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4-Sulfophenylphosphonic Acid: A Novel Precursor to Fabricate Polyfunctional Acid Materials

Enzo Montoneri,*,† Guido Viscardi,†,‡ Stefano Bottigliengo,† Roberto Gobetto,§
Michele R. Chierotti,§ Roberto Buscaino,†,‡ and Pierluigi Quagliotto†,‡

Dipartimento di Chimica Generale ed Organica Applicata, NIS Centre of Excellence, and Dipartimento di Chimica I.F.M., Università di Torino, C. M. D'Azeglio 48, 10125 Torino, Italy

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A major application of polyfunctional acid materials is the fabrication of solid electrolytes exhibiting proton conductivity in the solid state for operation in fuel cells at medium temperature (<160 °C). Because the advancement of research on solid proton conductors depends on the availability of new precursors, a new acid organosulphur phosphorus compound, i.e., the hydrated 4-sulfophenylphosphonic acid $H_2O_3PC_6H_4SO_3H_2 \cdot 2\ H_2O$ (**IA**), has been synthesized by the Tavs reaction starting from the 4-bromo(diethyl)-sulfonate precursor. This synthetic route is opposite that reported for the synthesis of many other aromatic sulfophosphonic acids, which are obtained by sulfonation of the aromatic phosphonic acid precursor. The reason for the different synthetic route in the former case lies in the fact that sulfonation of benzenephosphonic acid yields only metasubstituted derivatives. Investigation of the solid-state structure at variable temperature indicates that **IA** yields the anhydrous compound $H_2O_3PC_6H_4SO_3H_2$ (**IB**) at 190−210 °C. Solid state ^{13}C and ^{31}P NMR data and FT-IR measurements are consistent with intermolecular H-bonding between the sulfonic and phosphonic acid groups, and/or protonation of the phosphonic acid by the sulfonic acid group, depending on the presence of water. $Ar-SO_3^-H_3O^+\cdots O=P(Ar)(OH)_2\cdots OH_2 \rightleftharpoons Ar-SO_3^-H_3O^+\cdots O=P(Ar)(OH)-O^-\cdots H_3O^+$; $Ar-SO_3^-H_3O^+\cdots O=P(Ar)(OH)_2\cdots OH_2 \rightleftharpoons Ar-SO_3^-H_2O\cdots[HO-P(Ar)(OH)_2]^+\cdots OH_2$; $Ar-SO_3^-H_2O\cdots[HO-P(Ar)(OH)_2]^+\cdots OH_2 \rightleftharpoons Ar-SO_3^-H_2O\cdots(HO)_2P(Ar)=O\cdots H_3O^+$; $\underset{\textbf{IA}}{\{SO_3^-[H(H_2O)_2H_2O_3P]^+Ar\}_n} \rightleftharpoons \underset{\textbf{IB}}{\{SO_3^-[H_3O_3P]^+Ar\}_n} + 2nH_2O$.
These interactions are very important in determining proton conductivity in relation to the possible use of **IA** as solid electrolyte component in fuel cells operating at medium temperature. On this basis, 4-sulfophenylphosphonic acid seems an interesting precursor for the fabrication of solid proton conducting electrolytes.

Introduction

A major application of polyfunctional acid materials is the fabrication of solid electrolytes exhibiting proton conductivity in the solid state for operation in fuel cells.[1] Sulfonic acid polymers as DuPont Nafion exhibit high proton conductivity only in a high-humidity environment.[2] In these materials, the acid anion group is covalently attached to the polymer backbone; only the proton is mobile, and water, by virtue of its H-bonding properties, is capable of building the ideal pathway for the proton transfer. Water loss due to operation at medium temperature <160 °C yields lower conductivity. Thus, hydration stability of solid electrolytes at these temperatures is of primary importance. On the other hand, high humidity causes excessive electrolyte swelling, change of its dimensions, and damage of the electrolyte−electrode contacts. A very intriguing scope in modern research on solid-state proton conductors is the development of materials exhibiting high conductivity in the dry state or at low relative humidity (RH) at medium temperature. Polymers containing N imidazole or imine rings protonated by H_3PO_4[3] and polyphosphazenes protonated by H_3PO_4 in combination with sulfonated organic polymers[4] have been synthesized at this purpose. The rationale for devising such materials is to have functional groups of different acid strengths in the electrolyte in order to enhance proton mobility in the solid state, without the need for high water amounts. Depending on the relative acid strength of the other functional groups, H_3PO_4 may act as proton donor and/or proton acceptor. A main drawback of these systems, however, is the possible loss of H_3PO_4 during operation of the conductivity cell. This problem might be circumvented by use of compounds having both the proton donor and the proton acceptor groups covalently bonded to the same molecule. To this purpose, several polyfunctional phosphonic acids have been synthesized and studied for their proton conductivity properties. These compounds contain either sulfonic acid functions[5−11] or imidazole rings[12,13] covalently

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* Corresponding author. E-mail: enzo.montoneri@unito.it.

† Dipartimento di Chimica Generale ed Organica Applicata, Università di Torino.

‡ NIS Centre of Excellence, Università di Torino.

§ Dipartimento di Chimica I.F.M, Università di Torino.

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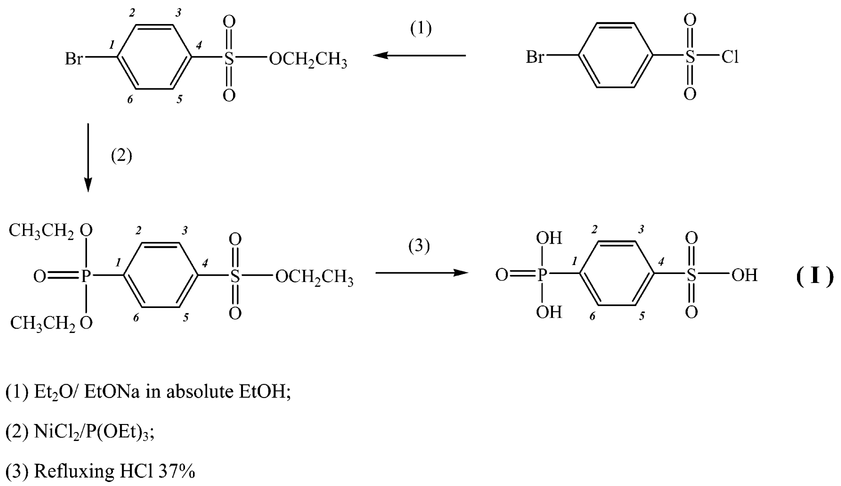
Scheme 1[a]



[a] (1) Et_2O/EtONa in absolute EtOH; (2) $NiCl_2/P(OEt)_3$; (3) refluxing HCl 37%.

bonded to the phosphonic acid molecule. Because the research on solid proton conductors is still quite active and its advancement depends on the availability of new precursors, we report herein after the synthesis of a new compound, 4-sulfophenylphosphonic acid (**I**). Because the primary requirement for assessing performance expectations for new polyfunctional acid precursors in fuel cell electrolytes is to understand the nature and stability of their H-bonding structure as a function of temperature, we have also characterized **I** in the solid state by NMR and IR spectroscopy, either in the synthesized hydrated form (**IA**) and in the anhydrous form (**IB**) obtained by heating **IA** at 190−210 °C.

Experimental Section

Reagents. All reagents were purchased from Sigma-Aldrich, unless otherwise indicated.

Physical Measurements. All ^1H, ^{13}C, and ^{31}P NMR solution ($CDCl_3$ or CD_3OD) spectra, except the ^{13}C NMR spectra of **I**, were recorded at room temperature on a JEOL Eclipse Plus 400 spectrometer operating at frequencies of 400, 100, and 162 MHz, respectively. The ^{13}C NMR spectra of **I** were recorded on a Bruker Avance 600 spectrometer operated at 151 MHz. All chemical shifts (δ) are reported in parts per million (ppm). For ^1H and ^{13}C spectra, δ values were measured by using the residual protic solvents as internal standard and then converting to values referred to internal TMS. For ^{31}P spectra, δ values are referred to external 85% H_3PO_4. Coupling constants (J) are reported in Hz. The solid state ^{13}C and ^{31}P CPMAS NMR spectra of **I** were recorded at room temperature on a JEOL GSX 270 spectrometer operating at 270 MHz for ^1H, 68 MHz for ^{13}C, and 109 MHz for ^{31}P. A standard cross-polarization pulse sequence was used with a contact time of 3.5 ms, a 90° pulse of 4.5 μs, recycle delays of 10 s and a number of 600−2000 transients. Cylindrical 5 mm o.d. zirconia rotors with sample volume of 120 μL were employed. A ^{13}C NQS (non-quaternary suppression) experiment was performed on **I**A and **I**B samples for the detection of quaternary C resonances and their J constants.

The GC MS spectra were acquired on a Thermo Finnigan Trace MS Plus spectrometer. The electrospray ionization (ESI) MS spectra were acquired on a Thermo Finnigan LCG Advantage Max instrument operating in the ESI mode under the following conditions: spray voltage 3.25 kV; capillary temperature 270 °C; capillary voltage −5 V; tube lens offset 0.

Thermal analyses were performed at 10 °C/min temperature program under a 20−60 mL/min N_2 flow by TA Instrument Hi-Res TGA 2950 and Perkin-Elmer Pyris 6 DSC instruments.

FT-IR spectra were obtained on samples as KBr tablets by a Bruker IFS 88 spectrometer with a DTGS detector operating under the following conditions: scanning numbers 128; resolution 4 cm^{-1}. The spectra were registered on the same sample, first at room temperature and then during heating under a vacuum for 1 h at 90 °C and 1 h at 210 °C.

Titration was carried out with a Crison Compact Titrator Version S + pH meter, using a Crison glass electrode calibrated with standard buffers at pH 7 and 4. The titration apparatus consisted of a water-jacketed 100 mL beaker fitted with a screw stopper, which allowed the insertion of a microburet, an electrode, and a temperature sensor. Water from a constant temperature bath maintained at 25 °C was circulated through the jacketed beaker. Product **I** (0.0152 g) was weighted into the titration vessel, 40 mL of deionized water was added, and the resulting solution was titrated with 0.0097 N aqueous NaOH. The titrant solution was standardized with an HCl solution that had been previously standardized with primary standard anhydrous sodium carbonate.

Synthesis of IA. The synthesis of IA was accomplished starting from commercial *p*-bromobenzenesulphonyl chloride in three steps according to reaction 1 in Scheme 1 reported in the Results and Discussion section.

Reaction 1 in Scheme 1 was carried out according to a previously reported procedure.[14] The sulfonyl chloride (0.23 mol) in an argon-blanketed three-necked flask was first dissolved in 176 mL of

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Table 1. ^{1}H, ^{13}C, and ^{31}P NMR Data for Hydrated (IA) and Anhydrous (IB) 4-sulfophenylphosphonic Acid and Their Precursors: Chemical Shift (δ, ppm), Signal Multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, tt = triplet of triplets, q = quartet, m = multiplet), Number of Atoms by Signal Integration (n H, n P, n C), Coupling Constants (J, Hz), Assignments, C and H Numbered as in Scheme 1

		$BrArSO_3Et$ in $CDCl_3$	$Et_2O_3PArSO_3Et$ in $CDCl_3$	**IA** or **IB** in CD_3OD	**IA** in solid state	**IB** in solid state
^{1}H	CH_3	δ 1.30, t, 3H, $^{3}J_{H-H}$ 7.2.	δ 1.30, q, 9H			
^{1}H	CH_2	δ 4.12, q, 2H, $^{3}J_{H-H}$ 7.2	δ 4.13, m, 6H			
^{1}H	H2,6	δ 7.68, d, 2H, $^{3}J_{H-H}$ 8.8	δ 7.96, d, 4H, $^{3}J_{H-H}$ 8.4	δ 7.85, dd, 2H, $^{3}J_{H-H}$ 8.4, $^{3}J_{P-H}$12.8		
^{1}H	H3,5	δ 7.7, d, 2H, $^{3}J_{H-H}$ 8.8	δ 7.96, d, 4H, $^{3}J_{H-H}$ 8.4	δ 7.92, dd, 2H, $^{3}J_{H-H}$ 8.4, $^{4}J_{P-H}$ 3.6		
^{13}C	CH_3	δ 14.81, s,1C	δ 14.81, s, 1C			
^{13}C	CH_3		δ 16.37, d, 2C, $^{3}J_{P-C}$ 6.1			
^{13}C	CH_2		δ 62.85, d, 2C, $^{2}J_{P-C}$ 5.3			
^{13}C	CH_2	δ 67.40, s,1C	δ 67.65, s, 1C			
^{13}C	C1	δ 128.93, s, 1C	δ 134.85, d, 1C, $^{1}J_{P-C}$ 187.6	δ 135.49, d, 1C, $^{1}J_{P-C}$186.3	δ 132.5, d, 1C, $^{1}J_{P-C}$ 186	δ 126.5, d, 1C, $^{1}J_{P-C}$ 184
^{13}C	C2,6	δ 132.64, s, 2C	δ 132.60, d, 2C, $^{2}J_{P-C}$ 10.0	δ 132.86, d, 2C, $^{2}J_{P-C}$ 10.7	δ 131.0, s, 1C and δ 135.6, s, 1C	δ 134.0, s, 2C
^{13}C	C3,5	δ 129.38, s, 2C	δ 127.68, d, 2C, $^{3}J_{P-C}$ 15.4	δ 127.73, d, 2C, $^{3}J_{P-C}$ 15.2	δ 125.1, s, 1C and δ 128.0, s, 1C	δ 127.9, s, 2C
^{13}C	C4	δ 135.55, s, 1C	δ 140.10, s, 1C	δ 150.17, s,1C	δ 144.8, s, 1C	δ 145.4, s, 1C
^{31}P			δ15.97, s, 1P	δ 15.58, tt, 1P, $^{3}J_{P-H}$ 12.9, $^{4}J_{P-H}$ 3.7	δ 13.00, s, 1P	δ 23.32, s, 1P

anhydrous Et_2O. The flask was cooled to 20 °C with a cold water bath. A solution of EtONa (0.23 mol) in 234 mL of absolute EtOH was added dropwise to the sulfonyl chloride solution over 5 h by means of a dropping funnel and a magnetic stirrer. The reaction was carried out until the solution was negative to the phenolphthalein test, which indicated that all EtONa was used up. At this point a milky suspension was present in the flask. Deionized water (220 mL) was then added and Et_2O was removed by means of a rotary evaporator. The aqueous phase was extracted with three 80 mL portions of $CHCl_3$. The combined $CHCl_3$ extracts were washed with two 180 mL portions of saturated sodium bicarbonate solution and then with 140 mL portions of deionized water until the pH of the collected washing was neutral. The organic solution was then dried with anhydrous sodium sulfate, filtered, evaporated at reduced pressure, and cooled in a freezer to yield a crystalline precipitate. This was suspended in cold petroleum ether, filtered, and air-dried to a white solid. The product was identified as *p*-bromobenzene(diethyl)sulfonate on the basis of the following analytical data: $R_f = 0.21$ (by TLC on F_{254} silica gel with 95:5 V/V petroleum ether:ethyl acetate); GC/MS *m*/*e* (% relative intensity) 266 (53), 264 (73), 238 (43), 236 (53), 221 (66), 219 (100), 174 (37), 172 (43), 158 (17), 157 (57), 156 (27), 155 (97), 145 (17), 143 (20), 141 (23), 93 (32), 77 (17), 76 (80), 75 (93), 74 (40), 65 (18), 50 (55); NMR data in Table 1. In the GC/MS spectrum, the parent (P) molecular peak at 265 was not observed, but the P + 1 peak at 266 was present. The NMR spectrum, however, was well consistent with the expected sulfonate. The product yield was 67 w/w % relatively to the starting sulfonyl chloride.

Reaction 2 in Scheme 1 was carried out in a 100 mL three-necked glass flask immersed in an oil heating bath kept at 180−195 °C. The flask was equipped with a dropping funnel, an inert gas inlet, and a distillation column kept at 60 °C by external heating, which terminated with a condenser and a receiving flask to collect all material boiling above 60 °C. The *p*-bromobenzene(diethyl)-sulfonate (0.053 mol), obtained in the previous step, was first melted at 180 °C in the reaction flask. Anhydrous $NiCl_2$ (0.0032 mol) was added to the molten sulfonate under magnetic stirring. $P(OEt)_3$ (0.069 mol) was added slowly over 6 h from the dropping funnel to the reaction flask. A slow argon flow was maintained throughout the apparatus during the reaction in order to ease the evolution of EtBr in the gas phase during the reaction. Indeed, this compound was continuously collected in the receiving flask during the reaction, which was assumed to be terminated when distillation of EtBr ceased. The reaction mixture was then distilled (51 °C) under a vacuum (3×10^{-2} Torr) to eliminate unreacted $P(OEt)_3$ and low-boiling byproducts as $EtPO_3Et_2$. The residue (a white solid suspended in a dense yellow liquid) was taken up with ethyl acetate and filtered. The solid residue was washed repeatedly with ethyl acetate until the color turned green. The anhydrous solution of ethyl acetate was evaporated under a vacuum to yield a green-yellow liquid, which was purified by flash chromatography on silica gel 60 (approximately 1 L) using pure ethyl acetate as eluent. The eluate was evaporated to yield the product, a colorless liquid which was identified as *p*-(diethoxyphosphonyl)benzene(diethyl) sulfonate on the basis of the following analytical data: $R_f = 0.59$ (TLC on F_{254} silica gel with ethyl acetate); GC/MS *m*/*e* (% relative intensity) 322 (8), 295 (11), 277 (7), 267 (30), 249 (20), 239 (12), 221 (48), 213 (34), 185 (37), 174 (19), 158 (100), 140 (46), 139 (46), 127 (21), 109 (20), 103 (32), 93 (21), 81 (21), 77 (74), 65 (67), 50 (10), 45 (13); NMR data in Table 1. It may be observed that, contrary to the case of the 4-bromobenzene(diethyl)sulfonate, in the GC/MS *m*/*e* spectrum of 4-(diethoxyphosphonyl)benzene-(diethyl) sulfonate, the parent molecular peak at 322 *m*/*e* was observed. Also, the NMR data in Table 1 show a few distinguishing features for the 4-(diethoxyphosphonyl)benzene(diethyl) sulfonate: (i) the ^{1}H CH_3 and CH_2 signal multiplicity is increased relative to that found for the bromosulfonate because of coupling of H with P; (ii) no separate signals could be picked out for the H2,6 or H3,5 protons, but all four protons are shifted downfield relative to the same signal in the bromosulfonate because of the replacement of Br with the stronger electron withdrawing PO_3Et_2 group; (iii) for the same reason, the C1 and C4 signals are shifted downfield relatively to the same signals in the bromosulfonate; (iv) well distinct signals are observed for the ethyl C atoms bonded to the sulfonate and phosphonate functions. These features are well consistent with the chemical identity of the 4-(diethoxyphosphonyl)-benzene(diethyl) sulfonate. This product was obtained in 61 w/w % yield relative to the starting 4-bromobenzene(diethyl)sulfonate.

Reaction 3 in Scheme 1 was carried out in a 25 mL reaction flask equipped with a reflux column. Concentrated HCl (9 mL) was added to 3.53 g (0.011 mol) p-(diethoxyphosphonyl)benzene-(diethyl) sulfonate, obtained as above. The two immiscible reagents gave a two-liquid phases mixture which was refluxed 24 h to yield a homogeneous yellow liquid phase. The mixture was evaporated in a vacuum until a solid started to precipitate from a dark yellow solution. The solid product was filtered, vacuum-dried, and stored over P_2O_5 and KOH pellets. The product was identified as

4-sulfophenylphosphonic acid (**I**) on the basis of the following analytical data: GC/MS *m*/*e* (% relative intensity) 238 (100) for the parent molecular peak, and 236 (99), 225 (22), 219 (18), 203 (19), 185 (27), 174 (89), 172 (96), 157 (62), 155 (60), 145 (40), 143 (40), 128 (21), 123 (35), 119 (27), 105 (20), 93 (37), 77 (27), 76 (67), 75 (88), 74 (50), 65 (49), 55 (32), 50 (61), 43(54) for the fragmentation pattern; negative ESI/MS *m*/*e* [ions] 237 $[H_2(O_3PArSO_3)]^-$, 259 $[HNa(O_3PArSO_3)]^-$, and 118 $[H(O_3PArSO_3)]^{2-}$; NMR data in CD_3OD in Table 1; absorption frequencies in the FT-IR (KBr pellet) spectrum as reported in the Results and Discussion section. The negative ESI/MS were acquired with several solutions of different compositions in water, methanol, and water/methanol mixtures with and without the addition of NaOH as discussed in the Results and Discussion section. The product yield was nearly quantitative relative to the starting *p*-(diethoxyphosphonyl)benzene(diethyl) sulfonate.

Results and Discussion

Synthesis and Characterization of I in Solution. Basic reactions to obtain phosphonic and sulfonic acids are the phosphonation and the sulfonation of a suitable organic precursor. The synthesis of products containing both SO_3H and PO_3H_2 functional groups requires the design of a proper reaction sequence. Previous sulfophenylphosphonic acids, i.e., benzenephosphono-3-sulfonic acid (**II**)[6] or benzenephosphono-3,5-disulfonic acid (**III**)[8] and biphenyl-4,4′-diphosphono-2,6,2′-trisulphonic acid (**IV**),[10] have been prepared by sulfonation of the parent phosphonic acid. In these cases, because of the electron withdrawing effect of the PO_3H_2, the sulfonation of the benzenephosphonic acid occurs only in the ring meta-positions. The synthesis of **I** therefore required a reverse approach, i.e., the phosphonation of the sulfonate derivative (reaction 1 in Scheme 1). Although the reaction of arylbomides and $P(OEt)_3$ in the presence of $NiCl_2$ catalyst is well-known as the Tavs reaction,[14] the phosphonation of *p*-bromobenzene(diethyl)sulfonate (reaction 2 in Scheme 1) is a new reaction never reported previously. This reaction was performed by dropping $P(OEt)_3$ into the *p*-bromobenzene(diethyl)sulfonate containing the catalyst because the required temperature was higher than the boiling point of $P(OEt)_3$. In this fashion, a temperature of 180−195 °C was guaranteed in the reaction vessel by slow addition of the phosphate and continuous distillation of EtBr from the reaction solution. Accumulation of unreacted $P(OEt)_3$ in the reaction vessel would have lowered the reaction temperature because of the refluxing low-boiling reagent. In our case, a matter of concern was the chemical stability of the *p*-bromobenzene(diethyl)sulfonate under the experimental conditions. Indeed, the reaction required 6 h at the above temperature for its completion (no more evolution of EtBr). The results however showed that for *p*-bromobenzene(diethyl)sulfonate, the reaction occurs satisfactorily, and hydrolysis of *p*-(diethoxyphosphonyl)benzene(diethyl)sulfonate easily yielded the desired 4-sulfophenylphosphonic acid **I.** The overall product yield was 40 w/w % relative to the starting sulfonyl chloride.

Product **I** is soluble in water, methanol, and dimethylsulfoxide. Its structure was well-confirmed by NMR and mass spectra and potentiometric titration data. The ^1H, ^{13}C, and ^{31}P NMR spectra in CD_3OD contained, respectively, two signals of equal intensity, four signals, and one signal, which are assigned as reported in Table 1. The assignments of the resonance signals were made on the basis of J_{P-H} and J_{P-C} values that are consistent with previously reported values for compounds **II**,[6] **III**,[8] and **IV.**[10] The observed chemical shifts, in either the ^1H or ^{13}C spectrum, point out the stronger electron-attracting effect of the SO_3H group compared to that of PO_3H_2. Indeed, the δ values for H3 and H5 protons are higher than those for H2 and H6 and the δ value for C4 is higher than for C1. These effects have been observed also in the spectra of compounds **II**,[6] **III**,[8] and **IV.**[10] The ^{31}P δ value of product I in CD_3OD (15.6 ppm in Table 1) is in the range of the values reported for benzenephosphonic acid (17.5 ppm)[6] and the aromatic sulfophosphonic acids **II** (14.9 ppm),[6] **III** (12.3 ppm),[8] and **IV** (9.9−12 ppm).[10]

Titration of the aqueous solution of product **I** with sodium hydroxide gave rise to two inflection points in a 2:1 equiv/equiv ratio, the first at pH 5.09 assigned to the sulfonic acid proton and the first phosphonic acid proton, and the other at pH 8.90 assigned to the second weaker phosphonic acid proton. The total product acid equivalent content was 11.1 mequiv/g against the 12.6 mequiv/g theoretical value for the anhydrous sulfophenylphosphonic acid. On the basis of these data, it was calculated that the reaction product **I** contained about 12% H_2O. This figure was consistent with the results of the TGA analysis discussed below, which yielded 12.7% H_2O content in product **I**. The data suggest that **I** is the hydrated 4-sulfophenylphosphonic acid, $H_2O_3PC_6H_4SO_3H_2 \cdot 2\,H_2O$ (**IA**).

The product molecular mass was confirmed by the GC mass spectrum (see Experimental Section) showing the parent $H_2O_3PC_6H_4SO_3H_2$ molecular peak, which was also the base peak, at 238 *m*/*e*. Further definitive evidence was obtained by electrospray ionization (ESI) mass spectrometry. In the ESI technique, polar molecules are ionized prior to acceleration into mass spectrometers. The process involves the formation of small, highly charged droplets that undergo solvent evaporation with subsequent ion transfer to the mass spectrometer. Almost any molecule carrying a net charge in solution may transfer to the gas phase.[16] As **I** has three acid protons, it could yield in principle the singly, doubly, and triply charged ions $H_2O_3PArSO_3^-$, $[HO_3PArSO_3]^{2-}$, and $[O_3PArSO_3]^{3-}$. However, in the ESI mass technique, a delicate balance must be maintained between two opposing factors, i.e., the total number of ions must be low enough to avoid space charge effects but high enough to allow detection of individual compounds.[17] Several solutions of different compositions in water, methanol, and water/methanol mixtures, with and without the addition of NaOH, were therefore used to acquire ESI mass spectra. Three main peaks were observed in these experiments, i.e., at 237 *m*/*e* for $[H_2(O_3PArSO_3)]^-$, 118 *m*/*e* for $[H(O_3PArSO_3)]^{2-}$, and at 259 *m*/*e* for $[HNa(O_3PArSO_3)]^-$. The spectrum acquired with the fully titrated product $Na_3(O_3PArSO_3)$ at 4 10^{-6} mol/L in

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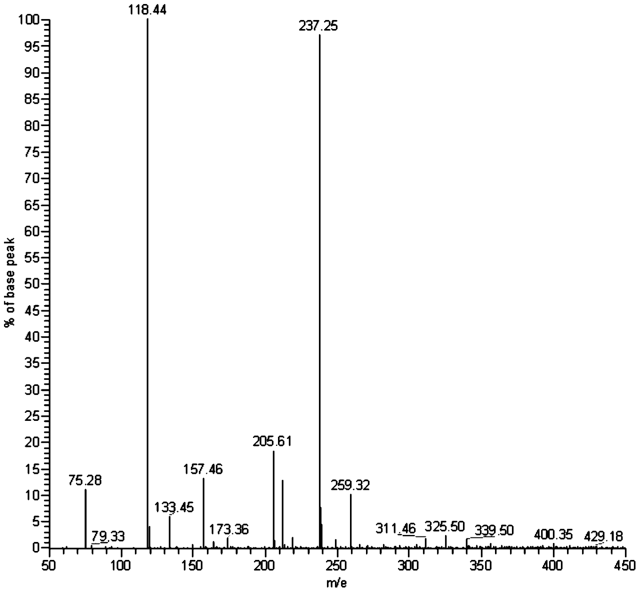

Figure 1. Negative ion ESI mass spectrum of 4-sulfophenylphosphonic acid acquired with a $Na_3(O_3PArSO_3)$ 4×10^{-6} mol/L H_2O/MeOH solution containing 0.4% V/V H_2O.

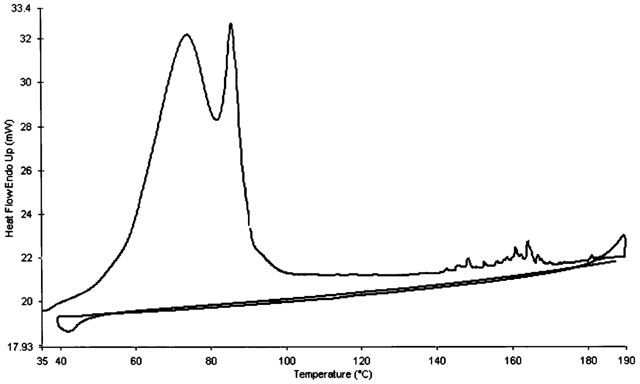

Figure 2. DSC scan of 4-sulfophenylphosphonic acid.

H_2O/MeOH containing 0.4 V/V % H_2O is reported in Figure 1. The relative ratios of the above three peaks were found to depend on the solution composition used for the acquisition of the ESI spectrum. Product **I** in MeOH at 4×10^{-5} mol/L concentration gave only the 237 *m*/*e* peak with 100% intensity. The maximum 100% intensity of the 118 *m*/*e* peak was reached under the conditions reported for the spectrum in Figure 1 and a maximum 26% intensity of the 259 *m*/*e* peak was reached with $Na_3(O_3PArSO_3)$ at 1×10^{-5} mol/L in H_2O/MeOH containing 0.99 V/V % H_2O. The 78 *m*/*e* peak for the triply charged $[O_3PArSO_3]^{3-}$ ion was never observed. Because the data well-confirmed the molecular formula of our product, no further study of the mass spectra beyond our scopes was performed.

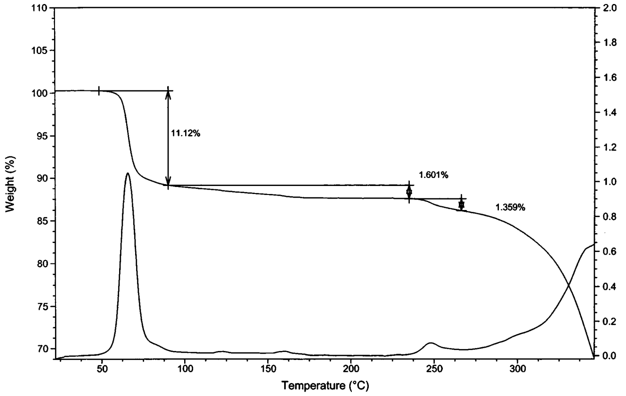

Figure 3. TGA scan of 4-sulfophenylphosphonic acid.

Characterization of IA in the Solid State. *Thermal Analyses.* Support of titration data pointing out the molecular formula **IA** for 4-sulfophenylphosphonic acid, as synthesized, came from thermal analyses. The DSC scan (Figure 2) exhibited two heat-absorption stages: the former over the 25−100 °C temperature range was relatively intense and broad, the latter in the 140−190 °C range was smaller. These endothermic processes are all likely to be associated with the evaporation of hydration water present in **IA** and not to the product melting. Indeed, no peaks were observed upon cooling from 190 °C to room temperature and heating back again to 190 °C. From the TGA scan in Figure 3, the water loss in the 25−230 °C range is shown to amount to 12.7% of the product weight. The weight loss corresponds to the loss of about two H_2O moles per mole of anhydrous acid (theoretic value: 13.1%). These water molecules are likely to be associated with the two acid functional groups, i.e., $PO_3H_2{\cdot}H_2O$ and $SO_3H{\cdot}H_2O$. The water loss occurs over a rather wide temperature range, as already observed for other sulfonic and sulfophosphonic acids.[3,5−11] This behavior is likely to arise from the water protonation equilibria by the two acid groups having different strengths (reactions 1 and 2).

$$PO_3H_2 + H_2O \rightleftharpoons PO_3H^{-}H_3O^{+} \qquad (1)$$

$$SO_3H + H_2O \rightleftharpoons SO_3H^{-}H_3O^{+} \qquad (2)$$

Indeed, another work reports that the molar enthalpy of vaporization of one water mole protonated by the SO_3H group as in reaction 2 is significantly higher than that of unprotonated water.[18]

FT-IR Spectroscopy. The FT-IR spectrum of compound **IA** is reported in Figures 4 and 5. The following absorption frequency (ν, cm^{-1}) assignments are given by comparison with the data previously reported for **II**[6] and other phosphonic acids:[3,12] ν (cm^{-1}) 3408 O−H stretching; 3082 and 3028 ring C−H stretching; 2733, 2355, 2323 and 2258 PO−H and/or SO−H stretching; 1645 O−H bending, 1391 aromatic C−C stretching, 1300−1100 P=O and/or S=O stretching, 1100−900 P−O and/or S−O stretching, 833 C−H out-of-plane bending. These data are well-consistent with compound **IA**. By comparison with compound **II**,[6] the most significant distinguishing spectral features appear the absorption bands in the 850−680 cm^{-1} frequency range, which rise from the ring C−H out-of-plane vibration. Compound **IA** exhibits a strong sharp band at 833 cm^{-1}, whereas compound **II** yields two bands at 800 and 680 cm^{-1}.[6] According to literature,[19] these features are, respectively, consistent with a 1,4- and a 1,3-disubstituted benzene ring, as indeed occurs in **IA** and **II**, respectively. In addition to being consistent with the substitution pattern in **IA**, the spectrum in Figure 1 provides

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(19) Silverstein, R. M.; Bassler, G. C.; Morril, C. T. *Spectrometric Identification of Organic Compounds*, 5th ed.; John Wiley & Sons: New York, 1991.

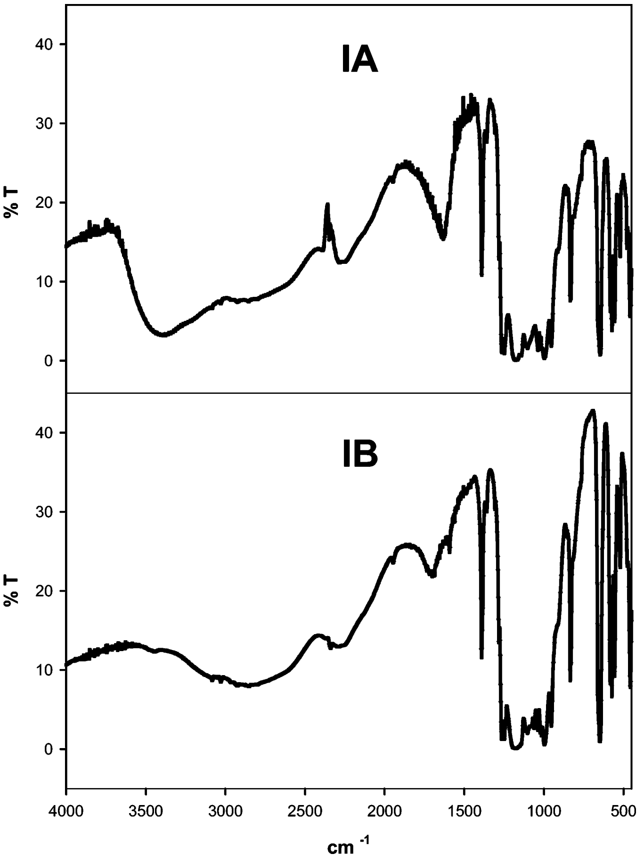

Figure 4. FT-IR spectra of hydrated (**IA**) and anhydrous (**IB**) 4-sulfophenylphosphonic acid in the 450−4000 cm^{-1} range.

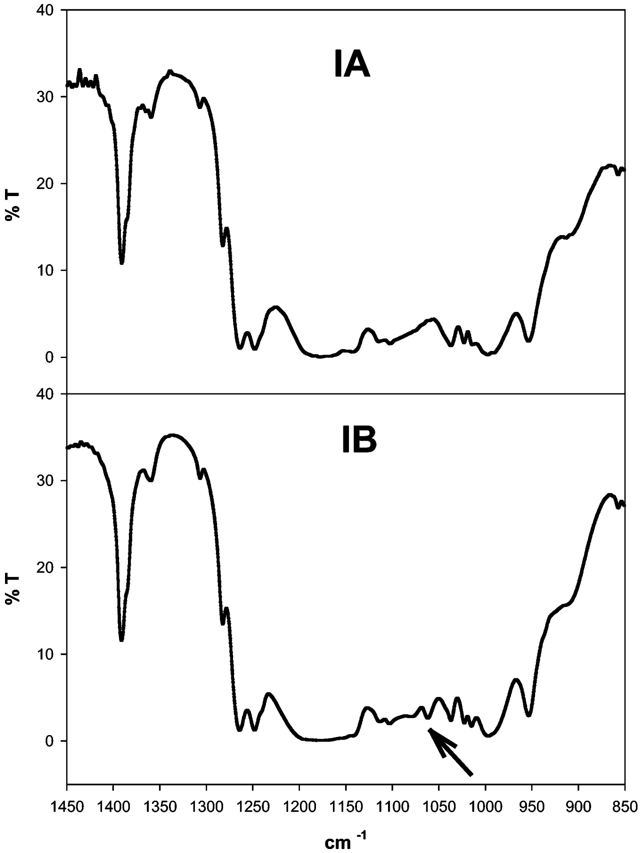

Figure 5. Expanded FT-IR spectra of hydrated (**IA**) and anhydrous (**IB**) 4-sulfophenylphosphonic acid in the 850−1450 cm^{-1}range.

important information about the structure of this compound in the solid state. The presence of water is confirmed by the O−H stretching and bending bands, respectively falling at 3383 and 1616 cm^{-1}. The band pattern in the 2800−2000 cm^{-1} range is typical of acid material and may yield useful hints related to structural H-bonds and proton conductivity.[1] Absorption bands in this frequency range arise from bond stretching vibrations of O−H and N−H functional groups engaged in H-bonded chains such as O···H···O and/or N···H···O. In such systems, proton conductivity is expected on the basis of the proton transport through H-bonds. Increasing band splitting in the above IR frequency range and shifting of the band pattern to lower frequency is expected to occur as the energy barrier between the potential minima and the distance between proton acceptor sites in the H-bonded system decrease. Absorption frequency values $\leq$2700 cm^{-1} indicate strong H bonds (with O···O distance $\leq$2.60 Å), and lower frequency values indicate shorter O···O distance.[3] In the case of compound **IA**, the FT-IR spectrum shows two main broad bands centered at 2726 and 2260 cm^{-1}, with the second one having a shoulder doublet at 2342 cm^{-1}. These absorption frequency values are consistent with rather short O···O distances, probably in the 2.4−2.6 Å range as reported for monetite and for 3-fluoro,6-sulfobenzylphosphonic acid $HO_3S-Ar(F)-CH_2-PO_3H_2\cdot H_2O$ (**VI**).[3] These rather short O···O distances have been shown to be possible in **VI**, but not in the 4-fluoro,3-sulfobenzylphosphonic acid isomer, because in the former, a complete intramolecular proton transfer from the stronger SO_3H group to the weaker PO_3H_2 group helps the formation of a stable eight-member ring enclosing the S−O2−H4−O4−P−C7−C1−C2 atoms, with the water molecule lying out of the ring and partially protonated by the $PO_3H_3^+$ group. For this compound, several O···distances have been found at the 2.42 and 2.64−2.69 Å level. Whereas the longer O···O distances have been proven to involve the O atoms in the above eight-member ring, the unusually short 2.42 Å distance has been attributed to the O−H···O interaction between the protonated phosphonic acid group and the water molecule, in which partial proton transfer from the former to the latter is evident. By comparison, for compound **IA**, intramolecular protonation of the phosphonic acid by the sulfonic acid group is not possible. However. **IA** has two water molecules, and water protonation may occur both by the SO_3H and the PO_3H_2 groups (reactions 3−5).

$$Ar-SO_3^{-}H_3O^{+}\cdots O{=}P(Ar)(OH)_2\cdots OH_2 \rightleftharpoons Ar-SO_3^{-}H_3O^{+}\cdots O{=}P(Ar)(OH)-O^{-}\cdots H_3O^{+} \quad (3)$$

$$Ar-SO_3^{-}H_3O^{+}\cdots O{=}P(Ar)(OH)_2\cdots OH_2 \rightleftharpoons Ar-SO_3^{-}H_2O\cdots[HO-P(Ar)(OH)_2]^{+}\cdots OH_2 \quad (4)$$

$$Ar-SO_3^{-}H_2O\cdots[HO-P(Ar)(OH)_2]^{+}\cdots OH_2 \rightleftharpoons Ar-SO_3^{-}H_2O\cdots(HO)_2P(Ar){=}O\cdots H_3O^{+} \quad (5)$$

As these 1,4 disubstituted molecules are likely to yield polymeric structures held by intermolecular ionic and H-bonds, a wide range of O···O distances is possible.[3]

NMR Spectroscopy. The ^{13}C NMR spectrum of solid **IA** (Figure 6) shows relevant differences compared to the solution spectrum (Table 1). In the former, the small $^{3}J_{P-C}$

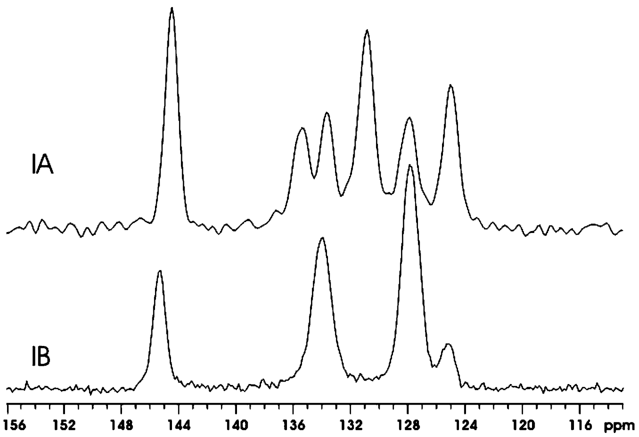

Figure 6. Solid state ^{13}C NMR spectra of hydrated (**IA**) and anhydrous (**IB**) 4-sulfophenylphosphonic acid.

and $^{2}J_{P-C}$ coupling constants cannot be measured because of line broadening, whereas the larger $^{1}J_{P-C}$ constant (186 Hz) could be measured. The two signals at 133.9 and 131.0 were, indeed, found to compose the expected doublet for the C1 resonance, which was calculated to be centered at 132.5 ppm. The excess signal at 131 ppm and the signal at 134.7 ppm were assigned to the C2 and C6 nuclei on the basis of the proximity of these chemical shifts with those assigned to the same C atoms in the solution spectrum. By the same criterion, the other signals were assigned. The most significant difference between the solid-state spectrum (Figure 6, **IA**) and the solution spectrum (Table 1) appears to be the signal pattern for the protonated C nuclei. Whereas two signals are observed in the solution spectra, one for the C2 and C6 nuclei and one for the C3 and C5 nuclei, in the solid state, these nuclei give four signals, one for each of the 4 C nuclei. This behavior is well-known in the solid state, where atoms symmetric in solution are not equivalent in the crystal, leading to different signals. A similar situation was reported for compound **IV**[10] in solution, where the C2 and C6 atoms bonded to the SO_3H groups in the symmetrically substituted ring were found to give two different signals, respectively, at 141. 4 and 142.8 ppm, whereas in **III**, the two C's substituted by SO_3H (C3 and C5) give one signal at 143.7 ppm. For **IV**, the inequality of the C2 and C6 δ values was explained with one of the two SO_3H groups in the symmetrically substituted rings, i.e., the SO_3H group bonded at the C2 atom, which was H-bonded to the third SO_3H group bonded at the second ring C2′ atom. In the case of solid **IA**, the observed inequalities of the C2−C6 and C3−C5 nuclei are likely to reflect the reduced molecular mobility in the solid state, where the ionic functional groups are frozen in a particular conformation that does not bring the same amount of magnetic shielding on each of the two ortho C atoms pairs. Furthermore, in this conformation, the electron-withdrawing effect of the two polar groups seems reduced, as may be observed from the overall upfield shift of the ring C and the P resonances relative to the solution resonances.

Characterization of Anhydrous 4-Sulfophenylphosphonic Acid (IB) in the Solid State. *NMR Spectroscopy.* The thermal analyses data discussed above indicated that **IA** converts to the anhydrous compound $H_2O_3PC_6H_4SO_3H_2$ (**IB**) upon heating to 190−230 °C. To further support the interpretation of the TGA and DSC scans, we recored the NMR spectra of the product recovered from the above heat treatment. The solution ^{1}H, ^{13}C, and ^{31}P NMR spectra of the thermally aged product were identical to the solution spectra of **IA**, thus demonstrating that no significant product degradation occurred in the former by the heat treatment. The solid state ^{13}C and ^{31}P NMR spectra of the thermally aged product were, however, significantly different from the solid-state spectra of **IA**, as may be readily visualized in Figure 6. Figure 6, **IB**, shows four main signals, i.e., at 145.4 ppm assigned to C4, 134.0 ppm assigned to C2 and C6, and 127.9 and 125.1 ppm. The resonance signal of the C1 atom is a doublet of which only the signal at 125.1 ppm can be selectively identified, whereas the other is included in the broad strong resonance band centered at 127.9 ppm. From this pattern and on the basis of the $^{1}J_{P-C}$ value found in the solution and solid-state spectra of **IA**, we calculated the chemical shift of the C1 signal for **IB** to be 126.5 ppm. The excess signal at 127.9 ppm, above which the intensity could be expected for the C1 signal, was assigned to the C3 and C5 nuclei on the basis of proximity of the chemical shift with the values found for these C atoms in solid **IA**. By the same criterion, the other signals were assigned. Compared to the spectrum of **IA**, Figure 6, **IB**, shows that in the anhydrous compound **IB**, the inequalities of the C atoms ortho to the polar groups are not observed and all signals have slightly moved downfield except for the C1 signal, which is found strongly shifted toward lower frequencies. Concurrently, the ^{31}P signal in the anhydrous compound **IB** appears strongly shifted at higher frequencies (Table 1). The data suggest that a further conformational change occurs in **IB** compared to **IA.** Particularly significant seems the higher-frequency shift of the P atom in **IB**. Previous data obtained for benzenephosphonic acid[6] and for the monosulfonated (**II**)[6] and disulfonated (**III**)[8] derivatives at the ring meta-C atoms report a continuous low-frequency shift of the P atom from 17.5 ppm in benzenephosphonic acid to 14.9 ppm in **II** and 12.3 ppm in **III**. This trends seems to be related to the increasing electron-withdrawing power of the benzene ring, which presumably causes increasing deprotonation due to ionization of the PO_3H_2 group. A similar trend was observed in the case of 1,10-(1-H-imidazol-5-yl)decanephosphonic acid,[12] where the ^{31}P δ value for the compound in the solid state shifts from 43.8 to 24.9 by the change in the PO_3H_2 group to the PO_3Na_2 form. On the basis of these data, the ^{31}P δ value of 13 ppm observed for **IA** suggests that the PO_3 group in this compound is considerably deprotonated according to reactions 6−8. On the contrary, the strong high-frequency shift of the P atom to 23.3 ppm in **IB** points out that, in the absence of water, deprotonation of the PO_3H_2 group to the phosphonate anion is strongly hindered. Under these circumstances, protonation of the PO_3H_2 group to $PO_3H_3^+$ seems more likely. The spectral changes may be well-consistent with the structural change depicted in reaction 6

$$\{SO_3^-[H(H_2O)_2H_2O_3P]^+Ar\}_n \rightleftharpoons \{SO_3^-[H_3O_3P]^+Ar\}_n + 2nH_2O \quad (6)$$

which occurs upon dehydration of **IA** to **IB.**

FT-IR Spectroscopy. To support reaction 6, we recored FT-IR spectra for the synthesized product **IA** in the same temperature range at which the TGA and DSC scans indicated that the product dehydration occurs. Figures 4 and 5 report the spectrum of **IA** recorded at room temperature and the spectrum recorded at the final temperature of 210 °C, which we assign to **IB**. For our discussion, we consider the spectral region divided in two main ranges, respectively, above and below 1600 cm^{-1}, with the former containing O−H stretching and bending bands and the latter containing bands that arise from the aromatic ring and the SO and PO bonds. Spectral changes in the region above 1600 cm^{-1} are readily evident from Figure 4. The spectrum of **IB**, compared to the spectrum of **IA**, shows a strong decrease in the O−H absorption bands at 3383 and 1616 cm^{-1}, whereas the bands in the 2800−2000 cm^{-1} range seem not much changed both in position and relative intensity. Given the absence of water in **IB** at 210 °C, as suggested by the TGA-DSC measurements, the bands in the 2800−2000 cm^{-1} range for this compound are likely to arise almost exclusively by the O···H···O bond network in which O and H atoms of the two acid functional groups are involved, without significant participation of water molecules. It may also be observed that in this situation, the shoulder doublet at 2342 cm^{-1} is more evident. Spectral changes in the region below 1600 cm^{-1} are less readily observed because of overlapping of the strong absorptions arising from S═O and P═O stretching vibrations in the 1300−1100 cm^{-1} range and of the S−O and P−O stretching vibrations in the 1100−900 cm^{-1} range. However, from the expanded spectral region (Figure 5), a band at 1061 cm^{-1} may be picked out for **IB** and not for **IA**. Previous work has reported shifting of P═O absorption bands to lower frequency (i.e., from 1214 to 1078 cm^{-1}) because of the change in the PO_3H_2 group to the sodium salt form.[12] In the specific case of this work, the band at 1061 cm^{-1} observed for **IB** is likely consistent with lengthening of the PO bond distance in **IB** compared to **IA**. Given the results of the ^{31}P NMR spectra in Table 1, the observed change of bond length seems caused by the protonation of the phosphonic acid group to $P(OH)_3^+$ by the SO_3H group occurring in the anhydrous compound **IB**. As neither **IA** nor **IB** could be obtained as single crystals, solid state ^1H NMR spectroscopy[13] seems the only mean to assess the above proposed interpretation of our experimental data and to determine the effects of the **IA-IB** structural change on proton mobility.

Conclusions and Future Perspectives

A new acid organosulphur phosphorus compound, 4-sulfophenylphosphonic acid, has been synthesized by the Tavs reaction starting from 4-bromobenzene(diethyl)sulfonate. This synthetic route was necessary, because sulfonation of benzenephosphonic acid yields only the meta-substituted derivatives. Investigation of the solid-state structure of this compound at variable temperature indicates that the synthesized hydrated product (**IA**) yields the anhydrous compound **IB** at 190−230 °C. The IR and NMR data consistently indicate that in the above 4-sulfophenylphosphonic acid intermolecular H-bonding between the sulfonic and the phosphonic acid groups, and/or protonation of the phosphonic acid by the sulfonic acid group, may occur depending on the presence of water. These interactions are very important in determining proton conductivity in relation to the possible use of **IA** as solid electrolyte component in fuel cells operating at medium temperature. Unfortunately, neither **IA** nor **IB** could be obtained as single crystals, and therefore assessment of the proposed structures by X-ray diffraction was not possible. In a similar case, presented by 1,10-(1-H-imidazol-5-yl)decanephosphonic acid, solid state ^1H NMR spectroscopy[13] sufficed to investigate more deeply the H-bonding interactions proposed by FT-IR and ^{13}C and ^{31}P NMR spectroscopy[12] and to obtain more specific evidence of proton mobility in the solid state. The data in this work certainly offer scope for further investigation in this direction.

As in the introduction section of this work specific reference has been made to the development of solid electrolytes for fuel cell operation at low humidity, we should stress now the point that such materials, in addition to high proton conductivity at low humidity, must have a relatively large number of other requirements, such as mechanical flexibility; chemical, physical and mechanical stability; and low permeability to the feed gases. Small molecules, such as 4-sulfophenylphosphonic, obviously cannot meet all these requirements and must be looked upon as precursors or doping agents of solid polymer electrolytes (SPE). In particular, a new trend for the improvement of the conductivity properties of SPE at low humidity, such as the perfluorinated alkyl sulfonic acid Nafion polymer made by DuPont, is the addition of stable organic acids that could perform as proton carriers in place of water.[20] As 4-sulfophenylphosphonic seems to fall in this category of compounds, assessment of its proton mobility by ^1H NMR spectroscopy coupled with proton conductivity measurements at variable temperature and humidity will allow us to assess its full potential as doping agent of proton-conducting solid polymer electrolytes to operate at low humidity.

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