Tetrahedron Letters No.9, pp. 1055-1057, 1968. Pergamon Press. Printed in Great Britain.

RADICAL ANIONS FROM QUINOLINE AND ITS METHYL DERIVATIVES

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(Received in UK 5 October 1967)

E.S.R. signals from radical anions obtained by reduction of quinoline and its methyl derivatives with potassium pellets in oxygen free THF solution have been detected (Fig. 1). To overcome the band broadening due to electron exchange between the radical and the corresponding base (1), spectra were recorded at 70°C: samples containing nitrogen under pressure were employed to enhance the boiling point of the solution. Analysis of the spectrum of the quinoline radical anion (Fig. 1) provides a set of electron-proton and electron-N^{14} coupling constants. To assign the a_H values to the different positions of the quinoline ring, E.S.R. spectra of monomethyl derivatives were also recorded.

Unfortunately, owing to the great number of non equivalent protons, the spectra of monomethyl quinolines could not be completely resolved. Consequently the whole set of coupling constants could not be determined for these derivatives, excepting the case of 4-CH_3 quinoline. All the a_{CH_3} values, however, could be determined because of the 1:3:3:1 characteristic intensity ratio.

The following procedure was thus employed for assigning the a_H values obtained from the quinoline E.S.R. spectrum to the ring protons. From the overall splitting of every methyl derivative spectrum was substracted three times the value of the a_{CH_3} coupling constant: the difference between these values and the quinoline radical anion overall splitting (30.4 gauss) should give the a_H values of protons replaced by the -CH_3 groups. Obviously such an evaluation strictly depends on the degree of perturbation induced by the methyl group on the coupling constants of the individual protons and nitrogen and consequently on the overall splitting ($\sum 2a_iI_i$). From the examples reported in literature (2..6) it can be inferred that such an effect should not exceed one gauss:moreover,at least in the case of 4-CH_3 quinoline,it can be exactly evaluated, and amounts to 0.64 gauss. Extending this result to the other methyl quinolines the method allows the assignment of a_H coupling constants differing more than this amount. The correctness of such a procedure was checked in the case of 3-CH_3 and 6-CH_3 quinolines. For the radicals of these compounds a_H values could be directly assigned to positions 3 and 6 since in both cases one of the two smallest constants (0.6 and 0.8 gauss) is not present. These coupling constants agree with those assigned on the basis of the overall splitting, as above reported (first row of Table 1). The assignment was attempted also for the other protons: the results are listed in Tab. 1.

TABLE 1

Assignment of the a_H coupling constants to the hydrogens of the quinoline radical anion

Exp. values for quinoline	Positions	a_H calculated from $-CH_3$ derivatives(*)
0.6_0 - 0.8_0	3 - 6	0.8(3) - 0.8(6)
2.2_8 - 2.5_0	7 - 8	3.0(7) - 2.2(8)
3.8_8 - 4.2_2	5 - 2	3.8(5) - 4.2(2)
8.9_2	4	8.3(4)

*) Numbers in parentheses refer to the ring position.

It is here shown that owing to the presence of the methyl group the assignment has to be limited, for each proton, to a couple of values, and good agreement is generally observed with the assignment made for the acridine radical anion recently reported (7).

Further works are in progress to compare these results with the calculated spin density distribution.

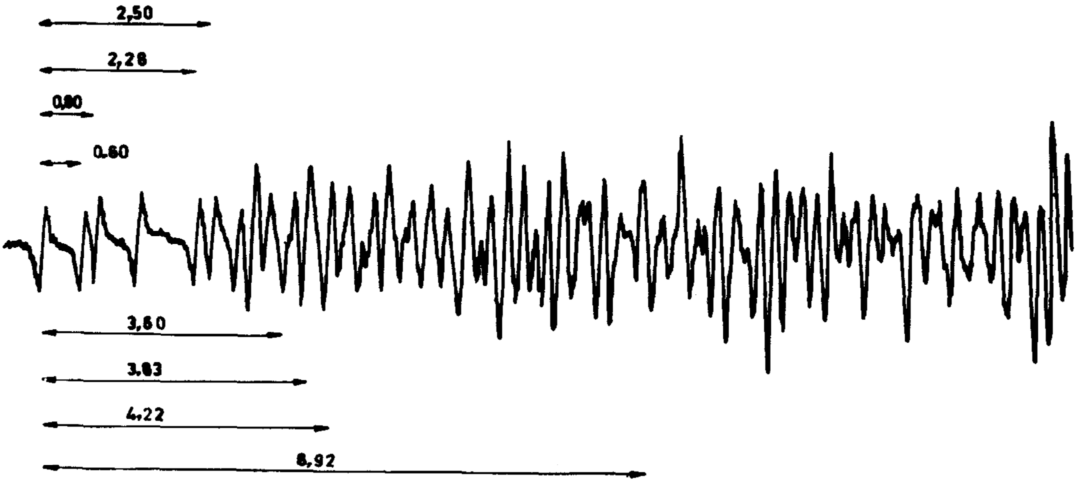

Fig. 1 - E.S.R. half spectrum of the quinoline radical anion. The coupling constants are expressed in gauss.

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