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

Charged Nitronyl Nitroxide Biradicals as Building Blocks for Molecular Ferrimagnetics

Daisuke Shiomi [a], Kazuhiko Ito [a], Masahiro Nishizawa [a], Syuichiro Hase [a], Kazunobu Sato [b], Takeji Takui [b] & Koichi Itoh [a]

[a] Department of Material Science, Graduate School of Science, Osaka City University, Osaka, 558-8585, Japan

[b] Department of Chemistry, Graduate School of Science, Osaka City University, Osaka, 558-8585, Japan

Version of record first published: 24 Sep 2006

Mol. Cryst. and Liq. Cryst., 1999, Vol. 334, pp. 99-108
Reprints available directly from the publisher
Photocopying permitted by license only

Charged Nitronyl Nitroxide Biradicals as Building Blocks for Molecular Ferrimagnetics

DAISUKE SHIOMI[a], KAZUHIKO ITO[a], MASAHIRO NISHIZAWA[a], SYUICHIRO HASE[a], KAZUNOBU SATO[b], TAKEJI TAKUI[b] and KOICHI ITOH[a]

[a]*Department of Material Science and* [b]*Department of Chemistry, Graduate School of Science, Osaka City University, Osaka 558–8585, Japan*

A crystal-engineering approach to organic ferrimagnetics is reported. Coulombic energy between cationic biradical with S=1 and anionic radical with S=1/2 is a promising driving force of co-crystallizing the hetero-molecular assemblage in a controllable manner. As a cationic component of "organic salt ferrimagnetics", two kinds of nitronyl nitroxide biradicals, 2,6- and 3,5-substituted pyridine derivatives, were examined. It was predicted from semi-empirical molecular orbital calculations that both the 2,6- and 3,5-derivatives have the triplet ground states both in the neutral and cationic states. The molecular ground state of the 2,6-biradical in the neutral state was found to be triplet from magnetic susceptibility measurements, while the susceptibility and ESR measurements suggested a singlet ground state for the 3,5-biradical.

Keywords: organic ferrimagnet; nitronyl nitroxide; crystal engineering; organic salt; pyridinium cation

INTRODUCTION

A Quantum Effect Disturbing Ferrimagnetic Spin Alignment

Organic molecule-based magnetism and magetics have been the focus of current topics in an interdisciplinary area of physics and chemistry[1]. Although organic ferromagnets as well as transition metal-based molecular ferrimagnets have been

found[1], genuinely organic molecule-based ferrimagnet has not been documented yet.

In a previous study[2], we have examined an alternating chain of spin-1/2 and spin-1 in terms of numerical calculations of a finite-size Heisenberg spin Hamiltonian. In the Hamiltonian, the spin-1 site was a composite system of two S=1/2 spins coupled by finite ferromagnetic interaction, which is the simplest model for colinear organic ferrimagnetics. From the calculations, a ferrimagnetic-like ground state with net magnetic moments arising from differing S's was obtained only when the spatial symmetry of the intermolecular antiferromagnetic interactions was assumed to be very high (J_{AF} = J'_{AF}). Lowering of the symmetry brought about quasi-degeneracy of the ground- and low-lying spin states with differing spin multiplicities. The quasi-degeneracy gave apparently free S=1/2 spins instead of the ferrimagnetic-like high-spins. The instability of the ferrimagnetic-like ground state was due to a decrease in energy associated with formation of intermolecular singlet (S=0) pairs, *i.e.*, a quantum effect of antiferromagnetically coupled spins, as illustrated in Fig.1. The singlet pair was supposed to suppress a long-range ferrimagnetic spin-correlation, or a divergence of $\chi_p T$, at low temperature.

The first and unique model system for organic ferrimagnetics has been

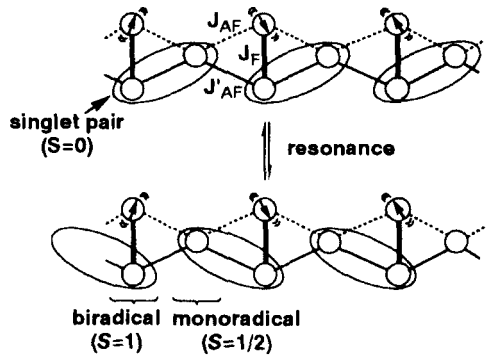


FIGURE 1 Schematic drawing of the colinear ferrimagnetic chain composed of ground-triplet (S=1) biradicals and mono-radicals (S=1/2). The circles denote the spin-1/2 sites which are coupled by intramolecular ferromagnetic (J_F) and intermolecular anti-ferromagnetic (J_{AF}, J'_{AF}) interactions. The ovals represent the intermolecular singlet-pairs.

found in a molecular complex of a spin-1/2 radical and a spin-1 biradical[3]. The decrease in $\chi_p T$ at low temperature observed for the complex is consistent with the above quantum effect of spin ensemble[2,4]. In order to establish the validity of the above theoretical model and obtain a guiding principle for constructing organic molecule-based ferrimagnetics, molecular complexes with various crystal structures and intermolecular interactions should be studied in view of the magneto-structural relationship in the hetero-molecular systems.

A Crystal Engineering Approach to Organic Ferrimagnetics

In general, co-crystallization of distinct molecules, *e.g.*, a spin-1/2 radical and a spin-1 biradical, in the asymmetric unit of a lattice involves a decrease in entropy that must be compensated by a further decrease in potential energy in the crystal lattice[5]. In the present study, a novel crystal-engineering approach is proposed which is necessary for crystallizing organic open-shell molecular complexes in a controllable manner. Coulombic energy in ionic salts can be utilized as a promising driving force of co-crystallization when a biradical cation and a monoradical anion are combined in a crystal. The strategy is termed as "organic salt ferrimagnetics".

As a cationic component in "organic salt ferrimagnetics", pyridine-substituted nitronyl nitroxide biradicals, 2,6- and 3,5-bis(4',4',5',5'-tetramethyl-4',5'-dihydro-1'*H*-imidazol-2'-yl)pyridine bis-1',1''-oxyl bis-3',3''-*N*',*N*''-oxide), or 2,6- and 3,5-pyridine bis(α-nitronylnitroxide), abbreviated as 2,6- and 3,5-PYBNN (Fig.2), are examined in this study. Alkylpyridinium cations of the molecules can be combined with anion monoradicals such as carboxylate[6] or phenolate[7] (Fig.2), to give model compounds of "organic salt ferrimagnetics". Semi-empirical molecular orbitals (MO's) are calculated for

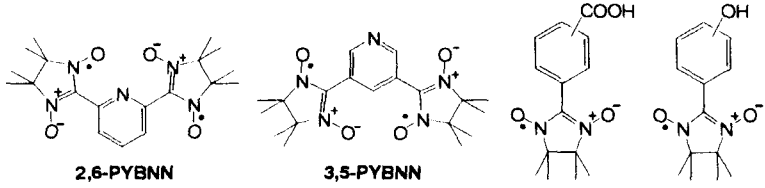
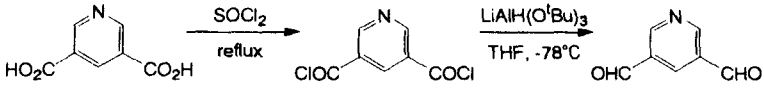


FIGURE 2 Nitronyl nitroxide radicals as building blocks for "organic salt ferrimagnetics".

the neutral pyridines and pyridinium cations. The molecular ground states of the neutral biradicals are discussed from static susceptibility and ESR measurements.

EXPERIMENTAL

The biradicals were synthesized from 2,6- or 3,5-pyridinedicarboxaldehyde and 2,3-bis(hydroxylamino)-2,3-dimethylbutane[8]. 3,5-pyridinedicarboxaldehyde, which is not commercially available, was synthesized from 3,5-pyridinedicarboxylic acid[9,10] (Scheme I). The magnetic susceptibility was measured on a Quantum Design SQUID magnetometer MPMS2 with an applied field of 100 mT. The ESR spectra were measured in a glassy solution of ethanol on a Bruker ESR spectrometer ESP300.



Scheme I Synthetic route of 3,5-pyridinedicarboxaldehyde.

RESULTS AND DISCUSSION

Molecular Orbital Calculation

It is examined whether the ground-state spin multiplicities of 2,6-PYBNN and 3,5-PYBNN change on ionization. For simplicity, hydrogen atoms are substituted for the tetramethylethylene group in the nitronyl nitroxide, which is referred to as "reduced structure". No environmental effect, *i.e.*, electrostatic interaction with neighboring pyridinium cations or counter anions, is taken into account in the MO calculation. The Hamiltonian is in the INDO level[11] and an unrestricted HF (UHF) method is adopted.

Figure 3 shows the MO energy levels calculated for 2,6-PYBNN with the reduced molecular structure both for the neutral (Fig.3a) and cationic (Fig.3b) states. In the neutral biradical, the α-HOMO is mainly localized on the pyridine nitrogen, while the next highest MO's localized on the nitronylnitroxide

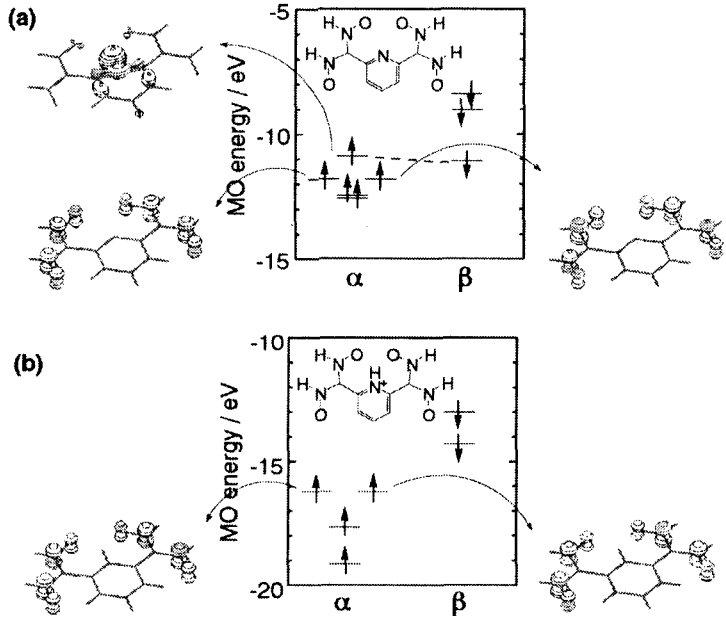


FIGURE 3 Energies and orbital pictures of the topmost occupied orbitals calculated for the neutral (a) and cationic (b) state of 2,6-PYBNN with the reduced structure. Only the orbitals of π-nature, except for α-HOMO in (a), are presented. The β-MO's with orbital-symmetry similar to that of the α-HOMO's are out of range of the figure. The electronic configuration of the ground triplet state is depicted by the arrows.

group are singly occupied and doubly degenerate, giving a triplet state. It is noteworthy that the singly occupied MO's remain doubly degenerate on cationization as depicted in Fig.3b. In both the neutral and cationic states, MO calculations assuming a singlet state gave higher energy than those of the triplet state.

The MO calculations for 3,5-PYBNN has yielded the similar result; the triplet ground state both for the neutral and cationic states. From the calculations, the biradicals 2,6-PYBNN and 3,5-PYBNN are found to be suitable for building blocks in "organic salt ferrimagnetics".

Magnetic Susceptibility and ESR Spectra

Magnetic susceptibility of 2,6-PYBNN

Temperature dependence of the magnetic susceptibility χ_p of 2,6-PYBNN measured for powder samples is depicted in Fig.4. The decrease in χ_pT with lowering temperature exhibited a stationary behavior around 10 K. This temperature dependence of χ_pT is essentially the same as that initially reported by Sugano *et al.*[12]. The observed temperature dependence of χ_pT is explained by a model of biradical dimer as given by a Heisenberg spin Hamiltonian[13]

$$H = -2J_1(S_{A1} \bullet S_{A2} + S_{B1} \bullet S_{B2}) - 2J_2 S_{A2} \bullet S_{B1}, \quad (1)$$

where S_{A1} and S_{A2} are the spin-1/2 operators of molecule A in the dimer. The two spins are coupled by the intramolecular exchange interaction J_1. The other molecule B in the dimer carrying the spins S_{B1} and S_{B2} are coupled with A by the intermolecular exchange interaction J_2 at the sites S_{A2} and S_{B1}. It has been known that the Hamiltonian (1) is the unique solution which reproduces the observed χ_pT value in the stationary region (0.37 emu K mol^{-1})[13]. The solid line in Fig.4 is calculated from Eq.(1) with the optimized parameters; J_1/k_B = +8.0 K, J_2/k_B = −52.0 K, g=2.006. The intramolecular exchange interaction of 2,6-PYBNN has been shown to be ferromagnetic, giving a possible building block suitable for "organic salt ferrimagnetics".

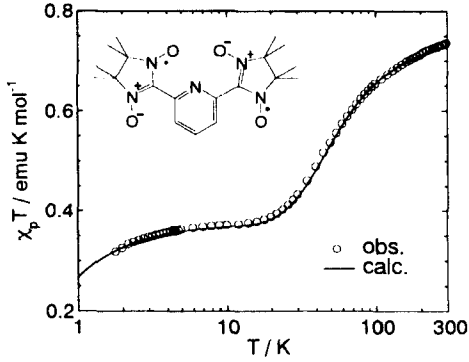


FIGURE 4 Temperature dependence of the paramagnetic susceptibility of 2,6-PYBNN. The solid line is calculated from the four-spin model, Eq.(1).

Magnetic susceptibility of 3,5-PYBNN

The $\chi_p T$ value of 3,5-PYBNN decreased at low temperatures as shown in Fig.5, indicating that the dominant interaction in a solid state is antiferromagnetic. No specific behavior of $\chi_p T$ such as the stationary temperature dependence in 2,6-PYBNN was observed. We cannot identify the sign of the intramolecular interaction from the result. The solid line in Fig.5 was calculated from Curie-Weiss law for S=1/2 assuming the purity of 98.0%, the Weiss constant θ = -6.0 K, and the g-factor g=2.006. The fit to the observed data is not satisfactory. The mean field approximation would be an oversimplified model for the exchange-coupled spin system of 3,5-PYBNN and does not give more than a qualitative estimate of the dominant magnetic interaction in the crystal.

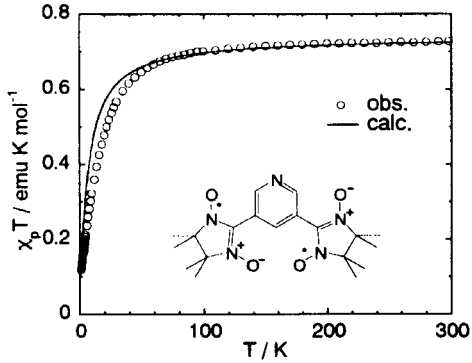


FIGURE 5 Temperature dependence of the paramagnetic susceptibility χ_p of 3,5-PYBNN. The solid line is calculated from Curie-Weiss law of S=1/2 with the Weiss constant of θ = -6.0 K.

Solution ESR of 3,5-PYBNN

In order to identify the intramolecular interaction of 3,5-PYBNN, ESR spectra in a glassy solution were measured. The ESR spectra exhibited a single line without any fine structure characteristic of triplet species; ESR signals from spin-1/2 impurities overlap the triplet signal. Intensity of the overall signal evaluated by integration is plotted as a function of temperature in Fig.6. The maximum of the intensity at 5 K suggests that the ground state of the isolated

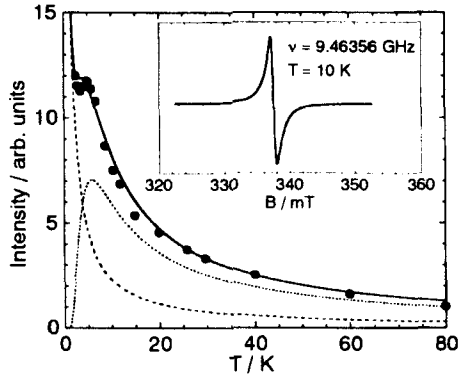


FIGURE 6 Temperature dependence of the ESR signal intensity measured for a glassy solution of 3,5-PYBNN. The broken and dashed lines denote the calculations of the singlet-triplet equilibrium with the intramolecular interaction, $J/k_B = -4.7$ K, and Curie law, respectively, the summation of which is given by the solid line. The inset shows the ESR spectrum recorded at 10 K.

molecule is singlet. The observed temperature dependence of the intensity was reproduced by assuming a singlet-triplet equilibrium for the 3,5-biradical and Curie law for the spin-1/2 impurity. The intramolecular exchange interaction was found to be antiferromagnetic; $J_{intra}/k_B = -4.7$ K. *Meta*-linkage of unpaired electrons in π-aromatic rings does not necessarily give a high-spin ground state particularly for heteroatomic π-conjugation[14]. This is exemplified in 3,5-PYBNN.

Cationization of 2,6-PYBNN

The cationization of 2,6-PYBNN has not succeeded yet because of poor reactivity in mild conditions for the biradical: Cationization by *N*-methylation with CH_3I or methylfluorosulphonate at room temperature resulted in the recovery of the biradical. Refluxing with the alkylation agents caused decomposition of the biradical to give ESR-silent materials. Reaction with HCl or HBr gas gave an oily mixture including monoradicals.

CONCLUSION

A crystal-engineering approach to organic molecule-based ferrimagnetics has been proposed. In the strategy of "organic salt ferrimagnetics", Coulombic interaction between cationic biradical and anionic radical is a possible driving force of co-crystallization. As cationic components of "organic salt ferrimagnetics", two kinds of nitronyl nitroxide biradicals, 2,6- and 3,5-PYBNN, were examined. Although the 2,6-biradical had a triplet ground state in the neutral state, it refused to react with *N*-alkylation agents in mild conditions probably because of the steric hindrance of the bulky nitronyl nitroxide group. The ground spin state of the 3,5-biradical has been found to be singlet from the susceptibility and glassy-solution ESR measurements. The simple extension of "π-topology rule" for spin alignment in carbon-based π-electron network[15] is invalidated for heteroatomic π-systems. Introduction of substituents with electronic charge into biradicals needs more sophisticated molecular design.

Acknowledgments

The authors (D. S. and K. S.) acknowledge the Ministry of Education, Science and Culture, Japan for Grants-in-Aid for Encouragement of Young Scientists (No. 09740528 and 10740275).

References

[1] For recent overviews, see: *Proceedings of the Vth International Conference on Molecule-based Magnets,* Osaka, 1996, edited by K. Itoh, J.S. Miller, and T. Takui (Gordon and Breach, New York, 1997); *Mol. Crysl. Liq. Cryst.,* **305, 306** (1997).

[2] D. Shiomi, M. Nishizawa, K. Sato, T. Takui, K. Itoh, H. Sakurai, A. Izuoka, and T. Sugawara, *J. Phys. Chem. B,* **101,**3342 (1997).

[3] A. Izuoka, M. Fukada, R. Kumai, M. Itakura, S. Hikami, and T. Sugawara, *J. Am. Chem. Soc.,* **116,** 2609 (1994).

[4] M. Nishizawa, D. Shiomi, K. Sato, T. Takui, K. Itoh, H. Sakurai, A. Izuoka, T. Sugawara, H. Sawa, and R. Kato, *Mol. Cryst. Liq. Cryst.,* **306,**191 (1997).

[5] G.R. Desiraju, *Crystal Engineering: The Design of Organic Solids*(Elsevier, Amsterdam, 1989), Chaps. 2 and 11.

[6] K. Inoue and H. Iwamura, *Chem. Phys. Lett.,* **207,** 551 (1993).

[7] J. Cirujeda, E.H. Gasio, C. Rovira, J.L. Stanger, P. Turek, and J. Veciana, *J. Mater. Chem.,* **5,** 243 (1995).

[8] E.F. Ullman, J.H. Osiecki, D.G.B. Boocock, and R. Darcy, *J. Am. Chem. Soc.,* **94,** 7049 (1972).

[9] F.J. Villani and M.S. King, *Org. Synth.,* Coll. Vol. **IV,** 88 (1963).

[10] H.C. Brown and B.C. Subba Rao, *J. Am. Chem. Soc.,* **80,** 5377 (1958).

[11] Gaussian94 (Gaussian, Inc.) with a keyword "INDO".

[12] T. Sugano, M. Tamura, and M. Kinoshita, *Synth. Met.,* **55–57,** 3305 (1993).

[13] D. Shiomi, M. Tamura, H. Sawa, R. Kato, and M. Kinoshita, *J. Phys. Soc. Jpn.,* **62,** 289 (1993).

[14] For example, see: J.Y. Bae, M. Yano, K. Sato, D. Shiomi, T. Takui, T. Kinoshita, K. Abe, K. Itoh, and D.I. Hong, this proceedings.
[15] K. Itoh, *Pure Appl. Chem.*, **50,** 1251 (1978).