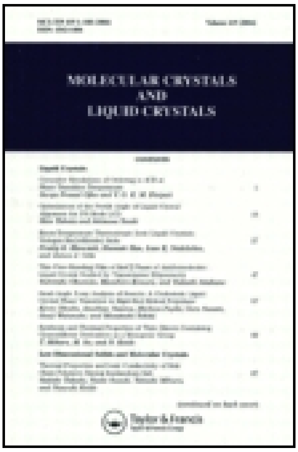

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Organic Molecule-Based Ferrimagnetism as Studied by Numerical Calculations of a Model Hamiltonian

Daisuke Shiomi [a], Masahiro Nishizawa [a], Kazunobu Sato [a], Masaki Mito [b], Kazuyoshi Takeda [b] & Takeji Takui [a]

[a] Departments of Materials Science and Chemistry, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka, 558-8585, Japan

[b] Department of Applied Quantum Physics, Graduate School of Engineering, Kyushu University, Hakozaki, Fukuoka, 812-8581, Japan

Version of record first published: 18 Oct 2010

To cite this article: Daisuke Shiomi, Masahiro Nishizawa, Kazunobu Sato, Masaki Mito, Kazuyoshi Takeda & Takeji Takui (2002): Organic Molecule-Based Ferrimagnetism as Studied by Numerical Calculations of a Model Hamiltonian, Molecular Crystals and Liquid Crystals, 376:1, 495-500

To link to this article: http://dx.doi.org/10.1080/713738430

Mol. Cryst. Liq. Cryst., Vol. 376, pp. 495-500
Copyright © 2002 Taylor & Francis
1058-725X/02 $12.00 + .00

Organic Molecule-Based Ferrimagnetism as Studied by Numerical Calculations of a Model Hamiltonian

DAISUKE SHIOMI[a], MASAHIRO NISHIZAWA[a],
KAZUNOBU SATO[a], MASAKI MITO[b], KAZUYOSHI TAKEDA[b]
and TAKEJI TAKUI[a]

[a]*Departments of Materials Science and Chemistry, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan and*
[b]*Department of Applied Quantum Physics, Graduate School of Engineering, Kyushu University, Hakozaki, Fukuoka 812-8581, Japan*

Abstract: A physical picture of spin alignments in organic molecule-based ferrimagnets is deduced from quantum Monte Carlo (QMC) simulations of magnetic susceptibility. It is found from the QMC calculations on the basis of a Heisenberg spin Hamiltonian that the ferrimagnetic spin alignment in S=1 and S=1/2 alternating molecular chains is equivalent to a ferromagnetic alignment of effective S=1/2 spins appearing in the unit cells of the heteromolecular chains. A spin polarization effect affording the effective ferromagnetic interactions is demonstrated in terms of a Heitler-London approximation.

Keywords organic ferrimagnet; Heisenberg spin Hamiltonian; spin polarization; quantum Monte Carlo simulation; magnetic susceptibility

INTRODUCTION

Organic open-shell molecules tend to have antiferromagnetic intermolecular interactions in their molecular assemblages such as in crystalline solids. Therefore, intuitively, it is natural that the antiferromagnetic interactions between neighboring molecules with different spin quantum numbers, e.g., S=1 and S=1/2, bring about antiparallel spin alignment, leading to the possible occurrence of an ordered state with net magnetization in molecular assemblages. The tendency of antiferromagnetic interactions underlies the first documented proposal of organic ferrimagnetics.[1] The ferrimagnetic spin ordering, however, has never been documented so far in organic molecular crystalline solids. This presents a remarkable contrast to the discovery of transition metal-based molecular ferrimagnets.[2] In this context, organic molecule-based ferrimagnetics has been a long-standing issue in terms of materials challenge in chemistry.[3]

In our previous papers,[4] we have discussed the possibility of ferrimagnetic order occurring in organic molecular crystals both from theoretical calculations of a Heisenberg spin Hamiltonian of an S=1/2 and S=1 alternating chain[4a,b] and from crucial experiments[4c] on the first and only model compound for genuinely organic ferrimagnets documented so far.[4d] We have shown that organic molecule-based ferrimagnets are characterized by the following two features:[4a-c] First, the spin density in an open-shell molecule is distributed over many atomic sites and hence the intermolecular interactions have a multi-centered or multi-contact nature. Second, in most cases, intramolecular interactions in stable organic S>1/2 molecules are in the same order of magnitude as the intermolecular ones. Thus, the magnetic degree of freedom within the S>1/2 molecules should be taken into account for understanding the nature of ferrimagnetism in molecule-based materials.

In the present study, numerical calculations of magnetic susceptibility are made in terms of a model Hamiltonian possessing the above features. The model Hamiltonian under study is given by

$$H = \sum_{i=1}^{N}[-2J_1\mathbf{S}_{i,\mathrm{b1}} \bullet \mathbf{S}_{i,\mathrm{b2}} - 2J_2\mathbf{S}_{i,\mathrm{b2}} \bullet \mathbf{S}_{i,\mathrm{m}} - 2J_3\mathbf{S}_{i,\mathrm{m}} \bullet \mathbf{S}_{i+1,\mathrm{b2}} - 2J_2'\mathbf{S}_{i,\mathrm{b1}} \bullet \mathbf{S}_{i,\mathrm{m}} - 2J_3'\mathbf{S}_{i,\mathrm{m}} \bullet \mathbf{S}_{i+1,\mathrm{b1}}], \tag{1}$$

where $\mathbf{S}_{i,\mathrm{b1}}$, $\mathbf{S}_{i,\mathrm{b2}}$, and $\mathbf{S}_{i,\mathrm{m}}$ denote the spin-1/2 operators. $\mathbf{S}_{i,\mathrm{b1}}$ and $\mathbf{S}_{i,\mathrm{b2}}$ are coupled by the intramolecular ferromagnetic interaction, J_1, to give the biradical site, which is coupled with the neighboring monoradical with $S_{i,\mathrm{m}}$=1/2 by the antiferromagnetic interactions, J_2, J_2', J_3, and J_3'. In Figure 1 is schematically shown the Hamiltonian (1). The magnetic degree of freedom within the biradical molecule is given by the finite interaction J_1, while the multi-centered or multi-contact intermolecular

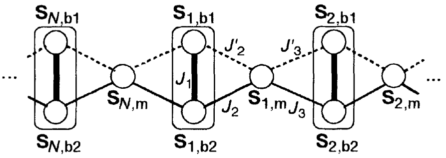

FIGURE 1 Schematic drawing of the spin Hamiltonian Equation (1). See the text for detailed notations.

interactions are signified by the ratio J_2'/J_2, which is assumed to be equal to J_3'/J_3. The dimerization, or alternation, of the intermolecular interaction along the chain is defined by the ratio J_3/J_2, which is assumed to be equal to J_3'/J_2'. A physical picture for the ferrimagnetic spin alignment in organic molecular assemblages is proposed in quantum terms, emphasizing a spin polarization effect in the molecular aggregation of the biradicals and monoradicals.

RESULTS AND DISCUSSION

Simulation of Magnetic Susceptibility

Since intermolecular interactions are primarily antiferromagnetic in ferrimagnetic systems, the product of susceptibility and temperature χT decreases on lowering the temperature.[2,4] A non-compensating magnetization, however, gives rise to an upturn and a divergence in χT at low temperatures: The appearance of the minimum in χT is a fingerprint of ferrimagnetic spin systems.[2,4] For low-dimensional antiferromagnetic spin systems, the minimum in χ or χT usually has a simple linear dependence on the relevant exchange interaction constants.[5] The influence of the multi-centered exchange interactions on the divergence in χT is examined by simulating the minimum value $\chi T_{\min}$ and the temperature $T_{\min}$ as functions of the interaction parameters.

The temperature dependence of susceptibility was calculated by the quantum Monte Carlo simulation method[4b,6] on an NEC supercomputer SX-5 at the Computer Center of the Institute for Molecular Science. The periodic boundary condition is imposed with $3N=30$ of $S=1/2$ spins in the Hamiltonian (1).

In Figure 2 are plotted the $\chi T_{\min}$ (a) and $T_{\min}$ values (b) as functions of the interaction ratio $|J_2/J_1|$. The solid symbols in Figure 2(a) denote the $\chi T_{\min}$ values calculated for the uniform chain ($J_3/J_2 = J_3'/J_2' = 1$). When the intermolecular interactions are weak ($|J_2/J_1|<0.3$), the $\chi T_{\min}$ value is independent of $|J_2/J_1|$. As the intermolecular interactions are larger ($|J_2/J_1|>0.3$), the $\chi T_{\min}$ value decreases. The lower symmetry of the two-fold intermolecular interactions $J_2'/J_2=J_3'/J_3<1$ gives the smaller minimum in χT. The dimerization, or the alternation, of the intermolecular interactions along the chain results in a drop in $\chi T_{\min}$ as shown by the open symbols in Figure 2(a) for $0.1 \leq J_3/J_2 \leq 0.9$ in both the regions, $|J_2/J_1|<0.3$ and $|J_2/J_1|>0.3$. On the other hand, effects of the dimerization on the $T_{\min}$ values do not manifest themselves. The

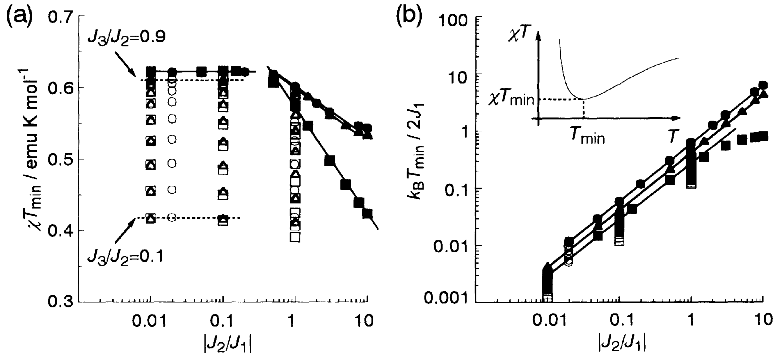

FIGURE 2 Simulated χT_{min} (left) and T_{min} (right). The solid and the open symbols denote the uniform chain (J_3/J_2=J_3'/J_2'=1) and the dimerized chains with the interactions alternation of J_3/J_2 =J_3'/J_2'=0.1 to 0.9. The symmetries of the intermolecular interactions are J_2'/J_2=J_3'/J_3=1 (circles), 0.5 (triangles), and 0 (squares). The solid and the dashed lines are to guide the eye.

normalized temperature $k_B T_{\mathrm{min}}/2J_1$ is approximately linear with respect to the interaction ratio $|J_2/J_1|$ as depicted in Figure 2(b).

As the interaction ratio J_3/J_2 (= J_3'/J_2') deviates from unity and approaches zero, the alternating molecular chain of the biradicals and the monoradicals should be regarded as an assemblage of biradical-monoradical pairs. In the pair, the biradical and the monoradical are coupled by the antiferromagnetic interaction, J_2 or J_2', to give a supramolecule in the doublet (S=1/2) state; there appears an effective S=1/2 spin in the repeat unit of the chain. The assemblage of the S=1/2 spins is consistent with the limiting value of $\chi T_{\mathrm{min}} \rightarrow 0.4$ emu K mol^{-1} for J_3/J_2(=J_3'/J_2')$\rightarrow 0$ as shown in Figure 2(a), which corresponds to the Curie law of S=1/2 with g=2.

Spin Polarization Effects in Heteromolecular Chains

Intermolecular ferromagnetic interactions between S=1/2 organic radicals have been understood in terms of the spin polarization effect within the S=1/2 molecules.[7] The spin polarization provides the spin density distribution with positive and negative densities in the molecule. Intermolecular orbital overlaps between neighboring molecules at the atomic sites of opposite signs of spin densities give rise to a ferromagnetic interaction between the molecules, which is schematically shown in Figure 3(a).

The ferrimagnetic spin alignment in our heteromolecular chain is

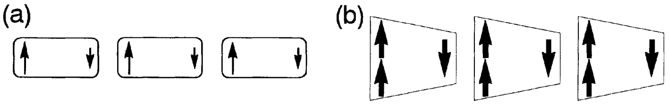

FIGURE 3 Schematic diagrams for the spin polarization in the S=1/2 chain (a) and the biradical-monoradical dimerized chains (b). The arrows indicate the positive or negative spin polarization.

examined in the light of a spin polarization effect in the supramolecule of the biradical and the monoradical. The spin polarization in the supramolecule is deduced from the Heisenberg model

$$h = -2j_1\mathbf{S}_{b1} \bullet \mathbf{S}_{b2} - 2j_2\mathbf{S}_{b2} \bullet \mathbf{S}_{m} - 2j_2'\mathbf{S}_{b1} \bullet \mathbf{S}_{m}, \tag{2}$$

which corresponds to the Heitler-London model applied to the supramolecule and is equivalent to the unit cell of the chain Hamiltonian (1). The ferromagnetic interaction j_1 and the antiferromagnetic interactions j_2 and j'_2 give the doublet (S=1/2) ground state of the supramolecule. The spin densities of the three molecular sites are calculated by diagonalizing the Hamiltonian (2) as

$$\rho_{b1} \equiv < S_{b1}^z > = \tfrac{1}{6}\{1 + (1 - 2j_2 + j_2')/A\}, \tag{3a}$$

$$\rho_{b2} \equiv < S_{b2}^z > = \tfrac{1}{6}\{1 + (1 + j_2 - 2j_2')/A\}, \tag{3b}$$

$$\rho_{m} \equiv < S_{m}^z > = \tfrac{1}{6}\{1 + (-2 + j_2 + j_2')/A\}, \tag{3c}$$

$$A = \sqrt{j_2^2 + j_2'^2 - j_2 j_2' - j_2 - j_2' + 1}. \tag{3d}$$

It is found from Equation (3) that for arbitrary values of $j_1>0$, $j_2<0$, and $j'_2<0$, the supramolecule has the resultant positive spin density in the biradical moiety, while the sizable negative polarization appears preferentially in the monoradical moiety:

$$0 \leq \rho_{b1}, \rho_{b2} \leq 1/2, \quad -1/6 \leq \rho_m \leq 0. \tag{4}$$

The spin polarization in the supramolecule, Equation (4), brings about ferromagnetic interactions between the supramolecules in the alternating chain as schematically shown in Figure 3(b). Thus, the ferrimagnetic spin state in the alternating chain of the biradicals and monoradicals is equivalent to the ferromagnetic alignment of the effective S=1/2 spins on the supramolecules, when the intermolecular interactions along the chain are dimerized.[8]

Given an intermolecular interaction $|J_2|$, the $T_{\min}$ value is governed by the smaller interaction $|J_3|$ as shown by the open symbols in Figure 2(b): $|J_3|$ is the effective intermolecular interaction for the supramolecules of S=1/2. It is concluded that an elaborate tuning for the multi-centered interactions is necessary for accomplishing the ferrimagnetic spin alignment at high temperatures, which is based on the spin polarization within the organic open-shell molecules and molecular packings governing the intermolecular interactions.

Acknowledgments
This work has been Grants-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

References and Notes

[1] A.L. Buchachenko, Dokl. Akad. Nauk. Eng. Ed., **244**, 107(1979).

[2] For example, see: a) O. Kahn, Y. Pei, M. Verdaguer, J.P. Renard, J. Sletten, J. Am. Chem. Soc., **110**, 782(1988). b) A. Caneschi, D. Gatteschi, J.P. Renard, P. Rey, R. Sessoli, Inorg. Chem., **28**, 1976(1989). c) M. Hagiwara, Y. Narumi, K. Minami, K. Tatani, K. Kindo, J. Phys. Soc. Jpn., **68**, 2214(1999).

[3] For recent overviews of molecule-based magnetism, see a) Magnetic Properties of Organic Materials, ed. P.M. Lahti, Marcel Dekker, New York, (1999). b)Molecular Magnetism, ed. K. Itoh and M. Kinoshita, Gordon and Breach, Amsterdam (Kodansha, Tokyo), (2000).

[4] a)D. Shiomi, M. Nishizawa, K. Sato, T. Takui, K. Itoh, H. Sakurai, A. Izuoka, T. Sugawara, J. Phys. Chem. B, **101**, 3342(1997). b) D. Shiomi, K Sato, T. Takui, J. Phys. Chem. B, **104**, 1961(2000). c) M. Nishizawa, D. Shiomi, K Sato, T. Takui, K. Itoh, H. Sawa, R. Kato, H. Sakurai, A. Izuoka, T. Sugawara, J. Phys. Chem. B, **104**, 503 (2000). d) A. Izuoka, M. Fukada, R. Kumai, M. Itakura, S. Hikami, T. Sugawara J. Am. Chem. Soc., **116**, 2609(1994).

[5] L.J. de Jongh, A.R. Miedema, Adv. Phys., **23**, 1(1974).

[6] M. Troyer, B. Ammon, E. Heeb, D. Caromel in Lecture Notes in Computer Science, Vol. 1505, ed. D. Caromel, R.R. Oldenhoeft, M. Tholburn, Springer, Berlin, pp.191-198(1999).

[7] a) H.M. McConnell, J. Chem. Phys., **39**, 1910(1963). b) K. Awaga, T. Sugano, M. Kinoshita, Chem. Phys. Lett. **141**, 540(1987).

[8] The description of the effective S=1/2 spins on the supramolecules is valid only for highly dimerized intermolecular interactions along the chain, J_3/J_2=J_3'/J_2'<<1, where an S=1/2 is a good quantum number for describing the magnetic properties of the unit cell.