

A Prerequisite for Purely Organic Molecule-Based Ferrimagnetics: Breakdown of Simple Classical Pictures

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Spin state energies were calculated for an antiferromagnetic linear chain composed of a doublet ($S = 1/2$) radical and a biradical with a triplet ($S = 1$) ground state by numerical diagonalization of a finite-size Heisenberg–Dirac spin Hamiltonian. A ferrimagnetic-like ground state with a spin value of $S = N/2$ (N stands for the number of repeating units) appears if the intermolecular antiferromagnetic exchange interactions are uniform between all the $S = 1/2$ sites. This finding is consistent with a simple picture of differing and neighboring spin angular moments S 's ordered in sublattices in an antiparallel manner. On the other hand, quasi-degenerate low-lying states appear as the spatial symmetry of the intermolecular antiferromagnetic interactions is lowered. The quasi-degeneracy destabilizes the ferrimagnetic-like ground state. This instability is inherent in multicentered antiferromagnetic interactions between open-shell organic molecular systems, suggesting a prerequisite for long-range magnetic order in purely organic molecule-based ferrimagnetics. Such prerequisite has never been reported until now. The results of the calculations are invoked to explain the susceptibility and the spin–spin relaxation time measured for the first model system for purely organic ferrimagnetics, a nitronyl nitroxide-based molecular crystal composed of an $S = 1/2$ and $S = 1$ molecules (Izuoka, A.; Fukuda, M.; Kumai, R.; Itakura, M.; Hikami, S.; Sugawara, T. *J. Am. Chem. Soc.* **1994**, *116*, 2609–2610.)

Introduction

Organic molecule-based magnetism and magnetics have been the focus of current topics in a multidisciplinary area of the pure and applied sciences.¹ After the discovery of the first purely organic ferromagnet of Curie temperature $T_C = 0.64$ K,^{2,3} efforts to study organic molecule-based magnetic materials have been concentrated on the full understanding of the underlying mechanism for intermolecular ferromagnetic interactions and on materials challenges for higher T_C organic ferromagnets as well as molecular functionality magnetics.¹ On the other hand, purely organic molecule-based ferrimagnets have not been documented thus far, in which intermolecular exchange interactions are primarily antiferromagnetic but net magnetic moments arise from differing moments ordered in the sublattice or from the difference between the sublattice magnetizations.

One of the most salient features of organic open-shell molecules as building blocks of magnetic materials is the isotropic nature of intermolecular exchange interactions.⁴ This feature results from the low symmetry of the organic molecules and weak spin–orbit interactions compared with those of transition-metal ions. Particularly, for antiferromagnetic spin systems including ferrimagnets, both the isotropic nature of electron spins and the low lattice dimensionality (spatial dimensionality) in nature commonly appearing in organic solids underlie large quantum fluctuation of the spins. The quantum fluctuation favors a diamagnetic singlet ($S = 0$) pair more than an antiparallel alignment of adjacent spins. Vanishing magnetic moments due to the singlet pair formation prevent long-range magnetic order or reduce transition temperatures to antiferro-

magnetic or ferrimagnetic ordered states. Thus, the quantum nature inherent in the exchange interactions in the organic materials is of crucial importance for establishing a rationale for purely organic ferrimagnetics.

Is it possible to construct ferrimagnetics from the substantially isotropic Heisenberg–Dirac spin systems in purely organic crystals? Are simple pictures⁵ analogous to metal ionic ferrimagnetics formative enough for organic ferrimagnetics? Organic ferrimagnetics were proposed on the theoretical side at early times.⁵ Formidable obstacles to purely organic ferrimagnetics, however, have never been considered. Giving answers to the above questions, we present a physical picture for the ground state of a “spin $1/2$ and spin 1 alternating chain” obtained from numerical calculations of both spin state energies and temperature dependence of magnetic susceptibility, χ . The above model is the simplest collinear organic ferrimagnetics, and the calculation is based on a finite-size Heisenberg–Dirac spin Hamiltonian. We invoke the calculation to examine the magnetic susceptibility of the first model system for purely organic ferrimagnetics, an organic molecular complex.⁶ The crystal of the complex is composed of an alternating collinear-chain of an $S = 1/2$ radical and a biradical with a triplet ($S = 1$) ground state. For elucidating microscopic magnetic environments of the electron spins in the linear-chain compound, transverse relaxation time (spin–spin relaxation time), T_2 , of the crystal is also discussed which was measured using a pulsed EPR technique.

Experimental Section

The spin state energy and magnetic susceptibility were calculated by exact numerical diagonalization of a Heisenberg–Dirac spin Hamiltonian for finite-size model systems. The computation was carried out using the facilities of the Super-

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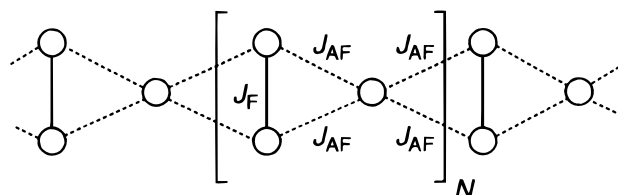


Figure 1. Schematic drawing of the Heisenberg-Dirac Hamiltonian with the uniform intermolecular antiferromagnetic interactions, J_{AF} , in N of the repeating units. J_F denotes the intramolecular ferromagnetic interaction. The open circles represent the spin $1/2$ sites.

computer Center, The Institute for Solid State Physics, The University of Tokyo. Preliminary calculations of the magnetic susceptibility were made on a Sony NWS-5000TG workstation at our departments. The static magnetic susceptibility of the molecular complex was measured for the randomly oriented polycrystalline sample using a Quantum Design MPMS SQUID magnetometer with an applied field of 0.1 T in the temperature range 2–300 K. The magnetization curve was measured below 6 K with an applied field up to 6 T. The transverse relaxation time measurements using a spin echo technique were carried out on a Bruker FT-EPR spectrometer ESP380E equipped with a dielectric cavity with a tunable Q value of 100–5000.

Results and Discussion

1. Numerical Calculation of Susceptibility and Spin Eigenstate Energies. (1) *Symmetric Hamiltonian.* The spin state energies and the temperature dependence of χT were calculated for a finite-size alternating linear-chain of doublet ($S = 1/2$) and triplet ($S = 1$) molecules. At the triplet site, two $S = 1/2$ spins are coupled by a ferromagnetic exchange interaction J_F . Both the $S = 1/2$ spins interact with the $S = 1/2$ spins on the neighboring doublet sites. The model is schematically illustrated in Figure 1. The Heisenberg-Dirac spin Hamiltonian examined for uniform exchange interactions is given as follows:

$$H = -2J_F \sum (S_{3i-2} \cdot S_{3i-1}) - 2J_{AF} \sum (S_{3i-2} \cdot S_{3i} + S_{3i-1} \cdot S_{3i} + S_{3i} \cdot S_{3i+1} + S_{3i} \cdot S_{3i+2}) \quad (1)$$

where the summation runs over $i = 1, 2, \dots, N$, and N stands for the number of the repeating units. S_j ($j = 3i - 2, 3i - 1, 3i, 3i + 1, 3i + 2$) is the spin $1/2$ operator on the j th site. The total number of the spin $1/2$ sites is given by $3N$. A periodic boundary condition, $S_{3N+1} = S_1$, was adopted in the calculation for avoiding an "edge effect" as expected in linear chain models with free edges. The expectation value of S^2

$$\langle S^2 \rangle = \langle S^+ S^- + S_z^2 - S_z \rangle = S(S + 1) \quad (2)$$

for each eigenstate was also calculated using the eigenvectors obtained in the diagonalization procedure of the Hamiltonian (1). All the calculations were made for a spin subspace with the z -component of the total spin:

$$S_z^{\text{total}} = \sum S_z^i = \begin{cases} 0 & (\text{even } 3N) \\ 1/2 & (\text{odd } 3N) \end{cases} \quad (i = 1, 2, \dots, N) \quad (3)$$

The state energies were calculated for the rings of up to 21 $S = 1/2$ sites by Lanczos method.⁷ The temperature dependence of magnetic susceptibility was simulated for the rings of up to 12 $S = 1/2$ sites by using the state energies obtained from Householder method. The calculations were done for the system of $J_F \sim |J_{AF}|$ in order to compare the results with the experiments for a molecular crystal with inter- and intramolecular exchange interactions being comparable as described below.

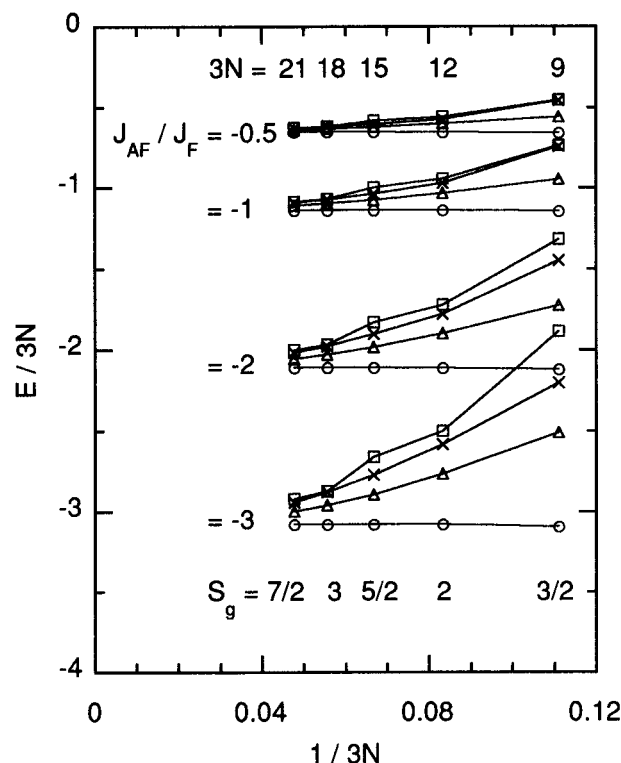


Figure 2. Eigenstate energies of low-lying spin states for the model Hamiltonian shown in Figure 1. $3N$ denotes the total number of the $S = 1/2$ sites. The circle represents the ground-state energy. The triangle, the cross, and the square are the low-lying excited states. The spin quantum number S_g of the ground state is also shown for each $3N$.

The ground-state eigenenergy and S value are shown in Figure 2 together with those of three low-lying excited states for representative ratios of $J_F:J_{AF}$. For any ring-size ($3N$) and interaction ratio ($J_F:J_{AF}$) examined, a "ferrimagnetic-like" ground state appears: The ground-state spin value is $S_g = N(1 - 1/2) = N/2$ which is consistent with a simple picture of the formal one-dimensional representation, i.e., the neighboring N spin pairs of $S = 1/2$ and $S = 1$ aligned in an antiparallel manner. It has turned out that the ferrimagnetic-like ground state appears even when the $S > 1/2$ site consists of a composite system of two isotropic (i.e., ideally quantum) $S = 1/2$ spins coupled by any finite ferromagnetic interaction (J_F).

For examining the thermally excited states of the doublet-triplet alternating linear chain, the temperature dependence of χT was calculated for $3N = 6, 9$, or 12 by diagonalizing the Hamiltonian (1) with respect to the eigenvectors of S_z^{total} as basis vectors. As shown in Figure 3, the calculated χT value exhibits a minimum between $T_{\min} = J_F/k_B$ and $2J_F/k_B$. The minimum in χT as a function of temperature is generally indicative of the ferrimagnetic-like behavior in low-dimensional lattices.^{8,9} In a chain composed of two kinds of spins S_1 and S_2 ($S_1 > S_2$) coupled antiferromagnetically, the ground state of the chain has a spin $S_g = N(S_1 - S_2)$ (N : the number of the repeating units). The highest energy corresponds to $S_h = N(S_1 + S_2)$. Between these two levels, spin states with S values ($S_g < S < S_h$) are distributed. In the high-temperature limit, all the states are populated to give a χ value expected for $3N$ mol of free $S = 1/2$ spins. On lowering the temperature, the high-energy states with $S = S_h, S_h - 1, \dots$ are depopulated first, resulting in a decrease in χT . At low temperature, the low-lying excited states with $S_g - 1, S_g - 2, \dots$, which are located just above the ground state, are depopulated and the χT value is increased. The minimum in χT in Figure 3 indicates that the thermal excitation behavior of the doublet-triplet alternating chain under study

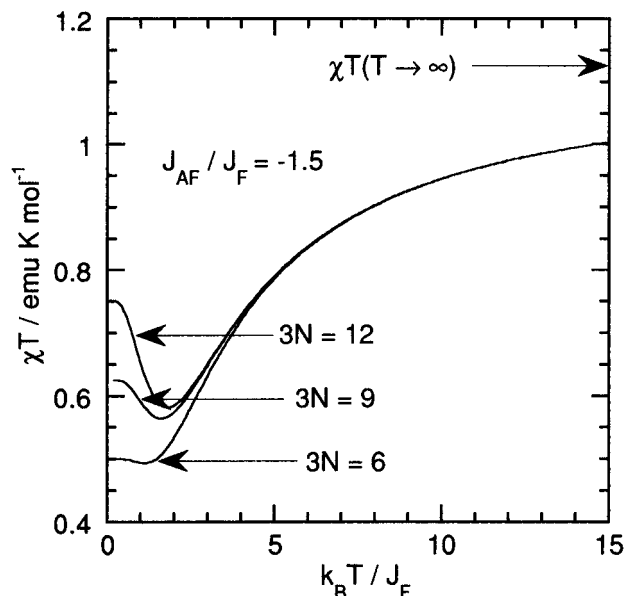


Figure 3. Calculated temperature dependence of χT for the model Hamiltonian in Figure 1. The high-temperature limit of χT is also indicated.

is not affected by the composite nature of the triplet sites represented by a finite J_F .

Next we consider the low-temperature magnetic behavior of the alternating chain of macroscopic size by increasing N in the above calculations. In the limit of $T = 0$, χT should approach a finite value corresponding to the ground-state spin value of $S_g = N/2$ for the single repeating unit with three $S = 1/2$ sites:

$$\chi T(T=0) = N_A g^2 \mu_B^2 (N+2)/36k_B \propto N \quad (4)$$

where N_A , g , μ_B , and k_B stand for Avogadro number, g -factor, Bohr magneton, and Boltzmann constant, respectively. With increasing N to a macroscopic scale, the low-temperature limit of χT diverges:

$$\chi T \rightarrow \infty \quad (N \rightarrow \infty) \quad (5)$$

suggesting the possible occurrence of ferrimagnetics.

The temperature dependence of the χT value calculated for the system with multicentered J_{AF} 's (the minimum and the possible divergence as functions of temperature) is essentially the same as those for spin chains composed of $S = 1/2$ spin and "rigid" $S > 1/2$ spin; in the chains, the neighboring $S = 1/2$ and $S > 1/2$ spins are coupled by a single J_{AF} .⁸⁻¹¹ Furthermore, the absolute value of χT for the model with the multicentered J_{AF} 's reproduces those with the "rigid" spins: Figure 4 shows the calculated T_{\min} and χT_{\min} as functions of $J_F/|J_{AF}|$. Within $J_F/|J_{AF}| = 3-4$, both the T_{\min} and χT_{\min} values reach the limit of $J_F = +\infty$ which has been calculated for the chains composed of "rigid" $S = 1$ spins ($J_F = +\infty$).⁹ It is concluded that the composite nature of the $S = 1$ sites characterized by finite J_F and multicentered J_{AF} seem to scarcely affect bulk magnetic properties, when intermolecular J_{AF} 's are uniform, i.e., all the J_{AF} 's have the same value.

(2) *Asymmetric Hamiltonian.* As described above, when all the intermolecular antiferromagnetic interactions couple the neighboring $S = 1/2$ sites uniformly, the ferrimagnetic-like ground state, together with the divergence of χT , appears even for the isotropic (i.e., Heisenberg-type) spins which favor the singlet pair formation more than the "Neel state" or antiparallel alignment of the adjacent spins. Here we have to examine the

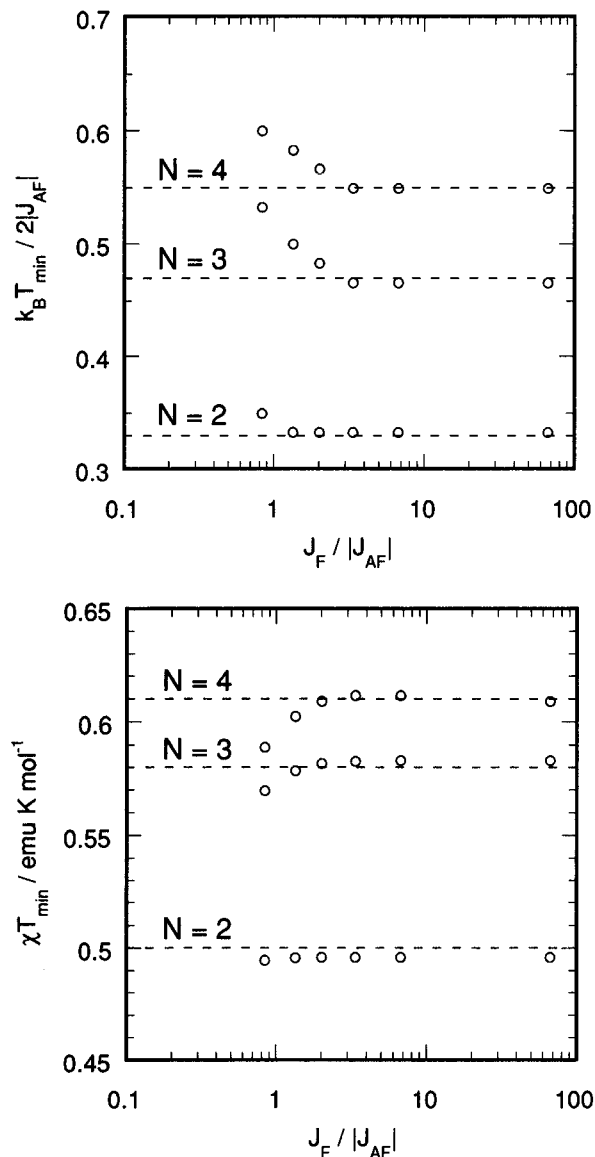


Figure 4. Position of the minimum in χT , T_{\min} (top) and χT_{\min} (bottom), as functions of $J_F/|J_{AF}|$ calculated for the model Hamiltonian in Figure 1. The dashed lines indicate the limit of $J_F/|J_{AF}| \rightarrow +\infty$ for the chain size of $N = 2, 3, 4$.⁹

influence of the spatial-symmetry lowering of intermolecular antiferromagnetic interactions J_{AF} 's on the spin states of the chain for the following two reasons. First, the model with a uniform J_{AF} is unrealistic for the crystalline solids composed of organic open-shell molecules. Second, removal of the translational uniformity of J_{AF} 's might give rise to an energy gap above a "diamagnetic" (or singlet) ground state as is analogized with a site alternation in an $S = 1/2$ antiferromagnetic linear chain.¹²

The following Heisenberg–Dirac Hamiltonian with lowered symmetry of J_{AF} is exploited:

$$H = -2J_F \sum (S_{3i-2} \cdot S_{3i-1}) - 2 \sum (J_{AF1} S_{3i-2} \cdot S_{3i} + J_{AF2} S_{3i-1} \cdot S_{3i} + J_{AF3} S_{3i} \cdot S_{3i+1} + J_{AF4} S_{3i} \cdot S_{3i+2}) \quad (i = 1, 2, \dots, N; S_{3N+1} = S_1) \quad (6)$$

where J_{AF1} , J_{AF2} , J_{AF3} , and J_{AF4} are allowed to differ from each other and the periodic boundary condition is retained. To obtain both the S value and the degeneracy, including accidental ones, simultaneously for low-lying eigenstates, the canonical orthogonalization procedure^{13,14} has been taken first. Then, with respect

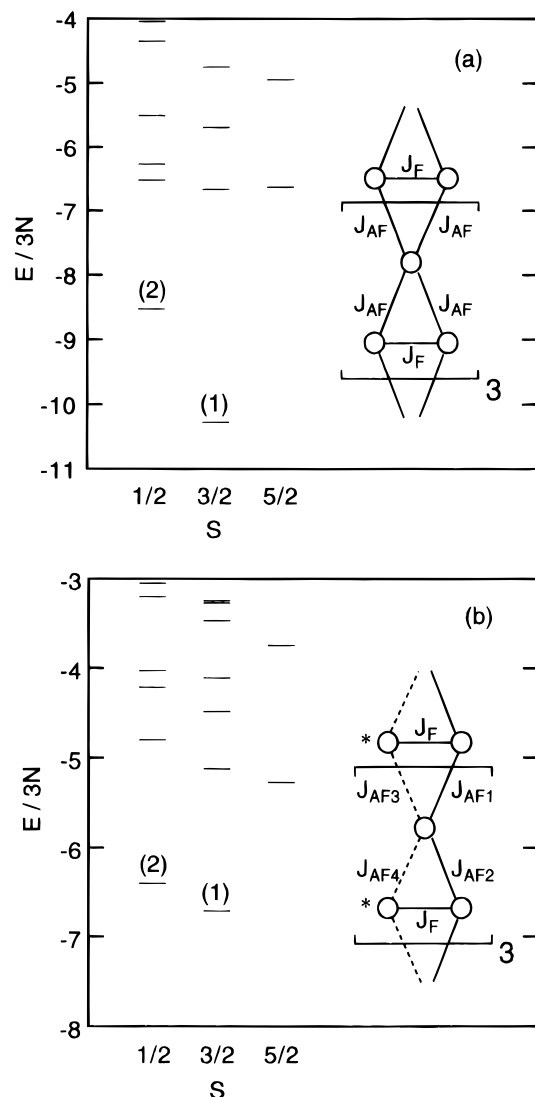


Figure 5. State energies of the $3N = 9$ system calculated for the symmetric (a, top) and asymmetric (b, bottom) Hamiltonians shown in the insets. The exchange interaction parameters are $J_F = 1$, $J_{AF} = -1$ in (a) and $J_{AF1} = -1$, $J_{AF2} = -1.1$, $J_{AF3} = 0$, $J_{AF4} = 0$ in (b). The starred circles indicate the “apparently decoupled” $S = 1/2$ spins. The degeneracies of the ground and first-excited states are shown in the parentheses. For the detailed notations, see the text.

to the eigenvectors of S^2 thus obtained, diagonalization by Householder method has been carried out. In Figure 5, the low-lying eigenstates of the asymmetric Hamiltonian (6) are compared with those of the symmetric Hamiltonian (1) for $3N = 9$. For the both models in Figure 5, the ground state is quartet ($S_g = N/2 = 3/2$). However, in the asymmetric model for a nonuniform case of $|J_{AF1}| \sim |J_{AF2}| \gg |J_{AF3}| \sim |J_{AF4}|$ given in Figure 5b, the first excited state with $S = 1/2$ is quasi-degenerate with the quartet ground state. Quasi-degeneracy of a single quartet and two doublet states corresponds to three $S = 1/2$ spins which are magnetically independent. Thus, when the difference in J_{AF} values is not negligible compared with the thermal energy (i.e., at very low temperature), the $N = 3$ chain with the asymmetric antiferromagnetic interactions behaves as three decoupled $S = 1/2$ spins. In the low-temperature limit, χT should approach a finite value:

$$\chi T = N_A g^2 \mu_B^2 / 4k_B = 0.38 \text{ emu K mol}^{-1} \quad (g = 2.0) \quad (7)$$

for a single repeating unit with an “apparently decoupled” $S = 1/2$ spin. The finite value is smaller than the χT minimum in

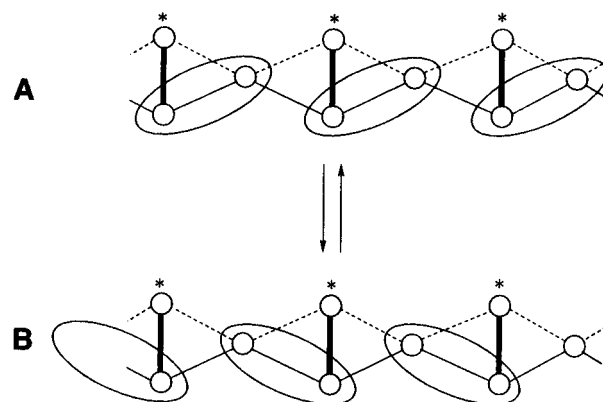


Figure 6. Schematic representation of the ground state of the Heisenberg spin system with the asymmetric intermolecular antiferromagnetic interactions. The open circles denote spin $1/2$ sites. The heavy solid lines represent the intramolecular ferromagnetic interactions. The light solid and dashed lines show the intermolecular antiferromagnetic interactions. The ovals denote the singlet ($S = 0$) pairs. Two resonance structures are given as A and B. The starred circles indicate the “apparently decoupled” $S = 1/2$ spins. For the detailed notations, see the text.

Figure 3. Thus, the quasi-degeneracy resulting from the spatial symmetry reduction of J_{AF} 's brings about a decrease in χT at low temperature. As a consequence, it is predicted that the doublet–triplet alternating chain with nonuniform asymmetric J_{AF} 's exhibits both a minimum and a maximum at lower temperature followed by a decrease in χT on lowering the temperature toward 0 K. The ground state of such chain is quite different from the ferrimagnetic-like state; apparently noninteracting $S = 1/2$ spins remain in the low-temperature limit.

Unfortunately, the quasi-degeneracy equivalent to “a single $S = 1/2$ spin per the repeating unit” has not been verified for general $3N$ owing to the memory-size limitation for computing in terms of the combination of the canonical orthogonalization and Householder diagonalization procedures. However, it is suggested that the quasi-degeneracy destabilizes the ferrimagnetic-like ground state found in the uniform antiferromagnetic systems. This instability is regarded as inherent in multicentered antiferromagnetic interactions connecting ground-state multiplet molecules with the neighboring doublet molecules. It is concluded that the spatial symmetry of intermolecular antiferromagnetic interactions is vitally important for the spin-state distribution in the vicinity of the ground state when internal magnetic degree of freedom in an $S > 1/2$ spin site is not negligible (i.e., finite J_F associated with the multicentered J_{AF} 's). In such cases weak spin polarization underlying intramolecular spin alignment leads to the occurrence of nearby excited states with differing low-spin multiplets.

A possible picture of the ground state is schematically illustrated in Figure 6 for the quantum spin system characterized by asymmetric intermolecular interactions, $|J_{AF1}| \sim |J_{AF2}| \gg |J_{AF3}| \sim |J_{AF4}|$. The intermolecular antiferromagnetic interactions, J_{AF} 's, are shown as light lines; the solid ones denote the larger J_{AF} 's and the dashed ones the smaller J_{AF} 's. At low temperature the singlet ($S = 0$) pairs appear at the sites with the larger J_{AF} values which are depicted as ovals in Figure 6. When the alternation of the J_{AF} values along the chain is neglected, the singlet pairs resonate as shown in A and B in Figure 6. The resonance should leave starred $S = 1/2$ spins apparently decoupled. This “apparently decoupled” spin brings about a paramagnetic behavior of a single $S = 1/2$ spin per repeating unit. If the alternation of J_{AF} values along the chain is large, the singlet pair is expected to localize at every other site. However, the “apparently decoupled” spin might still

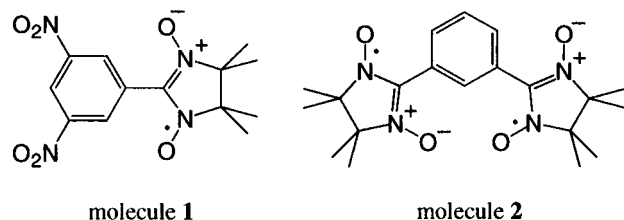


Figure 7. Molecules 1 and 2.

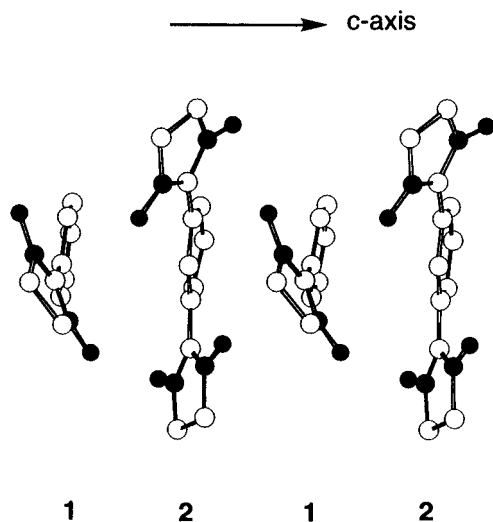


Figure 8. Linear-chain structure of the molecular complex 1+2 along the crystallographic *c* axis. The nitroxide (N–O) groups are denoted by the closed circles. The methyl groups and the nitro groups are omitted for clarity. It has been proposed that the electrostatic interaction between the nitro group and the nitroxide group on the adjacent molecules plays an important role in the crystal packing.⁶

appear at every other site. The “apparently decoupled spin” is acceptable by considering that the intramolecular ferromagnetic interactions seem no longer efficient when one of the ferromagnetically coupled spins in the molecule disappears owing to the singlet pair formation. The suppression of ferromagnetic interaction due to singlet pair formation has been demonstrated in the spin state found in a dimer of antiferromagnetically coupled triplet molecules.⁴

2. A Model Compound for Doublet–Triplet Alternating Linear Chain. (1) *Susceptibility and Magnetization.* The calculated results described above are compared with a model organic compound based on nitronyl nitroxide radical. Izuoka et al. has reported the crystal structure and static magnetic susceptibility of a molecular complex crystal that consists of alternating chains of a doublet radical **1** and a biradical **2** (Figures 7 and 8).⁶ The molecular ground state of **2** has been found to be triplet ($S = 1$) in a mixed crystal of **2** diluted in a diamagnetic compound.¹⁵ The intramolecular exchange interaction of **2** has been determined to be $J_F/k_B \sim +20$ K.¹⁵ To our knowledge, the complex is the first model system for purely organic ferrimagnetics with well-characterized molecular and crystal structure although ferrimagnetic phase transition has not been observed from the crystal yet.

The temperature dependence of χT below 30 K is depicted in Figure 9.¹⁶ As shown in the figure, the χT value took a minimum at $T_{\min} = 6$ K. In light of the calculated results, the minimum at $T_{\min} = 6$ K is regarded as indicative of ferrimagnetic-like spin correlation (or short-range magnetic order) which develops along the alternating chain of the complex around T_{\min} . The occurrence of the ferrimagnetic-like short-range order has been confirmed by the magnetization curve measured around T_{\min} . The thermally averaged spin number has been found to

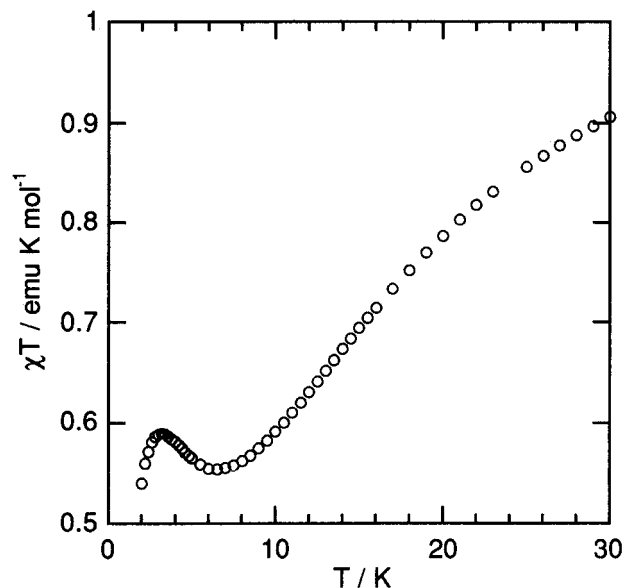


Figure 9. Temperature dependence of χT measured for the polycrystalline sample of the molecular complex 1+2.

be $S = 1-3/2$ from the fitting of the observed curvature to Brillouin function.¹⁷ It can be stated that the ground state or low-lying excited states have a thermally averaged spin magnetic moment of $S = 1-3/2$ in the chain; i.e., the ferrimagnetic-like spin correlation extends over two or three repeating units.

The χT value took a maximum at $T_{\max} = 3$ K and decreased at lower temperature. Usually, a decrease in χT at low temperature for magnetic linear-chain materials is attributed to additional interchain antiferromagnetic interactions. For the complex 1+2, however, such a conventional interpretation might not be a rationale for χT below T_{\max} : First, the methyl groups facing each other between the chains have low spin density in the molecules and thus are expected to have little contribution to the interchain interactions of the order of $k_B T_{\max}$. Second, relatively short interatomic distance is found between **1** and **2** instead of **1** and **1** or **2** and **2** between the chains.⁶ This molecular arrangement in the crystal tends to favor three-dimensional ferrimagnetic spin correlation which gives rise to the divergence of χT when only the distance is taken into account as a dominant factor responsible for interchain magnetic interactions. Therefore, the decrease in χT below T_{\max} is attributed to the spin state distribution within the chain.

It is predicted from the calculations in section 1(2) that the divergence of χT is suppressed when the spatial symmetry of intermolecular antiferromagnetic interactions is lowered. Considering the lattice symmetry (space group $P1$)⁶ of the crystal under study, the intermolecular antiferromagnetic interactions lack pseudo- C_2 symmetry around the chain axis such as $J_{AF1} = J_{AF3}$ or $J_{AF2} = J_{AF4}$ in the model Hamiltonian (6). Therefore, the appearance of the maximum and the decrease in χT for the complex 1+2 is reasonably attributed to the intermolecular singlet-pair formation.

(2) *Spin–Spin Relaxation Time.* In the above discussions both for the calculations and the observed susceptibility, the point is to distinguish the singlet pair formation from the antiparallel alignment of spins. In this respect, we have to elucidate experimentally the partial disappearance of magnetic moments due to the singlet pair formation. For this purpose, transverse relaxation time (spin–spin relaxation time), T_2 , of the complex 1+2 was measured using a pulsed EPR technique. The T_2 value was measured by Hahn’s echo method ($\pi/2-\pi$ pulse sequence) on the single crystals of the complex with static magnetic field parallel as well as perpendicular to the chain, or

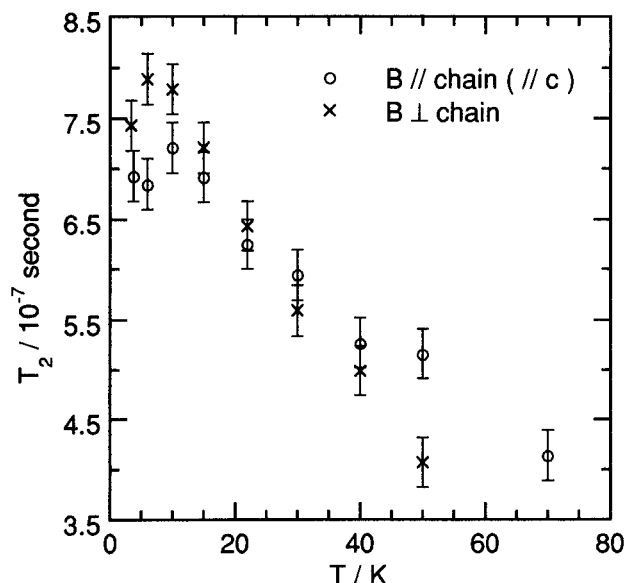


Figure 10. Temperature dependence of the spin–spin relaxation time, T_2 , measured on the single crystals of the complex **1+2**. The static field was applied parallel or perpendicular to the chain (\parallel c -axis).

to the crystallographic c -axis. By monitoring the echo peak intensity with incrementing the interval τ between the $\pi/2$ and π pulses, echo decay curves were obtained. The T_2 value was estimated as the time constant of the exponential decay of the echo intensity as a function of τ .

The experimental results are given in Figure 10. For both parallel and perpendicular orientations of the static field, the T_2 values increased gradually with lowering the temperature and showed a plateau of 7.5×10^{-7} s below 10 K. For low-dimensional antiferromagnetic systems, transverse relaxation rate $1/T_2$ or resonance line width of continuous-wave EPR is known to vary considerably in the low-temperature range of $T \sim |J_{AF}|/k_B$ (J_{AF} : the antiferromagnetic exchange interaction along the chain).¹⁸ This kind of variation in T_2 has been attributed to antiferromagnetic spin correlation extended over the low-dimensional lattice. For the complex **1+2**, the temperature dependence of $1/T_2$ reflecting the spin–spin relaxation in the solid state is quite different from those of conventional low-dimensional antiferromagnetic systems. The T_2 value determined through echo decay is a measure of the lifetime of homogeneous spin packets undergoing magnetic interactions with surrounding magnetic moments. The observed increase in T_2 , i.e., a reduction in spin–spin relaxation rate $1/T_2$ in the high-temperature region above T_{\min} indicates that the relaxation between the magnetic moments is suppressed as T lowers. In other words, the spatial distribution of the magnetic moment becomes more sparse with decreasing temperature. The plateau of T_2 below T_{\min} can be interpreted as a competing effect of the partial “tailing-off” of the magnetic moment and the short-range order between surviving spins at low temperature. The relaxation time measurements evidence the occurrence the partial disappearance of magnetic moments due to the singlet pair formation.

Conclusion

The spin state distribution and temperature dependence of magnetic susceptibility were examined for a one-dimensional alternating chain of spin $1/2$ and spin 1. The $S = 1$ site is a composite system of two isotropic $S = 1/2$ spins coupled by finite ferromagnetic interaction. This arrangement underlies typically molecular spin framework of organic open-shell systems. For this model system, the ferrimagnetic-like ground

state appeared in the numerical calculation of a finite-size Heisenberg–Dirac spin Hamiltonian with antiferromagnetic interactions connecting all the $S = 1/2$ sites uniformly. The ferrimagnetic-like ground state is not disturbed by the composite nature of the $S > 1/2$ sites with the ferromagnetic interactions which are comparable with both the intermolecular antiferromagnetic interactions and the thermal energy. However, by lowering the spatial symmetry of the antiferromagnetic interactions, we have found the quasi-degeneracy of the low-lying states. The quasi-degeneracy destabilizes the ferrimagnetic-like ground state. The instability of the ferrimagnetic-like spin structure is associated with the singlet ($S = 0$) pair formation at the sites with relatively large antiferromagnetic interactions. It is predicted that the instability suppress the divergence of χT or the effective magnetic moments at low temperature.

The magnetic properties of the molecular complex composed of nitronyl nitroxide-based radical molecules with different spin multiplicities were investigated as the first “real” model system of low-dimensional organic ferrimagnetics. The complex crystal is comprised of an assembly of doublet–triplet molecular collinear chains. As predicted from the calculation of the finite-size model Hamiltonian, both the minimum and maximum in χT were observed in the susceptibility measurements, corresponding to the occurrence of the ferrimagnetic-like short-range order and the singlet pair formation, respectively. The gradual formation of the singlet pair, i.e., the “tailing-off” of the magnetic moments, in the chain has been corroborated qualitatively by the spin–spin relaxation time measurements using a pulsed EPR spectroscopy.

Since Buchachenko’s proposal,⁵ many efforts have been made to construct organic molecule-based ferrimagnetic materials. All molecule-based ferrimagnetics reported so far, however, contained transition-metal ions.¹⁹ One of the difficulties in achieving ferrimagnetic order in the organic molecule-based materials stems from the isotropic exchange interaction of organic molecules in nature, which favors “quantum mechanically disordered ground states”, that is, the singlet pair formation between the adjacent $S = 1/2$ spins. The singlet pairs bring about the paramagnetic $S = 1/2$ spins rather than ferrimagnetic-like spin structure as shown in the calculations. Simple classical pictures for ferrimagnetics analogous to atomic-based magnetic order are lacking in essential part of organic ferrimagnetics.

In considering that achieving a stable ferrimagnetic-like ground state is not equivalent to realizing long-range ferrimagnetic order, a prerequisite for organic ferrimagnetics can be proposed from the present study: The spatial symmetry of intermolecular antiferromagnetic interactions is crucial to stabilizing ferrimagnetic-like ground states. The spatial symmetry becomes important only when the intermolecular antiferromagnetic interactions have multicentered features. In this sense, from the viewpoint of intermolecular exchange interactions, elaborate designs based on molecular orbital consideration is needed as the next step, requiring ground-multiplet molecules with the spin density distributed over the whole molecular frame and with robust spin polarization. For producing a direct experimental evidence in support of the appearance of the “apparently decoupled $S = 1/2$ spins”, single-crystal continuous-wave EPR experiments on the complex **1+2** are now in progress.

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