



ELECTRON PARAMAGNETIC RESONANCE STUDIES ON THE CHELATION OF ALKALI METAL CATIONS BY RADICAL-ANIONS. II. RADICALS DERIVED FROM *o*-DI-(PENTAMETHYLBENZOYL)-BENZENE (1).

B. J. HEROLD (2)

L. J. ALCÁCER

A. J. FERRER CORREIA

A. J. PEREIRA DOMINGOS

M. CELINA RODRIGUES LAZANA

J. DOS SANTOS VEIGA (3)

Laboratório de Química Orgânica

Instituto Superior Técnico

Lisboa 1

e

Laboratório de Física e Engenharia Nucleares

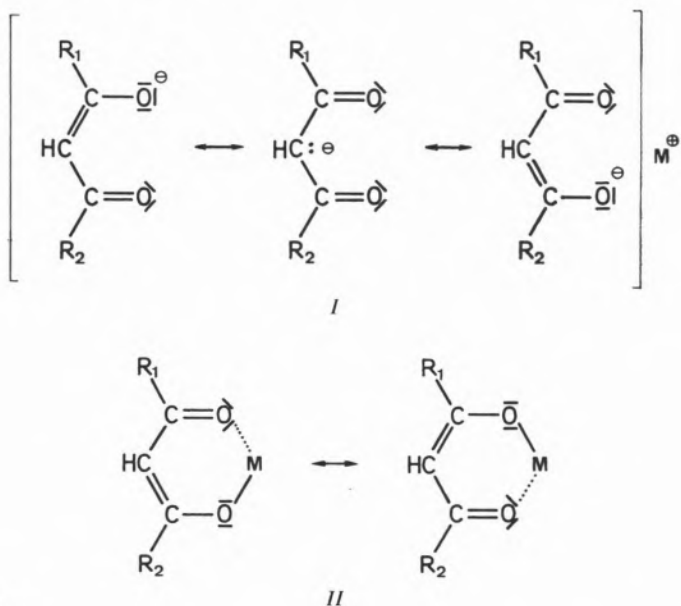
Sacavém

o-di-(pentamethylbenzoyl)-benzene was synthesized from sym.-phthaloyl chloride and pentamethylbenzene. The stable free radicals obtained by reaction of this ketone with Li, Na, K, Rb and Cs in tetrahydrofuran were studied by EPR. The spectra are analogous to those of the corresponding radicals of *o*-dimesitylbenzene. A linear relationship between the electron spin densities, at the metal nucleus and $r^{-1/2}$ was observed (r being the ionic radius of the alkali metal cation). These results are discussed in terms of chelation. Chelation of alkali metal cations is briefly reviewed. In the discussion of the results special emphasis is given to the problem of providing an explanation for the exceptionally high spin density at the nucleus of the alkali metal compared with other cases already known.

1 — INTRODUCTION

The chelation of alkali metal cations has frequently been thought responsible for certain features on the behaviour of enolate anions of β -dicarbonyl compounds. It is known from the early work of SIDGWICK and BREWER (2) that alkali metal derivatives of β -dicarbonyl compounds can be classified into two kinds:

- Those which show «saltlike» behaviour (insoluble in nonhydroxylic solvents and, on heating, decomposition without melting).
- Those which show «nonpolar» behaviour (distinct solubility in nonhydroxylic solvents and a definite melting point). From these properties the authors conclude that the first kind have an ionic structure (I) and the second a 2-covalent structure (II).



If one accepts the existence of covalent oxygen-metal bonds in these derivatives, the smaller the ionic radius of the alkali metal, the more covalent these bonds have to be. One would therefore expect the lithium derivatives to show «nonpolar» behaviour more often than the potassium derivatives.

(1) First paper of this series: ref. 1.

(2) Address: Laboratório de Química Orgânica. Instituto Superior Técnico. Lisboa 1.

(3) From the University of Coimbra.

The examples of Table 1, taken from Sidgwick and Brewer's paper, show, however, that the experimental results contradict this idea.

We do not know of any explicit attempts to explain this apparent contradiction, and this illustrates the kind of difficulties met when trying to make interpretations in this field.

Table 1

Alkali metal derivatives of β -dicarbonyl compounds

β -dicarbonyl compound	Li	Na	K
$\text{CH}_2 (\text{COOC}_2\text{H}_5)_2$	—	a)	—
$\text{N} \equiv \text{C} - \text{CH}_2 - \text{COOC}_2\text{H}_5$	—	a)	b)
$\text{CH}_3 - \text{CO} - \text{CH}_2 - \text{COOC}_2\text{H}_5$	a)	b)	b)
$\text{CH}_3 - \text{CO} - \text{CH}_2 - \text{CO} - \text{CH}_3$	a)	a)	—
$\text{C}_6\text{H}_5 - \text{CO} - \text{CH}_2 - \text{CO} - \text{CH}_3$	a)	a)	b)

a) alkali derivative with «saltlike» behaviour.

b) alkali derivative with «nonpolar» behaviour.

More recently ZAUGG and SCHAEFER (3) have studied cation and solvent effects on the ultraviolet spectra of alkali metal salts of β -dicarbonyl compounds. They concluded that most acyclic β -dicarbonyl compounds preferentially assume a U-shape on salt formation and remain in some form of association, even in aqueous solution. The observed bathochromic shifts with increasing cation radius are understood by the authors as a consequence of the perturbation of the molecular energy levels of the anion by the cation field. This, however, assumes always an essentially ionic structure for the chelates.

ZAUGG et al. (4) have supplied an important clue for the understanding of the differences in properties of «saltlike» and «nonpolar» alkali metal derivatives of β -dicarbonyl compounds by determining the molecular weight of the sodio-derivative of butylmalonic acid diethyl ester dissolved in benzene. Cryoscopic measurements showed that the molecular weight is greater than 10000, which is evidence that this compound exists in benzene as an ion pair aggregate of high association number. This conclusion rules out the possibility of interpreting the solubility and low melting point of this derivative in terms of a supposed covalent character of the oxygen metal bond as shown in struc-

ture II, and Zaugg et al. point out the possibility of its falling into the electrolyte classification denoted by KRAUS (5) as «type 2» in which one ion is large and one ion is small. Unlike the two other types in the Kraus classification «type 2» shows a particular tendency towards formation of ion-pair aggregates of high association number in solvents of low dielectric constant like benzene.

In our opinion all these facts indicate that the differences in solubilities and melting points between the compounds termed «saltlike» and «nonpolar» by SIDGWICK and BREWER (2) cannot be due to the nature of the bond between the chelate group and the alkali metal and this must always be considered as essentially ionic. A satisfactory explanation must rather be sought in the influence of the relative sizes of the cations and anions, and of the shapes of the anions on the associating abilities of the ion pairs as suggested by ZAUGG et al. (4). The investigation of these problems could give a sounder basis for the interpretation of the differing behaviour of alkali metal derivatives of β -dicarbonyl compounds with respect to

- Their reactions as bidentate, nucleophilic reagents
- Their extraction into organic solvents from aqueous solutions.

With regard to (b) it is very difficult from the present state of our knowledge to foresee which organic ligands will be able to extract alkali metal ions from aqueous solutions into nonhydroxylic solvents, by chelation, only a few reports have concerned such systems (6, 7, 8, 9).

Apart from their theoretical, analytical and technical aspects, studies on this subject may provide a model for sodium and potassium metabolism in biological systems, particularly for those cases in which there is a certain degree of specificity for the alkali metal ion.

Recently there appeared a series of papers entitled «On the Stability Constants of Uramil-diacetic Acids», which allowed certain conclusions about the actual structure of these abnormally stable complexes (10, 11).

Although the determination of stability constants is a convenient method to study chelates which are stable towards water, other methods have to

be used when the chelates are rapidly decomposed by water.

Electron-paramagnetic-resonance (EPR) spectroscopy has turned out to be a suitable method in certain cases for the study of the chelation of alkali metals. To use this method, however, it is necessary to generate chelates in which the chelating agent is not just an anion but a radical-anion.

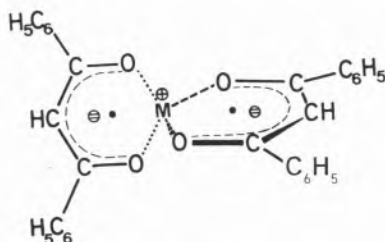
There are two possibilities in studying the chelation of alkali cations by EPR-spectroscopy.

Case 1: The splittings caused by the interaction between the electron spin and the spin of the metal nucleus can be observed and measured (1, 12, 13) when the electron spin density at the alkali metal nucleus is high enough.

Case 2: When this density is too low to produce a measurable splitting due to a particular metal in the liquid phase it is still possible, albeit more indirect, to get information about chelation from the effect of different metals on the proton splitting (14, 15, 16).

The lack of information about chelation in certain liquid phase EPR-spectra in case 2 (15, 17-20) can be compensated for in some instances by recording the EPR-spectra in rigid media:

Randomly oriented paramagnetic species in rigid matrices produce EPR signals. In particular it is possible to detect species with triplet ground states by the characteristic lineshape of their EPR-spectrum. H. VAN WILLIGEN (21) and S. I. WEISSMANN (22) succeeded in proving by this technique that the radical-dianion of dibenzoylmethane forms biradicals by coordination of two radical-dianions with one or two metal ions. Formula III represents one of the proposed structures



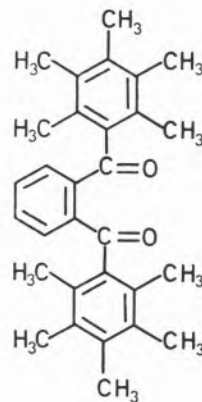
III

The free radicals generated by the reduction of o-dimesitylbenzene (V) by alkali metals (1) are an example of case 1, as the electron spin density at the nucleus of the alkali metal is exceptionally high in this case. The lack of dependence of such EPR spectra on the nature of solvent and temperature is evidence for an effective chelation (a «tight ion pair») (14). The rough linearity of the electron spin density at the metal nucleus with $r^{-1/2}$ agrees with the electron affinities, and was suggested as being perhaps the «normal» trend for ion-pairs because complications from the solvent and extensive movements of the cation compared to other ion-pairs are largely eliminated by the effective chelation (14).

2 — RESULTS

We wish to report now some analogous EPR-spectra in the radical solutions obtained from o-di-(pentamethylbenzoyl)-benzene (IV) and also additional experiments done with radicals derived from o-dimesitylbenzene (V).

o-di-(pentamethylbenzoyl)-benzene (IV) had to be synthesised. The method chosen is analogous to the Friedel-Crafts reaction used in the preparation of o-dimesitylbenzene (V) (23).



IV

Because of the close similarity between the synthesis of this compound and of o-dimesitylbenzene (V) no rigorous structure proof was made but the

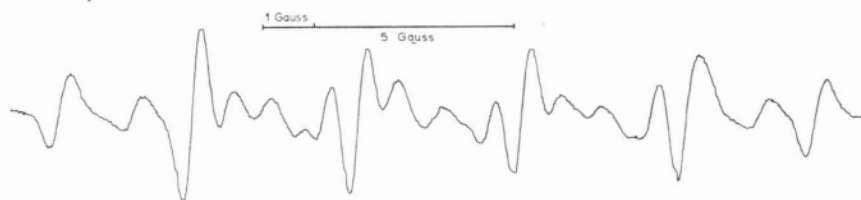


Fig. 1 — EPR-spectrum of the monolithium derivative of *o*-DPMB (IV).

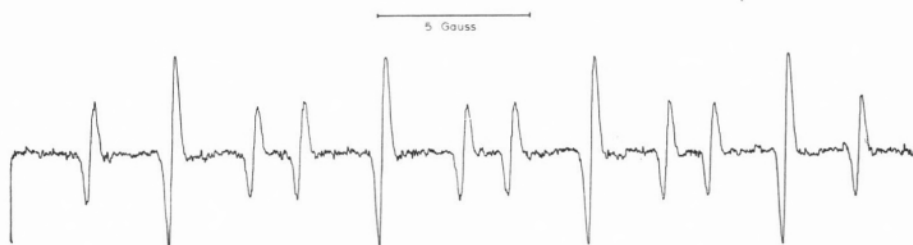


Fig. 2 — EPR-spectrum of the monosodium derivative of *o*-DPMBB (IV).

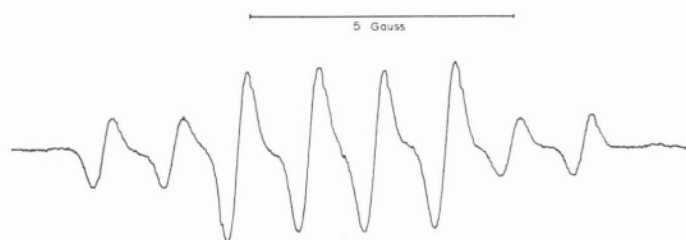


Fig. 3 — EPR-spectrum of the monopotassium derivative of *o*-DPMBB (IV).

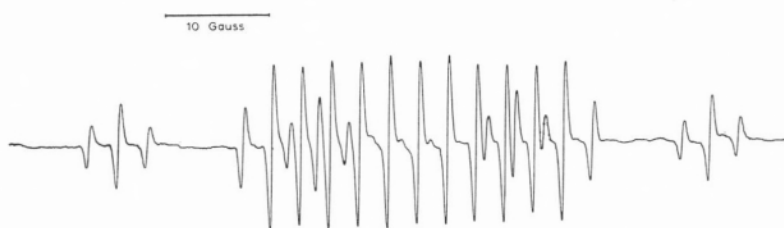


Fig. 4 — EPR-spectrum of the monorubidium derivative of *o*-DPMBB (IV).



Fig. 5 — EPR-spectrum of the monocesius derivative of *o*-DPMBB (IV).

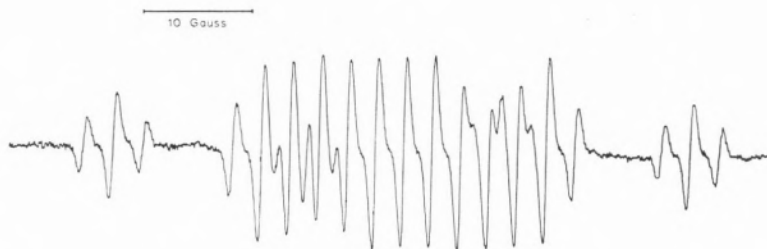
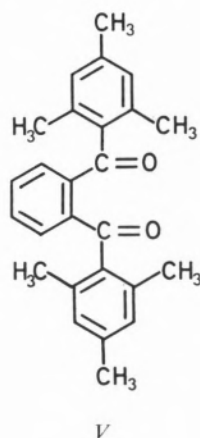


Fig. 6 — EPR-spectrum of the monorubidium derivative of o-DMB (V).

NMR and IR-spectra as well as the elementary analysis were in accordance with the proposed structure.



The mononegative radical anions of o-di-(pentamethylbenzoyl)-benzene (V) were generated by reaction with alkali metals in tetrahydrofuran under dry nitrogen. The EPR-spectra (Fig. 1-5) were very similar to the corresponding spectra obtained with o-dimesitylbenzene (V) (1) (Fig. 6).

Table 2 shows the electron spin densities at the metal nucleus calculated from the observed values of the splittings.

Again it is possible to verify a linear correlation between the electron spin density at the cation (a_M/a) and $r^{-1/2}$, not only for o-dimesitylbenzene (Fig. 7) but also for o-di-(pentamethylbenzoyl)-benzene (Fig. 8). The measurements were also extended to the case of rubidium.

The variations of the splittings with temperature were again almost undetectable. In the case of

Table 2

Hyperfine coupling constants and spin densities for the radicals

Cation	r	$r^{-1/2}$	a	o-DMB (V)		o-DPMBB (IV)	
				a_M	a_M/a	a_M	a_M/a
Li	0.78	1.132	143.5	3.75 (*)	0.0261 (*)	3.24	0.0226
Na	0.98	1.010	316	6.95 (*)	0.0220 (*)	6.38	0.0202
K	1.33	0.866	82.4	1.33 (*)	0.0161 (*)	1.39	0.0169
Rb ⁸⁵	1.48	0.824	360	5.2	0.0145	5.3	0.0147
Rb ⁸⁷	1.48	0.824	1240	17.5	0.0141	18.4	0.0148
Cs	1.65	0.781	820	10.2 (*)	0.0124 (*)	11.22	0.0137

r — Goldschmidt ionic radius of cation

a — atomic hyperfine coupling constants in Gauss calculated as in ref. 1) from values of optical spectra (24).

a_M — hyperfine coupling constants to the cation in Gauss.

o-DMB — o-dimesitylbenzene (V).

o-DPMBB — o-di-(pentamethylbenzoyl)-benzene (IV).

(*) Values taken from ref. 1.

cesium and potassium no significant variation could be detected in measurements between -50 and $+50^{\circ}\text{C}$. In the case of lithium there was a slight variation with temperature: At -70°C the splitting a_{Li} was 3.1 Gauss and at $+60^{\circ}\text{C}$ 3.6 Gauss. With sodium it is doubtful if the observed variation between 6.86 Gauss at -70°C and 6.56 Gauss at $+60^{\circ}\text{C}$ should be considered significant. The spectrum of *o*-dimesitylbenzene monosodium was also recorded in tetrahydrofuran saturated with sodium tetraphenylboranate. Practically the same spectrum was obtained as in the absence of sodium tetraphenylboranate. The variation in linewidth was within the experimental error, showing that the ion-pair does not exchange sodium ions at a measurable rate. Excess ketone again

of *o*-dibenzoylbenzene with sodium immediately dimerises (26) with the formation of a C-C bond, the radical obtained from *o*-dimesitylbenzene (V) is stable.

3 — DISCUSSION

The spectra of the radical obtained from *o*-di-(pentamethylbenzoyl)-benzene (IV) confirm our initial assumption that in the radical generated by the reaction of *o*-dimesitylbenzene (V) with alkali metals the mesityl groups are not conjugated with the phenylene ring whose π -electron-system contains the unpaired electron. If this were not the case then on changing from *o*-dimesitylbenzene

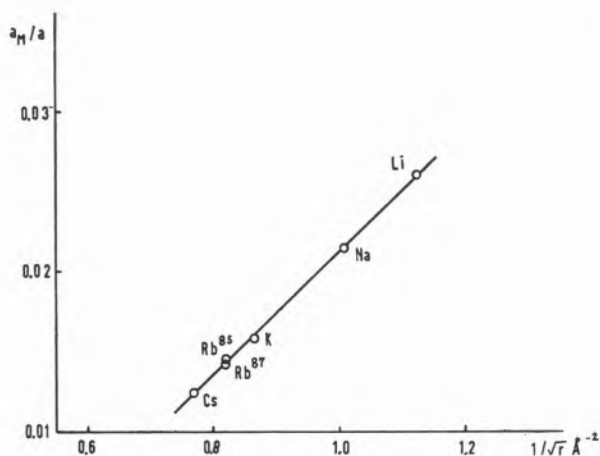


Fig. 7 — Plot of electron spin densities at the metal nucleus against $r^{-1/2}$ for radicals from *o*-DMB (V).

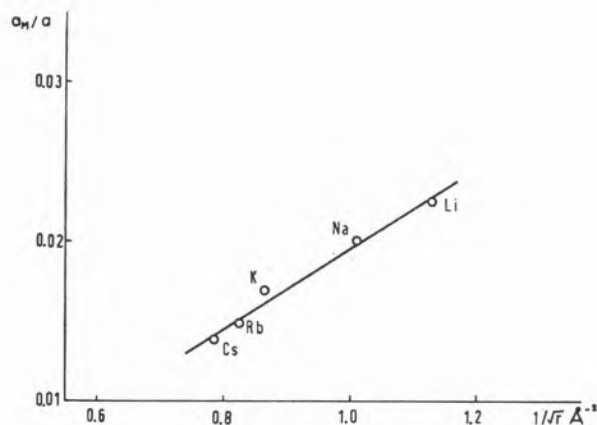


Fig. 8 — Plot of electron spin densities at the metal nucleus against $r^{-1/2}$ for radicals derived from *o*-DPMBB (IV).

does not alter the linewidth. These experiments show that any kind of ion exchange in this radical is too slow to be detected using this method (¹). According to van WILLIGEN (25) it is not possible to detect biradical species in a frozen solution of *o*-dimesitylbenzene monosodium in methyltetrahydrofuran. Repetition of these experiments confirmed these results and showed that no dimers analogous to III are present in appreciable concentration. The reason for this is almost certainly the large steric hindrance due to the mesityl groups. This steric hindrance is also illustrated by the fact that whereas the radical expected from the reaction

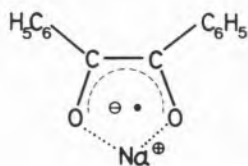
(V) to *o*-di-(pentamethylbenzoyl)-benzene (IV) a different hyperfine pattern would arise in the spectrum.

At first sight it even appears that assuming this noncoplanarity there should be no difference at all between the EPR-spectra of the radicals generated by reduction of *o*-dimesitylbenzene (V) and *o*-di-(pentamethylbenzoyl)-benzene (IV). The results, however, show that there is a small difference in the magnitude of the hyperfine splitting cons-

(¹) We wish to express our gratitude to Prof. S. I. Weissmann for suggesting this experiment.

tants which indicates a slightly different distribution of the electron spin densities.

It is very interesting to compare the values of the spin densities obtained by us for a_M/a with the values for other cases where chelation was proved or is to be expected. In the case of the ketyls of benzil (12, 13) in tetrahydrofuran the value determined for a_M/a is 0.0018 which is about ten times smaller than the values for *o*-dimesitylbenzene (V) and *o*-di-(pentamethyl-benzoyl)-benzene (IV). The possibility of formation of a 5-membered ring in benzil-sodium should however favor the formation of a chelate (VI) (18).



VI

In the case of the dibenzoylmethane-dianion-radical there is evidence from the EPR-spectra in rigid matrices that biradical chelates are formed with the alkali metal cations (III) (21, 22). In the liquid phase EPR-spectra, however, no splittings due to the alkali metal nuclei were observed (15).

It would be interesting now, to know if it is possible to make the generalization that 5 or 6-membered chelate rings of radical species containing alkali metals always show much smaller alkali metal splittings in their EPR spectra than the radical species with 7-membered chelate rings which we have been studying. Together with the knowledge of the geometry of the chelate ring in the radicals generated by alkali metal reduction of *o*-diarylbenzenes this would enable us to draw conclusions about the mechanism of interaction between the electron spin and the nuclear spin of the alkali metal. At present we can only be positive about the noncoplanarity of the nodal plane of the orbital occupied by the single electron and the planes of the two aryl groups attached to the carbonyl carbon atoms. However, it seems sensible to suggest that the nodal plane of the orbital of the single electron is the plane of the *o*-disubstituted benzene ring. Concerning the exact location of the oxygen atoms and the metal cation no definite conclusions can be drawn from the experimen-

tal data available at present, although we still think that the alkali metal cation is to be found in the immediate vicinity of the oxygen atoms.

As it is known that most 7-membered rings are not planar (¹) the possibility of the oxygen and (or) the alkali metal nuclei not being in the same plane as the *o*-disubstituted benzene ring has to be taken into consideration. Only after obtaining positive evidence about the geometry of the chelate ring will we be able to discuss the mechanism of interaction between the electron spin and the nuclear spin.

If one supposes that the C-O bonds are coplanar with the phenylene ring and only the alkali metal cation is out of plane, then the validity of the molecular orbital calculations (27) which allow us to attribute the observed splittings caused by two equivalent protons to the positions 4 and 5 is not affected.

Table 3

Infrared spectra of the diketones

<i>o</i> -DMB a)	<i>o</i> -DPMBB b)
1676 cm ⁻¹	1682 cm ⁻¹
1663 cm ⁻¹	1665 cm ⁻¹

(a) *o*-dimesitylbenzene (V).

(b) *o*-di-(pentamethylbenzoyl)-benzene (IV).

4 — EXPERIMENTAL

4.1 — EPR SPECTRA

Samples for the EPR spectra were prepared using the same method as before (1). Spectra were recorded on a Varian V-4502-04 EPR spectrometer using a 12-in magnet.

4.2 — PREPARATION OF *O*-DI-(PENTAMETHYLBENZOYL)-BENZENE (IV)

50 g of anhydrous aluminium chloride were added to a solution of 104 g (0.7 mole) of pentamethylbenzene (dried by azeotropic distillation with carbon disulfide) in 108 g of dry carbon disulfide.

(¹) We are grateful to Prof. Dr. H. J. Bestmann and some of his collaborators for raising this point.

28.5 g (0.14 mole) of sym-phthaloyl chloride were then added slowly whilst keeping the mixture at room temperature. After 14 hours of stirring at room temperature the reaction mixture was hydrolysed by the addition of dilute hydrochloric acid. Solvent and excess pentamethylbenzene were then removed by steam distillation. The residue (insoluble in water) was washed several times with ether to remove the remaining pentamethylbenzene and other impurities followed by hot, aqueous sodium carbonate until the washing liquor did not produce a precipitate upon acidification. The residue was then recrystallised from benzene. Colourless crystals of o-di-(pentamethylbenzoyl)-benzene (IV) were obtained, m.p. 325.5-327°C (Leitz heating stage microscope, uncorrected) Yield 41.4 g (0.097) 78 %.

IR-spectrum ⁽¹⁾: o-dimesitylbenzene (V) and o-di-(pentamethylbenzoyl)-benzene (IV) both exhibit a double carbonyl peak at ca. 1650 cm⁻¹ and 1700 cm⁻¹ (Table 3) (KBr disc; spectrometer: Perkin Elmer 421).

NMR-spectrum ⁽²⁾: The NMR spectrum of o-di-(pentamethylbenzoyl)-benzene (IV) in CDCl₃ was run on a Varian HA 100 NMR spectrograph at room temperature. It shows two complex groups of lines whose hyperfine splitting patterns are not well enough resolved to be analysed. The integration of the peaks due to the methyl groups situated between 2.1 and 2.3 p.p.m. gives 134, and the integration of the aromatic hydrogen peaks yields 18 leading to the expected ratio of 30:4.

Anal: Calcd. for C₃₀H₃₄O₂ (426.57): C, 84.46; H, 8.04.
Found: C, 84.29; H, 7.84.

ACKNOWLEDGEMENTS

The authors express their gratitude to the NATO scientific Affairs Division for supporting this research work by grant no. 182. M.C.R.L. acknowledges gratefully a research scholarship given by «Companhia Soda Póvoa», Lisbon. A. J. P. D. acknowledges gratefully a scholarship given by «Companhia União Fabril». The authors are also indebted to Dr. Ray Wotton for his help in the preparation of the manuscript.

BIBLIOGRAPHY

1. Herold, B. J., Correia, A. F. N. and Veiga, J. S., *J. Am. Chem. Soc.*, **87**, 2661 (1965).
2. Sidgwick, N. V. and Brewer, F. M., *J. Chem. Soc.*, 2379 (1925).
3. Zaugg, H. E. and Schaefer, A. D., *J. Am. Chem. Soc.*, **87**, 1857 (1965).
4. Zaugg, H. E., Horrom, B. W. and Borgwardt, S., *J. Am. Chem. Soc.*, **82**, 2895 (1960).
5. Kraus, C. A., *J. Chem. Educ.*, **35**, 324 (1958).
6. Guter, G. A. and Hammond, G. S., *J. Am. Chem. Soc.*, **78**, 5166 (1956).
7. Hesse, G. and Böckmann, K. W. F., *Liebigs Ann. Chem.*, **563**, 37 (1949).
8. Plieninger, H., Kanellakopulos, B. and Stumpf, K., *Angew. Chem.*, **79**, 155 (1967).
9. Jensen, B. S., *Acta Chem. Scand.*, **18**, 739 (1964).
10. Irving, H. and Silva, J. J. R. F., *J. Chem. Soc.*, 448 (1963).
11. Silva, J. J. R. F., *Rev. Port. Quím.*, **7**, 88, 163, 230 (1965).

⁽¹⁾ We are indebted to Dr. Maria Clara F. S. Lopes for running the IR-spectra at the Centro de Investigação da C. U. F., Sacavém.

⁽²⁾ We are indebted to Dr. U. Scheidegger (Zürich) for running this spectrum at the University of Coimbra.

12. Luckhurst, G. R. and Orgel, L. E., *Mol. Phys.*, **7**, 297 (1963).
13. Evans, A. G., Evans, J. C. and Godden, G. H., *Trans. Faraday Soc.*, **63**, 136 (1967).
14. Symons, M. C. R., *J. Phys. Chem.*, **71**, 172 (1967).
15. Bauld, N. L. and Brown, M. S., *J. Am. Chem. Soc.*, **89**, 5413 (1967).
16. Khakar, M. P., Prabhanda, R. S. and Das, M. R., *J. Am. Chem. Soc.*, **89**, 3100 (1967).
17. Maruyama, K., *Bull. Chem. Soc. Japan*, **37**, 553 (1964).
18. Corvaja, C., Nordio, P. L. and Giacometti, G., *J. Am. Chem. Soc.*, **89**, 1751 (1967).
19. Russell, G. A., Talaty, E. R. and Horrocks, R. H., *J. Org. Chem.*, **32**, 353 (1967).
20. Müller, E., Günter, F. Scheffler, K., Ziemeck, P. and Rieker, A., *Liebigs Ann. Chem.*, **688**, 134 (1965).
21. Willigen, H. van, «Dissertation», Univ. Amsterdam, 1965.
22. Willigen, H. van and Weissmann, S. I., *Mol. Phys.*, **11**, 175 (1966).
23. Fuson, R. F., Speck, S. B. and Hatchard, W. R., *J. Org. Chem.*, **10**, 55 (1945).
24. Kusch, P. and Taub, H., *Phys. Rev.*, **75**, 1477 (1949).
25. Willigen, H. van, Private Communication.
26. Herold, B. J., *Tetrahedron Letters*, **2**, 75 (1962).
27. Correia, A. F. N. and Veiga, J. S., *Rev. Port. Quím.*, **6**, 67 (1964).

Recebido 16 . Junho . 1969.

RESUMO

Sintetizou-se *o*-di-(pentametilbenzoil)-benzeno a partir de cloreto sim. de ftaloilo e pentametilbenzeno. Estudaram-se por meio de espectrografia de RPE os radicais livres estáveis obtidos por reacção desta cetona dissolvida em tetra-hidrofurano com Li, Na, K, Rb e Cs. Os espectros são semelhantes aos dos correspondentes radicais do *o*-dimesitoilbenzeno. Verificou-se a dependência linear entre as densidades de spin electrónico $r^{-1/2}$ (sendo r o raio iónico do catião do metal alcalino). Estes resultados são discutidos como sendo um caso de quelação. Na discussão dos resultados dá-se ênfase especial ao problema de obter uma explicação para a densidade de spin excepcionalmente elevada no núcleo do metal alcalino, em comparação com outros casos conhecidos.