

The EPR, Endor and Triple Spectra of Anthracene Cation Radicals Generated by Thallium(III)trifluoroacetate in Trifluoroacetic Acid.

JORMA ELORANTA and SEPPO KASA

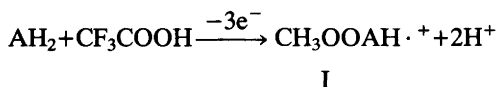
Department of Chemistry, University of Jyväskylä, SF-40100 Jyväskylä 10, Finland

Several different cation radicals are observed in the oxidation of anthracene in solution as monomer.¹⁻³ and as dimer.² When the oxidizing agent is Tl(III)-ion and the solvent trifluoroacetic acid,³ the reaction takes place in two stages.^{4,6}

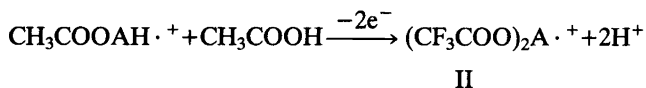
Similar reactions have been found in trichloroacetic acid and tribromoacetic acid.⁵

Where AH₂=anthracene and Tl³⁺=an oxidizing agent, the reaction⁶ is

Reaction stage 1:



Reaction stage 2:



The radical cation of 9,10(trifluoroacetoxy)-anthracene has the fluorine in the δ -position. The fluorine coupling has earlier been obtained by simulation of the EPR spectrum.^{4,6} This coupling might be verified from the ENDOR spectrum if it were obtainable, but very few Endor spectra of fluorine compounds in solution are known,⁷⁻¹⁰ especially F Endor spectrum of the radical cation has been measured by Evans *et al.*¹¹ The general Triple spectrum gives the relative signs of coupling constants and the special Triple spectrum the relative number of protons.

Experimental. We employed a Bruker EPR system ER 200D-SRC (with Varian 12" magnet) equipped with the data system Aspect 2000. This system consists of EPR, Endor and general and special Triple capabilities. The high vacuum samples were prepared as before.¹³

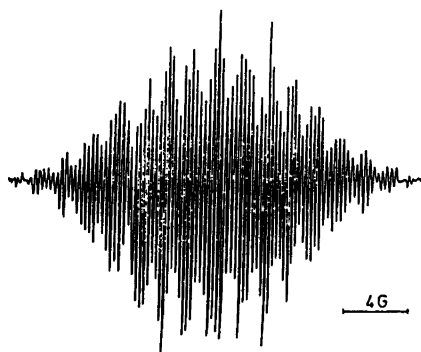


Fig. 1. The EPR spectrum of the radical I in trifluoroacetic acid at 255 K.

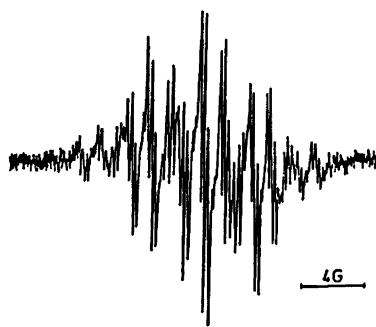


Fig. 2. The EPR spectrum of the radical II in trifluoroacetic acid at 255 K.

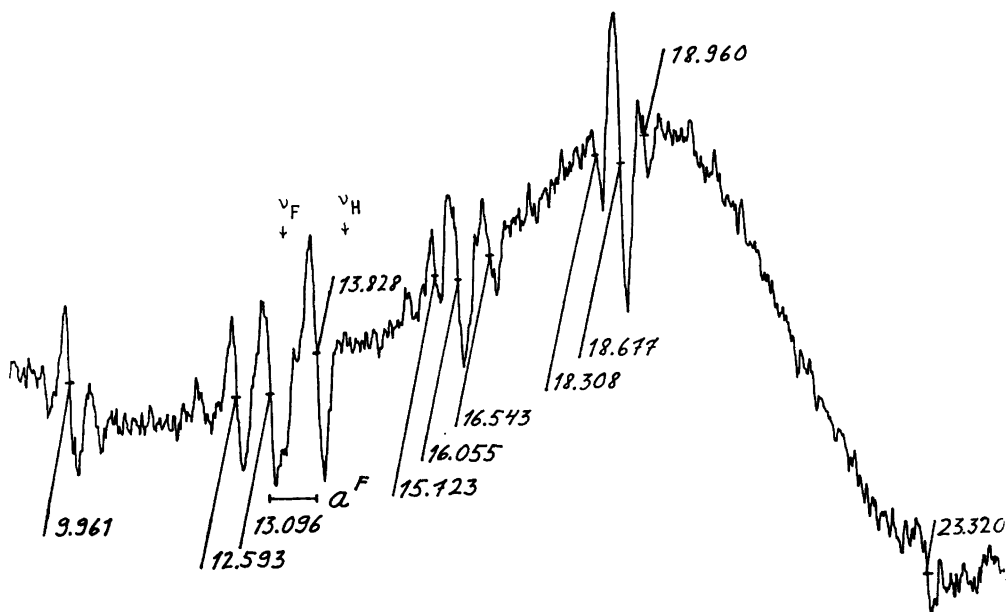


Fig. 3. The Endor spectrum of the mixture of radicals I and II at 255 K. The baseline is noisy during the reaction.

The anthracene was from Fluka AG ("puriss"). Its purity was checked by UV spectroscopy. Trifluoroacetic acid and thallium(III)trifluoroacetate were Merck products for spectroscopy.

Bond lengths and bond angles taken from Pople and Beveridge were used in the INDO calculations.¹²

Results and discussion. Though the radical I is shortlived at 255 K, it exists just long enough to make an EPR measurement feasible (Fig. 1).

The mixture of the radicals I and II is seen in the Endor spectrum of Fig. 3. The EPR spectrum of the radical II is presented in Fig. 2 and the corresponding Endor spectrum in Fig. 4a. The fluorine and proton couplings are seen in the Endor spectra.

The calculated and measured ν_F values are both 13.46 MHz.

The general Triple spectra of the radical II are shown in Fig. 4b, c and d. When the 18.6 MHz proton peak is pumped (Fig. 4b), the intensities of the lower field proton peaks increase, showing that the coupling constants of these two protons have the same sign.

The fluorine coupling constant has the opposite sign to that of the protons according to Fig. 4b. This is verified in Fig. 4c and d.

Negative coupling constants of the protons of the anthracene cation radical are obtained by INDO method,¹² which indicates a positive sign for the fluorine coupling constant.

The mean value of the coupling constants of the two triplets 2.85 and 3.30 G of the radical I (Table 1) is almost equal to the coupling constant of the quintet of the radical II. The similar behaviour is seen in the positions (2.7) and (3.6).

The measured coupling constants vary less than 0.01 G when different peaks are pumped.

In Fig. 5, the projection of the side chain of the radical I can be seen and the projection is perpendicular to the anthracene plane. The dihedral angles,¹⁴ used to calculate the coordinates of the side chain atoms, have to be chosen such that the fluorine atoms will lie

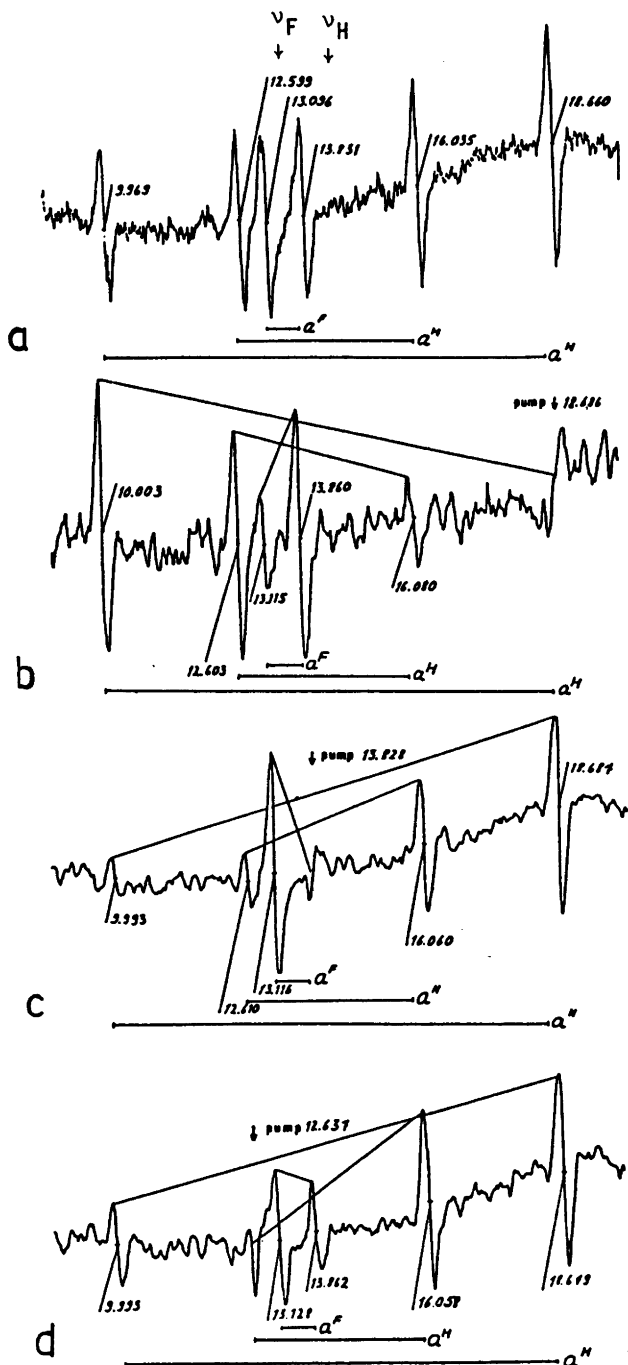


Fig. 4. (a) The Endor spectrum of the radical II. (b), (c) and (d) General Triple spectra of the radical II with different pumping frequencies. Spectra recorded at 255 K.

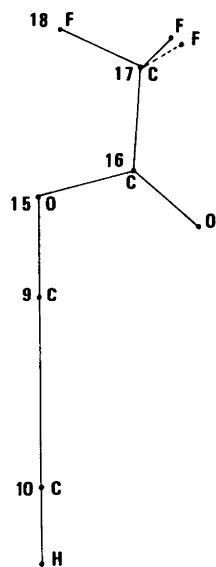


Fig. 5. The computer projection of radical I. The skeleton of the anthracene is perpendicular to the plane of the paper.

outward of the π orbitals of the anthracene. Otherwise the fluorine coupling constants would be about 1000 G.

Endor spectra confirm the coupling of fluorine which are in the δ -position toward the aromatic ring.

INDO calculations for the radical I (Table I) give reasonable results for the values and signs of the coupling constants. The signs of the fluorine coupling constants are positive. INDO calculations were not possible for the radical II owing to the orbital limitations.

Radical cations are usually more unstable than anions and specially favorable conditions are needed to get F Endor spectra in solution. Probably the $-(C=O)-C-$ group hinders the line broadening of radicals I and II in the present F Endor spectra, affecting the relaxation time of fluorine.

Table I. Coupling constants (G) measured from Endor and Triple spectra at 255 K. Calculated by Indo.

	a^F	$a^H(1.8)$	$a^H(4.5)$	$a^H(2.7)$	$a^H(3.6)$	$a^H(9)$
Radical I						
Measured	0.260	2.85	3.30	1.58	1.00	6.41
Calculated	1.5	-2.3	-3.3	-1.2	-0.04	-7.8
Radical II	0.262		3.09		1.22	-
Pumping frequency (MHz)						
18.686	0.264		3.09		1.24	-
16.071	0.260		3.08		1.23	-
13.828	0.254		3.08		1.23	-
12.637	0.261		3.09		1.22	-

1. Lewis, I.C. and Singer, L.S. *J. Chem. Phys.* 43 (1965) 2712.
2. Howarth, O.W. and Fraenkel, G.K. *J. Am. Chem. Soc.* 88 (1966) 4514.
3. Elson, I.H. and Kochi, J.K. *J. Am. Chem. Soc.* 95 (1973) 5060.
4. Eloranta, J. and Sippula, A. *Finn. Chem. Lett.* (1975) 170.
5. Eloranta, J. and Ijäs, M. *Finn. Chem. Lett.* (1975) 174.
6. Sullivan, P.D., Menger, E.M., Reddoch, A.H. and Paskovich, D.H. *J. Phys. Chem.* 82 (1978) 1158.
7. Lubitz, W., Dinse, K., Möbius, K. and Biehl, R. *Chem. Phys.* 8 (1975) 371.
8. Plato, M., Lubitz, W. and Möbius, K. *J. Phys. Chem.* 85 (1981) 1202.
9. Gerson, F., Heckendorn, R., Cowan, D., Kini, A. and Maxfield, M. *J. Am. Chem. Soc.* 105 (1983) 7017.
10. Evans, J.C., Rowlands, C.C., Herold, B.J. and Empis, J.M.A. *J. Chem. Soc. Perkin Trans. 2* (1984) 389.
11. Evans, J.C., Sorkhabi, Nouri, M.H. and Rowlands, C.C. *Tetrahedron* 38 (1982) 2581.
12. Pople, J. and Beveridge, D. *Approximate Molecular Orbital Theory*, McGraw-Hill, New York 1970, p. 132.
13. Eloranta, J., Hämäläinen, E., Salo, E., Mäkelä, R. and Kekäläinen, U. *Acta Chem. Scand. A* 37 (1983) 383.
14. Baird, N.C. and Dewar, M.J.S. *QCPE Program (COORD)* 136 (1973).

Received July 26, 1984.