115534-23-1; (2*R*,4*S*)-**25b**, 115534-22-0; (2*S*,4*R*)-**25b**, 115534-24-2; (2*R*,4*R*)-**26a**, 115534-19-5; (2*S*,4*R*)-**26b**, 115534-20-8; (2*S*,4*S*)-**27a**, 115534-25-3; (2*R*,4*R*)-**27a**, 115534-27-5; (2*R*,4*S*)-**27b**, 115534-26-4; (2*S*,4*R*)-**27b**, 115534-28-6; (*S*)-(+)-**28**, 59965-08-1; (*R*)-(−)-**28**, 6154-33-2; (±)-**29**, 115534-29-7; (±)-**30**, 115648-41-4; (±)-**31**, 115534-30-0; **32**, 115534-31-1; $CH_3CH_2C(OEt)_3$, 115-80-0; $CH_3CH_2CO_2H$, 79-09-4; ${}_t$BuMe$_2$SiCl, 18162-48-6; methylmalonaldehyde, 16002-19-0; acetylene, 74-86-2; isobutyraldehyde, 78-84-2; pivalaldehyde, 630-19-3; cyclohexanecarboxaldehyde, 2043-61-0; 2,2,2-triphenylethanal, 42365-04-8; benzaldehyde, 100-52-7; mesitaldehyde, 487-68-3; 1,1,2-triphenyloxirane, 4479-98-5; phenyl isocyanate, 103-71-9.

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# Bisannelated Derivatives of 2,2′-Bipyridine

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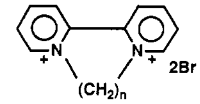
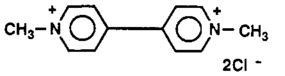
A series of 3,3′-polymethylene 2,2′-bipyridines has been treated with 1,*n*-dibromoalkanes ($n$ = 2–4) to afford a corresponding series of bisannelated bipyridinium dibromides. The conformational properties of this series of salts were examined by high-field NMR. As the molecule becomes less planar, the UV absorption maxima shift toward shorter wavelength, and the reduction potentials become more negative. For the least planar system, both electron-transfer steps are found to be irreversible.

Diquaternary derivatives of 2,2′-bipyridine and 4,4′-bipyridine are important electron-transfer agents in biological and other photocatalytic systems. Both 1,1′-dimethylene-2,2′-bipyridinium dibromide (**1a**, diquat) and 1,1′-dimethyl-4,4′-bipyridinium dichloride (**2**, paraquat) function as effective herbicides by viture of their ability to reversibly accept one electron to form a radical cation and thus interfere with the electron-transfer step in photosynthesis.[1] Paraquat, also known as methyl viologen, has been extensively utilized to transfer an electron from the photoexcited state of $Ru(bpy)_3^{2+}$ to an appropriate catalyst, which can then reduce water to evolve hydrogen gas.[2]

1a n = 2
b n = 3
c n = 4





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Variously substituted viologens have been examined as quenchers, electron relays, and herbicides. As expected, electron-withdrawing groups tend to destabilize the radical cation intermediate and shift the first reduction to more negative potential while electron-releasing substituents have the opposite effect.[3] Steric effects also can play an important role in determining the redox[4] and spectroscopic[5] properties of these diquaternary salts. The radical cation **3**, formed after one-electron reduction of diquat, is stabilized by resonance delocalization of the odd electron throughout both pyridine rings. Although of less importance from an electrocatalytic point of view, the fully reduced species **4** is of interest because the aromaticity of both pyridine rings has been destroyed and a formal double bond now exists between them. Both steps are favored by coplanarity of the pyridine rings, and thus one finds that lengthening the 1,1′-bridge to a trimethylene or tetramethylene unit accordingly increases both reduction potentials (see Table I). Electron-transfer quenching of photoexcited $Ru(bpy)_3^{2+}$ is similarly diminished as the 2,2′-bipyridinium unit becomes less planar.[4b,6] Nevertheless, Okura and co-workers have reported that **1b** and **1c** are more effective than **2** for photoinduced hydrogen evolution where zinc tetraphenylporphyrin trisulfonate is the photosensitizer.[7]

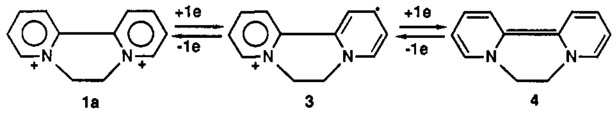

**Table I. Ultraviolet Absorption Data and Reduction Potentials for *N*,*N*′-Bridged Bipyridinium Dibromides**

| compound | $\lambda_{max}$ ($\epsilon \times 10^{-4}$)[a] | $E_{1/2}$, V (vs SCE)[b] redn 1 | redn 2 |
|---|---|---|---|
| **1a** | 308 (2.03) | −0.35 (80) | −0.82 (80) |
| **1b** | 289 (1.54) | −0.52 (80) | −0.83 (80) |
| **1c** | 273 (1.13) | −0.64 (80) | irrev |
| **6d** | 350 (1.32), 335 (1.42) | −0.39 (80) | −0.89 (80) |
| **6e** | 330 (1.51) | −0.39 (80) | −0.85 (80) |
| **6f** | 325 (1.6) | −0.40 (70) | −0.82 (80) |
| **6g** | 317 (1.28) | −0.48 (90) | −0.93 (90) |
| **6h** | 299 (1.29) | −0.60 (90) | −1.03 (90) |
| **6i** | 296 (1.31) | −0.65 (100) | −1.01 (100) |
| **6j** | 314 (1.19) | −0.56 (80) | −0.92 (80) |
| **6k** | 294 (1.2) | −0.72 (40) | irrev |
| **6m** | 286 (1.26) | irrev | irrev |

[a] Absorption maxima reported in nanometers for $10^{-4}$ M solutions in $H_2O$ at 25 °C. [b] Potentials are in volts vs SCE for saturated $CH_3CN$ solutions, 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 parentheses.

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(1) Summers, L. A. *The Bipyridinium Herbicides*; Academic: New York, 1980.

(2) (a) Keller, P.; Moradpour, A.; Amouyal, E.; Kagan, H. B. *Nouv. J. Chim.* **1980**, *4*, 377. (b) Graetzel, M. *Acc. Chem. Res.* **1981**, *14*, 376.

(3) (a) Pirzada, N. H.; Pojer, P. M.; Summers, L. A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1976**, *31B*, 115. (b) Jones, G., II; Malba, V. *J. Org. Chem.* **1985**, *50*, 5776.

(4) (a) Homer, R. F.; Tomlinson, T. E. *J. Chem. Soc.* **1960**, 2498. (b) Amouyal, E.; Zidler, B. *Isr. J. Chem.* **1982**, *22*, 117. (c) Tsukahara, K.; Wilkins, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 2632.

(5) (a) Calder, I. C.; Spotswood, T. McL.; Tanzer, C. I. *Aust. J. Chem.* **1967**, *20*, 1195. (b) Vögtle, F.; Brombach, D. *Chem. Ber.* **1975**, *108*, 1682. (c) Campâ, C.; Camps, J.; Font, J.; de March, P. *J. Org. Chem.* **1987**, *52*, 521.

(6) Takuma, K.; Shuto, Y.; Matsuo, T. *Chem. Lett.* **1978**, 983.

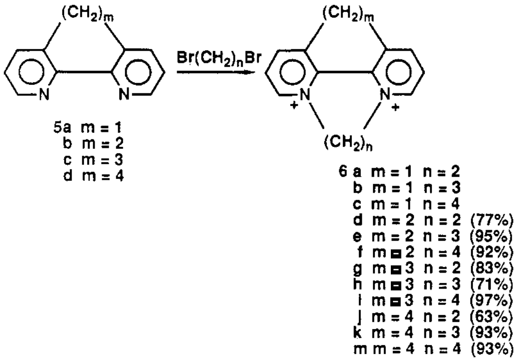
(7) Okura, I.; Kaji, N.; Aono, S.; Kita, T. *Inorg. Chim. Acta* **1984**, *86*, L79.

0022-3263/88/1953-4745$01.50/0

We have recently prepared a series of monoannelated derivatives of 2,2′-bipyridine in which a 3,3′-bridge controls the conformation of the molecule. In preliminary work we prepared 1,1′-dimethylene-bridged derivatives of these annelated bipyridines and demonstrated that their first and second reduction potentials were negatively shifted with increasing length of the 3,3′-bridge.[8] In this study we have extended the series to include longer diquaternary bridges, which show a more pronounced effect on the conformational and redox properties of the system.

## Results and Discussion

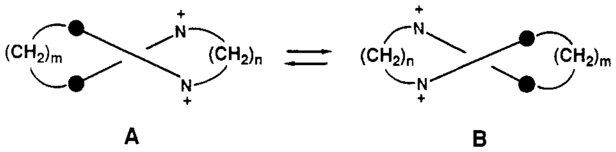
The salts **6d-m** were prepared by refluxing a solution of **5b-d** in the appropriate 1,*n*-dibromoalkane. In most cases the desired salt precipitated upon cooling. Yields ranged from 63 to 98%. The salts were purified by recrystallization from ethanol–ether and identified primarily on the basis of their 300-MHz $^1$H NMR spectra.



The synthetic results with the monomethylene-bridged system **5a** were inconclusive. $^1$H NMR spectroscopy showed at least two sets of aromatic resonances for systems presumed to be **6b** and **6c**. These anomalies were further supported by $^{13}$C and FAB mass spectral data. We have re-evaluated our previous report, which claimed preparation of **6a**.[8] An inspection of molecular models indicates that the monomethylene bridge in **5a** pulls the two nitrogens away from each other so that *N,N′*-dimethylene bridging appears to be impossible. Since we are uncertain as to the structures of compounds **6a–c**, they will be omitted from future discussion.

With regard to the structure of the salts **6d–m**, careful analysis of the NMR spectra provides information about the possible fluxional nature of the system as well as the electronic environment of the pyridine rings. In previous work we have demonstrated that for 3,3′-bridged pyridines **5b,c**, conformational inversion is rapid at room temperature while this process is slow for **5d** on the NMR time scale. Spotswood and Tanzer have investigated a series of dimethyl-substituted bridged bipyridinium salts similar to **1a–c** where the methyl groups occupied either the 3,3′-, 4,4′-, or 5,5′-positions.[4a] For the 3,3′-substituted series they found NMR evidence for magnetic nonequivalence of the methylene protons $\alpha$ to the pyridinium nitrogen. For the 4,4′-substituted series the trimethylene and tetramethylene bridged salts appeared to be rigid while only the tetramethylene-bridged derivative of the 5,5′-dimethyl-substituted salts appeared to be rigid. These observations are in accord with more recent results of Font and co-workers who found that trimethylene-bridged derivatives of 4,4′-disubstituted bipyridinium salts were conformationally rigid.[5c]

In the absence of other substituent effects, one can generalize by saying that an *N,N′*- or 3,3′-dimethylene bridge tends to flatten 2,2′-bipyridine causing the inversion barrier between forms A and B to be too low to observe conveniently by NMR. Conversely, a tetramethylene bridge introduces rigidity on the NMR time scale. Furthermore, a bridge between the N,N′-positions, leading to a diquaternary salt, is more influential than a 3,3′-bridge of the same length. Thus the trimethylene-bridged system **1b** is conformationally rigid by NMR while **5c** is conformationally mobile.



We find that when a two-carbon and a four-carbon bridge are used to annelate 2,2′-bipyridine, it is the 3,3′-bridge that dictates the conformation. Both **6f** and **6j** are rigid by NMR as is evidenced by the nonequivalence of the dimethylene bridge protons (supplementary material, Figure 2). When the bridging combination in **6** is a two carbon and three carbon one, we find the *N,N′*-trimethylene bridged derivative **6e** to be conformationally rigid while the 3,3′-trimethylene bridged **6g** shows three broad unresolved peaks evidencing coalescence at about room temperature. Warming the sample to 80 °C sharpens the dimethylene bridge singlet at 5.27 ppm as well as the trimethylene bridge pattern at 3.0 and 2.76 ppm. When the corresponding 3,3′-tetramethylene derivative **6j** is heated to 100 °C, no change in the dimethylene bridge signal is observed.

The aromatic protons of **6** show a pattern characteristic of a 2,3-disubstituted pyridine, and chemical shift data is summarized in supplementary Table II. The most consistent variation is found for $H_6$, which shifts downfield with decreasing planarity of the system. Interestingly this trend contrasts with the neutral precursors **5a–d** where $H_6$ for the least planar system **5d** is the highest field resonance. For these 3,3′-bridged bipyridines, $H_6$ becomes more shielded with increased twisting about the 2,2′-bond leading to less delocalization. For the diquaternary salts this decreased delocalization due to twisting leads to intensification of positive charge on nitrogen and concomitant deshielding of the adjacent C–H bond. This same effect is observed to a lesser degree for $H_5$.

Table I summarizes the ultraviolet data for the series of salts under discussion. The absorption maxima show a very consistent variation toward higher energy as the systems become less planar.[4a] The decrease in intensity of these absorptions is less consistent but shows a general trend wherein absorptions for the more planar systems are generally more intense. The bisannelated systems **6** show lower energy absorptions as compared to the monoannelated ones, **1**, which is probably due to an alkyl inductive effect as has been noted previously for simple pyridine absorptions.[10]

The half-wave reduction potentials for **6d–m** have been determined by cyclic voltammetry in acetonitrile, and the results are summarized in Table I. For all but the least planar systems, both reduction steps were found to be quasi-reversible in that the difference between the anodic and cathodic peak potentials for a given wave were ≥60 mV. Transfer of the first electron occurs at increasingly

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(8) Thummel, R. P.; Lefoulon, F.; Mahadevan, R. *J. Org. Chem.* **1985**, *50*, 3824.

(9) Spotswood, T. McL.; Tanzer, C. I. *Aust. J. Chem.* **1967**, *20*, 1213.

(10) Thummel, R. P.; Kohli, D. K. *J. Org. Chem.* **1977**, *42*, 2742.

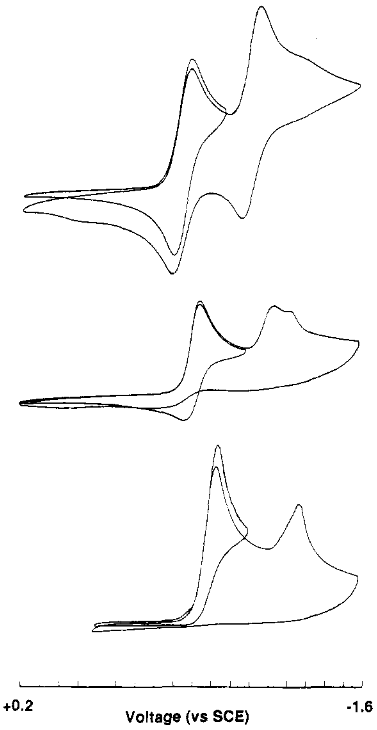

**Figure 1.** Cyclic Voltammograms of Diquaternary Salts **6i** (top), **6k** (middle), and **6m** (bottom) in acetonitrile containing 0.1 M TBAP at 25 °C with a sweep rate of 200 mV/s.

negative potential as the molecules become less planar as has been observed in earlier work.[8] The second reduction step appears to be less sensitive to conformation. It is of interest to compare **6i,k,m**, which are the most distorted from planarity. The cyclic voltammograms for these systems are illustrated in Figure 1. For **6m**, which has a 3,3′- and *N,N*′-tetramethylene bridge, both reduction steps are clearly irreversible. For **6k**, which has a 3,3′-tetramethylene and an *N,N*′-trimethylene bridge, the first step appears to be reversible but not the second. When these two bridges are interchanged as in **6i**, both steps are at least quasi-reversible. In this case it appears that a tetramethylene bridge is more influential on conformation when it occupies the 3,3′-position.

Irreversibility implies that the species formed upon reduction undergoes some other process faster than it can be oxidized back to the reduction precursor. The typical processes that might interfere with reoxidation include a subsequent chemical reaction, a conformational change, or adsorption of the reduced species onto the electrode surface.

The first reduction of the diquaternary salts **6** leads to a radical cation similar to **3**. This species is stabilized by electron delocalization, which is favored by coplanarity of the pyridine rings. The addition of a second electron to **6** would provide a neutral species similar in structure to the pentaene **4**. Clearly the 2,2′-double bond in **4** enforces near planarity of the bipyridine system.

The formation of species such as **3** and **4** may involve a conformational change as a discrete step, which occurs subsequent to electron transfer. Normally the energy barrier for this process is low enough that it does not interfere with the reversibility of electron transfer. For systems such as **6k** and **6m**, however, we know from NMR studies that this barrier has become appreciable and so its importance cannot be ignored. This same question has been addressed by Parker and co-workers in a study involving the reduction of lucigenin to 10,10′-dimethyl-9,9′-biacridylidene where they observed enhanced reversibility at lower temperatures.[11] We examined the redox behavior of **6m** at −45 °C in acetonitrile but observed no appreciable change from the results at 25 °C. The possible formation of a highly reactive diradical rather than a closed shell pentaene such as **4** cannot be ruled out. Related studies on other bridged biaryl systems are being directed toward stabilization of species such as **4** and subsequent examination of their electron-donor properties.

## Experimental Section

Nuclear magnetic resonance spectra were recorded on a Nicolet NT-300 WB spectrometer in $D_2O$ with chemical shifts reported in parts per million downfield from internal sodium 3-(trimethylsilyl)-1-propanesulfonate (DSS). Electronic absorption spectra were recorded on a Perkin-Elmer 330 spectrophotometer. The preparation of bipyridines **5a–d** has been reported previously.[8] 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 that consisted 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 cracked-glass bridge filled with 0.1 M TBAP in acetonitrile. Deaeration of all solutions was performed by passing high purity nitrogen through the solution for 5 min and maintaining a blanket of nitrogen over the solution while making measurements. Reagent grade acetonitrile was distilled twice from $P_2O_5$ 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.[12]

**Preparation of Bipyridinium Dibromides.** In a typical experiment, a mixture of 2 mmol of the 3,3′-annelated 2,2′-bipyridine **5**[8] and 2 mL of the 1,*n*-dibromoalkane was stirred at 120 °C overnight, during which time a precipitate formed. The reaction mixture was then cooled, diluted with 10 mL of diethyl ether, and filtered. The precipitate was washed with diethyl ether and dried under vacuum. Further purification, when necessary, was effected by recrystallization from ethanol/ether. The salts were characterized by their 300-MHz $^1H$ NMR spectra (see supplementary Table II) and C, H, N combustion analyses (see supplementary Table III). Yields are reported with structure **6**.

**Acknowledgment.** Financial support from the Robert A. Welch Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant CHE-8607935) is gratefully acknowledged. F.L. also wishes to acknowledge support from a Stella Erhardt Memorial Fellowship and a Grant-in-Aid of Research from Sigma Xi, the Scientific Research Society.

**Supplementary Material Available:** A table of $^1H$ NMR chemical shift data and a table of combustion analytical data as well as a figure showing the $^1H$ NMR signals for the dimethylene bridge protons of **6f** and **6j** (3 pages). Ordering information is given on any current masthead page.

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(11) Ahlberg, E.; Hammerich, O.; Parker, V. D. *J. Am. Chem. Soc.* **1981**, *103*, 844.

(12) Bard. A. J.; Faulkner, L. R. *Electrochemical* Methods; Wiley: New York, 1980; p 227.