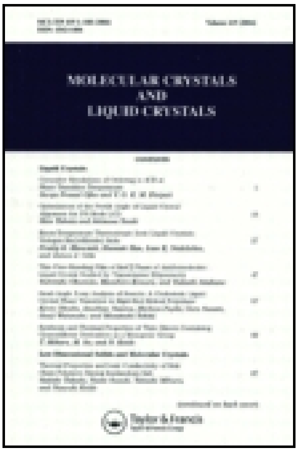

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Theoretical Studies of the Ferromagnetic Inter-Molecular Interaction of P-Carboxylate Phenyl Nitronyl Nitroxide

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THEORETICAL STUDIES OF THE FERROMAGNETIC INTERMOLECULAR INTERACTION OF P-CARBOXYLATE PHENYL NITRONYL NITROXIDE

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Abstract Ab initio and semiempirical MO calculations were carried out for dimers of p-carboxylate phenyl nitronyl nitroxide, whose geometries were extracted from the X-ray diffraction results. It was shown that the effective exchange integrals for the nearest neighbor dimer are largely positive (ferromagnetic), in accord with the experimental results. The direct potential exchange interactions between SOMOs are operative, giving the large J_{ab} values, but the spin polarization plus other higher-order terms reduce their magnitudes. Implications of these results are discussed in relation to molecular design of high T_c crystalline organic ferromagnets.

INTRODUCTION

Previously[1], molecular orbital calculations were carried out for dimers of phenyl nitronyl nitroxide (PNNO) derivatives with donor and acceptor groups in order to elucidate effective exchange interactions (J_{ab}) in their several different stacking modes. It was shown that the sign and magnitude of the calculated J_{ab} values are highly dependent on stacking modes of these species[1]. The ferromagnetic transition temperature (T_c) was also estimated by using the calculated effective exchange integrals (J_{ab}) in the case of β- and γ-phases of p-NPNN[2,3], being consistent with the experimental values by Kinoshita et al.[4-6].

Recently, Inoue et al.[7] reported synthesis of p-carboxylate phenyl nitronyl nitroxide (p-(1-oxyl-3-oxido-4,4,5,5-tetramethyl-2-imidazolin-2-yl) benzoic acid) **(1)** and its lithium-methanol ($1^{\cdot}\bullet Li^{+}\bullet MeOH$) **(2)** and lithium D-substituted methanol crystals ($1^{\cdot}\bullet Li^{+}\bullet MeOD$)) **(3)**. They performed the magnetic measurements of the crystals **2** and **3**, which manifested that dimers have a short intermolecular contact between the oxygen atom in nitronyl nitroxide (NN) group and the alpha carbon atom in the nearest-neighbor NN group with T-shape conformation. These lithium salts provided not only the first example of ferromagnetic dimers of radical anions but also the largest J_{ab} value ever reported for exchange couplings between PNNO derivatives.

Judging from the above characteristics[7], it is particularly interesting and important to investigate theoretically the origins of the large J_{ab} values in the crystals in order to design high-T_c organic ferromagnetic materials. Here, calculations based on molecular orbital (MO)[8-10] and density functional theory (DFT)[11] will be carried out in order to determine the intermolecular effective exchange integrals for clusters, whose geometries are taken from the X-ray diffraction experiments[7].

THEORETICAL BACKGROUND

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

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

where the kinetic (KE) and potential (PE) exchange terms are, respectively, given by the SOMO-SOMO overlap S_{ab} and the intermolecular exchange integral K_{ab} between them. The spin polarized (SP) term is given by the product of spin densities ($\rho_{a(b)}$) induced by the SP effect[8]. These three terms are useful to explain and design ferromagnetic interactions and organic ferromagnetism. For example, the simple rules to predict the magnetic interactions were derived from these terms, leading to the following classifications[9] :

Case I (KE<0, PE<0; J_{ab}<0), (2a)
Case II (KE≈0,PE>0; J_{ab}>0), (2b)
Case III (KE≈0,PE≈0,SP>0; J_{ab}>0), (2c)
Case IV (KE≈0,PE≈0,SP<0; J_{ab}<0). (2d)

The cases I and II are understood intuitively with the symmetries of SOMOs, and the orbital symmetry rule is resulted in order to predict and explain the strong ferromagnetic interactions between nitroxides[9]. The effective exchange interactions between free radicals are usually antiferromagnetic ($J_{ab} < 0$)[1] since the KE interaction stabilizes the low spin (LS) state (Case I). However, if the orientation of radical components is controlled in order to reduce the KE term, the ferromagnetic interaction ($J_{ab} > 0$) is expected at a moderate intermolecular distance (Case II) because of the nonzero Coulombic exchange integral (PE=K_{ab}) as shown in the case of nitroxide dimer[9]. On the other hand, when both the KE and PE terms become almost zero, the SP term arising from the indirect throughbond and throughspace interactions becomes important (Case III,IV). For example, β-phase crystal of p-NPNN corresponds to the case III[2]. If the KE term becomes zero and the PE term is largely positive (Case II), the effective exchange integral is expected to be a larger positive value. Thus ferromagnetic interactions represented by the KE and PE terms can become much stronger than those caused by SP effect (Case III) because the SOMO-SOMO direct interaction is usually about ten times as large as SP effect[9].

In order to confirm the above simple rules, ab initio configuration interaction (CI) method by the use of the complete active space (CAS) selected on the basis of the occupation numbers of the UHF natural orbitals (UNO), i.e., UNO CAS CI, is carried out in order to calculate the SOMO-SOMO direct interaction terms, i.e. the KE and PE terms, together with spin polarization (SP) and other electron correlation (EC) terms responsible for the higher-magnetic interactions. On the other hand, the DFT method based on unrestricted Kohn-Sham (UKS) with Becke(B)-Lee-Yang-Parr (LYP) functional, DFT UKS B-LYP, and semi-empirical INDO methods are successfully employed in order to calculate spin densities in relation to the SP term[10,11].

In addition to the KE, PE and SP terms given by APUHF, higher-order intermolecular interactions may contribute to the effective exchange interactions,

$$J_{ab}(APUHF\ \ X) = J_{ab}(APUHF) + J_{ab}(higher-order\ \ term) \qquad (3)$$

where X denotes the post UHF, i.e., Møller-Plesset (MP) or coupled-cluster (CC), method[8,9]. Since these post Hartree Fock calculations involve the higher-order interactions responsible for electron correlation effects, they improve J_{ab}(APUHF) values which often overestimate the SP effect. So, the J_{ab} values by APUMPn and APUCCSD(T)[8-10] should have better agreement with the experimental results than the values by APUHF method.

CRYSTAL STRUCTURES

Since dimer structures[7] were found in the crystals of **2** and **3**, an exchange-coupled dimer model was applied to elucidate the magnetic susceptibility data. Figures 1A and B illustrate the orientations ($\mathbf{a_1,b_1,c_1,d_1,a_2,b_2,c_2,d_2}$) of **2** and **3**, respectively, in their X-ray crystal structures. From fig. 1, the following characteristics were drawn:

(1) Both the structures reveal that one of the terminal oxygen of the nitronylnitroxide approaches significantly the α-carbon atom of the other imidazolinyl unit. The nearest C-O distances between the radical groups are, respectively, 3.246 and 3.309 Å for the dimers $\mathbf{A_1(a_1\text{-}b_1)}$ and $\mathbf{A_2(a_2\text{-}b_2)}$ which are composed of monoanion of **1**.

(2) On the other hand, the second, third and forth nearest distances between $\mathbf{1}^{-}$ in fig. 1A are 5.404 , 6.087 and 7.360 Å , respectively, for the dimers $\mathbf{B_1(a_1\text{-}c_1)}$, $\mathbf{C_1(a_1\text{-}d_1)}$ and $\mathbf{D_1(a_1\text{-}e_1)}$ in the crystal **2**. While, the corresponding distances are 5.090, 5.378 and 5.538 Å, respectively, for the dimers $\mathbf{B_2(a_2\text{-}c_2)}$, $\mathbf{C_2(a_2\text{-}d_2)}$ and $\mathbf{D_2(a_2\text{-}e_2)}$ in the crystal **3**.

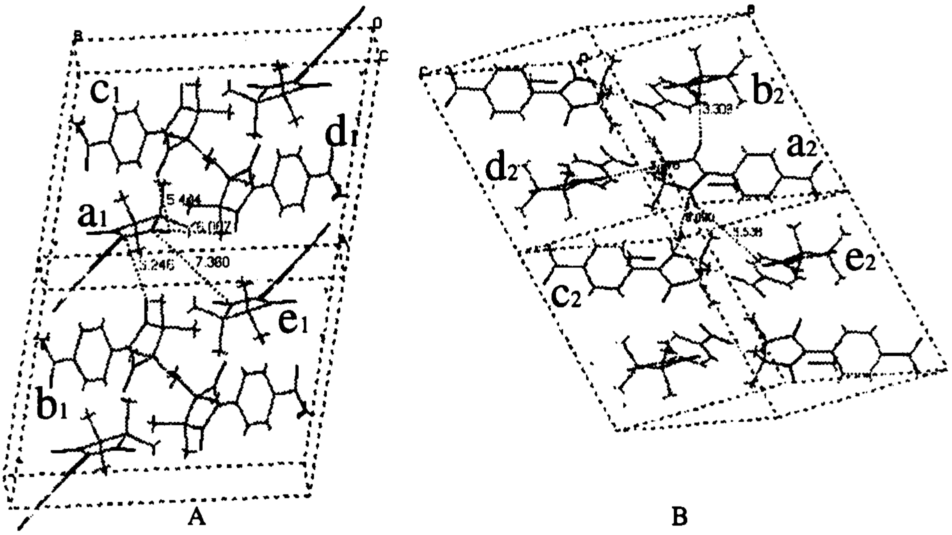

FIGURE 1 Crystal structures of $\mathbf{2}(\mathbf{1}^{-}\bullet Li^{+}\bullet MeOH)$ and $\mathbf{3}(\mathbf{1}^{-}\bullet Li^{+}\bullet MeOD)$.

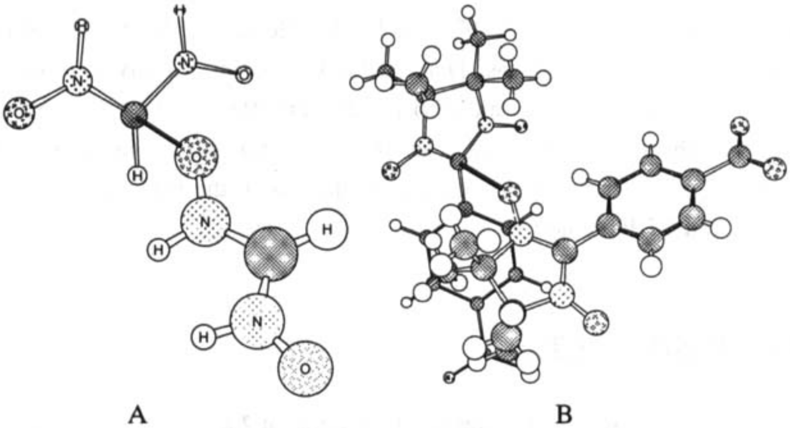

FIGURE 2 Simplied model **A1'** and Full model **A1(a1-b1)**.

Here, we will perform the theoretical calculations of the dimers A_1 and A_2 which have the shortest distance between the monoanion $\mathbf{1}^{-}$ in **2** and **3**, respectively. First, we extracted the simplified models A_1' and A_2' from the X-ray structures, which remain the only two nitronyl nitroxide (ON-C-NO) skeletons. Figure 2A shows the molecular coordinates for one (A_1') of these dimers, since their geometries are similar each other except for the intradimer distance. The C-H distances in these models were optimized by the PM3 semi-empirical method. From fig. 2A, the simplied dimer exhibits the short intermolecular contact between the oxygen atom in nitronyl nitroxide (NN) group and the alpha carbon atom in NN group with vertical T-shape conformation. On the other hand, fig. 2B shows the full geometry of the dimer A_1, where Li^{+}, MeOH and MeOD were neglected in order to clarify the direct effective exchange interaction between **1**$^{\cdot}$.

CALCULATIONS FOR THE SIMPLIED DIMER MODEL

Ab initio post Hartree-Fock and DFT calculations were carried out for the simplified dimers, **A**$_1$' and **A**$_2$', in order to elucidate the origin of the ferromagnetic effective exchange integral |J_{ab} |. Table 1 gives the J_{ab} values obtained by several computational methods . From table 1, the following conclusions are drawn:

(1)All the methods give the positive J_{ab} values and the absolute values of dimer **A**$_1$' are larger than those of dimer **A**$_2$' in each calculation. The ratios, J_{ab} (**A**$_1$')/J_{ab} (**A**$_2$'), by these computational methods are in good agreement with the ratio derived from experiment data[7].

(2)APUHF/4-31G methods overestimate the positive J_{ab} values because of the large SP effect. The Møller Presset (MP) perturbation methods cannot correct the overestimation occurred in the UHF calculation even at the fourth-order level.

(3) UNO CASCI by the use of the two active UNOs and two electrons {2,2} method involving only SOMO-SOMO direct interactions (KE and PE terms) gives the positive J_{ab} values which are in good agreement with the experimental values[7].

TABLE 1 J_{ab} values calculated by several theoretical methods for both dimer A_1 and A_2.

methods	J_{ab} /cm^{-1} **2** (**1**$^{\cdot}$•Li$^+$•MeOH)	**3** (**1**$^{\cdot}$•Li$^+$•MeOD)
Simplied model	A_1'	A_2'
APUHF[a)]	27.88	22.37
APUMP2[a)]	23.98	19.98
APUMP3[a)]	25.75	21.22
APUMP4SDTQ[a)]	26.31	21.67
UNOCASCI{2,2}[a)]	10.08	7.42
UNOCASSCF{2,2}[a)]	16.40	13.46
UNOCASCI{6,6}[a)]	8.26	6.36
UNOCASSCF{6,6}[a)]	8.86	6.76
APUB-LYP[a)]	19.81	16.12
INDO	9.72	7.18
Full model with whole atoms	A_1	A_2
INDO	5.666	3.979
Experiment[b)]	10.219	7.239

a) 4-31G basis set were used.

b) an exchage-coupled dimer model were employed.

(4) The UNO CASSCF{2,2} method gives quite larger J_{ab} values than UNO CAS CI {2,2}. It is essential to include orbital relaxations by the SCF procedure in the UNO CASCI {2,2} calculation.

(5) UNO CASCI and UNO CASSCF methods by the use of the six-active UNO and six-active electrons {6, 6} give similar J_{ab} values, which are smaller than that of UNO CASSCF {2,2}, but are close to the experimental values. The SP plus electron correlation (EC) terms given by the former two methods reduce the magnitude of J_{ab} arising from the direct PE effect.

(6) DFT UKS B-LYP 4-31G methods give quite larger J_{ab} values than UNO CASCI {6,6}, which is insufficient for quantitative calculations of intermolecular J_{ab} values.

(7) The J_{ab} values by INDO are close to the experimental values, although the calculations are performed for the simplied dimers.

In order to explain and understand the above conclusion (3), let us consider the shape of SOMO. Figure 3A illustrates the stacking of two SOMOs, and the solid and dotted lines indicate, respectively, the in-phase and out-of-phase combinations of the π-orbitals. From fig. 3A, it can be seen that SOMOs have nodes and two nitronylnitroxide groups stack each other in balance to eliminate the SOMO-SOMO overlap, i.e., KE term, whereas the PE term still remains because of the short intradimer distance. This indicates that the direct potential exchange (PE) interaction between SOMO electrons plays an essential role for the ferromagnetic interaction between the nitronyl nitroxide group.

Figure 3B illustrates the spin densities calculated by the UB-LYP/4-31G method. As shown previously[10,11], the UKS B-LYP method can give the more reasonable spin densities for open shell species than the UHF method. From fig. 3B it is found that positive densities populated on the N and O atoms of the nitronyl nitroxide (NN) group and the negative density is induced on its α-carbon atom. The terminal O atom with positive spin density on one NN group contacts with the α-carbon atom with negative spin density on the other NN group, indicating the ferromagnetic interaction via the intermolecular spin polarization (SP) mechanism[1-3,7]. However, the positive J_{ab} value

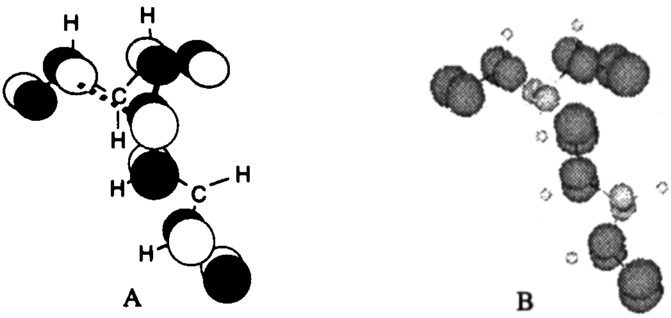

FIGURE 3 SOMO-SOMO direct interaction (A) and spin densities (threshold 0.01) by UBLYP/4-31G (B) in the simplied model A1'.

given by the SP effect is improved by the higher-order effects as confirmed by UNO CASSCF {6,6}. This in turn indicates that the direct potential exchange interaction is responsible for the large ferromagnetic interaction between the NN group in the crystals **2** and **3**, which supports our no-overlap and orientation principle[9] for organic ferromagnetism.

CALCULATIONS FOR THE FULL DIMER MODEL

(A) Electronic property of the monomer

The preceding model calculations indicated the essential role of the SOMO-SOMO interaction. Therefore, let us examine the magnetic orbitals of the monoanion $\mathbf{1}^{-}$. Figures 4A, B and C illustrate the HOMO, SOMO and LUMO, respectively, determined by the UNO analysis. From fig. 4B, it is noticed that SOMO orbital of $\mathbf{1}^{-}$ is localized with the nitronyl nitroxide (NN) group, ON-C-NO, as in the case of the above simplied model. Therefore, the SOMO-SOMO direct interaction should be expected even for the dimer $\mathbf{A}_1$ of the nearest neighbor monoanion $\mathbf{1}^{-}$.

Figures 4D and E depict the spin density populations on monomer $\mathbf{a}_1$ in dimer $\mathbf{A}_1$ in fig. 1 by the UHF/4-31G and UBLYP/4-31G method, respectively. It is seen that spin densities on the ON-C-NO group are similar to those of the model system in fig. 2A. However, spin densities are induced even on the benzene ring because of the SP effect[10,11]. As shown previously, the magnitudes of the induced spin densities by the B-LYP method are quite similar to those of the experiments obtained for PNNO derivatives by the neutron diffraction technique[13], although the UHF method largely overestmates them and the spin projection is crucial for the improvement[11].

(B) *Jab* value for the full dimer model

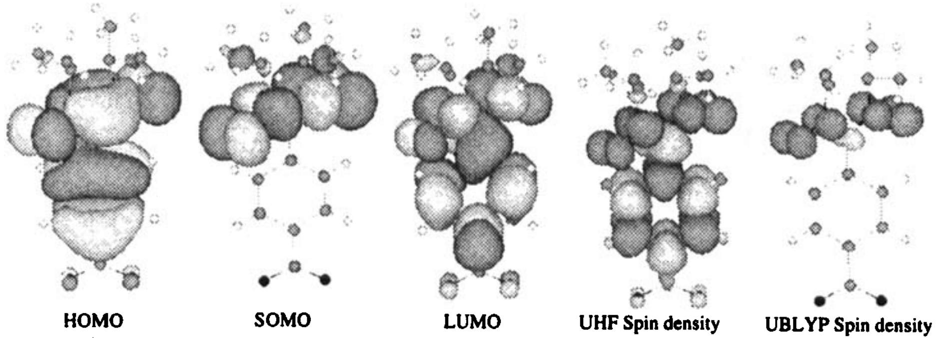

FIGURE 4 The structures of MOs and the spin densities (threshold 0.005) of the dimer **A1**.

In order to study magnetic properties observed for crystals of **2** and **3**, their full molecular skeletons must be taken into account because HOMO and LUMO are delocalized over not only the ON-C-NO group but also the benzene ring as illustrated in figs. 4A and C, indicating that indirect effective exchange interactions are operative. Since the J_{ab} values in table 1 and previous calculations[1-3] showed that the INDO semiempirical method works well for qualitative calculations of J_{ab} values, it was applied to the dimers $\mathbf{A}_1$ and $\mathbf{A}_2$ in fig. 2B, which have the nearest intradimer distance extracted from the X-ray study of the crystals of **2** and **3**. Table 1 gives the calculated J_{ab} values for these dimers. The J_{ab} values by INDO correspond to about 55% of the experimental values. Interestingly, the calculated ratio, $J_{ab}(\mathbf{A}_1)/J_{ab}(\mathbf{A}_2)$, is about 1.424/1, in good agreement with the ratio 1.412/1 derived from the magnetic measurements for the crystals **2** and **3**. Thus the semiempirical INDO calculation at least reproduces the observed tendency. The more reliable UNOCAS SCF calculations are in progress in our laboratory.

CALCULATIONS FOR THE SECOND, THIRD AND FORTH NEAREST DIMERS

Through the above section only the dimer $\mathbf{A}_1$ and $\mathbf{A}_2$ having the nearest intradimer distances have been taken into account and we could explain theoretically their magnetic behaviors. In this section, the INDO calculations were also performed for the second, third and forth nearest dimers in both crystals of **2** and **3** in order to elucidate their magnetic contributions. Table 2 summarizes the calculated J_{ab} values. From table 2, it is found that only the first nearest dimers have large J_{ab} values, and the second, third and fourth nearest dimers have smaller J_{ab} values than 1 cm^{-1}. These results may be explained by dependence of J_{ab} values on intermolecular distances (R) : J_{ab} values decrease with the increase of R in an exponential manner. Therefore the calculated results are understood

TABLE 2 J_{ab} values (INDO) for each dimers in **2** and **3**.

dimer		distance /Å	J_{ab} (INDO) /cm^{-1}
2 (1^-•Li$^+$•MeOH)			
dimer $\mathbf{A}_1$	($\mathbf{a}_1$-$\mathbf{b}_1$)	3.246	5.666
dimer $\mathbf{B}_1$	($\mathbf{a}_1$-$\mathbf{c}_1$)	5.404	0.061
dimer $\mathbf{C}_1$	($\mathbf{a}_1$-$\mathbf{d}_1$)	6.087	-0.001
dimer $\mathbf{D}_1$	($\mathbf{a}_1$-$\mathbf{e}_1$)	7.360	0.000
3 (1^-•Li$^+$•MeOD)			
dimer $\mathbf{A}_2$	($\mathbf{a}_2$-$\mathbf{b}_2$)	3.309	3.979
dimer $\mathbf{B}_2$	($\mathbf{a}_2$-$\mathbf{c}_2$)	5.090	0.005
dimer $\mathbf{C}_2$	($\mathbf{a}_2$-$\mathbf{d}_2$)	5.378	0.043
dimer $\mathbf{D}_2$	($\mathbf{a}_2$-$\mathbf{e}_2$)	5.538	0.111

intuitively from the crystal structures in fig. 1. In fact, the effective interactions become weaker as R increase in the case of **2**. The interaction in dimer $\mathbf{B}_1$ is only 0.06 cm^{-1}, and the interactions in dimers $\mathbf{C}_1$ and $\mathbf{D}_1$ are negligible. On the other hand, the J_{ab} values of the dimers $\mathbf{B}_2$, $\mathbf{C}_2$ and $\mathbf{D}_2$ in **3** exhibit the reverse dependency, showing that the orientations between the monoanion $\mathbf{1}^-$ become crucial. In summary, the tendency obtained by the INDO calculations is consistent with the experimental results derived form the exchange-coupled dimer models[7].

DISCUSSIONS AND CONCLUDING REMARKS

Judging from the present ab initio and semiempirical calculations, the nearest intermolecular O-C(α) distance in the dimer was responsible for the difference between J_{ab} values of the crystals **2** and **3**. The difference between crystal structures of **2** and **3** was lattice constants and molecular packing style. The true isotope effect (H, D) might not contribute to the effective exchange interactions. In addition it will be reasonable to conclude that the Li cation and methanol play no important role for the ferromagnetic intradimer interaction of the monoanion $\mathbf{1}^-$ though they are not treated explicitly in our studies.

The simplied model extracting the nitronyl nitroxide groups could give a useful guide for theoretical understanding of the effective exchange interaction. The UNO CASSCF by the use of two SOMOs and two unpaired electrons {2,2} demonstrates that SOMO is essentially localized on this group, and the SOMO-SOMO potential exchange (PE) interaction is predominant for explaining the ferromagnetic interactions observed for the dimers $\mathbf{A}_1$ and $\mathbf{A}_2$. On the other hand, the spin polarization (SP) plus higher-order magnetic interactions estimated by the UNO CASCI{6,6} method rather reduce the positive J_{ab} value via the PE mechanism in the case of the molecular packings of $\mathbf{1}^-$ revealed by the X-ray diffraction experiments[7]. The ab initio UNO CASSCF of the full dimers is desirable in this regard.

The INDO method gives reasonable J_{ab} values which are about one half of the experimental values[7]. This is the same even for clusters of phenyl nitronyl nitroxide (PNNO) derivatives in general[1-3]. The APUHF INDO method is useful for qualitative calculations of J_{ab} values for larger organic radical systems.

The J_{ab} values for the dimers $\mathbf{B}_1$, $\mathbf{C}_2$ and $\mathbf{D}_2$ by INDO remain positive, indicating the nonnegligible contributions to magnetic behaviors in the crystals. In fact, this may be the reason why the temperature dependence of the effective magnetic moments μ_{eff} per molecule of the crystalline samples of **2** does not become 2.0 even at the near 0 K in the fig. 2 in the reference[7]. So, in order to study more explicit magnetic behaviors experimental studies at much lower temperature region are desirable than at already reported region.

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