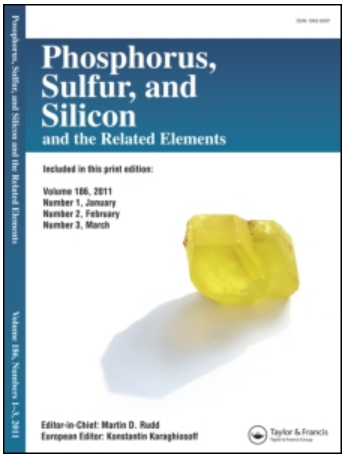

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1,10-(1-H-IMIDAZOL-5-YL)DECANEPHOSPHONIC ACID: A NEW COMPOUND WITH BASIC AND ACIDIC SITES TO FABRICATE PROTON-CONDUCTING SOLID ELECTROLYTES

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1,10-(1-H-IMIDAZOL-5-YL)DECANEPHOSPHONIC ACID: A NEW COMPOUND WITH BASIC AND ACIDIC SITES TO FABRICATE PROTON-CONDUCTING SOLID ELECTROLYTES

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2-(tert-butyldimethylsilyl)-5-(10-bromodecyl)-1-(N,N-dimethylsulfamoyl)-imidazole and $NaPO_3Et_2$ react at room temperature to yield the corresponding imidazole diethyl phosphonate, which when refluxed with concentrated HBr yields 1,10-(1-H-imidazol-5-yl)decanephosphonic acid hydrobromide (VI). Compound VI titrated with the required mole equivalents of NaOH yields 1,10-(1-H-imidazol-5-yl)decanephosphonic acid (VII) and 1,10-(1-H-imidazol-5-yl)decane (sodium)phosphonates (VIII). CP-MAS NMR (^{13}C, ^{31}P, and ^{15}N) and IR spectroscopy indicate that only compound VII is likely to yield a polymeric structure where each phosphonic acid group is H bonded to the imidazole ring of the same molecule and to the imidazole ring of another molecule. For this reason, solid-state proton conductivity in VII is likely to be favored.

Keywords: 1,10-(1-H-imidazol-5-yl)decanephosphonic acid; imidazole; phosphonic acids; solid proton conductors

Several phosphonic acids have been synthesized previously[1] and studied for their proton conductivity properties.[2–4] These compounds contain sulphonic acid groups and/or fluorine atoms in the alkyl or aryl C chain to increase proton conductivity. Although several materials fabricated with the sulpho-phosphonic acids have been shown to have

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high proton conductivity in the solid state, their performance requires high relative humidity (RH). H-bonded water molecules between acid functions are necessary to provide the proton transfer path.

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 RH at medium temperature. Polymers containing N imidazole[5–8] or imine[9] rings protonated by H_3PO_4 where the proton may transfer through phosphate anions, have been suggested possible proton conductors under these conditions. A main drawback of these systems is possible loss of H_3PO_4 during operation of the conductivity cell.

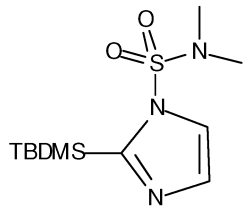
It seemed to us that the problem of electrolyte loss during operation of proton conductivity cells might have been circumvented by using a compound having either the proton donor and the proton acceptor groups covalently bonded in the same molecule. We therefore undertook the synthesis of 1,10-(1-H-imidazol-5-yl)decanephosphonic acid. Procedures for the synthesis of several (ω-substituted alkyl)-1-H-imidazoles are reported in literature.[10,11] These compounds have interest in medicinal chemistry for their potential as histamine-receptor antagonists. However, no alkyl imidazole substituted with a PO_3H_2 group seems to have been synthesized so far. We wish to report now the synthesis and characterization of such compound.

RESULTS AND DISCUSSION

Product Synthesis

Established pathways for the synthesis of phosphonic acids involve the reaction of a bromo-substituted organic C in refluxing excess $P(OEt)_3$ or with equimolar $NaPO_3Et_2$ at room temperature, followed by hydrolysis of the reaction product to the free acid. For our needs, no 5-[ω-bromo alkyl]-1-H-imidazole was commercially available; this reagent had therefore to be specifically synthesized. The synthesis of the 5-[10-bromo decyl]-1-H-imidazole, coupled with the phosphonation reaction and isolation of the free phosphonic acid, involved several steps and required the choice of alternatives. In fact, according to the literature, the synthesis a 5-[ω-haloalkyl]-1-H-imidazole could be performed in two ways[10,11] via 2-(tert-butyldimethylsilyl)-1-(N,N-dimethylsulfamoyl)-imidazole (I).

This intermediate compound is necessary since the substitution of H at position 5 of the imidazole ring by alkylation requires adequate protection of the ring positions 1 and 2 by the N,N-dimethylsulfamoyl and by the tert-butyldimethylsilyl (TBDMS) groups, respectively.



(I)

According to Vollinga et al.,[10] 1-(N,N-dimethylsulfamoyl)imidazole in THF is first reacted with nearly equimolar amount of butyl lithium (BuLi) in hexane at -70°C, and tert-butyldimesilyl chloride in THF is added afterwards to obtain I. The reaction mixture containing this compound is then reacted with BuLi in hexane without any prior work up to obtain the Li derivative of I [Im′-Li, Im′ = 2-(tert-butyldimethylsilyl)-1-(N,N-dimethylsulfamoyl)-imidazol-5-yl)], and then with 1-chloro-10-iododecane, to yield 2-(tert-butyldimethylsilyl)-5-(10-chlorodecyl)-1-(N,N-dimethylsulfamoyl)-imidazole (II), according to the reaction

$$\text{Im}'\text{-Li} + \text{I-CH}_2(\text{CH}_2)_8\text{CH}_2\text{Cl} \rightarrow \underset{\text{(II)}}{\text{Im}'\text{-CH}_2(\text{CH}_2)_8\text{CH}_2\text{Cl}} + \text{LiI} \quad (1)$$

According to Lee et al.,[11] I is synthesized as above and isolated. The product in THF is reacted with equimolar amount of BuLi in hexane. The reaction mixture containing Im′-Li is added to a THF solution containing a three-fold mole excess of the 1,ω-dibromoalcane to yield 2-(tert-butyldimethylsilyl)-5-(ω-bromoalkyl)-1-(N,N-dimethylsulfamoyl)-imidazole (III),

$$\text{Im}'\text{-Li} + \text{Br-CH}_2(\text{CH}_2)_n\text{CH}_2\text{Br} \rightarrow \underset{\text{(III)}}{\text{Im}'\text{-CH}_2(\text{CH}_2)_n\text{CH}_2\text{Br}} + \text{LiBr} \quad (2)$$

This procedure, however, appears to be reported only for the synthesis of compounds with relatively short aliphatic C chain (i.e., n = 1–4 in III).

For our scope, the 5-[10-bromodecyl]-imidazole derivative (i.e., III for n = 8) was more suitable than the chlorodecyl derivative II due to the higher reactivity of the bromo-substituent in the next phosphonation reaction. Although the synthesis by Vollinga et al.[10] had the advantage of not requiring the isolation of I, this feature would have been offset by the need to perform an additional step[12] to convert the chlorodecyl derivative (II) into the bromodecylderivative (III for n = 8) and also by the use of the expensive 1-chloro-10-iododecane reagent to perform the reaction in Equation (1).

For our scope we chose to proceed according to Lee et al.[11] One problem we found with this synthesis is that the bromodecylderivative (III

for n = 8), during its formation, further reacted with the unconverted Li derivative of I (Im′-Li) to yield the 1,10-di-[2-(tert-butyldimethylsilyl)-1-(N,N-dimethylsulfamoyl)-imidazol-5-yl]decane (IV),

$$\text{Im}'\text{-CH}_2(\text{CH}_2)_8\text{CH}_2\text{Br} + \text{Im}'\text{-Li} \rightarrow \underset{\text{(IV)}}{\text{Im}'\text{-CH}_2(\text{CH}_2)_8\text{CH}_2\text{-Im}'} + \text{LiBr} \quad (3)$$

The occurrence of side reaction in Equation (3) was found to depend on maintaining an adequate excess of dibromoalkane in the solution to which the Im′-Li derivative was transferred. With slight adjustment of Lee et al.'s procedure[11] reported for the short C chain dibromoalkanes, we were able to run the reaction in Equation (2) with 1,10-dibromodecane up to 80% yield of 2-(tert-butyldimethylsilyl)-5-(10-bromodecyl)-1-(N,N-dimethylsulfamoyl)-imidazole (III for n = 8).

For the further phosphonation step, we chose the room temperature reaction with $NaPO_3Et_2$,

$$\text{Im}'\text{-CH}_2(\text{CH}_2)_8\text{CH}_2\text{Br} + \text{NaPO}_3\text{Et}_2 \rightarrow \underset{\text{(V)}}{\text{Im}'\text{-CH}_2(\text{CH}_2)_8\text{CH}_2\text{-PO}_3\text{Et}_2} + \text{NaBr} \quad (4)$$

rather than the reaction with boiling $P(OEt)_3$, as we feared that operation at this temperature might cause side reactions involving the imidazole-protecting groups at position 1 and 2. Phosphonation by $NaPO_3Et$ indeed occurred with a good 89% yield.

Hydrolysis to convert the PO_3Et_2 group to PO_3H_2 was performed by HBr at reflux temperature to yield 1,10-(1-H-imidazol-5-yl)decanephosphonic acid hydrobromide (VI),

Im(HBr)-$CH_2(CH_2)_8CH_2$-PO_3H_2, Im = 1-H-imidazol-5-yl, according to the reaction

$$\text{V} + 4\text{H}_2\text{O} + \text{HBr} \rightarrow \underset{\text{(VI)}}{\text{Im(HBr)-(CH}_2)_{10}\text{PO}_3\text{H}_2} + 2\,\text{EtOH} + \text{TBDMS-OH} + \text{S(NMe}_2)\text{O}_3\text{H} \quad (5)$$

Titration of this compound with NaOH gave 1,10-(1-H-imidazol-5-yl)decanephosphonic acid (VII) and its sodium salts (VIII)

$$\text{VI} + \text{NaOH} \rightarrow \underset{\text{(VII)}}{\text{Im} - \text{CH}_2(\text{CH}_2)_8\text{CH}_2\text{-PO}_3\text{H}_2} + \text{NaBr} + \text{H}_2\text{O} \quad (6)$$

$$\text{VII} + 2\text{NaOH} \rightarrow \underset{\text{(VIII)}}{\text{Im-CH}_2(\text{CH}_2)_8\text{CH}_2\text{-PO}_3\text{H}_n\text{Na}_{(1+\text{m})}} + 2 - \text{n}\,\text{H}_2\text{O},$$

$$\text{n} + \text{m} = 1, \quad (7)$$

The isolation of the hydrobromide (VI) and of the sodium salts (VIII), in addition to the free acid (VII) and the comparison of the spectroscopic data for all products, allowed a better characterization of the new compound obtained in this work.

Product Characterization

Compound III for n = 8 was well identified in agreement with literature data,[10,11] (see Experimental section below). Compounds VI and VIII, derived from III according to the reactions in Equations (4)–(7), were well identified by their ^{1}H, ^{13}C, and ^{31}P spectra (both ^{1}H coupled and ^{1}H decoupled) in solution. Signals assignments and H and C ratios (Tables I and II) obtained from these spectra were consistent with the structural formulas for both compounds, as indicated in the reactions in Equations (5) and (7). The ^{31}P spectra for VIII in solution showed two signals (Table II), suggesting the presence of more than one salt form, as shown in the reaction in Equation (7). Compared to the parent intermediate III for n = 8 (Table I), the solution spectra of VI and VIII

TABLE I Assignment (RSA),[a] Chemical Shift (δ, ppm),[b] Multiplicity (s, d, t, m),[c] Relative H Ratios (pH),[d] Coupling Constant (J, Hz) for Signals in the ^{1}H NMR Spectra of III for n = 8, IV, VI, and VIII in Solution

RSA	III for n = 8 ($CDCl_3$)	IV ($CDCl_3$)	VI (MeOD)	VIII (D_2O)
$SiMe_2$	δ 0.38, s, 6H	δ 0.38, s, 12H		
Me_3CSi	δ 1.00, s, 9H	δ 1.00, s, 18H		
H_2C3–8	δ 1.30–1.44, m, 12H	δ 1.30–1.41, m, 12H	δ 1.30–1.70, m, 12H	δ 1.2–1.4, m, 16H[h]
H_2C9	δ 1.67, m, 2H	δ 1.67, m, 4H[e]	δ 1.7, m, 6H[g]	δ 1.55, m, 2H
H_2C2	δ 1.85, m, 2H	see H_2C9[e]	see H_2C9[g]	see H_2C3-8[h]
H_2C10	δ 2.69, t, 2H , J 7.20	δ 2.69, t, 4H , J 7.20[f]	δ 2.70, t, 2H, J 7.87	δ 2.50, t, 2H, J 7.18
Me_2N	δ 2.83, s, 6H	δ 2.82, s, 12H		
H_2C1	δ 3.40, t, 2H , J 6.85	see H_2C10[f]	see H_2C9[g]	see H_2C3-8[h]
HC4′	δ 6.93, s, 1H	δ 6.93, s, 2H	δ 7.30, s, 1H	δ 6.78, s, 1H
HC2′			δ 8.79, s, 1H	δ 7.58, s, 1H

[a] C atoms numbered as in Figure 1, i.e., ring position numbered clockwise starting from N-1 (NH in the pure imidazole ring), C in aliphatic chain numbered starting from C-X (X = Br in III, second imidazole ring in IV, P in VI and VIII) as C1.

[b] Referred as reported in the Experimental section.

[c] Singlet (s), doublet (d), triplet (t), multiplet (m).

[d] p as relative number of atoms.

[e] Signal assigned to both H_2C2 and H_2C9.

[f] Signal assigned to both H_2C1 and H_2C10.

[g] Signal assigned to the protons in H_2C1, H_2C2 and H_2C9.

[h] Signal assigned to the protons in H_2C1, H_2C2 and H_2C3–8.

TABLE II Chemical Shift (δ, ppm),[a] Multiplicity (s, d, t, m),[b] Relative C Ratios (pC),[c] Coupling Constant (J, Hz), and Assignment[d] for Signals in the ^{13}C, ^{31}P, and ^{15}N NMR Spectra of Compounds VI–VIII in Solution and in the Solid State

Nucleus in solution or in solid state	NMR data and signals assignment		
	VI	VII	VIII
^{13}C in MeOD (VI) and D_2O (VIII)	δ 22.55, d, 1C, $^{3}J_{PC}$ 4.61,C3		δ 24.97, d, $^{1}J_{PC}$132.12, C1
	δ 23.96, 1C, C_{al}		δ 28.33, C_{al}
	δ 26.72, d, 1C, $^{1}J_{PC}$ 137.60,C1		δ 28.56, C_{al}
	δ 28.27, 1C, C_{al}		δ 28.63, C_{al}
	δ 28.64, 1C, C_{al}		δ 28.76, C_{al}
	δ 28.90, 2C, C_{al}		δ 28.85, C_{al}
	δ 29.06, 1C, C_{al}		δ 28.93, C_{al}
	δ 29.25, 1C, C_{al}		δ 30.36, C_{al}
	δ 30.37, d, 1C,$^{2}J_{PC}$ 16.14, C2		δ 31.25, d, $^{2}J_{PC}$ 16.72, C2
	δ 115.26, 1C, C4′		δ 117.40, 1C, C4′
	δ 133.18, 1C, C2′		δ 135.49, 1C, C2′
	δ 134.48, 1C, C5′		δ 137.66, 1C, C5′
^{31}P in MeOD (VI) and D_2O (VIII)	δ 30.66		δ 24.07 δ 24.12
^{13}C CP-MAS	δ 26.46, C_{al}	δ 28.32, C_{al}	δ 34.10, 10C, C_{al}
	δ 32.78, C_{al}	δ 34.65, C_{al}	
	δ 114.00, C4′	δ 113.43, C4′	δ 112.03, C_{im}
		δ 131.97, C2′	δ 123.10, C_{im}
	δ 135.85, C2′ and C5′	δ 136.71, C5′	δ 130.50, C_{im}
			δ 136.85, C_{im}
			δ 140.73, C_{im}
			δ 143.02, C_{im}
^{31}P CP-MAS	δ 43.82	δ 35.95	δ 24.92
			δ 26.14
^{15}N CP-MAS (5 ms contact time)	δ 157.3	δ 154.2	δ 226.6
	δ 144.4		δ 147.3

[a]Referred as reported in the Experimental section.
[b]Singlet (s), doublet (d), triplet (t), multiplet (m).
[c]p as relative number of atoms.
[d]C atoms numbered as in Figure 1, i.e., ring position numbered clockwise starting from N-1 (NH in the pure imidazole ring), C in aliphatic chain numbered starting from C—P as C1; C_{im} as unidentified ring C, C_{al} as unidentified aliphatic C.

showed the signal for aliphatic H bonded to C10 at nearly the same value for H at C10 in III (Table I). However, for VI and VIII, the signals for H bonded to C1 appeared considerably shifted upfield. This upfield shift is well consistent with bonding of the C1 methylene group to P.[13] Another feature is that the imidazole ring protons bonded to C2′ and C4′ appeared shifted to lower field for VI compared to VIII, and the amount of the shift was higher for the H at C2′ than for H at C4′.

The low field shifts for VI appear consistent with protonation of N-3 by HBr and with delocalization of the positive charge over the two ring N atoms as depicted in Figure 1. Thus, H at C2′ taken in between the two protonated N atoms experiences the greater amount of shift. Solution NMR spectra for VII could not be obtained due to its insolubility. As VII is an intermediate compound in the chemical transformation of VI to VIII (see the reactions in Equations (6) and (7)), the structural formula of VII results also identified from the solution spectra of VI and VIII.

The free phosphonic acids (VII) exhibited very peculiar properties and spectroscopic features compared to the hydrobromide (VI) and the sodium salts (VIII). While the latter compounds are soluble in MeOH (VI) and water (VIII), the free acid is insoluble in any common solvent. Its water suspension yields a neutral pH. Addition of acid or base to the water suspension of VII, however, makes it soluble, as this compound converts into VI or VIII, respectively (see Figure 1). The DSC trace of VII showed a sharp intense endothermic peak at 220°C upon heating from room temperature to 250°C at 10°C/min under N_2 flow, and a low-intensity broad exothermic peak at about 140°C upon cooling back to room temperature. The thermal gravimetric analysis (TGA) trace showed no weight loss up to 240°C, a 3.7% loss from 240–395°C, and extensive thermal degradation above 400°C. The hydrobromide VI showed a sharp intense endothermic peak at 145°C during heating and no peak upon cooling.

^{13}C, ^{15}N, ^{31}P, and CP MAS nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy in the solid state have been employed to elucidate the different structural properties that may affect solid-state proton mobility for the free acid (VII), the hydrobromide (VI), and the sodium salts (VIII). The spectra are shown in Figures 2–4, and the data are summarized in Tables II and III. The interpretation of the results is based on the hypothetical structures represented in Figure 1.

The most significant features of the CP MAS NMR spectra are as follows. For the three aromatic C atoms, the spectrum of VI (Figure 2a) exhibits only two signals, while in the spectrum of VII (Figure 2b) the three aromatic C atoms give three distinct signals. The upfield signal at δ 113–114 assigned to C4′ (Table II) has nearly the same chemical shift value for both compounds. At lower field, VI exhibits one band at δ 135.85, which is assigned to both C2′ and C5′, while VII shows two distinct bands at δ 131.97 for C2′ and at δ 136.71 for C5′. A possible explanation for the different patterns shown by the two compounds is that in VI the strong electron-withdrawing effect played by HBr protonating the ring N atoms is experienced more by C2′ than by C5′, and it just so happens that the δ values for the two C atoms are very close.

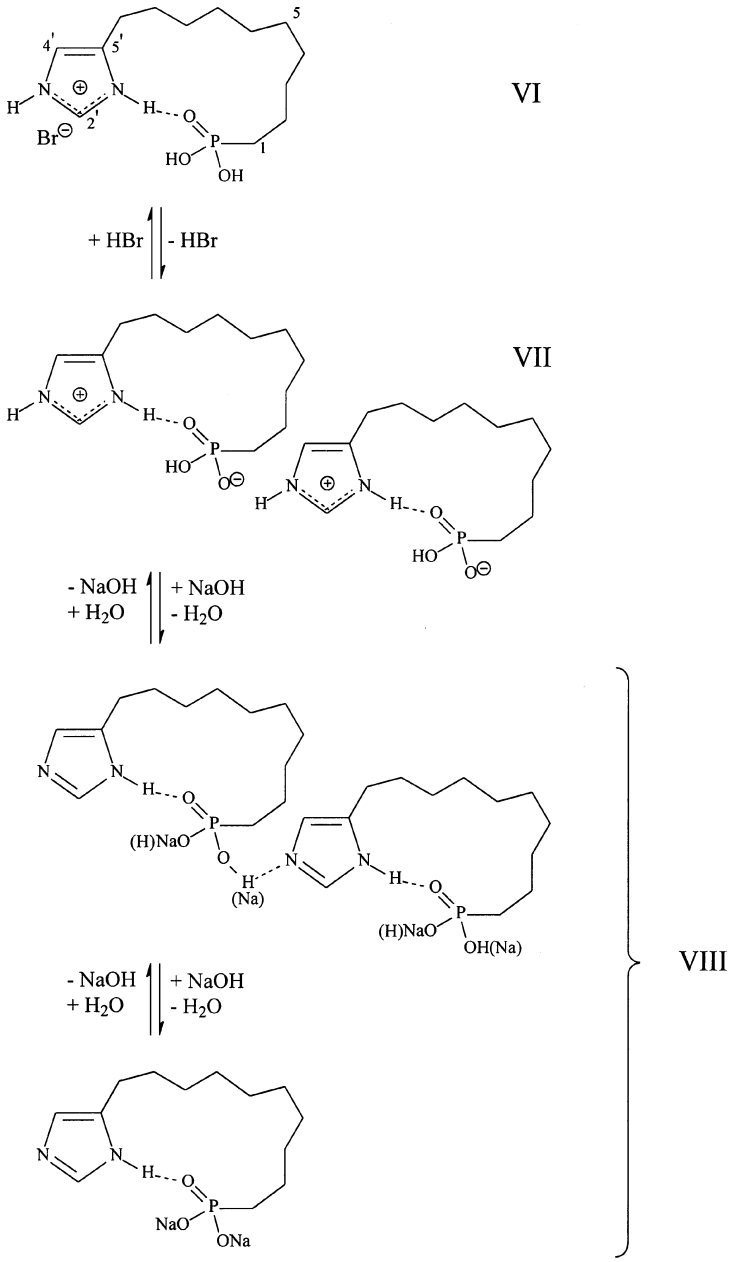


FIGURE 1 Structures for products VI, VII, and VIII in the solid state and reagents mole/P atom participating to the reactions in solution for their isolation.

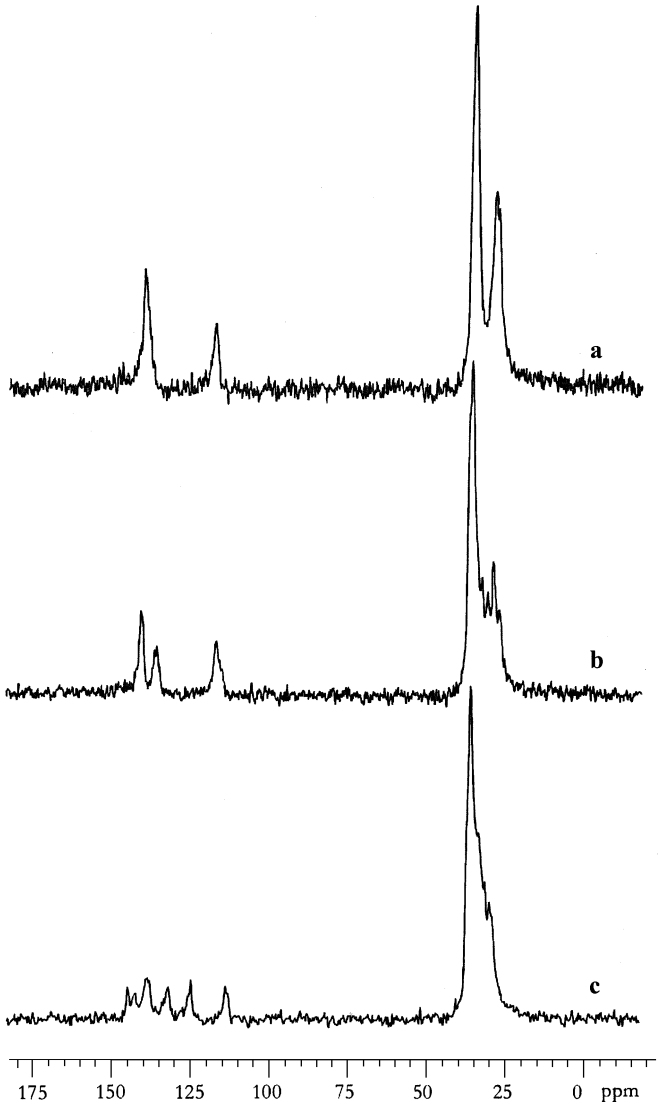


FIGURE 2 ^{13}C CP-MAS (7.0–8.0 kHz) spectrum for (a) VI ,(b) VII, and (c) VIII.

This interpretation appears reasonable if one considers that the better-resolved solution spectrum showed two distinct signals for C2′ and C5′ with a chemical shift difference of only 1.3 ppm (Table II). The stronger electron-withdrawing effect on C2′ has also been evidenced from the solution ^{1}H spectra above.

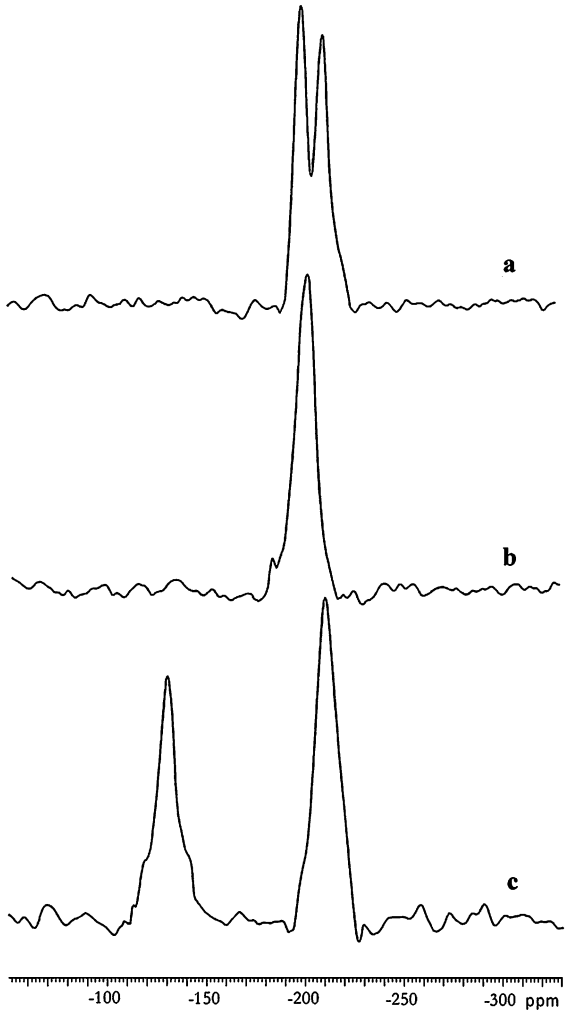


FIGURE 3 ^{15}N CP-MAS (4.0–5.0 Hz) spectrum for (a) VI, (b) VII, and (c) VIII.

Compared to VI and VII, the ^{13}C CP MAS spectrum of VIII was very interesting. This spectrum (Figure 2c and Table II) exhibits six signals for aromatic C (C_{im}). In Figure 1 VIII is represented as a mixture of two salts, the disodium and the acid sodium salts. It may be readily envisioned that the $-PO_3(NaH)$ group is capable of yielding more H bonding interaction with the imidazole ring than is the $-PO_3(Na)_2$. Consequently, more than one type of imidazole ring with variable electron density distribution may be expected to be present for the salts

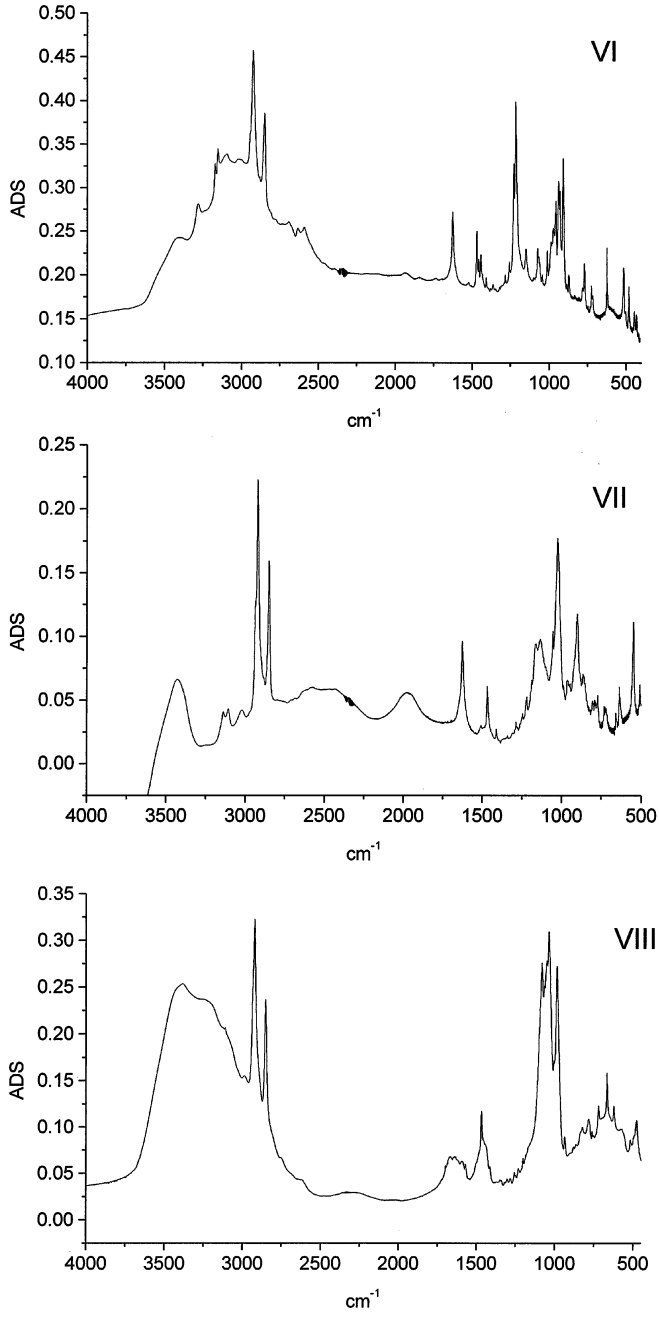


FIGURE 4 IR spectra of compounds VI, VII, and VIII.

TABLE III Absorption Frequencies (ν, cm^{-1}) and Assignments for the IR Spectra of Compounds VI–VIII

	Absorption frequency (ν, cm^{-1})		
Assignment	VI	VII	VIII
Stretching of OH in H_2O and ring NH	3407	3427	
Ring N—H^+ stretching	Broad absorption from 3300 to 2800	Broad absorption from 3200–2800	Broad absorption from 3600 to 2800
Imidazole ring N—H stretching	3387		3382
Imidazole ring C—H stretching	3156	3134	
Imidazole ring N—H stretching	3100	3100	3116
Imidazole ring N—H stretching	3028	3027	3016
CH stretching in CH_2	2928	2920	2920
CH stretching in CH_2	2849	2840	2850
PO—H stretching	2691	2574	2757
PO—H stretching	2628	2430	2616
PO—H stretching	2577	1974	2273
Ring skeletal bonds stretching	1621	1632	1641
Ring skeletal bonds stretching	1470	1474	1467
P═O stretching	1214	1174–1140	1078
P—O stretching		1035	1035
P—O stretching	936–907	907	983

mixture VIII. On this basis, our interpretation for the spectrum in Figure 2c is that the six ^{13}C signals arose from at least two imidazole rings interacting with the $-PO_3(NaH)$ and the $-PO_3(Na)_2$ groups in different ways. As VIII was obtained by adding NaOH to VII up to pH 8.5, the presence of the two-salt mixture is consistent with previous data showing that the imidazole ring in histidine is not completely deprotonated up to pH 9.[14,15]

Another very interesting observation on the ^{13}C NMR data for VIII is that, unlike the ^{13}C CP MAS spectrum (Figure 2c), the solution ^{13}C NMR spectrum (Table II) exhibited only three signals for the imidazole ring C. Yet, the ^{31}P spectra, in the solid state and in solution, exhibited two signals (Table II). These facts evidence that, although in both the solution or the solid state both $-PO_3(NaH)$ and $-PO_3(Na)_2$ are present at the same time, the direct interaction of the phosphonate groups with the imidazole ring occurs only in the solid state. In water, these groups

are likely to be surrounded by solvent molecules, and their different effects on the ring electron distribution are leveled out.

As we have pointed out in the Introduction section of this work, the interaction of the phosphonic groups, $-PO_3(H)_2$, or $-PO_3(NaH)$ and $-PO_3(Na)_2$, with the imidazole ring in the solid state is mostly important for the proton conductivity properties. The analysis of the ^{31}P CP MAS chemical shift values in conjunction with the ^{15}N CP MAS spectra provides further significant information on these interactions. Table II shows that the ^{31}P resonance for VII occurs at higher field than that of VI. This suggests higher ionization of the $-PO_3H_2$ group in VII, as represented in Figure 1. The ^{31}P signals for VIII are further shifted to higher field relatively to VII, consistently with the presence of the more ionized $-PO_3H^-$ Na^+ and $-PO_3^{2-}$ 2 Na^+ groups. The ^{15}N CP MAS spectra contain two resonance signals for VI (Figure 3a), one signal for VII (Figure 3b) and two signals for VIII (Figure 3c). Figure 1 shows that for three compounds VI, VII, and VIII, as well as for histidine and for protonated histidine,[14,15] three canonical-type N atoms are present: pyridine-like (>N:); pyrrole-like (>N—H); and pyrrole-like within a protonated imidazole ring (+>N—H). For the powder sample of the histidine sodium salt, the signals for >N—H and >N: fall at 147 ppm and 228 ppm, respectively.[16]

H bonding and/or protonation of the imidazole ring causes the above signals to shift in opposite directions. Thus, for the powder sample of histidine hydrocloride, the >N—H signal falls at 152 ppm and the +>N—H signal falls at 155 ppm. Accordingly, our interpretation for the spectra in Figures 3a–c is that the different signal patterns are caused by the different acidity and/or ionization of the phosponic acid and phosphonate groups, which has been pointed out above for the three compounds VI–VIII. As depicted in Figure 1, compound VI has two protonated N atoms in a similar magnetic environment. These give rise to two signals at 144.4 ppm and 157.3 ppm. The small chemical shift difference between the two signals can be then explained in term of the presence of an intramolecular H-bond interaction between the phosphonic group and the pyrrole-like N-1 within the protonated imidazole ring. The loss of HBr in VII is likely to favor protonation of the ring by the phosphonic group and/or the formation of a strong H-bond interaction between the partially deprotonated phosphonic group and the imidazole ring. The formation of a polymeric structure where each $-PO_3H_2$ group was H bonded to the imidazole ring of the same molecule and to the imidazole ring of another molecule (Figure 1) is quite likely in this case. The N sites in this compound are therefore almost equivalent, and here (Figure 3b) a single signal is observed at 154.2 ppm. The further addiction of NaOH to VII yields compound VIII, which, similar

to the histidine sodium salt,[16] exhibits two signals at 226.6 ppm and at 147.3 ppm (Figure 3c). As already pointed out, the structure of VIII is more complicated than that for a single chemical species, since the $-PO_3H^-\ Na^+$ and the $-PO_3^{2-}\ 2Na^+$ groups (Figure 1) are both likely to be present. To get more insight into the nature of the above two signals in Figure 3c, we recorded the ^{15}N CP MAS spectrum for VIII with a shorter contact time, i.e., 3 ms instead of 5 ms. With such short contact time value (3 ms), cross polarization is reached only for very short N—H distances,[17] and signals due to deprotonated N or to N involved in long H bonds disappear. Indeed, in the ^{15}N CP MAS spectrum recorded at 3 ms we found that only the signal at 226.6 ppm disappeared. This confirms the assignment of the 226.6 ppm signal in Figure 3c to the pyridine-like (>N:). As shown in Figure 1, this N atom may be either deprotonated (for VIII in the disodium salt form) and involved in long H bonds (due to the presence of the $-PO_3H^-\ Na^+$ group). Indeed, on theoretical ground, the acid proton in the $-PO_3H^-\ Na^+$ group is not strong enough to protonate the imidazole ring, in any case not as strong as the $-PO_3H_2$ group in VII, and therefore the former is more likely to yield relatively weak H bonds with N-3.

Further information about the solid-state structure of compounds VI–VIII was obtained from IR spectra (Figure 4). Neat imidazole has the most intense band at 1056 cm^{-1}. As this band has quite low intensity in the reported spectra, we conclude that most of the observed bands arise from the aliphatic C atoms bonds and from the phosphonic group in compounds VI–VIII. Possible bands assignments are given in Table III. Significant differences in the IR spectra are as follows.

The P=O stretching frequencies at 1214 cm^{-1} in VI appear shifted to lower and lower frequency in compounds VII and VIII, respectively. Concurrently, the bands assigned to P—O are significantly enhanced in intensity in the spectrum of VII and VIII. This band pattern and absorption intensities modifications are normally observed by the change of the $-PO_3$ group from the protonated form to the salt form.[4] In the specific case of this work, the changes observed in the phosphonate group absorption region are consistent with lengthening of the P=O bond due to higher dissociation of the $-PO_3M_2$ group on passing from VI (M = H) to VII (M = H) and to VIII (M = H and Na, or Na only). This result appears well consistent with the upfield shift observed for the ^{31}P resonance. Indeed, the IR P=O stretching frequency and the ^{31}P δ values in Table II for the three compounds in the solid state appear nicely correlated in linear fashion.

In the range above 2000 cm^{-1}, compound VI exhibits a very broad and strong absorption, extending from 2800–3300 due +>NH stretching. Three other absorption maxima assigned to PO—H stretching may

be picked out in the 2500–2700 cm^{-1} range. In the same range above 2000 cm^{-1}, compound VII yields a better resolved absorption pattern than compound VI. For VII, the +>NH stretching band in the 2800–3300 range is relatively less intense, and the PO—H bands are more evident, shifted to lower frequency and more separated one from the other. In the same range, the spectrum of VIII is dominated by the ring N—H stretching at 3382 cm^{-1}, consistently with the lower concentration +>NH in the salts mixture represented in Figure 1. Also, the absorptions in 2800–2000 cm^{-1} range are quite low, as less or no PO—H bands are expected for this compound.

The IR absorption pattern for compounds VII is well consistent with formation of H bonded chains such as O···H···O and/or N···H···O. In such systems, proton conductivity is expected based on the proton transport through H-bonds.[18] At this regard, particular significance acquires the band pattern in the 2800–2000 cm^{-1} IR frequency range. It has already been pointed out that only compound VII exhibits very evident absorption bands in this range.

Increasing bands splitting in the 2800–2000 cm^{-1} 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. The relationships between conductivity and the above IR spectroscopic feature was reported by Montoneri et al.[19] in the case of inorganic acid phosphates. For the specific case of imidazole-based solid electrolytes, this same relationship may also be observed in other work[20,21] upon comparing the IR spectra and conductivities of polybenzilimidazole-phosphoric acid blends, poly(4-vinylimidazole)-phosphoric acid blends, and the pristine polymers. Table IV reports these IR data and the conductivity values measured for different materials and for compounds VI–VIII. It is well evident that the presence of acid POH functions definitely lowers the average absorption frequency in the 2800–2000 cm^{-1} range. Based on the data reported in the literature,[19–22] the low PO-H frequency observed for compound VII allows us to expect significantly better conductivity properties than for VI and VIII.

For a possible explanation of the lower distance between proton acceptor sites in compounds VII compared to compound VI and VIII, we hypothesize that whereas for compound VII a polymeric structure as depicted in Figure 1 is quite likely, a similar arrangement for VI or VIII is less likely. For VI, due to the stronger acidity of HBr, the intermolecular protonation or H bonding of the imidazole ring N-3 atom by the PO_3H_2 group is less favored; this group would be pushed away from the imidazole ring of a second molecule due to the positive charge of the N-3 atom protonated by the stronger HBr acid. For VIII, the effects

TABLE IV Average Absorption Frequency (ν) in the 2000–2800 cm^{-1} IR Range and/or Conductivity (Ω^{-1} cm^{-1}) for a Few Materials Reported in Literature and for Compounds VI–VIII

		Conductivity and experimental conditions		
Material	ν, cm^{-1}	Ω^{-1} cm^{-1}	T, °C	Environment
$AlPO_4$[18]	3130	10^{-2}	100–200	5 atm steam pressure
$H_2AlP_3O_{10}$[18]	2625	nearly 10^{-1}	100–200	5 atm steam pressure
Polybenzimidazoles)-H_3PO_4[20]	2609	10^{-4}	25	dry
Polybenzimidazoles[20]	none	$<10^{-11}$	25	dry
poly(4-vinylimidazole)-H_3PO_4[21]	2578	nearly 10^{-3}	25	dry
Poly(4-vinylimidazole)[21]	none	$<10^{-12}$	25	dry
Poly(dipropylphosphazene)-H_3PO_4[22]	2520	10^{-4}	69	dry
Poly(dipropylphosphazene)-H_3PO_4[22]	2520	10^{-3}	52	33% RH[a]
VI	2632			
VII	2326			
VIII	2549			

[a]Relative humidity.

of the low acidity of the salts mixtures on H bonding has already been pointed out above. For both VI and VIII, therefore, the interaction of phosphonic groups with the imidazole ring is not particularly favored, and the net result would be the increase of the distance between O and N proton acceptor sites. The effects of these structural arrangements on solid-state proton conductivity will be the subject of a future work.

EXPERIMENTAL

Reagents

All reagents were purchased from Aldrich, Milan (1).

Physical Measurements

Thermal analysis was performed by TG-DTA Seiko 6300 (TGA) and Seiko 6200 (DSC) instruments operated in N_2 at 10°C/min. IR spectra were recorded as KBr pellets on a Nicolet Fourier transform infrared (FTIR) Magna 560 instrument. Mass Spectra (FAB) were recorded on a VG 7070 EQ-HF instrument. Solution NMR spectra were recorded at room temperature on Bruker and JEOL EX 400 (^{1}H frequency

399.78 MHz) instruments with standard conditions. Chemical shifts (δ, ppm) were referred to the solvent residual chemical shift, and in the case of phosphorus chemical shifts were referred to the signal of 85% phosphoric acid. CP MAS solid-state NMR spectra were recorded at room temperature on a Jeol GSE 270 equipped with a Doty probe operating at 270 MHz for ^{1}H, 67.8 MHz for ^{13}C, 27.25 MHz for ^{15}N, and 109.6 MHz for ^{31}P. The spectra were recorded at different spinning speeds. Cylindrical 6 mm o.d. zirconia rotors with sample volume of 120 μl were employed. For all samples the magic angle was carefully adjusted from the ^{79}Br spectrum of KBr by minimizing the line width of the spinning sideband satellite transitions. For ^{13}C spectra a standard cross-polarization pulse sequence has been 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 (7.0–8.0 KHz spin rate). In the case of ^{15}N, samples were spun at 4–5 KHz, a contact time of 5 ms (unless otherwise indicated), a repetition time of 15 s, and a spectral width of 35 KHz were used for accumulation of 3000–4000 scans. ^{31}P spectra were recorded with a 7.5–8.0 KHz spin rate, 3.5 ms of contact time, and 15 s of recycle time. Throughout this article, chemical shifts in the solid state are referred to TMS for ^{13}C resonance, to 85% phosphoric acid for ^{31}P resonance, and to external $(NH_4)_2SO_4$ for ^{15}N resonance. According to our measurements the ^{15}N resonance for $(NH_4)_2SO_4$ falls at -355.8 ppm from CH_3NO_2.

Preparation of Compounds VI, VII and VIII

Two runs were carried for the synthesis of III for n = 8. In the first one, a solution containing Im′-Li in THF (69.3 mmol in 500 ml) at −70°C, prepared according to Lee et al.,[11] was transferred to a suspension of 1,10-dibromodecane in THF (208 mmol in 250 ml) kept at −70°C. After 1 h the temperature of the mixture was allowed to rise to room temperature and was stirred for 3 h. The solvent was removed and the residue was purified by flash chromatography on silica. The column was first eluted with petroleum ether to collect the unreacted 1,10-dibromodecane, and then with ethyl acetate/hexane (1/4) to collect first pure 2-(tert-butyldimethylsilyl)-5-(10-bromodecyl)-1-(N,N-dimethylsulfamoyl)-imidazole (III for n = 8) and then 1,10-di-[2-(tert-butyldimethylsilyl)-1-(N,N-dimethylsulfamoyl)-imidazol-5-yl]decane (IV). The second run was performed as the first one, but 1,10-dibromodecane in THF (208 mmol in 250 ml) was kept at 0°C in order to operate with a homogenous solution of this reagent. The product (III for n = 8) yields were 53% in the first run and 80% in the second run. Product III for n = 8 was identified by its molecular weight (FAB measurement) and its $^{1}HNMR$ spectrum (Bruker 400 MHz,

$CDCl_3$). The ^1H NMR data for this compound are reported in Table I. These data are well consistent with those reported for the chlorodecyl derivative (II).[10] The most significant difference between III for n = 8 and II is the chemical shift for the H atoms bonded to the halogenated C (δ 3.40 for CH_2Br in III and δ 3.53 for CH_2Cl in II). By comparison, the ^1H chemical shift for CH_2Br in the bromohexyl derivative (δ 3.42 for III for n = 4)[11] has nearly the same value reported here for III for n = 8. Product IV was identified by its ^1H NMR spectrum (Bruker 400 MHz, $CDCl_3$). The ^1H NMR data for this compound are reported in Table I. The proton ratios are well consistent with its structure. Compared to III for n = 8, IV shows no signal for CH_2Br protons, and therefore has one signal for the equivalent protons at C9 and at C2 and one signal for the equivalent protons at C10 and at C1.

The phosphonation of compound III for n = 8 was carried out with $NaPO_3Et_2$ in anhydrous THF (37 mmol in 100 ml). This reagent was obtained from commercial HPO_3Et_2 as reported in literature.[23] The $NaPO_3Et_2$ solution in THF was dropped slowly under argon into an equimolar solution of III for n = 8 in 100 ml THF at 0°C. The reagents mix was kept overnight at room temperature. Afterwards, the white precipitate was filtered and washed with fresh THF. The collected liquid phase was vacuum evaporated to remove the solvent. The residue was taken up in $CHCl_3/H_2O$, and the organic phase was separated and dried under vacuum to yield V in 89% yield. Compound V was taken up with 175 ml of concentrated HBr and refluxed for 24 h. Afterwards, HBr was vacuum evaporated. The residue was taken up with EtOH, dried under vacuum, washed with CH_3CN, and filtered. The filtered solid was taken up again with EtOH. Crystallization from this solvent allowed us to collect pure VI in 20% yield. Compound VI was taken up with 100 ml water to yield a suspension. An equimolar amount of solid NaOH was added under stirring to this suspension to neutral pH. The solid was filtered, washed with MeOH, and dried to yield VII in 93% yield. Compound VII was taken up with water and added with a 0.1 N NaOH solution in 2/1 NaOH/VII mole ratio. Under this condition, a clear solution having pH = 8.5 was obtained. The solution was vacuum evaporated and dried to obtain solid VIII in nearly stoichiometric yield.

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