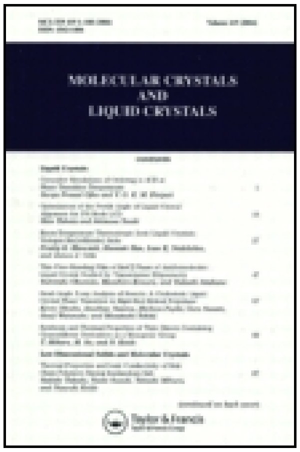

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Theoretical Studies of Magnetic Interactions in P-Cyanophenyl Nitronyl Nitroxide Crystal

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THEORETICAL STUDIES OF MAGNETIC INTERACTIONS IN *p*-CYANOPHENYL NITRONYL NITROXIDE CRYSTAL

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Abstract Magnetic interactions in crystal of *p*-cyanophenyl nitronyl nitroxide (*p*-CNPNN) were theoretically investigated. Semiempirical and *ab initio* molecular orbital calculations were performed for pair models of *p*-CNPNN molecules in the crystal. Effective exchange integrals (J_{ab}) are positive for the pairs of neighboring molecules in a sheet parallel to the *ac*-plane of the crystal, suggesting pseudo-two-dimensional ferromagnetic interaction in the *ac*-plane. Close contact between *p*-CN-phenyl group and NO group of the adjacent molecules plays a dominant role for the ferromagnetic interaction. Inter-sheet interaction is weak and the sign of J_{ab} depends on the pairs.

INTRODUCTION

In a series of our theoretical studies of ferromagnetic interaction in organic radical crystals, it was shown that the sign and magnitude of the effective exchange interaction (J_{ab}) strongly depend on stacking modes of radical molecules in the crystal.[1-4] Recently many experimental efforts to construct the stacking modes which exhibit strong ferromagnetic interaction have been paid by synthesizing a variety of nitroxide derivatives.[5-8]

Recently Hosokoshi *et al.* reported the magnetic property of *p*-cyanophenyl nitronyl nitroxide (2-(4'-cyanophenyl)-4, 4, 5, 5-tetramethyl-4, 5-dihydro-1*H*-imidazolyl-1-oxyl-3-oxide, abbreviated as *p*-CNPNN).[9] The magnetic susceptibility above 4 K can be explained by the ferromagnetic square-lattice Heisenberg model with $J = 0.52\ \mathrm{cm}^{-1}$. It is suggested from the structure analysis that the origin of the two dimensional ferromagnetic behavior may be attributed to the intermolecular contacts between nitronyl nitroxide groups and cyanophenyl groups in a sheet parallel to the *ac*-plane.

It is particularly interesting and important to investigate theoretically the origin of the two-dimensional magnetic behavior in this crystal. In this paper we report the molecular orbital (MO)[10-12] calculations to determine the intermolecular effective exchange integrals for several pair models whose geometries are extracted from the X-ray structure[9] in the crystal.

THEORETICAL BACKGROUND

As shown previously,[11] the effective exchange integral J_{ab} for radical pair is generally expressed by three different terms under the approximately spin-projected unrestricted Hartree-Fock (APUHF) approximation, *i. e.*,

$$J_{ab}(\mathrm{APUHF})=J_{ab}(\mathrm{KE})+J_{ab}(\mathrm{PE})+J_{ab}(\mathrm{SP}). \quad (1)$$

The kinetic (KE) and the potential (PE) exchange terms are, respectively, determined by SOMO-SOMO overlap S_{ab} and the intermolecular exchange integral K_{ab}. The spin polarization term (SP) is given by the product of spin densities ($\rho_{a(b)}$) induced by spin polarization effect.[10] The ferromagnetic interaction in molecular crystals can be explained by these terms. A simple classification to describe the magnetic interaction was derived.[11]

Case I	$(J_{ab}(\mathrm{KE})<0,\ J_{ab}(\mathrm{PE})>0;\ J_{ab}<0)$	(2a)
Case II	$(J_{ab}(\mathrm{KE})\approx 0,\ J_{ab}(\mathrm{PE})>0;\ J_{ab}>0)$	(2b)
Case III	$(J_{ab}(\mathrm{KE})\approx 0,\ J_{ab}(\mathrm{PE})\approx 0,\ J_{ab}(\mathrm{SP})>0;\ J_{ab}>0)$	(2c)
Case IV	$(J_{ab}(\mathrm{KE})\approx 0,\ J_{ab}(\mathrm{PE})\approx 0,\ J_{ab}(\mathrm{SP})<0;\ J_{ab}<0)$	(2d)

Cases I and II are understood intuitively by the symmetry of SOMO-SOMO contact. The effective exchange interaction between closely located radical groups is usually antiferromagnetic ($J_{ab}<0$)[1] since the KE interaction stabilizes the low spin (LS) state (Case I). However, if the mutual orientation of radical groups is controlled to reduce the KE term, the ferromagnetic interaction ($J_{ab}>0$) is expected at a short intermolecular distance (Case II) because of the nonzero Coulombic exchange integral ($J_{ab}(\mathrm{PE})=K_{ab}$) as studied in the case of simple nitroxide pair model.[11] On the other hand, the SP term induced by the indirect through-bond and through-space interactions becomes important when the distance between the two radical groups is large (Cases III and IV). For example, β-phase crystal of *p*-NPNN corresponds to the case III.[2] The sign of $J_{ab}(\mathrm{SP})$ depends on the phase of spin alternation by spin polarization effect.

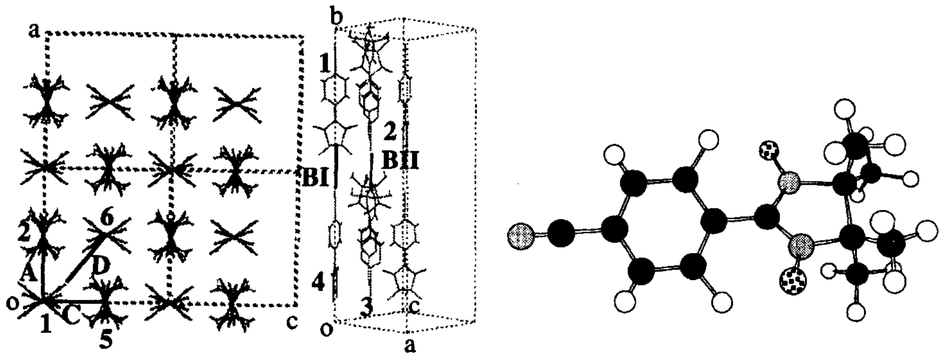
Ab initio configuration interaction (CI) method by use of the complete active space (CAS) selected on the basis of the occupation numbers of the UHF natural orbitals (UNO) *i. e.*, UNO CASCI, and UNO CASSCF methods are used for estimation of the

SOMO-SOMO direct interaction terms (KE and PE).[13, 14] Semiempirical INDO methods have been successfully employed to calculate J_{ab} in eq. 1.

CRYSTAL STRUCTURE

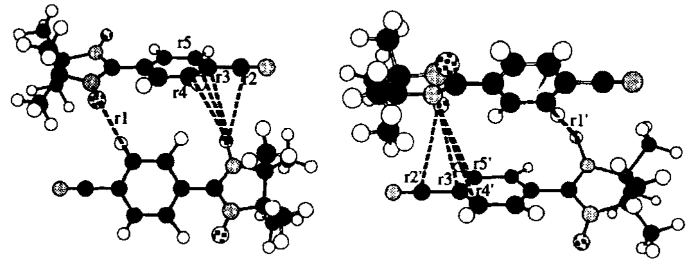
Figure 1(a) illustrates the packing arrangement of *p*-CNPNN molecules (**1** through **6**) in the crystal and Figure 1(b) shows the geometry of *p*-CNPNN molecule. There are two crystallographically independent molecules.[9] One of the molecules corresponds to **1**, **4** or **6** (group **I**) and the other to **2**, **3** or **5** (group **II**). Since disorder of the methyl groups in group **I** was suggested and correct geometry of the methyl groups was not determined, the geometry of the methyl groups in group **II** was used for group **I** in our MO calculations. The sheet structure parallel to the *ac*-plane is outstanding. Within the sheet, each molecule in **I** is surrounded by four molecules in **II** and *vice versa*. As shown in Figure 2, relatively short distances were found between the carbon atom of the cyano group and the terminal oxygen atom of the nitroxide group, *i. e.*, r2 along the a-axis and r2' along the c-axis. Close contact between the terminal oxygen atom of the nitroxide group and the carbon atoms of the phenyl group was also found. The molecular packing along the a-axis is very similar to that along the c-axis. From the crystal structure the magnetic interaction in the *ac*-plane is interested.

The theoretical calculations were performed for the pairs of *p*-CNPNN molecules, **A (1-2)**, **BI (1-4)**, **BII (2-3)**, **C (1-5)** and **D (1-6)**, in the crystal shown in Figure 1 by use of semiempirical INDO method. More accurate UNO CASCI and UNO CASSCF methods were used for the simplified pair models.



(a) (b)

FIGURE 1 Crystal structure (a) and molecular geometry (b) of *p*-CNPNN



along a-axis (**A**) along c-axis (**C**)

r1: 3.49Å	r2: 3.47Å	r3: 3.47Å	r4: 3.55Å	r5: 4.13Å
r1': 3.45Å	r2': 3.466Å	r3': 3.433Å	r4': 3.81Å	r5': 3.82Å

FIGURE 2 Pairs of *p*-CNPNN molecules along the a- and c-axes

CALCULATIONS FOR *p*-CNPNN PAIRS

In order to study the magnetic property observed for *p*-CNPNN crystal, the semi-empirical INDO calculation was carried out for whole molecular skeleton (pairs **A**, **BI**, **BII**, **C** and **D**). Table I shows the calculated J_{ab} values. The INDO method gives reasonable values for J_{ab} as compared with the experiment.[9] The pairs **A** and **C** on the *ac*-plane show large positive J_{ab} values. The reason of the large positive J_{ab} may be explained by short intermolecular distances for the pairs **A** and **C**. The INDO calculation suggests that pseudo-two-dimensional ferromagnetic interaction exists in the molecular sheet parallel to the *ac*-plane and interaction between the sheets (**BI** and **BII**) is weak. This result qualitatively explains the experimental result by Hosokoshi *et al.*[9]

TABLE I J_{ab} values for the pairs of *p*-CNPNN molecules shown in Figure 1

	J_{ab} /cm^{-1}				
methods	**A**	**BI**	**BII**	**C**	**D**
INDO/UHF	0.541	0.003	-0.003	0.301	0.000
experiment (square-lattice Heisenberg model)[9]	0.52				

CALCULATIONS FOR SIMPLIFIED PAIR MODELS

In order to elucidate the magnetic interaction path in the pairs described above, various computations were carried out for the simplified pair models.

(A) Simplified models for the pairs A and C

Different simplified pair models shown in Figure 3 were considered to designate the role of cyano, phenyl and methyl groups for the intermolecular magnetic interaction. $\mathbf{A}_1$ and $\mathbf{C}_1$ are the most simplified pair models, in which only the nitronyl nitroxide groups are considered. Cyano groups of **A** and **C** are replaced by hydrogen atoms in the pairs $\mathbf{A}_2$ and $\mathbf{C}_2$, whereas cyanophenyl groups are replaced by hydrogen atoms in the pairs $\mathbf{A}_3$ and $\mathbf{C}_3$. In the pairs, $\mathbf{A}_4$ and $\mathbf{C}_4$, methyl groups of **A** and **C** are replaced by hydrogen atoms.

Table II shows J_{ab} values calculated for the simplified models by several computational methods. Large and positive values of J_{ab} were obtained by use of INDO method for the model pairs, $\mathbf{A}_2$, $\mathbf{A}_4$, $\mathbf{C}_2$ and $\mathbf{C}_4$. These results indicate that cyanophenyl group contributes dominantly to the intermolecular ferromagnetic interaction in the pairs, **A** and **C**. Particularly the phenyl group seems to be important for the ferromagnetic interaction in the pairs, **A** and **C**. Direct interaction between nitronyl nitroxide groups is negligible as shown in the pair models, $\mathbf{A}_1$ and $\mathbf{C}_1$. It is note worthy that J_{ab} values calculated by UNO CASCI {2, 2} and UNO CASSCF {2, 2} methods predominantly reflect the direct SOMO-SOMO interactions, KE and PE terms in Eq. 1. Therefore, the ferromagnetic interactions in **A** and **C** pairs are classified into Case III.

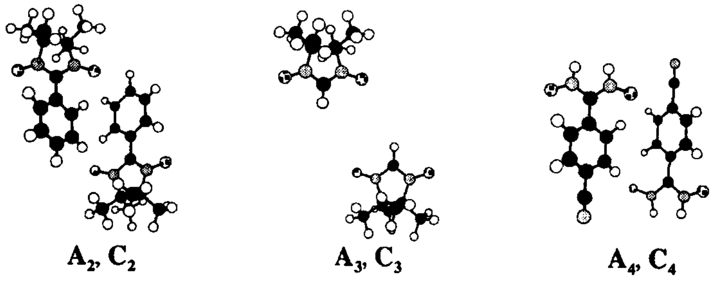


FIGURE 3 Simplified models for the pairs A and C

TABLE II J_{ab} values for the simplified models of pairs, **A** and **C**, shown in Figure 1

	J_{ab} /cm^{-1}				
methods	**A**	**A$_1$**	**A$_2$**	**A$_3$**	**A$_4$**
INDO	0.541	0.000	0.643	0.000	0.636
UNO CASCI{2, 2}$^{a)}$		0.000			0.019
UNO CASSCF{2, 2}$^{a)}$		0.000			

a) 4-31G basis set was used.

	J_{ab} /cm^{-1}				
methods	**C**	**C$_1$**	**C$_2$**	**C$_3$′**	**C$_4$**
INDO	0.301	0.000	0.331	0.000	0.374
UNO CASCI{2, 2}$^{a)}$		0.000			0.005
UNO CASSCF{2, 2}$^{a)}$		0.000			

a) 4-31G basis set was used.

(B) Simplified models for the pairs BI, BII and D

The inter-sheet magnetic interaction was estimated by use of simplified models of the pairs **BI** (1-4) and **BII** (2-3) shown in Figures 1 and 4. Model pairs **BI$_1$** and **BII$_1$** consist of two nitronyl nitroxide molecules. In **BI$_2$** and **BII$_2$** only the interacting components of *p*-CNPNN molecules are retained and terminal components are simplified, *i. e.*, atoms located between the two nitronyl nitroxide groups of the pairs are maintained.

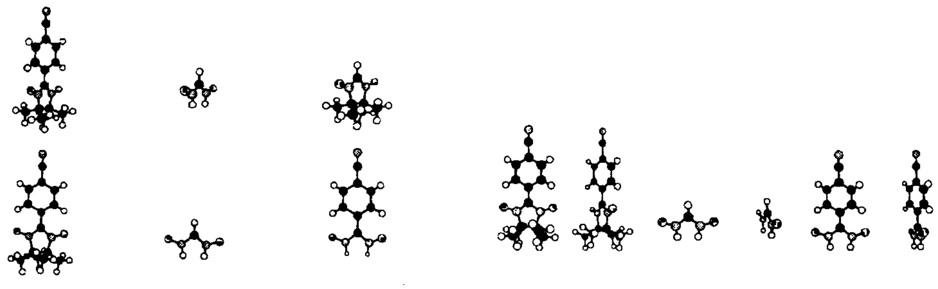


FIGURE 4 Simplified models of the pairs, **B** and **D**

Table III J_{ab} values for the simplified models of the pairs, **B** and **D**

	J_{ab} /cm^{-1}								
methods	**BI**	**BI$_1$**	**BI$_2$**	**BII**	**BII$_1$**	**BII$_2$**	**D**	**D$_1$**	**D$_2$**
INDO	0.003	0.000	0.003	-0.003	0.000	-0.003	0.000	0.000	0.000
UNO CASCI{2, 2}[a)]		0.000	0.000		0.000	0.000		-0.001	-0.001
UNO CASSCF{2, 2}[a)]		0.000	0.000		0.000	0.000			0.000

a) 4-31G basis set was used.

Table III shows that the direct interactions are negligible in the models **BI$_1$**, **BII$_1$**, **BI$_2$** and **BII$_2$** as indicated by UNO CASCI {2, 2} and UNO CASSCF {2, 2} methods. INDO method revealed a small antiferromagnetic interaction for model **BII$_2$** as in the case of **BII**. On the other hand, model **BI$_2$** have small ferromagnetic interaction as in the case of **BI**. These results suggest a weak magnetic interaction between the molecular sheets parallel to the *ac*-plane.

Finally the magnetic interaction in the pair **D** was examined. Simplified model pair **D$_1$** consists of two nitronyl nitroxide molecules, whereas hydrogen atoms of **D$_1$** were replaced by cyanophenyl groups in **D$_2$** as shown in Figure 4.

INDO, UNO CASCI {2, 2} and UNO CASSCF {2, 2} gave negligibly small J_{ab} values, indicating the negligible magnetic interaction in the pair **D** compared with the ferromagnetic interactions in the pairs, **A** and **C**. Therefore, the ferromagnetic interaction in the molecular sheet parallel to the *ac*-plane is concluded to be quasi-square-lattice type, in accord with the experiment.[9]

CONCLUDING REMARK

Characteristic magnetic interaction in *p*-CNPNN crystal was studied by semiempirical and *ab initio* calculations. Effective exchange integral J_{ab} was calculated for several pair molecules in the crystal. Quasi-two-dimensional ferromagnetic interaction in the molecular sheet parallel to the *ac*-plane was revealed. The phenyl group of *p*-CNPNN molecule plays a dominant role for the ferromagnetic interaction. The methyl and cyano groups slightly contribute to cancel the ferromagnetic interaction. J_{ab} values, 0.541 and 0.301 cm^{-1}, in the molecular sheet (Table I) obtained by INDO method may be compared with the experimental one ($J = 0.52$ cm^{-1}) derived from magnetic susceptibility measurement by assuming the square-lattice Heisenberg model.[9]

ACKNOWLEDGMENT

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