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Ab initio studies of ferromagnetic properties of a nitronyl nitroxide radical and a nucleoside with π -conjugated nitroxide spin label

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Full potential linearized augmented plane-wave calculations have been performed to study the electronic band structure and the ferromagnetic (FM) properties of the organic radical 2-(4,5,6,7-tetrafluorobenzimidazol-2-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl and a nucleoside with π -conjugated nitroxide spin label. The calculation reveals that the origin of the ferromagnetic properties of these two compounds all come from the spin polarization effect. It is found that the unpaired electrons in these two compounds are localized in a molecular orbital constituting primarily of π^* (NO) orbital, and the main contribution of the spin magnetic moment comes from the NO free radical. © 2007 American Institute of Physics. [DOI: 10.1063/1.2732830]

Organic radical magnets have been studied by various methods in recent years.^{1–3} Nitroxide radical was one of the most important radicals for the design of organic magnets since the discovery of the purely organic ferromagnet, *p*-nitrophenyl nitronyl nitroxide.⁴ With proper relation in the crystal network, nitronyl nitroxide can propagate magnetic interactions from one molecule to another. The introduction of a hydrogen bonding site as an orientation controlling unit has been used as one useful way to control the molecular arrangement in organic magnetic materials. In this letter, we present the magnetic properties of (1) a nitronyl nitroxide radical 2-(4,5,6,7-tetrafluorobenzimidazol-2-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl (F4BImNN)⁵ and (2) a nucleoside with π -conjugated nitroxide spin label,⁶ which all have hydrogen bonded chains.

The intermolecular close contacts of F4BImNN are shown in Fig. 1. Hydrogen bonded chains along the *c* axis link N1–H in each F4BImNN to O2–N4 of the NN group in a neighboring molecule. Yoshioka *et al.* proposed⁷ that ferromagnetic (FM) exchange in BImNN arises from N–O···C close contacts of 3.16 Å with favorable overlap between sites of opposite sign spin density [Fig. 1(b)], so major NO spin densities have the same sign. The corresponding N3–O1···C8' contacts in F4BImNN are 3.139(4) Å. The chains of N3–O1···C8' contacts in F4BImNN suggest that FM chain exchange interactions can occur.

The structure of spin labeled nucleoside is shown in Fig. 2. Both intrachain (O5'–H···O3') and interchain (N3–H···O5', O3'–H···O14) classical hydrogen bonds are found. The closest intrachain contact between the neighboring molecules, O14–C12 of 3.37 Å, may be viewed approximately as a π - π overlap between the positive spin density of the nitroxide and negative spin density at the *meta* position of the benzene ring. Based upon the McConnell model, such interaction should be ferromagnetic.⁸ Short interchain contacts, such as O2–C11 of 3.16 Å along the *b* axis, are also found. These two contacts may be responsible for the stron-

ger intrachain ferromagnetic coupling and the weaker interchain antiferromagnetic coupling of compound (2).

Here we use the accurate full potential linearized augmented plane-wave (FP-LAPW) method in WIEN2K code⁹ and the generalized gradient approximation¹⁰ to calculate the electronic structure and the ferromagnetic properties of these two compounds. The experimental crystal structures of F4BImNN and nucleoside have been adopted for the calculation,^{5,6} which are all fixed geometric structures. The sphere radii of O, N, C, and H have been chosen as 1.2, 1.2, 1.0, and 0.6 a.u., respectively. The plane-wave cutoff energy is about 260 eV.

The calculated total density of states (DOS) of the molecule and the partial density of states (PDOS) of 2*p* orbital of O, N, and C for compounds (1) and (2) are shown in Figs. 3(a) and 3(b). From Fig. 3, we found that the energy difference between the up-spin valence band and the down-spin band gives the spin splitting of the valence band of about 0.80 eV for compound (1) and 0.70 eV for compound (2). According to the DOS distribution, we note that the up- and down-spin subbands of compound (1) almost come from O1, O2, N3, and N4 atoms, and those of compound (2) mainly come from O14 and N13 atoms, with a little contributions from C and the other O and N atoms, so the magnetic moment is mainly localized on the free radicals. Figures 3(a) and 3(b) also show that there is hybridization between O 2*p* and N 2*p* orbitals. The unpaired electrons in compounds (1) and (2) are localized in the molecular orbital constituted primarily of the π^* (NO) orbital, which is formed from 2*p* (π) atomic orbital of N and O. In this way, the net spin magnetic moment is formed from the free radicals. As for neighboring carbon atoms, there is overlapping of orbitals inducing the net spin magnetic moment. Just because of the localized electrons of free radicals and the net spin magnetic moment of carbon atoms, their ordered spin arrangement in three-dimensional network results in FM state.

In order to further investigate the magnetic interaction and the spin density distribution, we also carry out a full geometry optimization of the two experimentally known crystal structures, which allows the cell parameter and all atoms to relax. The optimized cell parameters of compound (1) are *a*=8.7711(4) Å, *b*=21.2570(2) Å, *c*=8.9510(0) Å,

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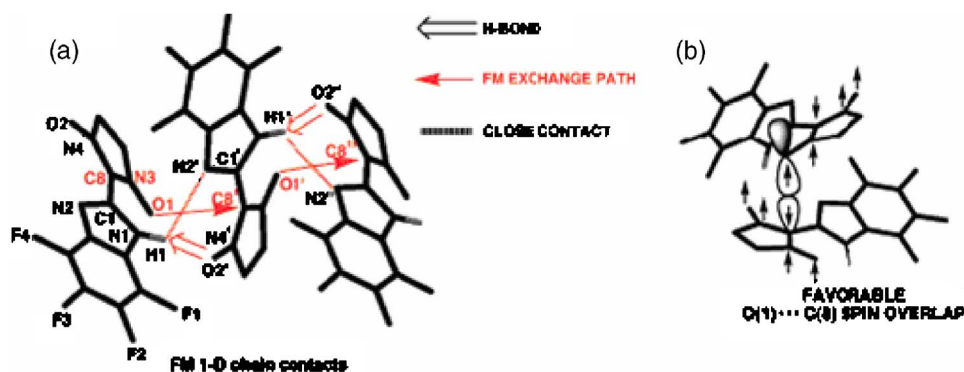


FIG. 1. (Color online) Schematics of F4BImNN crystal packing: (a) intermolecular chain contacts and (b) favorable spin overlap between molecules in the chain.

and $\beta=110.388(1)^\circ$, and those of compound (2) are $a=6.8867(0) \text{ \AA}$, $b=14.7127(2) \text{ \AA}$, $c=9.9418(0) \text{ \AA}$, and $\beta=107.173(8)^\circ$. The optimized distance of $\text{N3}-\text{O1}\cdots\text{C8}'$ contacts in F4BImNN is 3.205 \AA , and those of closest intra-chain contact $\text{O14}-\text{C12}$ and short interchain contacts $\text{O2}-\text{C11}$ of compound (2) are 3.579 and 3.324 \AA , respectively. The optimized cell parameter and the bond length are a little different from those of the experimental values.^{5,6} However, for both compounds, the shape of the DOS and the magnetic moments of the total molecule and each atom are almost unchanged. However, the spin splitting of the valence band becomes small, and the spin splitting energy is about 0.73 eV for compound (1) and 0.60 eV for compound (2).

For further consideration, we give the spin moments on atoms in Table I for compounds (1) and (2). From Table I, one finds that the magnetic moments almost come from N and O atoms, which form the free radicals, with a little contribution from other atoms. The calculated total magnetic moment of each compound is about $1.000 \mu_B/\text{molecule}$, which is in good agreement with the theoretical value of compounds (1) and (2) ($1.0 \mu_B/\text{molecule}$). The spin distribution of compound (1) is almost equally shared by each NO group, but the spin population of O atom is a little larger than that of N atom. This result is consistent with the almost equal distribution found in other *R*-nitrogen radicals on the two nitrogen and oxygen atoms¹¹ but contrasts with what was found by Gillon *et al.*,¹² who found dissymmetry spin distribution between the NO groups of *R*-nitrogen radicals. For free nitronyl nitroxide radical, the unpaired electron is not localized but conjugated among the four atoms of the two NO groups. There is a little negative spin population localized on the central C8 carbon atom, comparing well with what was found in other *R*-nitrogen radicals.¹¹⁻¹³ The presence of carbon sites (C8) carrying spin population of oppo-

site signs may allow for intermolecular coupling involving nonorthogonal orbitals, leading to ferromagnetic interaction. The chains of $\text{N3}-\text{O1}\cdots\text{C8}'$ contacts in compound (1) suggest that FM chain exchange interactions can occur, as is shown in Fig. 1(b). Previous experiment have shown that when one NO group of the nitronyl nitroxide participates in the formation of hydrogen bond, the spin population on its bound or coupling atom would be weakened.¹⁴⁻¹⁶ In compound (1), the hydrogen bond is along $[\text{N4}']\text{O2}'\cdots[\text{H1}]\text{N1}$, but we find that the spin population is equally shared by each NO group; hence very small unpaired electrons of the NO groups are delocalized to atom N1, which is positive and almost equal to zero. Then we believe that

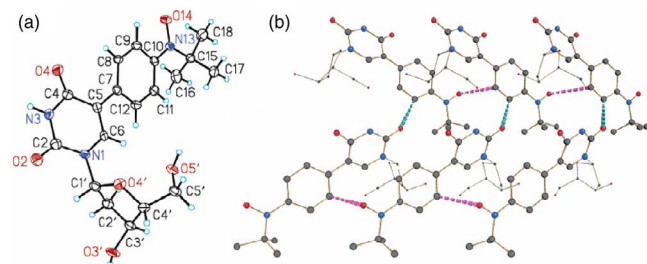


FIG. 2. (Color online) (a) Molecular structure and conformation of compound (2). (b) Three unit cells showing molecular packing of compound (2) into chains along the crystallographic *a* axis. Intercepted lines correspond to the selected short intermolecular distances shown in magenta ($\text{O14}\cdots\text{C12}$) and turquoise ($\text{O2}\cdots\text{C11}$).

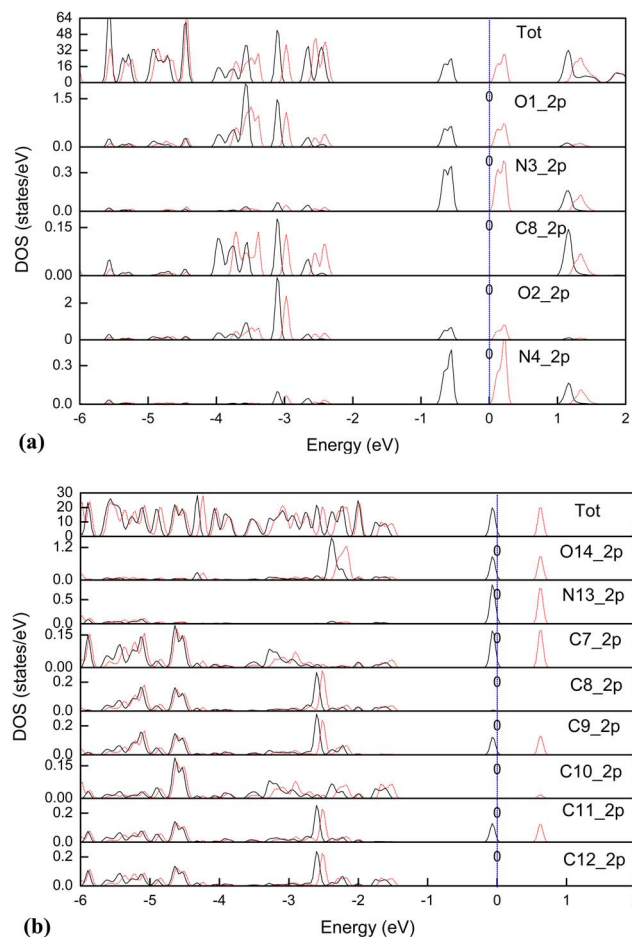


FIG. 3. (Color online) Calculated total density of states (DOS) for molecule and the partial density of states (PDOS) for O, N, and C atoms. (The solid and dotted lines denote majority and minority spins, respectively. The Fermi levels are located at 0 eV .) (a) For compound (1) and (b) for compound (2).

TABLE I. Calculated magnetic moments in μ_B for the atoms of compounds (1) and (2).

Compound (1)				Compound (2)			
Site	Spin	Site	Spin	Site	Spin	Site	Spin
O1	0.1351	C4	0.0030	O14	0.1066	C9	0.0162
N3	0.0770	C5	0.0036	N13	0.1006	C10	-0.0080
O2	0.1334	C6	0.0034	O2	0.0028	C11	0.0163
N4	0.0776	C7	0.0031	O3'	0.0035	C12	-0.0053
C8	-0.0121	F1	0.0003	O4'	0.0002	C15	-0.0020
C1	0.0013	F2	-0.0002	O5'	0.0000	C16	0.0048
C2	-0.0017	F3	0.0002	C7	0.0205	C17	0.0042
C3	-0.0018	F4	-0.0001	C8	-0.0049	C18	0.0001

[N4']O2'...[H1]N1 interactions are not ideal for hydrogen bonding. From Table I we also can find that because of the spin polarization within the π orbital of the carbon atoms of *p*-phenylene of compound (2), the sign of these carbon atoms is alternated as $-/+/-/+$. According to McConnell,⁸ the atoms of positive spin density are coupled most strongly to atoms of negative spin density in neighboring molecules, which gives a ferromagnetic exchange interaction favoring parallel (total) spin momentum on neighboring molecules. The sites with positive sign of spin density and negative sign of spin density of *p*-phenylene are in line with our results discussed above for compound (2). Our results are in agreement with the experimental observation,⁶ and the closest intrachain contact between the neighboring molecules is O14...C12, which is viewed as a π - π overlap between the positive spin density of the nitroxide and negative spin density at the *meta* position of the benzene ring; based on the McConnell model, such interaction should be ferromagnetic. Because of the spin delocalization effect, there is significant delocalization of spin density into the uracyl moiety. Short interchain contacts, such as O2...C11, are along the *b* axis; however, the O2 of the uracyl moiety possesses a rather small spin population, which is just $0.0028 \mu_B$. These two contacts (O14...C12 and O2...C11) are responsible for the stronger intrachain ferromagnetic coupling and the weaker interchain antiferromagnetic coupling of compound (2). In compound (2), the interchain hydrogen bond is along O3'-H...O14; from Table I, we can find that partially unpaired electrons of the NO groups are delocalized to atom O3', which results in small and positive spin populations on atom O3'.

In conclusion, we have studied the origin of the magnetism and the magnetic interactions in compounds (1) and (2) by employing *ab initio* method of the FP-LAPW. The analy-

sis of the DOS, the electronic band, and the spin density reveals that the spin magnetic moment is $1.0 \mu_B$ per molecule for each compound, and the magnetic moment is mainly from the π^* (NO) orbital. The calculation reveals that the origin of the ferromagnetic properties of these two compounds comes from the spin polarization effect.

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