J. Am. Chem. Soc. 1994, 116, 4523–4524

Intramolecular Exchange Interaction in a Novel Cross-Conjugated Spin System Composed of π-Ion Radical and Nitronyl Nitroxide

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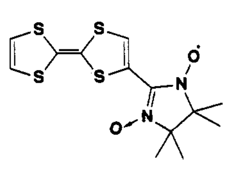
Received January 4, 1994

Recently, several molecular ferromagnets based on purely organic compounds have been reported.[1] Development of a novel organic spin system, which carries both localized and itinerant electron spins,[2] is an important step toward realizing an organic counterpart of transition metal ferromagnets with s–d or s–f interaction. We have prepared novel nitronyl nitroxide (NN) derivatives (**1** and **2**) which carry a tetrathiafulvalene (TTF) or a *p*-benzoquinone (BQ) group at the nodal carbon of NN. When such an open-shell donor **1** or acceptor **2** is converted into charge-transfer complexes or conductive ion–diradical salts, an organic Kondo system or organic magnetic metal[3] might be realized, depending on the degree and sign of the exchange interaction in these complexes. Thus, an examination of the intramolecular exchange interaction in the ion–diradical species generated by redox reactions of **1** or **2** should be crucial in this respect. A comparison of the spin correlation in these species with that of neutral non-Kekulé hydrocarbons, such as trimethylenemethane (TMM) or tetramethyleneethane (TME),[4] and of their charged radical systems[5] is also interesting.



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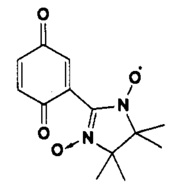

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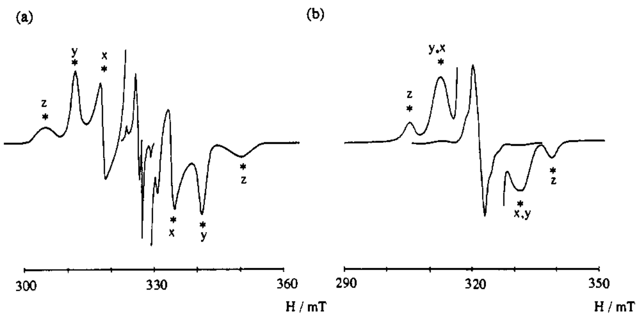

Figure 1. ESR spectra of (a) $\mathbf{1}^{\bullet+}$ in MTHF matrix at 110 K ($\nu = 9.1779$ GHz) and (b) $\mathbf{2}^{\bullet-}$ in frozen DMF at 25 K ($\nu = 9.0392$ GHz). The triplet lines are marked by asterisks. The resonance fields of triplet signals are (a) 304.47, 311.35, 318.23, 333.90, 341.33, and 350.27 mT and (b) 305.35, 312.76, 314.44, 328.83, 331.43, and 338.89 mT. Central lines are of neutral radical **1** or **2** with anisotropic *g* values and hyperfine structures. The broadening of the *z* lines in spectrum a is presumably caused by the hyperfine splitting of nitrogen atoms of the NN moiety.

The open-shell donor **1** and acceptor **2** were prepared from formyl TTF or formyl *p*-hydroquinone according to the ordinary method for preparing NN derivatives. The IR and mass spectral data of **1** and **2** are consistent with the desired structure.[6] ESR spectra of **1** and **2** in benzene show double quintet signals ($\Delta H_{msl} = 0.089$ mT) with $a_N = 0.757$ mT (2N), $a_H = 0.060$ mT (1H) at $g = 2.0063$ and quintet signals ($\Delta H_{msl} = 0.169$ mT) with $a_N = 0.722$ mT (2N) at $g = 2.0072$, respectively. An X-ray crystal analysis of **2** reveals the nonplanar structure of **2**; each NN moiety of two independent molecules in an asymmetric unit rotates by 60.17(7)° or 66.31(7)° from the planar structure.[7]

The donor **1** was oxidized by excess I_2 in 2-methyltetrahydrofuran (MTHF) to afford a green solution. The ESR spectrum of the oxidized species in a frozen matrix of MTHF at 100 K showed a set of fine structure signals due to the triplet species (Figure 1a) along with a signal ($g = 4.030$) of $\Delta m_s = 2$ in a half-field region. Zero-field splitting parameters and anisotropic *g* values of the triplet species were determined by a computational simulation to be $D = 0.0214$, $E = 0.0022$ cm^{-1}, and $g_x = 2.0111$, $g_y = 2.0094$, and $g_z = 2.0031$, respectively.[8] These parameters indicate that the obtained fine structure is due to the cation diradical $\mathbf{1}^{\bullet+}$.[9] The temperature dependence of the signal intensity in THF glass was measured in the temperature range 50–150 K (Figure 2). The plot reveals that the triplet signals are derived from thermally populated species and that two spins interact antiferromagnetically. Using a S–T model, the exchange interaction ($|J|/k_B$) was estimated to be about 100 K (Figure 2).

The acceptor **2** was reduced by sodium in DMF to afford a red solution, and the ESR spectrum of the reduced species was measured in a frozen matrix. The triplet signals with $D = 0.0157$, $E = 0.0011$ cm^{-1}, and $g_x = 2.0068$, $g_y = 2.0045$, and $g_z = 2.0055$[8] were observed as shown in Figure 1b along with a signal ($g = 4.019$) of $\Delta m_s = 2$, supporting the structure of $\mathbf{2}^{\bullet-}$. The temperature dependence of the triplet signals was measured in the temperature range of 6–150 K, and the Curie plot indicates that the triplet is the ground state of $\mathbf{2}^{\bullet-}$ (Figure 2).

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(6) **1**: mp 77.9 °C dec; IR (KBr) $\nu_{C=C} = 1461, 1559$ cm^{-1}, $\nu_{NO} = 1422, 1378$; MAS (FAB) $(M^+ + 1)_{obs} = 360.06$, $M^+_{calc} = 359.00$. **2**: mp 103.2 °C dec; IR (KBr) $\nu_{C=O} = 1668$ cm^{-1}, $\nu_{NO} = 1415, 1372$; MAS (FAB) $M^-_{obs} = 263.09$, $M^-_{calc} = 263.10$.

(7) Crystal data: $C_{13}H_{15}N_2O_4$, $M = 263.27$, monoclinic, space group $P2_1/n$, $a = 17.805(2)$ Å, $b = 17.983(3)$ Å, $c = 8.4745(7)$ Å, $\beta = 94.07(1)°$, $V = 2706.6(6)$ Å^3, $Z = 8$, $D_c = 1.292$ g cm^{-3}. $R = 0.043$ for 3456 independent reflections $[|F_o| \geq 3\sigma(|F_o|)]$ and 464 parameters.

(8) The triplet signals were tentatively assigned to a pair of *x*, *y*, and *z* lines from the inside to the outside, respectively.

(9) The *g* value of $\mathbf{1}^{\bullet+}$ ($g = {}^1/_3(g_x + g_y + g_z) = 2.0079$) corresponds to the average between unsubstituted nitronyl nitroxide radical NN-H ($g = 2.0063$) and TTF cation radical ($g = 2.0084$).

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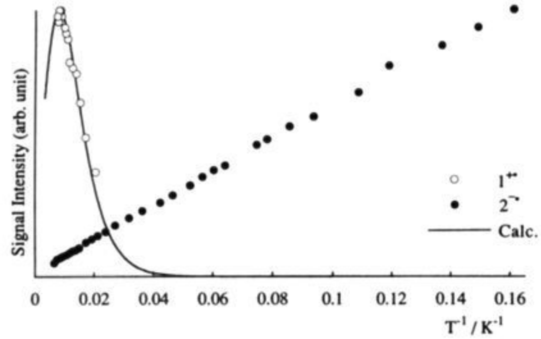

Figure 2. Temperature dependences of the ESR signal intensities for $1^{\bullet+}$ and $2^{\bullet-}$. Open and solid circles indicate the intensity of the *y* line at 311.35 mT for $1^{\bullet+}$ and the *z* line at 338.89 mT for $2^{\bullet-}$, respectively. The temperature dependence of the signal intensities due to signals of $\Delta m_s = 2$ for both $1^{\bullet+}$ and $2^{\bullet-}$ is consistent with that of the signals of $\Delta m_s = 1$. The solid line is a theoretical curve calculated using a S–T model ($2J/k_B = -200$ K).

In order to understand the results of the relatively large antiferromagnetic interaction in $1^{\bullet+}$ and the ferromagnetic interaction in $2^{\bullet-}$, cyclic voltammetry was measured for the open-shell donor **1** and acceptor **2**. The oxidation potentials of **1** were recorded at 0.32, 0.77, and 1.00 V (*vs* Ag/AgCl), corresponding to the first and second oxidation potentials of the TTF moiety and the first one of the NN, respectively.[10] The close resemblance of the first and second oxidation potentials of **1** to those of TTF itself suggests that $1^{\bullet+}$ has an open-shell diradical structure, in which each unpaired electron is distributed separately on the TTF and NN moieties. This tendency of the spin distribution is a reflection of the electronic features of the cross-conjugated system. Since the electronic structure resembles that of a disjoint system, such as TME in which two electron spins reside in separate allyl moieties of degenerate SOMOs, the exchange interaction should not be substantial.[4,11,12] An *ab initio* calculation with the model system of the planar form of $1^{\bullet+}$ predicts that $1^{\bullet+}$ has a large positive exchange interaction due to a spin polarization effect.[4b] However, this prediction contradicts the experimental result. A very large CI calculation on TME reveals that the ground-state spin multiplicity of TME depends heavily on the dihedral angle between the two allyl moieties.[11a] Thus in order to examine the ground state of $1^{\bullet+}$ theoretically, a CI calculation of similar level may be required.

In sharp contrast with the case of donor **1**, the reduction potential (−0.23 V) of **2** is found to be shifted 0.2 V lower, compared with that of BQ.[10] This result suggests that the energy level of the LUMO of **2** is lowered due to an interaction between the BQ and NN moieties (Figure 3). The MO calculation supports the above interpretation: coefficients of the SOMO in $2^{\bullet-}$ are located exclusively in the NN moiety, while those of the SOMO′ (LUMO of **2**) are distributed not only over the BQ moiety but also over the NN to some extent.[13] Thus, significant exchange interaction can occur between the localized spin in the NN moiety and the delocalized spin in the π^* orbital, leading to the triplet ground state of $2^{\bullet-}$: this spin system can be classified in the nondisjoint class of diradicals.[4,12] It should be noted that the electronic configuration of $2^{\bullet-}$ resembles that of a photoexcited triplet state, in reference to participation of a π^* orbital.[14]

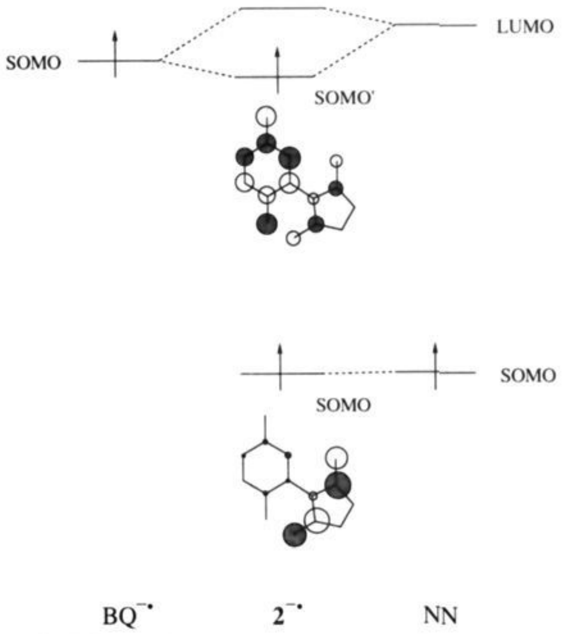

Figure 3. Schematic drawing of the electronic configuration of $2^{\bullet-}$ and coefficients of the SOMO and SOMO′ orbitals of $2^{\bullet-}$. The electronic interaction between BQ and NN moieties is also depicted.

In summary, two types of intramolecular exchange interaction were found in ion–diradicals derived from an open-shell donor or acceptor. In particular, the intramolecular ferromagnetic interaction demonstrated in the latter should be applicable to the construction of molecular magnetic systems with charge-transfer interactions.

Acknowledgment. This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Area "Molecular Magnetism" (Area No. 228/04 242 104) from the Ministry of Education, Science and Culture, Japan. We wish to thank Prof. K. Yamaguchi at Osaka University for a helpful discussion. We thank also Profs. K. Itoh, T. Takui, and Y. Teki at Osaka City University for providing an ESR simulation program.

Supplementary Material Available: ESR spectra of neutral **1** and **2** in a glassy matrix and ESR spectrum simulations for $1^{\bullet+}$ and $2^{\bullet-}$ including experimental details (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(10) The first and second oxidation potentials of TTF are observed at 0.34 and 0.71 V, and the reduction potential of BQ is at −0.44 V under the same experimental conditions: in CH_2Cl_2 solution; 0.1 M $(n\text{-Bu})_4NClO_4$ as supporting electrolyte; Pt electrode.

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