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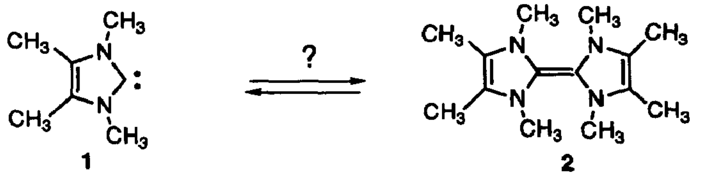
Bridged Bibenzimidazolium Salts and Their Conversion to Ureaphanes

Zhiqiang Shi and Randolph P. Thummel*

Department of Chemistry, University of Houston, Houston, Texas 77204-5641

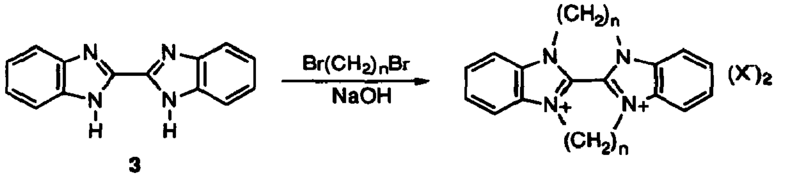
Abstract: The reduction of N,N'-polymethylene bridged 2,2'-bibenzimidazolium salts with *tetrakis*(dimethylamino)ethylene in air provides ureaphanes whose conformations are dependent upon the length of the bridging chain.

Arduengo and coworkers have elegantly demonstrated the unusual stability of nucleophilic carbenes derived from the imidazole nucleus.[1] These species (1) may be generated from the corresponding imidazolium salts by simple deprotonation and appear to be reluctant to dimerize to tetraazafulvalenes. We have previously examined the chemistry of N,N'-*bis*-annelated analogues of **2** which were generated by reduction of the corresponding biimidazolium salts.[2] These species were also unstable and could not be isolated.



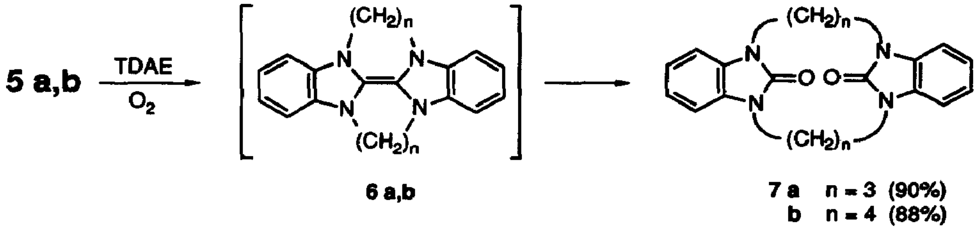
Benzo-fusion raises the reduction potentials of imidazolium salts which should render species similar to **2** more stable.[3] In this report we describe the preparation of N,N'-*bis*-annelated 2,2'-bibenzimidazolium salts and the consequences of their reduction.

Treatment of 2,2'-bibenzimidazole (3)[4] with excess 1,3-dibromopropane or 1,4-dibromobutane and recrystallization of the crude product from methanol results in moderate yields of the N,N'-*bis*-annelated salts **4a,b**.[3] Silver hexafluorophosphate converts these salts into their more soluble hexafluorophosphates.



4a n = 3, X = Br (40%)
b n = 4, X = Br (30%)
5a n = 3, X = PF$_6$ (85%)
b n = 4, X = PF$_6$ (90%)

A convenient reducing agent for these salts is *tetrakis*(dimethylamino)ethylene (TDAE). When an acetonitrile solution of **5a** or **5b** is treated excess TDAE, the solution immediately turns red but becomes colorless after stirring for 3 hours in the presence of air. Subsequent workup provides a white or pale yellow solid which at first we suspected might be a *bis*-carbene. Closer examination of the ^{13}C NMR evidenced a peak at 153.2 ppm which is more typical for the C=O of a urea. The IR of both compounds also showed a strong band in the region of 1650-1660 cm^{-1}.



Although the ^{13}C NMR spectra of **7a** and **7b** were very similar,[5] their ^{1}H NMR's were quite different. The aliphatic region of **7a** showed four well resolved multiplets at 4.71 (4H), 3.77 (4H), 2.95 (2H), and 1.87 (2H) ppm while **7b** showed only two broad singlets at 3.70 (8H) and 1.83 (8H) ppm. In the aromatic region, **7a** showed an eight proton multiplet at 6.61 ppm while **7b** gave two four proton multiplets at 6.96 and 6.84 ppm. From this data we conjectured that **7a** was conformationally rigid in a *syn*-conformation which would account for shielding of its aromatic protons, while **7b** was conformationally mobile in an *anti*-conformation. Furthermore, cooling of **7b** to -10° C caused the singlet at 3.70 ppm to decoalesce into two signals while further cooling to -40° C caused the singlet at 1.83 ppm to decoalesce into two signals. For other bridged biaryls we have previously noted that the bridge methylenes may show different coalescence temperatures.[6] On the other hand, warming of **7a** to 200° C did not appreciably alter its NMR spectrum, indicating that the *syn*-conformation was quite stable.

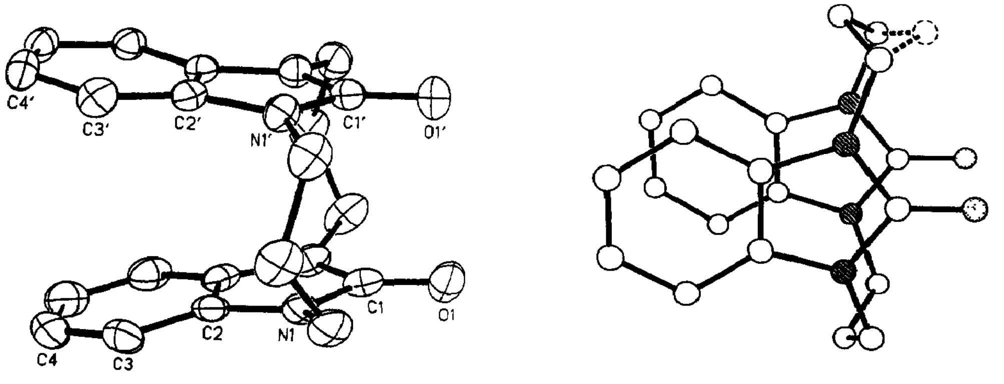


Figure 1. X-ray structure of **7a** (side and top view).

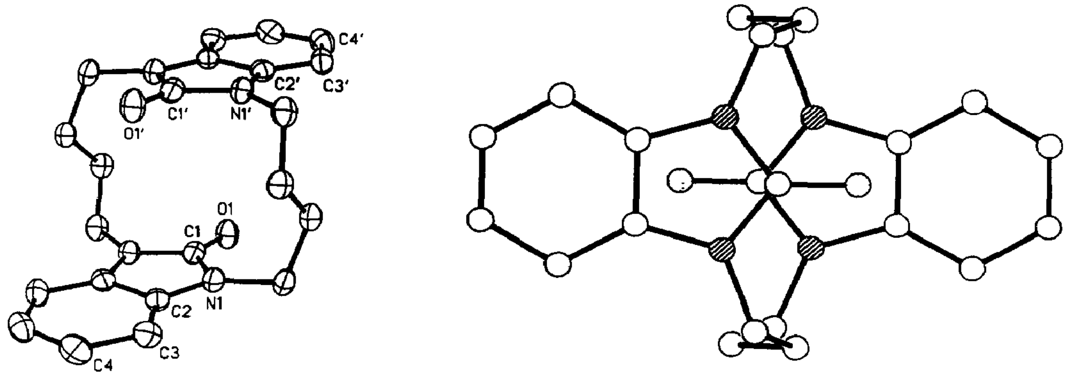


Figure 2. X-ray structure of **7b** (side and top view).

Our NMR hypotheses were borne out by single crystal x-ray analyses which showed the expected conformations for **7a** and **7b**, as illustrated in figures 1 and 2. The two benzimidazolone rings of **7a** are nearly parallel to one another, their planes forming an angle of only 19°. There is some disorder in the trimethylene bridge with the central -CH_2- preferring to be *anti* to the C=O group. Molecular mechanics calculations[7] are in reasonable agreement with the measured structures and provide total energies which tell us that the *anti* -conformer is more stable with **7a** showing a considerably larger energy difference between the two possible conformers (see table 1).

Table 1. Structural Characteristics and Minimized Energies of Ureaphanes **7a** and **7b**.[7]

	7a		**7b**	
	X-ray	MMX *(syn)*	X-ray	MMX*(anti)*
O_1-$O_{1'}$	2.95 Å	2.71 Å	4.98 Å	4.38 Å
C_1-$C_{1'}$	3.02	2.90	4.09	4.05
N_1-$N_{1'}$	3.09	3.00	4.24	4.68
C_2-$C_{2'}$	3.40	3.43		
C_3-$C_{3'}$	3.78	3.80		
C_4-$C_{4'}$	4.16	4.17		
Energy *(syn)*		30.47 kcal/mole[a]		29.57 kcal/mole
Energy *(anti)*		22.84		26.51

(a) Three trimethylene bridge conformations were possible with one or both central methylenes oriented *syn* or *anti* to the carbonyl. Data is given for the minimum energy (*anti, anti*) conformer.

It appears that **7a,b** are formed *via* a dioxetane derived from the addition of oxygen to **6a,b**. Tetramethylene bridges in **7b** allow rapid, irreversible conversion to the more stable *anti*-conformer while the shorter bridges in **7a** lock it into the higher energy *syn*-form. A similar situation has been observed for related 2,2'-disubstituted metacyclophanes which do not undergo *syn-anti* interconversion.[8]

The spectroscopic properties of these ureaphanes were consistent with their structures. Their long wavelength UV absorptions were similar with **7a** showing a band at 280 nm (ε 1230) and **7b** showing a band at 285 nm (ε 910). Their emission spectra were quite different, however, with **7b** showing strong emission at 310 nm while **7a** gave a band at 369 nm with less than 10% the same intensity.[9] This behavior is characteristic of excimer formation which would be expected from the *syn*-conformation of **7a**.

We are continuing to examine the chemistry of species such as **6a,b** as well as other conformationally rigid analogues of **7a**.

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References and Notes

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5. ^{13}C NMR (75 MHz, $CDCl_3$) **7a**: δ 153.2, 128.3, 120.7, 108.0, 40.2, 21.5; **7b**: δ 153.2, 130.0, 120.8, 107.1, 40.7, 24.9.

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7. Calculations were performed using the programs PC MODEL and MMX available from Serena Software, Bloomington, IN.

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9. Both molecules were excited at 283 nm where their optical densities were equal.

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