INTRAMOLECULAR HYDROGEN BOND AND HYPERFINE SPLITTING AT THE HYDROXYL GROUP

I. Dihydroxyanthrasemiquinones

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The ESR spectra of 1, 2-, 1, 4-, 1, 5-, and 1, 8-dihydroxyanthrasemiquinone were measured. A hyperfine splitting at the protons of the hydroxy groups participating in the formation of stable intramolecular hydrogen bonds with the carbonyl oxygen atoms is observed for all radicals. The spin density was calculated by the MO LCAO method in the Hu'ckel approximation, taking into consideration the configurational interaction according to McLachlan. Two models were used: the Pullman two-center models, one with and one without consideration of hydrogen bonds. The existence of the splittings indicates the participation of H-bonds in the transfer of the $\pi$ conjugation. A transfer of the spin density to the proton of the H-bond takes place principally from a proton-acceptor atom. It has been shown that the formation of intramolecular hydrogen bonds has a significant effect on the distribution of the spin density in the radical. Reasons are given for the advantage of the qualitative usefulness of the Pullman model in the calculation of H-bonds.

The ESR spectra of the anion-radicals of hydroxy-substituted anthraquinone have hardly been studied at all [1–3]. These radicals may conveniently serve as objects for the study of the effect of an intramolecular hydrogen bond (IHB) on ESR spectra. In connection with this, we measured the spectra of the anion-radicals of several di-, tri-, tetra-, and hexahydroxy-substituted anthraquinones. The spectra of the 1, 2-, 1, 5-, 1, 8-, and 1, 4-dihydroxy derivatives will be considered in this paper.

EXPERIMENTAL

The radicals were produced by hydrosulfite reduction in water—alcohol alkali solutions; the pH was 7.2–7.9. The spectra were recorded at room temperature on RE-1301 and EPA-2 instruments. The sensitivity of the EPA-2 instrument was \(5 \times 10^{-10}\) and that of the RE-1301 instrument was \(2 \times 10^{-12}\) mole of DPPH. Deuteration was accomplished in a solution of CH$_3$OD or in a mixture of CH$_3$OD and D$_2$O. The error in the determination of the splitting was ±0.1 Oe.

The spectrum of 1, 2-dihydroxyanthrasemiquinone (Fig. 1a) consists of four groups of lines; each one of the lines is split into a doublet and each component of the latter is split into a quadruplet. There is an even number of lines in the spectrum. All six C–H protons participate in the hyperfine splitting, whereby they fall into two groups each containing three equivalent* protons. The existence of a doublet may be due to a splitting at the proton of one of the hydroxy groups. The values for the splitting of the doublet and the two quadruplets are given in Table 1. The reconstructed spectrum (see Fig. 1a) is in good agreement with the observed one.

The spectrum of deuterated 1, 2-dihydroxyanthrasemiquinone (Fig. 1b) consists of an odd number of lines; it also consists of four groups of lines (1:3:3:1). A splitting of 1.57 Oe is maintained in the spectrum, but the doublet splitting disappears. This indicates that the doublet splitting occurs at the proton of a hydroxy group.

The spectrum of 1, 5-dihydroxyanthrasemiquinone (Fig. 2a) consists of seven triplets with a near-binomial intensity ratio. Within the triplets, the intensity ratio is close to 1:2:1, which corresponds to a splitting at two equivalent protons. The splitting between triplets is equal to 1.37 Oe and that within a triplet is 0.38 Oe. When the protons of the hydroxy groups are replaced by deuterium, then the spectrum of this radical (Fig. 2b) consists of seven lines with a near-binomial intensity ratio and with the same splitting (1.37 Oe); there is no triplet splitting. This indicates that the triplet splitting is caused by the protons of the two hydroxy groups and the six protons of the ring are practically equivalent.

*Not only protons which are strongly equivalent as far as their symmetry is concerned, but also protons for which the difference between the splittings lies within the experimental error of the determination will be called equivalent.
Fig. 2. ESR spectrum of 1, 5-dihydroxyanthrasemiquinone. a) Nondeuterated compound; b) deuterated compound.

Fig. 3. ESR spectrum of 1, 8-dihydroxyanthrasemiquinone. a) Nondeuterated compound; b) deuterated compound.

Fig. 4. ESR spectrum of 1, 4-dihydroxyanthrasemiquinone. a) Nondeuterated compound; b) deuterated compound.