Theoretical Studies of Magnetic Interactions in 2′, 5′-Dihydroxyphenyl Nitronyl Nitroxide Crystal

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THEORETICAL STUDIES OF MAGNETIC INTERACTIONS IN 2', 5'-DIHYDROXYPHENYL NITRONYL NITROXIDE CRYSTAL

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444, Japan; [3]Department of Chemistry, Faculty of Science, Kanagawa University,
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Abstract   In order to investigate the ferromagnetic interaction in the α phase of
2', 5'-dihydroxyphenyl nitronyl nitroxide (HQNN), semiempirical and *ab initio*
molecular orbital calculations were carried out for several pair models of HQNN
molecules extracted from the crystal structure. It was shown that the effective
exchange interaction (J_{ab}) for the nearest neighbor molecules is ferromagnetic,
being in agreement with the experimental result. The hydroxyl groups and the
methyl groups contribute to the ferromagnetic interaction in the α phase of
HQNN crystal.

INTRODUCTION

Ferromagnetic behavior in organic radical crystals attracts a great interest.[1-6] Molecular
orbital calculations have been carried out for pair 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 calculated J_{ab} values depend sensitively on
the stacking mode of the 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.

Recently, Sugawara, *et al.* reported the magnetic behavior of α phase of 2',
5'-dihydroxyphenyl nitronyl nitroxide (2-(2', 5'-dihydroxyphenyl)-4, 4, 5, 5-tetramethyl-4,
5-dihydro-1*H*-imidazolyl-1-oxy-3-oxide, abbreviated as HQNN).[12] This crystal undergoes
a ferromagnetic phase transition at low temperature and intermolecular hydrogen bond is
formed between oxygen atom of nitronyl nitroxide (NN) group and hydrogen atom of
hydroxyl group. It is particularly interesting and important to investigate theoretically

the origin of the ferromagnetic 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 HQNN molecules in the crystal. The computational procedures employed here were described in detail in the previous paper.[7-10]

THEORETICAL BACKGROUND

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

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

The kinetic (KE) and potential (PE) exchange terms are, respectively, determined by SOMO-SOMO overlap S_{ab} and intermolecular exchange integral K_{ab}. The spin polarization (SP) term is given by the product of spin densities ($\rho_{a(b)}$) induced by the spin polarization effect.[7] The ferromagnetic interaction in molecular crystals can be explained by these terms. A simple classification of the magnetic interaction was derived.[9, 10]

Case I	$(J_{ab}(\text{KE})<0, J_{ab}(\text{PE})>0; J_{ab}<0)$	(2a)
Case II	$(J_{ab}(\text{KE})\approx0, J_{ab}(\text{PE})>0; J_{ab}>0)$	(2b)
Case III	$(J_{ab}(\text{KE})\approx0, J_{ab}(\text{PE})\approx0, J_{ab}(\text{SP})>0; J_{ab}>0)$	(2c)
Case IV	$(J_{ab}(\text{KE})\approx0, J_{ab}(\text{PE})\approx0, J_{ab}(\text{SP})<0; J_{ab}<0)$	(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 nonzero Coulombic exchange integral $(J_{ab}(\text{PE})=K_{ab})$ as studied in the case of simple nitroxide pair model.[9] On the other hand, the SP term induced by the indirect interactions through bond and space becomes important when the distance between the two radical groups is large (Case III, IV). For example, β-phase of p-NPNN corresponds to the case III.[2] The sign of $J_{ab}(\text{SP})$ depends on the phase of spin alternation by the SP 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, has been used to estimate the SOMO-SOMO direct interaction terms (KE and PE).[9, 10, 13, 14] Semiempirical INDO method has been successfully employed to calculate J_{ab} values which include all terms in eq. 1.

CRYSTAL STRUCTURE

Figure 1(a) illustrates the packing arrangement of HQNN molecules (**1** through **5**) in the crystal and Figure 1(b) shows the geometry of a HQNN molecule with numbering scheme.[12] The following features are remarked from the X-ray structure analysis.

(i) The hydroxyl group (O(1')H) forms a strong intramolecular hydrogen bond (O(1')...O(1) : 2.507Å) with one of the NO groups (N(1)-O(1)). This hydrogen bond induces a remarkable deformation of the NN group. The bond lengths of N(1)-O(1) and C(1)-N(1)
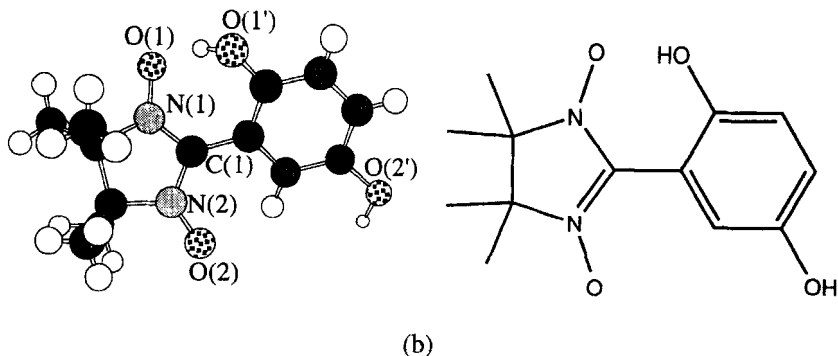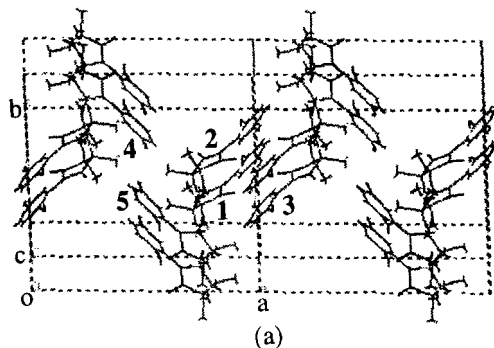

(a)

(b)

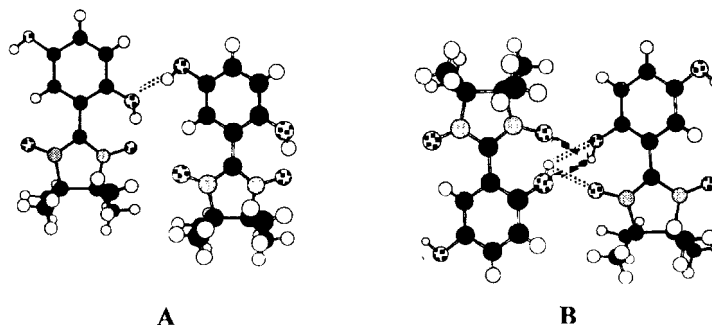FIGURE 1   Crystal structure (a) and molecular geometry (b) of HQNN

FIGURE 2   Pairs which have intermolecular hydrogen bonds

at the hydrogen-bonded side are 1.303 and 1.332Å, respectively, whereas those of N(2)-
O(2) and C(1)-N(2) at the opposite side are 1.272 and 1.367Å, respectively.

(ii) The hydroxyl group O(1')H of molecule 1 also participates in an intermolecular
hydrogen bond with the O(2')H group of the translated molecule (2) along the c-axis,
resulting in a one-dimensional hydrogen-bonded chain along the c-axis. A similar one-
dimensional chain runs parallel to the previous one related with inversion symmetry
between the two facing molecules. Two NN groups related by inversion symmetry are
located in proximity with the short NO...ON of distance 3.159Å presumably due to two
bifurcated hydrogen bonds between the two hydroxyl groups as shown in Figure 2B.
These two arrays form a herringbone type structure.

The theoretical calculations were performed for all possible pairs, A (1-2), B
(1-3), C (1-4), D (1-5) and E (2-5) by use of the semiempirical INDO method. *Ab initio*
UNO CASCI and CASSCF calculations[13, 14] were carried out for simplified pair models.

CALCULATIONS FOR HQNN PAIR MOLECULES

In order to elucidate the ferromagnetic property observed for the HQNN crystal, we
carried out semiempirical INDO calculations for five pair models of HQNN molecules.
Table I shows the calculated J_{ab} values. Semiempirical INDO method can reproduce
qualitatively the experimental results.[12] The pair B in Figure 2 which has bifurcated
hydrogen bonds (OH...OH and OH...O-N) shows the largest J_{ab}. J_{ab} values of other
pairs are smaller than a half of J_{ab} for 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}

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

| methods | | J_{ab}/cm^{-1} | | | |
	A	B	C	D	E
INDO/UHF	0.013	0.041	-0.003	0.010	0.008

decreases exponentially with the increase of R.[7, 8] Other contributions will be discussed later.

CALCULATIONS FOR THE SIMPLIFIED PAIR MODELS

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

(A) Simplified models for the pair A

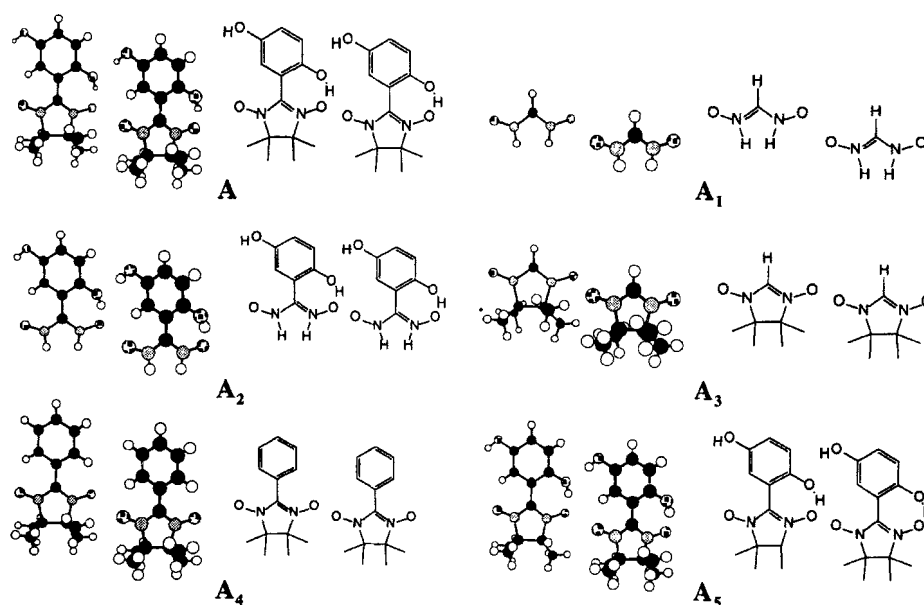The simplified pair models, A_1 through A_5 shown in Figure 3 were considered. The

FIGURE 3 Different simplified pair models for A in Figure 2

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

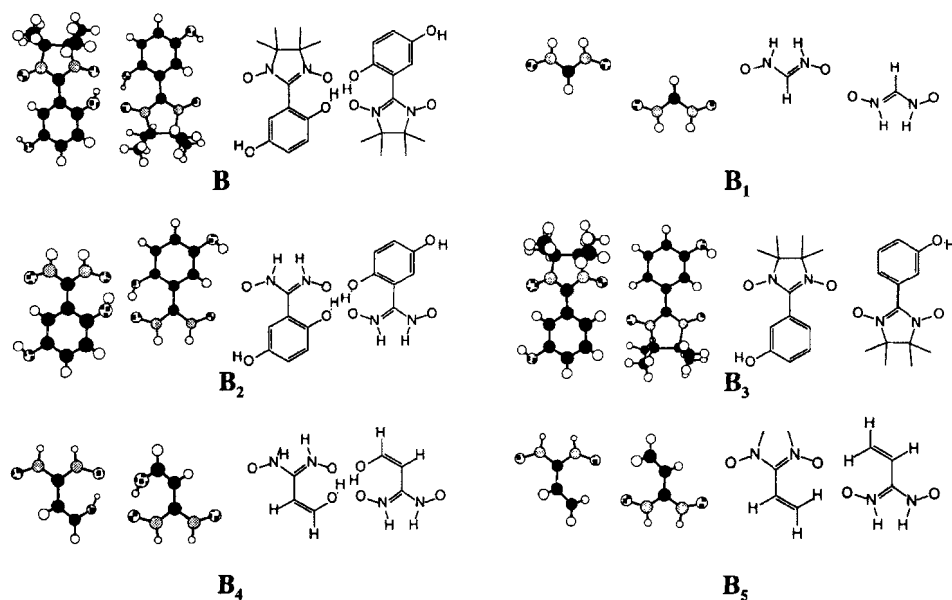| methods	J_{ab}/cm^{-1}					
	A	**A$_1$**	**A$_2$**	**A$_3$**	**A$_4$**	**A$_5$**
INDO	0.013	0.000	-0.001	0.009	0.005	-0.004
UNO CASCI{2, 2}[a]		0.003	0.006			
UNO CASSCF{2, 2}[a]		0.002	0.002			

a) 4-31G basis set was used.

model **A$_1$** consists of two nitronyl nitroxides (ON-C-NO) and the model **A$_2$** consists of two nitronyl nitroxides with hydroquinone moieties. In the model **A$_3$** hydroquinone moieties of **A** are replaced by hydrogen atoms, in **A$_4$** hydroxyl groups of **A** are replaced by hydrogen atoms and in **A$_5$** one of the methyl groups of **A** is replaced by hydrogen atom. The methyl group locates in close proximity to adjacent N-O group. 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 calculation suggests that the methyl group in close proximity to adjacent N-O group is significant for the intermolecular ferromagnetic interaction (positive J_{ab} value). Replacement of the methyl group by hydrogen atom leads to very weak antiferromagnetic interaction in **A$_5$**.

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

(B) Simplified models for the pair **B**

J_{ab} values were calculated for the simplified pair models, **B$_1$** through **B$_5$** shown in Figure 4. The models **B$_1$** and **B$_2$** are simplified in the same way as **A$_1$** and **A$_2$**. For the model **B$_3$**, hydroxyl groups linked to N-O radical group by bifurcated hydrogen bond in model **B** are replaced by hydrogen atoms. In the model **B$_4$** hydroxy ethylene groups linked to opposite N-O radical group by bifurcated hydrogen bond are attached to **B$_1$**. The hydroxyl groups of **B$_4$** are replaced by hydrogen atoms in **B$_5$**. 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 **B$_2$** and **B$_4$**, which have intermolecular hydrogen bonds, and negative J_{ab} values for pairs **B$_1$**, **B$_3$** and **B$_5$**, which do not have

FIGURE 4   Different simplified pair models for **B** in Figure 2

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

methods	**B**	**B$_1$**	**B$_2$**	**B$_3$**	**B$_4$**	**B$_5$**
			J_{ab} /cm^{-1}			
INDO	0.041	-0.030	0.121	-0.138	0.141	-0.505
UNO CASCI{2, 2}$^{a)}$		-1.554	0.142		0.148	-1.002
UNO CASSCF{2, 2}$^{a)}$		-1.036	0.014		0.016	-1.848

a) 4-31G basis set was used.

intermolecular hydrogen bonds. These results indicate that the intermolecular hydrogen bond plays an important role for the ferromagnetic interaction in the pair **B**.

(ii) Comparisons between *ab initio* and INDO results show that semiempirical INDO method gives reasonable J_{ab} values for all models.

Table III suggests that the hydrogen bonds in model **B** play a dominant role for the intermolecular ferromagnetic interaction. For investigating this interaction more precisely the hydroxyl groups of the model **B$_4$** were rotated simultaneously about the

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TABLE IV J_{ab} vs. rotation angle of OH group

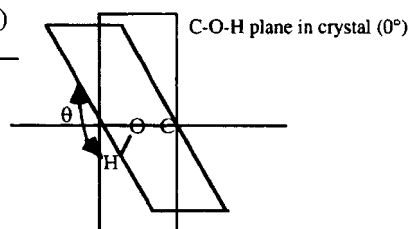| θ	J_{ab} (INDO)	θ	J_{ab} (INDO)
0°	0.141	180°	-0.545
30°	1.179	210°	-0.530
60°	7.088	240°	-0.061
90°	4.339	270°	4.288
120°	-0.055	300°	7.028
150°	-0.529	330°	1.172

C-O-H plane in crystal (0°)

FIGURE 5 Rotation of hydroxyl group

respective C-O axis with rotation angle R (Figure 5). J_{ab} value was calculated by INDO method for every 30° of the rotation angle. Table IV shows the J_{ab} values for the pair $\mathbf{B_4}$ with different angles. When the rotation angle is in between 120° and 240°, the J_{ab} value turns into negative. It is noted that break of the hydrogen bonding in the pair $\mathbf{B_4}$ leads to antiferromagnetic interaction.
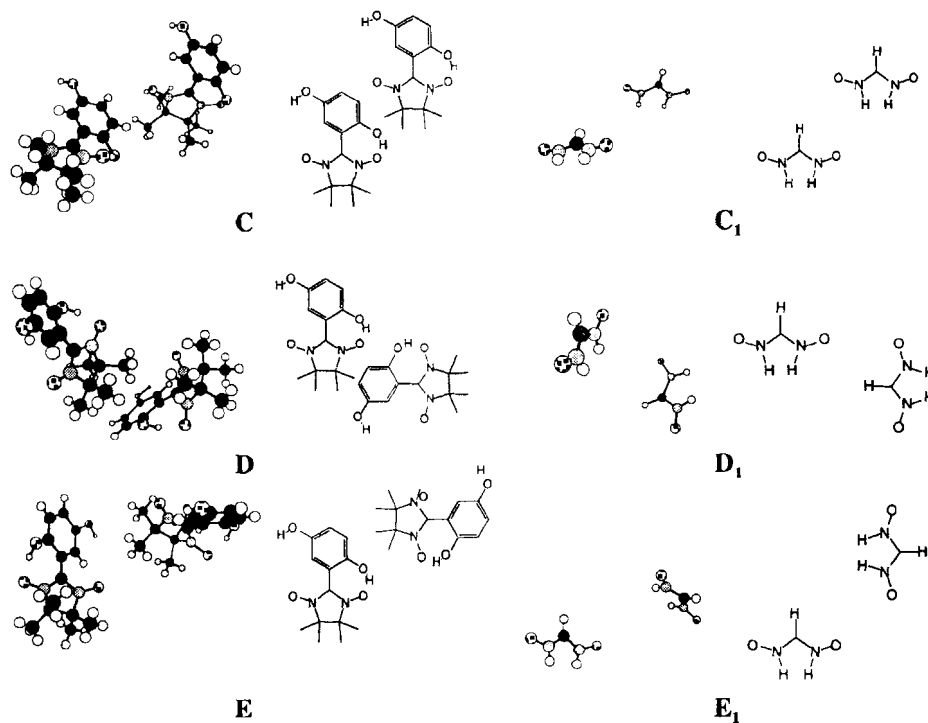
(C) Simplified models for the pairs C, D and E

The simplified models $\mathbf{C_1}$, $\mathbf{D_1}$ and $\mathbf{E_1}$ shown in Figure 6 were considered. Table V shows the calculated J_{ab} values. These pairs are simplified in the same way as $\mathbf{A_1}$. All J_{ab} values calculated by the INDO method are small compared with the pairs $\mathbf{A}$ and $\mathbf{B}$ because of the long intermolecular distances.

TABLE V J_{ab} for the simplified models for the pairs C, D and E

methods	J_{ab} /cm^{-1}					
	C	C_1	D	D_1	E	E_1
INDO	-0.003	0.000	0.010	0.000	0.008	0.000
UNO CASCI{2,2}[a]		0.000		0.000		0.000
UNO CASSCF{2,2}[a]		0.000				

a) 4-31G basis set was used.

FIGURE 6 Simplified pair models for C, D and E

CONCLUDING REMARK

Ab initio and semiempirical calculations indicate that magnetic interaction through the bifurcated hydrogen bonds in the pair **B** is dominant for the ferromagnetic property of α-HQNN crystal. The J_{ab} value of the pair **B** is almost three times larger than that of other pairs (**A**, **C**, **D** and **E**). The pair **B** has bifurcated hydrogen bonds and the simplified models of **B** without hydrogen bonds show negative J_{ab} values. The simplified model **B$_4$** 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 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 **B**.

The J_{ab} value of the pair **A** is positive in the case that all the methyl groups remain. Close contact between the methyl group and adjacent N-O radical group is important for the intermolecular ferromagnetic interaction rather than hydrogen bonding

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in the pair **A**.

There is intermolecular antiferromagnetic interaction for the pair **C**, but this is too small to prevent the ferromagnetic interactions in the crystal.

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