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ELECTRON PARAMAGNETIC RESONANCE OF THE 10,10-DIPHENYL- -9-ANTHRONE KETYL

The EPR spectra of the ketyls obtained from 10,10-diphenyl-9-anthrone by reduction with alkali metals and by electrolysis were determined and are interpreted by comparison with the spectra simulated on a computer. The assignment of the various hyperfine splitting constants to the different protons present in the molecule was based on a Hückel molecular orbital calculation.

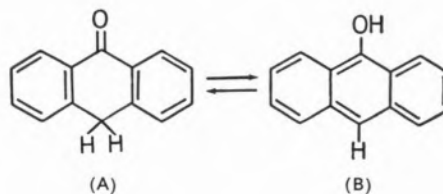
1 — INTRODUCTION

During some studies on the radicals obtained by reduction of o-dibenzoylbenzene, which will be published in short, the question came up, whether the electron paramagnetic resonance (EPR) spectra observed were originated by a species with the same carbon skeleton, or by a species in which a cyclization had already occurred. The existence of such cyclization reactions was proved by isolation of the quenching products, some of which were anthraquinone and anthracene derivatives (1-5).

This arose the interest of the authors of this paper to search the literature and to do some experimental work on radical-anions of such compounds as possible intermediates in the reduction and cyclization processes of o-dibenzoylbenzene.

EPR-spectra of the anthra-semiquinones in several solvents were already known (6-8), and there were two reports about a supposed radical-anion of anthrone (9, 10). The latter spectra were however narrow and did not account satisfactorily for all the protons in the anthrone radical-anion. This led recently TABNER and ZDYSIEWICZ (11) to reinvestigate the reduction of anthrone and to assign the formerly observed EPR-spectra (9, 10) to the semiquinone of anthraquinone.

By changing the experimental conditions of the anthrone reduction they were able to obtain a spectrum consistent with a mixture of the radical-anions of anthrone and anthranol, which is not unexpected, as they point out, because anthrone itself exists as keto-enol equilibrium mixture of anthrone (A) and anthranol (B).



When the authors of the present paper decided to start the research work which is presently reported the paper of TABNER and ZDYSIEWICZ (11) was not yet available to them. They were however already aware of the fact that the reduction of anthrone might lead to a complex series of reactions and were also doubtful of the assignment of the

EPR-spectra made in the first reports (9, 10) on the reduction of anthrone.

Instead of reinvestigating the anthrone reduction like TABNER and ZDYSIEWICZ (11) did, a compound was chosen, where no further reactions after the first reduction step were to be feared. For this reason it was decided to study the reduction of the non-enolisable 10,10-diphenyl-9-anthrone (DPA).

2 — EXPERIMENTAL

10,10-Diphenyl-9-anthrone (DPA) was synthesized by a known procedure (12-14). Samples of radical-anions obtained by the reduction of DPA with alkali metals (lithium, sodium and potassium) were prepared in pyrex tubes (fig. 1) directly adaptable to a vacuum line and to the EPR cavity. The solvent used, tetrahydrofuran, was distilled directly into the sample tube at a low pressure (5×10^{-3} mm Hg)

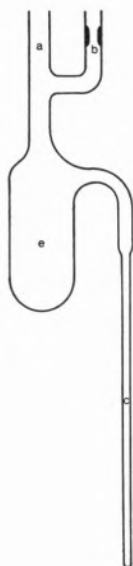


Fig. 1

Tube for the preparation of EPR-samples by reaction with alkali metals.

from a flask where it was kept dry in the presence of a sodium mirror with the characteristic blue colour of the benzophenone ketyl. For the electrolysis was used a quartz flat cell in connection with a simple device (fig. 2) where the solution was

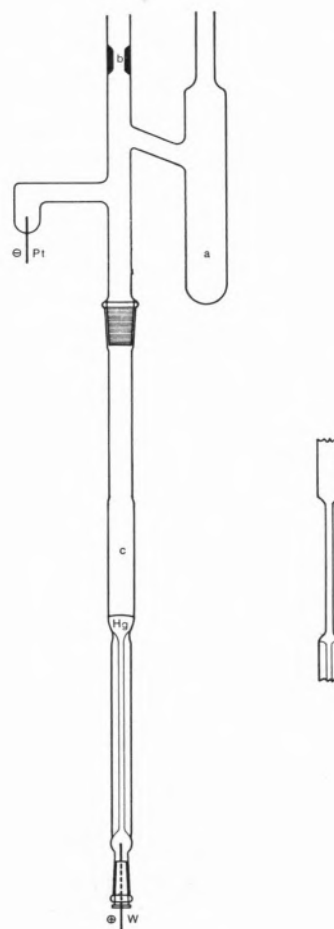


Fig. 2

EPR-sample tube for electrolysis.

initially deaerated. As solvent *N,N*-dimethylformamide was used and as supporting electrolyte tetrabutylammonium iodide in a concentration of 0,1M, the initial concentration of the ketone being 2×10^{-3} M. The applied electric tension was adjusted by means of a simple potentiometer so that it was just enough to produce the radical. The EPR spectrometer used was a Varian model 4502-04 with a 12 inch-magnet.

3 — RESULTS

The EPR-spectra of the DPA ketyls are represented in figs. 3 to 6, together with the simulated spectra calculated after the measured coupling constants, using a program written by one of us (P. B. C.) for

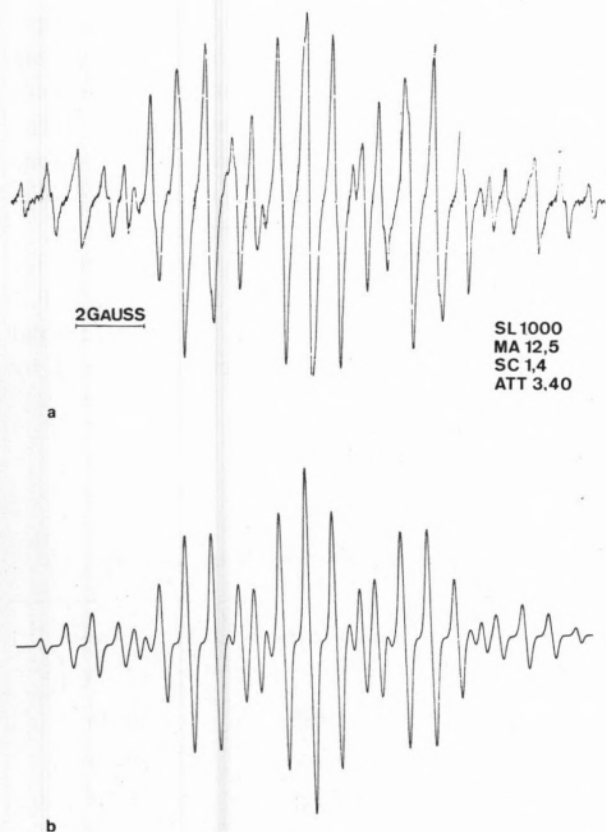


Fig. 3

Observed (a) and simulated (b) EPR-spectra of DPA ketyl obtained by electrolysis. The linewidth is 0.17 G.

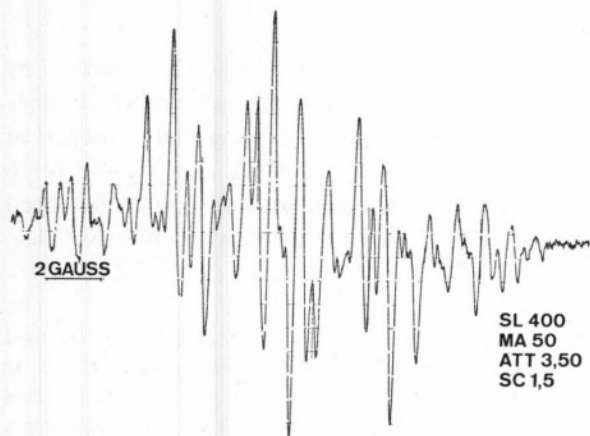


Fig. 4

EPR-spectrum of DPA ketyl obtained by reduction with lithium.

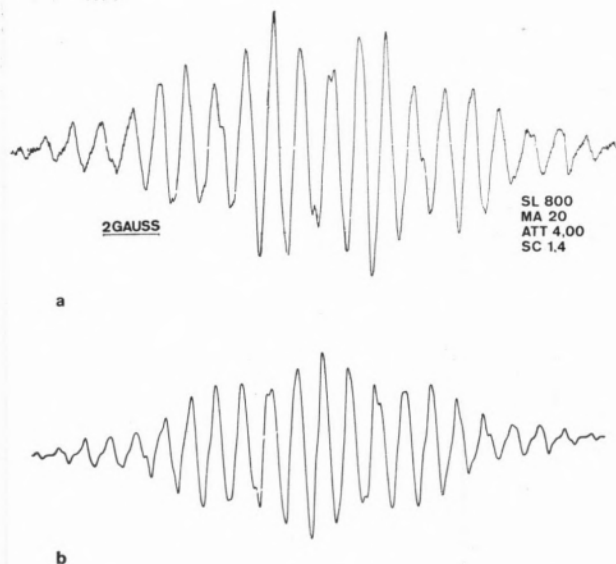


Fig. 5

Observed (a) and simulated (b) EPR-spectra of DPA ketyl obtained by reduction with sodium. The linewidth is 0.17 G.

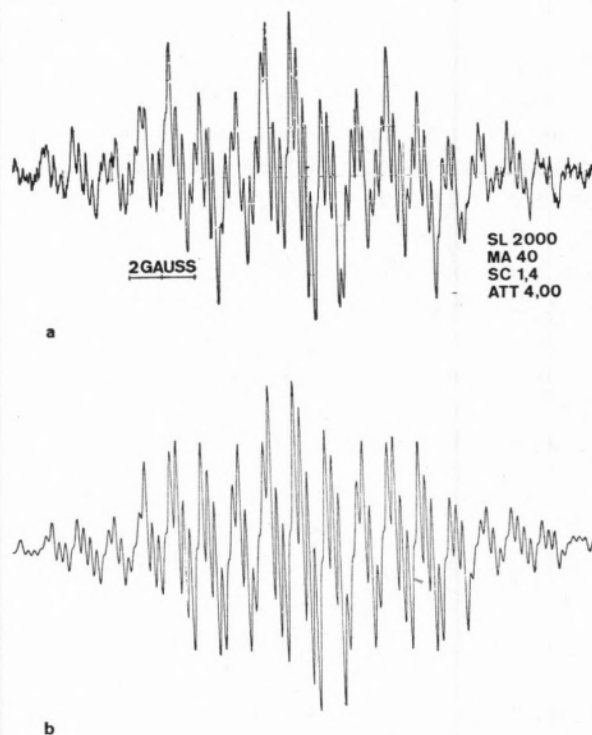


Fig. 6

Observed (a) and simulated (b) EPR-spectra of DPA ketyl obtained by reduction with potassium. The linewidth is 0.17 G.

Table I

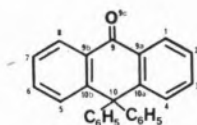
Hyperfine coupling constants in Gauss to the protons (a_H) and to the alkali metal (a_{Me}) in DPA Ketyl

	$a_{H1,8}$	$a_{H2,7}$	$a_{H3,6}$	$a_{H4,5}$	a_{Me}
Electrolysis	3.70	2.90	0.86	0.76	—
Sodium	3.80	2.85	0.95	0.76	0.93
Potassium	3.80	2.85	0.95	0.76	0.19

simple molecules like DPA (1), assuming the shapes of the curves are gaussian with a linewidth of 0.17 G. Table I shows the hyperfine splitting constants observed for the ketyls obtained by electrolytic reduction and by chemical reduction with sodium and potassium; the lithium spectrum was not simulated because it shows the same general aspect of the ketyl spectrum obtained by electrolysis, except that it appears to be a little more complex, which is probably due to the fact that lithium has two natural isotopes with nuclear spin different from zero.

At least twenty-nine lines are visible in the spectrum of the ketyl obtained by electrolysis whose relative intensities are 1:4:6:4:2:1:10:20:20:1:10:8:2:23:32:23:2:8:10:1:20:20:10:1:2:4:6:4:1.

A simple Hückel molecular orbital calculation was performed for the DPA molecule using the 1620/5.0.009 IBM program adapted to FORTRAN IV; this program was previously tested for the benzophenone ketyl giving electron spin densities that were in perfect agreement with those given by RIEGER and FRAENKEL (15).



In the M.O. calculation for DPA we have assumed that the two phenyl groups in position 10 would exert a $-I$ electron withdrawing effect, and so a positive Coulomb parameter for the carbon atoms

10a and 10b (16) was chosen. The parameters relative to the carbonyl group were varied according to the conclusions obtained by DEHL and FRAENKEL (17) for various cyclic ketyls and by GENDELL, FREED and FRAENKEL (18) for 9,10-anthrasemiquinone as studied in ethanol-water and in dimethylsulfoxide. The best values encountered were: $\delta_o = 1.2$; $\gamma_{eo} = 1.6$; $\gamma_{ec} = 1.2$ with the inductive parameter for carbon atoms at positions 10a and 10b, $\delta_c = 0.1$. Table II shows the calculated and experimental spin densities for the EPR spectrum obtained by electrolysis.

Table II

Calculated and experimental spin densities

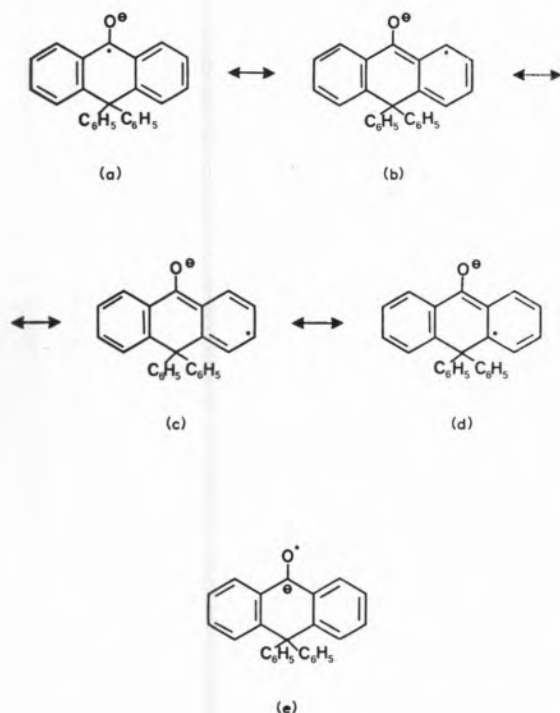
Position	Calculated (Hückel)	Experimental
1,8	0.082	0.116
2,7	0.007	0.034
3,6	0.103	0.148
4,5	0.002	0.030
9	0.176	—
9c	0.171	—
9a, 9b	0.042	—
10a, 10b	0.091	—

4 — DISCUSSION

The EPR-spectrum of DPA-ketyl obtained by electrolytic reduction presents a number of lines larger than twenty-five, showing that protons in positions 1 and 4 (or 5 and 8), and 2 and 3 (or 6 and 7) are not identical, similar to what has been verified very recently for the ketyl of anthrone (11).

(1) The program for the simulation of EPR spectra used presently by the authors can be applied to spectra with up to 5 coupling constants of nuclei $I = \frac{1}{2}$ and one coupling constant of a nucleus with $I = \frac{3}{2}$. A copy of the program, named «ANTRONA» in FORTRAN IV, can be obtained from the authors. Each simulation takes up 8 to 10 minutes to be performed in a NCR4100 computer.

On the basis of the valence bond theory it is to be expected that the contributing structures (a), (b), (c) and (d) must be important, besides (e)



which is confirmed by the Hückel M. O. calculation (see table II), allowing us the assignments of the hyperfine splitting constants to protons in DPA ketyl in the way shown in table I.

The order of magnitude of the observed splittings is rather in accordance with the spectrum published by TABNER and ZDYSIEWICZ (11) for the radical-anion of anthrone and anthranol than with the former reports (9, 10), which lends support to their interpretations.

The presence of the alkali metal changes only slightly the free electron spin density in the aromatic system (table I). The alkali metal hyperfine splitting constants are small but measurable.

For lithium it was not yet possible to obtain reliable values for the splitting constants from the spectra. As for the initial reasons for this research, the spectra of the adducts of alkali metals to o-dibenzoylbenzene differ so widely from the spectra reported in this paper and elsewhere (11), that there is no reason to suspect that these spectra stem from cyclization products with an anthrone skeleton.

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RESUMO

Determinaram-se os espectros de RPE dos cetilos obtidos a partir da 10,10-difenil-antrona-(9) por redução com metais alcalinos e por electrólise. Interpretam-se por comparação com os respectivos espectros simulados num computador. A atribuição das várias constantes hiperfinas de separação aos diferentes prótons da molécula foi feita com base num cálculo de orbitais moleculares de Hückel.