N,N′-Bridged Derivatives of 2,2′-Bibenzimidazole†

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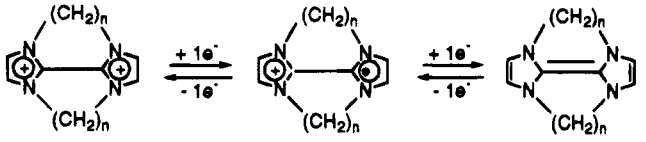
A series of 2,2′-bibenzimidazolium salts has been prepared by N,N′-bridging using dihaloalkanes. These salts may be reduced by either one or two electrons to the corresponding cation radical or neutral 2,2′-bibenzimidazolinylidene. The latter species undergoes a chemiluminescent reaction with dioxygen to afford conformationally unique ureaphanes. Two benzimidazole molecules may be joined by N,N′-bridges to form bis(benzimidazolium) salts which may be deprotonated with sodium hydride. Subsequent intramolecular 2,2′-coupling leads to the same 2,2′-bibenzimidazolinylidenes. The structural features of the ureaphane oxidation products have been studied by X-ray crystallography and NMR. An equimolar mixture of a 2,2′-bibenzimidazolium salt and the corresponding 2,2′-bibenzimidazolinylidene will coproportionate to form the analogous cation radical.

Introduction

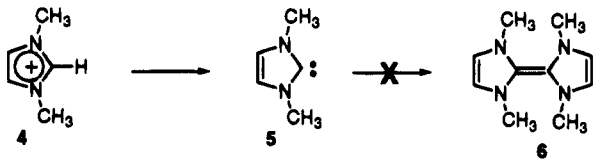
In an earlier study, we examined the preparation and properties of a series of 2,2′-biimidazoles incorporating one or two *N,N′*-polymethylene bridges.[1] The mono-bridged species were examined as ligands for Ru(II) analogous to 3,3′-polymethylene-bridged 2,2′-bipyridines.[2] The doubly bridged 2,2′-biimidazolium salts **1** were of interest because of their redox behavior. Two distinct reductions could be observed, the first leading to the cation radical **2** and the second providing the neutral tetraazaethylene derivative **3**. This latter species is particularly interesting because it is an aza-analogue of tetrathiafulvalene (TTF) which is an important donor used to form potentially conducting charge transfer salts. Important differences between **3** and TTF are the presence of the more electronegative nitrogens which tend to decrease the oxidation potential and the ability to modulate redox properties through control of the bridge length.



1 (n = 2-4) **2** **3**

In no instance were we able to isolate the neutral species **3**; all procedures required reduction potentials for the step **2** to **3** in the range of −1.28 to −1.49 V. The inaccessibility of **3** is somewhat surprising in light of the fact that tetraaminoethylenes are often stable species[3] and 4,4′,5,5′-tetrahydro derivatives of **3** have been reported.[4] Similarly, the highly colored cation radical intermediates **2** can be observed but not isolated.

Subsequently, Arduengo and co-workers reported the preparation of stable N,N′-disubstituted imidazolidenyl carbenes **5** *via* the deprotonation of the corresponding imidazolium salts **4**.[5] In no instance were dimers such as **6** observed, which was consistent with our inability to obtain species such as **3**.[6]



For the corresponding 4,5-benzo-fused systems, however, Bourson had reported that deprotonation of 1,3-diphenyl-2,2′-bibenzimidazolium iodide led to the corresponding dibenzimidazolinylidene dimer.[7] Hünig observed a similar result for the sodium hydride-promoted deprotonation of 1,3-dimethylbenzimidazolium chloride.[8] These observations coupled with the fact that 2,2′-bibenzimidazolium analogues of **1** can be reduced at more positive potentials,[9] indicating greater stability of the reduction products, prompted us to undertake a careful study of such species.

Synthesis of the Salts

The preparation of 2,2′-bibenzimidazole (**7**) is readily accomplished by the condensation of *o*-diaminobenzene with oxamide.[10] Further treatment of **7** with excess 1,3-dibromopropane or 1,4-dibromobutane in DMF provided

† Dedicated to Professor Bruce F. Rickborn on the occasion of his 60th birthday.

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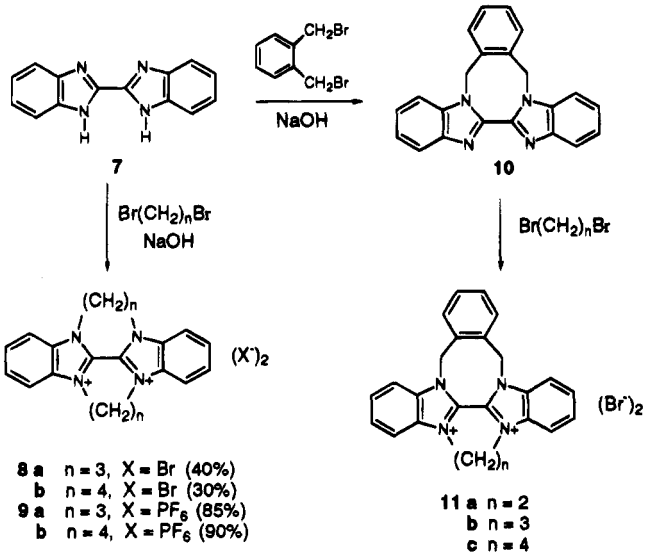
Scheme 1



the doubly bridged salts in good yields. The water soluble bromides **8** may be converted into the acetonitrile soluble hexafluorophosphates **9**. We were unable to prepare the bis-dimethylene bridged species (n = 2) because of the excessive strain required to incorporate the second bridge.

When **7** is treated with *o*-xylylene dibromide, the monobridged species **10** is obtained. Subsequent reaction of **10** with 1,*n*-dihaloalkanes provided the doubly bridged salts **11** (Scheme 1). We were unable to prepare the bis-(*o*-xylyl) bridged salt.

An alternative approach to the systems of interest might involve deprotonation of a bis(benzimidazolium) salt. These salts could be prepared by the treatment of benzimidazole with a 1,*n*-dihaloalkane to first provide the N,N′-bridged species **13**. A subsequent bis-alkylation with a second equivalent of 1,*n*-dihaloalkane then afforded the salts **14**.[8] The trimethylene bridged system **14a** was accompanied by about 4% of a cyclic tetramer **15**. When **12** is treated with *o*-xylylene dibromide the monobridged species **16** is obtained which can, in turn, be bridged a second time with 1,*n*-dihaloalkanes to provide the salts **17** or a second time with *o*-xylylene dibromide to afford the salt **18** (Scheme 2).

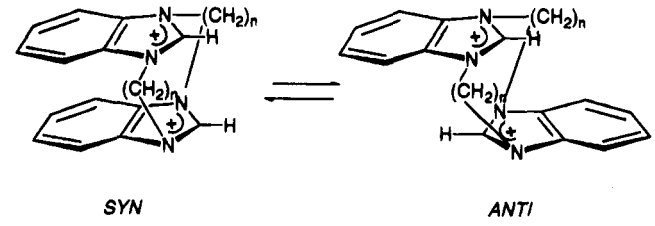
Properties of the Salts

The physical properties of the N,N′-bridged salts of 2,2′-bibenzimidazole may be correlated with the shape or geometry of the molecule (see Table 1). To estimate these geometries we performed molecular mechanics calculations which provided a good estimate of the dihedral angle between the two benzimidazole rings.[11] The systems having shorter bridges (**8a** and **11a**) are more planar while the system with two tetramethylene bridges is the least planar. The energy of UV absorption diminishes as a system becomes more planar or more delocalized, and this behavior is totally consistent with the trend observed in Table 1 where an approximately linear relationship exists between the absorption maximum and the dihedral angle (see Figure 1).

Bibenzimidazolium salts undergo two discrete one-electron reductions yielding first a cation radical and finally the neutral 2,2′-dibenzimidazolinylidene. The redox properties are governed in a fashion similar to the electronic absorption spectra so that the most planar systems are the most easily reduced and show the greatest separation between the two reduction waves. The stability of the intermediate cation radical can be correlated to the difference between E_1 and E_2 according to the expression $\log K_{RCAT} = (E_2 - E_1)/0.059$,[12] and values for K_{RCAT} are listed in Table 1. From this data it would be expected that **8a** and **11a** would provide the most stable cation radicals.

The conformational properties of the salts can be assessed by analyzing their methylene proton resonances in the ^{1}H NMR.[1,13] For the trimethylene bridged **8a**, the α-methylene protons appear at 4.90 ppm and the β-methylenes at 2.93 ppm. The equivalence of these geminal protons indicates that conformational rotation about the 2,2′-bond is rapid at room temperature on the NMR time scale. Conversely, **8b** shows four distinct signals in the methylene region at 5.04, 4.27, 2.43, and 2.05 ppm, indicating that at room temperature this system is conformationally rigid. The α,α′-*o*-xylyl bridged systems can be similarly analyzed by considering the $ArCH_2N$ methylene signal. In **11a,b** this methylene resonance appears as a singlet at 6.47 and 6.23, respectively, indicating rapid conformational inversion. For **11c**, however, these protons give an AB quartet centered at 6.06 ppm indicating a conformationally rigid system.

For the bis(benzimidazolium) salts (Scheme 2), the effect of N,N′ bridging is somewhat different. Since the two halves of the molecule are no longer joined by a 2,2′-bond they have more conformational freedom. One can envision two extreme situations wherein the benzimidazole moieties are aligned in a parallel *syn* arrangement or parallel *anti* arrangement. It is likely that π-stacking effects in the bridging process would initially lead to the *syn* arrangement, and if the bridges are sufficiently long, inversion to an *anti* arrangement is possible. The NMR evidence bears out this premise in that the bis(trimethylene)-bridged system **14a** shows both the α- and β-methylene groups as two distinct pairs of geminal signals, indicating a rigid *syn* conformation. On the other hand, the bis(tetramethylene)-bridged system **14b** has more conformational flexibility, and hence, its NMR shows only two methylene signals at 4.65 and 2.06 ppm, indicating rapid interconversion between the two possible *anti*-conformations. For the bis(*o*-xylyl)-bridged system **18** the



four carbons connecting the two benzimidazoles are more restricted since two of them are incorporated in a benzene ring, and thus, intermediate behavior is observed. The system is rigid at room temperature, and two broad nonequivalent geminal methylene signals are observed. Heating the sample to 40 °C causes these peaks to

(11) Calculated using the programs PC MODEL and MMX available from Serena Software, Bloomington, IN.

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Scheme 2

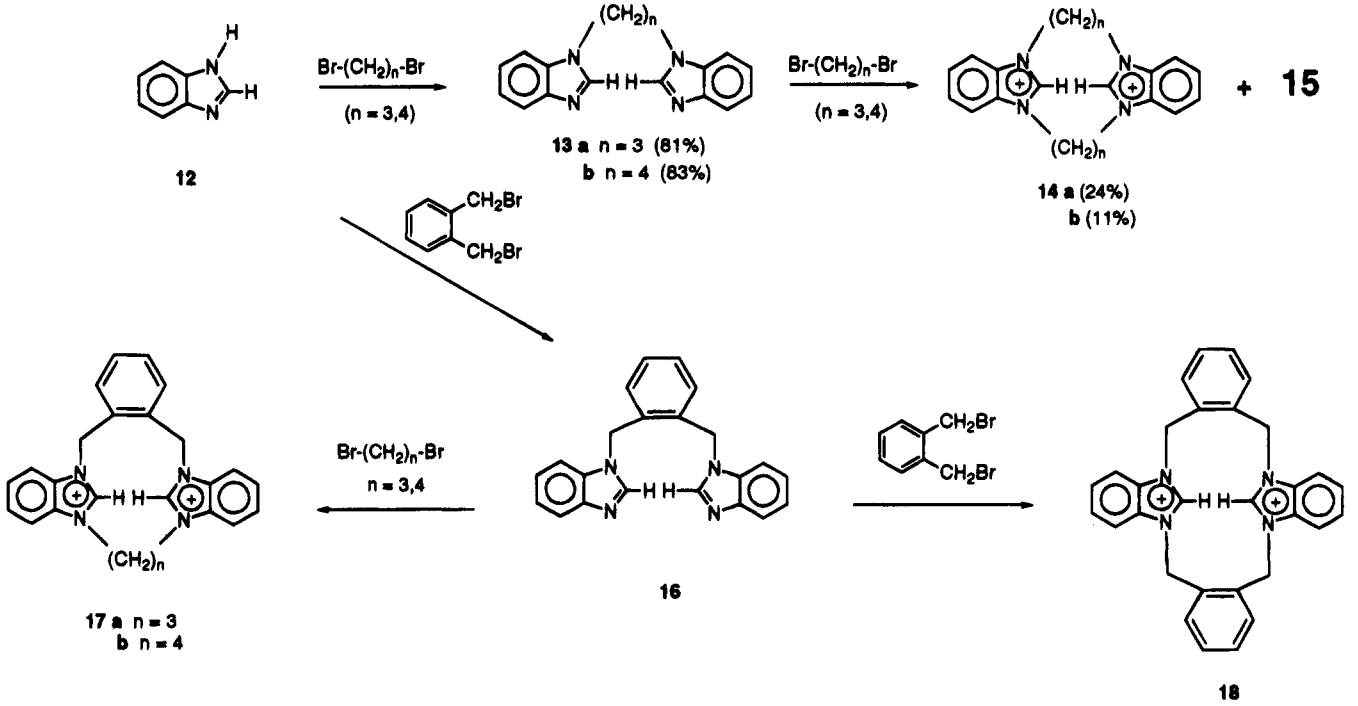


Table 1. Calculated Geometries, Absorption Maxima, and Electrochemical Data for 2,2'-Bibenzimidazolium Salts

compd	dihedral angle[a] (deg)	λ_{max} (MeOH) (nm)	E_1[b] (V)	E_2[b] (V)	K_{RCAT}[c]
8a[d]	20	353	−0.55 (60)	−0.87 (80)	2.7×10^5
8b[e]	54	325	−0.81 (100)	−0.94 (110)	1.6×10^2
11a[d]	17	368	−0.50 (120)	−0.81 (120)	1.8×10^5
11b[d]	32	346	−0.59 (100)	−0.74 (100)	3.5×10^2
11c[e]	46	329	−0.71 (130)	−0.85 (160)	2.4×10^2

[a] Calculated using the programs PC MODEL and MMX available from Serena Software, Bloomington, IN. [b] Potentials are in volts *vs* SCE measured in 0.1 M TBAP at room temperature. The number in parentheses is the difference between the cathodic and anodic waves (mV). [c] $\log K_{RCAT} = (E_2 - E_1)/0.059$. [d] In DMSO. [e] In CH_3CN.

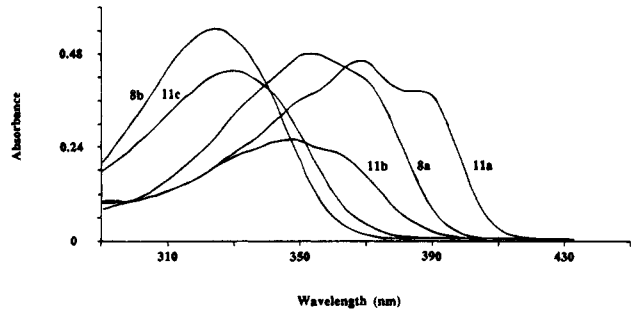
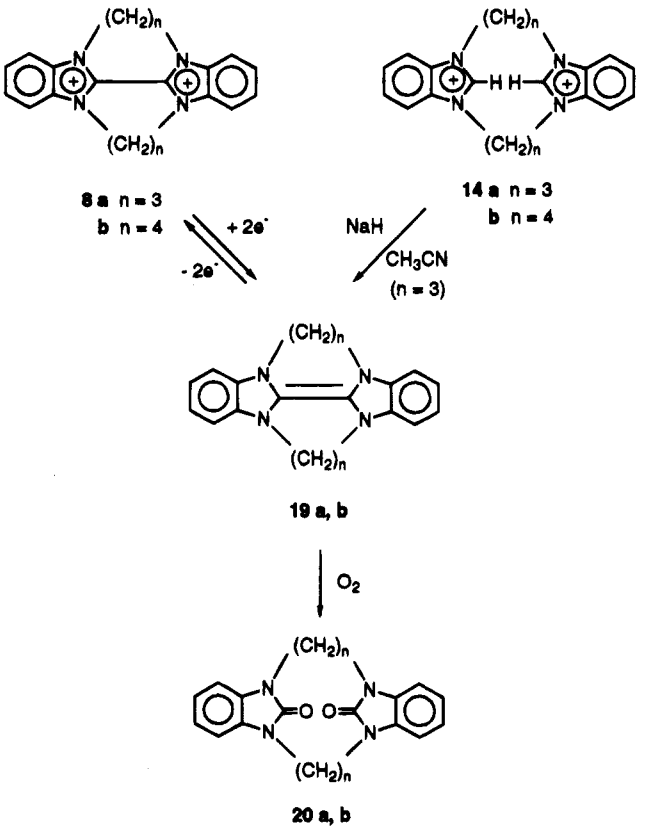


Figure 1. Long wavelength region of the UV absorption spectra of **8a,b** and **11a–c** (2.06×10^{-5} M CH_3OH).

coalesce, and an inversion barrier of 14.6 kcal/mol can be calculated.

Generation of 2,2'-Dibenzimidazolinylidene

The electrochemical generation of 2,2'-dibenzimidazolinylidene (**19**) was examined by the bulk electrolysis of the salts **8a,b**. A suspension of **8a** in CH_3CN containing 0.1 M TBAP was stirred, and a potential of −1.10 V, more negative than the E_2 for **8a**, was applied. The suspension slowly dissolved, and an intense red color appeared which indicated initial formation of the cation radical. As the reduction proceeded, the red color gradually faded. After the current had decreased to zero, a yellow crystalline material **19a** was obtained in 62% yield. Similar electrolysis of **8b** was carried out by applying a potential of −1.40 V, more negative than the E_2 of **8b**. During the electrolysis, a purple color appeared, presumably due to intermediate formation of the cation radical. As the electrolysis proceeded, the purple color faded and subsequent workup provided orange crystalline **19b** in 43% yield.



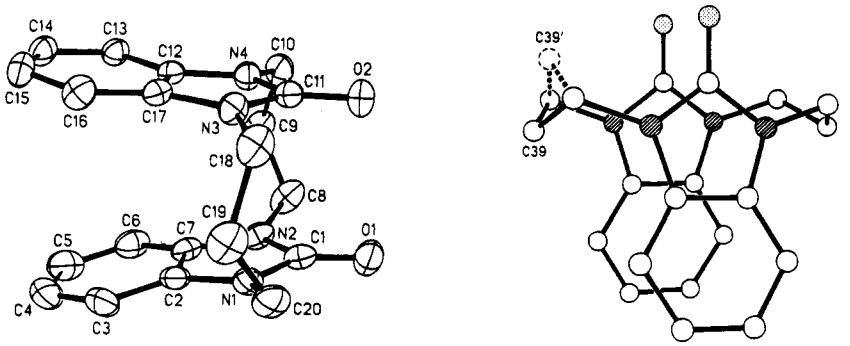


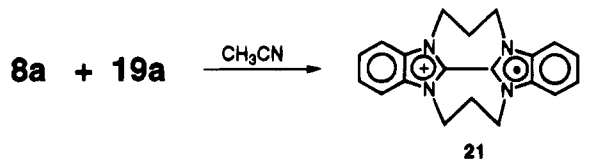
Figure 2. X-ray structure of **20a**. Left: ORTEP plot of side view of one molecule in the unit cell with atom-numbering scheme. Right: top view of second molecule in the unit cell showing disorder in trimethylene bridge.

In the ^{1}H NMR the benzo-protons of **19a** exhibited an AA'BB' pattern centered at 6.74 (4H) and 6.26 (4H) ppm. The bridge methylenes showed two multiplets at 2.98 (8H) and 1.36 (4H) ppm. For **19b** the benzo-protons appeared at 6.76 (4H) and 6.23 (4H) ppm and the bridge methylenes at 3.23 (8H) and 1.36 (8H) ppm. The relatively high field aromatic signals for both compounds demonstrate that they are electron rich. In the ^{13}C NMR **19a,b** showed the expected number of lines, and their IR spectra evidenced strong absorptions at 1595 and 1602 cm^{-1} characteristic of a tetraaminoethylene C=C stretch. The cyclic voltammograms for both species were identical to those obtained for the precursor salts. There is no evidence for a bis(carbene).

Dibenzimidazolinylidene **19b** is accompanied by 15% of a byproduct whose NMR shows aromatic multiplets at 6.83 and 6.29 ppm and aliphatic multiplets at 3.16, 2.80, 1.51, and 1.30 ppm. These signals were not due to the ureaphane **20b** (*vide infra*). Unfortunately, this byproduct could not be isolated or characterized due to the extreme air-sensitivity of these compounds.

When **14a** was treated with excess sodium hydride in CH_3CN under Ar, a gas was generated. After gas evolution stopped, filtration gave a yellow solution which was cooled to provide the air sensitive crystalline **19a** in 68% yield. It is tempting to explain the formation of this dibenzimidazolinylidene by the double deprotonation of **14a** to provide a bis-carbene which then undergoes dimerization. It is more likely, however, that a mono-carbene is initially formed which then attacks the nearby benzimidazolium cation, the adduct losing a proton at C2 to provide the final **19a**.

Coproportionation of **8a** and **19a** in CH_3CN generated a deep red solution. After solvent removal, the cation radical **21** was obtained as a red-black solid which exhibited a strong ESR signal in acetonitrile solution.



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Ureaphane Formation

When a 2–3 mg solid sample of **19a,b** is exposed to air it emits a bright yellow light for 5–10 min and then becomes white. These same white solids can also be generated by carrying out the electrolysis of **8a,b** or the deprotonation of **14a,b** in the presence of air. The reduction of the bridged bibenzimidazolium salts could be more conveniently accomplished by using a chemical reducing agent. For this purpose tetrakis(dimethylamido)ethylene (TDAE) was found to be quite effective so that the treatment of **9a,b** with this species in air gave **20a,b** directly. These two ureaphanes exhibited very similar properties, showing a carbonyl carbon resonance at 152.3 ppm and a C=O IR stretching frequency at 1700 cm^{-1}.[14]

Although the ^{13}C NMR spectra of **20a** and **20b** were similar, their ^{1}H NMR spectra were quite different. The aliphatic region of **20a** showed four well-resolved multiplets at 4.71 (4H), 3.77 (4H), 2.95 (2H), and 1.87 (2H) ppm while **20b** showed only two broad singlets at 3.70 (8H) and 1.83 (8H) ppm, indicating that the geminal methylene protons of **20a** are nonequivalent and the molecule is conformationally rigid while **20b** appears to be conformationally mobile. In the aromatic region, **20a** showed an eight proton multiplet at 6.61 ppm while **20b** gave two four proton multiplets at 6.96 and 6.84 ppm. From this data we conjectured that **20a** was held in a rigid *syn*-conformation which would account for shielding of its aromatic protons, while **20b** was in a mobile *anti*-conformation. Furthermore, cooling of **20b** to −10 °C caused the singlet at 3.70 ppm to split into two signals while further cooling to −40 °C caused the singlet at 1.83 ppm to split into two signals. From this data a barrier of 11.2–12.4 kcal/mol may be calculated for the interconversion of the two *anti*-conformations. Warming of **20a** to 200 °C did not appreciably alter its NMR spectrum, indicating that the *syn*-conformation was quite stable.

These NMR-based structural hypotheses are borne out by single crystal X-ray analyses which show **20a** to be held in a *syn* conformation with the two benzimidazolone rings parallel to one another forming an angle of 19° between the planes containing each ring (Figure 2). The distance between the centroids of the two six-membered rings is 3.78 Å, and the O–O distance is 2.95 Å. Although the molecule appears to present an attractive cavity, it is too narrow to allow the intercalation of a guest. There is some disorder in one of the trimethylene units where the central methylene can be *syn* or *anti* to the carbonyl group. The X-ray data are fit best by a model that is 88% *anti* and 12% *syn*.

Molecular mechanics calculations were performed on both the *syn* and *anti* conformations of **20a,b**, and these are summarized in Table 2 along with some pertinent X-ray distances. For **20a** the agreement between the

(14) This is a revision of our earlier reported value of 1650–1660 cm^{-1}; Shi, Z.; Thummel, R. P. *Tetrahedron Lett.* **1994**, *35*, 33.

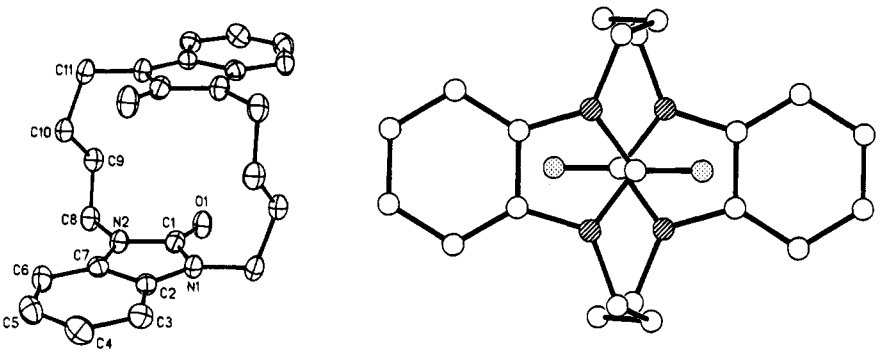


Figure 3. X-ray structure of **20b**. Left: ORTEP plot of side view with atom-numbering scheme. Right: top view.

Table 2. X-ray Structure Characteristics (Å) and Minimized Energies (kcal/mol) of Ureaphanes 20a,b and 22

	20a		20b		22	
	X-ray	MMX (*syn*)[a]	X-ray	MMX (*anti*)	X-ray	MMX
$O_1-O_{1'}$	2.95	2.71	4.98	4.38	3.14	3.00
$C_1-C_{1'}$	3.02	2.90	4.09	4.05	3.13	3.05
$N_1-N_{1'}$	3.09	3.00	4.24	4.68	3.13	3.09
$C_2-C_{2'}$	3.40	3.43			3.34	3.45
$C_3-C_{3'}$	3.78	3.80			3.53	3.80
$C_4-C_{4'}$	4.16	4.17			3.69	4.14
energy (*syn*)[a]	30.47		29.57			
energy (*anti*)	22.84		26.51			

[a] Three conformations of the trimethylene bridges were possible with one or both central methylenes oriented *syn* or *anti* to the carbonyl. Data are given for the *anti,anti* minimum energy conformer.

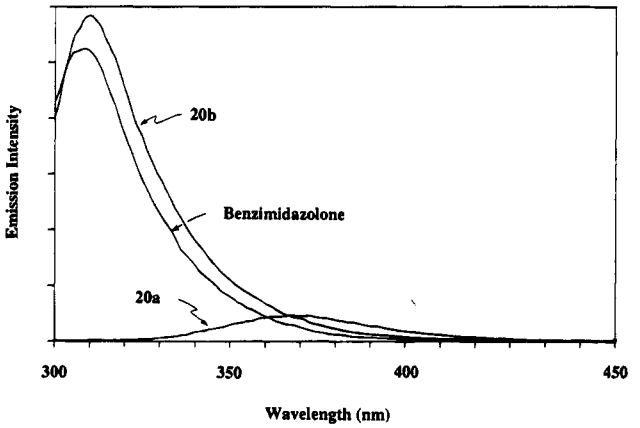
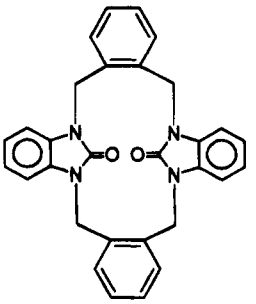


Figure 4. Emission spectra of **20a,b** and benzimidazolone (2.06×10^{-5} M CH_3OH) with excitation at 283 nm.

measured and calculated structures is quite good, although the O−O repulsion is somewhat underestimated. It is this O−O repulsion which prohibits the conformational inversion of **20a** and thus stabilizes the higher energy *syn* conformation. For **20b** the increased flexibility afforded by the longer bridges allows the initially formed *syn*-ureaphane to conformationally invert to the more stable *anti*-form (Figure 3).

The electronic absorption and emission properties of these ureaphanes are consistent with their structures. Their long wavelength UV absorptions show a band at 280 nm (ϵ 1230) for **20a** and a band at 285 nm (ϵ 910) for **20b** which are similar to the absorption of benzimidazolone at 280 nm (ϵ 700). When **20a,b** and benzimidazolone are excited at 283 nm where their optical densities are approximately equal, **20b** and benzimidazolone show similar strong emissions at 310 and 308 nm, respectively, while **20a** gives two weak bands at 305 and 369 nm (Figure 4). Further examination indicated that when the concentration of benzimidazolone was higher than 10^{-4} M the emission intensity at 308 nm decreased due to intermolecular excimer formation. The small band at 305 nm for **20a** is characteristic of the emission from the benzimidazolone ring and the band at 369 nm is characteristic of the emission from an intramolecular excimer, consistent with the *syn*-conformation of **20a**.



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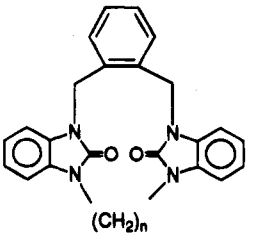
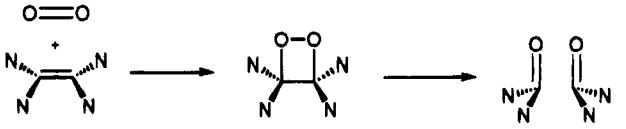


23 a n = 2
b n = 3
c n = 4

A bis-*o*-xylyl bridged benzimidazolone **22** could be generated by deprotonation of the corresponding salt **18** in the presence of air. Although we are unable to isolate the dibenzimidazolinylidene intermediate, we expect that this species reacts with dioxygen to form a dioxetane which then cleaves to the bis(urea). The consequences



of this oxidative pathway on the conformation of **22** are interesting. Due the comparatively limited flexibility of the *o*-xylyl bridges, **22** can exist only in a *syn*-conformation. Nevertheless, the *o*-xylyl bridges can behave like flaps which may be directed either up or down. Formation of a dioxetane intermediate dictates that the *o*-xylyl bridges will initially be directed downward forming a bowl-shaped molecule. This structure was confirmed by X-ray analysis, and the structure is illustrated in Figure 5. Note that the benzimidazolone rings do not eclipse one another; their skewing is caused by the O−O repulsion as well as the flagpole interaction between the *o*-xylyl methylenes. Molecular mechanics predicts a somewhat less parallel arrangement of the benzimidazolones but does show the same skewing effect.

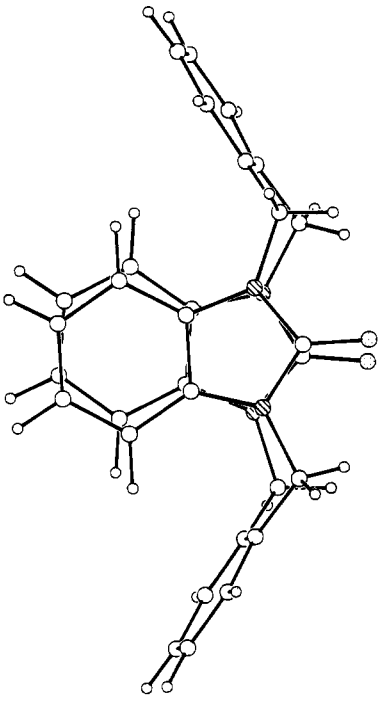
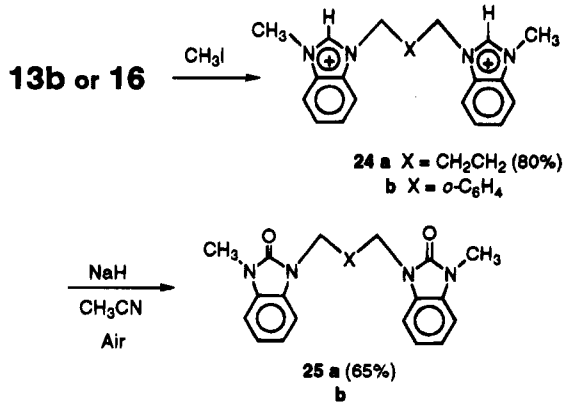


Figure 5. X-ray structure of **22**. Top view.

Other ureaphanes having one *o*-xylyl and one polymethylene bridge (**23a–c**) could be generated in a similar fashion, either by aerobic TDAE-promoted reduction of the 2,2′-bibenzimidazolium salts or by deprotonation of the appropriate bis(benzimidazolium) species in the presence of air. The NMR spectra of **23a–c** show nonequivalent geminal protons for both the *o*-xylyl methylenes as well as the polymethylene bridges, indicating that all three ureaphanes are conformationally rigid. Their benzimidazolone protons appear at about 6.5 ppm suggesting a *syn* parallel arrangement of these two rings as was seen for **20a** and **22**.

Two systems were examined having only one N′,N′-bridge connecting the two benzimidazolium moieties (**24a,b**). Deprotonation in the presence of air provided the bis(ureas) **25a,b** in yields of 65% and 40%, respectively. The tetrameric material **17** which was formed as a minor product in the preparation of **3** was also subjected to deprotonation in the presence of air to provide the benzimidazolone tetramer **26** in 69% yield. Htay and Meth-Cohn have reported a similar tetramethylene bridged trimer which results from the coupling of benzimidazolone with 1,4-dibromobutane.[15]



The structure of **26** was not obvious from its NMR and could only be verified by X-ray analysis. It is noteworthy

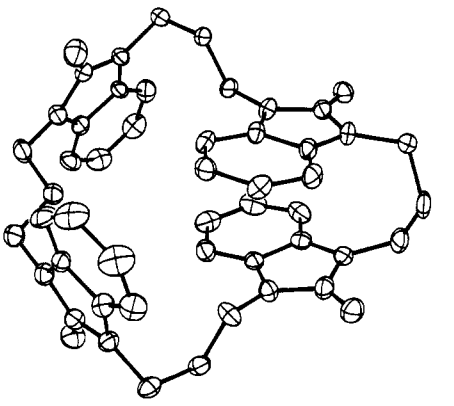
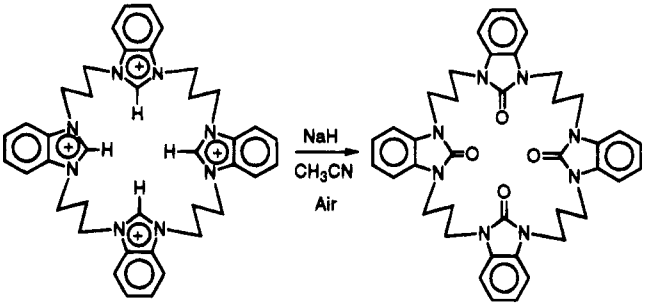


Figure 6. X-ray structure of tetramer **26**.

that the four carbonyl groups do not all point in the same direction but rather alternate up and down (Figure 6). If a bis(dibenzimidazolinylidene) is involved as an intermediate in the formation of **26**, such a species could be formed by the interaction of either two adjacent or two opposing benzimidazolium cations. Considering the general mechanism for bis(urea) formation, the alternate up and down conformation which is observed supports the crosswise interaction of benzimidazolium cations and the involvement of an intriguing orthogonally oriented bis(dibenzimidazolinylidene). Insufficient material was available to allow the isolation of such a species.



15 **26**

In this study we have demonstrated that N,N′-derivatives of 2,2′-dibenzimidazolinylidene can be generated by reduction of bridged salts of 2,2′-bibenzimidazole or deprotonation of similarly bridged bis(benzimidazolium) salts. These species undergo facile reaction with dioxygen to form dioxetanes which decompose to ureas with concommitant chemiluminescence. The conformation of the resulting urea is dictated by this oxidation, and future work will address the formation of larger conformationally unique ureaphanes and their complexation with metal cations. Cation radicals are readily accessible from either controlled reduction of 2,2′-bibenzimidazolium salts or oxidation of the dibenzimidazolinylidenes. The properties of these species are under further investigation.

Experimental Section

Nuclear magnetic resonance spectra were obtained on a General Electric QE-300 spectrometer at 300 MHz for ^{1}H and 75 MHz for ^{13}C, and chemical shifts are reported in parts per million downfield from Me_4Si referenced to the solvent peaks. For ^{1}H: 7.26 ($CDCl_3$), 2.49 (DMSO-d_6), 4.63 (D_2O), 7.15 (C_6D_6), and 1.93 (CD_3CN). For ^{13}C: 77.0 ($CDCl_3$), 39.5 (DMSO-d_6),

(15) Htay, M. M.; Meth-Cohn, O. *Tetrahedron Lett.* **1976**, 79.

128.0 (C_6D_6), 118.2, and 1.3 (CD_3CN). ESR spectra were measured on Bruker 300-ESR spectrometer. Fluorescence spectra were recorded on a Perkin-Elmer LS-50 luminescence spectrometer. Infrared, UV–vis, and cyclic voltammetry measurements were performed as described previously.[1] Melting points were measured with a capillary melting point apparatus and are not corrected. Elemental analyses were performed National Chemical Consulting, Inc., Tenafly, NJ.

Bulk electrolyses were carried out in an H-configuration cell with platinum working and auxiliary electrodes in a cathode compartment separated from a KCl saturated reference electrode in anode compartment by a fritted-glass disk. A solution of the salt to be electrolyzed in 0.1 M TBAP in CH_3CN (5 mL) was stirred continuously in the cathode compartment. The anode compartment was filled with 0.1 M TBAP in CH_3CN (4 mL). A negative potential generated on a BAS Synthetic Potentiostat-2 was applied. All manipulations were carried out under Ar.

Reagent grade acetonitrile was distilled under Ar from CaH_2 and was stored under Ar in Schlenk flask. Tetrahydrofuran (THF) was distilled from Na and was stored under Ar in Schlenk flask. NaH, 60% dispension in mineral oil, was washed twice with hexane, dried *in vacuo*, and stored under Ar. 1,1,3,3-Tetramethylguanidine was distilled and stored under Ar. $POCl_3$ was distilled before use. Other chemicals and solvents were commercial reagent grade and used without further purification. 2,2'-Bibenzimidazole (**7**) was synthesized according to a known procedure.[10]

1,1':3,3'-Bis(trimethylene)-2,2'-bibenzimidazolium Dibromide (8a)[8] and 1,1':3,3'-Bis(trimethylene)-2,2'-bibenzimidazolium Dihexafluorophosphate (9a). A mixture of **7** (6.0 g, 0.026 mol), 1,3-dibromopropane (2.5 g, 0.15 mol), and NaOH (2.1 g, 0.068 mol) in DMF (60 mL) was refluxed for 18 h. After cooling, the solution was combined with H_2O (800 mL) and filtered. The filtrate was evaporated, and the residue was crystallized from CH_3OH to give **8a** as a yellow solid (3.8 g, 30%), mp > 300 °C: ^1H NMR (D_2O) δ 7.97 (m, 4H), 7.77 (m, 4H), 4.88 (t, 8H, J = 6.3 Hz), 2.85 (m, 4H). A solution of $AgPF_6$ (1.5 g, 5.8 mmol) in H_2O (10 mL) was added to a solution of **8a** (1.0 g, 2.1 mmol) in H_2O–CH_3CN (1:5, 20 mL) and a light yellow solid precipitated immediately. CH_3CN (40 mL) was added, and the mixture was filtered. The filtrate was evaporated, and the residue was recrystallized from CH_3CN–H_2O to provide **9a** as a pale yellow material (1.2 g, 90%), mp > 300 °C: ^1H NMR (CD_3CN) δ 8.11 (m, 4H), 7.95 (m, 4H), 4.90 (t, 8H, J = 6.3 Hz), 2.93 (quintet, 4H), 2.15 (s, H_2O); ^{13}C NMR (CD_3CN) δ 134.8, 134.0, 130.8, 114.9, 47.1, 27.8; IR (KBr) 3040, 2880, 1575, 1435, 1400, 1340, 1065, 850, 750 cm^{-1}. Anal. Calcd for $C_{20}H_{20}N_4P_2F_{12}$: C, 39.60; H, 3.30; N, 9.24. Found: C, 39.40; H, 3.32; N, 8.94.

1,1':3,3'-Bis(tetramethylene)-2,2'-bibenzimidazolium Dibromide (8b) and 1,1':3,3'-Bis(tetramethylene)-2,2'-bibenzimidazolium Dihexafluorophosphate (9b). Following the procedure described for **8a**, a mixture of **7** (6.0 g, 0.026 mol), 1,4-dibromobutane (3.0 g, 0.15 mol), and NaOH (2.1 g, 0.068 mol) in DMF (60 mL) provided **8b** as pale yellow crystals (4.1 g, 30%), mp > 300 °C: ^1H NMR (D_2O) δ 8.02 (m, 4H), 7.79 (m, 4H), 5.01 (dd, 4H, J = 6.4, 15.0 Hz), 4.19 (dd, 4H, J = 10.2, 4.0 Hz), 2.28 (m, 4H), 2.02 (m, 4H). As described for **9a**, a solution of $AgPF_6$ (1.0 g, 3.8 mmol) in H_2O (10 mL) was added to a solution of **8b** (0.5 g, 1.1 mmol) in H_2O–CH_3CN (1:5, 20 mL) to provide **9b** as a pale yellow material (0.58 g, 90%), mp > 300 °C: ^1H NMR (CD_3CN) δ 8.17 (m, 4H), 7.99 (m, 4H), 5.04 (m, 4H), 4.27 (m, 4H), 2.43 (m, 4H), 2.15 (s, H_2O), 2.05 (m, 4H); ^{13}C NMR (CD_3CN) δ 134.5, 132.1, 131.0, 115.0, 48.3, 26.7; IR (KBr) 3020, 2875, 1580, 1445, 1410, 1320, 1100, 870, 730 cm^{-1}. Anal. Calcd for $C_{22}H_{24}N_4P_2F_{12}$ – 1 H_2O: C, 40.49; H, 3.98; N, 8.59. Found: C, 40.32; H, 3.73; N, 8.52.

1,1'-(α,α'-*o*-Xylyl)-2,2'-bibenzimidazole (10). In a 100 mL round bottom flask, 20% aqueous KOH (5 mL) was added to a well-stirred suspension of **7** (1.0 g, 4.3 mmol) and α,α'-dibromo-*o*-xylene (1.13 g, 4.3 mmol) in CH_3CN (30 mL). After the mixture was stirred for 12 h at room temperature, water (20 mL) was added. Filtration of the mixture provided a yellow-green solid which was dissolved in $CHCl_3$, and the undissolved impurities were removed by filtration. The filtrate was evaporated, and **10** was obtained as a green solid (1.2 g, 80%), mp > 300 °C: ^1H NMR (DMSO-d_6) δ 7.85 (m, 2H), 7.75 (overlapping m, 4H), 7.40 (overlapping m, 6H), 5.29 (s, 4H), 3.33 (m, H_2O); ^{13}C NMR ($CDCl_3$) δ 145.1, 143.6, 135.4, 133.5, 129.8, 129.3, 124.4, 123.3, 121.4, 109.7, 48.6; IR (KBr) 3200, 1590, 1460, 1420, 1370, 1340, 1090, 890, 750 cm^{-1}.

1,1'-(α,α'-*o*-Xylyl)-3,3'-dimethylene-2,2'-bibenzimidazolium Dibromide (11a). A mixture of **10** (0.22 g, 0.65 mmol) and 1,2-dibromomethane (3.0 g, 16 mmol) was heated at 130 °C for 2 h. After cooling, $CHCl_3$ (10 mL) was added and the reaction mixture was filtered to provide a yellow solid (0.22 g, 65%) which was recrystallized from ethanol–water to provide **11a**, mp > 300 °C: ^1H NMR (DMSO-d_6) δ 8.89 (d, 2H, J = 8.1 Hz), 8.32 (d, 2H, J = 7.9 Hz), 8.00 (quintet, 4H), 7.88 (dd, 2H, J = 3.5, 5.4 Hz), 7.56 (dd, 2H, J = 3.5, 5.4 Hz), 6.47 (s, 4H), 5.22 (s, 4H), 3.38 (H_2O); ^{13}C NMR (DMSO-d_6) δ 133.6, 133.3, 131.8, 131.6, 131.0, 130.1, 129.6, 129.4, 114.5, 114.4, 48.4, 42.2; IR (KBr) 2950, 1580, 1440, 1350, 1230, 1090, 890, 760 cm^{-1}. Anal. Calcd for $C_{24}H_{20}N_4Br_2$ – 2 H_2O: C, 51.43; H, 4.28; N, 10.00. Found: C, 51.76; H, 4.44; N, 9.86.

1,1'-(α,α'-*o*-Xylyl)-3,3'-trimethylene-2,2'-bibenzimidazolium Dibromide (11b). A mixture of **10** (0.23 g, 0.68 mmol) and 1,3-dibromopropane (2.5 g, 13 mmol) was heated at 120 °C for 2 h. After cooling, $CHCl_3$ (10 mL) was added and the reaction mixture was filtered to provide **11b** as a pale yellow solid (0.26 g, 68%) which was recrystallized from ethanol–water, mp > 300 °C: ^1H NMR (DMSO-d_6) δ 8.60 (dd, 2H, J = 3.1, 5.5 Hz), 8.43 (dd, 2H, J = 3.5, 5.7 Hz), 7.98 (m, 4H), 7.93 (dd, 2H, J = 3.3, 5.3 Hz), 7.55 (dd, 2H, J = 3.3, 5.3 Hz), 6.23 (s, 4H), 5.05 (broad t, 4H, J = 5.1 Hz), 3.38 (H_2O), 2.93 (broad t, 2H, J = 6.1 Hz); ^{13}C NMR (DMSO-d_6) δ 134.7, 133.2, 132.9, 131.8, 131.1, 130.1, 129.2, 129.1, 114.6, 114.4, 50.6, 44.3, 29.4; IR (KBr) 2940, 1580, 1430, 1350, 1250, 1090, 1010, 890, 790, 760 cm^{-1}. Anal. Calcd for $C_{25}H_{22}N_4Br_2$ – 2.5 H_2O: C, 51.02; H, 4.59; N, 9.52. Found: C, 51.38; H, 4.65; N, 9.95.

1,1'-(α,α'-*o*-Xylyl)-3,3'-tetramethylene-2,2'-bibenzimidazolium Dibromide (11c). A mixture of **10** (0.53 g, 1.72 mmol) and 1,3-dibromobutane (2.5 g, 12 mmol) was heated at 120 °C for 12 h. After cooling, $CHCl_3$ (10 mL) was added and the reaction mixture was filtered to provide **11c** as a pale yellow solid (0.53 g, 56%) which was recrystallized from ethanol–water, mp > 300 °C: ^1H NMR (DMSO-d_6) δ 8.47 (dd, 2H, J = 3.1, 6.4 Hz), 8.42 (dd, 2H, J = 3.2, 6.4 Hz), 7.98 (m, 6H), 7.58 (dd, 2H, J = 3.4, 5.2 Hz), 6.06 (AB quartet, 4H), 5.25 (m, 2H), 4.79 (m, 2H), 3.38 (H_2O), 2.38 (m, 2H), 2.03 (m, 2H); ^{13}C NMR (DMSO-d_6) δ 133.8, 133.7, 133.5, 130.9, 130.8, 129.9, 129.1, 128.9, 114.6, 114.4, 49.6, 47.0, 26.0; IR (KBr) 2940, 1580, 1440, 1370, 1250, 1090, 1010, 890, 790, 760 cm^{-1}. Anal. Calcd for $C_{26}H_{24}N_4Br_2$ – 1.5 H_2O: C, 53.88; H, 4.66; N, 9.67. Found: C, 53.82; H, 4.71; N, 9.28.

1,3-Bis(*N*-benzimidazolyl)propane (13a). In a 100 mL round bottom flask, 25% aqueous NaOH (15 mL) was added to a mixture of benzimidazole (5.0 g, 42 mmol) and 1,3-dibromopropane (4.2 g, 21 mmol) in CH_3CN (30 mL). After the mixture was stirred for 40 h at room temperature, the solvent was evaporated. The residue was dissolved in $CHCl_3$ (100 mL), and filtration gave a clear $CHCl_3$ solution. The solution was evaporated, and the residue was recrystallized from ethyl acetate–hexane to provide **13a** as a white solid (4.7 g, 81%), mp 120–1 °C: ^1H NMR ($CDCl_3$) δ 7.85 (s, 2H), 7.84 (d, 2H, J = 7.9 Hz), 7.29 (m, 6H), 4.17 (t, 4H, J = 6.9 Hz), 2.52 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 143.9, 142.6, 133.3, 123.3, 122.5, 120.7, 109.3, 41.8, 29.4; IR (KBr) 3050, 2930, 1600, 1480, 1430, 1275, 1195, 1100, 890, 740 cm^{-1}.

1,4-Bis(*N*-benzimidazolyl)butane (13b). A solution of 25% aqueous NaOH (30 mL) was added to a solution of benzimidazole (10.0 g, 84 mmol) and 1,4-dibromobutane (9.1 g, 42 mmol) in CH_3CN (60 mL). The mixture was stirred for 24 h at room temperature, and the solvent was evaporated. The residue was dissolved in $CHCl_3$ (150 mL) and dried with $MgSO_4$. Filtration gave a clear solution. After hexane (100 mL) was added, the solution was cooled at –20 °C to provide crystals of **13b** (10.2 g, 83%), mp 157–8 °C: ^1H NMR ($CDCl_3$) δ 7.85 (s, 2H), 7.84 (d, 2H, J = 7.9 Hz), 7.29 (m, 6H), 4.17 (t, 4H, J = 6.9 Hz), 1.91 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 143.7, 142.6, 133.4, 123.0, 122.2, 120.5, 109.4, 44.4, 27.1; IR (KBr) 3035,

2925, 1600, 1470, 1440, 1420, 1375, 1280, 1245, 1160, 1100, 900, 730 cm^{-1}.

1,1′:3,3′-Bis(trimethylene)bis(benzimidazolium) Dibromide (14a) and the Corresponding Tetramer (15). In a 1 L round bottom flask, a mixture of **13a** (2.0 g, 7.25 mmol) and 1,3-dibromopropane (1.46 g, 7.25 mmol) in CH_3CN (700 mL) was heated at reflux for 5 days. The solution was evaporated, and the residual white solid was dissolved in hot ethanol (95%, 500 mL). The solution was cooled to −20 °C for 24 h, and a white solid precipitated. Filtration provided the *N*-trimethylene-*N*′-benzimidazolium tetramer **15** (0.18 g, 5%), mp > 300 °C: ^1H NMR (DMSO-d_6) δ 10.52 (s, 4H), 8.21 (m, 8H), 7.77 (m, 8H), 4.73 (t, 16H, J = 6.3 Hz), 3.40 (s, H_2O), 2.70 (m, 8H); ^{13}C NMR (DMSO-d_6) δ 142.5, 131.3, 126.7, 113.7, 43.7, 28.0; IR (KBr) 3010, 1605, 1550, 1440, 1350, 1220, 1110, 900, 750 cm^{-1}. The filtrate was concentrated to 100 mL and kept at room temperature for 24 h. Precipitation occurred, and filtration provided **14a** as a pale white solid (0.83 g, 24%), mp > 300 °C: ^1H NMR (DMSO-d_6) δ 10.12 (s, 2H), 7.77 (m, 4H), 7.27 (m, 4H), 5.00 (t, 4H, J = 12.0 Hz), 4.88 (d, 4H, J = 14.7 Hz), 2.86 (m, 2H), 2.45 (m, 2H), 3.40 (H_2O); ^{13}C NMR (DMSO-d_6) δ 142.9, 129.9, 126.7, 113.7, 46.8, 23.4; IR (KBr) 3030, 1600, 1550, 1440, 1415, 1390, 1220, 1100, 900, 750 cm^{-1}.

1,1′:3,3′-Bis(tetramethylene)bis(benzimidazolium) Dibromide (14b). In a 1 L round bottom flask was heated a mixture of **13b** (1.18 g, 4.07 mmol) and 1,4-dibromobutane (0.88 g, 4.07 mmol) in CH_3CN (600 mL) at reflux for 5 days. After cooling, the mixture was filtered and **14b** was obtained as a white solid (0.22 g, 11%), mp > 300 °C: ^1H NMR (DMSO-d_6) δ 10.37 (s, 2H), 8.12 (m, 4H), 7.67 (m, 4H), 4.65 (broad s, 8H), 3.38 (s, H_2O), 2.06 (broad s, 8H); ^{13}C NMR (DMSO-d_6) δ 142.1, 131.1, 126.7, 113.7, 45.8, 25.0; IR (KBr) 2950, 1600, 1550, 1440, 1425, 1340, 1220, 1100, 900, 750 cm^{-1}.

α,α′-Di(*N*-benzimidazolyl)-*o*-xylene (16). A mixture of benzimidazole (3.0 g, 25 mmol), α,α′-dibromo-*o*-xylene (3.6 g, 12.7 mmol), and KOH (1.6 g, 25 mmol) in DMF (50 mL) and H_2O (20 mL) was stirred at room temperature for 6 h. H_2O (50 mL) was added to the reaction mixture, and stirring was continued for another 1 h. The mixture was filtered to provide material which was recrystallized from ethyl acetate−hexane (1:1) to provide **16** as a pale yellow solid (2.39 g, 57%), mp 174−6 °C: ^1H NMR ($CDCl_3$) δ 7.85 (d, 2H, J = 7.8 Hz), 7.78 (s, 2H), 7.26−7.40 (m, 6H), 7.14 (d, 2H, J = 7.4 Hz), 7.07 (m, 2H), 5.29 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 144.0, 142.8, 133.8, 133.0, 129.4, 129.1, 123.4, 122.6, 120.7, 109.7, 46.3; IR (KBr) 3030, 2940, 1580, 1460, 1420, 1320, 1240, 1170, 1090, 890, 740 cm^{-1}. Anal. Calcd for $C_{22}H_{18}N_4$: C, 78.11; H, 5.32; N, 16.57. Found: C, 77.67; H, 5.42; N, 16.41.

1,1′-(α,α′-*o*-Xylyl)-3,3′-trimethylenebis(benzimidazolium) Dibromide (17a). A mixture of **16** (0.8 g, 2.4 mmol) and 1,3-dibromopropane (0.6 g, 2.9 mmol) in CH_3CN (300 mL) was heated at reflux for 4 days. The solution was concentrated to 50 mL. After cooling, the mixture was filtered to provide **17** as a white solid (0.46 g, 35%) which was recrystallized from ethanol (95%), mp > 300 °C: ^1H NMR (DMSO-d_6) δ 8.88 (s, 2H), 7.84 (m, 6H), 7.73 (d, 2H, J = 8.2 Hz), 7.37 (t, 2H, J = 8.0 Hz), 7.28 (t, 2H, J = 8.0 Hz), 6.10 (d, 2H, J = 14.6 Hz), 5.48 (d, 2H, J = 14.6 Hz), 4.78 (m, 4H), 3.38 (H_2O), 2.91 (m, 1H), 2.37 (m, 1H); ^{13}C NMR (DMSO-d_6) δ 141.7, 134.5, 131.9, 131.5, 130.3, 129.2, 127.0, 126.9, 113.9, 113.2, 48.4, 46.8, 23.1; IR (KBr) 2910, 1590, 1450, 1420, 1210, 1120, 920, 770 cm^{-1}. Anal. Calcd for $C_{25}H_{24}N_4Br_2 - 1.5\ H_2O$: C, 52.91; H, 4.76; N, 9.88. Found: C, 52.67; H, 4.94; N, 9.85.

1,1′-(α,α′-*o*-Xylyl)-3,3′-tetramethylenebis(benzimidazolium) Dibromide (17b). A mixture of **16** (0.3 g, 0.89 mmol) and 1,4-dibromobutane (2.5 g, 12 mmol) in CH_3CN (200 mL) was heated at reflux for 24 h. The solution was concentrated to 5 mL. After cooling, filtration provided **17b** as a white solid (0.09 g, 20%) which was recrystallized from ethanol (95%), mp > 300 °C: ^1H NMR (DMSO-d_6) δ 8.97 (s, 2H), 7.98 (d, 2H, J = 8.3 Hz), 7.90 (m, 2H), 7.80 (m, 2H), 7.68 (d, 2H, J = 8.3 Hz), 7.41 (t, 2H, J = 8.0 Hz), 7.30 (t, 2H, J = 8.0 Hz), 5.87 (broad s, 4H), 4.31 (broad s, 4H), 3.38 (H_2O), 2.05 (broad s, 4H); ^{13}C NMR (DMSO-d_6) δ 140.9, 134.3, 132.0, 131.3, 130.1, 130.0, 127.1, 127.0, 113.4, 112.9, 48.3, 47.5, 26.5; IR (KBr) 2900, 1540, 1440, 1400, 1170, 1090, 880, 740 cm^{-1}. Anal. Calcd for $C_{26}H_{26}N_4Br_2 - H_2O$: C, 54.55; H, 4.90; N, 9.79. Found: C, 54.51; H, 4.88; N, 9.30.

1,1′:3,3′-Bis(α,α′-*o*-Xylyl)bis(benzimidazolium) Dibromide (18). A mixture of **16** (1.0 g, 2.96 mmol) and α,α′-dibromo-*o*-xylene (0.94 g, 3.55 mmol) in CH_3CN (200 mL) was heated at reflux for 12 h. After cooling, the mixture was filtered to give a gray solid. The solid was dissolved in water and filtered. The filtrate was evaporated to provide **18** as a white solid (0.85 g, 50%) which was recrystallized from ethanol (95%), mp > 300 °C: ^1H NMR (DMSO-d_6) (room temperature) δ 9.11, (s, 2H), 8.08 (broad s, 4H), 7.83 (broad s, 4H), 7.16 (broad s, 4H), 7.50−6.80 (broad s, 4H), 6.21 (broad s, 4H), 5.61 (broad s, 4H), 3.38 (H_2O); ^{13}C NMR (DMSO-d_6) δ 141.4, 134.7, 132.4, 131.2, 129.9, 126.6, 113.6, 49.0 (broad); IR (KBr) 2940, 1540, 1440, 1410, 1300, 1170, 1090, 880, 730 cm^{-1}. The same compound gave a more resolved ^1H NMR at 120 °C: ^1H NMR (DMSO-d_6) δ 9.21 (s, 2H), 8.04 (s, 4H), 7.78 (s, 4H), 7.36 (s, 4H), 7.33 (s, 4H), 5.94 (s, 8H), 2.92 (s, H_2O). Anal. Calcd for $C_{30}H_{26}N_4Br_2 - 1.5\ H_2O$: C, 57.23; H, 4.61; N, 8.90. Found: C, 57.46; H, 4.65; N, 9.03.

1,1′:3,3′-Bis(trimethylene)-2,2′-bibenzimidazolinylidene (19a). Method A. A potential of −1.10 V was applied to **9a** (100 mg, 0.13 mmol) in CH_3CN (5 mL) with 0.1 M TBAP contained in the cathode compartment of the bulk electrolysis cell. Initially, an intense red color appeared which indicated formation of the radical cation. As the reduction proceeded, the red color slowly faded. After the current had decreased to zero, a yellow solution with a small amount of yellow precipitate was obtained. The mixture was transferred to a Schlenk flask (25 mL) and cooled to −20 °C. Filtration provided yellow crystals of **19a** as a highly air-sensitive material (25 mg, 62%): ^1H NMR (C_6D_6) δ 6.74 (m, 4H), 6.26 (m, 4H), 2.98 (t, 8H, J = 5.6 Hz), 1.36 (m, 4H) ^{13}C NMR (C_6D_6) δ 140.5, 128.4, 119.5, 105.6, 48.7, 28.7; IR (Nujol) 2960, 2925, 1595, 1495, 1450, 1260, 1100, 1030, 800, 745 cm^{-1}.

Method B. A mixture of **14a** (1.0 g, 2.1 mmol) and NaH (0.35 g, 14.6 mmol) in CH_3CN (40 mL) was stirred at room temperature under Ar for 3 h. The reaction mixture was filtered through Celite under Ar to give a yellow solution. The solution was cooled to −30 °C for several days, and a yellow crystalline solid precipitated. More precipitate was obtained by the addition of diethyl ether. Filtration provided **19a** as a yellow material (0.45 g, 68%) which showed spectral properties identical to the material obtained from method A.

1,1′:3,3′-Bis(tetramethylene)bibenzimidazolinylidene (19b). A potential of −1.40 V was applied to **9b** (90 mg, 0.12 mmol) in CH_3CN (5 mL) with 0.1 M TBAP contained in the cathode compartment of the bulk electrolysis cell. Initially, an intense purple color appeared, indicating formation of the radical cation. Upon further reduction, the purple color slowly faded. After the current had decreased to zero, an orange solution with a small amount of orange precipitate was obtained. The mixture was transferred to a Schlenk flask and cooled to −20 °C. Filtration provided orange air-sensitive crystals (15 mg, 43%) which exhibited two sets of NMR signals. The major component showed the following spectral properties: ^1H NMR (C_6D_6) δ 6.76 (m, 4H), 6.23 (m, 4H), 3.23 (broad s, 8H), 1.36 (m, 8H); ^{13}C NMR (C_6D_6) δ 142.3, 120.0, 105.3, 50.2, 29.5 (one signal was not observed); IR (Nujol) 2920, 1602, 1500, 1385, 1310, 1240, 1150, 810, 770 cm^{-1}. The minor component showed the following spectral properties: ^1H NMR (C_6D_6) δ 6.83 (m, 4H), 6.29 (m, 4H), 3.16 (m, 4H), 2.80 (m, 4H), 1.51 (m, 4H), 1.30 (m, 4H). Due to their air sensitivity, these compounds were not separated.

1,1′:3,3′-Bis(trimethylene)bis(benzimidazolone) (20a). Method A. In a 50 mL round bottom flask was dissolved **9a** (50 mg, 0.083 mmol) in CH_3CN (10 mL). Tetrakis(dimethylamino)ethylene (TDAE, 0.1 mL, 0.4 mmol) was added dropwise, and the solution immediately turned red. After the solution was stirred in air for 3 h, the red color disappeared and the solution became pale white. The solution was evaporated, and the residue was dissolved in toluene (10 mL) and refluxed for 30 min. The insoluble material was removed by filtration, and the filtrate was evaporated to provide a pale yellow solid which was recrystallized from $CHCl_3$ to give **20a** as pale yellow crystals (25 mg, 90%), mp > 300 °C: ^1H NMR

($CDCl_3$) δ 6.61 (m, 8H), 4.71 (dt, 4H, J = 1.9, 14.0 Hz), 3.78 (dt, 4H, J = 3.3, 15.0 Hz), 2.95 (m, 2H, J = 2.9, 15.5 Hz), 1.86 (dt, 2H, J = 1.9, 15.4 Hz), 1.71 (s, H_2O); ^{13}C NMR ($CDCl_3$) δ 153.2, 128.3, 120.7, 108.0, 40.2, 21.5; IR (KBr) 3030, 2890, 1700, 1580, 1470, 1380, 1285, 1170, 875, 740 cm^{-1}.

Method B. A mixture of **14a** (0.1 g, 0.2 mmol) and NaH (0.10 g, 4.2 mmol) in CH_3CN (20 mL) was stirred for 1 h. The mixture was heated to reflux and filtered hot. The filtrate was concentrated to obtain a yellow solid which was recrystallized from $CHCl_3$–CH_3OH to provide pale yellow crystals (54 mg, 73%) having spectral properties identical to the material prepared under method A above.

Single Crystal X-ray Diffraction Analysis of 20a. A pale gold irregular fragment having approximate dimensions 0.60 × 0.55 × 0.55 mm was mounted in a random orientation on a Nicolet R3m/V automatic diffractometer. The radiation used was Mo Kα (λ = 0.710 73 Å) monochromatized by a highly ordered graphite crystal. The crystal data for **20a** are as follows: orthorhombic; space group *Pbca* with a = 18.081(6) Å, b = 19.234(5) Å, c = 19.501(5) Å, V = 6782 Å^3, and Z = 16. The molecular formula is $C_{20}H_{20}N_4O_2$, the molecular weight is 348.44, and the calculated density is 1.36 g/cm^3. Intensities were measured using the ω scan technique, with the scan rate depending on the count obtained in rapid prescans of each reflection. Two standard reflections were monitored after every 2 h or every 100 data collected, and these showed no significant variation. During data reduction Lorentz and polarization corrections were applied; however, no correction for absorption was made due to the very small absorption coefficient.

The structure was solved by the SHELXTL direct methods program, which revealed the positions of most of the nonhydrogen atoms in the asymmetric unit, consisting of two independent molecules. Remaining atoms were found in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were entered in ideal calculated positions and constrained to riding motion, with a single variable isotropic temperature factor for all of them. One of the carbon atoms was found to be disordered over two different positions, and based on analysis of the isotropic temperature factors involved, the occupancy factors assigned were 55%:45% for C39:C39'. The disordered atoms did not refine well, and eventually distance constraints had to be applied using values found for the equivalent location in the other independent molecule. Due to the disorder, no attempt was made to include hydrogens on C38, C39, or C40. After all shift/esd ratios were less than 0.1, convergence was reached at R = 0.046, R_w = 0.036.[16]

1,1':3,3'-Bis(tetramethylene)bis(benzimidazolone) (20b). Method A. TDAE (0.1 mL, 0.4 mmol) was added to a solution of **9b** (60 mg, 0.085 mmol) and the solution immediately turned purple. After the solution was stirred in air for 2 h, the color faded and water (30 mL) was added. The mixture was filtered to provide a pale white solid which was recrystallized from $CHCl_3$ to give **20b** as colorless crystals (28 mg, 88%), mp > 300 °C: ^1H NMR ($CDCl_3$) δ 6.96 (m, 4H), 6.84 (m, 4H), 3.70 (broad s, 8H), 1.91 (broad s, 8H), 1.70 (s, H_2O); ^{13}C NMR ($CDCl_3$) δ 153.2, 130.0, 120.8, 107.0, 40.7, 24.9; IR (KBr) 3040, 2910, 1700, 1590, 1470, 1430, 1380, 1180, 890, 750 cm^{-1}.

Method B. A mixture of **14b** (0.1 g, 0.2 mmol) and NaH (0.1 g, 4.2 mmol) in CH_3CN (10 mL) was stirred at room temperature in air for 1 h, and H_2O (10 mL) was added. The mixture was filtered to give a solid which was recrystallized from $CHCl_3$/CH_3OH to provide colorless crystals (40 mg, 54%) showing spectral properties identical to the material prepared under method A above.

Single Crystal X-ray Diffraction Analysis of 20b. A pale yellow block having approximate dimensions 0.40 × 0.48 × 0.50 mm was mounted in a random orientation on a Nicolet R3m/V automatic diffractometer. The sample was placed in a stream of dry nitrogen gas at −50 °C. The radiation used was Mo Kα (λ = 0.710 73 Å) monochromatized by a highly ordered graphite crystal. The crystal data for **20b** are as follows: monoclinic; space group $P2_1/n$ with a = 21.356(4) Å, b = 7.536(1) Å, c = 8.673(2) Å, β = 97.00(1)°, V = 1385 Å^3, and Z = 2. The molecular formula is $C_{22}H_{24}N_4O_2$ − 2$CHCl_3$, molecular weight is 615.24, and the calculated density is 1.47 g/mL. Intensities were measured using the ω scan technique, with the scan rate depending on the count obtained in rapid prescans of each reflection. Two standard reflections were monitored after every 2 h or every 100 data collected, and these showed no significant variation. During data reduction Lorentz and polarization corrections were applied; however, no correction for absorption was made due to the small absorption coefficient.

The structure was solved by the SHELXTL direct methods program, which revealed the positions of all of the nonhydrogen atoms in the asymmetric unit, consisting of one-half molecule situated about an inversion center and one molecule of chloroform solvent in a general position. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were entered in ideal calculated positions and constrained to riding motion, with a single variable isotropic temperature factor for all of them. After all shift/esd ratios were less than 0.1, convergence was reached at R = 0.039, R_w = 0.032.[16]

Generation of the Radical Cation of 1,1':3,3'-Bis(trimethylene)-2,2'-bibenzimidazolium Dihexfluorophosphate (21). Method A. A solution of **9a** (10 mg) in 0.1 M TBAP/dry CH_3CN (5 mL) was stirred continuously in the cathode compartment of the bulk electrolysis cell. The anode compartment was separated from the cathode by a porous glass frit and filled with 0.1 M TBAP in dry CH_3CN (2 mL). A negative potential (E_0 = −0.60 V) was applied, and the yellow solution instantly turned red. After 20 min of electrolysis, the original current of 10 mA had dropped to 3 mA. The deep red solution (1 mL) was transferred into a Schlenk ESR tube and analyzed. At room temperature the solution showed a strong ESR signal with g = 2.0034.

Method B. A mixture of **19a** (97 mg, 0.16 mmol) and **9a** (51 mg, 0.16 mmol) was stirred in CH_3CN under Ar until all the solid was dissolved and a deep red color appeared. The solution showed a strong ESR signal identical to the one obtained in method A. The solution was evaporated and a highly air-sensitive reddish black solid was obtained (110 mg, 74%).

1,1':3,3'-Bis(α,α'-*o*-Xylyl)bis(benzimidazolone) (22). A mixture of **18** (0.27 g, 0.45 mmol) and 1,1',3,3'-tetramethylguanidine (0.5 mL) in CH_3CN (5 mL) was stirred at room temperature in air for 3 h. The white precipitate was filtered, washed with water, and recrystallized from $CHCl_3$ to provide **22** as a colorless solid (0.14 g, 65%), mp > 300 °C: ^1H NMR ($CDCl_3$) δ 7.70 (m, 4H, J = 3.9, 4.9 Hz), 7.54 (m, 4H, J = 3.9, 4.9 Hz), 6.16 (m, 4H, J = 3.2, 5.7 Hz), 5.85 (broad s overlapping m, 8H), 4.55 (d, 4H, J = 14.5 Hz), 1.68 (s, H_2O); ^{13}C NMR ($CDCl_3$) δ 153.0, 135.7, 133.9, 129.2, 128.8, 120.1, 108.7, 46.4; IR (KBr) 3030, 2920, 1700, 1460, 1390, 1340, 1100, 1020, 890, 780, 730 cm^{-1}.

Single Crystal X-ray Diffraction Analysis of 22. A colorless block having approximate dimensions 0.60 × 0.30 × 0.20 mm was mounted in a random orientation on a Nicolet R3m/V automatic diffractometer. The sample was placed in a stream of dry nitrogen gas at −50 °C, and the radiation used was Mo Kα (λ = 0.710 73 Å) monochromatized by a highly ordered graphite crystal. The crystal data for **22** are as follows: monoclinic; space group $I2/c$ with a = 14.771(3) Å, b = 11.756(2), c = 14.722(3) Å, β = 118.03(1)°, V = 2257 Å^3, and Z = 4. The molecular formula is $C_{30}H_{24}N_4O_2$, the molecular weight is 472.58, and the calculated density is 1.39 g/mL. Intensities were measured using the ω scan technique, with the scan rate depending on the count obtained in rapid prescans of each reflection. Two standard reflections were monitored after every 2 h or every 100 data collected, and these showed no significant variation. During data reduction Lorentz and polarization corrections were applied; however, no cor-

(16) The author has deposited atomic coordinates for **20a,b**, **22**, and **26** structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

rection for absorption was made due to the very small absorption coefficient.

The structure was solved by the SHELXTL direct methods program, which revealed the positions of all of the non-hydrogen atoms in the asymmetric unit, consisting of one-half molecule situated about a 2-fold axis. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were entered in ideal calculated positions and constrained to riding motion, with a single variable isotropic temperature factor for all of them. After all shift/esd ratios were less than 0.1, convergence was reached at $R = 0.039$, $R_w = 0.037$.[16]

1,1′-(α,α′-*o*-Xylyl)-3,3′-dimethylenebis(benzimidazolone) (23a). A solution of **11a** (0.20 g, 0.38 mmol) in CH_3CN (10 mL) upon the addition of TDAE (0.26 g, 1.29 mmol) became immediately red. After being stirred in air at room temperature for 3 h, the mixture became pale yellow and a precipitate appeared. The solvent was evaporated; the residue was washed twice with water and recrystallized from $CHCl_3/CH_3OH$ to provide **23a** as a pale white solid (70 mg, 50%), mp > 300 °C: ^{1}H NMR ($CDCl_3$) δ 7.72 (dd, 2H, J = 3.6, 5.2 Hz), 7.53 (dd, 2H), 6.49 (d, 4H, J = 4.3 Hz), 6.31 (m, 2H), 6.01 (d, 2H, J = 8.0 Hz), 5.75 (d, 2H, J = 14.5 Hz), 4.70 (m, 2H), 4.56 (d, 2H, J = 14.5 Hz), 3.77 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 154.3, 135.5, 134.5, 129.9, 129.2, 129.1, 120.7, 120.6, 108.9 (2), 46.5, 30.1; MS (EI) 397 $(M + H)^+$, 369, 361; IR (KBr) 2940, 1705, 1480, 1420, 1370, 1100, 880, 720 cm^{-1}. Anal. Calcd for $C_{24}H_{20}N_4O_2$: C, 72.73; H, 5.05; N, 14.14. Found: C, 72.54; H, 5.25; N, 14.34.

1,1′-(α,α′-*o*-Xylyl)-3,3′-trimethylenebis(benzimidazolone) (23b). Method A. TDAE (0.32 g, 1.6 mmol) was added to a suspension of **11b** (0.10 g, 0.20 mmol) in CH_3CN (10 mL), and the mixture immediately became red. After being stirred in air for 3 h, the mixture turned pale yellow and a precipitate appeared. The solvent was evaporated, and the residue was washed with water twice to provide **23b** as a white solid (40 mg, 50%), mp > 300 °C: ^{1}H NMR ($CDCl_3$) δ 7.72 (dd, 2H, J = 3.6, 4.5 Hz), 7.55 (dd, 2H), 6.52 (overlapping t and d, 4H), 6.30 (t, 2H, J = 7.5 Hz), 5.91 (d, 2H, J = 7.9 Hz), 5.82 (d, 2H, J = 12.3 Hz), 4.70 (t, 2H, J = 13.8 Hz), 4.53 (d, 2H, J = 12.3 Hz), 3.77 (d, 2H, J = 14.8 Hz), 2.96 (m, 1H), 1.91 (d, 1H, J = 15.8 Hz), 1.68 (s, H_2O); ^{13}C NMR ($CDCl_3$) δ 153.2, 135.8, 134.0, 129.3, 128.9, 128.3, 120.5, 120.2, 108.8, 107.9, 46.5, 40.2, 21.6; IR (KBr) 2930, 1700, 1470, 1400, 1360, 1090, 890, 730 cm^{-1}.

Method B. To a solution of **17a** (0.10 g, 0.19 mmol) in CH_3CN (10 mL) was added NaH (0.50 g, 20 mmol). The solution immediately turned yellow. After being stirred in air for 1 h, the mixture became white and a precipitate appeared. Filtration provided a white solid which was washed with water and dissolved in $CHCl_3$. The $CHCl_3$ solution was dried over $MgSO_4$, filtered, and concentrated to yield a white solid (30 mg, 40%) having spectral properties identical to the material prepared under method A above.

1,1′-(α,α′-*o*-Xylyl)-3,3′-tetramethylenebis(benzimidazolone) (23c). Method A. Upon the addition of tetraaminoethylene (TDAE, 0.16 g, 0.8 mmol) a solution of **11c** (0.09 g, 0.16 mmol) in CH_3CN (15 mL) became deep red. After the solution was stirred in air for 2 h, precipitation occurred and the mixture became pale white. The solid was filtered and washed twice with CH_3CN to provide **23c** (40 mg, 59%), mp > 300 °C: ^{1}H NMR ($CDCl_3$) δ 7.71 (m, 2H), 7.57 (m, 2H), 6.45 (m, 4H), 6.30 (broad s, 2H), 5.82 (m, 4H), 4.55 (d, 2H, J = 14.1 Hz), 4.05 (broad m, 2H), 3.46 (broad m, 2H), 2.39 (broad m, 2H), 1.91 (broad m, 2H), 1.68 (s, H_2O); ^{13}C NMR ($CDCl_3$) δ 153.1, 135.7, 133.6, 129.3, 129.1, 128.7, 120.3, 120.2, 109.1, 106.4, 46.4, 42.5, 26.0; IR (KBr) 2940, 1700, 1470, 1390, 1350, 1170, 1100, 890, 730 cm^{-1}. Anal. Calcd for $C_{26}H_{24}N_4O_2 - 0.5$ H_2O: C, 72.06; H, 5.77; N, 12.93. Found: C, 72.54; H, 5.69; N, 12.27.

Method B. NaH (0.5 g, 20 mmol) was added to a solution of **17b** (0.20 g, 0.36 mmol) in CH_3CN (15 mL), and the mixture immediately became yellow. After the mixture was stirred in air for 1 h, a white solid precipitated. Water (10 mL) was added, and the mixture was filtered. The solid was dissolved in $CHCl_3$ and the solution was dried over $MgSO_4$. Evaporation provided a white material (0.07 g, 46%) having spectral properties identical to the material prepared under method A above.

3,3′-Dimethyl-1,1′-tetramethylenebis(benzimidazolium) Diiodide (24a). In a 50 mL round bottom flask was added iodomethane (0.70 g, 4.9 mmol) to a solution of **13b** (0.50 g, 1.7 mmol) in CH_3CN (15 mL), and the mixture was heated at reflux for 6 h. After being cooled to −20 °C, the mixture was filtered and washed twice with CH_3CN to provide **24a** as a white solid (0.80 g, 80%), mp > 300 °C: ^{1}H NMR (DMSO-d_6) δ 9.72 (s, 2H), 8.10 (m, 2H), 8.02 (m, 2H), 7.69 (m, 4H), 4.56 (m, 4H), 4.06 (s, 6H), 1.99 (m, 4H); ^{13}C NMR (DMSO-d_6) (one quaternary carbon is not observed) δ 142.6, 131.8, 130.9, 126.5, 113.6, 113.5, 46.0, 33.4, 25.5; IR (KBr) 3020, 2945, 1600, 1480, 1410, 1320, 1240, 1090, 880, 750 cm^{-1}.

3,3′-Dimethyl-1,1′-(α,α′-*o*-Xylylene)bis(benzimidazolium) Diiodide (24b). In a 100 mL round bottom flask were dissolved **16** (0.5 g, 1.48 mmol) and iodomethane (0.84 g, 6 mmol) in CH_3CN (15 mL). The solution was heated at reflux for 3 h. After cooling, the mixture was filtered and the resulting solid was washed twice with CH_3CN and dried to provide **24b** (0.80 g, 87%), mp 290−3 °C: ^{1}H NMR (DMSO-d_6) δ 9.59 (s, 2H), 8.05 (d, 2H, J = 8.1 Hz), 7.88 (d, 2H, J = 8.2 Hz), 7.71 (t, 3H), 7.64 (t, 3H), 7.43 (m, 2H), 7.25 (m, 2H), 5.98 (s, 4H), 4.05 (s, 6H), 3.38 (s, H_2O); ^{13}C NMR (DMSO-d_6) δ 143.0, 131.94, 131.88, 130.8, 129.4, 129.0, 126.7, 126.6, 113.73, 113.65, 47.4, 33.4; IR (KBr) 2950, 1540, 1430, 1330, 1220, 1100, 890, 740 cm^{-1}. Anal. Calcd for $C_{24}H_{24}N_4I_2$: C, 46.30; H, 3.86; N, 9.00. Found: 47.02; H, 3.99; N, 9.15.

1,1′-Dimethyl-3,3′-tetramethylenebis(benzimidazolone) (25a). A mixture of **24a** (0.15 g, 0.26 mmol) and NaH (0.15 g, 6 mmol) in CH_3CN (20 mL) was stirred at room temperature for 3 h. The reaction mixture was evaporated, and the residue was extracted with ethyl acetate. The ethyl acetate solution was evaporated, and the residue was purified by chromatography on aluminum oxide (10 g) eluting with ethyl acetate−ether to provide **25a** as a pale orange solid (60 mg, 65%), mp > 300 °C: ^{1}H NMR ($CDCl_3$) δ 7.08 (m, 4H), 6.98 (m, 4H), 3.93 (m, 4H), 3.40 (s, 6H), 1.83 (m, 4H), 1.70 (s, H_2O); ^{13}C NMR ($CDCl_3$) δ 154.5, 130.0, 129.2, 121.2, 121.1, 107.6, 107.4, 105.5, 40.6, 27.1, 25.6; IR (KBr) 3040, 2910, 1700, 1585, 1480, 1410, 1380, 1210, 1100, 890, 735 cm^{-1}.

1,1′-(α,α′-*o*-Xylyl)-3,3′-dimethylbis(benzimidazolone) (25b). A mixture of **24b** (0.23 g, 0.37 mmol) with NaH (0.20 g, 8.3 mmol) in CH_3CN (15 mL) was stirred at room temperature in air for 2 h. The mixture was evaporated, and the residue was extracted with $CHCl_3$ (50 mL). The $CHCl_3$ solution was dried over $MgSO_4$ and evaporated to provide **25b** as a pale yellow solid (60 mg, 40%) which was recrystallized from $CH_2Cl_2-CCl_4$, mp 234−7 °C: ^{1}H NMR ($CDCl_3$) δ 7.24−6.95 (m, 10H), 6.79 (d, 2H, J = 7.8 Hz), 5.24 (s, 4H), 3.47 (s, 6H), 1.68 (s, H_2O); ^{13}C NMR ($CDCl_3$) δ 154.5, 133.8, 130.1, 129.2, 128.0, 127.8, 121.5, 121.4, 108.4, 107.5, 42.5, 27.3; IR (KBr) 2890, 1690, 1460, 1410, 1375, 1100, 900, 740 cm^{-1}. Anal. Calcd for $C_{24}H_{22}N_4O_2 - 1/4$ H_2O: C, 71.55; H, 5.59; N, 13.91. Found: C, 71.49; H, 5.70; N, 14.01.

Benzimidazolone Tetramer 26. A mixture of **15** (0.1 g, 0.2 mmol) and NaH (0.1 g, 4 mmol) in CH_3CN (20 mL) was stirred at room temperature in air for 3 h. The mixture was evaporated, and the residue was extracted with $CHCl_3$ to give a brown solution. The solution was refluxed with charcoal for 10 min. After filtration, the solvent was evaporated and the residue washed twice with ether to provide **25** as a pale yellow solid (50 mg, 69%). The solid was recrystallized from CH_2Cl_2/CH_3OH to give white crystals which were subjected to X-ray diffraction analysis, mp > 300 °C: ^{1}H NMR ($CDCl_3$) δ 6.79 (m, 8H), 6.71 (m, 8H), 3.75 (t, 16H, J = 7.1 Hz), 2.52 (m, 8H), 1.70 (s, H_2O); ^{13}C NMR ($CDCl_3$) δ 153.5, 128.7, 121.0, 107.5, 38.6, 25.5; IR (KBr) 3030, 2920, 1700, 1590, 1480, 1430, 1380, 1180, 900, 740 cm^{-1}.

Single Crystal X-ray Diffraction Analysis of 26. A pale yellow rectangular column having approximate dimensions 0.20 × 0.25 × 0.60 mm was mounted in a random orientation on a Nicolet R3m/V automatic diffractometer. The sample was placed in a stream of dry nitrogen gas at −50 °C. The radiation used was Mo Kα (λ = 0.710 73 Å) monochromatized

by a highly ordered graphite crystal. The crystal data for **26** are as follows: monoclinic; space group $P2_1/c$ with a = 11.316(2) Å, b = 33.892(6) Å, c = 10.509(1) Å, β = 110.24(1)°, V = 3782 Å^3, and Z = 4. The molecular formula is $C_{40}H_{40}N_8O_4 - CH_3OH$, molecular weight is 728.93, and the calculated density is 1.28 g/mL. Intensities were measured using the ω scan technique, with the scan rate depending on the count obtained in rapid prescans of each reflection. Two standard reflections were monitored after every 2 h or every 100 data collected, and these showed no significant change. During data reduction Lorentz and polarization corrections were applied; however, no correction for absorption was made due to the small absorption coefficient.

The structure was solved by the SHELXTL direct methods program, which revealed the positions of most of the atoms in the molecule. Remaining atoms were located in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were entered in ideal calculated positions and constrained to riding motion, with a single variable isotropic temperature factor for all of them. A very diffuse area of disordered solvent was located, which is presumed to be methanol. This was treated by introducing C or O atoms at each of the seven sites having the largest peaks in a difference map, and refining them independently with occupancy factors of about 30%. After all shift/esd ratios were less than 0.1 (except in the disordered solvent), convergence was reached at R = 0.057, R_w = 0.046.[16]

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **10**, **13a,b**, **14a,b**, **15**, **19a,b**, **20a,b**, **22**, **23b,c**, **24a**, **25a**, and **26** (20 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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