Investigation of Proton Dynamics and the Proton Transport Pathway in Choline Dihydrogen Phosphate Using Solid-State NMR

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Abstract

Choline dihydrogen phosphate has previously been shown to be a good ionic conductor as well as an excellent host for acid doping, leading to high proton conductivities required for e.g., electrochemical devices including proton membrane fuel cells and sensors. A combination of variable-temperature ^{1}H solid-state NMR and 2D NMR pulse sequences, including ^{31}P and ^{13}C CODEX and ^{1}H BaBa, show that the proton conduction mechanism primarily involves assisted transport via a restricted three-site motion of the phosphate unit around the P-O bond that is hydrogen bonded to the choline and exchange of protons between these anions. In other words, proton transport at ambient temperatures appears to occur most favorably along the crystallographic *b* axis, from phosphate dimer to dimer. At elevated temperatures exchange between the protons of the hydroxyl group on the choline cation and the hydrogen-bonded dihydrogen phosphate groups also contributes to the structural diffusion of the protons in this solid state conductor.

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Introduction

Research into fuel cell technology is motivated by the need to develop a replacement for fossil fuels as our main energy source. The traditional materials used for electrolyte applications in fuel cells are polymer membrane systems such as Nafion, a perfluorinated ionomer. These membranes typically only operate well under humid conditions, thus requiring an operating temperature lower than 100°C. Several different systems have been explored as alternatives to polymer membranes including solid acid compounds,[1] phosphoric acid polybenzimidazoles (PBI)[2] and phosphoric acid polyphosphazenes[3]. Choline dihydrogen phosphate (DHP) is a novel organic ionic plastic crystal that has recently shown promise for the electrolyte component in fuel cells.[4,5] It has a low volatility, high thermal stability and fast ionic conductivity (10^{-3} S/cm) in the plastic crystalline phase (140°C). Doping of this plastic crystal material with phosphoric acid sees a significant improvement in ionic conductivity and a high proton diffusivity, higher than either the dihydrogen phosphate anion or the choline cation.[5] Understanding the structure and dynamics in such plastic crystal systems and the nature of the proton conduction is of significant physical chemistry interest that will influence the design of new, low volatility solid state proton conductors.

Solid-state nuclear magnetic resonance (NMR) is a powerful technique for the study of both local structure and dynamics. Proton double-quantum filtered (^{1}H DQF) experiments have been used in the study of a large number of systems for determination of the packing arrangement of the hydrogen-bonding motifs.[6-11] These experiments access the information inherent to through-space dipolar coupling and the relative strength of the measured dipolar coupling can be used as a probe of molecular mobility.

Here we establish the assignment of the proton resonances and the hydrogen-bonding structure of choline DHP by correlating the X-ray diffraction (XRD) structure to the ^{1}H NMR spectrum using heteronuclear and DQF homonuclear correlation techniques. After determining the hydrogen-bonded proton network, a combination of experiments were used to develop a description of the microscopic processes that give rise to proton transfer in choline DHP. Variable-temperature ^{1}H NMR studies are used to characterise the local proton mobility by observing the narrowing and/or coalescence of the resonances.[10-13] The centreband-only detection of exchange (CODEX) pulse sequence measures the reorientation of a molecule by studying the changes in chemical shift anisotropy (CSA) with time.[14] It enables determination of the number of sites involved in the reorientation and the timescale of the motion. Using these techniques, we explore whether the high conductivity of choline DHP results from transport of protons by rotation of the phosphate anions and/or the hydroxyl groups of the choline cation in a Grotthuss-type mechanism via structural diffusion.[15] Another possible means for proton transport is through vehicle transport, where the phosphate anion moves as a complete unit through the structure. By elucidating the molecular level mechanism of proton conduction in choline DHP, we can improve upon the design properties for electrolyte systems based on organic ionic plastic crystals.

Results and Discussion

^{1}H NMR: Structure and Influence of Drying Conditions

The one-dimensional ^{1}H MAS NMR spectrum of choline DHP (**Figure 1**) at ambient temperature (307 K) shows six distinct proton resonances in three distinct regions:

hydrogen-bonded (14-9 ppm), water (9-7 ppm) and aliphatic (4-2 ppm). The relative ratios for the isotropic chemical shifts of the aliphatic protons (9:2:2 for resonance A, B and C, assigned on the inset) correspond to those determined by solution-state NMR.[4] Solid-state NMR can elucidate packing arrangements and intermolecular interactions not available to solution state because of rapid exchange of the hydrogen-bonded protons.

The ^{1}H solid-state NMR spectrum of choline DHP shows two distinct resonances that correspond to hydrogen-bonded protons (resonances E and F). The X-ray crystal structure of choline DHP was reported recently (e.g. **Figure 2**)[16] showing the presence of three unique O-H…O hydrogen bonds. Each phosphate anion has two similar hydrogen bonds to another phosphate unit (O4-H4O-O2 in **Figure 2**), forming a dimer, and two hydrogen bonds with the hydroxyl group of two different choline cations. The latter two hydrogen bonds have the choline hydroxyl acting as a hydrogen bonding donor group and an acceptor respectively. For clarity, these two bonds will be referred to as the *phosphate-choline donor* (O5-H5O-O1) and the *phosphate-choline acceptor* (O3-H3O-O5) hydrogen bonds. The phosphate-phosphate dimers are connected to each other through the hydrogen bonds to the hydroxyl groups. This arrangement, where each phosphate anion is hydrogen-bonded to two cations and one anion, results in columns of choline DHP molecules along the *a* axis. The assignment of these proton chemical shifts to the crystallographic hydrogen bonds cannot be made based on the heteroatomic distances alone. The differences between the bond distances are small, only 0.03 Å, while the chemical shift difference is greater than 3 ppm. The relative ratio for the two hydrogen bonds is 2:1 for resonance E and F respectively, indicating there are two hydrogen-bonded environments represented at the lower frequency. The local

environments, including H-O and O-H…O bond distances, of the phosphate-phosphate and phosphate-choline donor hydrogen bonded protons are similar (**Table 1**) and therefore they are tentatively assigned to resonance E (confirmed by the correlation experiments below). This assignment will be confirmed through the use of heteronuclear and homonuclear correlation NMR techniques. Moreover, since the crystal structure was obtained at 193 K, these solid-state NMR methods help ascertain that the hydrogen bonding arrangement is similar at temperatures within the operating range of fuel cell applications.

Figure 3 includes ^{1}H MAS NMR spectra at ambient temperature of choline DHP treated by varying the drying time. The sample that has not been treated is referred to as "wet". The water protons resonance in the "wet" sample is very narrow, suggesting a highly mobile species. As the drying time increases, the water resonance decreases in signal intensity, broadens and moves to higher frequency. This suggests that it is possible to remove some of the water from the structure, but that even after extensive heat treatment, some water remains tightly bound. It has been observed previously in hydrogen-bonded structures, for example in SiO_2-Nafion composites, that there are strong hydrogen-bonding sites available that trap water molecules,[17] consistent with the results observed here. The aliphatic resonances appear to broaden after heat treatment, which might indicate that the structure is now slightly condensed so that the aliphatic protons experience a stronger dipolar interaction with the surrounding protons that is less completely averaged or perhaps there is an increase in disorder in the sample that is most reflected in the aliphatic resonances. The following experiments were all performed upon the sample dried for three days at 80 °C under vacuum (**Figure 3c**). Even in these

'dry' samples, isothermal TGA analysis at 110 °C has suggested that around 2% water may still be present in the choline DHP material.[5] This corresponds to the brittle crystalline phase of choline DHP and, according to a recent detailed investigation of the thermal behaviour of this material,[5] this phase is constant throughout the entire temperature range studied here (up to 330 K).

^{1}H-^{31}P HETCOR and ^{1}H-^{1}H 2D DQ MAS NMR: Assignment and Determination of Hydrogen-Bonding Arrangement

The accurate assignment of the two hydrogen-bonded resonances can be made using the short-range contact information provided by the homonuclear and heteronuclear dipolar couplings and is essential to be able to study the local dynamics. Heteronuclear ^{1}H-^{31}P correlation (HETCOR) experiments were performed to determine which hydrogen-bonding species include the phosphate group. The ^{31}P spectrum of choline DHP at ambient temperature shows one resonance at 0.5 ppm (**Figure 4**). There are correlations to all of the protons except for those of the water molecules. This means that all of the hydrogen-bonded resonances can be attributed to hydrogen bonds involving the phosphate group. This is supported by the crystal packing arrangement in **Figure 2**. It is clear that the strength of the ^{1}H-^{31}P correlation is stronger for resonance F than resonance E. The H-P bond distance between the proton of the choline acceptor hydrogen bond and the phosphorus is significantly shorter (2.02 Å) than the other two hydrogen bonds (2.15 and 2.77 Å), producing a stronger dipolar coupling consistent with the assignment of resonance F to the proton of the phosphate-choline acceptor hydrogen bond.

The elucidation of the packing environment is often best investigated by looking at the proximities of the protons to each other using DQ filtered experiments.[6,7] Protons that are mobile on the timescale of the experiment are motionally averaged and filtered from the spectra. In the 1D DQF 30 kHz MAS NMR spectrum of fully dried choline DHP acquired using the Back-to-Back (BaBa) pulse sequence[6,18] at ambient temperature (**Figure 5a**), only the water protons are filtered out, indicating that at 307 K, the protons of the water molecules are the only protons mobile on the timescale of the DQF experiment (33 μs). None of the protons associated with the choline DHP structure are mobile at ambient temperature on this fast timescale. By extending the length of the recoupling (excitation) time, the BaBa sequence can be used to detect weak dipolar couplings which are partially dynamically averaged by local mobility. **Figure 5c** shows the 1D ^{1}H DQF spectrum after six rotor periods (198 μs) where the hydrogen-bonded resonances are both filtered out.

In a 2D ^{1}H-^{1}H DQF experiment, correlations between like protons are found on the diagonal ($2\omega_A$, ω_A) and between unlike protons occur on either side of the diagonal ($\omega_A + \omega_B$, ω_A) and ($\omega_A + \omega_B$, ω_B). **Figure 6** shows the ^{1}H 2D DQF spectrum for choline DHP at 30 kHz and ambient temperature. The strong self-correlation between the aliphatic protons dominates the diagonal at the top right quadrant of the spectrum. The data shows that the three hydrogen-bonded protons (resonances E and F) are dipolar coupled with themselves (self-correlations E-E and F-F in **Figure 6**) and with each other (cross peaks E-F). This implies that not only are the two hydrogen-bonded phosphate anions close to each other and close to a hydroxyl, but that there must also be two hydrogen-bonded choline groups close to each other, again consistent with the hydrogen-bonding network

determined from XRD results. Close inspection of the slices in the 2D spectrum show that resonance F is not spatially close to the methyl groups (C) on the ammonium head group. Looking at the proton-proton proximities in the crystal structure, all of the hydrogen bonds are located close to the aliphatic protons except for the proton of the phosphate-choline acceptor hydrogen bond that is >5.4 Å away from the methyl protons. This is further evidence supporting the assignment of resonance E and F to the phosphate-phosphate/phosphate-choline donor and the phosphate-choline acceptor hydrogen bonds respectively.

The homonuclear and heteronuclear correlation NMR spectroscopy confirms the recently reported packing motif determined from XRD[16] with all the possible hydrogen-bonding contacts.

^{1}H NMR: Identifying and Quantifying Dynamic Processes

The behaviour of the resonances with temperature (307 – 330 K) is shown in **Figure 7a** for the sample dried for three days. Several trends are observed with increasing temperature. The resonances of the aliphatic protons narrow slightly with temperature and show a small shift to lower frequency (change of about 0.1 ppm). Similar to the behaviour observed upon drying, the water resonance shifts to higher frequency with temperature and broadens. At first glance, this observation seems inconsistent with the water molecules being mobile. Generally, mobile species narrow and tend towards lower frequency with increasing temperature. However, the resonance is completely filtered out during the BaBa acquisitions (**Figure 7b**), confirming the fast mobility. The broadening of the resonance and the shift to high frequency suggests that the water

protons are exchanging with the hydrogen-bonded resonances and that the resonances would eventually coalesce at higher temperatures. It is clear that resonances E and F shift to lower frequency with temperature, possibly both coalescing with the water protons. **Figure 8** shows a two-dimensional exchange (EXSY)[19] spectrum with a mixing time of 5 ms at ambient temperature that is consistent with this observation. While DQF experiments allow investigation of dipolar coupling of rigid protons, 2D EXSY studies are used to investigate the mobile water protons, as well as interactions between the rigid and mobile components. The cross peaks are evidence for chemical exchange between different protons. The cross peaks between resonances E and F in **Figure 8** support the packing arrangement where the two hydrogen bonds are close to each other in space. It appears that there is also a weak exchange between resonance E and the water protons. Whether the water is only exchanging on the microscopic level or if it is involved in long-range transport is unclear. However, the dried choline DHP sample exhibits high proton conductivity,[4] indicating that the water does not play an essential role in the conduction process.

The most significant change with temperature is the very marked narrowing of resonance E at 330 K (from a line width of 970 Hz to 110 Hz) which is filtered out completely in the DQF spectrum (**Figure 7b**). The behaviour in the wet sample (not shown) was similar. Resonance E narrowed completely with increasing temperature, with no additional resonance or broad component present, indicating that both the hydrogen bonds assigned to resonance E experience a significant increase in mobility at this temperature. The narrowing of the resonance corresponding to the phosphate-phosphate and phosphate-choline donor hydrogen bonds means these protons are more

mobile than the phosphate-choline acceptor hydrogen bond. Structural diffusion mechanisms are often characterised by reorganisation of the hydrogen-bonding network to facilitate proton transport through the solid. From these results concerning the mobility of the hydrogen-bonded protons, we propose that the rotation of the phosphate group and the reorientation of these hydrogen bonds is the dominant step in the proton transport. Moreover, the protons are being primarily passed from phosphate unit to phosphate unit, possibly involving the hydroxyl groups of the choline through rearrangement of the phosphate-choline donor hydrogen bond.

^{31}P CODEX: Study of Anion Dynamics

To study the reorientation of the phosphate unit, the CODEX pulse sequence was used to examine changes in the CSA over time.[14] After a mixing time (τ_{mix}), if chemical exchange occurs within the molecule the CSA will not be in the same position and the magnetisation will not be completely refocused, causing attenuation of the CODEX signal. The smaller the motion, the longer the time needed to produce significant dephasing. The dephasing is determined by Nt_r where N is the number of loops of the recoupling 180° pulses and t_r is a rotor period, 0.1 ms in these experiments.

The application of the CODEX pulse sequence requires two separate steps. First, by varying the amount of dephasing and keeping the mixing time constant and at a long value, a master curve is constructed. After sufficient dephasing, the CODEX signal will plateau and the final value is related to the total number of sites involved in the reorientation according to the following equation[14]:

$$E_\infty = \frac{(M-1)}{M} f_m \qquad (1)$$

where E_∞ is the normalised signal intensity (ratio of the CODEX signal to the reference intensity where the mixing time was 0.1 ms, the minimum increment), M is the number of sites and f_m is the fraction of mobile sites involved in the exchange. The ^{31}P master curve for choline DHP at ambient temperature is shown in **Figure 9a**. The x axis is determined by the product of the span of the CSA (δ) and the number of rotor periods of dephasing applied. The span was determined from a simulation that reproduces as closely as possible a static ^{31}P powder pattern of choline DHP. The CSA parameters were $\eta = 0.98 \pm 0.02$ and $\delta = 18.3 \pm 0.3$ kHz. These parameters are similar to those of benzimidazole methane phosphonate (Bi-mPA).[10] The ^{31}P CODEX signal for choline DHP attenuates to about 60% after 50 rotor periods of dephasing. Within experimental error, this is indicative of a three-site reorientation of the phosphate around the C_{3v} axis. It is possible that not all of the phosphate sites ($f_m < 100\%$) are participating in the reorientation which could explain the plateau being slightly less than the expected 66.6%.[14] This restricted three-site motion is consistent with the motion of the phosphate unit around the P-O bond that is tethered to the choline acceptor hydrogen bond. The variable-temperature experiments confirmed that this hydrogen bond is the least mobile within the choline DHP structure.

The second part of the CODEX experiment is to measure the timescale of the reorientation of the phosphate units. This is accomplished by varying the mixing time while holding the amount of dephasing constant at 80 rotor periods (where the CODEX signal is clearly fully attenuated). **Figure 9b** shows the ^{31}P CODEX exchange curve for choline DHP at ambient temperature, plotted as the normalised signal intensity versus mixing time. The curve was fit to a single exponential using the following equation:

$$E_{\infty} = A(1 - \exp(-t_m / \tau_c)) \qquad (2)$$

where τ_c is the correlation time of the exchange process that causes the attenuation of the CODEX signal. The inverse of the correlation time is the frequency at which the reorientation is occurring. The correlation time determined at ambient temperature is 290 ± 10 ms. Comparing this to correlation times for phosphate reorientation in Bi-mPA, the reorientation was almost three times faster for Bi-mPA (75 ± 6 ms),[10] suggesting that the hydrogen-bonding arrangement in choline DHP is stronger.

^{13}C CODEX: Study of Cation Dynamics

The ionic conductivity of choline DHP is an order of magnitude higher than 1-butyl-3-methylimidazolium DHP.[4] It was proposed that this difference could result from the hydroxyl group of the choline cation participating in the proton transport mechanism.[4] The 1D ^{1}H variable-temperature studies suggest that one of the hydrogen bonds involving the choline hydroxyl group is mobile. ^{13}C CODEX experiments are used to quantify the contribution of the choline cations, both the carbon chain and the hydroxyl group, to the conductivity. The variable-temperature data show that the aliphatic protons only narrow slightly with increasing temperature. They are also not eliminated from the DQF spectra, even at high temperature, suggesting they are not highly mobile species. Finally, there was no coalescence with the hydrogen-bonded resonances, indicating that the protons are not quickly being passed from the phosphate units to the aliphatic protons (not faster than the separation between them in Hz, or ~200 μs). The ^{13}C CP MAS NMR spectrum at ambient temperature is shown in **Figure 10**. The three resonances are labelled A, B and C correspond to the methyl groups attached to the quaternary ammonium group, the

carbon attached to the ammonium and the C-O carbon, respectively. Resonance A is completely absent and can only be observed for short constant times (mixing time + Z filter = 100 msec). **Figure 11** shows the ^{13}C CODEX exchange curves for resonance B and C of choline DHP at ambient temperature. To determine a correlation time, the amount of dephasing was set to three rotor periods. Unfortunately, further dephasing of the signal resulted in poor quality spectra, limiting the ability to determine the number of sites involved in the exchange. Resonance C is not observed at constant times longer than 3 sec.

The correlation time determined at ambient temperature for resonance B and C is 1.6 ± 0.4 sec. This timescale is slower than that of the phosphate anion reorientation, but it does indicate that the choline molecule may indeed play a part in the structural diffusion of the protons.

Mechanism of Proton Transport:

The proximity of the hydrogen-bonded protons is important for allowing a hopping mechanism for proton transport. The reorientation of the phosphate group is key for the structural diffusion of protons in choline DHP. This occurs by a three-site rotation that passes protons from phosphate unit to phosphate unit and, unique to this system, through the hydroxyl groups of the choline cation. We should note that previous studies of ion transport in plastic crystal materials have suggested that vacancy defects may also play an important role in the conduction mechanism.[20-23] Indeed as temperature increases and the number of defects also increases, the contribution of vacancy defects to ion transport may become more significant. For choline DHP, increases in temperature through the various

solid-solid phase transitions would likely lead to increased rotational freedom for the anion as well as the possibility of anion/cation defects which both facilitate conduction. From the NMR data presented here, the proton transport mechanism certainly favours the 'paddle wheel' mechanism of proton conduction, similar to the processes described for high temperature inorganic plastic crystals such as Li_2SO_4 and Na_3PO_4.[24,25]

Only one of the hydrogen bonds to the hydroxyl group appears to be involved in fast long-range motion which suggests a complicated transport pathway. Rather than motion straight down the *a* axis, the protons can move along one of two possible pathways: along the *b* axis from phosphate dimer to dimer or along the *a* axis in a zig-zag pathway down the column from phosphate to hydroxyl. The ^{31}P and ^{13}C CODEX data indicates that the former mechanism is the most energetically efficient and dominant pathway for proton diffusion. The latter mechanism involves motion from the phosphate-choline donor site to an adjacent phosphate-choline donor site along the *b* axis, thereby not involving the phosphate-choline acceptor hydrogen bond. This mechanism of proton transport is illustrated schematically in **Figure 12**. **Figure 12a** shows a representation of the static crystal structure[16] where the green triangular planes represent the C_{3v} axes of rotation of the phosphate anions. The protons in red (proton A) represent the phosphate-choline acceptor hydrogen bonds that are not involved significantly in proton transport at ambient temperature. For proton motion to occur, protons B, B' and D (green) move to the nearest oxygen atoms (**Figure 12b**). Subsequently, the phosphate anions rotate in a cogwheel fashion to provide free oxygen sites. In **Figure 12c,** the proton of the phosphate-choline donor hydrogen bond (proton D') has moved to the oxygen atom of the adjacent choline unit. Finally, proton C transfers to the closest free oxygen atom, the

hydroxide of the choline cation (**Figure 12d**). **Figure 12a** and **12d** are identical, but the different labels (A-D) of the protons allow us to follow the possible pathway of the proton migration.

As detailed in **Figure 12**, the phosphate-choline acceptor hydrogen-bonded proton is not involved in the most favourable pathways. However, resonance F does shift towards lower frequency with temperature, which indicates that the phosphate-choline acceptor hydrogen bond is weakening and becoming more dynamic. It possibly plays a minor role in proton transport straight down the *a* axis which could become more significant at even higher temperatures.

Experimental Details

Synthesis of Choline DHP. (2-Hydroxy-ethyl)-trimethyl-ammonium dihydrogenphosphate [Choline][DHP, (50 g) was synthesised by slow addition of an aqueous solution (85%) of phosphoric acid (26.68 g) to 45 % methanoic choline hydroxide solution (68.98 g) in an ice bath whilst stirring for 2 hours at room temperature. The filtrate was evaporated to obtain a pure white solid in 98 % yield. The resultant white solid was recrystallised from ethanol at 273 K. This material is prone to water uptake and hence the samples were stored in a nitrogen filled dry box after drying.

Solid-State NMR. ^{1}H MAS NMR spectra were acquired at a Larmor frequency of 500.1 MHz using a Bruker AV-500 (11.7 T) spectrometer. The variable-temperature studies were performed on a triple-resonance probe supporting rotors of 2.5 mm outer diameter with a spinning frequency of 30 kHz. The spectra are referenced to adamantane (1.63

ppm). The ^{1}H spectra were acquired using a 90° pulse length of 2.5 μs and a recycle delay of 5 sec. The temperature was calibrated using $Sm_2Sn_2O_7$ as a shift thermometer.[26] ^{1}H DQ MAS NMR experiments were performed with one cycle of the back-to-back (BaBa) recoupling sequence. The t_1 increments were set equal to one rotor period. The 1D ^{1}H MAS NMR experiments were collected with 64 transients. The 2D ^{1}H-^{1}H DQ MAS NMR and 2D EXSY spectra were obtained with 8 transients and 512 slices in the indirect dimension. Phase-sensitive detection in t_1 was achieved through States-TPPI.

The ^{1}H-^{31}P HETCOR experiment was conducted at 11.7 T using a triple-resonance probe supporting rotors of 2.5 mm outer diameter. The spectra are referenced to $NH_4H_2PO_4$ (0.9 ppm). A 90° pulse length of 2.5 μs was used with 64 transients and 256 slices in the indirect dimension.

The ^{31}P and ^{13}C CODEX data were acquired at 11.7 T using a triple-resonance Bruker probe supporting rotors of 4 mm outer diameter. The CODEX experiments were conducted using a 1 ms contact time for cross-polarisation from ^{1}H to both ^{31}P and ^{13}C and 5 μs 180° ^{31}P and ^{13}C pulses. The MAS frequency used was 10 kHz, which translates to 0.1 ms as the lowest increment for the mixing time, τ_{mix}. All other data points use a mixing time that is an integer of 0.1 ms intervals. The reference spectrum was acquired using 0.1 ms for the mixing time and 3 s for the Z-filter, while the completely attenuated spectra were obtained using 3 s for the mixing time and 0.1 ms for the Z filter. For the ^{13}C CODEX data, at least 1024 transients had to be acquired to achieve sufficient signal-to-noise.

Conclusion

An advanced multinuclear (^{1}H, ^{13}C and ^{31}P) NMR approach that probes both the structure and the dynamics of the proton conducting solid phase of choline dihydrogen phosphate has revealed (i) details of its hydrogen-bonded network, and (ii) the dominant proton transport mechanism. From DQF spectra it is clear that the nature of the structure here consists of two hydrogen-bonded phosphate anions together with the hydroxyl group from the choline cation, as well as hydrogen-bonded choline groups. This confirms definitively the suggested proton positions from the crystallographic structure. NMR independently probes the cation and anion dynamics in the range 307 to 330 K, leading to an understanding of the mechanism of proton transport. This data suggests that the preferred proton pathway is between phosphate dimers along the crystallographic *b* axis via a mechanism including rotation of the phosphate tetrahedra.

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Table 1: Summary of selected bond distances for the three hydrogen bonds in choline DHP (phosphate-choline acceptor, phosphate-phosphate and phosphate-choline donor are H3O, H4O and H5O respectively). The bond numbering corresponds to **Figure 2**.

Bond Type	Bond Distance (Å)
O3-H3O	0.79
O3-H3O-O5	1.79
O4-H4O	0.93
O4-H4O-O2	1.60
O5-H5O	0.94
O5-H5O-O1	1.63

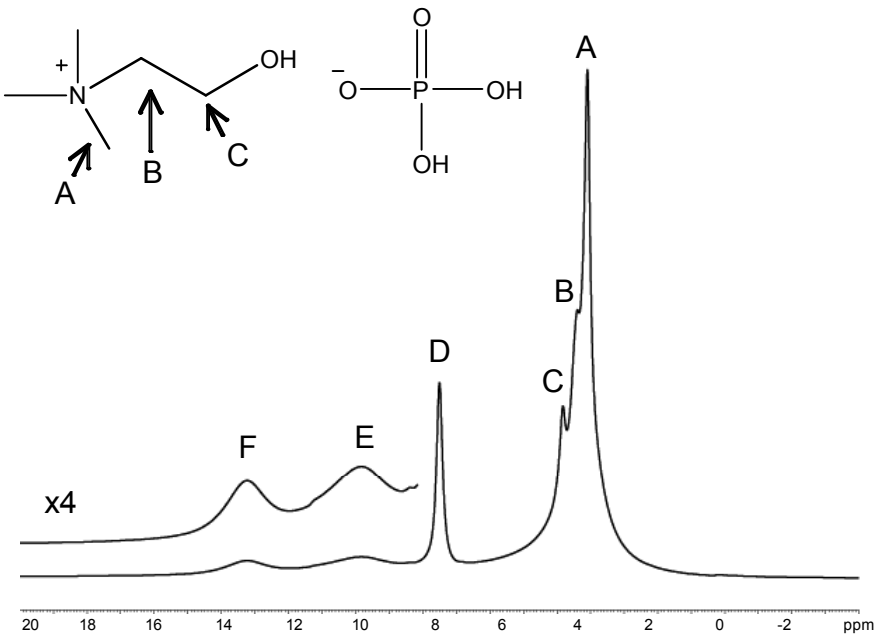

Figure 1: ^{1}H MAS NMR spectrum of choline DHP at 30 kHz and ambient temperature. The insert represents the three different aliphatic protons (A-C).

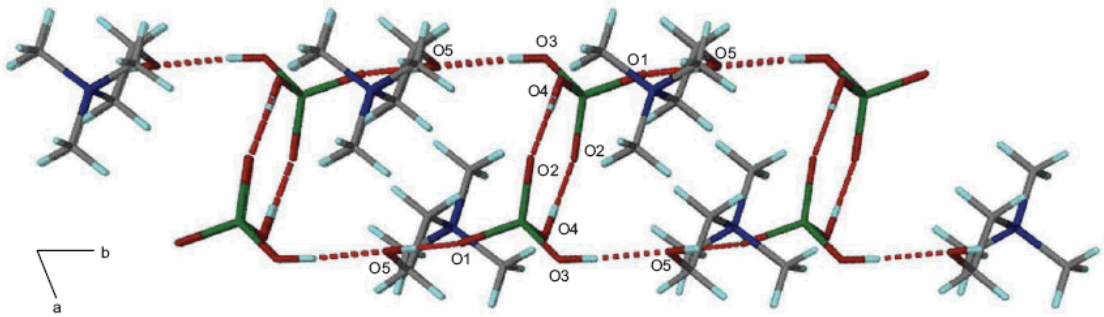

Figure 2: The molecular packing arrangement of choline DHP. The phosphorus atoms are represented in green, the oxygens in red, the nitrogens in dark blue, the carbons in gray and the protons in light blue. The dashed lines represent the intermolecular O-H…O hydrogen bonds. The oxygen atom labels are consistent with the crystallographic information from ref. 16.

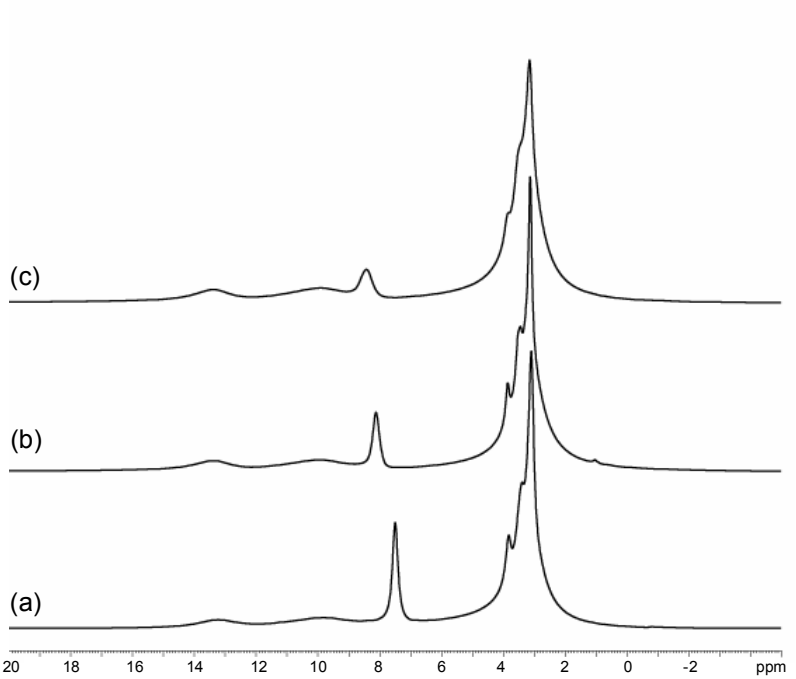

Figure 3: ^{1}H MAS NMR of choline DHP at 30 kHz and ambient temperature under different drying times: (a) wet; (b) dried overnight at 80 °C under vacuum. Note that the very weak resonance at ~1 ppm is an artifact that remains unassigned; (c) dried for three days at 80 °C under vacuum.

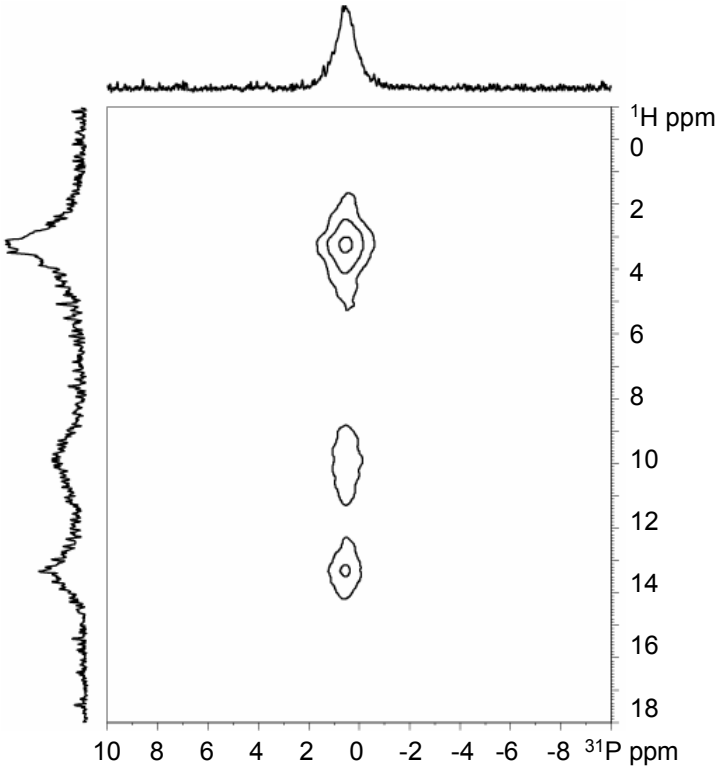

Figure 4: 2D ^{1}H-^{31}P HETCOR spectrum of dried choline DHP acquired at 30 kHz and ambient temperature, using a cross polarization contact time of 1 ms.

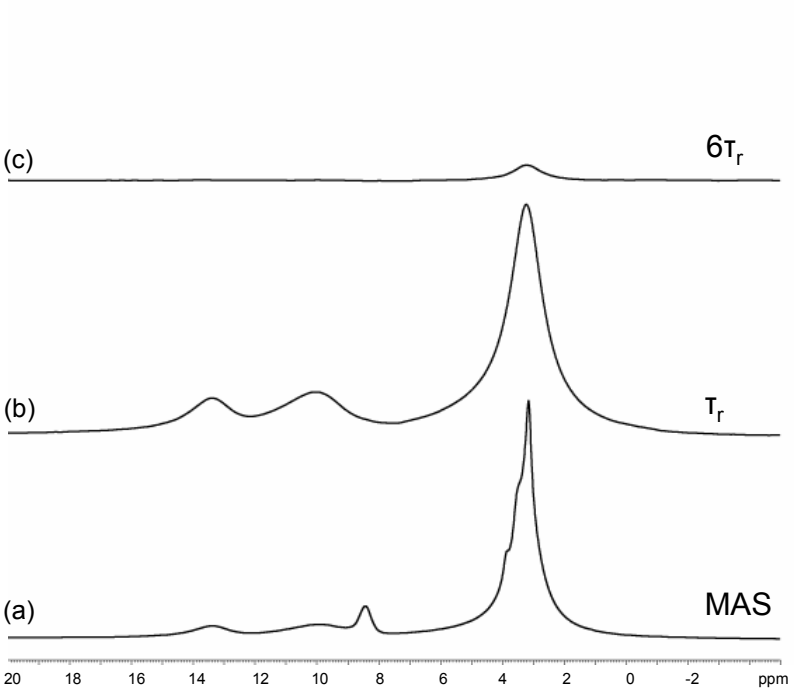

Figure 5: (a) ^{1}H MAS and (b)-(c) DQF spectra of dried choline DHP acquired at 30 kHz and ambient temperature. The number of rotor periods of recoupling used is indicated.

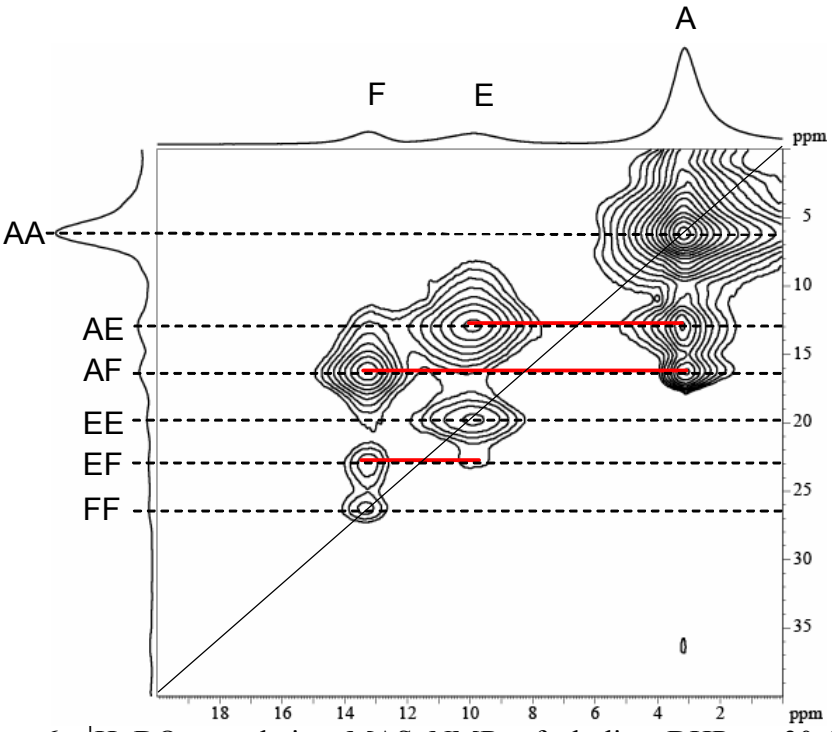

Figure 6: ^{1}H DQ correlation MAS NMR of choline DHP at 30 kHz and ambient temperature with one rotor period of recoupling. The protons are labeled A (aliphatic protons A-C) and E and F are the hydrogen-bonded resonances. The red lines indicate the cross peaks.

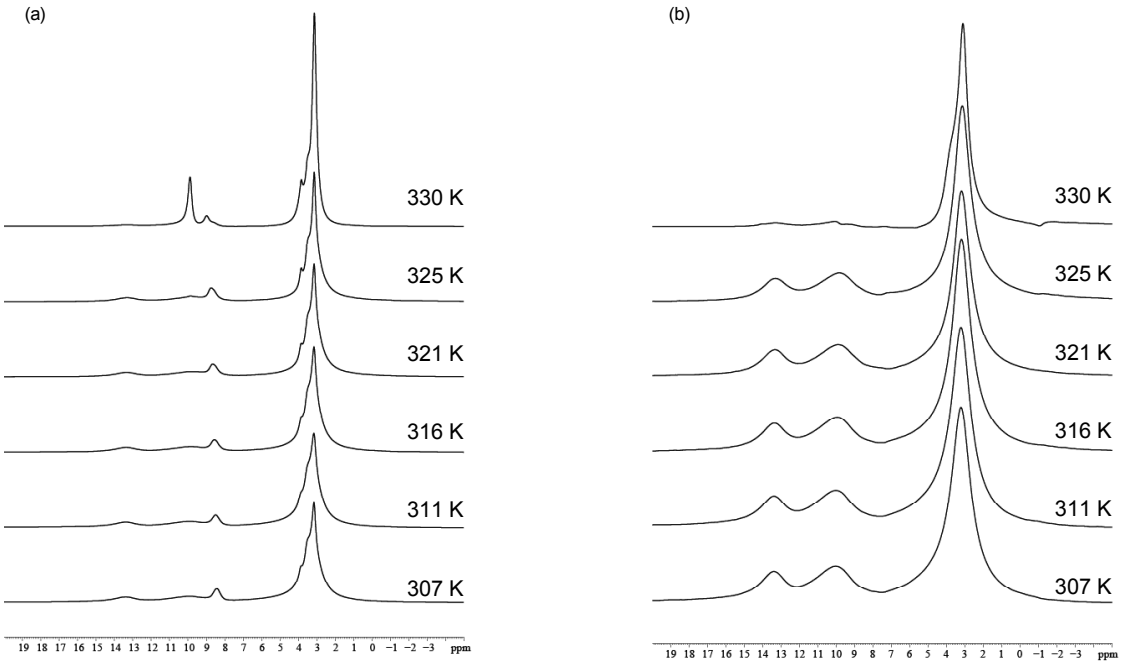

Figure 7: ^{1}H variable-temperature MAS NMR spectra acquired at 30 kHz. (a) ^{1}H MAS and (b) DQF using the BaBa pulse sequence and one rotor period of recoupling.

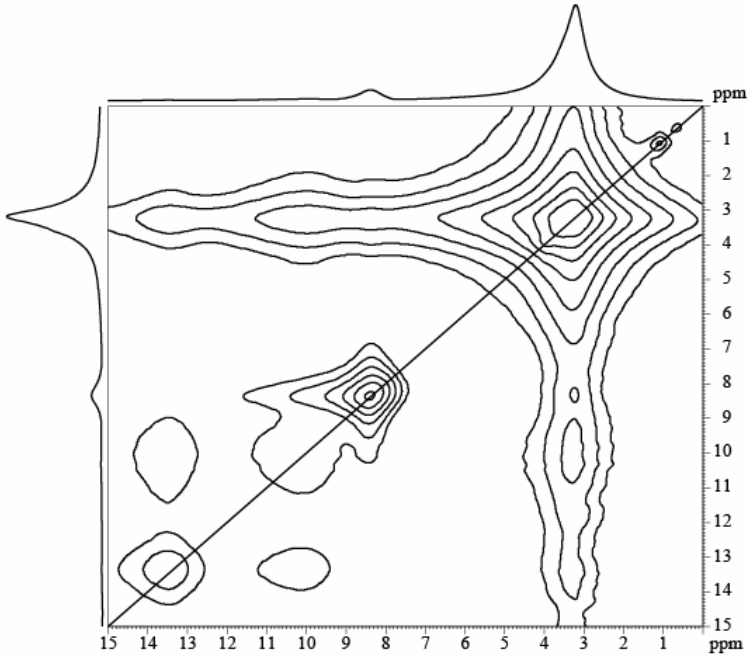

Figure 8: ^{1}H 2D EXSY spectrum of choline DHP at 30 kHz and ambient temperature, with a mixing time of 5 ms.

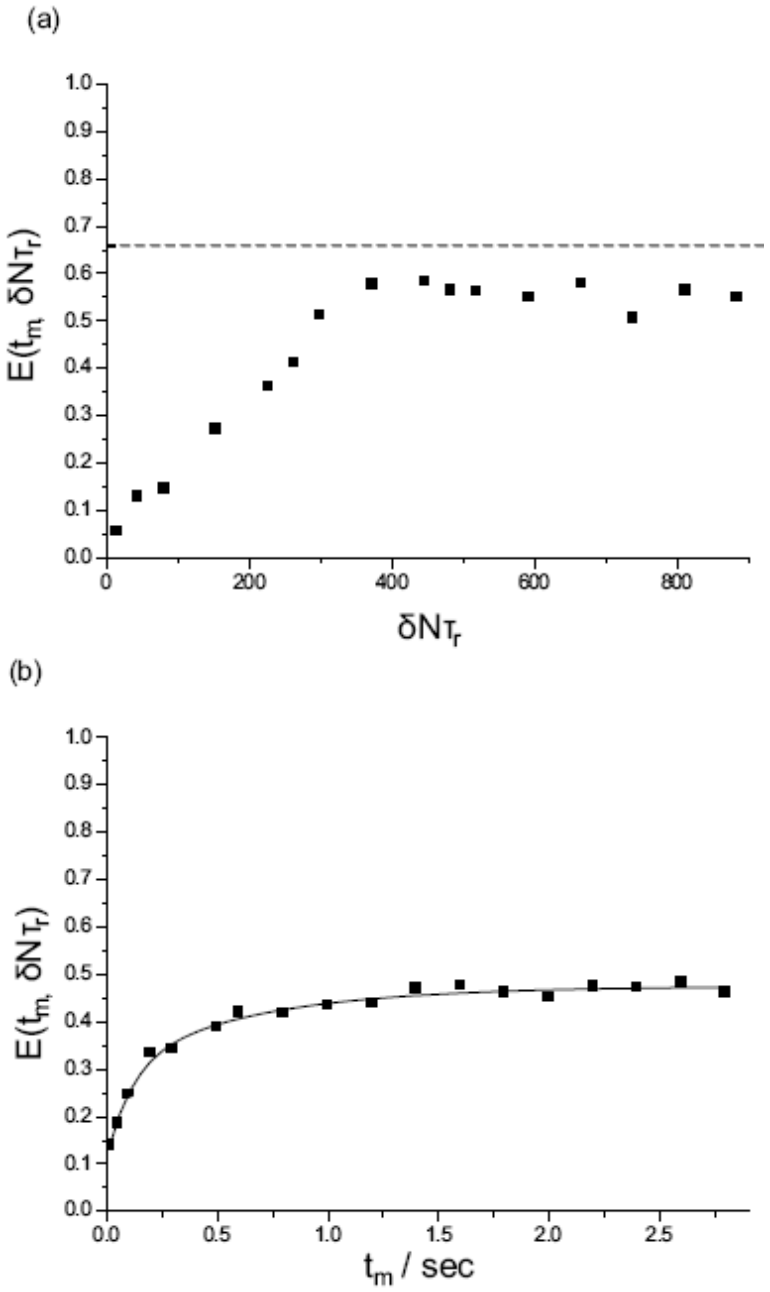

Figure 9: (a) The master curve for choline DHP at ambient temperature showing a plateau at approximately 60%, corresponding to a three-site reorientation. The dashed line represents the theoretical plateau of a master curve for a three-site jump; (b) ^{31}P CODEX exchange curve for choline DHP. The single exponential fit gave a time constant of 290 ± 10 ms.

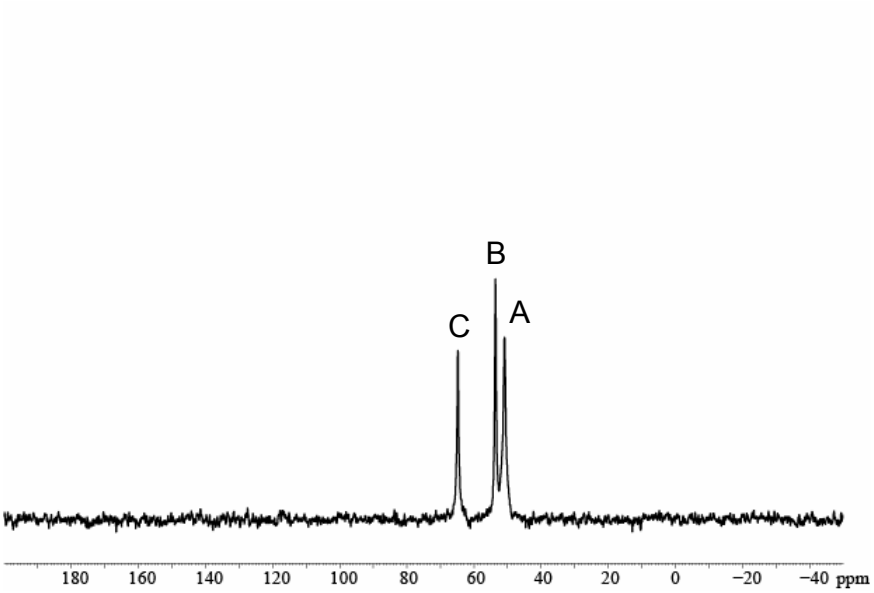

Figure 10: ^{13}C CP MAS NMR spectrum of choline DHP at 10 kHz and ambient temperature. The contact time was 1 ms.

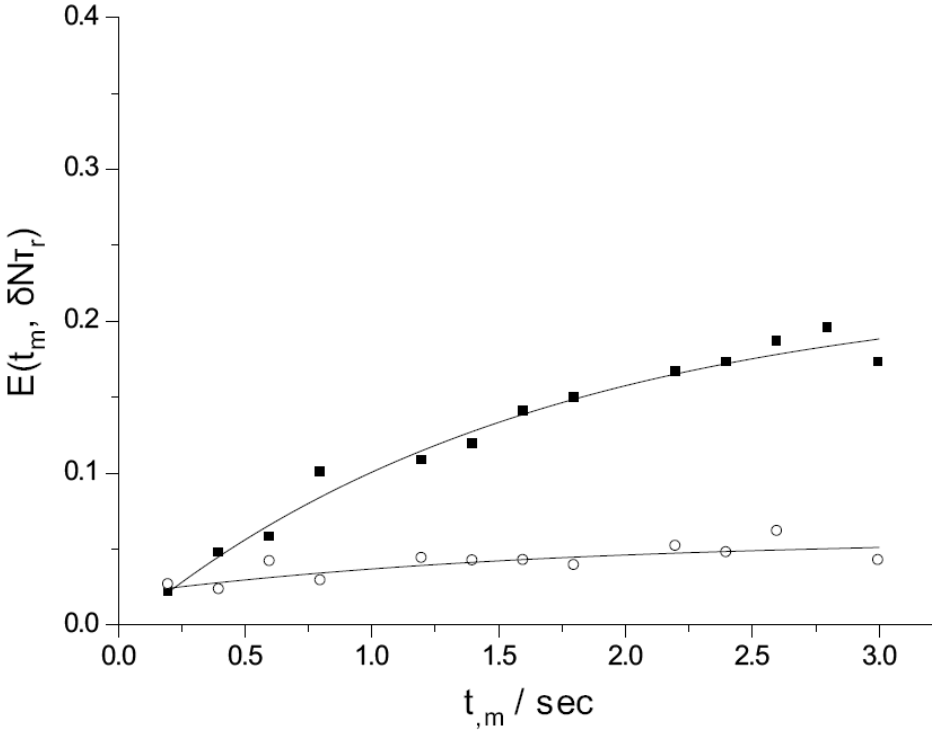

Figure 11: ^{13}C CODEX exchange curve for choline DHP at ambient temperature. The single exponential fits for both carbon B (filled squares) and carbon C (open circles) gave time constants of 1.6 ± 0.4 sec.

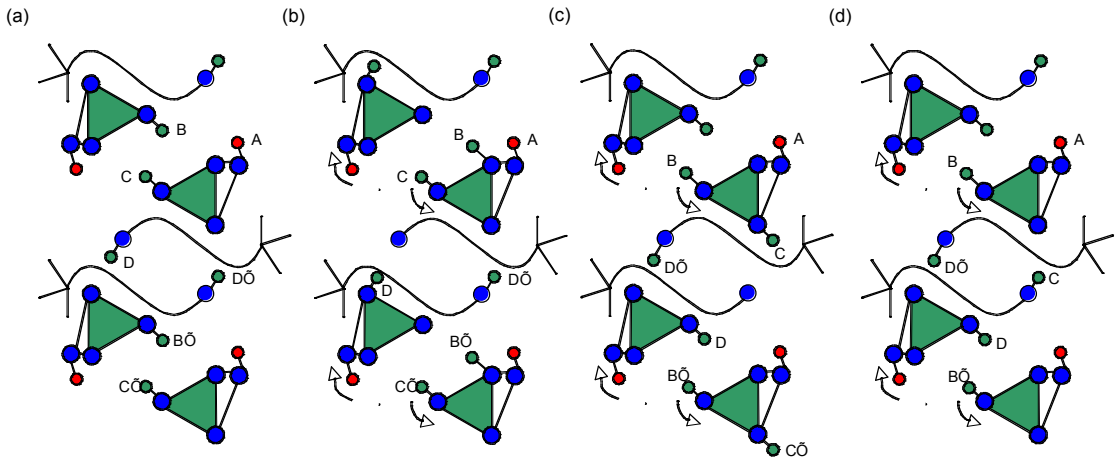

Figure 12: The mechanism of proton transport for choline DHP. The green triangular planes are the C_{3v} axes of rotation and the oxygen atoms, mobile protons and immobile protons (phosphate-choline acceptor hydrogen bond) are represented in blue, green and red respectively. The black arrows represent the three-fold rotation of the phosphate groups. The details of the mechanism are described in the text.

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Graphical contents entry

A combination of solid state NMR techniques reveal the details of the proton conduction mechanism via phosphate group rotation in the organic ionic conductor choline dihydrogen phosphate.