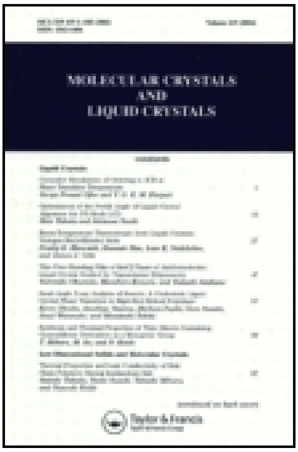

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Theoretical Study of Effective Exchange Integrals for Ferromagnetic Phenylenevinylene Polymers with Nitroxddes. Possibilities of Organic Ferro-or Ferri-Magnetic Solids

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THEORETICAL STUDY OF EFFECTIVE EXCHANGE INTEGRALS FOR FERROMAGNETIC PHENYLENEVINYLENE POLYMERS WITH NITROXIDES.
POSSIBILITIES OF ORGANIC FERRO- OR FERRI-MAGNETIC SOLIDS

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Abstract Molecular orbital calculations were carried out for pendant-type ferromagnetic phenylenevinylene oligomers with nitroxide groups in order to elucidate variations of the effective exchange integrals with oligomer size, conformational change and spin defects generated in the dehydrogenation process of NOH groups in the precursor oligomers. It was shown that the ferromagnetic effective exchange interactions between the nearest neighbor nitroxides are about 50-80 cm^{-1}, but they decrease with the internal rotation and spin defect. The interchain interactions between the oligomers are antiferromagnetic, and therefore they should be controlled by introduction of spacer group, showing a possibility to obtain the high T_C organic ferrimagnet induced by one-electron transfer between the oligomer and spacer.

INTRODUCTION

Previously [1,2], we have examined theoretical possibilities of magnetic modifications of conducting polymers by introduction of radical groups which can be considered as spin sources. Ab initio UHF MO calculations were carried out in order to elucidate effective exchange interactions (J_{ab}) between radical groups through π-networks with and without holes, which were introduced by chemical oxidation, photo-induced one-electron transfer etc. It was shown that phenylenevinylene polymer is one of potential candidates for pendant-type ferromagnetic polymers with radical groups as side chains, since (1) the J_{ab} values are quite large because of the planarity of the π-network and (2) the sign of the effective exchange integrals are variable depending on oxidation and deoxidation of the π-

networks, and (3) therefore the dynamic control of the magnetism seems feasible by changing the hole concentration in the main skeleton.

Recently Nishide et al. [3] synthesized the oligomers having poly-(phenylenevinylene) skeletons with phenoxy or nitroxide radical group as spin source. Their magnetic measurements revealed that the intramolecular effective exchange interactions are indeed ferromagnetic, and the J_{ab} values are in the range 20-40 cm^{-1}. Since this polyradical is a first example of the pendant-type ferromagnetic oligomers, it is particularly interesting and important to examine the origins of the through-bond ferromagnetic exchange couplings between nitroxides [4,5]. For the purpose, we will perform the first principle density functional (DFT) and semiempirical (INDO) calculations of ferromagnetic phenylenevinylene oligomers in order to elucidate variations of J_{ab} with the oligomer size N, conformational change and spin defects generated in the synthesis process.

THEORETICAL CALCULATIONS OF TWO SITE MODELS

(A) Comparison between ab initio DFT and INDO methods

First of all, we performed both ab initio unrestricted Kohn-Sham (UKS) Becke(B) or Slater (S)-Lee-Yang-Parr (LYP), i.e., UKS-B(S)-LYP [6-8], and INDO calculations of ortho-meta(o,m') and meta-meta(m,m') isomers of trans-stilbene bis(imnonitroxide) as illustrated in Figure 1. The 4-31G basis set was used for the UKS -B(S)-LYP calculations. Table 1 summarizes the calculated J_{ab} values. From Table 1, the J_{ab} values by B-LYP/4-31G are 76 and -22 cm^{-1}, respectively, for the (o,m') and (m,m')-isomers.

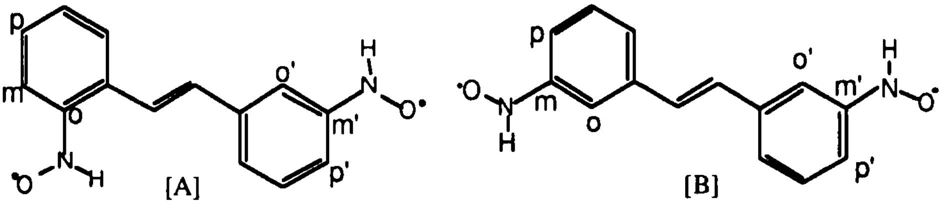

FIGURE 1 Molecular structure of the ortho(o),meta(m')[A]- and meta(m),meta(m')[B]- isomers of trans-stilbene bis(nitroxide)

TABLE 1 Effective exchange integrals calculated for trans-stilbene bis(nitroxide)

	INDO	B-LYP	S-LYP
o,o'	-92.5		
o,m'	54.0	75.7	52.2
o,p'	-95.0		
m,m'	-35.0	-22.4	-11.0
m,p'	57.8		
p,p'	-102.5		

The INDO values are compatible with the ab initio UKS BLYP values, indicating that the INDO UHF approximation is useful for qualitative calculations of more larger systems. However, these calculated values are larger by two- or three-times than the observed value for the trans-stilbene bis(t-butylnitroxide) [3], indicating the necessity of further theoretical investigations.

(B) Variations of J_{ab} with substitution positions of radical groups.

The INDO calculations were performed in order to elucidate the sign and magnitude of the J_{ab} values for six isomers of trans-stilbene bis(nitroxide) [1]. The calculated J_{ab} values are given in Table 1. The signs of J_{ab} are variable, depending on the substitution positions of nitroxide, and they are in accord with predicted results [1] based on the spin polarization (SP) rule. The magnitude of the J_{ab} values is insensitive to the syn- or anti conformations if the molecular planarity is retained [9]. Figure 2 illustrates the spin density populations by the INDO and DFT calculations for the (o, m')- and (m, m')-isomers. The spin density populations are consistent with the SP effect used for derivation of the intramolecular spin alignment rules.

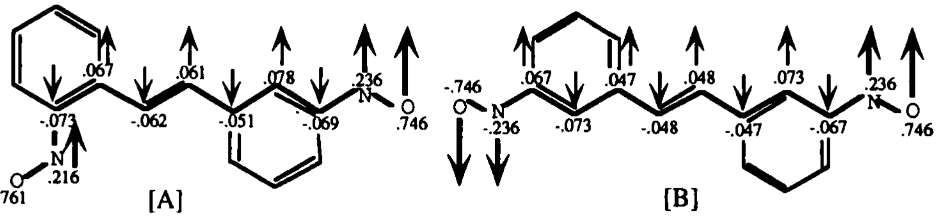

FIGURE 2 Spin density populations for (o,m')[A]- and (m,m')[B]- isomers of trans -stilbene bis(nitroxide)

(C) Variation of J_{ab} with conformation changes

The calculated J_{ab} values in Table 1 are generally larger than the experimental values by Nishide et al. [3]. This may be responsible for the nonplanarity of the nitroxide group since t-butyl group is introduced in order to suppress the radical reactivity of nitroxide. In order to confirm this explanation, we have investigated variations of J_{ab} values with the rotation of the nitroxide group as illustrated in Figure 3. Table 2 summarizes the calculated results. The J_{ab} values decrease significantly with the internal rotation of the nitroxide group. The through-bond coupling is almost zero at the perpendicular conformation, indicating the importance of the conjugation of the π-network of trans-stilbene skeleton and the π*-SOMO of nitroxide radical.

TABLE 2 Variations of the Jab values with the rotational angles(α,β) of bis(nitroxide)[a)]

α;β/deg	0;0	0;30	0;60	0;90	30;30	60;60	90;90
o,o'	-92.5	-72.8	-27.4	-1.64	-48.3	-3.75	-0.00
o,m'	54.1	43.0	16.8	1.90	29.0	2.45	0.02
o,p'	-94.9	-74.0	-26.5	-0.98	-49.5	-3.93	-0.01
m,m'	-35.0	-27.8	-10.7	-1.18	-22.0	-3.25	-0.04
m,p'	57.8	45.4	16.6	0.62	36.1	5.10	0.03
p,p'	-102.5	-79.7	-28.5	-1.07	-62.1	-8.03	-0.01

a) see Figure 3.

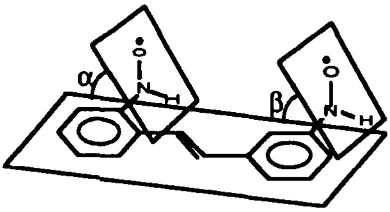

FIGURE 3 The internal rotations of bis(nitroxide) group α and β denote the rotational angles.

INTRACHAIN EFFECTIVE EXCHANGE INTERACTIONS

(A) Calculations of J_{ab} values of N-site oligomers

In order to examine the oligomer size-dependency of J_{ab}, the J_{ab} values for the N-site oligomers were calculated under the assumption that (1) the overlaps between SOMOs are not so large and (2) therefore the Heisenberg (HB) model can be used for through-bond exchange couplings between nitroxides. The J_{ab} values are easily calculated by the combinations of the UHF (or UKS) MO method plus HB model under the assumption of the uniform magnetic chain with one J_{ab} as illustrated in Figure 4A,

$$J_{ab} = \frac{{}^{LS}E - {}^{HS}E}{{}^{HS}\langle S^2 \rangle - {}^{LS}\langle S^2 \rangle - \Delta} \qquad (1)$$

where

$$\Delta = \begin{cases} (N-1)(N-3)/4 \ldots\ldots (N;\text{odd}) \\ (N-2)^2/4 \ldots\ldots\ldots\ldots (N;\text{even}) \end{cases} \qquad (2)$$

It is noteworthy that the present approximate spin projection (AP) scheme for UHF (or UKS) is size-consistent, guaranteeing the necessary condition for theoretical studies of extended systems [4].

Eqs. 1 and 2 were applied to elucidate the dependence of J_{ab} values on the oligomer size N, which was illustrated in Figure 5. From Figure 5, it is clear that J_{ab} values increase with the increase of the site number N and converge to a saturated value even at N=11. This tendency is in good agreement with the experimental tendency [3, 5] Therefore, the extrapolation procedure is possible to estimate the J_{ab} value at $N=\infty$ as follows

$$J = 126.3 - 42.7 \exp[-0.680 (N-2)] \qquad (3)$$

The J_{ab} values at the infinite length is estimated to be about 126 cm^{-1} for the oligomer in Figure 4A. This value is , however, much larger than the observed values [3, 5], suggesting the nonplanarity of the π-networks in the phenylenevinylene oligomers.

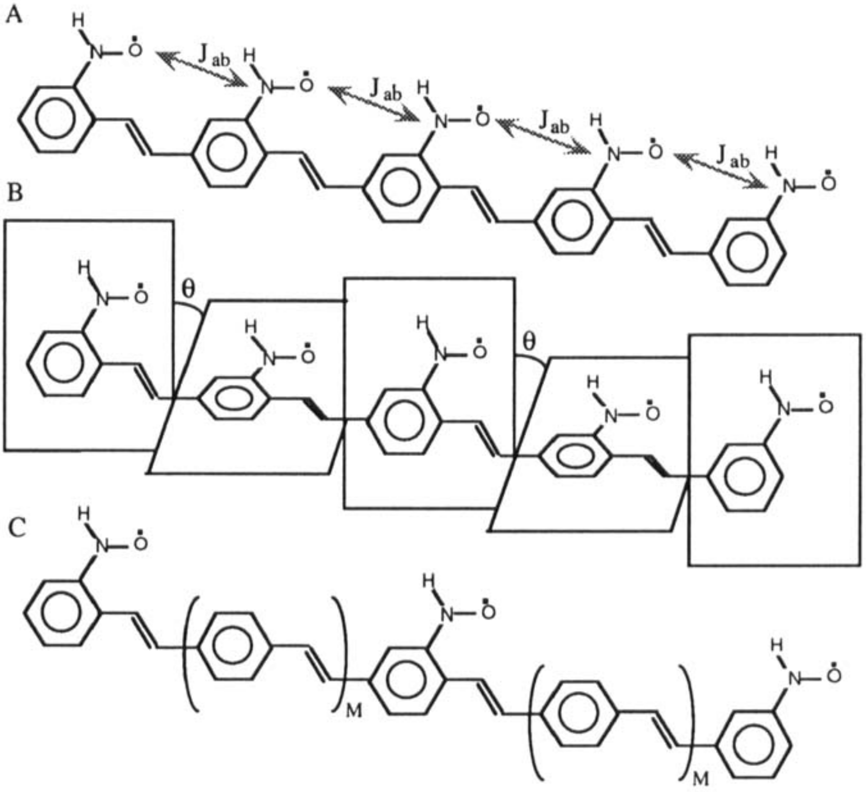

FIGURE 4 (A) Uniform chain of phenylenevinylene polymers with nitroxides. (B)Internal rotation of phenylnitroxide group. (C) Spacing units (M) of radical group.

(B) Variations of J_{ab} with the conformational change and spin defects

In order to examine the conformational change of J_{ab} values, we have investigated the rotations of the phenyl group in the main skeleton of oligomers as illustrated in Figure 4B. Table 3 summarizes the calculated J_{ab} values. The J_{ab} values decrease with increase of the rotational angle (θ) because of the suppression of the p-conjugation within the main chain. This tendency is the same even if the cluster size increases to the case N=6. The reduced J_{ab} values can partly explain quite smaller J_{ab} values observed by Nishide et al. [3] as compared with the theoretical values. However, judging from their experimental data, the other origin arising from the synthetic process might be operative to decrease the J_{ab} value, suggesting to the fact that spin defects (namely nonradical unit: *tert*-BuNOH group) remain in the oligomers since nitroxide radicals are chemically generated by the dehydrogenation of the NOH groups. Therefore, we examined the through-bond interactions by changing the numbers (M) of spacing units in the π-networks as illustrated in Figure 4C. The calculated J_{ab} values decreased to one-fifth if one nonradical unit (M=1) is inserted. Thus the J_{ab} value decreases in an exponential manner with the increase of M as shown in Figure 6. From these results, we can conclude two origins, the internal rotation of π-network and the spin defect, to explain the experimental tendencies revealed for the ferromagnetic phenylenevinylene oligomers [3, 5].

TABLE 3 Variation of Jab values with the internal rotation of phenylnitroxide[a)]

θ/deg	0	30	60	90	120	150	180
N=2	83.4	61.4	23.6	5.72	23.6	61.3	83.5
3	105.3	75.8	28.3	6.43	28.1	75.6	106.1
5	120.1	84.5	30.8	6.80	30.5	84.3	121.5
7	125.4	87.5	31.6	6.92	31.3	87.4	127.0

a) see Figure 4B

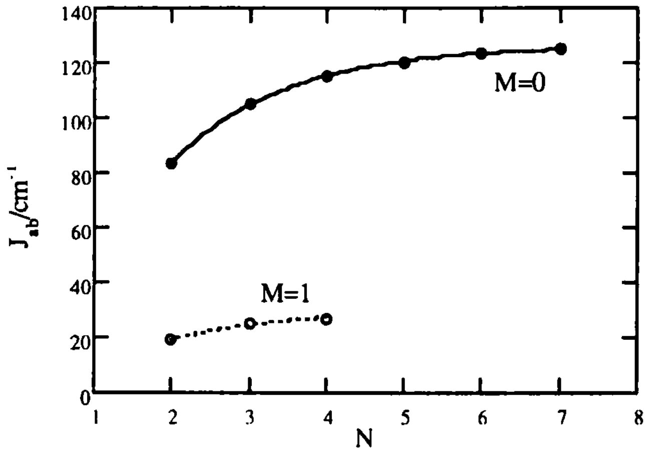

FIGURE 5 Variations of the J_{ab} values with the cluster size N

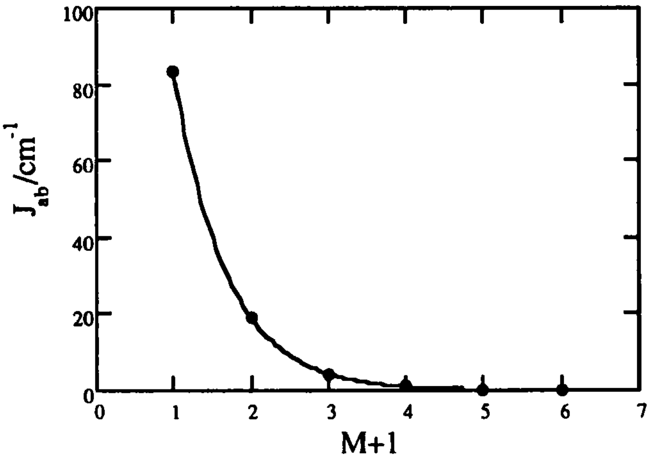

FIGURE 6 Variations of the J_{ab} values with the number (M) of spacing unit. (see Figure 4C.)

INTERCHAIN EFFECTIVE EXCHANGE INTERACTIONS

(A) Control of interchain interactions and superparamagnetism

The ESR experiments [3] indicated that the interchain interaction between the oligomers is antiferromagnetic. Therefore, controls of the interchain interactions are extremely important to accomplish ferro- or ferri-magnetic solids. Judging from the size (N)-dependence of the intrachain J_{ab} value, it is saturated for the high-spin oligomers with radical sites N= 8-15, which should be superparamagnetic in nature [10]. Therefore, if we use these oligomers as radical components for organic ferromagnetic solids, optimal control of the interchain interaction is essential since the ferromagnetic transition temperature (T_C) is approximately given by $T_C = C (J J')^{1/2}$ (C: const.) where J' denotes the interchain effective exchange integral. However, as is well known, the ferromagnetic interchain interactions (J') are usually weak for organic systems even if intermolecular stackings are well controlled, suggesting a possibility to synthesize the high-T_C organic ferromagnetic solids. For the purpose, the ferromagnetic high-polymers without spin defect are desirable.

(B) Possibilities of ferrimagnetic CT solids

The other strategy to obtain organic magnetic materials is to use relatively strong antiferromagnetic intermolecular interactions between organic molecules, leading to the concept of organic ferrimagnets [11]. For example, the introduction of spacer groups to control interchain interactions is feasible as illustrated in Figure 7, where one electron transfer is possible between the oligomer and spacer. As a spacer, we can consider TCNE, TCNQ, tetrafluoroTCNQ etc. as electron acceptor (A) and employ TTF derivatives , TDAE etc. as electron donors (D). Since antiferromagnetic interactions between organic radical species are strong in general, many theoretical possibilities are conceivable to obtain high-T_C organic ferrimagnets depicted in Figure 7, where the net spin moment , (N-2)/2, survives for each DA pair constructed of the oligomer cation or anion with (N-1)/2 spin and $A^{\cdot -}$(or $D^{\cdot +}$) with 1/2 spin.

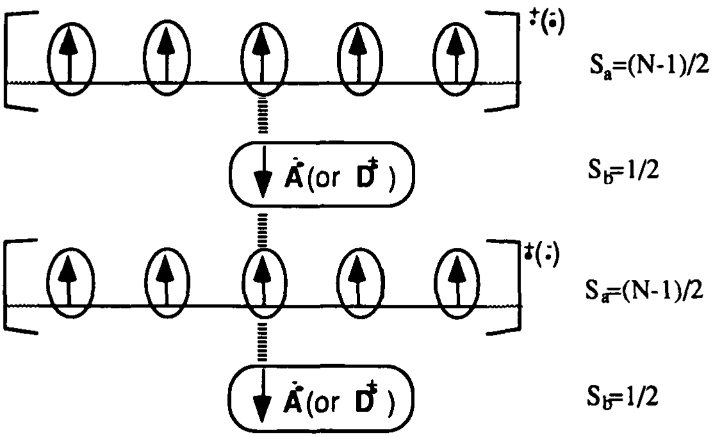

FIGURE 7 Organic CT ferrimagnets composed of high-spin oligomer and spacer (donor or acceptor).

(C) Possibilities of photoinduced CT ferrimagnets

The photo-induced one-electron transfer between the high-spin oligomer and electron donor (or acceptor) are also conceivable if selections of D or A are appropriate to allow the dynamic control from the superpara- to ferri-magnetic states (vice versa) by photo-switching as illustrated in Figure 8. For the purpose, a oligomer plus D(or A) system under consideration should be near the neighborhood of the neutral-ionic transitions as illustrated in Figure 8. The switching function by light will be one of the final goals in molecular based magnets [12].

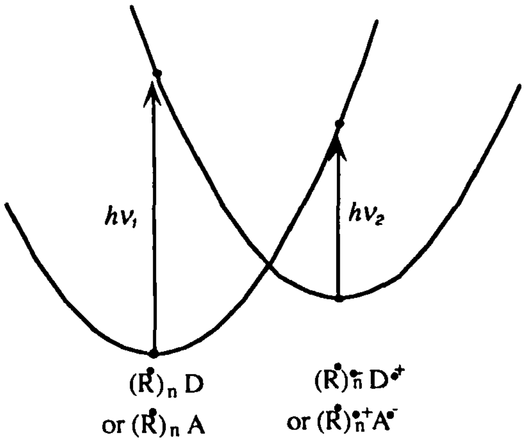

FIGURE 8 photo-switching type organic CT ferrimagnets composed of the oligomer $(R)_n$ and spacer (D or A).

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