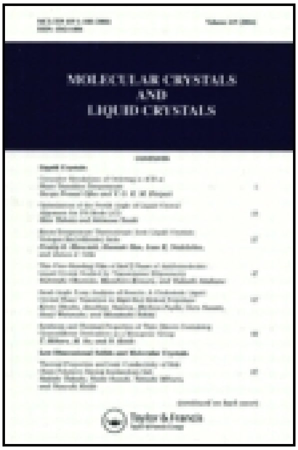

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Theoretical Studies of Intra- and Inter- Magnetic Interactions in TMAO(1,3,5,7 - Tetramethyl - 2, 6- Diazaadamantane N, N′ - Dioxyl)

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Theoretical Studies of Intra- and Inter- Magnetic Interactions in TMAO(1, 3, 5, 7 - Tetramethyl - 2, 6- Diazaadamantane N, N' - Dioxyl)

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Ferromagnetic properties of TMAO organic crystal, especially α-form crystal, are studied theoretically. There are two nitroxide groups, that is, both intramolecular magnetic interaction in one molecule and inter-molecular interaction between two molecules are expected in contrast to many organic ferromagnetic crystalline species that have been reported by other groups. Obtained J_{ab} values for intra- and inter- molecular interactions are positive and small positive for only a few pairs, respectively. Cooperation of two types of magnetic coupling is essential to realize bulk ferromagnetic behavior.

Keywords: TMAO; Ferromagnetic interaction; *ab initio* MO calculation; Effective exchange interaction

INTRODUCTION

Recently, Rassat and co-workers reported experimental measurements of α- and β- phases of a crystalline nitroxide biradical, that is, TMAO (1, 3, 5, 7 - tetramethyl - 2, 6 - diazaadamantane N, N' - dioxyl) (**1**) and showed that for α-phase it had a positive Weiss constant of 10 K and exhibited a ferromagnetic transition at 1.48 K[1,2,3]. This biradical contains two NO radical groups at the opposite sides in one molecule and magnetic coupling between each site can be propagated through carbon atoms. In this point this crystal differs from other previous ferromagnetic crystals which contain only one NO radical site[4,5,6,7,8]. On the other hand, one NO radical site locates in close contact with one site on the next molecule without forming the local dimer bonding which is familiar for *p*-NNBA$^-$ [5,9], Ph-CH=N-TEMPO[7,10] and so on, and linear zigzag NO paths appear. Two molecules on each chain also approach each other closely on NO radical sites[11,12,13,14] and it is expected that spatial networks of magnetic interactions appear. Thus, two types of magnetic interactions, that is, intra- and inter- magnetic interactions are expected in this crystal and coupling between these magnetic interactions is worth evaluating.

Recently, in series of TEMPO and NPNN compounds etc., the orbital and/or spin polarization on the β-position hydrogen (β-H) of $-CH_3$ or $-CH_2$ groups is found to play an important role[8,10,15]. Pressure-induced magnetic transition may be caused by the shortening or rotation of these groups by the pressurization[16,17,18]. Here, this β-H effect is also studied by calculating J_{ab} values.

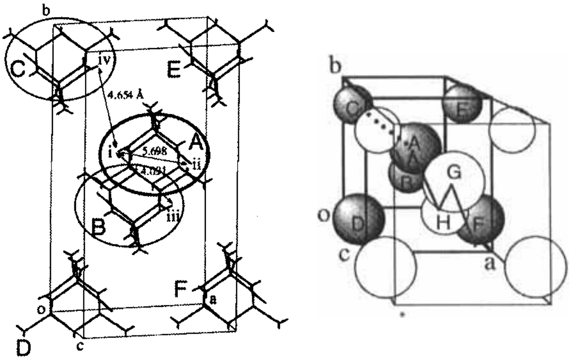
CRYSTAL STRUCTURES

The TMAO compound which consists of a purely organic non-ionic material has been reported in detail by Rassat and co-worker and their papers propose that it exhibits two crystalline forms (α- and β- forms) where packing styles are different from each other[1,2,3]. The α-form crystal undergoes a ferromagnetic transition at low temperature and the data of magnetic measurement were reported in their papers. It possess a Curie temperature of 1.48 ± 0.02 K and a positive Curie-Weiss temperature ($\theta = 10$ K), while the magnetic behavior in the β-form crystal was not reported. In addition, X-ray structural measurement was carried out in their papers and particularly the last paper contained accurate positions of not only heavy atoms, such as carbon, nitrogen and oxygen atoms, but also hydrogen atoms. Here, we employed the most accurate structural data for the α-form particularly, since its detailed magnetic behavior had been researched. The TMAO crystal in the α-form has unit cells classified by a space group of *C2/c* and cell parameters are a = 8.381(3) Å, b = 14.495(3) Å, c = 10.351(3) Å, and β = 105.35(2) °. The structure of all TMAO molecules is assumed to be rigid and not influenced by molecular packing.

Figure 1A illustrates a unit cell of the α-form crystal, for which theoretical calculations will progress. In this figure, let us consider molecule **A** as reference and two radical NO sites indicate **i** and **ii**. In addition to molecule **A**, the adjacent molecules are also indicated as **B**, **C**, **D**, **E** and **F**. Each NO group has three close NO neighbors, i.e. one is located on the opposite side of the same molecule and the others occupy the adjacent side of the next molecules. Distances between oxygen atoms on each NO-group are 5.698 (**i** to **ii** on **A**), 4.091 (**i** to **iii** on **B**) and 4.654 Å (**i** to **iv** on **C**). The NO's network with intra- and inter- molecular chains will compose spatial magnetic interactions. Much detailed theoretical studies depended on quantum chemistry techniques will be made on the following sections.

INTRA-MOLECULAR FERROMAGNETIC INTERACTION

First of all, we have to investigate intra-molecular magnetic interaction in a TMAO molecule. Figure 2 illustrates real TMAO and several modified models. Here, model I is actual structure without simplification in the crystal. In model II and III two (**a** and **b**) and four (**a**, **b**, **c** and **d**) methyl groups, which are close to one side and both sides of NO groups, are replaced by hydrogen atoms respectively in order to elucidate effects of β-hydrogen atoms and/or methyl groups etc. Here, C-H bond lengths in the models II and III were recalculated by the PM3 optimization method in the MOPAC program package



A B

FIGURE 1 Crystal structure of TMAO

under the condition that all another atoms are fixed. The last model IV implies only direct through-space interaction, though through-bond interactions with carbon atoms are expected in the other models. It is worth paying attention that difference between indirect coupling through bond and direct one through space comes into the spotlight, when we go through the process of these calculations.

The obtained J_{ab} values are summarized in Table I. Here, INDO, *ab initio* UHF, CASSCF and DFT calculations are carried out and 4-31G basis set is employed for the purpose. The DFT techniques depend on the spin-unrestricted Kohn-Sham (UKS) equation with suitable exchange functionals and correlation functionals. In this investigation UBLYP and UB3LYP methods were employed in order to compare behavior of DFT methods. Though the other DFT methods are also feasible with the GAUSSIAN94 program package, our previous papers reported that the method combined Becke-88 for exchange functional and LYP for correlation functional could give the most accurate values. UNO CASCI{2,2} and UNO CASSCF{2,2} methods are also performed to evaluate only SOMO-SOMO direct interaction. In addition, for the model IV, UMP2 and UMP4 methods, which are Møller-Plesset perturbation theory, and UCCSD(T) method were applied, whereas these methods were not feasible for model I, II and III because of the large size of models.

First, let us analyze the evaluated data for model I. All the calculated J_{ab} values for model I are positive, indicating all methods support ferromagnetic interaction. Magnitude of the J_{ab} values are near to the experimental results, that is, Curie-Weiss temperature (θ = 10 K ≈ 7 cm^{-1}). UHF method gives

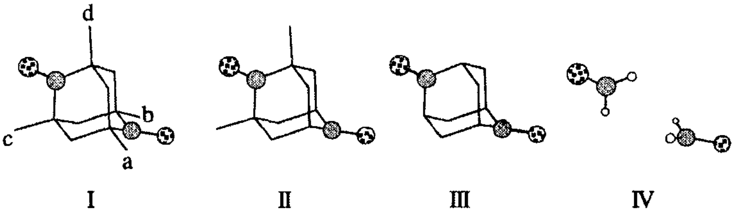


FIGURE 2 Models for studying intra-molecular magnetic interactions

TABLE I J_{ab} values for model I, II, III and IV.

Methods	J_{ab} /cm^{-1} I	II	III	IV
INDO	2.162	1.783	1.527	-0.126
UHF [a)]	16.141	14.594	13.437	1.966
UMP2 [a)]				3.857
UMP4 [a)]				3.689
UCCSD(T) [a)]				3.340
UNO CASCI{2,2} [a)]	4.502	4.257	4.076	0.327
UNO CASSCF{2,2} [a)]	4.244	3.991	3.813	0.410
UBLYP [a)]	18.344	17.819	17.809	-0.059
UB3LYP [a)]	16.470	15.700	15.274	2.145

a) 4-31G basis set was used.

about eight times as large a value as INDO method. Judging from our previous papers, UHF method tends to give too large values because of overestimation of the spin polarization (SP) effect, although values with INDO method are usually slightly small. This tendency also can be realized and a intermediate values between those derived by UHF and INDO methods may be often suitable. In addition, DFT methods, especially UB3LYP method, give similar J_{ab} values to the UHF method and the balance of both reliability of result and CPU time is very good. The J_{ab} values derived with UNO CASCI{2,2} and UNO CASSCF{2,2} methods are positive, about 4 cm^{-1}. This positive values show that SOMO-SOMO direct interaction is essential. Judging from the positive values with UNO CASCI{2,2} method, interaction between two SOMOs delocalizing on both NOs seems to contribute to ferromagnetic interaction.

Figure 3A illustrates shapes of SOMOs and occupation numbers given with natural orbital (NO) analyses. Here, for model I each SOMO corresponds to 61th and 62th MOs. In this figure each orbital can be classified into σ-, π-, π^*-, π'- and σ'- type. The marks ' (prime) indicate higher order orbitals because of double zeta orbitals of the employed 4-31G basis set.

methods. These results mean that methyl groups (**a**, **b**, **c** and **d**) of a TMAO molecule have negligible effect for ferromagnetic intramolecular interaction and variation of shape of SOMOs and spin densities are small.

Finally, we discuss model IV since it has no through-bond interaction. It is notice that the absolute values of J_{ab} obtained by INDO and UHF methods are about ten times as small as those for model I. UNO CASCI{2,2} and UNO CASSCF{2,2} methods give also small positive values. These results say that direct interaction through space between both H_2NOs is very small and through-bond path in model I is essential.

INTER-MOLECULAR FERROMAGNETIC INTERACTION

In the above section only intra-molecular magnetic interaction which appears in each TMAO molecule has been taken into account and we can explain theoretically their magnetic behaviors. Here, let us develop the investigation of magnetic interactions to inter-molecular magnetic coupling in this section. In α-form crystal, six TMAO molecules are packed in monoclinic unit cells and the four are shared by the next cells. Figure 1B illustrates straightforwardly how each molecule occupies its spatial position, where one ball indicates one TMAO molecule and shaded and white balls are individually packed into same unit cells. This figure is equivalent to Fig. 1A and the notations **A**, **B**, **C**, **D**, **E** and **F** are common to both figures. Let us consider molecule **A** as a reference. Orientation and relation between two molecules can be studied efficiently with crystal symmetry. In Table II the J_{ab} values calculated by INDO and UHF/4-31G method for each molecular pair are summarized. From this table, it is found that only pairs **A**-**B** (=**A**-**H**) and **A**-**C** have small ferromagnetic interaction, although J_{ab} values derived for the other pairs are almost zero and it is suitable to neglect contribution of them. In this regard, it is noteworthy to discuss implications of the calculated results in relation to the spatial ferromagnetism observed for crystals. The suitable orientation and shortening of intermolecular distances may turn out to be essential factors for the non-zero J_{ab} values, as compared with the other no-coupled pairs such as pairs **A**-**D** and so on. Spatial relations of these

Occupation numbers on the SOMOs are equal to 1.00 and imply single occupation of electrons. Two localized MOs of each radical site are oriented to each other perpendicularly and have *C2* symmetric operation. From this figure SOMOs are delocalized over the connecting α- and β- carbons as can be recognized from the remaing small lobes. The orbitals spread over α- and β-C atoms enable two radical sites to couple each other. Magnetic interaction given by UNO CASCI{2,2} method turns out to be positive.

Pairs of 60th and 63th MOs, 59th and 64th MOs, etc. indicate pairs of natural orbitals. These MOs as well as SOMOs may play an important role of magnetic interactions and higher order effects beyond only direct couplings between SOMOs are also expected. Thus, these *ab initio* calculations support existence of this higher contribution. For this purpose, spin density analysis would help us to investigate magnetic coupling between each NO site. In Fig. 3B results by UHF methods for model I are showed. This figure can point out remarkable contribution of inserted atoms, that is, existence of α- and β- C atoms enable two radical sites at both ends to interact each other.

Next, studies for models II and III need to be made. It is noteworthy that similar J_{ab} values are obtained for models I, II and III by each method, though the values for model I are slightly larger than those for the II and III. Same tendency is found in the result by UNO CASCI{2,2} and CASSCF{2,2}

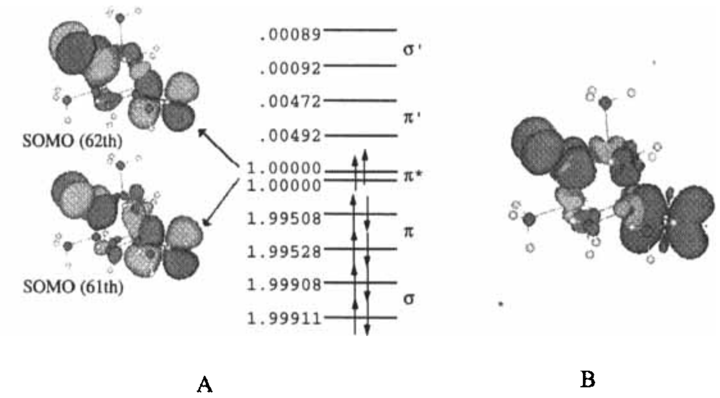


FIGURE 3 (A) Occupation numbers and SOMOs (B) Spin density

molecules are extracted and illustrated in Fig. 4A. Crystal symmetry reproduces equivalent pairs such as pair **A**-**H** to pair **A**-**B** etc. and zigzag chains propagate ferromagnetic coupling periodically. The other pair **A**-**C** makes two chains combine each other. Thus, these networks in the α-form TMAO crystal are necessary to accomplish spatial organic ferromagnetic interactions of two dimensions at least. Moreover, though pair **A**-**E** has a very small positive J_{ab} value, i.e. 0.001 cm^{-1}, three dimensional networks may be formed.

Next, we must look more carefully into studying for pair **A**-**B** which have positive J_{ab} value in order to elucidate the origin of the inter-molecular ferromagnetism. Figure 4B illustrated models V and VI, though model V is quivalent to pair **A**-**B**. In this pair two NO radical sites stack in anti-parallel manner and three interaction paths, i.e., NO ··· NO, α-H ··· O and β-H ··· O are expected. Model VI was employed in order to eliminate the β-H interaction. To this end, the $-CH_2$ groups were replaced with -NH groups as isoelectronic structures. The obtained data are summarized in Table II additionally. The minus and smaller J_{ab} values for model VI may indicate the β-hydrogen path ($\mathrm{NO}\uparrow - \mathrm{C}\downarrow - \mathrm{C}\uparrow - \mathrm{H}\downarrow \cdots \mathrm{NO}\uparrow$) is essential for the intermolecular ferromagenetic interaction.

CONCLUDING REMARK

Semiempirical, ab initio UHF, CASSCF and DFT calculations were carried out for evaluating the effective exchange integrals J_{ab} for both intra- and inter-molecular magnetic interactions in α-form TMAO crystal. Through-bond

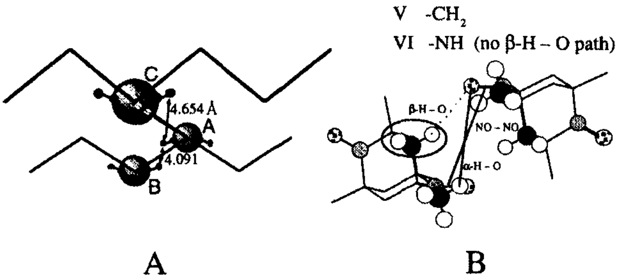


FIGURE 4 (A) Zigzag magnetic interactions (B) Models V (= **A**-**B**) and VI

TABLE II J_{ab} values for various molecular pairs in TMAO crystal. Models V and VI are illustrated in Fig. 4B.

	J_{ab} /cm^{-1}	
	INDO	UHF/4-31G
A-**B** (V) (=**A**-**H**)	0.008	0.700
A-**C**	0.013	0.129
A-**D**	0.000	0.000
A-**E**	0.000	0.001
A-**F** (=**B**-**C**)	0.000	0.000
A-**G**	0.000	0.000
VI	-0.008	0.253

coupling in one molecule corresponds to the former and relatively large ferromagnetic interaction is realized. On the other hand, through-space couplings between two molecules correspond to the latter and only small ferromagnetic interactions for pairs **A**-**B** and **A**-**C** and no interaction for the others are made clear. These cooperation might run in ferromagnetic intermolecular networks of three dimensions, at least two dimensionals without pair **A**-**E**. These agree with the experimental measurements by Rassat et al. Our theoretical calculations suggest that the bulk magnetism of this crystal is delicate in nature because the magnitude of the intermolecular exchange integrals is not large. It is important to analyze and control magnetic coupling for all essential molecular pairs to design macroscopic organic ferromagnetic crystalline species. With regard to this, existence of two radical groups in one molecule is essential. Intra-molecular ferromagnetic interaction helps the radical spins induced on one side to be transmitted to the other side. The TMAO crystal has the advantage of bulk ferromagnetism owing to its symmetry, though dimerization of two molecules often occured in another familiar organic ferromagnetic species.

Acknowledgments

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