

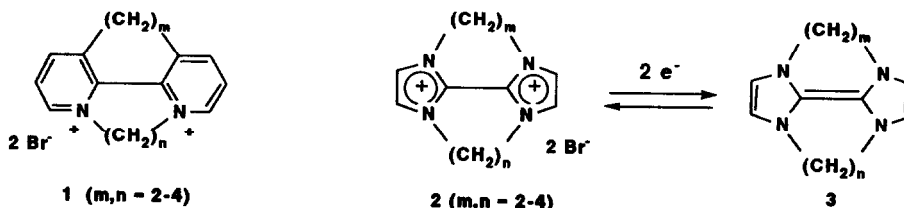
## SYNTHESIS AND PROPERTIES OF BRIDGED 2,2'-BITHIAZOLIUM SALTS

Veronique Goulle, Sara Chirayil, and Randolph P. Thummel\*

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

**Summary:** Bridged and methylated bithiazolium salts have been prepared by alkylation of 2,2'-bithiazole. The electronic absorption spectra and reduction potentials have been measured and stable radical cations of the di- and trimethylene bridged species have been prepared.

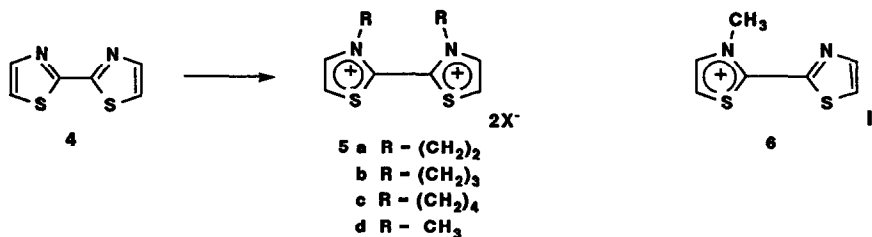
Recent work in our laboratories has been directed toward a study of the effect of bridging on a variety of azabiaryl molecules.<sup>1</sup> Such bridging has been found to influence both the physical and chemical properties of the biaryl molecule with important implications on the coordination chemistry of these systems.<sup>2</sup> In the case of 2,2'-bipyridine<sup>3</sup> (bpy) and 2,2'-biimidazole<sup>4</sup> (biim) the introduction of an N,N'-bridge can lead to diquatery salts such as 1 and 2. These salts are capable of behaving as reversible electron acceptors whose reduction potentials are dependent upon both the electronic nature of the biaryl nucleus as well as the length of the polymethylene bridges.



The fully reduced form of the biimidazolium salts 3 were of particular interest for two reasons. First, they are derivatives of tetraaminoethylene, a neutral organic species having a very low ionization potential.<sup>5</sup> Secondly, they are aza-analogs of tetrathiafulvalene (TTF) which is an important donor used in the formation of charge transfer systems.<sup>6</sup> We have found that the reduction potentials for 2 are too negative to allow for the convenient preparation of 3 as a stable species. This discovery prompted us to investigate diquatery salts of 2,2'-bithiazole whose redox chemistry should be intermediate between that of 2 and the oxidized form of TTF.

When 2,2'-bithiazole (4) is treated with a 1,n-dihaloalkane, the corresponding N,N'-bridged bithiazolium salts 5a-c are obtained. The reaction does not work for 1,4-dibromobutane but does succeed in 63% yield when 1,4-diiodobutane is employed. Excess methyl iodide leads only to

the mono-methylated derivative **6** while the dimethylated material **5d** can be prepared with trimethyloxonium tetrafluoroborate.

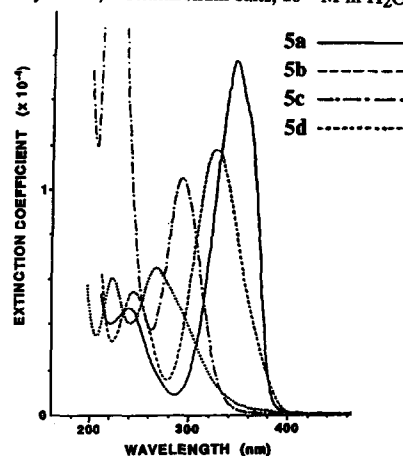


These five compounds were all characterized by their <sup>1</sup>H and <sup>13</sup>C NMR spectra. The aliphatic region of **5a** and **5b** indicated magnetic equivalence of the geminal methylene protons pointing to rapid conformational inversion at room temperature on the NMR time scale. The tetramethylene system **5c** showed two broad four proton singlets at 2.08 and 4.56 ppm, indicating that the system is close to coalescence and implying an inversion barrier of less than the 10.6 kcal/mole measured for N,N'-tetramethylene-2,2'-bimidazole.

Figure 1 illustrates the electronic absorption spectra for the series of salts **5a-d**. As the length of the N,N'-bridge increases from 2-4 carbons the absorption maximum decreases from 346 to 295 nm reflecting the increased non-planarity of the system. The dimethylated derivative **5d** extends this trend with an absorption at 270 nm. This system can achieve planarity so that it is not clear whether its high energy absorption is due to a large dihedral angle between the thiazolium rings or the fact that their planar conformation is transoid rather than cisoid as in **5a**. The steady decrease in extinction coefficient along the series implies poorer Franck-Condon overlap between the states and supports the former explanation for **5d**. The strong absorption at 227 nm ( $\epsilon$  31,700) for **5c** is associated with the iodide counterion.

The reduction potentials for **5** and **6** are summarized in Table 1 along with the analogous potentials for TTF and a bridged derivative of **1** and **2**. We observe two quasi-reversible reduction waves at very similar potentials for **5a** and **5b** while only a single nearly irreversible wave is observed for **5c** at more negative potential. These data imply similar conformations for the RCAT forms of **5a** and **5b** while **5c** would be less planar and hence less stabilized by

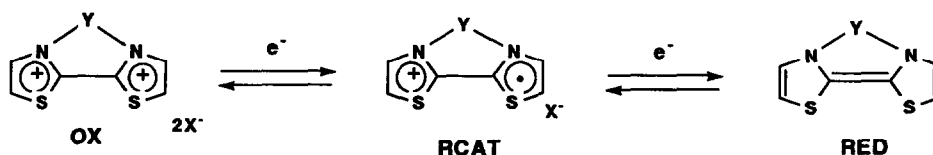
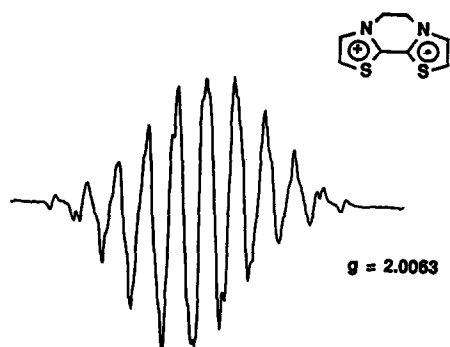
Figure 1. Electronic absorption spectra of bis-alkylated 2,2'-bithiazolium salts, 10<sup>-4</sup> M in H<sub>2</sub>O.



**Table 1. Reduction Potentials of Quaternary Salts<sup>a</sup>**

Compound	E <sub>1</sub>	E <sub>2</sub>
5a	-0.57 (100)	-0.13 (100)
5b	-0.50 (85)	-0.13 (85)
5c		-0.42 (320)
5d	-0.54 (120)	-0.41 (110)
6		-0.88 (ir)
2 (m = 2, n = 3)	-1.38 (110)	-1.14 (50)
1 (m = n = 2)	-0.89 (80)	-0.39 (80)
TTF (OX form)	+0.38 <sup>b</sup>	+0.77 <sup>b</sup>

(a) Potentials are measured by cyclic voltammetry in the oxidative direction to be consistent with other literature values. They are given in volts vs. SCE for saturated solutions in DMSO, 0.1 M in TBAP recorded at 25 ± 1°C at a scan rate of 200 mV/sec. 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. (b) Measured in CH<sub>3</sub>CN; reference 7.

**Figure 2. ESR spectrum of the radical cation generated by electrolysis of the PF<sub>6</sub><sup>-</sup> salt of 5a at -0.29V in CH<sub>3</sub>CN, 0.1 M in TBAPF<sub>6</sub>.**

resonance delocalization. The same analysis would hold for the RCAT form of 5d while its RED form could adopt a planar transoid conformation accounting for its relatively high value of E<sub>2</sub>. The monomethyl derivative 6 behaves like an N-substituted thiazole and evidences a less favorable, irreversible reduction. It is interesting that the first reduction potentials for 5a and 5b are nearly intermediate between those of 2 (m = 2, n = 3) and TTF which predict a value of -0.19 V. This implies that the substitution of nitrogen for sulfur in these systems has an approximately additive effect.

Of primary concern in systems of this type is the nature of the RCAT form since stable salts of similar species show promise as organic conductors. We carried out a bulk electrolysis of 5a and 5b as their hexafluorophosphate salts in acetonitrile applying potentials of -0.29 and -0.32 V respectively. Application of these potentials caused the solutions to immediately turn orange and measurement of the current drop as a function of time indicated the transfer of one electron. After electrolysis both solutions showed an ESR signal and the spectrum for 5a RCAT is shown in figure 2. Bulk electrolysis of 5a at -0.75 V indicated the transfer of only 1.39 electrons indicating that formation of the neutral RED form was less straightforward.

An interesting temperature dependency was observed for more concentrated acetonitrile solutions of 5a. If a tube containing this solution was cooled in dry ice/acetone to below -52°C, it

turned from orange to green. When only part of the tube was cooled, the cooled portion turned green while the uncooled portion remained orange. This process was completely reversible but was not evident for **5b** or more dilute samples of **5a**. At present our best explanation for this phenomenon is a reversible dimerization which is concentration dependent.<sup>8</sup>

The reduction of **5a** and **5b** can also be accomplished by treating an aqueous solution with zinc metal and precipitating the RCAT form with sodium tetraphenylborate. The solid thus obtained is dissolved in acetonitrile and filtered to remove excess zinc. Evaporation provides the RCAT tetraphenylborate which gives a satisfactory elemental analysis as a hydrate and an ESR signal with a *g* value nearly identical to that of the electrochemically generated material. Attempts are underway to prepare this material in crystalline form.

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