Tetrahedron Vol 37, pp 605 to 609
© Pergamon Press Ltd, 1981 Printed in Great Britain

0040 4020/81/0201 0605/$02.00/0

AN ESR INVESTIGATION OF TRIPLE IONS DERIVED FROM 1,2,4,5-TETRAMESITOYLBENZENE

M. CELINA R. L. R. LAZANA and BERNARDO J. HEROLD
Centro de Processos Quimicos da Universidade Técnica P-1096 Lisboa Codex, Portugal
and
NEIL M. ATHERTON
Department of Chemistry, The University, Sheffield S3 7HF, England

(*Received in U.K.* 28 *April* 1980)

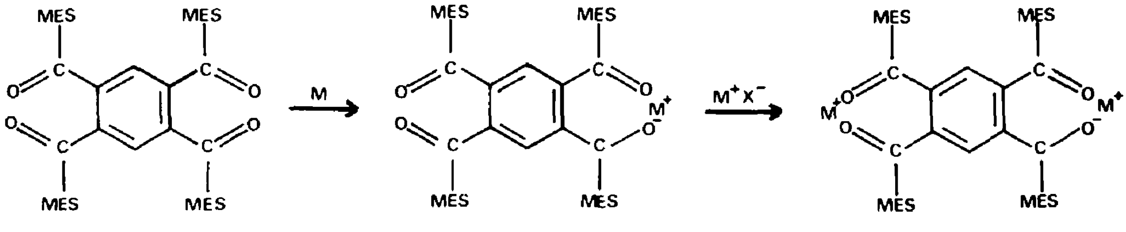
Abstract Stable triple ions were obtained in MTHF solution from the ion pairs of 1,2,4,5-tetramesitoylbenzene (TMB) radical anion and alkali metal cations by reaction with soluble alkali metal salts Their ESR spectra are highly resolved. MO calculations with parameters which lead to spin density values as nearly as possible equal to the experimental ones allow estimates of the oxygen-metal distances. The relatively most stable triple ions are the ones with the smallest estimated oxygen metal distances.

Triple ions are of interest because they may occur as intermediates in intermolecular exchange reactions of ion pairs and there have been several ESR-investigations of triples comprising an organic radical-anion and two alkali metal cations. Systems studied include those where the radical-anion was derived from pyrazine[1–6] or from a quinone.[7–11] The ESR spectra of ion pairs involving the anions of these molecules show linewidth alternation under suitable conditions reflecting the occurrence of intramolecular cation exchange. The spectra of the triple ions also show linewidth effects, asymmetric broadening of the hyperfine components and the origin of these has been extensively discussed.[4–6] Recently Chen and Wan[12] reported triple ions involving the radical-anions of furil and of di-t-butylazodicarboxylate in which well defined chelation of the cations can be envisaged. The ESR-spectra of these systems are strikingly well resolved and those of the tightly bound sodium complexes do not show dramatic linewidth effects. We have for many years been interested[13–18] in the chelate ion-pairs formed by the radical-anions of *o*-diaroylbenzenes and report here on the formation of a triple ion by such a molecule, 1,2,4,5-tetramesitoylbenzene (**1** TMB). The ion pairs of the radical-ion of this molecule and alkali ions have already been described.[16]

RESULTS AND DISCUSSION

When an equivalent amount of sodium tetraphenylboranate is added to a solution of the sodium ion pair **2** in 2-methyltetrahydrofuran (MTHF) the ESR-spectrum of the ion pair disappears and a much more highly resolved spectrum (Fig. 1) is obtained, which is easily recognized as the spectrum of a triple ion **3** from the splitting pattern of the two ^{23}Na ($I = 3/2$) nuclei consisting of 7 groups of lines with amplitudes proportional to 1:2:3:4:3:2:1.

A similar effect is observed when lithium tetraphenylboranate is added to a solution of the lithium ion pair in MTHF (Fig. 2). In analogous experiments with potassium tetraphenylboranate and caesium cyanotriphenylboranate no change of the ESR-spectrum of the ion pairs was observed. Simulations of the spectra are included in Figs 1 and 2

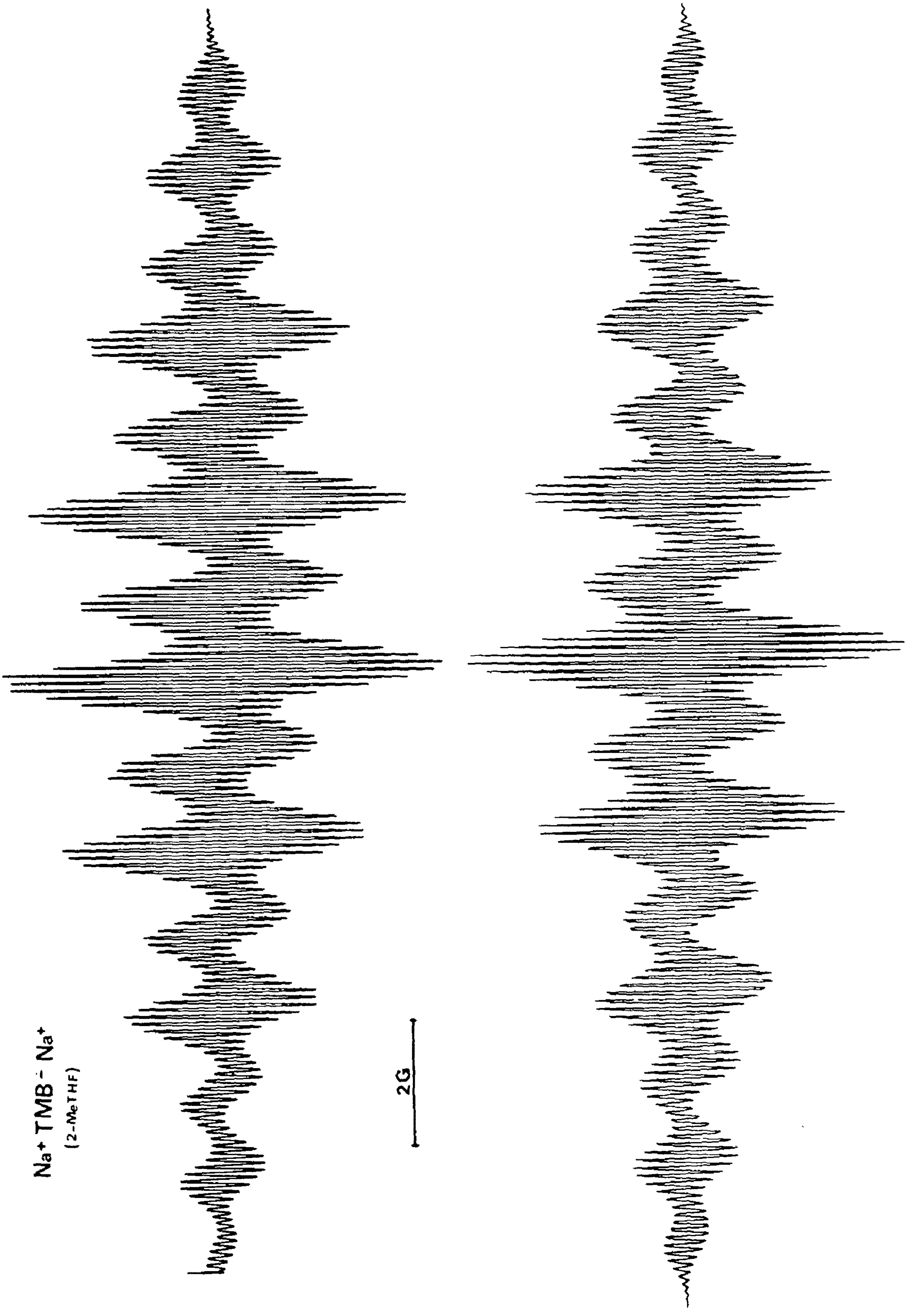


1 (TMB)

2 (TMB$^{\dot{-}}$ M^{+})

3 (M^{+} TMB$^{\dot{-}}$ M^{+})

MES (mesityl) ≡ 2,4,6-trimethylphenyl


Na+ TMB- Na+
(2-MeTHF)
2G

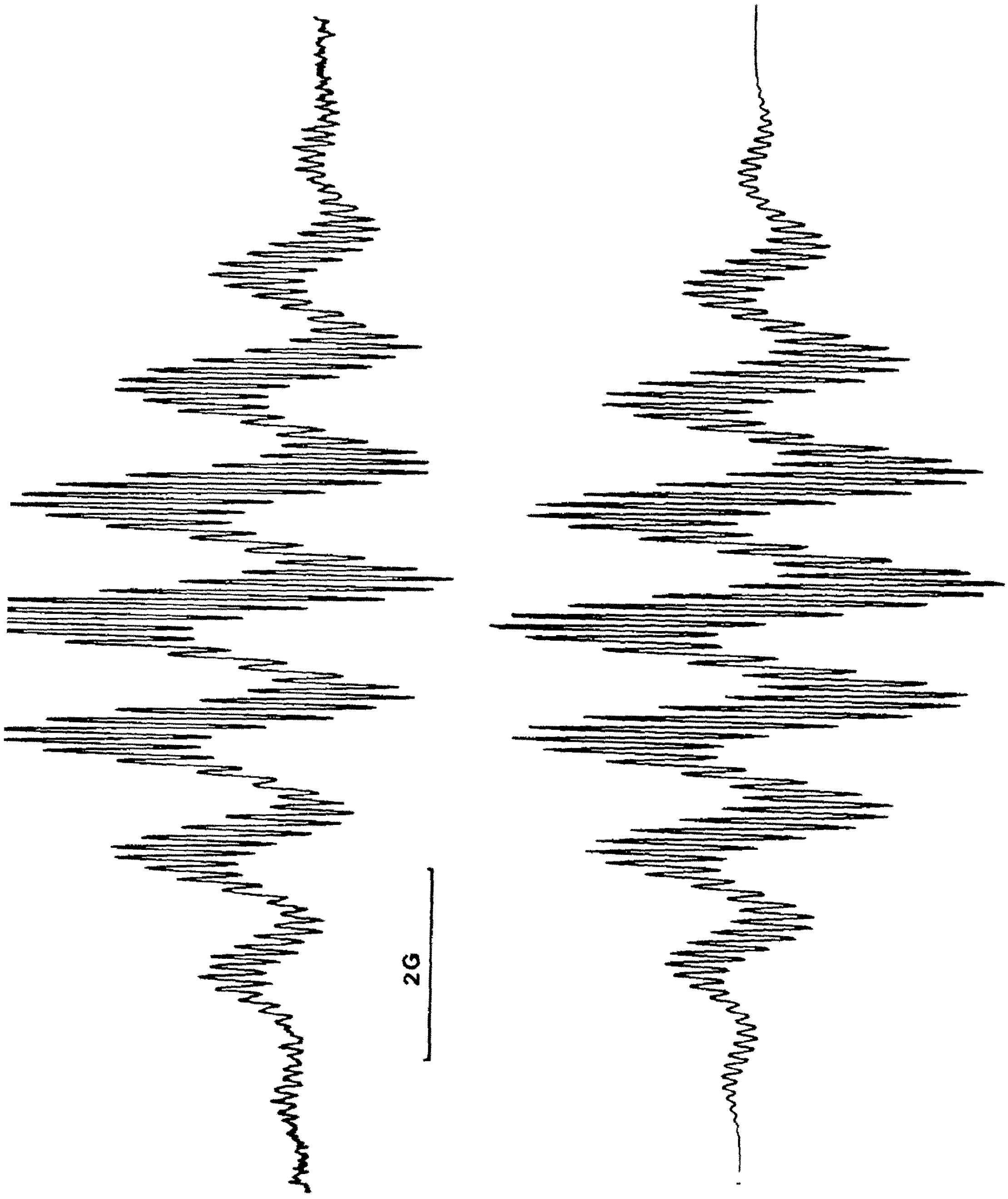


Fig. 2 ESR spectra of lithium triple ion of TMB in MTHF at room temperature: (a) experimental spectrum; (b) computer simulated spectrum, linewidth 0.11 G.

and the coupling constants thus deduced are shown in Table 1. It is interesting to note that the small proton coupling constants of the twelve Me groups (36 protons) appear in these spectra whereas in the corresponding ion pairs the linewidth is much higher than these couplings. This presumably reflects the greater symmetry and rigidity of the triple ions compared to the ion pairs. The couplings in the ion pairs[16] are included in Table 1 for comparison with the triple ions. The coupling constants of protons 3 and 6 in the triple ions are approximately equal to the coupling constants in the ion pairs but the metal coupling constants are only 60%.

The spin density at the alkali metal nuclei has been calculated using the method of Goldberg and Bolton[20] which had been used by Corvaja *et al.*[21] for the ion pairs of metal cations with the *o*-dimesitoylbenzene radical-anion. All interactions between the ions except the direct overlap term $\langle \psi^{\pi}_{m-1} | ns \rangle$ were neglected. In Hückel MO calculations with the McClelland correction[22] on the TMB$^-$M$^+$ ion pairs, which were improved in relation to the already published ones[16], values of $\alpha_c + 1.2\beta$ and $\alpha_c + 1.9\beta$ were used for the Coulomb integrals of the O atoms remote from and adjacent to the metal ion respectively. For the triple ions the latter value was used for all four O atoms.

Figure 3 shows plots of the spin densities at the metal nuclei as a function of the metal oxygen distance r_{OM} for both ion pairs and triple ions. The distances corresponding to the metal couplings observed at room temperature in MTHF are shown in Table 1.

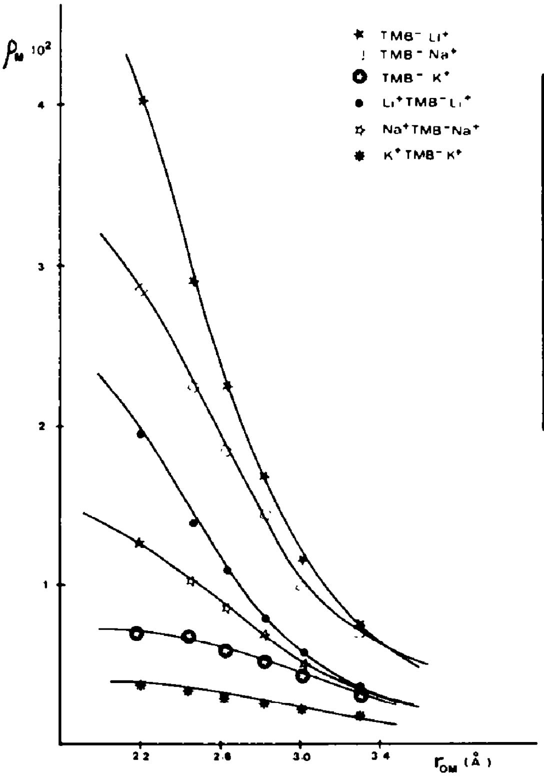


Fig. 3. Plot of calculated spin density at the metal nucleus vs oxygen-metal distance in Å for ion pairs and triple ions of TMB

The relative stabilities of the triple ions have been investigated by adding lithium tetraphenylboranate or sodium tetraphenylboranate to solutions of ion pairs of TMB with Li, Na, K or Cs (Table 2). Li displaces K or Cs but not Na and Na displaces all the other metals. The establishment of the new equilibria was faster than could be followed by ESR except for the replacement of Na by Li: when lithium tetraphenylboranate was added to solution of Na ion pairs the superposed spectra of the Li and Na triple ions were first observed and these changed to that of just the Na triple ion after about 30 min. No evidence for long lived mixed triple ions (Li$^+$ TMB$^-$ Na$^+$) was seen. The observation that the Na triple ion is the most stable is consistent with the results of the calculated oxygen metal distances (Table 1). It is also interesting to note that Chen and Wan[12] found that in the system they studied the Na complexes were the most stable.

EXPERIMENTAL

The samples of triple ions for ESR-measurements were prepared by adding an equivalent amount of the tetraphenylboranate to the soln of the ion pairs through a break-seal in a twinbodied all glass vacuum sealed apparatus.

TMB was synthesised in our laboratory.[16] Lithium, potassium and caesium tetraphenylboranates were prepared from the sodium salt by Bhattacharyya's method.[19] Caesium cyanotriphenylboranate was prepared from the sodium salt by reaction with caesium chloride in aqueous soln

ESR-measurements were made using Varian V-4502-04 with a 12 inch magnet and Bruker ER 200tt spectrometers.

Spectra were simulated using a program, which assumes Lorentzian line shape, written for a ICL 4130 computer with an on line plotter.

Table 1. Hyperfine splitting constants in Gauss and oxygen-metal distances in Å for ion pairs and triple ions of TMB

	a_M(G)	$a_{H_{3,6}}$(G)	$a_{H_{(CH_3)}}$(G)	r_{OM}(Å)
Li$^+$TMB$^-$	2.26	1.36	—	2.86
Li$^+$TMB$^-$Li$^+$	1.247	1.247	0.12	2.76
Na$^+$TMB$^-$	4.47	1.40	—	2.88
Na$^+$TMB$^-$Na$^+$	2.62	1.227	0.122	2.64

Table 2. TMB triple ions obtained from reactions of ion pairs with alkali metal tetraphenylboranates

ADDED SALT / ION PAIR	Li$^+$ Ph$_4$B$^-$	Na$^+$ Ph$_4$B$^-$
TMB$^{\dot-}$Li$^+$	Li$^+$TMB$^{\dot-}$Li$^+$	Na$^+$TMB$^{\dot-}$Na$^+$
TMB$^{\dot-}$Na$^+$	Na$^+$TMB$^{\dot-}$Na$^+$	Na$^+$TMB$^{\dot-}$Na$^+$
TMB$^{\dot-}$K$^+$	Li$^+$TMB$^{\dot-}$Li$^+$	Na$^+$TMB$^{\dot-}$Na$^+$
TMB$^{\dot-}$Cs$^+$	Li$^+$TMB$^{\dot-}$Li$^+$	Na$^+$TMB$^{\dot-}$Na$^+$

Acknowledgements— We are grateful for the financial support provided by the Instituto Nacional de Investigação Cientifica (Portugal), for permission to use the ESR spectrometers of Laboratório Nacional de Engenharia e Tecnologia Industriais and Centro de Quimica Estrutural da Universidade Técnica de Lisboa and for permission to use the computing facilities of Instituto Gulbenkian de Ciência of the Fundação Calouste Gulbenkian. We also thank Dr. H. M. Novais for his help, Dr. J. M. S. Calazans for assistance in programming our calculations and Eng. Téc. F.C. de Matos for technical assistance with the ESR-spectrometer.

REFERENCES

[1] S. A. Al-Baldawi and T. E. Gough, *Can. J. Chem.* **48**, 2798 (1970).

[2] S. A. Al-Baldawi and T. E. Gough, *Ibid.* **49**, 2059 (1971).

[3] C. Gooijer, D. M. de Leeuw and C. MacLean, *J. Magn. Res.* **17**, 46 (1975).

[4] T. E. Gough, *Ibid* **26**, 403 (1977).

[5] C. Gooijer and W. Oosterbeek, *Ibid.* **33**, 669 (1979).

[6] C. Gooijer, E. J. Baerends and W. Oosterbeek, *J. Chem. Soc.* Faraday Trans. II 1423 (10) (1979).

[7] T. E. Gough and P. R. Hindle, *Can. J. Chem.* **47**, 1698 (1969).

[8] T. E. Gough and P. R. Hindle, *Ibid.* **47**, 3393 (1969)

[9] T E. Gough and P. R. Hindle, *Trans. Faraday Soc.* **66**, 2420 (1970).

[10] T. E. Gough and P. R. Hindle, *Can. J. Chem.* **48**, 3959 (1970).

[11] K. S. Chen and N. Hirota, *J. Am. Chem. Soc.* **94**, 5550 (1972).

[12] K. S. Chen and J. K. S. Wan, *Ibid.* **100**, 6051 (1978).

[13] B. J. Herold, A. F. Neiva Correia and J. dos Santos Veiga, *Ibid.* **87**, 2661 (1965).

[14] B. J. Herold, L. J. Alcácer, A. J. Ferrer Correia, A. J. Pereira Domingos, M. Celina, R. L. R. Lazana and J. dos Santos Veiga, *Rev. Port. Quim* **11**, 188 (1969).

[15] B. J. Herold, H. M. Novais, M. Celina, R. L. R. Lazana and P. B. Correia, *Ibid.* **13**, 78 (1971).

[16] B. J. Herold, M. Celina R. L R. Lazana and H. M. Novais, *Tetrahedron* **33**, 517 (1977).

[17] N. M. Atherton, XXIII*rd International Congress of Pure and Applied Chemistry*, Vol. 4, 469 (1971).

[18] N. M. Atherton and B. Day, *J. Chem. Soc.* Faraday Trans. II 69 (12) 1801 (1973).

[19] D. N. Bhattacharyya, C. L. Lee, J. Smid and M. Szwarc, *J. Phys. Chem.* **69**, 608 (1965).

[20] I. B. Goldberg and I. R. Bolton, *J. Phys. Chem.* **74**, 1965 (1970).

[21] L. Pasimeni, M. Brustolon and C. Corvaja, *J. Chem. Soc.* Faraday Trans. II 70 (4), 734 (1974).

[22] B. J. McClelland, *Trans. Faraday Soc.* **57**, 1458 (1961).