Improved Correlation Analysis of Electron Spin Resonance Spectra: Pyridylmethyl Radicals

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2-, 3-, and 4-Pyridylmethyl (picolyl) radicals have been prepared in fluid solution by hydrogen or halogen abstraction from the corresponding hydride or chloride. The weak e.s.r. spectra have been analysed by improved correlation methods: results agree with INDO calculations about as well as do those for benzyl radicals. All three radicals have higher spin density at the α-position than does benzyl: the order is 4 > 2 > 3 > benzyl. Improvements in correlation techniques required for this analysis include a method for finding the centre of a spectrum without prior determination of the coupling constants, and MULTIPEAK, a method of establishing new coupling constants, which uses the whole information available in the spectrum and which is particularly useful in the analysis of spectra with numerous doublet splittings.

Pyridylmethyl (picolyl) radicals represent an interesting structural modification to the well studied benzyl radical, but the difficulty of obtaining high enough concentrations and the extra complexity of their structure has hitherto prevented their observation in fluid solution. A study of these radicals in adamantane matrices[1] led to surprising results, especially for the 3-pyridylmethyl radical. In view of our interest in the analysis of weak and complex spectra by correlation methods,[2] we decided to make an experimental e.s.r. study of these radicals.

Results and Discussion

We prepared 2-, 3-, and 4-pyridylmethyl (picolyl) radicals in the cavity of the e.s.r. spectrometer either by hydrogen abstraction from the methylpyridine (picoline) or by chlorine abstraction from the pyridylmethyl chloride. The e.s.r. spectra were invariably of poor quality (typical examples are shown in the Figure) as would be anticipated in view of the extra complexity (compared with benzyl) caused by the 1:1:1 nitrogen splitting, and the extra coupling constants (in the 2- and 3-isomers) arising from the unsymmetrical nature of the molecule. Analysis of spectra as weak as these poses two problems: firstly, the assignment of coupling constants and secondly to ensure as far as possible that the assignment is correct and unambiguous.

Analysis of the E.s.r. Spectra.—We start our discussion with the 4-pyridylmethyl radical as the simplest of the three isomers, and which therefore should be the easiest to analyse even though the spectrum is very weak. The analysis of the spectrum of this radical turned out to be an excellent exemplification of the procedure described in our previous paper,[2] using alternately MATCH (to locate the best position of a test spectrum consisting of as much information as is currently available about the spectrum) and SEEK (to locate new coupling constants one by one until the analysis is complete). A modification of MATCH enables us to vary the coupling constants and line widths one at a time up and down by one unit, to obtain better matching to the experimental spectrum as the analysis continues, and, for the final analysis, it allows the estimation of parameters more closely than the nearest integer by finding the position of the maximum product function on a three-point quadratic curve.

Table 1. MATCH and SEEK analysis of a 4-pyridylmethyl e.s.r. spectrum[a]

MATCH (M) or SEEK (S)	T	T	T	T	N	w	C	P
M						12	914	2 777
S				323		12	914	3 268
M				322		12	977	3 429
M					322	11	977	3 395
S			63	322		12	977	5 406
M			63	322		12	977	5 406
M				322	63	12	977	5 666
S			92	322	63	12	977	6 009
M			92	322	63	12	977	6 009
S		23	92	322	63	12	977	7 005
M		24	93	322	62	10	977	7 646
M		23.8	92.9	321.8	62.3	10.4	977	
S	1	24	93	322	62	10	977	7 659
M		24	93	62	322	10	977	6 373
M		24	62	322	93	10	977	5 760
M		62	93	322	24	11	977	5 877

[a] Analysis carried out on a 1904 point digitized spectrum: interval between points *ca.* 0.053 G. T = 1:2:1 triplet splitting from 2 protons; N = 1:1:1 triplet from the nitrogen atom; w = width factor (see reference 2), Gaussian derivative shape assumed, see text; C = apparent spectrum centre; and P = product function/1 000.

The procedure as applied to 4-pyridylmethyl is summarized in Table 1. The most prominent line (in retrospect the low-field line of the central nitrogen triplet) was located at 914 with a width factor of 12.† SEEK found a triplet splitting of 323. MATCH refined this to 322, relocated the centre at 977, and indicated that this coupling was not a nitrogen 1:1:1. SEEK next found a triplet splitting of 63; on this occasion MATCH indicated that this splitting was due to the nitrogen. Further triplets at 92 and 23 were found by SEEK: no change in the spectrum centre was found by MATCH, and best estimates for the coupling constants were found by varying each up and down by one unit and using a quadratic fit to find the best value from the product function.

A further run of SEEK showed a triplet at 1, an indication that the line shape is not as assumed. A slightly better fit is found with a Lorentzian shape, but the true shape is almost certainly distorted by the high modulation amplitude used to give the optimum signal to noise ratio. A further run of SEEK showed no further triplet in the range 1—350, and successive

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† The analysis of spectra is discussed in terms of splittings and line-width factors expressed in channel number units of the digitized spectrum. 1 Channel No. ≈ 0.053 G.

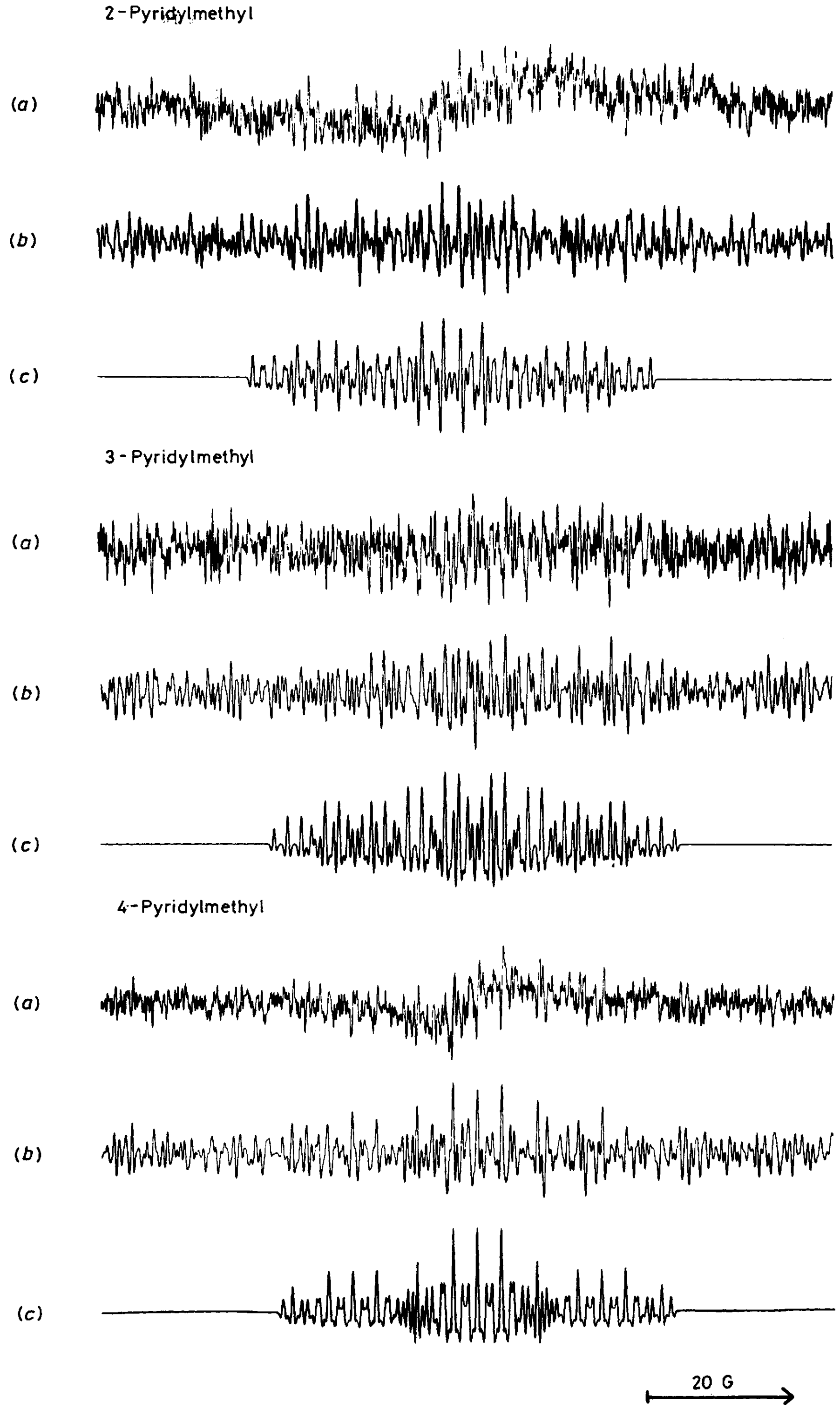


Figure. E.s.r. spectra of 2-, 3-, and 4-pyridylmethyl radicals. (*a*) Raw spectra; (*b*) spectra digitally filtered with a Gaussian derivative shape to give a second-derivative type of presentation (positions of lines emphasized) as described in reference 2; and (*c*) simulation using coupling constants shown in Table 2 [format as in (*b*)]

trials of the other coupling constants as the nitrogen 1:1:1 all gave lower values of the product function. Thus on the single assumption that the spectrum consists only of triplet splittings, we obtain an unequivocal analysis of the spectrum, together with confirmation that the analysis is complete and that no further couplings are involved. Our interpretation is confirmed for this radical by the good agreement with the adamantane matrix spectrum[1] (perfect agreement of coupling constants between fluid solution and adamantane spectra is not to be expected; benzyl radicals were found to exhibit slight differences in the two media).

Two features of these results may be of value in assessing the validity of the assignments for the 2- and 3-isomers (see below). Comparison of the experimental results with the INDO calculations[1] shows that the INDO calculations overestimate the *meta* couplings to an even greater extent than for benzyl, the *ortho* couplings are overestimated to a similar extent in the benzyl and 4-pyridylmethyl radicals, and the calculations overestimate the nitrogen coupling constant in 4-pyridylmethyl by a factor of approximately two.

Perhaps more significantly, the triethylsiloxy arylnitroxides (II)[3] have less spin density on the aryl ring than do the pyridylmethyl radicals (I): the ratio of coupling constants for 4-pyridylmethyl compared with the 4-pyridylnitroxide vary in the range 0.5—0.6.

Assignment of Couplings in 2- and 3-Pyridylmethyl Radicals.—The direct MATCH and SEEK analysis did not provide an analysis for the 2- and 3-pyridylmethyl radicals, which have, in principle, different coupling constants at each position. The large number of lines of similar size means that SEEK will sometimes choose sums or differences of coupling constants. We have refined the correlation techniques and devised a number of heuristics to help in this situation.

Firstly, we autocorrelate the spectrum. The maxima of the autocorrelogram should include the true coupling constants, along with sums and differences. If the spectrum shows very broad background variations, it is advantageous first to filter the spectrum using a differentiating filter (performed by using MATCH with a single Gaussian derivative peak with a line width which gives the optimum product function at the most intense line position).

It has been our experience that for any analysable spectrum, the largest (principal) off-zero autocorrelation maximum has corresponded to a true coupling constant. A large maximum at double the separation of the principal maximum indicates the presence of a multiplet due to the presence of one or more atoms with spin $> \frac{1}{2}$ or more than one spin $\frac{1}{2}$ atom with the same splittings. The next most intense autocorrelation maximum (ignoring multiples of the principal value) will also very probably be a true coupling. For benzylic radicals (including pyridylmethyl), the α-couplings will be sufficiently clear of the others to be little affected by chance coincidences of sums of other couplings, so that the correlations in this region should give a maximum at the true coupling, and since two protons are involved, a significant peak is to be expected at twice the α-CH$_2$ coupling. Using the above criteria, MATCH was used to find the best multiplicities of these prominent coupling constants (including the possibility that one of the couplings belongs to a nitrogen atom) using the maximization of the product function as a criterion of fit.

For 2-pyridylmethyl, the largest autocorrelation maxima were at 29 (0.375), 57 (0.293), 86 (0.213), and 320 (0.213). The large value at 57 suggests that this may be a true coupling too, rather than a multiplet artifact. Use of MATCH gave best values for two protons at 29, and a nitrogen at 57. The value of 86 may well be a combination of 29 + 57, but the 320 peak cannot be a combination of the other intense autocorrelation maxima, and thus is identified as the α-CH$_2$ triplet. Variation of these values one at a time allows an optimized fit of proton couplings of 24, 29, 320, and 322, with a nitrogen coupling of 58, width = 11.

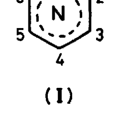
This leaves two couplings to be determined. For this we used an improved correlation technique, MULTIPEAK. This program takes a basic pattern (in this case as defined by the above coupling constants) and finds the 'best' offset positions to repeat it any desired number of times to give the best fit with the observed spectrum (details in the Experimental section). In this instance, four peaks were needed, and were identified as being at points 812.5, 910.5, 927.5, and 1 025.5. Since these unequivocally correspond to couplings of 98 and 115, the analysis is complete. MATCH was used to optimize the couplings and widths. SEEK established that with these coupling constants and provisional spectrum centre, no better fit could be found with any additional doublet or triplet coupling constant in the range 1—350, and MULTIPEAK established that no better fit for a doublet could be found for any of the 25 autocorrelation maximum values, with no assumption about the position of the spectrum centre. In support of this analysis, the position of the spectrum centre as determined by MATCH agrees with the position of the centre found by an alternative technique that does not involve any analysis of the spectrum's coupling constants.

The spectrum of 3-pyridylmethyl showed largest autocorrelation maxima at 97 (0.391), 313 (0.320), and 61 (0.306). By proceeding as above, MATCH suggested proton splittings of 94, 96, 99, 311, and 314 after optimization. MULTIPEAK (search for six peaks) gave no convincing pattern, so the procedure was repeated with an extra hydrogen or nitrogen coupling at 36 or 61, high and hitherto unused autocorrelation maxima. This resulted in two alternative analyses, 1 (36, 94, 96, 99, 311, 314), N(24), centre 1 031, $P = 8\,041$ K or 1 (94, 96, 99, 252, 311, 314), N(36), centre 983, $P = 8\,123$ K. The former analysis has the lower product function and a spectrum centre which does not correspond to that found independently, whereas the latter has a very unlikely proton coupling constant (252, *ca.* 13.4 G). SEEK applied to both tentative coupling patterns suggested further doublet couplings at 96 and 216, respectively: the production of such extra couplings by SEEK after all the expected couplings have been assigned is often an indication of an incorrect analysis.

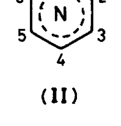
Accordingly, one of the couplings in the 97 region was removed. MATCH gave an optimized pattern of 1 (95, 98, 312, 314), $w = 11$. MULTIPEAK was now tried with this pattern plus successively a proton coupling corresponding to all the 13 autocorrelation maxima $\leqslant 156$, searching for a six-peak pattern. The best fit was for an extra proton coupling constant of 36, giving $P = 8\,914$ K, no obvious pattern of peaks. Similarly, a search for a nitrogen splitting among all autocorrelation values less than 100 also gave a best value of 36 for this coupling, $P = 8\,711$ K, and four peaks in a pattern which gave the two remaining proton couplings as 36 and 120, respectively. Alternatively, MULTIPEAK using a pattern of 1 (36, 95, 98, 312, 314), $w = 11$ plus a proton splitting varying up to 156 gave a maximum for a proton coupling constant of 120 with three peaks separated at distances corresponding to a 1:1:1 nitrogen triplet of 36.

MATCH showed the centre to be at 982.5 in accord with the independent estimate of the position of the centre. SEEK and MULTIPEAK showed no further coupling constant in the range 1—350, providing extra evidence that the correct analysis has been obtained.

Reproducibility.—Three independent e.s.r. spectra were run for each isomer of (I), and calibrated individually with



(I)



(II)

Table 2. E.s.r. coupling constants of pyridylmethyl radicals (I) and triethylsiloxypyridylnitroxides (II)[a]

Compound	Position of N	a_N	a_2	a_3	a_4	a_5	a_6	a_{7a}	a_{7b}	Note
(I)	2	3.05(2)		1.27(1)	6.05(2)	1.58(1)	5.22(1)	16.80(6)	16.96(4)	This work
(I)	2	1.35		1.40	6.30	4.60	5.20	16.45		Ref. 1
(I)	2	6.9		4.9	−6.6	4.9	−7.3	−15.7	−16.8	INDO, ref. 1
(II)	2	1.45		0.8	2.85	0.8	2.95	13.45		Ref. 3
(I)	3	1.95(1)	5.20(3)		6.37(1)	1.75(0)	5.12(2)	16.51(2)	16.59(4)	This work
(I)	3	6.79	5.20		1.98	~0?	~1.98?	16.27		Ref. 1
(I)	3	−4.4	−7.7		−6.7	4.4	−7.4	−17.0	−17.1	INDO, ref. 1
(II)	3	1.08	3.2		3.4[b]	1.08	3.0[b]	14.2		Ref. 3
(I)	4	3.35(1)	4.96(1)	1.23(1)				17.20(1)		This work
(I)	4	3.32	5.05	1.10				16.98		Ref. 1
(I)	4	6.8	−7.2	4.5				−16.2		INDO, ref. 1
(II)	4	1.8	3.0	0.7				12.85		Ref. 3
(I)			5.15	1.78	6.26			16.35		Ref. 2
(I)			5.08	1.95	6.25			16.1		Ref. 1
(I)			−6.4	3.6	−5.6			−17.0		INDO, ref. 1
(II)			3.1	1.04	3.1			14.76		Ref. 3

[a] Numbering system as in diagrams of (I) and (II) to facilitate comparisons between analogous positions. This does not conform to conventional numbering. Coupling constants in Gauss, figures in parentheses represent the standard deviation of three determinations, in units of 0.01 G. Lorentzian line shape assumed. The two α-CH_2 coupling constants for 2- and 3-pyridylmethyl have been optimized separately. See text for discussion of the reality of these differences. [b] Order inverted from reference 3. See text.

Mn^{2+}/SrO. The results are shown in Table 2 and exhibit a high degree of internal consistency as shown by the standard deviations. The maximum divergence of coupling constants was 0.11 G and the average standard deviation was 0.02 G. The two α-CH_2 couplings were allowed to vary individually for the 2- and 3-isomers and gave apparent slight differences. At least part of this difference may be an artifact: for a genuine triplet, a better line shape than the assumed Lorentzian may be obtained by treating the component as two slightly different doublets; true Lorentzian triplets of splitting intermediate between two integral values may also be better fitted in this way. Additionally, second-order effects will tend to distort the shape of the central lines. In an analysis of a 4-pyridylmethyl spectrum in which all the couplings were allowed to vary individually, differences of about 0.05 G were found between 'identical' couplings. The fact that these differences were found for both the small and large splittings suggests that this difference is mainly due to the line shape and non-integral coupling constant effects, though MATCH analysis of the central and outside groups of lines gave a greater apparent width to the central lines, in accord with a second-order splitting contribution. Thus the values for the differences in α-CH_2 coupling constants derived for the 3- and 2-pyridylmethyl radicals should be treated with caution, but the greater difference computed for the 2-pyridylmethyl radical suggests that here at least the close proximity of the nitrogen atom causes an observable difference between the two coupling constants.

Comparisons with Other Spectra and with INDO Calculations.—As noted earlier, there is good agreement between our analysis and that of Lloyd and Wood for 4-pyridylmethyl,[1] but for the other isomers there is considerable disagreement. This cannot be merely a matter of alternative patterns that give similar-looking simulations: simulations using our coupling constants look quite different from the spectra and simulations obtained by Lloyd and Wood for the 2- and 3-isomers. In support of our figures we note that they are more broadly in line with the INDO calculations[1] and perhaps more significantly, with the published e.s.r. spectra of the nitroxides, (II).[3] In the nitroxides, it is expected that less of the spin density will be localized on the ring. For all positions in the ring in benzyl and all the pyridylmethyl radicals, 16 sites in all, the ratio of couplings at a particular position in the nitroxide radical (II) to the corresponding position in the pyridylmethyl or benzyl radical (I) varies only in the range of 0.47 to 0.63.

Our proton coupling constants indicate that the nitrogen atom in pyridylmethyl radicals only causes minor changes in spin densities from those at corresponding positions in the benzyl radical. If we assume that the spin density at the 1-position in benzyl is the same as at the 3- and 5-positions, we derive $Q_H = -27.57$ G. Applying this figure to the pyridylmethyl radicals, and assuming that the (negative) spin density at the C(1) position is the average of that at C(3) and C(5) [C(3) only for the 3-isomer], we obtain the spin densities at nitrogen as 0.1340, −0.0787, and 0.1502 for the 2-, 3-, and 4-isomers, respectively. These figures may be used to derive $Q_N{}^N$ and $Q_{CN}{}^N$ from equation (1). The best least-squares fit gives $Q_N{}^N = 22.2$ and $Q_{CN}{}^N = -0.5$ G: these values 'predict' the three nitrogen couplings with a maximum error of 0.03 G. The $Q_N{}^N$ value lies within the range found by earlier workers for nitrogen-containing anion radicals[4] and the (less certain) $Q_{CN}{}^N$ value is small and of opposite sign as expected from the coupling mechanisms involved, and in qualitative agreement with values which can be derived from ^{13}C-substituted benzyl radicals[5] ($Q_C{}^C = 40.9$, $Q_{CC}{}^C = -12.8$ G).

$$a_N = Q_N{}^N\rho_N + Q_{CN}{}^N(\rho_C + \rho_{C'}) \qquad (1)$$

We have used the Lloyd and Wood INDO calculations[1] based on regular hexagonal geometry in this paper. More detailed studies show that by optimizing the geometry of the benzyl radical a better *para* to *ortho* ratio can be obtained,[6] but the higher value at the *para* position is not predicted and the *meta* coupling is still unacceptably high. In view of this, the considerable effort of optimizing the geometry of the pyridylmethyl radicals, especially the non-symmetric 2- and 3-isomers, appears unjustified. Our experimental figures suggest that, as expected, the same broad pattern is observed for pyridylmethyl as for benzyl radicals. The *meta* (3 and 5) couplings are much smaller than the INDO-calculated values. The nitrogen couplings are just under half of the INDO computed values, and the presence of nitrogen in the 2- and 4-positions seems to depress the coupling constants of the protons adjacent to it. On the whole, we have followed the INDO predictions in assigning positions, but we assign the 6.4 G coupling in 3-pyridyl to the 6-position [4-position in the numbering shown for (I)] on the basis of a study of a radical specifically deuteriated at this position,* and the assignments made[3] in the corresponding nitroxide (II) should probably be modified in accordance with this.

Spin Density at the α-Position and Stabilization.—The α-CH_2 coupling constants for all the pyridylmethyl radicals are greater than for benzyl itself, the order being 4- > 2- > 3-pyridylmethyl > benzyl. INDO calculations[1] do not predict this order at all, and imply that 2- and 4-pyridylmethyl radicals should have smaller α-coupling constants than benzyl; a similar conclusion was reached by calculations based on McLachlan's method,[7] in agreement with simple Hückel theory.

The variations in spin density at the α-position are also of interest in connection with the recent suggestion of a substituent constant scale for free-radical reactions based on the spin density at the α-position in benzyl radicals:[8] it is presumed that decrease in spin density is proportional to stabilization. The 3- and 4-isomers of methylpyridine have only about 0.44 and 0.33 of the reactivity of toluene towards hydrogen abstraction by t-butoxyl radicals,[9] but this is thought to relate to polar destabilization of the transition state rather than to the stability of the radicals formed. On the other hand, Barton and Stein[10] have recently measured, by very-low-pressure pyrolysis, the activation energies for 2-, 3-, and 4-ethylpyridine to give the corresponding pyridylmethyl radicals and methyl. Compared with the corresponding reaction of ethylbenzene to give a benzyl radical and a methyl radical, $\Delta E_a = 5.9 \pm 3.0, -1.2 \pm 1.8$, and 2.1 ± 1.8 kJ mol^{-1}, respectively. The corresponding changes in coupling constant are $+0.5_3$, $+0.2_0$, and $+0.8_5$ G, respectively, which cannot be said to provide strong support for the proportionality between change in coupling constant and stabilization energy at least in this system, though it must be stressed that the numbers are all small and the uncertainties relatively large.

Conclusions

In favourable cases such as 4-pyridylmethyl, a completely objective analysis of a weak e.s.r. spectrum can be made by correlation methods, including the establishment of the fact that no further coupling constants are present, in this instance on the single assumption that all the couplings are triplets. For the more complex 2- and 3-pyridylmethyl radicals, a rational analysis is possible but an element of judgement is needed. The correctness of the correlation analysis is supported by: (1) the agreement of the centre of the spectrum with that determined separately, (2) the positive indication of the absence of further couplings, (3) the broad agreement of the coupling constants with the results of INDO calculations, and (4) the close parallel of the coupling constants with those exhibited by triethylsiloxypyridyl nitroxide radicals (II).

Experimental and Computational Details

2-Bromo-3-methylpyridine and 6-bromo-3-methylpyridine were prepared from the corresponding amines by the method of Case,[11] and converted into the corresponding deuteriated compounds by treatment with n-butyl-lithium at −60 °C followed by addition of D_2O.[12] Purities were >97% by g.l.c. 2-D-3-Methylpyridine: δ_H 2.3 (3 H, s), 7.2 (1 H, m), 7.5 (1 H, d), 8.4 (1 H, d). 6-D-3-Methylpyridine: δ_H 2.3 (3 H, s), 7.2 (1 H, d), 7.5 (1 H, d), 8.5 (1 H, s), in agreement with the values of reference 12.

Radicals were generated photolytically at *ca.* −40 °C in the cavity of the e.s.r. spectrometer either by hydrogen abstraction from the methylpyridine (3-isomer only) or from the corresponding pyridylmethyl chloride (all three isomers). The apparatus is as described previously,[2] except that the data system has been replaced by a Strumech SEED microcomputer connected to the Varian E104A e.s.r. spectrometer by a 12-bit AD/DA converter. Approximately 4K points were accumulated in an 8-min scan: this number was reduced to *ca.* 2K by averaging pairs of points before commencing correlation analysis.

The correlation analysis was normally carried out using an assumed Gaussian shape: at the final stage a Lorentzian shape was tried, which usually gave a slightly improved fit, and the data in Table 2 are on the basis of a Lorentzian shape. Since the spectra were run with a relatively large modulation amplitude (0.5 G) to optimize the signal to noise ratio, considerable distortion of the line shape is expected.

Centre Finding.—To find the centre of a spectrum without any analysis of individual line positions, a '180° rotated' spectrum was created by reversing the order of points in the original spectrum and multiplying each value by −1. The '180° rotated spectrum' was then cross-correlated with the original spectrum, and the offset (rotated spectrum to the right of the original taken as positive) required to give the highest cross-correlation coefficient was determined, allowing the spectrum centre to be calculated by equation (2).

$$\text{Position of centre} = \frac{1 + \text{number of points} + \text{offset}}{2} \qquad (2)$$

MULTIPEAK.—This is a program to find the 'best' remaining pattern of lines, given a partial analysis of the spectrum. A variation of MATCH uses the partial information available to find possible line positions (corresponding to product function maxima) and the positions of all such possible lines and the product function for each of these positions are evaluated. A preliminary analysis of the spectrum is carried out by assigning line positions on a basis similar to elections held for multiple member constituencies with a quota: the quota here is [(sum of product functions + 1)/(number of lines + 1)], and lines not allocated immediately are allotted so as to give the largest value for [(product function)/(units allocated to a particular line)]. Two or more lines may be allocated to the same position.

This preliminary pattern of lines is used (with the initial partial analysis) to provide a full prospective analysis of the spectrum, and the product function is obtained by comparison with the experimental spectrum. The pattern is then changed by removing each 'line' in turn and seeing if a higher product function is obtained if it is replaced by a 'line' in one of the other possible positions. This procedure is repeated until no further improvement in product function is observed.

Acknowledgements

We thank the S.E.R.C. for a research studentship (to C. J. R.), the Royal Society for an equipment grant to update our data system, Dr. A. Hudson for helpful discussions, and Mr. P. R. Chitty and Mr. S. M. Kroll for development of the hardware and software required to link our e.s.r. spectrometer, the microcomputer, and the main-frame computer.

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* The weak spectrum of this radical was analysed by MATCH, using the couplings established for the non-deuteriated compound. Proton couplings were removed one at a time and replaced by a deuterium 1:1:1 of 1/6.5 of the protium splitting. The highest value of the product function was obtained when the 6.4 G coupling was removed in this way.

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Received 29th March 1984; *Paper* 4/508