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ESR-SPECTRA OF RADICAL ANIONS OF MACROCYCLIC AROMATIC COMPOUNDS II 1):

TRIBENZO-CYCLODODECAHEXAENE AND TRIBENZO-CYCLODODECATRIENETRIINE

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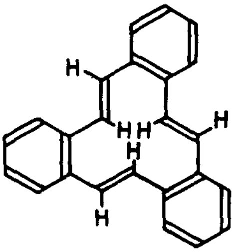
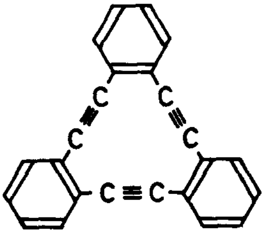
In a series of investigations of radical anions of macrocyclic aromatic compounds 1) we have measured the ESR-spectra of 1:2,5:6,9:1o-tribenzo-cyclododeca-1.3.5.7.9.11-hexaene (I) and of 1:2,5:6,9:1o-tribenzo-cyclododeca-1.5.9-triene-3.7.11-triine (II), the syntheses of which have been reported recently 2,3).



I



II

While II is undoubtedly planar with D_{3h}-symmetry, the UV and NMR-spectra of I indicate a non-planar structure caused by the repulsion of the three inner protons [2]. The experimental spin densities should provide information about the delocalisation of the unpaired electron and the symmetry of both the radical anions.

The negative ions were prepared with potassium (I) and sodium (II) in dimethoxyethane; the preparation of the anion of I with sodium gave a more complicated and less well resolved spectrum probably due to additional sodium splitting. The ESR-spectra measured with a Varian V-45oo spectrometer at room temperature are shown in fig.1 and 2 together with the theoretical reconstructions. The calculation is based on the assumption that the unpaired electron interacts with 3 groups of 6 equivalent protons in I and with 2 groups of 6 equivalent protons in II. The agreement between the experimental and the calculated spectra confirms the correctness of the assumptions on which the calculations are based, in particular the equivalence of the 6 bridge protons in I.

In addition, fig.1 shows the spectrum of I at -7o°C. It results from the spectrum at room temperature by disappearing of every second HFS-component, i.e. every component for which the sum of the three magnetic quantum numbers m_I is even. This interesting phenomenon is being investigated in detail and will be published elsewhere.

The measured coupling constants in Gauss and the spin densities obtained with $Q = -23.7$ Gauss at the adjacent carbon atoms are summarized in table 1. The Hückel spin densities

Fig.1

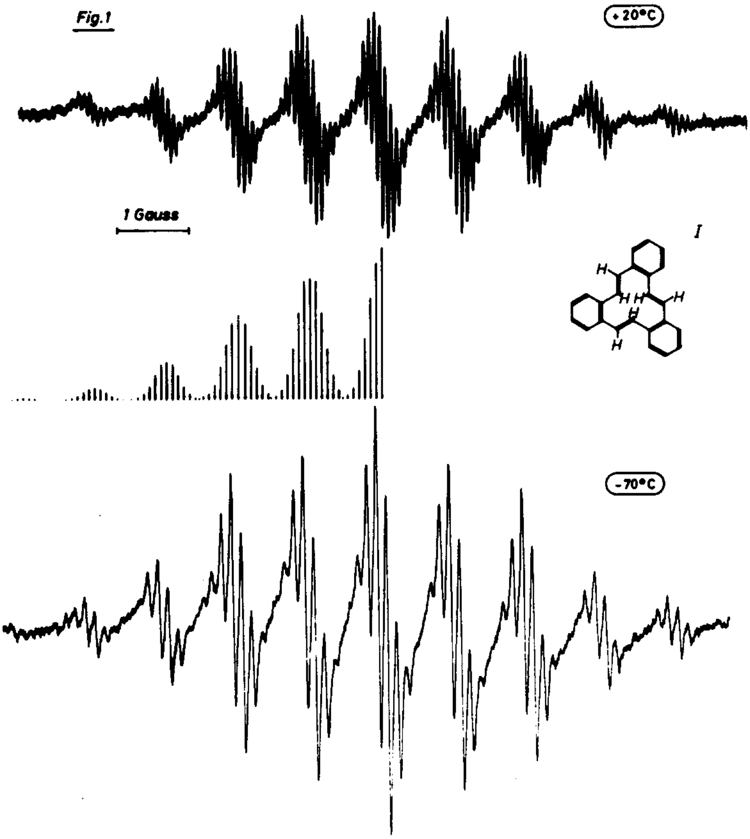


Table 1

type of protons	radical I coupling constant $-a_i$ [G]	radical I exp.spin densities ρ_i	radical II coupling constant $-a_i$ [G]	radical II exp.spin densities ρ_i
H_A	0.077±0.005	0.0033	0.092±0.005	0.0039
H_B	0.90±0.02	0.038	1.34±0.02	0.056
H_C	1.05±0.02	0.044	---	---

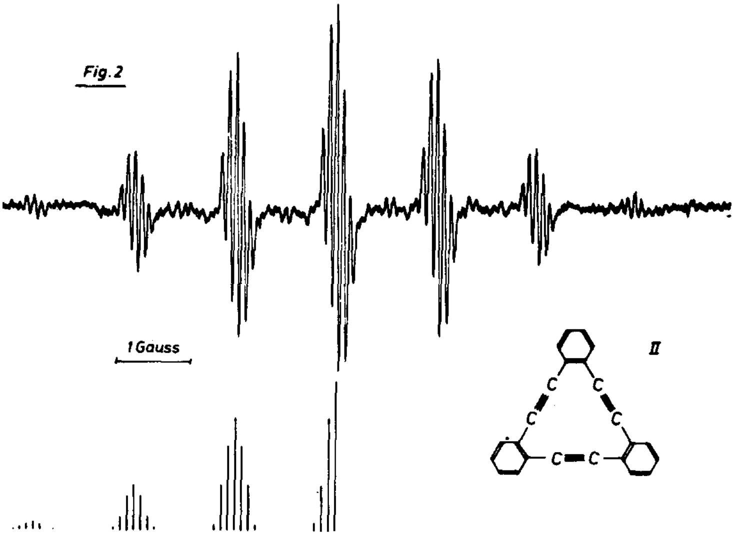


Fig. 2

calculated for comparison are ρ = o.o169 for the α-protons (adjacent to the bridges) and ρ = +o.o289 for the ß-protons of both radicals and ρ = +o.o784 for the bridge protons of I. The poor agreement between these and the experimental spin densities is perhaps not surprising considering the fact that neither the triple bond in II nor any deviation of planarity in I is taken into account in the simple Hückel calculation. Nevertheless, the assignment of the smallest coupling constants to the α-protons in both I and II is very probable, but it remains open which of the two larger coupling constants of I belongs to the ß-protons and which to the bridge protons.

We have also measured the radical anions of the related molecules stilbene and diphenyl-acetylene in order to obtain additional information for the assignment of the coupling constants in I and II. However, a meaningful correlation between these anions and those of compounds I and II could not be obtained. Since the ESR-spectra of these molecules have recently appeared in the literature 4), they are not reproduced here; our coupling constants agree with those given in 4) within the experimental error of o.o3 Gauss.

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1) Part I: P.H.H.Fischer, K.H.Hausser and H.A.Staab, Z.Naturforschg. 19a, 816 (1964).

2) H.A.Staab, F.Graf and B.Junge, Tetrahedron Letters 1966, 743.

3) H.A.Staab and F.Graf, Tetrahedron Letters 1966, 751.

4) C.S.Johnson and R.Chang, J.Chem.Phys. 43, 3183 (1965).