Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 05 Dec 2006.

To cite this article: Takashi Kawakami, Shusuke Yamanaka, Hidemi Nagao, Wasuke Mori, Mikmaru Kamachi & Kizashi Yamaguchi (1995): Theoretical Approaches to Molecular Magnetism II: No-Overlap and Orientation Principles for Ferromagnetic Interactions, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 272:1, 117-129

To link to this article: http://dx.doi.org/10.1080/10587259508055279

Mol. Cryst. Liq. Cryst., 1995, Vol. 272, pp. 117–129
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THEORETICAL APPROACHES TO MOLECULAR MAGNETISM II: NO-OVERLAP AND ORIENTATION PRINCIPLES FOR FERRO-MAGNETIC INTERACTIONS

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Abstract No-overlap and orientation principles for ferromagnetic interactions between organic radicals were derived on the basis of approximately spin-projected UMP4(2) and UCC SD(T)/4-31G computations for several typical radical pairs. Ferromagnetic intermolecular interactions are feasible at T-shape and rhombus conformations in parallel interplane orientations for radical pairs because of no-overlap between π^*-type SOMOs (no kinetic exchange) and nonzero-potential exchange via the SOMO-SOMO through-space contact, whereas antiferromagnetic kinetic exchange interactions are predominant at many other conformations.

INTRODUCTION

The orbital symmetry (OS) rules or Kanamori-Goodenough (KG) rules[1,2] play important roles for qualitative explanation, understanding and prediction of the signs of effective exchange integrals between transition metal ions. In our other series of papers[3-5] entitled " Heisenberg models for radical reactions" , the OS and KG rules have been extended to derive several selection rules for organic radical reactions on the basis of overlap and orientation principles for radical pairs. The extended KG (EKG) rules predicted that favored radical reactions occur so as to maximize kinetic exchange (KE) interactions which give rise to stable covalent pairs of spins. Thus, radical reactions are classified into kinetic exchange (KE)-allowed and -forbidden types. These are also referred to as spin-symmetry allowed and forbidden on the basis of the magnetic double group theory.[3-5]

In order to accomplish ferromagnetic interactions between organic radicals, the KE-term should disappear, leading to the no-overlap between SOMOs. Therefore, the reverse principles, no-overlap and orientation principles, are required

for achieveing no covalent bonding between spins and ferromagnetic exchange interactions between organic radicals as emphasized previously.[6,7] Here, we wish to extend no-overlap and orientation principles for ferromagnetic exchange interactions between organic radicals in several cases.

THEORETICAL BACKGROUNDS

Theory

As shown previously[7], the intermolecular effective exchange integral J_{ab} is expressed by three different terms under the approximately spin-projected unrestricted Hartree-Fock (APUHF) approximation

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

where the kinetic (KE) and potential (PE) exchange terms are approximately given by the SOMO-SOMO overlap S_{ab} and the intermolecular exchange integral K_{ab}, respectively. The J_{ab}(SP)-term is given by the product of spin densities ($\rho_{a(b)}$) induced by the SP effect.[7]

$$J_{ab}(\mathrm{KE}) = - CS_{ab}^2 \quad (\mathrm{C: constant}) < 0 \quad (2)$$

$$J_{ab}(\mathrm{PE}) = J_{ab}(\mathrm{SDPI}) = K_{ab} > 0 \quad (3)$$

$$J_{ab}(\mathrm{SP}) = J_{ab}(\mathrm{SDPII}) = - \Sigma A \rho_a \rho_b \quad (\mathrm{A: constant}) \quad (4)$$

where the parameters C and A can be determined nonempirically by ab initio computations as shown in paper I in this series.[8]

It was well-known that the KE and PE terms stabilize the antiferro- and ferro-magnetic spin states, respectively.[6-8] The effective exchange interactions between free radicals are usually anti-ferromagnetic since the kinetic exchange (KE) interaction stabilizes the low-spin (LS) state. Therefore organic ferromagnetism is KE-forbidden as shown in the case I in Table I.[9] It was already emphasized that the suppression of the KE term is essential for ferromagnetic intermolecular interaction, leading to the no-overlap principle.[6] In this regards, perpendicular interplane orientations instead of parallel one are often required.[10] In addition to the no-overlap principle, mutual orientations of organic radicals should be controlled so that the J_{ab}(PE)-term becomes larger than the $|J_{ab}(\mathrm{KE})|$-term. Then ferromagnetic interaction is potential exchange (PE)-allowed as shown in the case II in Table I. When KE- and PE-terms are negligible, SP-term plays a key role for determination of signs of J_{ab} as shown in cases III and IV in Table I. These are referred to as SP-allowed and -forbidden cases for ferromagnetic

interactions between organic radicals such as p-NPNN.[10]

Orbital Symmetry Rules

Let us first consider very simple examples of SOMO-SOMO interactions as

TABLE I Selection rules for organic ferromagnetism

case	KE	PE	SP	J_{total}	Notations
I_a	< 0	> 0	> 0	< 0	KE-forbidden
I_b	< 0	> 0	< 0	< 0	KE-forbidden
II_a	~ 0	> 0	> 0	> 0	PE-allowed
II_b	~ 0	> 0	< 0	> 0	PE-allowed
III	~ 0	~ 0	> 0	> 0	SP-allowed
IV	~ 0	~ 0	< 0	< 0	SP-forbidden

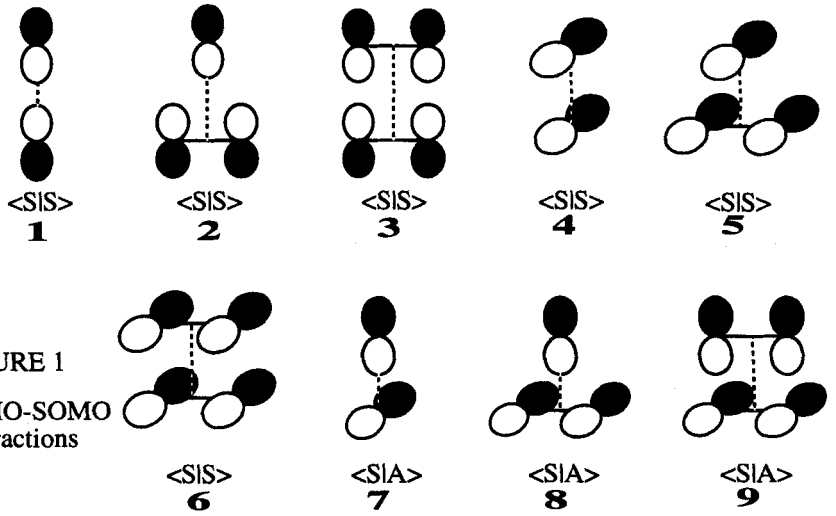
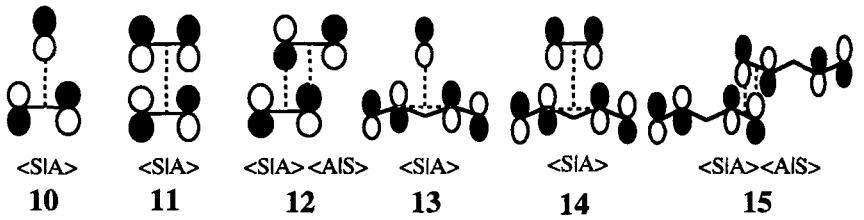


FIGURE 1
SOMO-SOMO interactions

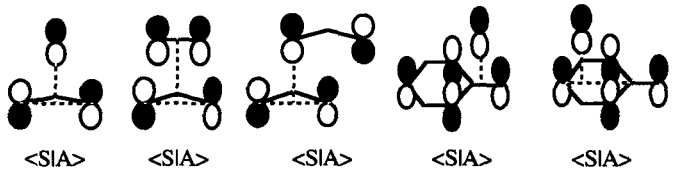
illustrated in Fig. 1. As examined previously,[3-7] the kinetic exchange (KE) interaction is orbital-symmetry allowed in orientations **1-3** and the σ-type bondings are feasible, leading to the case I in Table I. The KE-interaction is also orbital-symmetry-allowed in orientations **4-6** accompanied by the π-type bondings, giving rise to the formation of antiparallel spin alignment, namely the singlet pair. On the other hand, it is orbital-symmetry forbidden for the σπ-type orientations **7-9**,

indicating that ferromagnetic interaction is KE-allowed. Moreover, the potential exchange (PE) term is not zero because of the orbital symmetry , together with close contact between SOMOs. The ferromagnetic interaction is PE-allowed in orientations **7-9** , in conformity with the intermolecular Hund rule.



10 **11** **12** **13** **14** **15**

FIGURE 2 SOMO-SOMO interactions



16 **17** **18** **19** **20**

Following the intermolecular Hund picture,[10] the effective exchange interactions have been believed to be antiferromagnetic in the case of parallel orientations of organic radicals because of the nonzero-overlap between SOMOs, namely the case I in Table I. However, the KE-term often becomes almost zero even in the parallel orientation because of the zero SOMO-SOMO overlap. For example, the orbital overlap between SOMOs becomes almost zero even at parallel conformations **10-20** in Fig. 2, for which the PE term is still nonzero, giving rise to the ferromagnetic interactions in the case II in Table I. [7] As shown in **10-15**, the π^*-nature of SOMO play an important role for ferromagnetic interactions since the orbital overlap disappeared even in these parallel stacking modes. Similarly the nonbonding MO (NBMO) plays an important role for ferromagnetic interactions in the parallel orientations **16-20**.

AB INITIO CALCULATIONS

In addition to the KE, PE and SP terms in Eq. (1) given by APUHF, higher-order intermolecular interactions such as the van-der-Waals interactions may contribute to the effective exchange interactions. Here, the UHF Moller-Plesset (MP) and coupled-cluster (CC) SD(T) method followed by the approximate spin projection,

APUMP4 and APUCC SD(T), were carried out for the low- and high-spin states of radical pairs, and the effective exchange integrals were obtained as previously. [11,12] The reliability of these computational methods and the 4-31G basis set used in this work were examined

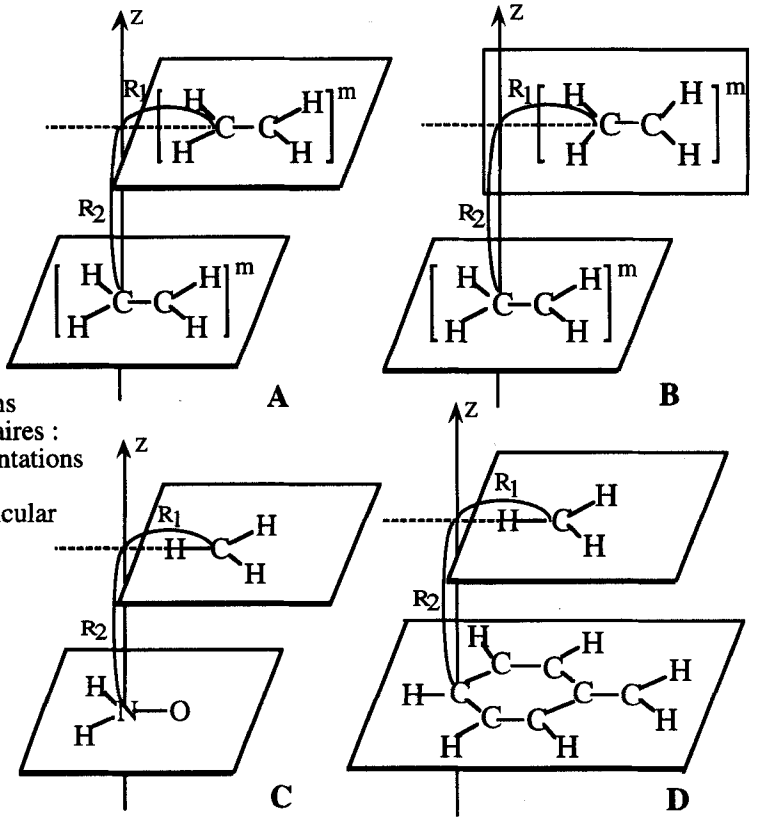


FIGURE 3

Conformations for radical paires : paralled orientations A, C and D, and perpendicular one B.

previously , comparing with spin-restricted CASSCF and CASPT2(D) results.[11,12]

In order to confirm the no-overlap and orientation principles in Figs. 1 and 2, we here examined typical systems as illustrated in Fig. 3. Model A denotes the face-to-face interaction between the cation radical (m=+1) of ethylene or between anion radical (m=-1) of ethylene, where R_1 and R_2 are taken as the sliding and interplane distances, respectively. The orientations **3** in Fig. 1 and **11** in Fig. 2 correspond to the case R_1=0.0 and R_2 = 3.4 Å. On the other hand, model B shows the perpendicualr approach between the cation radicals of ethylene, where R_1 and R_2 are also taken as the sliding and interplane distances, respectively. The orientation **9** in Fig. 1 corresponds to the case; R_1=0.0 and R_2 = 3.4 Å in model B. The models C and D show, respectively, the face-to-face interaction between

dihydronitroxide and methyl radical, and between benzyl radical and methyl radical. The orientations **10**, **19** and **20** correspond to the specific geometries with ferromagnetic interactions at appropriate R_1 and R_2 values as shown below.

Comparison between Parallel and Perpendicular Orientations

Both parallel and perpendicular conformations were examined in order to confirm the intermolecular Hund rule for radical pairs. The APUMP4(2)/4-31G calculations were performed for the cation radical dimer of ethylene in model A and B in Fig. 3. Fig. 4A and 4B illustrate, respectively, variations of effective exchange integrals (J_{ab}) for models A and B with the sliding distance R_1 at the fixed interplane distance R_2=3.4 Å.

From Fig. 4, the following notices are available:

(1) The J_{ab}-values are are negative (antiferromagnetic) thoughout the sliding deformation in the parallel orientation in model A, whereas these are always positive (ferromagnetic) in the case of perpendicular orientation in model B. The APUMP4/4-31G calculations confirmed the intermolecular Hund rule.

(2) The magnitudes of the J_{ab}-values are not so dependent on the computational methods in both cases, showing that the higer-order correlation corrections are not serious.

(3) The maximum magnitude for negative J_{ab}-values is about -800 cm^{-1} for the parallel orientation A, whereas the maximum positive value for the perpendicular orientation is about 70 cm^{-1} at the APUMP4/4-31G level.

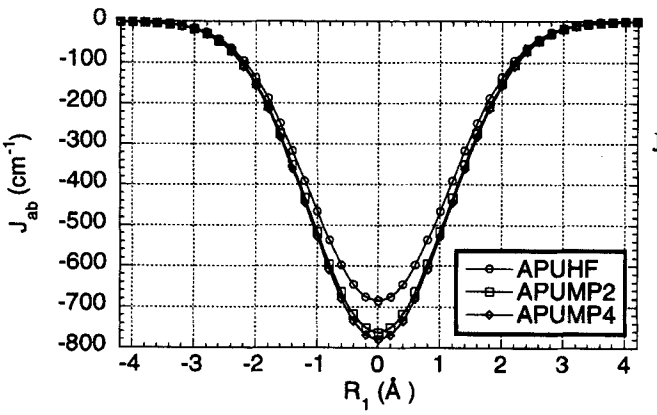
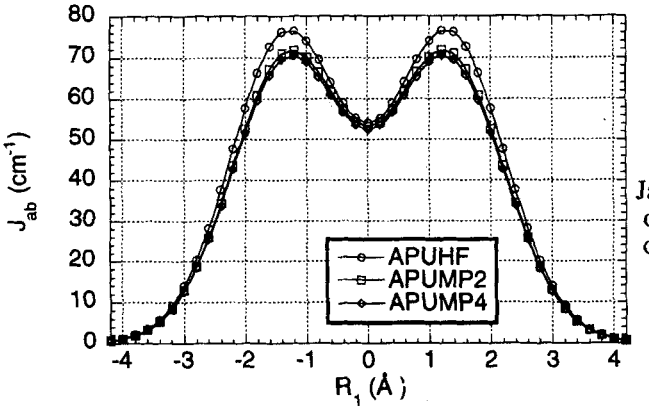


FIGURE 4A

Jab-values for dimer of the cation redical of ethylene in Fig. 3A



FIGUE 4B
Jab-values for dimer of the cation redical of ethylene in Fig. 3B

The positive J_{ab}-value via the potential exchange (PE) mechanism is far larger than the spin polarization (SP) mechanism as shown in the case of β-phase of p-NPNN. The intermolecular Hund rules are recognized for **3** and **9** in Fig. 1. The situations were similar in other cases in Fig. 1.

Importance of π*-SOMO for Ferromagnetic Interaction

In order to clarify the importance of π*-nature of *SOMO* for ferromagnetic interaction , let us consider the intermolecular interaction between dihydronitroxide and methyl radical as illustrated in Fig. 3C. Since the π*-type SOMO of nitroxide has a node near the center of the N-O bond, the pπ* orbital overlap $S_{p\pi^*}$ should disappear at a bridge structure as illustrated by **10** in Fig. 2

$$S_{p\pi^*} = S_{12} - S_{13} = 0 \qquad (5)$$

where $S_{12(3)}$ denotes the orbital-overlap between the atomic orbitals *1* and *2*(*3*). Therefore the effective exchange integral J_{ab} in eq. 1 should become positive (ferromagnetic) at this structure because of the nonzero potential exchange. The J_{ab}-values were calculated for this parallel interplane stacking mode by APUMP2(4) and APUCC/4-31G. Fig. 5 shows variations of the calculated effective exchange integrals with R_1.

From Fig.5, the following characteristics were drawn:

(1) The J_{ab}-values are positive in the bridge structure **10**, whereas these values are negative at the no-bridge conformations. The post Hartree-Fock calculations involving correlation corrections support qualitative predictions by the no-

overlap principle.

(2) The maximum positive J_{ab}-value is about 65 cm^{-1} by the APUCC/4-31G method

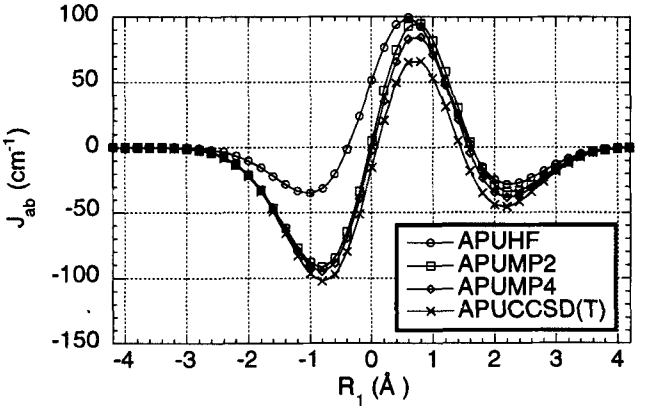


FIGURE 5 Jab-values for the nitroxide-methyl radical pair in Fig. 3B

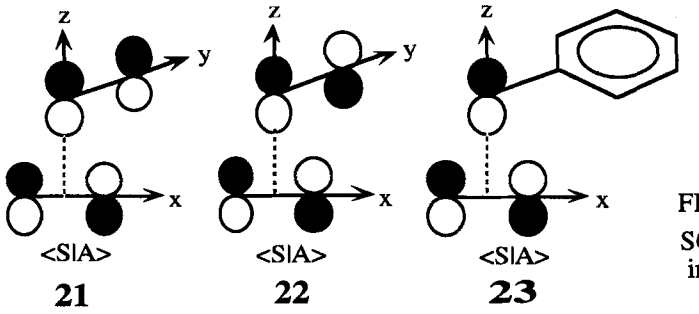


FIGURE 6 SOMO-SOMO interaction

at the bridge structure with the sliding distance R_1 = 0.8 Å. The potential exchange interaction is rather strong even at the van der Waals contact between nitroxides.

The magnitude of positive J_{ab}-value for the dihydronitroxide-methyl radical pair is quite larger than spin polarization (SP) term in Eq. (3). The parallel spin arrangement in Fig. 3C indicates that the potential exchange (PE) K_{ab} in Eq. (2), instead of the SP term, plays a dominant role for the ferromagnetic exchange interaction in a SOMO-SOMO contact region. The ferromagnetic exchange interaction between nitroxides and alkyl radical is feasible by the potential exchange (PE) term, even though the SOMO-SOMO direct contact is weak.

Three-center interactions **21-23** in the T-shape conformations in Fig. 6 satisfy the no-overlap principle becuase of the π^*-nature for one of SOMOs , suggesting the ferromagnetic interactions. In fact, previous APUCC/4-31G and

6-31G* calculations showed that the ferromagnetic interaction is feasible for nitroxide dimer with the T-shape conformation **22**.[9] The positive J_{ab}-value calculated for the T-shape conformation **22** is also compatible with the ferromagnetic interaction between TEMPO derivatives, 4-Benzylideneamino-2,2,6,6-tetramethylpiperidin-1-oxy[13].

Importance of Rhombus Conformation for Ferromagnetic Interaction

In order to confirm the no-overlap but parallel orientation principle for ferromagnetic interactions, the face-to-face stacking of anion radical (m=-1) of ethylene (model A in Fig. 3) was examined by changing the sliding distance (R_1) at the fixed interplane distance (R_2=3.4 Å). Because of the π^*-nature of SOMO for the species, the SOMO-SOMO overlap should disappear at the rhombus conformation as illustrated in **12** of Fig. 2.

$$S_{\pi^*\pi^*} = (S_{14} + S_{23}) - (S_{13} + S_{24}) = 0 \qquad (6)$$

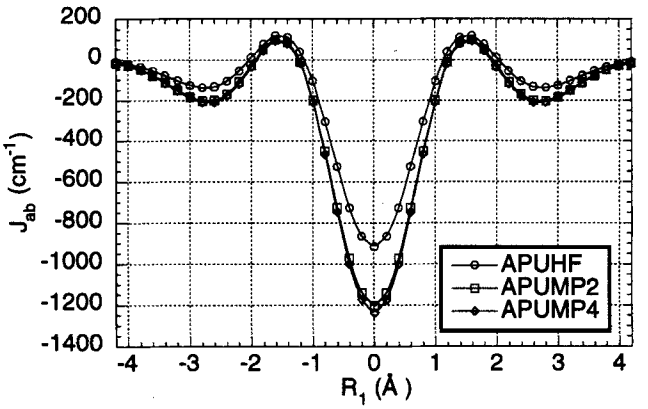


FIGURE 7

Jab-values for dimer of anion redical of ethylene in Fig. 3A

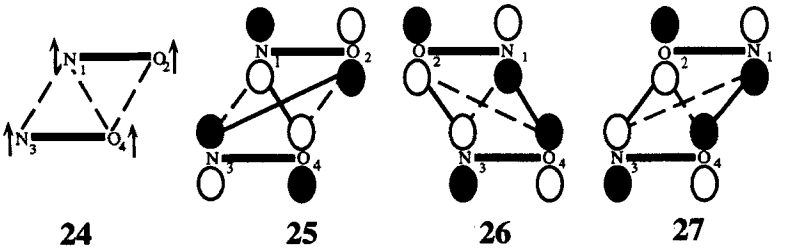


FIGURE 8 SOMO-SOMO intercaction

Therefore the KE-term is almost zero, but the potential exchange (PE) term remains

nonzero because of the close SOMO-SOMO contact. In order to confirm this prediction, the APUMP4(2) calculations were carried out. Fig. 7 shows variations of the calculated J_{ab}-values with the sliding distance R_1.

From Fig. 7, the following conclusions were drawn:

(1) The J_{ab}-values become positive (ferromagnetic) near the rhombus conformation **12** in Fig. 2, whereas these are negative near the rectangular conformation **3** in Fig. 1.

(2) The maximum positive J_{ab}-value by the APUMP4/4-31G method is 93 cm^{-1} at the rhombus conformation with the sliding distance R_1 =1.4 Å.

The spin structure for triplet state for the rhombus dimer exhibits the parallel spin alignment **24** as illustrated in Fig. 8. Therefore, the potential exchange (PE) term overweighs the kinetic exchange (KE) term in the rhombus conformation, showing an important role of the no-overlap but parallel orientation for the ferromagnetic interaction between π*-SOMOs

Previous APUMP2/4-31G calculations showed that the ferromagnetic interaction is possible even for the parallel syn-stacking mode of dihyronitroxide ($0° < \theta < 90°$ in model B of ref. 14) as illustrated in Fig. 8. Previous calculations also showed that the ferromagnetic interaction is feasible even for the parallel anti-stacking mode of dihyronitroxide ($140° < \theta < 180°$ in model C in ref. 14). Because of the π*-nature of SOMO for nitroxide, the SOMO-SOMO overlap should disappear as shown in Eq. (6) at the rhombus conformations **25-27** in Fig. 8. Then the J_{ab}-value should be positive (ferromagnetic) because of the nonzero potential exchange at these compact stackings.

The almost anti-parallel stacking mode of adamantane bisnitroxide by Rassat et al.[15] exhibits the ferromagnetic intermolecular interaction. Since the dimer of the species is too large, the anti-parallel stacking mode of dimethyl nitroxide was examined as its model by changing the interplane distance (R_2) at the fixed sliding distance R_1.[9] The J_{ab}-values at R_1=1.6 Å decreased sharply with the increase of R_2, but they remained positive in sign even in the larger intermolecular region ($R_2 > 4.2$ Å). Thus the through-space ferromagnetic interaction via the potential exchange mechanism is feasible even at $R_2 = 4.2$ Å. Since the nearest neighbor contact between the nitroxide group is about 4.2 Å in the case of the bisnitroxide, the intermolecular J_{ab}-value should be small but positive (< 0.1 cm^{-1}).

The above results mean that ferromagnetic intermolecular interactions are feasible via direct potential exchange mechanism even for simple nitroxides such as

dimethylnitroxide, unsubstituted nitronylnitroxide if stacking modes of these species are well-controlled as illustrated by **10-15** in Fig. 2 Similarly, π^*-type SOMOs should be also promising for ferromagnetic intermolecular interactions between anion radicals of vinyl group , carbonyl group , etc. In fact, previous semi-empirical calculations showed the ferromagnetic interaction between quinone anion radicals.[7]

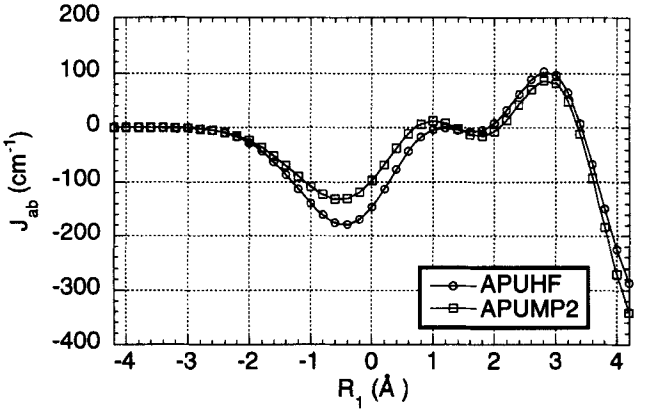


FIGURE 9

Jab-value for benzyl and methyl radical pair

Importance of NBMO for Ferromagnetic Interactions

In order to check the no-overlap but parallel orientation principle, the face-to-face stacking mode between benzyl and methyl radicals was examined by changing the sliding distance (R_1) at the fixed interplane distance (R_2=3.4 Å) as shown in Fig. 3D. Fig. 9 shows variations of the J_{ab}-values with the sliding distance R_1 calculated by the APUMP2/4-31G method.

From Fig. 9, the following conclusions were obtained:

(1) The J_{ab}-values become positive (ferromagnetic) at two conformations **19** and **20** in Fig. 2 because of zero SOMO-SOMO overlaps, whereas these are negative in other conformations.

(2) The magnitudes of the ferromagnetic interactions are 86 and 13 cm^{-1} at **19** with R_1=2.8 Å and **20** with R_1=1.0 Å, respectively.

The potential exchange term overweighs the kinetic exchange term at the conformations **19** and **20**, indicating the importance of the no-overlap but parallel orientation for the ferromagnetic interaction between NBMO and p-SOMO. The positive J_{ab}-values via the PE mechanism are quite larger than those of the SP

mechanism.

The ferromagnetic exchange interactions between NBMOs in allyl[7] and benzyl radicals[16] were examined previously in details. It was found that the effective exchange interaction between allyl radical is ferromagnetic at the conformation **18**.[7] Both the PE and SP mechanisms favor the ferromagnetic interactions between benzyl radicals in appropriate conformations where the KE-terms become zero. Therefore these are classified into the case IIa in Table 1.

CONCLUSION

No SOMO-SOMO overlap principle proposed previously[6-12,16] is applicable to organic radical crystals which exhibit the ferromagnetic effective exchange interactions. Here, it should be emphasized that the π^*-nature (orbital symmetry) of SOMO for organic radicals plays an important role to reduce the orbital-overlap (OO) antiferromagnetic term even in parallel interplane orientations. On the other hand, the potential exchange (PE) term is still nonzero because of SOMO-SOMO through-space contacts in the orientations, giving rise to ferromagnetic intermolecular interactions. Thus no-overlap and orientation principles are required for ferromagnetic interactions as illustrated in several examples.

On the other hand, indirect ferromagnetic interactions are feasible via spin-polarization (SP) mechanisms of π-networks when the direct OO and PE interactions are negligible because of far distant separations of SOMO. For example, the indirect exchange via the SP effect on phenyl ring was feasible for p-NPNN and other related species, and therefore the ferromagnetic interactions are SP-allowed in the case of β-phase crystals of p-NPNN. Thus, controls of spatial orientations of phenyl nitroxides or phenyl nitronylnitroxides are also important for their ferromagnetic intermolecular interactions.

In conclusion, present and previous computations conclude that the no overlap and orientation principles in Table I are useful guides for molecular design of organic ferromagnets. The orbital symmetry rules for kinetic exchange interactions are also derived for several cases. They are utilized for derivations of symmetry rules for organic ferromagnetism.

ACKNOWLEDGEMENT

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas of Molecular Magnetism (No. 04242101). The authors also thanks Asahi Glass Foundation for partial financial support of the project.

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