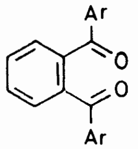
An Electron Spin Resonance Investigation of the Reduction of *o*-Diaroylbenzenes by Group III Metals

By **M. Cândida B. Loiá** and **Bernardo J. Herold**, Centro de Processos Quimicos de Universidade Technica, P–1096 Lisboa Codex, Portugal
Neil M. Atherton,* Department of Chemistry, The University, Sheffield S3 7HF

The e.s.r. spectra obtained when various *o*-diaroylbenzenes are reduced with Group III metals have been studied. Fluid solutions have spectra which show large metal hyperfine splittings and which are believed to arise from triple ions comprising a radical-anion, a dianion, and a metal ion. The temperature dependence of the intensity of the spectra of these species indicates that they are in equilibrium with species which do not have S ½. In two cases where reduction was effected with aluminium the frozen solution spectra indicate the presence of triplet-state species, presumed to be triple ions containing two radical anions.

o-BIS(POLYMETHYLBENZOYL)BENZENES (1) are known to react with alkali metals yielding ion-pairs of alkali cations and radical-anions, which have been studied by e.s.r. in solution [1-4] and ENDOR.[5,6] With main Group II metals biradical species (2b; $M^{n+} = Mg^{2+}$, Ca^{2+}, Sr^{2+}, or Ba^{2+}) are formed. These have been described by Brustolon *et al.*,[7] who calculated the zero-field splitting parameter D as a function of the oxygen–metal distance, r_{OM}, and thus estimated this distance from the experimental D values.

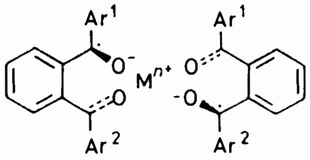


(1)

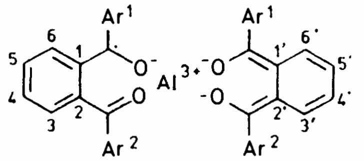
a; $Ar^1 = C_6H_5$, $Ar^2 = 2,4,6\text{-}C_6H_2(CH_3)_3$

b; $Ar^1 = Ar^2 = 2,4,6\text{-}C_6H_2(CH_3)_3$

c; $Ar^1 = Ar^2 = C_6(CH_3)_5$



(2)



(3)

In this note we report the extension of studies of these molecules to include reduction with Group III metals.

EXPERIMENTAL

Radicals have been prepared from three compounds, *o*-dimesitoylbenzene (1b) (*o*-DMB), 1-benzoyl-2-mesitoylbenzene (1a) (*o*-BMB), and *o*-bis(pentamethylbenzoyl)benzene (1c) (*o*-DPMBB). Commercially available *o*-DMB was used and the other two compounds were synthesised as described in the literature.[3,8] The reduction was carried out with metal amalgams using standard techniques. The solvents used were kept under vacuum over benzophenone ketyl. The e.s.r. spectra were recorded with a Varian V-4502-04 spectrometer, except those used in the concentration measurements which were recorded in a Varian New Century E-line spectrometer.

RESULTS AND DISCUSSION

Well resolved spectra are obtained at room temperature from solutions of *o*-DPMBB reduced with aluminium in 2-methyltetrahydrofuran (MTHF). An example is shown in Figure 1. The hyperfine splitting arises from interaction with a ^{27}Al nucleus ($I = 5/2$) and two groups of four equivalent protons. The coupling constants are listed in the Table. The spectrum of Figure 1 appears immediately on shaking the solution with the amalgam and reaches its full intensity in, typically, 15 min, after which it is stable for many weeks at room temperature. During the early stages of the reduction additional weak lines, which we have not been able to analyse, can be seen, but these are not persistent and are a very minor product which could arise from impurities.

Coupling constants of e.s.r. spectra in solution of radicals obtained by reduction of *o*-bis(polymethylbenzoyl)benzenes (1) in MTHF by Group III metals

Metal	*o*-BMB	*o*-DMB	*o*-DPMBB
^{139}La ($I = 7/2$)	Very broad spectrum	a_{La} 11.5 G	a_{La} 9.7 G
^{89}Y ($I = 1/2$)	Very broad spectrum	a_Y 2.44 G,[a] a_H 1.22 G[a,b]	a_Y 1.33 G, a_H 1.33 G[b]
^{27}Al ($I = 5/2$)	a_{Al} 15.3 G	a_{Al} 10.8 G	a_{Al} 13.1 G, a_H 1.2 G,[b] a_H' 0.6 G[c]

[a] In this case the spectrum was measured in tetrahydrofuran. [b] Tentative assignment: hydrogen atoms 4, 5, 4′, and 5′. [c] Tentative assignment: hydrogen atoms 3, 5, 3′, and 6′.

The structure we propose for the radical whose spectrum is shown in Figure 1 is a triple ion (3) of one radical-anion, one dianion, and Al^{3+}, $A^-Al^{3+}A^{2-}$, the electron spin and the negative charges being completely delocalised over both ketone structures, although we would not suppose that the whole structure is planar. It does not seem possible that the well resolved spectrum observed could originate from a weakly coupled biradical, for, following Carrington and Luckhurst,[9] we estimate that the spectrum of such a biradical would have a linewidth of *ca.* 30 G, to be compared with the 0.5 G observed. We have compared the intensity of the spectrum obtained on aluminium reduction with that obtained on alkali-metal reduction, which we take to proceed completely to the monoanion. These experiments shows that the species responsible for the spectrum of Figure 1 is the major product of the reaction of *o*-DPMBB with aluminium and that the stoicheiometry is consistent with the formation of the triple-ion (3).

The solution spectra obtained on reduction of *o*-BMB and *o*-DMB with ^{27}Al also show aluminium hyperfine splitting but the proton couplings are not resolved. The spectra obtained from *o*-DMB and *o*-DPMBB reduced with yttrium or lanthanum also show metal splittings but the linewidths are greater than those in the Al–*o*-DPMBB spectrum. Reduction of *o*-BMB with lanthanum or yttrium gives rise to very broad spectra with no resolved hyperfine splittings. Values of all the hyperfine couplings that could be measured are included in the Table. Overall the quality of resolution of the spectra deteriorates with decreasing rigidity of the substrate and with increasing radius of the cation. The observed metal couplings have been converted into valence shell *s*-orbital populations using the data tabulated by Morton and Preston[10] but no obvious trends are discernible.

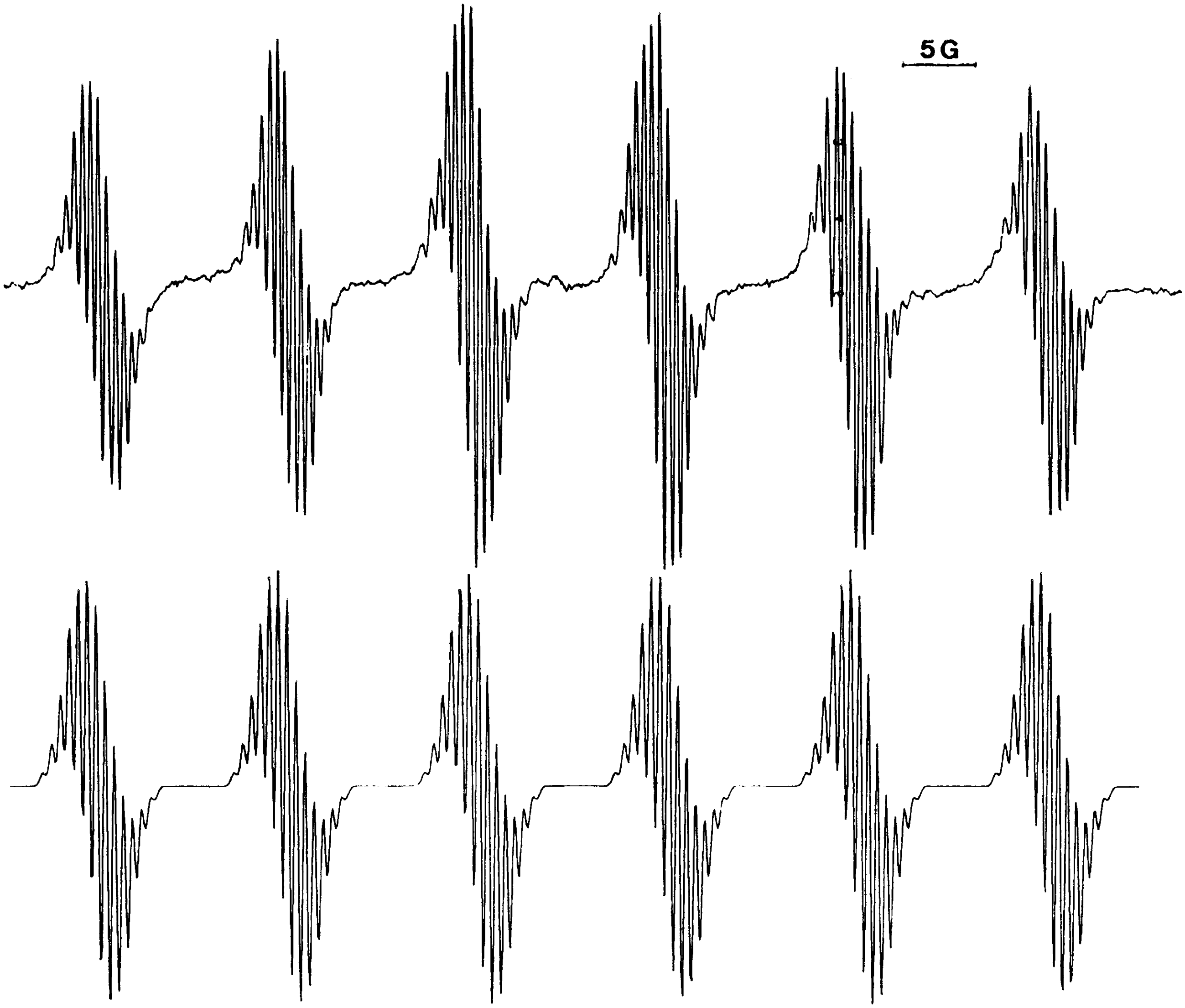


FIGURE 1 E.s.r. spectrum of *o*-DPMBB–Al in MTHF at room temperature (above) and a simulation using the coupling constants given in the Table (below)

The temperature dependence of the fluid solution spectra of Al–*o*-DMB and Al–*o*-DPMBB has been examined. On going down from room temperature, the intensities of the spectra decrease reversibly with no severe line broadening. The observations are recorded graphically in Figure 2 in the form of plots of the logarithm of the radical concentration against reciprocal temperature. Relative radical concentrations were assumed proportional to the integrated intensities of the spectra approximated by relationship (1) where $2\gamma'_{\text{max.}}$ is the peak-to-peak distance of the

$$I \propto \gamma'_{\text{max.}}(H_{\text{pp}})^{2} \qquad (1)$$

derivative and ΔH_{pp} the peak-to-peak width of the derivative[11] and a correction for the Boltzmann distribution was employed. It is clear that the radicals are in equilibrium with some species which do not have $S = 1/2$. An appealing possibility is that there is a disproportionation (2) for this could account for the observation of triplet species in rigid solutions and a plot of the form shown in Figure 2 should be linear when the equilibrium lies to the right, as is observed. However the e.s.r. measurements do not prove the existence of the equilibrium (2), and there are several other possibilities. The limiting low temperature slopes of the lines in Figure 2 correspond to enthalpy changes of -65.8 and -80 kJ mol^{-1} for *o*-DPMBB and *o*-DMB respectively.

$$2\,A^{2-}\,Al^{3+}\,A^{-} \rightleftharpoons A^{-}\,Al^{3+}\,A^{-} + A^{3-}\,Al^{3+}\,A^{2-} \qquad (2)$$

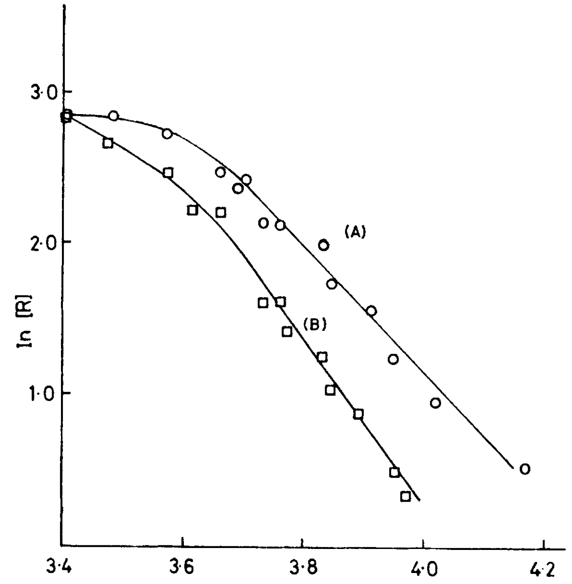


FIGURE 2 Plot of ln (relative radical concentration), ln[R]F *versus* $1/T$ for *o*-DPMBB–Al (A) and *o*-DMB–Al (B) in MTH

Frozen MTHF solutions of Al–*o*-DMB and Al–*o*-DPMBB have spectra characteristic of triplet species. The zero-field splitting parameters are *D* 160 G, *E* 3.0 G for *o*-DMB and *D* 164 G, *E* 4.3 G for *o*-DPMBB. These parameters were determined from comparison of the experimental spectra with spectra simulated using the program developed by Pijpers.[12] Experimental and simulated spectra for *o*-DPMBB are shown in Figure 3. The linewidth used in that simulation was 6.0 G while the value used for *o*-DMB was 9.0 G. For all other combinations of La, Y, and Al with the three ketones no triplet species could be detected.

The structure we propose for the triplet species is $A^{-}Al^{3+}A^{-}$ (2), which may be regarded as a complex of two radical-anions with a cation. A complex involving three organic molecules, which might have a quartet

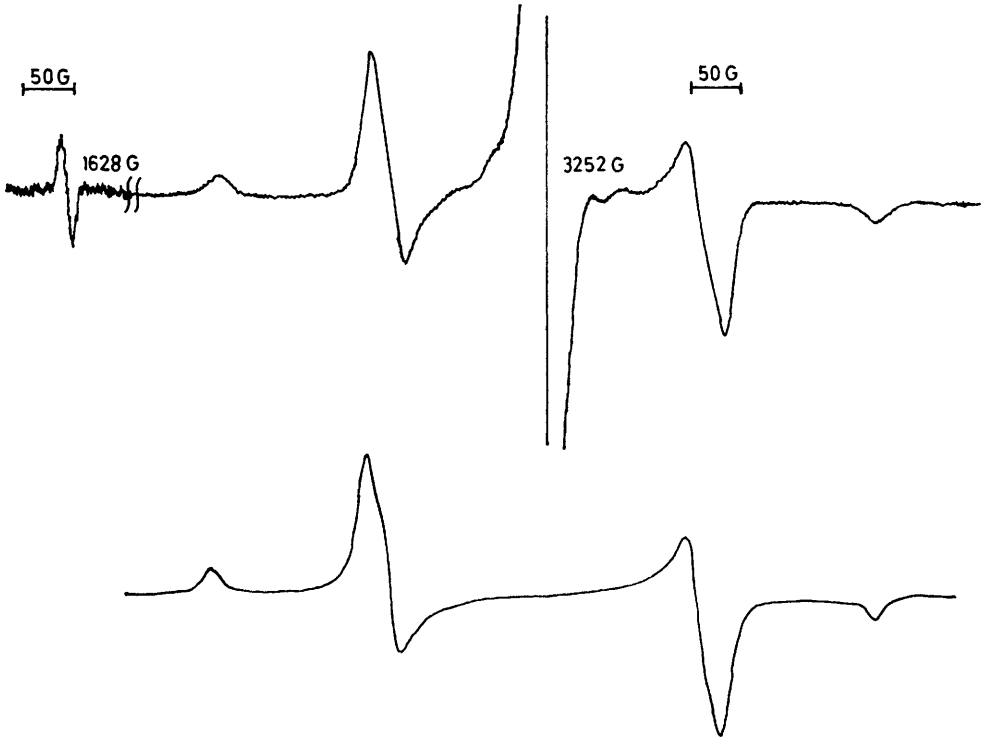


FIGURE 3 E.s.r. spectrum of *o*-DPMBB–Al in MTHF at 77 K (above) and a simulation constructed as described in the text (below)

ground state, seems most improbable on steric grounds. Further, the spectra can be perfectly satisfactorily simulated on the assumption that they arise from randomly oriented triplet species.[13]

As has already been pointed out for the alkaline earth biradical triple ions [7] the non-zero values for E indicate that the radical-anions are not perpendicular to each other. Tetrahedral, or near-tetrahedral, co-ordination of the metal is possible if the carbonyl groups are rotated out of the plane of the phenylene ring to which they are attached.

Using the above mentioned plot of D *versus* r_{OM} [7] one obtains a value of r_{OM} 2.03 Å for Al–*o*-DMB and 2.1 Å for Al–*o*-DPMBB. These are of the order of magnitude of the sum (1.91 Å) or the van der Waals radii of the oxygen and the metal,[14] and provide support for the structure (2) proposed.

We thank Instituto Nacional de Investigação Científica (Portugal) for financial support, the Laboratório Nacional de Engenharia e Tecnologia Indistriais (Portugal) for allowing the use of its e.s.r. spectrometer, the Fundação Calouste Gulbenkian for the use of its computing facilities, the S.R.C. for an equipment grant, and NATO for a travel grant for M. C. B. L. We thank also Professor C. Corvaja for giving us a listing of the program developed by Pijpers *et al.*[12] and Dr. H. M. Novais for advising M. C. B. L. on questions related to e.s.r. spectroscopy.

[0/641 *Received, 30th April*, 1980]

REFERENCES

[1] B. J. Herold, A. F. Neiva Correia, and J. dos Santos Veiga, *J. Amer. Chem. Soc.*, 1965, **87**, 2661.

[2] B. J. Herold, L. J. Alcacer, A. F. Ferrer Correia, A. J. Pereira Domingos, M. Celina R. Lanzana, and J. dos Santos Veiga, *Rev. Port. Quim.*, 1969, **11**, 188.

[3] B. J. Herold, H. M. Novais, M. C. R. Lazana, and P. B. Correia, *Rev. Port. Quim.*, 1971, **13**, 78.

[4] L. Pasimeni, M. Brustolon, and C. Corvaja, *J.C.S. Faraday II*, 1974, 734.

[5] N. M. Atherton and B. Day, *J.C.S. Faraday II*, 1973, 1801.

[6] H. van Willigen, M. Plato, R. Biehl, K. P. Dinse, and K. Möbius, *Mol. Phys.*, 1973, **26**, 793.

[7] M. Brustolon, L. Pasimeni, and C. Corvaja, *Chem. Phys. Letters*, 1973, **21**, 194.

[8] M. S. Newman, *J. Org. Chem.*, 1961, **26**, 2630.

[9] A. Carrington and G. R. Luckhurst, *Mol. Phys.*, 1964, **8**, 125.

[10] J. R. Morton and K. F. Preston, *J. Magnetic Resonance*, 1978, **30**, 577.

[11] J. E. Wertz and J. R. Bolton, Electron Spin Resonance,' McGraw-Hill, New York, 1972, p. 34.

[12] F. W. Pijpers, H. van Willigen, and J. J. Th. Gerding, *Rec. Trav. chim.*, 1967, **86**, 511.

[13] E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, 1964, **41**, 1763.

[14] L. H. Ahrens, *Geochim. Cosmochim. Acta*, 1952, **2**, 155.