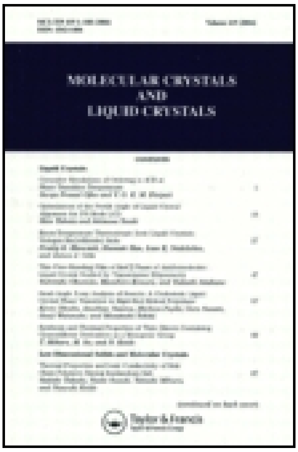

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Magnetic Behavior of N-(Arylthio)-2, 4, 6-Triphenylanilino Radical Crystals

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MAGNETIC BEHAVIOR OF N-(ARYLTHIO)-2,4,6-TRIPHENYLANILINO RADICAL CRYSTALS

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Abstract In order to find the conditions which prevent the dimerization among molecules in the crystal, we have searched long-range antiferromagnetic ordered purely organic systems, such as linear chain organic antiferromagnets. The dimerization is one of the most difficult problems be solved in order to obtain the organic ferrimagnets. This paper deals with the magnetic behavior of polycrystals of m-nitro, p-nitro, and 3,5-dichloro-N-(arylthio)-2,4,6-triphenylanilino radicals. We have found that all of them exhibit long-range antiferromagnetic chain behaviors (at least larger than 7 spins). The temperature dependence of the magnetic susceptibility of the m-nitro radical crystal was well analyzed in terms of a Heisenberg infinite alternating-linear-chain model with J/k = -26 K and the alternating parameter $\alpha = 0.92$. The temperature dependence of the ESR line-width was also consistent with the data of the magnetic susceptibility. The other two compounds have shown similar magnetic behaviors with the larger J/k values. The mechanism of their large antiferromagnetic interaction and the condition for the long-range ordering have been discussed.

INTRODUCTION

The purely organic ferrimagnet is one of the most important targets in the study of the molecular-based magnetic materials.[1] Organic molecules with large antiferromagnetic interaction in the crystal can be utilized for one of the two components in organic ferrimagnetic systems. The dimerization between molecules in the crystal arising from the large antiferromagnetic interaction is, however, one of the most common phenomena to be excluded in order to obtain the organic ferrimagnets or the organic antiferromagnets, since the dimerization cuts off the long-range magnetic interaction, leading to the short-range ordering. Therefore, in order to obtain the magnetic systems with long-range spin ordering via antiferromagnetic interaction, it is important to find the conditions which prevent the dimerization among organic molecules in the crystal. As part of the program to obtain purely organic ferrimagnets,[1] we have searched the organic molecular crystals with a large intermolecular antiferromagnetic interaction. The investigation of such antiferromagnetic systems may give clues to prevent the dimerization and also to construct the purely organic molecular ferrimagnetic systems with higher critical temperatures.

STRATEGY TO PREVENT THE DIMERIZATION

The dimerization between the organic molecules in the molecular crystal can be expected to occur when there is large antiferromagnetic interaction, since such antiferromagnetic interaction leads to the bond formation without any restriction of the Pauli's principles. In the case, in which the molecular orbital occupied by an unpaired electron is localized in the molecule, the tendency to form the chemical bond is expected to increase, since the bond formation leads the large binding energy between their orbitals in the adjacent molecules. On the other hand, the delocalization of the molecular orbital with an unpaired electron decreases the binding energy via the antiferromagnetic coupling as shown in the following discussion. For the estimate of the energy for the dimerization, we adopt the effective exchange energy based on the VB theory,[2] Jex, as the generalized form[3] to the arbitrary spins, S^A and S^B of the relation given by McConnell:[4]

$$J_{ex} = -\Sigma J_{ij}^{eff}\, \rho_i^A \cdot \rho_j^B/(4S^AS^B), \qquad (1)$$

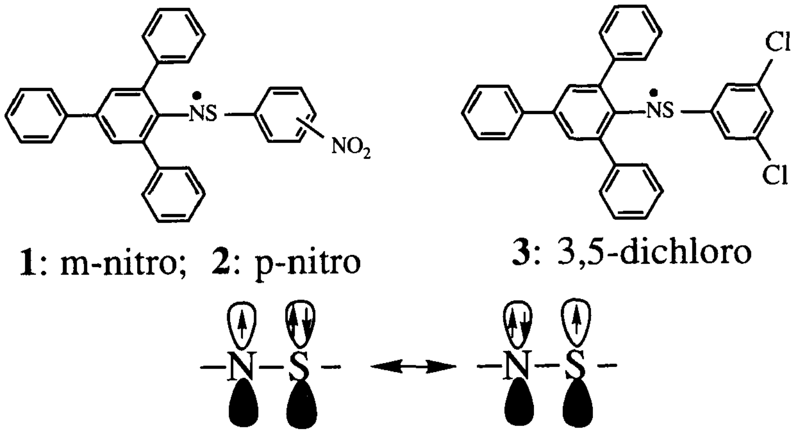
and

$$J_{ij}^{eff} = -2|T_{ij}|^2/U + K_{ij} \qquad (2)$$

where ρ_i (ρ_j) is the spin density on the i-th (j-th) carbon site in the molecule A(B). T stands for the electron transfer integral between the sites i and j, and U and K are the effective on-site Coulomb repulsion and the exchange integral, respectively. When the unpaired electron is delocalized, the expected values of the denominator in Eq. (1) decrease, since the product of the spin densities has smaller values than that of the localized case. Therefore, if we choose molecules, over which the orbital with the unpaired electron is delocalized, we can expect the smaller binding energy at all binding sites. This leads to prevent the dimer formation resulting from the bond formation at the particular carbon sites with the large unpaired electron density. We also expect that total intermolecular exchange energy does not decrease significantly in the delocalized case. Under these considerations, we have examined the molecular crystals of the derivatives of the N-(arylthio)-2,4,6-triphenylanilino radical in which the π nonbonding orbital is delocalized over the molecule as discussed in the next section.

MOLECULES AND THEIR ELECTRONIC STRUCTURES

Figure 1 shows the three kinds of the derivatives (**1**: m-nitro; **2**: p-nitro; **3**: 3,5-dichloro) of the N-(arylthio)-2,4,6-triphenylanilino radical. The simple molecular orbital calculations of these molecules give the following electronic structures. The ca. 40 % amount of the unpaired electron is delocalized to the five phenyl rings. The remainder is also delocalized between the sulfur atom and the adjacent nitrogen via the π conjugation. These molecules are stabilized by the conjugative delocalization of the unpaired electron from the nitrogen to the sulfur as shown in Figure 1. This is the reason why these triphenylanilino radical species are stable even at room temperature.



unpaired electron

40 % : <u>delocalized to five phenyl rings</u>

60 % : localized at the sulfur and the adjacent nitrogen

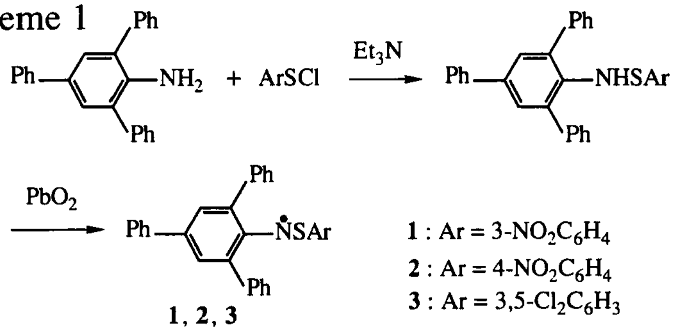
FIGURE 1 Stable radicals and their electronic structures.

EXPERIMENTAL

(i) Syntheses of the Stable Radicals, 1,2, and 3

The stable radicals **1** - **3** were prepared according to scheme 1.[5] Thus, 2,4,6-triphenylaniline was treated with substituted benzenesulfenyl chlorides in the presence of Et_3N, and the N-(arylthio)-2,4,6-triphenylanilines obtained were oxidized with PbO_2 in benzene.

Scheme 1



1, 2, 3

1 : Ar = $3\text{-}NO_2C_6H_4$
2 : Ar = $4\text{-}NO_2C_6H_4$
3 : Ar = $3,5\text{-}Cl_2C_6H_3$

(ii) Magnetic Susceptibility and ESR Measurements

The stable radicals used for the ESR and the susceptibility measurements were repeatedly recrystallized from hexane-ethylacetate for **1** and **2** and from hexane for **3**. After these purification, their samples were dried at ca. 50 °C for 4h in vacuum. The temperature dependence of the magnetic susceptibilities was examined from 1.8 K to 300 K using a Quantum-Design MPMS2 SQUID magnetometer. The correction of the diamagnetic component for the susceptibility was carried out by the Pascal's sum rule of the atomic contributions and the structural corrections. The ESR spectra were also measured from 1.7 K to room temperature with a Bruker ESP300 spectrometer equipped with an Oxford variable temperature controller ESR910. The polycrystalline powder samples were used for all the magnetic susceptibility measurements. The temperature dependence of the ESR spectra was examined for the polycrystalline sample. Unfortunately, we did not have any information on the crystal structural data, since the sizable crystals for the X-ray analysis could not be obtained.

RESULTS AND DISCUSSION

(A) m-Nitro-N-(arylthio)-2,4,6-triphenylanilino Radical, 1

Figures 2(a) and 2(b) show the temperature dependence of the molar magnetic susceptibility χ_{mol} and a plot of $\chi_{mol}T$ vs. T of the radical **1** obtained at 1.0 Tesla, respectively. The characteristic behavior of these temperature dependences did not change at lower magnetic field. The susceptibility χ_{mol} has the maximum at 30 K as shown in Figure 2(a). $\chi_{mol}T$ value exhibits a significant decrease at $T < 100$ K. The behavior indicates the presence of large antiferromagnetic interactions among the radicals **1** in the crystal. The temperature dependence was well interpreted in terms of an alternating ***infinite*** linear-chain model[6] with $J/k = -26$ K (antiferromagnetic) and $\alpha = 0.92$. The calculated values are denoted by the solid curves in Figures 2(a) and 2(b). The Hamiltonian of this one-dimensional system is given by

$$\mathcal{H} = -2J \sum (S_{2i}\cdot S_{2i-1} + \alpha S_{2i}\cdot S_{2i+1}), \qquad (3)$$

where α is the alternating parameter. Since a small value for α indicates the tendency of the dimerization, the value of α=0.92 which is close to unity means that the dimerization is well prevented in this molecular crystal.

The polycrystalline sample of **1** exhibits a powder-pattern ESR spectrum characteristic of the doublet species with an axially symmetric g anisotropy ($g_{//}$ = 2.010, $g_{\perp}$ = 2.002) at room temperature. The hyperfine splitting which has been observed in solution is completely smeared out in this polycrystalline sample, indicating the exchange interaction taking place among the radical species. The temperature dependence of the ESR spectrum is shown in Figure 3. With decreasing temperature, the line-width of the spectrum increased from 298 K to 20 K. The line broadening is more prominent at the direction of $g_{//}$ than that of $g_{\perp}$, indicating that the interacting chain

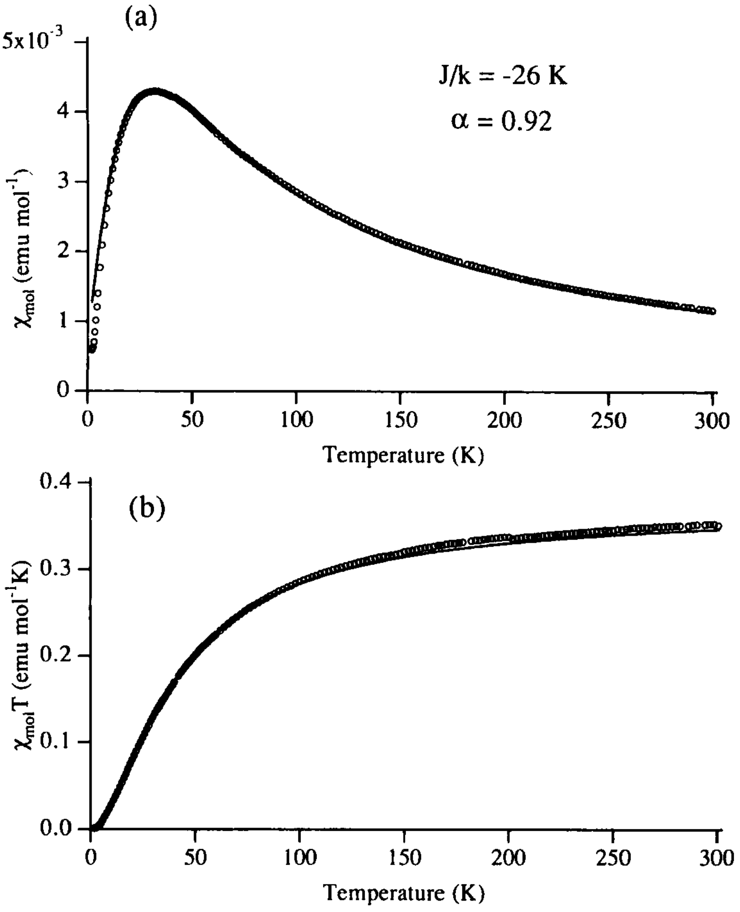


FIGURE 2 Temperature dependence of χ_{mol} and $\chi_{mol}T$.
(a) χ_{mol} vs. T, (b) $\chi_{mol}T$ vs. T.

is nearly parallel to the $g_\perp$ direction. In addition, Figure 3 also shows that the significant exchange-narrowing occurs below 10 K in agreement with the presence of the antiferromagnetic interaction of J/k=-26K as described above. These ESR behaviors are consistent with the results of the magnetic susceptibility measurements.

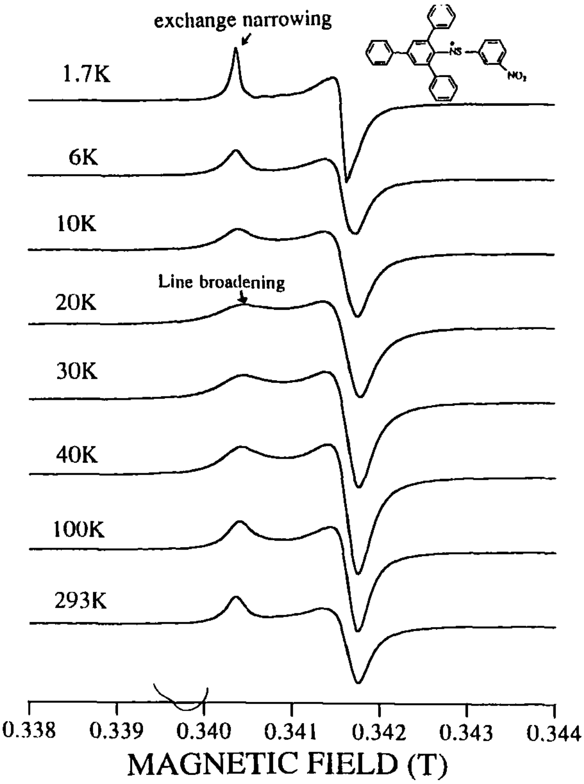


FIGURE 3 Temperature dependence of the powder-pattern ESR spectrum of the polycrystalline sample of **1**.

(B) p-Nitro-N-(arylthio)-2,4,6-triphenylanilino Radical, 2

In order to know the magnetic properties of another stable radical crystal with the delocalized π unpaired orbital, we have measured the magnetic susceptibility of the radical **2**. The preliminary results are shown in this article, since the final analysis and the measurements on more purified samples are in progress. Figures 4(a) and 4(b) show the temperature dependences of χ_{mol} and $\chi_{mol}T$ of **2**, respectively. At present, these data cannot be fitted using the ***infinite*** chain model such as a regular Heisenberg infinite-chain model or the alternating linear chain model described in section (A). These magnetic behaviors could be analyzed by the statistical mixture of ***finite-size*** regular Heisenberg linear chains ($\alpha = 1$ in Eq. (3), finite chain length N) with 7-spin chain clusters (80%) and 8-spin clusters (20%) with J/k = -55 K as denoted by the solid curves in Figure 4. The magnetic properties of these finite-size linear chain were calculated numerically according to the same procedures as given by Bonner-Fisher.[7]

Since the spin concentration of the radical crystal of **2** is obtained ca. 86% in the present preliminary analysis, this system cannot be of an infinite spin ordering as a result of the percolation of nonmagnetic species among the radical chain. This result, however, indicates that the higher spin concentration in the crystal **2** may lead to a quasi one-dimensional organic antiferromagnet. The intermolecular exchange interaction of J/k = -55 K is relatively large, compared with other purely organic systems except for the dimers.[8] ESR spectra of the polycrystalline sample of **2** showed the significant exchange narrowing below 20 K. It should be reminded that the ESR spectra of radical **1** with the exchange interaction of J/k= -26 K exhibit the significant narrowing below 10 K as described in section (A). The behavior of the ESR spectra of **2** is, therefore, consistent with the presence of the large intermolecular antiferromagnetic interaction of J/k = -55 K, which was determined by the analysis of the temperature dependence of the magnetic susceptibility.

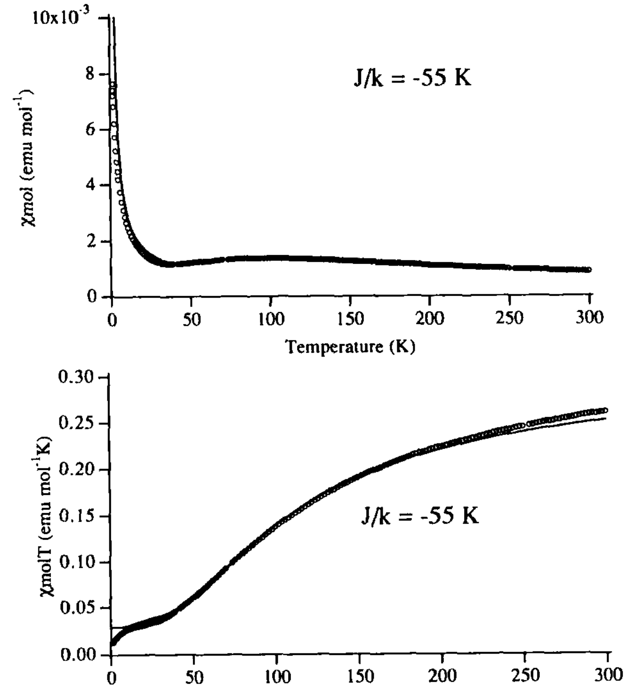


FIGURE 4 Temperature dependence of χ_{mol} and $\chi_{mol}T$. (a) χ_{mol} vs. T, (b) $\chi_{mol}T$ vs. T. (7 spin cluster 80%; 8 spin cluster 20%, radical concentration 86%)

(C) 3,5-dichloro-N-(arylthio)-2,4,6-triphenylanilino Radical, 3

In order to clarify the role of the substituted groups for the intermolecular magnetic interaction, we have also studied the stable radical **3** which has the chloro substituents at 3 and 5 positions instead of the nitro group. The magnetic behaviors of **3** is quite similar to those of the radical **2**. Thus, it has a large antiferromagnetic interaction similar in magnitude to **2** and the temperature dependence of the magnetic susceptibility was well analyzed using a finite-size linear chain cluster model. This finding indicates that the substituted groups are not essential for the large antiferromagnetic interaction. Therefore, it is concluded that the large antiferromagnetic interaction arises from the orbital overlap among the delocalized unpaired π orbital on the phenyl rings of **1** - **3**.

CONCLUSIONS

In this work, we have presented the strategy to prevent the dimerization among the radicals in the molecular crystals. In order to demonstrate the validity of this strategy, we have investigated the magnetic properties of three radicals **1** - **3** with the unpaired π orbital delocalized over the molecule. All of these examples show the occurrence of long-range magnetic-chain behaviors (at least 7 spin chain clusters) with large antiferromagnetic interactions, which is in agreement with our strategy. In this work, we have succeeded to obtain the infinite linear-chain antiferromagnetic system with the large intermolecular exchange interaction of $J/k= -26K$, which can be used for one of the two components in the organic ferrimagnetic systems.

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