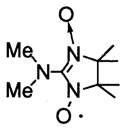
# Ground State Triplet Cation Diradicals Generated from *N,N*-Dimethylamino Nitronyl Nitroxide and Its Homologues through One-Electron Oxidation

Hiromi Sakurai, Reiji Kumai, Akira Izuoka, and Tadashi Sugawara*
*Department of Pure and Applied Sciences, Graduate School of Arts and Sciences, The University of Tokyo,*
*3-8-1 Komaba, Meguro, Tokyo 153*

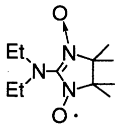
(Received July 12, 1996)

*N,N*-Dimethylamino nitronyl nitroxide (**1**) and its homologues were prepared. One-electron oxidation of these open-shell donors were fond to afford ground state triplet species based on the ESR spectroscopic measurements. The electronic structure of $\mathbf{1}^{+\bullet}$ is characterized by the presence of the two singly occupied orbitals (SOMO and SOMO') and can be regarded as a hetero-analogue of trimethylenemethane.

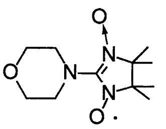
Construction of an organic ferromagnetic metal is a current target in materials science.[1] For this purpose it is crucial to prepare radical ion salts which exhibit spin ordering of localized spins through conduction electrons. Requirement for a building block of such radical ion salts is that a donor is ought to carry a localized spin which couples ferromagnetically with an unpaired electron generated by one-electron oxidation of itself. As a prototype of such open-shell donors, *N,N*-dimethylamino nitronyl nitroxide (**1**) and its homologues (**2, 3**) have been prepared. Here we report a characteristic electronic structure of the cation diradicals of these open-shell donors **1**-**3** generated through one-electron oxidation. These cation diradicals turned out to exist as ground state triplet species and their electronic structure was revealed to be closely related to that of trimethylenemethane (**TMM**),[2-4] having two degenerated SOMOs.



**1**



**2**



**3**

Provided that the electronic structure of the open-shell donor, which is composed of a donor site and a radical site, can be interpreted by a perturbational molecular orbital method,[5] the electronic features for the open-shell donor to generate a ground state triplet species upon one-electron oxidation may be documented as follows. HOMO of the open-shell donor should be located above SOMO (Figure 1(a)). If SOMO is the highest MO, one-electron oxidation is supposed to afford a closed-shell cationic species. This should not be the case. The desired situation becomes available if *homo* of the donor site interacts with *nhomo* of the radical site rather than with *somo* based on the symmetry of the relevant partial molecular orbitals. This electronic interaction raises the energy level of HOMO. Such an exotic electronic structure can be maintained if the on-site Coulombic repulsion of SOMO is larger than the orbital energy difference (ΔE) between HOMO and SOMO. According to the PM3/UHF calculation[6] on **1**, it turns out that a large spin polarization of HOMO places its β spin higher than the α spin of SOMO (Figure 1(b)). Thus one-electron oxidation removes the β spin of HOMO to afford a ground state triplet species.

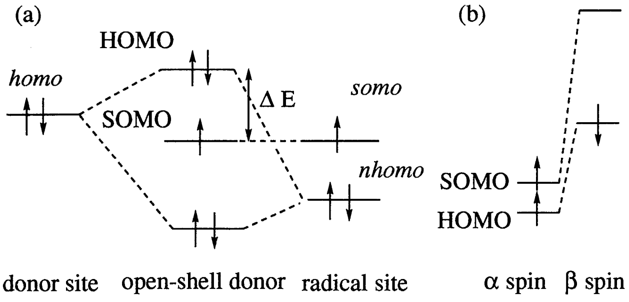
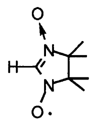
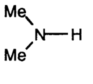
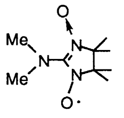
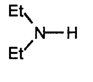
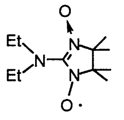
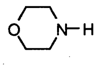
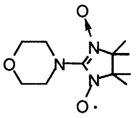


**Figure 1.** (a) Schematic drawing of the electronic configuration of an open-shell donor. (b) Spin polarization in **1** caluculated by the PM3/UHF method. A planar molecular structure is assumed for calculation.

As an open-shell donor which satisfies the above requirement, we have designed nitronyl nitroxide derivatives substituted with *N,N*-dimethylamino (**1**), *N,N*-diethylamino (**2**) or morpholino (**3**) groups. Open-shell donors were synthesized by treating bromo nitronyl nitroxide[7] with secondary amines.[8] The structure of **1** was proved by X-ray crystallography.[9]

Oxidation potentials of these open-shell donors **1**-**3** determined by cyclic voltammetry are listed in Table 1 together with reference compounds. The oxidation potentials of **1**-**3** are lower than those of the parent compounds, suggesting the electronic interaction between the donor site and the radical site as discussed above. It is to be noted that the oxidation potential of **1** is the lowest (0.53 V) among others.

**Table 1.** Cyclic voltammogram data for open-shell donors and referance compounds

| compounds | $E_{1/2}$[a] / V | compounds | $E_{1/2}$[a] / V |
|---|---|---|---|
|  | 0.83 | | |
|  $Me_2N{-}H$ | 1.22 (irr.) |  **1** | 0.53 |
|  $Et_2N{-}H$ | 1.49 (irr.) |  **2** | 0.60 |
|  | 1.20 (irr.) |  **3** | 0.58 |

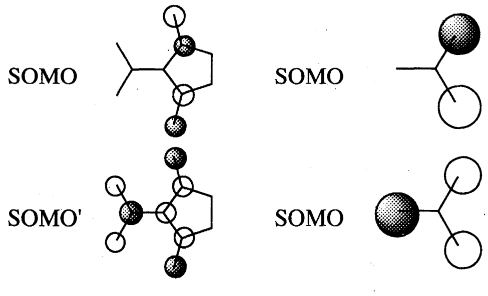
[a] Experimental conditions: acetonitrile solution; 0.1 M ($n$-Bu)$_4$N•ClO$_4$ as a supporting electrolyte; Pt electrode.

The obtained open-shell donor **1** was oxidized by iodine in THF solution at room temperature, and an ESR spectrum of the oxidized species (**1**$^{+\bullet}$) was measured in a frozen matrix. The fine structures assignable to the triplet species were observed with zero-field splitting parameters of $|D| = 0.0276$ cm$^{-1}$, $|E| = 0.0016$ cm$^{-1}$ (Table 2). The $D$ parameter of **1**$^{+\bullet}$ is smaller than the estimated value based on the point-dipole approximation and is similar to that of **TMM** ($|D| = 0.024$ cm$^{-1}$, $|E| < 0.001$ cm$^{-1}$).[2] This tendency could be attributed to the presence of a negative spin density induced at the α-carbon of nitronyl nitroxide as pointed out in the case of **TMM**.[4,10] The above result will be an evidence for the close resemblance of the electronic structure between **1**$^{+\bullet}$ and **TMM**. The Curie plot of the triplet signal afforded a straight line in the temperature range of 7.5 - 100 K. The result strongly suggests that the oxidized species exists as the cation diradical with a triplet ground state.[11] As we mentioned above, this situation becomes possible due to the large on-site Coulombic repulsion of SOMO which is localized on the nitronyl nitroxide group. Low reduction potentials of nitronyl nitroxides (usually lower than -0.7 V) supports the above interpretation. The results concerning to other cation diradicals **2**$^{+\bullet}$, **3**$^{+\bullet}$ were exactly the same as in the case of **1**$^{+\bullet}$ (Table 2).

**Table 2.** Zero-field splitting parameters for cation diradicals in THF frozen matrix at 8 K

| | $\lvert D \rvert$ / cm$^{-1}$ | $\lvert E \rvert$ / cm$^{-1}$ |
|---|---|---|
| **1**$^{+\bullet}$ | 0.0276 | 0.0016 |
| **2**$^{+\bullet}$ | 0.0273 | 0.0017 |
| **3**$^{+\bullet}$ | 0.0272 | 0.0018 |

Figure 2 shows the coefficients of SOMOs for **1**$^{+\bullet}$ and **TMM** both calculated by a PM3/RHF method.[6] The distribution of coefficients of SOMO and SOMO', the latter of which is derived from HOMO through one-electron oxidation, resembles two degenerated SOMOs of **TMM** closely, although degeneracy of SOMO and SOMO' is removed in **1**$^{+\bullet}$. Whereas the coefficients of SOMO' are spread over the entire molecule, those of SOMO are localized on the nitronyl nitroxide group. Besides, SOMO shares the coefficients of atomic orbitals of the nitronyl nitroxide group with SOMO'. Judging from the distribution of coefficients of SOMO and SOMO' of **1**$^{+\bullet}$, **1**$^{+\bullet}$ can be classified into a category of a non-disjoint type.[12] This electronic feature, therefore, will be the reason for the triplet ground state multiplicity of **1**$^{+\bullet}$. In fact, a PM3/UHF calculation[6] reveals that the triplet state of **1**$^{+\bullet}$ is more stable than the singlet by 9.7 kcal / mol.



**1**$^{+\bullet}$ **TMM**

**Figure 2.** Coefficients of SOMOs for **1**$^{+\bullet}$ and **TMM** calculated by a PM3/RHF method.

In summary, the electronic structure of **1**$^{+\bullet}$ and its homologues are characterized by the presence of two non-degenerated SOMO and SOMO'. The intramolecular ferromagnetic interaction in these cation diradicals is rationalized well by the non-disjoint character in reference to SOMO and SOMO'. Thus **1**$^{+\bullet}$ and its homologues **2**$^{+\bullet}$, **3**$^{+\bullet}$ can be regarded as a hetero-analogue of **TMM** based on their electronic features. The intramolecular ferromagnetic coupling between the delocalized spin on the donor site and the localized spin on the radical site in these cation diradicals can play an important role for aligning localized spins on the radical sites when the mixed valence complexes are prepared using these open-shell donors.

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.

## References and Notes

1 E. Dormann, M. J. Nowak, K. A. Williams, R. O. Angus, Jr., and F. Wudl, *J. Am. Chem. Soc.*, **109**, 2594 (1987); K. Yamaguchi, M. Okumura, and T. Fueno, *Synth. Metals*, **41-43**, 3631 (1991); R. Kumai, M. M. Matsushita, A. Izuoka, and T. Sugawara, *J. Am. Chem. Soc.*, **116**, 4523 (1994); R. Kumai, H. Sakurai, A. Izuoka, and T. Sugawara, *Mol. Cryst. Liq. Cryst.*, **279**, 133 (1996); T. Sugano, T. Fukasawa, and M. Kinoshita, *Synth. Metals*, **41-43**, 3281 (1991); S. Nakatsuji, S. Satoki, K. Suzuki, T. Enoki, N. Kinoshita, and H. Anzai, *Synth. Metals*, **71**, 1819 (1995); T. Sugimoto, S. Yamaga, M. Nakai, M. Tsujii, H. Nakatsuji, and N. Hosoito, *Chem. Lett.*, **1993**, 1817.
2 P. Dowd, *J. Am. Chem. Soc.*, **88**, 2587 (1966).
3 R. J. Baseman, D. W. Pratt, M. Chow, and P. Dowd, *J. Am. Chem. Soc.*, **98**, 5726 (1976).
4 W. T. Borden, "*Diradicals*," ed. by W. T. Borden, Wiley-Interscience, New York (1982), pp24-36.
5 W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.*, **99**, 4587 (1977).
6 J. J. Stewart, *J. Comp. Chem.*, **10**, 209 (1989).
7 D. G. B. Boocock and E. F. Ullman, *J. Am. Chem. Soc.*, **90**, 6873 (1968).
8 ESR spectrum of **1**, **2** or **3** in benzene solution shows a quintet signal with $a_N = 0.74$ mT (2N) at $g = 2.0059$ for **1**, $a_N = 0.75$ mT (2N) at $g = 2.0060$ for **2**, and $a_N = 0.73$ mT (2N) at $g = 2.0056$ for **3**, respectively.
9 Crystal data: $C_9H_{18}N_3O_2$, FW = 200.26, *monoclinic*, space group $P2_1/n$, $a = 11.084(4)$ Å, $b = 11.497(4)$ Å, $c = 9.263(3)$ Å, $\beta = 106.03(3)$ °, $V = 1134.5(7)$ Å$^3$, $Z = 4$, $Dc = 1.172$ gcm$^{-3}$. $R = 0.0625$ for 1464 independent reflections ($F_{obs} > 3\sigma(F_{obs})$).
10 H. M. McConnell, *J. Chem. Phys.*, **35**, 1520 (1961).
11 A liner Curie plot would also be obtained if the singlet-triplet splitting is *ca.* 10 cal / mol or less.
12 W. T. Borden, *Mol. Cryst. Liq. Cryst.*, **232**, 195 (1993).