

B. J. HEROLD (1)

H. M. NOVAIS

M. CELINA L. R. LAZANA

P. B. CORREIA

Laboratório de Física e Engenharia Nucleares, Sacavém
Instituto Superior Técnico, Lisboa



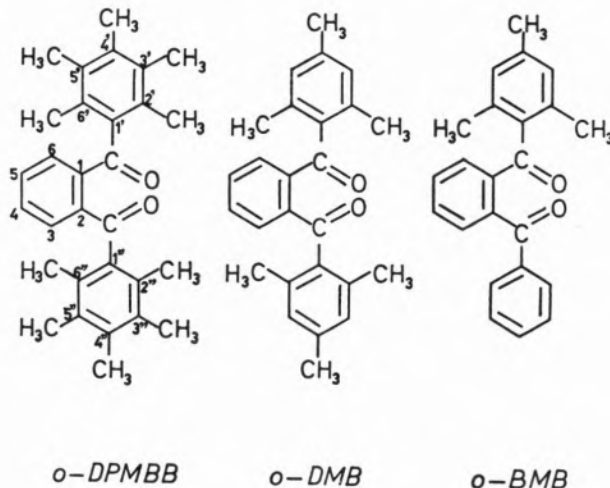
ELECTRON PARAMAGNETIC RESONANCE STUDIES ON THE CHELATION OF ALKALI METAL CATIONS BY RADICAL-ANIONS (2)

III—Radicals derived from o-benzoylmesitoylbenzene

The radicals obtained by alkali metal reduction of o-benzoylmesitoylbenzene are studied through their EPR-spectra. These spectra are compared with those obtained analogously from o-di-(pentamethylbenzoyl)-benzene and o-dimesitoylbenzene. The differences between these spectra are interpreted qualitatively.

1. INTRODUCTION

Previous studies of the ketyls produced by reaction of o-di-(pentamethylbenzoyl)-benzene (o-DPMBB) [1] and o-dimesitoylbenzene (o-DMB) (1,2) with alkali metals have shown a rough linearity between the electron spin density at the metal nucleus and $r^{-1/2}$, r being the ionic radius of the metal. The electron spin density is given by a_M/a , where a_M is the observed metal splitting and a the hyperfine splitting constant for the free atom.



It was verified that the slope of a_M/a versus $r^{-1/2}$ was smaller for o-DPMBB than for o-DMB.

In order to investigate whether a diminution of the number of the methyl substituents in the aryl groups always causes the angular coefficient of the straight line to become larger, the EPR-spectra of the ketyls of o-benzoylmesitoylbenzene (o-BMB) and o-dibenzoylbenzene were studied. The present paper only deals with the former case.

2. EXPERIMENTAL AND RESULTS

o-BMB was prepared according to Newman (3). The corresponding ketyls were obtained by reduction with alkali metals in the proportion of two atoms of metal to one molecule of the diketone (3), using

(1) Address: Laboratório de Química Orgânica, Instituto Superior Técnico, Av. Rovisco Pais, Lisboa-1.

(2) Papers I and II of this series: ref. (2) and (1).

(3) The use of two equivalents of metal instead of one seems a paradox way to obtain a radical-anion. This question is being studied at present.

Table 1

Hyperfine coupling constants and spin densities for the radicals obtained by metal-reduction of o-BMB

Alkali Metal	r	$r^{-1/2}$	a	a_M	a_M/a	a_H
Li	0.78	1.132	143.5	4.6	0.0321	2.22
Na	0.98	1.010	316	7.44	0.0235	2.43
K	1.33	0.866	82.4	1.24	0.0150	2.95
^{85}Rb	1.48	0.824	360	4.5	0.0125	2.53
^{87}Rb	1.48	0.824	1240	15.2	0.0123	
Cs	1.65	0.781	820	7.8	0.0095	2.59

 r — Goldschmidt ionic radius of the cation a — atomic hyperfine coupling constants in Gauss a_M — hyperfine coupling constants to the cation in Gauss a_H — hyperfine coupling constants to protons.

tetrahydrofuran as a solvent (spectra fig. 2-6). The samples were prepared by well known techniques (2). Table 1 lists the hyperfine coupling constants of the metal nuclei and of the protons observed. It lists also the atomic hyperfine coupling constants of the respective metals, given in Gauss by the expression (4):

$$a = \frac{\Delta\nu}{2.8} \frac{2}{2I + 1}$$

where $\Delta\nu$ is the hyperfine structure separation in MHz in the atomic spectrum (Zeeman effect) and I is the nuclear spin of the metal.

The EPR spectrometer used was a Varian V-4502-04 equipped with a 12-in magnet.

3. DISCUSSION

In fig. 1 the electron spin densities a_M/a at the metal nuclei are plotted against $r^{-1/2}$, r being the ionic radius of the alkali metal.

Together with the plot for the radicals obtained by metal reduction of o-BMB the plots for the corresponding radicals of o-DMB and o-DPMBB are given.

The slope of the lines decreases with an increasing number of methyl groups attached to the two aryl groups of the diarylbenzene.

It has been proved (1,2) that the radicals obtained by alkali metal reduction of o-DPMBB and o-DMB are intimate ion pairs where, however, a certain degree of covalency of the oxygen metal bond can be considered to exist and increases as the ionic radius of the metal decreases.

Studies with Stuart models show that the differences between the behaviour of o-DPMBB and o-DMB (fig. 7) cannot be accounted for by a steric effect because the 3', 5', 3'' and 5'' methyl groups in o-DPMBB do not hinder the molecule from assuming the same geometry as o-DMB. The main intramolecular steric interactions in these molecules stem from the methyl groups of the 2', 6', 2'' and 6'' positions of the two aryl groups. Therefore it is also unnecessary to consider a steric effect to explain the analogous differences between o-DMB and o-BMB (fig. 8) because, being of the same order of magnitude and signal, they are most probably of the same nature.

The explanation must be sought therefore on the basis of the electron donating effect of the methyl

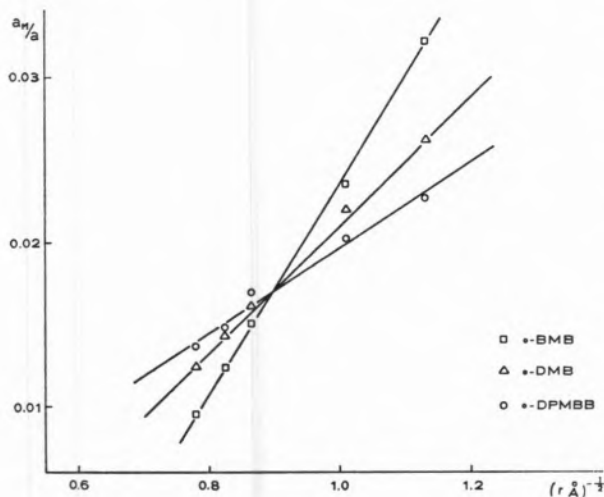


Fig. 1 — Plot of electron spin density a_M/a as a function of $r^{-1/2}$.

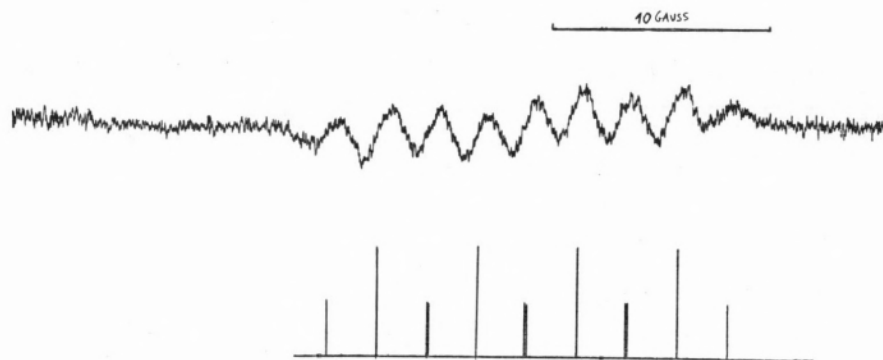


Fig. 2 — E. P. R. spectrum of the monolithium radical of o-BMB.

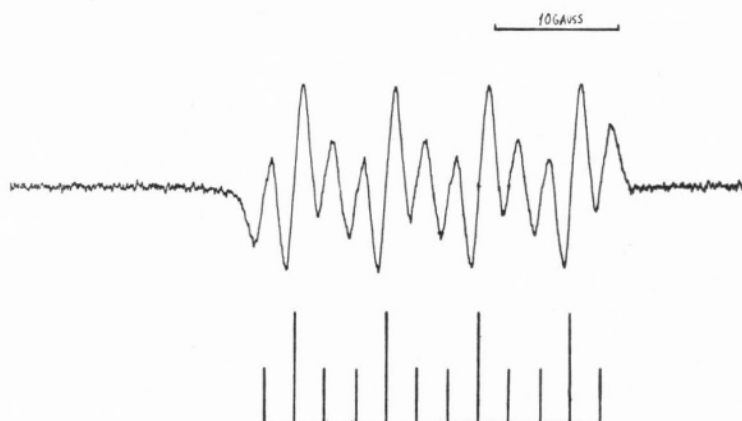


Fig. 3 — E. P. R. spectrum of the monosodium radical of o-BMB.

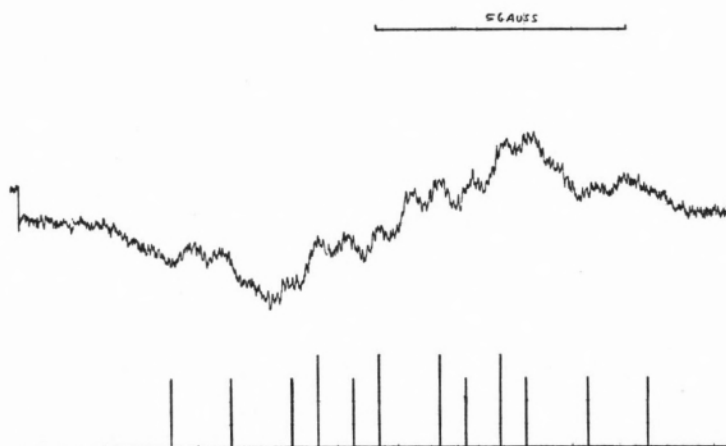


Fig. 4 — E. P. R. spectrum of the monopotassium radical of o-BMB.

groups. The analysis of the EPR-spectra of the radicals obtained by alkali metal reduction of o-DMB and o-DPMBB (1,2) shows, in accordance with molecular model studies, that the two aryl groups are almost perpendicular to the phenylene

group. Hence a resonance effect can be excluded and only inductive effects will be relevant.

The phenyl groups are known to have an electron attracting inductive ($-I$) effect (5, 6, 7). The higher the number of methyl groups attached to

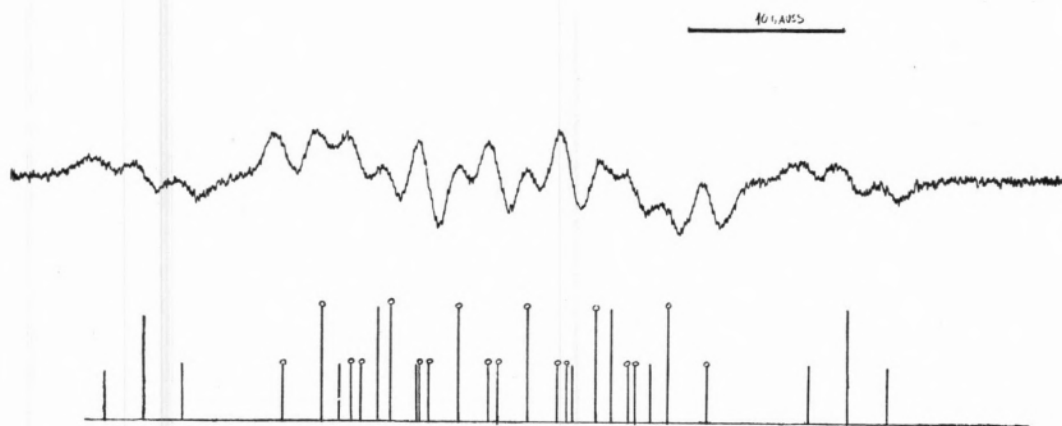


Fig. 5 — E. P. R. spectrum of the monorubidium radical of *o*-BMB.

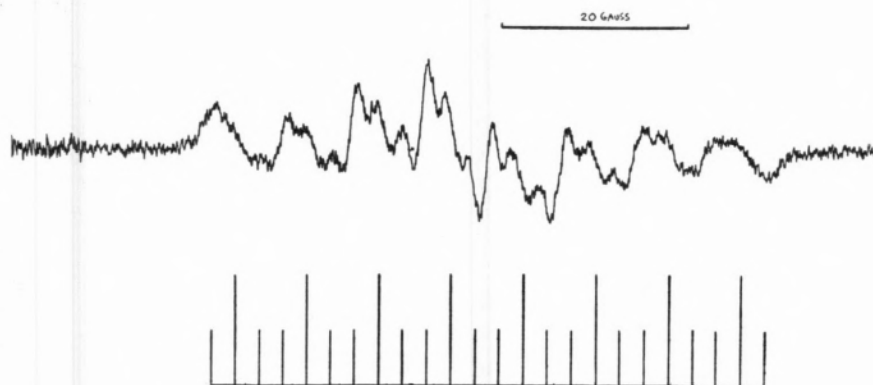


Fig. 6 — E. P. R. spectrum of the monocesium radical of *o*-BMB.

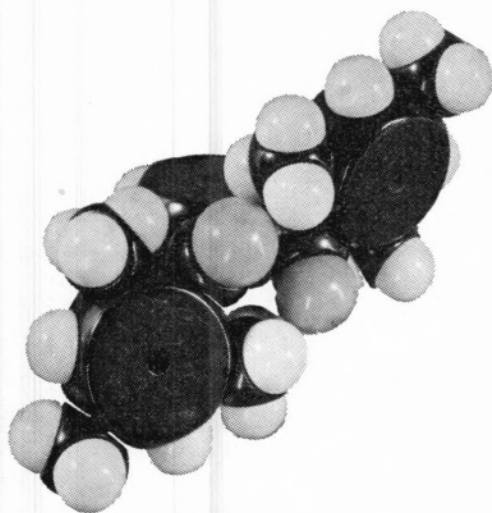


Fig. 7 — Stuart model of *o*-DMB.

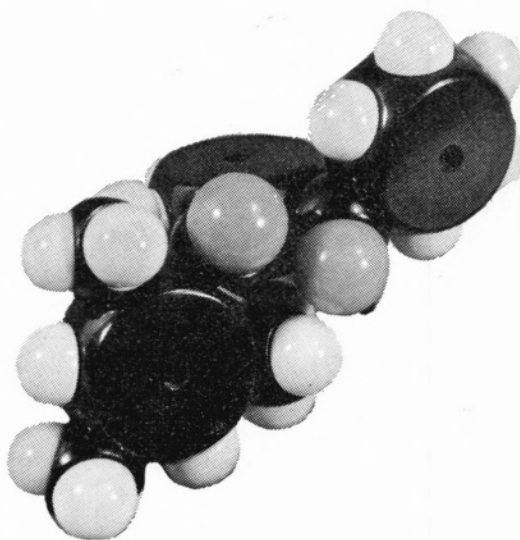
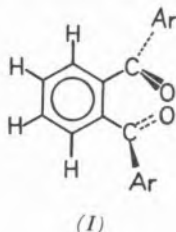


Fig. 8 — Stuart model of *o*-BMB.

the phenyl ring, the smaller is the electron attracting inductive ($-I$) effect of the aryl group.

The molecular models of the *o*-diarylbenzenes show also that the oxygen atoms of the carbonyl groups cannot be accommodated in the plane of the phenylene ring and most probably protrude into the opposite sides of this plane (I).



The same considerations apply also to the radical-anion since the larger negative charge density on the oxygen atoms will increase the repulsion between them.

This effect will be attenuated by the electron attracting properties of the two aryl groups. Hence it will increase in the following order:



Supposing that the metal ion is located in the vicinity and at equal distances from the oxygen atoms, the increase in the distance between the oxygen atoms will decrease the spin polarizing effect of the unpaired electron of the anion upon an internal *s* orbital of the metal cation (1).

This effect will certainly be more important with cations of comparatively small size like lithium and sodium and would account for the increase of the value of a_M/a in the radicals corresponding to these metals in the following order:



The influence of the cation upon the geometry of the CO groups and its polarizing effect upon the orbital of the single electron becomes less important with the increase in its ionic radius.

With potassium, rubidium and cesium the differen-

ces in the spin density a_M/a between the three di-*o*-diarylbenzenes must be sought mainly in purely internal interactions of the radical-anion: The less electron-attracting the aryl groups are, the higher will be the spin density a_M/a at the metal nucleus, if one considers that this spin density in these radical-anions was verified to increase with the global electron density as is shown by the proportionality between a_M/a and $r^{-1/2}$.

Therefore the spin densities a_M/a will increase in the following order for potassium, rubidium and cesium as is verified in the plot of fig. 1:



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RESUMO

Os radicais obtidos por redução do *o*-benzoilmesitoilbenzeno com metais alcalinos são estudados através dos seus espectros de RPE. Estes espectros são comparados com os obtidos análogamente a partir do *o*-di-(pentametilbenzoil)-benzeno e do *o*-dimesitoilbenzeno. Interpretam-se qualitativamente as diferenças entre estes espectros.

(1) Recent work by E. WARHURST and A. MARGARET WILDE (8) shows that in the radicals obtained by alkali metal reduction of 1,2-naphthoquinone and acenaphthenequinone the metal hyperfine splitting constant is to be accounted for by an indirect spin polarization of the inner *s* electrons of the cation by the unpaired electron of the anion. It is assumed that in the case under investigation the mechanism is the same.