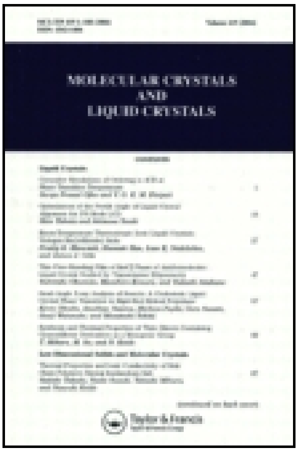

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Spin Alignment and Large Negative Spin Polarization Induced by π-Topology in Organic High-Spin Molecules

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SPIN ALIGNMENT AND LARGE NEGATIVE SPIN POLARIZATION INDUCED BY π-TOPOLOGY IN ORGANIC HIGH-SPIN MOLECULES

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Abstract This paper deals with intramolecular spin alignment in organic high-spin molecules and focus especially on a large negative spin polarization induced by π-topology. Utilizing a topological connectivity of π-electron network, spin inverted moiety with large negative spin densities can be realized in organic high-spin molecules, which are models of polymer-based ferrimagnets. As an example, two different organic high-spin molecules, 3,4'-diphenylmethylenbis(phenylmethylene) and 4-(diphenylmethylene)-4'-(m-phenylenbis(phenylmethylene))-ether, have been investigated. In order to clarify the electronic structure, the spin density distributions have been determined by single-crystal ESR and ENDOR experiments. The analysis of the ^{1}H- and ^{13}C-hyperfine tensors gives a clear evidence of the large negative spin polarization. The spin alignment in these molecules is discussed in terms of the VB picture based on a generalized Hubbard model.

INTRODUCTION

Organic ferro-/ferrimagnetic polymer is a challenging topics in the field of molecular magnetism.[1] For the ferrimagnetic spin ordering in polymers, it should be realized that one molecular spin moiety with spin S_i in the repeating constructing unit is inverted against the other with an inequivalent spin S_j by antiferromagnetic coupling, as illustrated in Figure 1. Such a spin inversion leads to an unusually large negative spin polarization in the spin inverted moiety. In other words, the existence of a large negative spin polarization gives a clear evidence of a ferrimagnetic spin-inversion. Studies of the spin structures of model compounds will clarify a physical insight into the ferrimagnetic spin ordering in polymer-based magnetic materials.

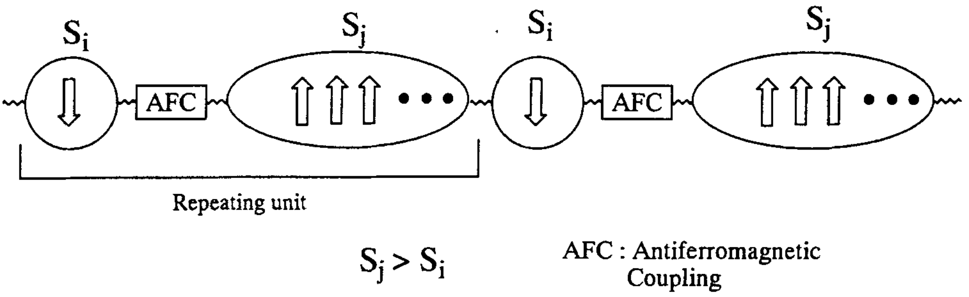


FIGURE 1 Schematic design of polymer-based ferrimagnets

In this paper, we report a single-crystal ESR and ENDOR study of the electronic structures of two different organic high-spin molecules, 3,4-diphenyl-methylenbis(phenylmethylene) (3,4'-DPBPM) **1** and 4-(diphenyl-methylene)-4'-(m-phenylenbis(phenylmethylene))-ether (4T4'Q-ether) **2**. In these two compounds, a large negative spin polarization induced by π-topology is predicted by considerations based on a valence-bond picture discussed later in this paper. The determination of the proton and ^{13}C hyperfine tensors will give clear evidences of such a spin inversion and of the large negative spin densities at the carbene sites in the spin-inverted moiety.

SPIN STATES OF 3,4'-DPBPM and 4T4'Q-ETHER

Molecule **1**, which is a topological isomer of 3,3'-DPBPM with a septet ground state,[2] has a quite different electronic structure from those of 3,3'-DPBPM as well as other organic high-spin molecules so far reported: The number of unpaired electrons in localized σ nonbonding orbitals is not equal to that in delocalized π orbitals (three unpaired σ electrons and one unpaired π electron). The spin states determined by our ESR experiments are shown in Figure 2. Thus, molecule **1** has the triplet ($S=1$) ground state with low-lying excited quintet spin state ($S=2$).[3] The localized σ spin at the carbene site labeled by asterisk is expected to be a down-spin configuration, since the pseudo π-spin density wave (the up-and-down spin network of the π spin) is formed in the delocalized π-orbital network and the localized σ spin become spin parallel to the π spin at each carbene site as a result of the ferromagnetic coupling through the one-center exchange integral. For the other model compound in which the spin inversion is induced by topology, we chose 4T4'Q-ether **2**, which is a model of organic polymer-based ferrimagnets, corresponding one repeating units shown in Figure 1. This molecule has been designed as follows: the triplet (S=1) diphenylmethylene[4] moiety and the quintet (S=2) m-phenylenbis(phenylmethylene)[5] moiety are antiferromagnetically coupled to each other via an ether bridge. Thus, **2** has been composed of two organic hetero-spins ($S_i=1$ and $S_j=2$) by the superexchange interaction via a $p\pi$-orbital on oxygen atom. The spin states determined by our ESR experiment is also shown in Figure 2.[6] The spin inversion is expected for the triplet moiety of **2**, leading to a large negative spin polarization at the carbene site labeled by asterisk. In order to clarify such spin inversion directly, we have synthesized the compounds labeled at the carbene site by ^{13}C isotope with nuclear spin I=1/2. The carbene position is shown by asterisk. The ^{13}C hyperfine tensor gives a direct information of π and σ spin densities at the carbene site. Partially deuterated compounds of **1** and **2** were also synthesized to give the exclusive identification of ^1H-ENDOR signals and to facilitate the correct assignment of the signals.

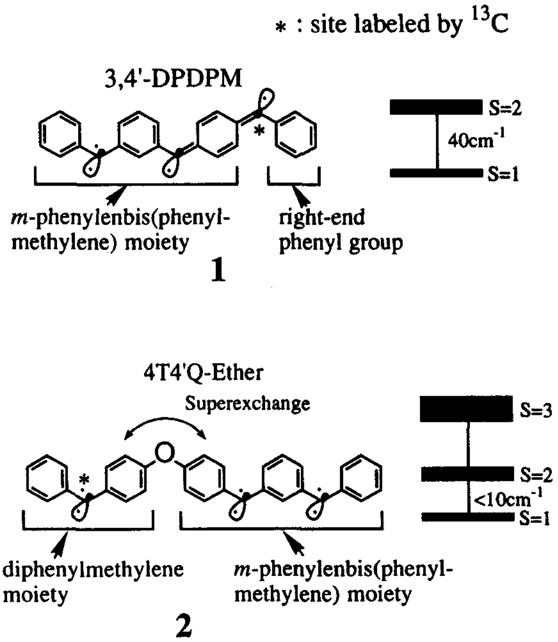


FIGURE 2 Model compounds with large negative spin densities

EXPERIMENTAL

We used mixed single crystals in all the ESR and ENDOR experiments. Each polycarbene was generated at 2 - 4 K by the photolysis of the corresponding diazo precursors incorporated in a host single crystal of benzophenone. We prepared also the partially deuterium labeled compounds, in order to reduce the spectrum density at the ^1H-ENDOR experiments, which makes easy the signal assignment. The EPR and ENDOR spectra were measured on a JES-SK K-band ESR spectrometer, a home-made X-bnd ENDOR spectrometer and a Bruker ESP300/350 ESR/ENDOR spectrometer operating at X-band equipped with an Oxford EPR910 variable temperature controller.

RESULTS AND DISCUSSION

(A) ESR/ENDOR Spectra and Spin Density Distribution of Molecule 1

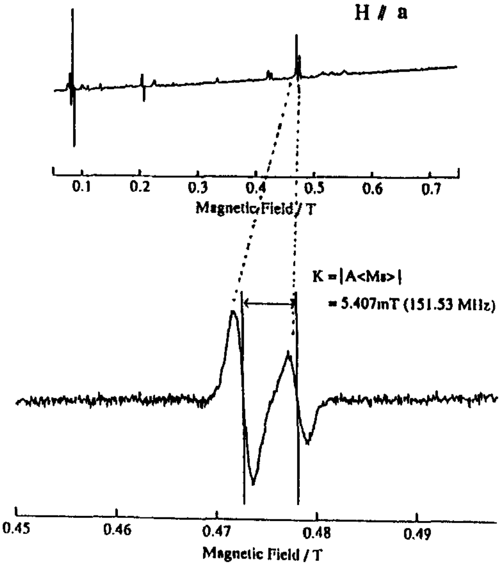


FIGURE 3 Typical ESR spectra of the ^{13}C labeled compound of **1**

Figure 3 shows the typical ESR spectra of the carbon 13 labeled compound of **1** observed at 1.7 K for the magnetic field applied parallel to the *a* axis of a benzophenone single crystal. Immediately after photolysis at 4 K, only the signals (T_+ and T_-) due to triplet ground state were observed. With increasing temperature, the four well-resolved signals (Q_{A+}, Q_{B+}, Q_{B-}, Q_{A-}) characteristic of a quintet state began to appear at ca. 50 K and increasing their intensity (not shown). The energy gap ΔE between the triplet ground state and the quintet low-lying excited state was estimated to be 40 cm^{-1} from the temperature dependence of ESR signal intensity. The spin Hamiltonian parameters were determined to be g= 2.003 (isotropic), D=+0.2336 cm^{-1}, E=-0.0107 cm^{-1} for the triplet ground state and g= 2.003 (isotropic), D=+0.0685 cm^{-1}, E=-0.0024 cm^{-1} for the low-lying quintet excited state.[3]

Figures 4(a) - 4(c) show typical ^1H-ENDOR spectra at 4 K for partially deuterium labeled compounds of **1** shown in the insert, which have been observed by monitoring the ESR transition T_+ (Ms= 0 - 1). The free proton frequency, $\nu_N = g_N\mu_N H/h$, is indicated in Figure 4. Since the ENDOR frequency is given by $\nu_{ENDOR} = |A_{zz}M_S - g_N\mu_N H|/h$ to the first order of the perturbation theory of well-known spin Hamiltonian, the shift from ν_N gives the zz tensor element (A_{zz}) of the ^1H hyperfine coupling constants (hfcc). The signals near ν_N in Figure 4 arise from the electron spin sublevel of

$M_S = 0$, and others from that of $M_S = +1$. Since the nuclear g factor, g_N of proton is positive, the signal appearing at a frequency lower (higher) than ν_N corresponds to a positive (negative) hfcc. Thus, the absolute sign and the magnitude of hfcc's can be determined at each orientation of the external magnetic field on the sample. The angular dependence of the ESR and ENDOR transitions were measured for the rotation of the external magnetic field in the three crystallographic planes, ab, bc, and ca of the single crystal. All the ^{1}H hyperfine tensors were determined from the analysis of the angular dependence. The π spin density on the carbon site adjacent to the hydrogen atom detected by the ENDOR experiment was obtained from the isotropic term A_F of the hfcc with the help of McConnell's equation[7] $A_F=Q\rho^{\pi}/2S$ ($Q= -66.5$ MHz).

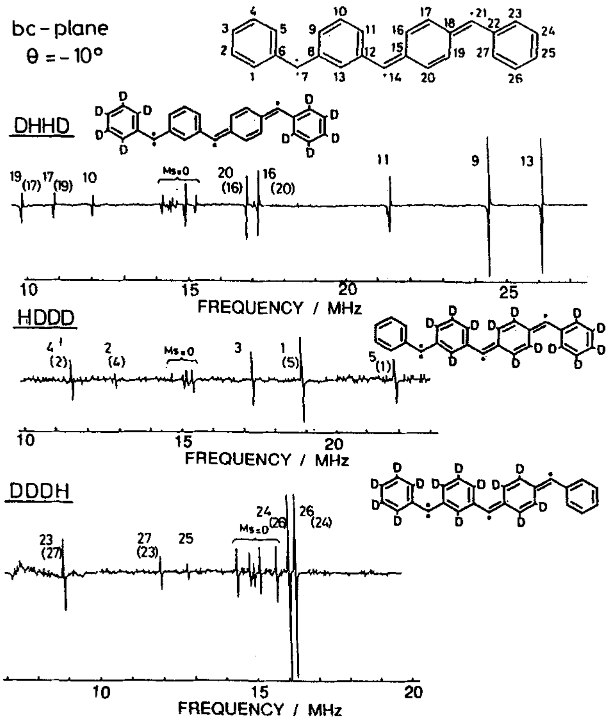


FIGURE 4 Typical 1H-ENDOR spectra of three different partially deuteleum labeled compounds

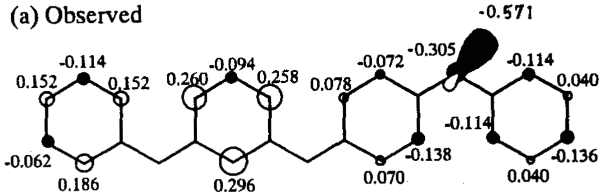
For the experiments using the ^{13}C labeled compound of **1**, each ESR transition splitted into a doublet due to the hfcc of ^{13}C isotope of the carbene site. The anisotropic terms A_{aniso} of the ^{13}C hyperfine tensor gives a direct information both of the π spin density ρ^{π} and the σ spin density ρ^{σ} on the carbene site, according to the following equation.

$$A_{aniso} = 1/(2S)\left[\begin{pmatrix} -B & & \\ & -B & \\ & & 2B \end{pmatrix}\rho^{\sigma} + \begin{pmatrix} -B & & \\ & 2B & \\ & & -B \end{pmatrix}\rho^{\pi}\right] \quad (1),$$

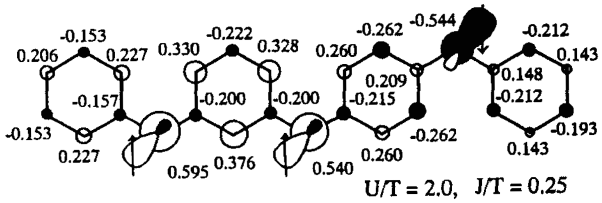
where B= -89.0 MHz.[8] Since, we could not succeed to detect ^{13}C-ENDOR signal, only the magnitude of the ^{13}C hfcc was determined experimentally from the hfcc spltting of the ESR transitions and, therefore, the absolute sign is unknown.

Figure 5(a) depicts the experimentally determined π spin densities on the carbon atoms and π and σ spin densities at the end carbene site labeled by ^{13}C isotope. The π spin densities of the carbon atoms without α-protons and π and σ spin densities of the other carbene sites were not obtained from the present experiments. It should be noted that there are three carbon sites with negative π spin density and two those with positive one in the right end phenyl group of **1**. In addition, their observed negative ones are larger in magnitude than the positive ones, indicating that a large negative spin polarization occurs in the right-end phenyl group. On the other hand, the phenyl groups of the m-phenylenbis-(phenylmethylene) moiety of **1**, the positive π spin densities are larger than the negative ones. These findings show clearly that the spin inversion occurs in the right-end phenyl group. These salient feature of the spin inversion can be well understood as follows, according to the consideration based on the topology in π electron network.

(a) Observed



(b) Hubbard Model Calculation



(c) Physical Picture of the Spin Alignment

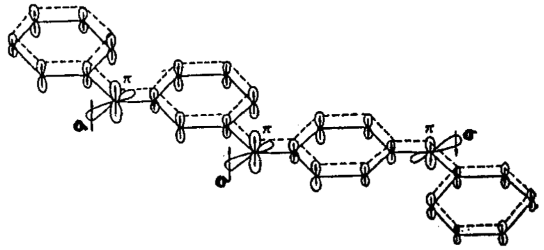


FIGURE 5 π and σ spin density distributions of the triplet ground state of 1

In order to understanding of the spin alignment of **1**, we have carried out semi-empirical UHF calculation using a generalized Hubbard model.[3,9]

$$\mathcal{H} = -T \sum_{m,m',\sigma} a^{\dagger}_{m',\sigma} a_{m,\sigma} + (U/2) \sum_{m,\sigma} n_{m,-\sigma} n_{m,\sigma} - J \sum_{k,m} [S^{z}_{k} S^{z}_{m} + (S^{+}_{k} S^{-}_{m} + S^{-}_{k} S^{+}_{m})] . \qquad (2)$$

The calculated spin densities are shown in Figure 5(b). The one unpaired π electron is distributed over the carbon skelton with alternating the sign of the spin density from carbon to carbon, according to the valence-bond picture of the spin correlation. We terms the topological nature of the π spin-up and spin-down network as a pseudo π spin density wave (pseudo π-SDW). The three σ electrons are exchange-coupled ferromagnetically to the π spins at each divalent carbon atoms. We have shown the physical picture for the spin alignment in Figure 5(c). This spin structure is consistent with the observed spin density distribution in Figure 5(a) and give an explanation for the spin inversion in the right end phenyl group. This means that the spin inversion in the right-end phenyl group is induced by π-topology. Although we could not determine the absolute sign of the π and σ spin densities on the right-end carbene site labeled by ^{13}C, we can safely conclude that the sign should be negative (the opposite sign against those on the other two carbene sites) both from the consideration of the simple valence-bond picture in the spin alignment (the formation of the pseudo π-SDW) and from the result of the theoretical calculation shown in Figure 5(b). The magnitude of both the π and σ spin densities on the right-end carbene site, which has been determined from the ^{13}C-hyperfine tensor by our experiment, is significantly large as shown in Figure 5(a), giving a direct evidence for the existence of large negative densities induced by π-topology.

(B) Spin Density Distribution and Spin Alignment of Molecule 2

The π spin density distribution on the phenyl groups determined by our ^{1}H-ENDOR experiment of **2** have been already published.[10] In this work, we measured the angular dependence of the ^{13}C hyperfinere splitting in the ESR spectra arising from the carbene site of the diphenylmethylene moiety denoted by the asterisk in Figure 2, in order to obtain the information about the π and σ spin densities on the carbene site. We focus our discussion on the spin inversion of the diphenylmethylene moiety. Typical ESR transitions showing ^{13}C-hyperfine splitting clearly is given in Figure 6, in which the external magnetic field has been applied parallel to the direction of 25 degree from the *a* axis in the ab plane. The largest hyperfine splitting in three crystallographic planes, ab, bc, and ca, was ca. 103 MHz, which is about one-half of that of the isolated diphenylmethylene molecule.[5] This results means that the spin densities on the carbene sites of the diphenyl-methylene moiety in molecule **2** meight be also ca. one-half of the isolated diphenylmethylene molecule itself. The detailed analysis and ^{13}C-ENDOR experiment to determine the smaller hyperfine splitting within the ESR line width are in progress. Typical ESR and ^{1}H-ENDOR spectra observed at 2 K are shown in Figure 7. The external magnetic field was applied parallel to the crystallographic *c* axis of the mixed crystal. ENDOR spectra were measured by monitoring T+ (Ms=0 - +1) ESR transition.

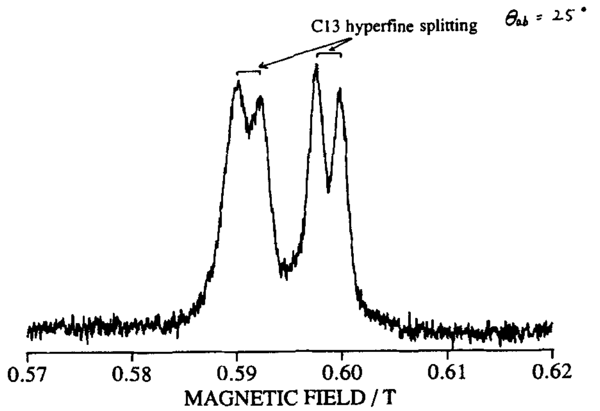
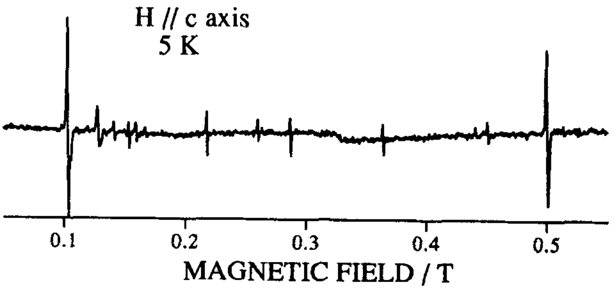


FIGURE 6 Typical ^{13}C hyperfine splitting observed in the ESR spectrum of **2**

Figure 7 shows the spin density distribution of the triplet ground state, which has been already reported in our previous paper.[10] The observed spin density distribution shows that the left-end phenyl group in diphenylmethylene moiety have three carbon sites with negative spin densities larger in magnitude than positive spin densities of the remain two carbon sites. This finding shows clearly that the spin densities in the diphnylmethylene moiety are opposite in sign to the non-interaction diphenylmethylene molecule itself and the unpaired spin in this moiety is inverted against the another moiety, m-phenylen-bis(phenylmethylene) moiety. This spin structure is corresponding to the ferrimgnetic spin ordering

(a) ESR spectrum



(b) ^{1}H-ENDOR spectrum

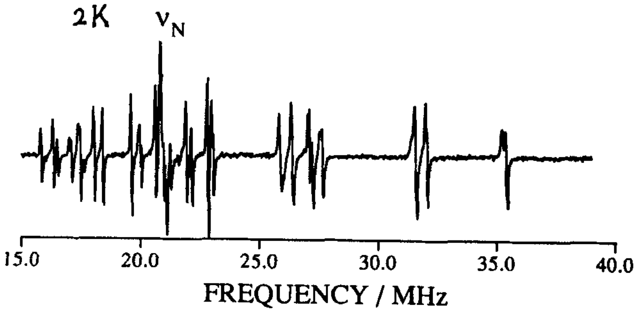
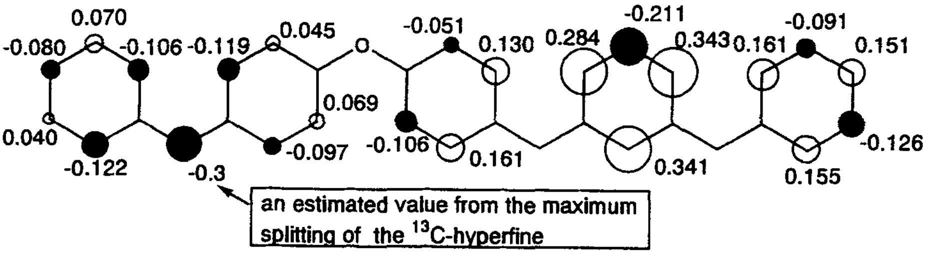


FIGURE 7 Typical ESR and ^{1}H-ENDOR spectra of **2**

shown in Figure 1. In this case, the spin inversion occurs by the antiferromagnetic superexchange interaction through the doubly-occupied pπ orbital on the oxygen atom. Moreover, it should be noted that the σ and π spin densities estimated from the magnitude of the ^{13}C-hyperfine splitting are about one-half of those of the isolated diphenylmethylene molecule. This result agrees well with the theoretical prediction obtained from the quantum mechanical vector addition of the spin angular momentum.[10a] A relationship which relates the spin densities of the whole molecule to those of the isolated non-interacting constituents molecules[10a] can be derived using the Clebsch-Gordan coefficient and a operator technique of the angular momentum. Thus,



an estimated value from the maximum splitting of the ^{13}C-hyperfine

FIGURE 8 Observed π spin density distributions of the triplet ground state of **2**

the quantum mechanical group theoretical calculation predicts following characteristic nature. For the resultant triplet states (|Si - Sj| = 1) in the present hetero-spin system constructed by the interaction of two molecules with spin Sj=1 and spin Sj=2, respectively, the spin density of the interacting quintet moiety, m-phenylene-bis(phenylmethylene) moiety in the present case, is reduced to be 3/4 of that of the non-inteacting constituent molecule and the spin density of the interacting triplet diphenylmethylene moiety reduced to be -1/2 of that of the non-interacting triplet constituent itself. The characteristic signs and magnitudes of the observed spin densities in Figure 8 are well interpreted using the relationship.

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