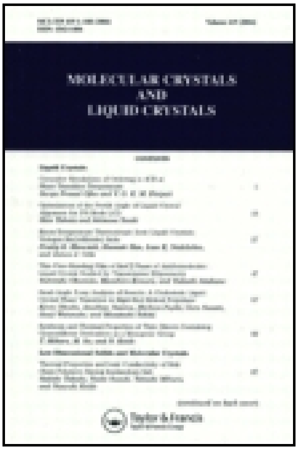


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Ferro- and Antiferromagnetic Behaviors of Stable Free Radical Crystals of N-(Arylthio)-2,4,6-Triarylphenylaminyls

Yoshio Teki [a] [b] , Yuko Tajima [a] , Koichi Itoh [a] , Sadaharu Ueno [c] , Yuichi Kitagishi [c] & Yozo Miura [c]

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

[b] Institute for Molecular Science, Myodaijicyou, Okazaki, 444, JAPAN

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

Version of record first published: 24 Sep 2006.

To cite this article: Yoshio Teki , Yuko Tajima , Koichi Itoh , Sadaharu Ueno , Yuichi Kitagishi & Yozo Miura (1996): Ferro- and Antiferromagnetic Behaviors of Stable Free Radical Crystals of N-(Arylthio)-2,4,6-Triarylphenylaminyls, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 278:1, 301-308

To link to this article: http://dx.doi.org/10.1080/10587259608033688

Mol. Cryst. Liq. Cryst., 1996, Vol. 278, pp. 301–308
Reprints available directly from the publisher
Photocopying permitted by license only

FERRO- AND ANTIFERROMAGNETIC BEHAVIORS OF STABLE FREE RADICAL CRYSTALS OF *N*-(ARYLTHIO)-2,4,6-TRIARYLPHENYLAMINYLS

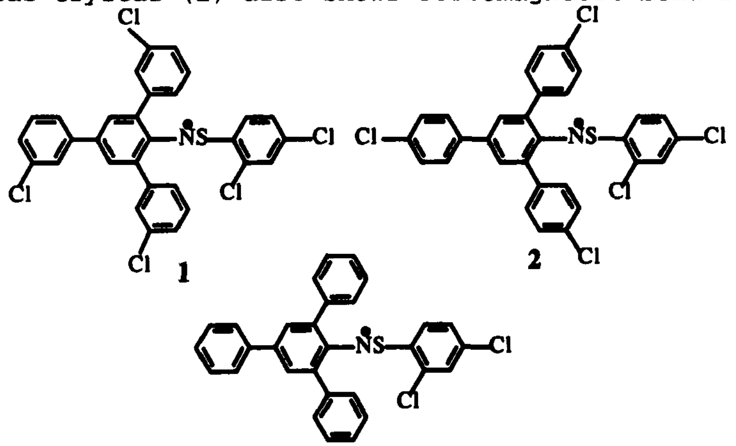
YOSHIO TEKI,[a,b] YUKO TAJIMA,[a] KOICHI ITOH,[a] SADAHARU UENO,[c] YUICHI KITAGISHI,[c] YOZO MIURA[c]
[a]Department of Material Science, Faculty of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558, JAPAN, [b] Institute for Molecular Science, Myodaijicyou, Okazaki 444, JAPAN, [c]Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558, JAPAN

Abstract As promising candidates for organic molecule-based ferromagnets, we have investigated several stable thioaminyl radicals in the solid states. In addition to *N*-[(2,4-dichlorophenyl)thio]-2,4,6-tris(3-chlorophenyl)-phenylaminyl (**1**) which we have already reported (Mol. Cryst. Liq. Cryst., in press (1995)), other thioaminyl radical crystal showing ferromagnetic behaviors have been found. Thus, *N*-[(2,4-dichloro-phenyl)thio]-2,4,6-tris(4-chlorophenyl)phenylaminyl (**2**) radical shows one-dimensional ferromagnetic behavior. The magnetic behavior has been well interpreted in terms of the one-dimensional Heisenberg model with ferromagnetic intermolecular interactions of $J/k = 14.0$ K. In contrast, *N*-[(2,4-dichlorophenyl)thio]-2,4,6-tris(4-chlorophenyl)-phenylaminyl (**3**) shows antiferromagnetic behavior described by an alternating linear chain model with $J/k = -8.4$ K and $\alpha=0.55$.

INTRODUCTION

Organic free radicals and their intermolecular magnetic interactions in the solid states have widely been investigated in the field of the molecular magnetism. Almost of such studies, however, have been limited to stable nitroxide and nitronyl nitroxide free radicals in which the unpaired electron is localized in the N-O function. Some of the nitroxide and nitronyl nitroxide radicals show bulk ferromagnetic transitions at very low temperatures;[1-5] e.g. 2-(4-nitrophenyl)nitronyl nitroxide has a Curie temperature (*Tc*) of 0.60 K. As a result of their localization of the unpaired electron, the intermolecular interactions are small in magnitude. Only 3-(4-chloro-phenyl)-1,5-dimethyl-6-thiooxoverdazil radical crystals have been recently reported as an example of a ferromagnetic free radical with a delocalized spin structure.[6]

As part of our program directed toward purely organic molecule-based magnetism we have studied a new class of stable free radicals, N-(aryltho)-2,4,6-triarylphenylaminyl.[7,8] These stable radicals have the delocalized spin structures. The unpaired electron in a singly occupied molecular orbital (SOMO) is extensively delocalized over the whole molecule; ~40% of the unpaired spin is on the nitrogen and ~20% is on the sulfur, the residual spin being delocalized onto the five phenyl ring via π-conjugation. This extensive delocalization of the unpaired spin is characteristic of this radical, being in contrast to nitroxide and nitronyl nitroxide radicals reported so far. We have already reported that *N*-[(2,4-dichlorophenyl)thio]-2,4,6-tris(3-chlorophenyl)phenylaminyl (**1**) shows ferromagnetic intermolecular interaction.[9] The temperature dependence of the magnetic susceptibility was interpreted well in terms of the one-dimensional Heisenberg model with *J/k* = +5.7 K. Recently, we have found that *N*-[(2,4-dichlorophenyl)thio]-2,4,6-tris(4-chloro-phenyl)phenylaminyl radical crystal (**2**) also shows ferromagnetic behavior. . In



1

2

3

contrast to these two radicals, *N*-[(2,4-dichlorophenyl)-thio]-2,4,6-tris(phenyl)phenylaminyl (**3**) radical crystal has shown antiferromagnetic behavior. In this paper, we report on their magnetic behaviors.

EXPERIMENTAL

Magnetic Susceptibility Measurements

We have already reported the preparation of stable free radical **1**. The free radicals, **2** and **3**, were also synthesized by the similar procedures. The radical samples used for the magnetic studies were carefully purified by repeated recrystallization from hexane and dried for 5 h in vacuum. For the magnetic susceptibility measurements polycrystalline samples were used.

RESULTS AND DISCUSSION

Only a brief summary of the results on **1** is given here because the magnetic behavior has been already reported.[9]. The temperature dependence of the molar susceptibility (χmol) of the polycrystalline sample of **1** is well interpreted by a regular one-dimensional Heisenberg model with ferromagnetic intermolecular interaction of J/k = 5.7 K. However, the crystal structure is still unknown because the suitable size of the crystal is not obtained. Hereafter, we describe the magnetic behaviors of **2** and **3** in this paper.

(i) *N*-[(2,4-dichlorophenyl)thio]-2,4,6-tris(4-chlorophenyl)-phenylaminyl (**2**)

Figure 1 shows the temperature dependence of $\chi_{mol}T$ values of the polycrystalline sample of **2**. All of the susceptibility data have been corrected for the diamagnetic contribution estimated from the Pascal's sum rule. The reciprocal susceptibility is also shown in figure 1. The $\chi_{\mathrm{mol}}T$ values begin to increase around 50 K and

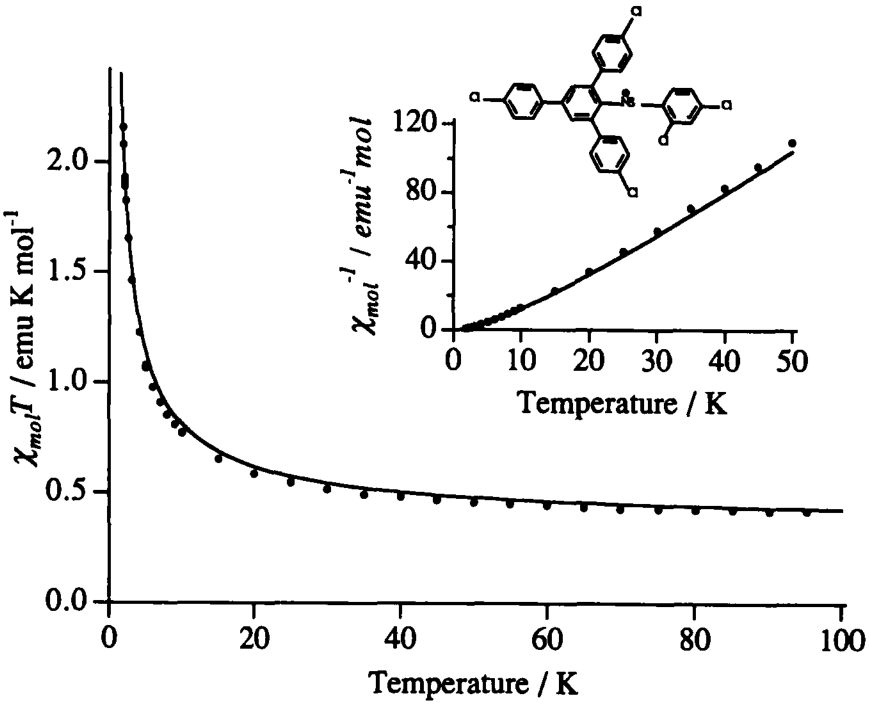


FIGURE 1. Temperature dependence of $\chi_{mol}T$ of N-[(2,4-dichlorophenyl)thio]-2,4,6-tris(4-chlorophenyl)phenylaminyl, **2**

sharply increase at a temperature lower than 10 K. This magnetic behavior exhibits that the magnetic interactions among the radicals are ferromagnetic in the crystals. On the other hand, the $\chi_{mol}T$ value (0.41 - 0.42 emu K mol^{-1}) in the high temperature region of 200 - 300 K is close to the theoretical value (0.376 emu K mol^{-1}) for the noninteracting S = 1/2 spin system of free electron with g value (2.0054), indicating that the spin concentration of **2** is ~100%. The difference between the observed values 0.41-0.42 at 200 - 300 K and 0.376 of the free spin value is attributable to the influence of the ferromagnetic intermolecular interaction remaining even at the high-temperature region. Thus, even at 200-300 K, the spins interact with each other in this crystal. The reciprocal susceptibility is also shown in Fig. 1 as an inset. The solid curves in both figures were theoretically calculated on the basis of the high-temperature series expansion for the magnetic susceptibility of the one-dimensional regular Heisenberg model which is given by [10]

$$\chi_{mol} = \frac{Ng^2\mu_B{}^2}{4kT} \times \left[\frac{1.0+5.797992X+16.90265X^2+29.37689X^3+29.83296X^4+14.03692X^5}{1.0+2.798992X+7.00868X^2+8.053864X^3+4.574311X^4}\right]^{3/2} \quad (1)$$

where X= $J/2kT$ and N is the Avogadro number. The intermolecular exchange interaction (J/k) is ferromagnetic and its best fit value has been obtained as +14.0 K using the experimental data below 100 K. The magnitude of the ferromagnetic intermolecular interaction is large compared with other pure organic ferromagnetic molecular crystals. In this calculation we used the Curie constant ($C=Ng^2\mu_B{}^2S(S+1)/3kT$) of 0.376 emu K mol^{-1} which was obtained using g = 2.0054 as determined from the ESR signal at room temperature. The fit between the observed and calculated values is quite well. It is, therefore, concluded that the magnetic behavior of this material can be explained by an ideal one-dimensional Heisenberg ferromagnet with an isotropic J value. The external magnetic field dependence of the magnetization (M_{mol}) measured at 1.7 - 10 K is shown in Fig. 2. The solid curves represent the magnetization

$$M_{mol}(\eta) = N\mu_B B(\eta)/n \quad (2)$$

which is calculated for S = 2 - 10 states constructed by S = 1/2 species, where $B(\eta)$ is the simple Brillouin function with $\eta = g\mu_B H/kT$ without the correction of the molecular field (λM) arising from the short-range ordering[12] and n is the number of spins used to construct a magnetic cluster with a spin quantum number S. Therefore, n is equal to $2S$ and the saturation magnetization of all curves reaches a constant value of ca. 5580 emu G mol^{-1} in the high field/temperature region. It is also obvious from Figure 2 that the magnetization grows slowly and the slopes of the curves in the low-field region become steeper with decreasing temperature. The experimental data in the low field/temperature region fit well with the Brillouin function drawn for S = 6.5 at 2.0 K (see, the inset of Figure 2). In order to check whether this material becomes a ferromagnet or not, further low temperature measurements of the magnetic susceptibility are in progress.

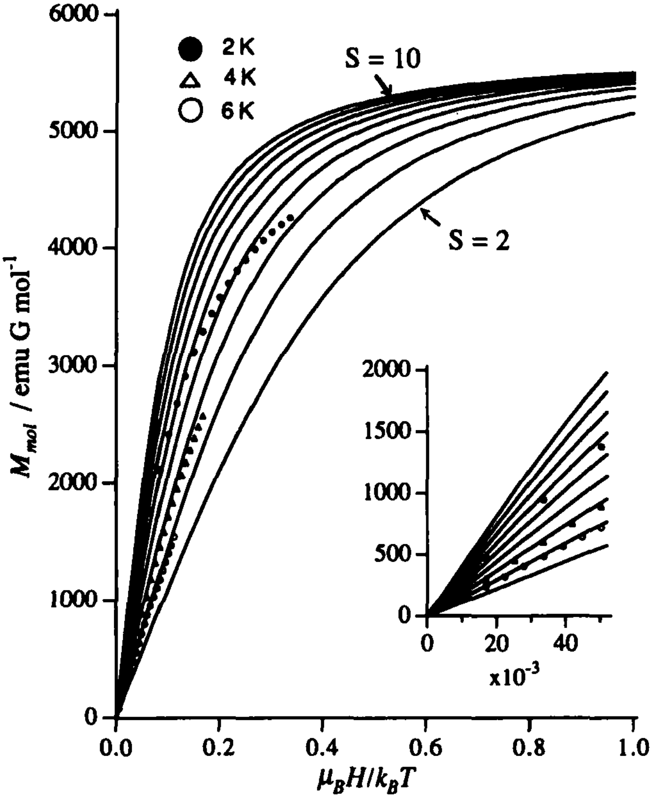


FIGURE 2. The magnetization isotherms for **2** at 2.0, 4.0 and 6.0 K.

(ii) *N*-[(2,4-dichlorophenyl)thio]-2,4,6-triphenylphenylaminyl (**2**)

Figure 3(a) and 3(b) show the temperature dependence of χ_{mol} and a plot of $\chi_{mol}T$ vs.T of the radical **3**, respectively. As shown in Figure 3(b), the intermolecular interaction in this crystal is antiferromagnetic in contrast to **1** and **2**. The least-square fitting analysis was carried out using the data lower than 100 K. The temperature dependence was well interpreted in terms of the following alternating linear-chain model with J/k = -8.4 K (antiferromagnetic) and an alternating parameter, α = 0.55.

$$\mathcal{H} = -2J\sum_{i}\{S_{2i}S_{2i-1} + \alpha S_{2i}S_{2i+1}\} \tag{3}$$

The solid curves in both figures were theoretically calculated on the basis of the high-temperature series

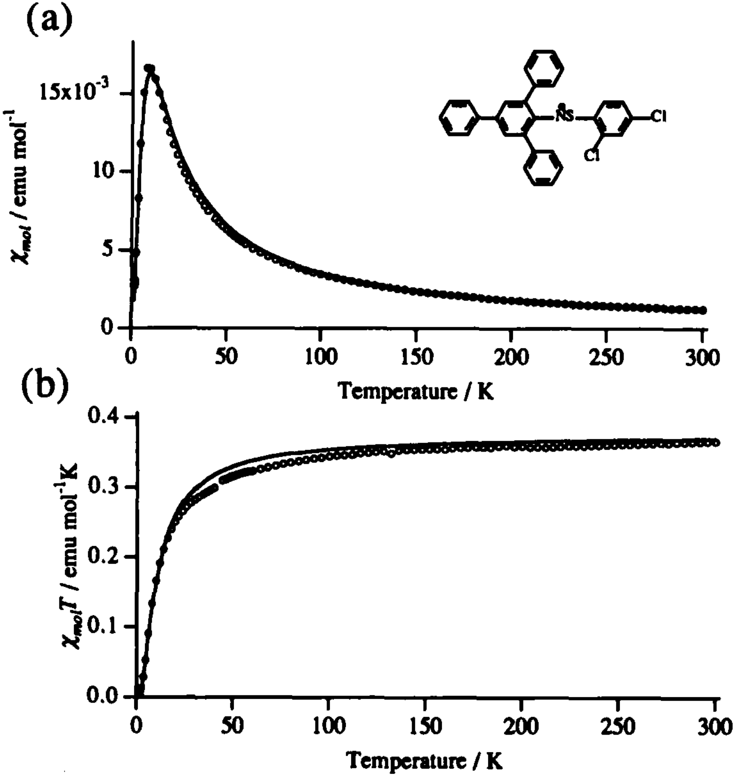


FIGURE 3. Temperature dependence of χ_{mol} and $\chi_{mol}T$ of **3**. (a) χ_{mol} vs. T, (b) $\chi_{mol}T$ vs. T

expansion.[11] The X-ray structural analysis was succeessful only for this material **3**. Although the crystal structural data are unknown for radicals **1** and **2**, the origin of the change of the sign of the intermolecular magnetic interaction might be due to their crystal structures.

CONCLUSIONS

A new example of the ferromagnetic molecular crystal of a stable thioaminyl radical with the delocalized unpaired π

electron in the molecule has been obtained. Thus, the molecular crystals of **1** and **2** show ferromagnetic intermolecular interaction. The magnitude of their FM interaction is fairly large. We can, therefore, conclude that thioaminyl radicals are one of the promising candidates for organic molecule-based ferromagnets.

ACKNOWLEDGMENTS

The present work was partly supported by Grant-in-Aid for Scientific Research on Priority Area "Molecular Magnetism" (Area No.228 04242105/06218226) from the Ministry of Education, Science and Culture, Japan.

REFERENCES

1. M. Kinoshita, P. Turek, M. Tamura, K. Nozawa, D. Shiomi, Y. Nakazawa, M. Ishikawa, M. Takahashi, K. Awaga, T. Inabe, and Y. Maruyama, Chem. Lett., 1225 (1991).
2. R. Chiarelli, M.A. Novak, A. Rassat, and L. Tholence, Nature, 363, 147 (1993).
3. P.-M. Allemand, K.C. Khemani, A. Kuch, F. Wudl, K. Holczer, S. Donovan, G. Gruner, and J.D. Thompson, Science, 235, 301 (1991).
4. T. Nogami, K. Tomioka, T. Ishida, H. Yoshikawa, M. Yasui, F. Iwasaki, H. Iwamura, N. Takeda, and M. Ishikawa, Chem. Lett., 29 (1994); T. Ishida, H. Tsuboi, T. Nogami, H. Yoshioka, M. Yasui, F. Iwasaki, H. Iwamura, N. Takeda, and M. Ishikawa, Chem. Lett., 919 (1994).
5. T. Sugawara, M. M. Matsushita, A. Izuoka, N. Wada, N. Takeda, and M. Ishikawa, J. Chem. Soc., Chem. Commun., 1723 (1994).
6. K. Mukai, K. Nedachi, J.B. Jamai, and N. Achiwa, Chem. Phys. Lett., 214, 559 (1993).
7. Y. Miura, A. Tanaka, and K. Hirotsu, J. Org. Chem., 56, 6638 (1991).
8. Y. Teki, Y. Miura, A. Tanaka, T. Takui, and K. Itoh, Mol. Cryst. Liq. Cryst., 233, 119 (1993).
9. Y. Teki, K. Itoh, T. Takui, Y. Miura, Y. Kitagishi, and S. Ueno, Mol. Cryst. Liq. Cryst., in press (1995).
10. G.A. Baker, Jr., G.S. Rushbrooke, and H.E. Gilbert, Phys. Rev., 135A, 1272 (1964).
11. W. Duffy, Jr. and K. P. Barr, Phys. Rev., 165, 647 (1968).