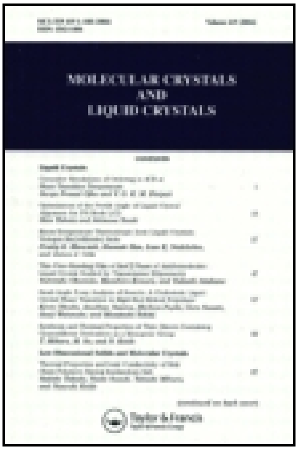

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Theoretical Studies of Magnetic Interactions in 3', 5'-Dihydroxyphenyl Nitronyl Nitroxide Crystal

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In order to investigate the ferromagnetic interaction in the 3', 5'-dihydroxyphenyl nitronyl nitroxide (RSNN), semiempirical and *ab initio* molecular orbital calculations were carried out for several pair models of RSNN molecules extracted from the X-ray crystal structure. It was shown that the effective exchange interaction (J_{ab}) for the nearest neighbor pair is ferromagnetic in accordance with the experimental results. For the pairs related with the double hydrogen bonds, the sign of the calculated J_{ab} values mainly corresponds with the experimental result, however partialy conflict. The hydroxyl groups contribute to the magnetic interaction in the RSNN crystal.

Keywords: molecular magnetism; nitronyl nitroxide; hydrogen bond; effective exchange integral

INTRODUCTION

Ferromagnetic behavior in organic radical crystals attracts a great interest.[1-6] Molecular orbital calculations have been carried out for pair and cluster models of phenyl nitronyl nitroxide (PNNO) derivatives to elucidate effective exchange interaction (J_{ab}) in their crystals.[1] It was shown that the sign and magnitude of the J_{ab} values calculated from the MO theory depend sensitively on the stacking mode of radical molecules.[1] The spin alignment rules were derived on the basis of the calculated results for PNNO derivatives.[7-11] Several calculations[7, 11] also suggested that molecular assembly and intermolecular magnetic interactions may be controlled by intermolecular hydrogen bonds. Particularly, bifurcated hydrogen bonds play an important role for the sign of J_{ab} values in the α phase of 2', 5'-dihydroxyphenyl nitronyl nitroxide (HQNN).[12]

Recently, Sugawara *et al.* reported the magnetic behavior of 3', 5'-dihydroxyphenyl nitronyl nitroxide (2-(3', 5'-dihydroxyphenyl)-4, 4, 5, 5-tetramethyl-4, 5-dihydro-1*H*-imidazolyl-1-oxy-3-oxide, abbreviated as RSNN).[13] In this crystal, a double intermolecular hydrogen bond is formed between the oxygen atom of nitronyl nitroxide (NN) group and the hydrogen atom of the hydroxyl group. This crystal undergoes a ferromagnetic intrapair interactions and an antiferromagnetic interpair interactions at low temperature. It is particularly interesting and important to investigate theoretically the origin of the magnetic interaction in this crystal to understand the role of the hydrogen bonds.

In this paper, we report the molecular orbital (MO) calculations for several pair models of RSNN molecules in the crystal. For the purpose of obtaining J_{ab} values in the order of 10^{-3}cm^{-1}, both total energy and densities in the order of 10^{-10} a.u. are required.[2, 3] The theoretical background and the computational procedures employed here were described in detail in the previous paper.[7-11]

CRYSTAL STRUCTURE

Fig. 1(a) illustrates the packing arrangement of RSNN molecules (**1** through **5**) with a space group of $P2_1/n$ in the crystal. Fig. 1(b) shows the geometry of a RSNN molecule with the numbering scheme.[13] The following features are remarked from the X-ray structure analysis.

(i) Compared with α-HQNN, RSNN have no intramolecular hydrogen bond. Therefore, there is no bond alternation in the NN group, and the twist angle between the NN group and the phenyl ring (23.3 degrees) is smaller than that of HQNN.

(ii) The hydroxyl groups O(1')H and O(2')H of molecule **1**, **4** and **5** also participate in intermolecular hydrogen bonds with the oxygen atoms of NN groups of two adjacent molecules at the both sites, resulting in a one-dimensional hydrogen-bonded chain along the diagonal of ac-plane (see Fig. 2). The distances of the hydrogen bonds are the same on one side of the molecule (d_1 =1.84Å; between **1** and **4**), they are slightly longer on the other side (d2 = 1.89Å; between **1** and **5**). Two types of similar one-dimensional chains run parallel to the previous one related with inversion symmetry between the two facing molecules. The oxygen of the NN group (O(2)) is located close to the C(1) of the NN group of the dimeric counterpart with the intermolecular distance of 3.727Å as depicted in **1**-**2** of Fig. 1(a). Since the overlap of the NN groups between pairs 1-3 is poor, the NN groups are located remote form each other.

The theoretical calculations were performed for all the possible pairs,

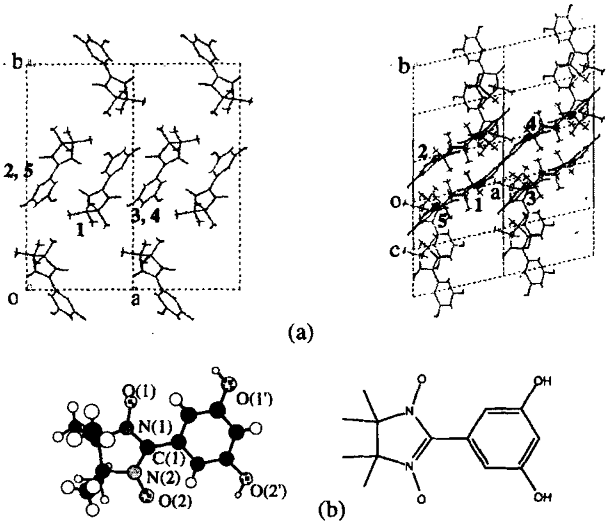

FIGURE 1 Crystal structure (a) and molecular geometry (b) of RSNN

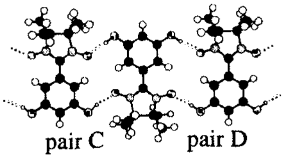

FIGURE 2 The hydrogen bonded chain

A(**1-2**), **B** (**1-3**), **C** (**1-4**) and **D** (**1-5**), by using of the INDO, UBLYP and UB3LYP methods. *Ab initio* UNO CASCI and CASSCF calculations[14, 15] were also carried out for simplified pair models (see Figs 3, 4 and 6).

CALCULATIONS FOR RSNN PAIR MOLECULES

In order to elucidate the magnetic property observed for the RSNN crystal, we carried out semiempirical INDO and *ab initio* calculations for four pair models of RSNN molecules. Table I shows the calculated J_{ab} values. Semiempirical INDO and UBLYP methods can reproduce qualitatively the experimental results for the pair **A** and **B**.[13] The pair **A** in Fig. 2 which has close contact between each NN groups (N-O...C) shows the largest J_{ab}. J_{ab} values of the pair **B** are slightly smaller than those of the pair **A**. On the other hand, the pair **C** and **D** have small $|J_{ab}|$ values in comparison with those of the pair **A** and **B**. One of the origins of this significant feature may be attributed to the dependence of J_{ab} on the interatomic distance (R). The J_{ab} decreases exponentially with the increase of R.[7, 8] Other contributions will be discussed later.

TABLE I J_{ab} values for the pairs shown in figure 1

	J_{ab}/cm^{-1}			
methods	**A**	**B**	**C**	**D**
INDO/UHF	0.782	0.613	-0.010	0.065
UBLYP/4-31G	2.718	2.693	-0.086	-0.046
UB3LYP/4-31G	4.971	3.449	0.048	0.219

CALCULATIONS FOR THE SIMPLIFIED PAIR MODELS

To study possible mechanisms of the ferromagnetic interaction in the RSNN crystal in detail, theoretical calculations with various methods were performed for the several simplified pair models.

(A) Simplified models for the pair A

The simplified pair models, $\mathbf{A}_1$ shown in Fig. 3 were considered. The model $\mathbf{A}_1$ consists of two nitronyl nitroxides (ON-C-NO). Positions of the substituted hydrogen atoms were optimized by PM3 (semiempirical method). Table II shows the calculated J_{ab} values and gives the following results.

(i) INDO and UBLYP calculations for model $\mathbf{A}_1$ can reproduce qualitatively the result of the full pair **A**. It suggests that NN groups of this pair are significant for the intermolecular ferromagnetic interaction(positive J_{ab} value).

(ii) UNO CASCI {2, 2} and UNO CASSCF {2, 2} methods by using of two active UNOs and two unpaired electrons give positive J_{ab} values, suggesting large contribution of direct SOMO-SOMO coupling to the ferromagnetic interaction.

A **$\mathbf{A}_1$**

FIGURE 3 Different simplified pair models for **A**

TABLE II J_{ab} values for the simplified models of the pair **A**

	J_{ab} /cm^{-1}	
methods	**A**	$\mathbf{A}_1$
INDO	0.782	1.518
UBLYP/4-31G	2.718	8.473
UMP2/4-31G		1.978
UNO CASCI{2, 2}$^{a)}$		1.349
UNO CASSCF{2, 2}$^{a)}$		13.694
UNO CASSCF{6, 6}$^{a)}$		2.484
UNO CASSCF{10, 10}$^{a)}$		2.271

a) 4-31G basis set was used.

(B) Simplified models for the pair B

J_{ab} values were calculated for the simplified pair models, $\mathbf{B}_1$ and $\mathbf{B}_2$ shown in Fig. 4. The models $\mathbf{B}_1$ is simplified in the same way as $\mathbf{A}_1$. The model $\mathbf{B}_2$ consists of two nitronyl nitroxides with dihydroxyphenyl moieties, and the hydroxyl groups of $\mathbf{B}_2$ are replaced by hydrogen atoms in $\mathbf{B}_3$. Table III shows the J_{ab} values obtained by several computational methods. The following conclusions were drawn from Table III:

(i) All the methods give positive J_{ab} values for pairs $\mathbf{B}_2$ and $\mathbf{B}_3$, which have phenyl rings, and negligible J_{ab} values for pair $\mathbf{B}_1$, which does not have phenylrings. These results indicate that the phenyl ring plays an important role for the ferromagnetic interaction in the pair **B**, and NN groups scarcely contribute to positive J_{ab} values.

(ii) Comparisons between the J_{ab} values of the model $\mathbf{B}_2$ and that of the model $\mathbf{B}_3$ show that hydroxyl groups do not play an important role for the intermolecular interaction in the pair **B**.

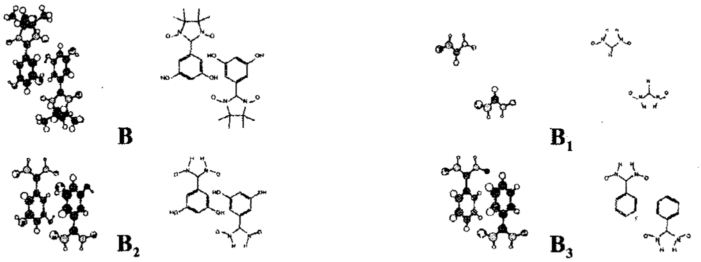

FIGURE 4 Different simplified pair models for **B**

TABLE III J_{ab} values for the simplified models for the pair **B**

	J_{ab} /cm^{-1}			
methods	**B**	$\mathbf{B}_1$	$\mathbf{B}_2$	$\mathbf{B}_3$
INDO	0.613	0.000	1.460	1.590
UBLYP/4-31G	2.693			3.672
UNO CASCI{2, 2}$^{a)}$			0.032	0.005
UNO CASSCF{2, 2}$^{a)}$			2.031	1.941
UNO CASSCF{6, 6}$^{a)}$			1.337	0.709

a) 4-31G basis set was used.

(C) Simplified models for the pairs C and D

The simplified models $\mathbf{C}_1$ through $\mathbf{C}_4$ and $\mathbf{D}_1$ through $\mathbf{D}_4$ shown in Fig. 5 were considered. Table IV shows the calculated J_{ab} values. The model $\mathbf{C}_1$ and $\mathbf{D}_1$ are simplified in the same way as $\mathbf{A}_1$, and the model $\mathbf{C}_2$ and $\mathbf{D}_2$ are simplified in the same way as $\mathbf{B}_2$. For the model $\mathbf{C}_3$ and $\mathbf{D}_3$, the hydroxyl groups linked to N-O radical group by hydrogen bond in $\mathbf{C}_2$ and $\mathbf{D}_2$ are replaced by hydrogen atoms. In the model $\mathbf{C}_4$ and $\mathbf{D}_4$, hydroxy butadiene groups linked to opposite N-O radical group by hydrogen bond are attached to $\mathbf{C}_1$ and $\mathbf{D}_1$.

(i) INDO and UNO CASSCF methods give negative J_{ab} values for model $\mathbf{C}_2$ and $\mathbf{C}_4$, which have intermolecular hydrogen bonds, and positive J_{ab} values for model $\mathbf{C}_3$ which does not have intermolecular hydrogen bonds. These results indicate that the intermolecular hydrogen bond plays an important role for the magnetic interaction in the pair **C**.

(ii) The absolute values of J_{ab} for the model $\mathbf{D}_2$ make a difference form that of $\mathbf{D}_4$. It suggests that the intermolecular hydrogen bonds are significant for the intermolecular interaction in pair **D**.

(iii) Comparisons among INDO, UBLYP/4-31G and UNO CASSCF results show that semiempirical INDO method gives reasonable J_{ab} values for all models, and UNO CASSCF method gives reasonable J_{ab} for the models which have phenyl rings.

(iv) All J_{ab} values of these models calculated by the INDO method are smaller than those of pairs **A** and **B**.

Table IV suggests that the hydrogen bonds in model **C** and **D** play a dominant role for the intermolecular ferromagnetic interaction. For investigating this interaction more precisely, the hydroxyl groups of the model $\mathbf{C}_4$ and $\mathbf{D}_4$ were rotated simultaneously about the respective C-O axis with rotation angle θ (Fig. 6). J_{ab} value was calculated by INDO method for every 30° of the rotation angle. Figure 7 shows the J_{ab} values for the model $\mathbf{C}_4$ and $\mathbf{D}_4$ with different angles. When the rotation angle of the model $\mathbf{C}_4$ is in between 30° and 240°, the J_{ab} value turns into positive. Regarding the model $\mathbf{D}_4$, J_{ab} value turns into negative with rotation angle 60°. It is noted that break of the hydrogen bonding in the model $\mathbf{C}_4$ leads to ferromagnetic interaction, and in the model $\mathbf{D}_4$ that leads to antiferromagnetic interaction. For the model

TABLE IV J_{ab} for the simplified models for the pairs **C** and **D**

	J_{ab} /cm^{-1}				
methods	**C**	**C$_1$**	**C$_2$**	**C$_3$**	**C$_4$**
INDO	-0.010	0.000	-0.010	0.025	-0.066
UBLYP/4-31G	-0.086		0.064		0.816
UNO CASSCF{2, 2}$^{a)}$			-0.005	0.025	-0.005
UNO CASSCF{6, 6}$^{a)}$			-0.007	-0.031	

a) 4-31G basis set was used.

	J_{ab} /cm^{-1}				
methods	**D**	**D$_1$**	**D$_2$**	**D$_3$**	**D$_4$**
INDO	0.065	0.000	0.075	0.035	0.314
UBLYP/4-31G	-0.046		0.209		1.369
UNO CASCI {2, 2}$^{a)}$			0.008	-0.022	0.007
UNO CASSCF{2, 2}$^{a)}$			-0.005	0.080	-0.007
UNO CASCI{6, 6}a)			0.178	-0.306	0.582
UNO CASSCF{6, 6}$^{a)}$			0.017	0.044	0.231
UNO CASCI{10, 10}$^{a)}$			0.017	-0.237	

a) 4-31G basis set was used.

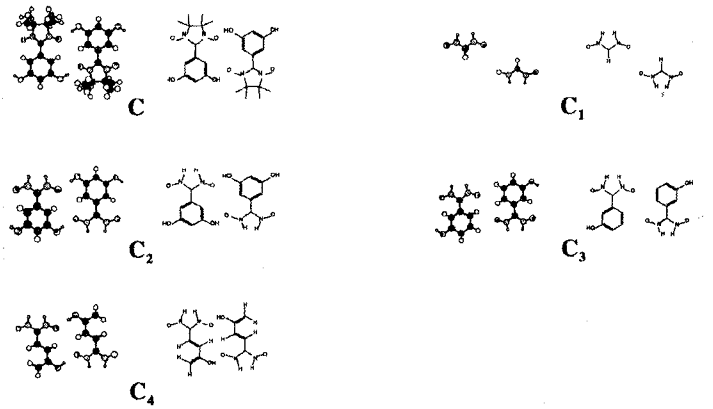

FIGURE 5 Simplified pair models for **C** in figure 2
(models for **D** are constructed with the same way as models for **C**)

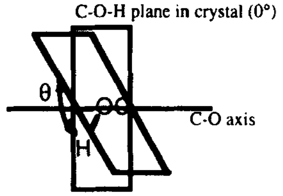

FIGURE 6 Rotation of hydroxyl group

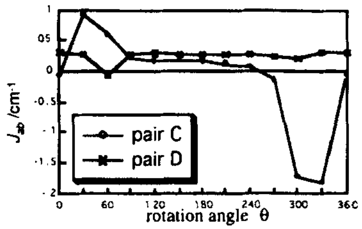

FIGURE 7 J_{ab} vs. rotation angle of OH group

C_4, the rotation of hydoroxyl group changes more sensitively the sign of J_{ab} values than the model D_4. This implies that the pressure effect is an interesting experimental task in the future.

CONCLUDING REMARK

The J_{ab} values of the pair **A** are much larger than that of pair **C** and **D**. The UNO CASSCF {2, 2} result shows that the SOMO-SOMO potential exchange (PE) interaction is dominant for the intermolecular ferromagnetic interactions of pair **A**, while the through-bond interaction is predominant in the pair **B**.

Ab initio and semiempirical calculations indicate that the hydrogen bonds are dominant for the intermolecular magnetic interactions. The J_{ab} values of the simplified models without hydrogen bond are much different from the full pair **C** and **D**. The model C_4 and D_4 gave a useful guide for understanding of the role of the hydrogen bond: the sign of J_{ab} value depends on the rotation angle of the hydroxyl groups. The J_{ab} values of the model C_4 change more sensitively than those of D_4. Assuming that the rotation of the hydroxyl group is caused by the pressure effect, the influence of this effect for the pair **C** is larger than that of the pair **D**. The UNO CASSCF method with two SOMOs and two unpaired electrons {2, 2} demonstrates that the SOMO-SOMO potential exchange (PE) interaction is not important for the ferromagnetic interaction in the pair **C** and **D**.

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