Tetrahedron Vol. 43, No. 22, pp. 5329 to 5334, 1987
Printed in Great Britain.

0040-4020/87 $3.00+.00

THE ASSIGNMENT OF THE HYPERFINE COUPLING CONSTANTS OF ASYMMETRICAL N,N'-DIARYL-; N,N'-DIALKYL-; AND N-ALKYL-N'-ARYL-4,4'-BIPYRIDYLIUM RADICAL CATIONS

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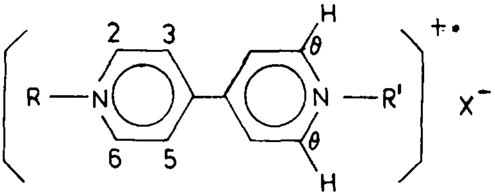
(*Received in UK* 9 *September* 1987)

Abstract - ESR and multiple resonance spectra were obtained for the radical cations of asymmetrical diquaternary 4,4'-bipyridylium compounds in which alkyl and aryl quaternising groups occur in a mixed fashion. The effect of these groups on the bipyridylium protons has shown clear trends which are used to predict the assignment for positions which cannot readily be deuterated.

The original report of the hyperfine coupling constants of the paraquat radical cation ($PQ^{+\cdot}$, $R=R'=CH_3$) by Johnson and Gutowsky in 1963 [1] assigned the smaller pyridyl proton coupling of 0.133 mT to the ortho protons (position 2) and the larger coupling of 0.157 mT to the meta (3) positions. Later work by Lamy et al[2] reversed this assignment and concluded that the couplings of 0.133 and 0.157 mT should be assigned to the meta and ortho positions respectively.



The recent ENDOR study of the deuterated analogues of paraquat and the N,N'-diphenyl-4,4'-bipyridylium radical cation ($DPB^{+\cdot}$) by Evans et al[3] resolved the ambiguity and revealed that Johnson and Gutowsky's original assignment was correct. They found that there is a reversal in the relative magnitudes of the H_2 and H_3 couplings in $PQ^{+\cdot}$ and $DPB^{+\cdot}$ so that the H_3 couplings (aH_3) is larger than that of H_2 (aH_2) in $PQ^{+\cdot}$ but vice versa for the pyridyl protons of $DPB^{+\cdot}$.

Most recently, we have prepared symmetrical N,N'-diaryl-4,4'-bipyridylium radical cations in which the quaternising groups are nitrogen heterocycles[4] and a proportionality has been established between the electron withdrawing properties of the quaternising group and the ratio aH_2/aH_3. We now extend this relationship to the asymmetrical aryl and alkyl diquaternary compounds in which $R \neq R'$ and where either may be aryl or alkyl. The radical cations of N-alkyl-N'-aryl-4,4'-bipyridylium salts were of particular interest and a number of deuterated analogues were prepared to facilitate the assignment of coupling constants.

EXPERIMENTAL

Materials:

N-phenyl-4,4'-bipyridylium chloride was kindly provided by ICI and used without further purification. N-(2-pyrimidyl)-; N-ethyl- and N-(n-propyl)-4,4'-bipyridylium monoquaternary salts were prepared by the reaction between 1:1 molar ratios of 4,4'-bipyridyl and 2-chloropyrimidine, iodoethane and 1-iodopropane respectively. The asymmetrical N-alkyl-N'-aryl-4,4'-bipyridylium salts were prepared by the reaction between the appropriate N-aryl- monoquaternary salt and excess iodoalkane. The N-phenyl-N'-(2-pyrimidyl)- salt was prepared by the reaction between the N-phenyl- monoquaternary salt and excess 2-chloropyrimidine. The asymmetrical dialkyl salts were prepared by the reactions of N-ethyl and N-(n-propyl)-4,4'-bipyridylium salts with excess iodomethane. The structures and purities of the diquaternary salts and their intermediate monoquaternary salts were confirmed by proton NMR and field desorption mass spectrometry.

Procedure:

The radical cations were prepared by passing anaerobic methanolic solutions over tin or a freshly prepared zinc film or by photolysis, the radical cations generated being independent of the method of reduction. ESR, ENDOR and TRIPLE resonance spectra were recorded on a Varian E109 spectrometer interfaced with a Bruker digital ENDOR attachment.

RESULTS AND DISCUSSION

The radical cations were green where R and R' were both aryl groups, blue where R and R' were alkyl groups and blue-green for the mixed system. All were stable for several months under anaerobic conditions. The ENDOR spectra of the N-ethyl-N'-phenyl-4,4'-bipyridylium radical cation (2) (for structures and radical numbers see table 1) and its 2,6,2',6' (ortho)-tetradeuterated analogue, recorded at -70°C are shown in Figs 1a and 1b respectively. Fig. 2 shows the ENDOR spectrum of the N-phenyl-N'-(2-pyrimidyl)- radical cation (4) while the ESR spectrum of the N-ethyl-N'-methyl- radical cation (5) (recorded at ambient temperature) is in Fig. 3. Fig. 4 is the ENDOR spectrum of the N-methyl-N'-propyl-diquaternary radical cation, (6) together with its General TRIPLE resonance spectrum. While General TRIPLE experiments indicate only the relative signs of the coupling constants, previous INDO calculations on analogous compounds[5] allow unequivocal assignment of absolute values (see Table 1). The ESR spectra decreased with decreasing temperature as previously reported for similar radical cations.[6,7]

Fig 1a

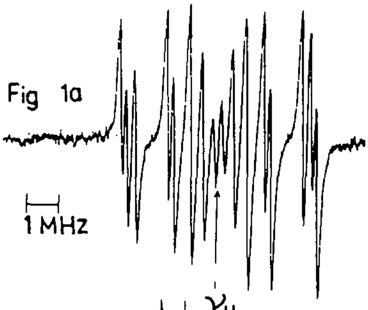


Fig 1b

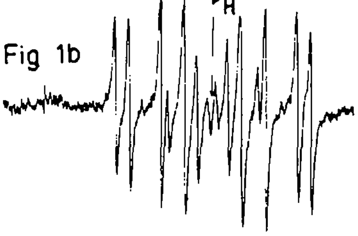


Fig 2

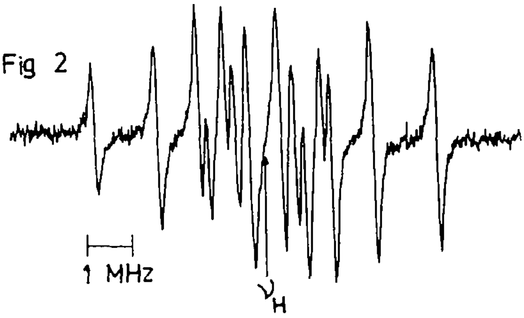


Fig 3

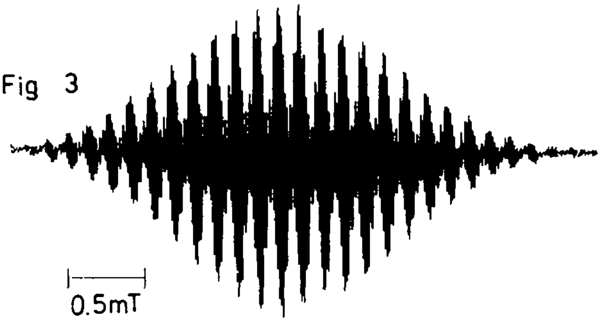
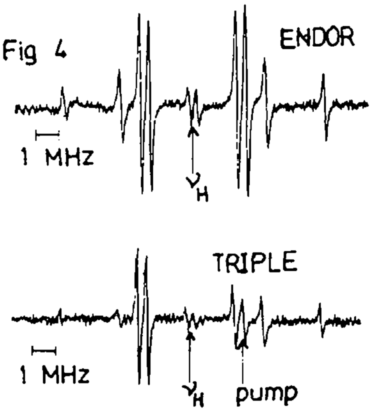


Fig 4



Bipyridylium protons: The theoretical calculations made by Evans et al[3] established that the reversal in the magnitudes of aH_2 and aH_3 in $PQ^{+\cdot}$ and $DPB^{+\cdot}$ was the result of steric hindrance between the groups R substituted at the nitrogen atoms and the ortho (2,6,2',6') bipyridyl protons. The ortho protons do not experience as great a repulsion when R = CH_3 as when R = Ph. Decreasing the N-C-H angle (Θ) from 126^0 to 114^0 causes the aH_2 coupling to decrease with a concomitant increase in aH_3 and so for $PQ^{+\cdot}$ where the (Θ) is 114^0, aH_3 becomes larger than aH_2. In $DPB^{+\cdot}$ where the (Θ) is thought to be 120^0, aH_2 remains larger than aH_3. An extension of this work by the same group to a consideration of electron-donating and withdrawing groups substituted into the phenyl rings of $DPB^{+\cdot}$ [5,7] has shown that in all cases whether the substituent is an electronegative fluroine atom or an electron-releasing methyl group, the largest coupling constant can be unequivocally assigned to the ortho (2) positions while the smaller is due to the meta (3) positions.

In addition to its dependence on the steric bulk of the quaternising group, the ratio aH_2/aH_3 is related to two other factors:[4,5,7]

(i) Ortho substitution into the phenyl ring which causes twisting of the phenyl ring out of the bipyridyl plane and which brings about a reduction in aH_2/aH_3.

(ii) The electron-donating or withdrawing effects of the quaternising group.

Selective deuterations were carried out to facilitate the interpretation of the ENDOR spectra. For this purpose the 2',6'-dideuterated analogue of the N-methyl-N'-phenyl-4,4'-bipyridylium radical cation (1) (ortho bipyridyl protons on the phenyl side deuterated) was prepared together with the 2,6,2',6'-tetradeuterated analogues of radicals (1), (2), (5) and (6) and the (trideuteriomethyl) analogues of (1), (3), (5) and (6). Table 1 gives the proton coupling constants of all radical cations considered together with the structures and numbering systems. The assignments were based on the ENDOR spectra of the various deuterated derivatives and on the premise that $aH_2 > aH_3$ for N-aryl systems but $aH_3 > aH_2$ for N-alkyl systems.

A consideration of Table 2 in which symmetrical and asummetrical derivatives are compared reveals that aH_2/aH_3 (on the R side) reaches a maximum when R is most electronegative and R' is most electropositive (and is at a minimum when vice versa). The increase in both aH_2/aH_3 and $aH_2 + aH_3$ as R becomes more electron-withdrawing and R' more electron-donating enables one to predict the assignment of the meta bipyridyl protons (3 and 3') in the N-phenyl-N'-(2-pyrimidyl)-4,4'-bipyridylium radical cation (4).

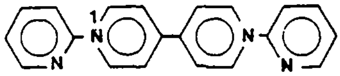
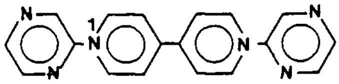
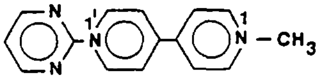
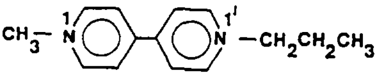
Of the observed bipyridyl couplings of 0.265, 0.167, 0.102 and 0.090 mT, only the coupling of 0.102 mT can be assigned unambiguously to the 2 position with the aid of a deuterated analogue. The largest coupling of 0.265 mT we assign to the 2' position on the basis of a previous study of pyrimidyl compounds.[4]

Although one might assign the remaining couplings of 0.167 and 0.090 mT to the 3' and 3 positions respectively, contrary to this, the clear trends in Table 2 suggest that the reverse assignment is correct. It is therefore proposed that, in this radical cation, the coupling constant of the meta bipyridyl position is greater than that of the ortho position (3>2) on the phenyl side.

Nitrogen couplings: The nitrogen couplings which could be obtained for symmetrical N,N'-diaryl-radical cations where the aryl groups were nitrogen heterocycles[4] and asymmetrical N,N'-disubstituted radical cations are shown in (i).

The nitrogen couplings which could be observed for those radical cations with heterocyclic quaternising outer rings are in the range 0.270 to 0.350 mT and all are considered to have positive signs. The observable nitrogen couplings were smaller than those of $PQ^{+\cdot}$ (0.423 mT)[3] and $DPB^{+\cdot}$ (0.380 mT)[3] and it is suggested that this is due to conjugation between the outer heterocyclic ring and the rest of the radical molecule. The increased delocalisation of the unpaired electron into the outer rings is then presumably at the expense of the bipyridyl nitrogens. The largest nitrogen coupling observed for these radicals was assigned to the 1 (methyl side) position of the N-methyl-N'-(2-pyrimidyl)-4,4'-bipyridylium radical cation and the smallest coupling detected was assigned to the 1' position of the same cation radical. It is suggested that a

(i)

Radical Cation$^{+\cdot}$	Position	Coupling Constant (mT)
	1	0.330
	1	0.284
	1 1'	0.350 0.270
	1,1'	0.360

mechanism is in operation whereby unpaired electron spin density can move from the bipyridyl moiety into the orbital of the lone pair on a nitrogen in the 8 or 12 (ortho) positions of an outer heterocyclic ring. The effect of unpaired spin being pulled from the carbon in position 2 into the outer ring may be, in turn, a removal of unpaired spin density from the bipyridyl nitrogen and hence a decrease in the coupling. This phenomenon would account for the decrease in the bipyridyl nitrogen coupling on passing from the N,N'-bis(2-pyridyl)- radical cation to the 1' position of the N-methyl-N'-(2-pyrimidyl)-4,4'-bipyridylium radical cation.

No couplings have been detected for nitrogen atoms in the outer quaternising rings of the radical cations studied and preliminary INDO calculations of the N,N'-bis(2-pyrimidyl)-4,4'-bipyridylium radical cation, indicate that these couplings are small (0.02 mT).

As expected, the nitrogen coupling of the dialkyl radical cation N-methyl-N'-propyl-4,4'-bipyridylium (1 and 1' positions equivalent) was the largest measured (0.360 mT) although this value was rather less than the nitrogen couplings of PQ$^{+\cdot}$ or n-propylquat$^{+\cdot}$ previously reported (0.423 and 0.415 mT respectively[9]).

Coupling constants of the quaternising groups: As previously shown all protons in the ortho and para positions of phenyl and pyrimidyl rings have negative couplings while all couplings from protons in the meta positions are small and positive and this is consistent with the presence of a node in the wave functions at the 9 and 11 positions. For those asymmetrical radical cations quaternised by a phenyl group, the ortho (8,12) positions differ from the para (10) position and by analogy with DPB$^{+\cdot}$ [5] the slightly larger coupling is assigned to the ortho protons and the smaller to the para position.

The decrease in the coupling of the methyl group on going from PQ$^{+\cdot}$ (0.409 mT)[3] to the N-methyl-N'-phenyl- and N-methyl-N'-(2-pyrimidyl) cation radicals (0.378 and 0.341 mT respectively) is presumably due to increased delocalisation of the unpaired electron into the bipyridyl rings on the phenyl and pyrimidyl sides at the expense of both the methyl group and the nitrogen to which it is attached.

Acknowledgements

One of us (CRM) wishes to thank the SERC for a research studentship.

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Table 1

Coupling Constants of asymmetrical N,N'-disubstituted-4,4'-bipyridylium radical cations.

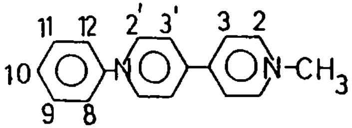
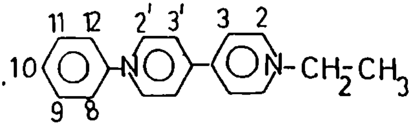
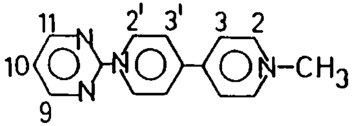
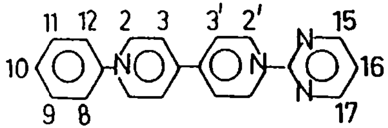
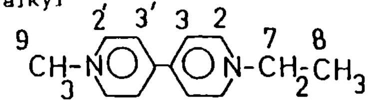
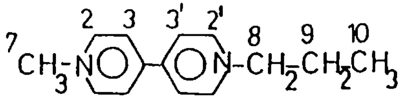
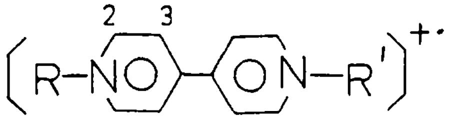
Radical Cation$^{+\cdot}$	Coupling Constants (mT)									
N-alkyl-N'-aryl-	2	2'	3	3'	8,12	9,11	10	CH_3	CH_2	
1. 	-0.097	-0.201	-0.184	-0.122	-0.064	+0.033	-0.059	+0.378	-	
2. 	-0.099	-0.202	-0.183	-0.112	-0.064	+0.033	-0.057	-0.010	+0.214	
3. 	-0.052	-0.315	-0.199	-0.096	ND	+0.025	-0.031	+0.341	-	
N,N'-diaryl-	2'	2	3'	3	8,12	9,11	10	14,18	15,17	16
4. 	-0.265	-0.102	-0.090	-0.167	-0.049	+0.026	-0.044	ND	+0.022	-0.0
N,N'-dialkyl	2',2		3',3		9	7	8			
5. 	-0.135		-0.165		+0.405	+0.230	-0.010			
	2',2		3',3		7	8	9	10		
6. 	-0.135		-0.165		+0.404	+0.226	-0.011	ND		

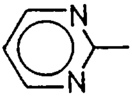
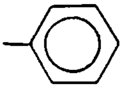
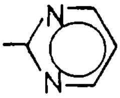
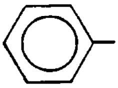
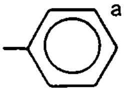
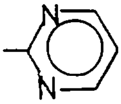
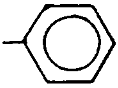
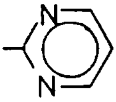
Table 2

The effect of asymmetrical quaternising groups on the bipyridyl proton couplings.



increasing inductive effect of R

increasing inductive effect of R'

R	R'	aH_2^*	aH_3^*	aH_2/aH_3	$aH_2 + aH_3$
	$-CH_3$	0.315	0.096	3.28	0.411
		0.265	0.090	2.94	0.355
		0.198	0.102	1.94	0.300
	$-CH_3$	0.201	0.112	1.79	0.313
	$-CH_2CH_3$	0.202	0.112	1.80	0.314
		0.159	0.140	1.14	0.299
		0.102	0.167	0.61	0.269
CH_3-	$-CH_3$ [a]	0.136	0.168	0.81	0.304
	$-CH_2CH_3$	0.135	0.165	0.82	0.300
	$-CH_2CH_2CH_3$	0.135	0.165	0.82	0.300
		0.097	0.184	0.53	0.281
		0.052	0.199	0.26	0.251

*all hfcs given in mT and negative in sign a) Ref. 3.