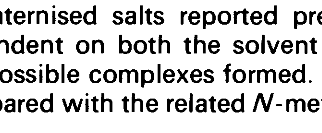
An Electron Spin Resonance, ENDOR, TRIPLE Resonance, and INDO Study of the Radicals formed by the Reduction of Monoquaternised *N*-Alkyl- and *N*-Aryl-4,4′-bipyridylium Salts

Dennis W. Clack, Jeffrey C. Evans,* Caroline R. Morris, and Christopher C. Rowlands
Chemistry Department, University College, Cardiff, CF1 1XL

The radicals formed by the reduction of *N*-monoquaternised-4,4′-bipyridylium salts (both alkyl and aryl) were studied by electron spin and multiple resonance and INDO calculations. Unlike the diquaternised salts reported previously,[1,2] the radicals formed by monoquaternary salts are highly dependent on both the solvent and the reductant used and this behaviour is described in terms of the possible complexes formed. The neutral radicals of *N*-methyl- and *N*-phenyl-4,4′-bipyridylium are compared with the related *N*-methyl-*N*′-phenyl-4,4′-bipyridylium diquaternised radical cation.

Although many uses have been described for the diquaternary derivatives of 4,4′-bipyridyl, for instance as herbicides,[3] electrochromic displays,[4] and film development accelerators,[5] far less interest has been shown in the monoquaternised compounds. Since their initial preparation by Emmert in 1923,[6] only a few uses for them have been described[7–9] and little is known of their radical chemistry.

Ross and Krieger[10] in their study of monoquaternary and diquaternary salts (symmetrical and asymmetrical) of 4,4′-bipyridyl, were unable to reduce the *N*-methyl- and *N*-ethyl-4,4′-bipyridylium salts with alkaline sodium dithionite solution although they could routinely obtain radicals from the diquaternary salts using the same reductant. Roullier and Laviron[11] were able to produce radicals by electrochemical reduction of *N*-methyl-4,4′-bipyridylium in aqueous solution but since they operated entirely in acidic media (pH 2—5.3), the species studied was the radical cation (1) and not the neutral radical.



(1)

In this study of the monoquaternised derivatives, no radicals were formed by irradiation of a solution of the salt in alcohol and it is clear that $E_{\frac{1}{2}}$ is substantially more negative than for the corresponding diquaternised compounds. The radicals obtained by reduction of the monoquaternised salt, using several methods, were characterised and their differences explained in terms of the probable species formed.

Experimental

Materials.—*N*-Phenyl-4,4′-bipyridylium chloride was kindly provided by I.C.I. and used without further purification. *N*-(2-Pyrimidyl)- and *N*-alkyl-4,4′-bipyridylium monoquaternary salts were prepared by the reaction between 1:1 molar ratios of 4,4′-bipyridyl and 2-chloropyrimidine and the appropriate iodoalkane, respectively. The *N*-methyl-*N*′-phenyl-4,4′-bipyridylium diquaternary salt was prepared by the reaction of the *N*-phenyl-monoquaternary salt with excess of iodomethane. Zinc complexes of the monoquaternary salts were prepared in a manner similar to that of Ferraro and Davies.[12] The structures and purities of the prepared salts were determined by ^{1}H n.m.r., CHN analysis, and field desorption mass spectrometry.

N-(2-*Pyrimidyl*)-4,4′-*bipyridylium chloride* [see structure (2)]: δ 10.05 (2 H, d, 2,6), 9.09 (2 H, d, pyrimidyl 4,6), 8.76 (2 H, d, 2′,6′), 8.60 (2 H, d, 3,5), 7.97 (2 H, d, 3′,5′), and 7.85 (1 H, t, pyrimidyl 5); *m/z* 235.0 (100%) and 156.0 (1.17).

Zinc complex of N-*methyl*-4,4′-*bipyridylium chloride* (Found: C, 38.41; H, 3.30; N, 8.11. Calc. for $C_{11}H_{11}Cl_3N_2Zn$: C, 38.52; H, 3.23; N, 8.17%).

Zinc complex of N-*phenyl*-4,4′-*bipyridylium chloride* (Found: C, 47.60; H, 3.64; N, 6.74. Calc. for $C_{16}H_{13}Cl_3N_2Zn$: C, 47.44; H, 3.24; N, 6.92%).

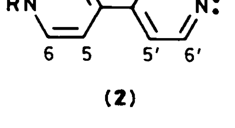
Zinc complex of N-(2-*pyrimidyl*)-4,4′-*bipyridylium chloride* (Found: C, 41.37; H, 2.69; N, 13.42. Calc. for $C_{14}H_{11}Cl_3N_4Zn$: C, 41.31; H, 2.72; N, 13.77%).

Procedure.—Reduction of the monoquaternised salts by (i) a freshly prepared zinc film in methanol, (ii) zinc in acetonitrile, and (iii) an alkali metal film in tetrahydrofuran (THF) or 2-methyl-THF or at the cathode of an electrochemical cell in dimethylformamide (DMF) with 10^{-1}M-tetrabutylammonium perchlorate as supporting electrolyte generated several different species. Radicals prepared by method (i) decomposed within days but those generated by methods (ii) or (iii) were stable for several weeks under anaerobic conditions. The diquaternary salt *N*-methyl-*N*′-phenyl-4,4′-bipyridylium was reduced by tin in methanol or by photolysis, the stable blue-green radical cation formed being independent of the method of reduction. The zinc complexes of the *N*-phenyl-and *N*-methyl-monoquaternary salts were reduced by zinc in methanol while that of *N*-(2-pyrimidyl)-4,4′-bipyridylium was reduced by tin in methanol and all three were unstable, decomposing within days.

The e.s.r., ENDOR, and TRIPLE resonance spectra were recorded on a Varian E109 e.s.r. spectrometer interfaced with a Bruker ENDOR/TRIPLE resonance system immediately after mixing. Computer simulations of the e.s.r. spectra were carried out using a fast Fourier transform program[13] on a Horizon North Star microprocessor.

Results and Discussion

(i) *Reduction by Zinc in Methanol.*—

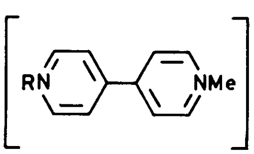


R = 2-pyrimidyl, phenyl, methyl, ethyl, or propyl

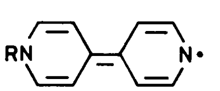
(2)

Radicals of the *N*-alkyl monoquaternary salts reduced by zinc in methanol were blue while *N*-aryl salts were green. The intensity of the radicals produced decreased with decreasing temperature as previously described for *N,N'*-disubstituted 4,4'-bipyridylium radical cations.[1,2] Figures 1 and 2 show the ENDOR spectra of the *N*-(2-pyrimidyl)- and *N*-phenyl-4,4'-bipyridylium radicals, respectively while the e.s.r. spectrum of the *N*-methyl-4,4'-bipyridylium radical run within 24 h of preparation is shown in Figure 3.

Reduction of compounds of type (**2**) by zinc in methanol gave, in all cases, radicals of type (**3**)



(3)



(4)

Thus, the ENDOR spectrum of *N*-(2-pyrimidyl)-4,4'-bipyridylium was identical to the spectrum of the *N*-methyl-*N'*-(2-pyrimidyl)-4,4'-bipyridylium radical cation[14] (reduced by irradiation in methanol, by zinc or by tin), the reduction of *N*-methyl-4,4'-bipyridylium gave the paraquat radical cation ($PQ^{+\bullet}$) and so on. Table 1 summarises the radicals formed.

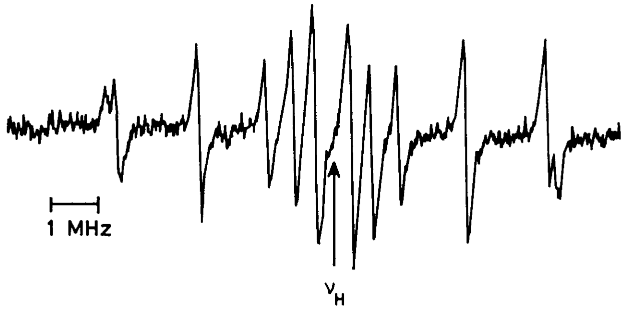


Figure 1. ENDOR spectrum of *N*-(2-pyrimidyl)-4,4'-bipyridylium radical reduced by zinc in methanol

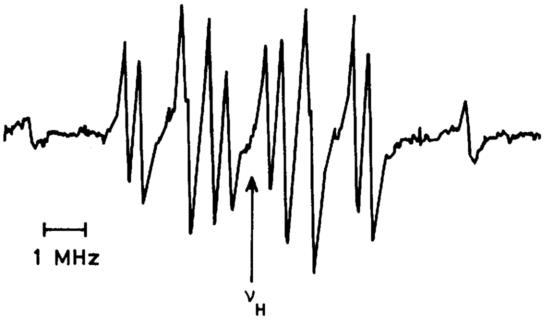


Figure 2. ENDOR spectrum of *N*-phenyl-4,4'-bipyridylium radical reduced by zinc in methanol

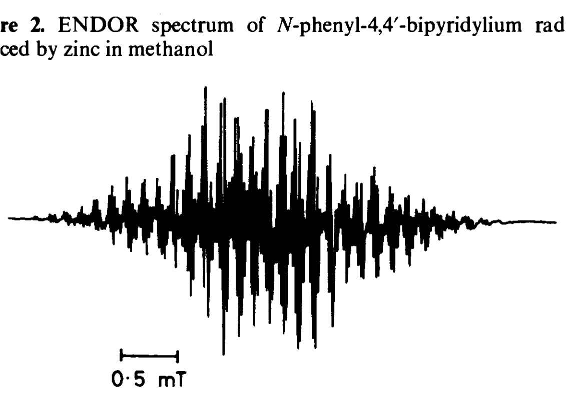
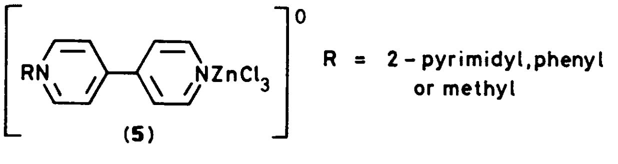


Figure 3. E.s.r. spectrum of *N*-methyl-4,4'-bipyridylium radical reduced by zinc in methanol

The nucleophilic attack on methanol solvent and abstraction of the methyl group is not a reaction associated with the unquaternised nitrogens of 4,4'-bipyridyl or its monoquaternised salts. The formation of paraquat by the reaction between 4,4'-bipyridyl and methanol requires very stringent forcing conditions[15] (200 °C, 200 atm, and in the presence of concentrated HCl) and it proved impossible in the course of this work to generate paraquat by heating *N*-methyl-4,4'-bipyridylium in methanol at atmospheric pressure no matter how long the mixture was allowed to reflux. Hence it appears that the unquaternised nitrogen of these monoquaternised salts will only react with methanol and affect the nucleophilic substitution of the OH group (which in the absence of acid is a very poor leaving group) once the neutral radical (**4**) has been formed by reduction with zinc.

From the above evidence it is most likely that the reaction sequence by which radicals of type (**3**) are produced starts by reduction of the monoquaternised salt to its neutral radical (**4**) by zinc and the immediate complexation of the Zn^{2+} by either the bipyridylium cation (**2**) or the neutral radical (**4**).

That the monoquaternised 4,4'-bipyridylium cations react with Zn^{2+} ions has been unequivocally established by mixing aqueous solutions of $ZnCl_2$ and the monocation to form zinc complexes in a manner similar to Ferraro and Davies.[12] Elemental analysis (C, H, N, Cl) both in this study and in previous work[16] indicates that the species formed by mixing aqueous solutions of $ZnCl_2$ and a monoquaterised salt of type (**2**) (R = 2-pyrimidyl, phenyl, or methyl) are of general formula (**5**).



(5)

When complexes of type (**5**) were reduced by zinc or tin in methanol, the ENDOR spectra obtained revealed that radicals of type (**3**) (R = 2-pyrimidyl, phenyl, or methyl) had been formed.

Since reduction, by zinc, of a monoquaternised derivative of 4,4'-bipyridyl and a zinc complex of the same salt in methanol yield identical radicals, it seems most probably that a labile Zn^{2+} complex of the monoquaternised salt is formed and breaks down to produce radicals of type (**3**) [though we do not discount the possibility that neutral radicals of type (**4**) can directly attack methanol in what would be an S_N2 reaction].

The origin of the methyl group of radicals (**3**) when R = 2-pyrimidyl or phenyl is quite clear but for the *N*-methyl-4,4'-bipyridylium radical, it is possible that the neutral radical or the labile zinc complex react with the monocation and abstract a methyl group from it to form $PQ^{+\bullet}$ (and 4,4'-bipyridyl as a side product). To investigate this possibility, a quantity of *N*-trideuteriomethyl-4,4'-bipyridylium was reduced on zinc in MeOD and left until the ENDOR spectrum revealed lines of coupling 0.413 mT which represent abstraction of a methyl group from the solvent rather than a CD_3 group from another monoquaternised species (approximately two weeks).

There is clear evidence in the e.s.r. spectra of the *N*-methyl-, 2,6-dideuterio-*N*-methyl-, and *N*-trideuteriomethyl-4,4'-bipyridylium salts reduced on zinc in methanol for a transition from a monoalkylated radical which is probably a zinc complex radical (see Figure 3 which shows the characteristic 1:3:3:1 pattern of a single methyl group) to the dialkylated radical cation ($PQ^{+\bullet}$ or a deuteriated analogue). The ENDOR spectrum of the zinc complex of the *N*-methyl compound reduced on zinc in

Table 1.

[Monoquaternised salt]$^+$	Reductant, solvent	[Radical obtained]$^{+\bullet}$
N-(2-Pyrimidyl)-4,4′-bipyridylium	Zn,MeOH	*N*-Methyl-*N*′-(2-pyrimidyl)-4,4′-bipyridylium[14]
N-Phenyl-4,4′-bipyridylium	Zn,MeOH	*N*-Methyl-*N*′-phenyl-4,4′-bipyridylium[14] (Figure 2)
2,6-Dideuterio-*N*-phenyl-4,4′-bipyridylium	Zn,CD_3OD	2′,6′-Dideuterio-*N*-(trideuteriomethyl)-*N*′-phenyl-4,4′-bipyridylium
N-Methyl-4,4′-bipyridylium	Zn,MeOH	*N*,*N*′-Dimethyl-4,4′-bipyridylium ($PQ^{+\bullet}$)
2,6-Dideuterio-*N*-methyl-4,4′-bipyridylium	Zn,CD_3OD	2,6-Dideuterio-*N*-methyl-*N*′-(trideuteriomethyl)-4,4′-bipyridylium
N-Trideuteriomethyl-4,4′-bipyridylium	Zn,CD_3OD	*N*,*N*′-Bis(trideuteriomethyl)-4,4′-bipyridylium ($[^2H_6]PQ^{+\bullet}$)
N-Ethyl-4,4′-bipyridylium	Zn,MeOH	*N*-Ethyl-*N*′-methyl-4,4′-bipyridylium[14]
N-(n-Propyl)-4,4′-bipyridylium	Zn,MeOH	*N*-Methyl-*N*′-(n-propyl)-4,4′-bipyridylium[14]

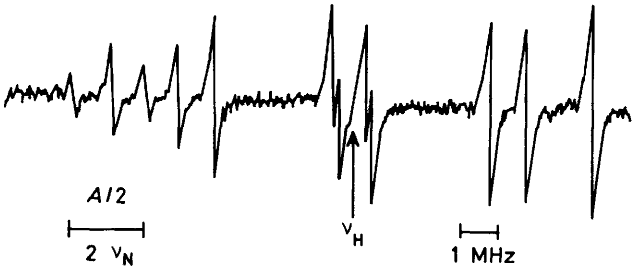


Figure 4a. ENDOR spectrum of *N*-methyl-4,4′-bipyridylium radical reduced by potassium in THF

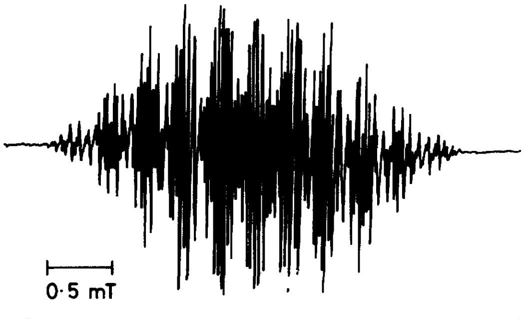


Figure 4b. E.s.r. spectrum of *N*-(trideuteriomethyl)-4,4′-bipyridylium radical reduced by potassium in THF

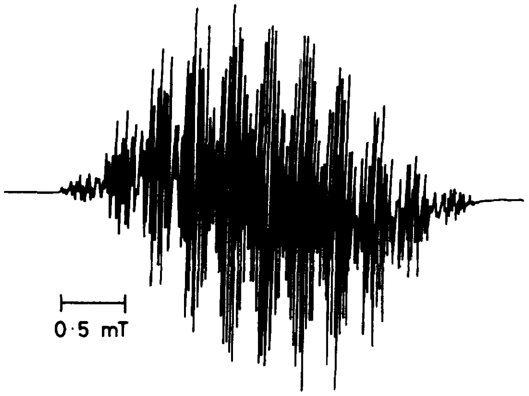


Figure 4c. Computer simulation of e.s.r. spectrum of *N*-(trideuteriomethyl)-4,4′-bipyridylium radical reduced by potassium in THF

methanol and run within one hour of preparation has shown, in addition to the expected coupling of $PQ^{+\bullet}$ (-0.139, -0.165, and $+0.413$ mT), less intense lines of coupling 0.112, 0.190, and 0.401 which do not originate from the neutral radical and which are probably due to the radical of the zinc complex.

A study of the radical generated by the reaction of 4,4′-bipyridyl and $ZnPh_2$ in THF with potassium by Kaim[17] revealed that the couplings of the nitrogens and the bipyridyl protons differed very little from the couplings of the unco-ordinated bipyridyl and it therefore seems that the zinc–nitrogen bond is weak and has little effect on the couplings of the bipyridyl ligand or, by analogy, on the monoquaternised 4,4′-bipyridylium ligand.

(ii) *Reduction on Zinc in Acetonitrile.*—The radical of the *N*-phenyl-4,4′-bipyridylium salt reduced by zinc in acetonitrile was purple. Unlike radicals generated by method (i), radicals produced by methods (ii) and (iii) did not change in concentration on lowering the temperature.

Both the e.s.r. and ENDOR spectra of the radical produced by the reduction of *N*-phenyl-4,4′-bipyridylium by zinc in acetonitrile (which yield proton couplings of 0.335, 0.242, 0.079, 0.038, and 0.018 mT) were quite unlike the spectra of the *N*-methyl-*N*′-phenyl radical cation. Indeed, it is hard to imagine that the nucleophilic attack of the *N*-phenyl salt (or its radical) on the solvent, which breaks the C–O bond of methanol, could break the C–C bond of acetonitrile to form the *N*-methyl-*N*′-phenyl-4,4′-bipyridylium radical.

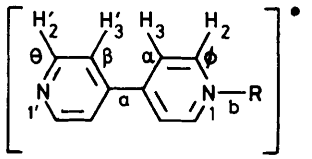
The reaction between zinc halides and acetonitrile has long been known to produce complexes of general formula $Zn{\cdot}X_2{\cdot}2MeCN$ ($X = Cl^-, Br^-, I^-$).[18,19] It is proposed that when *N*-phenyl-4,4′-bipyridylium chloride is dissolved in MeCN and passed over a zinc film, the initial reaction is reduction of the salt to the neutral radical as described for methanol solvent. The Zn^{2+} ions may then form a tetrahedral complex as before with the monoquaternised salt or its radical in one of the co-ordinate positions while acetonitrile and chloride ions compete for the other three postions. Since there is no evidence for any unco-ordinated bipyridylium radicals in acetonitrile, they must all be bound in stable complexes with zinc and it seems that an acetonitrile ligand must occupy at least one (if not two or all three) of the remaining co-ordinate positions to account for the increased stability of the complex (relative to the stability of the complex formed in methanol).

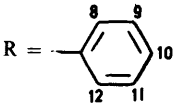
The possibility that complex ions such as $ZnCl_2(MeCN)_2$ are formed and may go on to exchange ligands or disproportionate as described by Libus[20] is not discounted but this could not be followed in the course of this e.s.r. experimentation (no couplings from ^{67}Zn, 4% abundance, $I = 5/2$ detected).

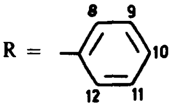
(iii) *Reduction on an Alkali Metal in* THF.—The radicals prepared by reduction of both *N*-alkyl and *N*-aryl-4,4′-bipyridylium monoquaternary salts on alkali metals in THF were red. The ENDOR spectrum of the *N*-methyl-4,4′-bipyridylium radical reduced on potassium in THF together with the e.s.r. spectrum of its *N*-trideuteriomethyl analogue and the latter's computer-simulated spectrum are shown in Figures 4a, 4b, and 4c, respectively.

Reduction of the monoquaternised salts of type (**2**) (R = phenyl, methyl, ethyl, or n-propyl) on sodium or potassium produced the same species as reduction at the cathode of an electrochemical cell (see Table 2). It therefore seems that the neutral monoquaternised bipyridyl radical and the alkali metal

Table 2. Observed and theoretical coupling constants for the monoquaternised bipyridylium neutral radicals



	Coupling constants (mT)					
	1	1′	2	2′	3	3′
$R = \overset{7}{\mathrm{Me}}$						
Observed	+0.533	+0.222	−0.338	−0.020	+0.048	−0.267
Theoretical a = 1.50 Å, b = 1.45 Å, α = β = 126°, θ = 120°, φ = 114°	+0.514	+0.197	−0.540	+0.090	+0.173	−0.203
$R = \overset{7}{\mathrm{C}}\mathrm{H_2}\text{-}\overset{8}{\mathrm{Me}}$						
Observed	+0.523	+0.224	−0.341	−0.020	+0.040	−0.265
$R = \overset{7}{\mathrm{C}}\mathrm{H_2}\text{-}\overset{8}{\mathrm{C}}\mathrm{H_2}\text{-}\overset{9}{\mathrm{Me}}$						
Observed	+0.517	*b*	−0.338	−0.017	+0.038	−0.267
R = 						
Observed	*b*	*b*	−0.419		0.092[a] 0.046[a]	−0.25
Theoretical a = 1.50 Å, b = 1.47 Å, α = β = 126°, θ = φ = 120°	+0.507	+0.190	−0.567	+0.088	+0.190	−0.198

	Coupling constants (mT)					
	7	8	9	10	11	12
$R = \overset{7}{\mathrm{Me}}$						
Observed	+0.468					
Theoretical a = 1.50 Å, b = 1.45 Å, α = β = 126°, θ = 120°, φ = 114°	+0.5004					
$R = \overset{7}{\mathrm{C}}\mathrm{H_2}\text{-}\overset{8}{\mathrm{Me}}$						
Observed	+0.265	−0.040				
$R = \overset{7}{\mathrm{C}}\mathrm{H_2}\text{-}\overset{8}{\mathrm{C}}\mathrm{H_2}\text{-}\overset{9}{\mathrm{Me}}$						
Observed	+0.267	−0.038	*b*			
R = 						
Observed						
Theoretical a = 1.50 Å, b = 1.47 Å, α = β = 126°, θ = φ = 120°		−0.097	+0.032	−0.069	+0.032	−0.09

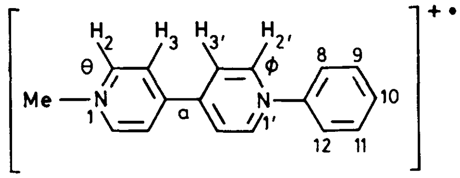
[a] See text. [b] Not determined.

ion are best represented as a solvent-separated ion pair rather than the type of intimate ion pair formed by reduction of pyrazine[21] or the covalently bonded radical complexes exemplified by the zinc complexes of (i) and (ii). In his work on the paramagnetic complexes formed between reduced 2,2′-bipyridyl and organometallic cations of type R_nM^+, Kaim[22] found a similar variation in the type of radical formed. Of the radicals studies $[(R_nM)\mathrm{bipy}]^{\bullet}$ where $R_nM^+ = K^+, Na^+, Li^+, PhMg^+, PhZn^+, Me_2Ga^+, PhBe^+, R_2Al^+$, the alkali metals at the beginning of the series formed ion pairs while the latter members formed genuine covalent complexes.

Assignment of Coupling Constants.—INDO calculations were carried out for these asymmetrically substituted bipyridyl radicals for a range of different geometries defined by the parameters a, b, θ, and φ (Table 2), employed previously for the symmetrically substituted radical species.[23] The two pyridine rings were assumed to lie coplanar.[23,24]

The proton coupling constants of the *N*-methyl-*N*′-phenyl-4,4′-bipyridylium radical cation[14] (which are in good agreement with the INDO calculations) indicate that this radical cation can be considered as two discrete moieties. On the *N*-methyl side of the radical, the *ortho* (2,6) protons may approach the methyl groups quite closely (see Table 3, θ = 114°) and as shown previously[23] the effect of this is that the coupling from the *ortho* bipyridyl protons (aH_2) is less than that of the *meta* bipyridyl protons (aH_3) on the methyl side (the protons are behaving like those of paraquat$^{+\bullet}$). However, on the *N*′-phenyl side, the steric bulk of the phenyl group hinders the approach of the *ortho* (2′,6′) protons (φ = 120°) so that $aH_{2'}$ is greater

Table 3. Observed and theoretical coupling constants for *N*-methyl-*N*′-phenyl-4,4′-bipyridylium radical cations



	Coupling constants (mT)											
	1′	1	2′	2	3′	3	7(Me)	8	9	10	11	12
Observed			−0.201	−0.097	−0.112	−0.184	+0.378	−0.064	+0.033	−0.059	+0.033	−0.064
Theoretical a = 1.40 Å, θ = 114°, φ = 120°	0.455	0.463	−0.130	−0.106	−0.101	−0.119	+0.428	−0.084	+0.031	−0.050	+0.031	−0.084

than $aH_{3'}$ as previously described[23] for the *N*,*N*′-diphenyl-4,4′-bipyridylium radical cation.

The coupling constants for the neutral radical derived from monosubstituted *N*-methyl-4,4′-bipyridylium (Table 2) show that unlike the asymmetrically diquaternised *N*-methyl-*N*′-phenyl-4,4′-bipyridylium radical cation (see above) the spin distribution in the two pyridyl rings cannot be regarded as derived from independent moieties of the 4,4′-bipyridyl anion[24] and paraquat cation[23] systems. In these latter two species the pyridyl ring proton coupling constants are all negative in sign.

For the neutral radical the experimental results and assignments based on deuteriated analogues are in reasonable agreement with the INDO calculations. The calculated coupling constants for the two non-equivalent N atoms are in very good agreement with the observed values, where the value of the methyl nitrogen increases compared with paraquat while that of the unmethylated nitrogen atom decreases. The most significant change from paraquat cation and bipyridyl anion is that the coupling constant aH_3 is positive for the *N*-methyl radical and this change of sign is endorsed by the calculations. These also suggest that coupling constant $aH_{2'}$ is positive; however, its value is small.

The ENDOR spectra of the *N*-ethyl- and *N*-(n-propyl)-bipyridylium neutral radicals show the same set of four coupling constants instead of the expected six (no coupling expected from the methyl group of the propyl radical) presumably due to accidental degeneracies, and the general TRIPLE spectra of these radicals were of little value for the same reason. The spectra however show marked similarity to the *N*-methyl radical and by analogy with the latter, the four couplings could be assigned with some confidence.

The ENDOR spectrum of the *N*-phenyl-4,4′-bipyridylium neutral radical was poorly resolved but clearly shows four proton coupling constants (0.419, 0.25, 0.092, and 0.046 mT) with the possibility of a fifth small coupling at 0.008 mT.

The INDO calculations suggest that the coupling constants 0.419 and 0.25 may be reasonably assigned to positions 2 and 3′ respectively (*cf.* the *N*-methylpyridyl radical). It is not possible to assign unequivocally the remaining positions; however, the calculations again indicate a change of sign for the coupling constant at position 3, but this is calculated to be larger than either of the two unassigned coupling constants of 0.092 and 0.046 mT.

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