

Synthesis of azole phosphonates precursors for proton-exchange membrane for application in high temperature PEM fuel cells

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Abstract

This work reports the synthesis and characterization of phosphonate-, hydroxybisphosphonate- and aminobisphosphonatebenzimidazole derivatives substituted at N-1 position and new regioisomers phosphonate- and aminobisphosphonatebenzotriazole derivatives substituted at N-1 or N-2 positions. The compounds were characterized by NMR, IR spectroscopy and mass spectrometry (low and high resolution) allowing the assignment of their structure, including the identification of regioisomers. These azoles will be precursors of mesoporous silica host to produce novel membranes materials with high proton conductivity for intermediate temperature PEMFCs.

Keywords: PEMFC, PEM, benzimidazole, benzotriazole, phosphonates

1 Introduction

The increasing demand for clean and efficient energy has motivated the search for new materials to develop environmental friendly energy utilizations. A fuel cell is a device that can provide electrical energy with high efficiency and low environmental impact, converting the chemical energy stored in fuel, such as hydrogen, methanol, ethanol, etc., directly and efficiently to electrical energy. Fuel cells are zero pollution systems with the potential to become alternative clean and efficient energy conversion devices [1-3].

Among the various kinds of fuel cells, the proton-exchange membrane fuel cells (PEMFCs) are considered promising power sources, due to their high power density and high power-to-weight ratio. A key material for the operation of PEMFC is the proton-exchange membrane (PEM). PEM has been focus of many studies, in recent years, to obtain membranes with high proton conductivity, low electrical conductivity, low permeability to fuel and oxidant, good chemical/thermal stability, good mechanical properties and low cost [1-3].

The temperature is a key factor in the operation of (PEMFCs) due to its relation to water content of fuel cell. The operation above 100°C increases its performance due to faster electrode reaction without CO poisoning of the Pt electro-catalyst, easier water management and high energy efficiency [1-3].

Usually, PEM are made of organic polymers containing acidic functionalities (ex. Nafion[®]), but the proton transport properties of these membranes strongly depend on their water content and, consequently, limit their operation temperatures up to 90°C [1-3].

These limitations have fostered the interest in research and development of new alternative membranes. Among them, as alternative to the perfluorosulphonic polymers, a variety of membranes have been developed, such as polybenzimidazole (PBI)-doped, composites of Nafion and metal oxides, sulfonated polymers based on aromatic hydrocarbons, and organosiloxane-based on inorganic-organic hybrids with various acidic species [1-3]. Recently, the use of polymers with phosphonate groups have been investigated as PEMs with higher chemical and thermal stabilities and a greater water retention capacity when compared with sulfonic groups membranes, allowing their operation at elevated temperatures [4].

The aim of this work is to develop novel membranes with high proton conductivity for application in high temperature PEM fuel cells, from organic-functionalized mesoporous silica material, synthesized from a bridged organosilica precursors of the general formula $(RO)_3Si-R'-Si(RO)_3$, where R represents alkyls groups and R' is a bridge organic groups such as benzimidazole or benzothiazole functionalized with phosphonate or

bisphosphonate groups (Figure 1). Varying the organic spacer group of the organosilica precursors allows the fine tuning of chemical and physical properties of the mesoporous organosilica materials (POM). These hybrid compounds also combine the high temperature stability of polysilsesquioxanes with the proton conductivity of benzimidazole and benzotriazole derivatives.

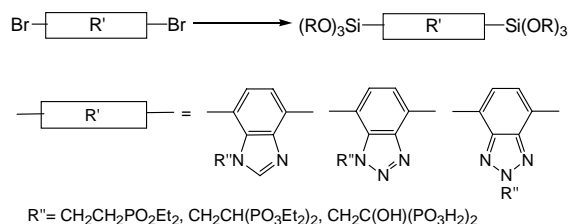


Fig. 1. General bridged organosilane precursors.

In this communication, we report on the synthesis and characterization of phosphonate-, hydroxybisphosphonate- and aminobisphosphonate benzimidazole derivatives substituted at N-1 position and new regioisomers phosphonate- and aminobisphosphonatebenzotriazole derivatives substituted at N-1 or N-2 positions. The compounds were characterized by NMR, IR spectroscopy and mass spectrometry (low and high resolution) allowing the assignment of regioisomers. These compounds will be precursors of mesoporous silica host to produce novel membranes materials with high proton conductivity for intermediate temperature PEMFCs.

2 Experimental

NMR spectra were recorded on Bruker AMX 300 and on a Bruker Avance II 300 (^1H 300 MHz, ^{13}C -75 MHz, ^{31}P 121 MHz) and on a Bruker Avance II 400 (^1H 400 MHz, ^{13}C -100 MHz, ^{31}P 162 MHz) spectrometers. Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz.

Infrared spectra were recorded on a Perkin Elmer FT-IR system spectrum BX Fourier Transform spectrometer, using KBr discs.

Low resolution and high resolution (HRMS) mass spectra analyses were performed at the 'C.A.C.T.I. - Unidad de Espectrometria de Masas' at the University of Vigo, Spain, on a VG AutoSpect M, MicroTOF (Bruker Daltonics) or APEX-Q (Bruker Daltonics) instrument.

Melting points were determined on a Reichert Thermovar melting point apparatus and are not corrected.

2,1,3-benzothiadiazole **1** is commercially available (Aldrich). Benzimidazole **4** and benzotriazole **5** were synthesized in a three step synthesis by

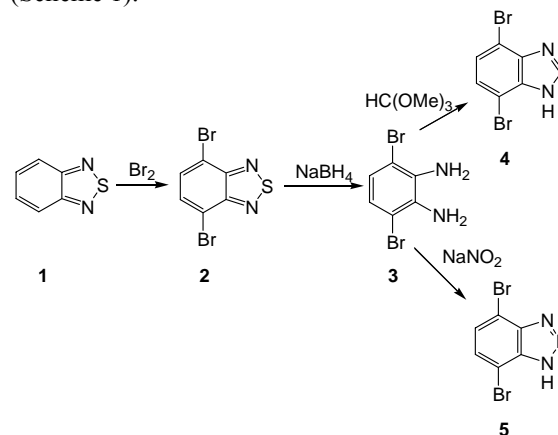
modifying the synthetic procedures reported (Scheme 1) [5].

Phosphonate-, hydroxybisphosphonate- and aminobisphosphonate were synthesized in several steps following modification of organic procedures already described by Teixeira *et al.* for the synthesis of indazole derivatives [6,7].

3 Results and Discussion

The synthesis of the dibromates benzimidazole **4** and benzotriazole **5** spacer precursors is summarized in Scheme 1. Compound **2** was prepared in high yield by bromination of commercially available 2,1,3-benzothiadiazole **1**. Reduction of **2** with NaBH_4 or by an alternative method using $\text{NaBH}_4/\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ cat. gave 1,2-diamine **3** in moderated yield [5].

Cyclization of 1,2-diamine **3** to 4,7-dibromobenzimidazole **4** was performed by reaction with trimethylorthoformate in acid conditions. The 4,7-dibromobenzotriazole **5** was formed in the presence of sodium nitride in acetic acid in good yield (Scheme 1).



Scheme 1. Synthesis of 4,7-dibromobenzimidazole **4** and 4,7-dibromobenzotriazole **5**

In order to prepare the benzimidazole phosphonates and bisphosphonates several strategies were followed with different kind of reagents (Scheme 2). All products were obtained in good yields.

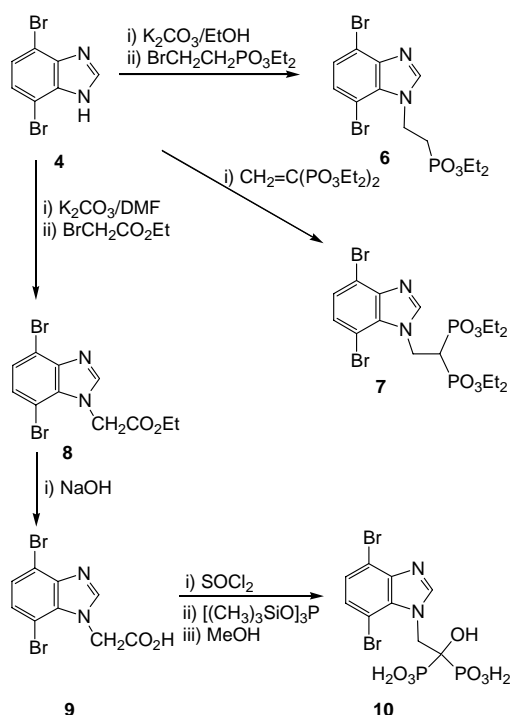
The reaction of 4,7-dibromobenzimidazole **4**, diethyl 2-bromoethylphosphonate and potassium carbonate in EtOH gave phosphonate **6** in very good yield (Scheme 2).

The synthesis of aminoethylidenebisphosphonate **7** substituted at N-1 position was performed by reaction of 4,7-dibromobenzimidazole **4** with tetraethyl ethylidene-1,1-bisphosphonate in THF (Scheme 2).

For the synthesis of hydroxybisphosphonate was necessary to prepare an ester and the corresponding

carboxylic acid. So, the benzimidazole ester derivative **8** was obtained starting from 4,7-dibromobenzimidazole **4** by nucleophilic substitution reaction of halo ester (BrCH₂CO₂Et). Basic hydrolysis of the ester derivative **8** allowed the synthesis of the corresponding carboxylic acid **9** (Scheme 2).

Bisphosphonate **10** was synthesized following the method of Lecouvey *et al.* [8], by reaction of carboxylic acid **5** with SOCl₂, to produce *in situ* the corresponding acid chloride, followed by reaction with tris(trimethylsilyl)phosphite and hydrolysis (Scheme 2).



Scheme 2. Synthesis of benzimidazole derivatives substituted at N-1 position (**6-10**).

Compounds **6-10** were fully characterized by NMR (including bidimensional techniques), IR spectroscopy and mass spectrometry (low and high resolution).

The bisphosphonate structure of compound **10** was readily identified by analysis of NMR data. Figure 2 shows the NMR spectra of bisphosphonate **10**.

The ¹H NMR spectrum of **10** shows a triplet at 5.19 (*J*_{HP}=10 Hz) ppm for the protons on carbon (A) with the subsequent coupling with two equivalent phosphorous nuclei (Figure 2 a).

The ¹³C NMR spectrum shows a triplet at 73 ppm (*J*_{CP}=139 Hz) consistent with a quaternary carbon (B) (disappearing in DEPT 135 ¹³C NMR mode) coupling with the two equivalent phosphorous nuclei, which supported the proposed structures

with two phosphonate groups attached to the same carbon (Figure 2b).

The proton decoupled ³¹P NMR spectrum of **10** shows a singlet at 17 ppm showing that two phosphorus atoms are chemically and magnetically equivalent (Figure 2c).

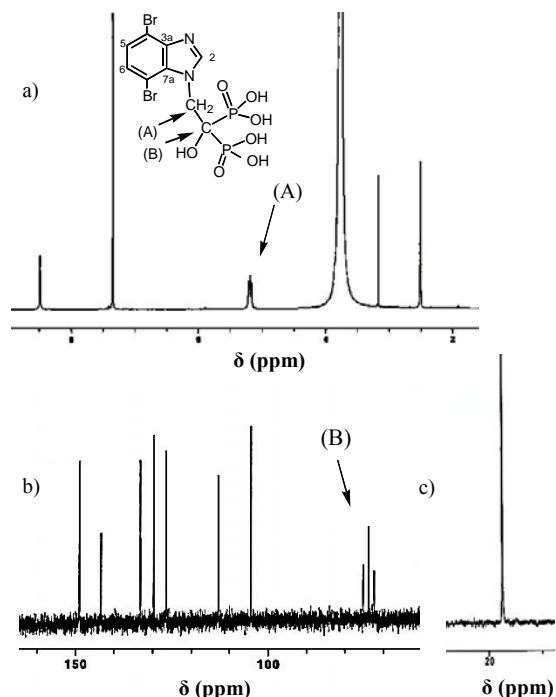


Fig. 2. The ¹H (a), ¹³C (b) and ³¹P NMR (c) spectra of bisphosphonate **10** in DMSO.

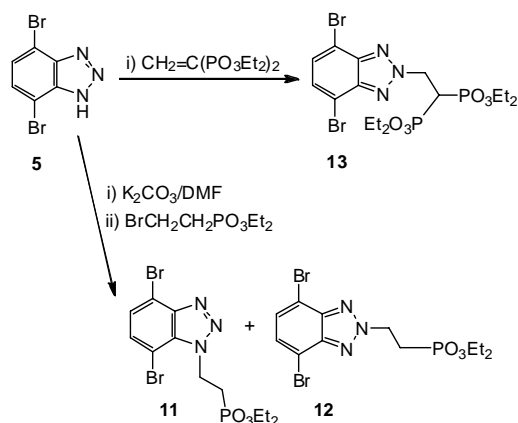
Electron Impact Ionization (EI) Mass Spectrometry was used to show the molecular ion of all compounds, which confirmed proposed molecular formulae for compounds **6-9**. The compound **10** was submitted to Electrospray Ionization (ESI) Mass Spectrometry to show the molecular ion of this compound, which confirmed its proposed molecular formula.

Like the benzimidazole, the benzotriazoles derivatives are also planar and rigid, and electron conjugation spacers, with different electron properties according to the bonded groups. Varying the synthetic procedure of 1,2-diamine **3** cyclization (Scheme 1), in the presence of sodium nitride in acetic acid, it allows the synthesis of the precursor 4,7-dibromo-benzotriazole **5**.

Scheme 3 shows the synthetic route for the synthesis of phosphonate- and aminobisphosphonatebenzotriazole derivatives substituted at N-1 or N-2 positions. The reaction of 4,7-dibromobenzotriazole **5**, diethyl 2-bromoethylphosphonate and potassium carbonate in DMF gave regioisomers **11** and **12**, with the N-2 derivative **12** as major regioisomer (70% yield) and

the N-1 derivative **11** as minor regioisomer (17% yield) (Scheme 3). Compounds **11** and **12** were separated by column chromatography to provide the pure phosphonates. The unambiguous assignment of benzotriazole derivatives substituted at N-1 and N-2 was carried out by ^1H - and ^{13}C -NMR spectroscopy, DEPT and two-dimensional NMR techniques.

Figure 3 and 4 shows the NMR spectra of compounds **11** and **12**. These spectroscopic data are in agreement with the ^{13}C -NMR spectra of 1N- and 2N-substituted benzotriazole reported in the literature [9].



Scheme 3. Synthesis of benzotriazole derivatives substituted at N-1 or N-2 position (**11-13**).

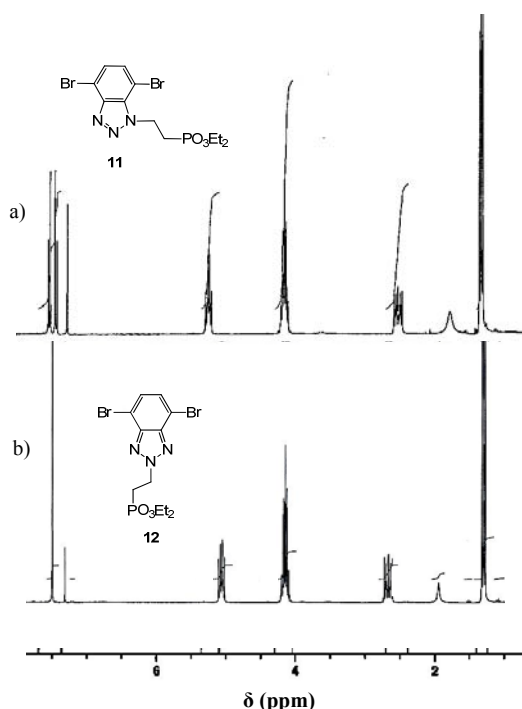


Fig. 3. ^1H NMR spectra of benzotriazole derivatives in CDCl_3 : (a) phosphonate **11** and (b) phosphonate **12**.

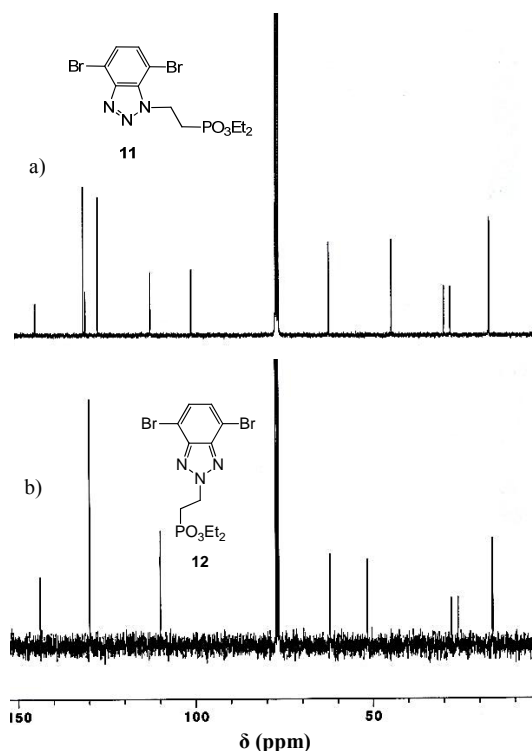


Fig. 4. ^{13}C NMR spectra of benzotriazole derivatives in CDCl_3 : (a) phosphonate **11** and (b) phosphonate **12**.

The synthesis of aminoethylidenebisphosphonate **13** substituted at N-2 position was performed by reaction of 4,7-dibromobenzotriazole **5** with tetraethyl ethylidene-1,1-bisphosphonate in THF (Scheme 3).

Compounds **11** - **13** were fully characterized by NMR (including bidimensional techniques), IR spectroscopy and mass spectrometry (low and high resolution).

Electron Impact Ionization (EI) Mass Spectrometry spectra show the molecular ion of all compounds, which confirmed the proposed molecular formulae for compounds **11** - **13**.

4 Conclusions

Several new azole derivatives were synthesized to become precursors for novel membranes materials. From 4,7-dibromobenzimidazole new phosphonate-, hydroxybisphosphonate- and aminobisphosphonatebenzimidazole derivatives substituted at N-1 position were synthesized in good yields. New regioisomers phosphonate- and aminobisphosphonatebenzotriazole derivatives substituted at N-1 or N-2 positions were synthesized in good yields, from 4,7-

dibromobenzotriazole. These compounds were fully characterized by NMR, IR spectroscopy and mass spectrometry (low and high resolution) allowing the assignment of regioisomers.

The evaluation of these compounds as precursors of mesoporous silica host to produce novel membranes materials is under investigation and will be reported in due course.

Acknowledgements

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