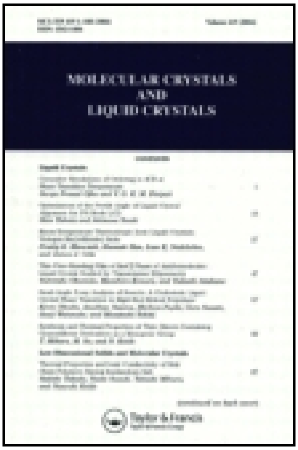

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Electronic States and Spin Characterization of Polyanionic High-Spin Molecules and Clusters Derived from 1,3-Dibenzoylbenzene Derivatives as Studied by ESR/Electron Spin Transient Nutation Spectroscopy

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Electronic States and Spin Characterization of Polyanionic High-Spin Molecules and Clusters Derived from 1,3-Dibenzoylbenzene Derivatives as Studied by ESR/Electron Spin Transient Nutation Spectroscopy

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The systems under study were 1,3-dibenzoyl benzene (**1**), its methyl derivatives (**2**,**3**), and 2,6-dibenzoyl pyridine (**4**), all of which have topologically pseudogenerate π-LUMO's. The corresponding dianions are expected to form triplet ground states and the anionic molecular assemblages expected to form polyanionic high-spin clusters. The polyanionic molecules and clusters were generated by chemical reduction and investigated by cw/FT pulsed ESR spectroscopy. Alkali metal-bridged high-spin clusters were identified directly by FT pulsed ESR-based 2D Electron Spin Transient Nutation (2D-ESTN) spectroscopy. We found ground-state quintet, quartet, and triplet dimers originating in the oligoketone with pluri-electron doping. We determined all the zero-field splitting parameters, g-values, and the concentration ratio of the high-spin systems with the help of spectral simulation.

Keywords: polyanionic high-spin organic molecules; polyanionic high-spin cluster; ESR; electron spin transient nutation spectroscopy; topological pseudo degenerate molecular orbital; heteroatomic perturbation

INTRODUCTION

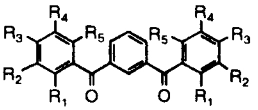
The recent development of the field of organic magnetism/molecule based magnetism crucially owes the fact that the study of organic magnetics has brought about important conceptual advances in chemistry and physics. Purely organic magnetism, defined typically as ferromagnetism originating in purely organic building spin-blocks composed of only light atoms such as C, H, N, O and S is apparently a controversial issue simply because organic substances are intrinsically diamagnetic. The search for organic magnetic materials is, thus, an important issue of the interplay between theory and experiment in physics and rapidly growing spin chemistry.

One of the highlighted advances has been that the use of topological symmetry in the electron network of non-charged π-conjugated homoatomic hydrocarbons gives rise to the unlimited number of the degeneracy in non bonding molecular orbital (NBMOs)(coined as topological degeneracy),[1] which contrasts with the limitation of usual orbital degeneracy. The limitation of the latter essentially arises from the geometrical (group-theoretical) symmetry nature of organic systems comprised of multi-nuclear centers. In this context, group theoretical argument alone never predicts the possible existence of organic molecular high-spin systems with spin multiplicity S greater than 3/2 in their electronic ground state. The very exploitation of the π-topological degeneracy gives birth to purely organic neutral high-spin molecules with S=2.[1]

In contrast to an extensive and continuing study of neutral molecular high-spin systems, it is not until recently that polyionic molecular high-spin systems have drawn much attention as models for studying multicharge fluctuation vs. spin polarization in homoatomic[2,3] and heteroatomic polycationic[4-8] high-spin systems, the documented reports and studies on polyanionic high-spin molecules and clusters appeared as early as 1970's,[9,10] following a pioneering work on triplet ketyl-clusters formed by alkaline metal ion bridges.[11] Recently, diketone-based intermolecular polyanionic clusters have been studied; metal bridge-based intermolecular quartet and quintet clusters with features of small zero-field splitting parameters have been claimed to be well characterized.[12] Stable polyionic magnetic systems[13] are the focus of current topics as models for multifunctionality molecule-based magnetic materials. Such systems have been considered as models for organomagnetic metals.

The systems under study are of hetero-atomic π-conjugation and expected to undergo dynamic spin polarization which is π-topologically controlled for both polycationic and polyanionic cases, leading to super high-spin ground states or ferromagnetic ground state for extended π-conjugation systems. Instead of "topological degeneracy" used for π-NBMOs, a concept of topological "pseudo superdegeneracy" of π-HOMOs or π-LUMOs is used, where "pseudo" and "super" degeneracy originate in heteroatomic perturbation and topological symmetry of π-conjugation network, respectively.

In this paper, our approach to molecular designs is topology-based in heteroatomic π-conjugation and polyketone-based. 1,3-Dibenzoylbenzene derivatives (see **1**-**4**), the precursors of polyanionic model oligomers have pseudo degenerate LUMO's with lower energy. The degeneracy is topology-controlled. Corresponding polyanions were prepared by wet processes of chemical reductions in solution. Unequivocal spin identifications of complicated fine-structure spectra in organic rigid glasses were carried out by invoking pulsed ESR-based 2D-Electron Spin Transient Nutation (2D-ESTN) spectroscopy. It has turned out that the complication is due to the contribution of molecular high-spins in various weights generated due to clustering. Theoretical treatments in terms of high-spin cluster Hamiltonian interpreted the experimentally derived fine-structure parameters for the high-spin ketone-based oligomers with pluri-charge.



1; R_1,R_2,R_3,R_4,R_5=H
2; R_1,R_4=CH_3
R_2,R_3,R_5=H
3; R_1,R_3,R_5=CH_3
R_2,R_4=H

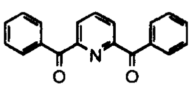


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FIGURE 1 Polyketone-based molecules for pluri-anionic high-spin systems.

EXPERIMENTAL

Precursor diketones are dibenzoylbenzene-based which have pseudo degenerate

LUMOs. The corresponding anionic molecules were prepared by the chemical reduction of the diketones with alkali metal at 200-300K. The reduction was carried out in a sealed-off glass assembly with a cell for ESR measurements under high vacuum. Solvent used in the present work is 2-methyltetrahydrofuran (MTHF) because it forms a glass at low temperature. MTHF solvent was dehydrated by alkali metals and degassed. ESR measurements were made with a JEOL JES-FE2XG X-band ESR spectrometer at 110K and also with a Bruker ESP 300 spectrometer equipped with an oxford ESR910 temperature controller. Pulsed ESR measurements were made with a Bruker spectrometer ESP380E spectrometer equipped with a dielectric resonator and 1kW traveling wave tube amplifier for microwave excitation. The ESTN experiments were performed by a three pulse sequence, which consists of a nutation pulse (for microwave excitation) and a pair of $\pi/2$-π pulses (for detection).[14-18] We adopted a 4-step phase cycling, monitoring a 2-pulse Hahn echo, $S(t_1)$, after the nutation pulse with a different pulse length t_1. Two-dimensional (2D) ESTN spectra were constructed as a function of swept static magnetic field.

Computer simulations[19] of fine-structure spectra were undertaken in order to extract spin Hamiltonian parameters and to decompose the mixed spin state ESR spectra. The simulation used was based on the second-order perturbation theory because the observed D value was much smaller than microwave energy.

RESULTS AND DISCUSSION

Intermolecular ferromagnetic interaction of monoanions via alkali metal cations occurred in MTHF. By reduction of diketone **1** with alkali metal, an ion-pair $\mathbf{1}^{\bullet-}$ K^+ and biradicalar spin-triplet clusters were formed. The spin triplet cluster was metal-bridged monoanionic diketone radicals because the fine-structure parameter depended on the temperature and radius of counter cationic metal. Monoanionic molecular assemblages from **2**,**3**, and **4** also formed spin-triplet clusters. Table I are summarized the observed fine-structure parameters of these triplet species. The triplet state with such small *D* values originates in intermolecular spin coupling between monoanion molecules via positive ions.

TABLE I Fine-structure parameters of the intermolecular triplet clusters formed via alkaline metal ion bridges.

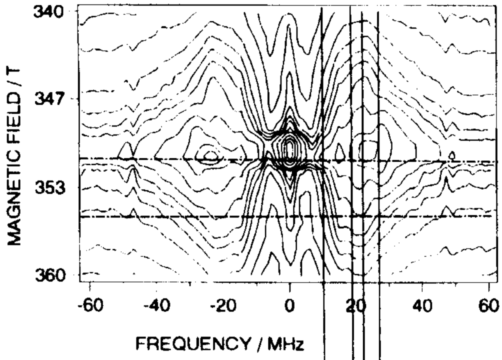
	$1^{\bullet-}M_21^{\bullet-}$	$2^{\bullet-}M_22^{\bullet-}$	$3^{\bullet-}M_23^{\bullet-}$	$4^{\bullet-}M_24^{\bullet-}$
$D/10^4 cm^{-1}$	50,108(Na)			98(Na)
		105(K)	68(K)	
				122(Na-K)
$E/10^4 cm^{-1}$	0,0			2
		0	0	
				0
Temp(K)	110	110	110	5

Chemical reduction of **1** with K yielded the complicated fine-structure ESR spectrum, as shown in Fig. 2(a), suggesting that the high-spin species exist in the sample. But determination of quantum numbers S's from the observed spectrum was not straightforward because it was a superposed spectrum of various high-spin species.

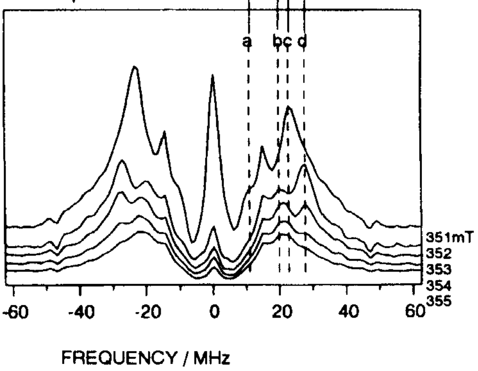
FIGURE 2 (a) Observed ESR spectrum of $1^{n\cdot}K^{+}_{n+m}1^{m\cdot}$.
(b) Simulated ESR spectrum based on 2D-ESTN spectroscopy.

In order to determine the spin quantum number S of the observed high-spin species, 2D-ESTN measurements were made at 4.2K. The spin quantum number S was determined clearly by 2D-ESTN spectroscopy as shown below. It is a useful method to investigate spin mixtures containing various high-spin species in the sample.

(a) Contour Plot



(b) Slice ESTN Spectra



FIFURE 3 (a) Contour plot of the field-swept 2D-ESTN spectra of $1^{n-}K_{n+m}1^{m-}$ (b) Slice spectra of the field-swept 2D-ESTM spectra from 351 to 355mT.

Fig. 3 shows a contour plot of the 2D-ESTN spectra and slice ESTN spectra observed from $1^{n-}K_{m+n}1^{m-}$. In the extremely weakly limit of the microwave irradiation field ($H_1 << H_D$), the nutation frequency is expressed as

$$\omega_n = \omega_1 \sqrt{S(S+1) - M_S(M_S - 1)} \tag{1}$$

for an $|S, M_S\rangle \leftrightarrow |S, M_S - 1\rangle$ ESR allowed transition, where H_1 and H_D stand for the microwave irradiation Hamiltonian and fine-structure term, respectively. The nutation frequency depended on S and M_s as well as ω_1 ($\omega_1 = \gamma B_1$: B_1=microwave magnetic field). Table II gives the observed reduced nutation frequencies ω_n/ω_1 compared with the calculated value by Eq. (1). The sample contained the species with spin quintet and quartet states.

TABLE II Observed nutation frequency ratios ω_n/ω_1 compared with the calculated ones for $1^{n\cdot}K_{n+m}1^{m\cdot}$.

	S	$M_S \rightarrow M_S'$	ω_n/ω_1 (Observed)	ω_n/ω_1 (Calculated)
a	1/2		1	1
b	3/2	$\pm 3/2 \rightarrow \pm 1/2$	1.80	$\sqrt{3}$
c	2	$\pm 2 \rightarrow \pm 1$	2.06	2
	3/2	$1/2 \rightarrow -1/2$		
d	2	$\pm 1 \rightarrow 0$	2.51	$\sqrt{6}$

The observed cw-ESR spectrum was a superposition of the spin quintet, quartet, triplet, and doublet ESR spectra. The cw-ESR spectrum was decomposed into randomly oriented ESR spectra from various spin states by spectral simulation. The superposition of the simulated spectra reproduced the observed ESR spectra satisfactory (Fig. 2(b)). The spin Hamiltonian parameters for the quintet, quartet and two triplet species were estimated to be S=2, g=2.001, D=0.00585cm^{-1}, E=0cm^{-1} ; S=3/2, g=2.001, D=0.0066cm^{-1}, E=0cm^{-1} ; S=1, g=2.001, D=0.0115cm^{-1}, E=0cm^{-1} and S=1, g=2.001, D=0.0090cm^{-1}, E=0cm^{-1}, respectively. The relative weight of quintet, quartet, two triplet and doublet states in the superposed spectra were 1: 3.1: 0.25: 0.21: 7, corresponding to the concentration ratio of various spin species.

Fig. 4 shows the temperature dependence of the intensity of the forbidden ESR signal of the intermolecular triplet $\mathbf{1}^{\bullet-}\mathrm{K}_2^+\mathbf{1}^{\bullet-}$. The horizontal axis is the inverse of the temperature. The analysis of the temperature dependence was made under the assumption of the singlet-triplet model. Under the high temperature approximation, $kT >> h\nu \approx 0.3\ \mathrm{cm}^{-1}$, the signal intensity is expressed by the following equation

$$I(T) \propto \frac{1}{3+\exp(-\Delta E/kT)}\frac{1}{T}, \qquad (2)$$

where I is the signal intensity and ΔE is the singlet-triplet energy gap. The solid line in the Fig. 4 is the theoretical curve for the ground-state triplet with $\Delta E = 1000\mathrm{K}$. It was concluded that the observed triplet state is a ground state. It suggests that intermolecular quintet and quartet species are in a ground state. The experimental results showed that the intensities of the ESR signal of the quintet and quartet species decreased as temperature increased.

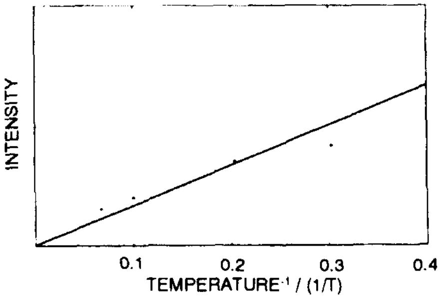


FIGURE 4 Temperature dependence of the ESR signal intensity of the forbidden transition of the intermolecular triplet $\mathbf{1}^{\bullet-}\mathrm{K}_2^+\mathbf{1}^{\bullet-}$.

Chemical reduction of **2**,**3**, and **4** with K, also yielded cw-ESR spectra o various high-spin species. The spectra were reproduced the superposition o quintet, quartet, triplet, and doublet spectra by spectral simulation. The fine-structure parameters dirceved from the simulation are summarized in Table III. Table IV gives the relative contributing weight of various spin states spectra. These quintet, quartet, and triplet species are the metal-bridged high-spin clusters; the quintet species is composed of a pair of triplet dianions and the quartet species is composed of a pair of the triplet dianion and doublet monoanion. The formation of the triplet dianion agrees with a theoretical interpretation of the observed fine-structure constants for the high spin clusters in terms of rather large D values of intramolecular triplet dianions. The triplet dianions derived from **1**,**2**,**3**, and **4** formed the alkali metal-bridged dimer with four pseudo-degenerate frontier orbitals which are capable of accommodating four parallel electrons in the ground state.

TABLE III Spin Hamiltonian parameters derived from the spectral simulation for polyanionic species of **1-4**.

	S	g	D /10^{-4}cm^{-1}	E /10^{-4}cm^{-1}
$\mathbf{1}^{n-}K_m\mathbf{1}^{l-}$	2	2.001	58.5	0
	3/2	2.001	66	0
	1	2.001	90	0
	1	2.001	115	0
$\mathbf{2}^{n-}K_m\mathbf{2}^{l-}$	2	2.005	52.6	6
	3/2	2.005	54.5	0
	1	2.005	65	0
$\mathbf{3}^{n-}K_m\mathbf{3}^{l-}$	2	2.000	75	16
	3/2	2.000	68	0
	1	2.000	98	0
$\mathbf{4}^{n-}K_m\mathbf{4}^{l-}$	2	2.005	57	14
	3/2	2.005	55	0
	1	2.005	89	0
	1	2.005	35	0

The D values of the quintet states are similar to these of the quartet states. This finding explained in terms of a coupled spin Hamiltonian approach. The D value of the triplet dianion molecule is estimated by using the coupled spin Hamiltonian approach; $D_{S=1}$= 0.0378cm^{-1}, which is comparable with the D value of a triplet dianion derived from tribenzoylbenzene, D=0.0310cm^{-1}.[20] More detailed analyses of the estimation of the D values for high-spin clusters will be published elsewhere.

TABLE IV Relative weights of various spin-state spectra contributing superposed spectra.

S	$1^{n-}K_{n+m}1^{m-}$	$2^{n-}K_{n+m}2^{m-}$	$3^{n-}K_{n+m}3^{m-}$	$4^{n-}K_{n+m}4^{m-}$
2	1	1	1	1
3/2	3.1	2	1.4	4
1	0.25	0.12	0.6	2
1	0.21			25
1/2	7	50	3	50

CONCLUSION

It is concluded that the use of pseudo-degenerate LUMOs is workable for generating polyanionic high-spin organic molecules and high-spin clusters. The formation of the pseudo-degenerate LUMOs near zero energy in unit of β arises from the topology of π-electron network and heteroatomic perturbation, which modulates molecular orbitals in terms of change in the coulomb integral and the resonance integral. Excess electrons occupy the pseudo-degenerate LUMOs in such a manner that dynamic π-spin polarization is additive, leading to high-spin ground states.

It is demonstrated that 2D-ESTN spectroscopy is useful to discriminate between high-spins in spin mixtures.

Acknowledgments

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