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# Structural and vibrational characteristics of amphiphilic phosphonate salts

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## ABSTRACT

1-Decylphosphonic acid (1), ammonium 1-decylphosphonate ( $NH_4C_{10}H_{21}PO_3H$ ) (2), ethylenediaminium 1-decylphosphonate 1,5 hydrate ( $enH_2C_{10}H_{21}PO_3 \cdot 1.5H_2O$ ) (3) and calcium 1-decylphosphonate ( $Ca(C_{10}H_{21}PO_3H)_2$ ) (4) were prepared and characterized by IR and Raman spectroscopy. The structures of 2 and 3 were determined by single crystal X-ray diffraction analysis. Compound 2 crystallizes in the  $P\bar{1}$ space group of triclinic system with two molecules in the asymmetric unit cell whereas compound 3 crystallizes in C2/c space group of monoclinic system with four molecules in the unit cell and both exhibit layered supramolecular structures generated by ionic interaction, H-bonding and alkyl chain interdigitation in the case of 3. The FT-IR and Raman spectra have been assigned in the range 4000–500 cm<sup>-1</sup> for all compounds, and reveal the *trans* conformation of alkane chain in all compounds.

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## 1. Introduction

Phosphonic acids  $(\text{RPO}_3H_2)$  can be consider as analogs of carboxylic acids in which a -COOH group is replaced by a  $-\text{PO}_3H_2$ group, and a R is the alkyl or aryl organic moiety. The geometry of the phosphonic group is nearly tetrahedral. In the recent years, an intensive development of metal phosphonate chemistry is observed due to their possible applications in materials chemistry [1]. Both metal phosphonates and phosphonic acids salts are able to create very interesting structures with specific functions and find application as catalysts, sorbents, sensors and ion exchangers. They can enhance the properties to bulk of materials, inhibit a corrosion, store gas or adsorb drugs [2–13].

The cell membrane plays an important role for existence of a living cell. It protects the cell from infiltrating internal components, directs molecular and ionic transport in and out of the cell, and assists in intercellular communication. The main body of membrane is made of phospholipid bilayer in which some amount of integral membrane proteins and other biomolecules are embedded [14]. Structural and functional features like molecular recognition and energy transduction make the cell membrane a suitable model for novel biosensors or therapeutics [15].

Compounds with long-alkyl chains show a tendency to form supramolecular structures containing characteristic wide hydrophobic layers [16–18]. The conformation and orientation of alkyl chains in the crystals of hybrid organic–inorganic metal

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alkylphosphonates was studied using X-ray diffraction data, IR and Raman spectroscopy [19–21]. Raman spectroscopy was applied in the study on the conformation of the alkyl chains in natural lipid materials coming from acetylcholine receptor of *Torpedo marmorata* or from human erythrocytes [22,23]. The conformational behavior of phosphatidylcholine and phosphatidyl acid membranes against temperature was studied by FTIR method [24]. The synthetic lipid, dioleyl phosphate, was applied as an component of the artificial lipid membrane [25]. The literature data on 1-decylphosphonic acid are very scarce, the X-ray diffraction patterns of the acid, its mono and disodium salts and their selected IR and Raman bands were presented and discussed [26]; 1-decylphosphonic acid was applied in the study of the mixed self-assembled monolayers of Co-porphyrin and *n*-alkane phosphonates on gold [27].

In this paper we describe the synthesis of 1-decylphosphonic acid and its ammonium, ethylenediaminium and calcium salts, the infrared and Raman studies and the single crystal x-ray study of ammonium and ethylenediaminium salt.

## 2. Experimental

## 2.1. Materials and methods

All materials used in this work were of reagent pure quality and were used as obtained.

### 2.1.1. Infrared spectroscopy

IR spectra were recorded as KBr pellets using Perkin Elmer FTIR-2000 spectrophotometer.



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#### 2.1.2. Raman spectroscopy

The Raman spectra of solid samples were recorded in the range  $0-3600 \text{ cm}^{-1}$  with a Bruker FIS-88 TRA-10G-Raman instrument. The excitation was provided by a diode pumped neodymium laser at 1064 nm (150 mV Nd:YAG).

## 2.2. Syntheses

2.2.1. 1-Decylphosphonic acid,  $C_{10}H_{21}PO_3H_2$  (1)

1-Decylphosphonic acid was prepared according to a general procedure of Arbuzov reaction [1].

#### 2.3. X-ray data collection and structure determination

X-ray intensity data for the crystals **2** and **3** were collected using graphite monochromatic MoK $\alpha$  radiation on a four-circle  $\kappa$  geometry KUMA KM-4 diffractometer with a two-dimensional area CCD detector. The  $\omega$ -scan technique with  $\Delta \omega = 1.0^{\circ}$  for each image was used for data collection. The 820 images for six different runs covering over 99% of the Ewald sphere were performed. The unit cell parameters were refined by the least-squares methods. One image was used as a standard after every 40 images for monitoring of the crystal stability and data collection, and no correction on the relative intensity variations was necessary. Data collections were made

$$CH_{3}(CH_{2})_{8}CH_{2}Br \xrightarrow{P(OC_{2}H_{5})_{3},180-190^{\circ}C, 1.5 \text{ h}} CH_{3}(CH_{2})_{8}CH_{2}PO(OC_{2}H_{5})_{2} \xrightarrow{\text{conc. HCl and } H_{2}O, \text{ reflux}} CH_{3}(CH_{2})_{8}CH_{2}PO_{3}H_{2} \xrightarrow{\text{conc. HCl and } H_{2}O, \text{ reflux}} CH_{3}(CH_{2})_{8}CH_{3}(CH_{2})_{8}CH_{3}(CH_{2})_{8}CH_{3}(CH_{2})_{8}CH_{3}(CH_{2})_{8}CH_{3}(CH_{2})_{8}CH_{3}(CH_{2})_{8}CH_{3}(CH_{2})_{8}CH_{3}(CH_{2})_{8}CH_{3}(CH_{3})_{8}CH_{3}($$

2.2.1.1. Diethyl 1-decylphosphonate (**1b**). In a round-bottomed flask were placed 1-decyl bromide (**1a**, 5.75 g, 0.0260 mol) and triethyl phosphite (5.50 g, 0.0331 mol). The mixture was gradually heated to 180–190 °C and at this temperature it was kept for 1.5 h. Then all volatile components of reaction mixture were removed under reduced pressure of water aspirator to yield the crude product: 7.17 g (99%) as an oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.85 (t, <sup>2</sup>J<sub>HH</sub> = 6.9 Hz, 3H, CH<sub>3</sub>), 1.20–1.35 (m, 20H, methylene protons), 1.38–1.92 (m, 4H, methylene protons), 3.99–4.13 ppm (m, 4H, OCH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CDCl<sub>3</sub>):  $\delta$  34.41(s).

2.2.1.2. 1-Decylphosphonic acid (1). The crude diethyl 1-decylphosphonate (1b) (7.020 g, 0.0252 mol), conc. HCl (40 cm<sup>3</sup>) and water (40 cm<sup>3</sup>) were refluxed for 20 h. The crude product, initially as an oil after a short standing at room temperature, was solidified. It was filtered off, dried in air to yield white powder: 3.803 g. The acid was crystallized from hexane (10 cm<sup>3</sup>) to give pure 1: 2.348 g (42%), mp 98–100 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.46–0.55 (m, 3H), 0.87–1.20 ppm (m, 18H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CDCl<sub>3</sub>):  $\delta$ 25.10 (s). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  13.57, 22.36, 24.41, 24.46, 29.24, 29.48, 29.59 (d, <sup>1</sup>J<sub>CP</sub> = 130.6 Hz), 29.67, 31.50, 31.66 ppm.

## 2.2.2. Ammonium 1-decylphosphonate, $NH_4C_{10}H_{21}PO_3H(2)$

0.112 g (0.504 mmol) of 1-decylphosphonic acid was dissolved in 20 cm<sup>3</sup> of warm water and mixed with 0.252 cm<sup>3</sup> of 2.0 M ammonia (0.504 mmol). The solution was left to stay and yielded the colorless crystals after few days. Elemental Anal. Calc. for  $C_{10}H_{26}PO_3N$ : C, 50.19, H, 10.95; N, 5.85. Found: C, 50.52; H, 11.35; N, 4.95%.

## 2.2.3. Ethylenediaminium 1-decylphosphonate 1.5 hydrate, enH<sub>2</sub>C<sub>10</sub>H<sub>21</sub>PO<sub>3</sub> $\cdot$ 1.5H<sub>2</sub>O (**3**)

0.0493 g (0.222 mmol) of 1-decylphosphonic acid was dissolved in 12 cm<sup>3</sup> in warm water and mixed with an excess ethylenediamine (five drops). The solution was left to stay and yielded the pale yellow crystals after few days. Elemental Anal. Calc. for:  $C_{24}H_{68}N_4P_2O_9$ : C, 47.98; H, 11.07; N, 9.05. Found: C, 46.68; H, 10.71; N, 8.82%.

## 2.2.4. Calcium 1-decylphosphonate, $(Ca(C_{10}H_{21}PO_3H)_2)$ (4)

0.0497 g (0.224 mmol) of 1-decylphosphonic acid was dissolvedin 12 cm<sup>3</sup> of warm water and 0.0266 g (0.240 mmol) of calcium chloride was added. The white microcrystalline solid was precipitated immediately. The use of calcium oxide 0.0134 g (0.240 mmol)in the synthesis gave the same product after few days. Elemental Anal. Calc. for C<sub>20</sub>H<sub>44</sub>P<sub>2</sub>O<sub>6</sub>Ca: C, 49.78; H, 9.19. Found: C, 49.84; H, 9.04%. using the CrysAlis CCD program [28]. Integration, scaling of the reflections, correction for Lorenz and polarization effects and absorption corrections were performed using the CrysAlis Red program [28]. The structure was solved by the direct methods using SHELXS-97 and refined using SHELXL-97 programs [29]. The final difference Fourier maps showed no peaks of chemical significance. Details of the data collection parameters, crystallographic data and final agreement parameters are collected in Table 1. Visualization of the structure was made with the Diamond 3.0 program [30]. Selected geometrical parameters are listed in Table 2 and the geometry of hydrogen bonding interactions are collected in Table 3.

## 3. Results and discussion

## 3.1. Crystal structure

## 3.1.1. Crystal structure of ammonium 1-decylphosphonate (2)

The molecular structure of **2** as an ORTEP drawing is shown in Fig. 1, together with the atom numbering scheme. Selected interatomic distances and angles as well as the details of hydrogen bonding for compound **2** are given in Table 2. Ammonium 1-decylphosphonate crystallized in the monoclinic space group  $P2_1/n$ , with two molecules in the asymmetric unit cell. Crystal of **2** is built of  $C_{10}H_{21}PO_3H^-$  anions and  $NH_4^+$  cations.

The layered structure of the crystal of **2** is dominated by the complex system of hydrogen bonds between phosphonate group and ammonium ion (Table 3). The 1-decylphosphonate ions are situated in the head-to-head and tail-to-tail relation. The very wide amphiphilic layers (26.345(5) Å) parallel to the *ab* crystallographic plane are built of the hydrophilic central part and the external, hydrophobic part. The interlayer contacts are of the very weak Van der Waals type, the aliphatic chains do not interdigitate (Fig. 2a).

The strongest hydrogen bond,  $O(3)-H(O3)\cdots O(2)$ , joins the phosphonate groups lying along the line parallel to the *a* crystallographic axis. The hydrogen bonds involved with the N–(H1), N–(H2) and N–(H3) donor groups connect the phosphonate groups with ammonium ions forming thereby the thin layer parallel to the *ab* crystallographic plane (the ring motifs  $R_5^5$  (12),  $R_3^3$  (10),  $R_4^4$  (8) and  $R_4^4$  (12)) [31]), Fig. 2. This plane is connected with the same plane related by the symmetry operation i = 1 - x, 1 - y, 1 - z by the hydrogen bonds N–(H4)···(O2)<sup>i</sup> ( $R_4^2$  (8)) in the head-to-head relation of 1-decylposphonate ions. The phosphonate group is single donor and fivefold acceptor, whereas the ammonium ion is fourfold donor.

### Table 1

Crystallographic data for ammonium 1-decylphosphonate (2) and ethylenediaminium 1-decylphosphonate 1.5 hydrate (3).

Empirical formula	$NH_4C_{10}H_{21}PO_3H$	$(C_2H_4N_2H_6C_{10}H_{21}PO_3)_2 \cdot 3H_2O$
Formula weight (g mol <sup>-1</sup> )	239.29	618.76
Crystal system, space group	triclinic, P1	monoclinic, $C2/c$
a (Å)	4.6405(9)	42.783(6)
b (Å)	6.1363(12)	5.991(1)
<i>c</i> (Å)	26.345(5)	13.903(2)
α, β, γ (°)	95.23(1),91.28(1), 100.53(2)	94.42(1)
$V(Å^3)$	733.9(3)	3552.9(9)
Ζ	2	4
$D_{\rm calc}/D_{\rm obs}~({\rm g~cm^{-3}})$	1.083/1.08	1.157/1.15
$\mu (\mathrm{mm}^{-1})$	0.179	0.170
Crystal size (mm)	$0.28\times0.25\times0.22$	$0.19 \times 0.18 \times 0.15$
Radiation type, wavelength, $\lambda$ (Å)	ΜοΚα (0.71073)	ΜοΚα (0.71073)
Temperature (K)	295(2)	295(2)
$\theta$ range (°)	2.11-29.36	2.87-29.37
Absorption correction	Numerical	Numerical
$T_{\min}/T_{\max}$	0.9612/0.9742	0.9691/0.9766
Refs. collected/unique/observed	10299/3678/1888	23363/4588/2347
R <sub>int</sub>	0.0712	0.0590
Refinement on		
$R[F^2 > 2\sigma(F^2)]$	0.0514	0.0517
$wR(F^2 \text{ all reflections})$	0.0795	0.0958
Goodness-of-fit, S	1.006	1.001
$\Delta  ho_{ m max}$ , $\Delta  ho_{ m min}$ (e Å <sup>-3</sup> )	+0.196, -0.233	+0.223, -0.249

 $wR = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma wF_o^4\}^{1/2}; \ w^{-1} = 1 / [\sigma^2(F_o^2) + (0.0577P)^2 + 0.1293P] \text{ where } P = (F_o^2 + 2F_c^2) / 3.$ 

## Table 2

Selected bond lengths (Å) and angles (°).

(a) Ammonium 1-decylphosphonate ( <b>2</b> )			
P1-01	1.4948(13)	P1-02	1.5158(13)
P1-03	1.5622(13)	P1-C1	1.7845(19)
01-P1-02	114.63(7)	01-P1-03	112.91(7)
02-P1-03	105.30(8)	01-P1-C1	110.96(9)
02-P1-C1	107.52(8)	O3-P1-C1	104.87(9)
(b) Ethylenediaminium 1-decylphosphonate 1.5 hydrate ( <b>3</b> )			
P1-01	1.5130(11)	P1-02	1.5153(12)
P1-03	1.5181(12)	P1-C1	1.8011(17)
01-P1-02	111.46(7)	01-P1-03	111.75(7)
02-P1-03	112.19(7)	01-P1-C1	109.13(8)
02-P1-C1	105.90(8)	03P1-C1	106.06(7)

### Table 3

Hydrogen-bond geometry (Å, °).

D-H···A	D-H	H···A	D···A	D−H···A		
(a) Ammonium 1-decylphosphonate ( <b>2</b> )						
03-H3002 <sup>i</sup>	0.95(2)	1.56(2)	2.500(2)	174(2)		
N1–H1…O1 <sup>ii</sup>	1.02(2)	1.75(2)	2.773(2)	175(2)		
N1–H2…O1 <sup>iii</sup>	0.94(2)	1.93(2)	2.873(2)	175(2)		
N1–H3…O2	0.88(2)	2.09(2)	2.961(2)	170(2)		
$N1H4\cdots O2^{iv}$	1.03(2)	1.81(2)	2.838(2)	173(2)		
Symmetry codes: (i) x – 1, y, z; (ii) x + 1, y + 1, z; (iii) x, y + 1, z; (iv) – x + 1, –y + 1, –z + 1						
(b) Ethylenediaminium 1-decylphosphonate 1.5 hydrate ( <b>3</b> )						
N1-H1…O5	0.87(2)	2.32(2)	2.958(2)	130(2)		
N1–H1···O4 <sup>i</sup>	0.87(2)	2.34(2)	3.006(2)	134(2)		
N1–H2···O3 <sup>ii</sup>	0.93(2)	1.77(2)	2.688(2)	169(2)		
N1-H3…O1	0.94(2)	1.80(2)	2.726(2)	168(2)		
N2–H4…O4 <sup>i</sup>	0.91(2)	2.29(2)	2.969(2)	131(2)		
N2–H5···O2 <sup>iii</sup>	0.84(2)	1.84(2)	2.665(2)	166(2)		
N2–H6···O1 <sup>iv</sup>	1.00(2)	1.76(2)	2.752(2)	169(2)		
O4−H1 <i>W</i> 1···O3 <sup>ii</sup>	0.73(2)	2.20(2)	2.929(2)	170(2)		
$O4-H2W1\cdots O2^{v}$	0.92(2)	1.78(2)	2.678(2)	167(2)		
05-H1W2…03	0.83(2)	1.92(2)	2.733(2)	167(2)		
Symmetry codes: (i) -x, y, -z + 1/2; (ii) x, y - 1, z; (iii) x, -y + 2, z + 1/2; (iv) x, -y + 1, z + 1/2; (v) -x, -y + 1, -z						



Fig. 1. View of the molecular unit of  $NH_4C_{10}H_{21}PO_3H$  (2) with the atom labeling scheme. Displacement ellipsoid are drawn at the 50% probability level.



**Fig. 2.** The details of packing and hydrogen bond system in the crystal of **2**, a – packing in the crystal, b – hydrogen bonds affording the head-to-head connection between 1-decylposphonic ions *via* ammonium ions, c – hydrogen bond system perpendicular to *ab* crystallographic plane. Dashed lines represent the hydrogen bonds. Symmetry code: (i) x - 1, y, z; (ii) x + 1, y + 1, z; (iii) x, y + 1, z.



**Fig. 3.** View of the molecular unit of  $enH_2C_{10}H_{21}PO_3 \cdot 1.5H_2O$  (3) with the atom labelling scheme. Displacement ellipsoid are drawn at the 50% probability level.

The aliphatic chains in the crystal of **2** have the *trans* conformation. The distances between the carbon atoms in the adjacent chains in the hydrophobic layer are equal to 4.64 Å and 5.02 Å. The shortest distance between the carbon atoms from the neighbor layers is 4.32 Å.

3.1.2. Crystal structure of ethylenediaminium 1-decylphosphonate 1.5 hydrate  $(\mathbf{3})$ 

The molecular structure of **3** as an ORTEP drawing is shown in Fig. 3, together with the atom numbering scheme. Selected interatomic distances and angles as well as the details of hydrogen bonding for compound **3** are given in Tables 2 and 3.



**Fig. 4.** Packing in the crystal of **3** viewed along b xis (a) and details of the hydrogen bond system viewed along the a xis (b). Dashed lines represent the hydrogen bonds.

Ethylenediaminium 1-decylphosphonate crystallized in the monoclinic space group C2/*c*, with four molecules in the asymmetric unit cell. Crystal of **3** is built of  $C_{10}H_{21}PO_3^{2-}$  anions,  $NH_3CH_2CH_2NH_3^{2+}$ cations and water molecules.

The organization of the crystal of **3** is very similar to that of the crystal of **2**, Fig. 4a. The crystal structure of **3** is more compact than that of **2** because the aliphatic chains interdigitate. The density of **2** and **3** are equal to 1.083 and 1.157 g/cm<sup>3</sup>, respectively.

The phosphonate groups interact with ethylenediaminium cations through four strong hydrogen bonds (Table 3) and form the layer parallel to the bc crystallographic plane, composed of the thin hydrophilic part and wide hydrophobic part (the ring motifs:  $R_4^4$  (10) and  $R_4^4$  (18)), Fig. 4a and b. The hydrophilic layers related by the inversion symmetry operation, are joined by the weaker hydrogen bonds between water molecules, bearing the donor and acceptor functions, and  $C_{10}H_{21}PO_3^{2-}$  as well as  $enH_2^{2+}$ ions. No water-water interaction are observed. The water molecules are almost coplanar in relation to the plane parallel to the layer plane. The alkyl chains of neighbor layers interdigitate. The shortest distance between the carbon atoms in the hydrophobic part are: 4.22 and 5.52 Å, for interdigitating and coming from the same plane alkyl chains, respectively. The trans conformation of the alkyl chain in **3** is slightly disordered. In **2**, the C(5)-C(6), C(8)-C(9) and C(9)-C(10) distances are noticeably shorter than those in **3**, the difference between the respective C–C–C angles in the C(6)–C(10) part of the alkyl chains in **2** and **3** also exceeds  $3\sigma$ (Supplementary material).

## 3.2. Vibrational spectra

Vibrational spectroscopy is very suitable method for studying the conformation of alkyl chain in natural and synthetic products [19–24]. The position, intensity and shape of the bands generated by the v(C-H) vibrations in the methylene group as well as stretching and deformation modes of carbon skeletal are correlated with chain conformation and packing in the chain assemblies [32–35].

The infrared and Raman spectra of 1-decylphosphonic acid (1), ammonium 1-decylphosphonate (2), ethylenediaminium 1-decylphosphonate 1,5 hydrate (3) and calcium 1-decylphosphonate (4) are shown in Figs. 5 and S1–S8. The positions and intensity of the vibrational bands found in the frequency region from 3500 cm<sup>-1</sup> to 400 cm<sup>-1</sup> are given in Table 4. Band assignment has been made by comparison with the results of the studies on alkyl phosphonic acids [36], alkyl chains [33–35], layered organicinorganic hybrid materials [20], tin(IV) alkyl phosphonates [21] and ethylenediaminium salt [37].

The most striking differences between the IR spectra of **1–4** are observed for the vibrations of phosphonate group, in the region 1250–900 cm<sup>-1</sup> where the v(P=O) and v(P-O(H)) modes are expected [21,36]. In this region the spectra of **1**, **2**, **3** and **4** display the specific character because the different state of phosphonic group protonation or different interactions of phosphonate ions with cations are found in the studied compounds. The IR bands are very strong with the multiple maxima, in the case of calcium compound the position and shape of the bands is similar to those reported for tin(IV) alkyl phosphonates [21].

The spectral features in the region of the C–H stretching vibrations obtained for the four studied compounds are very similar in both the IR and Raman spectra, Fig. 5. The  $v_{as}(CH_2)$  and  $v_s(CH_2)$ modes of methylene groups for all-*trans* alkyl chains are expected in the range 2916–2918 cm<sup>-1</sup> and 2846–2849 cm<sup>-1</sup>, respectively [19]. In the IR spectra of **1**, **2**, **3**, and **4** the position of the bands generated by the antisymmetric and symmetric stretching modes of [– (CH<sub>2</sub>)<sub>*n*</sub>–] groups are located at very similar wavenumbers, Table 4. This indicate that the alkyl chains adopt the *trans* conformation and is confirmed by the structural data obtained for compounds **2** and **3**.

The antisymmetric and symmetric C–H stretching modes of alkanes give rise to the Raman bands centered at 2880 and 2850 cm<sup>-1</sup>, respectively. The ratio of the intensity of these bands,  $I_{2880}/I_{2850}$ , is used to interpret the structure of hydrocarbons. The values of  $I_{2880}/I_{2850}$  equal ~2 for crystalline alkanes and decrease to 0.7 for alkanes in the liquid state [34]. The intensity of the band located at 2850 cm<sup>-1</sup> is sensitive to the lateral interchain interaction, the intensity of the band centered 2880 cm<sup>-1</sup> is sensitive to temperature. The  $I_{2880}/I_{2850}$  values found for **1**, **2**, **3** and **4** equal 1.56, 1.41, 2.12 and 1.75, respectively. The obtained values indicate that alkyl chains in the studied compounds are not distorted from the *trans* conformation.

Two medium intensity bands generated by the carbon–carbon stretching vibrations, observed in the Raman spectra of alkanes in the region of 1150–1050 cm<sup>-1</sup>, are characteristic for *trans* 



Fig. 5. IR and Raman spectra of (a) 1-decylphsphonic acid (1), (b) ammonium 1-decylphosphonate (2), (c) ethylenediaminium 1-decylphosphonate 1.5 hydrate (3) and (d) calcium 1-decylphosphonate (4).

## Table 4

IR spectra data for 1-decylphosphonic acid (1), ammonium 1-decylphosphonate (2), ethylenediaminium 1-decylphosphonate 1.5 hydrate (3) and calcium 1-decylphosphonate (4).

1		2		3		4		Band assignment <sup>a</sup>
IR	Raman	IR	Raman	IR	Raman	IR	Raman	
				3404 s				v(OH) <sub>H20</sub>
		3291 s,br		3252 s			٦	
2020 a ha		3208 s,br		3150 s,sh			7	v(NH)
3089 S,DF	2965 w	3045 S,DF	2961 w				ر 2954 w	
2958 vs	2936 w	2955 vs	2930 m	2954 s	2959 m	2956 s	2930 m	$v_{as}(CH_3)$
2921 vs		2918 vs		2922 vs		2919 vs		$v_{\rm as}(\rm CH_2)$
	2907 m		2917 m		2898 m		2903 m	$v_{as}(CH_3)$
2074		2898 s,sh		2070		2000		
2874 VS	2878 vs	2872 S	2878 vs	2870 m	2878 vs	2869 s	2882 vs	$v_{s}(CH_{3})$
2851 vs	2842 m	2851 vs	2844 s	2849 s	2859 s	2847 vs	2847 s	$v_{\rm as}(\rm CH_2)$
					2844 s			v <sub>s</sub> (CH <sub>2</sub> ) <sub>enH22+</sub>
	0704		2522		2812 vw		2722	
	2724 vw		2720 w	2560 s br	2713 vw	2345 m br	2720	Hydrogen bond vib
2297 s,br		2295 m		2500 3,51		2345 111,01	}	nyurogen bona vib.
,		1897 m		2126 m				
1702 m		1711 m		1725 vw		1638 vw	J	
		1671 m		1678 w				S(NILL)
				1647 III 1610 m			ļ	$\partial(\mathbf{NH})_{enH22+}$
				1561 m			1	10(011)H20
				1515 w			J	
1.400	1493 w	4 474	1494 w	1.400	1.460	1.467	1.405	
1466 s	1465 m	14/1 s	1466 m	1468 m	1469 m	1467 m	1465 m 1457 m	$\partial(CH_2)$
	1449 m	1460 s.sh	1453 m		1458		1449 m	$\delta(CH_2)$
	1450 m				1455		1440 m	()
1405 m	1436 m		1438 m		1430			$\delta(CH_2)$
1276 m		1412	1411 w	1418 vw	1418 1260 w	1413 vw		
1370 III 1354 w		1379 vw 1351 vw		1379 W 1343 vw	1360 W	1372 VW 1347 VW		$\sigma_{s}(CH_{3})$ $\omega(CH_{2})$
1332 w		1001 111		101010		1324 w		(CTT2)
1388 w								
1297 m	1295 m	1327 vw	1295 m	1291 vw	1296 m	1294 w	1295 w	$\omega(CH_2)$
12/2 m 1263 m		1260 v		1259 104		12/5 W 1261 w		$\delta(OH) \tau(CH_{-})$
1243 s		1200 V		1255 VW		1243 m		
1232 s		1235 m		1223 m		1229 m		
1202 s		1196 s		1189 vw	1189 vw	1197 s		$\delta(OH)$
				11/1 m		1180 s,sh		$v(\mathbf{P} - \mathbf{O})$
		1135 vs		1141 111		1144 VS		V(F=0)
1126 vw	1121 m		1121 w	1125 m	1126 m	1121 s,sh	1123 w	v(C-C)
					1079 w			v(C-N)
1080 s	1067 m	1110 sh,m	1062		1064 m		1062	v(P=O)
1067 s	1067 111	1060 m	1065 W	1089 m.sh	1064 111	1068 s	1003 W	$V(\mathbf{U}-\mathbf{U})$
1056 s		1000 111		1058 vs		1000 0		v(P-O)
1038 m				1034 vs		1045 vs	J	
1019 s		1020 s	1000	1005 a				(P. Q)
1000 Vs		1007 VS	1006 W	1005 s	985 m			v(P-O)
990 s		993 s		982 s	505 m	996 vw	٦	(C C)enH22+
959 s	957 vw	959 s		965 s		959 w		v(P-O)
947 vs	950 vw	938 vs		931 w,sh	000	925 vs		
	888 1/14/		890 1/14/	899 VW	898 W	891 m	890 w	v(C-C)
	000 111		050 VW	847 w		051 11	050 W	
				836 w	837 m			
			780 vw	797 w	769 w			()
789 s 772 m sh	788 W	779 m		783 w		783 m	785 w	$\gamma(OH)$
775 m,sm 718 s		718 m		770 w 723 w		717 m		v(PC)
615 vw		670 vw		678 vw		/ •••		, ( 2)
				648 vw			_	
530 s	527 vw	559 s		564 s		555 vs	ſ	\$( <b>PO</b> )
ວບວ m		512 M		223 m 495 s	491 vw	2∠1 M 488 m sh	$\succ$	0(PU)
467 s	464 vw	467 s	467 vw	479 s	151 000	474 s	J	
427 w		434 w				454 m		$\delta(CCC)$

<sup>a</sup> Abbreviations: vs – very strong, s – strong, m – medium, w – weak, vw – very weak, sh – shoulder, v – stretching,  $\delta$  – bending,  $\gamma$  – rocking,  $\omega$  – wagging.

conformation of the alkyl chains. In the spectra of the studied compounds the first band appears at 1121, 1121, 1126 and 1123 cm<sup>-1</sup>, where the second band is centered at 1067, 1063, 1064, 1063 cm<sup>-1</sup> for **1**, **2**, **3**, and **4**, respectively. Only in the spectrum of **3** the weak Raman band with the maximum at 1089 cm<sup>-1</sup> is observed. This band in the spectra of alkanes is characteristic for the *gauche* conformation of the chain [32]. We have assigned this band to the v(C-C) mode of ethylenediaminium cation because the structural study revealed that the alkyl chain adopts the *trans* conformation.

The occurrence of very broad, medium bands in the region  $2800-1600 \text{ cm}^{-1}$  in the spectra of compounds **1–4** (Table 4) is characteristic for strong hydrogen bonds [38].

## 4. Conclusions

1-decylphsphonic acid (1) as well as ammonium (2), ethylenediaminium (3) and calcium (4) 1-decylphosphonates have been obtained. The single crystal X-ray study of 2 and 3 reveal the layered structure of these compounds dominated by the complex systems of hydrogen bonds and ionic interactions between 1-decylphsphonate anions and ammonium cations in 2 and ethylenediaminium cations and water molecules in 3. The amphiphilic layers are composed of internal hydrophilic part and external hydrophobic parts. The alkyl chains are directed outside and do not interdigitate with neighbor layer in 2 and digitate in 3. The trans configuration of alkyl chains in 1–4 is confirmed by vibrational spectra.

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## Appendix A. Supplementary material

The IR and Raman spectra of compound **1–4** with the wave numbers explicitly marked are included. Additional material comprising full details of the X-ray data collection and final refinement parameters including anisotropic thermal parameters and full list of the bond lengths and angles for compounds **2** and **3** have been deposited with the Cambridge Crystallographic Data Center in the CIF format as supplementary publications Nos. 843514 and 843513. Copies of the data can be obtained free of charge on the application to CCDC, 12 Union Road, Cambridge, CB21EZ, UK, fax: +44 1223 336 033; email: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2011.10.051.

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