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Theoretical calculations of magnetic properties of the α-, β-, γ- and δ-phases of *p*-NPNN

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ABSTRACT

Hybrid density functional theory (HDFT) calculations have been carried out for clusters of *p*-NPNN extracted from the experimental crystal structures of the α-, β-, γ- and δ-phases in order to investigate the weak magnetic interactions between the organic radicals theoretically. From the systematic HDFT calculations for β- and γ-phase *p*-NPNN clusters, it was found that the magnetic long-range ferromagnetic and antiferromagnetic orderings would be presented in the β- and γ-phase *p*-NPNN crystals, respectively.

1. Introduction

An organic radical molecule *p*-NPNN [2-(4′-nitro-phenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-*N*-oxide] is well known to crystallize in four different phases, such as α-, β-, γ- and δ-phases [1–6]. The orthorhombic β-phase *p*-NPNN was found to be the first organic bulk ferromagnet below 0.6 K. On the other hand, the triclinic γ-phase *p*-NPNN showed antiferromagnetic transition at 0.65 K. In the case of the α- and γ-phases, a magnetic phase transition has not been found. Therefore, the *p*-NPNN systems are the appropriate examples for the theoretical study of the weak magnetic interaction for the molecular packing as the four different crystals of *p*-NPNN exhibit a variety of magnetism.

Previously, the semi-empirical molecular orbital method (INDO) was applied to calculations of intermolecular effective exchange integrals (J_{ab}) for clusters of various nitroxides, such as phenyl nitronyl nitroxides and *p*-NPNN [7–12]. The estimated magnetic phase transition temperatures for β- and γ-phase *p*-NPNN were roughly consistent with the experimental values determined for β- and γ-phase *p*-NPNN by measurements of heat capacity and magnetic susceptibility. Judging from the experimental result (T_c = 0.6 K) for the ferromagnetic β-phase of *p*-NPNN, J_{ab} values should be small positive quantity which gives rise to the difficulty of theoretical estimation. First-principle calculations of its sign and magnitude are crucial for theoretical elucidation and understanding of the mechanism of its organic ferromagnetism. Here, in order to determine the effective exchange integrals for all four phase of *p*-NPNN crystals, hybrid density functional theory (HDFT) calculations are carried out for *p*-NPNN clusters, whose geometries are taken from the X-ray structures of the four different crystals. A theoretical explanation is presented for the long-range magnetic orderings in the four phases of *p*-NPNN crystals. Additionally, Monte Carlo simulations and a generalized Langevin–Weiss (GLW) model are used to estimate its transition temperatures (T_c for the β-phase and T_N for the γ-phase) in order to elucidate the validity of the calculation results.

2. Calculation method and models

All the computations were performed by GAUSSIAN 03 program packages [12]. Unrestricted hybrid-DFT (UB3LYP and UB2LYP (0.35)) calculations was used for the model systems computations using 6-31G** basis set for C, N, O. In the used hybrid-DFT methods, E_{XC} is calculated by the following equation:

$$E_{XC} = P_2E_X^{HF} + P_1(P_4E_X^{Slater} + P_3E_X^{Becke88}) + P_6E_C^{VWN} + P_5E_C^{LYP} \quad (1)$$

P_1, P_2, P_3, P_4, P_5 and P_6 parameters for the B3LYP method are 1.0, 0.2, 0.72, 0.8, 0.81 and 1.0, respectively. On the other hand, P_1, P_2, P_3, P_4, P_5 and P_6 parameters for B2LYP (0.35) are 1.0, 0.35, 0.65, 0.65, 1.0 and 1.0, respectively.

In order to investigate the magnetic interaction in the model systems, the effective exchange integral of Heisenberg Hamiltonian was calculated using Yamaguchi equation as shown [7–9]:

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

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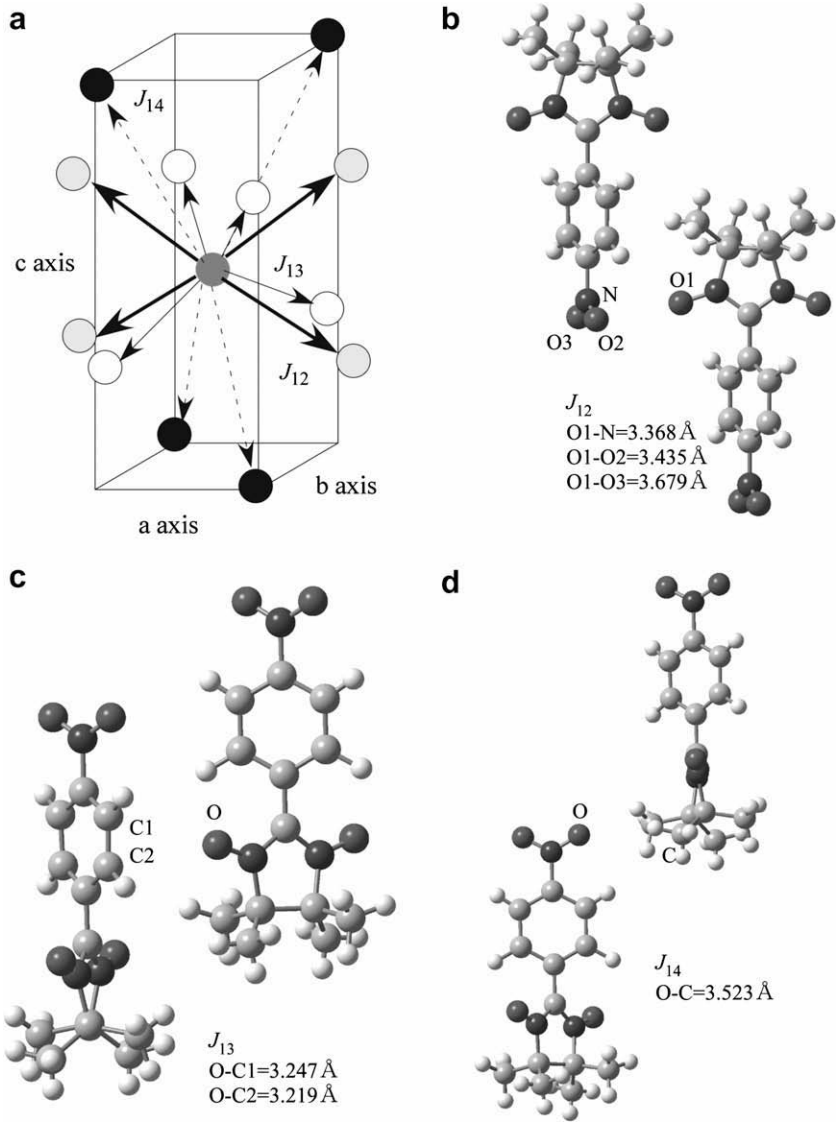

Fig. 1. (a) The crystal structure of the β-phase *p*-NPNN with the Fdd2 space symmetry. J_{1n} (n = 2–4) denotes the effective exchange interactions of (b) J_{12} type intermolecular interaction in the *ac* plane, (c) J_{13} type intermolecular interaction and (d) J_{14} type intermolecular interaction.

The ferromagnetic phase transition temperature is calculated by the Langevin–Weiss mean-field theory in combination with the calculated J values as shown [13–15]:

$$k_B T_c = \frac{2}{3} S(S+1) \sum J_{ij} \quad (3)$$

Moreover, in order to detail analysis of the magnetic transition temperatures of β- and γ-phase *p*-NPNN crystals, Monte Carlo ising spin simulation was also carried out. In these simulations, $12 \times 12 \times 12$ lattice with a periodic boundary condition was used. Especially, Wolff type cluster flipping method was applied for γ-phase *p*-NPNN model system [16].

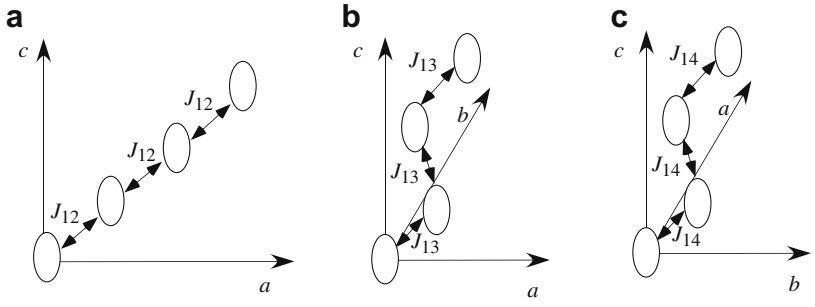

Fig. 2. The oligomers in the β-phase *p*-NPNN of (a) J_{12} type interaction, (b) J_{13} type interaction and (c) J_{14} type interaction.