Identification of Individual Couplings in E.S.R. Spectra by Deuteriation and Autocorrelation

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Comparison of the autocorrelogram of the e.s.r. spectrum of a free radical with that of a radical deuteriated at a specific position allows the objective determination of the coupling constant at that position even in spectra which are too weak or complex for analysis by conventional simulation methods.

As part of a programme to develop objective methods of analysis of e.s.r. spectra by correlation techniques,[1] we became interested in the information which might be derived from comparison of the spectrum of an organic free radical with that of a similar radical deuteriated at a particular position. We decribe here work on the benzyl radical, the four monodeuteriobenzyl radicals, and the α,α-dideuteriobenzyl radical to shed light on this problem.

Substitution of a proton by a deuteron at a specific position in a free radical replaces a doublet splitting by a 1 : 1 : 1 triplet

Table 1. Establishment of coupling constants for individual positions in benzyl radicals from autocorrelograms of e.s.r. spectra of benzyl and deuteriated benzyl free radicals.[a]

Position of Deuteriation	H coupling	Largest peak other than true value (and discrimination ratio) Method A	Method B	Method C	Method D
ortho	97	287 (1.34)	118 (1.42)	34 (1.05)	309 (1.28)
meta	33	98[b] (0.94)	98[b] (0.94)	65 (1.06)	65 (1.23)
para	117	320 (1.06)	307 (1.29)	319[b] (0.96)	307 (1.09)
α	309	344[b] (0.90)	214 (1.16)	54 (1.68)	98 (1.84)
α,α	309	55[b,c] (0.90)	341 (1.01)	323 (1.32)	323 (1.32)

[a] See text for methods used. Couplings in channel units (= *ca.* 0.053 G). (1 G = 10^{-4} T). [b] Incorrect coupling has higher value than true coupling. [c] Peak at 341 also has higher value than true coupling.

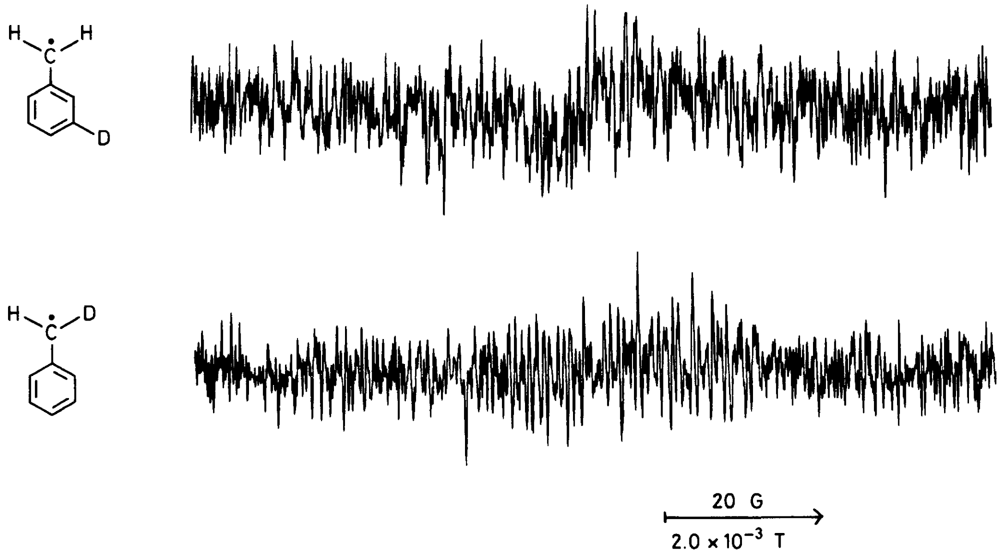

Figure 1. E.s.r. spectra of *m*- and α-deuteriobenzyl radicals.

in the e.s.r. spectrum. The ratio of the two coupling constants should be close to γ_H/γ_D = 6.514, but with differences that may be ascribed to the different zero-point energies of the two radicals in vibrational modes.[2] If a complete analysis of the spectrum is available, the coupling constant due to a particular proton can be identified by specific deuteriation followed by simulation analysis to see which doublet coupling has been removed and replaced with a 1 : 1 : 1 triplet of *ca.* a_H/6.514. However, in the absence of a complete analysis, a definite assignment cannot be made in this way. If the spectrum is reasonably intense, deuterium couplings can be assigned on the basis of the effect on total spectral width caused by specific deuteriation,[3] but this method fails if (as is commonly the case for spectra with high multiplicities) the outside lines are too weak to be seen.

Autocorrelation analysis offers the possibility of a solution to this problem. Maxima in a graph of correlation coefficient *vs.* horizontal displacement of the two 'copies' of the e.s.r. spectrum correspond to true coupling constants along with sums and differences: the determination of which maxima correspond to the true couplings in a complex spectrum is not easy.[4] The autocorrelogram of the e.s.r. spectrum of a deuteriated radical should differ from that of the protiated analogue by a lowering of the correlation coefficient at the position of the proton coupling constant (though also at positions corresponding to sums and differences of this coupling with others) and replacement with a new maximum near a_H/6.514 (with possible increases for combinations of this with other coupling constants too).

Thus the difference between the two autocorrelograms should provide a simple objective determination of the coupling constant at the position considered: there should be a maximum in the difference plot at this point. Column A in Table 1 shows the results obtained in this way for comparisons of *o*-, *m*-, *p*-, α-, and α,α-dideuteriobenzyl with benzyl itself. Discrimination is measured as the ratio of the biggest peak in this difference plot to the second biggest peak. It will be seen that this simple method only gives the correct result for two out of the five spectra considered, with the true coupling appearing as the second contender in two others and the third contender in the fifth.

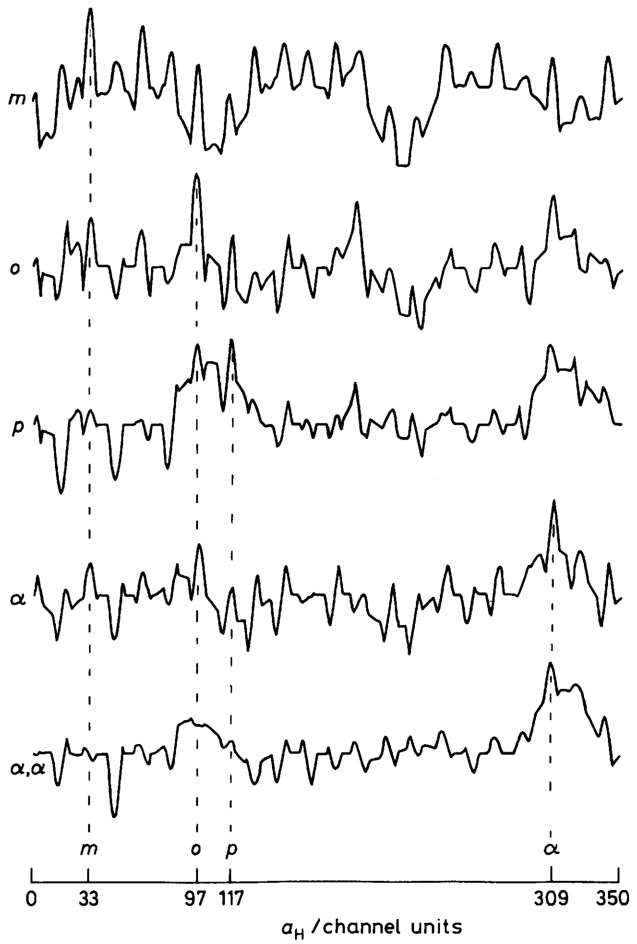

Figure 2. Determination of coupling constants at individual positions in the benzyl radical by method D. 1 Channel unit = *ca.* 0.053 G (1 G = 10^{-4} T).

This basic difference plot can be enhanced in two ways. Autocorrelograms of e.s.r. spectra have a wavelike appearance with negative values of correlation appearing between the positive values. This is due to the fact that for offsets just too big or small to match a coupling constant, the positive lobes in one spectrum will match the negative lobes of the lines in the other. These minima are of little significance in interpretation of a single autocorrelogram, but can have a big effect when differences of two correlograms are taken. To avoid this, we truncate the autocorrelograms so that all positive values are retained, but negative values are replaced by zeros. Application of this technique leads to the results in column B of the table, which shows that the correct result is obtained in four out of the five cases, with the *meta* coupling being the only one incorrectly assigned.

The second and more significant improvement is to make direct use of the increase in the value at the D coupling as well as the reduction in the value of the H coupling on deuteriation. A modified version of the difference plot (column A) is made with the x-axis scaled up by a factor of 6.514. This plot should show a maximum *negative* value at the H-coupling position, and subtraction of this plot from the original difference plot should give an enhanced plot. Column C in the table shows that this technique also succeeds in four out of the five cases, failing in this case only for the *para* coupling.

Both improvements in the technique can be combined: the correlograms are truncated and differenced as in B; this plot is expanded as in C and the difference between these two plots gives the results in column D. This refinement in technique gives the correct couplings in all five cases, with discrimination ratios of value for the true coupling compared with that for the next best value ranging from 1.84 to 1.09.

E.s.r. spectra of the deuteriated radicals were obtained by the method of reference 5; two examples are shown in Figure 1. The spectra have not been optimized since the object of this research has been to find methods which work on weak spectra. The *m*-deuteriobenzyl radical gives the poorest looking spectrum; presumably collapse of one of the *meta* couplings gives a new coupling which is small enough to broaden the lines significantly.

Figure 2 is a plot for all the radicals studied, according to the method of column D in the table. It will be seen that in each case the true coupling appears clearly from the plot.

This procedure should be useful in establishing definite coupling constants for particular positions in radicals whose spectra are too complex for direct analysis, and experiments in this area are under way. Small deviations from the theoretical 6.514 ratio of a_H/a_D for the radicals considered in this communication will be discussed in the full paper.

We thank the S.E.R.C. for a research studentship (to C. J. R.) and The Royal Society for an equipment grant.

Received, 26th June 1984; Com. 895

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