

2009

Preparation of substituted terephthalaic acids for use in novel polymers

Scott A. Simmons
University of Dayton

Follow this and additional works at: https://ecommons.udayton.edu/graduate_theses

Recommended Citation

Simmons, Scott A., "Preparation of substituted terephthalaic acids for use in novel polymers" (2009).
Graduate Theses and Dissertations. 5612.
https://ecommons.udayton.edu/graduate_theses/5612

This Thesis is brought to you for free and open access by the Theses and Dissertations at eCommons. It has been accepted for inclusion in Graduate Theses and Dissertations by an authorized administrator of eCommons. For more information, please contact mschlangen1@udayton.edu, ecommons@udayton.edu.

PREPARATION OF SUBSTITUTED TEREPHTHALAIC ACIDS FOR USE IN
NOVEL POLYMERS

Thesis

Submitted to

The College of Arts and Sciences of the

University of Dayton

In Partial Fulfillment of the Requirements for

The Degree

Master of Science in Chemistry

By

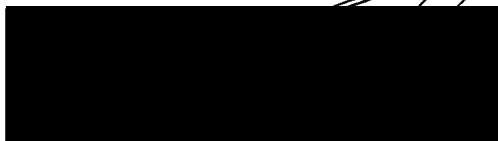
Scott A. Simmons

UNIVERSITY OF DAYTON

Dayton, Ohio

December 2009

APPROVED BY:



(Faculty Advisor)
Dr. Vladimir Benin
Associate Professor,
Department of Chemistry
University of Dayton
Committee Chair



(Faculty Committee Member)
Dr. R. Gerald Keil
Professor,
Department of Chemistry
University of Dayton



(Faculty Committee Member)
Dr. Shawn Swavey
Associate Professor,
Department of Chemistry
University of Dayton

ABSTRACT

PREPARATION OF SUBSTITUTED TEREPHTHALIC ACIDS FOR USE IN NOVEL POLYMERS

Name: Simmons, Scott, A
University of Dayton

Advisor: Dr. V. Benin

Currently there are few polymers that can be used in multiple applications with little or no modification. There presently exist polymers that can improve fuel cell performance and provide fire retardant ability but none that can do both. Therefore, our research intends to produce a polymer, or class of polymer with a unique chemical structure that will provide enhancements to many current applications. Recently synthesized phosphonic and boronic acid functionalized terephthalic acid are some of these structures that could be useful in multiple applications.

ACKNOWLEDGEMENTS

I would like to thank the University of Dayton, Department of Chemistry for providing financial assistance for this project and the graduate school for funding my summer work. I wish to express my deepest gratitude to Dr. Vladimir Benin for all his patience and encouragement. I would also like to thank Dr. Albert Fratini for his work on the X-ray crystal structure analysis. Thanks are also in order for Thuy Dang, Dr. Robert Keil and Dr. Shawn Swavey for their help and support.

TABLE OF CONTENTS

ABSTRACT.....	iii
ACKNOWLEDGEMENTS.....	iv
LIST OF ILLUSTRATIONS.....	vi
LIST OF TABLES.....	viii
LIST OF SYMBOLS/ABBREVIATIONS.....	ix
CHAPTER	
I. INTRODUCTION.....	1
II. RESULTS AND DISCUSSION.....	9
Part 1. Transition Metal Catalyzed Coupling.....	10
Part 2. Direct Nucleophilic Substitution.....	13
Part 3. Grignard Coupling Reactions.....	14
Part 4. Polymerization.....	18
Part 5. X-Ray Structural Analysis.....	21
Part 6. NMR Studies.....	24
III. EXPERIMENTAL.....	30
IV. CONCLUSIONS AND FUTURE RESEARCH.....	39
BIBLIOGRAPHY.....	43

LIST OF ILLUSTRATIONS

SCHEMES

1. Generalized synthetic routes to the target structures.....	10
2. Attempted preparation of diethyl 2,5-dimethylphenylphosphonate.....	11
3. Attempted preparation of dimethyl 2,5(diethoxyphosphoryl)terephthalate	11
4. Attempted preparation of 2-(2,5-dimethylphenyl)-4,4,5,5,-tetramethyl-1,3,2- dioxaborolane.....	12
5. Attempted preparation of 2,5-xylene diboronic acid.....	13
6. Attempted preparation of 2-(diethylphosphono)terephthalic acid.....	14
7. Preparation of 2-phosphonoterephthalic acid.....	14
8. Preparation of 2,5-dimethylphenylboronic acid	15
9. Oxidation of 2,5-Dimethylphenylboronic acid.....	16
10. Preparation of 1,4-Xylene-2,5-diboronic acid.....	17
11. Preparation of 2,5-diboronoterephthalic acid.....	18
12. Preparation of polyphosphonic acid-benzothiazole polymer (PAPBT)...	19
13. Preparation of polyphosphonic acid-hexafluorobenzoxazole (PAF6PBO)....	21
14. Reversible cleavage (hydration) of the anion of structure 13 in water.....	29

FIGURES

1. Schematic of a PEM fuel cell operation.....	2
2. Structure of Nafion.....	3
3. Generalized structure of proposed polymer repeat unit	5
4. Structures of the proposed target monomers	7
5. Viscosity of PAPBT.....	19
6. TGA data of PAPBT.....	20
7. TGA data of PAF ₆ PBO.....	21
8. ORTEP drawings of two orientations of structure 13.....	22
9. Crystal Packing Plots of structure 13.....	24
10. Variable temperature NMR data of compound 13 in D ₂ O.....	25
11. Variable temperature NMR data of compound 13 in DMSO- <i>d</i> ₆	25
12. Gas-phase calculated structure of the anionic part of compound 13. Data from a <i>B3LYP/6-31+G(d)</i> calculation.....	27
13. ¹ H NMR spectrum and proposed structure for the substance formed upon heating of a DMSO solution of 13 above 363 K.....	28

LIST OF TABLES

1. Selected bond lengths (in Å) and angles (in degrees) of structure 13.....23

LIST OF SYMBOLS/ABBREVIATIONS

1. CD_3OD : Methanol-*d*
2. CH_2Cl_2 : Methylene dichloride
3. D_2O : Deuterium Oxide
4. DIEA: Diisopropylethylamine
5. $\text{DMF-}d_7$: Dimethylformamide-*d*₇
6. DMSO: Dimethyl sulfoxide
7. $\text{DMSO-}d_6$: Methyl Sulfoxide-*d*₆
8. EtOAc: Ethylacetate
9. EtOH: Ethanol
10. H_2O : Water
11. HCL: Hydrochloric Acid
12. KMnO_4 : Potassium permanganate
13. KOH: Potassium hydroxide
14. MeOH: Methanol
15. MnO_2 : Manganese dioxide
16. mp: Melting point
17. NaCl: Sodium chloride
18. NaOH: Sodium hydroxide
19. NH_4Cl : Ammonium Chloride

- 20. NMR: Nuclear magnetic resonance
- 21. *P*: Para
- 22. PAF₆PBO: Polyphosphonic acid-hexafluorobenzoxazole
- 23. PAPBT: Polyphosphonic acid-benzothiazole polymer
- 24. PBI: Polybenzimidazole
- 25. PEM: Proton Exchange Membrane
- 26. PPA: Polyphosphoric acid
- 27. TGA: Thermogravimetric Analysis
- 28. THF: Tetrahydrofuran
- 29. TLC: Thin layer chromatography
- 30. wt: Weight

CHAPTER I

Introduction

Currently there are few polymers that can be used in multiple applications with little or no modification. There presently exist polymers that can improve fuel cell performance and provide fire retardant ability but none that can do both. Therefore, it is our goal to produce a polymer, or class of polymers, with a unique chemical structure that will provide enhancements to many current applications. Recently synthesized phosphonic and boronic acid functionalized terephthalic acids are two of these structures that could be useful in multiple applications.

With the prediction that fossil fuel supplies will run out in the near future there is a growing demand for alternative energy sources. One of these sources, the fuel cell, has been promoted for its ability to provide power which is clean and sustainable.¹

The fuel cell is an electrochemical conversion device that converts the chemical energy of a fuel (e.g. hydrogen) and oxygen into electricity at 40-50% efficiency. This efficiency is greater than that of an internal combustion engine or coal-fired power plant while requiring no moving parts which means that its maintenance needs are minimal.¹

One of the main types of fuel cell is the Proton Exchange Membrane Fuel Cell (PEM). This type of fuel cell was initially developed for use on the Gemini spacecraft. While the design proved successful, the cost of \$2000/kW limited its use to all but the most demanding applications. However, many recent advances in exchange membranes have shown the PEM to have the most promise for vehicular transportation and other portable power consuming applications due to its relative small size and power output.¹

The ability of the PEM fuel cell to produce power arises from the Proton Exchange Membrane. This class of fuel cells works by catalytically splitting H_2 fuel into protons and electrons and using the polymer membrane to separate the positively charged protons from the negatively charged electrons. The electrons are forced to travel through a circuit which generates the desired current. At the cathode the positively charged hydrogen and negatively charged electron are combined to form a byproduct, typically water, as shown in Figure 1.

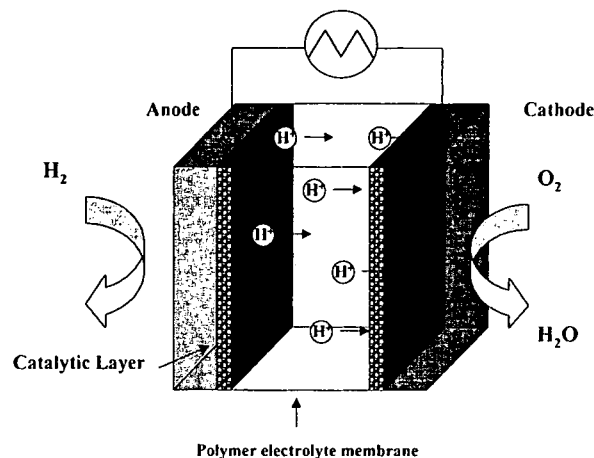


Figure 1. Schematic of a PEM fuel cell operation

For a PEM fuel cell to be commercially successful it must be low cost, have high proton conductivity (highly efficient) above 100 °C and below 0 °C, have good water uptake above 100 °C and be durable for many years.² Therefore, with the PEM being the heart of the fuel cell, much attention has been placed on its design. Currently, maximum performance is achieved by DuPont's Nafion™ membranes, whose structure is illustrated in Figure 2.

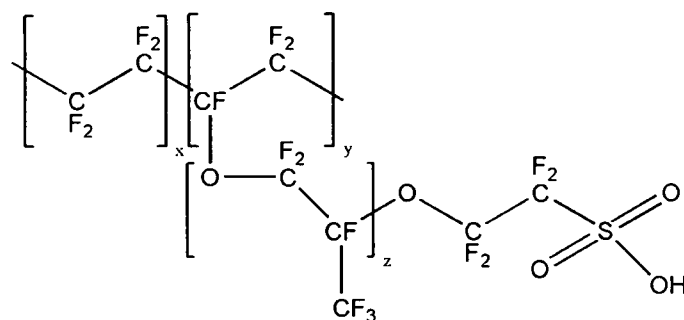


Figure 2. Structure of Nafion™

While the fluorinated polymer backbone of Nafion™ results in good water uptake and exhibits good mechanical and thermal stability, it also has many drawbacks which include high cost, low ionic conductivities at elevated temperatures (> 80 °C) and at low relative humidity, resulting in poor performance. Therefore, to achieve maximum performance the fluorinated backbone of Nafion™ needs to be fully hydrated. In the fully hydrated state the viscosity within the membrane is lower, generating greater ionic mobility and conductivity. This need for hydration requires a water management system to ensure proper function but results in higher cost and a narrow

operational window.² Such drawbacks are major impediments to widespread use of PEM fuel cells. Consequently, one of our research goals is finding a polymer membrane to improve upon the properties of Nafion and find a polymer system capable of operating "dry" or without the need for hydration. The introduction of a polymer system that could be operated dry would be a great improvement. A dry operating system would eliminate the need for a water management system and be able to operate at higher temperatures resulting in improved efficiency. Higher operating temperatures would also reduce costs by reducing the amount of catalyst required to split the H₂ fuel.

To find a polymer system that addresses these issues and overcomes the limitations of the Nafion membrane new polymeric structures have been proposed and studied. Specifically, it has been found that acid-base polymer systems in which a strong acid is incorporated into a basic polymer backbone are good proton conductors without requiring hydration. This proton conductivity is possible because the basic polymer backbone interacts with the strong acid and facilitates ion transport by the Grotthuss mechanism, eliminating the need for water entirely.³ One of these systems that has shown promise is the polybenzimidazole (PBI) class of polymers. The basic nature of the PBI polymer backbone has been shown to have higher proton conductivity at elevated temperatures (> 120 °C) and low relative humidity when doped with phosphoric acid. It was also shown that increased doping with phosphoric acid resulted in increased proton conductivity.^{3,4,5,6} In addition, the well known mechanical and thermal stability of PBIs, arising from

the rigid nature of the polymers, make them well suited for fuel cell use at high temperatures and low relative humidity.⁷ However, the PBI – phosphoric acid complex has the distinct disadvantage of phosphoric acid leeching from the polymer matrix over time, resulting in decreased performance and environmental hazards. Thus, to overcome this disadvantage while retaining the acid-base PBI properties required for effective ion transport we propose incorporating an organic acid functional group, specifically phosphonic and boronic acid into the polymer backbone to eliminate the possibility of leeching. Previous work has been done to maintain the acid-base properties by the incorporation of a sulfonic acid into the polymer chain. However, when exposed to heat the polymer would spontaneously desulfonate and lose the acid functionality.⁸ Therefore to improve upon this design we propose a substituted phosphonic and boronic acid structure, shown in Figure 3, in which the acid functionality, required for effective ion transport, is incorporated into the polymer backbone.

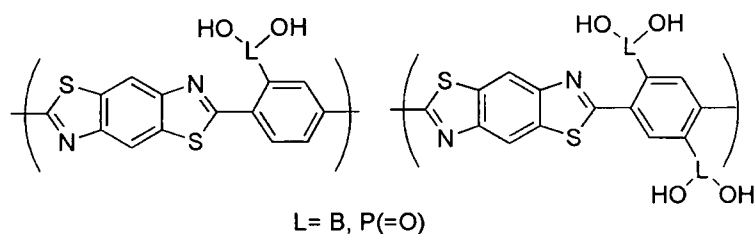


Figure 3. Generalized structure of proposed polymer repeat unit

In this configuration the acid functionality is very robust and will not leech from the polymer matrix, ultimately yielding a PBI based polymer that will minimize

water management issues and lead to a simplified design, resulting in a low cost fuel cell.

Fire safety is another intriguing aspect of our polymer design. The hydrocarbon backbone in the majority of polymers currently produced makes them inherently flammable. While the incorporation of several types of functional groups, such as halogen atoms, into the polymer chain can reduce flammability many drawbacks still remain. For example, polyvinylchloride is more flame resistant than polyethylene because the incorporation of a vinyl chloride can inhibit free radical reactions at the flame leading to self extinguishment.⁹ However, the leeching of HCl from the polymer over time poses distinct health and environmental dangers.

Our polymer design resolves the problem of leeching while continuing to be inherently flame resistant. This resistance is caused by the boronic or phosphonic pendant group's ability to form cross links between polymer chains when exposed to flame.¹⁰ These cross links prevent the material from flowing like a normal thermoplastic. It is this lack of flow that results in more of the carbon fuel being held in place, substantially increasing thermal stability of the underlying polymer. In addition the char that is formed when exposed to flame can engulf the underlying polymer preventing additional carbon fuel from being burned, ultimately leading to self extinguishing. While adding borate or phosphate additives is a common practice to lower the flammability of a polymer, the additives themselves can be problematic.¹¹ This is because the additive is not part of the polymer backbone structure; it is merely added

to the polymer matrix. Thus, overtime, the additives, which are often toxic, can leech out of the polymer matrix during use or recycling resulting in degradation to mechanical properties and health issues to the user. Our polymer design, which incorporates the robust phosphonic or boronic group into the polymer backbone, would eliminate these problems because the functional group could not be easily removed, resulting in a polymer that is inherently flame resistant for its entire life cycle.

We are therefore proposing the preparation of phosphonic acid or boronic acid substituted terephthalic acids as monomers for a new generation of inherently flame retardant, proton conducting polymers. Some proposed monomer units are shown in Figure 4.

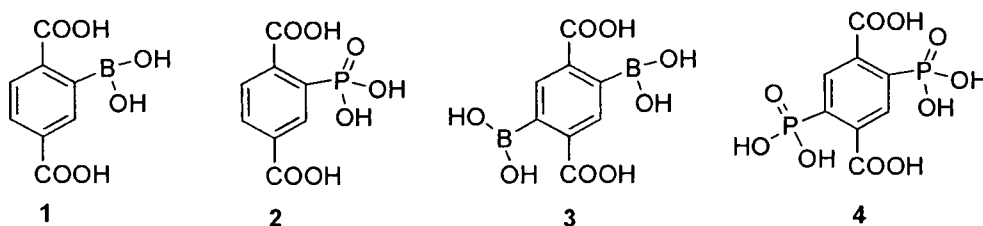


Figure 4. Structures of the proposed target monomers.

In summary, this monomer design would be ideal for use in fuel cell applications because the acid-base nature of the polymer would provide excellent proton transport while requiring little water and possessing, at the same time, good mechanical stability. The monomer design would also be ideally suited for lowering the flammability of currently produced polymers. By incorporating our monomer into the structure of many commonly used

polymers the flammability would be greatly reduced without the need for toxic additives.

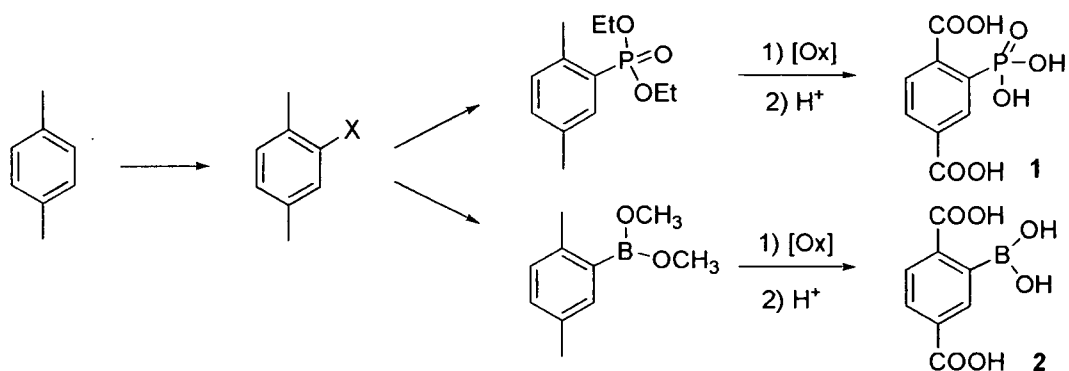
CHAPTER II

Results and Discussion

It has been the goal of our group to prepare separately phosphonic and boronic acid substituted terephthalic acids (**1**, **2**). In general, as shown in Scheme 1, these substituted terephthalic acids would be prepared by an initial halogenation of a hydrocarbon, such as *p*-xylene. The halogen would then be replaced by a phosphorous- or boron-containing functional group and the aromatic methyl groups would be oxidized to carboxylic acid units. Lastly, the phosphonic or boronic ester moiety would be hydrolyzed to yield the desired acid. Several synthetic routes are possible for the preparation of the targets and one of them relies on the use of transition metal catalyzed coupling. We started with attempts to utilize this particular approach because if our work was ever to be reproduced on a large scale, the use of catalyst would provide a route that did not involve sensitive conditions such as inert, water-free environment. However, so far, such attempts have proved unsuccessful. Another strategy relies on the generation and use of aryl Grignard reagents. Using Grignard reagents, we have been able to successfully couple the boron and phosphorous moieties to the *p*-xylene aromatic system.

Scheme 1

Generalized synthetic routes to the target structures



PART 1. Transition Metal Catalyzed Coupling

A. Attempted preparation of diethyl 2,5-dimethylphenylphosphonate

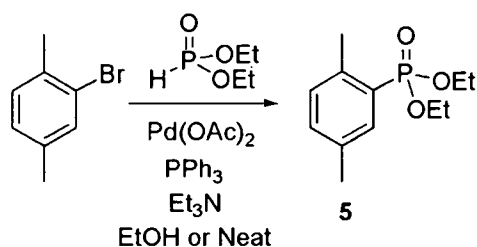
(5): The synthesis of target molecule **5** was attempted using a literature protocol.¹² Palladium acetate was used to catalyze the coupling of diethylphosphite and 2-bromo-*p*-xylene in the presence of triphenylphosphine and triethyl amine, in DMSO solvent, as shown in Scheme 2. This reaction, however, did not yield the desired product. The synthesis was also conducted in absolute EtOH, or without solvent. In each instance a mix of starting materials was isolated. In a separate attempt, tetrakis(triphenylphosphine)palladium was used as a coupling catalyst, in the presence of triethylamine and ethanol solvent, but again no desirable product was isolated, as evidenced by the NMR.

Our results were not entirely surprising, as it is increasingly evident that *ortho* substituted aromatic compounds are not receptive to transition

metal catalyzed coupling, possibly due to the steric bulk near the halogenated position.¹³

Scheme 2

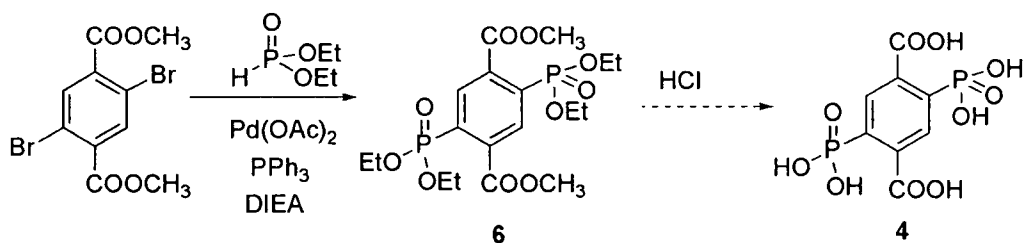
Attempted preparation of diethyl 2,5-dimethylphenylphosphonate



B. Attempted preparation of dimethyl 2,5-(diethoxyphosphoryl)terephthalate (6): In an attempt to introduce two phosphonic acid functional groups we carried out a coupling reaction with a palladium catalyst, as shown in Scheme 3.¹⁴ Palladium acetate was used with diethylphosphite and dimethyl 2,5-dibromoterephthalate, in the presence of diisopropylethylamine (DIEA) and triphenylphosphine, in ethanol solvent. However, only a mixture of starting materials was isolated.

Scheme 3

Attempted preparation of dimethyl 2,5(diethoxyphosphoryl)terephthalate

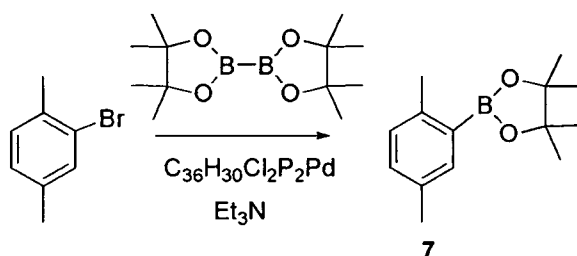


If structure **6** had been isolated, the ester would have been subsequently hydrolyzed to yield the desired terephthalic acid **4**, without the need for oxidation.

C. *Attempted preparation of 2-(2,5-dimethylphenyl)-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane (7)*: This synthesis was conducted using bis(triphenylphosphine)palladium(II) chloride as a catalyst.¹⁵ 2-Bromo-*p*-xylene was reacted with bis(pinacolato)diboron in the presence of triethylamine, in toluene, as shown in Scheme 4. However, NMR analysis revealed that only starting materials were collected.

Scheme 4

Attempted preparation of 2-(2,5-dimethylphenyl)-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane



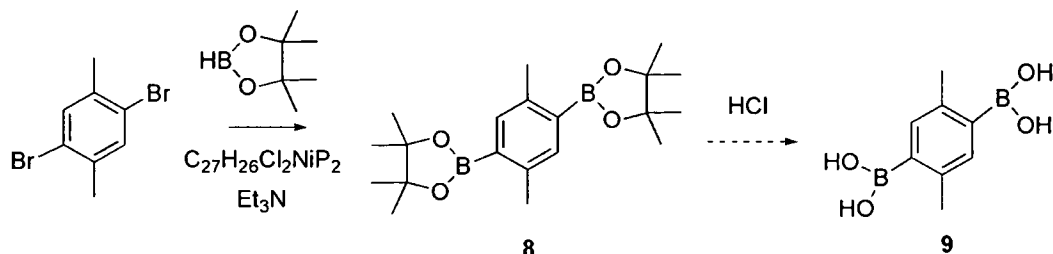
D. *Attempted preparation of 2,5-xylenediboronic acid (9)*: For this preparation a literature protocol was followed.¹⁶ 1,3-Bis(diphenylphosphino)propanenickel(II) chloride was used to couple 4,4',5,5'-tetramethyl-1,3,2-dioxaborolane with 2,5-dibromo-*p*-xylene in the presence of triethylamine, in toluene solvent, as shown in Scheme 5. This protocol first introduces the 2,5-dipinacolboronate ester **8**, which would be subsequently hydrolyzed to yield

the diboronic acid. However after hydrolysis only an inorganic salt was isolated and NMR data did not show presence of any organic structure.

According to a separate publication, target molecule **9** may be obtainable by using a diGrignard reagent.¹⁷ The diGrignard moiety would be formed using 2,5-dibromo-*p*-xylene and subsequently coupled to trimethyl borate under inert atmosphere.

Scheme 5

Attempted preparation of 2,5-xylene diboronic acid



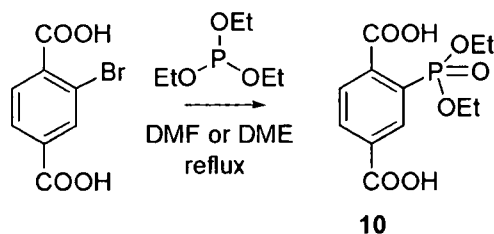
PART 2. Direct Nucleophilic Substitution

A. Attempted preparation of 2-(diethylphosphono)terephthalic acid (**10**):

To avoid the use of palladium catalyst and the need for oxidation, a direct nucleophilic substitution reaction of triethyl phosphite and 2-bromoterephthalic acid was attempted in toluene, as demonstrated in Scheme 6.¹⁸ NMR analysis revealed the starting 2-bromoterephthalic acid never reacted and was recovered in high quantity. To promote nucleophilic substitution the solvent was changed to dimethylformamide or dimethoxyethane. However, the starting 2-bromoterephthalic acid was again recovered in both reactions.

Scheme 6

Attempted preparation of 2-(diethylphosphono)terephthalic acid

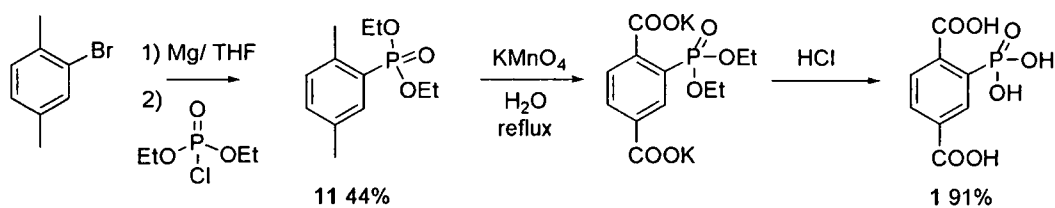


PART 3. Grignard Coupling Reactions

A. *Preparation of 2-phosphonoterephthalic acid (1)*: For this preparation, as shown in Scheme 7, the phosphorous functionality was introduced at the stage of a halogenated dialkylbenzene, using the latter as a precursor to a Grignard reagent. The reaction resulted in the generation of an aromatic phosphonic ester (**11**), which was oxidized by KMnO_4 to convert the alkyl groups into carboxylic acid moieties. The oxidation was followed by acidification, in which the phosphonic ester is also hydrolyzed.¹⁹

Scheme 7

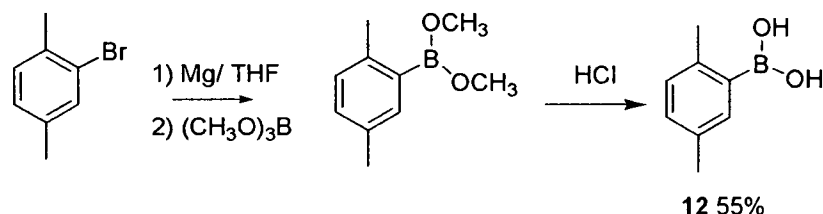
Preparation of 2-phosphonoterephthalic acid



B. *Preparation of 2,5-Dimethylphenylboronic acid (12)*: The synthesis of target molecule (**12**) was achieved in a manner shown in Scheme 8. In a preparation similar to a literature protocol, a Grignard reagent was reacted with trimethylborate to introduce the boronic ester.²⁰ The resulting ester was then hydrolyzed to form 2,5-dimethylphenylboronic acid (**12**) in a 55% yield.

Scheme 8

Preparation of 2,5-dimethylphenylboronic acid

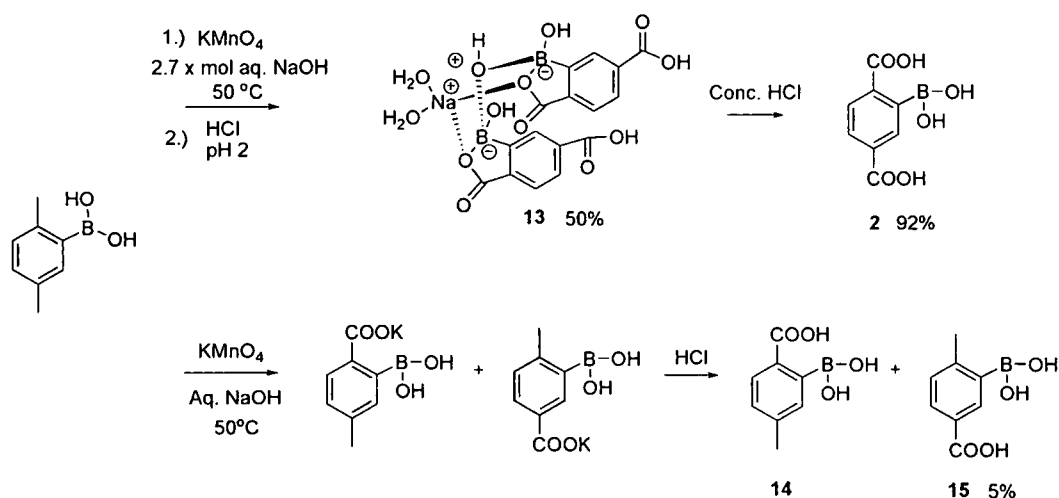


C. *Preparation of 2-boronoterephthalic acid (2)*. The conversion of **12** into the boronoterephthalic acid was achieved by oxidation with $KMnO_4$ in basic conditions.²¹ As reflected in Scheme 9, when NaOH was kept in a mol ratio of 2.7 times greater than $KMnO_4$, both methyl groups were oxidized. However, if the mol ratio was 1.5 times greater than $KMnO_4$, then only one methyl group was oxidized, preferentially forming one product (**16**) at a rate of 10:1. The identity of the major monooxidation product was established by comparison with literature data on structure 16.²² While this result is not useful for our research goals, the selective oxidation may be useful for other

applications such as Suzuki coupling reactions and its further study would be valuable.

Scheme 9

Oxidation of 2,5-Dimethylphenylboronic acid

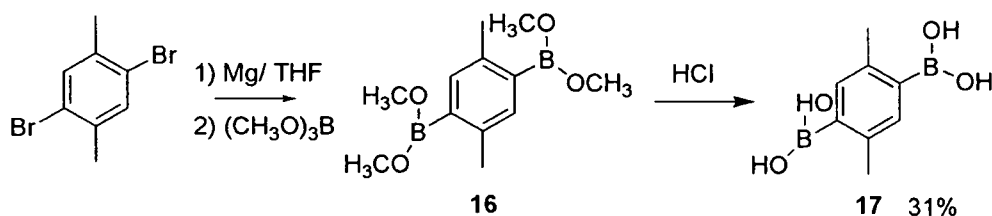


While oxidation of the two methyl groups proved to be fairly straightforward, the isolation of the fully protonated structure **2** required some extensive preliminary analysis. As shown in Scheme 9, acidification of the oxidation mixture to pH 2.0 actually led to the generation of the monosodium salt of a covalent dimer of 2-boronoterephthalic acid (Structure **13**). The structure of compound **13** was unambiguously demonstrated using X-ray structural analysis, which, in its turn, was necessitated by the peculiar NMR behavior of the compound, especially in polar aprotic solvents, such as DMSO and DMF. Detailed discussion of the NMR observations and the X-ray analysis is offered in Parts 5 and 6 of the Results and Discussion. Compound **2** was isolated only after subsequent treatment of **13** with conc. HCl.

C. *Preparation of 1,4-xylene-2,5-diboronic Acid (17)*: The diboronic acid **17** was prepared utilizing the chemistry reflected in Scheme 10.¹⁷ A Grignard reagent was used to introduce the boronic ester functionality. The success of Grignard reagent generation depended in this case on the grade of Mg used in the process, as well as the use of small amounts of Mg surface activators, such as I₂ and 1,2-dibromoethane. The boronic ester was introduced by the use of trimethyl borate. The resultant ester **16** was subsequently hydrolyzed with HCl to the desired diacid.

Scheme 10

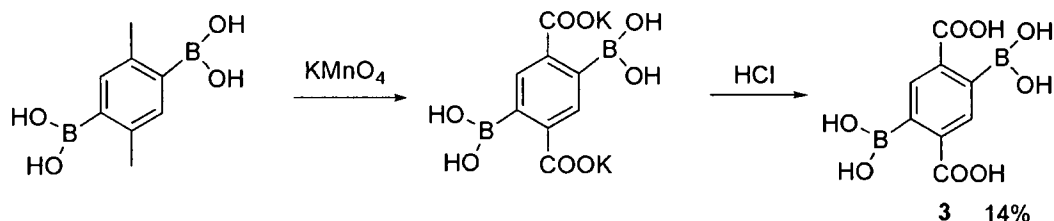
Preparation of 1,4-xylene-2,5-diboronic acid



D. *Preparation of 2,5-diboronoterephthalic acid (3)*. Similar to the case of generation of structure **2**, 1,4-xylene-2,5-diboronic acid was reacted with KMnO₄ in basic conditions (aq. NaOH) and hydrolyzed to yield the desired product (Scheme 11).²¹

Scheme 11

Preparation of 2,5-diboronoterephthalic acid



PART 4. Polymerization

A. Preparation of polyphosphonic acid-benzothiazole polymer (PAPBT)

(19): The polymerization to generate target structure (19), reflected in Scheme 12 was achieved using a step condensation mechanism. 2-Phosphonoterephthalic acid and 2,5-diamino-1,4-benzenedithiol were combined in 77 wt% polyphosphoric acid (PPA). Viscosity analysis, as shown in Figure 5, revealed that the polymer had a viscosity of 0.88 dL/g, indicating that a polymer of approximately 2,000 g/mol was formed. While this confirmed that some polymerization took place, the molecular weight is not nearly as high as a typical polymer such as polystyrene which will typically have a molecular weight exceeding 1,000,000 g/mol. TGA analysis, as shown in Figure 6, revealed thermal decomposition at 537 °C, which is encouraging because the significant mass loss does not occur until relatively high temperatures are reached.

The formation of a low molecular weight polymer could be the result of several factors including purity and reaction conditions. However, in this instance it is presumed that the rigid nature of both monomers was the cause

of the low molecular weight polymer being formed. It is assumed that the rigid nature of the main chain would not be flexible enough to allow for the formation of a high molecular weight polymer.

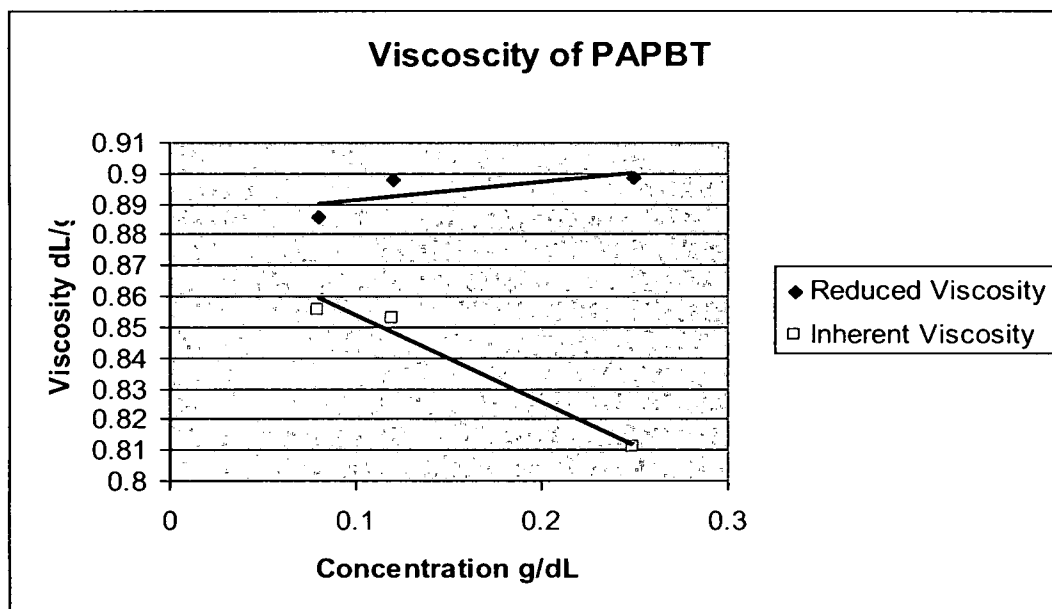
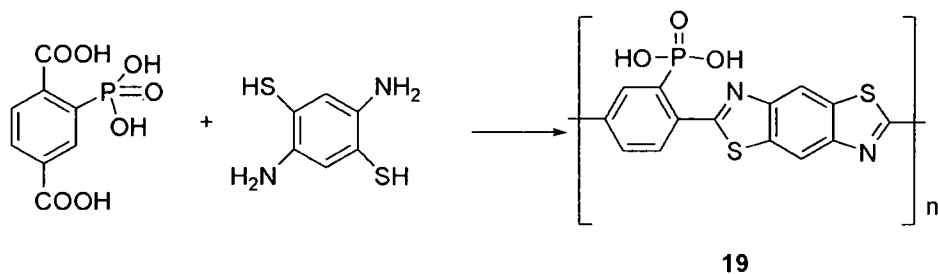


Figure 5. Viscosity of PAPBT (19).

Scheme 12

Preparation of polyphosphonic acid-benzothiazole polymer (PAPBT)



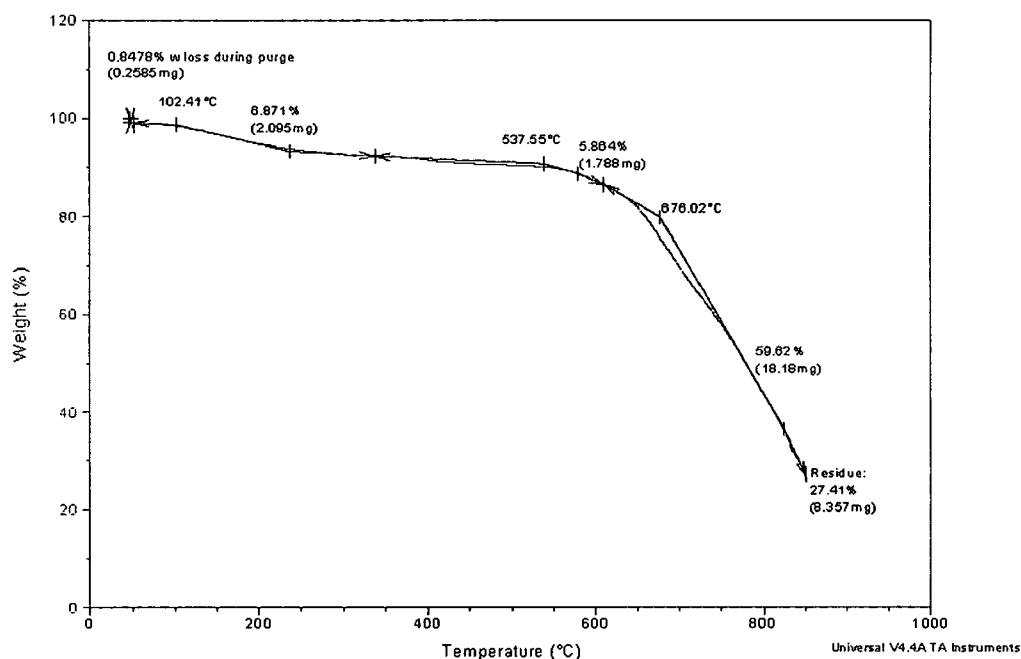


Figure 6. TGA data of PAPBT (19).

B. Preparation of polyphosphonic acid-hexafluorobenzoxazole (PAF6PBO) (20): In order to overcome the limitations of the rigid nature of the polymer formed from the 2,5-diamino-1,4-benzenedithiol, 4,4'-(perfluoropropane-2,2-diyl)bis(2-aminophenol), a more flexible monomer, was reacted with 2-phosphonoterephthalic acid in 83 wt% PPA. It was presumed that the hexafluoro linkage would make the polymer more flexible, in turn leading to greater reactivity and ultimately a higher molecular weight polymer. However, film casting of the polymer was unsuccessful indicating that a low molecular weight polymer was formed again. Thermal analysis data, shown in Figure 7, was collected in air and revealed that thermal breakdown occurred at 465 °C, which again is encouraging, in light of the desired high thermal stability of the polymer products.

Scheme 13

Preparation of polyphosphonic acid-hexafluorobenzoxazole (PAF₆PBO)

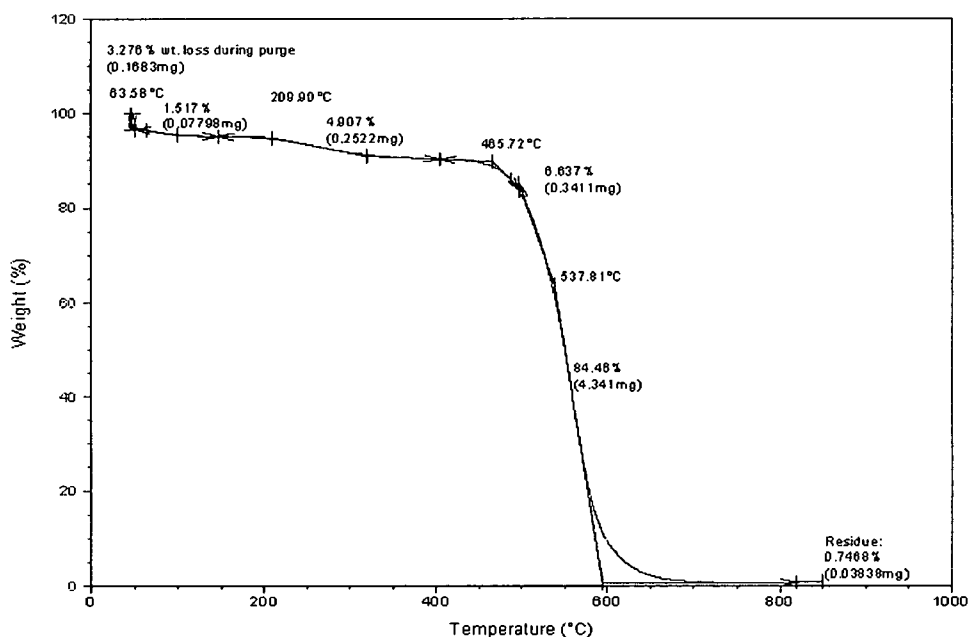
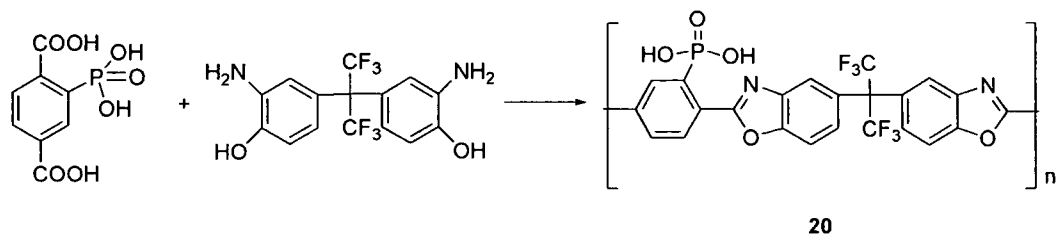


Figure 7. TGA data of PAF₆PBO (20)

PART 5. X-Ray Structural Analysis

X-Ray structural analysis was performed on a single crystal of structure **13** at 140 K. ORTEP plots of the asymmetric unit are shown in Figure 8. Compound **13** was confirmed to be a monosodium salt of the

covalently bonded dimer of 2-boronoterephthalic acid, with an oxygen link between the two boron centers.

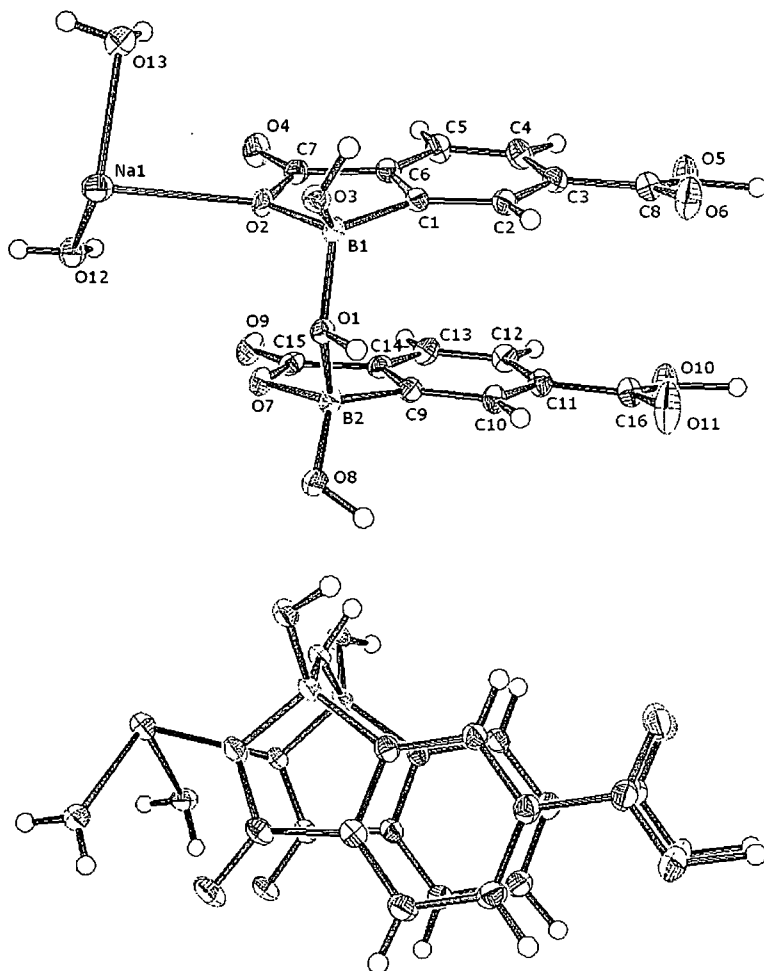


Figure 8. ORTEP drawings of two orientations of structure **13**.

The asymmetric unit exhibits an almost perfect stacking of the two aromatic rings, as evidenced by the value of the dihedral angle O3 - B1 - B2 - O8, which is approximately 2° . The dimer is highly symmetric with respect to the oxygen center O1, with the two B - O1 bonds having values of 1.55 Å. Each

boron center is part of a five-membered ring, which could be properly described as a cyclic, mixed carboxylic-boronic acid anhydride ring. Each boron center has a hydroxyl group attached to it, and the B – OH distances are virtually identical (about 1.43 Å). The carboxyl groups, as expected, are co-planar with the aromatic rings. In the asymmetric unit, each sodium atom is coordinated to two molecules of water, and the two Na – H₂O distances are very similar (2.34 and 2.39 Å correspondingly). Table 1 lists selected values of bond distances and bond dihedral angles.

Table 1. Selected bond lengths (in Å) and angles (in degrees) of structure **13**.

Structural parameter	Value
B1 - O1	1.555 (2)
B2 - O1	1.552 (2)
B2 - O8	1.433 (3)
B1 - O3	1.426 (2)
Na1 - O2	2.583 (15)
B1 - O2	1.528 (2)
B2 - O7	1.515 (2)
C7 - O4	1.215 (2)
B2 - O1 - B1	132.09 (15)
O13 - Na1 - O12	104.37 (8)
O3 - B1 - O2	111.64 (15)
O9 - C15 - C14	127.53 (17)

Two plots of the crystal packing of structure **13** are shown in Figure 9. Association in the crystal is realized in two different ways: 1) By coordination of oxygen centers from the five-membered rings to sodium ions, and 2) By complimentary hydrogen bonding of the carboxyl groups, in a fashion typical for carboxylic acids in general. The hydrogen bond distances within the carboxylic acid dimer are 1.38 and 1.42 Å.

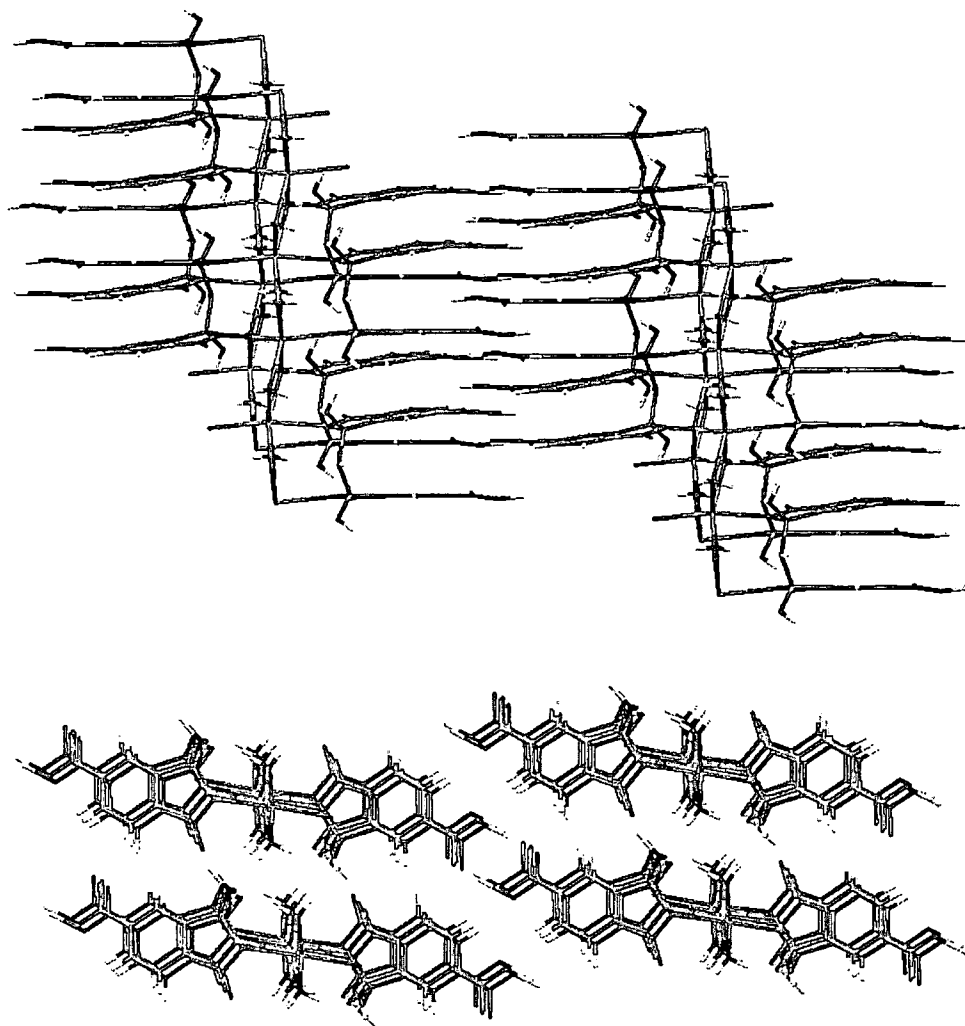


Figure 9. Crystal packing plots of structure 13.

PART 6. NMR Studies

As mentioned earlier, collecting NMR data for structure **13** in several different solvents led to some interesting observations. The NMR spectrum collected in D_2O exhibited the typical pattern for a 1,2,4-trisubstituted benzene ring, namely a doublet, a doublet of doublets and a singlet, as shown in Figure 10.

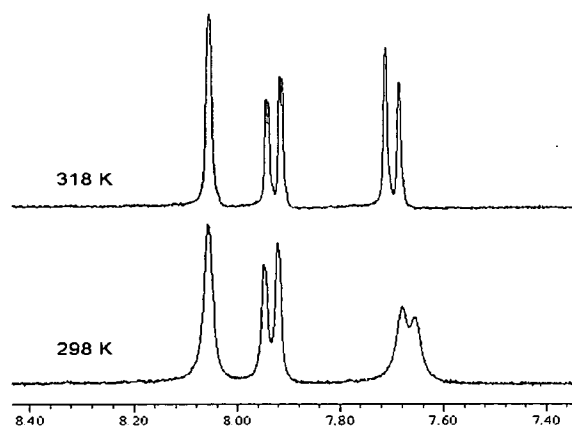


Figure 10. Variable temperature NMR data of compound **13** in D₂O.

On the other hand, NMR data collected at room temperature in DMSO-*d*₆ or DMF-*d*₇ exhibited each two sets of aromatic signals, of the same pattern (that of a 1,2,4-trisubstituted benzene ring), and of equal intensity (Figure 11).

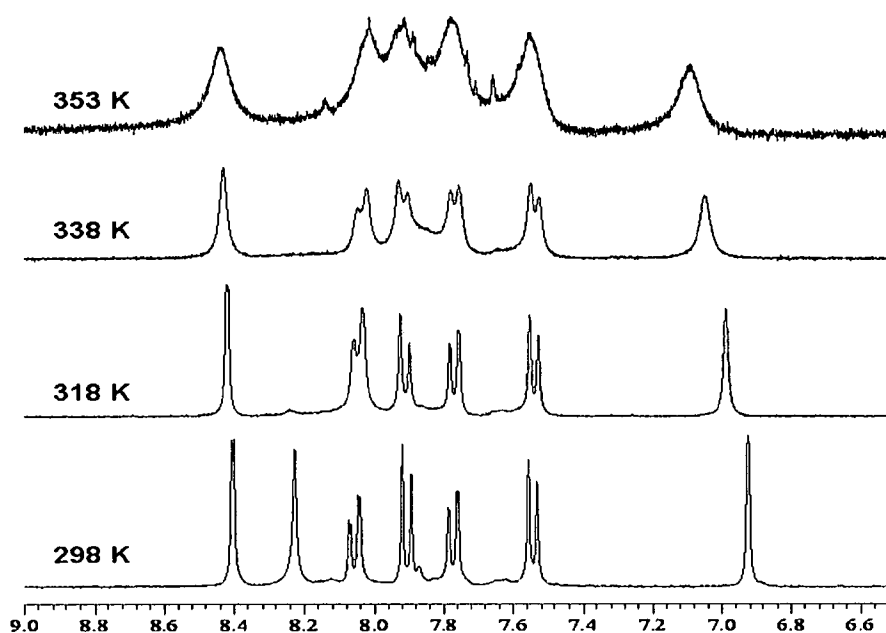


Figure 11. Variable temperature NMR data of compound **13** in DMSO-*d*₆.

Prior to obtaining explicit knowledge on the structure of **13**, several different hypotheses were advanced to account for the unexpected NMR pattern in DMSO and DMF. One of them was based on a proposed hydrogen-bonded dimerization of 2-boronoterephthalic acid, placing the two aromatic rings in different chemical environments. Another explanation was based on the potential donor – acceptor interaction with the solvent. From the successfully carried X-ray analysis we know at present that structure **13** does indeed have two aromatic rings, although in the solid state they are in an identical environment. As mentioned in the previous section, the dihedral angle O3 – B1 – B2 – O8 is roughly 2° in the solid state, and the structure is highly symmetrical. However, in the calculated gas-phase structure (and possibly also in the structure in solution) the same dihedral angle (O3 – B1 – B2 – O8) was found to have an approximate value of 75° (Figure 12). In other words, when not packed in the solid state, the dimer is no longer symmetrical and the two aromatic rings (and the hydrogen atoms belonging to them) are in different environments. The calculated NMR spectrum of this non symmetrical dimer gives well-separated signals for all six aromatic hydrogen atoms, with chemical shifts ranging from 7.06 - 8.11 ppm. The experimentally determined range is 6.92 - 8.40 ppm in DMSO-*d*₆ and 7.24 – 8.64 ppm in DMF- *d*₇. One reasonable explanation therefore would be that the spectra collected in DMSO-*d*₆ and DMF-*d*₇ arise from this non-symmetrical dimer structure.

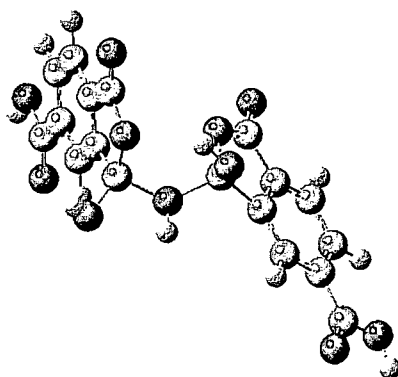


Figure 12. Gas-phase calculated structure of the anionic part of compound **13**. Data from a *B3LYP/6-31+G(d)* calculation.

In order to gain further understanding, NMR data was collected at elevated temperatures in both DMSO-*d*₆ and DMF-*d*₇. In each instance, when the temperature was raised, significant broadening of the signals occurred, as shown in Figure 11. This broadening could most likely be accounted for by an increased rate of rotation around the B – O1 bond in the dimer. However, before coalescence is reached, the dimer undergoes thermal decomposition, very likely amounting to an overall dehydration process for each unit of 2-boronoterephthalic acid. The newly observed species (Figure 13), whose spectrum becomes evident at and above 363 K, is permanent and the spectral features do not change upon cooling. However, full reversibility is observed if samples of **13** are heated up to 353 K.

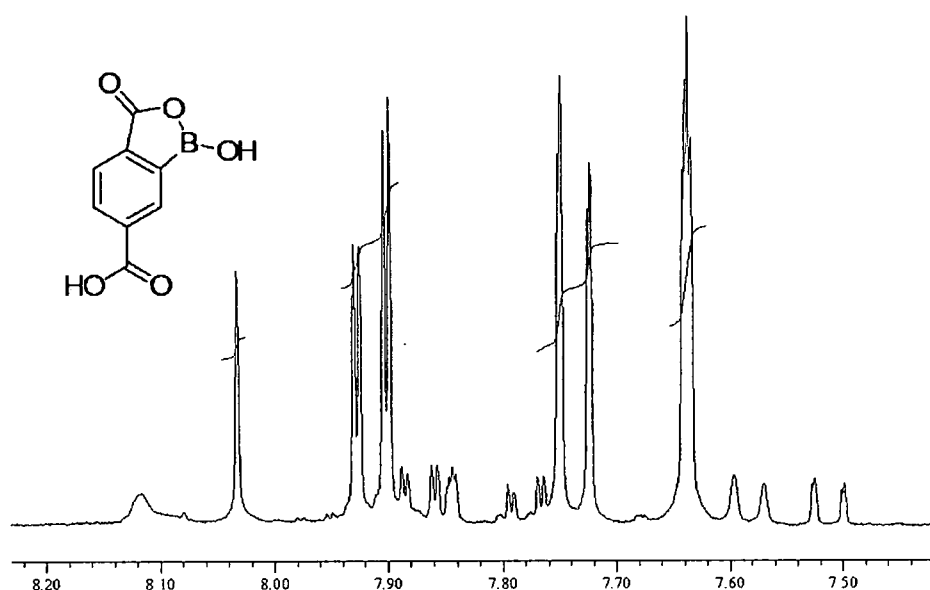
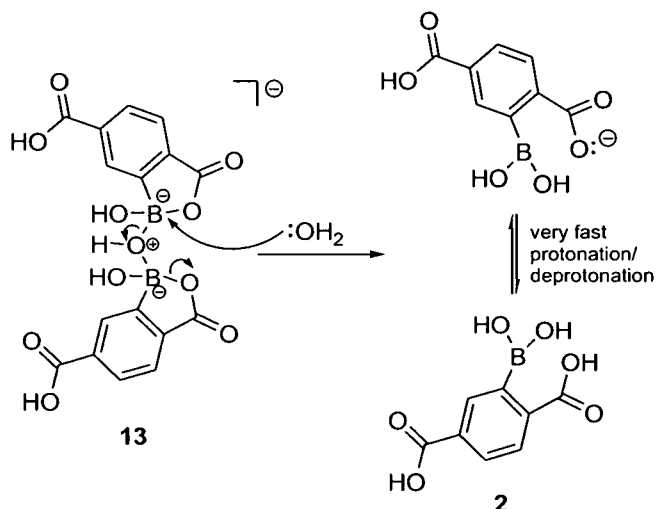


Figure 13. ^1H NMR spectrum and proposed structure for the substance formed upon heating of a DMSO solution of **13** above 363 K.

The observed NMR spectrum in D_2O , with a single set of aromatic signals, can be accounted for by cleavage of the dimer in solution. D_2O (or H_2O) is a nucleophilic, protic solvent. It is possible that in its presence the dimer is converted into two units of 2-boronoterephthalic acid (i.e. it is hydrated), as shown in Scheme 14. In such a case one would expect a single set of aromatic signals in the NMR spectrum. Such explanation, however, is valid only if the cleavage of the dimer is reversible, since it is a well-known fact that the compound can be recrystallized from water without any structural change.

Scheme 14

Reversible cleavage (hydration) of the anion of structure **13** in water.



Another explanation of the observed NMR behavior could be based on the extensive hydrogen bonding present in D_2O . It could lock the dimer into the symmetrical configuration, identical to that present in the crystal structure. In such structure the hydrogen atoms are in the same environment, which would correspond to only one set of peaks. Of the two hypotheses, the former seems to be better supported by experimental evidence. When **13** is protonated in concentrated HCl and transformed into 2-boronoterephthalic acid, the NMR spectrum of the resultant substance in D_2O is identical to the NMR spectrum of **13** in D_2O .

CHAPTER III

Experimental

X-ray crystallography of sodium 1,1'-oxoniobis(6-carboxy-1-hydroxy-3-oxo-1,3-dihydrobenzo[c][1,2]oxaborol-1-uide) (13). A colorless crystal of approximate dimensions 0.042 mm x 0.213 mm x 0.477 mm was mounted on a glass fiber. The X-ray intensity data were measured at 140 K on an Oxford Diffraction Xcalibur3 system equipped with a graphite monochromator and an Enhance (Cu) X-ray source ($\lambda=1.54178$ Å) operated at 2 kW power (50 kV and 40 mA). The detector was placed at a distance of 45 mm from the crystal. Final cell constants were obtained through a global refinement of all reflections. Intensity data were collected employing the *CrysAlisPro* CCD software program.²³ Data frames using φ and ω scans were integrated with the *CrysAlisPro* RED.²³ The ω scan width was 1.0°. The integration of the data yielded a total of 6368 reflections to a maximum 2θ angle of 135.0° (0.83 Å resolution). The structure was solved and refined using Bruker SHELXTL (v6.10).²⁴ Crystal data: C₁₆H₁₅B₂O₁₃Na, MW = 459.89, Z = 2, triclinic P-1, a = 6.7216(4), b = 7.1116(3), c = 19.2629(11) Å, α = 80.232(4), β = 81.827(5)°, γ = 83.005(4)°, V = 893.71(8) Å³, ρ_{calc} = 1.709 g cm⁻³, 3037 unique reflections, 2386 with I > 2 σ (I), μ = 1.482 mm⁻¹, anisotropic, hydrogen atoms were located in difference Fourier map and refined

isotropically, $R = 0.0503$ all reflections, $R = 0.0375 > 2\sigma(I)$, $wR = 0.0993$ all reflections, $wR = 0.0933 > 2\sigma(I)$, residual electron density minimum -0.347 , residual electron density maximum 0.232 \AA^{-3} .

Attempted synthesis of 2,5-dimethylphenylphosphonate (5):

Tiethylamine (1.67 mL, 0.012 mol), 2-bromo-*p*-xylene (1.85 g, 10.00 mmol), palladium acetate (0.045 g, 2 mol%), triphenylphosphine (0.078 g, 3 mol%) and diethylphosphite (1.53 mL, 12.00 mmol) were added to 50 mL of anhydrous ethanol and stirred under nitrogen, in a dry three neck flask for 18 hours. The solvent was removed under reduced pressure and the residue was filtered through a short silica gel column using successively hexane (150 mL), and dichloromethane (150 mL), ethylacetate (150 mL). Yellow oil was obtained (2.34 g), NMR was obtained and showed that the starting material was isolated.

Attempted synthesis of 2,5-dimethylphenylphosphonate (5): 2-

Bromo-*p*-xylene (2.08 mL, 15.00 mmol), triethylamine (2.24 mL, 16.00 mmol), tetrakis(triphenylphosphine)palladium(II) (0.093 g, 4 mol%), diethyl phosphite (2.05 mL, 16.00 mmol), and anhydrous ethanol (15 mL) were combined under nitrogen atmosphere. The reaction mixture was refluxed for 24 hours. The solvent was removed under reduced pressure and the residue was filtered through a short silica gel column using successively methylene chloride and ethyl acetate. TLC analysis revealed the starting material.

Attempted synthesis of dimethyl 2,5-(diethoxyphosphoryl)

terephthalate (6): Dimethyl 2,5-dibromoterephthalate (0.35 g, 1.00 mmol),

$\text{Pd}(\text{OAc})_2$ (0.018 g, 8 mol%), triphenylphosphine (0.026 g, 10 mol%) N,N-diisopropyletylamine (0.38 mL, 2.20 mol), diethylphosphite (0.28 mL, 2.20 mol) and ethanol were combined in nitrogen atmosphere and refluxed for eight hours. The solvent was removed under reduced pressure and the resulting oil was purified by high vacuum distillation at 60 °C. The remaining residue was purified by flash chromatography using successively hexane, methylene chloride and ethyl acetate, yielding a small amount of yellow oil. NMR analysis revealed the starting diethylphosphite was isolated.

Attempted synthesis of 2-(diethylphosphono)terephthalic acid (10):

2-Bromoterephthalic acid (1.23 g, 5.00 mmol) and triethylphosphite (1.44 mL, 8.30 mmol) were added to toluene (25 mL) under nitrogen. The reaction mixture was allowed to stir at 25 °C for 5 days and then the solvent was removed under reduced pressure. A white solid was precipitated with hexanes and vacuum filtered. The mp (240 °C) and NMR showed the product to be the starting terephthalic acid.

Diethyl 2,5-dimethylphenylphosphonate (11): To a suspension of magnesium powder (1.42 g, 58.42 mmol) and anhydrous THF (80 mL) were added several drops of dibromoethane and 2-bromo-*p*-xylene. The solution was heated with a heat gun until reflux began. 2-Bromo-*p*-xylene (6.72 mL, 48.68 mmol) was then added dropwise at a rate to maintain reflux. Upon completed addition the solution was stirred at 60 °C for 1 hr and allowed to cool to room temperature. The reaction mixture was transferred dropwise into a solution of diethylchlorophosphate (7.00 mL, 48.68 mmol) in THF (20 mL) at

0 °C. Stirring was continued for 1 hr, then at 60 °C for 12 hours. A solution of aqueous NH_4Cl was added and the organic layer separated. The aqueous layer was saturated with NaCl and the organic layers were combined, dried with MgSO_4 and reduced to minimal volume under reduced pressure. The residue was then filtered through a short silica gel column using successively hexane : CH_2Cl_2 (1:1), hexane : EtOAc (1:3) and EtOAc. The solvent was removed under reduced pressure to yield a colorless oil (4.40 g, 44%). ^1H NMR (CDCl_3) δ 1.25 (t, J = 6.0 Hz, 6H), 2.26 (s, 3H), 2.45 (s, 3H), 3.95-4.12 (m, 4H), 7.04 (d, J = 6.0 Hz, 1H), 7.14 (d, J = 6.0 Hz, 1H), 7.66 (d, J = 1.5 Hz, 1H)

2-Phosphonoterephthalic acid (1): Diethyl 2,5-dimethylphenyl phosphonate (4.33 g, 17.80 mmol) and water (90 mL) were heated to reflux. KMnO_4 (11.23 g, 71.50 mmol) was added over a 1 hr period in 1 - 2 g portions using a solid addition funnel, which was periodically washed with small amounts of water. The solution was then refluxed at 110 °C overnight. The MnO_2 was vacuum filtered and filtrate concentrated to 1/3 original volume. HCl was added and the mixture refluxed for four hours. The solution was cooled to room temperature and let stand at 15 °C overnight. The resulting white solid was vacuum filtered and washed with cold water, yielding a white powder (4.00 g, 91%). Mp 295 °C – 297 °C ^1H NMR ($\text{DMSO}-d_6$) δ 2.49 (t, J = 3.0 Hz, 3H), 7.83 (dd, J_1 = 9.0 Hz, J_2 = 6.0 Hz, 1H), 8.00 (dt, J_1 = 9.0 Hz, J_2 = 3.0 Hz, 1H), 8.41 (dd, J_1 = 1.5 Hz, J_2 = 3.0 Hz, 1H)

Attempted synthesis of 2,5-xylene diboronic acid (9): 2,5-Bromo-*p*-xylene (1.47 mL, 11.00 mmol), 4,4',5,5'-tetramethyl-1,3,2-dioxaborolane (pinacol borane) (2 mL, 13.80 mmol), 1,3 bis(diphenylphosphino)propanenickel(II) chloride (0.172 g, 0.318 mmol), triethylamine (11.82 mL, 85.00 mmol) and toluene were combined in dry nitrogen atmosphere. The reaction mixture was refluxed for 24 hours and washed with NH₄Cl. The organic and aqueous layers were separated and the aqueous layer was extracted with ether. The organic solvent was removed under reduced pressure and the residue was hydrolyzed using MeOH (20 mL) and HCl (20 mL, 3M). The solution was refluxed for 3 hours and the MeOH was removed under reduced pressure to yield an oily product.

Attempted synthesis of 2-(2,5-dimethylphenyl)-4,4',5,5'-tetramethyl-1,3,2-dioxaborolane (7): 2-Bromo-*p*-xylene (0.34 mL, 2.50 mmol), bis(pinacolato)diboron (1.00 g, 3.90 mmol), bis(triphenylphosphine)palladium(II) chloride (1.05 g, 1.50 mmol) and triethylamine (2.78 mL, 20.00 mol) were combined in toluene (40 mL) under nitrogen in a dry three neck flask. The reaction was allowed to reflux for 24 hours and quenched with NH₄Cl. The aqueous layer was washed with ether and the organic layer collected. Solvent was removed under reduced pressure to a minimal volume and passed through a short silica gel column using successively: hexane (100 mL), hexane: CH₂Cl₂ (3:1, 150 mL), hexane: CH₂Cl₂ (1:1, 150 mL), EtOAc (100 mL) and MeOH (100 mL). NMR was collected and revealed the starting material.

2,5-Dimethylphenylboronic acid (12): To a suspension of magnesium powder (1.00 g, 41.00 mmol) and anhydrous THF (80 mL) several drops of dibromoethane and 2-bromo-*p*-xylene were added. The solution was heated with a heat gun until reflux began. 2-Bromo-*p*-xylene (5.02 mL, 36.00 mmol) was then added dropwise at a rate to maintain reflux. Upon completed addition the solution was stirred at 60 °C for 1 hr and allowed to cool. The reaction mixture was transferred dropwise into a solution of trimethylborate (8.51 mL, 75.00 mmol) in THF (20 mL) at -78 °C. The reaction mixture was stirred at room temperature for 12 hr. HCl (2M, 37.5 mL) was added and the mixture stirred at room temperature for 24 hours. Water (80 mL) and ether (80 mL) were then added and the organic layer collected. The solvent was removed under reduced pressure and the resulting white solid was recrystallized from toluene to yield a white solid (2.99 g, 55%). Mp 171-173 °C ¹H NMR (CDCl₃) δ 2.39 (s, 3H), 2.76 (s, 3H), 7.15 (d, J = 9.0 Hz, 1H) 7.24 (dd, J₁ = 9.0 Hz, J₂ = 3.0 Hz, 1H) 7.99 (d, J = 3.0 Hz, 1H)

Sodium-1,1'-oxoniobis(6-carboxy-1-hydroxy-3-oxo-1,3-dihydro benzo[c][1,2]oxaborol-1-uide); (Sodium salt dimer, 13): 2,5-Dimethyl phenylboronic acid (1.35 g, 9.01 mmol) was dissolved in NaOH (50% wt, 9.0 mL) and water (18.0 mL) and heated to 50 °C. KMnO₄ (6.55 g, 41.40 mmol) in 72 mL H₂O was added dropwise over a one hour period. The solution was kept at 50 °C for and additional three hours and then cooled to 0 °C. The pH was adjusted using conc. HCl to 8 and the mixture was filtered. The filtrate was further acidified to pH 2 at 0 °C. Under reduced pressure the solvent was

removed and the resulting white solid was recrystallized from to yield 1.01 g (52%). Did not melt below 350 °C ^1H NMR (D_2O) δ 7.60 (d, J = 6.90 Hz, 1H), 7.88 (d, J = 9.00, 1H), 8.01 (s, 1H); ($\text{DMSO}-d_6$) (ppm) δ 6.92 (s, 1H), 7.53 (d, J = 7.78, 1H), 7.75 (dd, J_1 = 1.22 Hz, J_2 = 7.81 Hz, 1H), 7.89 (d, J = 8.08 Hz, 1H) 8.03 (dd, J_1 = 1.69 Hz, J_2 = 8.12 Hz, 1H), 8.22 (s, 1H), 8.39 (d, J = 1.49 Hz, 1H); (CD_3OD) (ppm) δ 7.85 (d, J = 7.58 Hz, 1H) 8.01 (dd, J_1 = 1.37 Hz, J_2 = 7.97 Hz, 1H) 8.13 (d, J = 0.88 Hz, 1H); ^{13}C NMR (CD_3OD) δ 126.76, 130.51, 131.88, 134.99, 140.74, 169.96, 174.21.

2-Boronoterephthalic acid (2): The sodium salt dimer **13** (1.01 g) was suspended in concentrated HCl (4 mL) and stirred at room temperature for four hours. The resulting suspension was then left in the refrigerator for two days. The suspension was filtered and the white solid collected (0.92 g, 92%). The solid did not decompose below 350 °C. ^1H NMR (D_2O) (ppm) δ 7.73 (d, J = 7.7 Hz, 1H), 7.98 (dd, J_1 = 1.4 Hz, J_2 = 8.0 Hz, 1H), 8.12 (s, 1H); ($\text{DMSO}-d_6$) (ppm) δ 7.64 (d, J = 7.8 Hz, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.96 (s, 1H), 8.03 (s)

4-Borono-4-methylbenzoic acid and 2-borono-4-methylbenzoic acid (14, 15): 2,5-Dimethylphenylboronic acid (0.87 g, 5.08 mmol) was dissolved in NaOH (50% wt, 3.3 mL) and H_2O (6.6 mL) and heated to 50 °C. KMnO_4 (5.49 g, 34.76 mmol) in 60 mL H_2O was added dropwise over a one hour period. The solution was kept at 50 °C for an additional three hours and then cooled to 0 °C. The pH was adjusted using conc. HCl to 8 and then filtered. The filtrate was further acidified to pH 2 at 0 °C. Under reduced

pressure the solvent was removed and the resulting white solid was recrystallized from acetonitrile. (0.15 g, 5%). Mp 157 – 167 °C ^1H NMR (DMSO- d_6) δ 2.55 (s, 3H), 3.39 (s, 2H), 7.28 (d, J = 9.0 Hz, 1H) 7.86 (dd, J_1 = 3.0 Hz, J_2 = 9.0 Hz, 1H), 8.08 (s, 1H)

1,4-Xylene-2,5-diboronic acid (17): In a dry, air free three neck flask, magnesium powder (0.664 g, 0.027 mol) and THF (60 mL) were combined with a small amount of iodine and dibromoethane (0.20 mL, 0.002 mol). The solution was then heated until the brown color dissipated. 1,4-dibromo-2,5-dimethyl benzene (3.00 g, 0.0114 mol) in THF (10 mL) was then added at a rate to maintain reflux. Upon completed addition the mixture was refluxed overnight. The Grignard solution was then added dropwise into trimethylborate (2.58 mL, 0.022 mol) in THF (20 mL) at -78°C. Upon completed addition the solution was stirred at room temperature overnight. HCl (22.7 mL, 2M) was then added and stirred at room temperature overnight. Water (80 mL) and ether (80 mL) were then added and the organic layer collected. The solvent was removed under reduced pressure and the resulting white solid was washed with toluene and chloroform to yield a white solid. (0.68 g, 31%). Did not decompose below 350 °C ^1H NMR (DMSO- d_6) δ 2.32 (s, 3H), 6.53 (brs) 7.17 (s, 1H), 7.88 (brs).

2,5-Diboronoterephthalic acid (3): 1,4-Xylene-2,5-diboronic acid (0.83 g, 4.28 mmol) was dissolved in NaOH (50% wt, 2.12 mL) and water (8.48 mL) and heated to 50 °C. KMnO_4 (3.11 g, 19.68 mmol) in 34.25 mL H_2O was added dropwise over a one hour period. The solution was kept at

50 °C for and additional three hours and then cooled to 0 °C. The pH was adjusted using conc. HCl to 8 and then filtered. The filtrate was further acidified to pH 2 at 0 °C. Under reduced pressure the solvent was removed and the resulting white solid was washed with acetonitrile to yield 0.14 g (14%). Did not decompose below 350 °C ^1H NMR (D_2O) (ppm) δ 7.99 (s, 2H); ^{13}C NMR ($\text{DMSO}-d_6$) (ppm) δ 124, 140, 160, 171.

Polyphosphonic acid – benzothiazole polymer (19): 2-Phosphonoterephthalic acid (2.00 g, 8.10 mmol) was combined with benzothiazole (1.985 g, 8.10 mmol) in polyphosphoric acid (77% wt, 22.59 g). The reaction mixture was heated at 140 °C for 24 hours. The temperature was then raised to 160 °C for 24 hours and then raised to 180 °C for three hours. Water was added and the resulting solid was washed in a solid phase extractor for three days and oven dried to yield a grey solid (2.264 g). Viscosity analysis, revealed the polymer had a viscosity of 0.88 dL/g and TGA analysis revealed thermal decomposition at 537 °C.

Polyphosphonic acid – hexafluoropolybenzoxazole polymer (20): 2-Phosphonoterephthalic acid (1.1542 g, 4.689 mmol) was combined with hexafluoropolybenzoxazole (1.7174 g, 4.689 mmol) in polyphosphoric acid (83% wt, 18.3116 g). The reaction mixture was heated at 140 °C for 24 hours the temperature raised to 160 °C for 24 hours and then raised to 180 °C for 3 hours. Water was added and the resulting solid was washed in a soxhlet extractor for 3 days and oven dried to yield a grey solid (2.2899 g). Thermal analysis was performed and revealed thermal breakdown to occur at 465 °C.

CHAPTER IV

Conclusions and Future Research

The objective of this research effort was the synthesis of novel monomers for use in specialty polymers. It was desired to synthesize a polymer that could improve upon the current fuel cell standard, Nafion, by not requiring water in its use while simultaneously offering a fire retardant benefit. This research sought to prove that a PBI polymer backbone with a phosphonic or boronic acid pendant could achieve the afore mentioned goals by transporting protons between the basic imidazole and acidic pendant, while an inherent fire retardant ability would be provided from the cross linking ability of the phosphonic and boronic moieties.

To achieve the research goal a synthetic method capable of effectively producing a mono- or disubstituted phosphono- or boronoterephthalic acid was sought. We first attempted to utilize transition metal catalysis to couple the desired phosphonic and boronic functional groups to a halogenated dialkylbenzene. This method, however, proved unsuccessful, which is not surprising because it is increasingly known that *ortho* substituted dialkylbenzenes are quite unreactive in transition metal catalyzed coupling processes.

When transition metal catalyzed coupling proved unsuccessful a direct nucleophilic substitution route was attempted. In particular, we tried to introduce directly the phosphonic functionality into a halogenated terephthalic acid. However this again proved unsuccessful, possibly for two reasons. The first of these is related to the low solubility of the starting material. The halogenated terephthalic acid could never be fully solubilized, which meant that it had little chance to react with the phosphite ester. Also at issue could be the large steric bulk near the halogen to be substituted. This steric hindrance could prevent the phosphite from reacting with the halogen.

Our research successfully generated three of the target monomers by employing Grignard reagents. The desired monosubstituted phosphonoterephthalic acid and the mono and di-substituted boronoterephthalic acid have been successfully generated utilizing this method.

Two attempts were made to generate polymers from the phosphonoterephthalic acid, but the result in each case was only a low molecular weight polymer. However, preliminary TGA data was encouraging because thermal decomposition was shown to occur only at temperatures above 400 °C which is ideal for fuel cell and fire retardant applications.

X-ray structural analysis was also performed to rationalize the NMR data collected of what was originally thought to be 2-boronoterephthalic acid. The analysis showed that if not subjected to very strongly acidic conditions the 2-boronoterephthalic acid will form a stable monosodium salt dimer. The

^1H splitting pattern of this compound showed a significant dependence on the solvent used. We propose that the different splitting patterns, as shown in Figures 10 and 11, arise from the dimeric structure in DMSO and DMF solvents and the cleaved dimer in D_2O . In D_2O the cleaved dimer forms 2-boronoterephthalic acid resulting in the expected splitting pattern. Further, when structure **13** is treated with concentrated HCl only one set of peaks is observed in DMSO indicating the likely formation of 2-boronoterephthalic acid.

Our research efforts lead us to conclude that it is possible to utilize Grignard reagents to generate mono- and disubstituted phosphono- and boronoterephthalic acids and our experience so far has demonstrated that they can be successfully used as monomers in polymer synthesis. The information presented herein can be further utilized to generate rigid rod polymers for various purposes.

Future Research

Future research calls for the preparation of 2,5-diphosphono terephthalic acid. After this monomer has been successfully synthesized the four target monomers will be input into polymerization reactions, in order to generate high molecular weight PBI-phosphonic or boronic acid polymers. In addition to these research goals it is our intention to continue the study of the monooxidation of 2,5-dimethylphenylboronic acid. The selective oxidation of this compound may have wide ranging applications. Also of interest would be

the synthetic utility of the boronic acids, as reagents in Suzuki coupling or related transition metal catalyzed coupling reactions.

BIBLIOGRAPHY

1. Sopian, K.; Daud, W. R. *Renewable Energy* **2006**, 31, 719-27.
2. Rikukawa, M.; Sanui, K. *Prog. Poly. Sci.* **2000**, 25, 1463-1502.
3. Carollo, A.; Quaterone, E.; Tomasi, C.; Mustaralli, P.; Belotti, F.;
Magistris, A.; Maestroni, F.; Parachini, M.; Garlaschelli, L. And Righetti, P.
P. Journal of Power Sources **2006**, 160, 175.
4. Chuang, S-W and Hsu, S L-C, *J. Poly. Sci., Polym. Chem.* **2006**, 44,
4508.
5. Wainright, J.S.; Wang, J-t.; Weng, D.; Savinell, R.F.; M. Litt. *J.*
Electrochem. Soc. **1995**, 142(7), L121.
6. Schecter, A.; Savinell, R. F. *Solid State Ionics* **2002**, 147, 181.
7. Tomlin, D. W.; Fratini, A. V.; Hunsaker, M. And Adams, W. W. *Polymer*
2000, 41, 9003.
8. Branion, S.; Benin, V. "Preparation of Novel Monomers for Rigid Rod
Polymers" M.S Thesis, University of Dayton, **2006**
9. Westbrook, C. K. *Combustion Science and Technology* **1980**, 23, 191-
202.
10. Pawlowski, K. H.; Schartel, B. *Proceedings of 17th Annual BCC*
Conference on Flame Retardancy May 22-24, **2006**
11. Levchik, S. V.; Weil, E. D. *J. Fire Sci.* **2006**, 24, 345-364.

R002594646

12. Goossen, L. J.; Dezfali, M. K. *Synlett* **2005**, 3, 445-448.
13. Billingsley, K. L.; Barder, T. E.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2007**, 3, 5359-5363.
14. Zhishan, B.; Zhang, C.; Severin, N.; Rabe, J. P.; Scluter., A. D. *Macromolecules* **2000**, 33, 2688-2694.
15. Thompson, A. L. S.; Kabalka, G. W.; Akula, M. R.; Huffman, J. W. *Synthesis* **2005**, 4, 0547-0550.
16. Iovine, P. M.; Kellett, M. A.; Redmore, N. P.; Therien, M. P. *J. Am. Chem. Soc.* **2000**, 122, 8717-8727.
17. Cairns, J. F.; Snyder, H. R. *J. Org. Chem.* **1964**, 29, 2810-2812.
18. Prasad, G. S.; Manjunath, M.; Reddy, K. R. K. K.; Reddy, O. V. S.; Reddy, C. S. *Arkivoc* **2006**, xvi, 128-135.
19. Brannion, S.; Benin, V. *Synthetic Comm.* **2006**, 36, 2121-2127.
20. Chen, Z.; Lee, N. H. S.; Huang, W. *Macromolecules* **2003**, 36, 1009-1020.
21. Tao, B.; Goel, S. C.; Singh, J.; Boykin, D. W. *Synthesis* **2002**, 8, 1043-1046.
22. Achmatowicz, M.; Thiel, O.; Wheeler, P.; Bernard, C.; Huang, J.; Larsen, R.; Faul, M. *J. Org. Chem.* **2009**, 74, 795-809.
23. Oxford Diffraction (2005). *CrysAlisPro CCD and CrysAlisPro RED*. Versions 171.33.32, Oxford Diffraction Ltd., Abingdon, Oxfordshire, UK.
24. Sheldrick, G.M. (2000). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.