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Magnetism in organic diradical ion salts based on nitronyl nitroxide

Tadashi Sugano [a,*], Stephen J. Blundell [b], William Hayes [b], Peter Day [c]

[a] *Department of Chemistry, Meiji Gakuin University, Kamikurata, Totsuka, Yokohama 244-8539, Japan*
[b] *Department of Physics, University of Oxford, Clarendon Laboratory, Parks Road, Oxford OX1 3PU, United Kingdom*
[c] *Royal Institution of Great Britain, 21 Albemarle Street, London W1S 4BS, United Kingdom*

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Abstract

Magnetism in organic diradical ion salts prepared from the diradicals, pyridine-2,6-diylbis(nitronyl nitroxide) [(2,6-PYBNN)$^{\cdot\cdot}$] and phenol-2,4-diylbis(nitronyl nitroxide) [(2,4-POBNN)$^{\cdot\cdot}$], were investigated by using SQUID magnetometers. The diradical cation salt (2,6-PYBNN)$^{\cdot\cdot+}$Cl$^-$ shows intramolecular ferromagnetic (FM) interaction with the exchange coupling constant $J/k = +9.0$ K and intermolecular antiferromagnetic (AFM) interaction with the Weiss constant $\theta = -0.75$ K in the low temperature phase below 4.5 K. Although the intramolecular FM interaction is close to that observed in the neutral diradical 2,6-PYBNN$^{\cdot\cdot}$, the intermolecular AFM interaction is significantly reduced from $J'/k = -57$ K due probably to the increase of intermolecular distances by the incorporation of Cl$^-$ ions into the salt. We also present and discuss the magnetic behavior in the diradical cation salt $(2,6\text{-PYBNN})^{\cdot\cdot+}\mathrm{BF_4}^-$ and the diradical anion salt $(\mathrm{C_4H_9})_4\mathrm{N}^+$(2,4-POBNN)$^{\cdot\cdot-}$.

Keywords: Magnetism; Diradical ions; Organic crystals; Ionic crystals; Nitronyl nitroxide

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1. Introduction

While a rich variety of purely organic and organic molecule-based ferromagnets have been reported [1–3], purely organic ferrimagnets consisting of two molecular components have not appeared to be obtained yet. To obtain purely organic ferrimagnets, it is necessary to prepare a combination of two magnetic centers with different spin multiplicities. A way to make such a combination is preparations of molecular complexes, in which $S = 1/2$ (mono)radicals and $S = 1$ diradicals are alternately stacked with intermolecular antiferromagnetic (AFM) interactions. It is therefore essential to prepare stable organic diradicals with intramolecular ferromagnetic (FM) interactions.

Of many kinds of organic radicals, nitronyl nitroxide (2-substituted 4,4,5,5-tetramethyl-4,5-dihydro-3-oxido-1*H*-imidazol-3-ium-1-oxyl) derivatives are known often to be stable in ambient atmosphere [4]. Furthermore, the derivatives can be purified through chromatography and crystallized even from a hot solution in many cases. We have therefore been preparing diradicals [5]; 2,6-bis(1-oxyl-3-oxido-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-3-ium-2-yl)pyridine [pyridine-2,6-diylbis (nitronyl nitroxide) for a trivial name and abbreviated as (2,6-PYBNN)$^{\cdot\cdot}$ hereafter], and 2,4-bis(1-oxyl-3-oxido-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-3-ium-2-yl) phenol [phenol-2,4-diylbis(nitronyl nitroxide) for a trivial name and abbreviated as (2,4-POBNN)$^{\cdot\cdot}$].

To prepare molecular complexes made of mono- and di-radical molecules, it is advantageous to use radical ions, because combinations of radical cations and anions easily yield salts, in which both mono- and di-radicals are incorporated, while those of neutral

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[*] Corresponding author. Tel.: +81 45 8632123; fax: +81 45 8632124.
E-mail addresses: sugano@mail.meijigakuin.ac.jp, sugano@law.meijigakuin.ac.jp (T. Sugano).

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molecules are sometimes hard to give complexes. This result prompts us to prepare diradical-ion salts and complexes to obtain compounds composed of mono- and di-radicals. In this paper, we present magnetic behavior of two diradical cation salts of (2,6-PYBNN)$^{\cdot\cdot}$ and a diradical anion salt of (2,4-POBNN)$^{\cdot\cdot}$ by investigating temperature dependence of magnetic susceptibility and magnetization isotherms at low temperatures.

2. Experimental

The diradicals, of which molecular structures are shown in Fig. 1, were prepared according to the procedures reported [4] and purified through column chromatography. The diradical cation salt (2,6-PYBNN)$^{\cdot\cdot+}$Cl$^-$ was prepared by the reaction between the neutral diradical (2,6-PYBNN)$^{\cdot\cdot}$ in a dichloromethane solution and hydrogen chloride diluted in an aqueous solution, while the diradical cation salt (2,6-PYBNN)$^{\cdot\cdot+}$BF$_4{}^-$ was obtained by the reaction of the diradical in dichloromethane with tetrafluoroboric acid dissolved in methanol. The diradical anion salt $(C_4H_9)_4N^+$(2,4-POBNN)$^{\cdot\cdot-}$ was prepared by dissolving the neutral diradical (2,4-POBNN)$^{\cdot\cdot}$ directly into a methanol solution of tetrabutylammonium hydroxide. The molecular structures of these diradical ion salts are also shown in Fig. 1. The magnetization isotherms up to 7 T and magnetic susceptibility over the temperature range from 1.8 to 300 K was measured by using two Quantum Design MPMSXL7 SQUID (superconducting quantum interference device) magnetometers. The contribution of the diamagnetism to the susceptibility was subtracted by extrapolating the temperature dependence of susceptibility to high temperatures, at which the Curie–Weiss law is applicable.

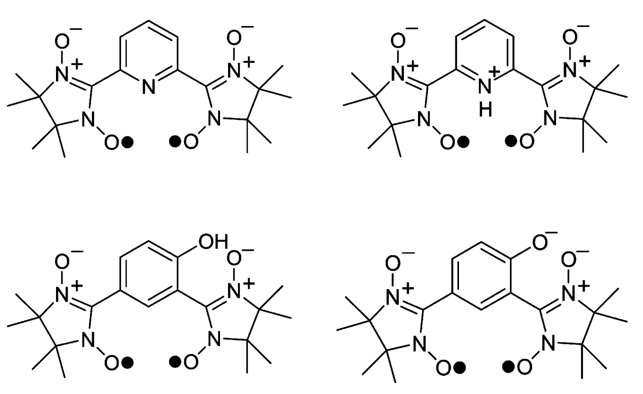

Fig. 1. The molecular structures of the diradicals (2,6-PYBNN)$^{\cdot\cdot}$ (top left) and (2,4-POBNN)$^{\cdot\cdot}$ (bottom left), the diradical ion (2,6-PYBNN)$^{\cdot\cdot+}$ (top right), and the diradical anion (2,4-POBNN)$^{\cdot\cdot-}$ (bottom right).

3. Results and discussion

Fig. 2 shows the temperature dependence of the product of paramagnetic susceptibility χ_p and temperature T of the diradical cation salts (2,6-PYBNN)$^{\cdot\cdot+}$Cl$^-$ (represented by open circles) and (2,6-PYBNN)$^{\cdot\cdot+}$BF$_4{}^-$ (open triangles) together with that of neutral diradical (2,6-PYBNN)$^{\cdot\cdot}$ (crosses). As shown in Fig. 2, the product, χ_pT, of (2,6-PYBNN)$^{\cdot\cdot}$ decreases monotonously upon lowering the temperature down to about 20 K. However, a plateau is observed below 20 K. This magnetic behavior is already interpreted [5] successfully in terms of the four-spin linear tetramer model [6] with the intramolecular FM interaction $J/k = +10$ K and intermolecular AFM interaction $J'/k = -57$ K, where J and J' is respectively the intra- and inter-molecular exchange coupling constants and k is the Boltzmann constant.

In (2,6-PYBNN)$^{\cdot\cdot+}$BF$_4{}^-$, χ_pT decreases monotonously down to 1.8 K as shown in Fig. 2. This behavior is interpreted by considering the interacting triplet molecule model by using the following equation [7]

$$\chi_pT = (2Ng^2\mu_B^2/k)\{3 + \exp[2J/(kT)]\}^{-1}[T/(T-\theta)], \tag{1}$$

where N is the number of molecules, g the g factor, μ_B the Bohr magneton and θ the Weiss constant. By fitting the experimental data to Eq. (1), $J/k = +9.0$ K and $\theta = -15.5$ K are obtained as represented by the solid line for open triangles in Fig. 2. The intramolecular coupling constant $J/k = +9.0$ K is FM and close to $J/k = +10$ K obtained for (2,6-PYBNN)$^{\cdot\cdot}$, which is the precursory neutral diradical of the salt. In contrast, the intermolecular interaction J'/k is reduced from -57 to -15.5 K, which is derived from the Weiss constant θ by using the relation for $S = 1/2$ spins based on the molecular mean-field theory [8]

$$J'/k = 2\theta/z, \tag{2}$$

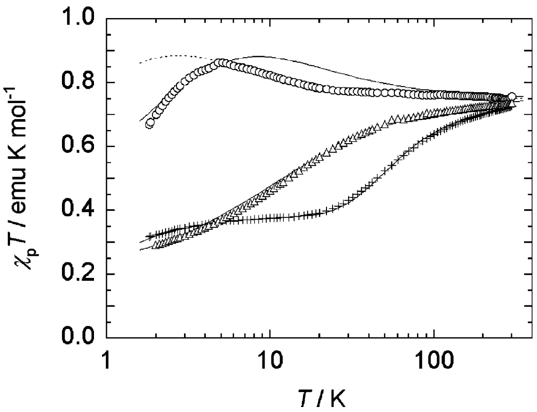

Fig. 2. Temperature dependence of χ_pT of (2,6-PYBNN)$^{\cdot\cdot+}$Cl$^-$, (2,6-PYBNN)$^{\cdot\cdot+}$BF$_4{}^-$ and (2,6-PYBNN)$^{\cdot\cdot}$ are shown by the open circles, open triangles and crosses, respectively. Theoretical fitting for each compound by using Eq. (1) (see the text) is represented by a solid or dashed line.