Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Molecular Structure 791 (2006) 111–116

Journal of
MOLECULAR
STRUCTURE

www.elsevier.com/locate/molstruc

Polyoxaalkyl esters of phenylboronic acids as new podands

A. Sporzyński [a], A. Miśkiewicz [a], B. Gierczyk [b], R. Pankiewicz [b], G. Schroeder [b], B. Brzezinski [b,*]

[a] *Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warszawa, Poland*
[b] *Faculty of Chemistry, Adam Mickiewicz University, ul Grunwaldzka 6, 60-780 Poznan, Poland*

Received 12 December 2005; accepted 5 January 2006
Available online 21 February 2006

Abstract

Three oxaalkyl esters of phenylboronic acid and one oxaalkyl ester of phenyldiboronic acid have been synthesized and their ability to form complexes with Li^+ and Na^+ cations has been studied using multinuclear NMR, ESI mass spectrometric and PM5 semiempirical methods. It has been demonstrated that the esters of phenylboronic acid form 1:1 complexes with Li^+ and Na^+ cations whereas the ester of phenyldiboronic acid can additionally form complexes of 1:2 stoichiometry. The stability constants of these complexes have been determined to show that with increasing number of oxygen atoms in the oxaalkyl chains the complexes of increasing stability are formed. The exemplary 1:1 and 1:2 structures of the complexes of esters with Li^+ and Na^+ cations, respectively, are given. They show that the cations are coordinated within a pseudo-crown structures formed by oxaalkyl chains.

Keywords: Phenylboronic acids; Oxaalkyl esters; ^1H NMR; ^{13}C NMR; ^7Li NMR; ^{23}Na NMR; ESI MS; Complexes; Stability constants; Pseudo-crown structure

1. Introduction

Arylboronic acids have found a wide range of applications in organic synthesis, of which the most important reactions are Suzuki coupling [1] and Petasis synthesis [2]. Another rapidly developing field is the biological and pharmaceutical application of boron compounds [3,4].

In recent years podands, open-chain ligands in contrast to the crowns, have attracted increasing interest as anion activators in homogeneous and heterogeneous systems. Podand molecules including polyoxaalkyl chains (inorganic esters of inorganic acids with ethylene glycol) show the ability to form complexes with metal cations [5]. Further, It has been demonstrated that tris(polyoxaalkyl) borates and tris(polyoxaalkyl) phosphates form channels with protons or cations [6–9]. Within these channels the protons or cations show large polarizability due to their fast fluctuations.

A new class of borate podands such as polyoxaalkyl esters of phenylboronic and phenylenediboronic acids have been synthesized and their ability to form complexes with metal cations has been studied using NMR spectroscopic and ESI MS method. The stability constants of the complexes are determined and the structure of the complexes is discussed.

2. Experimental

Ethylene glycol monomethyl ether, diethylene glycol monomethyl ether and triethyleneglycol monomethyl ether (Aldrich) were commercial products of Aldrich and were used without any purification. Phenylboronic and phenylenediboronic acids were synthesized following the procedures given in Ref. [10].

2.1. Preparation of esters **1–4**

Phenylboronic and phenylenediboronic esters (**1–4**) were obtained in the reactions shown in Scheme 1. To (0.0517 mol) of phenylboronic acid, (0.110 mol) of respective ethylene glycol monomethyl ether was added. After addition of 50 cm^3 of benzene the vessel was connected to a Dean-Stark trap, placed in an oil bath and heated for 10 h. The excess of alcohol was distilled off in vacuum (water pump). The products were purified by bulb-to-bulb distillation at ca. 10^{-3} Torr. Yields: **1**: 61%, **2**: 57%, **3**: 54%, **4**: 38%.

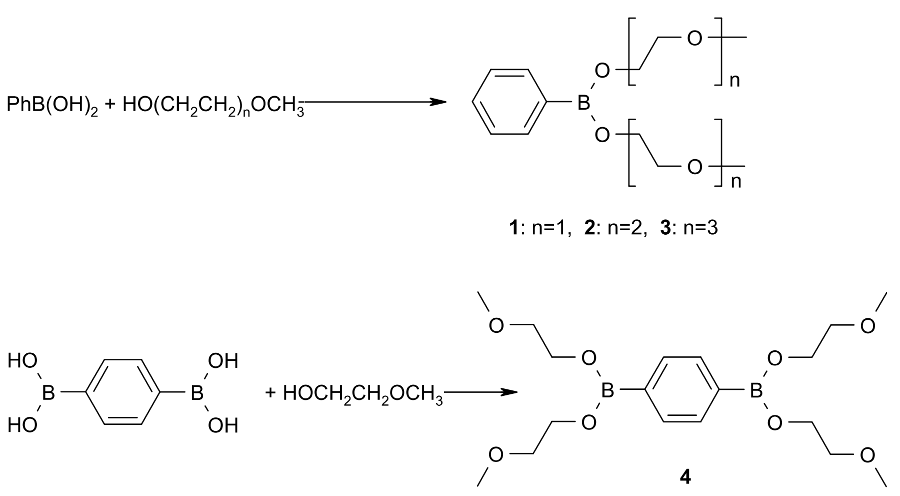
2.2. Preparations of complexes

$LiClO_4$, $NaClO_4$ and acetonitrile (Aldrich) were used for the preparations of complexes. The solutions were obtained

---

* Corresponding author. Tel.: +48 61 8291330; fax: +48 61 8658008.
E-mail address: bbrzez@main.amu.edu.pl (B. Brzezinski).

0022-2860/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2006.01.013



Scheme 1. Synthesis of the esters **1–4**.

by dissolving the respective esters (**1–4**) and the salt in analytical concentrations. For ^{7}Li and ^{23}Na measurements the concentration of the salt was constant (0.2 mol dm^{-3}) and the concentration of the ester was varied, whereas for the ^{1}H and ^{13}C measurements the concentration of the ester was constant (0.2 mol dm^{-3}) and the concentration of the salt was varied.

All solvents were spectroscopic grade and were dried over 3 Å molecular sieve.

All preparations and transfers of solutions were carried out in a carefully dried glove box under nitrogen atmosphere.

2.3. NMR measurements

The NMR spectra were recorded in CD_3CN using a Varian Gemini 300 MHz spectrometer. All spectra were locked to deuterium resonance of CD_3OD or CD_3CN, respectively. The error in parts per million values was 0.01.

All ^{1}H NMR measurements were carried out at the operating frequency 300.075 MHz; flip angle, pw = 45°; spectral width, sw = 4500 Hz; acquisition time, at = 2.0 s; relaxation delay, $d_1 = 1.0$ s; $T = 293.0$ K and TMS as the internal standard. No window function or zero filing was used. Digital resolution = 0.2 Hz/point.

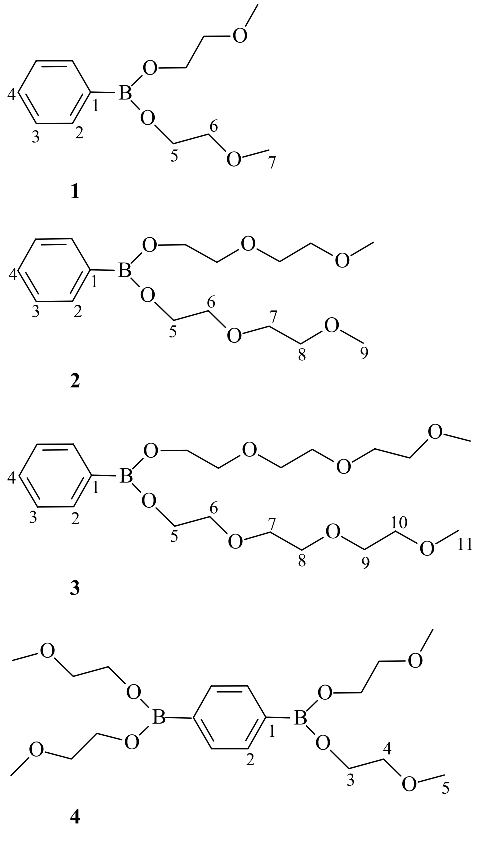
^{13}C NMR spectra were recorded at the operating frequency 75.454 MHz; pw = 60°; sw = 19,000 Hz; at = 1.8 s; $d_1 = 1.0$ s; $T = 293.0$ K and TMS as the internal standard. Line broadening parameters were 0.5 or 1 Hz.

^{7}Li NMR measurements were made in the following conditions: LiCl in D_2O (1 mol dm^{-3}) as external standard, sfrq = 116.621 MHz; pw = 25°; sw = 20,000 Hz; at = 1.0 s; $d_1 = 0.5$ s; $T = 293.0$ K. Digital resolution 0.6 Hz/point. No window function or zero filing was used.

^{23}Na NMR spectra were taken at: sfrq = 79.373 kHz; sw = 20,000 Hz; pw = 70°; at = 1.0 s; $d_1 = 1.0$ s; $T = 293.0$ K and 1 mol dcm^{-3} solution of NaCl/D_2O as the external standard. Digital resolution = 0.7 Hz/point. No window function or zero filing was used.

2.4. ESI mass spectrometry

The ESI (electrospray ionization) mass spectra were recorded on a Waters/Micromass (Manchester, UK) ZQ mass spectrometer equipped with a Harvard apparatus syringe pump. The sample solutions were prepared in acetonitrile (1:1) at a concentration of approximately 10^{-4} M. The samples were infused into the ESI source using a Harvard pump at the flow rate of 20 μl min^{-1}. The ESI source potentials were: capillary 3 kV, lens 0.5 kV, extractor 4 V. In the case of standard ESI



Scheme 2. Structures and atom numbering of the esters **1–4** studied.