

Electronic structure of the organic half-metallic magnet 2-(4-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl 3-N-oxide

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Ab initio calculations have been performed to study the electronic band structure and ferromagnetic properties of the organic radical *p*-NPNN. The density of states, the total energy, and the spin magnetic moment were calculated. The calculations revealed that the δ phase of *p*-NPNN has a stable ferromagnetic ground state and the spin magnetic moment per molecule is $1.0\mu_B$, which is in good agreement with the experimental value. It is found that an unpaired electron in this compound is localized in a single occupied molecular orbital (SOMO) constituted primarily of $\pi^*(\text{NO})$ orbitals and the main contribution of the spin magnetic moment comes from the $\pi^*(\text{NO})$ orbitals. By analysis of the band structure, we find that the δ -phase crystal of *p*-NPNN may be a half-metallic magnet.

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I. INTRODUCTION

Recently, there has been considerable interest in the discovery of ferromagnetic (FM) order in a class of purely organic compounds.¹⁻⁵ While the majority of organic and organometallic radicals exhibit antiferromagnetic (AFM) intermolecular interactions, a few radicals have been confidently proved to possess FM interactions. These materials may display a wide variety of magnetic behaviors, including paramagnetism, antiferromagnetism, and ferromagnetism. Among the few known compounds of this type of organic radicals is the crystal of 2-(4-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl 3-N-oxide (*p*-NPNN).^{4,5} The structural formula of the *p*-NPNN molecule with the atom labeling scheme is shown in Fig. 1. The crystals of *p*-NPNN were prepared by the method described in Ref. 6.

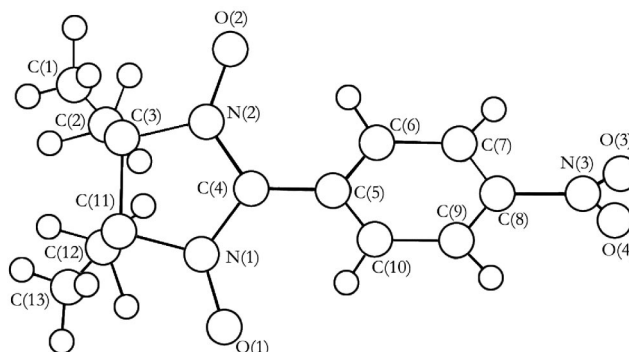
The magnetization at low temperatures and the ac susceptibility measurements suggest that FM order occurs in the present spin system below the Curie temperature T_C . This is the first organic ferromagnet which is composed of a simple radical having well-defined chemical and crystal structure and consisting only of the light elements of H, C, N, and O. The crystal engineering strategies which are used to have the free radicals interacting are inspired from supramolecular chemistry⁷ and are based mostly on hydrogen bond networks to direct the crystal packing. This has been recently demonstrated to work quite efficiently in a few cases, so that FM interactions and magnets were rationally achieved.⁸

The *p*-NPNN radical crystallizes in four different forms: α , β , γ , and δ (also known as β_h) phases. The orthorhombic β phase is the most stable one and undergoes an ordering transition to a FM state at 0.6 K due to the presence of intermolecular three-dimensional ferromagnetic interactions,⁹ while the triclinic γ phase shows one-dimensional ferromagnetic interactions but it orders antiferromagnetically at $T_N=0.65$ K.¹⁰ The γ phase was initially believed to be

ferromagnetic but was later shown to be antiferromagnetic. The interpretation of the experiments on the γ phase was quite contentious at first, until it was realized that the γ phase was thermodynamically unstable with respect to the β phase even at low temperature.¹¹ Only very few investigations have been devoted to the monoclinic α and δ phases. Static magnetic susceptibility measurements show results indicative of FM interactions in the α , β , and δ phases, and these three phases of *p*-NPNN exhibit qualitatively the same magnetic behavior as a function of temperature.¹²

In the δ -phase crystal of *p*-NPNN, the phenyl ring is almost coplanar with the nitro group, but forms an angle of 50.3° with the plane of the nitronyl nitroxide, O1-N1-C4-N2-O2. The projection of the crystal structure of the δ phase of *p*-NPNN along the *b* axis is shown in Fig. 2. Weak intermolecular contacts between the O atoms in the NO groups and N atoms in the NO₂ groups are possible, and the δ -phase crystal of *p*-NPNN forms a two-dimensional network by these contacts. N(3) of the NO₂ group is located almost at the mid point between O(1') and O(2'') in the neighboring radicals. O(1') \cdots N(3) and N(3) \cdots O(2'') distances are 3.359 and 3.372 Å, respectively, and the angle O(1') \cdots N(3) \cdots O(2'') is 175.9° . The nitrophenyl plane is almost perpendicular to the O(1') \cdots N(3) \cdots O(2'') vector.¹³

Theoretically the magnetic properties of the β phase and

FIG. 1. Atom labeling diagram of *p*-NPNN.

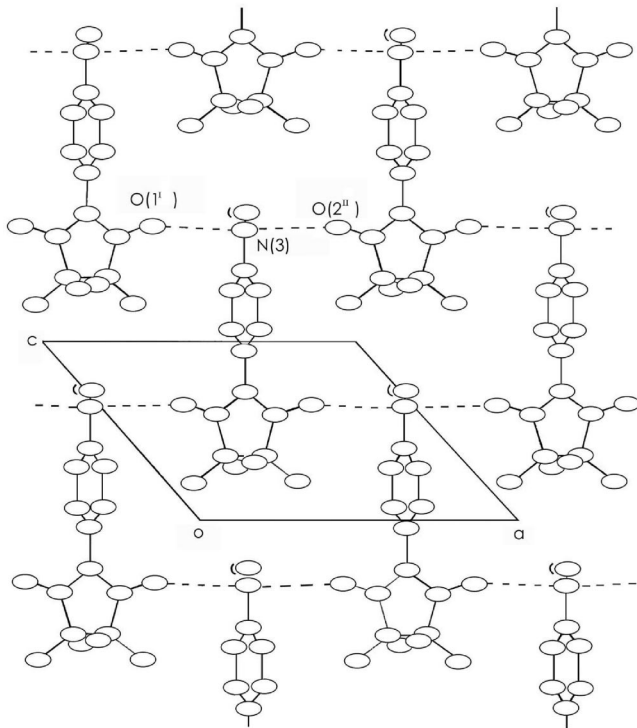


FIG. 2. Projection of the structure of the δ phase of p -NPNN along the b axis. Symmetry operations: (I) $x, y, z+1$; and (II) $x+1, y, z+1$.

γ phase of p -NPNN have been investigated with different methods.^{14,15} Considering the complex magnetic properties and the possible conductivity due to intramolecular and intermolecular charge transfer (CT) of the p -NPNN, detailed knowledge of the electronic band structure and magnetic properties, especially for the δ phase, is required to understand the mechanism of the FM interactions and the conductivity of this compound.

II. RESULTS AND DISCUSSION

The calculations presented in this work were performed by employing density-functional theory (DFT) with the generalized gradient approximation (GGA),¹⁶ using the full-potential linearized augmented plane-wave (FP-LAPW) method, which is among the most accurate band structure methods presently available. In this method no shape approximation on either potential or the electronic charge density is made. We use the wien97 (Ref. 17) package, which allows inclusion of local orbitals in the basis, improving upon linearization and making a possible consistent treatment of semicore and valence states in one energy window, hence ensuring proper orthogonality. In the present calculation, the lattice parameters of the δ -phase crystal of p -NPNN we used are $a=10.960$ Å, $b=19.350$ Å, $c=8.257$ Å, $\beta=131.61^\circ$. Atomic sphere radii (R_i) of 1.0, 1.0, 0.8, and 0.5 a.u. were used for N, O, C, and H, respectively; 100 k points in the first Brillouin zone were adopted in the calculations. The plane-wave cutoff energy is 278 eV.

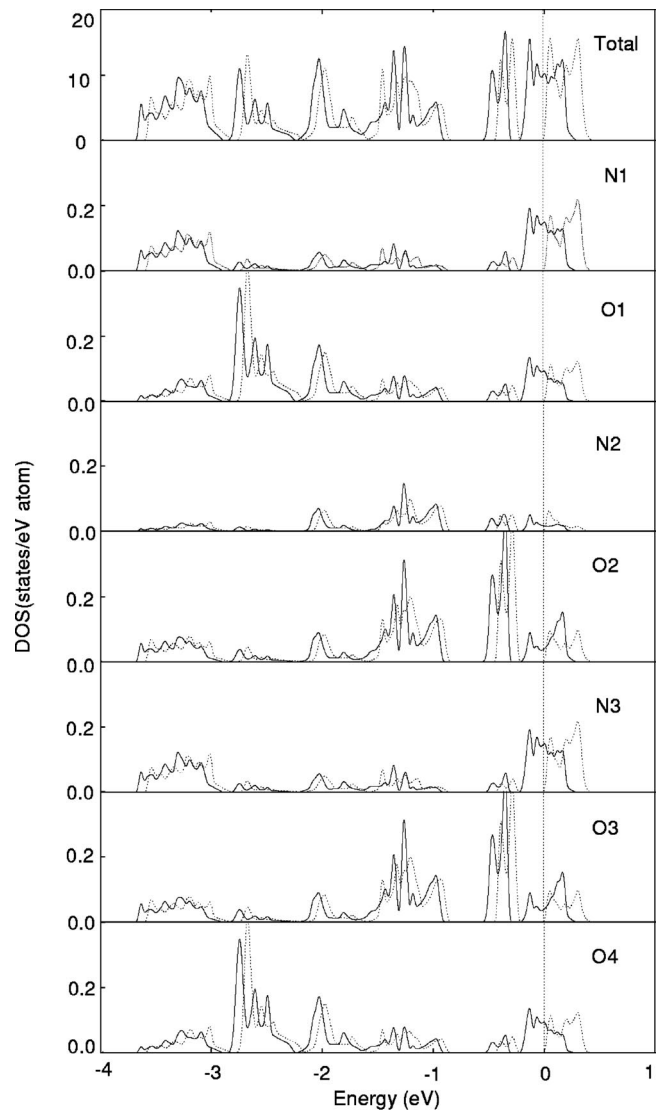


FIG. 3. Density of states of the δ phase of p -NPNN (solid line: spin-up states; dotted line: spin-down states).

To study the electronic structure and magnetic properties of the δ phase of p -NPNN, we performed FP-LAPW calculations of the electronic band structure. Figure 3 shows the total density of states (DOS) of the cell and the total atomic DOS of the atoms, such as N and O atoms. Because the DOS distribution near the Fermi level determines the magnetic properties, we concentrate our attention upon the DOS in the vicinity of the Fermi level, which range from -4 eV to 1 eV, as seen in Fig. 3. In the vicinity of the Fermi level, the total DOS distribution of spin-up and -down states are obviously split, and so are the ordered spin arrangements formed by the exchange interaction. The band structure can manifestly illustrate the band splitting. Figure 4 gives the electronic band structure of the δ phase of p -NPNN [For simplicity, we only plot the band structure in the range where there exists overlap between the spin-up highest occupied molecular orbital (HOMO) and the spin-up lowest unoccupied molecular orbital (LUMO) to discuss the half-metallic magnet character in the following.] In Fig. 4, the coordinates of the k points L ,

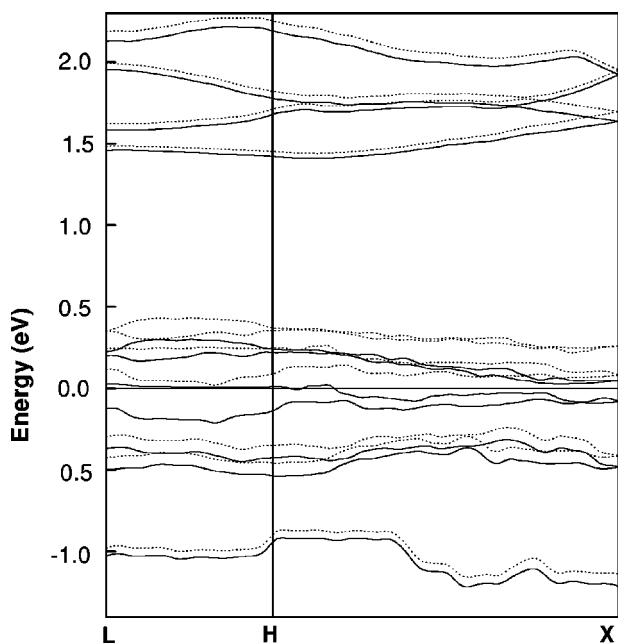


FIG. 4. Electronic band structure of the δ phase of p -NPNN. The horizontal solid line denotes the Fermi level. The solid lines denote the spin-up electronic band structure. The dotted lines denote the spin-down electronic band structure.

H , and X are $(1/2, 1/2, 0)$, $(17/50, 1, 0)$, and $(17/50, 1, 1/2)$, respectively. From Fig. 4, we find that two spin-up valence bands are below the Fermi level, but the two corresponding spin-down valence bands are above the Fermi level. One valence band is split into two subbands: one is the spin-up occupied valence band; the other is the spin-down unoccupied band. In the present calculations, the supercell contains two molecules, so the spin magnetic moment is about $1.0 \mu_B$ /molecule.

We concentrate our attention upon the total atomic DOS in the range from -0.5 eV to the Fermi level in the Fig. 3. The total atomic DOS of N and O atoms is nearly only from p_y orbitals in the energy range. For simplicity, we do not additionally give the partial DOS of the p_y orbitals of these atoms. It is found that, in the energy range, the partial DOS of N1 p_y , O1 p_y and N3 p_y , O4 p_y orbitals have the similar peaks and character, which means that there is a hybridization between N1 p_y , O1 p_y and N3 p_y , O4 p_y orbitals. The hybridization makes the $2p(\pi)$ atomic orbitals of N1 O1 and N3 O4 forming the $\pi^*(\text{NO})$ orbitals. The single occupied molecular orbital (SOMO) is mainly formed from these two $\pi^*(\text{NO})$. The unpaired electron of the δ -phase of p -NPNN is localized in the SOMO constituted primarily of the $\pi^*(\text{NO})$ orbitals, which is formed from the $2p(\pi)$ atomic orbitals of N1, O1 and N3, O4. An examination of Table I and Fig. 3 reveals that the unpaired electron of the δ phase of p -NPNN is localized in the $\pi^*(\text{N1O1})$ and $\pi^*(\text{N3O4})$ orbitals with identical probability. The major part of the spin magnetic moment is from these two NO radicals

The π^* bonds are formed in N1, O1 and N3, O4 radicals, π bonds in N2, O2 and N3, O3 radicals. As suggested in Ref. 4, the intramolecular CT takes place from N2 to O2 and from N3 to O3 by a low-energy shifting $\pi-\pi^*$ transition due to

TABLE I. Calculated magnetic moments in μ_B for the atoms of the δ phase of p -NPNN.

Site	Spin	Site	Spin
N1	0.305	C2(C12)	-0.055
N2	0.046	C3(C11)	-0.021
N3	0.305	C4	-0.002
O1	0.191	C5	-0.078
O2	0.046	C6(C10)	0.013
O3	0.046	C7(C9)	0.019
O4	0.191	C8	0.055
C1(C13)	-0.006		

introducing a substituent. The unpaired electron of the δ phase of p -NPNN is localized in the N1, O1 and N3, O4 radicals with identical probability. This indicates that the two possible resonance structure of the δ -phase crystals of p -NPNN, as seen in the Fig. 5, exists with identical probability.

From the total DOS in Fig. 3, we find that the energy gap in the spin-down subbands is opened. The spin-up total DOS is continuous in the vicinity of the Fermi level. From Fig. 4, we can find that there exists an overlap between the spin-up HOMO and spin-up LUMO. The detailed calculations indicate that the overlap is 0.01 eV. The spin-up subbands exhibit metallic properties. Considering that the δ -phase crystals of p -NPNN has a large delocalization of the unpaired electron on the nitro group, intramolecular and intermolecular CT, this result should be believable. The spin-down subbands exhibit insulator properties and the spin-up subbands metallic properties. The metal and insulator behaviors coexist in the δ phase of p -NPNN. The δ phase of p -NPNN may be a half-metallic magnet. To our knowledge, such a half-metallic magnet consisting only of the light elements H, C, N, and O has not been reported yet. If the δ phase of p -NPNN is really a half-metallic magnet; it is important to spin electronics.

In Table I, the spin magnetic moments of the δ phase of p -NPNN are given. The major part of the spin magnetic moment is from the N1, O1 radical and N3, O4 radical with a little contribution from other O, C, and N atoms. The spin order of p -NPNN is similar to that of the organic radical galvinoxyl.¹⁸ Alternating $+/-/+$ spin populations along all paths linking the NO radicals confirm that the ferromagnetic exchange interaction of the NO radicals passes through the

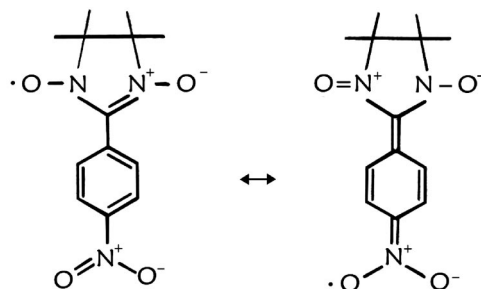


FIG. 5. The two possible resonance structure of the δ phase of p -NPNN.

polarized spin populations. Kinoshita *et al.*⁵ showed that at very low temperatures the saturation magnetic moment per molecule is about $1.0\mu_B$. It is well known that the saturation magnetization is the same as the spontaneous magnetization at the same temperature. The present calculation gives a spontaneous magnetic moment of $1.0\mu_B$ /molecule, which is in good agreement with the experimental value.^{5,12,13} The supercell adopted in the present calculation contains two molecules. The present calculation gives a spontaneous magnetic moment of $2.0\mu_B$ per supercell. This indicates that there is a FM intermolecular interaction in the system. Let us consider the magnetic coupling between two neighboring radicals, coupled by the intermolecular CT interaction. In this CT compound, the donor and acceptor are the same compound. From Fig. 4, we can find that the spin-down valence orbitals of the two molecules of the supercell are not occupied. The FM intermolecular interaction in this system could be explained by the model of Torrance *et al.*¹⁹ In this case, the intermolecular CT takes place from N(3) to O(1') and O(2'') of the neighboring radicals. The CT resonance occurs without losing the intramolecular exchange energies. This resonance results in the FM intermolecular interaction.

The self-consistent field (SCF) iterations converge to a FM state; the total energy in the FM state $E = -51\,152.313$ eV. An artificial nonmagnetic (NM) state was used to obtain the total energy for the NM state $E = -51\,152.270$ eV. Thus

the total energy difference between the FM state and the NM state is 0.043 eV. There are 214 valence electrons in the supercell, so the energy difference between the FM state and the NM state per electron is estimated to be 0.2 meV. Thus the FM state is stabler than the NM state. It is reasonably consistent with ac magnetic susceptibility measurements which show that the ferromagnetic couple only exists only at low temperature.^{5,12,13}

In conclusion, we have studied the electronic band structure and the ferromagnetic properties of the δ phase of *p*-NPNN by employing DFT with the GGA. It is shown that the δ phase of *p*-NPNN has a ferromagnetic phase at low temperatures. An analysis of the DOS of the δ phase of *p*-NPNN reveals that the spin magnetic moment is $1.0\mu_B$ per molecule and the magnetic moment is mainly from the $\pi^*(\text{NO})$ orbitals, which is in good agreement with the experimental result. There exists a FM intermolecular interaction. The important point is that the δ phase of *p*-NPNN may be a half-metallic magnet.

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