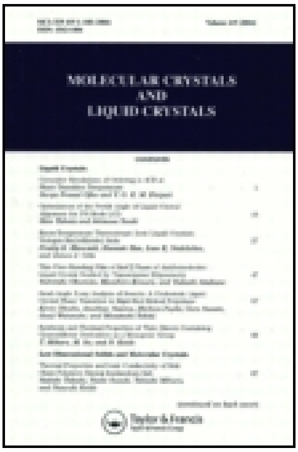

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MAGNETIC PROPERTIES AND CRYSTAL STRUCTURES OF 1,5-BIS(4-NITROPHENYL)-3-*t*-BUTYLVERDAZYL RADICALS

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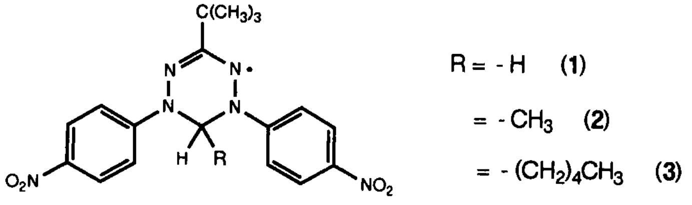
Abstract The crystal structures and magnetic properties of 1,5-bis(4-nitrophenyl) derivatives of verdazyl free radicals (**1**–**3**) are described. The magnetic properties of **1** are explained by the singlet-triplet model with the coupling constant $2J_{AF}/k_B$ = 93 K. The susceptibility of **2** was fitted by the Bonner-Fisher model with J_{AF}/k_B = 5.6 K. These results were in good agreement with the molecular arrangement in the crystal. The susceptibility of **3** obeyed the Curie-Weiss law with the Weiss constant $\theta = -0.5$ K. The magnetic intermolecular interactions were significantly suppressed by introducing the substituent at the 6-position.

INTRODUCTION

Recently, the magnetic properties of organic free radicals and metal complexes are intensely investigated seeking for ferromagnetic interactions between the spins in solids.[1] Among others, the nitronyl nitroxide-type free radical having nitro group, *p*-nitrophenyl nitronyl nitroxide has shown a ferromagnet transition at low temperature.[2] However, the intermolecular magnetic interactions in nitronyl nitroxide-type free radicals, either ferromagnetic or antiferromagnetic, are relatively small due to the strong localization of an unpaired electron at nitroxide group,[3] which makes it difficult to investigate the relationship between the molecular arrangement and magnetic properties.



Scheme I

Verdazyl-type free radicals, first synthesized by Kuhn's group[4] are also known as stable free radicals. The magnetic properties of the solids are studied for various kinds of derivatives.[5] Recently, Allenmand *et al.* have reported that a verdazyl radical having nitro groups shows a ferromagnetic intermolecular interaction.[6] The unpaired electrons in verdazyl radicals have a large population on four nitrogen atoms of the center ring. However, they also have a significant amount of population on the aromatic substituent at 1- and 5-positions. Namely the degree of localization of unpaired electrons is not so large compared with that of nitronyl nitroxide radicals,[7] which enables close spin interactions through the contacts of substituent aromatic groups. In this study, we examine the structures and magnetic properties of three verdazyl radicals having nitrophenyl groups at 1- and 5-positions (Scheme I) to clarify the conditions for realizing stronger intermolecular magnetic interactions.

EXPERIMENTAL

Verdazyl-type radicals were synthesized according to the literature.[4] X-ray diffraction data were collected using a RIGAKU AFC-5 fourcycle diffractometer for a crystal of **1** and an ENRAF-NONIUS CAD4 diffractometer for a crystal of **2**. Crystal data are shown in Table I. Temperature dependence of magnetic susceptibility was measured by Faraday method using a Kahn electric balance and an Oxford superconductor magnet.[8]

Table I. Summary of Crystal Data.

compound	**1**	**2**
space group	$Pna2_1$	$P2_1/c$
a, Å	17.316(5)	15.126(1)
b, Å	18.391(7)	12.231(1)
c, Å	11.901(5)	11.575(1)
β, deg	105.56(1)	107.667(4)
V, Å^3	3790(2)	2040.3(3)
Z	8	4
ρ(calc), g cm^{-3}	1.34	1.294

RESULTS AND DISCUSSION

Verdazyl 1

Figure 1 shows the crystal structure of **1**. The crystal is composed of head-to-head radical dimer. Four radical dimers are aligned in a unit cell in such a manner that each dipole moment is canceled. Figure 2 shows the interdimer molecular arrangements. The intermolecular short contacts between the nitrophenyl groups are clearly seen in Fig. 2 compared with those between the center ring having a bulky *t*-butyl group. This suggests that the magnitude of the intermolecular contact is enhanced by introducing polar nitro groups.

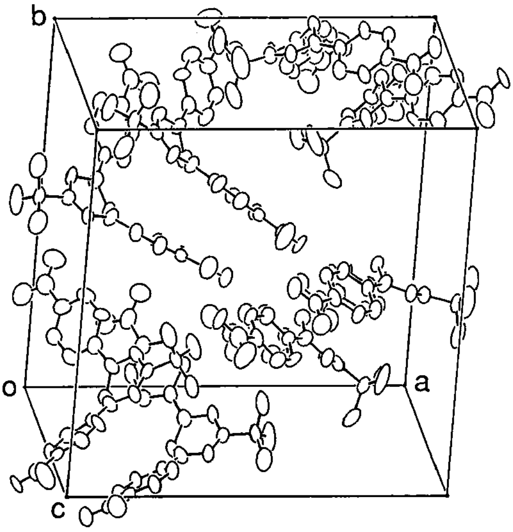


FIGURE 1. The crystal structure of verdazyl radical **1**.

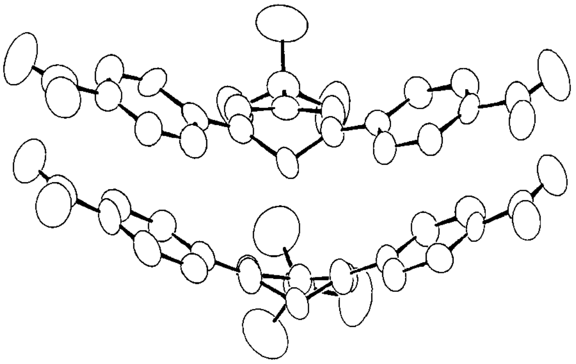


FIGURE 2. The interdimer molecular arrangement of **1**

Figure 3 shows the temperature dependence of magnetic susceptibility of **1**. The susceptibility increases with a decrease in temperature reaching a maximum at around 100 K. Below that temperature the susceptibility decreases with decreasing temperature and again slightly increases at low temperatures due to the contribution of the Curie spins at lattice defects. These results strongly suggest the relatively large interdimer antiferromagnetic interactions. In fact, the observed temperature dependence of susceptibility is explained by the singlet-triplet model taking the Curie spins into account. The solid curve in Fig. 3 is a theoretical curve,

$$\chi_P = \frac{C}{T}\frac{4\exp(-2J_{AF}/k_BT)}{1+3\exp(-2J_{AF}/k_BT)} + \frac{C_{imp}}{T}$$

with $2J_{AF}/k_B = 93$ K, $C = 0.376$ emuKmol^{-1} and $C_{imp} = 0.0037$ emuKmol^{-1}. The antiferromagnetic interaction is the strongest in this radical solid as far as we are aware for the verdazyl-type free radicals.

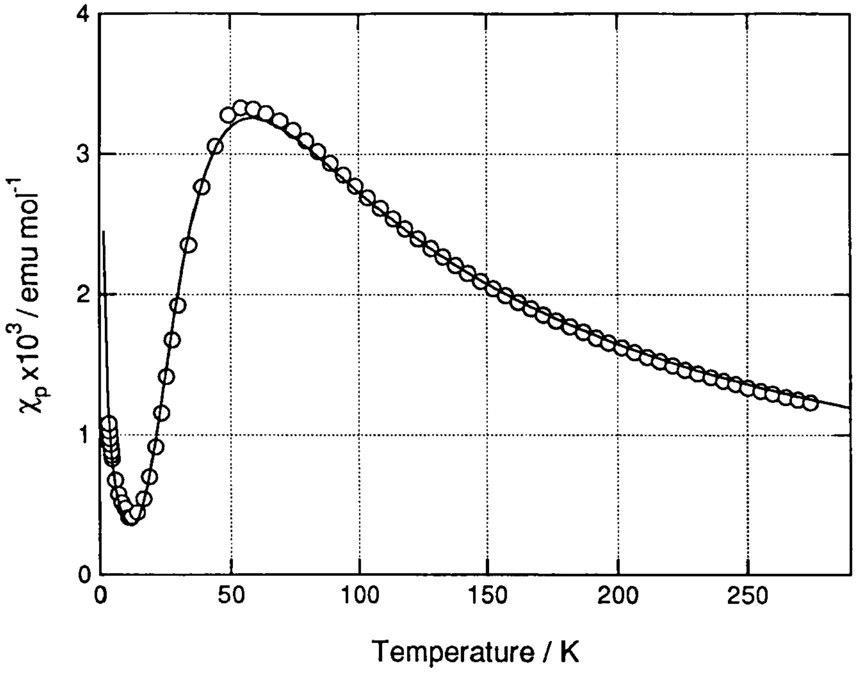


FIGURE 3. Temperature dependence of susceptibility of **1**. The solid curve is the theoretical fit (see text).

Verdazyl **2**

The molecules in the crystal of **2** form a 1-dimensional regular stack along the c axis as is shown in Fig. 4. Figure 5 shows a view of the unit cell projected along c axis. In the 1-dimensional chain, one of the two nitrophenyl groups of the molecule has short contacts with one of the two neighboring molecules, while the other nitrophenyl group is located near the other neighboring molecule. Molecules could not form dimers as is seen in crystal of **1** probably due to the steric hindrance of the methyl group introduced at center ring.

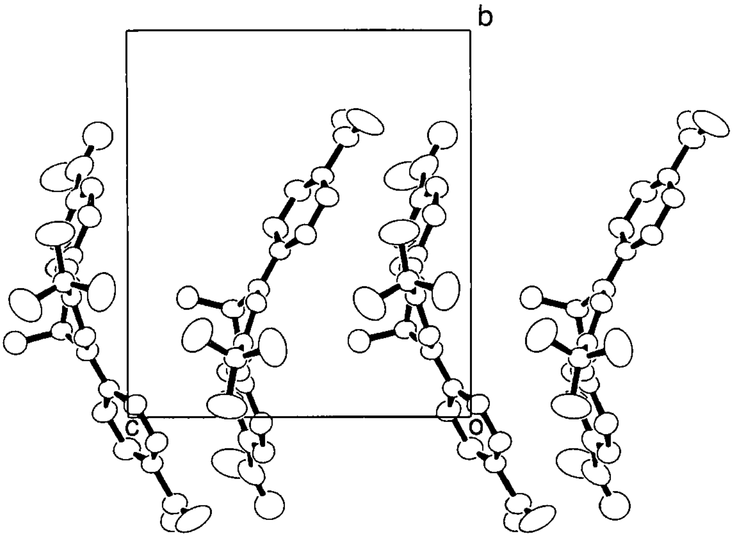


FIGURE 4. 1-dimensional stacking chain in verdazyl **2** projected along the a axis.

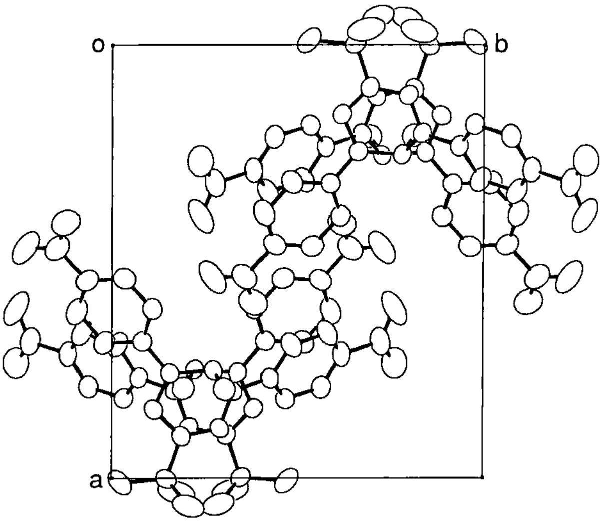


FIGURE 5. A view of the unit cell projected along the c axis.

Figure 6 shows the temperature dependence of the magnetic susceptibility of **2**. The inset shows the low-temperature portion of the same curve enlarged in abscissa. The susceptibility increases with a decrease in temperature down to around 10 K and decreases below that temperature. However, the susceptibility seems to have a finite value at 0 K. These results indicate the weak antiferromagnetic interactions in the 1-dimensional chains in the crystal. The solid curve in Fig. 5 represents a theoretical curve of the Bonner-Fisher model,

$$\chi_p = \frac{C}{T}\left\{\frac{1+5.7979916K+16.902653K^2+29.376885K^3+29.832959K^4+14.036918K^5}{1+2.7979916K+7.0086780K^2+8.6538644K^3+4.5743114K^4}\right\}^{\frac{2}{3}}$$

where $K = J/2k_BT$ with $J_{AF}/k_B = 5.6$ K and $C = 0.376$ emuKmol^{-1}. The facts that the magnetic susceptibility is explained by the 1-dimensional antiferromagnetic chain and that the weaker intermolecular magnetic interactions compared with that of **1** are in good agreement with the molecular arrangement of **2** in the crystal.

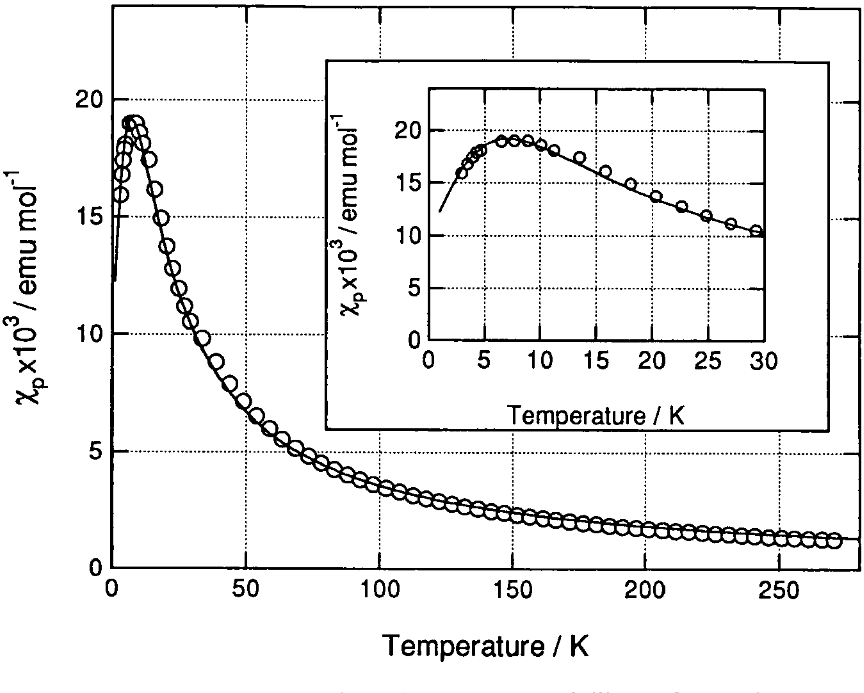


FIGURE 6. Temperature dependence of susceptibility of **2**. The inset shows the low-temperature portion of the same curve enlarged in abscissa. The solid curve is the theoretical fit (see text).

Verdazyl **3**

Figure 7 shows the temperature dependence of the magnetic susceptibility of **3**, the inset indicating the linear relationship between the inverse susceptibility and temperature. The susceptibility obeys the Curie law in the measured temperature range and the magnetic intermolecular interactions are very small. The solid curve in Fig.7 represents the Curie–Weiss law,

$$\chi_p = \frac{C}{T-\theta}$$

with C = 0.376 emuKmol^{-1} and θ = −0.5 K. The intermolecular magnetic interactions are strongly suppressed by introducing a longer alkyl chain at the 6-position.

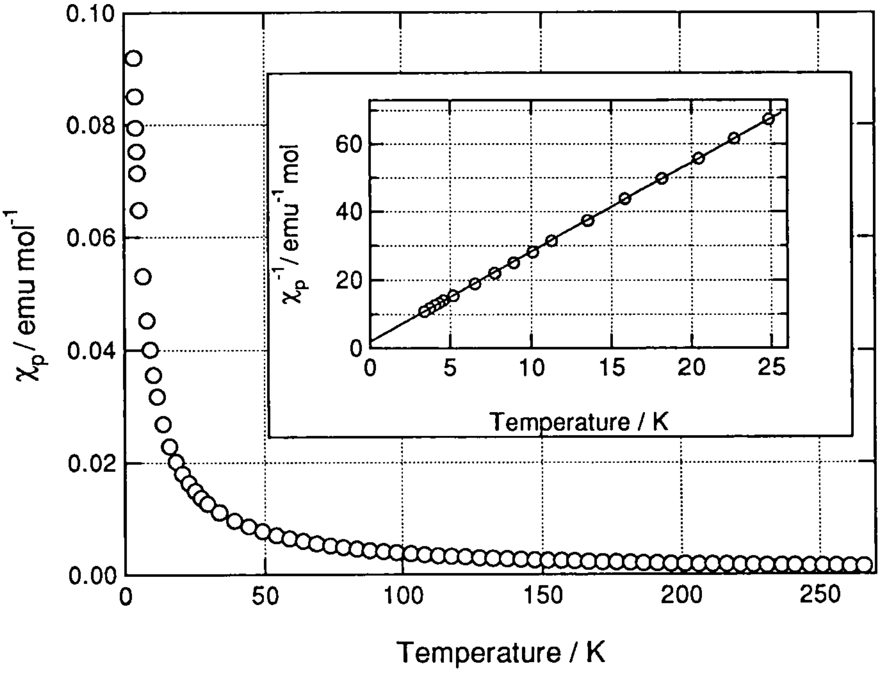


FIGURE 7. Temperature dependence of susceptibility of 3. The inset indicates the linear relationship between the inverse susceptibility and temperature. The solid line is the theoretical fit (see text).

CONCLUSION

The magnetic properties of verdazyl radicals **1** and **2** were explained by an antiferromagnetic dimer model and a 1-dimensional antiferromagnetic spin chain, respectively. Each magnetic property was in good agreement with the molecular arrangement in the crystal. These molecular arrangements should be determined by the attractive force between the nitrophenyl groups of neighboring molecules. Intermolecular distance of **1** is short due to the attractive force of the nitrophenyl groups resulting in strong antiferromagnetic intermolecular interactions. The interaction is strongly suppressed by the introduction of the alkyl group at the 6–position.

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