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The ESR Spectra of the Anthanthrene and Binaphthylene Dioxide Cation-radicals

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Synopsis. The ESR spectra of the anthanthrene and binaphthylene dioxide cation-radicals were recorded and analysed.

Some aromatic hydrocarbons have been known to form stable cation-radicals when dissolved in concentrated sulfuric acid and to exhibit ESR spectra with well-resolved hyperfine structures. Perylene and tetracene are notable examples.[1,2] During the course of our work on photoemission from solid aromatic compounds, we noted that anthanthrene and a compound with the same framework, binaphthylene dioxide, have ionization potentials close to those of the above-mentioned hydrocarbons. Therefore, an examination of the ESR spectra of their cation-radicals was undertaken.

When 98% sulfuric acid solutions are diluted enough to resolve the hyperfine structure, the anthanthrene cation-radical gives sixty-one lines, with a total span of 27.6 G. The left-hand half of the spectrum is shown in Fig. 1. All the intervals except those in the terminal quintet are equal to d, while those in the quintet are 2d. The separation between the terminal quintet and the neighboring one, 9d, gives the second smallest coupling constant. As the total span is equal to 68d, the only possible constants for the remaining protons are 10d and 11d.[3] Therefore, a pair of the protons does not contribute to the hyperfine structure. The stick diagram reconstructed with these constants reproduces well the relative intensities of the experimental lines. McConnell has derived the $a_i=Q\rho_i$ relationship, which shows that the proton-coupling constant, a_i, of the aromatic free radical is proportional to the spin density, ρ_i, at the attached carbon atom, i.[4] As the HMO spin densities at the carbon atoms

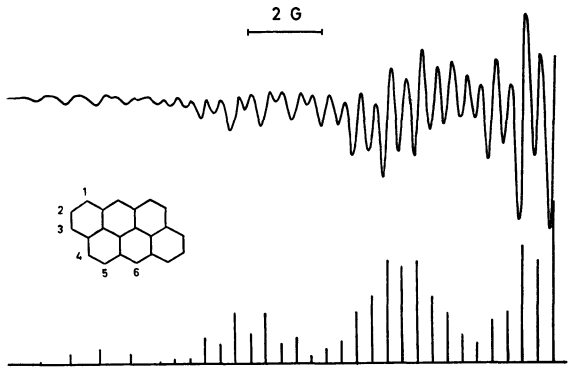

Fig. 1. First derivative of ESR spectrum of the anthanthrene cation-radical and the reconstructed stick diagram.

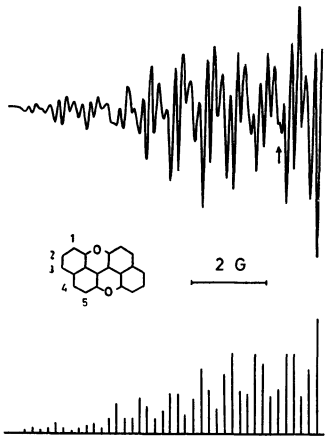

Fig. 2. First derivative of ESR spectrum of the binaphthylene dioxide cation-radical and the reconstructed stick diagram.

are 0.1074, 0.0003, 0.0969, 0.0436, 0.0431, and 0.1414 in the order of numbering given in Fig. 1, the large constants, 4.46, 4.06, and 3.65 G, may be assigned to the protons attached to the carbon atoms, 6, 1, and 3, and their equivalents respectively. The quintet with the spacing of 0.81 G arises from the coupling with the protons on the 4 and 5 carbon atoms and their equivalents.

The spectrum of the binaphthylene dioxide cation consists of seventy-seven lines, with an approximately equal spacing, d, if we ignore the partial resolution indicated by an arrow (see Fig. 2). The total span decreases to 15.7 G upon the introduction of two oxygen atoms into the framework. As the assignment of coupling constants did not seem easy, we employed the computing program proposed by Pomponiu and Balaban.[5] The summation of all the line intensities indicates that all the protons in this radical contribute to the hyperfine structure. The most probable partition of the thirty-eight intervals into five non-zero integers is d, 3d, 8d, 11d, and 15d. The stick diagram computed with these values appears to be consistent with the experimental spectrum. On the basis of the total span, the coupling constants can be approximated as 0.21, 0.62, 1.65, 2.27, and 3.10 G. The HMO spin densities on the carbon atoms calculated with the parameters of $\alpha_o=\alpha_C+2.0\beta_{CC}$ and $\beta_{CO}=0.8\beta_{CC}$[6] are 0.0591, 0.0175, 0.0754, 0.0947, and 0.0001, in the order of numbering in Fig. 2. The order of spin densities is different from that in the hydrocarbon cation-radical, but it is not affected by α_o even if this value is varied by $\pm 0.5\beta_{CC}$. Therefore, the largest constant may safely be assigned to the protons on the 4 carbon atom and the equivalent, and the second

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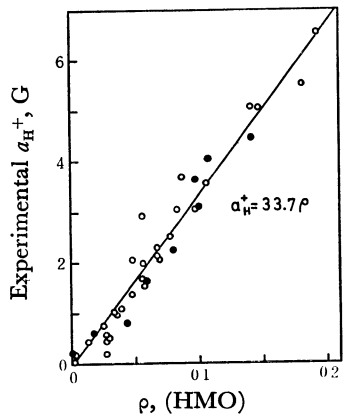

Fig. 3. Relation between experimental coupling constants, a_H^+, and HMO spin densities, ρ, for the anthanthrene and binaphthylene dioxide cations (●) and for other aromatic hydrocarbon cations (○).

largest, to those on the 3 carbon atom and the equivalent. On the other hand, the protons with the smallest constant are undoubletly attached to the 5 carbon atom and its equivalent, and those with the second smallest, to the 2 carbon atom and its equivalent. This cation-radical was found to be not quite stable; that is, a modification of the central part of the spectrum could be noted three days after the dissolution.

In order to verify the above choice of coupling constants, the constants for the present cation-radicals are plotted in Fig. 3 by shaded circles against the spin densities determined by the simple HMO theory. The plots show a linear relationship as good as those indicated by open circles for the eleven aromatic hydrocarbon cations compiled by Lewis and Singer.[7] We employed Q=33.7 G in this figure, following Griffith and Poole.[8]

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