

The ESR-Spectra of Radical Anions Generated from 5,12-Dihydrotetracene in Dimethoxyethane and in Liquid Ammonia

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The radical anion of 5,12-dihydrotetracene was prepared by the action of metallic potassium using dimethoxyethane as solvent. The ESR-spectra were recorded at various temperatures and the optical spectra in the visible region at room temperature. The anion radicals of 5,12-dihydrotetracene and tetracene were also generated in liquid ammonia, and they showed identical ESR-spectra.

The cation radical of 5,12-dihydrotetracene in trifluoroacetic acid was oxidized immediately to the tetracene cation radical.

The spectra of 5,12-dihydrotetracene in the UV and visible regions have been investigated earlier; an equilibrium has been observed to form between tetracene and 5,12-dihydrotetracene radical anions in dimethoxyethane.¹

The mono- and dinegative ions of tetracene can easily be identified on the basis of the spectrum in the visible region.²

The purpose of this work is to study whether it is possible to measure the ESR-spectrum of the 5,12-dihydrotetracene radical anion before the possible formations of the tetracene radical anions.

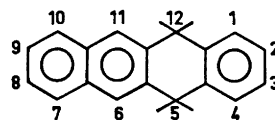
Liquid ammonia was chosen as an alternative solvent, since the concentration of solvated electrons in alkali metal reduction is high,^{3,4} and thus the equilibrium might remain on the side of 5,12-dihydrotetracene radical anion.

EXPERIMENTAL

1,2-Dimethoxyethane was purified as described previously.¹ The ammonia was a product of Merck and the degree of purity was

99.9%. It was distilled in the high vacuum line.

Tetracene was a product of K & K Laboratories, Inc. the visible spectrum we obtained agreed with that presented in the literature.^{5,6}



5,12-Dihydrotetracene was a product of Fluka AG. After purification⁷ we obtained a spectrum in the UV and visible regions, consistent with that in the literature.⁷

Trifluoroacetic acid and thallium(III) trifluoroacetate were Merck's products for spectroscopy.

The samples were prepared in high vacuum and the same ampoule contained ESR-cuvette and 1 cm and 1 mm optical cuvettes, which were of quartz glass. When liquid ammonia was used as solvent, the optical cuvettes did not tolerate room temperature, but broke down.

The ESR-spectra were recorded with Varian E-9 and E-12 spectrometers equipped with variable temperature control and with Varian 620/L-SS 100 computer facilities.

The spin density calculations and the simulations of the spectra were performed using the Univac 1108 central computer for Finnish universities.⁸ In order to perform INDO calculations for tetracene and 5,12-dihydrotetracene, it was necessary to expand the OCPE program to allow the basis set to be more than 80 orbitals. The following parameters were used in the INDO-calculations: $r_{C-C}(\text{arom.}) = 0.140$ nm, $r_{C-H}(\text{arom.}) = 0.1083$ nm, $r_{C-C}(\text{aliph.}) = 0.148$ nm⁹ and $r_{C-H}(\text{aliph.}) = 0.1093$ nm. The bond angles in positions 5 and 12 were 109.5°.

Optical spectra were measured with a Beckman DK-2A spectrophotometer.

Table 1. Coupling constants (G) of the radical anion of 5,12-dihydrotetracene in dimethoxyethane at 193 K.

Position	Exp. Anion	Calc. Anion	Calc. Cation
6,11	5.03	-6.5	-6.4
7,10	4.40	-4.6	-5.0
5,12(ax)	3.18	3,3	5.9
5,12(eq)	3.18	0.7	0.9
8,9	1.70	-0.8	-1.0
1,4	0.20	-0.13	-0.06

RESULTS AND DISCUSSION

Dimethoxyethane as solvent. The results of spin density calculations of the 5,12-dihydrotetracene anion by the INDO-method agree satisfactorily with the experimental values (Table 1). If we make comparisons between the anions of the 5,12-dihydrotetracene, naphthalene,¹⁰ and 1,2,3,4-tetrahydroanthracene,¹¹ we can observe that the coupling constants do not change in the equal positions noticeably.

Alternating line width as the temperature was varied between 180 and 233 K, was not observed, but instead some minor changes in intensities occurred.

It is perhaps rather surprising that the coupling constants of axial and equatorial protons were equal even at low temperature, but a similar result has also been observed with the anion of 9,10-dihydroanthracene.¹² The INDO-calculations show that the spin densities in the 1,2,3,4-positions are very small.

The sample was stored under liquid nitrogen between the measurements, although the optical spectra were recorded at room temperature. Immediately after measurements of the optical spectrum, the sample was cooled down and the resulting ESR-spectrum remained unchanged. When the sample was kept a few days at room temperature, a spectrum shown in Fig. 2 was recorded. It is, however, a mixture of different spectra.

The mononegative ion of tetracene has two narrow and very high absorption maxima at the wavelengths 402 nm and 824 nm and the dinegative ion of tetracene has at 619 nm a gently sloping absorption maximum.²

The curve labelled 1 in Fig. 3 shows the absorption peaks at 520 nm and 550 nm and they are due to the anion of 5,12-dihydrotetracene¹ and there are no peaks caused by the anions of tetracene. The ESR-spectrum was measured immediately, but there was still no ESR signal. The curve labelled 2 in Fig. 3 shows increasing concentration of the anion of 5,12-dihydrotetracene and immediately we can observe an ESR-spectrum (Fig. 1). In Fig. 3 there is no sign of the mononegative anion of tetracene, but the curve labelled 4 shows the absorption peak of the dinegative anion of tetracene and we can see the decomposition in the ESR-spectrum at the same time (Fig. 2).

When the sample was opened, nothing but tetracene and a small amount of 5,12-dihydrotetracene could be found.

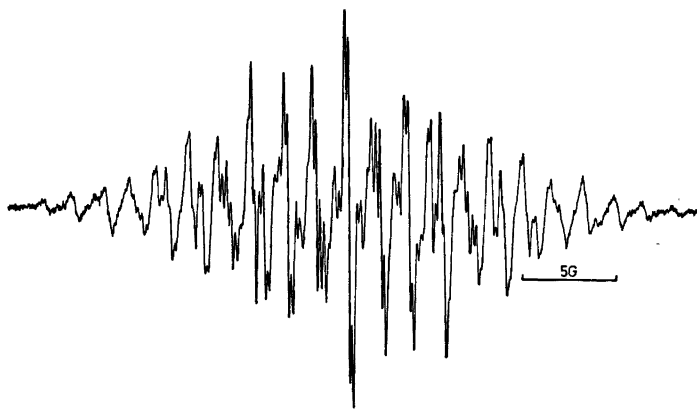


Fig. 1. The ESR-spectrum of the radical anion of 5,12-dihydrotetracene in dimethoxyethane at 193 K.

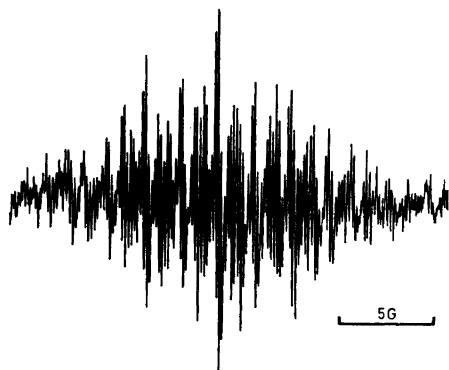


Fig. 2. The ESR-spectra of the radical anions generated from 5,12-dihydrotetracene after the decomposition in dimethoxyethane at room temperature.

When we observe the absorption of the dinegative anion of tetracene in the optical spectrum, the ESR-spectrum simultaneously shows that more than one radical was formed. The dinegative ion of tetracene has no triplet ground state and it cannot give any ESR-signal. This means that there is obviously one (or more) radical(s), whose structure lies between the anion of dihydrotetracene and the dinegative ion of tetracene.

Liquid ammonia as solvent. The radical anions of tetracene and 5,12-dihydrotetracene were generated by sodium-metal reduction. Fig. 4 shows the ESR-spectrum of the anion generated from 5,12-dihydrotetracene and Fig. 5

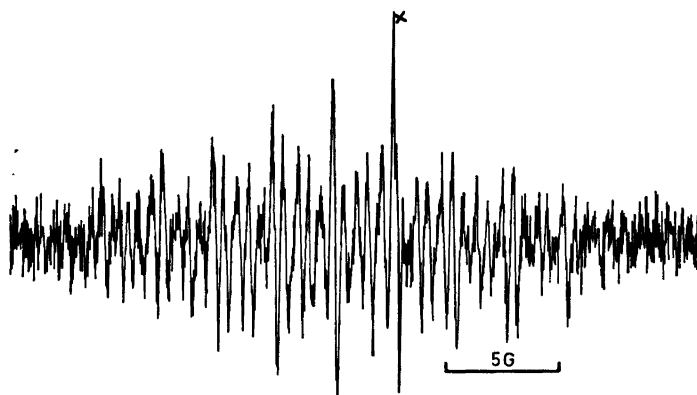


Fig. 4. The ESR-spectrum of the radical anion generated from 5,12-dihydrotetracene in liquid ammonia via sodium-metal reduction at room temperature. The peak of the solvated electrons is marked with x.

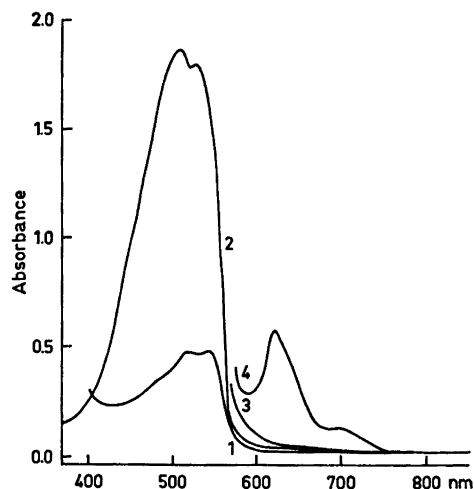


Fig. 3. The optical spectra of the anions generated from 5,12-dihydrotetracene in the visible region in dimethoxyethane at room temperature. Curve 1 is obtained using a 1 cm cuvette and the other curves using 1 mm cuvettes.

the ESR-spectrum of the anion generated from tetracene. The peak due to solvated electrons can also be seen in Fig. 4.

On the basis of the ESR-spectra in Figs. 4 and 5, both ions have the same structure; there is, however, a relatively strong noise. The same anion is generated both from dihydrotetracene and tetracene in liquid ammonia even at a low temperature, though the ion is stable also at room temperature. Alternat-

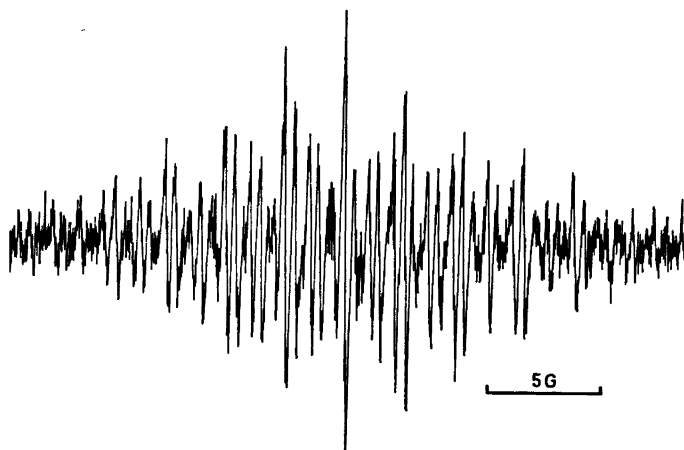


Fig. 5. The ESR-spectrum of the radical anion generated from tetracene in liquid ammonia via sodium-metal reduction at room temperature.

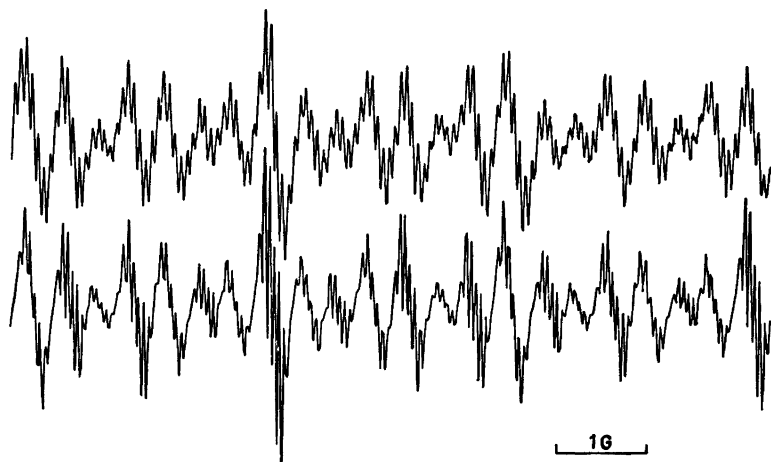


Fig. 6. The part of the ESR-spectrum of the radical anion generated from tetracene in liquid ammonia at 253 K. The lower curve represents a simulated spectrum (the Lorentz line shape) with a line width of 0.03 G and with experimental coupling constants mentioned in Table 2.

Table 2. Coupling constants (G) of the radical anion generated from tetracene and 5,12-dihydrotetracene in liquid ammonia at 253 K.

Position	Exp.	Calc.(dihydrotetracene)	
6,11	5.30	-6.5	-5.5
7,10	5.30	-4.6	
5,12(ax)	2.64	3.3	2.0
5,12(eq)	2.23	0.7	
8,9	1.50	-0.8	
1,4	0.07	-0.13	
Na ⁺	0.06	-	

ing line width due to the temperature was not observed.

In Fig. 6 the small quartet splitting of sodium ($m_1 = 3/2$) can be seen and hence the presence of an ion pair with the radical anion.

The experimental coupling constants presented in Table 2 differ slightly from the values in Table 1. The structure of the anion generated in liquid ammonia has more resemblance to the structure of 5,12-dihydrotetracene anion than to that of the tetracene anion.

The experimental coupling constants of the

axial and equatorial protons differ in positions 5 and 12, but only slightly. This means that the anion is nearly planar and the time averaged value is not concerned, as in dimethoxyethane even at a low temperature.

Trifluoroacetic acid as solvent. An attempt was made to prepare the cation radical of 5,12-dihydrotetracene by oxidation with thallium(III) trifluoroacetate. As a result we obtained the cation radical of tetracene.¹³ The same result was obtained using trichloroacetic acid as solvent.¹⁴ In fact, this was expected, since even in reducing circumstances 5,12-dihydrotetracene anion is oxidized to tetracene anion.

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