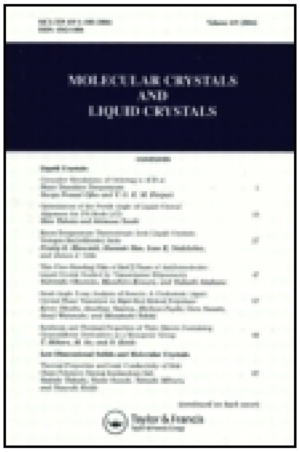

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MAGNETIC INTERACTION VIA β-HYDROGEN ATOMS IN TEMPO DERIVATIVES

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Abstract Theoretical studies of the ferromagnetic property of phenyl-CH=N-TEMPO were carried out. The effective exchange integrals (J_{ab}) were calculated for the nearest neighbour molecules in the crystal and the ferromagnetic interaction was revealed. To study the role of the hydrogen atoms, modified pair models were considered. It was concluded that the bridged β-hydrogen atoms dominantly contribute to the ferromagnetic interaction in the phenyl-CH=N-TEMPO crystal.

INTRODUCTION

Organic ferromagnets have been receiving continuous interest in recent years. [1-5] Many experimental and theoretical studies have been carried out to elucidate the mechanism of the magnetic interaction. Theoretical studies based on molecular orbital calculations have been performed in our group for various molecular systems, *i.e.*, *p*-NPNN, TMAO and their derivatives, in cooperation with experimental studies. It was shown that the magnetic interaction between organic radicals can be characterized quantitatively by the effective exchange integral (J_{ab}).

Recently, Nogami *et al.* reported ferromagnetic behavior of Phenyl-CH=N-TEMPO (4-benzylideneamino-2,2,6,6-tetramethylpiperidin-1-oxyl) (**1**). [5] This crystal shows Weiss temperature of +0.74 K and undergoes ferromagnetic phase transition at T_c = 0.18 K. Related compounds of the TEMPO derivatives also show ferromagnetic behaviors. A common structural feature was found for these TEMPO derivatives: β-hydrogen atoms, *i.e.*, methyl hydrogen atoms and/or methyene hydrogen atoms, locate in close contact with the neighboring nitroxide (NO) radical group in the crystal.

In the previous papers, we proposed the hydrogen bridging effect that the ferromagnetic interaction can be mediated by the hydrogen atoms.[6,7] A series of TEMPO derivatives seem a suitable system for the precise investigation of the hydrogen bridging effect. We here report the detailed theoretical studies on these species. Calculations based on molecular orbital (MO) theory[6] were carried out to evaluate the intermolecular effective exchange integrals for pair molecules in the crystal. Particularly, we wish to elucidate the origin of the ferromagnetic interaction in the crystals in relation to designing the organic ferromagnetic materials.

THEORETICAL BACKGROUND

The effective exchange integral J_{ab} is generally expressed by three different terms under the approximately spin-projected unrestricted Hartee-Fock (APUHF) method[8,9],

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

where the kinetic (KE) and potential (PE) exchange terms are given by the overlap integral (S_{ab}) and exchange integral (K_{ab}) between SOMOs, respectively. The spin polarization (SP) term is given by the product of spin densities ($\rho_{a(b)}$) induced by the SP effect. Analysis of J_{ab} by these terms is useful to understand and to design the ferromagnetic interaction for constructing the organic ferromagnets.

The condision J_{ab} (KE)<0 means that the orbital overlap leads to a strong antiferromagnetic interaction between radical groups as understood intuitively. However for the condition of $S_{ab}\approx 0$, the first term in Eq. (1) vanishes and the J_{ab} is determined by the second and third terms. If the PE term remains, J_{ab} value is positive and ferromagnetic interaction appears. We already investigated the systems satisfying this condition, *i.e.*, various stacking models of nitroxide derivatives[8-10] and ionic crystals of *p*-carboxyl phenyl nitronyl nitroxide[3,11]. We could successfully explain the strong ferromagnetic interaction in these crystals in terms of our orbital symmetry rule.[8-10] For the last case, if not only the KE term but also the PE term is almost negligible because of a lack of the direct interaction between radical groups, the SP term dominates the sign and the magnitude of the J_{ab} value. Namely, indirect magnetic interaction by the SP effect through bonds and space plays an important role. For example, the β-phase of *p*-NPNN corresponds to this case.[12,13]

Since the spin density on the hydrogen atom is usually small, the hydrogen atom was not taken into account for explanation of the ferromagnetic interaction in crystals. However, the weak magnetic interaction via the hydrogen bridging is a current interest in relation to the ferromagnetic phase transitions at low temperature in several organic ferromagnets recently discovered. [4,5] Our previous theoretical calculations suggest that the hydrogen bridging is effective for the weak intermolecular ferromagnetic exchange interaction. [6] Two different mechanisms for the effective exchange interaction via hydrogen bridging are conceivable. One is the hyperconjugation between the hydrogen atom and SOMO of nitroxide group, which is called as "hydrogen bridging hyperconjugative effect" . The potential exchange between hyperconjugated SOMOs provides a ferromagnetic exchange interaction. The other is the spin polarization (SP) effect via the hydrogen atom bridging, though the spin density induced on the hydrogen atom by the nitroxide radical group is small. This mechanism is referred to "the hydrogen bridging SP effect".

CRYSTAL STRUCTURES

Figure 1 illustrates the two unit cells of the crystal. Ph-CH=N-TEMPO crystallizes in a monoclinic unit cell, $P2_1/c$, and cell parameters are a = 12.6835 Å, b = 11.7402 Å, c = 11.0236 Å, and β = 111.399 °. [5] In this figure, let us consider the molecule **A** as a reference. Molecular pair **A-B** is expected to have the largest intermolecular magnetic interaction, because two adjacent NO groups locate in close proximity. The theoretical calculations for this pair were carried out in detail. This pair is depicted in Figure 2, and it is shown that not only the direct interaction between N_1O_1 and N_2O_2 but also the indirect interaction paths I and II may be expected. The distances between the oxygen atom of

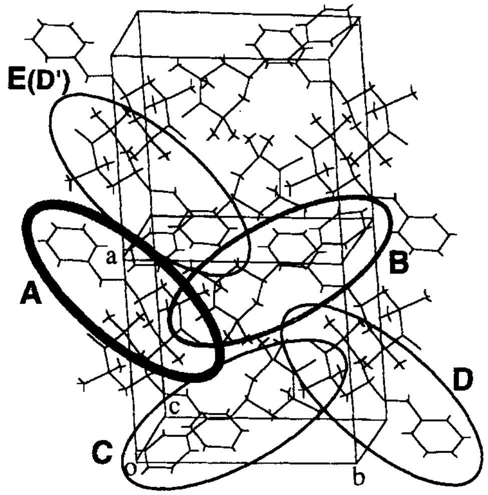


FIGURE 1 The crystal structure of phenel-CH=N-TEMPO.

FIGURE 2 Direct and indirect interaction paths in the nearest neighbor pair **A**-**B**.

NO group and the hydrogen atom of methyl group are 2.878 Å and 3.316 Å for paths I and II, respectively. These hydrogen bridging paths are interesting for the ferromagnetic interaction in the crystal.

The nitroxide radical groups are arranged to construct a two-dimensional sheet, where the distances between the adjacent NO groups are 5.62 Å and 6.15 Å for the nearest and second nearest pairs, respectively. The intersheets distance is 11.89 Å. In addition to the pair **A**-**B**, pairs **A**-**C**, **A**-**D** and **A**-**E** were studied. The pairs **A**-**C** and **A**-**D** are the second and the third nearest neighbors, respectively. The pair **A**-**E** represents the intersheet interaction (see Figure 7).

CALCULATIONS FOR PAIR A-B

Figure 3 illustrates simplified models of the pair **A**-**B**. Model I is the actual structure in the crystal. In model II ph-CH=N- group is replaced by a hydrogen atom to study the role of the phenyl ring for the magnetic interaction. In model III$_a$ β and γ methylene frameworks are replaced by hydrogen atoms and only the CH_3CH_2NOH frame is considered in model IV$_a$. When we go through the process of the simplification, *i.e.*, **A** → **A'** → **A''** → **A'''** and **B** → **B'** → **B''** → **B'''**, the interaction localized near the NO radical groups comes into the spotlight.

Ab initio UHF and INDO calculations were carried out for these models to elucidate the path of the ferromagnetic effective exchange interaction. Here, the 4-31G basis sets were used, since we performed calculations with various basis sets and it was concluded

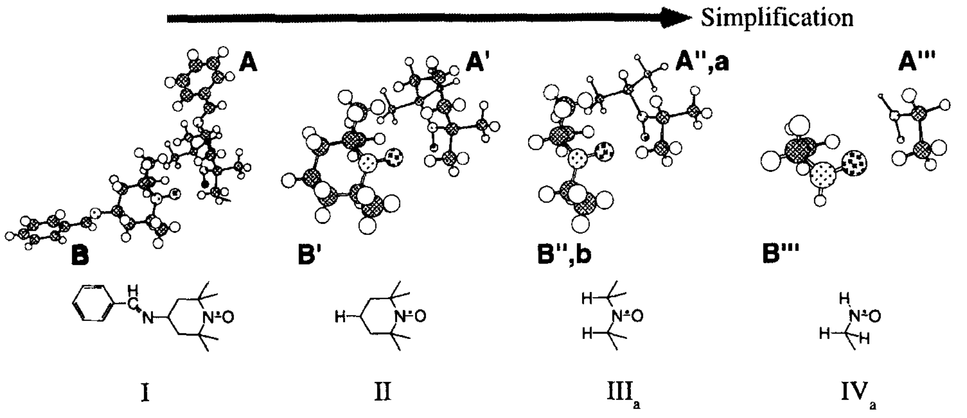


FIGURE 3 Simplified models of pair **A**-**B**.

TABLE 1 J_{ab} values for pair **A**-**B** and its simplified models.

	J_{ab} /cm^{-1}			
methods	I	II	III$_a$	IV$_a$
INDO	0.010	0.010	0.009	0.021
UHF [a)]	0.164	0.170	0.155	0.125
UNO CASCI{2,2} [a)]			0.149	0.120
UNO CASSCF{2,2} [a)]			0.145	0.110

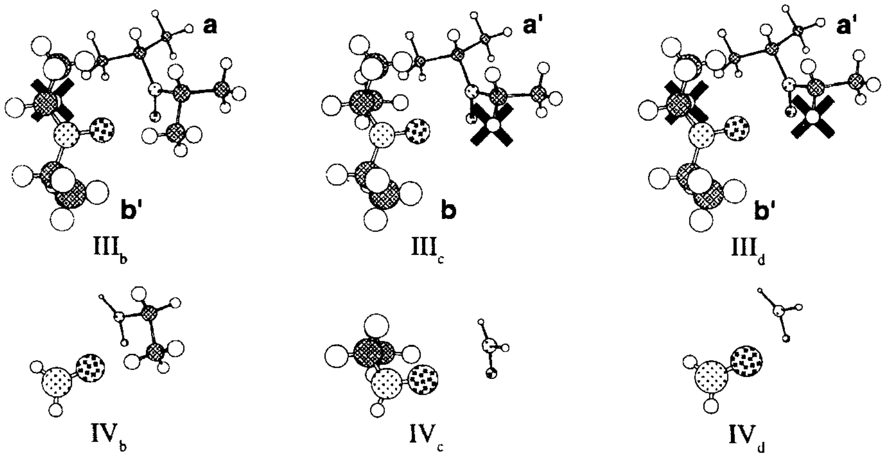
a) 4-31G basis set was used.

that the 4-31G basis sets can give relatively good result.[6] For the simplified models III$_a$ and IV$_a$ the UNO CASCI{2,2} and UNO CASSCF{2,2} /4-31G methods were also employed, whereas these methods are not feasible for complicated models I and II. Table 1 shows the J_{ab} values obtained by these computations. J_{ab} values for all models are positive, indicating a ferromagnetic interaction for pair **A**-**B**. It is noteworthy that similar J_{ab} values were obtained for all models I, II, III$_a$ and IV$_a$. This result means that ph-CH=N- and methylene groups of TEMPO framework have negligible effect for the magnetic interaction. Judging from the spin density calculated by the INDO method, the induced spin density on the hydrogen atom is consistent with spin density expected from the SP rule, and therefore the explanation of the ferromagnetic interaction based on the SP effect may be feasible. In addition to the spin polarization mechanism, the SOMO-SOMO interaction seems to contribute to the ferromagnetic interaction through the hydrogen bridging. This was pointed out by the result that the UNO CASCI{2,2} and UNO CASSCF{2,2} methods gave relatively large J_{ab} values for models III$_a$ and IV$_a$.

CALCULATIONS FOR SIMPLIFIED MODELS

As mentioned in the previous section, two kinds of indirect magnetic interaction paths I and II are expected to exist in the nearest neighbor pair **A**-**B**. In order to investigate these contribution, simplified models with decomposing the two interaction paths were considered.

Figure 4 illustrates the simplified models, where molecules **A''** and **B''** in model III_a shown in Figure 3 are renamed as **a** and **b**, respectively. In model III_b one of the methyl groups of the molecule **b** was replaced by a hydrogen atom (marked by a cross), leading to the break of the hydrogen bridging path II of model III_a, while in model III_c a methyl group of molecule **a** was replaced by a hydrogen atom (marked by a cross), leading to the break of the hydrogen bridging path I of model III_a. In model III_d both interaction paths I and II are broken by replacing the methyl groups with hydrogen atoms (marked by crosses). The J_{ab} values calculated by the INDO method for model III_a through III_d are listed in Table 2. Although scatter of the calculated J_{ab} values is not small,



III_b III_c III_d

IV_b IV_c IV_d

FIGURE 4 Simplified models of III_a and IV_a in Figure 3.

TABLE 2 J_{ab} values for simplified III_a through III_d and IV_a through IV_d shown in Figures 3 and 4.

	J_{ab} /cm^{-1} [a]			
	subscript (a)	(b)	(c)	(d)
III	0.009	0.003	-0.005	-0.001
IV	0.021	0.018	0.000	0.000

a) INDO method was used.

the ferromagnetic interaction (J_{ab} = 0.009 cm^{-1}) in model III$_a$ decreased by breaking the hydrogen bridging paths I and II. The result suggests that the hydrogen bridging paths I and II contribute to the ferromagnetic interaction and the ferromagnetic interaction mediated by path I seems large compared with that of path II. As listed in Table 2, a similar trend was obtained for J_{ab} values of more simplified models IV$_b$ through IV$_d$ shown in Figure 4. The model IV$_b$ lacks in the hydrogen bridging path II, the model IV$_c$ lacks in the path I and the model IV$_d$ lacks in both paths I and II.

As discussed above, Table 1 suggests that the SOMO-SOMO interaction through the hydrogen bridging seems to contribute to the ferromagnetic interaction and Table 2 indicates that hydrogen bridging paths I and II contribute to the ferromagnetic interaction. Combining these two results, it is concluded that in addition to the spin polarization mechanism hyperconjugated SOMO should spread over the hydrogen atoms of the methyl groups. The spin polarization and hyperconjugation mechanism may be also affected by chemical modification of molecular group outside the interaction path. In

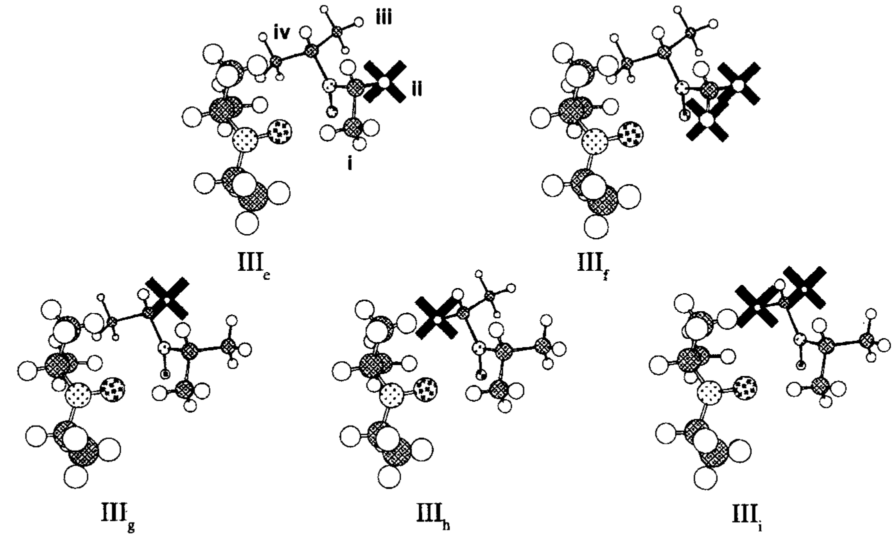


FIGURE 5 Models to elucidate the effect of the other β-methy group.

TABLE 3 J_{ab} values for models III$_e$ through III$_i$ shown in Figure 5.

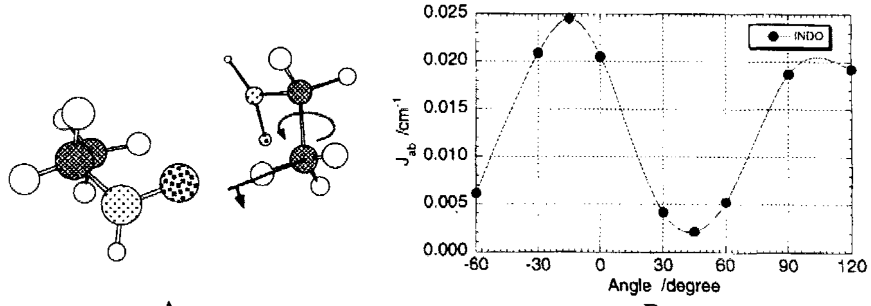
	J_{ab} /cm^{-1} ^{a}				
	subscript (e)	(f)	(g)	(h)	(i)
III	0.019	-0.004	0.008	0.008	0.008

a) INDO method was used.

order to investigate the secondary effect of the methyl group outside the hydrogen bridging, J_{ab} value was calculated for model pairs III_e through III_i shown in Figure 5. In model III_e methyl group **ii** of model III_a is replaced by a hydrogen atom, while in model III_f methyl groups **i** and **ii** are replaced by hydrogen atoms. In model III_g methyl group **iii** is replaced by hydrogen atom, in model III_h **iv** is replaced and both **iii** and **iv** are replaced by hydrogen atoms in model III_i. J_{ab} values calculated by the INDO method are listed in Table 3. Chemical modification of the methyl group **ii** (model III_e), which locates in proximity with the methyl group participating in the intermolecular ferromagnetic interaction, gave a significant change of J_{ab}. In addition, model III_f lacking the interaction path I, too, gave almost the same J_{ab} value as III_c. Other modifications of the remote methyl groups from the interaction path (methyl group **i**) gave no effect on J_{ab} (III_g through III_i) and gave the same tendency as III_a. Those calculations suggest that supplement of the methyl group near the interaction path modifies the spin polarization and/or hyperconjugation.

In the calculations described above, the methyl groups participating in the interaction path were replaced by hydrogen atoms. It is clear that the methyl group **i** is important for the intermolecular ferromagnetic interaction. However, it is not clarified which one of the carbon and hydrogen atoms of the methyl group is essential for the magnetic interaction.

Finally, in order to discuss this point the rotation of the methyl group around the C-C bond was considered as shown in Figure 6A. The INDO calculation was carried out for several rotation angles between -60 and 120 degree. Origin of the rotation angle corresponds to the geometry of the pair determined by X-ray diffraction experiments. Figure 6B depicts the result of calculation and remarkable angle dependence of J_{ab} was found. The maximum of J_{ab} appears at about -15 degree (0.026 cm^{-1}) and the minimum appears at about +45 degree (0.002 cm^{-1}). The distances between β-hydrogen and oxygen atom of adjacent NO group are 2.774 Å and 3.128 Å, respectively. The distance between



A B

FIGURE 6 J_{ab} as a function of the rotation angle of the methyl group **i**.

β-carbon atom and oxygen atom is fixed at 3.736 Å. This result clearly indicates that orientation of the hydrogen atoms is important for the intermolecular magnetic interaction. It is noted that "the hydrogen bridging hyperconjugative effect" and/or "the hydrogen bridging SP effect" occurs in this system. More accurate calculations for this system are in progress in our laboratory.

CALCULATIONS FOR OTHER PAIRS

Discussion of the pair **A**-**B** was described in the previous sections. In this section we investigate theoretically other pairs to elucidate bulk magnetic behavior. In Figure 7 positions of the molecules **A** through **E** shown in Figure 1 are illustrated. J_{ab} values calculated by the INDO and *ab initio* UHF/4-31G methods are also shown. In a two-dimensional sheet effective exchange interaction of pair **A**-**B** is ferromagnetic, while J_{ab} value of pair **A**-**C** is antiferromagnetic. A ferromagnetically interacted molecules construct a chain. The nearest interaction between the ferromagnetic chains is antiferromagnetic and intersheet interaction is very weak. Our theoretical calculations suggest that bulk ferromagnetism of the ph-CH=N-TEMPO crystal is difficult to predict and will be delicate in nature. Experimentally, a ferromagnetic phase transition at 0.18 K and positive Weiss temperature of +0.74 K in the high temperate phase were reported.

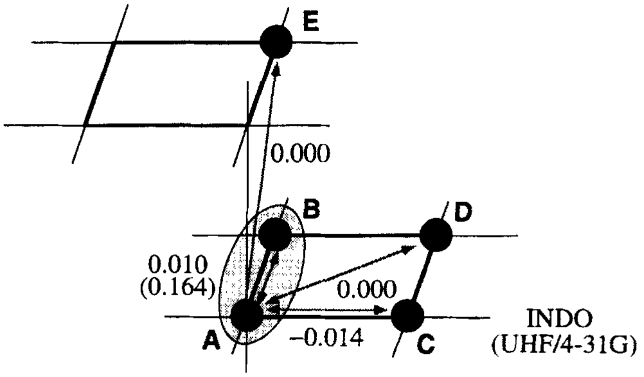


FIGURE 7 Various pairs**A**-**B**, **A**-**C**, **A**-**D** and **A**-**E** in the crystal.

CONCLUDING REMARK

Semiempirical and *ab initio* calculations were carried out for evaluating the effective exchange interaction for the pairs of adjacent molecules in the ph-CH=N-TEMPO crystal. Direct interaction of adjacent naked NO radical groups is weak. It was found that the hydrogen bridging between methyl hydrogen atom and adjacent NO group is essential for the ferromagnetic interaction. The ferromagnetic interaction runs along a chain. Interchain interaction is calculated to be antiferromagnetic. These two conflicting interactions exist in a molecular sheet and intersheet interaction is very week. Our theoretical calculations suggest that the bulk magnetism of this crystal is delicate in nature because the ferromagnetic and antiferromagnetic interaction coexists and is almost the same magnitude. More accurate and advanced calculations are required.

However, it is noteworthy that we realized the hydrogen bridging effect for the intermolecular ferromagnetic interaction in this crystal. Other example of the hydrogen bridging effect was also found for the ferromagnetic interaction through the hydrogen bonding in 2',5' dihydroxyphenyl nitronyl nitroxide crystal.[14]

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