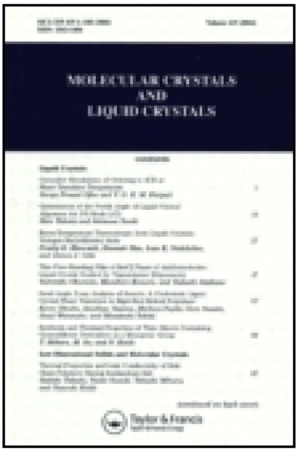

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New Aspects of High-Spin Chemistry

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NEW ASPECTS OF HIGH-SPIN CHEMISTRY

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Abstract As a novel high-spin molecule, a through-bond spin-frustrated organic molecule 4,4',4"-trisdiphenylmethyleneamine (TDMA) and its anion and cation was studied by cw-ESR spectroscopy. TDMA is a spin frustrated system composed of three S=1 units coupled antiferromagnetically. This molecule was shown to have a triplet ground-state which is asymmetrical in its exchange interaction as well as its molecular conformation. The TDMA ions were generated at low temperature via successive radiolysis and photolysis of its diazo precursor. It was shown that the ground states of the anion and cation are quartet and sextet, respectively. This means that upon ionization the ground state changed from the intermediate-spin state of TDMA to the high-spin state of the ions, showing the interrelation between spin alignment and excess charge in a molecular field. On the other hand, in order to identify and discriminate the spin multiplicities of complicated spin assemblages in amorphous materials, we have developed electron spin transient nutation spectroscopy based on FT pulsed ESR and applied it to a pseudo one-dimensional high-spin polymer with effective spin $S \geq 2$.

INTRODUCTION

High-spin chemistry has played an important role in the development of the research field of the molecular-based magnetism. In particular, organic high-spin molecules have conveyed new conceptual advances in chemistry, physics and related fields because they have provide topologically controllable orbital degeneracy which is essential for intramolecular through-bond spin alignment. These topological properties are inherent in spin alignment and spin ordering in organic molecules and magnetic polymers. As one of the new aspects of high-spin chemistry we have been pursuing, we describe in this paper the first example of spin frustration in a high-spin molecule which arises as the result of a particular topological spin arrangement. It is shown that frustration favors an asymmetric spin alignment in the molecule rather than a symmetric one. In addition. introduction of an excess electron or a hole dramatically changes spin alignment in the case of this frustrated molecule.

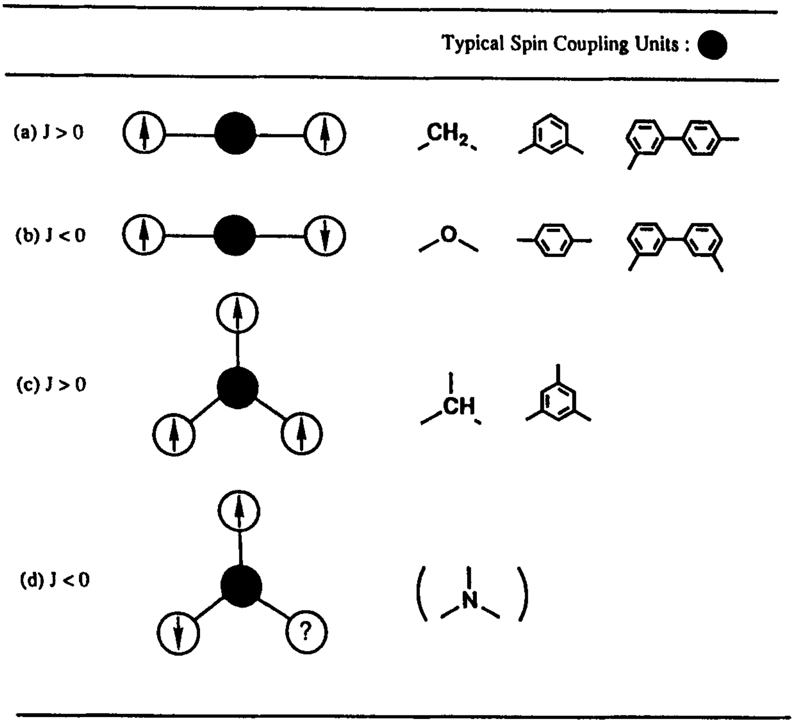
Another aspect concerns a technical methodology of FT pulsed ESR for the study of organic magnetism. We have developed electron spin transient nutation spectroscopy and have shown for the first time its inherent potentiality for the identification and discrimination of molecular spin multiplicities of complicated spin assemblages in amorphous materials. This spectroscopy was applied to a quasi one-dimensional organic high-spin polymer, which was found to possess effective molecular high-spins with the spin $S \geq 2$.

SPIN FRUSTRATED HIGH-SPIN MOLECULES

High-spin molecules are ideal models for studying the spin alignment in magnetic polymers where the through-bond mechanism plays a dominant role. For analyzing the spin alignment in such a model compound with more than one spins, it is convenient to regard the compound as composed of moieties functioning as spin units and of those functioning as spin coupling units or spin couplers. Spin coupling units are either ferromagnetic ($J > 0$) or antiferromagnetic ($J < 0$) depending on their electronic structures. Thus if two spins interact with each other, the resulting state is either a high-spin state (a) or a low-spin state (b), respectively, as schematically shown in Table I.

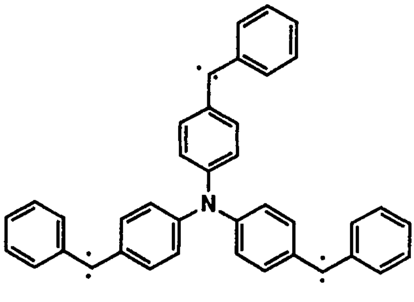
On the other hand, if three spins are connected by a bridge which ferromagnetically couples each pairs of the spins, we expect unequivocally a high-spin state. However, if the coupling is antiferromagnetic, we cannot describe the resulting spin state by a single electron configuration in which all the spin couplings are antiferromagnetic. The interaction in the spin system of this sort is called "spin frustration" [1] where the spin system is characterized by the existence of

TABLE I Various types of spin coupling units.



competing interactions. The spin Hamiltonian of such a system can be described by $H = -2 \sum_{ij} J_{ij} S_i S_j$ where $J_{ij} < 0$ and ij runs over only the nearest neighbors. Spin frustration is conceptually important for the study of random magnetic materials such as spin glasses as well as molecules and is the focus of contemporary topics in magnetism.

This part deals with the first example of a through-bond spin frustration in an organic high-spin molecule, 4,4',4"-trisdiphenylmethyleneamine, which is abbreviated as TDMA.



TDMA

The three spin units in this molecule undergo competing antiferromagnetic interactions intramolecularly via the central nitrogen atom bridge, where the spin units are ground-state triplet diphenylemethylenes. The electronic structure and the underlying mechanism dictating the spin alignment are elucidated.

Topological Spin Control via Through-bond Magnetic Couplings

We briefly summarize in TABLE I the spin coupling units which have been studied so far in our laboratory. If spins are connected via the 1,3- and 1,3,5-linking sites of the benzene ring or the 3,4'-sites of the biphenyl ring, the spins interact ferromagnetically with each other.[2-5] On the other hand, if spins are connected via the 1,4-sites of the benzene ring or the 3,3'-sites of the biphenyl ring, antiferromagnetic interactions take place.[6-8] In these cases, the through-bond spin couplings are controlled by the topology of pi spin networks associated with robust spin polarizations mechanism. Their spin structures have been extensively studied, and methodology for such spin control in organic systems has well been established.[9-14]

In the case of the methylene bridge (CH_2-), [15,16] the two coupled spins interact ferromagnetically with each other, if a hyperconjugation via a pseudo-pi-orbital is effective against the molecular torsion about the C-C bonds. On the other hand, in the case of the ether bridge (-O-),[17,18] the two coupled spins interact antiferromagnetically through a filled pi orbital of the oxygen atom, which is referred to as a superexchange mechanism. This is essentially due to the charge transfer interaction via the oxygen atom in its excited electron configurations. Recently, we have applied the superexchange mechanism to an organic hetero-atomic system, demonstrating an unusually large negative spin polarization in this system which serves as a model for organic ferrimagnets,[18]

In order to design the through-bond spin frustrated system, we have utilized here the superexchange interaction by adopting the trivalent nitrogen atom, which antiferromagnetically couples the three spin units,[19] instead of the divalent oxygen atom mentioned above. Similar systems may be designed using a trivalent phosphorus atom.

ESR Fine Structure of Neutral TDMA

The sample of randomly oriented TDMA was prepared by dissolving its trisdiazo precursor in 2-methyltetrahydrofuran (2MTHF) which was then degassed and frozen. For single crystal work, the trisdiazo precursor was incorporated into a benzophenone-d_{10} single crystal. Mixed single crystals were grown in a diethylether solution by slow cooling. TDMA was generated at liquid helium temperature by the irradiation of the trisdiazo precursor with a SAN-EI UVF-351S 300 W high-pressure mercury lamp. The ESR measurements were carried out on an X-band Bruker ESP300 spectrometer with a TE_{102} cavity.

The randomly oriented sample observed at 2.6 K gave an ESR spectrum characteristic of S = 1. The ga value and the fine structure parameters obtained by means of spectral simulation are $g = 2.003$, $|D| = 0.388$ cm^{-1} and $|E| = 0.019$ cm^{-1}. On the other hand, those of non-interacting triplet diphenylmethylene in a benzophenone single crystal are $D = 0.40505$ cm^{-1} and $E = 0.01918$ cm^{-1}. [20] The signal intensity of the randomly oriented ESR spectrum decreased with increasing temperature, indicating that the observed triplet state is the ground state.

The non-zero E value mean that this molecule does not take a conformation with C_3 symmetry but a distorted one. This asymmetric conformation suggests that the three exchange interactions are also asymmetric.

Single crystal ESR spectra were measured at 2.0 K. When the magnetic field was applied parallel to the crystallographic a axis of the benzophenone-d_{10} crystal ($P2_12_12_1$ space group), only one set of the fine structure characteristic of the triplet state was observed in addition to the forbidden transition at a half field. This strongly indicates that a single magnetic species of TDMA was generated by the photolysis of the three diazo groups, and that the possibility of partial photolysis is excluded.

Since no other signals were detected on raising the sample temperature from 2.0 K to 70.0 K, other magnetic excited states must be located at least 300 cm^{-1} above the triplet ground state. The analysis of the fine structure of the single crystal spectra is currently under way.

Effective Spin Hamiltonian

The effective Heisenberg spin Hamiltonian for the present system of the three spin units is given by

$$H = -2(J_{12}S_1 \cdot S_2 + J_{23}S_2 \cdot S_3 + J_{31}S_3 \cdot S_1). \tag{1}$$

We first assume as a simple treatment $J_{12} = J_{23} = J_{31}/\alpha = J$, where α is a parameter which expresses the asymmetry of the magnetic interaction in the system. If $\alpha = 1$, the interaction is isotropic. The energy of the spin state derived from Equation (1), is written as

$$\begin{aligned} E(S,S',S_1,S_2,S_3) = &- J[S(S+1) + (\alpha - 1)S'(S'+1) \\ &- \{S_1(S_1+1) + S_3(S_3+1)\} - S_2(S_2+1)], \end{aligned} \tag{2}$$

where $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3$ and $\mathbf{S}' = \mathbf{S}_3 + \mathbf{S}_1$. In the case of the present system of the three triplet spins ($S_1 = S_2 = S_3 = 1$), we obtain

$$E(S,S',1,1,1) = -J\{S(S+1) + (\alpha - 1)S'(S'+1) - 4\alpha - 2\}. \tag{3}$$

Figure 1 shows the energy diagram for $J < 0$ described by Equation (3). The triplet state is an intermediate-spin state. The diagram indicates that the ground state is singlet for $0.5 < \alpha < 2$, whereas triplet for $\alpha < 0.5$ or $\alpha > 2$. In order to reproduce the present experimental result, i.e., the ground state triplet, the latter should apply to our spin system. This means that the system undergoes an asymmetric exchange interaction.

As an advanced treatment for the asymmetric exchange interactions, we introduce an additional measure of the asymmetry by describ-

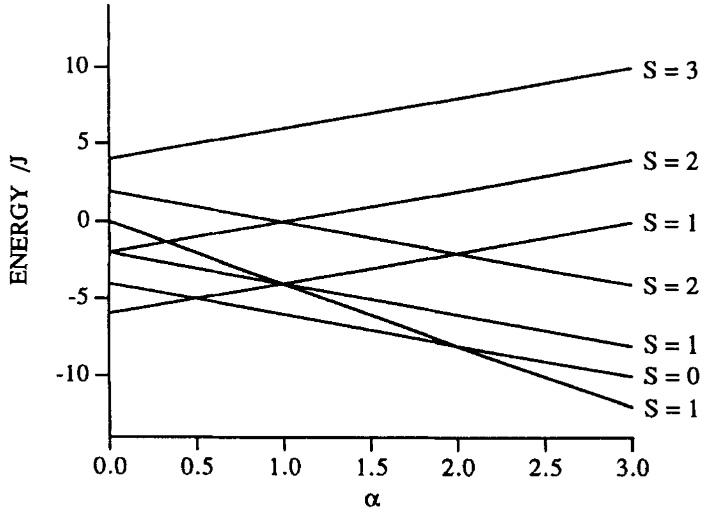


FIGURE 1 Energy diagram of the spin states obtained by the effective spin Hamiltonian (1).

ing the spin Hamiltonian as

$$H = -2J(S_1.S_2 + \alpha S_2.S_3 + \beta S_3.S_1). \tag{4}$$

where α and β are the asymmetry parameters of the exchange interactions. Numerical calculation gave a two-dimensional map of the energy surfaces of the lowest singlet and triplet states. Although we do not describe the results here, the tendency is similar to that of the one-dimensional case shown in Figure 1, viz, in the region where both of α and β nearly equal to unity, the singlet state is lower than the triplet state against the experimental result.

Above qualitative arguments based on these Heisenberg model Hamiltonians strongly suggest that the spin frustration favors the asymmetric exchange interaction in the triplet ground state in order to stabilized the spin system. This conclusion is consistent with the observed non-zero E value described in the preceding section.

Spin Alignment in neutral TDMA

The simple molecular orbital theory at Hückel level still serves as an excellent tool for understanding the role of topology in spin alignment in spite of its simplicity. The energy diagram is shown in Figure 2 where for simplicity the three terminal phenyl groups were replaced with hydrogen atoms and the empirical parameters used are $\alpha_N = \alpha_C + 1.5\beta$, and $\beta_{CN} = 0.8\beta$.[22] HOMO's of the pi system are doubly degenerate NBMO's which are occupied by three pi electrons, whereas the nonbonding orbitals (n), which lie in the molecular plane (σ) and are localized on each of the divalent carbon atoms, are triply degenerate and singly occupied.

Therefore, there are two types of magnetic spins in this system, i.e., three delocalized pi spins and three localized "n" spins. This leaves one unpaired spin in the pi system. Then the other unpaired spin of the triplet ground state must be in the n system. As a result, two of the three localized n spins are to be paired, leaving one unpaired n spin which is parallel to the unpaired pi spin in the triplet ground state. It is evident from Figure 2 that the triplet state is the intermediate-spin state between the singlet and quintet states.

The exchange interaction between the n and pi electrons on the divalent carbon atom is expected to be ferromagnetic because of the one center exchange interaction, and, therefore, the n and pi spins should

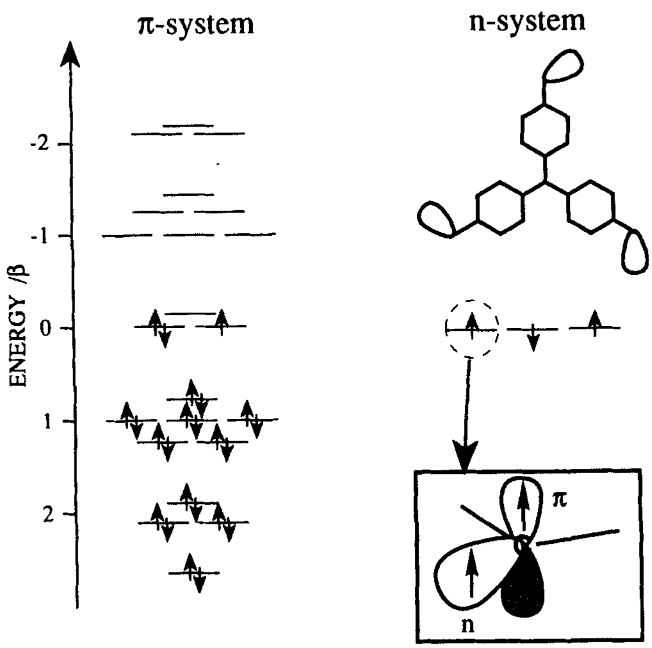


FIGURE 2 Energy diagram of TDMA where the terminal phenyl groups are replaced with hydrogen atoms for simplicity.

be parallel on the divalent carbon atom. The situation above uniquely determines the principal spin alignment in this frustrated system: the unpaired pi spin is distributed over the molecule and its largest spin density appears on the three divalent carbon atoms in such a way as up, up, and down, while the localized n spin on each divalent carbon atom is parallel to the pi spin on it.

This picture is consistent with the experimental fact that the fine structure parameters D and E of this frustrated system TDMA are not much different from those of non-interacting diphenylmethylene (DPM). The D and E values of the TDMA are essentially determined by the one center n-pi spin-spin interaction on the divalent carbon atoms.[21] Since the superexchange interaction through the nitrogen atom bridge is the secondary effect via the excited state, the spin density on the bridge is small. As a result, the spin distribution within each DPM unit of TDMA may not be much affected by the spin coupling unit. Therefore, this spin frustrated system may be regarded as three weakly interacting DPM via the trivalent nitrogen atom bridge. Moreover, both TDMA and DPM have the same spin ($S = 1$), so that their spin projection factors are also the same, justifying the experimental fact mentioned above.

This argument also indicates that the spin distribution in the DPM unit of TDMA is nearly the same as that of non-interacting DPM but its sign as a whole is different in such a way that one of the three DPM units has the sign as a whole opposite (negative) to that of the remaining two. In addition, the spin distribution on the bridge is small. This asymmetric spin distribution among the three spin units may be caused by the molecular distortion mentioned in the preceding section. In addition, a large negative spin appears on the divalent carbon atom of that DPM unit which has a negative spin as a whole. This is an another example of an unusually large negative spin desity.[18]

Spin Alignment in ionized TDMA

One of the most interesting aspects of the spin alignment of this frustrated system is whether the spin multiplicity of the ground state changes upon ionization from the intermediate-spin ground state to a high-spin ground state. This problem is associated with the interrelation between spin alignment and excess charge in a molecular field. This is interesting from a more general point of view because this interrelation appears to be of central importance in the area not only of organic magnetism but also of high temperature superconductors in connection with electric conduction through copper oxide planes.[23,24]

We have already explored such novel organic ions using m-phenylenebis(phenylmethylene) as an example which has a high-spin (quintet) ground state.[25-28] In the case of this prototype high-spin molecule where spin units are linked via meta substitution (case (a) in Table I), the parallel spin configuration is very stable owing to the spin polarization mechanism, resulting in the high-spin (quartet) ground state upon ionization to both its anion and cation. However, as summarized in Table I the spin coupling of this molecule (a) and that of the present frustrated molecule (d) are quite different. As a results, an interchange of the ground-state spin multiplicity between low-spin and high-spin may be expected for this frustrated molecule upon ionization.

The ionization was carried out by means of gamma-ray radiolysis of a solute in a frozen solution as in the previous experiments.[25-28] It has been well established that if we choose 2-methyltetrahydrofuran

(2-MTHF) or butyl chloride (BuCl) as a solvent, the anion or the cation of the solute is generated, respectively. In either case, an excess electron or a hole is generated by ionization of the matrix solvent. As in the previous experiments, we first ionized the diazo precursor of TDMA to yield its radical ion (S = 1/2). Upon photobleaching this ion, we finally obtained either type of ions depending on the choice of the solvent.

We first describe the case of the TDMA anion. Gamma-ray irradiation of the frozen 2-MTHF solution at 77 K yielded the radical ion of the solvent in addition to that of the diazo precursor. The former gave strong narrow ESR spectrum around g = 2.00 which prevented from the observation of the latter spectrum. However, upon irradiation of this sample with a λ >620 nm light at 77 K, the narrow ESR spectrum in the range of 0.32-0.34 T dramatically changed into the one spreading over the wide range of 0-0.6 T as shown in Figure 3a. The signals denoted by T were identified as due to the triplet state of neutral TDMA. The other new signals were ascribed to the TDMA anion.

This assignment has been confirmed by spectral simulation shown

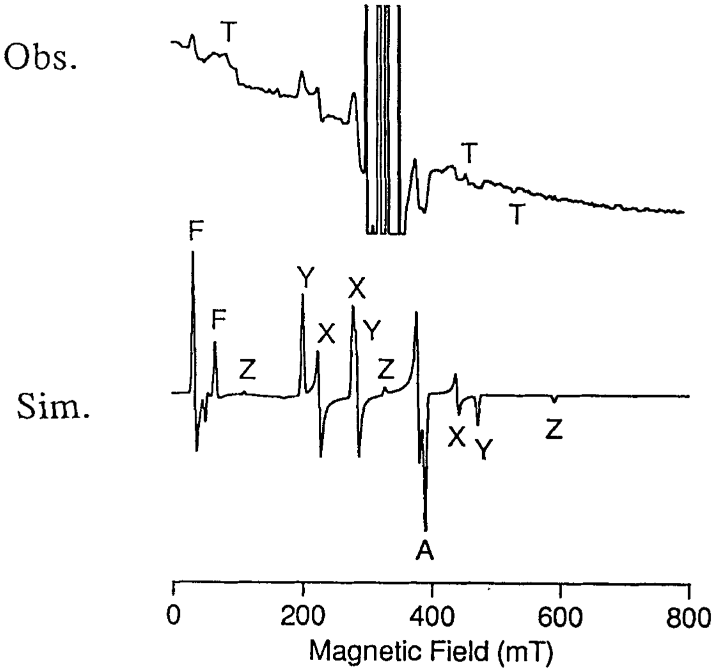


FIGURE 3 ESR spectra observed (a) and simulated (b) for the quartet state of the TDMA anion.

in Figure 3b where S = 3/2, D = 0.123 cm^{-1}, and E = 0.005 cm^{-1} are the best fit parameters. The peaks at the stationary fields corresponding to the principal axes of the fine structure tensor are denoted by X, Y, and Z. The stationary fields due to the forbidden transitions marked by F and the off-axis extra line marked by A are also shown. The excellent agreement between the simulated and observed spectra clearly proves that the TDMA anion is in the quartet state, which was determined to be the ground state by the measurement of the temperature dependence of its signal intensity.

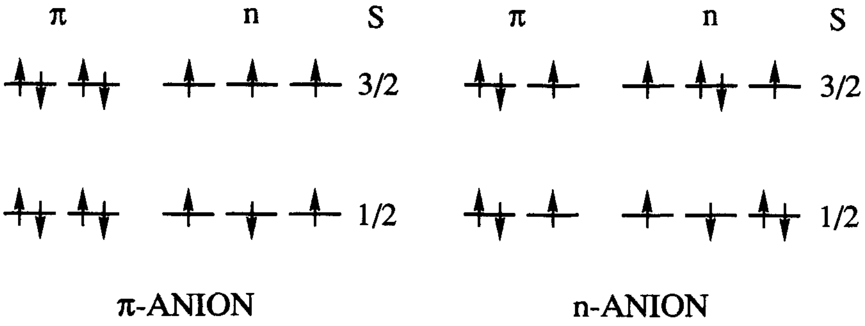


FIGURE 4 Possible spin configurations for the anion.

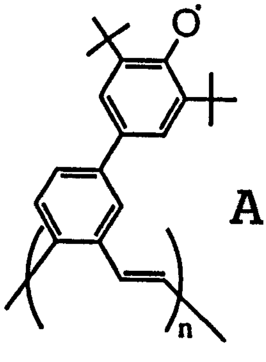
The spin configuration of the quartet ground state of the anion may be understood on the basis of the energy diagram for the neutral parent molecule presented in Figure 2. There are five key orbitals, i.e., two NBMO's and three n orbitals. Addition of an excess electron to the pi NBMO's or the n orbitals yields a pi-anion or an n-anion, respectively. Their possible spin configurations are depicted in Figure 3, the spin being either 3/2 (high-spin) or 1/2 (low spin). According to the present experiment, the high-spin state either of the pi-anion or of the n-anion is the ground state. However, the pi-anion is unlikely, since there is no spin left in the pi system so that the spin-spin interaction is essentially of the n-n type[29] among the localized n spins with large distances.[30] In that case, the D value may be more than one order of magnitude smaller than the observed value.[29] Therefore, the formation of the n-anion with the high-spin ground state was concluded.

In the case of the TDMA cation, the procedure quite parallel to that of the anion was carried out except that BuCl was employed as a solvent instead of 2-MTHF. Photobleaching of the radical cation of the diazo precursor also gave the ESR spectrum widely spreading over the range of 0-0.6 T. Simulation of this spectrum indicated the sextet (S = 5/2) ground state with the parameters g = 2.003, $|D| = 0.072\ \mathrm{cm}^{-1}$, and $|E| = 0.002\ \mathrm{cm}^{-1}$. For the cation spectrum, however, its signal to noise ratio was not sufficient enough to draw their final values. Hence improvement of the quality of the spectrum is currently going on. The sextet is the highest spin multiplicity expected for the pi-cation in which the five parallel spins singly occupy the five key orbitals depicted in Figure 4 as a results of the removal of one pi spin from the filled NBMO of the parent TDMA molecule.

In conclusion, in the case of the present frustrated molecule, the spin alignment changes from the low-spin to the high-spin ground state by the addition of an excess electron or a hole, in contrast to the case of m-phenylenebis(phenylmethylene) previously studied.

SPIN IDENTIFICATION BY ELECTRON SPIN NUTATION SPECTROSCOPY

In order to characterize magnetic properties of complex systems such as organic high-spin polymers or exchange-coupled spin clusters, we have developed electron spin transient nutation spectroscopy based on FT pulsed ESR techniques. The nutation method has been for the first time exploited for the identification of effective molecular spin multiplicities of a quasi one-dimensional organic high-spin polymer A.[31]



A

This study showed that the molecular high spins with the spin quantum number $S \geq 1$ featured in the nutation spectra of the polymer A in the solid state. It was concluded that the polymer was characterized as the mixture of molecular high-spin assemblages, supporting that the results from the static susceptibility measurements of polymer A suggested the existence of high-spin assemblages with an average spin $S \geq 1$.

Methodology of quantum spin transient nutation has been developed in NMR/NQR spectroscopy in order to measure the spin Hamiltonian in terms of the rotating frame. It was not until recently that the nutation method was introduced as pulsed ESR spectroscopic techniques.[32,33] Isoya et al. have determined the effective spin quantum number S of the nickel impurity in synthetic diamond to be S=3/2 by the nutation technique. This assignment was capable because of the non-vanishing fine-structure constants due to a distortion of the impurity site from tetrahedral symmetry.[32] Astashkin and Schweiger have demonstrated that electron spin transient nutation method facilitates the ESR transition assignment of complex spectra of transition metal ions in single crystals.[33]

With increasing effective molecular spin quantum number S and molecular size of pi-conjugated high-spin or magnetic polymers, cw ESR spectroscopy manifests its inherent disadvantages in discriminating high spin from S=1/2 in the mixture of various spin assemblages. The purpose of this section is to demonstrate the inherent potentiality of FT pulsed ESR spectroscopy to identify molecular spin multiplicities of a complicated spin assemblages in amorphous materials. Detailed description and fundamental bases for electron spin transient nutation spectroscopy will be given elsewhere.[34]

Nutation Spectrum of Single and Multiple Quantum Transitions: Nutation Frequency in the Extreme Limit $H_D \gg H_1$

The effect of a coherent microwave field $\mathbf{B}_1$ perpendicular to the magnetic field $\mathbf{B}_0$ is given by the Hamiltonian in the rotating frame as

$$H_1 = -\omega_1 S_y[\exp(i\omega t) + \exp(-i\omega t)] \tag{5}$$

with $\omega_1 = -\gamma B_1$.

For a high-spin state with a spin quantum number S, the fine-structure term H_D features in the total spin Hamiltonian, where

$$H_D = \omega_D(S_Z^2 - \mathbf{S}^2/3) + \omega_E(S_X^2 - S_Y^2) \tag{6}$$

in the principal-axis coordinate system of the fine-structure tensor **D**.

For vanishing H_D or $H_D \gg H_1$, the ensemble of high spins precesses at the frequency ω_1 on resonance, where ω_1 is independent of S. For non-vanishing H_D, the nutation (or precession) is modified due to the presence of H_D and is not describable by a single frequency. In the extreme limit of $H_D \gg H_1$, however, the nutation frequency ω_n is simply given by

$$\omega_n = \omega_1[S(S + 1) - M_S M_S']^{1/2} \tag{7}$$

where M_S and M_S' express the electron spin sublevels involved in the ESR transition.[32,33] The rotating frame matrix element corresponding to the transition is given to first order

$$<S,M_S \mid H_{1R} \mid S,M_S'> = -\omega_1[(S + M_S)(S - M_S')]^{1/2} \tag{8}$$

where $M_S'=M_S-1$ for allowed ESR transitions and $H_{1,R} = -\omega_1 S_y$. Thus for $H_D \gg H_1$ the nutation spectrum depends on S and M_S. For integral spins, $S=1,2,3,\ldots$, $\omega_n = \omega_1[S(S+1)]^{1/2}$ for $|S,M_S=1> \longleftrightarrow |S,M_S'=0>$ or $|S,M_S=0> \longleftrightarrow |S,M_S'=-1>$ transition. Therefore, even if the ESR transitions involving $|S, M_S=0>$ level overlap due to the small ω_D values in the cw ESR spectrum, the spin quantum number S can be discriminated in the nutation spectrum. For half-integral spins, $S=3/2$, $5/2$, ..., the fine-structure term in first order $\omega_D(2M_S-1)$ appearing in the transition field is vanishing for the $|S,M_S=1/2> \longleftrightarrow |S,M_S'=-1/32>$ transition The corresponding nutation frequency ω_n is given as $\omega_n = \omega_1(S+1/2)$. Thus the nutation spectra due to $S=1/2$ and other half-integral spins are distinguishable from each other even if the fine-structure splitting does not feature in the cw ESR spectrum.

Nutation frequencies arising from the multiple quantum transition are considerably reduced due to the scaling effect of the effective field which spin ensemble experience in the rotating frame. The scaling effect is a salient feature appearing in the nutation spectrum from high spins. A detailed account of this feature is given elsewhere.[34]

Experimental Method

The nutation experiment can be made in either observing the FID or electron spin echo (or rotary echo) signal $s(t_1,t_2)$ as time-domain spectroscopy (time axis t_2) by incrementing the time interval t_1 of microwave pulse excitation parametrically. The two time variables t_1 and t_2. are independent. $s(t_1,t_2)$ measured as a function of t_1 and t_2 is converted into a 1D or 2D frequency-domain spectrum by Fourier transformation. Our nutation experiment on the polymer A was carried out by the FID-detected method. A current Bruker, Inc. ESP 300E/380 2D FTESR spectrometer equipped with a dielectric cavity of tunable Q_u=100-5000 was used. The microwave pulse was amplified with a 1 KW pulsed traveling wave tube (TWT) amplifier.

The polymer A as a model for quasi 1D organic ferromagnets was elaborately designed based on through-bond approach to high-T_c polymer ferromagnets. The sample preparation of the polymer will be published elsewhere.[31]

Spin Identification of the Quasi 1D Polymer A

Figure 5 shows a cw ESR spectrum of the solid-state polymer A observed at 6.7 K. The ESR line shape was Lorentzian, indicating the exchange-narrowing taking place in the system. Figure 5(a) and (b) show the microwave amplitude dependence of the on-resonance nutation spectra of the polymer A. Figure 7 shows 2D representation of the 1D Fourier-transformed FID signal $s(t_1,t_2)$ as a function of the time-domain nutation defined by the time-axis t_1 segmentation, noting that the FID signal $s(t_1,t_2)$ was Fourier-transformed only along the time-axis t_2 into the frequency-domain power spectra. The FID signal $s(t_1,t_2)$ was obtained with good signal-to-noise ratios by incrementing the interval t_1, as seen in Figure 7. In Figure 6 several prominent nutation-frequency components are seen depending on the microwave amplitude. They were reproducible and were not distinguishable at elevated tempera-

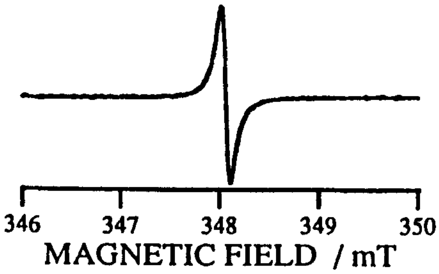


FIGURE 5 A cw ESR spectrum of high-spin polymer A at 6.7 K.

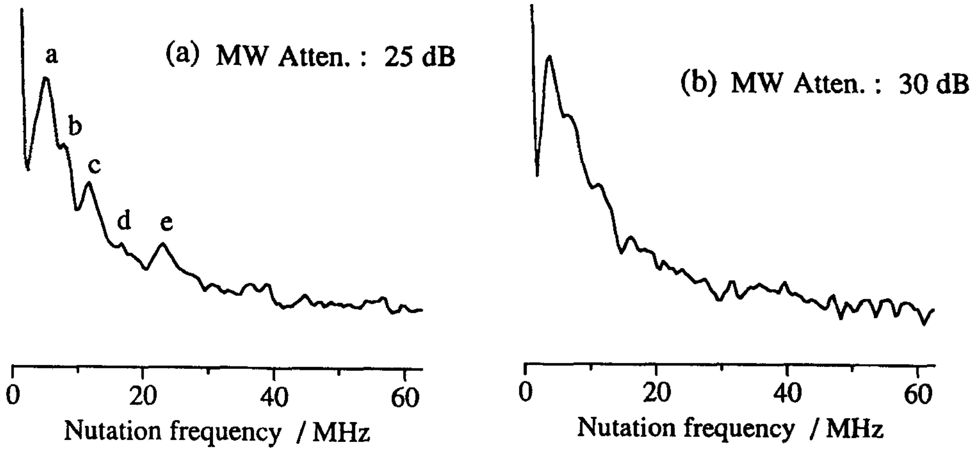


FIGURE 6 Nutation spectra of high-spin polymer A observed at 6.7K. Microwave attenuation: (a) 25 dB, (b) 30 dB.

tures. In the extreme limit of $H_D >> H_1$, the nutation peak at $\omega_n(S_1)$ denoted by a, b, c, d, and e were identified as S=1/2, 1, 2, 3, and 4, respectively ($\omega_n/\omega = 1$, 1.63, 2.37, 3.45, and 4.74 as compared with $[S(S+1)]^{1/2}$= —, 1.41, 2.45, 3.46, and 4.47, respectively). These were evaluated by elaborating the nutation frequency $\omega_n(S=1/2)$ of the reference standard (a DPPH single crystal).

The nutation experiment on the polymer A clearly identified that the polymer in the solid state was the mixture of high-spin assemblages

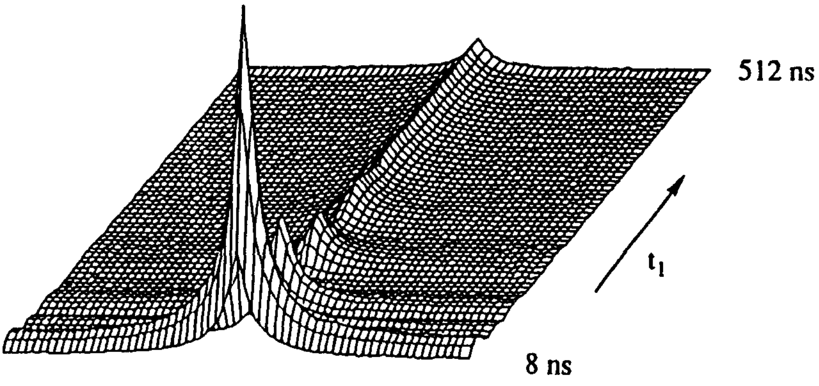


FIGURE 7 A 2D representation of the 1D Fourier FID signal $s(t_1,t_2)$ of polymer A as a function of the time-domain nutation defined by the time-axis t_1.

with various spin quantum numbers S_i's some of which exceed two. This findings supports the experimental result from the magnetization curve fitting for the polymer A: the Brillouin function fitting gave the effective spin S=2. The magnetization curve fitting is insensitive to and ensemble of various spin quantum number S_i's. Particularly, this problematic procedure becomes difficult with increasing number of S_i's expected for extended spin structures of magnetic polymers or spin clusters. The present nutation experiment demonstrates that electron spin transient nutation techniques are more suitable for spectroscopic discrimination of S_i's for high-spin ensembles, noticing that one of the difficulties of the nutation method is time resolution.

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