Synthesis and Characterization of *ortho*-Xylyl Linked *Bis*-benzimidazolium Salts (Part-II)

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A number of N-alkylbenzimidazoles were synthesized by reactions of benzimidazole with alkyl halides (PentBr, HexBr, OctBr, DecBr). The subsequent treatment of the resulting N-alkylbenzimidazoles with 1,2-*bis*-(bromomethylene) benzene afforded corresponding *bis*-benzimidazolium salts. All the compounds were characterized by spectroscopic techniques (NMR and FT-IR) and microanalysis. Molecular structures of selected compounds were established through single crystal X-ray diffraction studies.

Key Words: Benzimidazolium salts, N-Heterocyclic carbenes, Crystal structures.

INTRODUCTION

N-Heterocyclic carbenes (NHCs) have become universal ligands in organometallic and inorganic coordination chemistry¹ as their metal complexes have widespread biological²⁻⁵ and catalytic⁶⁻¹² applications. Our group is actively working on the synthesis and characterization of imidazole and benzimidazole based azolium salts and their metal (Ag, Pd, V, Hg) complexes with biological and catalytic applications. The recent work in our group comprises the synthesis of series of xylyl (*ortho*, *meta* and *para*) linked *bis*-benzimidazolium salts with alkyl substitutions (ethyl-decyl) and their metal (Ag and Hg) complexes. We reported a part of *ortho*-xylyl linked *bis*-benzimidazolium salts¹³ and selected crystal structures¹⁴ from *ortho* series. Herein we report the remaining part of this series with few more crystal structures.

EXPERIMENTAL

The FT-IR spectra were recorded on a Perkin-Elmer system 2000 spectrometer in KBr (for solids) and on thallium bromide disks (for liquids). The ¹H and ¹³C NMR spectra were obtained on a Bruker DPX-500 instrument from solutions in DMSO-*d*₆. The melting points were determined using Stuart Scientific SMP-1 (UK). The CHN microanalyses were carried out by using a Perkin Elmer 2400 LS Series CHN/S analyzer.

Synthesis of N-substituted benzimidazoles (I-IV): All the N-substituted benzimidazole compounds (I-IV) were prepared according to the method developed by Starikova *et al.*¹⁵, with minor modifications. In general, potassium hydroxide (1.5 equivalent) was added to a solution of benzimidazole (1 equivalent) in DMSO (30-40 mL for 0.01-0.02 M of reactants)

and mixture was stirred for 0.5 h at RT (25-27 °C) and respective alkyl halide (1 equivalent) was added dropwise under vigorous stirring. After 2 h, the mixture was poured into 200-300 mL of water and extracted with chloroform (6 mL × 25 mL), the combined extract was filtered through 5 plies of Whatman filter papers in order to dry the extract. This process of filtration was repeated twice to collect crystal clear solution of desired compound which was finally evaporated under reduced pressure. Desired compounds were obtained as thick yellowish fluids and characterized by spectroscopic (FT-IR and NMR) techniques before further use.

N-Pentylbenzimidazole (I): Thick yellowish fluid. Yield 5.21 g (92.37 %). For characterization refer¹⁶.

N-Hexylbenzimidazole (II): Thick yellowish fluid. Yield 5.72 g (94.24 %). ¹H NMR (500 MHz, DMSO-*d*₆): δ 0.77 (3H, t, CH₃, *J* = 7.00 Hz), 1.19 (6H, br.m, 3 × CH₂), 1.72 (2H, Pent, CH₂, *J* = 7.00 Hz), 4.14 (2H, t, CH₂-N, *J* = 7.00 Hz), 7.17 (2H, m, Ar 2 × CH), 7.47 (1H, d, Ar 1 × CH, *J* = 7.5 Hz), 7.65 (1H, d, Ar 1 × CH, *J* = 8.00 Hz), 8.12 (1H, s, NCHN); ¹³C{¹H NMR}(125.1 MHz, DMSO-*d*₆): 13.54 (CH₃), 21.82, 25.67, 29.20, 30.58 (4 × CH₂), 44.01 (R-CH₂-N) 109.86, 119.29, 121.08, 121.93, 133.60 (Ar-C) 143.50 (NCHN, d, *J* = 8.75 Hz). FT-IR (KBr, ν_{max}, cm⁻¹): 3434 (C_{aliph}-N_{benzimi}); 3077, 3056 (C-H_{arom}); 2957, 2931, 2859 (C-H_{aliph}), 1615 (C_{arom}-C_{arom}); 1496, 1459, 1286, 1365 (C_{arom}-N_{benzimi}).

N-Octylbenzimidazole (III): Thick yellowish fluid. Yield 5.72 g (93.44 %). ¹H NMR (500 MHz, DMSO-*d*₆): δ 0.84 (3H, t, CH₃, *J* = 7.00 Hz), 1.17-1.23 (10H, br.m, 5 × CH₂), 1.75 (2H, Pent, CH₂, *J* = 7.00 Hz), 4.18 (2H, t, CH₂-N, *J* = 7.00 Hz), 7.21 (2H, m, Ar 2 × CH), 7.52 (2H, d, Ar 1 × CH, *J* = 8.00 Hz), 7.68 (1H, d, Ar 1 × CH, *J* = 8.00 Hz), 8.19 (1H,

s, NCHN); $^{13}\text{C}\{^1\text{H NMR}\}$ (125.1 MHz, DMSO- d_6): 13.65 (CH_3), 21.92, 26.03, 28.39 (CH_2), 28.46 ($2 \times \text{CH}_2$, d, $J = 8.75$ Hz), 29.28, 31.06 (CH_2), 43.98 ($\text{R-CH}_2\text{-N}$), 109.96, 119.32, 121.08, 121.92, 133.68 (Ar-C) 143.64 (NCHN, d, $J = 17.51$ Hz). FT-IR (KBr, ν_{max} , cm^{-1}): 3422 ($\text{C}_{\text{aliph}}\text{-N}_{\text{benzimi}}$); 3056 (C-H_{arom}); 2956, 2929, 2857 ($\text{C-H}_{\text{aliph}}$), 1615 ($\text{C}_{\text{arom}}\text{-C}_{\text{arom}}$); 1496, 1459, 1286, 1365 ($\text{C}_{\text{arom}}\text{-N}_{\text{benzimi}}$).

N-Decylbenzimidazole (IV): Thick yellowish fluid. Yield 7.14 g (92.37 %). $^1\text{H NMR}$ (500 MHz, DMSO- d_6): δ 0.822 (3H, t, CH_3 , $J = 7.00$ Hz), 1.17 - 1.21 (16H, br.m, $8 \times \text{CH}_2$), 1.75 (2H, Pent, CH_2 , $J = 7.00$ Hz), 4.19 (2H, t, $\text{CH}_2\text{-N}$, $J = 7.00$ Hz), 7.20 (2H, m, Ar $2 \times \text{CH}$), 7.54 (1H, d, Ar 1 $\times \text{CH}$, $J = 8.00$ Hz), 7.65 (1H, d, Ar 1 $\times \text{CH}$, $J = 8.00$ Hz), 8.19 (1H, s, NCHN); $^{13}\text{C}\{^1\text{H NMR}\}$ (125.1 MHz, DMSO- d_6): 13.73 (CH_3), 21.98, 26.03, 28.44 (CH_2), 28.57 ($2 \times \text{CH}_2$, d, $J = 16.26$ Hz), 28.82 ($2 \times \text{CH}_2$, d, $J = 1.25$ Hz), 29.29 (CH_2), 43.98 ($\text{R-CH}_2\text{-N}$), 110.05, 119.33, 121.12, 121.95, 133.71 (Ar-C) 143.74 (NCHN, d, $J = 31.27$ Hz). FT-IR (KBr, ν_{max} , cm^{-1}): 3428 ($\text{C}_{\text{aliph}}\text{-N}_{\text{benzimi}}$); 3055 (C-H_{arom}); 2929, 2855 ($\text{C-H}_{\text{aliph}}$), 1615 ($\text{C}_{\text{arom}}\text{-C}_{\text{arom}}$); 1496, 1459, 1286, 1366 ($\text{C}_{\text{arom}}\text{-N}_{\text{benzimi}}$).

Synthesis of bis-benzimidazolium salts (V-VIII): The synthesis of ligands (V-VIII) was carried out by same method as we reported previously¹³. All the bis-benzimidazolium salts were collected as powderous material directly from reaction medium and dried under vacuum for 24 h. The physical appearances, yields and instrumental characterizations are mentioned under respective headings.

3,3'-(1,2-Phenylenebis(methylene))bis(1-pentylbenzimidazolium) dibromide monohydrate (V.2Br): White powder. Yield 0.55 g (16.81 %), m.p. 212-216 °C. $^1\text{H NMR}$ (500 MHz, DMSO- d_6): 0.87 (6H, t, $2 \times \text{CH}_3$, $J = 7.00$ Hz), 1.31-1.36 (8H, m, $4 \times \text{CH}_2$), 1.91 (4H, pent, $2 \times \text{CH}_2$, $J = 7.5$ Hz), 4.50 (4H, t, $2 \times \text{N-CH}_2\text{-R}$, $J = 7.50$ Hz), 6.10 (4H, s, $2 \times \text{N-CH}_2\text{-Ar}$), 7.20 (2H, q, Ar $2 \times \text{CH}$, $J = 3.5$ Hz), 7.41 (2H, q, Ar $2 \times \text{CH}$, $J = 3.50$ Hz), 7.65 (2H, t, Ar $2 \times \text{CH}$, $J = 7.5$ Hz), 7.71 (2H, t, Ar $2 \times \text{CH}$, $J = 7.50$ Hz), 7.98 (2H, d, Ar $2 \times \text{CH}$, $J = 8.0$ Hz), 8.16 (2H, d, Ar $2 \times \text{CH}$, $J = 8.50$ Hz), 9.93 (2H, s, $2 \times \text{NCHN}$); $^{13}\text{C}\{^1\text{H NMR}\}$ (125.1 MHz, DMSO- d_6): 13.72 (CH_3), 21.57 (CH_2), 28.44 ($2 \times \text{CH}_2$, d, $J_{\text{C}3,4} = 43.78$ Hz), 46.85 ($\text{R-CH}_2\text{-N}$), 47.57 (Ar- $\text{CH}_2\text{-N}$), 114.01 (Ar-C, d, $J = 16.26$ Hz), 126.78 (Ar-C, d, $J = 11.25$ Hz), 128.66, 129.30, (Ar-C), 131.12 (Ar-C, d, $J = 16.26$ Hz), 132.01 (Ar-C) and 142.59 (NCHN). FT-IR (KBr, ν_{max} , cm^{-1}): 3446, 3380 ($\text{C}_{\text{aliph}}\text{-N}_{\text{benzimi}}$); 3117, 3028 (C-H_{arom}); 2991, 2953, 2933, 2860 ($\text{C-H}_{\text{aliph}}$), 1633, 1607, 1560 ($\text{C}_{\text{arom}}\text{-C}_{\text{arom}}$); 1196, 1429, 1459, 1485 ($\text{C}_{\text{arom}}\text{-N}_{\text{benzimi}}$). Anal. calcd. (%) for: $\text{C}_{32}\text{H}_{42}\text{N}_4\text{OBr}_2$: C, 58.45; H, 6.29; N, 8.52. Found (%): C, 58.10; H, 6.11; N, 8.40.

3,3'-(1,2-Phenylenebis(methylene))bis(1-hexylbenzimidazolium) dibromide monohydrate (VI.2Br): White powder. Yield 5.35 g (78.10 %), m.p. 242-244 °C. $^1\text{H NMR}$ (500 MHz, DMSO- d_6): δ 0.82 (6H, t, $2 \times \text{CH}_3$, $J = 7.00$ Hz), 1.23-1.36 (12H, br.m, $6 \times \text{CH}_2$), 1.90 (4H, Pent, $2 \times \text{CH}_2$, $J = 7.5$ Hz), 4.54 (4H, t, $2 \times \text{CH}_2\text{-N}$, $J = 7.5$ Hz), 6.24 (4H, s, $2 \times \text{Ar-CH}_2\text{-N}$), 7.23 (2H, q, Ar $2 \times \text{CH}$, $J = 3.5$ Hz), 7.39 (2H, q, Ar $2 \times \text{CH}$, $J = 3.50$ Hz), 7.62 (2H, t, Ar $2 \times \text{CH}$, $J = 7.5$ Hz), 7.68 (2H, t, Ar $2 \times \text{CH}$, $J = 8.00$ Hz), 8.07 (2H, d, Ar $2 \times \text{CH}$, $J = 8.5$ Hz), 8.17 (2H, d, Ar $2 \times \text{CH}$, $J = 8.00$ Hz), 10.10 (2H, s, $2 \times \text{NCHN}$); $^{13}\text{C}\{^1\text{H NMR}\}$ (125.1 MHz, DMSO- d_6): 13.72 (CH_3), 21.18, 25.36, 28.45, 30.56, 39.02 ($5 \times \text{CH}_2$), 46.89

($\text{R-CH}_2\text{-N}$), 47.74 (Ar- $\text{CH}_2\text{-N}$), 114.11 (Ar-C, d, $J = 30$ Hz), 126.68 (Ar-C, d, $J = 12.51$ Hz), 128.66, 129.19, (Ar-C, s), 131.13 (Ar-C, d, $J = 106$ Hz), 131.90, 132.08 (Ar-C) and 142.46 (NCHN). FT-IR (KBr, ν_{max} , cm^{-1}): 3435, 3386 ($\text{C}_{\text{aliph}}\text{-N}_{\text{benzimi}}$); 3111, 3029 (C-H_{arom}); 2997, 2958, 2931, 2858 ($\text{C-H}_{\text{aliph}}$), 1631, 1609, 1559 ($\text{C}_{\text{arom}}\text{-C}_{\text{arom}}$); 1192, 1429, 1446, 1485 ($\text{C}_{\text{arom}}\text{-N}_{\text{benzimi}}$). Anal. calcd. (%) for: $\text{C}_{34}\text{H}_{45}\text{N}_4\text{OBr}_2$: C, 59.57; H, 6.62; N, 8.17. Found (%): C, 59.44; H, 6.43; N, 8.17.

3,3'-(1,2-Phenylenebis(methylene))bis(1-octylbenzimidazolium) dibromide monohydrate (VII.2Br): White crystalline powder. Yield 7.25 g (97.76 %), m.p. 198-201 °C. $^1\text{H NMR}$ (500 MHz, DMSO- d_6): δ 0.82 (6H, t, $2 \times \text{CH}_3$, $J = 7.00$ Hz), 1.21 - 1.36 (20H, br.m, $10 \times \text{CH}_2$), 1.91 (4H, Pent, $2 \times \text{CH}_2$, $J = 7.50$ Hz), 4.54 (4H, t, $2 \times \text{CH}_2\text{-N}$, $J = 7.50$ Hz), 6.22 (4H, s, $2 \times \text{Ar-CH}_2\text{-N}$), 7.22 (2H, q, Ar $2 \times \text{CH}$, $J = 3.50$ Hz), 7.39 (2H, q, Ar $2 \times \text{CH}$, $J = 3.50$ Hz), 7.62 (2H, t, Ar $2 \times \text{CH}$, $J = 7.75$ Hz), 7.68 (2H, t, Ar $2 \times \text{CH}$, $J = 7.75$ Hz), 8.07 (2H, d, Ar $2 \times \text{CH}$, $J = 8.50$ Hz), 8.18 (2H, d, Ar $2 \times \text{CH}$, $J = 8.50$ Hz), 10.08 (2H, s, $2 \times \text{NCHN}$); $^{13}\text{C}\{^1\text{H NMR}\}$ (125.1 MHz, DMSO- d_6): 13.83 (CH_3), 21.96, 25.36, 25.74 ($3 \times \text{CH}_2$), 28.44 ($3 \times \text{CH}_2$, t, $J_{\text{C}5,6} = 10$ Hz, $J_{\text{C}6,7} = 6.25$ Hz), 46.89 ($\text{R-CH}_2\text{-N}$), 47.73 (Ar- $\text{CH}_2\text{-N}$), 114.12 (Ar-C, d, $J = 30$ Hz), 126.68 (Ar-C, d, $J = 11.25$ Hz), 128.65, 129.19, (Ar-C), 131.15 (Ar-C, d, $J = 10$ Hz), 132.10 (Ar-C) and 142.49 (NCHN). FT-IR (KBr, ν_{max} , cm^{-1}): 3439, 3388 ($\text{C}_{\text{aliph}}\text{-N}_{\text{benzimi}}$); 3107, 3024 (C-H_{arom}); 2994, 2928, 2856 ($\text{C-H}_{\text{aliph}}$); 1609, 1557 ($\text{C-H}_{\text{aliph}}$); 1198, 1429, 1446, 1483 ($\text{C}_{\text{arom}}\text{-N}_{\text{benzimi}}$). Anal. calcd. (%) for: $\text{C}_{38}\text{H}_{54}\text{N}_4\text{OBr}_2$: C, 61.54; H, 7.20; N, 7.55. Found (%): C, 61.63; H, 7.25; N, 7.60.

3,3'-(1,2-Phenylenebis(methylene))bis(1-decylbenzimidazolium) dibromide monohydrate (VIII.2Br): White powder. Yield 5.65 g (70.89 %), m.p. 148-150 °C. $^1\text{H NMR}$ (500 MHz, DMSO- d_6): δ 0.83 (6H, t, $2 \times \text{CH}_3$, $J = 7.25$ Hz), 1.22-1.34 (28H, br.m, $14 \times \text{CH}_2$), 1.90 (4H, Pent, $2 \times \text{CH}_2$, $J = 7.50$ Hz), 4.51 (4H, t, $2 \times \text{CH}_2\text{-N}$, $J = 7.50$ Hz), 6.16 (4H, s, $2 \times \text{Ar-CH}_2\text{-N}$), 7.21 (2H, q, Ar $2 \times \text{CH}$, $J = 3.50$ Hz), 7.40 (2H, q, Ar $2 \times \text{CH}$, $J = 3.50$ Hz), 7.64 (2H, t, Ar $2 \times \text{CH}$, $J = 7.75$ Hz), 7.69 (2H, t, Ar $2 \times \text{CH}$, $J = 7.75$ Hz), 8.03 (2H, d, Ar $2 \times \text{CH}$, $J = 8.50$ Hz), 8.16 (2H, d, Ar $2 \times \text{CH}$, $J = 8.00$ Hz), 10.09 (2H, s, $2 \times \text{NCHN}$); $^{13}\text{C}\{^1\text{H NMR}\}$ (125.1 MHz, DMSO- d_6): 13.86 (CH_3), 22.00, 25.76, (CH_2), 28.53 ($3 \times \text{CH}_2$, t, $J_{\text{C}4,5} = 12.50$ Hz, $J_{\text{C}5,6} = 7.50$ Hz), 28.82 ($2 \times \text{CH}_2$, d, $J_{\text{C}7,8} = 2.50$ Hz), 39.20 (CH_2), 46.88 ($\text{R-CH}_2\text{-N}$), 47.66 (Ar- $\text{CH}_2\text{-N}$), 114.06 (Ar-C, d, $J = 23.76$ Hz), 126.72 (Ar-C, d, $J = 10$ Hz), 128.67, 129.24, (Ar-C), 131.20 (Ar-C, d, $J = 12.5$ Hz), 132.06 (Ar-C) and 142.53 (NCHN). FT-IR (KBr, ν_{max} , cm^{-1}): 3395 ($\text{C}_{\text{aliph}}\text{-N}_{\text{benzimi}}$); 3124, 3025 (C-H_{arom}); 2923, 2853 ($\text{C-H}_{\text{aliph}}$); 1609, 1561 ($\text{C-H}_{\text{aliph}}$); 1204, 1429, 1457, 1481 ($\text{C}_{\text{arom}}\text{-N}_{\text{benzimi}}$). Anal. calcd. (%) for: $\text{C}_{42}\text{H}_{62}\text{N}_4\text{OBr}_2$: C, 63.23; H, 7.71; N, 7.02. Found (%): C, 61.95; H, 7.51; N, 6.81.

RESULTS AND DISCUSSION

Most of the naturally occurring and synthetically available imidazolium or benzimidazolium derivatives are of the non-bridged variety. It was therefore of great interest to investigate the addition of an alkyl spacer of 1,2-dimethylene benzene to such non-bridged systems, to be able to extend the application of direct electrophilic substitution of long-chain and branched alkyl chain methodology.

Syntheses: The reaction of two equivalents of N-alkyl benzimidazole with 1,2-*bis*-(bromomethylene)benzene in 1,4-dioxane at 100 °C for 24 h afforded the product in 72-99 % yield with an exception of **V.2Br** (yield 16.85 %).

We have already reported^{14,17,18} the synthesis of a variety of medium- and long-chain-derivatized mono- and *bis*-imidazolium and benzimidazolium salts by our simple, high-yielding and general synthetic method. We previously employed ethyl bromide, propyl bromide, *i*-propyl bromide, butyl bromide, benzyl chloride and heptyl bromide as the electrophiles¹³ and now show that the use of pentyl bromide, hexyl bromide, octyl bromide and decyl bromide is also successful. The method adopted for the synthesis of title compounds is selective for the 1-position heterocycle and the two-step process is essentially quantitative. Indeed, upon treating alkylbenzimidazole (**I-IV**) with *o*-xylyl dibromide [1,2-*bis*-(bromomethylene)-benzene], respective *bis*-benzimidazolium salt was observed, to give **V.2Br-VIII.2Br** in almost quantitative yield. All prepared compounds are completely soluble in polar solvents like DMSO, DMF, methanol and insoluble in common non-polar to slightly polar organic solvents like benzene, diethyl ether, *n*-hexane, toluene, *etc.*

Furthermore the use of 1,4-dioxane as reaction medium for the synthesis of *bis*-benzimidazolium salts is highly recommended because of its inert nature and moderate boiling point (101 °C). By using 1,4-dioxane, *bis*-benzimidazolium salts can be collected directly as solids from the reaction medium by filtration and can be purified by washing of fresh 1,4-dioxane (5 mL × 3 mL). It is important to note that solubility of these salts in 1,4-dioxane increases with the increase in chain length of alkyl substitutions due to decrease in polarity, for example compound **VIII.2Br** (decyl substituted) is completely soluble in hot 1,4-dioxane and was collected as solid by cooling the reaction medium to RT (overnight) in crystalline form whereas **V-VI.2Br** (pentyl and hexyl substituted) are insoluble/partially soluble in boiling 1,4-dioxane. In conclusion using inert solvent like 1,4-dioxane is a good choice to collect

the *bis*-benzimidazolium salts as halides. The synthesis can also be carried out in acetonitrile, methanol *etc.*, but collection of *bis*-benzimidazolium salts as halide in pure form will probably be difficult and anion conversion to PF₆ by metathesis route will probably become compulsory to achieve the purity.

FT-IR spectra of the compounds: IR spectrum of all the compounds has been analyzed in the form of KBr pellets of compounds (for solids) and thallium bromide disks (for liquids) over the scan range 4000-400 cm⁻¹. Representative IR spectra of the compounds and the functional assignments are shown in Figs. 1 and 2. It is of much importance to study the spectral features in both near and mid IR spectra, for their strong correlation to vibrational structures of the molecules. For all synthesized compounds, two strong and sharp stretching vibrations (3439-3380 cm⁻¹) appeared for the tertiary nitrogen of benzimidazolium ring in the observed spectra. The pure modes of the C-H stretching vibrational bands in both, alkyl benzimidazoles and *bis*-benzimidazolium salts appeared at around 3000-2900 cm⁻¹. This variation in the range is due to presence of C-H (*sp*³-*s*) stretching of alkyl chains and methylene (N-CH₂-Ar) group. A strong and sharp intense band observed in the range 1450-1400 cm⁻¹ ascribed to the stretching modes of vibrations of benzimidazole ring due to the presence of -HC=N- module¹⁹. It may be concluded that the reduction in the intensity of this band in benzimidazolium salts is probably caused by the conjugation of C=N bond with the benzimidazole ring and due to N-alkylation, where alkyl group acts as electron donating entity. In benzimidazole, the modes due to the ring vibrations are characteristically strong near 1400 and 1460 cm⁻¹ absorptions²⁰. The other ring vibrations are intense bands at around 1050 and 1220 cm⁻¹.

FT-NMR spectra of the compounds: FT-NMR spectrum of all the compounds has been analyzed in DMSO-*d*₆ over the scan range 0-16 δ ppm for ¹H NMR and 0-200 δ ppm for ¹³C NMR studies. ¹H NMR spectra of all the salts evidenced a sharp singlet in the range 9.93-10.10 δ ppm ascribed to the benzimidazolium ring (NCHN) acidic proton. This signal for

Scheme-I: Synthesis of N-alkyl benzimidazoles (**I-IV**) and 3,3'-(1,2-phenylenebis(methylene))bis(1-alkyl-benzimidazolium) bromides (**V-VIII**)

Fig. 1. FT-IR overlay spectrum of N-alkylated benzimidazoles (II, III and IV)

Fig. 2. FT-IR overlay spectrum of xylyl linked *bis*-benzimidazolium salts (V, VI, VII and VIII)

imidazole based salts was observed usually in up field region, due to the absence of an electron withdrawing phenyl group¹⁸. Resonances of the aromatic protons of benzimidazole as well as spacer were observed in the range 7.19-8.18 δ ppm as doublet of doublets, triplet of triplets and multiplets with comparable coupling constants. The signals caused by the methylene (N-CH₂-Ar) group, which connects xylyl unit with benzimidazolium units, displays sharp singlets in the range 6.10-6.23 δ ppm. Finally, the resonance of alkyl protons appeared in the range 0.80-4.55 δ ppm with comparable coupling constants.

Similarly, the structural assortments of the salts were further confirmed by the ¹³C NMR spectral technique. The spectrum of all the salts evidenced a distinguished peak in the most down field range 142.49-142.59 δ ppm ascribed to the benzimidazole ring carbon (NCN). Resonances of aromatic carbons were found in the comparable region around 113.80-132.50 δ ppm. Also, the methylene carbon (N-C-Ar) and alkyl chain carbon resonances were observed in the chemical shift regions 47.57-47.74 and 13.50-46.88 δ ppm, respectively (Table-1).

In addition it is evident that N-C-Ar carbon, in all cases, is more deshielded as compare to N-C-R carbon due to being sandwiched by two electron withdrawing groups because N-C-R group is attached to electron withdrawing and donor groups (Fig. 3). In future, such deshielding of N-C-Ar carbon will probably allow the substitution of protons with functional groups which may open new ways of cage like metal complexes.

Fig. 3. Relative deshielding of methylene groups, attached directly to benzimidazolium units in ¹H and ¹³C NMR

TABLE-1
CHARACTERISTIC SIGNALS OF *BIS*-BENZIMIDAZOLIUM SALTS IN NMR SPECTROSCOPY

¹ HNMR (δ ppm)			
R	N-CH ₂ -R	N-CH ₂ -Ar	NCHN
Butyl	4.50	6.10	9.93
Pentyl	4.53	6.23	10.10
Heptyl	4.53	6.22	10.08
Nonyl	4.51	6.16	10.09

¹³ CNMR (δ ppm)			
R	N-C-R	N-C-Ar	NCN
Butyl	46.87	47.57	142.59
Pentyl	46.89	47.74	142.46
Heptyl	46.89	47.73	142.49
Nonyl	46.88	47.66	142.53

Crystallography: The molecular structures with ethyl, propyl, heptyl and octyl substitutions from this series have successfully been solved^{14,21,22}. Each of the solved structure showed one/half water molecule attached through H-bonding (Figs. 4 and 5). Such compounds also showed a sharp peak at 3.36-3.44 δ ppm in ¹H NMR spectroscopy, indicating the hydrated water molecule (see additional information). The CHN analysis also supported the presence of water in each

molecule so molecular names of respective compounds have been assigned as monohydrate in this work.

Conclusion

A series of *bis*-benzimidazolium salts was prepared in two steps. First, the preparation of *N*-alkyl benzimidazoles by the reactions of benzimidazole with appropriate alkyl halide in presence of potassium hydroxide. Second, the subsequent treatment of respective *N*-alkyl benzimidazole derivatives with 1,2-dibromomethylbenzene in 1,4-dioxane at refluxing temperature afforded the title compounds in good yields. Crystal structures of selected compounds from this series have successfully been solved^{14,21}. Further studies need to be conducted to prepare the respective transition metal-NHC complexes of these salts.

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Fig. 4. Single crystal structure of an *o*-xylyl linked *bis*-benzimidazolium salt with propyl substitutions, showing a hydrated molecule of water²¹

Fig. 5. Single crystal structure of compound VII.2Br, showing a hydrated water molecule along with two bromide anions²²

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