In recent years, extensive studies on the structure of cuprates[27] and mechanism[28] of their reactions have been reported. Any reasonable explanation for the selectivity observed in this substitution requires a clearer picture of the specific carbamate–cuprate complex. Nevertheless, the level of asymmetric induction in this transformation is remarkable considering the six intervening bonds between the original and created stereogenic centers. Further studies on nucleophile and substrate variability as well as reagent structure are ongoing.

Acknowledgment. We are grateful to the National Science Foundation for support of this project (NSF-CHE-8515371, CHE-8818147). S.E.D. acknowledges support from the NSF for a Presidential Young Investigator Award (1985–1990) and the A. P. Sloan Foundation for a Fellowship (1985–1989). We thank Professor William H. Pirkle for his assistance with the HPLC analyses.

Supplementary Material Available: A general procedure for reactions of **2h** (3 pages). Ordering information is given on any current masthead page.

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Articles

2,2′:4,4″:4′,4‴-Quaterpyridyl: A Building Block for the Preparation of Novel Redox Reagents. 1. Preparation and Quaternization

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An efficient preparation of 2,2′:4,4″:4′,4‴-quaterpyridyl (qpy) from 4,4′-bipyridine is described, using palladium on charcoal. Conditions are described for the selective methylation of the nitrogen atoms present. This has allowed the preparation of mono- and dimethylquaternary salts that retain an α-diimine site for complexation to a metal. These quaternary salts can be used to prepare complexes in which metal ions are coordinated to viologen-type ligands. Electrochemical and spectroscopic measurements of the diquaternary salt derived from qpy suggest that it behaves as two separate or weakly interacting monoquat moieties.

Introduction

Bipyridines and polypyridines have attracted attention in recent years as synthetic components of useful redox reagents such as the viologens[1] and polypyridyl complexes of Ru(II) and other metal ions.[2] These reagents have played a central role in the study of photoactivated electron-transfer reactions and in applications to energy conversion,[2,3] synthetic methodology,[4] electrochromic devices,[5] and related areas.[6]

As knowledge in these areas has accumulated, a need has arisen for structurally more complex bipyridines, polypyridines, and analogues so that more specialized systems can be developed and explored. Of particular interest has been the incorporation of two or more distinct molecular entities into a single "supermolecule" and the design of modified reagents that can participate in transient supramolecular interactions. Examples of systems that have been studied include the bis- and polyviologens that function as multielectron acceptors,[7] metal complexes of 2,2′-bipyrazine, used in the photoreduction of carbon dioxide to methane,[8] and molecules containing a light-activated electron-donor site covalently linked to an electron-aceptor site to explore the role of structure on the electron-transfer process.[9] Also of interest are systems in which the conformational relationship among neighboring pyridyl units is either rigidly defined,[10] and/or is controllable by molecular modification,[11] and systems

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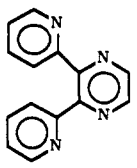
consisting of pyridine rings incorporated into macrocycles.[12]

Our recent efforts in this area have focused on the use of diimines that cannot only bind to a metal ion, or be quaternized, to create a redox-active chromophoric site, but that also allow for structural elaboration of this site. Earlier papers from this laboratory dealt with ligands **1** and **2**, which were used to prepare complexes of the type $[Ru(bpy)_2L)]^{2+}$. These complexes were elaborated by



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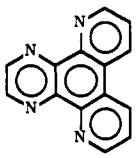

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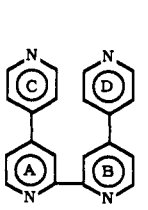
exploiting the two nitrogen atoms of L that are not coordinated to the metal. For example, a second ruthenium–diimine site, could be added, and in this way the first luminescent "dimers" $[(bpy)_2RuLRu(bpy)_2]^{4+}$ were prepared (L = **1** or **2**) and characterized.[13] Since luminescence measurements afford a powerful probe of excited state properties, there continues to be considerable interest in this type of compound, not only in our laboratory but in others. In this context, Petersen et al.[14] used ligand **1** to prepare $[RuL_3]^{2+}$, an ion containing three free diimine sites. Using these three sites, novel types of redox cluster compounds can be made. Petersen's group synthesized a cluster with a Ru(II) core and three appended iron centers. Similarly, Schmehl et al.[15] prepared a cluster with an iron core and three appended Ru(II) sites. Vogler and Kisslinger[16] have bridged Ru(II) and Re(I) centers, and Rillema et al. have bridged ruthenium and platinum centers.[17] Grätzel et al. recently showed that a binuclear ruthenium complex served as an efficient water oxidation photocatalyst.[18]

In light of the considerable interest in this type of system, we continue to develop novel diimine ligands that allow for the construction of interesting and potentially useful photocatalysts and redox reagents. It occurred to us that the quaterpyridyl **3** and its derivatives would provide a most useful and versatile class of compounds for extending the types of studies described above, by providing a basic building block for synthesizing reagents of a new and potentially useful type for fundamental studies of electron-transfer processes and of excited state photochemistry. This is the first in a series of papers that will detail our findings. In it we will describe an efficient preparation of the free quaterpyridyl ligand and will describe how it can be selectively monoquaternized to give ion **4**, or diquaternized to give the diquat ion **5**. In both ions, a diimine site remains free for coordination to a metal. The spectroscopic and electrochemical properties of the novel quaterpyridyls will be described. The quaternized quaterpyridyls provide electron-acceptor viologen-type sites in addition to the diimine nitrogen atoms. These features make the synthesis of new supermolecular clusters of metal-centered photoactive chromophores and redox-active viologen sites possible.



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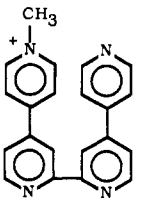

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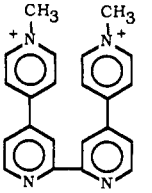

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Experimental Section

Reagents. 4,4'-Bipyridine was obtained from Aldrich as the dihydrate. Acetonitrile was either Aldrich gold label or Baker HPLC grade. Nitrogen gas was dried by passage through a column of P_2O_5, followed by a column of $CaCl_2$. All other reagents were used as received from chemical suppliers without further purification.

Synthesis of 2,2':4,4'':4',4'''-Quaterpyridyl (3). 4,4'-Bipyridine dihydrate (75 g) and 10% palladium on carbon (10 g) were heated at 125 °C for 72 h in a round-bottom flask equipped with a reflux condenser. After this time, the reaction mixture was cooled, chloroform (300 mL) was added, and the resulting slurry was refluxed for 30 min. The mixture was then filtered, and the chloroform was removed by distillation. Acetone (200 mL) was added to the solid residue and the mixture stirred. The slurry so obtained was filtered to yield a crop of crude quaterpyridyl product, which was set aside for later purification. The filtrate was collected and its volume reduced by about 50 mL by partial evaporation of the acetone, so as to yield more solid. The solid (a further batch of crude quaterpyridyl) was again collected by filtration and the filtrate once more reduced in volume. In this way more quaterpyridyl was obtained. This evaporation/filtration procedure was repeated several times, the acetone volume being reduced in 50-mL increments, until the solid obtained was found to be unreacted starting material (mp 71 °C) rather than the much higher melting quaterpyridyl (mp > 200 °C). The batches of crude quaterpyridyl were combined and recrystallized from ethanol. The procedure results in 5 g of the quaterpyridyl **3**, which is a colorless solid: mp 235 °C. C, H, N. Anal. Found: C, 73.02; H, 4.67; N, 17.02. Calcd: C, 73.15; H, 4.91; N, 17.06.

Synthesis of *N*-Methylquaterpyridinium Iodide (Iodide Salt of 4). Quaterpyridyl **3** (500 mg) and 1.0 mL of methyl iodide were dissolved in 70 mL of methylene chloride. The resulting solution was stoppered and allowed to remain at room temperature for 36 h. The solution was then poured into chloroform (200 mL), refluxed for 20 min, and filtered while hot. The yellow solid so obtained (100 mg) was found to be the *di*quaternary salt (see next preparation). The filtrate, containing unreacted qpy and the monoquaternary salt, was stripped of solvent under reduced pressure. The monomethyl quaternary salt (250 mg) was purified by crystallization from chloroform/methylene chloride or from ethanol. It is a pale yellow solid. C, H, N. Anal. Found: C, 53.25; H, 3.70; N, 11.66. Calcd: C, 53.62; H, 4.07; N, 11.96. To prepare the hexafluorophosphate salt, 100 mg of the iodide salt was added to 10 mL water and the solution was heated until all the solid dissolved. The solution was allowed to cool and then added to 15 mL of a saturated solution of ammonium hexafluorophosphate. The precipitate was allowed to digest at 0 °C for 2 h, and then the resulting slurry was filtered. The crude product was washed with 5 mL of water and then precipitated out of acetone using ether to yield 200 mg of the monoquaternary hexafluorophosphate salt.

Synthesis of *N*'',*N*'''-Dimethyl-2,2':4,4'':4',4'''-quaterpyridinium Iodide and Hexafluorophosphate (i.e., Salts of 5). The parent quaterpyridyl **3** (500 mg) and 2 mL of methyl

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iodide were refluxed in 50 mL of acetone for 4 h. The mixture was then filtered, and the solid so obtained was washed with acetone (20 mL) and then chloroform (4 × 10 mL). Recrystallization from ethanol yielded 300 mg of yellow platelets of the diquaternary iodide **5**. The substance yielded an immediate purple color with ferrous ion, confirming that the diimine nitrogen atoms of rings A and B had survived the quaternization reaction. Anal. Found: C, 44.03; H, 3.29; N, 9.15. Calcd: C, 44.46; H, 3.29; N, 9.43. The hexafluorophosphate salt of the diquaternary salt could be obtained in the same manner as for the monoquaternary salt (above).

Cyclic Voltammetry. Cyclic voltammograms were recorded on a PAR 173 system, as described in our earlier publications.[13a] Millimolar samples were examined in acetonitrile solution with 0.1 M tetra-*n*-butylammonium tetrafluoroborate as the supporting electrolyte. The cell was purged with nitrogen for 20 min prior to the recording of the voltammogram. The working electrode was a platinum disk, the auxiliary a platinum wire, and potentials were recorded versus the standard calomel electrode (SCE).

Results and Discussion

Preparation of Qpy. Throughout this discussion we shall use the abbreviation qpy to refer to compound **3**. The only earlier references to qpy have been a brief report over 50 years ago[19a] to the effect that a high temperature reaction of 4,4′-bipyridine and iodine had given a trace amount of a compound to which structure **3** was assigned and a recent mention in a review[19b] that qpy had been obtained during an attempt to prepare a macrocyclic polypyridyl by treating 4,4′-bipyridine with lithium diisopropylamide in tetrahydrofuran. No experimental details were given, nor have subsequently been published.

We initially contemplated preparing the qpy needed for our experiments by heating 4,4′-bipyridine with iodine as described in the older literature. However, the procedure proved to be quite unsuitable for routine preparations, involving tedious procedures, and giving extremely low and nonreproducible yields.

There are several catalytic systems that have been commonly used to couple simple pyridines in the 2,2′-positions. Of these, Raney nickel and palladium on activated carbon are most common.[20] In our hands the use of 10% Pd/C to couple together two 4,4′-bipyridine units, using the procedure described in the Experimental Section, provided the routine method of synthesis that we sought. The main problem with the procedure was the separation of a relatively large amount of uncoupled 4,4′-bipyridine from the quaterpyridyl product. Fractional crystallization was an effective separation procedure because 4,4′-bipyridine has a greater solubility than qpy in all solvents tested. Pure qpy could easily be obtained, and unreacted 4,4′-bipyridine was recovered and recycled. The qpy product proved to be identical with that obtained from the older Burstall method. Its mass and proton NMR spectra are consistent with structure **3**.

Quaternization of Qpy. One of the attractive features of qpy as a building block for creating interesting photoactive or electroactive substances is the diversity of nitrogen sites, which, with judicious choice of synthetic procedures, allows the binding of metal ions to the diimine nitrogen atoms of rings A and B and functionalization of these complexes through the nitrogens of rings C and D, too far apart to act in a chelating fashion. One avenue for functionalization is quaternization. Quaternization could, in principle, be done either prior to chelation to a metal through A and B nitrogens, or after such a chelation.

To establish that the first of these strategies had promise, we needed to show that quaternization could be carried out *selectively* on rings C and D, leaving the nitrogens on rings A and B undisturbed and available for coordination to a metal ion. We reasoned that this goal was realistic because the two nitrogen atoms of rings A and B are environmentally similar to those in 2,2′-bipyridine, which is fairly resistant to quaternization except under rather forcing conditions,[21] while those in rings C and D are similar to those in 4,4′-bipyridine, which are alkylated under mild conditions.[22] Thus one expects qpy to be selectively quaternized under mild conditions on rings C and D.

To test this, we treated qpy with methyl iodide in a variety of solvents. In refluxing acetone with excess methyl iodide, a clean yield of a beautiful yellow crystalline diquaternary salt was obtained, which we have been able to establish has structure **5**. It is more difficult to prepare a clean sample of the monoquaternary salt (the iodide salt of **4**). We initially attempted its preparation using 1 equiv of methyl iodide, using the same experimental conditions used to prepare **5**. This procedure yielded a mixture of diquat **5**, monoquat **4**, and unreacted starting material. Different solvents were investigated to improve the selectivity of the reaction. In relatively nonpolar solvents (hexane, ether) the reaction is too sluggish to be useful. In more polar solvents (chloroform, acetone, and alcohols), there is appreciable production of diquat. Best results were obtained by using methylene chloride as described in the Experimental Section. The monoquaternary salt so isolated has very attractive solubility properties. It is reasonably soluble in both aprotic organic solvents such as chloroform, as well as in protic solvents such as water and alcohols. The successful mono- and bismethylations on the nitrogen atoms of rings C and D establish that simple methodology can be used to discriminate between the different nitrogen atoms present in the quaterpyridyl molecule. Interestingly both the quaternary salts are water soluble, thus making them attractive reagents for analytical determinations of metal ions (most diimines, especially most polypyridyls, have limited water solubility).

Harsh alkylating conditions are required to proceed beyond the bisquaternization level. For example, treatment of qpy with trimethyloxonium tetrafluoroborate in 1,2-dichloroethane at 150 °C yielded a tris-quaternary salt (NMR showed nine methyl protons in the expected 2:1 ratio). It is an extremely hygroscopic salt, exhibiting similar anomalous behavior to that of other highly quaternized salts,[23] e.g., giving highly colored solutions in almost all solvents and showing evidence for facile formation of radical species. Quaternization of all four nitrogens of qpy to produce **6**, a potentially interesting "dimer" of methyl viologen, proved impossible under all conditions tried.

Carbon-13 NMR. ^{13}C NMR of Qpy. The 300-MHz decoupled ^{13}C NMR spectrum of 2,2′:2,4″:2′,4‴-quaterpyridine is shown in Figure 1. The spectrum shows the expected eight resonances. The values for the resonances of simpler pyridines used as models to interpret the qpy spectrum are listed in Table I. The numbering system used in this discussion and in Table I is illustrated in Figure 1.

In general, carbon atoms meta to the nitrogen atom in pyridines give signals in the range 118–124 ppm. In the

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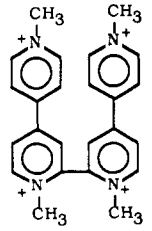

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spectrum of 2,2′:2,4″:2′,4‴-quaterpyridine, there are three resonances in this range, 119.0, 121.5, and 121.7, and three corresponding meta carbons in the quaterpyridyl (C3(3′), C5(5′), and C5″(C5‴)). Resonances in the 135–146 ppm range may be assigned to carbons in the 4-positions of pyridine rings such as C4(4′) and C4″(4‴) in **3**, and the resonances for these two carbons are at 145.6 and 146.6 ppm in the ^{13}C NMR spectrum of the quaterpyridyl. The carbon atoms ortho to the nitrogen atom (C2(2′), C6(6′), C2″(2‴), and C6(6‴) are further downfield, δ values in excess of 150 ppm, and there are three in the spectrum at 150.0, 150.6, and 156.6 ppm. Thus the ^{13}C NMR is consistent with the structure **3** for the quaterpyridyl.

^{13}C NMR of [QpyMe](I$^-$). The decoupled ^{13}C NMR spectrum of [QpyMe](I$^-$) is shown in Figure 2, and the chemical shifts are summarized in Table II. In the spectrum of [QpyMe](I$^-$) there are 17 resonances: one for the methyl group (48.1 ppm), six in a meta relation to a pyridine nitrogen atom (118–124 ppm), six ortho (147–156 ppm), and four para (135–146 ppm). The spectra confirm that there is a single methyl group in the molecule. The pattern of 17 resonances could be produced by di-, tri-, or tetraquaternized species. The spectrum is consistent with the structure **4** for the ion, but does not exclude the possibility that the methyl group is on ring A and not C. (However, other data indicate that this is not the case, see later discussion).

^{13}C NMR of [QpyMe$_2$](I$^-$)$_2$. The decoupled carbon spectrum of [QpyMe$_2$](I$^-$)$_2$ is shown in Figure 3, and the ^{13}C NMR chemical shifts for Qpy, [QpyMe$_2$](I$^-$)$_2$, and [QpyMe](I$^-$) are summarized in Table II. In the spectrum of [QpyMe$_2$](I$^-$)$_2$, there are the expected nine resonances, these include one for the methyl group (48.1 ppm), six in the range 118–124 ppm for carbons in a meta relation to a pyridine nitrogen atom, six ortho (147–156 ppm), and four para (135–146 ppm). The presence of nine resonances is consistent with structure **4**, but again by itself does not confirm that bismethylation occurs on rings C and D.

Proton NMR. ^1H NMR of Qpy. The ^1H NMR spectrum of 2,2′:2,4″:2′,4″-quaterpyridine is shown in Figure 4. The protons on ring C (D) are of the type AA′XX′. Protons H3″ and H6″ form an apparent doublet (rel area 4) at δ 7.65. Values for the coupling constants are likely to be of the same order as in other pyridines (Table III). Coupling constants of adjacent protons $J_{2,3}$ and $J_{5,6}$ are over three times the values for protons coupled across two nuclei ($J_{3,5}$ and $J_{4,6}$). Thus $J_{3'',2''}$ is expected to be large compared to $J_{3'',5''}$ and the AA′XX′ pattern closely resembles the A_2B_2 spectrum of 4,4′-bipyridine. The corresponding doublet expected for protons H2″ and H6″ in the quaterpyridyl is not resolved by our instrument and appears under the multiplet (rel area 6) at δ 8.68. Analogous protons, H2(2′) and H6(6′), in the spectrum of 4,4′-bipyridine appear at a similar δ value (8.70).

The three protons on ring A produce a spectrum of the AMX type, analogous to the AMXY spectrum of 2,2′-bipyridine. Protons H6(6′) are the furthest downfield, ortho to the nitrogen atom on a disubstituted ring, and due to

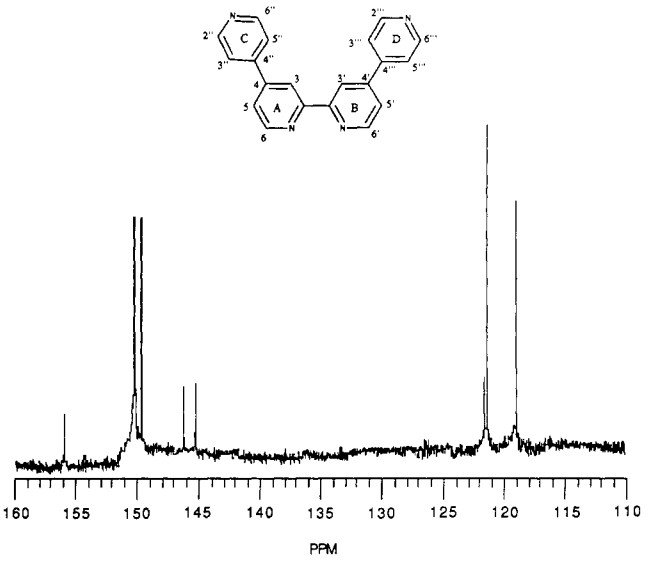


Figure 1. Decoupled 300-MHz ^{13}C NMR spectrum of Qpy (**3**) in $CDCl_3$.

Table I. ^{13}C NMR Resonances of Bipyridines[28]

C	Pyr	2,2′-bpy	2,4′-bpy	4,4′-bpy
2	148.9	155.7	153.6	150.1
3	123.2	120.6	120.0	120.8
4	135.5	136.4	136.2	144.8
5	123.2	123.2	123.0	120.8
6	148.9	148.7	149.3	150.1
2′		155.7	149.6	150.1
3′		120.6	120.2	120.8
4′		136.4	145.5	144.8
5′		123.2	120.2	120.8
6′		148.7	149.6	150.1

[a] $CDCl_3$ solutions, measured in ppm relative to TMS.

Table II. ^{13}C NMR Resonances[a] for Qpy,[b] [QpyMe]$^+$(I$^-$),[c] and [QpyMe$_2$]$^{2+}$(I$^-$)$_2$[c]

C	Qpy	[QpyMe]$^+$(I$^-$)	[QpyMe$_2$]$^{2+}$(I$^-$)$_2$
1	119.1	48.1	48.1
2	121.5	118.3	119.3
3	121.7	118.8	123.3
4	145.6	121.6	125.7
5	146.6	122.4	143.0
6	150.0	122.5	146.6
7	150.6	125.5	151.3
8	156.6	142.4	152.2
9		144.5	156.3
10		145.9	
11		146.5	
12		150.7	
13		151.0	
14		151.1	
15		152.1	
16		155.6	
17		156.4	

[a] Measured relative to TMS. [b] Saturated solution in $CDCl_3$. [c] Saturated solution in DMSO-d_6.

Table III. Coupling Constants for Bipyridines[29]

J[a]	2,2′-bpy	3,3′-bpy	4,4′-bpy
$J_{2,3}$			5.0[b]
$J_{3,4}$	8.0		
$J_{4,5}$	7.6	7.8	
$J_{5,6}$	4.8	4.9	5.0[b]
$J_{3,5}$	1.3		
$J_{4,6}$	1.8	1.6	

[a] Values given in Hertz, for samples in $CDCl_3$. [b] Authors report only an approximate value.

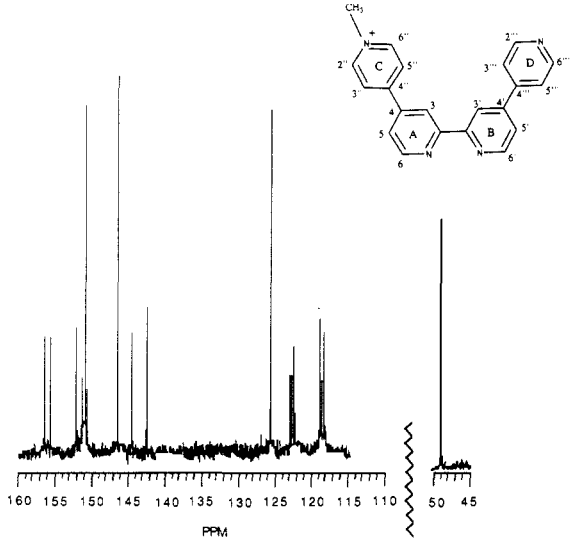


Figure 2. Decoupled 300-MHz ^{13}C NMR spectrum of $[QpyMe]^+(I^-)$ (**4**) in DMSO-d_6.

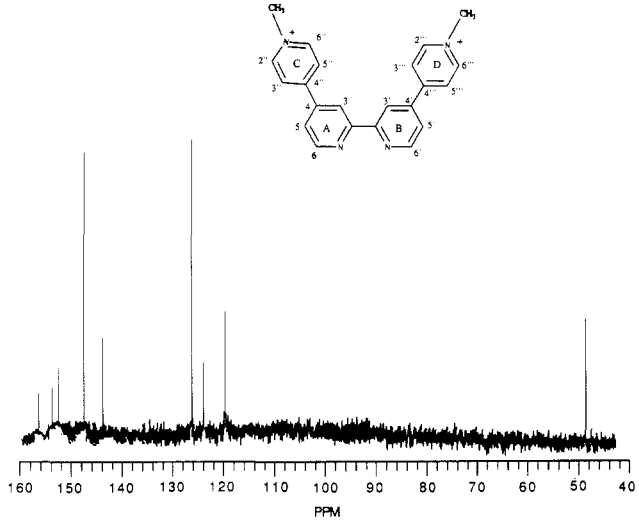


Figure 3. Decoupled 300-MHz ^{13}C NMR spectrum of $[QpyMe_2]^{2+}(I^-)_2$ (**5**) in DMSO-d_6.

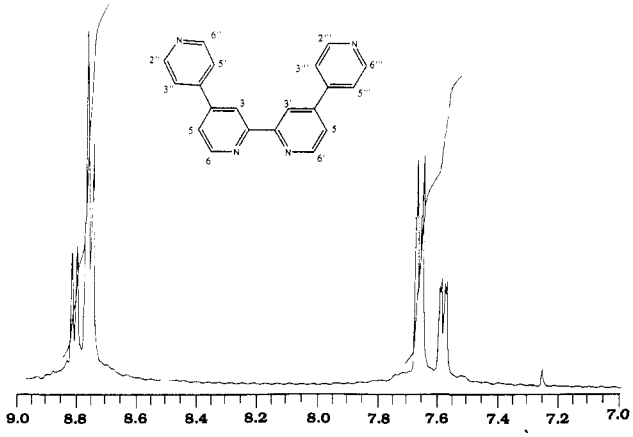


Figure 4. ^1H NMR spectrum (300-MHz) of Qpy (**3**) in $CDCl_3$.

the large magnitude of $J_{6,5}$, compared to $J_{6,3}$, appear as a doublet at δ 8.80 (rel area 2). Proton H5 is assigned to the quartet (rel area 2) at δ 7.65. The assignment of protons H3(3′) is based on the analogous protons in 2,2′-bipyridine. In the spectrum of 2,2′-bipyridine, protons H3(3′) are further downfield than H5(5′) at δ 8.40 and 7.23, respectively (Table IV). The larger than expected shift is

Table IV. Proton NMR Frequencies

H	Qpy (3)	$[QpyMe]^+$ (4)	$[QpyMe_2]^{2+}$ (5)	2,2′-bpy[28]	4,4′-bpy[28]
H2					8.70
H3	8.68	5.71	8.91	8.40	7.49
H4				7.74	
H5	7.68	8.00	8.20	7.23	7.49
H6	8.80	8.87	9.02	8.65	8.70
H2′					
H3′	8.68	8.56	8.91	8.40	8.70
H4′				7.74	
H5′	7.60	7.81	8.20	7.23	7.49
H6′	8.80	8.75	9.02	8.65	8.70
H2″	8.68	9.08	6.16		
H3″	7.65	8.60	8.71		
H4″					
H5″	7.65	8.60	8.71		
H6″	8.68	9.08	9.16		
H2‴	8.68	8.67	9.16		
H3‴	7.65	7.75	8.71		
H4‴					
H5‴	7.65	7.75	8.71		
H6‴	8.68	8.67	9.16		

[a] Solutions in $CDCl_3$, bpy = bipyridine.

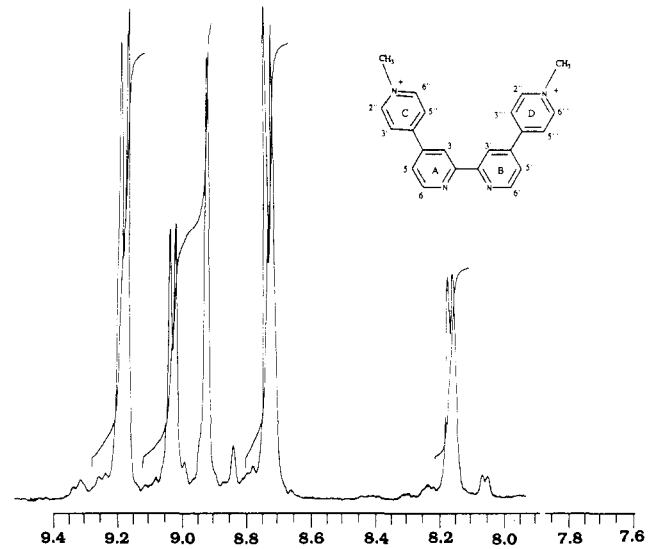


Figure 5. ^1H NMR spectrum (300-MHz) of $[QpyMe_2]^{2+}(I^-)_2$ (**5**) in DMSO-d_6.

thought to be due to a transoid conformation[24] in which the lone pairs on the nitrogen atoms deshield protons H3(3′) relative to H5(5′). The protons H3(3′) on the quaterpyridyl are likely to be subject to the same effect, and we believe them to lie under the multiplet (rel area 6) at δ 8.68. The proton chemical shifts for qpy are summarized in Table IV. Based on the ^{13}C and ^1H NMR spectra, we assign the structure **3** to the quaterpyridyl.

^1H NMR of $[QpyMe_2](I^-)_2$. The proton NMR spectrum of $[QpyMe_2](I^-)_2$ is shown in Figure 5. The numbering system used is illustrated in Figure 5, and Table IV summarizes the δ values for the signals in the spectrum. Integration of the spectrum of $[QpyMe_2](I^-)_2$ indicates that there are three aliphatic protons (δ 4.41) and 14 aromatic protons. The far downfield position of the singlet confirms that the methyl group is located on a quaternized nitrogen atom, and not on a ring carbon.

As is the case with the parent quaterpyridyl, protons on ring C (D) are of the type AA′XX′, and those on ring A (B) are AMX. Protons on ring C form apparent doublets

(24) Castellano, S.; Gunther, H.; Ebersole, S. *J. Phys. Chem.* **1965**, *69*, 4166.

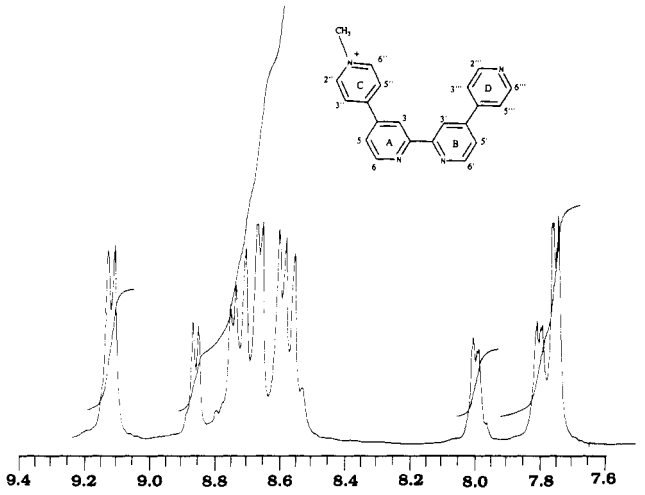


Figure 6. ^{1}H NMR spectrum (300-MHz) of [QpyMe]$^+$(I$^-$) (4) in DMSO-d_6.

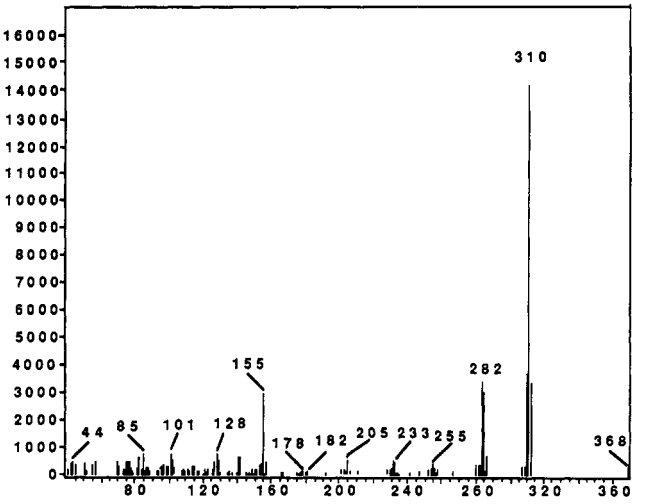


Figure 7. Mass spectrum (70eV) of Qpy (3).

at δ 8.71 (rel area 4) and δ 9.16 (rel area 4). The farthest downfield of these doublets at δ 9.16 is assigned to protons H2″ (6″), and protons H3″(5″) are in the upfield doublet at δ 8.71. In contrast to the parent quaterpyridyl, the three protons on ring A are clearly resolved in the spectrum. The farthest downfield of these is H6(6′) (doublet rel area 2) at δ 9.02. The protons farthest upfield in the aromatic region are H5(5′) at δ 8.20. The signal is broadened in comparison to that for H6(6′), and the splitting in the AMX quartet more evident. This is because the meta coupling constant $J_{3,5}$ is larger than the para, $J_{3,6}$. The final proton of the trio, H3, is nearly a singlet (rel area 2) at δ 8.91, due to the extremely small magnitude of both $J_{3,5}$ and $J_{3,6}$.

The ^{13}C NMR spectrum indicates that the molecule contains two environmentally equivalent methyl groups, that is, on either rings C and D, or on A and B. The important protons regarding the position of the methyl groups to rings C and D are those protons ortho to the nitrogen atoms, protons H6(6′) on rings A and B and H2″(2‴), H6″(6‴) on rings C and D. In the spectrum of the parent quaterpyridyl, the ortho protons associated with rings A and B are the farthest downfield at δ 8.80, with the ortho protons on rings C and D at δ 8.68. In the spectrum of the diquat, the protons in the ortho positions of rings C (H2″(6″)) and D (H2‴(6‴)) are further downfield than those on disubstituted rings A and B. If quaternization were to occur on rings A and B, the protons, in the spectrum of the diquat, on the disubstituted rings A and B (protons H6(6′)) would be the farthest downfield in the spectrum, not those on rings C and D.

^{1}H NMR of [QpyMe]$^+$(I$^-$). The spectrum of [QpyMe]$^+$(I$^-$) is shown in Figure 6. Integration of the spectrum indicates the presence of three aliphatic protons (singlet δ 4.40) and 14 pyridine protons. The position of the singlet is in the range expected for protons on a methyl quaternized pyridine ring. Figure 6 illustrates the numbering system used in the following discussion, and it is the same as that used for the interpretation of the spectrum of the diquat and the parent quaterpyridyl. Protons on rings C and D are of type AA′XX′, and rings A and B contain protons of type AMX. As in the spectrum of the diquat, protons H2″(6″) are the farthest downfield (δ 9.16), and these protons are observed at δ 9.08 (doublet rel area 2) in the spectrum of 4. The corresponding doublet (rel area 2) for the protons H3″(5″) is at δ 8.60.

The protons on ring D, H2‴(6‴) and H3‴(5‴), appear in the pair of doublets (rel area 2) at 8.67 (rel area 2) and δ 7.75 (rel area 2). The splitting of the doublet into a quartet is more obvious in the protons on ring D than C and allows the assignments of the quartets at δ 8.67 and 7.75 to be coupled to one another, and independent of the doublets at δ 9.08 and 8.60. The H6 signal in the spectra of the monoquat is the farthest downfield of any signal on rings A and B at δ 8.87 (rel area 2). Protons H3 and H3′ are likely to appear as singlets, as are the analogous proton in the spectrum of the diquat, and H3 will be farthest downfield at δ 8.71 (rel area 1). The signal for H6′ is at δ 8.57 (rel area 1). The last two assignments are of the distorted doublets (rel area 1) at δ 8.00 and 7.81, due to H5 and H5′, respectively.

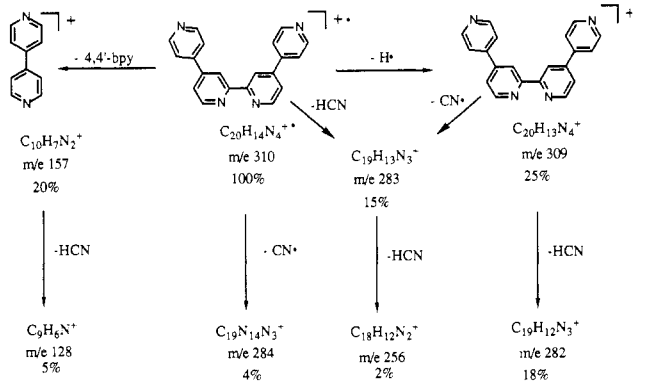
On the basis of a similar argument to that above for the diquat, ortho protons on ring C (H2″(6″) are further downfield than ortho protons on ring A (protons H6′) as a result of quaternization occurring on ring C, and the proton NMR spectrum is consistent with the structure 4.

Mass Spectrum of Qpy (3). The dominant fragmentation pathways in 2,2′-bipyridine[25] and 4,4′-bipyridine[26] are the expulsion of H•, CN•, HCN, and to a lesser extent C_2H_2. The base peak in both the mass spectra is the molecular ion, and hydrogen atom expulsion from the molecular ion gives the largest fragments (M − 1) in both 4,4′-bipyridine[26] (44% of base peak) and 2,2′-bipyridine[25] (42%). Expulsion of HCN from the molecular ion is favored over the loss of CN• in both 4,4′-bipyridine[26] (10% to 6%) and 2,2′-bipyridine[25] (20% to 10%). The expulsion of HCN greatly dominates the expulsion of H•, CN• or C_2H_2 from the M − 1 ion. High resolution mass spectra were used to discriminate the loss of CN• from the loss of C_2H_2, and it was found that expulsion of CN• dominates in both 2,2′-bipyridine[25] and 4,4′-bipyridine.[26] Pyridine–pyridine bond fission was found to be an important pathway in the fragmentation of 2,2′,2″-terpyridyl.[27] Doubly charged molecular ions are also significant in the spectra of 4,4′-bipyridine[26] (3.8%), 2,2′-bipyridine[25] (4.0%), and 2,2′,2″-terpyridyl (5.8%).[27]

The 70-eV mass spectrum of 2,2′:2,4″:2′,4‴-quaterpyridine (3) is shown in Figure 7. The base peak in the spectrum is molecular ion $C_{20}H_{14}N_4^+$ at m/e 310. The

(25) Keats, N. G.; Summers, L. A. *J. Heterocycl. Chem.* **1976**, *13*, 369.
(26) Keats, N. G.; Summers, L. A. *J. Heterocycl. Chem.* **1976**, *13*, 753.
(27) Osbourne, A. G. *Spect. Lett.* **1972**, *10*(10), 777.
(28) De Koning, A. J.; Budzelaar, P. H. M.; Boersma, J.; Van Der Kerk, G. J. M. *J. Organomet. Chem.* **1980**, *199*, 153–169.
(29) Spotswood, T. McL.; Tanzer, C. I. *Aust. J. Chem.* **1967**, *20*, 1227–42.

Scheme I



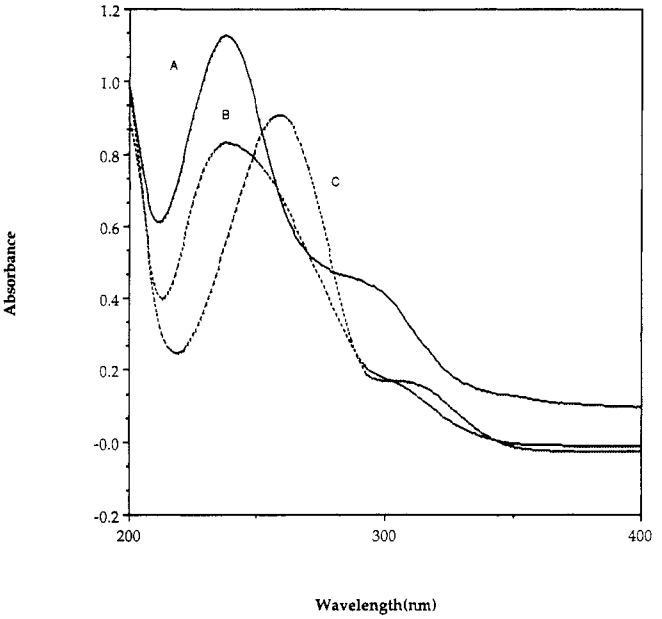


Figure 8. Ultraviolet spectra of 1×10^{-5} M solutions of compounds (A) **3**, (B) **4**, and (C) **5**.

largest fragment (Scheme I) results from the loss of a hydrogen atom from the molecular ion $C_{20}H_{13}N_4^+$ (25% of the base peak). Loss of HCN then gives $C_{19}H_{12}N_3^+$, *m/e* 282 (18%). Expulsion of HCN from the molecular ion results in $C_{19}H_{13}N_3^+$, *m/e* (15%), and of CN• results in the $C_{19}H_{14}N_3^+$ at *m/e* 284. It is likely that loss of C_2H_2 from the molecular ion also contributes to this peak. The peak at *m/e* 155 (20%) results from C–C bond fission, giving 4,4′-bipyridinium cation $C_{10}H_7N_2^+$, and it is also likely that the M^{2+} ion $C_{20}H_{14}N_4^{2+}$ contributes to the intensity of this peak. The bipyridinium cation then expels HCN to give the ion $C_9H_6N^+$, *m/e* 128 (5%).

Absorption Spectra. Figure 8 shows the absorption spectra of **3**, **4**, and **5** (the latter two as their iodide salts). The parent quaterpyridyl **3** shows strong bands at 290 nm and 238 nm. These are shifted to the red in the corresponding spectra of the mono- and diquaternary salts. However, while the spectrum of the monomethyl quaternary salt is broader than that of the parent quaterpyridyl, that of the dimethyl quaternary salt is essentially identical with that of the parent quaterpyridyl except for the red shift. In fact, the general appearance of the spectrum of the monomethyl salt in the region 320–230 nm can be approximated by summing the spectra of the parent quaterpyridyl and the dimethyl salt and dividing the intensity by two. This suggests that the 4,4-bipyridine and 4,4-monomethylpyridinium units contribute independently to the spectra.

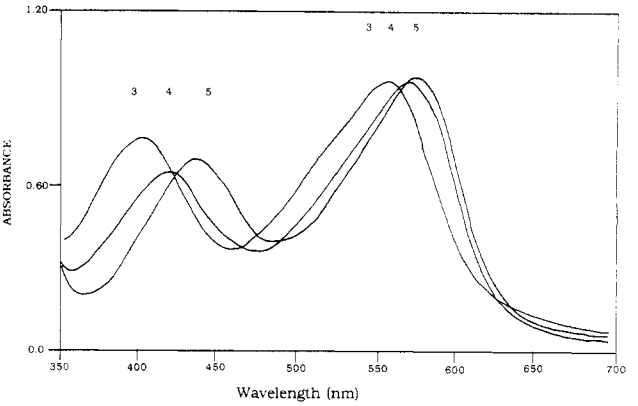


Figure 9. Visible spectra of ferrous complexes of **3**, **4**, and **5**.

Complexation. In order to test the chelating properties of qpy and its methylated complexes, as well as to confirm the availability of diimine nitrogens for complexation, ferrous complexes of **3**, **4**, and **5** were prepared. All three form deeply purple colored complexes upon addition of ferrous ammonium sulfate to methanolic solutions of the quaterpyridyls. The absorption spectra, which consist of MLCT bands, show a shift to lower energy with the addition of each methyl group (Figure 9). Complexation to ruthenium(II) is also possible. This creates luminescent complexes to be described in later papers of this series.

Cyclic Voltammetry of 4 and 5 as Their Hexafluorophosphate Salts. The voltammogram of the monomethyl salt of qpy shows one reversible couple at $E^{\circ\prime}$ = –0.79 V if the scan is performed from 0 to –1.2 V (Figure 10a). The position of the wave is independent of scan rate, and the ratio of the current for the cathodic half wave to the anodic is 0.98. In addition, there are no changes to the voltammogram after 20 scans at 100 mV/s. Extending the lower scan boundary to –2.1 V reveals several additional waves. The first on the anodic scan occurs at –1.66 V. The voltammogram, with these scan limits, quickly decomposes after a few scans at 100 mV/s. The ratio of the cathodic current to the anodic on the first wave ($E^{\circ\prime}$ = –0.79 V) decreases with each scan. The diquaternary salt shows two anodic and two corresponding cathodic reductions when scanned from 0.0 to –1.2 V (Figure 10b). The cathodic waves are at –0.84 and –0.92 V, and the cathodic portions are approximately –0.85 and –0.71 V. Because of the close spacing of these waves, there is some uncertainty in the calculation of their half-wave ($E^{\circ\prime}$) potentials. The ratios of the currents (cathodic to anodic) on both the waves is in excess of 0.98, indicative of a reversible process. $E^{\circ\prime}$ values for the waves are –0.78 and –0.86 V, respectively. The positions of the waves along the potential axis are independent of scan rate. Multiple scans produce no changes in the voltammogram. Scanning from 0.0 to –2.1 V gives results similar to that of the monomethyl salt, the current on the cathodic scan decreases, eventually falling into the base line, upon multiple scans at 100 mV/s.

The electrochemical behavior of the monoquat ion **4** is similar to that for *N*-methyl-4,4′-bipyridinium cation (under identical conditions as for **4**), in which the first reduction occurs at –0.84 V (measured vs the SCE). This potential is, within experimental error, the same as the first reduction in the monoquat (Scheme II). The diquat, ion **5**, contains two reductions in this potential region, at –0.84 and –0.92 V (Scheme II). The first reduction in the diquat forms the radical cation **8**, which can be further reduced to species **9**. Using simple resonance considerations, the species **9** must exist as a diradical. The electrochemical behavior of **5** is dissimilar to that of other viologens, such

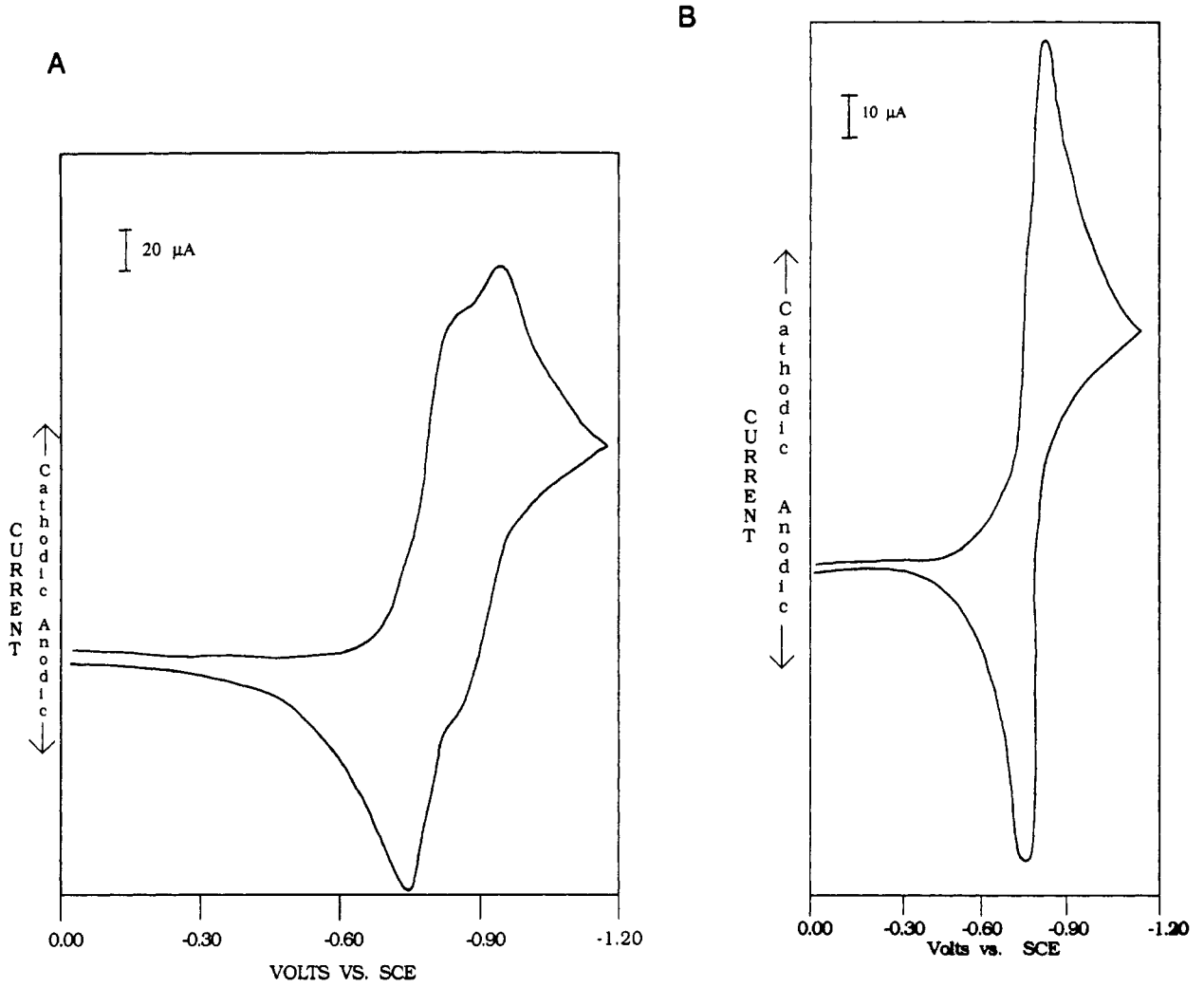
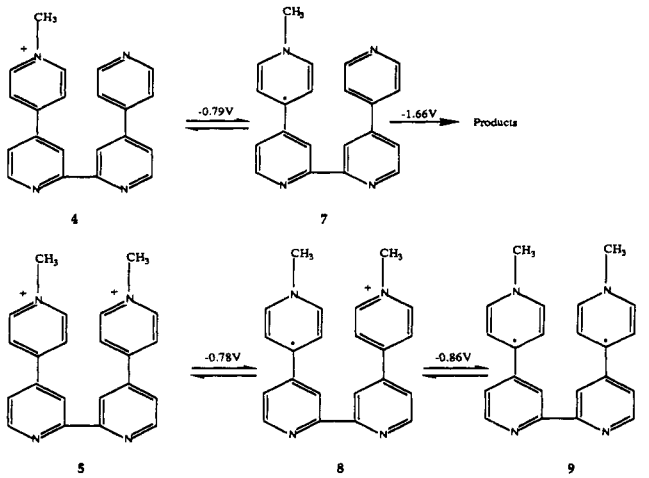
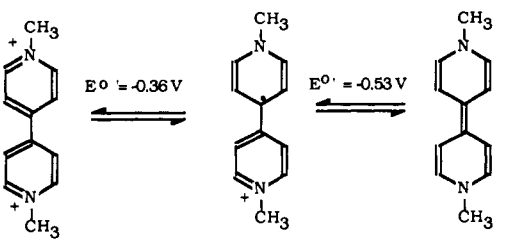


Figure 10. Cyclic voltammograms of (a) monomethyl quaternary salt **5** in acetonitrile and (b) dimethyl quaternary salt **6** in acetonitrile, conditions as described in Experimental Section.

Scheme II



Scheme III



as methyl viologen (Scheme III). In the CV of methyl viologen the two reduction waves are well spaced, and fully reversible. The diquat **5** behaves as two independent *N*-methyl-4,4'-bipyridinium units.

Conclusions

We report an efficient preparation of 2,2':4,4'':4',4'''-quaterpyridyl and have found conditions for selective quaternization based on the differing reactivities of the different types of nitrogen atoms present in the ligand. The redox chemistry of the dimethyl quaternary salt of the quaterpyridyl was explored by cyclic voltammetry. Addition of two electrons produces a diradical. This establishes the potential for the preparation of metal complexes in which two electrons can be carried on a single ligand. The quaterpyridyls described here will provide excellent building blocks for the construction of supermolecules containing clusters of photoactive and redox-active sites.

Acknowledgment. A.D.B. acknowledges PSC-BHE Grant 668256 from the City University of New York.

Registry No. **3**, 125330-07-6; **4**·I^-, 125330-08-7; **4**·PF_6^-, 125330-11-2; **5**·$2I^-$, 125330-09-8; **5**·$2PF_6^-$, 125330-13-4; **6**, 125330-14-5; Pyr, 110-86-1; 4,4'-bpy, 553-26-4; 2,2'-bpy, 366-18-7; 2,4'-bpy, 581-47-5; Fe, 7439-89-6.