A Solid-State NMR Study of Hydrogen-Bonding Networks and Ion Dynamics in Benzimidazole Salts

Jason W. Traer, James F. Britten, and Gillian R. Goward*

McMaster University, Department of Chemistry, 1280 Main Street West, Hamilton, ON, L8S 4M1, Canada

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On the basis of our solid-state NMR characterization of dynamics in two model salts, we draw the analogy to the fuel cell membrane candidate, phosphoric acid-doped poly(benzimidazole), and conclude that phosphate anion dynamics contribute to long-range proton transport, whereas the mobility of the polymer itself is not a contributing factor. This is contrasted with emerging membrane candidates, which rely on fully covalently bonded acid donors and acceptors, and target high-temperature PEM fuel cell operation in the absence of liquid electrolyte. The hydrogen-bonding structures of benzimidazolium phosphate and benzimidazolium methane phosphonate are established using X-ray diffraction paired with solid-state $^1$H DQF NMR. By comparing the dynamics of the phosphate and methane phosphonate anions with the dynamics of imidazolium and benzimidazolium cations, the relative importance of these processes in proton transport is determined. The imidazolium cation is known to undergo two-site ring reorientation on the millisecond time scale. In contrast, it is shown here that the benzimidazolium rings are immobile in analogous salts, on a time scale extending into the tens of seconds. Therefore, we look to the phosphate anions and demonstrate that the time scale of tetrahedral reorientation is comparably fast (50 ms). Moreover, the $^{31}$P CODEX NMR data clearly indicate a four-site jump process. In contrast, the methane phosphonate undergoes a three-site jump on a slower time scale (75 ms). A mechanism for a zigzag pathway of proton transport through the phosphonate salt crystallites is developed based on the $^{31}$P CODEX and $^1$H variable-temperature MAS NMR data.

Introduction

New proton conducting materials for polymer electrolyte membrane fuel cells (PEM-FCs) must offer increased performance at higher temperatures to reduce catalyst poisoning. Also, low-cost and superior durability are necessary in order for new membranes to be competitive in the automotive sector. Many membranes incorporating phosphates have been introduced to solve these problems. These are based on phosphoric acid poly (benzimidazole) (PBI) polymers. Such polymer–acid blends have excellent conductivity at higher temperatures (200 °C) but rely heavily on the liquid phosphoric acid electrolyte to maintain their high ionic conductivity. A recently proposed copolymer based on the combination of vinylphosphonic acid and vinylimidazole successfully incorporates the acid into the backbone of the polymer but fails to achieve acceptable ionic conductivities as compared to the liquid acid-containing membranes. Covalently attaching phosphonate to the polymer backbone eliminates the possibility of acid leaching, but the mobility of the acid group may now depend strongly on the mobility of the vinyl backbone. This tradeoff is the crux of the challenge faced by materials chemists in this field.

Design of new polymers with increased performance can be aided by determining the mechanism of proton transport that enables structural diffusion. The proton conduction mechanism of the benzimidazolium phosphates has yet to be comprehensively characterized on the microscopic scale. There are a number of viable mechanisms for proton transport in these solids that have been suggested based on macroscopic ionic conductivity measurements. The benzimidazolium ring in the polymer may act as a proton-donor site, and may facilitate proton transfer through segmental reorientation. For a bound acid, structural diffusion, often called the Grotthuss mechanism, is necessary. In contrast, a free acid molecule like phosphoric acid could behave as a vehicle for the proton transport or may also participate as a site for the Grotthuss style transport. To develop a better understanding of the dynamics available to these systems, two model compounds are introduced: benzimidazolium methane phosphonate (Bi–mPA) and benzimidazolium phosphate (Bi–PA). The model salts were judiciously chosen, as materials in which the Grotthuss style dynamics is the only mechanism of proton transport below the melt temperature of the lattice. Thereby, we isolate one of the possible mechanisms of proton transport in the benzimidazole–phosphate systems, and can characterize this mechanism quantitatively, independent of other influences. In considering the role of the cations, benzimidazolium salts are contrasted with a previous study of imidazolium methane sulfonate, where cation dynamics were clearly established. The anions are distinguished by their hydrogen-bonding motifs. Phosphate itself models the participation of phosphate in doped PBI, while methane phosphonate imitates the change in local hydrogen bonding upon covalently tethering the acid group to the polymer backbone. This strategy is an increasingly common synthetic means of improving high-temperature performance.

Methodology

To probe the structure and dynamics of the two model compounds, the complementary techniques of solid-state nuclear magnetic resonance (NMR) and X-ray diffraction were used. While X-ray diffraction is useful for determining the positions

* Corresponding author. Email: goward@mcmaster.ca. Phone: (905) 525-9140, x24176. Fax: (905) 522-2509.
of the heavy atoms, solid-state NMR can be used to study the hydrogen-bonding structure in detail, as well as providing a site-specific handle on the local dynamics.9,11

Establishing the structures of the salts was accomplished by correlating the single-crystal X-ray structures to the high-resolution solid-state 1H NMR spectra. The chemical shift range for hydrogen-bonded protons expands well past the normally observed chemical shifts of covalently bound protons. The chemical shifts of hydrogen-bonded protons are very sensitive to changes in the electron density of the hydrogen-bonding environment; this makes 1H NMR an excellent probe of hydrogen bonding and H+ conductivity. In doped poly(benzimidazole) and similar systems, the pathway for proton transport is dictated by the dynamics and structure of the hydrogen bonds, therefore determining the connectivity of the hydrogen-bonding network is the first step to determining the transport mechanism.12

Beyond the straightforward one-dimensional 1H MAS NMR data, detailed information about inter and intramolecular 1H–1H contacts can be obtained from two-dimensional double quantum filtered (DQF) homonuclear correlation spectra. The double quantum (DQ) pulse sequence excites a dipolar coupled spin pair by the application of orthogonal ninety degree pulses reconverging the dipolar coupled spins. The strength of dipolar coupling is quantum coherence generates a spectrum that represents only the dipolar coupled spins. The strength of dipolar coupling is inversely proportional to the cube of the distance between the two spins, so only the strongest of the dipolar couplings will produce resonances in the double-quantum spectrum. The two-dimensional version of the DQF spectrum can be used to correlate spin pairs and a packing environment for each spin can be elucidated. This is particularly useful when studying solid-state materials that do not produce highly crystalline phases, but also provides details of proton positions and dynamics that are inaccessible by standard X-ray methods.14,15

Increasing the temperature at which the 1H MAS spectra are acquired increases the thermal energy of the material and local dynamics may be observed by the narrowing and/or coalescence of the NMR resonances. The variable-temperature experiments provide a window into the dynamic phenomena of the ions in a site specific fashion. Beyond 1D 1H NMR, more advanced methods can be used to quantify the time scale and number of sites involved in dynamic processes. To study the reorientation of the phosphate tetrahedra and benzimidazole rings, a pulse sequence called the centerband-only detection of exchange (CODEX) is implemented.16 The pulse sequence is shown as Figure 1. CODEX measures the reorientation of a molecule by observing the influences on the chemical shift anisotropy (CSA) of the nuclei (13C or 31P). If chemical exchange occurs during the mixing time (tm), the CSA will not be in the same position as at the start of the mixing time and therefore the magnetization will not be entirely refocused during the reconversion portion of the pulse sequence: thus the CODEX signal will be attenuated. The total attenuation of the CODEX signal (E) is proportional to the length of the dephasing applied. The dephasing is controlled by the number of rotor periods (Nt_r) of excitation applied to the sample and the span of the CSA (δ). After sufficient dephasing and long mixing times, the CODEX signal will not be further attenuated and the final value of the attenuated signal can be related to the total number of sites involved in the reorientation. The number of sites (M) involved in the exchange is related to the signal by

$$E_w = \left( \frac{M - 1}{M} \right)^{\frac{t_m}{n_m}}$$

where n_m is the fraction of mobile sites involved in the exchange. For example, a ring flip should produce a final signal attenuated to 50% since the ring flip is a two site exchange. To measure the time scale of the exchange, the normalized signal intensity which is a function of the dephasing (Nt_r) is plotted against the mixing time for a given amount of dephasing. All the curves are then fitted to a single exponential of the form

$$E_w = A(1 - \exp(-t_m/t_\phi))$$

to find the correlation time, t_\phi, of the exchange process that causes the attenuation of the CODEX signal. The correlation time represents the period of the motion and the inverse of the correlation time is the frequency at which the exchange occurs. This correlation provides valuable information on the rates of critical exchange processes.

**Experimental**

Crystals of the Bi–mPA and Bi–PA compounds were obtained by saturating a solution in dimethylsulfoxide with the components in a 1:1 ratio. Upon standing in a closed environment, both solutions produced good quality crystals that were transparent and colorless. Trace amounts of dimethylsulfoxide found in the 1H MAS spectra were removed by heating the powders to 100–120 °C. The single-crystal X-ray diffraction data for the Bi–mPA was recorded using Cu Kα radiation with a wavelength of 1.54178 Å. The final R-factor for the structure solution was 3.21% with a space group of P21/c, and the details of the structure are available in the Supporting Information. The crystal structure of Bi–PA has been previously reported in the literature and therefore no further diffraction data was acquired.17 Powder X-ray diffraction data of both materials were acquired, in both cases confirming the high degree of crystallinity in the materials.

The high-field 1H NMR work was conducted at the National Ultrahigh Field NMR Facility for Solids in Ottawa, Canada. The magnetic field had a proton Larmor frequency of 900.20 MHz with 1H pulse lengths of 2.5 μs. Rotors of 2.5 mm outer diameter, with a sample volume of 10 μL were used to obtain MAS frequencies of 30 kHz.
An 11.74 T magnet was used for the $^{31}$P and $^{13}$C CODEX studies. The CODEX data was acquired with a MAS frequency of 10 kHz with a double resonance probe using rotors with a 4 mm outer diameter. For Bi-mPA a 3.5 s $^{1}$HT$_{1}$ was measured and 53 s $^{1}$HT$_{1}$ was measured for Bi-PA. These long relaxation times imposed long acquisition times on the experiments, with an average CODEX build-up curve requiring 72 h. A contact time of 3000 $\mu$s was used for the CODEX experiments.

The double-quantum filter spectrum was acquired using a Bruker AMX 600 system with a proton Larmor frequency of 600.16 MHz. The 50.3 kHz MAS spectrum was acquired using a proto-type probe with rotors of an outer diameter of 1.8 mm. The double quantum filter spectrum was acquired using $^{1}$H$_{cr}$.) The two-dimensional $^{1}$H-$^{1}$H DQF spectrum was acquired at 50.3 kHz MAS using $^{1}$H$_{cr}$ = $^{1}$H$_{r}$. The dipolar coupling between resonances that were used to distinguish the hydrogen bonding of Bi-mPA are marked on the spectrum as A′-B and B-D.

show the sp$^{2}$-hybridized carbon-hydrogen stretches of the benzimidazole at 3137 cm$^{-1}$, and Bi-mPA shows additionally, the sp$^{3}$-hybridized carbon-hydrogen of its methyl group at 2980 cm$^{-1}$. Hydrogen-bonding regions are very broad in both cases.

**Results and Discussion**

The mechanism of proton transport in the doped PBI system has been proposed based on impedance spectroscopy.$^{7}$ The drawback of using ionic conductivity for justification of a mechanism is that the measurement directly observes only the macroscopic behavior of the system. Therefore, data interpretation must rely on our chemical intuition to rationalize the mechanism of proton transport. The application of solid-state NMR to characterize the molecular-level local dynamics of various systems has proved valuable for understanding the structure and reorientations of molecules in the solid state.$^{14,16,20}$ In this study we utilize various solid-state NMR techniques to elucidate the molecular level mechanism of proton transport in benzimidazole based systems.

**Structural Considerations.** The two model compounds, benzimidazolium phosphate and benzimidazolium methane

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**Table 1:** Distances between Hydrogen-Bonded Heteroatoms from Crystal Structures

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Distance (Å)</th>
<th>Bond Type</th>
<th>Distance (Å)</th>
</tr>
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<tr>
<td>N(1)–O(2)</td>
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<td>N(1)–O(2)</td>
<td>2.675</td>
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<tr>
<td>N(2)–O(1)</td>
<td>2.644</td>
<td>N(2)–O(1)</td>
<td>2.602</td>
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<tr>
<td>O(2)–O(3)</td>
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<td>O(2)–O(3)</td>
<td>2.594</td>
</tr>
<tr>
<td>O(1)–O(4)</td>
<td>2.623</td>
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</tbody>
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**Figure 2.** (a) The four unique hydrogen bonds in Bi-PA; two N–H=O and four O–H=O hydrogen bonds. (b) The three unique hydrogen bonds in Bi-mPA; two N–H=O and one O–H=O hydrogen bond. Each diagram shows the asymmetric unit, with the hydrogen bonding of the heteroatoms expanded and labeled.

**Figure 3.** The $^{1}$H MAS proton spectra acquired at 500 MHz for (a) Bi-PA and (b) Bi-mPA acquired at 25 kHz MAS. Inset: $^{1}$H MAS data for Bi-PA at 900 MHz.

**Figure 4.** The two-dimensional $^{1}$H–$^{1}$H DQF spectrum of Bi-mPA, acquired at 50.3 kHz MAS using $^{1}$H$_{cr}$ = $^{1}$H$_{r}$. The dipolar coupling between resonances that were used to distinguish the hydrogen bonding of Bi-mPA are marked on the spectrum as A′-B and B-D.
phosphonate, differ by the addition of a methyl group to the phosphate. In Figure 2, the hydrogen-bonding environments of the two model compounds are illustrated.\textsuperscript{21,22,23} The cation to anion hydrogen bond distances for Bi–PA and Bi–mPA crystal structures are shown in Table 1, and unit cell parameters are available in the Supporting Information. The differences in the two structures result from changing a hydroxyl, which acts as a hydrogen bonding donor on the phosphate to a methyl group. This switch changes the number of hydrogen bonds linked to each anion; the methane phosphonate has four hydrogen bonds while the phosphate has six. The relative strength of these hydrogen bonds is indicated by their \(^1^H\) NMR resonances, and moreover, their dynamics.

The influence of the different hydrogen-bonding environments is observed in the \(^1^H\) MAS NMR spectra that are shown in Figure 3. First, the resonances can be generally classed as follows. The N–H=O hydrogen bonds of the Bi–PA and Bi–mPA compounds have the higher chemical shift (17–15 ppm) because they are stronger hydrogen bonds, while the O–H=O hydrogen bonds are weaker and have a lower chemical shift (12–10 ppm). All N–H=O hydrogen bonds are labeled as A or A’, O–H=O hydrogen bonds are given the designation B. The resonances at 9–6 ppm in Figure 3 are assigned to the aromatic protons of the benzimidazole ring, and are labeled C. The resonance centered at 1 ppm in Figure 3b is assigned to the methyl group of Bi–mPA, and is referred to as resonance D.

Beyond this general assignment, we aim to specify which protons are which, as related to the crystal structures of the two salts. The different sets of hydrogen-bonded resonances cannot be accounted for by the different heteroatomic distances alone. As seen in the crystal structures, full hydrogen bonding for all the proton donors in Bi–mPA requires that one oxygen atom is bifurcated to become an acceptor site for two hydrogen-bonded protons, whereas two oxygen atoms are bifurcated in Bi–PA. In Bi–PA, the N–H=O heteroatomic distances differ by 0.083 Å, and yet the chemical shift difference of the two resonances is only 0.7 ppm. Bi–mPA has similar heteroatomic distances, which differ by 0.073 Å; yet the two N–H=O hydrogen-bonded protons are separated by 1.7 ppm. In Bi–mPA, the N(2)–H=O(1) hydrogen bond is not bifurcated and is referred to as hydrogen bond A, the bifurcated N(1)–H=O(2) hydrogen bond is referred to as hydrogen bond A’, and the O(3)–H=O(2) is labeled hydrogen bond B. The chemical shifts related to the two benzimidazolium protons in Bi–PA do not correlate directly to the distances reported in Table 1, but rather the type of hydrogen bonding (bifurcated or not). For Bi–PA to have a complete set of hydrogen bonds, two of the oxygen atoms on the phosphate accept an additional proton. The third hydroxyl group of the phosphate causes both N–H protons in Bi–PA to hydrogen bond to a bifurcated oxygen atom. Although the hydrogen-bonding distances are important to the chemical shift, the bifurcation of the oxygen atoms has a greater effect on the chemical shift of the hydrogen atoms in Bi–PA. Using a proton frequency of 500 MHz, the two benzimidazolium N–H protons in the Bi–PA structure are unresolved in Figure 3a. Only at 900 MHz does the difference between the two sites start to manifest itself in the NMR spectrum (shown as an inset for Figure 3a). The small difference in the two chemical shifts is attributed to the small difference in heteroatom distances (0.057 Å). A \(^1^N\) CP MAS spectrum of Bi–mPA (not shown) confirms the different environments of the two nitrogen centers of the benzimidazole ring. The two \(^1^N\) resonances are separated by 8.3 ppm; therefore, the two sites are similar but not are equivalent.

The deconvolution of the 30 kHz \(^1^H\) MAS spectrum of Bi–mPA using Gaussian lineshapes gives a ratio for the hydrogen-bonded resonances of 1:1:1 within experimental error. This ratio matches the crystal structure which has two N–H=O protons and one O–H=O proton. Similarly, the deconvolution of the 30 kHz \(^1^H\) MAS spectrum of Bi–PA yielded two resonances at 15.1 & 14.3 ppm which corresponds to the two N–H=O protons and two resonances at 10.9 and 10.2 ppm which corresponds to the two O–H=O protons.

The three largest chemical shift resonances can be identified as the three unique hydrogen-bonded protons of the Bi–mPA crystal structure. The assignment of these three hydrogen-bonded protons is established by the \(^1^H\)–\(^1^H\) two-dimensional DQF spectrum, shown in Figure 4, corresponding data for Bi–PA is given as Supporting Information. It is important to note that all of the \(^1^H\) resonances in both materials pass through this \(^1^H\) double quantum filter. This is a clear indicator that there are no highly mobile protons with correlation times shorter than a rotor period, in this case 20 μs, in the samples at these temperatures, as their dipolar couplings would be attenuated by their dynamics, and therefore they would be efficiently "filtered".\textsuperscript{11} This allows us to conclude that proton dynamics are indeed occurring within the crystallites, and are not exclusive to amorphous, or semi-liquid regions.

The 2D DQF spectrum allows us to determine the local packing environment of the hydrogen atoms. This approach, of utilizing 2D \(^1^H\) DQF spectroscopy under fast MAS is a well-established tool which can be applied to crystalline or amorphous solids where interesting and unique packing motifs can be readily determined.\textsuperscript{14,15} Such spectra are readily interpreted: if two nuclei are dipolar coupled in a DQF spectrum, the sum of the two single quantum chemical shifts must equal the chemical shift of the resonances in the double quantum dimension. From the crystal structure, the two hydrogen bonded O(3)–H=O(2) and N(1)–H=O(2) protons that share the same oxygen in Figure 2 would have a stronger dipolar coupling to each other than to the third hydrogen bond (N(2)–H=O(1)). This dipolar coupling appears between the two proton resonances of 15 and 11 ppm; thus, the proton resonance at 17 ppm must be the proton

### Table 2: \(^1^H\) NMR Chemical Shift and Linewidths for Bi–PA and Bi–mPA, and Corresponding Assignments to Heteronuclei in the Respective Crystal Structures

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Chemical Shift (ppm)</th>
<th>Linewidth (± 30 Hz)</th>
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</thead>
<tbody>
<tr>
<td>Bi–PA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>N(2)–O(1)</td>
<td>15.2</td>
</tr>
<tr>
<td>A</td>
<td>N(1)–O(1)</td>
<td>14.3</td>
</tr>
<tr>
<td>B</td>
<td>O(2)–O(3)</td>
<td>10.9</td>
</tr>
<tr>
<td>B</td>
<td>O(1)–O(4)</td>
<td>10.2</td>
</tr>
<tr>
<td>C(^1)</td>
<td></td>
<td>8.0</td>
</tr>
<tr>
<td>C(^2)</td>
<td></td>
<td>6.5</td>
</tr>
<tr>
<td>Bi–mPA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>N(2)–O(1)</td>
<td>16.9</td>
</tr>
<tr>
<td>A</td>
<td>N(1)–O(2)</td>
<td>15.2</td>
</tr>
<tr>
<td>B</td>
<td>O(2)–O(3)</td>
<td>11.3</td>
</tr>
<tr>
<td>C(^1)</td>
<td></td>
<td>9.3</td>
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<td>C(^2)</td>
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<tr>
<td>C(^3)</td>
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<td>6.9</td>
</tr>
<tr>
<td>C(^4)</td>
<td></td>
<td>5.4</td>
</tr>
<tr>
<td>D</td>
<td>0.9</td>
<td>740</td>
</tr>
</tbody>
</table>
in the N(2)−H∞O(1) hydrogen bond. To distinguish between the two lower hydrogen-bonded resonances at 15.2 and 11.3 ppm, a second dipolar coupling is needed. The resonance at 11 ppm in the DQF spectrum shows a dipolar coupling to the methyl group labeled D in the spectrum, while a similar coupling is not observed between the resonance at 15 ppm and the methyl group. In the crystal structure the proton of the O(3)−H∞O(2) hydrogen bond is 1.4 Å closer to the center of the methyl group than the proton in the hydrogen bond N(1)−H∞O(2), which translates to a relatively stronger dipolar coupling of the O(3)−H∞O(2) hydrogen-bonded proton to the methyl group. Therefore the proton in the O(3)−H∞O(2) hydrogen bond is at 11 ppm and will be labeled B. On the basis of the B−D dipolar coupling, the resonance at 15 ppm must be the proton in the N(1)−H∞O(2) hydrogen bond since that resonance does not have a similar B−D coupling. The chemical shift information from the deconvolution of the 1D 1H MAS spectra of both compounds at 900 MHz and 30 kHz MAS is summarized in Table 2. With the complete assignment based on the combination of crystal structures and 1H NMR data for the two model compounds, the dynamics processes may now be characterized by NMR methods which probe site specific mobility.

Identifying and Quantifying Dynamic Processes. A simple set of experiments that can provide much information about the dynamics of a material is the variable-temperature 1H MAS NMR study. The 1H MAS variable-temperature spectra for Bi−PA and Bi−mPA are shown in panels a and b, respectively, of Figure 5. The variable-temperature data for Bi−mPA do not show any coalescence or significant line narrowing in the temperature range of our experiments. The Bi−mPA compound does exhibit coalescence of the A′ and B resonances. The absence of the coalescence with resonance A in the observed temperature range for Bi−mPA indicates that there is no motion occurring that would exchange the two N−H∞O hydrogen-bonded protons on the benzimidazolium ring. This preliminary data indicates that the dynamics in these salts are dominated by anion motion. From the frequency separation (3.5 kHz) of the resonances at ambient temperature, we can conclude that the dynamics are faster than this time scale (1/Δω = τc ~ 280 μs) once coalescence occurs. As well, the onset of coalescence in Bi−mPA occurs before coalescence in Bi−PA.
Anion Dynamics. We use the $^{31}$P CODEX NMR experiment to look at the dynamics of the anion more carefully. The CODEX pulse sequence is shown as Figure 1. The application of the CODEX pulse sequence is a two step process. The first step is to construct a master curve where the amount of dephasing is varied and the length of time for reorientation is held constant at a reasonable maximum value. In this case, the value of the mixing time is chosen to be 3 seconds. The plateau of the master curve is correlated to the number of sites involved in reorientation. The mixing time and the $z$-filter time period is incremented by whole rotor periods and the total number of rotor periods for the sum is kept constant to ensure a constant time. The $^{31}$P CODEX signal for Bi-PA (Figure 6a) attenuates to 74% after five rotor periods of dephasing. This attenuation corresponds to a four site reorientation of the phosphate tetrahedra. This motion is illustrated in Figure 7a. The reorientation of the phosphate anion involves an exchange of the two nonequivalent sites, and a three-dimensional $T_d$ rotation, which causes a large CSA rotation amplitude. The amount of dephasing needed to reach a plateau is determined by from the structures themselves, and the amplitudes of the reorientational motion involved. Large angle reorientations of the CSA are known to correspond to a rapidly dephasing CODEX signal. Thus, only five rotor periods of attenuation are required to reach the plateau for the phosphate exchange, consistent with the amplitude of the reorientation involved. The master curve for the Bi-mPA (Figure 6b) shows the attenuation of the $^{31}$P CODEX signal to 63% after 25 rotor periods of dephasing, which can be attributed to the three site rotation of the methane phosphonate. The restricted motion of the $^{31}$P site for Bi-mPA indicates that the CSA rotates only about the $C_{3v}$ axis, as shown in Figure 7b. The hydrogen bonding for the methane phosphonate anion occurs in a single plane perpendicular to the rotation axis; when switching between these similar environments, the apparent change of the $^{31}$P CSA is small and thus a large amount of dephasing is required to reach the defined plateau. For the two model compounds studied here, the static powder patterns for the $^{31}$P sites produce nearly symmetrical CSAs, with the Bi-mPA salt having a larger asymmetry parameter than its Bi-PA counterpart, the powder patterns are shown as Supporting Information. The smaller asymmetry parameter of Bi-PA is consistent with our chemical intuition since it would be expected that the bonding in the phosphate would be more symmetrical than the methane phosphonate. The CSA parameters are $\eta = 0.86$ and $\delta = 20.8$ kHz for Bi-PA and $\eta = 0.94$ and $\delta = 22.7$ kHz for Bi-mPA. These CSA values are used to determine the $x$-axis of the data in Figure 6, where $\Delta N\tau_r$ represents the product of the CSA span ($\delta$) and the number of rotor periods of dephasing applied ($N\tau_r$).

To measure the reorientation rates of the different anions the $^{31}$P CODEX exchanges curves were constructed by varying the mixing time while holding the amount of dephasing constant, at the values established in the preceding section. The $^{31}$P CODEX exchange curves of Bi-PA and Bi-mPA are shown as panels a and b, respectively, of Figure 8. The exchanges curves have been fitted to single exponentials to produce a correlation time for each reorientation. The room-temperature correlation time for Bi-PA is $56 \pm 3$ ms while the correlation time for Bi-mPA is $75 \pm 6$ ms. The decrease in correlation time for the methane phosphonate is somewhat surprising, since this anion has two fewer hydrogen bonds than the phosphate analogue. From this we conclude that the bifurcated hydrogen bonds are somewhat weaker than their single hydrogen-bonding counterpart and are therefore more easily broken and reformed. This is also seen in the relative chemical shifts of the hydrogen-bonded protons, where the single hydrogen bond, A, in Bi-mPA is observed at the highest frequency shift of 17 ppm.

The CODEX data shows that the methyl phosphonate anion and phosphate itself are very similar in the timescales of their molecular level dynamics. The key finding is that the anion reorientation is not inhibited by the presence of the methyl...
group. This anion reorientation is proposed to be a key step in the proton transport mechanism. The mechanism is explored further below. It is interesting to note that comparable tetrahedral anion dynamics have been characterized in solid acids such as CsHSO$_4$ using molecular dynamics simulations. In that case the superprotonic phase is distinguished from the lower temperature phase by a lowering of the symmetry in the crystal structure, commensurate with a decrease in the energy barrier to HSO$_4^-$ rotation.

**Cation Dynamics.** Having considered the dynamics of the anions in these salts, we now move to quantifying the participation of the benzimidazolium cations. Our preliminary data showed that the benzimidazolium ring flip of was not observed in the variable-temperature $^1$H NMR study due to the lack of coalescence of resonances A with the other hydrogen-bonded resonances in Bi$^{-}$mPA. In comparison, the imidazole ring flip in a previous study of imidazolium methane sulfonate occurs with a correlation time of several milliseconds. Here we investigate the cation dynamics using $^{13}$C CODEX NMR at ambient temperature. The benzimidazolium ring flip is expected to be slower than imidazolium itself because of the attached phenyl ring. The $^{13}$C resonance that represents the two carbon atoms that adjoin the imidazole ring to the phenyl was chosen for the data analysis, since these carbon atoms do not have a directly bonded proton and should be least affected by spin diffusion. The $^{13}$C CODEX exchange curves of Bi$^{-}$PA and Bi$^{-}$mPA are shown in panels a and b, respectively, of Figure 9. The $^{13}$C CODEX exchange curves use six rotor periods to provide adequate dephasing. Further dephasing of the signal resulted in poor quality spectra. Thus, a small number of rotor periods of dephasing was chosen to determine a correlation time. This limits our ability to determine the number of sites involved in the exchange but it is reasonable to assume that if a reorientation of the ring was occurring, the two-site ring flip of the benzimidazole is the most likely mechanism. The exchange curves of the two compounds show a long build up and the plateau of the curve has not been reached by 30 s for Bi$^{-}$mPA. The correlation time measured here is not attributed to the benzimidazolium ring flip but instead the observed dephasing is due to spin diffusion. No earlier plateau curve is observed for either compound, implying that the benzimidazolium ring does not flip on this time scale. If it does occur, it is on the same time scale as the spin diffusion which is on the order of seconds. The measured correlation times for Bi$^{-}$PA and Bi$^{-}$mPA are 0.42 ± 0.05 and 4.2 ± 0.3 s, respectively. The long correlation time for the measured $^{13}$C CODEX data for both benzimidazolium model compounds are in dramatic contrast of the imidazole methane sulfonate compound which was reported to have a correlation time of 29 ± 1 ms at 274 K. Therefore, the addition of the phenyl group to the imidazole ring serves to immobilize the cation in the benzimidazole compounds. Hence, we are able to conclude that the benzimidazole-based polymers do not utilize the benzimidazole ring reorientation in their proton-transfer process. The slow correlation times of the benzimidazolium rings imply that the major contributor to the ionic conductivity in benzimidazole based polymers is exclusively the acid dopant. Further, these experiments show that covalently tethering the anion to a polymer backbone will not substantially impede proton transport through a Grotthuss style reorientation. For imidazole-based polymers, proton diffusion through the structure by the two-site ring flip is a significant mechanistic step, with a time scale appropriate for contributing to long-range transport, whereas this is not the case for the benzimidazole-based polymers.

**Mechanism of Proton Transport.** The mechanism of proton transport for Bi$^{-}$mPA is based on the $^1$H MAS variable-temperature data and multinuclear CODEX data. Black Arrows represent rotation of the phosphonate anion and green arrows represent protons jumping from one anion to another.

![Figure 10](image-url)

**Figure 10.** The mechanism of proton transport for Bi$^{-}$mPA is based on the $^1$H MAS variable-temperature data and multinuclear CODEX data. Black Arrows represent rotation of the phosphonate anion and green arrows represent protons jumping from one anion to another.
groups are not shown for simplicity. For proton transfer to occur proton A′ (shown in white) moves to its nearest oxygen atom, as in Figure 10b. Subsequently, the adjacent phosphonate anions counter-rotate in an interlocking cogwheel fashion, to provide a free oxygen center for the A′ proton. This proton transfer between the phosphonates is paused in mid-rotation in Figure 10c. The phosphate anions rotate such that the protons zigzag through the structure; this pathway is highlighted by the green arrows. In Figure 10d, proton B (shown in green) is nearing the benzimidazole ring and proton A′ begins to form the O–H=O hydrogen bond. The final step returns the system to its equilibrium state, shown in Figure 10e where proton A′ and B have exchanged places. Thus, Figure 10a and 10e represent identical structures, where the color coding of the protons simply allows us to follow the proton path through the structure.

**Conclusion**

The two model compounds, Bi–PA and Bi–mPA, have unique hydrogen-bonding structures, which are determined through the combination of X-ray diffraction and high-resolution solid-state 1H MAS NMR. The 31P CODEX studies of these model compounds showed that the phosphate undergoes four-site reorientation whereas the methane phosphonate showed only a three-site reorientation. This rotation allows two-dimensional diffusion of the protons along a zigzag pathway, as illustrated in the model developed here. In contrast, the free phosphate facilitates a more isotropic motion of the protons in three dimensions. The results of this study can be generalized to conclude that the effect of binding the phosphate group to the backbone of a polymer slows down the rotational diffusion of the protons, but allow significant local dynamics, as observed in the methane phosphate model salt. Attaching the acid group to the backbone prevents any translational diffusion of the group but not impede the ability of the phosphonate to undergo a reorientation. This work showed that the rotational motion of the anions greatly outpaces any contribution of backbone dynamics by the benzimidazole ring, and therefore the former is the dominant mechanism of proton transport. This is demonstrated based on the relative correlation times of benzimidazolium versus imidazolium, characterized by 13C CODEX NMR. To increase the ionic conductivity of the tethered phosphonates, increased mobility of the side chains may be needed in order to offset the loss of the translational mechanism of proton transport by removing the free acid molecules.

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**Supporting Information Available:** IR spectra, 31P powder patterns and CSA fits, table of crystal data, X-ray crystallographic file (CIF) for Bi–mPA, and 1H 2D DQF NMR spectrum of Bi–PA. This material is available free of charge via the Internet at http://pubs.acs.org.

**References and Notes**