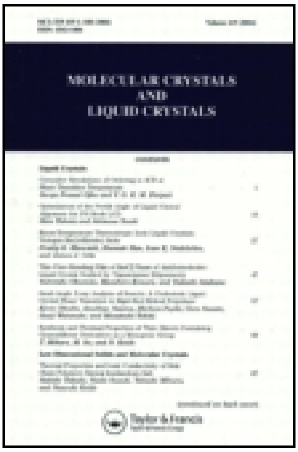

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Ground State Triplet Cation Diradicals having Non-Degenerated Singly Occupied Molecular Orbitals

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GROUND STATE TRIPLET CATION DIRADICALS HAVING NON-DEGENERATED SINGLY OCCUPIED MOLECULAR ORBITALS

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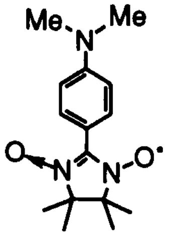
Abstract Open-shell donors (**1**, **2**) carrying a nitronyl nitroxide group (NN) at the para position of *N*, *N'*-dimethyl- or diphenylaniline were prepared and thier one-electron oxidation states were investigated by means of the ESR spectroscopic measurement. The cation diradicals of **1** and **2** turned out to be the ground state triplet species based on the non-disjoint character of thier electronic structures consisted of two non-degenerated SOMOs.

INTRODUCTION

Development of organic ground state triplet species is of great importance not only from the view point of spin chemistry but also from constructing organic magnetic materials.[1] The ground state triplet species reported hitherto can be classified into two categories: The one is one-centered diradicals[2] such as carbenes or nitrenes, and the other is multi-centered diradicals which have degenerated SOMOs[3,4] such as non-Kekulé hydrocarbons (trimethylenemethane[5] or *m*-xylylene[6]) or charged antiaromatics having high symmetry (cyclopenadienyl cation[7] or C_{60} dianion[8]).

Recently we have reported the ground state triplet anion diradical[9] derived from one-electron reduction of an open-shell acceptor, BQNN, in which *p*-benzoquinone (BQ) is substituted by a nitronyl nitroxide (NN) group. The anion diradical $BQNN^{-\bullet}$ can not be classified into the conventional categories afore mentioned, because it has two non-degenerated SOMOs: One of the SOMOs is delocalized over the entire molecule and the other is localized on the NN group.

As a cation diradical counterpart of this novel class of ground state triplet species, we have designed and prepared open-shell donors (**1**, **2**) carrying a nitronyl nitroxide group at *para* position of *N*, *N'*-dimethyl- or diphenylaniline, and examined the ground state spin multiplicity of the cation diradical $\mathbf{1}^{+\bullet}$ and $\mathbf{2}^{+\bullet}$ in terms of ESR spectroscopy.



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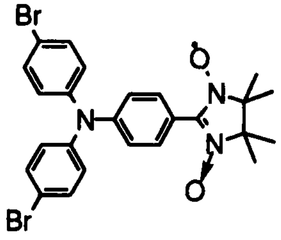

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EXPERIMENTAL

The open-shell donors **1**, **2** were prepared from the corresponding formyl derivatives. ESR spectra of **1** and **2** in benzene showed quintet signals with a_N = 0.77 mT (2N) at g = 2.0061 for **1**, and a_N = 0.75 mT (2N) at g = 2.0070 for **2**, respectively. The IR and mass spectral data were consistent with the structure of **1** and **2**. The donors **1** or **2** was oxidized by excess I_2 in tetrahydrofuran or 2-methyltetrahydrofuran. ESR spectra of the oxidized species were measured at cryogenic temperatures (6 ~ 110 K). Half-wave oxidation potentials $E_{1/2}$ *vs.* Ag/AgCl, were obtained by using cyclic voltammetry (**1** in acetonitrile, **2** in dichloromethane, in the presence of tetra-*n*-buthylammonium perchlorate as supporting electrolyte with a scanning rate of 200 mVs^{-1}). UHF calculations were carried out on the neutral radicals and the cation diradical using the PM3 Hamiltonian; MOPAC Ver. 6.00 (QCPE No. 445).[10]

RESULTS AND DISCUSSION

ESR Spectra of Cation Diradicals of Open-Shell Donors

ESR spectra of the oxidized species $\mathbf{1}^{+\bullet}$, $\mathbf{2}^{+\bullet}$ in rigid matrix showed fine structures due to triplet species at 6 K. The spectrum of $\mathbf{2}^{+\bullet}$ is shown in Figure 1. The anisotropic g-values of the triplet species were estimated to be g_x = 2.0098, g_y = 2.0083 and g_z = 2.0099 for $\mathbf{1}^{+\bullet}$ and g_x = 2.0109, g_y = 2.0097 and g_z = 2.0118 for $\mathbf{2}^{+\bullet}$, respectively. Zero-field splitting parameters of the triplet species were estimated to be D = 0.0266 cm^{-1}, E = 0.0021 cm^{-1} for $\mathbf{1}^{+\bullet}$ and D = 0.0261 cm^{-1}, E = 0.0019 cm^{-1} for $\mathbf{2}^{+\bullet}$, respectively. These relatively large D values indicate that the obtained triplet signals are not derived from the intermolecular interaction between two doublet species but due to the cation diradicals $\mathbf{1}^{+\bullet}$ and $\mathbf{2}^{+\bullet}$. The ground state spin multiplicity of $\mathbf{1}^{+\bullet}$ and $\mathbf{2}^{+\bullet}$ were examined cautiously by the temperature dependence of the triplet ESR signals in the temperature range of 6 ~ 110 K (Figure 2). The obtained Curie plots indicate that both $\mathbf{1}^{+\bullet}$ and $\mathbf{2}^{+\bullet}$ exist as the ground state triplet.

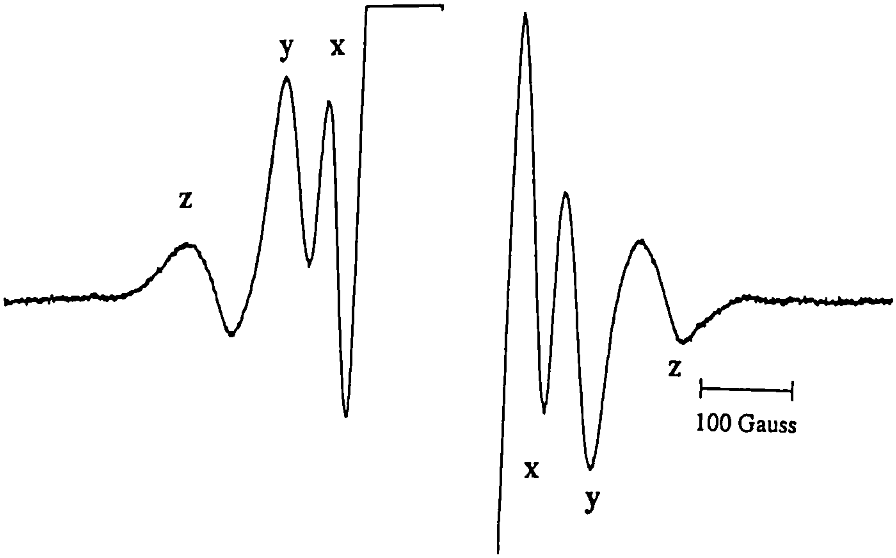

FIGURE 1 ESR spectra of $2^{+\bullet}$ in 2-methyltetrahydrofuran matrix at 6 K. Six transitions of the triplet species are assigned to be x, y, and z lines. Central strong signal is due to the neutral radical **2** . The broadening of the z lines are presumably caused by the hyperfine splitting of nitrogen atoms.

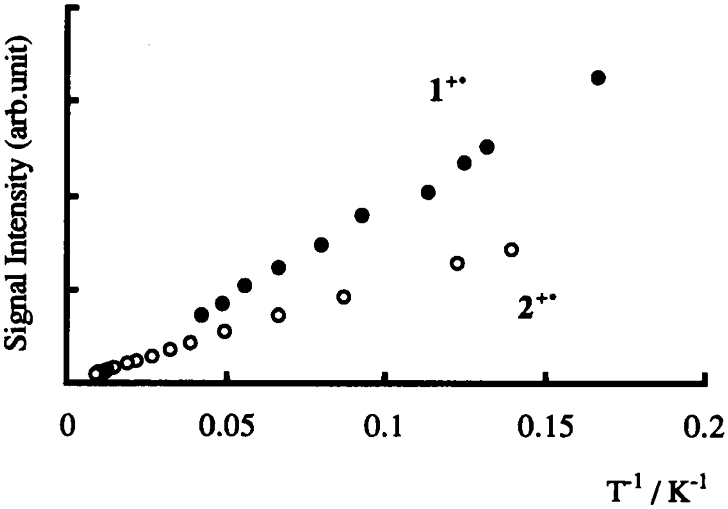

FIGURE 2 Plots of triplet signal intensties of $1^{+\bullet}$(●) and $2^{+\bullet}$(○) *vs.* inverse of temparatures.

Electronic Structure of Cation Diradicals of Open-Shell Donors

In order to rationalize the ground state spin multiplicity of $\mathbf{1}^{+\bullet}$ and $\mathbf{2}^{+\bullet}$, the MO calculations (PM3/UHF) were performed on these species. The coefficients of SOMO and SOMO' for $\mathbf{1}^{+\bullet}$ are shown in Figure 3. The cation diradical has two singly occupied molecular orbitals, SOMO and SOMO', the latter being derived from HOMO through one-electron oxidation. While the coefficients of SOMO of $\mathbf{1}^{+\bullet}$ and $\mathbf{2}^{+\bullet}$ are localized on the NN group, those of SOMO' distribute over the entire molecule framework, having significant coefficients on the NN group. Thus these diradicals can be regarded as a non-disjoint type according to Borden's classification.[4] Thus large exchange interaction for $\mathbf{1}^{+\bullet}$ and $\mathbf{2}^{+\bullet}$ will be expected between two electron spins residing in SOMO and SOMO', respectively.

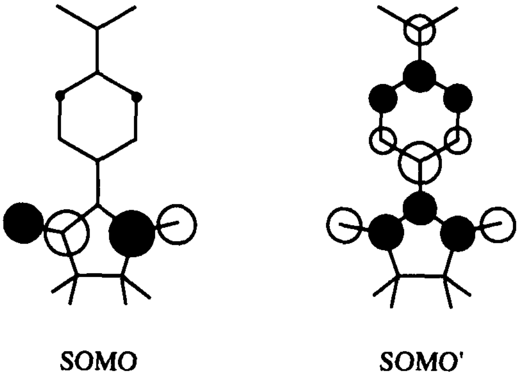

FIGURE 3 Coefficients of SOMO and SOMO' of one-electron oxidized open-shell donors $\mathbf{1}^{+\bullet}$.

Based on the above experimental results, the requirement of the singly oxidized open-shell donor to have a triplet ground state multiplicity can be summarized as follows. First, the donor moiety should be substituted by the radical moiety through a cross conjugated π-system, as the cation diradical can maintain the open-shell structure. Second, HOMO of the open-shell donor should be located above SOMO. Third, the exchange interaction should be larger than the energy difference between SOMO and SOMO' of the cation diradical. The third condition will be satisfied when the cation diradical has the non-disjoint character.

When the open-shell donor is assumed to be composed of the donor moiety (*N*, *N'*-dimethyaniline (DMA) in the case of **1**) and the radical moiety (NN in the cases of **1**) in terms of a perturbation MO method (Figure 4), the intramolecular electronic interaction can be interpreted as follows. If the interaction exists between *homo* of the donor moiety and *nhomo* of the radical moiety, the orbital energy of HOMO of the open-shell donor should be raised to exhibit a lower oxidation potential compared with the reference donor. Such an electronic feature, therefore, can be confirmed experimentally by measuring the cyclic voltammogram of the open-shell donor. The oxidation potentials of **1** and **2** were recorded at $E^{1}_{1/2} = +0.64$ and $E^{2}_{1/2} = +1.31$ V for **1** and at $E^{1}_{1/2} = +0.82$ and $E^{2}_{1/2} = +1.38$ V for **2** (*vs.* Ag/AgCl), respectively. It is to be noted that the first oxidation potentials of **1** and **2** are shifted to the lower side by 0.18 V and 0.41 V, respectively, compared with that of *N*,*N'*-dimethylaniline or tris(4-bromophenyl)amine, while the second oxidation potentials are not relatively affected by the substituents on the nitrogen atoms of aniline.

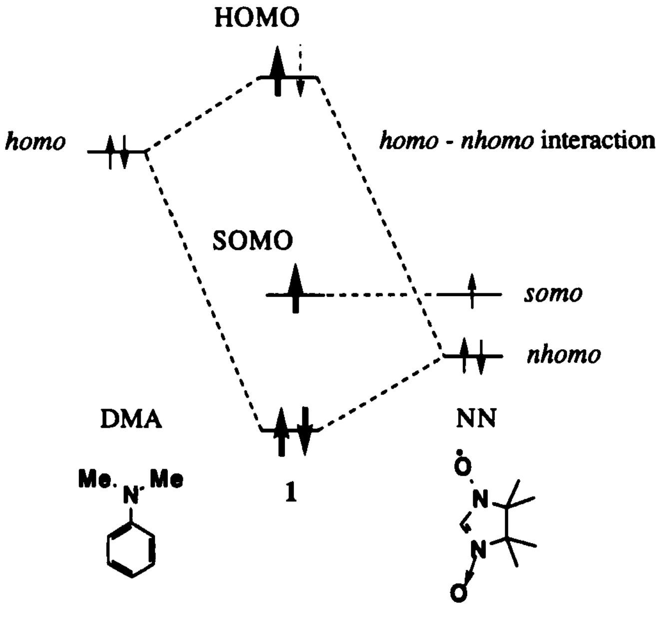

FIGURE 4 Schematic drawing of an electronic configuration of **1**. An electronic interaction (*homo-nhomo* interaction) between DMA and NN moieties is depicted. Removing an anti-parallel spin (a dashed arrow) of HOMO affords the triplet ground state $\mathbf{1}^{+\bullet}$.

CONCLUSION

Intramolecular exchange interaction of the cation diradical spin system ($\mathbf{1}^{+\bullet}$ and $\mathbf{2}^{+\bullet}$) which contains the delocalized spin and the localized one is well rationalized by non-disjoint character in reference to non-degenerated SOMO and SOMO'. One can expect that high-spin molecules of this type can be prepared according to the molecular design documented in the text. The intramolecular ferromagnetic coupling between the π-spin on the donor moiety and the localized spin on the radical moiety in these cation diradicals can play a crucial role for aligning localized spins through conducting electrons when mixed valence complexes are prepared using the open-shell donor.

ACKNOWLEDGMENT

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