Unambiguous Assignment of Electron Spin Resonance Spin Coupling Constants from Nuclear Magnetic Resonance Line Broadening Effects

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IN the analysis of a high resolution e.s.r. spectrum it is often difficult to make an unambiguous assignment of the proton coupling constants without examining specifically deuterated compounds. In this note we report a method which, in some cases, will give an unambiguous assignment without this labour. This method is based on the line broadening of the n.m.r. signals of a diamagnetic species, due to electron exchange with the paramagnetic species whose e.s.r. is under study.

Johnson and Tully[1] have shown that if there is rapid exchange between a diamagnetic and a paramagnetic species, then the broadening of the n.m.r. signals of the diamagnetic species should be dependent on the e.s.r. coupling constants of the paramagnetic species, while if exchange is slow no such dependence is expected. An example of the former case is given by Johnson and Tully[1] who showed that in isopropylbenzoquinone which is exchanging electrons with its semiquinone, the signals from the ring and methine protons are broadened by greater amounts than the signal from the methyl protons, while an example of the slow exchange case is to be found in proton exchange in tri-t-butylphenol.[2] We will give two cases which show that where there is rapid electron

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[1] C. S. Johnson and J. C. Tully, *J. Chem. Phys.*, 1964, **40**, 1744.
[2] R. W. Kreilick and S. I. Weissman, *J. Amer. Chem. Soc.*, 1962, **84**, 306.

exchange between a diamagnetic species A and the paramagnetic ion A^-, and the n.m.r. spectrum of A is of first order, then the n.m.r. signals of A are broadened by amounts which are roughly proportional to the e.s.r. spin coupling constants of A^-. This means that if the n.m.r. spectrum of A can be analysed with certainty, then the spin coupling constants of A^- can be assigned with equal certainty.

The proton n.m.r. spectra of 3,5-lutidine and 4,4′-bipyridyl have been measured in the presence of various concentrations of their negative ion radicals. The experiments were carried out in dry, de-oxygenated dimethoxyethane, the negative ions being produced by sodium metal. The concentration of radical could be controlled by the time of contact between the solutions and the metal. The n.m.r. spectra were measured on a Varian A60 spectrometer, without sample spinning. The results are summarized in the Table.

Compound	Posn.	Rel. broadening	Exptl. e.s.r. spin coupling constants (gauss)	Calc. Hückel spin densities
3,5-Lutidine	CH_3	1	0·80[3,4]	0·045[4]
	2, 6	3·3 ± 0·5	3·41	0·166
	4	6·9 ± 0·8	8·96	0·294
4,4′-Bipyridyl	α	1	0·45[5,6]	0·052[6]
	β	5·9 ± 0·8	2·32	0·068

Line widths, which are of the order of tens of cycles per sec., were measured by the width at half-height, and the broadening of the lines is expressed as the increase in line width after addition of paramagnetic species A^-. In the case of 3,5-lutidine the broadenings are given relative to the CH_3 signal, and in 4,4′-bipyridyl to the signal from the α protons. The relative broadenings are roughly independent of the concentration of A^- in the range studied. They are compared with experimental e.s.r. coupling constants, and calculated Hückel orbital spin densities. No changes of chemical shift were observed.

Although the experimental errors in measuring the line widths are large (the error could be reduced by making measurements on a large number of spectra and averaging), it can be seen that there is a fairly good correlation between the relative broadening of the n.m.r. signals and the e.s.r. coupling constants. In the case of 3,5-lutidine there is no ambiguity in the assignment of the e.s.r. lines, and this compound was merely studied to establish the relationship we have suggested. In the case of 4,4′-bipyridyl, however, the Hückel spin densities are not a reliable guide to the assignment of the e.s.r. coupling constants, and our experiment shows that the assignment given,[5,6] that is with the β position having the largest coupling constant, is correct.

The transverse relaxation times $(T_2)_{\rm p}$ of the paramagnetic species will be very much shorter than those in the diamagnetic species $(T_2)_{\rm d}$. Since with rapid exchange we see an average relaxation time, if $(T_2)_{\rm p}$ depends on spin density (and it is expected that this will be the case), then so also will the observed line widths. Further though less important grounds for a dependence of this sort arise from the chemical shifts seen in the paramagnetic species. What we observe is an average n.m.r. spectrum of A and A^- and if a proton is being subjected to a rapid change between two different environments, the observed line shape depends on the difference in its chemical shifts in these two environments. The larger this difference, the broader will be the signal. Since the chemical shifts of the protons in A^- are proportional to the spin densities,[7] there should be a correlation between the spin densities (or e.s.r. coupling constants) and the n.m.r. line widths.

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[4] C. A. McDowell and K. F. G. Paulus, to be published.

[5] R. L. Ward, *J. Amer. Chem. Soc.*, 1961, **83**, 3623.

[6] A. Carrington and J. dos Santos-Veiga, *Mol. Phys.*, 1962, **5**, 21.

[7] H. M. McConnell and C. H. Holm, *J. Chem. Phys.*, 1948, **28**, 749.