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Photoelectron Spectroscopic Studies of an α-nitronyl Nitroxide Radical: Mechanism of Ferromagnetic Intermolecular Interaction

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PHOTOELECTRON SPECTROSCOPIC STUDIES OF AN α-NITRONYL NITROXIDE RADICAL: MECHANISM OF FERROMAGNETIC INTERMOLECULAR INTERACTION

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Abstract An ultraviolet photoelectron spectrum of phenyl α-nitronyl nitroxide (PNN) has been studied in the gas phase, in order to understand the potentiality of the α-nitronyl nitroxide radical family yielding ferromagnetic intermolecular coupling. The observed spectrum has been well interpreted with the help of CNDO-CI calculation. Very strong spin polarization effect has been suggested, which is advantageous for the intermolecular ferromagnetic coupling.

INTRODUCTION

The quest for a non-polymeric organic ferromagnet has been intensified.[1] For this reason, the free radical family, α-nitronyl nitroxide, has attracted much interest: *p*-Nitrophenyl α-nitronyl nitroxide (*p*-NPNN) crystallizes into three different phases all of which exhibit ferromagnetic (FM) intermolecular interactions.[2-4] Very recently, the β- and γ-phases were found to have magnetic ordered states at very low temperatures.[5] Furthermore, *m*-*N*-methylpyridinium α-nitronyl nitroxide crystallizes into a trigonal space group with a two-dimensional triangular lattice, which includes both ferromagnetic and antiferromagnetic intermolecular interactions.[6]

The usefulness of photoelectron spectroscopy for studying molecular electronic structure has been well recognized. To understand the potentiality of the α-nitronyl nitroxide radical family yielding ferromagnetic intermolecular coupling, an ultraviolet photoelectron spectrum of phenyl α-nitronyl nitroxide (PNN; see Figure 1) has been studied in the gas phase.

EXPERIMENTAL

The PNN radical was prepared according to the method described in ref. 7.

Details of the photoelectron spectrometer were previously described elsewhere.[8] The excitation source was a He I (21.22 eV) discharge lamp. Electron energy was analyzed using a hemispherical deflector analyzer of 3 cm mean radius. the resolution of which is estimated to be about 40 m eV from FWHM of the peaks measured from argon. Sample material was charged and heated in a sample holder, from which the sample vapor was introduced to an ionization chamber. The heating temperature was controlled and maintained as low as possible to avoid possible thermal decomposition so that the signal intensity obtained was fairly high.

RESULTS AND DISCUSSION

Photoelectron spectrum

The photoelectron spectrum of PNN is shown in Figure 1. Vertical ionization potentials are listed in Table I. The first vertical ionization potential of PNN has been found to be 6.8 eV with an estimated uncertainty of ±0.05 eV. The second band is located at 7.8 eV with almost the same intensity as that of the first band. A doublet band is observed at 8.9 eV. In addition, there seems to be a small peak at 9.7 eV, on the tail of the doublet band. From 11 eV, broad and strong bands appear continuously.

TABLE I Vertical ionization potentials of PNN and TEMPO (in eV).

	1st	2nd	3rd	4th	5th	
PNN	6.8	7.8	8.8	8.9	9.6 ?	this work
TEMPO	7.31	8.94	9.27			ref. 9

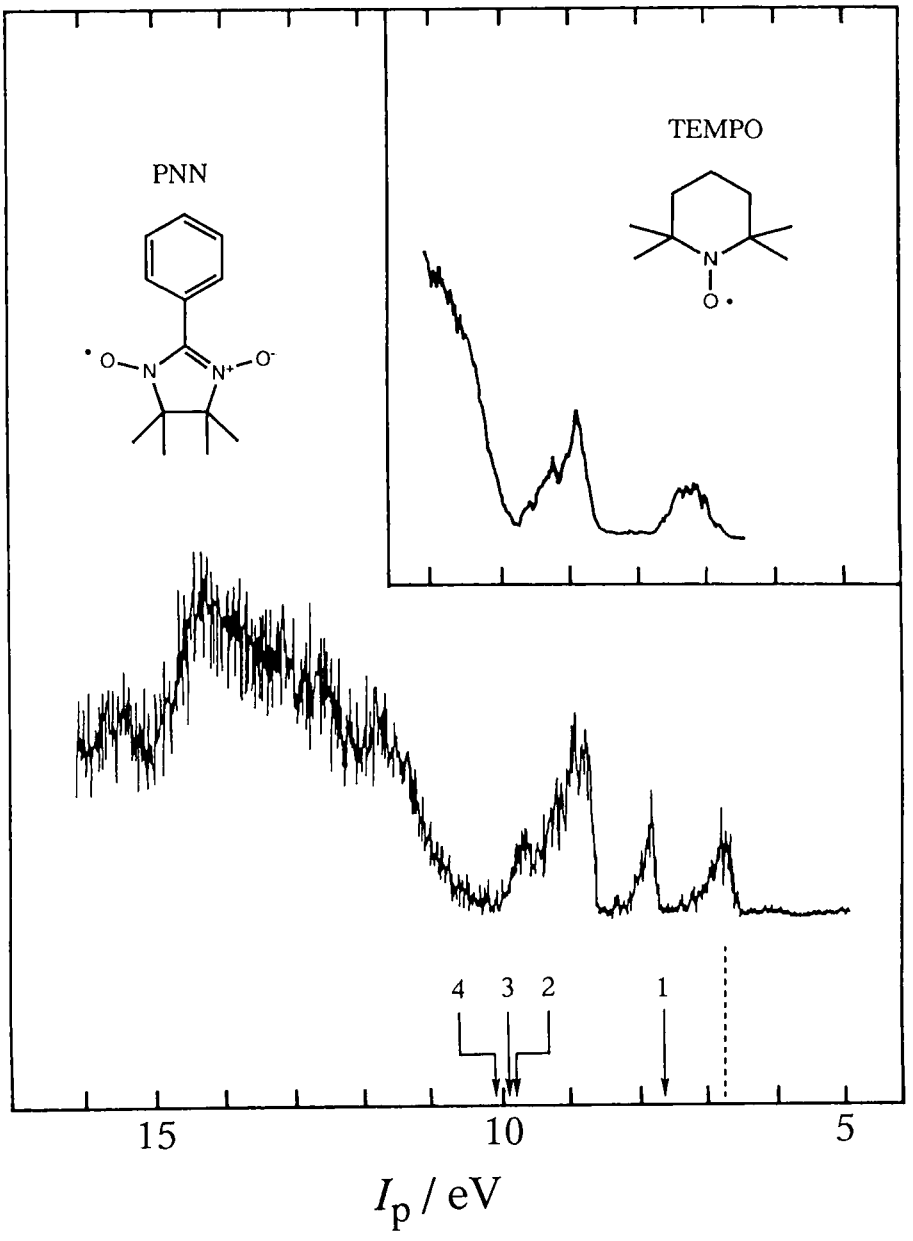

FIGURE 1 Photoelectron spectrum of the PNN radical. The inset shows a part of the photoelectron spectrum of TEMPO in ref. 9, just in comparison with that of PNN. The arrows indicate the positions of the calculated excitation energies of the PNN cation (See the text and Table II.).

Just in comparison with that of PNN, the inset of Figure 1 shows a part of the photoelectron spectrum of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) reported in ref. 9: The first band of TEMPO has been assigned to ionization of the unpaired electron occupied in the NO π^* orbital. The second and the third bands have been assigned to removal of the non-bonding electrons. The doublet splitting between them has been interpreted as the energy difference between the triplet and singlet states of the TEMPO cation left by ionization of one of the oxygen lone pair electrons.

MO calculation

In order to interpret the spectrum of PNN, we have performed CNDO calculations on the PNN radical and the PNN cation, using the geometry of the PNN free radical in the solid state,[10] commonly. The SOMO[11] of the PNN radical is formed by the anti-bonding combination between the π^* orbitals of the NO groups, making a node at the α-carbon atom. There is little penetration of the SOMO into the phenyl ring. On the other hand, the other frontier orbital, NHOMO, is composed of the two NO π^* orbitals, the α-carbon p_z orbital, and the phenyl π orbital. The NHOMO has population in both of the nitronyl nitroxide group, O-N-C-N-O, and the phenyl group. The ground state of the cation is indicated to be the singlet state where the unpaired electron of the radical is removed from the SOMO. The first ionization potential of PNN can be assigned to the energy needed for removal of the unpaired π electron.

TABLE II Calculated excitation energies of the PNN cation.

	Excitation energy /eV	Main contribution
1	0.83	^{3}(NHOMO→SOMO)
2	2.99	^{3}(n→SOMO)
3	3.02	^{1}(n→SOMO)
4	3.27	^{1}(NHOMO→SOMO)

The excitation energies of the PNN cation which correspond to the energy differences between the first ionization potential and the other ones, have been calculated by the CNDO-CI method. Table II shows the lowest four excitation energies of the PNN cation. The results are also shown by the arrows in Figure 1, where the energy of the

ground state is assumed to be equal to the first ionization potential of 6.8 eV. Each of the calculated excitations is written as a combination of various one-electron excitations, and the largest contribution among them is listed in Table II. The lowest excitation energy is 0.83 eV, which is mainly for the NHOMO-SOMO triplet excitation. This excitation energy can explain the second band of PNN. Namely, the second ionization potential could correspond to the energy needed for removal of the up-spin electron in NHOMO. The largest contributions to the second and the third excitation energies are the triplet and singlet excitations of the non-bonding electrons to the SOMO, respectively. These two are attributable to the doublet band at 8.9 eV. It is quite reasonable that the doublet bands of PNN and TEMPO look like each other, because they result from ionization of the oxygen lone pair electrons of the NO group. The fourth excitation is largely due to the NHOMO-SOMO singlet excitation, whose energy seems to explain the weak band at 9.7 eV.

The calculated excitation energies are found to correspond well to the observed ionization potentials of PNN. The first vertical ionization potential of 6.8 (±0.05) eV is attributed to that needed for removing the unpaired π-electron from SOMO, which leaves a singlet cation state. The bands at 7.8 and 9.7 eV are assigned to the triplet and singlet states of the nitroxide cation, respectively, which are formed by photoionization of the NHOMO π-electrons. The large energy separation between them would reflect the strong spin polarization effects of PNN. The doublet band at 8.9 eV can correspond to removal of the non-bonding electrons.

Mechanism of the ferromagnetic intermolecular interaction

It is considered that there is little difference in electronic structure between PNN and the organic ferromagnet, *p*-NPNN,[12] although PNN exhibits a weak antiferromagnetic intermolecular interaction in the solid state.[2] It would be meaningful to discuss the ferromagnetic properties of the α-nitronyl nitroxide radicals, upon examining the above results of PNN.

A charge transfer (CT) process within a dimer gives three CT configurations,[13] as is shown in Figure 2, where we take account only of SOMO and NHOMO in the radical. Among the three levels, $\mathbf{T_1}$ is triplet and the other two, $\mathbf{S_0}$ and $\mathbf{S_1}$, are singlets. It is worth noting here that a difference exists only in the cation molecule. In the case of the PNN radical dimer, the lowest state among the three would be $\mathbf{S_0}$, because the ground state of the PNN cation is concluded to be the singlet state resulting from removal of the unpaired electron. $\mathbf{S_0}$ stabilizes the antiferromagnetic coupling, as is shown in Figure 2. Accordingly, if PNN had ferromagnetic coupling, the intermolecular overlap between SOMO's should be very small. If this is zero, $\mathbf{S_0}$ makes no contribution to the ground

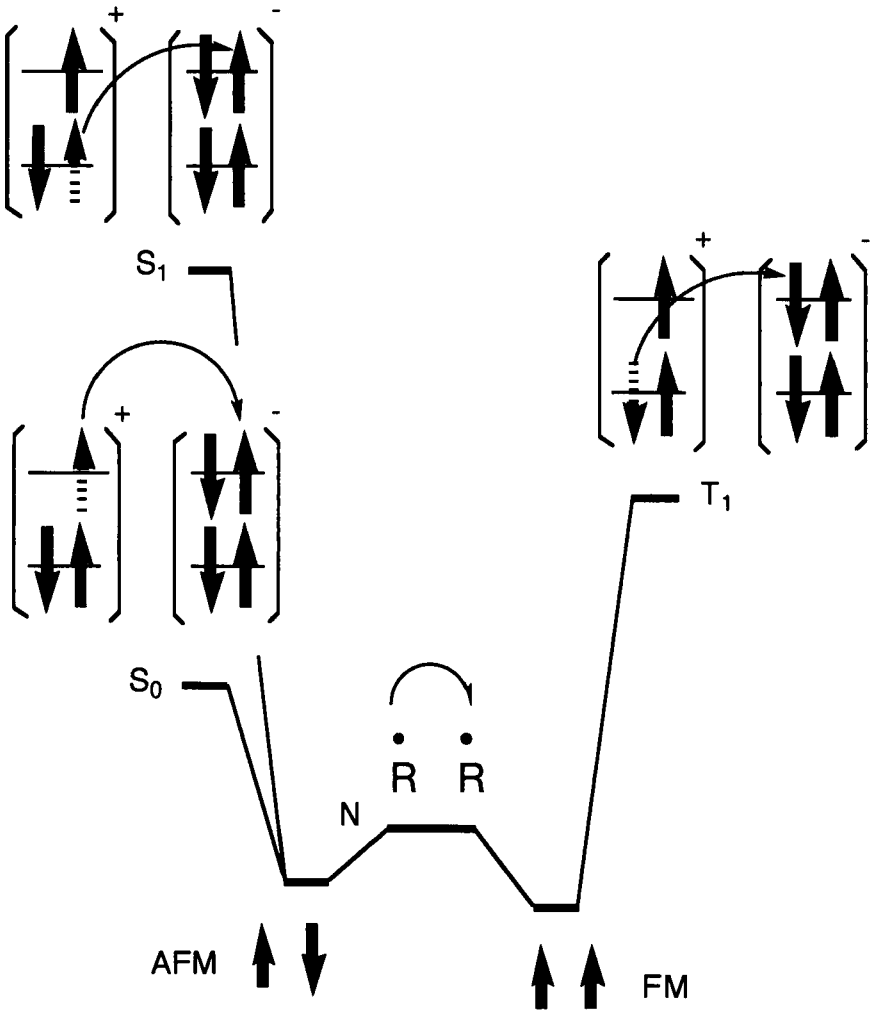

FIGURE 2. Three CT configurations in the radical dimer.

state magnetic coupling without depending on its configurational energy. On the other hand, both of $\mathbf{T}_1$ and $\mathbf{S}_1$ are given by the electron transfer from NHOMO to SOMO. $\mathbf{T}_1$ stabilizes the ferromagnetic coupling, while $\mathbf{S}_1$ makes an opposite contribution. The large energy difference in ionization energies for the up- and down-spin electrons in NHOMO suggests that the configurational energy of $\mathbf{T}_1$ is much lower than that of $\mathbf{S}_1$. This is a favorable condition to the ferromagnetic interaction, and could be one of the reasons for the potentiality of the ferromagnetic coupling in the α-nitronyl nitroxide family.

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11. SOMO is the singly-occupied MO. NHOMO and NLUMO are defined as the highest doubly-occupied and the lowest unoccupied MO, respectively.
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13. Strictly speaking, we have to take account of disproponation in order to apply the discussion to our material, α-nitronyl nitroxide.