

## Line Broadening in the EPR Spectrum of the Negative Radical Ion of 1,2,3,4-Tetrahydroanthracene

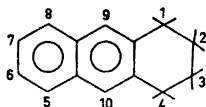
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The radical anion of tetrahydroanthracene was produced by reduction of the hydrocarbon with potassium in 1,2-dimethoxyethane and by electrolysis in dimethylformamide. Appreciable line broadening is observed with rising temperature in the EPR spectra of the radical ion in 1,2-dimethoxyethane recorded in the range from  $-90^{\circ}\text{C}$  to room temperature. The EPR spectra are compared with the spectra of the probable reduction and oxidation products of the tetrahydroanthracene anion.

Conformational change (chair boat) has been found to cause line broadening in the EPR spectra of the radical ions of tetrahydropyrene and hexahydropyrene in solution.<sup>1-3</sup> The radical ions of di-, tetra-, and octahydrophenanthrene have been studied by EPR spectrometry in 1,2-dimethoxyethane.<sup>4-6</sup> Line broadening has been observed by Iwaizumi and Bolton to result from ion pair formation in the EPR spectrum of the radical ion of dihydroanthracene.<sup>7</sup>

1,2,3,4-Tetrahydroanthracene has the structure:



In order to be able to identify the disproportionation products of the radical ion of tetrahydroanthracene, it was necessary to prepare and record the EPR spectra of the radical anions of anthracene, dihydroanthracene, and octahydroanthracene.

### EXPERIMENTAL

1,2,3,4-Tetrahydroanthracene was prepared under high pressure by hydrogenating 9,10-dihydroanthracene with the theoretical amount of hydrogen in the presence of Raney nickel. The products were analysed and purified by gas chromatography (Varian

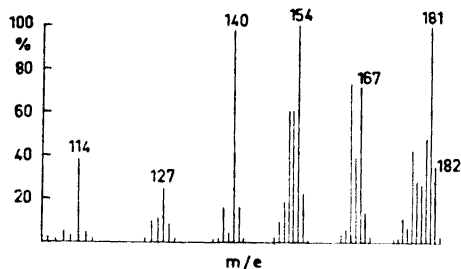


Fig. 1. The mass spectrum of 1,2,3,4-tetrahydroanthracene.

Autoprep 705). Four components were observed. Of these the component, in whose mass spectrum (Perkin-Elmer) the molecular ion peak was located at  $M^+ = 182$ , (Fig. 1), was collected with the gas chromatograph. The NMR spectrum (Perkin-Elmer) of the purified product showed that addition of hydrogen had occurred at positions 1, 2, 3, and 4.

1,2,3,4,9,10,11,12-Octahydrophenanthrene was prepared by the same method as tetrahydroanthracene. The molecular ion peak of the compound was located at  $M^+ = 186$ . The IR spectrum of 1,2,3,4,9,10,11,12-octahydrophenanthrene, which is reproduced in Fig. 2, differs clearly from the IR spectrum of symmetric 1,2,3,4,5,6,7,8-octahydrophenanthrene.

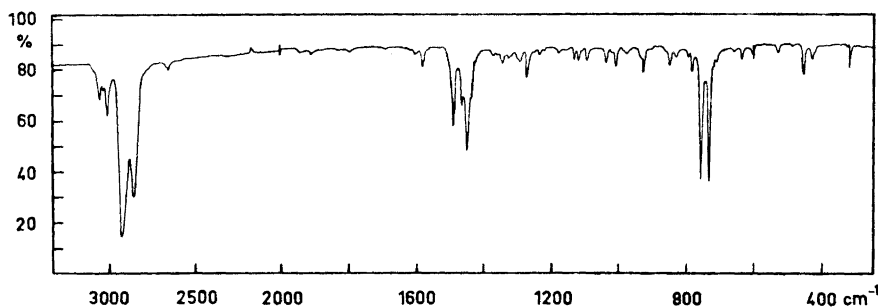


Fig. 2. The IR spectrum of 1,2,3,4,9,10,11,12-octahydrophenanthrene.

9,10-Dihydroanthracene was a commercial product, which was purified by gas chromatography.

The purification of the solvents and the preparation of samples in a high vacuum were carried out as described earlier.<sup>4</sup>

The EPR spectra were measured with a Varian E-12 spectrometer equipped with a Varian temperature regulator.

Molecular orbital, spin density and theoretical EPR spectrum calculations were performed at the Computer Centre of the University of Jyväskylä.

## RESULTS AND DISCUSSION

Iwaizumi and Bolton<sup>7</sup> found that there are three quintets in the EPR spectrum of the anion of 9,10-dihydroanthracene in dimethoxyethane at  $-87^\circ\text{C}$  and that the anion is unstable above  $-75^\circ\text{C}$ . They did not report what the decomposition products were. It is surprising that all four methylene

protons are equivalent at these low temperatures. In order to obtain a reference spectrum for possible decomposition products of tetrahydroanthracene, we measured the EPR spectrum of the 9,10-dihydroanthracene anion in dimethoxyethane and found it to be identical with the spectrum obtained by Iwaizumi and Bolton. At room temperature the EPR spectrum had changed into the spectrum of the anion of anthracene.

Coupling constants of the radical anion of 1,2,3,4-tetrahydroanthracene in 1,2-dimethoxyethane at  $-60^{\circ}\text{C}$  are collected in Table 1. The EPR spectra

Table 1. Coupling constants of the negative radical ion of 1,2,3,4-tetrahydroanthracene in 1,2-dimethoxyethane at  $-60^{\circ}\text{C}$ .

Positions	$a_{\text{H}}(\text{G})$
6, 7	1.69
1, 4	2.56
2, 3	0.16
5, 8	4.72
9, 10	4.90

of aromatic radical anions produced when potassium is used as reductant do not usually contain bands indicating coupling of potassium as signs of ion pair formation. Bands indicative of ion pair formation are not seen in Figs. 3, 4, and 5 (6). However, the variation of line width and intensity with temperature is considerable. The triplet  $^3a=1.69$  G due to the protons in positions 6 and 7 remains sharp at temperatures up to  $0^{\circ}\text{C}$ . The intensities of the lines of the protons at positions 1 and 4 rapidly approach the intensities of the quintet lines as the temperature rises above  $-60^{\circ}\text{C}$  and the lines are sharp up to  $0^{\circ}\text{C}$ . When, however, the temperature is lowered below  $-60^{\circ}\text{C}$ , the intensities

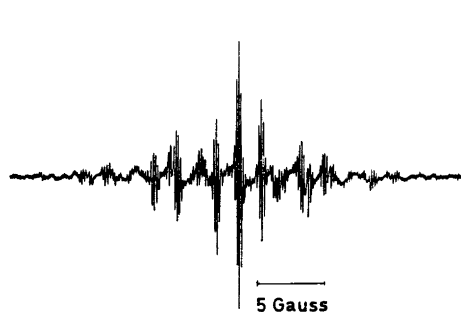


Fig. 3. EPR spectrum at  $-90^{\circ}\text{C}$  of the products of the reduction of 1,2,3,4-tetrahydroanthracene with potassium in 1,2-dimethoxyethane.

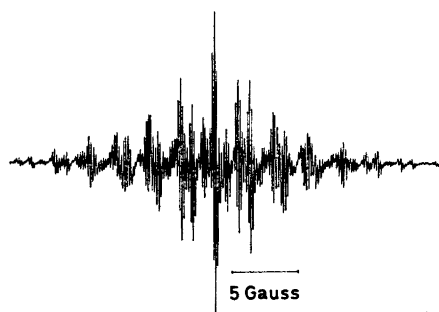


Fig. 4. EPR spectrum at  $-60^{\circ}\text{C}$  of the products of the reduction of 1,2,3,4-tetrahydroanthracene with potassium in 1,2-dimethoxyethane.

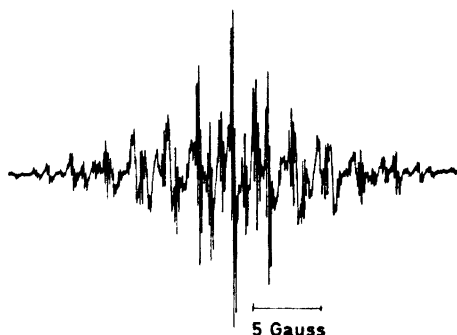


Fig. 5. EPR spectrum at  $-20^{\circ}\text{C}$  of the products of the reduction of 1,2,3,4-tetrahydroanthracene with potassium in 1,2-dimethoxyethane.

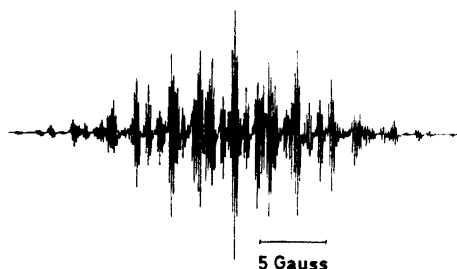


Fig. 6. Calculated spectrum with  ${}^5a = 4.72$  G,  ${}^6a = 2.56$  G,  ${}^7a = 1.69$  G, and  ${}^8a = 0.16$  G. Line width 0.05 G.

of the lines due to the protons at positions 1 and 4 diminish and the lines broaden.

The coupling constant 2.56 G is hardly visible at  $-90^{\circ}\text{C}$  and yet the overall length of the spectrum is the same. 1,2,3,4-Tetrahydroanthracene has two chair and two boat conformations. When the conformational change is slow, the change in the coupling constants of the protons on carbons 1 and 4 leads to the line broadening. This is clearly evident already at  $-90^{\circ}\text{C}$ . Because the solvent freezes, it was not possible to reach so low a temperature that the coupling constants of the axial and equatorial protons could be separately determined. When the temperature rises to  $-60^{\circ}\text{C}$ , the limit of rapid change is attained and the line becomes sharper with rising temperature. In this respect there is a clear difference compared with tetrahydrophenanthrene, the coupling constants of the axial and equatorial protons of which can be determined using dimethoxyethane as solvent. The conformational change evidently takes place much more easily with tetrahydroanthracene than with tetrahydrophenanthrene.

Conformational changes cannot, however, explain the extremely low intensities of the peaks due to the protons in positions 5, 8 and 9, 10 that are seen in Fig. 4. Though ion-pair coupling cannot be seen in the EPR spectrum of the tetrahydroanthracene anion, it is obvious that the rapid movement of the potassium ion above the plane of the aromatic moiety comes the intensities of the peaks of the protons in positions 5, 8 and 9, 10 to decrease as observed by Iwaizumi and Bolton in the case of the anion of 9,10-dihydroanthracene.<sup>7</sup>

The highest spin densities are observed in the positions 9, 10 and 5, 8 in the anion of tetrahydroanthracene. The potassium ion is located in this region and does not alter the intensities of the peaks of the protons in positions 6 and 7.

By varying the values of the coulombic integrals at positions 1, 4, 4a, and 9a and taking for the resonance integral  $\beta_{1-9a}$  and  $\beta_{4-4a}$  values greater than unity, the highest spin density is obtained for position 9, 10 by Hückel calculations. The tetrahydroanthracene anion is fairly stable and no changes were

seen in the EPR spectrum although the sample was allowed to warm to room temperature and re-cooled. The anion was produced also electrolytically in dimethylformamide at room temperature. It gave an EPR spectrum that was identical with the spectrum of the anion produced by reduction with potassium.

A radical anion was not obtained when symmetric octahydroanthracene was treated with potassium. Instead of asymmetric octahydroanthracene, we used 1,2,3,4,9,10,11,12-octahydrophenanthrene, the EPR spectrum of whose anion evidently must be almost identical with the spectrum of the anion of the corresponding octahydroanthracene.

The EPR spectrum of the anion of 1,2,3,4,9,10,11,12-octahydroanthracene in 1,2-dimethoxyethane at room temperature is shown in Fig. 7. It contains

Fig. 7. EPR spectrum at room temperature of the products of the reduction of 1,2,3,4,9,10,11,12-octahydrophenanthrene with potassium in 1,2-dimethoxyethane.



two triplets with coupling constants  $^3a(6,7) = 1.78$  G and  $^3a(5,8) = 4.77$  G that are fairly close in value to the corresponding coupling constants of the anion of tetrahydrophenanthrene.

When the EPR spectra of tetrahydroanthracene, anthracene, and 9,10-dihydroanthracene are compared, it is found that lines indicating presence of the last two anions are not present in the spectrum of tetrahydroanthracene. The conclusion is that no disproportionation has taken place. However, one cannot exclude the possibility that the anion of tetrahydroanthracene is reduced to the anion of asymmetric octahydroanthracene, as indicated by the coupling constants of the anion of asymmetric octahydrophenanthrene. The variations of the peak intensities with temperature and the stabilities of the intensities of the peaks of the protons in positions 6 and 7 show, however, that signs due to products of reduction are not either evident in the EPR spectrum of the radical anion of tetrahydroanthracene. As the temperature decreases, the influence of the hydrated ring in the anion of tetrahydroanthracene decreases, for the coupling constant  $^5a(5,8,9,10)$  is found to be 4.72 G at  $-90^\circ\text{C}$ . Its structure then resembles more the structure of the anion of naphthalene than that of 2,3-dimethylnaphthalene.<sup>8</sup>

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