An Electron Spin Resonance, ENDOR, and TRIPLE Resonance Study of Symmetrical *N,N'*-Disubstituted-4,4'-Bipyridylium Radical Cations in which the Quaternising Groups are Nitrogen Heterocycles

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

The e.s.r., ENDOR, and TRIPLE resonance results are reported for a novel series of symmetrical *N,N'*-diaryl-4,4'-bipyridylium radical cations in which the aryl groups are nitrogen heterocycles (pyridyls, pyrimidinyl, and pyrazinyl). A comparison is made between these systems and the previously reported fluorine- and methyl-substituted *N,N'*-diphenyl-4,4'-bipyridylium radical cations. Evidence is presented to suggest that steric hindrance in the *N,N'*-bis-(1-methyl-2-pyridyl) radical cation brings about a loss of ring planarity.

Earlier studies[1,2] of *N,N'*-diaryl-4,4'-bipyridylium radical cations have been confined to systems where the aryl groups have been phenyl or substituted phenyl groups. It has been shown that substitution of electron-withdrawing fluorine or electron-donating methyl groups into the phenyl rings has a marked effect on the spin density distribution within the radical. In this paper, we report an extension of the work to systems in which the aryl groups are nitrogen heterocycles and thus it has been possible to examine the effect of an electron-withdrawing substituent positioned within the carbon framework rather than substituted into the quaternising rings.

Experimental

Materials.—The *N,N'*-bis-(3-pyridyl)-4,4'-bipyridylium dichloride (**3**) and *N,N'*-bis-(2-pyrazinyl)-4,4'-bipyridylium dichloride (**7**) diquaternary salts were prepared in a manner similar to that of Allen[3] using the appropriate heterocyclic anilines.

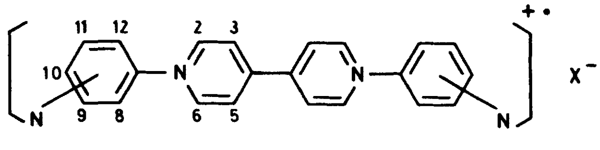
The *N,N'*-bis-(2-pyridyl)-4,4'-bipyridylium dichloride (**1**), *N,N'*-bis-(1-methyl-2-pyridyl)-4,4'-bipyridylium dichloride diiodide (**2**), and *N,N'*-bis-(2-pyrimidinyl)-4,4'-bipyridylium dichloride (**6**) salts were prepared by the reaction between 4,4'-bipyridyl and 2-chloropyridine, 2-chloro-1-methylpyridylium iodide, and 2-chloropyrimidine respectively. The diprotonated (**4**) and dimethylated (**5**) derivatives of the *N,N'*-bis-(3-pyridyl)-4,4'-bipyridylium dichloride salt were prepared by the reaction between the latter and an excess of acid and iodomethane respectively. The structures and purities of the prepared salts were determined by ^{1}H n.m.r., CHN analysis, and field desorption mass spectrometry.

Procedure.—Anaerobic methanolic solutions of the radical cations (*ca.* 10^{-4}M) were prepared by passing a solution of the di- or tetra-quaternary salt over tin or freshly prepared zinc films or by photolysis. In all cases, the radical cations obtained were independent of the method of reduction. E.s.r., ENDOR, and general TRIPLE resonance spectra were recorded on a Varian E109 spectrometer interfaced with a Bruker digital ENDOR, TRIPLE resonance attachment.

Results and Discussion

The Table gives the proton coupling constants of the radical cations together with the structure and numbering system. The radicals of compounds numbered (**1**), (**3**), and (**6**) were extremely stable with time while radicals (**2**), (**4**), and (**7**) decayed within days to diamagnetic species. Radical (**5**) was also unstable, yielding the unquaternised *N,N'*-bis-(3-pyridyl)-4,4'-bipyridylium radical cation (**3**) within hours of preparation. With the exception of radical (**2**) which was blue, all radicals considered were green. The e.s.r. spectrum decreased with decreasing temperature as previously reported for similar radical cations.[1,4]

Table. Coupling constants of symmetrical *N,N'*-diaryl-4,4'-bipyridylium radical cations



Radical cation	Quaternising group (R)	Coupling constants (mT)									
		2	3	8	9	10	11	12	Me	a_{H-2}/a_{H-3}	$\lambda_{max.}$/nm
(**1**)	2-Pyridyl	−0.175	−0.118	ND	+0.023	−0.068	+0.023	−0.068	—	1.48	447
(**2**)	1-Methyl-2-pyridyl	−0.362	−0.211	ND	+0.018	−0.039	+0.018	−0.039	+0.323	1.72	383
(**3**)	3-Pyridyl	−0.168	−0.130	−0.054	ND	−0.054	+0.033	−0.054	—	1.29	428
(**4**)	3-Pyridyl hydrochloride	−0.186	−0.113	−0.060	ND	−0.060	+0.028	−0.060	—	1.65	—
(**5**)	1-Methyl-3-pyridyl	−0.240	−0.158	−0.077	ND	−0.070	+0.018	−0.070	(+)0.128	1.52	428
(**6**)	2-Pyrimidinyl	−0.198	−0.102	ND	+0.019	−0.078	+0.019	ND	—	1.94	449
(**7**)	2-Pyrazinyl	−0.187	−0.109	ND	+0.024	−0.063	ND	−0.084	—	1.72	440

ND = not detected.

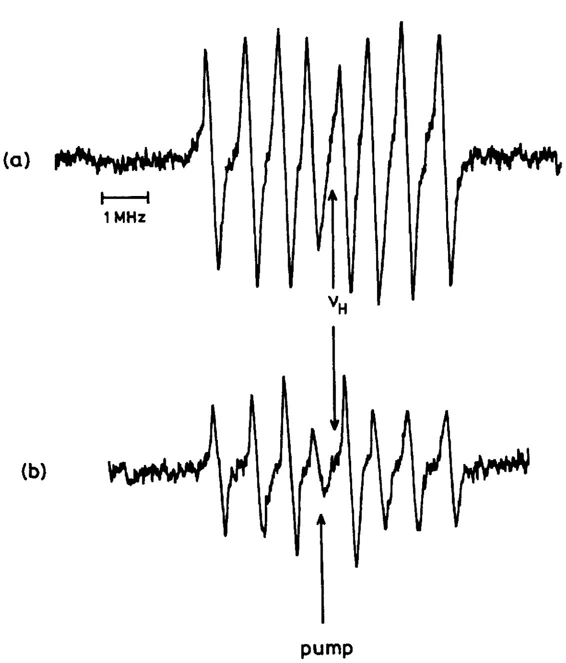


Figure 1. (a) ENDOR spectrum of *N,N'*-bis-(2-pyridyl)-4,4'-bipyridylium dichloride in methanol at −70 °C; (b) general TRIPLE spectrum of *N,N'*-bis-(2-pyridyl)-4,4'-bipyridylium dichloride in methanol at −70 °C

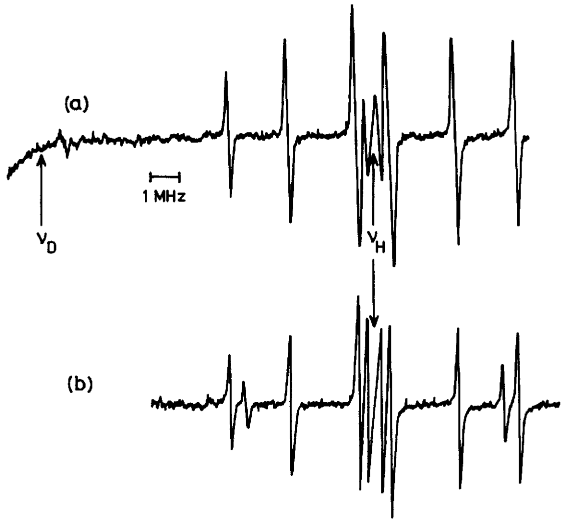


Figure 2. (a) ENDOR spectrum of *N,N'*-bis-(1-trideuteriomethyl-2-pyridyl)-4,4'-bipyridylium dichloride di-iodide in methanol at −70 °C; (b) ENDOR spectrum of *N,N'*-bis-(1-methyl-2-pyridyl)-4,4'-bipyridylium dichloride di-iodide in methanol at −70 °C

The ENDOR and general TRIPLE spectra of the radical cation (**1**) (at −70 °C) are shown in Figures 1(a) and 1(b) respectively while the ENDOR of the *N,N'*-bis-(1-trideuteriomethyl-2-pyridyl)-4,4'-bipyridylium radical cation used in the assignment of couplings of radical (**2**) is shown in Figure 2 together with the spectrum of the undeuteriated analogue.

Assignment of the Hyperfine Coupling Constants.—By analogy with the unequivocal assignments derived for the *N,N'*-diaryl-4,4'-bipyridylium radicals by Evans and co-workers,[5] the largest coupling constant is assigned to the equivalent 2,6,2',6'-(*ortho*) positions of the bipyridylium moiety, while the second largest [except for radical (**2**)] is due to the 3,5,3',5'-(*meta*) positions (in direct contrast to the assignment for *N,N'*-dialkyl systems). The heterocyclic substituted salts proved extremely susceptible to ring breakage in basic solution and it was not therefore possible to deuteriate the *ortho*-positions of the bipyridylium moiety to confirm these assignments directly. However, it has been shown[5] that the relative sizes of a_{H-2} and a_{H-3} are largely determined by steric factors which affect the positions of the *ortho*-(2,6,2',6') protons. Since the pyridine, pyrimidine, and pyrazine rings are comparable in steric bulk with phenyl rings it therefore seems appropriate to draw an analogy between them and the case of the *N,N'*-diphenyl-4,4'-bipyridylium radical cation (DPB$^{+\bullet}$) rather than the *N,N'*-dimethyl-4,4'-bipyridylium radical cation (PQ$^{+\bullet}$).

A comparison between the ENDOR spectra of the radical cations of (**2**) and its deuteriated analogue, *N,N'*-bis-(1-trideuteriomethyl-2-pyridyl)-4,4'-bipyridylium, reveals that the pair of absorptions at +0.323mT in the spectrum of the former have been removed in that of the latter and replaced by a deuterium splitting of 0.056mT (Figure 2, only the high-frequency deuterium line detected) in reasonable agreement with the expected value based on the proton and deuteron magnetrogyric ratios. Hence, the splitting of 0.323mT can be unequivocally assigned to the methyl protons of radical (**2**).

It has not been possible to determine whether the coupling constants of 0.158 and 0.128mT arise from the methyl protons and the 3,5,3',5'-(*meta*) positions respectively of radical cation (**5**) or *vice versa.* It is tentatively suggested that the larger coupling can be assigned to the *meta*-protons and this assignment provides a minimum value for the ratio a_{H-2}/a_{H-3} of the *N,N'*-bis-(1-methyl-3-pyridyl)- radical cation.

In most of the symmetrical disubstituted radicals studied, protons in the 8, 10, and 12 positions of the outer rings have equivalent negative couplings (*cf.* reference 5). However, this is not the case for radical cation (**5**) and the slightly larger coupling of 0.077mT is assigned to the 8 positions (which lie *ortho* to both quaternised nitrogens) rather than the 10,12 positions (0.070mT) which lie *ortho* to one quaternised nitrogen but *para* to the other.

A coupling constant of +0.330mT was obtained from the ENDOR spectrum for the 1,1' (bipyridylium) nitrogens of radical (**1**) but, in general, nitrogen couplings could not be obtained for these systems. Also no couplings have been detected for nitrogens in the outer quaternising heterocycles and preliminary INDO calculations indicate that these couplings are small [~0.02mT for the pyrimidinyl nitrogens of radical cation (**6**)].

Substituent Effects on the a_{H-2}/a_{H-3} Ratio.—The ratio a_{H-2}/a_{H-3} which has a value of 1.14[5] in the unsubstituted DPB$^{+\bullet}$ radical cation is dependent upon three factors:

(i) the in-plane bending of the *ortho*-protons which is related to the steric bulk of the quaternising group R.

(ii) the related effect of *ortho*-substitution into the phenyl ring which causes steric repulsion and twisting of the phenyl ring out of the bipyridylium plane.

(iii) the electron-donating or -withdrawing effects of the quaternising group R.

The slight reduction in steric repulsion when the phenyl ring of DPB$^{+\bullet}$ is replaced by the 2-pyridyl ring of radical cation (**1**) would be expected to cause an a_{H-2}/a_{H-3} ratio of less than 1.14 for radical cation (**1**). However, the ratio is greater than that of DPB$^{+\bullet}$ and this seems to be due to the through-bond electron-withdrawing nature of the unquaternised nitrogen lying *ortho* to the bipyridyl system. In radical cation (**6**) two unquaternised nitrogen atoms lie *ortho* to the bipyridyl moiety on each side and their combined electron-withdrawing effect produces a further increase in the a_{H-2}/a_{H-3} value to 1.94 [*cf.*

the *N,N'*-bis-(2-fluorophenyl)- (8-FPB$^{+\cdot}$) and *N,N'*-bis-(2,6-difluorophenyl)-4,4'-bipyridylium radical cations with a_{H-2}/a_{H-3} 1.22 and 1.34 respectively[2]].

A comparison of DPB$^{+\cdot}$ with the *N,N'*-bis-(3-pyridyl)-4,4'-bipyridylium radical cation (**3**) again reveals an increase in a_{H-2}/a_{H-3} to 1.29. In this case there are no steric effects which might affect the ratio but the unquaternised nitrogens of the 3-pyridyl rings can only exert their electron-withdrawing influence from a position *meta* to the bipyridylium moiety and so the a_{H-2}/a_{H-3} ratio (while larger than for DPB$^{+\cdot}$) is less than 1.48.

When the electronegative nitrogen is in the *meta*-position it still exerts a greater effect than a fluorine[2] or methyl[1] group substituted onto the phenyl ring in the 9-(*meta*) position. Similarly the radical cation (**7**) which has unquaternised nitrogen atoms both *ortho* and *meta* to the bipyridyl system has an a_{H-2}/a_{H-3} ratio of 1.72 which is greater than the ratio of the radical cation (**1**) (1.48) but less than that of the radical cation (**6**) (1.94). The a_{H-2}/a_{H-3} ratio of (**3**) (1.29) is increased to 1.65 for the diprotonated derivative (**4**) and to a (minimum) value of 1.52 for the dimethylated compound (**5**) and this is consistent with an increased inductive effect from a quaternised nitrogen in the *meta*-position when compared with a single unquaternised nitrogen (in the *meta*- or indeed in the *ortho*-position).

Effect of ortho *Quaternisation.*—The effect of quaternising a nitrogen in the 8-(*ortho*) position can be shown by a comparison between the radical cations (**1**) and (**2**). The a_{H-2}/a_{H-3} ratio of 1.48 for the unsubstituted compound is increased to 1.72 in the dimethylated compound and it is thus evident that the electron-withdrawing effect of the quaternised ($^{+}$N–Me) group (which increases the ratio) overrides the effect of ring twisting (which would tend to decrease it).

Evidence that steric repulsion between the *ortho*-methyl groups and the *ortho*-bipyridyl protons causes a twisting of the outer pyridyl rings from the bipyridyl plane arises from the following two considerations.

(i) A comparison of the couplings of the 2-pyridyl rings in radicals (**1**) and (**2**) reveals that the equivalent *ortho*- and *para*-positions (10,12) in radical (**1**) are almost halved in value (− 0.068 to −0.039mT) in the dimethylated derivative (**2**). This is attributed to the relative twisting in (**2**) which decreases the conjugation of the outer rings and hence lowers the unpaired spin density at the *ortho*- and *para*-carbon atoms. The effect of *ortho*-quaternisation on the *meta*-protons [+0.023 in (**1**) to +0.018mT in (**2**)] is rather less because spin density at the *meta*-carbons is mainly due to spin polarisation which is relatively unaffected by ring twisting.

While *ortho*-quaternisation causes a decrease in the *ortho*- and *para*-couplings, *meta*-quaternisation causes a corresponding increase. A comparison of the radical cation (**3**) (8,10,12 = −0.054mT) with its dimethylated analogue (**5**) (8 = −0.077; 10,12 = −0.070mT) reveals that in the absence of twisting (and the concomitant decrease in conjugation) the *ortho*- and *para*-couplings are increased as a result of nitrogen quaternisation.

(ii) The blue or hypsochromic shift to shorter wavelength on going from the radical cation (**1**) to its dimethylated derivative (**2**) is an indication of decrease in the length of the conjugated system on passing from the former to the later as a result of twisting in (**2**). See $\lambda_{max.}$ values in the Table.

The fact that the methyl splitting constant is so small in the *N,N'*-bis-(2-methylphenyl)-4,4'-bipyridylium radical cation (0.030 mT)[1] is evidence that the *ortho*-methyl protons in this radical do not overlap with the bipyridyl π system. In the radical cation (**2**), the methyl coupling is increased by an order of magnitude to +0.323mT. The positive sign of the coupling constant gives no indication as to whether the spin density is due to overlap with the π system or to spin polarisation (both would result in positive couplings) but the increased magnitude of the methyl protons coupling suggests most strongly that their geometry is suitable for direct overlap with the bipyridyl π system. Similarly, the methyl protons coupling of 0.017mT in the *N,N'*-bis-(3-methylphenyl)-4,4'-bipyridylium radical cation is increased to 0.128mT (sign unknown) in radical (**5**).

In conclusion:

(i) a nitrogen occupying a position in the outer quaternising rings always increases a_{H-2}/a_{H-3} and has more effect than an electron-withdrawing substituent substituted in the ring at the same position;

(ii) two nitrogens increase the value more than one;

(iii) an *ortho*-nitrogen increases it more than a *meta*-nitrogen;

(iv) a quaternised nitrogen (in any position) increases it more than an unquaternised one.

Acknowledgements

One of us (C. R. M.) thanks the S.E.R.C. for a research studentship. We would also like to thank the S.E.R.C. for a grant towards an ENDOR spectrometer.

References

1 J. C. Evans, A. G. Evans, M. H. Nouri-Sorkhabi, A. Y. Obaid, and C. C. Rowlands, *J. Chem. Soc., Perkin Trans. 2*, 1985, 315.
2 D. W. Clack, J. C. Evans, A. Y. Obaid, and C. C. Rowlands, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1653.
3 J. G. Allen, B.P. 1 514 466.
4 J. C. Evans, M. H. Nouri-Sorkhabi, and C. C. Rowlands, *Tetrahedron*, 1982, **38**, 2581.
5 D. W. Clack, J. C. Evans, A. Y. Obaid, and C. C. Rowlands, *Tetrahedron*, 1983, **39**, 3615.

Received 2nd *December* 1986; *Paper* 6/2324