Tris-imidazolium derivatives of isocyanuric acid. A lead for tripodal ionic liquids and anion receptors

Julio A. Seijas,* M. Pilar Vázquez-Tato*

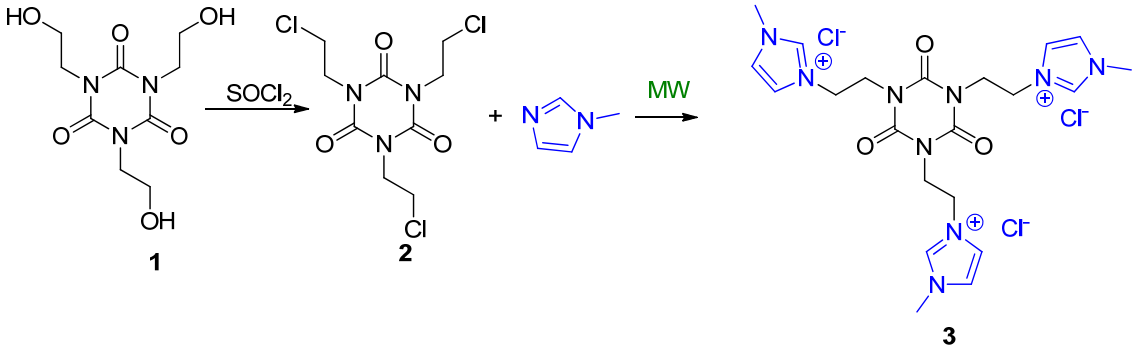
julioa.seijas@usc.es, pilar.vazquez.tato@usc.es

Department of Organic Chemistry. Facultade de Ciencias. Universidade de Santiago de Compostela. Campus Lugo. Aptdo. 280. 27080-Lugo. Spain.

Abstract: Tripodal topology of tris-imidazolium salts of isocyanuric acid derivatives is a field that has not been studied in detail. A strategy based on 1,3,5-tris(2-hydroxyethyl)-1,3,5-triazinane-2,4,6-trione was designed. This compound was converted into 3,3',3''-((2,4,6-trioxo-1,3,5-triazinane-1,3,5-triyl)tris(ethane-2,1-diyl))tris(1-methyl-1H-imidazol-3-ium) chloride in two steps through its trihalide derivative in good yields. This opens a new line of research for anionic receptors and polycationic ionic liquids.

Although polyimidazolium compounds have been studied in the last years, less attention has been paid to symmetrical ones, among these, tripodal ones are scarcely known. To our knowledge most of tripodal tris-imidazolium salts use benzene as nucleus [1] with only a few exceptions.[2] The availability of tripodal triazinetriones derived from isocianuric acid make of this type of compounds and ideal core for the synthesis of tripodal derivatives.[3]

Thus, in order to obtain 1,3,5-tris(2-chloroethyl)-1,3,5-triazinane-2,4,6-trione (**2**), the commercial precursor 1,3,5-tris(2-hydroxyethyl)-1,3,5-triazinane-2,4,6-trione (**1,** scheme 1) was treated with thionyl chloride under reflux to exchange its three hydroxyl groups by chlorine atoms. The substitution of the three haloalkane moieties was studied under microwave irradiation (100 W power during 2 minutes at 100 ºC), of 2 and N-methylimidazole (1:3) in solventless conditions, yielding 90% of 1,1',1''-((2,4,6-trioxo-1,3,5-triazinane-1,3,5-triyl)tris(ethane-2,1-diyl))tris(3-methyl-1H-imidazol-3-ium) chloride (**3**). This compound with a melting point lower than 100 ºC constitutes the lead of a new class of ionic liquids.



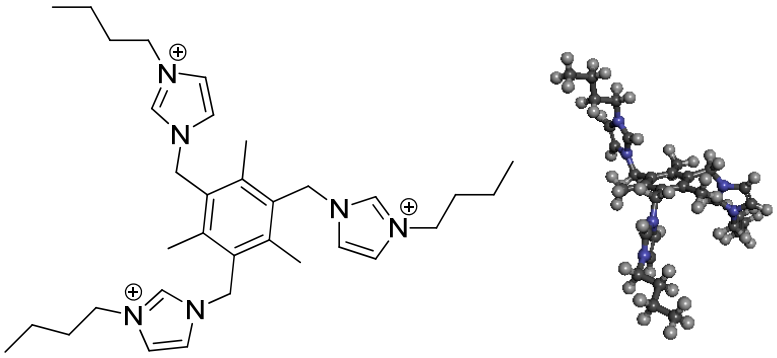
Scheme 1

Apart from the possibilities of tris imidazolium compound **3** as ionic liquid, an additional feature of interest is its similarity with some know anion receptors like 1,1',1''-((2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene))tris(3-butyl-1H-imidazol-3-ium)[6] (**4**, figure 1a).

In recent years, a relatively new cationic subunit for anion recognition [4] has been introduced, namely the 1,3-disubstituted imidazolium motif. While most other cationic anion complexing systems (e.g., protonated polyammonium, guanidinium, amidinium, and thiouronium) rely on a combination of electrostatic interactions and $^{+}$NH···A^{-} hydrogen bonds to achieve anion (A^{-}) recognition, receptors based on the imidazolium cation stabilize the corresponding anion complexes via a combination of electrostatic interactions and $^{+}$CH···A^{-} type hydrogen bonds. Therefore, compared to systems based on NH hydrogen bond donors, imidazolium-based receptors can offer a significant advantage, namely pH-independent binding. The fact that imidazolium can engage in CH-anion hydrogen-bonding interactions is now widely accepted.[5] For instance, such hydrogen bonds have been observed in a number of imidazolium halide salt structures determined by single crystal X-ray diffraction analysis.[5],[6]

Neutral anion receptors having amide, pyrrole, urea groups as binding sites form N–H anion hydrogen bonds.1 Most positively charged anion receptors have dealt with ammonium and guanidinium groups as binding sites interacting with the anions by either electrostatic forces or with N+–H···anion hydrogen bonds.1 In contrast, various positively charged imidazolium derivatives have been synthesized and studied as selective anion-receptors. Imidazolium group can make a strong interaction with anions through (C–H)+···X2 type ionic hydrogen bond because the charge–charge electrostatic interaction dominates.[7]

In 1999 Sato et al.[8] reported that the imidazolium-based tripodal receptor **4** (figure 1a) has considerable affinity for halide anions in polar solvent through electrostatic interactions and C-H.-X^- hydrogen bonds, the first example of C-H... X- hydrogen bond interaction of imidazolium in host-guest chemistry.



a b

Figure 1

In order to check the similarity of both kind of compounds we modelled the structure of trication **4** using MOPAC2012 software [9] with PM7 Hamiltonian with a Hf=568.71702 Kcal/mol the same minimization for trication **3** (figure 2) resulted in Hf=494.38815 Kcal/mol (figure 2).

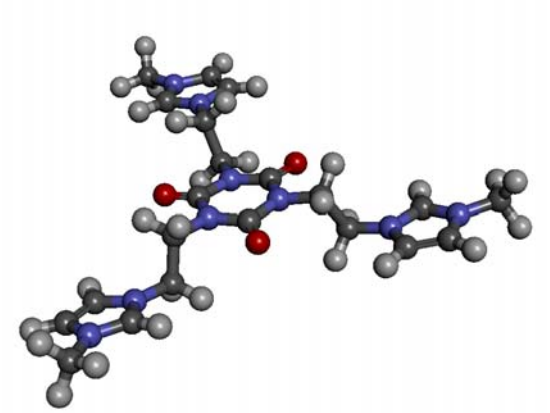
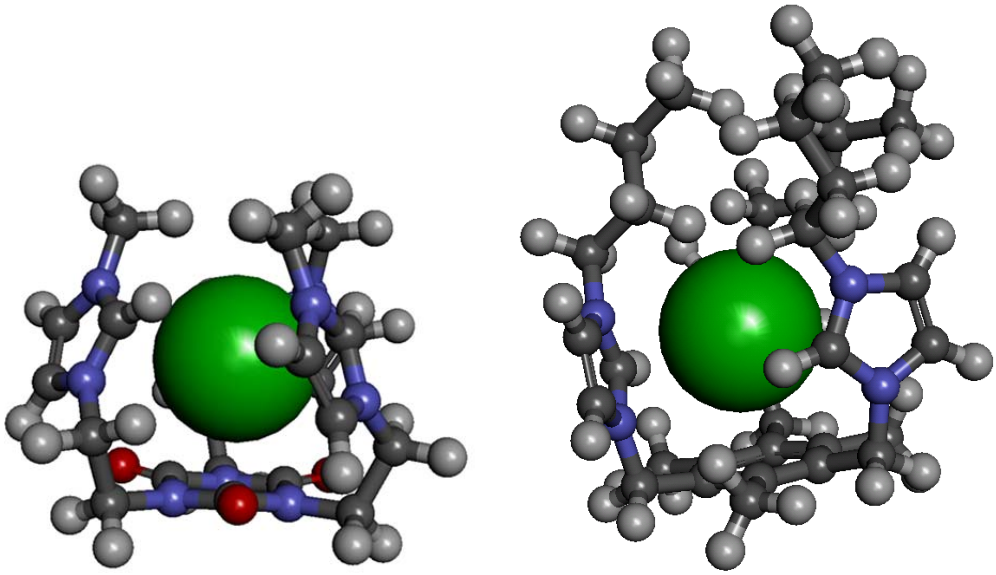


Figure 2

Both structures though comparable, have 74 Kcal/mol of difference. The same calculation for the structure postulated for **4** as ionic receptor (figure 3) resulted in 281.98145 Kcal/mol. Similar structure for compound **3** the Hf calculated was 208.23373 Kcal/mol, that is more stable than **4**.



a b

Figure 3 Minimized structures of 3 (a) and 4 (b)

In summary two step synthesis of a new tripodal ionic liquid derived from imidazolium and 1,3,5-triazine-2,4,6-trione was developed based on a solventless microwave key step. Besides, this constitutes a new lead in anion receptors chemistry since they present structural similarities with known anion receptors.

Experimental procedure

1,3,5-tris(2-chloroethyl)-1,3,5-triazinane-2,4,6-trione (**2**) [10] (949 mg, 3 mmol) and N-methylimidazole (738 mg, 9 mmol) and allylchloride were irradiated in a closed vessel, for 2 minutes at 100 °C (100W) in a Discovery microwave oven (CEM). The reaction mixture was dissolved in MeOH (1 mL) and CH_2Cl_2 (10 mL) is added. The upper phase was isolated and evaporated under vacuum to give 3,3',3''-((2,4,6-trioxo-1,3,5-triazinane-1,3,5-triyl)tris(ethane-2,1-diyl))tris(1-methyl-1H-imidazol-3-ium) (**3**) as a white solid (1.518 g, 90%). ^{1}H-NMR (DMSO-d_6) δ 9.74 (s, 1H), 7.93 (t, 1H, J= 1.8 Hz), 7.66 (t, 1H, J= 1.8 Hz), 4.47 (t, 2H, J= 5.2 Hz), 4.10 (t, 2H, J= 5.2 Hz), 3.87 (s, 3H, CH_3). ^{13}C-NMR (MeOD) δ 149.59 (s, C=O), 137.61, 123.67, 123.11, 47.74 (CH_2), 43.32 (CH_2), 35.38 (CH_3).

1,3,5-tris(2-chloroethyl)-1,3,5-triazinane-2,4,6-trione (**2**) ^{1}H-NMR (Cl_3CD) δ 4.20 (t, 2H, J= 6.4 Hz), 3.69 (t, 2H, J= 6.4 Hz).

Acknowledgements

Xunta de Galicia for financial support to “Rede Galega de Líquidos Iónicos (REGALIS)” and INCITE09 262346PR.

References

1.- Rit, A.; Pape, T.; Hepp, A.; Hahn, F. E. *Organometallics* **2011**, *30*, 334–347. González-Álvarez, J.; Blanco-Gomis, D.; Arias-Abrodo, P.; Díaz-Llorente; D.; N. Ríos-Lombardía, E. Busto, V. Gotor-Fernández, M. D. Gutiérrez-Álvarez, *J. Sep. Sci*. **2012**, *35*, 273–279. A. Pun, D. A. Hanifi, G. Kiel, E. O’Brien, and Y. Liu *Angew. Chem. Int. Ed.* **2012**, *51*, 13119 –13122. A. Rit, T. Pape, F. E. Hahn *J. Am. Chem. Soc.* **2010**, *132*, 4572–4573. R. Fang, Y. Liu, Z. Wang, X. Zhang *Polym. Chem*., 2013, 4, 900–903. Yuan, Y.; Jiang, Z.-L.; Yan, J.-M.; Gao, G.; Chan, A. S. C.; Xie, R.-G. *Synth. commun.* 30, 4555 (2000)

2.- F. Mutelet , J.-C. Moise, A. SkrzypczakJ. *Chem. Eng. Data* **2012**, *57*, 918 – 927. J. Pernak, A. Skrzypczak, G. Lota, E. Frackowiak *Chem. Eur. J.* 2007, 13, 3106 – 3112

3.- Seijas, J. A.; Carracedo-Taboada, M.; Feás, X.; Vázquez-Tato, M. P. *15th International Electronic Conference on Synthetic Organic Chemistry (ECSOC-15)* (a009) 2011. Seijas, J. A.; Labandeira-Peteiro, S.; Feás, X.; Vázquez-Tato; M. P. *15th International Electronic Conference on Synthetic Organic Chemistry (ECSOC-15)* (c002) 2011.

4.- *Anion Receptor Chemistry*. Sessler, J. L.; Gale, P. A.; Cho, W.-S. The Royal Society of Chemistry, 2006.

5.- Fannin Jr., A.A.;, King, L.A.; Levisky J.A.; Wilkes, J.S. *J. Phys. Chem.* **1984**, *88*, 2609.; Dieter, K.M.; Dymek Jr., C.J; Heimer, N.E.; Rovang J.W Wilkes, J.S. *J. Am. Chem. Soc.*, **1988**, *110*, 2722. Dymek Jr. C.J.; Stewart, J.J.P. *Inorg. Chem.*, **1989**, *28*, 1472. Abdul-Sada, A.K.; Greenway, A.M.; Hitchcock, P.B.; Mohammed, T.J.; Seddon K.R.; Zora, J.A. *J. Chem. Soc. Chem. Commun*., **1986**, 1753. Dymek Jr., C.J.; Grossie, D.A. Fratini A.V. and Adams, W.W. *J. Mol. Struct*., **1989**, *213*, 25.

6.- Abdul-Sada, A.K.; Al-Juaid, S.; Greenway, A.M; Hitchcock, P.B.; Howells M.J.; Seddon K.R and Welton, T. *Struct. Chem.*, **1990**, 1, 391; Wilkes, J.S.;Zaworotko,

M.J. *J. Chem. Soc. Chem. Commun.*, **1992**, 965. Arduengo III, A.J.; Dias, H.V.R.; Harlow R.L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 553. Hitchcock, P.B.; Seddon, K.R.; Welton, T. *J. Chem. Soc. Dalton Trans*., **1993**, 2639. Fuller, J.; Carlin, R.T.; de Long, H.C; Haworth D. *J. Chem. Soc. Chem. Commun.* **1994**, 299. Elaiwi, A.; P.B. Hitchcock, K.R. Seddon, N. Srinivasan, Y.-M. Tan, T. Welton and J.A. Zora, *J. Chem. Soc. Dalton Trans.,* 1995, 3467; Arduengo, III, A.J.; Krafczyk, R.; Schmutzler, R.; Craig, H.A,; Goerlich, J.R; Marshall, W.J.; Unverzagt, M. *Tetrahedron,* 1999, 55, 14523; M.L. Cole, C. Jones and P.C. Junk, New J. Chem., 2002, 262, 1296;

Holbrey, J.D.; Reichert, W.M., Rogers, R.D. *J. Chem. Soc. Dalton Trans.,* **2004**, 2267.

7,- Yoon, J.: Kim, S. K.; Singh, N. J.; Kim, K. S. *Chem. Soc. Rev*. **2006**, *35*, 355–360.

8.- K. Sate*, Sadao Arap, and T. Yamagishi *Tetrahedron Letters* 40 (1999) 5219-5222.

9.- MOPAC2012, James J. P. Stewart, Stewart Computational Chemistry, Colorado Springs, CO, USA, HTTP://OpenMOPAC.net (2012).

10.- Fukuoka, N.; Yasuda, H.; Nishimatsu, M.; Yamashita, T.; Fukui, K.; Osaki, Y. (2001), JP2001192373, CAN135:108117.