methods (AM1). The found conformers were optimized by the density functional theory (DFT).³⁴ The Becke's three parameter functional³⁵ with the Vosko *et al.*³⁶ local correlation part and the Lee *et al.*³⁷ non-local part, abbreviated as B3LYP, has been applied and the calculations were performed using the standard 6-31G(d,p) basis set.³⁸ The effect of the solvent on the calculated structures was taken into account through the polarized continuum model for chloroform. The ideal gas, rigid rotor, and harmonic oscillator approximations³⁹ were applied for studying the vibrational

frequencies and the thermodynamic properties of the compounds. All structures were in their energetical minimum, which was confirmed by the frequency calculations. The NMR parameters were calculated using the coupled perturbed density functional theory (CP-DFT) method with B3LYP functional and including the diamagnetic spin-orbit, paramagnetic spin-orbit, Fermi-contact and spin-dipolar terms. This functional is believed to give results that best fit the experimental data. A IGLOII base was applied to the calculations. For the calculation of scalar couplings were used the same solvent models as those employed for the geometry optimization. The computations by DFT, AM1 and MM+ methods were carried out using the Gaussian 03 suite of codes program.⁴⁰

Results and discussion

Syntheses

Ethyl and isopropyl esters of pyridylphosphonic acids 1''-3'' were obtained from the corresponding derivatives of 3-bromopyridine 1'-3' and diethyl (Hirao *et al.*,²⁴ procedure A, or diisopropyl phosphite (Montchamp *et al.*,²⁶ procedure B) in the presence of amine using two palladium catalyzed cross-coupling reactions (Scheme 1). Both used methods differ in the type and loading of catalyst. Yield of desired products varied from high to low. The ethyl and isopropyl esters 1''-3'' were chromatographically purified and spectroscopically characterized. The pure esters were hydrolyzed with 6 N hydrochloric acid at reflux to give corresponding pyridylphosphonic acids 1-3 with good yields.

Molecular and crystal structures

All compounds in solid state appear in zwitterionic form (NH⁺ and PO₃H⁻) with a proton transferred from the phosphonic (-PO₃H₂) group toward the nitrogen atom of the pyridine ring (Fig. 1). The proton transfer is manifested in the P-O bond lengths of the phosphonic group as well as in C-N-C angle of the pyridine ring. The deprotonated P-O bond in all compounds is intermediate between the P-OH bond and the formal double bond P=O (see Table 2). It is close in length to the double P=O bond in crystals 1 and 2. In crystal 3 the intermediate ($P \simeq O32$) and P \simeq O52) bonds become significantly longer and the protonated (P-O33 and P-O53) bonds become slightly shorter, which reflects the proton dynamic from both phosphonic groups toward the N_{pv} atom, as well as, between the phosphonic groups of neighbouring molecules. The protonation of the nitrogen atom is reflected also in the enlargement of the internal C-N-C angle $(121.59(12)^{\circ}$ in 1, $122.87(16)^{\circ}$ in 2 and $123.36(16)^{\circ}$ in 3) versus an average C-N-C angle of 117.3(2)° found in CSD for pyridine derivatives.¹⁹ This change is consistent with the valenceshell electron pair repulsion model (VSEPR),41 according to which the bonded pair of electrons affords a smaller region than the lone-pair. The C–O bond distances of 1.198(2) Å and 1.303(2) Å in 2 are typical for C=O and C-OH bonds of the non-dissociated carboxylic group, which proves that also in this compound the proton of the ring nitrogen atom N_{py} is transferred from the phosphonic group in 5-position.

The *meta*-position of the carboxylic group(s) *versus* the pyridine nitrogen atom in nicotinic and dinicotinic acids^{22,23} determines the molecular arrangement into polar layers *via*

O-H···N_{py}/N_{py}-H···O interactions. However, the crystal packing of these compounds takes place with a generation of an inversion center, since there are no specific interactions between the layers. Our design strategy was based on the postulate that by replacing the planar carboxylic group for the three-dimensional phosphonic group, we may promote an acentric three-dimensional arrangement due to hydrogen bonds formed between the monolayers. Indeed, all three compounds display non-centro-symmetric crystal structures. Compounds 1 and 3, which are phosphonic analogous of nicotinic and dinicotinic acids, crystallise in $Pna2_1$ and $P2_12_12_1$ space groups, respectively.



Fig. 1 The asymmetric units with the atom-labelling schemes for compounds 1-3. The displacement ellipsoids are given at the 50% probability level.



Fig. 2 (a and b) The interconnection between the [100] chains in [011] and $[01\overline{1}]$ directions to form two and three-dimensional hydrogen bonded network in **1**. (c) The crystal packing and the hydrogen-bonded network viewed along the chains. The O-H···O (assigned as 1) bonds are shown in

Moreover, compound **3**, containing two phosphonic groups, symmetrically arranged *versus* the pyridine N-atom, displays a chiral crystal structure with helical arrangement of the molecules in all three crystallographic directions. Note that $P2_12_12_1$, though belonging to the Sohncke family, is not a chiral space group. On the other hand, compound **2** can be considered as a derivative of the nicotinic acid with an additional functional group in 5-position or as a derivative of the dinicotinic acid in which one of the carboxylic groups is replaced with a phosphonic group. The total asymmetry of the zwitterion and the chemical and geometrical bias of the functional groups prevent recognition events governed by screw operators enforcing diamond relations in solid state and the compound crystallizes in *Fdd*2 space group.

Supramolecular networks

Numerous hydrogen bond interactions, established between the functional groups of the molecules, as well as the nitrogen site of the pyridine ring, are the main driving forces responsible for the molecular self-recognition and self-association leading to well defined crystal structures 1-3 (see Table 3).

There are two strong hydrogen bonds O33–H33···O31 of 2.5181(15) Å and N1–H1···O32 of 2.5559(16) Å in crystal **1**. The first of them is formed between the phosphonate groups of adjacent glide related zwitterions and serves to arrange them into chains along the *a*-crystallographic axis (Fig. 2a). The second hydrogen bond, established between the protonated N-atom and a phosphonate oxygen site, cross-links *n*-glide chains in [011] and $[01\bar{1}]$ directions in order to form 3D hydrogen-bonded network shown in Fig. 2b. The aromatic rings are arranged into stacks along the *a*-axis with 3.8297(11) Å and 3.8298(11) Å distances between their gravity centres (Fig. 2c).

The unit cell of crystal 2 contains 16 symmetry related zwitterions. Three different hydrogen bonds are used to link them into 3D hydrogen-bonded network. The shortest bond O53-H53...O51 (2.5195(19) A) is formed between the phosphonate groups of rotation related zwitterionic units and extends them into a chain along the *c*-crystallographic axis. The carboxylic groups, arranged from both sides along the chain, approach the phosphonate groups of two neighbouring chains via O32-H32···· O52 bond (of length 2.589(2) A), linking them into a formal monolayer parallel to (010) crystallographic plane (Fig. 3a). The aromatic rings are inclined versus the main plane of the monolayer and amassed into two different stacks along *c*-axis. There are no $\pi \cdots \pi$ interactions between the rings along the stacks. The hydrogen atom of the pyridine nitrogen sites and the carbonyl oxygen site of the carboxylic groups are arranged outward from both sides of the layers (Fig. 3b). However, the carbonyl O31 atom is inaccessible for hydrogen-bond formation since the geometrical and directional requirements of the interaction are incompatible with the symmetry constraints of the crystal network. Instead, the H1(N) atoms of one layer approach the phosphonate O52 atoms of two adjacent layers (N1-H1...O52), completing thus the 3D hydrogen-bonded network. On the other

red colour and the N–H \cdots O (assigned as 2) bonds in blue colour. The hydrogen bond numbering is consistent with that in Table 3.

hand, the carbonyl O31 atoms project the π system of the rings in the next glide-related layer establishing interlayer C=O··· π interaction (the C=O···Cg and O···Cg distances are 3.940(2) Å and 3.1542(18) Å, respectively and the angle C=O···Cg is 123.19(13)°) (Fig. 3c).

In crystal **3** the proton transfer takes place from one of the phosphonic groups, *meta*-positioned *versus* the pyridine nitrogen atom. The molecular symmetry is only slightly reduced, which is the probable reason for appearing of screw axes instead of glide



Fig. 3 The molecular organization in **2**. (a) A view of the hydrogenbonded monolayer. (b) A side view of the monolayer. (c) The 3D hydrogen-bonded network viewed along the *c*-crystallographic axis. The O-H···O and N-H···O bonds are shown in red and blue colours. The interlayer electron pair··· π interactions are shown in gray colour. The hydrogen bond numbering is consistent with that in Table 3.

planes in compound 2. The hydrogen-bonded extensions of the zwitterions are helical in all three crystallographic directions and the structure of the measured crystal is right-handed with a Flack parameter of 0.04(8).⁴² Nonetheless, the space group $P2_12_12_1$ is not a chiral group, since the even-fold screw operations do not produce enantiomorphic pairs.43 There are four strong proton donors in this system (compared to two in 1 and three in 2), which form three O-H···O and three N-H···O hydrogen bonds (listed in Table 3). Additionally, six C-H...O hydrogen bonds stabilize the crystal structure. The protonation of the pyridyl N_{py} atom prompts a marked migration of the phosphonic H32 atom toward the monodeprotonated phosphonate group of an adjacent zwitterion. The implemented hydrogen bond O32-H32... O52 is very strong (2.4711(17) Å) and links the zwitterionic units into a helical chain along the *b*-crystallographic axis. The folding of the *b*-helix is stabilized by $\pi \cdots \pi$ interactions established between the π electronic systems of the double bond P=O31 and the aromatic ring of the next molecule. (P= $O31 \cdots Cg =$ 3.8888(11) Å, $O31\cdots Cg = 3.4234(15)$ Å, $\angle P = O31\cdots Cg =$ 96.70(5)°) (see Fig. 4b). A moderate strong phosphonic-phosphonate interaction (O33-H33···O51 of 2.5458(18) Å) connects the a-translated b-helixes to form undulate molecular monolayers parallel to the (001) crystallographic plane (Fig. 4d). The implemented two-dimensional network is a grid with large $R_4^4(26)$ ring motifs enclosed between six phosphonic groups belonging to four molecules. Another O-H...O bond, donated from the phosphonate H53 hydrogen atom toward the phosphonic O31 oxygen site, executes helical arrangement along the *c*-crystallographic axis and serves to associate the monolayers (Fig. 4c and e). On the other hand the pyridine H1(N1) atom serves as triple hydrogen-bond donor in order to form hydrogen bonds with all three oxygen atoms of the phosphonate group (Fig. 4f). One of them (N1–H1···O52) executes the helical arrangement along aaxis $(2_1(X) \text{ operation})$, while the other $(N1-H1\cdots O53)$ is holding the translation related molecules along the *a*-helix, preventing thus its unfolding (Fig. 4a). The third bond N1-H1...O51 is firming the c-helix. Four C-H···O bonds stabilize the threedimensional network. The C2-H2···O32 bond (of 2.936(2) Å) is intramolecular, formed between the pyridine ring C2 atom (ortho-positioned versus N_{py}) and the phosphonic group, and serves to fix the configuration of the zwitterion. C6-H6...O31 is established along the *c*-helix and stabilizes it. The remaining two bonds (C2-H2···O33 and C4-H4···O52) are formed between the helices.

Nonlinear optical properties

The powder second harmonic generation (SHG) technique provides only a very general indication on the merit of a second-order nonlinear optical (NLO) material, but the results obtained attest to some potential of phosphonic acids for forming interesting crystal structures that, especially with introduction of stronger NLO chromophores, may lead to useful material properties. Table 4 shows the powder SHG results obtained for the three investigated compounds against urea. Clearly, compound **3** has an efficiency lower than the other two compounds.

Table 5 shows results obtained by the AM1 method for the three investigated molecules, each of them modelled as



Fig. 4 (a–c) The 1D helical arrangement of the molecules in 3: the *a*-helix, the *b*-helix and the *c*-helix. (d) The (001) monolayer. (e and f) The

a zwitterion and as a neutral molecule. The values listed in the table are the components and the value (length) of the vector part of the hyperpolarizability $\beta(-2\omega;\omega,\omega)$ computed for the fundamental frequency corresponding to photon energy of 0 eV and 0.5 eV. The vector parts of the hyperpolarizabilities of the molecules, computed by the AM1 method, are on the order of 10^2 atomic units ($\sim 10^{-30}$ esu), which is in agreement with these molecules exhibiting only moderate strength nonlinear effects. It should be noted, however, that while the vector part of the hyperpolarizability is a convenient quantity characterizing the nonlinearity of a polar molecules will depend on particulars of the employed nonlinear process and on the orientation of molecules in the material.

Infrared spectra

The IR spectra of the compounds 1–3 are presented in Fig. 5. The frequencies of the observed bands together with their tentative assignments are given in Table S1 in the ESI[†]. Generally one can state that the measured spectra reflect the structural peculiarities both at a molecular and at a supramolecular level. The different chemical groups in positions 1, 3 and 5 on the benzene ring of the compounds give rise to different band frequencies and intensities of the ring stretching vibrations C–H (3300–3000 cm⁻¹) and C–C (1630–1550 cm⁻¹) and especially of the ring deformation vibrations in the region 730–650 cm⁻¹. The *v*C–P band is observed at 940–955 cm⁻¹. The bands at 1708 cm⁻¹ (*v*C=O), 1316 cm⁻¹ (*v*C–OH) and 1266 cm⁻¹ (*v*C–C), observed in the spectrum of compound **2**, are connected with the vibrations of the carboxylic group.

The strong and broad absorption observed in the whole region $3500-1650 \text{ cm}^{-1}$ is connected with the stretching vibrations ν O–H and ν N–H. It provides evidence for the strong hydrogen bond interactions (P)O–H···O(P), (C)O–H···O(P), that organize the molecules of these compounds in solid state. The spectrum of the partly deuterated analogue of 1 displays a marked red shift and narrowing of the absorption and the observed frequency shift ν OH/ ν OD roughly corresponds to the ratio of the mass factors.

The positions of the gravity centre of the ν OH absorption in the spectra of the compounds correlate well with the lengths of the hydrogen bonds in them. On the other hand, the differentiated structure of the ν OH absorption, issued from strong resonance and coupling effects of the stretching vibrations with overtones and combinations of internal vibrations, reflects the structural relationships between the molecules.^{44,45} So, the four maxima (at 2650 cm⁻¹ and 2450 cm⁻¹ (band A), 2250 cm⁻¹ (band B) and 1735 cm⁻¹ (band C)) and two minima (at 2550 cm⁻¹ and 2400 cm⁻¹), observed in the spectrum of **1**, are a result from

packing patterns viewed along the *c*-axis. For transparency reasons the O–H···O (shown in red colour) and the N–H···O (shown in blue colour) hydrogen bonds are visualized in two separate pictures. The H1(N_{py}) atoms are removed from the picture (e) and the H atoms of the phosphonate groups are removed from picture (f). The (C)H-atoms of the benzene ring are removed from all pictures. The C–H···O bond is shown in green and the π ···Cg interaction in the *b*-helix is shown in gray colours. The hydrogen bond numbering is consistent with that in Table 3.



Fig. 5 The IR spectra of compounds 1–3. The spectrum of the partly deuterated compound 1 is shown in red colour.

couplings with overtone and combination of vibrations of the phosphonate group. For example, the minimum at 2550 cm⁻¹ is caused by the overtone of ν P=O vibration (1379 cm⁻¹), which is clearly observed as a weak bond in the deuterated spectrum. The spectrum of compound **2** displays maxima at 2400 cm⁻¹ (A), 2007 cm⁻¹ (B) and 1650 cm⁻¹ (C) with some additional structure,

which reflects both the existence of two different hydrogen bonds (P)O–H···O(P) (2.5195 Å) and (C)O–H···O(P) (2.589 Å) and coupling effects with overtones of the two different functional groups. The two bands observed at 2660 cm⁻¹ (A) and 2280 cm⁻¹ (B) in the spectrum of compound **3** arise from the two medium strong hydrogen bonds (O53–H53···O31 and O33–H33···O51).

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The broad absorption (band C), appearing in the region below 1600 cm⁻¹ of **3**, is due to the very short O32–H32–O52 hydrogen bond of 2.4711 Å, which has a great extent of a covalent character.46

The spectra in the fingerprint region $(1400-900 \text{ cm}^{-1})$ are very complicated and cannot be understood solely on the ground of intramolecular bonding considerations. For example, the two P-O bonds in 1 and 2. to which no H atom is attached, are very close in length while the third bond P-OH is significantly longer. Therefore, the three strong bands observed at 1275 cm⁻¹, 1192 cm⁻¹ and 1125 cm⁻¹ in **1** and at 1265 cm⁻¹, 1175 cm⁻¹ and 1125 cm⁻¹ in **2** are assigned to the $\nu_a PO_2$ and $\nu_s PO_2$, while the two strong bands at 1205 cm⁻¹ and 1133 cm⁻¹ in the spectrum of 3 are connected with the two independent stretching vibrations $\nu P=O$ of both phosphonic groups. On the other hand, the whole functional groups (-PO₃H₂ and -CO₂H) participate in the hydrogen bond interactions and reflect to a greater or smaller extent the proton motions in O-H...O bridges. In particular, the stretching vibrations of the long P-O(H) bonds are coupled with the deformation vibration δOH and γOH and split into several bands observed at 1060 cm⁻¹, 1037 cm⁻¹, and 986 cm⁻¹ in 1, at 1041 cm⁻¹, 1010 cm⁻¹, 978 cm⁻¹, and 915 cm⁻¹ in 2 and at 1026 cm⁻¹, 1000 cm⁻¹, and 958 cm⁻¹ in **3**.

The above discussion clearly shows that the differences observed in the spectra reflect not only the atom arrangement and the bonding relationships inside the molecules of the compounds 1-3, but also the structural peculiarities issued from the different connectivity patterns between the molecules in the crystals. In particular, they reflect the variable hydrogen-bond interactions responsible for the supramolecular organization of the compounds.

Solution NMR spectra

The NMR (^{1}H , $^{1}H{}^{1}H{}$, ^{31}P , $^{31}P{}^{1}H{}$), HHCosy) spectra both of the studied pyridylphosphonic acids 1-3 and of their esters 1'', 2''(A) and 3''(A) have been measured and analyzed. The spectra of the esters are composed of several multiplets in their aromatic region. For the reasons of their complexity and the literature inconsistency in the assignment of the NMR parameters for diethyl 3-pyridylphosphonate 1'',⁴⁷ we decided also to perform calculations at ab initio level. The theoretical and experimental results for chemical shifts are collected in Table S2[†] and for the coupling constants in Table S3 (given in the ESI[†]). We have found that all stable low energy conformers have C_s symmetry and the double bonds P=O and C=O lie in the symmetry plane of the molecules. However, their bond vectors are differently orientated and point toward the N_{py} atom or in the opposite direction (which is expressed in the Table S3[†] by 'up' or 'down' arrows). The torsion angles describing the orientations of the carboxyl and phosphonate groups in solid state are given in Table 2. This investigation reveals that the stable conformers in solution are different to those in the crystals.

Conclusions

One can state that, in agreement with our design considerations, all three compounds display non-centrosymmetric crystal structures with helical arrangement of the molecules at least in one direction. The crystal structure of 3,5-pyridinediyldiphosphonic acid 3 is chiral, with a helical propagation of the molecules in all three crystallographic directions. The pronounced differences in molecular conformation and torsion angles observed in solid state versus those in solution result from the proton transfer toward the N_{py} atom and the strong (P)O-H···O(P) and N_{py} - $H \cdots O(P)$ interactions between the zwitterions in the crystals. The lack of inversion center in the solid state structures allows for SHG and makes the compounds 1-3 interesting building blocks for nonlinear optical materials. On the other hand, the studied compounds are very attractive as polytopic ligands for design of coordination polymers. Synthesis and study of variable hybrid compounds with 3-pyridylphosphonic linkers are now in progress in our laboratory.

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