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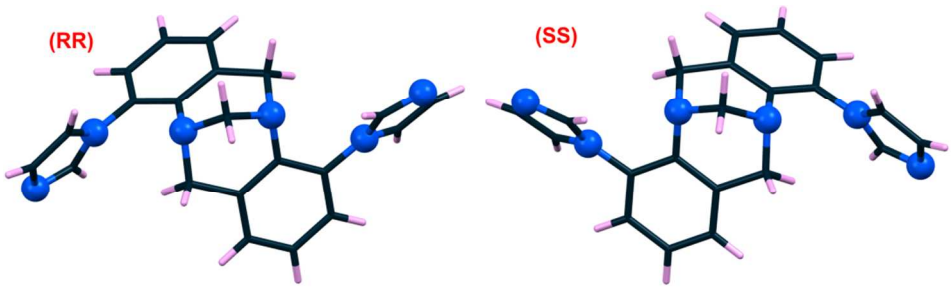
Graphical Abstract

The C_2-symmetrical 2,8- and 4,10-diimidazo methano dibenzo diazocines were synthesized and converted in to alkyl imidazolium salts.



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ARTICLE

Facile Access to Imidazole and Imidazolium Substituted Dibenzo-Diazocines

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The C2-symmetrical 2,8- and 4,10-diimidazo-methano dibenzo-diazocines have been successfully synthesized and structurally characterized. The single crystal structures of 2,8- and 4,10-diimidazo-methano dibenzo-diazocines are the first structurally characterized heterocyclic ring systems attached to the methano dibenzo-diazocines. Notably, the 2,8- and 4,10-diimidazo-methano dibenzo-diazocines are isolated without any additional groups (on benzene rings) by the condensation of *ortho* or *para* imidazo-aniline with paraformaldehyde in trifluoroacetic acid. The diimidazo-methano dibenzo-diazocines have been fully characterized. Furthermore, these newly prepared nitrogen rich heterocyclic compounds have been subjected for the selective alkyl or aralkylation reactions. The alkyl or aralkyl substituted products of diimidazo-methano dibenzo-diazocines have been fully characterized. Besides, the single crystal X-ray structures of methyl, isopropyl and 2-picolyl substituted derivatives of 4,10-diimidazo-methano dibenzo-diazocines have been reported for the first time.

Introduction

The heterocyclic compounds play a wide role as building block in natural products synthesis,[1a-1c] materials applications,[1d-1f] and catalysis.[1g,1h] The methanodibenzo-diazocine bearing C_2-symmetric chiral diamine (known as Tröger's base) is one such N-heterocyclic skeleton, which has attracted attention as artificial receptors,[2-4] asymmetric catalysis,[5] and chiral solvating agents.[6] The difunctionalization of methanodibenzo-diazocine at 2,8-, 4,10-, 1,7- and 3,9- are well known, which leads to symmetric disubstituted methanodibenzo-diazocine analogues. Several symmetric dinitro[7]/alkyl[8]/aryl[9]/ester[10]/halo[11] methanodibenzo-diazocine analogues have been successfully synthesized. Some of these molecules have been structurally characterized.

Among a wide range of substituted (on the benzene ring) methanodibenzo-diazocines, very few 4,10-disubstituted methanodibenzo-diazocine analogues are known, which are synthetically challenging.[12] 4,10–dihalo derivatives have been developed by Warmark and co-workers in low yields.[11] Later the same group has isolated the 4,10–dihalo substituted methanodibenzo-diazocine analogues from 2-halo anilines (without an additional substitution on the benzene ring) in slightly better yield (9–27%, see supporting information, table S1).[13] 4,10–dihalo substituted methanodibenzo-diazocine analogues were synthesized in good yields even in the presence of halogens as additional groups (on the benzene ring) (see supporting information, table S2).[14]

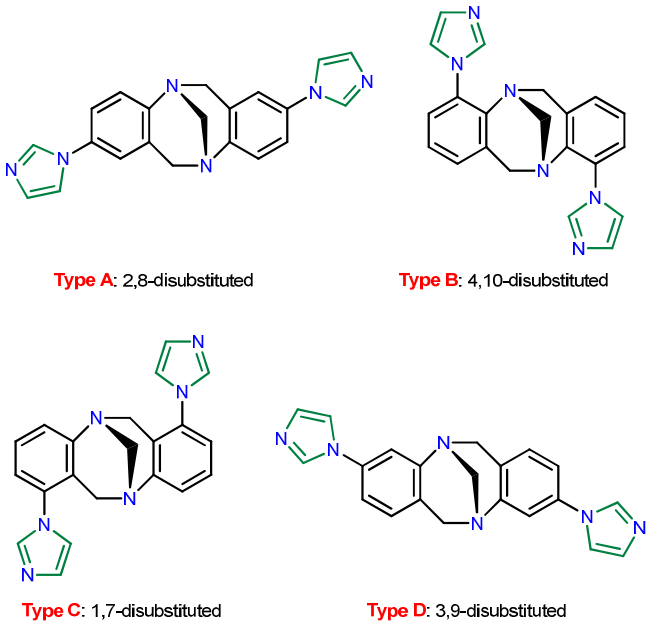


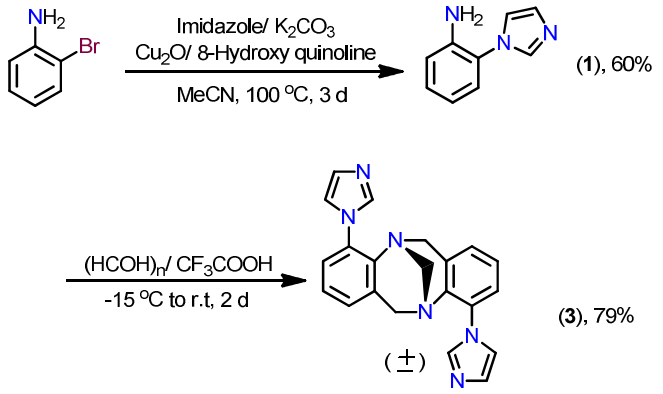
Chart 1. The possible symmetric diimidazole Tröger's base analogues.

Although the importance of century old methanodibenzo-diazocine skeleton has been a subject of focus in last several

decades,[2–16,17] examples based on methanodibenzo-diazocine tethered heterocyclic ring systems are still rare.[18,19] The only report available upto date is 2,8-diazolyl substituted Tröger's Bases (Type A, Chart 1) by Pardo *et al*.[19a] Notably, the symmetric disubtituted type B-D are not known. Since the electronegativity of imidazole is comparable with halogens,[19b] attempts have been made to isolate the structurally substituted diimidazole methanodibenzo-diazocine derivatives in the present work. The first structurally characterized 2,8- (Type A, Chart 1) and 4,10- (Type B, Chart 1) diimidazole derivatives of methanodibenzo-diazocine have been isolated. The diimidazole derivatives of methanodibenzo-diazocine have been synthesized in good yields from 2-imidazoaniline or 4-imidazoaniline without any additional group on benzene ring.

Results and discussion

As shown in scheme 1 and 2, the compounds **1** and **2** were synthesized by using inexpensive starting materials.[20] The 2-bromo or 4-bromo aniline was treated with imidazole in the presence of Cu_2O, 8–hydroxy quinolone and K_2CO_3 to afford **1** and **2**, respectively. The isolated yield for **1** (60%) is lower than the reported yield (86%), where the reaction was performed in the same route using Cs_2CO_3. Analytically pure compounds **1** and **2** were obtained by silica loaded column chromatography using MeOH/DCM mixture. The analytical and spectral data of **1** and **2** are consistent with the literature.[21]



Scheme 1. Synthesis of **1** and **3**.

1 was readily converted to methanodibenzo-diazocine **3** in 79% yield by condensation reaction between **1** with paraformaldehyde in the presence of trifluoroacetic acid (TFA) under ambient conditions (Scheme 1). Notably, Hansson *et. al* reported the similar synthesis in the absence of light.[13] However, from our experiment we observed that the presence of light did not affect the yield of **3**. The reaction progress was monitored by TLC. In TLC **3** and **1** showed the same R_f, but a distinct color change was observed after ninhydrin charring for **1**. The analytically pure compound **3** was obtained by silica loaded column chromatography using MeOH/DCM mixture. In HRMS, **3** showed a $[M+H]^+$ ion peak at 355.1651 in positive ESI mode, which is evidence in support of formation of **3**.

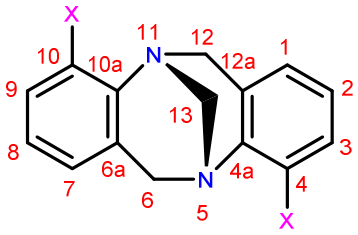
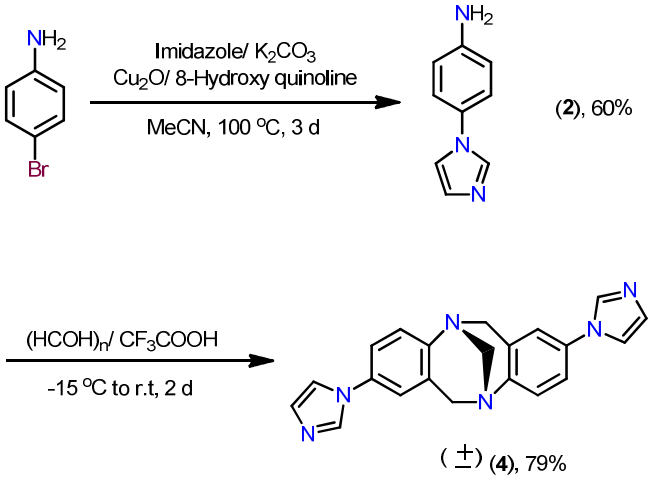


Chart 2. Structure of 4,10-disubstited Tröger's base analogs (X = F, Cl, Br and Imidazole (**3**)).[13]

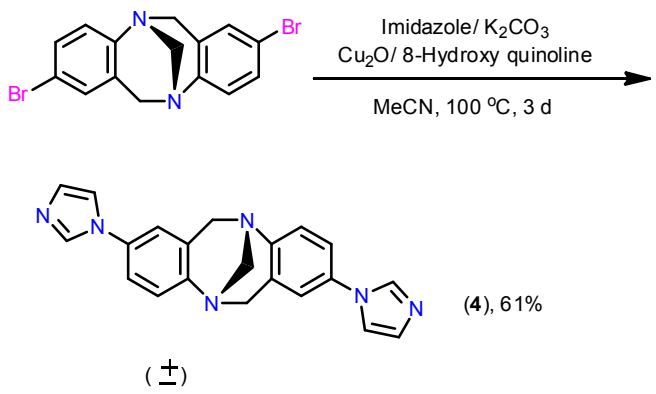
The multinuclear NMR (^1H and ^{13}C) spectra of **3** are comparable with 4,10-dihalo substituted methanodibenzo-diazocine derivatives due to the similar electronic properties of imidazole with halogens.[19] As shown in table S3, the ^1H NMR chemical shift values of **3** at 1-H/7-H, 2-H/8-H, 3-H/9-H positions are comparable with the values of 4,10-dihalo analogues, while the 6-H/12-H chemical shift values are upfield shifted in comparison with 4,10-dihalo analogues.[19b]



Scheme 2. Synthesis of **2** and **4**.

2,8-Diimidazo methano dibenzo-diazocine (**4**) was synthesized by the condensation reaction between **2** with paraformaldehyde in the presence of trifluoroacetic acid (TFA) under ambient conditions (Scheme 2).[13] Analytically pure **4** (56%) was obtained by silica loaded column chromatography using MeOH/DCM mixture. **4** was first reported by Pardo *et. al*[19a] with 30% yield from the condensation reaction between **2** and aqueous formaldehyde in presence of concentrated hydrochloric acid. However, in the present report, yield of **4** (56%) is appreciably improved when the condensation reaction between **2** and paraformaldehyde was carried out in the presence of trifluoroacetic acid. Alternatively, **4** can also be synthesized from reaction between 2,8-dibromo methano

dibenzo-diazocine with imidazole in the presence of Cu_2O and 8–hydroxy quinolone, K_2CO_3 in better yield (61%) (Scheme 3).



Scheme 3. Synthesis of **4**.

The solid state structures of **3** and **4** were unambiguously determined by single crystal X-ray analysis. Crystals suitable for the single crystal X-ray analysis were grown from the MeOH/DCM mixtures by slow evaporation at room temperature. A single enantiomer of **4** (S,S) was crystallized, while the mixture of enantiomers (R,R (**3a**) & S,S (**3b**)) of **3** were crystallized.[22,23] The selected structural parameters and metrics are listed in table S4 and S5.

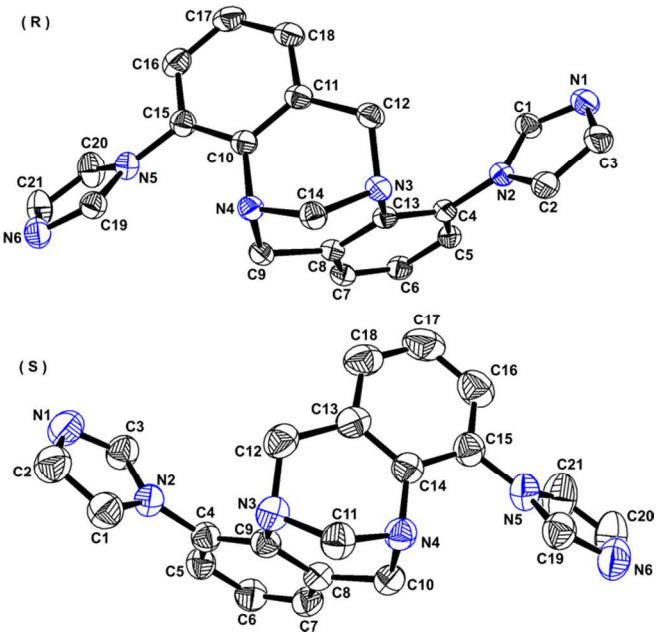


Figure 1. Molecular structure of **3a** (top) and **3b** (bottom). Hydrogen atoms and water molecule have been omitted for clarity.

Compounds **3a** and **3b** crystallized in the monoclinic space group, $P2_1/c$ (Fig. 1) with a water molecule.[22,23] Selected bond lengths and bond angles are assembled in table S4. Molecules **3a** and **3b** are the first structurally characterized R,R and S,S enantiomers of the dibenzo-diazocine skeleton linked to azole rings at the 4,10-positions of the benzene rings. The C–N bond distances and N–C–N bond angles in **3a** and **3b** are comparable.

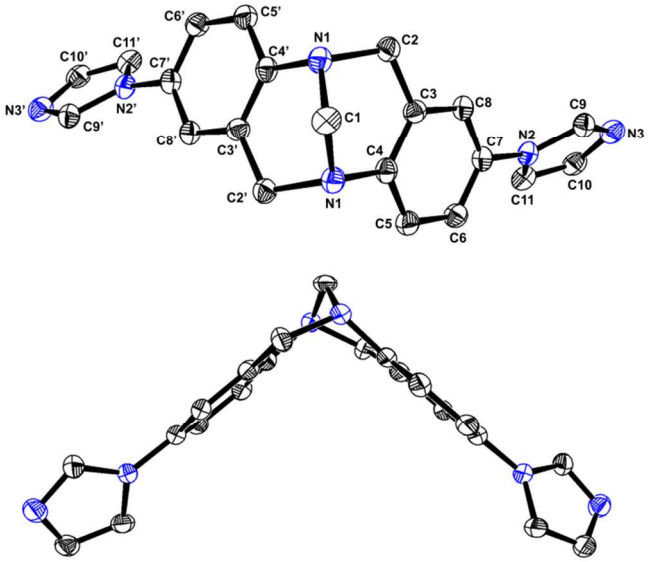


Figure 2. Molecular structure of **4**. Hydrogen atoms have been omitted for the clarity.

Compound **4** crystallized in the monoclinic space group, *C 1 2/c 1*(Fig. 2).[22,23] Selected bond lengths and bond angles are listed in table S5. As shown in figure 2, the "V" shaped dibenzo-diazocine skeleton is linked with imidazole at 2- and 8-positions. The benzene and imidazole rings are not on the same plane. The torsion angle between methanodibenzo-diazocine and imidazole, C(8)–C(7)–N(2)–C(9) is 47.16°. The C(2')–N(1)–C(4) angle is 112.59(12)°, which is much wider than 2,8-dimethyl-5,11-methano-5,6,11,12-tetrahydro-dibenzo-[*b,f*][1,5]diazocine (92.8-97.4°)[24] but comparable with 2,8-dibromo-5,11-methano-5,6,11,12-tetrahydro-dibenzo-[*b,f*][1,5] diazocine (112.83 and 111.55°).[25] The N(1)–C(2)–C(3) angle is 111.27(12)°. The N(1)–C(1)–N(1') angle is 111.45(18)° with N(1)–C(1) bond distance of 1.4667(18) Å. The N(1)–C(1)–N(1') angle found in **4** is smaller than that of 2,8-dimethyl-5,11-methano-5,6,11,12-tetrahydro-dibenzo-[*b,f*][1,5] diazocine (113.27°)[24] and 2,8-dibromo-5,11-methano-5,6,11, 12-tetrahydro-dibenzo-[*b,f*][1,5]diazocine (112.07°).[25] N(1)–C(2) bond distance is (1.4782(19) Å) slightly longer than N(1')–C(4) bond distance of 1.4381(19) Å.

The bond lengths and angles found in **3** are comparable to **4**. The N(3)–C(14)–N(4) and N(3)–C(11)–N(4) angles for **3a** and **3b** are 111.90(11)° and 112.00(16)°, respectively. The phenyl and imidazole rings of **3a** and **3b** are not in the same plane. The C(13)–C(4)–N(2)–C(2) and C(10)–C(15)–N(5)–C(19) torsion angles in **3a** are 62.39° and 48.70°, respectively, whilst those in

3b are C(9)–C(4)–N(2)–C(3), 122.05° and C(14)–C(15)–N(5)–C(19), 50.39°.

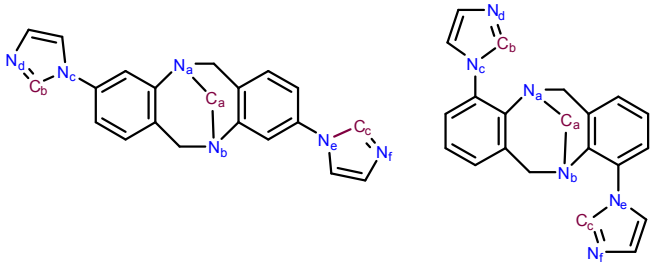


Chart 3

Although **3a** and **3b** are crystallized with a water molecule, the molecular packing of **3a** and **3b** are different. As shown in figure 3, **3a** depicts a strong N····H–O hydrogen bonding interaction between water and imidazolium nitrogen, while it is absent in **3b**. The N(1)····H(1b) hydrogen bond distance (2.061(2) Å) is slightly longer than N(4)····H(1a) (2.0(2) Å) and this can be explained by the favorable hydrogen bonding angle of N(6)····H(1a)–O(1) (173.01(2)°) compared to that of N(1)····H(1b)–O(1)(158.8(2)°). As shown in figure 4, molecule **4** shows a framework type of crystal packing in b axis without any van der Waals interactions.

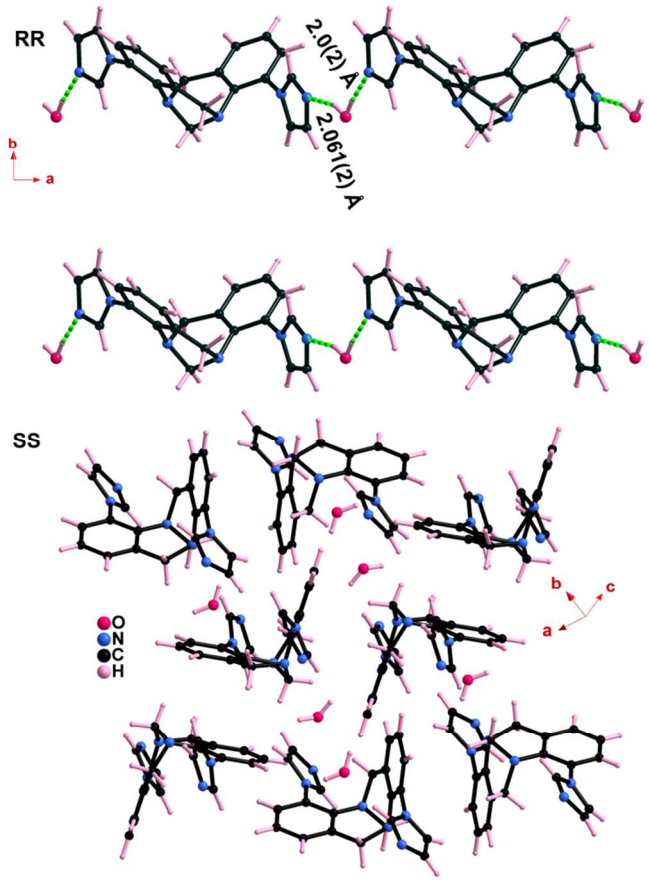


Figure 3. Top: N····H–O hydrogen bonding network in **3a** (View along c axis). Bottom: The molecular packing of **3b,** where the water molecules are not showing any hydrogen bonding interactions.

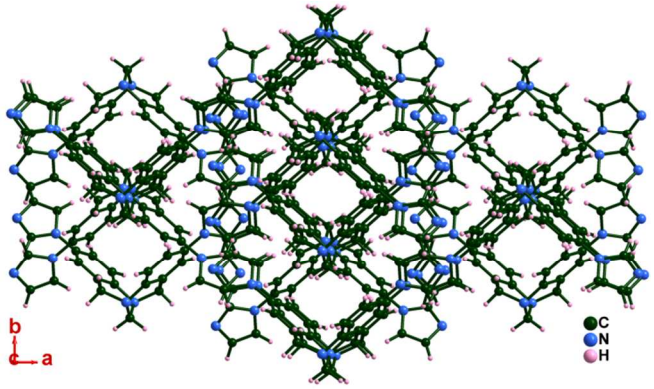
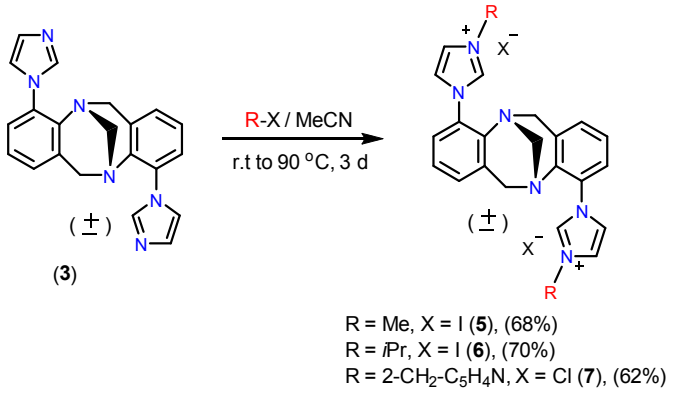


Figure 4. Framework type molecular packing in **4** (view along c axis).



Scheme 4. Synthesis of **5**-**7**.

The reaction between **3** and two equivalence of methyl iodide in acetonitrile for 3 days gave a stable white solid **5** with 68% yield at room temperature. Molecule **5** is fully characterized. The ^{1}H NMR chemical shift value of imidazolium NC*H*N is δ = 9.64 ppm and the ^{13}C NMR chemical shift value of imidazolium N*C*HN is δ = 137.66 ppm, which are further confirmed by HMBC and HSQC correlation spectra (see supporting information).

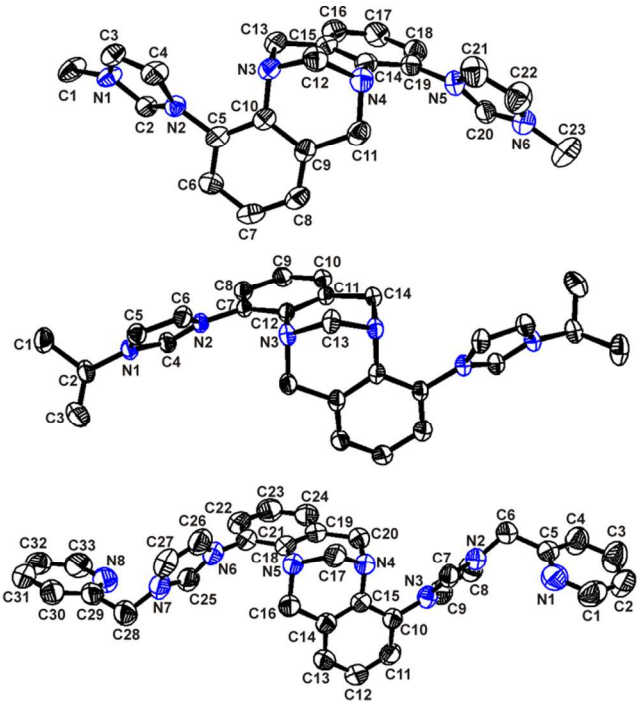


Figure 5. Molecular structure of **5** (top), **6** (middle) and **7** (bottom). Two iodine counter ions in **5** and **6** have been omitted for clarity. Two chlorine ions and one water molecule in **7** have been omitted for the clarity.

Compounds **6** and **7** were synthesized from **3** with 2 eq of *iso*propyl iodide and 2-picolyl chloride in acetonitrile at 90 °C for 3 days. Compounds **6** (70 %) and **7** (62 %) were obtained in very good yield and fully characterized. **6** is a white stable solid. In ^{1}H NMR, the imidazolium NC*H*N proton appears at δ = 9.72 ppm and in ^{13}C NMR N*C*HN carbon appears at δ = 135.97 ppm, which are further confirmed by HMBC and HSQC correlation. Compound **7** is a pinkish white solid and highly soluble in water. The imidazolium NC*H*N proton in **7** is slightly downfield shifted (δ = 10.01 ppm) compared to **6**. Similarly, the ^{13}C NMR chemical shift value of **7** is (δ = 138.41 ppm) downfield shifted compare to **6**.

Crystals suitable for the single crystal X-ray analysis were grown from MeOH/DCM mixture of **5** or **6** respectively, while **7** was obtained from an acetonitrile and methanol mixture (Fig. 5).[22,23] Molecules **5**-**7** crystallized in the monoclinic space group, $P2_1/c$ (for **5**), $C2/c$ (for **6**) and triclinic space group, $P\bar{1}$ (for **7**), respectively. Selected structural parameters are listed in table S4. The selected bond distances and angles of **5**-**7** are listed in table S5. The bond distances and angles of N-methyl/isopropyl/2-methyl-pyridine derivatives are comparable with **4**. Similarly, the N–C–N angle of methanodibenzo-diazocine in **3**-**7** is comparable. The single crystal structures of **6** and **7** are isolated in the form of RR, while the SS enantiomeric form is isolated for **5**. As shown in figures 6 and 7, the molecular packing of **5**-**7** are not comparable. The inter/intra molecular interactions in **5** and **6** are absent, while **7** shows a strong Cl····H–C hydrogen bonding interaction along with a π····π interaction between pyridine molecules. As shown in figure 7, a weak intermolecular pyridine-pyridine π····π interactions are observed. The pyridine-pyridine distances are 4.16 and 4.74 Å. The Cl····H hydrogen bonding distances and Cl····H–C hydrogen bonding angles are assembled in figure 7. The Cl····H–C hydrogen bonding interactions observed in **7** are considerably stronger[26]. The donor atoms involved in intermolecular hydrogen bonding interactions are H(28a), H(25), H(20b), H(9) and H(8), while the acceptor atoms involved in intermolecular hydrogen bonding interactions are Cl(2A) and Cl. The shortest hydrogen bonding distance is observed for H(9)····Cl(2A) (2.394(7) Å), while the hydrogen bonding distance between H(28a) and Cl(2A) is the longest bond distance (2.747(7) Å).

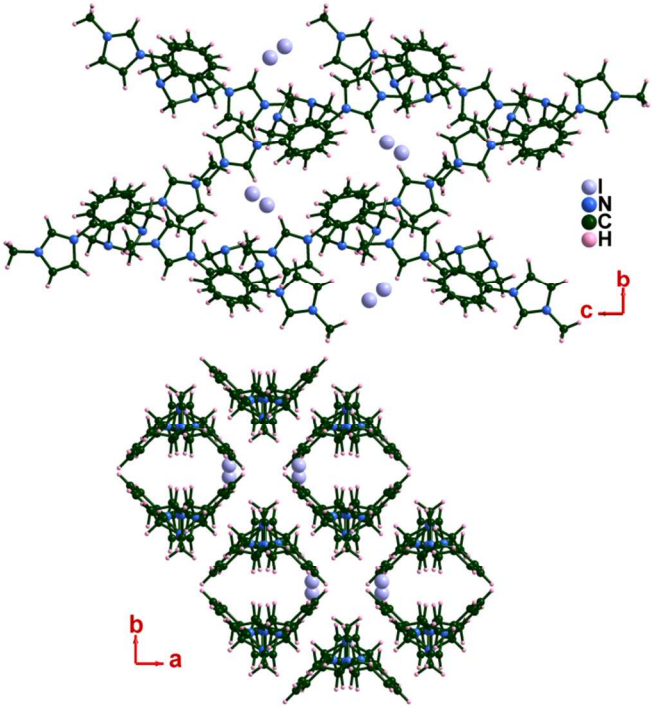


Figure 6. Top: The molecular packing of **5**. Bottom: The molecular packing of **6**.

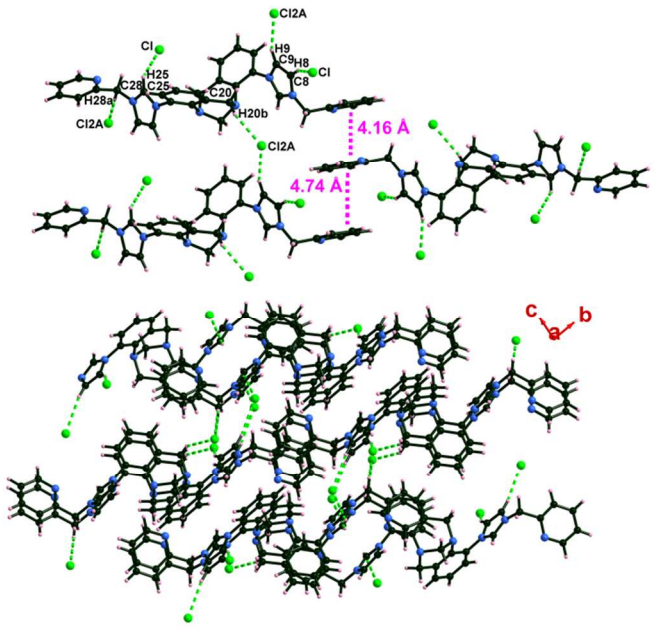
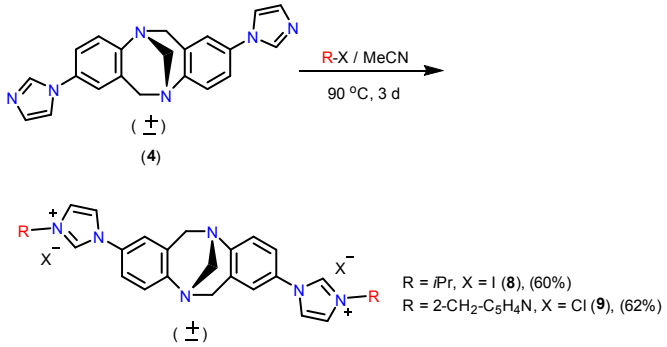


Figure 7. The Cl····H–C hydrogen bonding interactions and π····π interaction in **7**. Hydrogen bond distances (Å): Cl····H(8) 2.622(7), H(9)····Cl(2A) 2.394(7), H(28a)····Cl(2A) 2.747(7), H(25)····Cl 2.556(2), H(20b)····Cl(2A) 2.625(2). Hydrogen bond angles (°): Cl····H(8)–C(8) 155.74(7), C(9)–H(9)····Cl(2A) 158.14(7), C(28)–H(28a)····Cl(2A) 115.26(6), C(25)–H(25)····Cl 172.55(1), C(20)–H(20b)····Cl(2A) 150.03(2).



Scheme 5. Synthesis of **8** and **9**.

Compounds **8** and **9** were synthesized from **4** with 2 eq of isopropyl iodide and 2-picolyl chloride in acetonitrile at 90 °C for 3 days. Compounds **8** (60%) and **9** (62 %) were isolated in good yield as yellowish white hygroscopic solids. The yield of **8** and **9** are lower than **6** and **7**. Molecules **8** and **9** were fully characterized. The ^{1}H NMR chemical shift value of imidazolium NC*H*N proton (δ = 9.71 ppm for **8** and 10.09 ppm for **9**) and ^{13}C NMR chemical shift value of imidazolium N*C*HN carbon (δ = 133.84 ppm for **8** and 135.92 ppm for **9**) of **8** and **9** are nearly comparable. The ^{1}H NMR chemical shift values of 6H endo and 6H exo protons in **3** and **5-7** (6H endo δ = 3.30–3.66 ppm, 6H exo δ = 4.24–4.41 ppm) are upfield shifted compared with **4** and **8-9** (6H endo δ = 4.23–4.31 ppm, 6H exo δ = 4.76–4.80 ppm), due to the presence of the imidazole near to 6H in **3** (steric effect on 6H).

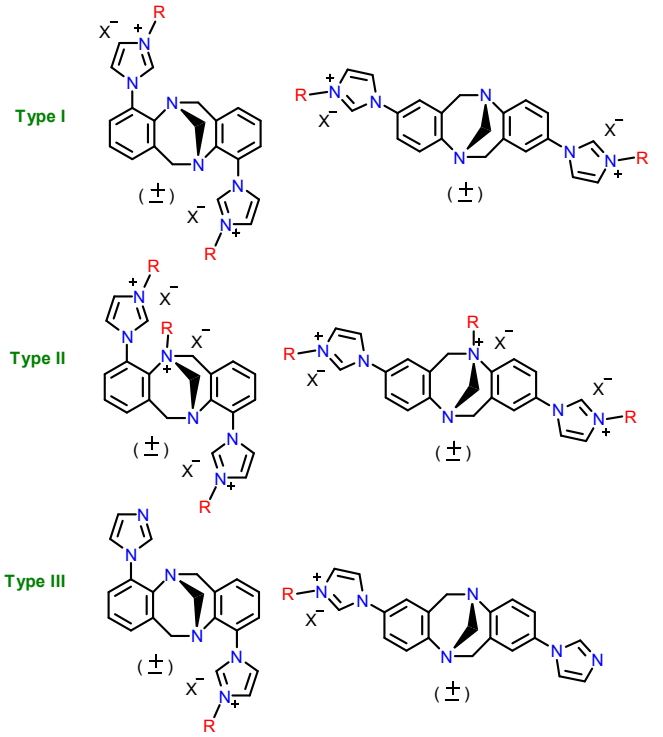
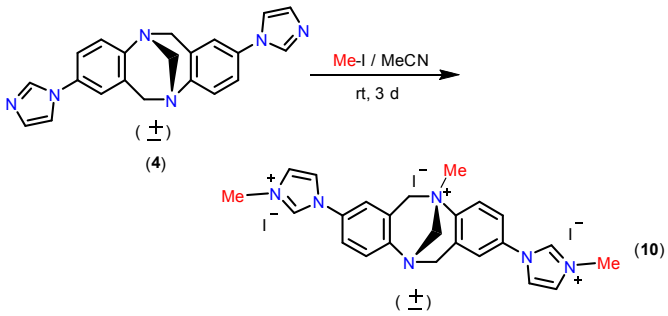


Chart 4. Possible products formation from the reaction between **3** or **4** with 2 equivalents of alkyl or aralkyl halide (RX).

Thus, type I products, **5-7**, obtained from the reaction between **3** and corresponding alkyl halides can be explained by the more nucleophilic nature of the imidazole nitrogen than methanodibenzo-diazocine nitrogen (Chart 4). Notably, type III products are not isolated. The NC*H*N proton NMR chemical shift values of **5-7** and **8-9** (δ = 9.64–10.01 and 9.72–10.09 ppm) are considerably downfield shifted compare to their parent molecules **3** and **4** (δ = 7.93 and 7.75 ppm, respectively) that indicates the addition of alkyl substituents at imidazole nitrogen (type I) (also confirmed by HMBC and single crystal X-ray diffraction technique).

Whereas the treatment of **4** with methyl iodide gave trimethylated imidazole methanodibenzo-diazocine derivative **10**, where one of the bridgehead nitrogen atoms of methanodibenzo-diazocine quaternized with 2 equivalents of methyl iodide (Scheme 6) (Fig. 8) (see supporting information).[27,18d] Notably, the quaternary product is not observed in the case of 4,10-diimidazo methanodibenzo-diazocine (**3**) with methyl iodide. Similarly, the quaternary product is not isolated when methanodibenzo-diazocine-bis methylene imidazole is treated with 1-(bromomethyl)-2,4,6-trimethylbenzene.[17] Formation of possible quaternary

ammonium salts[27,18d] from the reaction between alkyl halide or aralkyl halide and imidazole methanodibenzo-diazocine are shown in chart 4. The formation of type II product (**10**) from the reaction between **4** and methyl iodide was confirmed by ^{1}H, ^{13}C NMR and single crystal X-ray analysis (see supporting information, table S6).



Scheme 6. Synthesis of **10**.

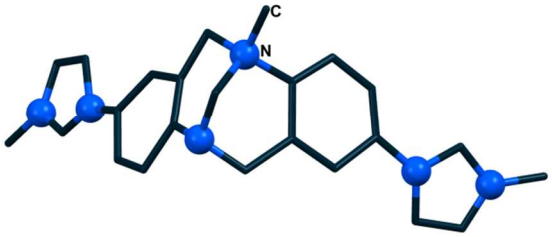


Figure 8. Molecular structure of **10**.

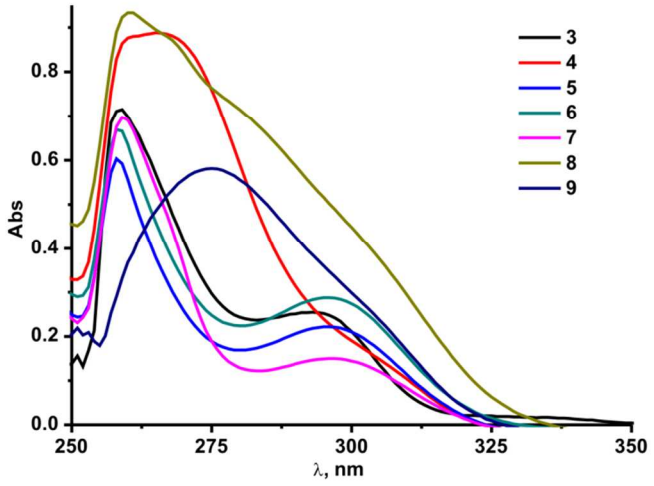


Figure 9. Uv-vis spectra of **3-9** in DMSO at room temperature (3.133 x 10^{-5} M).

The absorption spectra of the **3**, **4** and their azolium salts **5-9** in DMSO (3.133×10^{-5} M) are compared in figure 9. The UV−vis absorption spectra of 2,8-diimidazo methano dibenzo diazocine derivatives **4**, **8**, and **9** are distinctly different from 4, 10-diimidazo methanodibenzo-diazocine derivatives **3**, **5**, **6** and **7**. The UV−vis absorption spectra of **3**, **5-7** showed two absorption maxima; a sharp intense absorption at λ_{max}= 259 nm due to π-π* transition; broad and weak absorption around 294-297 nm (294 nm for **3**, 296 nm for **5**, 297 nm for **6** and **7**) due to n-π* transition. In the case of **4**, **8** and **9**, a broad strong absorption around λ_{max} = 265-276 nm (265 nm for **4**, 261 nm for **8**, and 276 nm for **9**) was observed.

HRMS analysis of compounds **5**, **6** and **8** showed ($C_{23}H_{24}IN_6^+$= 511.1086, $C_{27}H_{32}IN_6^+$ = 567.1708 and an $C_{27}H_{32}IN_6^+$ = 567.1708) the mass elimination of one counter ion (iodine) from the parent molecules. In the case of **7** and **9**, ($C_{33}H_{29}N_8^+$ = 537.2479 and $C_{33}H_{29}N_8^+$ = 537.2485) the mass elimination of two neutral molecules of HCl from the parent molecules were observed.

Experimental

Materials and methods

All manipulations were carried out under nitrogen using Schlenk vacuum line techniques and an argon glove box. The solvents were purchased from commercial sources and purified according to standard procedures.[28] Starting materials were purchased from commercial sources and used without further purification. FT−IR measurement (neat) was carried out on a Bruker Alpha-P Fourier transform spectrometer. The UV−vis spectra were measured on a T90+ UV−visble spectrophotometer. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF. NMR spectra were recorded on Bruker Ultrashield-400 MHz spectrometers at 25 °C unless otherwise stated. Chemical shifts are given relative to Me_4Si and were referenced to the solvent resonances as internal standards. The crystal structures of **3-7** and were measured on an Oxford Xcalibur 2 diffractometer. Data were collected at 150 K (for **3a**, **3b**, **4**, **6** and **7**) and 298 K (for **5** and **10**). Using Olex2,[22] the structures of **3-7** and **10** were solved with the olex2.solve structure solution program using Charge Flipping and refined with the olex2.refine[23] refinement package using Gauss-Newton minimisation. The final refinement of **10** was not performed due to poor X-ray data quality. In **7**, the hydrogen atoms were not included on water molecule for the final refinement. CCDC 979765 (**3a**), 979766 (**3b**), 979767 (**4**), 979768 (**5**), 979769 (**6**) and 979770 (**7**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

Synthesis of 1 and 2.
An oven dried 50 mL schlenk tube or sealed tube was charged with 2-bromo or 4-bromo aniline (0.2 g, 1.16 mmol), imidazole (0.11 g, 1.74 mmol, 1.5 eq), 8-hydroxy quinolone (0.033g, 0.23 mmol, 0.2 eq), Cu_2O (0.0083 g, 0.058 mmol, 0.05 eq) and K_2CO_3 (2.5 eq) then tube was evacuated for 3min. and re-filled with N_2 gas then solvent MeCN (10 mL) was added under N_2 gas at room temperature. The reaction mixture was heated at 100 ^oC for 3 days. After 3 days, (yellowish green reaction mixture) volatiles were evaporated under reduced pressure to get green residue then washed with DCM (5 x 15 mL). The organic extract was washed with water and brine solution. Volatiles were evaporated under reduced pressure to get crude compound. The compound was purified by column chromatography using 100-200 mesh size silica gel. The desired compound was eluted by 5% MeOH/DCM mixture.

Synthesis of 3 and 4.
Cooled (−15 ^oC) trifluoroacetic acid (20 mL) was added to **1** or **2** (1 g, 6.282 mmol) at −15 ^oC subsequently paraformaldehyde (0.4 g, 13.32 mmol) was added to the reaction mixture then stirred for 40 h at room temperature. The reaction progress was monitored by TLC. After completion of the reaction, the reaction mixture was poured into crushed ice (120 g), then 30% aq. ammonia solution (20 mL) was added to the reaction mixture (until pH = 9-10) then extracted with dichloromethane (3 x 30 mL) and the organic extract was washed with brine solution, dried over an anhydrous Na_2SO_4, organic solvent was evaporated under reduced pressure to result crude gummy compound. Crude compound was purified by column chromatography (100-200 silica gel) and the desired product was eluted by MeOH/DCM mixture.

3.
White solid. Yield 79% (based on **1**). M.P., 236-238 ^oC. FT–IR (neat): $\bar{\upsilon}$ 3442 (w), 3357 (w), 3093 (w), 2917 (w), 2854 (w), 1579 (w), 1492 (s), 1459 (m), 1335 (w), 1305 (m), 1238 (m), 1208 (m), 1060 (s), 935 (m), 785 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.93 (s, 2H, Im NC*H*N, 15-*H*), 7.39 (s, 2H, 18-*H*), 7.23 (s, 2H, 17-*H*), 7.10–7.08 (d, 2H, $J_{H,H}$ = 7.6 Hz, 2-*H*), 7.06–7.03 (t, 2H, $J_{H,H}$ = 7.6 Hz, 3-*H*), 6.83–6.81 (d, 2H, $J_{H,H}$ = 7.6 Hz, 1-*H*), 4.32 (s, 2H, 13-*H*), 4.28–4.24 (d, 2H, $J_{H,H}$ = 17.2 Hz, 6exo-*H*), 3.37–3.30 (d, $J_{H,H}$ = 17.2 Hz, 2H, 6endo-*H*) ppm.^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.94 (*C*-6a), 137.36 (*C*-15), 131.59 (*C*-4a), 129.59 (*C*-4), 129.30 (*C*-17), 126.80 (*C*-1), 124.50 (*C*-3), 123.77 (*C*-2), 119.77 (*C*-18), 66.79 (*C*-13), 54.18 (*C*-6) ppm. HRMS (+ESI): calcd. for $C_{21}H_{19}N_6^+$ ($[M+H]^+$) 355.1671; found 355.1651.

Synthesis of 5.
To a stirred solution of **3** (0.1 g, 0.282 mmol) in MeCN (4 mL), MeI (0.1 g, 0.704 mmol) was added under nitrogen gas atmosphere at room temperature, then the reaction mixture was stirred for 3 days at room temperature. The white solid was filtered and washed with MeCN and diethyl ether successively. Single crystals were grown in MeOH/DCM mixture by slow evaporation.

5.
White solid. Yield 68% (based on **3**). M.P., 328–330 ^oC. FT–IR (neat): $\bar{\upsilon}$ 3083 (w), 3001 (w), 2929 (w), 2886 (w), 2842 (w), 1572 (m), 1549 (m), 1466 (m), 1339 (w), 1229 (m), 1212 (m), 1143 (m), 1084 (m), 938 (m), 786 (s) cm^{-1}. ^1H NMR (DMSO–d_6, 400 MHz): δ 9.64 (s, 2H, Im NC*H*N, 15-*H*), 8.18 (s, 2H, 18-*H*), 8.01 (s, 2H, 17-*H*), 7.47–7.45 (d, 2H, $J_{H,H}$ = 7.6 Hz, 3-*H*), 7.29–725 (t, 2H, $J_{H,H}$ = 7.6 Hz, 2-*H*), 7.20–7.18 (d, 2H, $J_{H,H}$ = 7.6 Hz, 1-*H*), 4.41–4.38 (d, 2H, $J_{H,H}$ = 16.8 Hz, 6exo-*H*), 4.38 (s, 2H, 13-*H*), 4.03 (s, 6H, 19-*H*), 3.66–3.61 (d, $J_{H,H}$ = 17.6 Hz, 2H, 6endo-*H*) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ 140.93 (*C*-12a), 137.66 (*C*-15), 129.98 (*C*-4a), 129.06 (*C*-4), 128.84 (*C*-1), 124.63 (*C*-2), 124.40 (*C*-3), 123.50 (*C*-17), 123.11 (*C*-18), 65.28 (*C*-13), 53.96 (*C*-6), 36.24 (*C*-19) ppm. HRMS (+ESI): calcd. for $C_{23}H_{24}I N_6^+$ ($[M–I]^+$) 511.1107; found 511.1086.

Synthesis of 6-9.
To a stirred solution of **3** or **4** (1eq) in MeCN, isopropyl iodide or 2-picolyl chloride (2 eq) was added under nitrogen gas atmosphere at room temperature, then the reaction mixture was stirred for 3 days at 90 ^oC, after that the solid was filtered and washed with MeCN and diethylether successively. Single crystals were grown in MeOH/DCM or MeOH/MeCN mixture slow evaporation.

6.
White solid. Yield 70% (based on **3**). M.P., 289-291 ^oC (black). FT–IR (neat): $\bar{\upsilon}$ 3117 (w), 3077 (w), 2971 (w), 2946 (w), 2889 (w), 1545 (m), 1467 (m), 1340 (w), 1210 (m), 1143(m), 1088 (m), 934 (m), 791 (s) cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): δ 9.72 (s, 2H, Im NC*H*N, 15-*H*), 8.22 (s, 4H, 18-*H* and 17-*H*), 7.52–7.50 (d, 2H, $J_{H,H}$ = 7.6, 3-*H*), 7.29–7.25 (t, 2H, $J_{H,H}$ = 7.8 Hz, 2-*H*), 7.20–7.18 (d, 2H, $J_{H,H}$ = 7.6 Hz, 1-*H*), 4.85–4.79 (m, 2H, 19-*H*), 4.40–4.37 (d, 4H, $J_{H,H}$ = 13.6 Hz, 6exo-*H* merged with13-*H*), 3.61–3.56 (d, 2H, $J_{H,H}$ = 17.2 Hz, 6endo-*H*), 1.63–1.61 (d, 12H, $J_{H,H}$ = 6.8 Hz, 20-*H*) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ 141.02 (*C*-12a), 135.97 (*C*-15), 129.89 (*C*-4a), 129.16 (*C*-4), 128.97 (*C*-1), 124.57 (*C*-2), 124.40 (*C*-3), 123.60 (*C*-17), 120.41 (*C*-18), 65.37 (*C*-13), 53.79 (*C*-6), 52.78 (*C*-19), 22.26 (*C*-20) ppm. HRMS (+ESI): calcd. for $C_{27}H_{32}I N_6^+$ ($[M–I]^+$) 567.1733; found 567.1708.

7.
Pinkish white solid, Yield 62% (based on **3**). M.P., 272-276 ^oC (decomp.). FT–IR (neat): $\bar{\upsilon}$ 3637 (w), 3259 (w), 3130 (w), 3025 (w), 2970 (w), 2935 (w), 2855 (w), 1592 (w), 1543 (m), 1469 (s), 1439 (m), 1341 (w), 1220 (m), 1145 (m), 1088 (m), 936 (m), 789 (s), 759 (s) cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): δ 10.01 (s, 2H, Im NC*H*N, 15-*H*), 8.63–8.62 (d, 2H, $J_{H,H}$ = 4 Hz, 22-*H*), 8.20 (s, 2H,18-*H*), 8.11 (s, 2H, 17-*H*), 7.96–7.92 (t, 2H, $J_{H,H}$ = 7 Hz, 24-H), 7.64–7.62 (d, 2H, $J_{H,H}$ = 8 Hz, 25-*H*),7.52–7.50 (d, 2H, $J_{H,H}$ = 7.6 Hz, 3-*H*), 7.46–7.43 (qrt, 2H,

$J_{H,H}$ = 5.2 Hz, 23-*H*), 7.29–7.25 (t, 2H, $J_{H,H}$ = 7.8 Hz, 2-*H*), 7.19–7.17 (d, 2H, $J_{H,H}$ = 7.6 Hz, 1-*H*), 5.80 (s, 4H, 19-*H*), 4.40–4.36 (t, 4H, 13-*H* merged with 6exo-*H*), 3.64–3.60 (d, 2H, $J_{H,H}$ = 17.2 Hz, 6endo-*H*) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ 153.41 (*C*-20), 149.67 (*C*-22), 141.10 (*C*-12a), 138.41 (*C*-15), 137.67 (*C*-24), 130.05 (*C*-4a), 129.36 (*C*-4), 129.03 (*C*-1), 124.94 (*C*-2), 124.59 (*C*-3), 123.82 (*C*-23), 123.49 (*C*-18), 123.29 (*C*-17), 122.65 (*C*-25), 65.46 (*C*-13), 54.08 (*C*-6), 53.31 (*C*-19) ppm. HRMS (+ESI): calcd. for C_{33} H_{29} N_8 [M-(2-HCl)+H]$^+$) 537.2515; found 537.2479.

8.

White solid. Yield 60% (based on **4**). Hygroscopic solid. FT–IR (neat): $\bar{\upsilon}$ 3123 (w), 3064 (w), 2980 (w), 2923 (w), 2853 (w), 1551 (m), 1496 (m), 1378 (w), 1217 (m), 1156(m), 1087 (m), 990 (m), 782 (s) cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.71 (s, 2H, Im NC*H*N, 15-*H*), 8.20 (s, 2H, 18-*H*), 8.10 (s, 2H, 17-*H*), 7.61-7.58 (dd, 2H, $J_{H,H}$ =2.4, 6.4 Hz, 3-*H*), 7.50–7.49 (d, 2H, $J_{H,H}$ = 2.4 Hz, 1-*H*), 7.46–7.44 (d, 2H, $J_{H,H}$ = 8.8 Hz, 4-*H*), 4.80–4.76 (d, 2H, $J_{H,H}$ = 16.8 Hz, 6exo-*H*), 4.70–4.63 (m, 2H, 19-*H*), 4.36 (s, 2H, 13-*H*), 4.30–4.25 (d, 2H, $J_{H,H}$ = 17.2 Hz, 6endo-*H*), 1.52–1.51 (d, 12H, $J_{H,H}$ = 2.8 Hz, 20-*H*) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ 148.84 (*C*-12a), 133.84 (*C*-15), 130.13 (*C*-2), 129.44 (*C*-4a), 126.08 (*C*-4), 121.29 (*C*-17), 121.18 (*C*-18), 120.96 (*C*-3), 120.69 (*C*-1), 65.73 (*C*-13), 58.00 (*C*-6), 52.75 (*C*-19), 22.14 (*C*-20) ppm. HRMS (+ESI): calcd. for C_{27} H_{32} I N_6^+ ([M–I]$^+$) 567.1733; found 567.1708.

9.

White solid. Yield 62% (based on **4**). Hygroscopic solid. FT–IR (neat): $\bar{\upsilon}$ 3393 (m), 3079 (w), 2957 (w), 2919 (w), 2850 (w), 1594 (w), 1552 (m), 1494 (s), 1439 (m), 1341 (w), 1216 (m), 1074 (m) cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.09 (s, 2H, Im NC*H*N, 15-*H*), 8.53 (s, 2H, 22-*H*), 8.25 (s, 2H, 18-*H*), 8.01 (s, 2H, 17-*H*), 7.88 (s, 2H, 24-*H*), 7.62–7.52 (m, 6H, 3-*H*, 25-*H* and 1-*H)*, 7.45–7.40 (m, 4H, 4-*H* and 23-*H*), 5.65 (s, 4H, 19-*H*), 4.80–4.76 (d, 2H, $J_{H,H}$ =17.2 Hz, 6exo-*H*), 4.36 (s, 2H, 13-*H*), 4.31–4.26 (d, 2H, $J_{H,H}$ = 17.6 Hz, 6endo-*H*) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ 153.21 (*C*-20), 149.47 (*C*-22), 148.96 (*C*-2), 137.44 (*C*-24), 135.92 (*C*-15), 129.98 (*C*-4a), 129.59 (*C*-12a), 126.21 (*C*-4), 123.85 (*C*-17), 123.63 (*C*-23), 122.57 (*C*-25), 121.18 (*C*-18), 120.87 (*C*-3), 120.64 (*C*-1), 65.71 (*C*-13), 58.01 (*C*-6), 53.24 (*C*-19) ppm. HRMS (+ESI): calcd. for C_{33} H_{29} N_8 [M-(2-HCl)+H]$^+$) 537.2515; found 537.2485.

10.

To a stirred solution of **4** (0.1 g, 0.282 mmol) in MeCN (4 mL), MeI (0.1 g, 0.704 mmol) was added under nitrogen gas atmosphere at room temperature, then the reaction mixture was stirred for 3 days at room temperature. The white solid was filtered and washed with MeCN and diethyl ether successively. Single crystals were grown in MeOH/DCM mixture by slow evaporation. Yellowish white solid, Yield 53% (based on **4**). FT–IR (neat): $\bar{\upsilon}$ 3137 (w), 3084 (w), 2958 (w), 2923 (w), 2853 (w), 1613 (w), 1575 (m), 1506 (s), 1443 (w), 1348 (w), 1316 (w), 1231 (m), 1023 (m), 1001 (s), 821 (m). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.87 (s, 1H, Im NC*H*N, 15-*H*), 9.74 (s, 1H, Im NC*H*N, 15-*H*), 8.57–8.55 (d, 1H, $J_{H,H}$ =5.2 Hz, Ar*H*), 8.29–8.28 (d, 1H, $J_{H,H}$ = 2 Hz), 8.20–8.19 (d, 1H, $J_{H,H}$ =4 Hz, Ar*H*), 8.03–8.02 (d,d, 1H, $J_{H,H}$ =2.8, 6.4 Hz, Ar*H*), 8.01–8.00 (d, 1H, 3-*H*, $J_{H,H}$ =17.2 Hz, Ar*H)*, 7.96–7.95 (d, 1H, $J_{H,H}$ =1.6 Hz, Ar*H*), 7.93–7.92 (d, 1H, $J_{H,H}$ =1.6 Hz, Ar*H*), 7.84–7.83 (d, 1H, $J_{H,H}$ =2.8 Hz, Ar*H*), 7.803–7.80 (d, 1H, $J_{H,H}$ =1.2 Hz), 7.69 (s, 1H, Ar*H*), 5.69–5.66 (d, 1H, $J_{H,H}$ = 11.2 Hz, NCH_2Ar), 5.51–5.47 (d, 1H, $J_{H,H}$ = 16 Hz, NCH_2Ar), 5.22–5.19 (d, 1H, d, 1H, $J_{H,H}$ = 1.2 Hz, NCH_2Ar), 5.09–5.01 (t, 2H, d, 1H, $J_{H,H}$ = 16.4, 17.6 Hz, NCH_2N), 4.58–4.53 (d, 1H, d, 1H, $J_{H,H}$ = 17.6 Hz, NCH_2Ar), 3.93 (s, 3H, NCH_3), 3.92 (s, 3H, NCH_3), 3.87 (s, 3H, NCH_3) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ 143.20 (Ar*C*), 140.82 (Ar*C*), 136.33 (Ar*C*), 135.98 (Ar*C*), 135.38 (Ar*C*), 131.18 (Ar*C*), 130.61 (Ar*C*), 126.50 (Ar*C*), 124.54 (Ar*C*), 124.31 (Ar*C*), 123.58 (Ar*C*), 123.01 (Ar*C*), 122.35 (Ar*C*), 120.93 (Ar*C*), 120.86 (Ar*C*), 120.76 (Ar*C*), 120.61 (Ar*C*), 120.56 (Ar*C*), 76.04 (N*C*H_2N), 66.26 (N*C*H_2Ar), 56.44 (N*C*H_2Ar), 50.85 (N*C*H_3), 36.24 (N*C*H_3), 36.12 (N*C*H_3) ppm.

Conclusions

The rigid 4,10- and 2,8-diimidazo methano dibenzodiazocines (**3** and **4**) were synthesized in good yield from the condensation reaction between paraformaldehyde and corresponding imidazo anilines in the presence of trifluoro acetic acid. The yield of **4** was improved by two different routes. Molecules **3** and **4** were characterized by HRMS, FT-IR, ^{1}H NMR, ^{13}C NMR, DEPT, HMBC, HSQC, UV-vis and single crystal X-ray diffraction techniques. Furthermore the solid state structure of **3a** (R,R), **3b** (S,S) and **4** are reported for the first time. Interestingly the molecular packing of **3a** (R,R) and **3b** (S,S) are different. Besides the alkyl substituted 4,10- and 2,8-diimidazolium methano dibenzodiazocine salts, **5-9** were synthesized from selective alkylation of **3** and **4** with alkyl or aralkylhalide. Notably, the reaction between **4** and methyl iodide gave **10**. These newly prepared 4,10- and 2,8-diimidazolium methano dibenzodiazocine salts were fully characterized. Molecules **5-7** are the first structurally characterized alkyl substituted symmetric diimidazolium methano dibenzodiazocine derivatives. Molecular packing of **7** showed Cl···H–C hydrogen bonding interactions along with π···π interactions. We are currently exploring the chemistry of 1,7- (Type C, Chart 1) and 3,9- (Type D, Chart 1) diimidazole derivatives of methanodibenzo-diazocine compounds, which will be reported in due course.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [All spectra (FT-IR and NMR) of **1**-**10**. Single crystal X-ray parameters of **10**.]. See DOI: 10.1039/b000000x/

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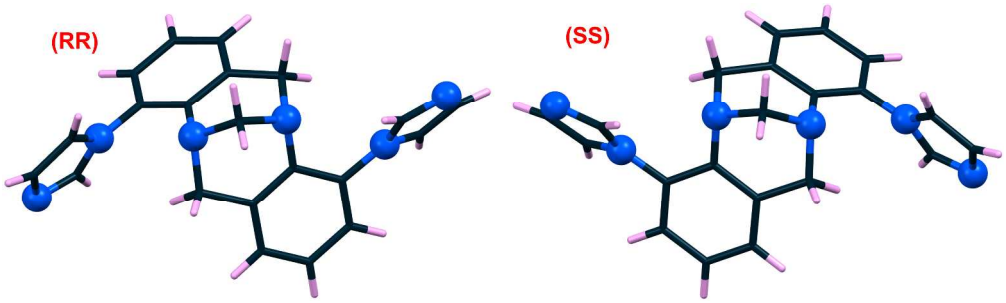

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