Bridged Derivatives of 2,2′-Biimidazole

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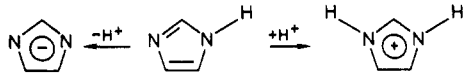
The reaction of 2,2′-biimidazole with 1,*n*-dihaloalkanes or *o*-xylylene dibromide leads to a series of N,N′-bridged derivatives. When these substances are treated with a second equivalent of 1,*n*-dihaloalkane, a series of bis-annelated biimidazolium salts is obtained. The conformations of these species are discussed with regard to their electronic absorption spectra and their 300-MHz ^{1}H NMR spectra. The barriers for conformational inversion are found to be lower than for the corresponding bis-annelated 2,2′-bipyridinium salts. The redox properties of these salts are measured in CH_3CN and DMSO, and their reductions are found to become increasingly more difficult and less reversible as the system becomes less planar. These results are explained primarily based on the greater N,N′-distance in 2,2′-biimidazole as compared with 2,2′-bipyridine.

The properties of biaryl molecules are strongly influenced by both electronic and steric factors. Interaction of two covalently bound π-systems is favored by a planar conformation, which provides the optimum environment for resonance delocalization. In this planar conformation substituents ortho to the bond connecting the two aryl rings often interact with one another, forcing the two rings out of coplanarity. The ability to control the conformation of a biaryl molecule clearly plays an important role in determining its properties. We have already demonstrated the importance of this effect for biaryls such as 2,2′-bipyridine,[1] 2,2′-biquinoline,[2] and 2,2′-bi-1,8-naphthyridine,[3] as well as 2,2′:6′,2″-terpyridine.[4] This paper will extend these studies to include 2,2′-biimidazole.

Imidazole is an intriguing aromatic molecule in that it can exist as a protonated or deprotonated species while retaining its aromaticity. Both of the charged forms exhibit symmetry which is lacking in the parent neutral compound. The potential applications of species such as



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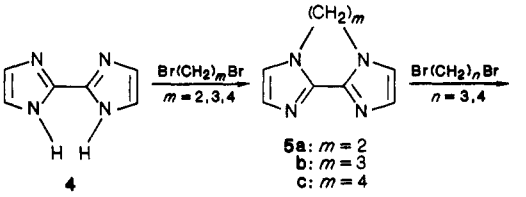
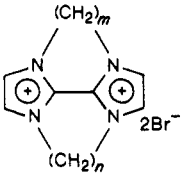
2 or 3 are amplified when they are incorporated in the dimeric analogue 2,2′-biimidazole. Thus the biimidazolium dication can potentially behave as an effective two-electron acceptor while the corresponding dianion possesses two bidentate chelating sites and might function as a bridging ligand.[5]

The molecule 2,2′-biimidazole (4) lends itself particularly well to the formation of bridged derivatives. Treatment of 4 with a 1,*n*-dihaloalkane in the presence of base leads readily to an N,N′-bridged neutral species **5**. Reaction with a second equivalent of 1,*n*-dihaloalkane quaternizes the two basic nitrogens of **5**, leading to the diquaternary salts **6**.

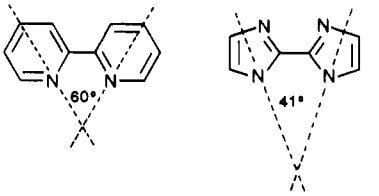
The five-membered rings of 4 create a 1,4-diaza system that differs significantly from the one found in 2,2′-bipyridine. Measurements from Dreiding models indicate a chelation angle of only 41° for 2,2′-biimidazole as compared with an angle of 60° for 2,2′-bipyridine. Assuming



4 **5a**: $m = 2$ **b**: $m = 3$ **c**: $m = 4$



6a: $m = 2$; $n = 3$ **b**: $m = 2$; $n = 4$ **c**: $m = n = 3$ **d**: $m = 3$; $n = 4$ **e**: $m = n = 4$



that the length of the 2,2′-bond is invariant,[6] this decreased chelation angle causes a significantly larger N,N′-distance in the biimidazole system. Bridging between these sites should be affected, and the dihedral angle between the imidazole rings resulting from bridging should be reduced. Estimates of this angle from molecular mechanics calculations give values of 11° (n = 2), 39° (n = 3), and 41° (n = 4).[9] These angles are up to 20° less than those calculated for the corresponding 3,3′-bridged 2,2′-bipyridines due to the increased N,N′-distance in **5**. Since the optimum bite angle for octahedral coordination of a bidentate chelator should be 90°, one would also expect the ligating properties of 4 to be somewhat diminished. The coordination chemistry of the bridged biimidazoles **5** is under investigation and will be reported elsewhere.[10]

Due to the increased N,N′-distance, the shortest doubly bridged system we were able to prepare was **6a**. Treatment

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(6) An X-ray structure analysis is available for a metal complex of 4,4′,5,5′-tetramethyl-2,2′-biimidazole.[7] Comparison of the 2,2′-bond length for this system with the analogous bond length for a coordinated derivative of 2,2′-bipyridine[8] shows a variance of less than 0.01 Å.
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(8) Thummel, R. P.; Lefoulon, F.; Korp, J. D. *Inorg. Chem.* **1987**, *26*, 2370.
(9) These estimates were made using the programs PC MODEL and MMX available from Serena Software, Bloomington, IN.
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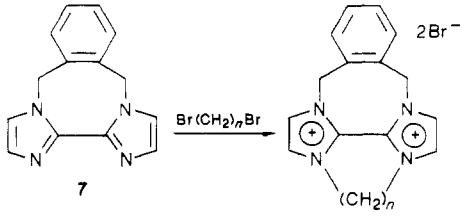
of **5a** with 1,2-dibromoethane or 1-bromo-2-chloroethane did not provide the salt **6** with $m = n = 2$. However we have observed such bridging in a recently prepared series of [1,1′:3,3′]bis(polymethylene)-2,2′-bipyridinium dibromides. For the case of 2,2′-bibenzimidazole, a salt analogous to **6** with $m = n = 2$ has been reported, although in yields of only 30–43%.[11,12] Hünig has commented on the difficulty of preparing this salt by direct treatment of 2,2′-bibenzimidazole with 1,2-dibromoethane.[12] We expect that benzo-ring fusion at the 4,5-positions of **4** would cause an increase in the N_1–C_2–N_3 bond angle, leading to a decrease in the N,N′-distance, which, in turn, would afford more facile bridging.

The bridged biimidazoles **5a** and **5b** were prepared earlier by Melloni and co-workers who used them as intermediates in the preparation of related pyrazine and diazepine derivatives.[13] More recently Deady has utilized the same compounds along with 1,1′-dimethyl-2,2′-biimidazole to investigate lone pair cooperativity effects in a study involving N-alkylation reactions.[14] Unfortunately Deady bases his arguments to explain the relative rates of alkylation of **5a** and **5b** on planar conformations for these molecules. Clearly they are not planar, and arguments related to steric hindrance and N–N distances must take this nonplanarity into account.

The highly distorted systems **5c** and **6e** would be expected to exhibit the most unusual properties. In these cases the imidazole subunits are bridged by one or two tetramethylene chains. A related four-carbon bridging unit would be the α,α′-(*o*-xylyl) moiety where all four carbons in the bridge would be constrained approximately in the plane of the phenyl ring. Due to this conformational constraint, it is expected that *o*-xylylene and tetramethylene bridges might impose somewhat different inversion barriers on the biimidazole system.

By treating 2,2′-biimidazole with 1 equiv of *o*-xylylene dibromide we obtain the mono-bridged species **7**. If this species is in turn treated with 1,*n*-dihaloalkanes, the biimidazolium salts **8a–c** can be prepared.



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8a: $n = 2$
b: $n = 3$
c: $n = 4$

Spectroscopic Properties

Figure 1 illustrates the ultraviolet absorption spectra for the series of N,N′-bridged 2,2′-biimidazoles **5a–c** and **7**. Two trends are apparent. As the N,N′-bridge becomes longer, the absorption energy increases, which is indicative of diminished π-delocalization resulting from less coplanarity of the two imidazole rings. This same effect is also manifested by a decrease in absorption intensity with increasing bridge length. The two four-carbon bridged systems, **5c** and **7**, show almost identical absorption energies, indicating that the conformations of their biimidazole moieties are nearly identical. The bridging

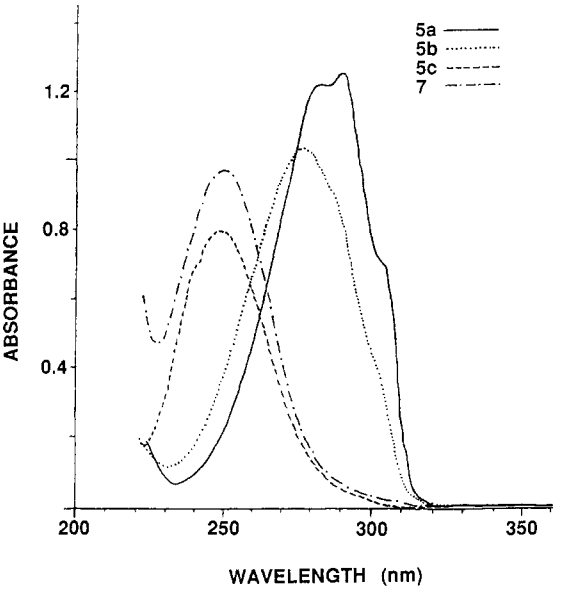

Figure 1. Ultraviolet absorption spectra for N,N′-bridged 2,2′-biimidazoles (10^{-4} M in 95% EtOH).

phenyl ring of **7** is homobenzylic and, in a conformation possessing a C_2 axis, it is arranged almost orthogonal to both imidazole rings so that no π-overlap is apparent.

The absorption maximum for imidazole in ethanol occurs at 270 nm while that for 1-methylimidazole occurs at 271 nm. The *N*-alkyl inductive effect appears to be essentially negligible. Knowing this, we can use the absorption value of 273 nm for biimidazole (**4**) to estimate its approximate conformation in solution as being close to that of **5b**. The two N–H bonds will most likely be directed away from one another in a transoid orientation.

The absorption maxima for the salts **6a–d** all occur in the range of 298–306 nm. The bis(tetramethylene)-bridged system, however, absorbs at considerably higher energy (268 nm), indicating that this system is the most highly distorted. The absorption maxima for the series **8a–c** occur at 313, 298, and 286 nm, respectively. These systems exhibit a consistent trend toward decreasing wavelength (higher energy) with increasing nonplanarity. It is interesting to note that although **5c** and **7** absorb at the same energy, the corresponding tetramethylene-bridged salts **6e** and **8c** do not. From its longer wavelength absorption, the latter system appears to be more planar.

The ^{1}H NMR spectra of bridged azabiaryl molecules provide useful information regarding the conformations of these species. For the corresponding 3,3′-polymethylene-bridged 2,2′-bipyridines we have examined the aliphatic region of their spectra to determine whether conformational rigidity was observable on the NMR time scale.[1] The two- and three-carbon bridged bipyridines show rapid conformational inversion as evidenced by magnetic equivalence of their geminal methylene protons. The 3,3′-tetramethylene bridged bipyridine, however, is found to be conformationally rigid, showing four distinct signals for nonequivalent geminal protons at the benzylic and nonbenzylic positions of the bridge. Warming the sample to 150 °C does not cause the signals to coalesce, implying an inversion barrier of greater than 20 kcal/mol.

The situation for the bridged biimidazoles **5** and **7** is somewhat different. The two- and three-carbon bridged systems **5a** and **5b** again appear to be conformationally mobile at room temperature. However, at 30 °C in $CDCl_3$, the tetramethylene bridged system shows two broad four-proton singlets at 1.96 and 3.90 ppm. As the sample is cooled to −50 °C these signals broaden considerably and

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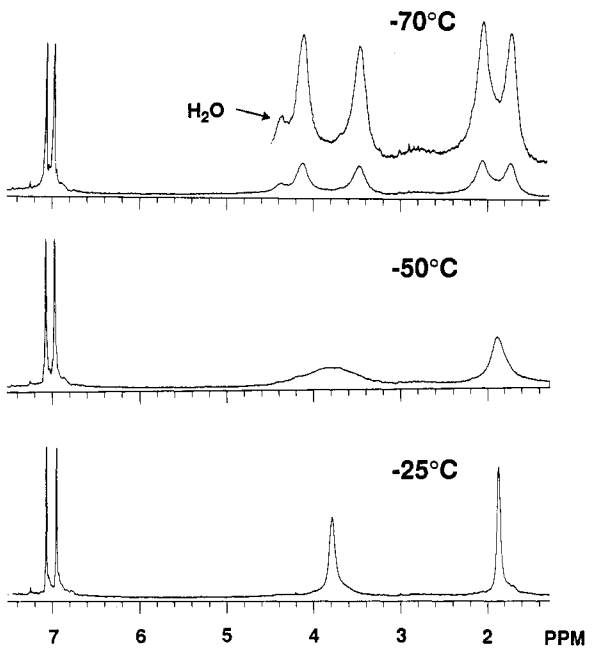


Figure 2. Variable temperature 300-MHz ^{1}H NMR study of 1,1′-tetramethylene-2,2′-biimidazole in $CDCl_3$.

at −70 °C they split into four signals while the imidazole peaks remain essentially unchanged (Figure 2). We estimate the coalescence temperature to be −55 °C from which we calculate a free energy of activation for the conformational inversion process of 10.6 kcal/mol.[15]

The transition state for conformational inversion of biaryl systems would require the two aromatic rings to become coplanar. Thus we can deduce that the greater N,N′-distance in the planar form of **4** as compared with 2,2′-bipyridine makes a significant difference in the transition-state energy for conformational inversion of the bridged derivatives **5**. This difference will have important implications in situations where the system is forced toward planarity as in bidentate chelation or reduction of salts such as **6**.

In considering the NMR spectra of the bis-annelated salts **6**, we again observe the barrier for conformational inversion to be lower than for the corresponding bis-annelated bipyridinium salts. The only system that is conformationally rigid at room temperature is **6e**, with two tetramethylene bridges, as evidenced by four distinct signals for the bridge protons at 4.78, 4.13, 2.32, and 2.00 ppm. When one bridge is shortened to three carbons, the remaining tetramethylene bridge in **6d** shows two broad singlets at 4.41 and 2.20 ppm, intermediate between the pairs of peaks for **6e**. For the 1,1′:3,3′-bis-annelated bipyridinium salts the presence of one tetramethylene bridge is always sufficient to induce conformational rigidity on the molecule.[16]

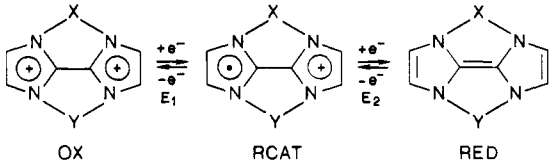
The conformational mobility of the *o*-xylylene-bridged salts **8a–c** can be assessed by inspection of the *o*-xylyl methylene protons. When this bridge is mobile on the NMR time scale, these protons appear as a sharp singlet as in the case of **8b** (δ 5.92). The trimethylene bridge protons also show a pattern typical for a mobile bridge. For the tetramethylene system, **8c**, the *o*-xylyl methylene protons show an AB quartet (δ 5.59) indicative of a rigid system. Surprisingly the dimethylene-bridged analogue **8a** shows a very broad singlet at 5.99 ppm for these same protons, indicating that the coalescence barrier decreases in the order **8c** > **8a** > **8b**. It appears that N,N′-bridging by a dimetylene unit in these salts allows less mobility than a trimethylene bridge, which can span this distance more comfortably. In going from **8a–c** the difference between the chemical shifts of the two imidazole protons decreases regularly from 0.21 to 0.07 ppm, indicating that these protons become less sensitive to shielding effects from the bridging phenyl ring as the molecule becomes more twisted.

In the ^{13}C NMR we observe an interesting trend for the C-2 resonance, which shifts steadily to higher field as one proceeds from **6a** to **6e**. The implication is that positive charge density at this carbon is decreasing as the delocalization becomes inhibited by nonplanarity.

Redox Behavior

Diquaternary salts of azabiaryl systems have been studied extensively with regard to their ability to undergo two one-electron reductions.[17] The ease with which these reductions occur and the reversiblity of this reduction process depend heavily on the structures of the intermediate radical cation and the neutral species which are formed.

Biimidazolium salts of the types **6** and **8** are capable of undergoing such redox chemistry. The dication would be the fully oxidized form OX; the radical cation would be the intermediate RCAT, and the fully reduced neutral species would be RED. The RED form is especially in-



teresting for two reasons. It is a derivative of tetraaminoethylene, a molecule in which there is considerable interest because of its low ionization potential.[18] Secondly, RED is an aza analogue of tetrathiafulvalene (TTF), which is an important donor used to form conducting charge transfer systems.[19] The two important differences between RED and TTF are the presence of the more electronegative nitrogen atoms and the incorporation of conformational effects governed by the bridges.

The dibenzo analogue of **6c** has been examined by Hünig and co-workers who measured reduction potentials of −0.63 and −0.87 V (DMF vs Ag/AgCl).[20] They also investigated the lower homologue with two ethano bridges and measured potentials of −0.53 and −1.39 V with the reversibility of the second reduction being questionable. The strain inherent in the RED system with two ethano bridges is readily apparent.

We have measured the redox potentials for the series **6a–e**, **8a–c**, and **9** in DMSO and CH_3CN and collected the data in Table I. Representative voltammograms are reproduced in Figure 3, and two definite trends are in evidence. The more planar systems (**6a**,**b**, **8a**) show two

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Table I. Reduction Potentials for Bis-Annelated Biimidazolium Salts[a]

compd	$E_{1/2}$(DMSO)	$E_{1/2}$(CH_3CN)
6a	−1.14 (50), −1.38 (110)	−1.18 (80), −1.42 (ir)
6b	−1.13 (110), −1.41 (105)	−1.11 (80), −1.49 (ir)
6c	−1.14 (130)	−1.12 (100), −1.28 (ir)
6d	−1.31 (ir)	−1.28 (ir)
6e	−1.37 (120)	−1.39 (ir)
9	−1.43 (ir)	−1.48 (ir)
8a	−1.03 (85), −1.44 (ir)	−1.42 (ir)
8b	−1.15 (ir), −1.24 (ir)	
8c	−1.24 (ir)	

[a] Potentials are given in volts for saturated solutions in DMSO or CH_3CN, 0.1 M in TBAP recorded at 25 ± 1 °C at a scan rate of 200 mV/s. The difference between cathodic and anodic peak potentials (mV) is given in parenthesis; (ir) means irreversible, and for these systems the potential given is the peak of the cathodic wave.

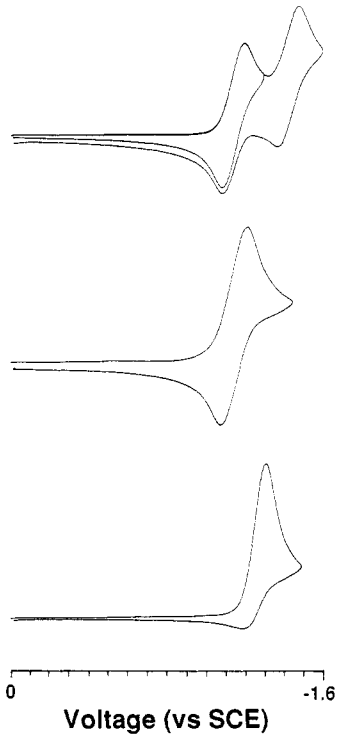
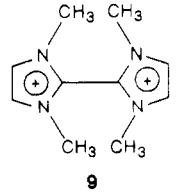


Figure 3. Cyclic voltammograms of biimidazolium salts **6a** (top), **6c** (middle), and **6d** (bottom) in DMSO containing 0.1 M TBAP at 25 °C with a sweep rate of 200 mV/s.

distinct reduction steps, but only the first reduction for **6a** is clearly reversible (in DMSO). The less planar systems **6d,e**, **9**, and **8c** all show a single irreversible wave, indi-



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cating that the species formed after reduction does not persist long enough to be reoxidized back to the initial OX species. It appears likely that a conformational change is occurring after reduction which then inhibits the loss of an electron. The lower barriers for conformational inversion which we have already documented earlier support this premise particularly in comparison with the analogous bis-annelated bipyridinium salts, which have higher inversion barriers and show more reversible behavior. Systems **6c** and **8b** exhibit intermediate behavior. One quasi-reversible wave is found for **6c** in DMSO (Figure 3) which splits into two waves in CH_3CN while **8b** shows two poorly resolved and irreversible waves in DMSO.

The second apparent trend is the shift to more negative potentials with increasing nonplanarity of the system, indicating that the species RCAT and RED are less stable when deprived of a more delocalized planar structure. In general the reduction potentials are too negative to allow convenient preparation of stable RED species for these series of compounds.

Experimental Section

Nuclear magnetic resonance spectra were obtained on a General Electric QE-300 spectrometer at 300 MHz for ^1H and 75 MHz for ^{13}C, and chemical shifts are reported in parts per million downfield from Me_4Si or sodium 3-(trimethylsilyl)propanoate-*2,2,3,3-d*$_4$ (in D_2O). Infrared spectra were obtained on a Perkin–Elmer 1330 spectrometer. Ultraviolet spectra were obtained on a Perkin-Elmer 330 spectrophotometer. All solvents were freshly distilled reagent grade, and all melting points are uncorrected. Elemental analyses were performed by Canadian Microanalytical Service, Ltd., New Westminster, B.C.

Cyclic voltammograms were recorded with a BAS CV-27 voltammograph and a Houston Instruments Model 100 X-Y recorder. A three-electrode system was employed consisting of a platinum button working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode. The reference electrode was separated from the bulk of the solution by a cracked-glass bridge filled with 0.1 M TBAP in the appropriate solvent. Deaeration of all solutions was performed by passing high purity nitrogen over the solution while making measurements. Reagent grade acetonitrile was distilled twice from P_2O_5 under nitrogen, and dimethyl sulfoxide was distilled from CaH_2 under nitrogen. The supporting electrolyte, tetra-*n*-butylammonium perchlorate (TBAP), was recrystallized from EtOAc/hexane, dried, and stored in a dessicator. Half-wave potentials were calculated as an average of the cathodic and anodic peak potentials.[21]

2,2′-Biimidazole (4).[22] Ammonia was bubbled slowly into 300 mL of 20% aqueous glyoxal as such a rate that the temperature was maintained at 40–50 °C. After 2 h the temperature fell below 30 °C, and after 10 h the reaction mixture was filtered to provide 22.9 g of crude product. This material was washed with H_2O, dissolved in 300 mL of hot ethylene glycol, and treated with decolorizing carbon. After a hot filtration, the product precipitated instantly to provide 8.8 g (4.2%) of white crystals: mp >300 °C; ^1H NMR (DMSO-d_6) δ 7.12 (s).

1,1′-Dimethylene-2,2′-biimidazole (5a). To a well-stirred suspension of 0.7 g (5.2 mmol) of **4** in 9 mL of DMF was added 0.9 mL of 35% aqueous NaOH. The mixture turned green and then black after which 1.59 g (11 mmol) of 1-bromo-2-chloroethane was added slowly. After the mixture was stirred overnight at room temperature, the solid precipitate was removed by filtration and washed with ethanol. The filtrate was evaporated to dryness, and the residue was washed several times with hot acetonitrile. The acetonitrile was evaporated, and the residue recrystallized from water to yield 0.36 g (43 %) of **5a**, which was further purified by sublimation (170 °C/0.45 mm): mp 216–217 °C (lit.[13] mp 214–216 °C); ^1H NMR (DMSO-d_6) δ 7.29 (s, $H_{4,4'}$), 7.02 (s, $H_{5,5'}$), 4.39 (s, CH_2CH_2); ^{13}C NMR (DMSO-d_6) δ 137.4 (C_2), 128.6 (C_4, J_{CH} = 189 Hz), 119.7 (C_5, J_{CH} = 192 Hz), 42.6 (CH_2, J_{CH} = 145.4 Hz); IR (KBr) 3170, 1590, 1480, 1420, 1340, 1275, 1110, 1060, 930, 780, 740 cm^{-1}.

1,1′-Trimethylene-2,2′-biimidazole (5b). Via the procedure outlined above for **5a**, 2.7 g (16 mmol) of **4** was treated with 3.64 g (18 mmol) of 1,3-dibromopropane to provide 0.89 g (32 %) of **5b** after recrystallization from water: mp 56 °C (lit.[14] mp 50–55 °C); ^1H NMR (D_2O) δ 7.14 (s, $H_{4,4'}$), 7.06 (s, $H_{5,5'}$), 4.27 (t, 4 H, NCH_2), 2.34 (m, 2 H, CH_2); ^{13}C NMR (D_2O) δ 138.3 (C_2), 128.0 (C_4, J_{CH} = 190 Hz), 123.2 (C_5, J_{CH} = 192.3 Hz), 47.6 (NCH_2, J_{CH}

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(22) Fieselmann, B. F.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1978**, *17*, 2078.

= 142.4 Hz), 26.0 (CH_2, J_{CH} = 131 Hz); IR (KBr) 3400 (b), 1415, 1390, 1315, 1300, 1250, 1125, 740 cm^{-1}.

1,1'-Tetramethylene-2,2'-biimidazole (5c). Via the procedure outlined above for **5a**, 0.4 g (3 mmol) of **4** was treated with 0.57 g (3.3 mmol) of 1-bromo-4-chlorobutane at 110 °C overnight. The residue obtained after the acetonitrile wash was further washed with hot acetone, and the insoluble material was removed by filtration. The filtrate was evaporated to give a thick oil, which solidified upon standing. This solid was chromatographed on 21 g of neutral alumina, eluting with 95:5 chloroform–methanol to yield 0.244 g (44%) of **5c**: mp 195–203 °C; ^1H NMR ($CDCl_3$) δ 7.19 (s, $H_{4,4'}$), 7.00 (s, $H_{5,5'}$), 3.90 (broad s, 4 H, NCH_2), 1.96 (broad s, 4 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 138.1 (C_2), 129.5 (C_4, J_{CH} = 190.4 Hz), 120.7 (C_5, J_{CH} = 187.8 Hz), 46.1 (NCH_2, J_{CH} = 138.5 Hz), 29.1 (CH_2, J_{CH} = 128.5 Hz); IR (KBr) 3070, 2900, 1460, 1400, 1330, 1260, 1225, 1095, 750 cm^{-1}.

1,1'-(α,α'-o-Xylylene)-2,2'-biimidazole (7). Via the procedure outlined above for **5a**, 0.5 g (3.7 mmol) of **4** was treated with 1.1 g (4.2 mmol) of *o*-xylylene dibromide at 120 °C overnight. Workup provided 1.07 g of crude product, which was washed with diethyl ether to provide 0.47 g (54%) of a white solid, which was further purified by sublimation (170 °C, 0.05 mmHg): mp 284–292 °C; ^1H NMR (DMSO-d_6) δ 7.49 (s, $H_{4,4'}$), 7.41 (m, ArH), 7.08 (s, $H_{5,5'}$), 5.08 (s, CH_2); ^{13}C NMR (DMSO-d_6) δ 139.2 (C_2), 134.0 (C_4), 130.0 and 128.7 (Ar-C), 122.3 (C_5), 48.9 (CH_2); IR (KBr) 3120, 1490, 1430, 1380, 1285, 1130, 785, 740 cm^{-1}.

1,1'-Dimethylene-3,3'-trimethylene-2,2'-biimidazolium Dihalide (6a). Method A. A mixture of 0.05 g (0.3 mmol) of **5a** in 1.5 mL of 1,3-dibromopropane was heated at 166 °C for 4 h. After cooling, the reaction mixture was filtered to provide 0.10 g (94%) of **6a**, which could be recrystallized from ethanol–water: ^1H NMR (D_2O, DSS) δ 7.93 (s, ArH), 7.92 (s, ArH), 4.93 (s, 4 H, ethano bridge), 4.78 (t, 4 H, NCH_2), 2.74 (quintet, CH_2); ^{13}C NMR (D_2O, dioxane) δ 130.9 (C_2), 128.5 (C_4), 126.8 (C_5), 53.8, 47.4, 26.3. Anal. Calcd for $C_{11}H_{14}N_4Br_2$: C, 36.46; H, 3.87; N, 15.47. Found: C, 36.53; H, 3.86; N, 15.28.

Method B. A mixture of 0.05 g (0.3 mmol) of **5b** in 1.5 mL of 1-bromo-2-chloroethane was treated as described under method A to provide 0.102 g (94%) of **6a** as the dihalide salt. This material showed spectral properties identical with that prepared by method A.

1,1'-Dimethylene-3,3'-tetramethylene-2,2'-biimidazolium Dibromide (6b). The reaction of 0.3 g (1.9 mmol) of **5a** in 10 mL of 1,4-dibromobutane as described above for **6a** afforded 0.66 g (92%) of **6b**, which was recrystallized from EtOH–H_2O: ^1H NMR (D_2O, DSS) δ 7.96 (s, ArH), 4.87 (s, 4 H, ethano bridge), 4.75 (m, 4 H, NCH_2), 2.32 (m, 4 H, CH_2); ^{13}C NMR (D_2O, dioxane) δ 130.4 (C_2), 129.4 (C_4), 127.2 (C_5), 52.0, 47.8, 26.5. Anal. Calcd for $C_{12}H_{16}N_4Br_2 \cdot 0.5H_2O$: C, 37.40; H, 4.41; N, 14.54. Found: C, 37.53; H, 4.23; N, 14.22.

1,1':3,3'-Bis(trimethylene)-2,2'-biimidazolium Dibromide (6c). To a well-stirred suspension of 1 g (7.5 mmol) of 2,2'-biimidazole (**4**) in 10 mL of DMF was added 0.6 g (15 mmol) of NaOH pellets dissolved in 0.75 mL of water. After 5 min, 6.6 g (32 mmol) of 1,3-dibromopropane was slowly added to the mixture. After 20 h of reflux, an additional 6.6 g (32 mmol) of 1,3-dibromopropane was added, and the mixture was refluxed for another 12 h. After cooling, filtration provided 2.5 g (89%) of **6c**, which was recrystallized from EtOH–MeOH (1:1): ^1H NMR (D_2O, DSS) δ 7.92 (s, 4 H, ArH), 4.77 (t, 8 H, NCH_2), 2.7 (quintet, 4 H, CH_2); ^{13}C NMR (D_2O, dioxane) δ 129.0 (C_2), 126.7 ($C_{4,5}$), 50.8 (NCH_2), 25.2 (CH_2). Anal. Calcd for $C_{12}H_{16}N_4Br_2 \cdot 2H_2O$: C, 34.95; H, 4.85; N, 13.59. Found: C, 35.16; H, 4.88; N, 13.58.

1,1'-Trimethylene-3,3'-tetramethylene-2,2'-biimidazolium Dihalide (6d). Method A. A mixture of 0.05 g (0.27 mmol) of **5c** in 2.0 g (13 mmol) of 1-bromo-3-chloropropane was heated at 105 °C overnight. After cooling, a white precipitate was collected by vacuum filtration to provide 0.087 g (84%) of **6d**, which was recrystallized from EtOH–H_2O: ^1H NMR (D_2O, TSP) δ 8.05 (s, ArH), 7.96 (s, ArH), 4.76 (broad s, 4 H, NCH_2), 4.53 (broad s, 4 H, NCH_2), 2.83 (quintet, 2 H), 2.20 (broad s, 4 H); ^{13}C NMR (D_2O, dioxane) δ 127.1 (C_2), 126.8, 126.7, 50.9, 46.7, 29.6, 24.5. Anal. Calcd for $C_{13}H_{18}N_4Br_2 \cdot H_2O$:[23] C, 38.23; H, 4.90; N, 13.72. Found: C, 38.50; H, 4.88; N, 13.71.

Method B. A mixture of 0.4 g (2.3 mmol) of **5b** in 10 mL of 1,4-dibromobutane was heated at 110 °C for 2 h. The reaction mixture was then diluted with 70 mL of H_2O and extracted twice with chloroform. The aqueous solution was then decolorized with activated charcoal, filtered, and evaporated to provide 0.41 g (46%) of **6d**, which was recrystallized from EtOH to provide material having identical spectral properties with that prepared under method A above.

1,1':3,3'-Bis(tetramethylene)-2,2'-biimidazolium Dibromide (6e). To a well-stirred suspension of 1 g (7.5 mmol) of 2,2'-biimidazole (**4**) in 50 mL of DMF was added 0.6 g (15 mmol) of NaOH pellets dissolved in 0.75 mL of water. After 5 min, 7 g (30 mmol) of 1,4-dibromobutane was added to the mixture, which was then refluxed for 44 h. After cooling, filtration provided 1.04 g (35%) of **6e**, which was recrystallized from EtOH–MeOH: ^1H NMR (D_2O, dioxane) δ 8.06 (s, 4 H, ArH), 4.77 (m, 4 H), 4.13 (t, 4 H), 2.32 (m, 4 H), 2.00 (m, 4 H); ^{13}C (D_2O, dioxane) δ 127.36 ($C_{4,5}$), 125.8 (C_2), 50.81 (NCH_2), 26.7 (CH_2). Anal. Calcd for $C_{14}H_{20}N_4Br_2 \cdot H_2O$: C, 39.81; H, 5.21; N, 13.27. Found: C, 40.04; H, 5.15; N, 13.32.

1,1'-Dimethylene-3,3'-(α,α'-o-xylylene)-2,2'-biimidazolium Dibromide (8a). A mixture of 0.06 g (0.25 mmol) of **7** and 1.8 g (12 mmol) of 1-bromo-2-chloroethane was stirred at room temperature for 4 h and at 90 °C overnight. The reaction mixture was filtered to provide 0.081 g (75%) of a white solid, which was washed well with acetonitrile and recrystallized from EtOH–H_2O: ^1H NMR (D_2O, TSP) δ 8.14 (s, 2 H, ImH), 7.93 (s, 2 H, ImH), 7.71 (d, 2 H, ArH), 7.61 (t, 2 H, ArH), 6.0 (broad s, 4 H, $ArCH_2N$), 4.84 (s, 4 H, ethano bridge); ^{13}C NMR (D_2O, dioxane) δ 132.1, 131.7, 131.4 (benzo ring), 126.5 and 124.2 (C_4, C_5), 122.2 (C_2), 52.7 44.9. Anal. Calcd for $C_{16}H_{16}N_4Br_2$:[23] C, 45.28; H, 3.77; N, 13.21. Found: C, 45.00; H, 3.82; N, 12.87.

1,1'-Trimethylene-3,3'-(α,α'-o-xylylene)-2,2'-biimidazolium Dibromide (8b). Via the procedure described above for **8a**, 0.07 g (0.3 mmol) of **7** was treated with 2.42 g (12 mmol) of 1,3-dibromopropane to provide 0.071 g (54%) of **8b**, which was recrystallized from EtOH–H_2O: ^1H NMR (D_2O, TSP) δ 8.17 (s, 2 H, ImH), 8.0 (s, 2 H, ImH), 7.70 (m, 2 H, ArH), 7.57 (m, 2 H, ArH), 5.92 (s, 4 H, $ArCH_2N$), 4.46 (t, 4 H), 2.79 (quintet, 2 H); ^{13}C NMR (D_2O, dioxane) δ 132.4, 131.6, 131.4 (benzo ring), 128.2 (C_2), 127.2 and 126.5 (C_4, C_5), 53.7, 47.7, 29.3. Anal. Calcd for $C_{17}H_{18}N_4Br_2 \cdot 1.5H_2O$: C, 43.87; H, 4.52; N, 12.04. Found: C, 43.72; H, 4.49; N, 12.06.

1,1'-Tetramethylene-3,3'-(α,α'-o-xylylene)-2,2'-biimidazolium Dibromide (8c). Via the procedure described above for **8a**, 0.07 g (0.3 mmol) of **7** was treated with 2.6 g (12 mmol) of 1,4-dibromobutane to provide 0.101 g (75%) of **8c**, which was recrystallized from EtOH–H_2O: ^1H NMR (D_2O, TSP) δ 8.20 (s, 2 H, ImH), 8.11 (s, 2 H, ImH), 7.52 (m, 4 H, ArH), 5.59 (AB quartet, 4 H, $ArCH_2N$), 5.28 (broad s, 2 H), 4.37 (m, 2 H), 2.38 (broad s, 2 H), 2.11 (quintet, 2 H); ^{13}C NMR (D_2O, dioxane) δ 130.8, 130.6, 130.3, 129.4, 127.7, 127.5, 53.3, 51.2, 26.7. Anal. Calcd for $C_{18}H_{20}N_4Br_2 \cdot 2H_2O$: C, 44.26; H, 4.92; N, 11.48. Found: C, 44.25; H, 4.92; N, 11.41.

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(23) Apparently anion exchange occurs during salt formation.