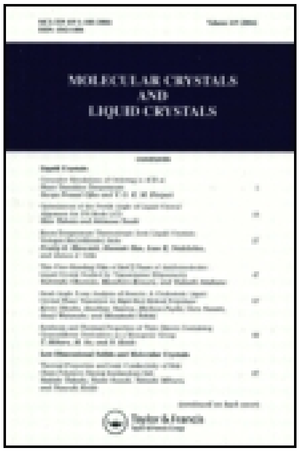

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A Single-Crystal Esr Study of Magnetism and Spin Dynamics in N-[(2,4-Dichlorophenyl)Thio]-2,4,6-Tripheyl-Phenylaminyl Radical Crystal

Yoshio Teki [a] , Yoshimasa Ohmura [a] , Koichi Itoh [a] & Yozo Miura [b]

[a] Department of Material Science, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka, 558, Japan

[b] Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka, 558, Japan

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A SINGLE-CRYSTAL ESR STUDY OF MAGNETISM AND SPIN DYNAMICS IN *N*-[(2,4-DICHLOROPHENYL)THIO]-2,4,6-TRIPHEYLPHENYLAMINYL RADICAL CRYSTAL

Yoshio Teki,[1]* Yoshimasa Ohmura,[1] Koichi Itoh,[1] and Yozo Miura[2]
Department of Material Science,[1] Faculty of Science; Department of Applied Chemistry,[2] Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558 Japan

Abstract A single-crystal ESR study of the magnetic properties of *N*-[(2,4-dichlorophenyl)thio]-2,4,6-triphenylphenylaminyl radical crystals is reported. The stable radical crystal shows a one-dimensional antiferromagnetic behavior which has described in terms of an alternating linear chain model with J/k_B = -7.5 K and an alternating parameter α=0.55. A detailed analysis of the angular and temperature dependence of the ESR linewidth and g-value has been carried out. The angular dependence of the line-width and line shape observed at 5 K has shown characteristic features expected for a one-dimensional magnetic system: $(3\cos^2\theta-1)^{4/3}$ angular dependence of line width and Lorentzian line shape at θ= 55°. Nagata's theory has applied for the analysis of the temperature dependence of the g-shift. However, the temperature dependence has been only qualitatively reproduced by the theory which is proposed for the one-dimensional regular Heisenberg model. We discuss on the origin of this unsatisfactory agreement. The magneto-structural correlation is also discussed based on the X-ray crystallographic and single-crystal ESR data.

INTRODUCTION

N-(Arylthio)-2,4,6-triarylphenylaminyl radicals are exceptionally stable and can be isolated as pure radical crystals.[1] These thioaminyl radicals are, therefore, a new class of stable free radicals as a promising candidate for organic molecular-based magnets. Most of the stable free radicals studied in the field of the molecular-magnetism have been limited to nitroxides and nitronyl nitroxides which have a localized unpaired electron spins.[2] The requirement of the large spin-polarization for the ferromagnetic intermolecular exchange[3] is easily realized for such localized spin-structures. Recently, the ferromagnetic exchanges have been found for the stable radicals with delocalized spin structures such as thioaminyl radicals[4,5] and thiooxoverdazyl radicals.[6] For thioaminyl radicals, three *N*-[(2,4-dichlorophenyl)thio]-2,4,6-tris(dichlorophenyl)phenylaminyl radicals have exhibited intermolecular ferromagnetic coupling with J/k_B = 1.8 - 14.0 K in the crystals. Although we have not yet succeeded to obtain the suitable single-crystals of these ferromagnetic thioaminyl radicals for the single-crystal X-ray structure analysis. On the other hand, a

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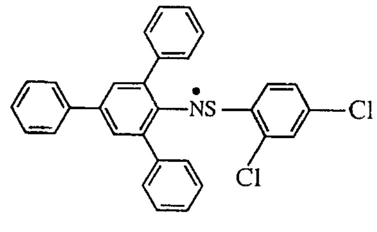
* Adjunct associate professor of Institute for Molecular Science (IMS). Part of this work was carried out at IMS.

structurally close, but antiferromagnetic, *N*-[(2,4-dichlorophenyl)thio]-2,4,6-triphenylphenylaminyl **1** has given sizable crystals′ and its molecular and crystal structures has been determined. In this paper we report a detailed single-crystal ESR study of the magnetism and spin dynamics of the antiferromagnetic radical **1**.



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EXPERIMENTAL

The free radical **1** was synthesized by the procedures which we have already reported.[1] The temperature dependence of the magnetic susceptibility was measured from 1.8 K to 298 K with a Quantum-Design MPMS2 SQUID magnetometer. The single-crystal ESR spectra were measured from 1.7 K to 298 K by an X-band Brucker ESR300 spectrometer equipped with an Oxford ESR910 variable temperature controller. The typically 5.0 x 1.0 x 0.2 mm size single-crystal was used for the ESR measurements. The single-crystal was mounted at the end of a quartz rod. In the X-ray crystal structural measurements, the black prismatic crystal of **1** was mounted on a glass fiber. All X-ray measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Cu-Kα radiation.

RESULTS AND DISCUSSION

(i) Magnetic Behaviors from 1.8 K to 298 K

The magnetic behavior of **1** from 1.8 K to 298 K was already reported in our previous paper.[5] We therefore describe only a brief summary of the results of the susceptibility

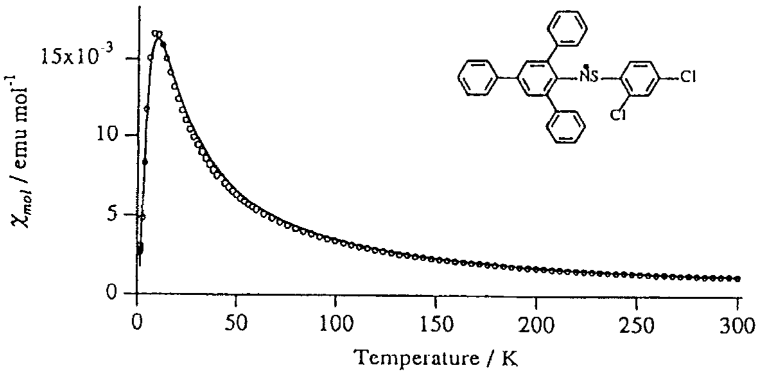

FIGURE 1. Temperature dependence of χ_{mol} of **1** from 1.7 K to 300 K.

measurements. Figure 1 shows χ_{mol} vs T plots of the polycrystalline sample of **1**. The temperature dependence of molar susceptibility (χ_{mol}) was well described in terms of an alternating linear chain model[7]:

$$H = -2J\Sigma[S_{2i}\cdot S_{2i-1} + \alpha S_{2i}\cdot S_{2i+1}]. \qquad (1)$$

The best-fit parameters are obtained to be J/k_B = -7.5 K and α=0.55.

(ii) Single-Crystal ESR

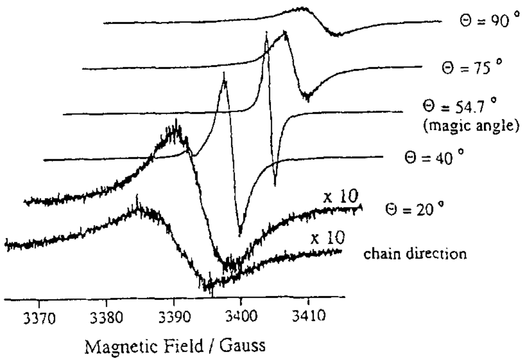

FIGURE 2. Angular dependence of ESR spectra observed at 5 K

ESR spectra have shown a drastic angular dependence of the g-value and line-width at low-temperatures. Figure 2 shows a stack plots of the ESR spectra observed at 5 K when the external magnetic directions have rotated from the interacting chain axis (a longest edge direction in the present single-crystal). The observed g values show an axial angular dependence as shown in Figure 3. The angular dependence of the g value is well fitted to the expression

$$g = g_{\perp} + (g_{//} - g_{\perp})\cos^2\theta \qquad (2)$$

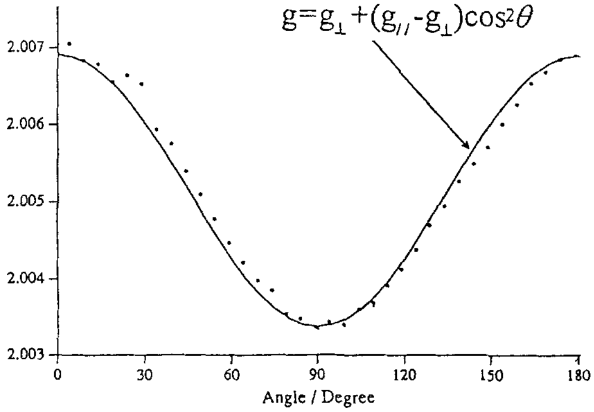

FIGURE 3. Angular dependence of g value observed at 5 K.

The spectra show the minimum line-width and Lorentzian line-shape at the magic angle direction (θ= 54.7°). The peak-to-peak line-width (ΔHpp) at 5 K is ca. 12 G at the interacting chain axis (θ = 0°), ca. 1 G at the magic angle direction, and 5.5 G at the perpendicular direction (θ = 90°). The variation of the peak-to-peak line-width as a function of θ observed at 5 K is shown in Figure 4. The variation shows the features expected for one-dimen-sional interacting spin system: $(3\cos^2\theta-1)^{4/3}$ angular dependence with minima at line width and Lorentzian line shape at θ = 54.7° and 126.3°. As shown by the solid line in Figure 4, the experimental data are well fitted to the following expression

$$\Delta H\mathrm{pp}(\theta)= A|3\cos^2\theta-1|^{4/3}+B \quad (3)$$

where A and B are constants.

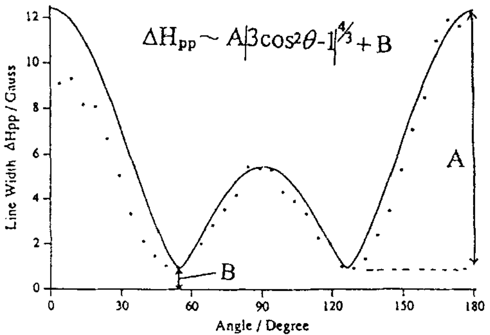

FIGURE 4. Angular dependence of ESR line width ΔHpp at 5 K.

Figure 5 shows the temperature dependence of the resonance field shifts (g-shifts) for the directions of θ = 0°, 54.7°, and 90°. As pointed out by Richards *et al.*,[8] there are two mechanisms for the g-shits in the exchange correlated spin systems. One is a classical effect which comes from the mean dipolar field. The other is the dynamical and quantum mechanical effect which comes from the exchange spin correlation. In the present system, the latter effect is dominant since the classical dipolar interaction is small in magnitude compared with the exchange interaction of J/k_B = -7.5 K. For the one-dimensional Heisenberg model, the theory which describes the angular and temperature dependence of the ESR line-width and the g-shifts has been proposed by Tazuke and Nagata.[9] The theory has well explained the angular and tempera-ture variations of the ESR spectra of $CsMnCuCl_3\bullet 2H_2O$ single-crystal. Since the magnetic properties of the present system has been well interpreted in terms of the alternating Heisenberg linear chain model with J/k_B = -7.5 K and α=0.55, the following modification of the effective exchange has been done when we apply the Nagata's theory[9] to our system.

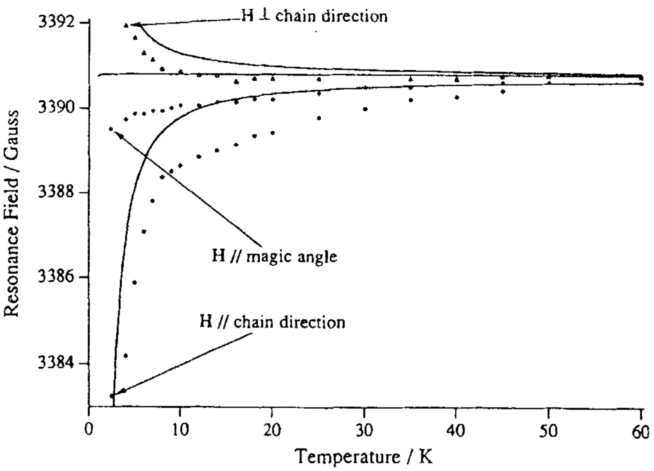

FIGURE 5. Temperature dependence of the resonance field. Solid curves are theoretical.

$$J_{eff} = \sqrt{J\alpha J}. \quad (4)$$

Thus, the averaged value of J and αJ has been used for the effective exchange interaction.

According to Nagata's theory, the temperature dependence of the resonance field H has been calculated by the following expressions,

$$h\nu = g\mu_B H[1 + (3\cos^2\theta - 1)\delta] \tag{5}$$

where

$$\delta = 3g^2\mu_B^2 S(S+1)\{(2+u/K)/(1-u)^2 - 2K/3\}/5k_BTr_0^3, \tag{6}$$

$$K = -2|J|S(S+1)/k_BT, \tag{7}$$

and

$$u = \coth K - 1/K. \tag{8}$$

The calculated results are shown by the solid curves in Figure 5. The solid curves explain the direction of the resonance field shifts and its magnitude. In the temperature region which the thermal energy k_BT is comparable with the exchange interaction, the agreement is somewhat unsatisfactory. This may be due to the simple approximation of equation (4). In the temperature region, it is expected that the effect of the amplitude alternation of the exchange interactions plays an important role for the g-shift since the coherent length among the spins becomes short as a result of the thermal fluctuation.

Under such conditions, the approximation of equation (4) is not valid and the equations (5) - (8) derived for the regular Heisenberg model can be not straightforwardly applicable to the alternating linear chain system. In order to reproduce the g-shift in the temperature region of $k_BT \sim J$, it will be necessary to make an exact numerical treatment of the spin-correlation function $\langle S_m^z S_{m+1}^z - S_m^x S_{m+1}^x \rangle$ etc. in the limited size spin system with the alternating exchange interaction.

(iii) X-ray Crystallographic Data and Magneto-Structural Correlation

A part of the X-ray crystallographic data was already reported in our previous paper.[1] The following X-ray analysis was made on the same single-crystal used in the ESR experiments. The space group was determined uniquely to be $P2_1/c$, a= 15.548(4) Å, b=6.328(5) Å, c=25.809(4) Å, β=104.40(2)°, Z=4. The full matrix least-squares refinement was carried out based on 2575 observed reflections and 340 variable parameters and converged with R=0.041 and R_w=0.039. Figure 6 shows the determined molecular and crystal structures of **1**. The N and S atoms are coplanar with the benzene ring A. This benzene ring makes a dihedral angle of 19.5° with the benzene ring E. The dihedral angle between the benzene rings A and D is 27.7°, while those between A and B and between A and C are 49.6° and 86.5°, respectively. On the basis of the crystallographic data, it is concluded that a conjugated π electron network is formed among the A, D, and E benzene rings and N and S atoms.

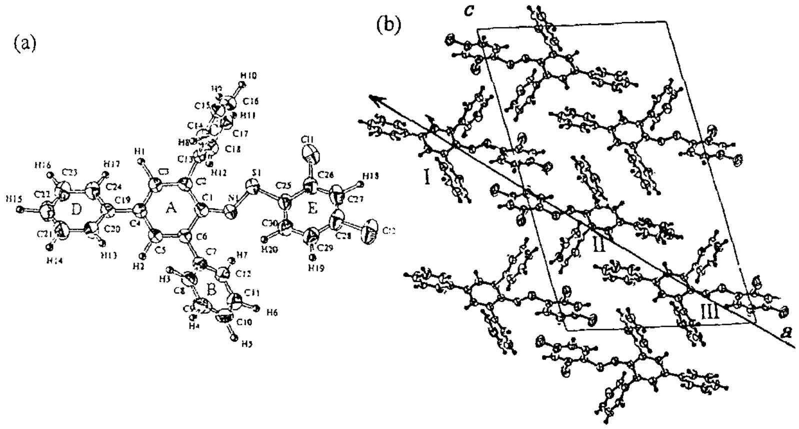

FIGURE 6. Molecular and Crystal structures of **1**. (a) molecular structure, (b) crystal structure

The interacting chain direction determined by the single-crystal ESR study is also shown in Figure 6(b). This interacting direction is located in the crystallographic *ac* plane. According to the molecular and the crystal structure, the π orbital on the benzene ring E in molecule I overlap with that of the benzene ring E in the neighboring molecule II, while the π orbital on the benzene ring D in II overlap with that in III. This crystal packing form is consistent with the magnetic property of the present crystal of **1**, the alternating linear chain Heisenberg model.

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REFERENCES

1. Y. Miura, A. Tanaka, and K. Hirotsu, J. Org. Chem., 56, 6638 (1991).
2. For recent overvies on this topic, see J. S. Miller, A. J. Epstein Eds., Mol. Cryst. Liq. Cryst., 271/272/273/274, 1-867 (1995).
3. K. Awaga, T. Sugano, and M. Kinoshita, Chem. Phys. Lett., 141, 540 (1987).
4. Y. Teki, K. Itoh, Y. Miura, Y. Kitagishi, and S. Ueno, Mol. Cryst. Liq. Cryst., 272, 23 (1995).
5. Y. Teki, Y. Tajima, K. Itoh, S. Ueno, Y. Kitagishi, and Y. Miura, Mol. Cryst. Liq. Cryst., 278, 301 (1996).
6. K. Mukai, K. Nedachi, J. B. Jamai, and N. Achiwa, Chem. Phys. Lett., 214, 559 (1993).
7. W. Duffy, Jr. and K. P. Barr, Phys. Rev., 165, 647 (1968).
8. P. M. Richards and M. B. Salamon, Phys. Rev., 9B, 32 (1974).
9. Y. Tazuke and K. Nagata, J. Phys. Soc. Jpn., 38, 1003 (1975).