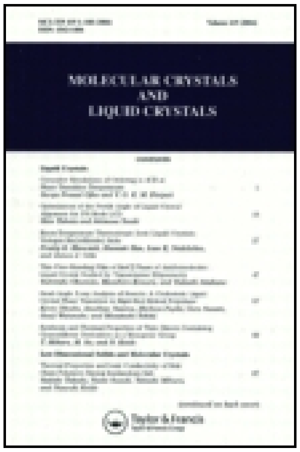


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

ESR Study of High Spin States Derived from Tribenzoylenebenzene

M. Căndida B. L. Shohoji [a] , M. Luisa T. M. B. Franco [a] , M. Celina R. Lazana [a] , Kazunobu Sato [b] , Takeji Takui [b] & Koichi Itoh [c]

[a] Department of Chemistry, Instituto Superior Técnico, Universidade Técnica de Lisboa, Av. Rovisco Pais, 1096, Lisboa Codex, Portugal

[b] Department of Chemistry, Osaka City University, Sumiyoshi-ku, Osaka, 558, Japan

[c] Department of Material Science, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka, 558, Japan

To cite this article: M. Căndida B. L. Shohoji, M. Luisa T. M. B. Franco, M. Celina R. Lazana, Kazunobu Sato, Takeji Takui & Koichi Itoh (1997): ESR Study of High Spin States Derived from Tribenzoylenebenzene, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 305:1, 353-365

To link to this article: http://dx.doi.org/10.1080/10587259708045072

Mol. Cryst. Liq. Cryst., 1997, Vol. 305, pp. 353–365
Reprints available directly from the publisher
Photocopying permitted by license only

ESR STUDY OF HIGH SPIN STATES DERIVED FROM TRIBENZOYLENEBENZENE

M. CÂNDIDA B. L. SHOHOJI[1], M. LUISA T. M. B. FRANCO[1], M. CELINA R. LAZANA[1], KAZUNOBU SATO[2], TAKEJI TAKUI[2] and KOICHI ITOH[3]
[1]Department of Chemistry, Instituto Superior Técnico, Universidade Técnica de Lisboa, Av.Rovisco Pais, 1096 Lisboa Codex, Portugal
[2]Department of Chemistry and [3]Department of Material Science, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan

Abstract By reduction of tribenzoylenebenzene **4** with lithium in 2-methyltetrahydrofuran (MTHF) an ion pair and a cluster with S = 1 were obtained whereas with potassium or sodium in MTHF in the presence of dicyclohexano-18-crown-6 (or a solvent of strong solvating power such as diglyme or hexamethyl-phosphoric triamide), different species with $S \geqq 1/2$ were detected. The ESR spectra of the randomly oriented pluri-anions in glassy matrix showed the existence of triplet species assigned to a dianion $[\mathbf{4}^{2(\cdot\,-)}(M^+)_2]$ and aggregates $[\mathbf{4}^{\cdot\,-}(M^+)_n\mathbf{4}^{\cdot\,-}]$ and quartet species $[\mathbf{4}^{2(\cdot\,-)}(M^+)_3\mathbf{4}^{\cdot\,-}]$. The quartet species was attributed to intermolecular high-spin clusters with the relatively small zero-field splitting parameter *D* and vanishing *E* value. Further reduction led to the formation of a more persistent species with a quartet ground state characterized by the zero-field parameters $D = +\ 0.0215\ \mathrm{cm}^{-1}$ and $E = 0\ \mathrm{cm}^{-1}$, assigned to a triradical-trianion $[\mathbf{4}^{3(\cdot\,-)}(M^+)_3]$, generated by three-electron doping per a single tribenzoylenebenzene molecule. The observed ^{1}H-ENDOR spectra and INDO calculations also confirmed the above identification. $\mathbf{4}^{3(\cdot\,-)}$ is a stable pluri-anionic high-spin molecule in solution.

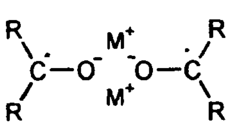
INTRODUCTION

The last decade has witnessed a rapid development of spin science which has given rise to diverse topics in this field. Among these, pluri-charged organic high-spin systems of elaborate molecular design have emerged as models for studying the interplay between charge fluctuation and spin polarization. The first experimental evidence of the existence of species with S = 1 formed by clusters of two alkali (or alkaline earth) metal ketyls **1**, was reported by Hirota and Weissman, who studied the rigid media ESR spectra of aromatic (benzophenone, xanthone and fluorenone) and aliphatic ketyls (pentamethyl and hexamethylacetone)[1-3]

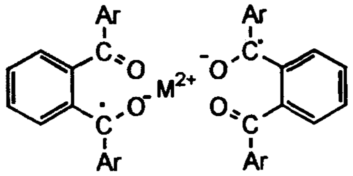
A few other triplets derived from ketones, such as benzoylacetone and dibenzamide were also reported[4] Later two other groups investigated biradicals **2** formed by clustering of two radical monoanions of 1,2-diaroylbenzenes and alkaline earth cations[5,6]

A species **3**, generated by reduction of a diketone, with a triplet state arising from intramolecular spin coupling was for the first time detected for 1,3-dimesitoylbenzene[7]

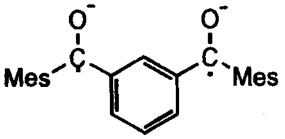
Higher spin states were expected to be reached in radical trianions derived from the corresponding 1,3,5-triaroylbenzenes. However, only clusters with $S = 1$ arising from intermolecular coupled radical centers were detected[8].



1

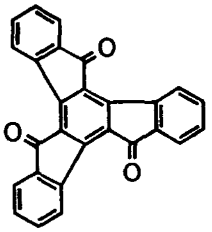


2



3

In the search for organic molecules with high spin states based on ketyls, we investigated by ESR spectroscopy the species obtained by the reduction with alkali metals of the discoidal and three-fold symmetric polyketone, tribenzoylenebenzene (diindeno [1,2-a:1',2'-c] fluorene-5,10,15-trione), **4**. In this work, we report an extension of the preliminary results previously published[9].



4

EXPERIMENTAL

In Lisbon, ketyls were prepared by reducing **4** with Li, Na and K in MTHF (2-methyltetrahydrofuran) under the presence of dicyclohexane-18-crown-6, MTHF/DG (diglyme) (2:1) and MTHF/HMPA (hexamethylphosphoric triamide) (40:1). They were investigated in the temperature range from 4.2 to 293K by means of ESR (X-band) and ENDOR spectroscopies using a Bruker ESP 300E spectrometer equipped with an EN 810 ENDOR unit. The temperature of the sample was monitored by means of either a Bruker ER400T variable temperature unit or an ESR900 liquid-helium flow cryostat manu-factured by Oxford Instruments. In order to avoid saturation, the microwave power was attenuated to 2.0 μ W in the experiments between 4.2 and 10K.

In Osaka, computer simulations of fine structure spectra were undertaken in order to identify the observed high spin states and to extract spin Hamiltonian parameters. The simulation was based on the Eigenfield method free from problematic avoidance of eigenenergy crossing. All the absorption lines including forbidden transitions, $\triangle M_s = \pm 2$ and ± 3 were calculated with Boltzmann distribution taken into account.

RESULTS AND DISCUSSION

The rate and degree of reduction of **4** with alkali metals in ethereal solvents depended not only on the redox potential of the metal but also on the ionising power of the medium. By reduction with lithium, an ion-pair $\mathbf{4}^{\cdot -}\mathbf{Li}^{+}$ and a biradicalar spin-triplet cluster with D = 0.0078 cm^{-1} and vanishing E, were formed. The relatively small value for D and vanishing E are characteristic of a biradicalar triplet anion cluster $[\mathbf{4}^{\cdot -}(\mathrm{Li}^{+})_2\mathbf{4}^{\cdot -}]$ which is comprised of the metal-bridged monoanion ketone radical. Figure 1 shows the ESR, ENDOR and general TRIPLE resonance spectra of the ion-pair. The magnitudes and signs for the hyperfine coupling constants presented in Table I were extracted from the ^{1}H-ENDOR and general TRIPLE spectra in solution.

INDO calculations were carried out with geometric parameters based on the fluorenone molecular structure and with the Li^{+} cation lying 2.24 Å above the carbon atom of the carbonyl group as given in Figure 1a, yielding the values for the theoretical hyperfine coupling constants which agree satisfactorily with the experimental ones (see Table I).

Higher electron-doping steps were reached by reduction with Na and K in MTHF under the presence of a crown-ether or in mixtures of MTHF with solvents of higher solvating power for cations such as DG and HMPA. Mainly the crown-ether was proved to be very suitable to avoid not only the formation of undesirable precipitates which make

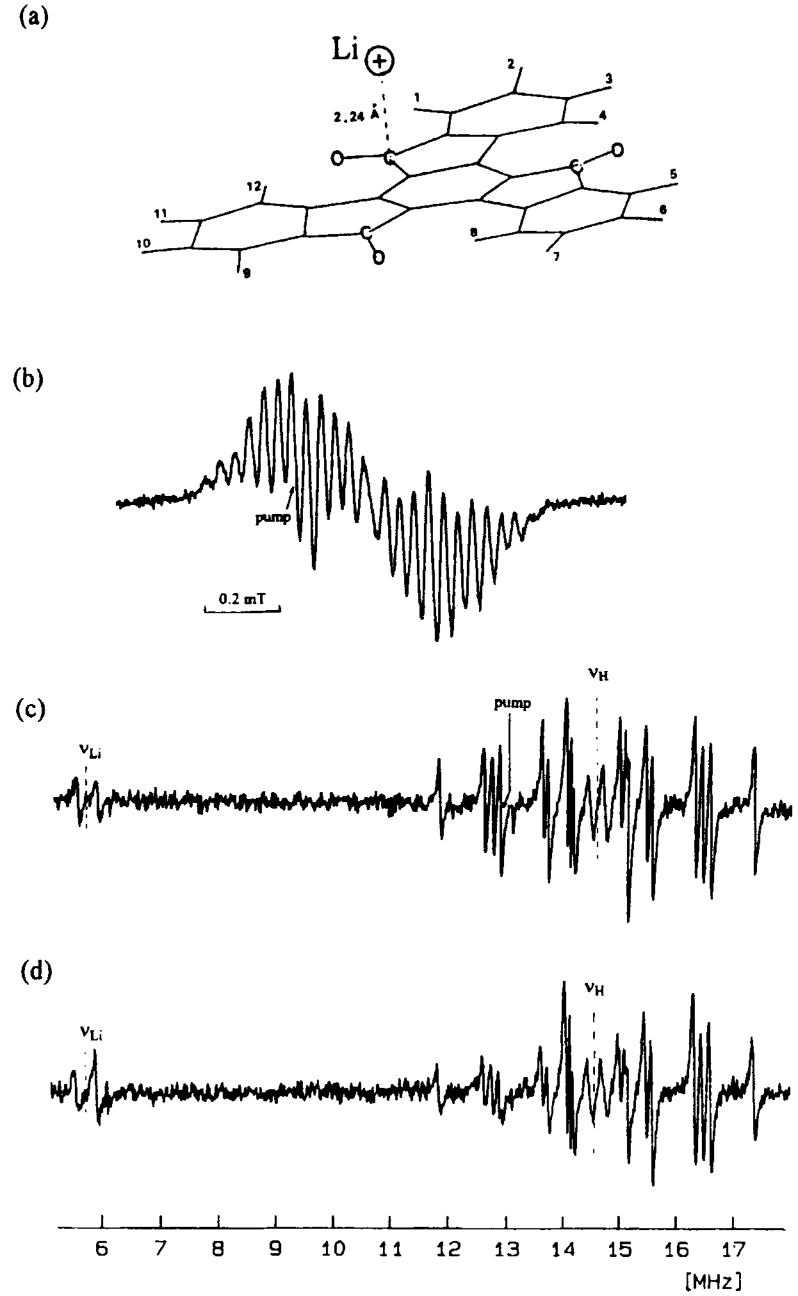


FIGURE 1. Molecular structure assumed in the INDO calculations (a) and spectra of $4^{\cdot -}Li^+$ ion pair in DME, at 193K: (b) ESR; (c) ^{1}H-ENDOR pumping at 338.05 mT; (d) general TRIPLE pumping at 12.796 MHz.

TABLE I. Experimental and calculated* hyperfine coupling constants (a^i x 10/mT) of $\mathbf{4}^{\cdot -}Li^+$ in DME, at 193K.

	a^1	a^2	a^3	a^4	a^5	a^6	a^7	a^8	a^9	a^{10}	a^{11}	a^{12}	a^{13}
Exp.	-1.42	0.29	-1.96	0.38	0.09	-1.22	0.09	-1.32	0.09	-0.69	0.09	-0.62	-0.13
Calc.	-1.37	0.43	-1.56	0.62	0.26	-0.54	0.30	-0.68	0.21	-0.48	0.25	-0.47	-0.14

*INDO calculation with geometric parameters based on the structure of fluorenone and the Li^+ lying 2.24 Å above the C carbonyl atom.

TABLE II Experimental and calculated* hyperfine coupling constants (a^i / mT) of $\mathbf{4}^{3(\cdot -)}(K^+)_3$ in glassy matrix of MTHF, at 90K.

	$a^{1,5,9}$	$a^{2,6,10}$	$a^{3,7,11}$	$a^{4,8,12}$
Exp.	-0.073	-0.057	-0.135	0.030
Calc.	-0.071	-0.039	-0.218	0.093

*INDO calculation with geometric parameters based on the structure of fluorenone.

the progress of the reaction very difficult, but also the formation of ion-pairs or aggregates. In fact, if an ion-pair is formed, the perturbation caused by the positive electrostatic field of the cation will destroy the triple pseudo-degeneracy (double and single near degeneracy) of the π -LUMO of **4**. In this case, chance for the formation of intramolecularly coupled high-spin species can be suppressed.

The first species with S > 1/2 obtained by the reduction of **4** with Na (or K) showed an ESR spectrum characteristic of randomly oriented triplet species. The computer simulation allowed the determination of the g value and zero-field splitting parameters: g = 2.01, D = 0.0310 cm^{-1} and E = -0.0020 cm^{-1} in DG/MTHF (2:1) at 103 K. The values of these parameters slightly depend on the temperature, solvent and counter-ion, suggesting that the triplet species is possibly attributable to clusters $[\mathbf{4}^{\cdot -}(Na^+)_2\mathbf{4}^{\cdot -}]$ with intermolecular electron spin coupling. This possible assignment was only apparently consistent with dilution experiments which showed that the intensity of the central line of the ESR spectra increases in relation to the ones of the triplet lines due to the dissociation of the aggregate. Nevertheless, the observed D value is too large to claim to arise from the intermolecularly coupled spins. D values for triplet states from ketone-based metal-bridged molecular anion clusters range up to 0.02 cm^{-1}. The observed large D value and non-vanishing E value can be only interpretable in comparison with the large D value and vanishing E from a quartet species described below, indicating that the triplet state characterized by such a large D value originates in intramolecular spin coupling in a triplet-state dianion $\mathbf{4}^{2(\cdot -)}(Na^+)_2$. A rationale is given by considering molecular structures and the projection factor for zero-field splitting parameters when compared.

Following the reduction of **4** with Na or K, the ESR spectrum was obtained as shown in Figure 2. The spectrum in Figure 2 was obtained with K. In the low field $\triangle M_s = \pm 3$ and ± 2 forbidden transitions appeared near 0.10 T and 0.16 T, respectively. A strong peak near 0.16 T is due to a triplet species and the other peaks were assigned to a quartet state with a considerably large line width. Anomalous line shapes appearing from 0.28 T to 0.38 T are attributed to overlapping of the triplet and quartet species with large variation of line width distribution. The spin Hamiltonian parameters for the triplet and quartet species were estimated to be g = 2.01, D = 0.037 cm^{-1}, E = 0 cm^{-1} and g = 2.01, D = 0.0179 cm^{-1}, E = 0 cm^{-1}, respectively. The quartet species with the smaller D value and

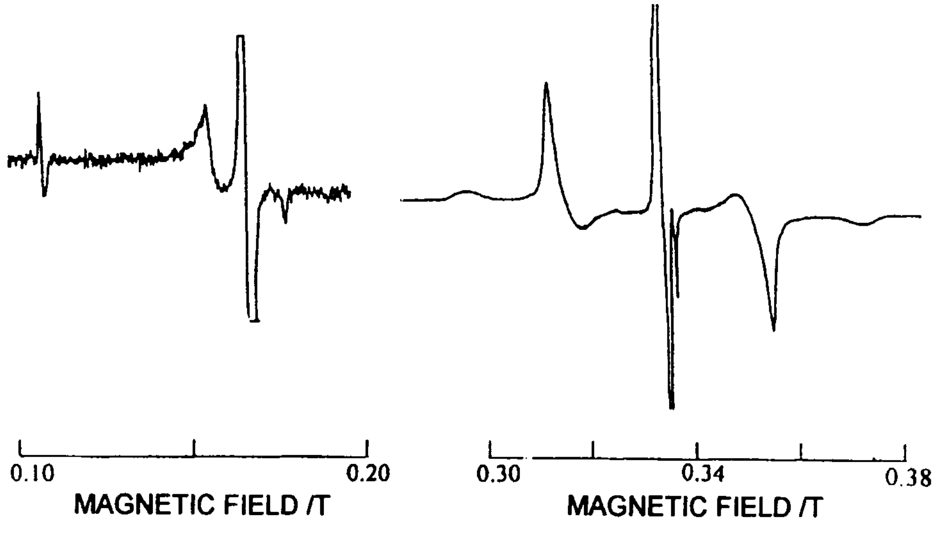


FIGURE 2. ESR spectrum observed from the mixture of the triplet state of $\mathbf{4}^{2(\cdot -)}(K^+)_2$ and the quartet state of $\mathbf{4}^{2(\cdot -)}(K^+)_3\mathbf{4}^{\cdot -}$ in MTHF at 4.4K, in which the former dominates.

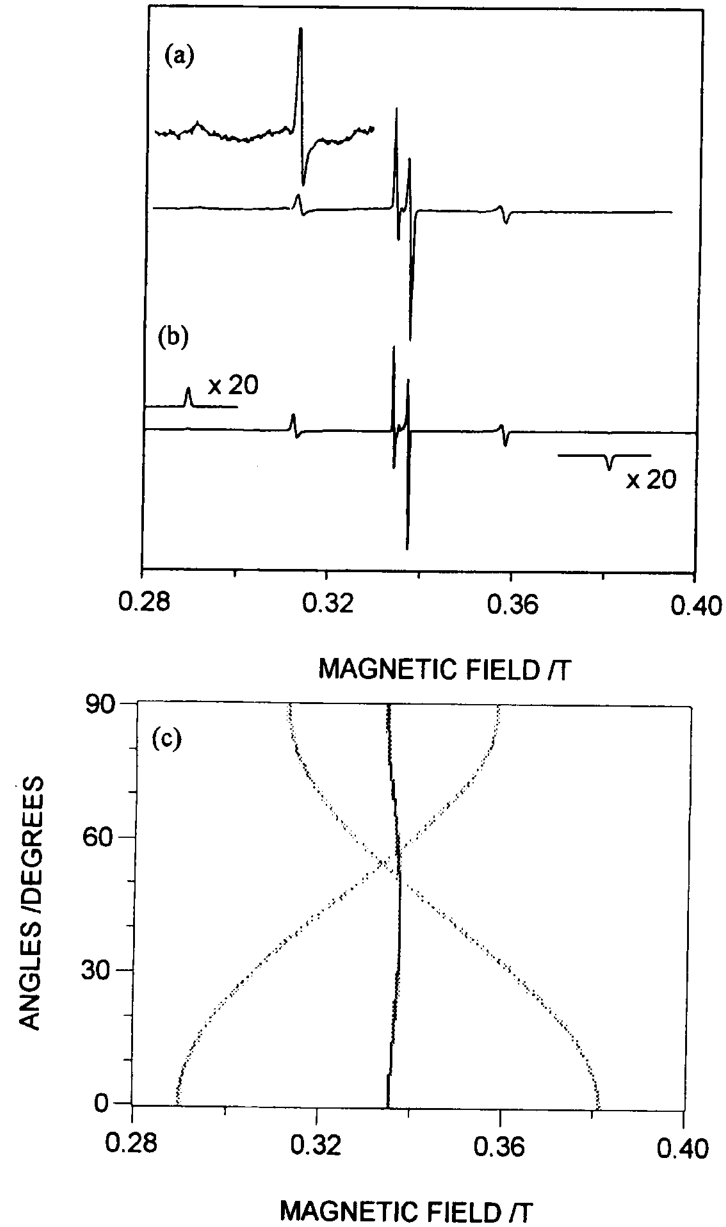


FIGURE 3. (a) Observed and (b) simulated ESR spectra ($\Delta M_s = \pm 1$) for the quartet state of $4^{3(\cdot\,-)}(K^+)$ in MTHF, at 90K. (c) Angular dependence of resonance fields and transition probabilities for random orientation. (d) Observed and (e) simulated ESR spectra ($\Delta M_s = \pm 2$ and ± 3). (f) Angular dependence of resonance fields and transition probabilities for random orientation.

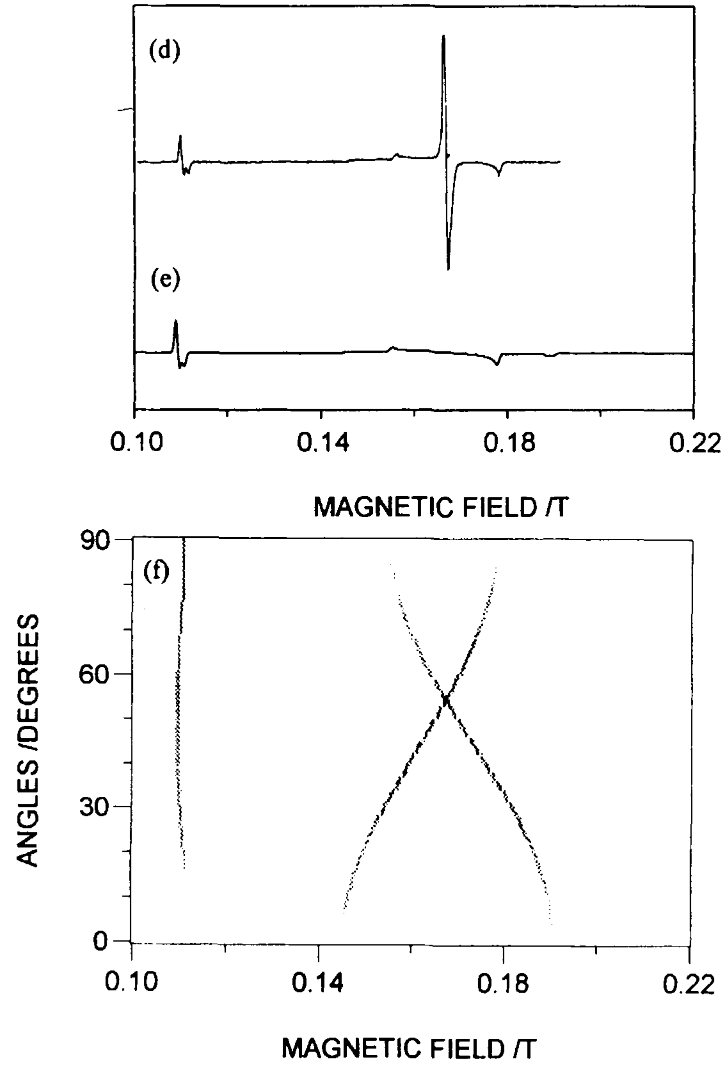


FIGURE 3. (a) Observed and (b) simulated ESR spectra ($\Delta M_s = \pm 1$) for the quartet state of $4^{3(\cdot\,-)}(K^+)$ in MTHF, at 90K. (c) Angular dependence of resonance fields and transition probabilities for random orientation. (d) Observed and (e) simulated ESR spectra ($\Delta M_s = \pm 2$ and ± 3). (f) Angular dependence of resonance fields and transition probabilities for random orientation.

large line width was attributable to intermolecularly spin coupled metal-bridged clusters such as $[\mathbf{4}^{2(\cdot -)}(M^+)_3\mathbf{4}^{\cdot -}]$ which is composed of the triplet dianion and doublet monoanion. The corresponding *D* value for the cluster spin-quartet is expected to range from 0.010 to 0.020 cm^{-1}, assuming $D = 0.031\ cm^{-1}$ for $\mathbf{4}^{2(\cdot -)}(M^+)_2$ and coupled spin Hamiltonian approach. The value of 0.010 corresponds to a weak limit of the vanishing intermolecular spin coupling between the triplet and doublet species.

After a new contact of the solution with the metal (Na, K), the spectrum of Figure 2 disappeared and an ESR spectrum showing a strong off-principal-axis extra line characteristic of species with half-integral spins and large *D* values compared with the line width of the single transition was obtained,[10] as shown in Figure 3a. Computer spectral simulations (see Figure 3b) produced satisfactorily well the experimental spectra with $S = 3/2$, $g = 2.010$ (isotropic) and the values of the zero-field splitting parameters, $D = 0.0215\ cm^{-1}$ and $E = 0.0000\ cm^{-1}$, showing unambiguously that an additional strong peak on the high field side near $g = 2$ is assigned to the off-principal-axis extra line which belongs to the quartet species and not to a quintet state species as concluded before [9].

The $\Delta M_s = \pm 2$ and $\Delta M_s = \pm 3$ forbidden transitions from the quartet state could be recorded in the wide range from 4.4 K to 90 K, as shown in Figure 3d. Due to the relatively large *D* value, the line corresponding to the $\Delta M_s = \pm 2$ transition is very anisotropic as shown by the angular dependence of resonance fields depicted in Figure 3f. The sharp line observed at 167 mT is due to small contamination by a triplet species. The line appeared with a rather strong intensity because of the small anisotropy of the $\Delta M_s = \pm 2$ forbidden transition of the triplet state. Salient features of the appearance of the off-axis exra line of the $\Delta M_s = \pm 1$ transition as well as the anisotropic nature of the $\Delta M_s = \pm 2$ transition are inherent in a quartet state with a relatively large *D* value. For spin-quartet species with relatively small *D* values, the appearance of the signal assignable to the $\Delta M_s = \pm 2$ forbidden transitions does not give enough evidence for the quintet spin state.

The quartet state was identified as resulting from intramolecular spin coupling in a triradical-trianion $\mathbf{4}^{3(\cdot -)}(K^+)_3$. The possibility of assigning the spectrum to a cluster was ruled out on the basis of the independence of the zero-field splitting of the solvent, temperature and cation and of the results of the dilution experiments. Assuming a similar three-fold symmetric molecular structure for the triplet state of a dianion $4^{2(\cdot\,-)}$ and considering the projection factor 2S-1 give $(2S-1)D = 0.043$ cm^{-1} and $E = 0$ cm^{-1} which can be compared with the observed $(2S-1)D = 0.0310$ cm^{-1} and $E = -0.002$ cm^{-1} (S = 1). The *D* value should be reduced more if two-electron doping per triply pseudo-degenerate orbitals is taken into account.

The temperature dependence of the ESR lines corresponding to the $\Delta M_s = \pm 3$ transition for the quartet $4^{3(\cdot\,-)}(K^+)_3$ is shown in Figure 4a. Since the line shape of the peak does not change with temperature, the intensity of the ESR signal was calculated by measuring the peak height of the derivative curve. Figure 4b shows the experimental data

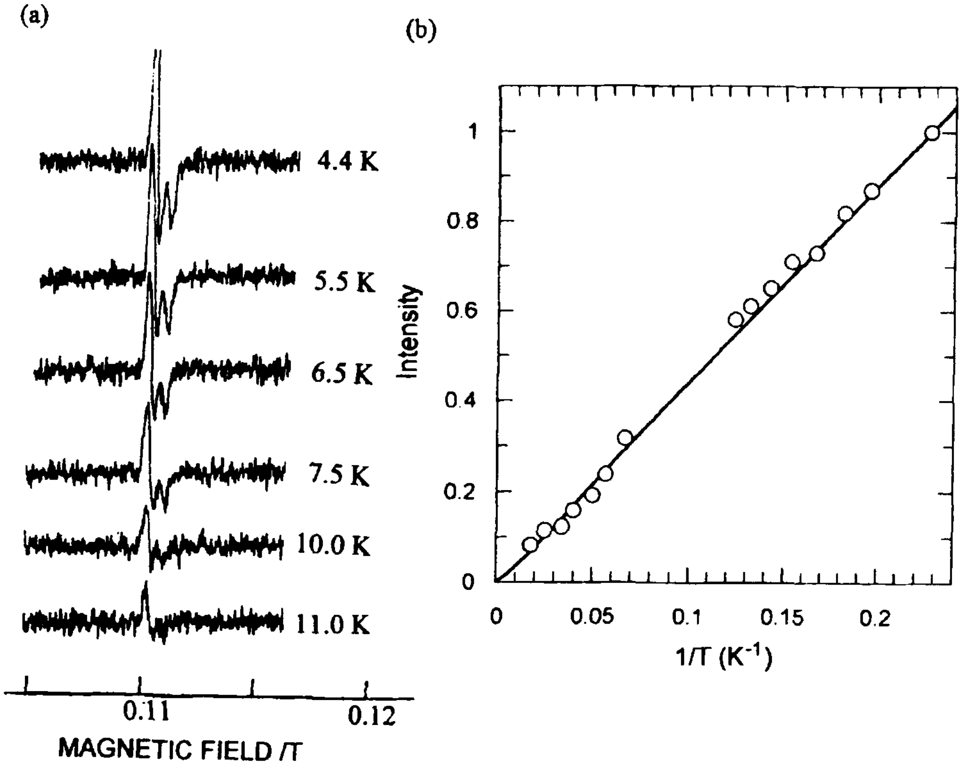


FIGURE 4. (a) ESR spectra at various temperatures of the $\Delta M_s = \pm 3$ transition for the quartet state of $4^{3(\cdot\,-)}(K^+)_3$. (b) Plot of the absorption intensity vs. T^{-1}

together with the theoretical curve calculated for a doublet-quartet energy gap. The experimental and theoretical intensities were normalized at 4.4K. A thermal excitation energy of $\triangle E_{d\text{-}q} \geqq 500$ J/mol could be evaluated from the experimental data and fitting above, leading to the conclusion that the ground state of $\mathbf{4}^{3(\cdot\,-)}(K^+)_3$ is a spin-quartet.

The ratio I_H/I_L of the intensity of the XY absorption peak appearing at high field to that at low field increased by 1.13 times from 4.2K to 9K, indicating a positive *D* value for the ground-state quintet. Also, the ^{1}H-ENDOR experiments confirm the sign of the *D* value. Figure 5 shows the ^{1}H-ENDOR spectra of $\mathbf{4}^{3(\cdot\,-)}(K^+)_3$ in glassy matrix of MTHF obtained by pumping the XY canonical peaks of the three transitions. By monitoring the

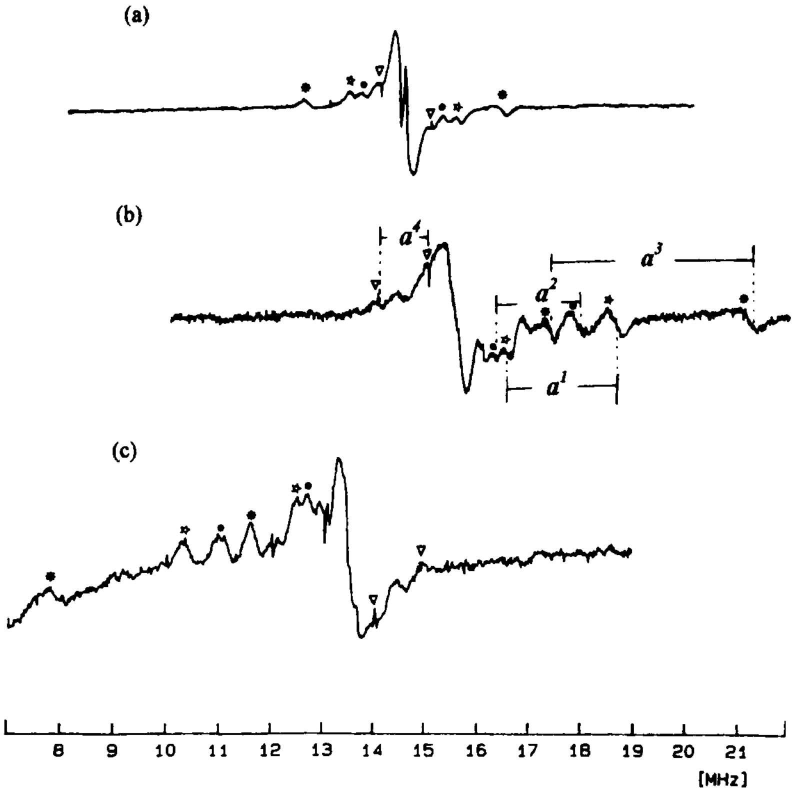


FIGURE 5. ^{1}H-ENDOR spectra of $\mathbf{4}^{3(\cdot\,-)}(K^+)_3$ in glassy matrix of MTHF, at 90K. Pumping: (a) 336.86 mT (XY-canonical peak of | -1/2>⇔1/2> transition, NS = 15; (b) 360.15 mT (XY-canonical peak of | 3/2>⇔ | 1/2> transition, NS = 90; (c) 315.26 mT (XY-canonical peak of | -3/2>⇔ | -1/2> transition, NS = 90. NS denotes the number of scans.

transition between $M_s = 1/2$ and $-1/2$ sublevels, the ENDOR spectrum is symmetric with respect to ν_H and the hyperfine coupling constants a can be determined from the separation of the pair of lines symmetrically located although the sign of a cannot be determined from this spectrum (see Figure. 5a). On the contrary, the spectra of Figure 5b and 5c corresponding to the $|3/2\rangle \Leftrightarrow |1/2\rangle$ and $|-3/2\rangle \Leftrightarrow |-1/2\rangle$ transitions, respectively, are asymmetric. From them, both the relative as well as absolute sign and the magnitude of a^i (see Table II) can be directly determined by considering the pair of lines located at $\nu_H - (3/2)a^i$ and $\nu_H - (1/2)a^i$ [11,12]. According to the theory, for the quartet state with a positive D value, the negative coupling constants, a^1, a^2 and a^3 appear at $\nu > \nu_H$ and $\nu < \nu_H$ when the high field and the low field XY absorption peaks were pumped, respectively.

A large positive D value with the vanishing E value is expected if strong intramolecular coupling occurs in an axially symmetric spin-quartet trianion like $\mathbf{4}^{3(\cdot-)}$

INDO calculations of hyperfine coupling constants for the quartet state of the triradical-trianion were carried out using the geometric parameters similar to those of the fluorenone strucure. The agreement between the experimental and the calculated values is satisfactory in spite of the approximations used, as seen in Table II. These results confirm the validity of the assignment of the quartet state to an intramolecular spin-coupled triradical-trianion.

In concentrated solutions, another species with $S = 1$ ($D = 0.0188$ cm^{-1} and $E = 0.0036$ cm^{-1}) assigned to unidentified aggregates coexists with the ground-state quartet species.

CONCLUSIONS

The detection of a quartet ground state for $\mathbf{4}^{3(\cdot-)}(K^+)_3$ suggests that the planar (or quasi-planar) and C_3-symmetric molecular structure of **4** allows the transfer of three electrons to the triply pseudo-degenerate π-LUMOs. This indicates the occurrence of robust spin polarisation which dictates high spin preference in the system under study. To our knowledge, $\mathbf{4}^{3(\cdot-)}$ is the first organic pluri-anionic molecule of high symmetry to be reduced to a spin state with $S > 1$. Other molecules with three-fold degeneracy of the LUMO such as buckminsterfullerence only yielded triplets upon ionization[13]. Therefore, $\mathbf{4}^{3(\cdot -)}$ is a good pluri-anionic model for theoretical and experimental studies of electron transfer and high spin formation.

REFERENCES

1. N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, **83**, 3533(1961).
2. N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, **86**, 2538(1964.
3. N. Hirota, *J. Am. Chem. Soc.*, **89**, 32(1967).
4. F. W. Pijpers, H. van Willigen and J. J. Th. Gerding, *Rec. Trav. chim. Pays Bas*, **86**, 511(1967).
5. M. Brustolon, L. Pasimeni and C. Corvaja, *Chem. Phys. Lett.*, **21**, 194(1973).
6. M. C. Loia, B. J. Helold, N. M. Atherton and H. M. Novais, *J. Chem. Soc., Faraday Trans.* 2, **77**, 1643(1981).
7. B. J. Herold, M. C. R. L. R. Lazana, M. C. B. L. Shohoji and N. M. Atherton, *Abstracts of the Geselschaft Deutcher Chemiker Meeting*, Berlin, 1979.
8. M. C. R. L. R. Lazana and M. C. B. L. Shohoji, *unpublished results.*
9. M. C. R. L. R. Lazana, M. L. T. M. B. Franco and M. C. B. L. Shohoji, *J. Chem. Res.(S)*, 48(1996).
10. Y. Teki, T. Takui and K. Itoh, *J. Chem. Phys.*, **88**, 6134(1988).
11. H. Kurreck, B. Kirste and W. Lubitz, *Electron Nuclear Double Resonance Spectroscopy of Radicals in Solution* (VCH Verlagsgesellschaft mbH, Weinheim, 1988), Chap. 8.
12. M. Matsushita, T. Nakamura, T. Momose, T. Shida, Y. Teki, T. Takui, T. Kinoshita and K. Itoh, *J. Am. Chem. Soc.*, **114**, 7470(1992).
13. M. Baumgarten, A. Gügel and L. Gherghel, *Adv. Mater.*, **5**, 458(1993).