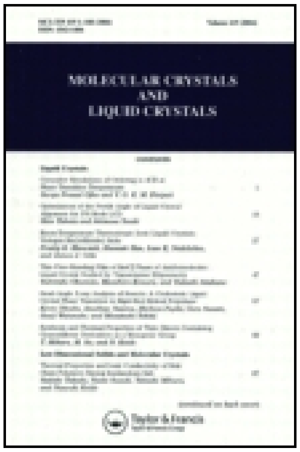

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Direct Evidence of the Spin Contraction in the Limited-Size Ferrimagnetic Organic Spin System: Determination of the Spin Densities at the Divalent Carbon and Theoretical Calculation of the Spin Contraction

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DIRECT EVIDENCE OF THE SPIN CONTRACTION IN THE LIMITED-SIZE FERRIMAGNETIC ORGANIC SPIN SYSTEM: DETERMINATION OF THE SPIN DENSITIES AT THE DIVALENT CARBON AND THEORETICAL CALCULATION OF THE SPIN CONTRACTION

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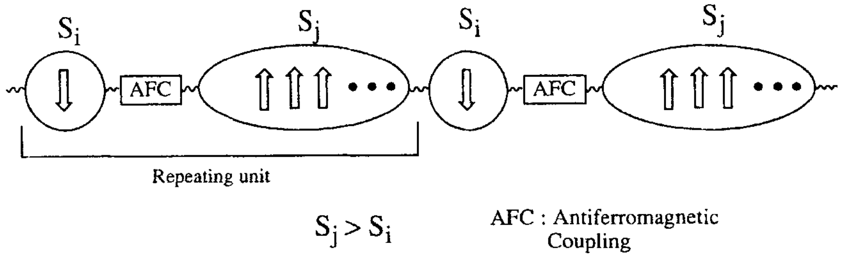
Abstract In order to clarify the quantum spin contraction in the limited-size organic spin systems, we have directly determined the σ and π spin densities on the ^{13}C-isotope labeled divalent carbon site of an organic high-spin molecule, 4-(diphenylmethylene)-4'-[*m*-phenylenebis(phenylmethylene)] ether **1**. **1** is the most simple model compound for topologically controlled ferrimagnetic spin ordering. The magnitude of the spin density on the divalent carbon site in the diphenylmethylene moiety of **1** is almost one-half of that of diphenylmethylene molecule. This finding gives a direct evidence of the spin contraction expected as a quantum effect on the limited-size ferrimagnetic spin system. We have also carried out the theoretical calculation of the spin-densities, spin-energies, and spin functions for the ferrimagnetic spin chain systems ($-S^A-S^B-S^A-S^B- \bullet\bullet\bullet$, $S^A \neq S^B$) with different chain lengths by the exact numerical calculation. With increasing number of the repeating unit $-S^A-S^B-$, the spin contraction has been recovered. The size dependency of the quantum spin contraction is discussed based on the theoretical calculation.

INTRODUCTION

In molecular magnetic systems, we can synthesize and construct the limited-size spin systems. This is one of the advantages in the field of 'molecular magnetism'. The quantum size-effect in such systems is one of the most interesting phenomena from the theoretical and experimental points of view. In the repeating constructing units of the ferrimagnetic molecular systems one molecular spin moiety with spin S_i should be inverted against the other with an inequivalent spin S_j by antiferromagnetic coupling, as illustrated in scheme 1. In the

Scheme 1 Schematic Design of Polymer-Based Ferrimagnet



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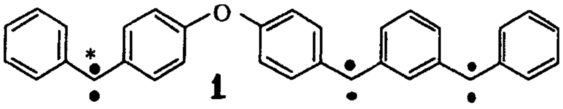
limited-size spin system with the ferrimagnetic spin ordering a contraction of the quantum spins is expected as described later.

In order to obtain the direct evidence of such a spin contraction, we labeled at the divalent carbon site of the diphenylmethylene moiety of 4-(diphenylmethylene)-4'-[*m*-phenylenebis(phenylmethylene)] ether **1** by carbon 13 isotope. Molecule **1** is a typical model compound of the topologically controlled organic polymer-based ferrimagnets in which the triplet (S=1) diphenylmethylene moiety and the quintet (S=2) *m*-phenylenebis(phenylmethylene) moiety are antiferromagnetically coupled with each other via an ether bridge. Thus, **1** is the most simple hetero-spin system (S_i=1 and S_j=2) by the superexchange interaction via the pπ-orbital on the oxygen atom. The ground state was determined to be the triplet (S=1) spin state by our previous ESR experiment.[1] The π spin densities on the phenyl groups were already reported in our previous paper.[2]



1

* : Carbon 13 labeled

In this paper, we report a single-crystal ^{13}C-ENDOR study and the direct determination of the spin densities on the divalent carbon site of the diphenylmethylene moiety. Since **1** is the most shortest ferrimagnetic organic spin system, the spin contraction is clearly expected to appear as a quantum size-effect. The aim of this work is to clarify the spin contraction directly. The theoretical calculations of the spin density and the spin contraction are carried out using the exact numerical calculation based on the Heisenberg model Hamiltonian approach.[3] The size dependency in the magnitude of the quantum spin contraction is also discussed based on the theoretical calculation.

THEORETICAL PREDICTION OF THE SPIN CONTRACTION

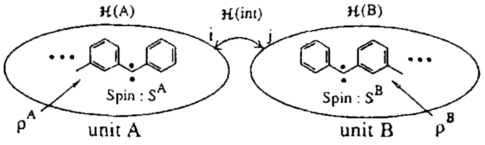
For the weakly-interacting two high-spin moieties shown in Figure 1, the total Hamiltonian of the whole molecule is given by

$$\boldsymbol{H} = \boldsymbol{H}(\mathrm{A}) + \boldsymbol{H}(\mathrm{B}) + \boldsymbol{H}(\mathrm{int}), \qquad \boldsymbol{H}(\mathrm{int}) << \boldsymbol{H}(\mathrm{A}), \boldsymbol{H}(\mathrm{B}), \tag{1}$$

where the first (second) term is the electronic Hamiltonian consisting of both orbital parts and spin parts for the unit *A*(*B*) and the third term is that for interaction. For the two unit spin systems, one of the authors (Y.T.) derived the following analytical relationship of the spin densities.[4, 2a] The spin density ρ_i^A on the carbon site i in the interacting *A* unit of the whole molecule can be expressed in terms of the corresponding spin density $\rho_{i0}{}^{A}$ in the isolated *A* molecule with the spin S^A and of the Clebsch-Gordan coefficient $C(S^A S^B S; m_A\, M\text{-}m_A)$:

$$\rho_i{}^{A}(S, M) = (1/S^A)\, \rho_i{}^{A} \sum_{m_A} m_A\, C(S^A S^B S; m_A\, M\text{-}m_A)^2 \tag{2}$$

where $S = S^A+S^B,\ S^A+S^B-1,\ \ldots\ldots,\ |S^A-S^B|$. The relationships in the most simple two hetero-spin systems with $S^A = 1/2$ and $S^B = 1$ and with $S^A = 1$ and $S^B = 2$ are listed in Table I (a) and I(b), respectively. The latter case corresponds to molecule **1**. This table shows that the magnitude of the spin densities of the unit moiety *A* in **1** is expected to be about one-half of that of triplet diphenylmethylene molecule. In addition, the corresponding spin densities have opposite signs with each other. This spin contraction arises from the restriction that the total spin quantum number *S* should be a good quantum number. Therefore, the spin contraction must be recovered in the large-size spin systems with a lot of degrees of freedoms of spins. Such size dependency of the spin contraction will be discussed later. In order to obtain the direct evidence of the spin contraction in the limited-size ferrimagnetic spin systems, we have determined the σ and π spin densities on the ^{13}C-isotope labeled divalent carbon site of **1** by the ENDOR experiments.



$$\mathcal{H} = \mathcal{H}(A) + \mathcal{H}(B) + \mathcal{H}(\text{int}),$$

$$\mathcal{H}(\text{int}) = -2J_{ij}{}^{\text{eff}} s_i{}^{A} \cdot s_j{}^{B},\quad \mathcal{H}(\text{int}) << \mathcal{H}(A), \mathcal{H}(B)$$

FIGURE 1 Weakly Interacting High-Spin Molecule

TABLE I Relaionships of the Spin Densities in the Weakly Interacting Hetero-Spin System

(a) $S^A = 1/2$, $S^B = 1$

$S = 3/2$

unit A	unit B
ρ_{i0}^{A}	ρ_{i0}^{B}

$S = 1/2$

unit A	unit B
$-\frac{1}{3}\rho_{i0}^{A}$	$\frac{2}{3}\rho_{i0}^{B}$

(b) $S^A = 1$, $S^B = 2$

$S = 3$

unit A	unit B
ρ_{i0}^{A}	ρ_{i0}^{B}

$S = 2$

unit A	unit B
$\frac{1}{3}\rho_{i0}^{A}$	$\frac{5}{6}\rho_{i0}^{B}$

$S = 1$

unit A	unit B
$-\frac{1}{2}\rho_{i0}^{A}$	$\frac{3}{4}\rho_{i0}^{B}$

EXPERIMENTAL

We used mixed single crystals of benzophenone-d_{10} containing the diazo precursor of **1**. The synthetic procedures of the carbon 13 labeled diazo precursor of **1** will be published elsewhere. **1** was generated at 2 K by the photolysis of the corresponding diazo precursor using an XBO 500W high-pressure mercury lamp. All ESR and ENDOR experiments were carried out with a Bruker ESP300/350 spectrometer equipped with an Oxford variable temperature controller ESR 910.

RESULTS AND DISCUSSION

A part of the ESR and ^{1}H-ENDOR studies of molecule **1** was already published in our previous paper.[2] In this paper, we focus the results of ^{13}C-ENDOR work and the direct evidence of the spin contraction as a quantum size-effect.

(a) ^{13}C-ENDOR Spectra of **1**

Figure 2 shows typical ESR and ^{13}C-ENDOR spectra of the triplet ground state of molecule **1** observed at 2 K. The external magnetic field applied parallel to the direction of 10 degree from *a* axis in the *ab* plane. Typical ^{13}C-ENDOR spectra shown in Figure 2(b) have observed by monitoring the ESR transition T_- (Ms = -1 - 0). Since the ENDOR spectra could be obtained for T_- and T_+ transitions only in *ab* and *ca* planes, we determined the off-diagonal element of the hyperfine tensors in *bc* plane from the hyperfine-splitting observed in the ESR spectra. Figure 3 shows the angular dependence of the ^{13}C-ENDOR frequency in the three crystallographic *ab*, *bc*, and *ca* planes (the experimental data in *bc* plane has been estimated from the hyperfine-splitting in the ESR transition and the nuclear Zeemann term). The solid curves are theoretical ones which have been calculated by the exact diagonalization of the following

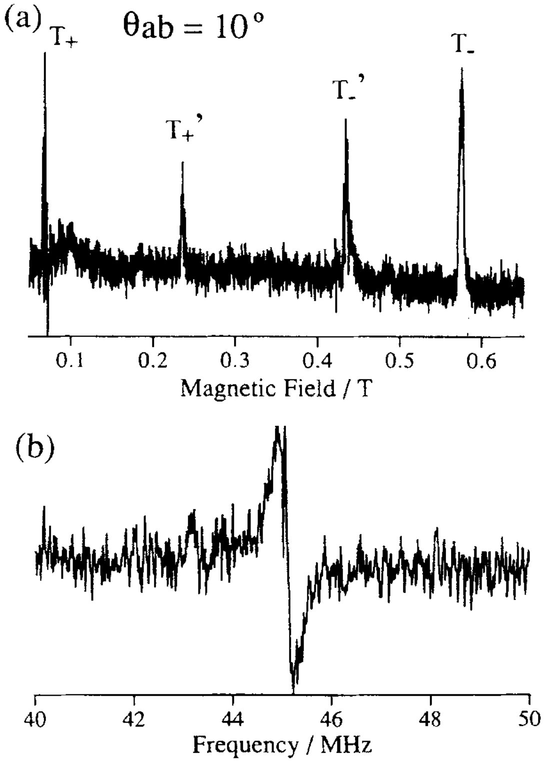


FIGURE 2 Typical ESR and ^{13}C-ENDOR Spectra Observed at 2 K. (a) ESR Spectrum, (b) ^{13}C-ENDOR Spectrum

spin Hamiltonain using the experimental determined ^{13}C-hyperfine tensor:

$$\boldsymbol{H}_{\mathrm{spin}} = \beta_e \boldsymbol{H}\cdot\boldsymbol{g}\cdot\boldsymbol{S} + \boldsymbol{S}\cdot\boldsymbol{D}\cdot\boldsymbol{S} + \boldsymbol{S}\cdot\boldsymbol{A}_{\mathrm{C13}}\cdot\boldsymbol{I} - g_{\mathrm{N}}\beta_{\mathrm{N}}\boldsymbol{H}\cdot\boldsymbol{I}_{\mathrm{C13}}, \qquad (3)$$

where $\boldsymbol{g}$, $\boldsymbol{D}$, and $\boldsymbol{A}_{\mathrm{C13}}$ are the electron g, the fine-structure, and the ^{13}C-hyperfine tensors, respectively. The terms g_{N}, β_e and β_{N} are the nuclear g-factor, electron Bohr magnetron and nuclear magnetron, respectively. The agreement between the experimental data and the calculated ones are excellent, indicating the high accuracy of the obtained hyperfine tensor.

The data analysis obtaining the accurate hyperfine tensor from the ENDOR spectra was carried out by the following procedures.[4] The data analysis FORTRAN programs were made by mainly one of the authors (Y.T.). The ENDOR frequency is given to first-order by

$$\nu_{\mathrm{ENDOR}} = |A_{zz}M_{\mathrm{S}} - g_{\mathrm{N}}\beta_{\mathrm{N}}\mathrm{H}|/h, \qquad (4)$$

where h is the Plank constant and H is the external magnetic field strength. We first obtained the crude hyperfine tensors from the first-order analysis of the angular dependence using a least-square fitting based on equation (4). Then, we refined the tensor by comparing the observed ENDOR frequencies with the calculated values obtained by the exact numerical diagonalization of the matrix of the spin Hamiltonian (3). All the spin Hamiltonian parameters were finally determined from the numerical diagonalization of the spin Hamiltonian (3). The obtained ^{13}C -hyperfine tensor on the divalent carbon site of the diphenylmethylene moiety in **1** is given in Table II. The anisotropic terms A_{aniso} of the ^{13}C-hyperfine tensor gives a direct information for both the π spin (ρ^{π}) and

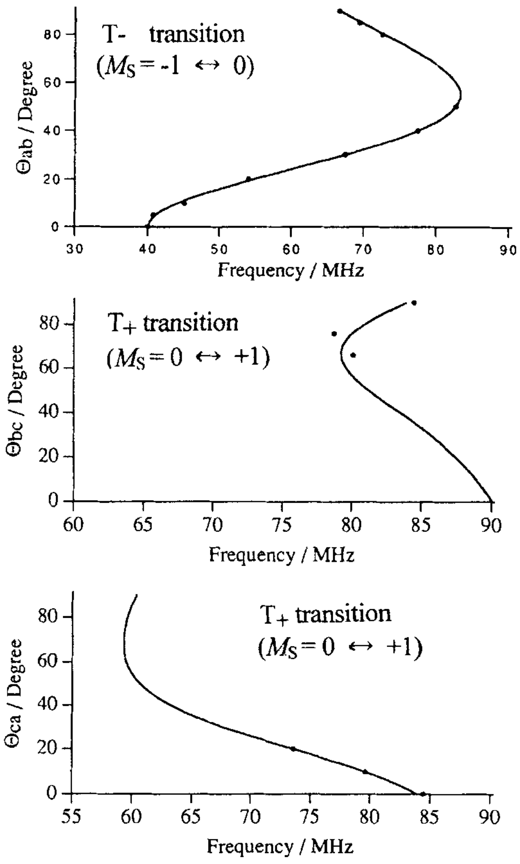


FIGURE 3 Angular Dependence of ^{13}C-ENDOR Frequencies

the σ spin densities (ρ^{σ}) on the divalent carbon site. Thus, these spin densities can be directly determined by the following equation.

$$A_{aniso} = \frac{1}{2S}\left[\begin{pmatrix} -B & & \\ & -B & \\ & & 2B \end{pmatrix}\rho^{\sigma} + \begin{pmatrix} -B & & \\ & 2B & \\ & & -B \end{pmatrix}\rho^{\pi}\right] \qquad (5)$$

where B = -89.0 MHz. The obtained spin densities are also listed in Table II. The magnitudes and absolute signs of the ^{13}C -hyperfine splittings of the diphenylmethylene moiety in **1** should be compared with those of the Hutchison's experiments.[5] The ^{13}C -hyperfine splittings on the divalent carbon sites of the diphenylmethylene molecule were already reported to be Axx = 115.4, Ayy = -189.6 and Azz = 214.8 MHz by Hutchison et al.[5] It should be notice that the determined ^{13}C -hyperfine splittings in **1** are about muinus one-half of those of the diphenylmethylene molecule. Thus, the present results clearly show that the σ and π spin densities at the divalent carbon sites in **1** are about one-half of those of the isolated diphenylmethylene molecule and the signs also opposite as predicted by the relationship shown in Table I(b). The present results are the clear example of the spin contraction. Thus, these findings give the direct evidences of the spin contraction on the limited-size molecular spin systems.

TABLE II Principal Values of the ^{13}C-Hyperfine Tensor and σ and π Spin Densities

	Principal Values				Spin Densities
	/ MHz	A_{iso} / MHz	A_{aniso} / MHz		
A_{XX}	-46.16		X	25.69	$\rho^{p\pi}$= -0.217
A_{YY}	75.15	-71.86	Y	-3.29	ρ^{2s}= -0.043 ┐→ ρ^{σ}=-0.403
A_{ZZ}	-94.26		Z	-22.40	$\rho^{p\sigma}$= -0.360 ┘

(b) Theoretical Calculation of the Spin Contraction as an Quantum Size Effect

In order to demonstrate that the observed spin contraction to be an quantum size-effect, we have carried out the following theoretical model calculations. For the reason of the simplicity, we treated here the most spimple hetero-spin systems in which the spins and in the repeating units -S^A-S^B- corresponds to be S^A =1/2 and S^B =1. We calculated the spin energies, the spin functions, and the spin densities of the ground states and the low-lying excited states for the several ferrimagnetic Heisenberg spin systems (-S^A-S^B-S^A-S^B- • • • -S^A-S^B-) with different chain lengths by the exact numerical calculations. The full matrix of the Heisenberg Hamiltonian was directly solved for the short chain systems by the numerical diagonalization. For the longer chain systems in which number of the repeating unit is larger than 3, we used the Lanczos method for the spin-energy calculations and the Converged Gradient (CG) method for the calculations of the spin functions.[3] In order to neglect the edge effects in the spin chain, we used a periodic boundary conditions in these calculations. Only the size-dependency of the expectation values of S^Z in the ground states is shown in Figure 4 since we interest here the quantum spin contraction. The $<S^Z>$ values of the local spins on each site i can be related to the spin density on each site i by

$$\rho_i = 2<S^Z_i>. \qquad (6)$$

The result of the shortest ferrimagnetic spin system (S^A-S^B) just fitted to the analytical solution in Table I(a) with the total spin S = 1/2. As clearly shown in Figure 4, the absolute values of $<S^Z>$ on each site have been increases with increasing number of the repeating units. This means that the spin contraction has been recovered with increasing size of the spin system. Thus, these theoretical calculations for the limited-size ferrimagnetic linear chain systems reveal that the present spin contraction is a size-effect of the quantum spin system.

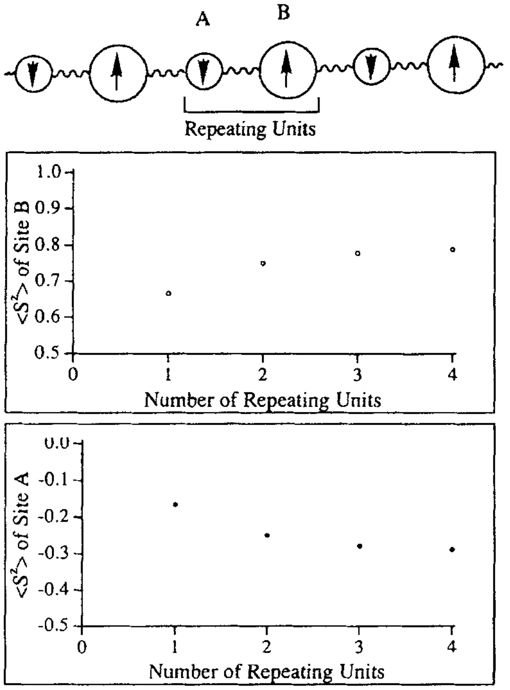


FIGURE 4 Size-Dependency of $<S^Z>$ Values on Each Site in the Ferrimagnetic Spin System

CONCLUSIONS

The spin contraction as a quantum size effect has been clearly observed in the high-spin organic molecule **1** which is the most shortest ferrimagnetic spin system by ^{13}C-ENDOR experiments. The size-effect has also been examined by the exact numerical calculations for the model systems with the ferrimagnetic spin ordering. These experimantal and theoretical findings give the direct evidence of the spin contraction predicted by equation (2) as an quantum size-effect.

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