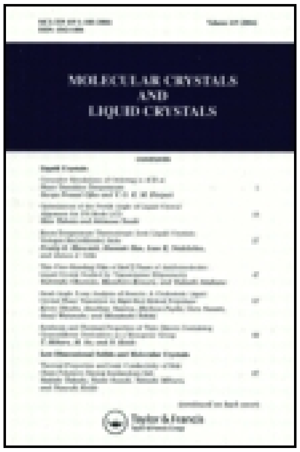

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Ground State Spin Multiplicity of Cation Diradicals Derived from Pyrroles Carrying Nitronyl Nitroxide

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GROUND STATE SPIN MULTIPLICITY OF CATION DIRADICALS DERIVED FROM PYRROLES CARRYING NITRONYL NITROXIDE

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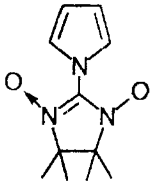
Abstract Pyrroles substituted by nitronyl nitroxide (**1**-**3**) have been prepared and the ground state multiplicity of their cation diradicals have been examined. The triplet was found to be the ground state for $\mathbf{2}^{+\cdot}$, $\mathbf{3}^{+\cdot}$, although the triplet signal was not observed for $\mathbf{1}^{+\cdot}$. The ground state spin multiplicity of these cation diradicals was rationalized in terms of the exchange interaction between unpaired electrons which reside SOMO and SOMO' of these species, respectively. A novel approach to polaronic high spin polymers obtained from 1,3-phenylene-bis(2'-*1H*-pyrrole) is also mentioned.

INTRODUCTION

Conducting property of doped polypyrroles is well documented in terms of a polaronic and/or a bipolaronic mechanism[1-4). If polypyrroles carrying a stable radical as a pendant group are prepared, both conductive and magnetic properties may be manifested by doping the polymer. Although polymers (or oligomers) bearing stable radicals as a pendant group[5,6) have been studied, dopable ones have not been reported. As a building block of such functionlized polypyrroles, we report here preparation of pyrrole derivatives substituted with a stable radical group of various substituted patterns and examine the magnetic interaction between unpaired electrons of the singly oxidized species.



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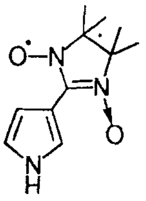

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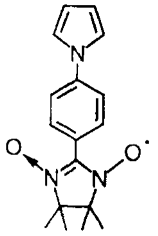

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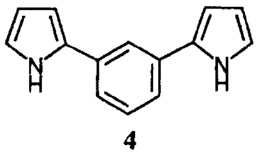
Recently we reported[7) ground state triplet cation diradicals derived from one-electron oxidation of open-shell donors. In order to realize organic ferromagnetic metals using such open-shell donors, it is crucial to construct a segregated columnar stacking of the donor units with a mixed valency. In the present approach, however, a conduction path should be easily constructed, by doping poly-pyrroles which are supposed to be formed through oxidation of functionalized pyrroles.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In the latter part of this paper, we describe a novel approach to construct polaronic high spin polymers. Since a polaronic mechanism, which has been proposed by Fukutome[8,9)], is considered to be effective for constructing high spin polymers, we designed 1,3-phenylene-bis(2'-*1H*-pyrrole) (**4**), where a *meta*-phenylene group is incorporated as a *π-topology controlling unit.* Oxidative polymerization of **4** is supposed to afford a doped poly-*meta*-phenylene-bipyrrole which consists of the polaronic spin containing bipyrrole units and the *meta*-phenylene units.

EXPERIMENTAL

Pyrrole derivatives (**1**-**3**) were prepared by the following reaction schemes (Figure 1). Pyrrole was treated with sodium hydride in dimethylformamide, and the resulted anion was reacted with 2-bromonitronyl nitroxide to give **1**. 3-Formylpyrrole (**5**) was obtained according to the literature[10)] method as shown below, and it was converted to a cyclic hydroxyl amine, which was oxidized by lead dioxide to give **2**. Reduction of 4-(Pyrrol-1-yl)benzoic acid by lithium aluminium hydride was followed by oxidation with pyridinium

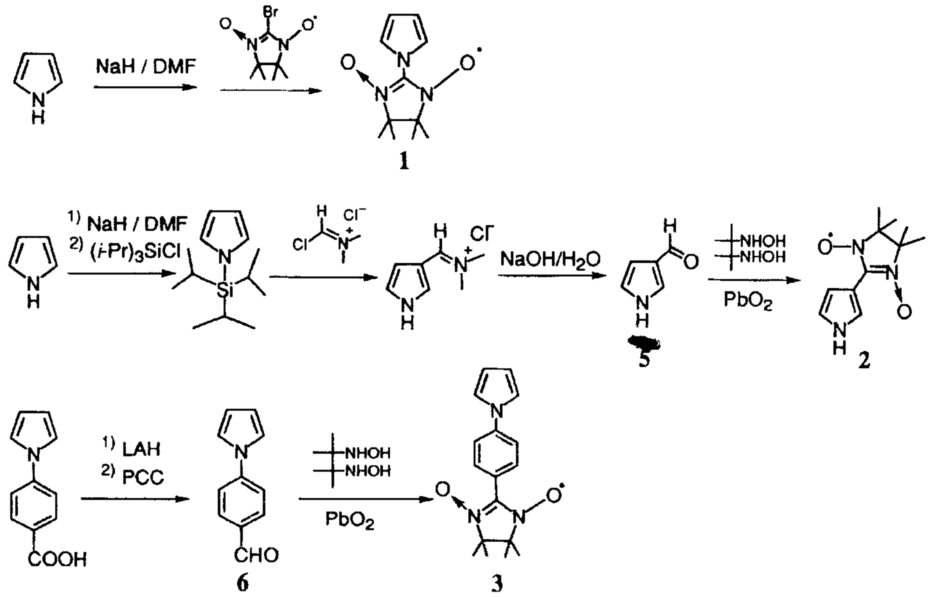


FIGURE 1 Synthetic schemes of pyrrolylNN derivatives

chlorochromate to give 4-formyl derivative (**6**). It was converted to nitonyl nitroxide derivative **3** by the same procedure as in the case of **2**.

Preparative method of **4** is similar to that of 1,4-phenylene-bis(2'-*1H*-pyrrole) which is shown in a literature[11] (Figure 2). 1,3-Dibromobenzene was dilithiated with *tert*-butyllithium, and reacted with 1,3-dioxolane-2-propanal. The resulted product was oxidated with pyridinium chlorochromate to give diacetal derivative (**7**). After acidic hydrolysis of **7**, the desired product **4** was obtained by Paal-Knorr synthesis using ammonium acetate and aqueous ammonia.

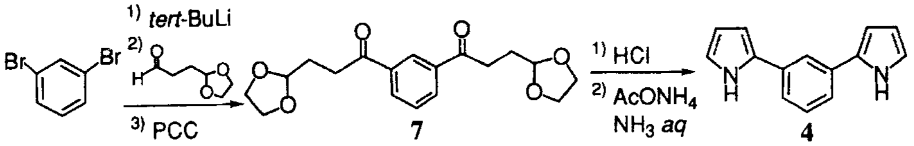


FIGURE 2 Synthetic scheme of 4

Cyclic voltammetry was measured in the presence of 0.1 M *n*-Bu_4NBF_4 in acetonitrile, using Ag/AgCl as a reference electrode, a scanning rate being 200 mV/sec. Pyrrole derivatives were oxidized by iodine in tetrahydrofuran, and ESR spectra of the oxidized species were recorded at cryogenic temperatures in a frozen matrix in the temperature range of 7.5-120 K.

Molecular orbital calculations were performed by the semiempirical PM3 method, using a MOPAC ver. 6.00 program.

RESULTS AND DISCUSSION

1) Development of a building block for high spin doped-polypyrroles

Redox potentials of pyrroles substituted with nitronyl nitroxide recorded by means of cyclic voltammetry are listed in Table I, together with those of pyrrole and *N*-phenylpyrrole. Oxidation potentials of pyrrole derivatives are smaller than those of the parent compounds. The results suggest the presence of electronic interaction between these two moieties (*vide infra*).

TABLE I Redox potentials of **1-3**

Samples	**1**	**2**	**3**	pyrrole	*N*-phenylpyrrole
$E_{1/2}{}^1$	+0.86V	+0.63	+0.81	+1.05	+1.35
$E_p{}^2$	+2.15	+2.05	+1.65		
$E_p{}^3$			+2.20		

Electrolytes : Bu_4NBF_4 ; Solvent : CH_3CN ; *vs.* Ag/AgCl

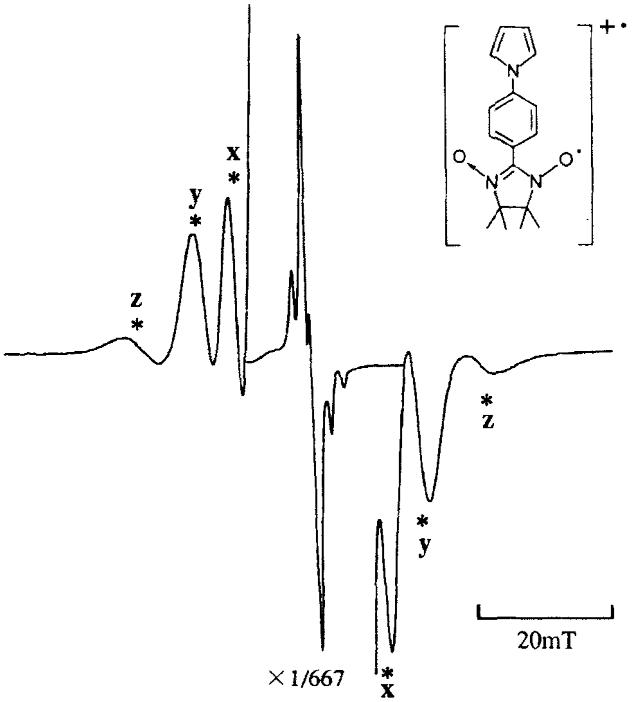


FIGURE 3 ESR spectra of **3**$^{+\cdot}$ in tetrahydrofuran matrix at 7.5 K. A central strong signal is due to the neutral radical **3**. Six transitions of the triplet species were assigned to x, y, and z lines. The g value for each lines are g_x=2.0092, g_y=2.0077 g_z=2.0096. The zero field parameters are calculated to be D=0.0257 cm^{-1}, E=0.0021 cm^{-1}.

ESR spectra of the oxidized species of **1**-**3** were measured in a frozen matrix of tetrahydrofuran at cryogenic temperatures. Whereas no signals assignable to a triplet species were detected in the case of **1**$^{+\cdot}$, distinct triplet signals were observed on **2**$^{+\cdot}$ and **3**$^{+\cdot}$ (Figure 3). The zero-field parameters of **2**$^{+\cdot}$ were evaluated to be D = 0.026 cm^{-1}, E = 0.002 cm^{-1}, and those of **3**$^{+\cdot}$ to be D = 0.0257 cm^{-1}, E = 0.0021 cm^{-1}. Curie plots of these triplet signals in the temperature range of 7.5-120 K revealed the triplet ground state multiplicity of **2**$^{+\cdot}$ and **3**$^{+\cdot}$.

The difference of the results of ESR measurements on **1**$^{+\cdot}$ and **2**$^{+\cdot}$ were explained by the electronic features of a singly-oxidized pyrrole substituted by a nitronyl nitroxide group (NN). When the pyrrole radical cation is substituted by NN at the *N*-position, both *somos* of pyrrole and NN parts have nodes at the connecting sites, leading to a disjoint[12)] type diradical **1**$^{+\cdot}$. On the other hand, if NN is introduced at the 3-position of pyrrole, this connection should afford a non-disjoint[12)] type diradical of **2**$^{+\cdot}$ (Figure 4).

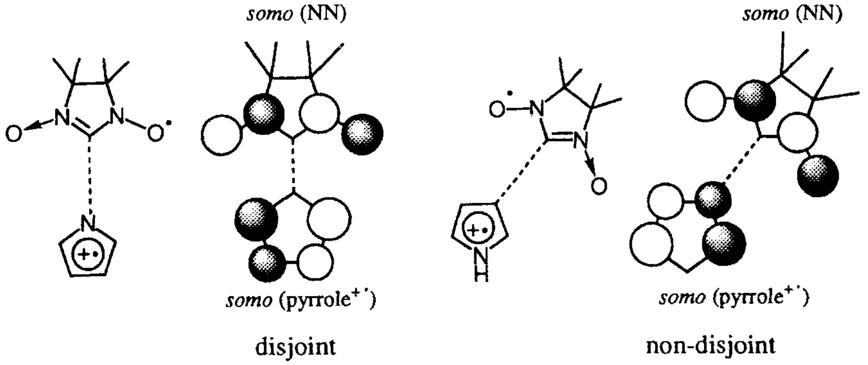


FIGURE 4 Connection patterns of a cation radical of pyrrole and a nitronyl nitroxide; disjoint type connection of the N-substitution (left), and non-disjoint type connection of the 3-substitution (right).

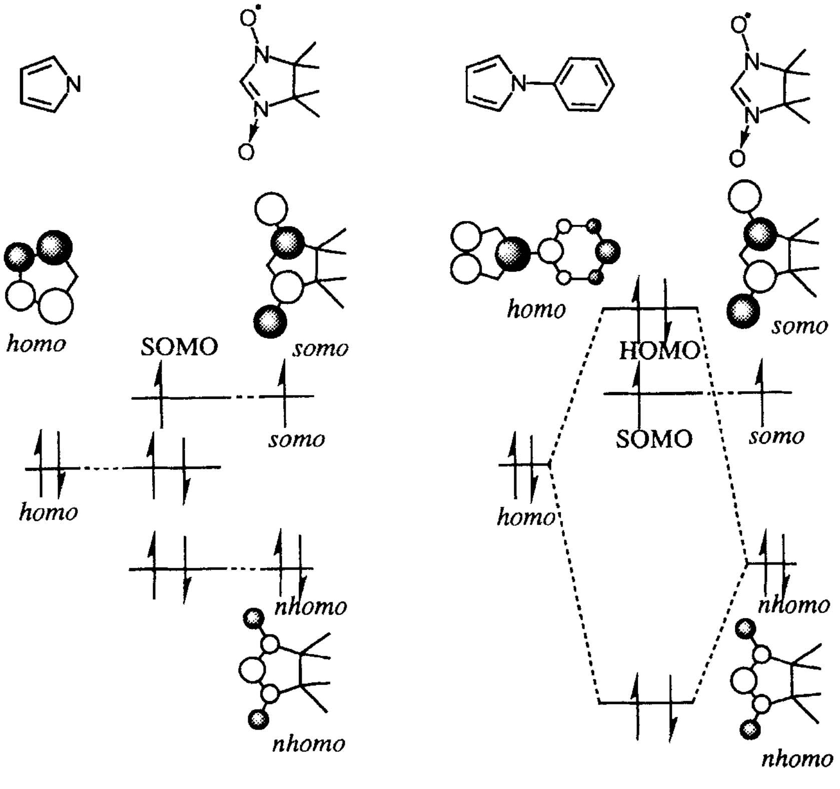


FIGURE 5 Schematic drawing of electronic interaction between partial orbitals of **1** (left) and **2** (right).

Showing a sharp contrast with the case of **1**, the ground state triplet cation diradical was detected for **3**, when a phenyl group was inserted between pyrrole and nitronyl nitroxide. The difference of the electronic structure of **1** and **3** may be rationalized by using a perturbational molecular orbital method (Figure 5). Pyrrolyl nitronyl nitroxide **1** is considered to be composed of a pyrrole unit and a nitronyl nitroxide (NN) unit, whereas **3** is divided into a pyrrolyl phenyl unit and a NN unit. When coefficients of each partial molecular orbital are taken into account, the interaction of *homo* of the pyrrole unit and *somo* of the NN unit of **1** should be small, giving rise to SOMO as the highest molecular orbital. Thus one-electron oxidation of **1** is supposed to afford a closed shell cation. On the other hand, the electronic interaction between *homo* of pyrrolyl phenyl unit and *nhomo* of NN should be considerably large, and pushes *homo* of pyrrolyl phenyl unit to HOMO of the entire molecule, leaving SOMO underneath. Such an electronic structure can be maintained due to the large on-site Coulombic repulsion of SOMO.

The electronic structure of **3** is also explained by the UHF calculation (Figure 6). HOMO is located higher than SOMO as in a perturbational MO treatment. Besides, the spin polarization of HOMO is significantly large, pushing the β spin orbital higher than the α. Thus one-electron oxidation of **3** should remove the β spin of HOMO, affording the ground state triplet cation diradical.

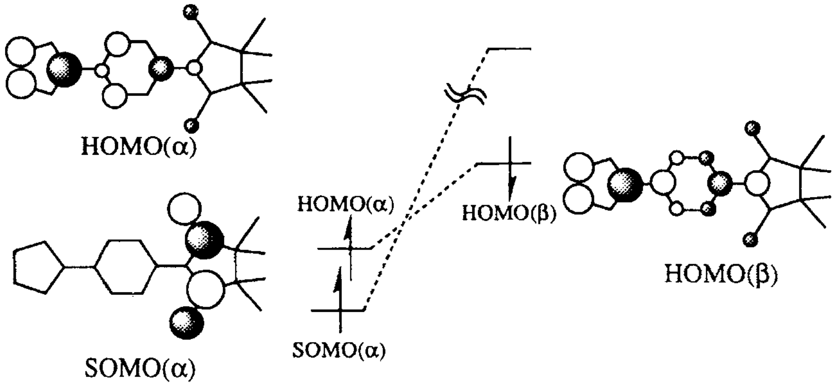


FIGURE 6 Spin-orbitals of **3** calculated by a UHF method

Reactivity of polymerization of pyrrole derivative can also be examined by cyclic voltammetric measurement. Lack of polymerization reactivity of **2** may be derived from the steric hindrance of the NN group at the 2-position. Although polymerization reactivity was not observed either in the case of **3**, electronic modification may enhances the reactivity of polymerization. Investigation along this line is in progress under these laboratories.

2) Novel approach to polaronic high spin polymers

If bipyrroles connected by *meta*-phenylene units are *p*-doped, polaronic high spin state of poly-*meta*-phenylene-bipyrrole should be generated. When the pyrrole derivative **4** in tetrahydrofuran solution was treated with iodine, it was polymerized and further doped to give a mixture of ground state triplet signals in the ESR spectrum. One set of the triplet signals (D = 0.025 cm^{-1}) were in accord with those observed when **4** in polyvinylchloride matrix was treated with iodine. The zero-field parameters of others were somewhat smaller than this.

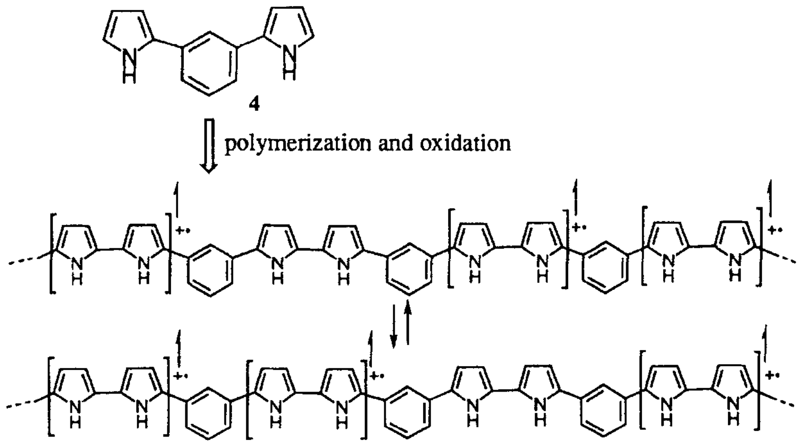
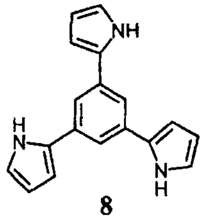


FIGURE 7 Formation of doped poly-*meta*-phenyene-bipyrrole

Magnetic property of the doped poly-*meta*-phenylene-bipyrrole was examined by means of SQUID measurements. A magnetization curve showed the average spin quantum number of about 1, suggesting that the high spin state can be realized in this system. The fact that the spin quantum number decreases with lowering temperatures suggests the presence of the antiferromagnetic interchain interaction. Since improved conditions of the oxidization of the polymer should increase the average spin quantum number, the system may be promising in obtaining high spin polymers. The 1,3,5-tris(pyrrole)benzene (**8**) is also in preparation to realize a two-dimensional high spin system.



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