Asian Journal of Chemistry; Vol. 24, No. 6 (2012), 2625-2628

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Synthesis and Characterization of *Ortho*-Xylyl Linked *Bis*-Benzimidazolium Salts

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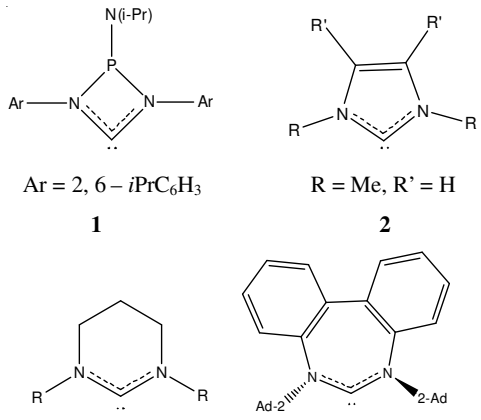
(*Received*: 7 June 2011; *Accepted*: 17 January 2012) AJC-10959

A number of *N*-alkylbenzimidazoles were synthesized by reactions of benzimidazole with alkyl halides (*i*-prBr, BuCl, BzCl, HeptBr, EtBr, PrBr). The subsequent treatment of the resulting *N*-alkylzoles 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.

Key Words: Benzimidazolium salts, N-Heterocyclic carbenes (NHCs), Metathesis, Crystal structure.

INTRODUCTION

N-Heterocyclic carbene (NHC) is a versatile class of ligand that has various types and classified on the basis of ring size. This starts from carbenes derived from four membered heterocycles and proceed up to seven membered heterocycles[1], among which perhaps five membered heterocyclic carbenes **2** are the most widely studied N-heterocyclic carbenes[2] (**Scheme-I**).



Ar = 2, 6 – *i*PrC$_6$H$_3$ (**1**); R = Me, R' = H (**2**); R = *i*Pr, Me (**3**); 2-Ad = 2- Adamantyl (**4**)

Scheme-I Classification of *N*-heterocyclic carbenes on the basis of ring size:**1-4**[3-7]

Five membered *N*-heterocyclic carbenes are further subdivided into various types, on the basis of N, N and H4/H5 substitutions, described well by Hahn and Jahnke[1]. Our group is actively working on imidazolin-2-ylidenes of this subclass. We have reported various open chain and close chain ligands (imidazole-linked cyclophanes), as well as their metal complexes[4-9]. Herein, we report a series of *N*-heterocyclic carbene ligands, based on benzannulated counterpart of this subclass. The area is new and recently similar compounds have been proved as effective catalysts for alcohols[10], Heck and Suzuki coupling reactions[11], arylation of aldehydes[12] and formation of probes for remote sensing[13].

EXPERIMENTAL

The IR spectra were recorded on a Perkin Elmer system 2000 spectrometer in KBr (for solids) and on thallium bromide disks (for liquids). The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DPX-400 and 300 instruments from solutions in DMSO-d_6 or CD_3CN-d_3. 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-VII): All the *N*-substituted benzimidazole compounds (**I-VII, Scheme-II**) were prepared and purified according to the method developed by Starikova *et al.*[14,15] and desired compounds were either obtained as oil or crystallized to solid (**III**). The basic characterization (bp, mp, ^{1}H NMR) was repeated for each compound and compared with literature[10,15-24] before further use.

Synthesis of *bis*-benzimidazolium salts (VIII-XIV): The synthesis of ligands (**VIII-XIV**) were carried out by adding respective *N*-alkylbenzimidazole (0.01 M) drop wise in a vigorously stirring solution of 1,2-*bis*(bromomethylene)benzene (0.005 M, 1.31 g) in 30 mL of 1,4-dioxane and refluxed for 24 h. The product either settled as a sticky brownish fluid at bottom of the flask (**VIII**) or precipitated directly as a powder material (**IX-XIV**). In the case when the product settled as a

brownish fluid the upper layer was decanted and product was washed with fresh 1,4-dioxane (3 × 5 mL). The resulting bromide salt was converted directly to its hexaflourophosphate counterpart by metathesis reaction using two equivalents of KPF_6 (1.84 g, 0.01 M) in 50 mL of methanol. The mixture was stirred for 3 h and filtered. The white precipitates were collected and washed with distilled water (2 × 5 mL), then left to dry at ambient temperature for one day and recrystallized by acetonitrile/water mixture. In the case when product appeared as solid the solution was filtered to collect the suspended material, washed with fresh 1,4-dioxane (3 × 5 mL), air dried for 24 h and ground to fine powder. The physical appearances, yields and instrumental characterizations are mentioned under respective headings.

3,3'-(1,2-Phenylene*bis*(methylene))*bis*(1-isopropyl-1H-benzimidazolium) (VIII.2PF$_6$). White powder. yield 4.96 g (70.10 %), m.p.: 260-264 ºC. ^{1}H NMR (400 MHz, d_6-DMSO): δ 1.67 (6H, d, 2 × CH_3, J = 6.6 Hz), 5.09 (2H, hept, *i*-Pr 2 × CH), 5.97 (4H, s, 2 × N-CH_2-Ar), 7.36 - 7.73 (8H, br.m, Ar 8 × CH), 7.82 (2H, d, Ar 2 × CH, J = 7.8 Hz), 8.19 (2H, d, Ar 2 × CH, J = 7.8 Hz) and 9.84 (2H, s, 2 × NCHN); ^{13}C{^{1}HNMR}100 MHz, d_6-DMSO: 22.25 (CH_3, J = 132.60 MHz), 48.37 (CH_2), 52.15 (i-Pr-CH), 114.18, 115.25 (Ar-C), 127.74, 128.94, 130.08, 131.64, 132.21, 132. 60 (Ar-C) and 141.82 (NCHN). FT-IR (KBr, ν_{max}, cm^{-1}); 3439 (C_{aliph}-$N_{benzimi}$); 3156, 3092 (C-H_{arom}); 2985, 2921, 2858 (C-H_{aliph}), 1609, 1560 (C_{arom}-C_{arom}); 1205 (C_{arom}-$N_{benzimi}$). Anal. cald. for $C_{28}H_{32}F_{12}N_4P_2$: C, 47.07; H, 4.51; N, 7.84 %. Found: C, 46.91; H, 4.50; N, 7.50 %.

3,3'-(1,2-Phenylene*bis*(methylene))*bis*(1-benzyl-1H-benzimidazolium) (**IX**.2Br): Beige coloured powder from crunchy lumps. Yield 1.30 g (96.15 %), m.p.: 268-270 ºC. ^{1}H NMR (300 MHz, d_6-DMSO): 5.87 (4H, s, 2 × CH_2), 6.21 (4H, s, 2 × CH_2) 7.30-8.05 (22H, br.m, Ar 22 × CH), 10.16 (2H, s, 12 × NCHN); ^{13}C{^{1}H NMR}100 MHz, d_6-DMSO: 48.79, 51.01 (CH_2), 114.96, 115.04 (Ar-C, J = 43.80 Hz), 127.75, 127.68, 129.23, 129.62, 129.84, 130.39, 131.75, 132.17, 132.83, 134.67 (Ar-C), 143.72 (NCHN). FT-IR (KBr, ν_{max}, cm^{-1}); 3417 (C_{aliph}-$N_{benzimi}$); 3109, 3028 (C-H_{arom}); 2955, 2923, 2858 (C-H_{aliph}); 1604, 1555 (C-H_{aliph}); 1188 (C_{arom}-$N_{benzimi}$). Anal. cald. for: $C_{36}H_{32}Br_2N_4$: C, 63.54; H, 4.74; N, 8.23 %. Found: C, 61.15; H, 4.68; N, 8.16 %.

3,3'-(1,2-Phenylene*bis*(methylene))*bis*(1-butyl-1H-benzimidazolium) (XI.2PF$_6$): Grey coloured powder from crunchy lumps. Yield 3.06 g (47.38 %), m.p.: 184-186 ºC. ^{1}H NMR (300 MHz, d_6-DMSO): 0.88 (6H, t, 2 × CH_3, J = 7.3 Hz), 1.34 (4H, sext, 2 × CH_2, J = 7.8 Hz), 1.87 (4H, q, 2 × CH_2, J = 7.2 Hz), 4.51 (4H, t, 2 × N-CH_2-R, J = 7.35 Hz), 6.20 (4H, s, 2 × N-CH_2-Ar), 7.26-7.68 (8H, br.m, Ar 8 × CH), 7.02 (2H, d, Ar 2 × CH, J = 8.1 Hz), 8.14 (2H, d, Ar 2 × CH, J = 8.1 Hz) and 9.98 (2H, s, 2 × NCHN); ^{13}C{^{1}H NMR} 100 MHz, d_6-DMSO: 14.29 (CH_3). 19.97 (CH_2, J = 66.90 Hz), 31.40, 47.62 (CH_2), 48.69 (N-CH_2-Ar), 114.88 (Ar-C, J = 41.70 Hz), 127.69, 127.71, 127.71, 127.88, 129.39, 130.29, 131.90, 132.01, 132.13, 132.86 (Ar-C), 142.91, 143.51 (NCHN). FT-IR (KBr, ν_{max}, cm^{-1}); 3342 (C_{aliph}-$N_{benzimi}$); 3120, 3021(C-H_{arom}); 2950, 2921, 2865 (C-H_{aliph}); 1606, 1560 (C_{arom}-C_{arom}); 1195 (C_{arom}-$N_{benzimi}$). Anal. cald. for: $C_{30}H_{36}Br_2N_4$; C, 48.52; H, 4.89; N, 7.55 %. Found: C, 48.41; H, 5.42; N, 7.17 %.

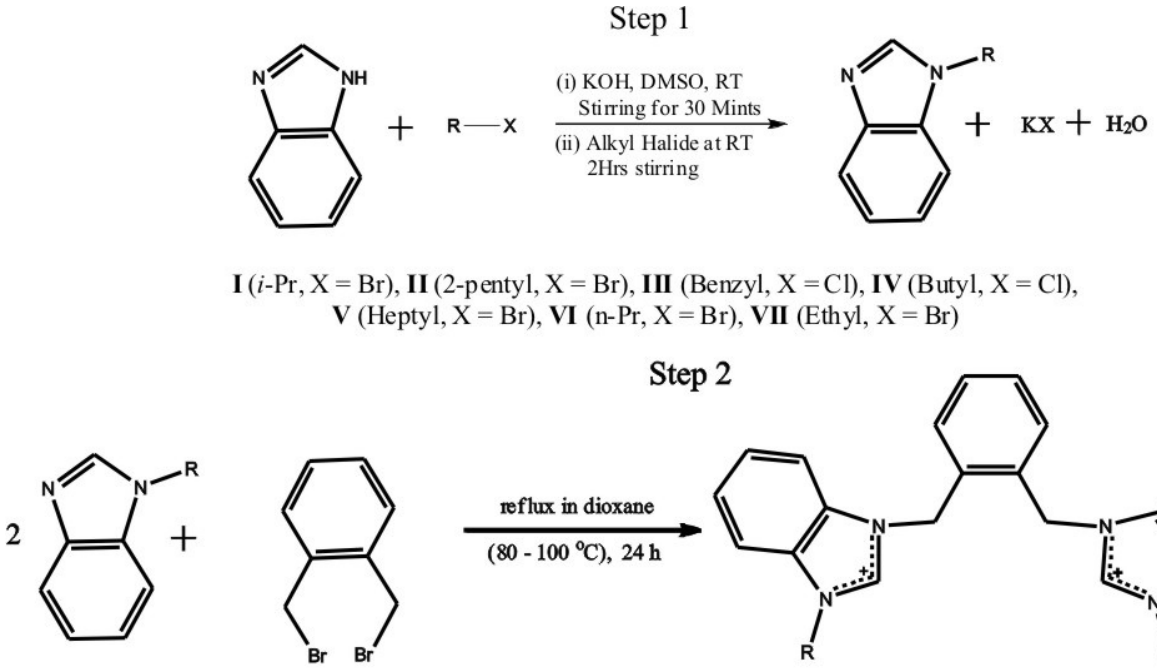
3,3'-(1,2-Phenylene*bis*(methylene))*bis*(1-heptyl-1H-benzimidazolium) (XII.2Br): White powder from soft lumps. Yield 1.72 g (49.38 %), m.p.: 226-228 ºC. ^{1}H NMR (300 MHz, d_6-DMSO): δ 0.79 (6H, t, 2 × CH_3, J = 6.6 Hz), 1.19-1.29 (16H, br.d, alkyl chain 8 × CH_2, J = 24.6 Hz), 1.88 (4H, pent., 2 × CH_2), 4.47 (4H, t, 2 × N-CH_2-R, J = 7.2 Hz), 6.11 (4H, s, 2 × N-CH_2-Ar), 7.20-7.68 (8H, br.m, Ar-CH), 7.95 (2H, d, Ar 2 × CH, J = 8.1 Hz), 8.11 (2H, d, Ar 2 × CH, J = 8.1 Hz) and 9.88 (2H, s, 2 × NCHN). ^{13}C{^{1}H NMR}; 10.02 (CH_3), 13.46, 18.57, 19.82, 26.50, 37.24 (alkyl chain 5 × CH_2), 49.85 (N-CH_2-R), 54.37 (N-CH_2-Ar), 114.20 (Ar-C), 126.74, 128.48, 128.66, 129.77, 130.88, 130.95, 134.71, 134.90 (Ar-C), 141.40, 143.08 (NCHN). FT-IR (KBr, ν_{max}, cm^{-1}); 3430, 3380 (C_{aliph}-$N_{benzimi}$); 3125, 3024 (C-H_{arom}); 2925, 2854 (C-H_{aliph}); 1606, 1560 (C_{arom}-C_{arom}); 1195 (C_{arom}-$N_{benzimi}$) Anal. cald. for: $C_{36}H_{48}Br_2N_4$; C, 62.07; H, 6.95; N, 8.04 %. Found: C, 61.93; H, 6.75; N, 7.93 %.

3,3'-(1,2-Phenylene*bis*(methylene))*bis*(1-propyl-1H-benzimidazolium) (XIII.2Br): White powder from soft lumps. Yield 1.83 g (62.67 %), m.p.: 250 - 252 ºC. ^{1}H NMR (300 MHz, d_6-DMSO): δ 0.92 (6H, t, 2 × CH_3, J = 7.35 Hz), 1.92 (4H, sext, alkyl 2 × CH_2, J = 7.2 Hz), 4.47 (4H, t, 2 × N-CH_2-R, J = 7.2), 6.14 (4H, s, 2 × N-CH_2-Ar), 7.40-7.69 (8H, br.m, Ar 8 × CH), 7.98 (2H, d, Ar 2 × CH, J = 8.4 Hz), 8.12 (2H, d, Ar 2 × CH, J = 7.5 Hz) and 9.91 (2H, s, 2 × NCHN); ^{13}C{^{1}H NMR}100 MHz, d_6-DMSO 300 MHz: δ 11.56 (CH_3), 22.93 (CH_2), 48.58 (CH_2), 49.20 (N-CH_2-Ar), 114.84 (J = 31.2 Hz), 127.63 (J = 28.8 Hz), 129.68, 130.32, 131.91, 132.06, 132.81 (Ar-C), 142.92, 143.61 (NCHN); FT-IR (KBr, ν_{max}, cm^{-1}); 3451, 3373 (C_{aliph}-$N_{benzimi}$); 3103, 3010 (C-H_{arom}); 2925, 2875 (C-H_{aliph}); 1607, 1554 (C_{arom}-C_{arom}); 1189, 1253 (C_{arom}-$N_{benzimi}$). Anal. cald. for: $C_{28}H_{32}Br_2N_4$; C, 57.55, H, 5.52, N, 9.59 %. Found: C, 56.86, H, 5.22, N, 8.67 %.

3,3'-(1,2-Phenylene*bis*(methylene))*bis*(1-ethyl-1H-benzimidazolium) (XIV.2Br): Beige coloured powder from soft lumps. Yield 2.40 g (86.33 %), m.p.: 270-272 ºC. ^{1}H NMR (300 MHz, d_6-DMSO): δ 1.52 (6H, t, 2 × CH_3, J = 7.2 Hz), 4.48 (4H, q, 2 × N-CH_2-R, J = 7.2 Hz), 6.07 (4H, s, 2 × N-CH_2-Ar), 7.22-7.69 (8H, br.m, 8 × Ar-CH), 7.91 (2H, d, Ar 2 × CH, J = 8.4 Hz), 8.07 (2H, d, Ar 2 × CH, J = 7.8 Hz) and 9.82 (2H, s, NCHN). ^{13}C{^{1}H NMR}100 MHz, d_6-DMSO 300 MHz: δ 14.91 (CH_3), 43.24 (CH_2), 48.53 (N-CH_2-Ar), 114.42,114.91, 115.23 (Ar-C), 127.23, 127.58, 128.12, 129.90, 130.13, 130.48, 131.85, 131.92,132.72, (Ar-C) 142.80, 143.17 (NCHN). FT-IR (KBr, ν_{max}, cm^{-1}); 3466, 3395 (C_{aliph}-$N_{benzimi}$); 3124, 3012(C-H_{arom}); 2928, 2768 (C-H_{aliph}); 1607, 1564 (C_{arom}-C_{arom}); 1180, 1264 (C_{arom}-$N_{benzimi}$). Anal. cald. for: $C_{26}H_{28}Br_2N_4$; C, 56.13; H, 5.07; N, 10.07 %. Found: C, 55.94; H, 4.91; N, 9.84 %.

RESULTS AND DISCUSSION

The synthesis was carried out by dual step route. In 1st step, a series of alkylated/benzylated benzimidazole compounds (**I-VII**) were prepared and in the 2nd step each, *N*-substituted benzimidazole was attached with the *o*-xylene dibromide by using dioxane as a reaction medium to get 2nd series of *N, N'*-o-xylyl linked *bis*(*N*-alkyl/benzyl benzimidazolium) salts (**VIII-XIV**, **Scheme-II**). The salts **VIII** and **XI**



Scheme-II: Synthesis of *N*-alkyl/benzyl benzimidazoles (**I-VII**) and 3,3'-(1,2-phenylenebis(methylene))bis(1-alkyl-1H-Benzimidazolium) salts (**VIII-XIV**)

were converted to PF_6 counter part by metathesis reaction for the ease of handling. All the compounds (**VIII-XIV**) were charac-terized by spectroscopic techniques (NMR and FT-IR) and microanalysis.

FT-IR spectrum of all the compounds has been analyzed in the form of KBr pellet over the scan range 4000 to 400 cm^{-1}. 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, strong and wide benzimidazolium ring tertiary nitrogen stretching vibrations appeared in the observed spectra (C_{aliph}-$N_{benzimi}$), at around 3475-3410 cm^{-1}. The pure modes of the C-H stretching vibrational bands in *bis*-benzimidazolium salts have appeared at around 3125-3010 cm^{-1}. These variations in this range are due to the presence of C-H fragments in aromatic backbones ($C\text{-}H_{arom}$), whereas strong and sharp peaks around 2985-2768 cm^{-1} represents C-H stretch of alkyl chains ($C\text{-}H_{aliph}$).

The compounds were further characterized by using NMR spectrophotometers (300 and 400 MHz) using appropriate deutrated solvents over the scan range 0 to 16 δ ppm for ^1H NMR and 0 to 200 δ ppm for ^{13}C NMR studies. In ^1H NMR the acidic proton (NCHN) signals ranged 9.82-10.16 ppm. It is already reported[25] that such a downfield movement of these protons is due to the presence of an electron withdrawing (phenyl) group at H4/H5 positions of imidazolium ring. Such a high acidity for this class of ligands gives them privilege over the imidazolium salts in field of organometallic chemistry.

A single crystal of salt XII.2Br from this series was grown by slow cooling of its hot saturated solution in DMSO-d_6. The crystal data is available online[26]. The crystal packing represents that the cations, anions and water molecules are connected *via* intermolecular O-H···Br, C-H···Br and C-H···O hydrogen bonds, forming a three dimensional network and one of the heptyl groups is disordered over two sets of sites.

Moreover, two benzimidazolium units are facing the same directions and so are suitable for the synthesis of bridging (dimeric) complexes at room temperature. In some cases the two units faces in the opposite directions resulting the polymeric formation of M-NHC complexes.

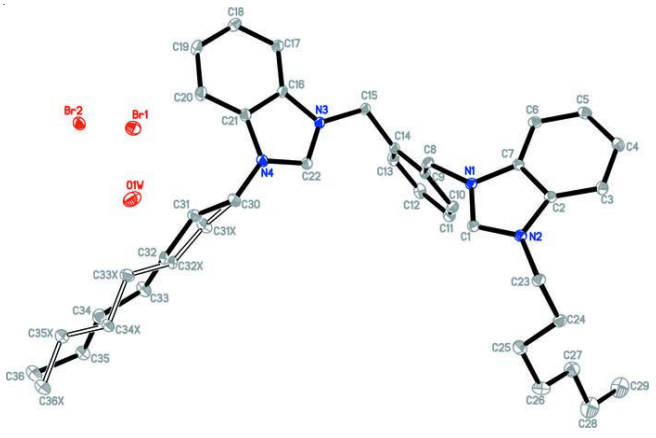


Fig. 1. Single crystal structure of XII.2Br[27]

ACKNOWLEDGEMENTS

One of the authors (RAH) thank Universiti Sains Malaysia (USM) for the Research University (RU) grants (1001/PKI MIA/811157) and (1001/PKIMIA/823082). While the corresponding author (MAI) is grateful to (IPS) USM for financial support [fellowship: USM.IPS/JWT/1/19 (JLD 6)].

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