An Electron Spin Resonance, ENDOR, and TRIPLE Resonance Study of Methyl-substituted *N,N'*-Diphenyl-4,4'-bipyridylium Dichloride Radical Cations

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The e.s.r. and ENDOR spectra of the radical cations of *N,N'*-diphenyl-4,4'-bipyridylium dichloride (DPQ), *N,N'*-bis-(4-methylphenyl)-4,4'-bipyridylium dichloride (*p*-mDPQ), *N,N'*-bis-(3-methylphenyl)-4,4'-bipyridylium dichloride (*m*-mDPQ), *N,N'*-bis-(2-methylphenyl-4,4'-bipyridylium dichloride (*o*-mDPQ), and *N,N'*-bis-(2,4,6-trimethylphenyl)-4,4'-bipyridylium dichloride (T-mDPQ) in methanol were studied over a range of temperatures. Values for the hyperfine coupling constants are given at −40 °C. It was found that the radical cation concentrations of DPQ$^{+\cdot}$, *p*-mDPQ$^{+\cdot}$, *m*-mDPQ$^{+\cdot}$, and *o*-mDPQ$^{+\cdot}$ decreased with decreasing temperature, this change being reversible, whilst that of T-mDPQ$^{+\cdot}$ did not. We explain the reversible change with temperature in terms of a monomer–dimer equilibrium, and the absence of such an equilibrium in the case of T-mDPQ$^{+\cdot}$ as due to the lack of planarity of the molecule, because of steric hindrance between the methyl groups and the pyridyl *ortho*-protons. The thermodynamic constants $\Delta G°$, $\Delta H°$, and $\Delta S°$, obtained for the dimerisation equilibria, are reported.

The use of bipyridylium salts (also known as viologens) as photochromic or electrochromic displays is well established, and such ability has been related to their ease of reduction. This one-electron reduction is completely reversible. Current research has been involved in studying how the stereochemistry of the bipyridylium salts affects the ability of these compounds to undergo successive oxidation–reduction cycles.[1] In this paper we are extending earlier work[2] on *N,N'*-alkyl-substituted bipyridylium salts (which undergo reversible dimerisations through π–π^* bonding) to aryl, and methyl-substituted aryl, *N,N'*-substituted bipyridylium salts (I) with a view to investigating how the stereochemistry of the substituted group affects their chemical behaviour. Consequently, we have now synthesized 4,4'-bipyridylium compounds which have phenyl and methyl-substituted phenyl groups attached to the nitrogen atoms of the pyridyl rings, as shown in (I), thus introducing steric hindrance to dimerisation. The use of ENDOR and general TRIPLE resonance spectroscopy has enabled us to obtain, accurately, hyperfine coupling constants together with their relative signs, and to be able to measure changes in them on substitution of methyl groups. The thermodynamic constants of the monomer–dimer equilibrium were obtained by e.s.r.

Experimental

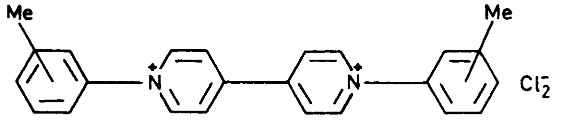
Materials.—*AnalaR methanol.* Dried (calcium sulphate), distilled under dinitrogen, and out-gassed on a high-vacuum system prior to use.

N,N'-*Diphenyl*-4,4'-*bipyridylium dichloride* (*DPQ*). Kindly provided by ICI Runcorn.

N,N'-*Bis*-(4-*methylphenyl*)-4,4'-*bipyridylium dichloride dihydrate* (p-*mDPQ*). Prepared by a similar method to that of Allen;[3] yellow crystalline product (Found: C, 64.7; H, 5.5; N, 6.0; Cl, 16.0%).

N,N'-*Bis*-(3-*methylphenyl*)-4,4'-*bipyridylium dichloride dihydrate*,[3] (m-*mDPQ*). Pale yellow crystals (Found: C, 65.3; H, 6.25; N, 6.4; Cl, 16.0%).

N,N'-*Bis*-(2-*methylphenyl*)-4,4'-*bipyridylium dichloride dihydrate*[3] (o-*mDPQ*). Yellow crystals (Found: C, 64.6; H, 5.4; Cl, 16.0%).



(I)

Calculated analysis for *p*-, *m*-, and *o*-mDPQ, C, 64.7; H, 5.8; N, 6.1; Cl, 15.5%.

N,N'-*Bis*-(2,4,6-*trimethylphenyl*)-4,4'-*bipyridylium dichloride dihydrate*[3] (*T-mDPQ*). Yellow crystals (Found: C, 67.4; H, 6.8; N, 5.2; Cl, 14.0%).

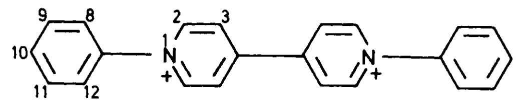
Calculated analysis, C, 67.1; H, 6.8; N, 5.6; Cl, 14.0%. The structures of the compounds were verified by n.m.r. spectroscopy.

Procedure.—Methanol solutions of the radical cations of the bipyridylium compounds were prepared as described previously[2] by reduction with zinc. The e.s.r. measurements were made using a Varian E109 spectrometer fitted with a variable-temperature unit E1002. ENDOR spectra were recorded using a Bruker Digital ENDOR unit, interfaced with the Varian E109 spectrometer. Radical cation concentration measurements were made by double integration of the e.s.r. signal and comparison with methanol solutions of diphenylpicrylhydrazyl under similar instrumental conditions.

Results

E.s.r., ENDOR, and TRIPLE Resonance Studies.—The technique of ENDOR enables one to obtain accurately hyperfine coupling constants (h.f.c.s) and also to measure small changes in the h.f.c.s so obtained. General TRIPLE experiments can then give information concerning the relative signs of the h.f.c.s. Consequently, these techniques were used to obtain the reported values in Table 1. Figure 1 shows the ^1H ENDOR spectra of *o*-mDPQ$^{+\cdot}$ and DPQ$^{+\cdot}$ as examples. It can be seen that the spectra contain groups of h.f.c.s centred about the free ^1H Lamor frequency (13.84 MHz at 325.0 mT). The assignments of the pyridyl coupling constant (for the methyl-

Table 1. Splitting constants (mT) for the radical cations $DPQ^{+\bullet}$, *p*-$mDPQ^{+\bullet}$, *m*-$mDPQ^{+\bullet}$, *o*-$mDPQ^{+\bullet}$, and T-$mDPQ^{+\bullet}$ at −40 °C



Radical cation	Position 1	2	3	8	9	10	11	12
$DPQ^{+\bullet}$	+0.380	−0.159	−0.140	−0.054	+0.031	−0.050	+0.031	−0.054
p-$mDPQ^{+\bullet}$	+0.380	−0.155	−0.140	−0.055	+0.030	+0.055[a]	+0.030	−0.055
m-$mDPQ^{+\bullet}$	+0.380	−0.158	−0.140	−0.053	−0.017[a]	−0.053	+0.028	−0.053
o-$mDPQ^{+\bullet}$	+0.400	−0.159	−0.150	+0.030[a]	+0.010	−0.022	+0.010	−0.036
T-$mDPQ^{+\bullet}$	+0.400	−0.156	−0.156	+0.024[a]	+0.008	+0.024[a]	+0.008	+0.024[a]

[a] Me groups.

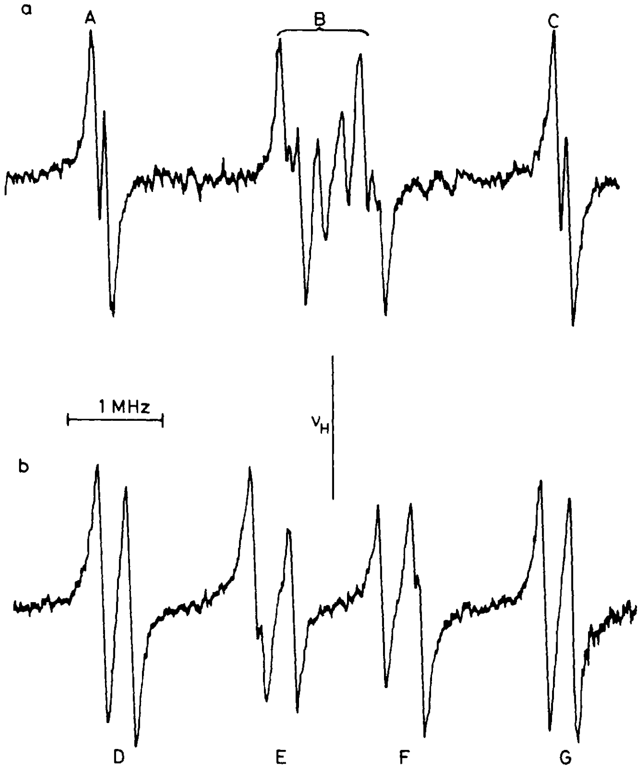


Figure 1. Proton ENDOR spectra of the radical cations *o*-mDPQ (a) and DPQ (b) in methanol at −40 °C. A, Pyridyl protons; B, phenyl and methyl protons; C, pyridyl protons; D, 2- and 3-pyridyl protons; E, 8-, 10-, and 9-phenyl protons; F, 9-, 10-, and 8-phenyl protons; G, 3- and 2-pyridyl-protons

substituted compounds) was carried out by deuteriation of the 2,2′-positions of the pyridyl ring. Figure 2 shows the ^1H and ^2H ENDOR spectrum for tetradeuteriated *o*-$mDPQ^{+\bullet}$.

It can be clearly seen that the pair of lines arising from the 2-position of the pyridyl ring have now disappeared from the proton ENDOR spectrum with the appearance of two lines centred about the free deuterium Lamor frequency, 2.12 MHz at 324.0 mT, *cf.* Figure 1a. The deuterium splitting was found to be 0.0255 mT which is approximately 1/6 of the proton value in this position. We believe this is the first time that deuterium ENDOR has been reported in these radical cations.

The assignment of the pyridyl proton hyperfine coupling constants for $DPQ^{+\bullet}$ has been previously made by us by selective deuteriation of the pyridyl ring.[4]

The methyl proton hyperfine coupling constants of the *o*-$mDPQ^{+\bullet}$ and *m*-$mDPQ^{+\bullet}$ were assigned on the basis of the relative sign determination as obtained from general TRIPLE resonance experiments. This is possible because when a methyl group replaces a proton a change in the sign of the hyperfine coupling constant can occur. Figure 3 shows the ENDOR and general TRIPLE resonance spectra of T-$mDPQ^{+\bullet}$. In this case only three h.f.c.s were observed in the proton ENDOR because the 2- and 3-pyridyl protons have become equivalent. The general TRIPLE resonance experiment Figure 3b shows the larger coupling to be opposite in sign to the remaining smaller two h.f.c.s. The *ortho*- and *para*-phenyl protons are of the same sign as the pyridyl proton, *i.e.*, negative. It can be seen, therefore, that substitution of a methyl group has resulted in a change of sign, *i.e.*, the 8-, 10-, 12-methyl protons are now opposite to the pyridyl protons and this results in the absorptions behaving differently during the general TRIPLE experiment.

In the case of the *p*-$mDPQ^{+\bullet}$, the result of a general TRIPLE experiment is inconclusive as the methyl protons and *ortho*-protons occur at the same frequency in the ENDOR spectrum. Consequently these peak heights do not change during a general TRIPLE resonance experiment as the effect of the opposite signs cancel.

Fast Fourier transform computer simulations[5] based on the assignments in Table 1 gave good agreement with all the experimental spectra.

Monomer–Dimer Equilibrium.—It was found that the e.s.r. spectra intensity decreased with decrease in temperature for the radical cations of $DPQ^{+\bullet}$, *p*-$mDPQ^{+\bullet}$, *m*-$mDPQ^{+\bullet}$, and *o*-$mDPQ^{+\bullet}$, but there was no change in intensity with temperature for T-$mDPQ^{+\bullet}$. We attribute this change to the dimerisation of the radical cations to form diamagnetic dimers.[2,6]

Using the method previously described[2] we have calculated the equilibrium constant, *K*, for equilibrium (1) where $M^{+\bullet}$ = monomer, and D^{++} = dimer.

The values obtained for *K* are give in Table 2. It is seen that *K* is constant over a wide range of dilutions, which confirms that the equilibrium involved is that of equation (1) and not a

$$M^{+\bullet} + M^{+\bullet} \rightleftharpoons D^{++} \qquad (1)$$

$$K = \frac{[D^{++}]}{[M^{+\bullet}]^2}$$

disproportionation reaction, (*i.e.*, Beer's law was not obeyed). Plotting log *K* against $1/T$ gave good straight lines, from which the thermodynamic values for equilibrium (1) were obtained. These values are given in Table 3.

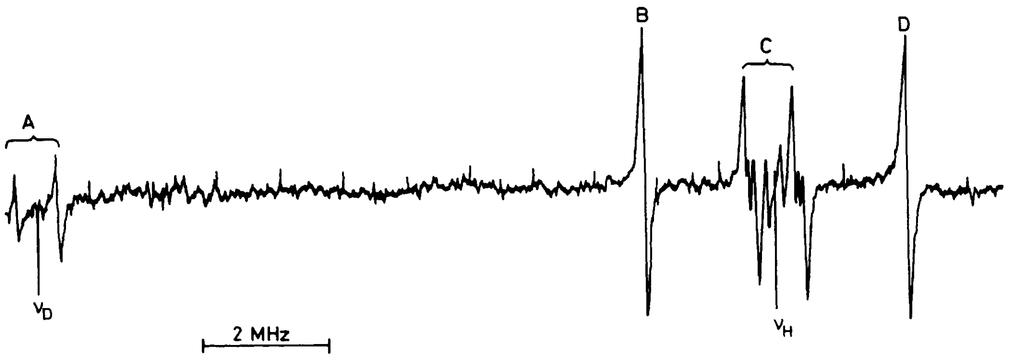


Figure 2. Deuterium and proton ENDOR spectrum of 2,2′,6,6′-tetradeuterio *o*-mDPQ radical cation in deuteriated methanol. A, 2-Pyridyl deuterons; B, 3-pyridyl protons; C, phenyl and methyl protons; D, 3-pyridyl protons

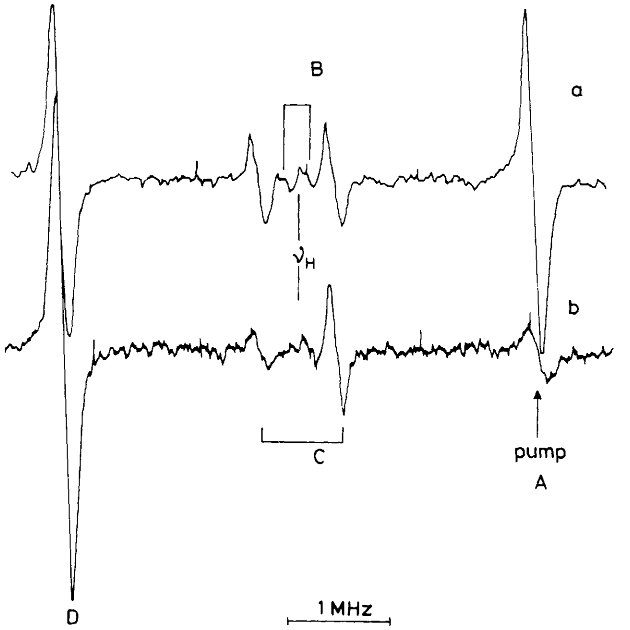


Figure 3. ENDOR (a) and general TRIPLE (b) spectra for T-mDPQ radical cation. A, Pyridyl protons; B, 9 and 11 *meta*-protons; C, 8, 10, and 12 methyl protons; D, pyridyl protons. 'Pump' means that line indicated has been partially saturated with r.f at which the line occurs.

Table 2. Effect of dilution on the concentration of monomer and dimer at −20 °C

Radical cation	10^4[Radical cation] (mol l^{-1})	10^4[Dimer] (mol l^{-1})	K/ mol^{-1} l	T/°C
DPQ$^{+\bullet}$	1.755	0.055	178	−16
	6.493	0.665	157	−16
	11.264	1.890	149	−16
p-mDPQ$^{+\bullet}$	1.632	0.0425	159	−15
	4.304	0.265	143	−15
	8.061	0.913	142	−15
	20.683	6.741	157	−15
m-mDPQ$^{+\bullet}$	1.36	0.095	513	−20
	2.46	0.305	503	−20
	3.67	0.695	516	−20
	6.16	1.970	519	−20
	11.96	7.020	490	−20
o-mDPQ$^{+\bullet}$	6.424	0.961	232	−52
	12.697	3.746	232	−52
	22.090	10.800	221	−52

Table 3. Thermodynamic constants for dimerisation of diquaternary 4,4′-bipyridylium radical cations at 25 °C. (T-mDPQ$^{+\bullet}$ does not dimerise)

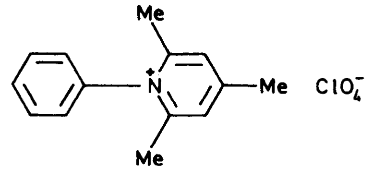
Radical cation	ΔG/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$\Delta S°$/ J K^{-1} mol^{-1}
DPQ$^{+\bullet}$	−6.84	−34.84	−93.85
p-mDPQ$^{+\bullet}$	−6.56	−41.93	−118.69
m-mDPQ$^{+\bullet}$	−6.84	−45.38	−129.29
o-mDPQ$^{+\bullet}$	−1.25	−32.93	−106.30

Discussion

E.s.r., ENDOR, and General TRIPLE Spectra.—The e.s.r. spectra were found to vary in intensity with change in temperature, but the coupling constants remained the same over the range of temperature studied thus showing that the species studied was the same over all temperatures. The ^{14}N coupling constants were obtained by inspection of the e.s.r. spectra and computer simulation.

Table 1 shows that the unpaired electron is delocalised throughout the entire molecule for all the radical cations. The results obtained for the *o*-mDPQ$^{+\bullet}$ and T-mDPQ$^{+\bullet}$, show lower hyperfine coupling constants for the phenyl ring protons, and slightly higher ^{14}N hyperfine coupling constants, than the other radical cations suggesting that the degree of delocalisation is less for these two radical cations. For T-mDPQ$^{+\bullet}$ the pyridyl ring hyperfine coupling constants are equal. INDO calculations[4] on similar systems show that such a result could be obtained if the two phenyl groups were twisted out of the plane of the bipyridyl rings. Experimental evidence in support of the non-planarity of *o*-mDPQ$^{+\bullet}$ and T-mDPQ$^{+\bullet}$ is found in an *X*-ray study of *N*-phenyl-2,4,6-trimethylpyridinium perchlorate (**II**) by Cameran *et al.*[7] They found that the phenyl ring is rotated through an angle of 83.5° and the C–N bond length is 1.47 Å. This bond length suggests a high degree of single bond character. If this is also true for T-mDPQ$^{+\bullet}$ then such a high degree of twisting would introduce steric hindrance to dimerisation and would account for the fact that T-mDPQ$^{+\bullet}$ does not dimerise. In the case of *o*-mDPQ$^{+\bullet}$, with only one methyl group present, the degree of twist will not be as great and this would allow the compound to dimerise, but not as readily as the others.

The fact that the methyl splitting constants are so small for *o*-mDPQ$^{+\bullet}$ and T-mDPQ$^{+\bullet}$ shows that these *o*-methyl protons do not overlap with the pyridyl π-system and that the steric



(II)

hindrance operates between the methyl protons and the pyridyl *ortho*-protons.

Monomer–Dimer Equilibrium.—The ΔG° values given in Table 3 for DPQ$^{+\bullet}$, *p*-mDPQ$^{+\bullet}$, and *m*-mDPQ$^{+\bullet}$ are virtually the same, thus reflecting that similar factors operate in the dimerisation of these compounds. In the case of *o*-mDPQ$^{+\bullet}$ the *ortho*-methyl group interferes sterically with the proton in the 2′-position of the pyridyl ring, and this causes a lack of coplanarity of the ring systems, so it is not surprising that the value for ΔG° is different for this particular compound. This more positive value shows that dimerisation is more difficult. This is supported by the fact that the e.s.r. signal for the T-mDPQ$^{+\bullet}$ molecule did not decrease on reducing the temperature showing that dimerisation did not occur. Molecular models show that the steric hindrance in the trimethyl derivative was much greater than in the mono *ortho*-methyl compound, *o*-mDPQ$^{+\bullet}$. This lack of coplanarity between the phenyl and pyridyl rings is so marked in T-mDPQ$^{+\bullet}$ that the radical cations are unable to form face-to-face dimers with π–π^* linking.

An important point arises in the comparison of *p*-mDPQ$^{+\bullet}$ and *m*-mDPQ$^{+\bullet}$. It seems strange that substitution of a methyl group into the *meta*-position should have a greater effect on ΔH° and ΔS° than substitution into the *para*-position. This might be due to the fact that the steric factors for dimerisation are due to the fact that the steric factors for dimerisation are different in these two cases, since the methyl groups in the dimerisation of *m*-mDPQ$^{+\bullet}$ can avoid steric interference with each other by being on opposite sides of the phenyl ring, whereas this possibility does not exist in the dimerisation of *p*-mDPQ$^{+\bullet}$. It is seen, however, that the ΔG° values are in the expected sequence.

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