Journal of Molecular Structure 922 (2009) 64–76

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Preparation and characterization of new low melting ammonium-based ionic liquids with ether functionality

Minna Kärnä, Manu Lahtinen *, Jussi Valkonen

Department of Chemistry, University of Jyväskylä, P.O. Box 35, FI-40014 Jyväskylä, Finland

ARTICLE INFO

Article history:
Received 3 November 2008
Received in revised form 19 January 2009
Accepted 20 January 2009
Available online 31 January 2009

Keywords:
Quaternary ammonium bromide
Tetrafluoroborate
Hexafluorophosphate
Ionic liquid
Thermal analysis
X-ray diffraction

ABSTRACT

Eighteen new and three previously known but insufficiently characterized $R\acute{R}_3N^+A^-$ and $R_2\acute{R}_2N^+A^-$ type (R = 2-ethoxyethyl or 4-methoxybenzyl, $\acute{R}$ = methyl, ethyl, *n*-propyl, *n*-butyl, *n*-pentyl or *n*-hexyl, A = Br, BF_4 or PF_6) quaternary ammonium (QA) salts were synthesized and characterized by using ^1H and ^{13}C NMR techniques, mass spectroscopy and elemental analysis. The bromide salts were synthesized either by treating dimethyl formamide with an ether functionalized alkyl bromide in the presence of potassium carbonate or by treating a tertiary amine with an ether functionalized alkyl bromide. The QA tetrafluoroborates and hexafluorophosphates were synthesized by metathesis reaction between a prepared QA bromide and HBF_4 or KPF_6. The crystal structures of four compounds were determined by X-ray single crystal diffraction and powder diffraction was used to study the crystallinity of the solid compounds and to compare the structural similarities between the single crystals and the microcrystalline bulk form. Thermal properties of all compounds were studied by using TG/DTA and DSC methods. The anion exchange had a clear lowering effect on the melting points and enhanced the thermal stability of the BF_4^- and PF_6^- salts compared to the analogous bromides. Most of the compounds melted clearly below 100 °C, of which four are liquid at room temperature.

1. Introduction

The seemingly ever growing interest on room temperature ionic liquids (RTILs) has turned the spotlight, along with many others, to quaternary ammonium-based compounds. Ionic liquids are of interest because of their unique characteristics, for example, low vapor pressure and extraordinary solvent properties, which have enabled their use in numerous applications and which have been widely discussed in several excellent publications or reviews and references therein [1–6].

Traditionally, the most widespread applications of ionic liquids lie in organic synthesis as solvents and catalysts [7,8]. Ionic liquids have in fact been described as designer solvents since their properties can be tuned by careful selection of ionic species [1,9]. They have also various electrochemical applications: in electric double layer capacitors (energy storage device) ionic liquids have been used as electrolytes due to their high conductivity and some quaternary ammonium-based ionic liquids have been reported to have more potential than the traditional aromatic type ionic liquids such as imidazolium or pyridinium due to their higher cathodic stability [10,11]. The quest for new energy sources has also led a great attention to dye-sensitized solar cells (DSSCs) in which ionic liquids could be used to replace the organic liquid electrolytes due to their non-volatility, non-flammability and high ionic conductivity, among other characteristics [12]. In addition to the most studied imidazolium-based ionic liquids, quaternary ammonium polyiodides have been tested as electrolytes in DSSCs [13]. Another solar application is the use of ionic liquids as heat-transfer fluids in electric power plants using parabolic trough solar collector technology [14–16]. Lately, some studies have suggested that ionic liquids could be used as a new class of lubricants or as additives in conventional lubricants. Certain quaternary ammonium-based ionic liquids have proven to be even more efficient lubricants than conventional hydrocarbon oils in reciprocal sliding tests [17]. Some ionic liquids containing a large amount of nitrogen are highly energetic materials which may be used in industrial or military applications [18]. A large number of tested applications consider only imidazolium-based ionic liquids which unfortunately are still rather expensive especially for large scale industrial applications. Quaternary ammonium and phosphonium-based ionic liquids, on the other hand, can also be made from readily available lower cost materials and thereby will be more applicable to industrial use if synthesized with reasonable yields [19–22]. Furthermore, the saturated quaternary ammonium cations are generally more resistant against oxidation and reduction than 1,3-substituted imidazolium cations that have certain degree of electrochemical instability and have some usability limitations in organic reactions [23,24]. Introducing an oxygen-containing side chain has proven to reduce the toxicity of imidazolium-based ionic liquids [25,26] and it might

* Corresponding author. Tel.: +358 14 2602624; fax: +358 14 2602501.
E-mail address: manu.lahtinen@jyu.fi (M. Lahtinen).

0022-2860/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2009.01.041

lead to a change of solvent properties [27,28]. Various methods to synthesize quaternary ammonium compounds has been known for a long time and a significant amount of publications exists [29–32]. Recently, a new method was developed by our group [33] for preparing $R_2\acute{R}_2N^+X^-$ type quaternary ammonium halides.

Relatively few studies on quaternary ammonium-based compounds with ether functionality have been made so far, for example, by Pernak [34], Das [35] and Hayamizu [36] and the number of existing compounds still remains fairly small comparing to, e.g., imidazolium-based compounds, and actually almost all are based to that cation. The number of simple acyclic non-chiral compounds is even smaller.

The aim of our studies is to find new quaternary ammonium-based compounds that have ionic liquid nature-compounds with a broad liquid range, low viscosity, good electrochemical properties and low melting point combined with good thermal stability. This is achieved by synthesizing new quaternary ammonium-based cations, pairing them with various anions, and performing systematic structural and thermoanalytical evaluations of the novel materials. Furthermore, based on special characteristics of the compounds potential application areas for the materials will be sought out in further studies.

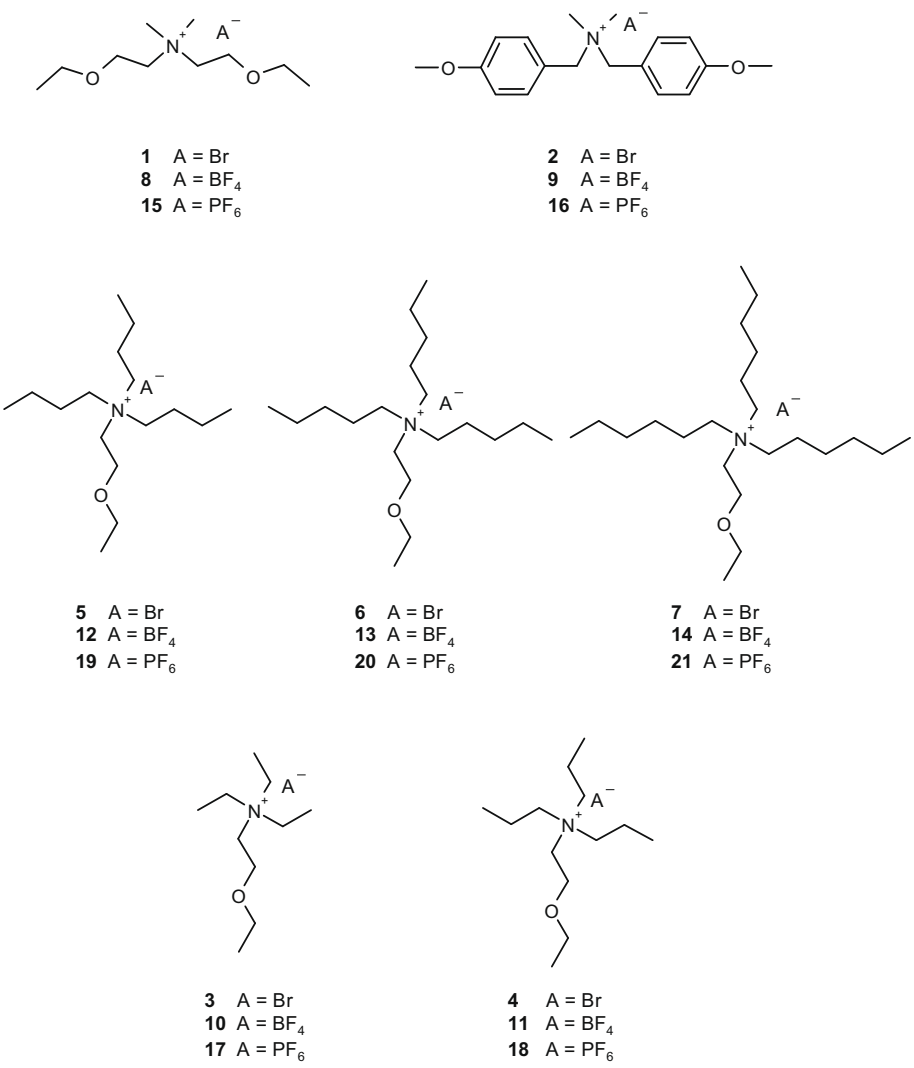
In this study, as a continuum to our previous ones, 18 new $R_2\acute{R}_2N^+A^-$ or $R\acute{R}_3N^+A^-$ type quaternary ammonium (QA) salts, in which A is bromide, tetrafluoroborate or hexafluorophosphate, Ŕ is an alkyl and R is an ether-bonded alkyl or aralkyl group, have been synthesized and characterized. In addition to these new compounds, three previously known but insufficiently characterized compounds [37–42] have been synthesized and characterized and used as precursors for six of the new QA salts. This study was oriented to structural characterization and thermal analysis and therefore the performed synthesis methods were not optimized. The ^1H and ^{13}C NMR spectroscopy, elemental analysis and ESI-TOF MS measurements are used to verify the accuracy and the purity of the compounds. Furthermore, X-ray powder diffraction was used to study the crystallinity of the compounds and to compare the consistency between the single crystal structures and their powdery forms. The thermal properties have been observed by TG/DTA and DSC and the effect of different anions on some characteristics of the compounds have been examined by comparing these results.

2. Experimental

2.1. Synthesis and analysis

2.1.1. General procedure

All reagents and solvents were purchased from manufacturers and used as received. Compounds **1** and **2** (Scheme 1) were prepared by using the one-pot synthesis route described by Ropponen



Scheme 1. Molecular structure of the compounds **1–21.**