We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists



186,000

200M



Our authors are among the

TOP 1% most cited scientists





WEB OF SCIENCE

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us? Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected. For more information visit www.intechopen.com



Glycoside-Based Ionic Liquids

Robert Engel Department of Chemistry and Biochemistry Queens College of the City University of New York USA

1. Introduction

A significant portion of our efforts over the past decade has been dedicated to the design and synthesis of polycationic organic salts, both for their use as metabolic regulators in a variety of settings, and for their use in the construction of ionic liquids. Following from this body of work we present this summary of efforts toward the development of a particular category of ionic liquid, those related to carbohydrates and their derived compounds, glycosides and related polyols.

Our synthetic endeavours have focused on the generation of a library of polycationic derivatives of carbohydrates and their derivatives. There is a fundamental rationale in contemplating such structures; if one is to fulfill the promise of ionic liquids as "designer solvents," (Plechkova & Seddon 2007) then one must consider structures with which significant and subtle variation in properties can be achieved with relatively minor changes in their structures. Carbohydrates and their related compounds (glycosides, polyols) clearly meet this requirement through the presence of multiple functionalities through which structural variation can be accomplished with relative ease.

Thus we turn our attention to the design of cationic (and particularly polycationic) derivatives related to glycosides, simple carbohydrates, and the reduced polyols. It is necessary that such parent structures bear functionalities that may be used readily for the incorporation of cationic sites. Most prominently, in all of these types of compounds, the presence of primary hydroxyl group(s) readily permits such cationic site incorporation. We will contemplate the reaction systems allowing such transformations in a later section of this treatment. Initially, however, we should note the limitations on the nature of the anion in ionic liquids generated from such structures if one is to allow facile production of the ionic liquid without side reactions that could modify the inherent organic (carbohydrate) structure.

Finally, we will contemplate the experimental strategies most amenable for such ionic liquids, as well as their particular applications that would appear to be significant.

2. Anionic choices

There has been a wide range of anions that have been used for the construction of ionic liquids. Historically, anions such as tetrachloroaluminate, which are highly reactive with water and other hydroxylic species, were involved for the construction of ionic liquids that were reasonably fluid at temperatures below 100°C. Unfortunately, tetrachloroaluminate is

itself quite reactive toward both water and other hydroxylic solvents and reagents, and therefore would be quite unsuitable for use with cations themselves bearing hydroxylic functionalities (Kubisa 2004).

Other commonly used anions for ionic liquids, such as tetrafluoroborate and hexafluorophosphate, also undergo hydrolysis at sufficiently rapid rates that would cause difficulties for their use with either aqueous solvents or hydroxylic cations. While the hexafluorophosphate anion undergoes hydrolysis most rapidly only under acidic conditions (Freire et al. 2010), the preparation of the ionic liquids using hexafluorophosphoric acid can lead to significant formation of the (hydrolyzed) phosphate salt (Lall et al. 2000). Similarly, the alternative approach for the preparation of the phosphate salts (liquid ionic phosphates, LIPs) involving the use of 98% phosphoric acid (Lall et al. 2002) similarly experiences difficulty when cations are used that bear hydroxylic sites. Presumably the "anion exchange" method (Lall et al. 2002) would not experience this difficulty, but this process is extremely inefficient for the preparation of any sizable quantity of material. Similarly, the tetrafluoroborate anion undergoes hydrolysis sufficient rapidly (Freire, et al. 2010) and can be anticipated to react with free hydroxylic functions such that it would not be a useful anion for ionic liquids based on carbohydrate and carbohydrate-related materials.

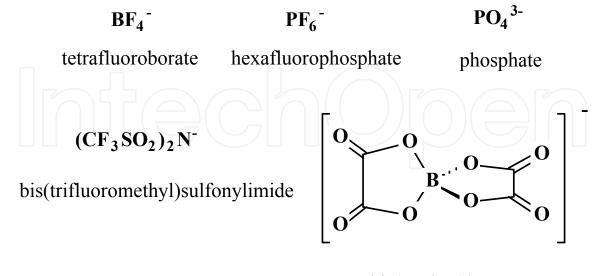
While these reactivity characteristics eliminate such anions from practical use with the polyhydroxylic cationic species of current interest, there remain a number of other anions that would be quite suitable. Of particular interest are those that remain unreactive in the presence of hydroxylic solvents (and cations) and may be incorporated by simple metathesis processes. For example, the bis(trifluoromethyl)sulfonylimide anion can be introduced through the addition of an equivalent amount of lithium bis(trifluoromethyl)sulfonylimide to an aqueous solution of the halide salt of the desired cationic (ammonium) species, which causes separation of the desired liquid salt from the aqueous remainder (Bonhôte et al. 1996). The ionic liquid can then be isolated by decantation and drying. In addition, use of the lithium bis(oxalato)borate salt in similar ionic exchange processes produces the "BOB" salts that are useful as anions for ionic liquids (Lishka et al. 1999; Xu & Angell 2001; Xu et al. 2002). The "BOB" anion is quite intriguing in that it has no hydrogen associated with it and exhibits a wide electrochemical stability window (Xu & Angell 2001). This intriguing anion has recently been used for the construction of ionic liquids bearing traditional cations (Lall-Ramnarine et al. 2009). In complement to the hydrophobic solubility characteristics presented by these anions, the phosphate salts provide aqueous solubility without dissolution in organic solvents. The anion structures are illustrated in Figure 1.

3. Cationic systems

The interest for us in the construction of new ionic liquids involved cationic components bearing more than one quaternary ammonium ion site within a given cationic species. These "polycations" were of particular interest given our involvement in the construction and use for a variety of purposes of polyammonium and polyphosphonium salts.

Polyammonium and polyphosphonium salts in several geometric categories were prepared, including dendrimers (Rengan & Engel 1990; Rengan & Engel 1991; Engel et al. 1991; Engel 1992; Rengan & Engel 1992; Engel et al. 1993a; Engel et al. 1993b; Engel 1995; Cherestes & Engel 1994; Cherestes et al. 1998), linear cationic arrays, "strings" (Fabian et al. 1997; Shevchenko & Engel 1998; Strekas et al. 1999; Engel et al. 1999; Cohen et al. 1998; Gordon et al. 2006), and cyclic systems, "rings" (Cohen et al. 1999; Cohen & Engel 2000; Cohen et al.

2000a; Cohen et al. 2000b). Examples of these categories of polycationic species are illustrated in Figures 2-4.



bis(oxalato)borate

Fig. 1. Common anions for ionic liquids

Efforts using the cyclodextrins led to increasing interest in a variety of carbohydrate monoand polycationic species. The polycationic cyclodextrin derivatives themselves exhibited most intriguing physical characteristics, particularly with regard to their serving as inclusion agents for a variety of anions (Cohen et al. 2000b). It was determined that the host:guest association was of a 1:1 nature, with association constants for guest nucleoside monophosphate anions being generally in the range 5-500; similarly, 1:1 association with acylated amino acids was observed, but with association constants found to be as great as 10⁵. Clearly the ring of charges about the top of the cyclodextrin torus held quite rigidly the charged species with the hydrophobic interior of the torus providing a "comfortable" space for the organic portion of the guest species. It is also intriguing that aqueous solubility of the polycationic cyclodextrin salts is significantly dependent on the associated anion. As the reaction is performed, a mixture of halide and tosylate anions would be anticipated to be associated with the product salts. However, a selectivity is observed, strictly halide forms of the salt precipitating readily from aqueous solution while tosylate forms of the salts remain in solution, the tosylate being at least partially associates as a guest species within the hydrophobic interior of the torus.

Carbohydrate derivatives bearing charged sites (as ammonium or phosphonium components) clearly held significant potential not only with the cyclodextrins, but also for other carbohydrate species owing to the wealth of functionality present within the structure and the possibilities for interaction with solvents and other external anionic components. Owing to the size of the cationic portion and the wealth of associated anionic species in a multitude of possible locations relative to the individual cationic sites, the possibilities of cationic carbohydrate derivatives for serving in ionic liquids are quite sizable.

In this regard a series of polyhydroxylic polyammonium species have been prepared, derived from carbohydrate precursors (Thomas et al. 2009a) and ionic liquids generated from them using phosphate and tosylate anions (Engel et al. 2007). Of particular note are the

syntheses of chiral tosylate associated ionic liquids derived from methyl α -D-glucopyranoside and mannose, as illustrated in Figure 5.

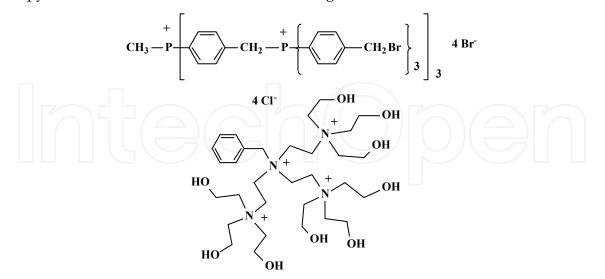


Fig. 2. Examples of polycationic dendrimers. top: a tetraphosphonium dendrimer; bottom: a tetraammonium dendrimer

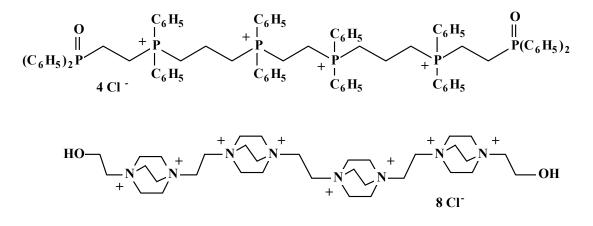


Fig. 3. Examples of polycationic "strings". top: a tetraphosphonium "string" species bottom: an octaammonium "string" species

It is notable that simple tosylate salts of these polyhydroxylic cations produce ionic liquids. This is an indication of the nature of the polyhydroxylic species bearing one or more cationic sites possessing several arrangements of cation and anion of relatively similar energies leading to an inability to form crystalline structures readily. Preliminary MM2 calculations concerning the relative energy minima available for polycationic salts of several common anions indicate a host of such relative minima to exist of relatively close energies (Engel 2011). In such a situation their formation of a simple crystalline structure at room temperature is disfavored and a liquid or glass material is to be anticipated. Indeed, one of the first ionic liquids generated in our laboratory was that from a derivative of a polyhydroxylic species as a chloride (Cherestes et al. 1998). In this effort, formation of a chiral ammonium salt derived from (S)-malic acid by reaction of the primary chloride with 1,4-diazabicyclo[2.2.2]octane produced the chloride salt as a viscous liquid that resisted all attempts at crystallization (Figure 6).

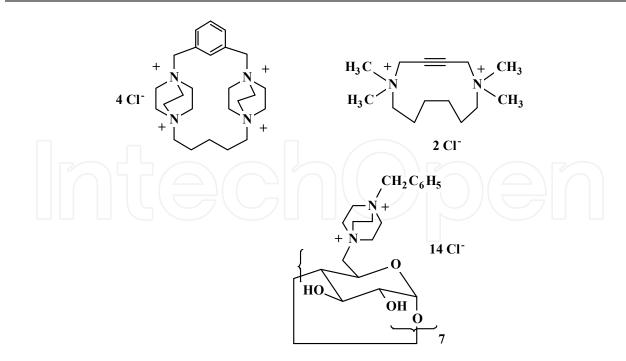


Fig. 4. Examples of polycationic rings. top left: a tetraammonium salt derived from 1,4diazabicyclo[2.2.2]octane; top right: a cyclic dicationic alkyne; bottom: a β -cyclodextrin derivative bearing fourteen ammonium sites.

As noted in Figure 5 (*vide infra*) the formation of the tosylates of polyhydroxylic species is a relatively simple matter. Tosyl chloride, in early efforts allowed to react in pyridine solution with hydroxylic substrates, reacts selectively with primary hydroxylic sites under aqueous conditions reminiscent of the simple Schotten-Baumann procedure for ester formation (Frantz et al. 2002), as has been used for a wide range of ester preparations. The selectivity of the tosylation reaction and the ability to perform it in aqueous medium (Thomas et al. 2009a) provide major advantages to this procedure, allowing facile formation of the tosylate ester and the equally facile subsequent displacement of the tosylate leaving group by an incoming tertiary amine nucleophile.

Using the simple approach of selective tosylation of primary hydroxyl sites followed by nucleophilic substitution by a tertiary amine reagent, quaternary ammonium salts of a wide range of structures derived from carbohydrate precursors have been prepared. for the cyclodextrin derivatives, per-tosylation of the available hydroxylic sites was established by early efforts at generating cyclodextrin derivatives (Cramer et al. 1969) with later modification to the procedure using aqueous medium.

Using the method of selective tosylation of primary hydroxyl sites, a variety of simple carbohydrate and their glycosidic and reduced derivatives have been generated and investigated (Thomas et al. 2009). Of particular concern were cationic and polycationic derivatives of methyl α -D-glucopyranoside, examples of which are illustrated in Figure 7.

It will be noted that a variety of tertiary amine species were used as nucleophiles in generating the cationic glycoside species from the appropriate tosylate. These included simple mono-basic reagents as had been used previously in the preparation of cationic components of ionic liquids, as well as a series of mono-basic/di-nitrogen reagents derived from 1,4-diazabicyclo[2.2.2]octane. These reagents are illustrated in Figure 8.

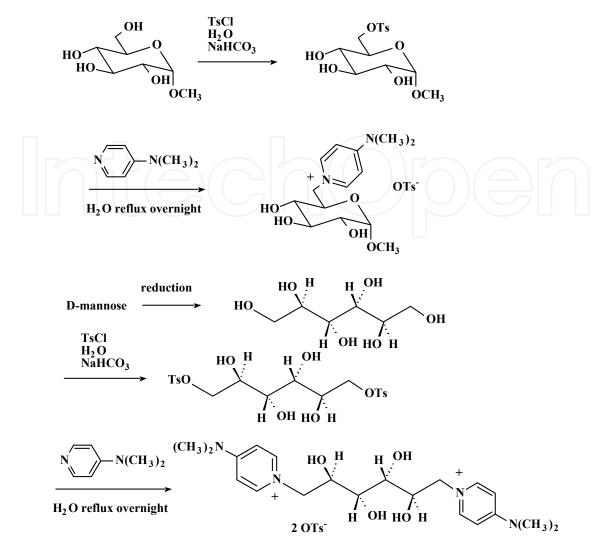
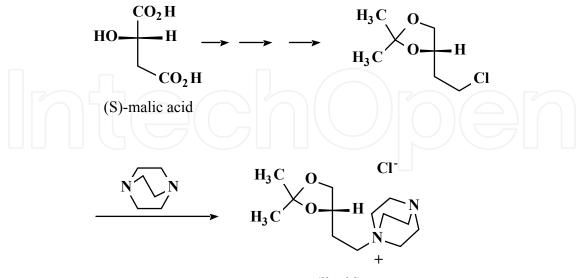


Fig. 5. Chiral ionic liquids prepared from carbohydrate derived precursors with tosylate anions. top: chiral tosylate ionic liquid based on methyl α -D-glucopyranoside; bottom: chiral tosylate ionic liquid based on derivative of D-mannose.

Several di-basic reagents were used for the linking of two glycosidic units, as illustrated in Figure 9. These types of reagents were utilized in the construction of several di-cyclodextrin species bearing a most intriguing structural feature (*vide infra*).

In addition to using methyl α -D-glucopyranoside as a scaffolding for the cationic components, reduced carbohydrates were used for the construction of materials bearing two cationic sites attached directly to the carbohydrate backbone (Thomas et al. 2009b). There are present in several of these species, examples being illustrated in Figure 10, additional cationic sites as components of integrated 1,4-diazoniabicyclo[2.2.2]octane components. All of these species bear potential for the construction of ionic liquids as the association of a variety of anions would be anticipated to exhibit numerous thermodynamic minima of close energy rendering the formation of crystalline species unlikely. The presence of the numerous hydrophilic oxygen sites and hydroxyl groups in such materials would provide intriguing solubilizing characteristics with both classically hydrophobic and hydrophilic anions. The variety of solubilizing characteristics is particularly numerous using the 1,4-diazoniabicyclo[2.2.2]octane adjuncts as the distal unit of these materials can be varied widely, from long and hydrophobic to multifunctional hydrophilic. As such, these materials

hold significant promise to fulfill the aim of ionic liquids as being "designer solvents" (Plechkova & Seddon 2007).



(liquid)

Fig. 6. Formation of an ionic liquid chloride salt derived from a polyhydroxylic precursor

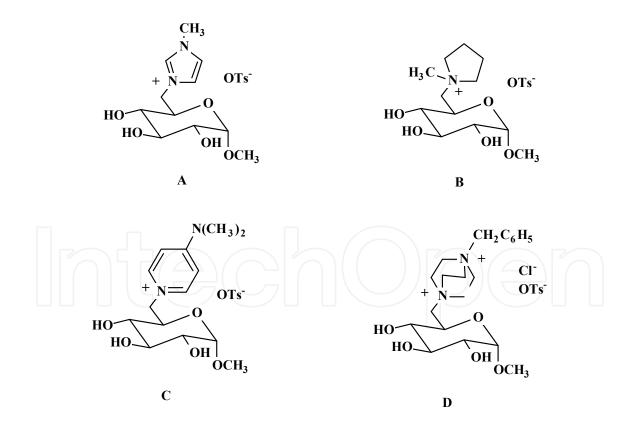


Fig. 7. Examples of cationic derivatives of methyl α-D-glucopyranoside as reported in Thomas et al. 2009b: **A**, derivative of *N*-methylimidazole; **B**, derivative of *N*-methylpyrrolidine; **C**, derivative of 4-dimethylaminopyridine; **D**, derivative of 4-benzyl-1-aza-4-azoniabicyclo[2.2.2]octane

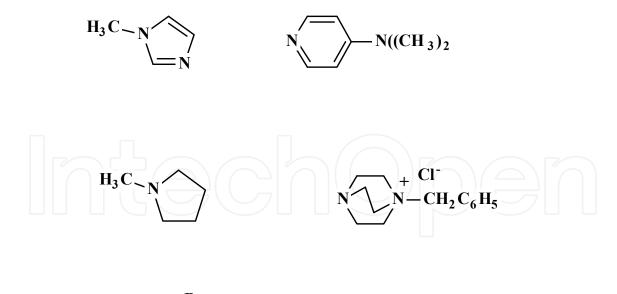
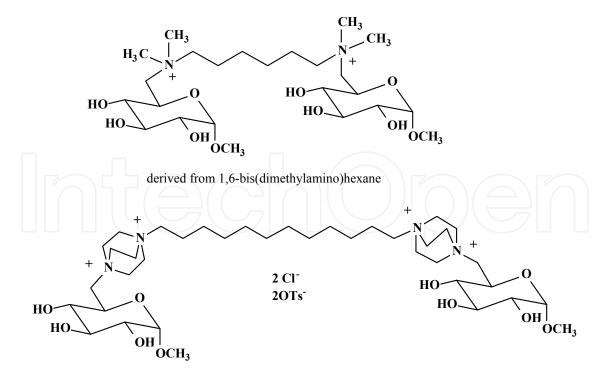




Fig. 8. Tertiary amines used in the formation of cationic derivatives of α-D-glucopyranoside as reported in Thomas et al. 2009b: these include (from top, left to right) *N*-methylimidazole, 4-dimethylaminopyridine, *N*-methylpyrrolidine, 4-benzyl-1-aza-4-azoniabicyclo[2.2.2]octane chloride, 4-octyl-1-aza-4-azoniabicyclo[2.2.2]octane bromide, and4-isobutyl-1-aza-4-azoniabicyclo[2.2.2]octane bromide



derived from 1,12-bis-(1'-azonia-4'-azabicyclo[2.2.2]octane) dichloride

Fig. 9. Constructs with two α -D-glucopyranoside units connected through linking di- and tetracationic bridges (Thomas et al 2009b)

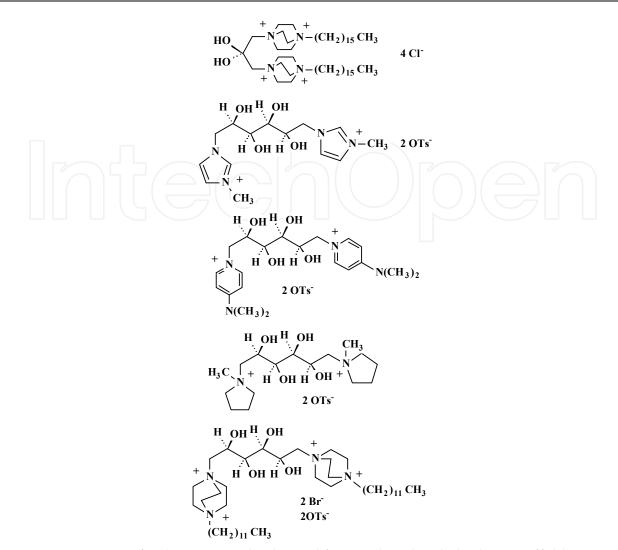


Fig. 10. Constructs of polycationic salts derived from reduced carbohydrate scaffoldings, including glycerol(top) and mannitol (lower structures). A host of potential structures bearing a variety of functionalities and subsequent solubilizing characteristics are available.

As noted (*vide supra*) a series of salts derived from cyclodextrins have been prepared in which the α, ω -bis(basic) reagents were used for the construction of a most intriguing category of host species. Both the α, ω -bis(dimethylamino)alkanes as well as the α, ω -bis(1'-azonia-4'azabicyclo[2.2.2]octane salts were used as bridging reagents linking two cyclodextrin units. These particular host molecules bear hydrophobic cyclodextrin interiors at each end as well as in the middle, with cationic sites near each end at the "top" portion of each of the cyclodextrin units. This structural category is shown in cartoon form in Figure 11. The particular significance of these structures is that they can serve as host for anions bearing a hydrophobic region (*e.g.* fatty acid anions) that holds them virtually permanently. Using MM2 calculations it is indicated that once such an anion is trapped inside the tube, it remains there perpetually, unable to "escape" to the surrounding solution (Engel et al. 2004).

While the cyclodextrins are most intriguing polysaccharides in that six, seven, or eight glucose unites are combined in a useful cyclic shape, other polysaccharides are also of interest. Polycationic derivatives of sucrose, a non-reducing disaccharide, have recently been

reported (Engel et al. 2011). The compounds of interest, each bearing six cationic sites as well as lipophilic chains, are notable as being significantly antibacterial in character. The sucrose structure provides three primary hydroxyl sites within each molecule through which the cationic sites can be introduced easily using the tosylation procedure noted previously (Thomas et al 2009). Several structures of interest are illustrated in Figure 12.

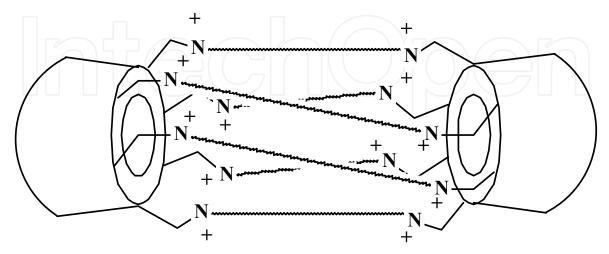


Fig. 11. Cartoon representation of a molecular version of the "Chinese Finger Puzzle" constructed from α, ω -bis(basic)alkane reagents and cyclodextrins modified by tosylation at each of their primary hydroxyl sites.

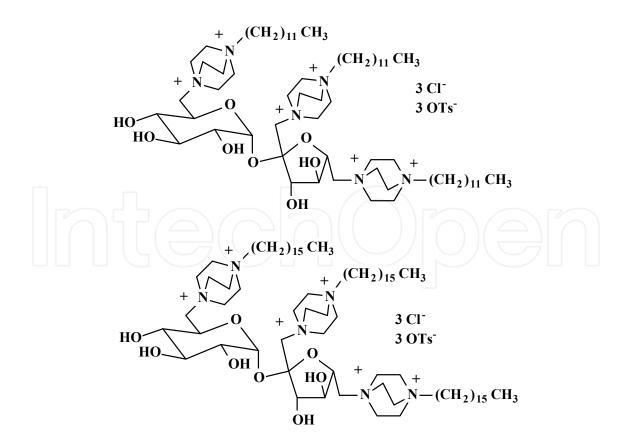


Fig. 12. Polycationic derivatives of sucrose

The significant antibacterial effect of the polycationic derivatives of sucrose is not unexpected. Antibacterial (and antifungal) characteristics are noted for even simple cationic derivatives of lipophilic materials, increasing as the density of charge and tethered sites of charge increase. Even greater antibacterial activity is noted for polycationic derivatives of oligosaccharide species such as soluble starch.

There remain to be exploited numerous variable structures based on carbohydrate and glycosidic systems to which are tethered cationic linkages. For examples are, simple carbohydrates of shorter chain length and their reduced derivatives, simple nucleosides, alginates, carrageenan, amino sugars, chitosan, and other nitrogen-containing carbohydrate species (see Figure 13).

These carbohydrate derivatives, including the oligosaccharides, are intriguing potential structures for cationic systems and ultimately ionic liquids owing not only to their particular structural characteristics, but also to their ready availability for large scale production.

4. Outlook

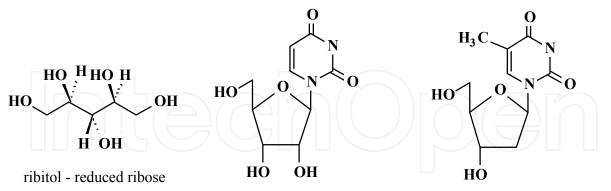
While only a portion of the carbohydrate and derived glycosidic species considered in the previous section have to date been converted into ionic liquids, they present a major source of materials for the generation of ionic liquids with tunable physical and chemical characteristics, among these being: solubilizing capabilities, fluidity, melting point, and reactivity, to itemize a few. If one is looking to actualize the potential of ionic liquids to serve as "designer solvents" (Plechkova & Seddon 2007) the glycosidic materials, along with their parent carbohydrates and their reduced derivatives provide readily available scaffoldings with facile conversion routes.

Caution need be taken in exploring these possibilities. The multifaceted functionality of the glycoside and related carbohydrate components place limitations on the nature of the associated anions and on the approaches used to incorporate them with the cations. For example, while it was quite reasonable to use crystalline phosphoric acid for the generation of liquid ionic phosphates from simple quaternary ammonium ion chloride salts bearing only alkyl groups on the ammonium species (Lall et al 2002), this approach will not be feasible with the carbohydrate-based systems; there would be anticipated to occur significant dehydration of the carbon structure rendering yields low and purification extremely difficult. Similarly, the approach toward such materials using HPF₆ would result in reaction of the free hydroxyl groups. It would appear to be necessary to generate the phosphate salts through the use of an ion-exchange approach.

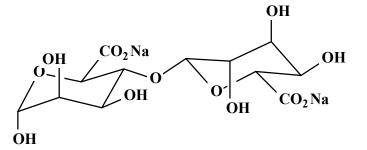
Other classical systems for ionic liquid construction would also require care, or might possibly be excluded from consideration owing to the presence of the reactive hydroxyl groups. Of particular note here would be the classical tetrachloroaluminates and the tetrachloroborates, both of which would be anticipated to undergo reaction with the polyhydroxylic cations in undesirable ways.

The major options thereby for ionic liquid construction using glycosides and their related carbohydrate and reduced-carbohydrate species are those that are unreactive in general, and particularly with hydroxylic reagents. These would include the bisoxalato borate and bis(trifluoromethyl)sulfonylimide anions (illustrated in Figure 1), both of which can be incorporated into ionic liquid materials by simple metathesis processes or ion-exchange. Other anions that can be incorporated into ionic liquid materials *via* ion-exchange processes include phosphate (albeit with low efficiency for large-scale conversions) or the substituted

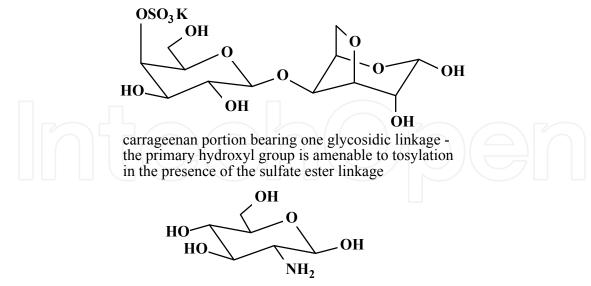
phosphate system, di(phenyl)phosphate anion (Thomas et al 2009b). The use of ionexchange for incorporating such phosphate diesters is tedious, but has the advantages of



uridine - simple nucleoside deoxythymidine - simple nucleoside



alginate portion bearing one glycosidic linkage - the carboxylate linkages are reducible to primary hydroxyl sites to accommodate facile incorporation of cationic sites



D-2-glucosamine - component of chitosan

Fig. 13. Glycoside and related structures suitable for facile preparation of cationic derivatives with ultimate conversion to ionic liquids. In each instance a primary hydroxyl is available or readily obtained by simple reduction for introduction of a quaternary ammonium (or phosphonium) site for salt construction.

precluding reaction of the target anion supplying reagent from undergoing reaction with a functionally sensitive cation, and allows further structural variation for tuning properties of the target ionic liquid. The variability of this type of anion, being an organic species in itself, is illustrated in Figure 14.

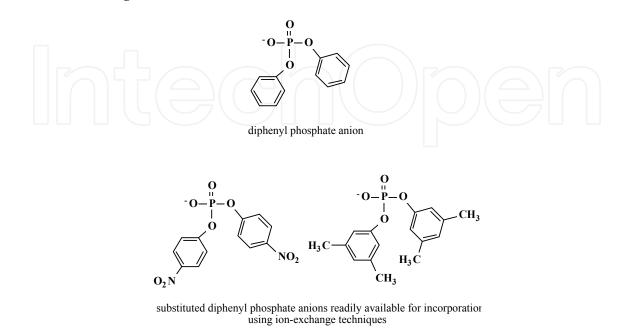
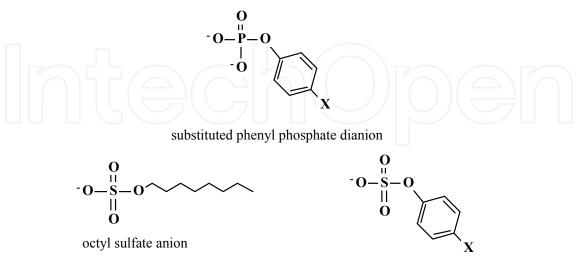


Fig. 14. Phosphate and substituted phosphate anions for ionic liquids.

Of course, the potential for ionic liquids being generated from glycosides and related carbohydrate-derived cations with tosylate anions remains. These have been observed in several instances, and the possibility remains for additional species to have similar behavior and characteristics. There are also possibilities, including the tunability of characteristics, through the use of mono-esters of phosphoric acid or sulfuric acid (see Figure 15), again



substituted phenyl sulfate anior

Fig. 15. Phosphate dianion and sulfate anions with structural and conformational variability for ionic liquid construction.

incorporated into the ionic liquid through ion-exchange or metathesis techniques. These again may be generated easily with a variety of substituents that will provide a broad range of chemical and physical characteristics to the materials. The fact that such anions as the partial esters of such inorganic acids are relatively bulky in nature with possibilities for variation in shape *via* bond rotation among a selection of conformations with closely lying relative minima also increases their potential to provide salts that are liquid at room temperature. The construction of these salts with glycosides and related carbohydrate derived cations can provide us with a significantly large selection of ionic liquids for a broad range of purposes.

5. Acknowledgements

The author wishes to thank his numerous students who have generated over the years most of the results discussed in this presentation that emanate from his laboratory. He also wishes to thank Queens College of The City University of New York for providing him the laboratory for his work and the Fellowship Leave during which this presentation was prepared.

6. References

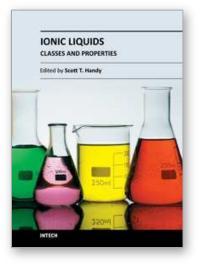
- Bonhôte, P., Dias, A.-P., Papageorgiou, N., Kalyanasundaram, K., & Grätzel, M. (1996). Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts. *Inorg. Chem.*, Vol. 35, No. 5, pp. 1168-1178, ISSN 0020-1669.
- Cherestes, A., & Engel, R. (1994). Dendrimeric Ion Exchange Materials. *Polymer*, Vol. 35, No. 15, pp. 3343-3344, ISSN 0032-3861.
- Cherestes, A., October, T., & Engel, R. (1998). Polycations. II. Chiral Ammonium Dendrimer Synthesis. *Heteroatom Chem.*, Vol. 9, No. 5, pp. 485-494, ISSN 1042-7163.
- Cohen, J.I., Traficante, L., Schwartz, P.W., and Engel, R. (1998). Polycations. 4. Synthesis and Antihydrophobic Effect of Polycationic Strings. *Tetrahedron Lett.*, Vol. 39, pp. 8617-8620, ISSN 0040-4039.
- Cohen, J.I., Rusinowski, A., Strekas, T.C., & Engel, R. (1999). Polycations. 6. Polycationic Heterocyclic Salts: Their Synthesis and Effect on Double Stranded DNA, *Heteroatom. Chem.*, Vol. 10, No. 7, pp. 559-565, ISSN 1042-7163.
- Cohen, J.I. & Engel, R. (2000). Polycations. 7. Polycationic Cyclic Alkynes, *Synth. Commun.,* Vol. 30, No. 12, pp. 2161-2164, ISSN 0039-7911.
- Cohen, J.I., Shteto, V., & Engel, R. (2000a). Polycations. 8. The Synthesis of Polycationic Rings, *Synthesis*, pp.1263-1268, ISSN 1088-4327.
- Cohen, J.I., Castro, S., Han, J.-a., Behaj, V., & Engel, R. (2000b). Polycations. IX. Polyammonium Derivatives of Cyclodextrins: Synthesis and Binding to Organic Oxyanions, *Heteroatom Chem.*, Vol. 11, No. 7, pp. 546-555, ISSN 1042-7163.
- Cramer, F., Mackensen, G., & Kensse, K. (1969). Über Einschlussverbindungen, XX. ORD-Spektren und Konformation der Glucose-Einhalten in Cyclodextrinen, *Chem. Ber.*, Vol. 102, No. 2, pp. 494-508, ISSN 1099-6082
- Engel, R. (1992). Cascade Molecules. Polymer News, Vol. 17, pp. 302-305, ISSN 0032-3918.
- Engel, R., Rengan, K., & Milne, C. (1991). Cationic Cascade Molecules. *Polym. Prepr.*, Vol. 32, p. 601, ISSN 0332-3934.

- Engel, R., Rengan, K., & Chan, C.-s. (1993a). Phosphorus Cascade Molecules, *Phosphorus and Sulfur*, Vol. 77, p. 221, ISSN 1042-6507.
- Engel, R., Rengan, K., & Chan, C.-s. (1993b). Cascade Molecules Centered About Phosphorus, *Heteroatom Chem.*, Vol. 4, No. 2/3, pp. 181-184, ISSN 1042-7163.
- Engel, R. (1995). Ionic Dendrimers and Related Materials, *Advances in Dendritic Macromolecules*, Vol. 2, pp.73-99, ISBN 1-55938-939-7.
- Engel, R., Shevchenko, V. Lall, S., Tropp, B., Lau, N., and Strekas, T. (1999). Synthesis and Biological Activities of Phosphorus-Containing Polycationic Strings. *Phosphorus and Sulfur*, Vol. 147, p. 83, ISSN 1042-6507.
- Engel, R., Coleman, D., & Thomas, M. (2004). Molecular Version of the Chinese Finger Puzzle, presented at the 228th Meeting of the American Chemical Society, Philadelphia, PA, August 2004.
- Engel, R., Lall-Ramnarine, S., Coleman, D., & Thomas, M. (2007). New cations for ionic liquids, including chiral adjuncts with phosphate and sulfonylimide anions. *Proceedings of the Ionic Liquids for Organic Synthesis Symposium*, American Chemical Society Symposium Series #950, pp. 259-266, ISBN 13:9780841274075.
- Engel, R. (2011). Unpublished work of this laboratory.
- Engel, R., Ghani, I., Montenegro, D., Thomas, M., Klaritch-Vrana, B., Castaño, A., Friedman, L., Leb, J., Rothman, L., Lee, H., Capodiferro, C., Ambinder, D., Cere, E., Awad, C., Sheikh, F., Rizzo, J., Nesbitt, L.-M., Testani, E., & Melkonian, K. (2011). Polycationic Glycosides. *Molecules*, Vol. 16, pp.1508-1518, ISSN 1420-3049.
- Fabian, J., October, T., Cherestes, T., & Engel, R. (1997). Polycations: Syntheses of Polyammonium Strings as Antibacterial Agents. *Synlett*, pp. 1007-1010, ISSN 0936-5214.
- Frantz, D.E., Weaver, D.G., Carey, J.P., Kress, M.H., & Dolling, U.H. (2002). Practical Synthesis of Aryl Triflates under Aqueous Conditions. Org. Lett., Vol. 4, No. 26, pp. 4717-4718, ISSN 1523-7060.
- Freire, M., Neves, C., Marrucho, I., Coutinho, J., & Fernandes, A. (2010). Hydrolysis of Tetrafluoroborate and Hexafluorophosphate Counter Ions in Imidazolium-Based Ionic Liquids. J. Phys. Chem., Vol. 114, No. 11, pp. 3744-3749, ISSN 1089-5647.
- Gordon, E., Cohen, J., Engel, R., & Abbott, G.W. (2006). 1,4-Diazabicyclo[2.2.2]octane Derivatives: A Novel Class of Voltage-Gated Potassium Channel Blockers. *Mol. Pharmacol.*, Vol. 69, No. 3, pp. 718-726, ISSN 0026-895X.
- Kubisa, P. (2004). Application of ionic liquids as solvents for polymerization processes. *Prog. Polym. Sci.*, Vol. 29, (January 2004), pp. 3-12, ISSN 0079-6700.
- Lall, S., Mancheno, D., Castro, S., Behaj, V., Cohen, J. & Engel, R. (2000). Polycations. X. LIPs, a New Category of Ionic Liquid Based on Polyammonium Salts. J. Chem. Soc., Chem. Commun., (November 2004), pp. 2413-2414, ISSN 1364-548X.
- Lall, S., Behaj, V., Mancheno, D., Casiano, R., Thomas, M., Rikin, A., Gaillard, J., Raju, R., Scumpia, A., Engel, R., & Cohen, J. (2002). Polycations-12. The Synthesis of Liquid Ionic Phosphates (LIPs) from Mono- and Polycationic Ammonium Halides. *Synthesis*, No. 11, pp.1530-1540, ISSN 0039-7881.
- Lall-Ramnarine, S., Castaño, A. Subramaniam, G., Thomas, M.F., Wishart, J. (2009). Synthesis, characterization and radiolytic properties of bis(oxalato)borate containing ionic liquids. *Radiation Phys. Chem.*, Vol. 78, No. 12. pp. 1120-1125, 0969-806X

Lishka, U., Wietelmann, & Wegner, M. (1999). German Patent DE 19829030.

- Plechkova, N., & Seddon, K. (2007). Ionic Liquids: "Designer" Solvents for Green Chemistry, In: *Methods and Reagents for Green Chemistry: An Introduction*, Tundo, P., Perosa, A., & Zecchini, F., Chapter 5, John Wiley & Sons, Inc., wiley.com/WileyCDA/ WileyTitle/productCd-0470124075.html.
- Rengan, K. and Engel, R. (1990). Phosphonium Cascade Molecules, J. Chem. Soc., Chem. Commun., pp. 1084-1085, ISSN 1364-548X.
- Rengan, K. & Engel, R. (1991). The Synthesis of Phosphonium Cascade Molecules, J. Chem. Soc., Perkin Trans. I, pp. 987-990, ISSN 0300-922X.
- Rengan, K. & Engel, R. (1992). Ammonium Cascade Molecules, J. Chem. Soc. Chem. Commun., p. 758, ISSN 1364-548X.
- Shevchenko, V. & Engel, R. (1998). Polycations. III. Synthesis of Polyphosphonium Salts for Use as Antibacterial Agents. *Heteroatom Chem.*, Vol. 9, No. 5, pp. 495-502, ISSN 1042-7163.
- Strekas, T.C., Engel, R., Locknauth, K., Cohen, J., & Fabian, J. (1999). Polycations. 5. Inducement of Ψ-DNA Circular Dichroism Signals for Duplex Deoxyribonucleotide Homopolymers by Polycationic Strings. *Arch. Biochem. Biophys.*, Vol. 364, No. 1, pp. 129-131, ISSN 0003-9861.
- Thomas, M., Montenegro, D., Castaño, A., Friedman, L., Leb, J., Huang, M.L., Rothman, L., Lee, H., Capodiferro, C., Ambinder, D., Cere, E., Galante, J., Rizzo, J., Melkonian, K., & Engel, R. (2009a). Polycations. 17. Synthesis and properties of polycationic derivatives of carbohydrates, *Carbohydrate Res.*, Vol. 344, No. 13, pp. 1620-1627, ISSN 0008-6215.
- Thomas, M., Rothman, L., Hatcher, J., Agarkar, P., Ramkirath, R. Lall-Ramnarine, S., & Engel, R. (2009b). Synthesis and Thermochemical Properties of Stereoisomeric Dihydroxy- and Tetrahydroxyalkylammonium Salts. *Synthesis*, No. 9, pp. 1437-1444, ISSN 0039-7881.
- Xu, K., Zhang, S., Jow, T.R., Xu, W., & Austen, C. (2002). A, LiBOB as Salt for Lithium-Ion Batteries - A Possible Solution for High Temperature Operation. *Electrochem. and Solid-State Letters*, Vol. 5, No. 1, pp. A26-A29, ISSN 0013-4651.
- Xu, W., & Angell, C.A. (2001). LiBOB and Its Derivatives: Weakly Coordinating Anions, and the Exceptional Conductivity of Their Nonaqueous Solutions. *Electrochem. and Solid-State Letters*, Vol. 4, No. 1, pp. E1-E4, ISSN 0013-4651.





Ionic Liquids - Classes and Properties Edited by Prof. Scott Handy

ISBN 978-953-307-634-8 Hard cover, 344 pages **Publisher** InTech **Published online** 10, October, 2011 **Published in print edition** October, 2011

Room temperature ionic liquids (RTILs) are an interesting and valuable family of compounds. Although they are all salts, their components can vary considerably, including imidazolium, pyridinium, ammonium, phosphonium, thiazolium, and triazolium cations. In general, these cations have been combined with weakly coordinating anions. Common examples include tetrafluoroborate, hexafluorophosphate, triflate, triflimide, and dicyanimide. The list of possible anionic components continues to grow at a rapid rate. Besides exploring new anionic and cation components, another active and important area of research is the determinination and prediction of their physical properties, particularly since their unusual and tunable properties are so often mentioned as being one of the key advantages of RTILs over conventional solvents. Despite impressive progress, much work remains before the true power of RTILs as designer solvents (i.e. predictable selection of a particular RTIL for any given application) can be effectively harnessed.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Robert Engel (2011). Glycoside-Based Ionic Liquids, Ionic Liquids - Classes and Properties, Prof. Scott Handy (Ed.), ISBN: 978-953-307-634-8, InTech, Available from: http://www.intechopen.com/books/ionic-liquids-classes-and-properties/glycoside-based-ionic-liquids



InTech Europe

University Campus STeP Ri Slavka Krautzeka 83/A 51000 Rijeka, Croatia Phone: +385 (51) 770 447 Fax: +385 (51) 686 166 www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai No.65, Yan An Road (West), Shanghai, 200040, China 中国上海市延安西路65号上海国际贵都大饭店办公楼405单元 Phone: +86-21-62489820 Fax: +86-21-62489821 © 2011 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the <u>Creative Commons Attribution 3.0</u> <u>License</u>, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

IntechOpen

IntechOpen