

A NEW CLASS OF IONIC SOLVENTS, ELECTROLYTES AND ENGINEERING FLUIDS BASED ON 1,3-ALKYLMETHYL-1,2,3-BENZOTRIAZOLIUM SALTS

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ABSTRACT

A new series of ionic liquids based on 1,3-alkylmethyl-1,2,3-benzotriazolium cation has been prepared. The spectroscopic, physical and electrochemical characteristics of this family of salts have been investigated with respect to potential usage as ionic solvents, electrolytes and engineering fluids. Incorporation of diverse anions including weak coordinating anion and pseudohalide with this benzotriazolium cation produces ionic liquids with advantageously low melting points and good thermal stability. Thermal analyses of these very stable salts included the determination of melting points (-65 to 164 °C) and decomposition temperatures (up to 291 °C). The electrochemical windows of representative benzotriazolium species has been investigated by cyclic voltammetry and determined to be ~ 3 V. The X-ray single crystal and spectroscopic studies revealed that weak hydrogen-bonding interactions between the benzotriazolium ring protons and the anions are present both in the solid state as well as in solution.

Keywords: ionic liquids, X-ray single crystal, thermal analysis, electrochemical analysis, benzotriazolium salt.

INTRODUCTION

In recent years the attention paid by the scientific community towards the use of ionic liquids as next generation electrolytes and "green" solvents has been ever increasing [1-6]. Ionic liquids have aroused increasing interest for their promising role in electrochemical applications [7] (e.g. batteries, electrochemical metal deposition and sensors); solvents for chemical synthesis [8], catalysis and biocatalysis [9] and as engineering fluids [10-14] (e.g. thermofluids, separation techniques, lubricants and liquid crystals) as a result of their unique chemical and physical properties and the relative ease with which these properties can be fine-tuned by altering the cationic or anionic moieties comprising the ionic liquid [15]. The spectrum of their physical and chemical properties is much larger than that of organic solvents.

Ionic liquids are those compounds composed of organic cations and inorganic or organic anions which are liquids at room temperature or whose melting points are slightly higher than ambient temperature: generally <100–150 °C [4]. Like inorganic molten salts, e.g. Na₃AlF₆ with m.p. = 1010 °C, they are composed entirely

of ions, but they may be distinguished from molten salts by their low melting points.

Research on ambient temperature ionic liquids has been directed largely toward common salts with alkylammonium, alkylphosphonium, *N*-alkylpyridinium and *N,N*-dialkyl-imidazolium cations and weakly coordinating anions [5, 16-18]. A very large fraction of the literature is devoted to 1,3-dialkylimidazolium salts **1** [1-6]. These ionic liquids or 'designer' solvents are truly amazing in that their liquid ranges and thermal stabilities can, in some cases do, exceed a 400°C range, and, in addition, they exhibit essentially no vapor pressure.

In connection with an ongoing project involving the chemistry of carbene analogue stable nitrenium ion, several novel salts based on 1,3-alkylmethyl-1,2,3-benzotriazolium cation **2** have been prepared. The side chains of this cation are structurally and functionally diverse compared to imidazolium cations, which are commonly used in ionic liquids.

New classes of ionic liquid are needed, both to further understanding of ionic liquid in general and also to find the appropriate combination of physical properties and performance geared towards industrial application.

EXPERIMENTAL SECTION

General Procedures

All reactions were performed under a dry N₂ atmosphere using standard Schlenk techniques. Solvents were dried and purified by conventional methods prior to use [19]. All chemicals were used as

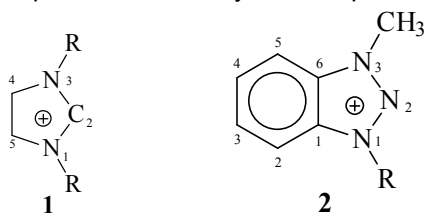


Fig 1. Structure of 1,3-dialkylimidazolium salts **1** and 1,3-alkylmethyl-1,2,3-benzotriazolium cation **2**

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received. ^1H spectra was recorded on a Bruker DPX 400 spectrometer with TMS as external references. Infrared spectra were recorded on a Perkin-Elmer FT-IR 2000 spectrometer. Mass spectra were recorded on a Finnigan MAT SSQ 7000. TG/DTA/DSC traces were recorded on a Netzsch STA 449C and melting points on an Electrothermal IA 9100 melting point apparatus. Elemental analyses were recorded on a LECO CHNS-932. X-ray intensities were measured by Dr. Axel Fischer, University of Magdeburg on a Bruker AXS Smart CCD-System and Siemens P4 diffractometer.

Synthetic Procedures

The first benzotriazolium salts were reported by Krollpfeiffer *et al.* in 1935 [20] who described the dialkylation of benzotriazole with an excess of alkyl iodide to give 1,3-dialkylbenzotriazolium iodides. 1-Methylbenzotriazole has been prepared using a number of different alkylating agents including dimethyl sulfate [21], trimethyl phosphate [22], methyl iodide [23] and dimethyl oxalate [24]. The 1-methylbenzotriazole prepared in this work utilised the procedure described by Masahiro *et al.* using dimethylmethylphosphonate as alkylating agent [25]. The second alkylation, forming the salt, was conducted using appropriate alkyl iodides or alkyl bromides in acetonitrile to form 1,3-alkylmethylbenzotriazolium halides.

1,3-Dimethyl-1,2,3-benzotriazolium *p*-toluenesulphonate [Bz01CH₃PhSO₃]. A solution of 1,3-dimethyl-1,2,3-benzotriazolium iodide in acetonitrile was added to a solution of silver *p*-toluenesulphonate in acetonitrile and stirred at room temperature for several hours. Solid silver iodide was filtered and the acetonitrile removed by vacuum. The product was then dried and stored in a vacuum desiccator. FTIR (KBr, cm⁻¹): 3435 m, 3113 m, 3079 m, 2956 m, 2873 w, 2361 w, 1905 w, 1810 w, 1609 m, 1493 m, 1480 m, 1456 m, 1401 m, 1348 m, 1317 m, 1269 m, 1208 s, 1191 s, 1152 m, 1124 s, 1034 s, 1012 s, 820 m, 800 m, 780 m, 765 m, 751 m, 683 s. $^1\text{H-NMR}$ (DMSO, 400 MHz): δ (ppm) = 8.33 (m, 2H ring); 7.98 (m, 2H, ring); 7.46 (m, 2H ring); 7.09 (m, 2H ring); 4.60 (s, 6H, -CH₃); 2.28 (s, 3H, -CH₃). CI-MS [m/z (%): Cl⁺ m/z 148.0 Bz01 and Cl⁻ m/z 171.1 CH₃C₆H₄SO₃⁻.

1,3-Butylmethyl-1,2,3-benzotriazolium *p*-toluenesulphonate [Bz02CH₃PhSO₃]. The title compound was prepared using the same method described for Bz01CH₃PhSO₃. FTIR (KBr, cm⁻¹): 3423 w, 2925 s, 2855 s, 1995 w, 1654 w, 1605 w, 1491 w, 1460 m, 1403 w, 1376 m, 1350 m, 1284 w, 1199 m, 1074 w, 1054 w, 1031 m, 1007 m, 849 w, 823 w, 781 m, 711 w, 679 m. $^1\text{H-NMR}$ (DMSO, 400 MHz): δ (ppm) = 0.96–1.00 (t, 3H, CH₃), 1.41–1.48 (sext, 2H, CH₂), 2.05–2.18 (quin, 2H,

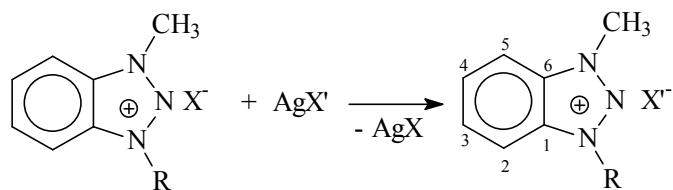
CH₂), 2.31 (s, 3H, C-CH₃), 4.71 (s, 3H, N-CH₃), 4.96–4.98 (t, 2H, N-CH₂), 7.04–7.07 (d, 2H, CH), 7.59–7.62 (d, 2H, CH), 7.80–7.83 (m, 2H, CH), 8.10–8.16 (m, 1H, CH), 8.29–8.34 (m, 1H, CH). ES-MS: ES⁺ m/z 189.9 Bz02 dan ES⁻ m/z 170.6 CH₃C₆H₄SO₃⁻.

1,3-Benzylmethyl-1,2,3-benzotriazolium *p*-toluenesulphonate [Bz03CH₃PhSO₃]. The title compound was prepared using the same method described for Bz01CH₃PhSO₃. FTIR (KBr, cm⁻¹): 3433w, 2925s, 2855s, 1996w, 1654w, 1604w, 1481w, 1460m, 1413w, 1376m, 1350m, 1284w, 1199m, 1075w, 1054w, 1031m, 1007m, 849w, 823w, 781m, 711w, 679m cm⁻¹. $^1\text{H-NMR}$ (DMSO, 400 MHz): δ (ppm) = 2.31 (s, 3H, Ph-CH₃), 4.63 (s, 3H, N-CH₃), 6.32 (s, 2H, N-CH₂), 7.04–7.07 (d, 2H, CH), 7.37–7.47 (m, 3H, CH), 7.52–7.56 (m, 2H, CH), 7.59–7.62 (d, 2H, CH), 7.80–7.83 (m, 2H, CH), 7.96–8.02 (m, 2H, CH), 8.35–8.42 (m, 2H, CH). ES MS: ES⁺ m/z 224 Bz03⁺ dan ES⁻ m/z 171 CH₃C₆H₄SO₃⁻.

1,3-Dimethyl-1,2,3-benzotriazolium dicyanamide [Bz04N(CN)₂]. The title compound was prepared using the same method described for Bz01CH₃PhSO₃ in ethanol. FTIR (KBr-Pellet, cm⁻¹): 3512 m, 3151 m, 3151 m, 3070 m, 2998 m, 2934 m, 2372 w, 1962 m, 1835 w, 1730 w, 1638 w, 1613 m, 1506 w, 1481 m, 1453 m, 1445 m, 1406 m, 1354 m, 1323 s, 1279 m, 1262 m, 1147 m, 1112 m, 1065 m, 1020 s, 1002 m, 903 m, 803 m, 780 s, 764 s, 689 w. $^1\text{H-NMR}$ (DMSO, 400 MHz): δ (ppm) = 8.34 (m, 2H ring), 8.00 (m, 2H, ring) und 4.61 (s, 6H, -CH₃). CI-MS: Cl⁺ m/z 148.0 Bz04 dan Cl⁻ m/z 65.9 N(CN)₂⁻.

1,3-Butylmethyl-1,2,3-benzotriazolium dicyanamide [Bz05N(CN)₂]. The title compound was prepared using the same method described for Bz01CH₃PhSO₃ in ethanol. FTIR (KBr-Pellet, cm⁻¹): 3486 s br, 3102 w, 3065 m, 3009 s, 2963 m, 2936 m, 2875 m, 2359 w, 2226 s, 2190 s, 2138 s, 1817 w, 1609 m, 1504 w, 1464 m, 1403 m, 1347 m, 1306 m, 1272 m, 1206 w, 1145 m, 1116 w, 1076 w, 1021 w, 1003 w, 951 w, 902 m, 805 w, 796 m, 776 m, 757 m, 659 w cm⁻¹. $^1\text{H-NMR}$ (DMSO, 400 MHz): δ (ppm) = 0.91–0.96 (t, 3H, CH₃), 1.32–1.45 (sext, 2H, CH₂), 1.96–2.06 (quin, 2H, CH₂), 4.61 (s, 3H, N-CH₃), 4.98–5.03 (t, 2H, N-CH₂), 7.97–8.03 (m, 2H, CH), 8.32–8.44 (m, 2H, CH). ES-MS: ES⁺ m/z 189.9 Bz05 dan ES⁻ m/z 65.5 N(CN)₂⁻.

1,3-Benzylmethyl-1,2,3-benzotriazolium icyanamide [Bz06N(CN)₂]. The title compound was prepared using the same method described for Bz01CH₃PhSO₃ in ethanol. FTIR (KBr-Pellet, cm⁻¹): 3484br, 3100m, 3064m, 3009s, 2694w, 2546w, 2363w, 2237s, 2192s, 2143s, 1995w, 1819w, 1609m, 1587w, 1496m, 1473s, 1456s, 1400m, 1366m, 1309m, 1273m, 1203m, 1182m, 1141m, 1087m, 1016m, 1002w, 953w, 904m,



X = Br⁻ and I⁻

R = CH₃, C₄H₉ and C₆H₅CH₂

X' = *p*-toluensulphonate and dicyanamide

Fig 2. Synthesis reaction of 1,3-alkylmethyl-1,2,3-benzotriazolium iodide

846w, 796m, 776m, 754m, 705m, 674w, 639w cm⁻¹. ¹H-NMR (DMSO, 400 MHz): δ (PPM) = 4.62 (s, 3H, N-CH₃), 6.30 (s, 2H, N-CH₂), 7.40-7.47 (m, 3H, CH), 7.52-7.56 (m, 2H, CH), 7.96-8.02 (m, 2H, CH), 8.33-8.40 (m, 2H, CH). ES-MS: ES⁺ *m/z* 224 Bz06⁺ dan ES⁻ *m/z* 65 N(CN)₂⁻.

RESULT AND DISCUSSION

Synthesis

A series of 1,3-alkylmethyl-1,2,3-benzotriazolium salts with weakly coordinating anion and pseudohalide as counter ion was prepared by metathesis of the silver salts of *p*-toluensulphonate and dicyanamide with the 1,3-alkylmethyl-1,2,3-benzotriazolium iodide (R = methyl and butyl) or bromide (R = benzyl) (Fig 2). The resulting compounds were characterized by ¹H-NMR spectroscopy, FTIR spectroscopy, mass analysis and elemental analysis, and found to be pure. The salts are not hygroscopic and are stable in air.

Infrared Spectroscopy

The aromatic C-H stretching vibrations in the benzotriazolium ring result in two highly characteristic infrared bands between 3100 - 3060 cm⁻¹. These are dependent on the presence and strength of hydrogen-bonding interactions between these protons and the anions of the ionic liquids [26-28].

For compound **Bz01I** the bands for ν (C(2&5)-H) and ν (C(3&4)-H) are observed respectively at 3095 and 3043 cm⁻¹. For compounds **Bz01CH₃PhSO₃** and **Bz01N(CN)₂** these vibrations are shifted to higher frequencies, with bands at 3113 and 3151 cm⁻¹ for ν (C(2&5)-H) and 3079 and 3070 cm⁻¹ for ν (C(3&4)-H), respectively. This shift is caused by a decrease in the strength of the C-H bonds in the benzotriazolium ring as their participation in hydrogen-bonding interactions increases [29]. In these salts an increase in the strength of the hydrogen bonds between the cation and the anion also resulted in lower ν (CH) stretching frequencies.

Table 2 Infrared spectral data for the aromatic stretching region (3100 - 3060 cm⁻¹) corresponding with C-H stretching frequencies in the benzotriazolium cation

Compound	Anion	ν (C(2&5)-H)	ν (C(3&4)-H)
Bz01I	I ⁻	3095	3043
Bz01CH₃PhSO₃	CH ₃ PhSO ₃ ⁻	3113	3079
Bz01N(CN)₂	N(CN) ₂ ⁻	3151	3070

Table 3 ¹H NMR chemical shifts (δ in ppm) of **Bz01I**, **Bz01CH₃PhSO₃** and **Bz01N(CN)₂** in dimethylsulfoxide-*d*₆

Compound	Anion	C(2&5)H	C(3&4)H	NCH ₃
Bz01I	I ⁻	8.38	8.01	4.63
Bz01CH₃PhSO₃	CH ₃ PhSO ₃ ⁻	8.34	8.00	4.61
Bz04N(CN)₂	N(CN) ₂ ⁻	8.34	8.00	4.61

¹H NMR Spectroscopy

The dependence of the ¹H NMR chemical shifts of the benzotriazolium ring protons on the various types of anions was investigated. The chemical shifts of C(2&4)-H, C(3&5)-H and NCH₃ for **Bz01I**, **Bz01CH₃PhSO₃** and **Bz01N(CN)₂** were measured in dry dimethylsulfoxide-*d*₆ at the same concentration (Table 3). The resonances for these protons proved slightly sensitive to the nature of the anion. The variations in chemical shifts were observed for the C(2&5)-H, C(3&4)-H and the NCH₃ resonances, which shifted as much as 0.01-0.04 ppm depending on the anion.

It has been noticed previously [29] that the chemical shifts of the imidazolium ring protons are anion- and concentration-dependent. This effect is strong for H-C(2) and weaker for H-C(4) and H-C(5). For these compounds it is known that two phenomena determine the chemical shifts of the protons on the ring: hydrogen-bonding interactions and ring stacking [17]. Hydrogen bonding causes the protons to shift to lower field and shielding of the protons from the magnetic field by the aromatic system of the imidazolium aromatic systems will result in a shift of the NMR signals to higher field [30]. This relationship is also slightly observed for benzotriazolium salts through anion series as presented in Tabel 3. At identical concentrations in dimethylsulfoxide-*d*₆, the chemical shifts of the ring protons C(2&5)H, C(3&4)H and NCH₃ increase slightly with anion basicity and thus hydrogen bonding ability.

Thermal Characteristic

Thermal characteristic of the compounds was assessed using simultaneous thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) in a nitrogen

Table 4. Melting points and liquid range of benzotriazolium salts **Bz01CH₃PhSO₃**, **Bz02CH₃PhSO₃**, **Bz03CH₃PhSO₃**, **Bz04N(CN)₂**, **Bz05N(CN)₂** and **Bz06N(CN)₂**

Compound	Anion	Melting Point (°C)	Decomposition Temperature (°C)	Liquid Range (K)
Bz01CH₃PhSO₃	CH ₃	164	291	127
Bz02CH₃PhSO₃	C ₄ H ₉	120	225	105
Bz03CH₃PhSO₃	C ₆ H ₅ CH ₂	143	205	62
Bz04N(CN)₂	CH ₃	131	256	125
Bz05N(CN)₂	C ₄ H ₉	-65 ^(a)	185	250
Bz06N(CN)₂	C ₆ H ₅ CH ₂	-34 ^(a)	155	189

atmosphere, heating at a rate of 3 °C/min. For the benzotriazolium salts **Bz01CH₃PhSO₃**, **Bz02CH₃PhSO₃**, **Bz03CH₃PhSO₃**, **Bz04N(CN)₂**, **Bz05N(CN)₂** and **Bz06N(CN)₂** the melting points and the thermal stability were determined (Table 4). All compounds are solids that melt well above room temperature, except for **Bz05N(CN)₂** and **Bz06N(CN)₂** for which DSC measurements indicated melting point at low temperature. The salts **Bz01CH₃PhSO₃**, **Bz02CH₃PhSO₃**, **Bz03CH₃PhSO₃**, and **Bz04N(CN)₂** are perhaps too high for most solvent and fluid applications but these salts may be of interest in solid electrolyte applications. All compounds were stable up to 150 °C. For all ionic liquids the decomposition process was complete above 300 °C.

Table 4 shows the effect of cation symmetry for a series of benzotriazolium salts. Melting points of organic salts have an important relationship to the symmetry of the ions. Increasing symmetry in the ions increases melting points, by permitting more efficient ion packing in the crystal cell. Conversely, a reduction in the symmetry of the cations causes a distortion from ideal close packing of the ionic charges in the solid state lattice, a reduction in the lattice energy, and depression of the melting points.

Cyclic Voltammetry

The measurement was conducted to **Bz05N(CN)₂** in a nitrogen filled glove-box at 100 °C using a glassy carbon working electrode, silver pseudo-reference electrode and platinum counter electrode. The ionic liquid has an electrochemical window of at ~ 3 Volts (V). The reductive and oxidative breakdown limits are in the ranges of -1 and 2 V versus Ag/Ag⁺. The reduction process, which is expected to involve the Bz05 cation, begin at approximately -1 V for dicyanamide anion. This limit is similar for ionic liquids of the imidazolium cation but not quite as impressive as limits seen for the pyrrolidinium cation [31].

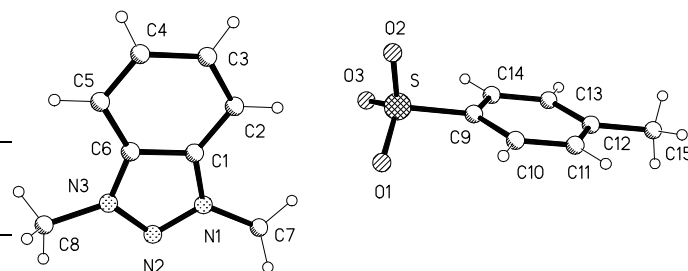


Fig 3. The structure of 1,3-dimethyl-1,2,3-benzotriazolium *p*-toluensulphonate **Bz01CH₃PhSO₃** in crystal

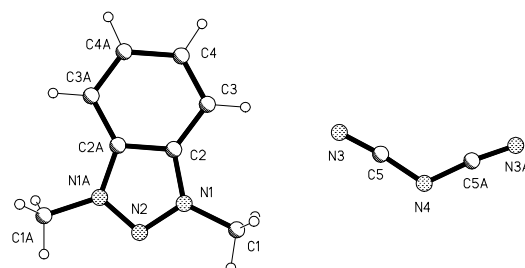


Fig 4. The structure of 1,3-dimethyl-1,2,3-benzotriazolium dicyanamide **Bz01N(CN)₂** in crystal

Structure

The structural features would be helpful to explain the physical and chemical properties of the compounds. Crystals suitable for single crystal X-ray structure determination were obtained for **Bz01CH₃PhSO₃** and **Bz04N(CN)₂**. Crystals of **Bz01CH₃PhSO₃** and **Bz04N(CN)₂** was obtained by slow evaporation of acetonitrile and ethanol respectively from a concentrated solution. The crystal structures of **Bz01CH₃PhSO₃** and **Bz04N(CN)₂** are represented in Fig 3 and 4.

The presence of a 1,3-dimethyl-1,2,3-benzotriazolium cation is common to all structures. Comparison of these cations shows just a little variation in their bond distances and angles. The internal dimensions of the ring are largely insensitive to its environment. 1,3-Dimethyl-1,2,3-benzotriazolium in **Bz01CH₃PhSO₃** and **Bz04N(CN)₂** are essentially planar. However, considering the ideal plane through C(1)-C(6) and N(1)-N(3) significant differences concerning the deviation from planarity are observed. The central rings are planar within 0.15 – 0.89 pm. The C(7,8)-atoms also deviate no more than 0.26 – 1.75 pm.

In the crystal of **Bz01CH₃PhSO₃** *p*-toluensulphonate anions are connected to chains along *c*-axis by two weak hydrogen bonding CH(15A)···O(3) and CH(15C)···O(3) (Fig 5).

The packing in the solid state structure of **Bz01CH₃PhSO₃** and **Bz04N(CN)₂** are characterized by a three-dimensional network of weak hydrogen bonded ions.

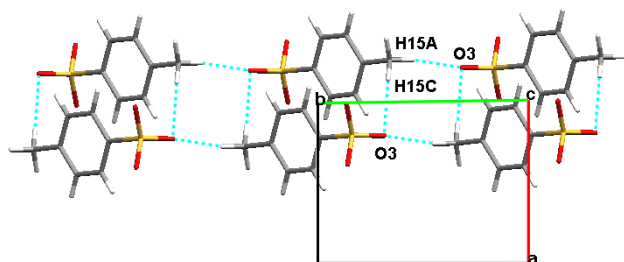


Fig 5. A chain of p-toluensulphonate anions by weak hydrogen bonding along c-axis

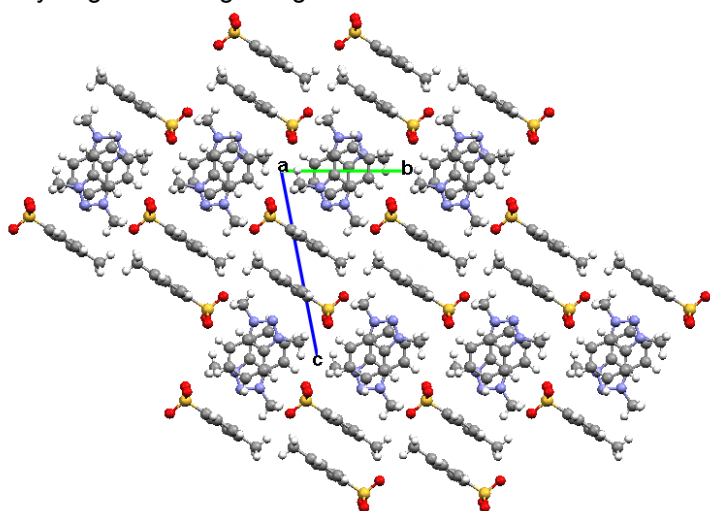


Fig 4. Packing diagram of 1,3-dimethyl-1,2,3-benzotriazolium p-toluensulpho-nate **Bz01CH₃PhSO₃** along a-axis (hydrogen bonds are omitted for clarity)

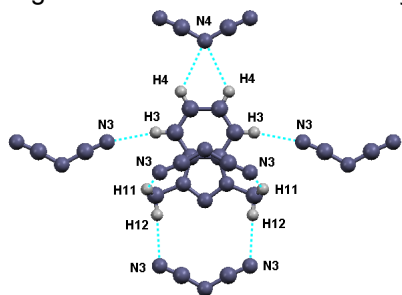


Fig 5. Packing diagram of 1,3-dimethyl-1,2,3-benzotriazolium dicyanamide **Bz04N(CN)₂** along c-axis

CONCLUSION

New thermally stable ionic liquids based on 1,3-alkylmethyl-1,2,3-benzotriazolium cation have been synthesized and characterized. The effects of variation of the anion and symmetry of cation on the physical properties of the salts with weakly coordinating anion and pseudohalide are reported. One of the interesting features of ionic liquids that benefits their use as ionic solvents, electrolytes and engineering liquids is the possibility of adapting their properties by choosing different cation-anion combinations. Marked variations in melting points appear to be primarily a function of the

anion and symmetry of cation. Work is being carried out to extend the understanding of the chemical and physical properties of these versatile novel compounds and to develop methodologies leading to even more dense liquids.

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