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THE ASSIGNMENT OF THE HYPERFINE COUPLING CONSTANTS FOR THE PYRIDYL PROTONS IN ARYL AND ALKYL N-SUBSTITUTED BIPYRIDYLIUM RADICAL CATIONS

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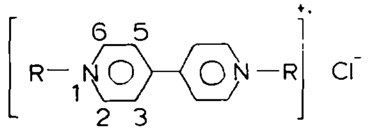
Abstract—The coupling constants for the pyridyl protons of the radical cations of N,N′-dimethyl-4,4′-bipyridylium dichloride PQ^{+} and N,N′-diphenyl-4,4′-bipyridylium dichloride DPQ^{+} have been unambiguously assigned from an ENDOR study of selectively deuterated compounds. The experimental results confirm the early theoretical assignments for PQ^{+} made by Johnson and Gutowsky; however subsequent assignments for DPQ^{+} based on this work have now been revised. The revision of the assignments and the difference between the two compounds are discussed using INDO molecular orbital calculations.

Johnson and Gutowsky[1] reported the hyperfine coupling constants for some alkyl N-substituted bipyridyl radical cations and assigned them on the basis of Huckel molecular orbital calculations. They found that for the N-Me substituted radical cation, paraquat $PQ^{+\cdot}$, the hyperfine coupling constants for the pyridyl ring protons were 0.133 mT for position 2 and 0.157 mT for position 3. The numbering system is shown in I. When the methyl group was replaced by a proton then the coupling constant at position 2 became greater than that at position 3.



I

Later work by Lamy *et al.*[2] disagreed with the assignments of Johnson and Gutowsky in that they attributed the largest pyridyl ring hyperfine coupling constant to position 2 on the basis of INDO calculations. They also reported a value for the methyl proton hyperfine coupling of 0.253 mT, considerably smaller than the value reported by Johnson and Gutowsky of 0.399 mT. Evans *et al.*[3] in a study of the radical cation of paraquat $PQ^{+\cdot}$ found similar values of the coupling constants to those obtained by Johnson and Gutowsky and used their assignments.

We have reinvestigated these substituted bipyridyl cations as we are now able to selectively deuterate the pyridyl ring, and can therefore unequivocably assign the coupling constants for the pyridyl ring protons. We report herein data for paraquat radical cation $PQ^{+\cdot}$ (R=Me), and DPQ^{+} radical cation (R=Ph) (ENDOR spectra reported earlier)[4] together with theoretical results from INDO molecular orbital calculations on these two radical cations and on the radical cation where R=H.

EXPERIMENTAL

Materials. N,N′-dimethyl-4,4′-bipyridylium dichloride PQ^{2+} and N,N′-diphenyl-4,4′-bipyridylium dichloride DPQ^{2-} were provided by ICI. N,N′-dimethyl-3,3′-5,5′-tetra-deutero-4,4′-bipyridylium dibromide was prepared in a manner similar to that of Colchester and Thomas[5] except that 3,4,5-trideutero-N-methyl pyridinium iodide was used as starting material.

N,N′-diphenyl-3,3′-5,5′-tetra-deutero-bipyridylium dibromide was prepared from 3,4,5-trideutero-N-phenylpyridinium iodide using the methods of Allen[6] and Colchester and Thomas.[5]

The structures and positions of deuteration were confirmed by ^{13}C and ^{1}H NMR. Specific deuteration at the 3,3′,5,5′-position of paraquat was established by ^{1}H (90 MHz Perkin–Elmer R32) and ^{13}C (90 MHz, Bruker WM-260) NMR spectroscopy in D_2O soln. In the ^{1}H spectrum [δ_H8.51 (3,3′-5,5′) 9.05 (2,2′-6,6′) doublets, J = 7 Hz for unlabelled material][7] the lower-frequency signal was absent, and the higher-frequency signal was a singlet. In the ^{13}C spectrum [δ_C 148.7 (2,2′,6,6′), 129.2 (3,3′,5,5′), 152.2 (4,4′), 51.1 (Me)(8) under broad-band decoupling, the signal at 129.1 was a triplet (J_{CD}27 Hz) with no sign of the singlet that unlabelled or differently labelled material would have given, while all the other signals were singlets.

MeOH was dried over $CaSO_4$ for 24 hr prior to distilling under dinitrogen and then outgassed under vacuum before use.

Procedure. MeOH solns of the radical cations were prepared by passing the solns over freshly prepared Zn films. Samples for ESR and ENDOR experiments were then sealed in quartz tubes under vacuum. The ESR experiments were carried out on a Varian E109 spectrometer fitted with a variable temp controller. ENDOR experiments were made using a digital Bruker ENDOR unit interfaced with the Varian E109.

RESULTS AND DISCUSSION

ESR and ENDOR spectra

Radical cation of N,N′-*dimethyl*-4,4′-*bipyridylium dichloride* PQ^{+} Figure 1 shows the proton ENDOR spectra for PQ^{+} and radical cation of N,N′-dimethyl-3,3′,5,5′-tetradeutero-4,4′-bipyridylium dibromide. The low resonance lines for the Me protons are not shown. It can be clearly seen that on deuterating the pyridyl ring in the 3,3′-positions the absorptions marked b and b′ disappear from the

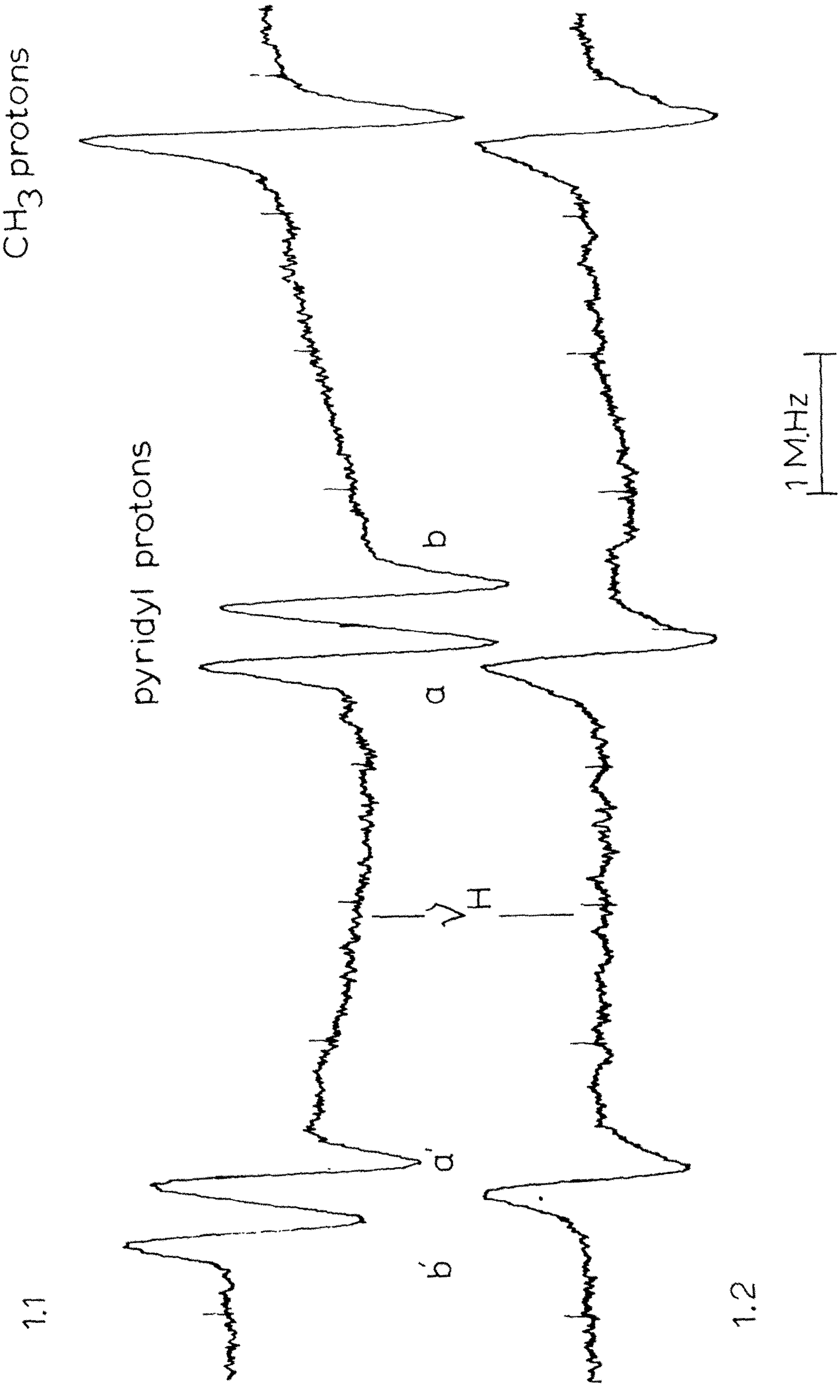
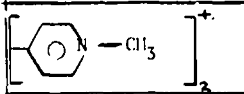
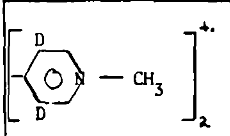
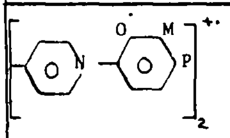
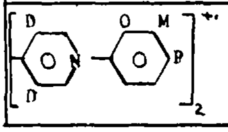


Fig. 1. Proton ENDOR spectra in methanol at −60°C for: (1.1) PQ$^{+\cdot}$. (1.2) N,N′ dimethyl 3,3′ 5,5′ tetradeutero 4,4′-bipyridylium radical cation.

Table 1. Experimental hyperfine coupling constants obtained from proton ENDOR and ESR measurements at −60°

COMPOUND	Splitting constant in mT						
	N	CH_3	2	3	0	m	p
	+0.423 0.423*	+0.409 0.399*	-0.136 0.133*	-0.168 0.157*			
	+0.423	+0.409	-0.136	not detected			
	+0.38		-0.159	-0.140	-0 054	+0.031	-0 050
	+0.38		-0.159	not detected	-0 054	+0.031	-0 050

*Johnson and Gutowsky(1)

Absolute sign of hyperfine coupling constant obtained from INDO calculation and confirmed by General Triple experiments.

proton ENDOR spectrum (Fig. 1.2). Thus it is possible to unambiguously assign each of the two ENDOR enhancements a, a′ and b, b′ (Fig. 1.1) to positions 2 and 3 respectively of the pyridyl ring. Table 1 gives the values for the proton hyperfine coupling constants obtained together with the ^{14}N hyperfine coupling constant obtained from an ESR experiment. These values are in good agreement with those reported by Johnson and Gutowsky[1] which are also shown in Table 1. The values obtained by Lamy[2] are different to those we report. They have assigned the larger pyridyl splitting to the 2 position and report a value for the Me protons of 0.2546 mT. Our ENDOR results show this value to be wrong.

Radical cation of N,N′-*diphenyl*-4,4′-*bipyridylium dibromide DPQ*$^{+}$. The proton ENDOR spectrum for DPQ^+ is shown in Fig. 2.1. Five absorptions are evident, two arising from the pyridyl ring protons and the remaining three from the phenyl ring protons. The ENDOR spectrum of the penta-deuterophenyl derivative is shown in Fig. 2.2. As can be seen there are now only two absorptions, which must arise from the pyridyl ring protons. Figure 2.3 shows the ENDOR spectrum of the radical cation of N,N′-biphenyl-3,3′-5,5′-tetra-deutero-4,4′-bipyridylium dibromide. The absorptions arising from the phenyl ring are evident together with one pair of absorptions remaining for the pyridyl ring protons, which can therefore be assigned to positions, 2,2′ and 6,6′. The values and their assignments are shown in Table 1. The assignment for the phenyl ring protons was made as before.[4]

It is clear from the results that there is a reversal in the relative values of the H_2 and H_3 coupling constants in these two compounds. The H_3 coupling constant (a_{H_3}) is larger than that of $H_2(a_{H_2})$ in PQ^+ but vice versa for DPQ^+. Thus our previous assignment[4] of the pyridyl coupling constants for DPQ^+ based on earlier results[1,3] for PQ^+ is not correct. The relative signs of the proton hyperfine coupling constants were obtained from a General Triple Resonance experiment[9] and the absolute sign taken from the INDO calculations (see below).

Preliminary results for the fluorine substituted phenyl paraquats suggest that these also behave like the unsubstituted cation, with $a_{H_3} < a_{H_2}$.

Theoretical calculations

Calculations have been made in order to establish the origin of the differing magnitudes of the H_2 and H_3 coupling constants for the methyl and phenyl derivatives. In addition the N,N-dihydro-4,4-bipyridylium radical cation was studied for comparison although unambiguous assignments on the basis of deuteriation and ENDOR are not available at present.

The calculations were made using the INDO - molecular orbital method[10] to derive orbital spin densities. These were converted to coupling constants using Pople's[11] best fit values for the quantity $|\phi_{SN}(R_N)|^2$.

Geometry. The initial geometry chosen was an average of those found in diquaternised bipyridinium salts,[12-14] with both pyridine rings lying co-planar and an interannular C–C bond distance of 1.46 Å. The early Huckel calculations of Johnson and Gutowsky[1] used $\beta_{C-C} = 1$ for this bond, which is equivalent to a bond distance of 1.40 Å. More recent INDO calculations by Lamy *et al.*[2] employed rather old struc-

Table 2. Calculated coupling constants a_{H_2} and a_{H_3} for PQ^+ interannular distance = 1.40 and 1.46 Å

.C-C ring Å	a_{H_2} (mT)	a_{H_3} (mT)
1.46	-0.132	-0.091
1.40	-0.121	-0.105

Fig. 2. Proton ENDOR spectra in methanol at −60°C for (2.1) DPQ$^+$. (2.2) Pentadeuterophenyl derivative of DPQ$^+$. (2.3) N,N′ diphenyl 3,3′-5,5′ tetradeutero 4,4′-bipyridylium radical cation.

tural data and used an interannular bond distance of 1.51 Å. The positions of the ring H atoms pose some problems. X-ray work on biphenyl has shown that the four *ortho* hydrogens are bent away from each other in order to minimise steric crowding when the rings are coplanar.[15,16] Thus the C–C–H angle normally observed in aromatic systems (120°) is reduced by up to 6°. Initial calculations were therefore made with the angles C_2–C_3–H_3 and C_3–C_2–H_2 both equal to 114°. Lamy *et al.*[2] did not state the positions they used for the H atoms.

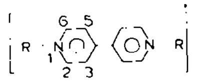
Results of M.O. calculations. The computations show that with the initial geometry used (interannular C–C = 1.46 Å) the coupling constant a_{H_2} is always greater in magnitude than a_{H_3} (both are negative) for all three compounds R = H, Me and Ph. Calculations run at the shorter interannular distance of 1.40 Å, a distance compatible with the parameters chosen by Johnson and Gutowsky in their Huckel calculations, produced no significant change in molecular energy and yet still yielded $a_{H_2} > a_{H_3}$, although the values lay closer together (see Table 2). It is significant that the calculations produce similar values for the coupling constants a_{H_2} and a_{H_3} for the cations with R = Me and Ph, but a_{H_2} is calculated to be substantially larger ($\simeq 10\%$) when R = H. Previous calculations[2] carried out using a larger interannular distance of 1.51 Å have resulted in an even wider separation between the a_{H_2} and a_{H_3} values.

Twisting of the two rings about the interannular bond also increased the difference between the a_{H_2} and a_{H_3} values ($a_{H_2} > a_{H_3}$), and so it is not responsible for the switch in a_{H_2} and a_{H_3} values in the dimethyl substituted compound.

Thus, INDO calculations which use a similar geometry for all three compounds are unable to account for the differing relative magnitudes of the a_{H_2} and a_{H_3} splitting constants. Johnson and Gutowsky[1] attributed the interchange of the values of these coupling constants in the unsubstituted (H) and the methyl derivative to the differing α(coulomb) terms for the nitrogen atoms in the two compounds.

One further factor which may be treated within the INDO scheme is the steric effect of the group R, substituted at the N atom. This may be accounted for by adjustment of the molecular geometry, but of course cannot be handled within the simple π-electron Huckel method. The results discussed above have been obtained for all three compounds using the ring hydrogen positions indicated by X-ray work,[13,14] i.e. C_2–C_3–H_3 = C_3–C_2–H_2 = 114°. However, the hydrogens bonded to the carbon atoms *ortho* to N may not experience as large a repulsion when R = H or Me as for R = Ph. Consequently, further calculations were made for all three compounds covering an in plane bending of the N–C–H angle from 114 to 126°. The results show that the *ortho* hydrogens can approach closer to the R group when R = H or Me, than when R = Ph because of the smaller steric bulk of these two groups. The lowest molecular ion energy corresponds to an angle N–C–H of 114° for R = Me and H but of 120° for R = Ph. The values of a_{H_2}, a_{H_3} and the a_N splitting constants arising from this change in angle are shown in Table 3. Decreasing the angle N–C–H from 126 to 114° causes the a_{H_2} splitting constant to decrease with a concomitant increase in a_{H_3} for all three compounds. It can be seen that because of this bending it is possible for a_{H_3} to become larger than a_{H_2} in the methyl derivative, whereas a_{H_2} remains larger than a_{H_3} in the phenyl compound. Although a bending of equal magnitude to that in the methyl case seems

Table 3. Calculated coupling constants (mT) for the pyridyl protons and the nitrogen atom for



Cl$^-$ (R = H, Me and Ph) for three values of the NCH_2 angle

	Angle NCH_2	126°	120°	114°
	a_{H_2}	-0.134	-0.126	-0.120
R=H	a_{H_3}	-0.103	-0.107	-0.111
	$a_{Nitrogen}$	0.409	0.414	0.421
	a_{H_2}	-0.121	-0.114	-0.108
R=Me	a_{H_3}	-0.105	-0.109	-0.114
	$a_{Nitrogen}$	0.427	0.432	0.439
	a_{H_2}	-0.122	-0.114	-0.108
R=Ph	a_{H_3}	-0.105	-0.111	-0.117
	$a_{Nitrogen}$	0.465	0.470	0.475

Footnote: Interannular bond distance = 1.40 Å

and angle $C(2)\hat{C}(3)H(3)$ = 114°

probable for the unsubstituted molecule, it appears that a_{H_2} never becomes smaller than a_{H_3} for the unsubstituted molecule.

Thus it is reasonable to conclude from the results that the switch over in the magnitudes of a_{H_2} and a_{H_3} between the methyl and phenyl substituted compounds is due to steric factors which determine the positions of the *ortho* hydrogens in the two compounds.

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