

Electronic structure of the organic half-metallic magnet: 2-(5-pyrimidinyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-3-oxoimidazol-1-oxyl

Ming-Hu Wu*

Department of Chemistry and Life sciences, Xianning College, Xianning, Hubei 437005, China
E-mail: minghuwu@hotmail.com

Wei-Dong Zou

Department of Physics, Xianning College, Xianning, Hubei 437005, China

An accurate full-potential density-functional method is used to study the magnetic and half-metallic properties in the pure organic materials: 2-(5-pyrimidinyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-3-oxoimidazol-1-oxyl. The total and partial density of states and atomic spin magnetic moments are calculated and discussed. It is found that the unpaired electrons in this compound are localized in a molecular orbital constituted primarily of $\pi^*(\text{NO})$ orbital, and the main contribution of the spin magnetic moment comes from the NO free radicals. It is predicted that this compound is half-metallic magnet. It is also found that there exists ferromagnetic intermolecular interaction in the compound.

KEY WORDS: *Ab initio* method, the organic magnet, electronic structure, half-metallic property

1. Introduction

The synthesis of ferromagnets using only organic is a challenge for synthetic chemists. In general, covalent bonding between atoms in organic compounds pairs off all available electrons resulting in a net spin $S = 0$, thus diamagnetic materials. However, there is a number of examples of pure organic compounds made from molecules containing free radicals with one unpaired electron and thus $S = 1/2$. The first pure organic compound which exhibits ferromagnetic behavior (β phase of (*p*-nitrophenyl) nitronyl nitroxide) has been reported by Tamura et al. [1]. With this context, Takahashi, Chiarelli, and Rey et al. have also succeeded in synthesizing this kind of pure organic ferromagnets [2–8]. At the same time, the mechanism of ferromagnetic interactions attracts interest of research and a good number of radical compounds are still studied

*Corresponding author.

now. Recently, an interesting property of organic magnetic materials: half-metallic property was found by our group [9]. In this paper, we investigate the half-metallic property of another organic magnetic material.

In 1993, Rey reported the structural characterization and magnetic properties of 2-(5-pyrimidinyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-3-oxoimidazol-1-oxyl [5]. In this compound, the asymmetric unit comprises one molecule of the nitroxide free radicals. This molecular is represented in figure 1. The unit cell of the compound comprises eight molecules of the nitroxide free radicals, which are arranged in pairs. The intermolecular arrangement is shown in figure 2. As shown in figure 2, one NO group of each molecule is directed inside the stack and the other directed outside the stack. Since, in a molecule, the five- and the six-membered ring are not coplanar (28.5°), within a stack, the conjugated fragments of two adjacent molecules (O1-N1-C1-N2-O2 and O1'-N1'-C1'-N2'-O2') make an angle of 48.5° . Just because of this type of geometrical structure, the magnetic behavior of the compound is determined. The temperature dependence of the magnetic susceptibility and the product of the magnetic susceptibility with the temperature for the compound have been studied by Lanfranc et al. [5]. They found that in this nitronyl nitroxide compound the intermolecular coupling of free radicals are ferromagnetic at intermediate temperature (about 14 K). In order to study the mechanism of ferromagnetic interactions in the compound, they proposed that the ferromagnetic interactions between the two NO radicals is transferred by the spin-polarized clouds of carbon atoms. To understand deeply the mechanism of the ferromagnetic interactions in this compound, a more detailed knowledge of the electronic band structure and the magnetic properties is still required.

In this paper, we adopt the density-functional theory (DFT) with generalized gradient approximation (GGA) [10] in order to calculate the electronic band structure and the ferromagnetic properties of this compound by the full potential linearized augmented plane wave (FPLAPW). We obtain the electronic structure, the partial density of states, and atomic spin magnetic moments of this compound. From the partial density of states and atomic spin magnetic moments, the mechanism of the ferromagnetic interactions and the half-metallic property in this compound is discussed.

2. Results and discussion

The first-principles electronic structure calculations employ the well-known FPLAPW method. In this method, no shape approximation either on the potential or on the electronic charge density is made. The calculations were performed using the WIEN97 [11] code which allows for inclusion of local orbitals in basis. Thus, it improves upon linearization and makes possible a consistent treatment of semicore and valence in one energy window. The exchange and correlation

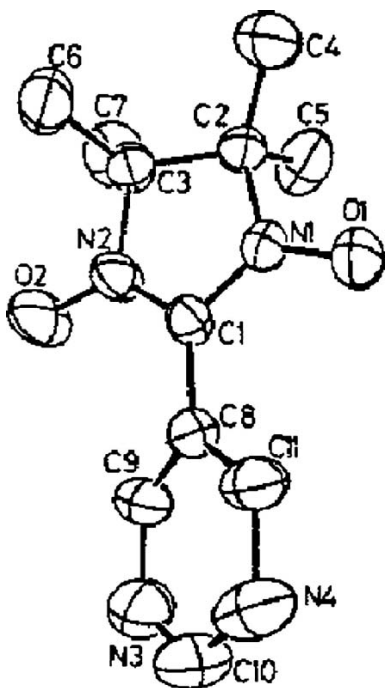


Figure 1. View of the molecular structure showing the atom numbering scheme.

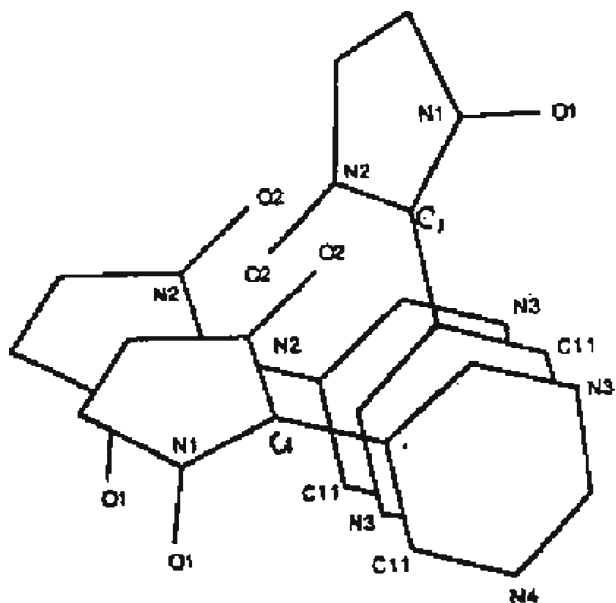


Figure 2. View of stack of molecules.

Table 1

Atomic spin magnetic moments of the titled compound. The spin magnetic moments on atoms defined as the difference of the average occupied ions between in spin up and spin down in the muffin tin sphere.

Atoms	Magnetic moment (μ_B)	Atoms	Magnetic moment (μ_B)
O1N1	-0.16994	C6	0.03088
O2N2	-0.10419	C7	0.03116
C1	0.02288	C8	0.02133
C2	0.02888	C9	0.02573
C3	0.02772	C10	0.02508
C4	0.03213	C11	0.02604
C5	0.03126		

effects are treated with the GGA according to Perdew–Burke–Ernzerhof [10]. In order to achieve a satisfactory degree of convergence, the plane-wave cut-off energy is 154 eV. Thirty k -points in the irreducible Brillouin zone (IBZ) are used in the spin-polarized approximations. According to experiment [5], the compound have tetragonal lattice. The lattice parameters we used in the present calculation are $a = 18.245 \text{ \AA}$, $b = 18.245 \text{ \AA}$, $c = 7.427 \text{ \AA}$.

To study the electronic structure and the magnetic properties of this compound, the total density of states (DOS) of the molecule is shown in figure 3. Because the DOS distribution near the Fermi level determines the magnetic properties, we focused upon the DOS in the vicinity of the Fermi level, which range from -3.0 to 1.0 eV (as seen in figure 3). In the range below -3 eV , it consists of the contribution of internal electrons, which give little contribution to the magnetism. From figure 3, we found that the total DOS below the Fermi level are sharp peaks, this means that all energy bands below the Fermi level are narrow and flat and the electrons are localized. In the vicinity of the Fermi level, the total DOS distribution of the up- and down-spin electrons is obviously splitted. One valence band is splits up into two subbands; one is for the up-spin valence band, and the other one is for the down-spin band. So the ordered spin arrangement of electrons is formed by the exchange-correlation of the electrons, which provide the static magnetic moment of this compound. To find out the contributions of atoms to the magnetism, we give the spin moments on atoms in table 1, which the spin moments defined as the difference of the average occupied ions between spin up and spin down in the muffin tin sphere. As it can be seen in the table, the value of the two free radicals are $-0.16994 \mu_B$ for the O1N1 group and $-0.10419 \mu_B$ for the O2N2 group, respectively, but the value of carbon atoms is below $0.031164 \mu_B$. These results suggest that the NO groups contribute the most and that the carbon atoms the less, respectively, to the magnetic character.

In order to understand better the mechanism of the magnetic interactions in this compound, we give figure 4a and b where the partial DOS of 2-p orbital

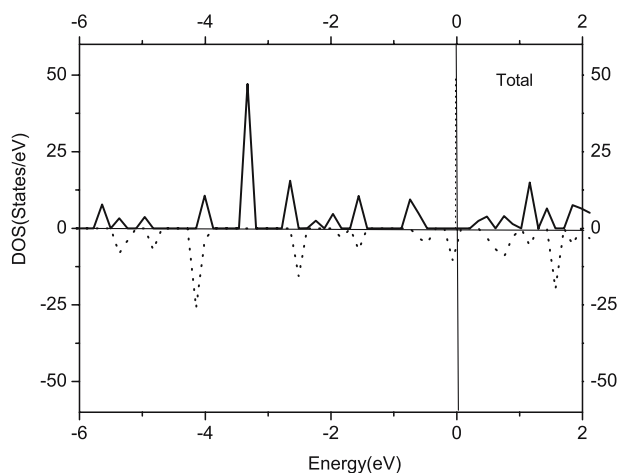


Figure 3. The calculated total density of states (DOS) for molecule. The solid and dot line denote majority and minority spin, respectively. The Fermi levels are located at 0 eV.

of O1, N1, and O2, N2 atoms is shown. It is found that the partial DOS of 2-p orbital of O1 and N1 atoms (O2 and N2 atoms) have similar peaks and character, which means that there is hybridization between the 2-p orbitals of O1 and N1 atoms (O2 and N2 atoms), respectively. The unpaired electron in the compound is localized in the molecular orbital constituted primarily of the $\pi^*(\text{NO})$ orbital, which is formed from 2p (π) atomic orbital of N1 and O1 (O2 and N2 atoms), respectively. In this way, the net spin magnetic moment is formed in between the two free radicals. In the present calculation, we calculate the spin magnetic moments on atoms, and we estimated the value of the spin magnetic moments of the two free radicals as: $-0.16994\mu_B$ for the O1N1 group and $-0.10419\mu_B$ for the O2N2 group. Further consideration, we calculate the spin magnetic moments of C1 atom which give the spin magnetic moment of $0.022884\mu_B$ for the C1 atom. Then opposite sign spin magnetic moment is formed between the two nitroxide free radicals. This result suggests that there exist ferromagnetic intermolecular interaction in the compound.

From the total DOS in figure 3, we found that the energy gap in the spin-up is opened and the value of the energy gap is 0.633 eV, while the spin-down total DOS is continuous in the vicinity of the Fermi level. So the spin-down subbands exhibit metallic properties and the spin-up subbands show insulator properties. The metallic and insulator behavior coexist in the 2-(5-pyrimidinyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-3-oxoimidazol-1-oxyl, so this compound may be a half-metallic magnet. To the best of our knowledge, such an organic half-metallic magnet consisting only of the light elements H, C, N, and O has not been reported yet. If this compound is

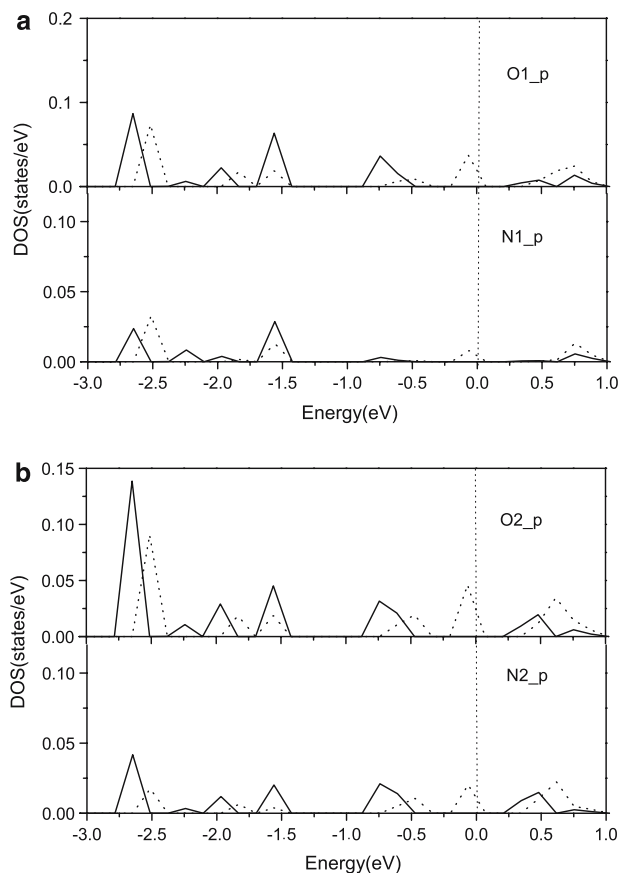


Figure 4. The calculated partial density of states (PDOS) for O1, N1 atoms (a), O2, N2 atoms (b). The solid and dot line denote majority and minority spin, respectively. The Fermi levels are located at 0 eV.

really a half-metallic magnet, it will be of importance in the field of spin electronics.

In conclusion, we have studied the electronic band structure and the ferromagnetic properties of the pure organic solid: 2-(5-pyrimidinyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-3-oximidazol-1-oxyl by employing DFT with GGA. It is shown that the most of the contribution to the magnetization of this compound comes from the NO groups. The spin magnetic moments of C1 atom bridges the two ON free radicals, and in this is how ferromagnetic intermolecular interaction in the compound is formed. It is predicted that this compound exhibits half-metallic character.

Acknowledgments

This work was supported by the group of Young Scientist Innovation Foundation of Hubei Province under the grant No: 2004T006, the Natural Science Foundation of Hubei Province under the grant No: 2004ABA111 and the Grand Project of Department of Education of Hubei Province under the grant No: Z200528001.

References

- [1] M. Tamura, Y. Nakazawa, D. Shiomi, K. Nozawa, Y. Hosokoshi, M. Ishikawa, M. Takahashi and M. Kinoshita, *Chem. Phys. Lett.* 186 (1991) 401.
- [2] M. Takahashi, P. Turek, Y. Nakazawa and M. Tamura, *Phys. Rev. Lett.* 67 (1991) 746.
- [3] R. Chiarelli, M.A. Novak, A. Rassat and J.T. Tholence, *Nature* 363 (1993) 147.
- [4] K. Mukai, K. Nedachi, J.B. Jamali and N. Achiwa, *Chem. Phys. Lett.* 214 (1993) 559.
- [5] F. Lanfranc de Panthou, D.F. Luneau, J. Laugier and P. Rey, *J. Am. Chem. Soc.* 115 (1993) 9095.
- [6] F. Palacio, G. Antorrena, M. Castro, R. Burriel, J. Rawson, J. Nicholas Smith, N. Bricklebank, J. Novoa and C. Ritter, *Phys. Rev. Lett.* 79 (1997) 2336.
- [7] F. M. Romero, R. Ziessel, M. Drillon, J.-L. Tholence, C. Paulsen, N. Kyritsakas and J. Fisher, *Adv. Mater.* 8 (1996) 826.
- [8] D. Luneau, *Curr. Opin. Solid State Mater. Sci.* 5 (2001) 123.
- [9] S.J. Luo and K. L. Yao, *Phys. Rev. B* 67 (2003) 214429.
- [10] J.P. Perdew, S. Burke and M. Ernzerhof, *Phys. Rev. Lett.* 77, (1996) 3865.
- [11] P. Blaha, K. Schwarz and J. Luitz, *WIEN97, A Full Potential Linearized Augmented Plane Wave Package for Calculation Crystal Properties* (Karlheinz Schwarz, Techn. Universit Wien, Austria, 1999), isbn 3-9501031-0-4.