Comparative Study by Electron Spin Resonance, ENDOR, and TRIPLE Resonance of the Radical Cations of Isomeric (1,4)-Pyridinophanes and the Analogous Compound *N,N'*-Dibenzyl-4,4'-bipyridylium

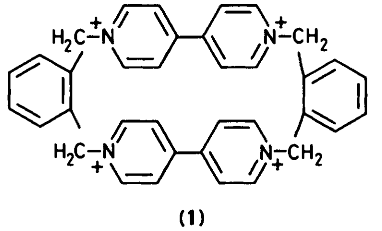
Jeffrey C. Evans,* Caroline R. Morris, and Christopher C. Rowlands
Chemistry Department, University College Cardiff, CF1 1XL

The e.s.r., ENDOR, and TRIPLE resonance spectra are reported for the radical cations of isomeric orthocyclo- and metacyclo-pyridinophanes. Evidence is presented which suggests that while both are doublet states, there is rapid inter-annular electron movement between the bipyridylium moieties only in the latter. Multiple resonance spectra of the straight-chain model *N,N'*-dibenzyl-4,4'-bipyridylium (benzylquat) show the previously undetected phenyl couplings and reveal discrete signals from the *ortho*- and *meta*-bipyridyl protons (previously thought equivalent).[1–4]

E.s.r. spectroscopy has been used in the study of cyclophane radical ions since the pioneering work of Weissman in 1958[5] and has been of particular importance in the study of intramolecular electron-transfer between the non-directly bonded aromatic moieties.

Pyridinophanes having two 4,4'-bipyridinium moieties linked *via* two *ortho*- or two *meta*-xylene bridges (orthocyclopyridinophanium and metacyclopyridinophanium, respectively) were first prepared by Hunig in 1983[6] and we report on the isomeric radical cations formed by reduction of the two macrocyclic tetra-cations.

The coupling constants derived from the ENDOR spectrum of the benzylquat radical cation are similar to those measured from the e.s.r. spectrum by Rieger and Rieger[1] and Shapiro *et al.*,[2] but differ from the work of Johnson and Gutowsky[3] and the previous study by Evans *et al.*[4]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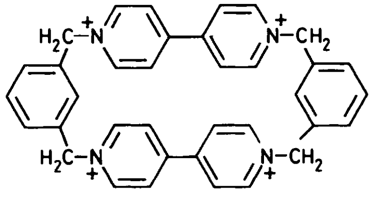
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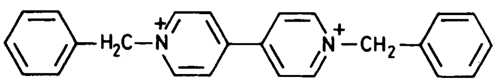
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Experimental

Materials—Samples of orthocyclopyridinophanium (**1**) and metacyclopyridinophanium (**2**) were kindly provided by Professor Dr. S. Hunig and the *N,N'*-dibenzyl-4,4'-bipyridinium dichloride (**3**) was kindly supplied by ICI.

Procedure.—The radical cation of the orthocyclopyridinophane was prepared by reduction on tin in methanol or in trifluoroacetic acid (there was no difference in e.s.r. or ENDOR spectra obtained by the two methods). The radical cations of the metacyclopyridinophane and benzylquat (**3**) were prepared by reduction on tin in methanol at room temperature. The e.s.r. experiments were carried out with a Varian E109 spectrometer and ENDOR experiments with a Bruker ENDOR attachment interfaced to the E109.

Results and Discussion

All three radical cations were blue and stable for several days under anaerobic conditions. Figure 1 shows the e.s.r. spectrum of the orthocyclopyridinophane radical cation recorded at room temperature while Figures 2(a) and 2(b) show the ENDOR and General TRIPLE spectra respectively, recorded at −70 °C. Figures 3(a) and 3(b) show the ENDOR and General TRIPLE spectra of the metacyclopyridinophane radical cation and the ENDOR and General TRIPLE of the benzylquat radical cation are shown in Figures 4(a) and 4(b) respectively. The intensity of the e.s.r. spectra of the radical cations of the phanes and benzylquat decrease with decreasing

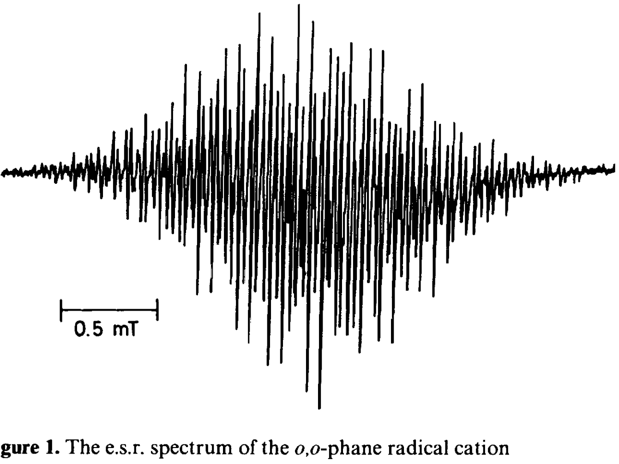


Figure 1. The e.s.r. spectrum of the *o,o*-phane radical cation

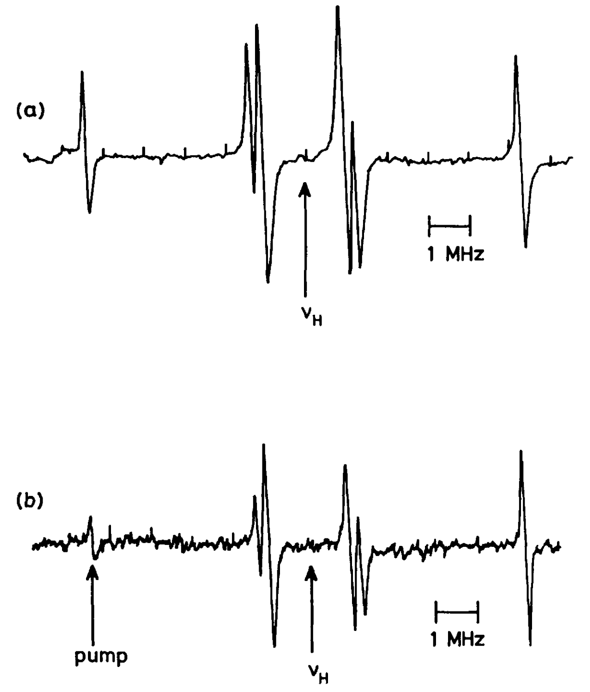


Figure 2. (a) ENDOR spectrum of the *o,o*-phane radical cation; (b) General TRIPLE resonance spectrum of the *o,o*-phane radical cation

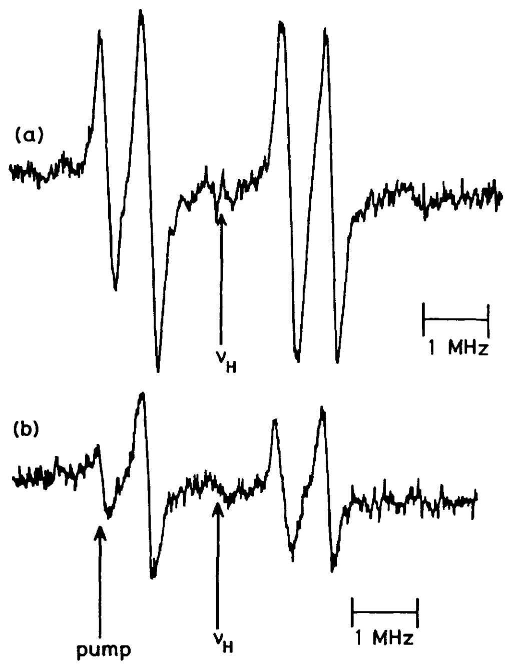


Figure 3. (a) ENDOR spectrum of the *m,m*-phane radical cation; (b) General TRIPLE spectrum of the *m,m*-phane radical cation

temperature as has been previously reported for *N,N'*-di-substituted-4,4'-bipyridylium radical cations.[7,8] The hyperfine coupling constants are given in the Table.

Although the cylcophanes are potentially four-electron acceptors,[6] it has been shown[9] that the product of reduction of orthocyclopyridinophanium (**1**) is the mono-radical. The difference between the first and second reduction potentials of (**1**) is very small, allowing simultaneous two electron-transfer

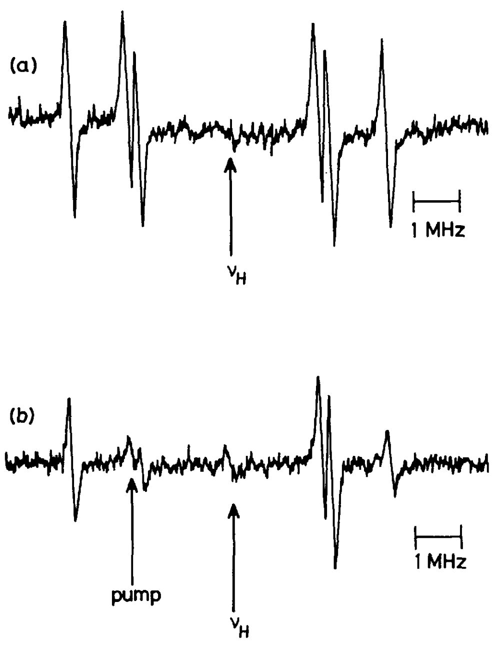
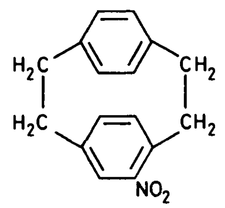


Figure 4. (a) ENDOR spectrum of the *N,N'*-dibenzyl-4,4'-bipyridylium radical cation; (b) General TRIPLE spectrum of the *N,N'*-dibenzyl-4,4'-bipyridylium radical cation



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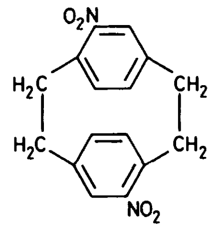

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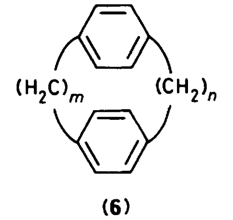

(6)

but this is followed by rapid co-proportionation (reverse of disproportionation) between the bi-radical and the parent tetra-cation to produce the mono-radical. By analogy, the product of reduction of the metacyclopyridinophanium is considered to be the mono-radical.

A study of the radical anion of the asymmetrical 4-nitro-[2.2]paracyclophane (**4**) by Gerson *et al.*,[10] revealed that the unpaired spin density is largely localised on the nitro-substituted benzene ring and is distributed in a manner resembling the radical anion of nitrobenzene.[11] The e.s.r. spectrum of the radical anion of 4,12-dinitro[2.2]paracyclophane (**5**), however, shows that spin density is evenly distributed between the two rings and the most prominent coupling constants are approximately halved[10] relative to nitrobenzene.

For radical anions of type (**6**) e.s.r. studies[12] bear out the expectation that the frequency of electron exchange between the

Table. Coupling constants of the radical cations of benzylquat and orthocyclo- and metacyclo-pyridinophane

	Proton coupling constant (mT)		
Radical cation	Methylene	Bipyridyl	Phenyl
Benzylquat	+0.247	−0.157, −0.141	≃0.005[a]
	0.265	0.150	b
	0.26	0.14	c
	0.414	≃0.150	d
Orthocyclopyridinophane	+0.072	−0.380, −0.091	—
Metacyclopyridinophane	0.118	0.074	≃0.007[e]

[a] This study. [b] Ref. 1. [c] Ref. 2. [d] Refs. 3 and 4. [e] General TRIPLE indicates only that the two largest couplings are opposite in sign.

two benzene rings is lowered with increasing number *m,n* of the methylene groups. The e.s.r. spectrum of the radical anion of (**6**) where $m = n = 4$ shows four equivalent protons of coupling comparable to the radical anions of *p*-dialkylbenzenes[13] so spin population is localised on one aromatic ring. It appears that both *m* and *n* must be equal to or larger than four in order to slow down the migration rate of the counter cation and therefore the exchange frequency of the electron spin so that it is lower than the hyperfine time-scale[12] and it is clear that the 'through-space' electron movement of the cyclophanes is quite unlike the 'through-bond' delocalisation in benzylquat$^{+\bullet}$ or bibenzyl$^{-\bullet}$[12]

By analogy with the 4-nitro[2.2]paracyclophane (**4**) radical anion it is assumed that there is preferential localisation of the unpaired electron onto the bipyridylium moieties of the phanes (rather than the phenyl rings) which is due to the higher electron affinity of the heterocyclic rings and the greater delocalisation of the unpaired spin over the extended π conjugated system of the bipyridyls. If one assumes that the larger coupling constant observed for the metacyclopyridinophanium is due to the methylene protons and the second largest to equivalent *ortho*- and *meta*-bipyridyl protons then one obtains a ratio of a_{H}cyclophane/a_{H}benzylquat of 0.48 for the $-CH_2-$ protons and 0.49 for the bipyridyl protons which correspond closely to the expected value of 0.5. It therefore seems likely that the radical cation of the metacyclopyridinophane is a doublet with the unpaired electron alternating rapidly between the bipyridylium groups.

While initial consideration of the relative sizes of the orthocyclopyridinophane radical cation coupling constants and comparison with the benzylquat radical cation suggest that the largest coupling constant of the cyclophane be assigned to the methylene protons one must conclude from the general TRIPLE experiments, that, in direct contrast to benzylquat$^{+\bullet}$, the smallest coupling of the orthocyclopyridinophane radical cation is due to the methylene groups. It may be that due to the steric arrangement of the cyclophane the 'pseudo-π' methylene σ orbitals cannot overlap appreciably with the delocalised multicentred π molecular orbitals of the bipyridylium moieties and hence spin density at the methylene protons due to hyperconjugation is small.

On the basis of this assignment, the splitting of the $-CH_2-$ group is reduced by a factor of 0.29 relative to benzylquat and the larger coupling of the bipyridylium protons is increased by a factor of 2.5 (with no coupling observed from the phenyl rings).

Clearly, the rapid inter-annular electron movement which lowers the metacyclopyridinophane radical cation couplings to half of their value in benzylquat, does not seem to occur in the orthocyclopyridinophane radical cation and one must envisage a situation in which the single unpaired electron of the latter is not able to freely jump between bipyridylium moieties. This could not be related to the phenomenon observed in radicals of type (**6**) where the electron is localised on one aromatic ring when the inter-annular distance is large enough[12] because the deck-to-deck distance is much greater in the metacyclo- (5.1 Å) than the orthocyclo-pyridinophane radical cations (2.9 Å)[2] but would, more likely, be associated with steric factors.

The coupling constants calculated for the benzylquat radical cation from its ENDOR spectrum have been compared with previous reports of the splitting constants derived from e.s.r. and n.m.r. spectra.[1–4] Our assignment is essentially the same as that of Rieger and Rieger[1] and Shapiro *et al.*,[2] although the previously reported degenerate bipyridylium splittings (0.150 mT) have been resolved by ENDOR into separate signals at 0.157 and 0.141 mT (whether $a_{\mathrm{H}_2} < a_{\mathrm{H}_3}$ as in the paraquat radical cation or $a_{\mathrm{H}_3} < a_{\mathrm{H}_2}$ as in the phenylquat radical cation has not yet been determined). Our assignment differs from Johnson and Gutowsky[3] and Evans *et al.*,[4] chiefly in their value for the splitting of the methylene protons. No previous study has reported a value for the very small phenyl couplings (≃0.005 mT) which lie within the e.s.r. linewidth and which could just be detected in the ENDOR spectrum (they are more prominent in the General TRIPLE spectrum).

Acknowledgements

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