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Sylwia Zięba<sup>1</sup>, Alina T. Dubis<sup>2</sup>, Andrzej K. Gzella<sup>3</sup>, Paweł Ławniczak<sup>1</sup>, Katarzyna Pogorzelec-Glaser<sup>1</sup>, Andrzej Łapiński<sup>1,\*</sup>

A new approach towards achieving proton conducting materials based on aromatic acid and heterocyclic base was proposed. It can lead to a new material in which all hydrogen bonding interactions are of the medium, or weak strength and rotations of the base and acid molecules are possible. If the above conditions are met, one can expect a high value of proton conductivity governed by the Grotthuss mechanism. Two salts of imidazole with benzoic acid having one carboxylic acid group and salicylic acid having a carboxylic and hydroxyl group located in the *ortho* position, were synthesized. Physical properties of these newly synthesized proton conducting salts were investigated using experimental and theoretical methods. The structures of these salts were studied by X-ray diffraction and <sup>1</sup>H and <sup>13</sup>C NMR techniques. The intermolecular interactions in the salts were analyzed by DFT calculations, within the QTAiM theory, and by the Hirshfeld surface analysis. The  $\pi$ - $\pi$  interactions, the proton conduction pathways, and the transport mechanism are also discussed.

# Introduction

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Over the past few years, new proton conducting materials have attracted much attention. Conducting materials can be used in a wide range of energy devices, including solid-state fuel cell as well as many types of electrolytes in sensors.<sup>1-6</sup> There is a growing technological need for solids capable of high ionic conductivity. A novel conducting material should show good conductivity of at least Nafion<sup>©</sup> perfluorocarbon sulphonic acid polymer (5×10<sup>-2</sup> S·cm<sup>-1</sup>)<sup>7</sup>, a melting point higher than 100 °C and its degradation should start at a temperature lower than its melting point. Many salts based on dicarboxylic acids and heterocyclic molecules such an imidazole, triazole, benzimidazole have been synthesized. For instance, a new complex of imidazolium proton transfer dipicolinate. benzimidazolium and imidazolium camphor sulfonate, 3,5dihydroxybenzoate, and 5-nitrosalicylic acid has been studied.<sup>8,9</sup> Imidazole has been found a very promising building unit of the conducting salts.

In the process of designing new materials showing desired properties, the prediction of occurrence of specific interactions

- <sup>c.</sup> Department of Organic Chemistry Poznan University of Medical Sciences
- Grunwaldzka 6, Poznan, Poland

between functional groups, the ability to form hydrogen bonds as well as the prediction of the crystal structure are of crucial importance at the chemical reaction stage. Acid-base reactions can lead to formation of either salts or co-crystals. On the basis of the pK<sub>a</sub> difference between the acid and the conjugate base, we can predict what material we can get.<sup>10</sup> Dicarboxylic acids are attractive substrates for crystal engineering due to their ability to hydrogen bonding formation, while the nitrogen-containing heterocyclic bases are known to form hydrogen bond networks to water.<sup>11,12</sup> The hydrogen bonding formation is also characteristic of heterocyclic acids with carboxyl groups.<sup>13,14</sup> Earlier studies have shown that the exchange of imidazole with triazole or benzimidazole,<sup>15-20</sup> leads to a change in the conductive properties of their salts: the electric conductivity equals  $10^{-1}$  and  $2 \times 10^{-4}$  S·m<sup>-1</sup> for imidazolium sebacate and benzimidazolium sebacate, respectively.

In this study, a new approach towards achieving a novel organic salt that could act as a proton conductor was proposed. The new material will have all intermolecular bonds of medium strength. This property allows rotations of the base and the acid molecules. The preparation of these materials was based on the interactions between the aromatic acid and heterocyclic base. Acid and base moieties are planar ring molecules. In the design process of the new proton conducting salt, it is worth knowing what effect the type of substitution pattern of the benzoic acid ring has on the physical properties of the material. For this purpose, we have synthesized two new salts that are composed of imidazole and benzoic acid (denoted as 1) and imidazole and salicylic acid (denoted as 2) (see Fig. 1a, b). In these salts, the acid moieties differ in the number of groups attached to the benzene ring. Benzoic acid is composed of a benzene ring with carboxylic group, whereas salicylic acid is formed of a benzene ring with carboxylic and hydroxyl groups, located in the ortho position. The substitution pattern of an aromatic ring

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<sup>&</sup>lt;sup>a.</sup> Institute of Molecular Physics

Polish Academy of Sciences Smoluchowskiego 17, Poznan, Poland

<sup>&</sup>lt;sup>b.</sup> Instytute of Chemistry

University of Bialystok Ciołkowskiego 1K, Bialystok, Poland.

<sup>\*</sup> Corresponding author: E-mail: lapinski@ifmpan.poznan.pl

The supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC), 12 UnionROAD, Cambridge CB2 1EZ (UK), /336-033, E-mail: deposit@ccdc.cam.ac.uk, World Wide Web: http://www.ccdc.cam.ac.uk (deposition No. for 1: CCDC1892005, for 2: CCDC 1892004).

influences the symmetry of the hydrogen bonding network, the melting point, the conductivity and activation energy of the substance.

The crystal structure, chemical environment, and symmetry of studied molecules were determined by the X-ray diffraction method and NMR technique. The thermal stability was assessed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), while the electrical properties were investigated using the impedance spectroscopy method. The Fourier transform infrared (FTIR) and Raman spectroscopies were applied to study the molecular dynamics of these proton conductors. The theoretical studies were performed using the Density Functional Theory (DFT), Quantum Theory of Atoms in Molecules (QTAIM), and Hirshfeld surface analysis.

To the best of our knowledge, the proton conduction of imidazolium benzoate and salicylate salt study by the DFT, QTAIM, or Hirshfeld surface analysis and spectroscopic study has not been reported yet (**1**, **2**). The main goal of this work was to find out whether the substitution pattern of the benzene ring could affect electrical conductivity within a set of imidazolium salts: imidazolium benzoate (**1**), imidazolium salicylate (**2**) and investigated previously <sup>21</sup> imidazolium orto-phthalate (**3**) and imidazolium terephthalate (**4**) (see Scheme 1).



Scheme 1 Schematic representations of the structure of salts 1-4.

The efficacy of spectroscopic data as descriptors of molecular dynamics of a proton conductor was also discussed. This work is a continuation of our earlier study on imidazolium salts<sup>21,</sup> and to the best of our knowledge, neither spectroscopic nor theoretical data of salt **1** and **2** have been previously reported.

## Materials and methods

#### Synthesis procedure

Salts **1** and **2** were obtained from solutions (ethyl acetate, Merc KGaA, 99.8%) containing imidazole (Sigma-Aldrich, purity >=99.5%), benzoic acid (POCH Gliwice, >=99.5%), and salicylic acid (Sigma-

Aldrich, 98%), respectively. The molar ratio of imidazole to acid was 1:1. All substrates were dissolved separately: Theo3010416n91Were combined, mixed, and stirred vigorously. The crude precipitate was filtered off and recrystallized from ethyl acetate. The crystals were isolated by filtration, washed out with cold ethyl acetate, and allowed to dry. Crystals of 1 and 2 are transparent plate crystallites 5 mm in length and about 4 mm in thickness.

#### **Experimental methods**

*Data collection*. A colourless plate crystal (AcOEt) of 0.31 x 0.22 x 0.14 and 0.24 x 0.22 x 0.11 mm was used to record 10482 and 16447 (MoKα-radiation,  $\theta_{max} = 29.68$  and 29.60°) intensities on a Rigaku SuperNova Dual four-circle diffractometer equipped with an Atlas CCD detector<sup>22</sup> using mirror monochromatized MoKα radiation from a high-flux microfocus source ( $\lambda = 0.71073$  Å) for salt 1 and 2, respectively. Accurate unit cell parameters were determined by least-squares techniques from the  $\theta$  values of 4317 and 6107 reflections,  $\theta$  range 4.02–29.02° and 4.28–29.22° for salt 1 and 2, respectively. The data were corrected for Lorentz polarization and absorption effects.<sup>22</sup> The 2348 and 2578 unique reflections ( $R_{int} = 0.035$  and 0.036) were used for structure determination for salt 1 and 2, respectively.

Structure solution and refinement. The structure was solved by the dual-space algorithm (SHELXT),<sup>23</sup> and refined against F<sup>2</sup> for all data (SHELXL-97).<sup>24</sup> The positions of the H atoms bonded to N (salt 1 and 2) and O (salt 2) were obtained from the difference Fourier maps and were refined freely. The remaining H atoms were placed geometrically in calculated positions and were refined with a riding model, with 1 C–H = 0.95 Å ( $C_{ar}$ H) and  $U_{iso}$ (H) =1.2 $U_{eq}$ (C). Final refinement for salt 1 converged with R = 0.0416 (for 2008 data with  $F^2 > 4\sigma(F^2)$ ), wR = 0.1100 (on  $F^2$  for all data), and S = 1.059 (on  $F^2$  for all data) and for salt 2, with R = 0.0450 (for 2173 data with  $F^2$ >  $4\sigma(F^2)$ ), wR = 0.1222 (on  $F^2$  for all data), and S = 1.087 (on  $F^2$  for all data). The largest peak and hole difference was 0.328 and -0.275 eÅ<sup>3</sup>, 0.260 and -0.297 eÅ<sup>3</sup> for salt **1** and **2**, respectively. The illustrations of molecular structures were drawn using ORTEP-3 for Windows.<sup>25</sup> The material was prepared for publication using WINGX,<sup>25</sup> OLEX<sup>26</sup>, and PLATON.<sup>27</sup> Both salt **1** and **2** were obtained in the yields of about 50 %. These crystals were used for X-ray diffraction, NMR, and conductivity studies. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at room temperature using an NMR Spectrometer Bruker Avance II 400 MHz and DMS solution with TMS (CH<sub>3</sub>)<sub>4</sub>Si was used as an internal standard.

A Bruker Equinox 55 spectrometer combined with an FT-IR Hyperion 2000 microscope in the spectral range from 650 to 4000 cm<sup>-1</sup> to a spectral resolution of 2 cm<sup>-1</sup>, were used to investigate optical properties. The spectra were recorded in perpendicular to the Crystallographic (natural) plane in the absorbance mode for the KBr pellets (c = 1: 500) at room temperature.

Thermal stability of salts **1** and **2** was characterized by differential scanning calorimetry (DSC) with a NETZSCH DSC 200F3 calorimeter under a nitrogen atmosphere. Thermogravimetric analysis (TGA) was carried out with a Perkin-Elmer TGA 4000 instrument under a nitrogen atmosphere. The samples for DSC studies were of about 7 mg, and the scan rates of 5, 10, and 15 K·min<sup>-1</sup> were applied. The measurements were performed in the

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range from 300 to 550 K. The samples for TGA studies were of similar mass, the temperature was varied from 300 to 550 K, at a heating rate of 10 K  $\cdot$  min  $^{\cdot1}$ .

The electrical properties of the investigated materials were studied using the impedance spectroscopy method. Salts **1** and **2** were powdered in the agate mortar; the powder was pressed at room temperature under 30 MPa to form cylindrical pellets (~0.4 mm thick and ~5 mm in diameter). Next, the electrodes were placed at the proper surface using Hans Wolbring GmbH silver paste. The real and imaginary components of the electrical impedance of the prepared samples were measured in the frequency range from 1 Hz to 10 MHz using the computer-controlled Alpha A High-Frequency Analyzer (Novocontrol GmbH). The Quatro Cryosystem stabilized the temperature of the sample to the accuracy of 0.1 K.

#### **Computational Methods**

Intermolecular intramolecular and interactions were investigated using Hirshfield surface and fingerprint plots generated by the CrystalExplorer 3.0 program.<sup>28</sup> Gaussian output wfn files were used as inputs for the AIM2000 program to calculate topological properties of the systems investigated. The bond and ring critical points were located (BCPs and RCPs), and their properties, such as electron densities at critical points ( $\rho_{BCP}$  and  $\rho_{\text{RCP}})$  and their Laplacians ( $\nabla^2\rho_{\text{BCP}}$  and  $\nabla^2\rho_{\text{RCP}})$ , were calculated.  $^{29}$  For the investigated molecules, the initial geometry was taken from the X-ray data for the single crystal of imidazolium benzoate (1) and imidazolium salicylate (2). The 6-311++G(d,p) Pople style basis set and the B3LYP hybrid density functional, which combines Becke's three-parameter nonlocal exchange potential with the nonlocal correlation functional of Lee, Yang, and Parr,<sup>30,31</sup> were used. The topological parameters of the critical points of O-H···O, N-H···O, and C-H…O hydrogen bond were established. The Gaussian 03 set of codes<sup>32</sup> was used to calculate the molecular geometry and spectroscopic properties by quantum chemical methods. The initial geometries of 1 and 2 were taken from X-ray data and applied in the geometry optimization job. Potential Energy Scan (PES) was used to determine the energy barrier of a rotating molecule. The different positions of the proton relative to proton donor and proton acceptor group and N-H...O=C dihedral angles were considered; the MP2/6-31G(d) theory level was used for this purpose.

### **Results and discussion**

#### Crystallographic and NMR investigations

On the basis of the X-ray analysis of compound **1** (1*H*-imidazol-3-ium benzoate (formula moiety:  $C_7H_5O_2^-$ ,  $C_3H_5N_2^+$ ) and **2**, (1*H*-imidazol-3-ium 2-hydroxybenzoate, formula moiety:  $C_7H_5O_3^-$ ,  $C_3H_5N_2^+$ ) it was confirmed that both compounds are salts. Salt **1** crystallizes in the monoclinic system, space group *P2*<sub>1</sub>/*n* with the cell parameters *a* = 8.7106(6), *b* = 12.3618(6), *c* = 9.2744(7) Å,  $\beta$  = 111.594(8)°, *V* = 928.56(12) Å<sup>3</sup>, *Z* = 4, *D*<sub>calc</sub> = 1.361 g/cm<sup>3</sup>,  $\mu$  = 0.097 mm<sup>-1</sup>, *T* = 130.0(1) K. Salt **2** (1*H*-imidazol-3-ium 2-hydroxybenzoate, formula moiety:  $C_7H_5O_3^-$ ,  $C_3H_5N_2^+$ ) crystallizes in the orthorhombic system, space group *Pbca* with lattice parameters *a* =11.0905(6), *b*  = 10.9922(5), *c* = 16.1833(8) Å, *V* = 1972.89(16) Å<sup>3</sup>,  $V_{\overline{L}}$ ,  $V_{\overline{L$ 



**Figure 1.** A view of molecules of **1** (a), **2** (b), **3** (c),<sup>21</sup> and **4** (d)<sup>21</sup> showing the atomic labeling scheme. Non-H atoms are drawn as 30% probability displacement ellipsoids, and H atoms are presented as spheres of arbitrary size.

The carboxylate group in the benzoic anion (1) as well as in the 2-hydroxybenzoate anion (2) are to a small degree displaced from the mean plane of the phenyl ring. The dihedral angle (C1b-)COO-/C1b-C6b is 9.06(19) and 5.9(2)° for 1 and 2, respectively. For 2, the spatial orientation of the carboxylate group is stabilized by the intramolecular hydrogen bond O10b-H10b-O9b. Geometrical parameters of interatomic distances of bond pairs C7b-O8b/C7b-O9b (salt 1: 1.2551(14)/1.2631(14) Å; salt 2: 1.2484(15)/1.2811(15) Å) show that in **2** they differ significantly (difference in length  $40\sigma$ ), while in **1** they are comparable (difference in length  $4\sigma$ ). For salt **1**, it indicates an almost uniform distribution of negative charge in the carboxylate group. In both crystals, the benzoic and 2hydroxybenzoic anions are connected by hydrogen bonds with two molecules of imidazolium cation, occupying in the crystal of 1 the x,y,z and 0.5-x,-0.5+y,0.5-z positions, in the crystal of **2** the x,y,z and 0.5+x, 1.5-y, 1-z positions. The dihedral angles between the imidazolium and anionic rings are 12.67(9), 75.01(4)° (for 1) and 8.30(9), 80.32(4)° (for 2). In the crystal of 1, the molecules related by the screw axis  $2_1$ , running this time along the *b* axis, are connected by the classical hydrogen bonds N1a-H1a-O9b and N2a-H2a···O8b<sup>i</sup> into chains, which are further joined by nonclassical hydrogen bonds C1a-H1aa…O9b<sup>ii</sup> in layers aligned in parallel to the plane (-101) (Fig. S1 and Table S1 in Supplementary

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Materials). Since C-atom in proton donating bond is not electronegative thus these systems are not in line with the classical definition of H-bond. In the chains, the molecules are arranged in a herringbone motif. In the crystal lattice of **1**, in addition to hydrogen bonds, the interactions C2a–H2aa… $\pi$ (Ph<sup>iii</sup>) and  $\pi$ (Ph)… $\pi$ (Ph<sup>iv</sup>) were found (see Fig. S3 in Supplementary Materials).

In the crystal of **2**, the molecules related by the screw axis 2<sub>1</sub> running this time along the *a* axis, are connected by the classical hydrogen bonds N1a–H1a···O9b and N2a–H2a···O8b<sup>i</sup> into chains, which are further connected by non-classical hydrogen bonds C2a–H1aa··O10b<sup>ii</sup> in layers that are aligned in parallel to the *ab* plane (Fig. S2, Table S2 in Supplementary Materials). It is worth noting that the molecules in the chains form a herringbone motif (Fig. S2b). Furthermore, in the crystal in addition to hydrogen bonds, the presence of interactions C3a–H3aa···π(Ph<sup>iii</sup>) and  $\pi$ (Ph)···π(Im<sup>iv</sup>),  $\pi$ (Im)···π(Ph<sup>iv</sup>) (iv: 1-*x*,1-*y*,1-*z*) was also found (see Table S2 and Fig. S4 in Supplementary Materials). The symbols Ph and Im denote phenyl and imidazolium rings, respectively. Perpendicular distance of Ph on ring Im is 3.4629(6) Å, while that of Im on ring Ph is 3.5601(6) Å.

The chemical structures of salts **1** and **2** were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectra. The chemical shifts are collected in Table S3 (see Supplementary Materials). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of salt **1** formed from benzoic acid and imidazole as well as the spectra of salt **2** formed from salicylic acid and imidazole are shown in Fig. S5 (see Supplementary Materials). The <sup>1</sup>H NMR spectrum of imidazole consists of a singlet at 7.02 ppm (H2a, H3a) and a singlet at 7.66 ppm (H1a). It is worth noting that imidazole H2a and H3a protons are magnetically equivalent. This equivalency originates from the fact that NH proton is very mobile and undergoes rapid exchange, so the imidazole structure is stabilized by resonance.

When salt 1 formed, there were some changes in the chemical shifts of the proton and carbon peaks in the acid and base moieties. Benzoic acid peaks H3b, H5b, are shifted upfield upon salt formation, while peak H4b is shifted downfield, relative to the chemical shifts of the neutral acid molecule. Imidazole peaks H1a are shifted upfield. There are no COOH signals in the <sup>1</sup>H spectrum of **1**. Salt **1** formation also caused low field displacements of imidazole C1a and C2a, whereas benzoic acid moiety peaks C3b, C5b and C1b were downfield shifted, which is attributed to proton transfer phenomenon.

The interaction of organic base such as imidazole with salicylic acid leads to a proton transfer from the acid to the base molecule, and as a result, the imidazolium cation and salicylate anion are formed. Salt **2** formation led to changes in the chemical shifts of the hydrogen and carbon atoms of acid and base parts of the salt. H3b and H4b peaks were shifted downfield upon salt **2** formation. Conversely, H5b and H6b peaks were shifted upfield compared with those corresponding to the acid molecule. Imidazolium cation peaks (H1a, H2a, and H3a) were shifted downfield as compared with those of the neutral imidazole. There were also upfield displacements of imidazole C1a, C2a, and C3a signals. The <sup>1</sup>H and <sup>13</sup>C NMR spectra have provided evidence of salt **1** and **2** formations.

Table S4 (see Supplementary Materials) presents structural data for imidazolium ions in salt **1** and salt **2**. The difference in the length of bonds between N1a–C1a and N2a–C1a equals to 0.002 and 0.004 Å for salt **1** and salt **2**, respectively. The length difference

between N1a–C3a and N2a–C2a equals 0.002 and 0.005 Å for salt 1 and salt 2, respectively. The difference between these bonds points out that they are structurally equivalent and the imidazole in the investigated salt is a symmetric molecule.<sup>33,34</sup> This symmetry can also be observed between the pairs of angles (C1a-N1a-C3a and C1a-N2a-C2a, N1a-C3a-C2a and N2a-C2a-C3a) which differ by 0.5 or less.

#### FT-IR spectral investigation

Salt **1** and **2** were characterized by means of infrared spectroscopy. This method provided information about the nature of bond vibrations, which allowed identification of a network of hydrogen bonds in the materials under study. Fig 2 shows the infrared spectra of salt **1** and **2** recorded for KBr pellet (the mass ratio was 1: 500). The most intense bands have been marked with wavenumbers. In the region 1650–1400 cm<sup>-1</sup> there are absorption bands which can be assigned to the in-plane skeletal vibration of the aromatic ring. These vibrations involve the expansion and contraction of the carbon-carbon and carbon-nitrogen bonds within the benzene as well as imidazole rings. The substitution pattern of the ring significantly influences the frequency and intensity of these vibrational bands. For instance, the v<sub>C=C</sub> band of **1** was observed at 1625 and 1602 cm<sup>-1</sup>, while the v<sub>C=C</sub> band of **2** was observed at 1625 and 1615 cm<sup>-1</sup>.



Figure 2. Infrared spectra of salts 1 and 2 in region 3600-800 cm<sup>-1</sup>.

Furthermore, the out-of-plane wagging vibrations of adjacent hydrogen atoms of substituted aromatic ring usually cause a strong absorption in the spectral region 900-690 cm<sup>-1</sup>. In the 1-substituted aromatic ring (1) and 1,2-substituted benzene ring (2), the vibrations of adjacent hydrogens were responsible for absorption in the region 900-770 cm<sup>-1</sup>. In monosubstituted benzenes (1), the five adjacent hydrogen atoms give rise to two absorption bands in the regions 770-730 and 710-690 cm<sup>-1</sup> (bands 722 cm<sup>-1</sup> and 717 cm<sup>-1</sup>), whereas in 1,2-substituted benzenes (2), the vibrations of four neighboring hydrogen atoms lead to the appearance of a single absorption in the region 770-735 cm<sup>-1</sup> (757 cm<sup>-1</sup>).

On the other hand, phenols are characterized by strong absorption, assigned to the O-H stretching modes. The position and shape of this band are sensitive to the electronic and steric features of the compounds as well as the physical state of the sample. Ortho-substituted phenols that possess a carbonyl group (2) are able, for steric reasons, to form intramolecular hydrogen bonded

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species. Their hydrogen bonding is strong due to resonance stabilization of the species. The absorption bands assigned to the C-O stretching and O-H bending vibrations were also of diagnostic value. The band assigned to phenolic C-O stretching was present at 1346 cm<sup>-1</sup>.

Salicylic acid is known to be stronger than benzoic one. The ionization constant of benzoic acid is pKa=4.20, whereas that of salicylic acid (o-hydroxybenzoic acid) is 2.97. It means that salicylic acid is almost 16 times stronger than benzoic acid.<sup>35</sup> The increase in acid strength produced by a o-hydroxy group is attributed to the intramolecular hydrogen bonding between the phenolic hydroxyl and the carboxyl groups. The chelation is possible for ortho isomer since it is expected to be stronger in the anion rather than in unionized acid. It stabilizes the anion more than the acid and thereby causes an increase in ionization.

The spectra of amine and carboxylic acid salt showed characteristic bands of the ionized carboxyl group observed in the range 3100-2000 cm<sup>-1</sup>. The IR spectra of charged amine derivatives  $(v_{C=NH+})$  revealed bands in the range of 3200-2800 cm<sup>-1</sup> assigned to the N-H stretching modes of ions. There are also multiple combinational bands in the range of 2800-2000 cm<sup>-1</sup> and the bands corresponding to the N-H bending vibrations in the 1600-1400 cm<sup>-1</sup> region (Fig. 2). The spectra of carboxylic acid salts did not show a band assigned to carbonyl group vibrations. Instead, intensive bands due to the asymmetric and symmetric stretching vibrations of the equivalent carbon-oxygen bonds were observed at 1565, 1389 cm<sup>-1</sup> and 1572, 1388 cm<sup>-1</sup> for salt 1 and 2, respectively. These bands provide evidence for the presence of carboxylate anion. Earlier spectroscopic studies<sup>36</sup> have indicated that the spectra of many acidic salts of carboxylic or dicarboxylic acids containing very strong symmetric hydrogen bonds  $(O - H - O)^{-}$  show only one  $(CO_2^{-})$ band instead of the bands assigned to  $v_{C=0}$  vibration of carboxylic groups.

Imidazolium ring subunit can form  $(N-H)^+-O^-$  hydrogen bonds with benzoate anion and  $(C-H)^+-O^-$  HB with phthalate anion.<sup>37</sup> It suggests complexation of the anion by N-H and C-H hydrogens, which means that the proton donating and accepting groups such as OH, NH, and CH are engaged in HB interaction. The stretching vibration of these groups produce bands in the range 3500-2500 cm<sup>-1</sup>. There are some differences in geometrical parameters and bond force (see Tables S1 and S2); between HB patterns of salts **1** and **2** (see Figs S1 and S2 in Supplementary Materials), therefore the frequencies of stretching and bending vibrations of proton donating and proton-accepting groups of salt **1** and **2** differ. For salt **2**, the v<sub>as(OHO-)</sub> band can be found at 1346 cm<sup>-1</sup>, this band occurs in the spectra of crystalline substances with strong bonds; thus, this band is absent in the spectrum of salt **1**.

In the range between 1900 and 2700 cm<sup>-1</sup>, the bands characteristic of the salt with a network of hydrogen bonds<sup>38</sup> are observed. The continuum showed a clear structure with two maxima at 1973, 2497 and 1959, 2604 cm<sup>-1</sup> for salt **1** and **2**, respectively. It indicated that these two bands resulted from three different species in equilibrium and not from an intramolecular effect, such as Fermi resonance, which supported the spectral assignment.<sup>38-40</sup>

IR studies showed that salt **2** has a more complex network of hydrogen bonds than salt **1**. NMR measurements showed that the

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#### Thermal stability analysis

cm<sup>-1</sup> characterize salts 1 and 2, respectively.

Thermal stability was studied using the DSC, TGA, and DTG methods. Figure 3 presents the thermograms recorded for salt **1** and **2**. The scans of thermal stability were measured on heating at 5, 10, and 15 K<sup>-</sup>min<sup>-1</sup> rates in the temperature range from 320 to 420 K. For both salts, one can observe a sharp endothermic peak related to the melting and decomposition processes. The position of this feature depends on the heating rates.

The onset temperature of the melting process of imidazole benzoate (1) was close to 365 K. Salt 1 reached the maximum degradation rate at about 373, 374, and 375 K for the heating rates of 5, 10, and 15 K<sup>-</sup>min<sup>-1</sup>, respectively. TGA measurement revealed that the mass loss started at about 353 K. The imidazolium salicylate melting process began at 393 K, and its maximum degradation rate was at about 402, 403, and 404 for the heating rates of 5, 10, 15 K<sup>-</sup>min<sup>-1</sup>, respectively. The mass loss started at about 379 K.



Figure 3. Differential scanning calorimetry (DSC) recorded for 5, 10, and 15 K<sup>-</sup>min<sup>-1</sup> rates (upper panels), thermogravimetric analysis (TGA) (lower panel, red line), and derivative thermogram (DTG) (lower panel, blue line) of salt 1 (a) and salt 2 (b).

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#### Intermolecular interactions analysis

The intermolecular interactions can be readily identifiable using 3D Hirshfeld surface (3D HS) and 2D molecular fingerprint plot analysis. The method permits distinction of different types of intermolecular interactions and provides insight into their nature. The Hirshfeld<sup>41</sup> surface was created for the crystal by partitioning space into regions in which the sum of the electron density of spherical atoms in the molecule (the promolecule) was higher than the corresponding sum over the crystal (the procrystal). The Hirshfeld surface<sup>42</sup> was calculated to use a molecular weight function w(r) which is defined as:

$$w(r) = \frac{\rho_{promolecule}(r)}{\rho_{procrystal}(r)} = \frac{\sum_{A \in molecule} \rho_A(r)}{\sum_{A \in crystal} \rho_A(r)}$$
(1)

The symbol  $\rho_A(r)$  is the spherically – averaged atomic electron density centered on nucleus A. The sum over the atoms, which belong to the molecule and the crystal is named as promolecule and procrystal, respectively. The Hirshfeld surface is constructed in a crystal as the region around a molecule where  $w(r) \ge 0.5$ . The promolecule contribution to electron density of the procrystal exceeds that from all other molecules in the crystal in this region. The 3D Hirshfeld surface mapping with  $d_e$  distance and fingerprint plots are shown in Fig. 4 for imidazole molecule (a) and acid molecules (b) for salts **1** and **2**.



**Figure 4.** The Hirshfeld surface for the imidazole molecule (a) and acid molecule (b) for salt **1** and **2** mappings with  $d_e$ ; the range of mapping: short distance – red through green to blue – long distance. Fingerprint plot  $d_e$  versus  $d_i$  for these features with contribution from specific pairs of atoms; characteristic features corresponding to the occurrence of hydrogen bonds are marked in red.

For the studied salt, the dominant interaction that takes parting hydrogen bonding is H...O; it was marked in the Hirsh feld suffice by the red area (short distance). Weaker and longer contacts were marked by the green and blue regions on the surface (Fig. 4).

The right panel of Fig. 4, shows the 2D molecular fingerprint  $d_{\rm e}/d_{\rm i}$  plot derived from 3D Hirshfeld surface. The distances from Hirshfeld surface to the nearest nucleus outside and inside the surface are  $d_e$  and  $d_i$ , respectively.<sup>43,44</sup> Each point on the 2D fingerprint plot corresponds to a unique  $(d_e, d_i)$  pair. The color of each point corresponds to the relative area of the surface assigned to this (de, di) pair, blue for a small contribution through green to red for points bringing the greatest contribution. The contribution involved in hydrogen bonds has a clear signature: sharp spikes at the bottom left of the plots. In the studied salts, we observed H...O and O"H interactions. For the imidazolium moiety, we found the sharp spike in the upper part (d<sub>i</sub><d<sub>e</sub>) associated with the acceptor atom (see Fig. 4a) and for acid molecules, in the lower one (d<sub>i</sub>>d<sub>e</sub>) associated with the donor (see Fig. 4b). For imidazolium, H...O interactions cover 20.4% and 27.5%, and for acids molecules, O"H interaction covers 24.3 % and 28.7 % of the total 3D HS for the salts with benzoic and salicylic acid, respectively.

In the studied salts, many other contacts existed, and their strength was weaker than that of van der Waals interaction. These contacts are indicated by yellow, orange to green areas in 3D Hirshfeld surface (Fig. 4). The H<sup>...</sup>H interactions brought a significant contribution (37.9% and 44.1%) to the Hirshfeld surface, for imidazolium, and 36.2% and 42.1% for anion in salt **1** and **2**, respectively. The C<sup>...</sup>H contact brings a contribution 12.3% and 13.2%, for imidazolium, and 15% and 15.7% for an acidic part in salt **1** and **2**, respectively. This contact resulted from the herringbone arrangement of molecules in the crystal. The  $\pi^{...}\pi$  interactions determine mutual orientation of molecules in the crystal. For imidazolium salicylate, this type of interaction is greater than 4.5%, and it covers 7.8% of the total HS 3D (see Fig. S6 in Supplementary Materials).

For 1H-imidazole-3-ium benzoate and 1H-imidazol-3-ium 2-hydroxybenzoate, numerous hydrogen bonds, especially  $N-H\cdotsO$  (see Table S1 and S2) were observed. The three-dimensional chain structure of salt **1** and **2** formed along the [010] and [100] directions through a network of hydrogen bonds between the imidazolium ions and the carboxylate groups.

The hydrogen bonds joining imidazole acting as a proton acceptor and acid the molecules acting as proton donors, that took part in the conduction mechanism are N(X)–H···O(X):  $(d_{N...0}=2.649 \text{ Å} and d_{N...0}=2.603 \text{ Å})$  and  $(d_{N...0}=2.679 \text{ Å} and d_{N...0}=2.695 \text{ Å})$  for salt **1** and salt **2**, respectively. According to the geometrical parameters,<sup>37,45</sup> the strength of hydrogen bond D–H···O for salt **1** and **2** can be classified as a moderate.<sup>45</sup> In salt **1**, there are C(X)–H···N(X)  $(d_{C...N}=3.509 \text{ Å})$ , C(X)–H···O(X)  $(d_{C...0}=3.203 \text{ Å})$ , and C(X)–H···H(X)  $(d_{C...H}= 3.190 \text{ Å})$  interactions. These hydrogen bonds are weak and stiffen the crystal structure. In salt **2** the intermolecular C(X)–H···O(X)  $(d_{C...H}= 2.528 \text{ Å})$  are present, which are weak and strong, respectively.

The hydrogen bonding interaction in the studied crystals was also analyzed using the quantum theory of atoms in molecules (QTAIM).<sup>46</sup> For the system investigated (see Figure S7 and Table S5

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in Supplementary Materials), the following parameters were considered: electron density ( $\rho_{BCP}$ ), the Laplacian of the electron density ( $\Delta\rho_{BCP}$ ), potential electron energy density ( $V_{BCP}$ ), kinetic electron energy density ( $G_{BCP}$ ), and the total electron energy density ( $H_{BCP}$ ) at the critical points. $^{47}$  The classification of hydrogen bonds using topological parameters at the critical points has been proposed by the Rozas' group.'^{48}

- $\Delta \rho_{BCP}$ >0, H<sub>BCP</sub>>0 for weak and medium hydrogen bond interaction,
- $\Delta \rho_{BCP}$ >0, H<sub>BCP</sub><0 for strong hydrogen bond interactions,
- $\Delta \rho_{BCP}$ <0, H<sub>BCP</sub><0 for very strong interactions.

For 1H-imidazol-3-ium benzoate (1) and 1H-imidazol-3-ium2-hydroxybenzoate (2), the values of  $\Delta \rho_{BCP}$  and  $H_{BCP}$  took positive or slightly negative values (-0.00689 and -0.000006) (see Table S5), which indicated them as closed-shell interactions.

The proton transport mechanism in the investigated salts: 1Himidazol-3-ium benzoate (1) and 1H-imidazol-3-ium 2hydroxybenzoate (2), was studied by theoretical methods. The conductivity pathway of protons along the [010] and [100] directions was parallel to the one-dimensional chains within the individual layers in the (101) and (010) planes (see Fig. 5 a and b) for 1 and 2, respectively. Since the distance between the chains was greater than the sum of van der Waals radii, there was no conductivity pathway between two chains.



Figure 5. A view of the one-dimensional chain in salt 1 (projection onto the (101) plane) (a) and salt 2 (projection onto the (010) plane) (b)

#### Impedance spectroscopy

The electrical properties of salts **1** and **2** were measured using impedance spectroscopy method for the polycrystalline samples of both salts in the form of pellets in the temperature range from 130 to 363 K for salt **1** and from 130 to ~378 K for salt **2**. Typical complex impedance responses of the materials in the form of Nyquist plots are presented in Fig. 6 a and b. Each plot consisted of a single semicircle, related to the bulk response of the measured sample. The measured complex impedance Z\* of a sample can be modeled using a parallel RC equivalent circuit:

$$Z^*(\omega) = \frac{R}{1 + (i\omega RC)^{1-\alpha}}$$
(2)

where R denotes the resistance, C - the capacity,  $\alpha$  - a fitting parameter and  $\omega$  =  $2\pi\nu$  – the angular frequency of measuring

field. Solid lines in Fig. 6 a,b represent the model it is experimental data. The resistivity R inferred from the fit was used to calculate the conductivity  $\sigma_{dc}$ , which corresponds to the conductivity of the sample.

The Arrhenius plot of electric conductivity  $\sigma_{dc}$  measured on the heating cycle is presented in Fig. 6 c. The activation energy was calculated from the relation:

$$\sigma_{dc}(T) = \sigma_0 exp\left(-\frac{E_a}{kT}\right) \tag{5}$$

where  $\sigma_0$  is the pre-exponential factor,  $E_A$  - the activation energy, k - the Boltzmann constant and T – absolute temperature. For both salts, electric conductivity increased with increasing temperature, which is typical of protonic conductors. It reached  $\sigma_{dc}$ =2.36×10<sup>-6</sup> S·m<sup>-1</sup> at T=353 K (1), and  $\sigma_{dc}$ =1.66×10<sup>-6</sup> S·m<sup>-1</sup> at T=368 K (2). Above these temperatures, a rapid increase in conductivity took place. The DSC and TGA measurements show that it was caused by the melting of the sample and changes in the sample geometry.



Figure 6. The Nyquist plot of complex impedance  $Z^*$  of benzoic acid (a) and salicylic acid (b) with imidazole salts. Data collected at T=353.2 K. The lines represent the impedance of the sample calculated from equation (2); Arrhenius plot of dc conductivity of salt 1 (open red circles) and 2 (open blue diamonds) with imidazole salts (c).

The studied salts may be classified as conductors in which protons are transported between two molecules according to the Grotthuss mechanism.<sup>49</sup>

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Figure 7. Potential Energy Scan (PES) performed for the translational of a proton between imidazole and benzoic acid (a) and salicylic acid (d), structures show two local minima, resulting from hydrogen bonding interactions. PES obtained for the rotation of imidazole around its pseudo-2-fold axis for salt 1 (b) and salt 2 (e) and the rotation of carboxyl groups in benzoic acid (c) and salicylic acid (f) around the C–C bond axis.

This mechanism can be described by two main steps: intrabond and interbond motion. During the intrabond motion, a proton jumps between two potential minima in a doublewell N–H…O hydrogen bond. During the interbond motion, protons shift between hydrogen bonds, during which the rotation of imidazole or acid molecule and carboxyl groups cause the link of a double-minimum hydrogen bond to be broken, the proton is transferred to the nearest vacant position, and a new hydrogen bond is formed. The NMR study<sup>20</sup> shows the proton motion related to the reorientations is a significantly faster process than proton motion between two-potential minimum in a double-well hydrogen bond.

For the investigated conducting materials, we calculated the energy barrier<sup>50</sup> within the double-well hydrogen bonds and for rotation of imidazole and acid molecules to transport proton between two molecules. The energy barrier within the double-well hydrogen bonds in the studied systems is similar and close to 0.10 eV. Fig. 7 a and d present the transfer of a proton from one site to another in N–H···O, where the N–H bond is broken and a new H–O bond is formed.

In the next step, we calculated the energy barriers for rotation by 180° of imidazole, acid molecule, and a carboxyl group. The activation energy for imidazole cation is equal to 2.10 and 1.71 eV for salt **1** and salt **2**, respectively (see Fig. 7 b and e). The activation energy for rotation of carboxyl group flip

around the C–C bond axis equals 1.15 eV and 1.44 for salt 1 and 2, respectively (see Fig. 7 c and f).

In general, in the crystal, the value of activation energy depends on many effects: interaction between hopping ions, the interaction between hopping ions and phonons (proton-phonon-coupling effect), the configuration of surrounding ions, etc. Besides, when we increase temperature, the probability and frequency of rotation also increase. In our opinion, the determined activation energy is in line with that obtained from the Arrhenius plot for electric conductivity measurements: 1.87 eV (for salt 1) and 1.50 eV (for salt 2).

Table 1 shows the conductivity of salt **1-4** and pKa of acid species. The lower the pKa, the higher the equilibrium constant  $K_a$  and the stronger the acid AH. According to the present knowledge, electron-withdrawing groups such as carboxyl (COOH) or hydroxyl (OH) groups considerably lower the pKa of carboxylic acids. For instance, the pKa of benzoic acid is 4.2, whereas pKa of salicylic acid is 2.89. As follows from Table 1, the conductivity of salt **1-4** increases with increasing acidity of AH (lower pK<sub>a</sub>).

The symmetry of 1H-imidazol-3-yl benzoate (1) and 2Himidazol-3-one benzoate-1-hydroxybenzoate (2) is monoclinic and orthorhombic, respectively. For the salt in which the carboxyl group is in ortho (3) and para (4) position, the symmetry is orthorhombic and monoclinic, respectively. The substitution of the carboxyl and hydroxyl groups in the acids affects the symmetry of the crystal obtained. For the four crystallographic structures examined, the

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**Table 1.** The conducting and thermal properties of salt **1-4**. Note:  $\sigma_{RT}$  means the electrical conductivity at room temperature, T is the melting point,  $\sigma_{T}$  is the conductivity at the melting point,  $E_{A}$  means activation energy, and  $pK_{a}$  is acid dissociation constant.

Salt	Imidazolium benzoate ( <b>1</b> )	Imidazolium salicylate ( <b>2</b> )	lmidazolium phthalat ( <b>3</b> ) <sup>21</sup>	lmidazolium terephthalate ( <b>4</b> ) <sup>21</sup>
$\sigma_{RT}$ [S·m <sup>-1</sup> ]	10-9	10-9	8·10 <sup>-9</sup>	10-9
T [K]	374	403	422	464
$\sigma_{\scriptscriptstyle T}[S{\cdot}m^{\cdot 1}]$	<b>2</b> ⋅10 <sup>-6</sup>	8·10 <sup>-6</sup>	2.10-1	10 <sup>-5</sup>
E <sub>A</sub> [eV]	1.87	1.50	1.15	1.10
$\ensuremath{pK_{a}}\xspace$ of acid	4.20	2.97	2.89	3.51



**Figure 8.** Parameters of the primitive unit cell (a, b, c) of salt **1-4** (a); temperature dependence of the O–H interaction in salts **1-4** (b).

One can also observe that the dimensions of the unit cell have a significant effect on the conductive properties. In salts **1**, **2**, and **4**, the conductivity is equal to  $10^{-6}$ - $10^{-5}$  S·m<sup>-1</sup>. The dimension of parameters *a*, *b*, and *c* of their primitive unit cells are similar (Fig. 8 a). For salt **3**, the dimensions are different: the primitive cell is an elongated cuboid. The structure of the cell translates into good conductivity of salt **3**, which is of the order of  $10^{-1}$  S·m<sup>-1</sup>. Upon

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substitution of the benzene ring with carboxyl or hydroxyl groups, the O···H interaction in N H···O hydrogen bond of Sifts and significantly affects the thermal stability (Fig. 8 b). The lowest thermal stability obtained for imidazolium benzoate with O···H interaction equals 20.4%, while the highest thermal stability is obtained for imidazolium terephthalate (at 464 K and O···H interaction equals 42.6%).

## Conclusions

This study has been undertaken to get insight into the correlation between the molecular structure and the conducting and thermal properties of new proton conductors. The imidazolium salts: imidazolium benzoate (1), imidazolium salicylate (2), imidazolium orto-phthalate (3), and imidazolium terephthalate (4) were investigated using experimental and theoretical methods.

In our work, we showed a relationship between molecular structure and thermal stability. The appropriate distribution of carboxylic acid groups in the anion translates into the number of O···H interactions in the crystal. The higher the percentage of this type of interactions observed, the higher the melting point. In the investigated salts, both counterions participate in the Grottuss mechanism. Their energy barrier for rotations is affected by the number and strength of hydrogen bonding interactions.

The presented research results showed that thanks to the use of cyclic acid and bases molecules, we were able to obtain a salt in which all hydrogen bonds have weak or medium power. It is still a challenge to choose an acid molecule with proper structure and symmetry, which will ensure a sufficiently low rotational barrier. This problem requires further detailed research.

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# Highlights

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The substitution pattern of the counterions affects electrical conductivity and thermal properties of the new proton conducting imidazolium salts.

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